Regioselective Difluoroallylation of Alkylidenemalonates with Trifluoromethyl Alkenes: Synthesis of *gem*-Difluoro-1,5-Dienes and Their [2 + 2] Photocycloaddition

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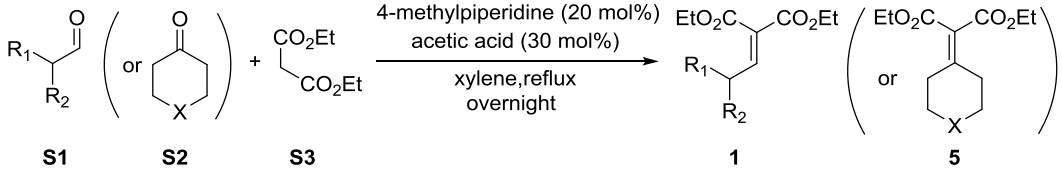
1. General information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.5 mm) or Sorbent Silica Gel 60 F254 plates. For column chromatography, 200-300 mesh silica gel (Qingdao, China) were used. Fluorescence spectra were collected on Hitachi F-4500 Fluorescence Spectrophotometer. High-resolution mass spectra (HRMS) were performed on ThermoFisher Q Exactive using orbitrap as the mass analyzer with an electrospray ionization (ESI) source, an electron impact ionization (EI) source, or an atmospheric pressure chemical ionization (APCI) source. Unless otherwise noted, ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were measured recorded on Brucker ARX 400 MHz or 600 MHz spectrometer at ambient temperature. Chemical shifts for ^{1}H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: δ 7.26 ppm). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: δ 77.16 ppm). Data are reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration.

2. Experimental procedures

2.1 Synthesis of alkylidene malonates.

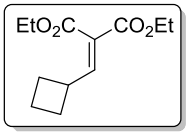


Alkylidene malonates **1** and **5** were prepared using Knovenagel condensation conditions according to literature methods.[1]

Alkyl aldehyde **S1** or cyclic ketone **S2** (22 mmol, 1.1 equiv), diethyl malonate **S3** (3.2 g, 20 mmol, 1.0 equiv), 4-methylpiperidine (396 mg, 4.0 mmol), glacial acetic acid (360 mg, 6.0 mmol), and 50 mL of xylene were added into a round bottom flask equip with a magnetic stir bar, a Dean-Stark trap and a reflux condenser. The resultant solution was refluxed for overnight. Then the reaction mixture was cooled down to room temperature, concentrated under reduced pressure and purified by flash chromatography (petroleum ether: ethyl acetate = 20:1) on silica gel to give alkylidene malonate product **1** or **5**.

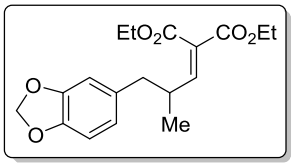
Diethyl 2-(2-methylpropylidene)malonate (**1a**),[2] diethyl 2-(cyclopentylmethylene) malonate (**1c**),[3] diethyl 2-(cyclohexylmethylene)malonate (**1d**),[1] diethyl 2-cyclopentylidenemalonate (**5a**)[4] and diethyl 2-(tetrahydro-4H-pyran-4-ylidene) malonate (**5b**)[4] are known compounds.

Diethyl 2-(cyclobutylmethylene)malonate (1b)



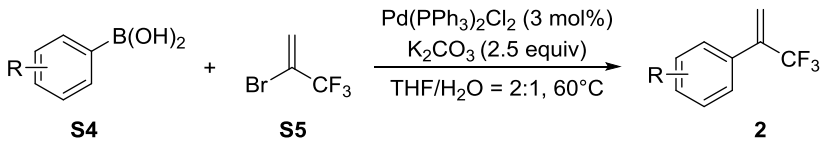
R_f: 0.5 (petroleum ether/ethyl acetate 20:1). Colorless liquid (Yield: 38%, 1.7 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 9.4 Hz, 1H), 4.33 – 4.23 (m, 4H), 3.40 – 3.29 (m, 1H), 2.28 – 2.21 (m, 2H), 2.04 – 1.97 (m, 3H), 1.96 – 1.91 (m, 1H), 1.36 –1.29 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ165.5, 164.2, 153.0, 126.4, 61.2 (d, *J* = 4.5 Hz)., 35.4, 28.5, 19.0, 14.1, 14.1. HRMS (ESI) calcd for $C_{12}H_{19}O_4$ $[M+H]^+$ 227.1278, found 227.1279.

Diethyl 2-(3-(benzo[d][1,3]dioxol-5-yl)-2-methylpropylidene)malonate (1e)



R_f: 0.3 (petroleum ether/ethyl acetate 20:1). Colorless liquid (Yield: 45%, 4.4 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (d, *J* = 10.6 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 6.63 (d, *J* = 1.6 Hz, 1H), 6.58 (dd, *J* = 7.9 Hz, 1.7 Hz, 1H), 5.93 (s, 2H), 4.30 – 4.21 (m, 4H), 2.88 – 2.83 (m, 1H), 2.69 (dd, *J* = 13.6 Hz, 6.5 Hz, 1H), 2.53 (dd, *J* = 13.6, 7.6 Hz, 1H), 1.33 – 1.29 (m, 6H), 1.06 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 164.0, 153.3, 147.6, 146.0, 132.7, 127.6, 122.1, 109.4, 108.1, 100.8, 61.3 (d, *J* = 8.2 Hz), 42.1, 36.5, 19.1, 14.1 (d, *J* = 3.9 Hz). HRMS (ESI) calcd for $C_{18}H_{23}O_6$ $[M+H]^+$ 335.1489, found 335.1491.

2.2 Synthesis of α-trifluoromethyl styrenes.



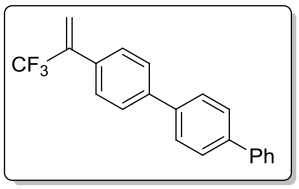
S4 **S5** **2**

α-Trifluoromethyl styrenes were prepared by the Pd-catalyzed Suzuki cross coupling of aryl boronic acids and 2-bromo-3,3,3-trifluoropropene (BTP) according to our previous reported method.[5,6]

To a Schlenk tube equipped a magnetic stir bar, aryl boronic acid (2.5 mmol, 1.0 equiv), K_2CO_3 (7.5 mmol, 0.85g, 3.0 equiv) and $Pd(PPh_3)_2Cl_2$ (36.6 mg, 3 mol%) were added. The vessel was evacuated and filled with argon (three times). THF (15 mL), H_2O (30 mL), and then 2-bromo-3,3,3-trifluoropropene (5 mmol, 0.52 mL), were injected via syringe. The reaction mixture was stirred at 60 ℃ overnight under an argon atmosphere. After cooling to room temperature, the solution was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired corresponding α-trifluoromethyl styrene **2**.

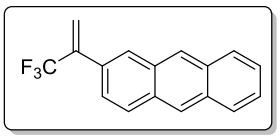
Except for **2k** and **2m**, other α-trifluoromethyl styrenes are known compounds.[5,6]

4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1',4',1''-terphenyl (2k)



R_f: 0.8 (petroleum ether). Light yellow solid (Yield: 67%, 543.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 8H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.3 Hz, 1H), 5.99 (d, *J* = 1.5 Hz, 1H), 5.84 (d, *J* = 1.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 140.7 (d, *J* = 2.2 Hz), 139.3, 132.7, 129.0, 127.9, 127.8, 127.6, 127.6, 127.3, 127.2, 126.2(d, *J* = 262.6 Hz), 120.4 (d, *J* = 5.8 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.59. HRMS (APCI) calcd for $C_{21}H_{15}F_3$ $[M]^+$ 324.1120, found 324.1113.

2-(3,3,3-trifluoroprop-1-en-2-yl)anthracene (2m)



R_f: 0.8 (petroleum ether). Light yellow solid (Yield: 55%, 374.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 17.0 Hz, 2H), 8.14 (s, 1H), 8.04 (d, *J* = 9.3 Hz, 3H), 7.57 (dd, *J* = 8.9 Hz, 1.8 Hz, 1H), 7.54 – 7.49 (m, 2H), 6.11 (d, *J* = 1.5 Hz, 1H), 6.00 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 138.7, 132.3, 132.1, 131.0, 130.1, 128.7, 128.3, 128.2, 127.3, 127.2, 126.1, 125.9, 125.8, 124.1, 123.5 (d, *J* = 274.1 Hz), 120.5 (d, *J* = 5.8 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.13. HRMS (APCI) calcd for $C_{17}H_{12}F_3$ $[M+H]^+$ 273.0886, found 273.0882.

2.3 General procedure for the base-mediated S_N2' reaction of alkylidenemalonate 1 and α-trifluoromethyl styrene 2.

To a 10 mL test tube equipped with a magnetic stir bar was charged with alkylidenemalonate **1** (0.20 mmol, 1.0 equiv), α-trifluoromethyl styrene **2** (0.20 mmol, 1.0 equiv), Cs_2CO_3 (0.50 mmol, 163.0 mg, 2.5 equiv) and 1.5 mL of DMSO. The vessel was evacuated and filled with nitrogen. The solution was stirred at 60 ℃ for 4 h. After the completion of the reaction, the mixture was filtered through a short path

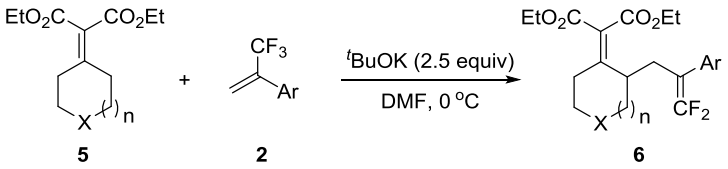
of silica gel eluting with ethyl acetate. The volatile compounds were removed *in vacuo* and the residue was purified by column chromatography on silica gel.

2.4 General procedure for the [2 + 2] photocycloaddition of 3.

3 **4**

To a 10 mL test tube equipped with a magnetic stir bar was charged with **3** (0.20 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (1 mol %, 1.3 mg) and 1.5 mL of DMSO. The vessel was evacuated and filled with nitrogen. The solution was stirred at room temperature irradiating by a 8 W blue LED for 24 h. After the completion of the reaction, the mixture was filtered through a short path of silica gel eluting with ethyl acetate. The volatile compounds were removed *in vacuo* and the residue was purified by column chromatography on silica gel.

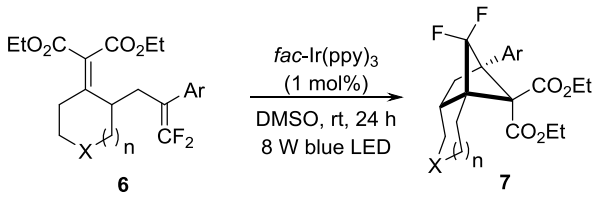
2.5 General procedure for the base-mediated S_N2' reaction of alkylidenemalonate 5 and α-trifluoromethyl styrene 2.



5 **2** **6**

To a 10 mL test tube equipped with a magnetic stir bar was charged with alkylidenemalonate **5** (0.20 mmol, 1.0 equiv), α-trifluoromethyl olefin **2** (0.20 mmol, 1.0 equiv), and 1.5 mL DMF. After stirring at 0 ℃ for 5 minutes, ^{t}BuOK (0.50 mmol, 56.1 mg, 2.5 equiv) was slowly added (no less than 5 minutes). The resultant solution was stirred at 0 ℃ for 4 h. Then, the reaction mixture was filtered through a short path of silica gel eluting with ethyl acetate. The volatile compounds were removed *in vacuo* and the residue was purified by column chromatography on silica gel.

2.6 General procedure for the [2 + 2] photocycloaddition of 6.



To a 10 mL test tube equipped with a magnetic stir bar was charged with **6** (0.20 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (1 mol %, 1.3 mg) and 1.5 mL of DMSO. The vessel was evacuated and filled with nitrogen. The solution was stirred at room temperature irradiating by a 8 W blue LED for 24 h. After the completion of the reaction, the mixture was filtered through a short path of silica gel eluting with ethyl acetate. The volatile compounds were removed *in vacuo* and the residue was purified by column chromatography on silica gel.

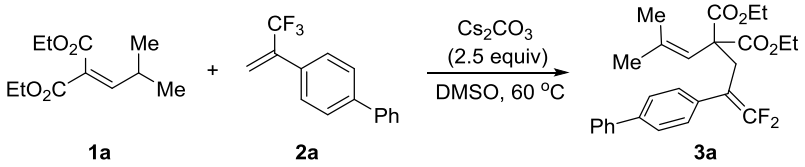
2.7 Synthesis of 4a on gram scale via two steps in one-pot.

1a (5 mmol) **2a** (5 mmol) **4a**, 79% (1.742 g)

To a 25 mL round equipped with a magnetic stir bar was charged with alkylidenemalonate **1a** (5 mmol, 1.07 g, 1.0 equiv), α-trifluoromethyl styrene **2a** (5 mmol, 1.24 g, 1.0 equiv), Cs_2CO_3 (7.5 mmol, 2.44 g, 2.5 equiv) and 15 mL of DMSO. The vessel was evacuated and filled with nitrogen. The solution was stirred at 60 ℃ for 4 h. After the completion of the reaction, *fac*-Ir(ppy)$_3$ (1 mol %, 32.5 mg) was added to the cooling mixture, which was irradiated by a 8 W blue LED for 72 h. The volatile compounds were removed *in vacuo* and the residue was purified by column chromatography on silica gel to give **4a** as a yellow liquid (79%, 1.742 g).

3. Optimization of reaction conditions

Table S1. Base-mediated S_N2' reaction of alkylidenemalonate **1a** and α-trifluoromethyl-(4-phenyl)styrene **2a**.[a]



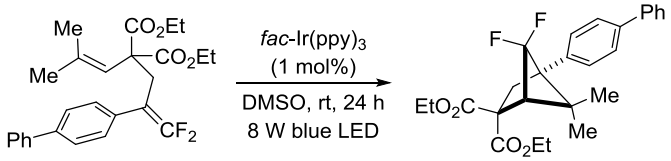
1a **2a** **3a**

Entry	Variation from the standard conditions	Yield (%)[b]
1	none	97 (95)[c]
2	At room temperature	90
3	At 80 ℃	82
4	^{t}BuOK as the base	15
5	NaH as the base	20
6	LiHMDS as the base	Trace
7	DMF as the solvent	88
8	MeCN as the solvent	28

[a] Standard conditions: alkylidenemalonate **1a** (0.2 mmol), α-CF_3-(4-phenyl)styrene **2a** (0.2 mmol), Cs_2CO_3 (0.5 mmol), DMSO (1.5 mL) at 60 ℃ for 24 h. [b] Yields were determined by ^{19}F-NMR using 4-bromobenzotrifluoride as the internal standard.
[c] Isolated yield in the parenthesis.

After the brief screen of the temperature, base, and solvent, we found that the best conditions for the S_N2' reaction of alkylidenemalonate **1a** and α-trifluoromethyl-(4-phenyl)styrene **2a** are the use of 2.5 equiv of Cs_2CO_3 as the base in the solvent of DMSO at 60 ℃ (Table S1, entry 1). The reaction also proceeds well at room temperature, albeit affording **3a** in a slightly diminished yield (Table S1, entry 2). Further increasing the reaction temperature to 80 ℃ decreased the yield of 3a to 82% (Table S1, entry 3). ^{t}BuOK, NaH and LiHMDS were less effective bases for the reaction (Table S1, entries 4-6). Product was obtained in 88% yield in DMF, while the use of MeCN as the solvent only led to the formation of **3a** in 28% yield (Table S1, entries 7 and 8).

Table S2. Visible light-promoted [2 +2] photocycloaddition of **3a**.[a]



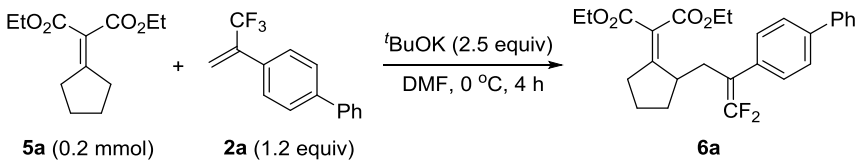
3a **4a**

Entry	Variation from the standard conditions	Yield (%)[b]
1	none	98 (96)[c]
2	4CzIPN (5 mol%) as the photocatalyst	91
3	$Ru(bpy)_3Cl_2$ as the photocatalyst	0
4	Eosin Y (5 mol%) as the photocatalyst	0
5	5 W blue LED	90
6	Without photocatalyst	0
7	In the dark	0

[a] Standard conditions: *gem*-difluoro-1,5-diene **3a** (0.2 mmol), *fac*-$Ir(ppy)_3$ (1 mol%), DMSO (1.5 mL) at room temperature for 24 h. [b] Yields were determined by ^{19}F-NMR using 4-bromobenzotrifluoride as the internal standard. [c] Isolated yield in the parenthesis.

fac-$Ir(ppy)_3$ is the best energy transfer photocatalyst to active *gem*-difluoro-1,5-diene **3a** (Table S2, entry 1). 4CzIPN was also efficient photocatalyst for such [2 + 2] photocycloaddition (Table S2, entry 2). However, $Ru(bpy)_3Cl_2$ and Eosin Y were ineffective for the reaction (Table S2, entries 3 and 4). When the reaction was irradiated by a 5 W blue LED, a slightly decreased yield was obtained (Table S2, entry 5). The control experiments suggested that both photocatalyst and light irradiation were essentially necessary for the reaction (Table S2, entries 6 and 7).

Table S3. Base-mediated S_N2' reaction of alkylidenemalonate **5a** and α-trifluoromethyl-(4-phenyl)styrene **2a**.[a]



5a (0.2 mmol) **2a** (1.2 equiv) **6a**

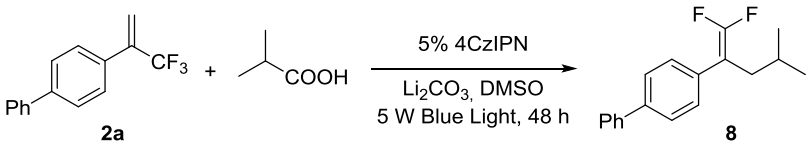
Entry	Variation from the standard conditions	Yield (%)[b]
1	none	98 (98)[c]
2	Cs_2CO_3 as the base	61
3	LiOH as the base	Trace
4	LiHMDS as the base	70
5	At room temperature	62
6	At 60 ℃	17
7	DMSO as the solvent	58
8	THF as the solvent	Trace

[a] Standard conditions: alkylidenemalonate **5a** (0.2 mmol), α-CF_3-(4-phenyl)styrene **2a** (0.2 mmol), ^{t}BuOK (0.5 mmol), DMF (1.5 mL) at 0 ℃ for 4 h. [b] Yields were determined by ^{19}F-NMR using 4-bromobenzotrifluoride as the internal standard. [c] Isolated yield in the parenthesis.

For the S_N2' reaction of **2a** with alkylidenemalonate **5a** deriving from cyclopentanone and diethyl malonate, γ-difluoroallylation product **6a** was obtained with excellent regioselectivity using ^{t}BuOK (2.5 equiv) as the base and DMF as the solvent at 0 ℃ (Table S3, entry 1). In this case, the use of Cs_2CO_3 as the base only provided **6a** in 61% yield (Table S3, entry 2). Other bases, such as LiOH and LiHMDS were also examined; but they were less effective than ^{t}BuOK (Table S3, entries 3 and 4). Higher reaction temperatures also decreased the yield of **6a** (Table S3, entries 5 and 6). Replacing the solvent DMF by DMSO afforded **6a** in 58% yield, while THF was unfavorable solvent for the reaction (Table S3, entries 7 and 8).

4. Mechanistic studies

4.1 Synthesis of *gem*-difluoroalkene 8

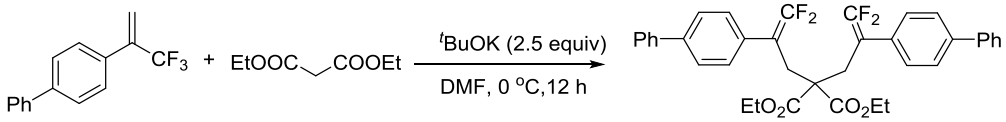


To a 10 mL test tube equipped with a magnetic stir bar was charged with α-trifluoromethyl-(4-phenyl)styrene **2a** (0.5 mmol, 124.1 mg, 1.0 equiv), isobutyric acid (1.0 mmol, 88.1 mg, 2.0 equiv), 4CzIPN (5 mol %, 19.7 mg), Li_2CO_3 (1.0 mmol, 73.9 mg, 2.0 equiv) and 2.5 mL of DMSO. The vessel was evacuated and filled with nitrogen. The solution was stirred at room temperature irradiating by 5 W blue LED for 48 h. After the reaction is completed, the solution was washed with H_2O, and the organic layer was extracted with ethyl acetate, dry with anhydrous Na_2SO_4. Then the volatile compounds were removed under vacuum, and the residue was purified through silica gel column chromatography using petroleum ether as elute to give *gem*-difluoroalkene **8** (91%, 123.9 mg) as a colorless liquid.

4.2 Intermolecular [2 + 2] photocycloaddition of 8 with cyclopentene

Placed the *gem*-difluoroalkene **8** (0.20 mmol, 54.5 mg, 1.0 equiv) synthesized by the above method in another 10 mL reaction tube, sequentially added *fac*-Ir(ppy)$_3$ (1 mol %, 1.3 mg) and 1.5 mL of DMSO. The vessel was evacuated and filled with nitrogen. Cyclopentene (4.00 mmol, 272.5 mg, 20 equiv) was added via a syringe. The solution was stirred at room temperature under the irradiation of a 8 W blue LED for 24 h. After the completion of the reaction, the mixture was filtered through a short path of silica gel eluting with ethyl acetate. The volatile compounds were removed *in vacuo* and the residue was purified by column chromatography on silica gel to give the [2 + 2] cycloaddition product **9** in the yield of 25% (17 mg).

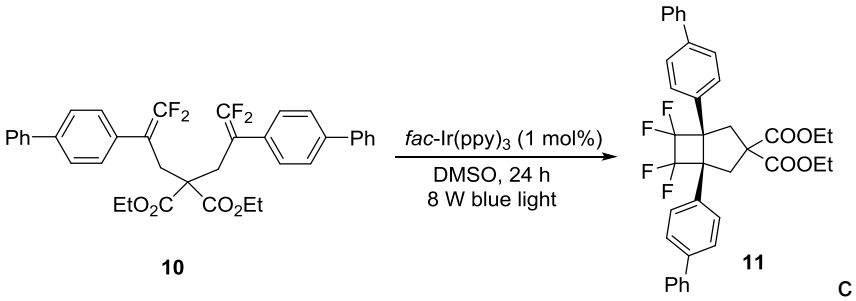
4.3 Synthesis of dual *gem*-difluoroallylated malonate 10.



2a **10**

To a 50 mL round bottomed flask equipped with a magnetic stirrer, α-trifluoromethyl-(4-phenyl)styrene **2a** (1.0 mmol, 248.2 mg, 2.0 equiv), diethyl malonate (0.50 mmol, 80.1 mg, 1.0 equiv) and 5.0 mL of DMF were added. Subsequently, ^{t}BuOK (1.25 mmol, 140.3 mg, 2.5 equiv) was slowly added to the reaction flask at 0 ℃. After the reaction was stirred at 0 ℃ for 12 h, the solution was washed with H_2O, and the organic layer was extracted with ethyl acetate, dry with anhydrous Na_2SO_4. Then the volatile compounds were removed under vacuum, and the residue was purified through silica gel column chromatography using petroleum ether/ethyl acetate (10:1) as elute to give product **11** in 88% yield.

4.4 Intramolecular [2 + 2] photocycloaddition of 10.



10 **11**

C

To a 10 mL test tube equipped with a magnetic stir bar was charged with **10** (0.20 mmol, 123.2 mg), *fac*-Ir(ppy)$_3$ (1 mol %, 1.3 mg) and 1.5 mL of DMSO. The vessel was evacuated and filled with nitrogen. The solution was stirred at room temperature irradiating by 8 W blue LED for 24 h. After the completion of the reaction, the mixture was filtered through a short path of silica gel eluting with ethyl acetate. The volatile compounds were removed *in vacuo* and the residue was purified by column chromatography on silica gel to give product **11** in 81% yield (99.8 mg).

4.5 UV-Vis absorption spectra

The energy transfer between the excited photocatalyst *fac*-Ir(ppy)$_3^*$ and **3a** was supported by the UV-Vis spectrum of **3a**, which only presents an absorbance peak around 300 nm. Therefore, the direct photo-activation of **3a** by visible light irradiation is less likely.

The spectra was recorded in a 1 cm Hellma Quartz cuvette with a cap provided with a Teflon septum using EtOAc as the solvent (concentration: 0.01 M).

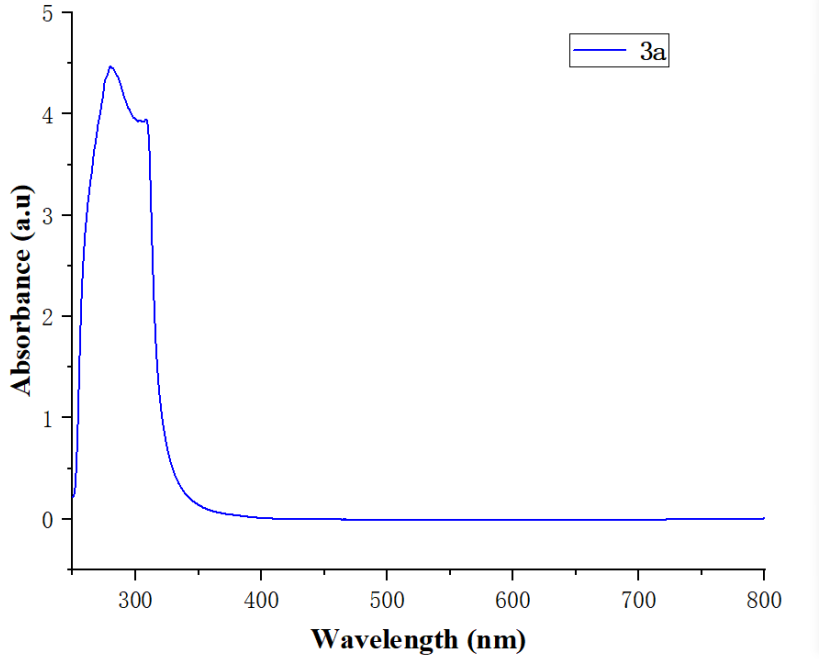


Figure S1. UV-Vis spectrum of **3a**.

4.6 Emission Quenching Experiments (Stern-Volmer Studies)

Fluorescence quenching experiments were recorded on a Fluorescence Spectrophotometer F4500. In each experiment, a solution of 1.0×10^{-4} M *fac*-Ir(ppy)$_3$ in DMSO was mixed with a DMSO solution of a quencher of various concentration in a screw-top 1.0 cm quartz cuvette. After degassing by sparging with argon for ten minutes, the resulting solution was irradiated at 465 nm, and fluorescence was measured at 550 nm. I_0 and I represent the intensities of the emission in the absence and presence of the quencher at 465 nm.

It was found that the excited photocatalyst *fac*-Ir(ppy)$_3$* could be quenched by **3a**,

according to the Stern–Volmer luminescence quenching studies (Figure S2).

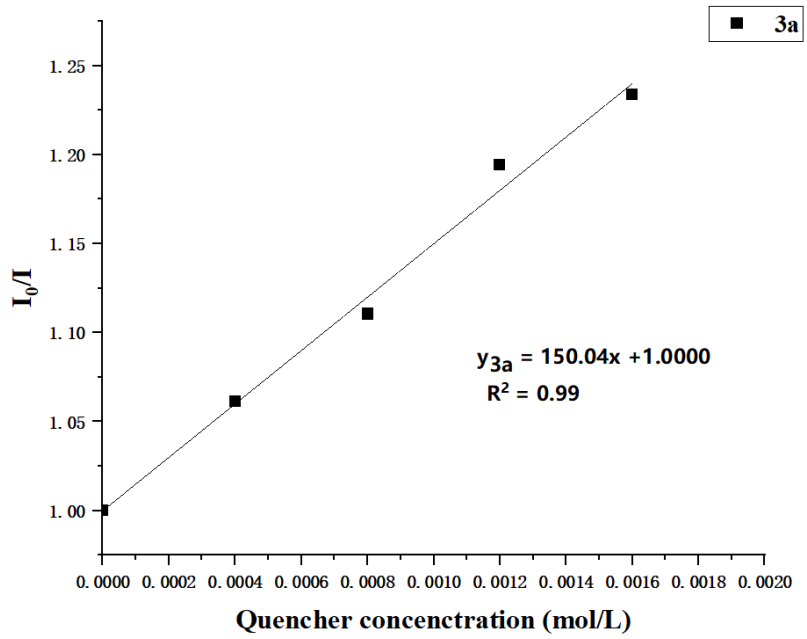


Figure S2. Stern-Volmer plot of **3a**

4.7 Cyclic voltammograms of substrate

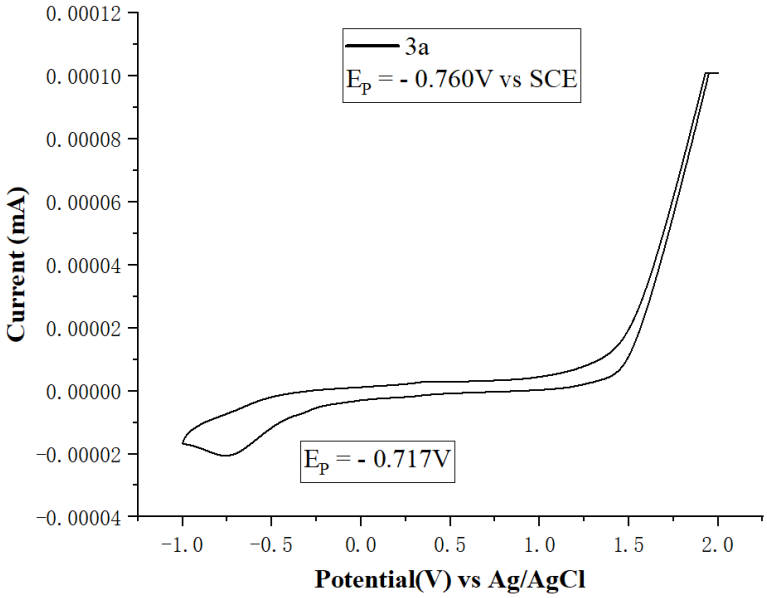


Figure S3. Cyclic voltammogram of **3a**

Cyclic voltammogram was performed using a CHI750E Electrochemical Analyzer with a platinum working electrode, an Ag^+ (0.01 M $AgNO_3$, 0.1 M NBu_4PF_6, MeCN)/Ag as reference electrode, a platinum wire counter electrode. All measurements were taken in nitrogen-sparged MeCN with 0.1 M Bu_4NPF_6 as supporting electrolyte where **3a** concentrations were 1 mM. The sweep rate was 10 mV/s and no reversible electrochemical event was observed in all cases. The values for Ep are referenced to SCE (Saturated Calomel Electrode) by deducting 0.043V to the measured potential.

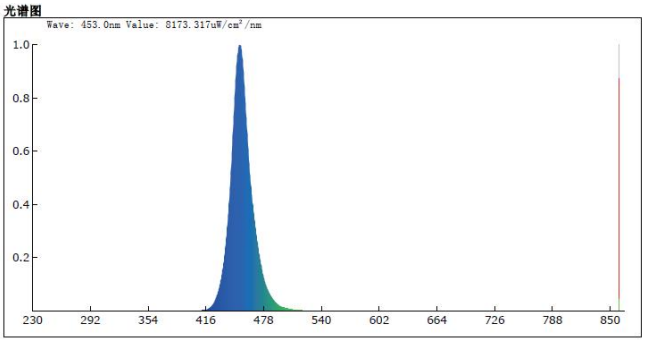
5. Light source

The reactions were performed using RLH-18 8-position Photo Reaction System, which manufactured by Beijing Rogertech Co. ltd based in Beijing, China (http://www.rogertech.cn/). This Photo reactor are equipped with eight 10 W blue light LEDs, and their power can be tuned by connecting a controller.

The emission spectrum of blue LEDs is about 416 to 510 nm, and its λ_{max} is 453.6 nm. The strength of irradiation @5 W is about 246 mW/cm^2.

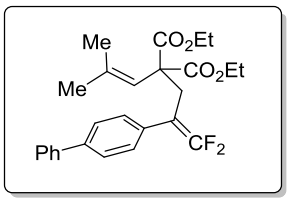
Irradiation vessel is borosilicate glass test tube. The reaction was irradiated through a high-reflection channel from blue LED to the test tube, which length is 2 cm without any filters.

The emission spectrum and the picture of the light source are shown below:



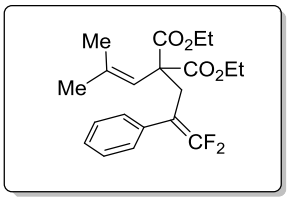
6. Compound characterization data

***Diethyl 2-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)-2-(2-methylprop-1-en-1-yl) malonate* (3a)**



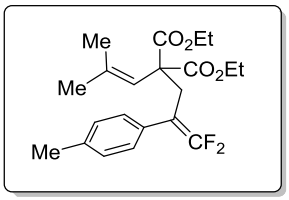
R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 95%, 84.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 4H), 7.45 – 7.41 (m, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 7.1 Hz, 2H), 5.69 (s, 1H), 4.04 – 3.89 (m, 4H), 3.29 (t, *J* = 2.2 Hz, 2H), 1.51 (s, 3H), 1.50 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.4, 154.6 (t, *J* = 289.9 Hz), 140.7, 140.1, 136.4, 132.7 (dd, *J* = 4.4 Hz, 2.3 Hz), 129.4 (t, *J* = 3.0 Hz), 128.8, 127.4, 127.0, 126.7, 120.5, 88.6 (dd, *J* = 20.6 Hz, 17.1 Hz), 61.6, 57.3 (t, *J* = 2.9 Hz), 34.0, 26.9, 18.2, 13.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -89.49 (d, *J* = 36.5 Hz), -89.77 (d, *J* = 36.5 Hz). HRMS (ESI) calcd for $C_{26}H_{28}F_2O_4Na$ $[M+Na]^+$ 465.1848, found 465.1840.

***Diethyl 2-(3,3-difluoro-2-phenylallyl)-2-(2-methylprop-1-en-1-yl)malonate* (3b)**



R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 90%, 65.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.25 – 7.20 (m, 3H), 5.69 (s, 1H), 4.03 – 3.96 (m, 2H), 3.94 – 3.86 (m, 2H), 3.27 (t, *J* = 2.1 Hz, 2H), 1.54 (s, 3H), 1.50 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.4, 154.5 (t, *J* = 289.6 Hz), 136.4, 133.7 (dd, *J* = 4.3 Hz, 2.3 Hz), 129.0, 128.0, 127.2, 120.4, 88.8 (dd, *J* = 20.4 Hz, 17.3 Hz), 61.4, 57.3 (t, *J* = 2.9 Hz), 34.0 (d, *J* = 2.4 Hz), 26.8, 18.2, 13.8.^{19}F NMR (377 MHz, $CDCl_3$) δ -89.97 (d, *J* = 36.8 Hz), -90.25 (d, *J* = 36.8 Hz). HRMS (ESI) calcd for $C_{20}H_{24}F_2NaO_4$ $[M+Na]^+$ 389.1535, found 389.1532.

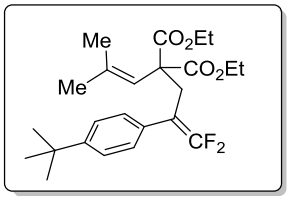
***Diethyl 2-(3,3-difluoro-2-(p-tolyl)allyl)-2-(2-methylprop-1-en-1-yl)malonate* (3c)**



R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 80%, 60.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 7.07 (m, 4H), 5.66 (s, 1H), 4.02 – 3.96 (m, 2H), 3.92 – 3.87 (m, 2H), 3.23 (d, *J* = 2.2 Hz, 2H), 2.30 (s, 3H), 1.53 (s, 3H),

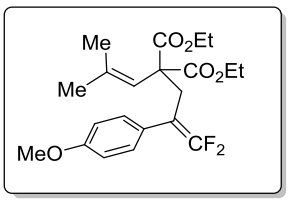
1.48 (s, 3H), 1.14 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 154.5 (t, *J* = 289.1 Hz), 136.9, 136.2, 130.6 (t, *J* = 3.5 Hz), 128.8 (t, *J* = 2.5 Hz), 128.6, 120.5, 88.6 (dd, *J* = 20.4 Hz, 17.4 Hz), 61.4, 57.3 (t, *J* = 2.8 Hz), 34.0 (d, *J* = 2.4 Hz), 26.8, 21.1, 18.2, 13.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -90.34 (d, *J* = 38.0 Hz), -90.63 (d, *J* = 38.0 Hz). HRMS (ESI) calcd for $C_{21}H_{27}F_2O_4$ $[M+H]^+$ 381.1872, found 381.1870.

***Diethyl 2-(2-(4-(tert-butyl)phenyl)-3,3-difluoroallyl)-2-(2-methylprop-1-en-1-yl) malonate* (3d)**



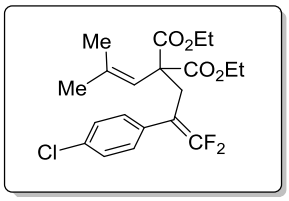
R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 82%, 69.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.66 (s, 1H), 4.00 – 3.92 (m, 2H), 3.88 – 3.80 (m, 2H), 3.23 (t, *J* = 2.1 Hz, 2H), 1.49 (d, *J* = 10.0 Hz, 6H), 1.29 (s, 9H), 1.12 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.4, 154.5 (t, *J* = 289.4 Hz), 150.0, 136.2, 130.6 (t, *J* = 3.3 Hz), 128.6 (t, *J* = 2.7 Hz), 124.9, 120.5, 88.5 (dd, *J* = 20.4 Hz, 17.4 Hz), 61.4, 57.3 (t, *J* = 2.8 Hz), 34.5, 34.1 (d, *J* = 2.6 Hz), 31.2, 26.8, 18.2, 13.8.^{19}F NMR (377 MHz, $CDCl_3$) δ -90.20 (d, *J* = 37.6 Hz), -90.56 (d, *J* = 37.5 Hz). HRMS (ESI) calcd for $C_{24}H_{33}F_2O_4$ $[M+H]^+$ 423.2341, found 423.2338.

***Diethyl 2-(3,3-difluoro-2-(4-methoxyphenyl)allyl)-2-(2-methylprop-1-en-1-yl) malonate* (3e)**



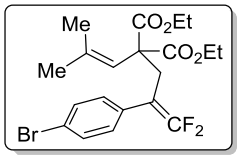
R_f: 0.4 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 86%, 68.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.3 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.69 (s, 1H), 4.05 – 3.80 (m, 4H), 3.80 (s, 3H), 3.23 (t, *J* = 2.2 Hz, 2H), 1.58 (s, 3H), 1.51 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 170.4, 158.7, 154.5 (t, *J* = 288.8 Hz), 136.2, 130.7 (t, *J* = 1.5 Hz), 125.7 (dd, *J* = 3.0 Hz, 1.5 Hz), 120. 5, 113.5, 88.3 (dd, *J* = 20.5, 17.6 Hz), 61.5, 57.3 (t, *J* = 1.5 Hz), 55.3, 34.1 (d, *J* = 2.2 Hz), 26.9, 18.2, 13.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -90.71 (d, *J* = 38.9 Hz), -90.93 (d, *J* = 38.8 Hz). HRMS (ESI) calcd for $C_{21}H_{27}F_2O_5$ $[M+H]^+$ 397.1821, found 397.1821.

***Diethyl 2-(2-(4-chlorophenyl)-3,3-difluoroallyl)-2-(2-methylprop-1-en-1-yl) malonate* (3f)**



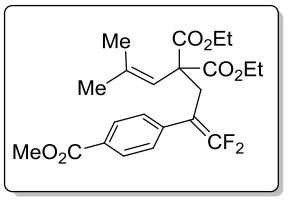
R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 85%, 68.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 5.64 (s, 1H), 4.06 – 3.91 (m, 4H), 3.23 (t, *J* = 2.1 Hz, 2H), 1.53 (s, 3H), 1.49 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 154.5 (t, *J* = 290.4 Hz), 136.5, 133.1, 132.3 (dd, *J* = 4.5 Hz, 2.3 Hz), 130.3 (t, *J* = 2.7 Hz), 128.2, 120.4, 88.1 (dd, *J* = 21.3 Hz, 17.1 Hz), 61.6, 57.3 (t, *J* = 2.7 Hz), 33.9 (d, *J* = 2.2 Hz), 26.8, 18.2, 13.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -89.11 (d, *J* = 35.2 Hz), -89.39 (d, *J* = 35.4 Hz). HRMS (ESI) calcd for $C_{20}H_{24}ClF_2O_4$ $[M+H]^+$ 401.1326, found 401.1325.

***Diethyl 2-(2-(4-bromophenyl)-3,3-difluoroallyl)-2-(2-methylprop-1-en-1-yl) malonate* (3g)**



R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 85%, 75.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 5.64 (s, 1H), 4.07 – 3.93 (m, 4H), 3.23 (t, *J* = 2.2 Hz, 2H), 1.54 (s, 3H), 1.49 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 154.4 (t, *J* = 290.5 Hz), 136.6, 131.2, 130.6 (t, *J* = 2.7 Hz), 121.3, 120.3, 88.1 (dd, *J* = 21.2 Hz, 17.1 Hz), 61.6, 33.9, 26.8, 18.2, 13.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -88.98 (d, *J* = 35.2 Hz), -89.26 (d, *J* = 35.1 Hz). HRMS (ESI) calcd for $C_{20}H_{24}BrF_2O_4$ $[M+H]^+$ 445.0821, found 445.0817.

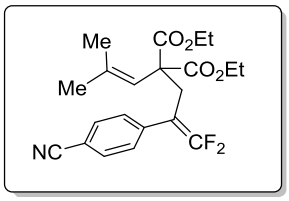
***Diethyl 2-(3,3-difluoro-2-(4-(methoxycarbonyl)phenyl)allyl)-2-(2-methylprop-1-en -1-yl)malonate* (3h)**



R_f: 0.3 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 88%, 74.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.62 (s, 1H), 4.07 – 3.88 (m, 7H), 3.28 (t, *J* = 2.1 Hz, 2H), 1.46 (s, 6H), 1.16 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 166.6, 154.6 (t, *J* = 291.3 Hz), 138.8 (t, *J* = 3.3 Hz), 136.6, 129.2, 128.9, 128.9 (t, *J* = 2.7 Hz), 120.4, 88.6 (dd, *J* = 21.0, 16.8 Hz), 61.6, 57.3 (d, *J* = 2.7 Hz), 52.1, 33.7 (d, *J* = 2.0 Hz), 26.7, 18.2, 13.8.

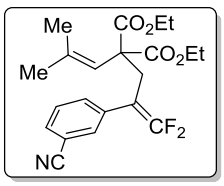
^{19}F NMR (377 MHz, $CDCl_3$) δ -88.10 (d, *J* = 32.7 Hz), -88.24 (d, *J* = 32.6 Hz). HRMS (ESI) calcd for $C_{22}H_{27}F_2O_6$ $[M+H]^+$ 425.1770, found 425.1778.

***Diethyl 2-(2-(4-cyanophenyl)-3,3-difluoroallyl)-2-(2-methylprop-1-en-1-yl) malonate* (3i)**



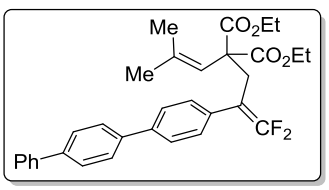
R_f: 0.3 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 78%, 61.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.57 (s, 1H), 4.09 – 3.92 (m, 4H), 3.25 (d, *J* = 2.2 Hz, 2H), 1.45 (s, 6H), 1.17 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 154.8 (t, *J* = 292.2 Hz), 139.2, 137.0, 131.9, 129.8 (t, *J* = 2.6 Hz), 120.5, 118.7, 111.1, 88.5 (dd, *J* = 21.2 Hz, 17.1 Hz), 61.8, 57.4, 33.8, 26.9, 18.3, 14.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -87.14 (d, *J* = 30.6 Hz), -87.25 (d, *J* = 30.5 Hz). HRMS (ESI) calcd for $C_{21}H_{24}F_2NO_4$ $[M+H]^+$ 392.1668, found 392.1673.

***Diethyl 2-(2-(3-cyanophenyl)-3,3-difluoroallyl)-2-(2-methylprop-1-en-1-yl)malonate* (3j)**



R_f: 0.3 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 93%, 72.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.49 – 7.43 (m, 2H), 5.59 (s, 1H), 4.09 – 4.01 (m, 2H), 4.01 – 3.94 (m, 2H), 3.25 (t, *J* = 2.1 Hz, 2H), 1.49 (s, 3H), 1.48 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.1, 154.8 (t, *J* = 291.5 Hz), 136.9, 135.4 (dd, *J* = 4.6, 2.1 Hz), 133.4, 132.4, 130.8, 128.95, 120.4, 118.3, 112.4, 87.8 (dd, *J* = 21.9 Hz, 16.9 Hz), 61.7, 57.2 (d, *J* = 2.8 Hz), 33.6 (d, *J* = 2.0 Hz), 26.7, 18.2, 13.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -87.82 (d, *J* = 32.0 Hz), -87.97 (d, *J* = 32.2 Hz). HRMS (ESI) calcd for $C_{21}H_{24}F_2NO_4$ $[M+H]^+$ 392.1668, found 392.1670.

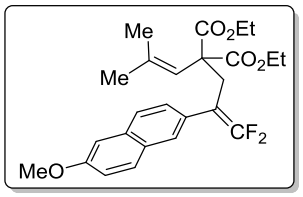
***Diethyl2-(2-([1,1':4',1''-terphenyl]-4-yl)-3,3-difluoroallyl)-2-(2-methylprop-1-en-1-yl) malonate* (3k)**



R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 89%, 92.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 6H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 7.5 Hz, 2H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.34 – 7.31 (m,

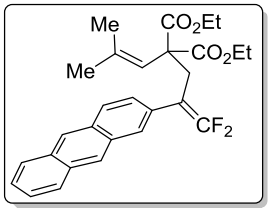
2H), 5.72 (s, 1H), 4.08 – 4.00 (m, 2H), 4.00 – 3.92 (m, 2H), 3.32 (t, *J* = 2.1 Hz, 2H), 1.55 (s, 3H), 1.53 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.4, 153.6 (t, *J* = 289.2 Hz), 140.7, 140.3, 139.5 (d, *J* = 4.4 Hz), 136.4, 132.9, 129.4 (t, *J* = 2.6 Hz), 128.8, 127.6, 127.4, 127.3, 127.0, 126.5, 120.5, 88.6 (dd, *J* = 20.5 Hz, 16.8 Hz), 61.5, 57.4, 34.0, 26.8, 18.2, 13.8.^{19}F NMR (377 MHz, $CDCl_3$) δ -89.40 (d, *J* = 36.4 Hz), -89.68 (d, *J* = 36.1 Hz). HRMS (ESI) calcd for $C_{32}H_{32}F_2NaO_4$ $[M+Na]^+$ 541.2161, found 541.2160.

***Diethyl 2-(3,3-difluoro-2-(6-methoxynaphthalen-2-yl)allyl)-2-(2-methylprop-1-en-1-yl) malonate* (3l)**



R_f: 0.4 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 94%, 83.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.64 (m, 2H), 7.59 (s, 1H), 7.29 (d, *J* = 8.6 Hz, 1H), 7.12 (d, *J* = 8.9 Hz, 1H), 7.08 (s, 1H), 5.69 (s, 1H), 3.95 – 3.88 (m, 5H), 3.84 – 3.77 (m, 2H), 3.34 (d, *J* = 2.3 Hz, 2H), 1.48 (s, 3H), 1.42 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 157.8, 154.7 (t, *J* = 289.6 Hz), 136.4, 133.6, 129.3, 128. 7 (d, *J* = 3.4 Hz), 128.5, 127.7 (t, *J* = 2.6 Hz), 127.4 (t, *J* = 2.5 Hz), 126.4, 120.4, 119.0, 105.5, 88.8 (dd, *J* = 20.1 Hz, 17.5 Hz), 61.5, 57.3 (t, *J* = 2.9 Hz), 55.3, 34.1 (d, *J* = 2.0 Hz), 26.8, 18.2, 13.8.^{19}F NMR (377 MHz, $CDCl_3$) δ -89.94 (d, *J* = 36.9 Hz), -90.08 (d, *J* = 36.9 Hz). HRMS (ESI) calcd for $C_{25}H_{29}F_2O_5$ $[M+H]^+$ 447.1978, found 447.1974.

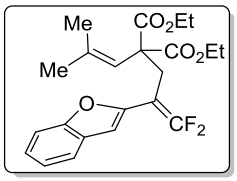
***Diethyl 2-(2-(anthracen-2-yl)-3,3-difluoroallyl)-2-(2-methylprop-1-en-1-yl)malonate* (3m)**



R_f: 0.5 (petroleum ether/ethyl acetate 20:1). Colorless liquid (Yield: 85%, 79.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 88.40 (s, 2H), 8.03 – 7.99 (m, 2H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.85 (s, 1H), 7.51 – 7.46 (m, 2H), 7.36– 7.33 (m, 1H), 5.73 (s, 1H), 3.98 – 3.90 (m, 2H), 3.88 – 3.79 (m, 2H), 3.42 (t, *J* = 2.1 Hz, 2H), 1.50 (s, 3H), 1.39 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 156.3 (d, *J* = 290.8 Hz), 136.6, 131.9 (d, *J* = 4.0 Hz), 131.2, 130.6, 128.2 (d, *J* = 4.3 Hz), 128.0, 127.8, 126.5, 126.2, 125.9, 125.5, 89.0 (dd, *J* = 20.2 Hz, 17.5 Hz), 61.5, 57.3, 34.0,

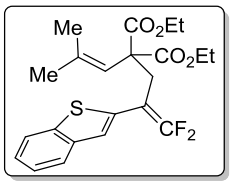
26.8, 18.2, 13.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -88.99 (d, *J* = 35.3 Hz), -89.23 (d, *J* = 35.0 Hz). HRMS (ESI) calcd for $C_{28}H_{29}F_2O_4$ $[M+H]^+$ 467.2028, found 467.2032.

***Diethyl 2-(2-(benzofuran-2-yl)-3,3-difluoroallyl)-2-(2-methylprop-1-en-1-yl) malonate* (3n)**



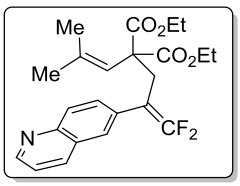
R_f: 0.5 (petroleum ether/ethyl acetate 20:1). Yellow liquid (Yield: 70%, 56.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.28 – 7.19 (m, 2H), 6.67 (d, *J* = 1.9 Hz, 1H), 5.69 (s, 1H), 4.19 – 4.06 (m, 4H), 3.39 (t, *J* = 2.1 Hz, 2H), 1.61 (s, 3H), 1.42 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 156.3 (d, *J* = 290.8 Hz), 136.6, 131.9 (d, *J* = 4.0 Hz), 131.2, 130.6, 128.2 (d, *J* = 4.3 Hz), 128.0, 127.8, 126.5, 126.2, 125.9, 125.5, 89.0 (dd, *J* = 20.2 Hz, 17.5 Hz), 61.5, 57.3, 34.0, 26.8, 18.2, 13.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -79.51 (d, *J* = 20.1 Hz), -84.79 (d, *J* = 20.5 Hz). HRMS (ESI) calcd for $C_{22}H_{25}F_2O_5$ $[M+H]^+$ 407.1665, found 407.1666.

***Diethyl 2-(2-(benzo[b]thiophen-2-yl)-3,3-difluoroallyl)-2-(2-methylprop-1-en-1-yl) malonate* (3o)**



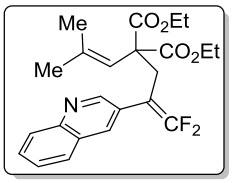
R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 66%, 55.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.24 (m, 3H), 5.75 (s, 1H), 4.09 – 3.94 (m, 4H), 3.30 (t, *J* = 2.2 Hz, 2H), 1.55 (s, 3H), 1.52 (s, 3H), 1.16 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.6, 155.7 (t, *J* = 297.5 Hz), 154.2, 149.2 (t, *J* = 6.4 Hz), 136.9, 128.7, 124.1, 122.9, 120.8, 119.6, 110.6, 104.9 (dd, *J* = 7.9 Hz, 3.6 Hz), 82.6 (dd, *J* = 27.0 Hz, 14.5 Hz), 61.7, 57.4, 30.9, 26.7, 18.3, 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -82.59 (d, *J* = 24.5 Hz), -85.60 (d, *J* = 24.2 Hz). HRMS (ESI) calcd for $C_{22}H_{25}F_2O_4S$ $[M+H]^+$ 423.1436, found 423.1438.

***Diethyl 2-(3,3-difluoro-2-(quinolin-6-yl)allyl)-2-(2-methylprop-1-en-1-yl)malonate* (3p)**



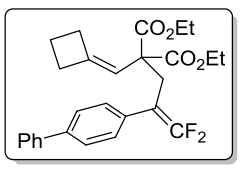
R_f: 0.3 (petroleum ether/ethyl acetate 5:1). Colorless liquid (Yield: 93%, 77.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 4.3 Hz, 1.7 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.67 (s, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.40 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.65 (s, 1H), 3.99 – 3.91 (m, 2H), 3.89 – 3.83 (m, 2H), 3.36 (t, *J* = 2.1 Hz, 2H), 1.46 (s, 3H), 1.36 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.3, 154.8 (t, *J* = 290.7 Hz), 150.6, 147.3, 136.6, 135.9, 132.1 (t, *J* = 3.4 Hz), 130.3, 129.0, 127.9 (t, *J* = 2.7 Hz), 127.8, 121.4, 120.4, 88.6(dd, *J* = 21.1 Hz, 17.0 Hz), 61.5, 57.3, 34.0 (d, *J* = 2.0 Hz), 26.7, 18.2, 13.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -88.77 (d, *J* = 34.5 Hz), -88.96 (d, *J* = 34.2 Hz). HRMS (ESI) calcd for $C_{23}H_{26}F_2NO_4$ $[M+H]^+$ 418.1824, found 418.1825.

***Diethyl 2-(3,3-difluoro-2-(quinolin-3-yl)allyl)-2-(2-methylprop-1-en-1-yl)malonate* (3q)**



R_f: 0.4 (petroleum ether/ethyl acetate 5:1). Colorless liquid (Yield: 94%, 78.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (t, *J* = 1.9 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 8.00 (s, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.72 (t, *J* = 7.0 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 5.64 (s, 1H), 4.02 – 3.95 (m, 2H), 3.95 – 3.85 (m, 2H), 3.39 (t, *J* = 2.1 Hz, 2H), 1.48 (s, 3H), 1.36 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 154.8 (t, *J* = 290.3 Hz), 136.6, 131.9 (d, *J* = 4.0 Hz), 131.2, 130.6, 128.2, 128.2, 128.0 (t, *J* = 2.9 Hz), 127.8, 126.5 (t, *J* = 2.6 Hz), 126.2, 125.9, 125.5, 120.4, 89.1 (dd, *J* = 21.2 Hz, 16.1 Hz), 61.5, 57.3 (d, *J* = 3.1 Hz), 34.0 (d, *J* = 2.2 Hz), 26.8, 18.2, 13.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -87.66 (d, *J* = 32.6 Hz), -88.29 (d, *J* = 32.4 Hz). HRMS (ESI) calcd for $C_{23}H_{26}F_2NO_4$ $[M+H]^+$ 418.1824, found 418.1824.

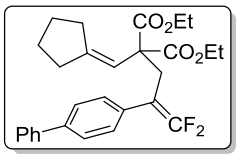
***Diethyl 2-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)-2-(cyclobutylidenemethyl) malonate* (3r)**



R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 61%, 55.5mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.7, 6.1 Hz, 4H), 7.49 – 7.45 (m, 2H), 7.40 – 7.33 (m, 3H), 5.58 (s, 1H), 4.08 – 3.99 (m, 2H), 3.97 – 3.91 (m, 2H), 3.26 (t, *J* = 2.1 Hz, 2H), 2.58 –

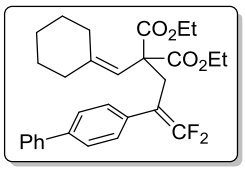
2.49 (m, 4H), 1.87 (q, *J* = 7.9 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 154.6 (t, *J* = 290.1 Hz), 145.1, 140.7, 140.2, 132.7, 129.4 (t, *J* = 2.5 Hz), 128.8, 127.4, 127.0, 126.7, 116.6, 88.5 (dd, *J* = 20.3 Hz, 17.3 Hz), 61.4, 57.1, 33.8 (d, *J* = 2.1 Hz), 32.0, 29.7, 17.1, 13.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -87.66 (d, *J* = 32.6 Hz), -88.29 (d, *J* = 32.4 Hz). HRMS (ESI) calcd for $C_{27}H_{28}F_2NaO_4$ $[M+Na]^+$ 477.1848, found 477.1853.

***Diethyl 2-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)-2-(cyclopentylidenemethyl) malonate* (3s)**



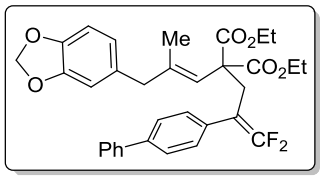
R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 83%, 77.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 4H), 7.49 – 7.44 (m, 2H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 5.82 (s, 1H), 4.08 – 3.96 (m, 4H), 3.30 (t, *J* = 2.0 Hz, 2H), 2.07 – 2.02 (m, 2H), 2.01 – 1.96 (m, 2H), 1.61 – 1.56 (m, 2H), 1.43 – 1.40 (m, 2H), 1.19 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.3, 154.5 (t, *J* = 289.9 Hz), 147.2, 140.7, 140.1, 132.9 (t, *J* = 3.4 Hz), 129.3 (t, *J* = 2.7 Hz), 128.8, 127.4, 127.0, 126.7, 116.3, 88.7 (dd, *J* = 20.6 Hz, 17.2 Hz), 61.5, 57.8, 35.2, 33.1 (d, *J* = 2.2 Hz), 28.4, 27.0, 25.4, 13.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -89.46 (d, *J* = 36.6 Hz), -89.68 (d, *J* = 36.4 Hz). HRMS (ESI) calcd for $C_{28}H_{31}F_2O_4$ $[M+H]^+$ 469.2185, found 469.2187.

***Diethyl 2-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)-2-(cyclohexylidenemethyl) malonate* (3t)**



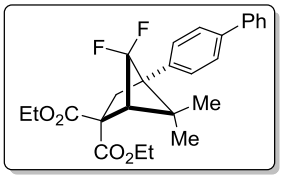
R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 97%, 93.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 4H), 7.45 – 7.41 (m, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 2H), 5.67 (s, 1H), 4.03 – 3.86 (m, 4H), 3.26 (t, *J* = 2.1 Hz, 2H), 1.97 (t, *J* = 5.6 Hz, 2H), 1.89 (t, *J* = 5.8 Hz, 2H), 1.45 – 1.35 (m, 6H), 1.15 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.8, 154.6 (t, *J* = 290.0 Hz), 143.9, 140.8, 140.3, 132.9 (dd, *J* = 4.5, 2.3 Hz), 129.6 (t, *J* = 2.5 Hz), 128.9, 127.5, 127.1, 126.8, 117.7, 88.7 (dd, *J* = 20.6 Hz, 17.3 Hz), 61.7, 57.1, 37.7, 35.2 (d, *J* = 2.2 Hz), 29.3, 27.9, 26.8, 26.3, 14.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -88.99 (d, *J* = 35.8 Hz), -89.39 (d, *J* = 36.0 Hz). HRMS (ESI) calcd for $C_{29}H_{33}F_2O_4$ $[M+H]^+$ 483.2341, found 483.2344.

***Diethyl 2-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)-2-(3-(benzo[d][1,3]dioxol-5-yl)-2-methylprop-1-en-1-yl)malonate* (3u)**



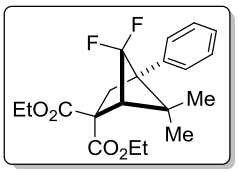
R_f: 0.3 (petroleum ether/ethyl acetate 20:1). Yellow liquid (Yield: 85%, 95.6 mg). This compound was obtained as a mixture of two *E/Z* isomers (*E/Z* = 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 10.1, 8.1 Hz, 4H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 2H), 6.71 (d, *J* = 7.9 Hz, 1H), 6.62 (s, 1H), 6.57 (d, *J* = 7.9 Hz, 1H), 5.94 (s, 0.2 H, *Z*-), 5.92 (s, 1.8 H, *E*-), 5.90 (s, 1H), 4.06 – 4.01 (m, 2H), 3.99 – 3.87 (m, 2H), 3.36 – 3.32 (m, 2H), 3.07 (s, 2H), 1.45 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.3, 154.6 (t, *J* = 285.4 Hz), 147.6, 145.9, 140.6, 140.2, 139.0, 133.3, 132.4 (d, *J* = 3.6 Hz), 129.4 (t, *J* = 1.5 Hz), 128.8, 127.4, 127.0, 126.7, 122.7, 121.7, 109.1, 107.9, 100.8, 88.6 (dd, *J* = 20.5 Hz, 17.2 Hz), 61.6, 57.4, 46.7 33.8, 16.2, 13.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -89.10 (d, *J* = 35.6 Hz), -89.33 (d, *J* = 36.1 Hz). HRMS (APCI) calcd for $C_{33}H_{33}F_2O_6$ $[M+H]^+$ 563.2240, found 563.2239.

***Diethyl 4-([1,1'-biphenyl]-4-yl)-5,5-difluoro-6,6-dimethylbicyclo[2.1.1]hexane-2,2-dicarboxylate* (4a)**



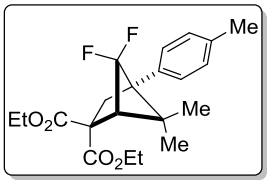
R_f: 0.4 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 96%, 85.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.31 (m, 3H), 4.29 – 4.21 (m, 4H), 3.37 (t, *J* = 2.1 Hz, 1H), 2.94 (s, 2H), 1.36 (d, *J* = 5.4 Hz, 3H), 1.31 (t, *J* = 6.6 Hz, 3H), 1.28 (t, *J* = 6.5 Hz, 3H), 1.12 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.1, 169.8, 140.7, 140.4, 132.8, 128.8, 127.4, 127.3, 127.1, 127.1, 124.1 (dd, *J* = 291.0 Hz, 286.2 Hz), 62.2 (d, *J* = 4.5 Hz), 60.4 (dd, *J* = 32.5 Hz, 16.6 Hz), 58.8 (t, *J* = 16.1 Hz), 57.3, 44.2 (dd, *J* = 13.5 Hz, 4.0 Hz), 39.2 (d, *J* = 3.2 Hz), 21.7 (d, *J* = 15.4 Hz), 20.8 (d, *J* = 9.0 Hz), 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ 95.14 (d, *J* = 183.4 Hz), -123.66 (d, *J* = 183.3 Hz). HRMS (ESI) calcd for $C_{26}H_{28}F_2O_4Na$ $[M+Na]^+$ 465.1848, found 465.1852.

***Diethyl 5,5-difluoro-6,6-dimethyl-4-phenylbicyclo[2.1.1]hexane-2,2-dicarboxylate* (4b)**



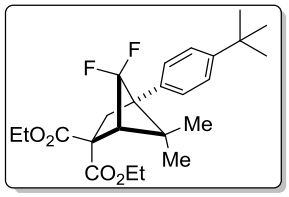
R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 77%, 56.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 5H), 4.30 – 4.20 (m, 4H), 3.37 (t, *J* = 2.2 Hz, 1H), 2.93 (s, 2H), 1.36 – 1.28 (m, 9H), 1.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 169.8, 133.9, 128.6, 127.5, 126.6, 122.7 (dd, *J* = 292.2 Hz, 286.5 Hz), 62.2 (d, *J* = 3.7 Hz), 60.6 (dd, *J* = 19.2 Hz, 14.5 Hz), 58.8 (dd, *J* = 17.6 Hz, 14.9 Hz), 57.3, 44.0 (dd, *J* = 14.1 Hz, 4.0 Hz), 39.3, 21.7 (d, *J* = 15.6 Hz), 20.7 (d, *J* = 8.8 Hz), 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -95.15 (d, *J* = 183.5 Hz), -123.73 (d, *J* = 183.3 Hz). HRMS (ESI) calcd for $C_{20}H_{24}F_2O_4Na$ $[M+Na]^+$ 389.1535, found 389.1527.

***Diethyl 5,5-difluoro-6,6-dimethyl-4-(p-tolyl)bicyclo[2.1.1]hexane-2,2-dicarboxylatee* (4c)**



R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 84%, 63.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 3.9 Hz, 4H), 4.28 – 4.22 (m, 4H), 3.35 (t, *J* = 2.2 Hz, 1H), 2.91 (s, 2H), 2.36 (s, 3H), 1.35 – 1.28 (m, 9H), 1.10 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.1, 169.8, 137.2 130.7, 129.3, 126.6, 124.1 (dd, *J* = 291.1 Hz, 286.9 Hz), 62.1 (d, *J* = 5.5 Hz), 60.3 (dd, *J* = 18.1 Hz, 13.6 Hz), 58.8 (dd, *J* = 17.7 Hz, 14.9 Hz), 57.3, 43.9 (dd, *J* = 13.6 Hz, 4.5 Hz), 39.2, 21.7 (d, *J* = 15.4 Hz), 21.1, 20.7 (d, *J* = 8.9 Hz), 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -95.31 (d, *J* = 183.5 Hz), -123.79 (d, *J* = 183.5 Hz). HRMS (ESI) calcd for $C_{21}H_{26}F_2O_4Na$ $[M+Na]^+$ 403.1691, found 403.1692.

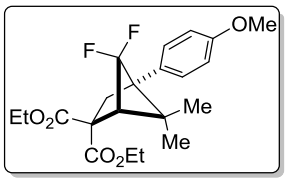
***Diethyl 4-(4-(tert-butyl)phenyl)-5,5-difluoro-6,6-dimethylbicyclo[2.1.1]hexane -2,2-dicarboxylate* (4d)**



R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 80%, 67.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 8.7 Hz, 2H), 4.31 – 4.29(m, 4H), 3.35 (t, *J* = 2.2 Hz, 1H), 2.92 (s, 2H), 1.35 – 1.29 (m, 18H), 1.27 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.1, 169.8, 150.3, 130.7, 126.4, 125.4, 124.2 (dd, *J* = 291.0 Hz, 286.0 Hz), 62.1 (d, *J* = 5.8 Hz), 60.3 (dd, *J* = 18.1 Hz,

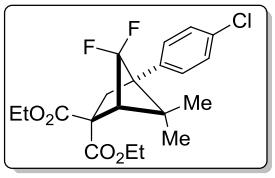
14.5 Hz), 58.8 (dd, *J* = 17.4 Hz, 14.8 Hz), 57.3, 44.0 (dd, *J* = 13.8 Hz, 4.1 Hz), 39.2 (d, *J* = 3.3 Hz), 34.5, 31.3, 21.8 (d, *J* = 15.4 Hz), 20.7 (d, *J* = 8.8 Hz), 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -95.25 (d, *J* = 183.1 Hz), -123.77 (d, *J* = 183.0 Hz). HRMS (ESI) calcd for $C_{24}H_{32}F_2O_5Na$ $[M+Na]^+$ 445.2161, found 445.2153.

***Diethyl 5,5-difluoro-4-(4-methoxyphenyl)-6,6-dimethylbicyclo[2.1.1]hexane -2,2-dicarboxylate* (4e)**



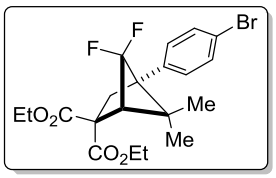
R_f: 0.4 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 83%, 65.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 4.28 – 4.23 (m, 4H), 3.81 (s, 3H), 3.34 (t, *J* = 2.2 Hz, 1H), 2.89 (s, 2H), 1.34 – 1.27 (m, 9H), 1.07 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.1, 169.8, 158.9, 127.9, 125.7, 124.2 (dd, *J* = 291.0 Hz, 286.0 Hz), 114.0, 62.1 (d, *J* = 4.1 Hz), 60.0 (dd, *J* = 18.4 Hz, 14.5 Hz), 58.7 (dd, *J* = 17.5 Hz, 14.9 Hz), 57.2 (d, *J* = 2.5 Hz), 55.2, 43.9 (dd, *J* = 13.9 Hz, 4.3 Hz), 39.1 (d, *J* = 3.4 Hz), 21.7 (d, *J* = 15.4 Hz), 20.6 (d, *J* = 9.8 Hz), 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -95.49 (d, *J* = 183.2 Hz), -123.82 (d, *J* = 183.1 Hz). HRMS (ESI) calcd for $C_{21}H_{26}F_2O_5Na$ $[M+Na]^+$ 419.1641, found 419.1634.

***Diethyl 4-(4-chlorophenyl)-5,5-difluoro-6,6-dimethylbicyclo[2.1.1]hexane -2,2-dicarboxylate* (4f)**



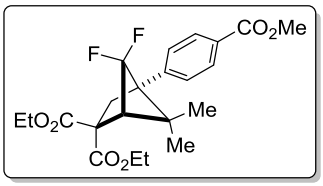
R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 78%, 62.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 4.28 – 4.22 (m, 4H), 3.37 (t, *J* = 2.2 Hz, 1H), 2.90 (s, 2H), 1.34 – 1.27 (m, 9H), 1.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 169.6, 133.5, 132.3, 128.8, 128.0, 123.9 (d, *J* = 291.9 Hz, 286.8 Hz), 62.2 (d, *J* = 4.2 Hz), 60.1 (dd, *J* = 18.5 Hz, 14.4 Hz), 58.8 (dd, *J* = 17.4 Hz, 14.9 Hz), 57.2, 44.1 (dd, *J* = 13.5 Hz, 4.2 Hz), 39.1, 21.6 (d, *J* = 15.6 Hz), 20.6 (d, *J* = 8.7 Hz), 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -95.30 (d, *J* = 183.4 Hz), -123.77 (d, *J* = 183.4 Hz). HRMS (ESI) calcd for $C_{20}H_{23}ClF_2O_4Na$ $[M+Na]^+$ 423.1145, found 423.1137.

***Diethyl 4-(4-bromophenyl)-5,5-difluoro-6,6-dimethylbicyclo[2.1.1]hexane-2,2-dicarboxylate* (4g)**



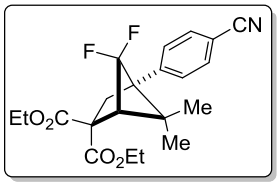
R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 79%, 70.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 4.28 – 4.22 (m, 4H), 3.37 (t, *J* = 2.2 Hz, 1H), 2.90 (s, 2H), 1.33 – 1.28 (m, 9H), 1.09 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 169.6, 132.8, 131.8, 128.4, 123.8 (dd, *J* = 291.4 Hz, 286.9 Hz), 121.62, 62.2 (d, *J* = 6.2 Hz), 60.1 (dd, *J* = 18.2 Hz, 15.1 Hz), 58.8 (dd, *J* = 17.4 Hz, 14.7 Hz), 57.2, 44.1 (dd, *J* = 13.4 Hz, 4.1 Hz), 39.1 (d, *J* = 3.5 Hz), 21.6 (d, *J* = 15.6 Hz), 20.6 (d, *J* = 8.9 Hz), 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -95.26 (d, *J* = 183.2 Hz), -123.76 (d, *J* = 183.2 Hz). HRMS (ESI) calcd for $C_{20}H_{23}BrF_2O_4Na$ $[M+Na]^+$ 467.0640, found 467.0644.

***Diethyl 5,5-difluoro-4-(4-(methoxycarbonyl)phenyl)-6,6-dimethylbicyclo[2.1.1]hexane-2,2-dicarboxylate* (4h)**



R_f: 0.4 (petroleum ether/ethyl acetate 5:1). Colorless liquid (Yield: 90%, 76.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 4.28 – 4.22 (m, 4H), 3.93 (s, 3H), 3.38 (t, *J* = 2.2 Hz, 1H), 2.94 (s, 2H), 1.34 – 1.27 (m, 9H), 1.13 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.8, 169.5, 166.7, 139.1, 129.8, 129.4, 126.6, 123.8 (dd, *J* = 291.0 Hz, 286.1 Hz), 62.2 (d, *J* = 6.6 Hz), 60.6 (dd, *J* = 18.3 Hz, 14.5 Hz), 58.9 (dd, *J* = 17.3 Hz, 14.7 Hz), 57.3, 52.1, 44.4 (dd, *J* = 13.2 Hz, 4.2 Hz), 39.2 (d, *J* = 3.2 Hz), 21.6 (d, *J* = 15.6 Hz), 20.8 (d, *J* = 8.7 Hz), 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -95.31 (d, *J* = 183.5 Hz), -123.79 (d, *J* = 183.5 Hz). HRMS (ESI) calcd for $C_{22}H_{26}F_2O_6Na$ $[M+Na]^+$ 447.1590, found 447.1585.

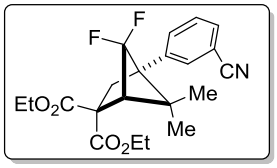
***Diethyl4-(4-cyanophenyl)-5,5-difluoro-6,6-dimethylbicyclo[2.1.1]hexane-2,2-dicarboxylate* (4i)**



R_f: 0.4 (petroleum ether/ethyl acetate 5:1). Colorless liquid (Yield: 91%, 71.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 4.27 – 4.22 (m, 4H),

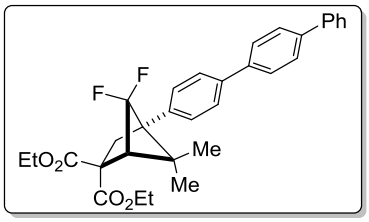
3.38 (t *J* = 2.2 Hz, 1H), 2.91 (s, 2H), 1.33 – 1.26 (m, 9H), 1.11 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.6, 169.3, 139.4, 132.4, 127.4, 123.6 (dd, *J* = 291.1 Hz, 286.3 Hz), 118.5, 111.6, 62.4 (d, *J* = 7.8 Hz), 60.5 (dd, *J* = 18.5 Hz, 14.5 Hz), 58.9 (dd, *J* = 17.3 Hz, 14.7 Hz), 57.2, 44.7 (dd, *J* = 13.0 Hz, 4.1 Hz), 39.1 (d, *J* = 3.0 Hz), 21.6 (d, *J* = 15.6 Hz), 20.7 (d, *J* = 8.6 Hz), 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -94.97 (d, *J* = 183.9 Hz), -123.59 (d, *J* = 183.9 Hz). HRMS (ESI) calcd for $C_{21}H_{23}NF_2O_4Na$ $[M+Na]^+$ 414.1487, found 414.1477.

***Diethyl 4-(3-cyanophenyl)-5,5-difluoro-6,6-dimethylbicyclo[2.1.1]hexane -2,2-dicarboxylate* (4j)**



R_f: 0.3 (petroleum ether/ethyl acetate 5:1). Colorless liquid (Yield: 80%, 62.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.3 Hz, 1H), 7.54 (s, 1H), 7.52 – 7.45 (m, 2H), 4.31 – 4.23 (m, 4H), 3.40 (t, *J* = 2.0 Hz, 1H), 2.92 (s, 2H), 1.34 – 1.31 (m, 6H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.12 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.6, 169.3, 135.5, 131.2, 131.1, 130.2, 129.5, 123.6 (dd, *J* = 291.3 Hz, 286.3 Hz), 118.5, 113.0, 62.4 (d, *J* = 8.1 Hz), 60.0 (dd, *J* = 18.5 Hz, 14.4 Hz), 58.8 (dd, *J* = 17.3 Hz, 14.8 Hz), 57.2, 44.5 (dd, *J* = 13.1 Hz, 4.1 Hz), 39.0 (d, *J* = 3.2 Hz), 21.6 (d, *J* = 15.4 Hz), 20.7 (d, *J* = 8.7 Hz), 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -95.06 (d, *J* = 183.8 Hz), -123.70 (d, *J* = 183.8 Hz). HRMS (ESI) calcd for $C_{21}H_{24}F_2NO_4$ $[M+H]^+$ 392.1668, found 392.1670.

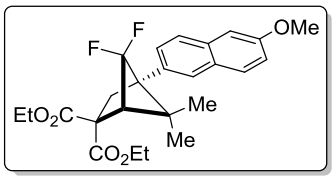
***Diethyl 4-([1,1':4',1''-terphenyl]-4-yl)-5,5-difluoro-6,6-dimethylbicyclo[2.1.1] hexane-2,2-dicarboxylate* (4k)**



R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 92%, 95.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 8H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 8.7 Hz, 3H), 4.31 – 4.25 (m, 4H), 3.40 (t, *J* = 2.1 Hz, 1H), 2.99 (s, 2H), 1.40 (d, *J* = 5.3 Hz, 3H), 1.37 – 1.32 (m, 6H), 1.16 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.1, 169.8, 140.7, 140.3, 139.9, 139.5, 132.9, 128.8, 127.5, 127.4, 127.2, 127.0, 125.1 (dd, *J* = 291.4 Hz, 286.5 Hz), 62.2 (d, *J* = 5.5 Hz),

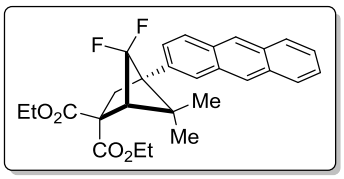
60.4 (dd, *J* = 18.1, 14.7 Hz), 58.9 (dd, *J* = 17.7 Hz, 16.6 Hz), 44.2 (dd, *J* = 13.6 Hz, 3.8 Hz), 39.3, 21.8 (d, *J* = 15.4 Hz), 20.8 (d, *J* = 8.8 Hz), 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -95.12 (d, *J* = 183.5 Hz), -123.64 (d, *J* = 183.3 Hz). HRMS (ESI) calcd for $C_{32}H_{32}F_2O_4Na$ $[M+Na]^+$ 541.2161, found 541.2153.

***Diethyl 5,5-difluoro-4-(6-methoxynaphthalen-2-yl)-6,6-dimethylbicyclo[2.1.1] hexane-2,2-dicarboxylate* (4l)**



R_f: 0.4 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 98%, 87.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.6 Hz, 2H), 7.68 (s, 1H), 7.35 (d, *J* = 9.1 Hz, 1H), 7.18 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.14 (s, 1H), 4.33 – 4.23 (m, 4H), 3.94 (s, 3H), 3.41 (t, *J* = 2.1 Hz, 1H), 3.07 – 2.96 (m, 2H), 1.39 – 1.29 (m, 9H), 1.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 169.9, 157.8, 133.7, 129.4, 128.9, 128.8, 127.1, 125.6, 124.9, 124.2 (dd, *J* = 292.9 Hz, 287.9 Hz), 119.2, 105.6, 62.2 (d, *J* = 4.5 Hz), 60.7 (dd, *J* = 18.3 Hz, 14.3 Hz), 58.8 (dd, *J* = 17.5 Hz, 14.8 Hz), 57.3, 55.3, 44.2 (dd, *J* = 13.8 Hz, 4.3 Hz), 39.3 (d, *J* = 3.3 Hz), 21.8 (d, *J* = 15.4 Hz), 20.8 (d, *J* = 8.8 Hz), 14.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -95.09 (d, *J* = 183.2 Hz), -123.49 (d, *J* = 183.1 Hz). HRMS (ESI) calcd for $C_{25}H_{28}F_2O_5Na$ $[M+Na]^+$ 469.1797, found 469.1790.

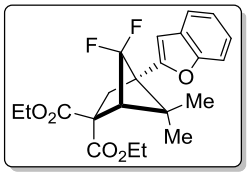
***Diethyl 4-(anthracen-2-yl)-5,5-difluoro-6,6-dimethylbicyclo[2.1.1]hexane -2,2-dicarboxylate* (4m)**



R_f: 0.6 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 81%, 74.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 2H), 8.04 – 7.99 (m, 3H), 7.92 (s, 1H), 7.52 – 7.47 (m, 2H), 7.35 (dd, *J* = 8.8, 1.7 Hz, 1H), 4.34 – 4.26 (m, 4H), 3.44 (t, *J* = 2.1 Hz, 1H), 3.12 – 3.02 (m, 2H), 1.41 (d, *J* = 5.5 Hz, 3H), 1.38 – 1.31 (m, 6H), 1.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 169.9, 132.0, 131.8, 131.3, 130.8, 130.8, 128.7, 128.2, 126.3, 126.10, 125.9, 125.6 (d, *J* = 8.0 Hz), 124.3 (dd, *J* = 291.1 Hz, 286.3 Hz), 123.9, 62.3 (d, *J* = 4.3 Hz), 61.0 (dd, *J* = 18.1 Hz, 14.3 Hz) , 58.9 (dd, *J* = 17.6 Hz, 14.7 Hz), 57.4, 44.4 (dd, *J* = 13.6 Hz, 4.2 Hz), 39.3

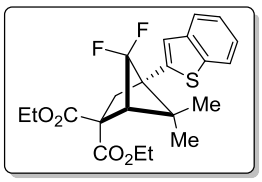
(d, *J* = 3.3 Hz), 21.9 (d, *J* = 15.5 Hz), 21.0 (d, *J* = 8.9 Hz), 14.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -94.87 (d, *J* = 183.3 Hz), -123.27 (d, *J* = 183.3 Hz). HRMS (ESI) calcd for $C_{28}H_{29}F_2O_4$ $[M+H]^+$ 467.2028, found 467.2026.

***Diethyl 4-(benzofuran-2-yl)-5,5-difluoro-6,6-dimethylbicyclo[2.1.1]hexane -2,2-dicarboxylate* (4n)**



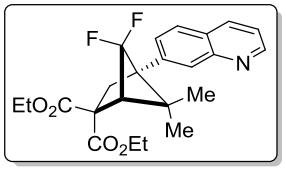
R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 93%, 75.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.33 – 7.23 (m, 2H), 6.69 (s, 1H), 4.33 – 4.24 (m, 4H), 3.40 (t, *J* = 2.1 Hz, 1H), 3.08 (s, 2H), 1.50 (d, *J* = 5.5 Hz, 3H), 1.36 – 1.29 (m, 6H), 1.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 169.5, 154.8, 149.9, 128.0 124.3, 122.9, 122.7 (dd, *J* = 292.1 Hz, 287.2 Hz), 120.9, 111.2, 105.2, 62.3 (d, *J* = 4.0 Hz), 58.9 (dd, *J* = 17.0 Hz, 14.9 Hz), 57.3, 56.7 (dd, *J* = 18.9 Hz, 14.7 Hz), 44.9 (dd, *J* = 12.6 Hz, 4.2 Hz), 36.4 (d, *J* = 3.3 Hz), 21.8 (d, *J* = 15.7 Hz), 20.5 (d, *J* = 9.4 Hz), 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -96.21 (d, *J* = 180.4 Hz), -124.42 (d, *J* = 180.3 Hz). HRMS (ESI) calcd for $C_{22}H_{25}F_2O_5$ $[M+H]^+$ 407.1665, found 407.1660.

***Diethyl 4-(benzo[b]thiophen-2-yl)-5,5-difluoro-6,6-dimethylbicyclo[2.1.1]hexane -2,2-dicarboxylate* (4o)**



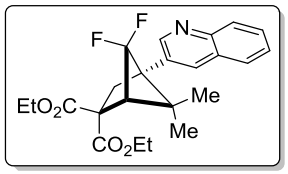
R_f: 0.6 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 97%, 82.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.4 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.35 – 4.23 (m, 2H), 7.26 (s, 1H), 4.32 – 4.23 (m, 4H), 3.43 (t, *J* = 2.1 Hz, 1H), 3.08 (d, *J* = 14.0 Hz, 1H), 3.10 – 3.00 (m, 1H), 1.44 (d, *J* = 5.5 Hz, 3H), 1.36 – 1.29 (m, 6H), 1.06 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.8, 169.5, 139.5, 139.3, 134.9, 124.4, 124.4, 123.5, 123.2 (dd, *J* = 292.7 Hz, 286.9 Hz), 122.5, 122.1, 62.3 (d, *J* = 6.6 Hz), 58.8 (dd, *J* = 17.1 Hz, 14.8 Hz), 58.5 (dd, *J* = 18.8, 14.8 Hz), 57.4, 45.1 (dd, *J* = 13.1 Hz, 4.2 Hz), 38.9 (d, *J* = 3.1 Hz), 21.6 (d, *J* = 15.6 Hz), 20.1 (d, *J* = 8.6 Hz), 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -96.29 (d, *J* = 181.1 Hz), -123.99 (d, *J* = 180.7 Hz). HRMS (ESI) calcd for $C_{22}H_{25}F_2O_4S$ $[M+H]^+$ 423.1436, found 423.1436.

***Diethyl 5,5-difluoro-6,6-dimethyl-4-(quinolin-6-yl)bicyclo[2.1.1]hexane -2,2-dicarboxylate* (4p)**



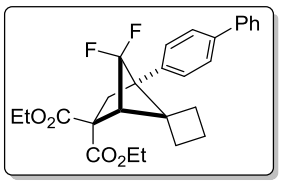
R_f: 0.5 (petroleum ether/ethyl acetate 5:1). Colorless liquid (Yield: 95%, 79.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 4.2 Hz, 1H), 8.13 (d, *J* = 7.7 Hz, 1H), 8.08 (d, *J* = 8.7 Hz, 1H), 7.71 (s, 1H), 7.57 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.41 – 7.39 (m, 1H), 4.30 – 4.21 (m, 4H), 3.41 (t, *J* = 2.1 Hz, 1H), 3.06 – 2.96 (m, 2H), 1.35 – 1.26 (m, 9H), 1.17 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 169.6, 150.6, 147.5, 136.0, 132.3, 129.9, 128.2, 127.8, 125.7, 124.0 (dd, *J* = 291.0 Hz, 286.3 Hz), 121.4, 62.2 (d, *J* = 8.3 Hz), 60.6 (dd, *J* = 18.3 Hz, 14.4 Hz), 58.9 (dd, *J* = 17.4 Hz, 14.8 Hz), 57.3, 44.4 (dd, *J* = 13.4 Hz, 4.0 Hz), 39.3 (d, *J* = 3.1 Hz), 21.7 (d, *J* = 15.5 Hz), 20.8 (d, *J* = 8.8 Hz), 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -95.13 (d, *J* = 183.5 Hz), -123.48 (d, *J* = 183.3 Hz). HRMS (ESI) calcd for $C_{23}H_{26}F_2NO_4$ $[M+H]^+$ 418.1824, found 418.1824.

***Dithyl 5,5-difluoro-6,6-dimethyl-4-(quinolin-3-yl)bicyclo[2.1.1]hexane -2,2-dicarboxylate* (4q)**



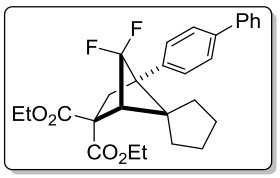
R_f: 0.5 (petroleum ether/ethyl acetate 5:1). Colorless liquid (Yield: 92%, 76.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 2.2 Hz, 1H), 8.14 – 8.05 (m, 2H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.73 (t, *J* = 7.3 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 4.34 – 4.23 (m, 4H), 3.45 (t, *J* = 2.1 Hz, 1H), 3.12 – 3.05 (m, 1H), 3.02 (d, *J* = 13.6 Hz, 1H), 1.38 (d, *J* = 5.4 Hz, 3H), 1.33 – 1.28 (m, 6H), 1.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 169.5, 148.7, 147.4, 134.0, 129.7, 129.3, 127.8, 127.7, 127.1, 126.9, 123.9 (dd, *J* = 291.2 Hz, 286.2 Hz), 62.4 (d, *J* = 6.6 Hz), 59.1 (dd, *J* = 18.6 Hz, 14.7 Hz), 58.9 (dd, *J* = 17.3 Hz, 14.8 Hz), 57.3, 44.6 (dd, *J* = 13.3 Hz, 4.2 Hz), 38.9, 21.8 (d, *J* = 15.5 Hz), 20.8 (d, *J* = 9.3 Hz), 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -94.92 (d, *J* = 183.3 Hz), -123.24 (d, *J* = 183.2 Hz). HRMS (ESI) calcd for $C_{23}H_{26}F_2NO_4$ $[M+H]^+$ 418.1824, found 418.1826.

***Diethyl 1-([1,1'-biphenyl]-4-yl)-6,6-difluorospiro[bicyclo[2.1.1]hexane -5,1'-cyclobutane]-3,3-dicarboxylate* (4r)**



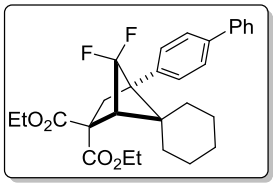
R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 93%, 84.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 4H), 7.54 – 7.44 (m, 4H), 7.40 – 7.35 (m, 1H), 4.34 – 4.21 (m, 4H), 3.45 (t, *J* = 2.4 Hz, 1H), 2.96 (dd, *J* = 12.6 Hz, 5.0 Hz, 1H), 2.81 (d, *J* = 12.7 Hz, 1H), 2.44 – 2.34 (m, 1H), 2.24 – 2.15 (m, 1H), 2.08 – 2.02 (m, 2H), 1.82 – 1.71 (m, 1H), 1.64 – 1.57 (m, 1H), 1.37 – 1.28 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.4, 169.4, 140.7, 140.5, 133.1, 128.8, 127.4, 127.3, 127.1, 127.0, 123.1 (dd, *J* = 301.6 Hz, 278.3 Hz), 62.2 (d, *J* = 11.3 Hz), 59. (dd, *J* = 19.3 Hz, 14.2 Hz), 57.7 (dd, *J* = 19.4 Hz, 16.0 Hz), 55.7 (d, *J* = 2.8 Hz), 51.3 (d, *J* = 11.8 Hz), 36.4, 27.2 (d, *J* = 6.2 Hz), 24.2 (d, *J* = 7.6 Hz), 15.2 (d, *J* = 4.2 Hz), 14.0, 14.0 . ^{19}F NMR (377 MHz, $CDCl_3$) δ -99.10 (d, *J* = 179.0 Hz), -131.18 (d, *J* = 179.1 Hz). HRMS (ESI) calcd for $C_{27}H_{29}F_2O_4$ $[M+H]^+$ 455.2028, found 455.2027.

***Diethyl 1-([1,1'-biphenyl]-4-yl)-6,6-difluorospiro[bicyclo[2.1.1]hexane -5,1'-cyclopentane]-3,3-dicarboxylate* (4s)**



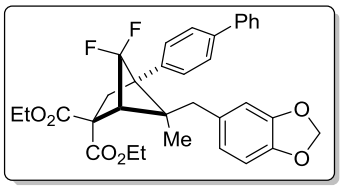
R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 94%, 88.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 4H), 7.48 – 7.37 (m, 2H), 7.42 – 7.34 (m, 3H), 4.37 – 4.22 (m, 4H), 3.43 (t, *J* = 2.2 Hz, 1H), 3.08 (dd, *J* = 12.8 Hz, 4.7 Hz, 1H), 2.92 (d, *J* = 12.8 Hz, 1H), 2.10 – 1.98 (m, 1H), 1.92 – 1.85 (m, 1H), 1.84 – 1.75 (m, 1H), 1.62 – 1.47 (m, 4H), 1.43 – 1.37 (m, 1H), 1.37 – 1.29 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.1, 169.8, 140.6, 140.4, 133.1, 128.8, 127.4, 127.3, 127.2, 127.0, 123.8 (dd, *J* = 294.8 Hz, 282.4 Hz), 62.2 (d, *J* = 13.4 Hz), 60.4 (dd, *J* = 18.9 Hz, 14.0 Hz), 58.8 (dd, *J* = 17.9 Hz, 15.2 Hz), 57.2 (d, *J* = 2.4 Hz), 55.4 (dd, *J* = 13.4 Hz, 3.6 Hz), 39.1, 31.1 (d, *J* = 11.7 Hz), 29.7 (d, *J* = 8.0 Hz), 26.0 (d, *J* = 5.0 Hz), 25.6, 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -98.76 (d, *J* = 181.2 Hz), -127.13 (d, *J* = 181.1 Hz). HRMS (ESI) calcd for $C_{28}H_{31}F_2O_4$ $[M+H]^+$ 469.2185, found 469.2185.

Diethyl 1-([1,1'-biphenyl]-4-yl)-6,6-difluorospiro[bicyclo[2.1.1]hexane-5,1' -cyclohexane]-3,3-dicarboxylate **(4t)**



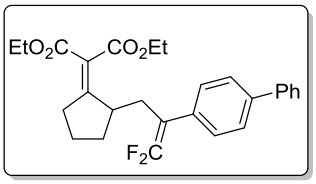
R_f: 0.4 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 95%, 91.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 4H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.34 (m, 3H), 4.40 – 4.14 (m, 4H), 3.65 (t, *J* = 2.4 Hz, 1H), 3.12 (dd, *J* = 12.7 Hz, 3.0 Hz, 1H), 2.89 (d, *J* = 12.8 Hz, 1H), 2.42 (d, *J* = 14.0 Hz, 1H), 1.81 – 1.67 (m, 3H), 1.50 – 1.15 (m, 12H).^{13}C NMR (151 MHz, $CDCl_3$) δ 170.1, 169.9, 140.7, 140.3, 132.5, 128.8, 127.5, 127.4, 127.1, 127.0, 124.7 (dd, *J* = 289.4 Hz, 282.4 Hz), 62.2 (d, *J* = 18.3 Hz), 61.1 (dd, *J* = 18.3 Hz, 13.3 Hz), 57.6, 56.3 (t, *J* = 15.8 Hz), 49.9 (d, *J* = 12.3 Hz), 37.7, 30.8 (d, *J* = 17.2 Hz), 28.8 (d, *J* = 7.5 Hz), 26.3, 24.4, 23.7, 13.9,13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -93.21 (d, *J* = 183.1 Hz), -120.80 (d, *J* = 183.1 Hz). HRMS (ESI) calcd for $C_{29}H_{32}F_2O_4Na$ $[M+Na]^+$ 505.2161, found 505. 2164.

Diethyl 4-([1,1'-biphenyl]-4-yl)-5-(benzo[d][1,3]dioxol-5-ylmethyl)-6,6-difluoro -5-methylbicyclo[2.1.1]hexane-2,2-dicarboxylate **(4u)**



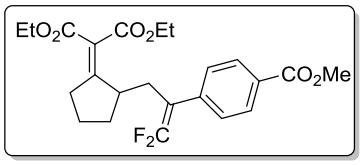
R_f: 0.3 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 89%, 100.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 4H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.38 – 7.33 (m, 3H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.70 – 6.62 (m, 2H), 5.91 (dd, *J* = 7.4, 1.5 Hz, 2H), 4.26 – 4.12 (m, 4H), 3.54 (t, *J* = 1.9 Hz, 1H), 3.42 (dd, *J* = 14.5 Hz, 3.1 Hz, 1H), 3.03 – 2.92 (m, 2H), 2.40 (dd, *J* = 14.6 Hz, 4.7 Hz, 1H), 1.29 (d, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 1.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 169.6, 147.4, 145.9, 140.6 (d, *J* = 7.2 Hz), 132.6, 128.8, 127.4, 127.4, 127.1, 122.9, 110.4, 108.0, 100.8, 62.2 (d, *J* = 15.1 Hz), 61.5 (dd, *J* = 18.3, 13.6 Hz), 57.3, 56.5 (dd, *J* = 17.2 Hz 15.0 Hz), 48.7 (dd, *J* = 13.8 Hz, 4.6 Hz), 40.6 (d, *J* = 15.5 Hz), 39.8, 18.4 (d, *J* = 8.2 Hz), 13.9, 13.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -93.60 (d, *J* = 185.9 Hz), -122.26 (d, *J* = 185.8 Hz). HRMS (ESI) calcd for $C_{33}H_{32}F_2O_6Na$ $[M+Na]^+$ 585.2059, found 585.2071.

***Diethyl 2-(2-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)cyclopentylidene)malonate* (6a)**



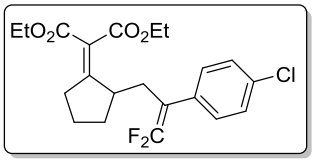
R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 98%, 89.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 4H), 7.50 – 7.44 (m, 4H), 7.39 (d, *J* = 7.2 Hz, 1H), 4.29 – 4.15 (m, 4H), 3.21 – 3.06 (m, 1H), 2.93 – 2.80 (m, 1H), 2.77 – 2.71 (m, 2H), 2.46 – 2.39 (m, 1H), 1.86 – 1.68 (m, 3H), 1.62 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 165.59, 165.29, 154.7 (dd, *J* = 298.1 Hz, 287.7 Hz), 140.6, 140.3, 131.6, 128.9, 128.8, 127.4, 127.1, 127.0, 121.5, 90.6 (dd, *J* = 19.0 Hz, 16.1 Hz), 61.0, 60.8, 42.6, 33.0, 29.6, 29.4, 22.5, 14.1, 14.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -90.00 (d, *J* = 41.5 Hz), -90.11 (d, *J* = 41.5 Hz). HRMS (ESI) calcd for $C_{27}H_{29}F_2O_4$ $[M+H]^+$ 455.2028, found 455.2038.

***Diethyl2-(2-(3,3-difluoro-2-(4-(methoxycarbonyl)phenyl)allyl)cyclopentylidene) malonate* (6b)**



R_f: 0.3 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 63%, 54.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) 8.05 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 4.26 – 4.14 (m, 4H), 3.92 (s, 3H), 3.11 – 3.03 (m, 1H), 2.84 – 2.61 (m, 3H), 2.45 – 2.35 (m, 1H), 1.77 – 1.73 (m, 2H), 1.66 – 1.51 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 166.8, 165.4, 154.9 (dd, *J* = 293.5 Hz, 288.4 Hz), 137.6 (t, *J* = 3.7 Hz), 129.8, 129.2, 128.5 (t, *J* = 3.4 Hz), 121.7, 90.8 (dd, *J* = 21.8 Hz, 13.0 Hz), 61.1, 60.9, 52.2, 42.4, 33.0, 29.5, 29.4, 22.5, 14.2, 14.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ -88.29 (d, *J* = 37.1 Hz), -88.52 (d, *J* = 37.1 Hz). HRMS (ESI) calcd for $C_{23}H_{27}F_2O_6$ $[M+H]^+$ 437.1770, found 437.1776.

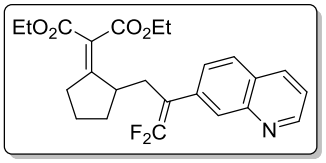
***Diethyl 2-(2-(2-(4-chlorophenyl)-3,3-difluoroallyl)cyclopentylidene)malonate* (6c)**



R_f: 0.5 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 81%, 66.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 4H), 4.28 – 4.14 (m, 4H), 3.12 – 3.01 (m, 1H), 2.88 – 2.75 (m, 1H), 2.73 – 2.62 (m, 2H), 2.42 – 2.33 (m, 1H), 1.80 – 1.72 (m,

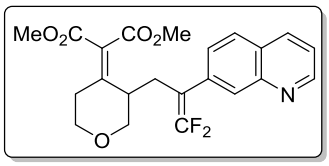
2H), 1.66 – 1.61 (m, 1H), 1.60 – 1.53(m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.6, 165.3, 154.6 (dd, *J* = 291.4 Hz, 287.7 Hz), 133.4, 131.1, 129.9 (t, *J* = 3.0 Hz), 128.6, 121.6, 90.2 (dd, *J* = 21.0 Hz, 14.6 Hz), 60.9, 60.8, 42.3, 32.9, 29.5, 29.4, 22.4, 14.1, 14.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -89.76 (d, *J* = 40.7 Hz), -89.91 (d, *J* = 40.7 Hz). HRMS (ESI) calcd for $C_{21}H_{24}ClF_2O_4$ $[M+H]^+$ 413.1326, found 413.1325.

Diethyl 2-(2-(3,3-difluoro-2-(quinolin-7-yl)allyl)cyclopentylidene)malonate **(6d)**



R_f: 0.3 (petroleum ether/ethyl acetate 5:1). Colorless liquid (Yield: 92%, 79.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.20 (d, *J* = 9.0 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.91 (s, 1H), 7.78– 7.75 (m, 1H), 7.42 (dd, *J* = 8.3 Hz, 4.2 Hz, 1H), 4.25 – 4.07 (m, 4H), 3.15 – 3.07 (m, 1H), 2.89 – 2.78 (m, 2H), 2.73 – 2.63 (m, 1H), 2.53 – 2.45 (m, 1H), 1.84 – 1.67 (m, 3H), 1.62 – 1.53 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.7, 165.3, 165.2, 154.9 (dd, *J* = 292.8 Hz, 287.7 Hz), 150.7, 147.5, 136.1, 130.9 (t, *J* = 3.9 Hz), 129.9 (t, *J* = 3.5 Hz), 129.5, 128.2, 127.6 (t, *J* = 3.4 Hz), 121.6, 121.4, 90.7 (dd, *J* = 22.1 Hz, 12.9 Hz), 60.9, 60.8, 42.5 (t, *J* = 2.6 Hz), 32.9, 29.6, 29.4, 22.5, 14.1, 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -88.93 (d, *J* = 39.1 Hz), -89.45 (d, *J* = 39.3 Hz). HRMS (ESI) calcd for $C_{24}H_{26}F_2NO_4$ $[M+H]^+$ 430.1824, found 430.1826.

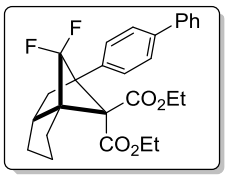
Dimethyl 2-(3-(3,3-difluoro-2-(quinolin-7-yl)allyl)tetrahydro-4H-pyran-4-ylidene) malonate **(6e)**



R_f: 0.2 (petroleum ether/ethyl acetate 5:1). Colorless liquid (Yield: 83%, 73.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 4.2 Hz, 1H), 8.21 – 8.16 (m, 1H), 8.10 (d, *J* = 8.8 Hz, 1H), 7.81 (s, 1H), 7.71 (dd, *J* = 8.8 Hz, 1.9 Hz, 1H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.11 (dd, *J* = 11.2, 6.1 Hz, 1H), 3.93 (d, *J* = 11.7 Hz, 1H), 3.73 (s, 3H), 3.50 – 3.40 (m, 2H), 3.39 (s, 3H), 3.06 (t, *J* = 3.4 Hz, 2H), 2.97 – 2.82 (m, 2H), 2.54 – 2.46 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.3, 165.2, 157.0, 154.8 (dd, *J* = 293.4 Hz, 289.4 Hz), 150.7, 147.4, 136.1, 131.1 (t, *J* = 3.9 Hz), 129.7 (t, *J* = 3.4 Hz), 129.6, 128.1,

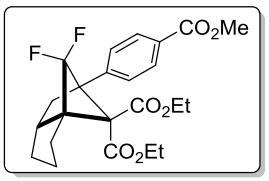
127.6 (t, *J* = 3.4 Hz), 123.9, 121.5, 89.8 (dd, *J* = 21.9 Hz, 13.7 Hz), 70.2, 68.5, 52.2, 52.0, 39.0 (d, *J* = 2.6 Hz), 29.0, 28.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -87.33 (d, *J* = 36.1 Hz), -88.71 (d, *J* = 36.1 Hz). HRMS (ESI) calcd for $C_{22}H_{22}F_2NO_5$ $[M+H]^+$ 418.1461, found 418.1461.

***Diethyl 2-([1,1'-biphenyl]-4-yl)-3,3-difluorohexahydro-1H-2,3a-methanopentalene -7,7-dicarboxylate* (7a)**



R_f: 0.4 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 95%, 86.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.61 (dd, *J* = 11.7 Hz, 7.7 Hz, 4H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.33 (m, 1H), 4.35 – 4.26 (m, 2H), 4.15 – 3.96 (m, 2H), 2.72 – 2.65 (m, 1H), 2.28 – 2.17 (m, 1H), 2.17 – 2.14 (m, 2H), 2.08 – 1.95 (m, 3H), 1.87 – 1.78 (m, 1H), 1.78 – 1.70 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 166.7(d, *J* = 9.1 Hz), 141.1, 140.1, 133.5, 128.7, 128.2, 127.2, 127.1, 126.7, 123.0 (dd, *J* = 299.3 Hz, 272.2 Hz), 69.8 (t, *J* = 17.7 Hz), 68.2 (dd, *J* = 19.0 Hz, 15.3 Hz), 63.6 (d, *J* = 19.3 Hz), 61.9, 61.4, 60.8, 42.9, 34.7, 26.5, 25.9 (d, *J* = 5.2 Hz), 20.1, 14.1, 13.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -108.55 (d, *J* = 176.3 Hz), -134.72 (d, *J* = 175.9 Hz). HRMS (ESI) calcd for $C_{27}H_{28}F_2O_4Na$ $[M+H]^+$ 477.1848, found 477.1841.

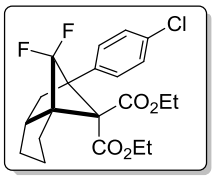
***3,3-difluoro-2-(4-(methoxycarbonyl)phenyl)hexahydro-1H-2,3a-methanopentalene -7,7-dicarboxylate* (7b)**



R_f: 0.3 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 69%, 60.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR δ 8.00 (d, *J* = 1.1 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.06 – 3.94 (m, 2H), 3.92 (s, 3H), 2.62 (t, *J* = 11.2 Hz, 1H), 2.25 – 2.18 (m, 1H), 2.15 – 2.06 (m, 2H), 2.05 – 1.94 (m, 3H), 1.84 – 1.76 (m, 1H), 1.67 (d, *J* = 7.7 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.98 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 166.7, 166.5 (d, *J* = 9.0 Hz), 139.77, 129.31, 129.05, 127.9, 122.8 (dd, *J* = 299.5, 272.4 Hz), 69.9 (t, *J* = 17.8 Hz), 68.2(dd, *J* = 19.1, 15.4 Hz), 63.7 (d, *J* = 19.4 Hz), 62.1, 61.6, 52.4, 43.1, 34.7, 26.6, 25.9 (d, *J*

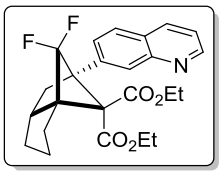
= 5.3 Hz), 20.1, 14.2, 13.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -108.38 (d, *J* = 176.4 Hz), -134.90 (d, *J* = 176.4 Hz). HRMS (ESI) calcd for $C_{23}H_{27}F_2O_6$ $[M+H]^+$ 437.1770, found 437.1769.

***Diethyl 2-(4-chlorophenyl)-3,3-difluorohexahydro-1H-2,3a-methanopentalene-7,7 -dicarboxylate* (7c)**



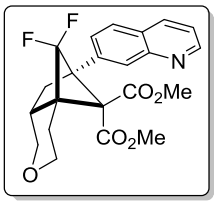
R_f: 0.4 (petroleum ether/ethyl acetate 10:1). Colorless liquid (Yield: 77%, 63.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 4.32 – 4.26 (m, 2H), 4.10 – 3.98 (m, 2H), 2.64 – 2.56 (m, 1H), 2.22 – 2.15 (m, 1H), 2.14 – 2.06 (m, 2H), 2.03 – 1.93 (m, 3H), 1.84 – 1.77 (m, 1H), 1.72– 1.64 (m, 1H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 166.5 (d, *J* = 9.1 Hz), 133.2, 132.9, 129.2, 128.7, 128.1, 124.7 (*J* = 299.0 Hz, 271.8Hz), 69.7 (t, *J* = 18.1 Hz), 67.7 (d, *J* = 15.8 Hz), 61.9, 61.4, 42.9, 34.6, 26.5, 25.8 (d, *J* = 5.2 Hz), 20.1, 14.1, 13.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -108.70 (d, *J* = 176.1 Hz), -134.93 (d, *J* = 176.2 Hz). HRMS (ESI) calcd for $C_{21}H_{24}ClF_2O_4$ $[M+H]^+$ 413.1326, found 413.1323.

***Diethyl 3,3-difluoro-2-(quinolin-7-yl)hexahydro-1H-2,3a-methanopentalene-7,7 -dicarboxylate* (7d)**



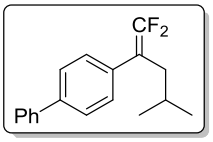
R_f: 0.3 (petroleum ether/ethyl acetate 5:1). Colorless liquid (Yield: 80%, 68.7mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.20 – 8.08 (m, 3H), 8.00 (s, 1H), 7.40 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.36 – 4.31 (m, 2H), 4.08 – 3.89 (m, 2H), 2.77 – 2.68 (m, 1H), 2.29 – 2.20 (m, 1H), 2.20 – 2.10 (m, 2H), 2.10 – 1.99 (m, 3H), 1.85 – 1.80 (m, 1H), 1.74 – 1.68 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 166.5, 150.3, 147.6, 136.3, 133.0, 129.8, 128.9, 127.8, 126.2, 122.9 (dd, *J* = 299.0 Hz, 271.8 Hz), 121.0, 69.8 (t, *J* = 17.8 Hz), 68.2 (dd, *J* = 18.1 Hz, 15.1 Hz), 63.7 (d, *J* = 19.2 Hz), 62.0, 61.4, 43.1, 34.8, 26.55, 25.8 (d, *J* = 5.3 Hz), 20.1, 14.1, 13.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -108.50 (d, *J* = 175.8 Hz), -134.70 (d, *J* = 175.8 Hz). HRMS (ESI) calcd for $C_{24}H_{26}NF_2O_4$ $[M+H]^+$ 430.1824, found 430.1830.

***Dimethyl 5,5-difluoro-6-(quinolin-7-yl)hexahydro-1H-4a,6-methanocyclopenta[c] pyran-8,8-dicarboxylate* (7e)**



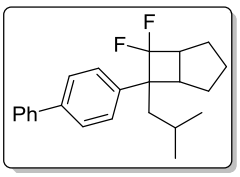
R_f: 0.2 (petroleum ether/ethyl acetate 5:1). Colorless liquid (Yield: 66%, 55.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.19 (dd, *J* = 8.3, 1.8 Hz, 1H), 8.12 (d, *J* = 1.3 Hz, 2H), 7.99 (s, 1H), 7.42 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.08 – 4.01 (m, 2H), 3.89 (s, 3H), 3.74 – 3.67 (m, 1H), 3.58 – 3.51 (m, 1H), 3.50 (s, 3H), 2.76 – 2.72 (m, 1H), 2.50 – 2.41 (m, 1H), 2.35 – 2.20 (m, 2H), 1.87 – 1.82 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 166.6 (d, *J* = 9.1 Hz), 150.5, 147.6, 136.3, 132.5, 129.5, 129.2, 127.9, 126.1, 122.9 (dd, *J* = 300.1 Hz, 274.0 Hz), 121.2, 68.9 (d, *J* = 5.9 Hz), 65.0 (d, *J* = 19.0 Hz), 64.7, 59.9 (t, *J* = 17.9 Hz), 53.3, 52.6, 35.3, 32.6, 24.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ -102.10 (d, *J* = 178.5 Hz), -132.91 (d, *J* = 178.5 Hz). HRMS (ESI) calcd for $C_{22}H_{22}NF_2O_5$ $[M+H]^+$ 418.1461, found 418.1462.

***4-(1,1-difluoro-4-methylpent-1-en-2-yl)-1,1'-biphenyl* (8)**



R_f: 0.8 (petroleum ether). Colorless liquid (Yield: 91%, 123.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 4H), 7.50 – 7.41 (m, 4H), 7.40 – 7.36 (m, 1H), 2.36 – 2.33 (m, 2H), 1.73 – 1.63 (m, 1H), 0.95 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.2 (dd, *J* = 290.4 Hz, 286.4 Hz), 140.6, 140.0, 133. 0 (t, *J* = 4.0 Hz), 128.8, 128.7 (t, *J* = 3.3 Hz), 127.4, 127.1, 127.0, 91.4 (dd, *J* = 22.0 Hz, 12.6 Hz), 36.6, 26.5, 22.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ -91.00 (d, *J* = 43.6 Hz), -91.49 (d, *J* = 43.0 Hz). HRMS (EI) calcd for $C_{18}H_{18}F_2$ $[M]^+$ 272.1371, found 272.1370.

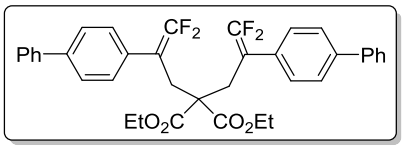
***6-([1,1'-biphenyl]-4-yl)-7,7-difluoro-6-isobutylbicyclo[3.2.0]heptane* (9)**



R_f: 0.8 (petroleum ether). Colorless liquid (Yield: 25%, 17.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 4H), 7.48 – 7.42 (m, 4H), 7.35 (d, *J* = 7.3 Hz, 1H), 6.02 – 5.95 (m, 1H), 5.84 – 5.82 (m 1H), 3.87 (d, *J* = 10.2 Hz, 1H), 3.30 – 3.18 (m, 1H), 2.72 (d, *J* = 17.8 Hz, 1H), 2.44 (m, 1H), 1.73 – 1.70 (m, 2H), 1.22 – 1.15 (m, 1H), 0.90 – 0.87 (m, 2H), 0.76 (d, *J* = 6.7 Hz, 3H), 0.60 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR

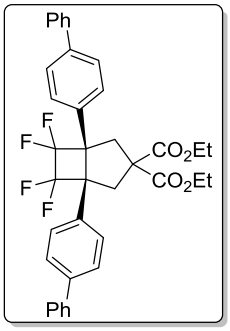
(151 MHz, $CDCl_3$) δ 140.7, 138.9, 134.8, 129.9 (d, *J* =2.3 Hz), 128.7, 128.3 (d, *J* =1.8 Hz), 127.2, 127.0, 126.7, 122.4 (dd, *J* = 295.6 Hz, 292.7 Hz), 61.2 (dd, *J* = 21.6, 19.0 Hz), 47.0 (dd, *J* = 15.8 Hz, 3.7 Hz), 45.8 (dd, *J* = 24.2, 21.2 Hz), 39.6 (d, *J* = 5.9 Hz), 31.7 (d, *J* = 6.7 Hz), 24.6, 23.5, 23.0, 22.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -85.26 (d, *J* = 189.4 Hz), -112.99 (d, *J* = 189.4 Hz). HRMS (EI) calcd for $C_{23}H_{26}F_2$ $[M]^+$ 340.1997, found 340.2000.

Diethyl 2,2-bis(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)malonate **(10)**



R_f: 0.4 (petroleum ether/ethyl acetate 10:1). Colorless solid (Yield: 88%, 271.1 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (t, *J* = 8.2 Hz, 8H), 7.44 (t, *J* = 7.6 Hz, 4H), 7.38 – 7.33 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 4H), 3.50 (q, *J* = 7.1 Hz, 4H), 3.11 (s, 4H), 0.99 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 154.5 (t, *J* = 289.9 Hz), 140.5 (d, *J* = 4.7 Hz), 131.3, 129.6, 128.8, 127.5, 127.0, 126.8, 88.4 (t, *J* = 18.1 Hz), 61.3, 56.5, 31.1, 13.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -88.40 (d, *J* = 36.3 Hz), -88.54 (d, *J* = 36.3 Hz). HRMS (ESI) calcd for $C_{37}H_{33}F_4O_4$ $[M+H]^+$ 617.2309, found 617.2319.

Diethyl 1,5-di([1,1'-biphenyl]-4-yl)-6,6,7,7-tetrafluorobicyclo[3.2.0]heptane -3,3-dicarboxylate **(11)**



R_f: 0.4 (petroleum ether/ethyl acetate 10:1). Colorless solid (Yield: 81%, 99.8 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.0 Hz, 4H), 7.49 (d, *J* = 8.5 Hz, 4H), 7.44 (t, *J* = 7.6 Hz, 4H), 7.38 – 7.34 (m, 2H), 7.14 (d, *J* = 8.2 Hz, 4H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.78 (d, *J* = 15.4 Hz, 2H), 3.26 (d, *J* = 15.6 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 170.1, 140.1 (d, *J* = 17.8 Hz), 134.5, 129.2, 128.8, 127.5, 127.0, 126.7, 64.8(d, *J* = 13.5 Hz), 62.4 (d, *J* = 7.4 Hz), 61. 6, 44.1, 14.0, 13.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -113.77 (d, *J* = 212.4 Hz), -117.38 (d, *J* = 212.3 Hz). HRMS (ESI) calcd for $C_{37}H_{33}F_4O_4$ $[M+H]^+$ 617.2309, found 617.2332.

7. X-ray structures of 4l and 11.

Method for single crystals cultivation: a pure solid sample (10.0 – 20.0 mg) was dissolved in ethyl acetate (0.2 mL) in a vial at room temperature, and hexane (2.0 mL) was added into the above solution slowly while keeping the sample completely dissolved. The vial was properly sealed with parafilm and kept at -20℃ to allow the slow evaporation of the solvents until a single crystal was obtained.

The crystal measurement of compound **4l and 11** was collected on a SuperNova single crystal diffract meter equipped with graphite-monochromated Cu Kα radiation (λ = 1.54184 Å). The X-ray data have been deposited at the Cambridge Crystallographic Data Center (**4l, CCDC: 2251699; 11, CCDC: 2244804**).

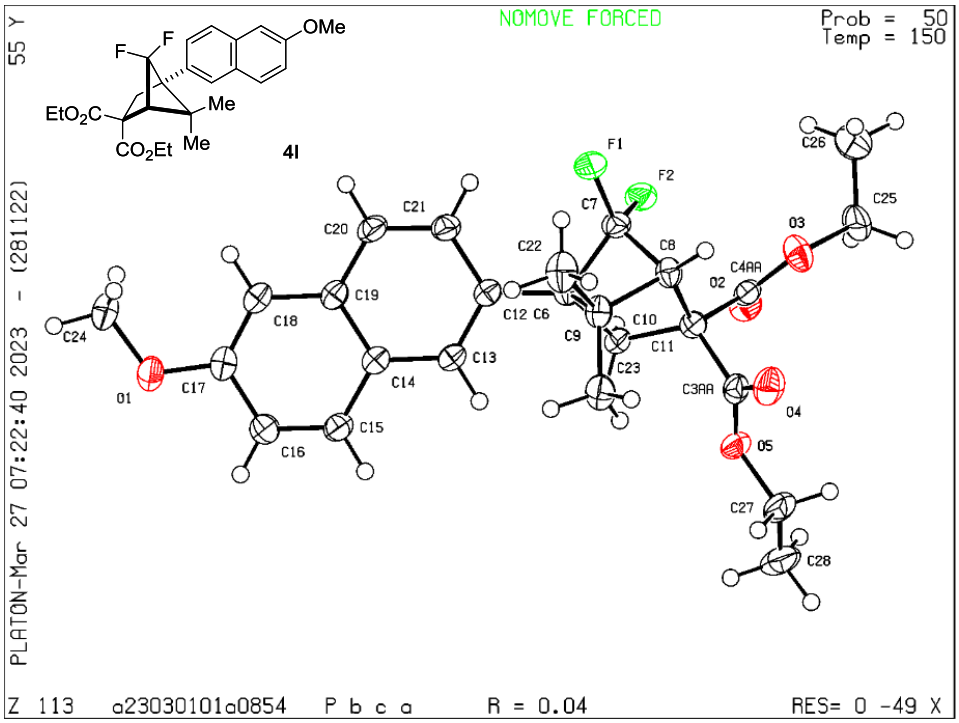


Figure S3. Representative ORTEP diagram of **4l**. Thermal ellipsoids are set at the 50% probability level.

Table S4 Crystal data and structure refinement for 4l.

Identification code	A23030101A0854
Empirical formula	$C_{25}H_{28}F_2O_5$

Formula weight	446.47
Temperature/K	149.99(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	7.61863(13)
b/Å	23.8201(4)
c/Å	24.6464(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4472.74(12)
Z	8
ρ_{calc}g/cm^3	1.326
μ/mm^{-1}	0.855
F(000)	1888.0
Crystal size/mm^3	0.2 × 0.1 × 0.06
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.174 to 146.19
Index ranges	-6 ≤ h ≤ 9, -28 ≤ k ≤ 29, -25 ≤ l ≤ 30
Reflections collected	15316
Independent reflections	4436 [R_{int} = 0.0346, R_{sigma} = 0.0280]
Data/restraints/parameters	4436/0/295
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0430, wR_2 = 0.1143
Final R indexes [all data]	R_1 = 0.0463, wR_2 = 0.1173
Largest diff. peak/hole / e Å^{-3}	0.27/-0.19

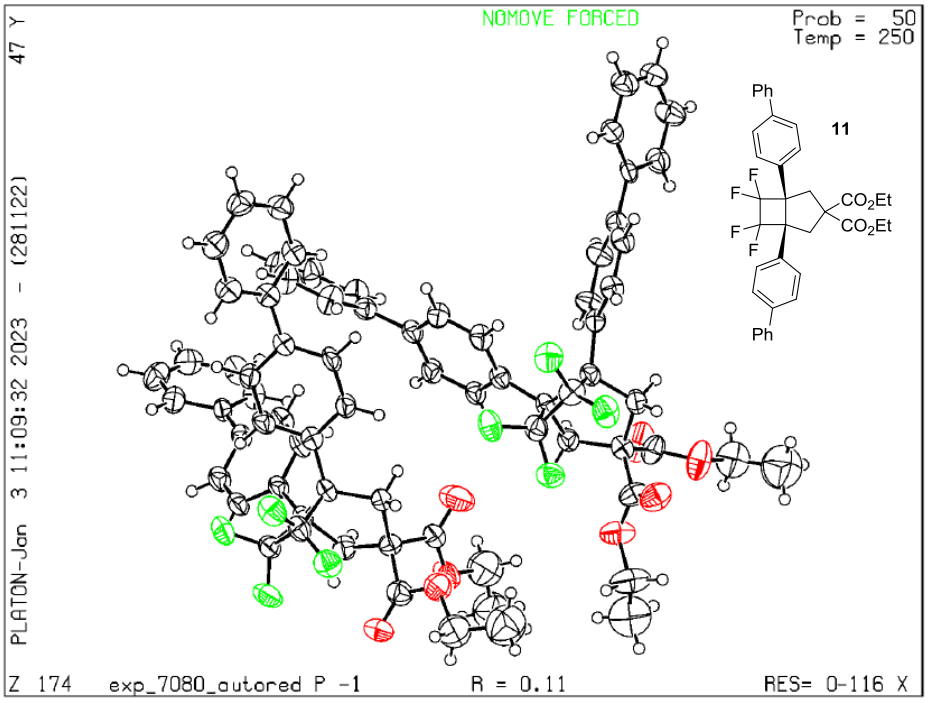


Figure S2. Representative ORTEP diagram of **11**. Thermal ellipsoids are set at the 50% probability level.

Table S5 Crystal data and structure refinement for 11.

Identification code	exp_7080_autored
Empirical formula	$C_{74}H_{63}F_8O_8$
Formula weight	1232.24
Temperature/K	250.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.4768(2)
b/Å	10.8350(3)
c/Å	27.4176(7)
α/°	95.513(2)
β/°	93.604(2)
γ/°	90.033(2)

Volume/Å^3	3091.75(13)
Z	2
ρ_{calc}g/cm^3	1.324
μ/mm^{-1}	0.848
F(000)	1286.0
Crystal size/mm^3	1 × 0.8 × 0.5
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.49 to 133.19
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -32 ≤ l ≤ 32
Reflections collected	48908
Independent reflections	48908 [R_{int} = ?, R_{sigma} = 0.0571]
Data/restraints/parameters	48908/65/817
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.1122, wR_2 = 0.2752
Final R indexes [all data]	R_1 = 0.1313, wR_2 = 0.2859
Largest diff. peak/hole / e Å^{-3}	0.98/-0.53

8. References

1. Guan, Y.; Attard, J. W.; Visco, M. D.; Fisher, T. J.; Mattson, A. E. *Chem. Eur. J.* **2018**, 24,7123 –7127.
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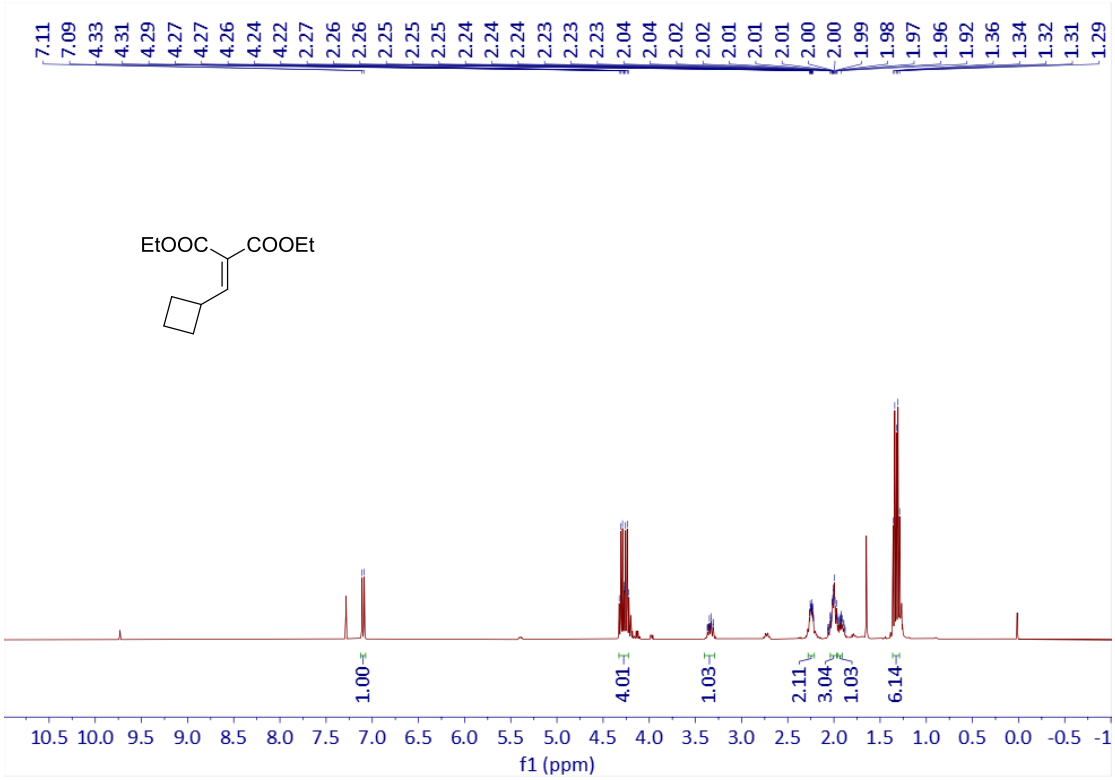
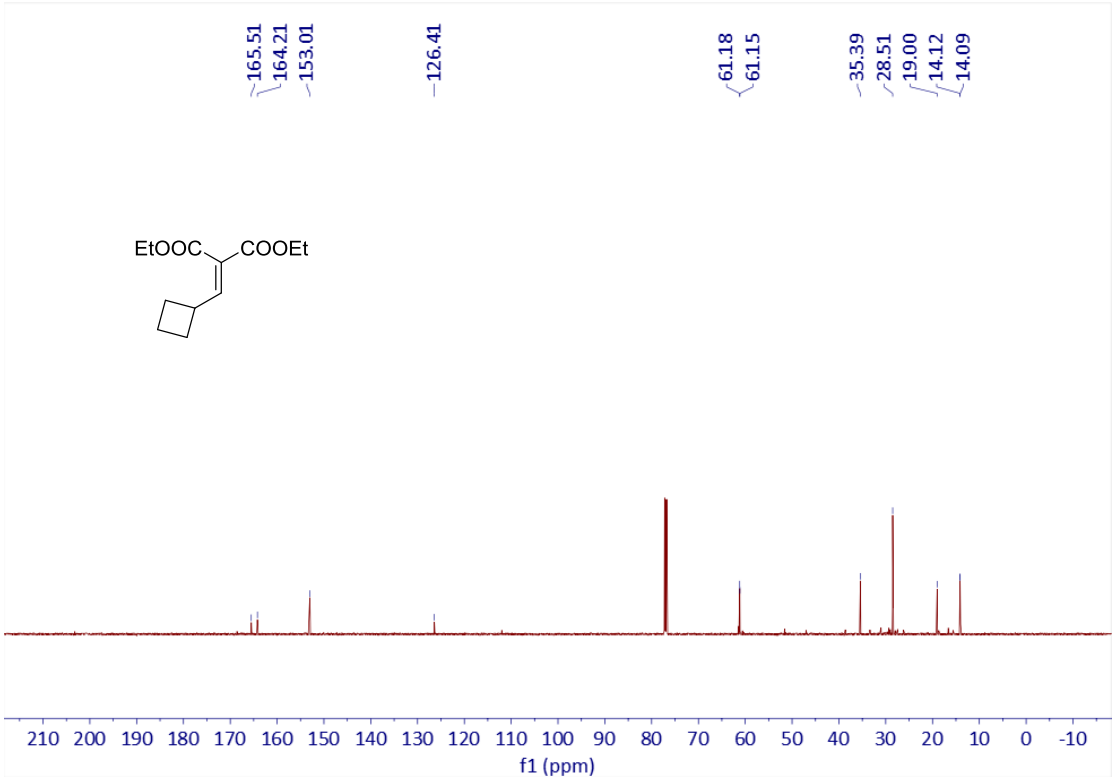
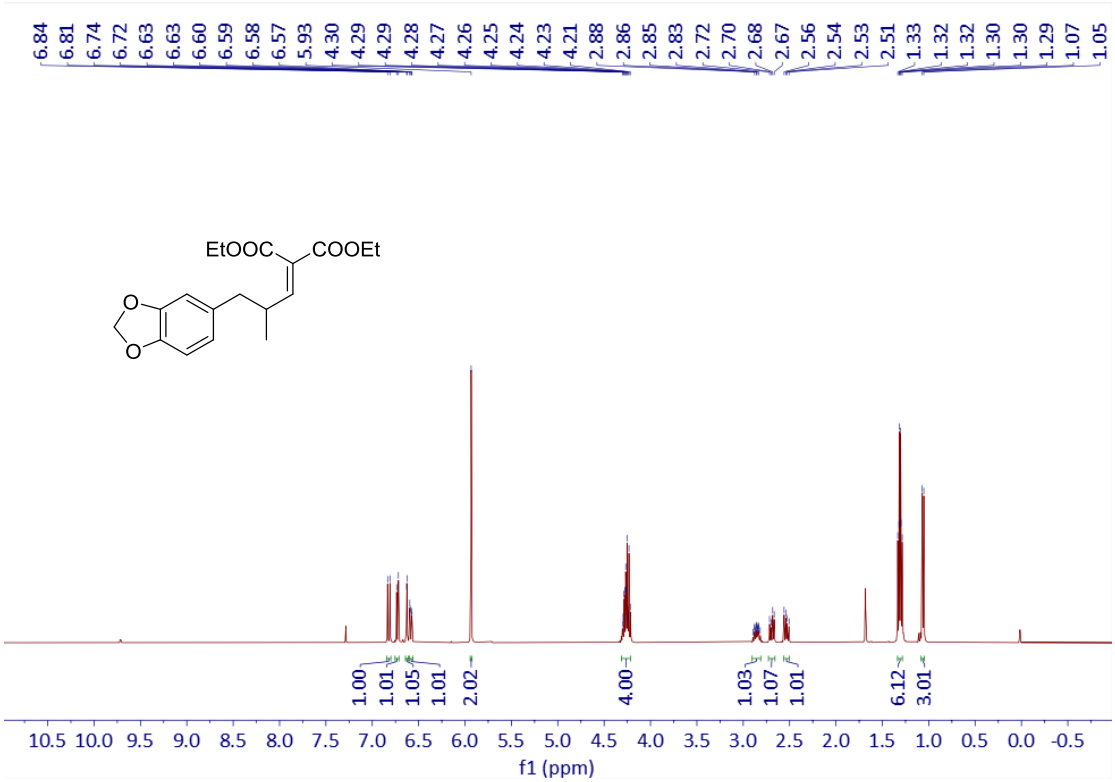
9. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra



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



^{13}C NMR of 1r (151 MHz, $CDCl_3$)



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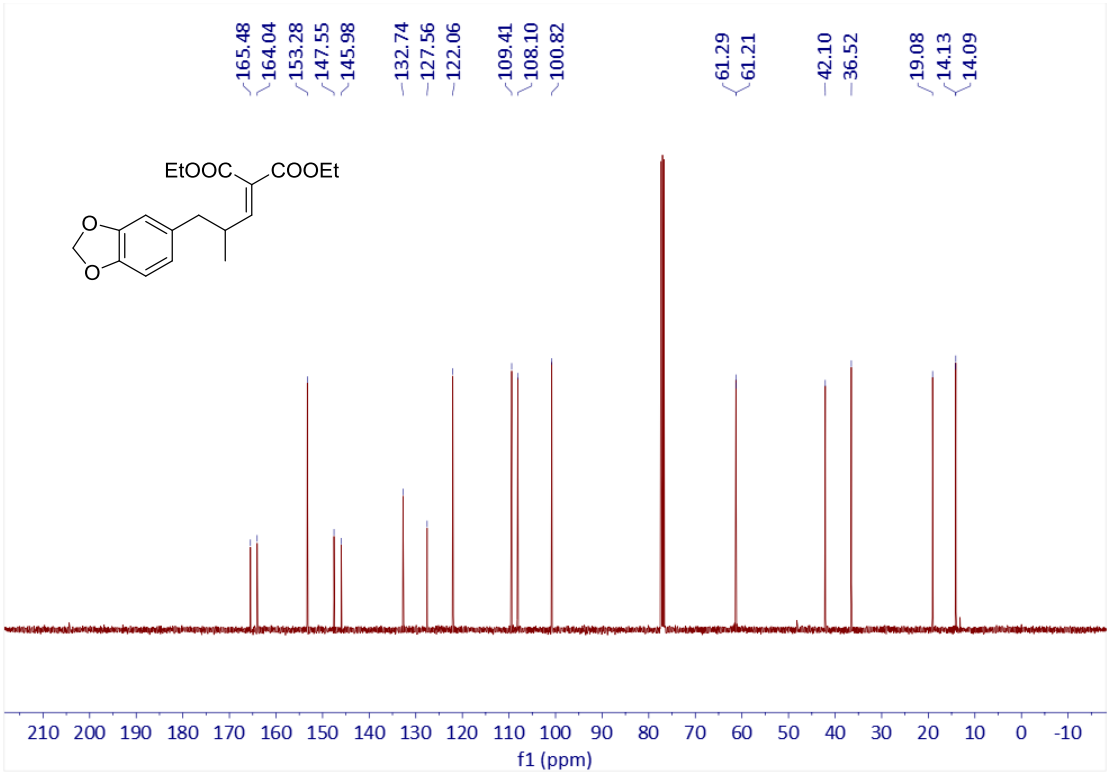
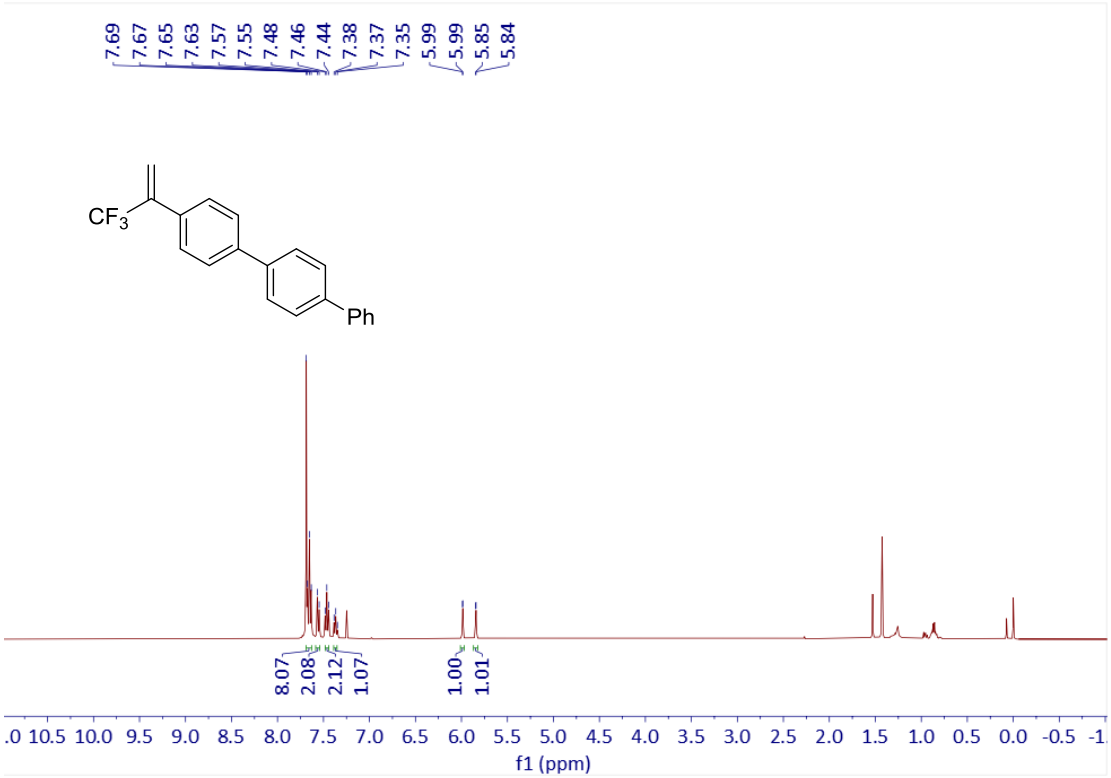
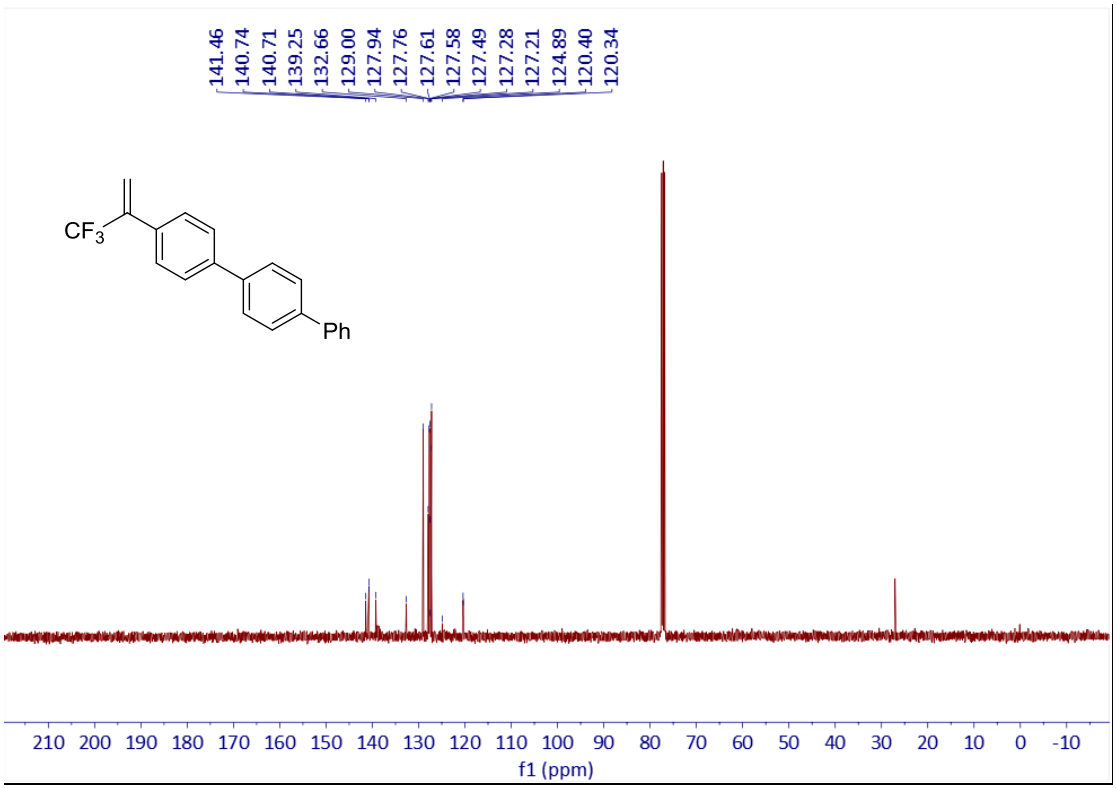


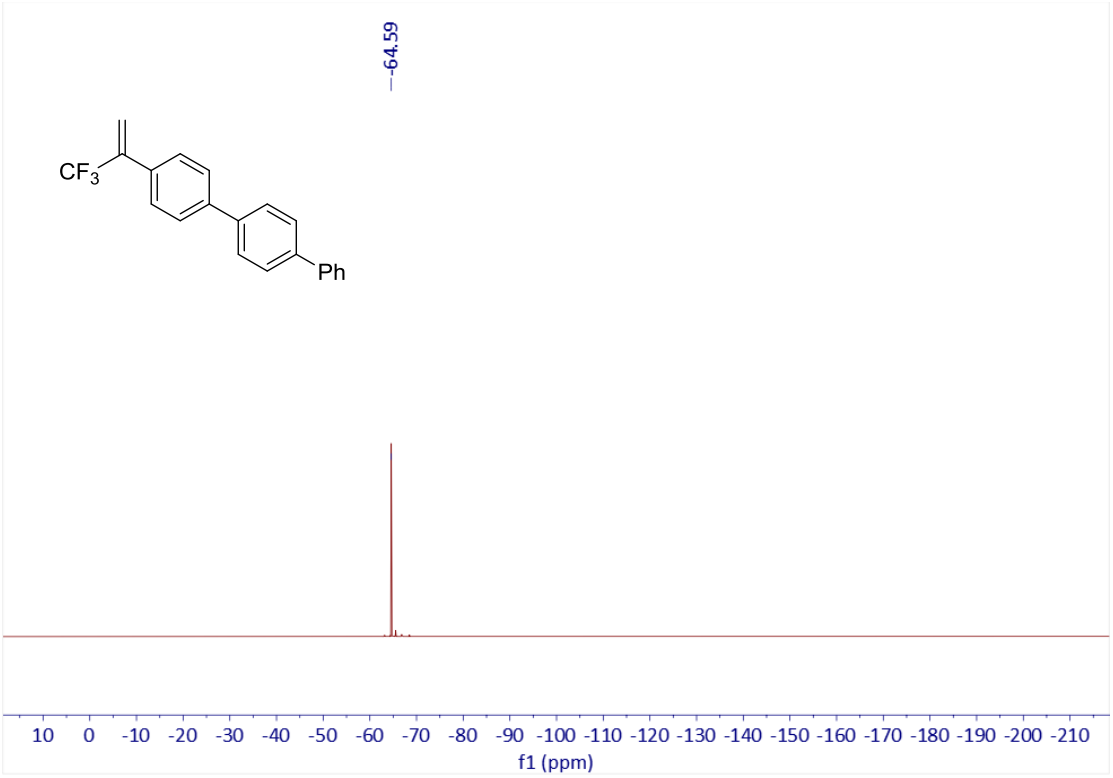
^{13}C NMR of 1u (101 MHz, $CDCl_3$)



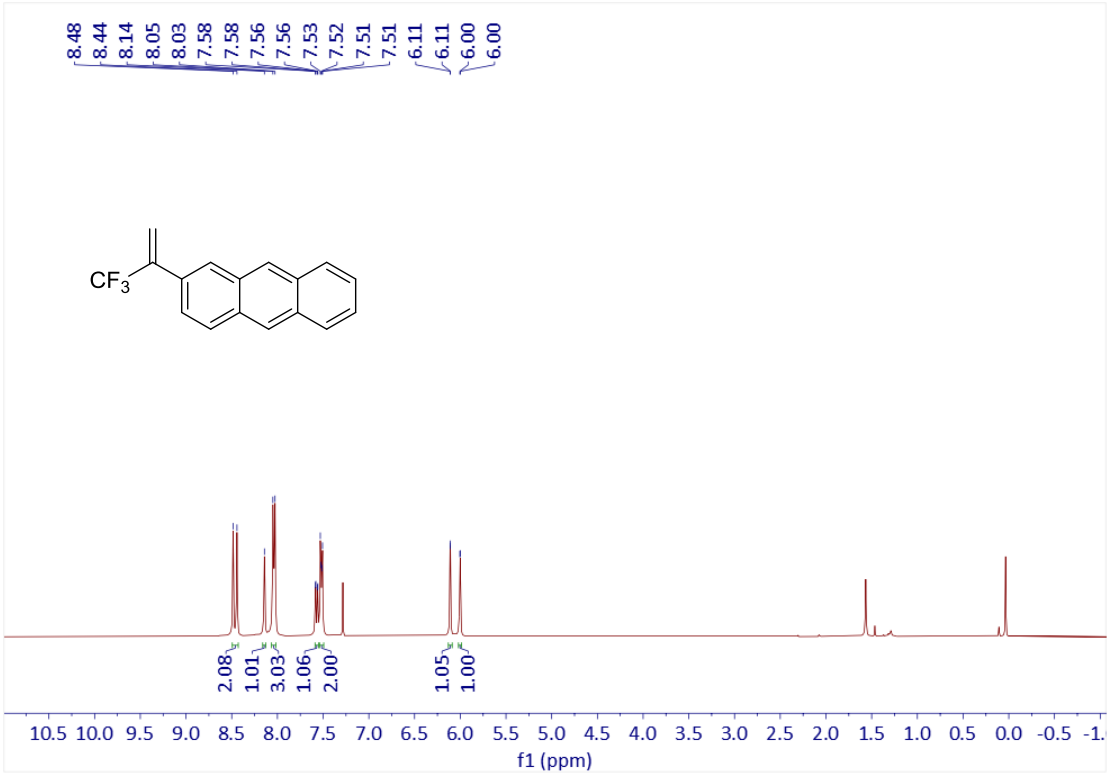
^{1}H NMR of 2k (400 MHz, $CDCl_3$)



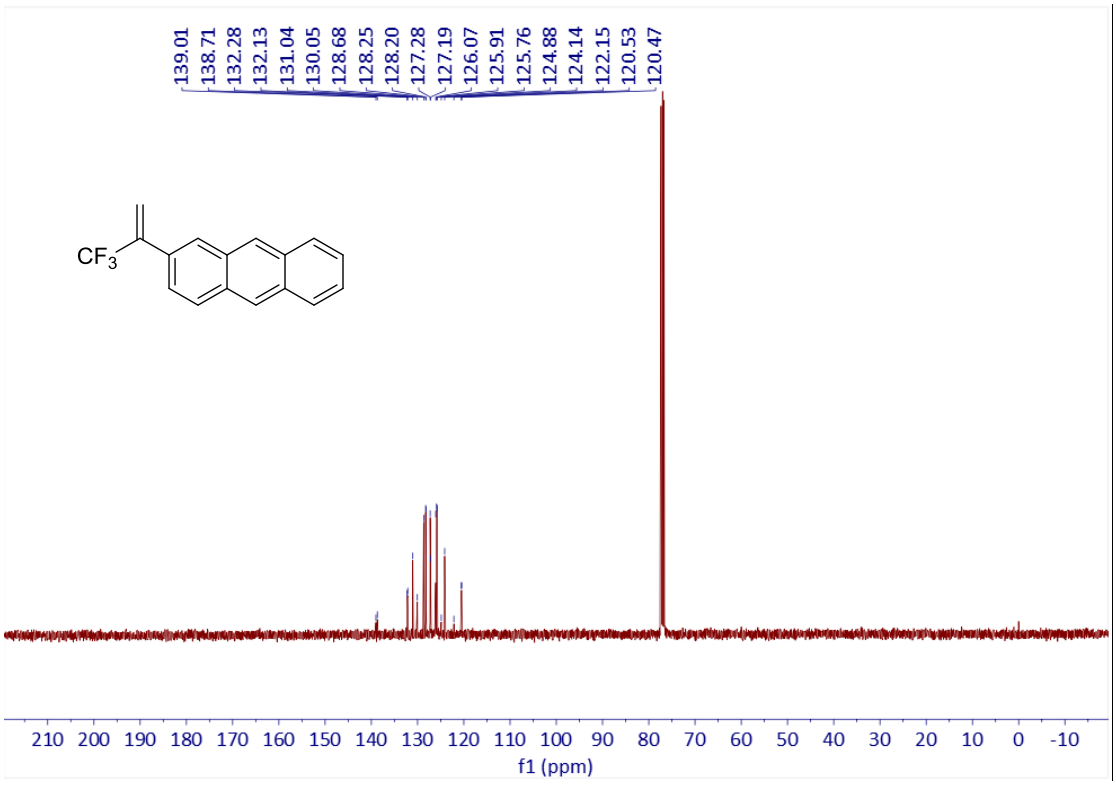
^{13}C NMR of 2k (101 MHz, $CDCl_3$)



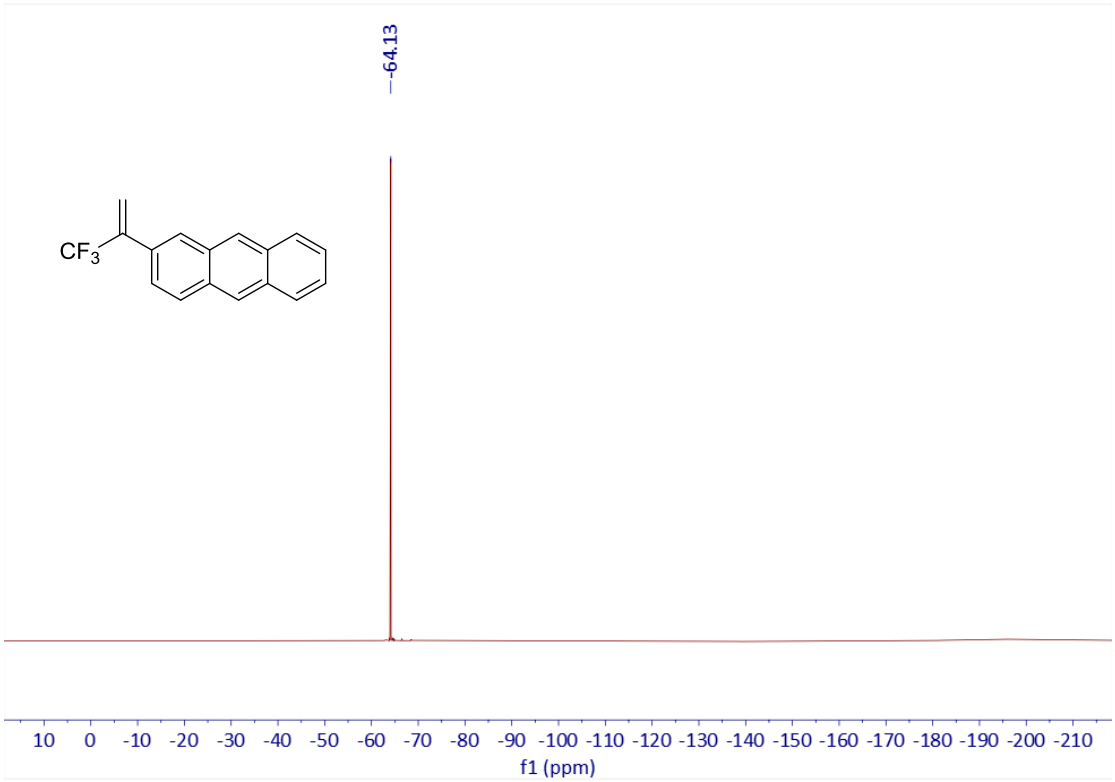
^{19}F NMR of 2k (377 MHz, $CDCl_3$)



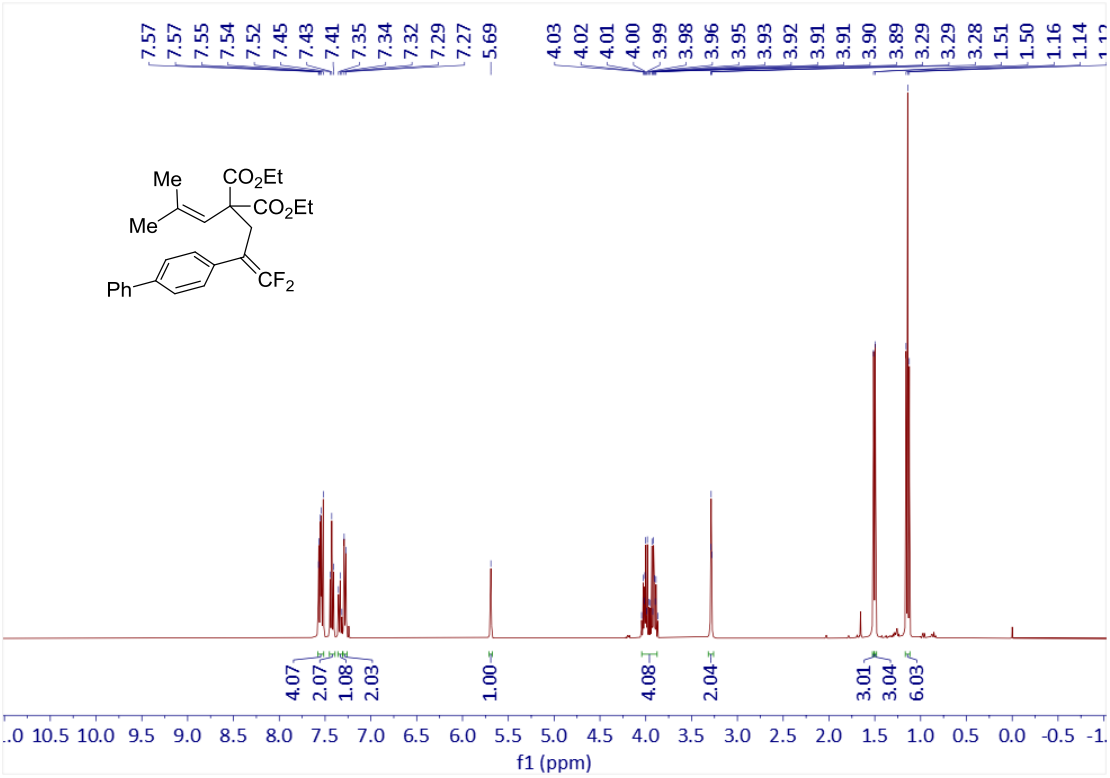
^{1}H NMR of 2m (400 MHz, $CDCl_3$)



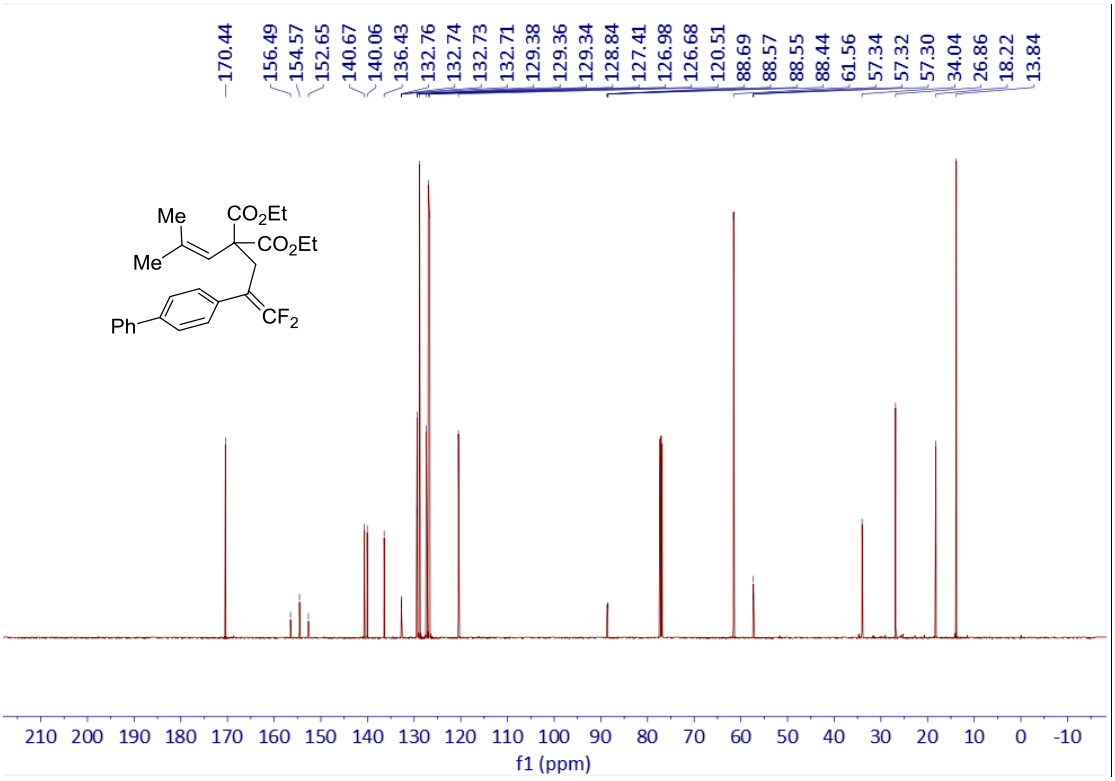
^{13}C NMR of 2m (101 MHz, $CDCl_3$)



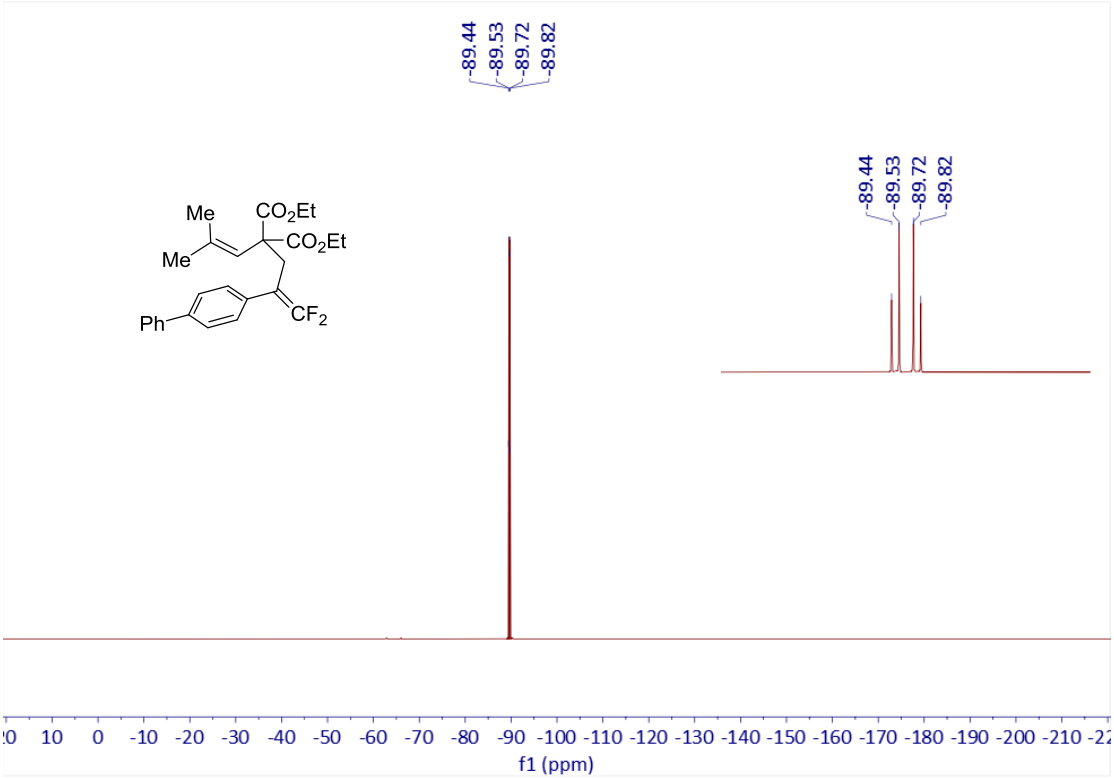
^{19}F NMR of 2m (377 MHz, $CDCl_3$)



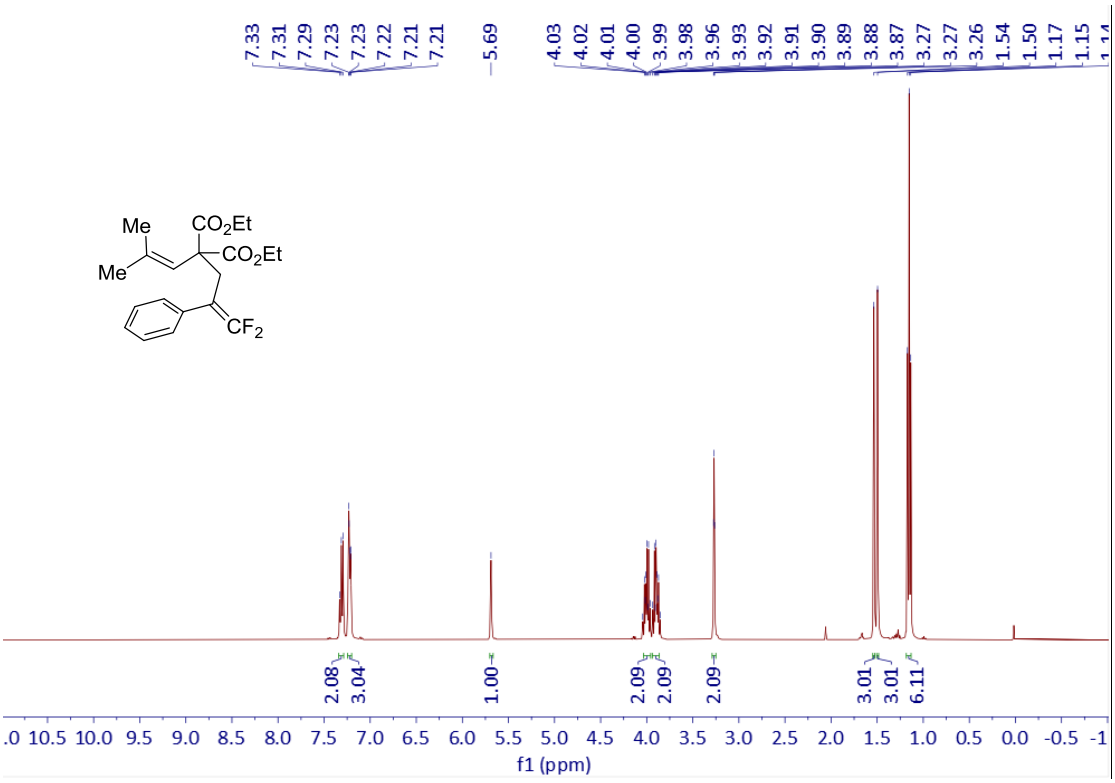
^{1}H NMR of 3a (400 MHz, $CDCl_3$)



^{13}C NMR of 3a (151 MHz, $CDCl_3$)



^{19}F NMR of 3a (377 MHz, $CDCl_3$)



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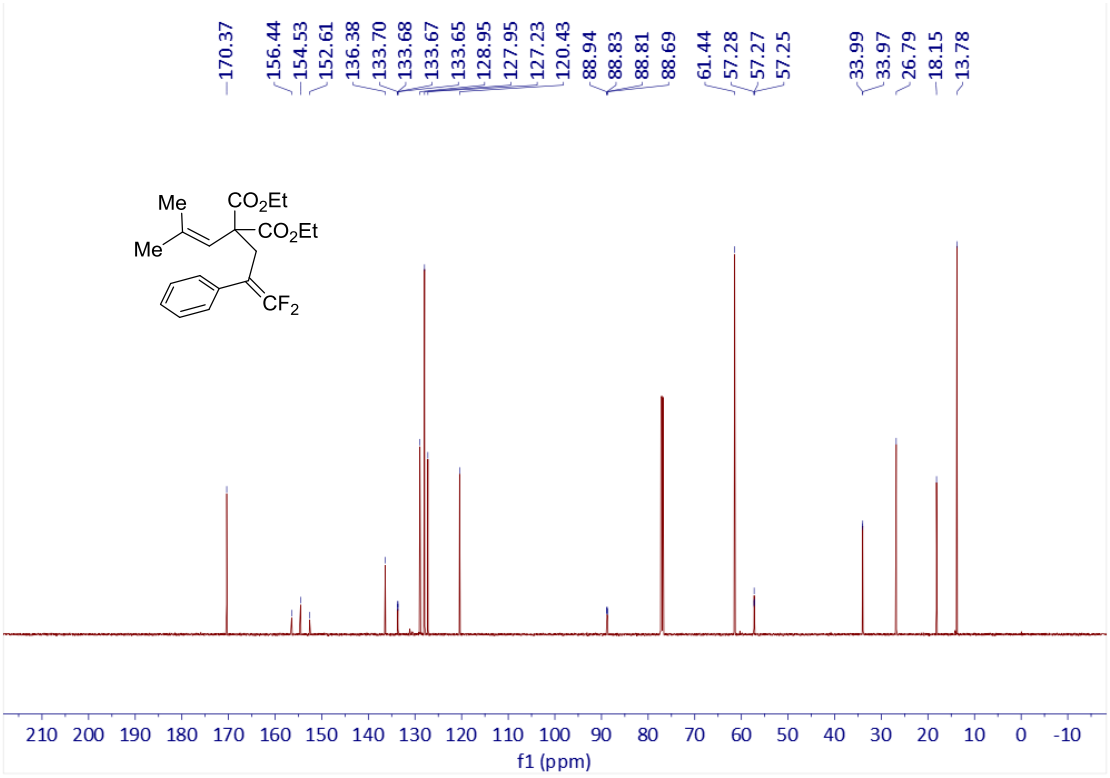

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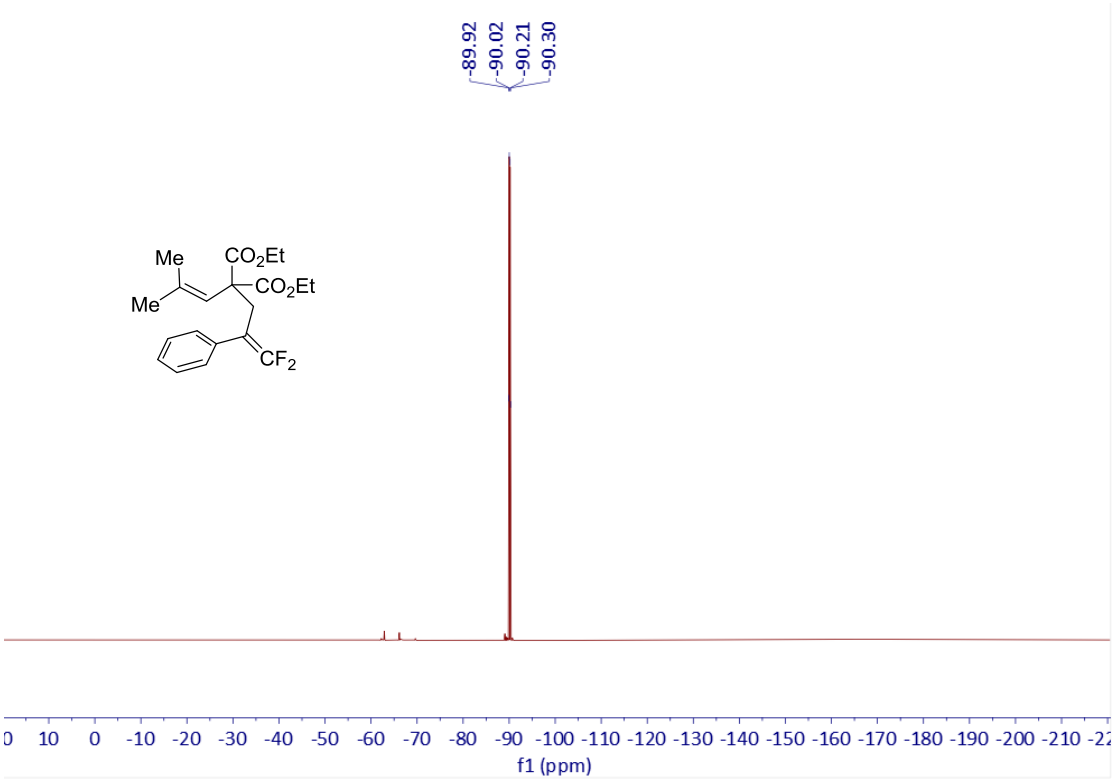
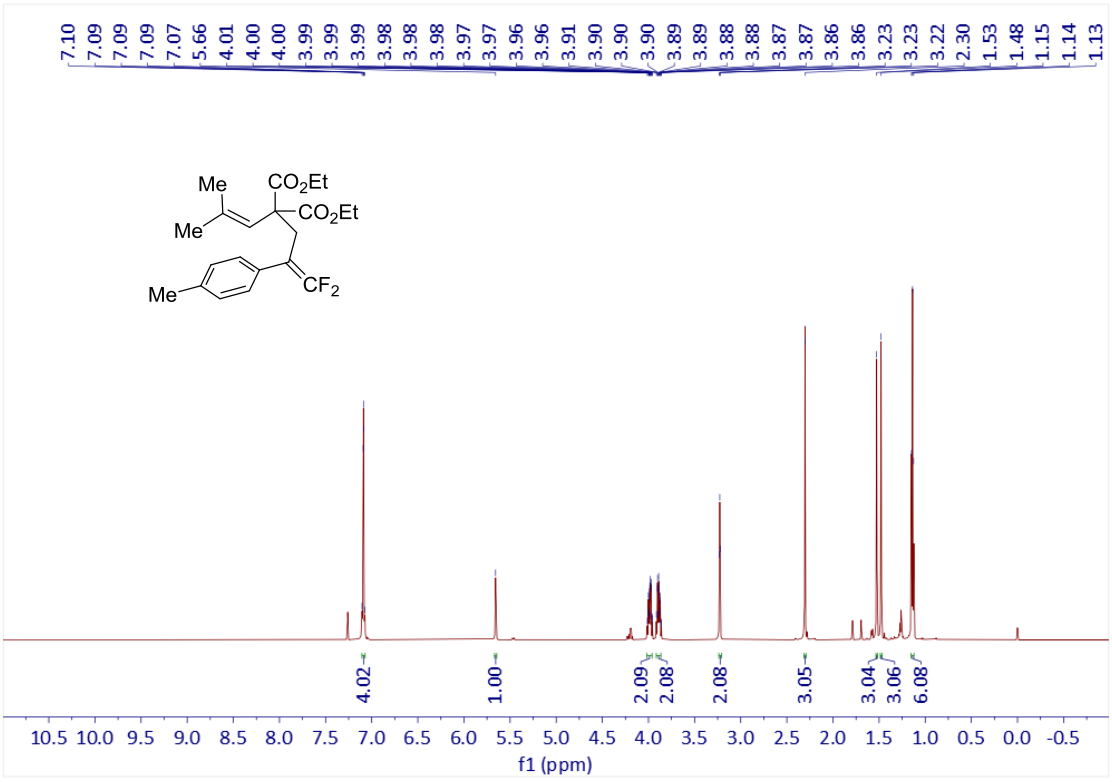


^{19}F NMR of 3b (377 MHz, $CDCl_3$)



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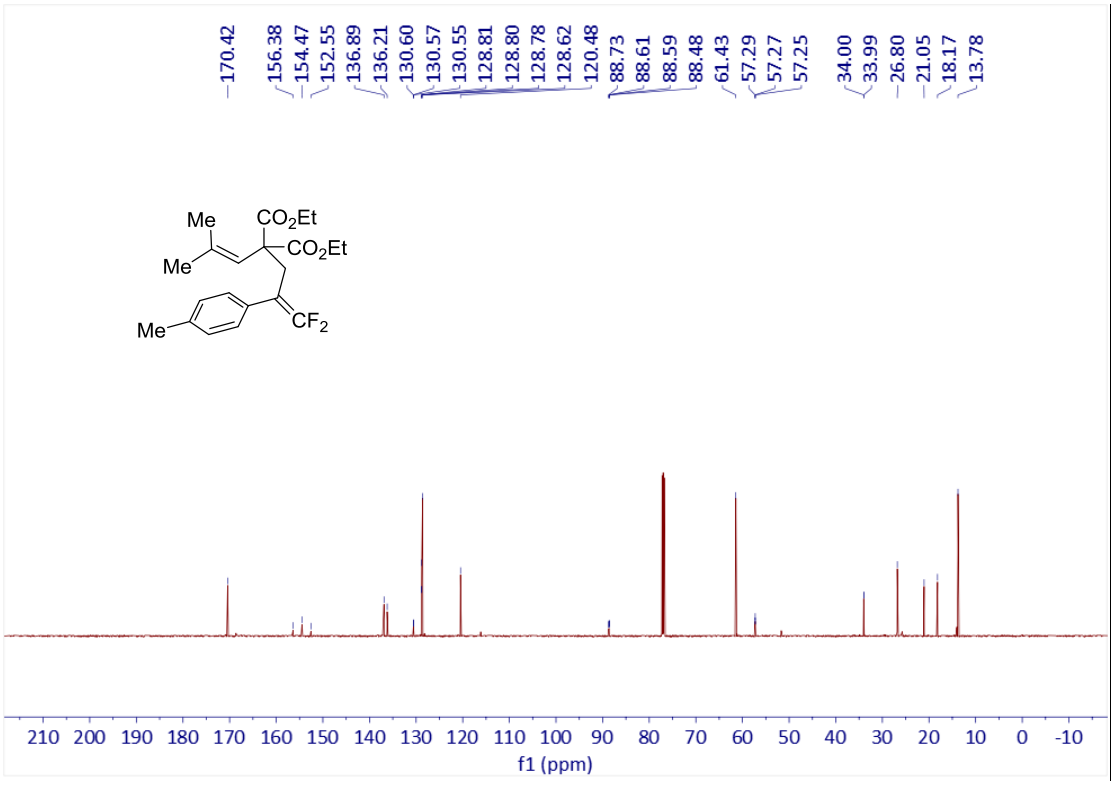
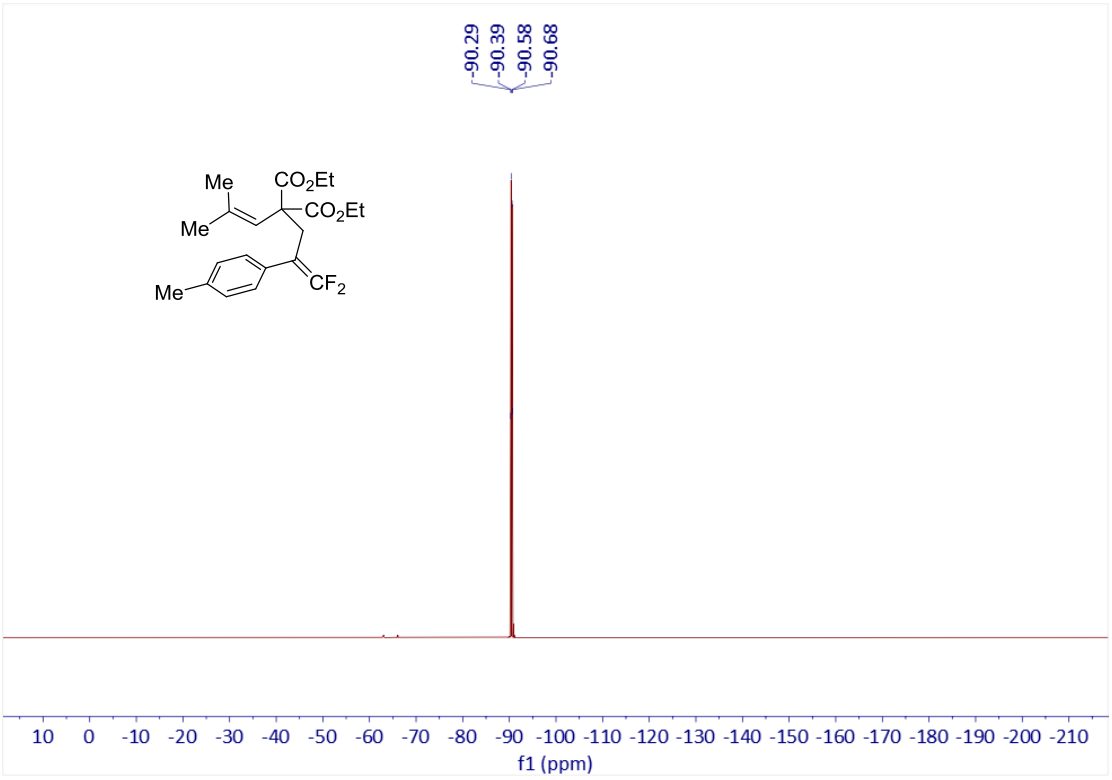


^{13}C NMR of 3c (101 MHz, $CDCl_3$)



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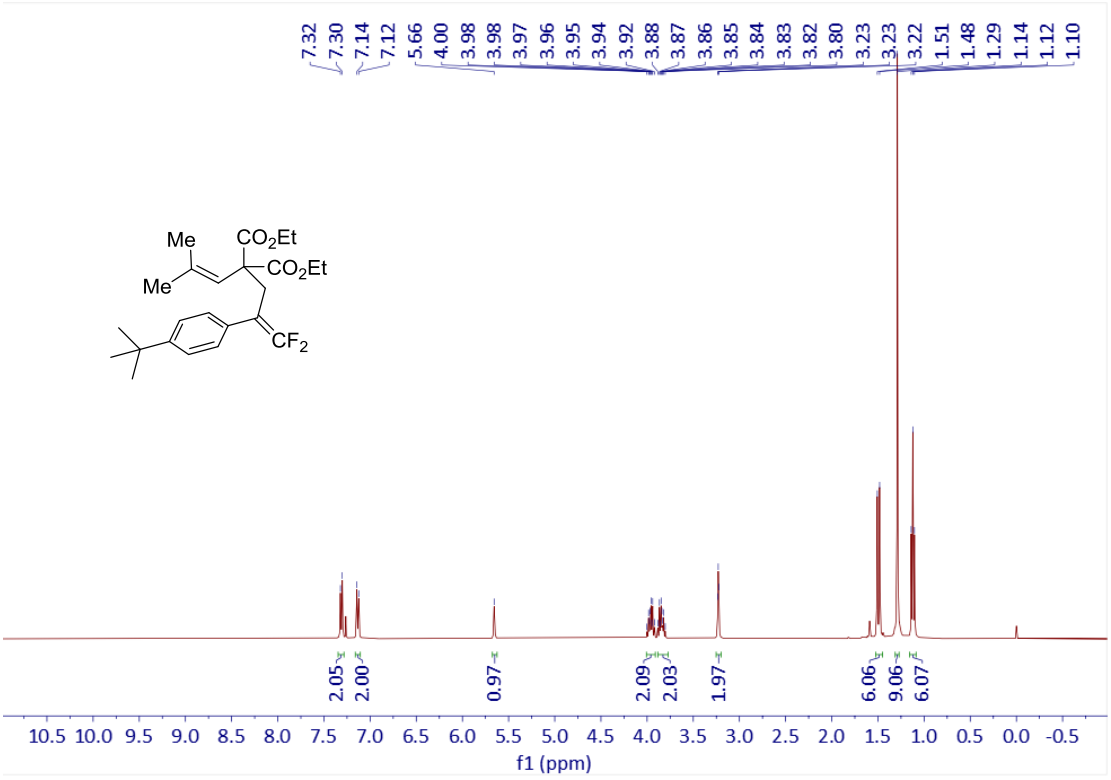

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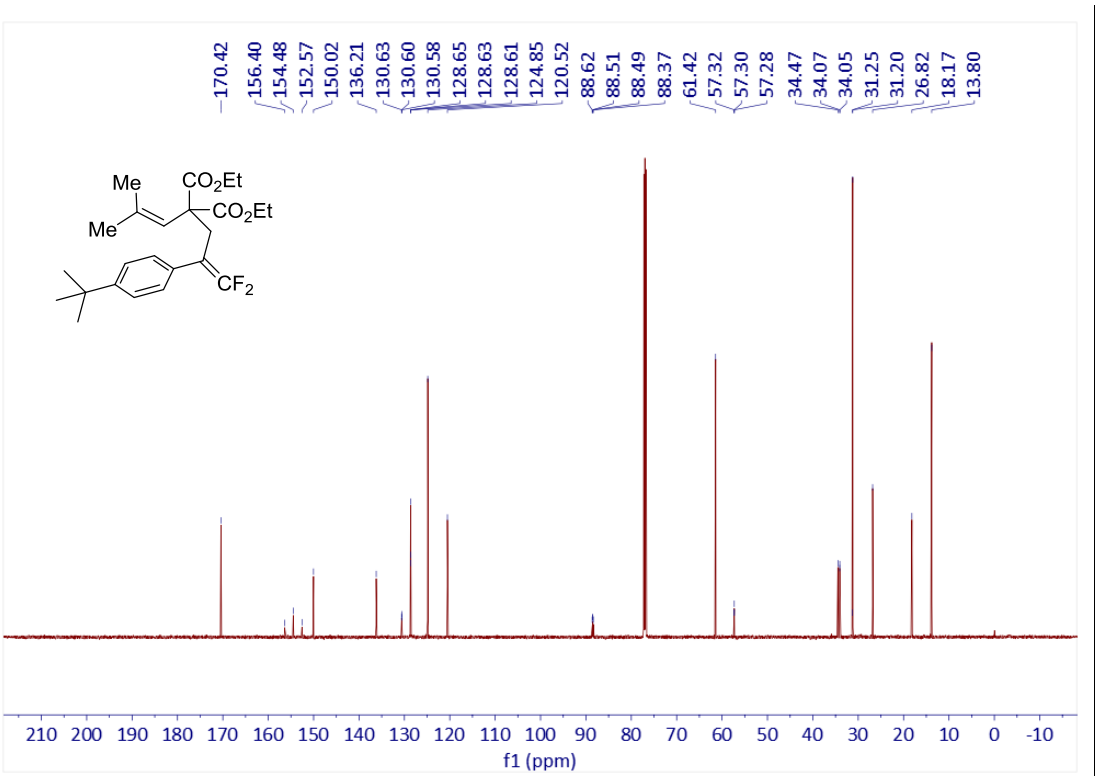
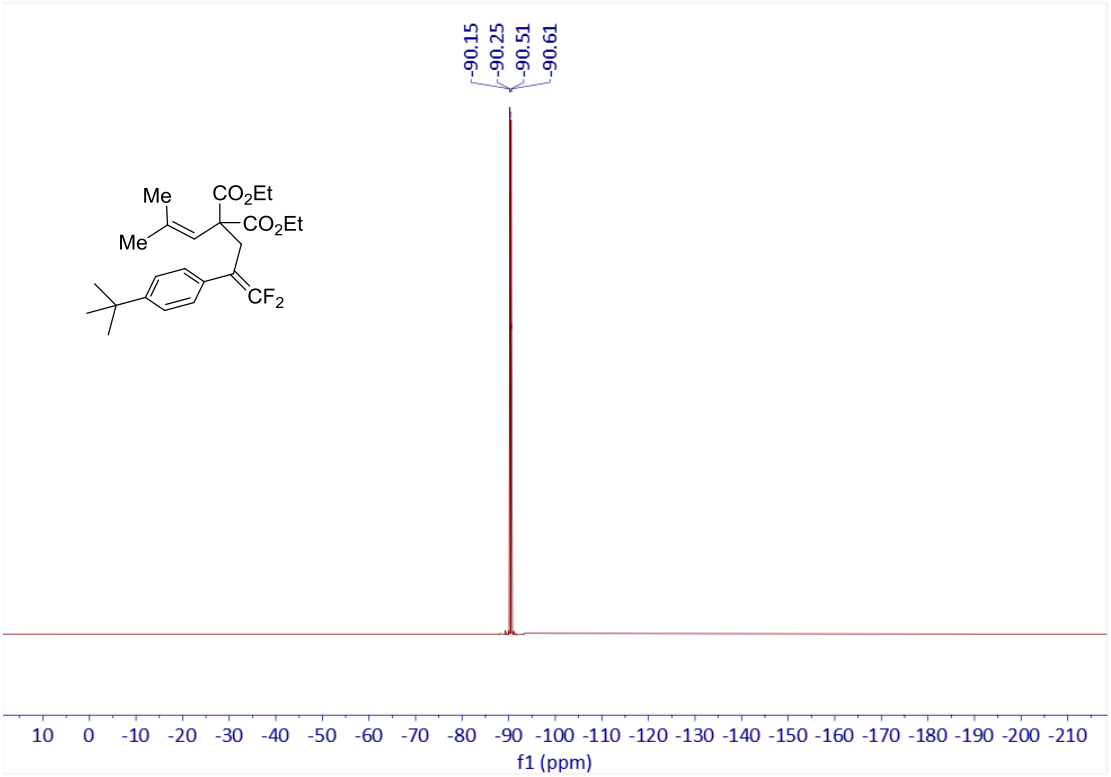


^{13}C NMR of 3d (151 MHz, $CDCl_3$)



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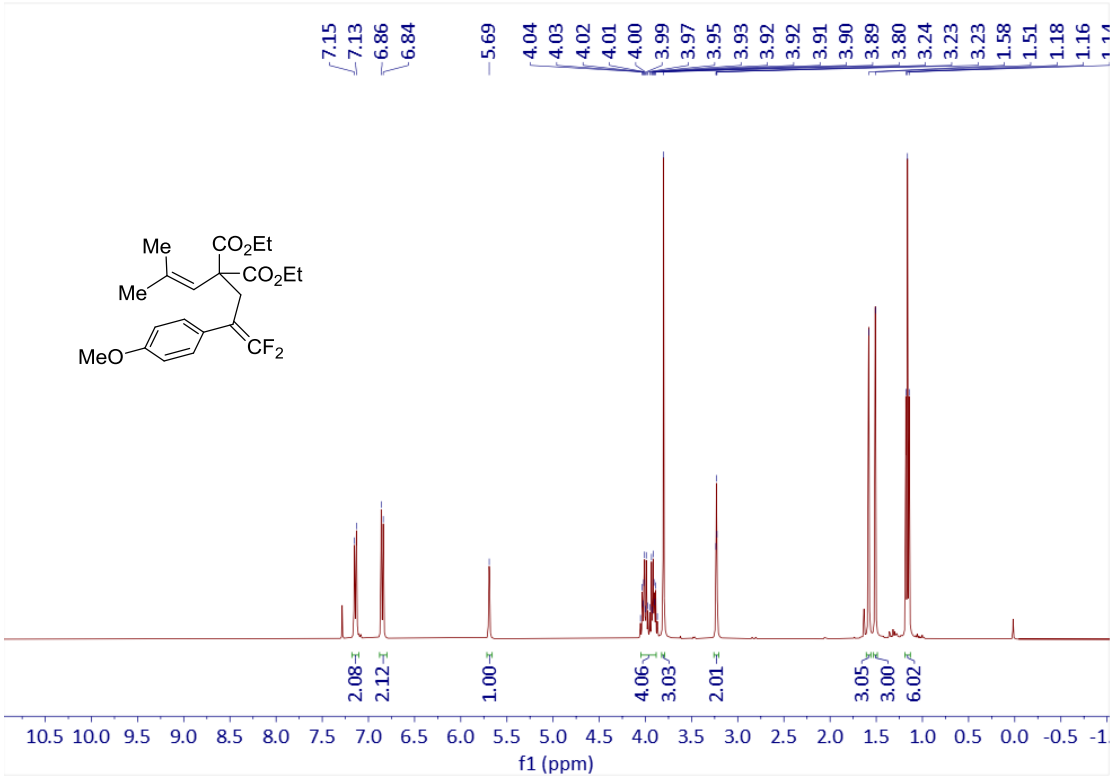

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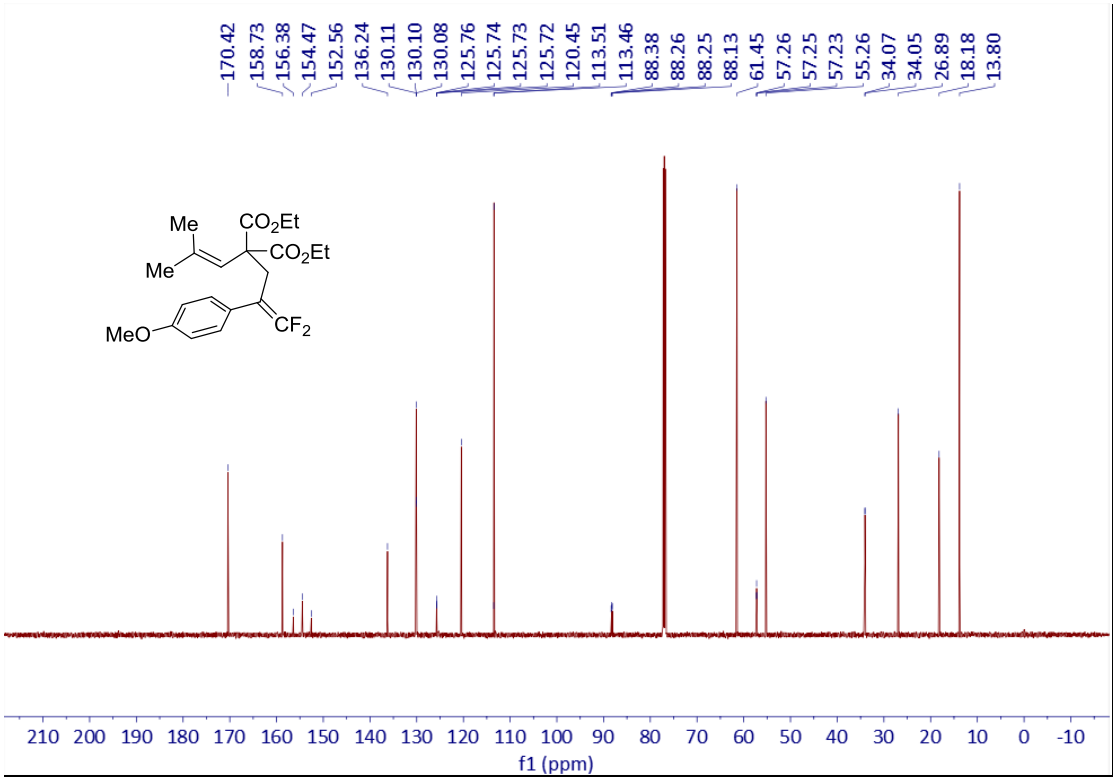

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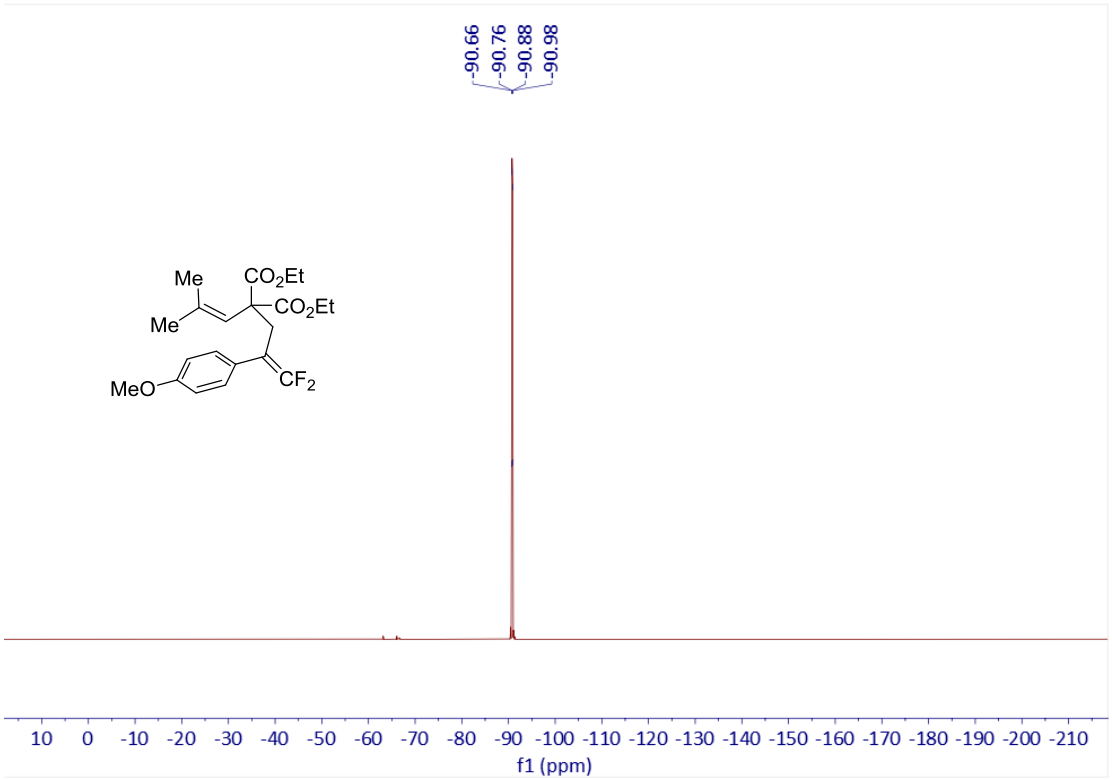

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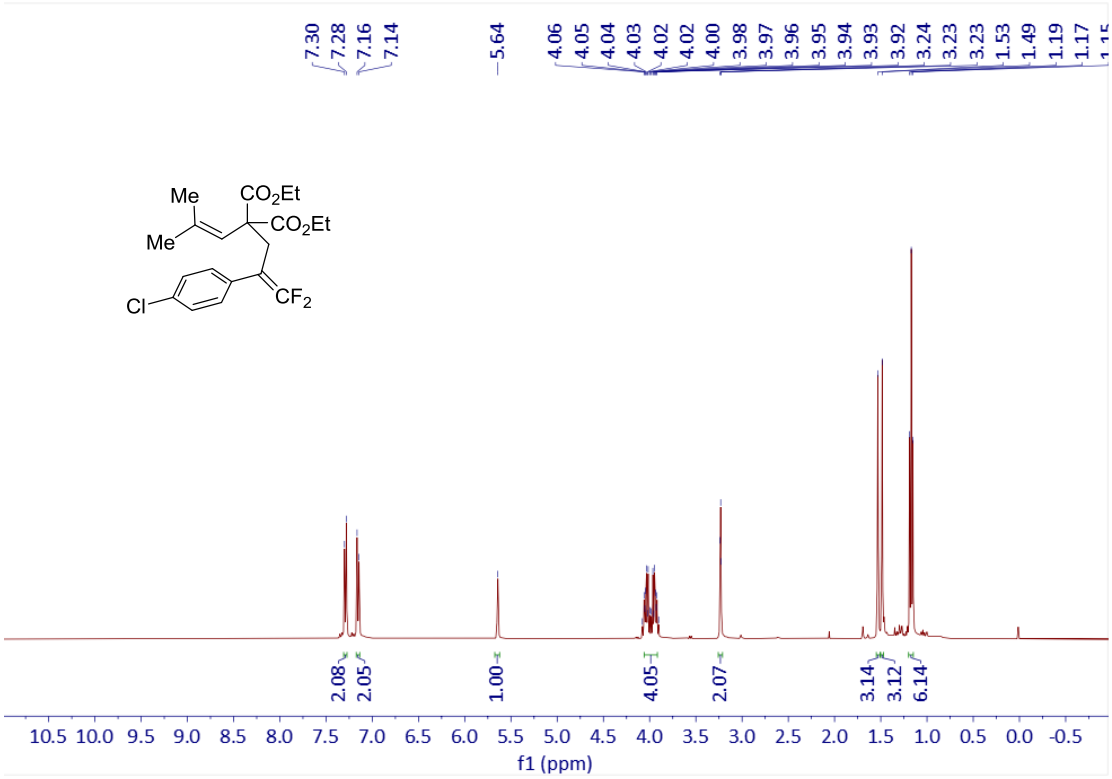

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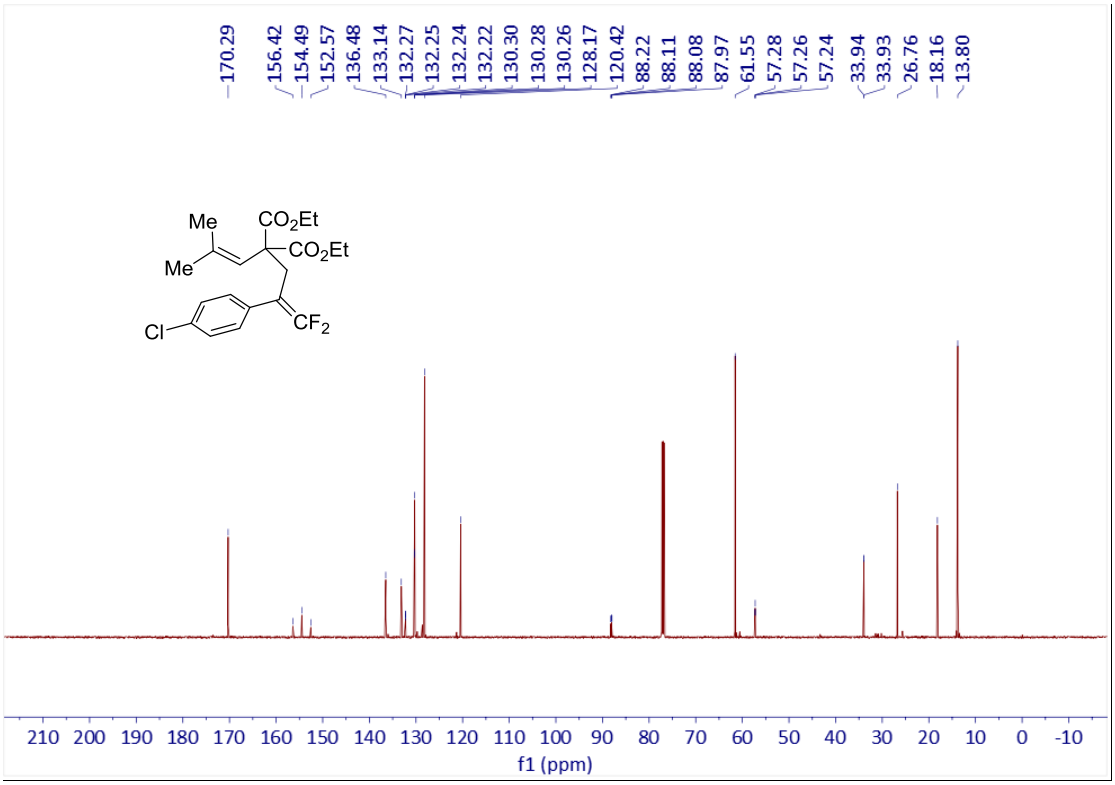

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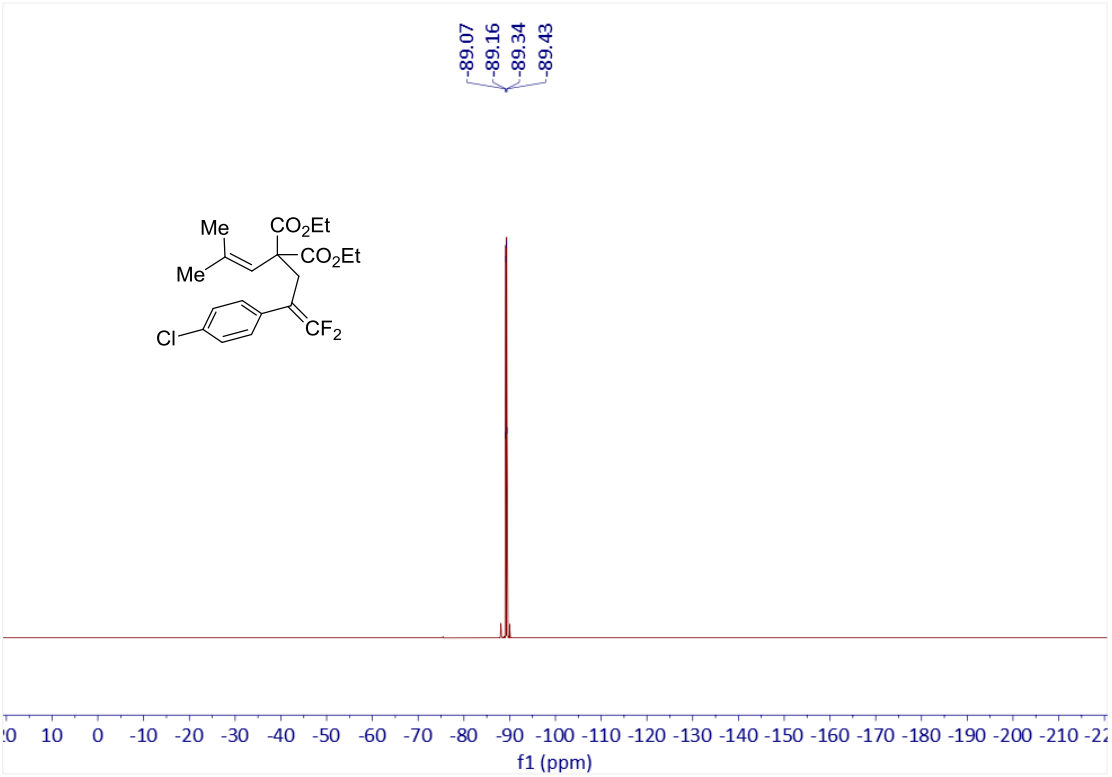

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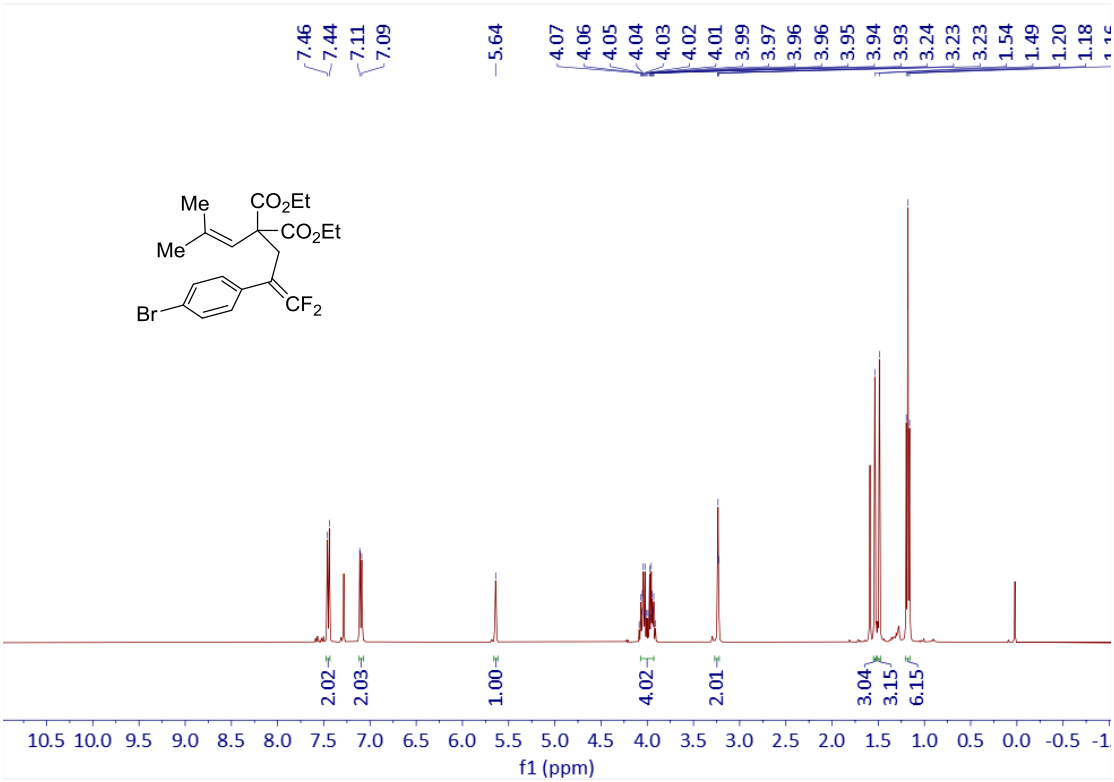
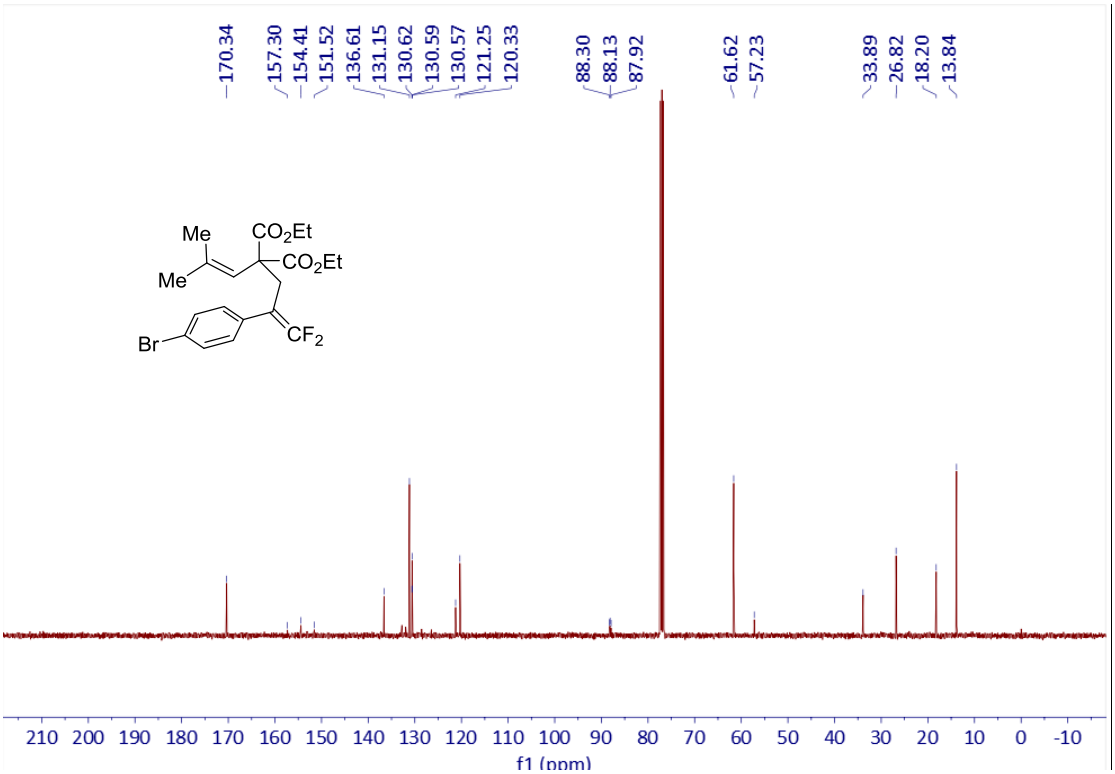


^{1}H NMR of 3g (400 MHz, $CDCl_3$)



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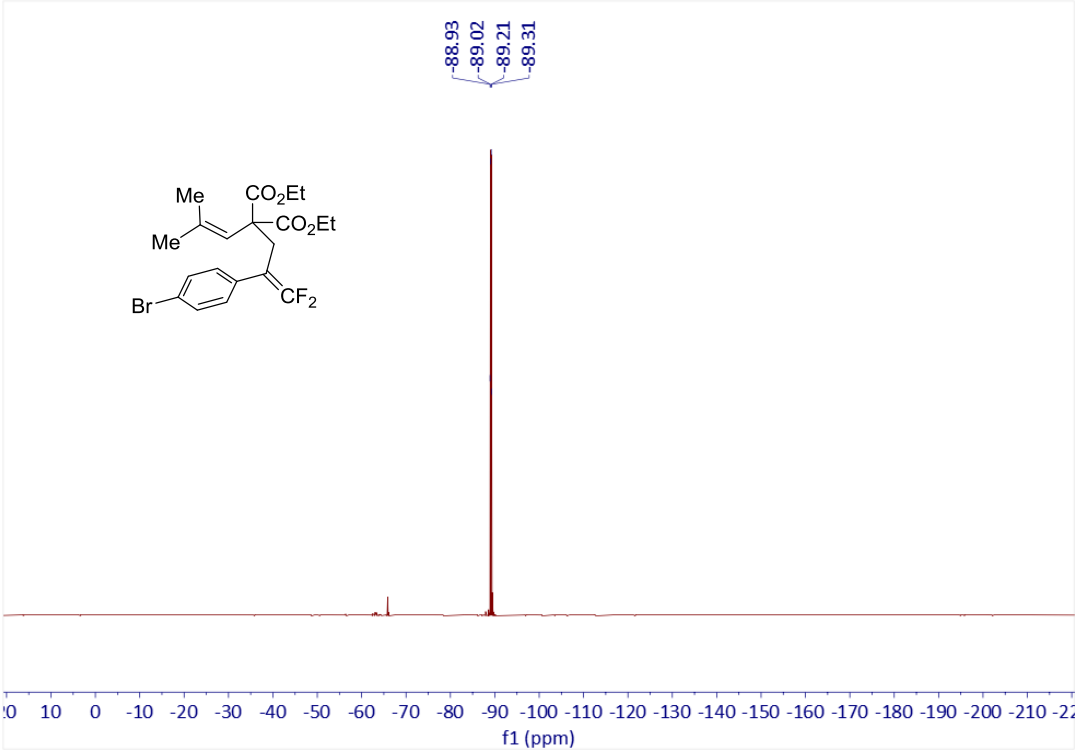
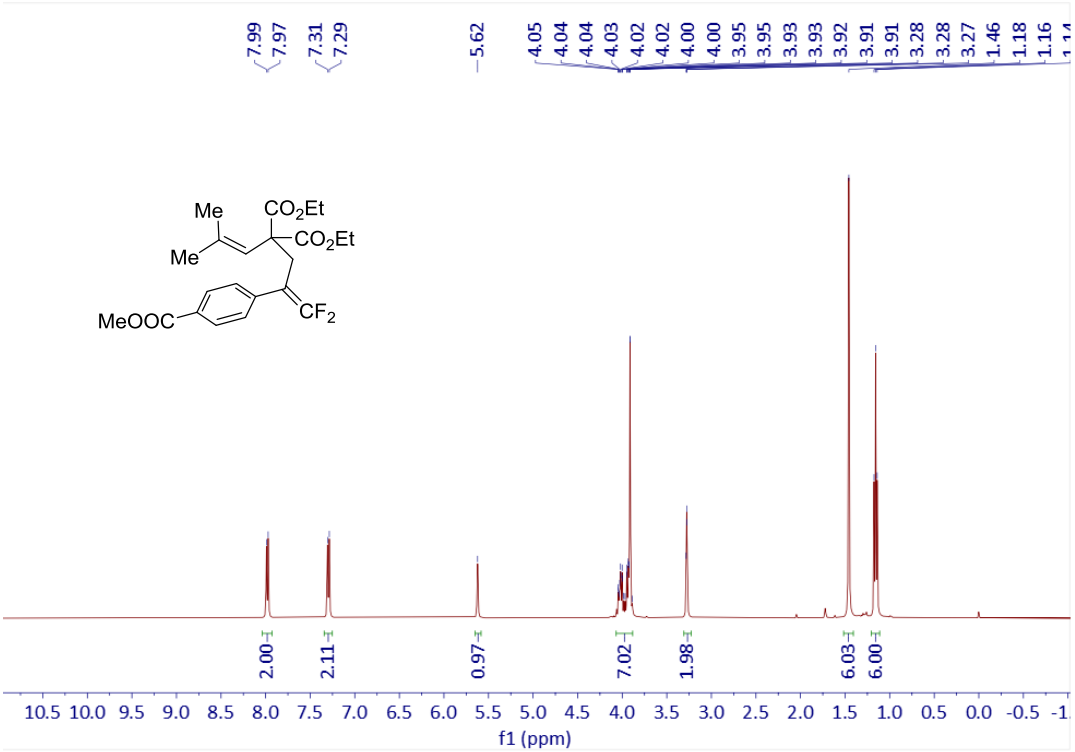


^{19}F NMR of 3g (377 MHz, $CDCl_3$)



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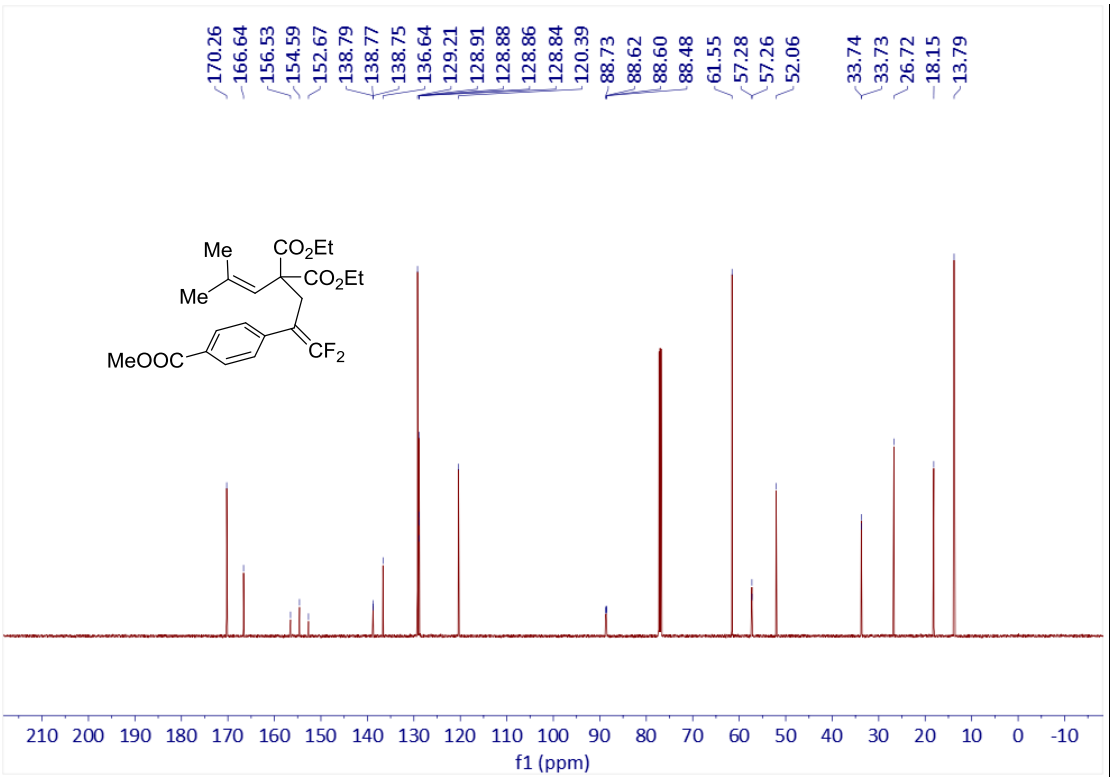

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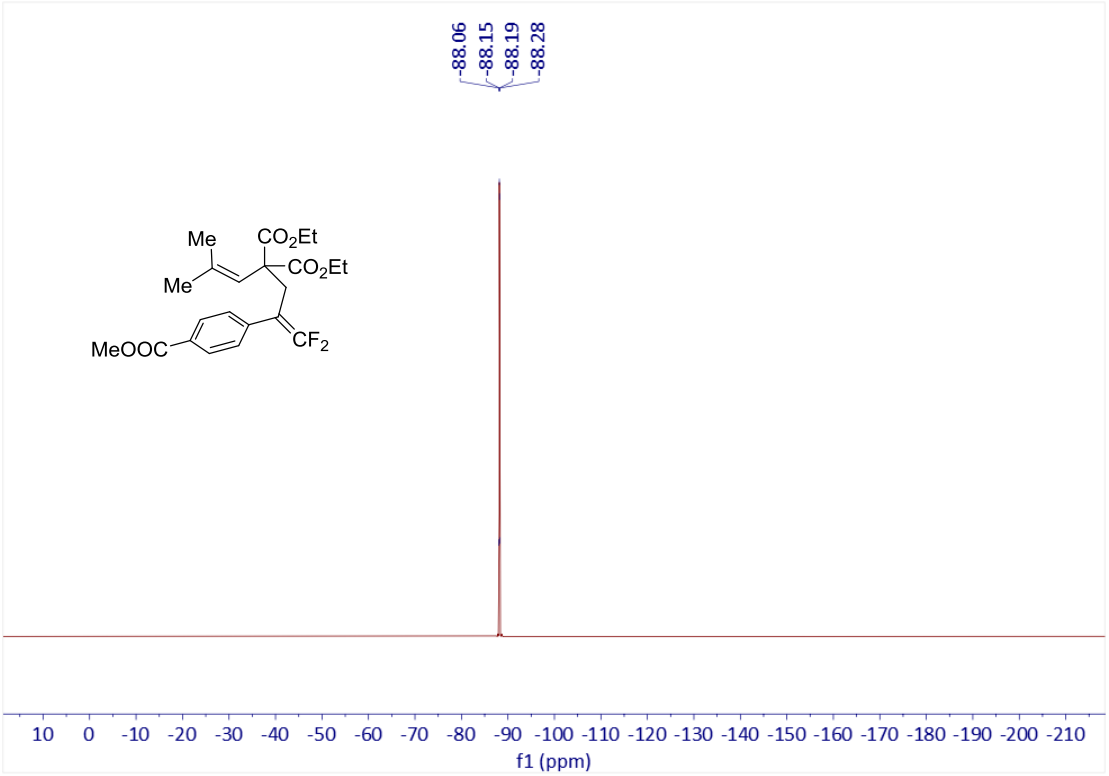
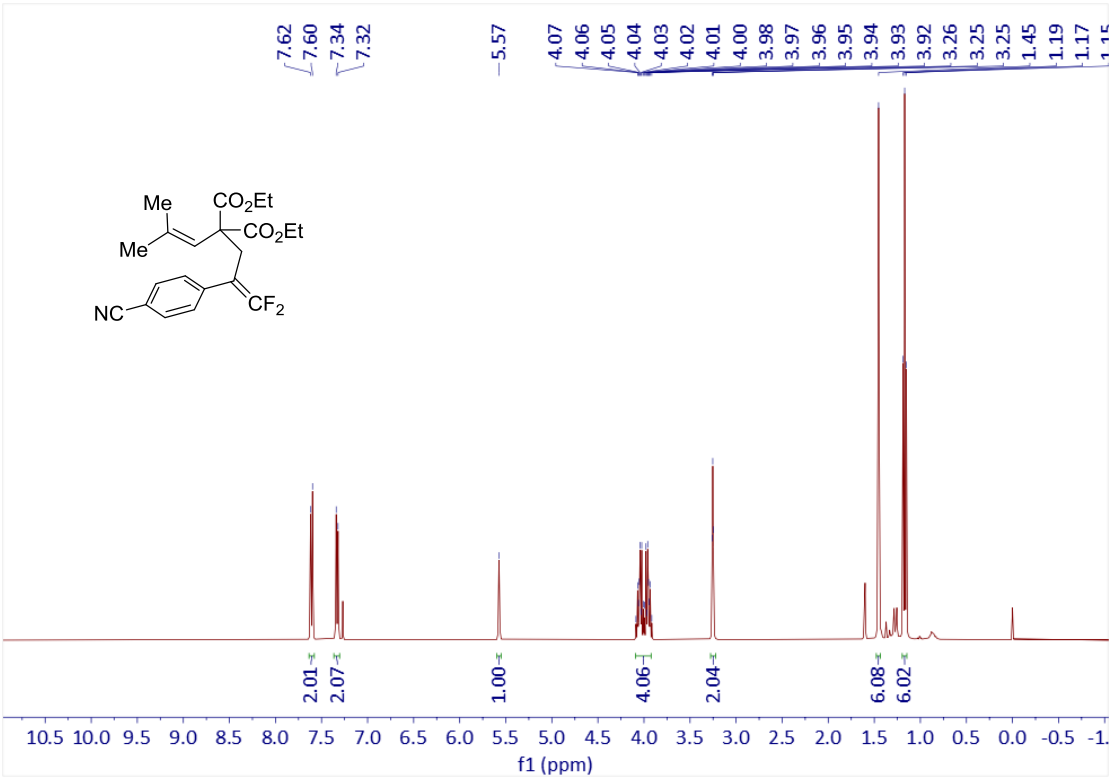


^{19}F NMR of 3h (377 MHz, $CDCl_3$)



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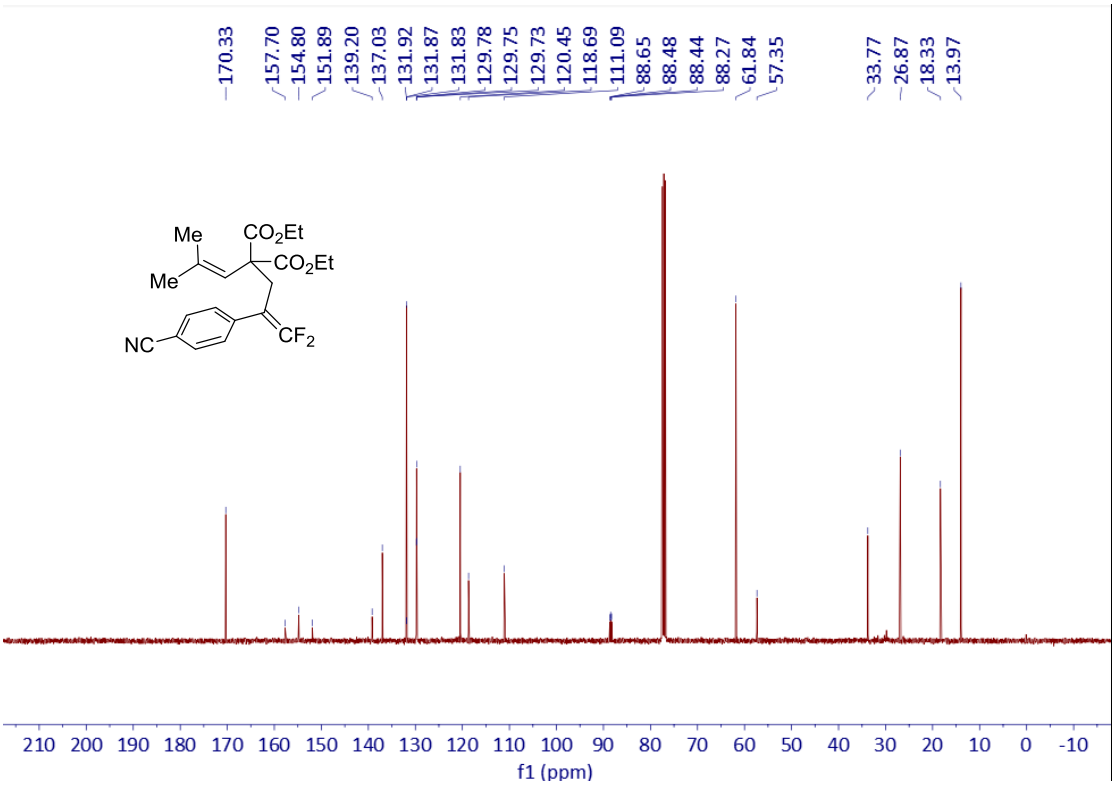

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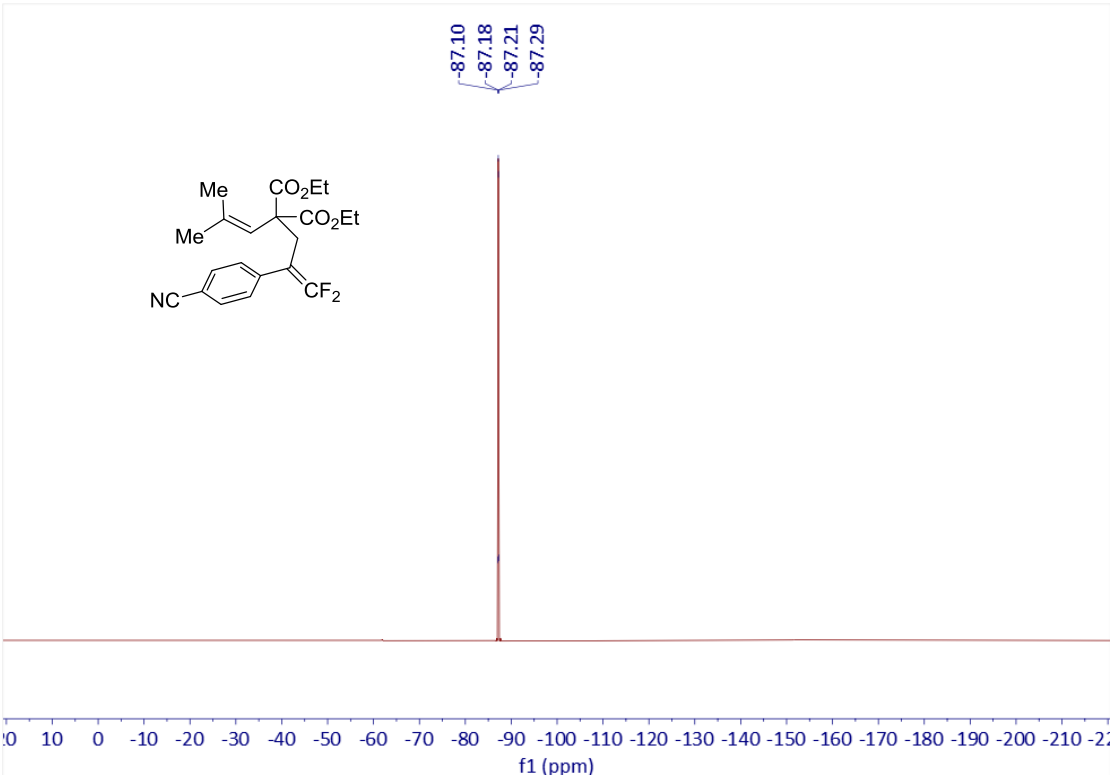

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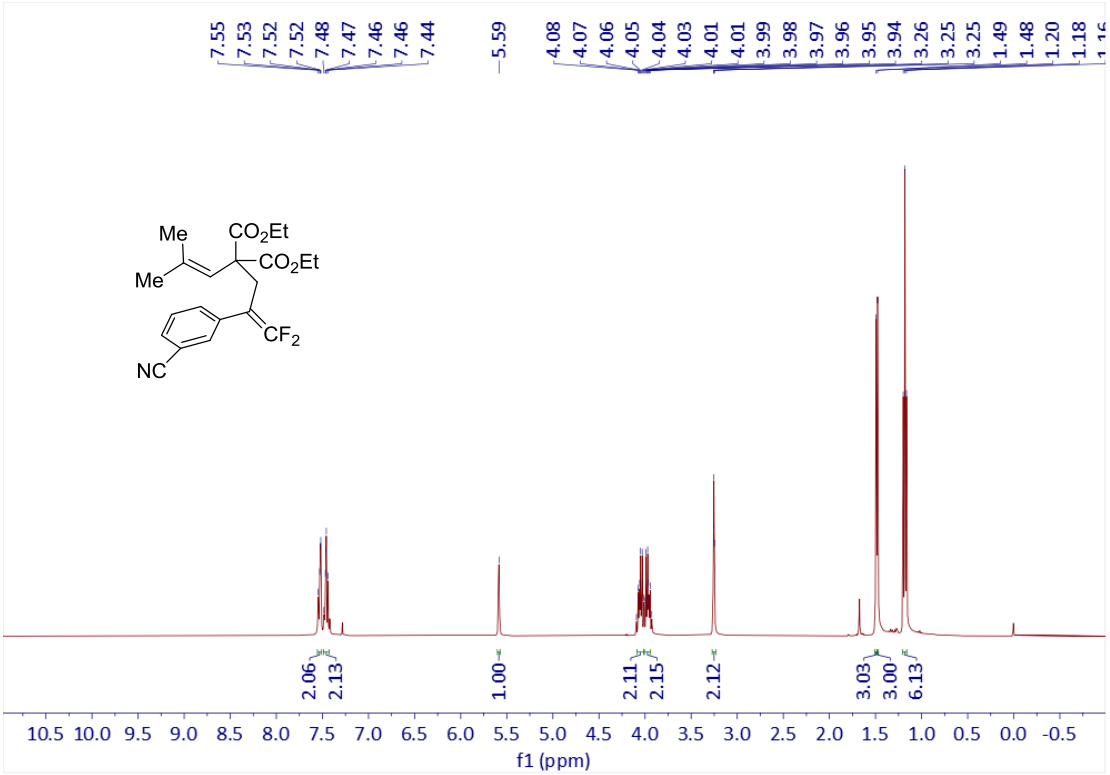

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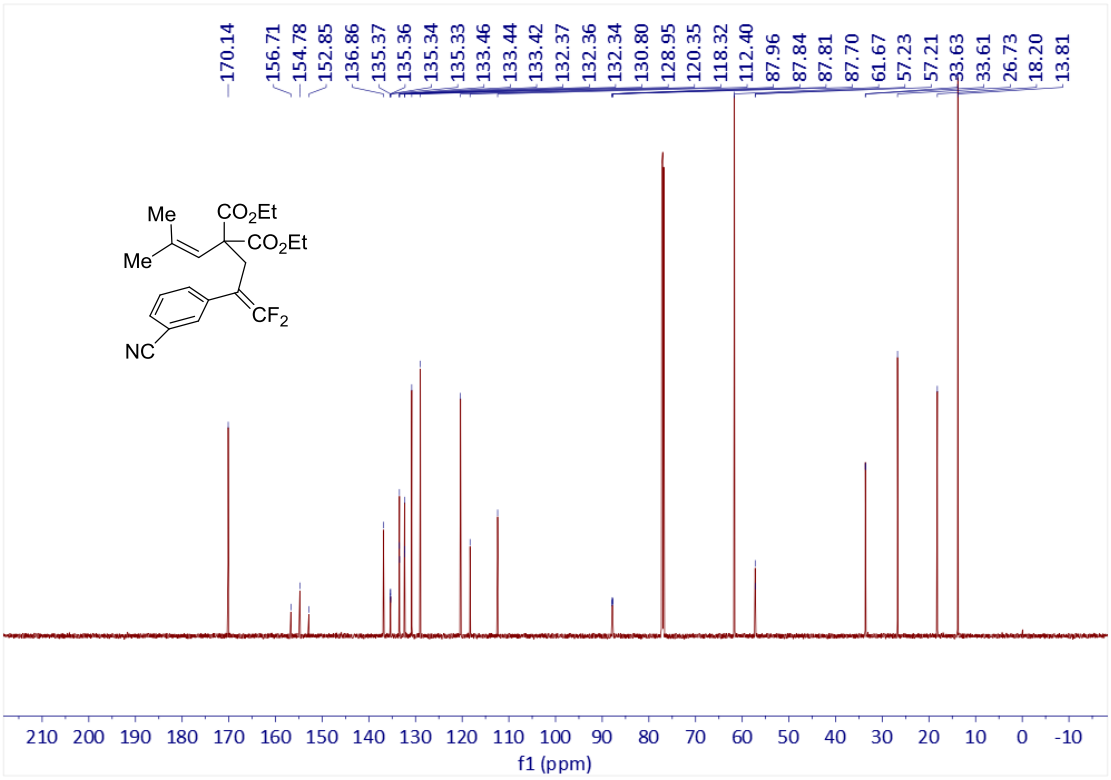
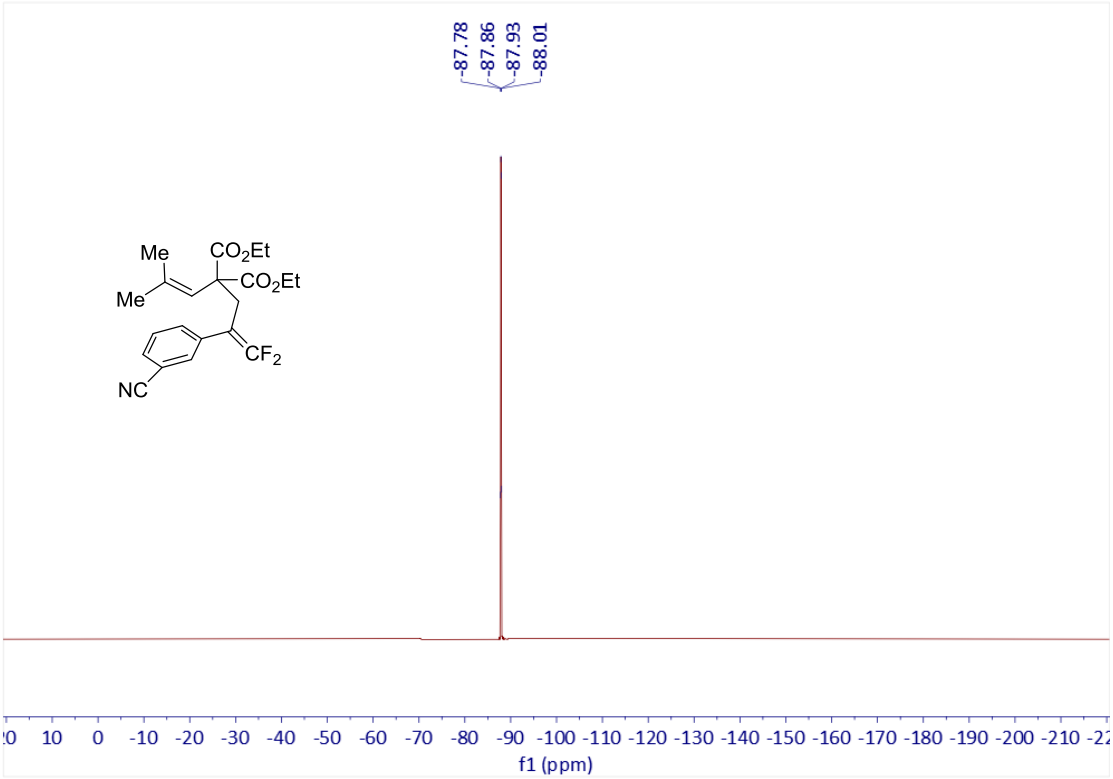


^{13}C NMR of 3j (151 MHz, $CDCl_3$)



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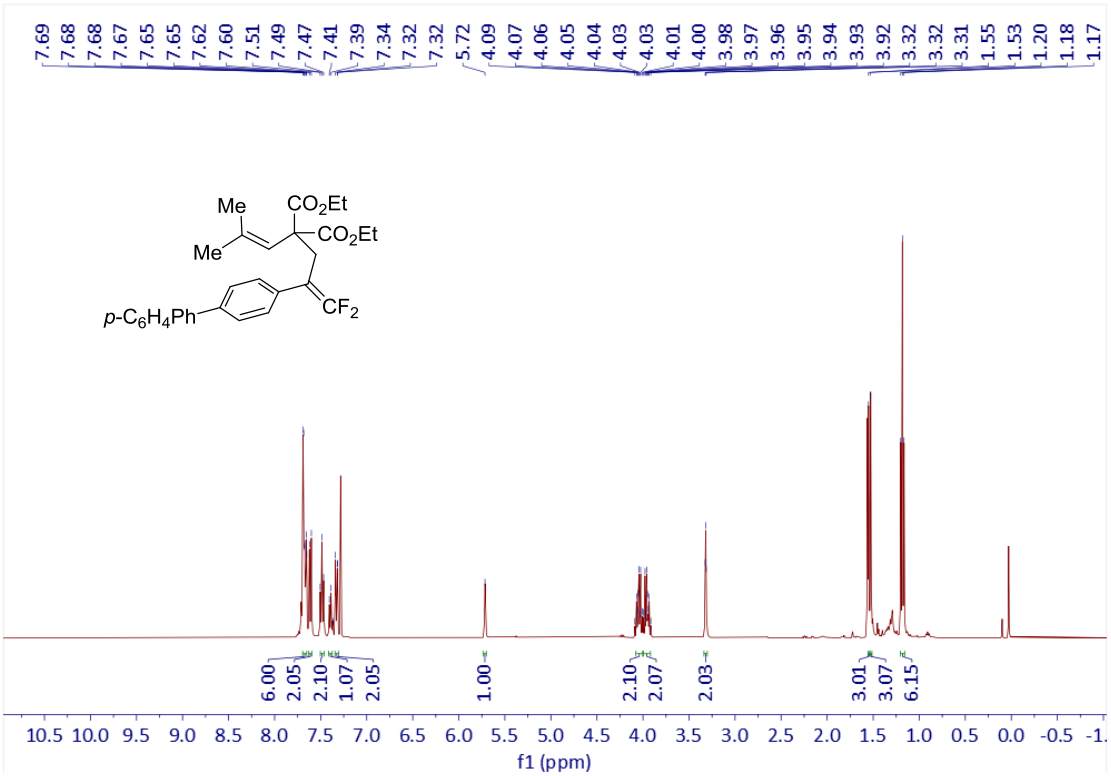

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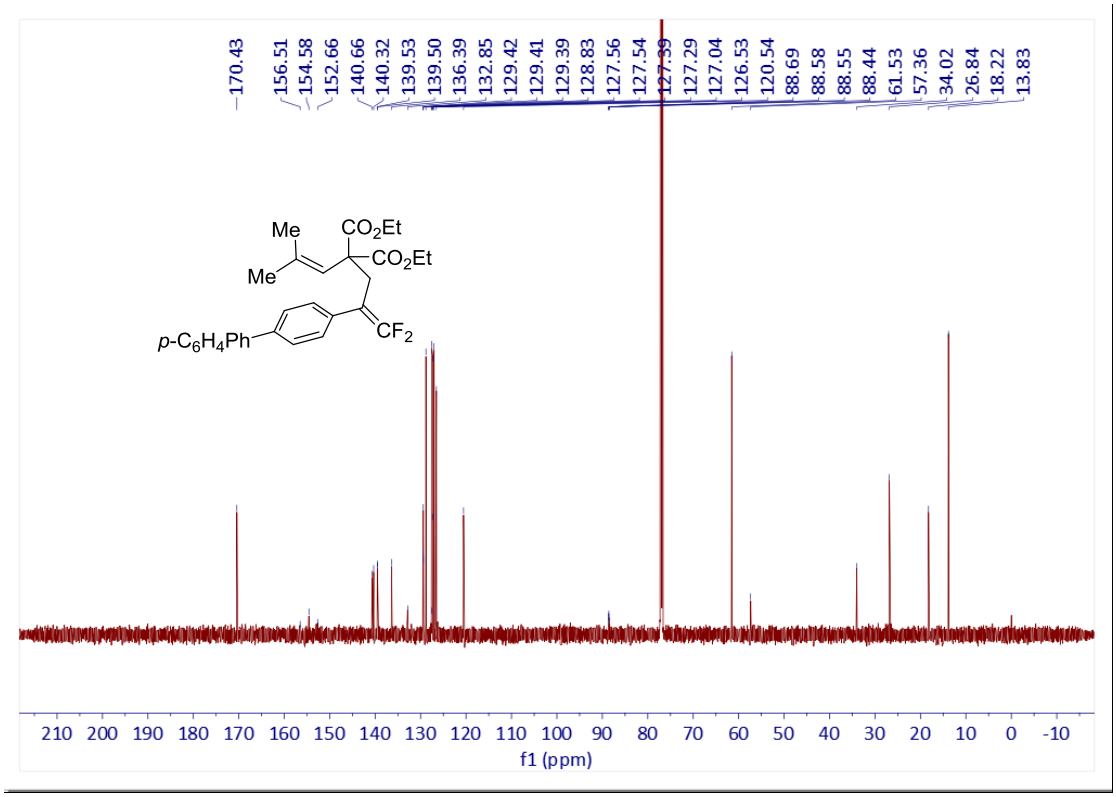
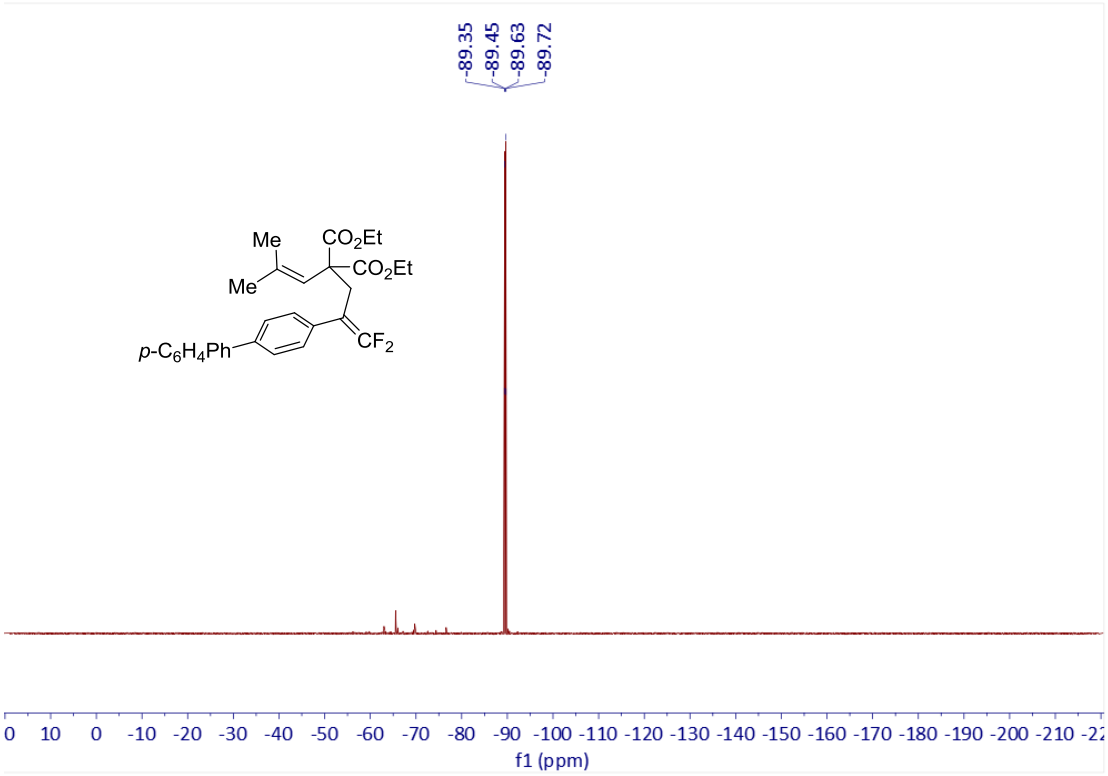


^{13}C NMR of 3k (101 MHz, $CDCl_3$)



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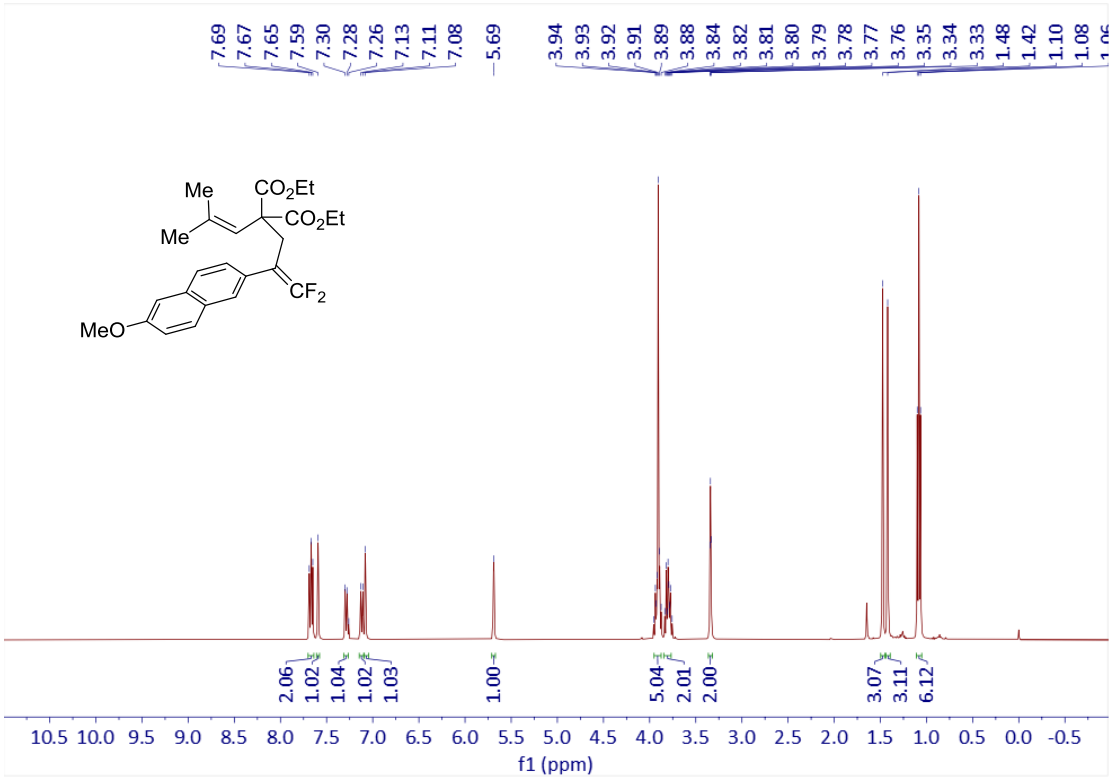

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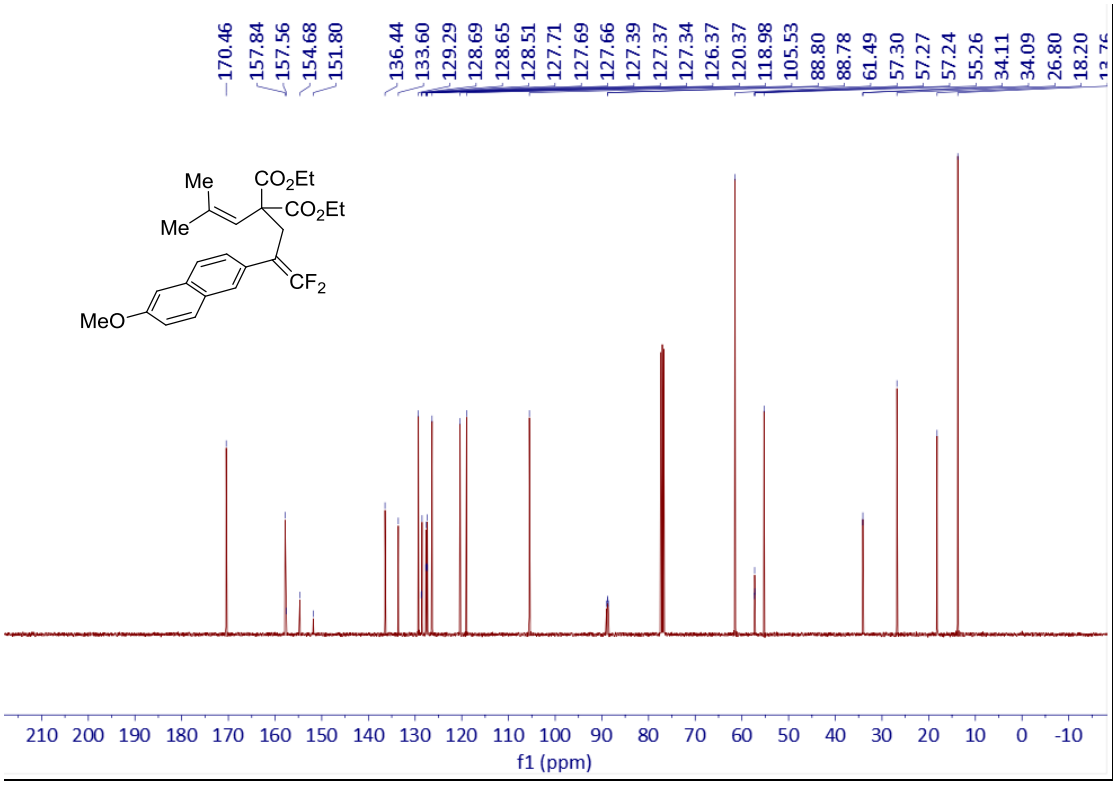

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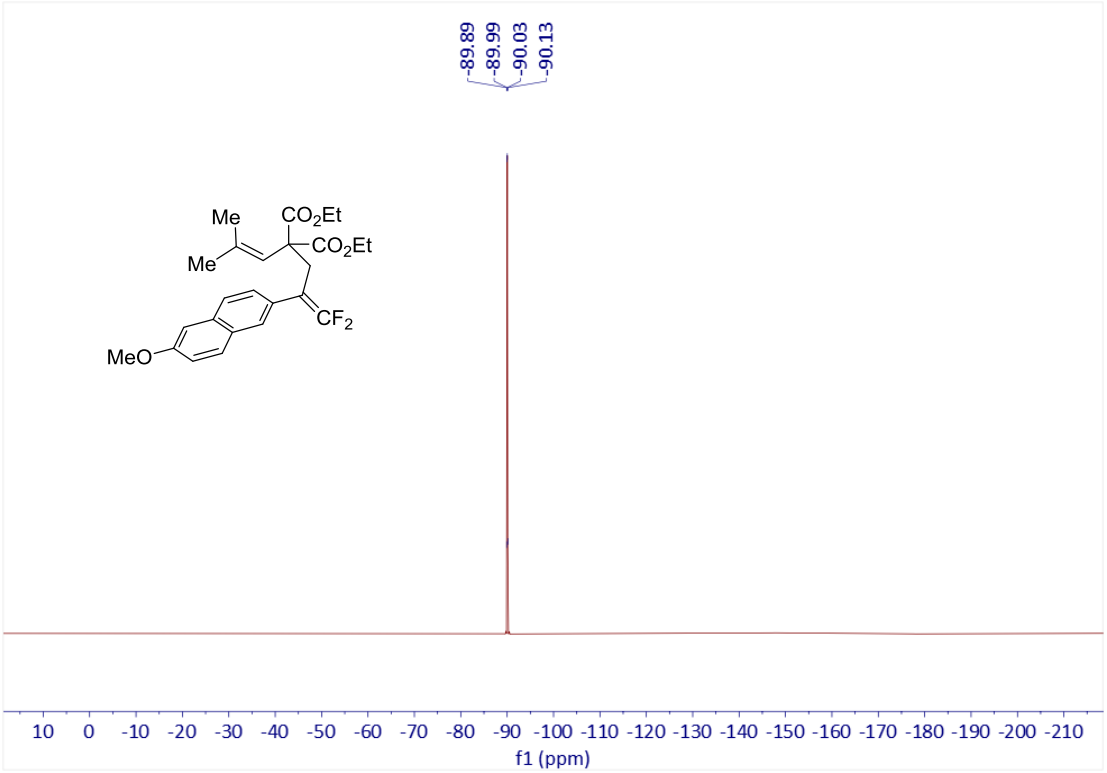

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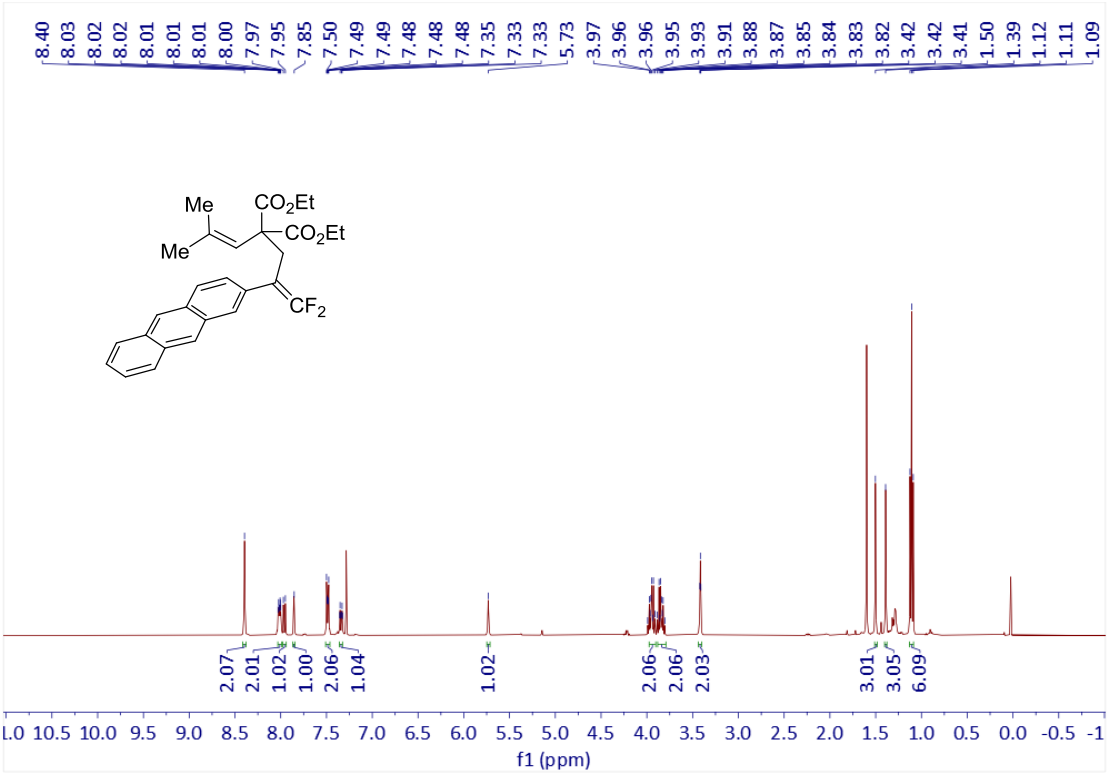

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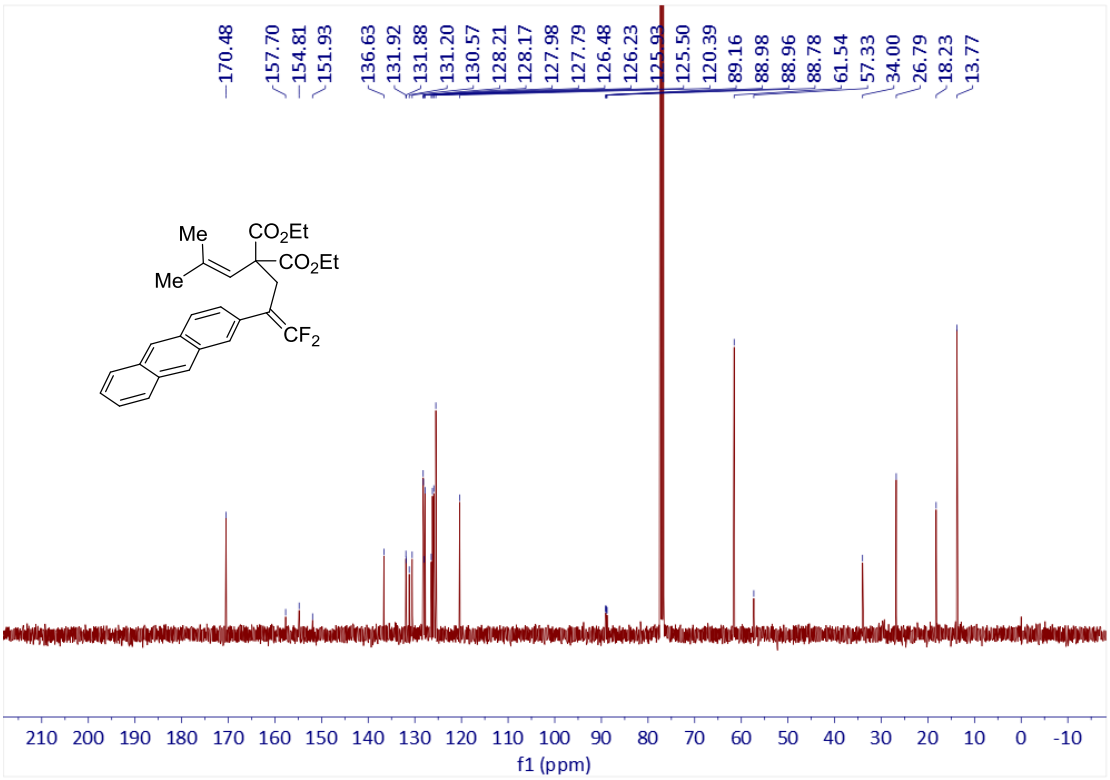

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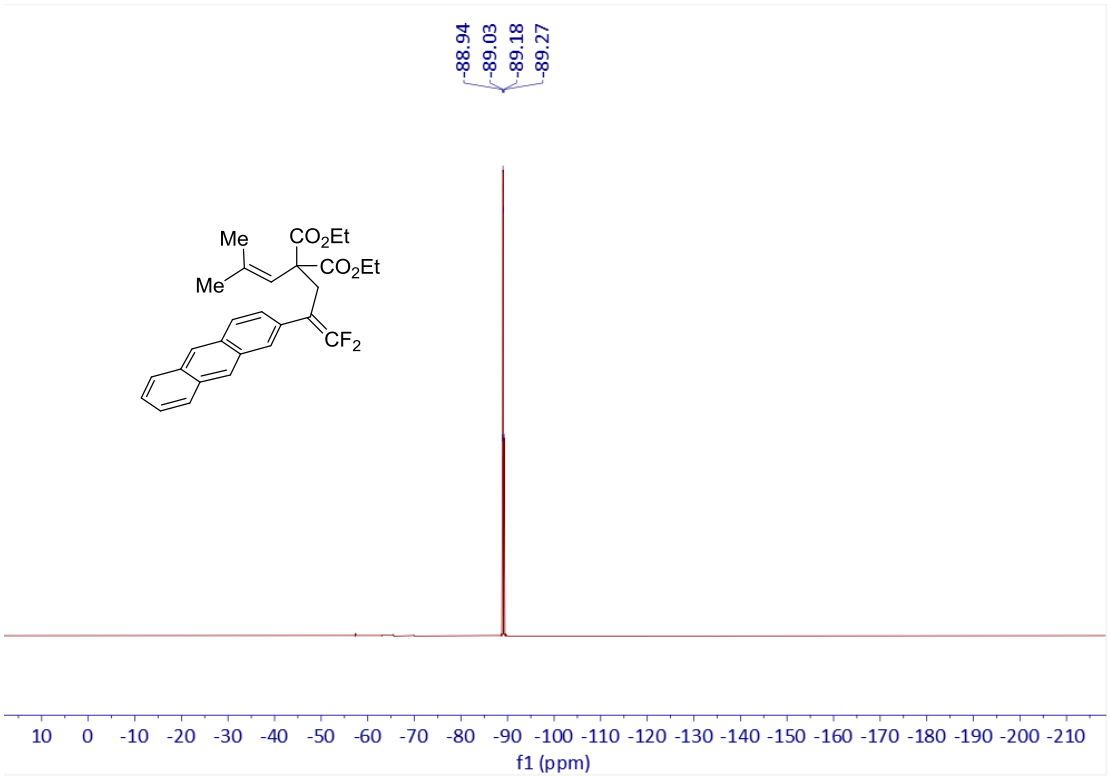
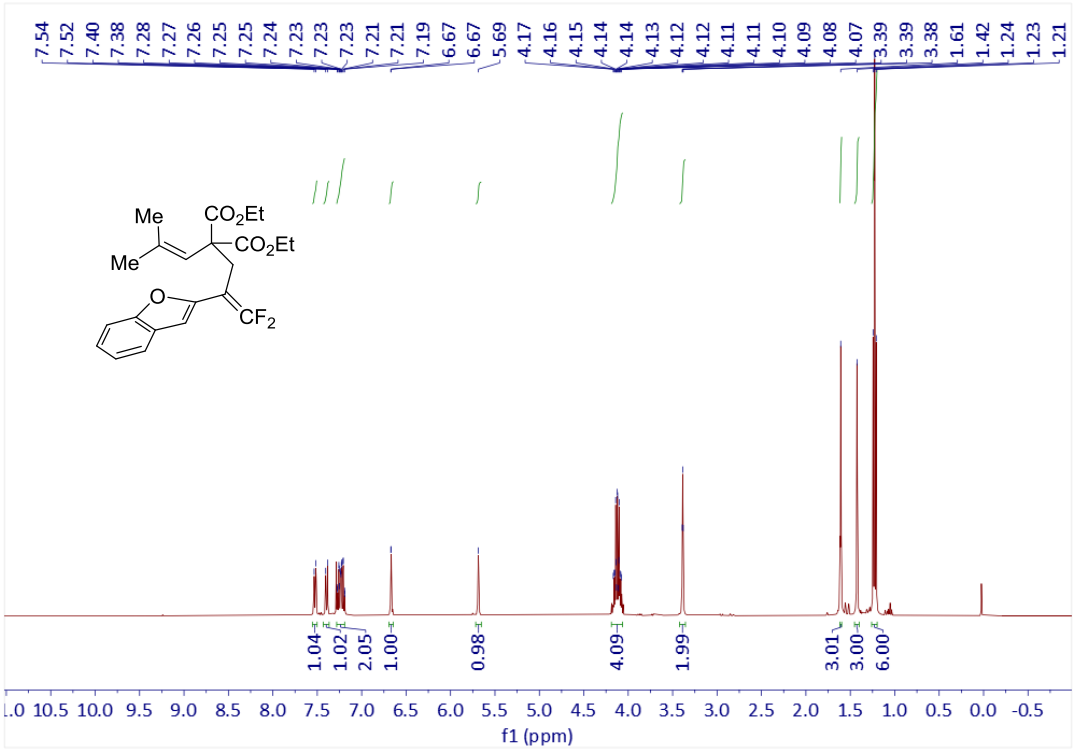


^{19}F NMR of 3m (377 MHz, $CDCl_3$)



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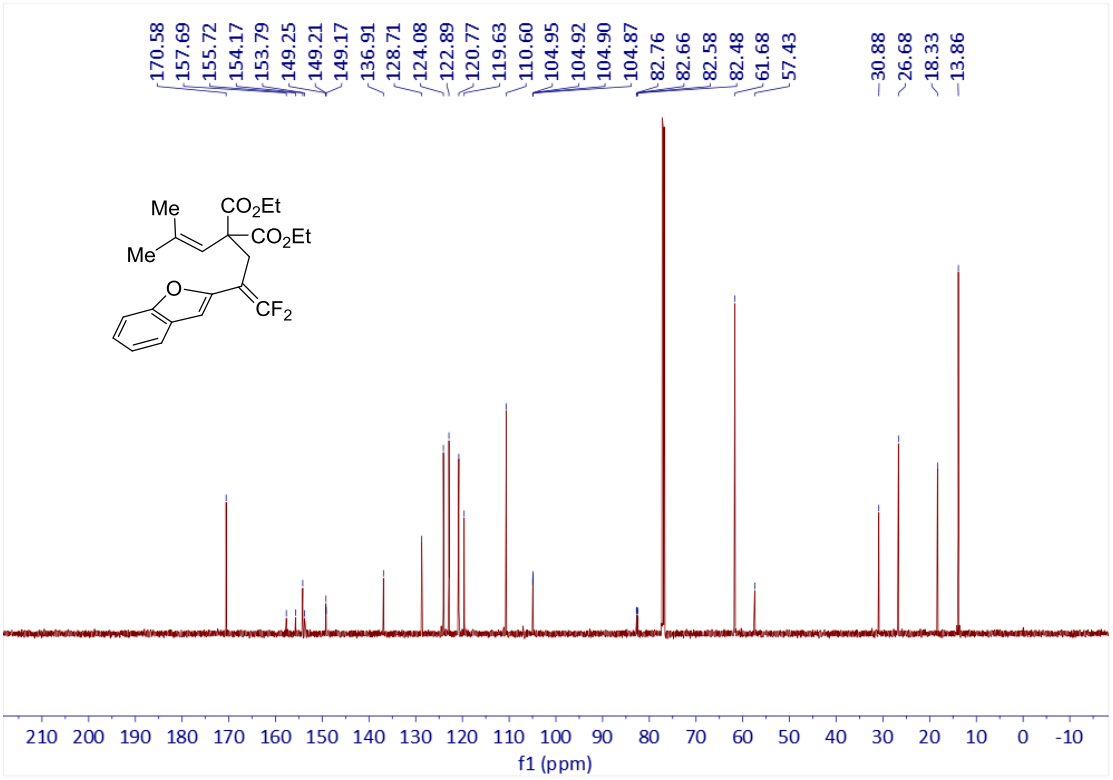

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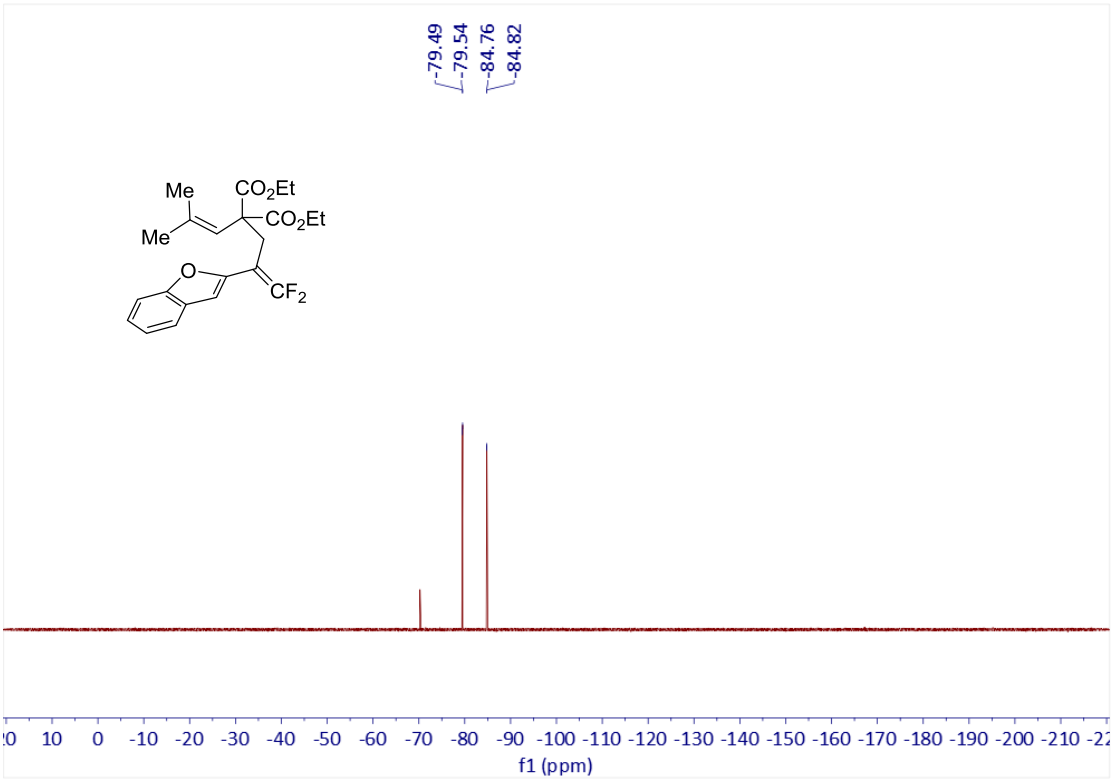
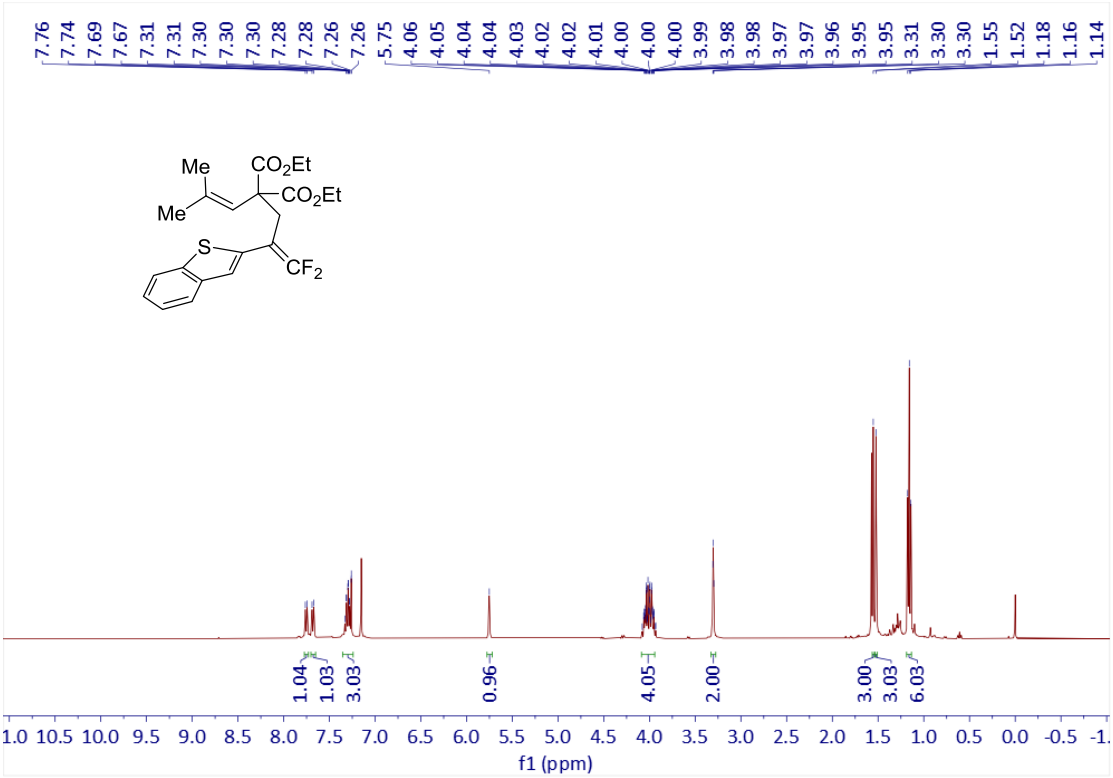
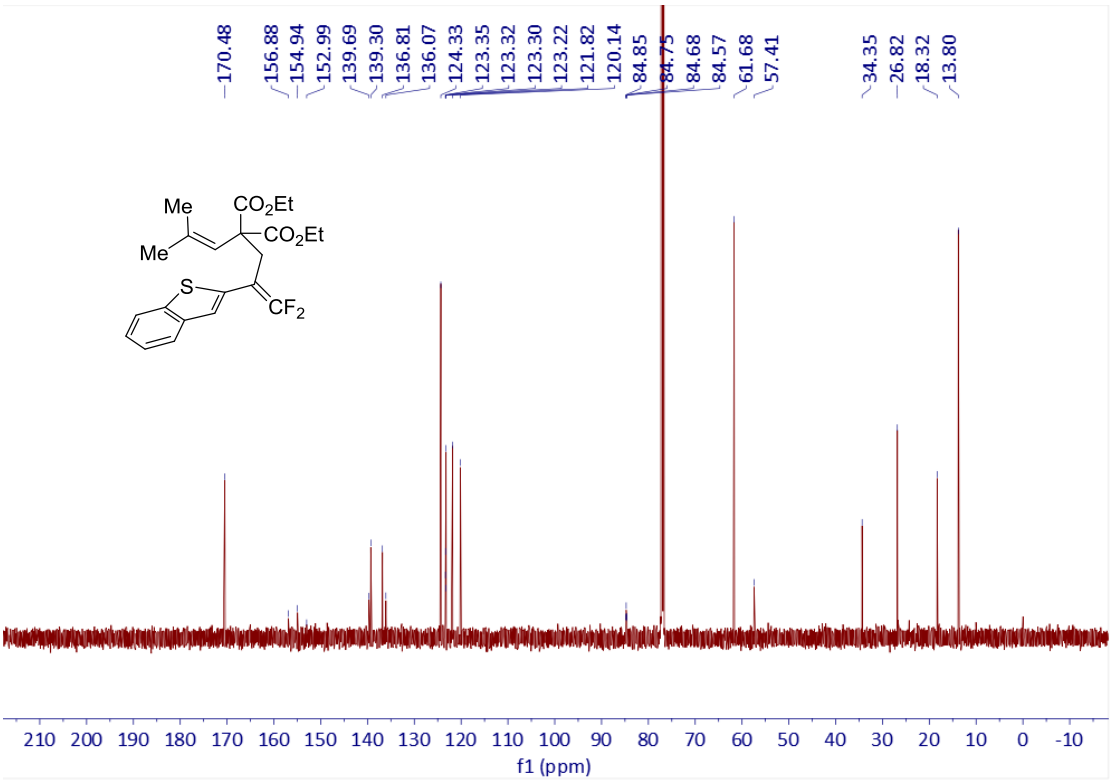


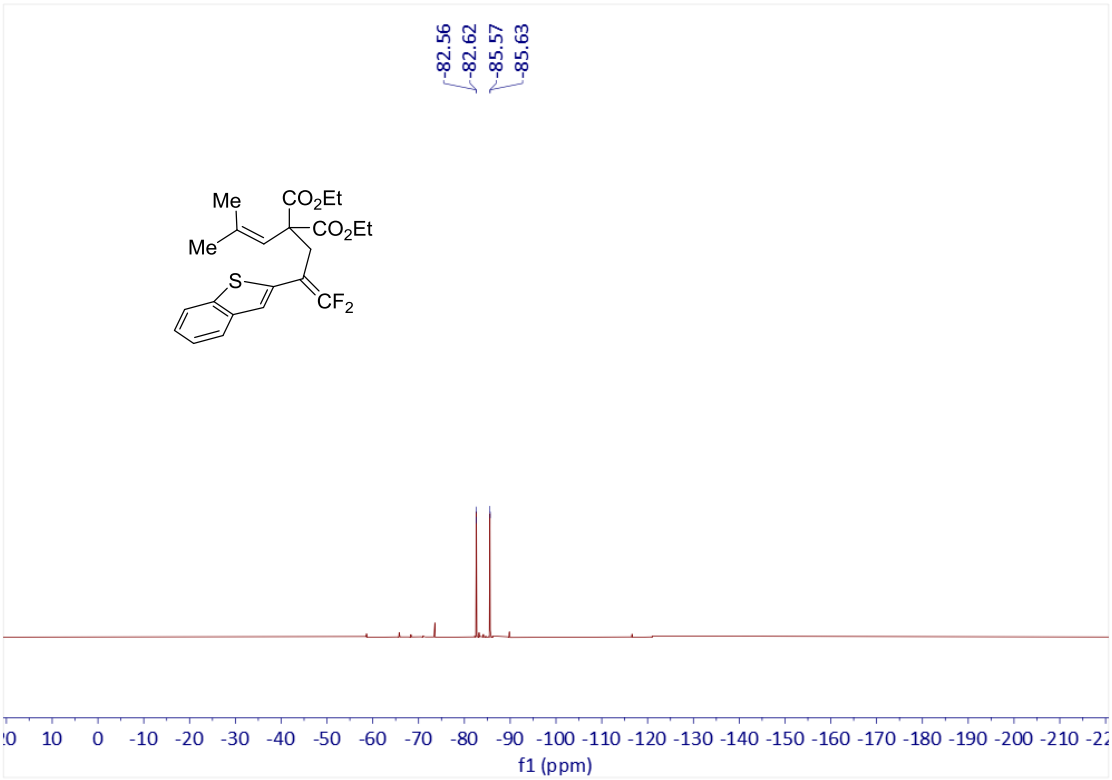
^{19}F NMR of 3n (377 MHz, $CDCl_3$)



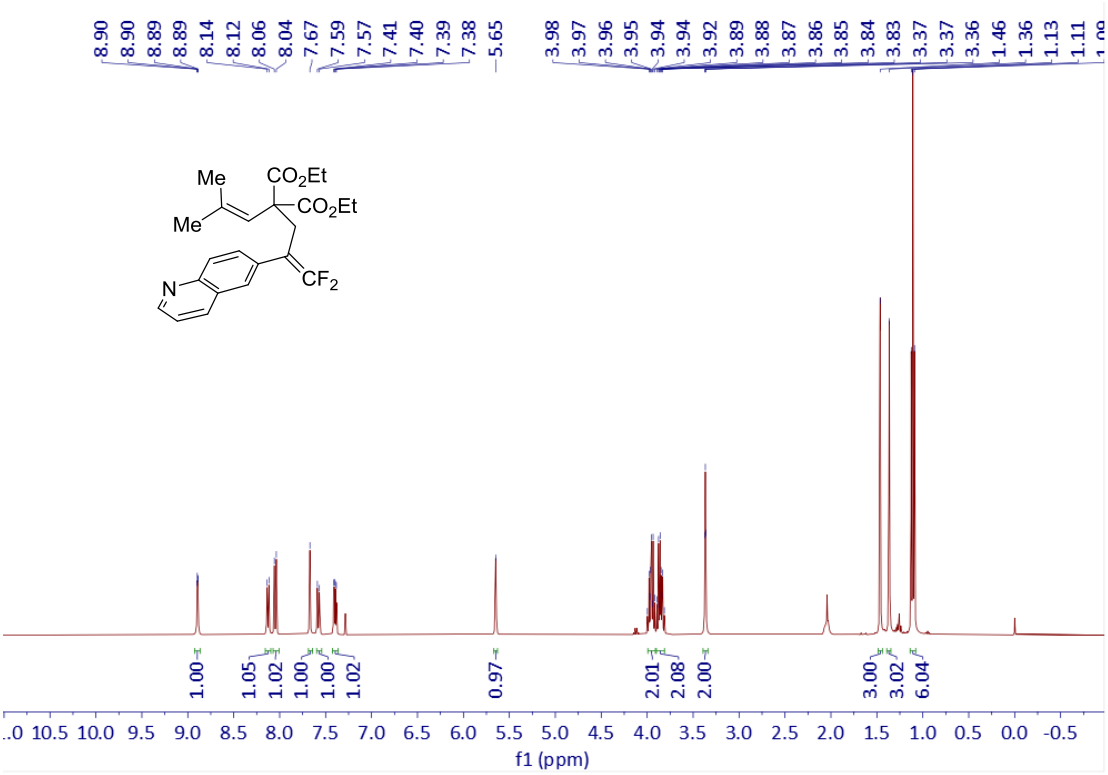
^{1}H NMR of 3o (400 MHz, $CDCl_3$)



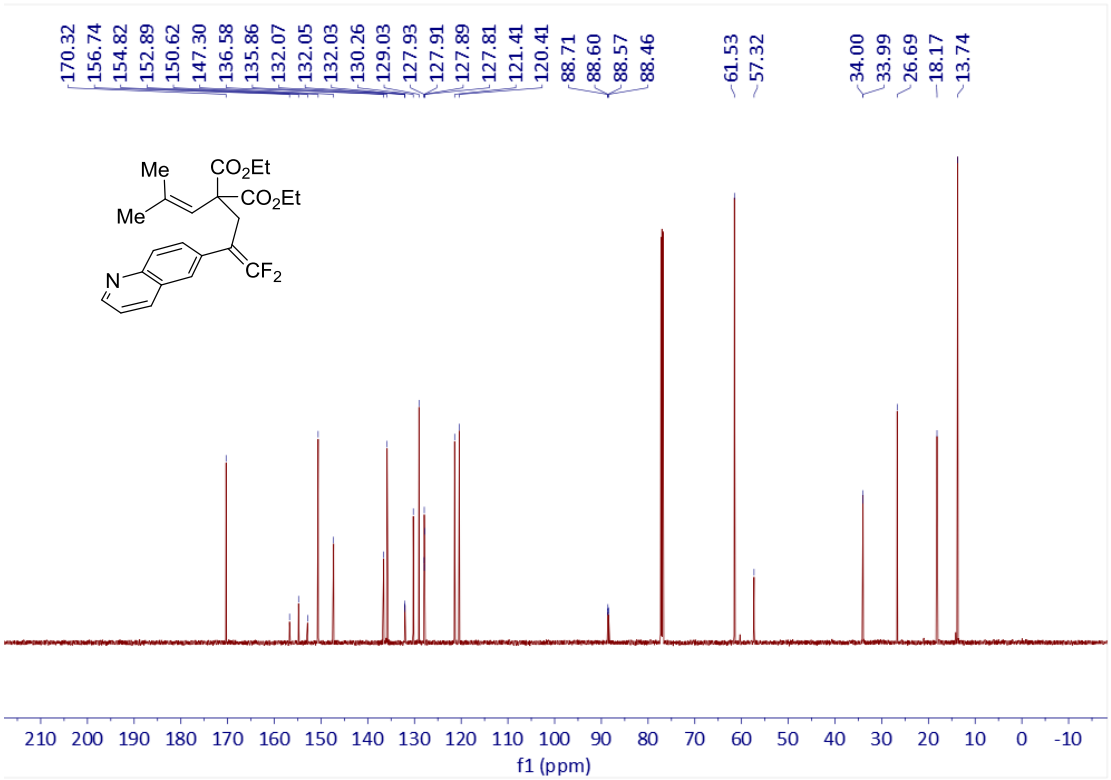
^{13}C NMR of 3o (151 MHz, $CDCl_3$)



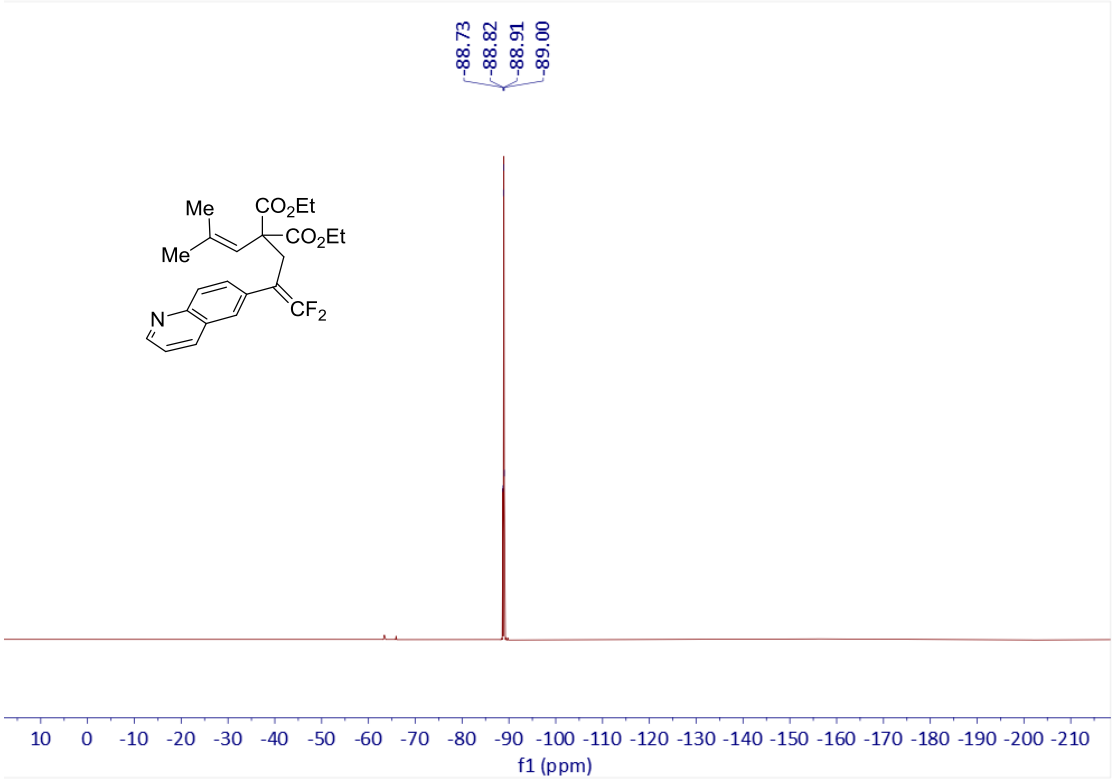
^{19}F NMR of 3o (377 MHz, $CDCl_3$)



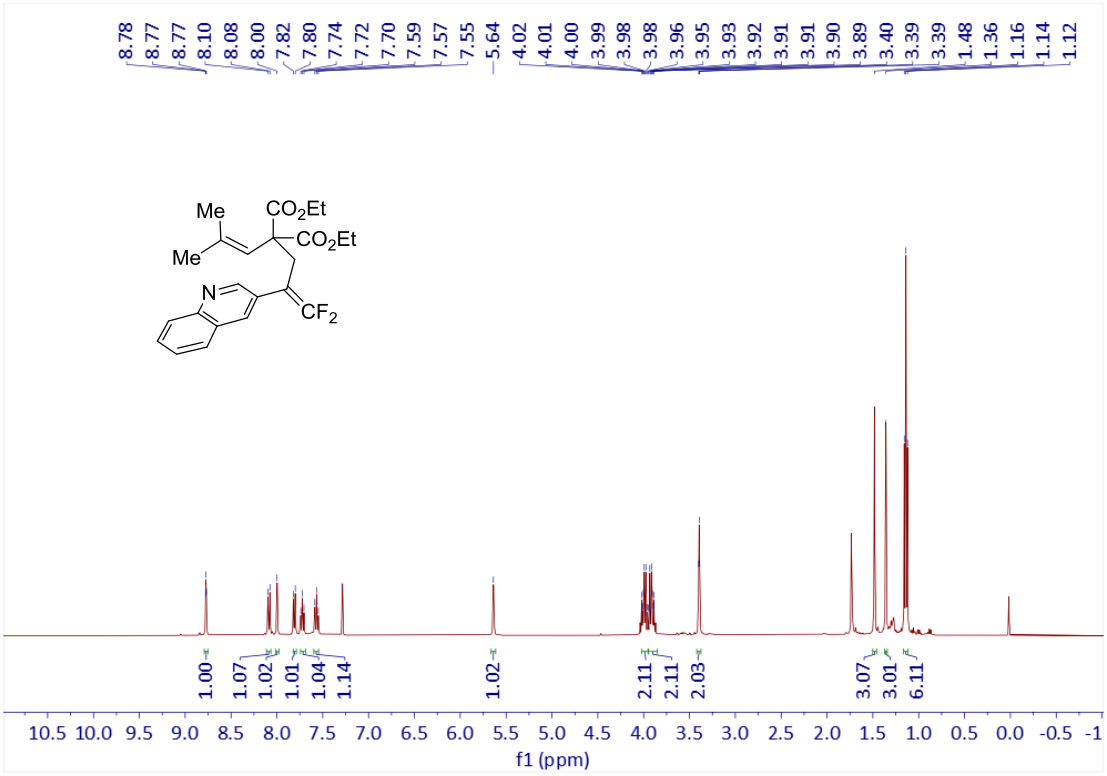
^{1}H NMR of 3p (400 MHz, $CDCl_3$)



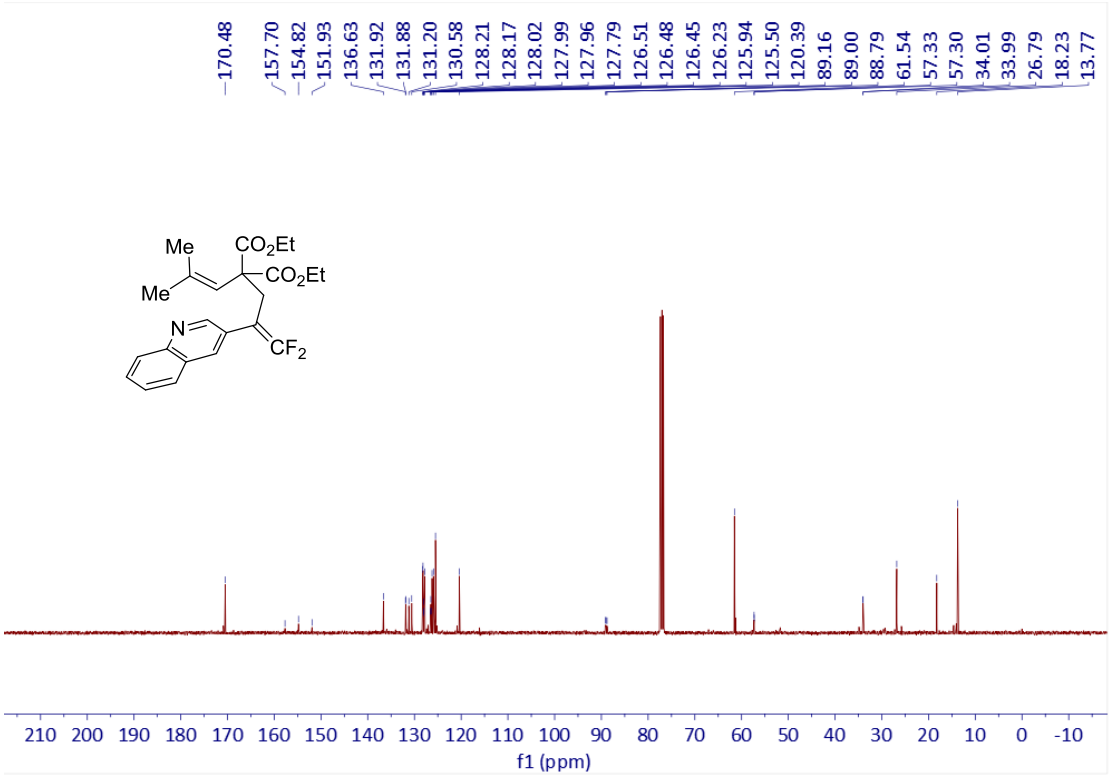
^{13}C NMR of 3p (151 MHz, $CDCl_3$)



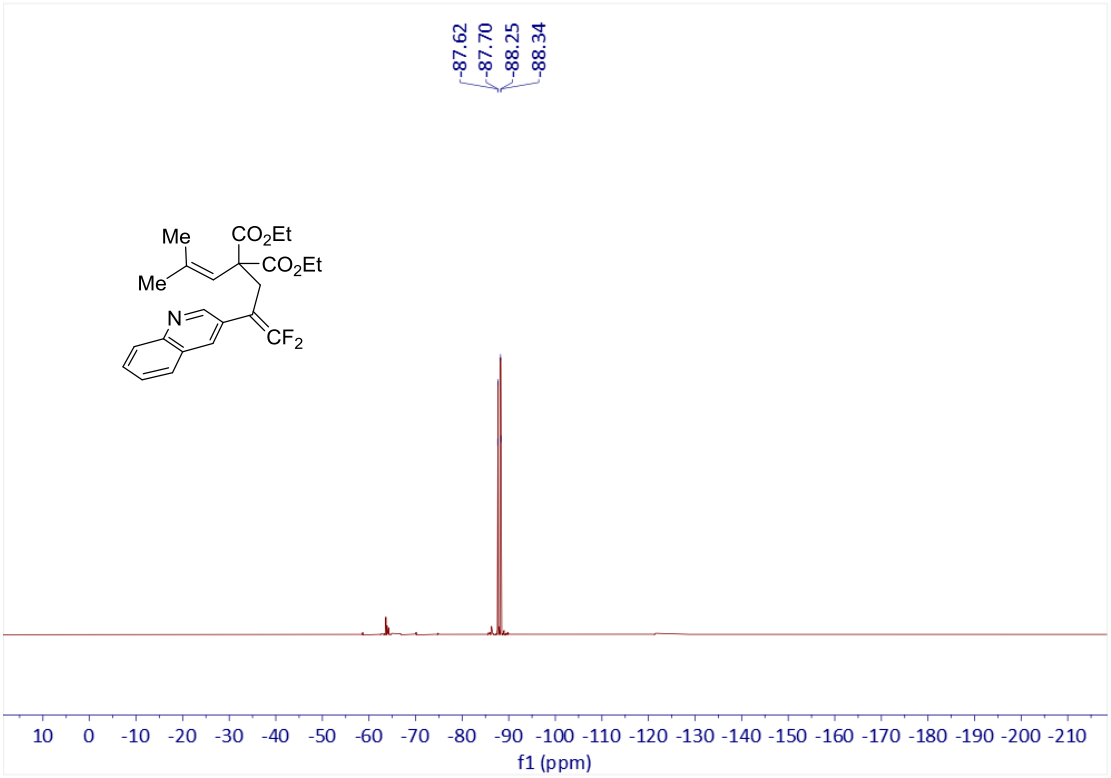
^{19}F NMR of 3p (377 MHz, $CDCl_3$)



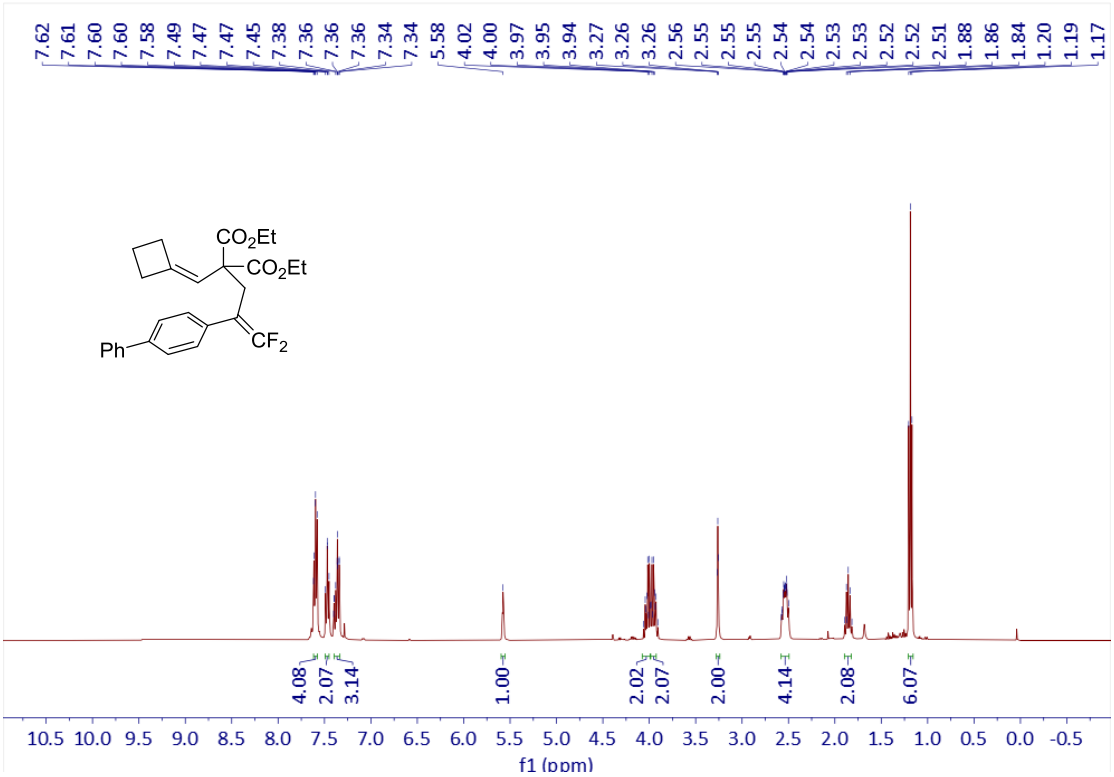
^{1}H NMR of 3q (400 MHz, $CDCl_3$)



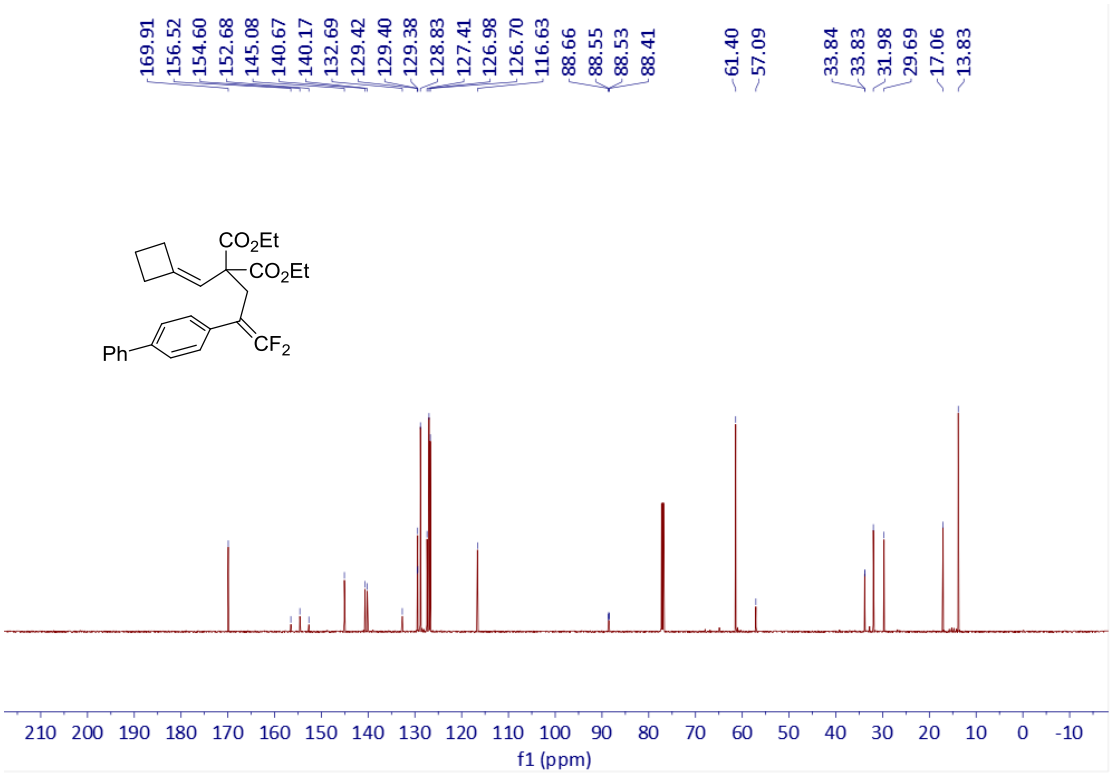
^{13}C NMR of 3q (101 MHz, $CDCl_3$)



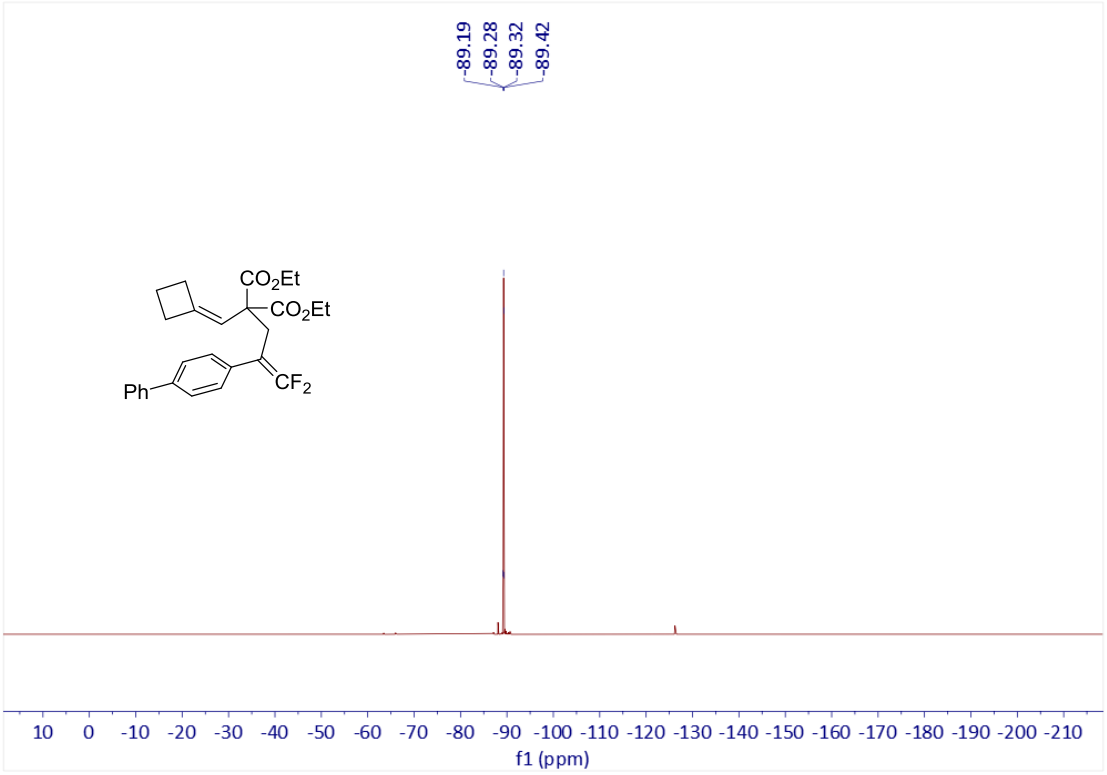
^{19}F NMR of 3q (377 MHz, $CDCl_3$)



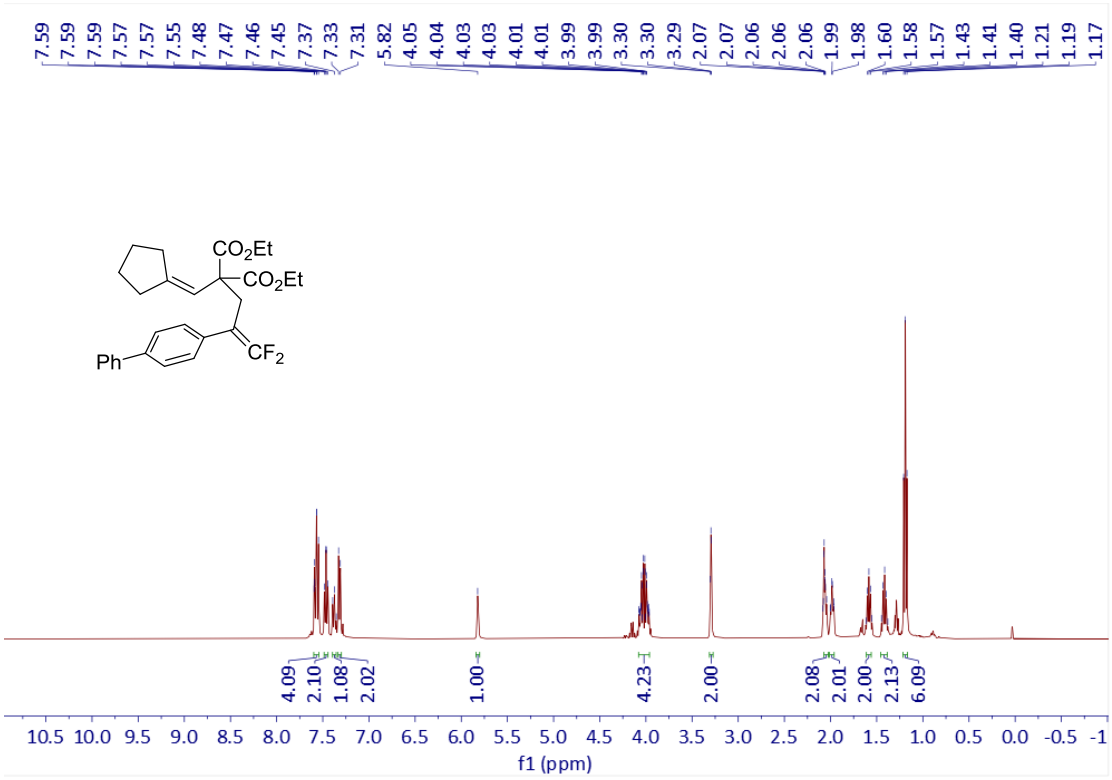
^{1}H NMR of 3r (400 MHz, $CDCl_3$)



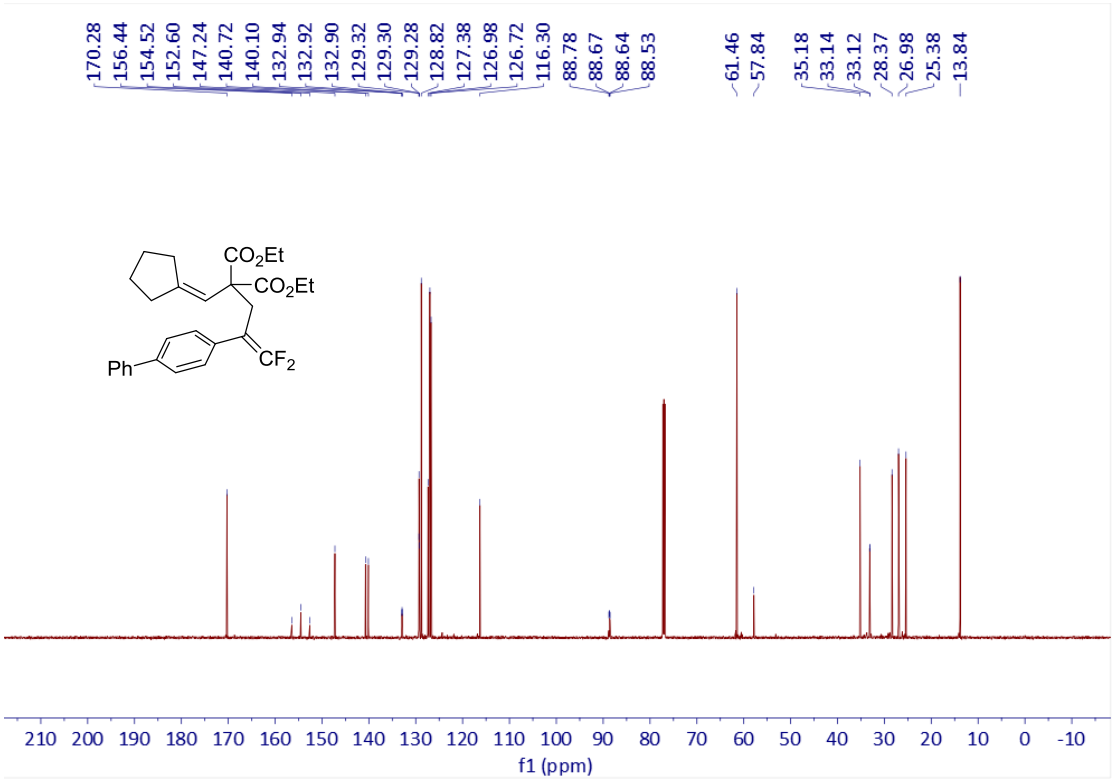
^{13}C NMR of 3r (151 MHz, $CDCl_3$)



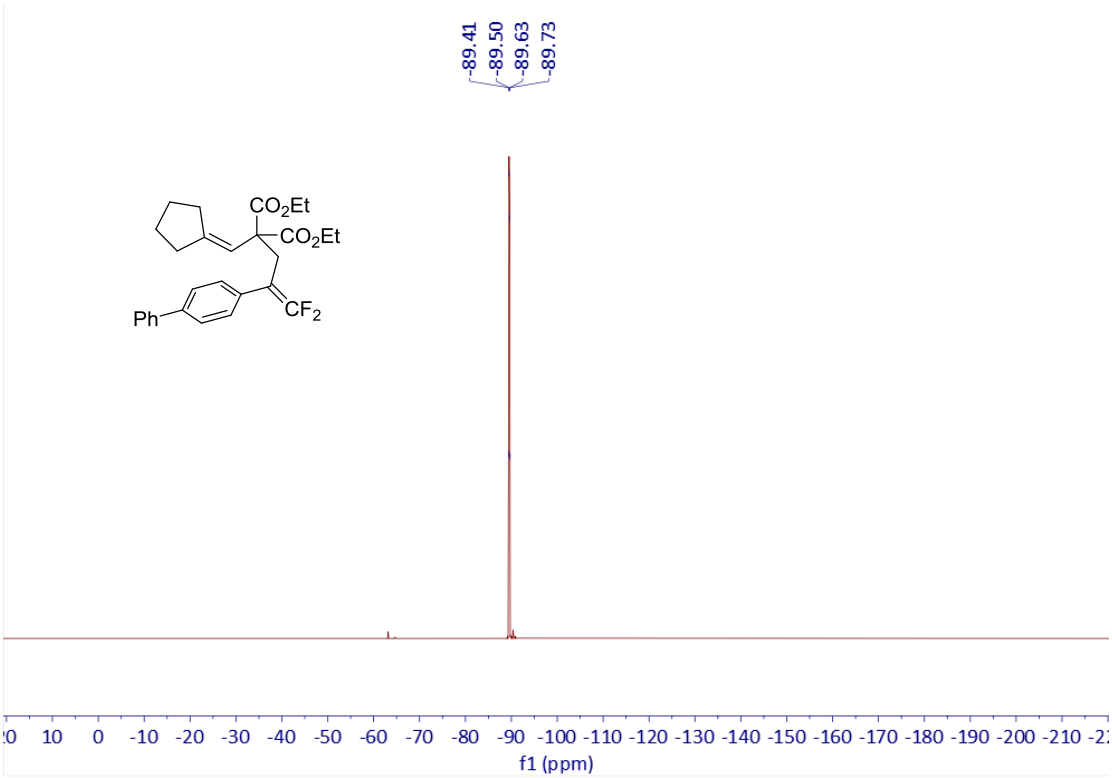
^{19}F NMR of 3r (377 MHz, $CDCl_3$)



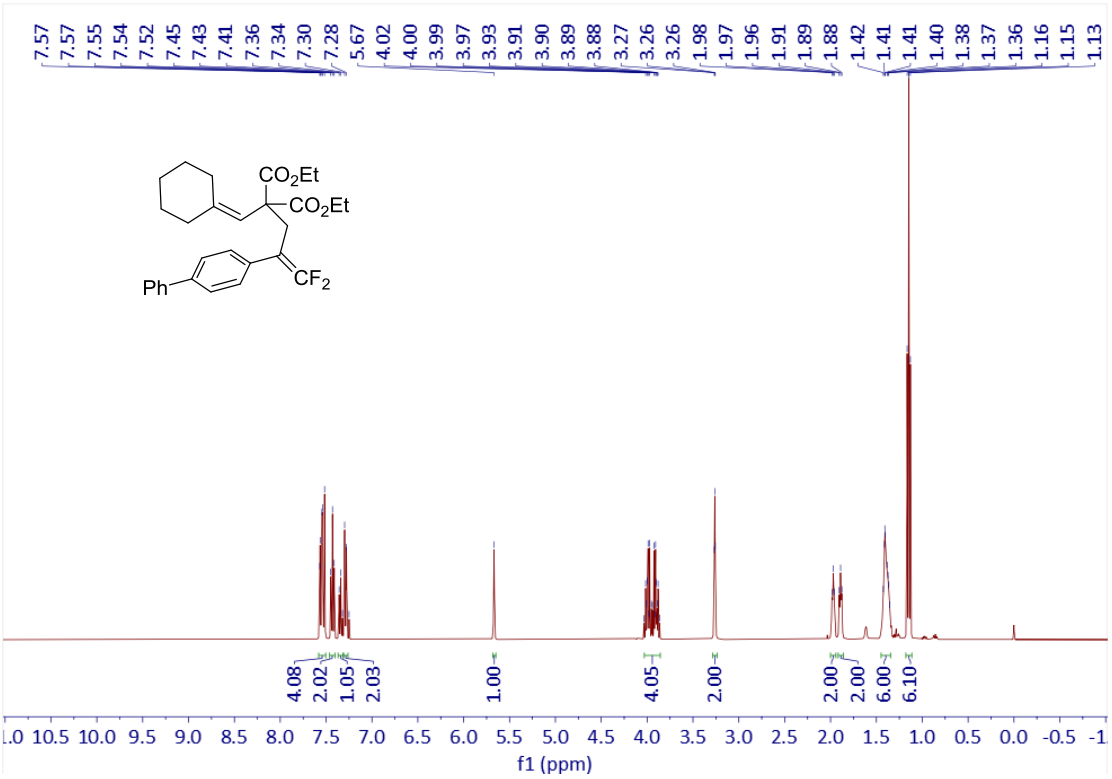
^{1}H NMR of 3s (400 MHz, $CDCl_3$)



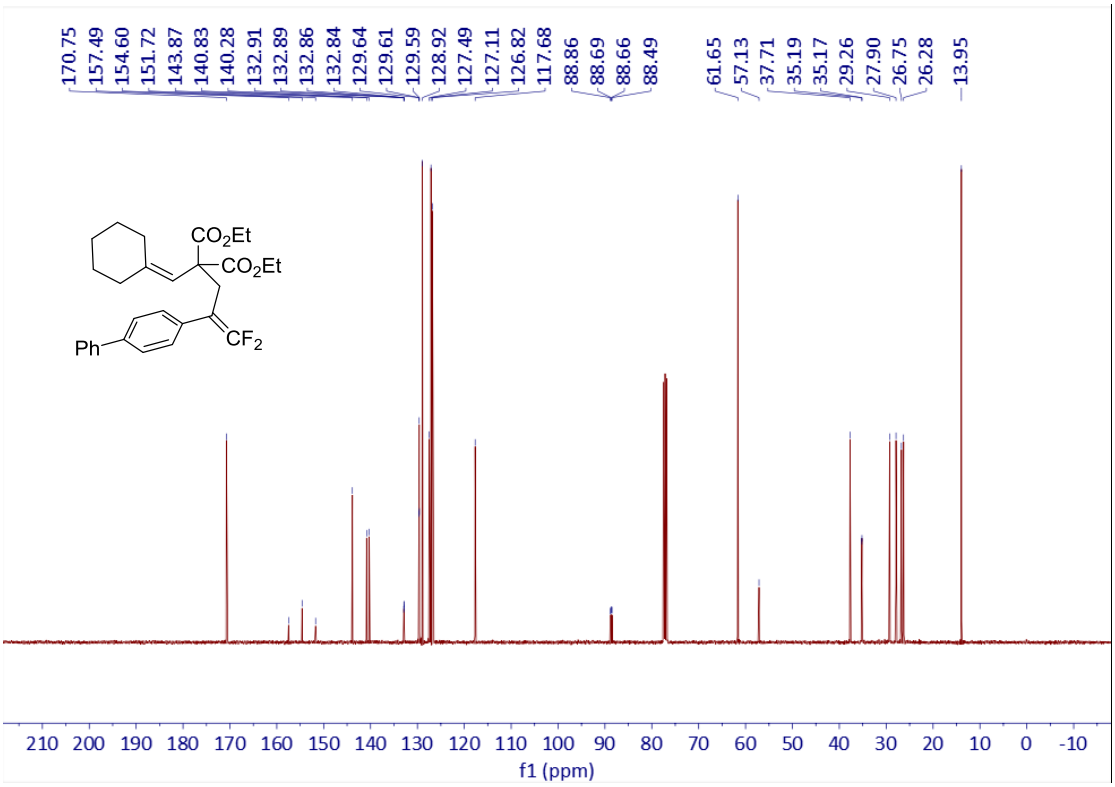
^{13}C NMR of 3s (151 MHz, $CDCl_3$)



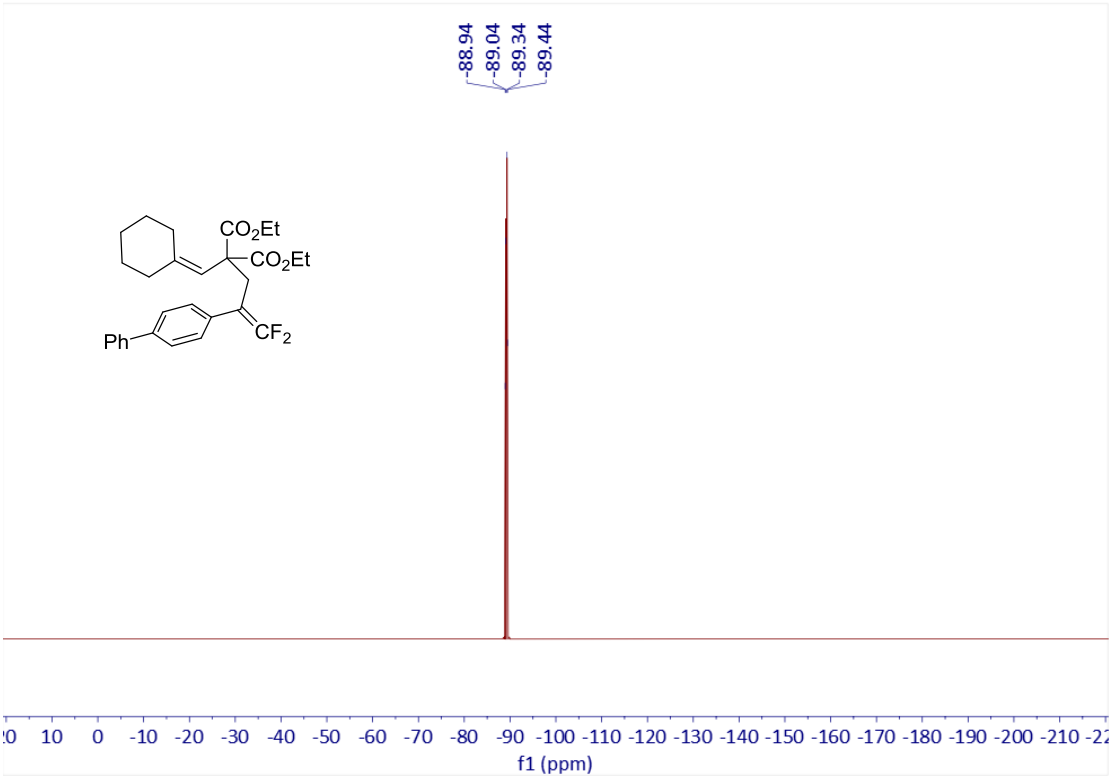
^{19}F NMR of 3s (377 MHz, $CDCl_3$)



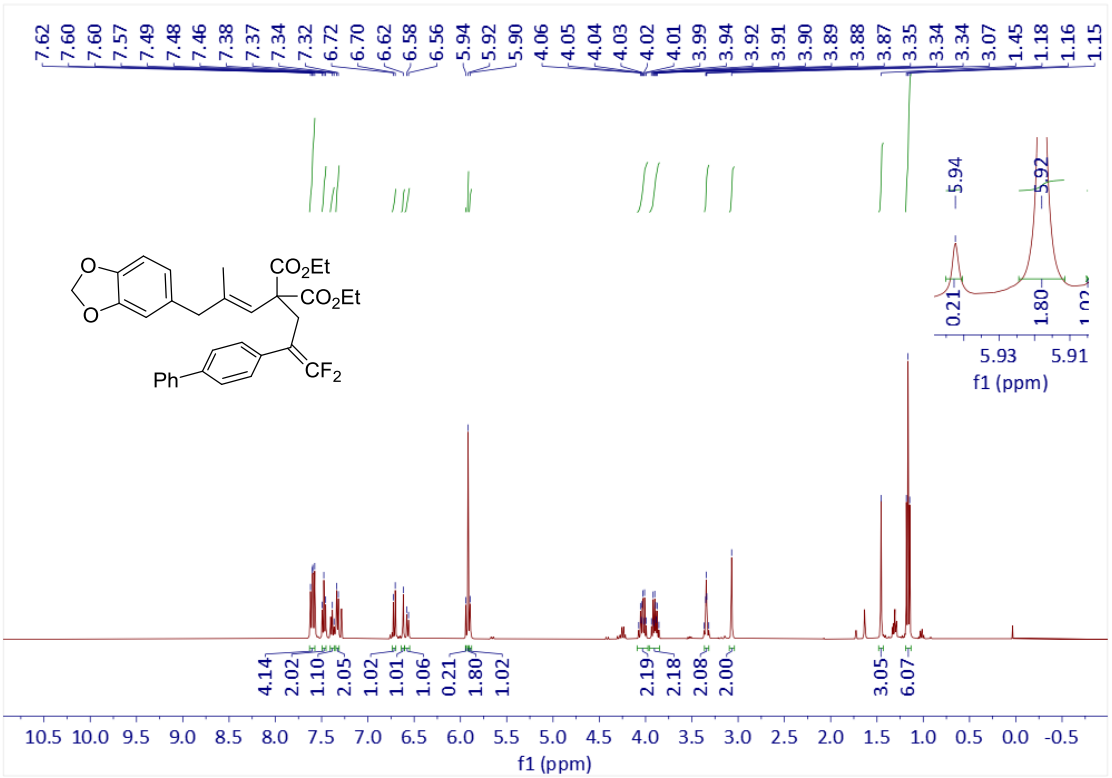
^{1}H NMR of 3t (400 MHz, $CDCl_3$)



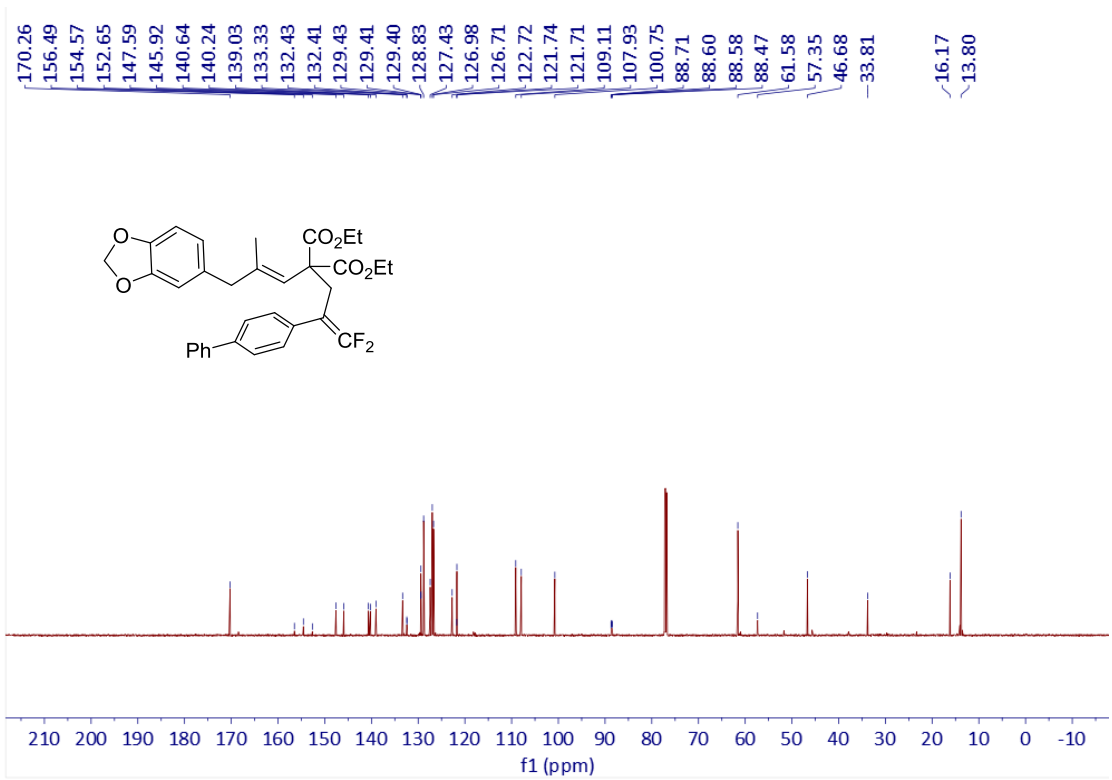
^{13}C NMR of 3t (151 MHz, $CDCl_3$)



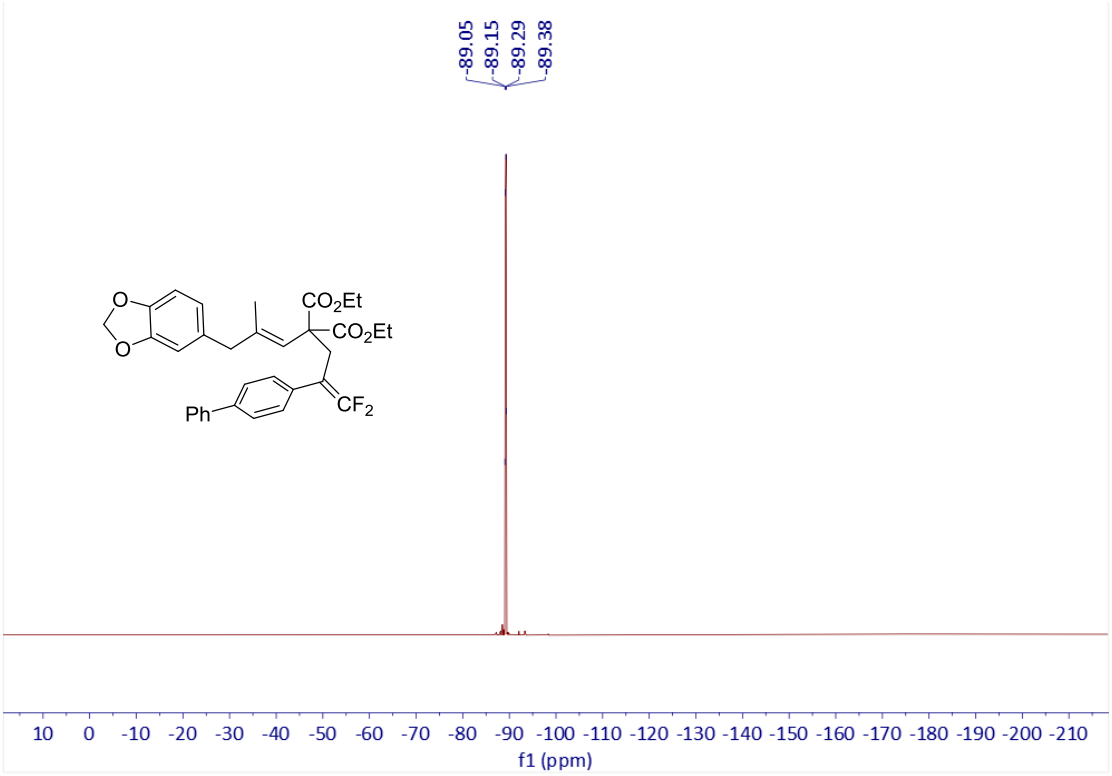
^{19}F NMR of 3t (377 MHz, $CDCl_3$)



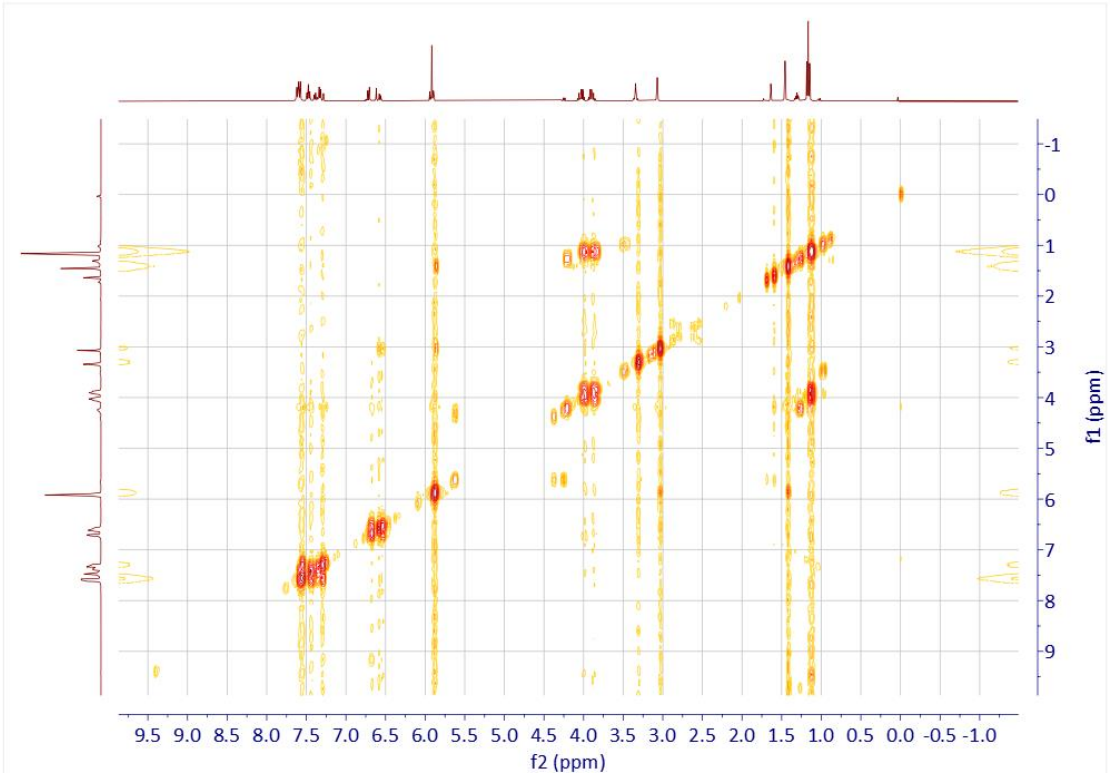
^{1}H NMR of 3u (400 MHz, $CDCl_3$)



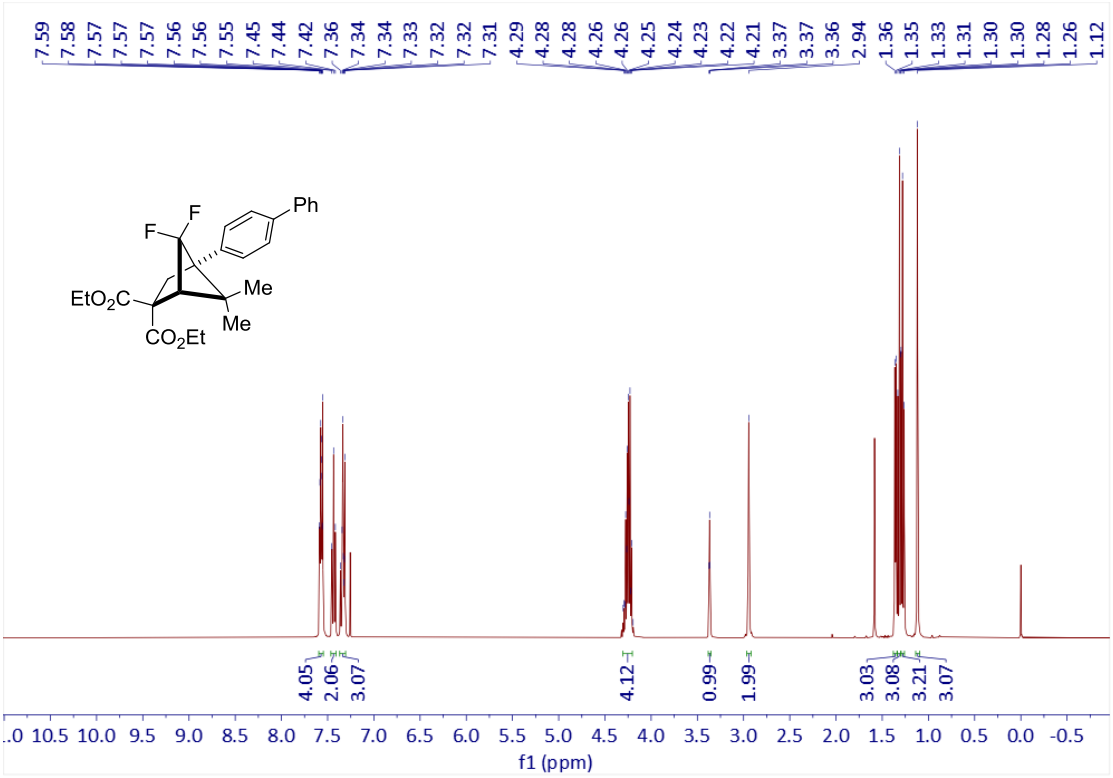
^{13}C NMR of 3u (151 MHz, $CDCl_3$)



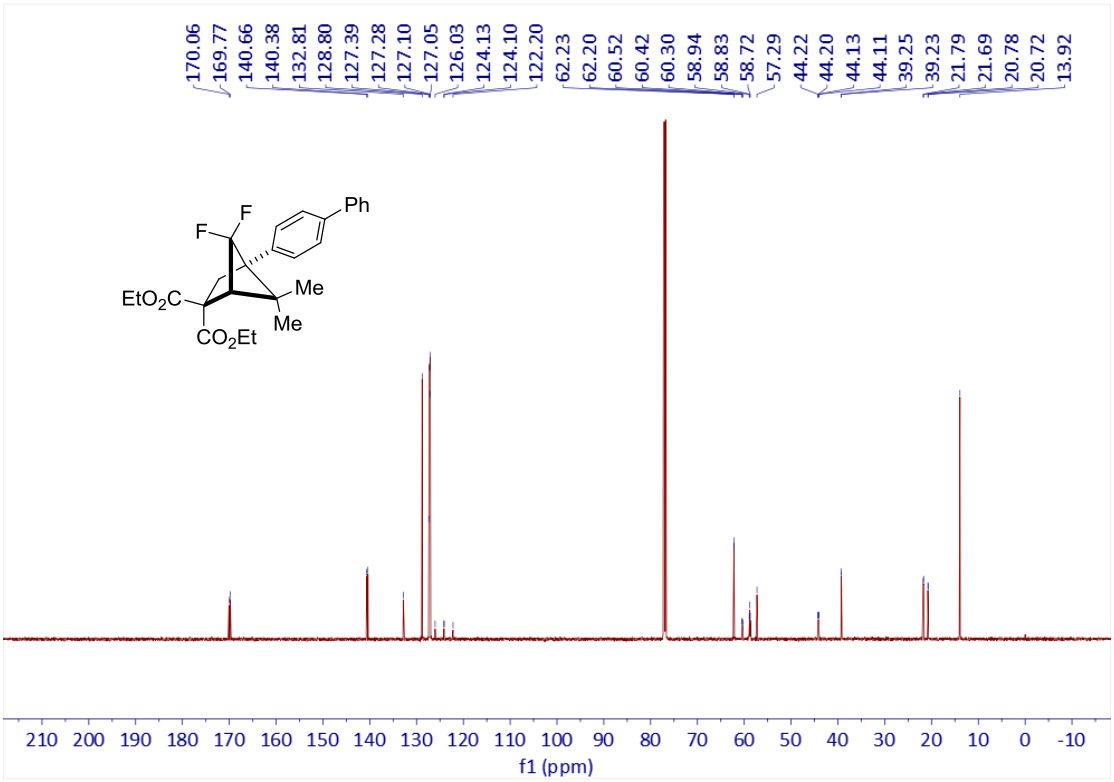
^{19}F NMR of 3u (377 MHz, $CDCl_3$)



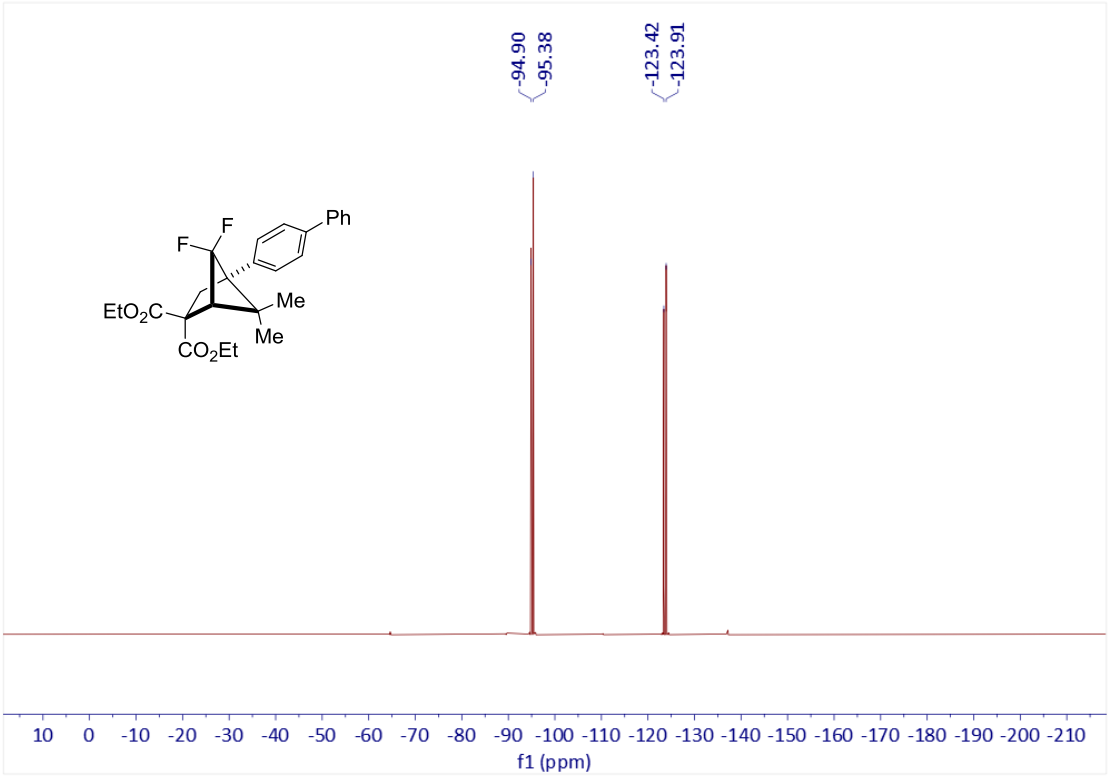
H-H COSY of **3u**



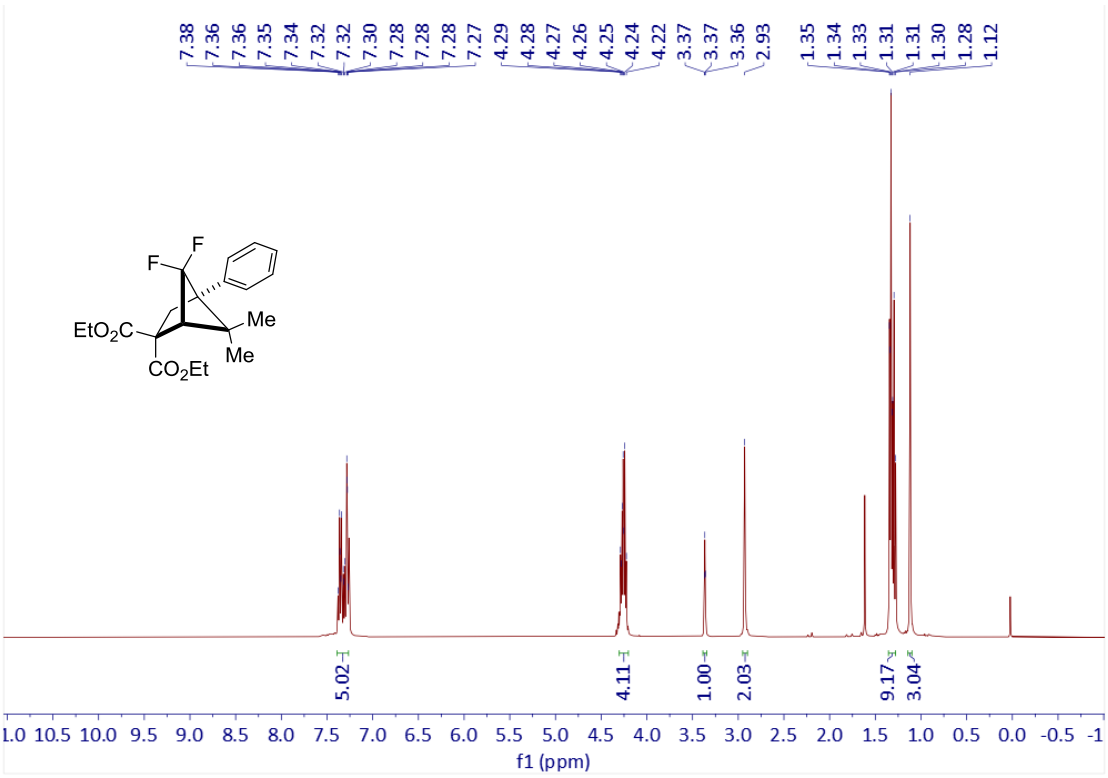
^{1}H NMR of 4a (400 MHz, $CDCl_3$)



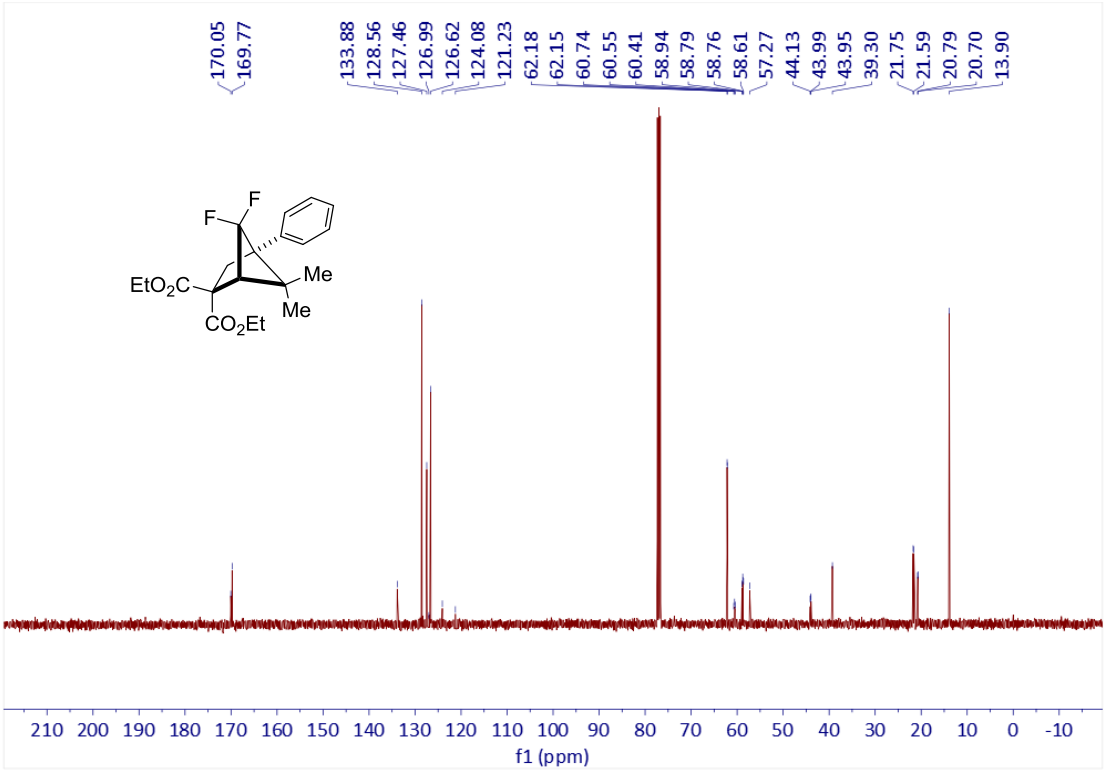
^{13}C NMR of 4a (151 MHz, $CDCl_3$)



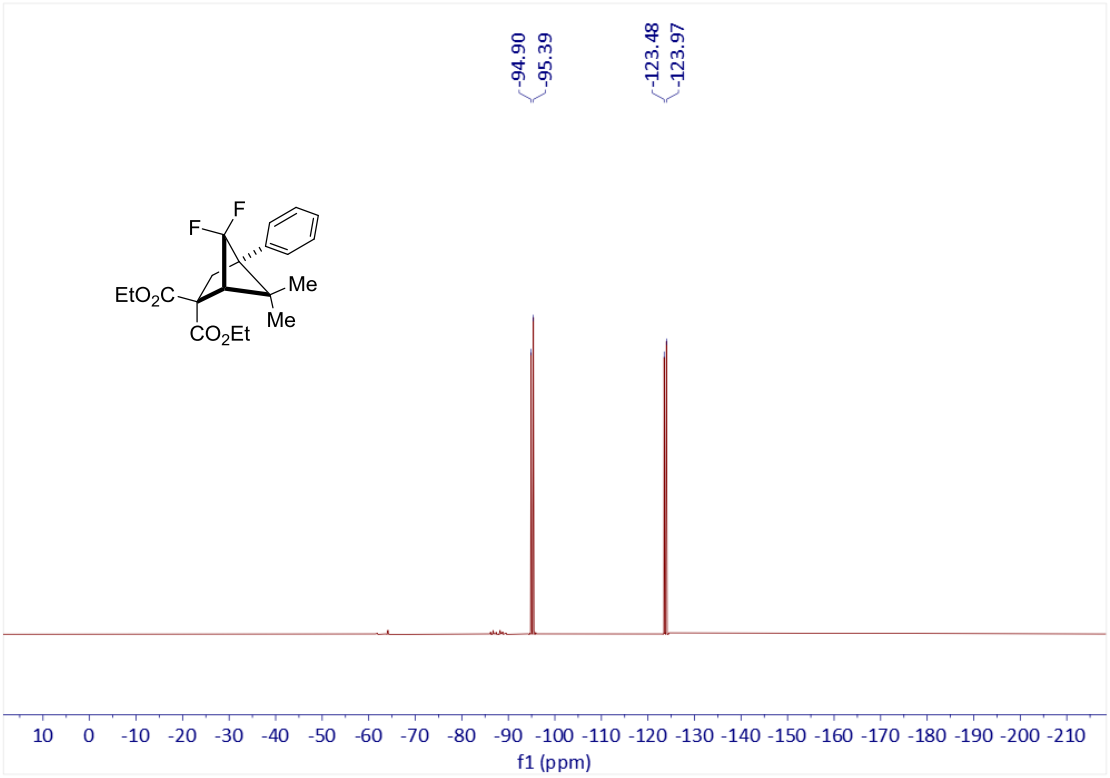
^{19}F NMR of 4a (377 MHz, $CDCl_3$)



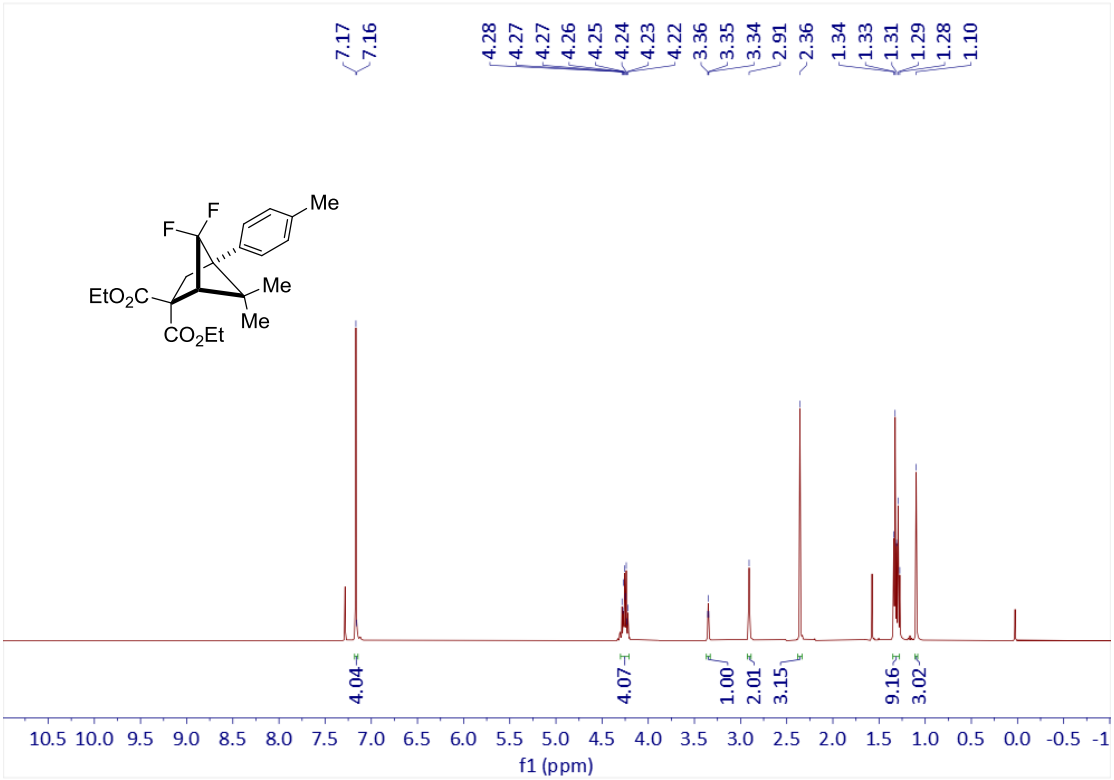
^{1}H NMR of 4b (400 MHz, $CDCl_3$)



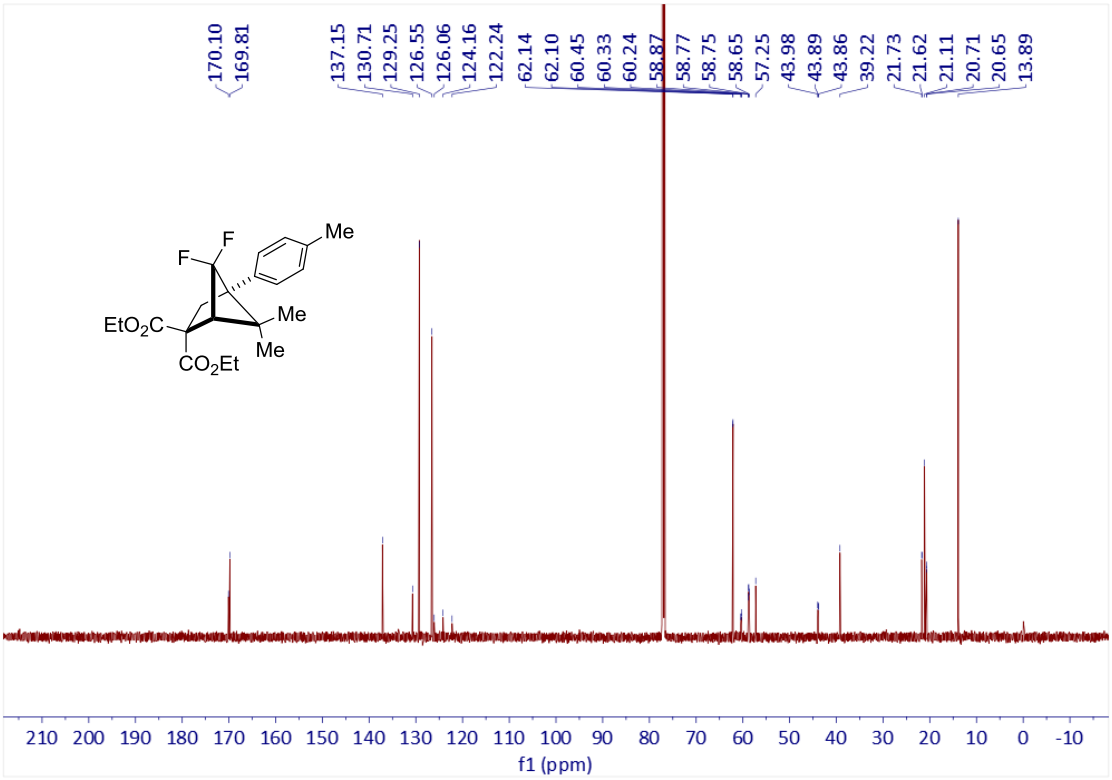
^{13}C NMR of 4b (101 MHz, $CDCl_3$)



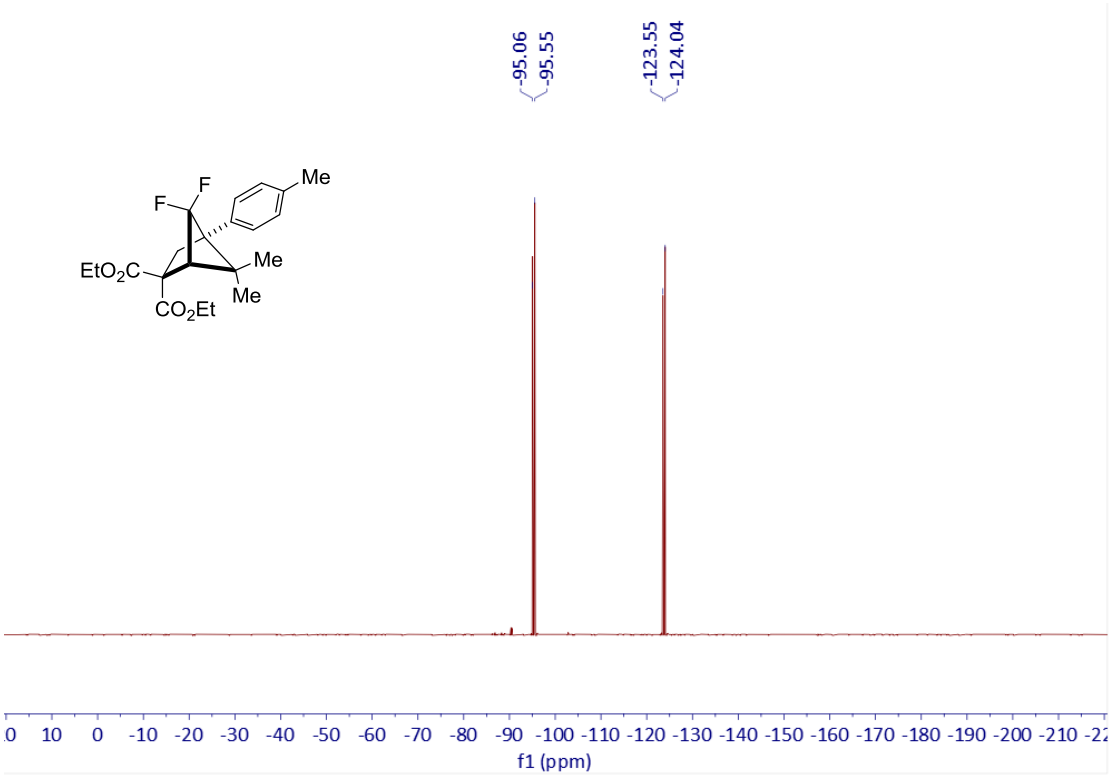
^{19}F NMR of 4b (377 MHz, $CDCl_3$)



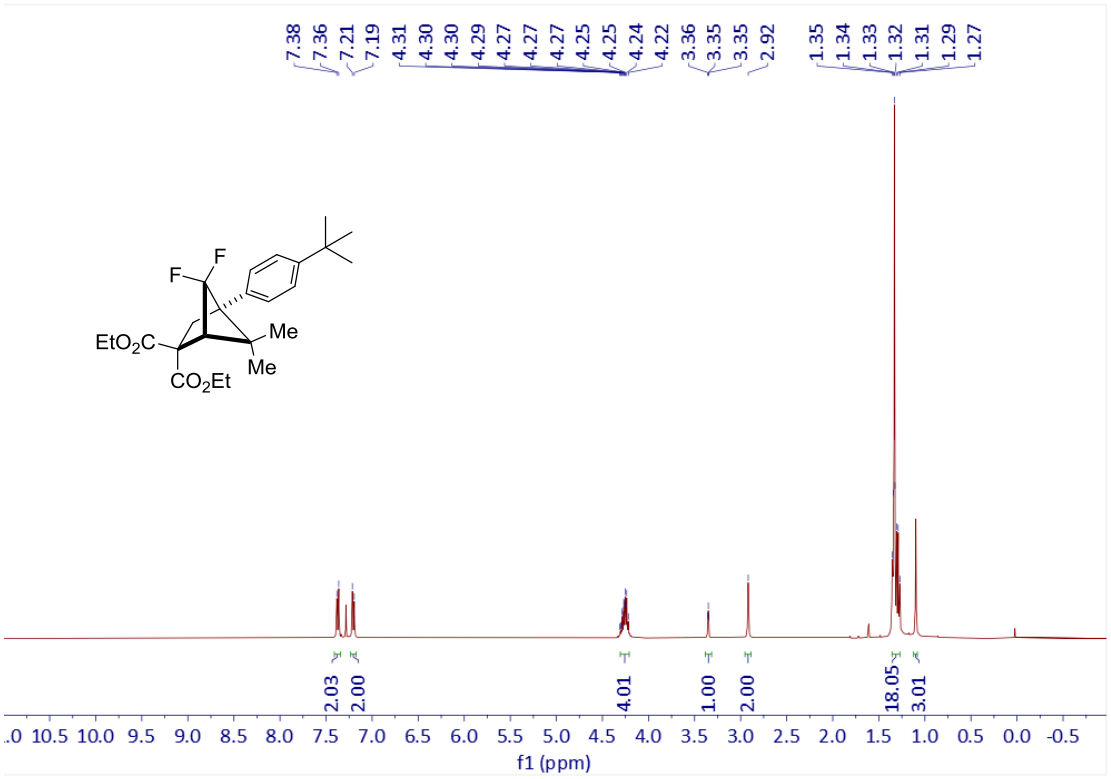
^{1}H NMR of 4c (400 MHz, $CDCl_3$)



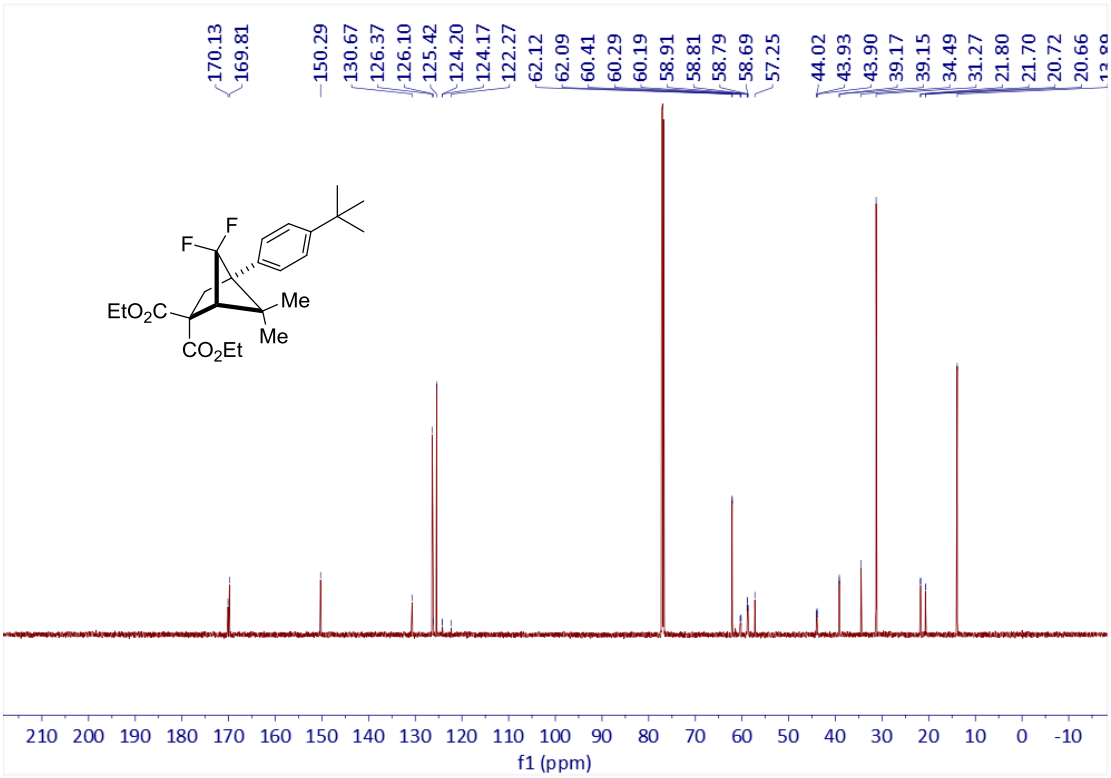
^{13}C NMR of 4c (151 MHz, $CDCl_3$)



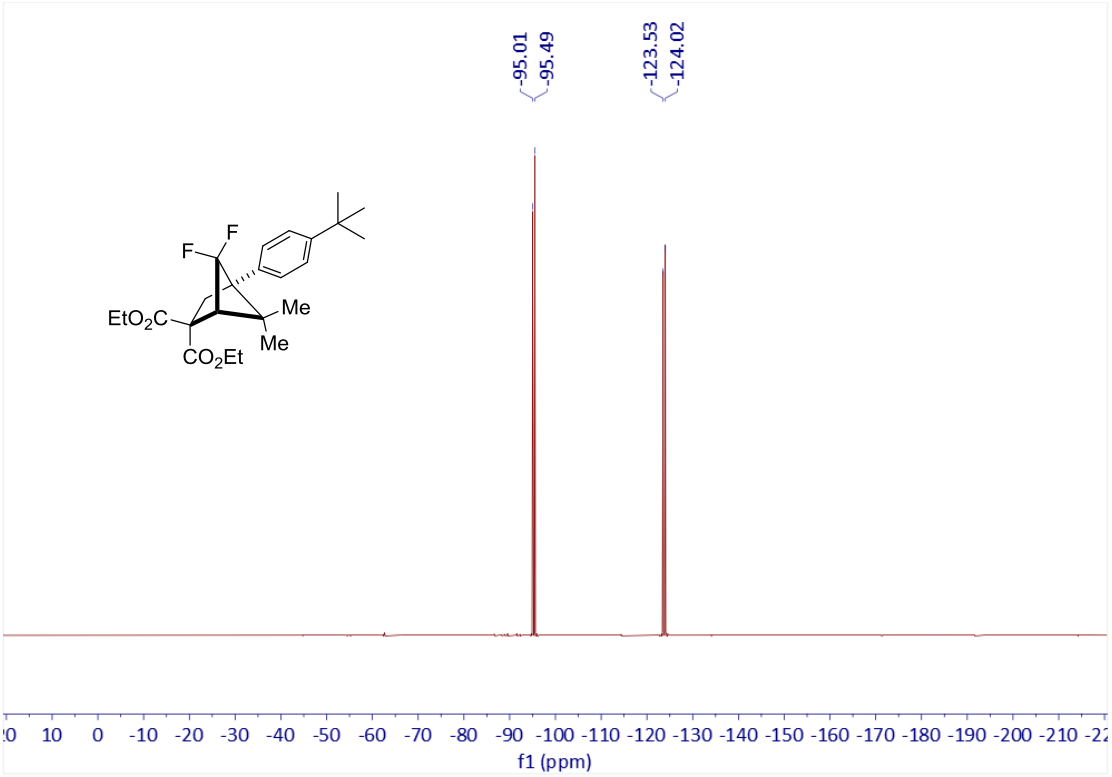
^{19}F NMR of 4c (377 MHz, $CDCl_3$)



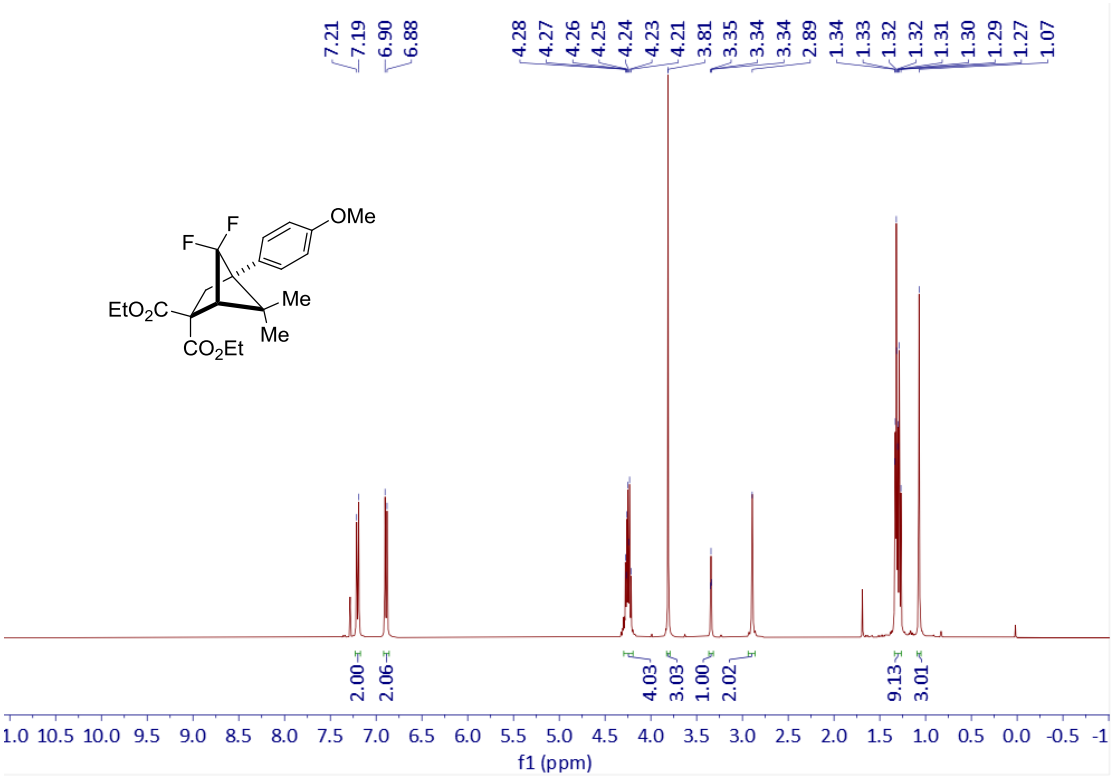
^{1}H NMR of 4d (400 MHz, $CDCl_3$)



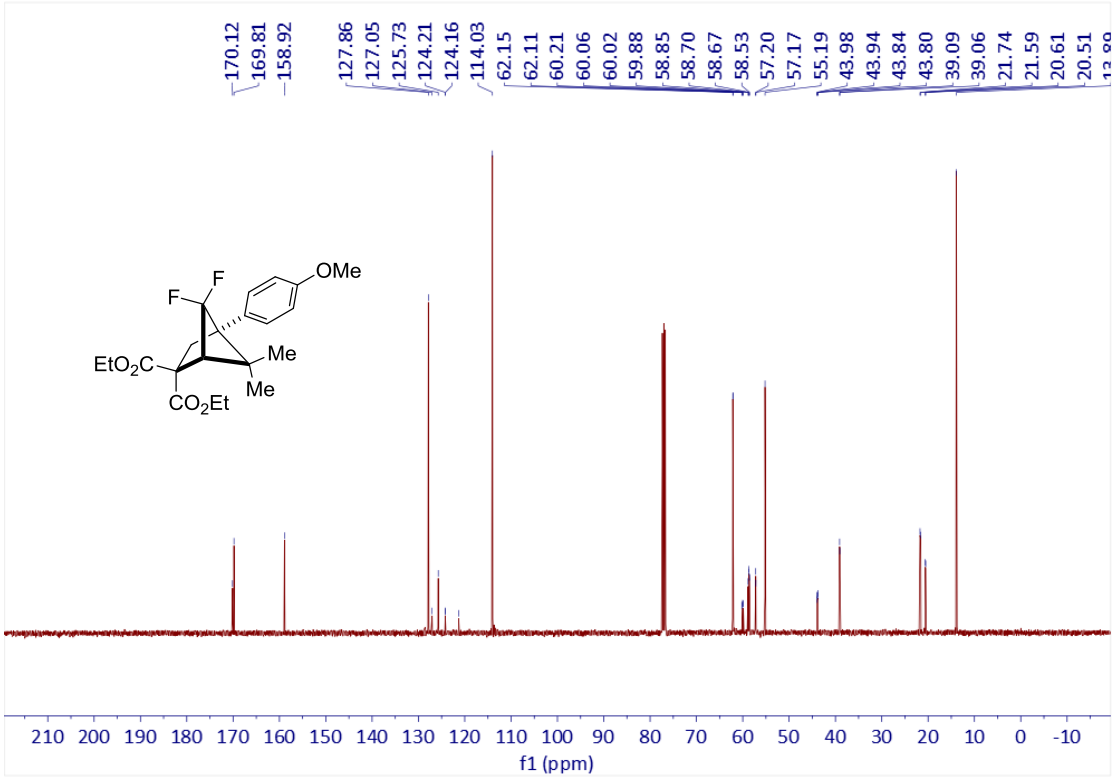
^{13}C NMR of 4d (151 MHz, $CDCl_3$)



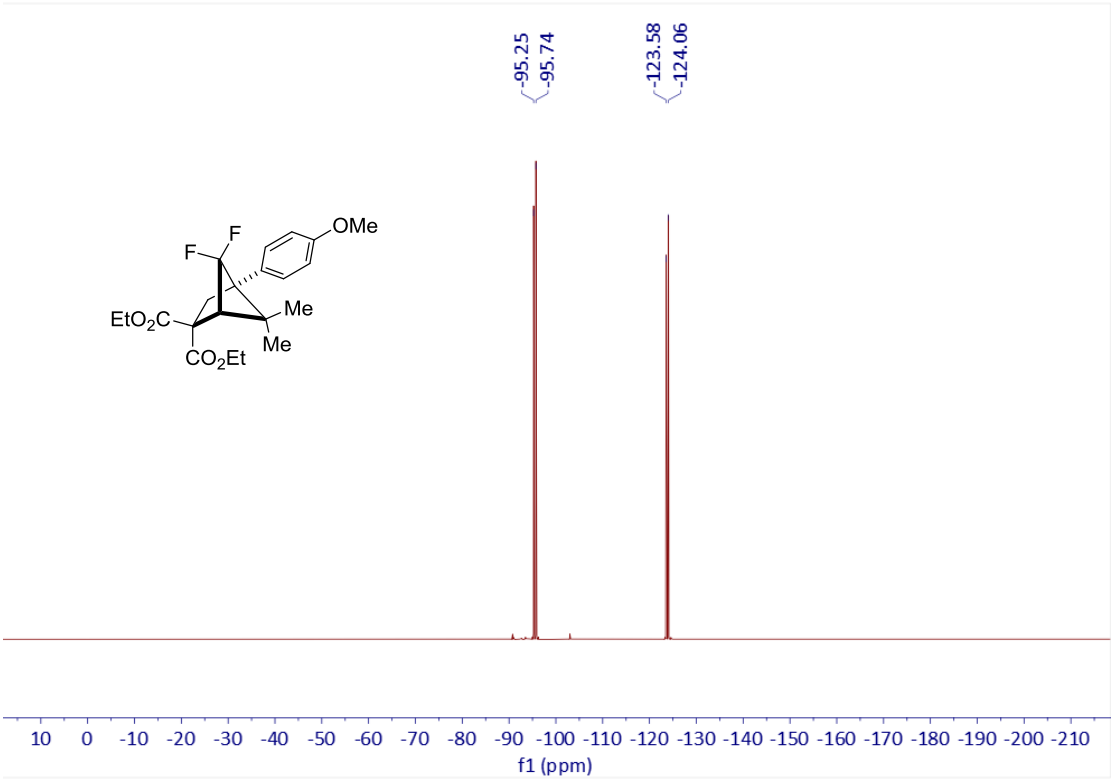
^{19}F NMR of 4d (377 MHz, $CDCl_3$)



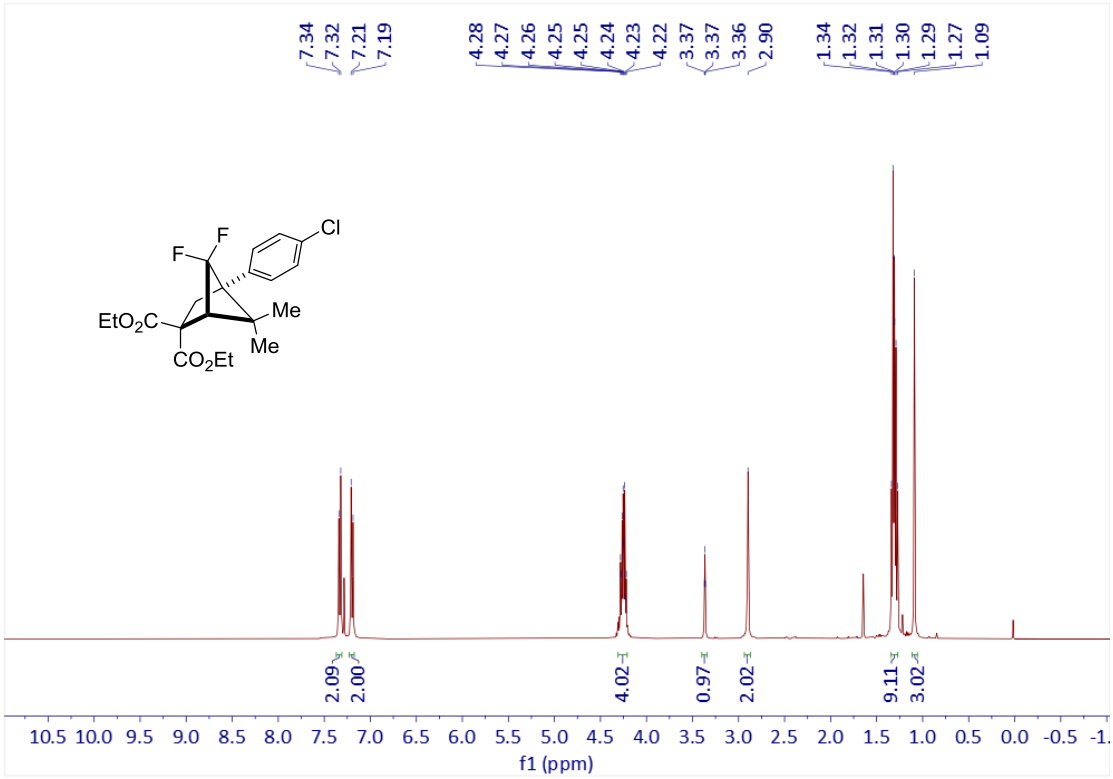
^{1}H NMR of 4e (400 MHz, $CDCl_3$)



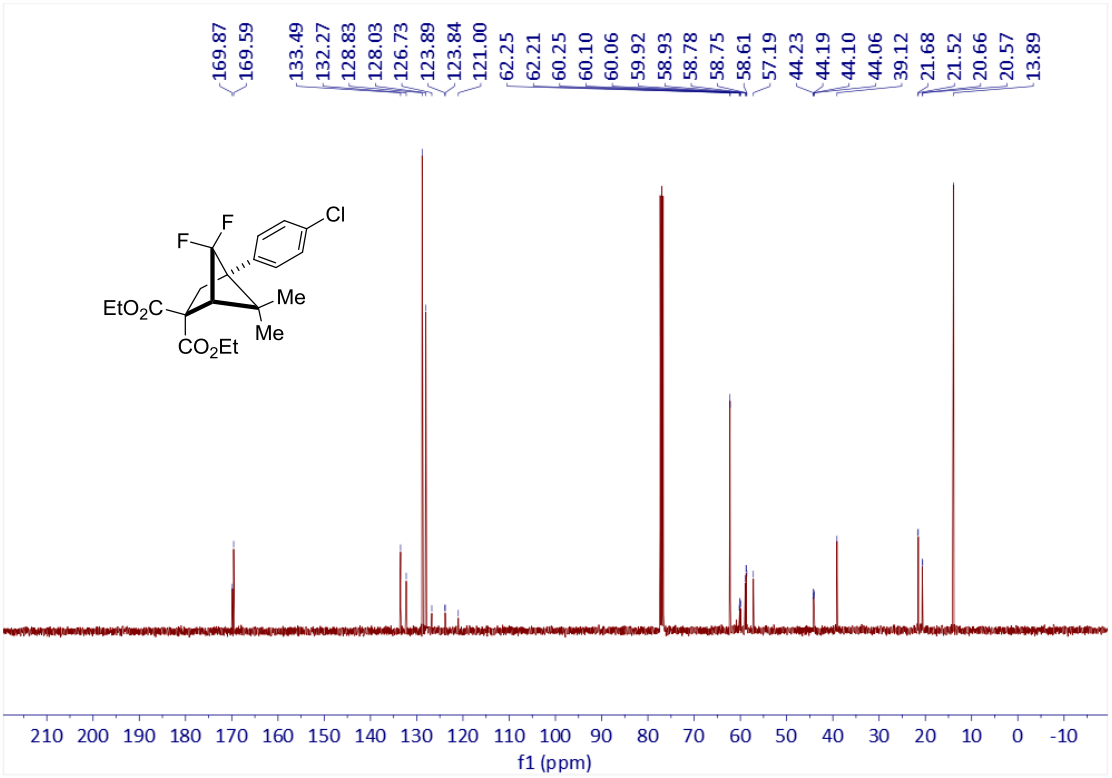
^{13}C NMR of 4e (151 MHz, $CDCl_3$)



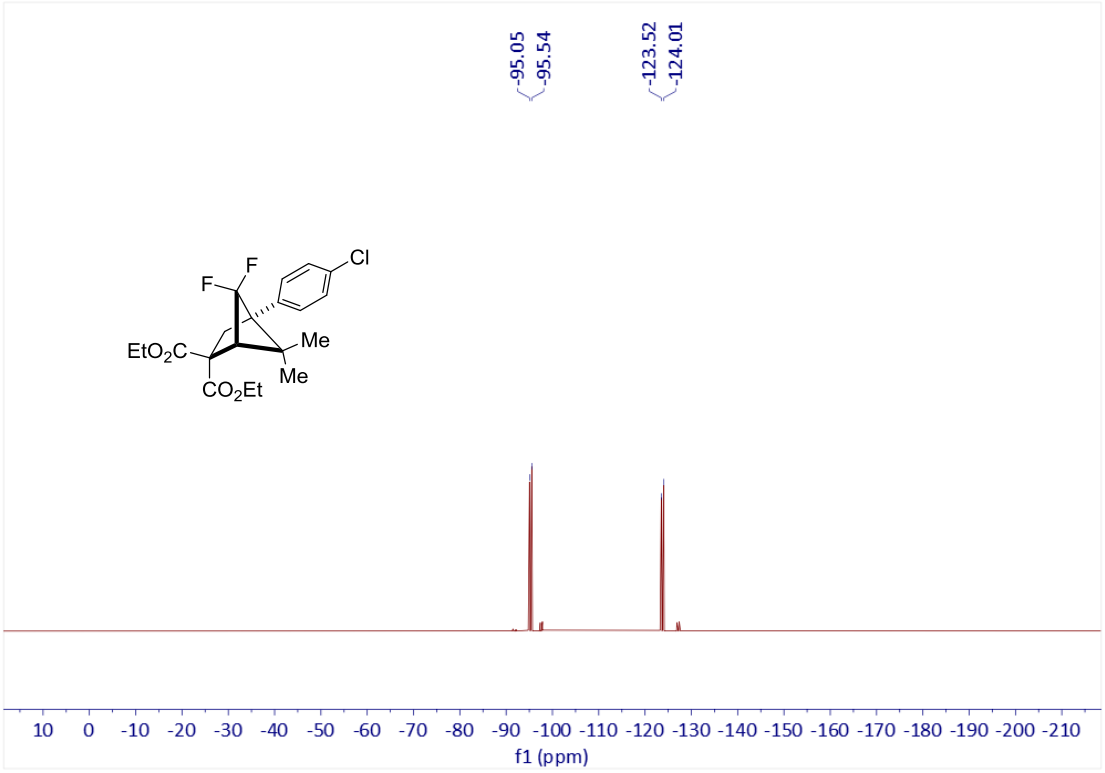
^{19}F NMR of 4e (377 MHz, $CDCl_3$)



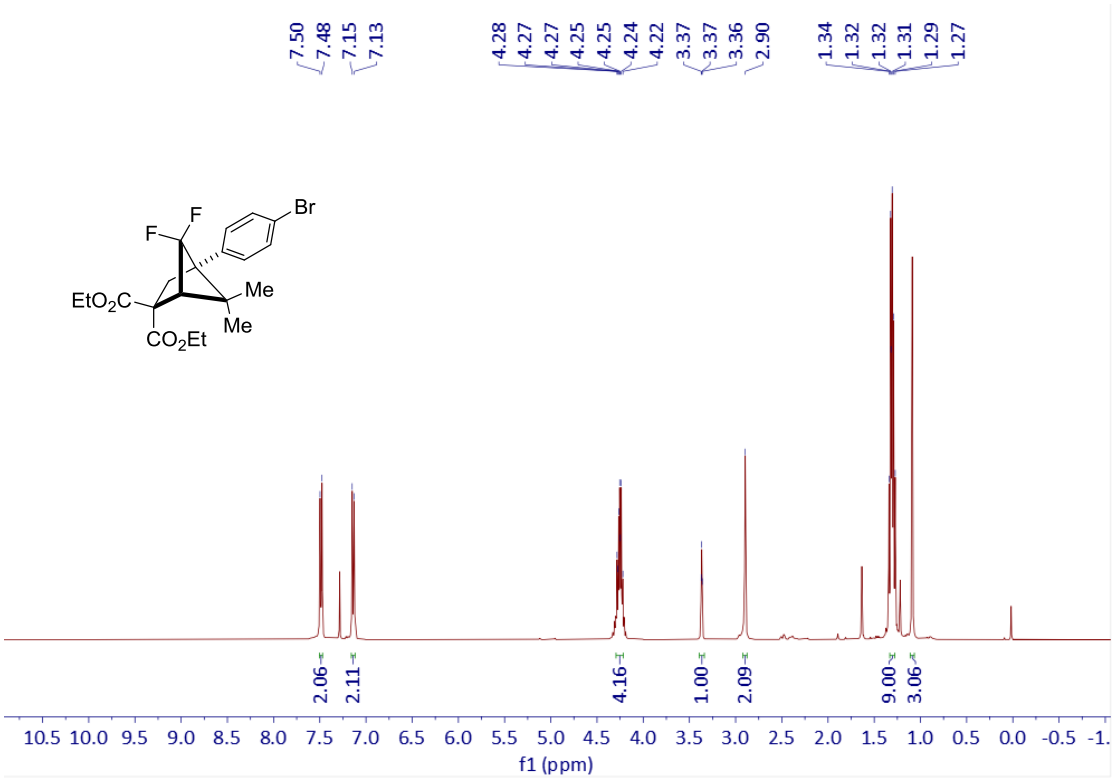
^{1}H NMR of 4f (400 MHz, $CDCl_3$)



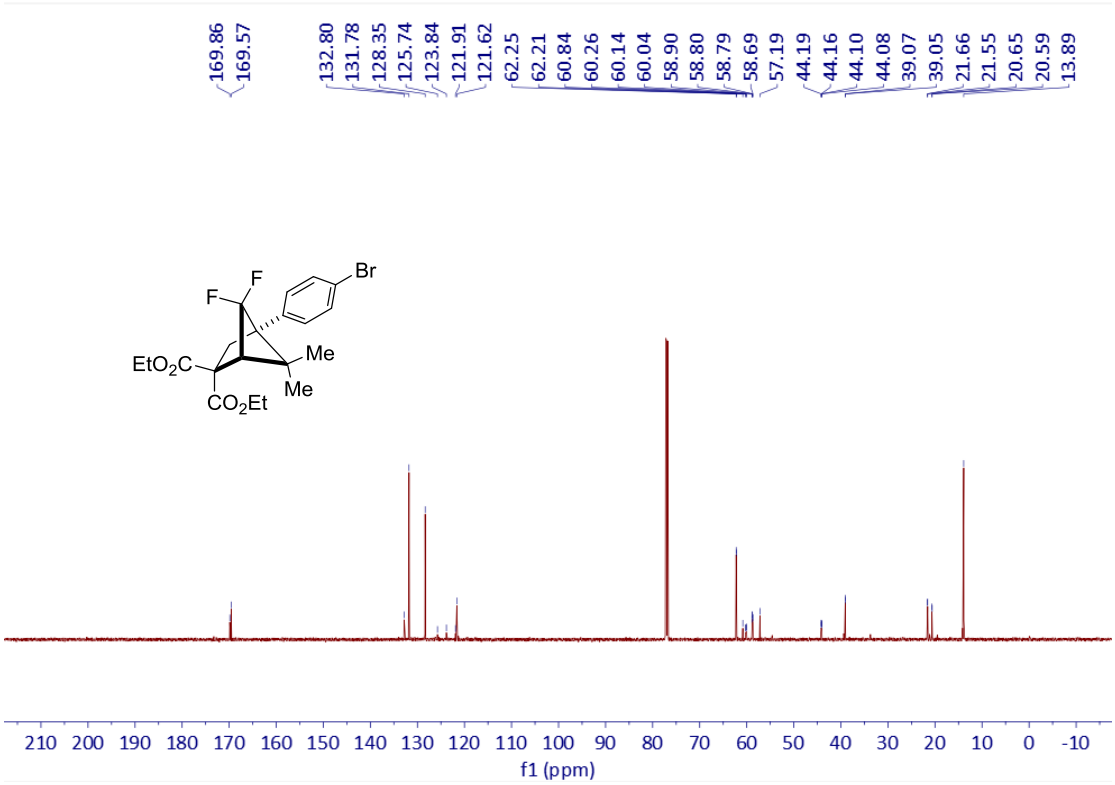
^{13}C NMR of 4f (101 MHz, $CDCl_3$)



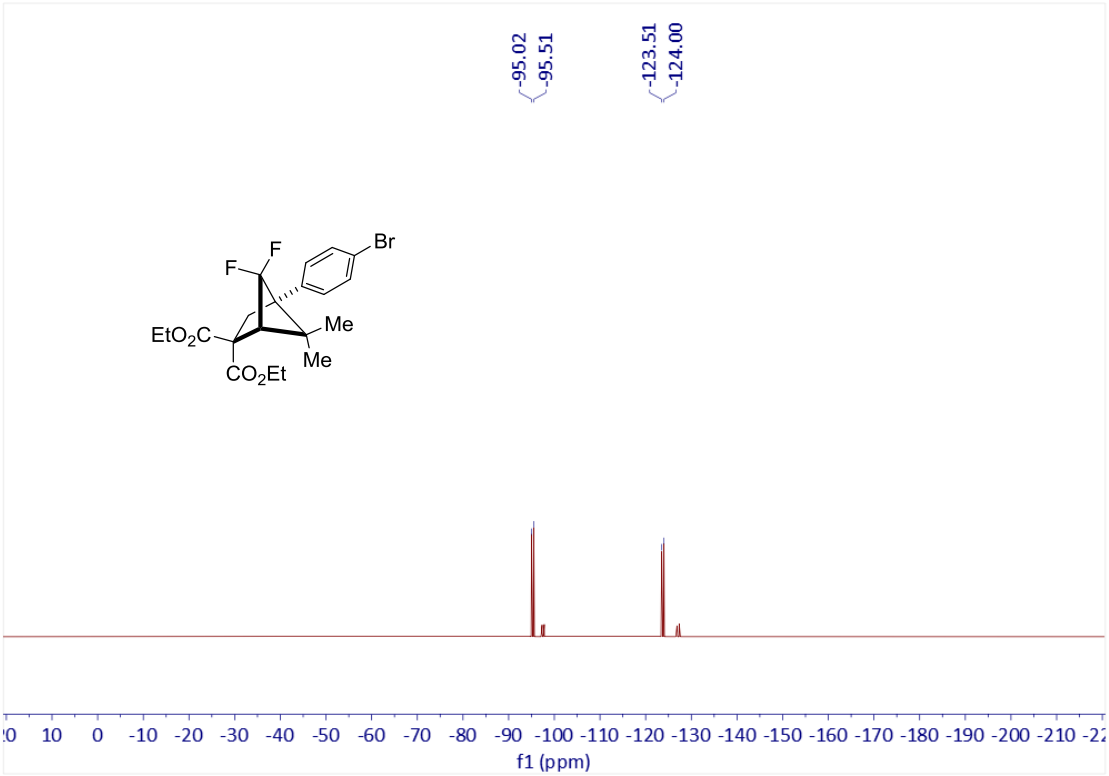
^{19}F NMR of 4f (377 MHz, $CDCl_3$)



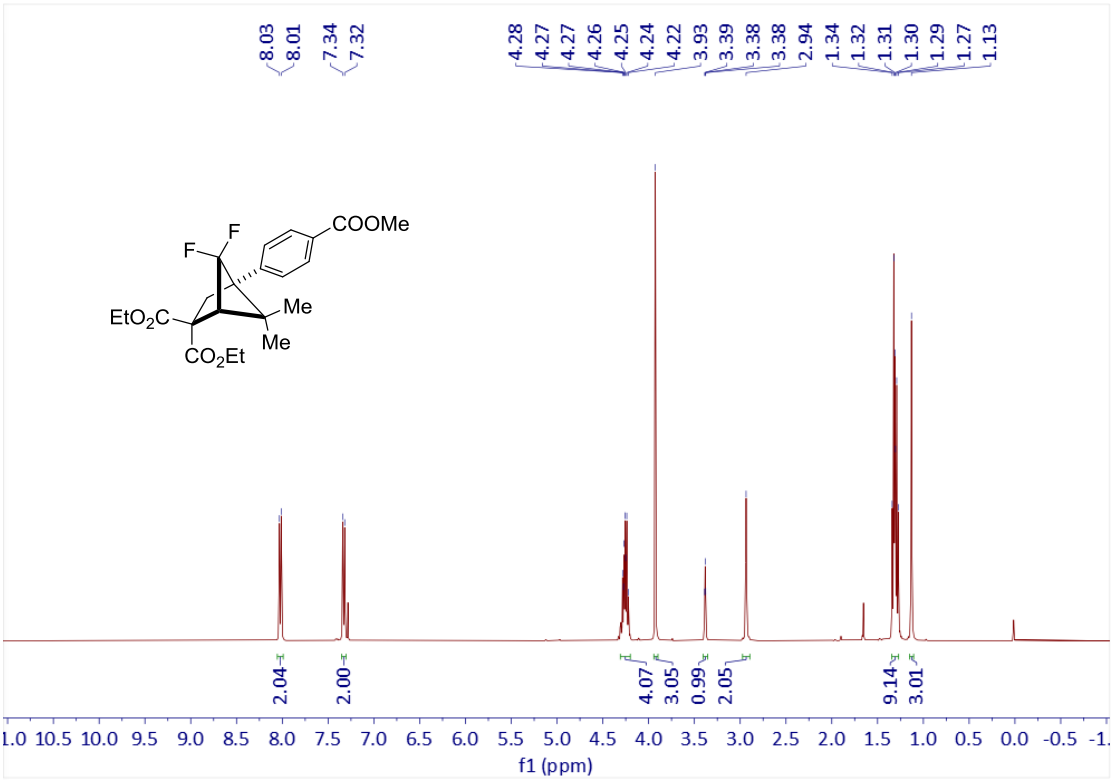
^{1}H NMR of 4g (400 MHz, $CDCl_3$)



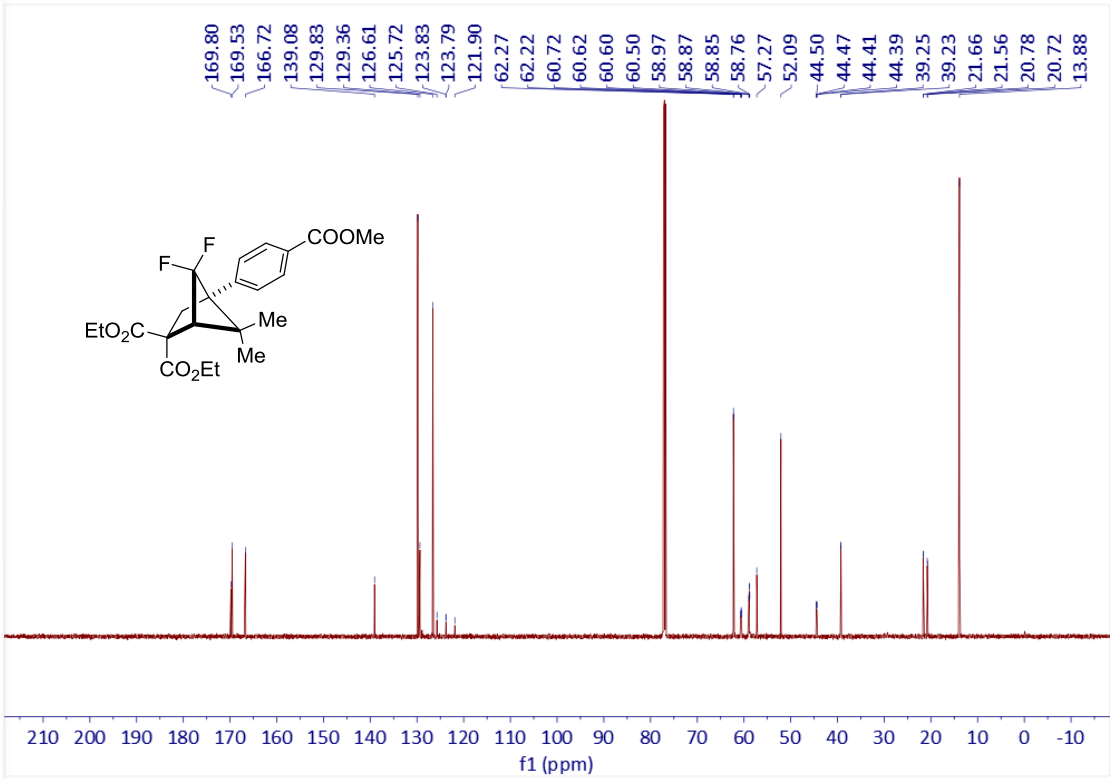
^{13}C NMR of 4g (151 MHz, $CDCl_3$)



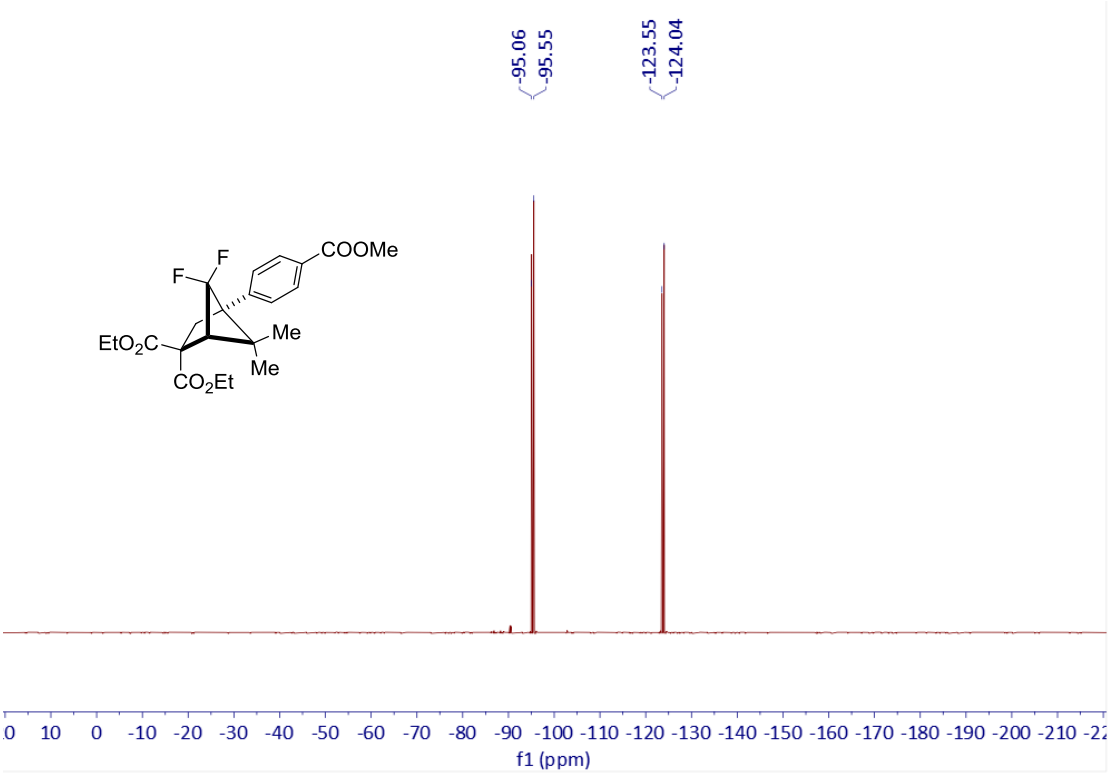
^{19}F NMR of 4g (377 MHz, $CDCl_3$)



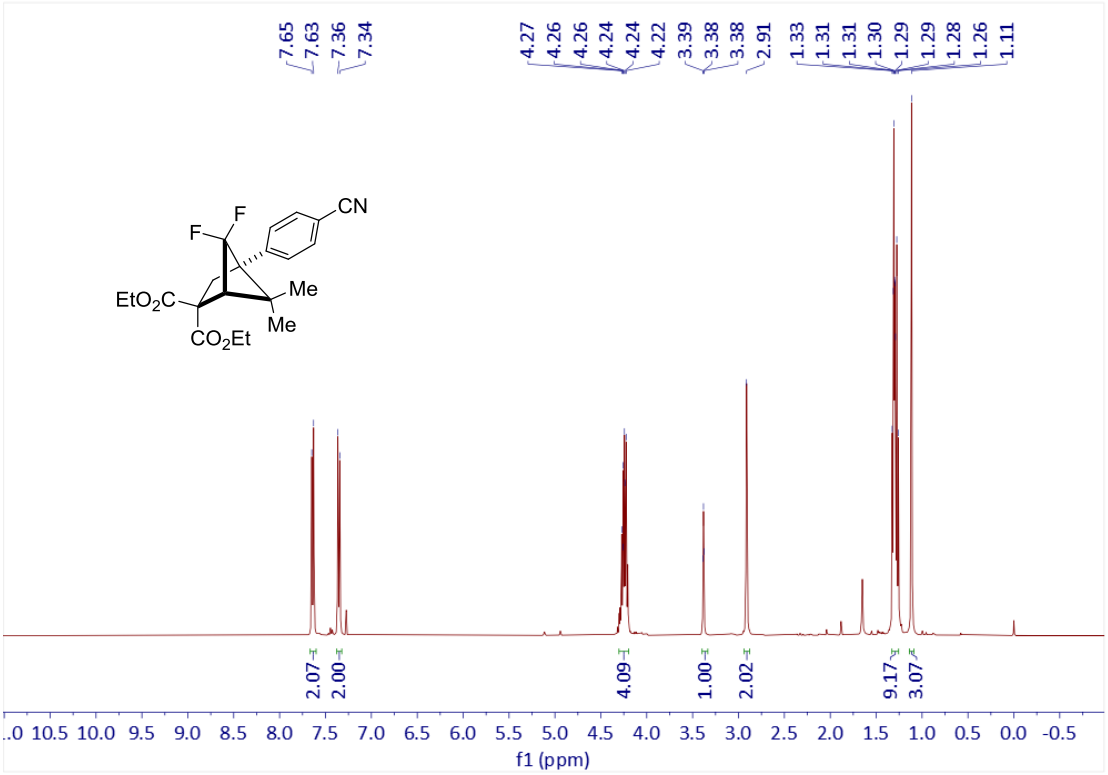
^{1}H NMR of 4h (400 MHz, $CDCl_3$)



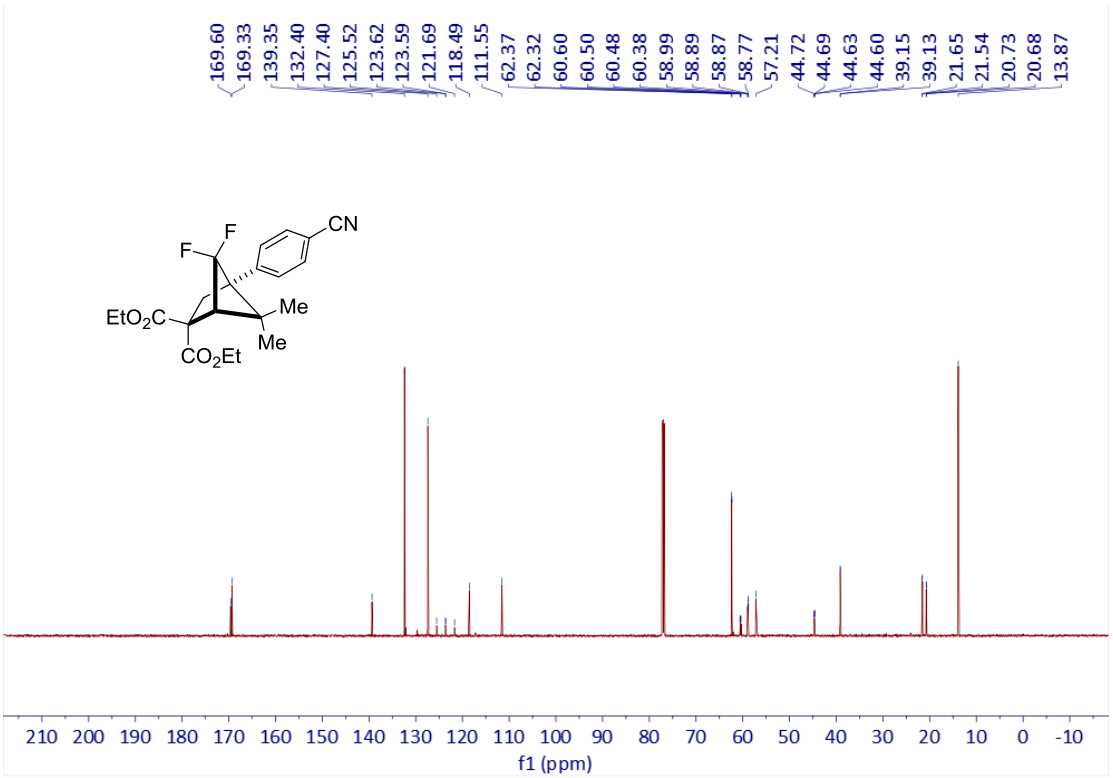
^{13}C NMR of 4h (151 MHz, $CDCl_3$)



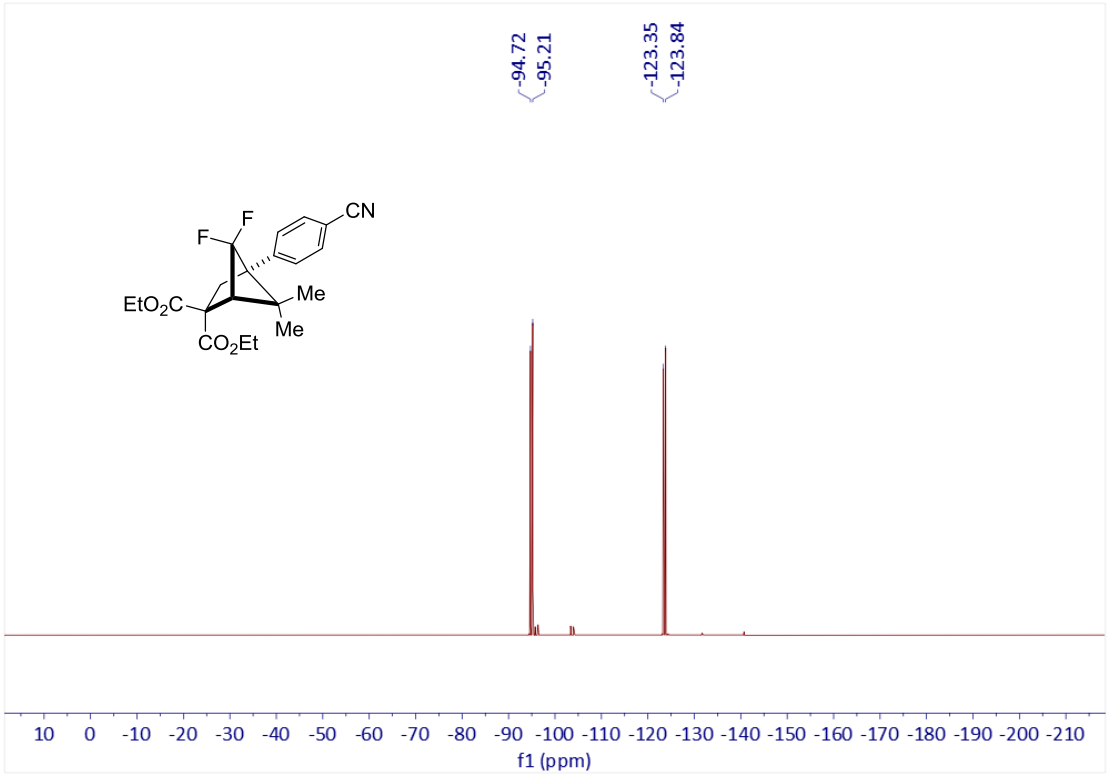
^{19}F NMR of 4h (377 MHz, $CDCl_3$)



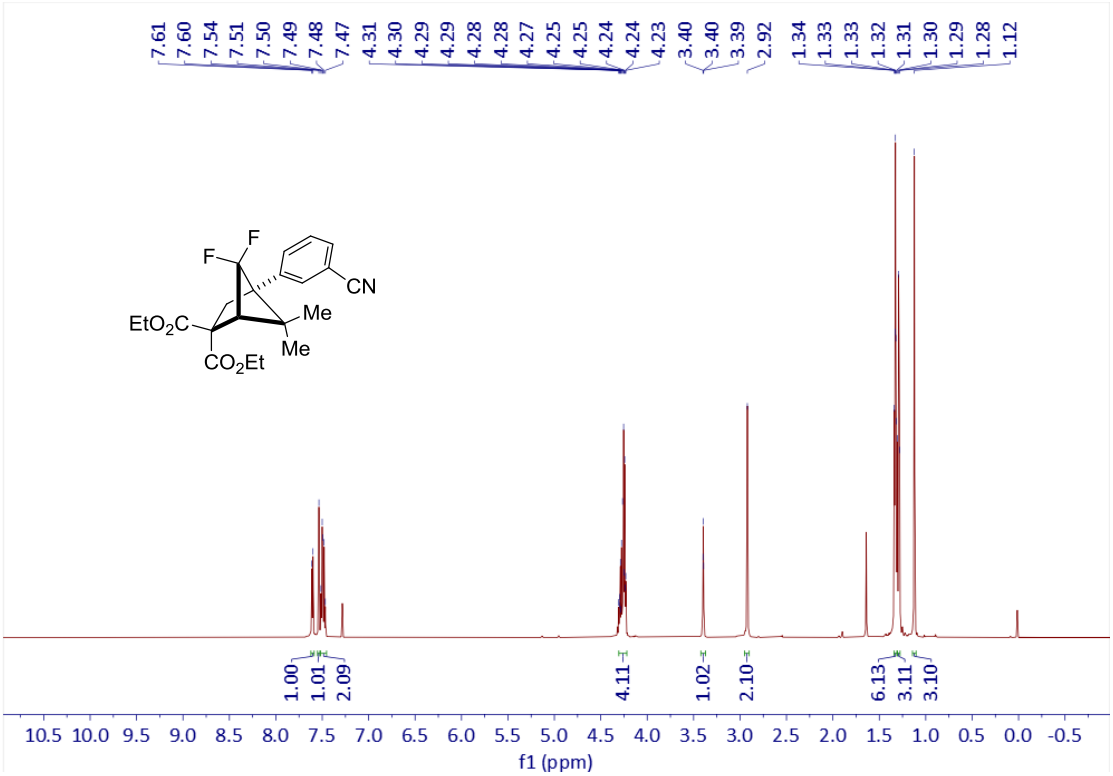
^{1}H NMR of 4i (400 MHz, $CDCl_3$)



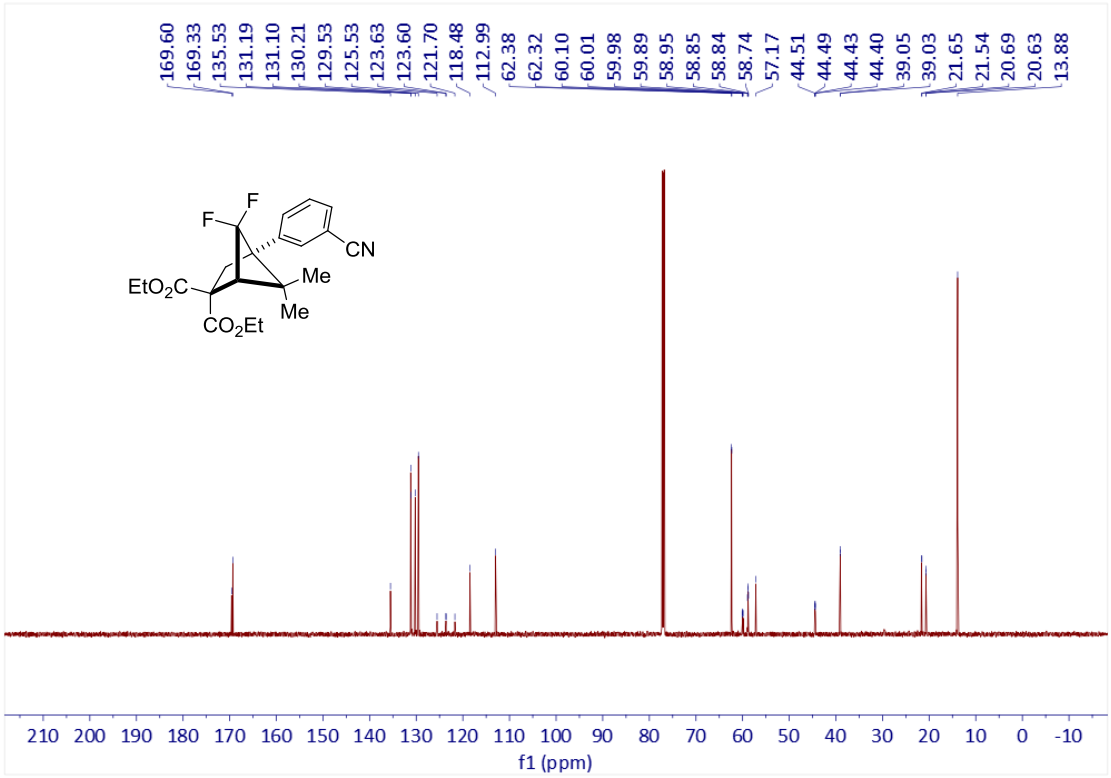
^{13}C NMR of 4i (151 MHz, $CDCl_3$)



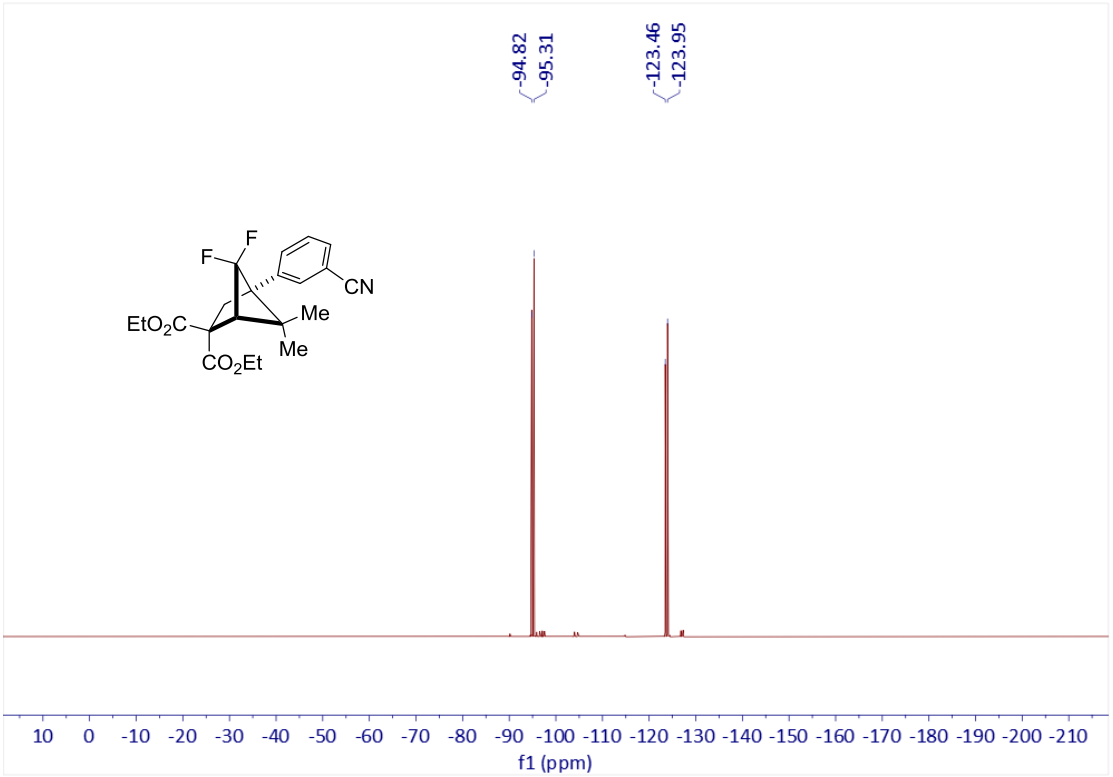
^{19}F NMR of 4i (377 MHz, $CDCl_3$)



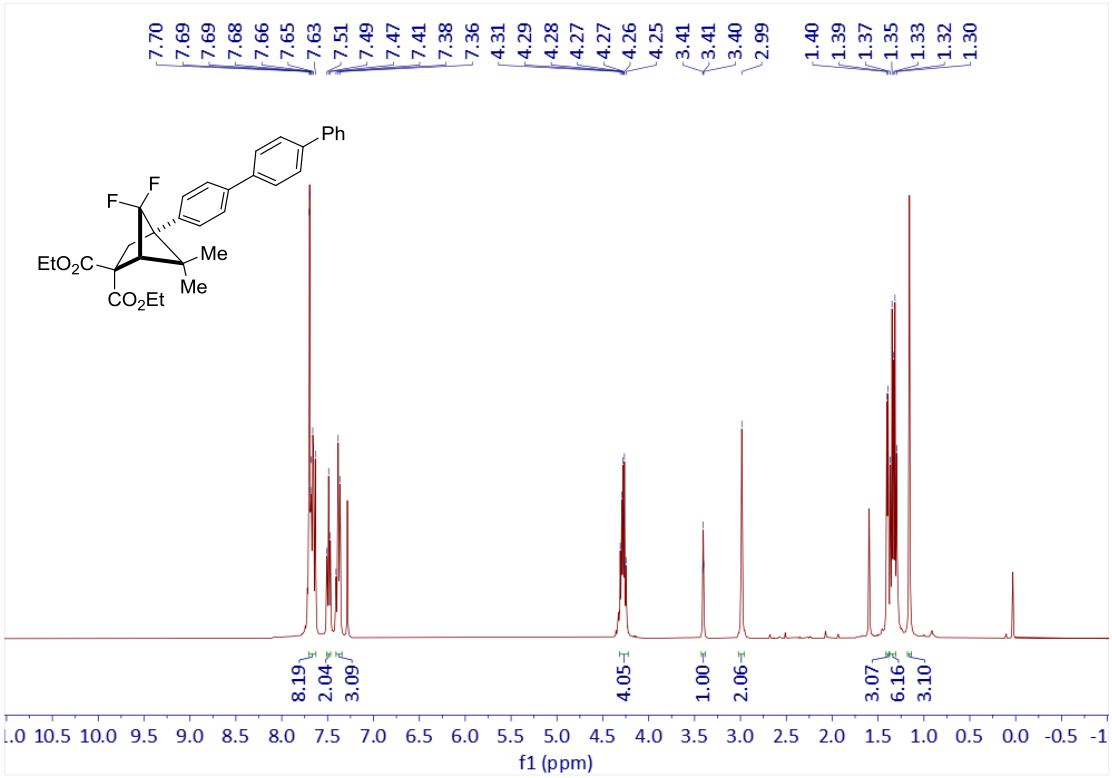
^{1}H NMR of 4j (400 MHz, $CDCl_3$)



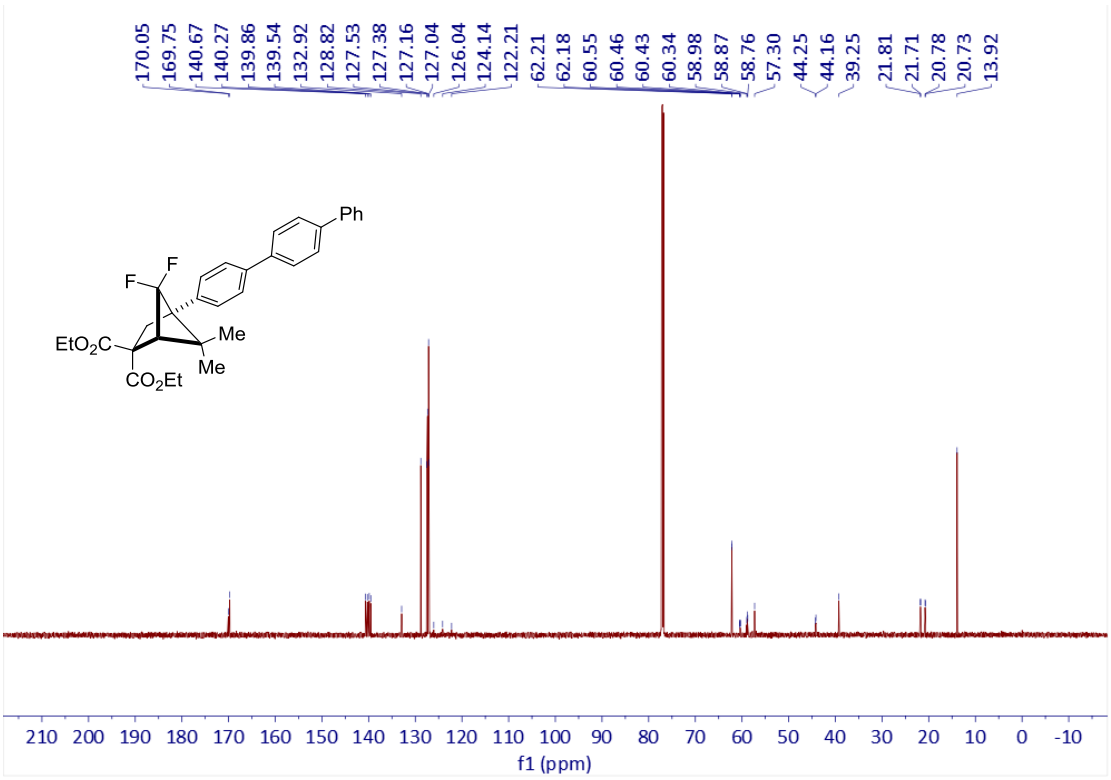
^{13}C NMR of 4j (101 MHz, $CDCl_3$)



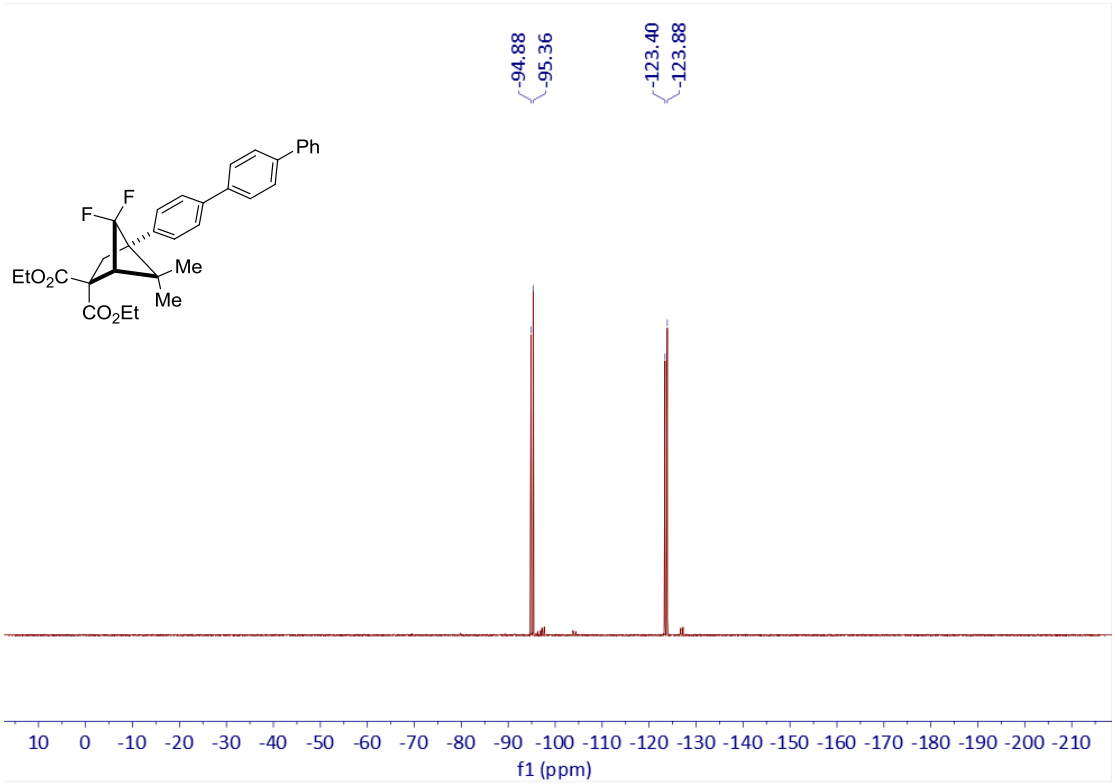
^{19}F NMR of 4j (377 MHz, $CDCl_3$)



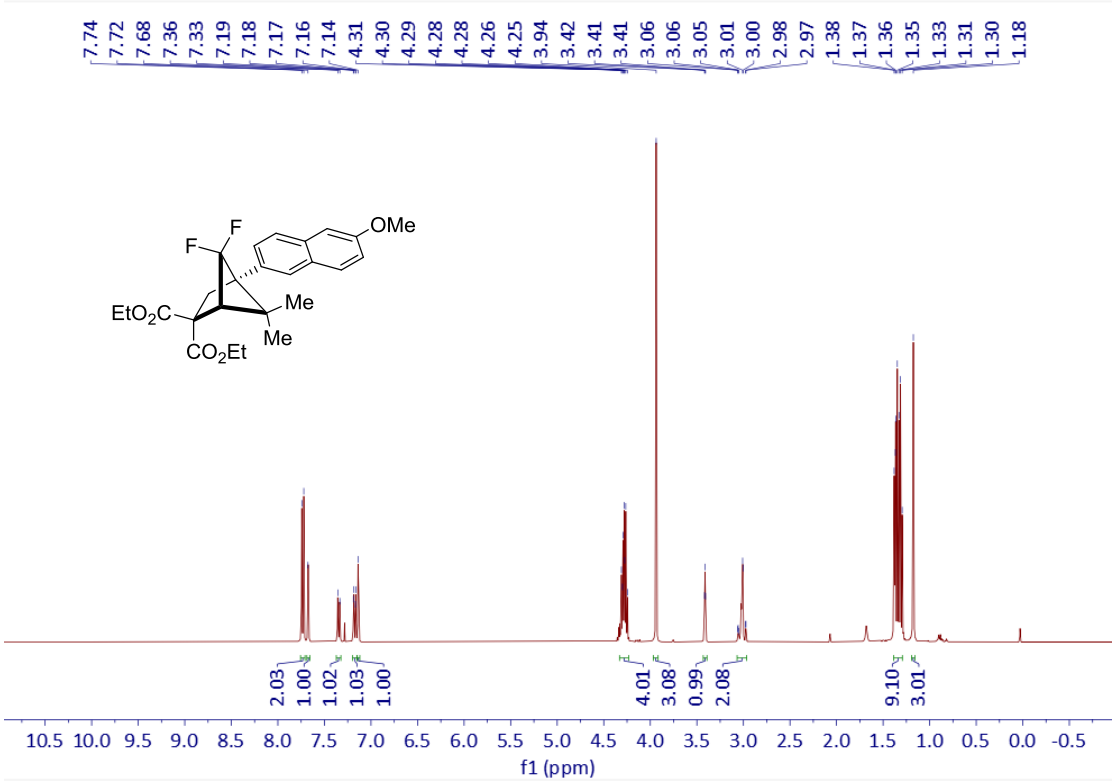
^{1}H NMR of 4k (400 MHz, $CDCl_3$)



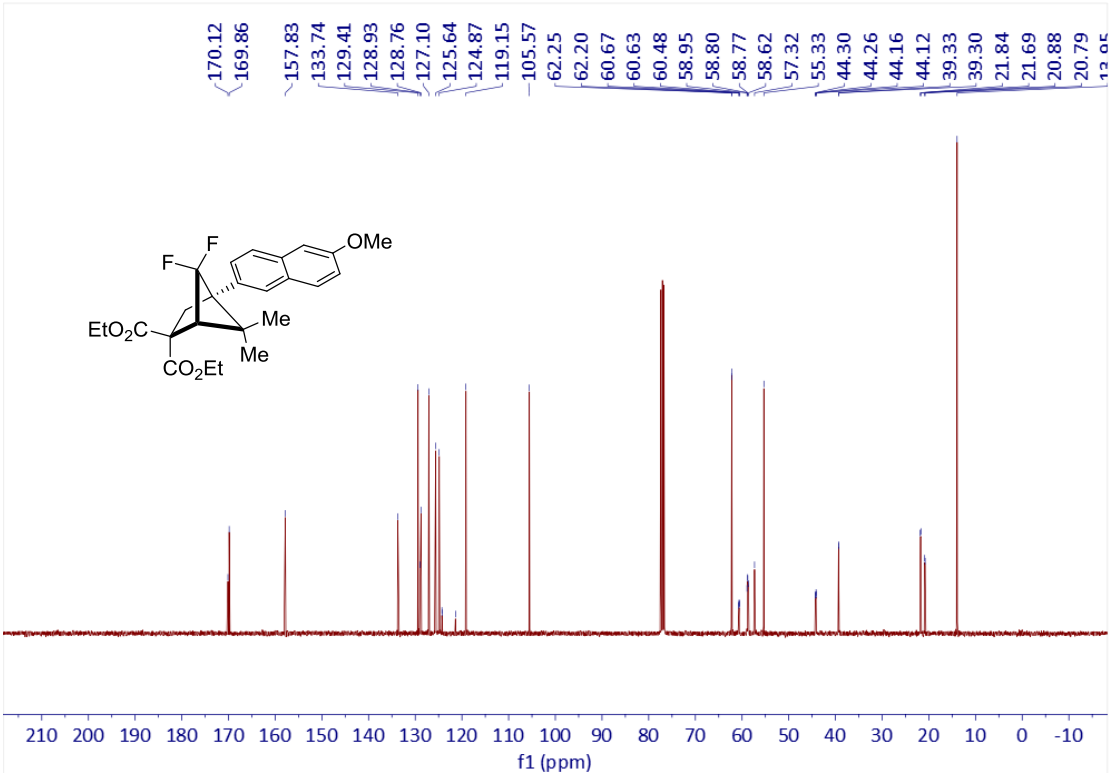
^{13}C NMR of 4k (151 MHz, $CDCl_3$)



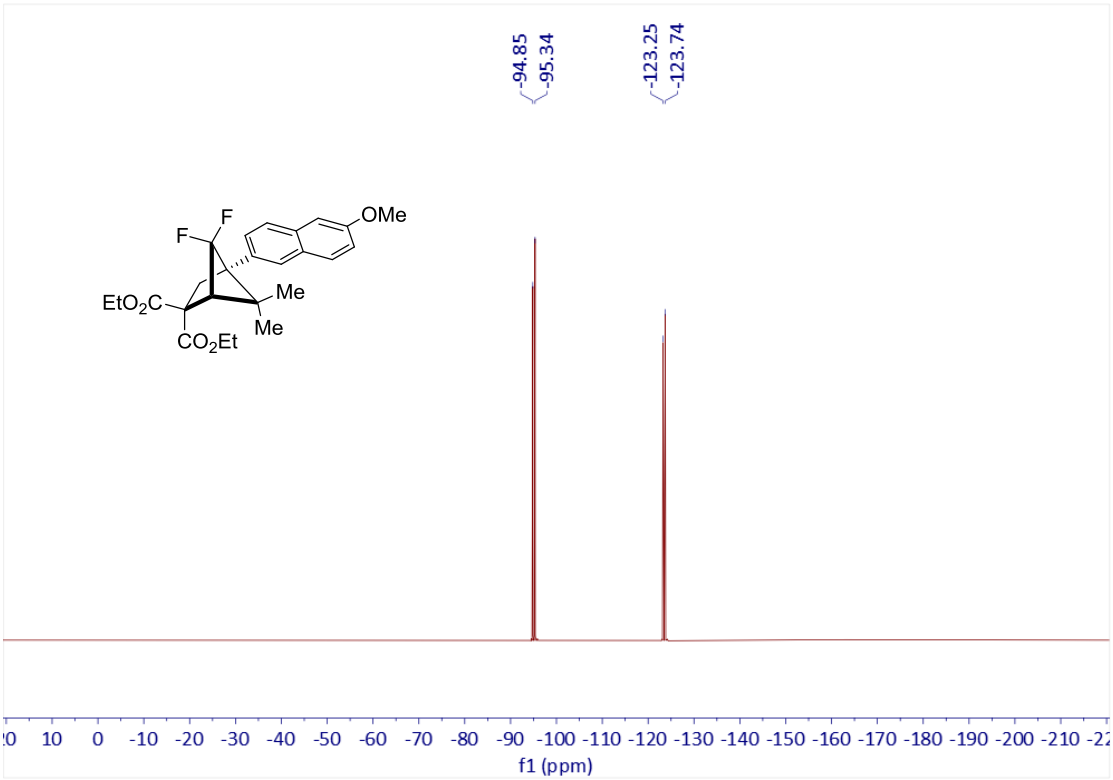
^{19}F NMR of 4k (377 MHz, $CDCl_3$)



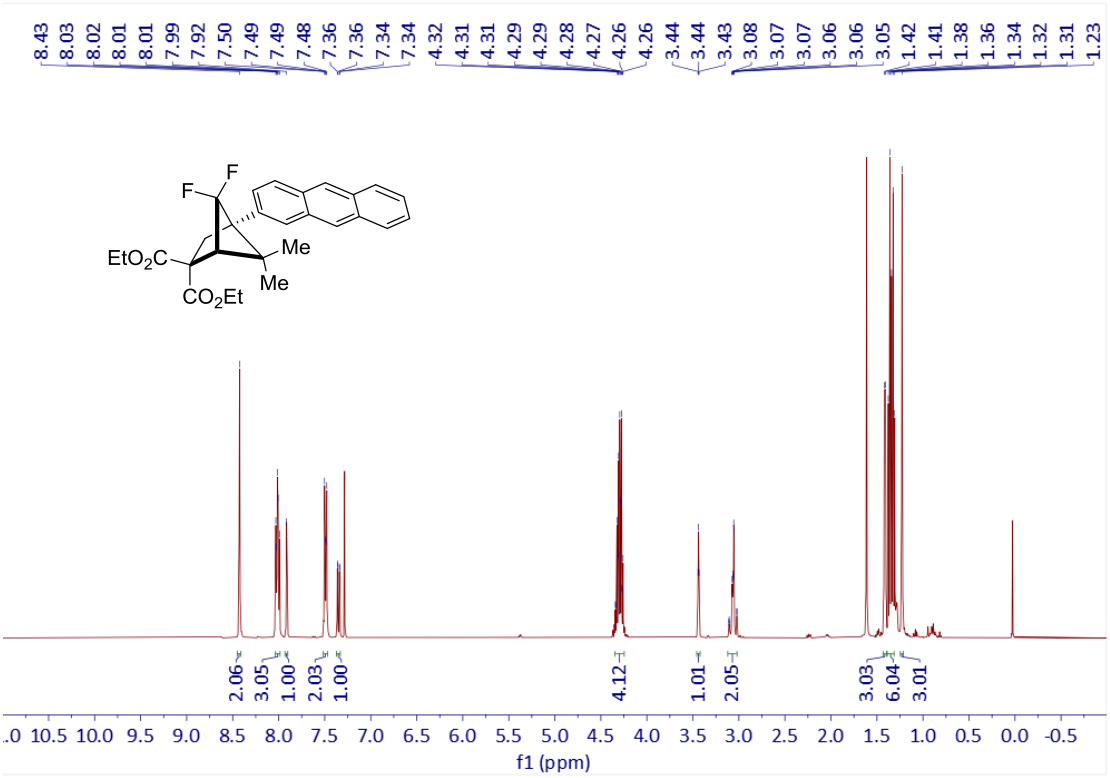
^{1}H NMR of 4l (400 MHz, $CDCl_3$)



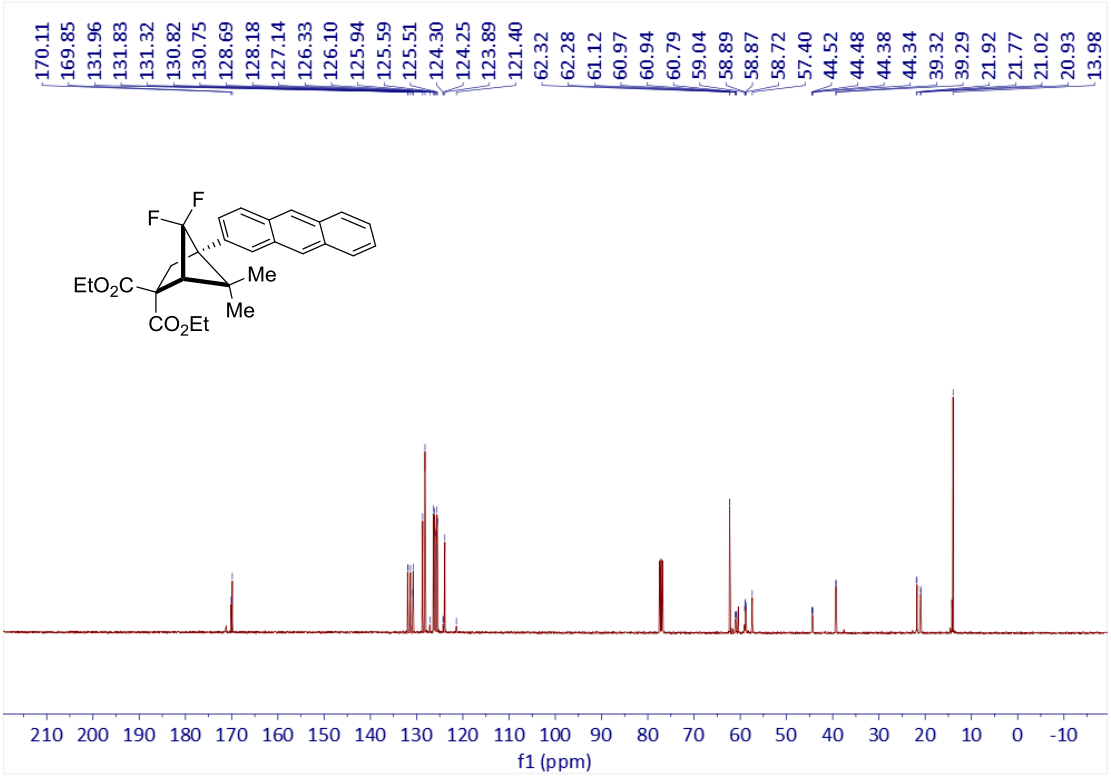
^{13}C NMR of 4l (101 MHz, $CDCl_3$)



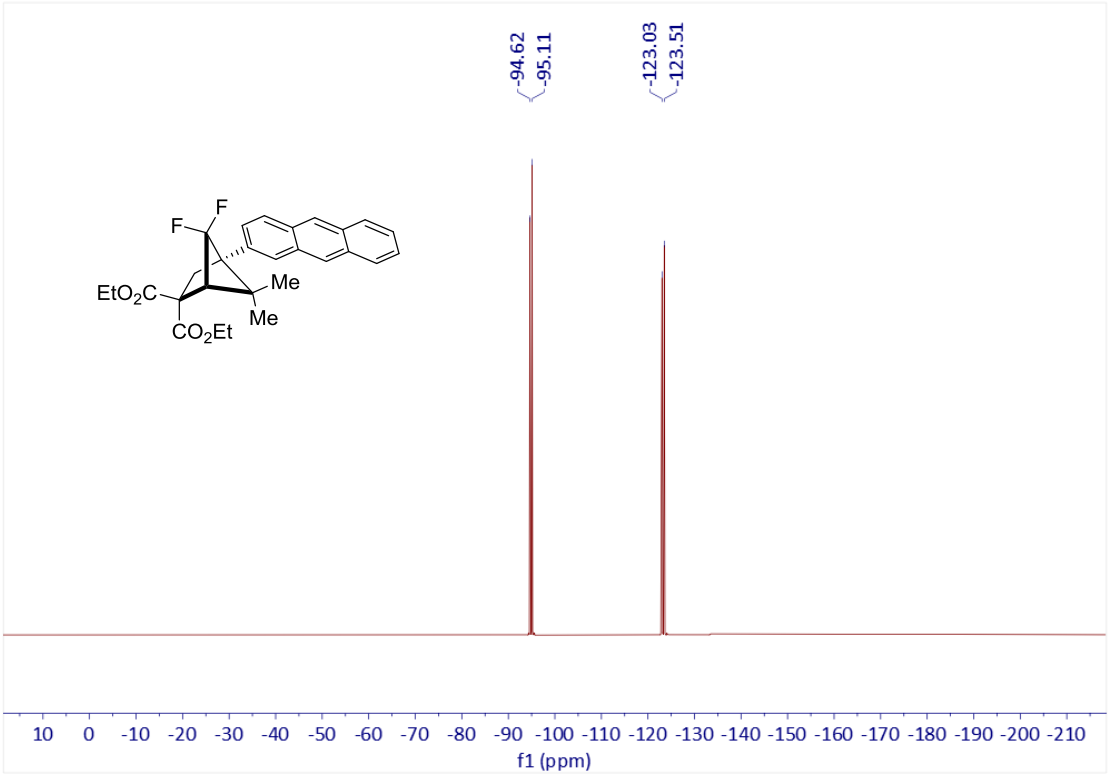
^{19}F NMR of 4l (377 MHz, $CDCl_3$)



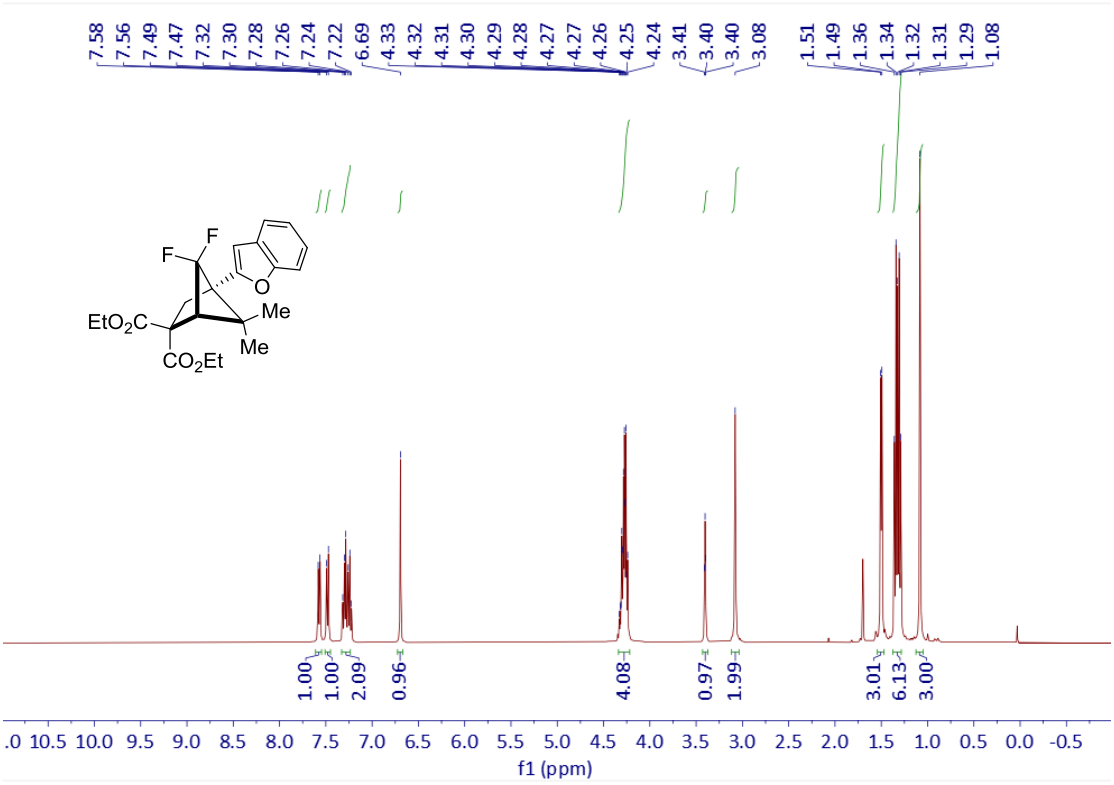
^{1}H NMR of 4m (400 MHz, $CDCl_3$)



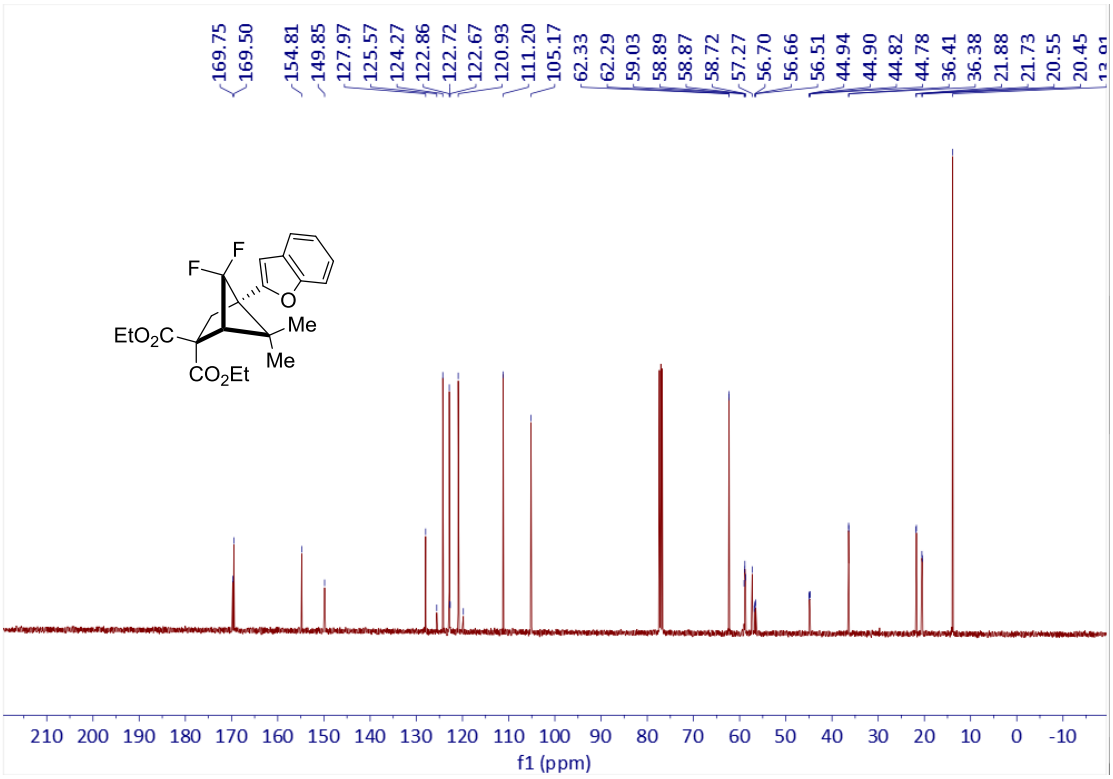
^{13}C NMR of 4m (101 MHz, $CDCl_3$)



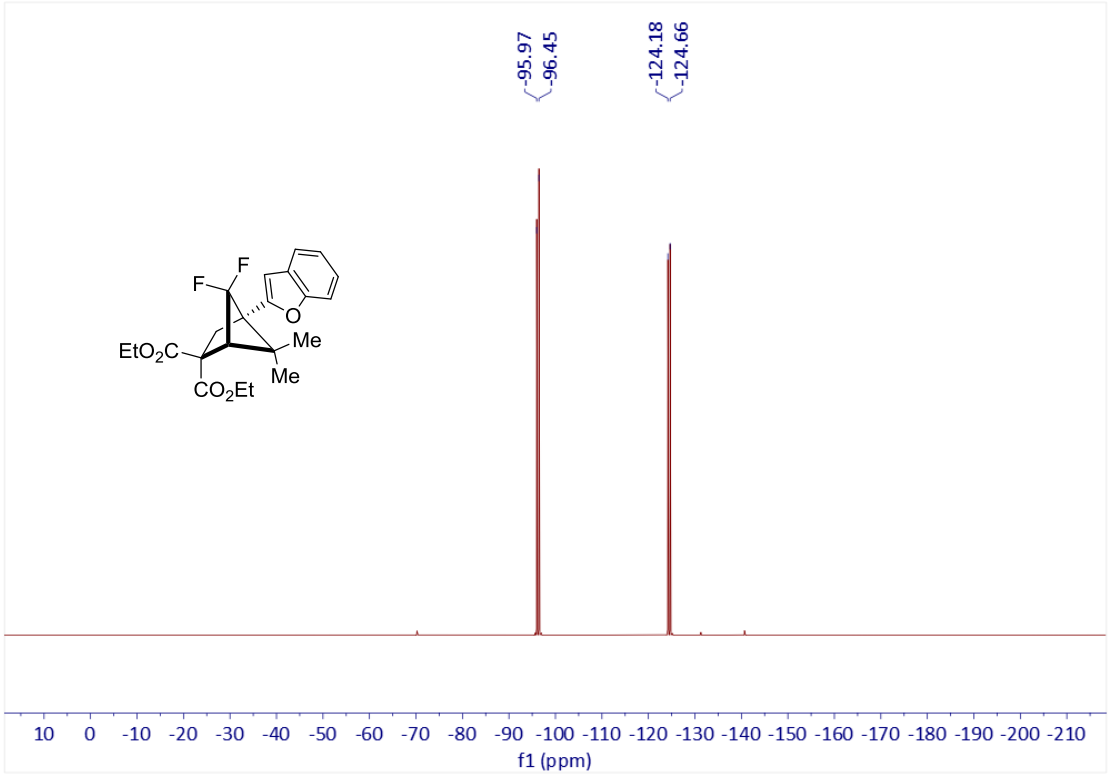
^{19}F NMR of 4m (377 MHz, $CDCl_3$)



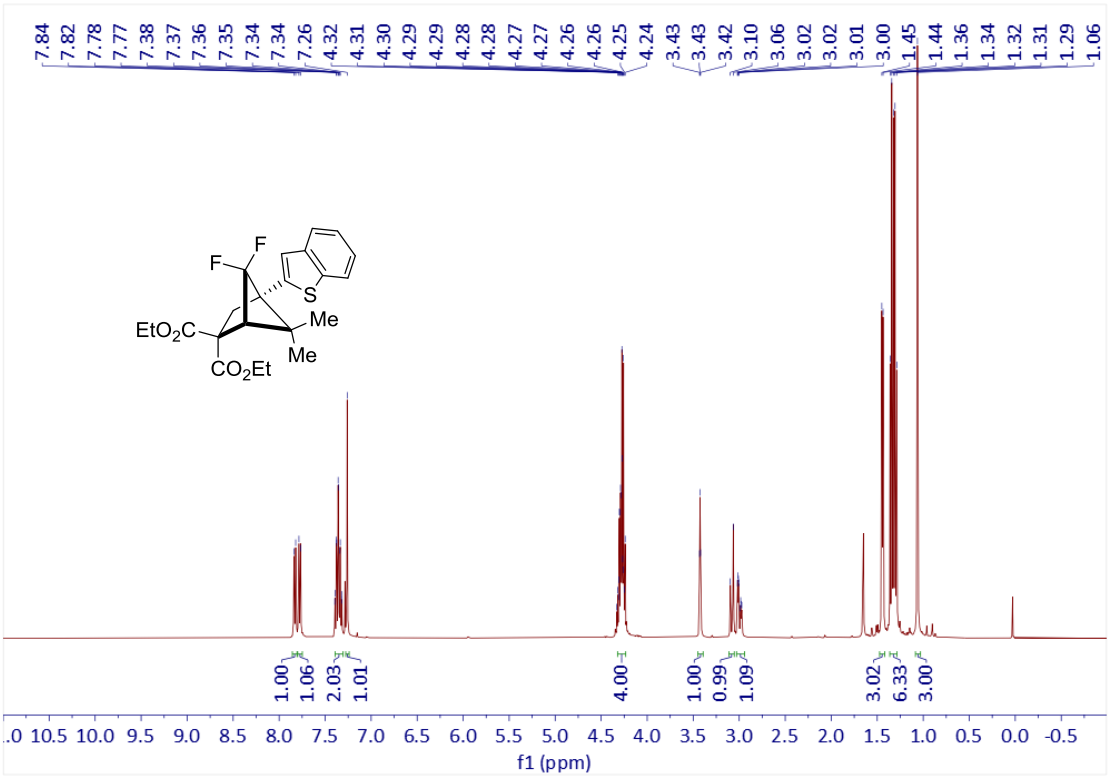
^{1}H NMR of 4n (400 MHz, $CDCl_3$)



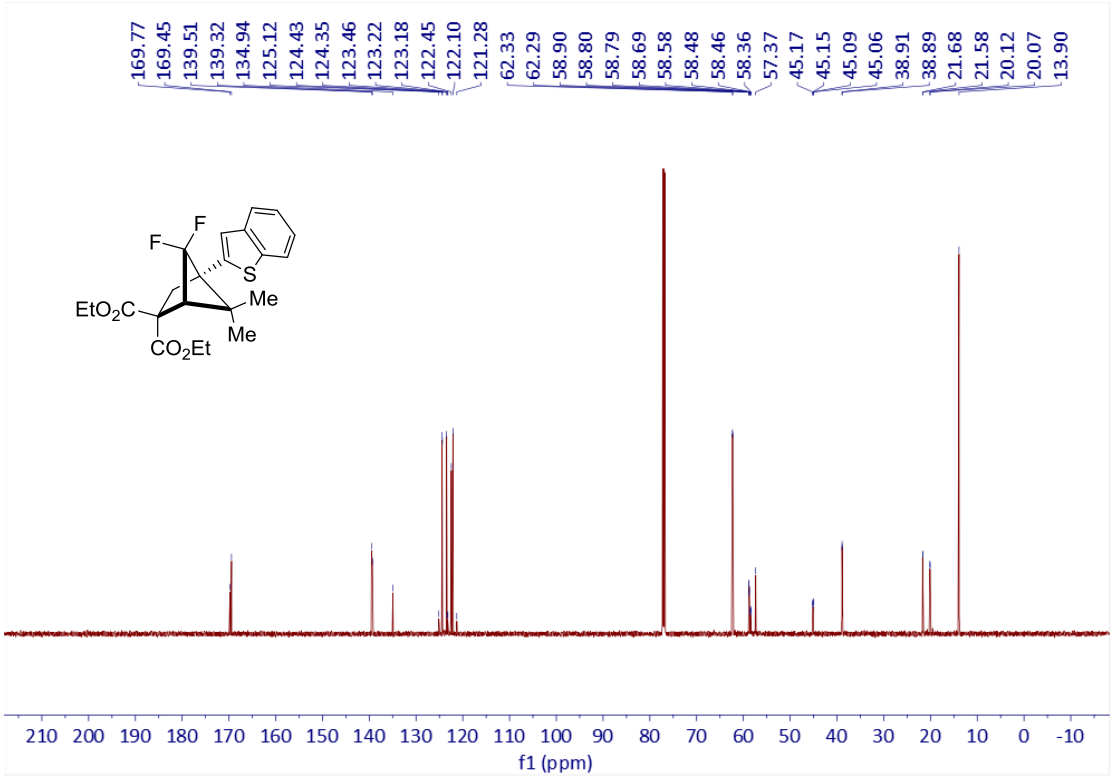
^{13}C NMR of 4n (101 MHz, $CDCl_3$)



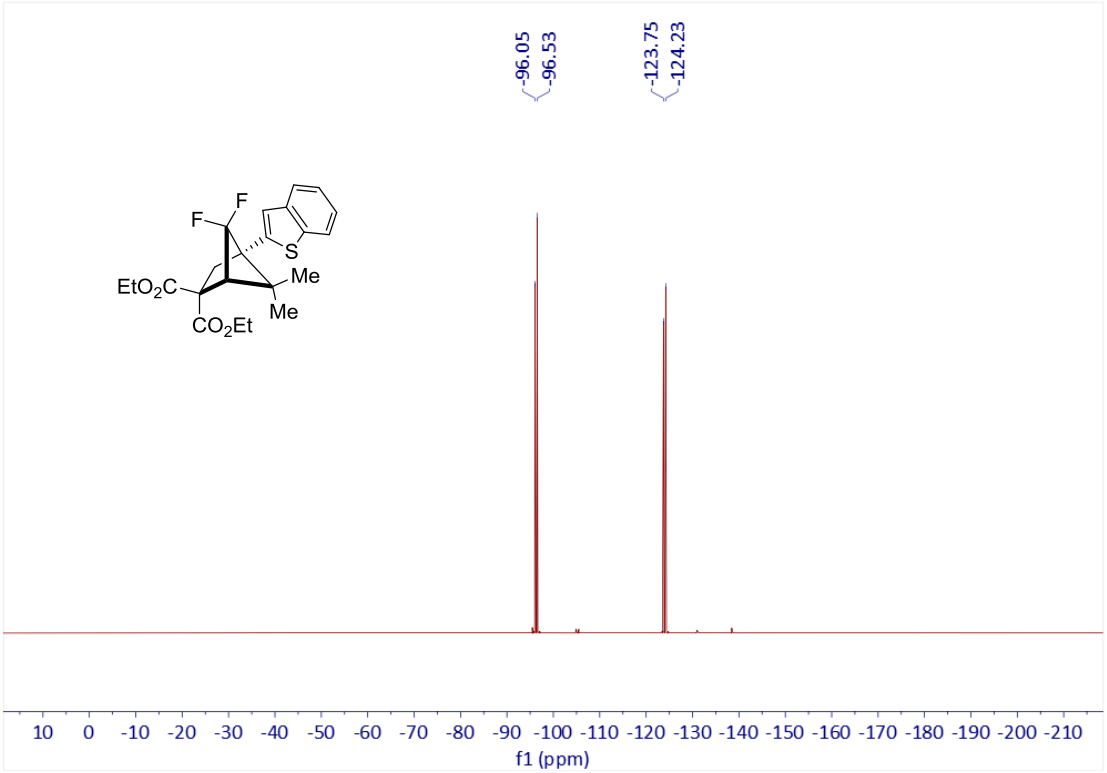
^{19}F NMR of 4n (377 MHz, $CDCl_3$)



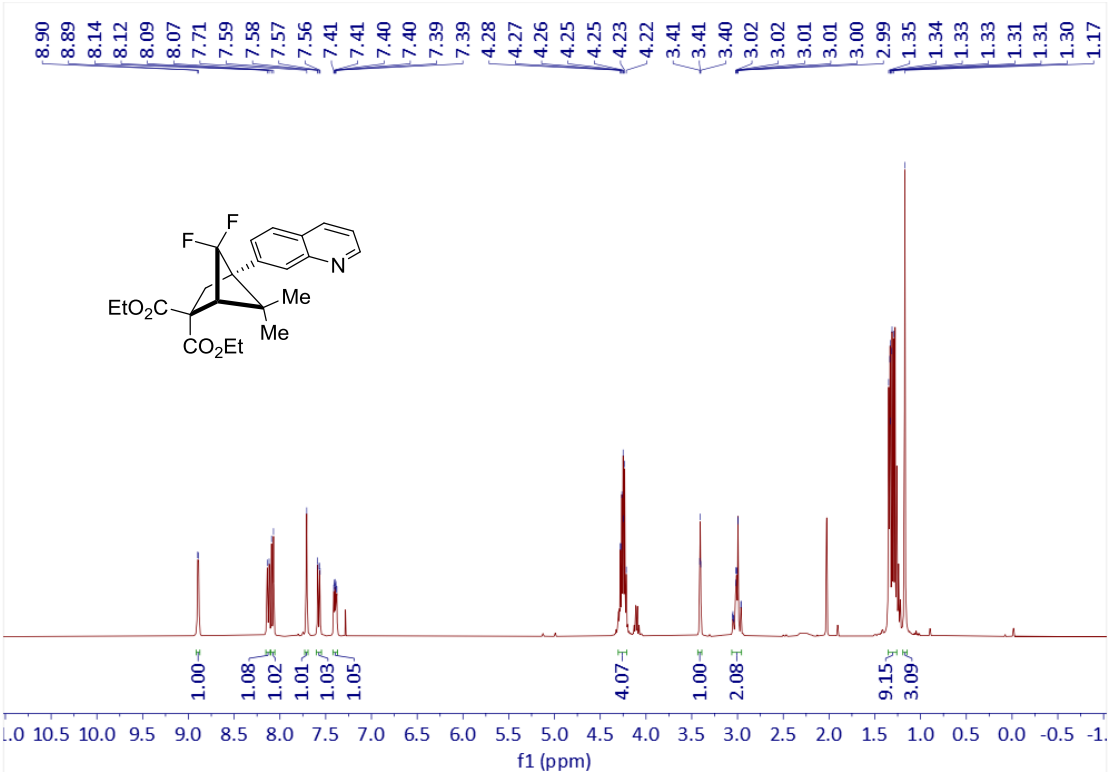
^{1}H NMR of 4o (400 MHz, $CDCl_3$)



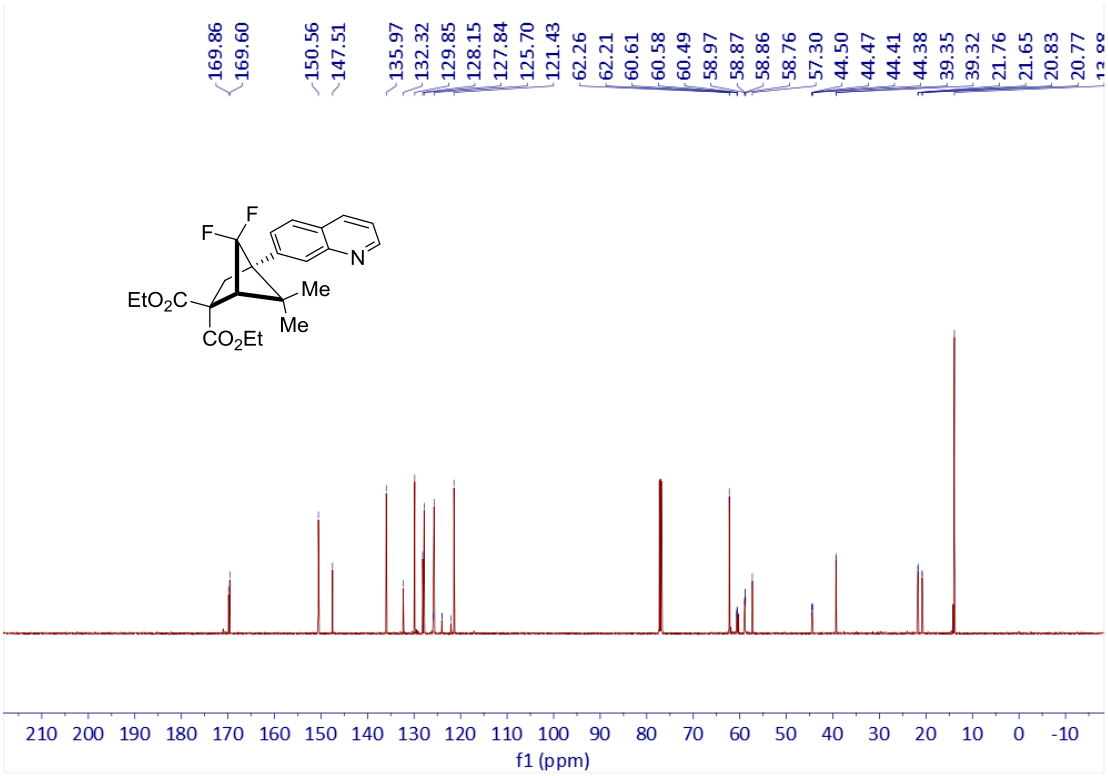
^{13}C NMR of 4o (151 MHz, $CDCl_3$)



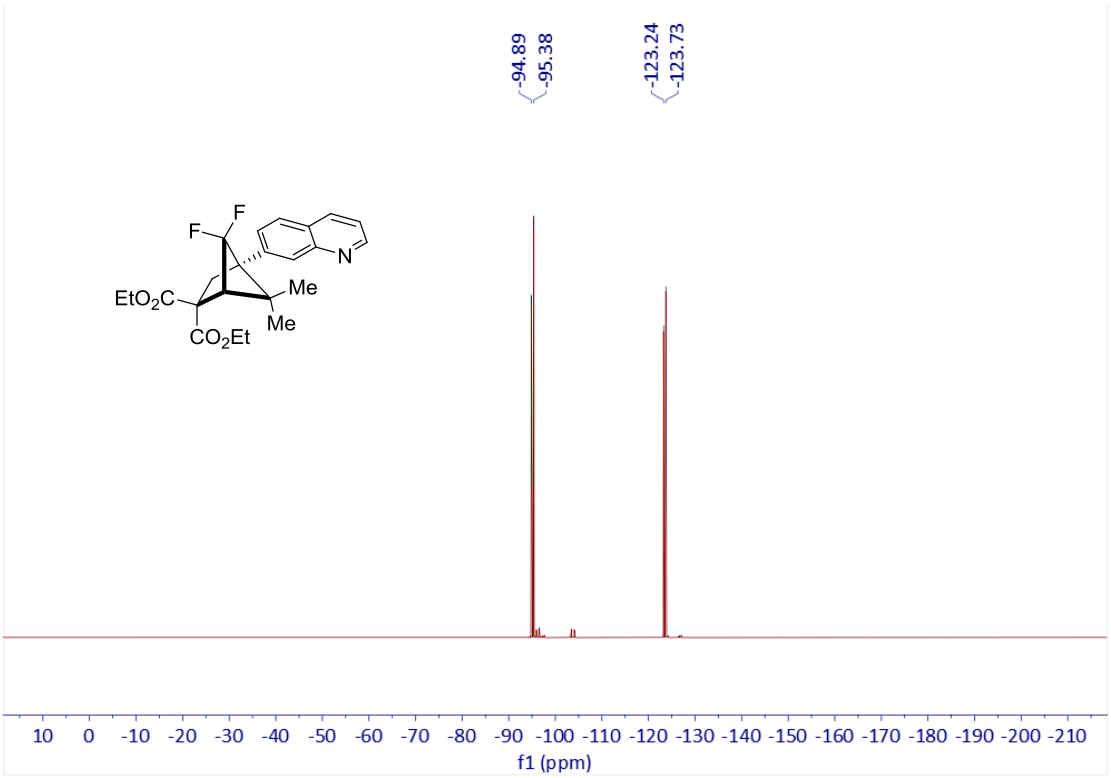
^{19}F NMR of 4o (377 MHz, $CDCl_3$)



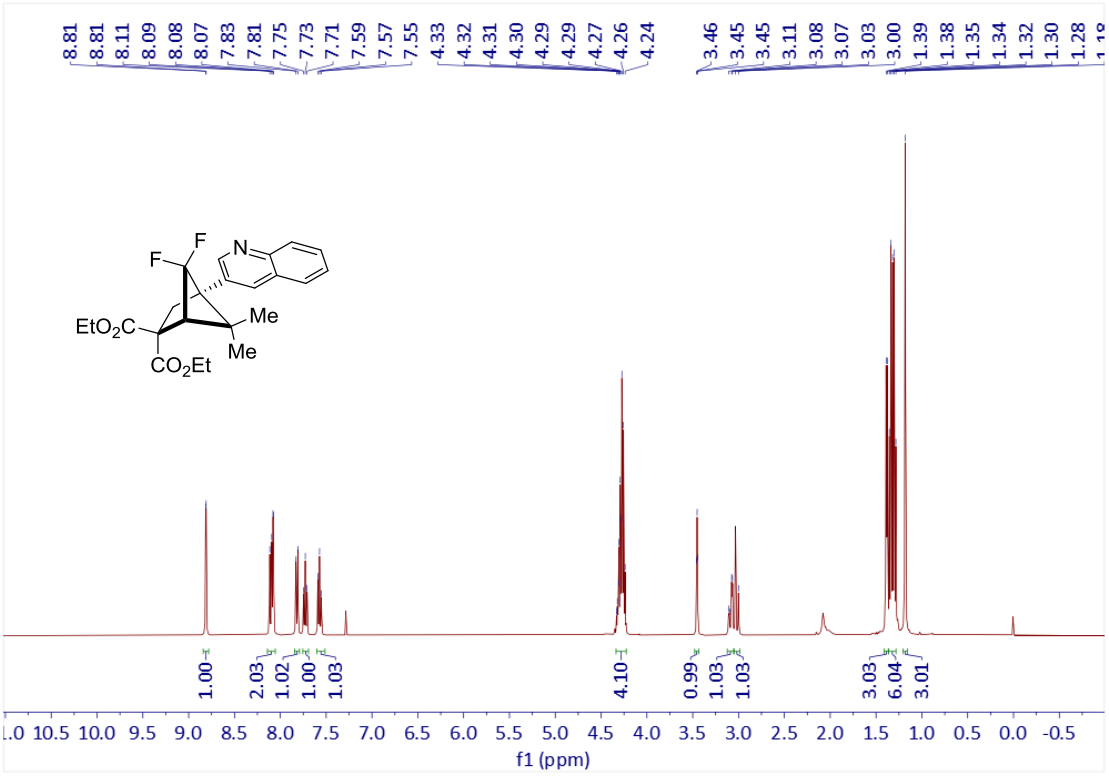
^{1}H NMR of 4p (400 MHz, $CDCl_3$)



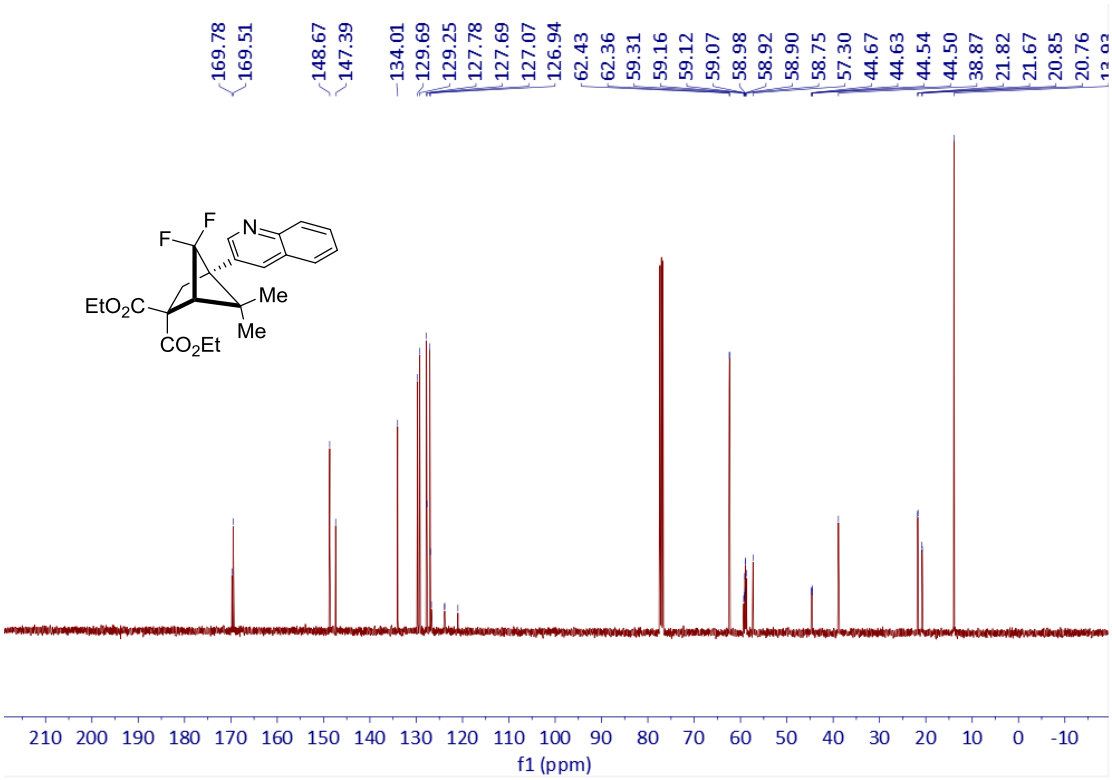
^{13}C NMR of 4p (151 MHz, $CDCl_3$)



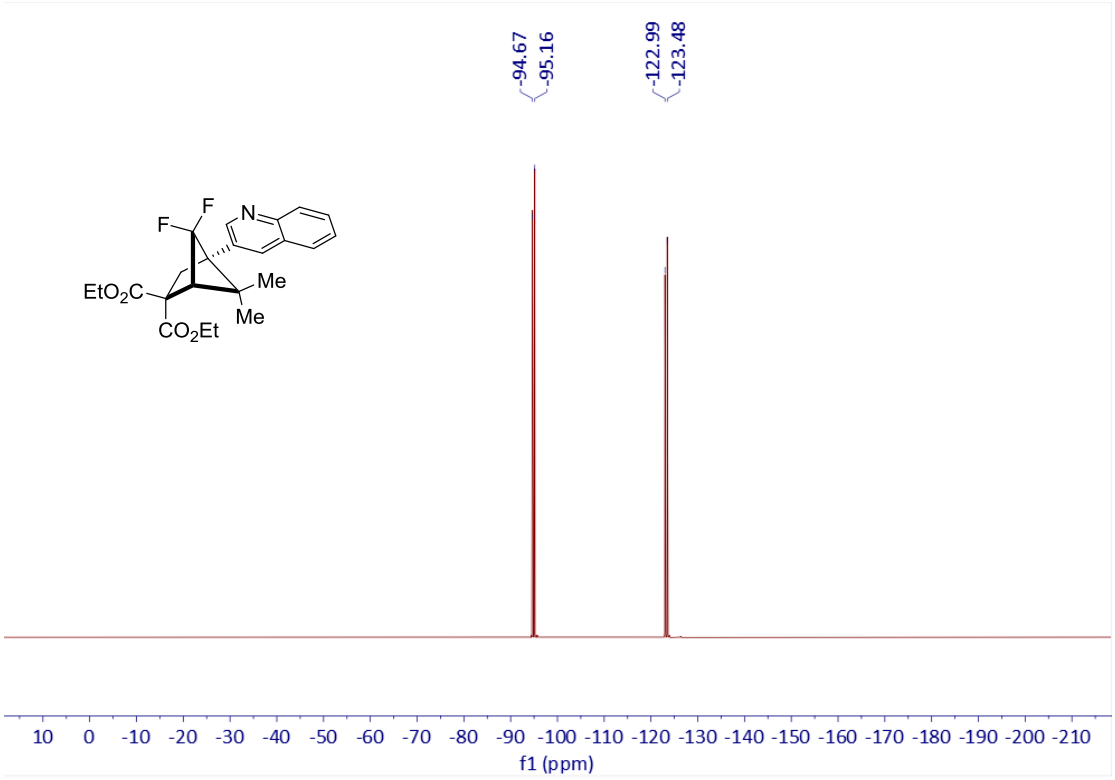
^{19}F NMR of 4p (377 MHz, $CDCl_3$)



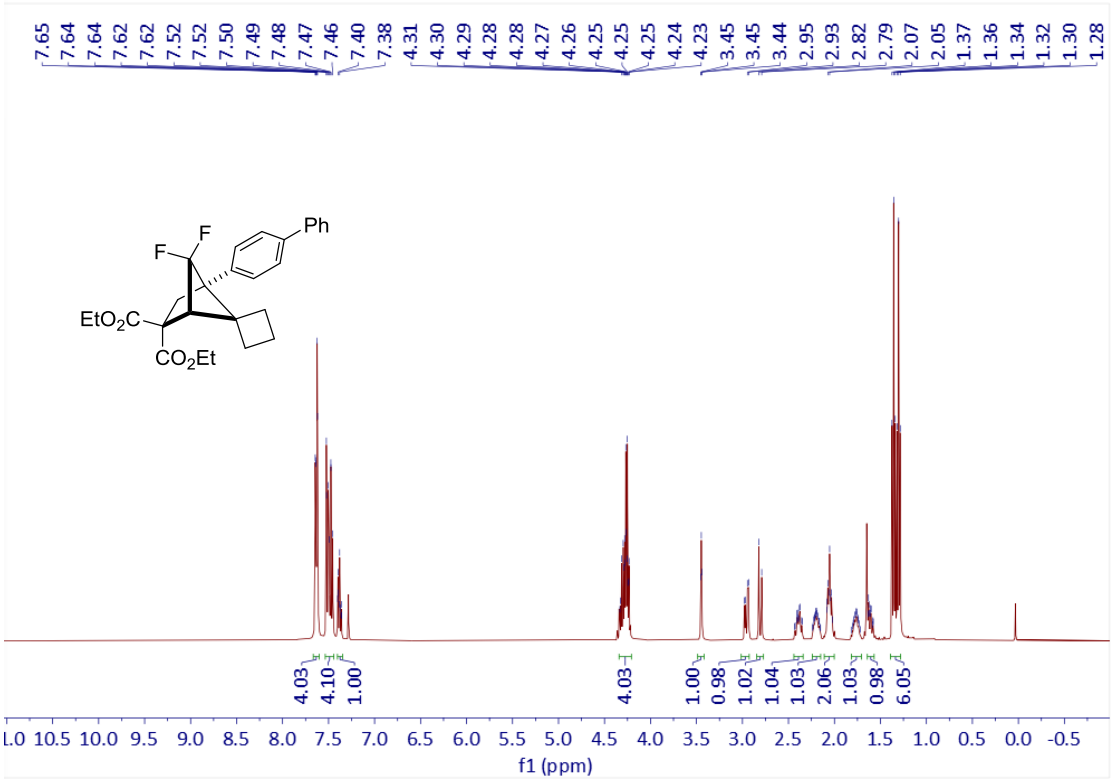
^{1}H NMR of 4q (400 MHz, $CDCl_3$)



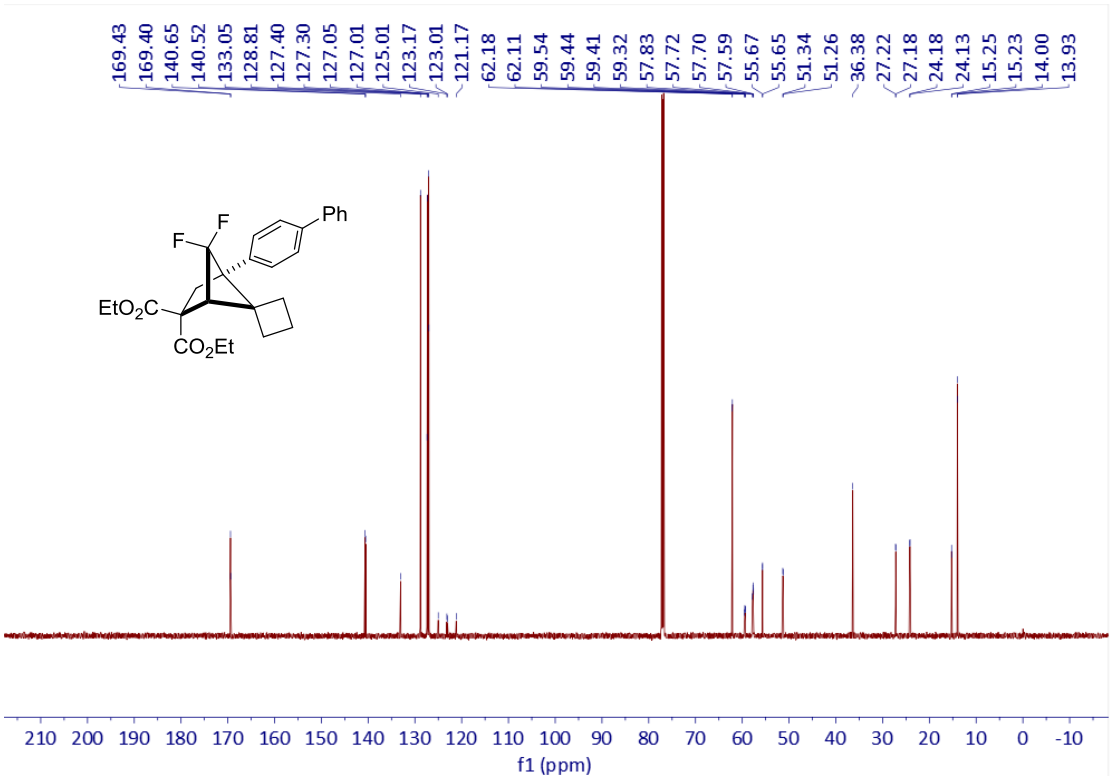
^{13}C NMR of 4q (101 MHz, $CDCl_3$)



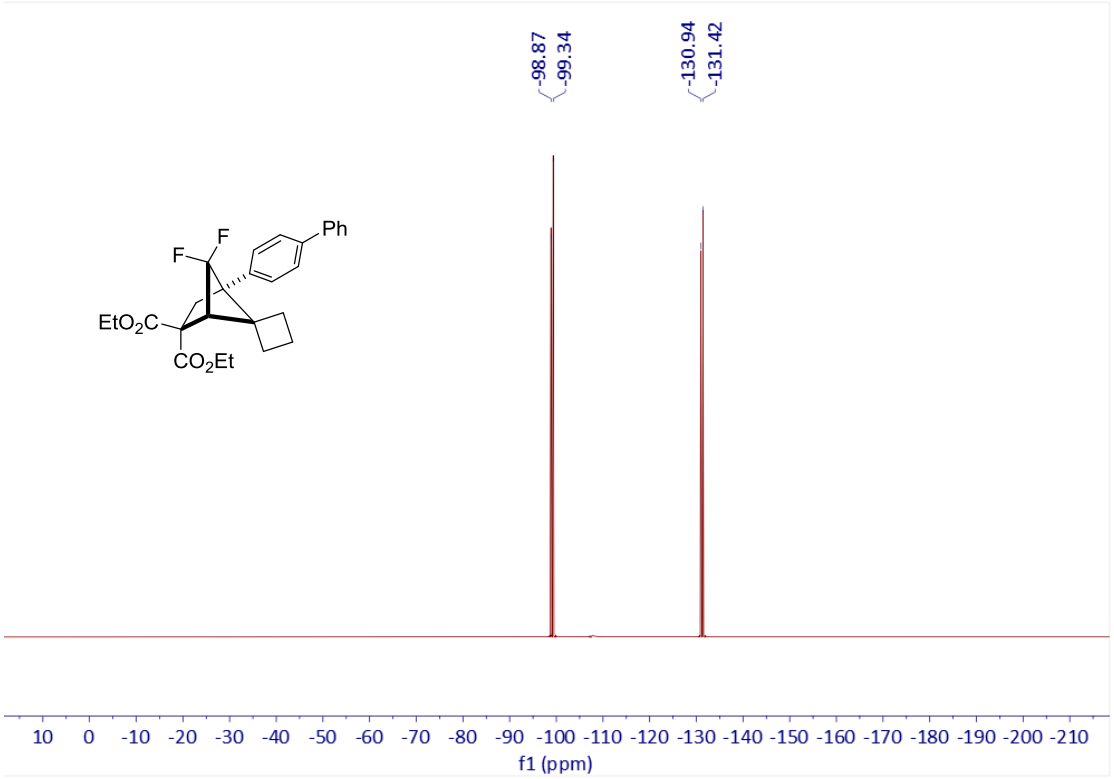
^{19}F NMR of 4q (377 MHz, $CDCl_3$)



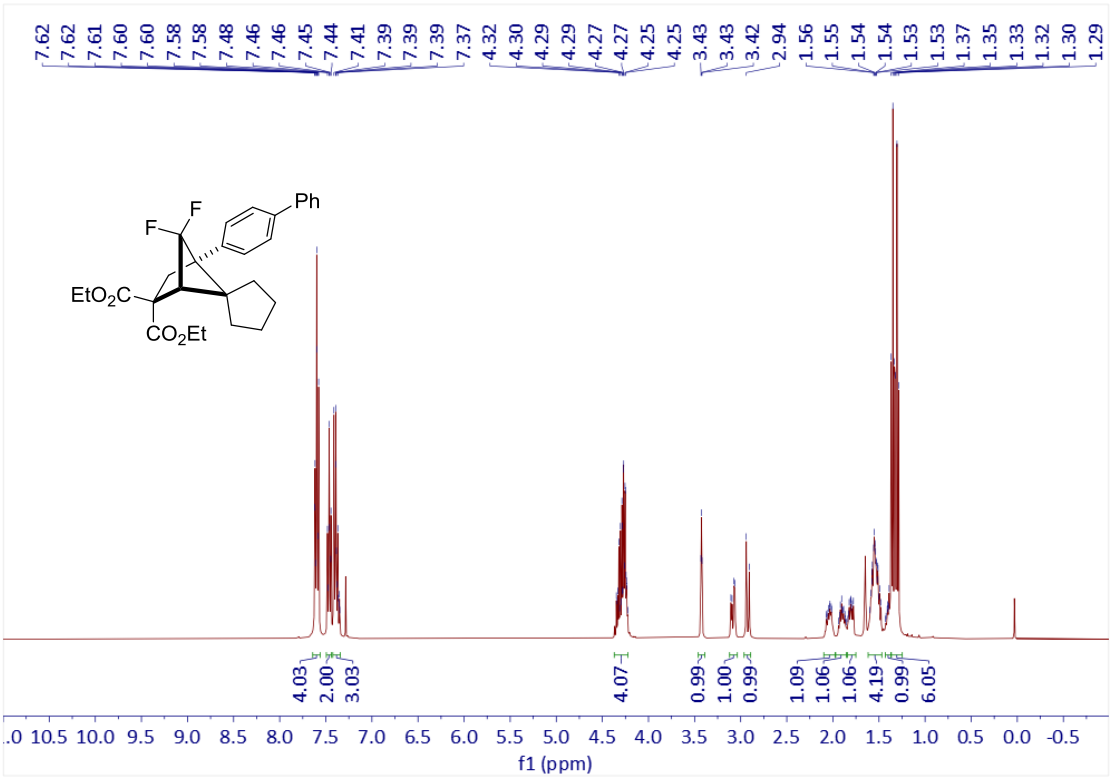
^{1}H NMR of 4r (400 MHz, $CDCl_3$)



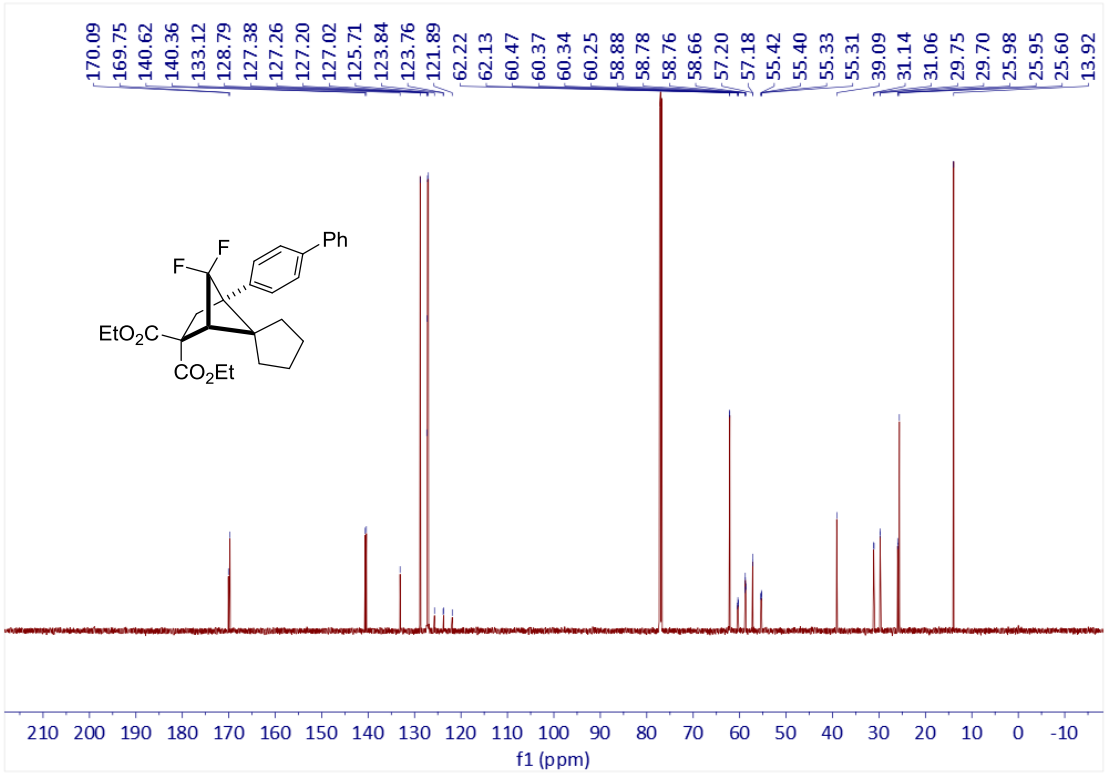
^{13}C NMR of 4r (151 MHz, $CDCl_3$)



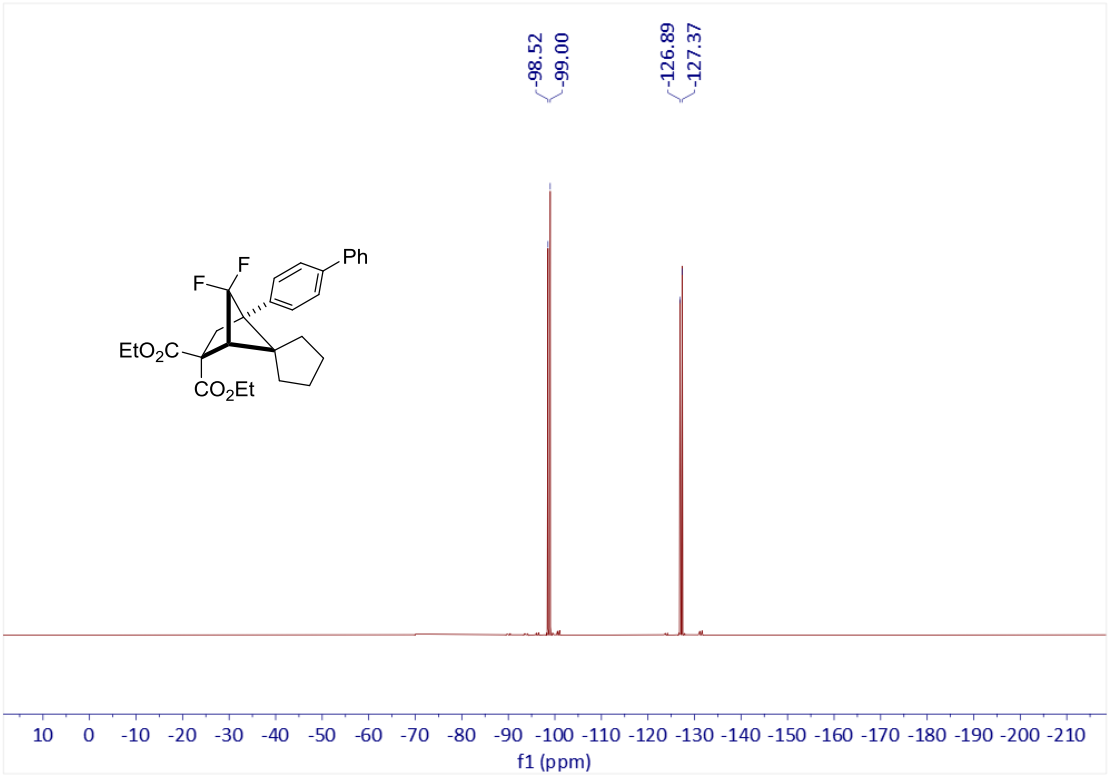
^{19}F NMR of 4r (377 MHz, $CDCl_3$)



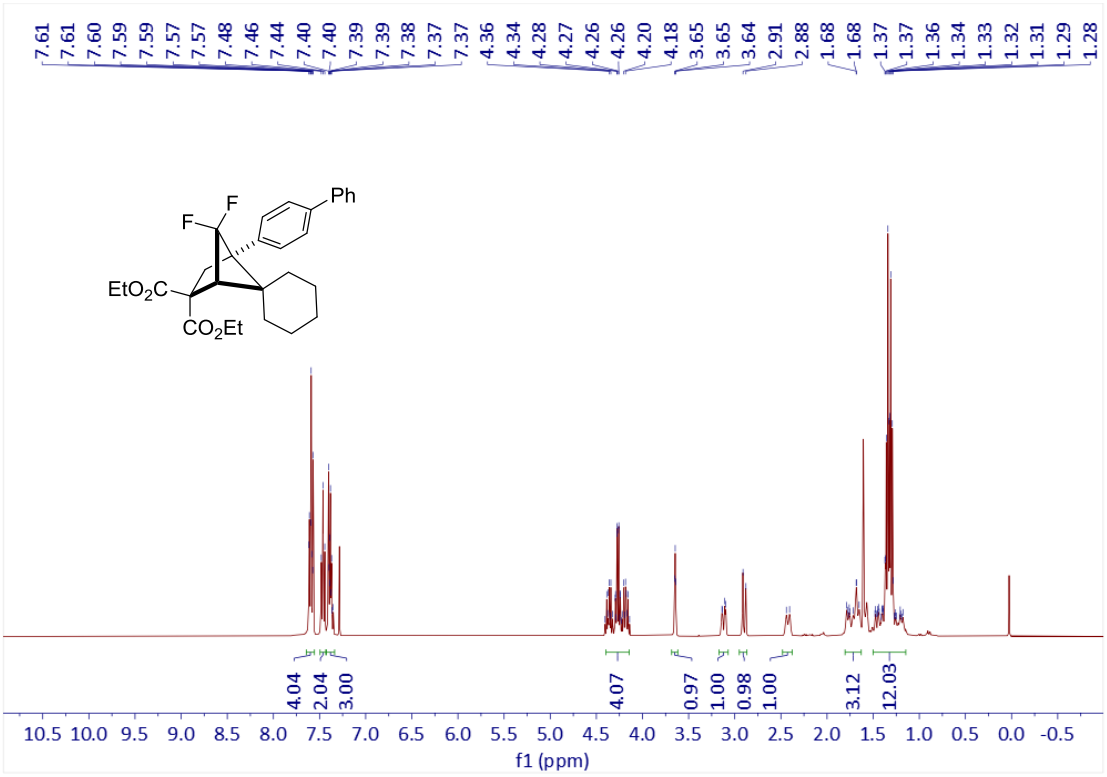
^{1}H NMR of 4s (400 MHz, $CDCl_3$)



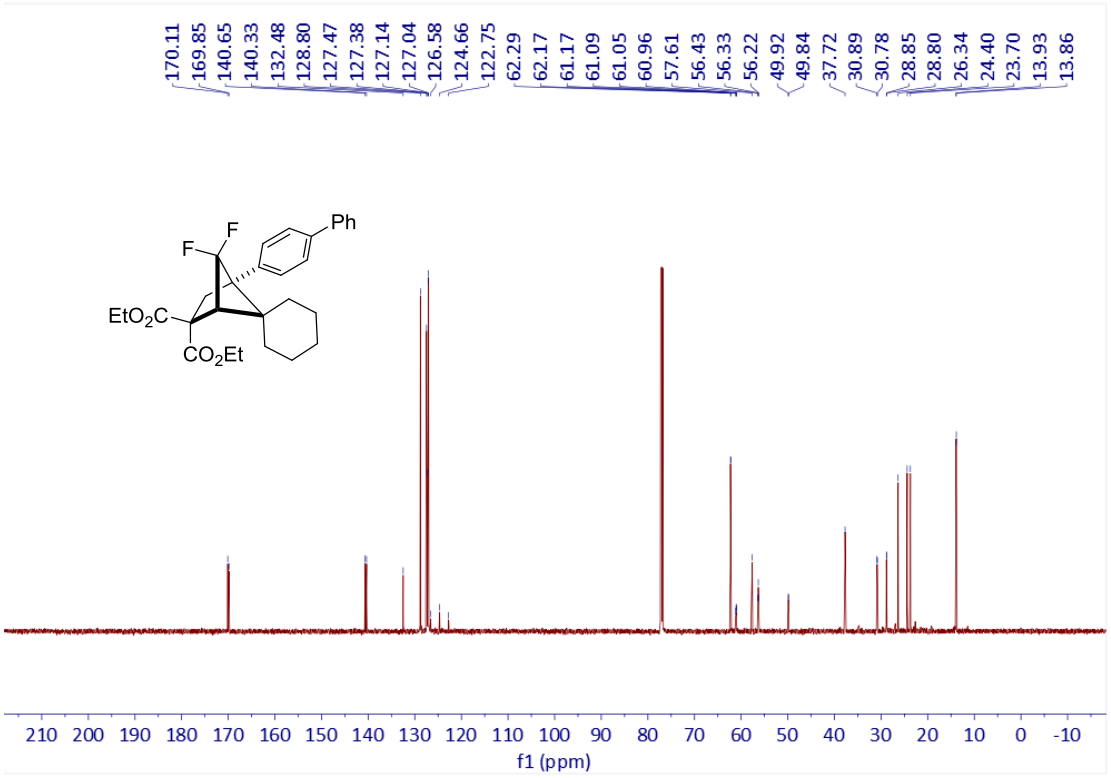
^{13}C NMR of 4s (151 MHz, $CDCl_3$)



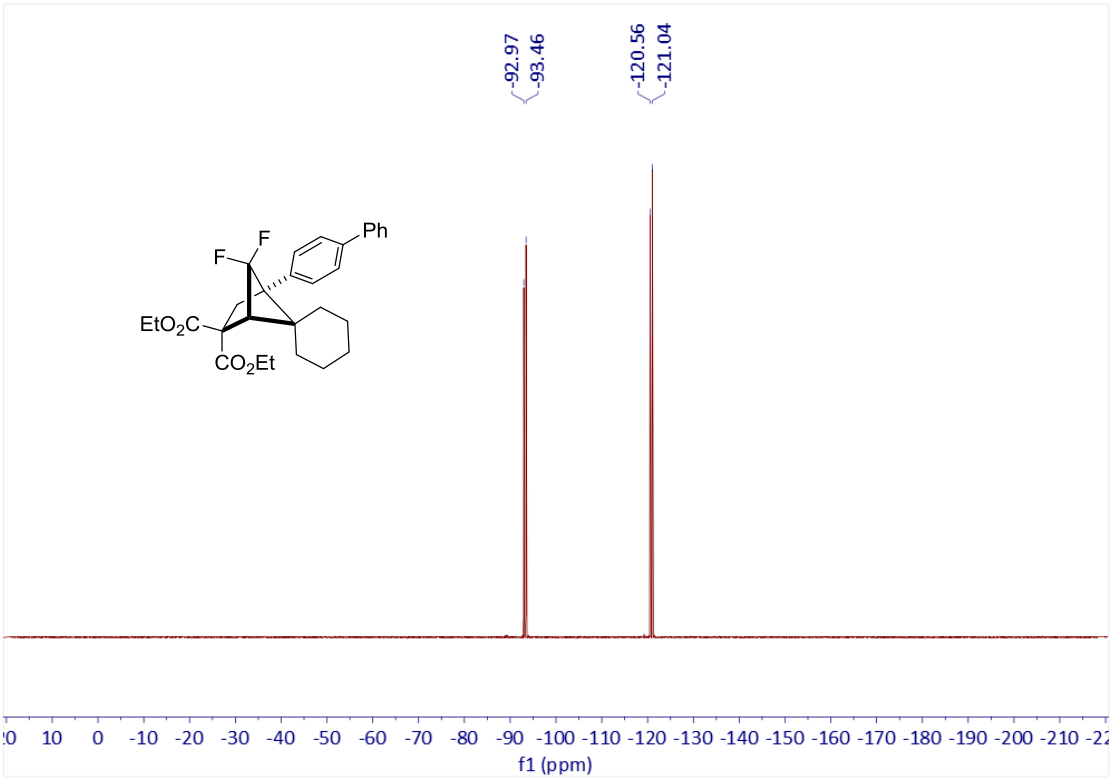
^{19}F NMR of 4s (377 MHz, $CDCl_3$)



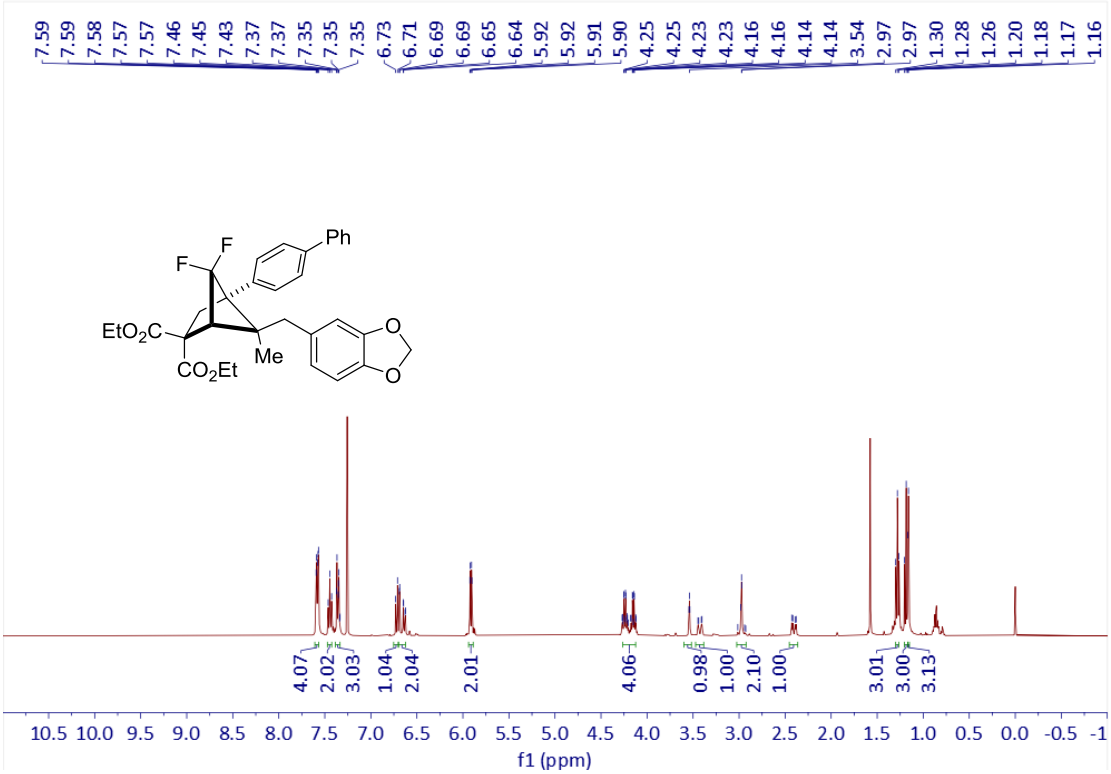
^{1}H NMR of 4t (400 MHz, $CDCl_3$)



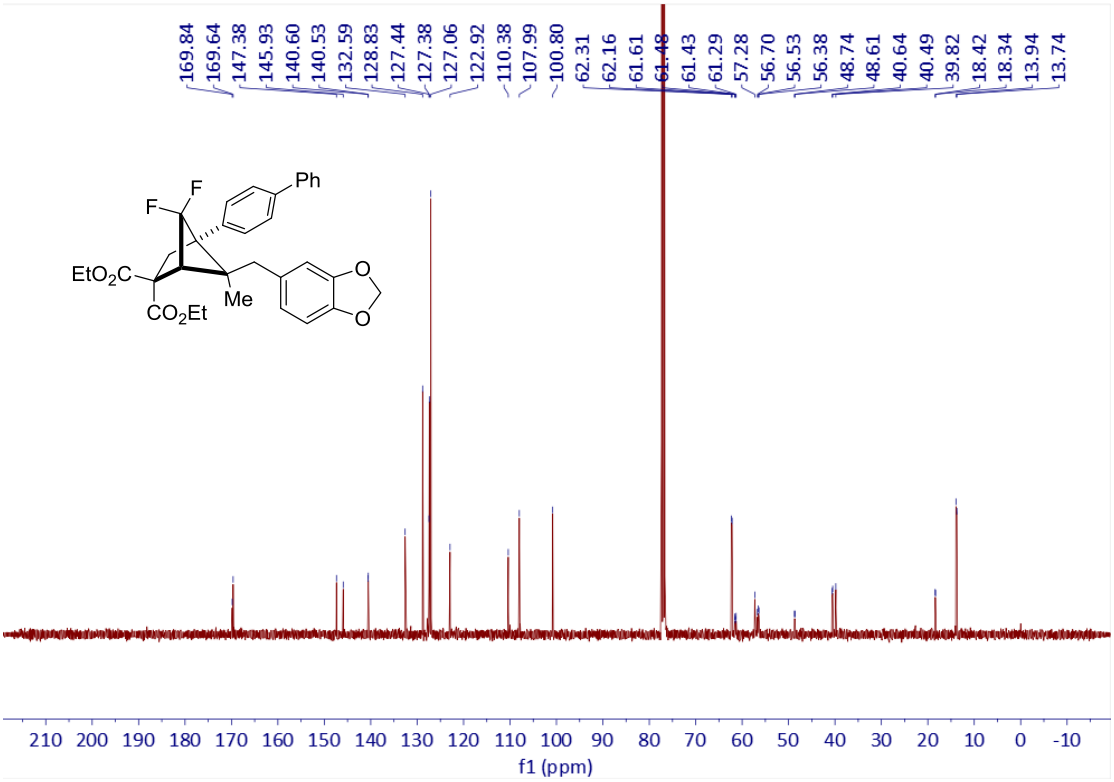
^{13}C NMR of 4t (151 MHz, $CDCl_3$)



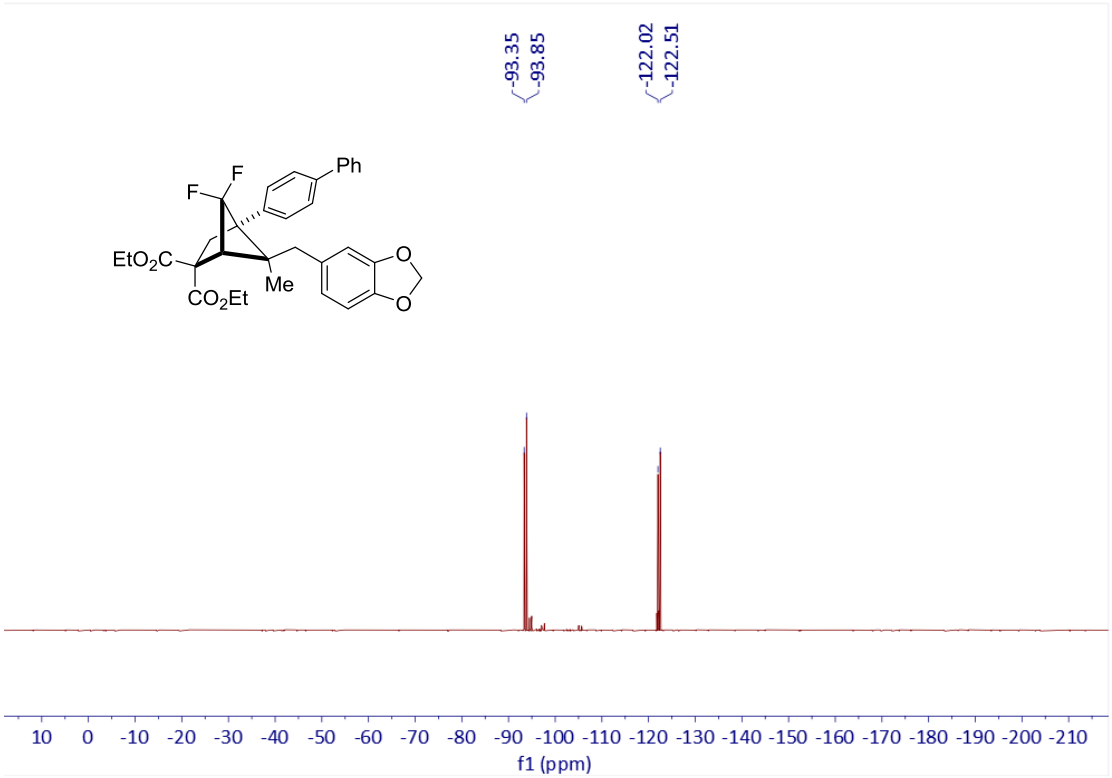
^{19}F NMR of 4t (377 MHz, $CDCl_3$)



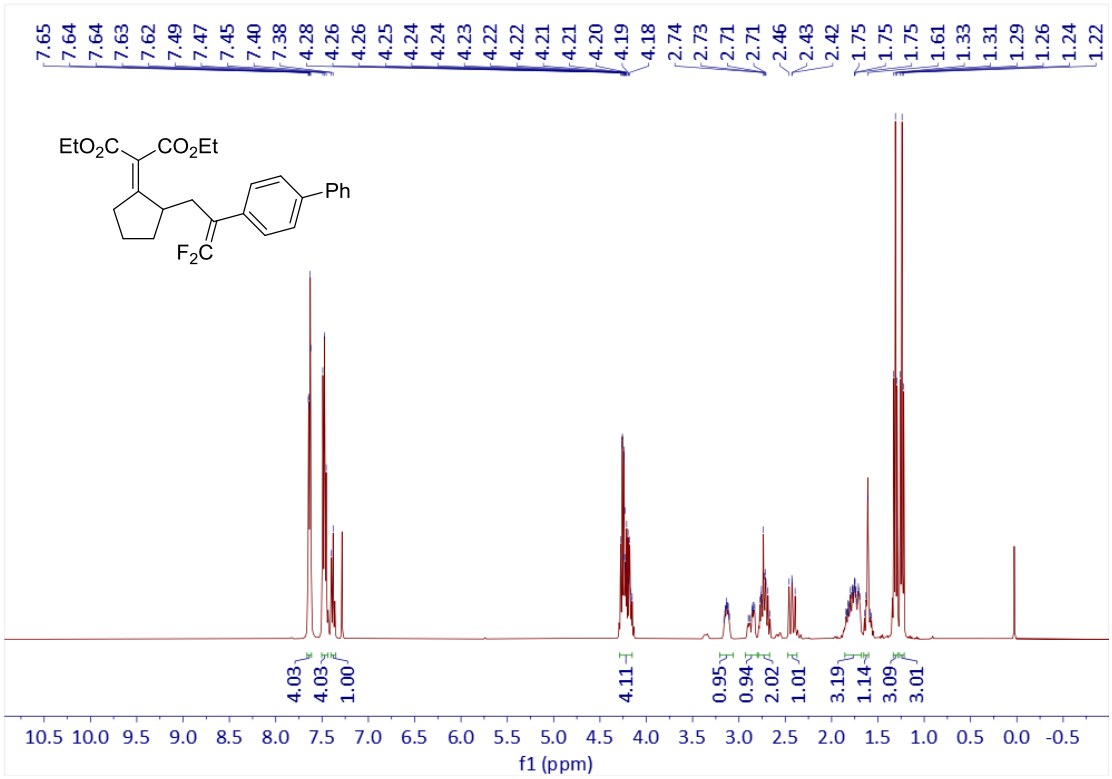
^{1}H NMR of 4u (400 MHz, $CDCl_3$)



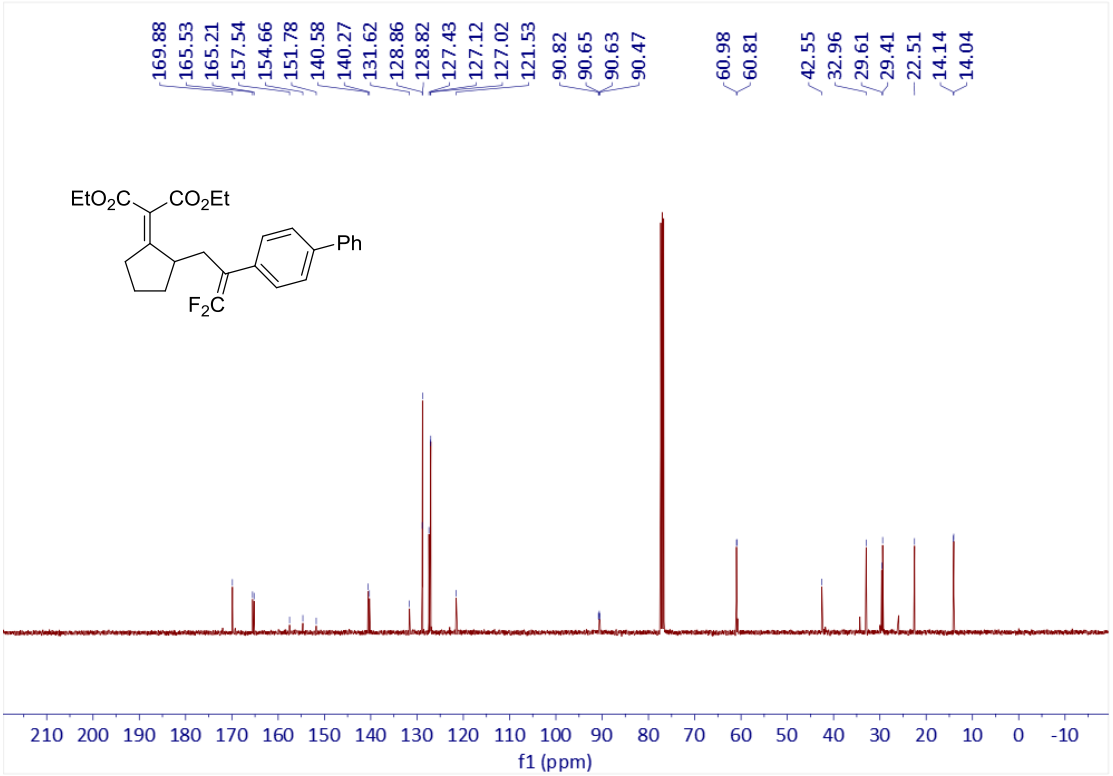
^{13}C NMR of 4u (101 MHz, $CDCl_3$)



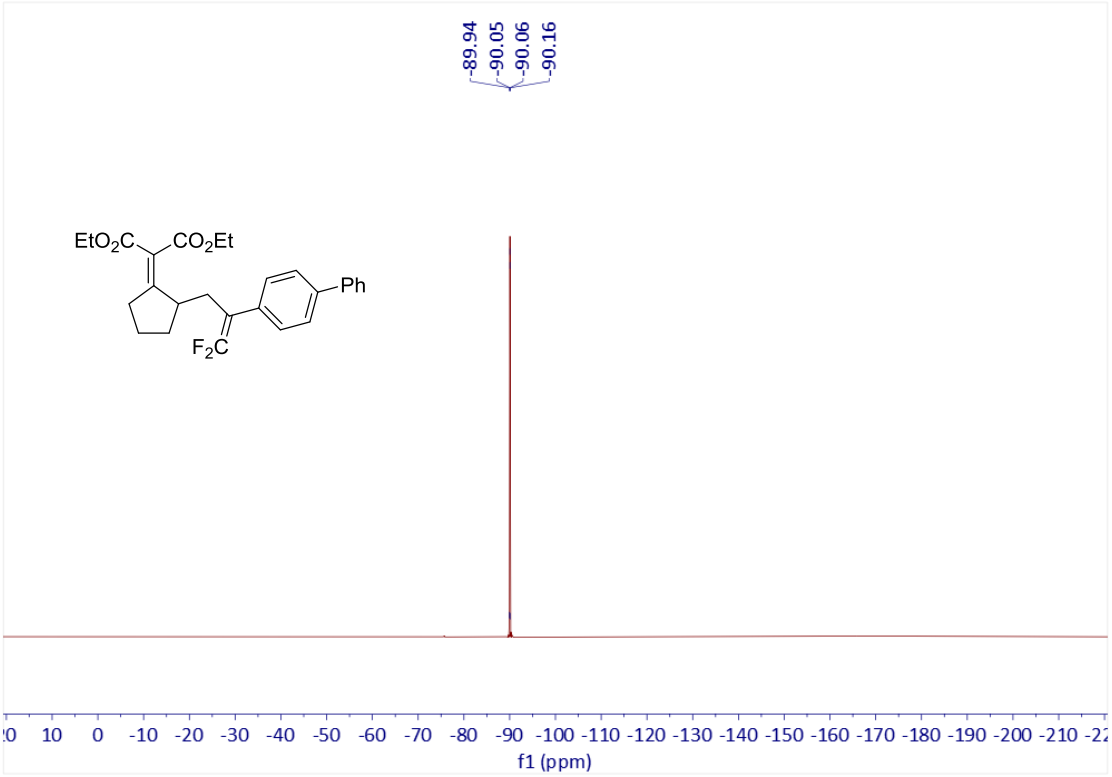
^{19}F NMR of 4u (377 MHz, $CDCl_3$)



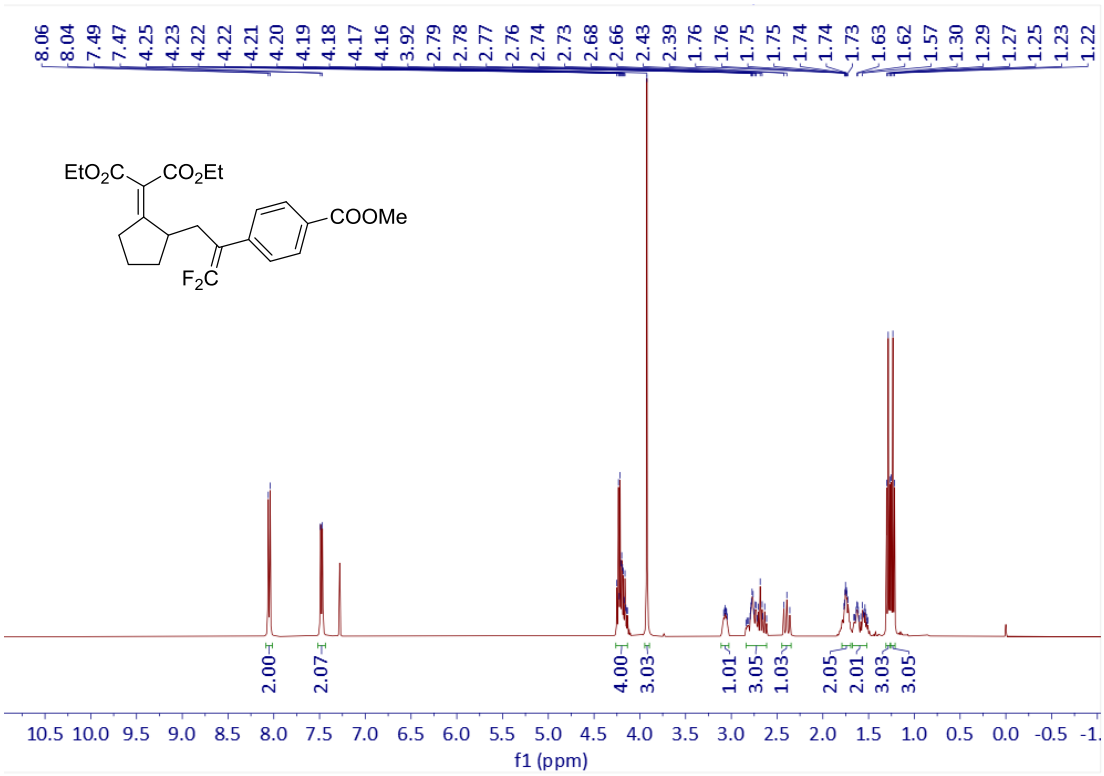
^{1}H NMR of 6a (400 MHz, $CDCl_3$)



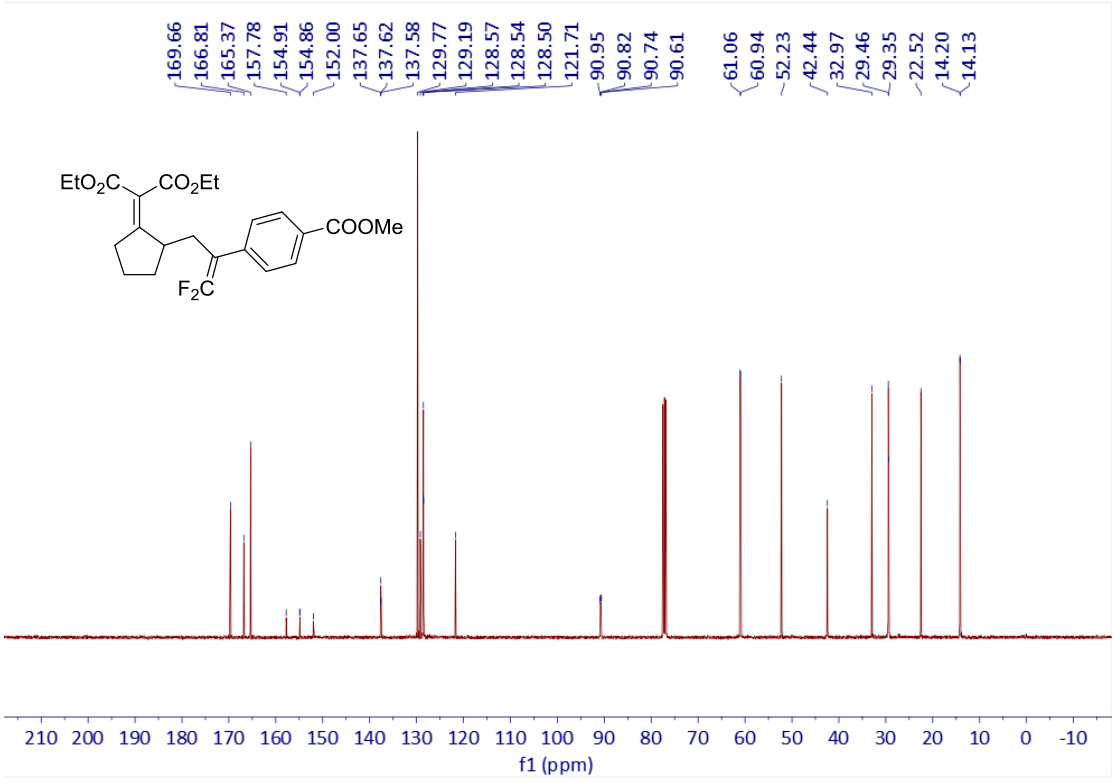
^{13}C NMR of 6a (101 MHz, $CDCl_3$)



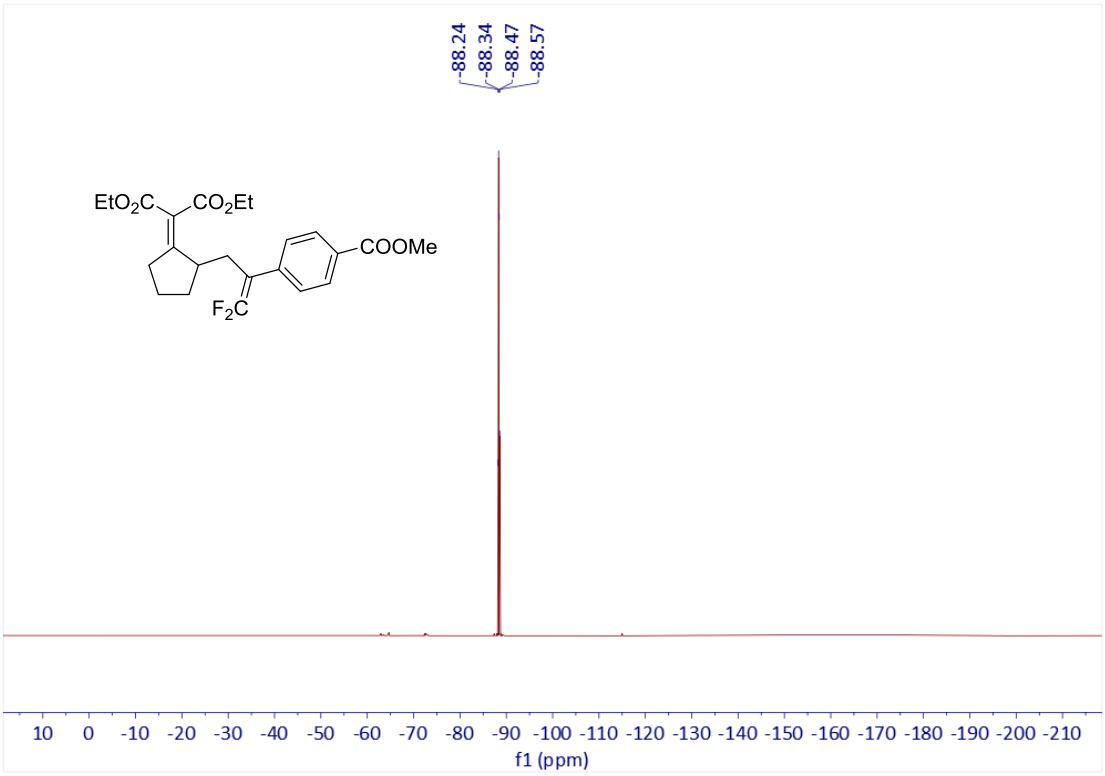
^{19}F NMR of 6a (377 MHz, $CDCl_3$)



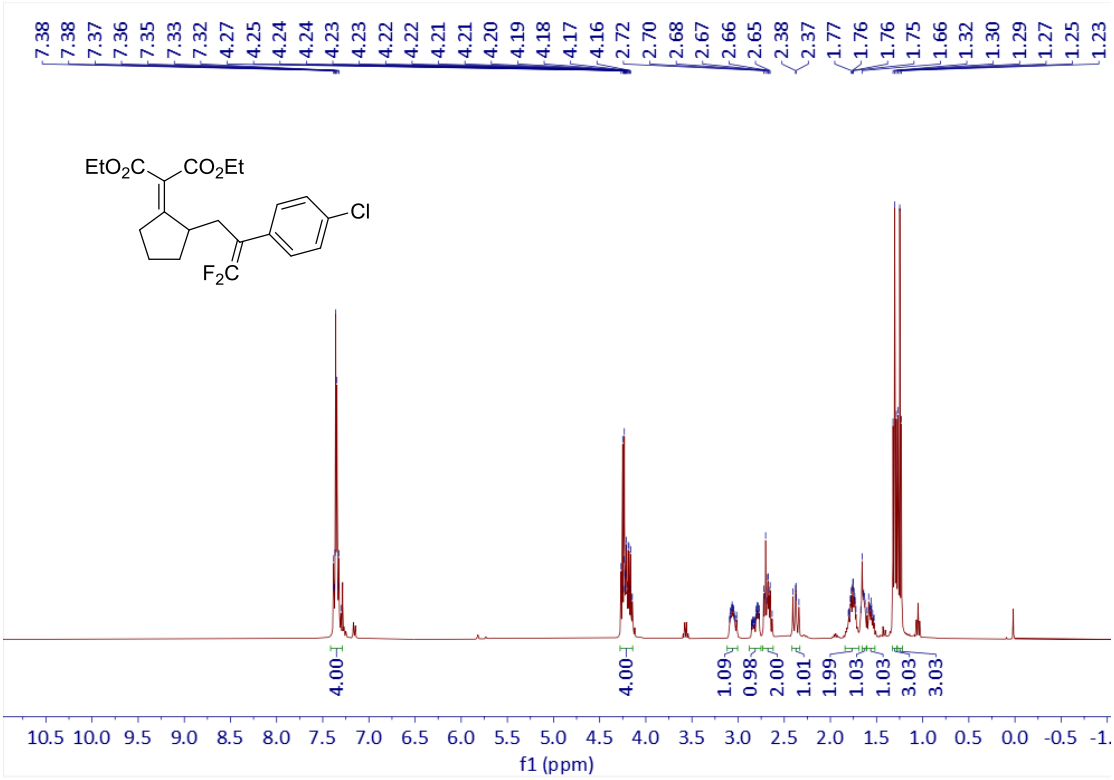
^{1}H NMR of 6b (400 MHz, $CDCl_3$)



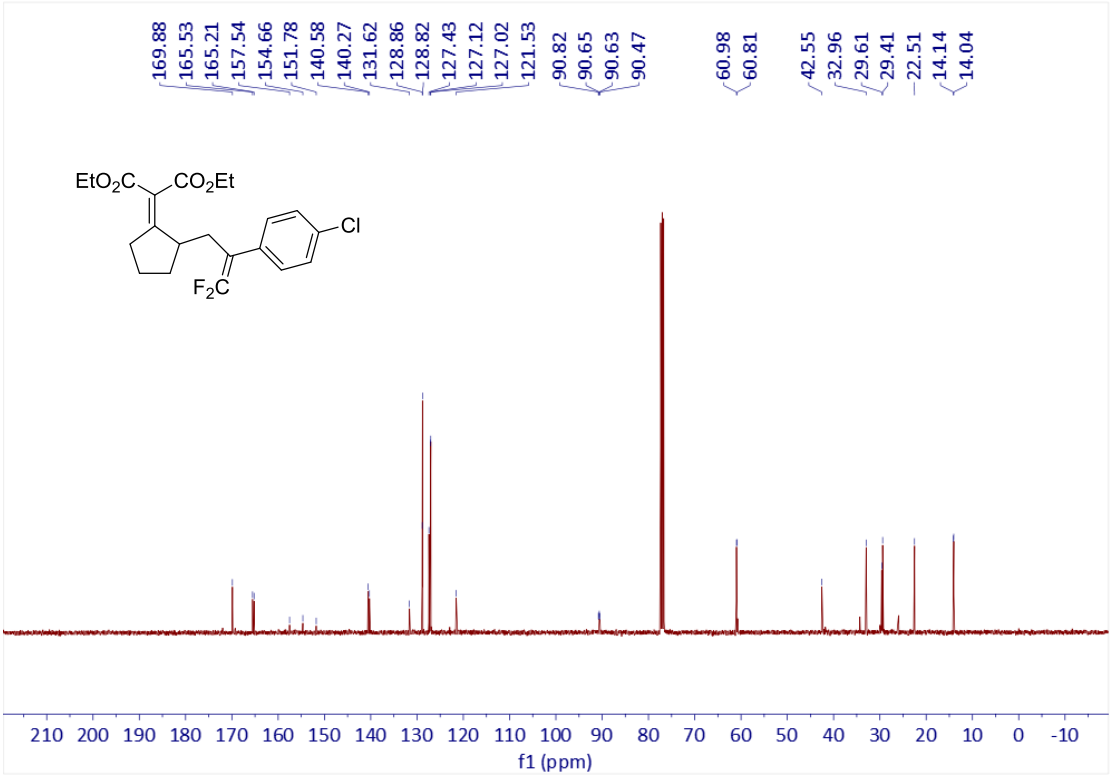
^{13}C NMR of 6b (101 MHz, $CDCl_3$)



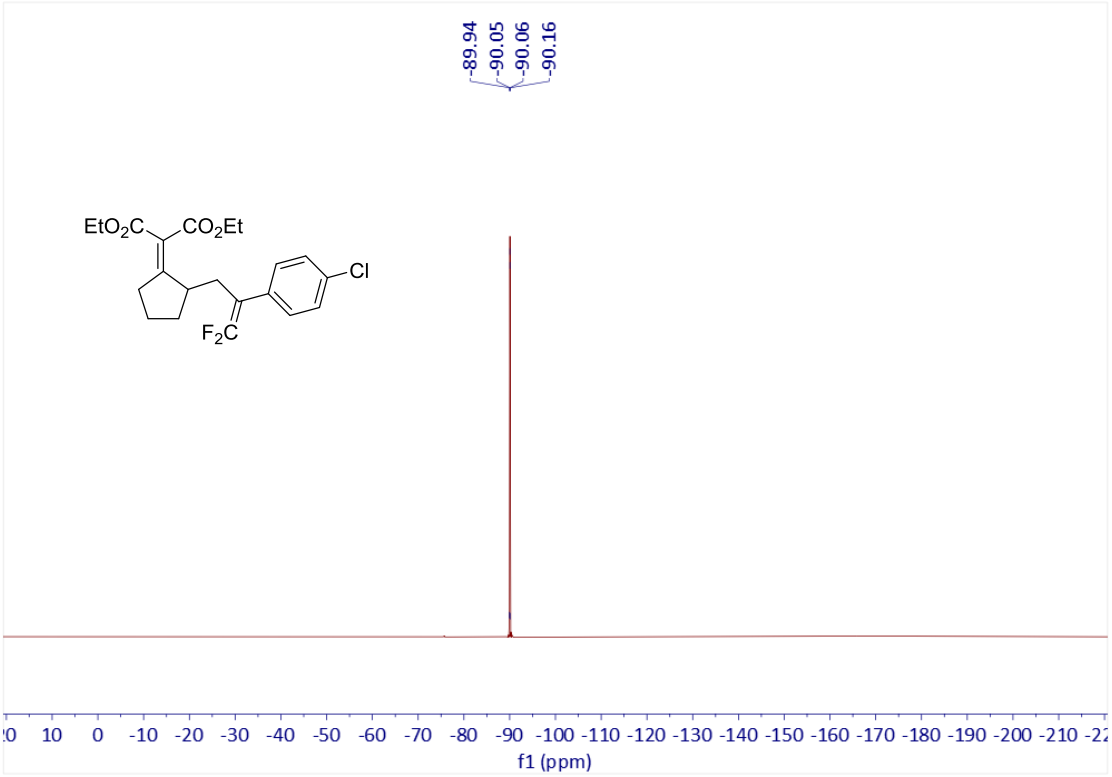
^{19}F NMR of 6b (377 MHz, $CDCl_3$)



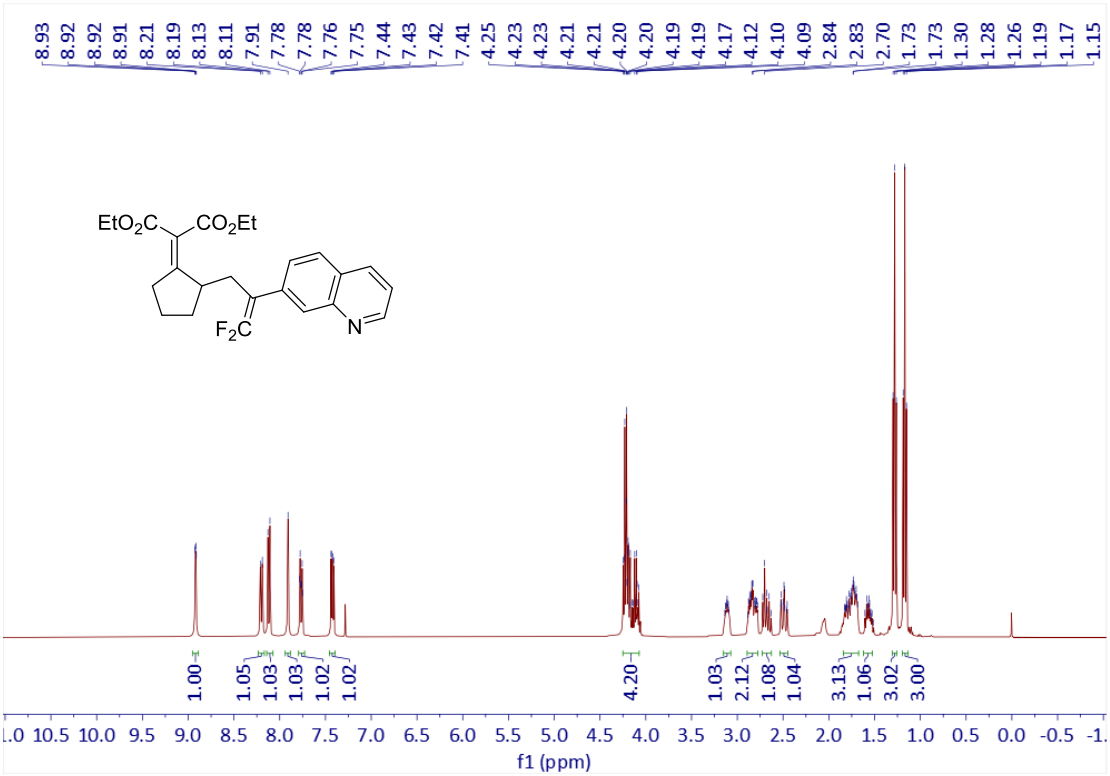
^{1}H NMR of 6c (400 MHz, $CDCl_3$)



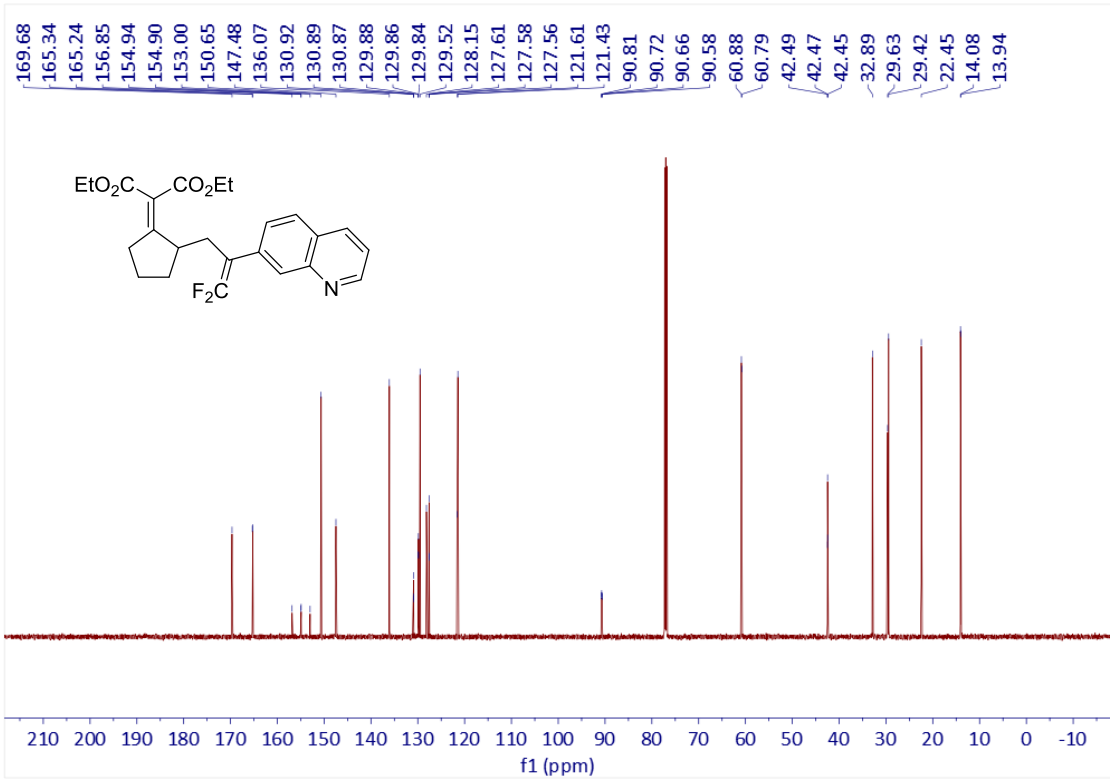
^{13}C NMR of 6c (151 MHz, $CDCl_3$)



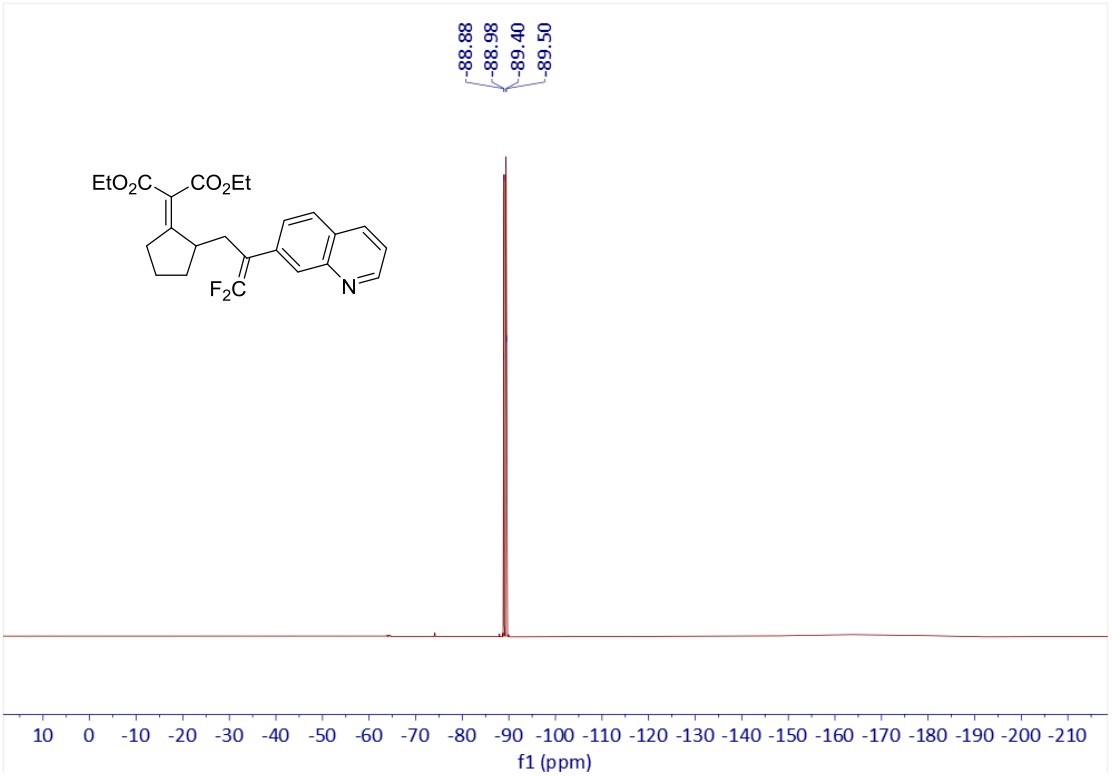
^{19}F NMR of 6c (377 MHz, $CDCl_3$)



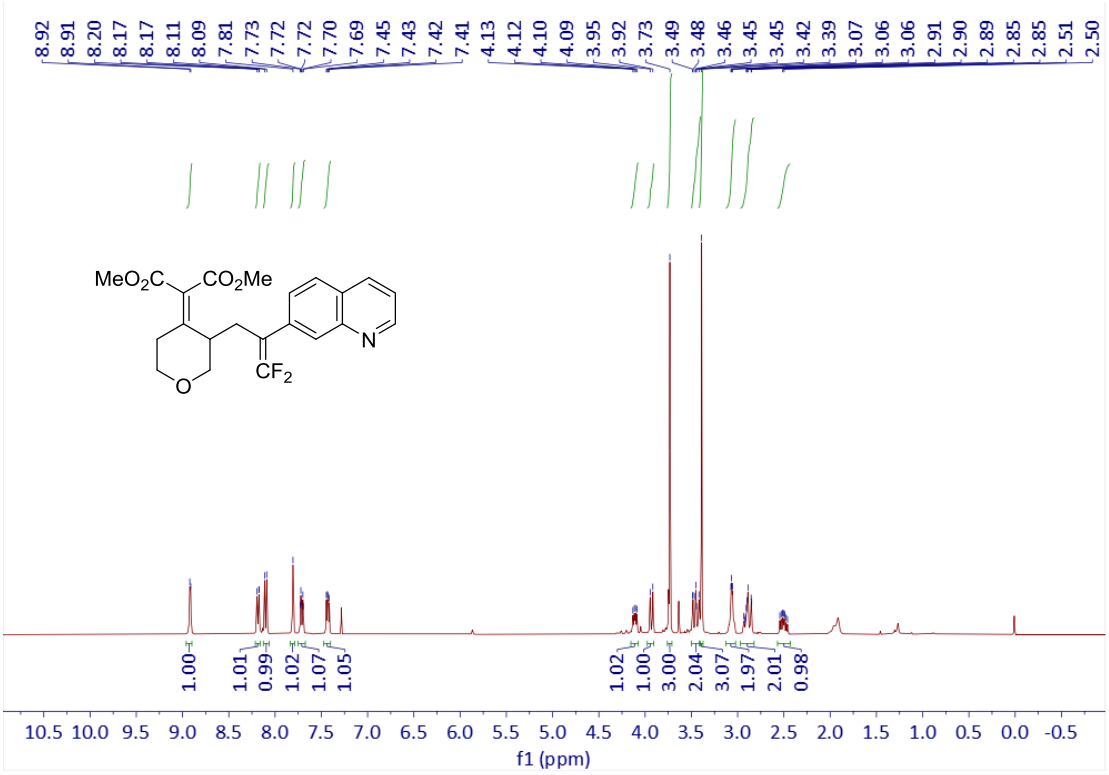
^{1}H NMR of 6d (400 MHz, $CDCl_3$)



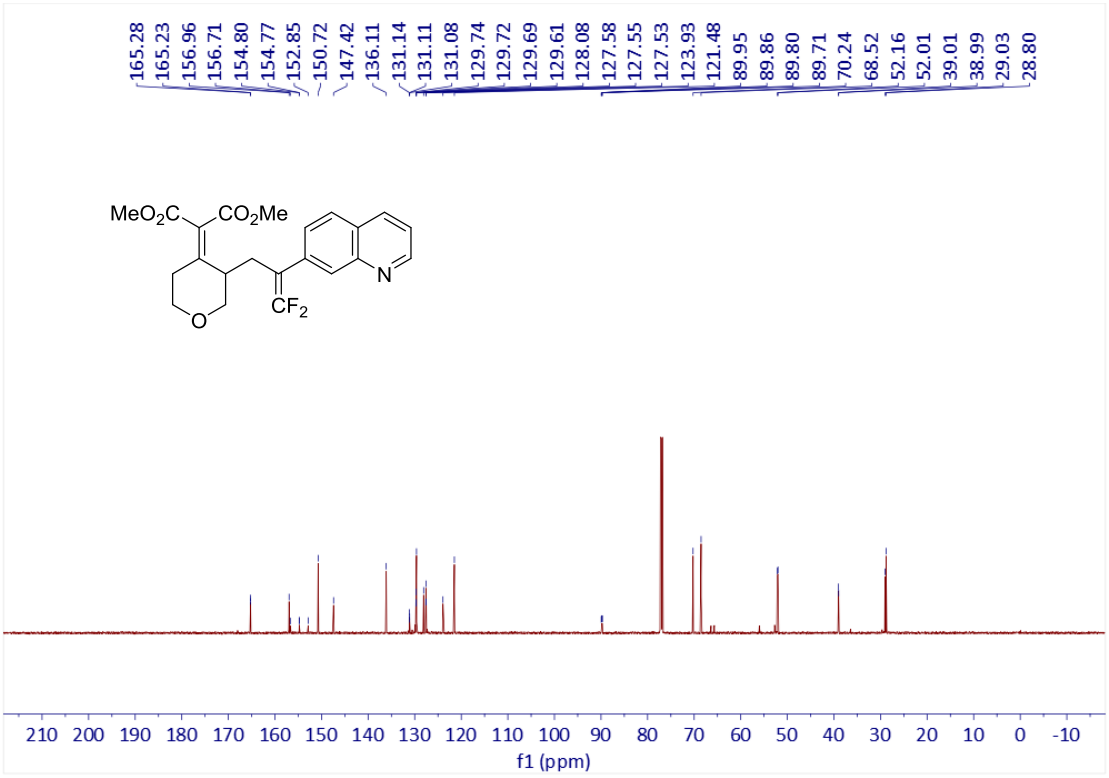
^{13}C NMR of 6d (151 MHz, $CDCl_3$)



^{19}F NMR of 6d (377 MHz, $CDCl_3$)

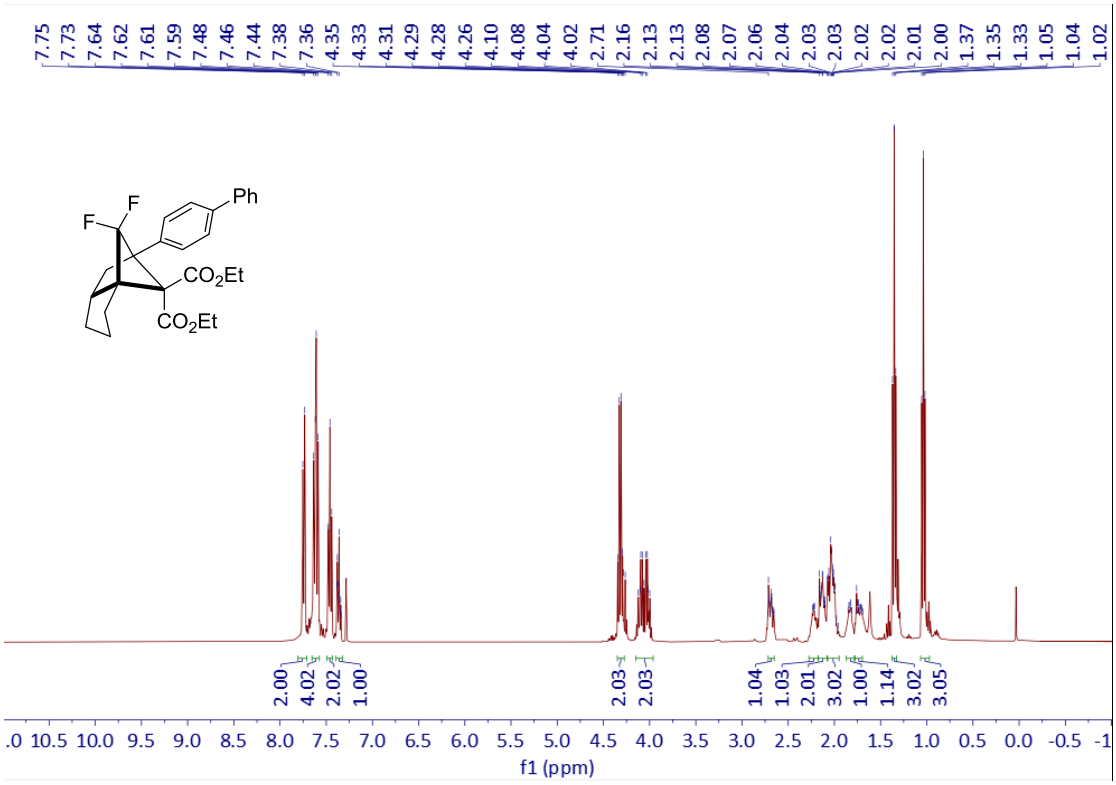


^{1}H NMR of 6e (400 MHz, $CDCl_3$)

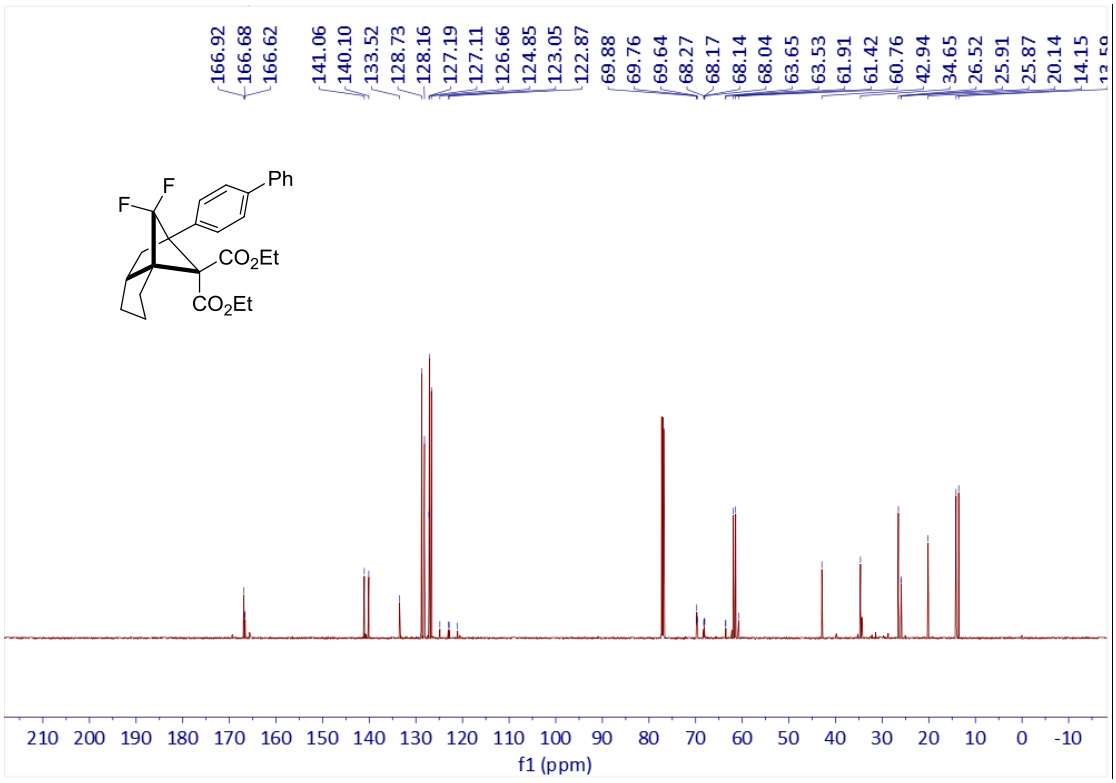


^{13}C NMR of 6e (151 MHz, $CDCl_3$)

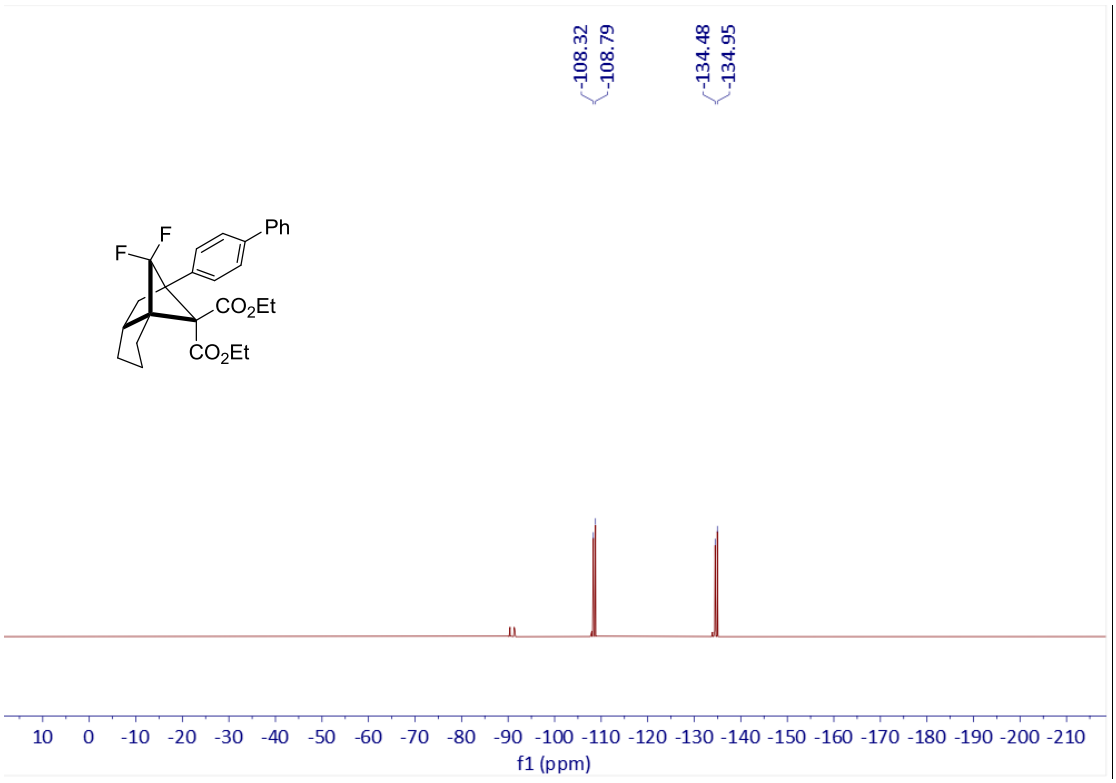
^{19}F NMR of 6e (377 MHz, $CDCl_3$)



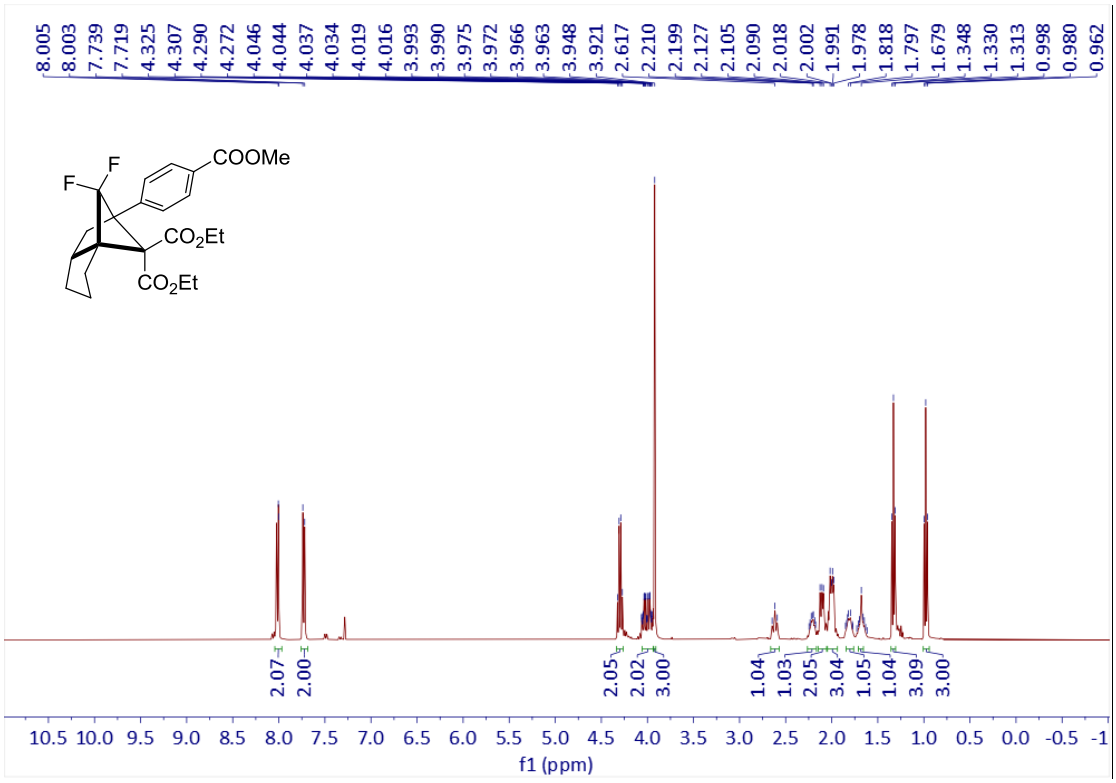
^{1}H NMR of 7a (400 MHz, $CDCl_3$)



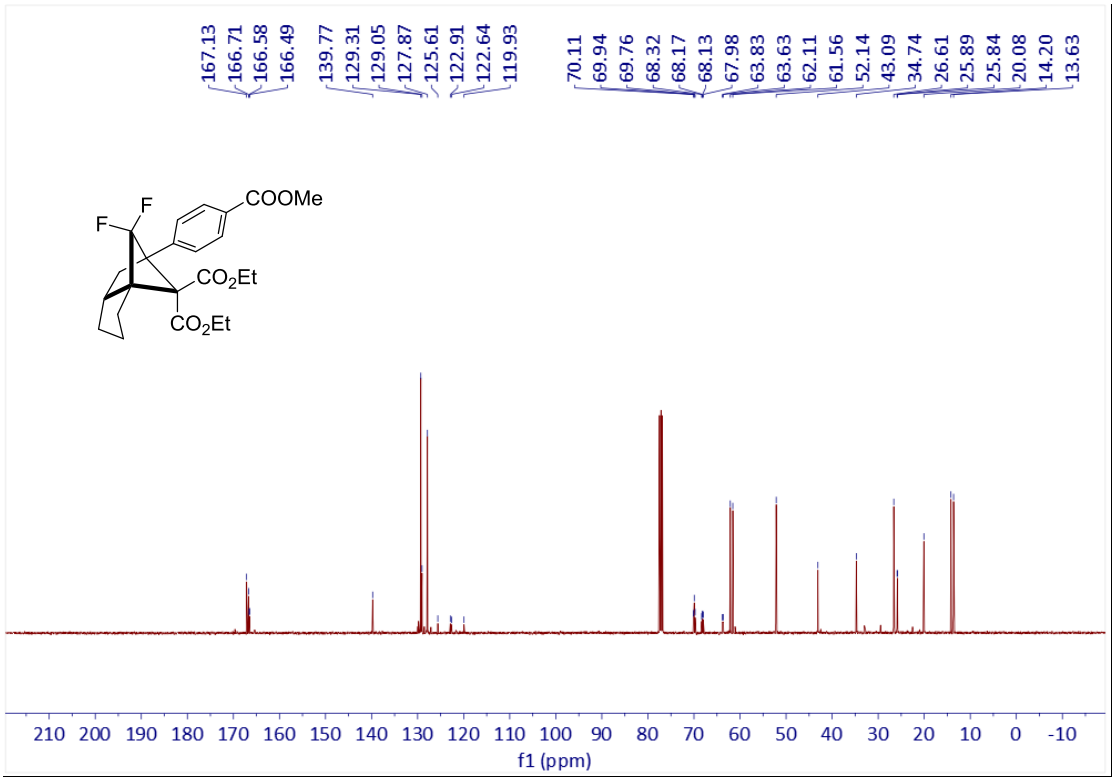
^{13}C NMR of 7a (151 MHz, $CDCl_3$)



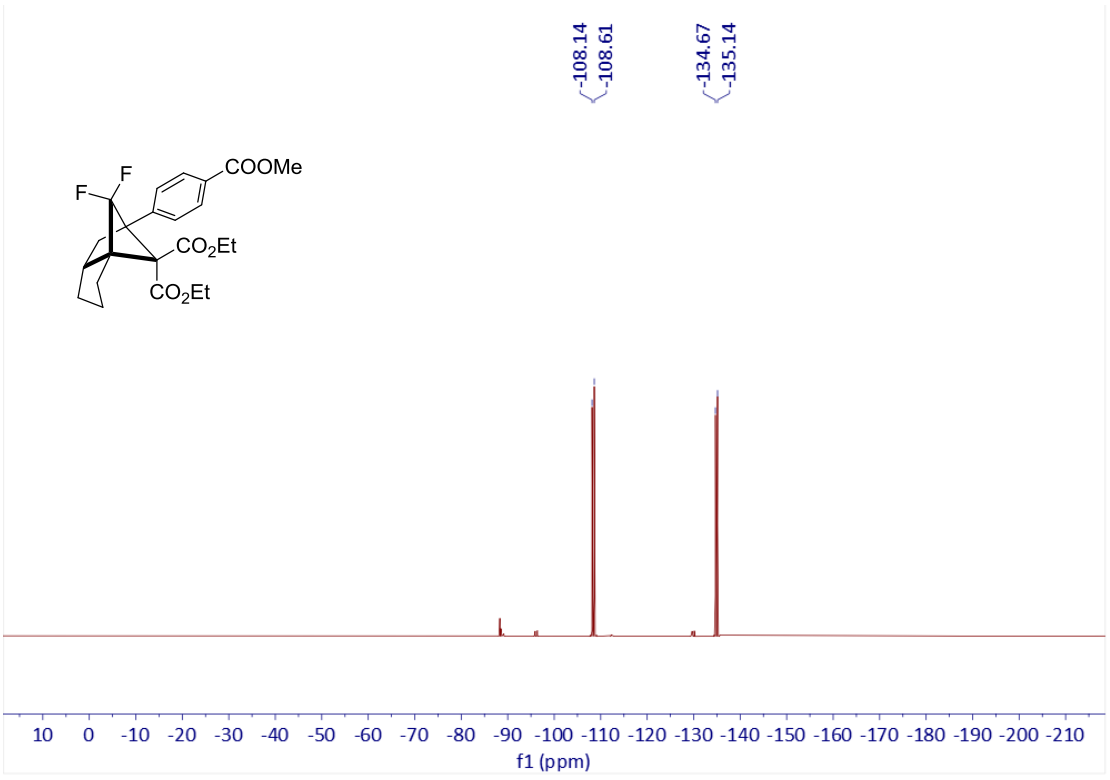
^{19}F NMR of 7a (377 MHz, $CDCl_3$)



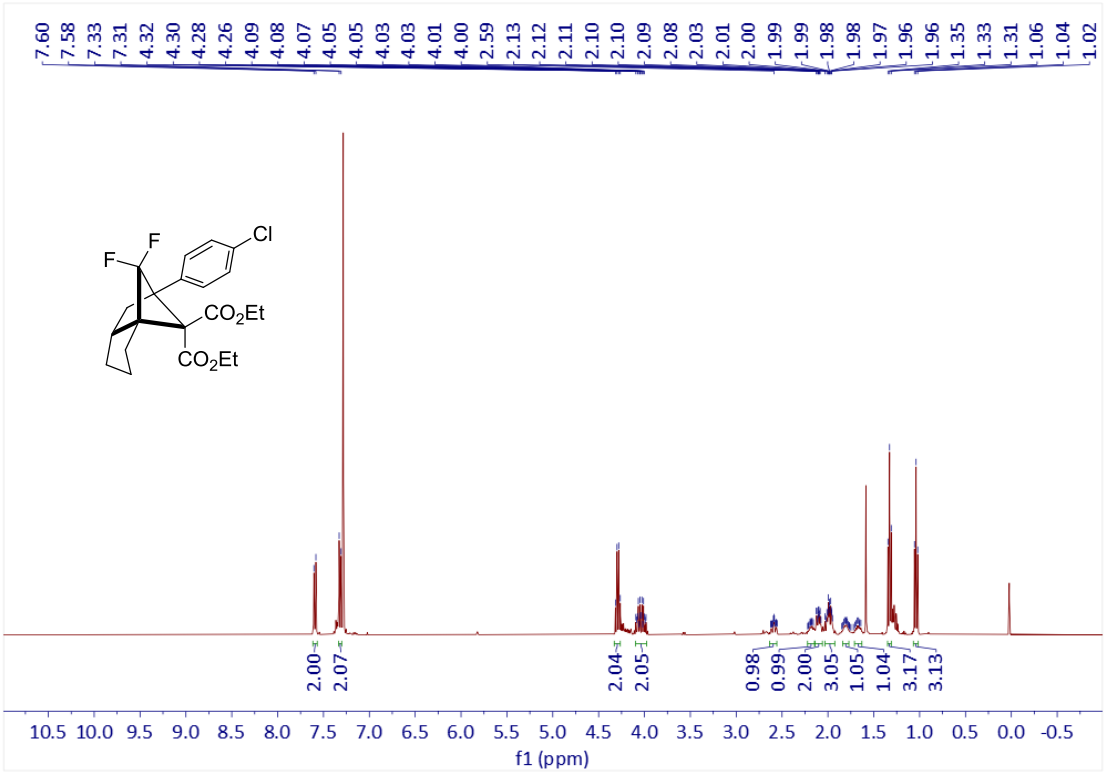
^{1}H NMR of 7b (400 MHz, $CDCl_3$)



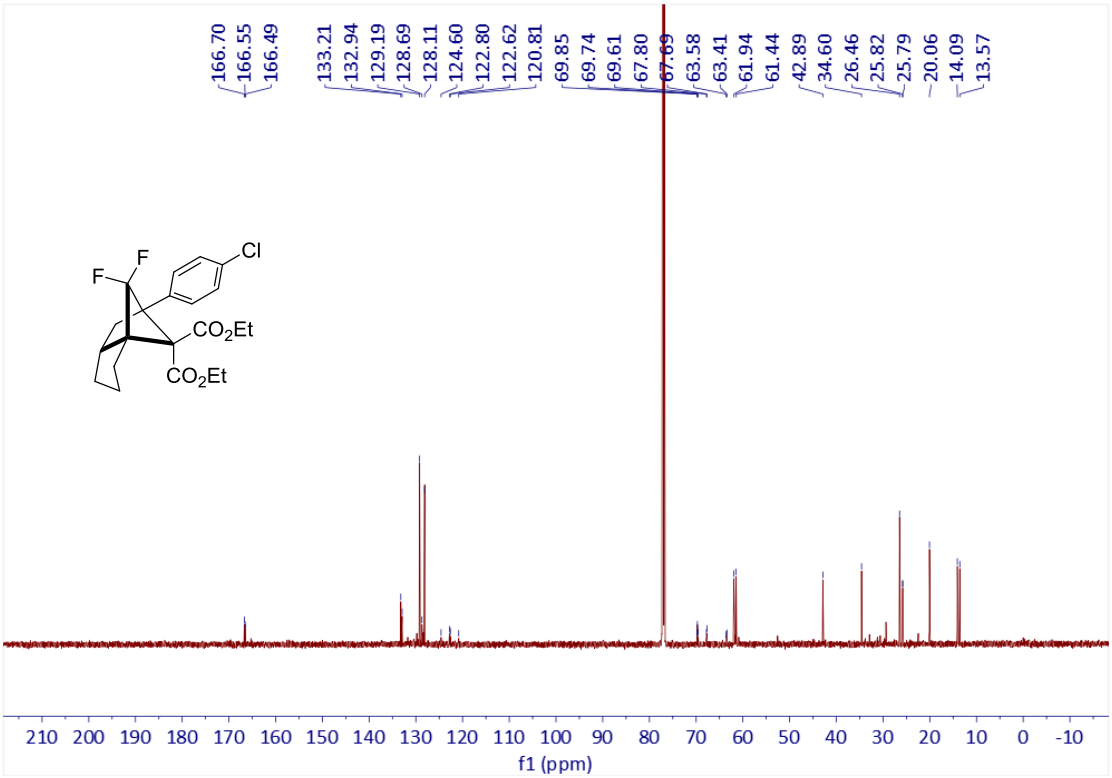
^{13}C NMR of 7b (101 MHz, $CDCl_3$)



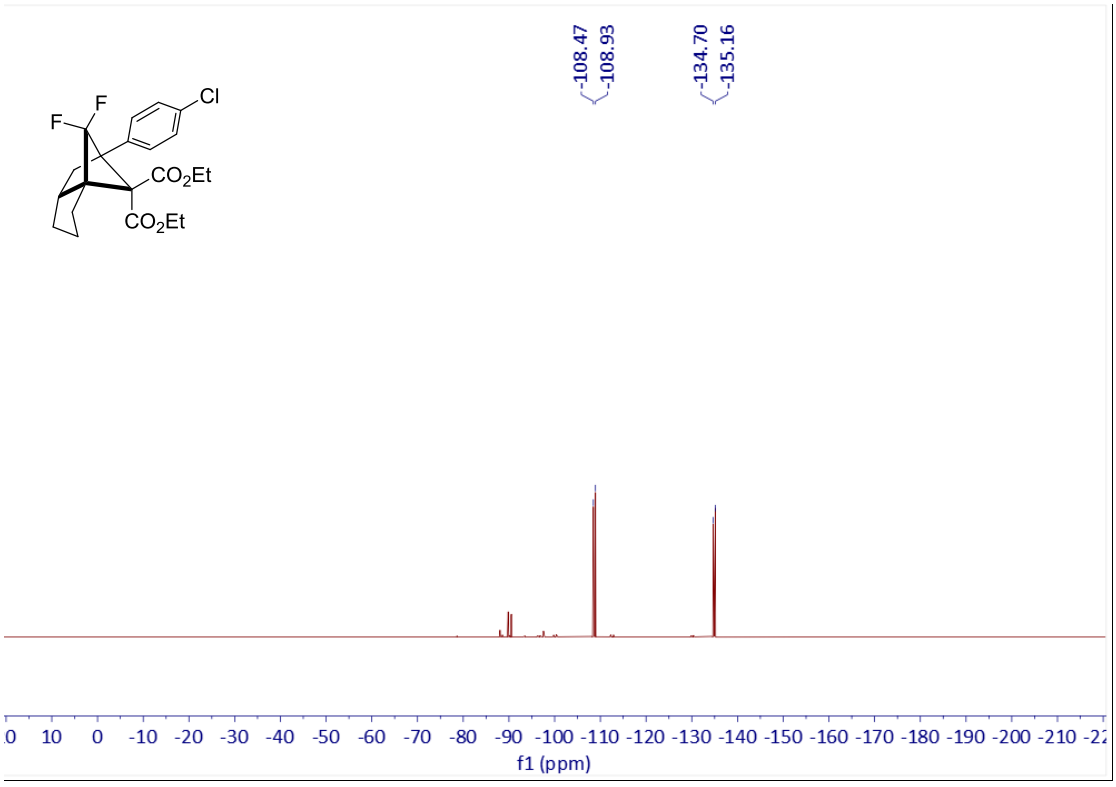
^{19}F NMR of 7b (377 MHz, $CDCl_3$)



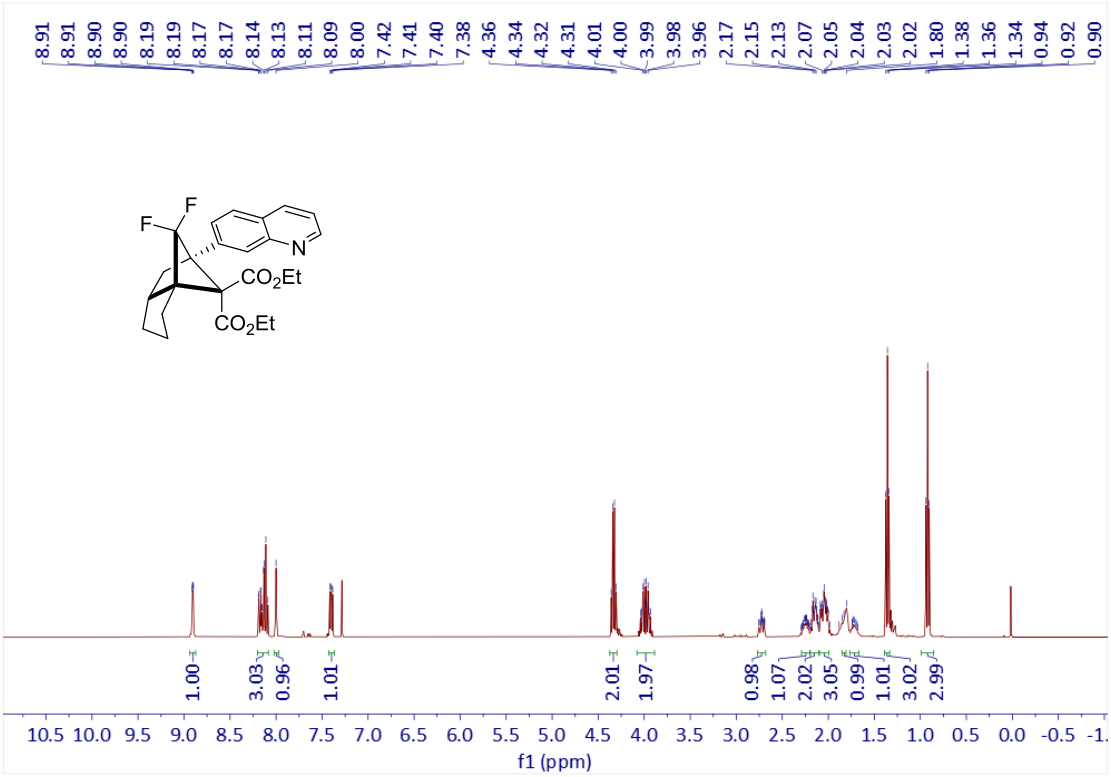
^{1}H NMR of 7c (400 MHz, $CDCl_3$)



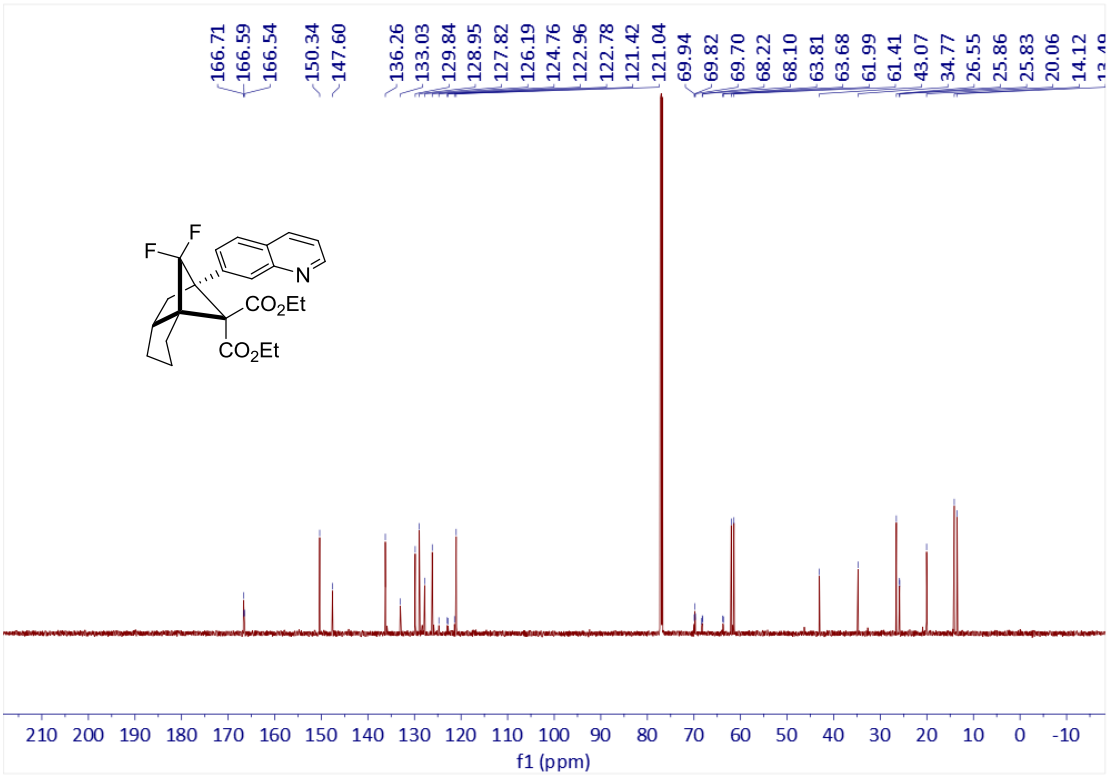
^{13}C NMR of 7c (151 MHz, $CDCl_3$)



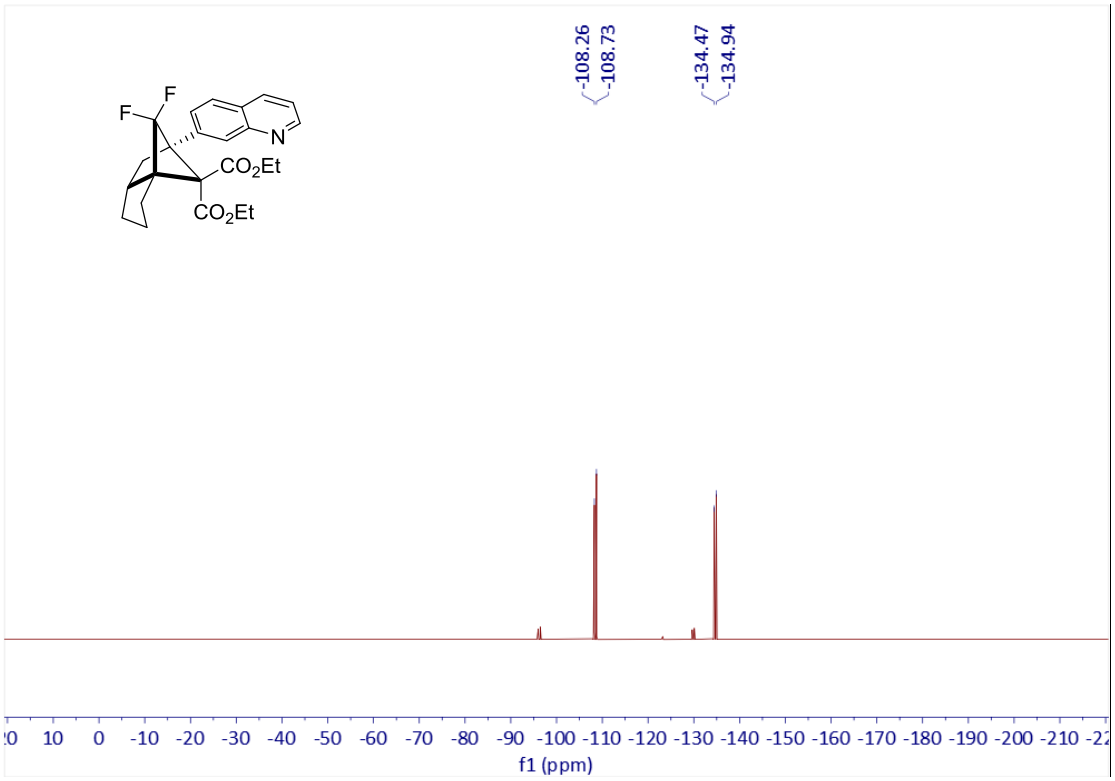
^{19}F NMR of 7c (377 MHz, $CDCl_3$)



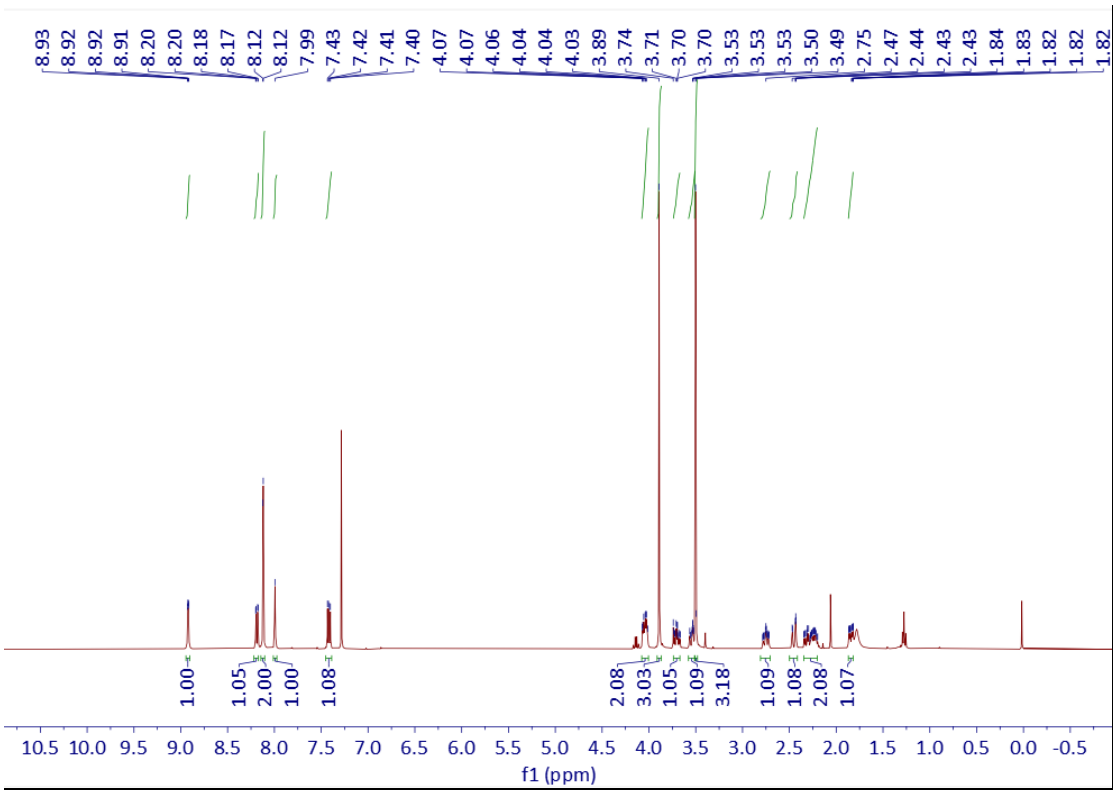
^{1}H NMR of 7d (400 MHz, $CDCl_3$)



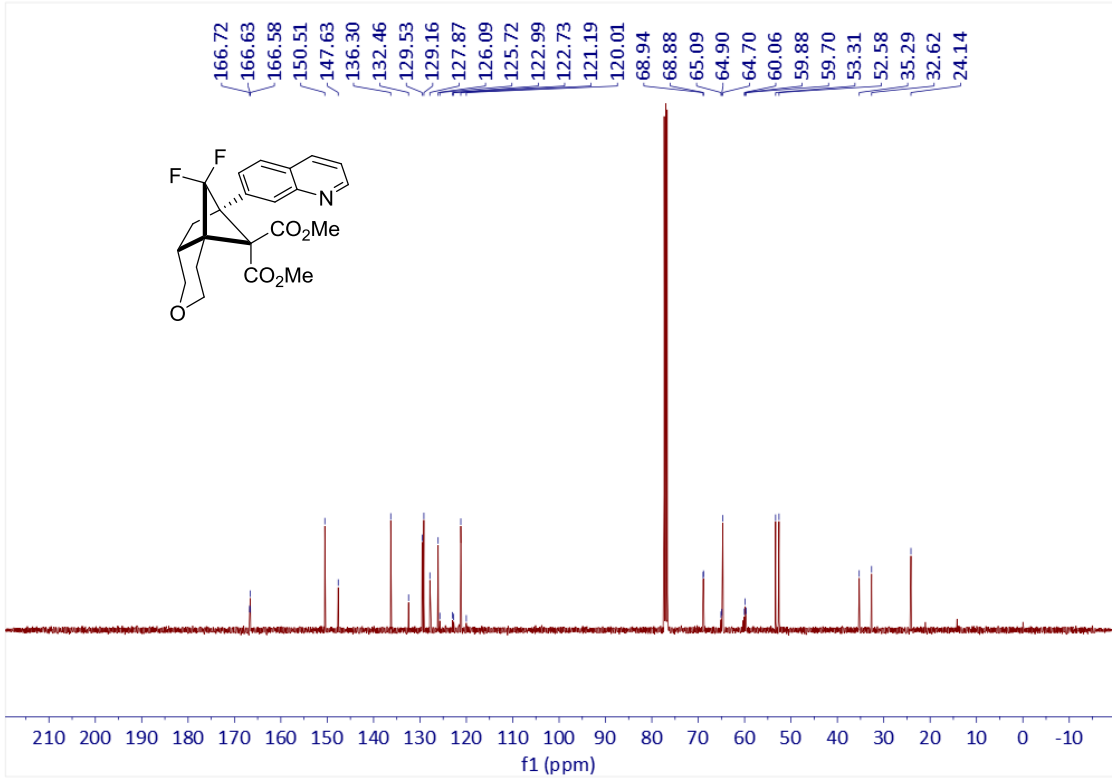
^{13}C NMR of 7d (151 MHz, $CDCl_3$)



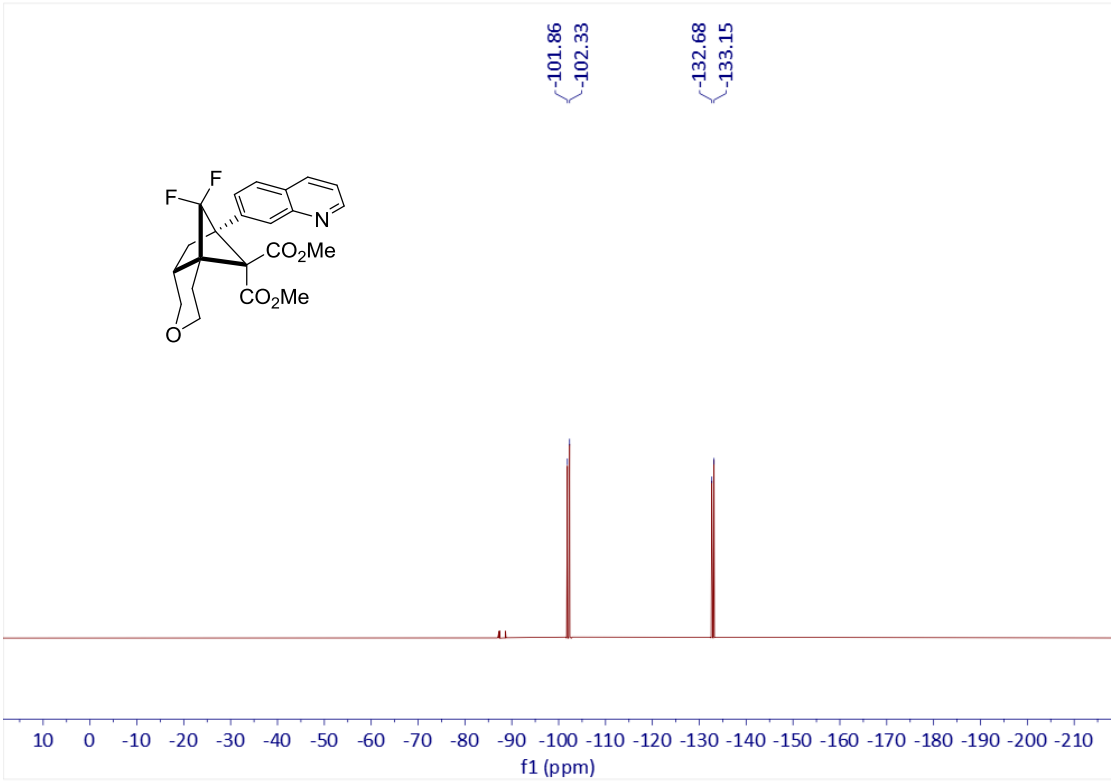
^{19}F NMR of 7d (377 MHz, $CDCl_3$)



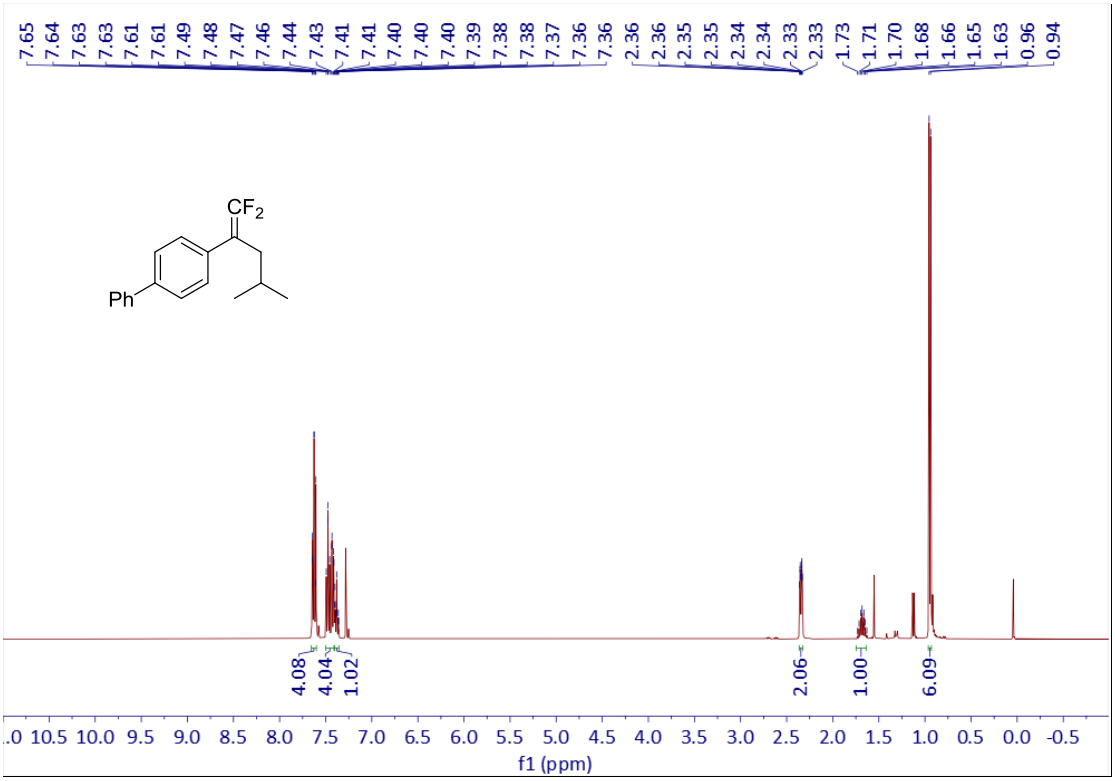
^{1}H NMR of 7e (400 MHz, $CDCl_3$)



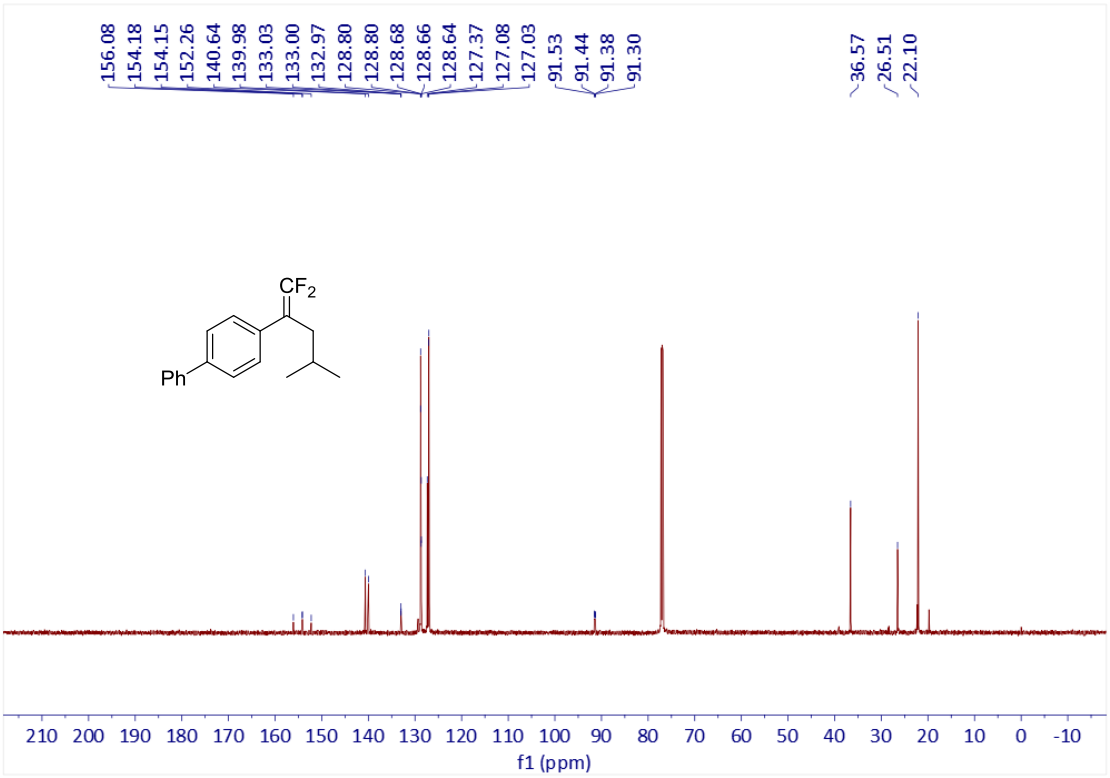
^{13}C NMR of 7e (151 MHz, $CDCl_3$)



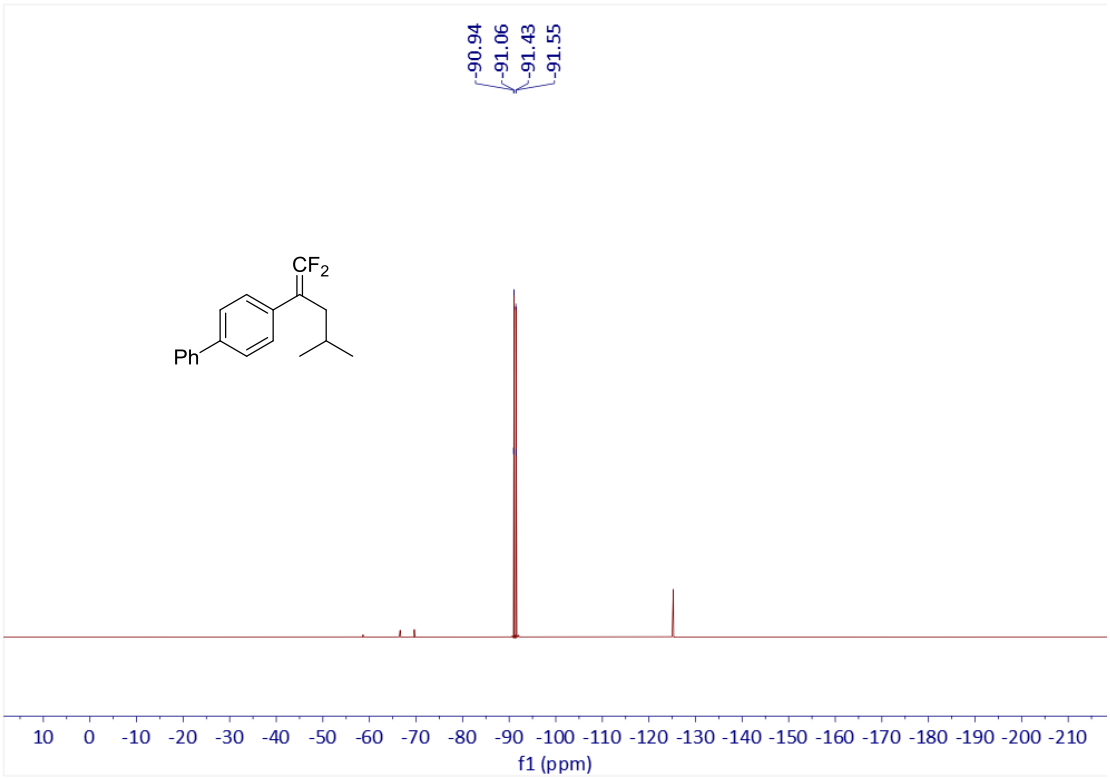
^{19}F NMR of 7e (377 MHz, $CDCl_3$)



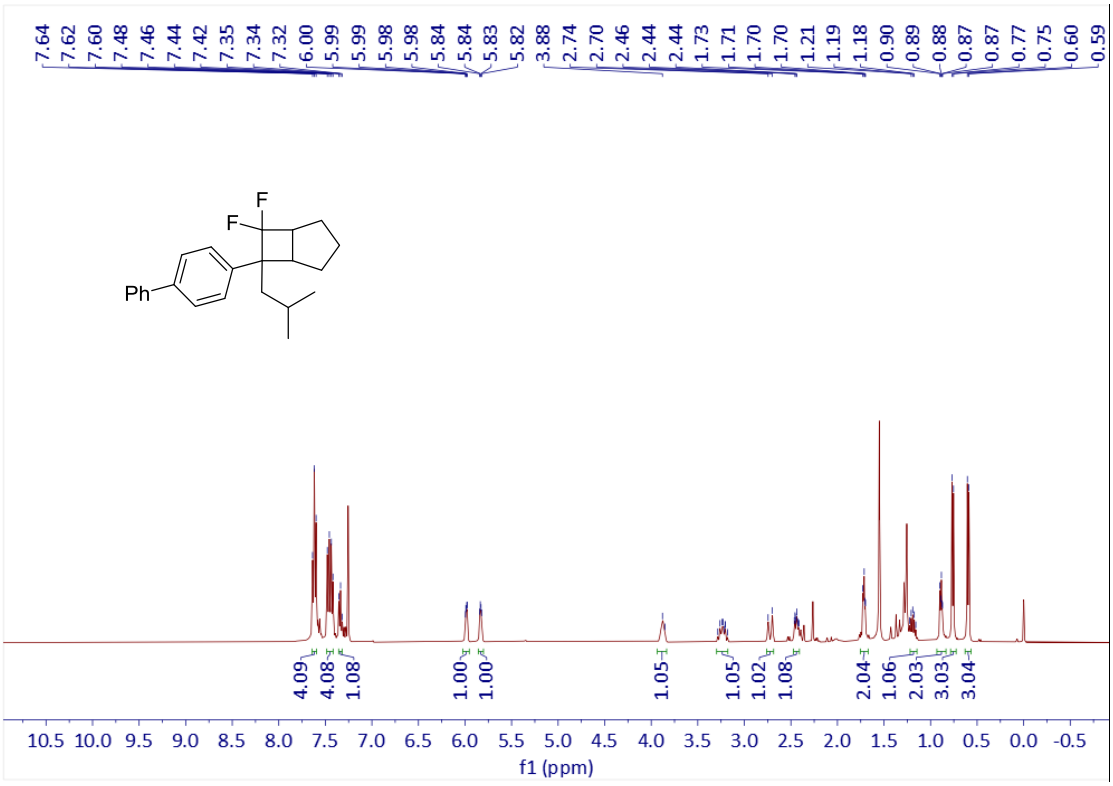
^{1}H NMR of 8 (400 MHz, $CDCl_3$)



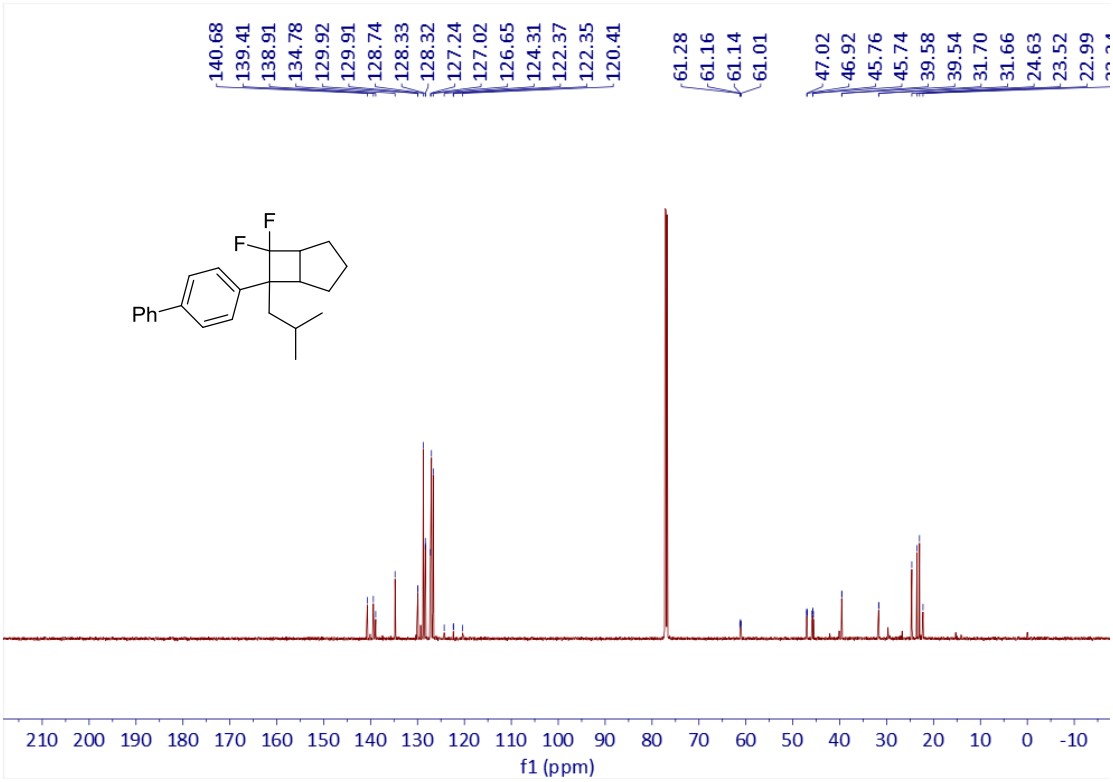
^{13}C NMR of 8 (151 MHz, $CDCl_3$)



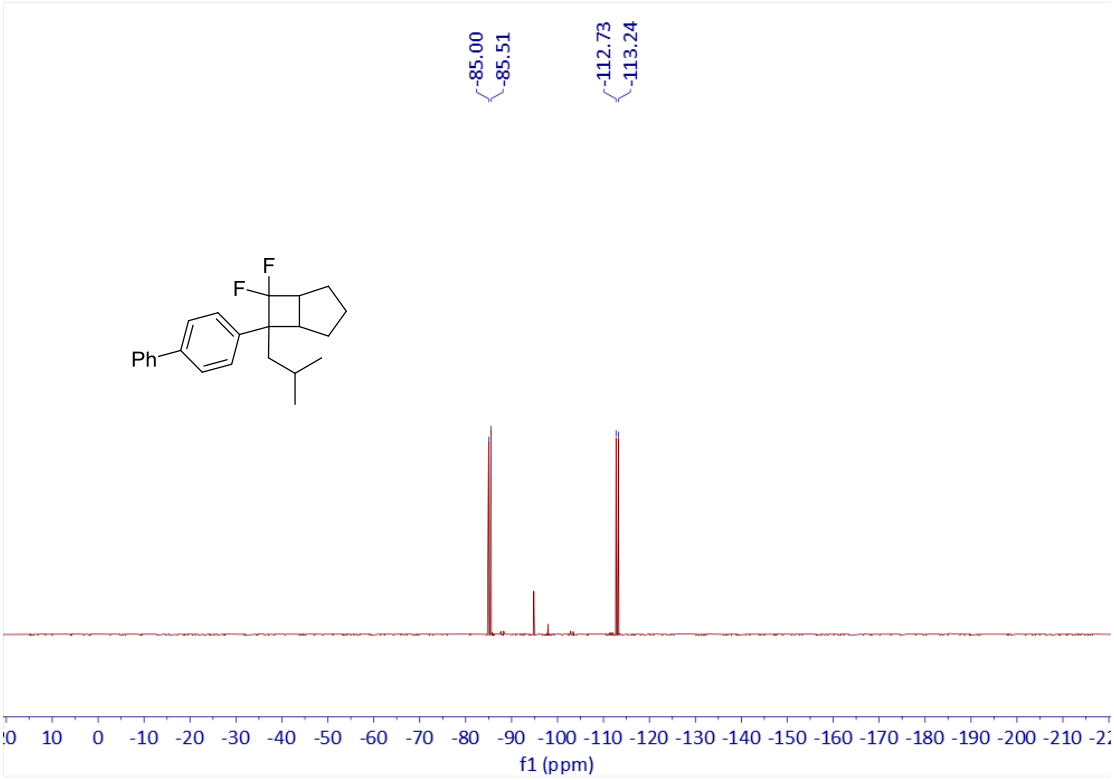
^{19}F NMR of 8 (377 MHz, $CDCl_3$)



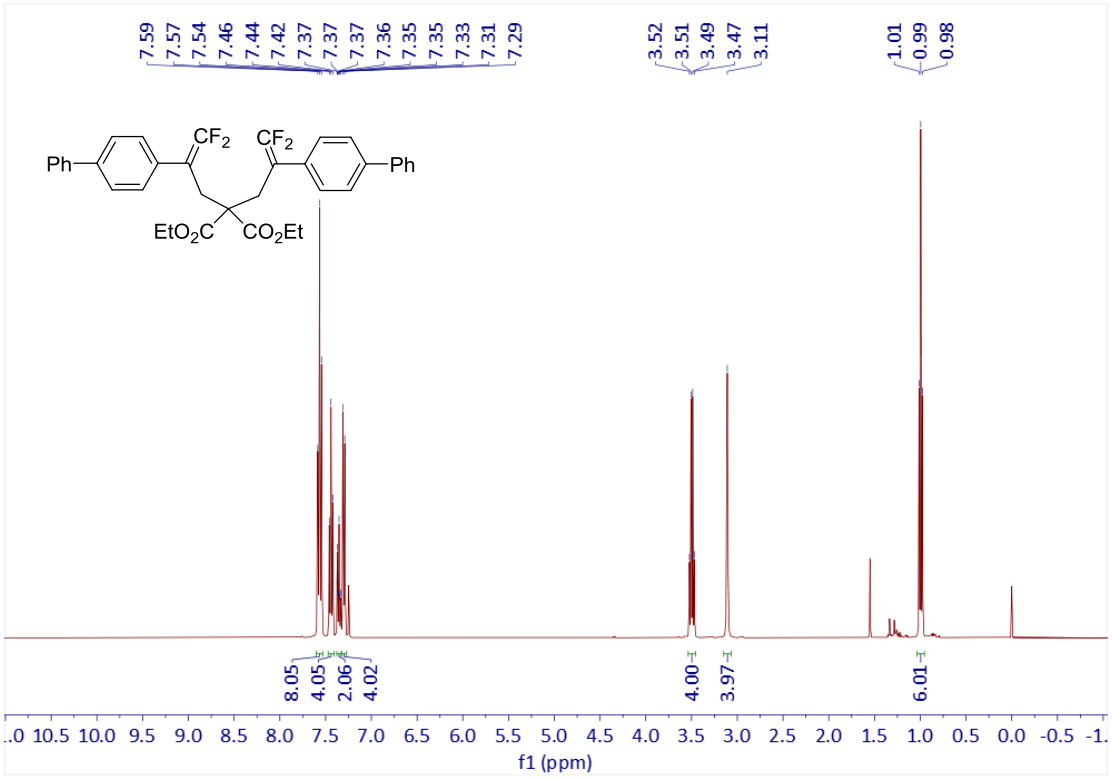
^{1}H NMR of 9 (400 MHz, $CDCl_3$)



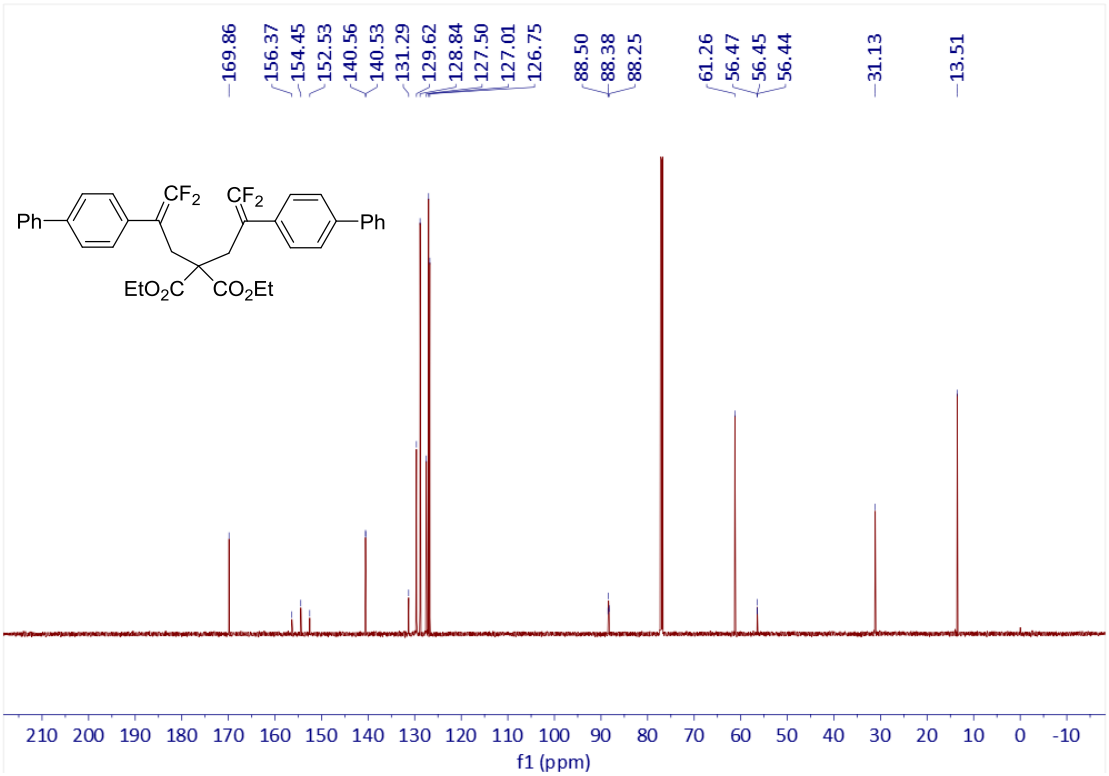
^{13}C NMR of 9 (151 MHz, $CDCl_3$)



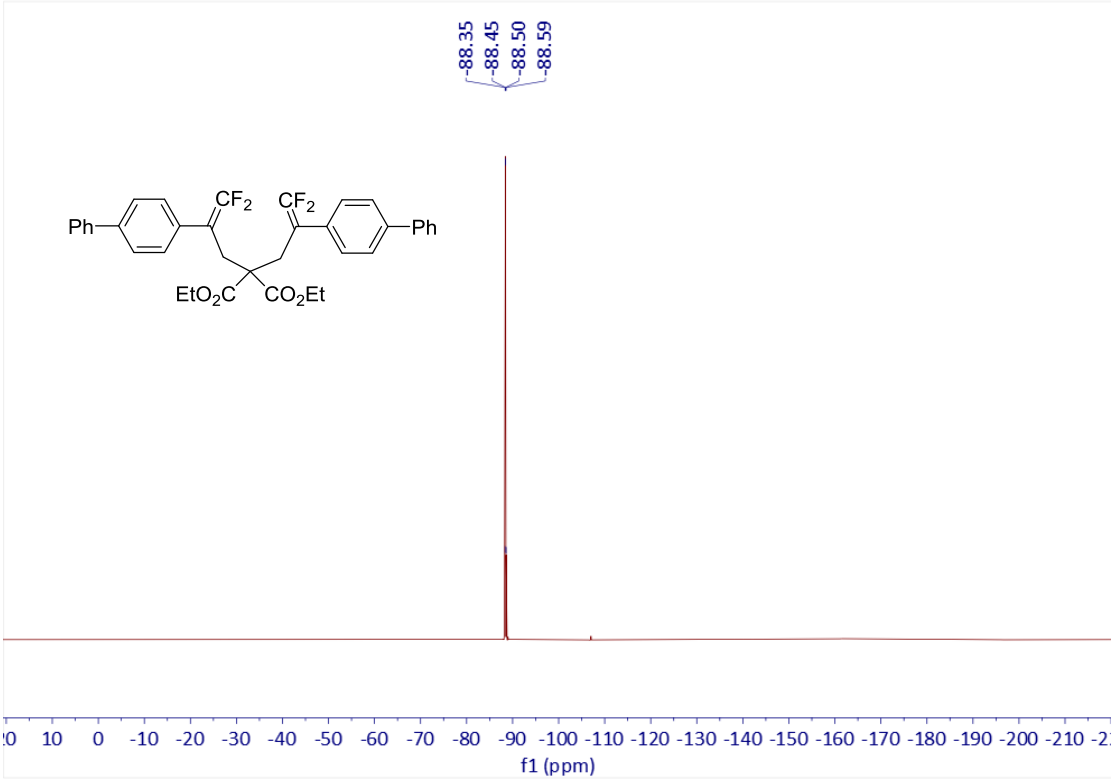
^{19}F NMR of 9 (377 MHz, $CDCl_3$)



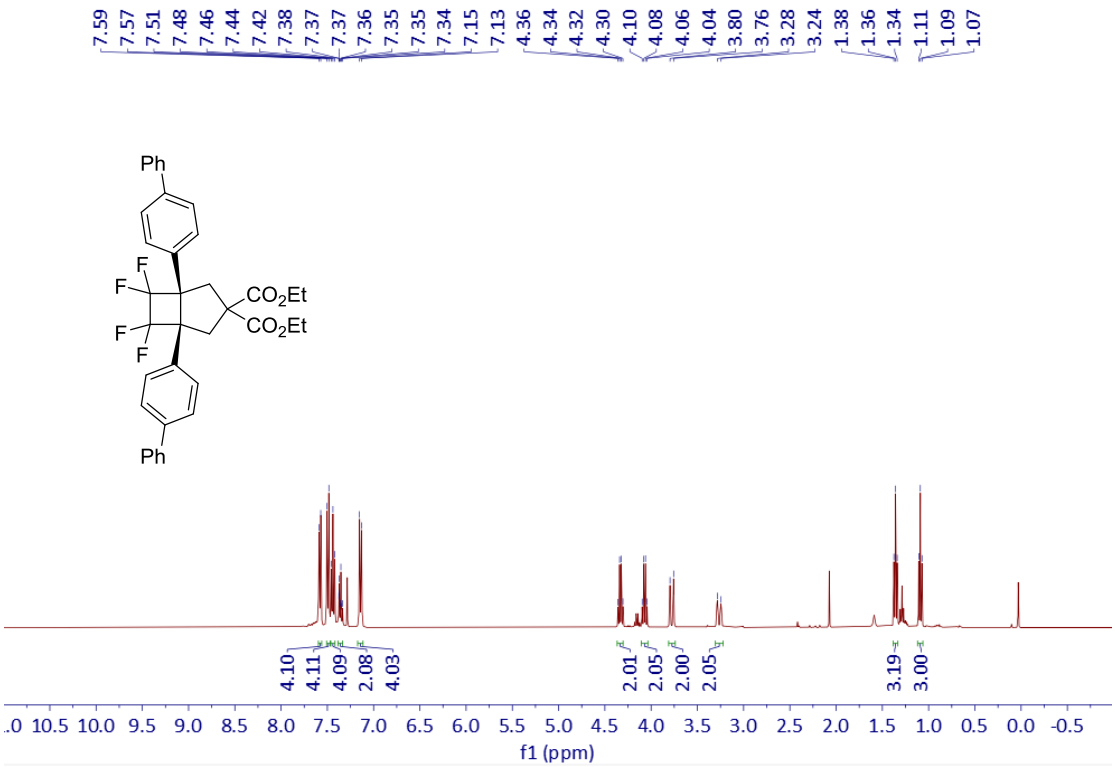
^{1}H NMR of 10 (400 MHz, $CDCl_3$)



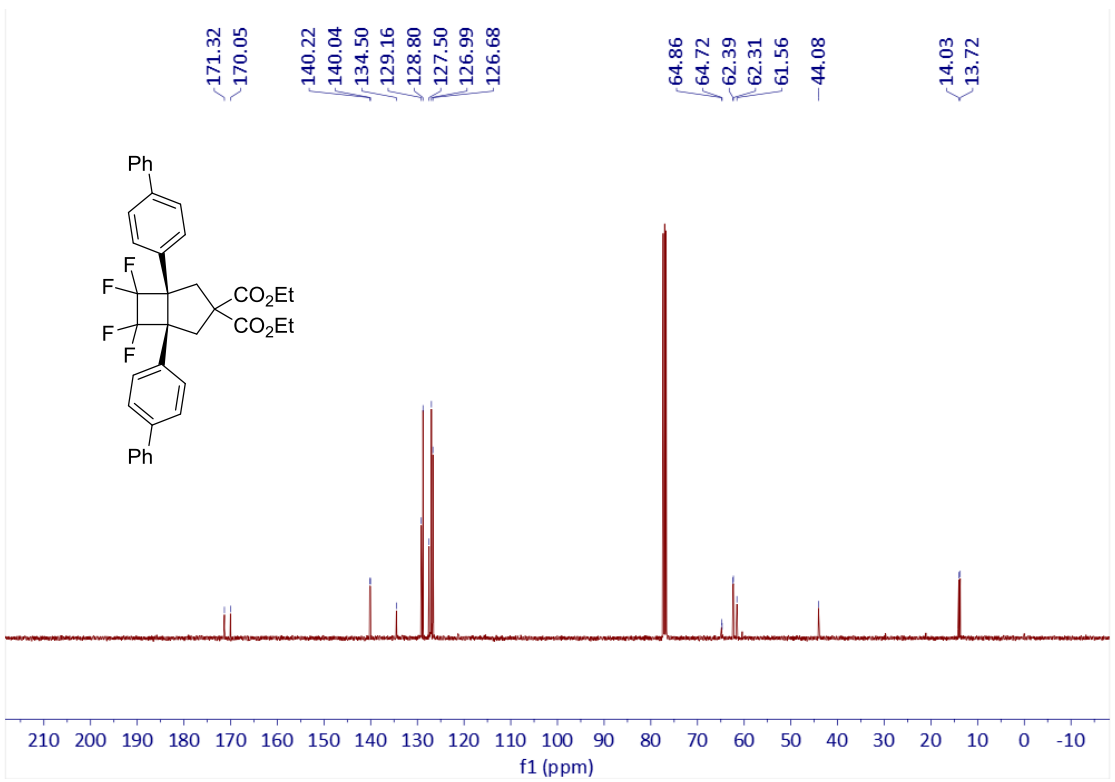
^{13}C NMR of 10 (101 MHz, $CDCl_3$)



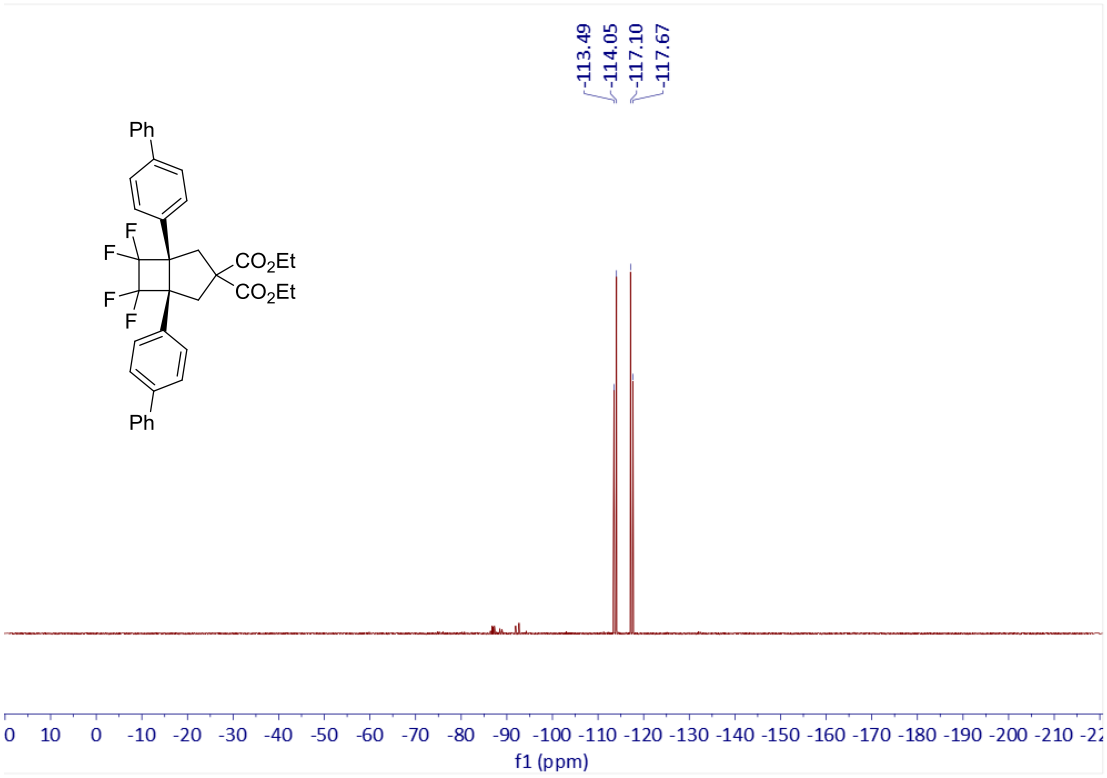
^{19}F NMR of 10 (377 MHz, $CDCl_3$)



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



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



^{19}F NMR of 11 (377 MHz, $CDCl_3$)