Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Deoxygenative *gem*-difluorovinylation of aliphatic alcohols

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1. General information

Unless otherwise noted, materials were purchased from commercial suppliers (Alfa, TCI and Sigma-Aldrich etc.), and used without further purification. All the solvents were treated according to general methods. All reactions were monitored by thin-layer chromatography (TLC) on silica gel plates using UV light as visualizing agent (if applicable). Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR spectra were recorded on 400 and 600 MHz spectrophotometers. Chemical shifts are reported in delta (δ (ppm)) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on Varian Mercury 100 MHz with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). ^{19}F NMR data were collected at 376 MHz with complete proton decoupling. The high resolution mass spectra (HRMS) were measured on a Shimadzu LCMS-IT-TOF mass spectrometer or DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer by ESI. Measured values are reported to 4 decimal places of the calculated value. The calculated values are based on the most abundant isotope. An oil bath was used for the synthesis of **2a**-**2k**. Cyclic Voltammetry (CV) experiments were recorded on a CHI760E electrochemical workstation.

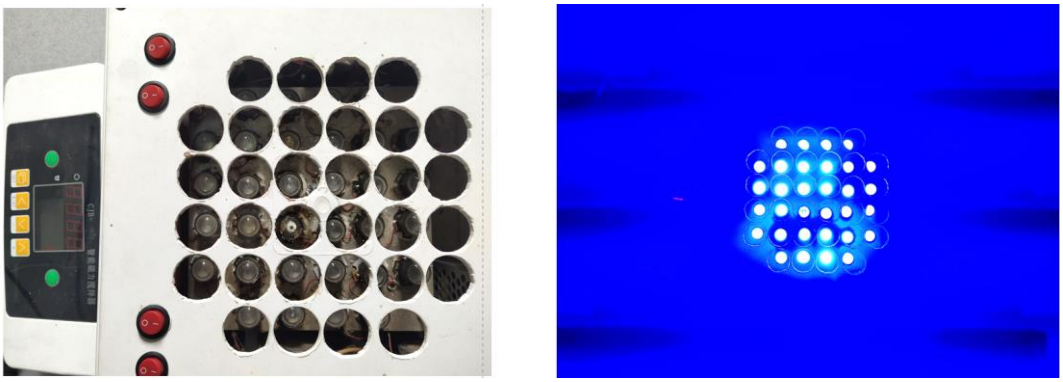
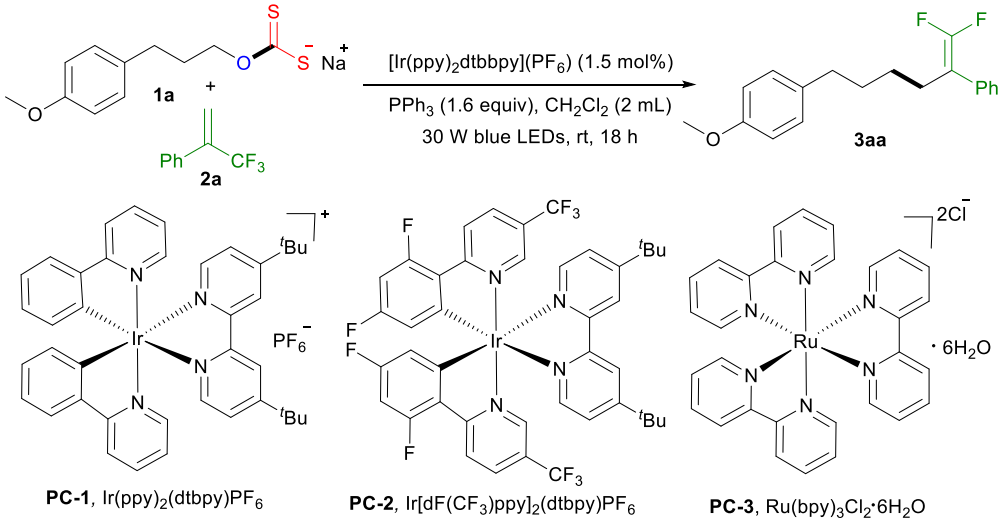


Figure 1. Reaction equipment

2. Screening of the reaction conditions.

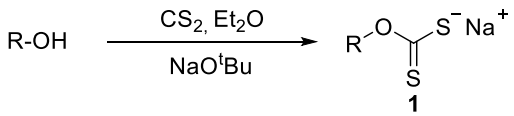


entry	deviation from standard conditions	yield[b] (%)
1	none	91(88)[c]
2	**PC-2** instead of **PC-1**	55
3	**PC-3** instead of **PC-1**	26
4	MeCN instead of CH_2Cl_2	77
5	DCE instead of CH_2Cl_2	69
6	toluene instead of CH_2Cl_2	trace
7	$PPh(OEt)_2$ instead of PPh_3	41
8	Na_2CO_3 or K_2CO_3 was added	18, 20
9	50 μL H_2O was added	69
10	no PC	0
11	no light irradiation	0
12	no PPh_3	0

[a]Reaction Conditions：**1a** (0.3 mmol), **2a** (0.2 mmol), photocatalyst (1.5 mol%), Ph_3P (1.6 equiv), solvent (2.0 mL), 30W blue LEDs at room temperature for 18 h. [b]GC yield using *n*-tetradecane as the internal standard. [c]Isolated yield.

3. Preparation of substrates

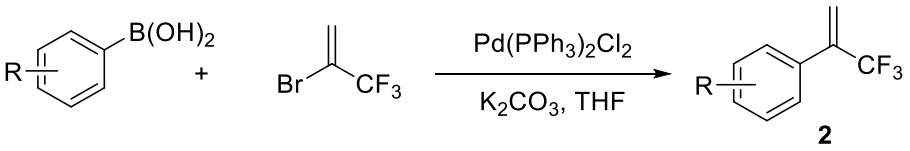
3.1 General procedure for preparation of product 1a-1o and 8.[1]



An oven-dried 250 mL flask equipped with a magneton was charged sequentially with alcohol (30 mmol), NaO^tBu (2.9 g, 30 mmol). The vessel was evacuated and filled with nitrogen (three times), followed by

addition of dry Et_2O (180 mL). Then stirred at room temperature for 30 min. The resulting solution was cooled to 0 ℃, followed by addition of CS_2 (6.9 g, 5.4 mL, 90 mmol) via syringe, then stirred at 0 ℃ for 3 h. The pale-yellow precipitate formed was collected by filtration, washed with Et_2O (3×30 mL), and dried in vacuo to afford the desired product **1**.

3.2 General procedure for preparation of product 2a-2k.[2]

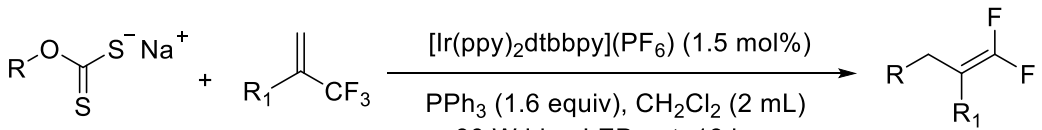


2

To a round-bottom flask equipped with a magnetic stir bar, arylboronic acid (20 mmol) and $Pd(PPh_3)_2Cl_2$ (210.6 mg, 1.5 mol%) were added. The vessel was evacuated and filled with nitrogen (three times), and then aqueous K_2CO_3 (2.0 M, 40 mL) and THF (60 mL) were added. After addition of 2-bromo-3,3,3-trifluoropropene (40 mmol, 4.2 mL), the solution was stirred at 60 ºC for 12 hours. The system was removed under reduced pressure and the residue was purified by column chromatography to afford the corresponding trifluoromethyl alkene (PE/EA=100:1).

4. General procedure and spectral data of the products

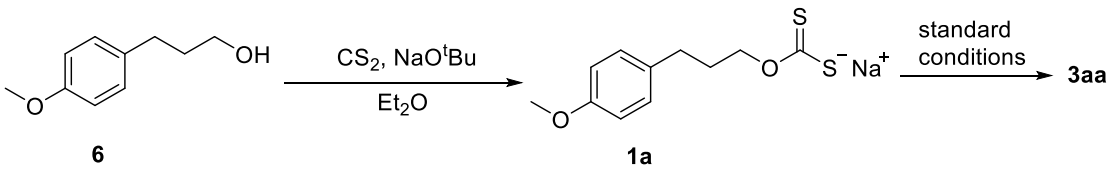
4.1 General procedure for preparation deoxygenative gem-difluorovinylation of alcohols.



1 **2** **3**

1 (0.3 mmol, 1.5 equiv.), alkene **2** (0.2 mmol, 1.0 equiv.), $[Ir(ppy)_2dtbbpy](PF_6)$ (2.7 mg, 1.5 mol%) and PPh_3 (83.8 mg, 0.32 mmol, 1.6 equiv.) were dissolved in CH_2Cl_2 (2 mL). Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times). After that, the reaction mixture was irradiated with a 30 W blue LEDs lamp, maintained at a temperature of 26 ℃, and stirred for 18 hours， as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel to afford pure product **3.**

4.2 one-pot reaction for 3aa and 3na.

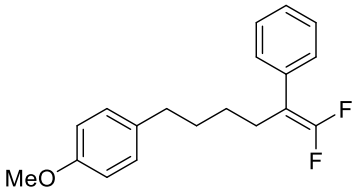


In a nitrogen-filled glovebox, alcohol **6** (50.0 mg, 0.3 mmol, 1.5 equiv) and NaO^{t}Bu (28.8 mg, 0.3 mmol, 1.5 equiv) were dissolved in Et_2O (2 mL). The resulting mixture was transferred out of the glovebox. Then the mixture was stirred at room temperature for 30 min. The resulting solution was cooled to 0 ℃ followed by addition of CS_2 (54.1 uL, 0.9 mmol) via syringe, then stirred at 0 ℃ for 3 h before removing the solvent in vacuo. The system was transferred into the glovebox, alkene **2** (30 uL, 0.2 mmol, 1.0 equiv.), [Ir(ppy)$_2$dtbbpy](PF$_6$) (2.7 mg, 1.5 mol%) , PPh_3 (83.8 mg, 0.32 mmol) were dissolved in CH_2Cl_2 (2 mL). After that, the reaction mixture was irradiated with a 30 W blue LEDs lamp, maintained at a temperature of 26 ℃, and stirred for 18 hours, as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel to afford pure product **3aa** as a colorless oil in 76% yield.

The synthesis of **3na** is the same as the above steps. **3na** as a colorless oil in 51% yield.

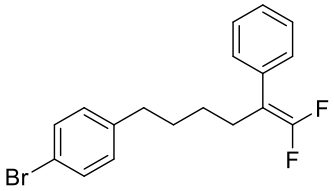
4.3 Spectral data of the products 3aa-3na, 4a-4c, 5ab-5ak and 9.

Product 3aa



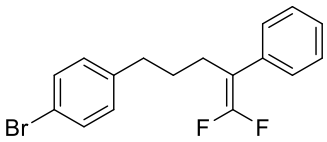
The crude product was purified by column chromatography, yielding **3aa** as a colorless oil (55.0 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 (d, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 2.5 Hz, 2H), 7.26 (d, *J* = 2.4 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 3.77 (s, 3H), 2.53 – 2.48 (m, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 1.62 – 1.54 (m, 2H), 1.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.6, 153.5 (dd, *J* = 261.9, 288.9 Hz), 129.2, 128.4, 128.2 (t, *J* = 3.2 Hz), 127.2, 113.6, 92.2 (dd, *J* = 16.8, 17.8 Hz), 77.0, 55.2, 34.5, 30.9, 27.4, 27.1 (t, *J* = 2.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -91.9 (s, 2F). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{21}F_2O^+$: 303.1555; found: 303.1558.

Product 3ba



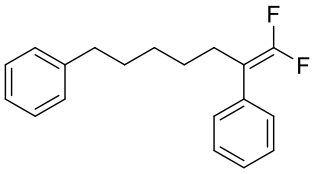
The crude product was purified by column chromatography, yielding **3ba** as a colorless oil (48.3 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 (t, *J* = 8.4 Hz, 4H), 7.21 – 7.16 (m, 3H), 6.90 (d, *J* = 8.1 Hz, 2H), 2.43 (t, *J* = 7.7 Hz, 2H), 2.33 (t, *J* = 7.5 Hz, 2H), 1.54 – 1.47 (m, 2H), 1.30 (m, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.6 (dd, *J* = 289.1, 289.9 Hz), 141.2, 133.6 (d *J* = 1.8 Hz), 131.3, 130.1, 128.4, 128.2 (t, *J* = 3.2 Hz), 127.2, 119.4, 92.1 (dd, *J* = 15.7, 18.6 Hz), 77.0, 34.8, 30.4, 27.3, 27.0 (t, *J* = 2.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -91.7 (d, *J* = 0.15 Hz, 2F). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{18}BrF_2^+$: 351.0554; found: 351.0563.

Product 3ca



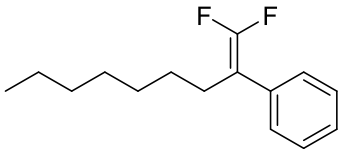
The crude product was purified by column chromatography, yielding **3ca** as a colorless oil (47.2 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 (t, *J* = 7.7 Hz, 4H), 7.22 – 7.15 (m, 3H), 6.89 (d, *J* = 8.3 Hz, 2H), 2.51 – 2.44 (m, 2H), 2.34 (m, 2H), 1.58 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 153.6 (t, *J* = 289.6 Hz), 140.7, 133.4 (d, *J* = 1.5 Hz), 131.3, 130.1, 128.4, 128.2 (t, *J* = 3.2 Hz), 127.3, 119.5, 92.0 (dd, *J* = 16.4, 18.5 Hz), 34.5, 29.1 (t, *J* = 2.5 Hz), 27.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -91.4 (d, *J* = 2.1 Hz, 2F). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{16}BrF_2^+$: 337.0398; found: 337.0403.

Product 3da



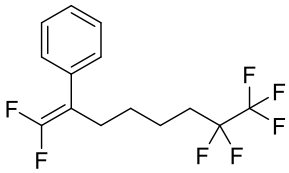
The crude product was purified by column chromatography, yielding **3da** as a colorless oil (48.1 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 – 7.24 (m, 2H), 7.22 – 7.18 (m, 4H), 7.16 (s, 1H), 7.07 – 7.05 (m, 3H), 2.48 (t, *J* = 7.7 Hz, 2H), 2.31 (t, *J* = 7.2 Hz, 2H), 1.55 – 1.47 (m, 2H), 1.33 – 1.23 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.5 (dd, *J* = 288.7, 289.9 Hz), 142.6, 133.8 (d, *J* = 2.4 Hz), 128.4 (overlap), 128.2, 128.2 (t, *J* = 2.7 Hz), 127.1, 125.6, 92.3 (dd, *J* = 15.6, 18.8 Hz), 35.8, 31.1, 28.6, 27.5 (t, *J* = 2.5 Hz), 27.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -91.9 (q, *J* = 44.8 Hz, 2F). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{21}F_2^+$: 287.1606; found: 287.1607.

Product 3ea



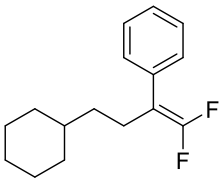
The residue was purified by column chromatography, yielding **3ea** as a colorless oil (40.0 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 – 7.25 (m, 2H), 7.24 (s, 1H), 7.22 – 7.17 (m, 2H), 2.33 – 2.28 (m, 2H), 1.30 – 1.26 (m, 2H), 1.20 – 1.16 (m, 8H), 0.78 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 153.6 (t, *J* = 289.3 Hz), 133.94, 128.4, 128.3 (t, *J* = 6.3 Hz), 127.1, 92.5 (t, *J* = 17.4 Hz), 31.8, 29.7, 28.9 (d, *J* = 3.9 Hz), 27.7 (t, *J* = 4.7 Hz), 27.7, 22.6, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -92.11 (d, *J* = 3.3 Hz, 2F). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{21}F_2^+$: 239.1606; found: 239.1607.

Product 3fa (known compound)



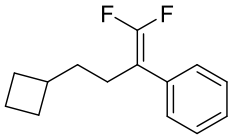
The crude product was purified by column chromatography, yielding **3fa** as a colorless oil (56.5 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 – 7.26 (m, 2H), 7.22 (d, *J* = 7.4 Hz, 3H), 2.39 – 2.35 (m, 2H), 1.96 – 1.83 (m, 2H), 1.55 – 1.50 (m, 2H), 1.40 – 1.33 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =153.7 (dd, *J* = 287.9, 291.5 Hz), 133.3 (dd, *J* = 2.7, 3.8 Hz), 128.5, 128.2 (t, *J* = 3.2 Hz), 127.4, 120.6 (qt, *J* = 285.3, 36.5 Hz), 115.7 (qt, *J* = 251.5, 37.5 Hz), 91.8 (dd, *J* = 13.9, 21.3 Hz), 77.0, 30.3 (t, *J* = 22.3 Hz), 27.3, 27.1 (t, *J* = 2.6 Hz), 19.6(t, *J* = 3.8 Hz) . ^{19}F NMR (376 MHz, $CDCl_3$) δ = -85.5 (s, 3F), -91.5 (q, *J* = 43.4 Hz, 2F), -118.3 (s, 2F).

Product 3ga



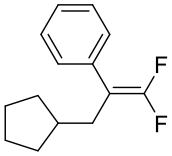
The crude product was purified by column chromatography, yielding **3ga** as a colorless oil (30.0 mg, 60 %).^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 – 7.25 (m, 2H), 7.24 – 7.17 (m, 3H), 2.38 – 2.27 (m, 2H), 1.64 – 1.57 (m, 4H), 1.54 (s, 1H), 1.18 – 1.11 (m, 4H), 1.10 – 0.96 (m, 2H), 0.82 – 0.74 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.4 (dd, *J* = 287.7, 290.5 Hz), 134.0 (dd, *J* = 1.6, 3.1 Hz), 128.4, 128.2 (t, *J* = 3.3 Hz), 127.1, 92.7 (dd, *J* = 14.0, 20.2 Hz), 77.0, 37.3, 35.5, 35.4 (t, *J* = 2.5 Hz), 26.6, 26.3, 25.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -92.1 (q, *J* = 45.0 Hz, 2F). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{21}F_2^+$: 251.1606; found: 251.1614.

Product 3ha



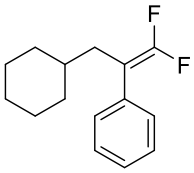
The crude product was purified by column chromatography, yielding **3ha** as a colorless oil (43.5 mg, 98 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 – 7.25 (m, 2H), 7.25 – 7.16 (m, 3H), 2.28 – 2.10 (m, 3H), 1.98 – 1.90 (m, 2H), 1.83 – 1.66 (m, 2H), 1.53 – 1.44 (m, 2H), 1.40 – 1.34 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 153.5 (dd, *J* = 287.8, 290.6 Hz), 133.9, 128.2 (t, *J* = 3.6 Hz), 128.3, 127.1, 92.4 (dd, *J* = 13.8, 20.9 Hz), 35.5, 35.0 (t, *J* = 2.4 Hz), 28.1, 25.4, 18.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -92.01 (d, *J* = 3.4 Hz, 2F). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{17}F_2^+$: 227.1242; found: 227.1248.

Product 3ia (known compound)



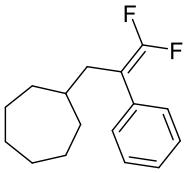
The crude product was purified by column chromatography, yielding **3ia** as a colorless oil (32.4 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 – 7.25 (m, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.21 – 7.17 (m, 1H), 2.32 (dt, *J* = 7.5, 2.4 Hz, 2H), 1.75 – 1.68 (m, 1H), 1.62 – 1.56 (m, 2H), 1.53 – 1.51 (m, 2H), 1.40 – 1.37 (m, 2H), 1.11 – 1.02 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.8 (dd, *J* = 287.1, 290.5 Hz), 134.0 (dd, *J* = 2.8, 4.3 Hz) 128.4 (t, *J* = 3.1Hz), 128.3, 127.1, 92.3 (dd, *J* = 12.8, 21.4 Hz), 77.0, 38.2 (t, *J* = 2.5 Hz), 33.6, 32.1, 25.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -92.4 (q, *J* = 45.0 Hz, 2F).

Product 3ja (known compound)



The crude product was purified by column chromatography, yielding **3ja** as a colorless oil (45.4 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 – 7.33 (m, 2H), 7.32 – 7.28 (m, 2H), 7.26 (s, 1H), 2.27 (dt, *J* = 7.3, 2.5 Hz, 2H), 1.69 – 1.59 (m, 4H), 1.56 (s, 1H), 1.29 – 1.20 (m, 1H), 1.16 – 1.06 (m, 3H), 0.97 – 0.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.0 (dd, *J* = 286.9, 291.2 Hz), 134.1 (dd, *J* = 3.0, 4.3 Hz), 128.3, 128.3 (t, *J* = 3.3 Hz), 127.1, 91.0 (dd, *J* = 12.7, 22.1 Hz), 77.0, 35.7 (t, *J* = 2.2 Hz), 35.2, 32.8, 26.4, 26.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -93.2 (q, *J* = 45.3 Hz, 2F).

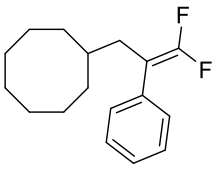
Product 3ka



The crude product was purified by column chromatography, yielding **3ka** as a colorless oil (44.5 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 – 7.25 (m, 2H), 7.23 –

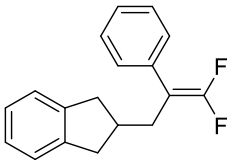
7.21 (m, 2H), 7.19 (d, *J* = 4.1 Hz, 1H), 2.22 (dt, *J* = 7.4, 2.5 Hz, 2H), 1.62 – 1.50 (m, 5H), 1.43 – 1.35 (m, 4H), 1.27 – 1.21 (m, 2H), 1.14 – 1.08 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.1 (dd, *J* =287.1, 290.7 Hz), 134.0 (dd, *J* =2.5, 4.1 Hz), 128.4, 128.4 (t, *J* = 2.9 Hz), 127.1, 91.7 (dd, *J* =13.2, 21.4 Hz), 77.0, 37.0 (t, *J* = 2.3 Hz), 35.7, 34.0, 28.4, 26.1.. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -91.9 (q, *J* = 44.4 Hz, 2F). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{21}F_2^+$: 251.1606; found: 251.1614.

Product 3la (known compound)



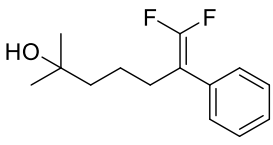
The crude product was purified by column chromatography, yielding **3la** as a colorless oil (50.7 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 – 7.25 (m, 2H), 7.23 – 7.17 (m, 3H), 2.21 (dt, *J* = 7.3, 2.4 Hz, 2H), 1.57 – 1.44 (m, 5H), 1.42 – 1.35 (m, 5H), 1.33 – 1.27 (m, 2H), 1.25 – 1.18 (m, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.0 (dd, *J* =287.1, 290.6 Hz), 133.9 (dd, *J* =2.1, 3.7 Hz), 128.3, 128.3 (t, *J* = 2.5 Hz), 127.1, 91.6 (dd, *J* =13.7, 21.0 Hz), 77.0, 35.4, 35.1 (t, *J* = 2.3 Hz), 31.4, 27.3, 26.0, 25.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -91.9 (q, *J* = 45.0 Hz, 2F).

Product 3ma



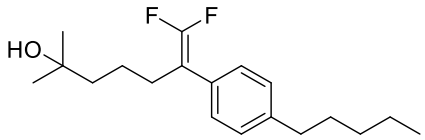
The crude product was purified by column chromatography, yielding **3ma** as a colorless oil (37.3 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 (d, *J* = 6.9 Hz, 4H), 7.19 (t, *J* = 6.7 Hz, 1H), 7.10 – 7.05 (m, 2H), 7.04 – 7.00 (m, 2H), 2.86 (dd, *J* = 15.5, 7.7 Hz, 2H), 2.63 – 2.45 (m, 4H), 2.42 – 2.35 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.0 (dd, *J* =288.0, 290.9 Hz), 143.0, 133.6 (d, *J* = 2.1 Hz), 128.5, 128.4 (t, *J* = 3.1 Hz), 127.3, 126.1, 124.4, 91.8 (dd, *J* = 14.2, 20.8 Hz), 77.0, 38.6, 38.0 (t, *J* = 2.6 Hz), 33.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -91.6 (q, *J* = 43.4 Hz, 2F). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{17}F_2^+$: 271.1293; found: 271.1294.

Product 4a



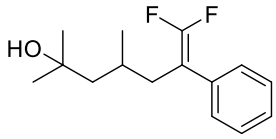
The crude product was purified by column chromatography, yielding **4a** as a colorless oil (29.3 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 (t, *J* = 7.4 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 3.6 Hz, 1H), 2.34 (t, *J* = 6.9 Hz, 2H), 1.42 – 1.33 (m, 4H), 1.07 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.6 (dd, *J* = 288.7, 290.0 Hz), 133.6 (d, *J* = 1.9 Hz), 128.4, 128.2 (t, *J* = 3.2 Hz), 127.2, 92.2 (dd, *J* = 15.6, 19.0 Hz), 77.0, 70.8, 43.0, 29.2, 22.5 (t, *J* = 2.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -91.7 (q, *J* = 44.0 Hz, 2F) m/z: $[M+Na]^+$ calcd for $C_{14}H_{18}F_2ONa^+$: 263.1218; found: 263.1218..

Product 4b



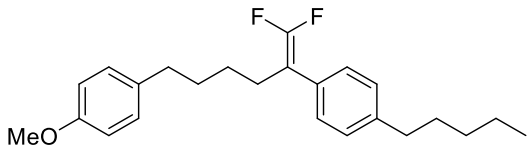
The crude product was purified by column chromatography, yielding **4b** as a colorless oil (24.8 mg, 40% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.21 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 2.62 – 2.56 (m, 2H), 1.74 – 1.52 (m, 4H), 1.51 – 1.38 (m, 4H), 1.35 – 1.30 (m, 4H), 1.15 (s, 6H), 0.89 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 153.6 (dd, *J* = 281.2, 290.0 Hz), 142.0, 130.7 (d, *J* = 2.6 Hz), 128.4, 128.0 (t, *J* = 3.3 Hz),92.0 (dd, *J* = 15.4, 19.5 Hz), 77.0, 70.8, 43.1, 35.6, 31.5, 31.0, 29.7 (d, *J* = 6.4 Hz), 29.2, 28.0, 22.5, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ =-92.0 (s, 2F). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{29}F_2O^+$: 311.2181; found: 311.2181.

Product 4c



The crude product was purified by column chromatography, yielding **4c** as a colorless oil (30.5 mg, 60% yield).^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.27 (d, *J* = 7.1 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.19 (td, *J* = 6.3, 5.5, 1.8 Hz, 1H), 2.49 – 2.43 (m, 1H), 2.19 – 2.13 (m, 1H), 1.56 – 1.49 (m, 1H), 1.44 (dd, *J* = 14.2, 4.4 Hz, 1H), 1.26 (dd, *J* = 14.2, 7.0 Hz, 1H), 1.06 (d, *J* = 5.6 Hz, 6H), 0.88 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 154.1 (dd, *J* = 287.0, 291.3 Hz), 133.6 (dd, *J* = 2.9, 4.3 Hz), 128.4, 128.3 (t, *J* = 3.1 Hz), 127.2, 91.5 (dd, *J* = 12.8, 21.8 Hz), 77.0, 71.4, 49.7, 36.2, 29.9 (d, *J* = 11.4 Hz), 27.6, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ =-91.6 (q, *J* = 44.1 Hz, 2F). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{20}F_2ONa^+$: 277.1374; found: 277.1124.

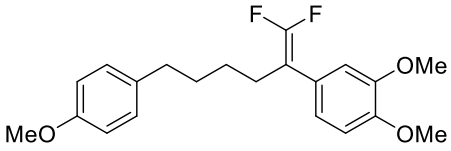
Product 5ab



The crude product was purified by column chromatography, yielding **5ab** as a colorless oil (69.2 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 3.70 (s, 3H), 2.54 – 2.49 (m, 2H), 2.43 (t, *J* = 7.7 Hz, 2H), 2.35 – 2.29 (m, 2H), 1.54 (d, *J* = 7.4 Hz, 2H), 1.50 (d, *J* = 5.9 Hz, 2H), 1.33 (m, *J* = 7.8 Hz, 2H), 1.29 – 1.23 (m, 4H), 0.85 – 0.80 (m, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.7, 153.6 (dd, *J* = 287.7, 289.8 Hz), 141.9, 134.5, 133.7 (d, *J* = 19.6 Hz), 129.2, 128.4, 128.0 (t, *J* = 3.3 Hz), 113.7, 92.1 (dd, *J* = 14.5, 20.0 Hz), 77.0, 55.2, 35.6, 34.6, 31.6, 31.0, 31.0, 27.4, 27.3(t, *J* = 2.7 Hz) , 22.5, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -92.1 (q, *J* = 44.9 Hz, 2F). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{31}F_2O^+$:

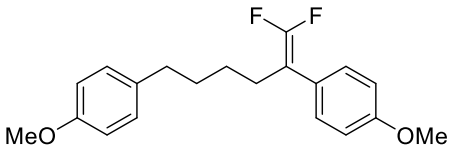
373.2337; found: 373.2339.

Product 5ac



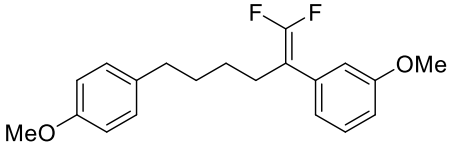
The crude product was purified by column chromatography, yielding **5ac** as a colorless oil (71.0 mg, 98 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.05 (d, *J* = 8.6 Hz, 2H), 6.84 (s, 2H), 6.81 (d, *J* = 8.5 Hz, 3H), 3.88 (d, *J* = 9.1 Hz, 6H), 3.78 (s, 3H), 2.52 (t, *J* = 7.7 Hz, 2H), 2.41 – 2.36 m, 2H), 1.63 – 1.55 (m, 2H), 1.40 (m, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ =157.6, 153.4 (dd, *J* = 283.9, 290.1 Hz), 148.7, 148.1, 134.4, 129.2, 120.7 (t, *J* = 3.4 Hz), 113.6, 111.5 (t, *J* = 3.6 Hz), 111.0, 91.9 (dd, *J* = 12.8, 21.9 Hz) 77.0, 55.9, 55.8, 55.2, 34.6, 30.9, 27.5, 27.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -92.9 (q, *J* = 46.7 Hz, 2F). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{21}H_{24}F_2O_3Na^+$: 385.1586; found: 385.1587.

Product 5ad



The crude product was purified by column chromatography, yielding **5ad** as a colorless oil (63.4 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.13 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 3.72 (d, *J* = 12.4 Hz, 6H), 2.43 (t, *J* = 7.7 Hz, 2H), 2.33 – 2.28 (m, 2H), 1.53 (d, *J* = 6.9 Hz, 1H), 1.47 (d, *J* = 7.7 Hz, 1H), 1.34 – 1.27 (m, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.6, 157.6, 153.4 (t, *J* = 288.1 Hz), 134.5, 129.3 (t, *J* = 3.2 Hz), 129.2, 125.8, 113.8, 113.6, 91.6 (dd, *J* = 16.6, 18.1 Hz), 77.0, 55.2, 34.6, 30.9, 27.4, 27.1 (t, *J* = 2.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ =-92.8 (s, 2F). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{20}H_{22}F_2O_2Na^+$: 355.1480; found: 355.1479.

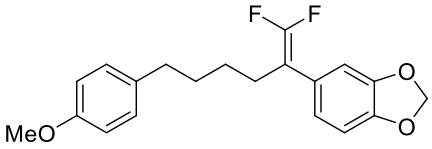
Product 5ae



The crude product was purified by column chromatography, yielding **5ae** as a colorless oil (55.8 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.18 (t, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.77 – 6.70 (m, 4H), 3.71 (d, *J* = 10.0 Hz, 6H), 2.43 (t, *J* = 7.7 Hz, 2H), 2.34 – 2.28 (m, 2H), 1.51 (d, *J* = 7.6 Hz, 1H), 1.47 (d, *J* = 7.7 Hz, 1H), 1.35 – 1.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.5, 157.6, 153.5 (dd, *J* = 287.3, 291.4 Hz), 135.1 (dd, *J* = 3.1, 4.6 Hz), 134.4, 129.3, 129.2, 120.7 (t, *J* = 3.2 Hz), 114.2 (t, *J* = 3.6 Hz), 113.6, 112.4, 92.2 (dd, *J* = 12.7, 22.2 Hz), 77.0, 55.2 (d, *J* = 1.9 Hz),

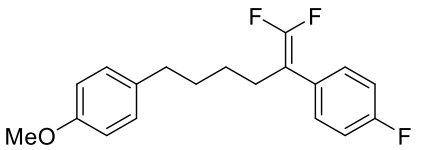
34.5, 31.0, 27.4, 27.2 (t, J = 2.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ =-91.3 (q, J = 43.8 Hz, 2F). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{20}H_{22}F_2O_2Na^+$: 355.1480; found: 355.1477.

Product 5af



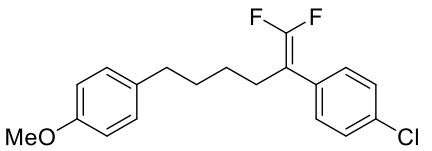
The crude product was purified by column chromatography, yielding **5af** as a colorless oil (51.9 mg, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.05 (d, J = 8.4 Hz, 2H), 6.83 (s, 1H), 6.80 (s, 1H), 6.78 (s, 1H), 6.77 – 6.68 (m, 2H), 5.97 (s, 2H), 3.79 (s, 3H), 2.52 (t, J = 7.7 Hz, 2H), 2.35 (t, J = 7.4 Hz, 2H), 1.60 – 1.55 (m, 2H), 1.42 – 1.35 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.7, 153.5 (dd, J = 286.8, 290.0 Hz), 147.7, 146.7, 134.4, 129.2, 127.4 (dd, J = 2.7, 4.6 Hz), 121.8 (t, J = 3.2 Hz), 113.7, 108.8 (t, J = 3.5 Hz), 108.2, 101.1, 92.0 (dd, J = 13.1, 22.6 Hz), 77.0, 55.2, 34.6, 30.9, 27.7, 27.0 (t, J = 2.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -92.2 (q, J = 45.9 Hz, 2F). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{21}F_2O_3^+$: 347.1453; found: 347.1439.

Product 5ag



The crude product was purified by column chromatography, yielding **5ag** as a colorless oil (48.7 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.19 – 7.14 (m, 2H), 7.00 – 6.92 (m, 4H), 6.76 – 6.71 (m, 2H), 3.71 (s, 3H), 2.43 (t, J = 7.7 Hz, 2H), 2.39 – 2.34 (m, 2H), 1.55 – 1.46 (m, 2H), 1.33 – 1.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.8 (d, J =247.5 Hz), 157.7, 153.5 (t, J = 289.4 Hz), 134.3, 129.9 (dt, J = 7.8, 7.8 Hz) 129.6 (dd, J = 1.6, 3.2 Hz), 129.2, 115.5, 115.3, 113.7, 91.5 (dd, J = 16.7, 19.0 Hz), 77.0, 55.2, 34.5, 30.8, 27.5, 27.0 (t, J = 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -91.9 (q, J = 44.8, 2F), -114.8 (s, 1F). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{20}F_3O^+$: 321.1461; found: 321.1467.

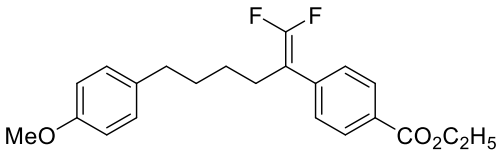
Product 5ah



The crude product was purified by column chromatography, yielding **5ah** as a colorless oil (55.8 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 (d, J = 8.6 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.6 Hz, 2H), 6.72 (d, J = 8.6 Hz, 2H), 3.70 (s, 3H), 2.42 (t, J = 7.7 Hz, 2H), 2.33 – 2.28 (m, 2H), 1.53 – 1.45 (m, 2H), 1.33 – 1.25 (m , 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.7, 153.6 (dd, J = 289.2, 290.6 Hz), 134.3, 133.0, 132.1 (d, J = 2.1 Hz), 129.5 (t, J = 3.3 Hz), 129.2, 128.6, 113.7, 91.5 (dd, J = 15.4,

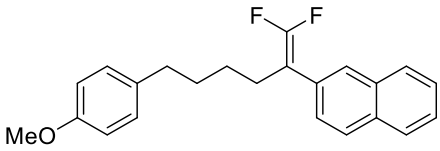
20.0 Hz), 77.0, 55.2, 34.5, 27.2, 27.0 (t, J = 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ =-91.0 (q, J = 42.5 Hz, 2F). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{20}ClF_2O^+$: 337.1165; found: 337.1170.

Product 5ai



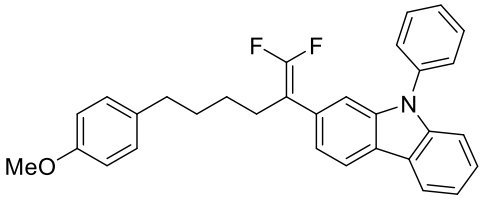
The crude product was purified by column chromatography, yielding **5ai** as a colorless oil (37.4 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 7.2 Hz, 2H), 6.96 (d, J = 8.6 Hz, 2H), 6.73 (d, J = 8.6 Hz, 2H), 4.31 (s, J = 7.1 Hz, 2H), 3.70 (s, 3H), 2.43 (t, J = 7.7 Hz, 2H), 2.40 – 2.34 (m, 2H), 1.52 – 1.46 (m, 2H), 1.34 – 1.29 (m, , 5H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.2, 157.7, 153.8 (dd, J = 289.1, 293.1 Hz), 138.4 (dd, J = 3.2, 4.2 Hz), 134.2, 129.6, 129.2 (overlap), 128.1 (t, J = 3.5 Hz), 113.7, 92.0 (dd, J = 12.5, 22.1 Hz), 77.0, 61.0, 55.2, 34.5, 30.8, 27.1 (t, J = 2.3 Hz), 27.1, 14.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ =-89.6 (q, J = 39.4 Hz, 2F). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{22}H_{24}F_2O_3Na^+$: 397.1586; found: 397.1587.

Product 5aj



The crude product was purified by column chromatography, yielding **5aj** as a colorless oil (67.6 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73 (dt, J = 9.7, 3.6 Hz, 3H), 7.65 (s, 1H), 7.43 – 7.34 (m, 2H), 7.32 (d, J = 8.6 Hz, 1H), 6.94 (d, J = 8.6 Hz, 2H), 6.69 (d, J = 8.6 Hz, 2H), 3.67 (s, 3H), 2.45 – 2.40 (m, 4H), 1.57 – 1.48 (m, 2H), 1.38 – 1.30 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.6, 153.8 (dd, J = 287.8, 291.4 Hz), 134.4, 133.2, 132.4, 131.1 (dd, J = 3.0, 3.9 Hz), 129.2, 128.0, 127.9, 127.6, 127.3 (t, J = 3.4 Hz), 126.2, 126.1 (t, J = 3.1 Hz), 126.0, 113.6, 92.3 (dd, J = 13.2, 21.8 Hz), 77.0, 55.2, 30.9, 27.4, 27.1 (t, J = 2.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -91.4 (q, J = 43.4 Hz, 2F). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{23}H_{22}F_2ONa^+$: 375.1531; found: 375.1539.

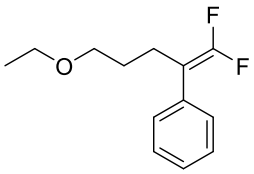
Product 5ak



The crude product was purified by column chromatography, yielding **5ak** as a colorless oil (86.0 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (dd, J = 10.7, 7.9 Hz, 2H), 7.56 – 7.50 (m, 2H), 7.49 – 7.45 (m, 2H), 7.42 – 7.37 (m, 1H), 7.32 (d, J

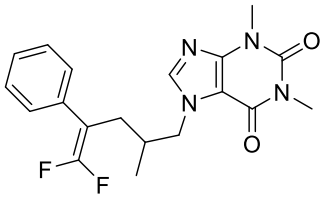
= 3.6 Hz, 2H), 7.24 – 7.18 (m, 2H), 7.13 (d, *J* = 8.2 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.70 – 6.65 (m, 2H), 3.65 (s, 3H), 2.41 – 2.35 (m, 4H), 1.53 – 1.45 (m, 2H), 1.35 – 1.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.6, 153.5 (dd, *J* = 287.4, 290.1 Hz), 141.3, 140.9, 137.5, 134.4, 131.5 (dd, *J* = 2.7, 4.4 Hz), 129.9, 129.1, 127.5, 127.1, 126.0, 123.0, 122.5, 120.3 (t, *J* = 3.0 Hz), 120.2, 120.1 (d, *J* = 8.7 Hz), 113.6, 109.8, 109.6 (t, *J* =3.2 Hz), 92.9 (dd, *J* = 13.4, 21.6 Hz), 77.0, 55.2, 34.6, 30.9, 27.8, 27.2 (t, *J* = 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ =-92.0 (q, *J* = 44.3 Hz, 2F). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{31}H_{27}F_2NO^+$: 468.2133; found: 468.2137.

Product 3na



The crude product was purified by column chromatography, yielding **3na** as a colorless oil (23.1 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 – 7.30 (m, 4H), 7.26 (s, 1H), 3.39 (dt, *J* = 11.0, 6.7 Hz, 4H), 2.52 – 2.46 (m, 2H), 1.68 – 1.62 (m, 2H), 1.18 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.6, 133.6, 128.4, 128.2 (t, *J* = 3.2 Hz), 127.2, 91.9, 77.0, 69.4, 66.1, 27.8 (t, *J* = 2.6 Hz), 24.3, 15.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -93.1 (d, *J* = 8.6 Hz, 2F). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{17}F_2O^+$: 227.1242; found: 227.1248.

Product 9



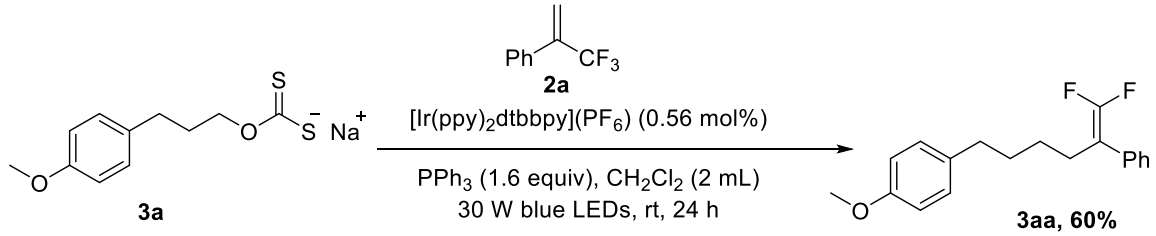
The crude product was purified by column chromatography, yielding **9** as a colorless oil (65.1 mg, 87 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 (s, 1H), 7.24 (t, *J* = 7.2 Hz, 2H), 7.20 – 7.17 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.13 (dd, *J* = 13.5, 7.0 Hz, 1H), 3.99 (dd, *J* = 13.5, 7.4 Hz, 1H), 3.52 (s, 3H), 3.28 (s, 3H), 2.39 – 2.33 (m, 1H), 2.30 – 2.22 (m, 1H), 2.11 – 2.03 (m, 1H), 0.84 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.9, 154.0 (dd, *J* = 288.4, 291.8 Hz), 151.6, 148.7, 132.9 (t, *J* = 2.8 Hz), 128.5, 128.1 (t, *J* = 3.2 Hz), 127.5, 107.1, 90.2 (dd, *J* = 15.2, 20.5 Hz), 77.0, 52.4, 33.1 (t, *J* = 2.3 Hz), 31.8, 29.7, 27.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -90.2 (q, *J* = 41.5 Hz, 2F). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{21}F_2N_4O_2^+$: 291.0275; found: 291.0280.

References: [1] H. M. Guo and X. Wu, *Nat. Commun*., 2021, **12**, 5635.

[2] P. J. Xia, Z. P. Ye, Y. Z. Hu, D. Song, H. Y. Xiang, X. Q. Chen and H. Yang, *Org. Lett*., 2019, **21**, 2658-2662.

5. Gram-scale reaction

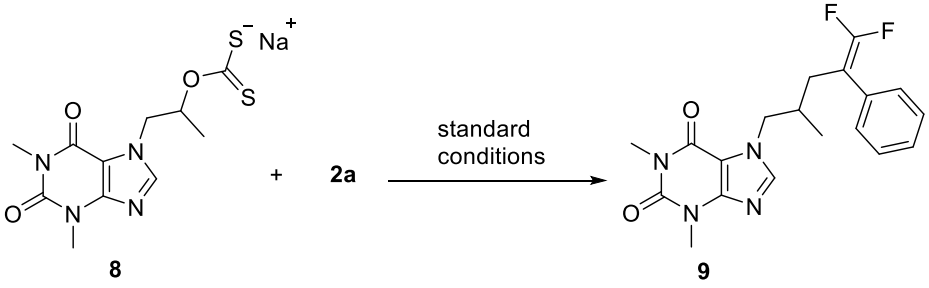
5.1 Procedure for gram-scale reaction



3a (793.0 mg, 3 mmol), alkene **2a** (300 uL, 2 mmol), $[Ir(ppy)_2dtbbpy](PF_6)$ (10.2 mg, 0.56 mol%) and PPh_3 (840 mg, 3.2 mmol) were dissolved in CH_2Cl_2 (20 mL). Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times). After that, the reaction mixture was irradiated with a 30 W blue LEDs lamp, maintained at a temperature of 26 ℃, and stirred for 24 hours, as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel to afford pure product **3aa** as a colorless oil in 60% yield**.**

6. Synthetic application

6.1 Preparation of compound 9



8 (100.9 mg 0.3 mmol, 1.5 equiv.), alkene **2a** (30 uL, 0.2 mmol), $[Ir(ppy)_2dtbbpy](PF_6)$ (2.7 mg, 1.5 mol%) and PPh_3 (83.8 mg, 0.32 mmol) were dissolved in CH_2Cl_2 (2 mL). Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times). After that, the reaction mixture was irradiated with a 30 W blue LEDs lamp, maintained at a temperature of 26 ℃, and stirred for 18 hours, as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel to afford pure product **9** as a colorless oil in 87% yield**.**

7. Mechanism studies

7.1 Light on-off experiments

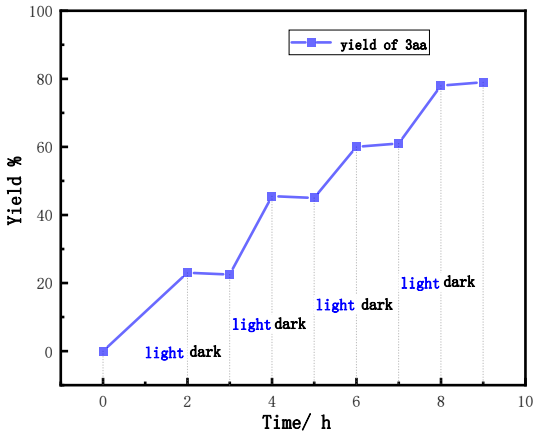
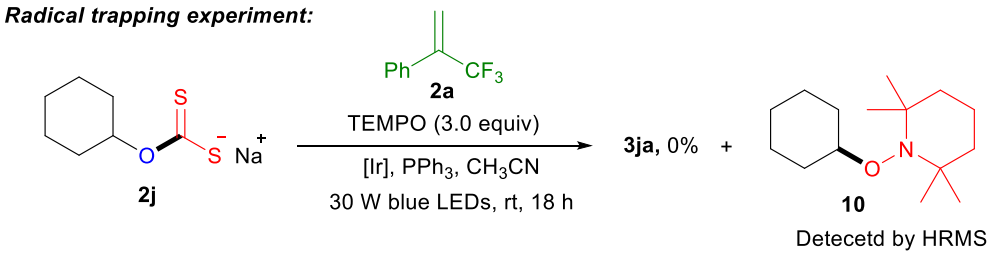


Figure 2. Light on-off experiments

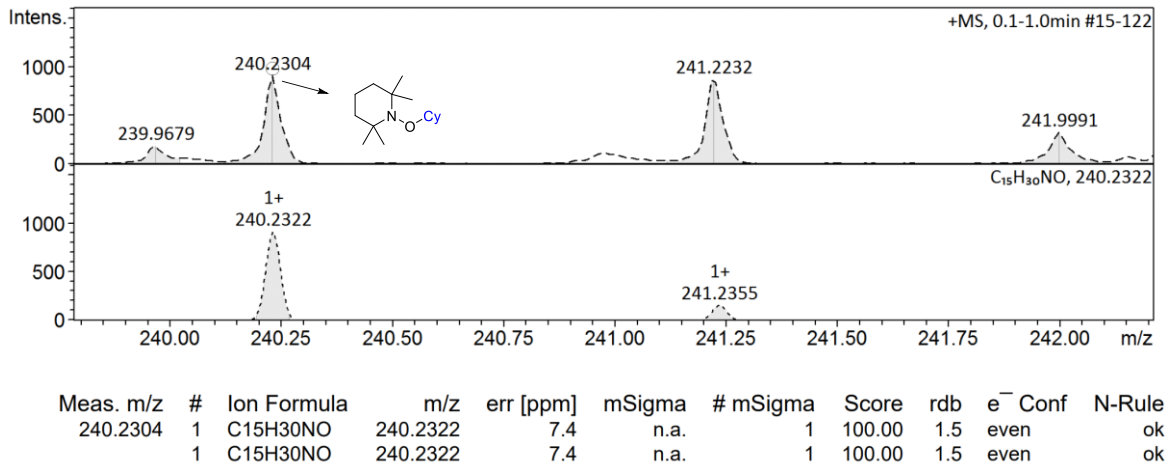
The yield of **3aa** was detected by GC using naphthalene as an internal standard. ***The results shows that a radical chain process is not the major reaction pathway, while it could not be completely ruled out at the current stage.***

7.2 TEMPO trapping experiment



2j (59.4 mg, 0.3 mmol), alkene **2a** (30 uL, 0.2 mmol), $[Ir(ppy)_2dtbbpy](PF_6)$ (2.7 mg, 1.5 mol%), PPh_3 (83.8 mg, 0.32 mmol) and TEMPO (93.7 mg, 0.3 mmol) were dissolved in MeCN (2 mL). Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times). After that, the reaction mixture was irradiated with a 30 W blue LEDs lamp, maintained at a temperature of 26 °C, and stirred for 18 hours. ***In the presence of TEMPO, the reaction was completely inhibited and the corresponding TEMPO-adduct can be detected by analysis of the crude reaction mixture by HRMS (ESI-TOF) m/z:***

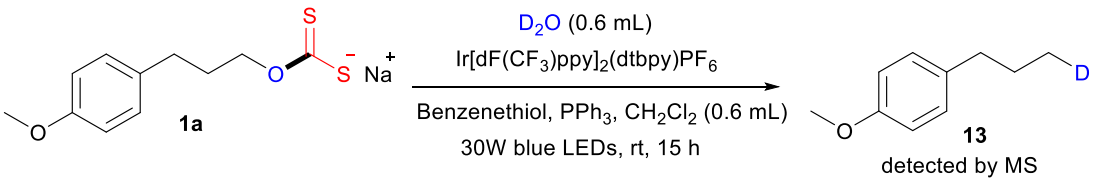
[M+H]$^+$ calcd for $C_{15}H_{30}NO^+$: 240.2322; found: 240.2304. This result demonstrated the radical pathway of this reaction.



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e¯ Conf	N-Rule
240.2304	1	C15H30NO	240.2322	7.4	n.a.	1	100.00	1.5	even	ok
	1	C15H30NO	240.2322	7.4	n.a.	1	100.00	1.5	even	ok

Figure 3. HMRS of 10

7.3 Deuterium-labelling experiment



1a (52.9 mg, 0.2 mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbpy)PF$_6$ (2.2 mg, 1 mol%), benzenethiol (7.1 uL, 0.03 mol) and PPh$_3$ (57.6 mg, 0.22 mmol) were dissolved in DCM (0.6 mL), followed by addition of D$_2$O (0.6 mL). Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times). After that, the reaction mixture was irradiated with a 30 W blue LEDs lamp, maintained at a temperature of 26 ℃, and stirred for 15 hours. The deoxygenative deuterium product **13** can be detected by GC-MS. ***This result indicated that the existence of an alkyl radical intermediate in this reaction.***

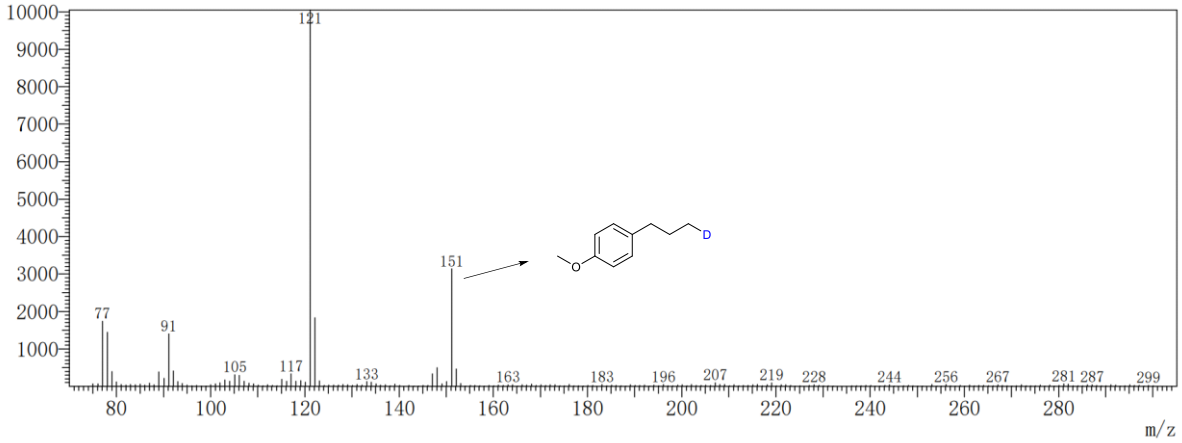


Figure 4. GC-MS of **13**

The mechanism was described as following:

Initially, the photoexcited Ir-catalyst ($E_{1/2}^{ox}$[*Ir(III)/Ir(II)] = +0.66 V vs SCE) is prone to oxidize xanthate anion **1** to form the sulfur-centered radical **1-A**. Then, radical **1-A** is readily coupled with Ph_3P to afford the key phosphoranyl radical **1-B**, followed by β-scission to give radical intermediate **C**. The fragmentation of **C** results in an alkyl radical **1-D** by the extrusion of carbonyl sulfide. The radical **1-D** undergoes HAT process with thiol to give the deuterated product and generate an electrophilic thiyl radical. The resulting thiyl radical is readily reduced by Ir(II) catalyst to give thiol anion with the regeneration of the ground-state photocatalyst for next catalytic cycle. Finally, the thiol anion abstracts one deuteron from D_2O to restart the thiol catalysis.

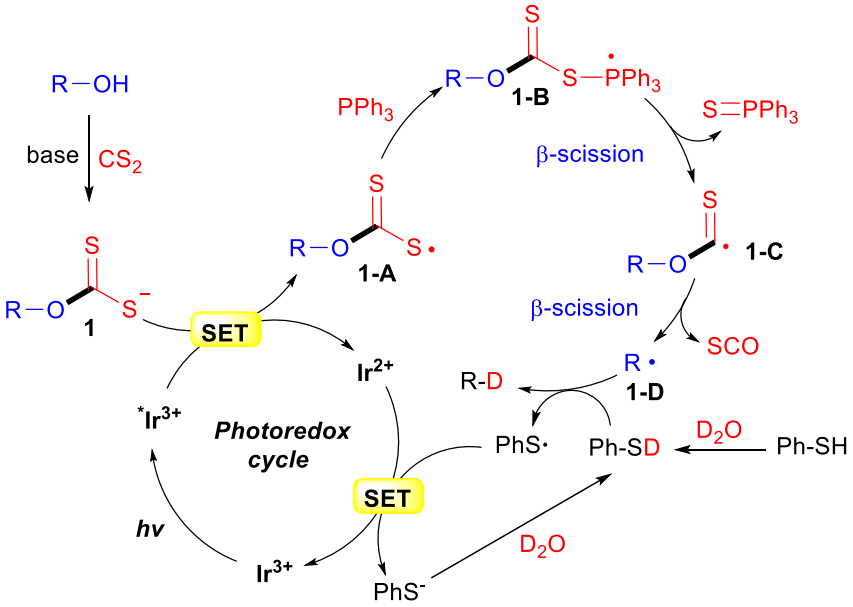


Figure 5. Proposed reaction mechanism.

7.4 Electrochemical studies

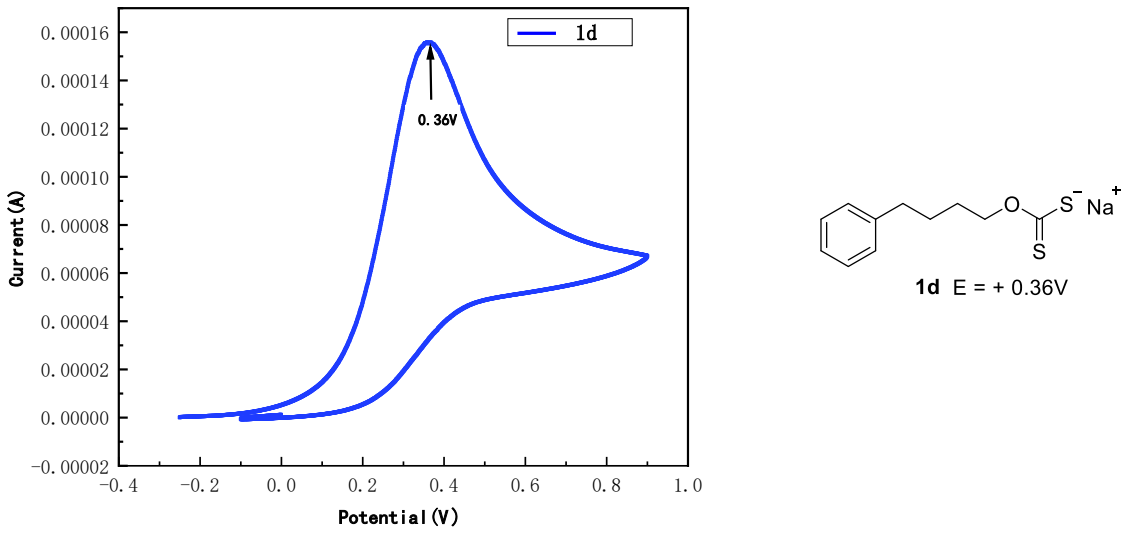
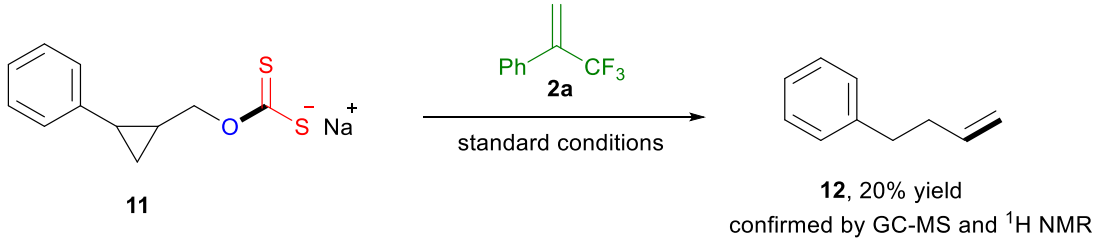


Figure 6. Cyclic voltammetry of **1d**

Cyclic voltammetry was performed in a three-electrode cell connected to a Schlenk line at room temperature. Pt wire as the auxiliary electrode, and saturated calomel electrode as the reference electrode. 20.0 mL of CH_3CN containing 0.1 M $^{n}Bu_4PF_6$ and 0.01 M **1d** were poured into the undivided three-necked flask (25 mL). Samples were examined at a scan rate of 0.1 V/s. The oxidation potential of xanthate salt **1d** ($E_{1/2}^{ox}$ = +0.36 V vs SCE) is lower than the oxidation potential of $^{*}Ir^{III}$ ($E_{1/2}^{ox}$[*Ir(III)/Ir(II)] = +0.66 versus SCE in MeCN).

7.5 Radical clock experiment



11 (73.8 mg, 0.3 mmol), alkene **2a** (30 uL, 0.2 mmol), $[Ir(ppy)_2dtbbpy](PF_6)$ (2.7 mg, 1.5 mol%) and PPh_3 (83.8 mg, 0.32 mmol) were dissolved in MeCN (2 mL). Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times). After that, the reaction mixture was irradiated with a 30 W blue LEDs lamp, maintained at a temperature of 26 ℃, and stirred for 18 hours. Ring opening product **12**

was detected by GC-MS, which indicated the existence of a radical intermediate.

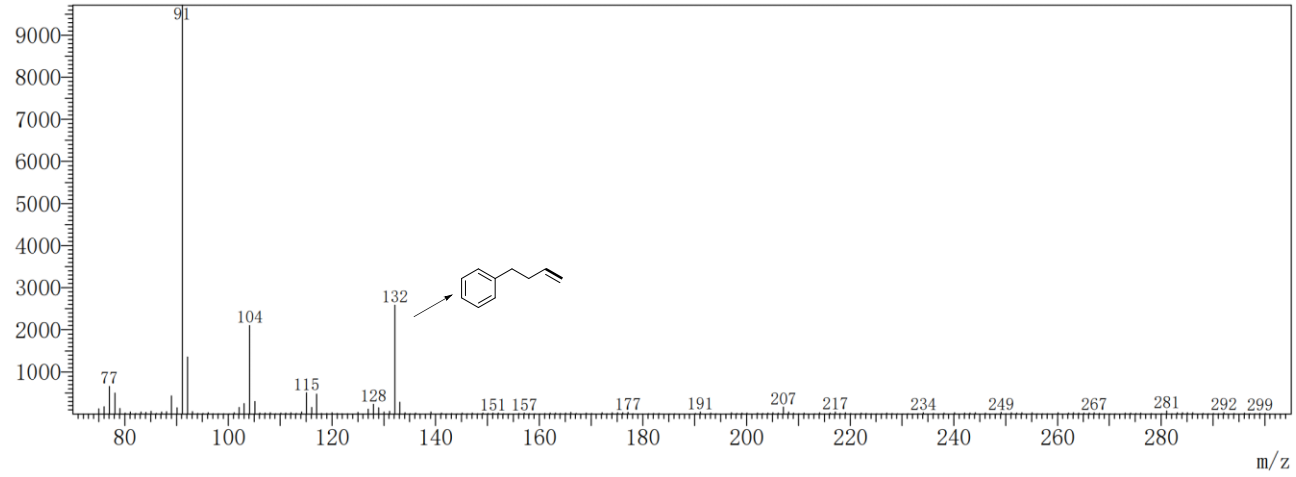


Figure 7. GC-MS of **12**

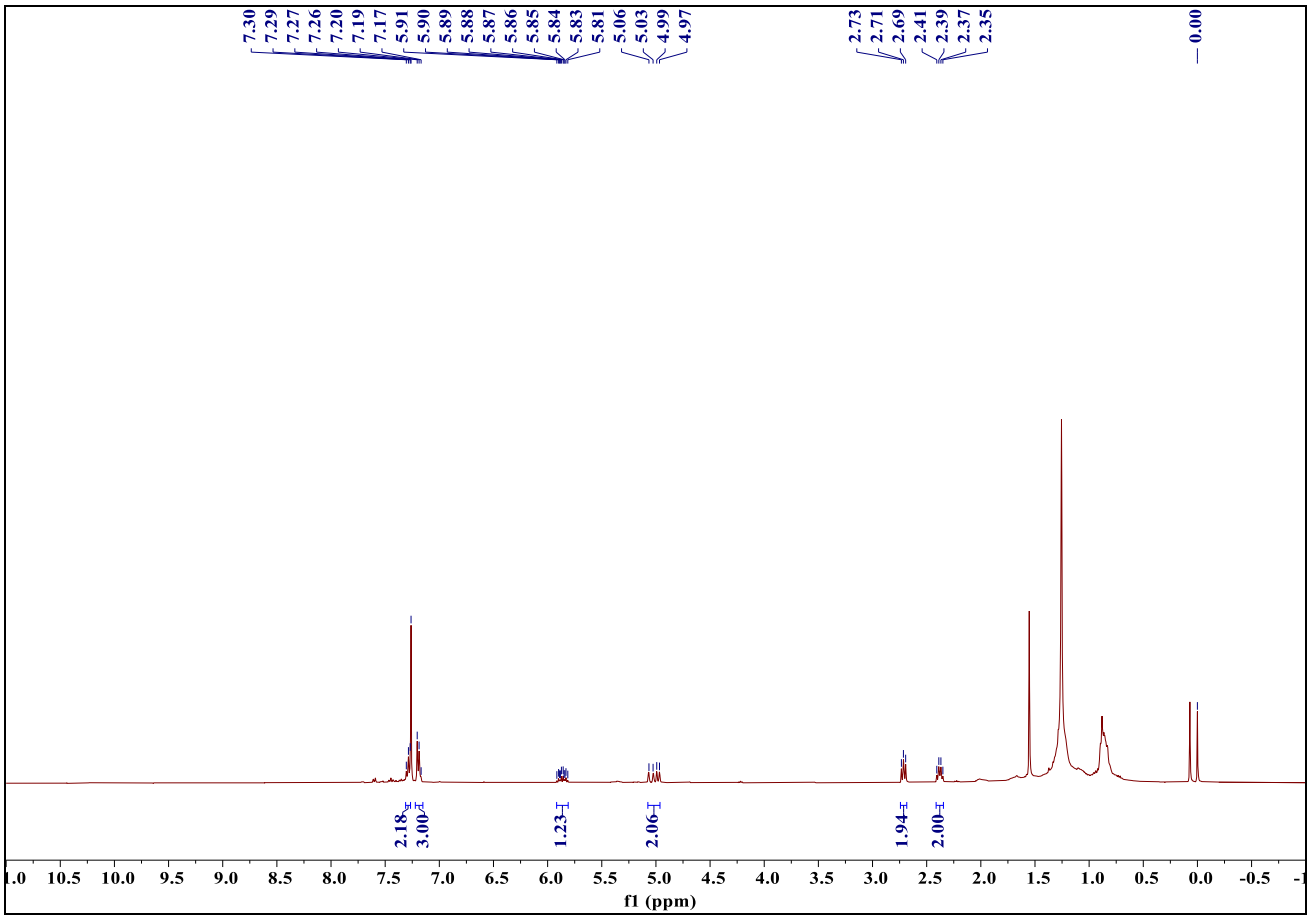
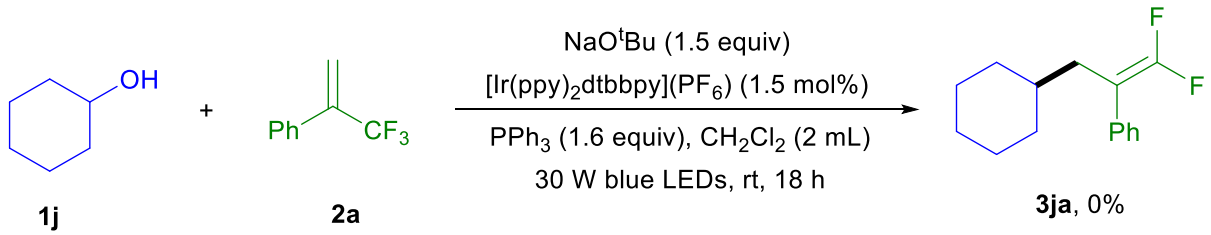


Figure 8. ^{1}H NMR spectra of **12**

7.6 Control experiment



1j **2a** **3ja**, 0%

1j (30.0 mg, 0.3 mmol), alkene **2a** (30 uL, 0.2 mmol), $[Ir(ppy)_2dtbbpy](PF_6)$ (2.7 mg, 1.5 mol%), PPh_3 (83.8 mg, 0.32 mmol) and NaO^tBu (28.8 mg, 1.5 equiv) were dissolved in CH_2Cl_2 (2 mL). Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times). After that, the reaction mixture was irradiated with a 30 W blue LEDs lamp, maintained at a temperature of 26 ℃, and stirred for 18 hours. **3aj** was not found in system. ***As a result, no reaction occurred, which demonstrated the importance of CS_2 in this reaction.***

7.7 Another possible reaction mechanism

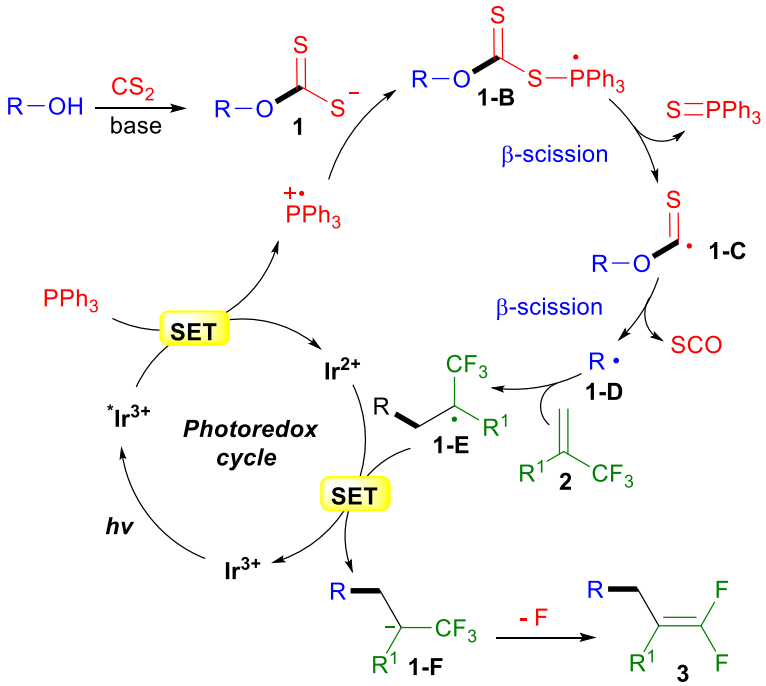
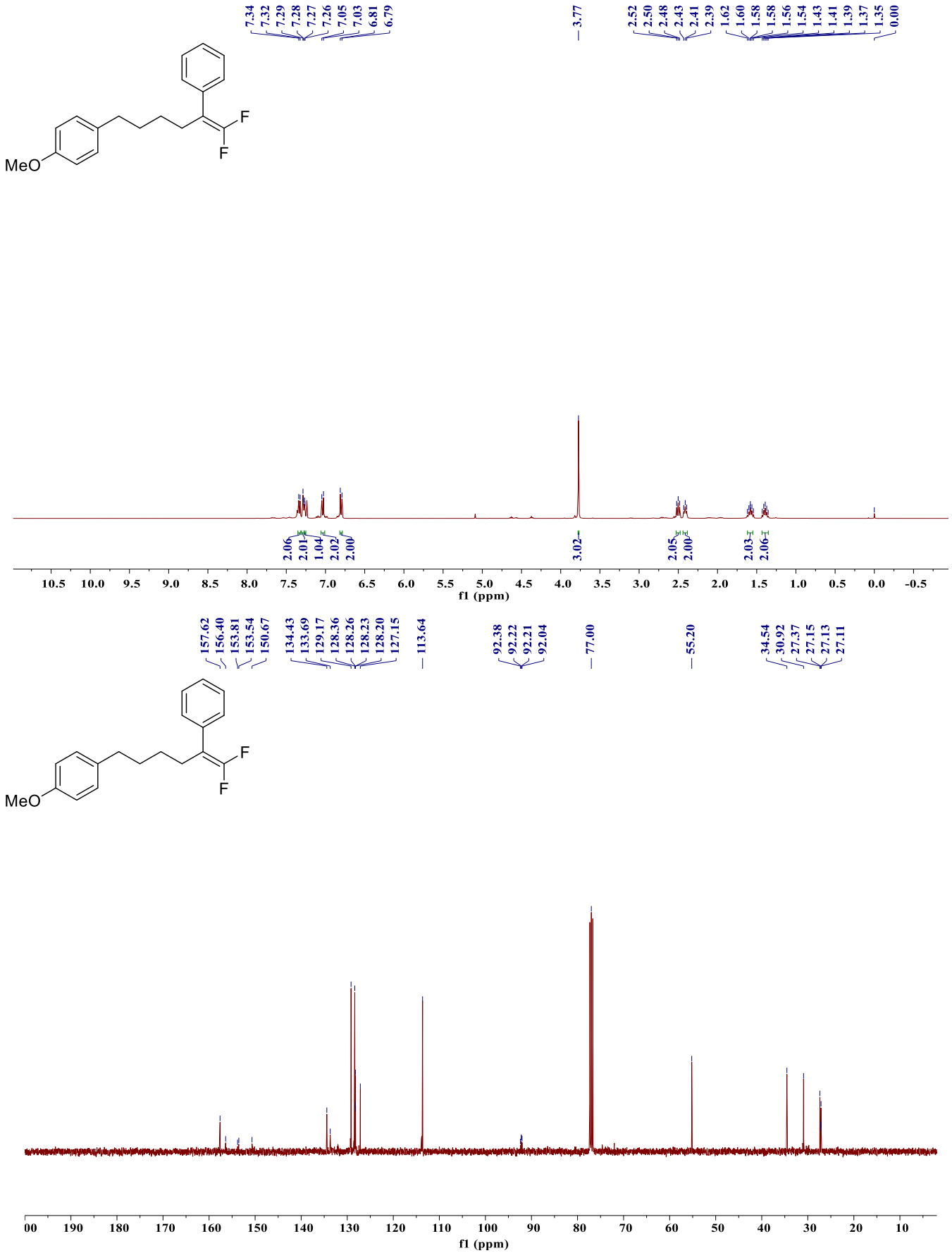


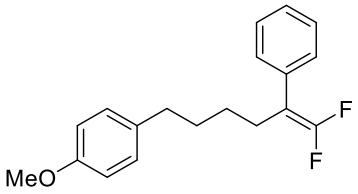
Figure 9. Another possible reaction mechanism

The photoexcited Ir-catalyst may oxidize Ph_3P to form phosphoranyl cation radical, which then reacts with xanthate anion to generate the key phosphoranyl radical **1-B**. This mechanism is also possible, but not the main reaction pathway.

8. NMR Spectra of products 3aa-3na, 4a-4c, 5ab-5ak and 9.

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3aa




MeO
F
F

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-20
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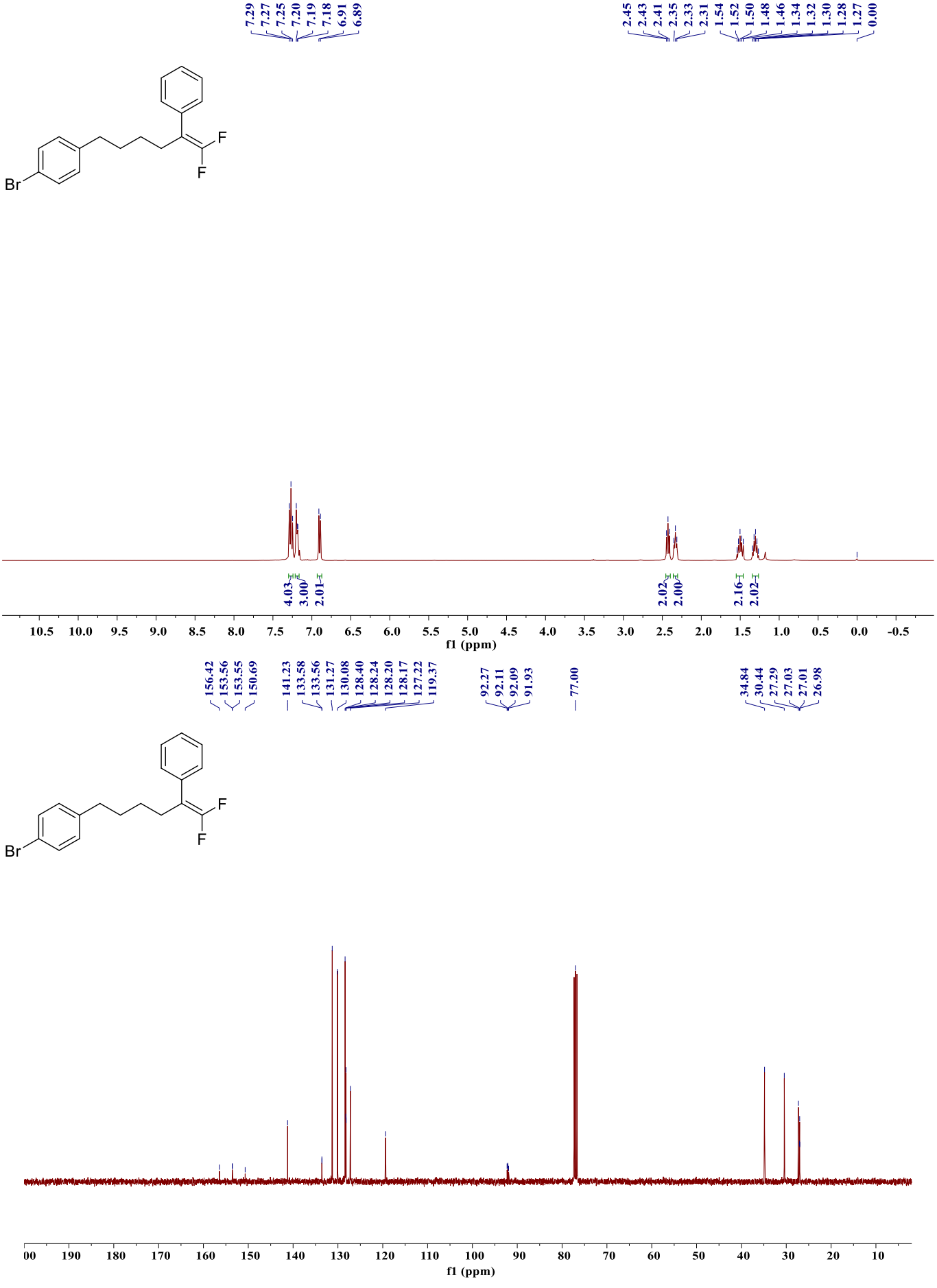
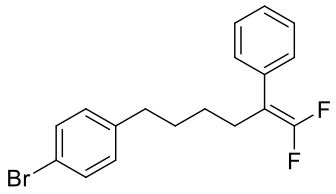
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3ba




Br
F
F

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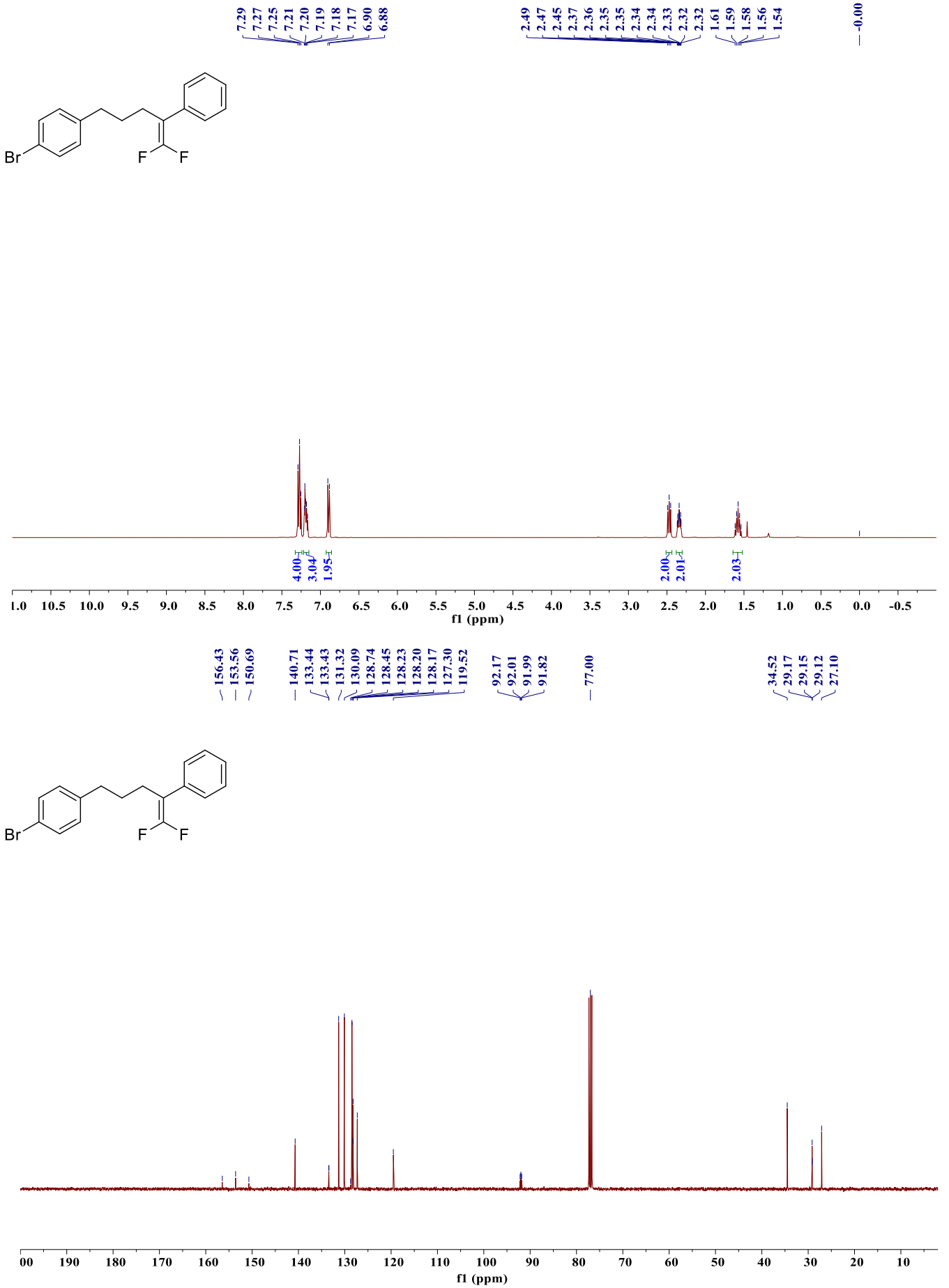
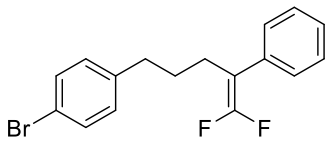
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of Product 3ca

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F
F

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-100
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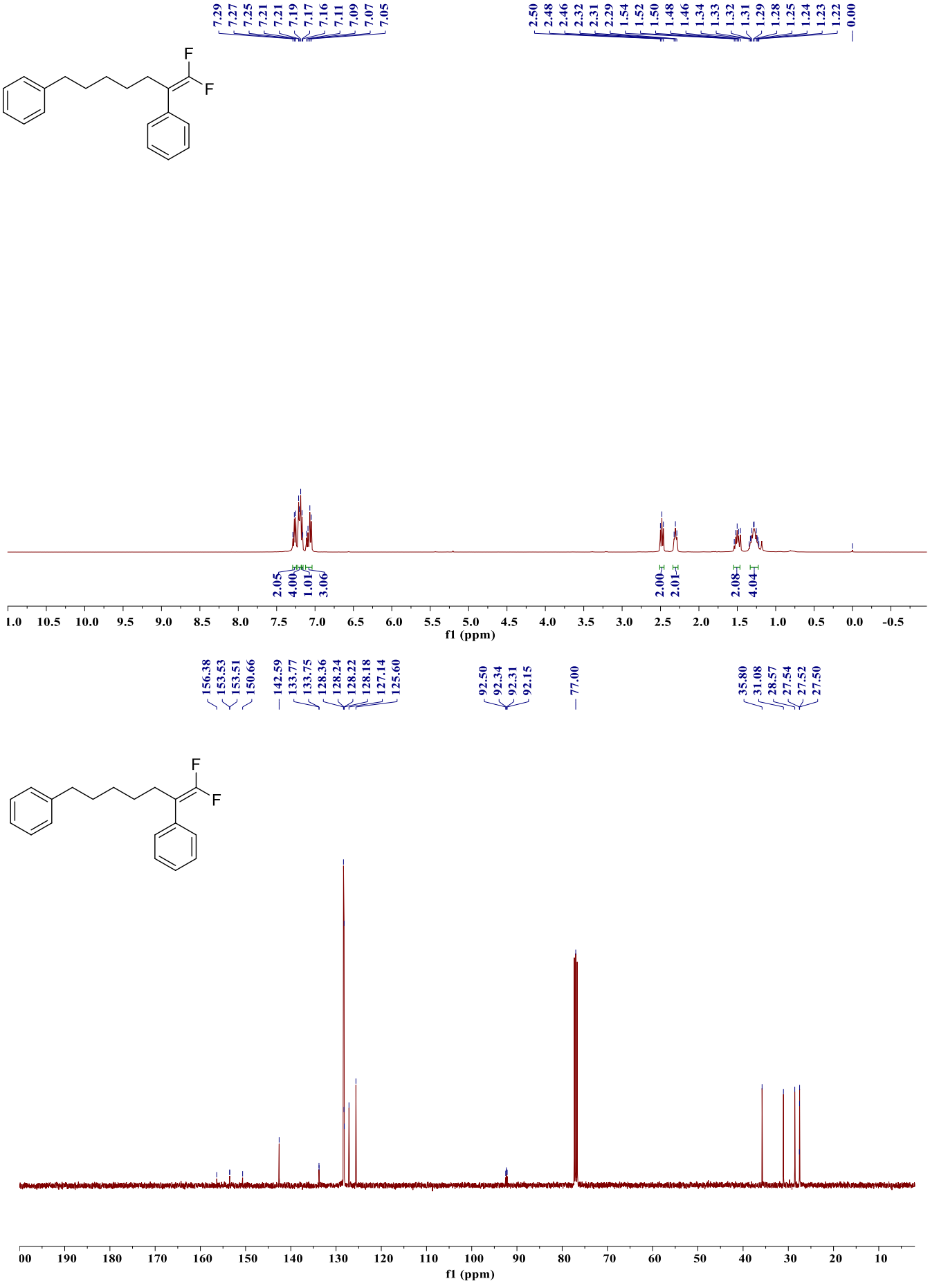
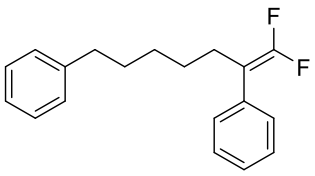
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3da




F
F

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-92.07
2.00
0
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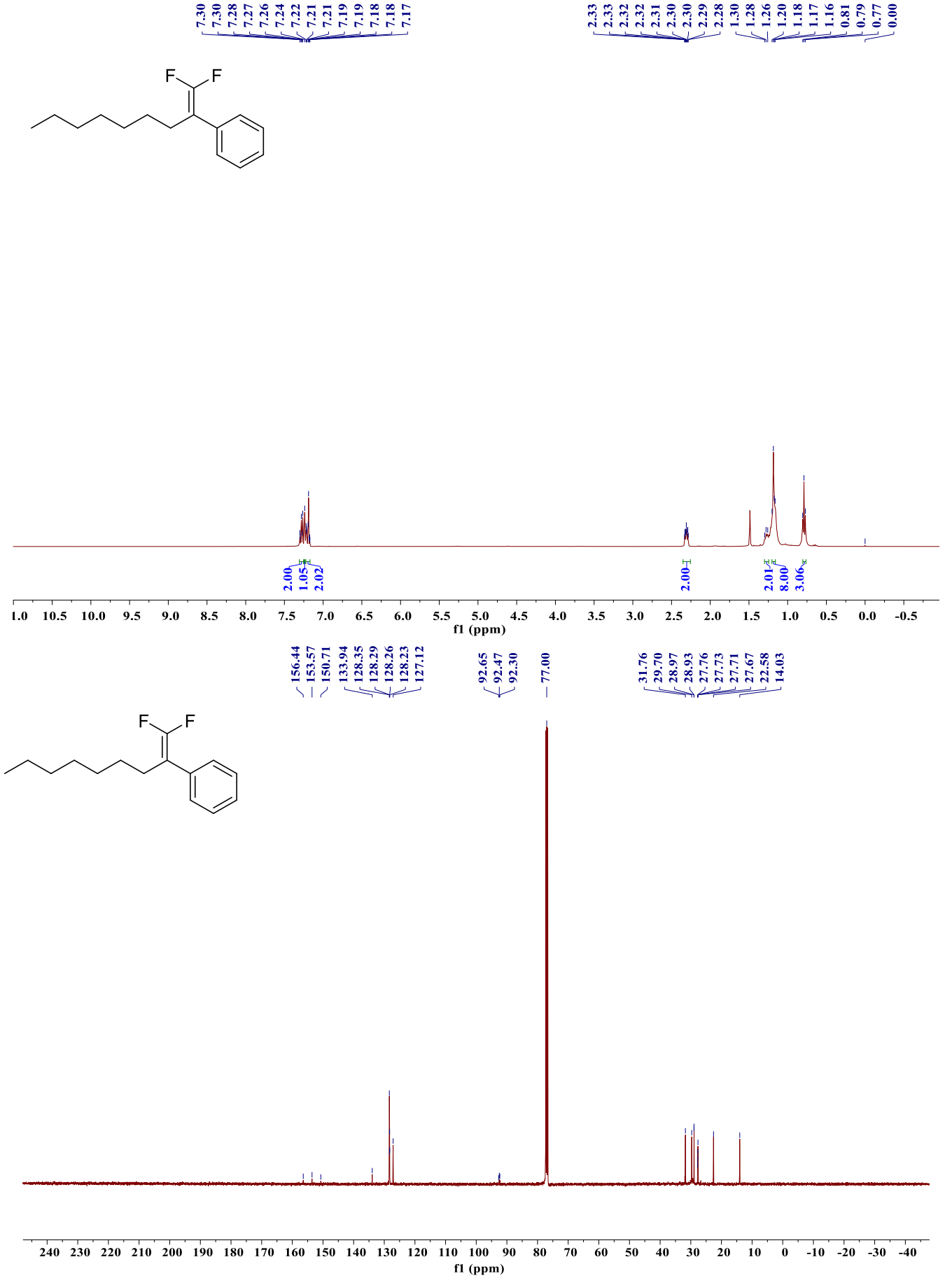
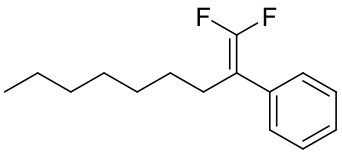
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of Product 3ea




F
F

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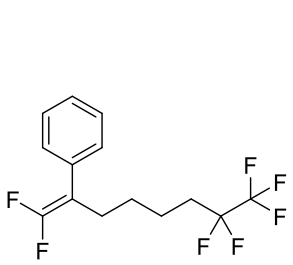
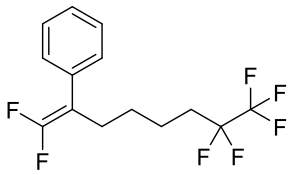
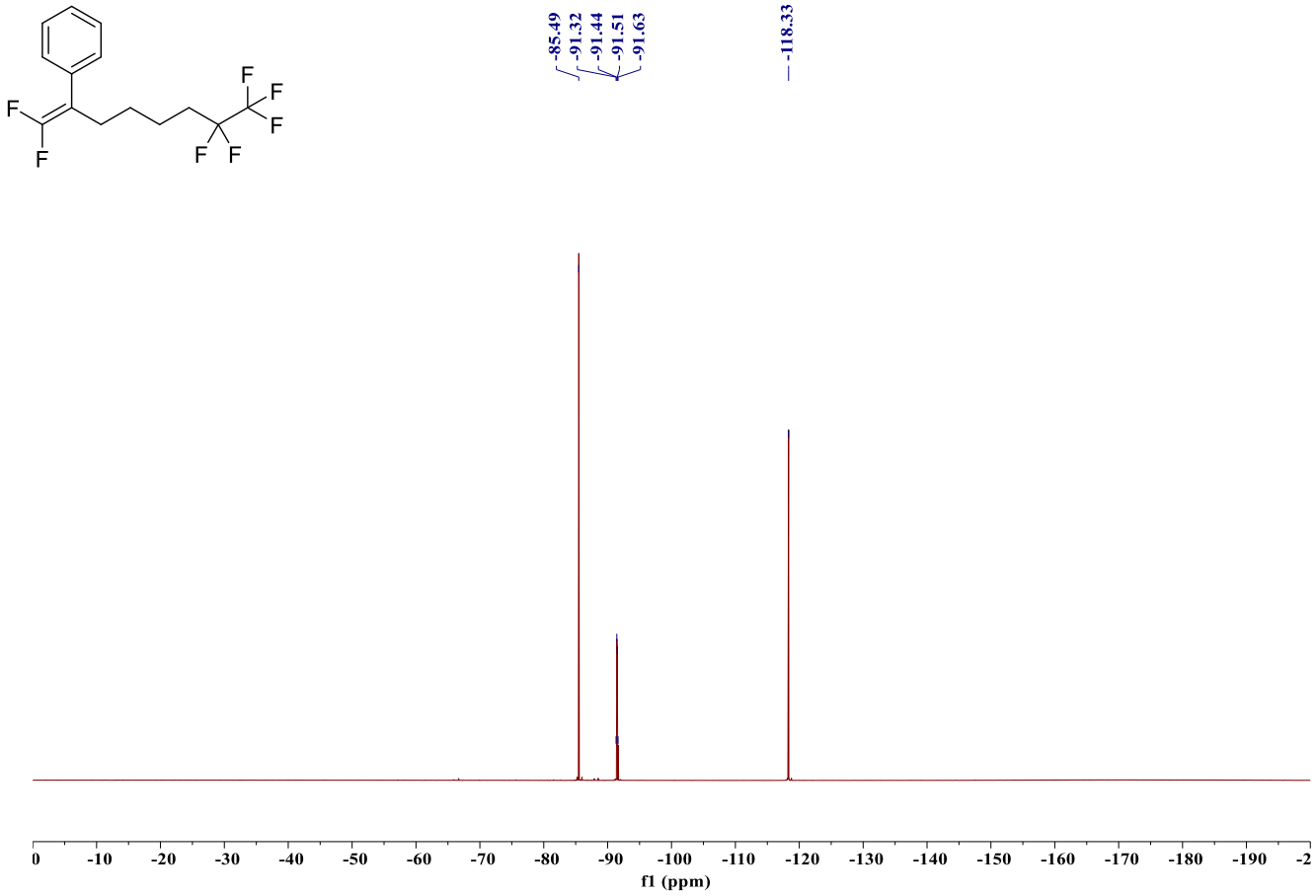
-92.11
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

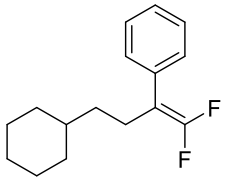
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3fa

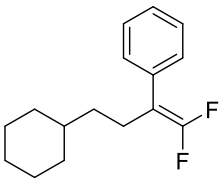


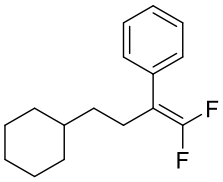



F
F
F
F
F
F
-85.49
-91.32
-91.44
-91.51
-91.63
-118.33
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3ga

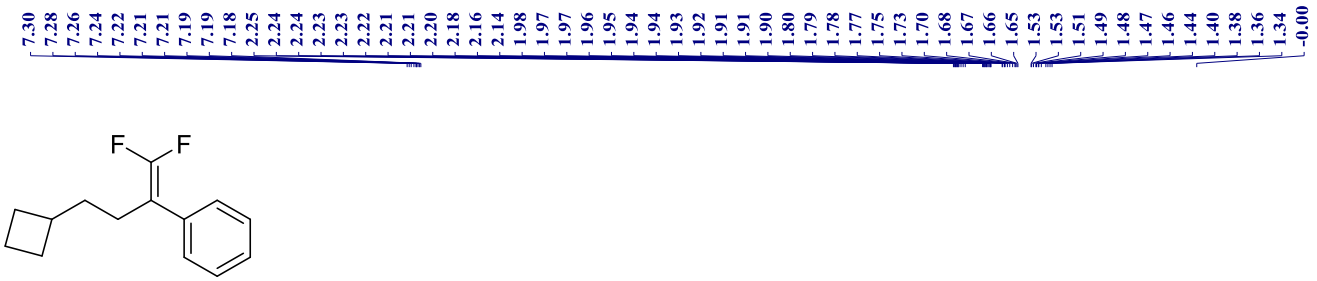


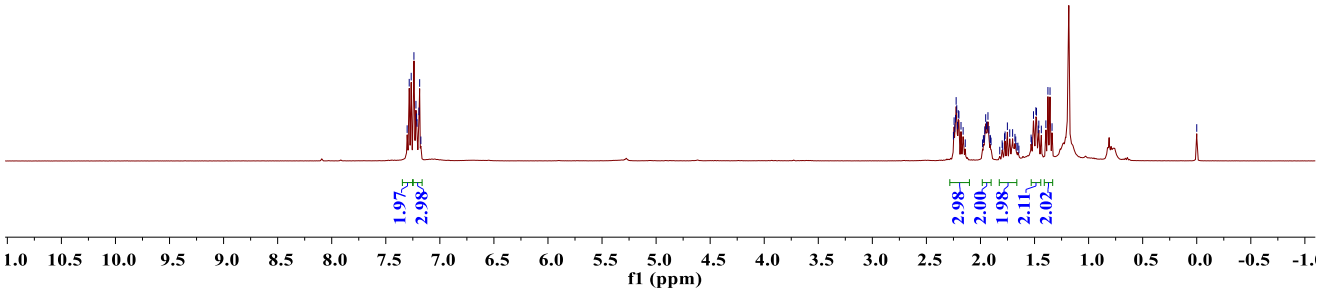


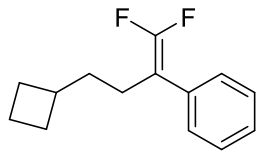

F
F

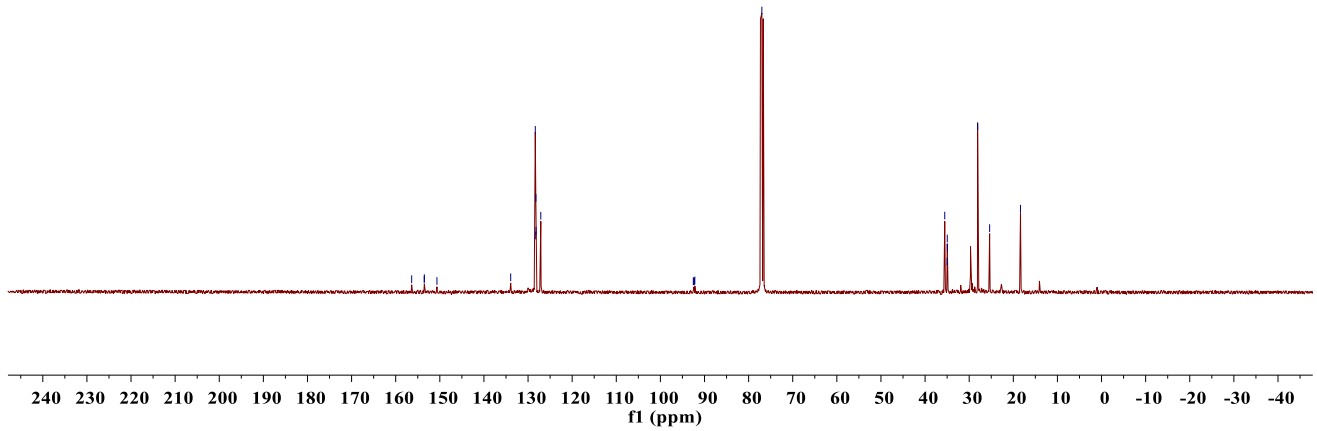
-92.00
-92.12
-92.12
-92.24
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

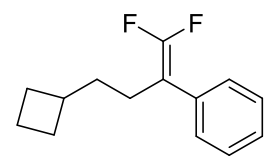
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra Product of 3ha





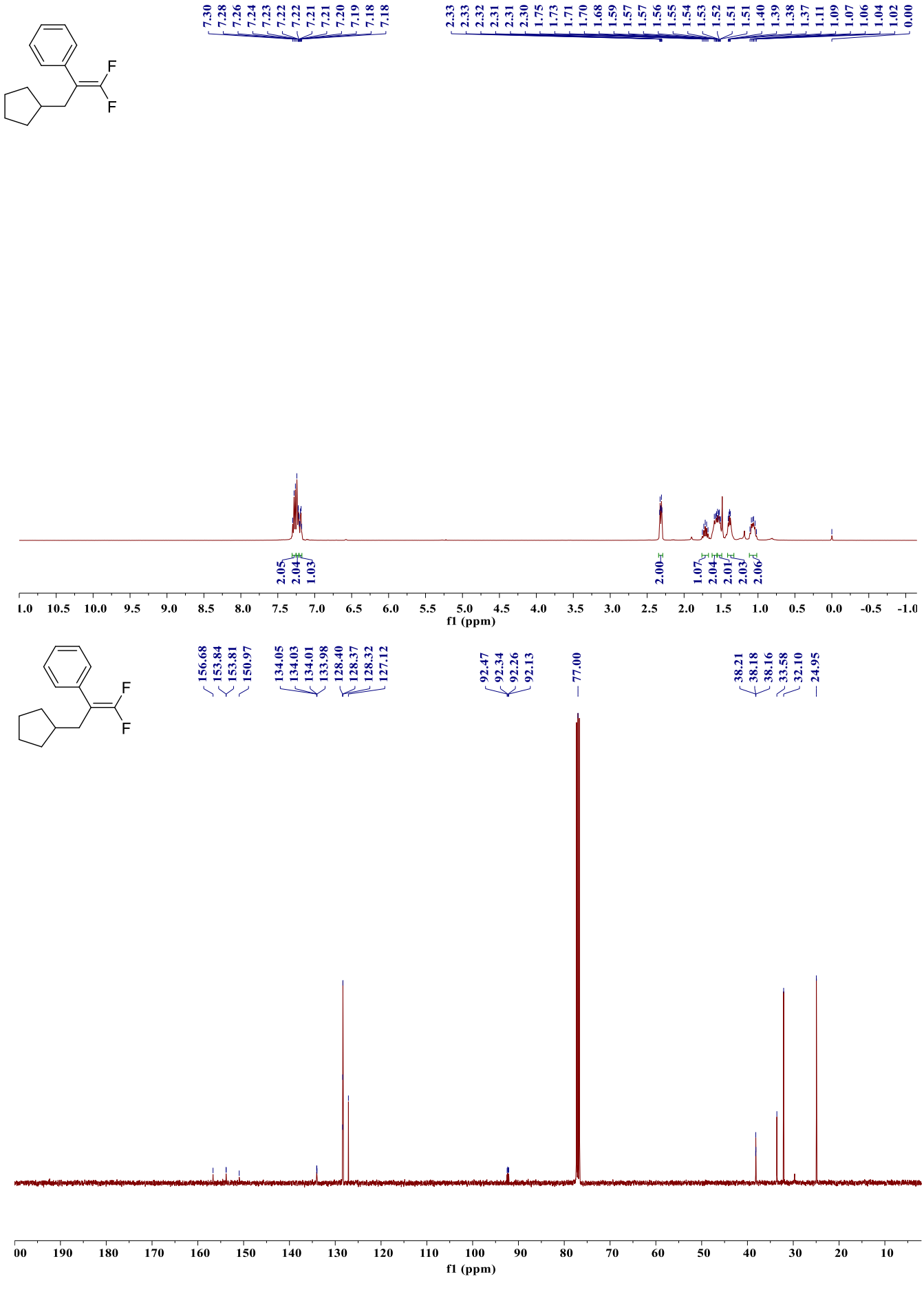


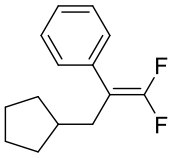



F
F

-92.01
-92.01
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

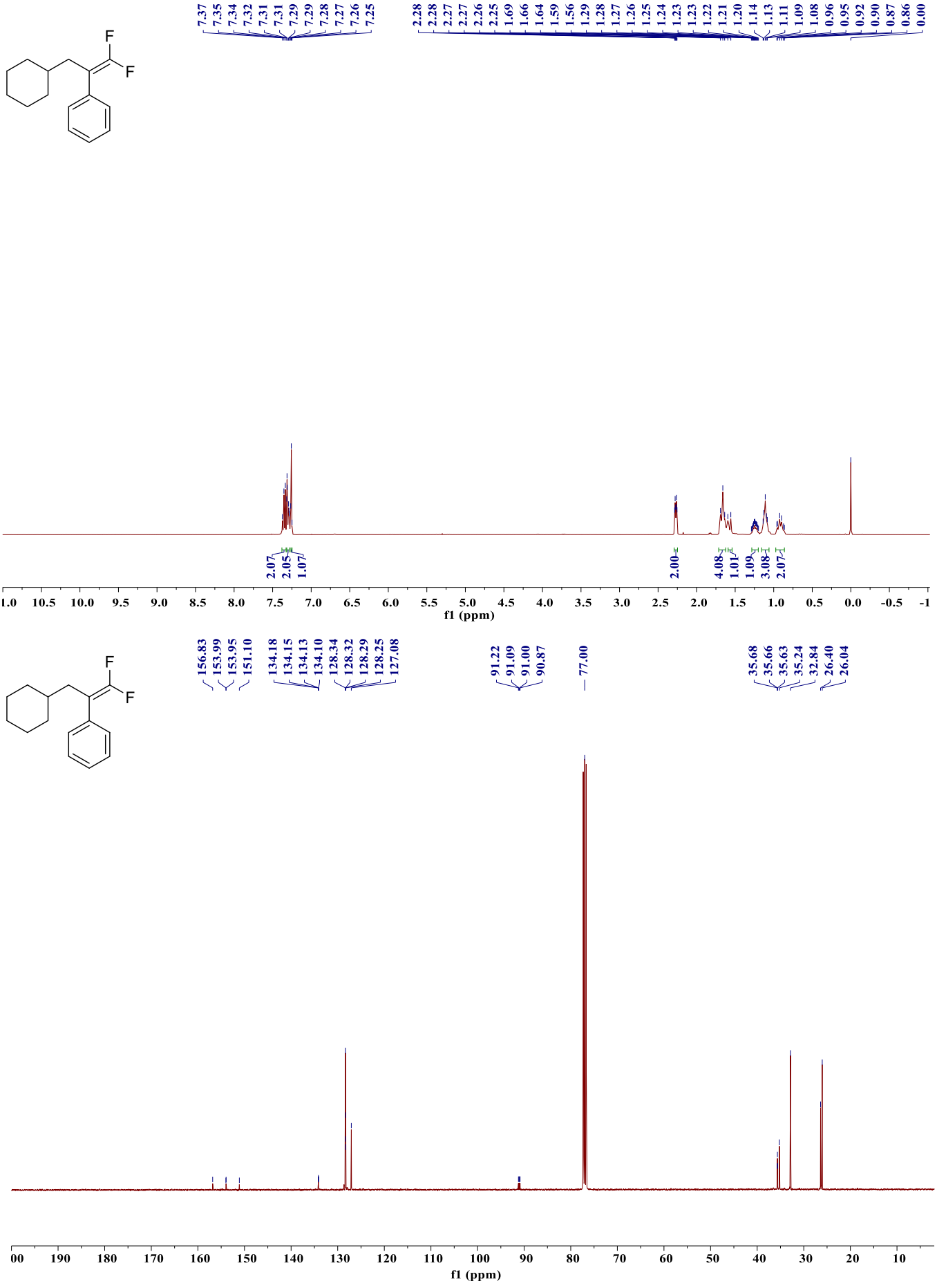
^{1}H NMR (400 MHz, $CDCl_3$) ,^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3ia

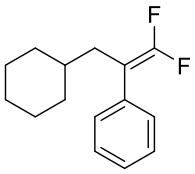



F
F

-92.19
-92.31
-92.53
-92.65
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

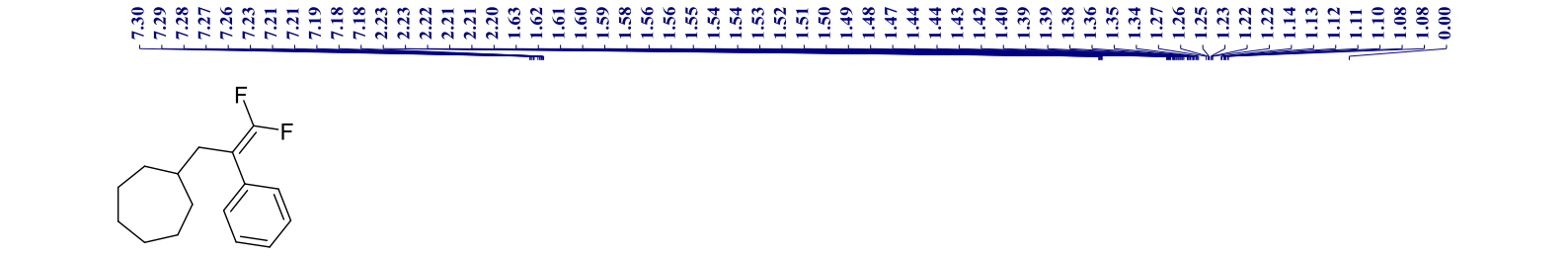
^{1}H NMR (400 MHz, $CDCl_3$) ,^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3ja

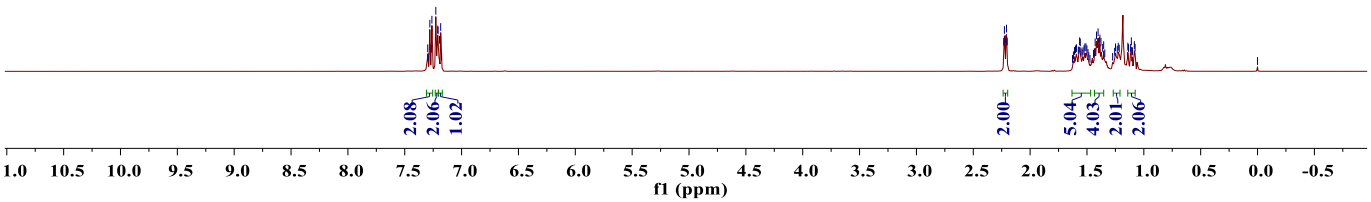


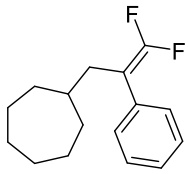

F
F

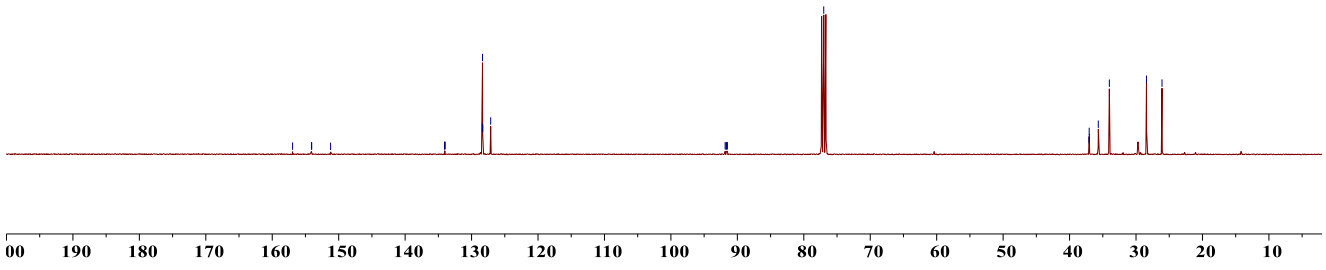
-92.88
-93.00
-93.38
-93.50
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

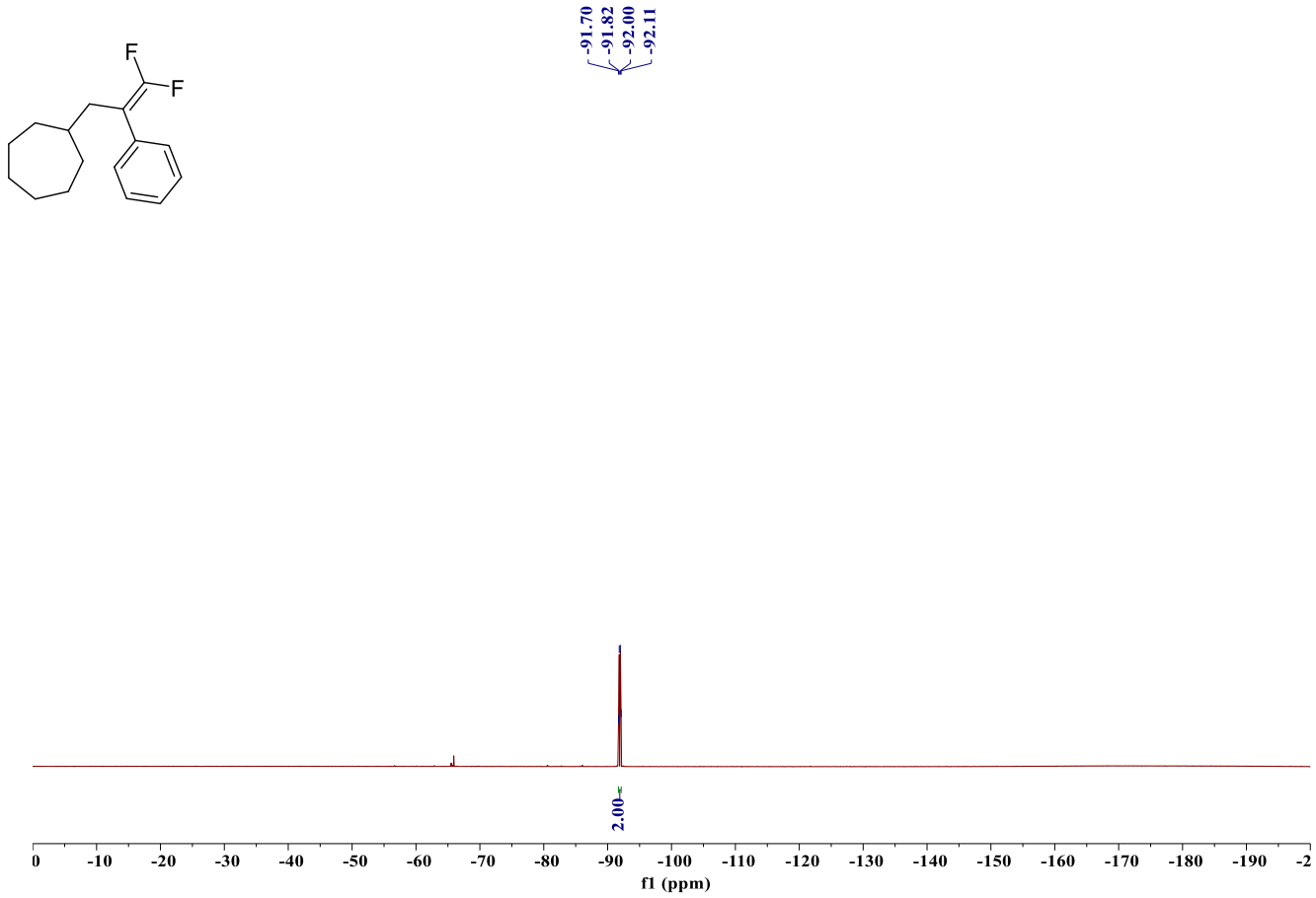
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3ka



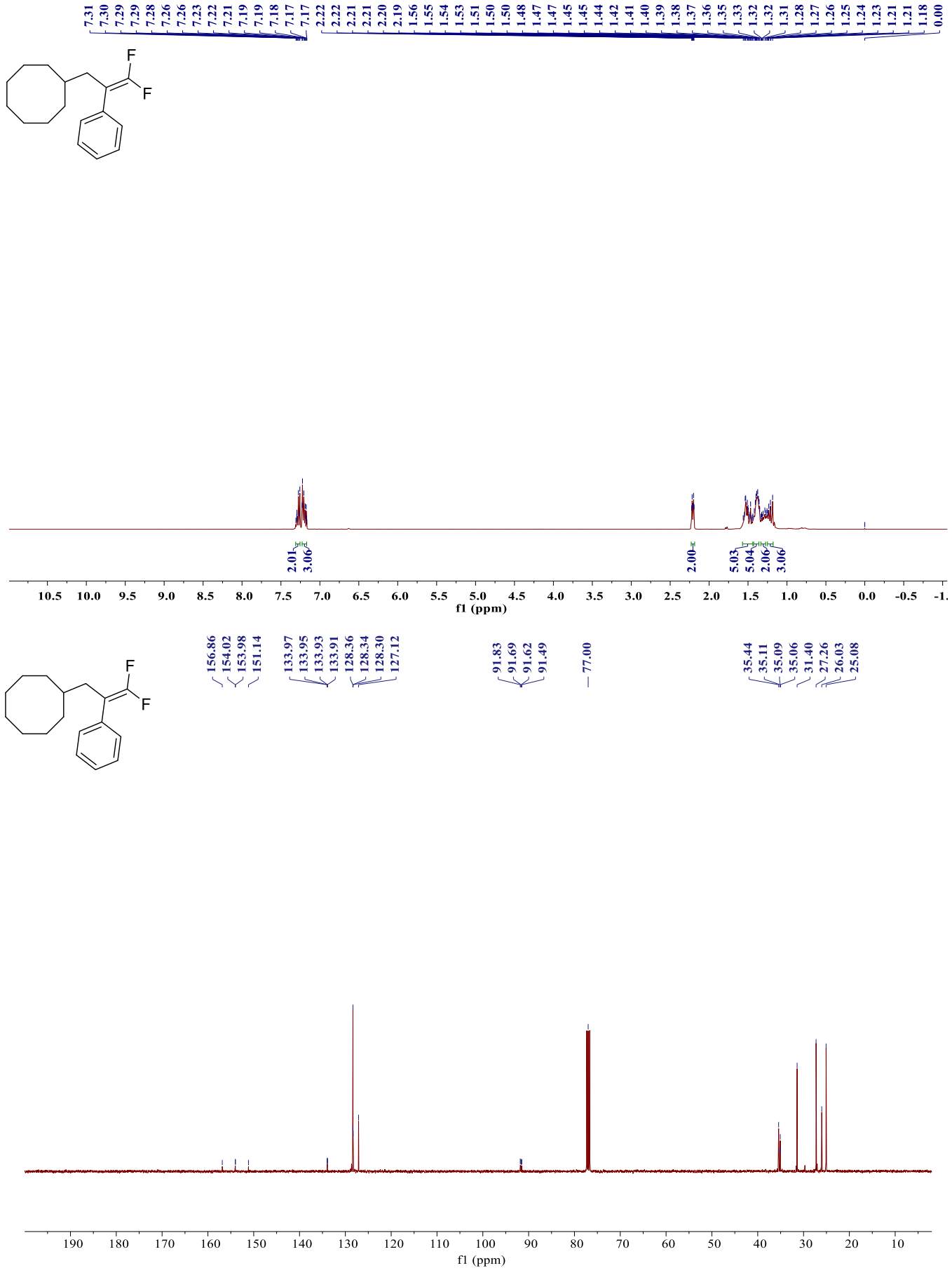


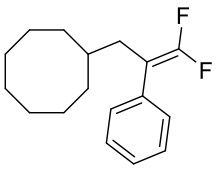





F
F
-91.70
-91.82
-92.00
-92.11
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

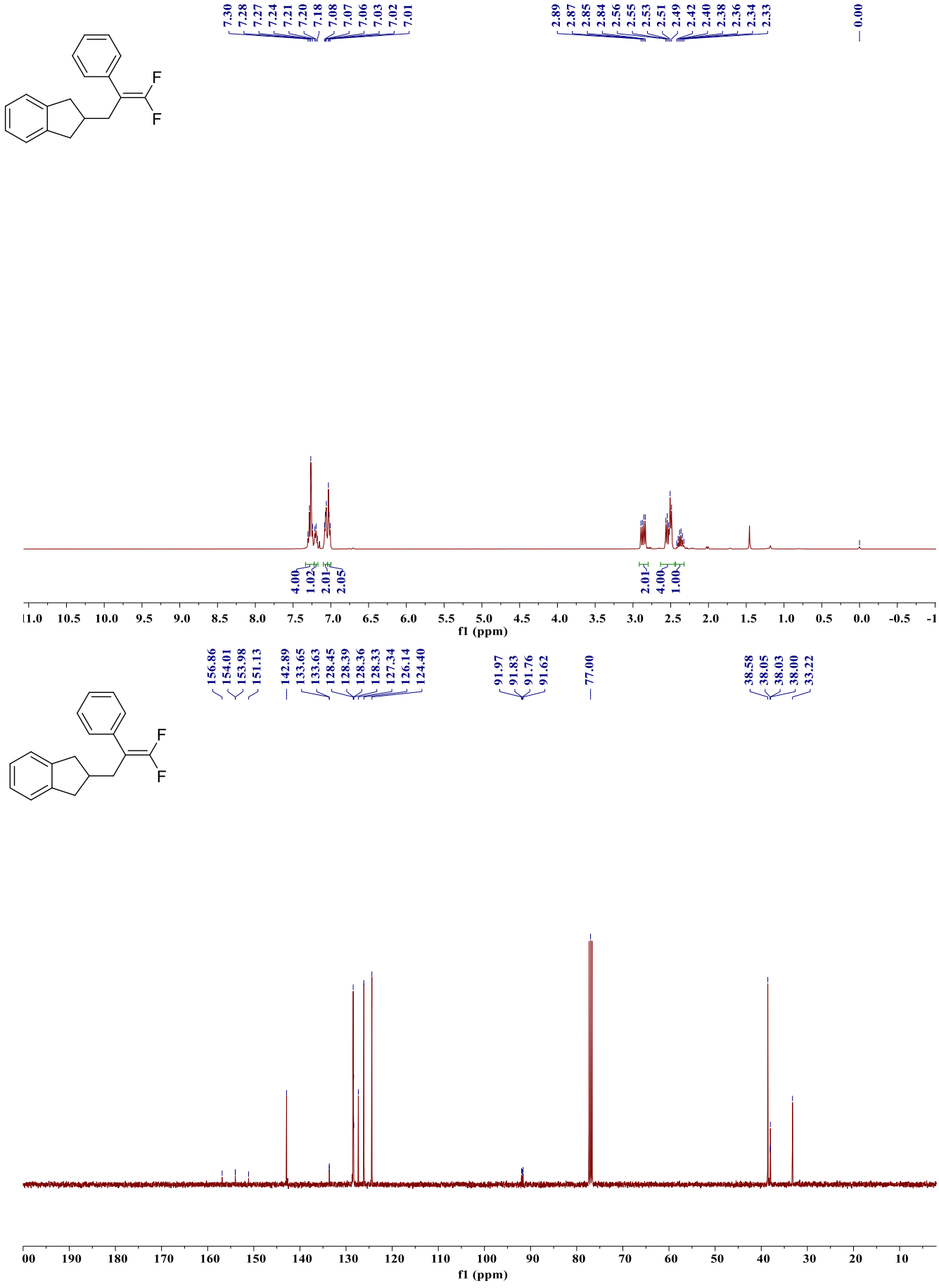
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3la

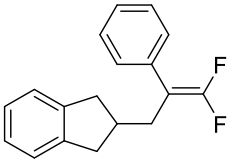



F
F

-91.75
-91.86
-91.94
-92.06
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

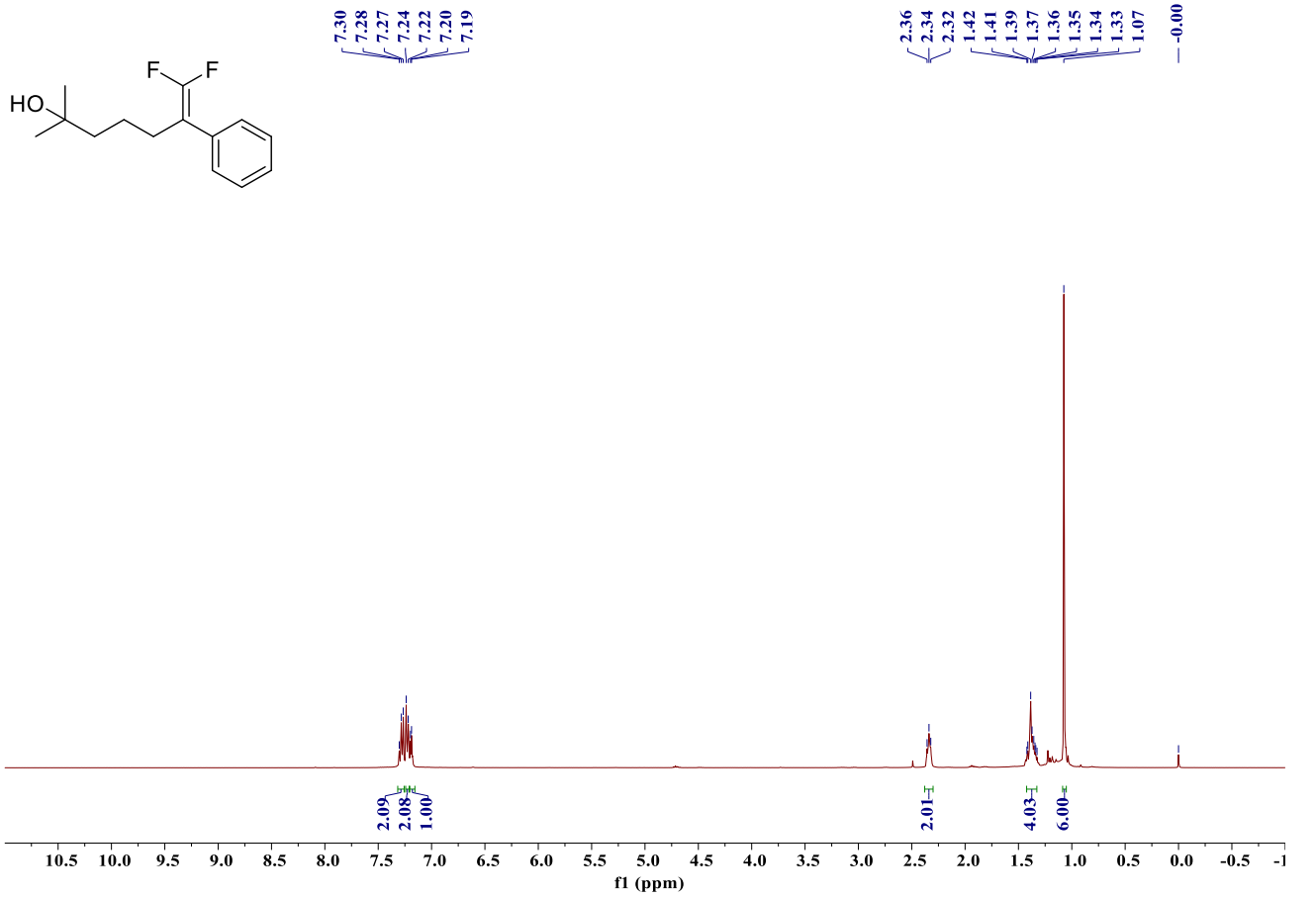
^{1}H NMR (400 MHz, $CDCl_3$) ,^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of 3ma

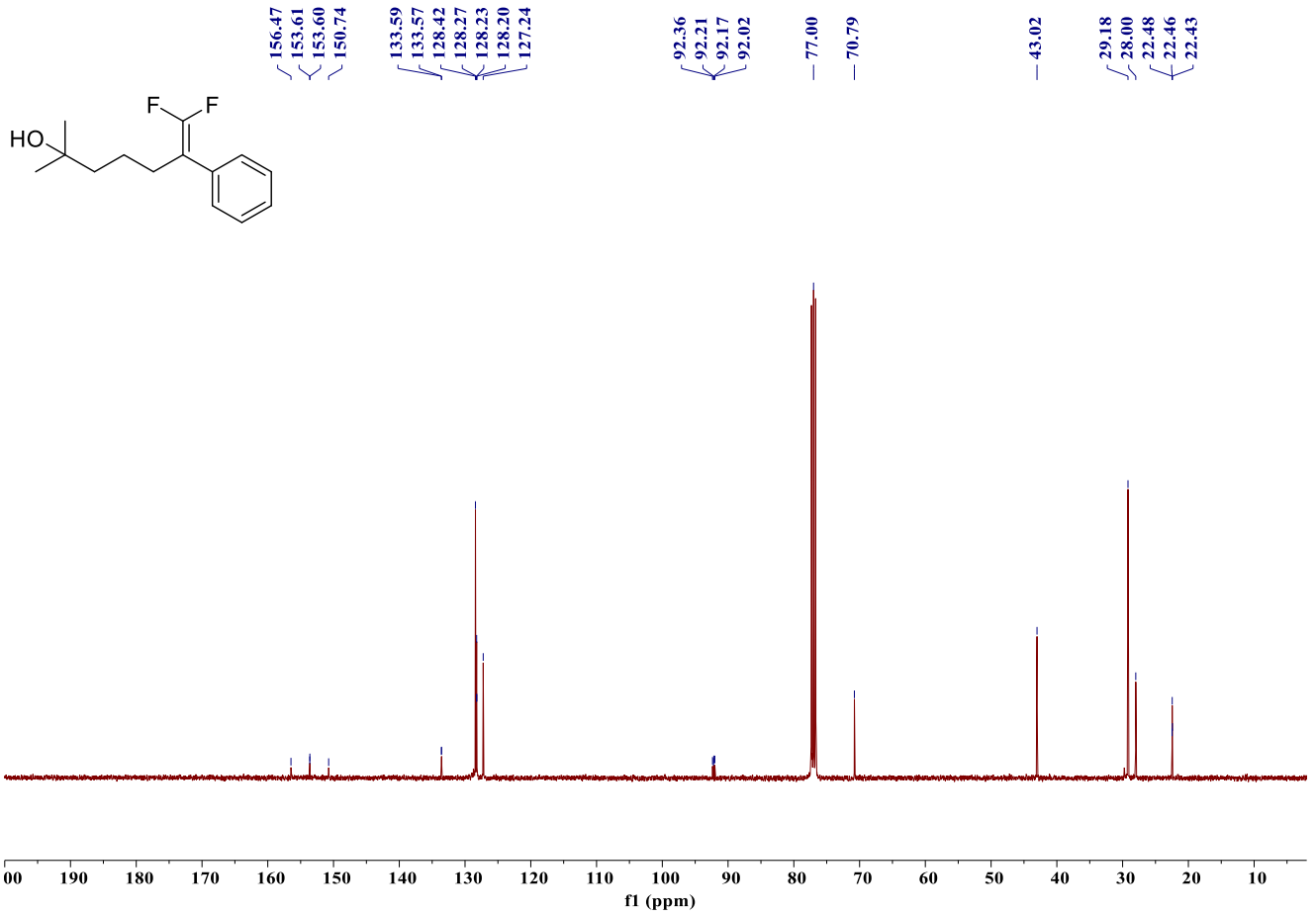


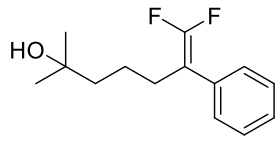

F
F

-91.48
-91.60
-91.67
-91.78
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 4a

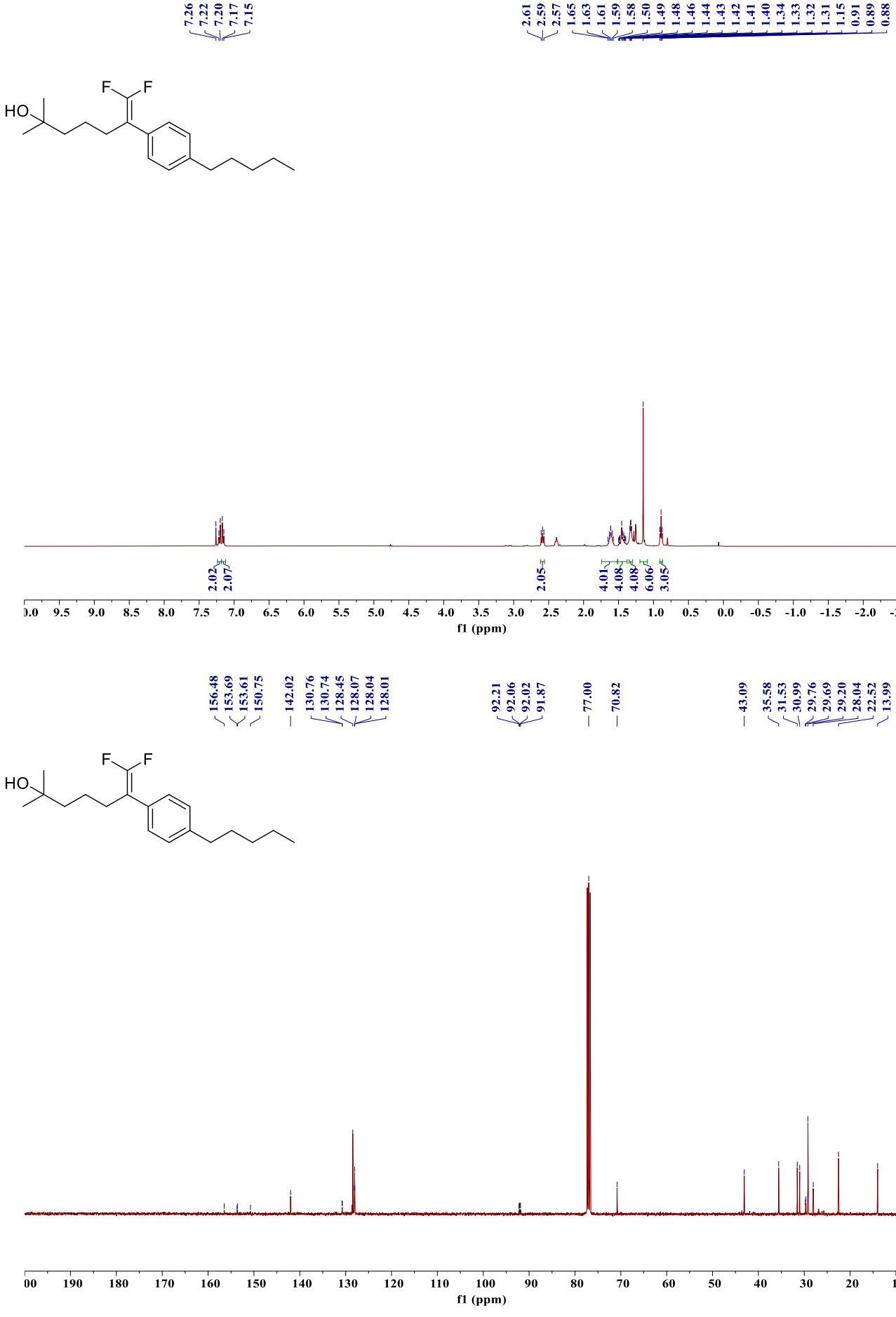


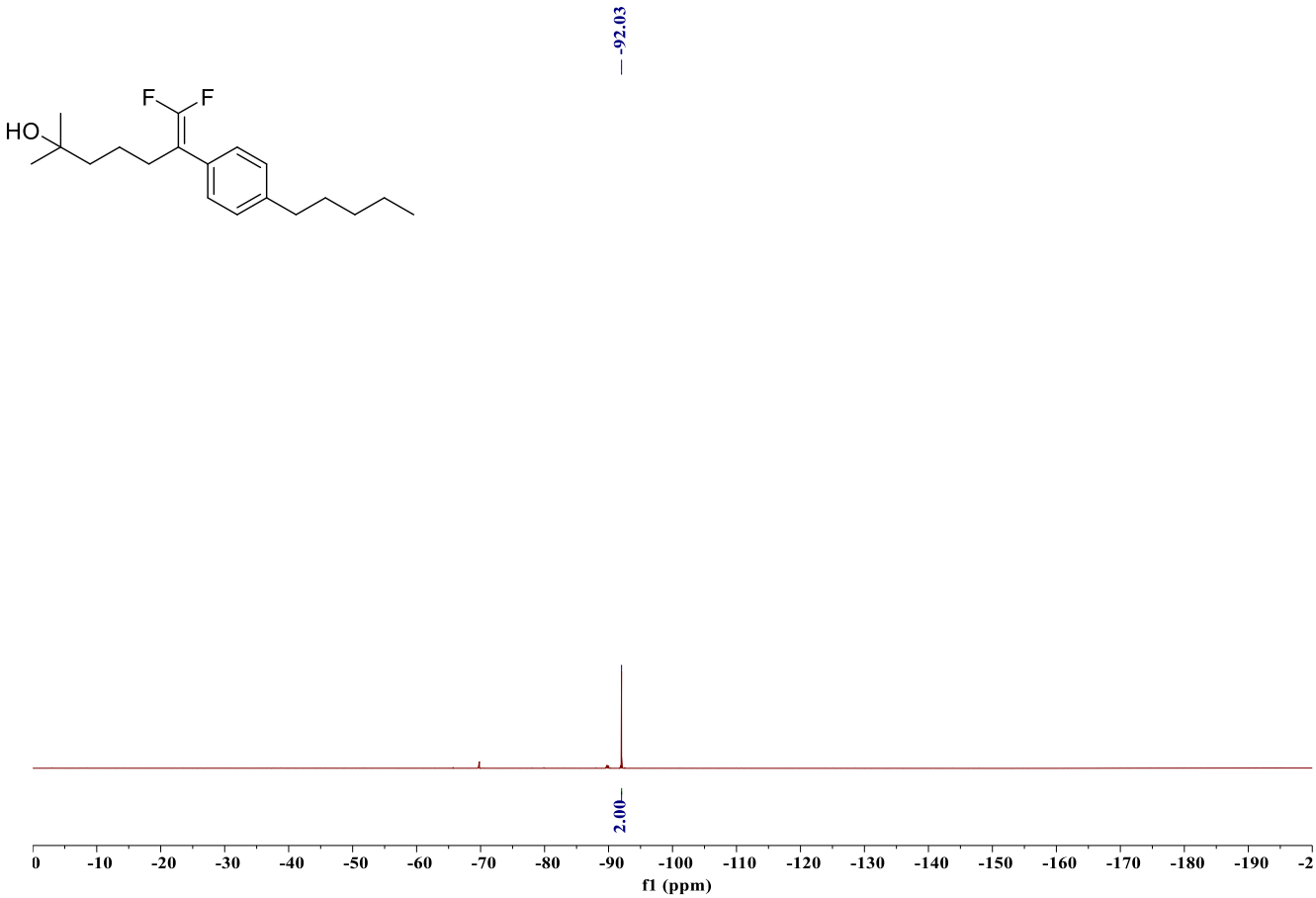



F
F
HO

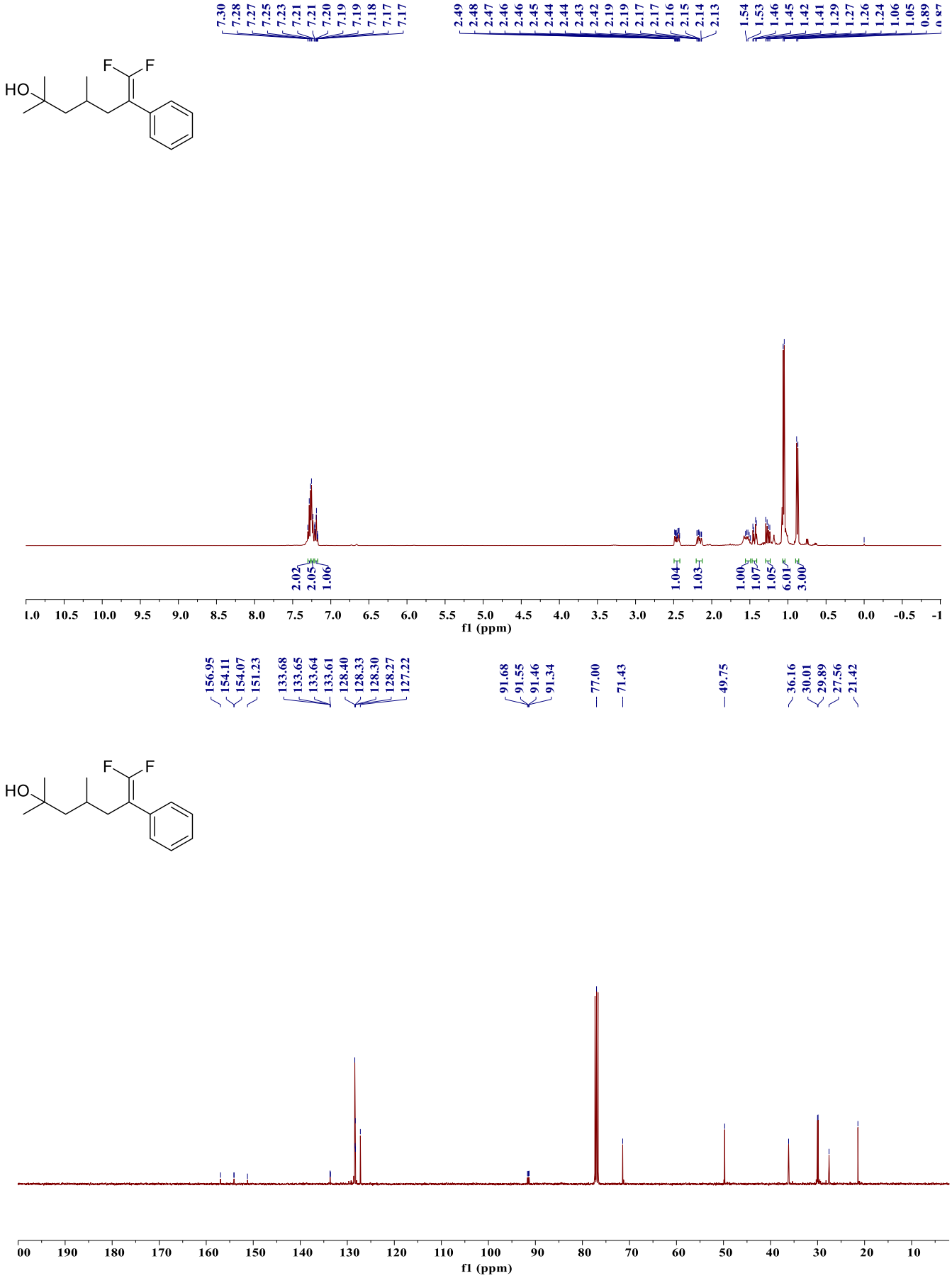
-91.62
-91.74
-91.76
-91.87
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

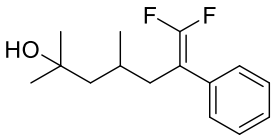
^{1}H NMR (600 MHz, $CDCl_3$), ^{13}C NMR (150 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 4b




F
F
HO
-92.03
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

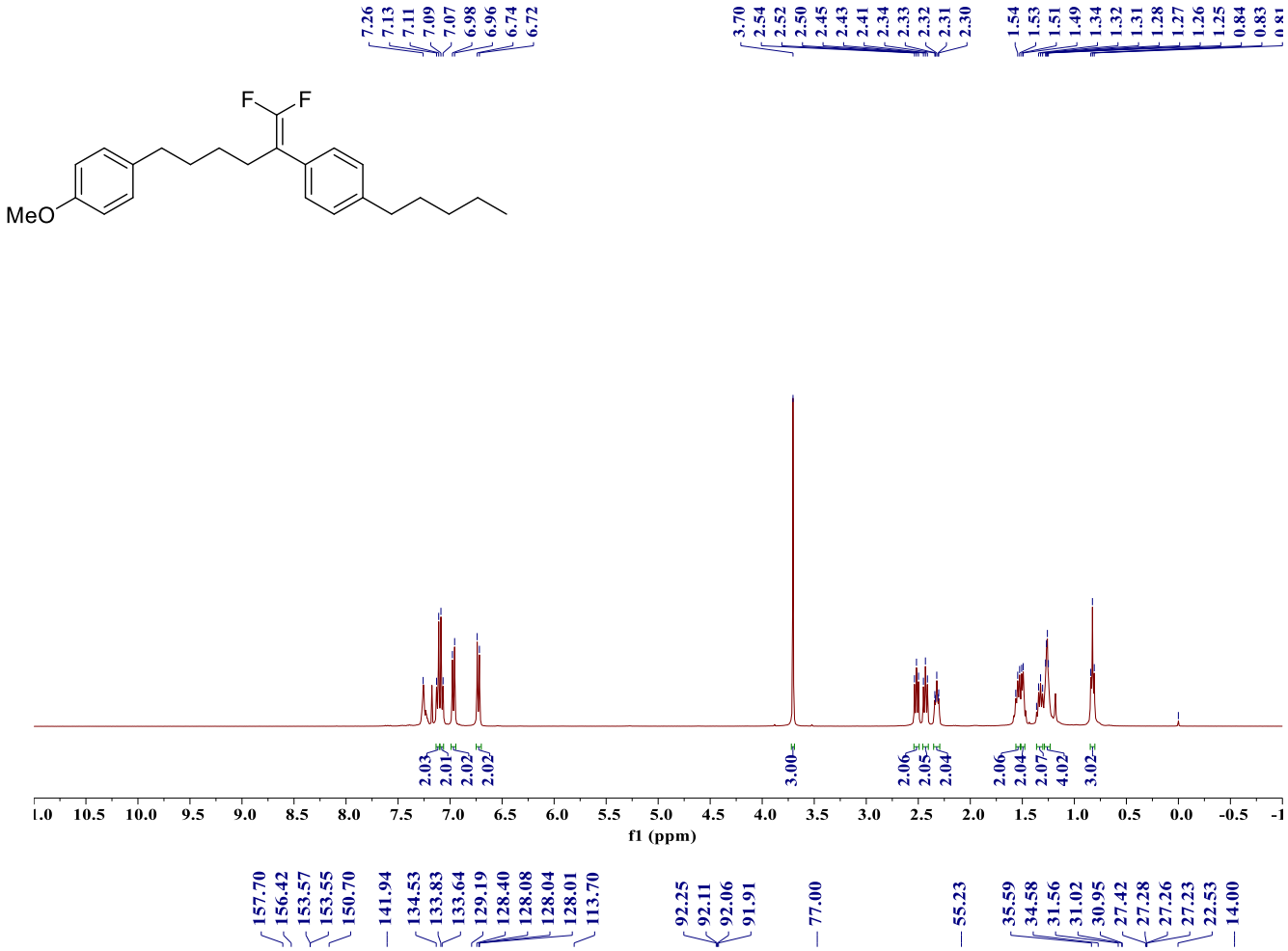
^{1}H NMR (600 MHz, $CDCl_3$), ^{13}C NMR (150 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 4c

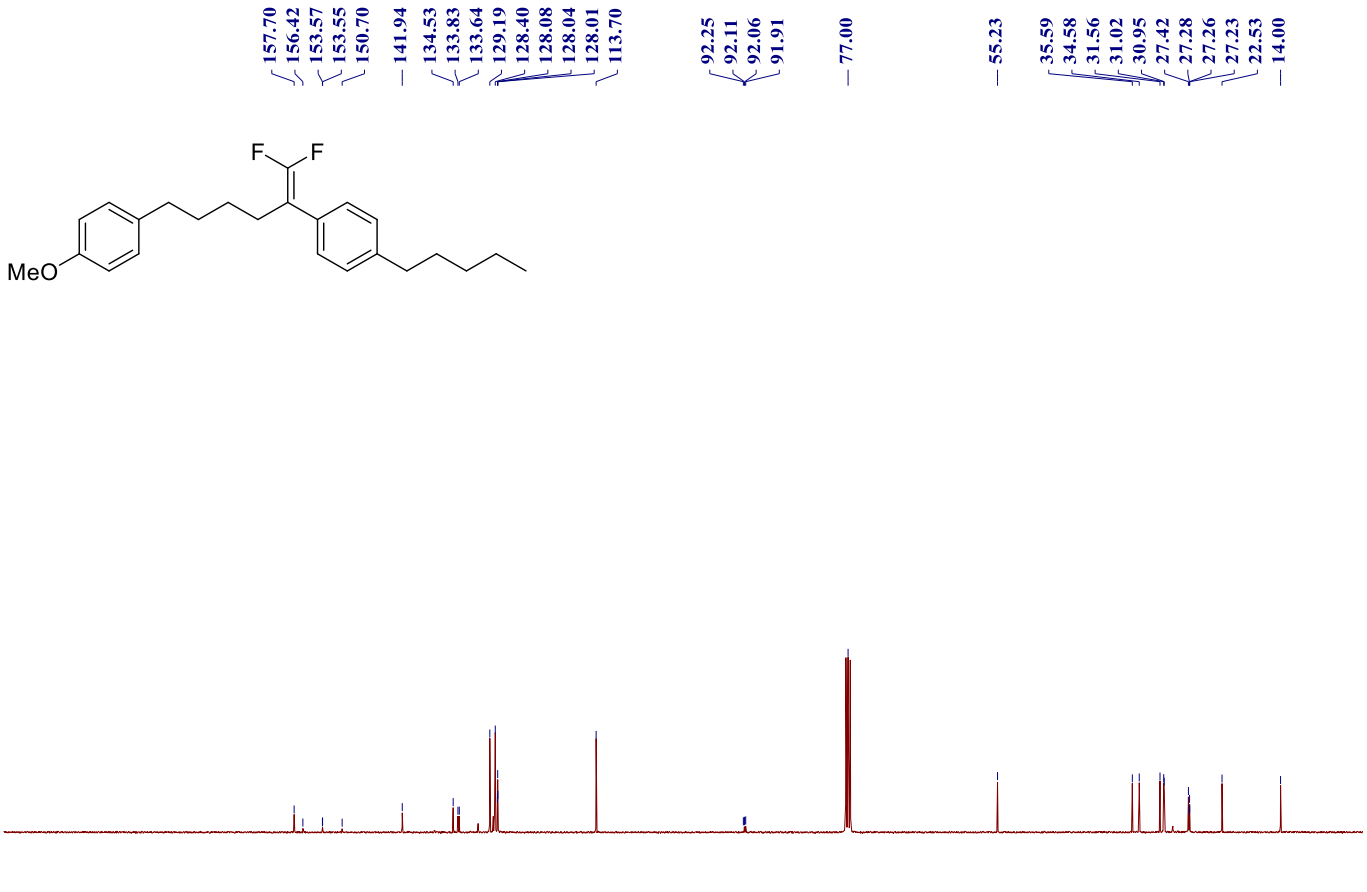


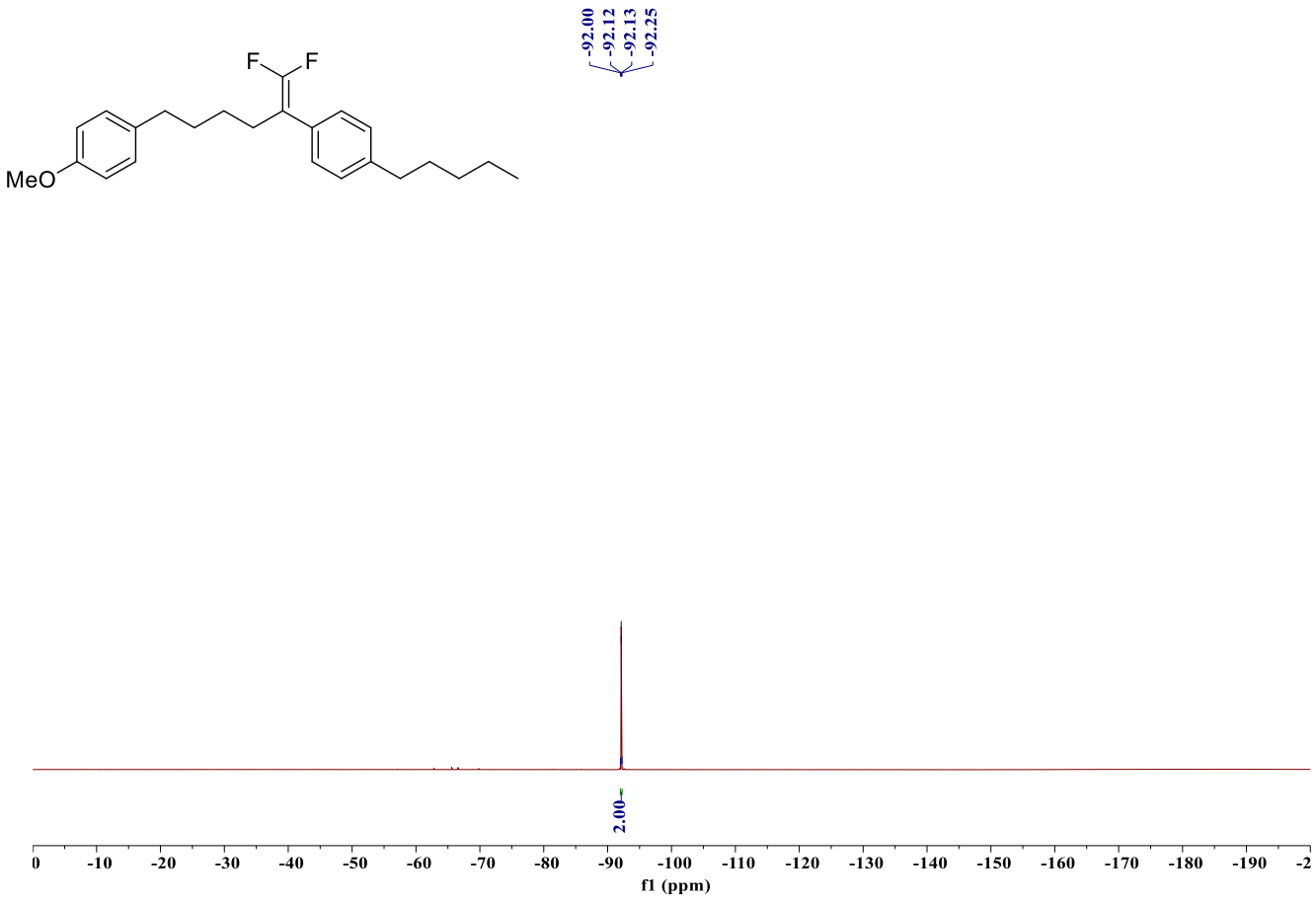

F
F
HO

-91.26
-91.38
-91.80
-91.91
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

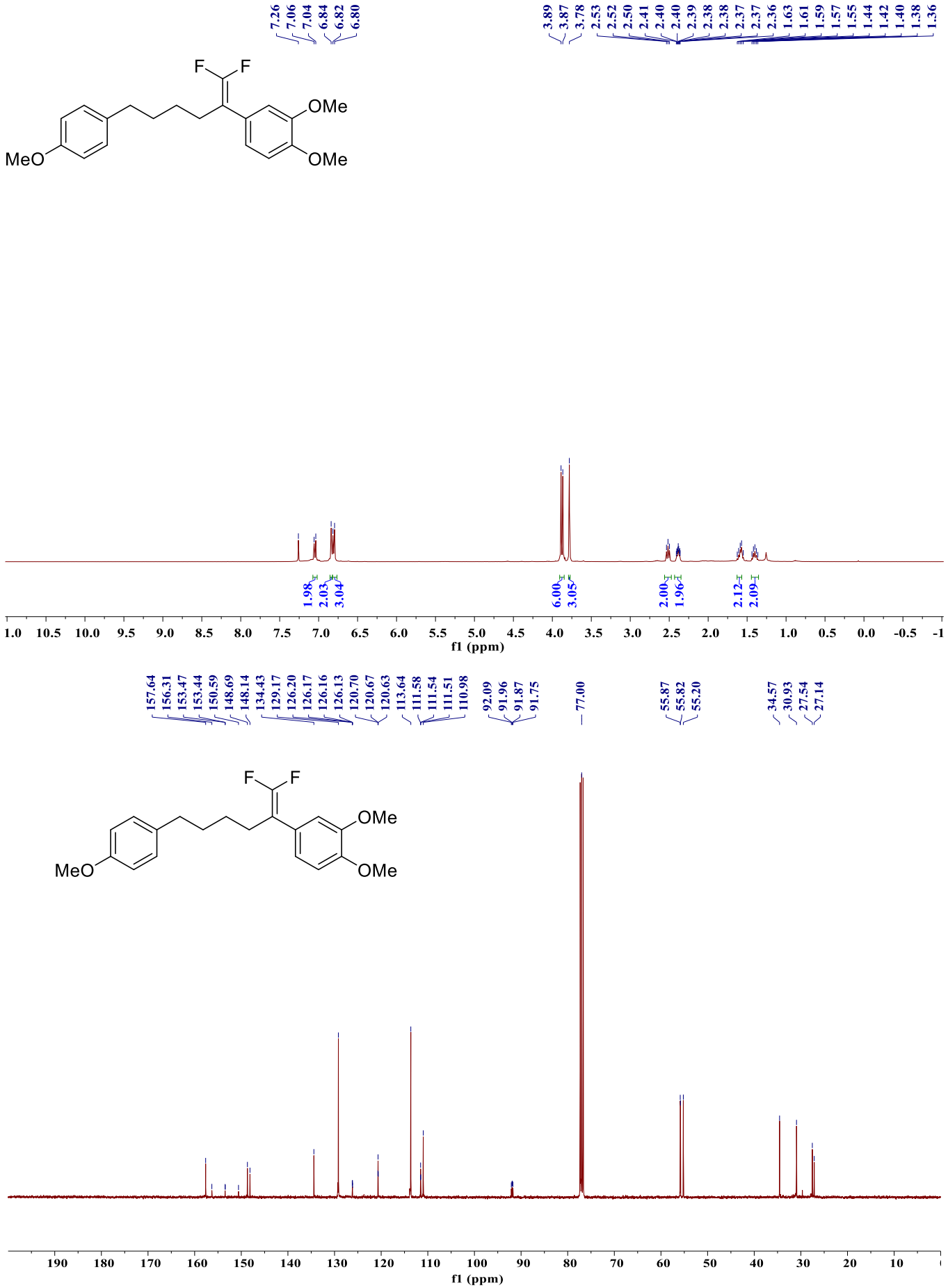
^{1}H NMR (400 MHz, $CDCl_3$) ,^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 5ab

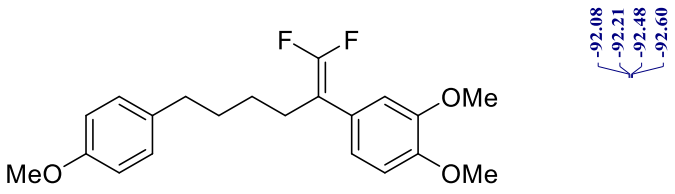





F
F
MeO
-92.00
-92.12
-92.13
-92.25
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

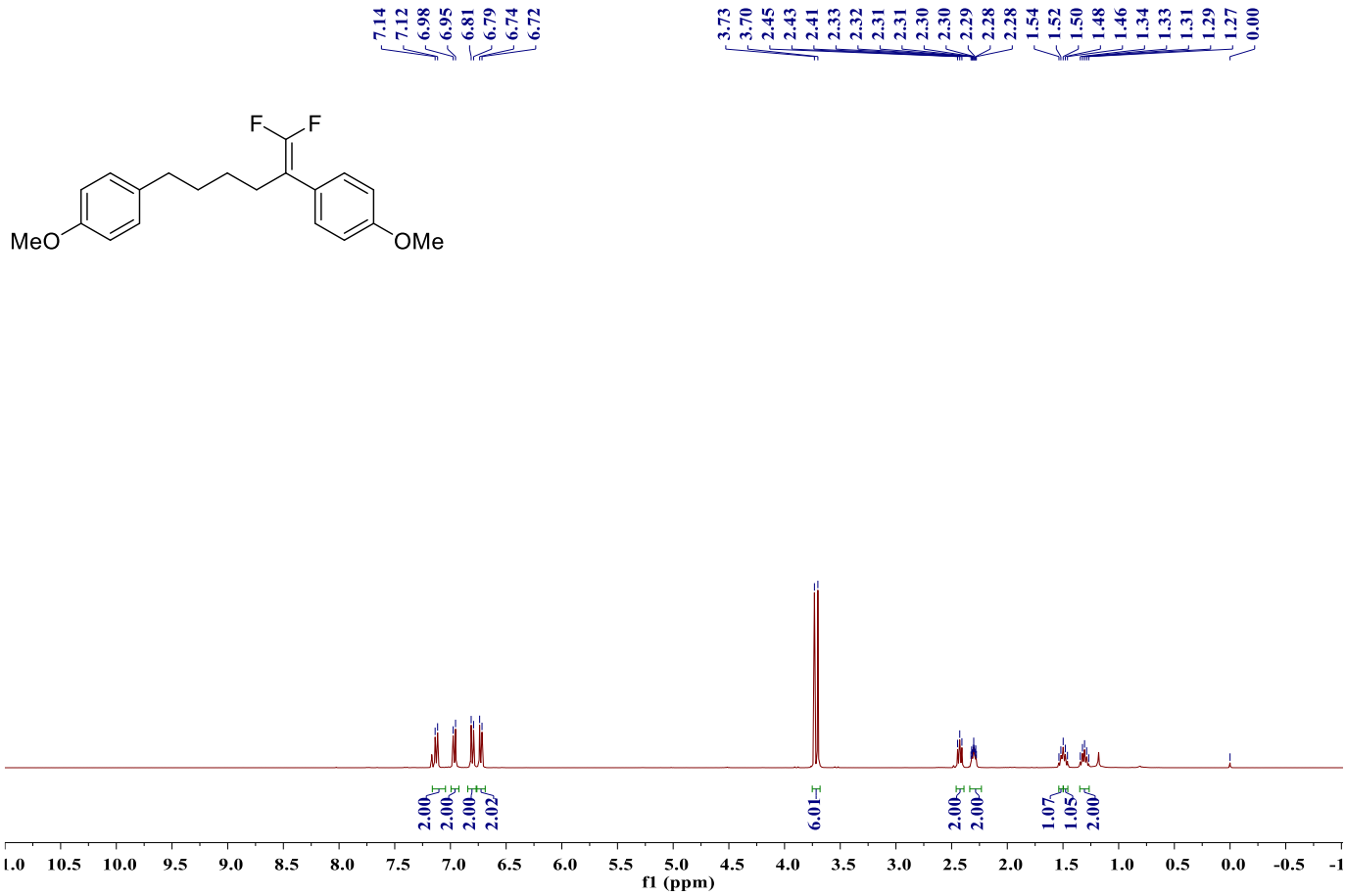
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of Product 5ac

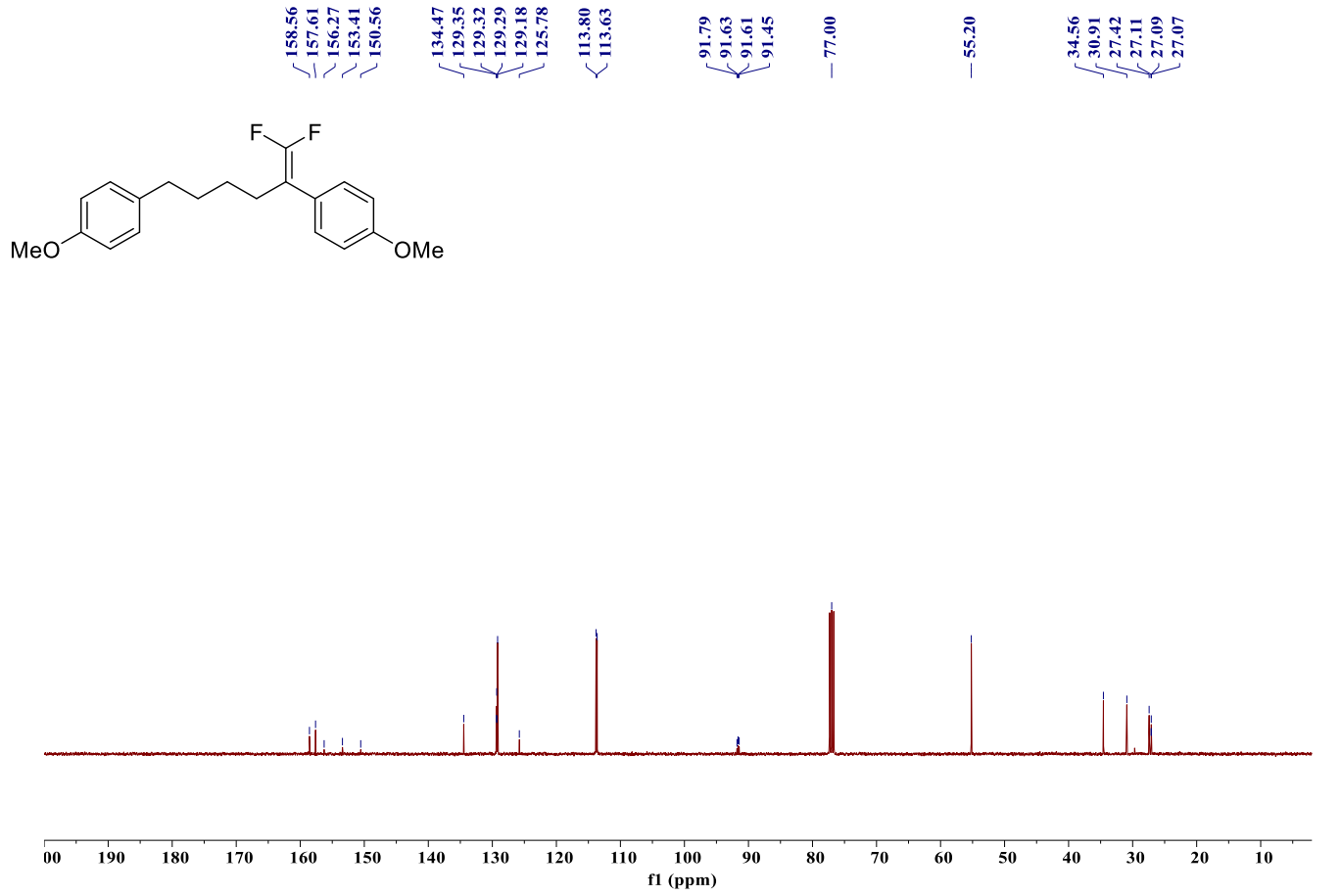


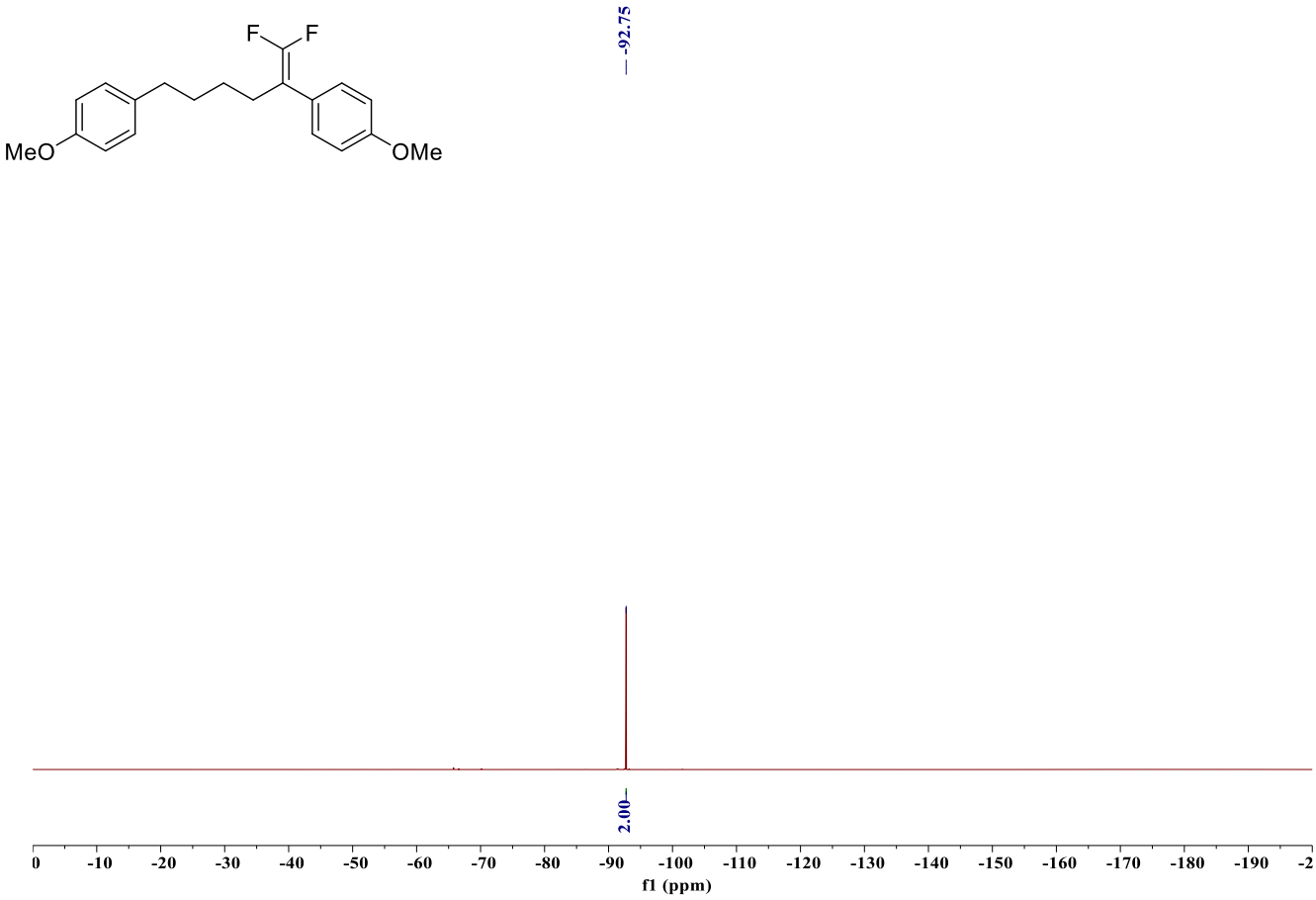

F
F
OMe
MeO
OMe

-92.08
-92.21
-92.48
-92.60
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

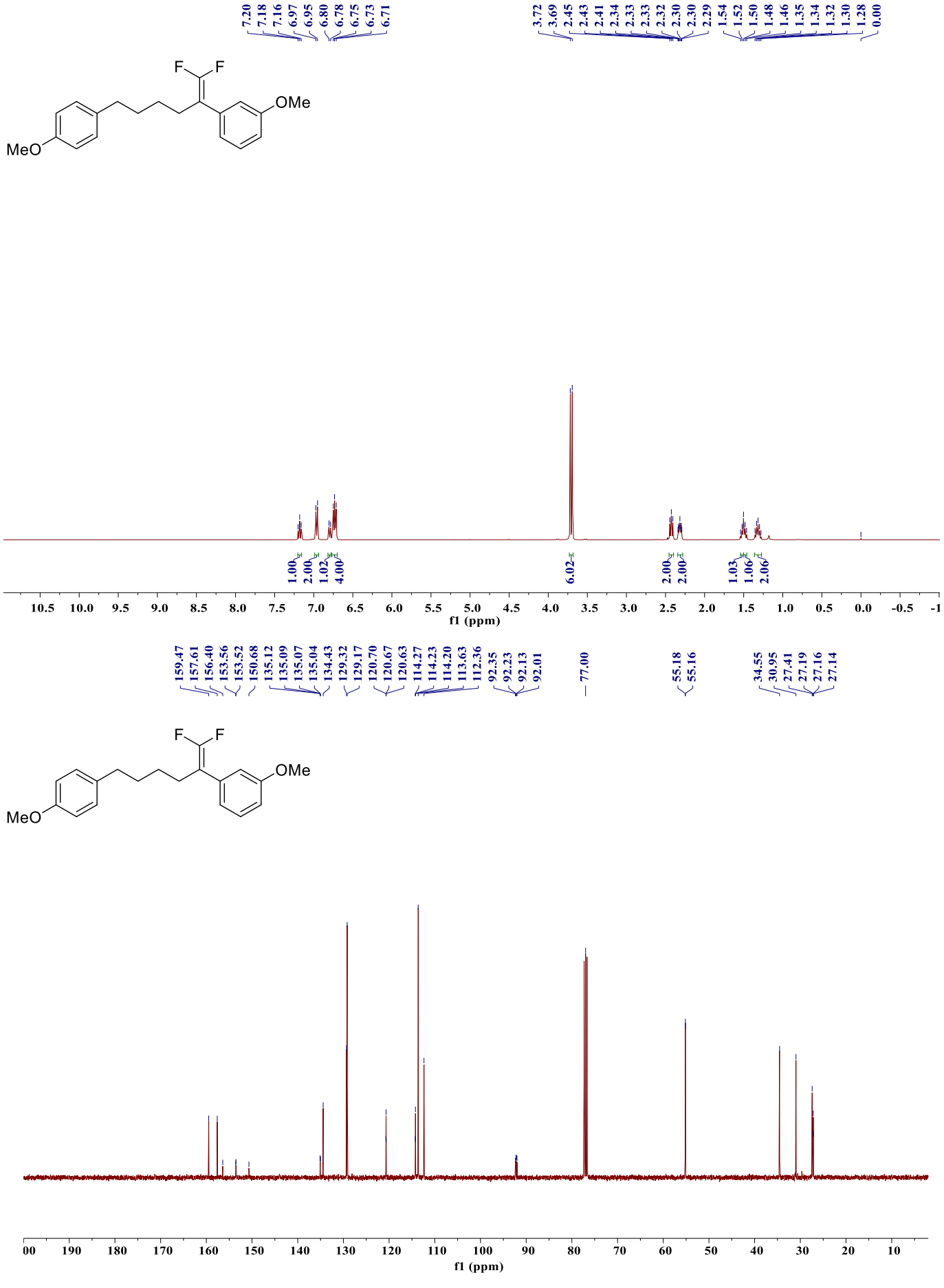
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 5ad

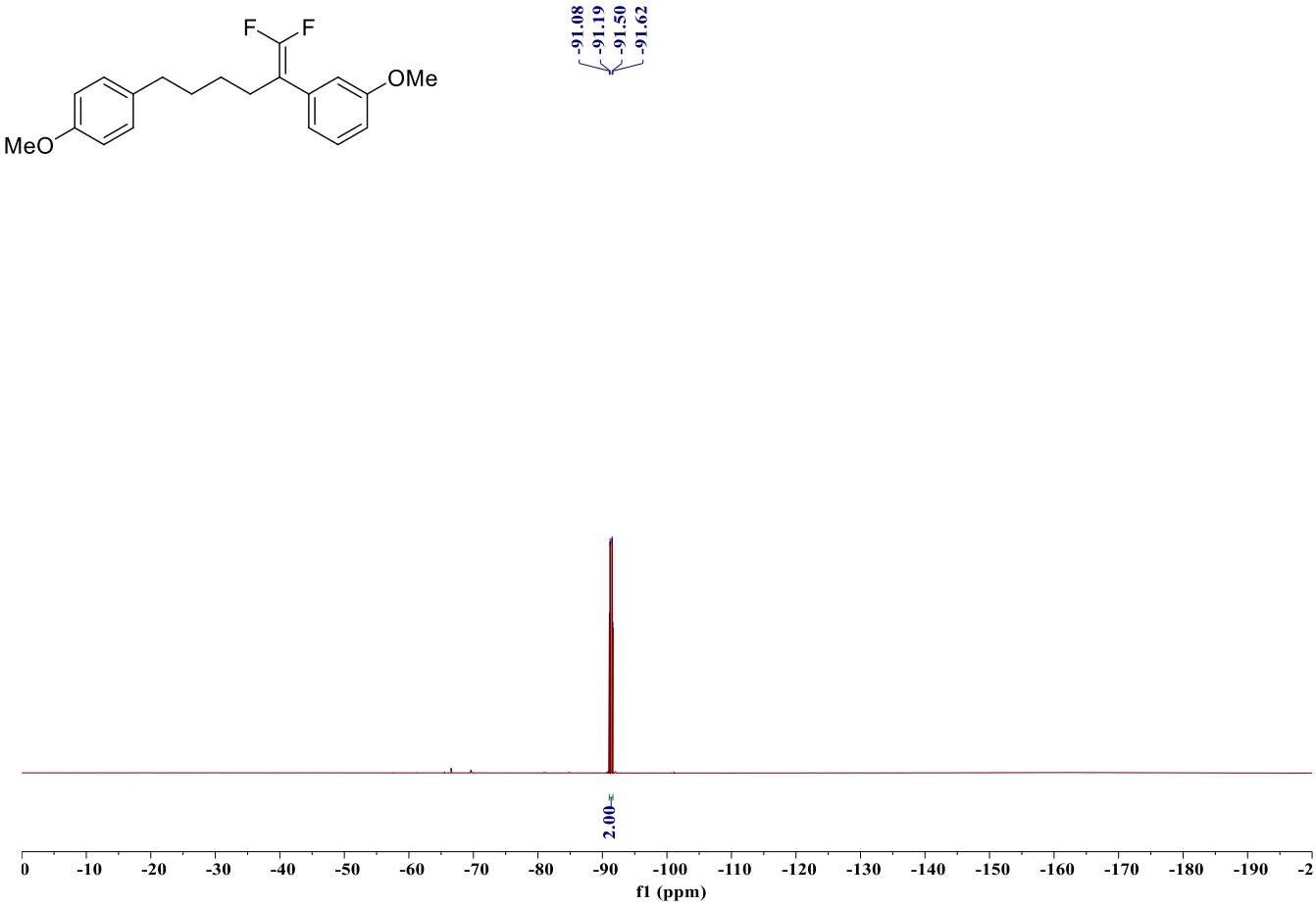




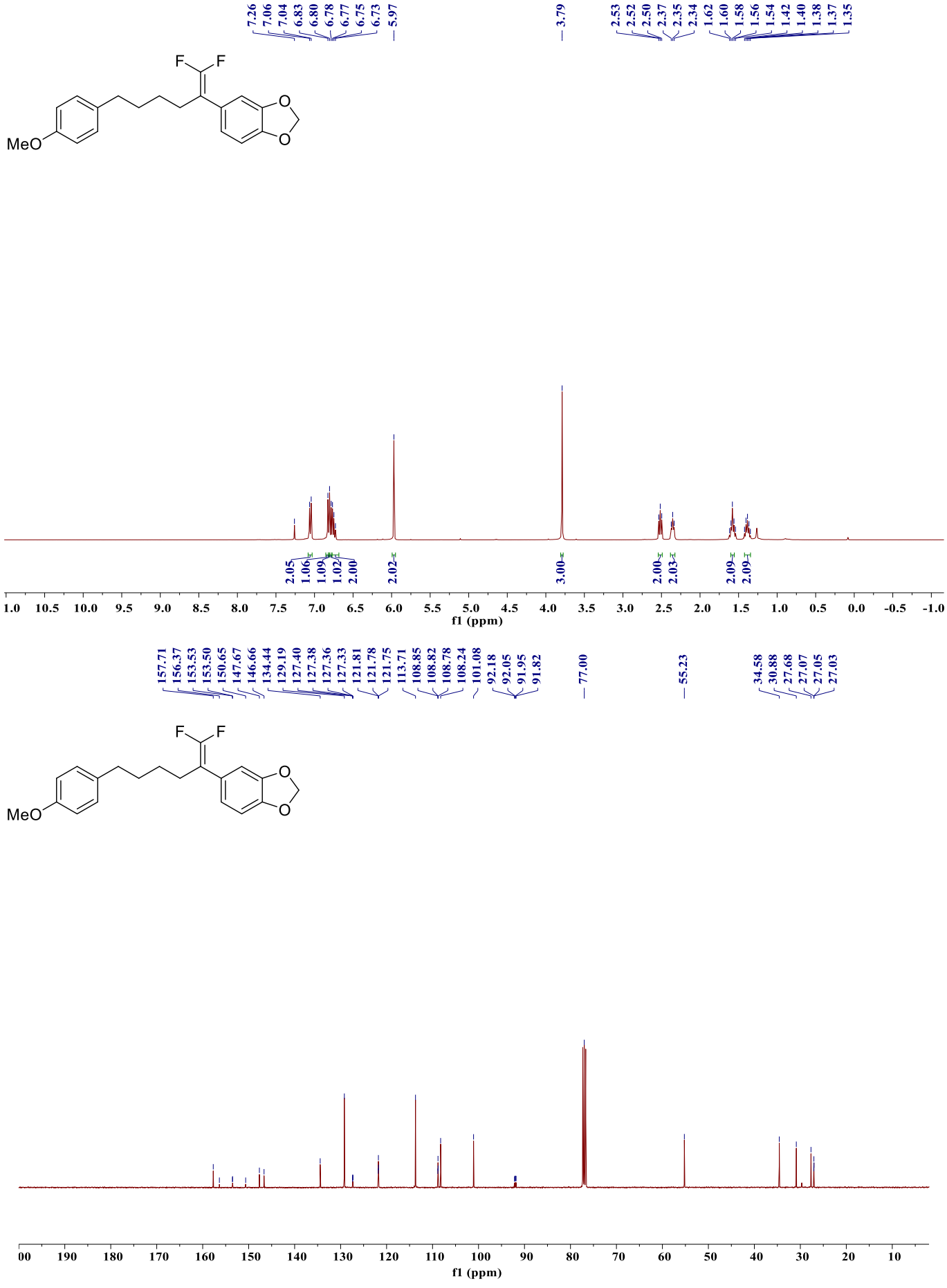

F
F
MeO
OMe
-92.75
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

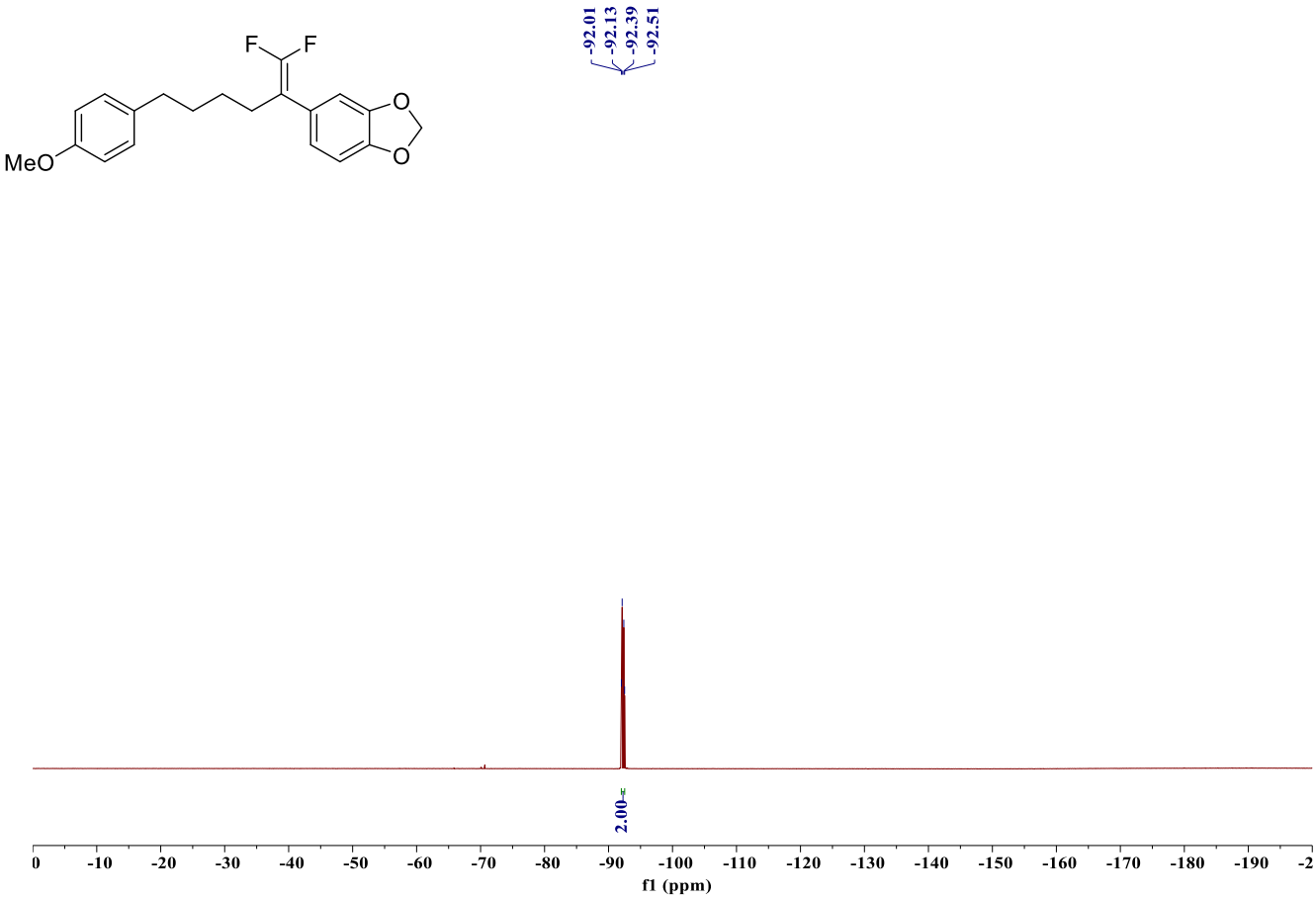
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 5ae



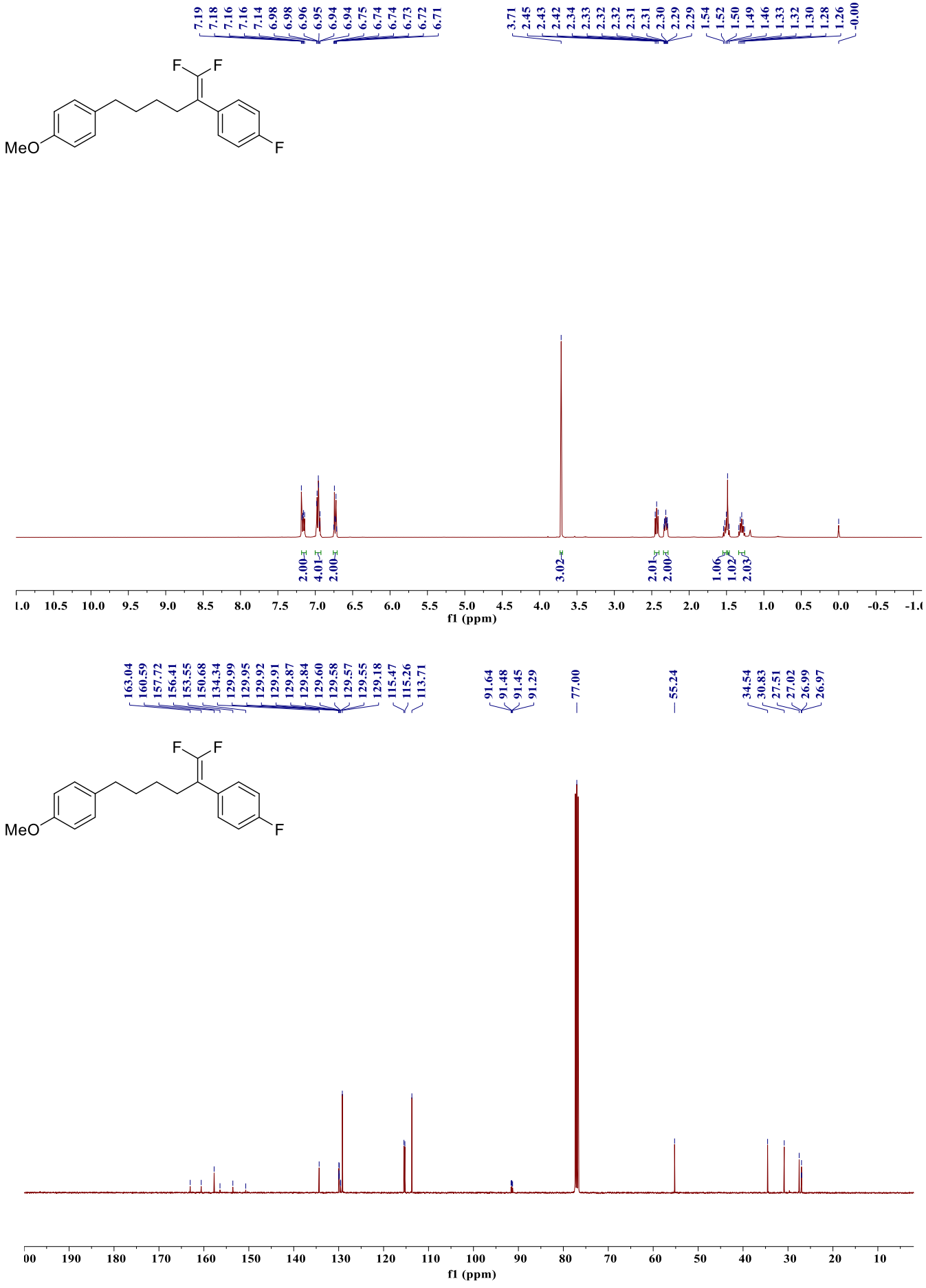

F
F
OMe
MeO
-91.08
-91.19
-91.50
-91.62
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

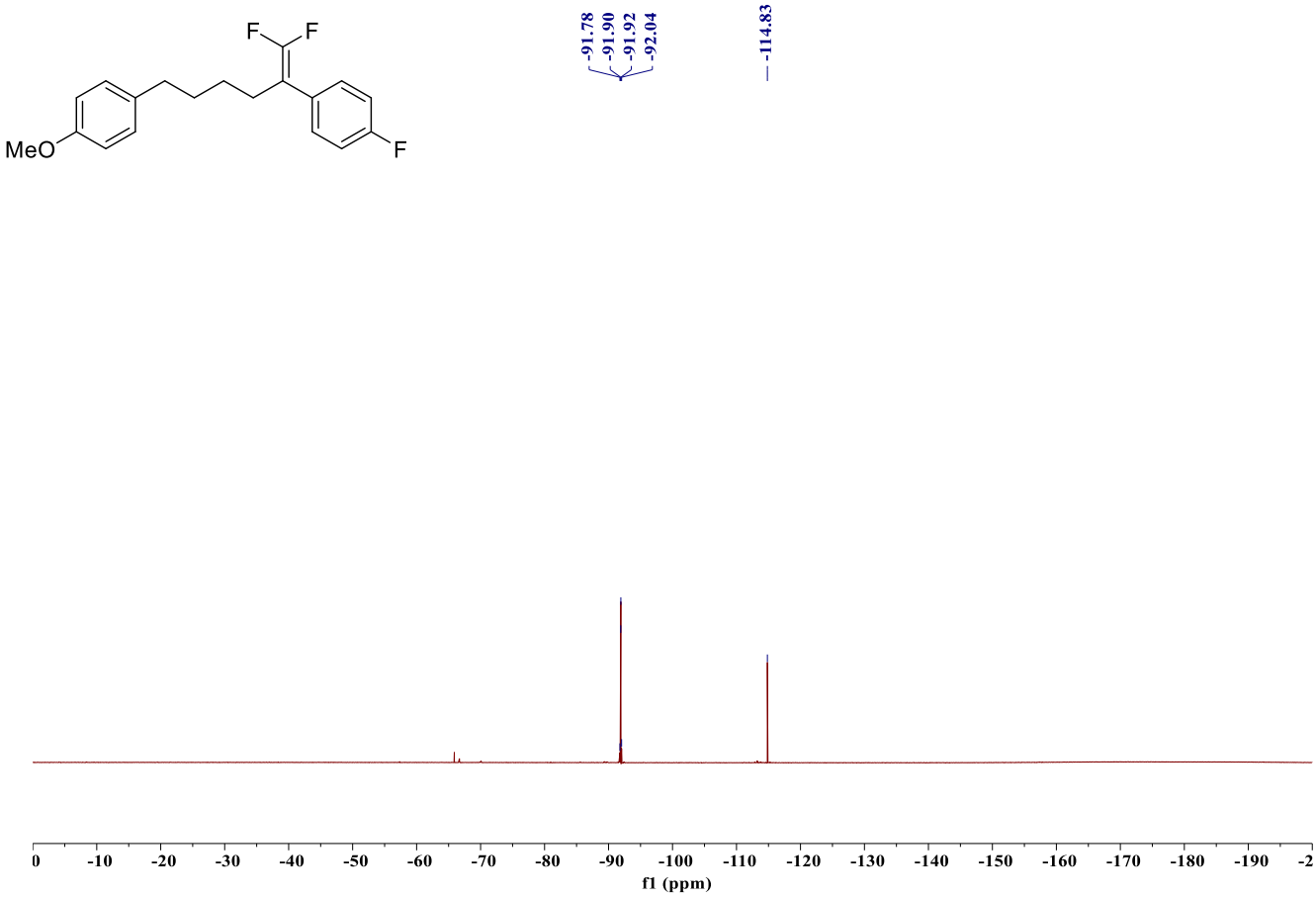
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 5af



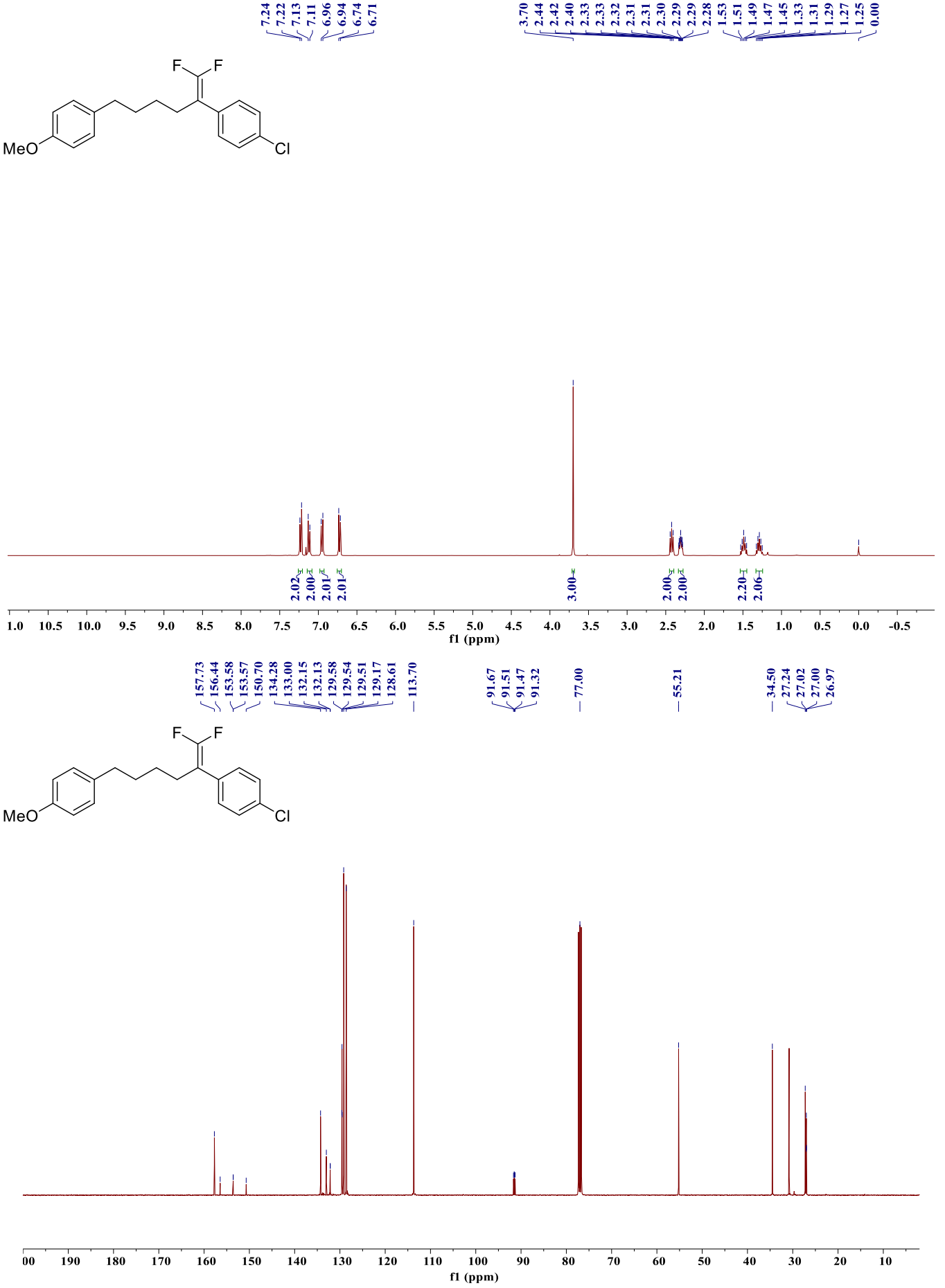

F
F
O
O
MeO
-92.01
-92.13
-92.39
-92.51
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

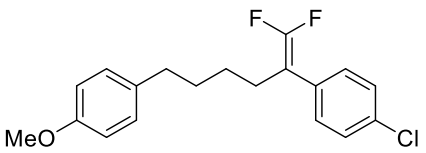
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 5ag



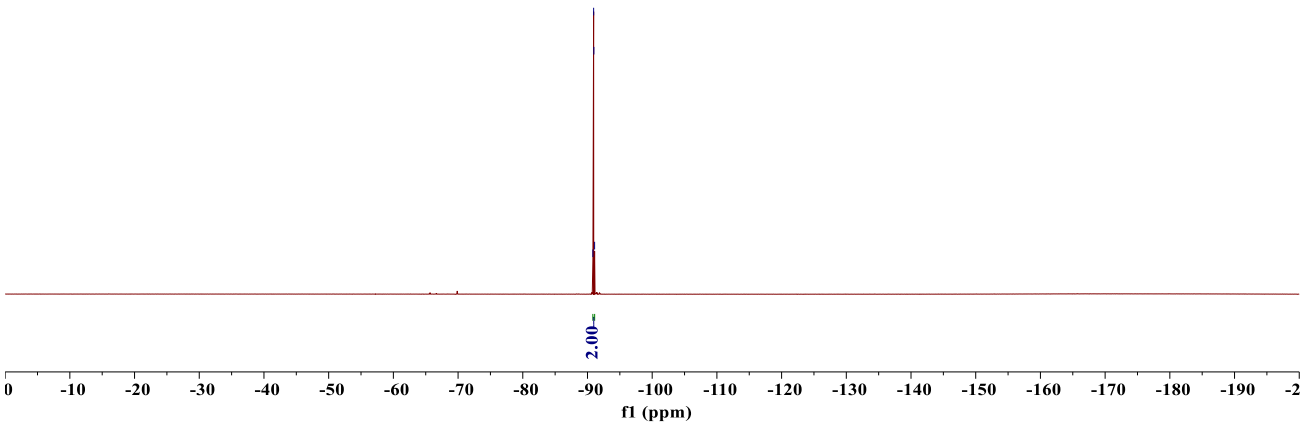

F
F
MeO
F
-91.78
-91.90
-91.92
-92.04
-114.83
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 5ah

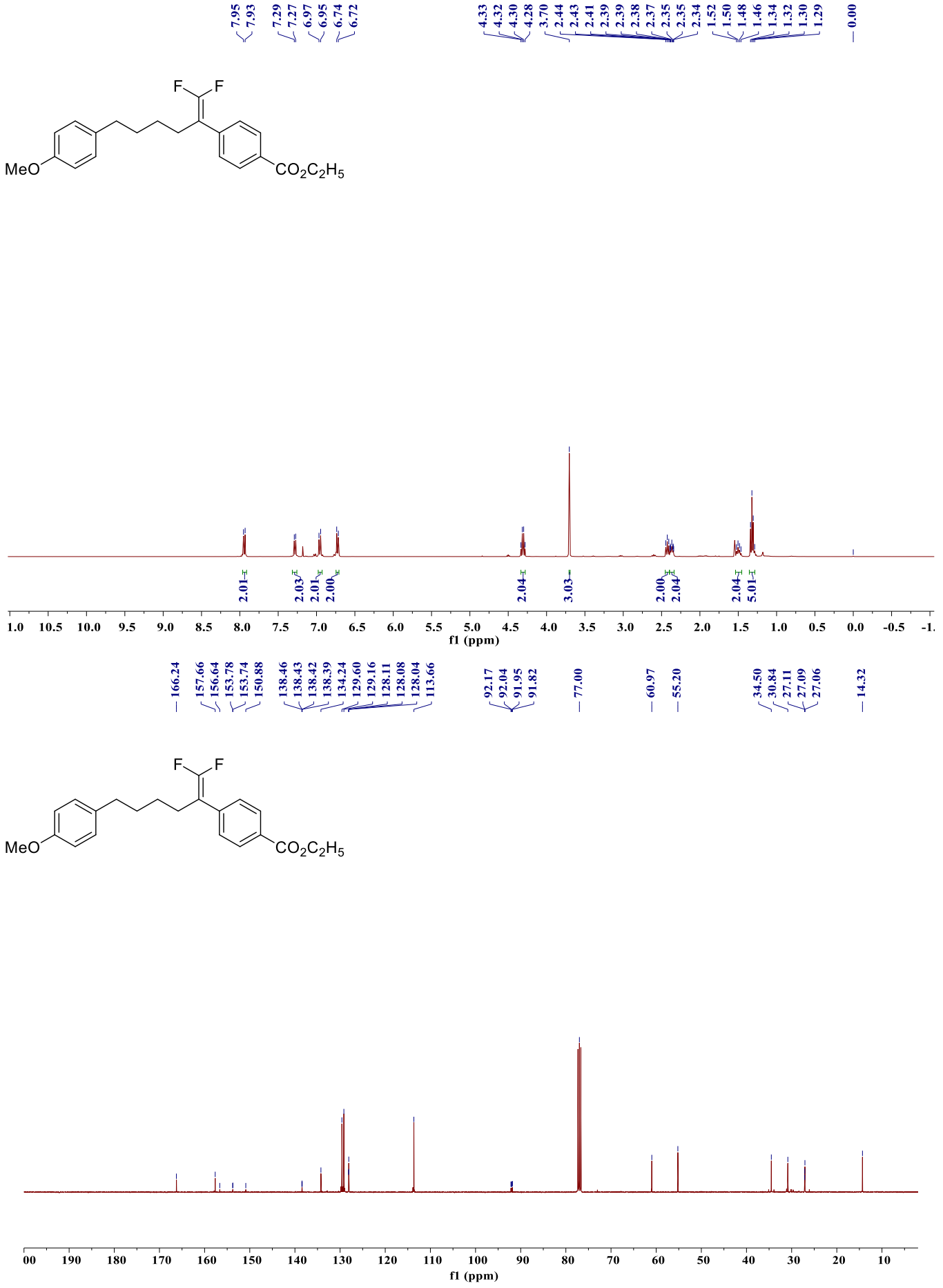


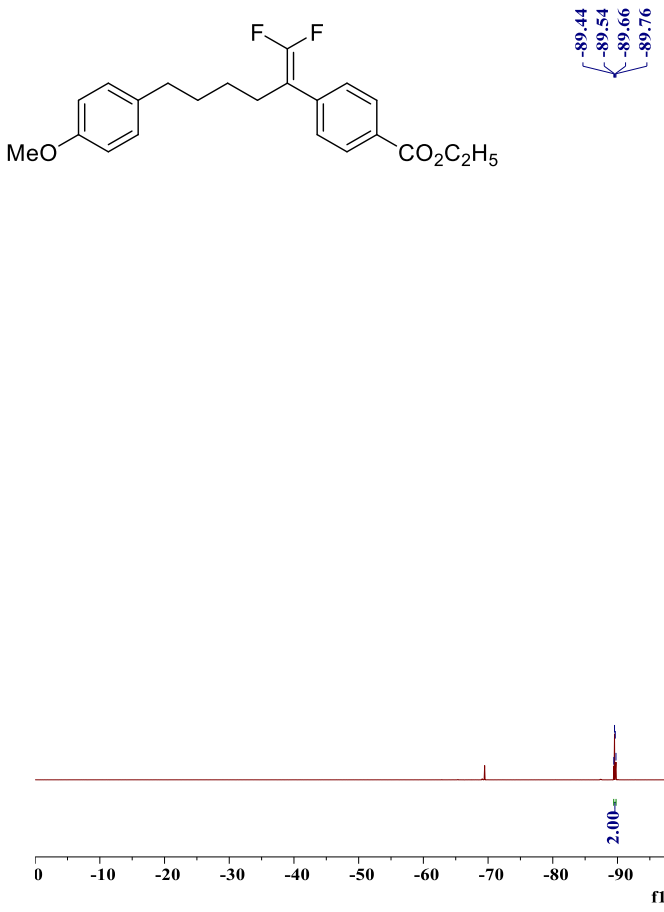

F
F
MeO
Cl


-90.84
-90.95
-90.99
-91.10

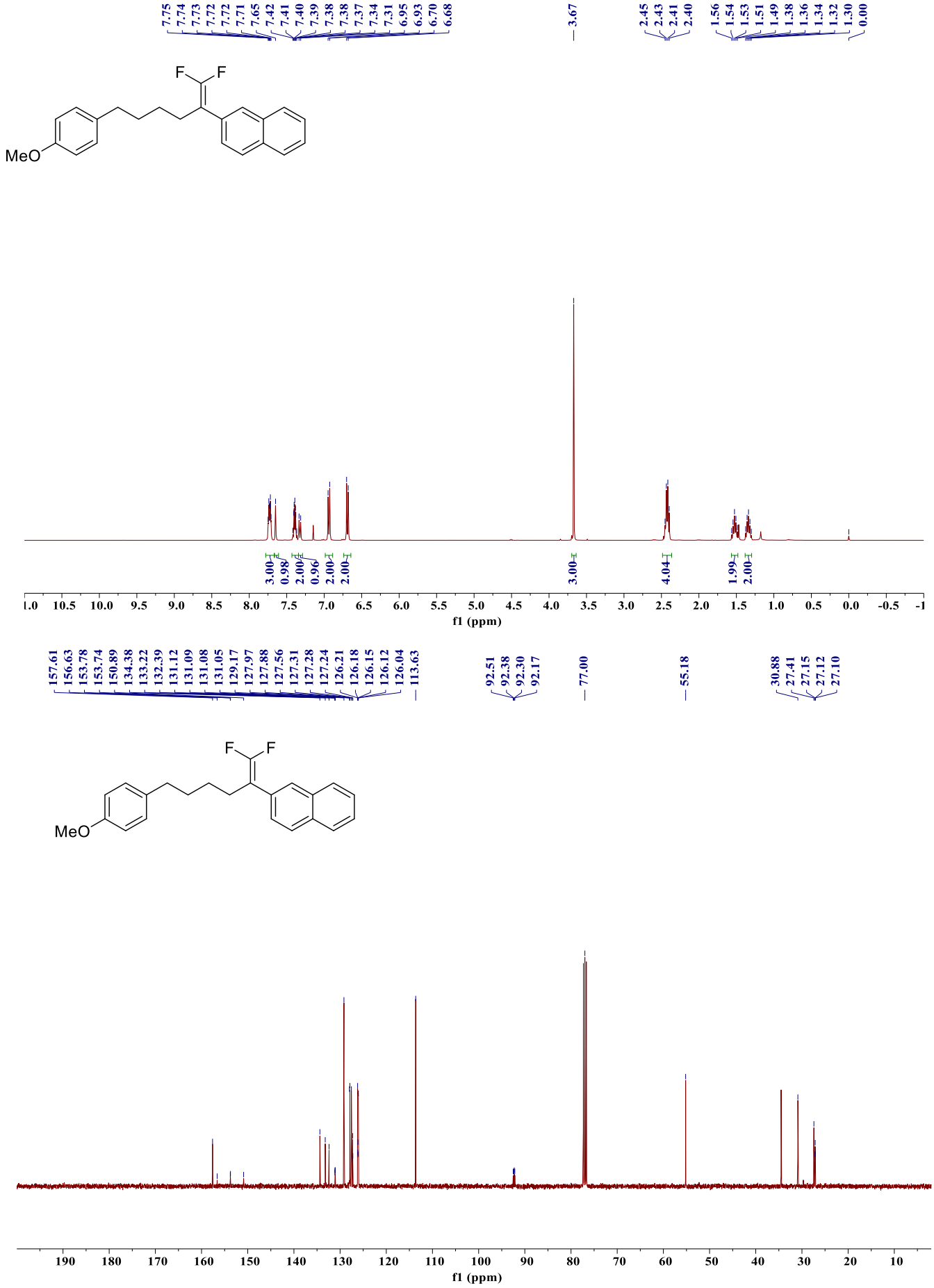

2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

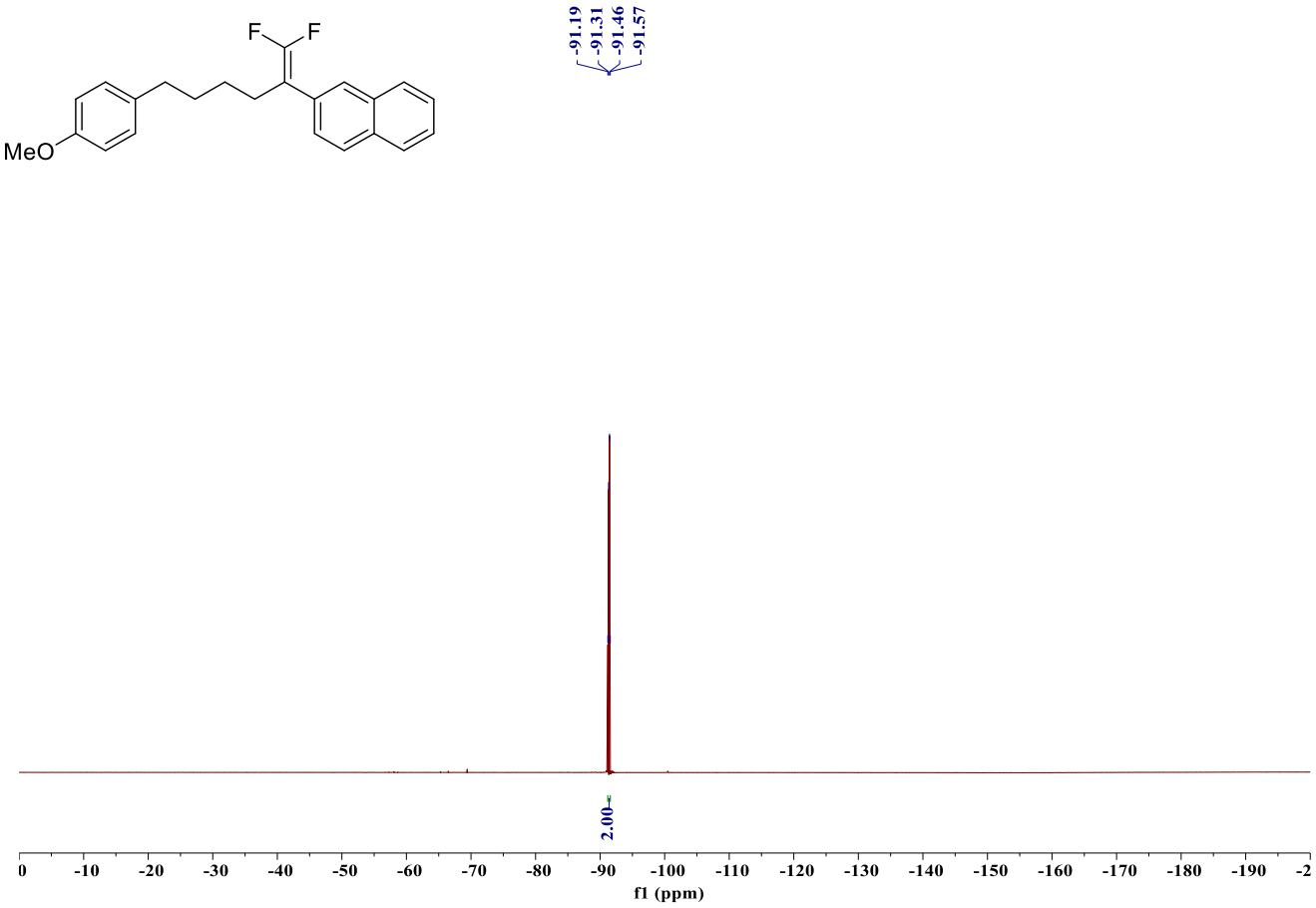
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 5ai



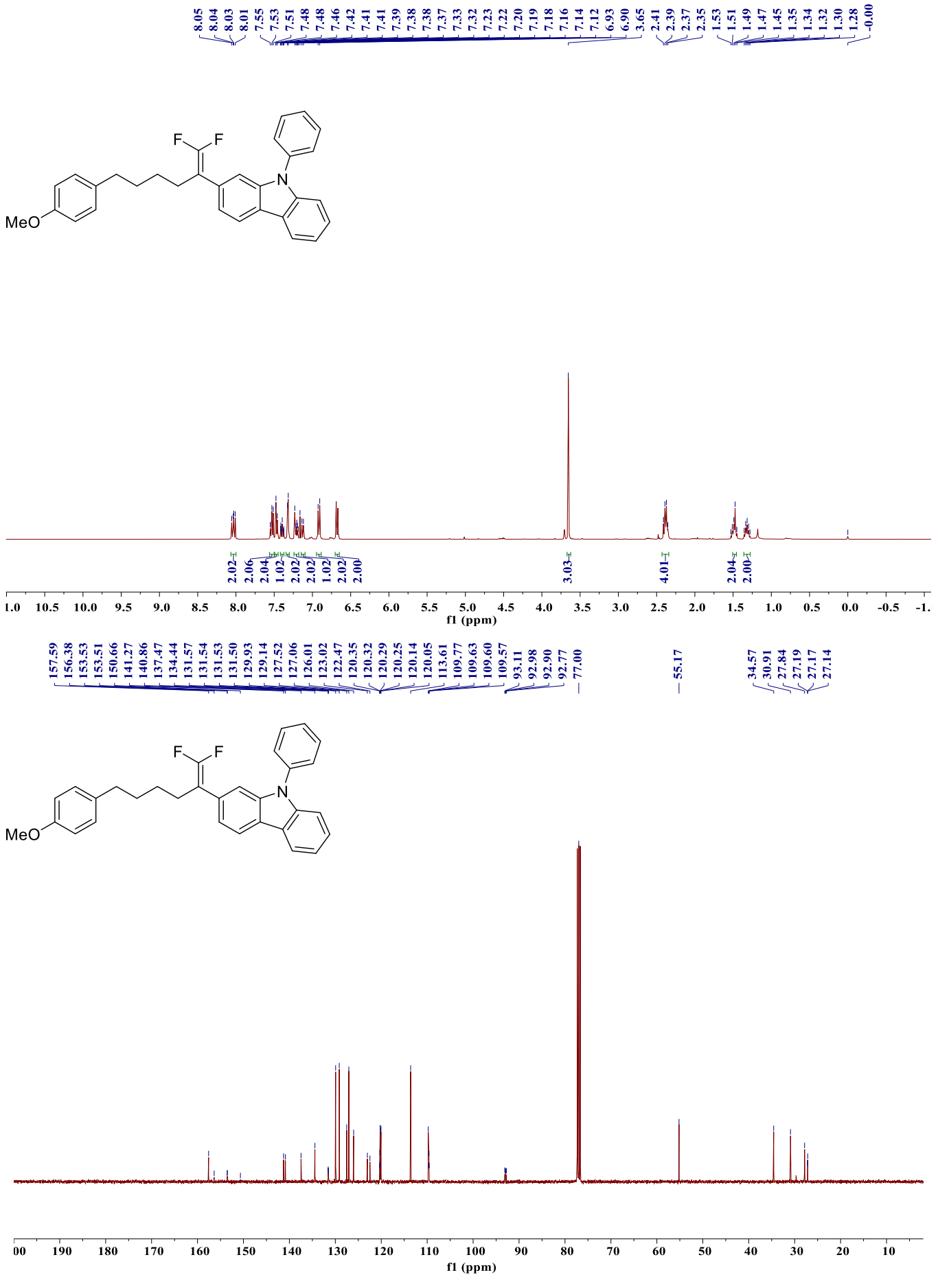

F
F
MeO
$CO_2C_2H_5$
-89.44
-89.54
-89.66
-89.76
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

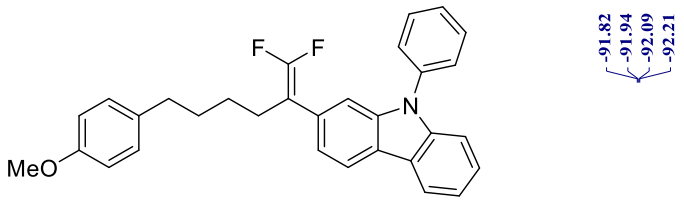
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 5aj




F
F
MeO
-91.19
-91.31
-91.46
-91.57
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

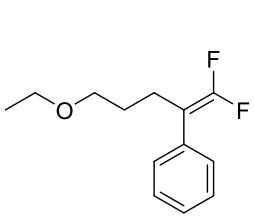
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 5ak

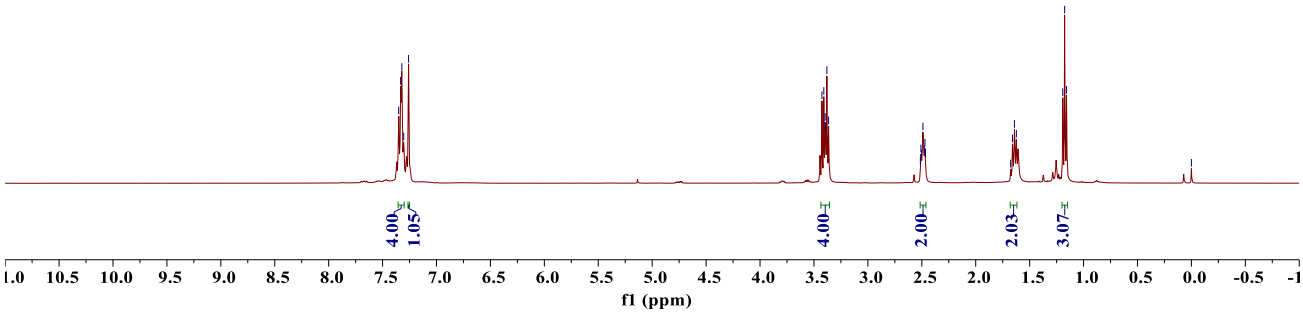


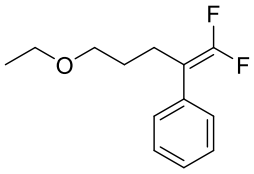

F
F
N
MeO

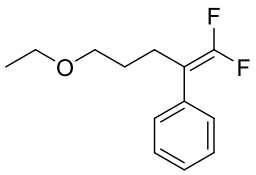
-91.82
-91.94
-92.09
-92.21
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3na



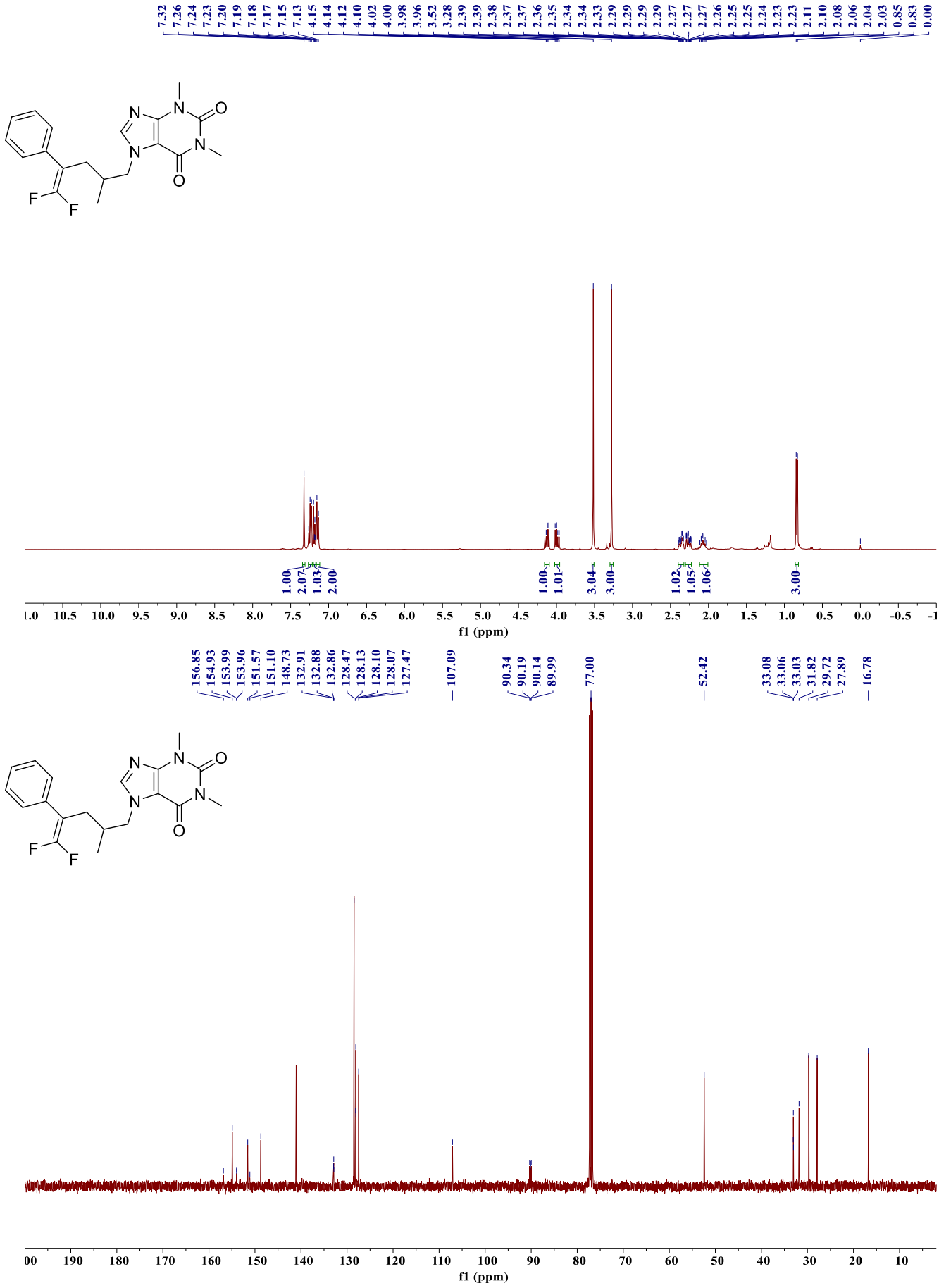


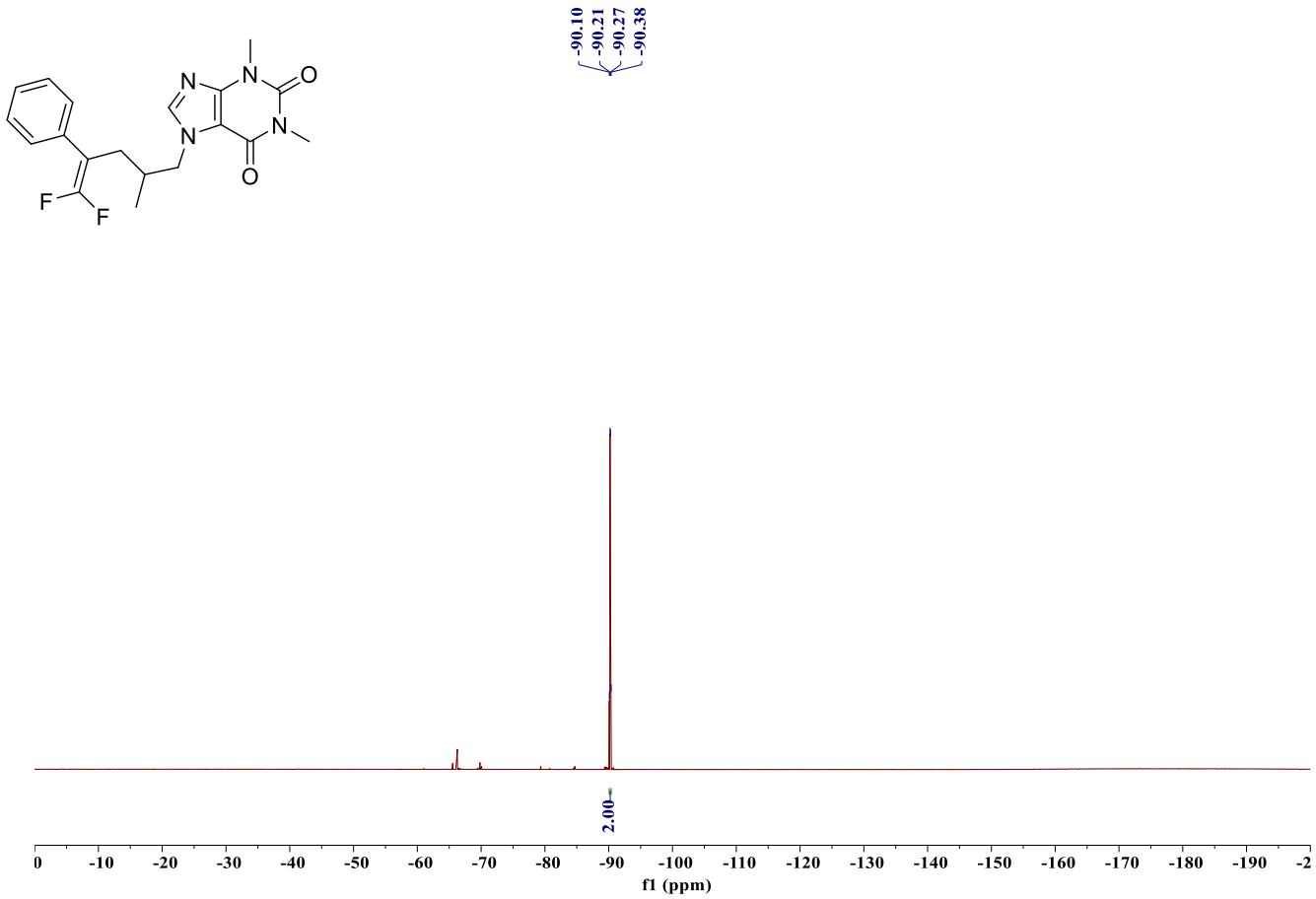



F
O
F

-93.11
-93.13
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 9




-90.10
-90.21
-90.27
-90.38
N
N
O
N
N
O
F
F
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)