*Supporting Information*

# Cr-Catalyzed Difluoromethylation of *α*-Trifluoromethyl Alkenes for Modular Synthesis of Polyfluorinated Compounds

Jiaran Yang, Hongxiang Li, Meiming Luo* and Xiaoming Zeng*

*Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, China*

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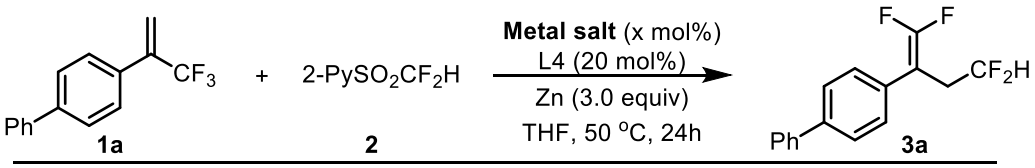
# 1. Materials and Methods

**General.** All reactions dealing with air- or moisture-sensitive compounds were carried out in a flame-dried and sealed Schlenk tube under atmosphere of nitrogen. Analytical thin-layer chromatography was performed on glass plates coated with silica gel (0.25 mm, 230–400 mesh) containing a fluorescent indicator (Merck). Flash silica gel column chromatography was performed on silica gel 60 N (spherical and neutral, 140–325 mesh) as described by Still. NMR spectra were measured on a Bruker AVANCE III HD spectrometer and reported in parts per million (ppm). $^{1}$H NMR spectra were recorded at 400 MHz in $CDCl_3$, $^{13}$C NMR spectra were recorded at 100 MHz in $CDCl_3$, $^{19}$F NMR spectra were recorded at 377 MHz in $CDCl_3$. $^{1}$H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, tt = triplet of triplets, m = multiplet), coupling constants (Hz), and integration. Analytical gas chromatography (GC) was carried out on a Thermo Trace 1300 gas chromatograph, equipped with a flame ionization detector. Mass spectra (GC-MS) were taken at Thermo Trace 1300 gas chromatograph mass spectrometer. High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (SCIEX X500R QTOF) equipped with ESI ionization source and TOF mass analyzer.

**Materials.** Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., Alfa Aesar, Adamas-beta, and other commercial suppliers and used as received. Solvents were dried over sodium (THF) by refluxing overnight and freshly distilled prior to use.

## 2. Optimizing Reaction Parameters

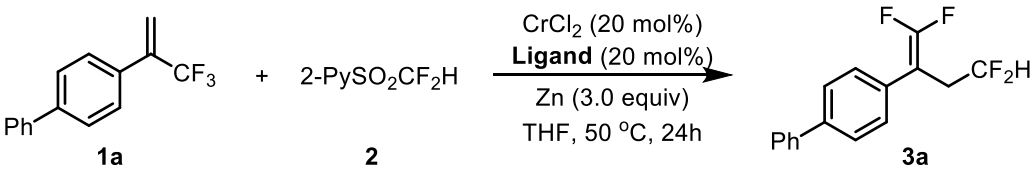
***Table S1.*** **Studying the Effect of Metal Salts**[a]



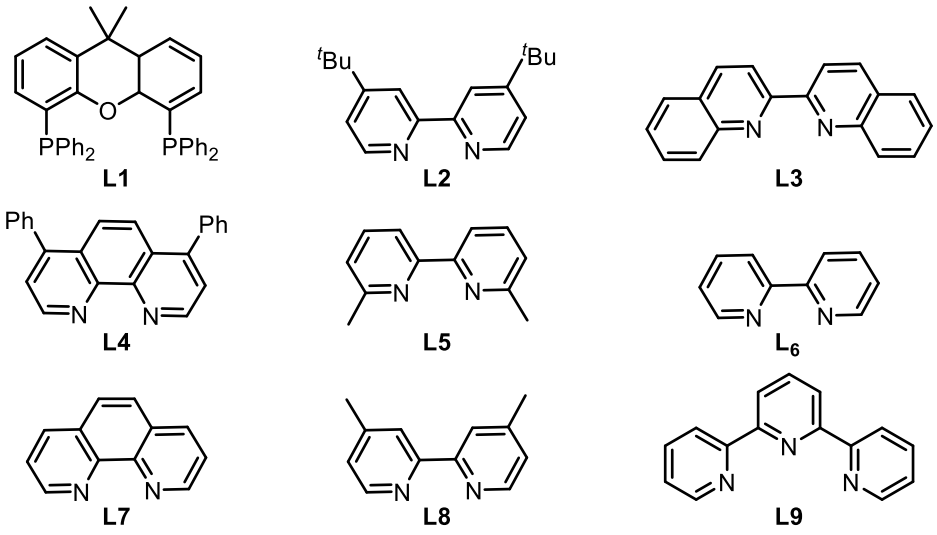

| Entry | Catalyst | x mol% | Yield of **3a**(%)[b] |
|---|---|---|---|
| 1 | -- | 20 | 13% |
| 2 | $FeCl_3$ | 20 | 10 |
| 3 | $CoCl_2$ | 20 | 23 |
| 4 | $NiCl_2$ | 20 | 20 |
| 5 | CuCl | 20 | 14 |
| 6 | CuBr | 20 | 29 |
| 7 | CuI | 20 | 12 |
| 8 | $CrF_3$ | 20 | 23 |
| 9 | $Cr(OAc)_2$ | 20 | 24 |
| 10 | $Cr(CO)_6$ | 20 | 74 |
| 11 | $CrI_3$ | 20 | 78 |
| 12 | $CrCl_3$ | 20 | 83 |
| 13 | $CrCl_2$ | 20 | **91(88)**[c] |
| 14 | $CrCl_2$ | 15 | 85 |
| 15 | $CrCl_2$ | 10 | 71 |
| 16 | $CrCl_2$ | 5 | 59 |

[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), metal salt (20 mol%), **L4** (20 mol%), Zn (0.6 mmol), and THF (0.5 mL) at 50 ℃ for 24 h. [b]Yields were determined by GC analysis using *n*-tridecane as internal standard. [c]Isolated yield.

***Table S2.*** **Studying the Effect of Ligands**[a]

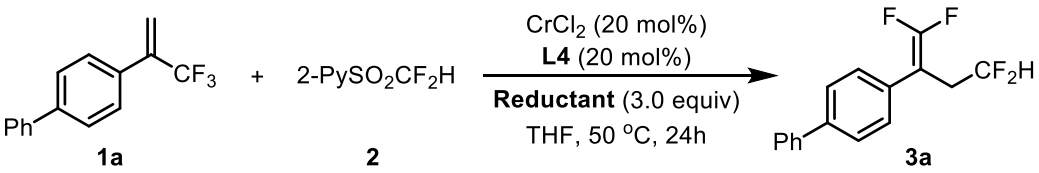



| Entry | Ligand | Yield of **3a** (%)[b] |
|---|---|---|
| 1 | -- | trace |
| 2 | **L1** | trace |
| 3 | **L2** | 78 |
| 4 | **L3** | 44 |
| 5 | **L4** | **91(88)**[c] |
| 6 | **L5** | trace |
| 7 | **L6** | 37 |
| 8 | **L7** | 25 |
| 9 | **L8** | 26 |
| 10 | **L9** | 74 |




[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), $CrCl_2$ (20 mol%), ligand (20 mol%), Zn (0.6 mmol), and THF (0.5 mL) at 50 ℃ for 24 h. [b]Yields were determined by GC analysis using *n*-tridecane as internal standard. [c]Isolated yield.

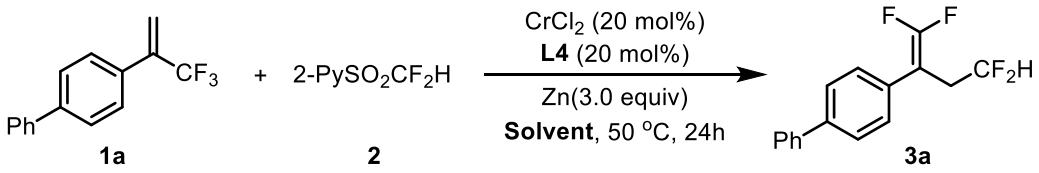
***Table S3.*** **Studying the Effect of Reductants**[a]




| Entry | Reductant | x equiv | Yield of **3a** (%)[b] |
|---|---|---|---|
| 1 | -- | | trace |
| 2 | Mn | 3 | 22 |
| 3 | Mg | 3 | 15 |
| 4 | Al | 3 | 30 |
| 5 | Zn | 3 | **91(88)**[c] |
| 6 | Zn | 2 | 78 |
| 7 | Zn | 1 | 50 |

[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), $CrCl_2$ (20 mol%), **L4** (20 mol%), reductant (0.6 mmol), and THF (0.5 mL) at 50 ℃ for 24 h. [b]Yields were determined by GC analysis using *n*-tridecane as internal standard. [c]Isolated yield.

***Table S4.*** **Studying the Effect of Solvents**[a]

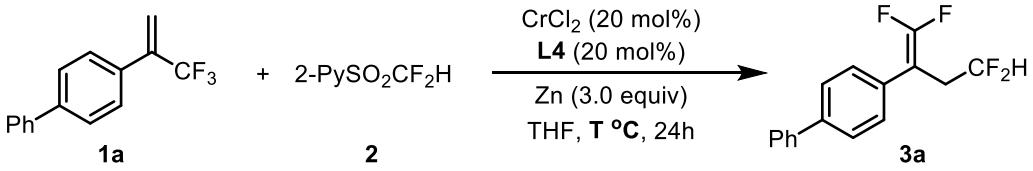



| Entry | Solvent | Yield of **3a** (%)[b] |
|---|---|---|
| 1 | DMA | 85 |
| 2 | DMF | 78 |
| 3 | MeCN | 80 |
| 4 | DMSO | 29 |
| 5 | Toluene | 34 |
| 6 | THF | **91(88)**[c] |
| 7 | EA | n.d[d] |
| 8 | 2-MeTHF | 23 |

[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), $CrCl_2$ (20 mol%), **L4** (20 mol%),

Zn (0.6 mmol), and Solvent (0.5 mL) at 50 °C for 24 h. [b]Yields were determined by GC analysis using *n*-tridecane as internal standard. [c]Isolated yield. [d]not detected.

***Table S5.*** **Studying the Effect of Temperature**[a]

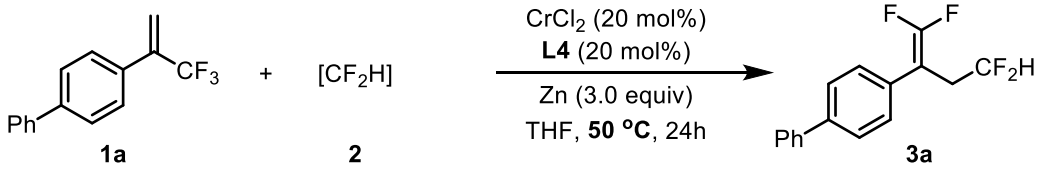



**1a** **2** **3a**

| Entry | Temperature (°C) | Yield of **3a** (%)[b] |
|---|---|---|
| 1 | 0 | trace |
| 2 | 30 | 36 |
| 3 | 50 | **91(88)[c]** |
| 4 | 80 | 77 |

[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), $CrCl_2$ (20 mol%), **L4** (20 mol%), Zn (0.6 mmol) and THF (0.5 mL) at T °C for 24 h. [b]Yields were determined by GC analysis using *n*-tridecane as internal standard. [c]Isolated yield.

***Table S6.*** **Studying the Effect of Difluoromethylating Reagents**[a]



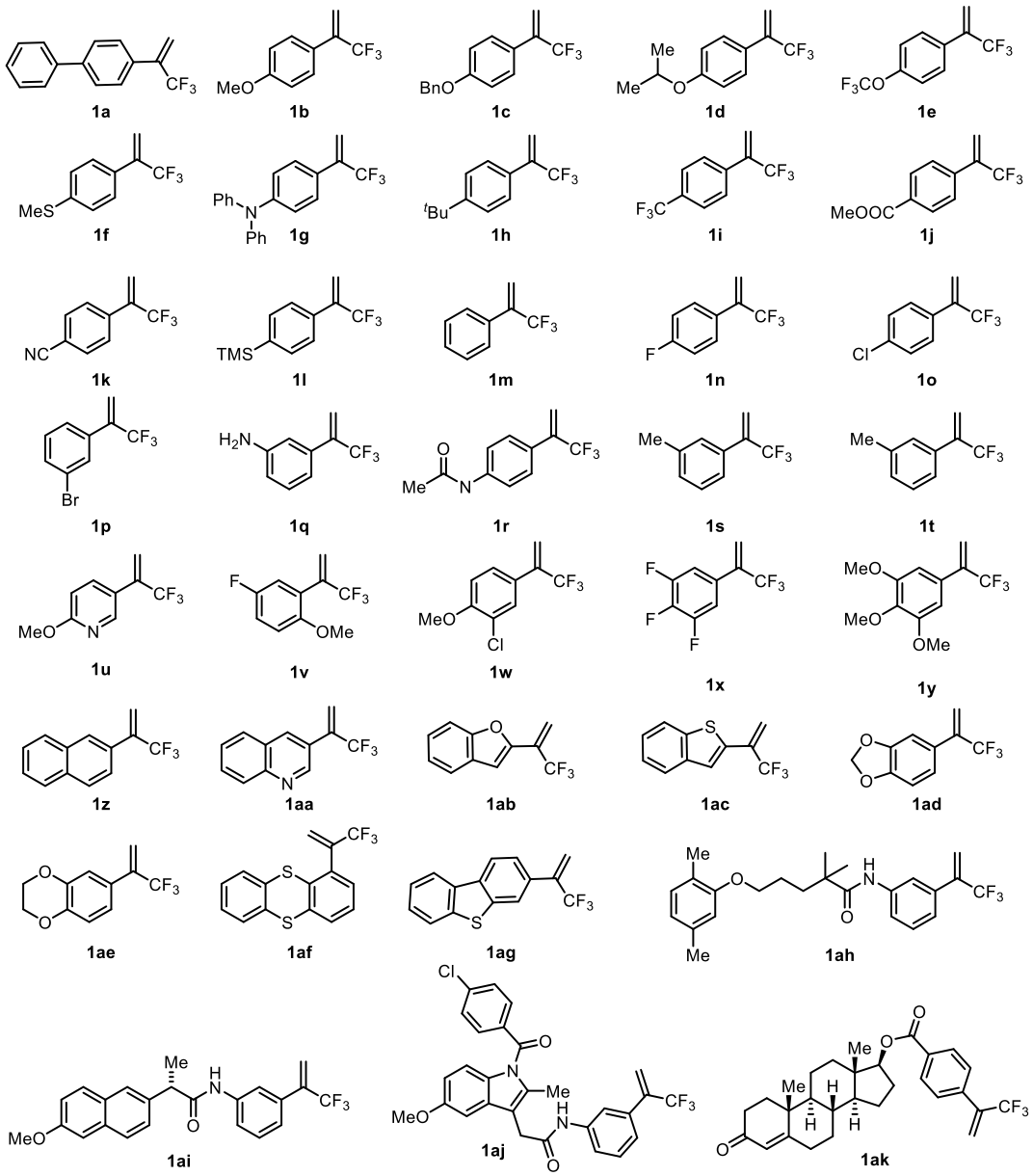

**1a** **2** **3a**

| Entry | [$CF_2H$] | Yield of **3a** (%)[b] |
|---|---|---|
| 1 | 2-$PySO_2CF_2H$ | **91(88)[c]** |
| 2 | $TMSCF_2H$ | n.d[d] |
| 3 | $HCF_2CO_2H$ | n.d[d] |
| 4 | $(CF_2HCO)_2O$ | n.d[d] |
| 5 | $NaSO_2CF_2H$ | n.d[d] |
| 6 | $Zn(SO_2CF_2H)_2$ | n.d[d] |
| 7 | $[Ph_3PCF_2H]^+Br^-$ | 73% |
| 8 | BTS-$CF_2H$ | n.d[d] |

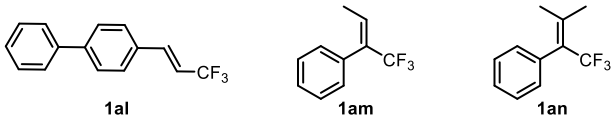
[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), $CrCl_2$ (20 mol%), **L4** (20 mol%),

Zn (0.6 mmol) and THF (0.5 mL) at 50 ℃ for 24 h. [b]Yields were determined by GC analysis using *n*-tridecane as internal standard. [c]Isolated yield. [d]not detected.

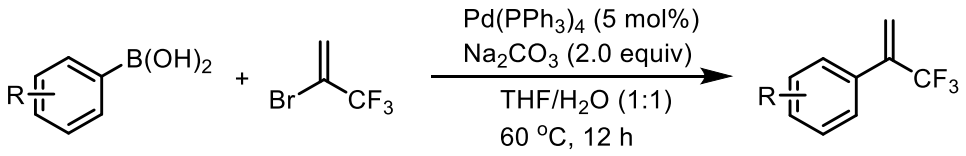
## 3. Procedure for the Preparation of Trifluoromethyl Alkenes




**Unsuccessful Substrates**



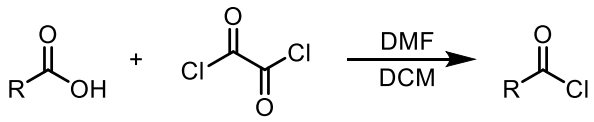
**General procedure for the synthesis of compounds 1a-1ah:**



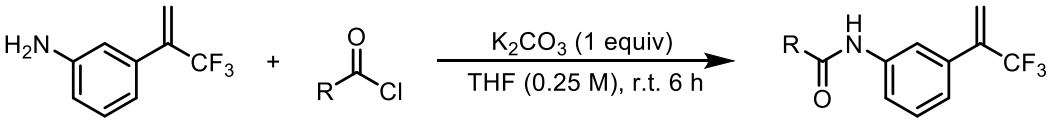

To a Schlenk tube equipped with stir bar, arylboronic acid (5 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (289 mg, 0.25 mmol, 5 mol%) were added. The vessel was evacuated and filled with argon (three times), and then aqueous $Na_2CO_3$ (1.38 g, 10 mmol, 2.0 equiv) and THF/$H_2O$ (10 mL/10 mL) were added. After addition of 2-bromo-3,3,3-trifluoro-1-propene (1.75 g, 10 mmol, 2 equiv), the solution was stirred at 60 ℃ with heating mantle for 12 hours (TLC tracking detection). The solvent was quenched with water, diluted with EtOAc (10 mL) and washed with brine (15 mL). The aqueous layer was extracted with EtOAc (3×10 mL). The combined organic layers were dried over $Na_2SO_4$, filtered and concentrated in vacuum and the residue was purified by column chromatography to afford the corresponding trifluoromethyl alkenes **1a-1ag**.[1]

**General procedure for the synthesis of compounds 1ag-1aj:**

1)




2)

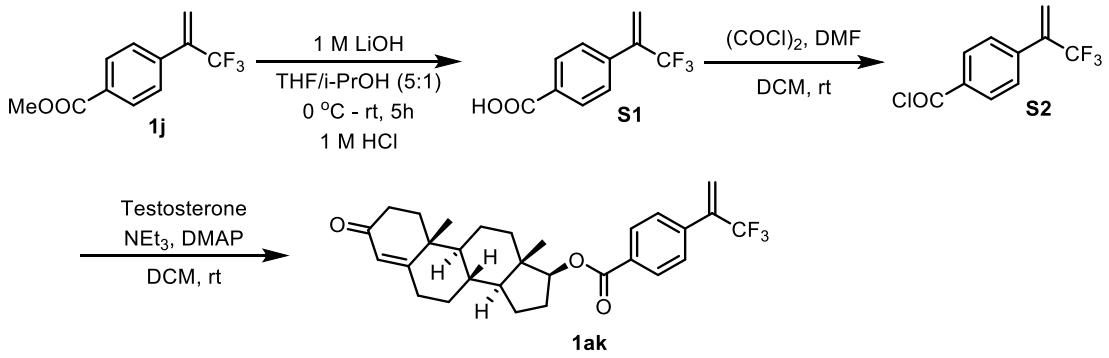



(1) To a mixture of Indomethacin, Gemfibrozil, (*S*)-Naproxen (5 mmol) and oxalyl chloride (0.84 ml, 10 mmol) in DCM (20 mL) was added DMF (0.5 mmol, 38 uL, 0.1 equiv) slowly. The reaction mixture was stirred at room temperature for 5 h, before it was evaporated under vacuum to give the crude acid chlorides, which were used in the next step without further purification.

(2) To a solution of 3-(3,3,3-trifluoroprop-1-en-2-yl)aniline (5 mmol, 935 mg, 1.0 equiv) in THF (20 ml) were added $K_2CO_3$ (690 mg, 5 mmol, 1.0 equiv) and the freshly prepared acid chlorides (1.0 equiv). This mixture was stirred at room temperature for 6h, before water was added to quench the reaction. The aqueous layer was extracted

with $Et_2O$ (3×20 mL) and the combined organic layers were dried over $Na_2SO_4$, filtered and removed under reduced pressure. The resultant crude product was purified through column chromatography over silica gel (petroleum ether/ethyl acetate) to give the trifuoromethyl alkene products.[2]

**General procedure for the synthesis of compounds 1ak:**



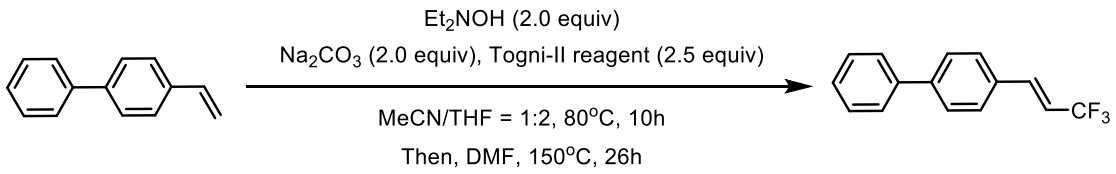

(1) To a 50 mL round bottom flask equipped with a stir bar was added **1j** (4.60 g, 20 mmol, 1.0 equiv) followed by THF (20 mL). The reaction mixture was cooled to 0 °C in an ice-water bath. After stirring for approximately 10 min, an aq. 1 M solution of LiOH (aq. 1.5 equiv) was added, followed by *i*-PrOH ($V_{THF\ /\ i\text{-}PrOH}$ = 5:1). After stirring for 10 min, the ice-bath was removed, and the solution was allowed to stir for 5 h at rt. The solution was concentrated in vacuo, and the resulting residue was dissolved in $H_2O$. This aqueous solution was transferred to a separatory funnel and washed with $Et_2O$ (3 × 20 ml). The pH of aq. layer was adjusted to ~1.0 with adding HCl (1M) and extracted with EtOAc (3 × 20 ml)). The combined organic layers were then dried over anhyrous $Na_2SO_4$ and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (DCM/MeOH = 10/1) to afford compound **S1** (3.89 g, 18 mmol) in 90% yield as a colorless oil.[3]

(2) To an oven-dried 100 mL round-bottom flask equipped with a stir bar was charged with 4-(3,3,3-trifluoroprop-1-en-2-yl)benzoic acid (2.16 g, 10.0 mmol, 1.0 equiv). The flask was purged with nitrogen three times, DCM (50 mL) and catalytic amount of DMF (two drops) were added via syringe. The reaction mixture was cooled to 0 °C and stired for 5 minutes. Then $(COCl)_2$ (2.54 g, 20 mmol, 2.0 equiv) was added dropwise and the resulting mixture was allowed to stir at room temperature for 12 h. The mixture was

concentrated under reduced pressure to afford acid chloride **S2** which was used directly in the next step without any further purification.

(3) To an oven-dried 100 mL round-bottom flask equipped with a stir bar was charged with testosterone (1.44 g, 5.0 mmol, 1.0 equiv) and DMAP (0.12 g, 1.0 mmol, 0.2 equiv). The flask was purged with nitrogen three times, DCM (25 mL) were added via syringe, followed by $Et_3N$ (0.46 g, 4.5 mmol, 1.5 equiv). The reaction mixture was cooled to 0 °C and stirred for 5 min. Then solution of compound **S2** (1.0 equiv) in $CH_2Cl_2$ (5 mL) was added dropwise and the resulting mixture was stirred at room temperature for 8 h. Then the reaction mixture was quenched with $H_2O$ (30 mL) and extracted with $CH_2Cl_2$ (3 × 15 mL). The combined organic layers were washed with brine (15 mL), dried over $Na_2SO_4$, and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (DCM/MeOH = 100/1) to afford compound **1ak** (1.94 g, 4.0 mmol) in 40% yield as a white solid.[4]

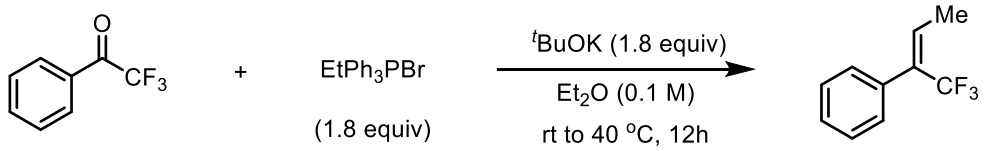
**Procedure for the synthesis of compound 1al:**




(1) Togni-II reagent (3.95 g, 12.5 mmol, 2.5 equiv) and $Na_2CO_3$ (1.06 g, 10.0 mmol, 2.0 equiv) were added to an oven-dried Schlenk flask with a stir bar. Then the flask was refilled three times with Nitrogen. Then 4-vinyl-1,1'-biphenyl (0.90 g, 5.0 mmol, 1.0 equiv) was added followed by injection of MeCN/THF(1/2) 45 mL. Finally, diethylhydroxylamine (988 μL, 10.0 mmol, 2.0 equiv) was added to the mixture. This solution was heated with vigorous stirring under nitrogen. Using TLC and GC-MS to monitor this reaction until 4-vinyl-1,1'-biphenyl was consumed.

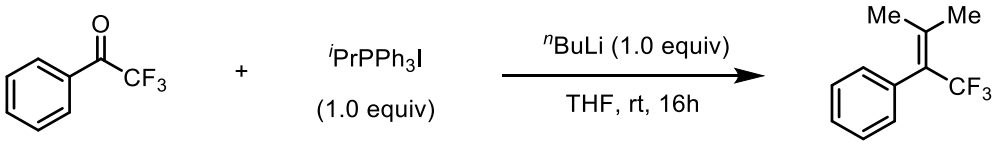
(2) After finishing step 1, 30 mL DMF was added into the flask. After heated to 150 °C for 26 hours, the resulting mixture was poured into 100 mL $H_2O$ and extracted with ethyl acetate (100 mL × 3). The combined organic layers were dried over $Na_2SO_4$, concentrated in vacuo, and purified by flash column chromatography (silica gel) to afford the trifluoromethylation product **1al**.[5]

**Procedure for the synthesis of compounds 1am:**



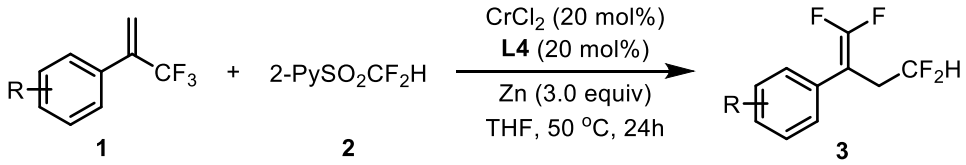

To a solution of ethyltriphenylphosphonium bromide (3.34 g, 1.8 equiv) in $Et_2O$ (50.0 mL) under $N_2$ atmosphere was added potassium tert-butoxide (1.02 g, 1.8 equiv) at room temperature. The resulting orange mixture was stirred for 2 h at room temperature. A solution of 2,2,2 trifluoro-1-phenylethan-1-one (0.87 g, 5.0 mmol) was added at room temperature. The reaction was heated and stirred for 12 hours at 40 °C . Then cooled to room temperature. The resulting mixture was extracted with $Et_2O$. The combined organic layers were washed with brine, and dried over anhydrous $Na_2SO_4$. Evaporation of the solvent followed by purification by flash chromatography on silica gel (Petrol ether) to provide the title compound as a colorless liquid.[6]

**Procedure for the synthesis of compounds 1an:**



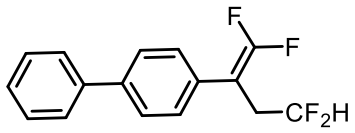

A 50 mL round bottom flask was charged with isopropyltriphenylphosphonium iodide (2.2 g, 5 mmol, 1 equiv) and THF (25 mL) under nitrogen atmosphere. A solution of n-butyllithium (2.5 M in hexanes, 2 mL, 5 mmol, 1.0 equiv) was added dropwise, and the now red mixture was stirred vigorously at room temperature. After 1h, 2,2,2 trifluoroacetophenone (0.7 mL, 5 mmol, 1.0 equiv) was added dropwise. The solution, now yellow, was stirred at room temperature. After 16h, the reaction was diluted with water (30 mL). The layers were separated, and the aqueous phase was extracted with diethyl ether (3 x 20 mL). The combined organic extracts were washed with saturated aqueous sodium chloride solution (20 mL) and was dried over $Na_2SO_4$. The solution was filtered and concentrated in vacuo. The crude residue was purified by flash column chromatography to give **1an**.[7]

## 4. General Procedure for the Cr-Catalyzed Allylic Difluoromethylation of *α*-Trifluoromethyl Alkenes




1 2 3

In a dried Schlenk tube were placed trifluoromethyl substituted alkene **1** (0.2 mmol, 1.0 equiv), 2-$PySO_2CF_2H$ **2** (58 mg, 0.3 mmol, 1.5 equiv), $CrCl_2$ (5.0 mg, 0.04 mmol, 20 mol%), **L4** (13.3 mg, 0.04 mmol, 20 mol%) and Zn powder (39 mg, 0.6 mmol, 3.0 equiv). Subsequently, freshly distilled THF (0.5 mL) was added by a syringe under atmosphere of nitrogen. The resulting solution was stirred at 50 °C for 24 h. After removal of the volatiles under vacuum, the crude product was purified by column chromatography on silica gel to afford the title compound **3**.




**3a**

**4-(1,1,4,4-Tetrafluorobut-1-en-2-yl)-1,1'-biphenyl**

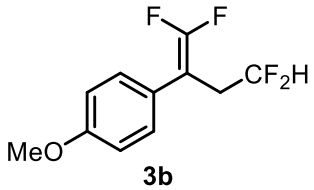
The general procedure was applied to **1a** (49.6 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 100/1) to afford the title compound **3a** (49.9 mg, 88% yield) as a white solid.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 4H), 7.50 – 7.37(m, 5H), 5.85 (tt, *J* = 56.3, 4.7 Hz, 1H), 3.00 (tdt, *J* = 16.0, 4.7, 2.3 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.2 (t, *J* = 290 Hz), 140.9, 140.41, 131.4 (t, *J* = 2.7 Hz), 129.0, 128.6 (t, *J* = 3.4 Hz), 127.7, 127.6, 127.2, 115.5 (tt, *J* = 241.0, 4.0 Hz), 85.8 – 85.4 (m), 33.6 (td, *J* = 24.3, 2.0 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -87.11 – 87.34 (m, 2F), -115.63 (t, *J* = 2.4 Hz, 2F).

Spectroscopic data are in accordance with those described in the literature.[8]




**3b**

**1-Methoxy-4-(1,1,4,4-tetrafluorobut-1-en-2-yl)benzene**

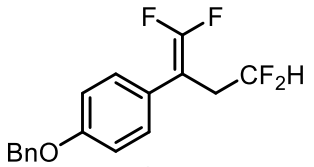
The general procedure was applied to **1b** (40.4 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 100/1) to afford the title compound **3b** (41.7 mg, 89% yield) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.9 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.76 (tt, *J* = 56.4, 4.7 Hz, 1H), 3.81 (s, 3H), 2.90 (tdt, *J* = 16.1, 4.8, 2.3 Hz, 3H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.28, 154.9 (t, *J* = 288.5 Hz), 129.46 (t, *J* = 3.2 Hz), 124.49 (t, *J* = 3.4 Hz), 115.22 (tdd, *J* = 241.3, 4.4, 3.1 Hz), 114.29, 85.5 – 85.1 (m), 55.35, 33.72 (td, *J* = 24.2, 2.2 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -88.71 – -89.10 (m, 2F), -115.75 – -115.76 (m, 2F).

HRMS ($ESI^+$) calcd for $C_{11}H_{10}F_4O$ $[M+H]^+$: 235.0741, found 235.0745.




**3c**

**1-(Benzyloxy)-4-(1,1,4,4-tetrafluorobut-1-en-2-yl)benzene**

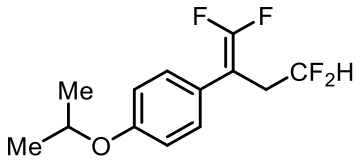
The general procedure was applied to **1c** (55.7 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound **3c** (47.8 mg, 77% yield) as a white solid.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.37 (m, 5H), 7.30 – 7.27 (m, 2H), 7.04 – 7.01 (m, 2H), 5.80 (tt, *J* = 56.4, 4.7 Hz, 1H), 5.11 (s, 2H), 2.94 (tdt, *J* = 16.0, 4.7, 2.3 Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl3) δ 158.5, 154.9 (t, *J* = 289 Hz), 136.8, 129.5 (t, *J* = 3.3 Hz), 128.8, 128.2, 127.6, 124.8 (t, *J* = 3.2 Hz), 115.2, 115.2 (t, *J* = 242.5 Hz, overlap), 85.3 (m), 70.2, 33.7 (td, *J* = 24.1, 2.1 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -88.50 – -88.87 (m, 2F), -115.75 – -115.76 (m, 2F).

HRMS (ESI$^+$) calcd for $C_{17}H_{14}F_4O$ [M+H]$^+$: 311.1054, found 311.1057.




**3d**

**1-Isopropoxy-4-(1,1,4,4-tetrafluorobut-1-en-2-yl)benzene**

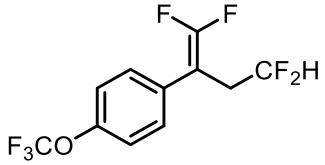
The general procedure was applied to **1d** (46 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 100/1) to afford the title compound **3d** (44.6 mg, 85% yield) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.22 (m, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.77 (tt, *J* = 56.2, 4.4 Hz, 1H), 4.56 (p, *J* = 6.0 Hz, 1H), 2.90 (tdt, *J* = 15.9, 4.7, 2.3 Hz, 3H), 1.35 (d, *J* = 6.1 Hz, 6H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.7, 154.9 (t, *J* = 280.1 Hz ), 129.5 (t, *J* = 3.3 Hz), 124.2 (t, *J* = 3.5 Hz), 116.0, 115.3 (tdd, *J* = 241.3, 4.6, 3.0 Hz), 85.4 (m), 70.0, 33.7 (td, *J* = 24.2, 2.3 Hz), 22.1.

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -88.72 – -89.15 (m, 2F), -115.83 (t, *J* = 2.4 Hz, 2F).

HRMS (ESI$^+$) calcd for $C_{13}H_{14}F_4O$ [M+H]$^+$: 263.1054, found 263.1060.




**3e**

**1-(1,1,4,4-Tetrafluorobut-1-en-2-yl)-4-(trifluoromethoxy)benzene**

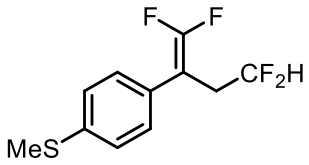
The general procedure was applied to **1e** (51.2 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to afford the title compound **3e** (47.8mg, 83% yield) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.25 – 7.23 (m, 2H), 5.80 (tt, *J* = 56.2, 4.6 Hz, 1H), 2.94 (tdt, *J* = 16.0, 4.6, 2.3 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.3 (t, *J* = 290.1 Hz), 147.9, 130.4 (t, *J* = 1.9 Hz), 128.9 (t, *J* = 3.3 Hz), 120.3, 119.6 (q, *J* = 257.5 Hz), 114.0 (tt, *J* = 241.7, 3.8 Hz), 84.2 – 83.8 (m), 32.6 (td, *J* = 24.2, 1.4 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -58.05(s, 3F), -87.06 (dt, *J* = 4.1, 2.2 Hz, 2F), -115.79 (t, *J* = 2.4 Hz, 2F).

HRMS (ESI$^+$) calcd for $C_{11}H_7F_7O$ [M+H]$^+$: 289.0458, found 289.0452.




**3f**

**Methyl(4-(1,1,4,4-tetrafluorobut-1-en-2-yl)phenyl)sulfane**

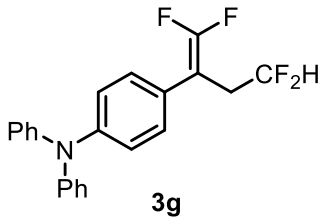
The general procedure was applied to **1f** (43.6 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound **3f** (35.0 mg, 70% yield) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.27-7.25 (m, 4H), δ 5.77 (tt, *J* = 56.4, 4.4 Hz, 1H), 2.92 (tdt, *J* = 16.0, 4.6, 2.3 Hz, 2H), 2.49 (s, 3H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.1 (t, *J* = 289.5 Hz), 138.7, 128.9, 128.6 (t, *J* = 3.3 Hz), 126.6, 115.1 (tt, *J* = 241.4, 3.9 Hz), 33.5 (td, *J* = 24.3, 1.7 Hz), 15.6.

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -87.44 – -87.72 (m, 2F), -115.69 – -115.70 (m, 2F).

HRMS (ESI$^+$) calcd for $C_{11}H_{10}F_4S$ [M+H]$^+$: 251.0512, found 251.0512.




**3g**

**N,N-diphenyl-4-(1,1,4,4-tetrafluorobut-1-en-2-yl)aniline**

The general procedure was applied to **1g** (74.3 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to afford the title compound **3g** (60.5 mg, 75% yield) as a colorless oil.

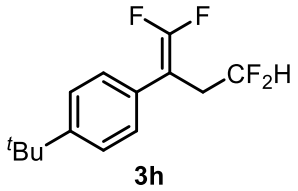
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 4H), 7.21 – 7.18 (m, 2H), 7.14 – 7.11 (m, 4H), 7.09-7.05 (m, 4H), 5.83 (tt, *J* = 56.5, 4.8 Hz, 1H), 2.93 (tdt, *J* = 15.9, 4.7, 2.3 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.1 (t, *J* = 289.3 Hz), 147.6, 147.5, 129.5, 128.9 (t, *J*

= 3.5 Hz), 125.6 (t, *J* = 3.5 Hz), 124.9, 123.5, 123.0, 115.3 (t, *J* = 240.7 Hz), 85.6(m), 33.6 (td, *J* = 24.2, 2.2 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -87.88 – -88.26 (m, 2F), -115.64 (t, *J* = 2.6 Hz, 2F).

HRMS ($ESI^+$) calcd for $C_{22}H_{17}F_4N$ $[M+H]^+$: 372.1370, found 372.1369.




**3h**

**1-(Tert-butyl)-4-(1,1,4,4-tetrafluorobut-1-en-2-yl)benzene**

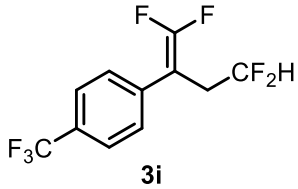
The general procedure was applied to **1h** (45.7 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE) to afford the title compound **3h** (29.2 mg, 56% yield) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$) ) δ 7.43 – 7.40 (m, 2H), 7.29 – 7.26 (m, 2H), 5.79 (tt, *J* = 56.4, 4.7 Hz, 1H), 2.94 (tdt, *J* = 15.9, 4.7, 2.3 Hz, 2H), 1.34 (s, 9H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.1 (t, *J* = 289.3 Hz), 151.1, 129.4, 127.9 (t, *J* = 3.3 Hz), 125.8, 115.2 (t, *J* = 240 Hz), 85.4(m), 34.7, 33.6 (td, *J* = 24, 2.2 Hz), 31.4.

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -87.88 – -88.19 (m, 2F), -115.82 (t, *J* = 2.3 Hz, 2F).

Spectroscopic data are in accordance with those described in the literature.[8]




**3i**

**1-(1,1,4,4-Tetrafluorobut-1-en-2-yl)-4-(trifluoromethyl)benzene**

The general procedure was applied to **1i** (48 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound **3i** (42.5 mg, 78% yield) as a colorless oil.

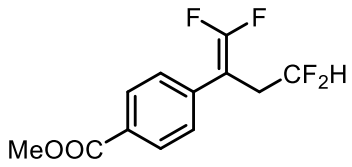
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 5.81 (tt, *J* = 56.1, 4.6 Hz, 1H), 2.97 (tdt, *J* = 16.0, 4.5, 2.3 Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl3) δ 155.4 (t, *J* = 291.5 Hz), 136.5 (tt, *J* = 3.4, 1.5 Hz), 130.2 (q, *J* = 32.9 Hz), 128.7 (t, *J* = 3.3 Hz), 125.9 (q, *J* = 3.7 Hz), 125.4 (q, *J* = 270.3 Hz),

114.9 (tdd, *J* = 241.9, 4.6, 3.1 Hz), 85.54 – 85.08 (m), 33.4 (td, *J* = 24.1, 2.2 Hz).

$^{19}$F NMR (376 MHz, CDCl3) δ -62.92(s, 3F), -85.67 – -86.03 (m, 2F), -115.67 (dd, *J* = 2.8, 1.3 Hz, 2F).

HRMS (ESI$^+$) calcd for $C_{11}H_7F_7$ [M+H]$^+$: 273.0509, found 273.0511.




**3j**

**Methyl 4-(1,1,4,4-tetrafluorobut-1-en-2-yl)benzoate**

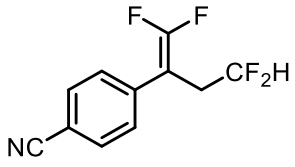
The general procedure was applied to **1j** (46.4 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to afford the title compound **3j** (42.0 mg, 80% yield) as a yellow oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.03 (m, 2H), 7.42 – 7.40 (m, 2H), 5.79 (tt, *J* = 56.2, 4.6 Hz, 1H), 3.92 (s, 3H), 2.96 (tdt, *J* = 16.0, 4.6, 2.3 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.6, 155.3 (t, *J* = 291 Hz), 137.29 (t, *J* = 3.0 Hz), 130.1, 129.7(t, *J* = 69.1 Hz ), 128.2 (t, *J* = 3.4 Hz), 114.9 (t, *J* = 242.1 Hz), 85.5(m), 52.3, 33.3 (td, *J* = 24.2, 2.0 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -86.01 – -86.22 (m, 2F), -115.94 (dt, *J* = 56.0, 16.2 Hz, 2F).

HRMS (ESI$^+$) calcd for $C_{12}H_{10}F_4O_2$ [M+H]$^+$: 263.0690, found 263.0695.




**3k**

**4-(1,1,4,4-Tetrafluorobut-1-en-2-yl)benzonitrile**

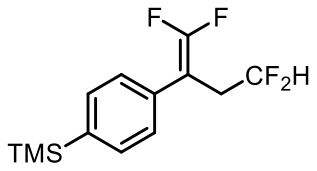
The general procedure was applied to **1k** (39.4 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to afford the title compound **3k** (37.1 mg, 81% yield) as a yellow oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.65 (m, 2H), 7.46 (dd, *J* = 8.6, 1.3 Hz, 2H), 5.82 (tt, *J* = 56.1, 4.4 Hz, 1H), 2.96 (tdt, *J* = 16.2, 4.5, 2.3 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.4 (dd, *J* = 295.4, 292.9 Hz), 137.6 (t, *J* = 4.2 Hz), 132.5, 129.0 (t, *J* = 3.6 Hz), 118.5, 114.7 (tdd, *J* = 242.2, 4.5, 3.1 Hz), 111. 8, 85.4 – 85.0 (m), 33.1 (td, *J* = 24.1, 2.1 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -84.28 (dd, *J* = 187.3, 26.6 Hz, 2F), -115.46 (dtd, *J* = 56.2, 16.1, 3.2 Hz, 2F).

HRMS ($ESI^+$) calcd for $C_{11}H_7F_4N$ $[M+H]^+$: 230.0588, found 230.0591.




**3l**

**Trimethyl(4-(1,1,4,4-tetrafluorobut-1-en-2-yl)phenyl)silane**

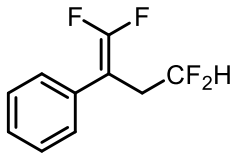
The general procedure was applied to **1l** (49.7 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound **3l** (42.0 mg, 75% yield) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 6.8 Hz, 1H), 5.81 (tt, *J* = 56.4, 4.7 Hz, 1H), 2.98 (tdt, *J* = 15.9, 4.7, 2.3 Hz, 2H), 0.32 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl3) δ 155.2 (t, *J* = 289.8 Hz ), 140.6, 133.9, 132.8 (t, *J* = 3.1 Hz), 127.5 (t, *J* = 3.3 Hz), 115.17 (tdd, *J* = 241.7, 4.5, 3.5 Hz), 86.1 – 85.6 (m), 33.6 (td, *J* = 24.3, 2.2 Hz), -1.1.

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -87.39 – -87.64 (m, 2F), -115.76 (t, *J* = 2.3 Hz, 2F).

HRMS ($ESI^+$) calcd for $C_{13}H_{16}F_4Si$ $[M+H]^+$: 277.1030, found 277.1028.




**3m**

**(1,1,4,4-Tetrafluorobut-1-en-2-yl)benzene**

The general procedure was applied to **1m** (34.4 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel PE to afford the title compound **3m** (28.6 mg, 70% yield) as a colorless oil.

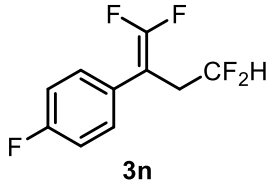
1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 5H), 5.78 (tt, *J* = 56.4, 4.7 Hz, 1H), 2.95

(tdt, $J$ = 16.0, 4.6, 2.2 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.1 (t, $J$ = 290 Hz), 132.5 (t, $J$ = 3.4 Hz), 128.9, 128.3 (t, $J$ = 3.3 Hz), 128.1, 115.14 (tdd, $J$ = 241.6, 4.3, 3.2 Hz), 85.7(m), 33.7 (td, $J$ = 24.4, 2.2 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -87.73 – -88.04 (m, 2F), -115.79 (t, $J$ = 2.6 Hz, 2F).

HRMS (ESI$^+$) calcd for $C_{10}H_8F_4$ $[M+H]^+$: 205.0635, found 205.0639.




**3n**

**1-Fluoro-4-(1,1,4,4-tetrafluorobut-1-en-2-yl)benzene**

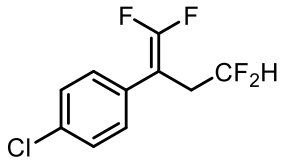
The general procedure was applied to **1n** (38.0 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel PE to afford the title compound **3n** (36.9mg, 83% yield) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.12 – 7.05 (m, 2H), 5.78 (tt, $J$ = 56.2, 4.6 Hz, 1H), 2.92 (tdt, $J$ = 16.0, 4.6, 2.3 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, $J$ = 247.9 Hz), 155.1 (t, $J$ = 291.1 Hz), 130.2 (dt, $J$ = 8.3, 3.3 Hz), 128.48 (q, $J$ = 3.3 Hz), 115.9 (d, $J$ = 21.7 Hz), 114.6 (tdd, $J$ = 240.4, 3.3, 1.0 Hz), 85.3 – 84.9 (m), 33.8 (td, $J$ = 24.2, 2.0 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -87.77 – -88.02 (m, 2F), -113.64 (s, F), -115.75 (t, $J$ = 2.4 Hz, 2F).

HRMS (ESI$^+$) calcd for $C_{10}H_7F_5$ $[M+H]^+$: 223.0541, found 223.0540.




**3o**

**1-Chloro-4-(1,1,4,4-tetrafluorobut-1-en-2-yl)benzene**

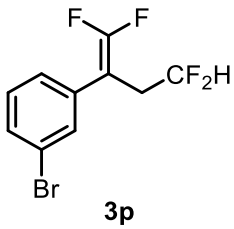
The general procedure was applied to **1o** (41.3 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 100/1) to afford the title compound **3o** (37.2 mg, 78% yield) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.29 – 7.26 (m, 2H), 5.79 (tt, *J* = 56.2, 4.6 Hz, 1H), 2.92 (tdt, *J* = 16.0, 4.6, 2.3 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.1 (t, *J* = 290.2 Hz), 134.0, 131.0 (t, *J* = 2.1 Hz), 129.7 (t, *J* = 3.3 Hz), 129.1, 115.0 (tt, *J* = 241.8, 3.9 Hz), 85.1(m), 33.5 (td, *J* = 23.9, 1.3 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -86.91 (dt, *J* = 8.8, 2.2 Hz, 2F), -115.63 (t, *J* = 2.1 Hz, 2F).

HRMS (ESI$^+$) calcd for $C_{10}H_7ClF_4$ $[M+H]^+$: 239.0245, found 235.0245.




**3p**

**1-Bromo-3-(1,1,4,4-tetrafluorobut-1-en-2-yl)benzene**

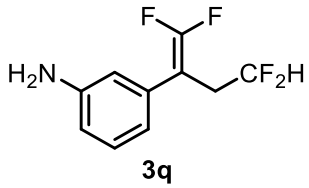
The general procedure was applied to **1p** (50.2 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel PE to afford the title compound **3p** (42.5 mg, 75% yield) as a yellow oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.27 – 7.23 (m, 2H), 5.79 (tt, *J* = 56.2, 4.6 Hz, 1H), 2.92 (tdt, *J* = 16.0, 4.6, 2.3 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.3 (dd, *J* = 293.3, 291.6 Hz), 134.7 (t, *J* = 3.6 Hz), 131.3 (t, *J* = 3.5 Hz), 131.2, 130.4, 127.0 (t, *J* = 3.3 Hz), 122.9, 114.9 (tdd, *J* = 241.9, 4.5, 3.2 Hz), 85.3 – 84.8(m), 33.5 (td, *J* = 24.3, 2.1 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -86.16 – -86.50 (m, 2F), -115.68(s, 2F).

HRMS (ESI$^+$) calcd for $C_{10}H_7BrF_4$ $[M+H]^+$: 282.9740, found 282.9745.




**3q**

**3-(1,1,4,4-Tetrafluorobut-1-en-2-yl)aniline**

The general procedure was applied to **1q** (37.4 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc =

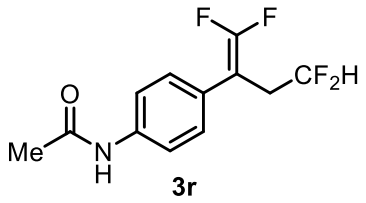
2/1) to afford the title compound **3q**(37.3 mg, 85% yield) as a yellow oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.8 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 1H), 6.63 (dd, *J* = 8.3, 1.8 Hz, 2H), 5.77 (tt, *J* = 56.4, 4.7 Hz, 1H), 3.71 (s, 2H), 2.90 (tdt, *J* = 15.9, 4.7, 2.2 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.0 (dd, *J* = 291.8, 289.9 Hz), 146.8, 133.4 (t, *J* = 3.6 Hz), 129.8, 118.4 (t, *J* = 3.1 Hz), 115.2 (tdd, *J* = 241.2, 4.6, 3.0 Hz)，114.9 (t, *J* = 3.4 Hz), 114.8, 86.1 – 85.7 (m), 33.6 (td, *J* = 24.3, 2.3 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -87.82 (dd, *J* = 335.6, 34.6 Hz, 2F), -115.96 (s, 2F).

HRMS ($ESI^+$) calcd for $C_{10}H_9F_4N$ $[M+H]^+$: 220.0744, found 220.0742.




**3r**

**N-(4-(1,1,4,4-tetrafluorobut-1-en-2-yl)phenyl)acetamide**

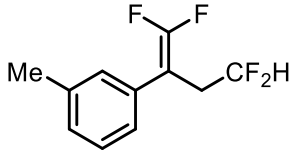
The general procedure was applied to **1r** (45.8 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford the title compound **3r** (44.4 mg, 85% yield) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.68 (s), 7.54 – 7.51 (m, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 5.78 (tt, *J* = 14.1, 1.1 Hz 1H), 2.90 (tdt, *J* = 16.0, 4.6, 2.3 Hz, 2H), 2.17 (s, 3H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 168.8, 155.1 (t, *J* = 289.6 Hz), 137.7, 128.9 (t, *J* = 3.1 Hz), 128.1 (d, *J* = 5.4 Hz), 120.2, 115.1 (t, *J* = 241.6 Hz), 85.3(m), 33.5 (td, *J* = 24.1, 1.5 Hz), 24.7.

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -87.80 (q, *J* = 34.4 Hz, 2F), -115.72(s, 2F).

HRMS ($ESI^+$) calcd for $C_{12}H_{11}F_4NO$ $[M+H]^+$: 262.0850, found 262.0843.




**3s**

**1-Methyl-3-(1,1,4,4-tetrafluorobut-1-en-2-yl)benzene**

The general procedure was applied to **1s** (37.2 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol).

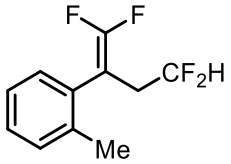
The crude product was purified by column chromatography on silica gel PE to afford the title compound **3s** (29.7 mg, 68% yield) as a yellow oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, J = 8.5, 7.4 Hz, 1H), 7.14 – 7.12 (m, 3H), 5.77 (tt, *J* = 56.4, 4.8 Hz, 1H), 2.93 (tdt, *J* = 15.9, 4.6, 2.3 Hz, 2H), 2.38 (s, 3H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.1 (t, *J* = 289.4 Hz), 138.6, 132.4 (t, *J* = 3.3 Hz), 129.0 (t, *J* = 3.1 Hz), 128.9, 128.8, 125.4 (t, *J* = 3.2 Hz), 115.2 (t, *J* = 240 Hz), 85.7(m), 33.7 (td, *J* = 24.5, 2.4 Hz), 21.6.

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -87.81 – -88.35 (m, 2F), -115.86 (dd, *J* = 2.6, 1.3 Hz, 2F).

HRMS ($ESI^+$) calcd for $C_{11}H_{10}F_4$ $[M+H]^+$: 219.0792, found 219.0791.




**3t**

**1-Methyl-4-(1,1,4,4-tetrafluorobut-1-en-2-yl)benzene**

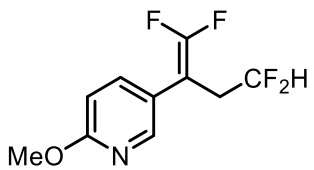
The general procedure was applied to **1t** (37.2 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE) to afford the title compound **3t** (30.1 mg, 69% yield) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.15 (m, 4H), 5.71 (tt, *J* = 56.3, 4.8 Hz, 1H), 2.85 (tdt, *J* = 16.1, 4.6, 2.0 Hz, 2H), 2.30 (s, 3H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.2 (t, *J* = 287.9 Hz ), 137.1 (dd, *J* = 2.3, 1.2 Hz), 131.7 (dd, *J* = 4.0, 1.7 Hz), 130.7, 129.7 (dd, *J* = 3.2, 1.1 Hz), 128.6, 126.3, 115.1 (tdd, *J* = 241.4, 4.8, 3.1 Hz), 84.4, 34.6 (td, *J* = 24.1, 2.6 Hz), 19.4 (d, *J* = 1.9 Hz).

$^{19}$F NMR (376 MHz, CDCl3) δ -88.39 (dd, *J* = 1924.1, 35.6 Hz, 2F), -116.08 (d, *J* = 2.1 Hz, 2F).

HRMS ($ESI^+$) calcd for $C_{11}H_{10}F_4$ $[M+H]^+$: 219.0792, found 219.0798.




**3u**

**2-Methoxy-5-(1,1,4,4-tetrafluorobut-1-en-2-yl)pyridine**

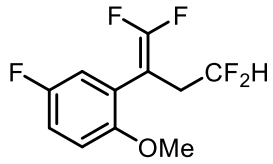
The general procedure was applied to **1u** (40.6 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the title compound **3u** (35.3 mg, 75% yield) as a yellow oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.7 Hz, 1H), 7.52 (ddd, *J* = 8.7, 2.6, 1.0 Hz, 1H), 6.75 (dd, *J* = 8.7, 0.8 Hz, 1H), 5.79 (tt, *J* = 56.2, 4.5 Hz, 1H), 3.93 (s, 4H), 2.88 (tdt, *J* = 16.0, 4.6, 2.3 Hz, 3H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.7, 155.1 (t, *J* = 291.6 Hz), 146.5 (t, *J* = 3.7 Hz), 138.4 (t, *J* = 3.3 Hz), 121.5 (t, *J* = 3.5 Hz), 115.2 (tdd, *J* = 240.0, 3.0, 1.4 Hz), 111.1, 83.1 – 82.7 (m), 53.7, 33.4 (td, *J* = 24.0, 2.2 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -87.15 – -87.49 (m, 2F), -115.61 (dd, *J* = 2.6, 1.5 Hz, 2F).

HRMS ($ESI^+$) calcd for $C_{10}H_9F_4NO$ $[M+H]^+$: 236.1889, found 236.1885.




**3v**

**4-Fluoro-1-methoxy-2-(1,1,4,4-tetrafluorobut-1-en-2-yl)benzene**

The general procedure was applied to **1v** (44.0 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound **3v** (37.8 mg, 75% yield) as a colorless oil.

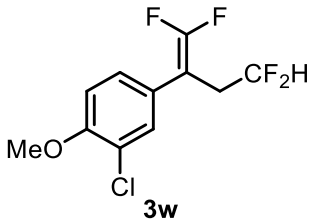
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.01 (ddd, *J* = 9.1, 7.9, 3.2 Hz, 1H), 6.92 (dd, *J* = 8.5, 2.8 Hz, 1H), 6.85 (dd, *J* = 9.0, 4.5 Hz, 1H), 5.74 (tt, *J* = 56.4, 4.7 Hz, 1H), 3.81 (s, 3H), 2.89 (tdt, *J* = 16.4, 4.5, 2.1 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.8 (d, *J* = 239.5 Hz), 154.8 (dd, *J* = 291.3, 289.3 Hz), 153.6 (t, *J* = 2.5 Hz), 122.4 (ddd, *J* = 7.9, 4.7, 1.9 Hz), 118.2 (t, *J* = 2.5 Hz), 118.0 (t, *J* = 2.5 Hz), 115.9 (d, *J* = 22.6 Hz), 115.5 (tdd, *J* = 241.3, 4.7, 3.1 Hz), 112.0 (d, *J* = 8.4 Hz), 83.0 – 82.6 (m), 56.1, 33.1 (td, *J* = 24.0, 2.1 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -86.22 (d, *J* = 33.0 Hz, 1F), -89.63 (dt, *J* = 32.9, 3.1 Hz,

1F), -115.75 – -115.76 (m, 2F), -123.69(s, 1F).

HRMS (ESI$^+$) calcd for $C_{11}H_9F_5O$ [M+H]$^+$: 253.1913, found 253.1915.




**3w**

**2-Chloro-1-methoxy-4-(1,1,4,4-tetrafluorobut-1-en-2-yl)benzene**

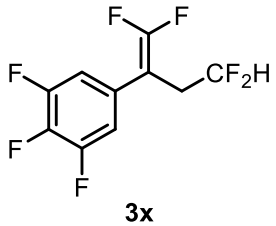
The general procedure was applied to **1w** (44.0 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound **3w** (41.8 mg, 78% yield) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 2.3, 1.0 Hz, 1H), 7.19 (dd, *J* = 8.6, 1.2 Hz, 0H), 6.93 (d, *J* = 8.6 Hz, 1H), 5.78 (tt, *J* = 56.2, 4.6 Hz, 1H), 3.91 (s, 3H), 2.89 (tdt, *J* = 16.0, 4.6, 2.3 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.1 (t, *J* = 289.5 Hz), 154.7, 130.1 (t, *J* = 3.4 Hz), 127.8 (t, *J* = 3.2 Hz), 125.6 (t, *J* = 3.6 Hz), 122.9, 115.2 (tdd, *J* = 240.0, 3.1, 1.3 Hz), 112.2, 84.9 – 84.6 (m), 56.3, 33.6 (td, *J* = 23.9, 1.7 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -87.44 – -87.81 (m, 2F), -115.71 – -115.72 (m, 2F).

HRMS (ESI$^+$) calcd for $C_{11}H_{10}F_4$ [M+H]$^+$: 269.0351, found 269.0355.




**3x**

**1,2,3-Trifluoro-5-(1,1,4,4-tetrafluorobut-1-en-2-yl)benzene**

The general procedure was applied to **1x** (45.2 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound **3x** (42.8 mg, 83% yield) as a colorless oil.

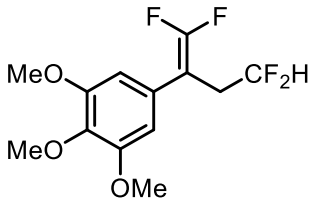
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.02 – 6.95 (m, 2H), 5.83 (tt, J = 56.0, 4.4 Hz, 1H), 2.89 (tdt, J = 16.2, 4.6, 2.3 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.4 (ddd, *J* = 293.9, 292.5, 1.2 Hz)， 151.4 (ddd, *J* =

250.4, 10.0, 4.4 Hz), 139.4 (dt, *J* = 253.5, 15.2 Hz), 128.8 (dddt, *J* = 11.4, 8.7, 6.3, 3.2 Hz), 114.7 (tt, *J* = 242.1, 3.7 Hz)，112.8 (ddt, *J* = 16.0, 6.6, 3.4 Hz)，84.5 – 84.3 (m), 33.3 (td, *J* = 24.1, 1.3 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -84.88 – -85.05 (m, 2F), -115.59 (dd, *J* = 3.0, 1.7 Hz, 2F), -133.53 (d, *J* = 20.4 Hz, 2F), -160.42 (t, *J* = 20.4 Hz, 1F).

HRMS (ESI$^+$) calcd for $C_{10}H_5F_7$ $[M+H]^+$: 259.0352, found 259.0355.




**3y**

**1,2,3-Trimethoxy-5-(1,1,4,4-tetrafluorobut-1-en-2-yl)benzene**

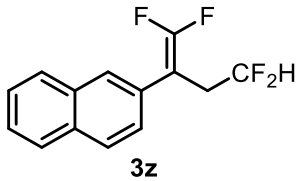
The general procedure was applied to **1y** (52.5mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to afford the title compound **3y** (53.0 mg, 90% yield) as a colorless solid.

$^1$H NMR (400 MHz, $CDCl_3$) δ 6.51 (d, *J* = 1.0 Hz, 2H), 5.78 (tt, *J* = 56.3, 4.7 Hz, 1H), 3.85 (s, 9H), 2.90 (tdt, *J* = 15.9, 4.7, 2.2 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.0 (t, *J* = 289.0 Hz), 153.4, 137.9, 127.9 (t, *J* = 3.6 Hz), 115.1 (tdd, *J* = 241.4, 4.5, 3.2 Hz), 105.7, 86.2 – 85.8 (m), 60.9, 56.3, 33.9 (td, *J* = 24.3, 2.2 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -87.19 – -88.30 (m, 2F), -115.84(s, 2F).

HRMS (ESI$^+$) calcd for $C_{13}H_{14}F_4O_3$ $[M+H]^+$: 295.0952, found 295.0949.




**3z**

**2-(1,1,4,4-Tetrafluorobut-1-en-2-yl)naphthalene**

The general procedure was applied to **1z** (44.4 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE / EtOAc = 100/1) to afford the title compound **3z** (37.1 mg, 73% yield) as a colorless oil.

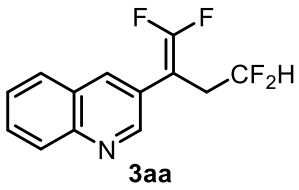
$^1$H NMR (400 MHz, CDCl3) δ 7.89 – 7.81 (m, 4H), 7.54 – 7.52 (m, 2H), 7.47 – 7.45

(m, 1H), 5.84 (tt, *J* = 56.3, 4.7 Hz, 1H), 3.06 (tdt, *J* = 15.9, 4.7, 2.2 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.3 (t, *J* = 291.6 Hz), 133.4, 132.8, 129.8, 128.6, 128.1, 127.8, 127.6 (t, *J* = 3.3 Hz), 126.7 (d, *J* = 2.5 Hz), 125.8 (t, *J* = 3.2 Hz), 115.2 (tt, *J* = 241.6, 3.8 Hz), 86.2 – 85.8 (m), 33.7 (t, *J* = 24.3 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -87.37 – -87.38 (m, 2F), -115.68 – -115.69 (m, 2F).

HRMS ($ESI^+$) calcd for $C_{14}H_{10}F_4$ $[M+H]^+$: 255.2349, found 255.2342.




**3aa**

**3-(1,1,4,4-Tetrafluorobut-1-en-2-yl)quinoline**

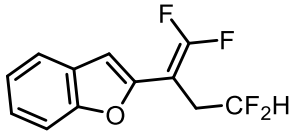
The general procedure was applied to **1aa** (44.6 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 4/1) to afford the title compound **3aa** (38.8 mg, 76% yield) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.90 (t, *J* = 2.1 Hz, 1H), 8.11 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.81 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.73 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.57 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 5.87 (tt, *J* = 56.0, 4.4 Hz, 1H), 3.05 (tdt, *J* = 16.1, 4.5, 2.2 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.7 (t, *J* = 291.4 Hz ), 149.9 (m), 147.4, 135.2 (t, *J* = 3.2 Hz), 130.2, 129.4, 128.0, 127.6, 127.5, 126.0 (t, *J* = 4.1 Hz), 114.9 (tdd, *J* = 242.2, 4.5, 3.1 Hz), 83.6 – 83.2 (m), 33.4 (td, *J* = 23.9, 1.7 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -85.01 – -85.80 (m, 2F), -115.39 (m, 2F).

Spectroscopic data are in accordance with those described in the literature.[8]




**3ab**

**2-(1,1,4,4-Tetrafluorobut-1-en-2-yl)benzofuran**

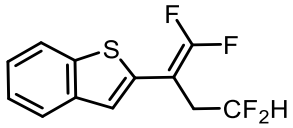
The general procedure was applied to **1ab** (42.4 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound **3ab** (38.1 mg, 78% yield) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.56 (m, 1H), 7.48 (dq, *J* = 8.3, 0.9 Hz, 1H), 7.32–7.23 (m, 2H), 6.79 (dd, *J* = 2.0, 1.0 Hz, 1H), 6.05 (tt, *J* = 56.5, 4.7 Hz, 1H), 3.06 (tdt, *J* = 15.6, 4.4, 2.0 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.1 (dd, *J* = 290.9, 7.6 Hz), 154.4 (t, *J* = 1.3 Hz), 148.3 (dd, *J* = 7.3, 5.4 Hz), 128.7, 124.7, 123.4, 121.1, 115.1 (tdd, *J* = 241.6, 4.4, 3.3 Hz), 111.2, 105.1 (dd, *J* = 9.9, 5.3 Hz), 80.3 – 79.8 (m), 30.6 (td, *J* = 25.1, 2.3 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -76.66 (d, *J* = 16.6 Hz, 1F), -84.19 (dt, *J* = 16.5, 3.4 Hz, 1F), -115.82 (dd, *J* = 3.4, 1.4 Hz, 2F).

HRMS (ESI$^+$) calcd for $C_{12}H_8F_4O$ $[M+H]^+$: 245.0584, found 219.0587.




**3ac**

**2-(1,1,4,4-Tetrafluorobut-1-en-2-yl)benzo[b]thiophene**

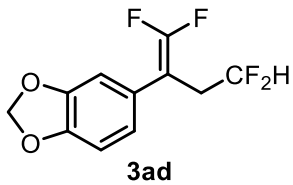
The general procedure was applied to **1ad** (45.6 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound **3ad** (39.6 mg, 76% yield) as a colorless solid.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.80 (m, 1H), 7.76 (dd, *J* = 6.8, 1.9 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.30 (s, 1H), 5.99 (tt, *J* = 55.5, 4.3 Hz, 1H), 3.13 – 2.97 (m, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.5 (dd, *J* = 298.6, 293.0 Hz), 139.5 (dd, *J* = 5.5, 1.8 Hz), 139.4, 134.7 (dd, *J* = 7.5, 3.4 Hz), 125.0, 124.8, 123.7, 122.7 (dd, *J* = 6.0, 4.8 Hz), 122.1, 114.9 (tdd, *J* = 242.3, 4.5, 2.9 Hz), 82.7 – 82.3 (m), 33.3 (td, *J* = 24.9, 2.7 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -79.50 (d, *J* = 21.6 Hz, 1F), -84.90 (dt, *J* = 21.3, 3.4 Hz, 1F), -115.16 (dd, *J* = 3.3, 1.3 Hz, 2F).

HRMS (ESI$^+$) calcd for $C_{12}H_8F_4S$ $[M+H]^+$: 261.0356, found 261.0362.




**3ad**

**5-(1,1,4,4-Tetrafluorobut-1-en-2-yl)benzo[*d*][1,3]dioxole**

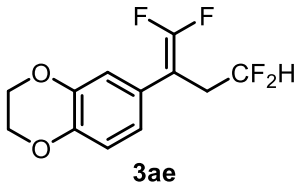
The general procedure was applied to **1ad** (43.2 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to afford the title compound **3ad** (43.7 mg, 88% yield) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 6.83 – 6.80 (m, 2H), 6.79 – 6.77 (m, 1H), 5.98 (s, 2H), 5.77 (tt, *J* = 56.3, 4.7 Hz, 1H), 2.87 (tdt, *J* = 15.9, 4.6, 2.3 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.0 (t, *J* = 290.7 Hz), 148.1, 147.4, 126.0 (t, *J* = 3.7 Hz), 122.0 (t, *J* = 3.2 Hz), 115.1 (tdd, *J* = 241.6, 4.6, 3.1 Hz), 108.9 (t, *J* = 3.4 Hz), 108.7, 101.5, 85.4(m), 33.9 (td, *J* = 24.2, 2.2 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -87.98 (dt, *J* = 36.2, 1.2 Hz, 1F), -88.62 (dt, *J* = 35.5, 2.7 Hz, 1F), -115.86 (t, *J* = 2.3 Hz, 2F).

Spectroscopic data are in accordance with those described in the literature.[8]




**3ae**

**6-(1,1,4,4-Tetrafluorobut-1-en-2-yl)-2,3-dihydrobenzo[b][1,4]dioxine**

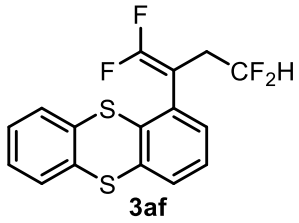
The general procedure was applied to **1ae** (46.0 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound **3ae** (44.6 mg, 85% yield) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 6.87 (d, *J* = 8.4 Hz, 1H), 6.85 – 6.84 (m, 1H), 6.80 (ddd, *J* = 8.4, 2.2, 1.1 Hz, 1H), 5.94 – 5.59 (m, 1H), 4.26 (m, 4H), 2.95 – 2.80 (m, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.0 (t, *J* = 288.9 Hz), 143.7, 143.4, 125.5 (t, *J* = 3.6 Hz), 121.4 (t, *J* = 3.4 Hz), 117.7, 117.3 (t, *J* = 3.3 Hz), 115.3 – 112.6 (m), 86.6 – 84.2 (m), 64.5 (d, *J* = 6.6 Hz), 33.7 (td, *J* = 24.3, 2.2 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -85.21 – -90.58 (m, 2F), -115.86 (dd, *J* = 2.9, 1.6 Hz, 2F).

HRMS ($ESI^+$) calcd for $C_{12}H_{10}F_4O_2$ $[M+H]^+$: 263.0617, found 219.0618.




**3af**

**7-(1,1,4,4-Tetrafluorobut-1-en-2-yl)-4a,10a-dihydrothianthrene**

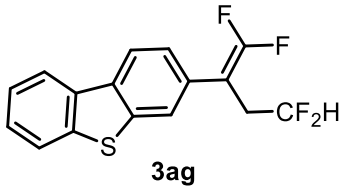
The general procedure was applied to **1af** (62.5 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound **3af** (42.7 mg, 62% yield) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 3H), 7.30 – 7.24 (m, 3H), 7.19 (dd, *J* = 7.7, 1.4 Hz, 1H), 5.75 (tt, *J* = 56.2, 4.7 Hz, 1H), 2.97 (tdt, *J* = 16.2, 4.4, 2.0 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.2 (dd, *J* = 293.3, 289.0 Hz), 137.0, 136.2 (dd, *J* = 3.3, 1.1 Hz), 136.1, 135.0, 132.4 (dd, *J* = 4.7, 1.8 Hz), 129.6, 129.2, 129.0, 128.8, 128.2, 128.1, 127.7, 115.0 (tdd, *J* = 241.7, 4.7, 3.2 Hz), 84.8 – 84.3 (m), 34.0 (td, *J* = 23.8, 1.7 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -84.24 (d, *J* = 31.4 Hz, 1F), -88.52 (dt, *J* = 31.2, 2.8 Hz, 1F), -115.59(s, 2F).

HRMS ($ESI^+$) calcd for $C_{16}H_{10}F_4S_2$ $[M+H]^+$: 343.0233, found 343.0240.




**3ag**

**2-(1,1,4,4-Tetrafluorobut-1-en-2-yl)dibenzo[b,d]thiophene**

The general procedure was applied to **1ag** (55.6 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound **3ag** (50.9 mg, 82% yield) as a colorless oil.

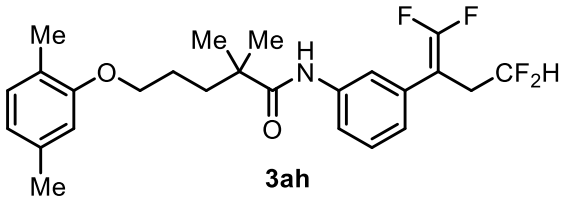
$^1$H NMR (400 MHz, $CDCl_3$) δ 8.17 (ddt, *J* = 7.6, 4.1, 2.0 Hz, 1H), 8.13 (m, 1H), 7.90 – 7.85 (m, 2H), 7.52 – 7.47 (m, 2H), 7.42 (ddd, *J* = 8.3, 1.8, 1.0 Hz, 1H), 5.87 (tt, *J* = 56.3, 4.7 Hz, 1H), 3.07 (tdt, *J* = 16.0, 4.6, 2.3 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.2 (t, *J* = 291.2 Hz), 134.0, 139.2, 136.1, 135.1, 128.8 (t, *J* = 2.6 Hz), 127.2, 126.7 (*t*, J = 3.1 Hz), 124.7, 123.2, 123. 0, 121.8, 121.4 (t,

*J* = 3.3 Hz), 115.4 (tt, *J* = 240.1, 3.8 Hz), 86.1 – 85.7 (m), 34.0 (td, *J* = 24.2, 2.0 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -87.55 – -87.78 (m, 2F), -115.59 (t, *J* = 2.3 Hz, 2F).

HRMS ($ESI^+$) calcd for $C_{16}H_{10}F_4S$ $[M+H]^+$: 311.0512, found 311.0519.




**3ah**

**5-(2,5-Dimethylphenoxy)-2,2-dimethyl-N-(3-(1,1,4,4-tetrafluorobut-1-en-2-yl)phenyl)pentanamide**

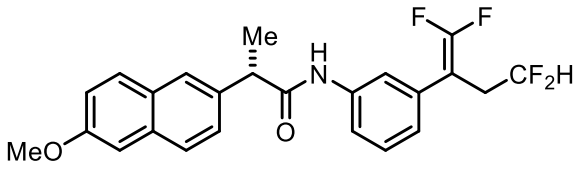
The general procedure was applied to **1ah** (83.9 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the title compound **3ah** (75.9 mg, 82% yield) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.54 (s, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.05 (dd, *J* = 20.6, 7.4 Hz, 2H), 6.70 – 6.64 (m, 2H), 5.78 (tt, *J* = 56.3, 4.8 Hz, 1H), 3.98 – 3.96 (m, 2H), 2.97- 2.86 (m, 2H), 2.32 (s, 3H), 2.20 (s, 3H), 1.85 (d, *J* = 4.9 Hz, 4H), 1.37 (s, 6H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.1, 156.9, 155.0 (t, *J* = 290Hz), 138.5, 136.6, 133.3 (dd, *J* = 4.2, 3.3 Hz ), 130.4, 129.3, 124.2 (t, *J* = 3.2 Hz), 123.6, 121.0, 120.0 (t, *J* = 3.4 Hz), 119.7, 115.0 (tdd, *J* = 241.5, 4.6, 3.0 Hz), 112.3, 85.8 – 85.4 (m), 67.9, 43.0, 37.7, 33.5 (td, *J* = 24.3, 2.2 Hz), 25.6, 25.2, 21.4, 15.9.

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -87.06 – -87.76 (m, 2F), -115.73 (dd, *J* = 2.8, 1.4 Hz, 2F).

HRMS ($ESI^+$) calcd for $C_{25}H_{29}F_4NO_2$ $[M+H]^+$: 452.2207, found 452.2205.




**3ai**

**(*S*)-2-(6-Methoxynaphthalen-2-yl)-N-(3-(1,1,4,4-tetrafluorobut-1-en-2-yl)phenyl)propenamide**

The general procedure was applied to **1ai** (79.9 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol).

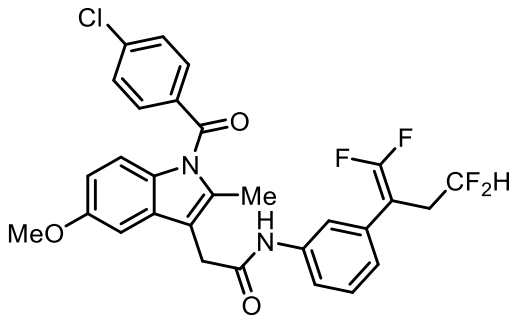
The crude product was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the title compound **3ai** (63.0 mg, 73% yield) as a white solid.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 3H), 7.51 (s, 1H), 7.43 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.27 (dd, *J* = 30.5, 8.9 Hz, 3H), 7.20 – 7.14 (m, 2H), 7.01 (d, *J* = 7.5 Hz, 1H), 5.71 (tt, *J* = 56.3, 4.7 Hz, 1H), 3.92 (s, 3H), 3.85 (q, *J* = 7.1 Hz, 1H), 2.86 (tdt, *J* = 16.0, 4.6, 2.2 Hz, 2H), 1.66 (d, *J* = 7.1 Hz, 3H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 172.8, 158.0, 155.0 (t, *J* = 289.7 Hz ), 138.4, 135.9, 134.1, 133.3 (t, *J* = 3.6 Hz), 129.4 (d, *J* = 3.9 Hz), 129.1, 128.0, 126.5, 126.2, 124.2 (t, *J* = 2.9 Hz), 119.5, 119.3, 115.0 (t, *J* = 239.4 Hz), 105.8, 85.4 (m), 55.5, 48.2, 33.5 (td, *J* = 24.2, 2.0 Hz), 18.7.

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -87.02 – -87.71 (m, 2F), -115.80(s, 2F).

HRMS ($ESI^+$) calcd for $C_{24}H_{21}F_4NO_2$ $[M+H]^+$: 432.1581, found 432.1579.




**3aj**

**2-(1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)-N-(3-(1,1,4,4-tetrafluorobut-1-en-2-yl)phenyl)acetamide**

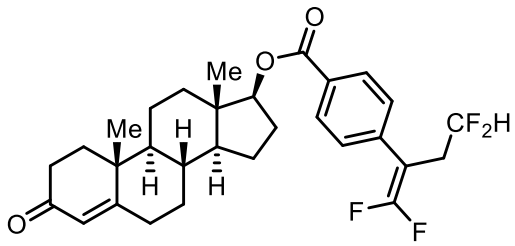
The general procedure was applied to **1aj** (105.2 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 1/1) to afford the title compound **3aj** (75.9 mg, 68% yield) as a white solid.

$^1$H NMR (400 MHz, None) δ 7.68 (s, 1H), 7.59 (dd, *J* = 8.6, 2.4 Hz, 2H), 7.46 (dd, *J* = 8.4, 2.5 Hz, 4H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.28 (t, *J* = 7.9 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 2.5 Hz, 1H), 6.89 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.73 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.74 (tt, *J* = 56.2, 4.7 Hz, 1H), 3.83 (s, 2H), 3.82 (s, 3H), 2.88 (tdt, *J* = 16.0, 4.7, 2.3 Hz, 2H), 2.45 (s, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 168.6, 168.5, 156.5, 155.0 (t, *J* = 289.8 Hz ), 139.7, 138.1, 136.8, 133.5, 133.3 (t, *J* = 3.8 Hz), 131.2, 131.1, 130.4, 129.4, 129.3, 124.5, 119.9 (t, *J* = 3.0 Hz), 119.8, 115.3, 114.7 (tdd, *J* = 240.0, 3.1, 1.5 Hz)), 112.4, 112.3, 101.0, 85.7 – 85.3 (m), 55.9, 33.5 (td, *J* = 24.5, 2.3 Hz), 33.4, 13.4.

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -86.96 – -87.51 (m, 2F), -115.71 – -115.72 (m, 2F)

HRMS ($ESI^+$) calcd for $C_{29}H_{23}ClF_4N_2O_3$ $[M+H]^+$: 559.1406, found 559.1410.




**3ak, 79%**

**(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 4-(1,1,4,4-tetrafluorobut-1-en-2-yl)benzoate**

The general procedure was applied to **1ak** (97.3 mg, 0.2 mmol) and **2** (58 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the title compound **3ak** (81.9 mg, 79% yield) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 5.79 (tt, *J* = 56.2, 4.5 Hz, 1H), 5.74 (s, 1H), 4.85 (t, *J* = 8.4 Hz, 1H), 2.96 (tdt, *J* = 16.0, 4.5, 2.2 Hz, 2H), 2.47 – 2.26 (m, 5H), 2.05 – 2.00 (m, 1H), 1.91 – 1.84 (m, 2H), 1.77 – 1.57 (m, 5H), 1.48 – 1.38 (m, 2H), 1.27 – 1.25 (m, 1H), 1.20 (s, 3H), 0.97 (s, 3H).

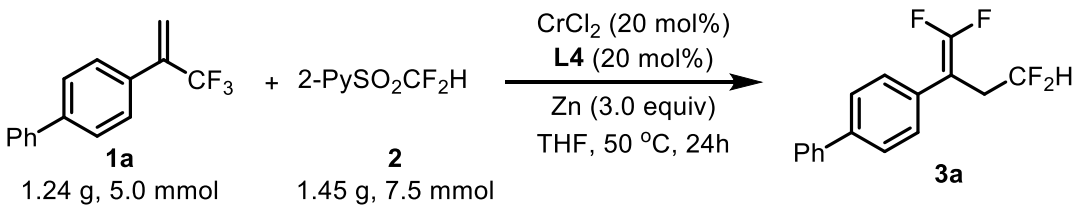
$^{13}$C NMR (100 MHz, $CDCl_3$) δ 199.6, 171.0, 166.0, 137.2 (t, *J* = 3.3 Hz), 130.2, 130.0, 128.2 (t, *J* = 3.4 Hz), 124.1, 116.1 (t, *J* = 236 Hz ), 85.6 (m), 83.3, 53.8, 50.4, 43.0, 38.7, 36.9, 35.8, 35.6, 34.1, 33.3 (td, *J* = 24.1, 1.7 Hz), 32.9, 31.6, 29.8, 27. 8, 23.7, 20. 7, 17.5, 12.4.

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -85.77 (q, *J* = 29.8 Hz, 2F), -115.67(s, 2F).

HRMS ($ESI^+$) calcd for $C_{30}H_{34}F_4O_3$ $[M+H]^+$: 519.2517, found 519.2519.

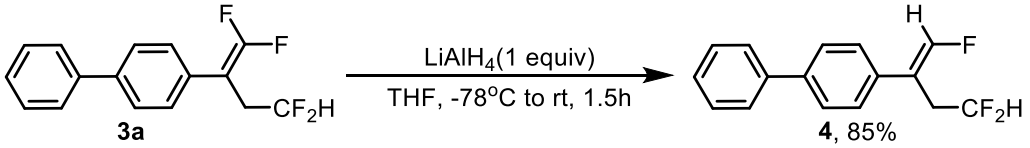
# 5. Synthetic Applications

## 5.1 Gram-Scale Synthesis




In a dried Schlenk tube were placed **1a** (1.24 g, 5 mmol), **2** (1.45g, 7.5 mmol), $CrCl_2$ (123 mg, 1 mmol, 20 mol%), **L4** (332.4 mg, 1 mmol, 20 mol%), Zn power (975g, 15 mmol). Subsequently, freshly distilled THF (12.5 mL) was added by a syringe under atmosphere of nitrogen. The resulting solution was stirred at 50 ℃ for 24 h. After the completion of the reaction, the mixture solution was concentrated under vacuum and the crude products were purified by column chromatography (PE/EtOAc = 100/1) to afford the desired compound **3a** (1.19 g, 85% yield) as a white solid.

**5.2 Transformations of 1a and 1j**




**Procedure for the synthesis of compound 4**: In a flame-dried glass tube, under an argon atmosphere, 4-(1,1,4,4-tetrafluorobut-1-en-2-yl)-1,1'-biphenyl **3a** (282.3 mg, 1.0 mmol, 1.0 equiv) was stirred in THF (0.2 M) at -78 °C for 0.25 h. $LiAlH_4$(1 equiv) was added to the mixture. The resulting solution was stirred at -78 °C for 0.5 h and warmed up to room temperature for another 1 h. The reaction was quenched with $NH_4Cl$. The reaction mixture was extracted with $Et_2O$ (3 × 5 mL), washed with brine, and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography with hexanes (100%) to afford the desired product **4** (44.6 mg, 85% yield) as a white solid.[9]

**(E/Z)-4-(1,4,4-Trifluorobut-1-en-2-yl)-1,1'-biphenyl**

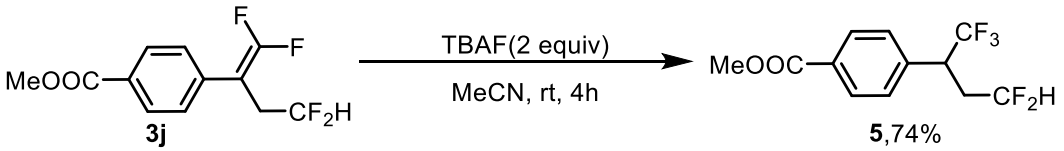
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.61 (m, 4H), 7.50 – 7.46 (m, 2H), 7.42 – 7.38 (m, 3H), 7.02 (d, *J* = 83.5 Hz, 1H), 5.94 (tt, *J* = 56.6, 4.9 Hz, 1H), 3.16 (tdd, *J* = 16.1, 4.9, 2.6 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 148.7 (d, *J* = 265.1 Hz), 141.1, 140.4, 134.2 (d, *J* = 8.2

Hz), 129.0, 127.7, 127.7, 127.2 (d, $J$ = 3.0 Hz), 127.1, 117.1 – 116.9 (m), 115.4 (td, $J$ = 241.5, 3.8 Hz), 32.8 (td, $J$ = 23.8, 3.7 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -114.32 (d, $J$ = 2.9 Hz, 2F), -125.31 (t, $J$ = 3.1 Hz, 1F).

HRMS (ESI$^+$) calcd for $C_{16}H_{13}F_3$ [M+H]$^+$: 263.1042, found 263.1045.




**Procedure for the synthesis of compound 5**: To a solution of compound **3j** (52.4 mg, 0.2 mmol, 1.0 equiv) in anhydrous MeCN (3.0 mL) was added TBAF (104.6 mg, 0.4 mmol, 2.0 equiv,) at rt. The reaction mixture was stirred for 4 hours. Next, the reaction mixture was concentrated in vacuo, and the residue was purified through column chromatography on silica gel (PE/EtOAc = 100/1) to give methyl 4-(1,1,1,4,4-pentafluorobutan-2-yl)benzoate **5** as a white solid (41.8 mg, 74 %).[10]

**Methyl 4-(1,1,1,4,4-pentafluorobutan-2-yl)benzoate**

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, $J$ = 8.3 Hz, 2H), 7.40 (d, $J$ = 8.0 Hz, 2H), 5.61 (tdd, $J$ = 56.1, 6.2, 3.5 Hz, 1H), 3.92 (s, 3H), 3.61 (pd, $J$ = 9.1, 4.5 Hz, 1H), 2.63 – 2.36 (m, 2H).

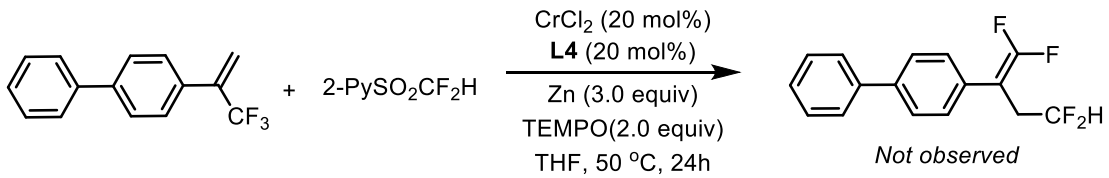
$^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.4, 137.9 (q, $J$ = 1.6 Hz), 131.0, 130.4, 129.1, 126.0 (d, $J$ = 279.8 Hz), 114.9 (t, $J$ = 240.1 Hz), 52.4, 45.3 – 44.5 (m), 34.3 – 33.8 (m).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -69.97(s, 3F), -117.34 (d, $J$ = 22.2 Hz, 2F).

HRMS (ESI$^+$) calcd for $C_{12}H_{11}F_5O_2$ [M+H]$^+$: 283.0752, found 283.0758.

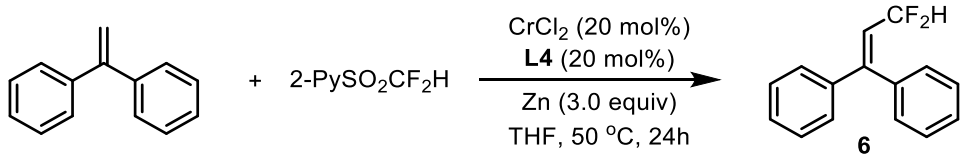
## 6. Mechanistic Studies

### 6.1 Radical-Trapping Expriments




The representative procedure was followed using 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl **1a** (49.65 mg, 0.20 mmol), 2-((difluoromethyl)sulfonyl)pyridine **2** (58 mg, 0.3 mmol) and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) (62.5 mg, 0.4 mmol)

Then we found that the coupling was completely inhibited without the production of related compound **3a**.




In a dried Schlenk tube were placed ethene-1,1-diyldibenzene (36.0mg, 0.2 mmol, 1.0 equiv), 2-$PySO_2CF_2H$ **2** (58mg, 0.3 mmol, 1.5 equiv), $CrCl_2$ (5.0 mg, 0.04 mmol, 20 mol%), **L4** (13.3 mg, 0.04 mmol, 20 mol%) and Zn powder (39 mg, 0.6 mmol, 3.0 equiv). Subsequently, freshly distilled THF (0.5 mL) was added by a syringe under atmosphere of nitrogen. The resulting solution was stirred at 50 °C for 24 h. After removal of the volatiles under vacuum, the crude product was purified by column chromatography on silica gel to afford compound **6** as a white solid.

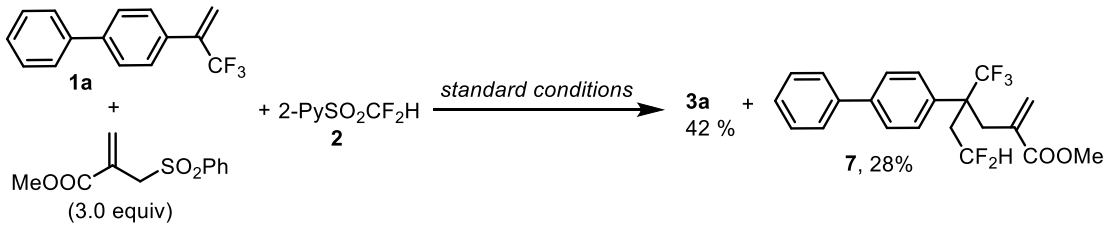
**(3,3-Difluoroprop-1-ene-1,1-diyl)dibenzene**

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 3H), 7.33 – 7.28 (m, 3H), 7.26 – 7.24 (m, 2H), 7.23 – 7.19 (m, 2H), 6.18 – 6.14 (m, 1H), 6.13 – 5.85 (m, 1H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 150.8 (t, $J$ = 12.8 Hz), 140.2 (t, $J$ = 1.3 Hz), 137.4 (t, $J$ = 2.1 Hz), 129.9 (t, $J$ = 1.7 Hz), 129.2, 128.8, 128.6, 128.6, 128.2 (t, $J$ = 1.3 Hz), 120.2 (t, $J$ = 26.7 Hz), 113.9 (t, $J$ = 229.4 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -106.82 (dd, $J$ = 55.1, 8.4 Hz, 2F).

HRMS ($ESI^+$) calcd for $C_{15}H_{12}F_2$ $[M+H]^+$: 231.0980, found 231.0988.




In a dried Schlenk tube were placed 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl **1a** (49.65 mg, 0.20 mmol), 2-((difluoromethyl)sulfonyl)pyridine **2** (58 mg, 0.3 mmol) and methyl 2-((phenylsulfonyl)methyl)acrylate (144.0 mg, 0.60 mmol, 3 equiv), $CrCl_2$ (5.0 mg, 0.04 mmol, 20 mol%), **L4** (13.3 mg, 0.04 mmol, 20 mol%) and Zn powder (39 mg, 0.6 mmol, 3.0 equiv. Subsequently, freshly distilled THF (0.5 mL) was added by a

syringe under atmosphere of nitrogen. The resulting solution was stirred at 50 °C for 24 h. After removal of the volatiles under vacuum, the crude product was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford product **3** (23.5 mg, 42% yield) as a white solid and compound **7** (22.3 mg, 28% yield) as a yellow oil.

**Methyl 4-([1,1'-biphenyl]-4-yl)-6,6-difluoro-2-methylene-4-(trifluoromethyl)hexanoate**

$^1$H NMR (400 MHz, CDCl3) δ 7.63 – 7.59 (m, 4H), 7.48 (dd, *J* = 20.7, 8.1 Hz, 4H), 7.40 – 7.35 (m, 1H), 6.25 (d, *J* = 1.1 Hz, 1H), 5.92 (tt, *J* = 55.6, 4.3 Hz, 1H), 5.35 (d, *J* = 1.2 Hz, 1H), 3.61 (s, 3H), 3.18 – 3.09 (m, 2H), 2.77 – 2.56 (m, 2H).

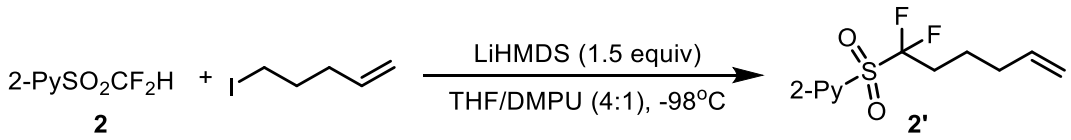
$^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.5, 141.1, 140.0, 134.8, 134.0, 130.6, 129.1, 128.2 (d, *J* = 2.0 Hz), 127.9, 127.3, 127.1, 115.5 (t, *J* = 239.1 Hz), 52.3, 37.4 (t, *J* = 24.2 Hz), 36.2, 29.8 – 29.5 (m).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -68.67 (dd, *J* = 5.3, 2.9 Hz, 3F), -108.96 – -111.17 (m, 2F).

HRMS ($ESI^+$) calcd for $C_{21}H_{19}F_5O_2$ $[M+H]^+$: 399.1378, found 399.1381.

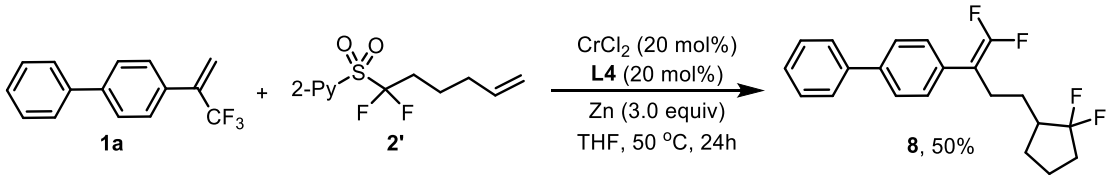
### 6.2 Radical cyclization

**The synthesis of compounds 2':**




To an oven-dried 100 mL round-bottom flask equipped with a stir bar was charged with sulfone **2** (75.4 mg, 0.39 mmol, 1.3 equiv), THF/DMPU (0.1 M with respect to alkyl iodide), and alkyl iodide (58.8 mg, 0.3 mmol, 1 equiv) under a $N_2$ atmosphere in a glovebox. The vial was cooled to -98 °C with a MeOH/liquid $N_2$ bath. LiHMDS (0.45 mL, 0.45 mmol, 1.5 equiv, 1.0 M in THF) was added over a period of 5 min, followed by quenching with sat. aq. $NH_4Cl$ at the same temperature. The mixture was allowed to warm to rt before diluting with EtOAc (10 mL) and water (10 mL), and the layers were separated. The aqueous layer was extracted with additional EtOAc (2 × 10 mL), then the combined organic layers were dried over $Na_2SO_4$ and concentrated in vacuo. The

mixture was then purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the product **2'** as a clear light-yellow oil. Characterization data matched the reported in the literature.[11]




In a dried Schlenk tube were placed **1a** (49.6 mg, 0.2 mmol), **2'** (78.4 mg, 0.3 mmol), $CrCl_2$ (5.0 mg, 0.04 mmol, 20 mol%), **L4** (13.3 mg, 0.04 mmol, 20 mol%) and Zn powder (39 mg, 0.6 mmol, 3.0 equiv). Subsequently, freshly distilled THF (0.5 mL) was added by a syringe under atmosphere of nitrogen. The resulting solution was stirred at 50 °C for 24 h. After removal of the volatiles under vacuum, the crude product was purified by column chromatography on silica gel (PE/EtOAc = 100/1) to afford the title compound **8** (34.8 mg, 50% yield) as a yellow oil.

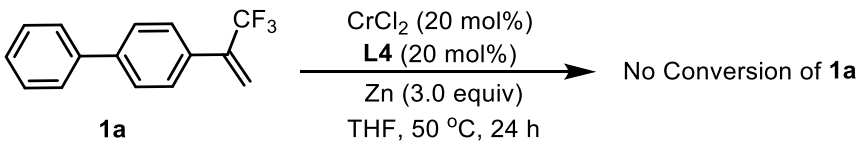
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.59(m, 4H), 7.47 – 7.34 (m, 5H), 2.58 – 2.45 (m, 2H), 2.19 – 1.95 (m, 4H), 1.81 – 1.63 (m, 3H), 1.47 – 1.35 (m, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.8 (dd, *J* = 290.3, 288.0 Hz), 140.7, 140.2, 132.5(t,*J* = 249.7 Hz), 132.45 (dd, *J* = 2.7, 1.4 Hz), 128.9, 128.7 (t, *J* = 3.4 Hz), 127.5, 127.3, 127.2, 92.1 (dd, *J* = 19.7, 14.9 Hz), 45.7 (t, *J* = 22.9 Hz), 35.3 (t, *J* = 25.1 Hz), 29.9, 29.9 (d, *J* = 7.3 Hz), 26.79 – 25.97 (m), 25.9, 20. 3 (dd, *J* = 5.6, 3.5 Hz), 45.7 (t, *J* = 22.9 Hz), 35.3 (t, *J* = 25.1 Hz), 29.5 (d, *J* = 7.3 Hz), 26.4 – 26.3 (m), 25.9, 20.3 (dd, *J* = 5.6, 3.5 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -90.82 (dd, *J* = 42.4 Hz, 7.3 Hz, 2F), -96.82 (d, *J* = 226.6 Hz, 1F), -105.20 (d, *J* = 226.8 Hz, 1F).

HRMS (ESI$^+$) calcd for $C_{21}H_{20}F_4$ $[M+H]^+$: 349.1574, found 349.1576.

### 6.3 Control Experiments




In a dried Schlenk tube were placed **1a** (49.6 mg, 0.2 mmol), $CrCl_2$ (5.0 mg, 0.04 mmol,

20 mol%), **L4** (13.3 mg, 0.04 mmol, 20 mol%) and Zn powder (39 mg, 0.6 mmol, 3.0 equiv). Subsequently, freshly distilled THF (0.5 mL) was added by a syringe under atmosphere of nitrogen. The resulting solution was stirred at 50 °C for 24 h. According to the analyses based on TCL, no conversion of **1a** was observed.

## 7. Cyclic Voltammetry Experiment

Linear sweep voltammetry was performed with an electrochemical analyzer. The voltammetric cell consisted of a glassy carbon working electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode. The analyte solution (0.1 M) was prepared in anhydrous $CH_3CN$, employing tetrabutylammonium perchlorate ($[^{n}Bu_4N]^+[ClO_4]^-$, 0.1 M) as the supporting electrolyte.

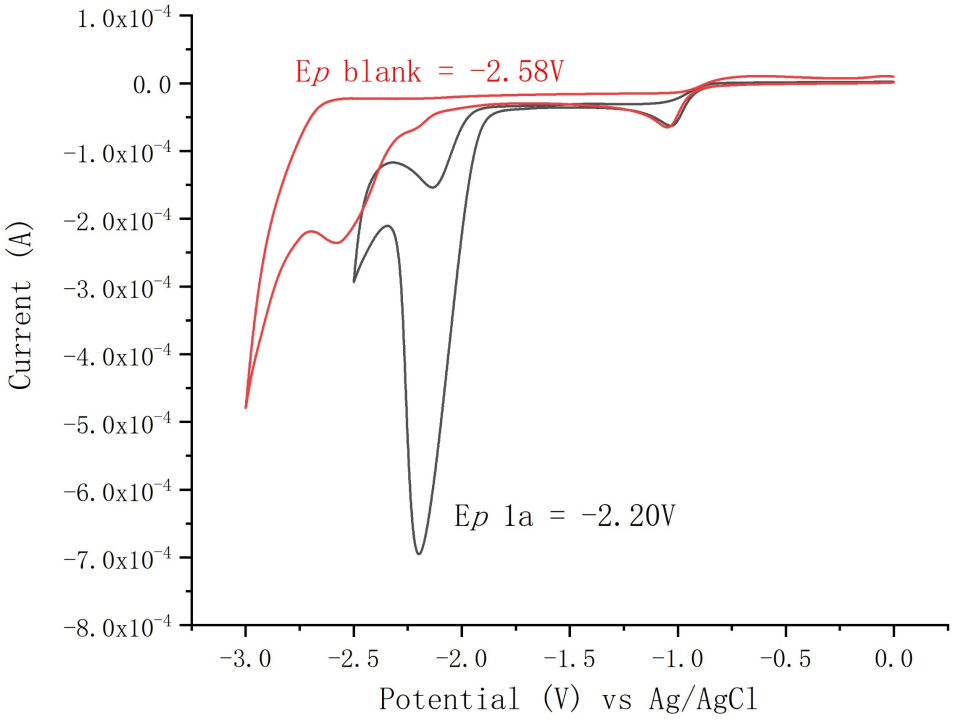



***Figure S1***. Measurement of the reduction potential of **1a**

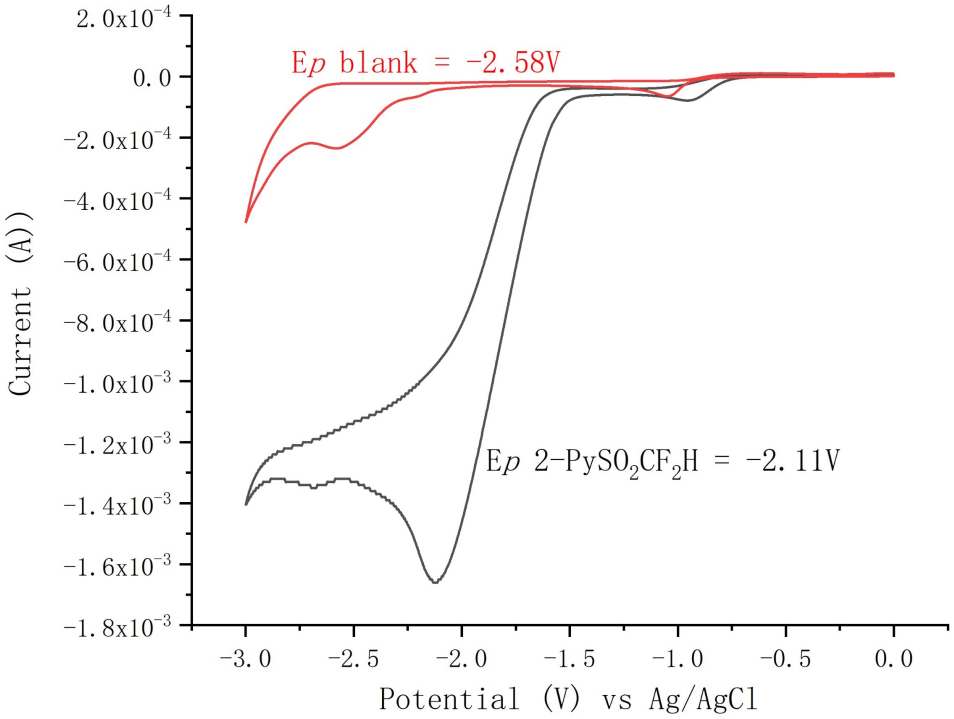



***Figure S1***. Measurement of the reduction potential of 2-$PySO_2CF_2H$

## 8. Supplementary References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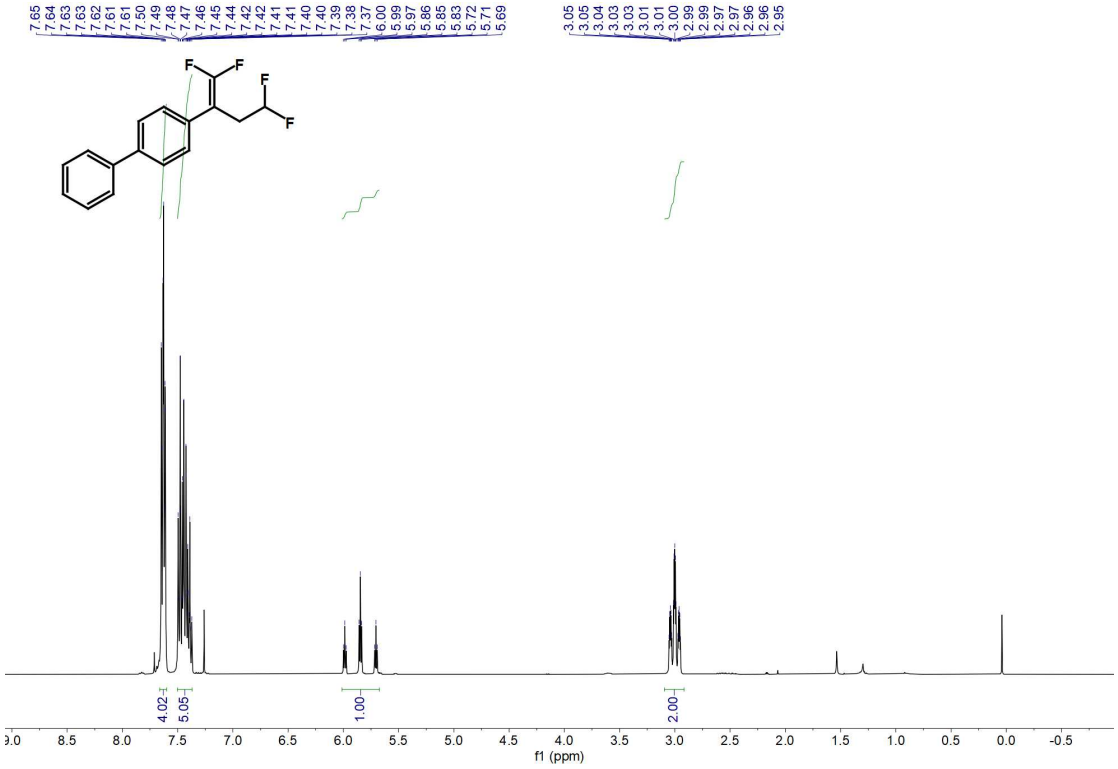
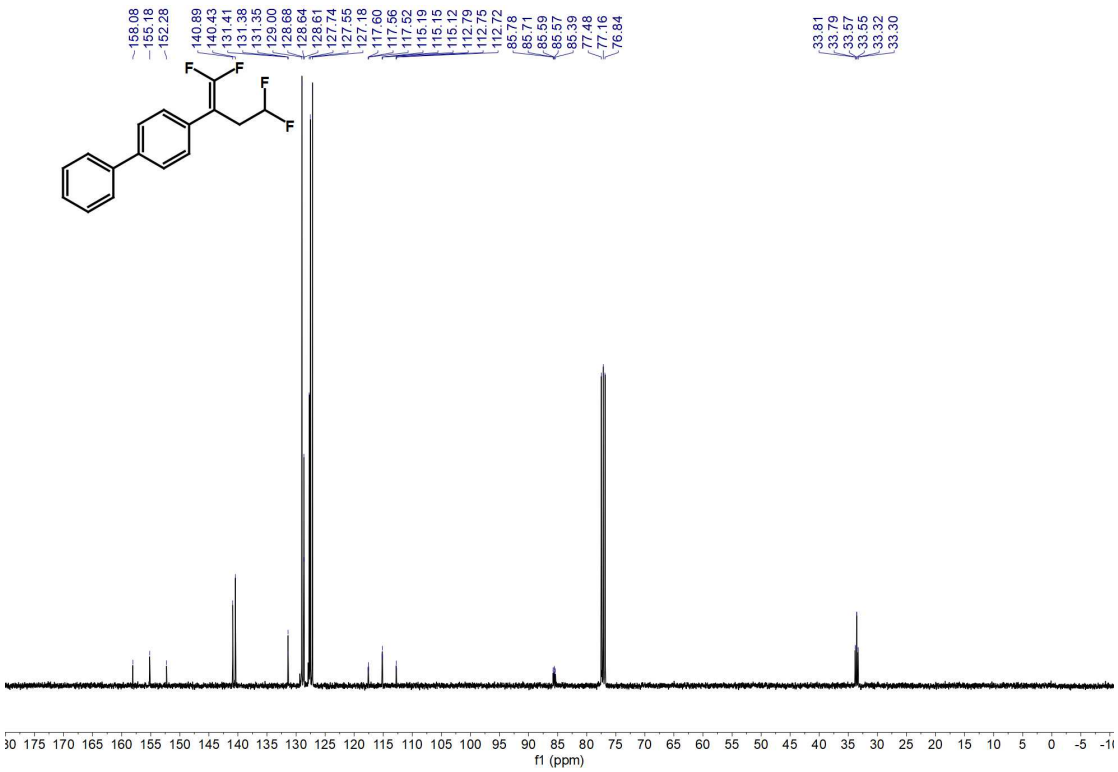
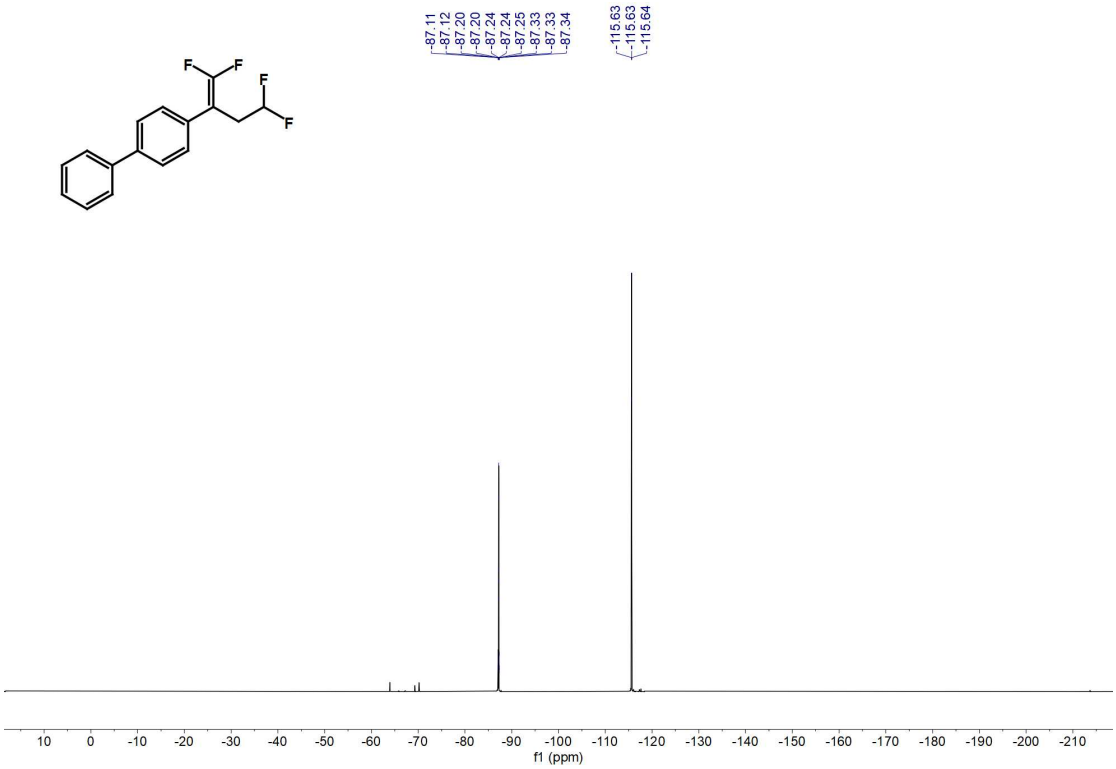
10. Zhang, Q.-Q.; Chen, S.-Y.; Lin, E.; Wang, H.; Li, Q. Regio- and Stereoselective Alkenylation of Allenoates with *Gem*-Difluoroalkenes: Facile Access to Fluorinated 1,4-Enynes Bearing an All-Carbon Quaternary Center. *Org. Lett.* **2019**, *21*, 3123–3126.
11. Miao, W.; Zhao, Y.; Ni, C.; Gao, B.; Zhang, W.; Hu, J. Iron-Catalyzed Difluoromethylation of Arylzincs with Difluoromethyl 2-Pyridyl Sulfone. *J. Am. Chem. Soc.* **2018**, *140*, 880–883.

# 9. NMR Spectra

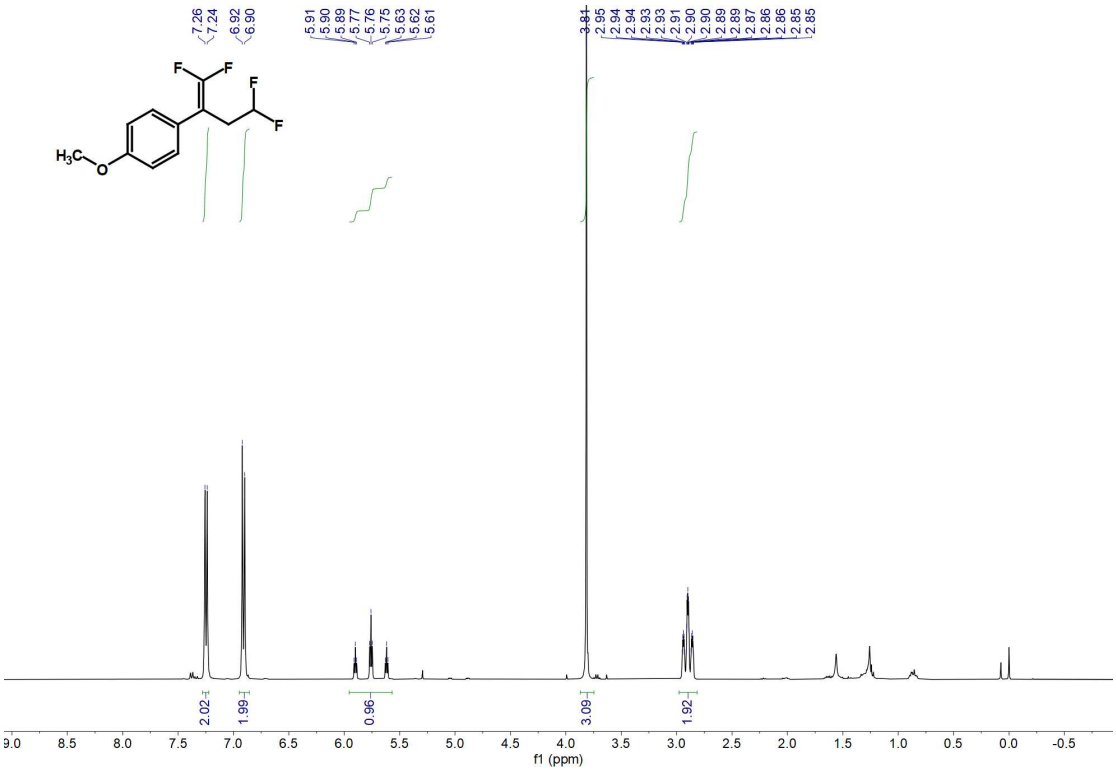
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3a**

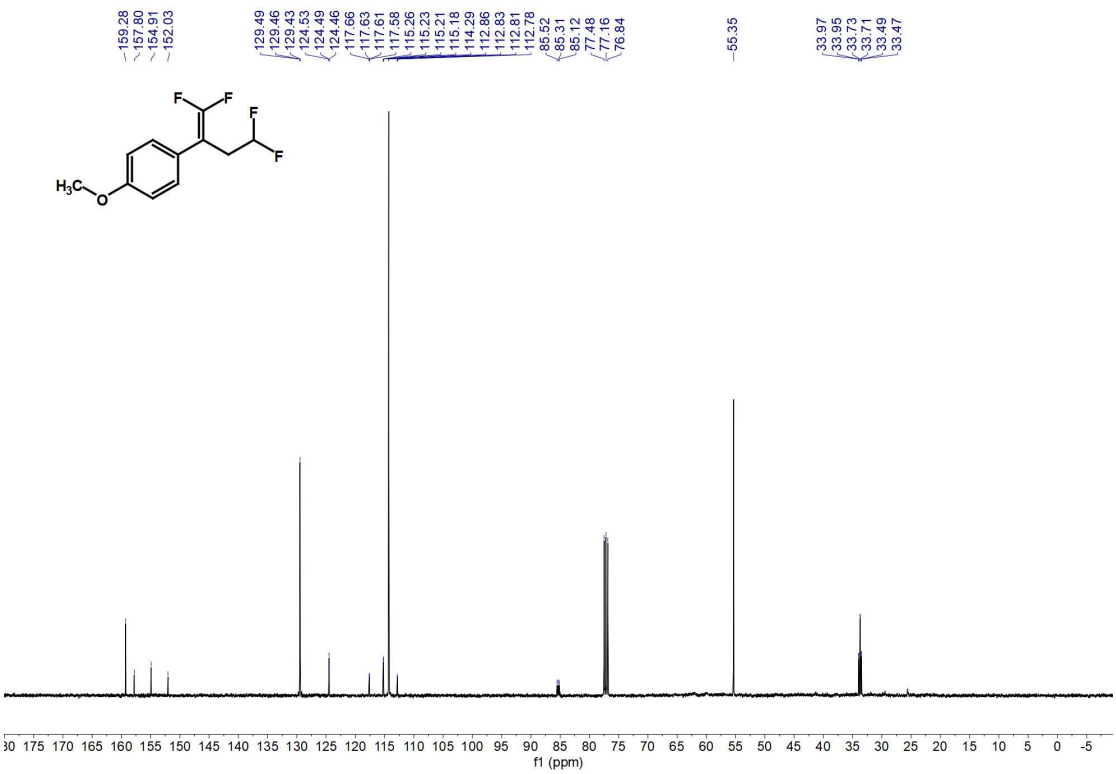





$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3b**

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124.46
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117.61
117.58
115.26
115.23
115.21
115.18
114.29
112.86
112.83
112.81
112.78
85.52
85.31
85.12
77.48
77.16
76.84
55.35
33.97
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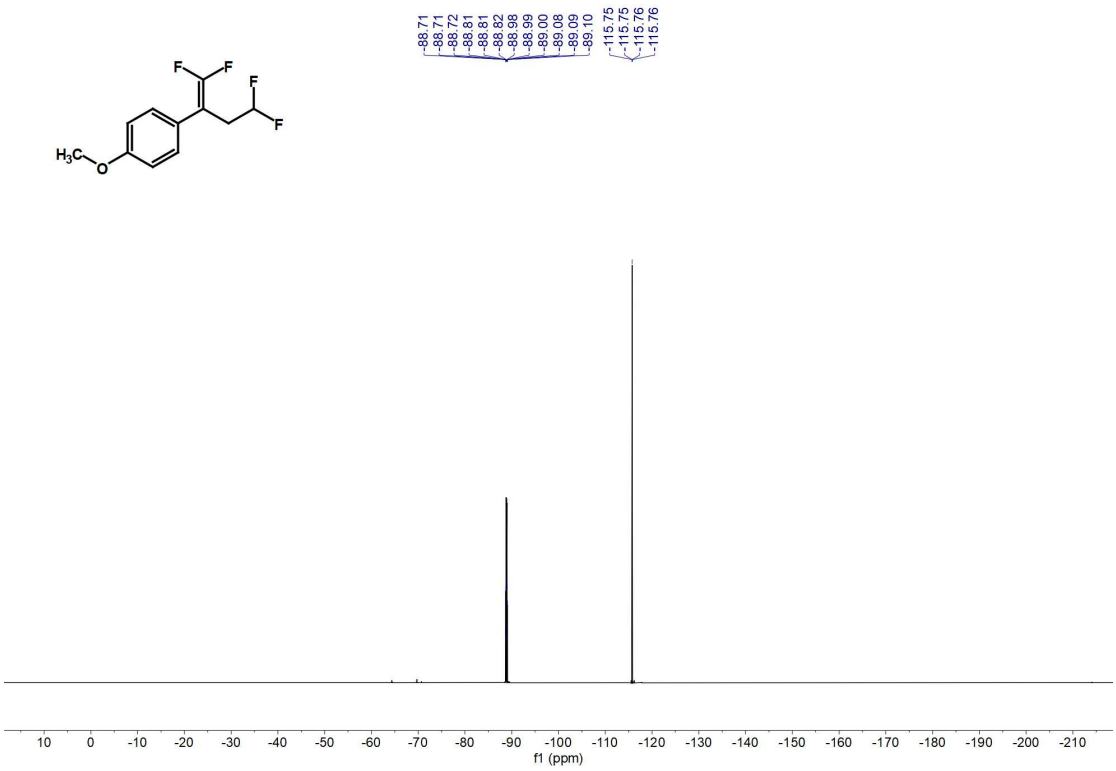
33.47
F
F
F
F
H3C
O
f1 (ppm)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-115.76
-115.76
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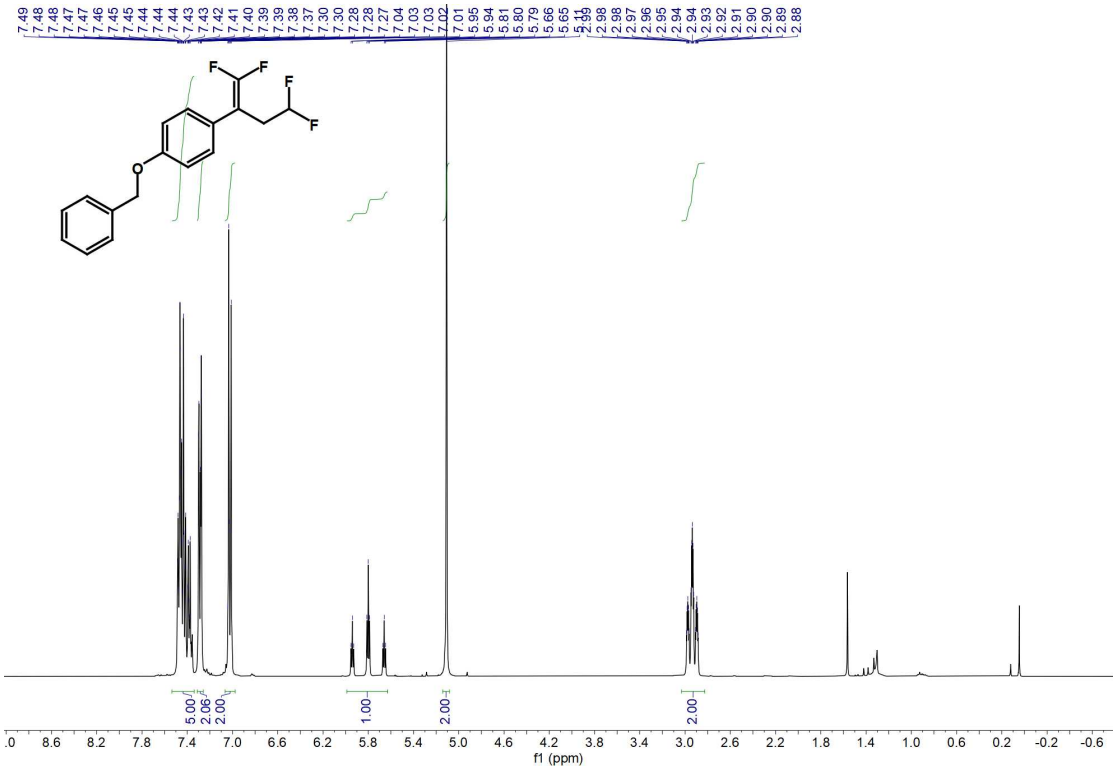
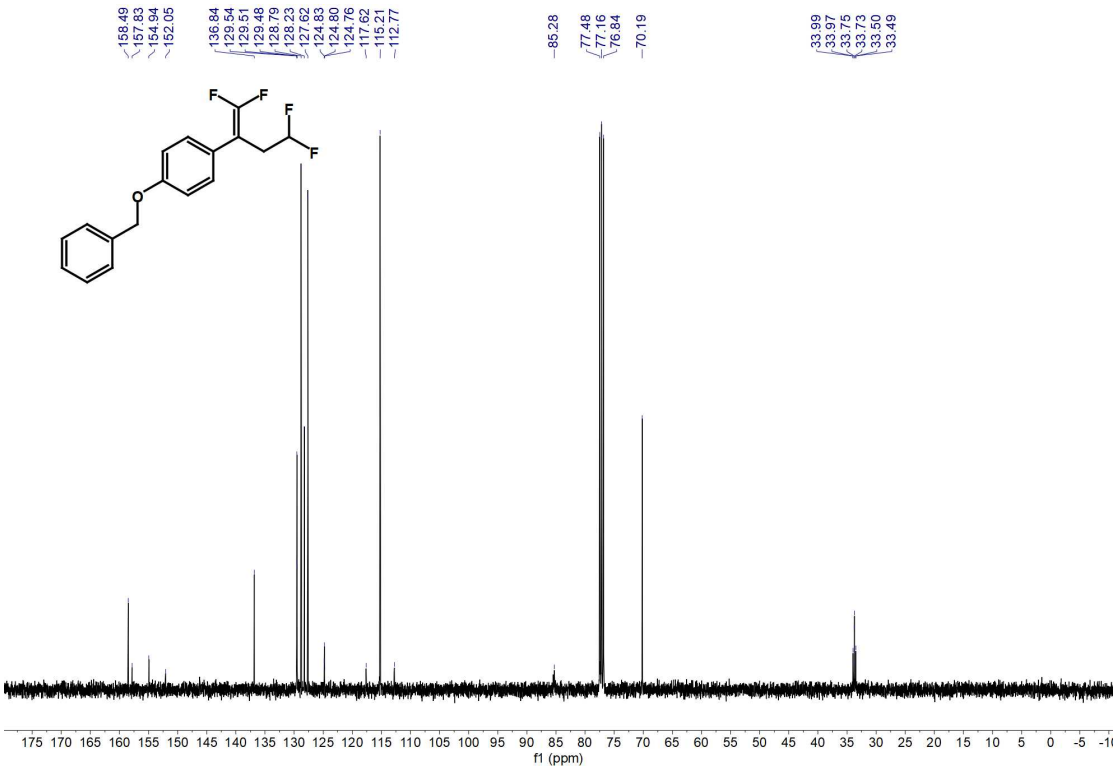
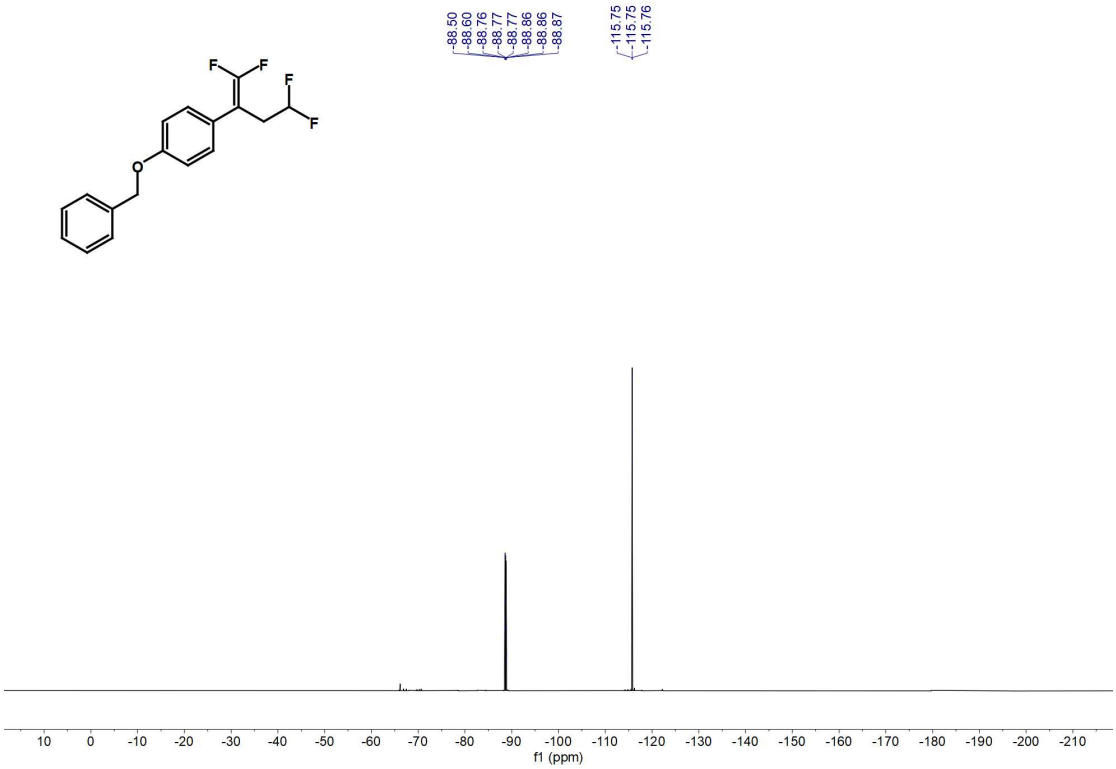
F
F
F
H3C
O
f1 (ppm)

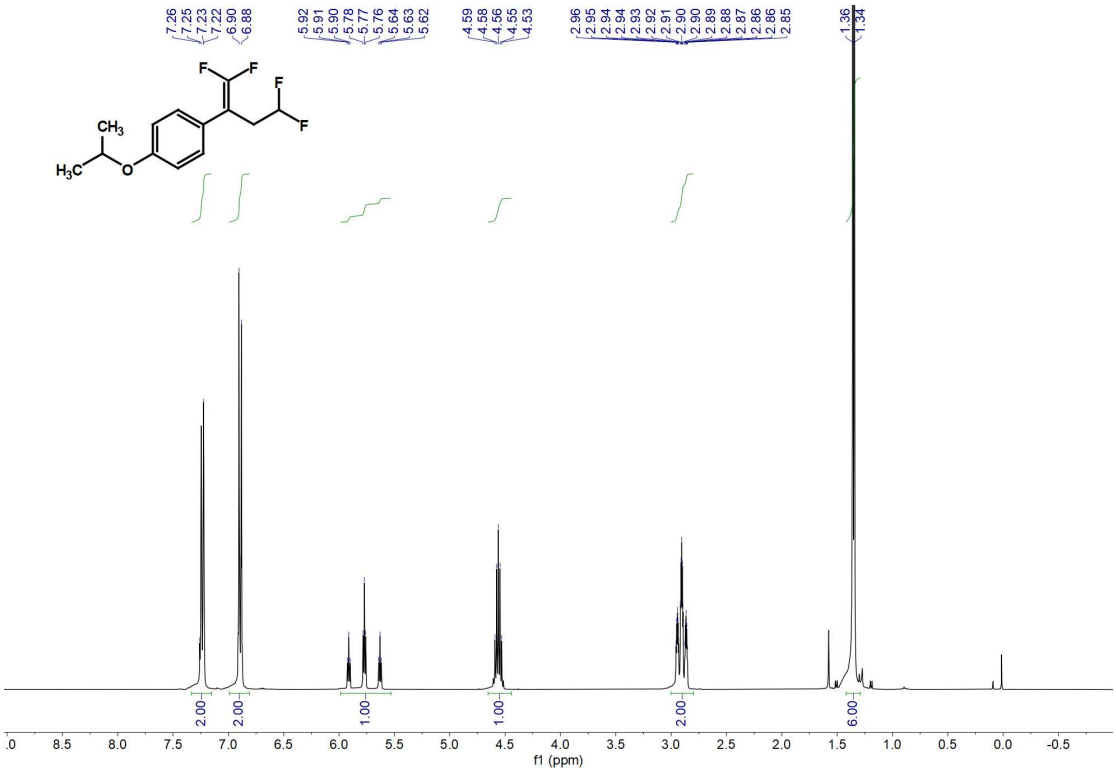
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3c**

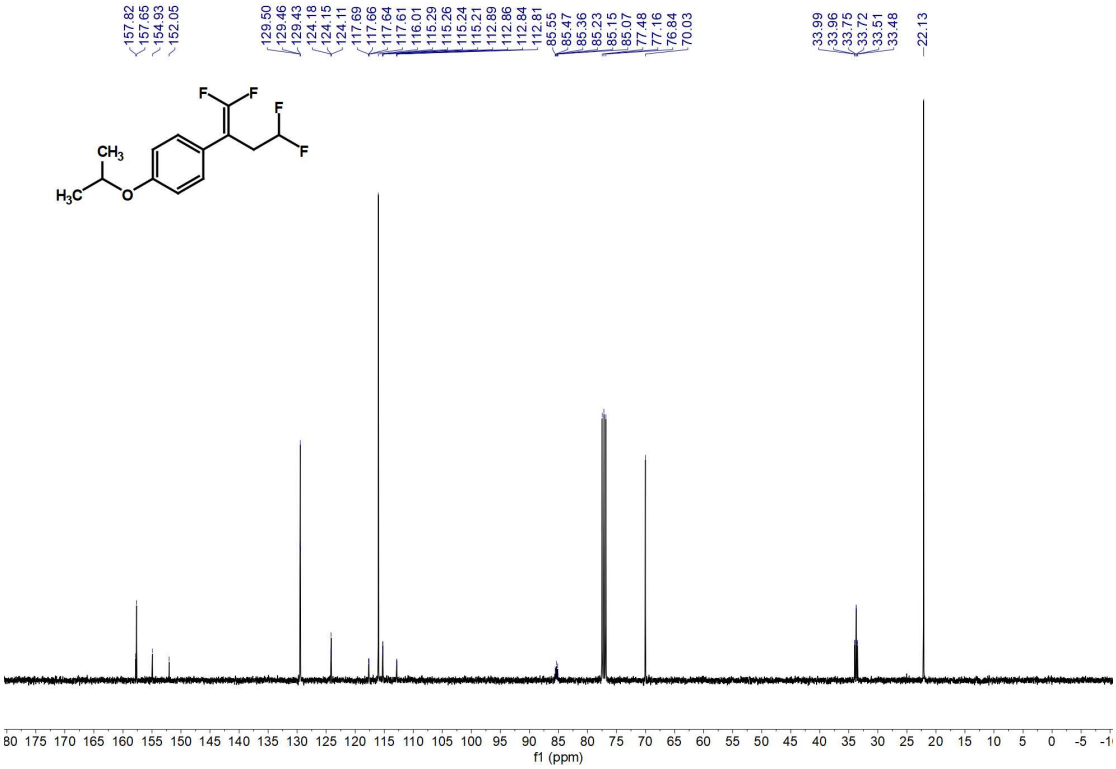





$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3d**

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112.89
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112.84
112.81
85.55
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85.23
85.15
85.07
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76.84
70.03
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H3C
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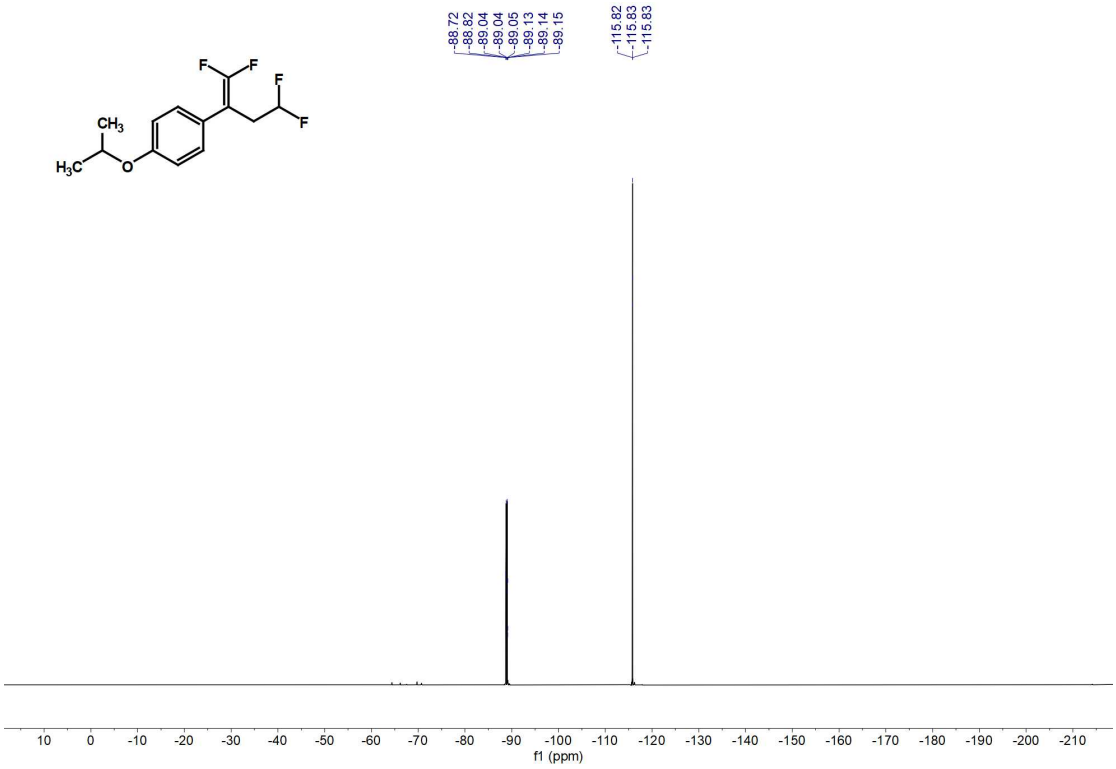
f1 (ppm)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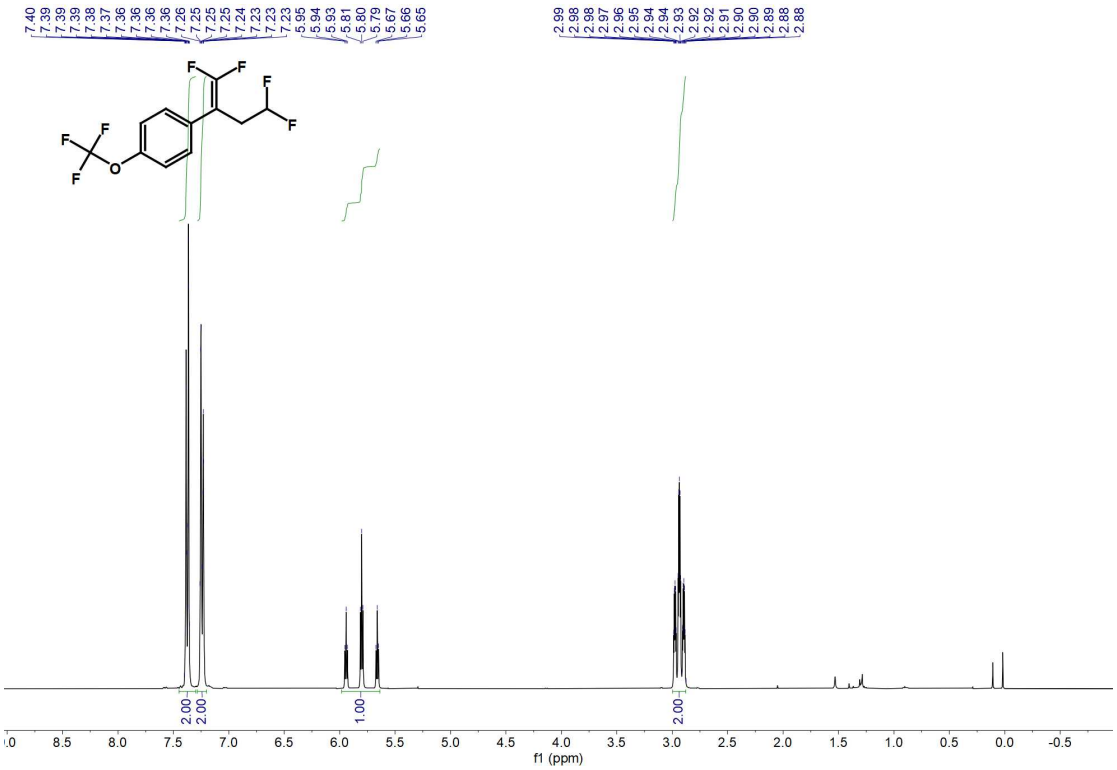
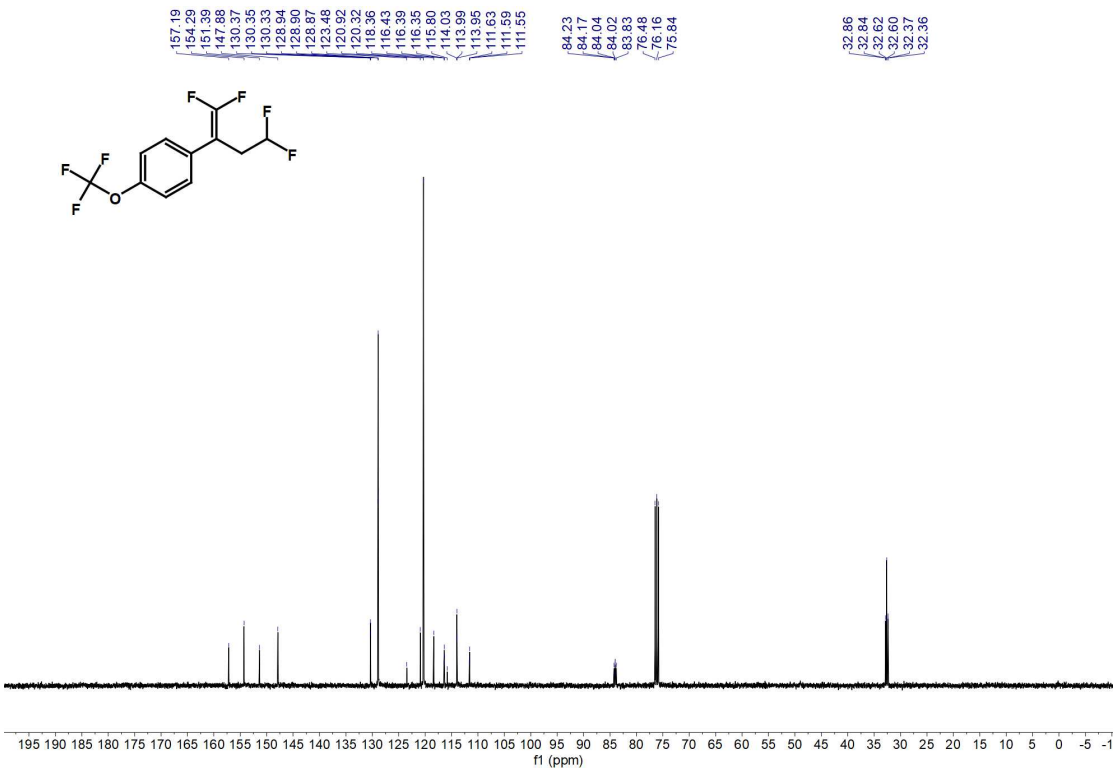
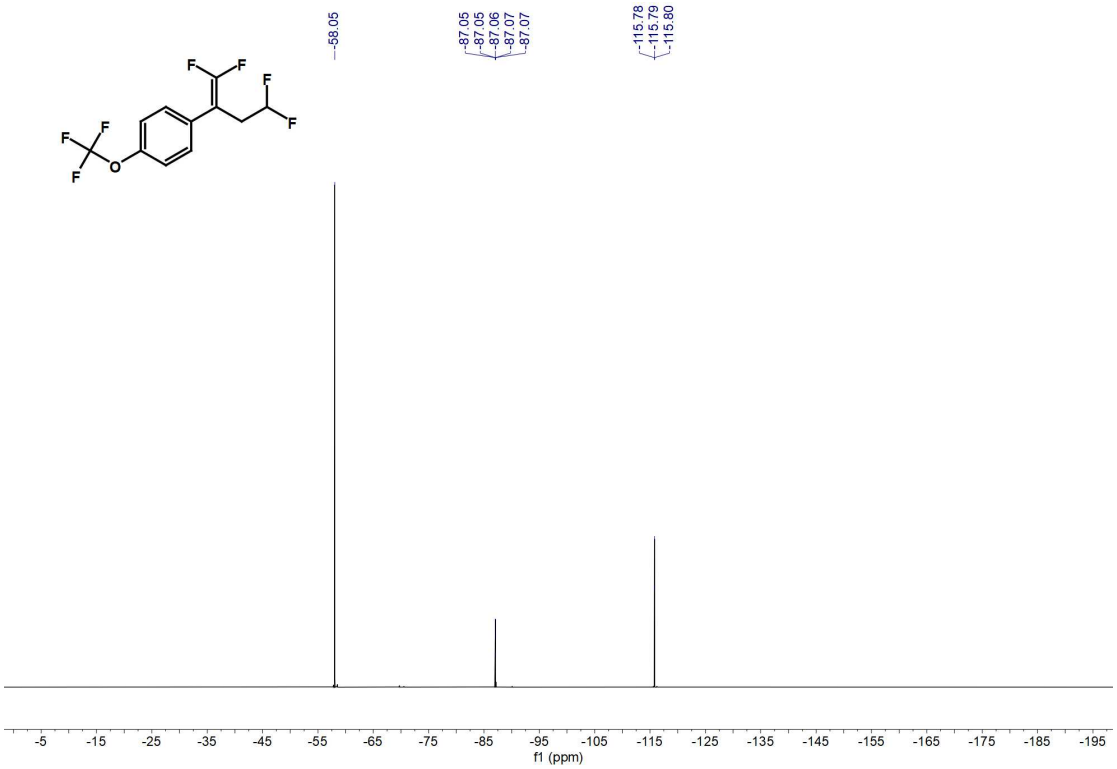
f1 (ppm)

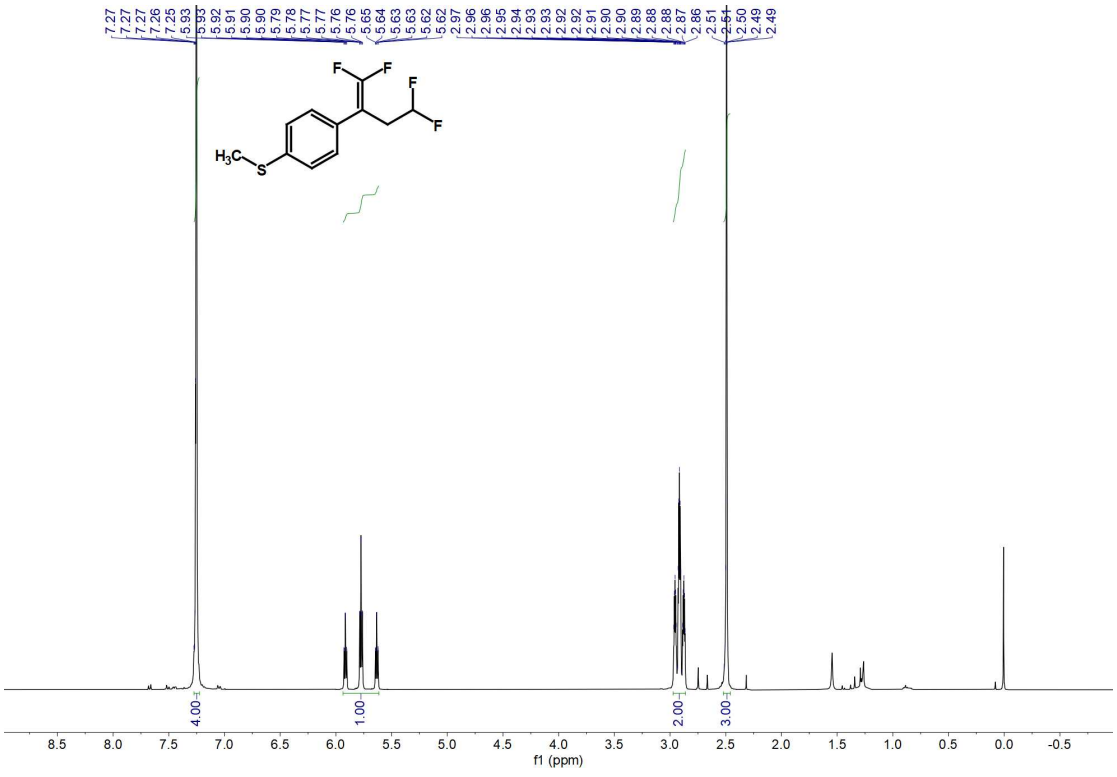
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3e**

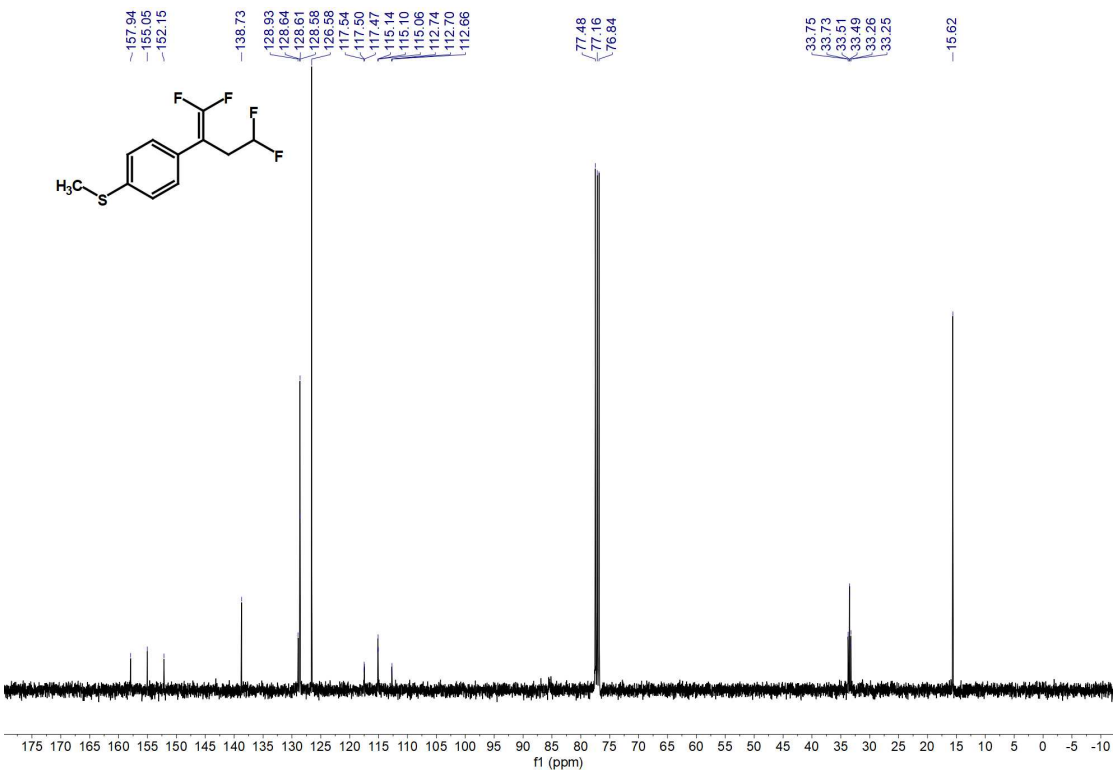





$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3f**

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77.16
76.84
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33.51
33.49
33.26
33.25
15.62
F
F
F
F
H3C
S
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10
f1 (ppm)


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-87.53
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F
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H3C
S
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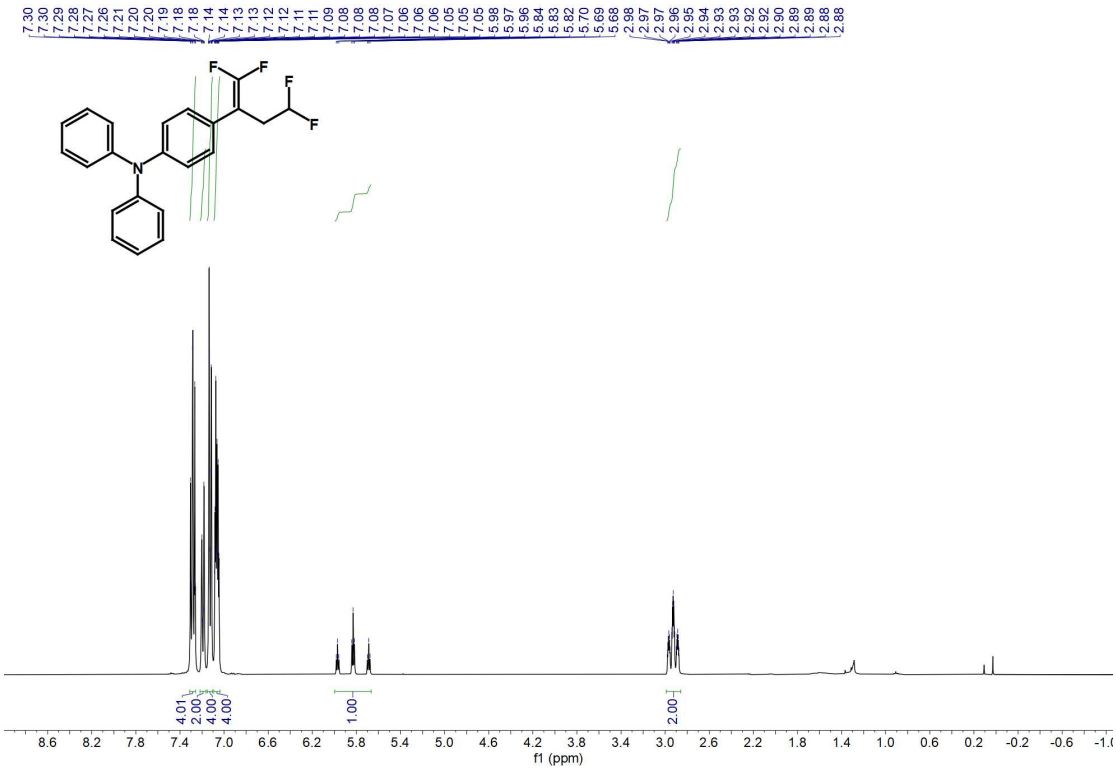
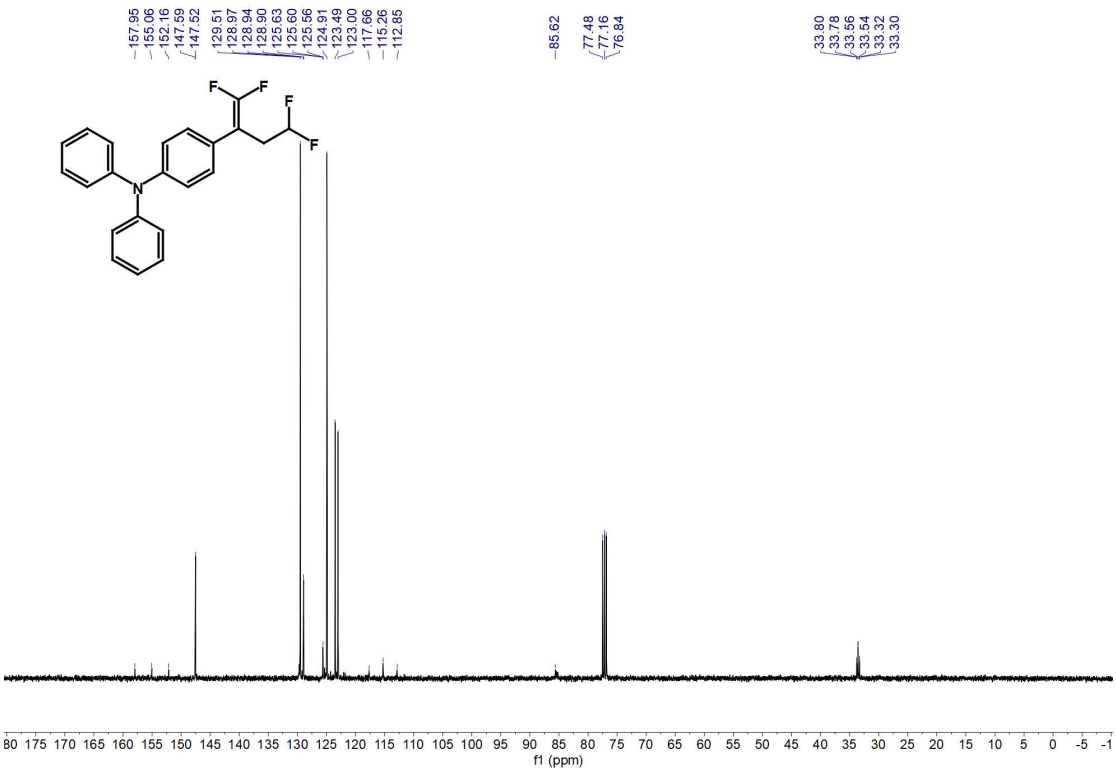
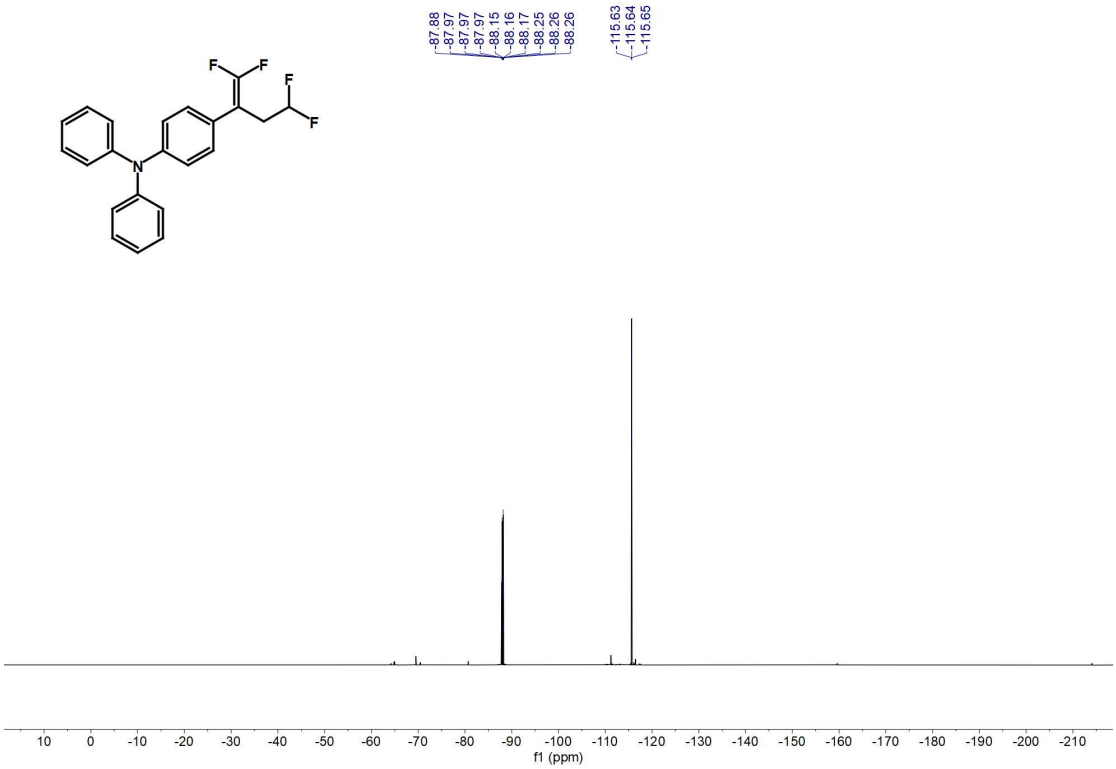
f1 (ppm)

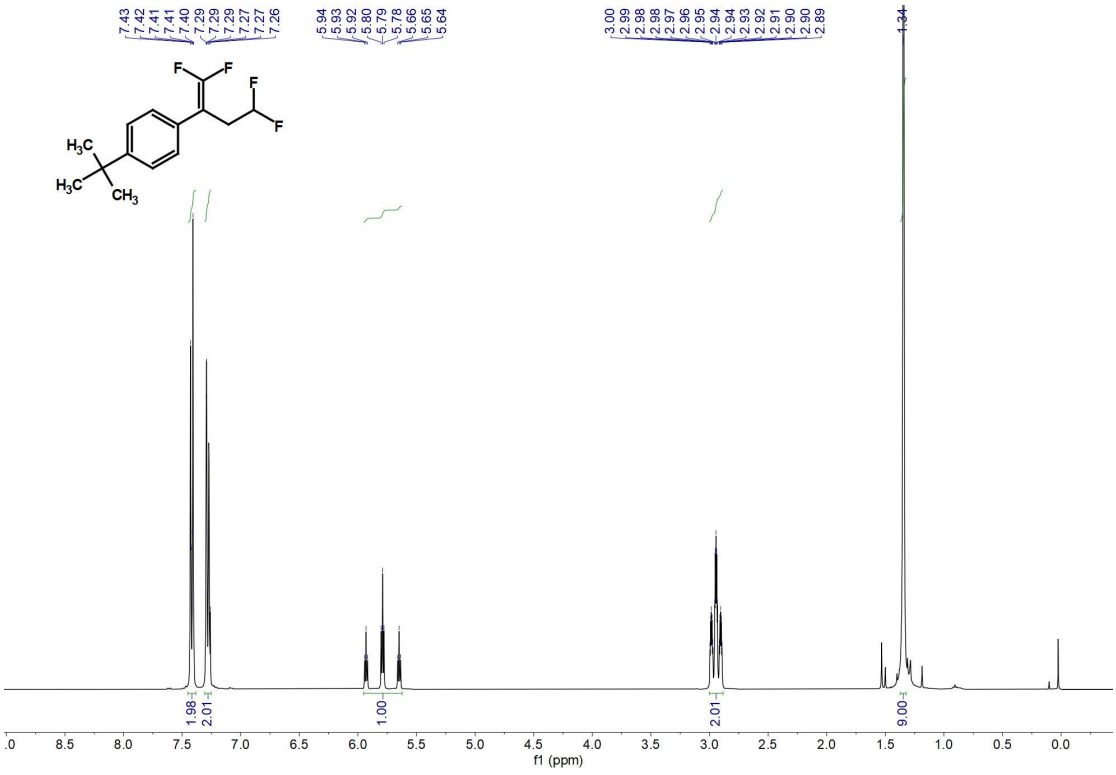
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3g**

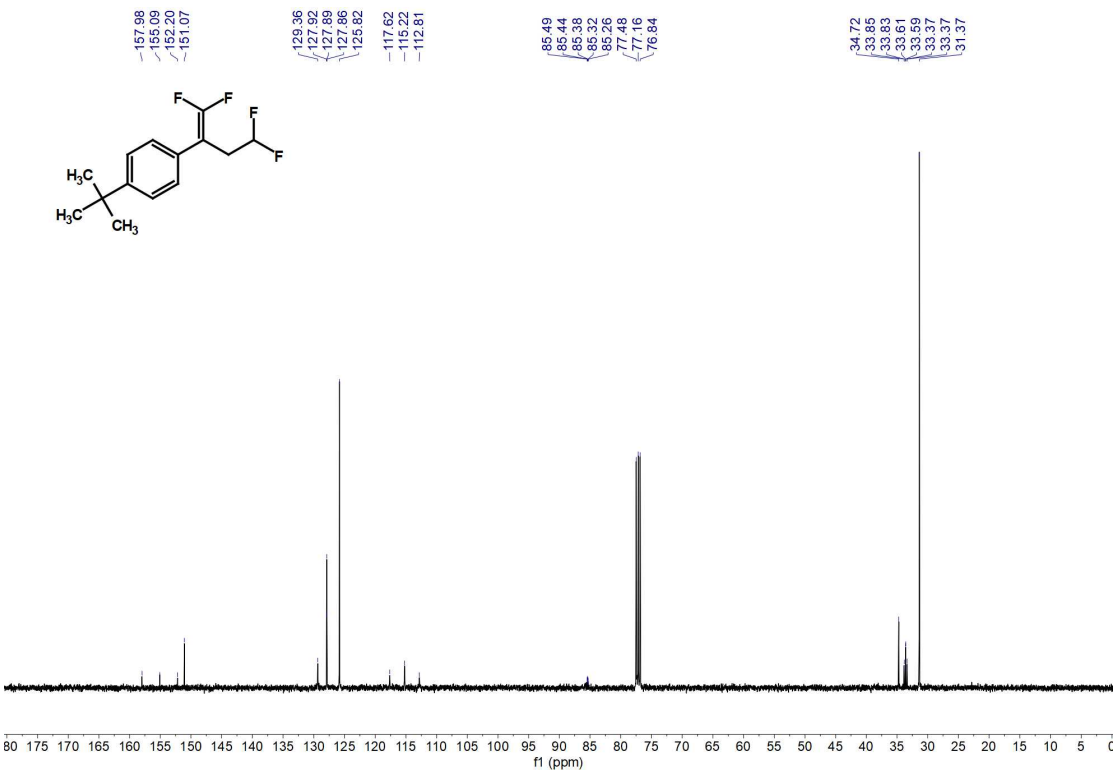




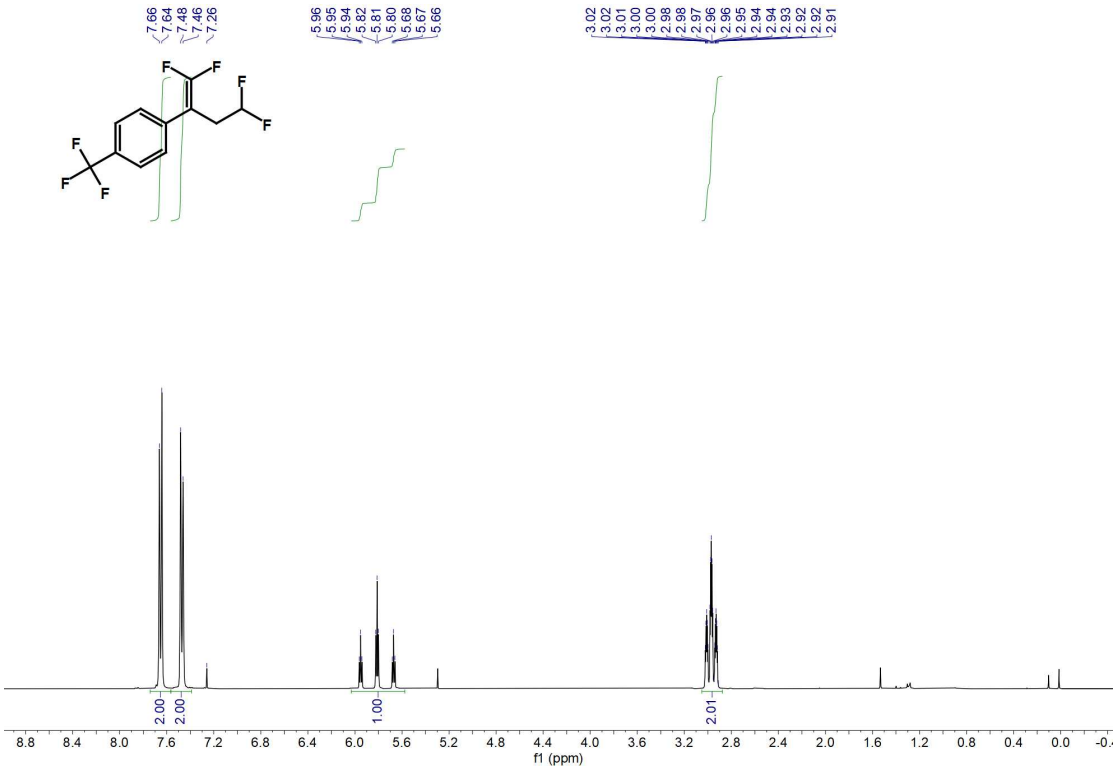

$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3h**

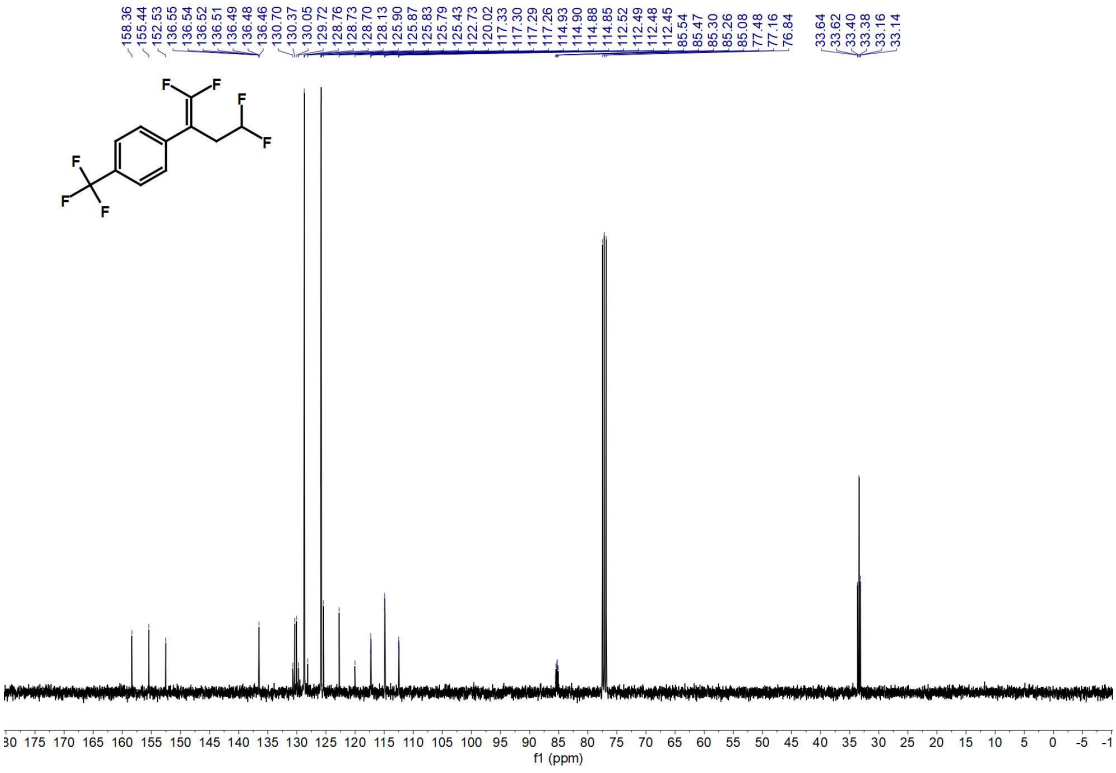


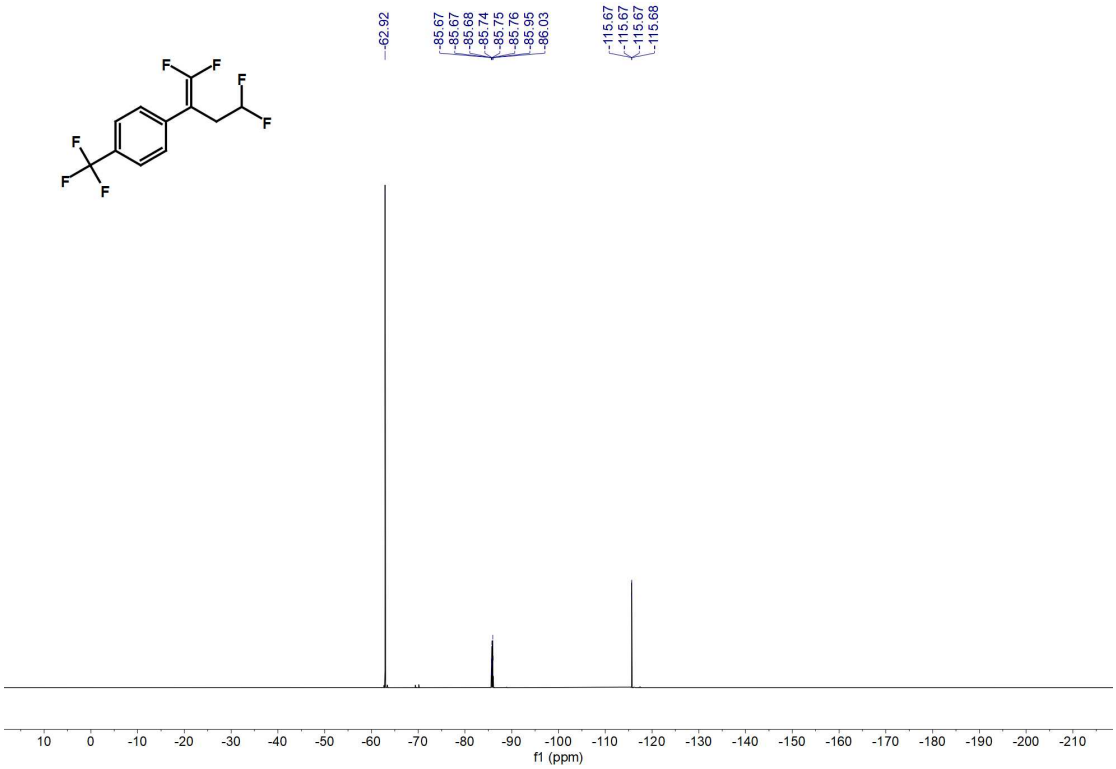

157.98
155.09
152.20
151.07
129.36
127.92
127.89
127.86
125.82
117.62
115.22
112.81
85.49
85.44
85.38
85.32
85.26
77.48
77.16
76.84
34.72
33.85
33.83
33.61
33.59
33.37
33.37
31.37
F
F
F
F
H3C
H3C
CH3
f1 (ppm)


-87.88
-87.98
-88.09
-88.09
-88.10
-88.18
-88.19
-115.82
-115.82
-115.83
F
F
F
F
H3C
H3C
CH3
f1 (ppm)

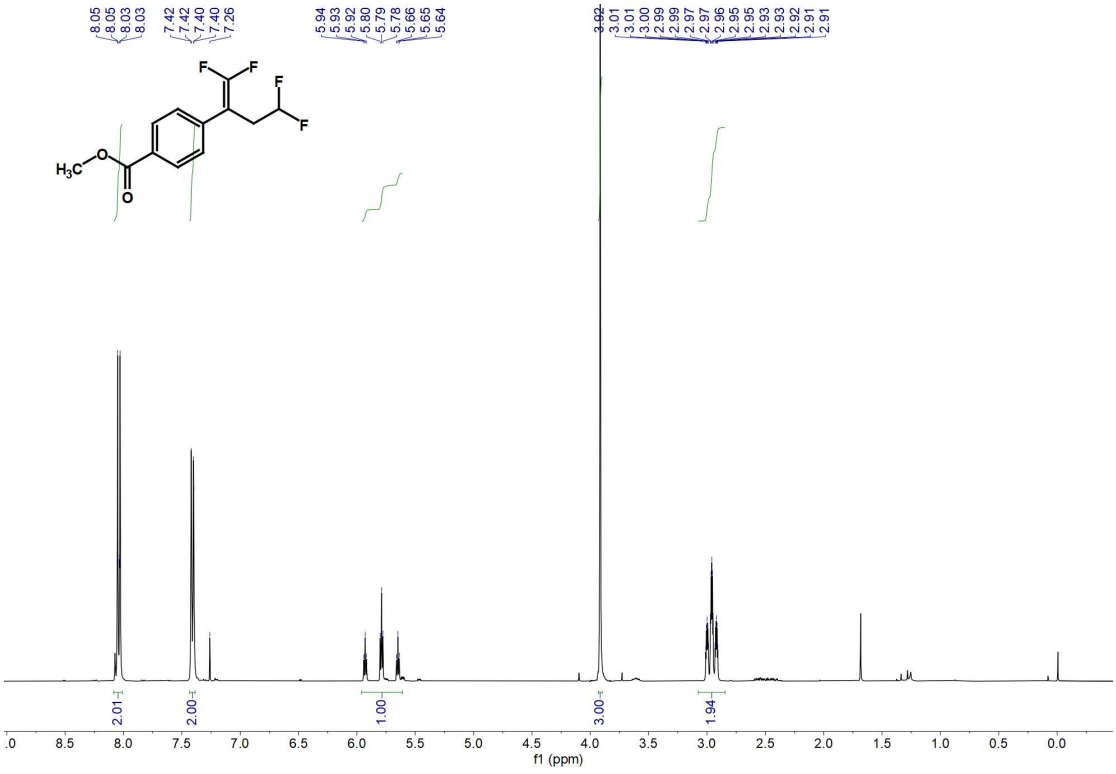
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3i**

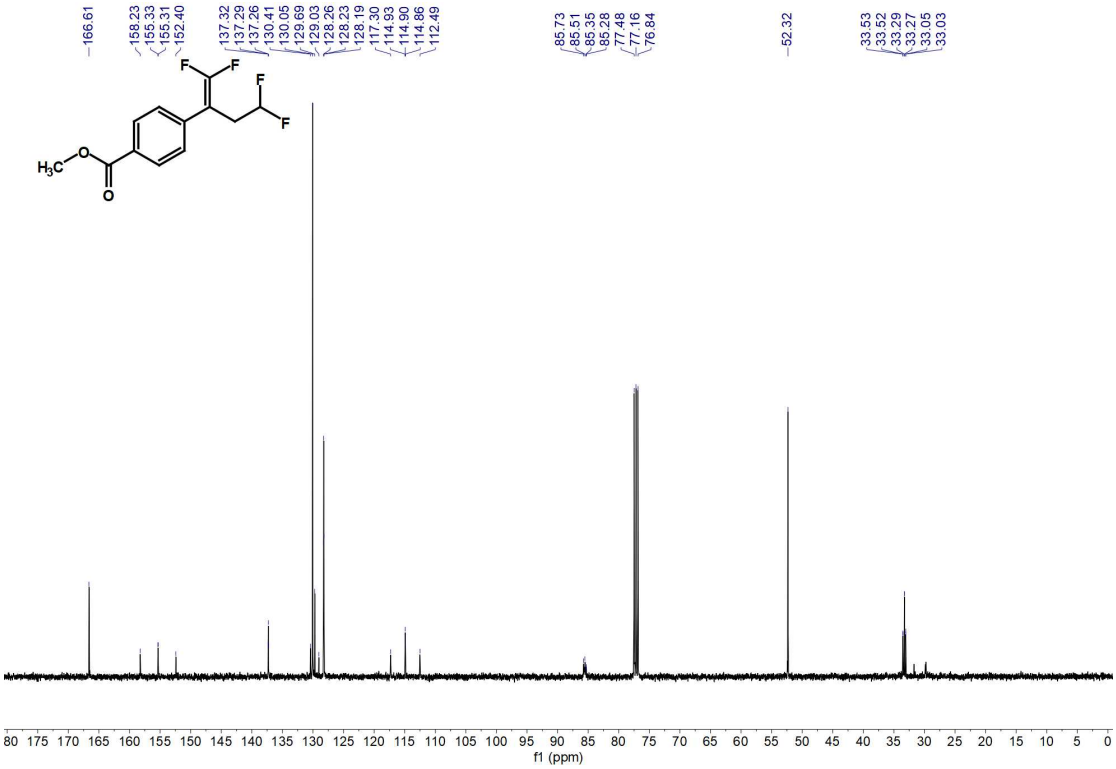


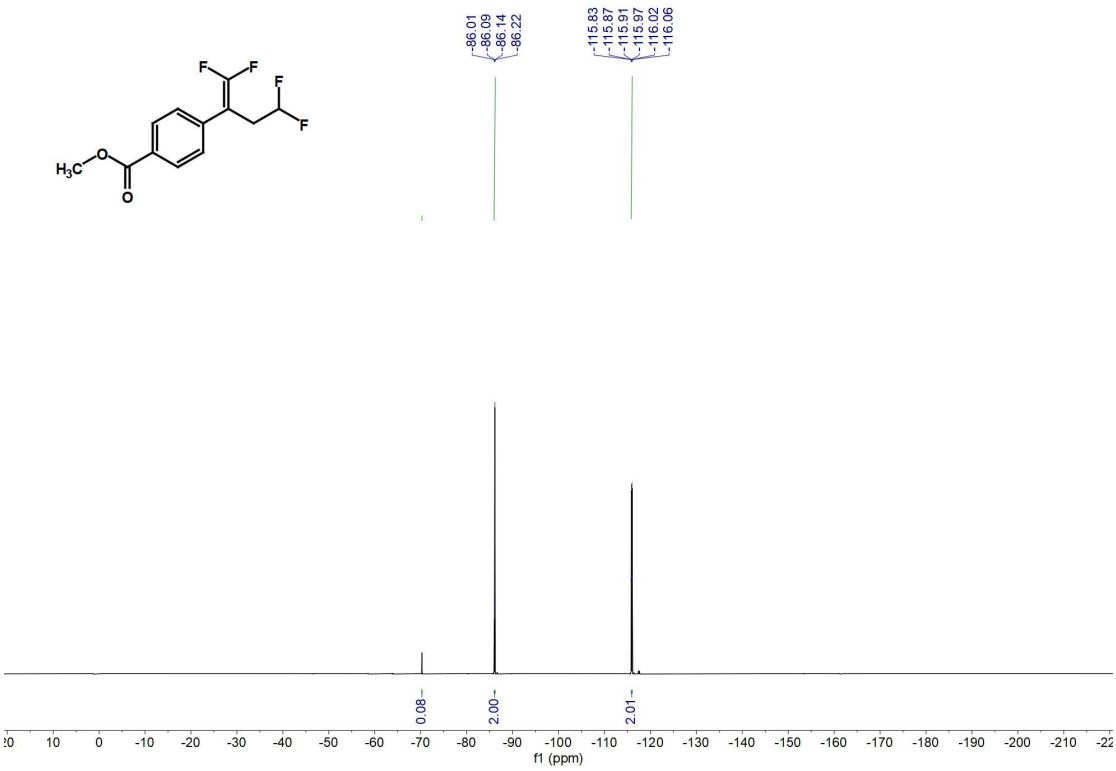





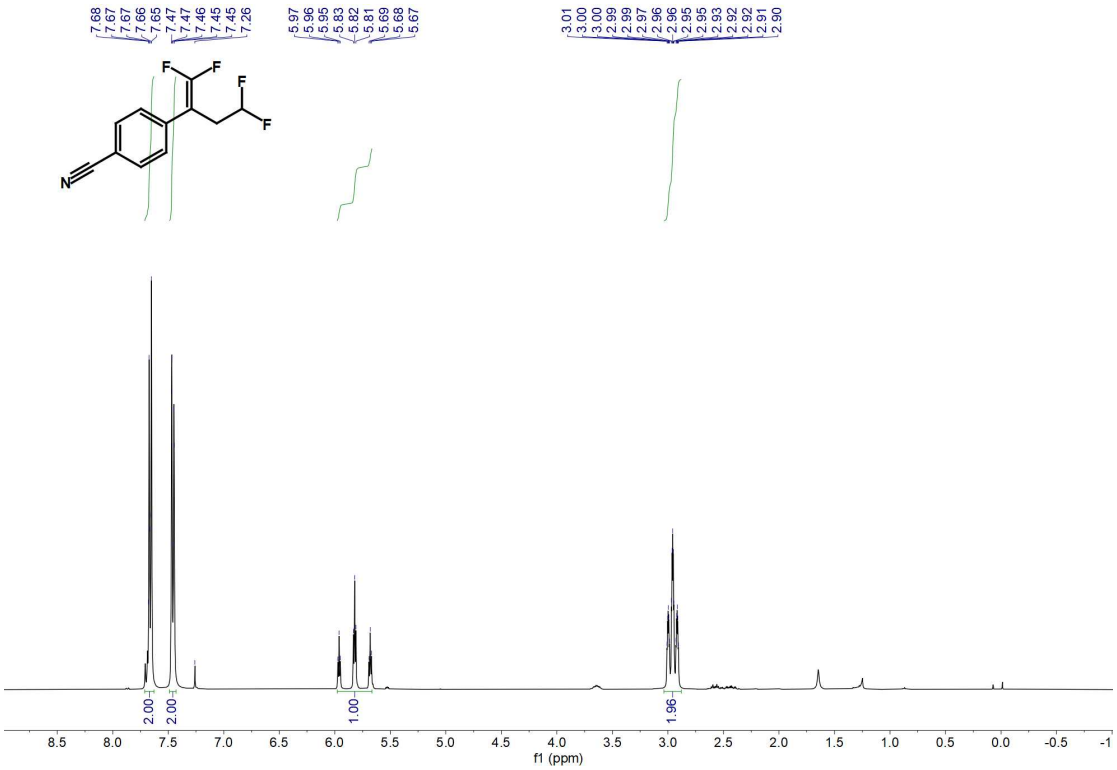

$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3j**

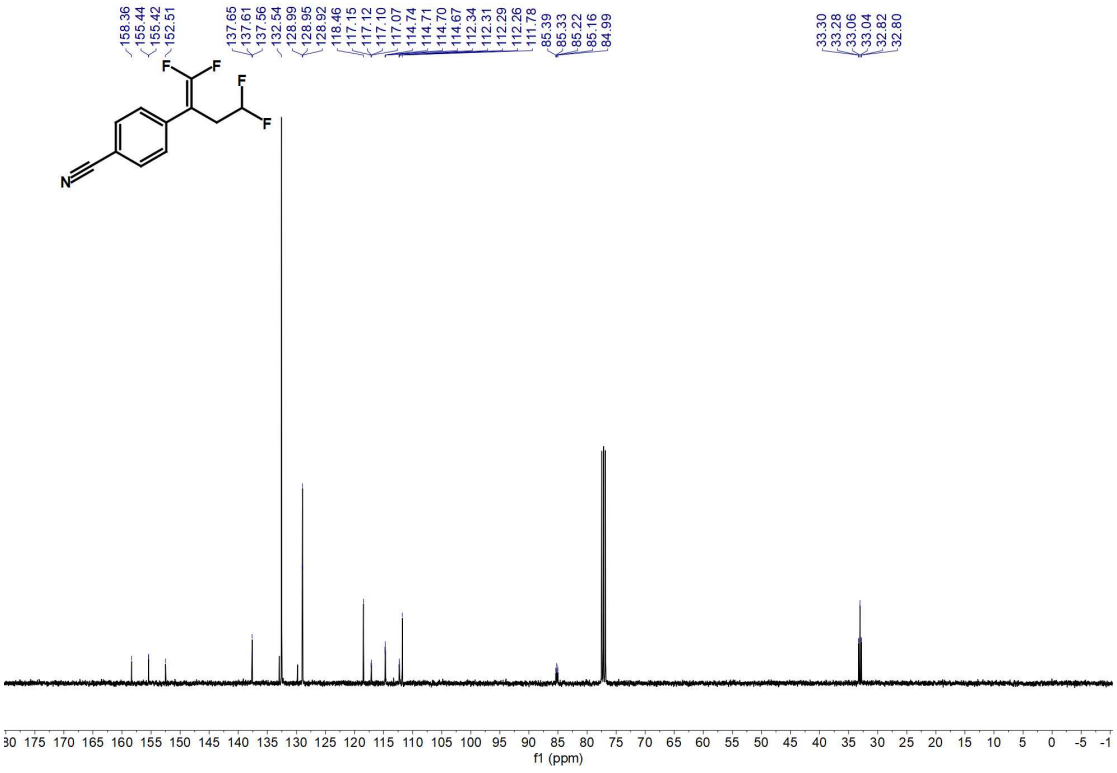


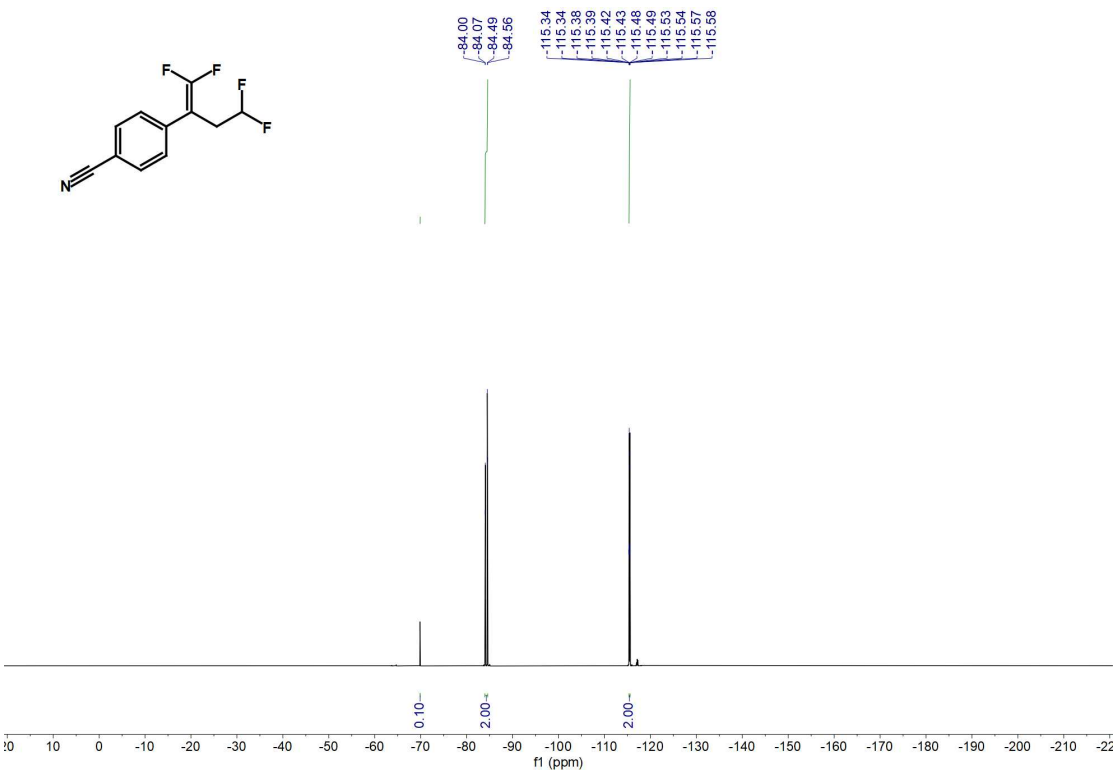

166.61
158.23
155.33
155.31
152.40
137.32
137.29
137.26
130.41
130.05
129.69
129.03
128.26
128.23
128.19
117.30
114.93
114.90
114.86
114.49
85.73
85.51
85.35
85.28
77.48
77.16
76.84
52.32
33.53
33.52
33.29
33.27
33.05
33.03
F
F
F
F
O
O
H3C
f1 (ppm)


86.01
86.09
86.14
86.22
115.83
115.87
115.91
115.97
116.02
116.06
F
F
F
F
O
O
H3C
0.08
2.00
2.01
f1 (ppm)

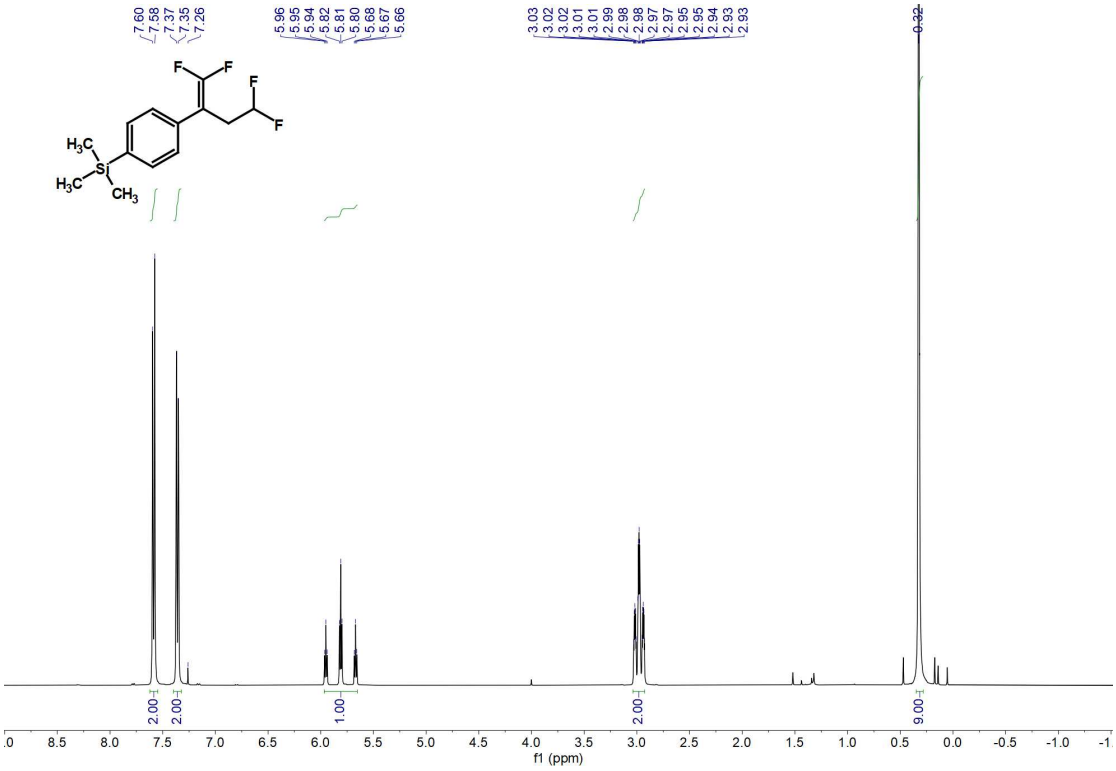
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3k**

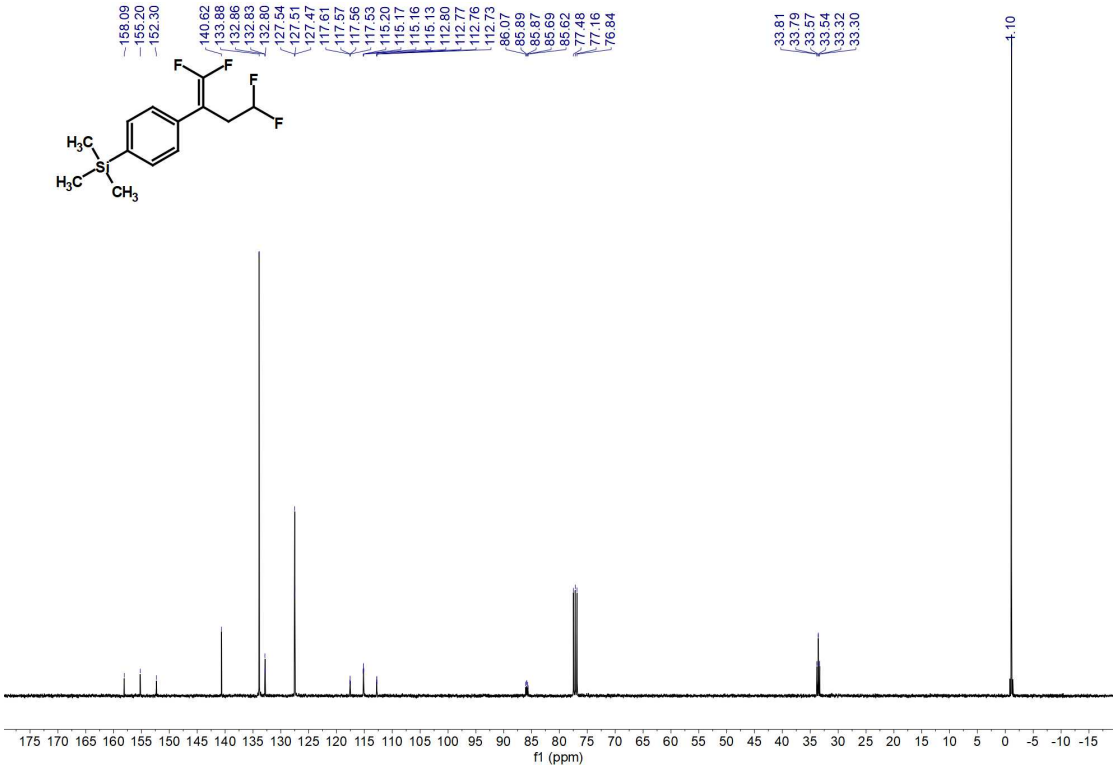


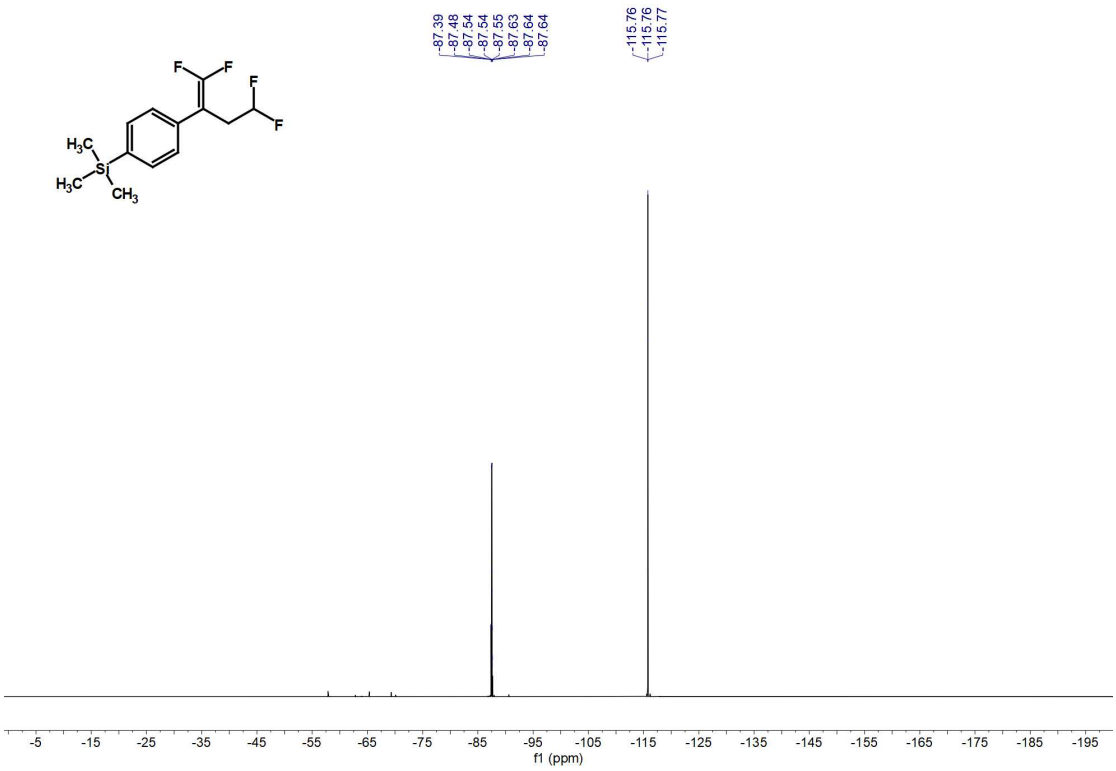





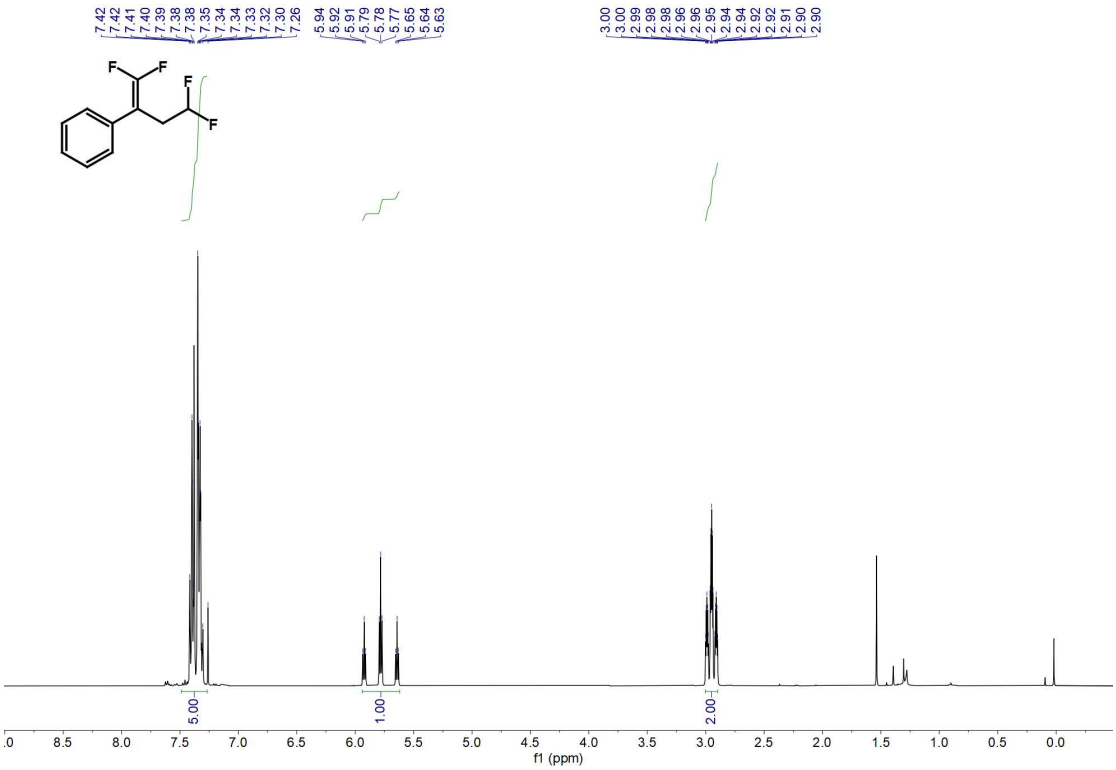

$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3l**

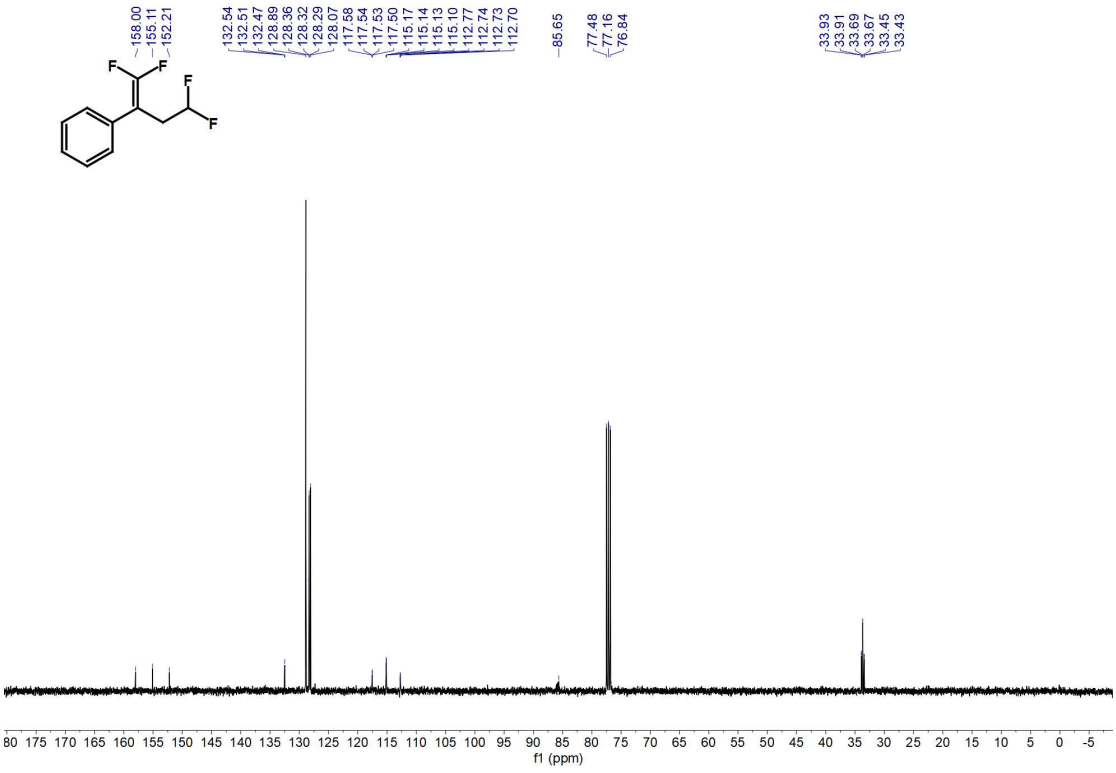


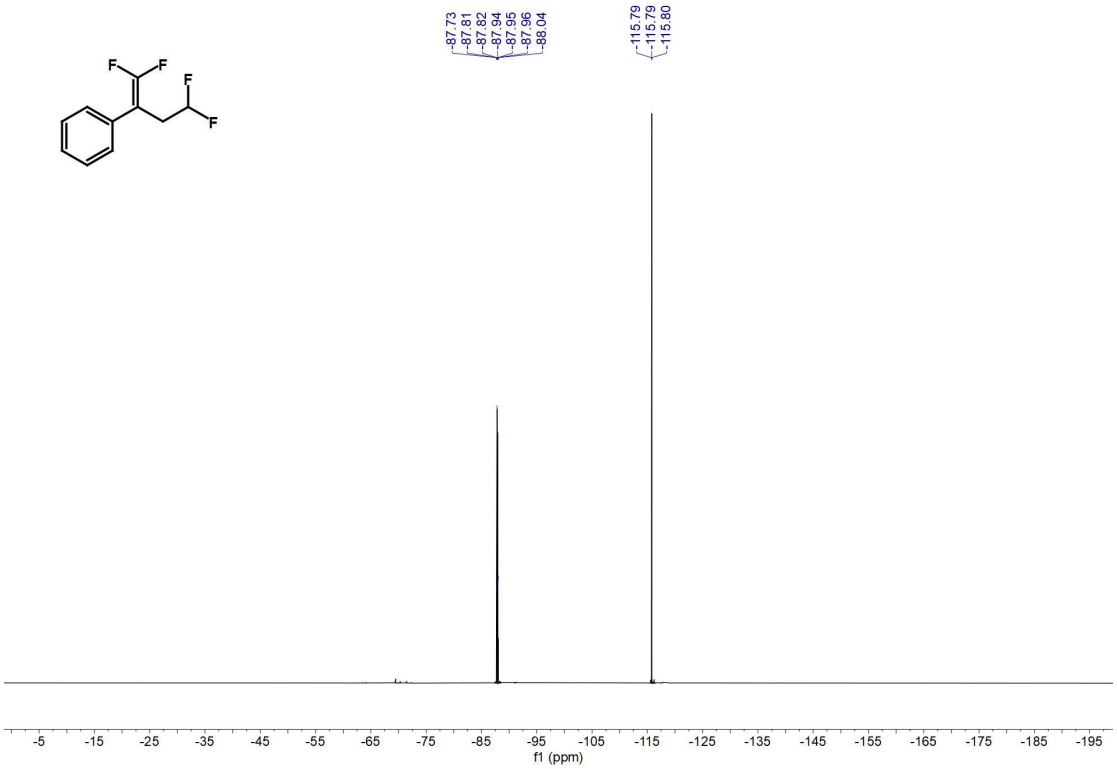

158.09
155.20
152.30
140.62
133.88
132.86
132.83
132.80
127.54
127.51
127.47
117.61
117.57
117.56
117.53
115.20
115.17
115.16
115.13
112.80
112.77
112.76
112.73
86.07
85.89
85.87
85.69
85.62
77.48
77.16
76.84
33.81
33.79
33.57
33.54
33.32
33.30
1.10
F
F
F
F
H3C
Si
H3C
CH3
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15
f1 (ppm)


-87.39
-87.48
-87.54
-87.54
-87.55
-87.63
-87.64
-87.64
-115.76
-115.76
-115.77
F
F
F
F
H3C
Si
H3C
CH3
-5 -15 -25 -35 -45 -55 -65 -75 -85 -95 -105 -115 -125 -135 -145 -155 -165 -175 -185 -195
f1 (ppm)

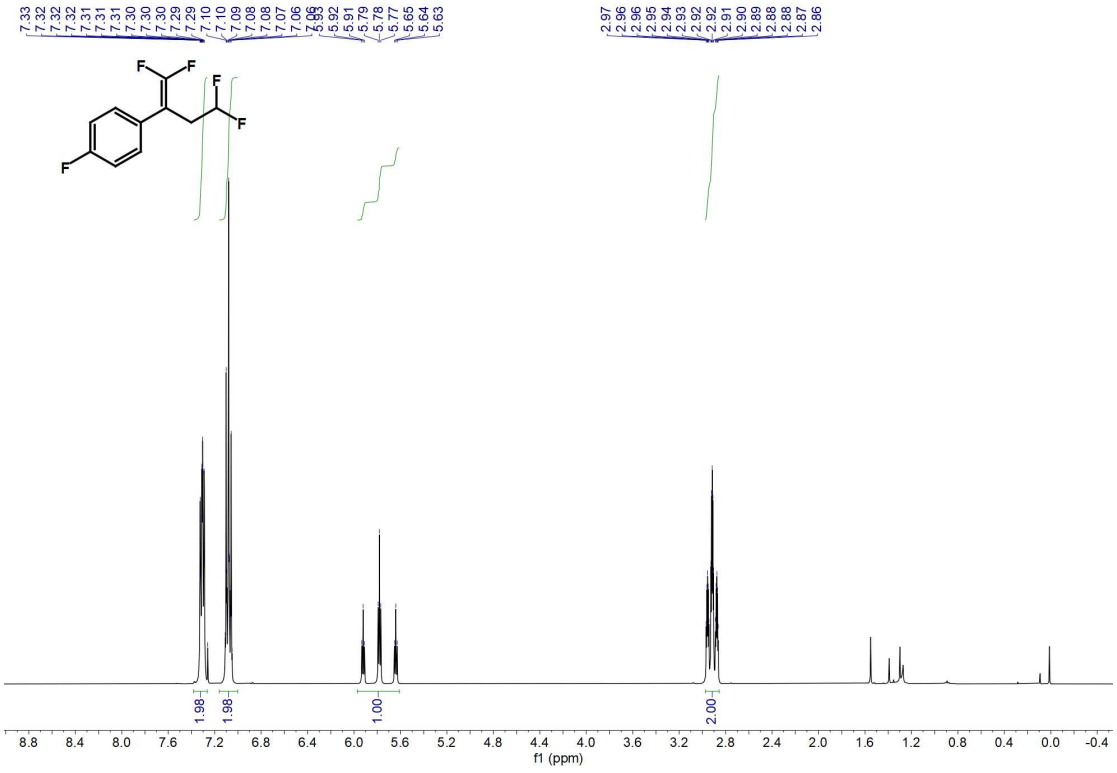
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3m**

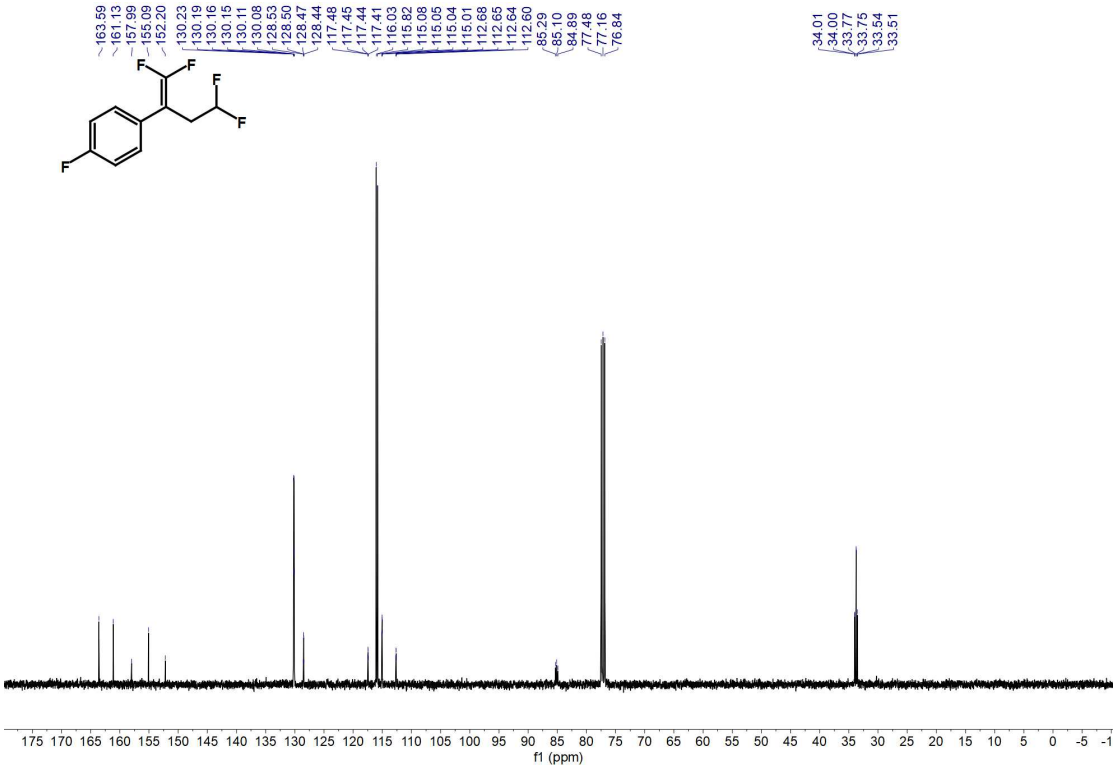





$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3n**




163.59
161.13
157.99
155.09
152.20
130.23
130.19
130.16
130.15
130.11
130.08
128.53
128.50
128.47
128.44
117.48
117.45
117.44
117.41
116.03
115.82
115.08
115.05
115.04
115.01
112.68
112.65
112.64
112.60
85.29
85.10
84.89
77.48
77.16
76.84
34.01
34.00
33.77
33.75
33.54
33.51
F
F
F
F
F
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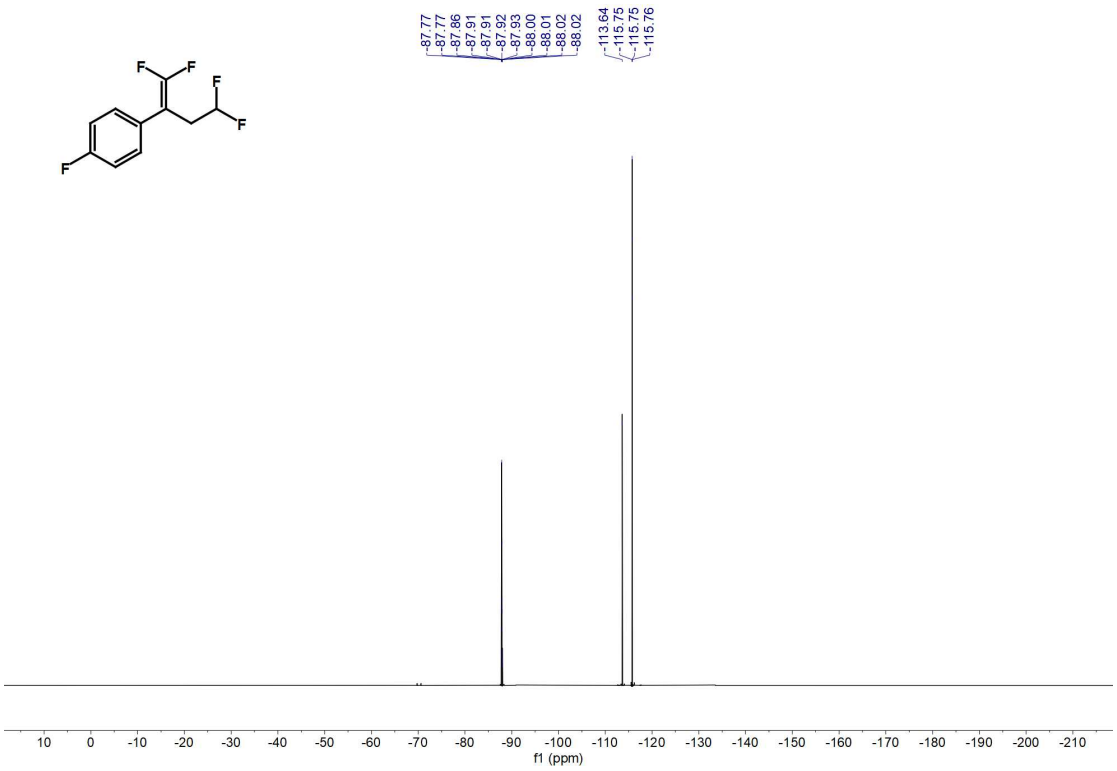
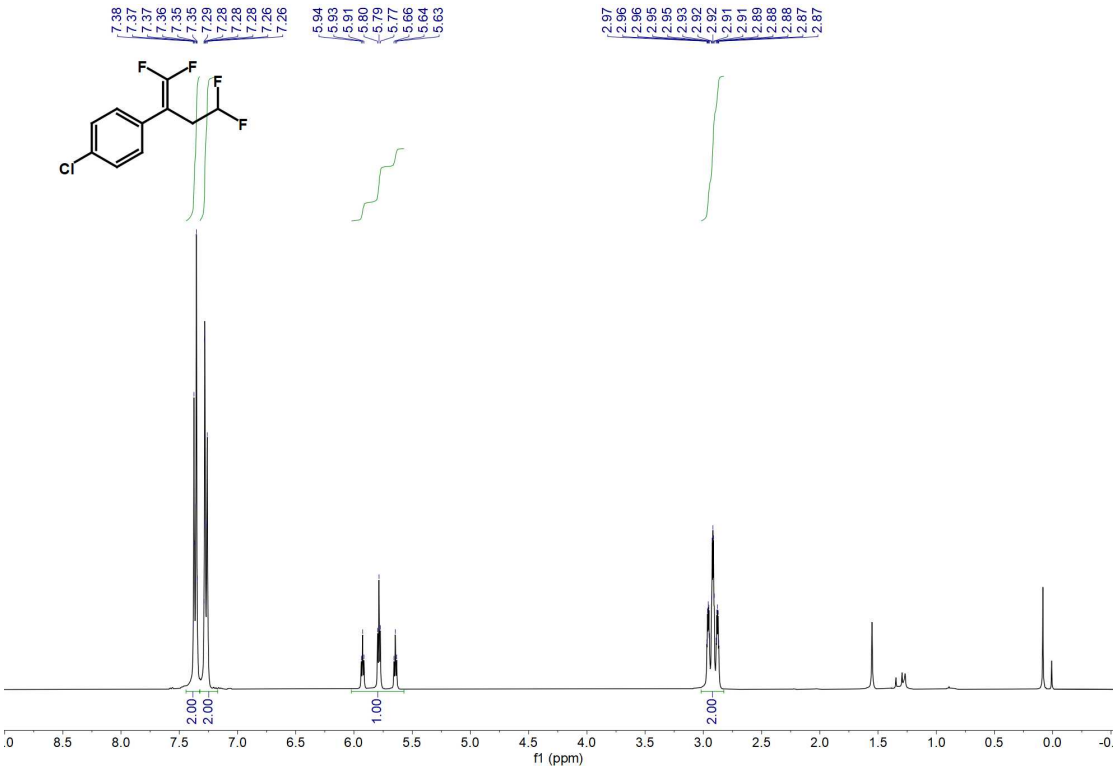
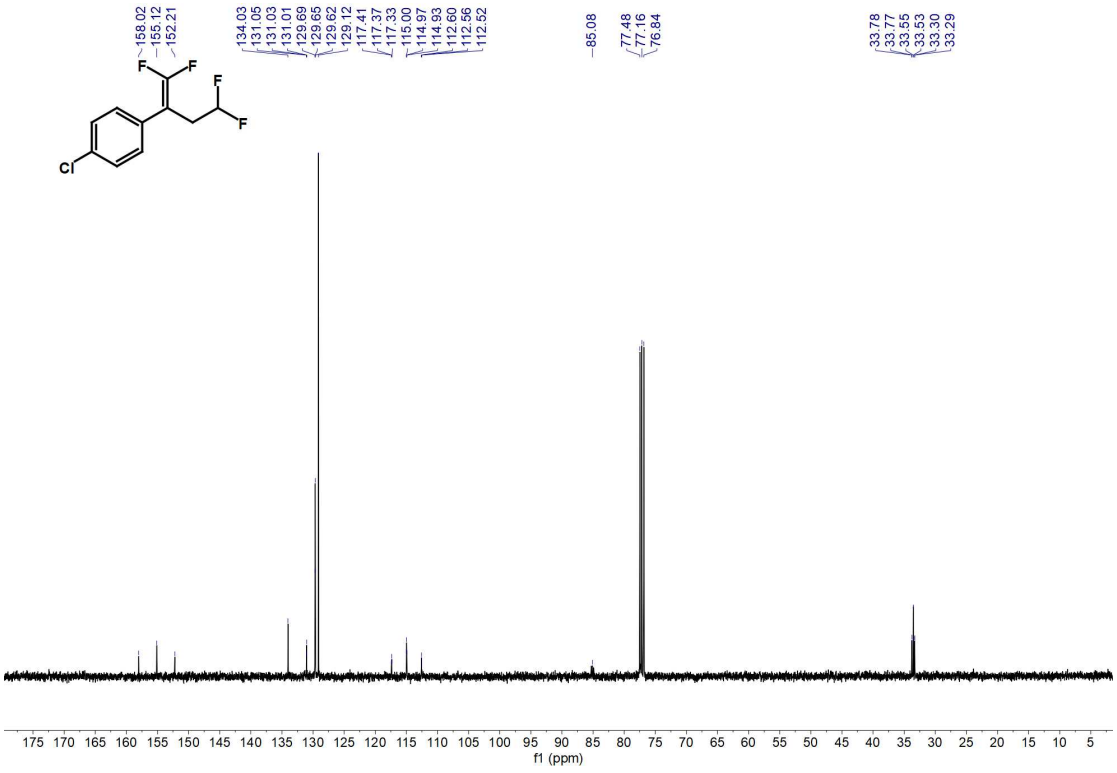
f1 (ppm)

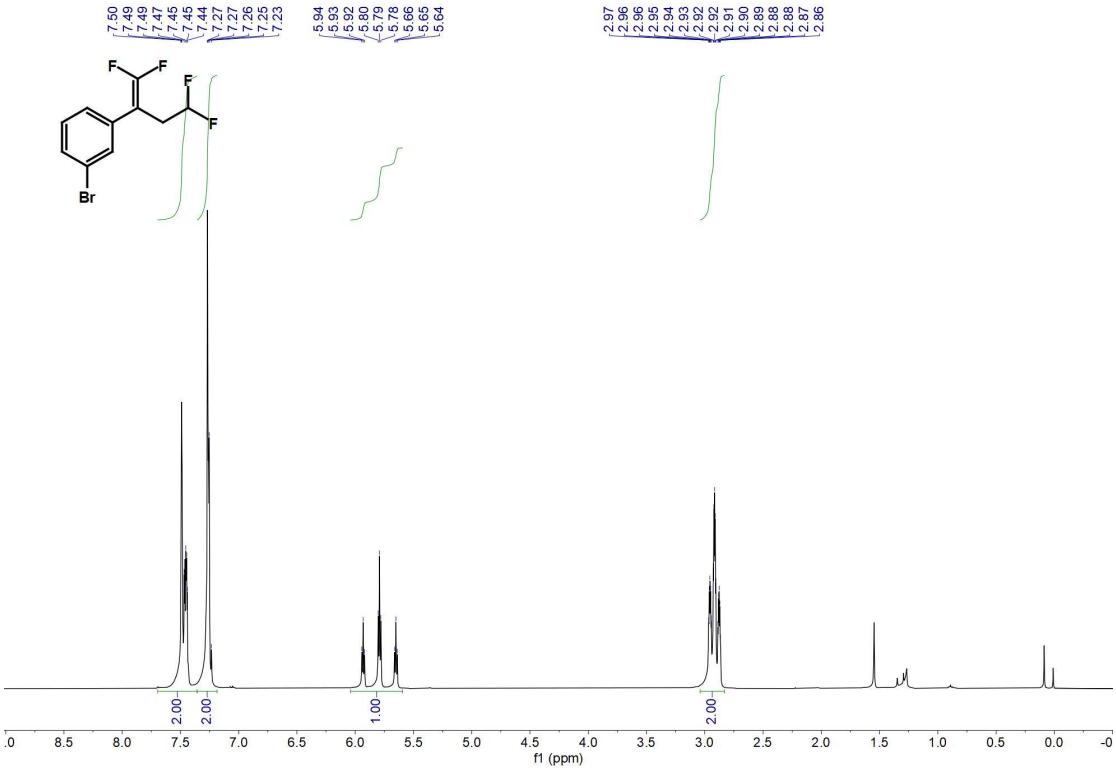

-87.77
-87.77
-87.86
-87.91
-87.91
-87.92
-87.93
-88.00
-88.01
-88.02
-88.02
-113.64
-115.75
-115.75
-115.76
F
F
F
F
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

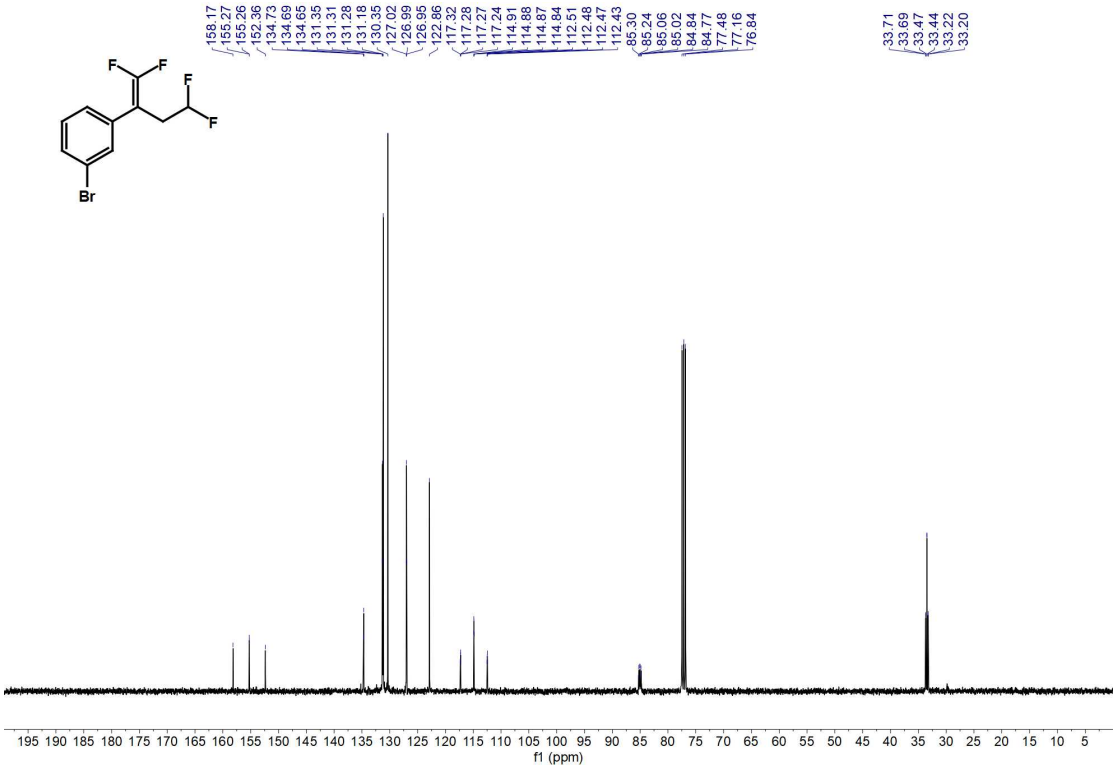
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3o**



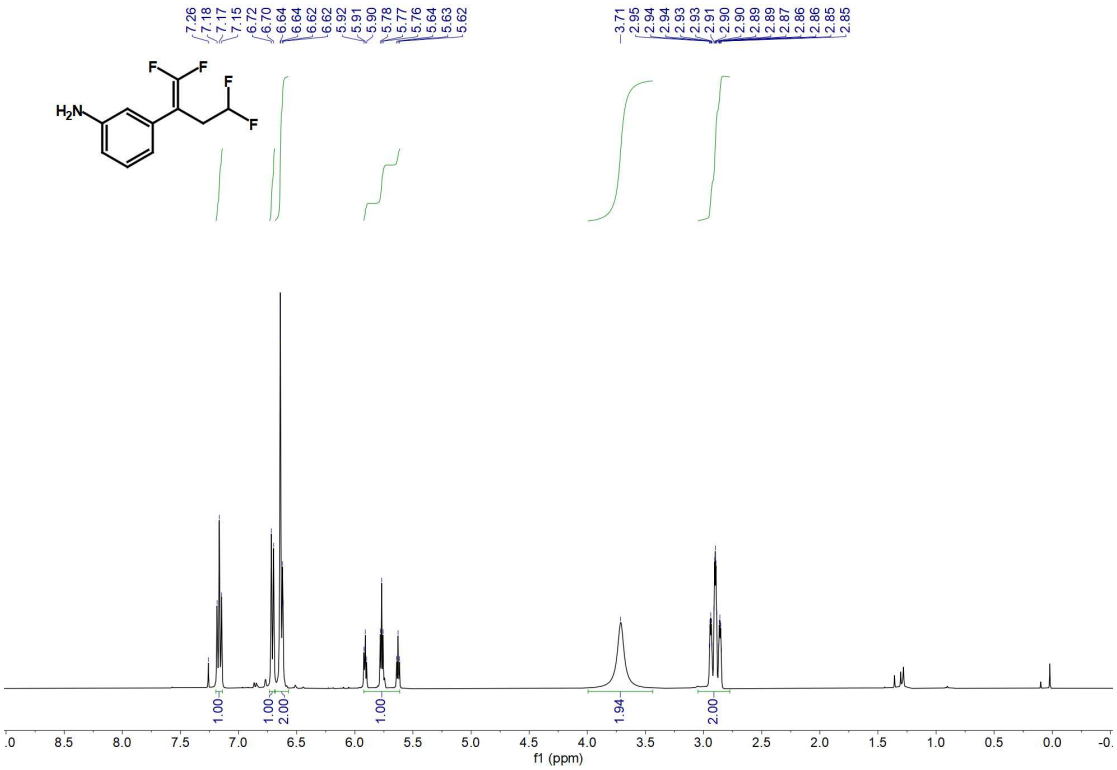

$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3p**

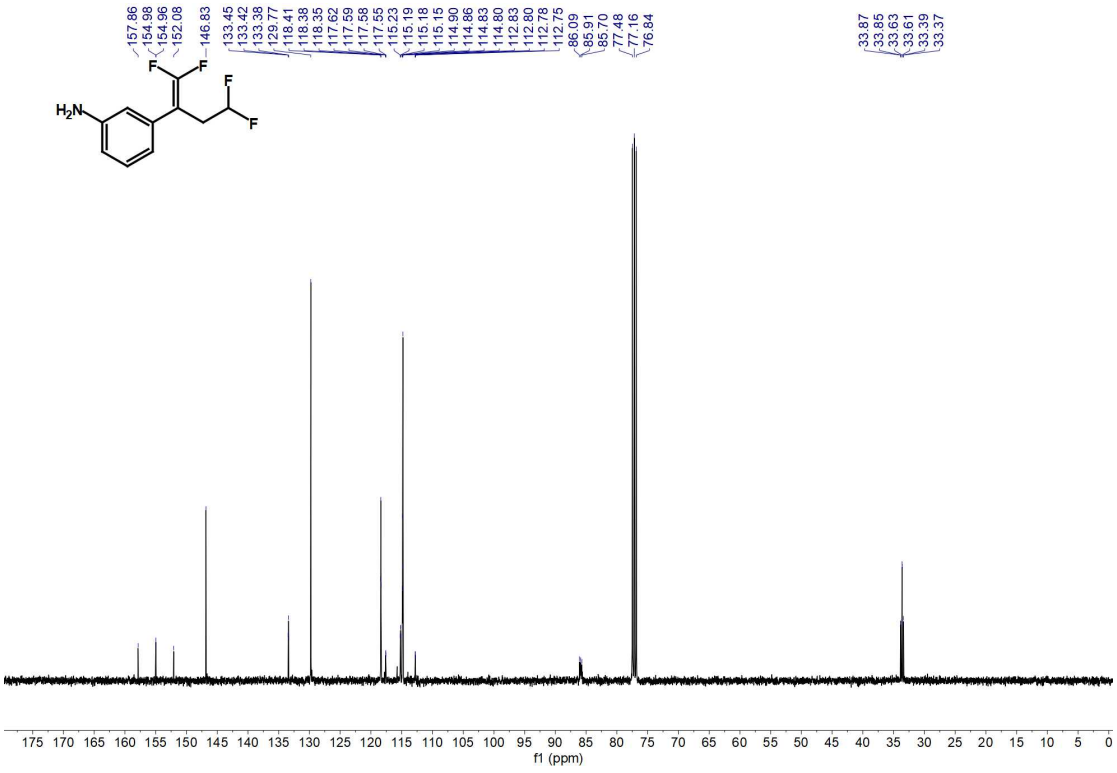



158.17
155.27
155.26
152.36
134.73
134.69
134.65
131.35
131.31
131.28
131.18
130.35
127.02
126.99
126.95
122.86
117.32
117.28
117.27
117.24
114.91
114.88
114.87
114.84
112.51
112.48
112.47
112.43
85.30
85.24
85.06
85.02
84.84
84.77
77.48
77.16
76.84
33.71
33.69
33.47
33.44
33.22
33.20
F
F
F
F
Br
195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

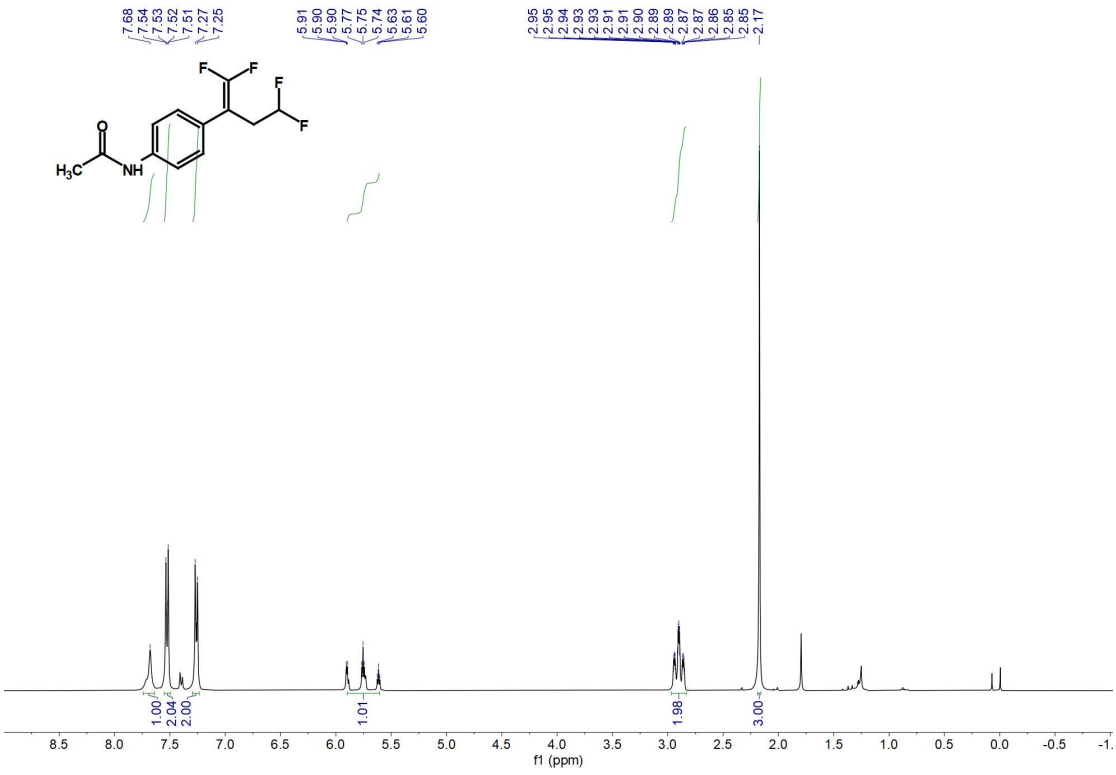

-86.16
-86.25
-86.41
-86.50
-115.68
F
F
F
F
Br
-20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -18
f1 (ppm)

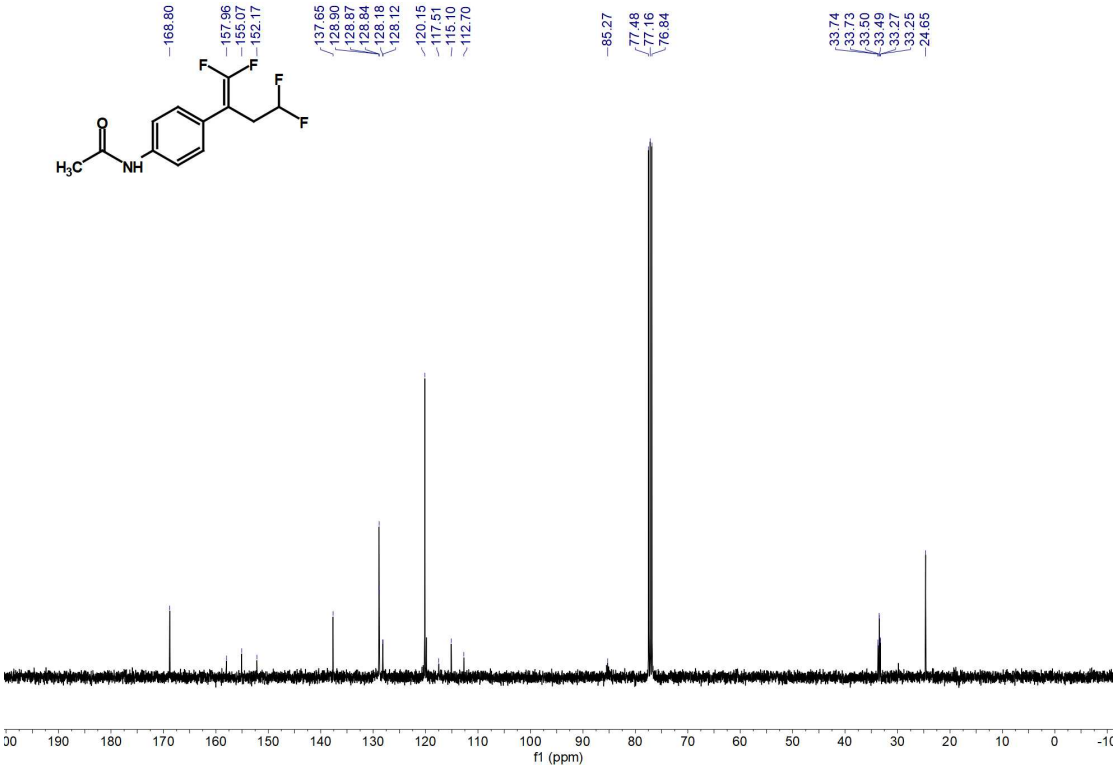
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3q**

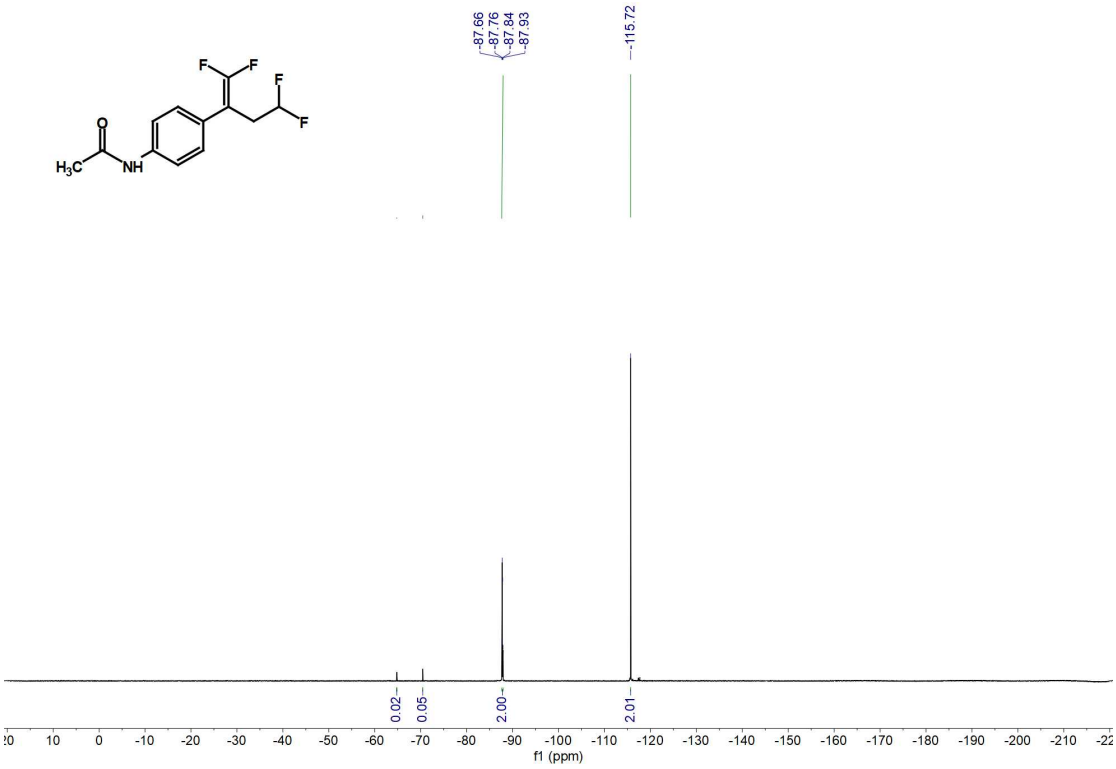


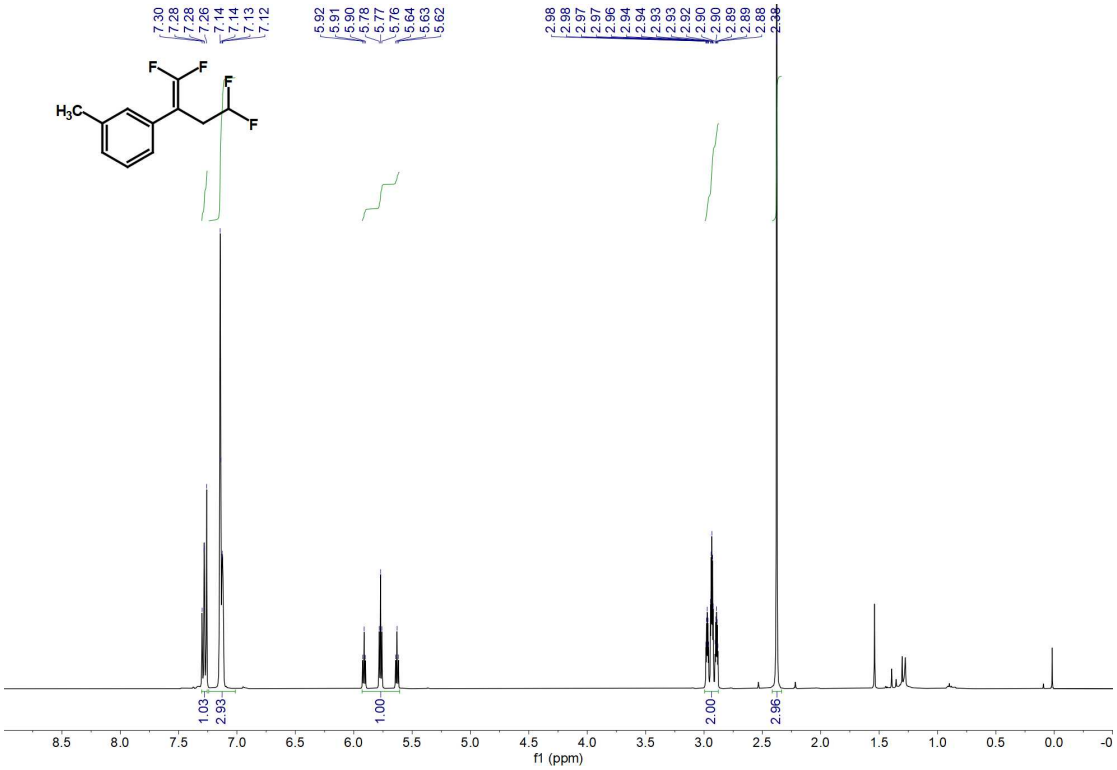

$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3r**

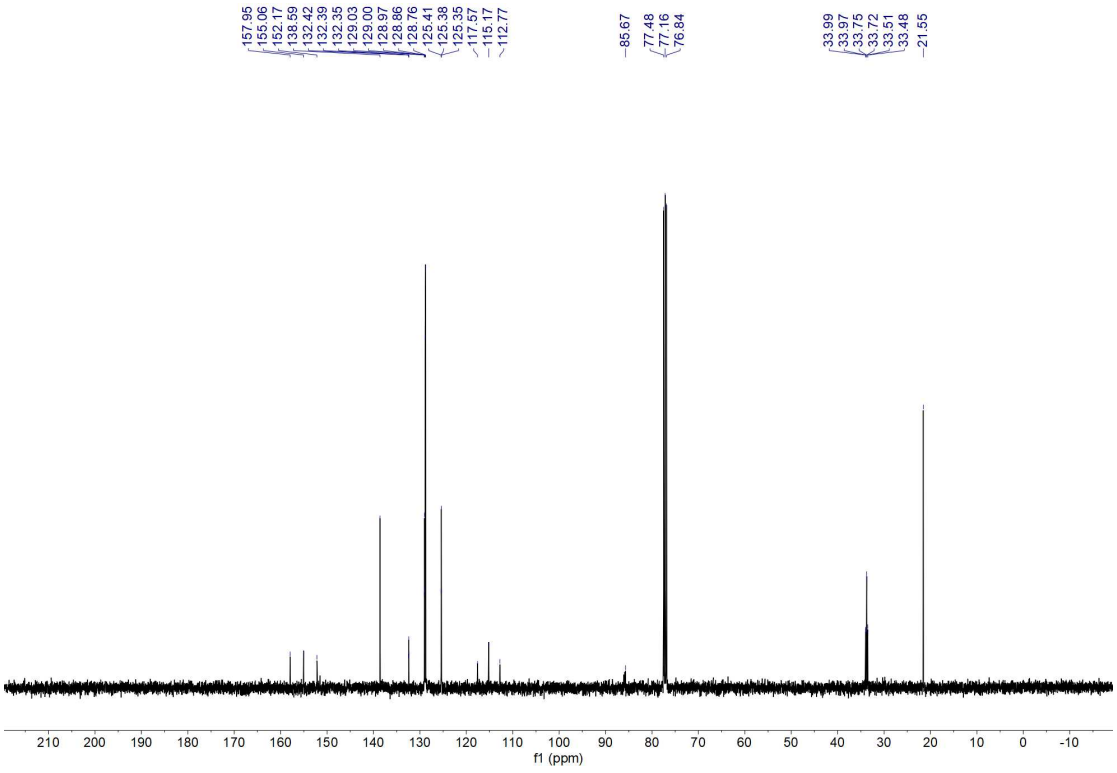


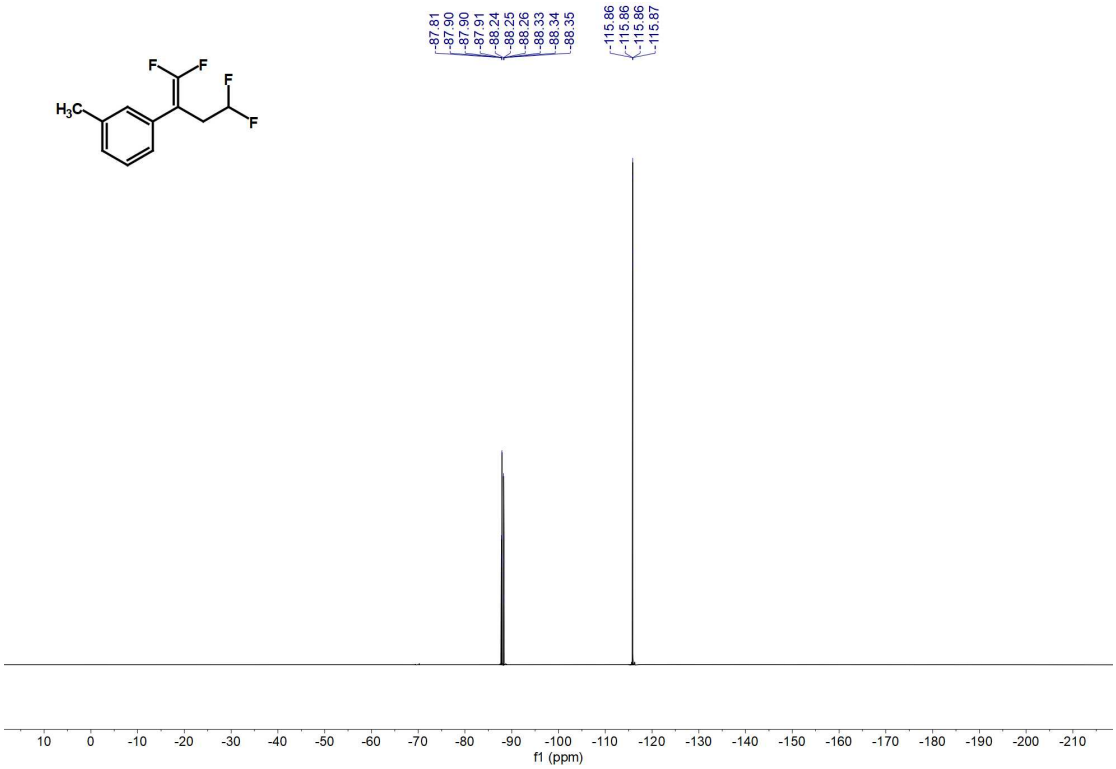

168.80
157.96
155.07
152.17
137.65
128.90
128.87
128.84
128.18
128.12
120.15
117.51
115.10
112.70
85.27
77.48
77.16
76.84
33.74
33.73
33.50
33.49
33.27
33.25
24.65
F
F
F
F
O
H3C
NH
f1 (ppm)


87.66
87.76
87.84
87.93
115.72
F
F
F
F
O
H3C
NH
0.02
0.05
2.00
2.01
f1 (ppm)

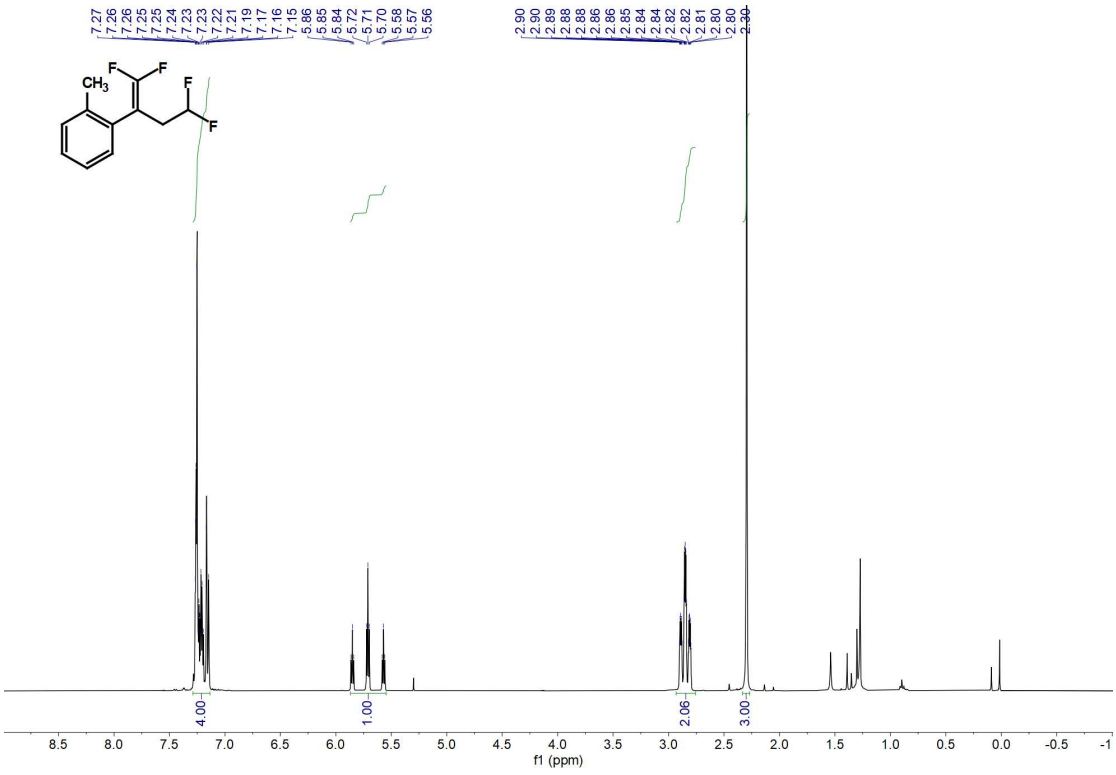
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3s**

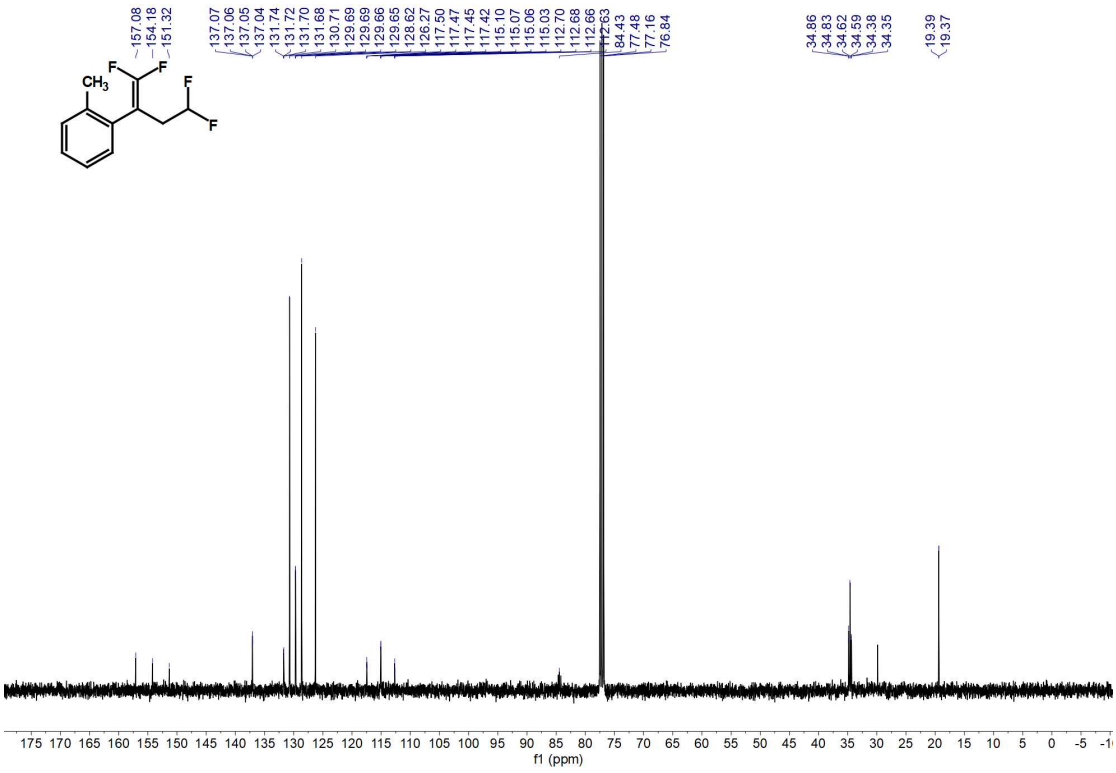




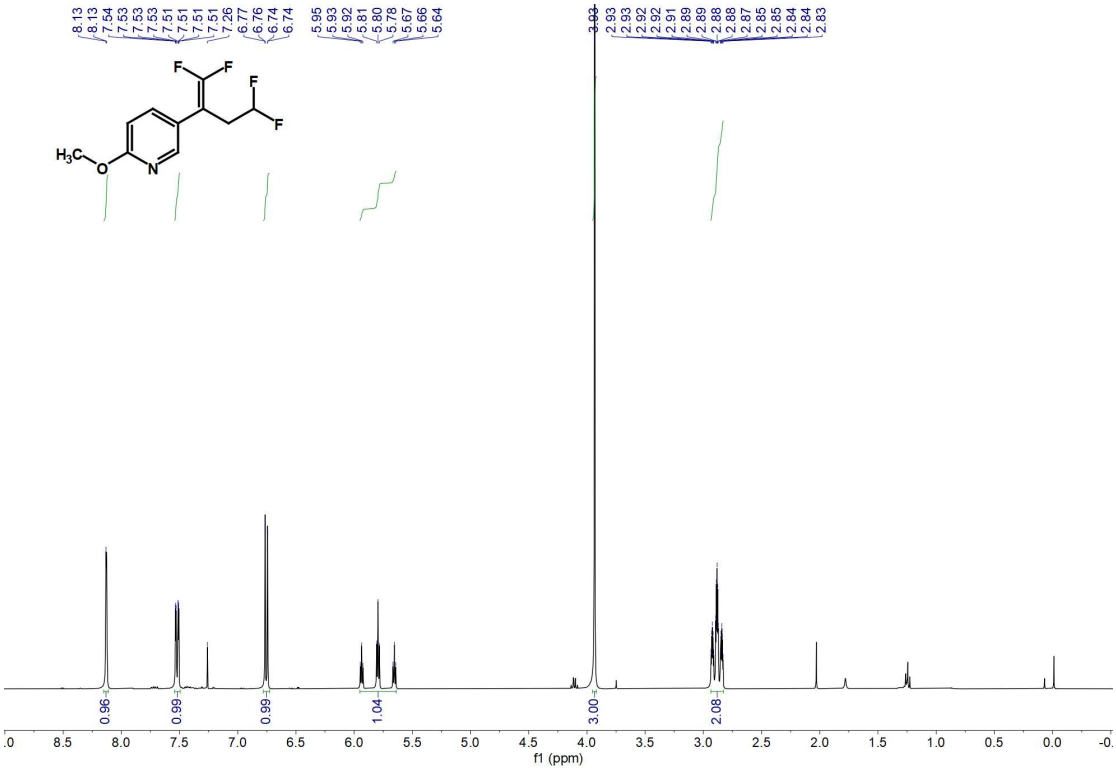

$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3t**

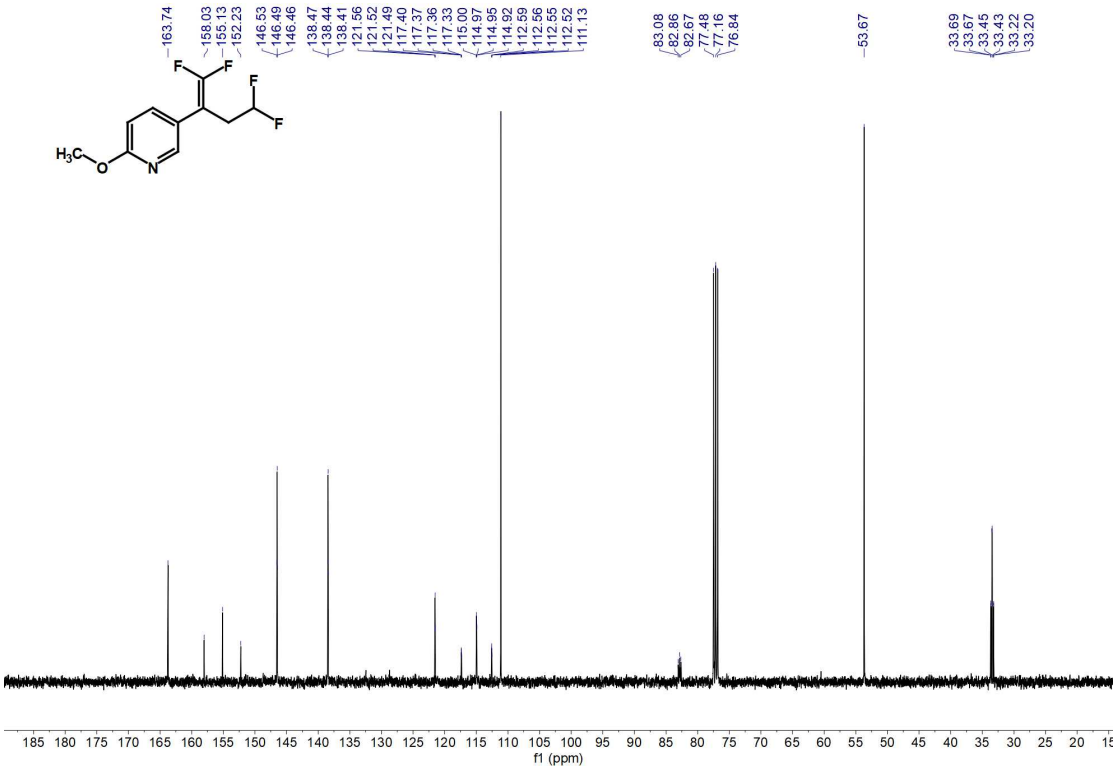



157.08
154.18
151.32
137.07
137.06
137.05
137.04
131.74
131.72
131.70
131.68
130.71
129.69
129.69
129.66
129.65
128.62
126.27
117.50
117.47
117.45
117.42
115.10
115.07
115.06
115.03
112.70
112.68
112.66
112.63
84.43
77.48
77.16
76.84
34.86
34.83
34.62
34.59
34.38
34.35
19.39
19.37
CH3
F
F
F
F
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)

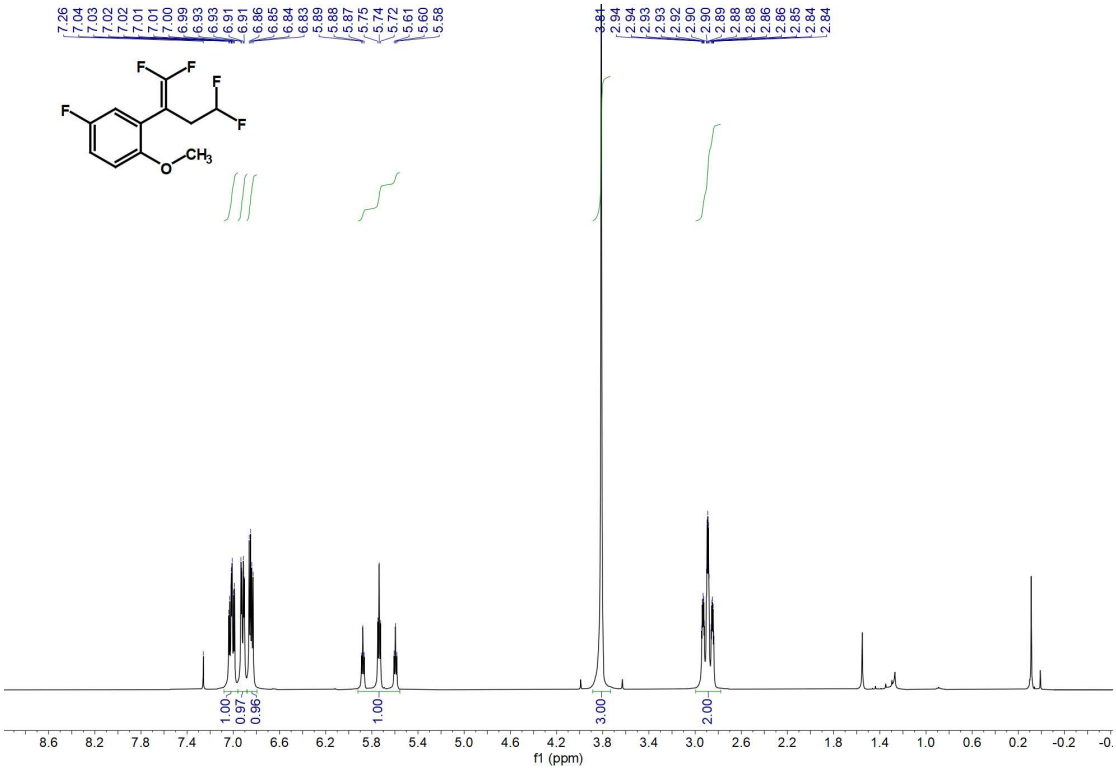

-85.79
-85.88
-90.90
-90.99
-116.07
-116.08
CH3
F
F
F
F
-58 -62 -66 -70 -74 -78 -82 -86 -90 -94 -98 -102 -106 -110 -114 -118 -122 -126 -130 -134 -138 -142 -146 -150 -15
f1 (ppm)

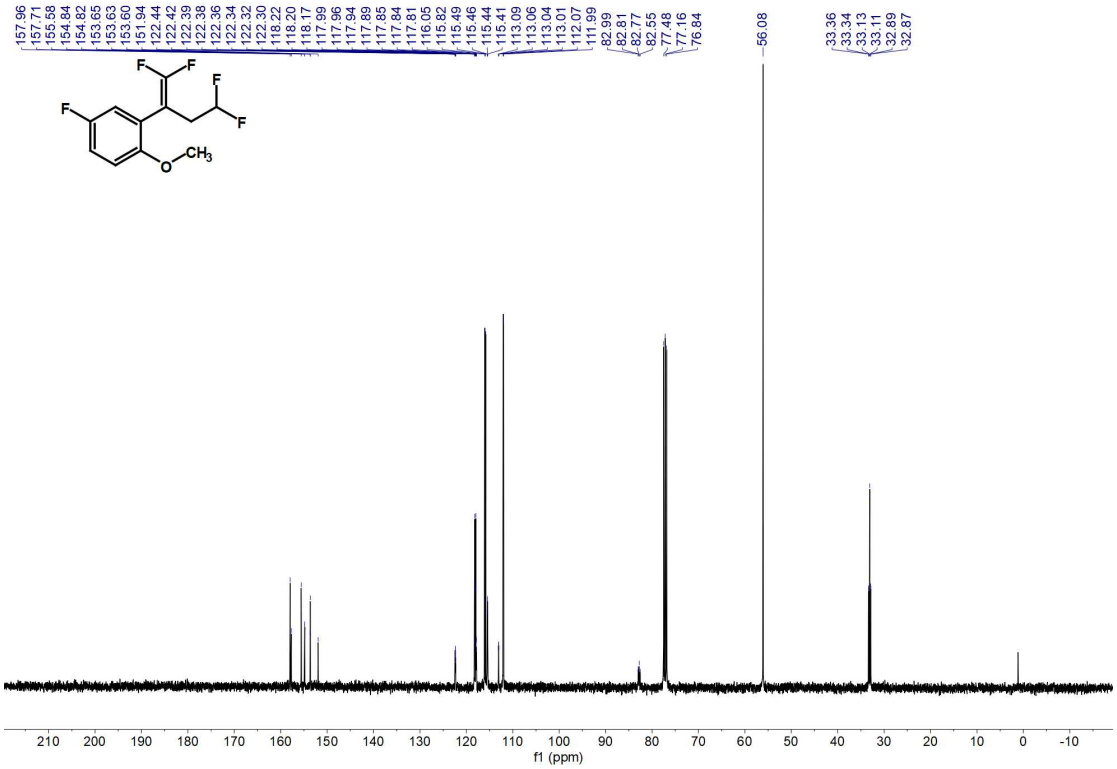
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3u**

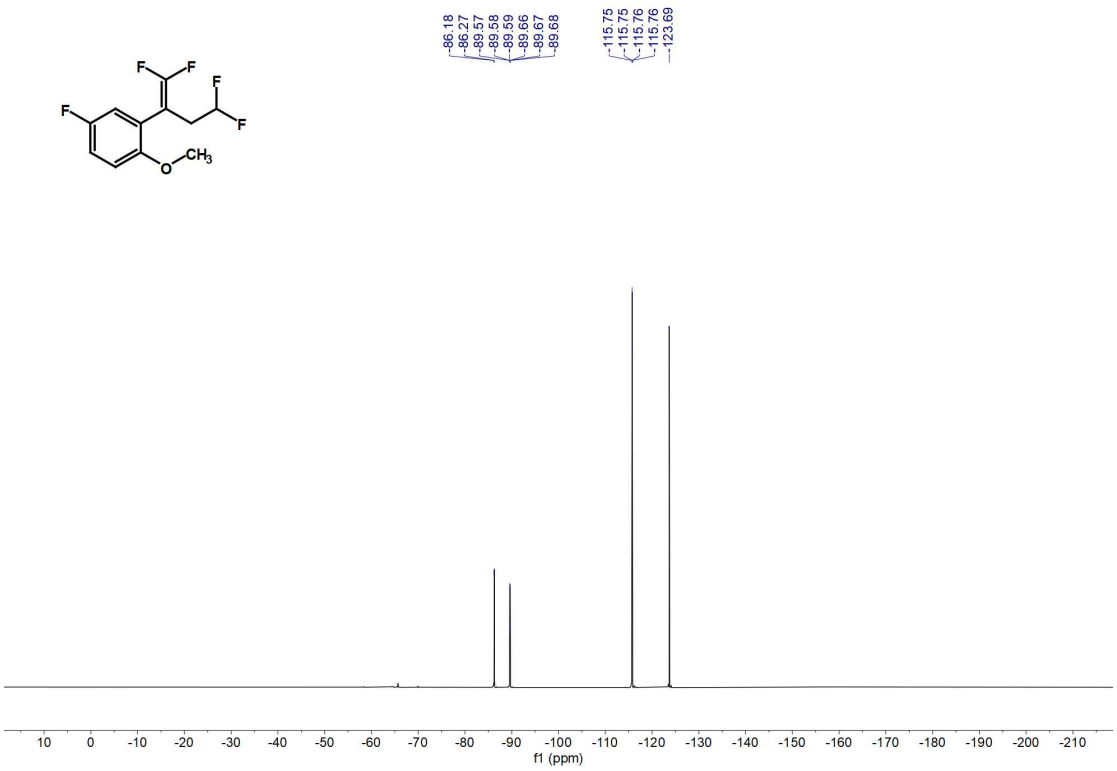


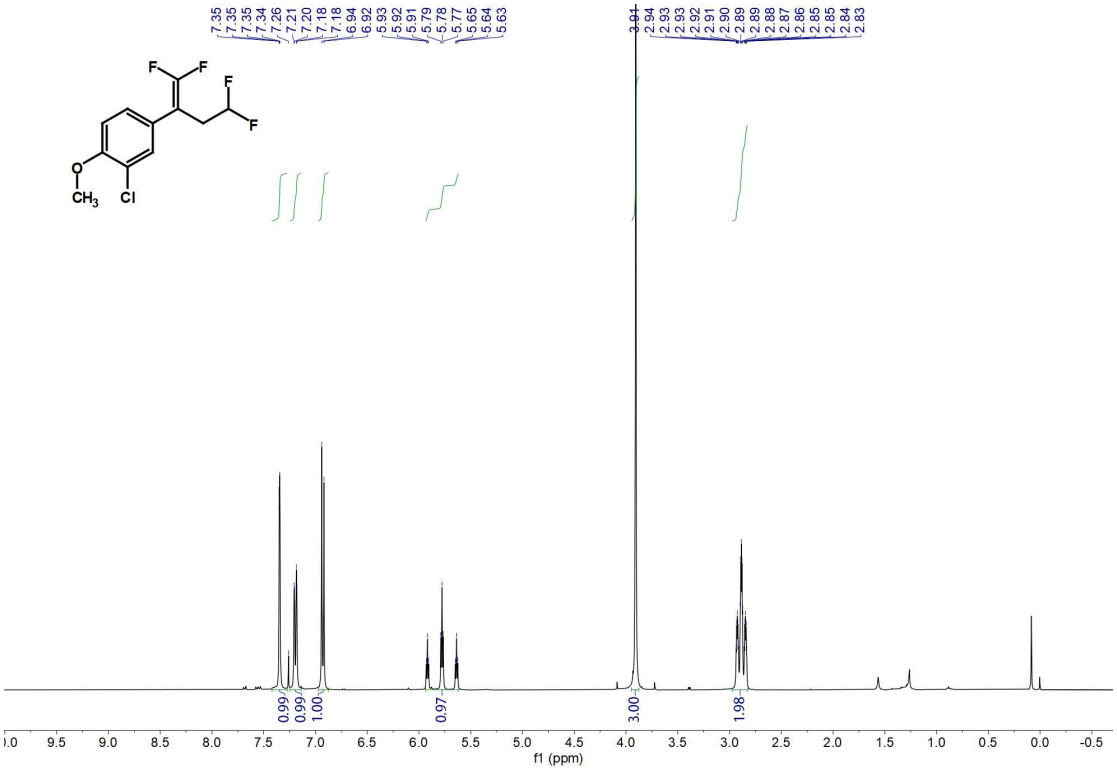

$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3v**

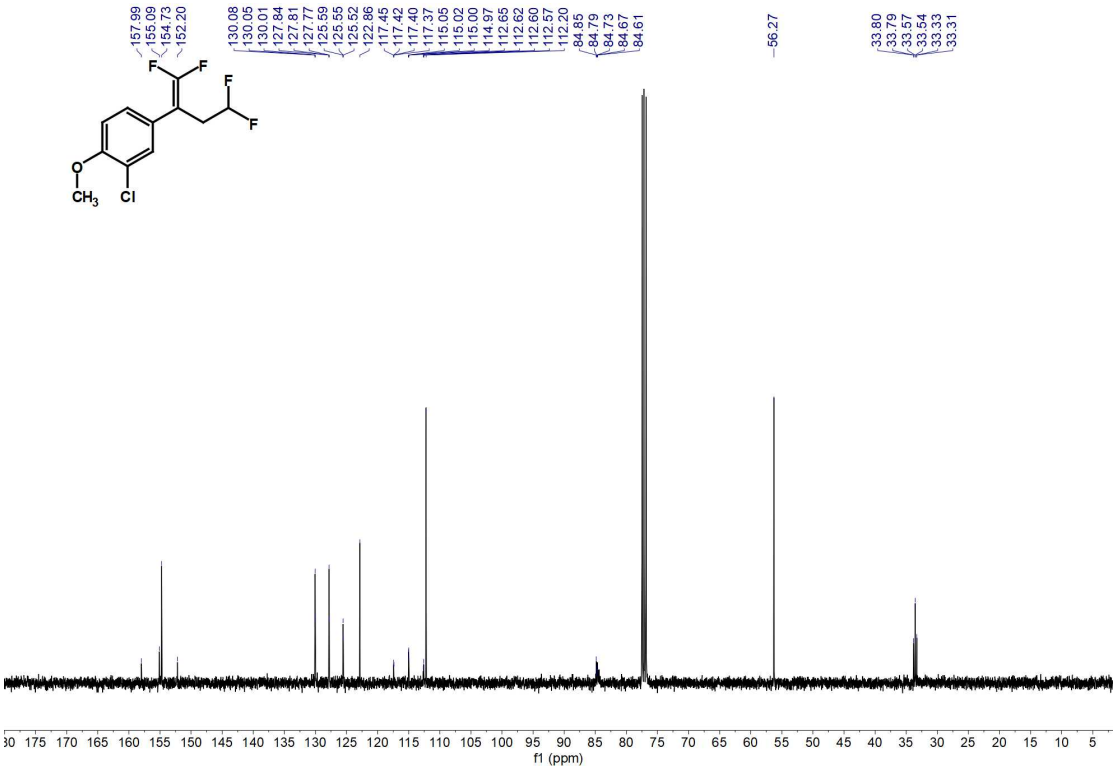


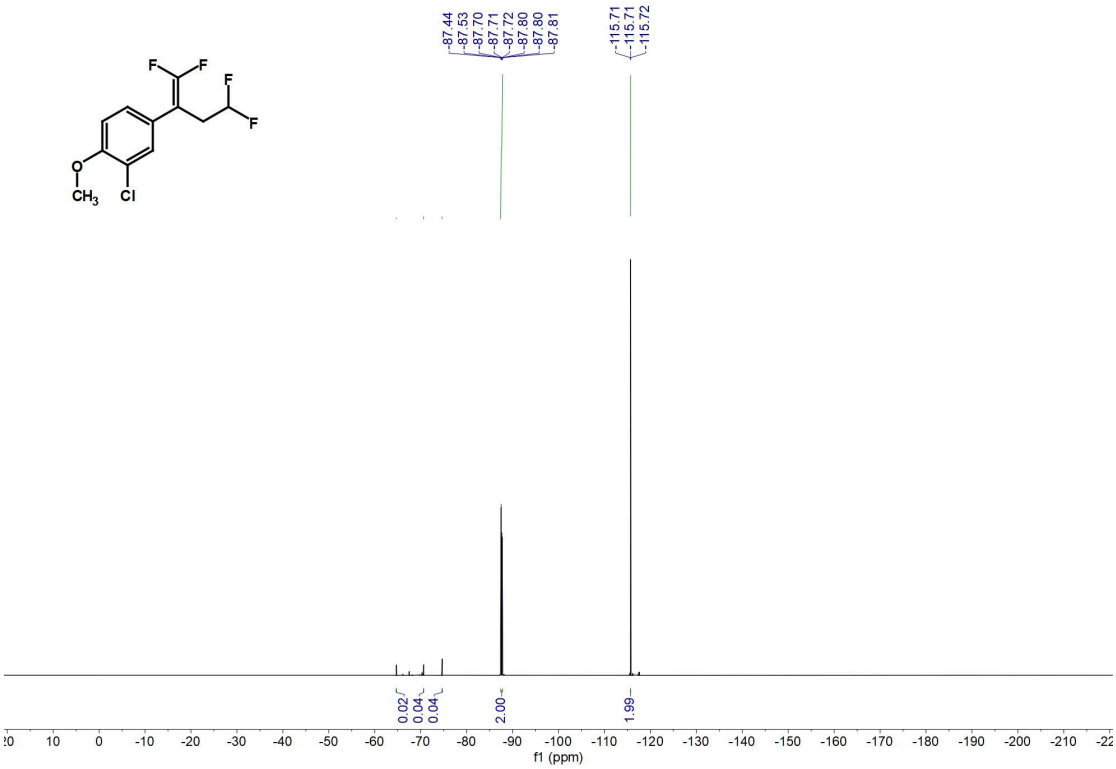

157.96
157.71
155.58
154.84
154.82
153.65
153.63
153.60
151.94
122.44
122.42
122.39
122.38
122.36
122.34
122.32
122.30
118.22
118.20
118.17
117.99
117.96
117.94
117.89
117.85
117.84
117.81
116.05
115.82
115.49
115.46
115.44
115.41
113.09
113.06
113.04
113.01
112.07
111.99
82.99
82.81
82.77
82.55
77.48
77.16
76.84
56.08
33.36
33.34
33.13
33.11
32.89
32.87
F
F
F
F
O
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-86.18
-86.27
-89.57
-89.58
-89.59
-89.66
-89.67
-89.68
-115.75
-115.75
-115.76
-115.76
-123.69
F
F
F
F
O
CH3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

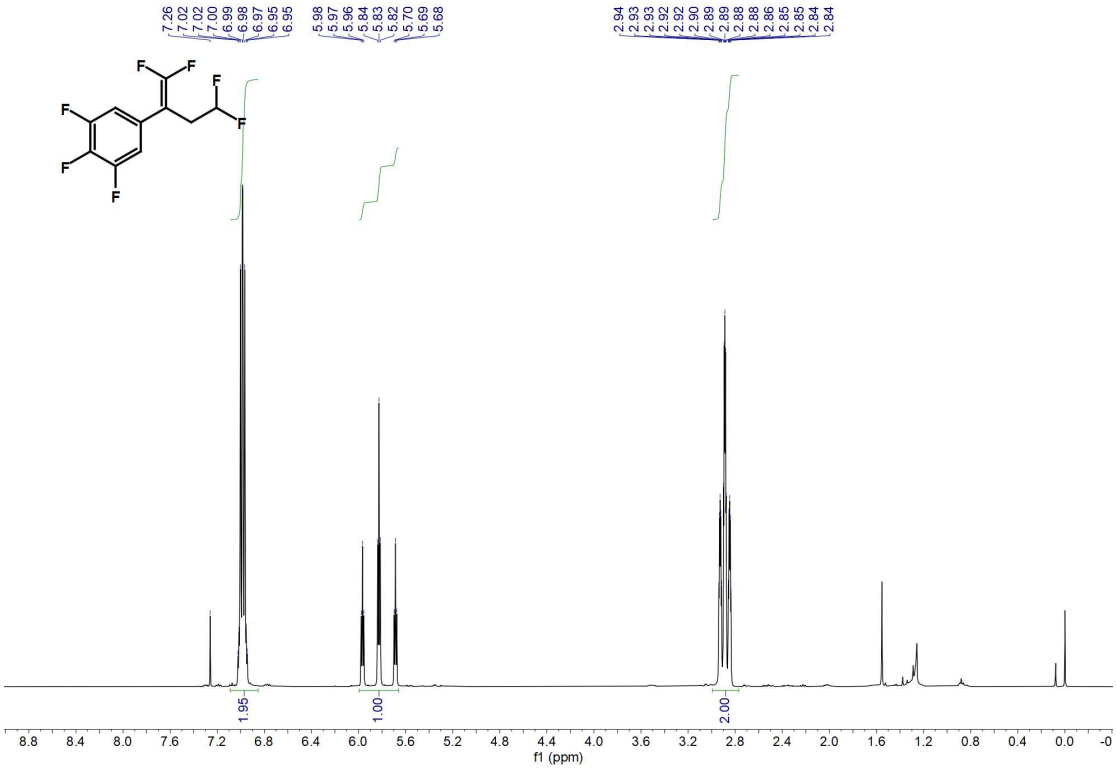
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3w**

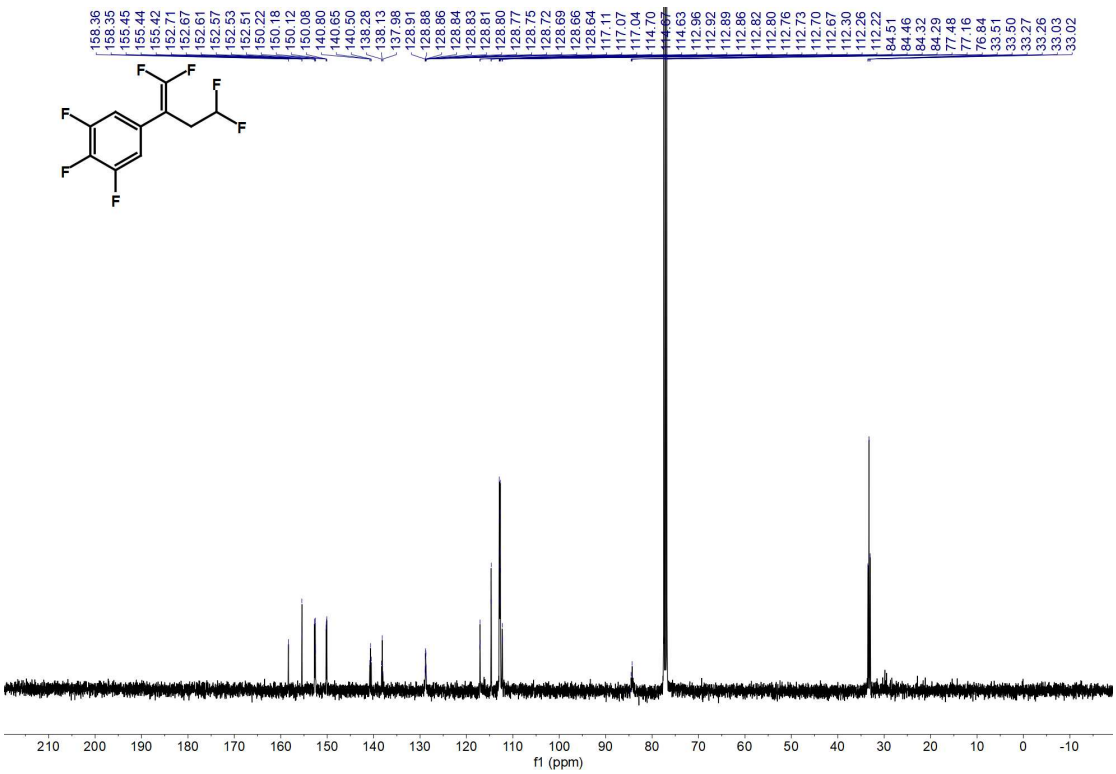





$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3x**

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152.61
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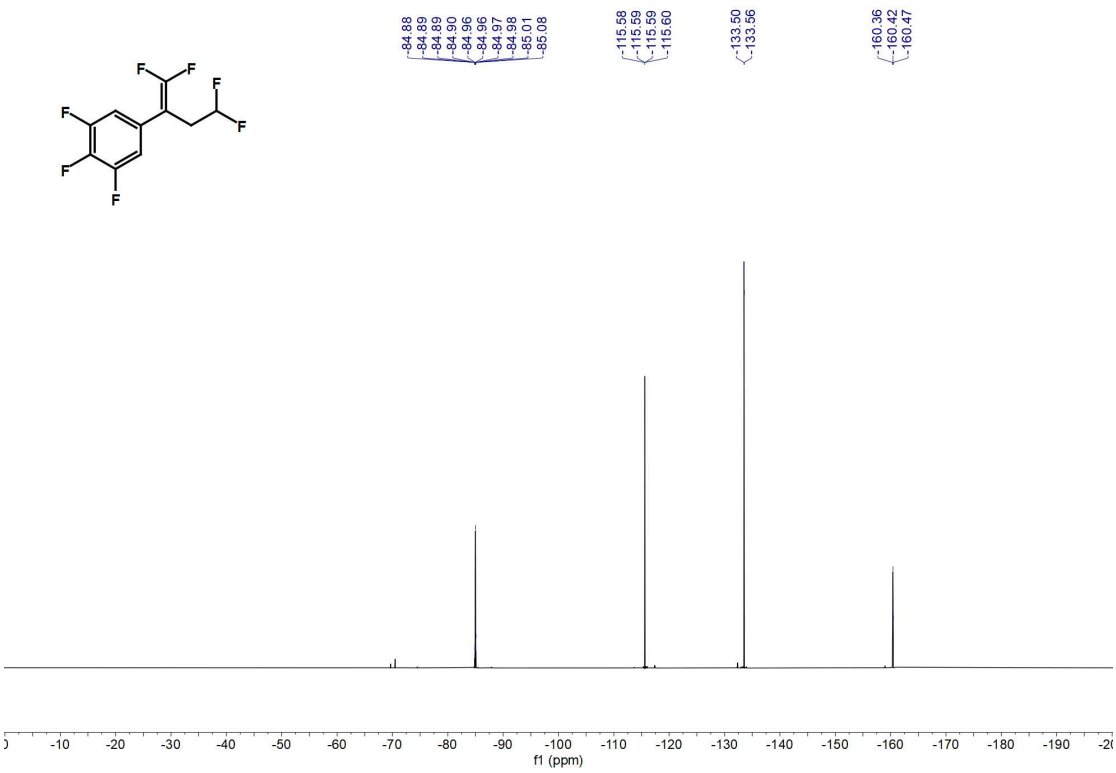
152.51
150.22
150.18
150.12
150.08
140.80
140.65
140.50
138.28
138.13
137.98
128.91
128.88
128.86
128.84
128.83
128.81
128.80
128.77
128.75
128.72
128.69
128.66
128.64
117.11
117.07
117.04
114.70
114.67
114.63
112.96
112.92
112.89
112.86
112.82
112.80
112.76
112.73
112.70
112.67
112.30
112.26
112.22
84.51
84.46
84.32
84.29
77.48
77.16
76.84
33.51
33.50
33.27
33.26
33.03
33.02
F
F
F
F
F
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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-84.89
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-84.96
-84.97
-84.98
-85.01
-85.08
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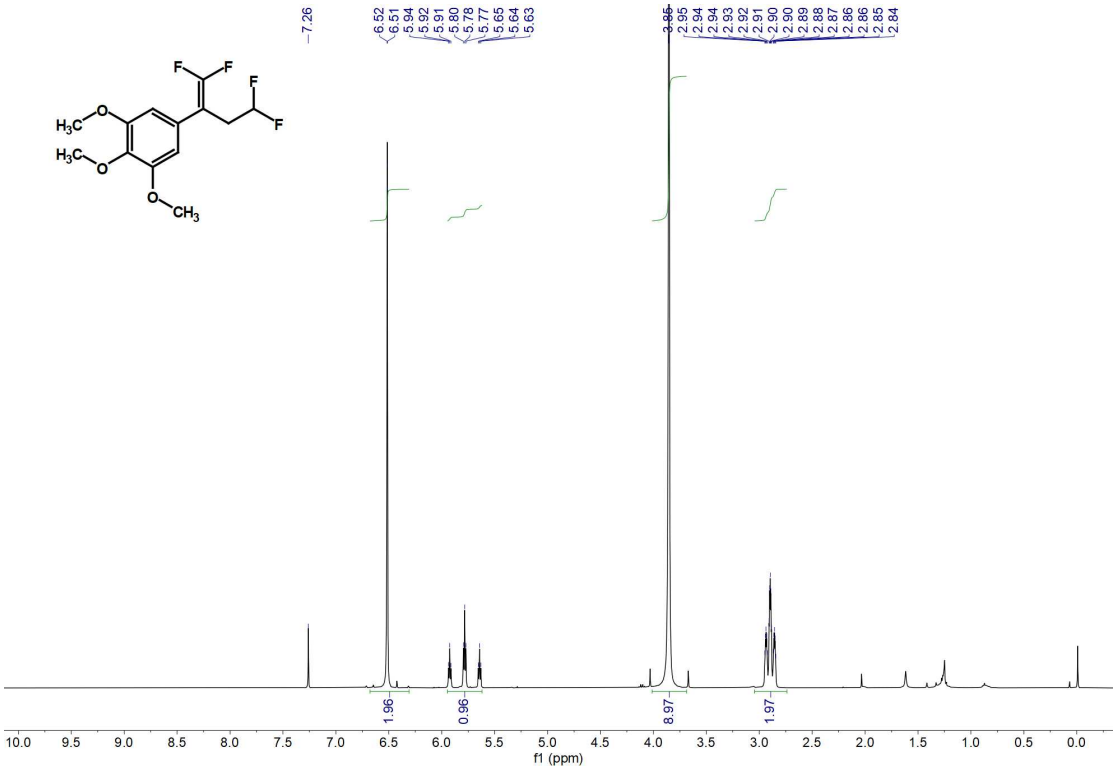
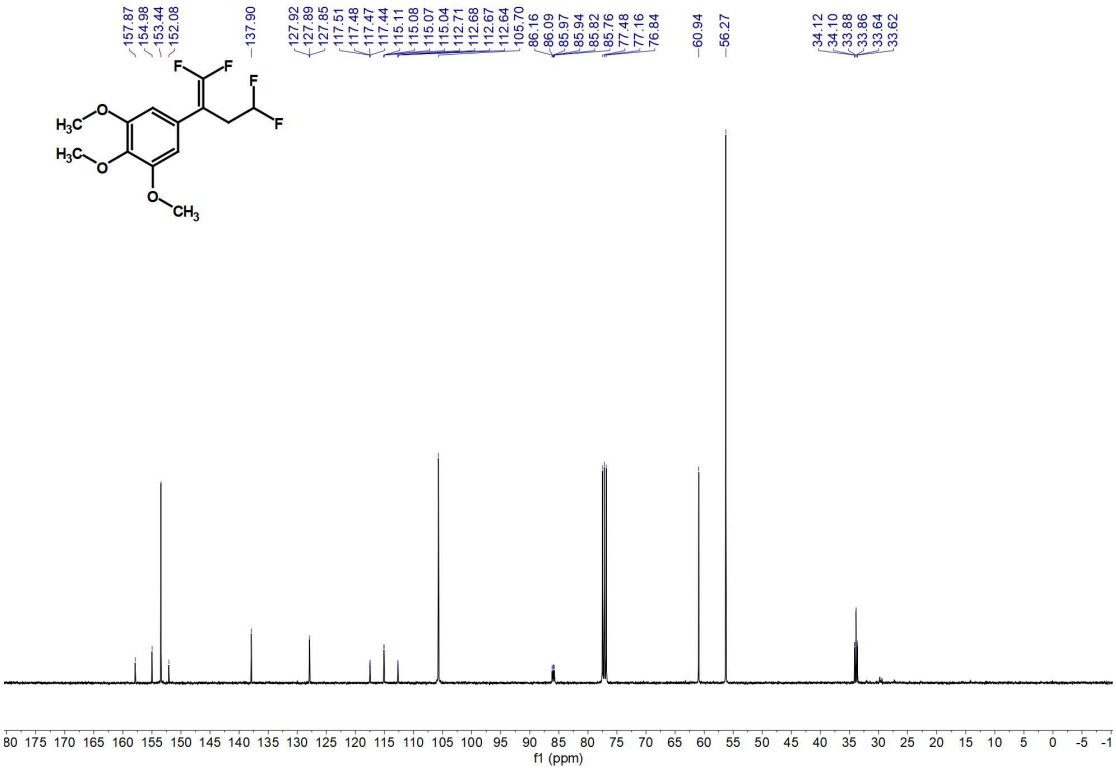
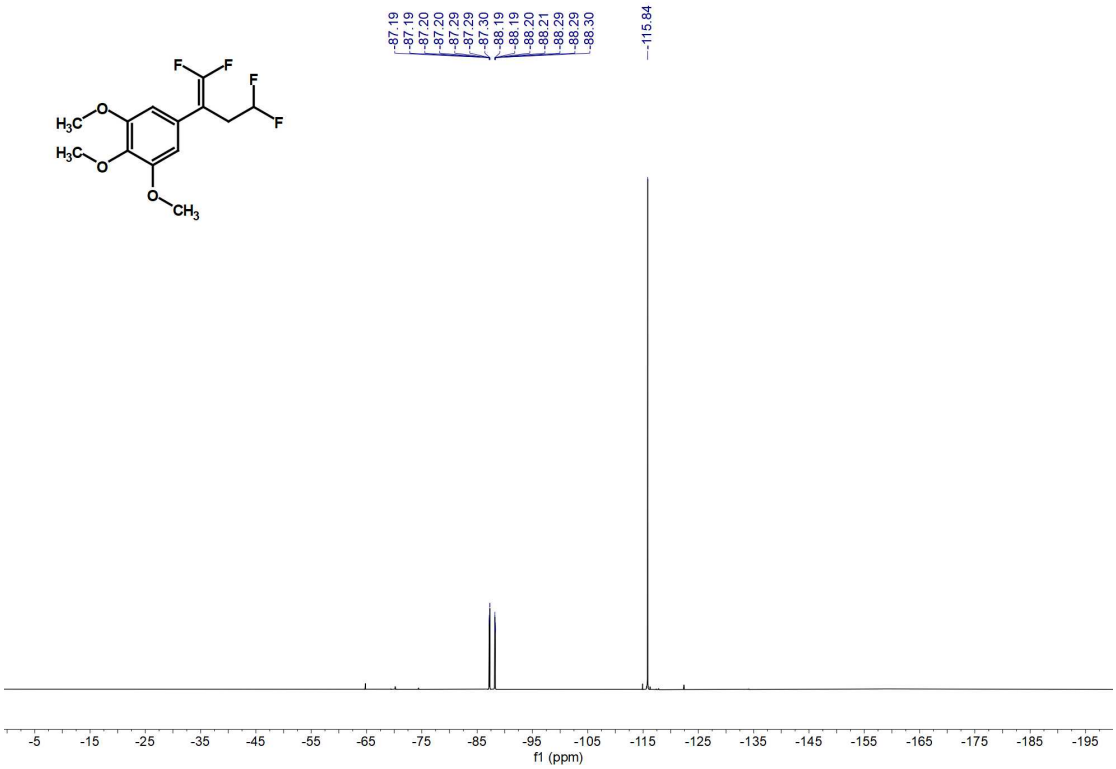
-115.59
-115.59
-115.60
-133.50
-133.56
-160.36
-160.42
-160.47
F
F
F
F
F
F
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

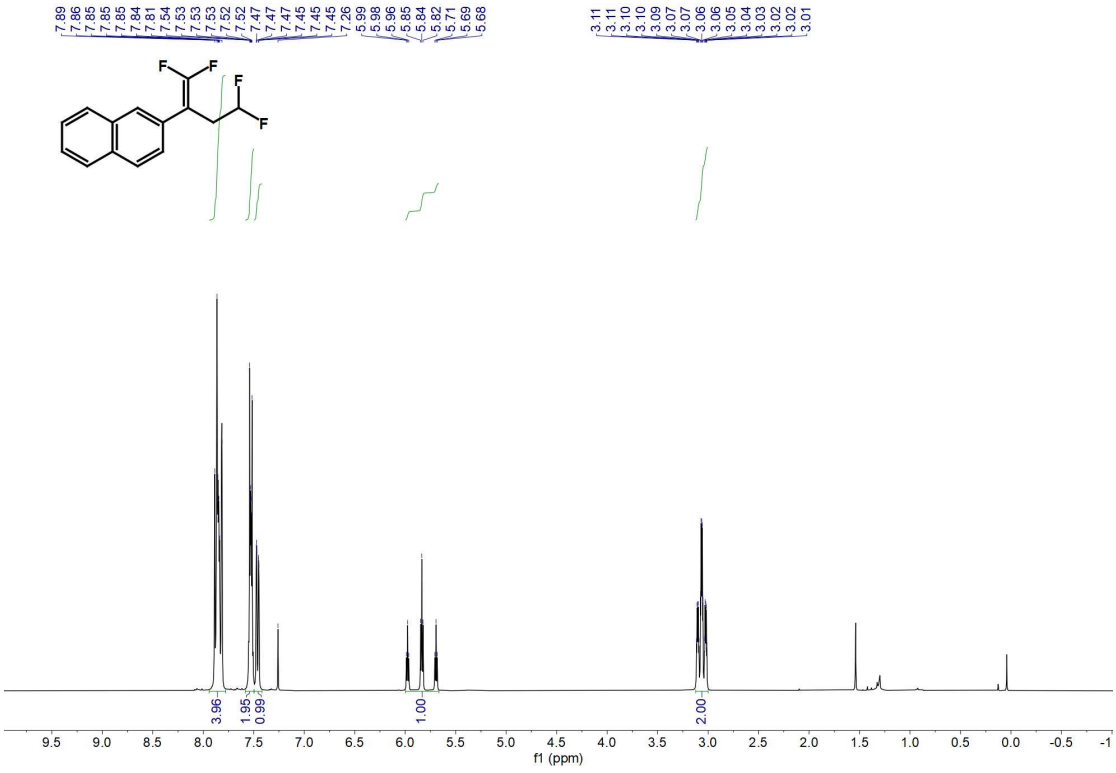
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3y**

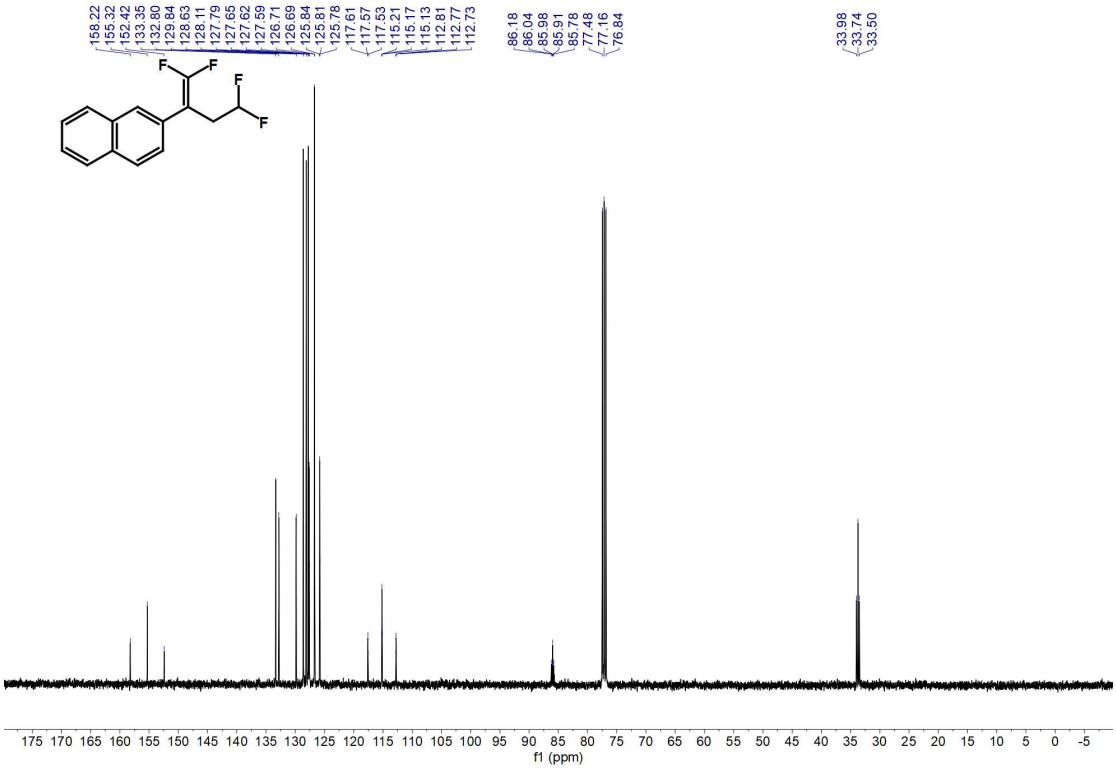





$^{1}$H, $^{13}$C, $^{19}$F NMR Spectra of **3z**




158.22
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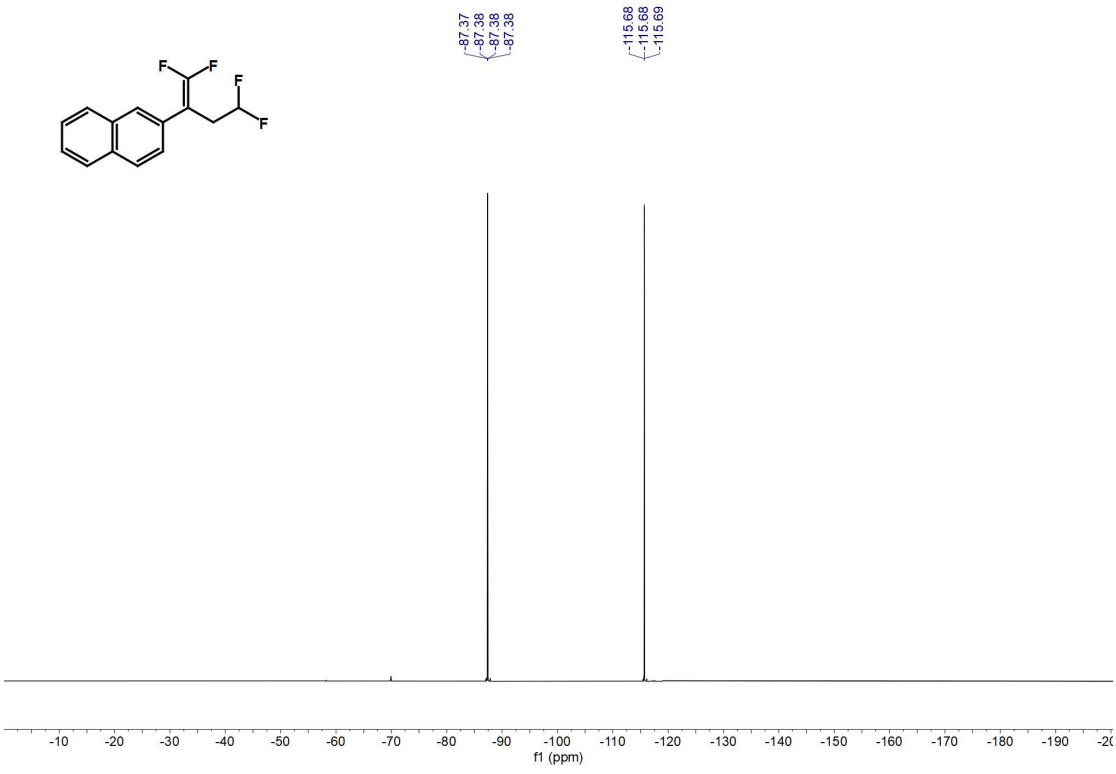
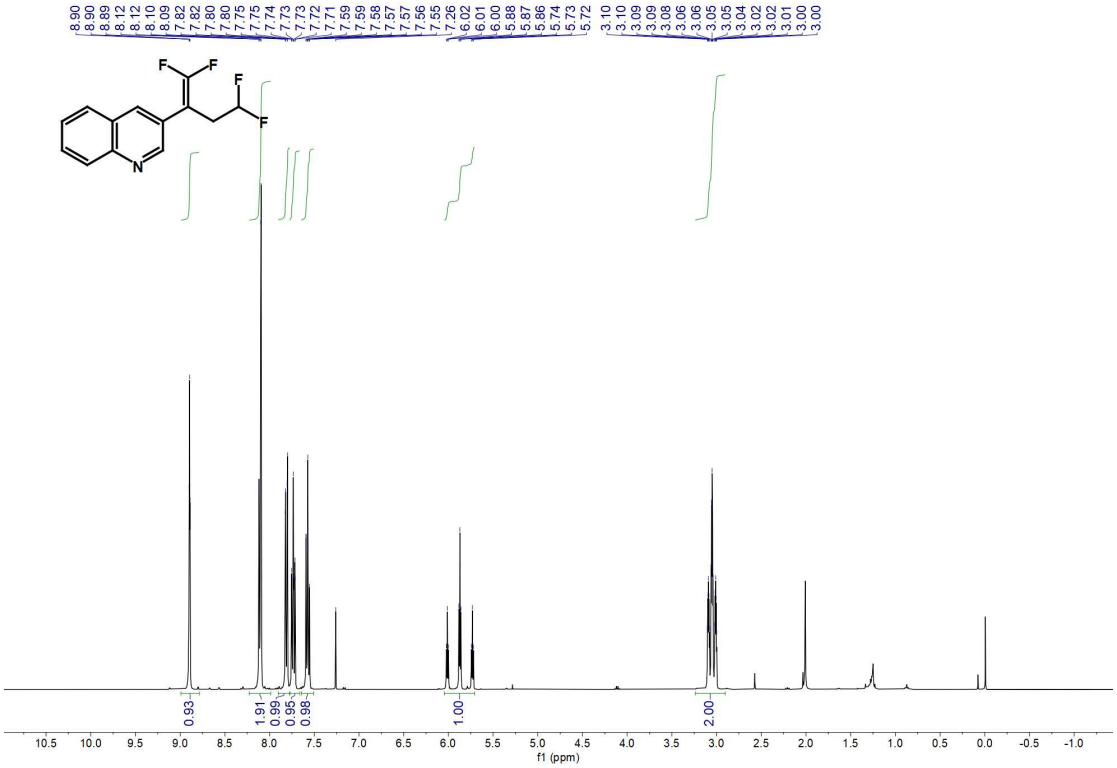
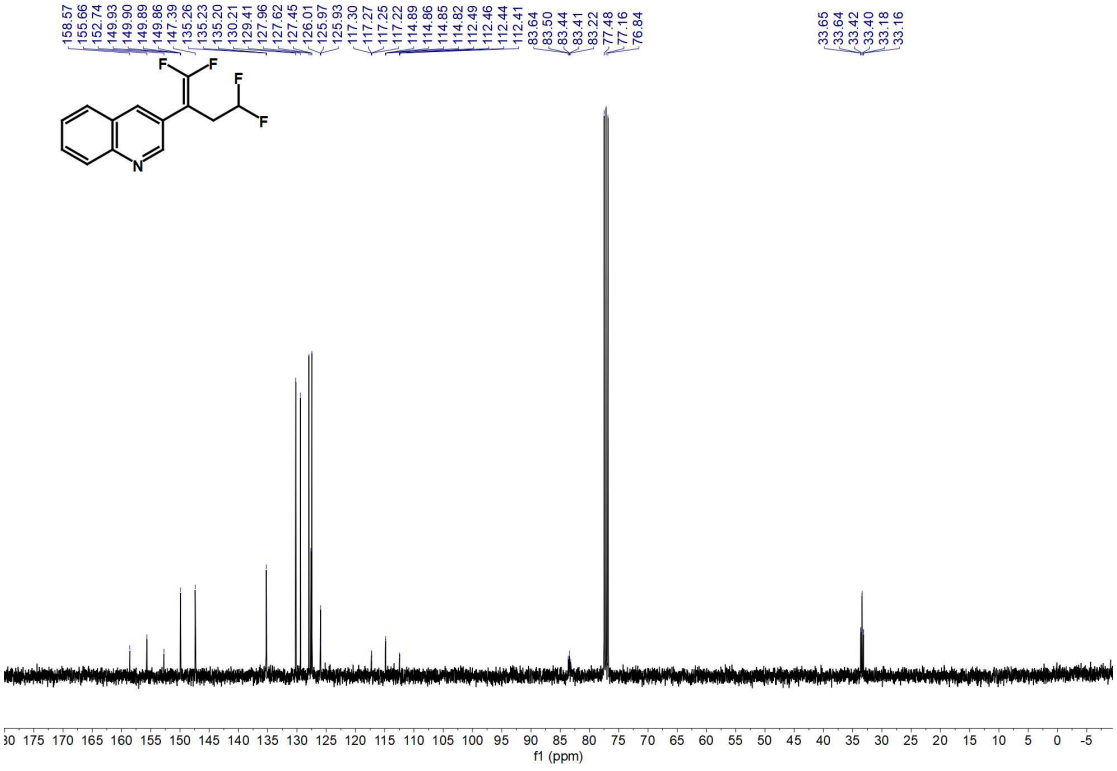
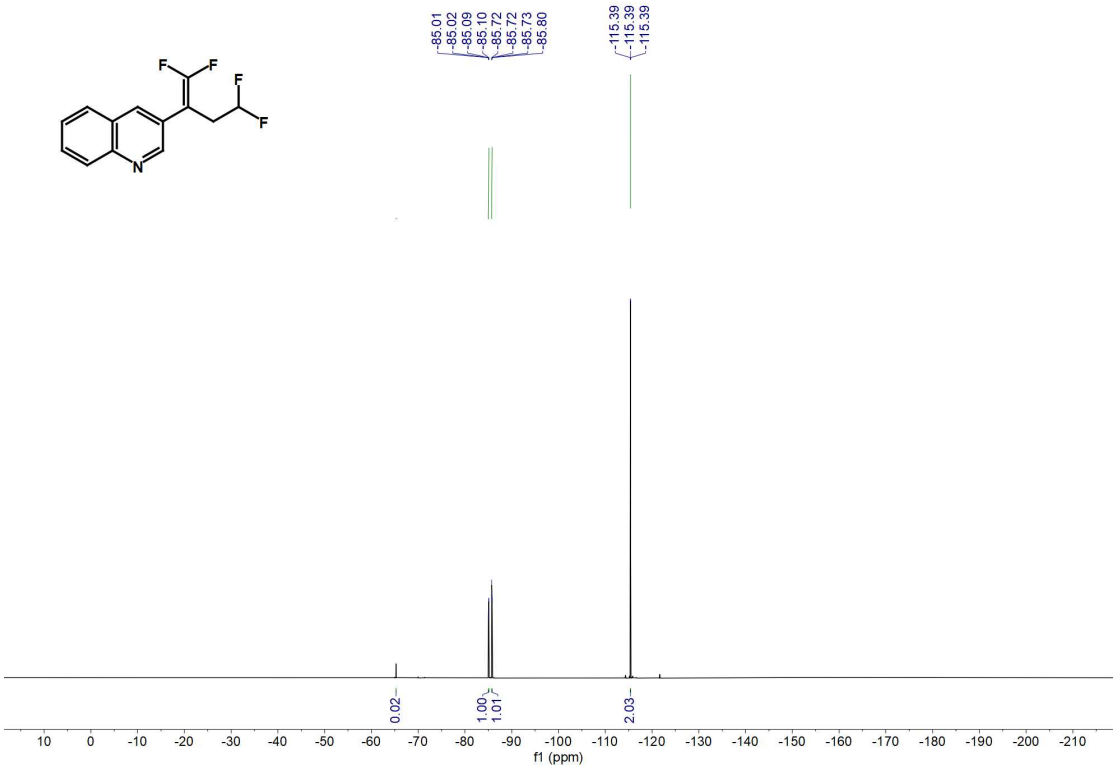
152.42
133.35
132.80
129.84
128.63
128.11
127.79
127.65
127.62
127.59
126.71
126.69
125.84
125.81
125.78
117.61
117.57
117.53
115.21
115.17
115.13
112.81
112.77
112.73
86.18
86.04
85.98
85.91
85.78
77.48
77.16
76.84
33.98
33.74
33.50
F
F
F
F
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)


-87.37
-87.38
-87.38
-87.38
-115.68
-115.68
-115.69
F
F
F
F
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)

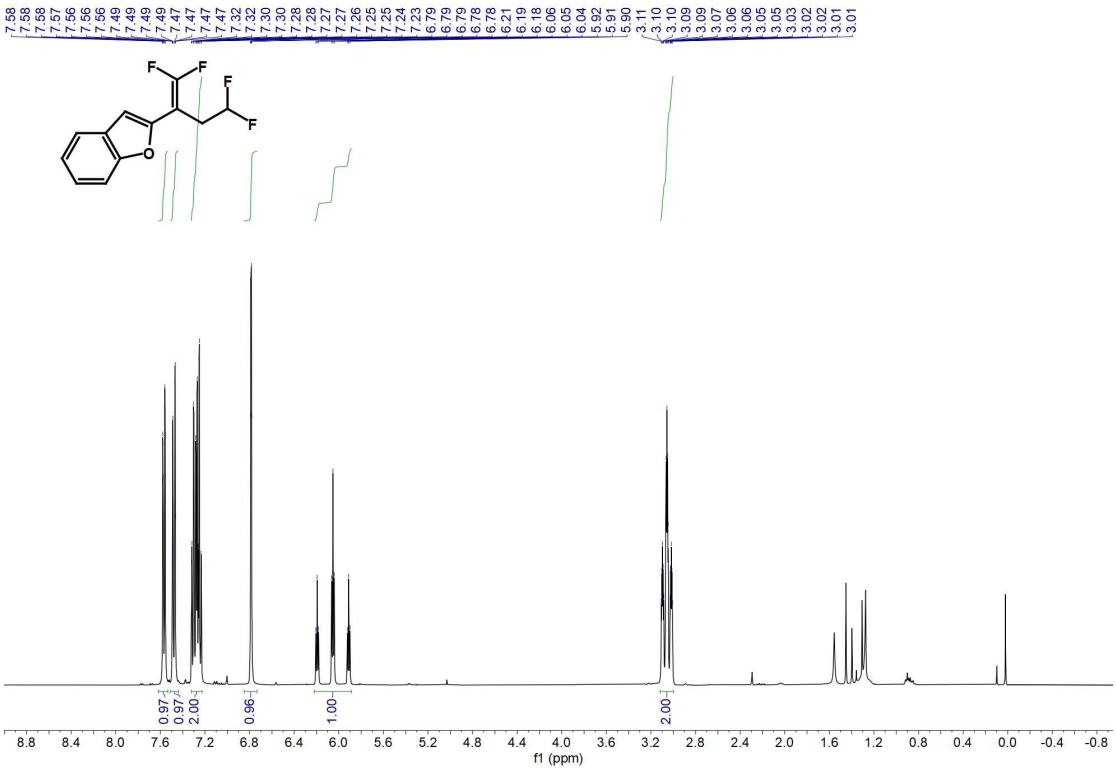
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3aa**

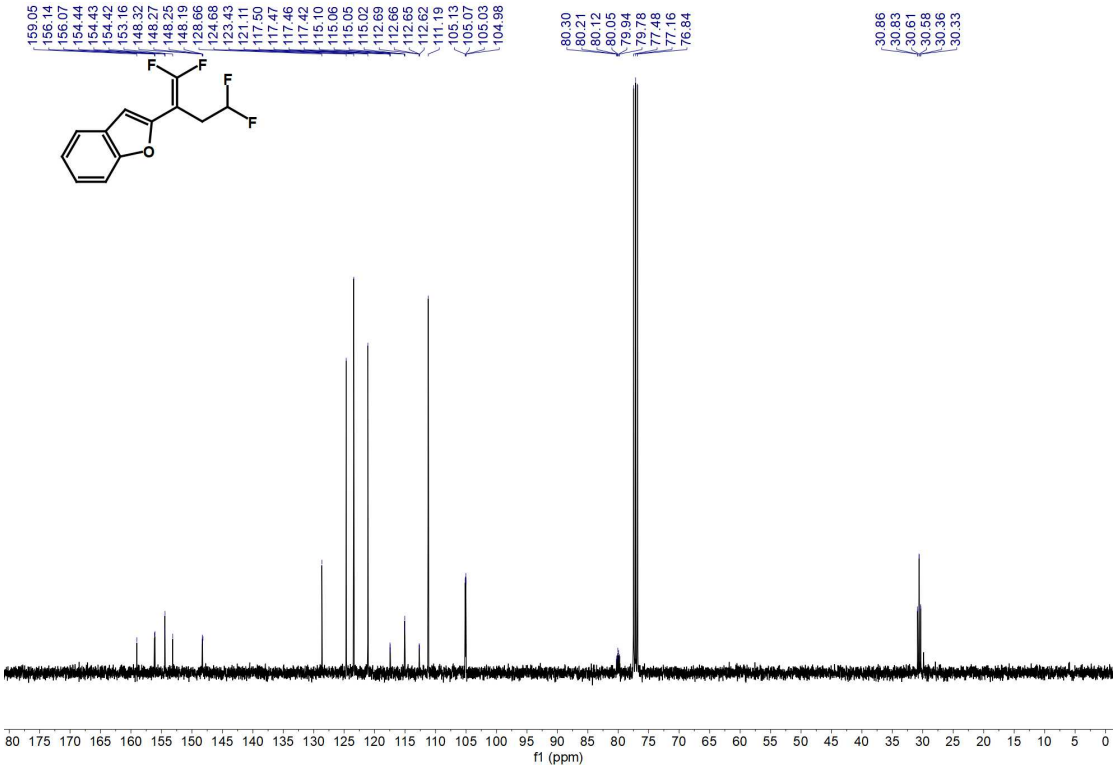


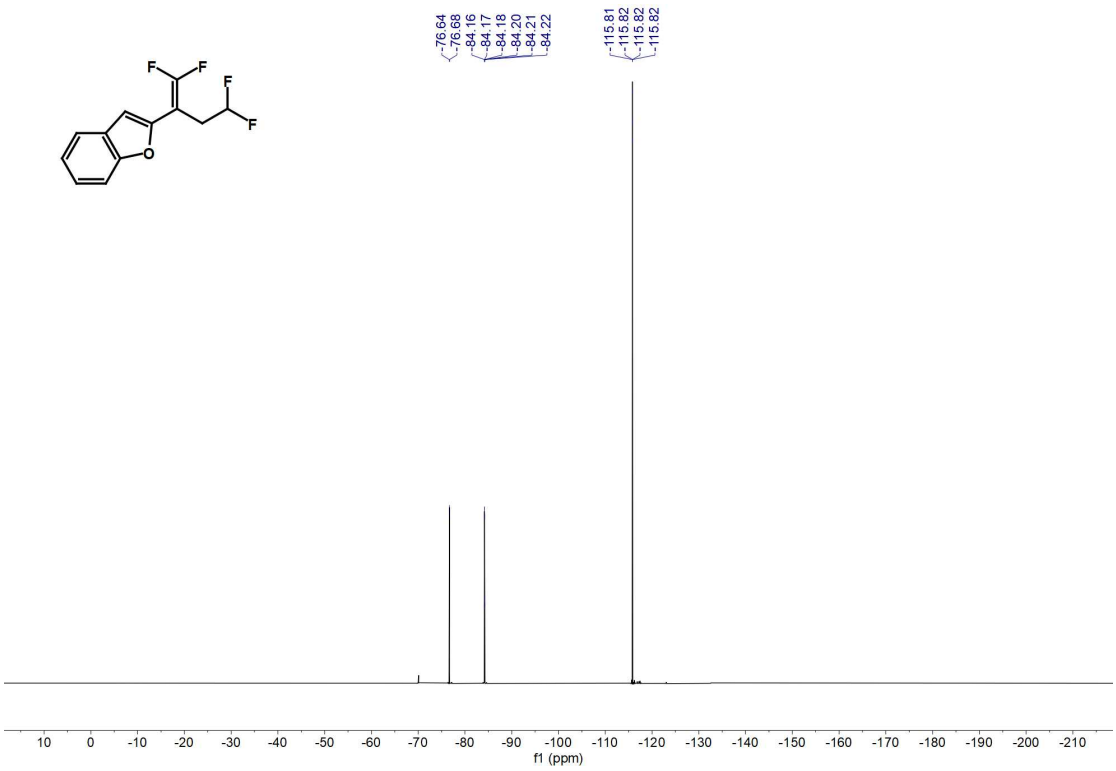






$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3ab**




159.05
156.14
156.07
154.44
154.43
154.42
153.16
148.32
148.27
148.25
148.19
128.66
124.68
123.43
121.11
117.50
117.47
117.46
117.42
115.10
115.06
115.05
115.02
112.69
112.66
112.65
112.62
111.19
105.13
105.07
105.03
104.98
80.30
80.21
80.12
80.05
79.94
79.78
77.48
77.16
76.84
30.86
30.83
30.61
30.58
30.36
30.33
F
F
F
F
O
80 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


-76.64
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-84.17
-84.18
-84.20
-84.21
-84.22
-115.81
-115.82
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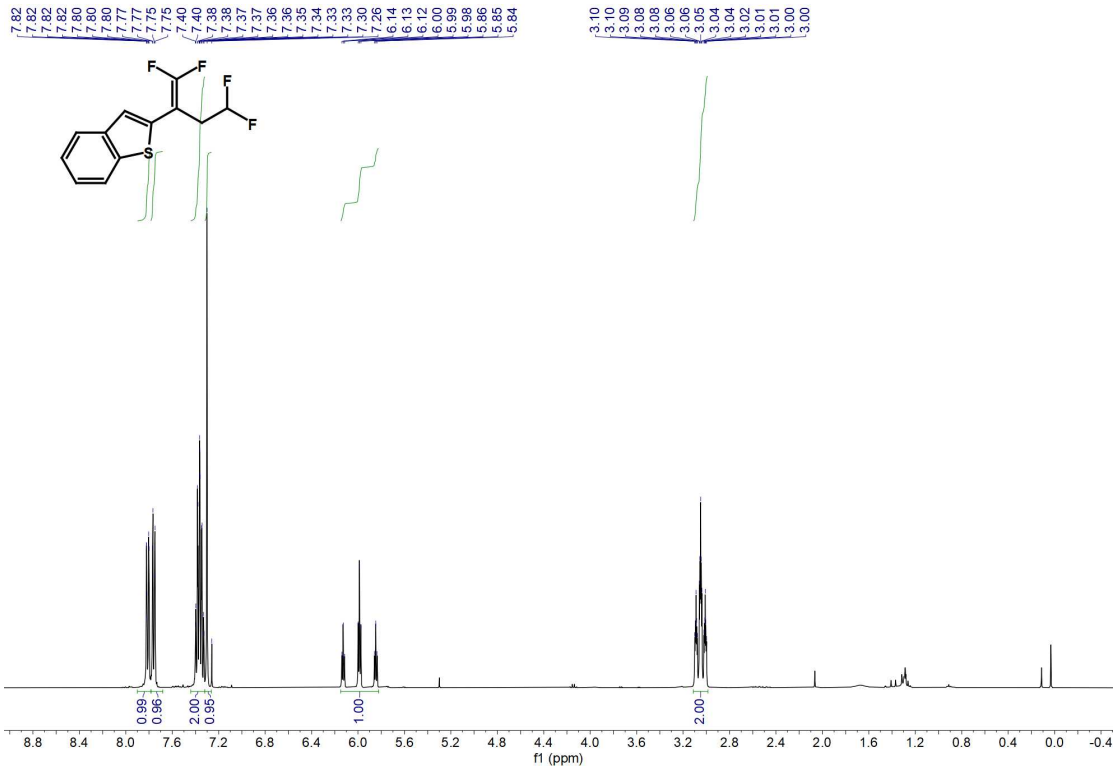
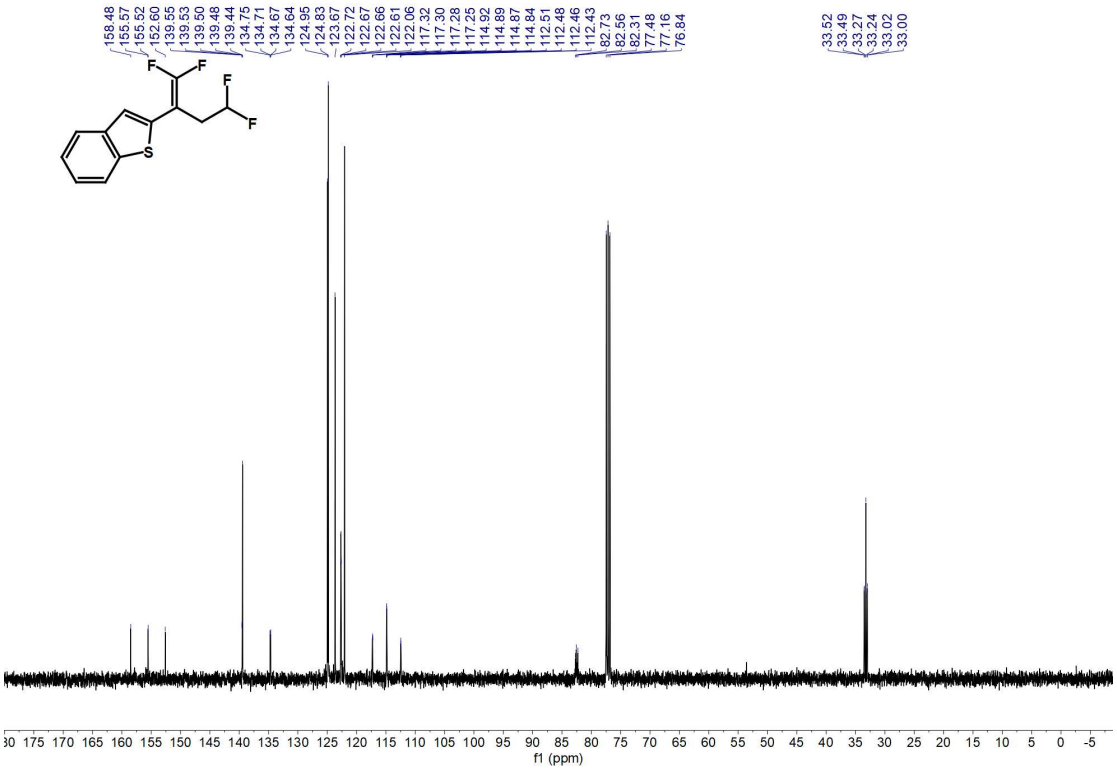
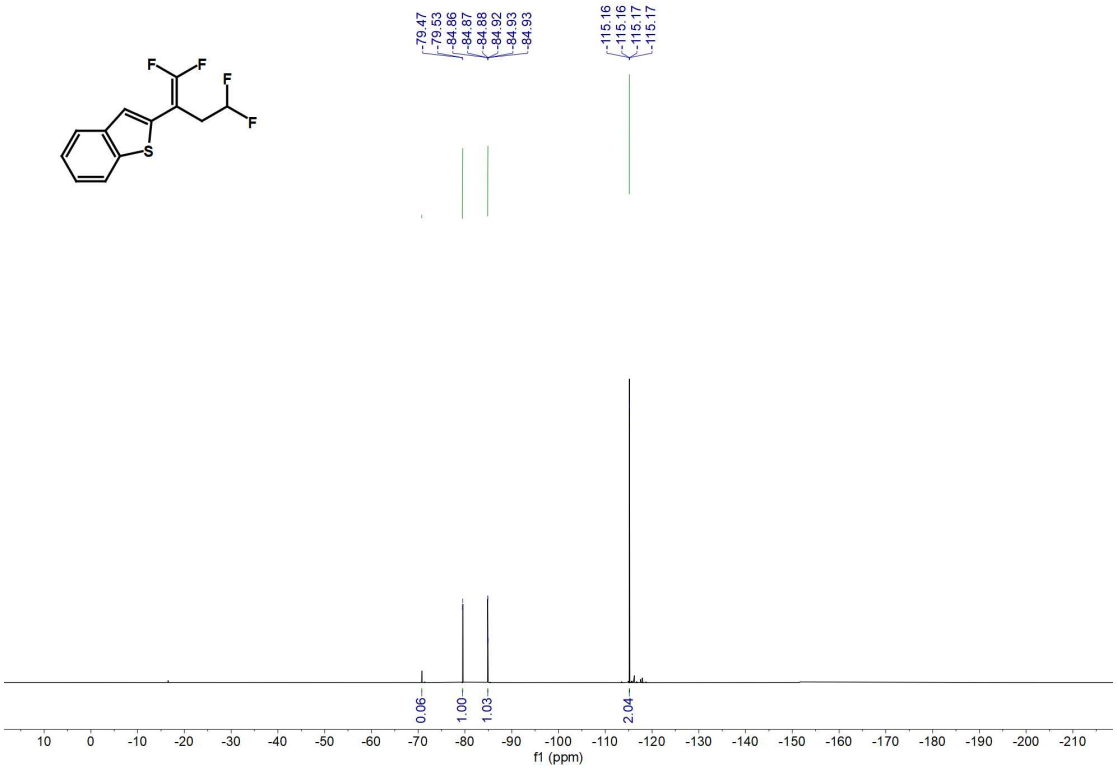
-115.82
F
F
F
F
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

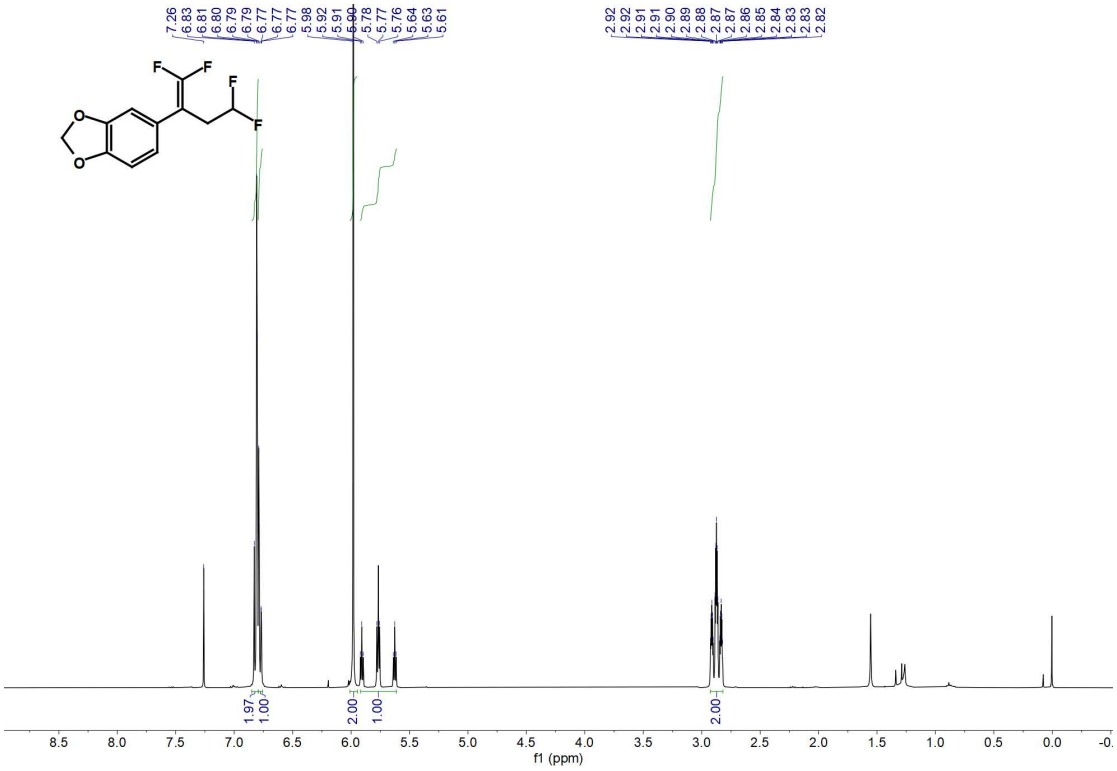
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of 3ac

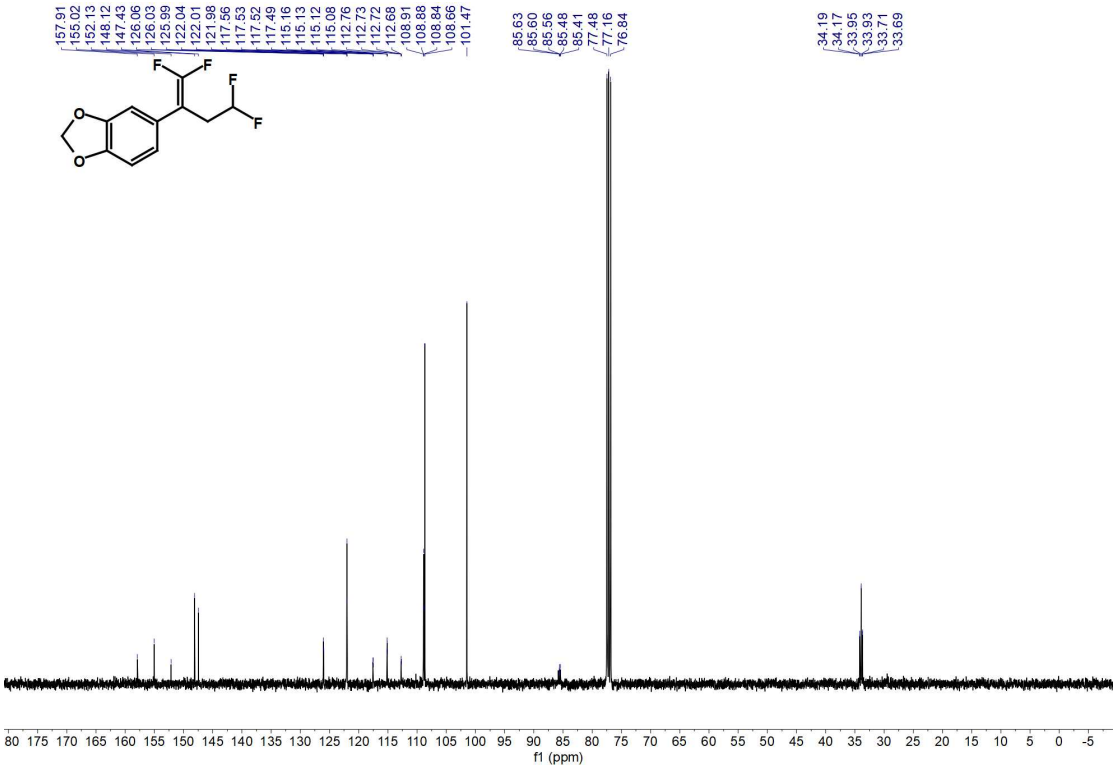





$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3ad**

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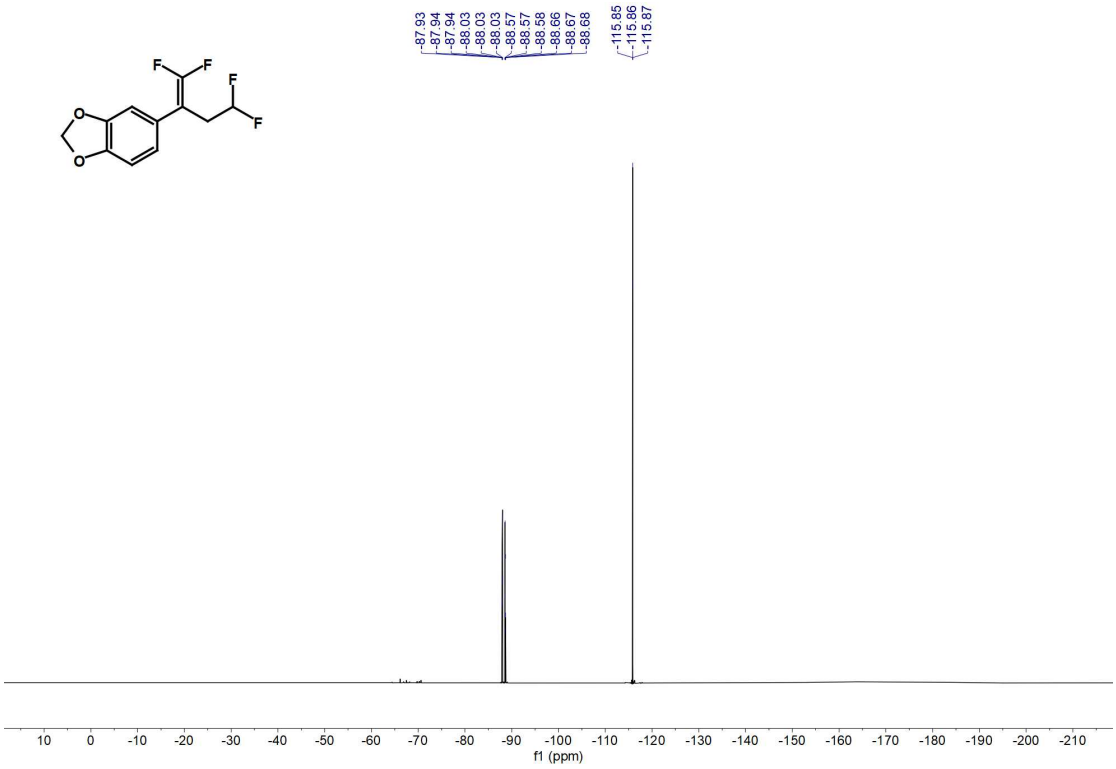
126.03
125.99
122.04
122.01
121.98
117.56
117.53
117.52
117.49
115.16
115.13
115.12
115.08
112.76
112.73
112.72
112.68
108.91
108.88
108.84
108.66
101.47
85.63
85.60
85.56
85.48
85.41
77.48
77.16
76.84
34.19
34.17
33.95
33.93
33.71
33.69
F
F
F
F
O
O
80 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)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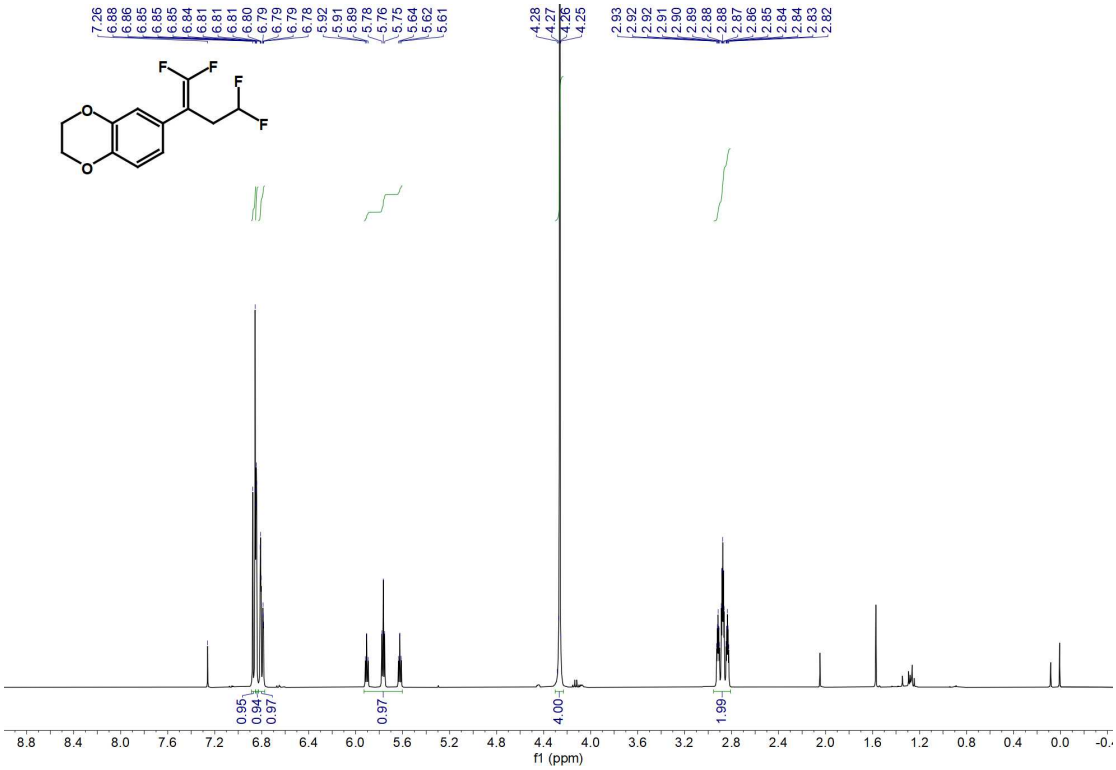
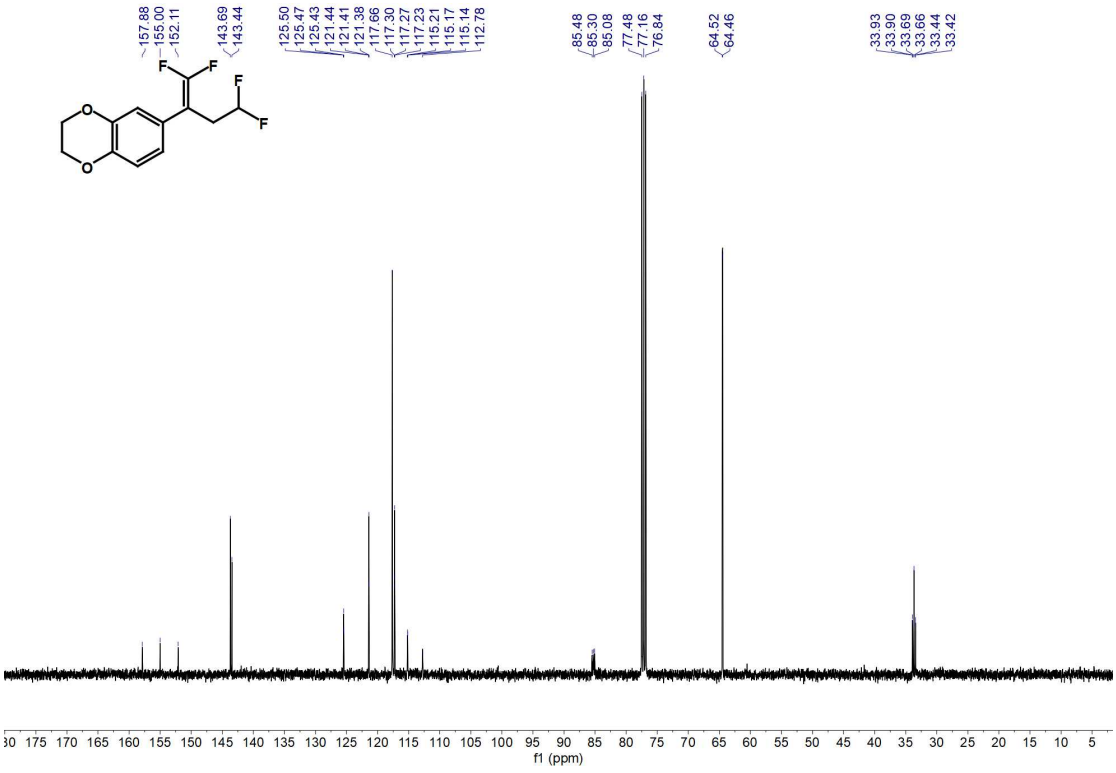
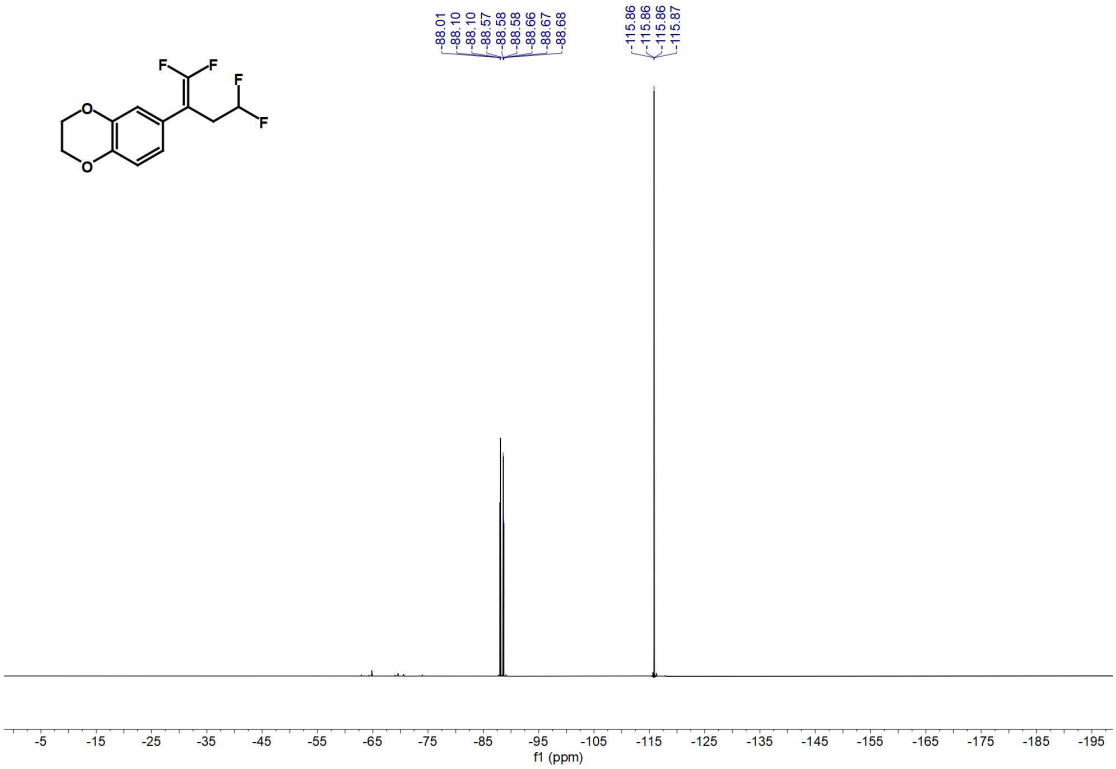
-87.94
-87.94
-88.03
-88.03
-88.03
-88.57
-88.57
-88.58
-88.66
-88.67
-88.68
-115.85
-115.86
-115.87
F
F
F
F
O
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

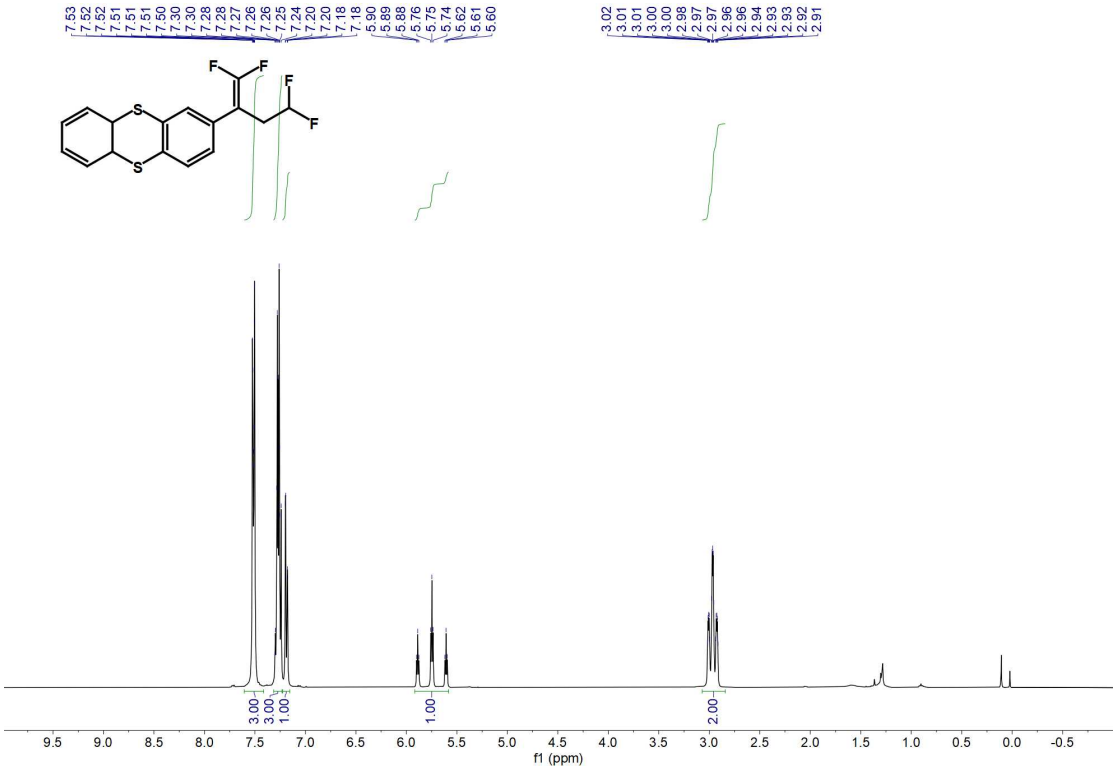
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3ae**

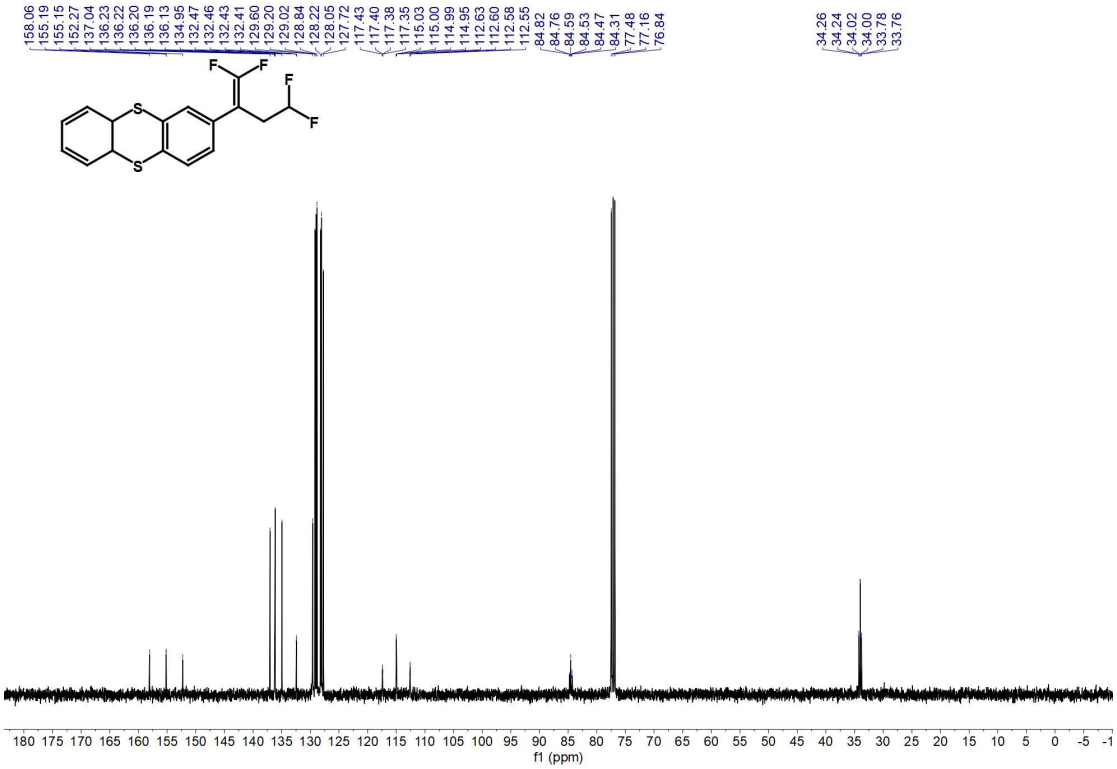





$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3af**

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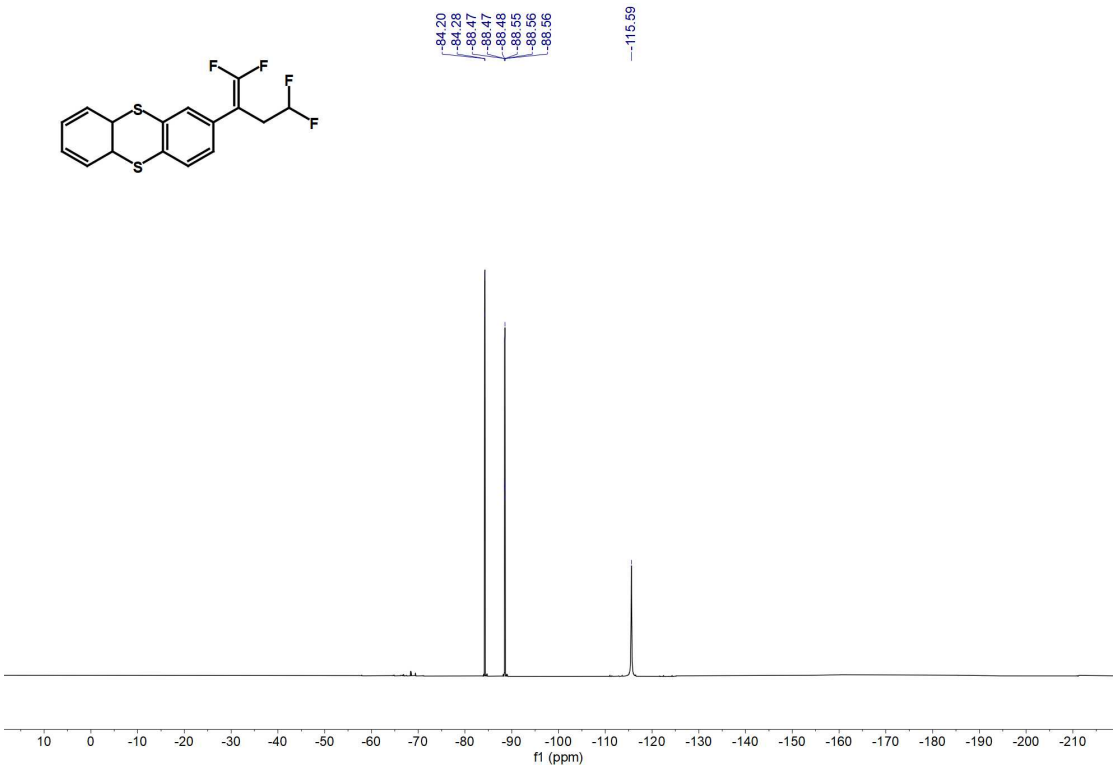
136.22
136.20
136.19
136.13
134.95
132.47
132.46
132.43
132.41
129.60
129.20
129.02
128.84
128.22
128.05
127.72
117.43
117.40
117.38
117.35
115.03
115.00
114.99
114.95
112.63
112.60
112.58
112.55
84.82
84.76
84.59
84.53
84.47
84.31
77.48
77.16
76.84
34.26
34.24
34.02
34.00
33.78
33.76
F
F
F
F
S
S
180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -1
f1 (ppm)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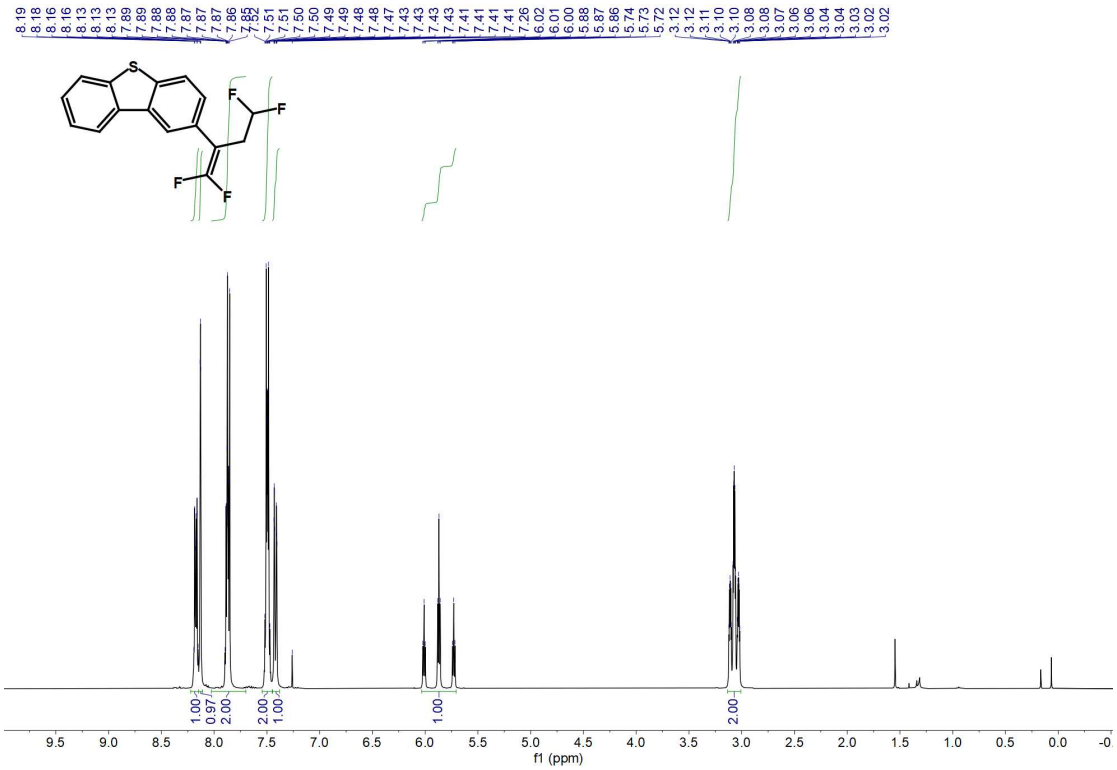
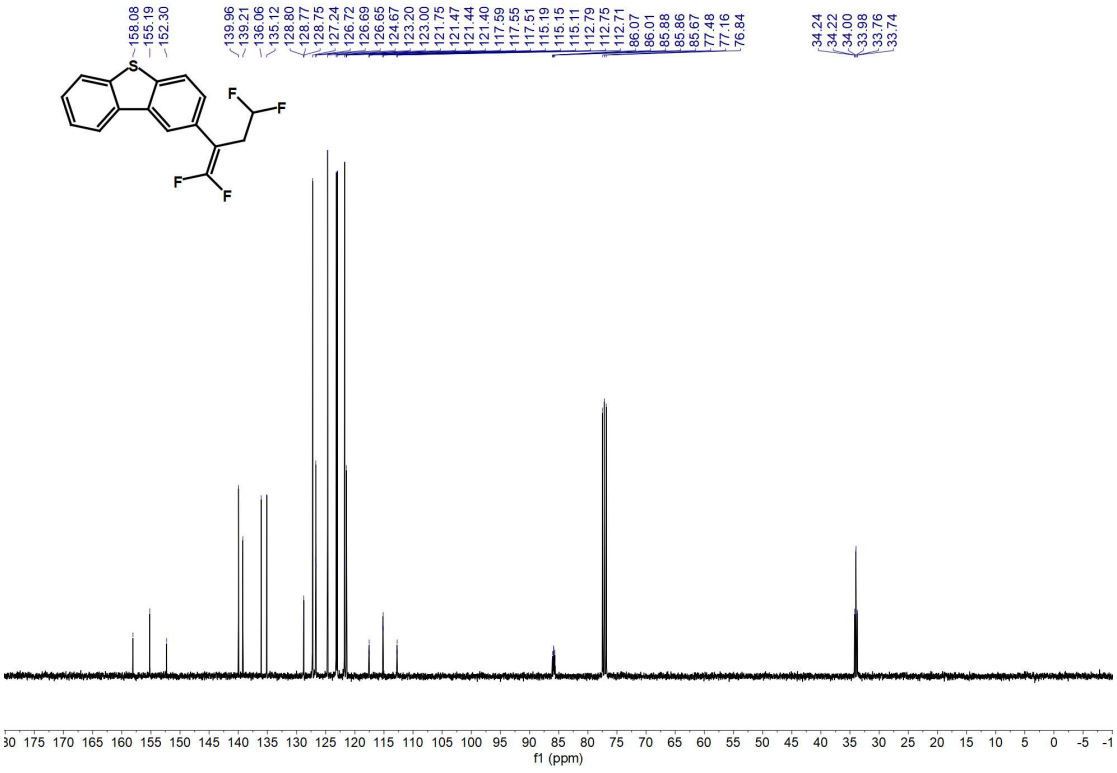
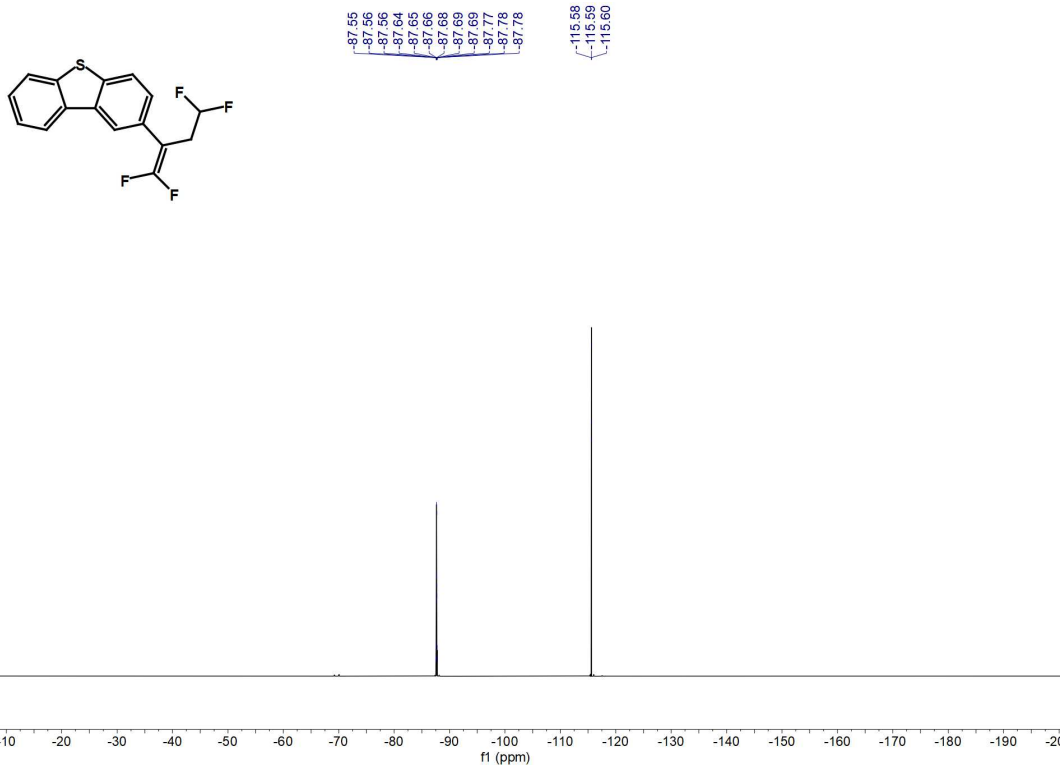
-84.28
-88.47
-88.47
-88.48
-88.55
-88.56
-88.56
-115.59
F
F
F
F
S
S
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

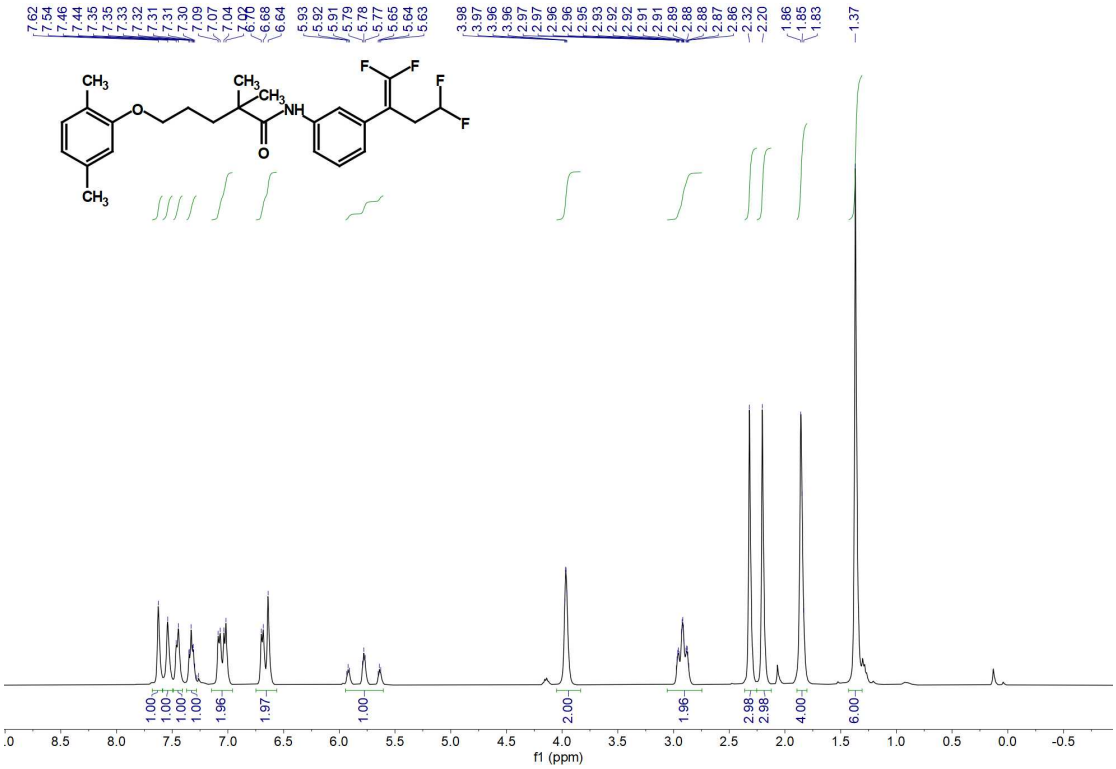
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3ag**

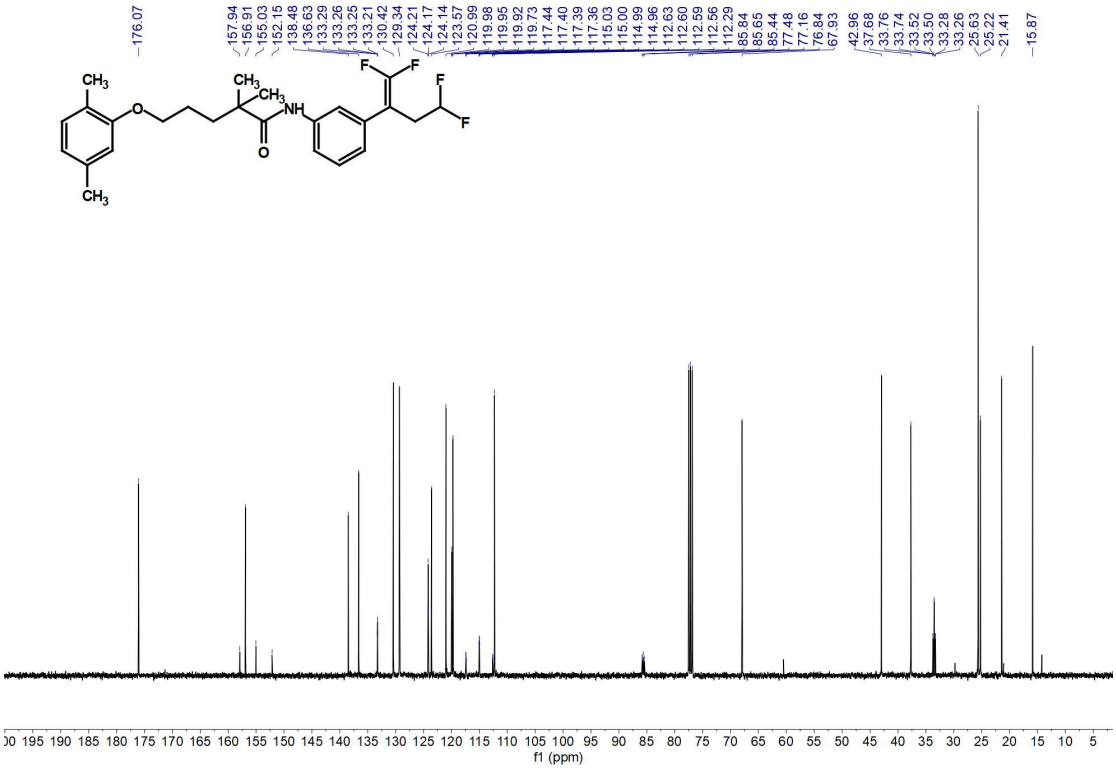





$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3ah**

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152.15
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133.29
133.26
133.25
133.21
130.42
129.34
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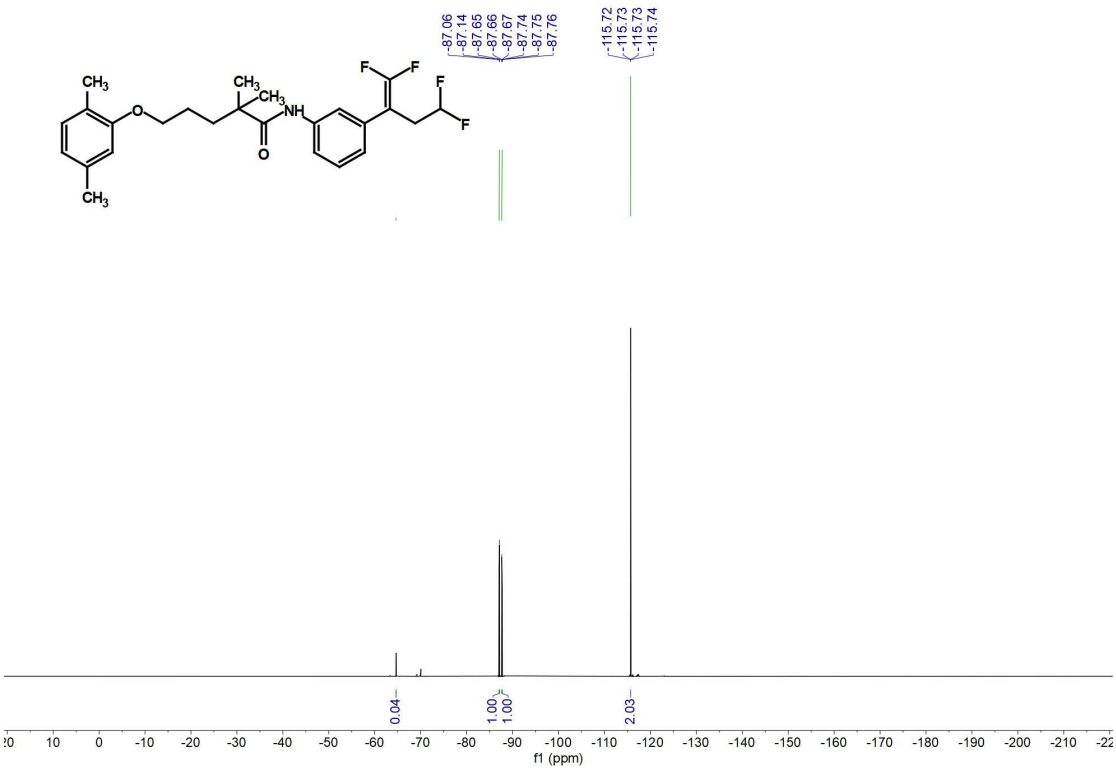
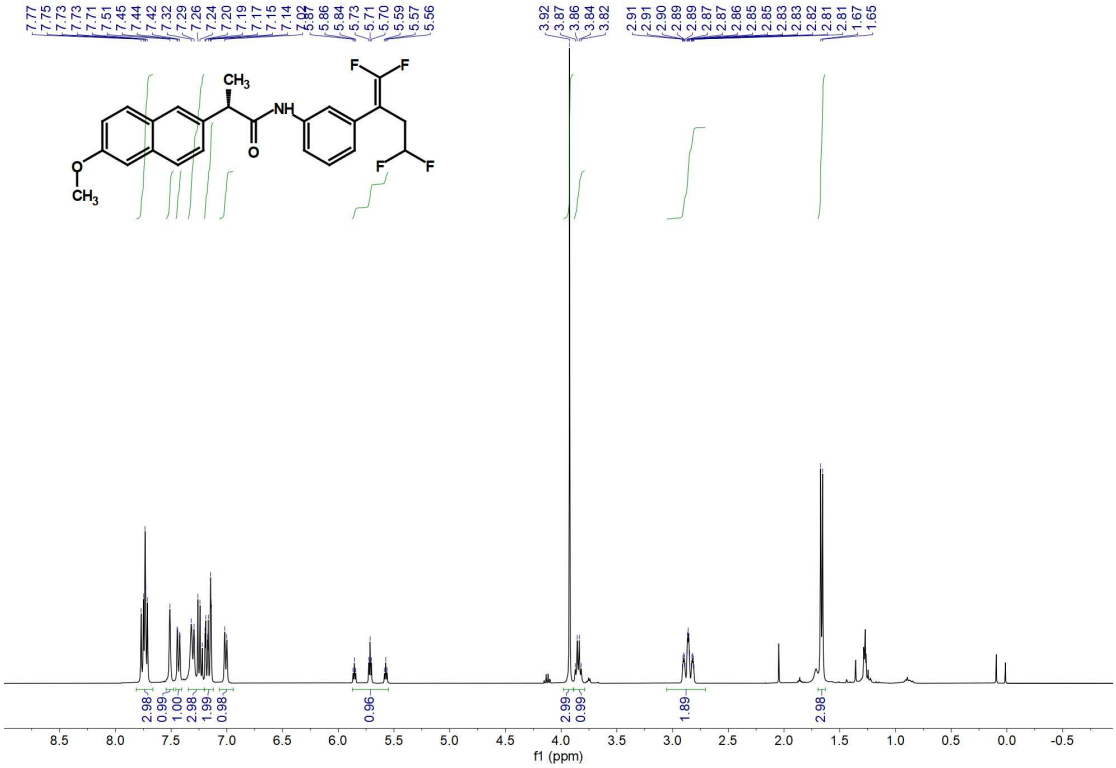
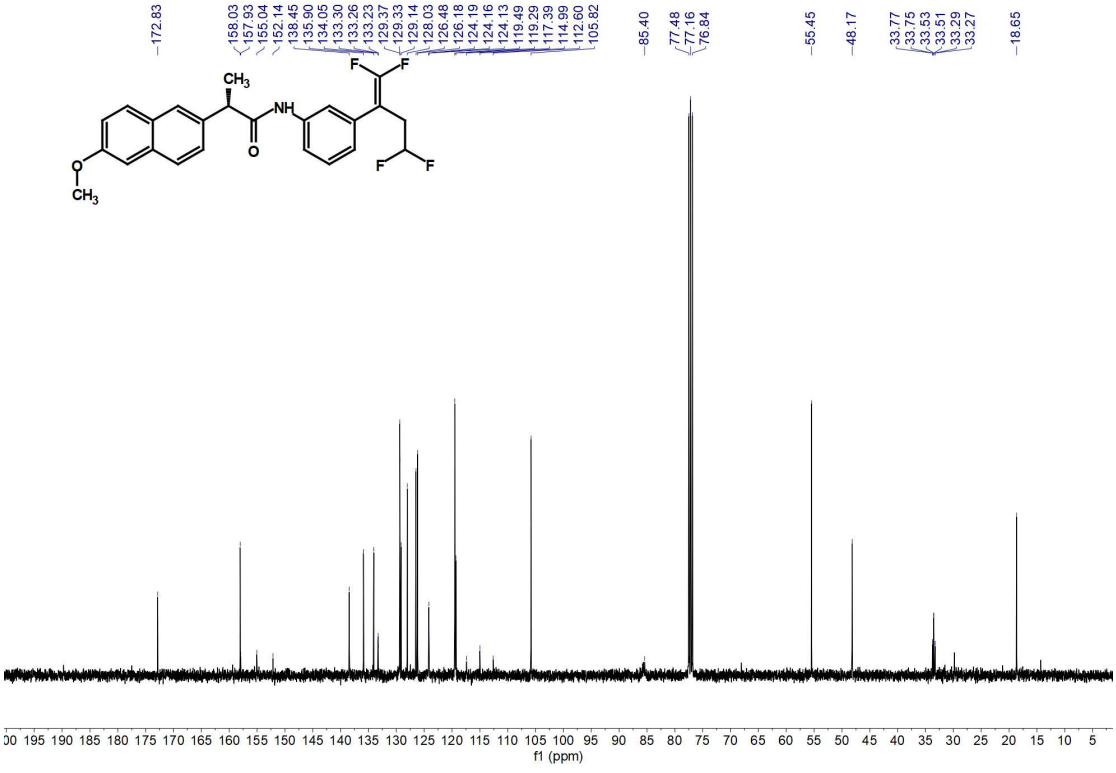
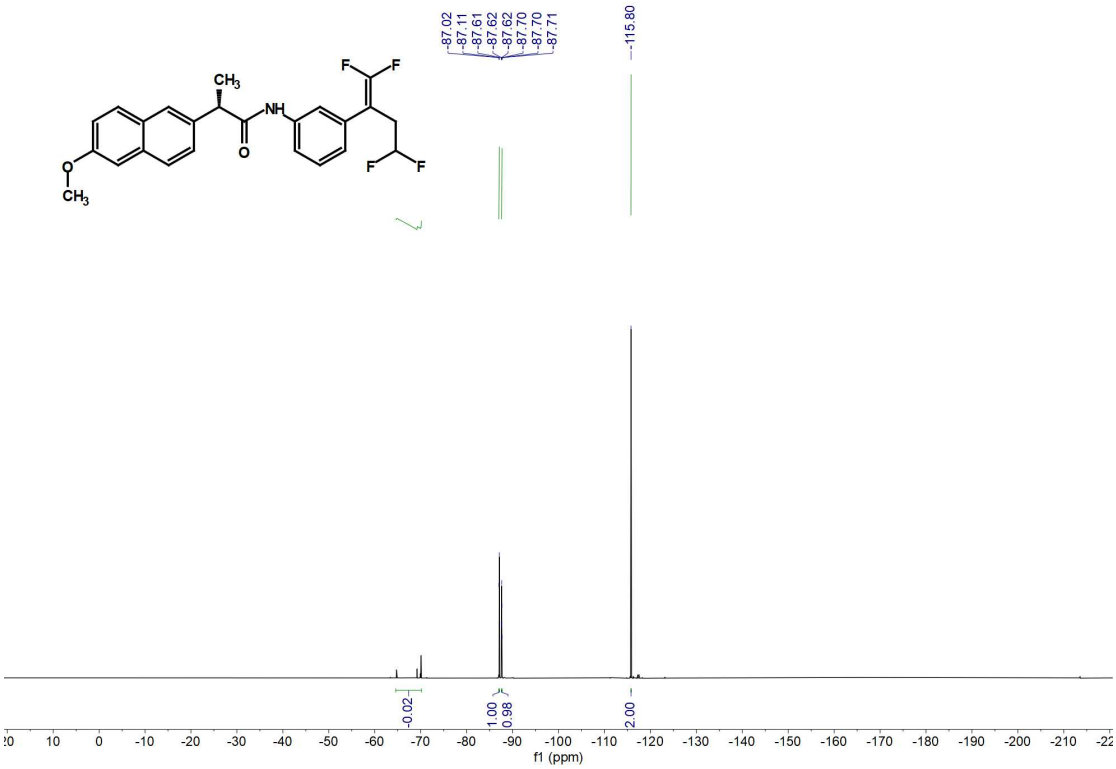
124.17
124.14
123.57
120.99
119.98
119.95
119.92
119.73
117.44
117.40
117.39
117.36
115.03
115.00
114.99
114.96
112.63
112.60
112.59
112.56
112.29
85.84
85.65
85.44
77.48
77.16
76.84
67.93
42.96
37.68
33.76
33.74
33.52
33.50
33.28
33.26
25.63
25.22
21.41
15.87
f1 (ppm)


87.06
87.14
87.65
87.66
87.67
87.74
87.75
87.76
115.72
115.73
115.73
115.74
0.04
1.00
1.00
2.03
f1 (ppm)

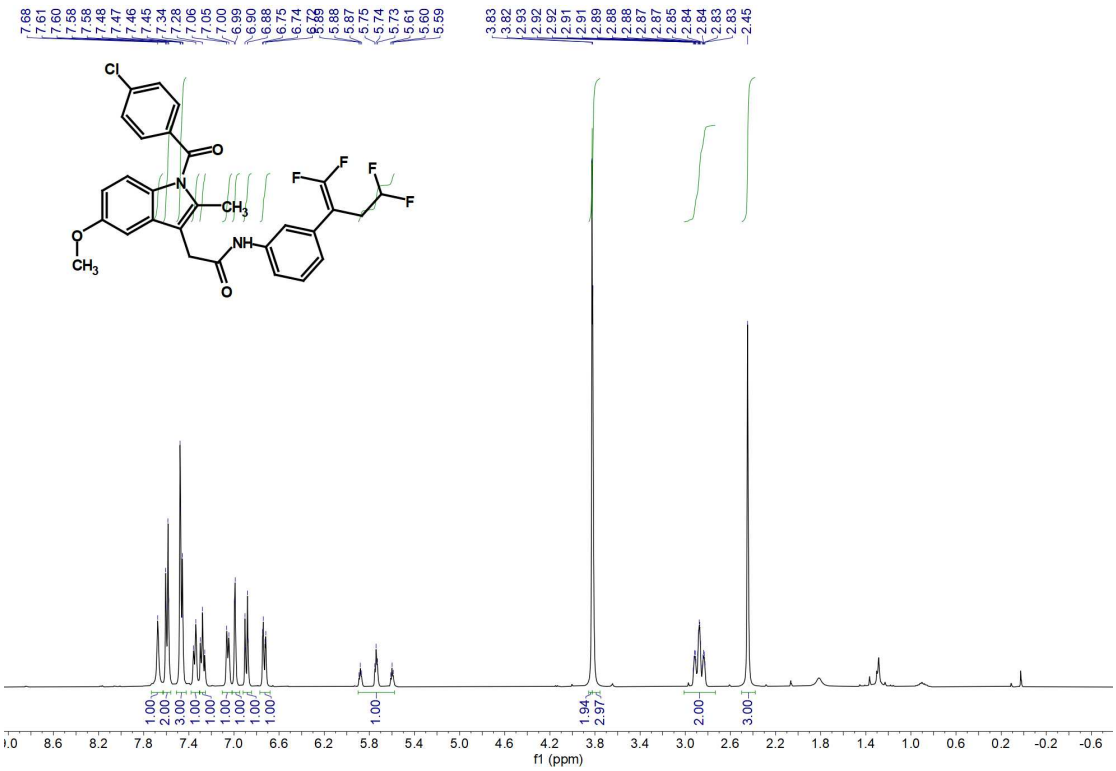
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3ai**

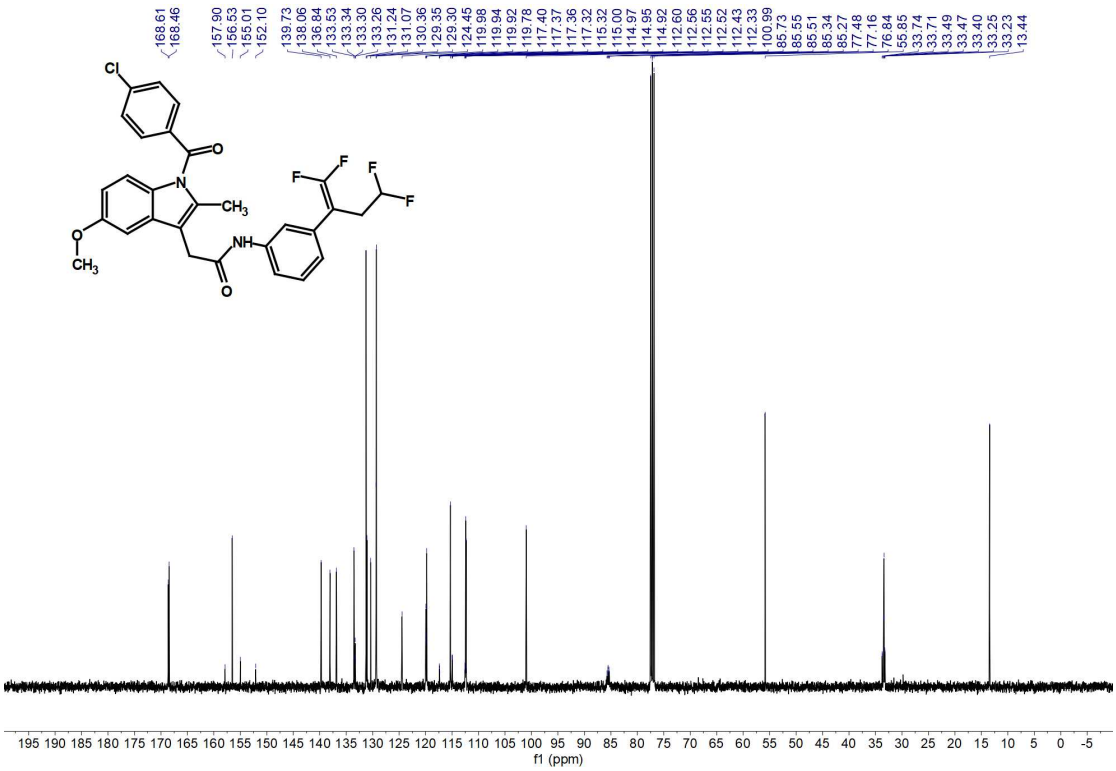


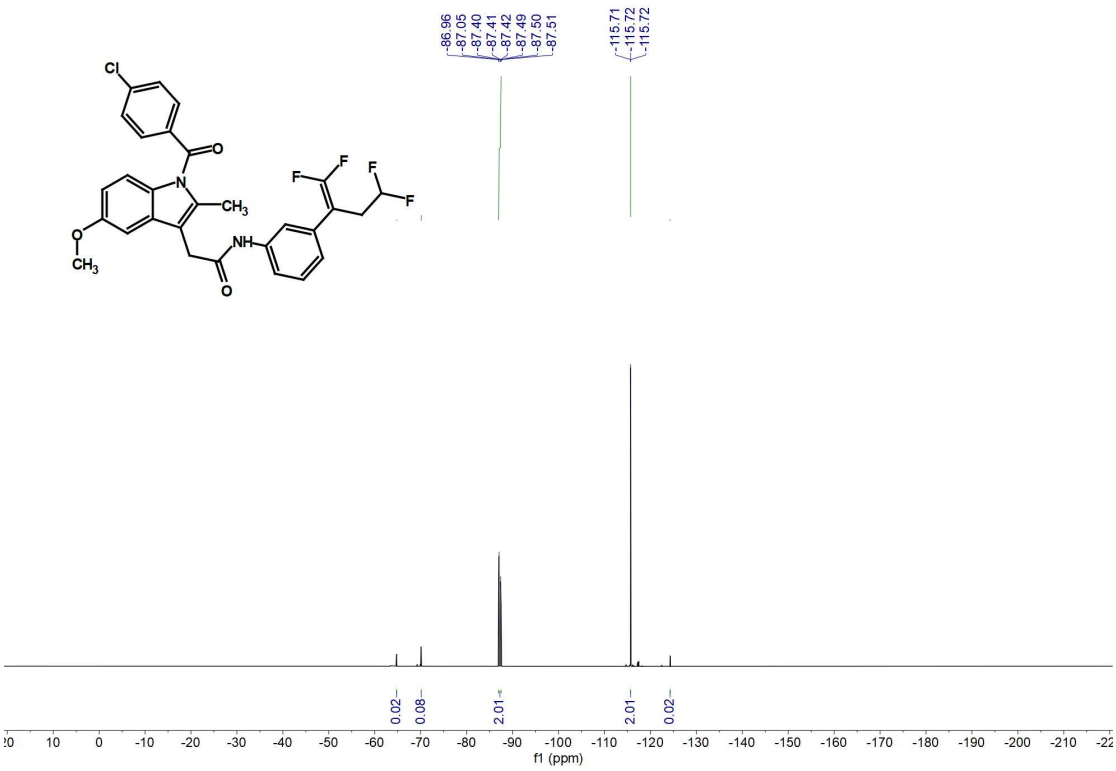





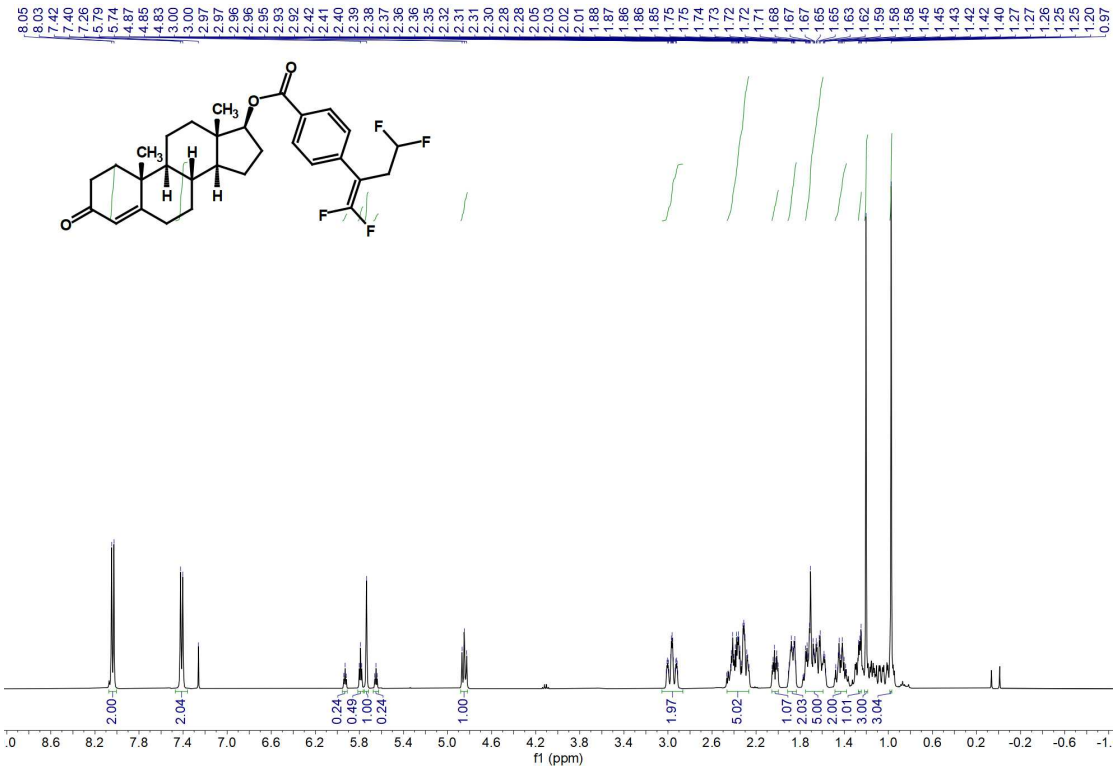

$^{1}$H, $^{13}$C, $^{19}$F NMR Spectra of **3aj**

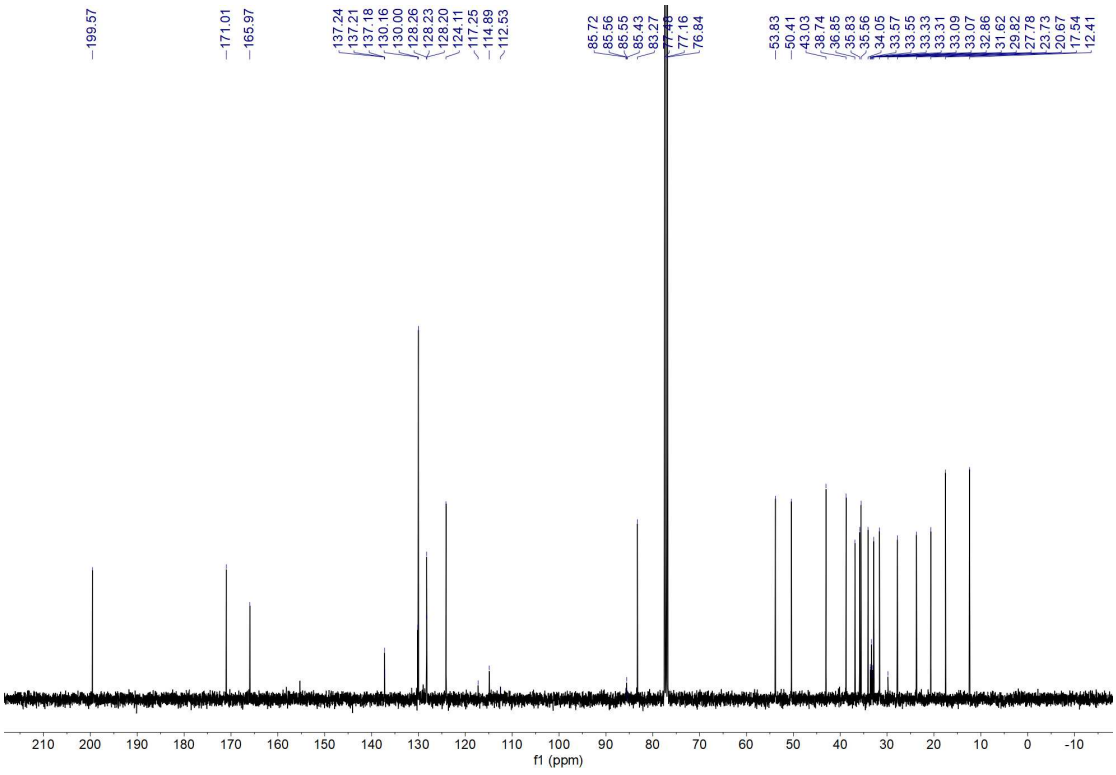


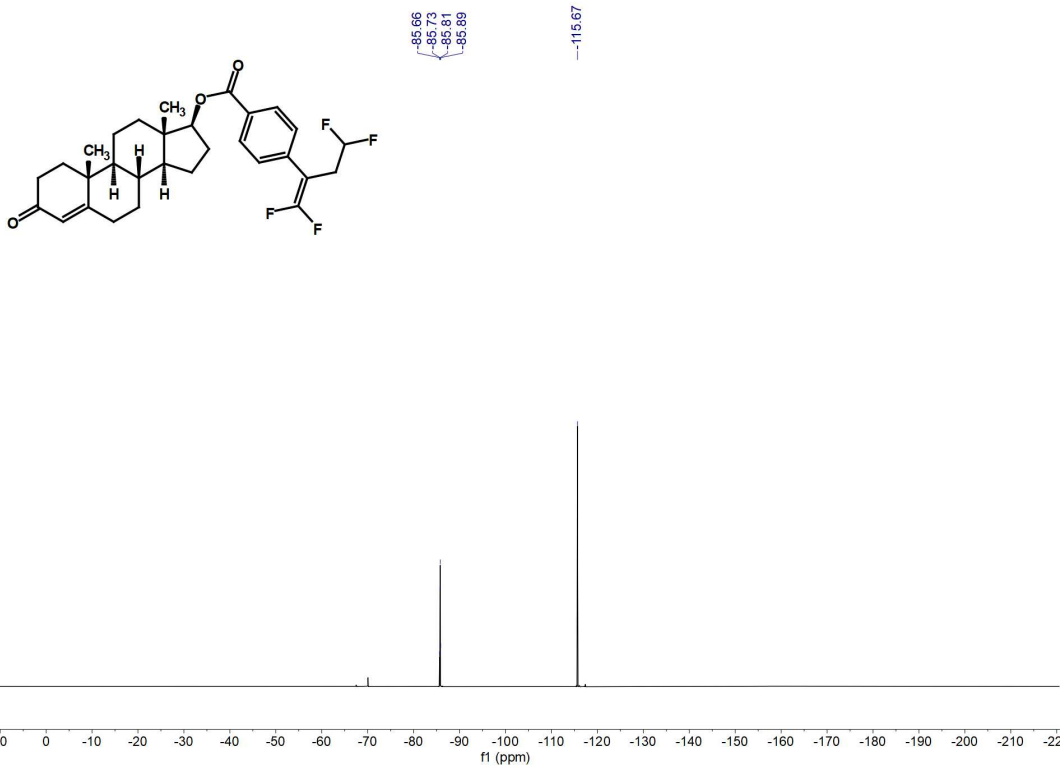

168.61
168.46
157.90
156.53
155.01
152.10
139.73
138.06
136.84
133.53
133.34
133.30
133.26
131.24
131.07
130.36
129.35
129.30
124.45
119.98
119.94
119.92
119.78
117.40
117.37
117.36
117.32
115.32
115.00
114.97
114.95
114.92
112.60
112.56
112.55
112.52
112.43
112.33
100.99
85.73
85.55
85.51
85.34
85.27
77.48
77.16
76.84
55.85
33.74
33.71
33.49
33.47
33.40
33.25
33.23
13.44
Cl
O
N
CH3
F
F
F
F
O
CH3
NH
O
195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)


-86.96
-87.05
-87.40
-87.41
-87.42
-87.49
-87.50
-87.51
-115.71
-115.72
-115.72
Cl
O
N
CH3
F
F
F
F
O
CH3
NH
O
0.02
0.08
2.01
2.01
0.02
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

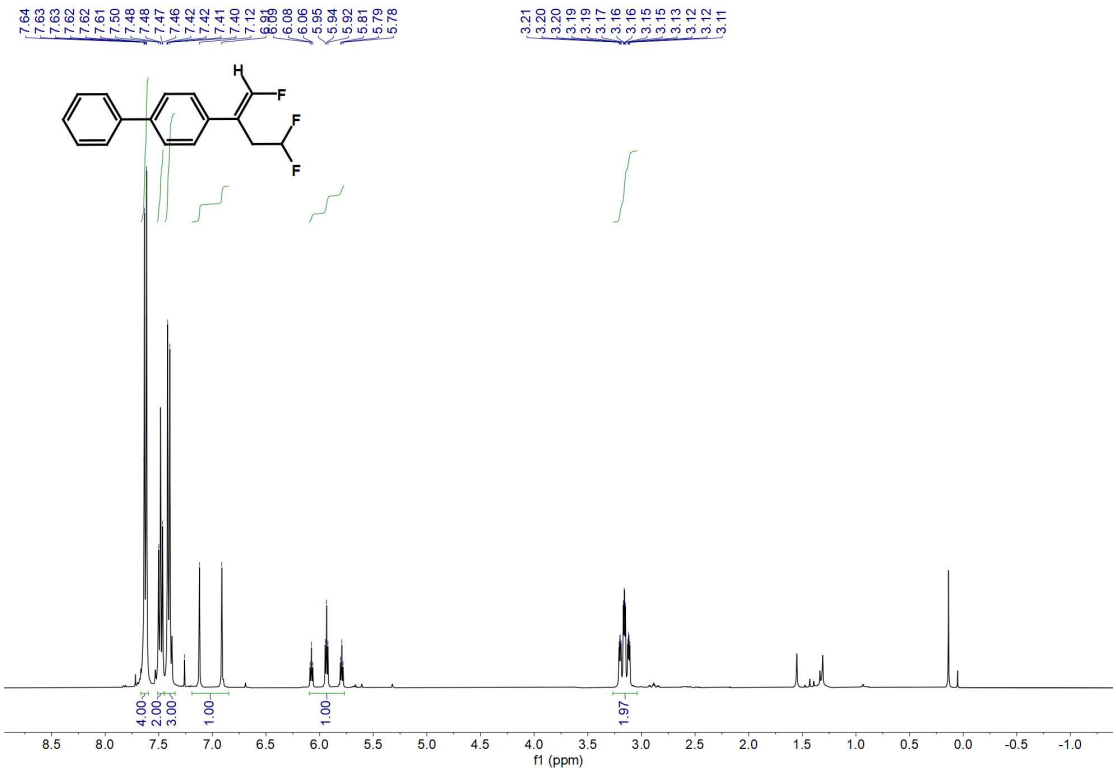
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **3ak**

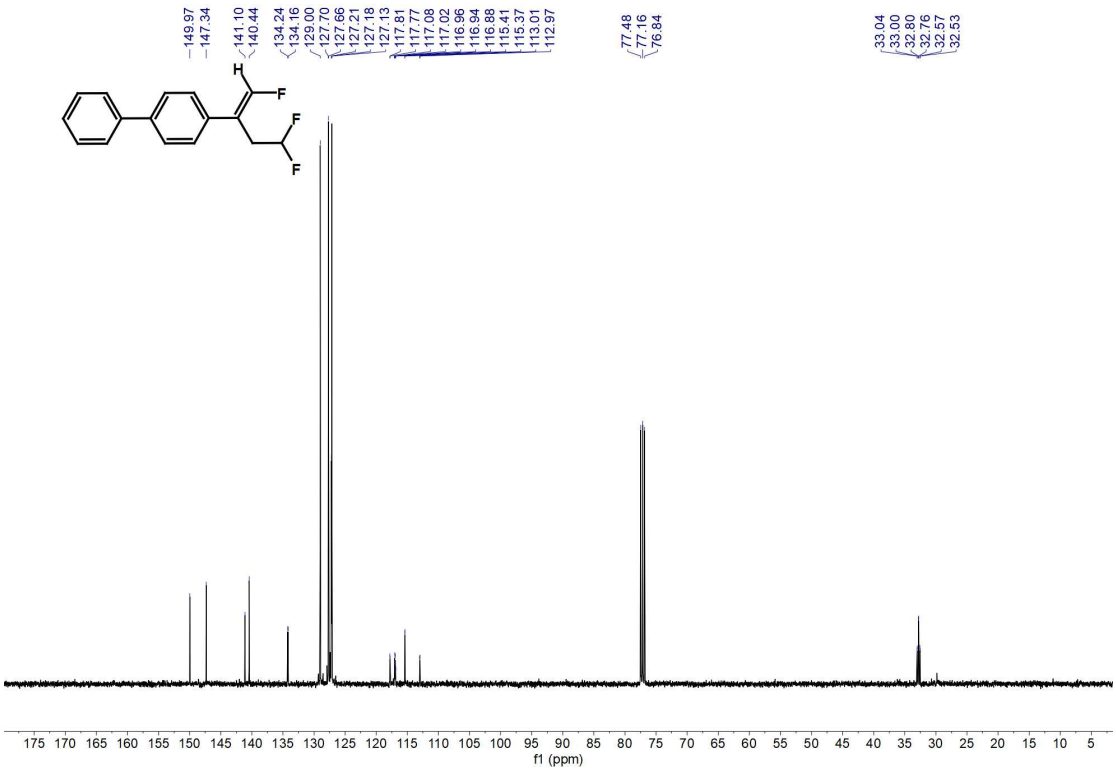




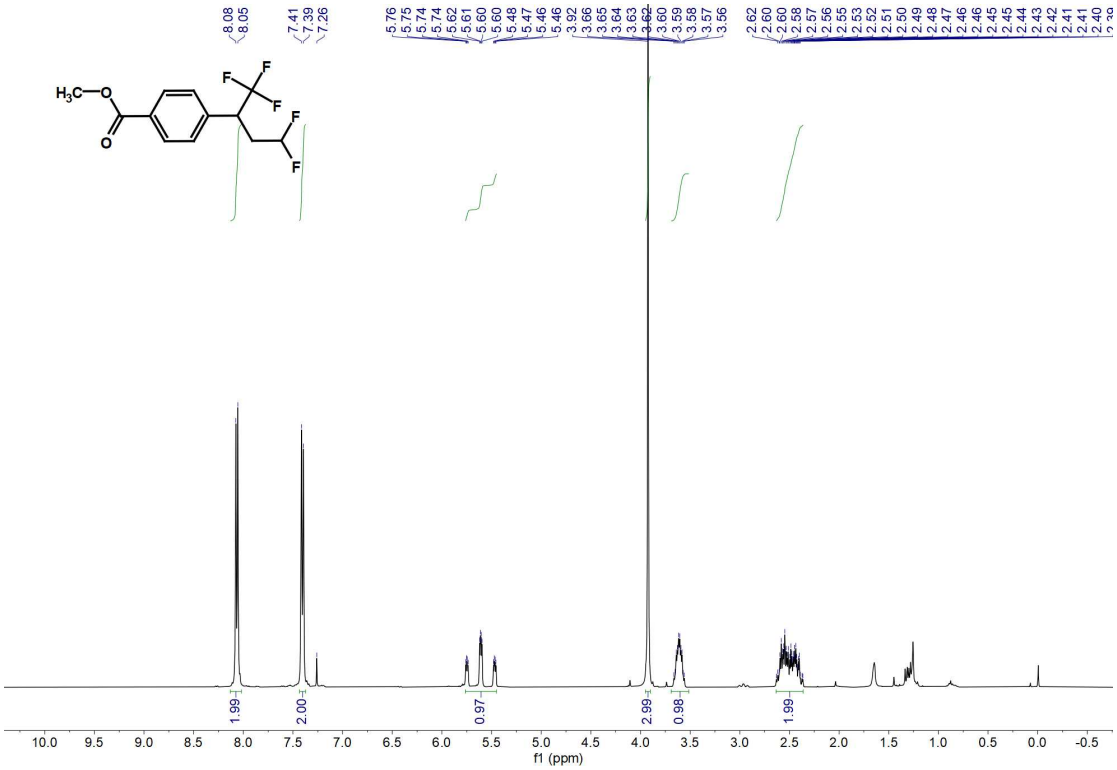

$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **4**

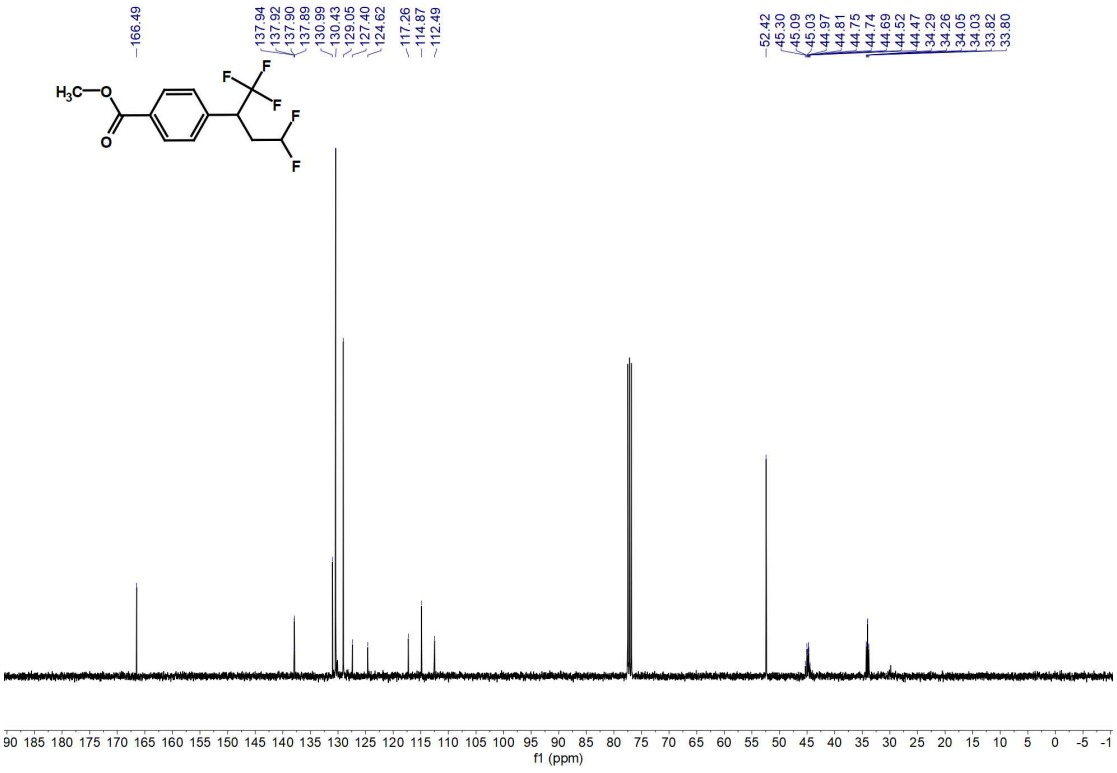


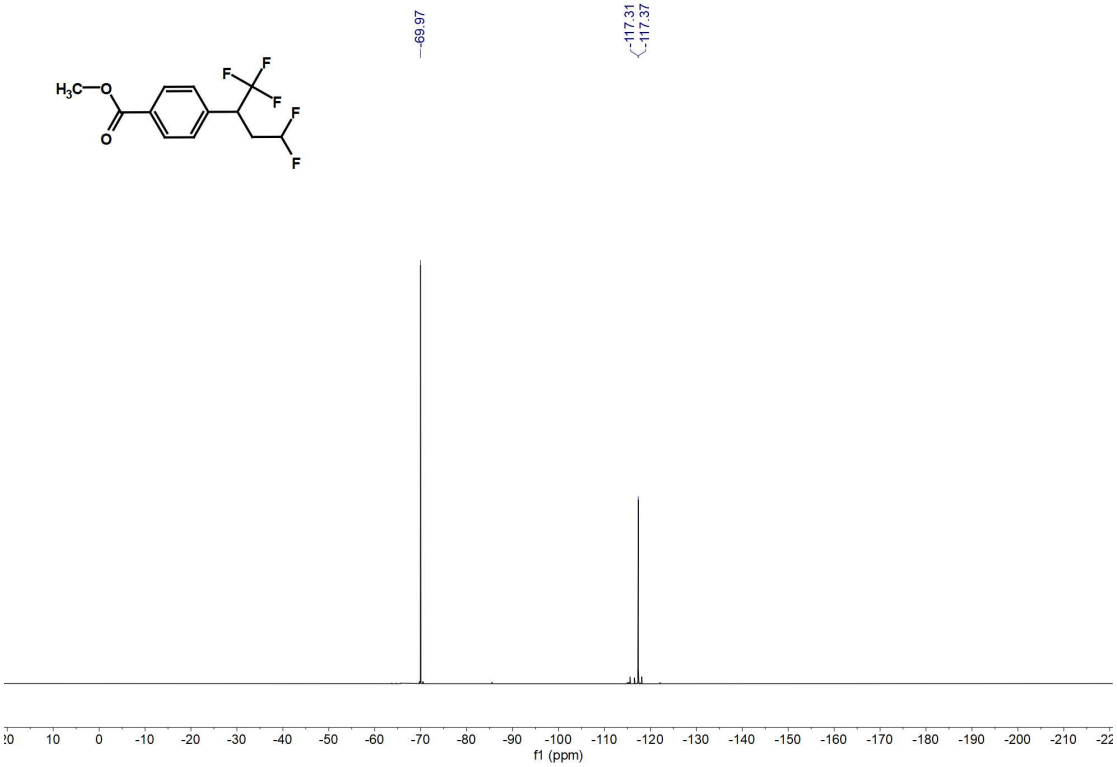

149.97
147.34
141.10
140.44
134.24
134.16
129.00
127.70
127.66
127.21
127.18
127.13
117.81
117.77
117.08
117.02
116.96
116.94
116.88
115.41
115.37
113.01
112.97
77.48
77.16
76.84
33.04
33.00
32.80
32.76
32.57
32.53
H
F
F
F
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)


H
F
F
F
4
-114.31
-114.32
-125.31
-125.31
-125.32
0.09
2.00
1.07
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

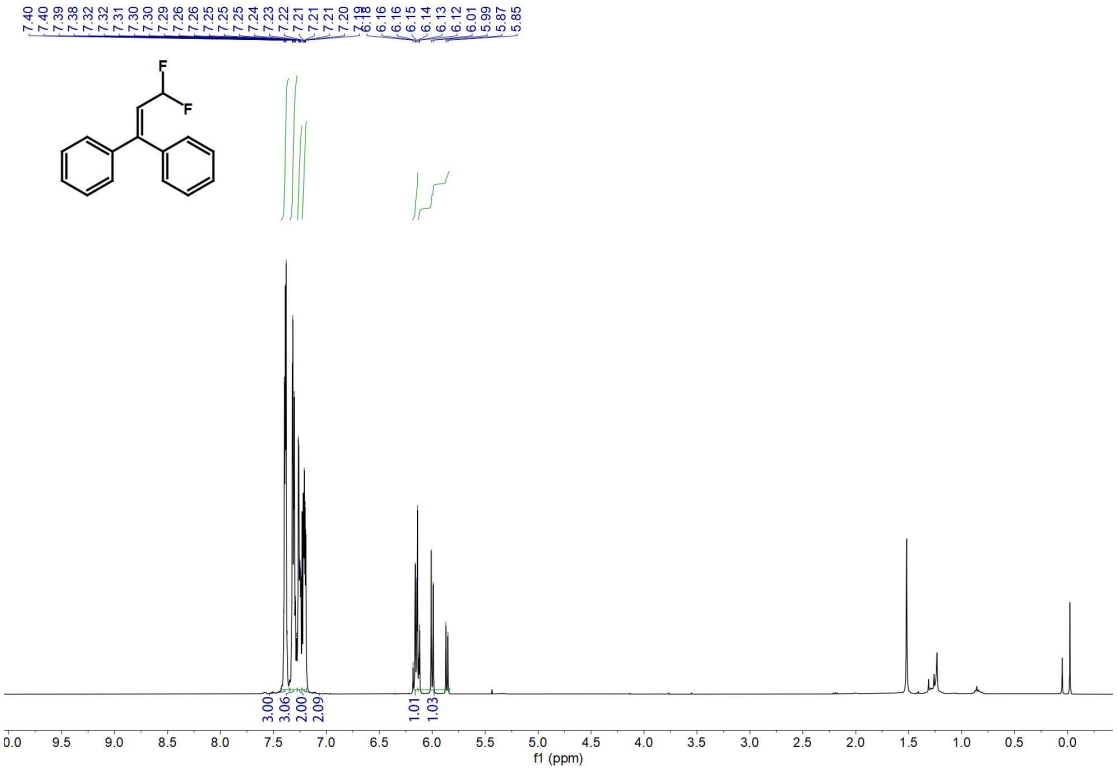
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **5**

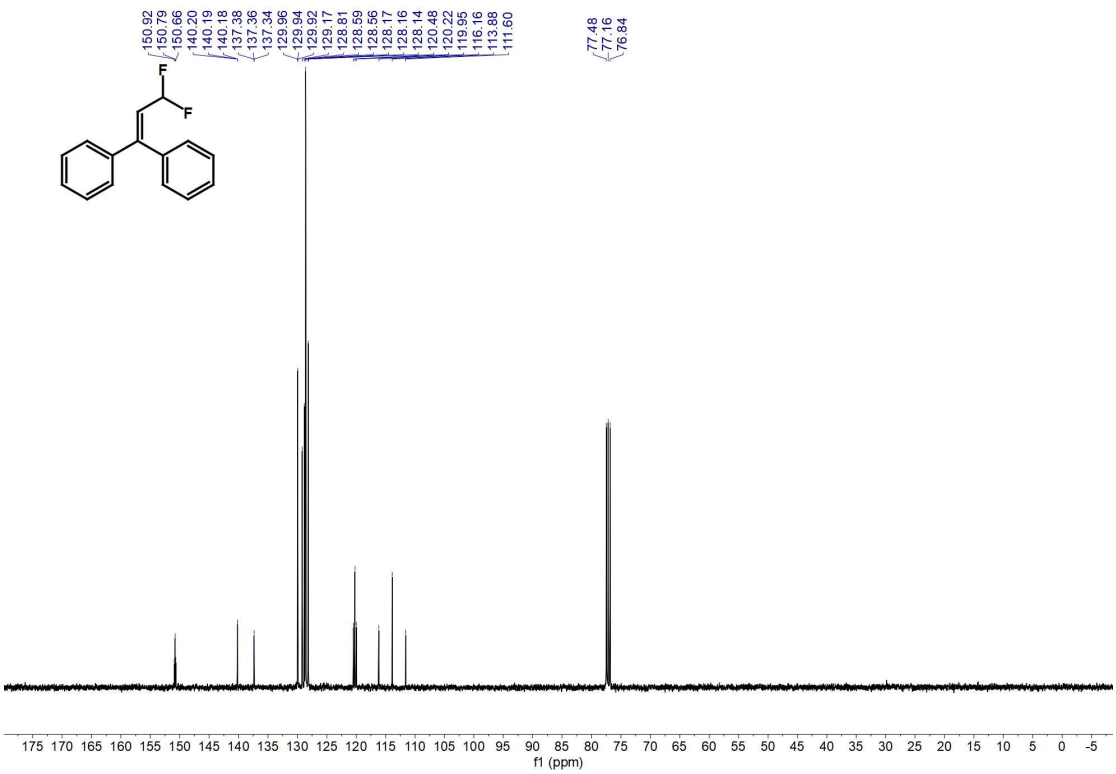


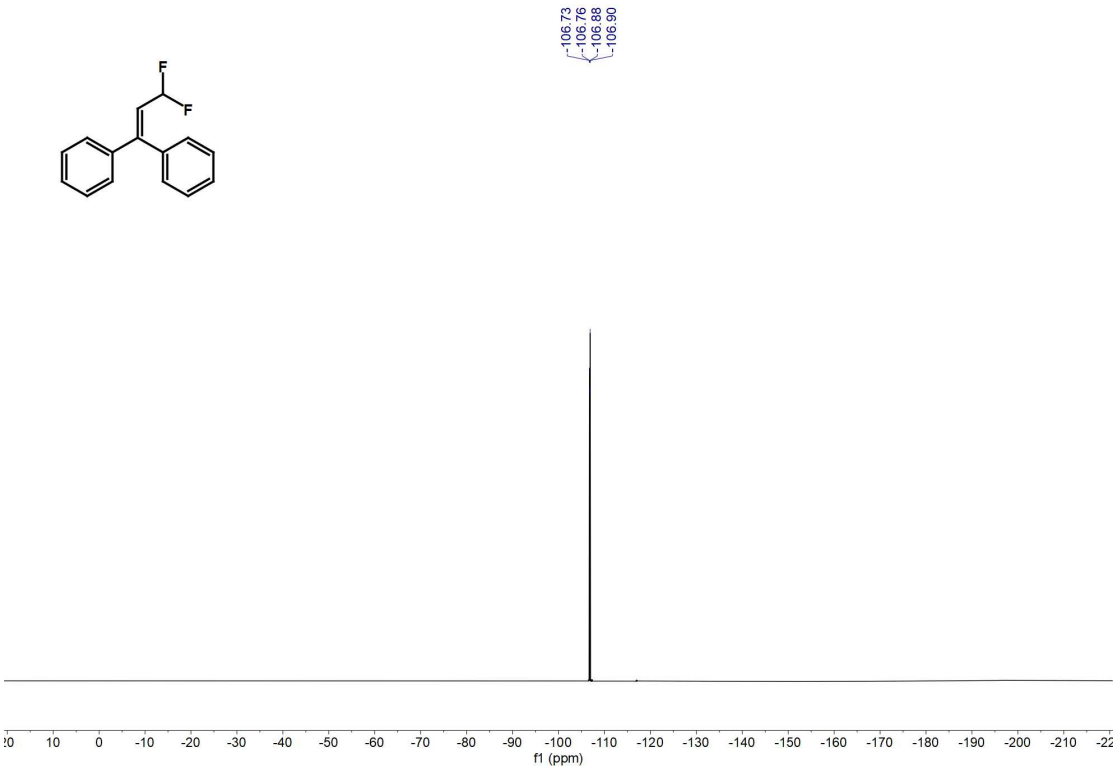





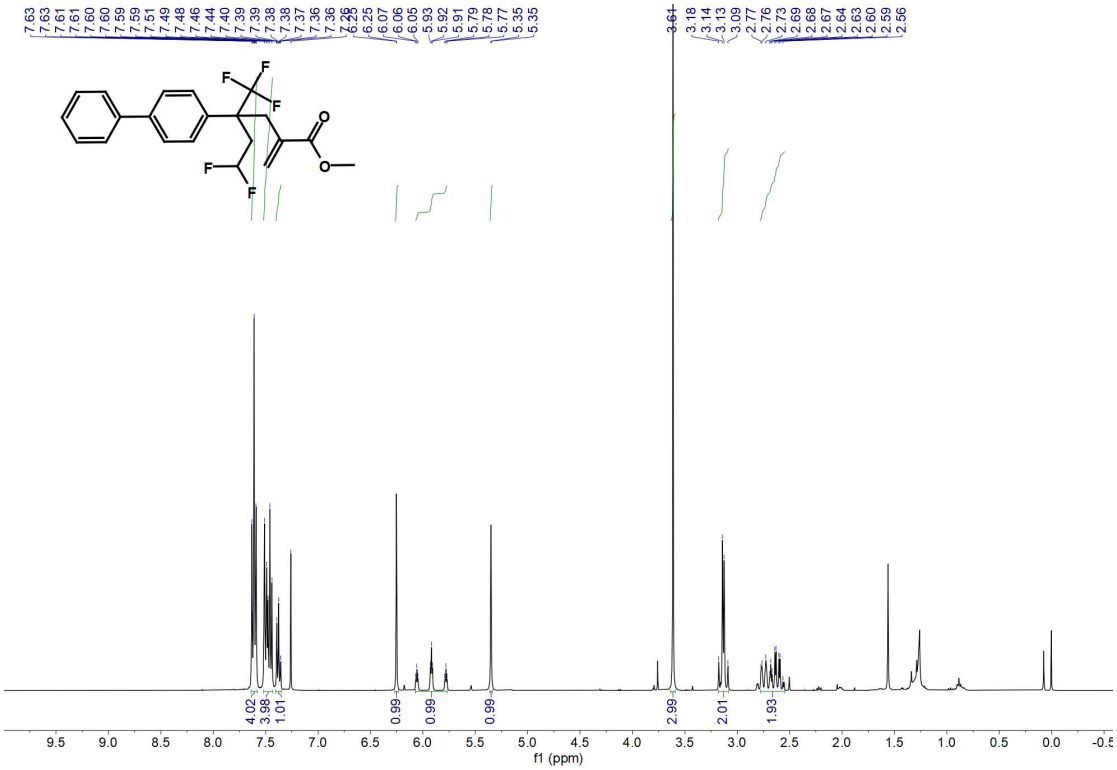

$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **6**

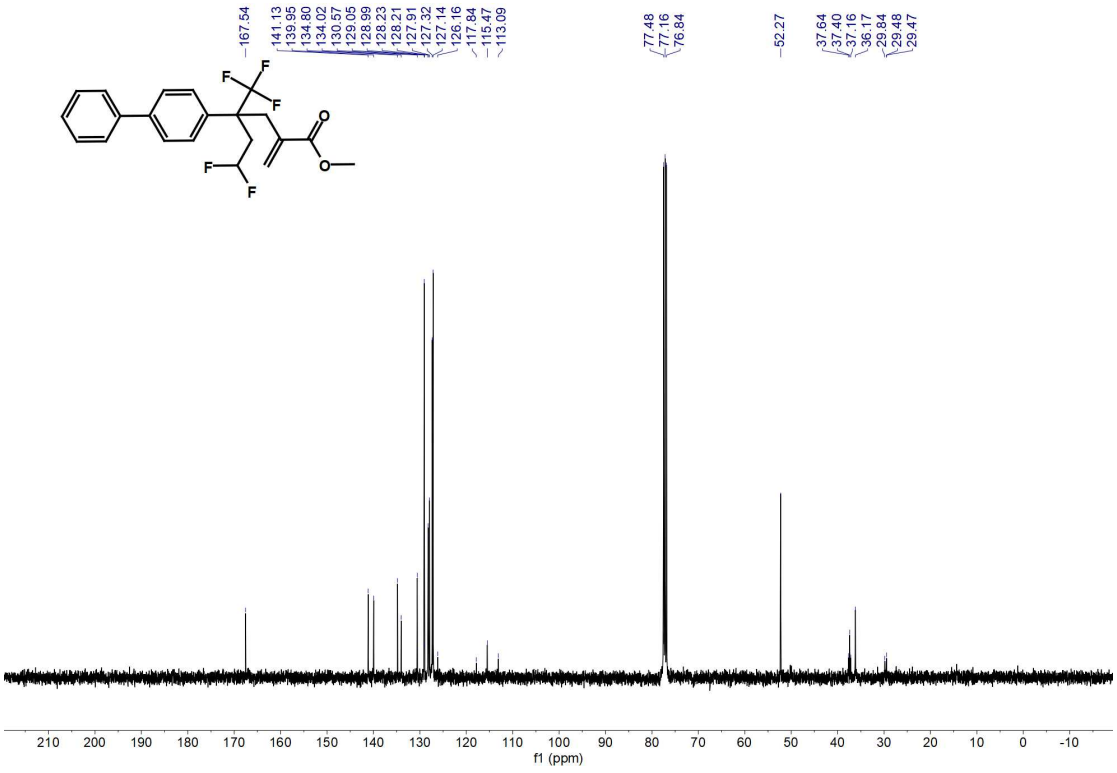


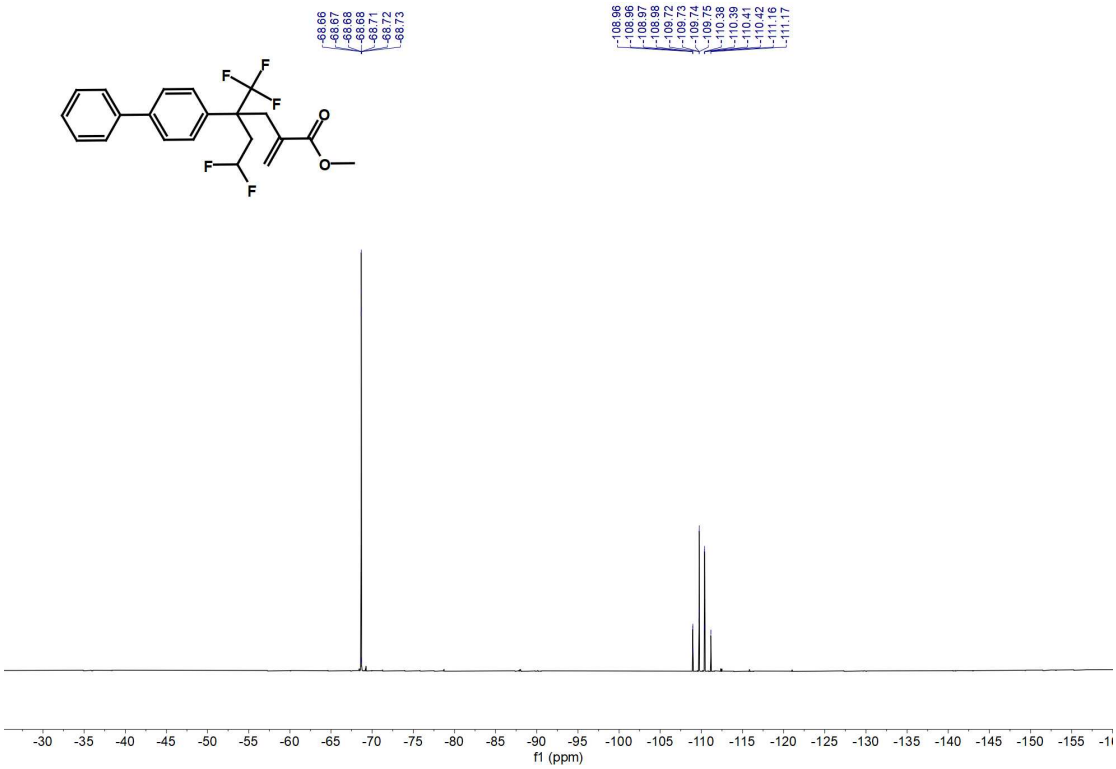

150.92
150.79
150.66
140.20
140.19
140.18
137.38
137.36
137.34
129.96
129.94
129.92
129.17
128.81
128.59
128.56
128.17
128.16
128.14
120.48
120.22
119.95
116.16
113.88
111.60
77.48
77.16
76.84
F
F
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)


-106.73
-106.76
-106.88
-106.90
F
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

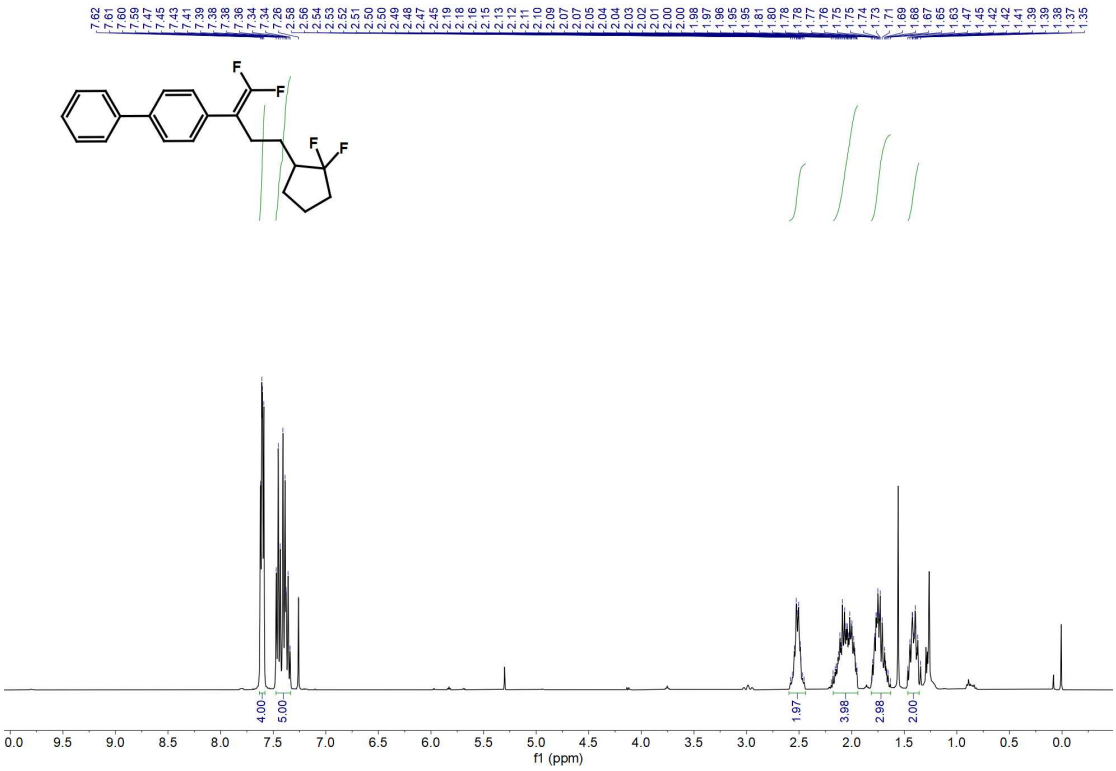
$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **7**

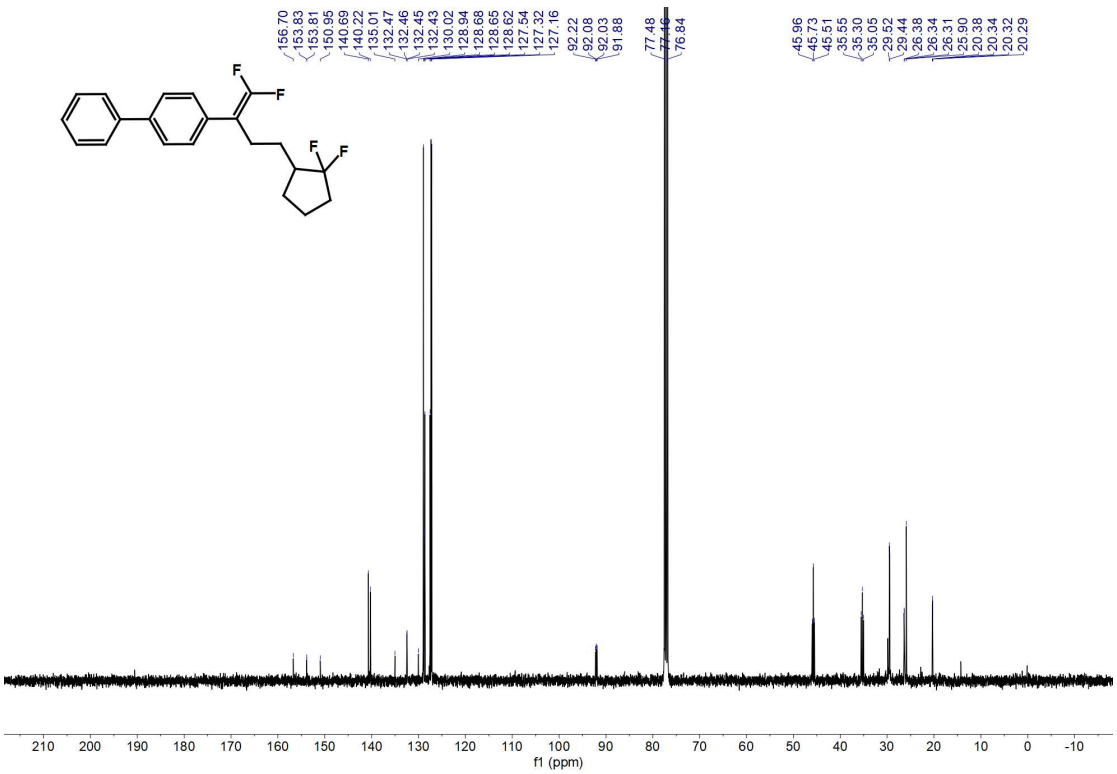


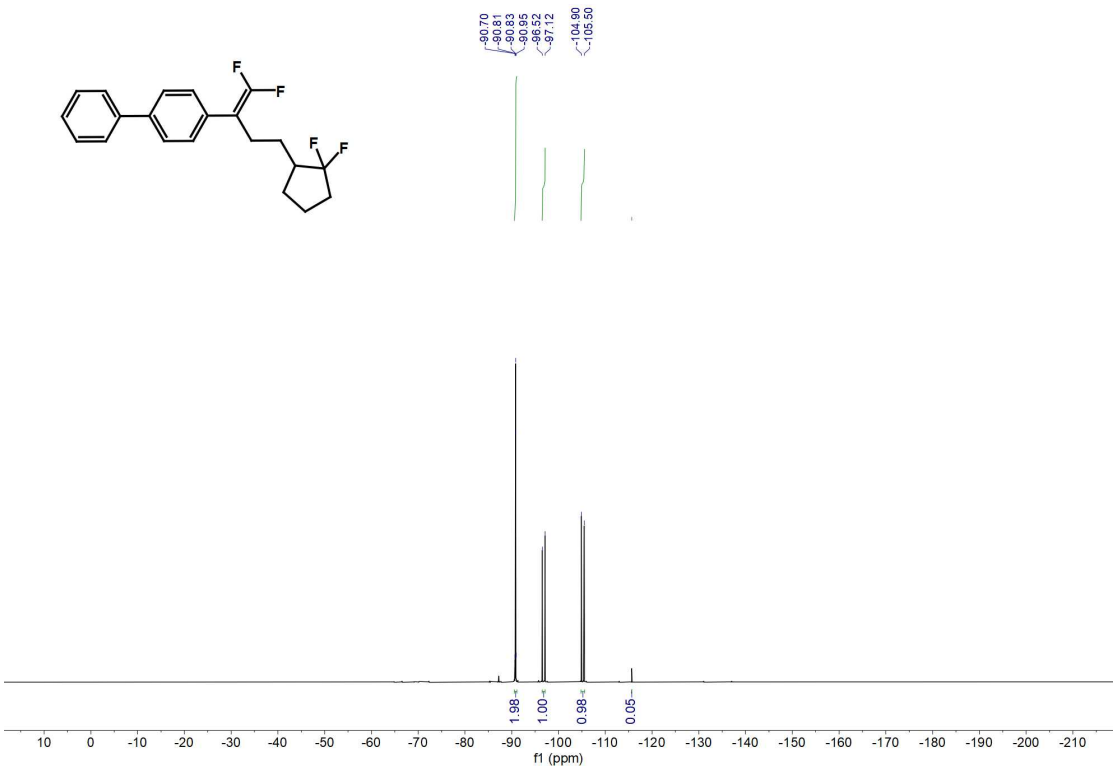






$^{1}H$, $^{13}C$, $^{19}F$ NMR Spectra of **8**




156.70
153.83
153.81
150.95
140.69
140.22
135.01
132.47
132.46
132.45
132.43
130.02
128.94
128.88
128.65
128.62
127.54
127.32
127.16
92.22
92.08
92.03
91.88
77.48
77.16
76.84
45.96
45.73
45.51
35.55
35.30
35.05
29.52
29.44
26.38
26.34
26.31
25.90
20.38
20.34
20.32
20.29
F
F
F
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


90.70
90.81
90.83
90.95
96.52
97.12
104.90
105.50
F
F
F
F
1.98
1.00
0.98
0.05
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)