Supporting Information

Photoredox Radical/Polar Crossover Enables C-H *gem*-Difunctionalization of 1,3-Benzodioxoles for the Synthesis of Monofluorocyclohexenes

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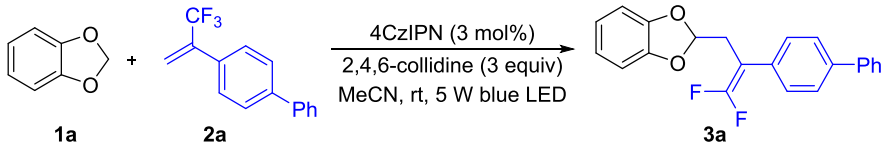
1. General

Unless otherwise noted, all reactions were performed in a 10 mL test tube at room temperature. Photo-irradiation was carried out with a 5 W blue LED. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were measured in $CDCl_3$ and recorded on Brucker ARX 400 MHz or 600 MHz spectrometer. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of $CDCl_3$ (7.26), to the carbon resonance of $CDCl_3$ (77.16). Coupling constants (J) were given in Hertz (Hz). The term m, q, t, d, s referred to multiplet, quartet, triplet, doublet, singlet. High resolution mass spectra (HRMS) were obtained on a Thermo MAT95XP GC-HRMS with an EI source or Thermofisher LTQ Orbitrap LC-HRMS mass spectrometer with an ESI source. α-CF_3 alkenes were prepared via the palladium catalyzed Suzuki coupling of commercially available 2-bromo3,3,3-trifluoropropene with various boric acids or α-(trifluoromethyl)ethenyl boronic acid with a series of aryl halides according to the previous reports.[1] Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. Experimental procedures

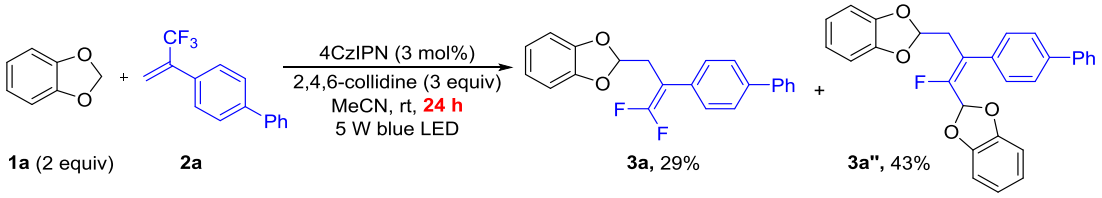
2.1 Typical procedure for the synthesis of *gem*-difluoroalkene 3a



To a dry test tube, α-trifluomethyl (*p*-phenyl)styrene **2a** (0.2 mmol, 49.6 mg), 4CzIPN (3 mol%, 4.7 mg) and 2,4,6-collidine (0.6 mmol, 72.6 mg) were added. The test tube was sealed with a septum and charged with nitrogen. Then 1,3-benzodioxole **1a** (0.4 mmol, 48.4 mg) was dissolved in 1mL of MeCN and added *via* a syringe. The reaction was irradiated with a 5 W blue LED at room temperature for 13 h. After consumption of the starting material, 10 mL of water was added and the mixture was extracted with ethyl acetate (3 × 10 mL), washed with brine and dried with anhydrous Na_2SO_4. The crude product was purified by column chromatography using petroleum ether/ethyl acetate (100: 1) as the eluent to give *gem*-difluoroalkene **3a** as colorless oil (54.6 mg, 78% yield).

Unless other note, *gem*-difluoroalkenes **3b**-**3o** were prepared according to the same procedure as described above. The reaction time for each reaction was indicated in the Scheme 3 in the manuscript. If the reaction time is longer than the given point, mono-fluorinated alkene **3′′** will be formed by the reaction of resultant *gem*-difluoroalkene **3** with 1,3-benzodioxole **1**.

Under standard conditions, prolonging the reaction time of **1a** and **2a** from 13 h to 24 h (Table 1, entry 11) provided desired product **3a** only in 29% yield, while mono-fluorinated alkene **3a′′** was obtained in 43% yield (Scheme S1).



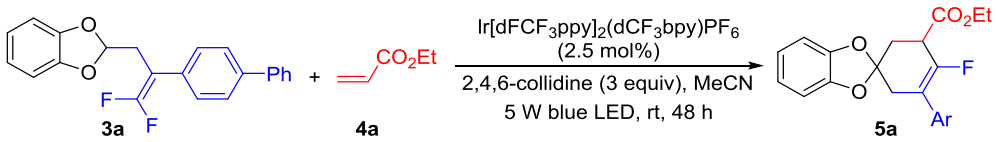
Scheme S1. The photocatalytic reaction of **1a** and **2a** for 24 h

2.2 Synthesis of 3a in gram-scale

To a dry 25 mL Schlenk flask charged with a magnetic stirring bar, **2a** (5 mmol, 1.24 g), 4CzIPN (3 mol%, 117.5 mg) and 2,4,6-collidine (15 mmol, 1.82 g) were added. Then 1,3-benzodioxole **1a** (10 mmol, 1.21 g) was dissolved in 10 mL of MeCN and added *via* a syringe

added under nitrogen atmosphere. The reaction was irradiated with a 5 W blue LED at room temperature for 13 h. After consumption of the starting material, 30 mL of dilute hydrochloric acid was added and the mixture was extracted with ethyl acetate (3 × 30 mL), washed with brine and dried with anhydrous Na_2SO_4. The crude product was purified by column chromatography using petroleum ether/ethyl acetate (100: 1) as the eluent to give *gem*-difluoroalkene **3a** as colorless oil (1.14 g, 65% yield).

2.3 Typical procedure for the synthesis of monofluorinated cyclohexene 5a



3a **4a** **5a**

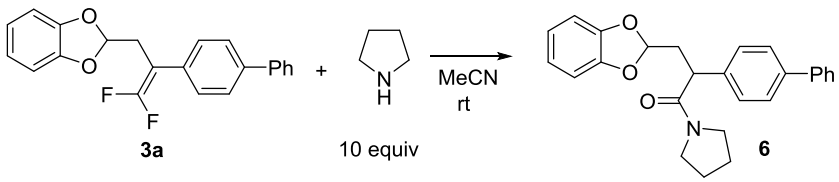
To a dry test tube, **3a** (0.2 mmol, 70.0 mg) $Ir(dFCF_3ppy)_2(dCF_3bbpy)PF_6$ (2.5 mol%, 5.7 mg), and 2,4,6-collidine (0.6 mmol, 72.6 mg) were added. The test tube was sealed with a septum and charged with nitrogen. Then ethyl acrylate **4a** (0.4 mmol, 40.0 mg) and MeCN (1mL) were added *via* a syringe. The resultant solution was irradiated with a 5 W blue LED at room temperature for 48 h. After consumption of **3a**, 10 mL of water was added. The reaction mixture was extracted with ethyl acetate (3 × 10 mL), washed with brine and dried with anhydrous Na_2SO_4. The crude product was purified by column chromatography using petroleum ether/ethyl acetate (20: 1) as the eluent to give **5a** as white solid (74.0 mg, 86% yield).

Unless other note, mono-fluorinated cyclohexenes **3b-3t** were prepared according to the same procedure as described above. All the reactions were irradiated for 48 h.

2.4 Synthesis of 5a in gram-scale

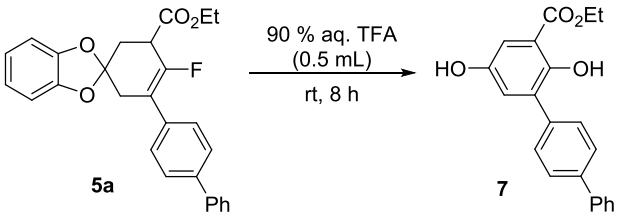
To a dry 25 mL Schlenk flask charged with a magnetic stirring bar, **3a** (3 mmol, 1.05 g) $Ir(dFCF_3ppy)_2(dCF_3bbpy)PF_6$ (2.5 mol%, 86 mg), and 2,4,6-collidine (9 mmol, 1.09 g) were added. Then ethyl methacrylate (6 mmol, 684 mg) and MeCN (10 mL) were added *via* a syringe under nitrogen atmosphere. The resultant solution was irradiated with a 5 W blue LED at room temperature for 48 h. After consumption of **3a**, 30 mL of dilute hydrochloric acid was added. The reaction mixture was extracted with ethyl acetate (3 × 30 mL), washed with brine and dried with anhydrous Na_2SO_4. The crude product was purified by column chromatography using petroleum ether/ethyl acetate (20: 1) as the eluent to give **5a** as white solid (0.88g, 68% yield).

2.5 Conversion of *gem*-difluoroalkene 3a to amide 6[2]



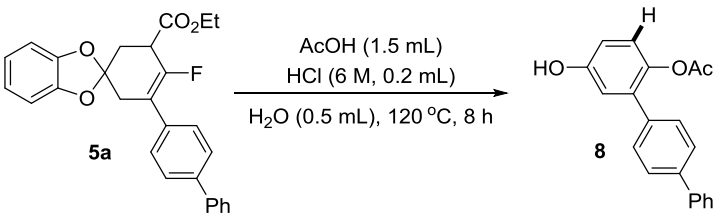
To a solution of **3a** (0.1 mmol, 35 mg) in MeCN (4 mL) was added pyrrolidine (1 mmol, 83 uL). The solution was stirred at room temperature for 8 h. Then 10 mL of water was added and the mixture was extracted with ethyl acetate (3 × 10 mL), washed with brine, dried with anhydrous Na_2SO_4. The crude product was purified by column chromatography using petroleum ether/ethyl acetate (20: 1) as the eluent to give amide **6** as white solid (67.8 mg, 85% yield).

2.6 Deprotection of 5a for the synthesis of 1,4-diphenol 7[3]



To a 10 mL test tube charged with **5a** (0.1 mmol, 43 mg), 90% aqueous trifluoroacetic acid solution (0.5 mL) was slowly added. The resultant mixture was stirred at room temperature for 8 h. Then 10 mL of saturated sodium bicarbonate solution was added. The organic layer was extracted with ethyl acetate (3 × 10 mL), washed with brine and dried with anhydrous Na_2SO_4. The crude product was purified by column chromatography using petroleum ether/ethyl acetate (20: 1) as the eluent to give 1,4-diphenol **7** as white solid (17.3 mg, 51% yield).

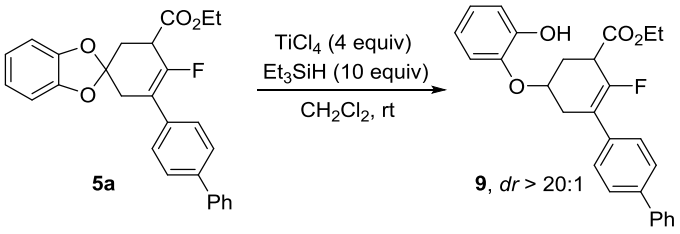
2.7 Synthesis of mono-acetyl substituted 1,4-diphenol 8 with the removal of the ester group[4]



In a round bottom flask equipped with condenser, **5a** (0.1 mmol, 43 mg) was dissolved in AcOH (1.5 mL), H_2O (0.5 mL) and 6 M HCl (0.2 mL). The reaction mixture was heated at 120 ^oC for 8 h. After consumption of **5a**, 10 mL of saturated sodium bicarbonate solution was added. The

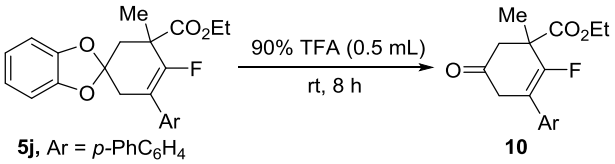
organic layer was extracted with ethyl acetate (3 × 10 mL), washed with brine and dried with anhydrous Na_2SO_4. The crude product was purified by column chromatography using petroleum ether/ethyl acetate (20: 1) as the eluent to give **8** as white solid (17.0 mg, 57% yield).

2.8 Reduction of 5a using triethylsilane[5]



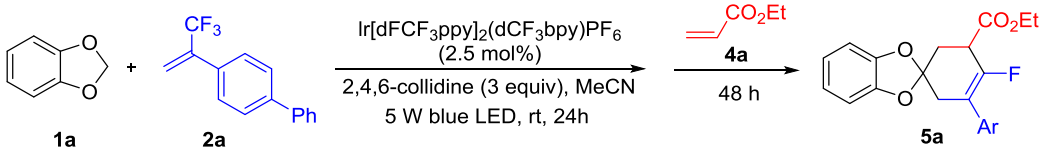
Titanium tetrachloride (0.4 mmol, 43.8 μL) was added dropwise to a stirred solution of **5a** (43.0 mg, 0.1 mmol) and triethylsilane (1 mmol, 159.3 μL) in dry CH_2Cl_2 (2 mL) at 0 ℃. After stirring at room temperature for 24 h, the reaction mixture was quenched with saturated aqueous Na_2CO_3 (3 mL) followed by extraction with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried over Na_2SO_4, The crude product was purified by column chromatography using petroleum ether/ethyl acetate (20: 1) as the eluent to **9** as white solid with >20:1 *dr* (69.9 mg, 81% yield).

2.9 Deprotection of 5j[3]



To a 10 mL test tube charged with **5j** (0.1 mmol, 44.4 mg), 90% aqueous trifluoroacetic acid solution (0.5 mL) was slowly added. The resultant solution was stirred at room temperature for 8 h. Then 10 mL of saturated sodium bicarbonate solution was added. The organic layer was extracted with ethyl acetate (3 × 10 mL), washed with brine and dried with anhydrous Na_2SO_4. The crude product was purified by column chromatography using petroleum ether/ethyl acetate (20: 1) as the eluent to give mono-fluorinated 3-cyclohex-1-one **10** as white solid (14.4 mg, 41% yield).

2.10 Synthesis of 5a by two steps in one-pot

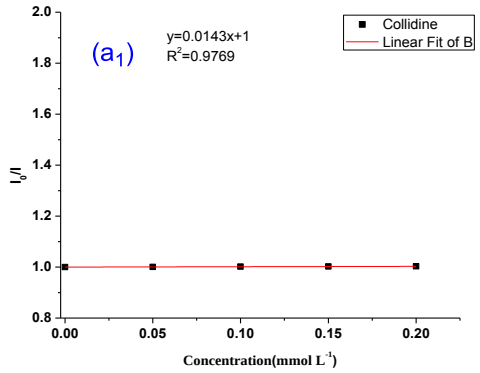


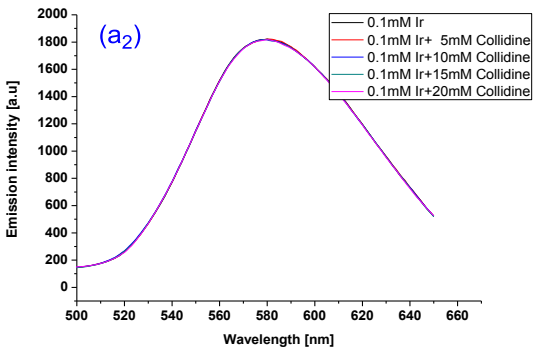
To a dry test tube, α-trifluomethyl (*p*-phenyl)styrene **2a** (0.2 mmol, 49.6 mg), 2,4,6-collidine (0.6

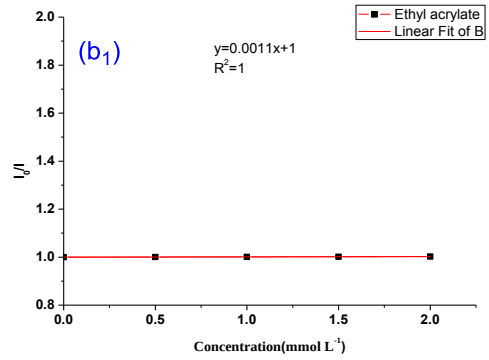
mmol, 72.6 mg) and $Ir(dFCF_3ppy)_2(dCF_3bbpy)PF_6$ (2.5 mol%, 5.7 mg) were added. The test tube was sealed with a septum and charged with nitrogen. Then 1,3-benzodioxole **1a** (0.2 mmol, 24.2 mg) was dissolved in 1mL of MeCN and added *via* a syringe. After the irradiation of a 5w blue LED at room temperature for 24 h, ethyl acrylate **4a** (0.4mmol, 40.0 mg) was added via a syringe. The reaction mixture continues to be irradiated for 48 h. Then, 10 mL of water was added. The organic layer was extracted with ethyl acetate (3 × 10 mL), washed with brine and dried with anhydrous Na_2SO_4. The crude product was purified by column chromatography using petroleum ether/ethyl acetate (20: 1) as the eluent to give **5a** as white solid (37.8 mg, 44 % yield).

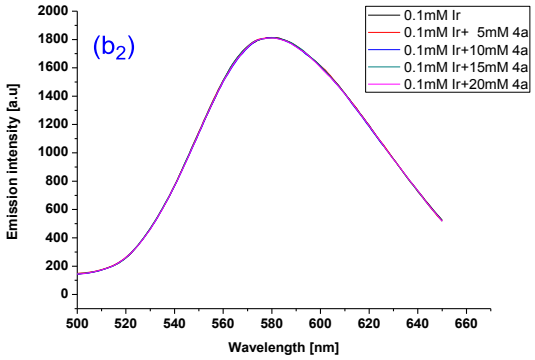
3. Emission Quenching Experiments (Stern-Volmer Studies)

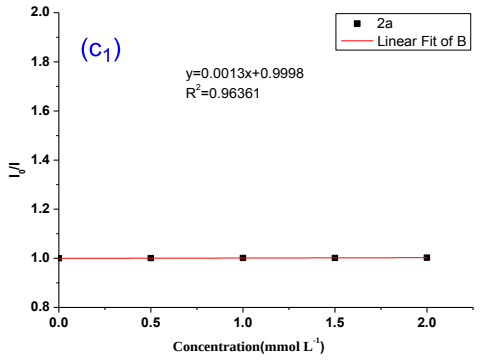
Fluorescence quenching experiments were recorded on a Fluorescence Spectrophotometer F4500. In each experiment, a solution of 0.01mM $Ir[dFCF_3ppy]_2(dCF_3bpy)PF_6$ (**Ir-1**) in MeCN was mixed with a MeCN solution of a quencher of various concentration in a screw-top 1.0 cm quartz cuvette. After degassing by sparging with argon for ten minutes, the resulting solution was irradiated at 465 nm, and fluorescence was measured at 580 nm. I^0 and I represent the intensities of the emission in the absence and presence of the quencher at 465 nm.

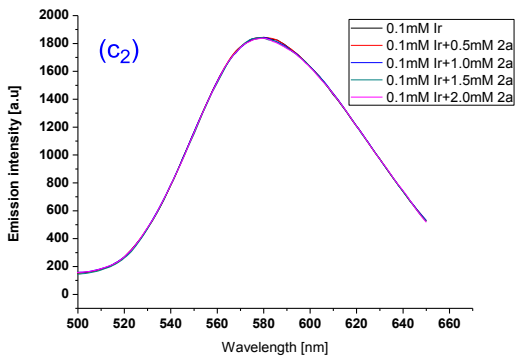












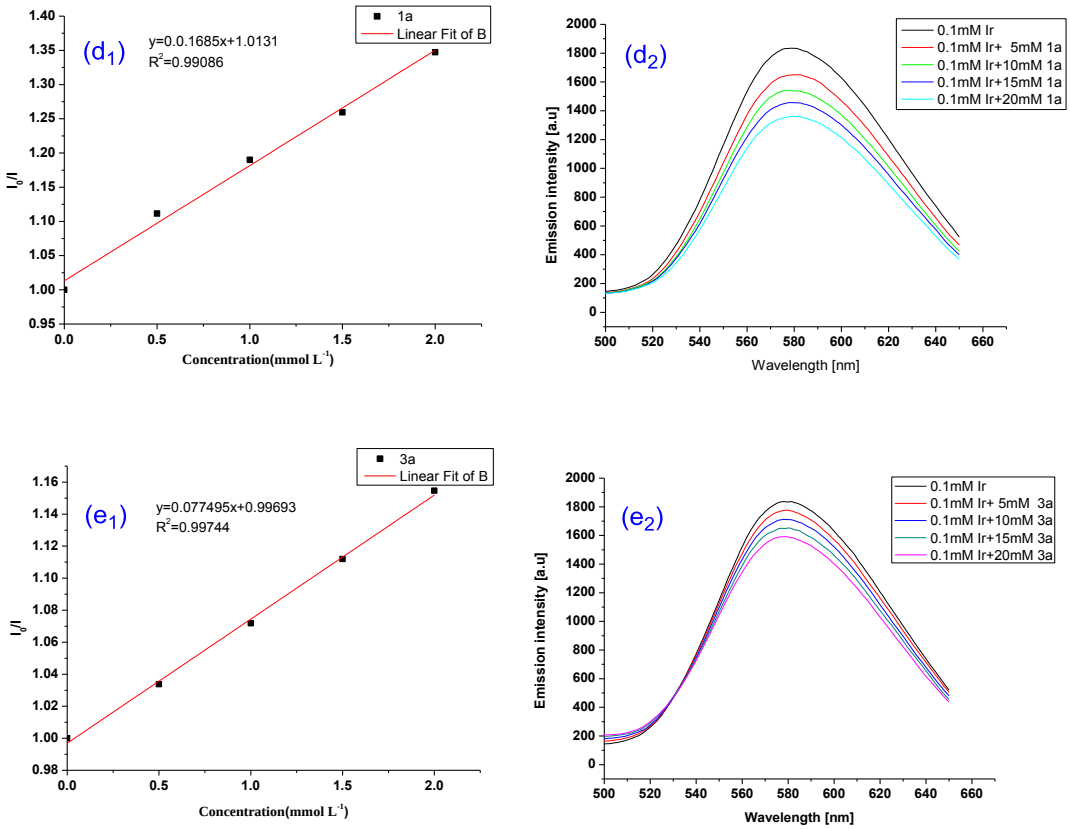


Figure S1. Emission quenching of excited photocatalyst [**Ir-1**]* by: (a) 2,4,6-collidine; (b) ethyl acrylate; (c) α-CF_3 (*p*-phenyl)styrene **2a**; (d) 1,3-benzodioxole **1a**; (e) *gem*-difluoroalkene **3a**.

It was found that the excited photocatalyst Ir* could be quenched by 1,3-benzodioxole (**1a**), mono-*gem*-difluoroallylated 1,3-benzodioxole (**3a**) respectively, while **2a**, ethyl acrylate and 2,4,6-collidine were ineffective for the quenching. According to the rate of slope (Figure S2), the reductive quenching of Ir* by **1a** was the most efficient.

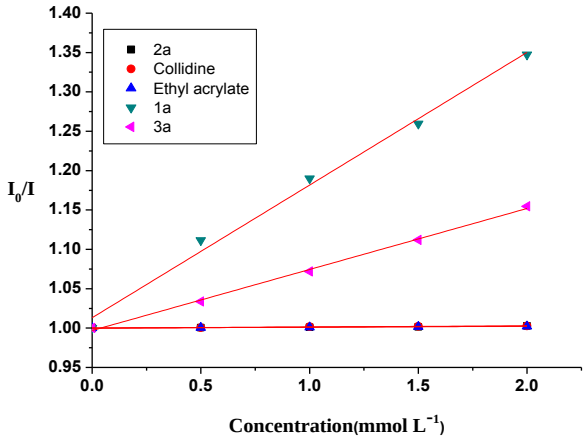


Figure S2. Combined Stern-Volmer plots

4. Cyclic voltammograms

Cyclic voltammetry data were recorded on a CHI750E Electrochemical Analyzer using a three-electrode cell at room temperature. A glassy carbon electrode was used as the working electrode and a platinum wire as the auxiliary electrode. The reference electrode was a saturated AgCl/Ag. t-Bu_4NPF_6 (0.1 M in MeCN) was used as the supporting electrolyte. Voltammograms were taken in N_2-sparged MeCN and the sweep rate was 100 mV/s. The concentration of measured compound was 1 mM. Considering the possible effects of base, one equivalent of 2,4,6-collidine was added.

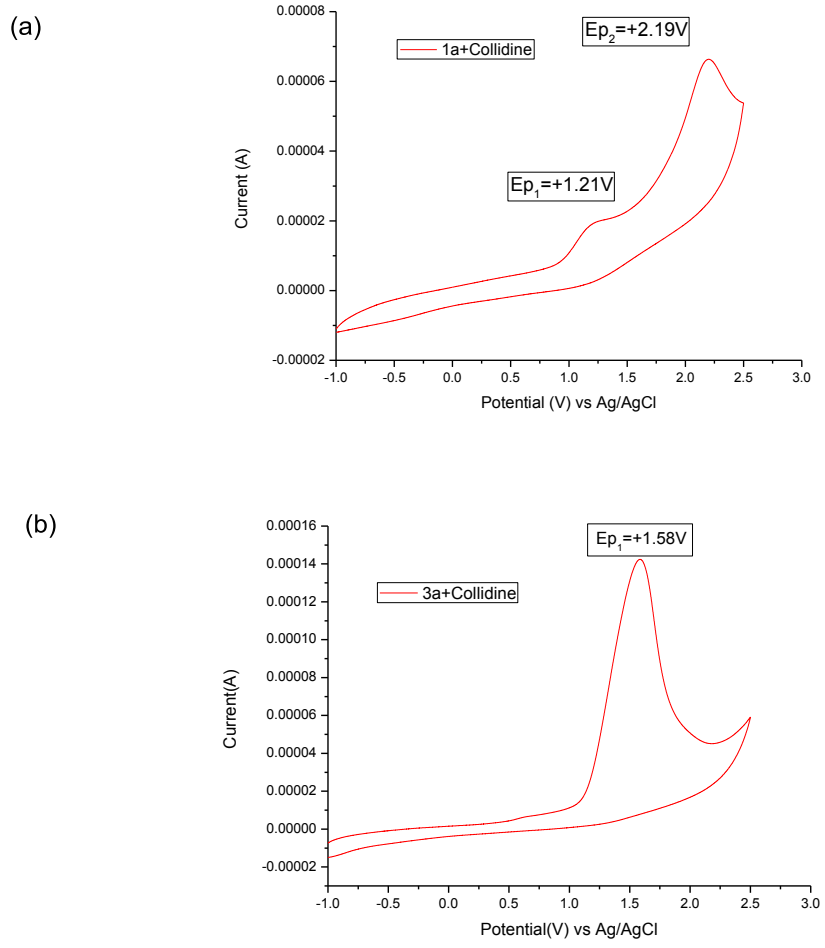
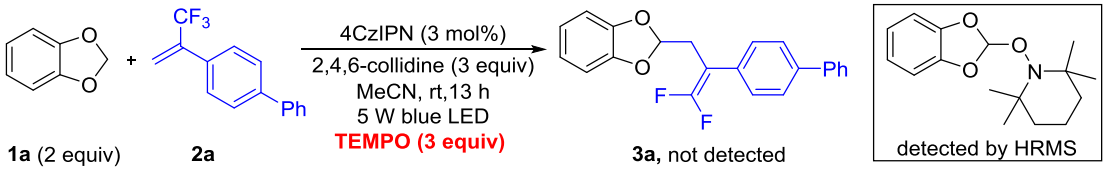


Figure S3 Cyclic voltammogram of (a) 1,3-benzodioxole **1a** ; (b) *gem*-difluoalkene **3a**

The peak potential for the irreversible oxidation of **1a** was measured as +1.21 V and the irreversible reduction of **3a** was measured as +1.58 V, which were referenced to saturated salomel slectrode (vs SCE) by reducing 0.042 V to the measured potential.

5. Radical trapping experiments



To a dry test tube, **2a** (0.2 mmol, 49.6 mg), 4CzIPN (3 mol%, 4.7mg), TEMPO (0.6 mmol, 93.7 mg) and 2,4,6-collidine (0.6 mmol, 72.6 mg) were added. The test tube was sealed with a septum and charged with nitrogen. Then 1,3-denzodioxole **1a** (0.4 mmol, 48.4 mg) and 1mL of MeCN were added. The reaction was irradiated with a 5 W blue LED at room temperature for 2 h and quenched by 10 mL of water. The mixture was extracted with ethyl acetate (3 × 10 mL), washed with brine and dried with anhydrous Na_2SO_4. The crude product was measured by ^{19}F-NMR and found that the formation of **3a** was completely suppressed. However, a **1a**-TEMPO adduct was found as detected by HRMS, whose spectra were shown below.

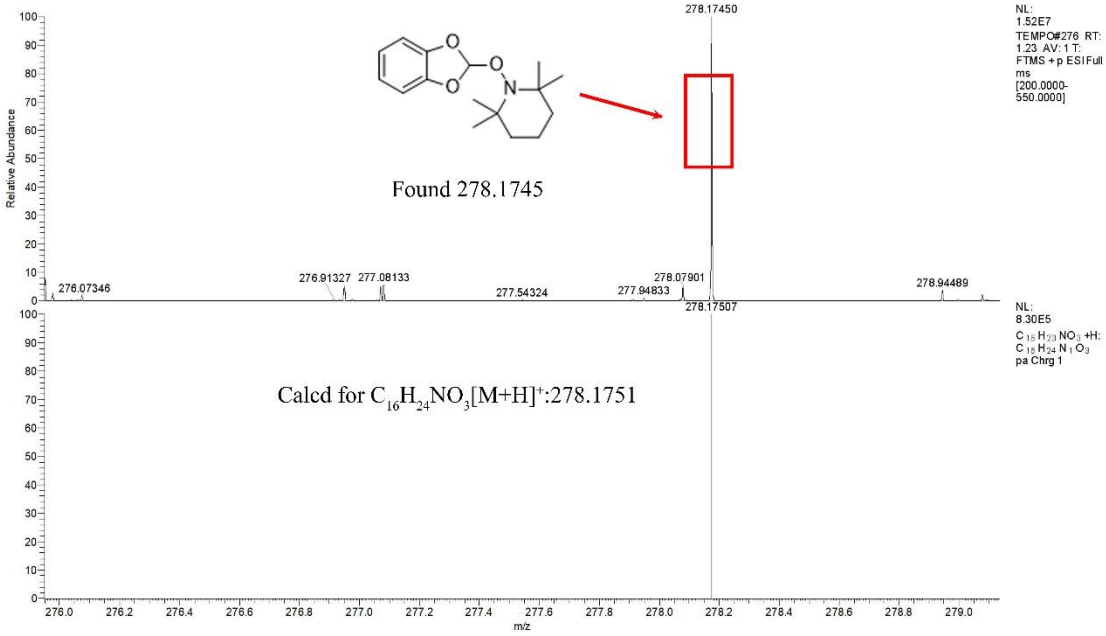


Figure S5. The HRMS of **1a**-TEMPO adduct

6. Light source and apparatus

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 λmax is 453.6 nm. The strength of irradiation @5 W is about 246 mW/cm^2. The emission spectrum of the light source is shown in the Figure S6.

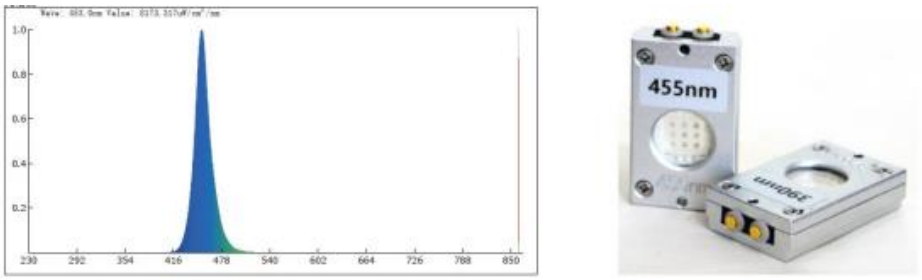


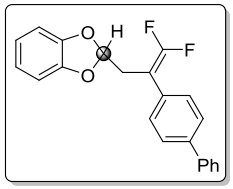
Figure S6 The emission spectrum and the picture of the light source

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. Figure S7 is the picture of the apparatus.

Figure S7. The picture of apparatus.

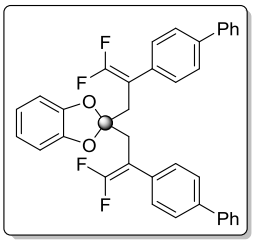
7. Characterization data

2-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)benzo[d][1,3]dioxole (3a)



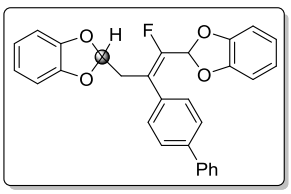
Colorless oil (54.6 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 4H), 7.49 – 7.40 (m, 5H), 6.86 – 6.77 (m, 4H), 6.21 (t, *J* = 4.9 Hz, 1H), 3.08 – 3.07 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.58 (d, *J* = 34.4 Hz), -87.72 (d, *J* = 34.4 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.0 (t, *J* = 289.5 Hz), 147.2, 140.5 (d, *J* = 4.9 Hz), 131.8, 128.9, 128.7 (t, *J* = 3.3 Hz), 127.5, 127.3, 127.1, 109.2 (t, *J* = 3.6 Hz), 108.6, 86.5 (dd, *J* = 21.2, 17.2 Hz), 33.7. HRMS (EI) calcd for $C_{22}H_{16}F_2O_2$ $[M]^+$: 350.1112; found: 350.1113.

2,2-bis(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)benzo[d][1,3]dioxole (3a′)



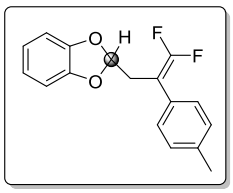
White solid (104.1 mg, 90% yield). M.p. 123.8-124.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.49 (m, 4H), 7.41 – 7.33 (m, 8H), 7.28 – 7.24 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 4H), 6.61 – 6.58 (m, 2H), 6.35 – 6.32 (m, 2H), 2.93 (s, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.17 (d, *J* = 32.2 Hz), -88.25 (d, *J* = 32.4 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.2 (t, *J* = 291.3 Hz), 147.5, 140.8, 140.2, 132.9 (t, *J* = 3.6 Hz), 129.0, 128.9, 127.6, 127.2, 127.0, 121.3, 117.9 (d, *J* = 3.5 Hz), 108.2, 87.0 (dd, *J* = 20.7, 17.5 Hz), 37.4. HRMS (ESI) calcd for $C_{37}H_{26}F_4O_2Na$ $[M+Na]^+$: 601.1761; found: 601.1749.

2,2'-(2-([1,1'-biphenyl]-4-yl)-1-fluoroprop-1-ene-1,3-diyl)bis(benzo[d][1,3]dioxole) (3a″)



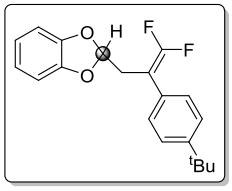
Colorless oil (38.9 mg, 43% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 4H), 7.45 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.40 – 7.34 (m, 3H), 6.81 (s, 4H), 6.79 – 6.72 (m, 4H), 6.51 (d, *J* = 21.0 Hz, 1H), 6.22 – 6.20 (m, 1H), 3.20 (dd, *J* = 5.2, 2.9 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.04. ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.1 (d, *J* = 264.6 Hz), 147.4 (d, *J* = 26.1 Hz), 141.7, 140.4, 133.6 (d, *J* = 6.5 Hz), 129.7 (d, *J* = 2.8 Hz), 129.0, 127.9, 127.6, 127.2, 121.8 (d, *J* = 25.1 Hz), 121.2 (d, *J* = 14.2 Hz), 109.0 (d, *J* = 3.2 Hz), 108.6 (d, *J* = 39.9 Hz), 103.5 (d, *J* = 26.1 Hz), 36.5 (d, *J* = 2.8 Hz). HRMS (ESI) calcd for $C_{29}H_{21}FO_4Na$ $[M+Na]^+$: 475.1316; found: 475.1311.

2-(3,3-difluoro-2-(p-tolyl)allyl)benzo[d][1,3]dioxole (3b)



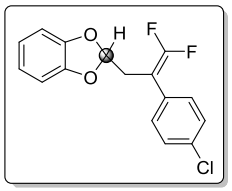
Colorless oil (36.9 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 4H), 6.81 – 6.74 (m, 4H), 6.12 – 6.10 (m, 1H), 2.98 (dt, *J* = 4.8, 2.3 Hz, 2H), 2.35 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.61 (d, *J* = 36.7 Hz), -88.74 (d, *J* = 36.4 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.8 (t, *J* = 288.0 Hz), 147.2, 137.5, 129.8, 129.3, 128.1 (t, *J* = 3.1 Hz), 121.5, 109.2 (t, *J* = 3.7 Hz), 108.6, 86.5 (dd, *J* = 20.9, 17.8 Hz), 33.8 (d, *J* = 2.1 Hz), 21.1. HRMS (EI) calcd for $C_{17}H_{14}F_2O_2$ [M]$^+$: 288.0960; found: 288.0956.

2-(2-(4-(tert-butyl)phenyl)-3,3-difluoroallyl)benzo[d][1,3]dioxole (3c)



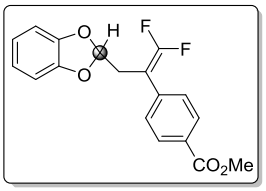
Colorless oil (42.9 mg, 65% yield). δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.86 – 6.73 (m, 4H), 6.15 (t, *J* = 5.0 Hz, 1H), 3.02 (dt, *J* = 4.8, 2.3 Hz, 2H), 1.35 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.43 (d, *J* = 37.6 Hz), -87.53 (d, *J* = 37.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0 (t, *J* = 290.4 Hz), 150.7, 129.8, 128.0 (t, *J* = 3.2 Hz), 125.6, 121.6, 109.3 (t, *J* = 3.6 Hz), 108.7, 86.6 (dd, *J* = 20.0, 19.1 Hz), 34.7, 33.8, 31.4. HRMS (EI) calcd for $C_{20}H_{20}F_2O_2$ [M]$^+$: 330.1426; found: 330.1426.

2-(2-(4-chlorophenyl)-3,3-difluoroallyl)benzo[d][1,3]dioxole (3d)



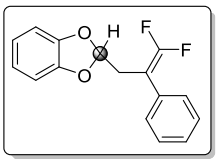
Colorless oil (36.3 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.81 – 6.79 (m, 2H), 6.73 (dd, *J* = 5.7, 3.3 Hz, 2H), 6.14 (t, *J* = 4.7 Hz, 1H), 2.99 – 2.97 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.24 (d, *J* = 33.4 Hz), -87.48 (d, *J* = 33.7 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.9 (t, *J* = 289.5 Hz), 147.1, 133.5, 131.5 (t, *J* = 3.8 Hz), 129.6 (t, *J* = 3.5 Hz), 128.7, 121.6, 109.0 (t, *J* = 3.6 Hz), 108.6, 86.0 (dd, *J* = 21.8, 17.4 Hz), 33.7. HRMS (EI) calcd for $C_{16}H_{11}ClF_2O_2$ [M]$^+$: 308.0411; found: 308.0410.

methyl4-(3-(benzo[d][1,3]dioxol-2-yl)-1,1-difluoroprop-1-en-2-yl)benzoate (3e)



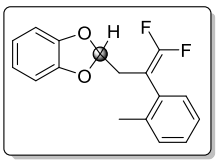
Colorless oil (30.0 mg, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 8.00 (m, 2H), 7.40 – 7.38 (m, 2H), 6.80 – 6.77 (m, 2H), 6.72 – 6.70 (m, 2H), 6.16 (t, *J* = 4.7 Hz, 1H), 3.93 (s, 3H), 3.04 (dt, *J* = 4.7, 2.3 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.72 (d, *J* = 30.3 Hz), -86.12 (d, *J* = 30.2 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.7, 155.1 (t, *J* = 289.5 Hz), 147.1, 137.9, 129.7, 129.2, 128.2 (t, *J* = 3.4 Hz), 121.6, 108.9 (t, *J* = 3.5 Hz), 108.6, 86.4 (dd, *J* = 21.0, 16.5 Hz), 52.2, 33.5. HRMS (EI) calcd for $C_{18}H_{14}F_2O_4$ $[M]^+$: 332.0854; found: 332.0855.

2-(3,3-difluoro-2-phenylallyl)benzo[d][1,3]dioxole (3f)



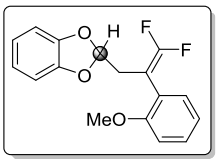
Colorless oil (34.0 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$ δ 7.39 – 7.27 (m, 5H), 6.81 – 6.73 (m, 4H), 6.12 (t, *J* = 5.0 Hz, 1H), 3.01 (dt, *J* = 4.8, 2.3 Hz, 2H).^{19}F NMR (376 MHz, $CDCl_3$) δ -88.21 (d, *J* = 37.6Hz), -88.31 (d, *J* = 33.8 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.0 (t, *J* = 290.9 Hz), 147.3, 133.0, 128.7, 128.5 – 128.3 (m), 127.8, 121.7, 109.2 (d, *J* = 3.9 Hz), 108.7 (d, *J* = 7.4 Hz), 86.9 (dd, *J* = 38.6 Hz), 34.0. HRMS (EI) calcd for $C_{16}H_{12}F_2O_2$ $[M]^+$: 274.0801; found: 274.0800.

2-(3,3-difluoro-2-(m-tolyl)allyl)benzo[d][1,3]dioxole (3g)



Colorless oil (42.0 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.14 – 7.09 (m, 3H), 6.81 – 6.73 (m, 4H), 6.13 – 6.10 (m, 1H), 2.98 (dt, *J* = 4.7, 2.3 Hz, 2H), 2.35 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.33 (d, *J* = 36.0 Hz), -88.58 (d, *J* = 35.9 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.8 (t, *J* = 289.5 Hz), 147.2, 138.2, 132.8 (t, *J* = 3.6 Hz), 129.0 (t, *J* = 3.0 Hz), 128.4, 125.4 (t, *J* = 3.0 Hz), 121.5, 109.1 (t, *J* = 3.7 Hz), 108.6, 86.7 (dd, *J* = 20.9, 17.8 Hz), 33.9 (d, *J* = 2.2 Hz), 21.4. HRMS (EI) calcd for $C_{17}H_{14}F_2O_2$ $[M]^+$: 288.0959; found: 288.0956.

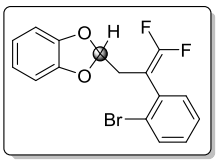
2-(3,3-difluoro-2-(3-methoxyphenyl)allyl)benzo[d][1,3]dioxole (3h)



Colorless oil (38.3 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.92 – 6.89 (m, 2H), 6.85 – 6.83 (m, 2H), 6.80 – 6.78 (m, 2H), 6.17 (t, *J* = 4.9 Hz, 1H), 3.83 (s, 3H), 3.04 – 3.02

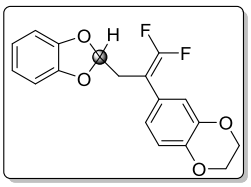
(m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.60 (d, *J* = 34.9 Hz), -88.08 (d, *J* = 35.0 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.6, 154.9 (dd, *J* = 292.0, 289.8 Hz), 147.2, 134.3 (t, *J* = 3.7 Hz), 129.6, 121.6, 120.7 (t, *J* = 3.2 Hz), 114.2 (t, *J* = 3.3 Hz), 113.2, 109.1 (t, *J* = 3.6 Hz), 108.6, 86.7 (dd, *J* = 21.4, 17.2 Hz), 55.2, 33.9 (d, *J* = 2.1 Hz). HRMS (EI) calcd for $C_{17}H_{14}F_2O_3$ $[M]^+$: 304.0905; found: 304.0906.

2-(2-(3-bromophenyl)-3,3-difluoroallyl)benzo[d][1,3]dioxole (3i)



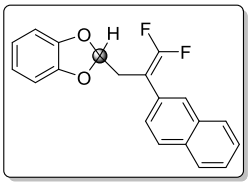
Colorless oil (42.8 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 2H), 7.25 (d, *J* = 6.9 Hz, 2H), 6.84 – 6.82 (m, 2H), 6.77 – 6.75 (m, 2H), 6.17 (t, *J* = 4.7 Hz, 1H), 3.00 (dt, *J* = 4.6, 2.3 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.75 (d, *J* = 30.1Hz), -86.85 (d, *J* = 33.8Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.0 (t, *J* = 291.9 Hz), 147.1, 135.2, 131.4, 130.7, 130.0, 127.0, 122.5, 121.7, 108.9 (d, *J* = 3.8 Hz), 108.6, 85.9 (dd, *J* = 21.0, 19.5 Hz), 33.7. HRMS (EI) calcd for $C_{16}H_{11}BrF_2O_2$ $[M]^+$: 351.9906; found: 351.9905.

6-(3-(benzo[d][1,3]dioxol-2-yl)-1,1-difluoroprop-1-en-2-yl)-2,3-dihydrobenzo[b][1,4]dioxine (3j)



Colorless oil (43.2 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 – 6.84 (m, 2H), 6.82 (dd, *J* = 2.0, 1.0 Hz, 1H), 6.80 – 6.78 (m, 2H), 6.78 – 6.75 (m, 2H), 6.12 – 6.10 (m, 1H), 4.26 (s, 4H), 2.93 (dt, *J* = 4.8, 2.2 Hz, 2H).^{19}F NMR (376 MHz, $CDCl_3$) δ -88.50 (d, *J* = 36.8 Hz), -88.90 (d, *J* = 36.8 Hz). ^{13}C NMR (150MHz, $CDCl_3$) δ 154.9 (t, *J* = 288.0 Hz), 147.3, 143.6, 143.2, 126.0 (d, *J* = 3.7 Hz), 121.6 (d, *J* = 8.9 Hz), 117.9 – 116.2 (m), 109.2 (t, *J* = 3.6 Hz), 108.7, 86.3 (dd, *J* = 21.6, 17.4 Hz), 64.5 (d, *J* = 12.5 Hz), 34.0. HRMS (EI) calcd for $C_{18}H_{14}F_2O_4$ $[M]^+$: 332.0854; found: 332.0855.

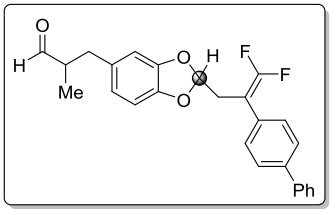
2-(3,3-difluoro-2-(naphthalen-2-yl)allyl)benzo[d][1,3]dioxole (3k)



Colorless oil (45.4 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 4H), 7.50 – 7.44 (m, 3H), 6.81 – 6.75 (m, 4H), 6.17 (t, *J* = 4.9 Hz, 1H), 3.10 (dt, *J* = 4.8, 2.3 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ

-87.64 (d, *J* = 34.7 Hz), -87.92 (d, *J* = 34.6 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.2 (t, *J* = 297.0 Hz), 147.2, 133.2, 132.6, 130.3 (d, *J* = 3.7 Hz), 128.2, 128.0, 127.8 – 127.5 (m), 126.4 (d, *J* = 7.3 Hz), 126.0 (t, *J* = 3.3 Hz), 121.6, 108.6, 86.9 (dd, *J* = 21.0, 17.0 Hz), 34.0 (d, *J* = 2.1 Hz). HRMS (EI) calcd for $C_{20}H_{14}F_2O_2$ $[M]^+$: 324.0957; found: 324.0956.

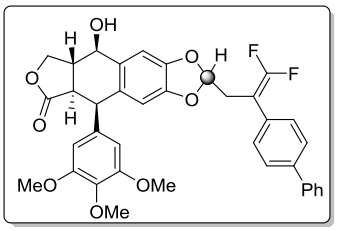
3-(2-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)benzo[d][1,3]dioxol-5-yl)-2-methylpropanal (3l)



Colorless oil (52.1 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 – 9.71 (m, 1H), 7.64 – 7.6 (m, 4H), 7.50 – 7.46 (m, 2H), 7.44 – 7.42 (m, 2H), 7.40 – 7.39 (m, 1H), 6.69 – 6.67 (m, 1H), 6.62 – 6.59 (m, 2H), 6.20 – 6.18 (m, 1H), 3.07 (dt, *J* = 4.8, 2.3 Hz, 2H), 3.00 (dd, *J* = 13.5, 5.8 Hz, 1H), 2.65 – 2.59 (m, 1H), 2.56 – 2.51 (m, 1H), 1.10 (dd, *J* = 6.9, 1.0 Hz, 3H).^{19}F NMR (376 MHz, $CDCl_3$) δ -87.66 (dd, *J* = 18.6, 3.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.64 (d, *J* = 3.5 Hz), -87.69 (d, *5j*

= 4.1 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 204.4, 157.4 – 152.8 (m), 147.5, 145.9, 140.4, 132.4, 131.8, 128.9, 128.6 (t, *J* = 3.3 Hz), 127.5, 127.2, 127.0, 121.8 (d, *J* = 2.8 Hz), 109.5 (t, *J* = 3.7 Hz), 109.2 (d, *J* = 2.8 Hz), 108.2, 86.5 (dd, *J* = 21.1, 17.3 Hz), 48.2, 36.4, 33.7 (d, *J* = 1.9 Hz), 13.2. HRMS (ESI) calcd for $C_{26}H_{22}F_2O_3Na$ $[M+Na]^+$: 443.1329; found: 443.1327.

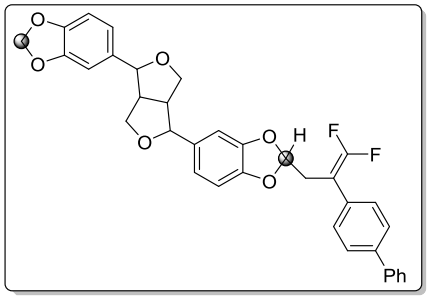
2-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)-9-hydroxy-5-(3,4,5-trimethoxyphenyl)-5,8,8a,9-tetrahydrofuro[3',4':6,7]naphtho[2,3-d][1,3]dioxol-6(5aH)-one (3m)



White solid (80.9 mg, 63% yield). M.p. 91.0-92.2 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 4H), 7.45 – 7.34 (m, 5H), 7.04 (s, 1H), 6.42 – 6.34 (m, 3H), 6.19 (t, *J* = 4.6 Hz, 1H), 4.72 (t, *J* = 5.2 Hz, 1H), 4.56 – 4.55 (m, 2H), 4.03 (t, *J* = 8.2 Hz, 1H), 3.80 (d, J = 6.4 Hz, 3H), 3.76 (s, 4H), 3.72 (s, 2H), 3.04 (dt, *J* = 4.5, 2.2 Hz, 2H), 2.80 – 2.78 (m, 2H), 2.50 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.53 (d, *J* = 7.5 Hz), -87.57 (d, *J* = 3.7 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.6 (d, *J* = 2.3 Hz), 157.0 – 152.9 (m), 152.6 (d, *J* = 10.4 Hz), 147.5 (d, *J* = 4.2 Hz), 147.4, 140.5, 140.3 (d, *J* = 10.2 Hz), 137.3, 137.2, 135.5 (d, *J* = 4.5 Hz), 133.2 (d, *J* =

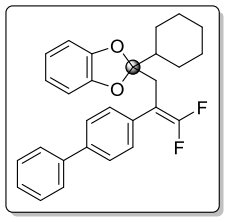
6.0 Hz), 131.7 (d, *J* = 14.9 Hz), 131.0 (d, *J* = 2.3 Hz), 128.9 (d, *J* = 3.6 Hz), 128.7 (t, *J* = 3.2 Hz), 128.6 (t, *J* = 3.3 Hz), 127.6 (d, *J* = 3.4 Hz), 127.2 (d, *J* = 5.1 Hz), 127.0 (d, *J* = 3.8 Hz), 110.1 (dd, *J* = 8.3, 4.9 Hz), 109.7 (d, *J* = 3.0 Hz), 108.5 (d, *J* = 19.8 Hz), 106.3, 88.0 – 84.4 (m), 72.7 (d, *J* = 2.6 Hz), 71.4, 60.8 (d, *J* = 3.8 Hz), 56.3 (d, *J* = 7.7 Hz), 45.3 (d, *J* = 4.4 Hz), 44.1, 40.7, 33.7. HRMS (ESI) calcd for $C_{37}H_{32}F_2O_8Na$ $[M+Na]^+$: 665.1957; found: 665.1939.

2-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)-5-(4-(benzo[d][1,3]dioxol-5-yl)tetrahydro-1H,3H-furo[3,4-c]furan-1-yl)benzo[d][1,3]dioxole (3n)



Yellow oil (83.8 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 4H), 7.47 – 7.42 (m, 4H), 7.40 – 7.38 (m, 1H), 6.88 – 6.86 (m, 1H), 6.82 – 6.77 (m, 4H), 6.74 – 6.71 (m, 1H), 6.22 (t, *J* = 4.9 Hz, 1H), 5.98 (s, 2H), 4.75 – 4.71 (m, 2H), 4.26 – 4.22 (m, 2H), 3.89 – 3.86 (m, 2H), 3.07 – 3.05 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.47 – -87.74 (m). ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.8 (t, *J* = 280.95 Hz), 148.0, 147.7, 147.1, 146.9, 140.4 (dd, *J* = 4.8, 2.2 Hz), 135.1, 135.0, 128.9, 128.6 (t, *J* = 3.4 Hz), 127.5, 127.2 (d, *J* = 3.9 Hz), 127.0 (d, *J* = 2.4 Hz), 119.4, 109.7 (d, *J* = 3.6 Hz), 108.2, 108.1, 106.5, 106.4, 101.1, 86.4 (dd, *J* = 21.0, 18.0 Hz), 85.8 (d, *J* = 1.8 Hz), 71.7 (d, *J* = 3.3 Hz), 54.3 (d, *J* = 3.6 Hz), 33.7. HRMS (ESI) calcd for $C_{35}H_{28}F_2O_6Na$ $[M+Na]^+$: 605.1731; found: 605.1746.

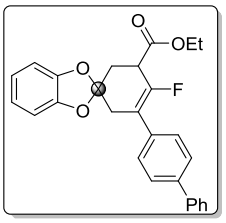
2-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)-2-cyclohexylbenzo[d][1,3]dioxole (3o)



Colorless oil (57.1 mg, 66% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.62 (m, 2H), 7.53 – 7.46 (m, 4H), 7.41 – 7.39 (m, 1H), 7.17 – 7.14 (m, 2H), 6.74 – 6.72 (m, 2H), 6.57 – 6.54 (m, 2H), 3.05 (s, 2H), 1.93 – 1.87 (m, 3H), 1.81 – 1.79 (m, 2H), 1.69 (t, *J* = 4.4 Hz, 1H), 1.24 – 1.13 (m, 5H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.88 (d, *J* = 34.0 Hz), -88.69 (d, *J* = 33.4 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.8 (t, *J* = 290.9 Hz), 147.9, 140.7, 139.8, 133.1 (t, *J* = 3.8 Hz), 128.8, 128.6 (t, *J* = 2.8 Hz), 127.3, 127.0, 126.6, 120.8, 120.5 (t, *J* = 3.0 Hz), 107.6, 87.0 (dd, *J* = 20.9, 16.8 Hz), 46.0, 34.5 (d, *J* = 2.0 Hz), 26.2, 26.1, 25.9. HRMS (ESI) calcd for $C_{28}H_{26}F_2O_2$ $[M+H]^+$: 433.1974; found:

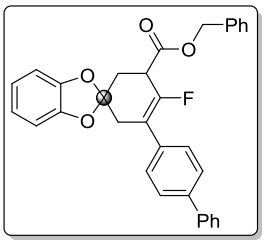
433.1964.

ethyl4'-fluoro-3'-(4-phenylphenyl)spiro[1,3-benzodioxole-2,1'-cyclohexan]-3'-ene-5'-carboxylate (5a)



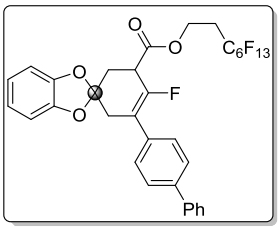
White solid (74.0 mg, 86% yield). M.p. 113.2-114.5 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.3, 1.7 Hz, 4H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.33 (dd, *J* = 8.3, 6.4 Hz, 1H), 6.84 – 6.76 (m, 4H), 4.26 (qd, *J* = 7.2, 2.4 Hz, 2H), 3.81 – 3.80 (m, 1H), 3.09 – 3.05 (m, 2H), 2.66 (dd, *J* = 13.2, 7.5 Hz, 1H), 2.53 – 2.51 (m, 1H), 1.30 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.30. ^{13}C NMR (150 MHz, $CDCl_3$) 170.6, 150.7 (d, *J* = 261.0 Hz), 146.7 (d, *J* = 5.7 Hz), 140.5 (d, *J* = 12.0 Hz), 134.0, 128.8, 128.2 (d, *J* = 4.8 Hz), 127.5, 127.0 (d, *J* = 13.6 Hz), 121.7 (d, *J* = 2.7 Hz), 114.7, 113.0 (d, *J* = 10.3 Hz), 109.0, 61.7, 43.0 (d, *J* = 26.1 Hz), 37.8 (d, *J* = 4.3 Hz), 34.7 (d, *J* = 6.8 Hz), 14.2. HRMS (ESI) calcd for $C_{27}H_{24}FO_4$ $[M+H]^+$: 431.1653; found: 431.1646.

benzyl4'-fluoro-5'-(4-phenylphenyl)spiro[1,3-benzodioxole-2,1'-cyclohexan]-3'-ene-5'-carboxylate (5b)



White solid (77.7 mg, 79% yield). M.p. 118.7-119.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 4H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.35 – 7.33 (m, 6H), 6.80 (d, *J* = 4.4 Hz, 3H), 6.67 (d, *J* = 6.8 Hz, 1H), 5.27 – 5.19 (m, 2H), 3.88 – 3.84 (m, 1H), 3.12 – 3.01 (m, 2H), 2.68 (dd, *J* = 13.4, 7.3 Hz, 1H), 2.50 (dd, *J* = 13.4, 7.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.10. ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 150.5 (d, *J* = 261.0 Hz), 146.7, 140.6 (d, *J* = 3.5 Hz), 135.6, 134.1, 128.9, 128.7, 128.4 (d, *J* = 19.2 Hz), 127.6, 127.1 (d, *J* = 11.9 Hz), 114.6, 113.3 (d, *J* = 10.9 Hz), 109.1 (d, *J* = 8.9 Hz). HRMS (ESI) calcd for $C_{32}H_{26}FO_4$ $[M+H]^+$: 493.1810; found: 493.1799.

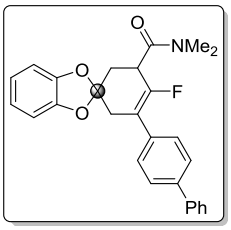
3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl4'-fluoro-3'-(4-phenylphenyl)spiro[1,3-benzodioxole-2,1'-cyclohexan]-3'-ene-5'-carboxylate (5c)



White solid (110.7 mg, 74% yield). M.p. 124.9-126.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.59 (m, 4H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.35 (m, 1H), 6.85 – 6.82 (m, 3H), 6.76

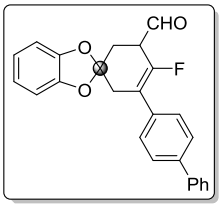
– 6.73 (m, 1H), 4.51 (t, *J* = 6.6 Hz, 2H), 3.83 – 3.82 (m, 1H), 3.08 (dt, *J* = 4.6, 2.1 Hz, 2H), 2.67 – 2.66 (m, 1H), 2.55 – 2.49 (m, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.75, -110.34, -113.52 (td, *J* = 13.2, 12.4, 5.5 Hz), -121.85 (p, *J* = 13.6 Hz), -122.85 (dp, *J* = 13.7, 4.7 Hz), -122.93 – -124.84 (m), -125.46 – -126.86 (m). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.3 (d, *J* = 2.3 Hz), 149.9 (d, *J* = 260.8 Hz), 146.5 (d, *J* = 4.9 Hz), 140.6 (d, *J* = 17.0 Hz), 133.8, 128.8, 128.2 (d, *J* = 4.8 Hz), 127.5, 127.0 (d, *J* = 8.4 Hz), 121.8, 114.4 (d, *J* = 2.0 Hz), 113.4 (d, *J* = 10.7 Hz), 108.9 (d, *J* = 18.0 Hz), 57.4, 42.7 (d, *J* = 26.1 Hz), 37.8 (d, *J* = 3.9 Hz), 34.5 (d, *J* = 6.6 Hz), 30.5 (t, *J* = 21.7 Hz). HRMS (ESI) calcd for $C_{33}H_{23}F_{14}O_4$ $[M+H]^+$: 749.1367; found: 749.1332.

4'-fluoro-N,N-dimethyl-3'-(4-phenylphenyl)spiro[1,3-benzodioxole-2,1'-cyclohexan]-3'-ene-5'-carboxamide (5d)



White solid (50.6 mg, 59% yield). M.p. 137.1-138.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 4H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.44 – 7.40 (m, 2H), 7.35 – 7.30 (m, 1H), 6.83 – 6.82 (m, 4H), 4.32 – 4.30 (m, 1H), 3.17 (s, 3H), 3.13 (dd, *J* = 6.0, 3.5 Hz, 1H), 3.03 (s, 3H), 3.00 – 2.99 (m, 1H), 2.76 (dd, *J* = 13.2, 11.1 Hz, 1H), 2.40 – 2.38 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.83. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 152.0 (d, *J* = 259.7 Hz), 146.9 (d, *J* = 32.6 Hz), 140.6 (d, *J* = 28.8 Hz), 134.3, 129.3 – 128.4 (m), 127.5, 127.1 (d, *J* = 16.3 Hz), 121.7 (d, *J* = 10.3 Hz), 115.6 (d, *J* = 2.3 Hz), 113.0 (d, *J* = 11.6 Hz), 109.0 (d, *J* = 6.2 Hz), 39.6, 39.3, 37.9 (dd, *J* = 10.9, 3.3 Hz), 36.4, 35.1 (d, *J* = 6.8 Hz). HRMS (ESI) calcd for $C_{27}H_{25}NFO_3$ $[M+H]^+$: 430.1813; found: 430.1803.

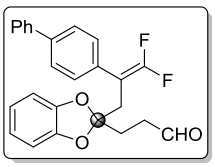
4'-fluoro-3'-(4-phenylphenyl)spiro[1,3-benzodioxole-2,1'-cyclohexan]-3'-ene-5'-carbaldehyde (5e)



White solid (29.3 mg, 38% yield). M.p. 140.8-141.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.62 – 7.58 (m, 4H), 7.46 – 7.43 (m, 2H), 7.37 – 7.34 (m, 3H), 6.85 – 6.77 (m, 4H), 4.32 – 4.27 (m, 1H), 3.13 – 3.07 (m, 1H), 2.82 – 2.75 (m, 1H), 2.68 – 2.62 (m, 1H), 2.35 (dd, *J* = 13.6, 11.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.80. ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.0 (d, *J* = 12.8 Hz),

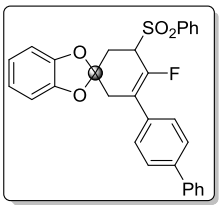
147.1, 146.8, 141.4, 140.8, 136.7, 129.3, 128.9, 128.2, 128.0, 127.5, 122.1 (d, *J* = 4.4 Hz), 116.8, 114.8, 109.4, 43.4 (d, *J* = 22.6 Hz), 40.9 (d, *J* = 6.1 Hz), 31.5. HRMS (ESI) calcd for $C_{25}H_{19}FO_3Na$ $[M+Na]^+$: 409.1210; found: 409.1201.

2-(2-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)benzo[d][1,3]dioxol-2-yl)acetaldehyde (5e′)



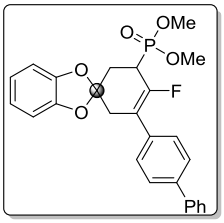
White solid (31.4 mg, 40% yield). M.p. 138.8-139.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.60 – 7.58 (m, 2H), 7.52 – 7.50 (m, 2H), 7.46 – 7.42 (m, 2H), 7.37 – 7.35 (m, 1H), 7.20 – 7.17 (m, 2H), 6.74 (dd, *J* = 5.7, 3.3 Hz, 2H), 6.57 (dd, *J* = 5.7, 3.3 Hz, 2H), 3.02 (t, *J* = 2.2 Hz, 2H), 2.56 (td, *J* = 7.3, 1.3 Hz, 2H), 2.30 (t, *J* = 7.3 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.18 (d, *J* = 32.8 Hz), -88.16 (d, *J* = 32.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 156.5 (d, *J* = 291.5 Hz), 147.3, 140.5, 140.1, 132.5, 128.8, 128.6 (t, *J* = 3.0 Hz), 127.4, 127.0, 126.8, 121.5, 118.0 (t, *J* = 3.2 Hz), 108.3, 86.9 (dd, *J* = 20.0, 17.0 Hz),37.0 (d, *J* = 8.0 Hz), 30.3. HRMS (APCI) calcd for $C_{25}H_{21}F_2O_3$ $[M+H]^+$: 407.1449; found: 407.1453.

5'-(benzenesulfonyl)-4'-fluoro-3'-(4-phenylphenyl)spiro[1,3-benzodioxole-2,1'-cyclohexan]-3'-ene (5f)



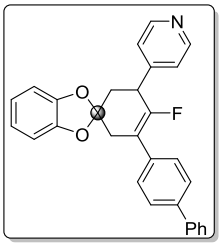
White solid (84.7 mg, 85% yield). M.p. 178.0-179.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.7 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.61 – 7.56 (m, 6H), 7.45 – 7.33 (m, 5H), 6.86 – 6.77 (m, 4H), 4.58 – 4.57 (m, 1H), 3.03 – 2.98 (m, 2H), 2.80 – 2.79 (m, 1H), 2.69 (dd, *J* = 13.8, 10.1 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.46. ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.9, 146.4 (d, *J* = 38.0 Hz), 141.1, 140.4, 138.6, 134.2, 133.4, 129.2, 129.1, 128.9, 128.3 (d, *J* = 4.4 Hz), 127.6, 127.1, 121.9 (d, *J* = 3.6 Hz), 117.7 (d, *J* = 11.1 Hz), 114.4, 109.1 (d, *J* = 3.9 Hz), 62.5 (d, *J* = 24.0 Hz), 38.0 (d, *J* = 3.1 Hz), 32.3 (d, *J* = 5.0 Hz). HRMS (ESI) calcd for $C_{30}H_{23}FO_4SNa$ $[M+Na]^+$: 521.1193; found: 521.1187.

diethyl [4'-fluoro-3'-(4-phenylphenyl)spiro[1,3-benzodioxole-2,1'-cyclohexan]-3'-en-5'-yl] phosphonate (5g)



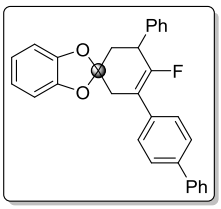
White solid (77.4 mg, 83% yield). M.p. 181.1-182.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 8.0, 1.9 Hz, 4H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.36 (m, 1H), 6.87 – 6.86 (m, 4H), 3.87 (dd, *J* = 18.6, 10.9 Hz, 6H), 3.63 – 3.56 (m, 1H), 3.19 – 3.13 (m, 1H), 3.02 (ddd, *J* = 16.8, 5.1, 2.5 Hz, 1H), 2.64 – 2.47 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.99 (d, *J* = 2.5 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.5 (dd, *J* = 258.5, 14.5 Hz), 146.8, 146.6, 140.5 (d, *J* = 4.6 Hz), 134.1, 128.8, 128.3 (d, *J* = 5.0 Hz), 127.5, 127.1, 127.0, 121.7 (d, *J* = 2.4 Hz), 114.5 (dd, *J* = 14.3, 1.9 Hz), 113.6 (d, *J* = 11.2 Hz), 109.0 (d, *J* = 12.2 Hz), 53.5 (dd, *J* = 6.6, 2.6 Hz), 52.9 (d, *J* = 6.9 Hz), 37.8 (t, *J* = 3.3 Hz), 35.7 (d, *J* = 25.9 Hz), 34.7 (d, *J* = 25.7 Hz), 32.6 (t, *J* = 6.0 Hz). HRMS (ESI) calcd for $C_{26}H_{25}FO_5P$ $[M+H]^+$: 467.1418; found: 467.1410.

4-[4'-fluoro-3'-(4-phenylphenyl)spiro[1,3-benzodioxole-2,1'-cyclohexan]-3'-en-5'-yl]pyridine (5h)



White solid (64.4 mg, 74% yield). M.p. 154.9-156.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 5.1 Hz, 2H), 7.62 – 7.56 (m, 6H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 5.1 Hz, 2H), 6.85 – 6.80 (m, 3H), 6.75 – 6.73 (m, 1H), 4.23 (t, *J* = 8.3 Hz, 1H), 3.22 – 3.13 (m, 2H), 2.65 – 2.61 (m, 1H), 2.31 (dd, *J* = 13.4, 9.9 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.91. ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.0 (d, *J* = 261.5 Hz), 150.2, 149.1, 146.7 (d, *J* = 15.1 Hz), 140.6 (d, *J* = 16.1 Hz), 134.1, 128.8, 128.2 (d, *J* = 4.9 Hz), 127.5, 127.1, 123.3, 121.7, 114.6, 113.4 (d, *J* = 11.0 Hz), 108.9 (d, *J* = 17.9 Hz), 42.3, 42.1, 40.2 (d, *J* = 6.3 Hz), 38.2 (d, *J* = 4.2 Hz). HRMS (ESI) calcd for $C_{29}H_{23}FNO_2$ $[M+H]^+$: 436.1707; found: 436.1699.

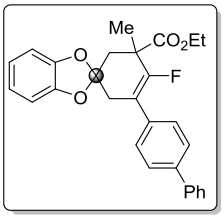
4'-fluoro-5'-phenyl-3'-(4-phenylphenyl)spiro[1,3-benzodioxole-2,1'-cyclohexan]-3'-ene (5i)



White solid (35.6 mg, 41% yield). M.p. 120.7-122.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 9.4, 7.1 Hz, 6H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.39 – 7.32 (m, 5H), 7.31 – 7.28 (m, 1H), 6.86 – 6.76 (m, 4H), 4.27 (s, 1H), 3.26 – 3.20 (m, 1H), 3.13 – 3.08 (m, 1H), 2.66 – 2.60 (m, 1H), 2.34 (dd, *J* = 13.4, 10.7

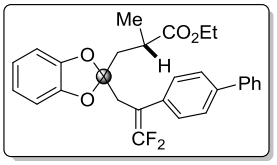
Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.33. ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.8 (d, *J* = 261.6 Hz), 147.0 (d, *J* = 15.3 Hz), 140.8, 140.4, 140.1, 134.8, 128.9 (d, *J* = 2.4 Hz), 128.4 (d, *J* = 5.1 Hz), 128.1, 127.5, 127.4, 127.2, 127.1, 121.7 (d, *J* = 4.6 Hz), 115.3 (d, *J* = 2.0 Hz), 112.1 (d, *J* = 11.5 Hz), 109.0 (d, *J* = 28.0 Hz), 43.0 (d, *J* = 26.1 Hz), 41.3 (d, *J* = 6.3 Hz), 38.4 (d, *J* = 4.2 Hz). HRMS (APCI) calcd for $C_{30}H_{24}FO_2$ $[M+H]^+$: 435.1755; found: 435.1757.

ethyl 4'-fluoro-5'-methyl-3'-(4-phenylphenyl)spiro[1,3-benzodioxole-2,1'-cyclohexan]-3'-ene-5'-carboxylate (5j)



White solid (74.6 mg, 84% yield). M.p. 111.6-113.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 4H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 6.83 – 6.78 (m, 3H), 6.72 – 6.70 (m, 1H), 4.26 (p, *J* = 7.3 Hz, 2H), 3.17 – 3.00 (m, 2H), 2.91 (dd, *J* = 13.6, 4.1 Hz, 1H), 2.16 (d, *J* = 13.6 Hz, 1H), 1.58 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.18. ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.7 (d, *J* = 4.1 Hz), 154.2 (d, *J* = 263.6 Hz), 146.8 (d, *J* = 14.8 Hz), 140.6 (d, *J* = 38.7 Hz), 134.5, 128.9, 128.5 (d, *J* = 4.7 Hz), 127.5, 127.2, 127.0, 121.7 (d, *J* = 14.9 Hz), 114.5 (d, *J* = 2.0 Hz), 111.9 (d, *J* = 12.2 Hz), 109.0 (d, *J* = 21.1 Hz), 61.7, 46.7 (d, *J* = 24.4 Hz), 42.7 (d, *J* = 4.8 Hz), 38.7 (d, *J* = 3.8 Hz), 22.6 (d, *J* = 4.4 Hz), 14.3. HRMS (ESI) calcd for $C_{28}H_{26}FO_4$ $[M+H]^+$: 445.1810; found: 445.1795.

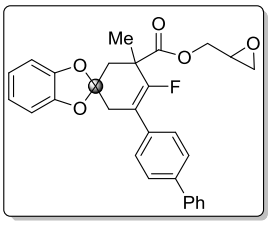
ethyl 3-(2-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)benzo[d][1,3]dioxol-2-yl)-2-methylpropanoate (5j′)



This compound can be obtained as a side product in 7% yield during the gram scale synthesis of **5j**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.48 (dd, *J* = 8.3, 6.9 Hz, 1H), 7.43 – 7.36 (m, 1H), 7.21 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.81 – 6.72 (m, 1H), 6.63 – 6.52 (m, 1H), 4.16 – 3.96 (m, 1H), 3.02 (t, *J* = 2.1 Hz, 1H), 2.69 (ddt, *J* = 13.1, 7.0, 3.5 Hz, 0H), 2.59 (dd, *J* = 14.7, 9.3 Hz, 1H), 1.97 (dd, *J* = 14.7, 3.5 Hz, 1H), 1.16 (d, *J* = 4.5 Hz, 1H), 1.15 – 1.12 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -87.19 (d, *J* = 32.4 Hz), -88.30 (d, *J* = 32.3 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 155.0 (t, *J* = 291.5 Hz), 147.4 (d, *J* = 9.0 Hz), 140.6, 139.9, 132.6 (t, *J* = 3.6 Hz),

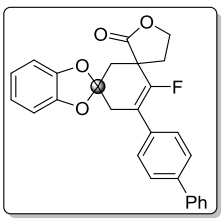
128.8, 128.6 (t, *J* = 3.0 Hz), 127.4, 127.0, 126.8, 121.3, 118.0 (t, *J* = 3.3 Hz), 108.2 (d, *J* = 6.1 Hz), 86.9 (dd, *J* = 20.8, 16.8 Hz), 60.5, 41.4, 37.1 (d, *J* = 1.9 Hz), 34.3, 18.7, 14.0.HRMS (ESI) calcd for $C_{28}H_{26F}O_4$ $[M+Na]^+$: 487.1691; found: 487.1689.

(oxiran-2-yl)methyl4'-fluoro-5'-methyl-3'-(4-phenylphenyl)spiro[1,3-benzodioxole-2,1'-cyclohexan]-3'-ene-5'-carboxylate (5k)



White solid (73.6 mg, 78% yield, *dr* = 1.4:1). M.p. 129.3-131.2 ^oC. ^1H NMR (400 MHz, $CDCl_3$)**:** δ 7.60 (d, *J* = 8.0 Hz, 4H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 6.82 – 6.80 (m, 4H), 6.73 – 6.72 (m, 1H), 4.54 (dd, *J* = 12.2, 3.1 Hz, 0.56 H, major), 4.47 (dd, *J* = 12.3, 3.1 Hz, 0.42 H, minor), 4.14 (dd, *J* = 12.2, 5.7 Hz, 0.42 H, minor), 4.07 (dd, *J* = 12.2, 5.8 Hz, 0.56 H, major), 3.28 – 3.22 (m, 1H), 3.07 – 2.82 (m, 1H), 2.71 – 2.67 (m, 1H), 2.19 (dd, *J* = 13.6, 4.1 Hz, 1H), 1.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) major diastereoisomer: δ 173.5 (d, *J* = 4.3 Hz), 154.9 (d, *J* = 3.4 Hz), 153.6 (d, *J* = 263.1 Hz), 146.7, 140.5 (d, *J* = 11.8 Hz), 134.3, 128.8, 128.3 (d, *J* = 4.8 Hz), 127.5, 127.1, 121.8, 121.7, 114.2, 112.3 (d, *J* = 12.7 Hz), 112.2 (d, *J* = 12.0 Hz), 108.9 (d, *J* = 15.7 Hz), 65.7, 49.3, 46.8, 46.5, 44.6, 42.7, 42.6, 38.5 (d, *J* = 3.8 Hz), 22.5 (d, *J* = 4.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.32 (minor), -117.41 (major). ^{13}C NMR (100 MHz, $CDCl_3$) minor diastereoisomer: 173.4 (d, *J* = 4.4 Hz), 154.9 (d, *J* = 3.4 Hz), 153.7 (d, *J* = 263.2 Hz), 146.5, 140.5 (d, *J* = 11.8 Hz), 134.2, 128.8, 128.3 (d, *J* = 4.8 Hz), 127.5, 127.0, 121.8, 121.7, 114.2, 112.3 (d, *J* = 12.7 Hz), 108.9 (d, *J* = 8.4 Hz), 65.6, 49.3, 46.8, 46.5, 44.5, 42.7, 42.6, 38.5 (d, *J* = 3.8 Hz), 22.5 (d, *J* = 4.4 Hz). HRMS (ESI) calcd for $C_{29}H_{26}FO_5$ $[M+H]^+$: 473.1759; found: 473.1738.

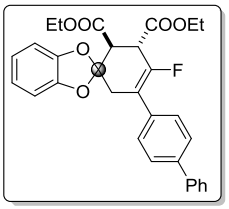
4'-fluoro-5'-(4-phenylphenyl)dispiro[1,3-benzodioxole-2,1'-cyclohexane-3',3''-oxolan]-4'-en-2''-one (5l)



White solid (53.9 mg, 63% yield). M.p. 198.4-199.8 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 4H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 6.86 – 6.80 (m, 4H), 4.48 (q, *J* = 7.9 Hz, 1H), 4.36 (q, *J* = 8.6, 6.3 Hz, 1H), 3.19 (dd, *J* = 16.9, 6.1 Hz, 1H), 3.11 – 3.09 (m, 1H), 2.91 – 2.88 (m, 1H), 2.78 (d, *J* = 13.6 Hz, 1H), 2.79 – 2.76 (m, 1H), 2.38 (ddd, *J* = 13.7, 5.9, 2.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.96. ^{13}C NMR (100 MHz, $CDCl_3$) δ

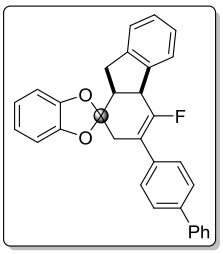
176.5, 152.2 (d, *J* = 258.9 Hz), 146.6, 146.4, 140.8, 133.3, 128.8, 128.4, 128.3, 127.6, 127.1 (d, *J* = 4.7 Hz), 122.0, 121.8, 114.5 (d, *J* = 2.3 Hz), 113.7, 113.6, 109.1, 108.9, 66.4, 48.0 (d, *J* = 25.9 Hz), 39.5 (d, *J* = 6.6 Hz), 38.1 (d, *J* = 4.0 Hz), 34.2 (d, *J* = 1.9 Hz). HRMS (ESI) calcd for $C_{27}H_{22}FO_4$ $[M+H]^+$: 429.1497; found: 429.1490.

trans-5',6'-diethyl 4'-fluoro-3'-(4-phenylphenyl)spiro[1,3-benzodioxole-2,1'-cyclohexan] -3'-ene-5', 6'-dicarboxylate (5m)



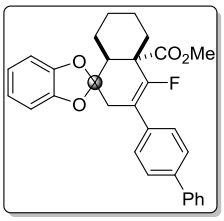
White solid (from maleate, 88.4 mg, 88% yield; from fumarate 83.3 mg, 83% yield). M.p. 119.4-121.2 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.58 (m, 4H), 7.53 – 7.51 (m, 2H), 7.45 – 7.42 (m, 2H), 7.36 – 7.34 (m, 1H), 6.83 – 6.77 (m, 4H), 4.30 – 4.27 (m, 2H), 4.18 (dd, *J* = 7.4, 2.0 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.79 (d, *J* = 7.4 Hz, 1H), 3.23 – 3.22 (m, 1H), 3.14 – 3.08 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.79. ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.4, 168.1, 149.1 (d, *J* = 261.0 Hz), 146.8, 146.4, 140.6 (d, *J* = 13.5 Hz), 133.6, 128.2 (d, *J* = 4.8 Hz), 127.5, 127.0 (d, *J* = 10.0 Hz), 121.9 (d, *J* = 17.5 Hz), 113.9 (d, *J* = 2.1 Hz), 112.7 (d, *J* = 10.8 Hz), 108.9 (d, *J* = 44.0 Hz), 62.1, 61.7, 49.7 (d, *J* = 7.0 Hz), 46.1 (d, *J* = 27.4 Hz), 37.8 (d, *J* = 3.9 Hz), 14.1, 13.8. HRMS (ESI) calcd for $C_{30}H_{27}FO_6Na$ $[M+Na]^+$: 525.1684; found: 525.1675.

cis-4'-fluoro-3'-(4-phenylphenyl)-2',4'a,9',9'a-tetrahydrospiro[1,3-benzodioxole-2,1'-fluorene] (5n)



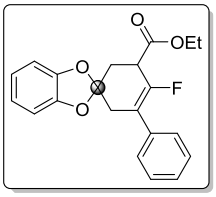
White solid (54.4 mg, 61% yield). M.p. 193.3-194.1 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 4H), 7.51 – 7.46 (m, 3H), 7.43 – 7.40 (m, 2H), 7.35 – 7.32 (m, 1H), 7.26 – 7.24 (m, 3H), 6.84 – 6.79 (m, 4H), 4.38 (d, *J* = 8.1 Hz, 1H), 3.38 (dd, *J* = 9.9, 7.8 Hz, 1H), 3.29– 3.18 (m, 3H), 3.06 – 2.99 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.08. ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3 (d, *J* = 261.3 Hz), 147.1 (d, *J* = 14.8 Hz), 141.4, 140.7, 140.0, 134.6, 128.8, 128.1 (d, *J* = 5.2 Hz), 127.9, 127.4, 127.0, 126.8 (d, *J* = 4.4 Hz), 126.0 (d, *J* = 2.4 Hz), 124.8, 121.5 (d, *J* = 12.5 Hz), 117.6 (d, *J* = 2.3 Hz), 108.9 (d, *J* = 16.1 Hz), 46.9, 46.7 – 46.4 (m), 35.0 (d, *J* = 4.8 Hz), 34.2. HRMS (EI) calcd for $C_{31}H_{23}FO_2$ $[M]^+$: 446.1680; found: 446.1677.

cis-methyl4'-fluoro-3'-(4-phenylphenyl)-4'a,5',6',7',8',8'a-hexahydro-2'H-spiro[1,3-benzodioxole-2,1'-naphthalene]-4'a-carboxylate (5o)



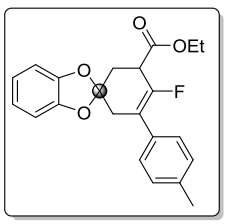
White solid (59.2 mg, 63% yield). M.p. 136.8-137.2 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (q, *J* = 7.9 Hz, 6H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.37 – 7.33 (m, 1H), 6.83 – 6.77 (m, 3H), 6.68 – 6.66 (m, 1H), 3.80 (s, 3H), 3.19 (dd, *J* = 17.5, 6.2 Hz, 1H), 2.96 (dd, *J* = 17.5, 5.5 Hz, 1H), 2.82 (dt, *J* = 11.5, 5.6 Hz, 1H), 2.41 (d, *J* = 13.8 Hz, 1H), 2.11 (d, *J* = 8.7 Hz, 1H), 1.84 (s, 1H), 1.70 (d, *J* = 11.5 Hz, 2H), 1.34 (d, *J* = 10.5 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.61. ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.1, 152.1 (d, *J* = 266.2 Hz), 146.6 (d, *J* = 46.7 Hz), 140.5 (d, *J* = 38.7 Hz), 134.4, 128.8, 128.3 (d, *J* = 5.1 Hz), 127.4, 127.0, 121.6 (d, *J* = 23.9 Hz), 116.9 (d, *J* = 2.5 Hz), 108.9 (d, *J* = 44.7 Hz), 52.6, 51.1 (d, *J* = 22.5 Hz), 44.3 (d, *J* = 4.3 Hz), 36.0 (d, *J* = 4.0 Hz), 31.1 (d, *J* = 6.4 Hz), 26.9, 24.2 (d, *J* = 15.1 Hz), 22.3. HRMS (ESI) calcd for $C_{30}H_{27}FO_4Na$ $[M+Na]^+$: 493.1786; found: 493.1779.

ethyl 4'-fluoro-3'-phenylspiro[1,3-benzodioxole-2,1'-cyclohexan]-3'-ene-5'-carboxylate (5p)



Colorless oil (55.2 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 2H), 7.38 – 7.34 (m, 2H), 7.29 – 7.28 (m, 1H), 6.84 – 6.76 (m, 4H), 4.26 – 4.24 (m, 2H), 3.79 – 3.78 (m, 1H), 3.05 – 3.02 (m, 2H), 2.67 – 2.62 (m, 1H), 2.53 – 2.47 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376MHz, $CDCl_3$) δ -111.13.^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7 (d, *J* = 2.3 Hz), 151.8, 149.2, 146.8 (d, *J* = 3.8 Hz), 135.2, 128.4, 128.1 – 127.6 (m), 121.8 (d, *J* = 2.0 Hz), 114.8 (d, *J* = 2.3 Hz), 113.5 (d, *J* = 11.1 Hz), 109.1, 61.8, 43.0 (d, *J* = 26.1 Hz), 38.1 (d, *J* = 4.1 Hz), 34.8 (d, *J* = 7.0 Hz), 14.3. HRMS (ESI) calcd for $C_{21}H_{20}FO_4$ $[M+H]^+$: 355.1340; found: 355.1335.

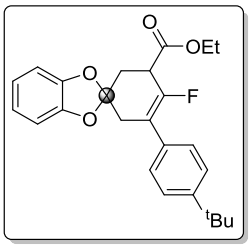
ethyl 4'-fluoro-3'-(4-methylphenyl)spiro[1,3-benzodioxole-2,1'-cyclohexan]-3'-ene-5'-carboxylate (5q)



Colorless oil (59.6 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.32 (m, 2H), 7.17 – 7.15 (m, 2H), 6.83 – 6.75 (m, 4H), 4.26 – 4.22 (m, 2H), 3.78 – 3.77 (m, 1H), 3.04 – 3.00 (m, 2H), 2.66 – 2.60 (m, 1H), 2.51 – 2.45 (m, 1H), 2.34 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).^{19}F NMR (376 MHz,

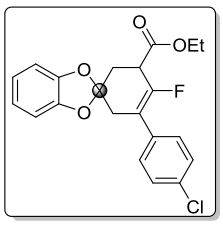
$CDCl_3$) δ -111.54.^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8 (d, *J* = 2.2 Hz), 151.5, 148.9, 146.8 (d, *J* = 3.6 Hz), 137.7, 132.2, 129.1, 127.8 (d, *J* = 4.6 Hz), 121.8 (d, *J* = 1.5 Hz), 114.8 (d, *J* = 2.4 Hz), 113.3 (d, *J* = 11.0 Hz), 109.0, 61.7, 43.0 (d, *J* = 26.3 Hz), 38.0 (d, *J* = 4.3 Hz), 34.8 (d, *J* = 7.0 Hz), 21.3, 14.3. HRMS (ESI) calcd for $C_{22}H_{21}FO_4Na$ $[M+Na]^+$: 391.1316; found: 391.1309.

ethyl 3'-(4-tert-butylphenyl)-4'-fluorospiro[1,3-benzodioxole-2,1'-cyclohexan]-3'-ene-5'-carboxylate (5r)



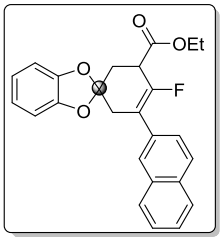
Colorless oil (64.8 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 4H), 6.83 – 6.75 (m, 4H), 4.27 – 4.21 (m, 2H), 3.79 – 3.78 (m, 1H), 3.06 – 3.01 (m, 2H), 2.66 – 2.60 (m, 1H), 2.51 – 2.45 (m, 1H), 1.31 (s, 9H), 1.28 (d, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.37. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8 (d, *J* = 2.1 Hz), 151.6, 150.9, 149.0, 146.8 (d, *J* = 3.4 Hz), 132.3, 127.6 (d, *J* = 5.0 Hz), 125.3, 121.8, 114.8 (d, *J* = 2.3 Hz), 113.1 (d, *J* = 10.8 Hz), 109.0, 61.7, 43.1 (d, *J* = 26.3 Hz), 37.9 (d, *J* = 4.3 Hz), 35.3 – 34.2 (m), 31.4, 14.3. HRMS (ESI) calcd for $C_{25}H_{27}FO_4Na$ $[M+Na]^+$: 433.1786; found: 433.1779.

ethyl3'-(4-chlorophenyl)-4'-fluorospiro[1,3-benzodioxole-2,1'-cyclohexan]-3'-ene-5'-carboxylate (5s)



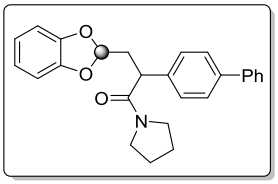
Colorless oil (58.2 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 4H), 6.87 – 6.78 (m, 4H), 4.30 – 4.25 (m, 2H), 3.83 – 3.77 (m, 1H), 3.09 – 2.97 (m, 2H), 2.69 – 2.64 (m, 1H), 2.55 – 2.49 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 3H).^{19}F NMR ($CDCl_3$) δ -109.90.^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4 (d, *J* = 2.2 Hz), 152.2, 149.6, 146.6 (d, *J* = 4.3 Hz), 133.5 (d, *J* = 8.4 Hz), 129.2 (d, *J* = 4.9 Hz), 128.5, 121.7 (d, *J* = 2.5 Hz), 114.4 (d, *J* = 2.2 Hz), 112.4 (d, *J* = 10.7 Hz), 109.0, 61.7, 42.9 (d, *J* = 25.9 Hz), 37.8 (d, *J* = 4.2 Hz), 34.6 (d, *J* = 7.0 Hz), 14.2. HRMS (ESI) calcd for $C_{21}H_{18}ClFO_4Na$ $[M+Na]^+$: 411.0770; found: 411.0763.

Ethyl 4'-fluoro-3'-(naphthalen-2-yl)spiro[1,3-benzodioxole-2,1'-cyclohexan]-3'-ene-5'-carboxylate (5t)



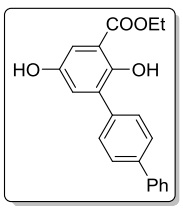
White solid (57.3 mg, 71% yield). M.p. 120.9-122.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 4H), 7.65 – 7.62 (m, 1H), 7.52 –7.49 (m, 2H), 6.88 – 6.80 (m, 4H), 4.33 – 4.28 (m, 2H), 3.89 – 3.85 (m, 1H), 3.20 – 3.17 (m, 2H), 2.75 – 2.69 (m, 1H), 2.60 – 2.54 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.55. ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 151.6, 149.9, 146.7 (d, *J* = 6.0 Hz), 133.1, 132.6 (d, *J* = 21.1 Hz), 128.2, 127.8, 127.5, 126.8 (d, *J* = 3.8 Hz), 126.2 (d, *J* = 6.6 Hz), 125.9 (d, *J* = 5.4 Hz), 121.7 (d, *J* = 3.1 Hz), 114.7 (d, *J* = 2.2 Hz), 113.4 (d, *J* = 10.8 Hz), 109.0, 61.7, 43.1, 38.1 (d, *J* = 4.0 Hz), 34.7 (d, *J* = 7.0 Hz), 14.2. HRMS (ESI) calcd for $C_{25}H_{22}FO_4$ $[M+H]^+$: 405.1497; found: 405.1491.

2-([1,1'-biphenyl]-4-yl)-3-(benzo[d][1,3]dioxol-2-yl)-1-(pyrrolidin-1-yl)propan-1-one (6)



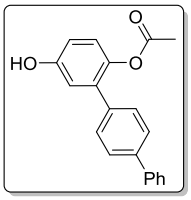
White solid (67.8 mg, 85% yield). M.p. 83.5-85.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 4H), 7.43 (t, *J* = 8.2 Hz, 4H), 7.33 (t, *J* = 7.3 Hz, 1H), 6.78 (d, *J* = 1.9 Hz, 4H), 6.10 (t, *J* = 4.8 Hz, 1H), 4.02 (dd, *J* = 8.6, 6.1 Hz, 1H), 3.53 – 3.51 (m, 1H), 3.45 – 3.39 (m, 2H), 3.25 – 3.23 (m, 1H), 2.89 – 2.84 (m, 1H), 2.33 (dt, *J* = 14.2, 5.5 Hz, 1H), 1.85 – 1.74 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 147.6 (d, *J* = 2.8 Hz), 140.6, 140.2, 137.8, 128.8, 128.5, 127.6, 127.4, 127.0, 121.4, 110.1, 108.5 (d, *J* = 5.8 Hz), 46.2 (d, *J* = 12.1 Hz), 44.6, 39.2, 26.0, 24.2. HRMS (ESI) calcd for $C_{26}H_{26}NO_3$ $[M+H]^+$: 400.1907; found: 400.1903

ethyl 2,5-dihydroxy-[1,1':4',1''-terphenyl]-3-carboxylate (7)



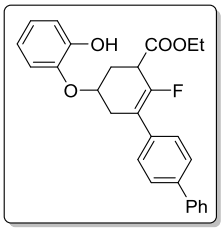
White solid (17.04 mg, 51% yield). M.p. 151.7-152.8 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.02 (s, 1H), 7.69 (s, 4H), 7.66 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.16 (d, *J* = 3.2 Hz, 1H), 4.70 (d, *J* = 2.2 Hz, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.2, 153.5, 147.3, 140.6 (d, *J* = 42.6 Hz), 135.9, 131.0, 129.7, 128.8, 127.3, 127.1 (d, *J* = 16.8 Hz), 124.5, 114.3, 112.8, 61.7, 14.2. HRMS (ESI) calcd for $C_{21}H_{18}O_4$ $[M+Na]^+$: 357.1097; found: 357.1092.

5-hydroxy-[1,1':4',1''-terphenyl]-2-yl acetate (8)



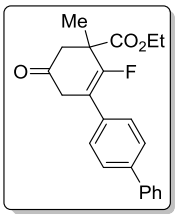
White solid (17.0 mg, 57% yield). M.p. 153.5-154.4 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.64 (m, 6H), 7.56 – 7.47 (m, 2H), 7.40 (d, *J* = 7.3 Hz, 1H), 7.08 (s, 1H), 6.95 (d, *J* = 2.5 Hz, 1H), 6.70 (d, *J* = 2.5 Hz, 1H), 4.90 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.9, 142.3, 140.7, 140.2 (d, *J* = 10.5 Hz), 139.8, 128.8, 127.9 – 127.2 (m), 127.1, 120.6, 115.1, 111.1, 21.5. HRMS (ESI) calcd for $C_{20}H_{15}O_3$ [M-H]$^-$: 303.1028; found: 303.1027.

ethyl 2-fluoro-5-(2-hydroxyphenoxy)-3,4,5,6-tetrahydro-[1,1':4',1''-terphenyl]-3-carboxylate (9)



White solid (69.9 mg, 81% yield). M.p. 159.6-161.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 4H), 7.44 – 7.40 (m, 4H), 7.35 – 7.33 (m, 1H), 6.94 – 6.89 (m, 3H), 6.81 – 6.79 (m, 1H), 6.71 (s, 1H), 4.87 – 4.86 (m, 1H), 4.29 – 4.25 (m, 2H), 3.54 (d, *J* = 7.9 Hz, 1H), 2.88 – 2.82 (m, 1H), 2.76 – 2.60 (m, 2H), 2.44 – 2.38 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.32.^{13}C NMR (150 MHz, $CDCl_3$) δ 173.6, 148.6, 143.2, 140.5 (d, *J* = 58.3 Hz), 134.7, 128.8, 128.3 (d, *J* = 4.0 Hz), 127.3, 127.0 (d, *J* = 14.3 Hz), 123.2, 119.7, 116.1, 115.4, 71.3, 62.1, 40.7 (d, *J* = 24.7 Hz), 32.1, 31.7 (d, *J* = 6.5 Hz), 14.0. HRMS (ESI) calcd for $C_{27}H_{26}FO_4$ [M+H]$^+$: 433.1810; found: 433.1806.

ethyl 2-fluoro-3-methyl-5-oxo-3,4,5,6-tetrahydro-[1,1':4',1''-terphenyl]-3-carboxylate (10)



White solid (14.4 mg, 41% yield). M.p. 115.3-116.8 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.59 (m, 4H), 7.54 – 7.45 (m, 4H), 7.38 (dd, *J* = 8.4, 6.2 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.52 – 3.29 (m, 2H), 3.04 (dd, *J* = 15.0, 3.9 Hz, 1H), 2.68 (d, *J* = 15.0 Hz, 1H), 1.60 (s, 3H), 1.34 – 1.30 (m, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -116.64. ^{13}C NMR (150 MHz, Chloroform-*d*) δ 203.9, 172.0, 155.0, 153.2, 140.8, 140.4, 133.4, 128.8, 128.1 (d, *J* = 5.0 Hz), 127.6, 127.1 (d, *J* = 9.2 Hz), 112.9 (d, *J* = 12.3 Hz), 62.2, 49.6 (d, *J* = 4.3 Hz), 47.8 (d, *J* = 26.0 Hz), 41.3 (d, *J* = 4.4 Hz), 31.4, 30.2, 20.8 (d, *J* = 4.9 Hz), 14.0.HRMS (ESI) calcd for $C_{22}H_{21}FO_3$ [M+Na]$^+$: 375.1367; found: 375.1366.

8. Reference

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2. X. Ariza, O. Pineda, J. Vilarrasa, G. W. Shipps, Y. Ma and X. Dai. *Org. Lett.*, 2001, **3**, 1399-1401.
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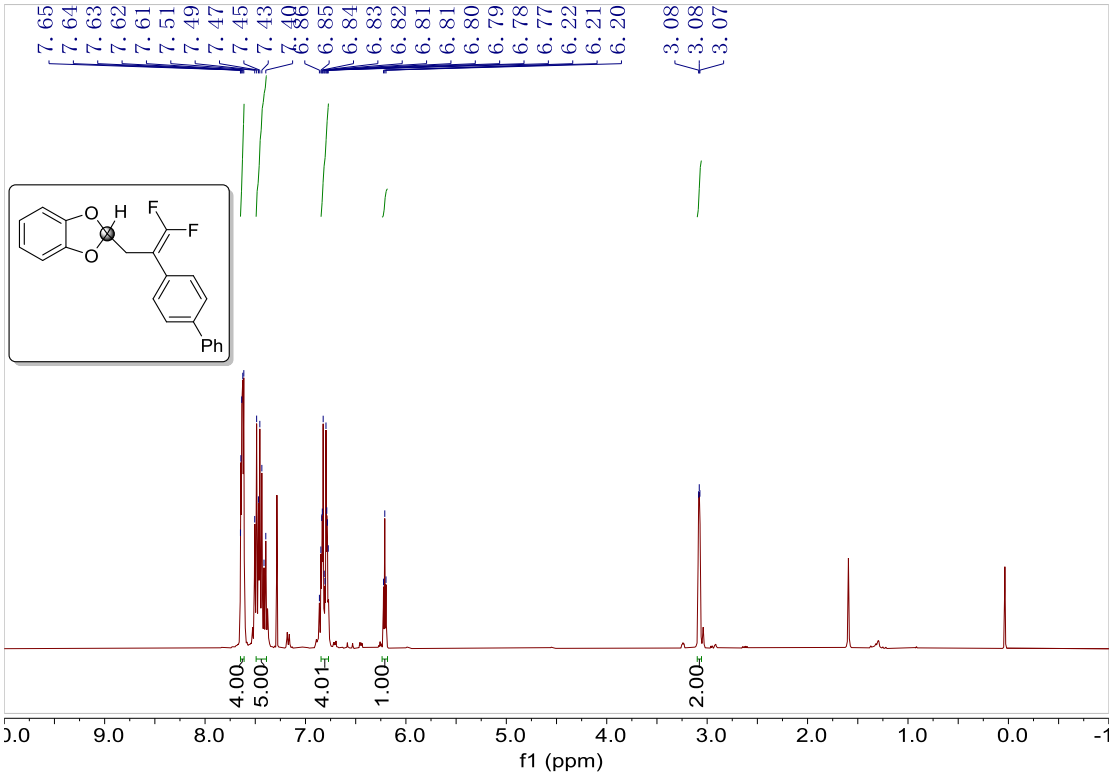
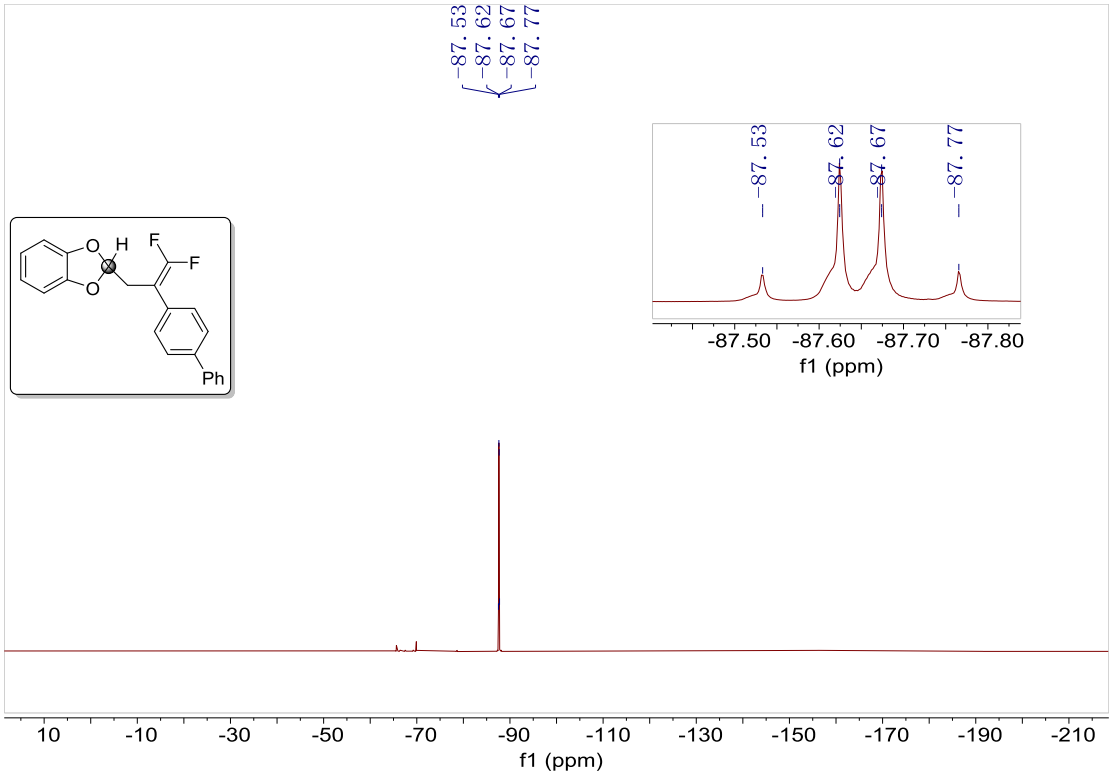
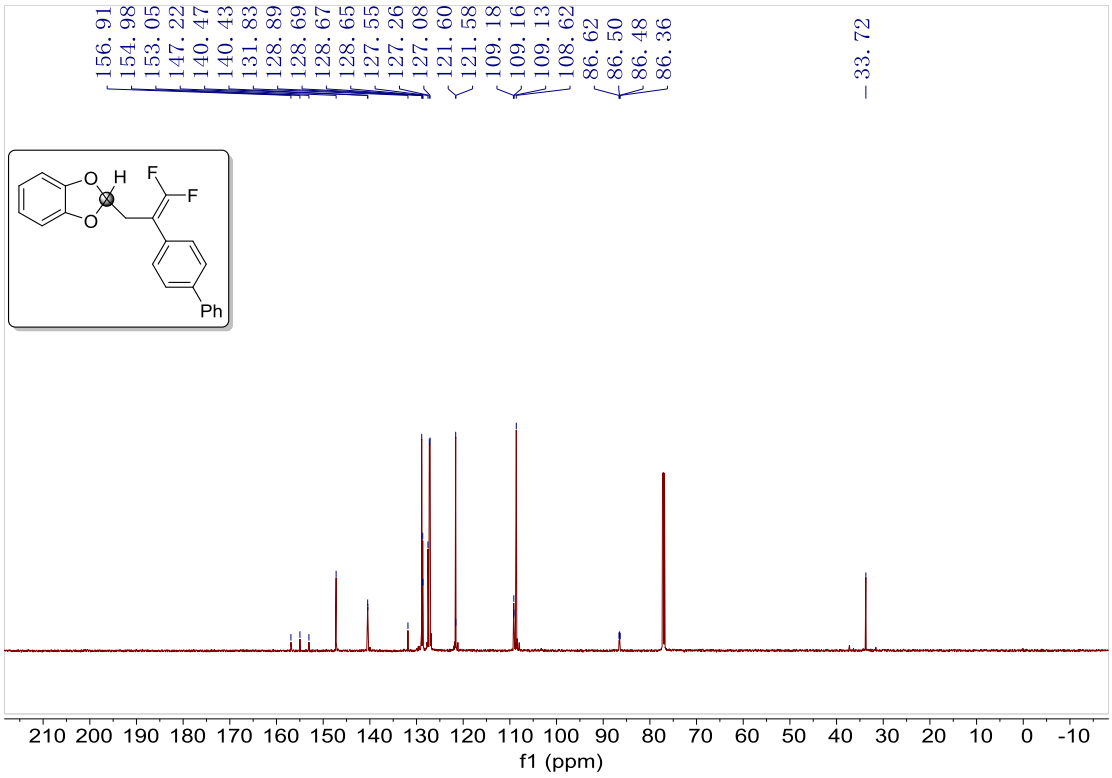
9. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra



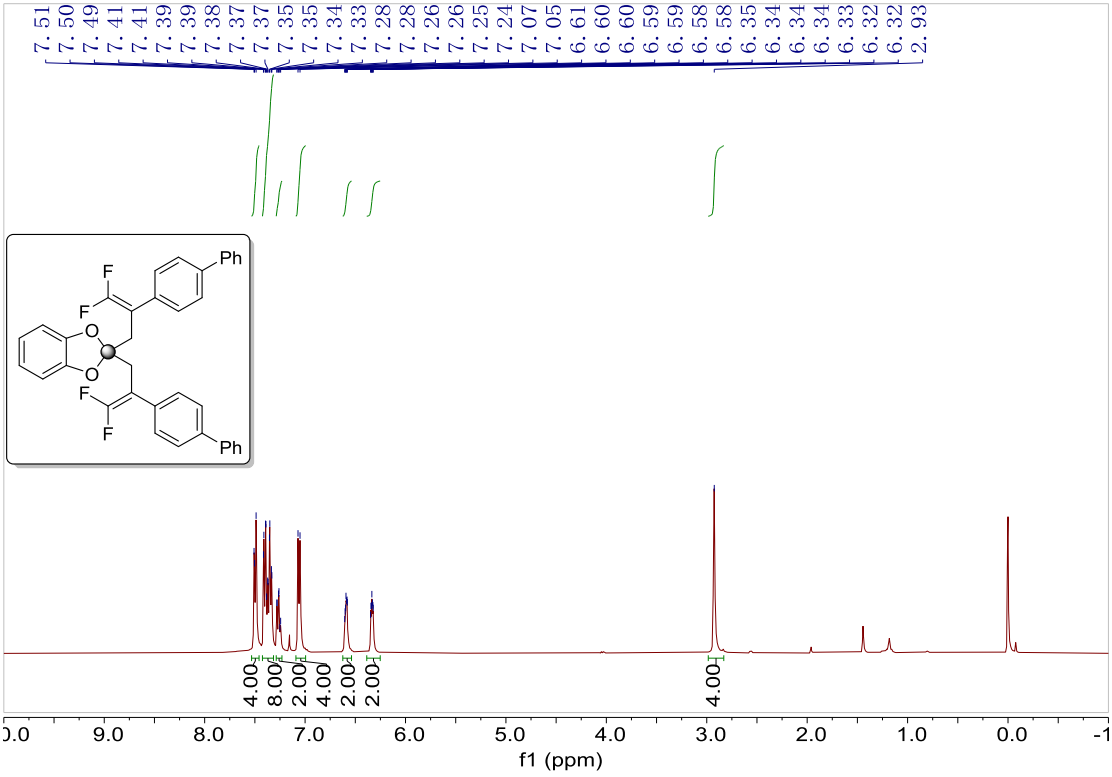
^{1}H NMR of 3a (400 MHz, $CDCl_3$)



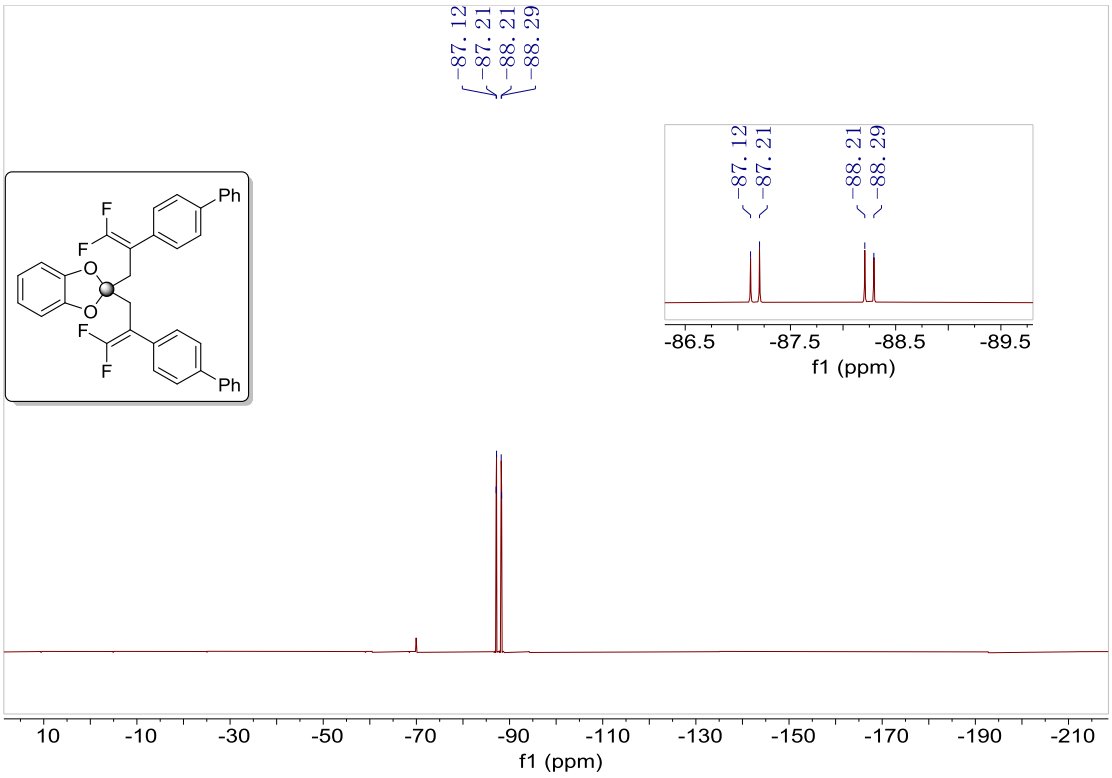
^{19}F NMR of 3a (376 MHz, $CDCl_3$)



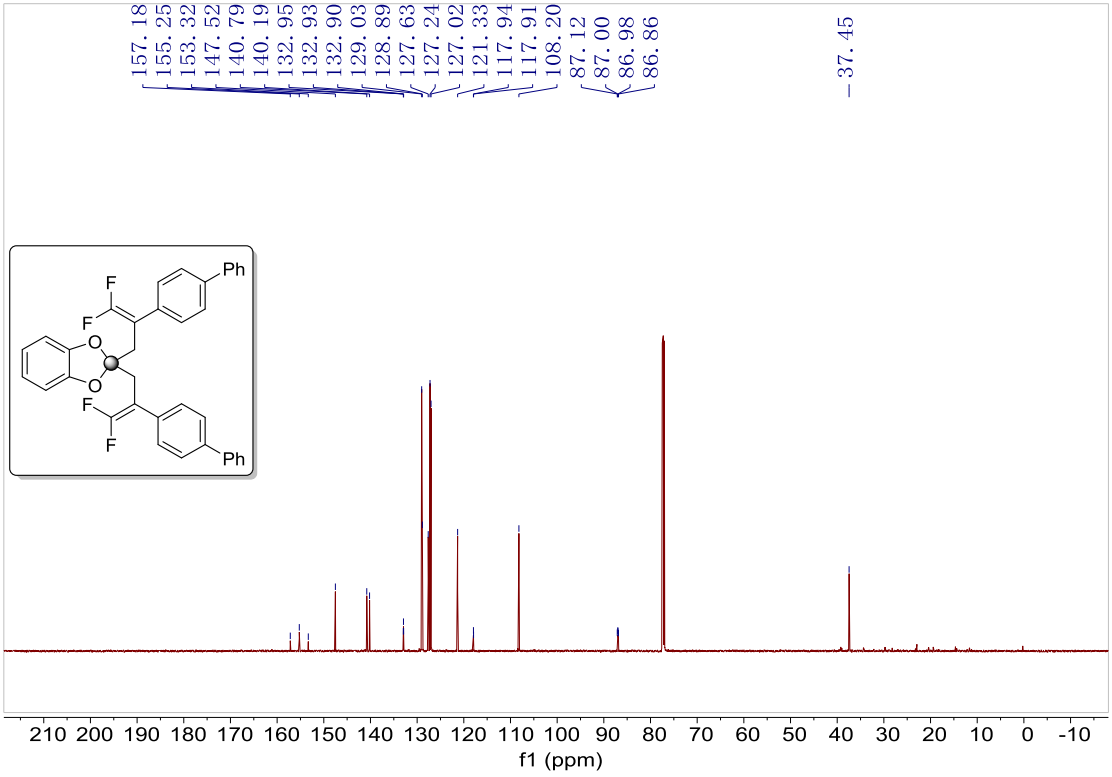
^{13}C NMR of 3a (150 MHz, $CDCl_3$)



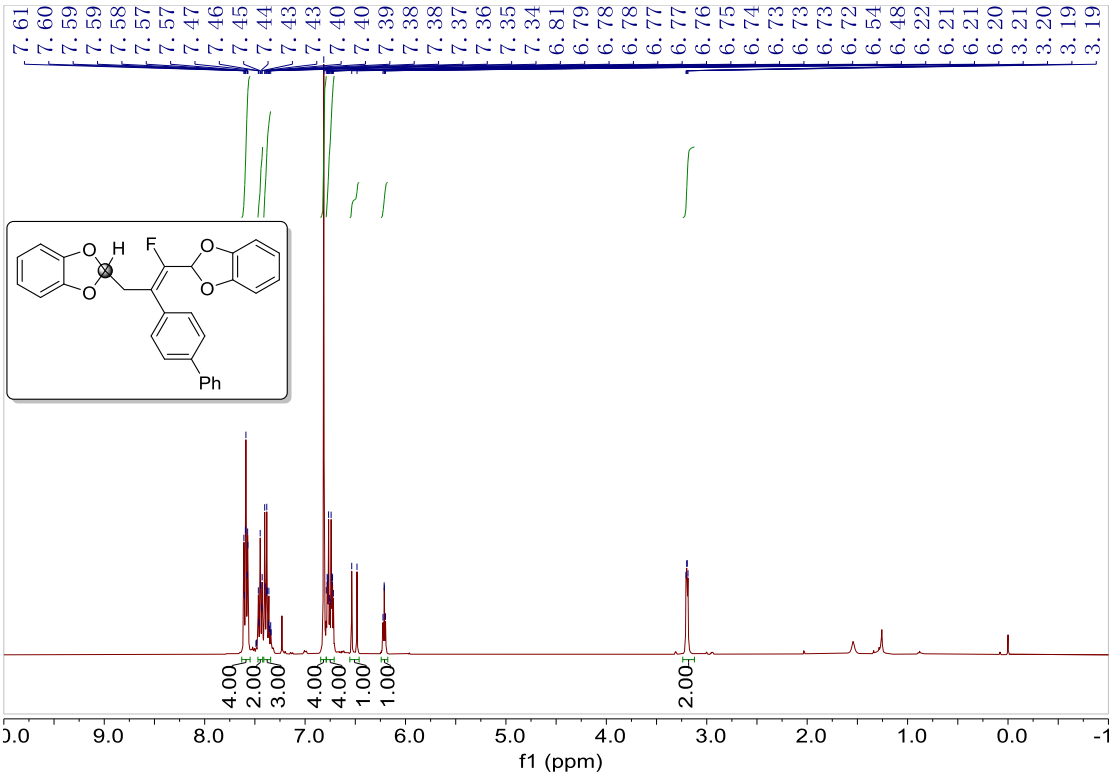
^{1}H NMR of 3a′ (400 MHz, $CDCl_3$)



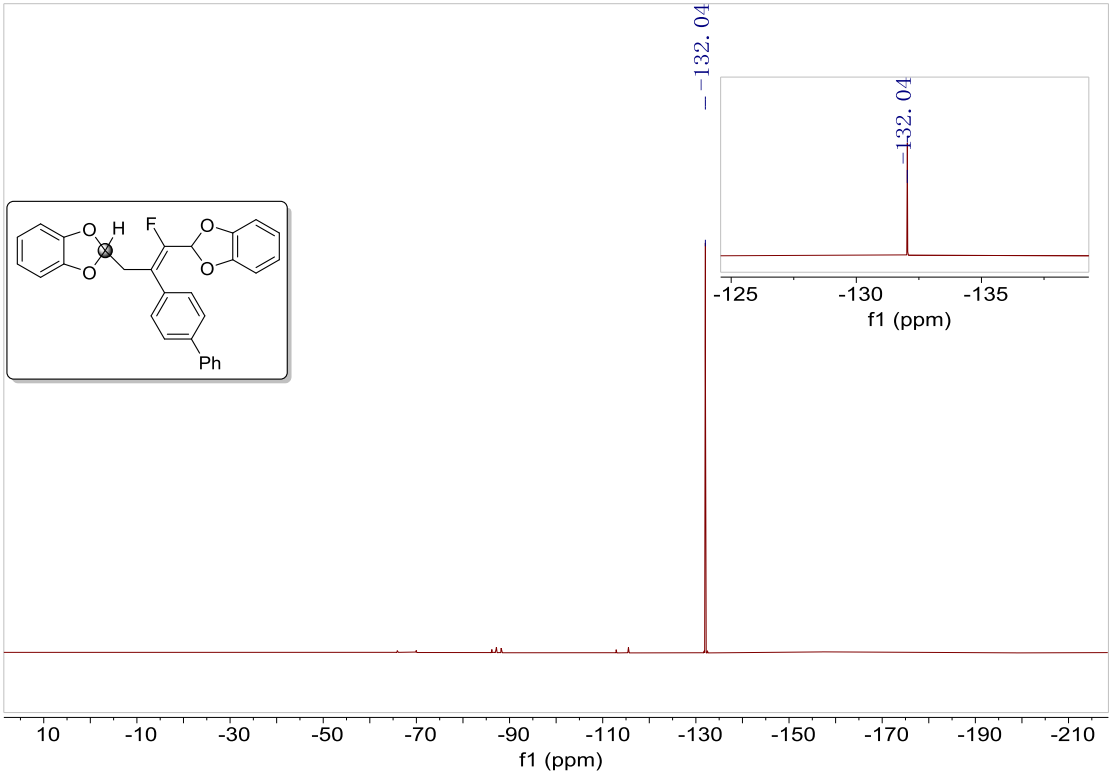
^{19}F NMR of 3a′ (376 MHz, $CDCl_3$)



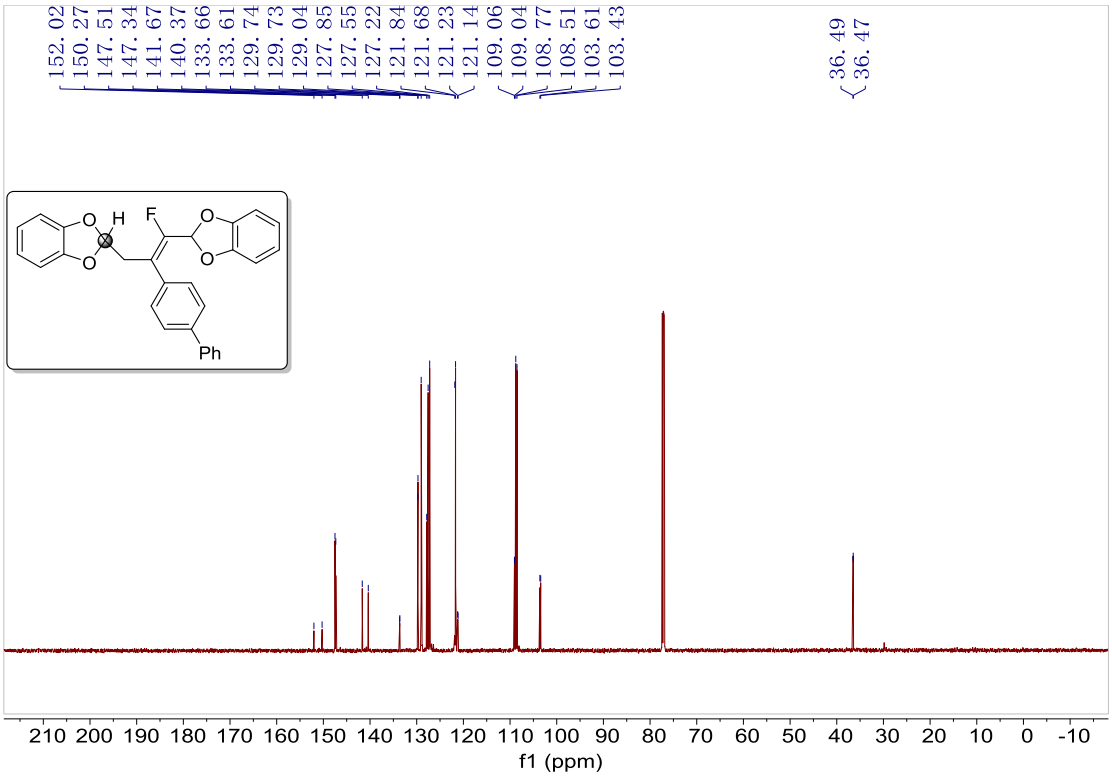
^{13}C NMR of 3a′ (150 MHz, $CDCl_3$)



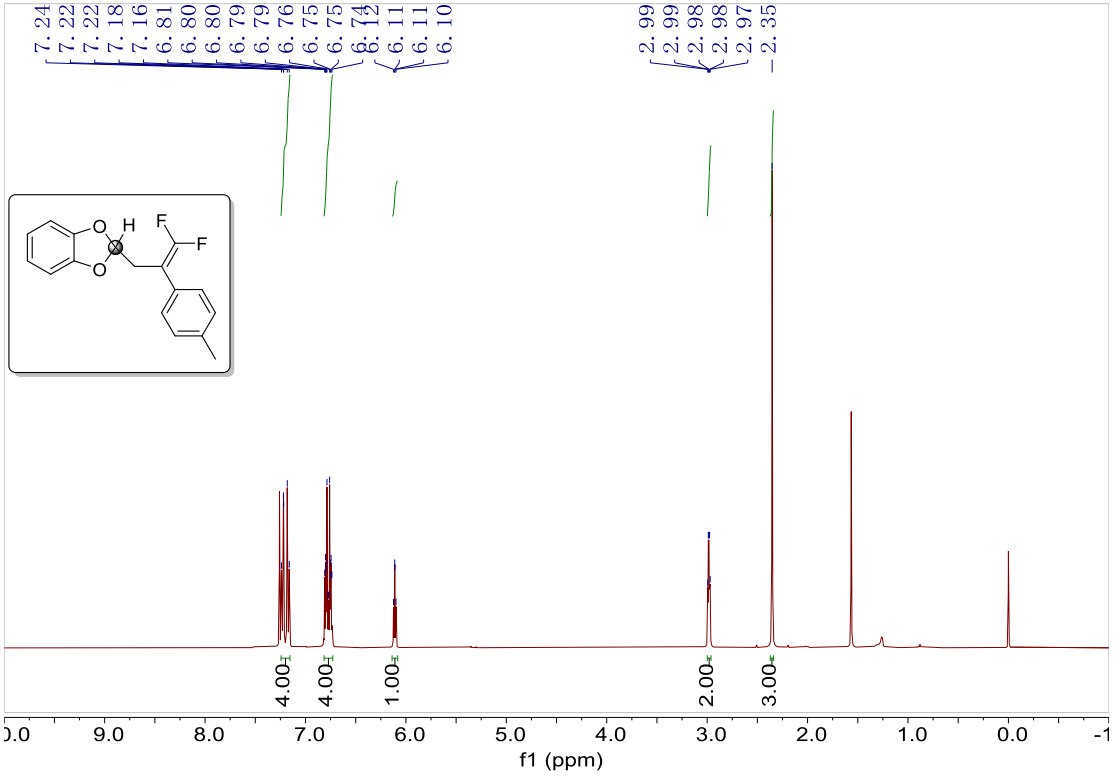
^{1}H NMR of 3a″ (400 MHz, $CDCl_3$)



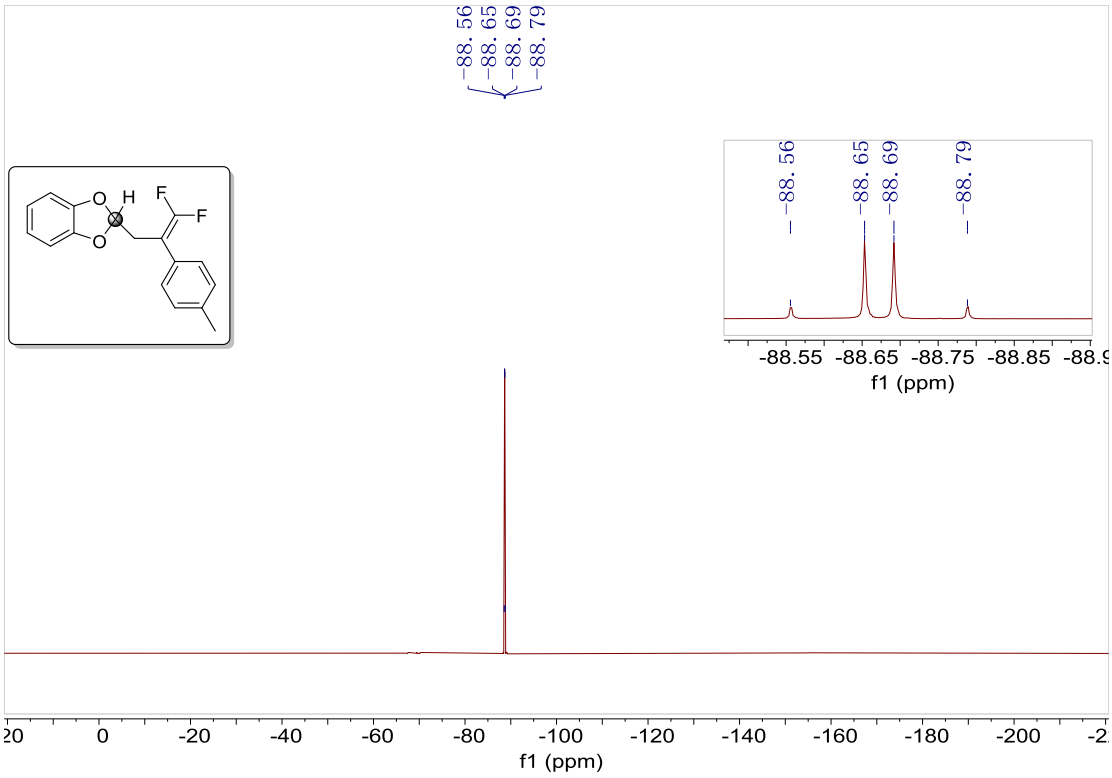
^{19}F NMR of 3a″ (376 MHz, $CDCl_3$)



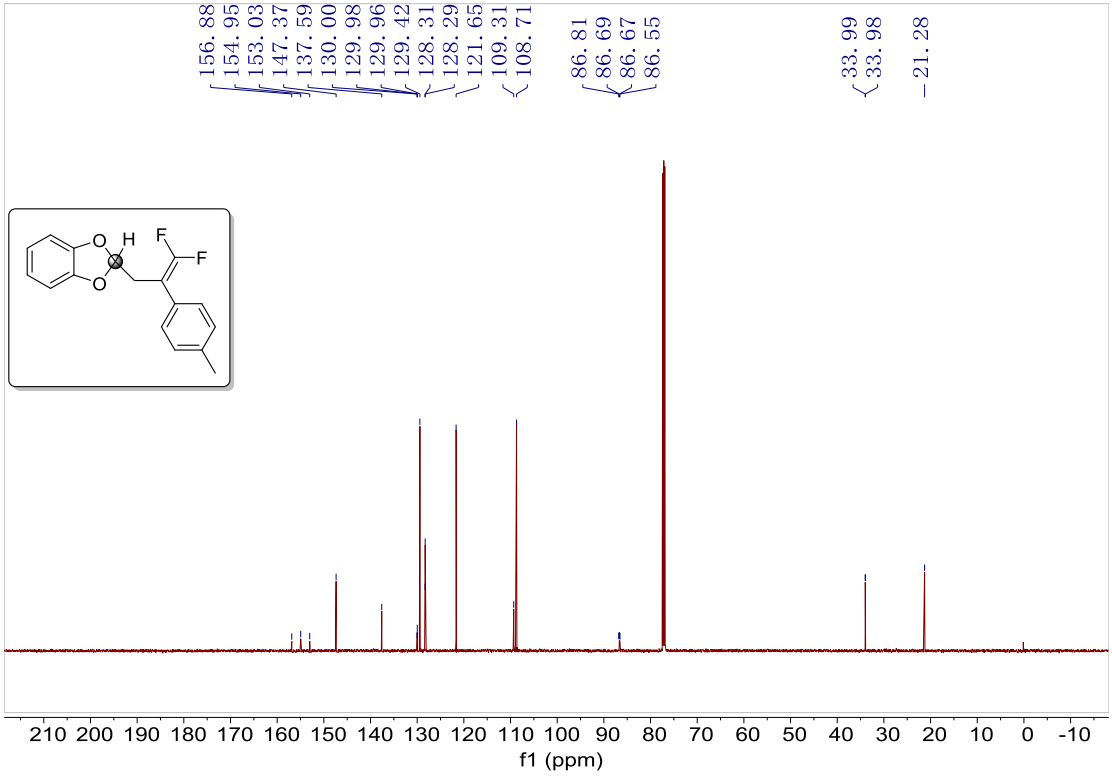
^{13}C NMR of 3a′′ (150 MHz, $CDCl_3$)



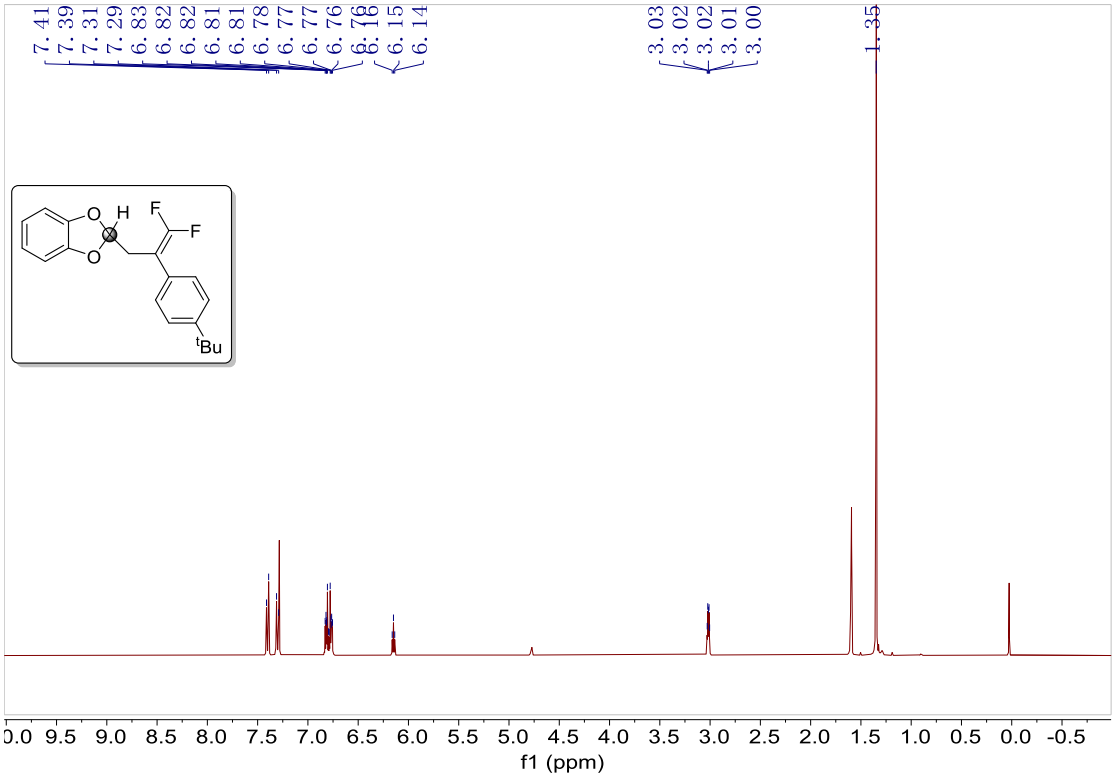
^{1}H NMR of 3b (400 MHz, $CDCl_3$)



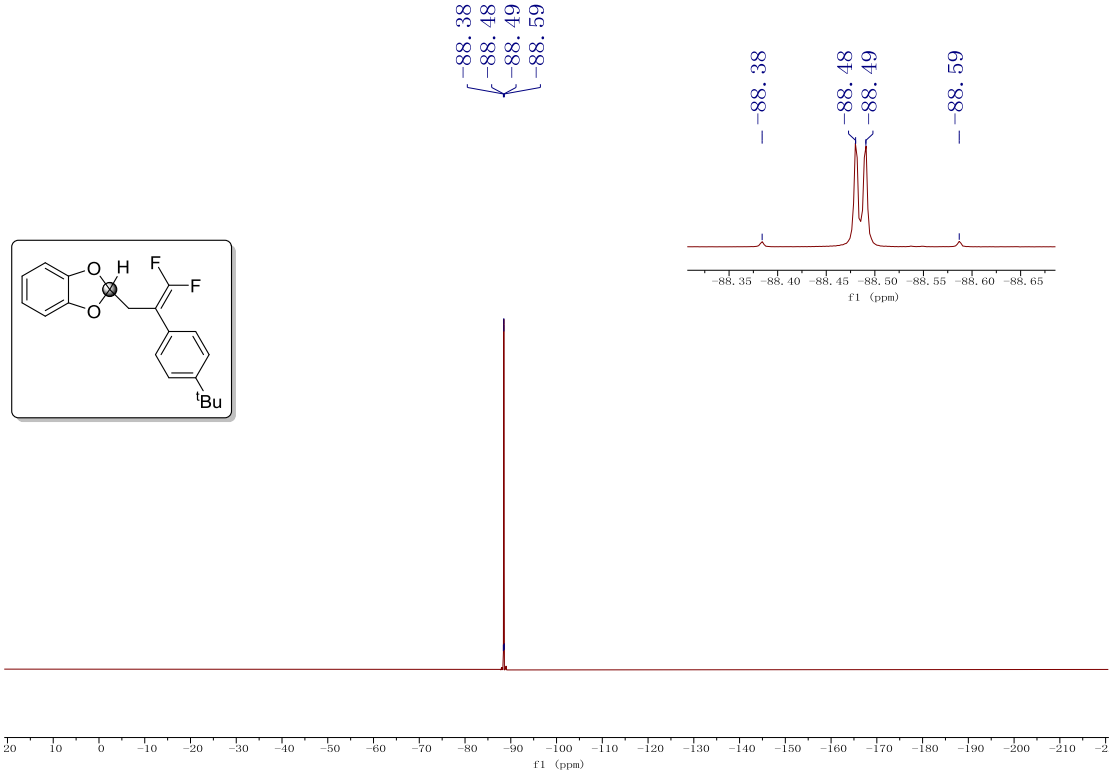
^{19}F NMR of 3b (376 MHz, $CDCl_3$)



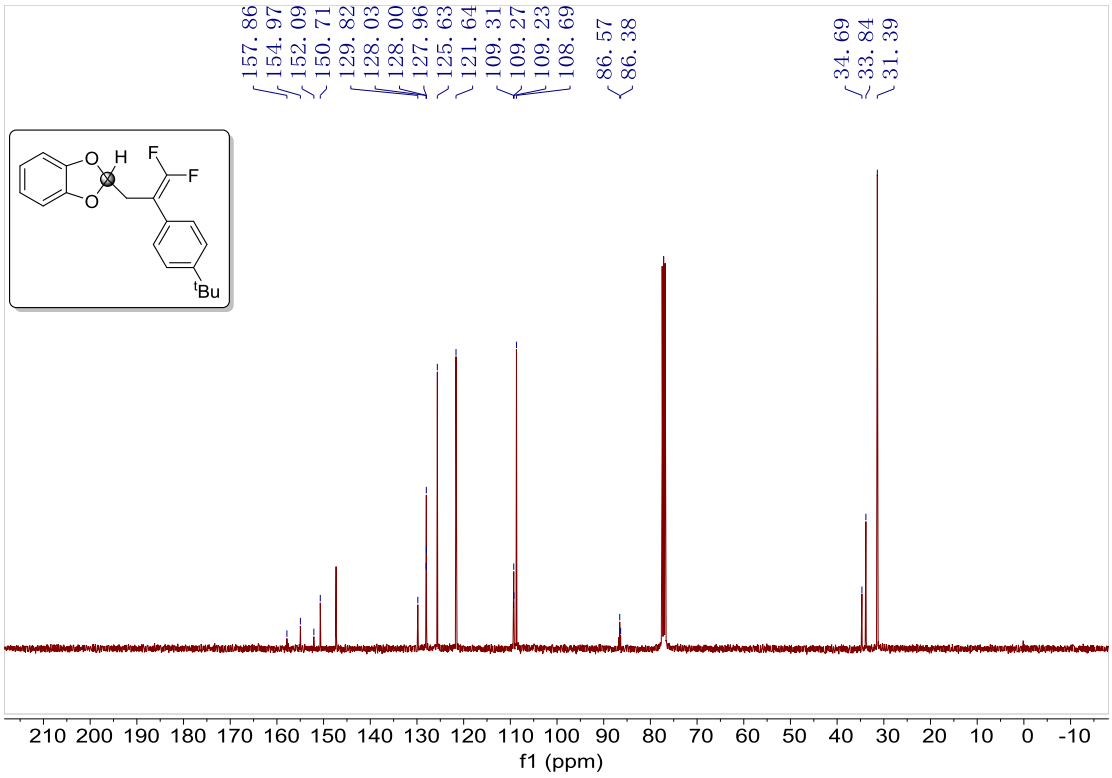
^{13}C NMR of 3b (150 MHz, $CDCl_3$)



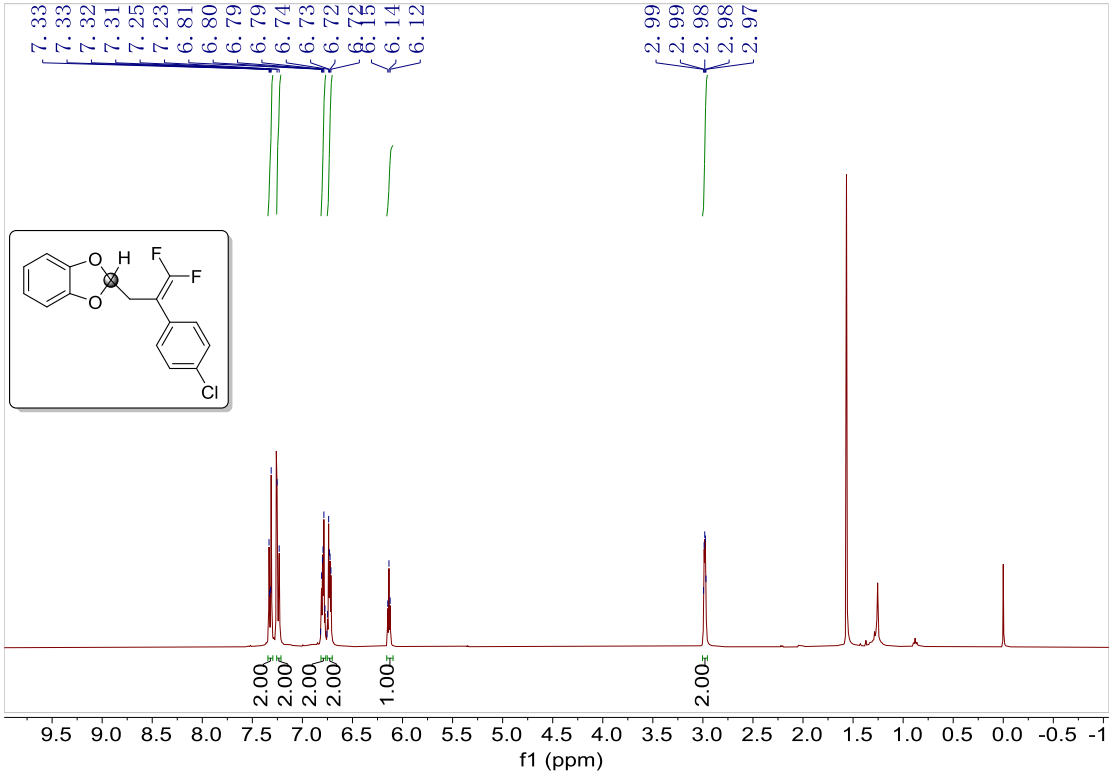
^{1}H NMR of 3c (400 MHz, $CDCl_3$)



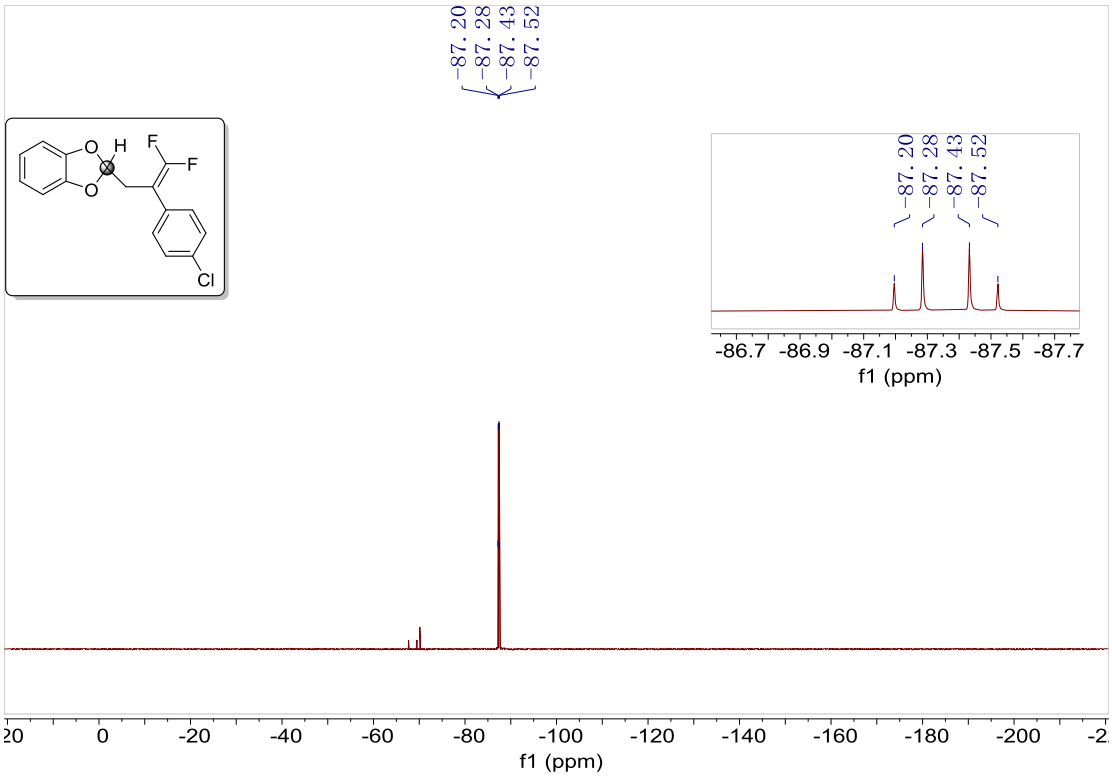
^{19}F NMR of 3c (376 MHz, $CDCl_3$)



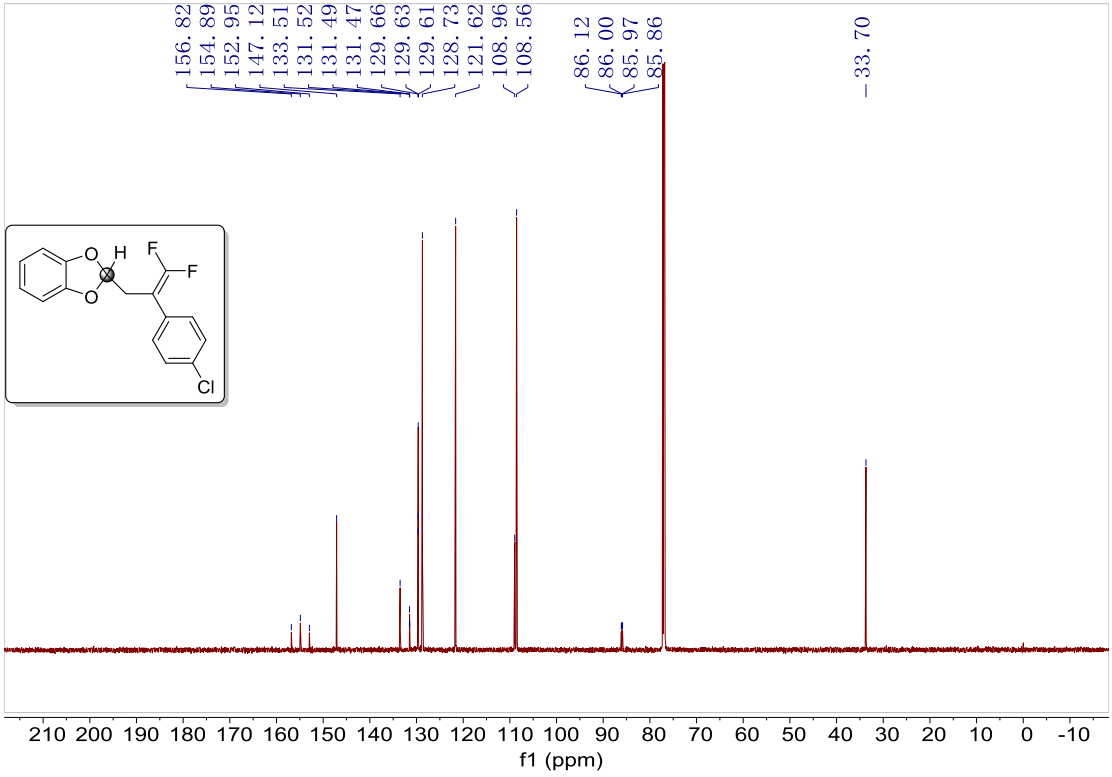
^{13}C NMR of 3c (100 MHz, $CDCl_3$)



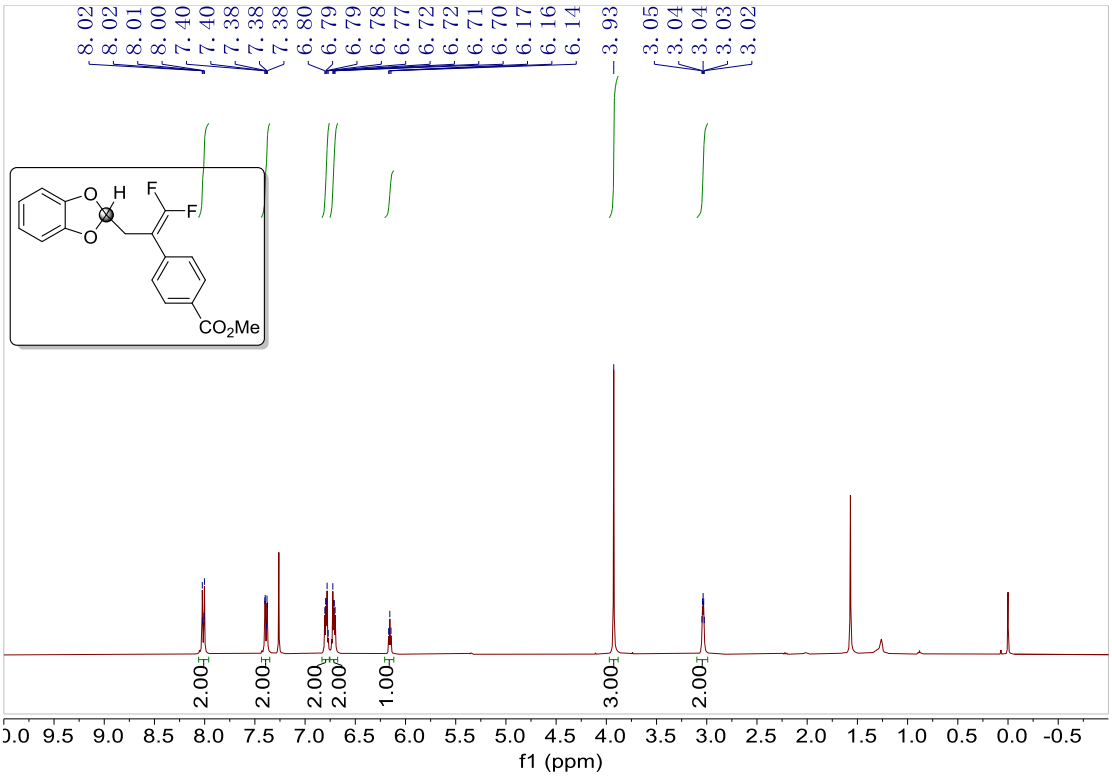
^{1}H NMR of 3d (400 MHz, $CDCl_3$)



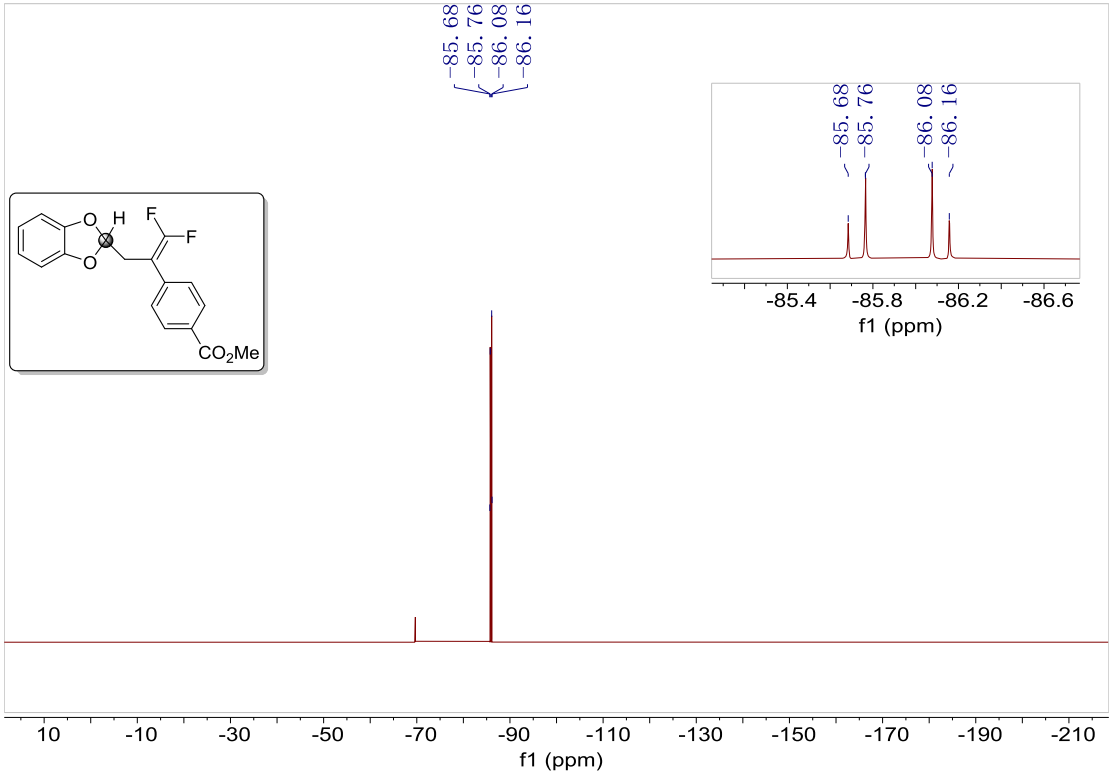
^{19}F NMR of 3d (376 MHz, $CDCl_3$)



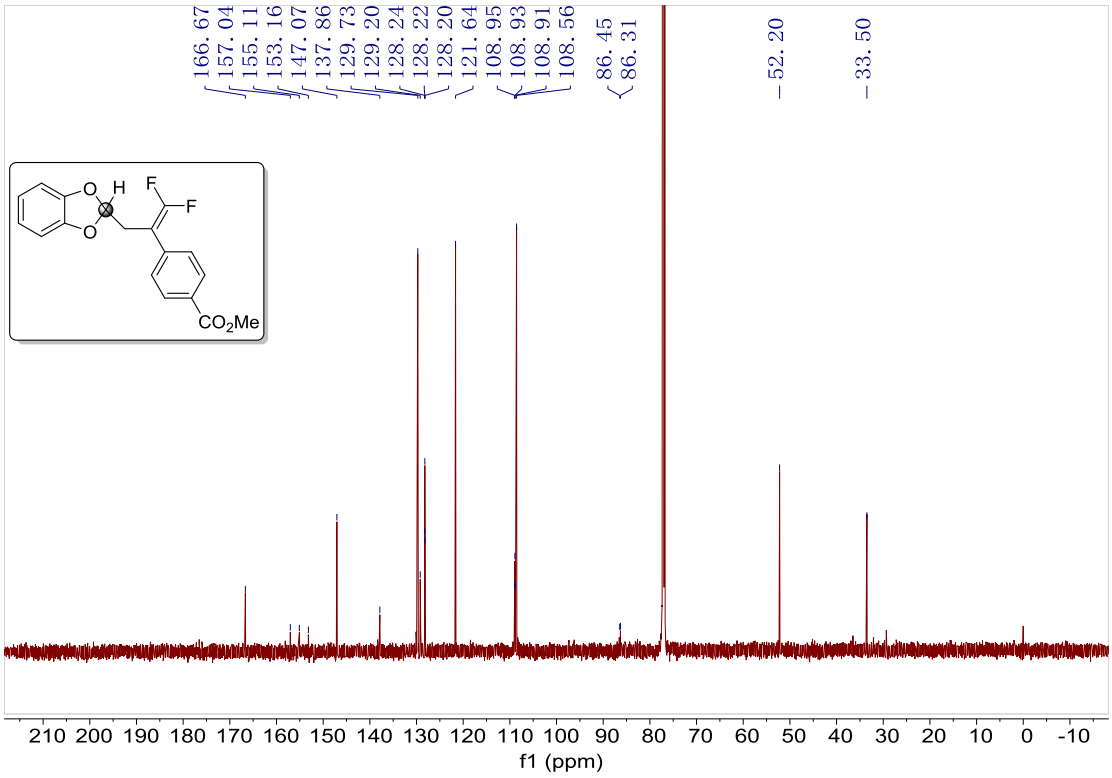
^{13}C NMR of 3d (150 MHz, $CDCl_3$)



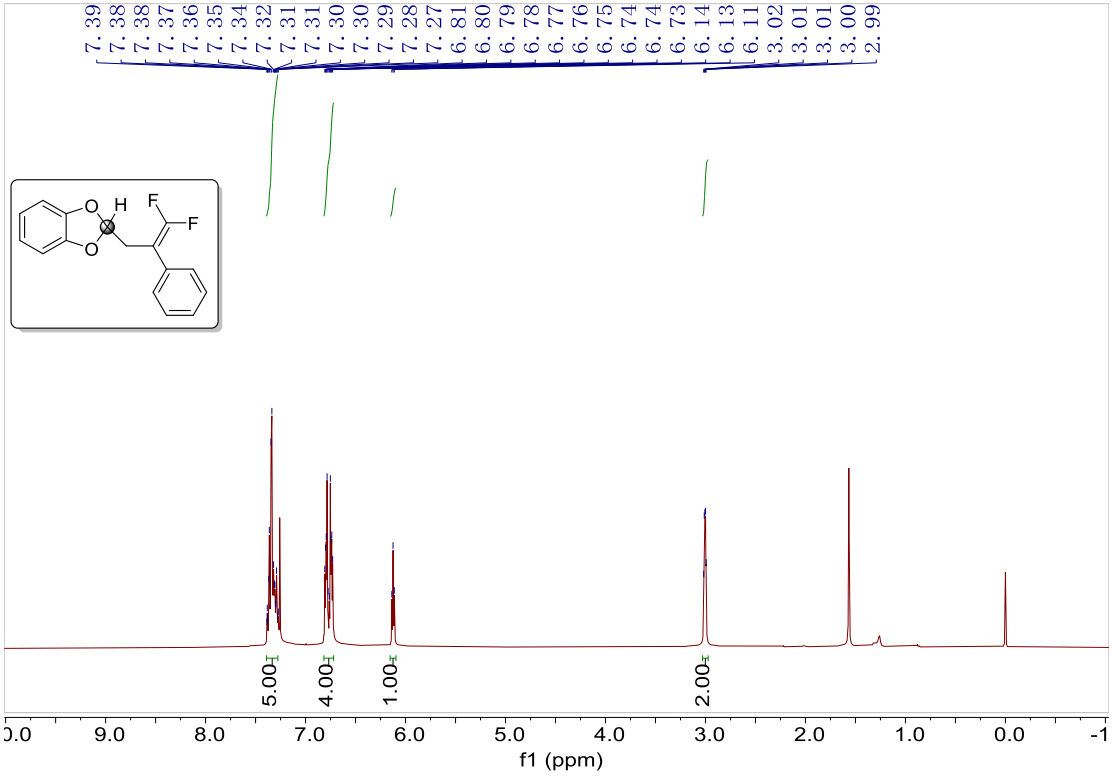
^{1}H NMR of 3e (400 MHz, $CDCl_3$)



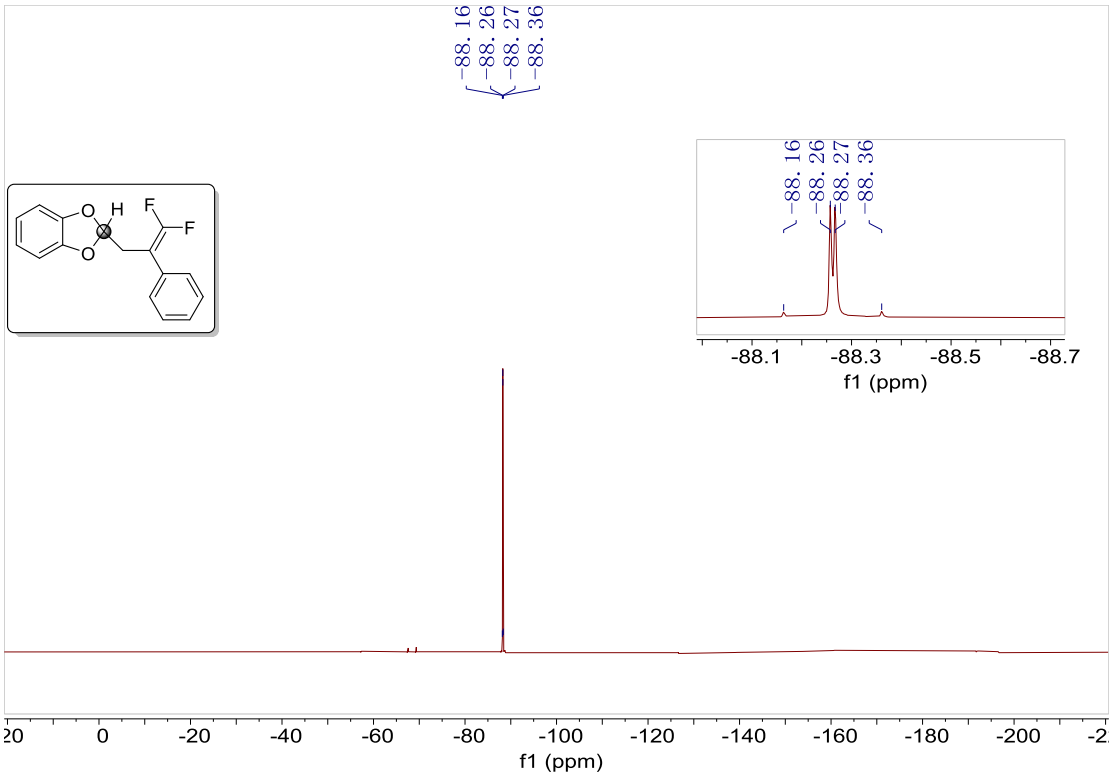
^{19}F NMR of 3e (376 MHz, $CDCl_3$)



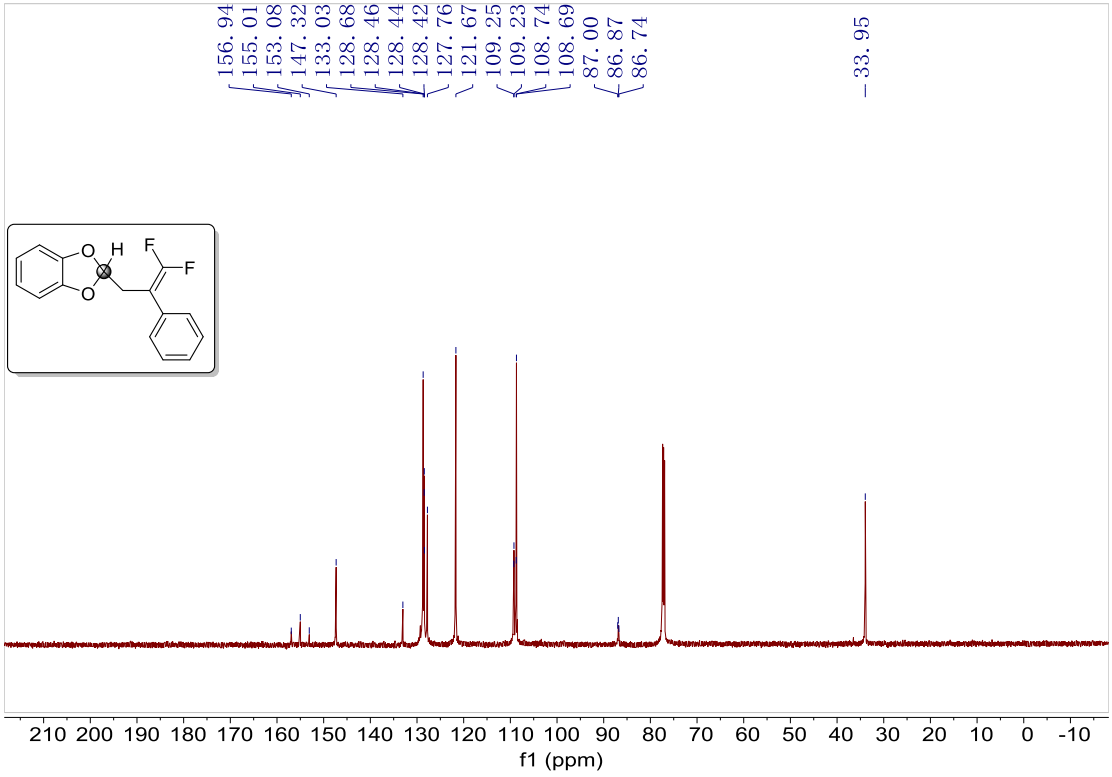
^{13}C NMR of 3e (150 MHz, $CDCl_3$)



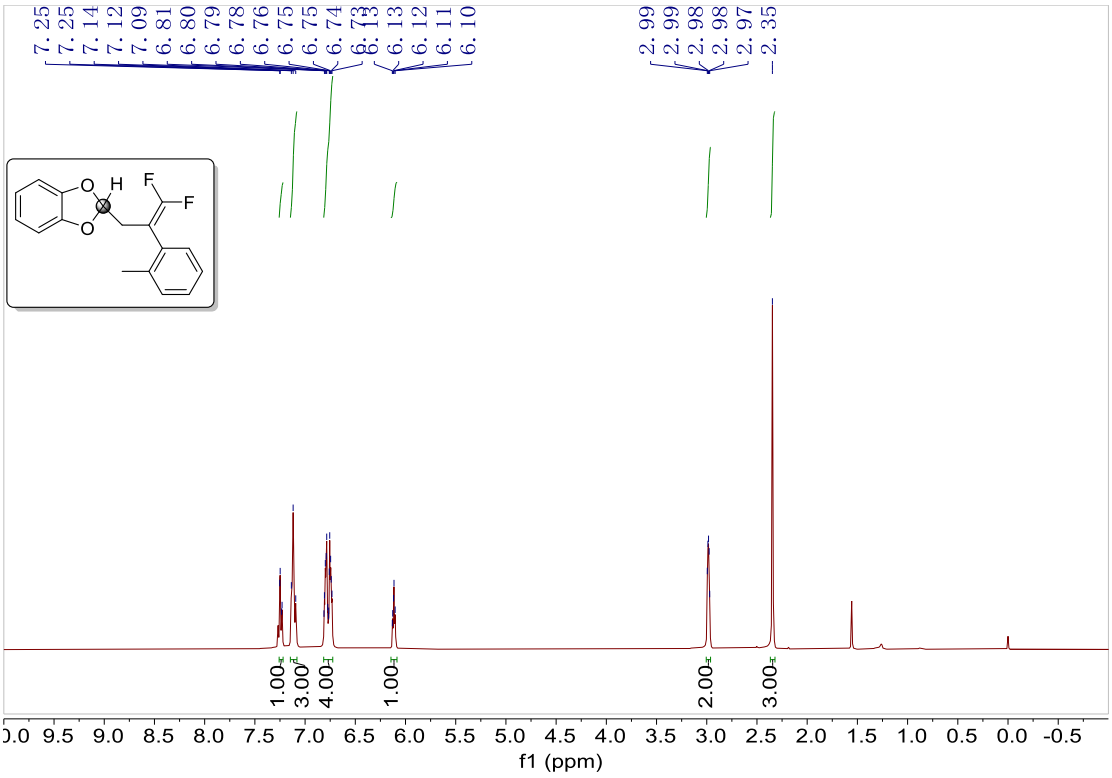
^{1}H NMR of 3f (400 MHz, $CDCl_3$)



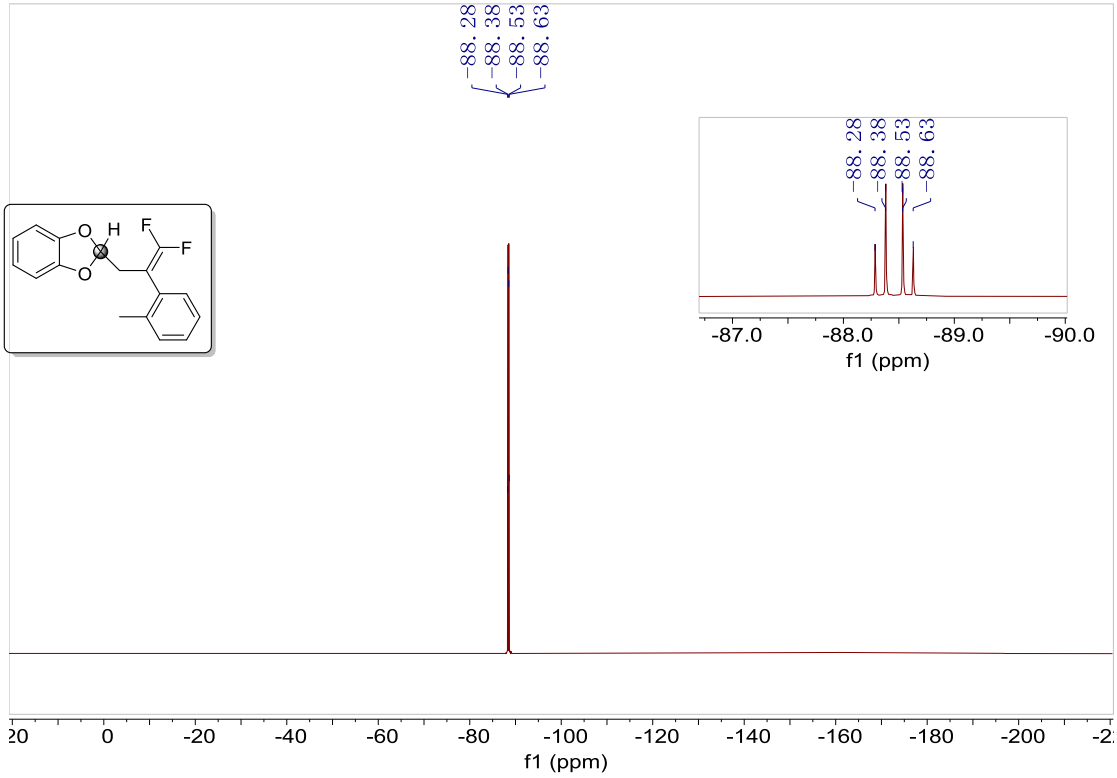
19F NMR of 3f (376 MHz, $CDCl_3$)



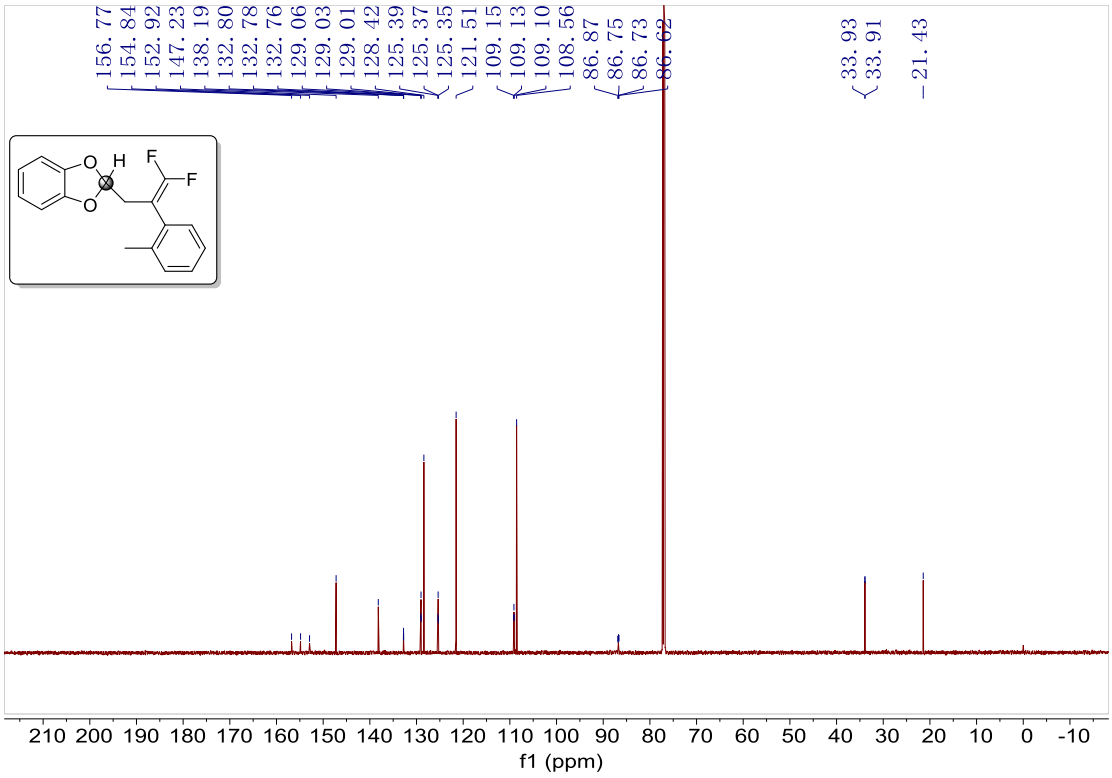
^{13}C NMR of 3f (150 MHz, $CDCl_3$)



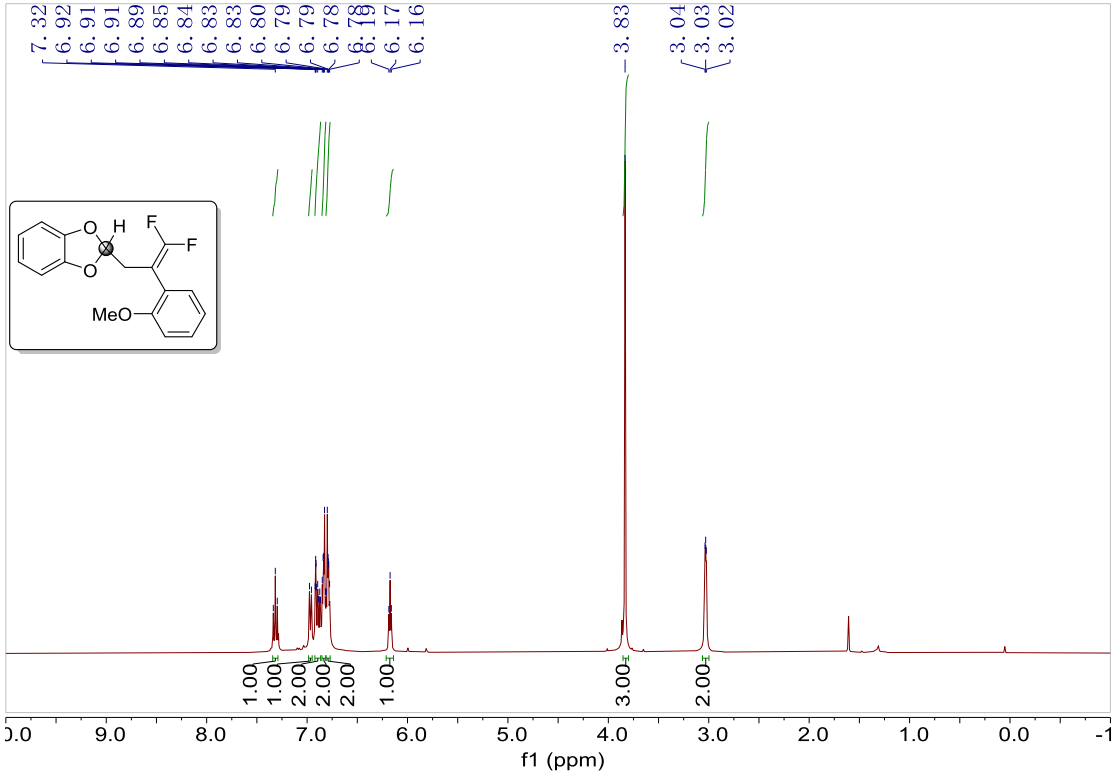
^{1}H NMR of 3g (400 MHz, $CDCl_3$)



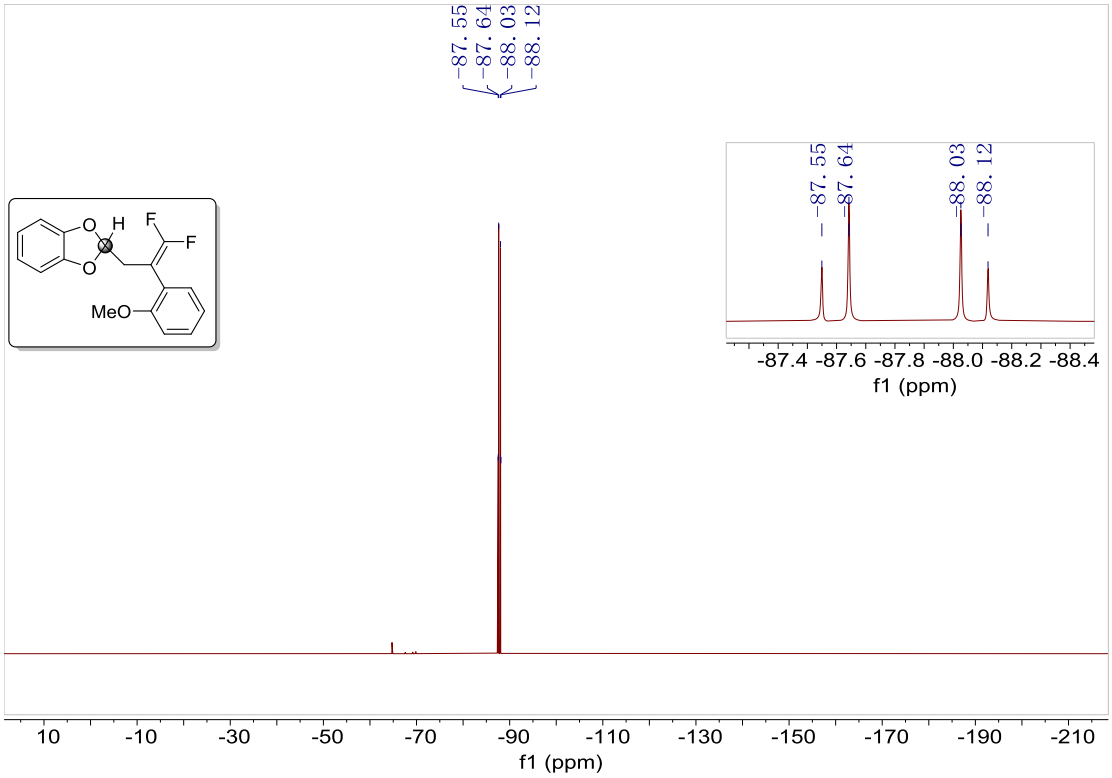
^{19}F NMR of 3g (376 MHz, $CDCl_3$)



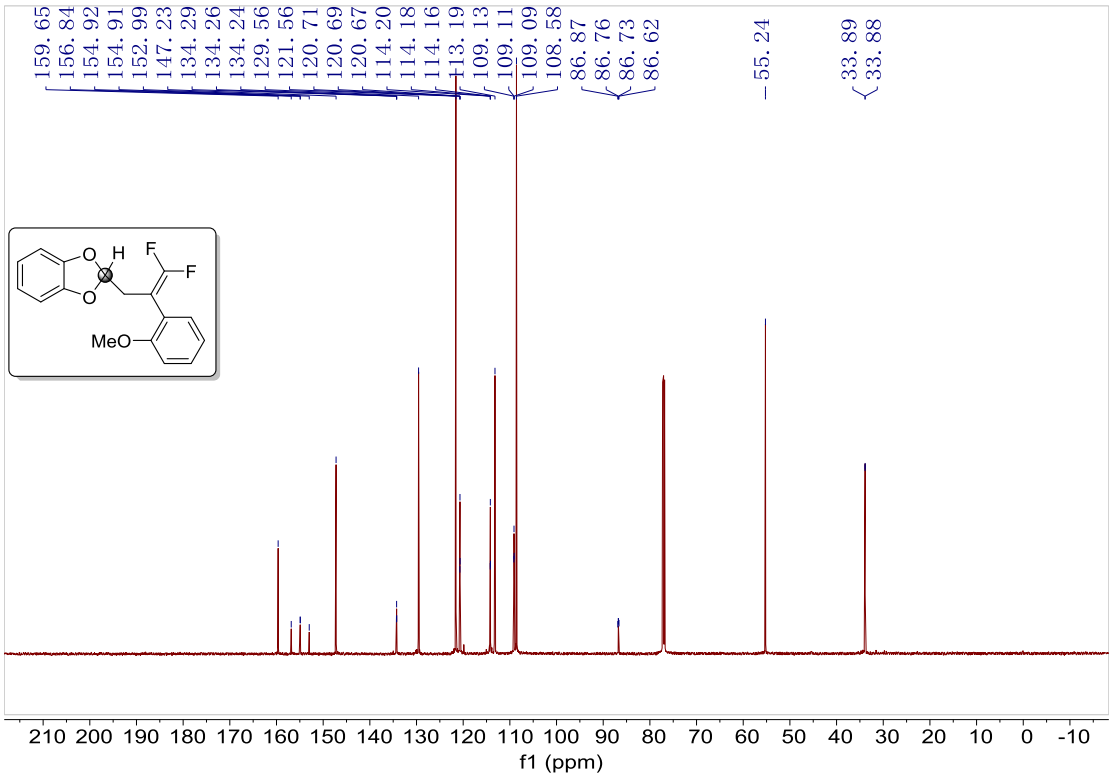
^{13}C NMR of 3g (150 MHz, $CDCl_3$)



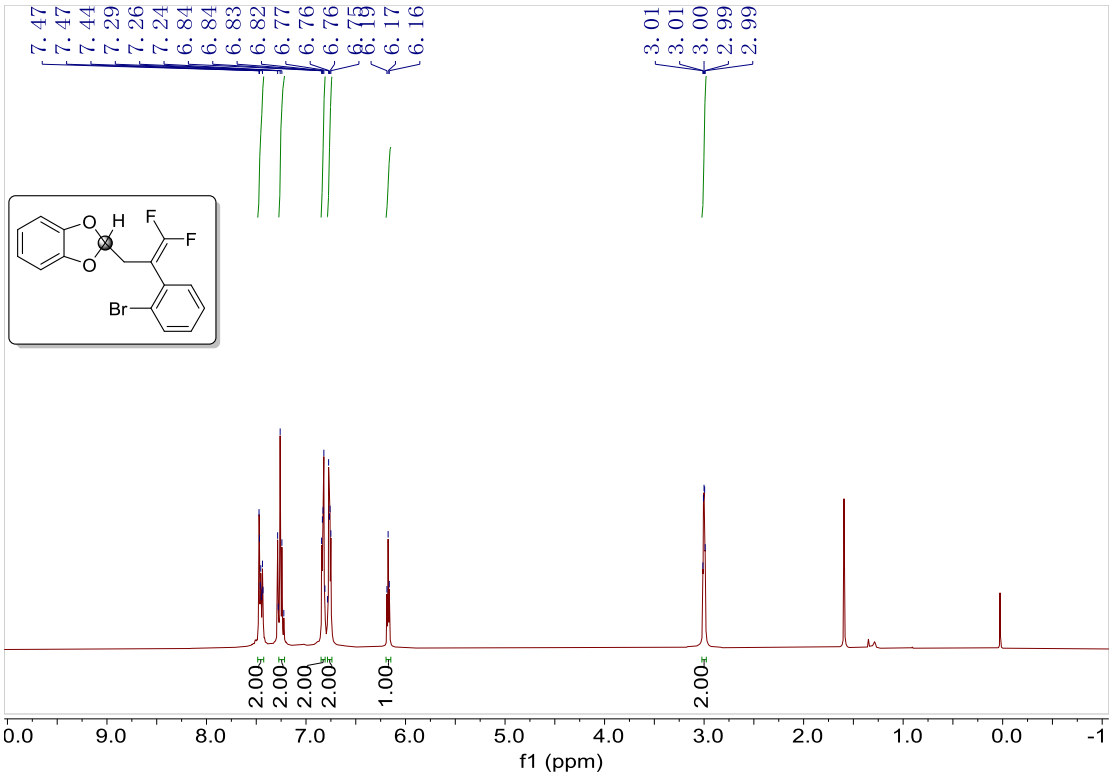
^{1}H NMR of 3h (400 MHz, $CDCl_3$)



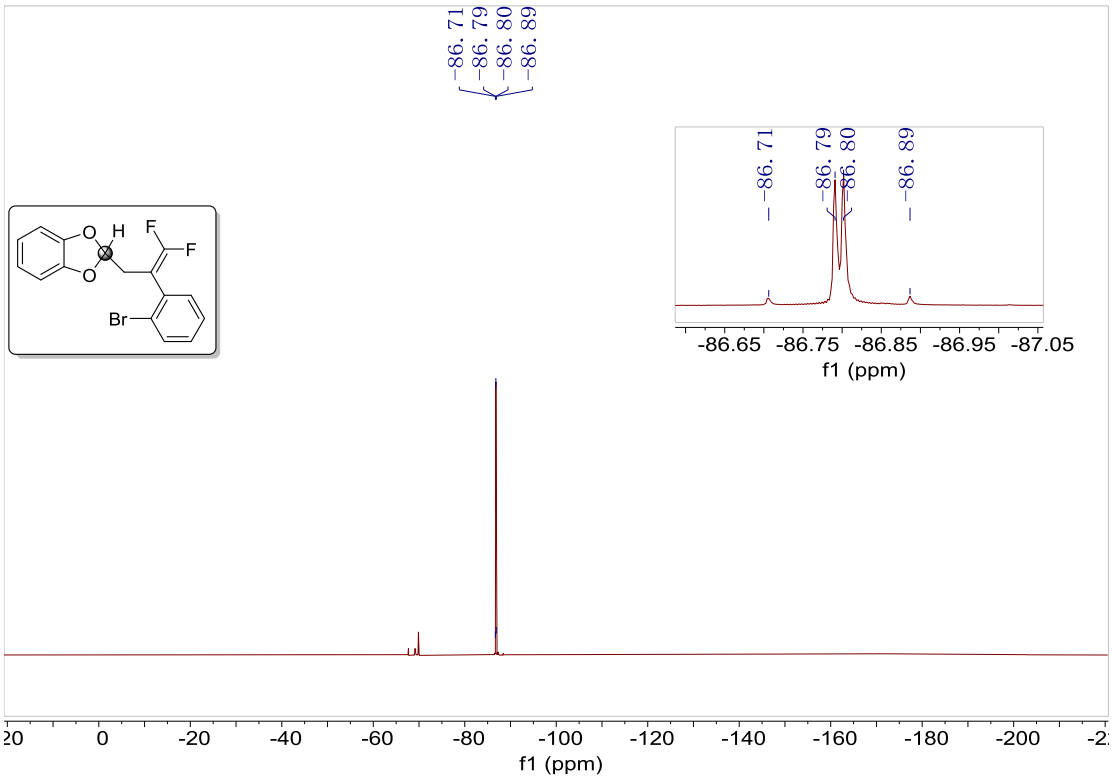
^{19}F NMR of 3h (376 MHz, $CDCl_3$)



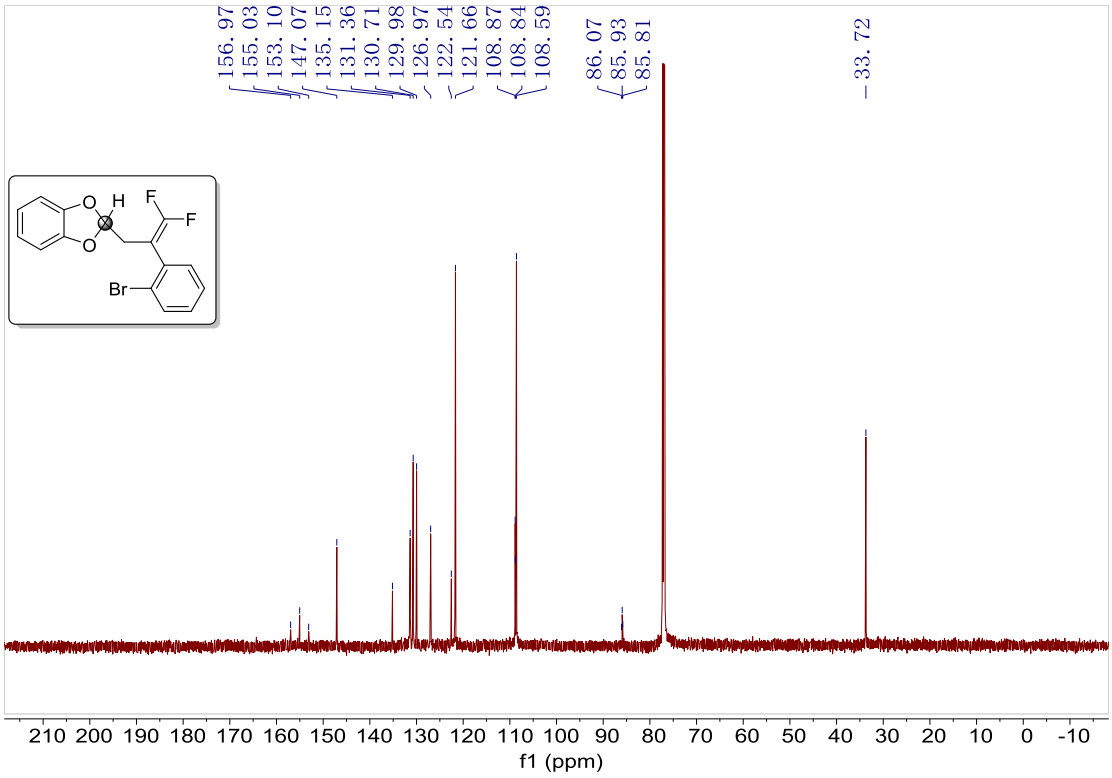
^{13}C NMR of 3h (150 MHz, $CDCl_3$)



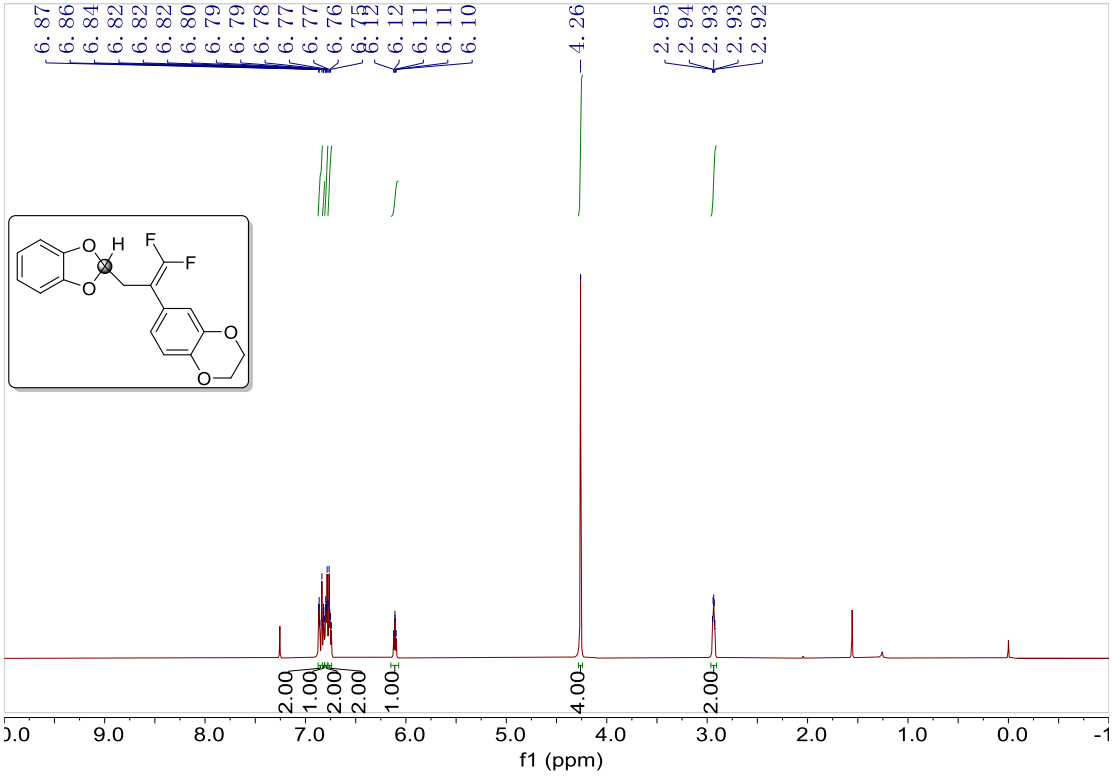
^{1}H NMR of 3i (400 MHz, $CDCl_3$)



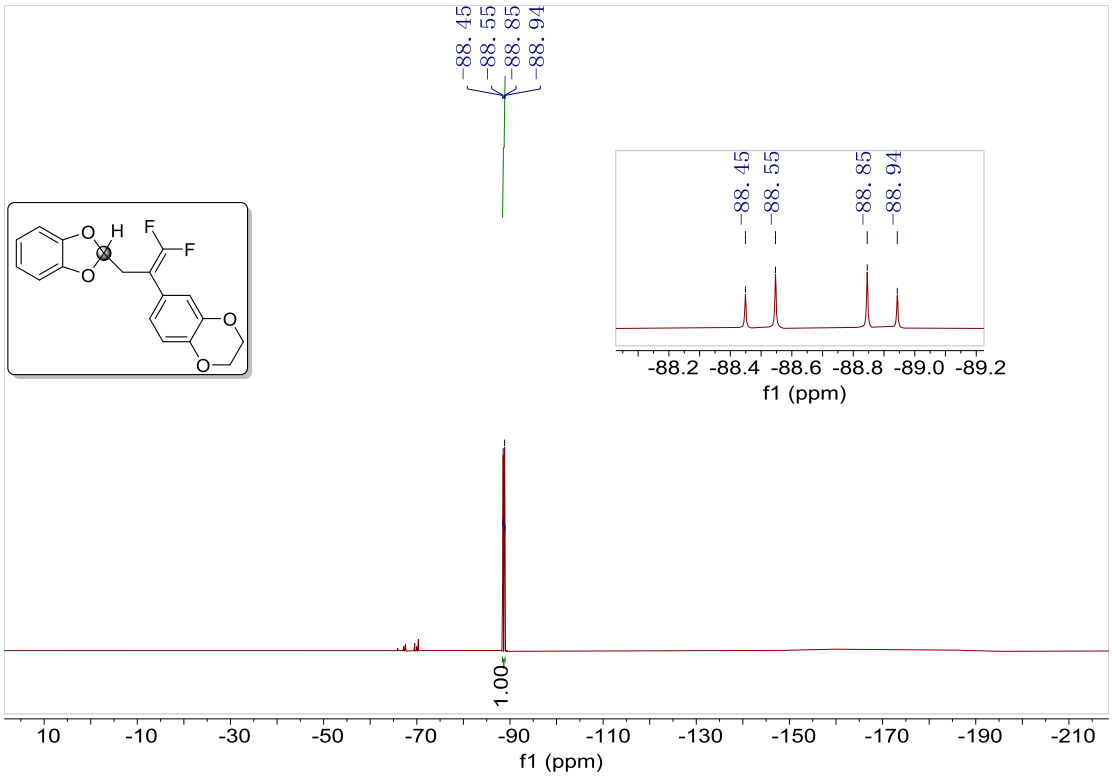
^{19}F NMR of 3i (376 MHz, $CDCl_3$)



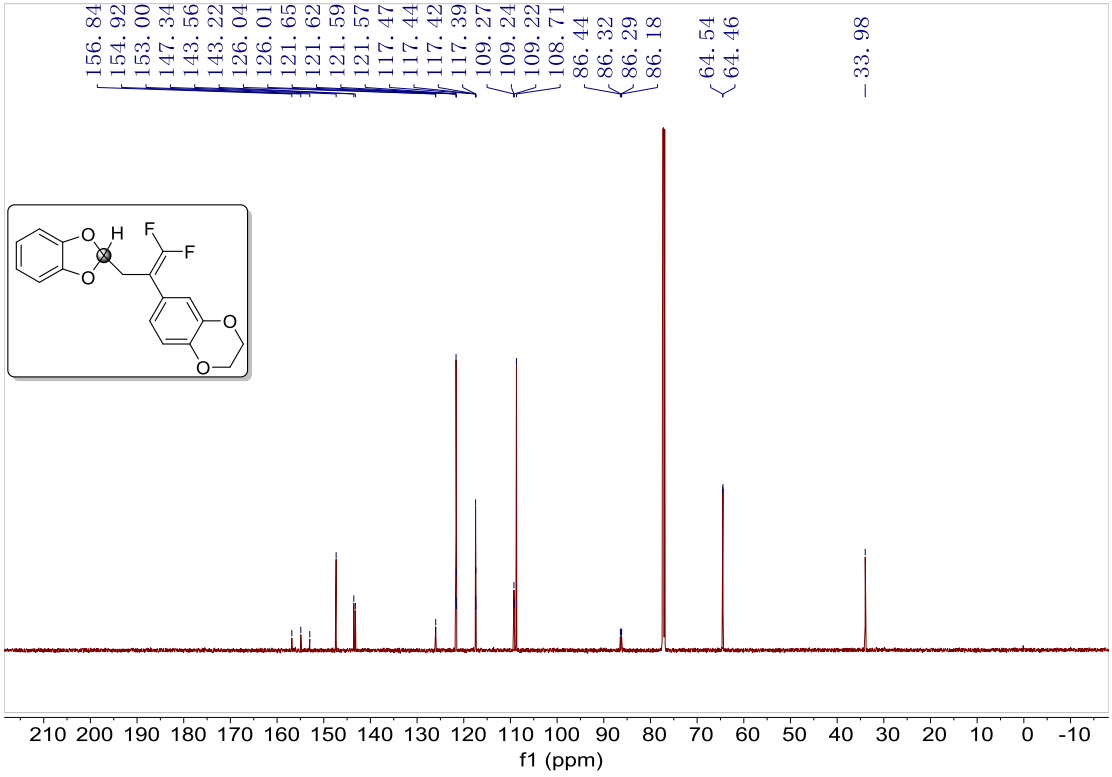
^{13}C NMR of 3i (150 MHz, $CDCl_3$)



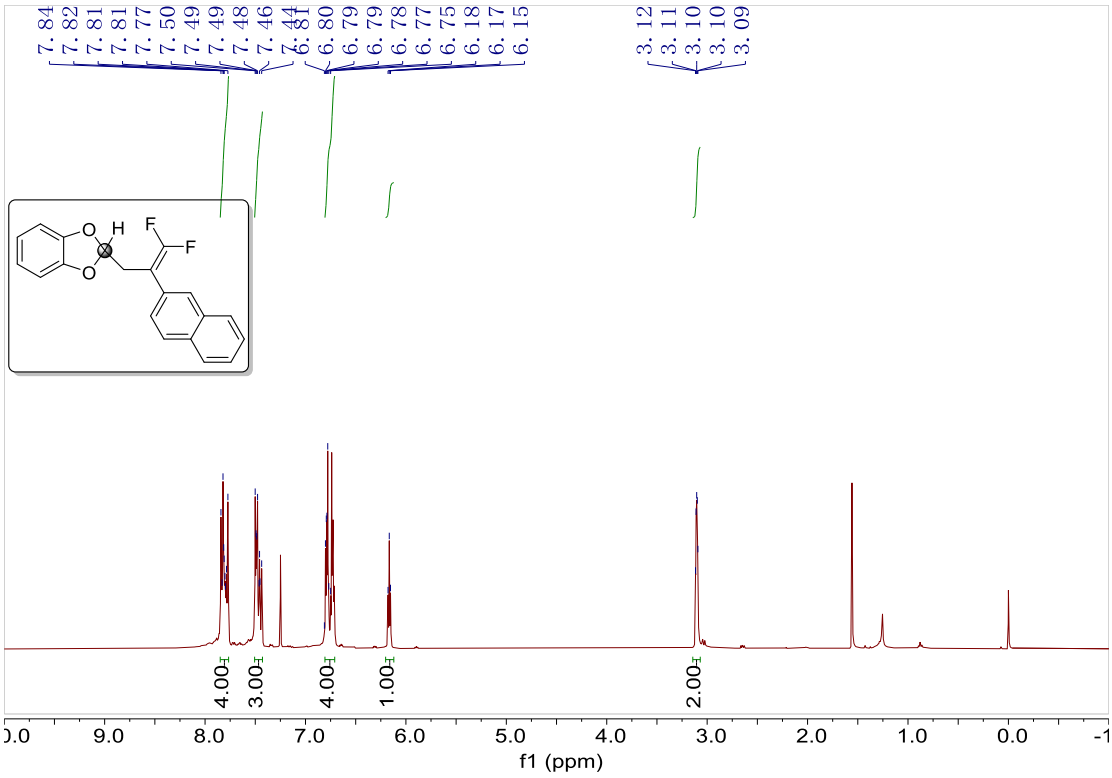
^{1}H NMR of 3j (400 MHz, $CDCl_3$)



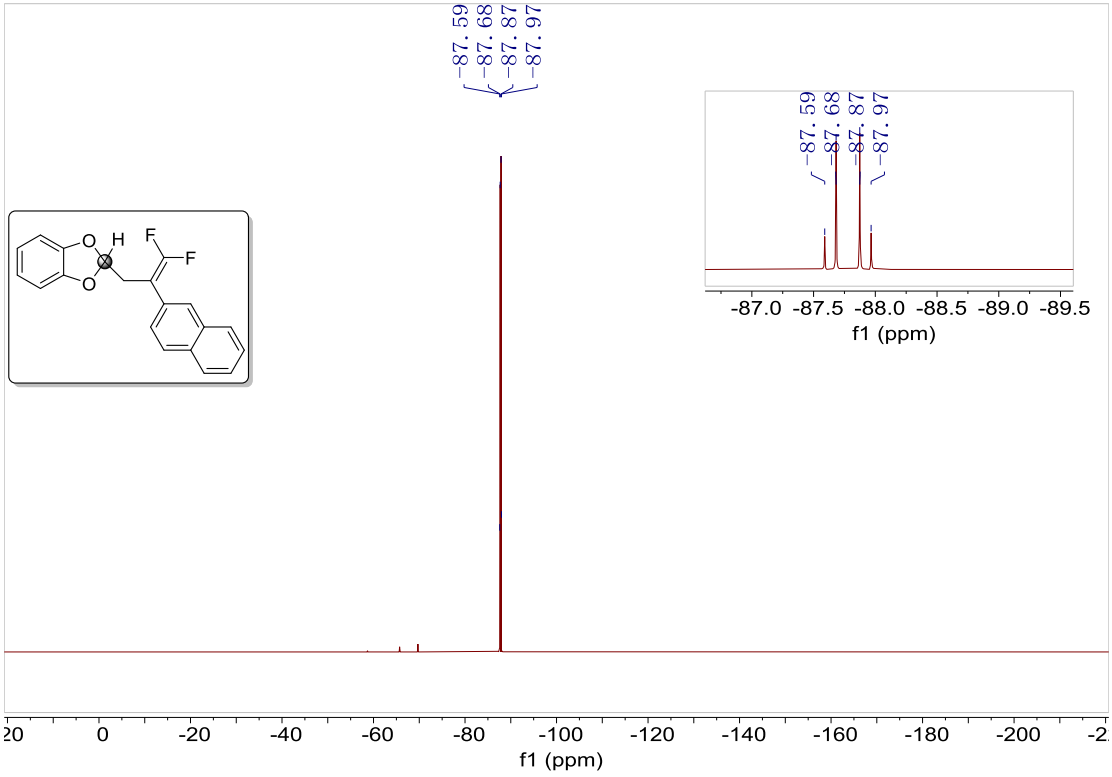
^{19}F NMR of 3j (376 MHz, $CDCl_3$)



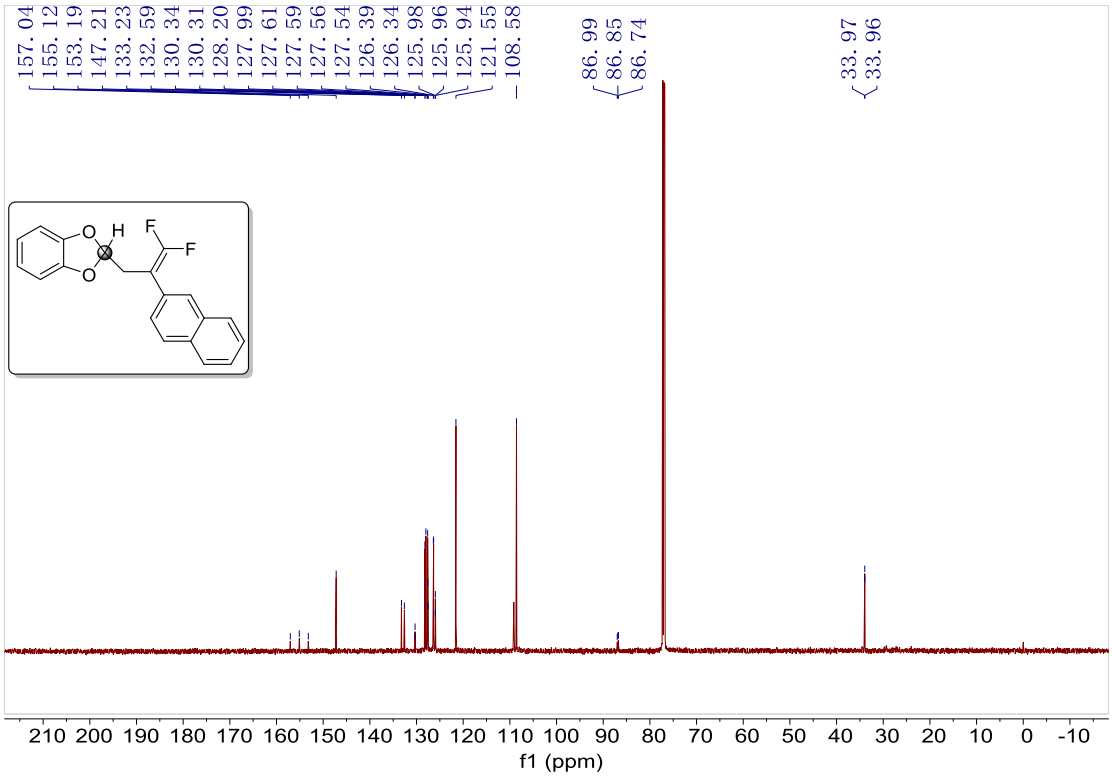
^{13}C NMR of 3j (150 MHz, $CDCl_3$)



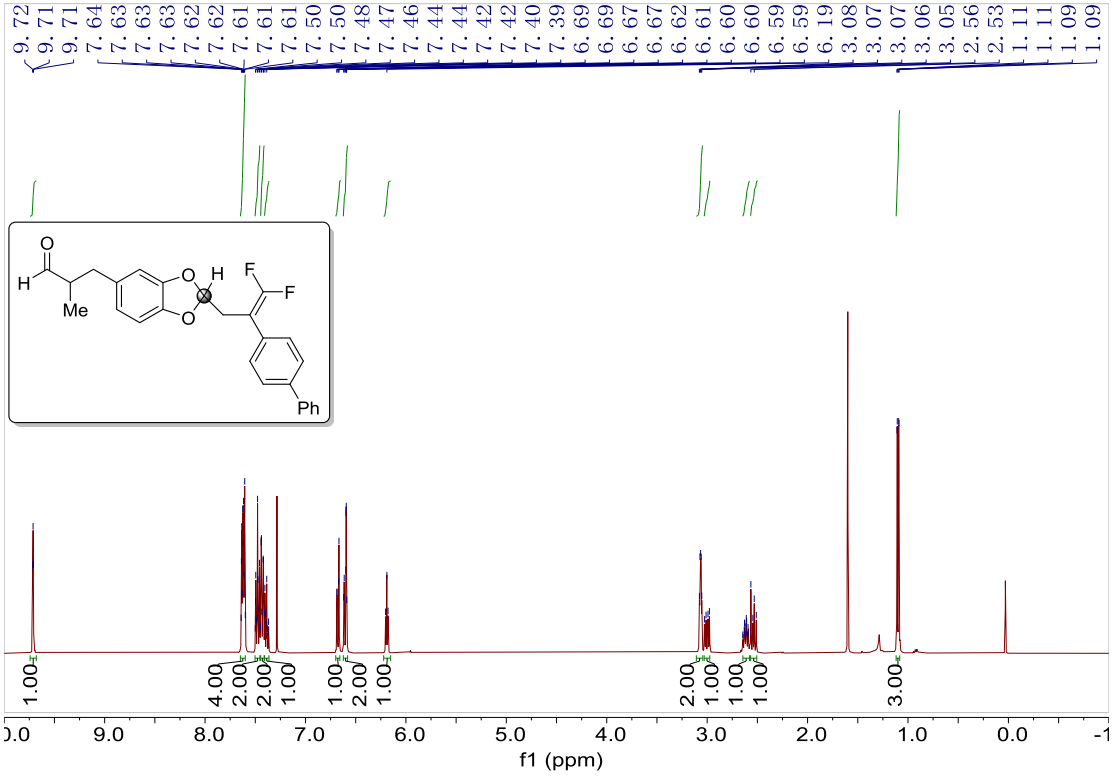
^{1}H NMR of 3k (400 MHz, $CDCl_3$)



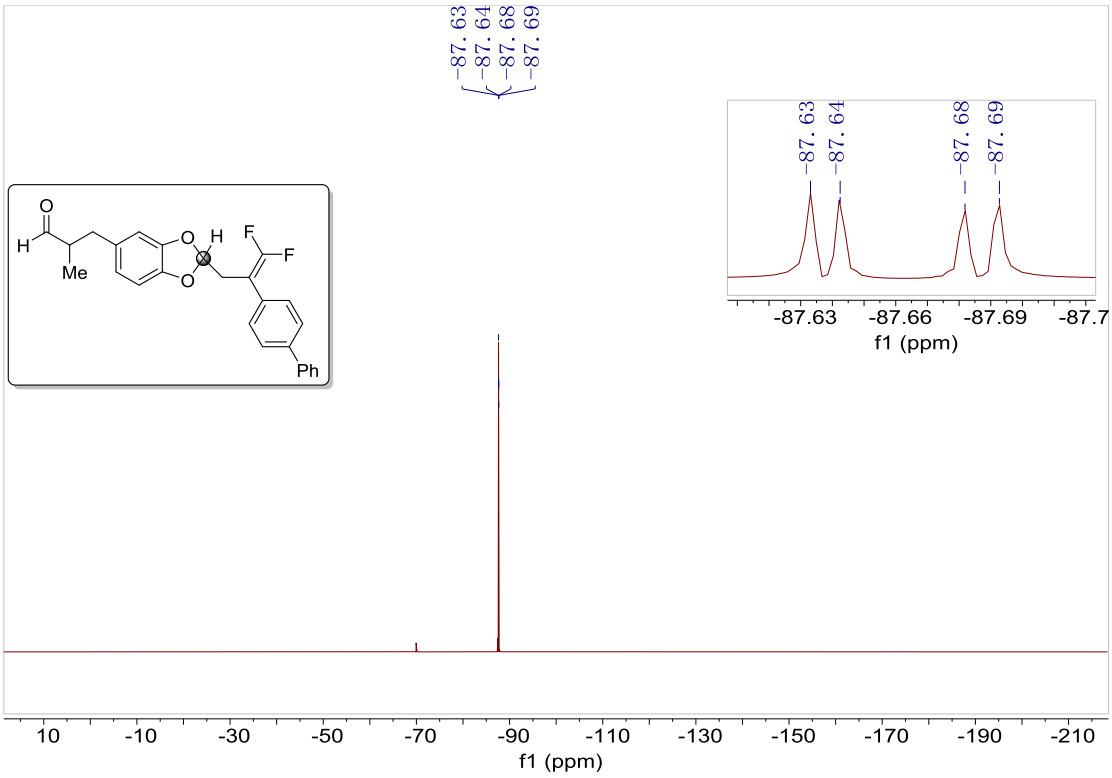
^{19}F NMR of 3k (376 MHz, $CDCl_3$)



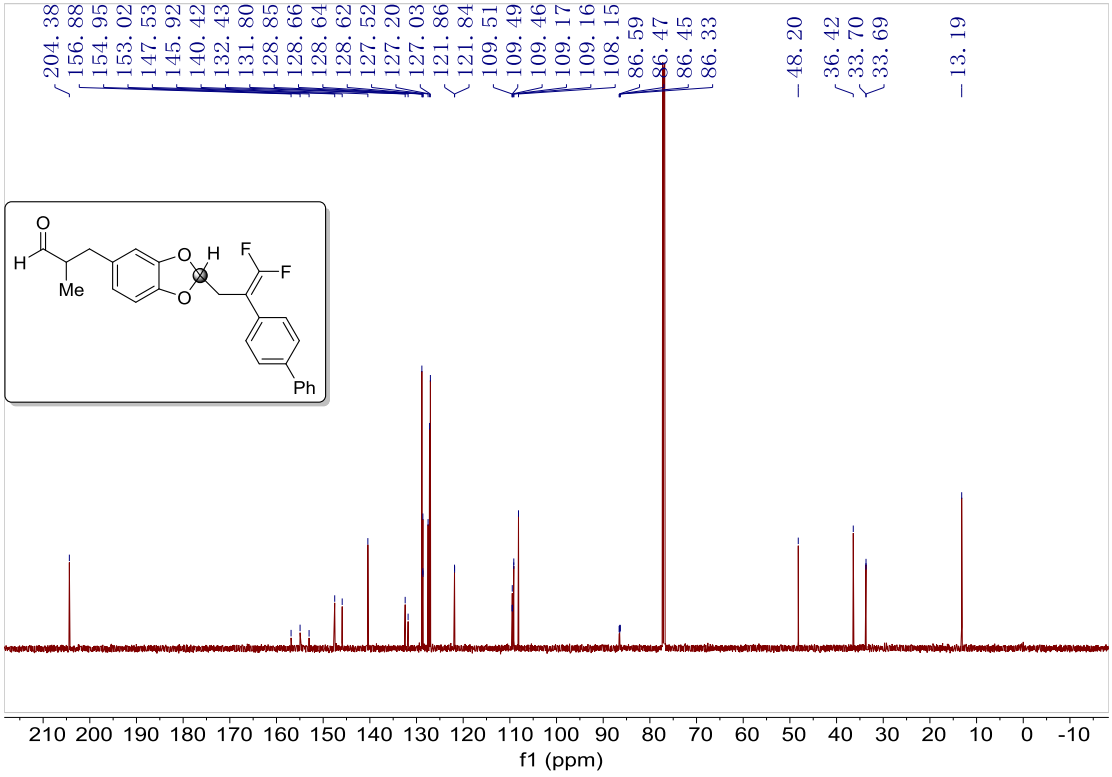
^{13}C NMR of 3k (150 MHz, $CDCl_3$)



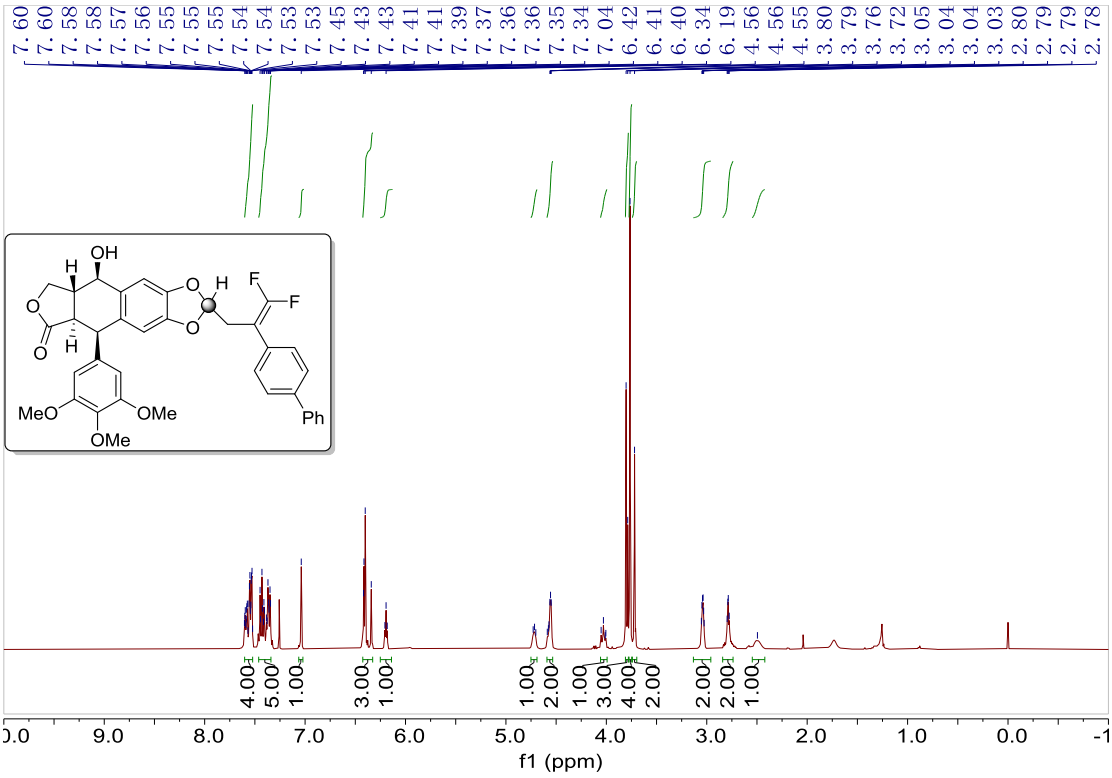
^{1}H NMR of 3l (400 MHz, $CDCl_3$)



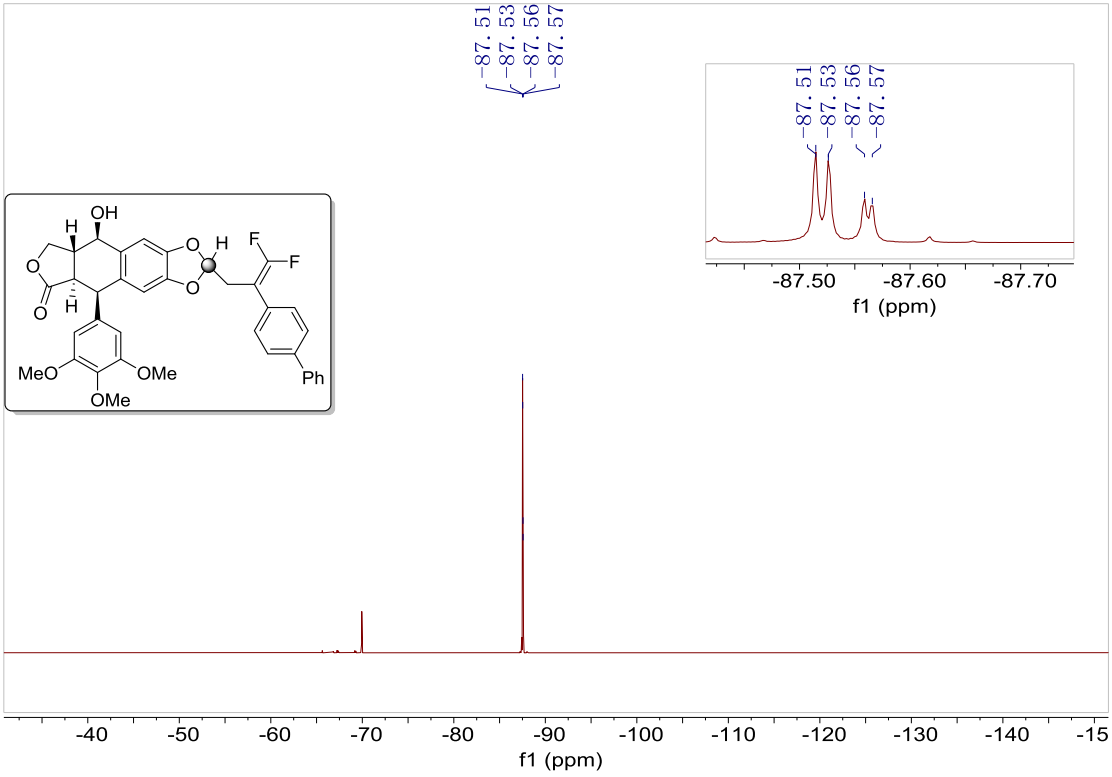
^{19}F NMR of 3l (376 MHz, $CDCl_3$)



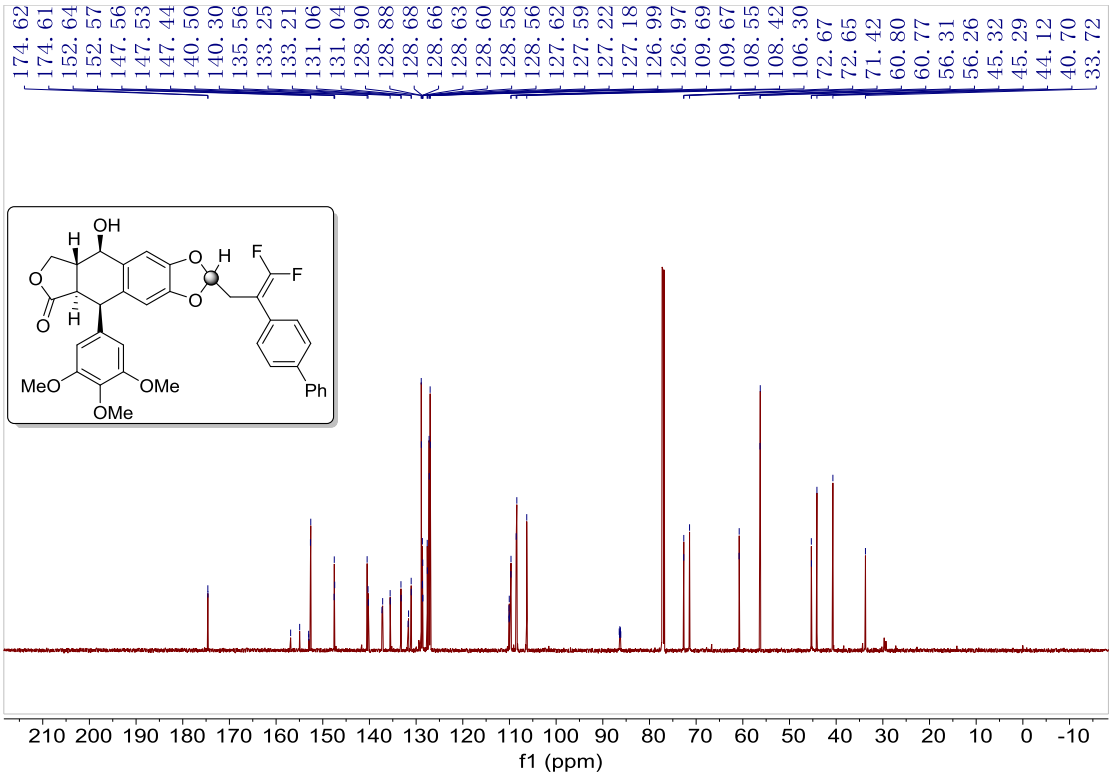
^{13}C NMR of 3l (150 MHz, $CDCl_3$)



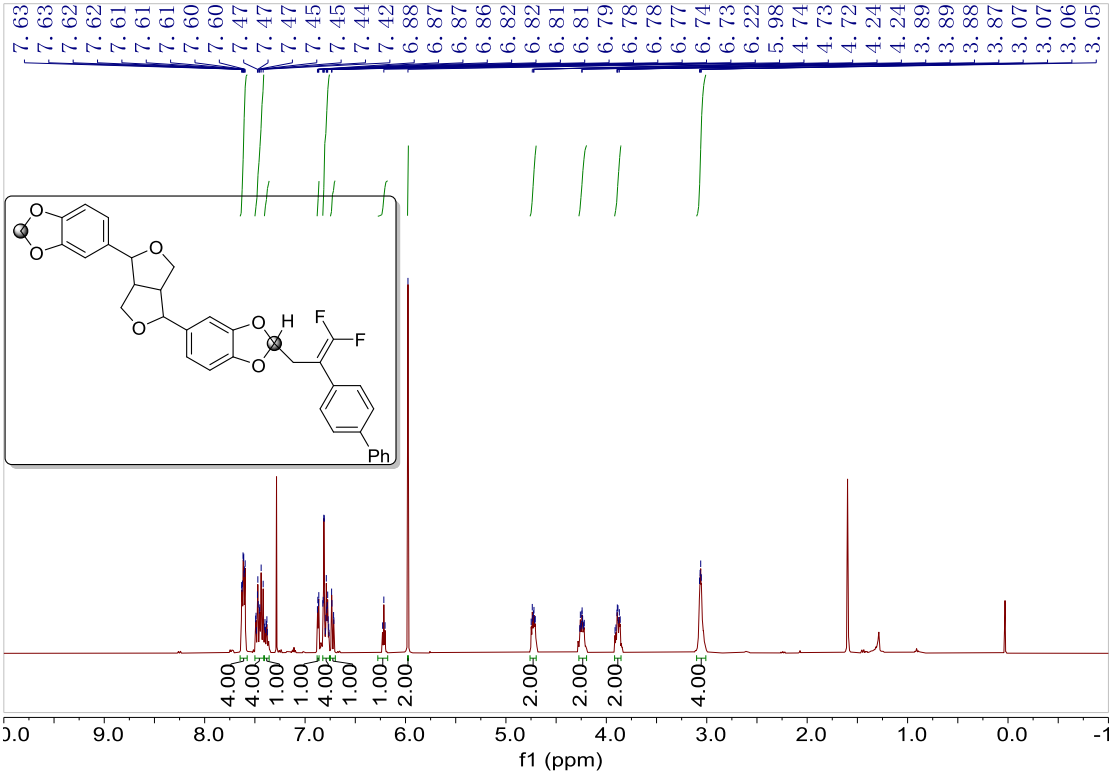
^{1}H NMR of 3m (400 MHz, $CDCl_3$)



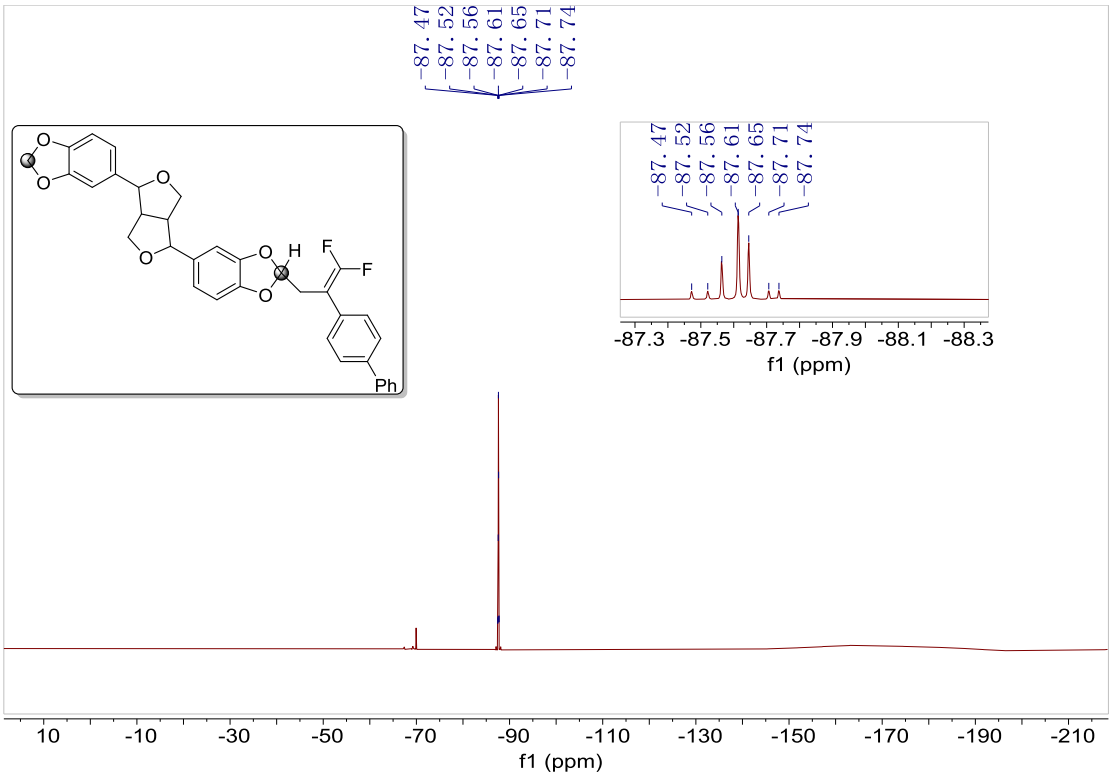
^{19}F NMR of 3m (376 MHz, $CDCl_3$)



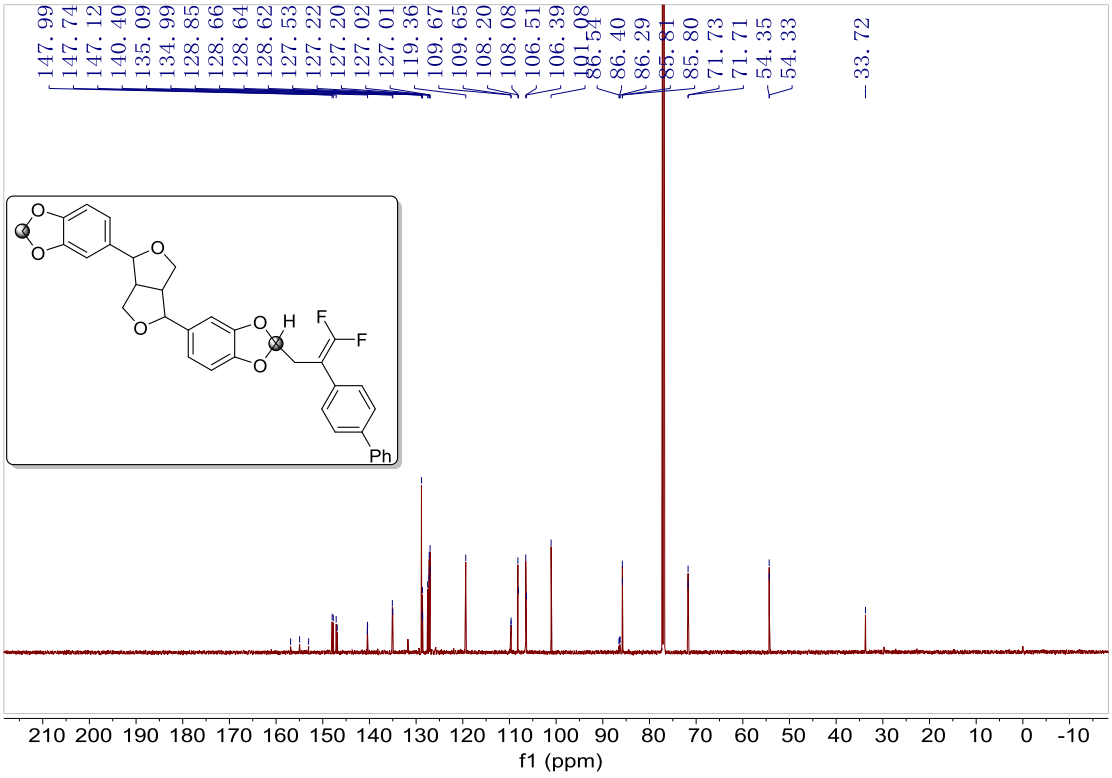
^{13}C NMR of 3m (150 MHz, $CDCl_3$)



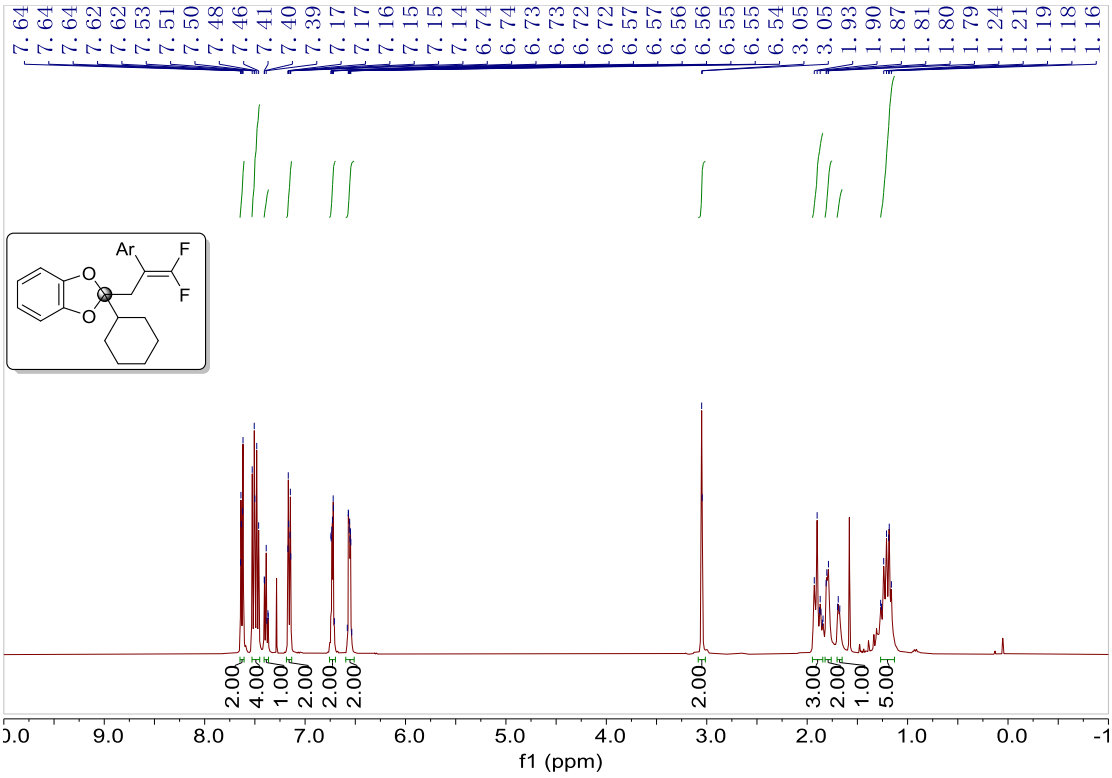
^{1}H NMR of 3n (400 MHz, $CDCl_3$)



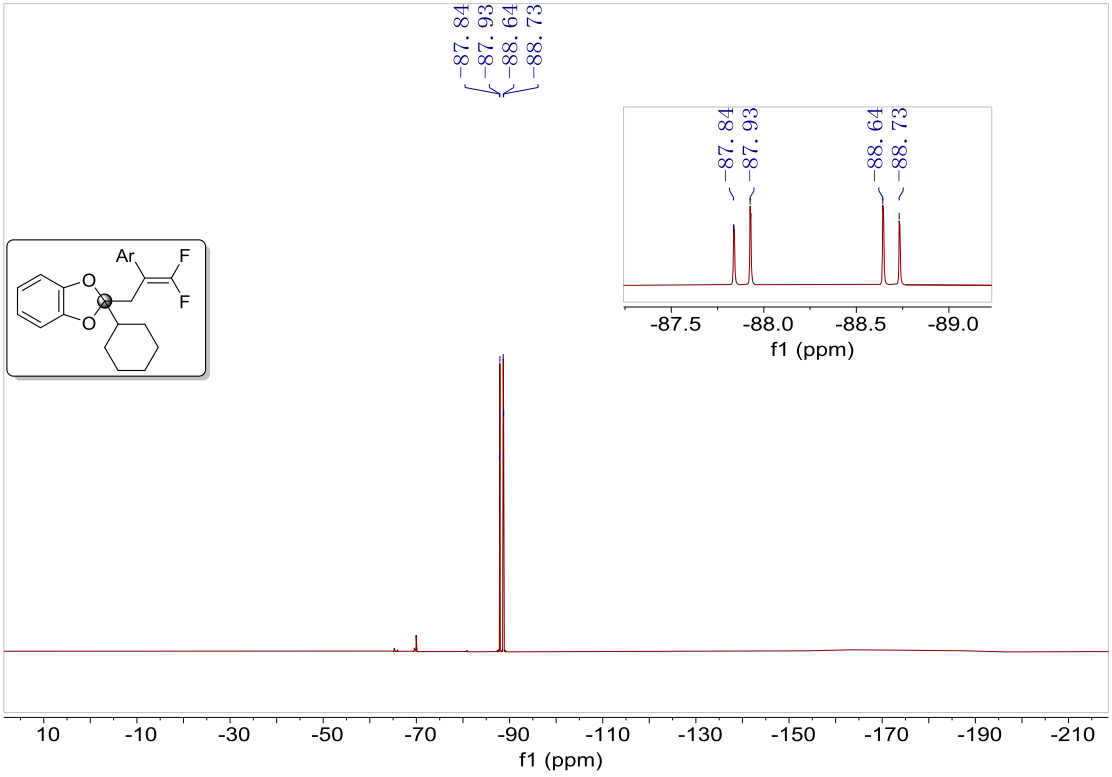
^{19}F NMR of 3n (376 MHz, $CDCl_3$)



^{13}C NMR of 3n (150 MHz, $CDCl_3$)



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



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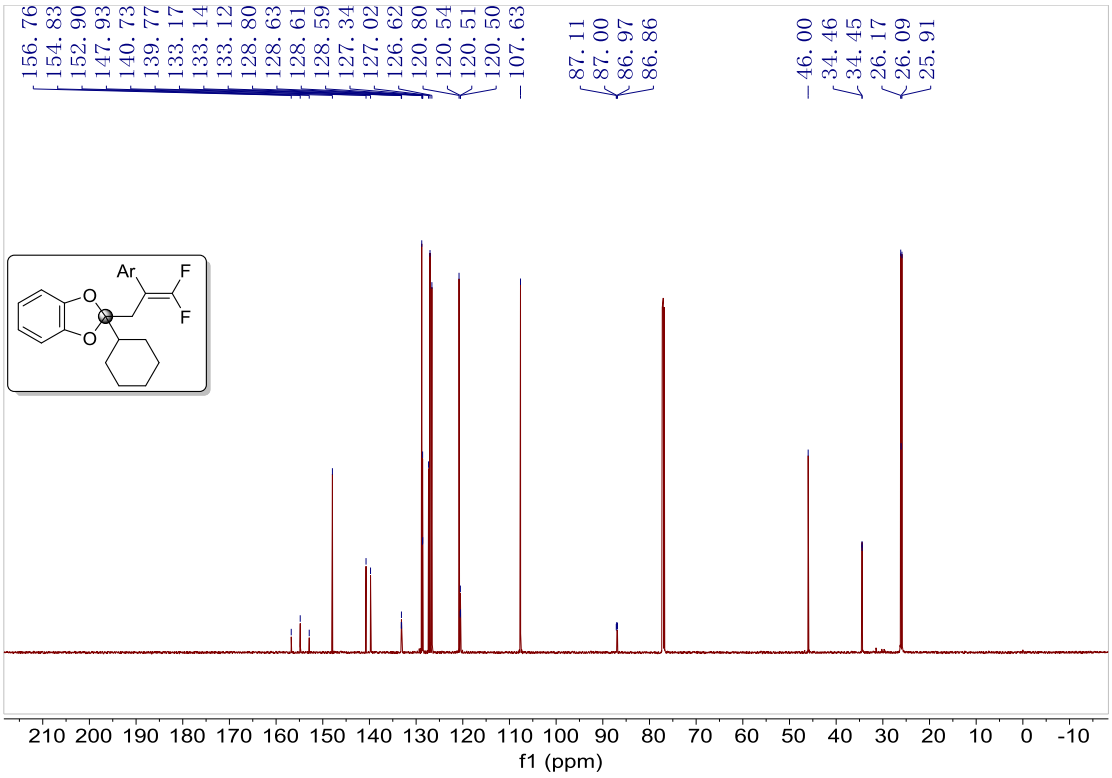

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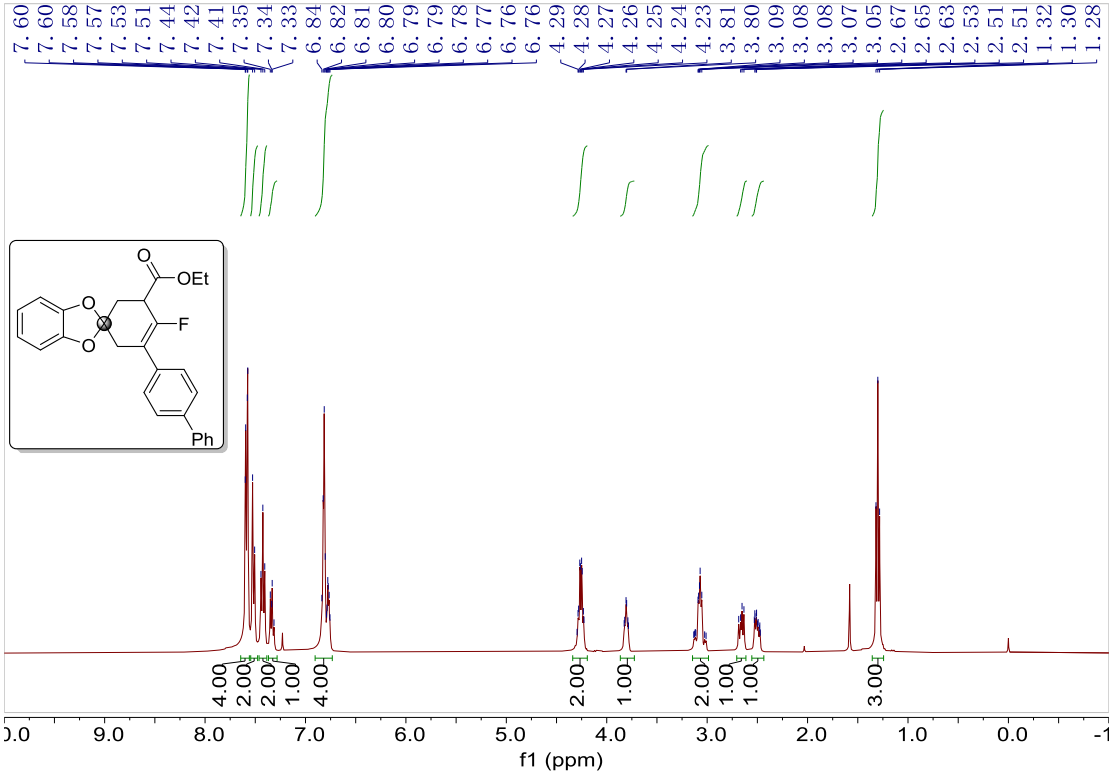
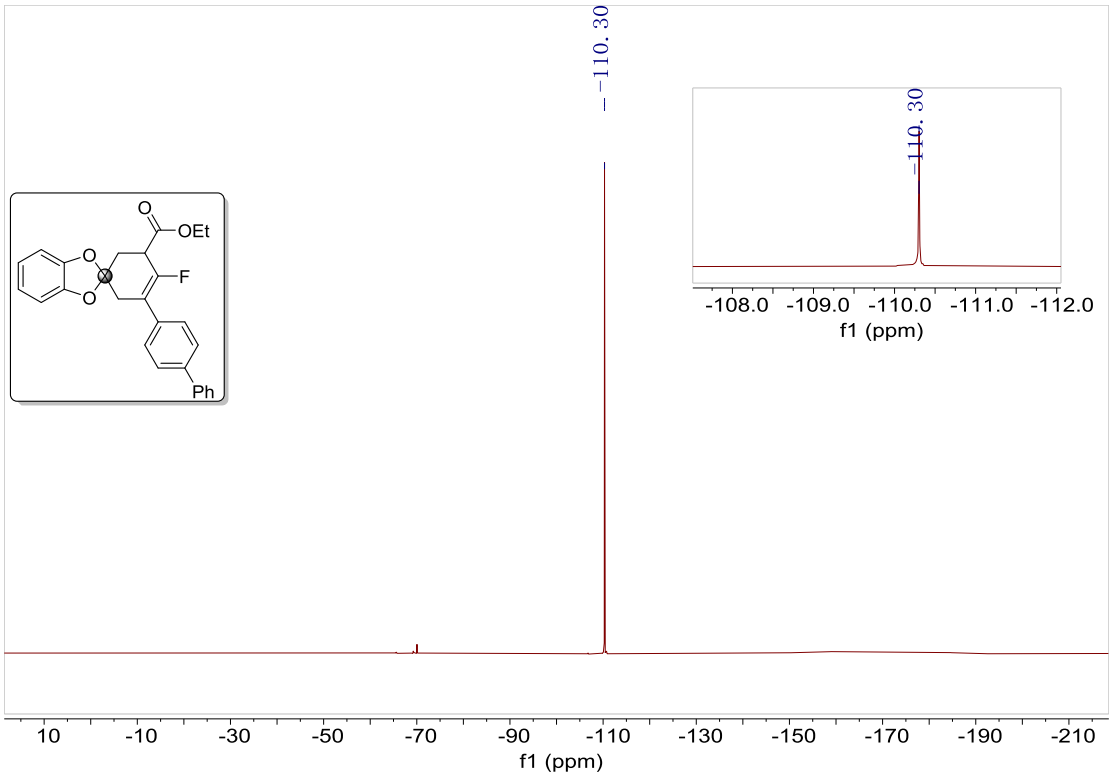
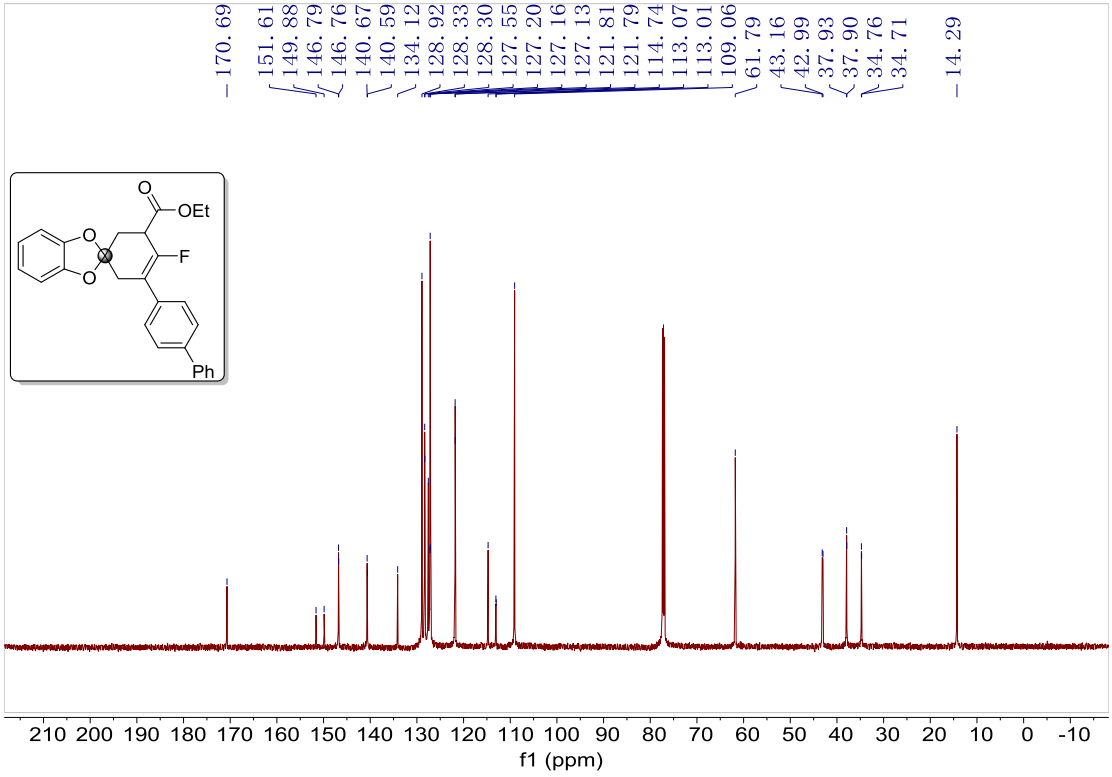


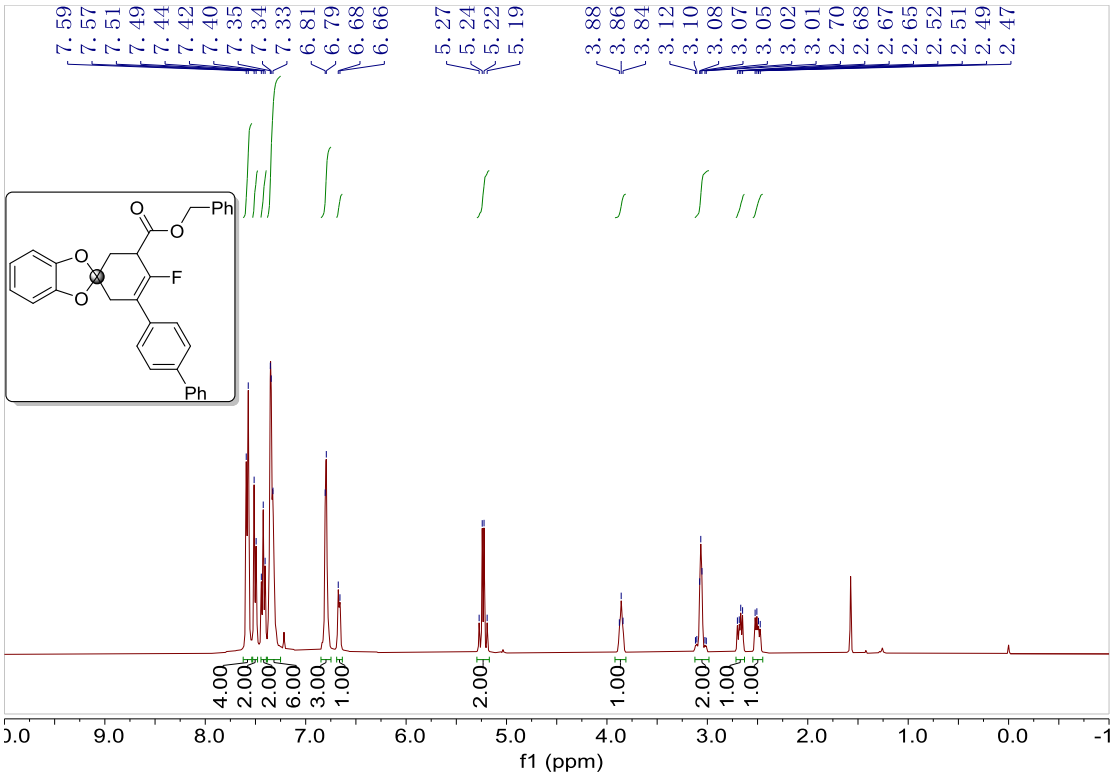
^{1}H NMR of 5a (400 MHz, $CDCl_3$)



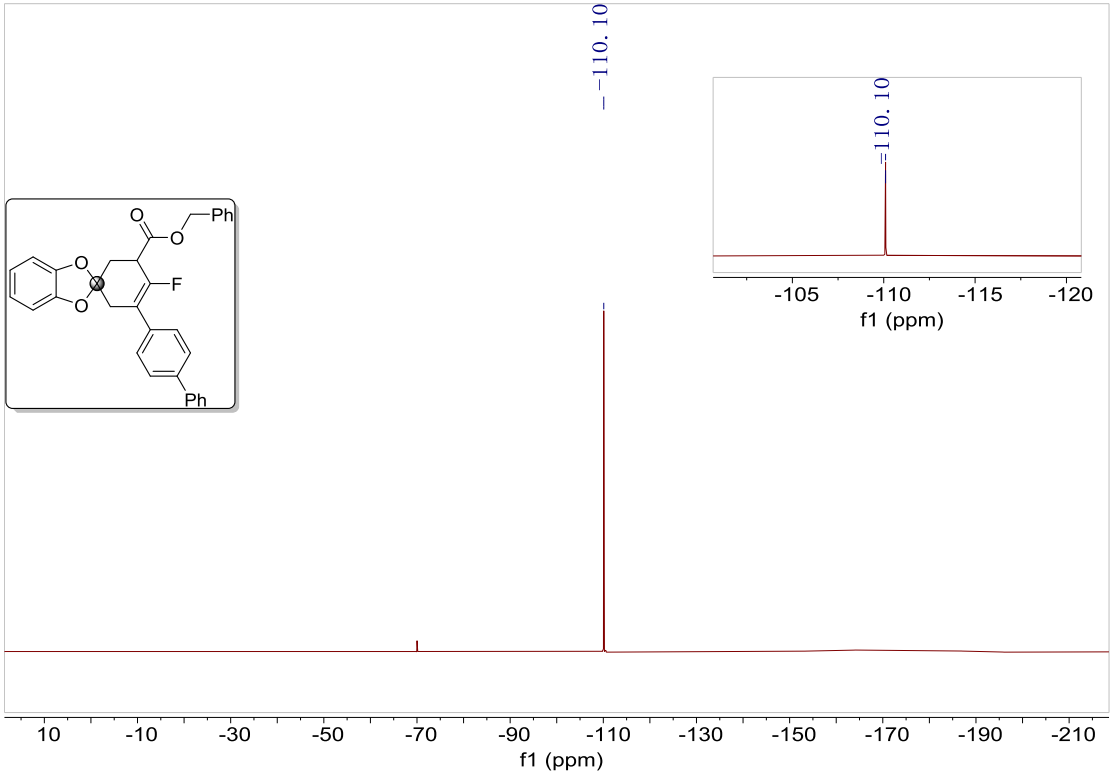
^{19}F NMR of 5a (376 MHz, $CDCl_3$)



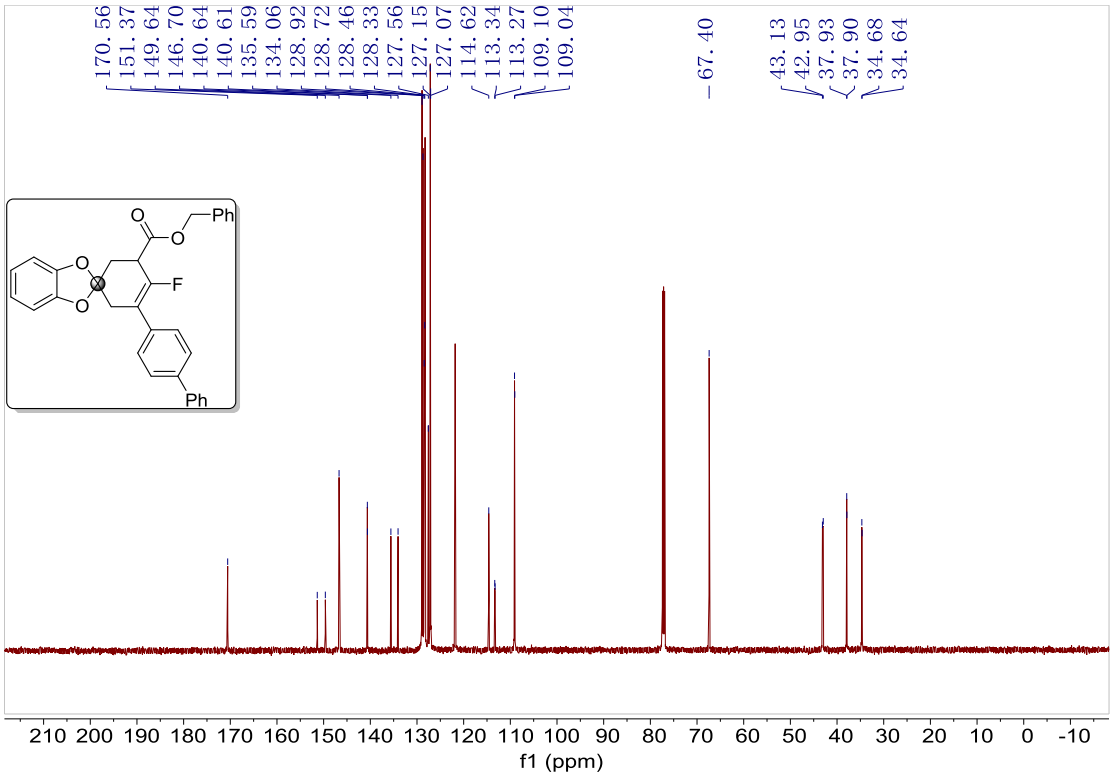
^{13}C NMR of 5a (150 MHz, $CDCl_3$)



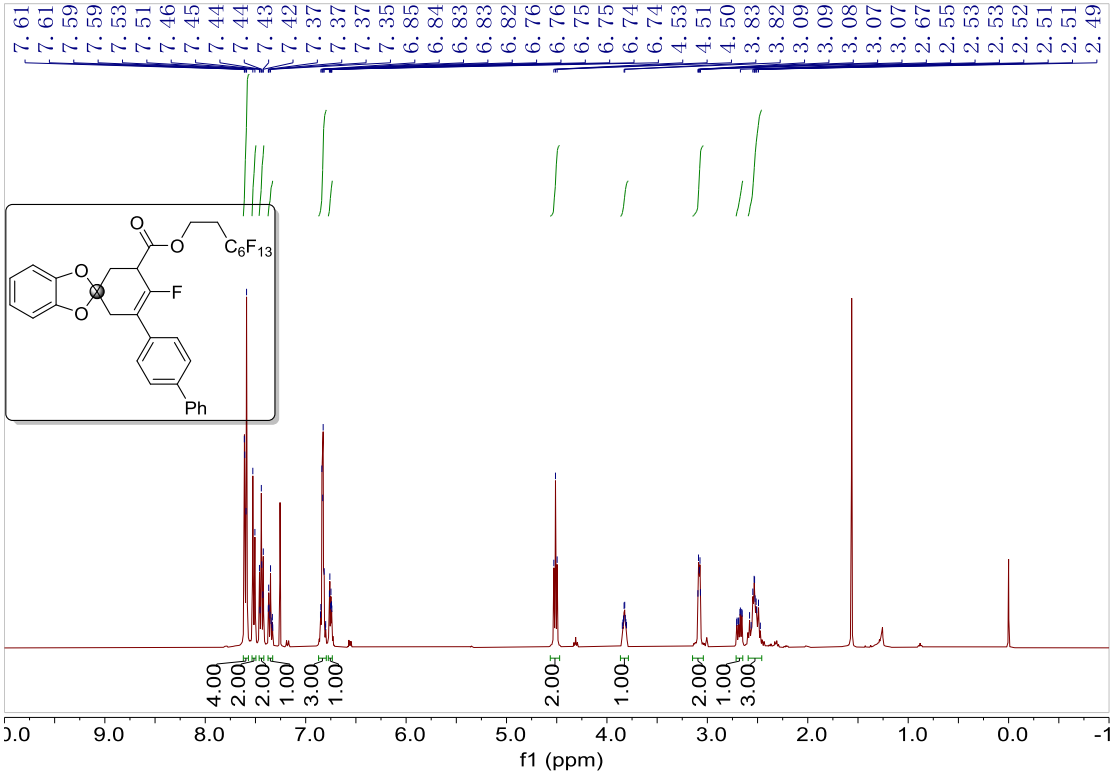
^{1}H NMR of 5b (400 MHz, $CDCl_3$)



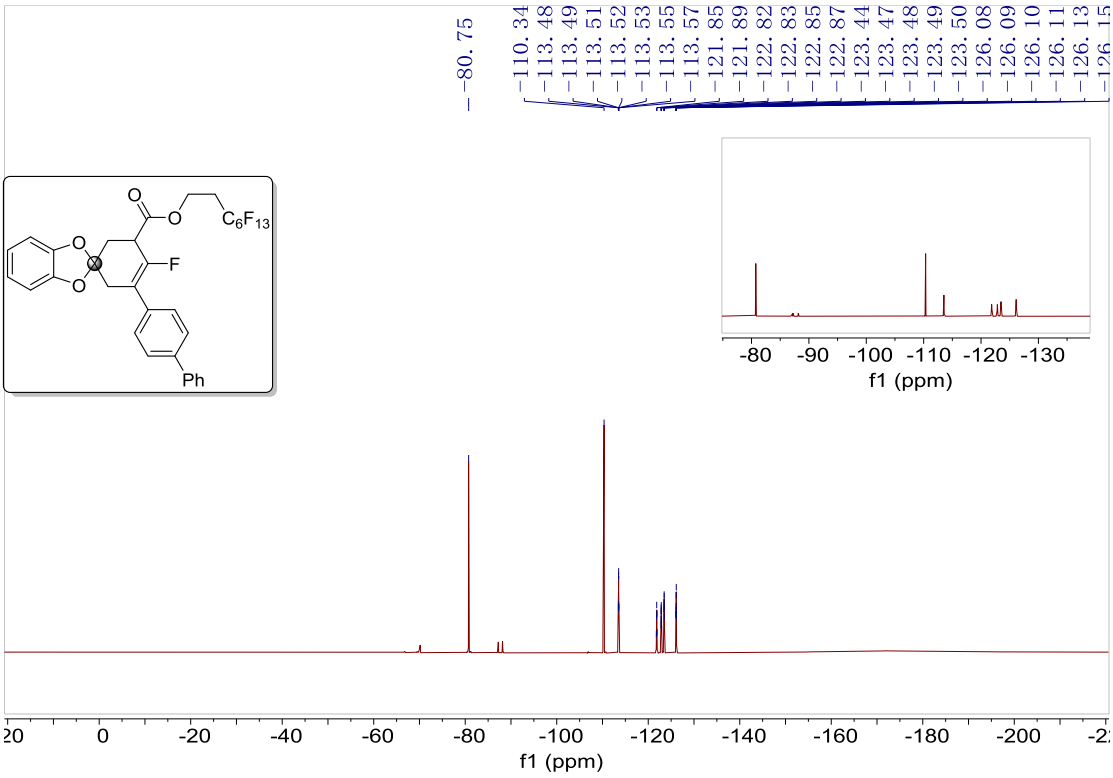
^{19}F NMR of 5b (376 MHz, $CDCl_3$)



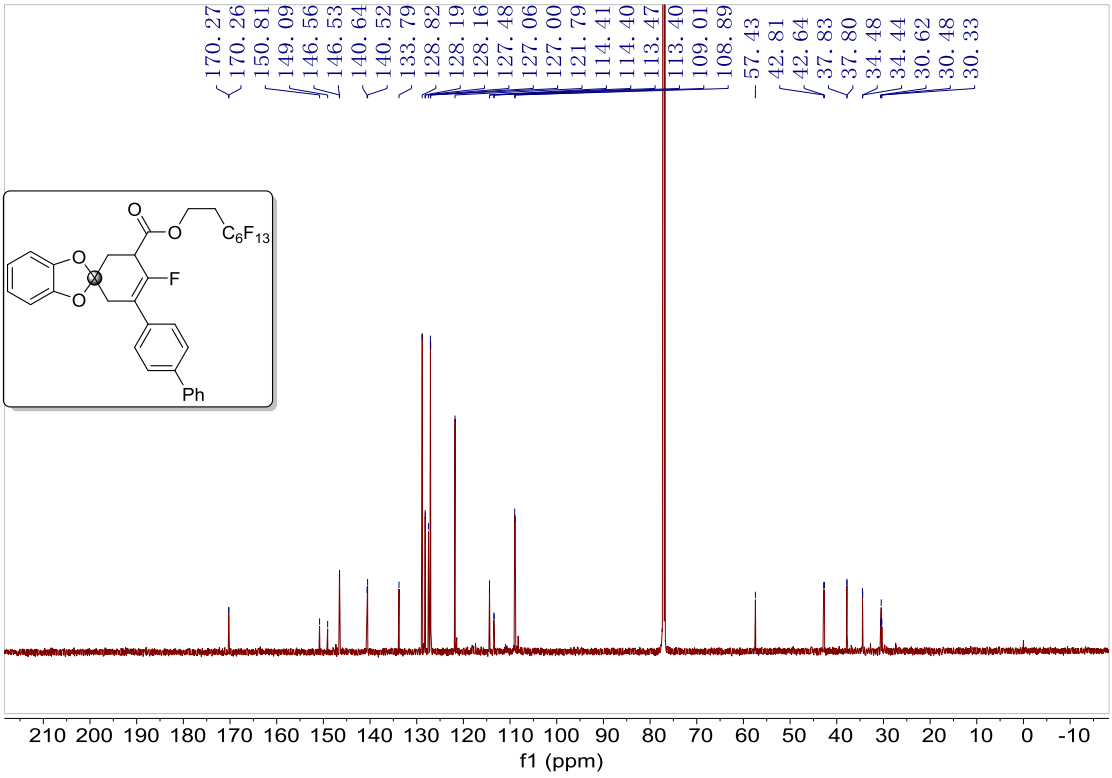
^{13}C NMR of 5b (150 MHz, $CDCl_3$)



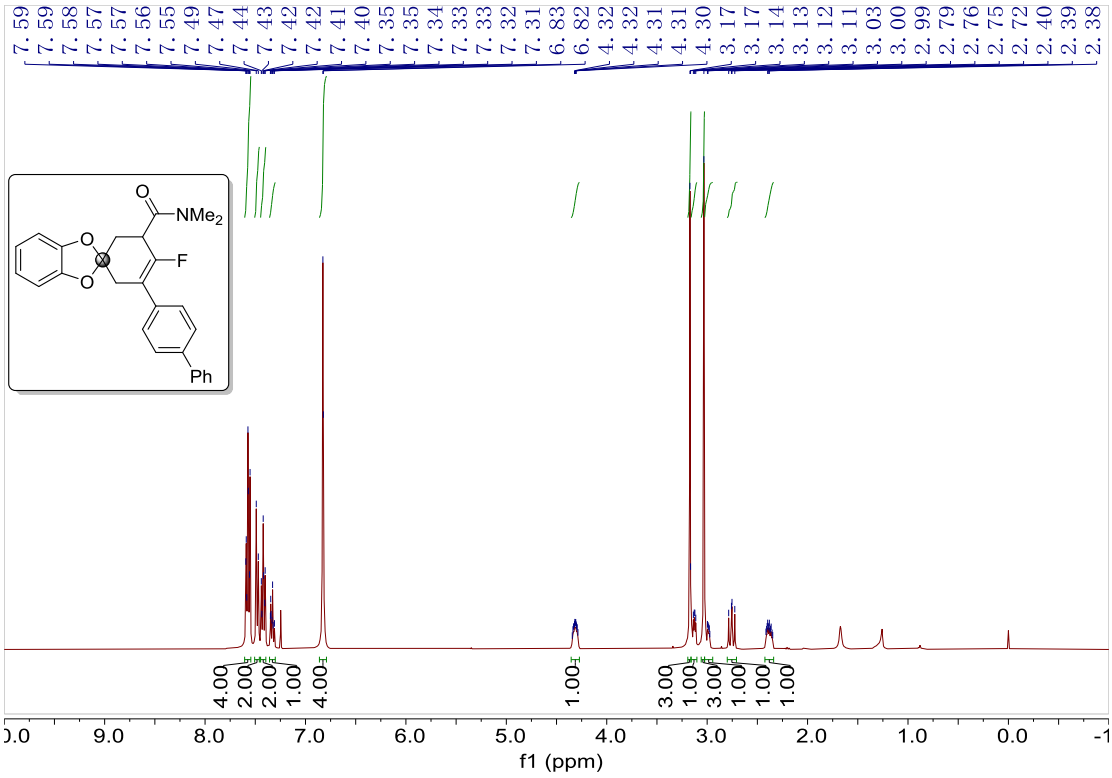
^{1}H NMR of 5c (400 MHz, $CDCl_3$)



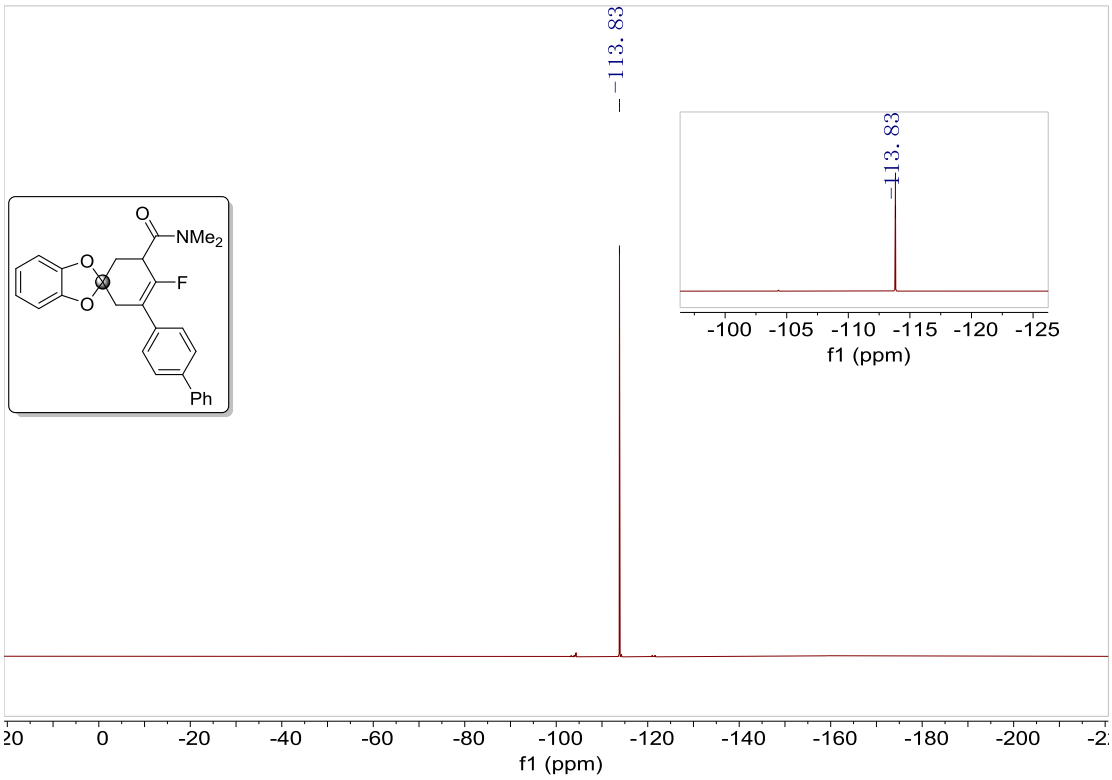
^{19}F NMR of 5c (376 MHz, $CDCl_3$)



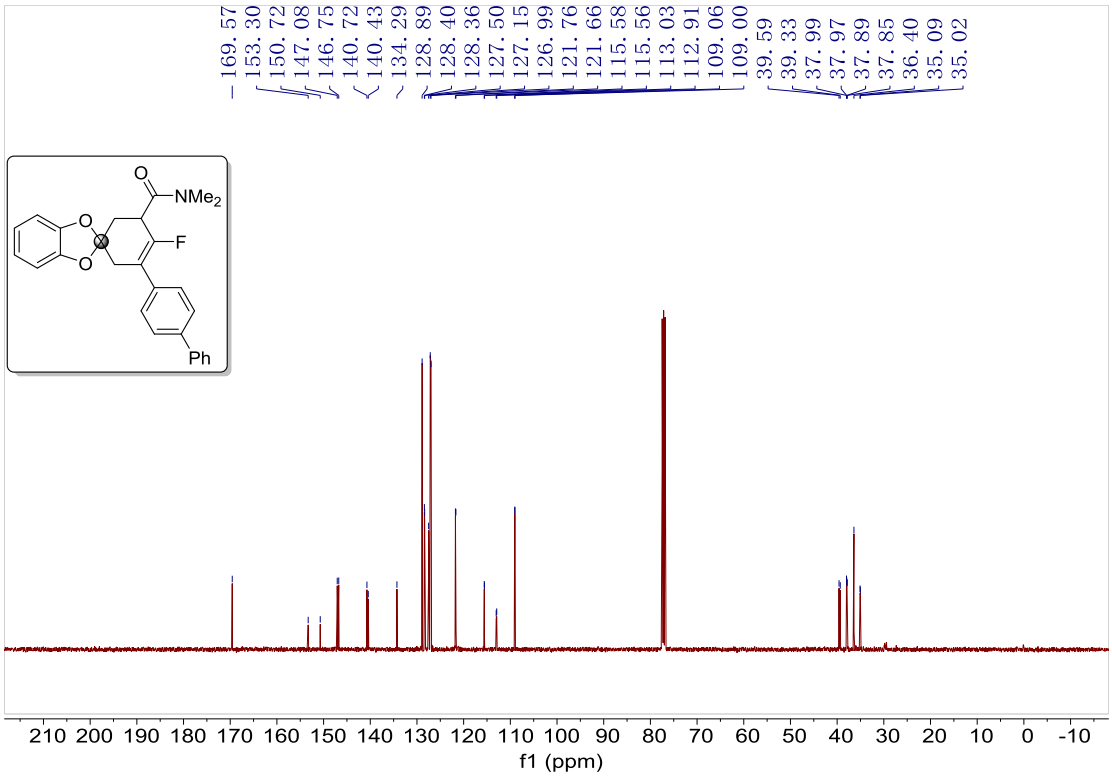
^{13}C NMR of 5c (150 MHz, $CDCl_3$)



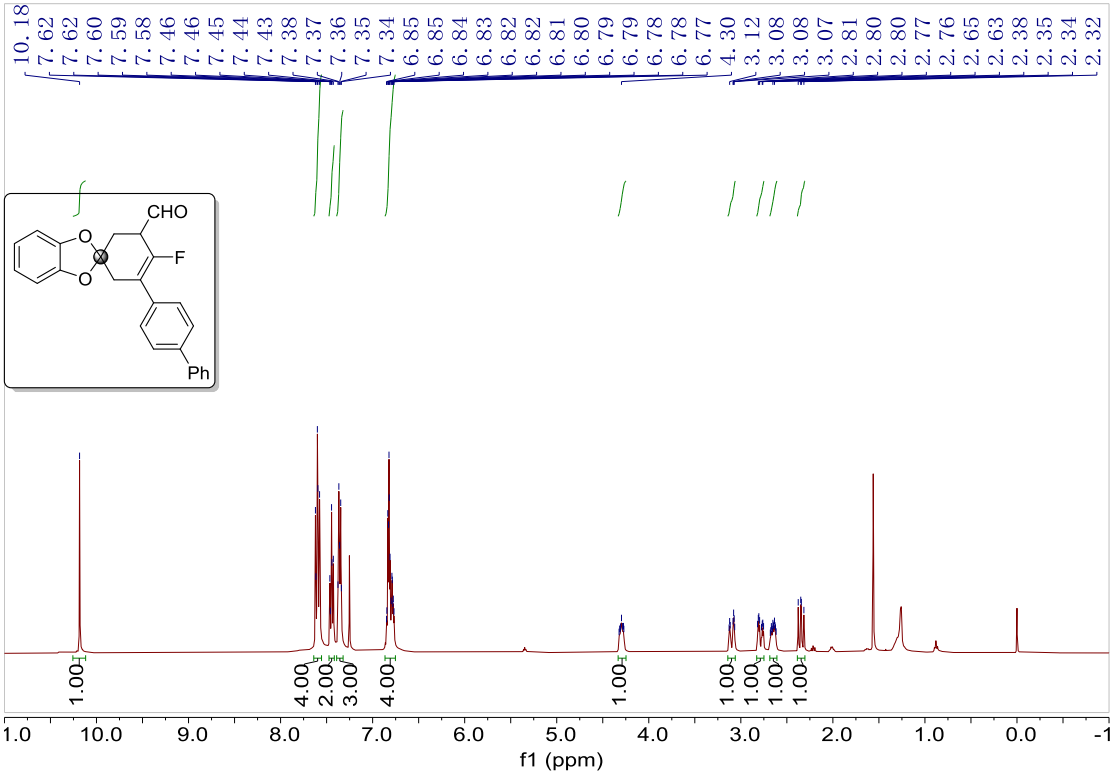
^{1}H NMR of 5d (400 MHz, $CDCl_3$)



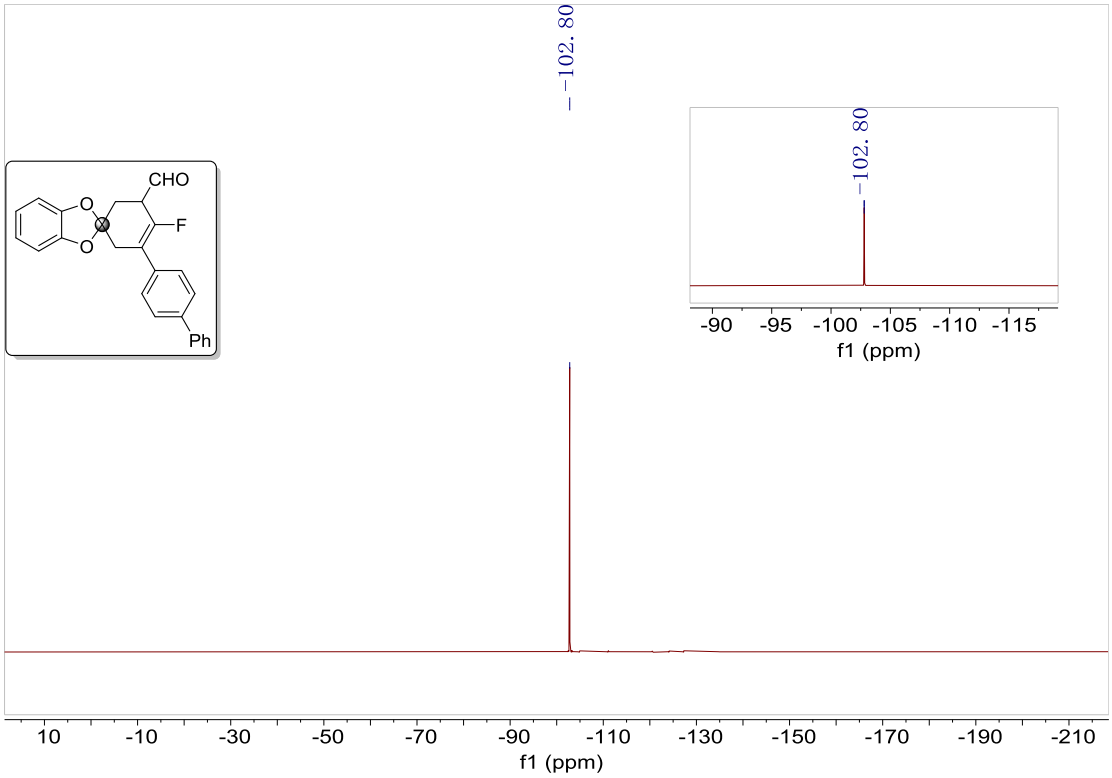
^{19}F NMR of 5d (376 MHz, $CDCl_3$)



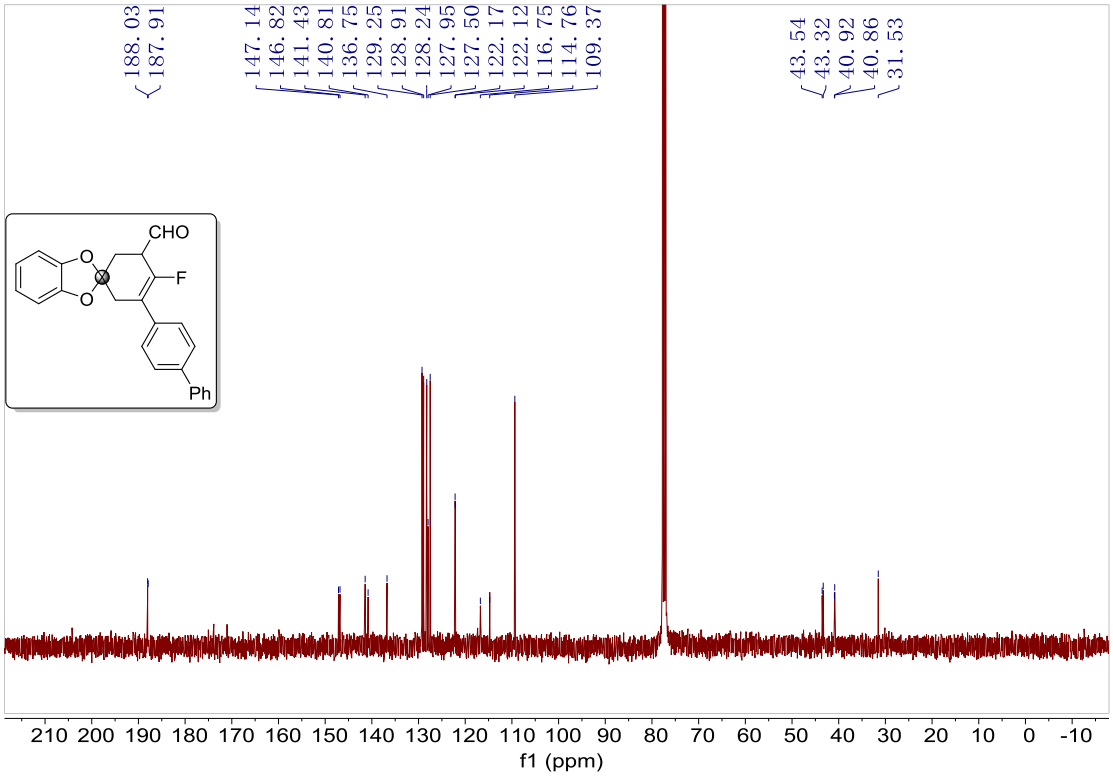
^{13}C NMR of 5d (150 MHz, $CDCl_3$)



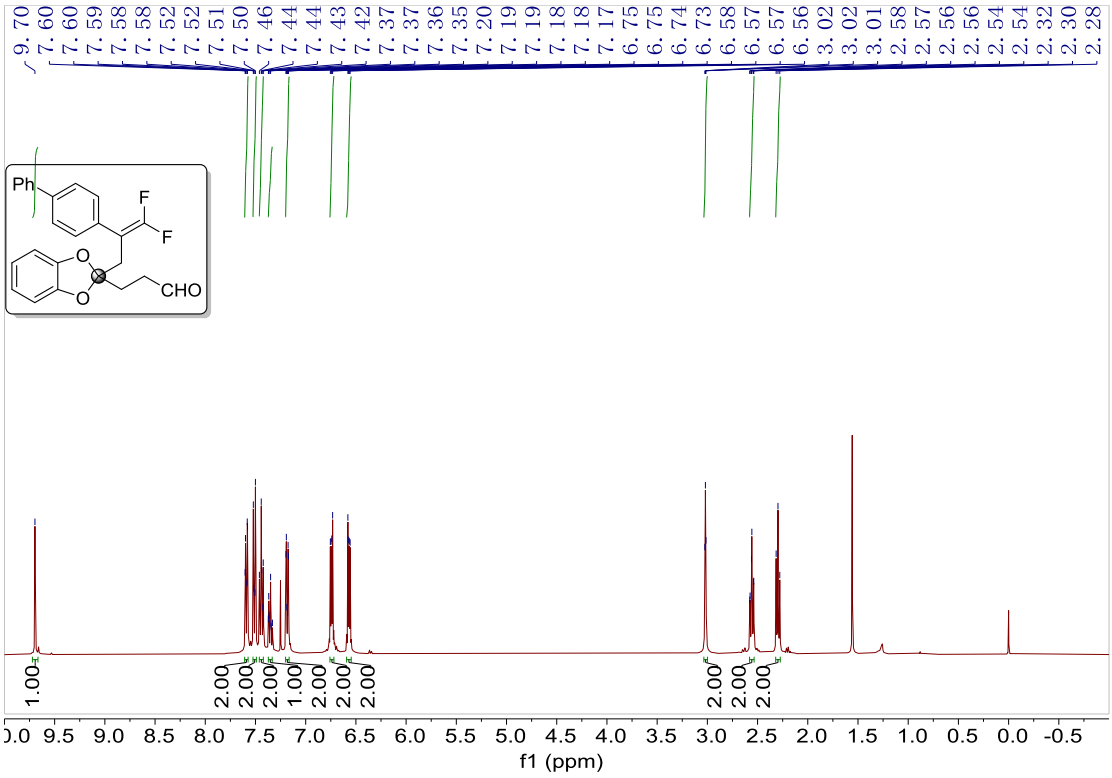
^{1}H NMR of 5e (400 MHz, $CDCl_3$)



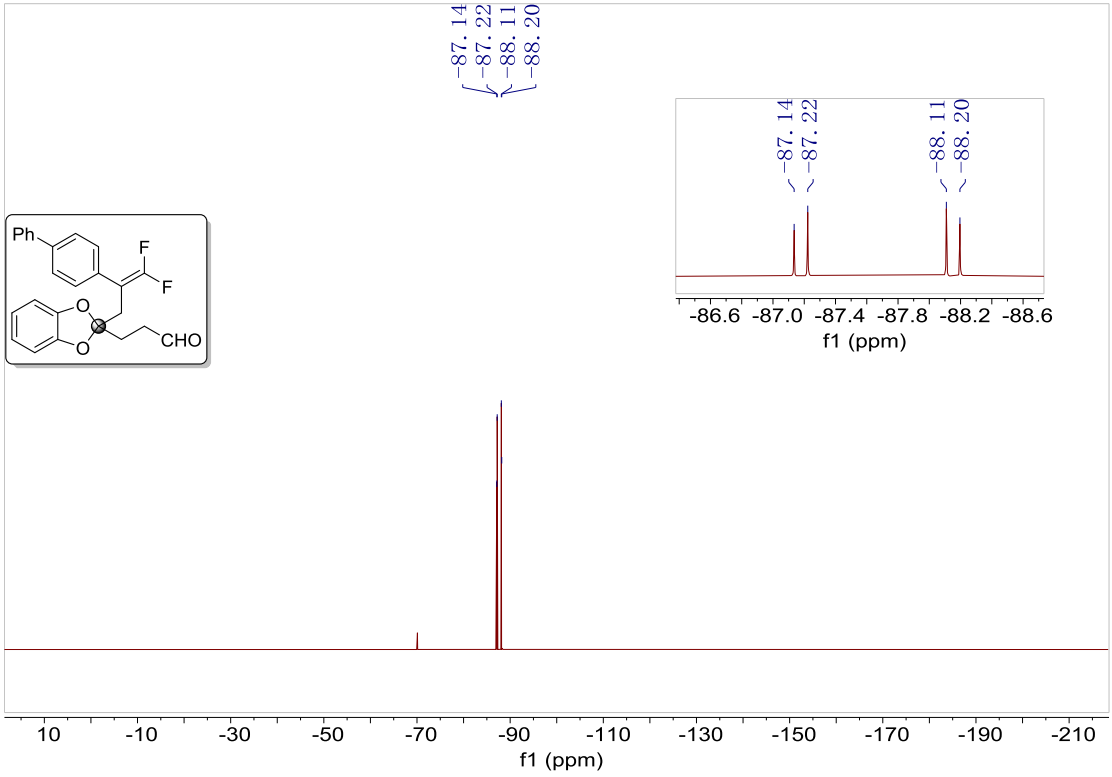
^{19}F NMR of 5e (376 MHz, $CDCl_3$)



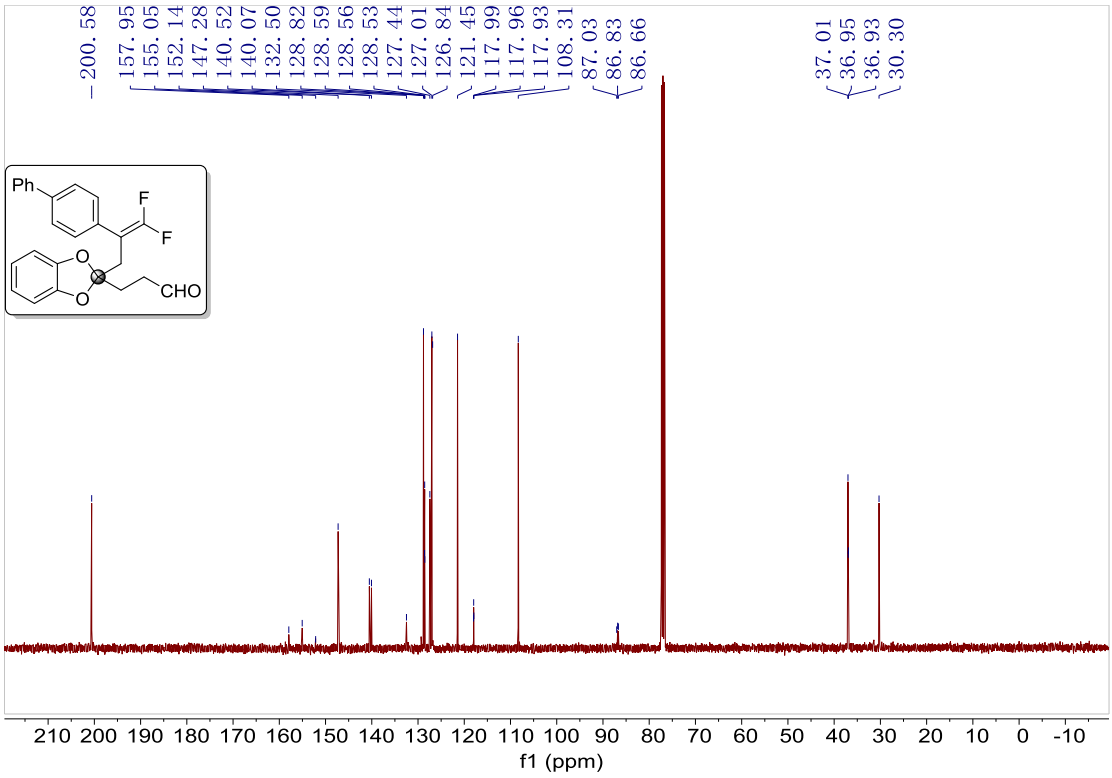
^{13}C NMR of 5e (100 MHz, $CDCl_3$)



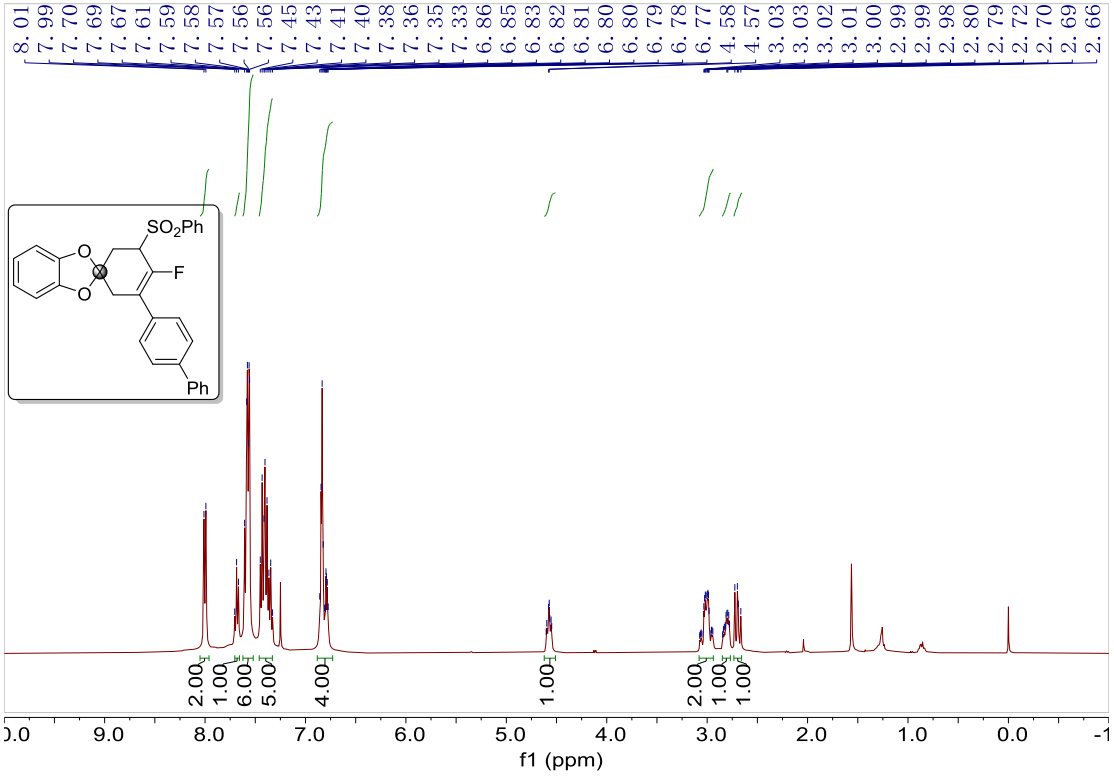
^{1}H NMR of 5e′ (400 MHz, $CDCl_3$)



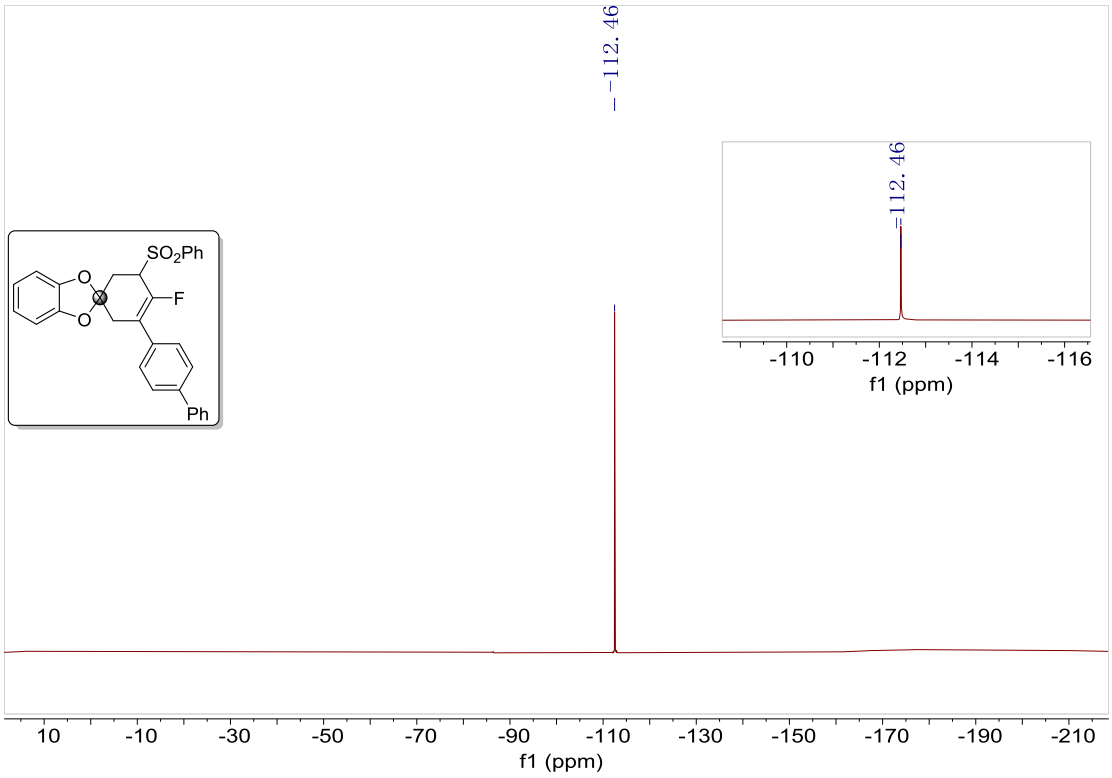
^{19}F NMR of 5e′ (376 MHz, $CDCl_3$)



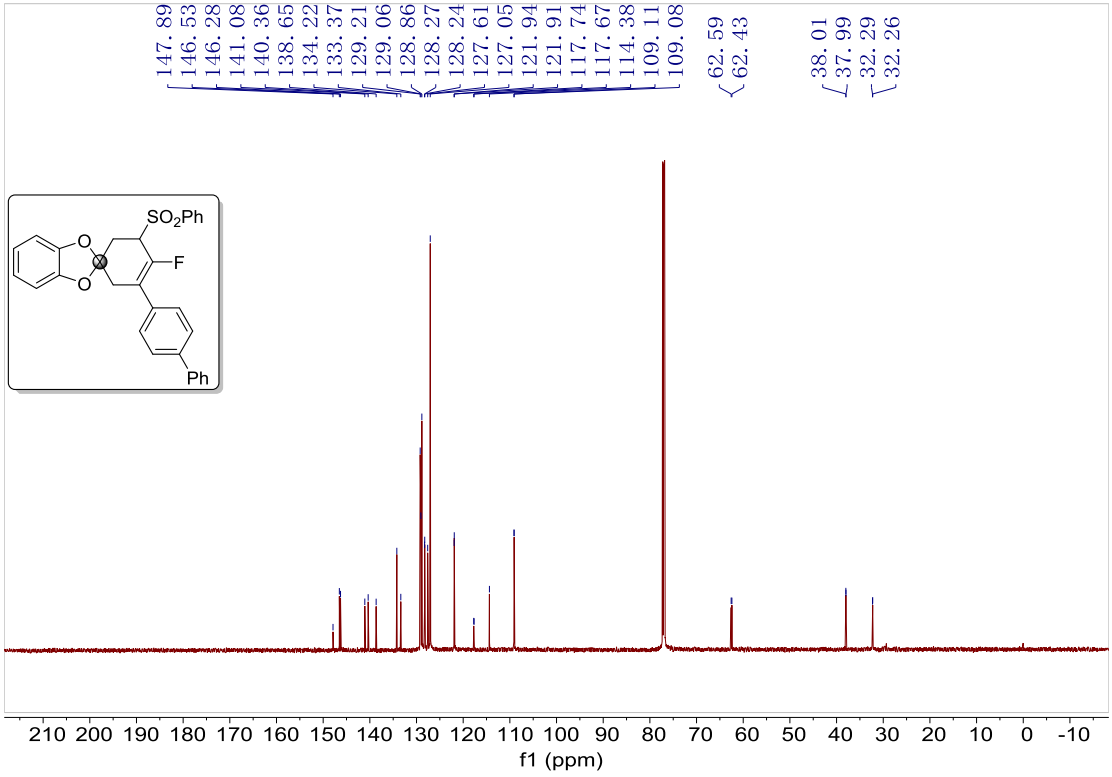
^{13}C NMR of 5e′ (100 MHz, $CDCl_3$)



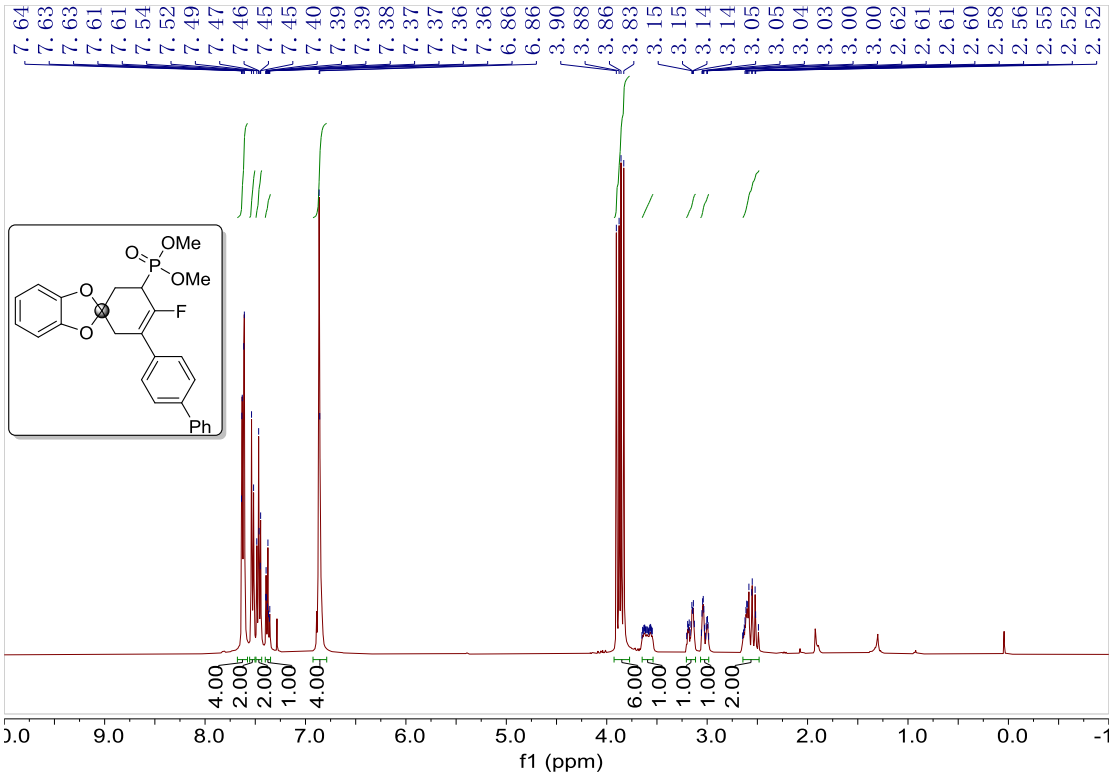
^{1}H NMR of 5f (400 MHz, $CDCl_3$)



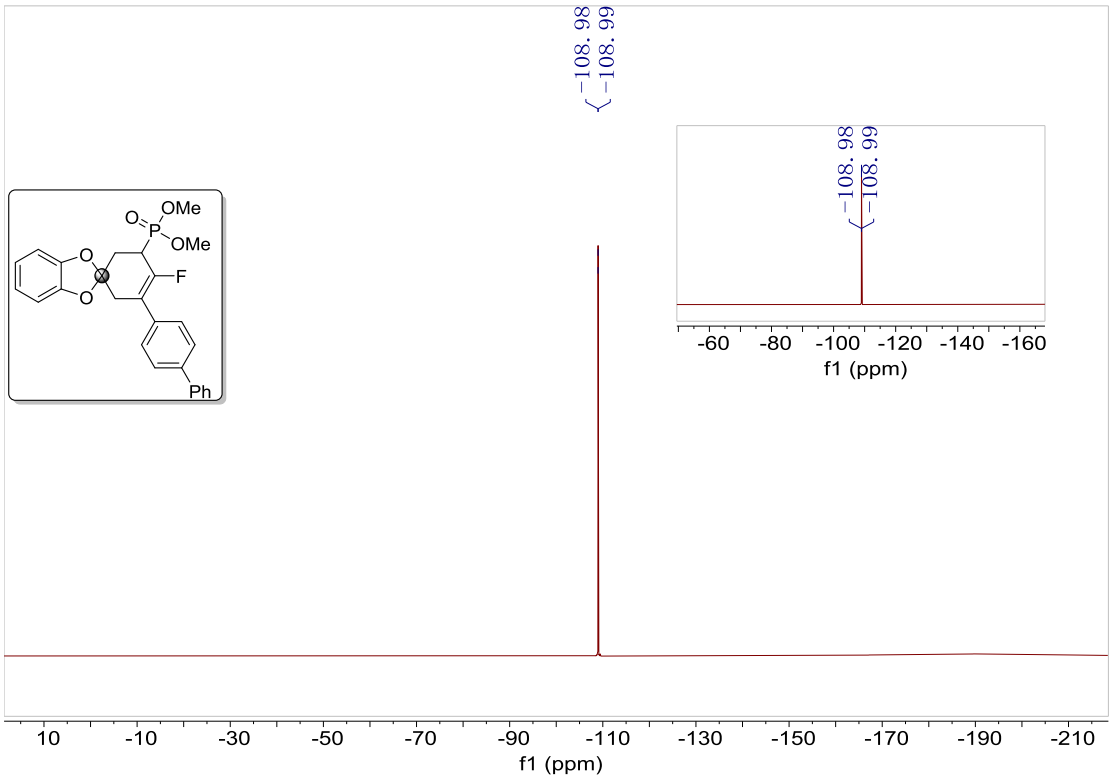
^{19}F NMR of 5f (376 MHz, $CDCl_3$)



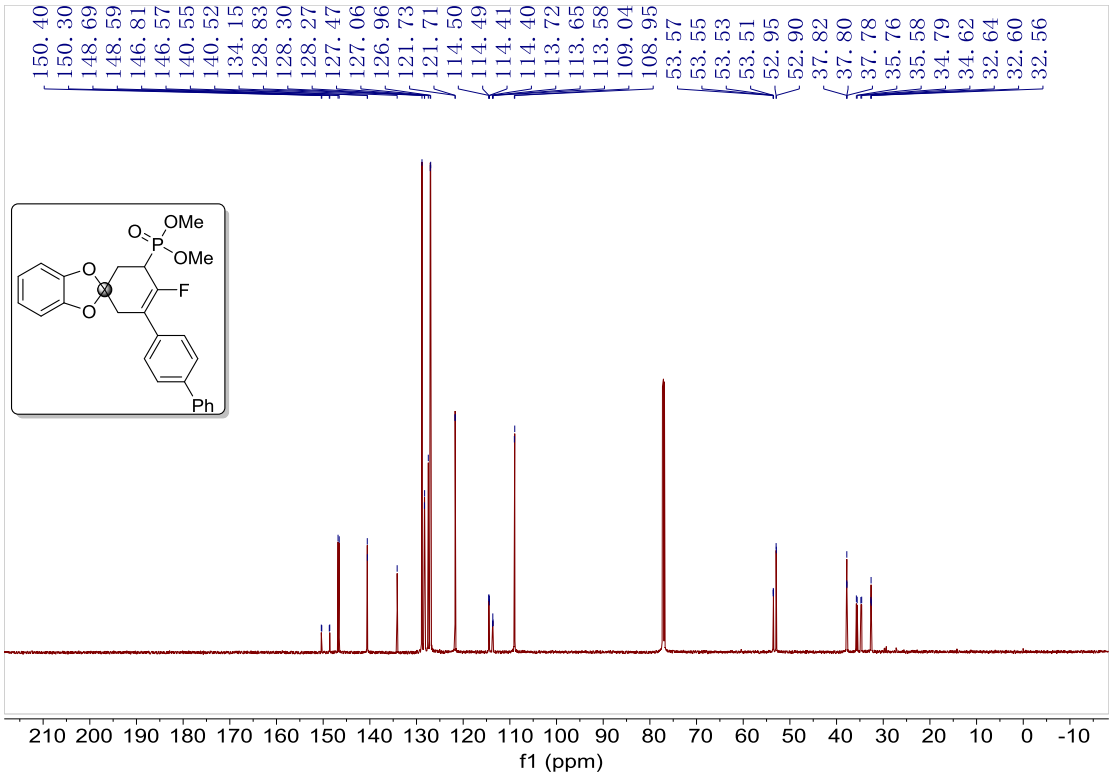
^{13}C NMR of 5f (150 MHz, $CDCl_3$)



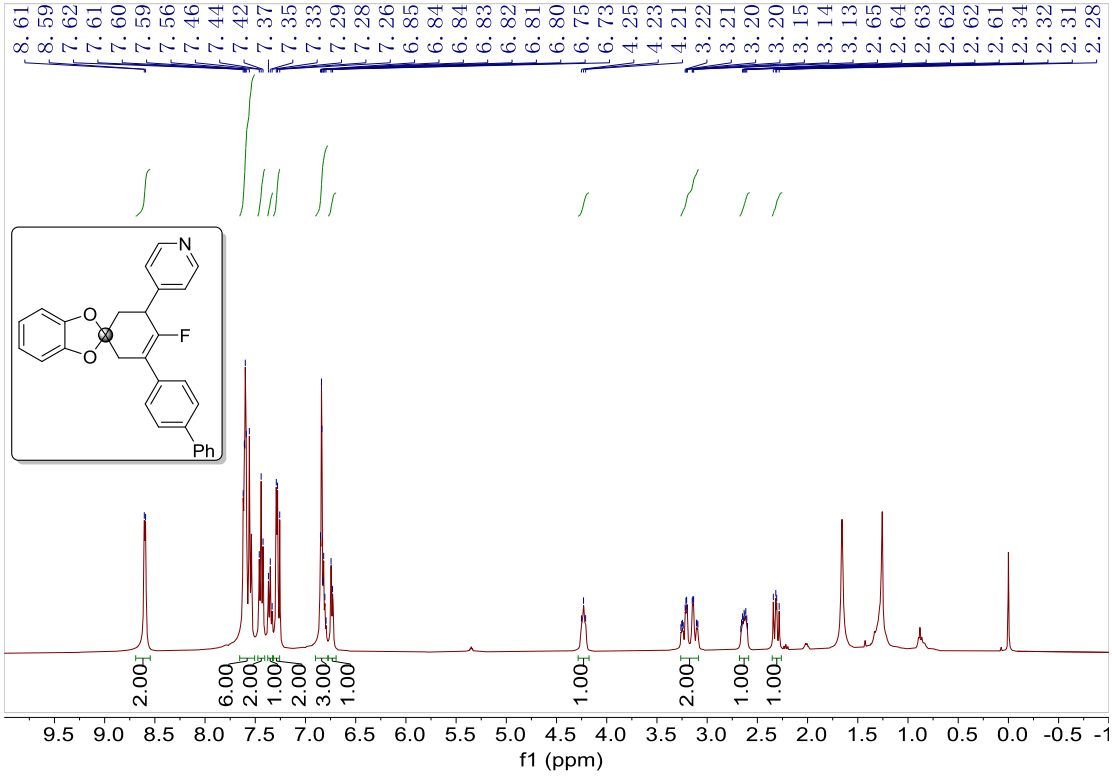
^{1}H NMR of 5g (400 MHz, $CDCl_3$)



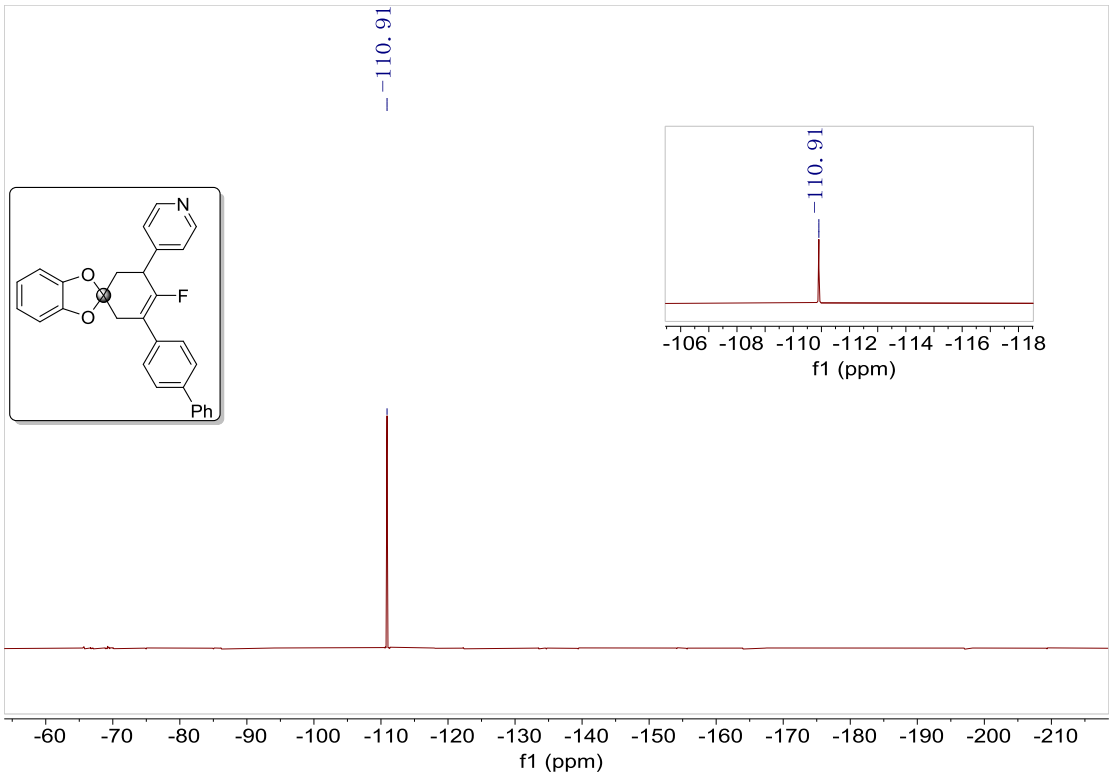
^{19}F NMR of 5g (376 MHz, $CDCl_3$)



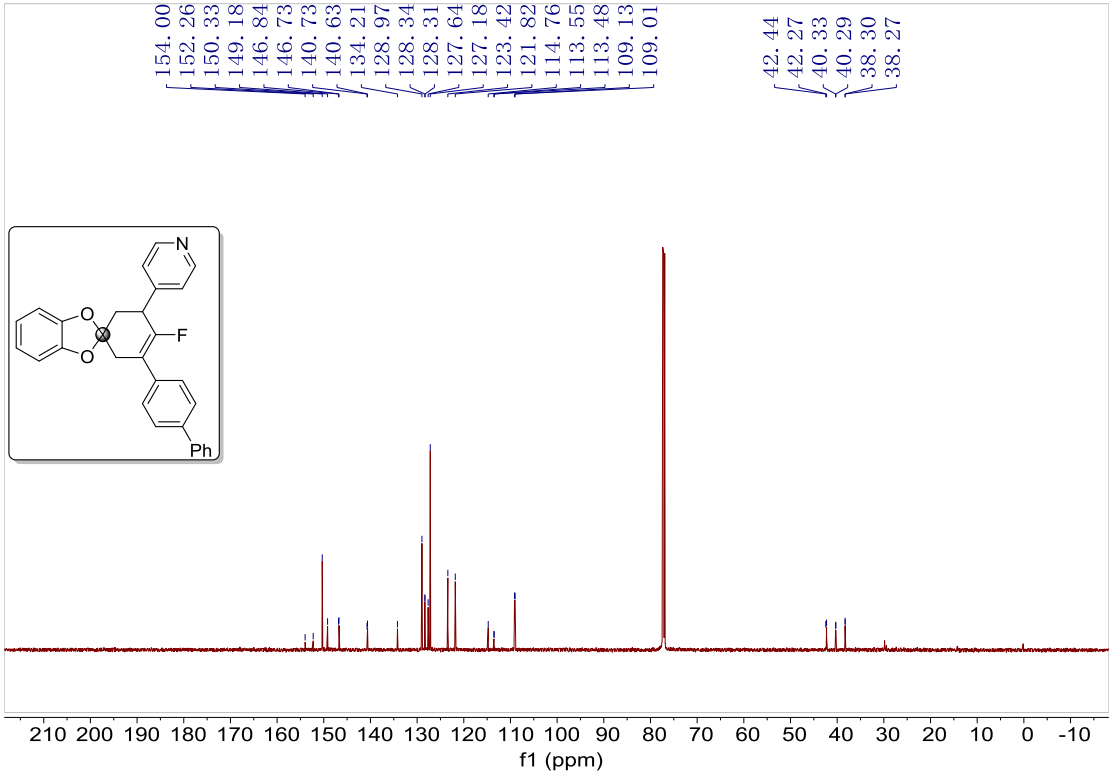
^{13}C NMR of 5g (150 MHz, $CDCl_3$)



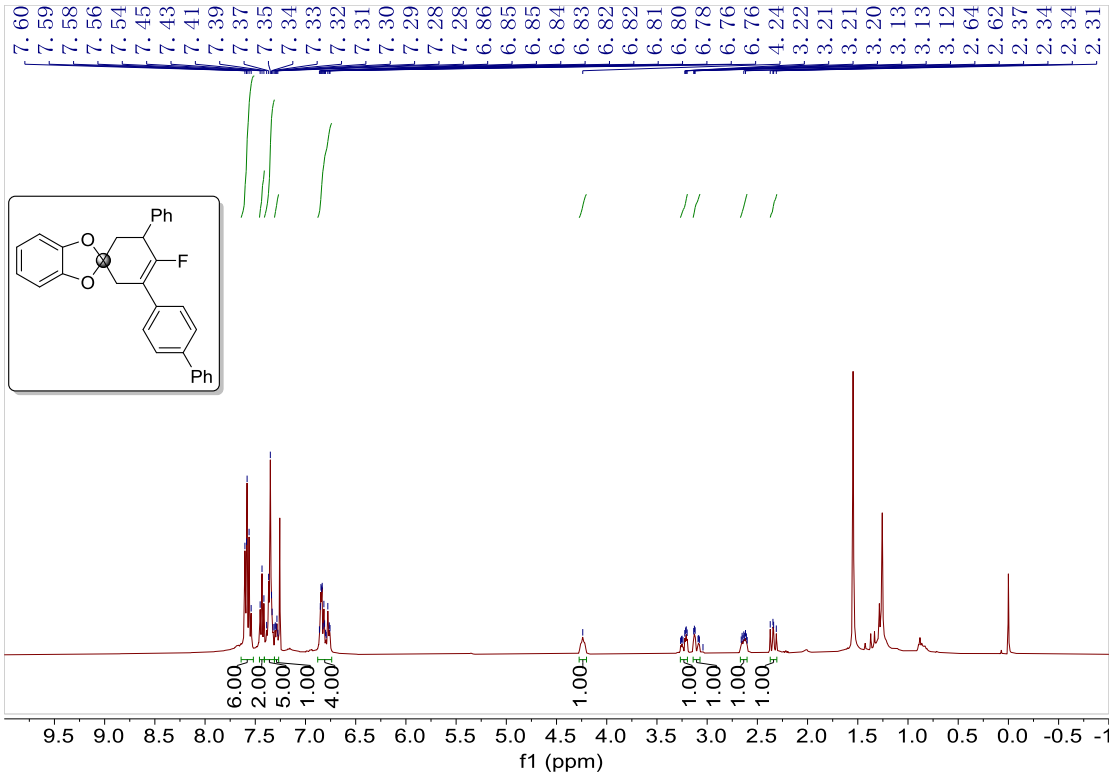
^{1}H NMR of 5h (400 MHz, $CDCl_3$)



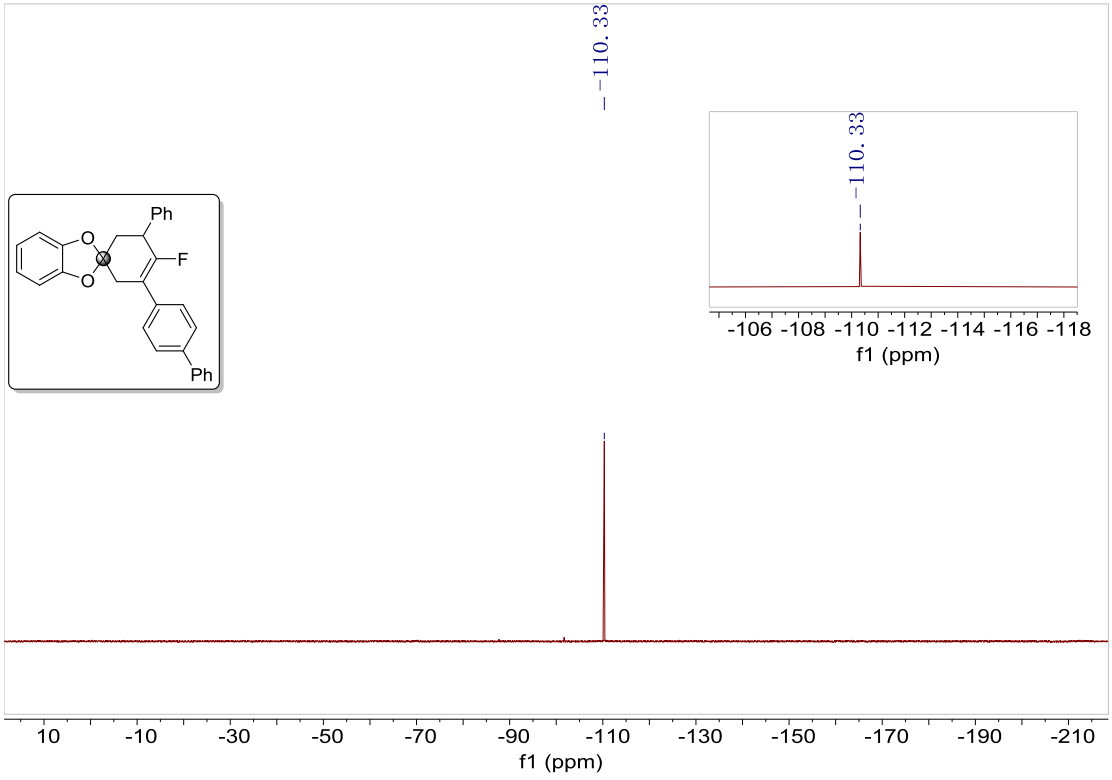
^{19}F NMR of 5h (376 MHz, $CDCl_3$)



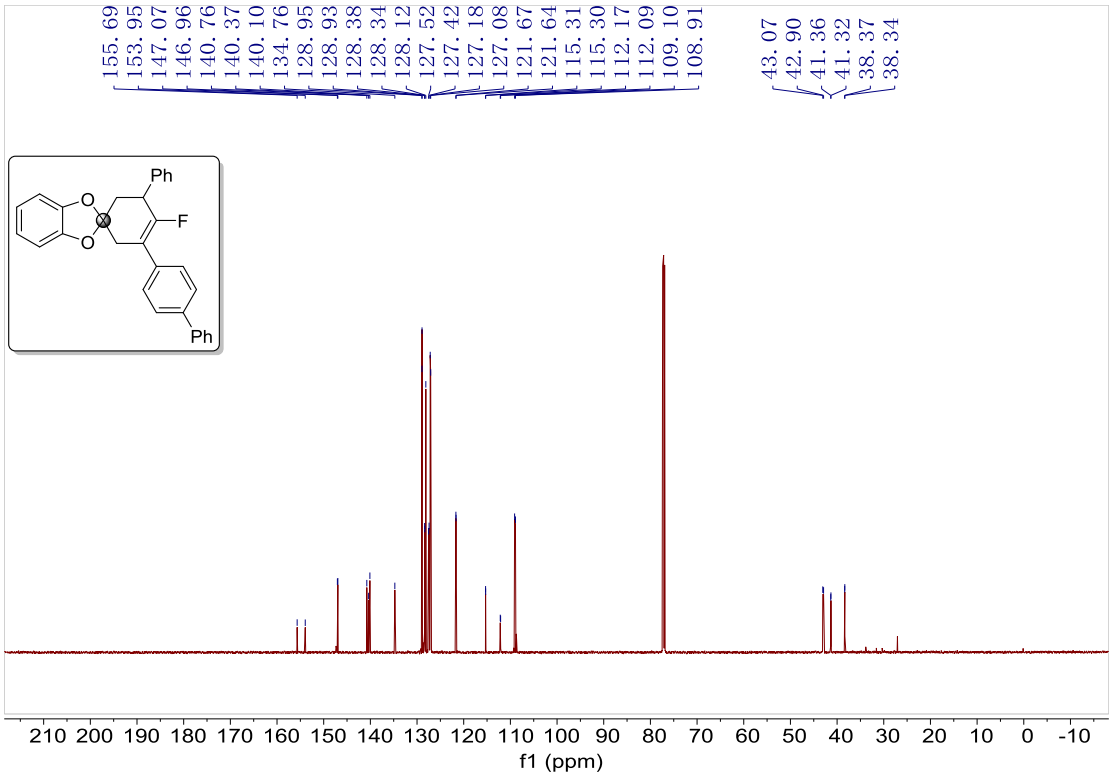
^{13}C NMR of 5h (150 MHz, $CDCl_3$)



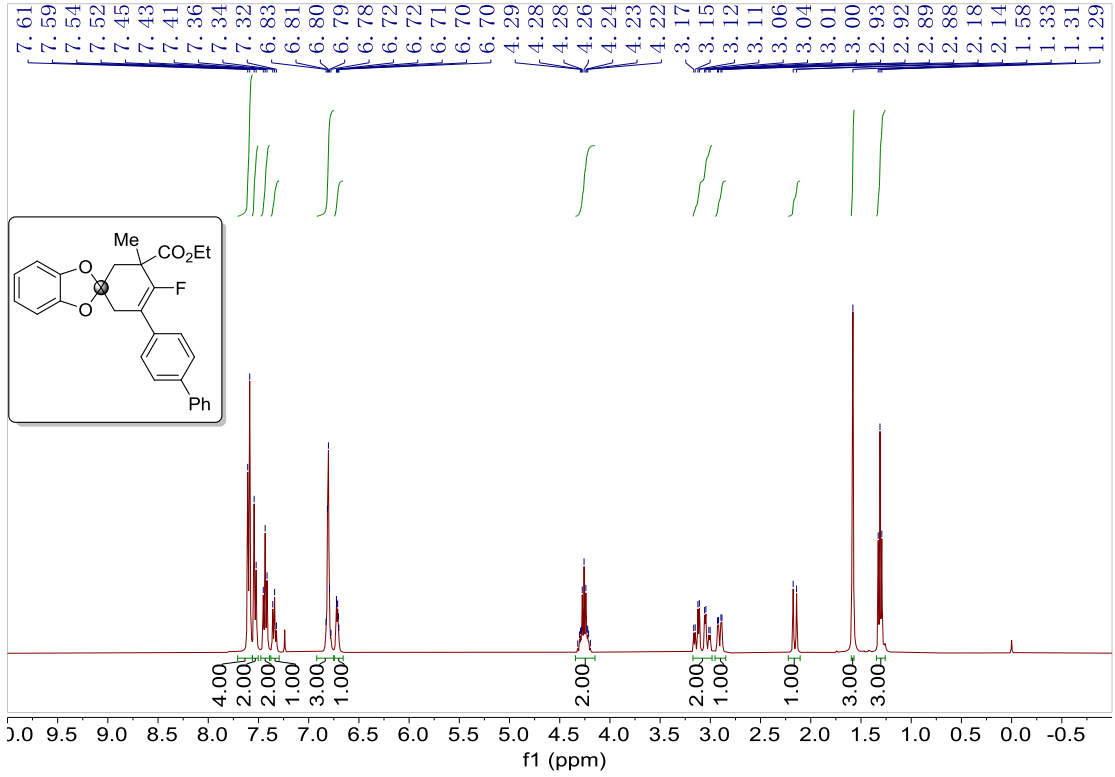
^{1}H NMR of 5i (400 MHz, $CDCl_3$)



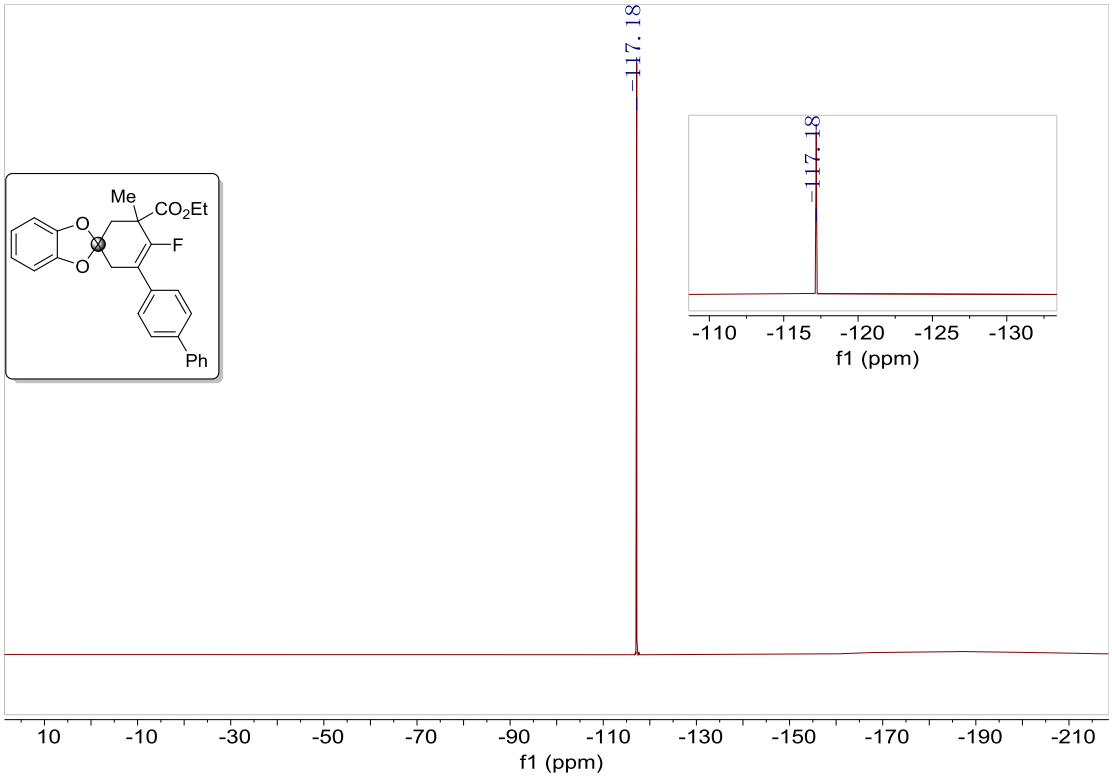
^{19}F NMR of 5i (376 MHz, $CDCl_3$)



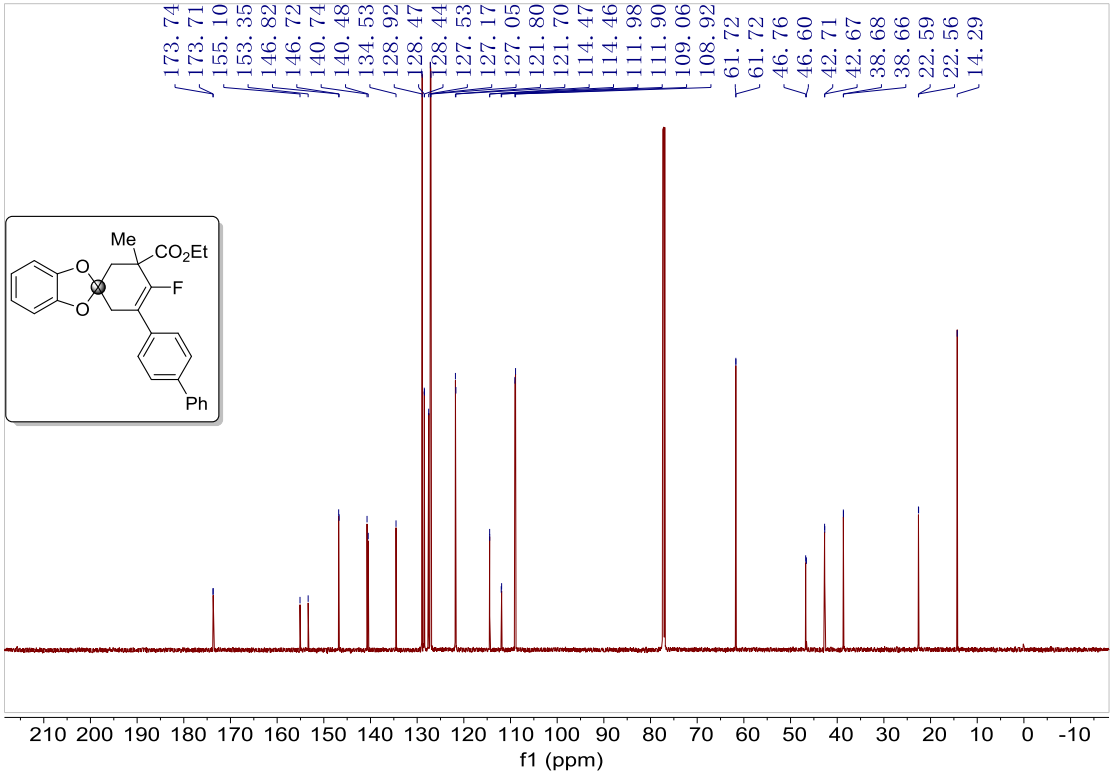
^{13}C NMR of 5i (150 MHz, $CDCl_3$)



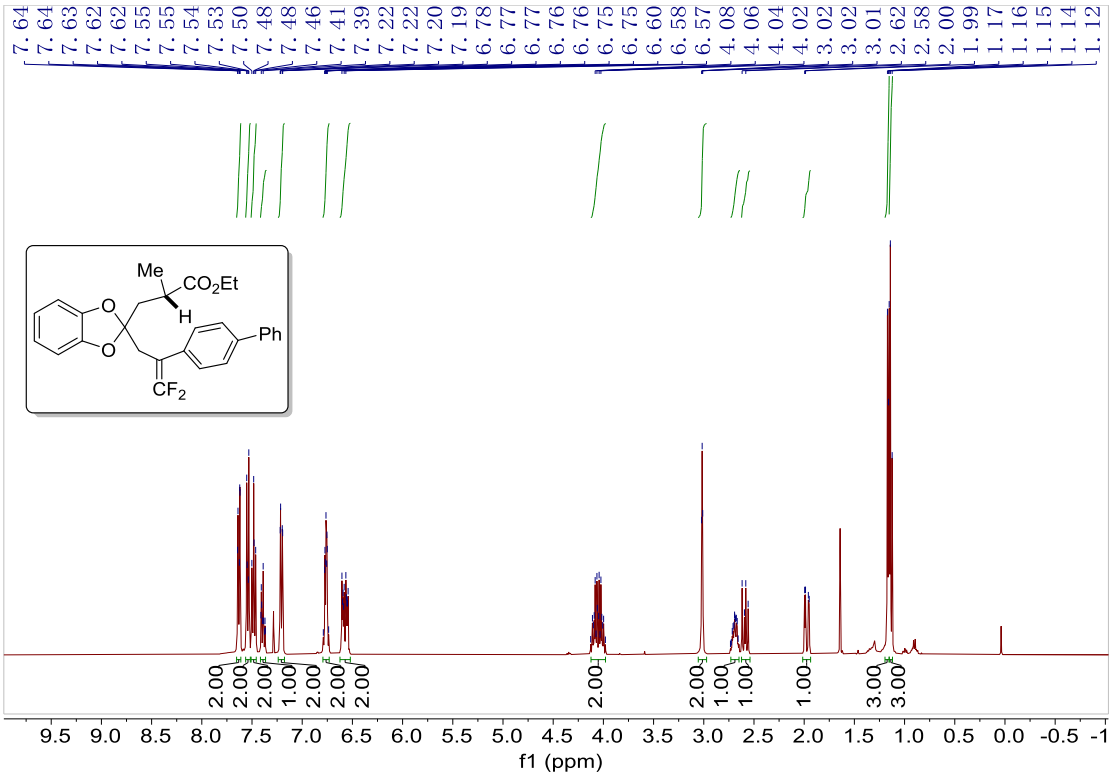
^{1}H NMR of 5j (400 MHz, $CDCl_3$)



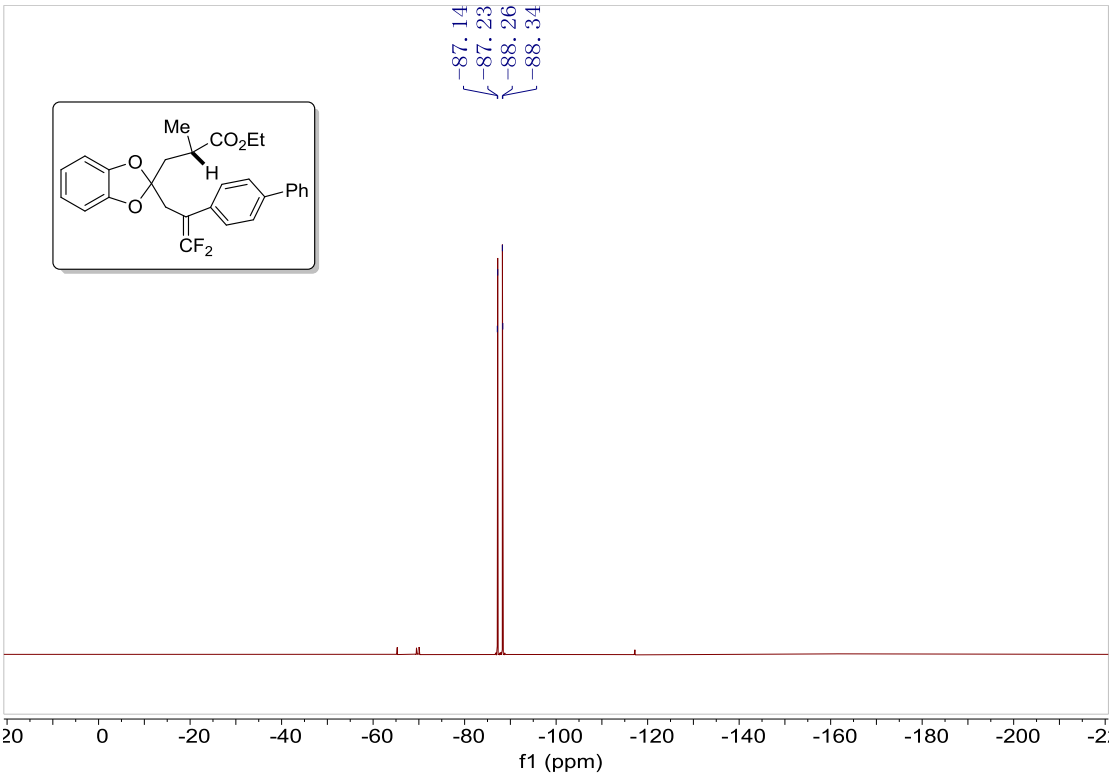
^{19}F NMR of 5j (376 MHz, $CDCl_3$)



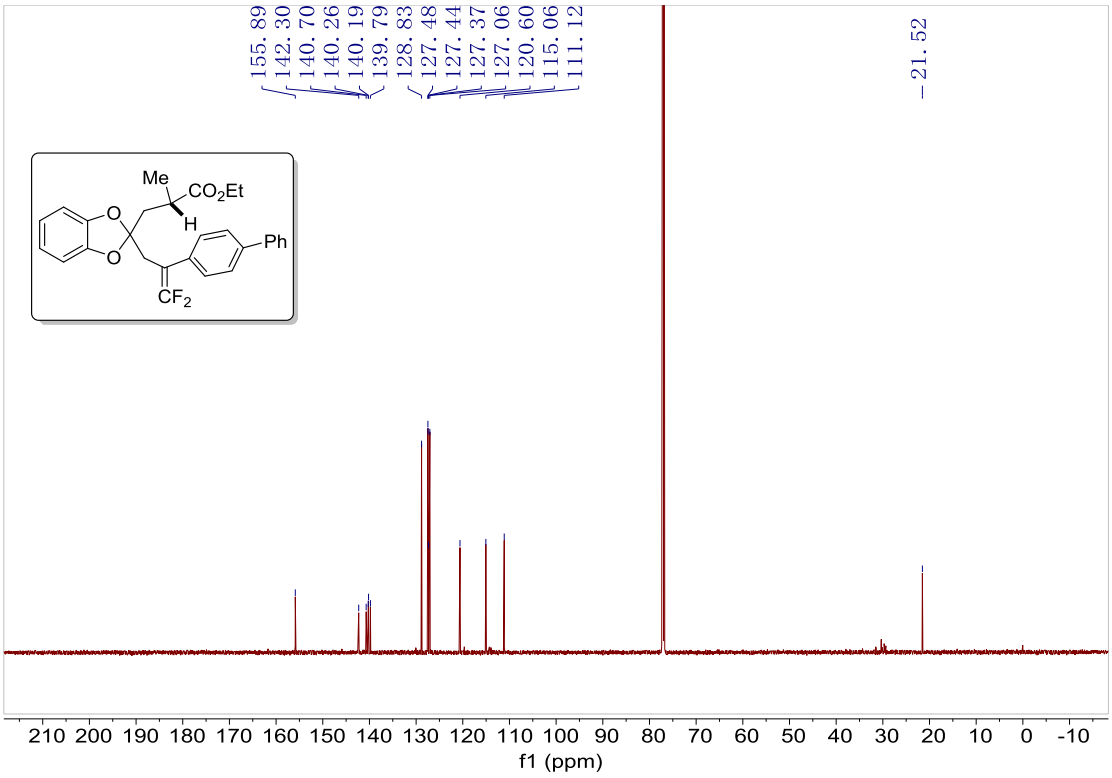
^{13}C NMR of 5j (150 MHz, $CDCl_3$)



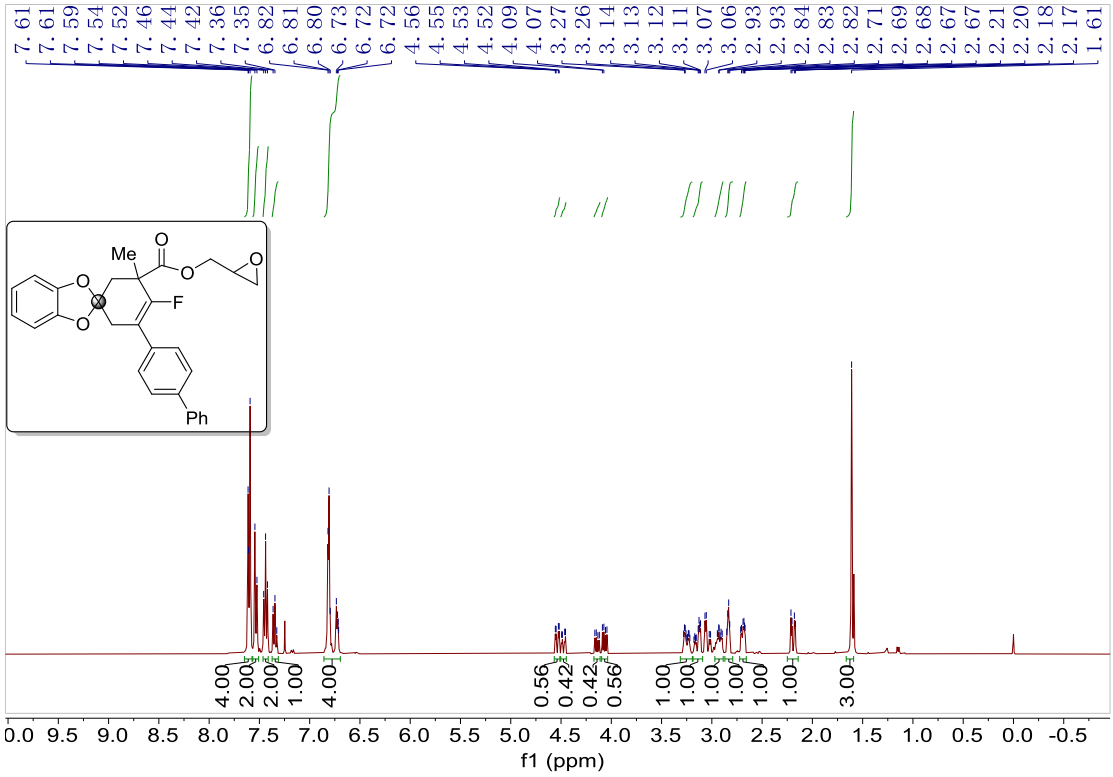
^{1}H NMR of 5j′ (400 MHz, $CDCl_3$)



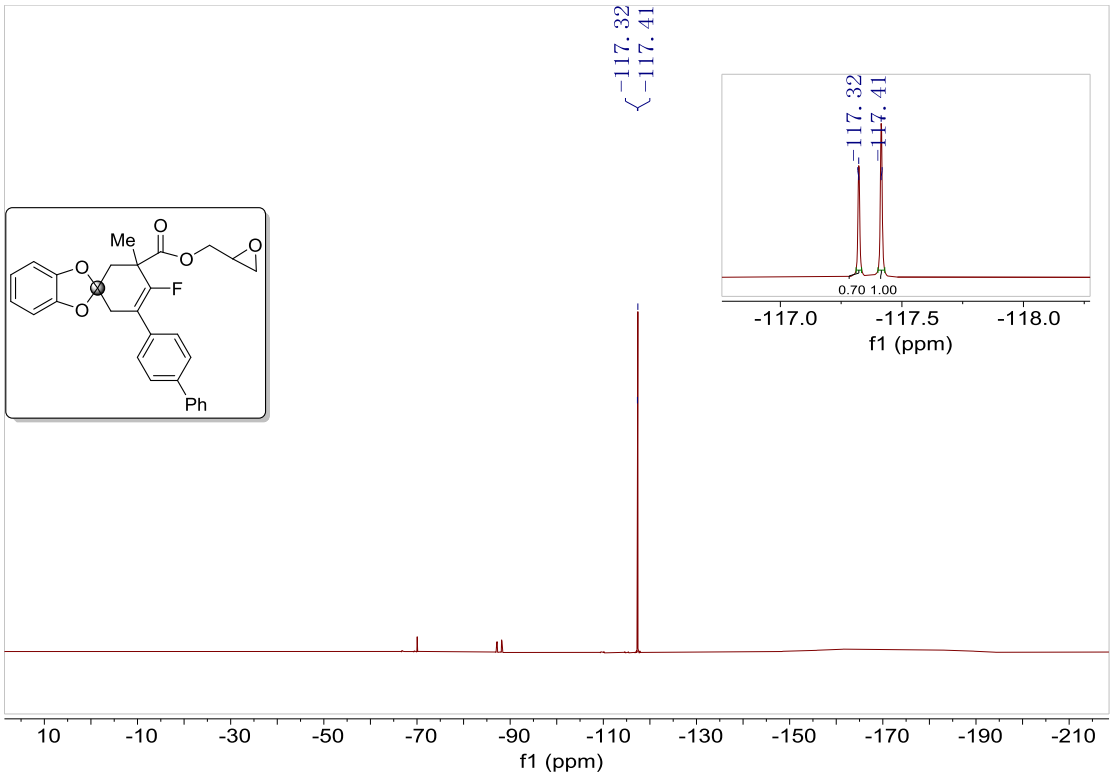
^{19}F NMR of 5j′ (376 MHz, $CDCl_3$)



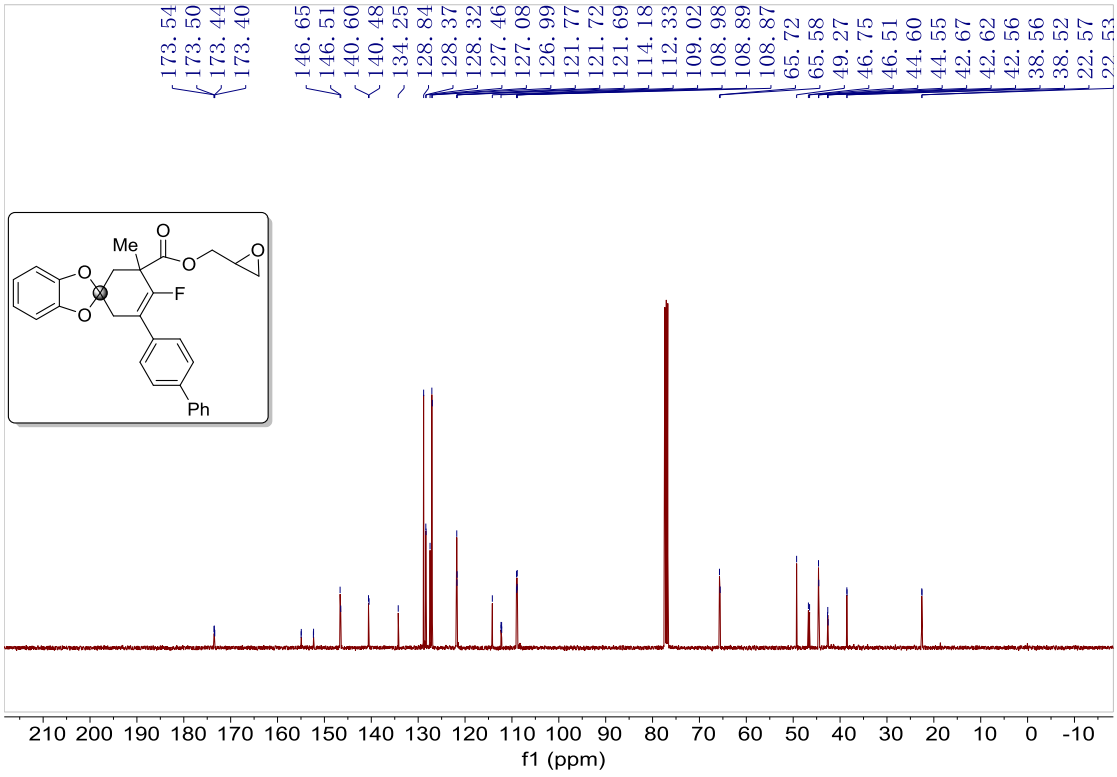
^{13}C NMR of 5j′ (150 MHz, $CDCl_3$)



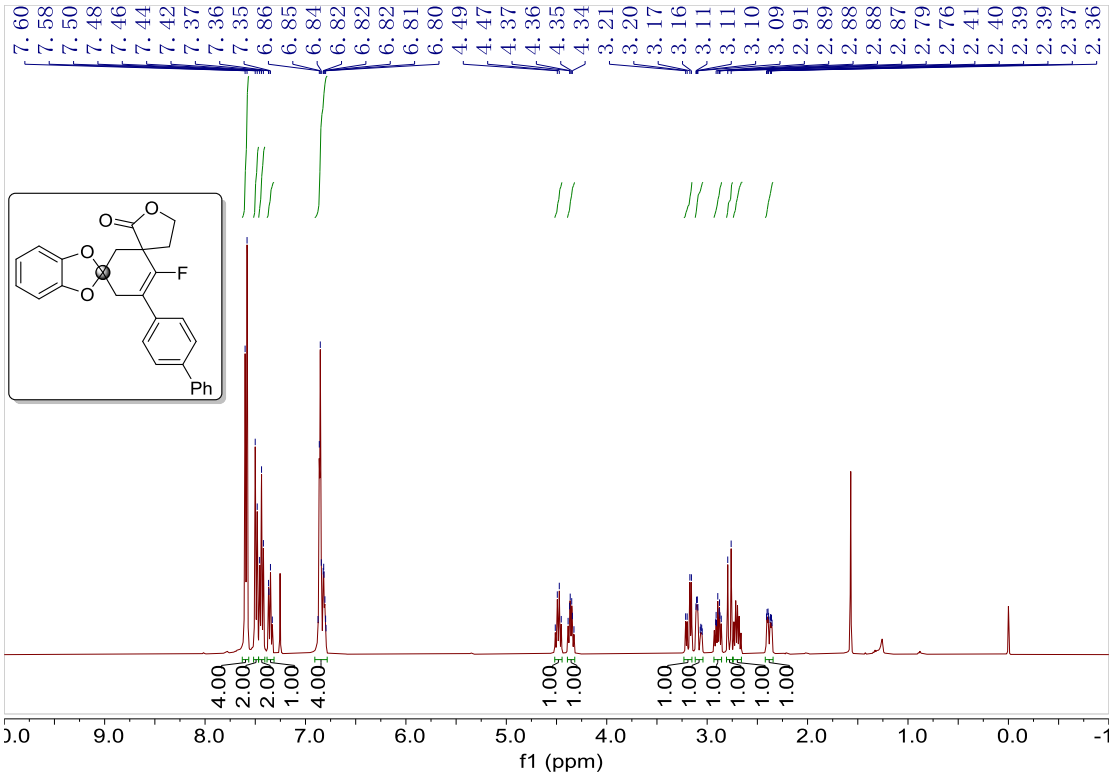
^{1}H NMR of 5k (400 MHz, $CDCl_3$)



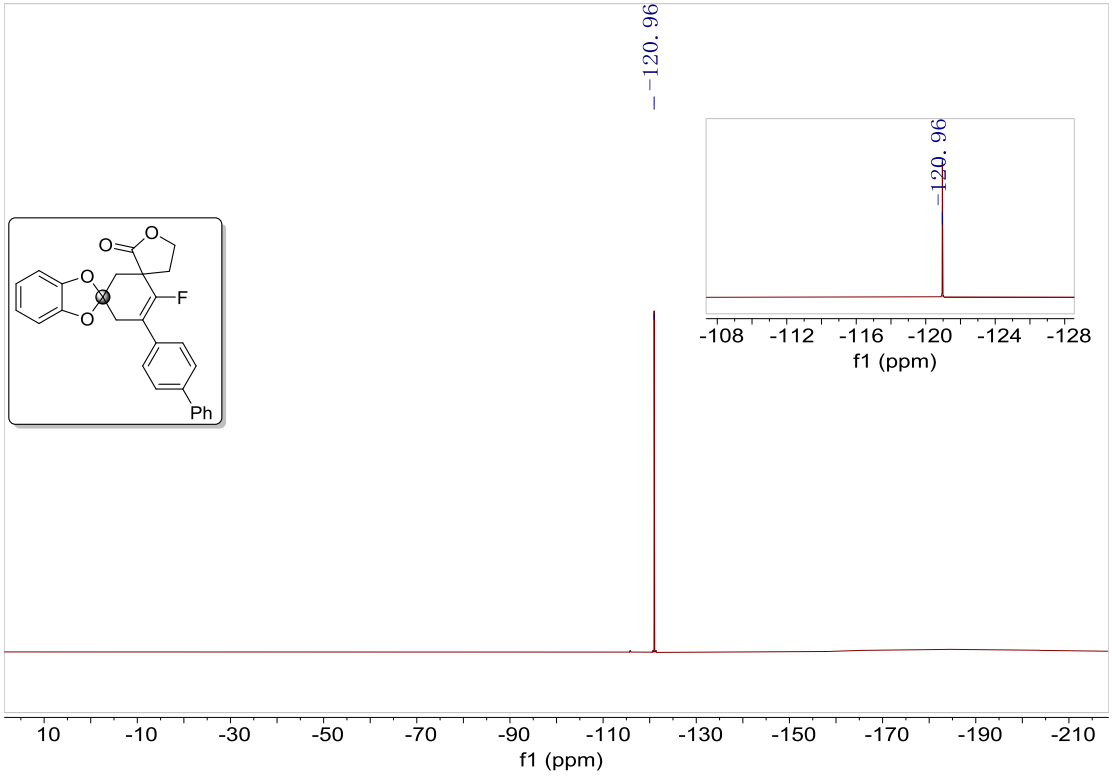
^{19}F NMR of 5k (376 MHz, $CDCl_3$)



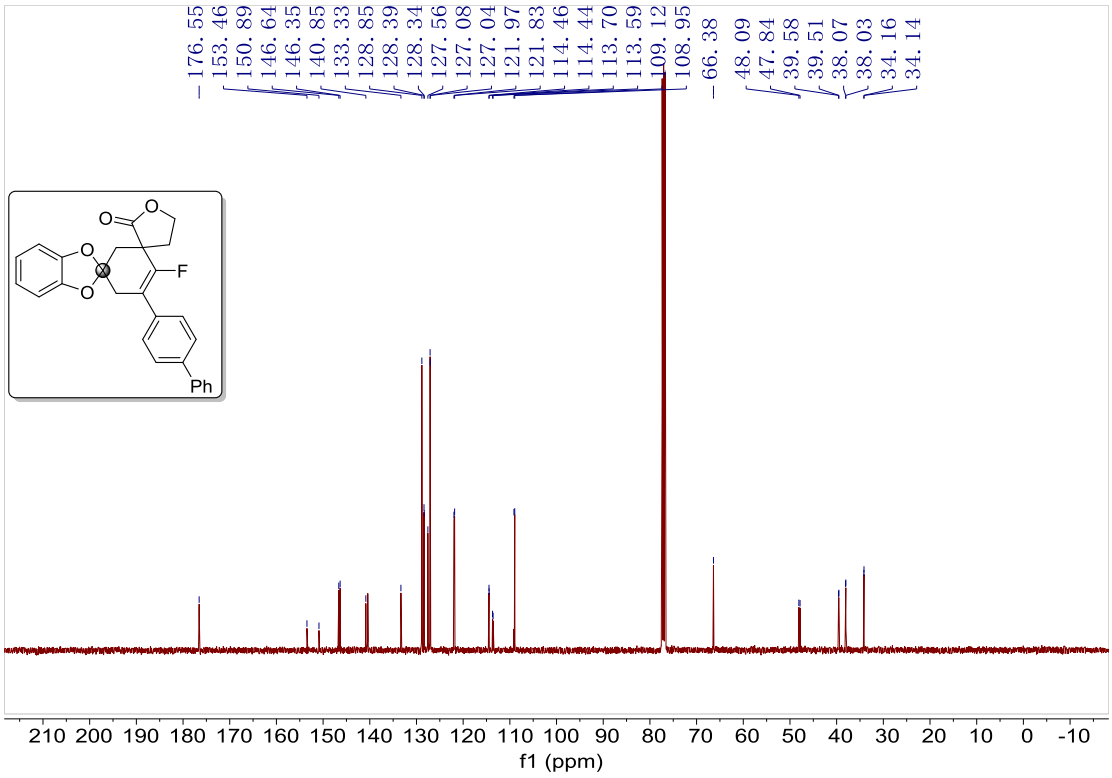
^{13}C NMR of 5k (150 MHz, $CDCl_3$)



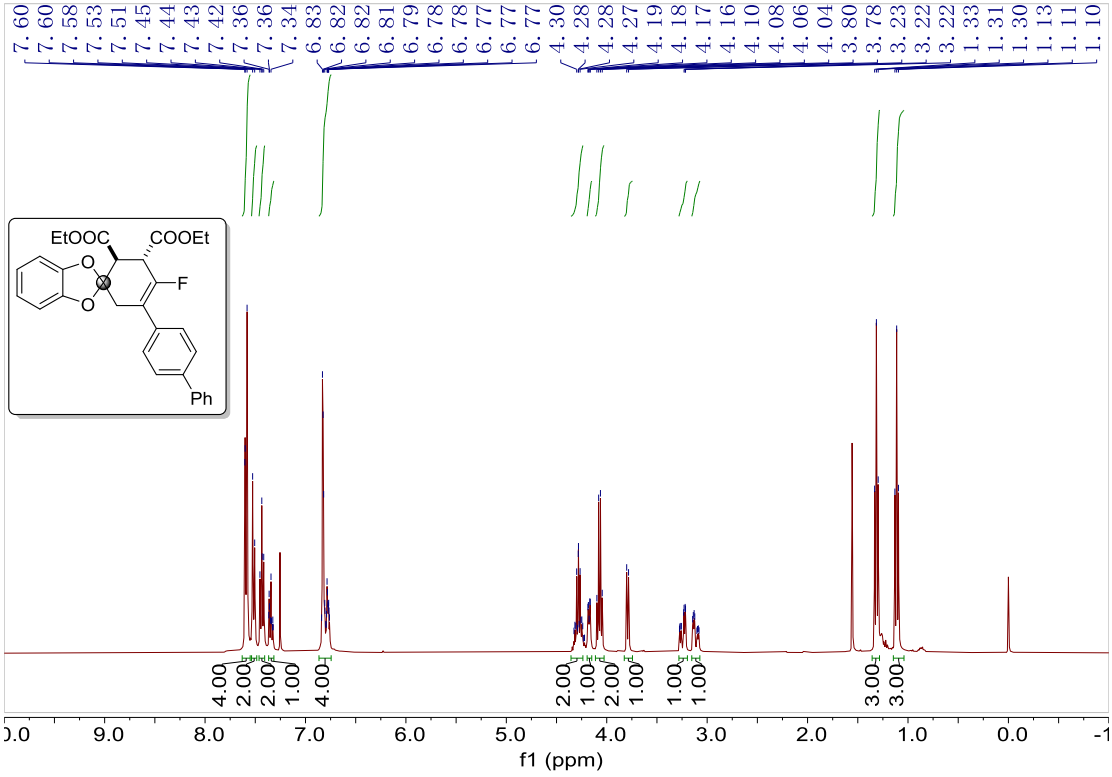
^{1}H NMR of 5l (400 MHz, $CDCl_3$)



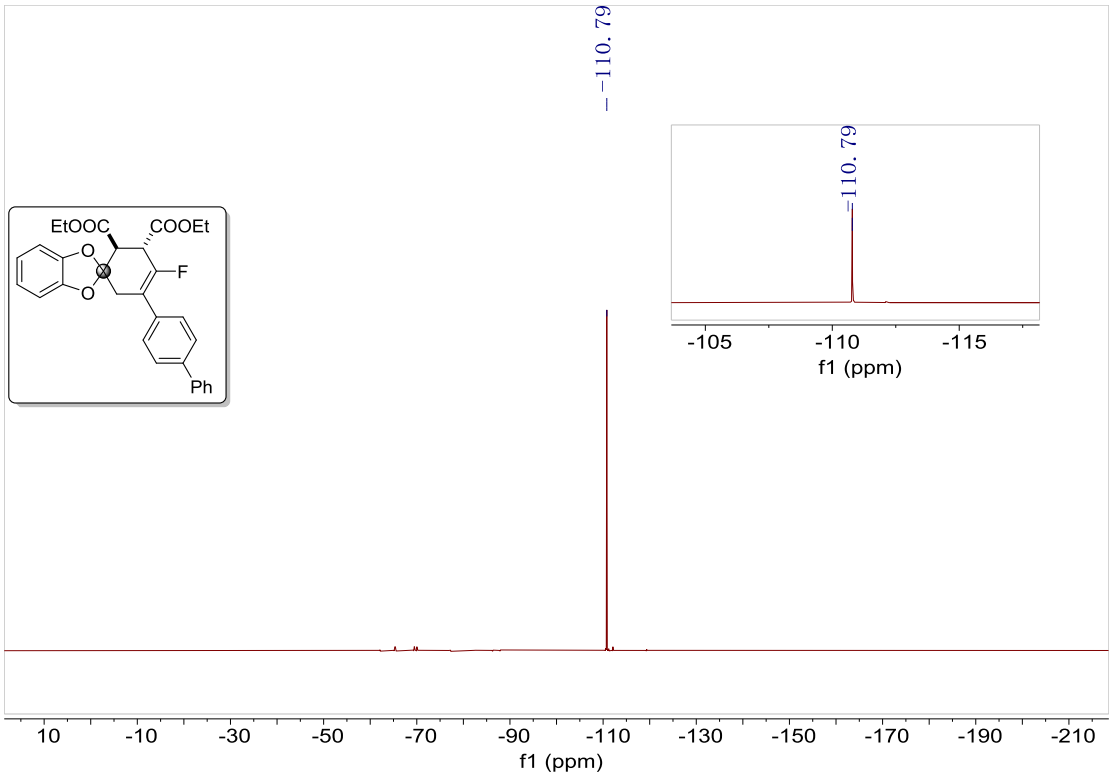
^{19}F NMR of 5l (376 MHz, $CDCl_3$)



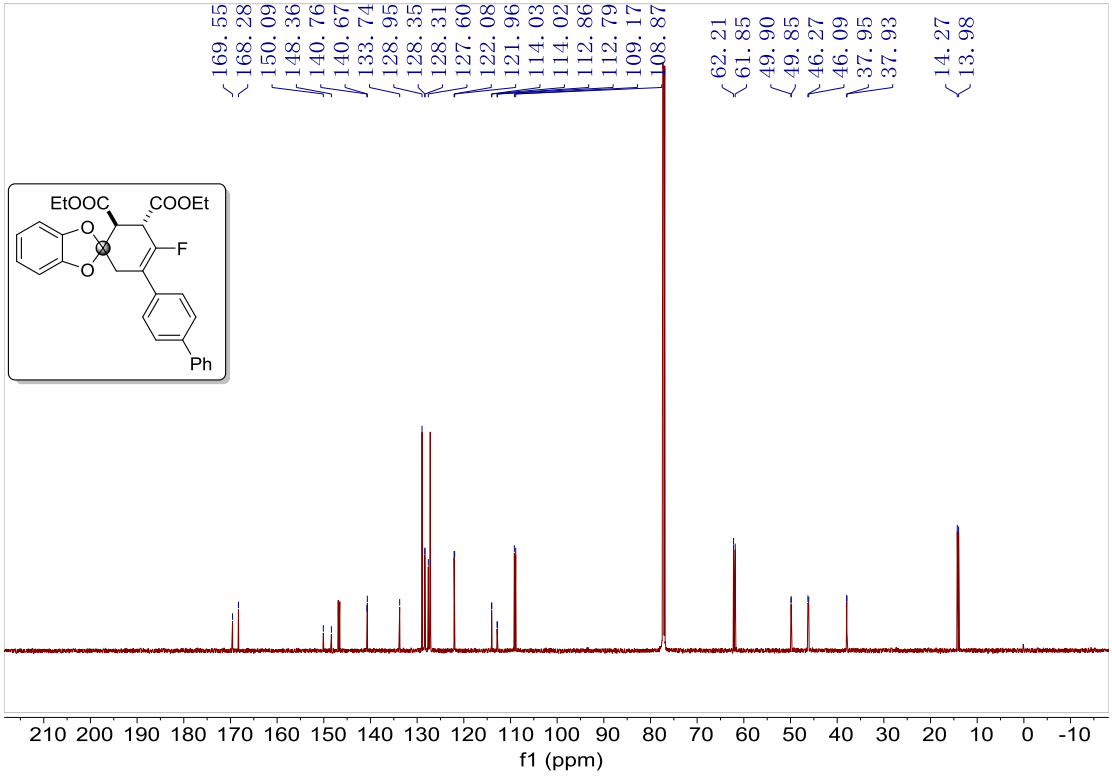
^{13}C NMR of 5l (150 MHz, $CDCl_3$)



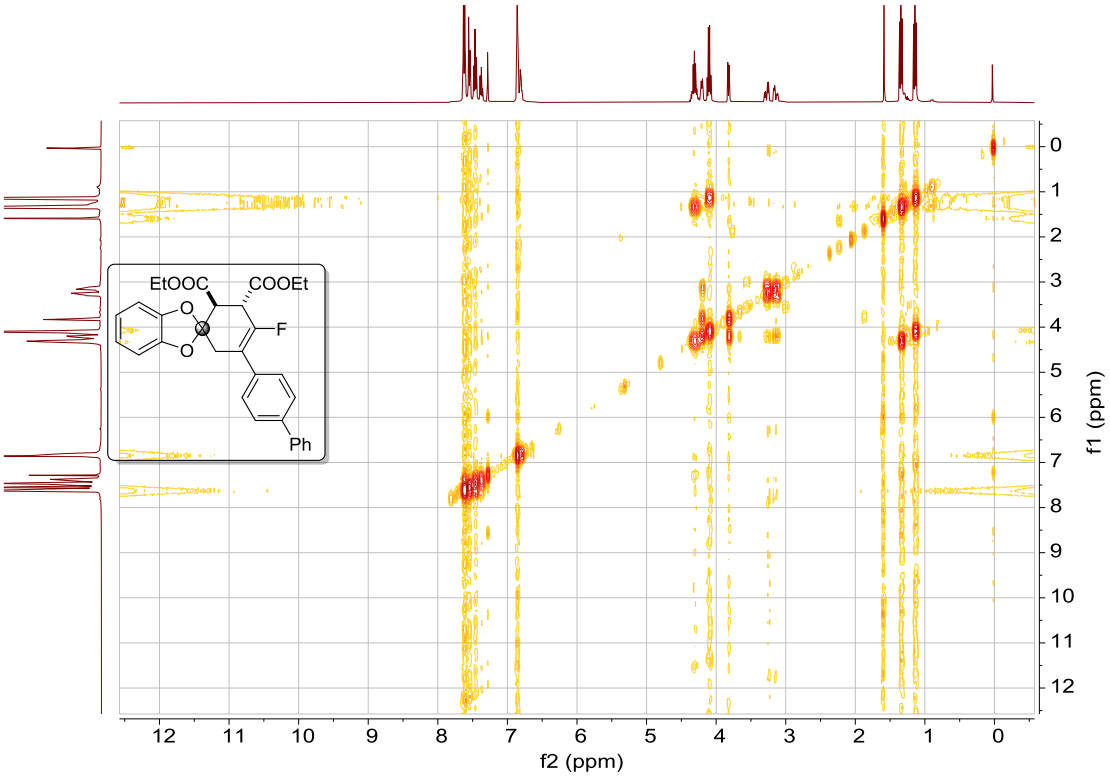
^{1}H NMR of 5m (400 MHz, $CDCl_3$)



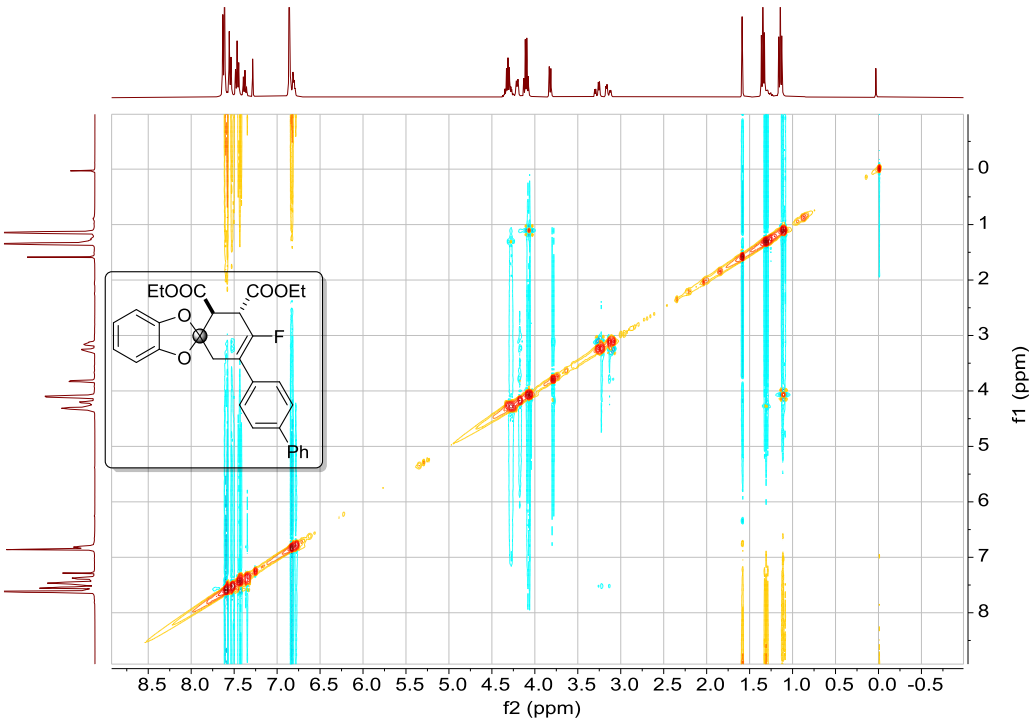
^{19}F NMR of 5m (376 MHz, $CDCl_3$)



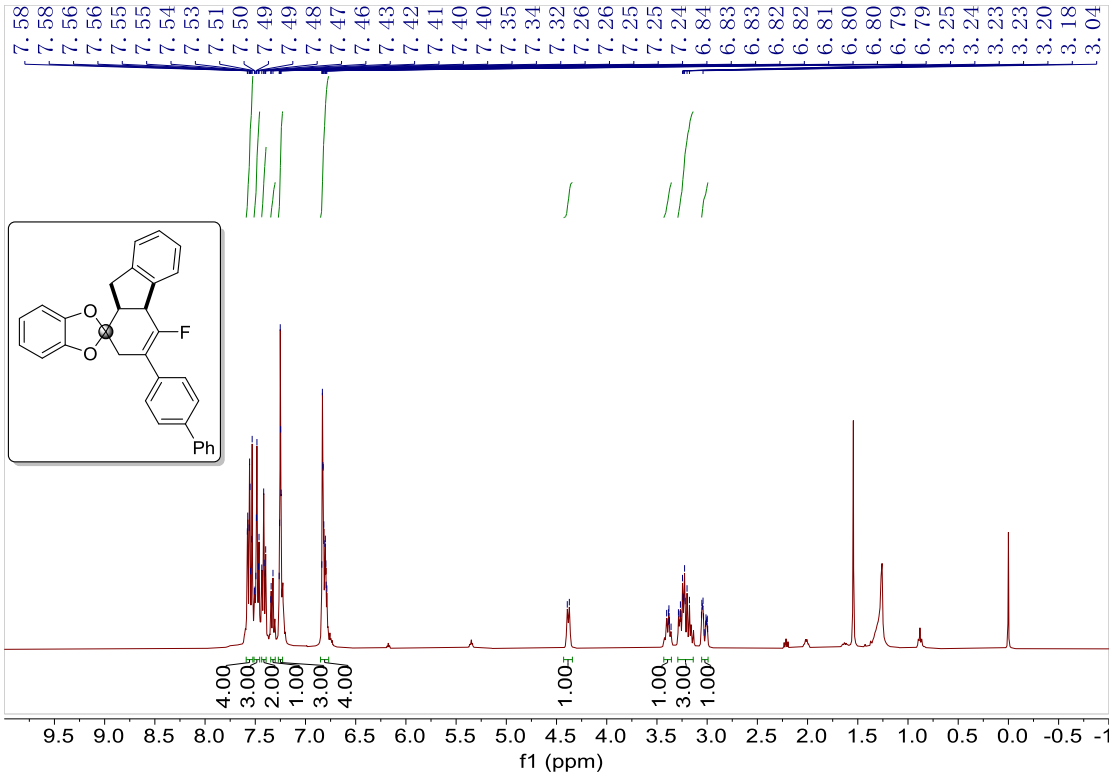
^{13}C NMR of 5m (150 MHz, $CDCl_3$)



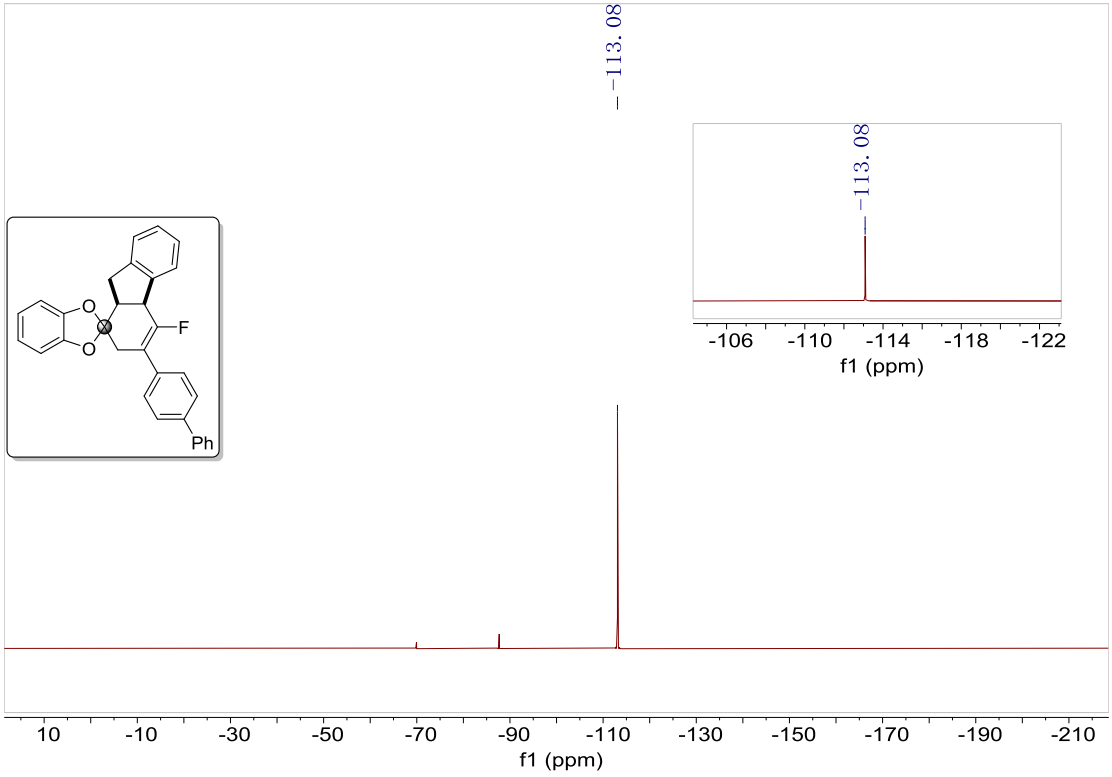
H-H COSY of 5m



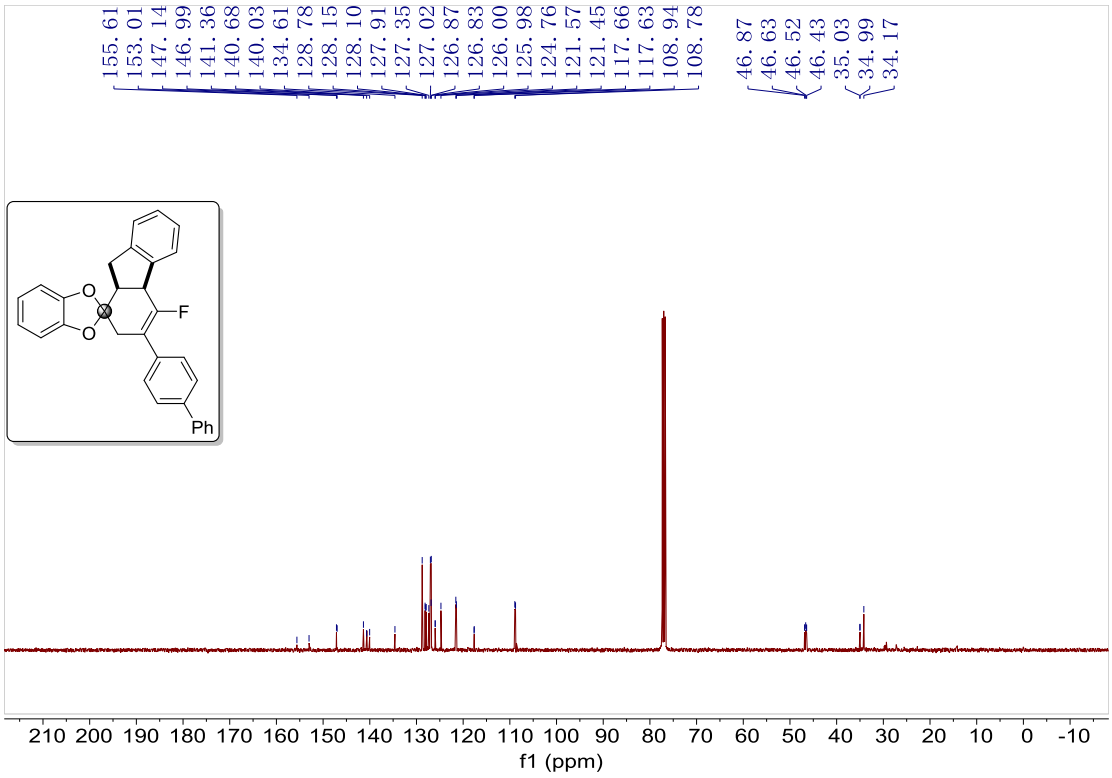
H-H NOESY of 5m



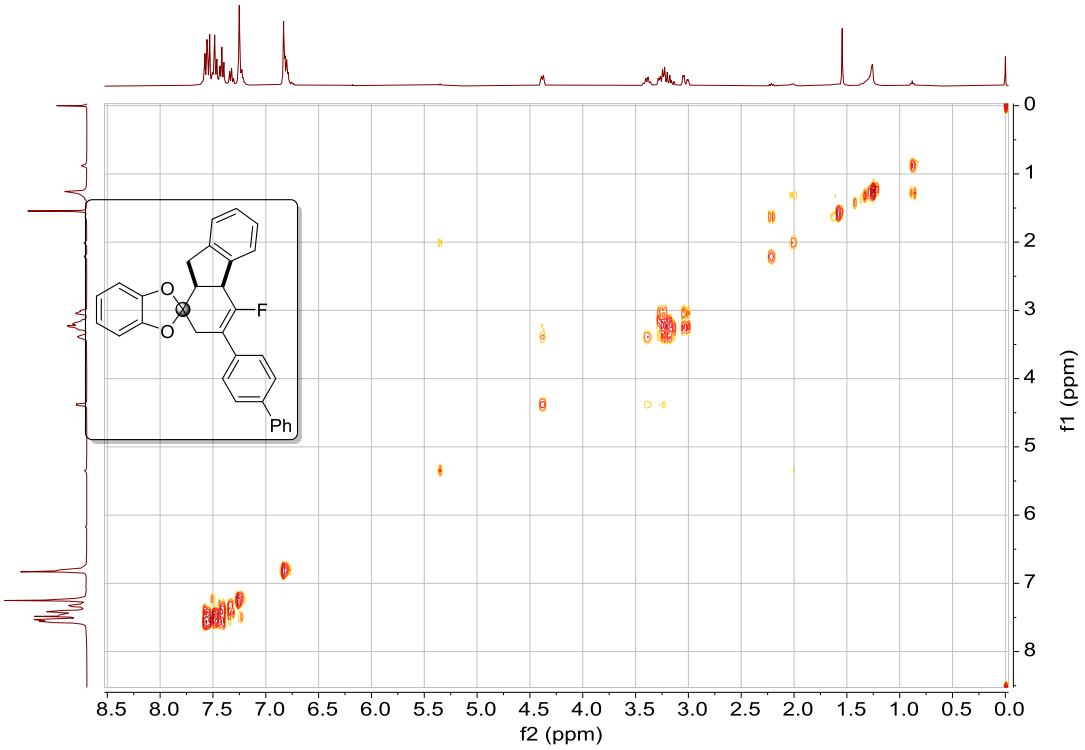
^{1}H NMR of 5n (400 MHz, $CDCl_3$)



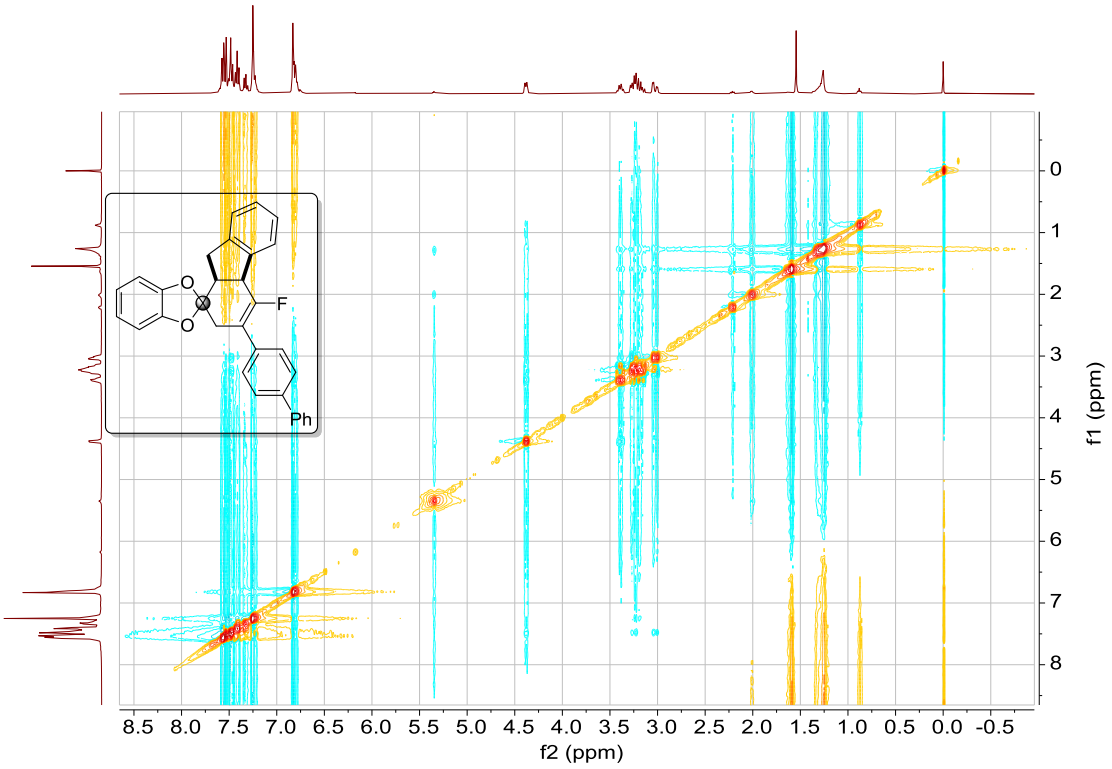
^{19}F NMR of 5n (376 MHz, $CDCl_3$)



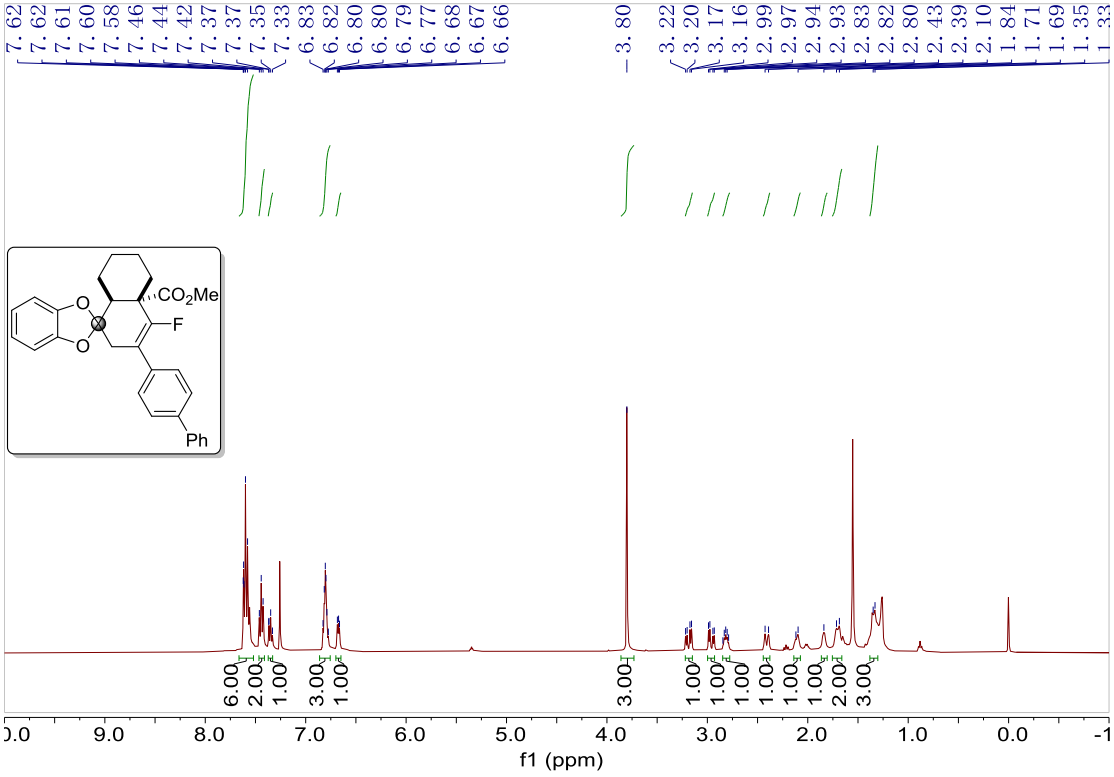
^{13}C NMR of 5n (150 MHz, $CDCl_3$)



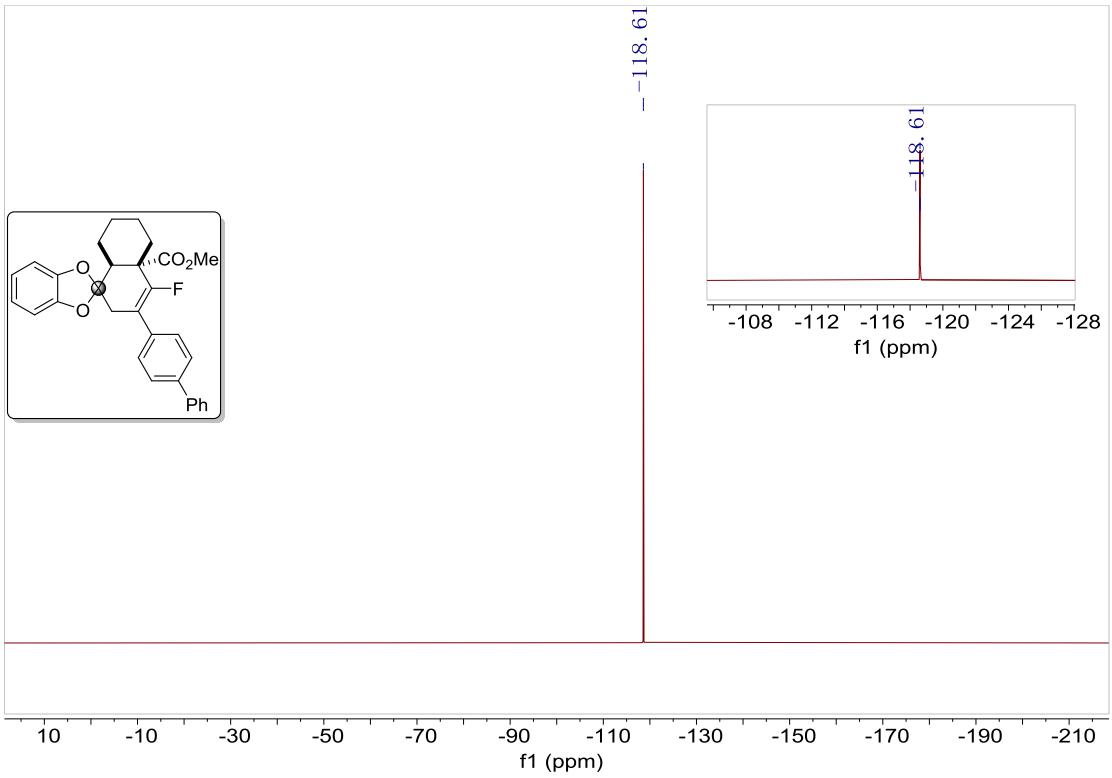
H-H COSY of 5n



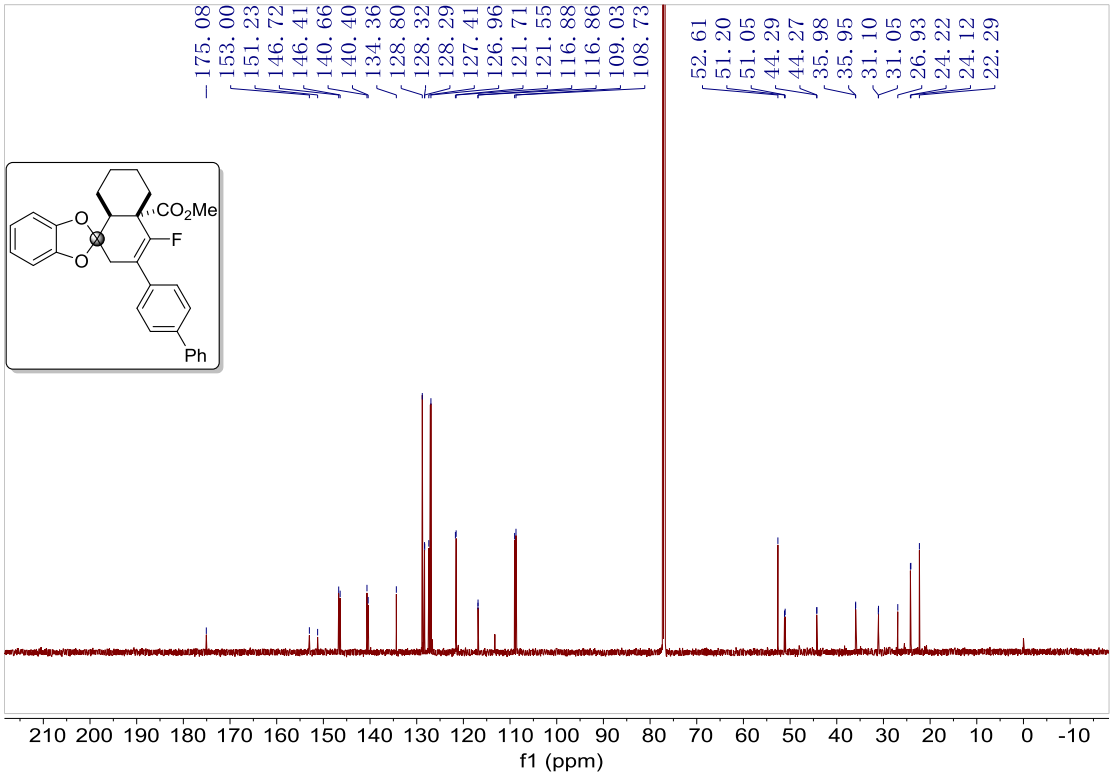
H-H NOESY of 5n



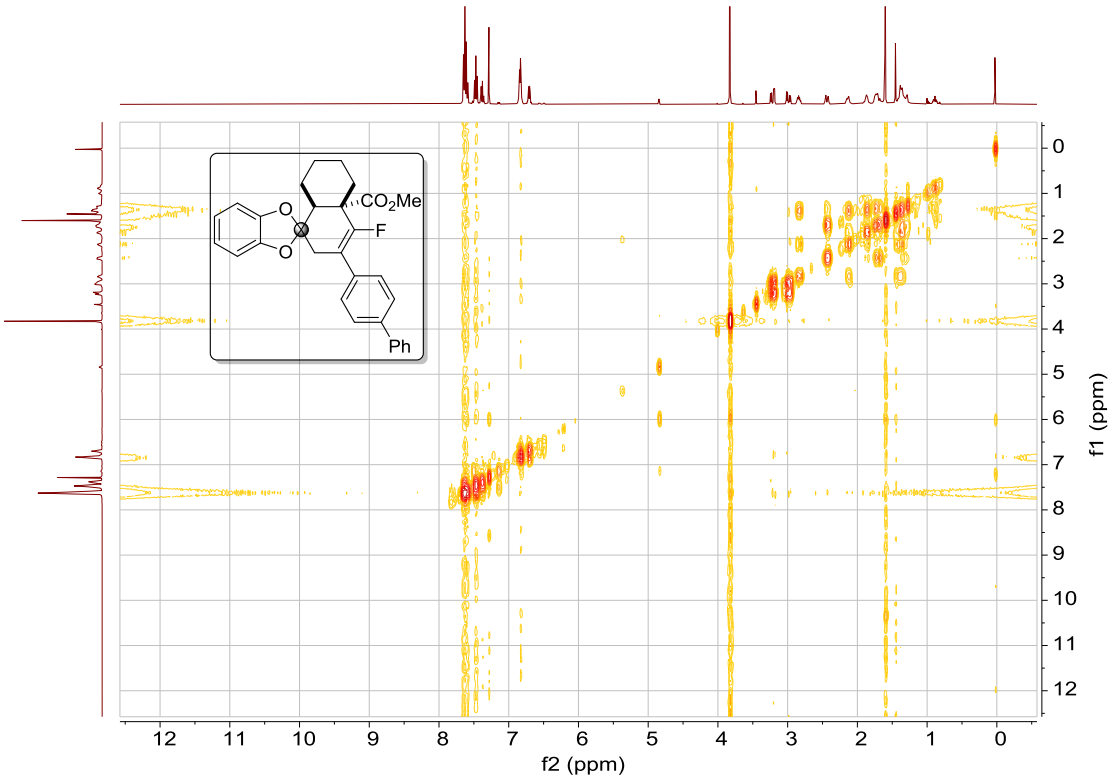
^{1}H NMR of 5o (400 MHz, $CDCl_3$)



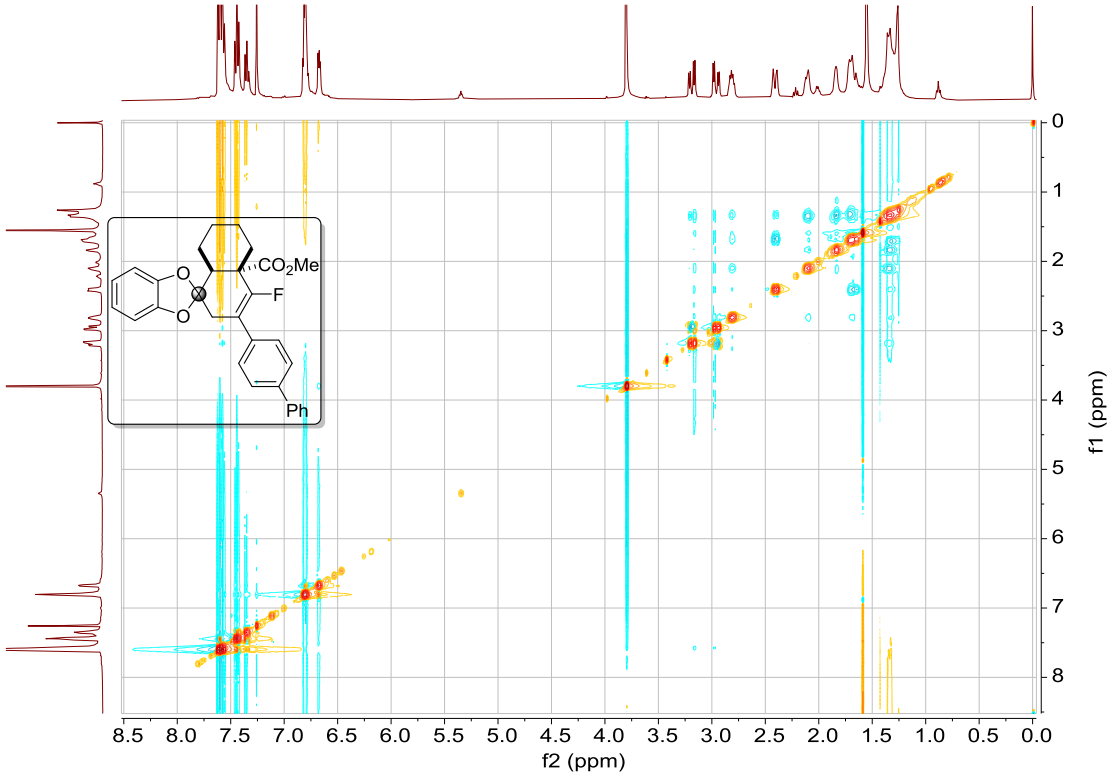
^{19}F NMR of 5o (376 MHz, $CDCl_3$)



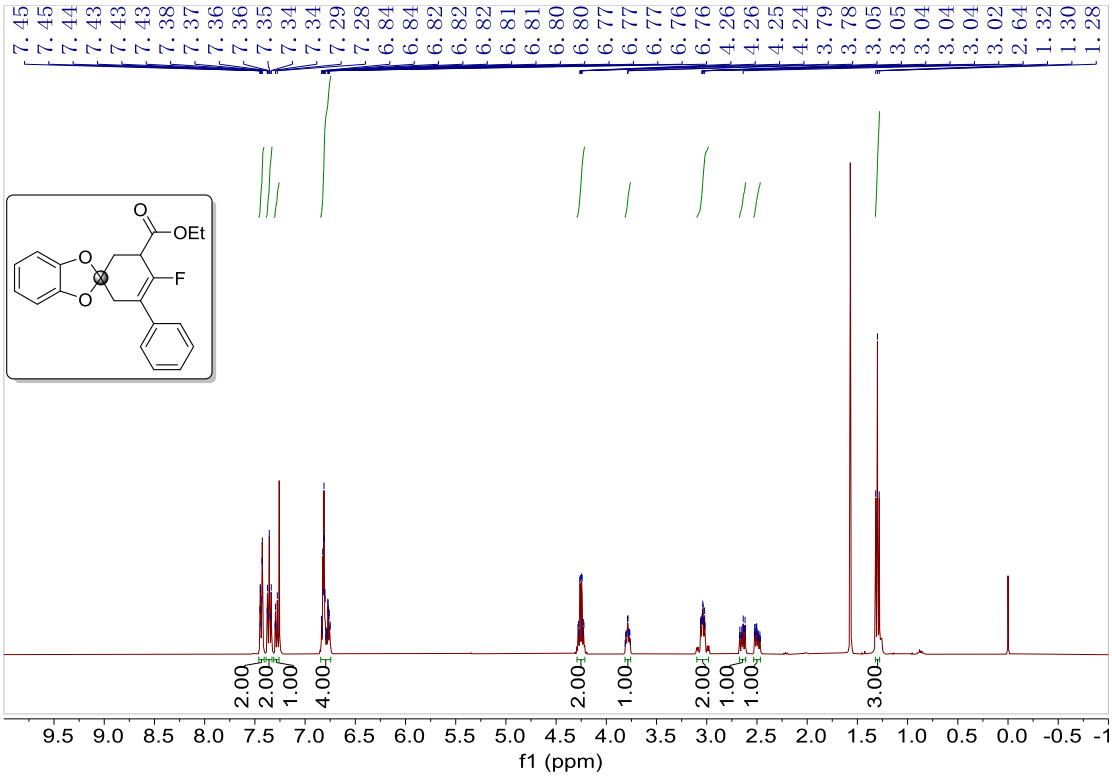
^{13}C NMR of 5o (150 MHz, $CDCl_3$)



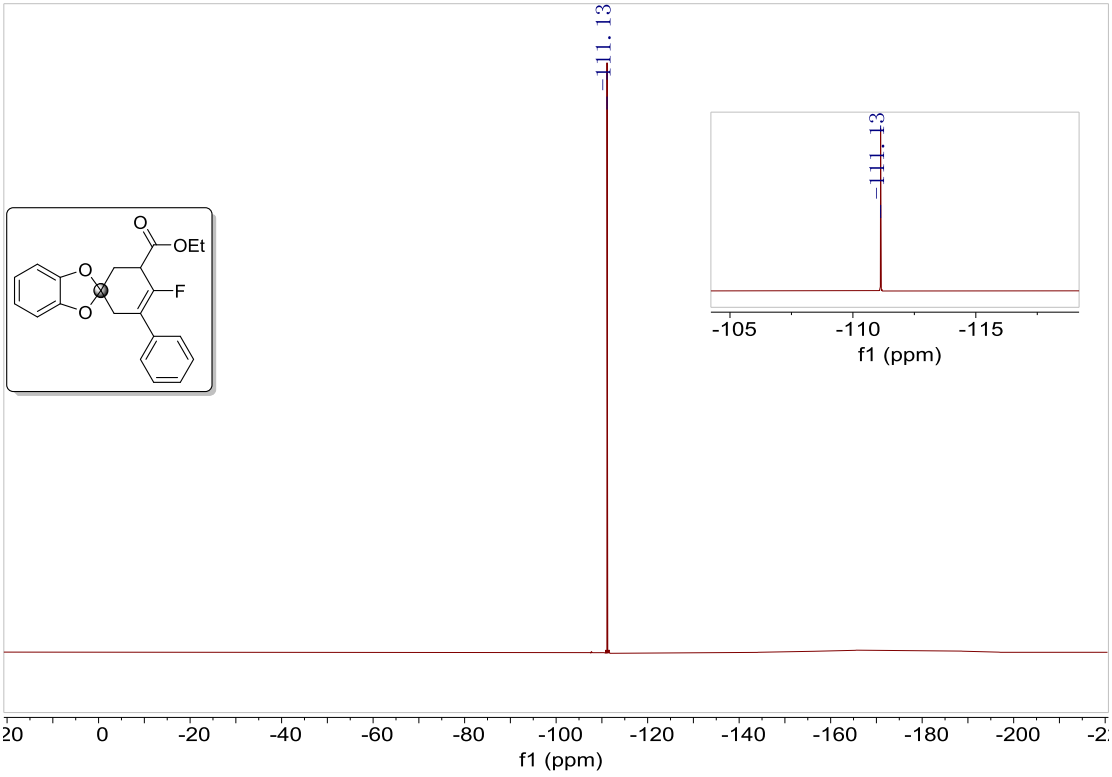
H-H COSY of 5o



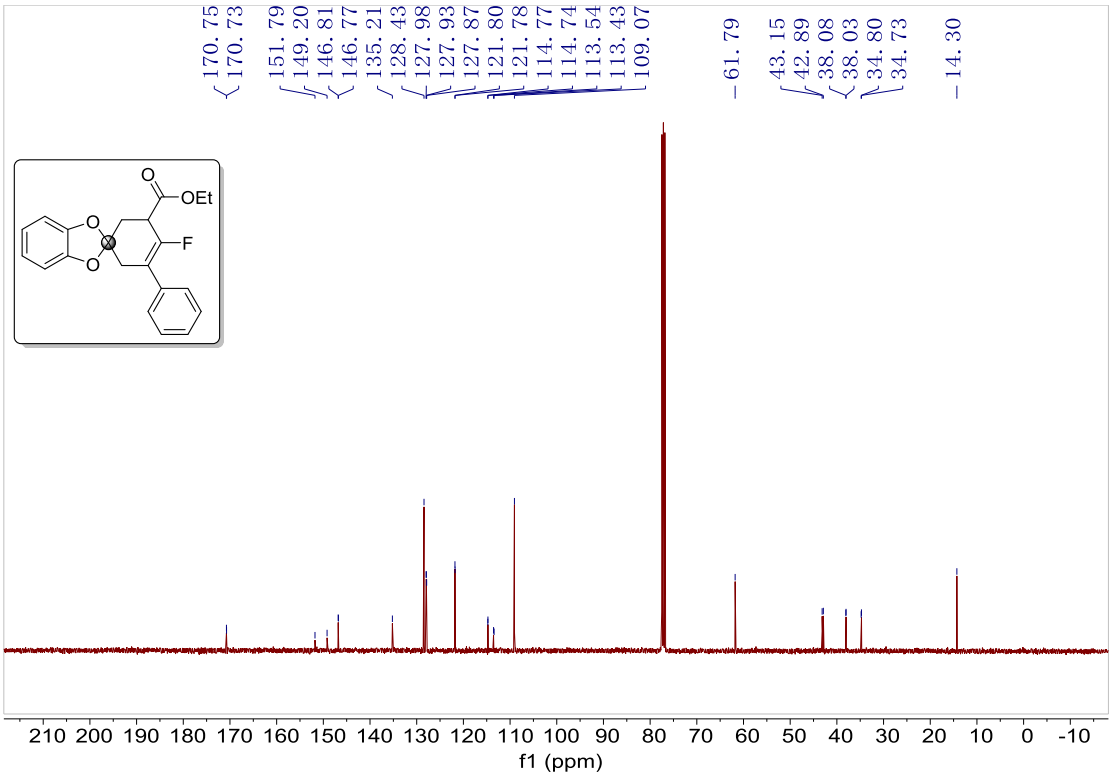
H-H NOESY of 5o



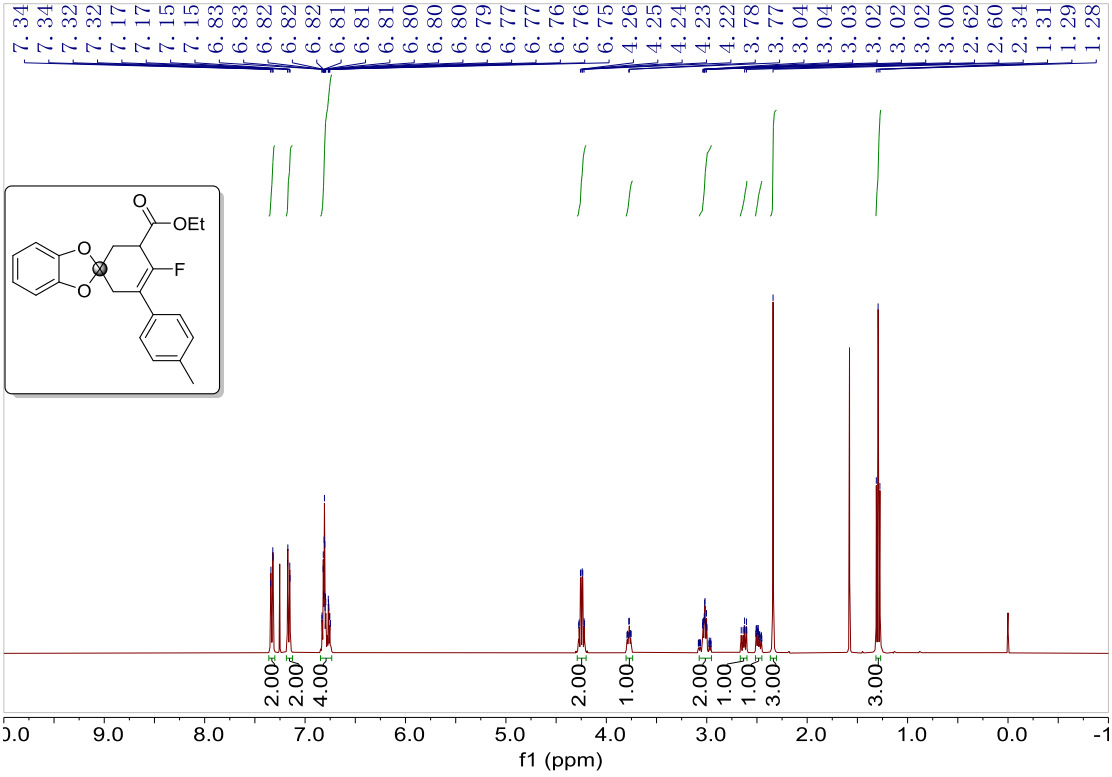
^{1}H NMR of 5p (400 MHz, $CDCl_3$)



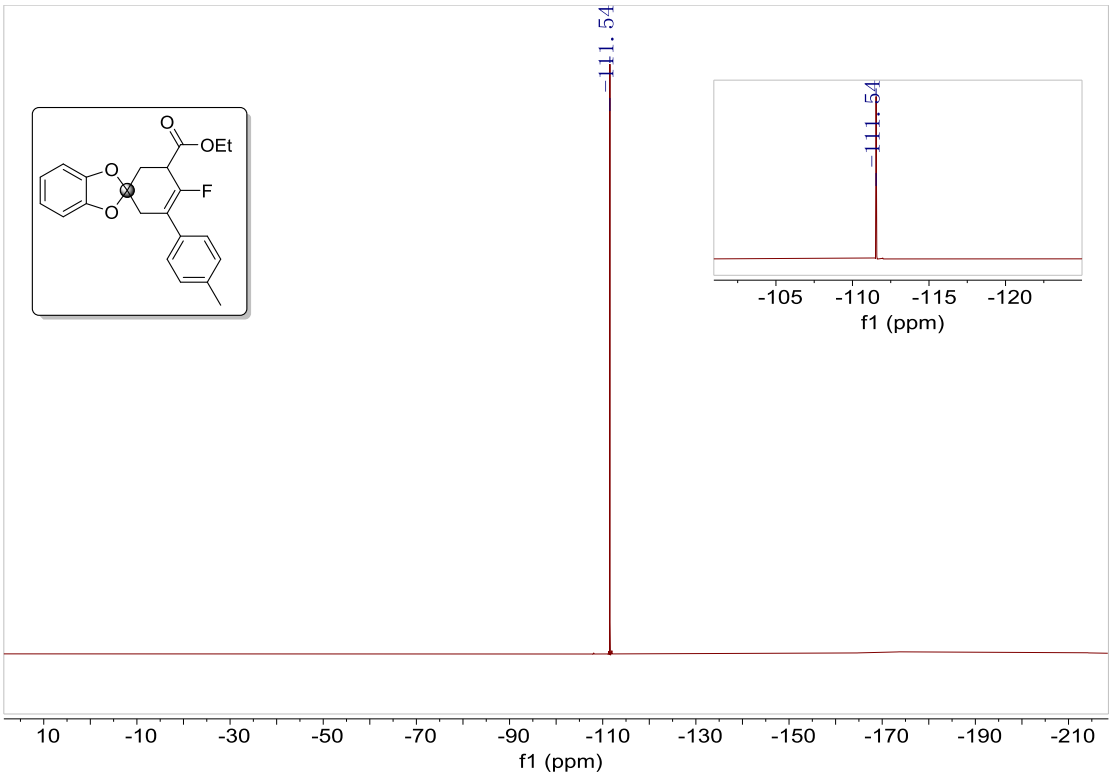
^{19}F NMR of 5p (376 MHz, $CDCl_3$)



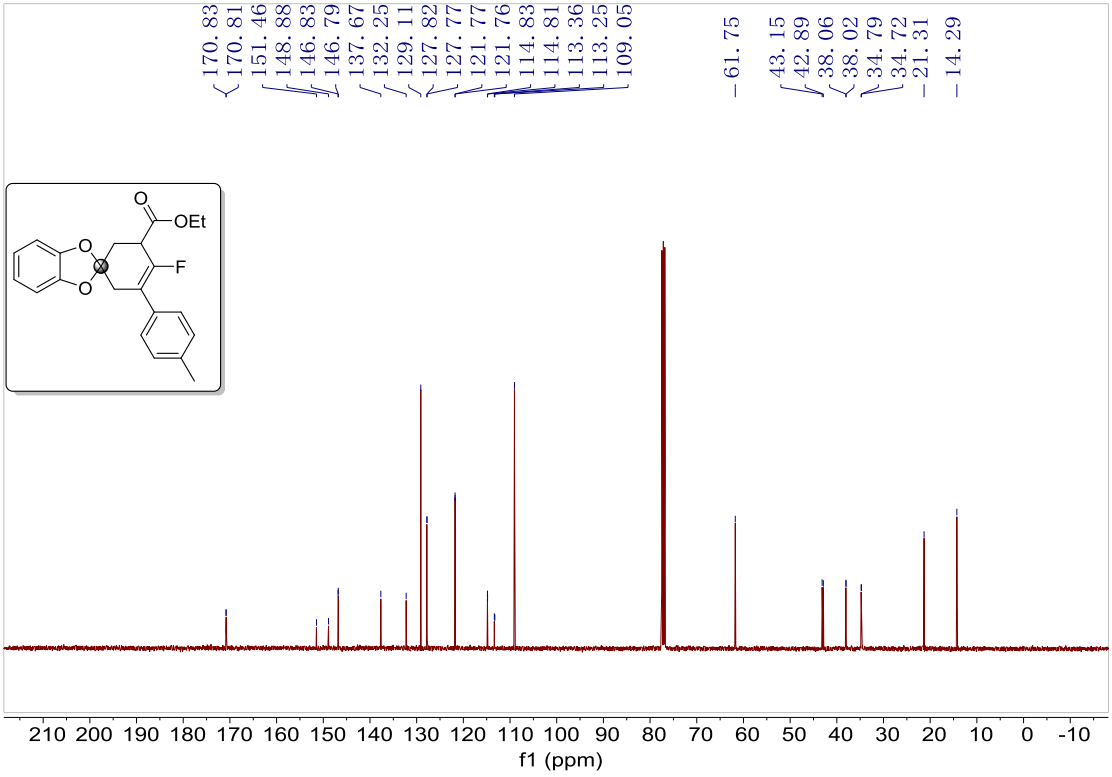
^{13}C NMR of 5p (100 MHz, $CDCl_3$)



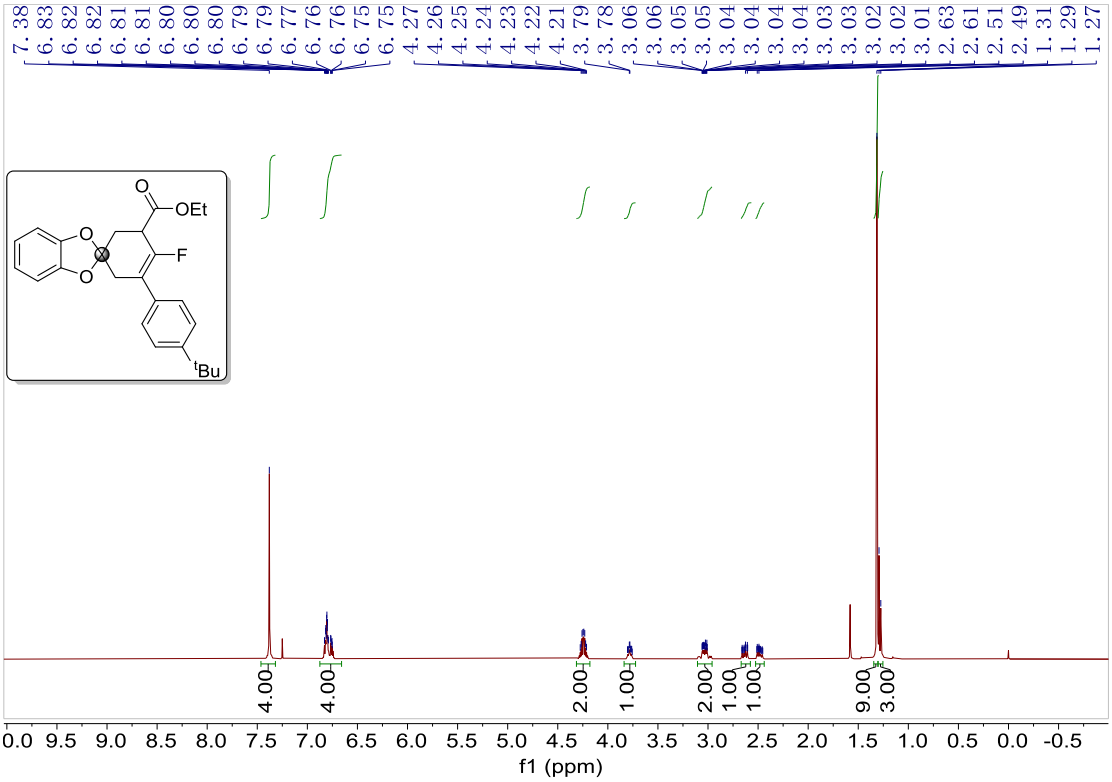
^{1}H NMR of 5q (400 MHz, $CDCl_3$)



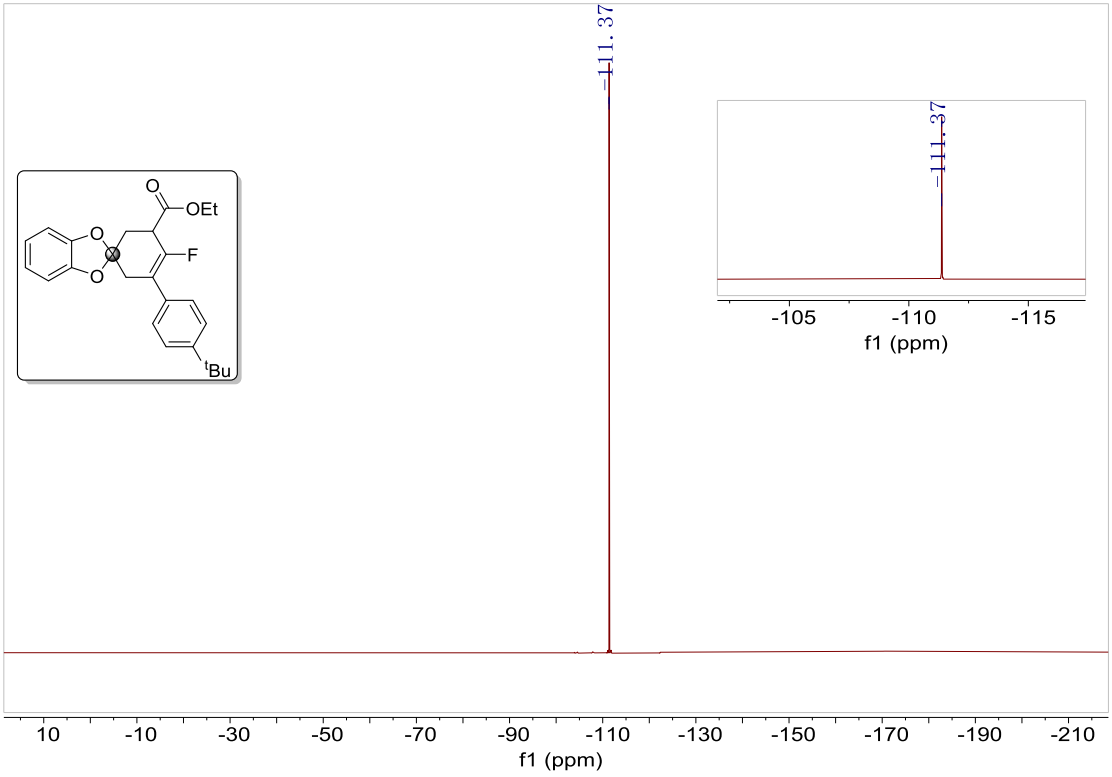
^{19}F NMR of 5q (376 MHz, $CDCl_3$)



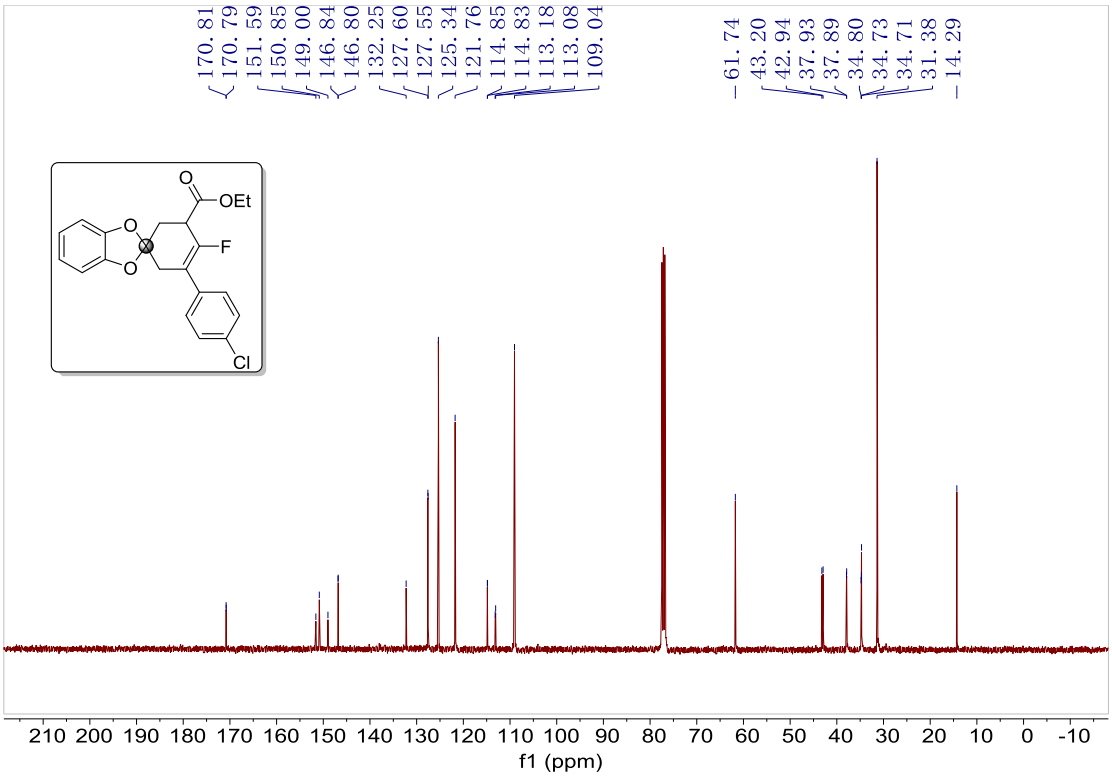
^{13}C NMR of 5q (100 MHz, $CDCl_3$)



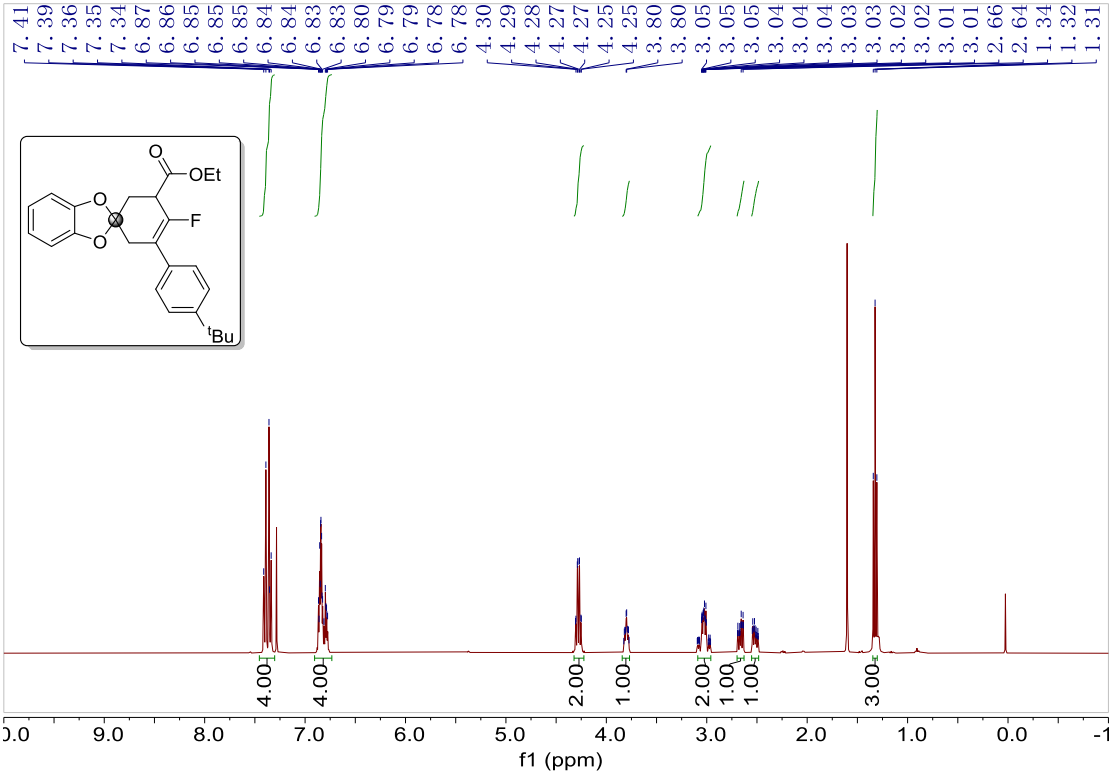
^{1}H NMR of 5r (400 MHz, $CDCl_3$)



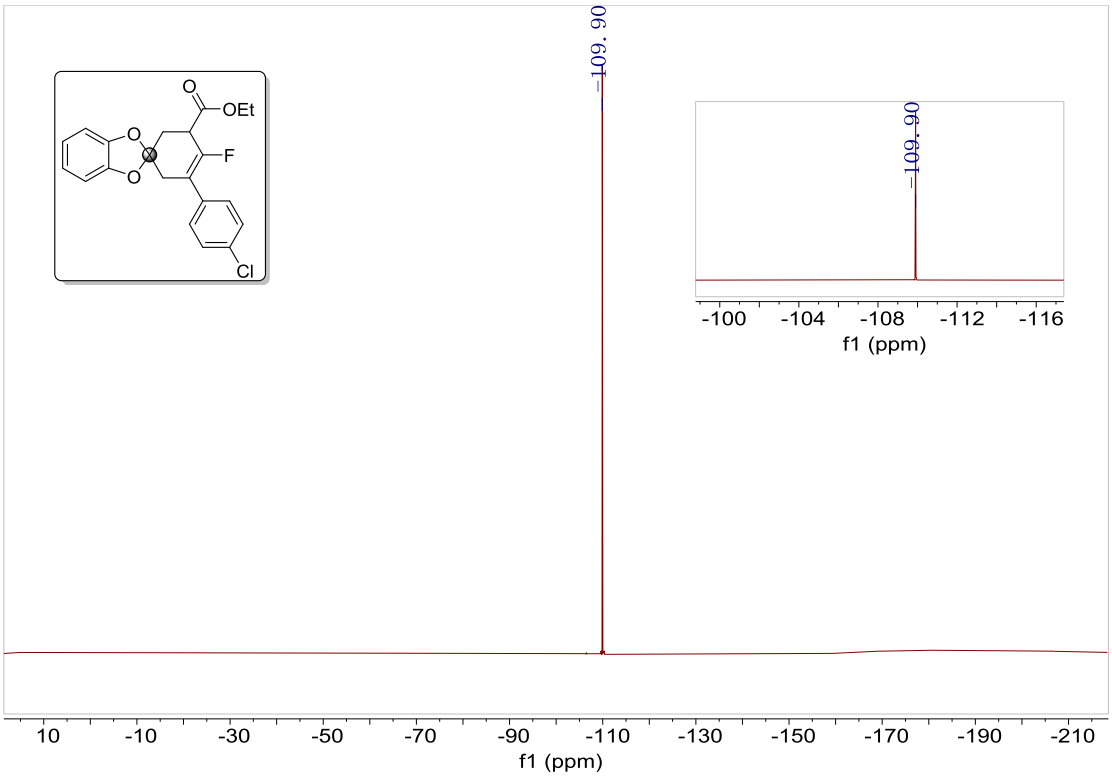
^{19}F NMR of 5r (376 MHz, $CDCl_3$)



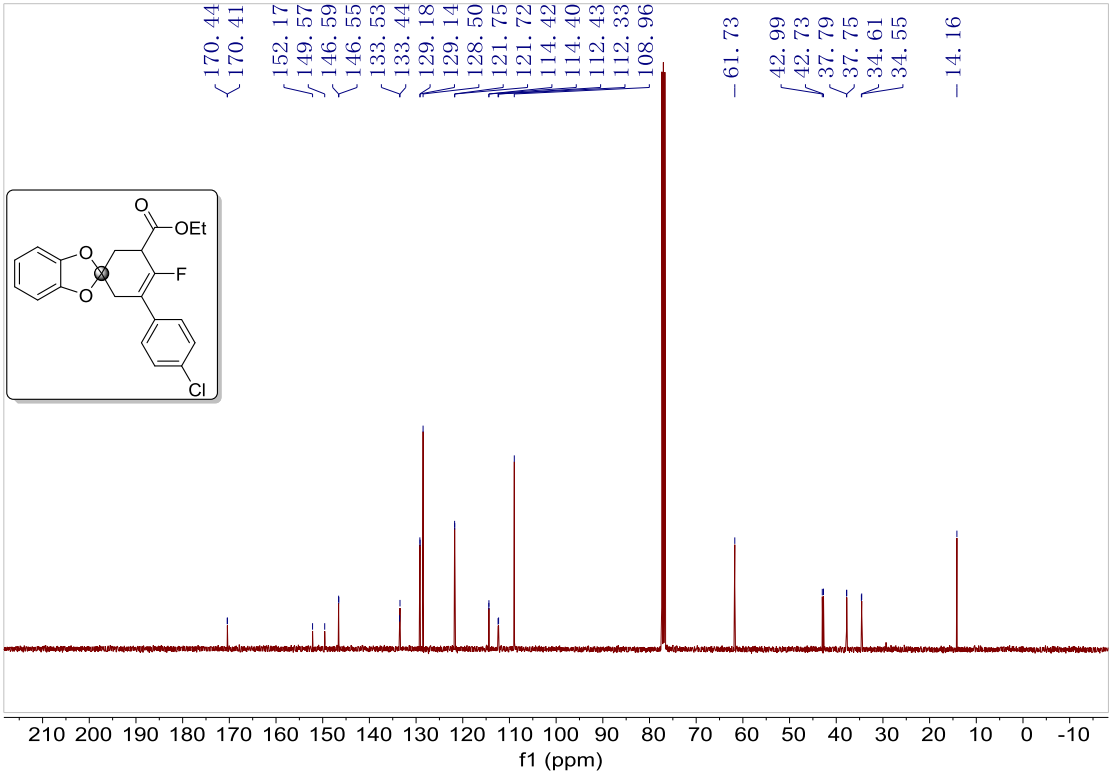
^{13}C NMR of 5r (100 MHz, $CDCl_3$)



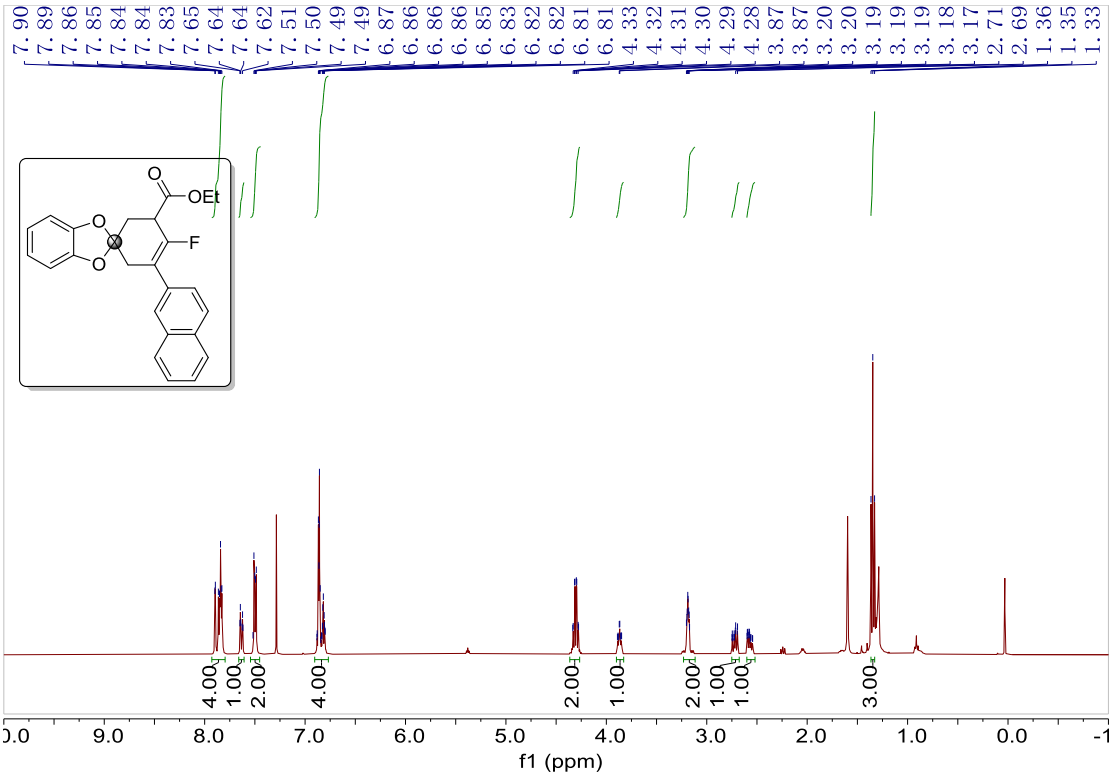
^{1}H NMR of 5s (400 MHz, $CDCl_3$)



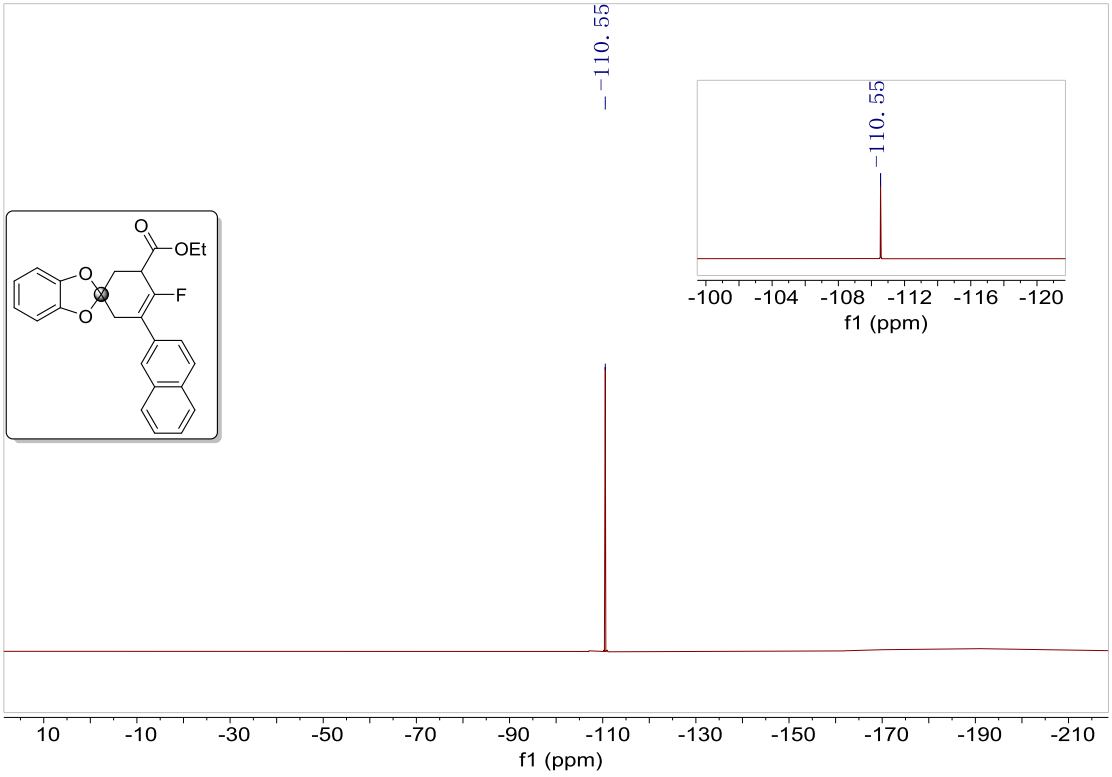
^{19}F NMR of 5s (376 MHz, $CDCl_3$)



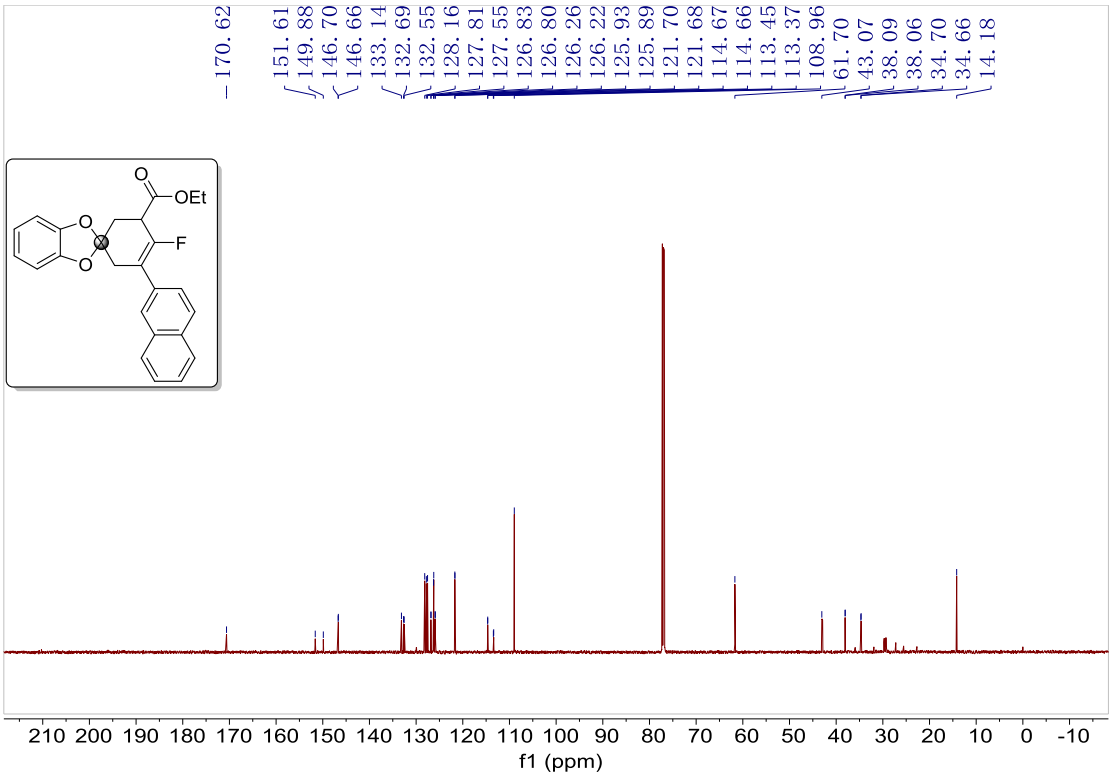
^{13}C NMR of 5s (100 MHz, $CDCl_3$)



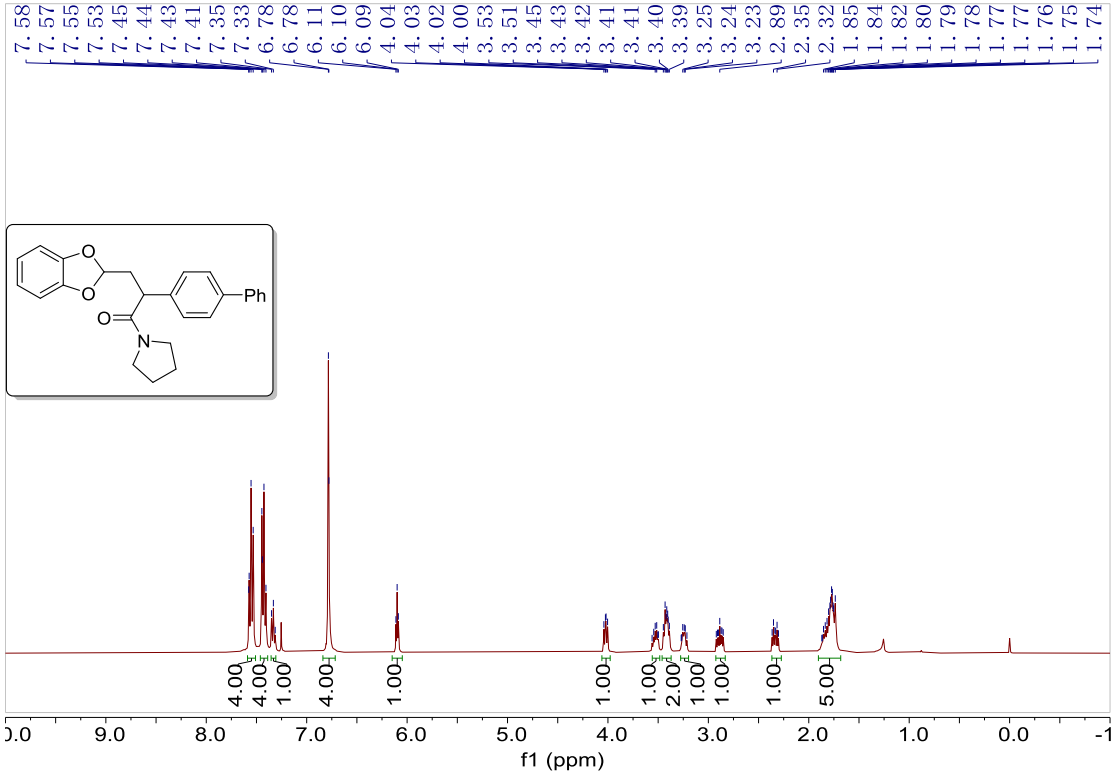
^{1}H NMR of 5t (400 MHz, $CDCl_3$)



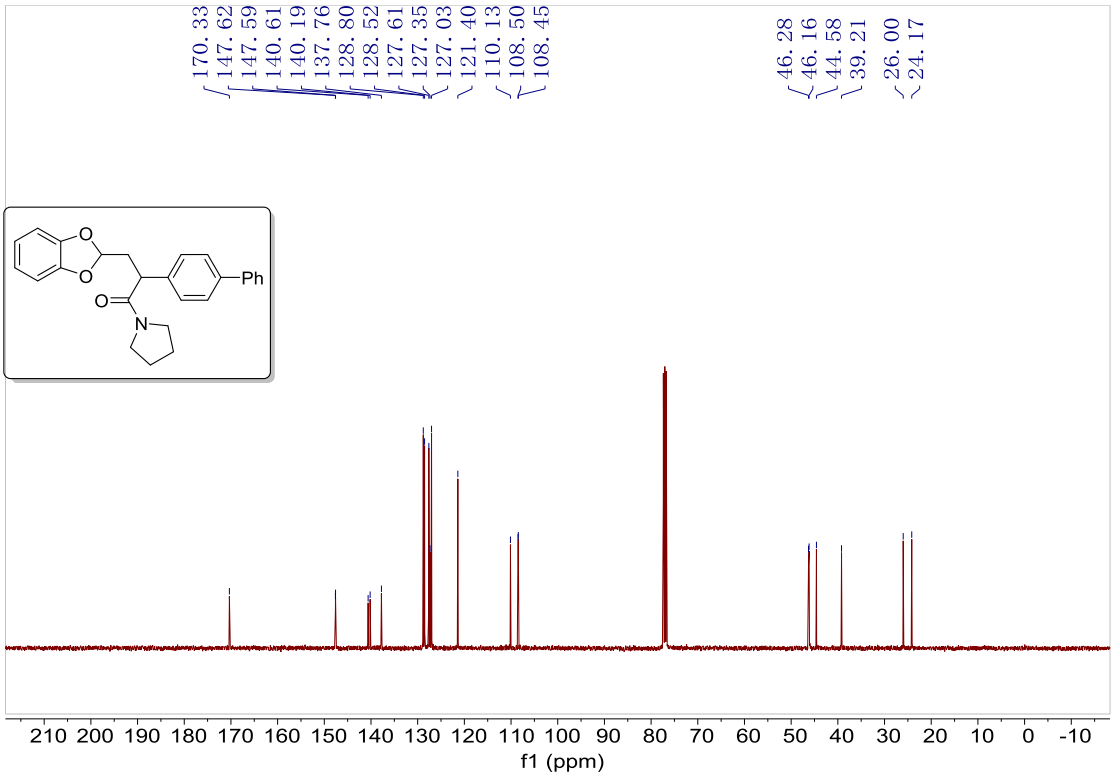
^{19}F NMR of 5t (376 MHz, $CDCl_3$)



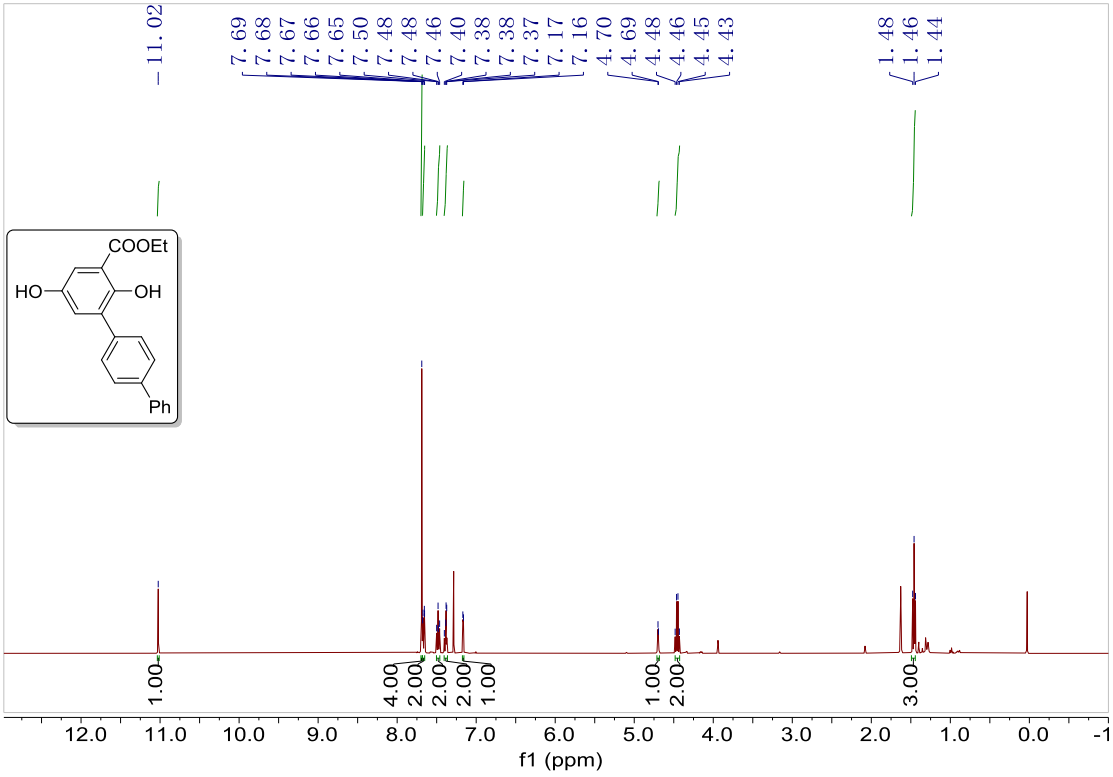
^{13}C NMR of 5t (150 MHz, $CDCl_3$)



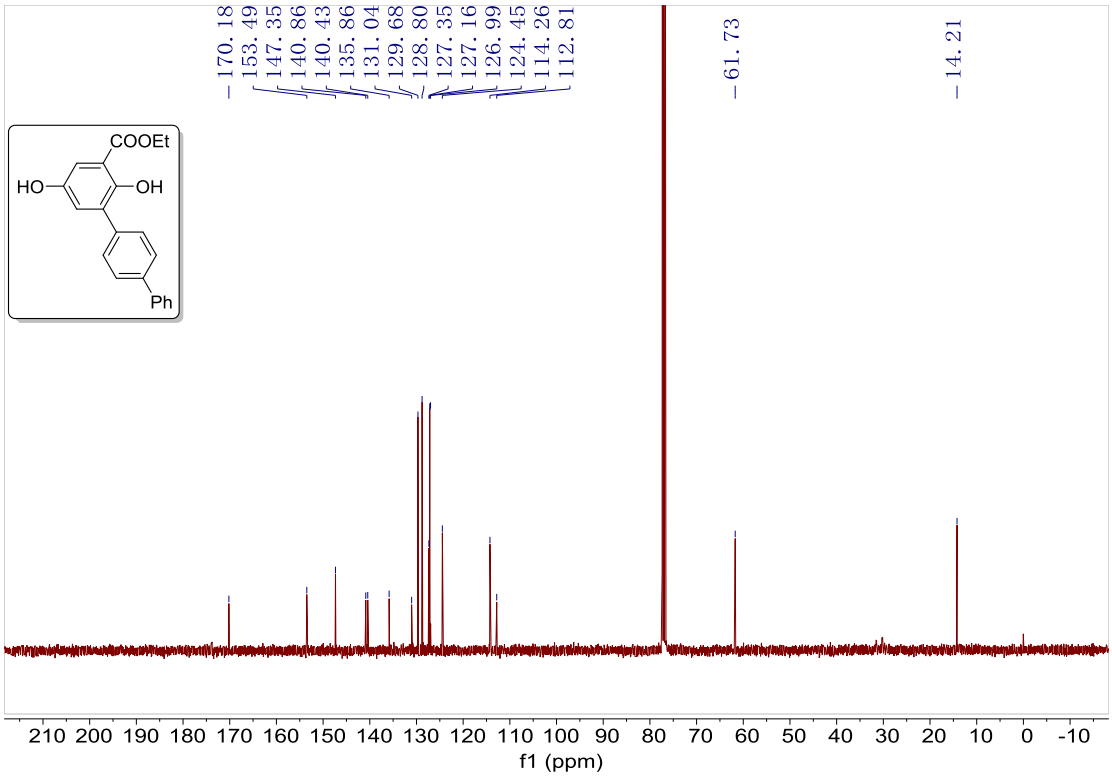
^{1}H NMR of 6 (400 MHz, $CDCl_3$)



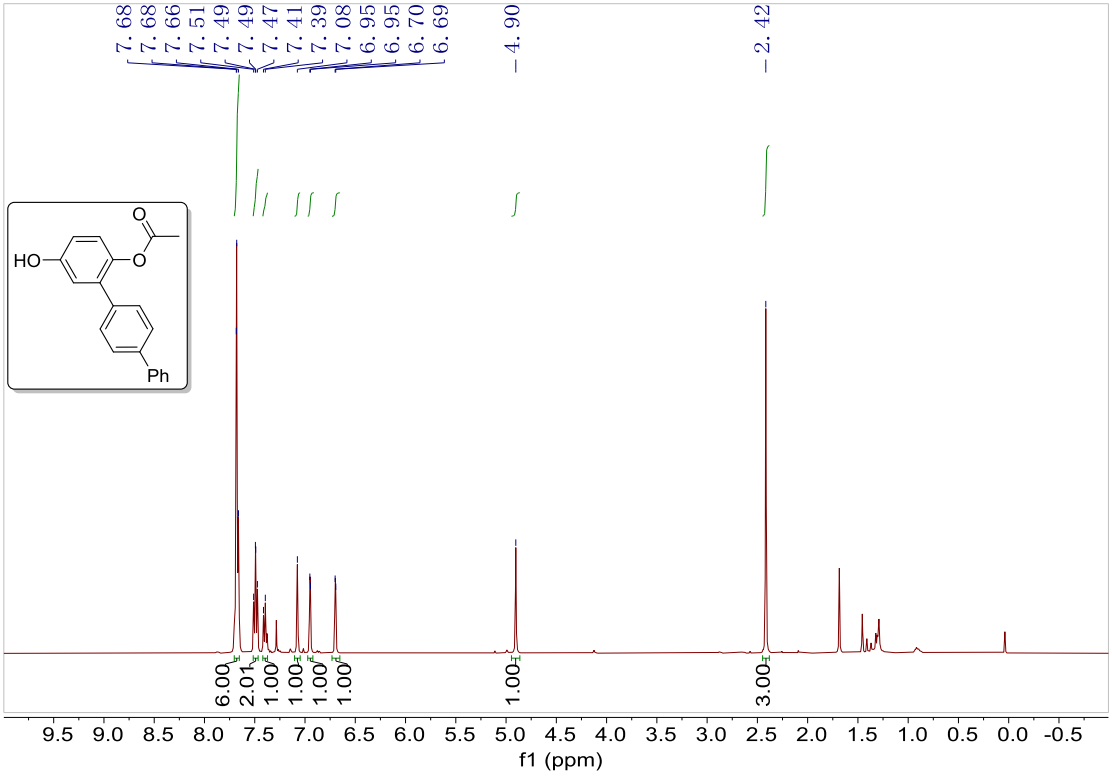
^{13}C NMR of 6 (150 MHz, $CDCl_3$)



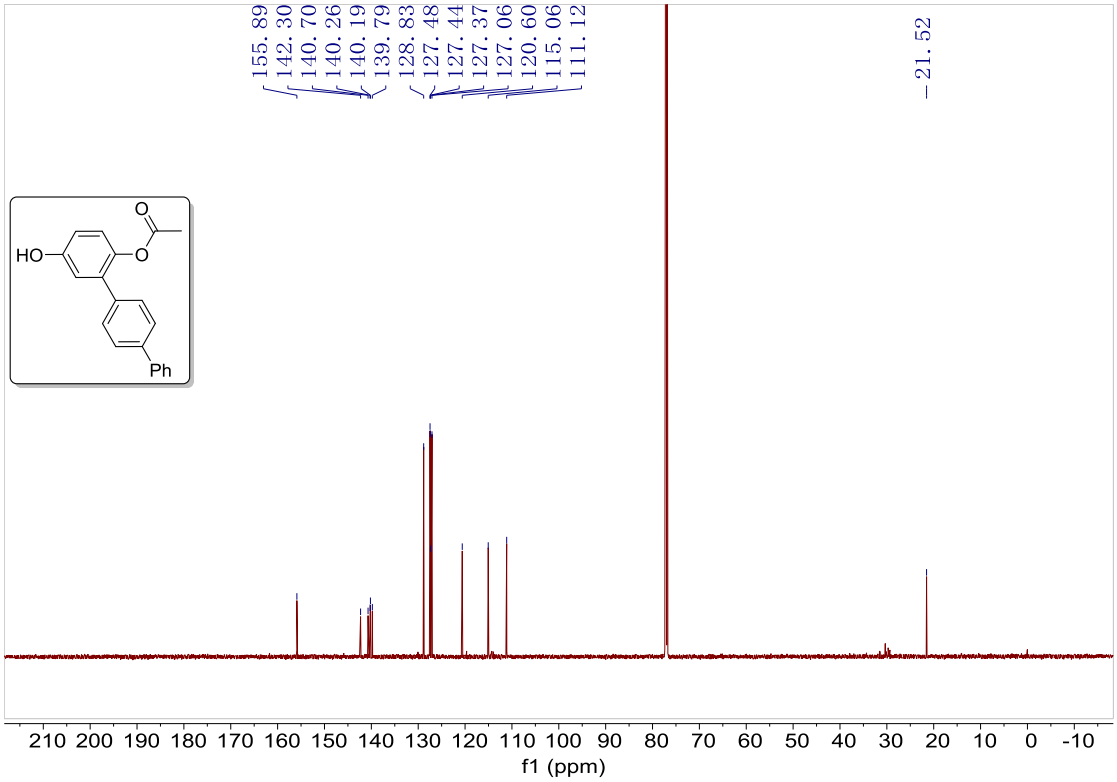
^{1}H NMR of 7 (400 MHz, $CDCl_3$)



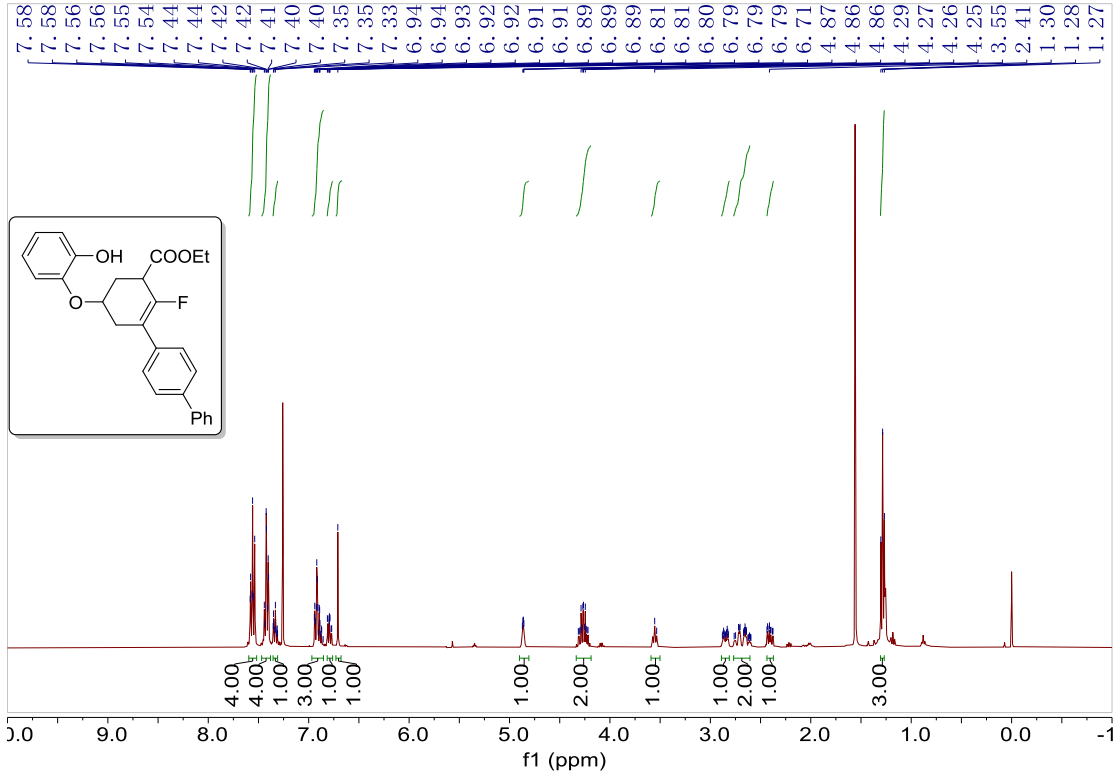
^{13}C NMR of 7 (100 MHz, $CDCl_3$)



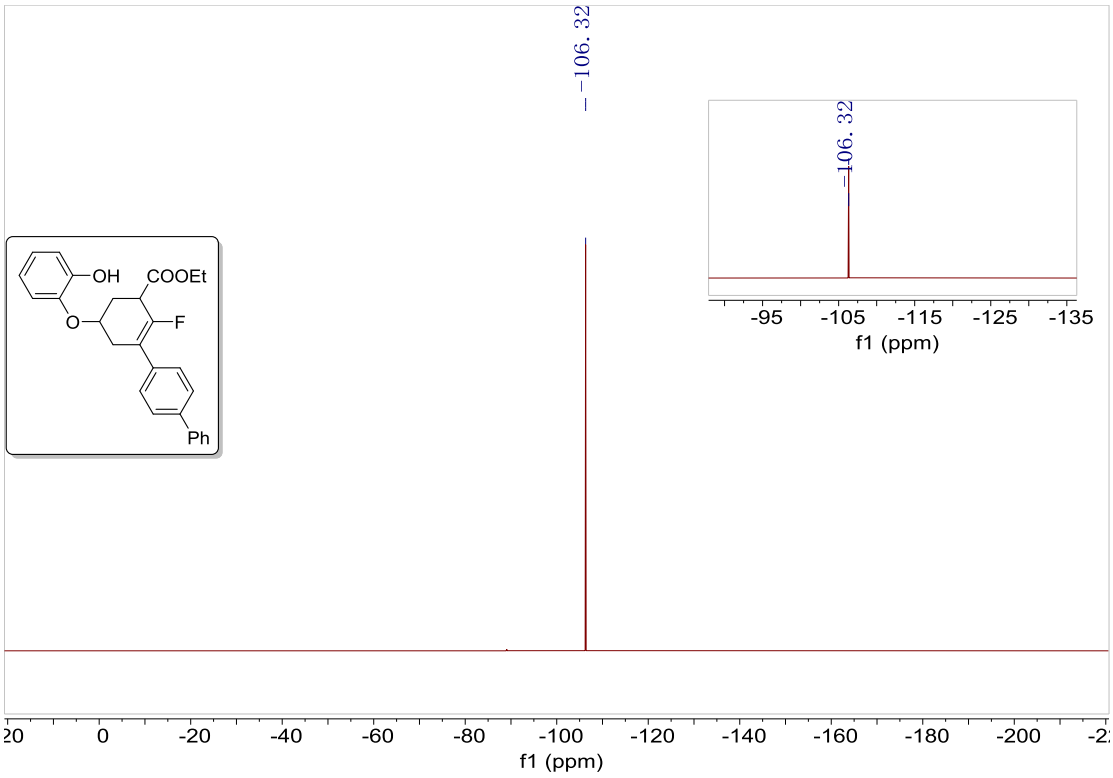
^{1}H NMR of 8 (400 MHz, $CDCl_3$)



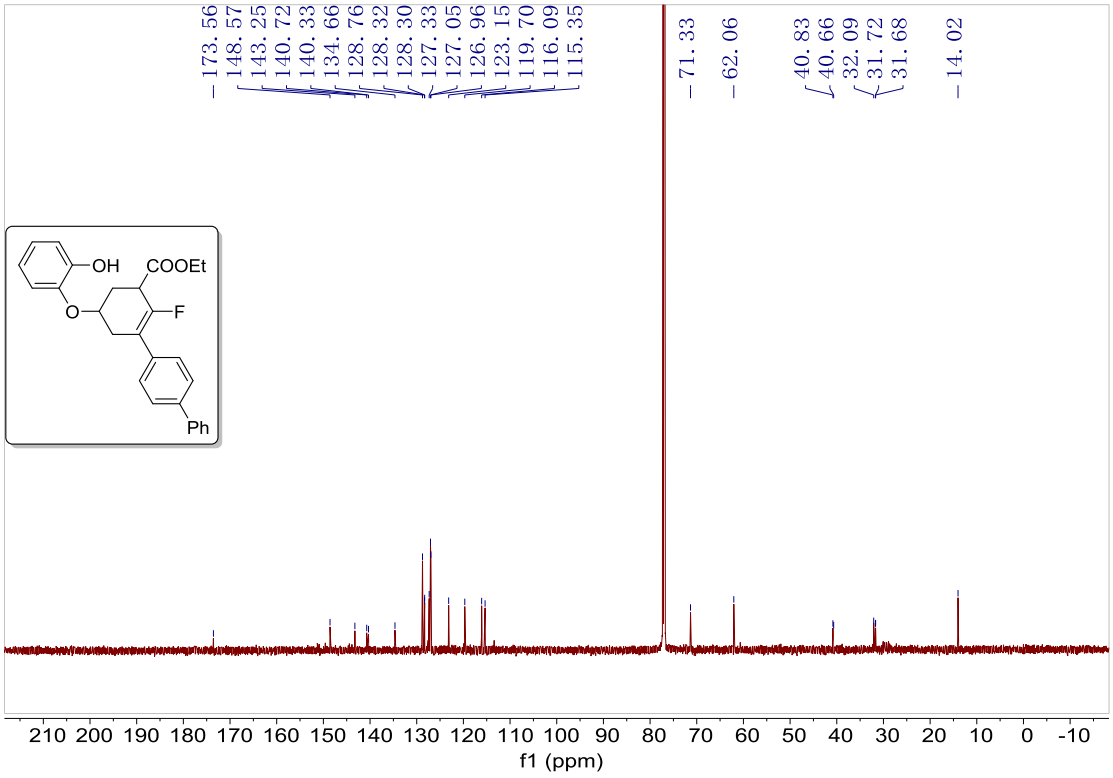
^{13}C NMR of 8 (150 MHz, $CDCl_3$)



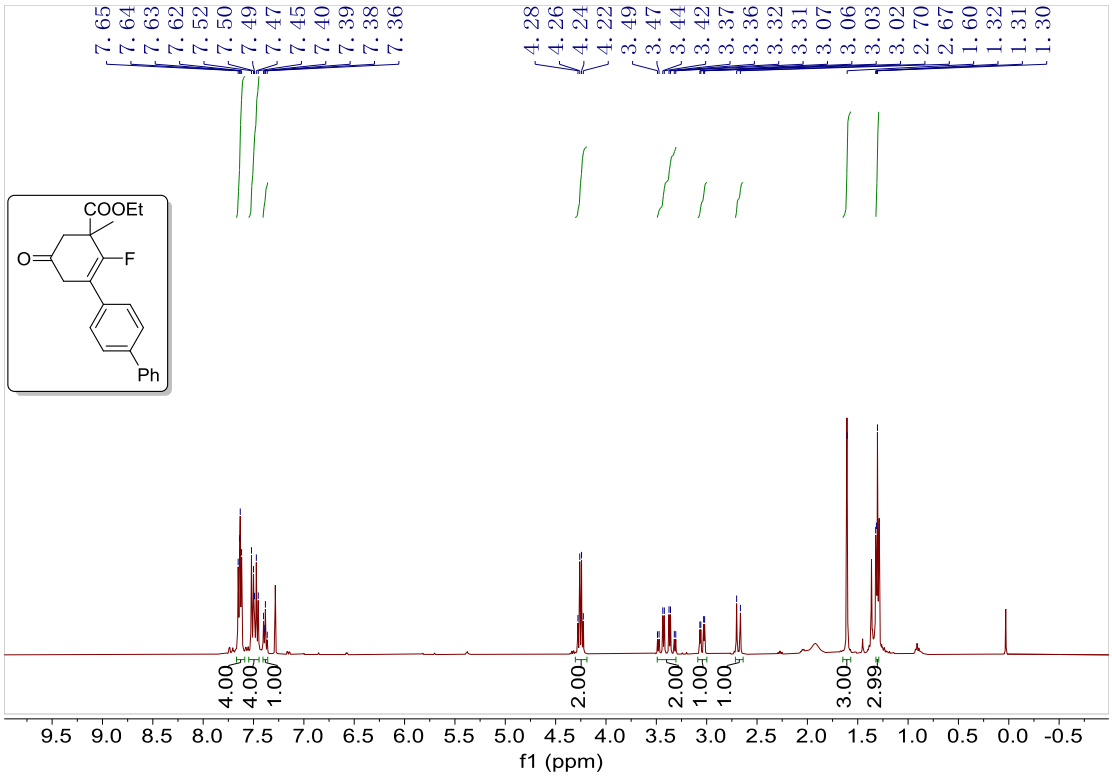
^{1}H NMR of 9 (400 MHz, $CDCl_3$)



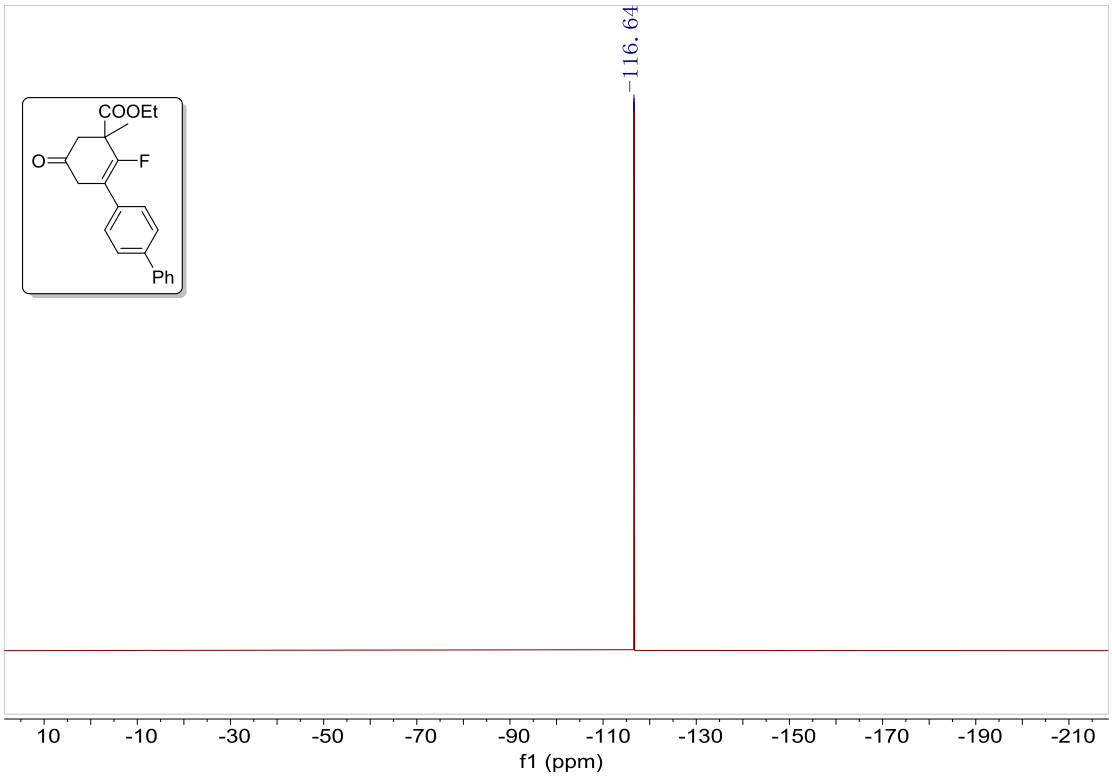
^{19}F NMR of 9 (376 MHz, $CDCl_3$)



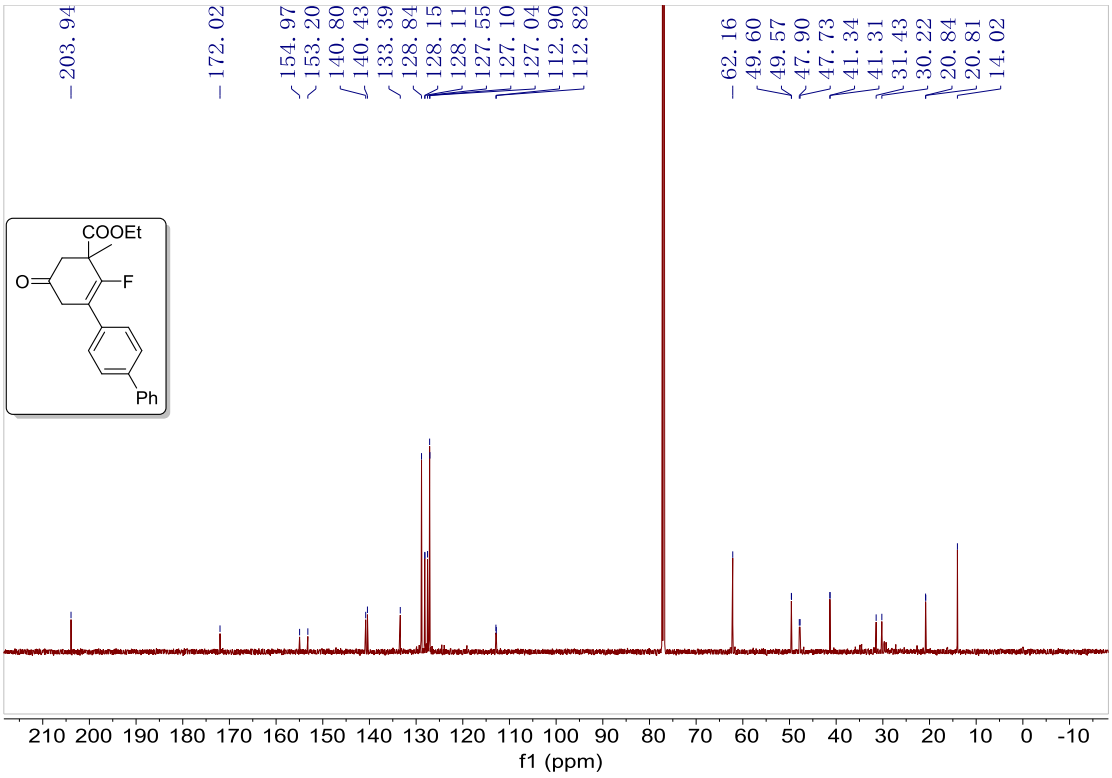
^{13}C NMR of 9 (150 MHz, $CDCl_3$)



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



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



^{13}C NMR of 10 (150 MHz, $CDCl_3$)