Supporting Information

Visible Light-Mediated β-C-H *gem*-Difluoroallylation of Aldehydes and Cyclic Ketones through C-F Bond Cleavage of 1-Trifluoromethyl Alkenes

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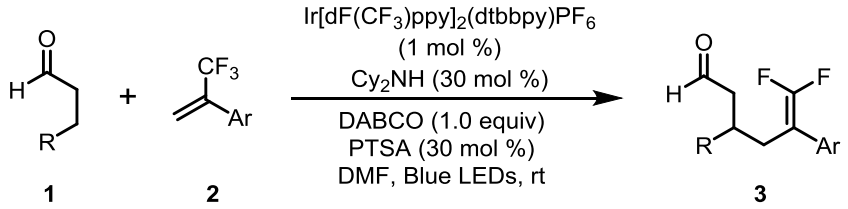
General

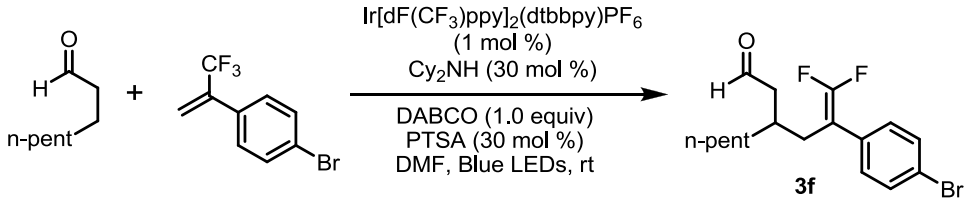
Unless otherwise noted, all reactions were performed in a 10 mL test tube at room temperature. Photo-irradiation was carried out with a 5 W blue LED. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ and recorded on Brucker ARX 400 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, t, d, s, dd referred to multiplet, triplet, doublet, singlet, doublet of doublet. High resolution mass spectra (HRMS) were obtained using orbitrap as the mass analyzer with an ESI source. α-CF_3 alkenes were prepared according to literature reported procedures.[1,2] All reagents and solvents were commercial available and directly used without any further purification.

General procedure for the β-gem-difluoroallylation of aldehydes



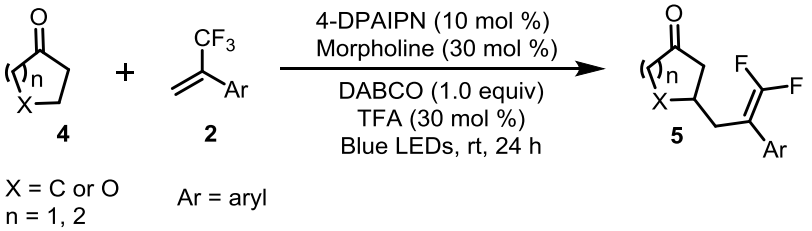
To a dry 10 mL vial equipped with a stir bar was added α-CF_3 alkene **2** (0.2 mmol), DABCO (22.4 mg, 0.2 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 1 mol %) and *p*-toluenesulfonic acid (10.3 mg, 30 mol %). The vial was sealed, degassed *via* vacuum evacuation for 5 minutes and backfilled with argon. Dicyclohexylamine (10.9 mg, 30 mol %), aldehyde **1** (0.4 mmol, 2.0 equiv), and DMF (2 mL) were added to the reaction vial. The reaction vial was irradiated with a 5 W blue LED light at room temperature for 24 hours. After consumption of the starting material, 10 mL water was added and the mixture was extracted with ethyl acetate, washed with brine and dried with anhydrous Na_2SO_4. Purification by silica column chromatography afforded the desired *β-gem*-difluoroallyation product (**3**).

Synthetic procedure for the compound 3f at 1 mmol scale



To a dry 50 mL vial equipped with a stir bar was added α-CF_3 (4-bromo)styrene (251 mg, 1 mmol), DABCO (112 mg, 1 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 1 mol %) and *p*-toluenesulfonic acid (51.6 mg, 30 mol %). The vial was sealed, degassed *via* vacuum evacuation for 5 minutes and backfilled with argon. Dicyclohexylamine (54.3 mg, 30 mol %), octanal **1a** (256 mg, 2 mmol), and DMF (10 mL) were added to the reaction vial. The reaction vial was irradiated with a 5 W blue LED light at room temperature for 24 hours. After consumption of the starting material, 30 mL water was added and the mixture was extracted with ethyl acetate, washed with brine and dried with anhydrous Na_2SO_4. Purification by silica column chromatography using petroleum ether/ethyl acetate (50:1) as the eluent afforded the desired *β-gem*-difluoroallylation product **3f** (247.7 mg) in 69 % yield.

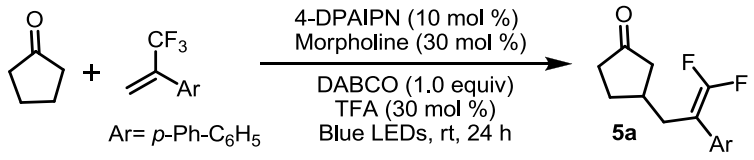
General procedure for the β-gem-difluoroallylation of cyclic ketones



To a dry 10 mL vial equipped with a stir bar was added α-CF_3 alkene **2** (0.2 mmol), DABCO (22.4 mg, 0.2 mmol), and 4-DPAIPN (16 mg, 10 mol %). The vial was sealed, degassed *via* vacuum evacuation for 5 minutes and backfilled with argon. Morpholine (5.2 mg, 30 mol %), cyclic ketone **4** (1.0 mmol, 5.0 equiv), trifluoroacetic acid (6.9 mg, 30 mol %), and DMF (2 mL) were added to the reaction vial. The reaction vial was irradiated with a 5 W blue LED light at room temperature for 24 hours. After consumption of the starting material, 10 mL water was added and the

mixture was extracted with ethyl acetate, washed with brine and dried with anhydrous Na_2SO_4. Purification by silica column chromatography afforded the desired *β-gem*-difluoroallyation product (**5**).

Synthetic procedure for the compound 5a at 1 mmol scale



To a dry 50 mL vial equipped with a stir bar was added α-CF_3 (4-phenyl)styrene **2a** (248 mg, 1 mmol), DABCO (112 mg, 1 mmol), and 4-DPAIPN (79.7 mg, 10 mol %). The vial was sealed, degassed *via* vacuum evacuation for 5 minutes and backfilled with argon. Morpholine (26 mg, 30 mol %), cyclopentanone **4** (420 mg, 5.0 mmol), trifluoroacetic acid (34.2 mg, 30 mol %), and DMF (10 mL) were added to the reaction vial. The reaction vial was irradiated with a 5 W blue LED light at room temperature for 24 hours. After consumption of the starting material, 30 mL water was added and the mixture was extracted with ethyl acetate, washed with brine and dried with anhydrous Na_2SO_4. Purification by silica column chromatography using petroleum ether/ethyl acetate (40:1) as the eluent afforded the desired *β-gem*-difluoroallyation product **5a** (206 mg) in 66% yield.

Experimental setup for the photocatalytic reactions

The reaction was carried out in a 10 mL Teflon-sealed microwave tube (biotage), approximately 5 cm from the light source. The blue LED was purchased from QJL, and its link is: https://item.taobao.com/item.htm?spm=a230r.1.14.20.4bfb368frEfkJn&id=558978956686&ns=1&abbucket=17#detail. The cover was removed before use and its emission spectrum is shown in Figure S1.

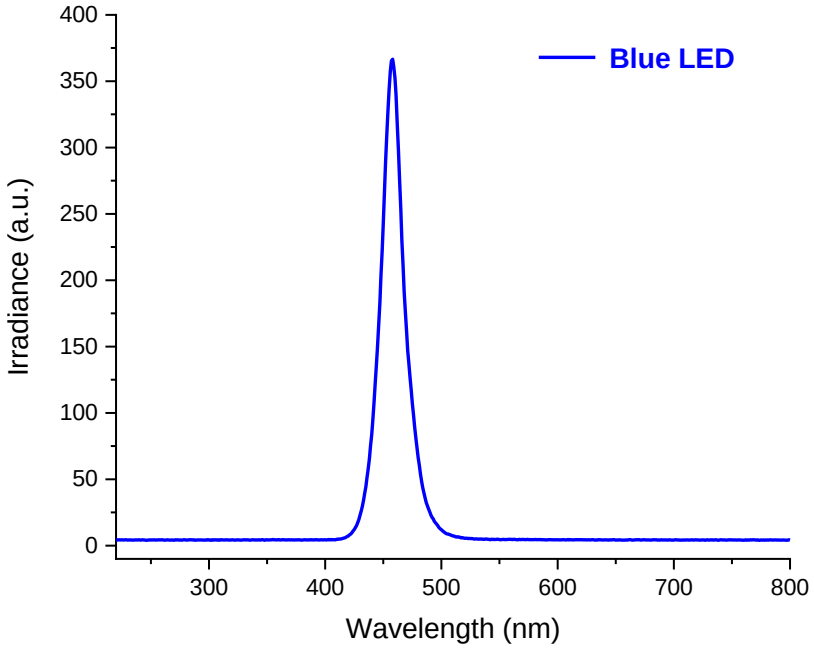
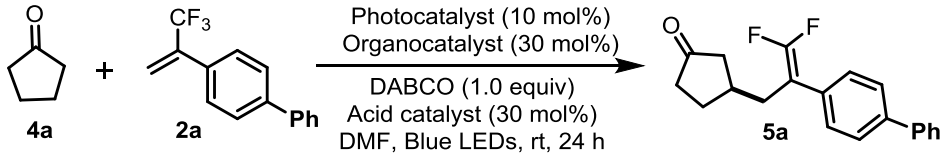


Figure S1 The emission spectra of blue LED.

Table S1. ***Optimization for the β-gem-difluoroallylation of cyclopentanone***

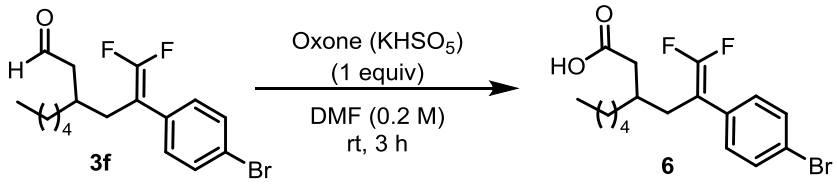


entry	photocatalyst	organocatalyst	acid catalyst	yield (%)[b]
1[c]	Ir-2	Cy_2NH	PTSA	30
2[c]	Ir-2	Cy_2NH	TFA	42
3[c]	Ir-2	morpholine	TFA	63
4[c]	Ir-1	morpholine	TFA	50
5	4DPAIPN	morpholine	TFA	77
6	4-CzIPN	morpholine	TFA	65
7	Eosin Y	morpholine	TFA	10
8	Rose bengal	morpholine	TFA	5
9	$MesAcrClO_4$	morpholine	TFA	trace
10[c]	$Ru(bpy)_3Cl_2$	morpholine	TFA	21
11	4DPAIPN	pyrrodine	TFA	68
12	4DPAIPN	piperidine	TFA	65
13	4DPAIPN	azapane	TFA	70
14[d]	4-DPAIPN	morpholine	TFA	0

[a] Reaction conditions: **4a** (1.0 mmol), **2a** (0.2 mmol), photocatalyst (10 mol%), organocatalyst (30 mol%), DABCO (0.2 mmol), acid catalyst (30 mol%), DMF (2 mL), 5W blue LED, rt, 24 h. [b] Yield was determined by ^{19}F NMR using benzotrifluoride as an internal standard. [c] 1 mol% of photocatalyst loading. [d] Reaction carried out in the absence of DABCO. DABCO: 1,4-diazabicyclo[2.2.2]octane. PTSA: *p*-toluenesulfonic acid. TFA: trifluoroacetic acid.

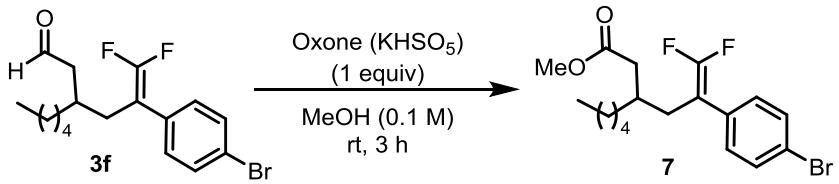
Synthetic applications of the products

1. Oxidation of aldehyde to carboxylic acid



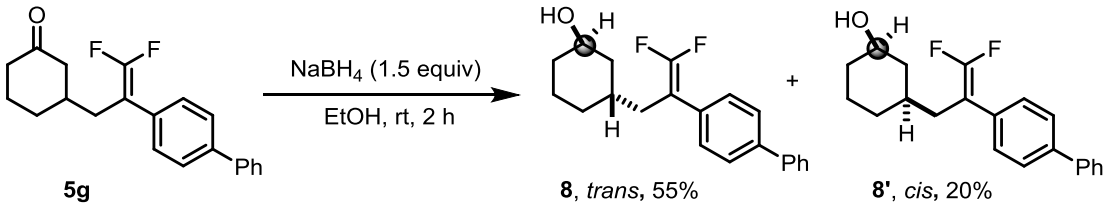
The aldehyde **3f** (71.8mg, 0.2 mmol) was dissolved in DMF (1 mL). Oxone (122.8 mg, 0.2 mmol) was added in one portion and stirred at room temperature for 3 hours. The reaction was monitored by TLC. After consumption of the starting material, reaction mixture was diluted with 1N HCl, extracted with EtOAc, washed with brine and dried over Na_2SO_4. Purification by silica column chromatography using petroleum ether/ethyl acetate (5:1) as the eluent afforded the desired carboxylic acid product **6** (57 mg) in 76% yield.

2. Oxidation of aldehyde to ester



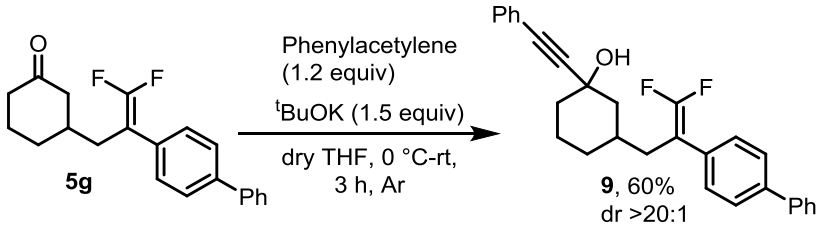
The aldehyde **3f** (71.8 mg, 0.2 mmol) was dissolved in MeOH (2 mL). Oxone (122.8 mg, 0.2 mmol) was added in one portion and stirred at room temperature for 24 hours. After the completion of the reaction, as monitored by TLC, reaction mixture was diluted with 1N HCl, extracted with EtOAc, washed with brine and dried over Na_2SO_4. Purification by silica column chromatography using petroleum ether/ethyl acetate (40:1) as the eluent afforded the desired carboxylic acid product **7** (54 mg) in 70% yield.

3. Reduction of cyclic ketone with $NaBH_4$



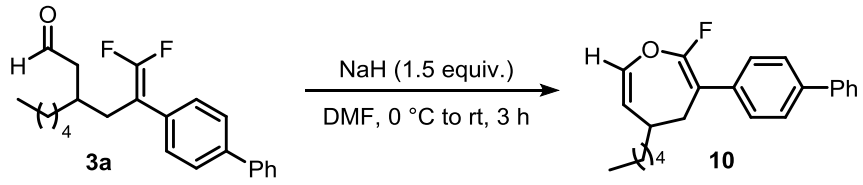
The ketone **5g** (100 mg, 0.3 mmol) was dissolved in EtOH (2 mL). $NaBH_4$ (17.1 mg, 0.45 mmol) was added in one portion and stirred at room temperature for 2 hours. After the completion of the reaction, as monitored by TLC, solvent was evaporated and diluted with water, extracted with EtOAc, washed with brine and dried over Na_2SO_4. Purification by silica column chromatography using petroleum ether/ethyl acetate (10:1) as the eluent afforded the two separable diastereomers **8** and **8'** in yields of 55% (54 mg) and 25% (19.7 mg), respectively.

4. Nucleophilic addition of terminal alkyne to cyclic ketone



To a solution of ^{t}BuOK (33.6 mg, 0.3 mmol) in dry THF was added phenylacetylene (24.5 mg, 0.24 mmol) at 0 ℃ under argon atmosphere. After the mixture was stirred at room temperature for 5 minutes, ketone **5g** (65.2 mg, 0.2 mmol) was added drop wise. The reaction mixture was stirred for 3 hours. After completion of the reaction, the resulting mixture was quenched with water and extracted with EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated in *vacuum*. The residue was purified by column chromatography using petroleum ether/ethyl acetate (10:1) as the eluent to give the product **9** with >20:1 diastereoselectivity (51.3 mg, 60%).

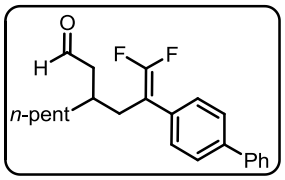
5. Intramoleular S_NV reaction for the synthesis of fluorooxepine



To a solution of *β-gem*-difluoroallyl aldehyde **3a** (71.2 mg, 0.2 mmol.) in dry DMF (2 mL), NaH (12 mg, 0.3 mmol, 60% dispersion in mineral oil) was added at 0 ℃. Then the reaction mixture was stirred for 3 hours at room temperature. The reaction was quenched with water and extracted with EtOAc (10 mL x 3), dried with anhydrous Na_2SO_4 and concentrated in *vacuo*. Purification by silica column chromatography using petroleum ether as the only eluent afforded the desired fluorodihydrooxepine product **10** (30 mg) in 44% yield.

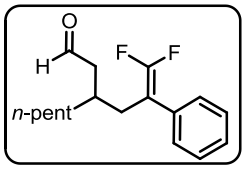
Compound characterization data

3-(2-(biphenyl-4-yl)-3,3-difluoroallyl)octanal (3a):



R_f: 0.6 (petroleum ether/ethyl acetate 20:1). Colorless oil (54 mg, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.68 (t, *J* = 2.0 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 4H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.40-7.34 (m, 3H), 2.55-2.35 (m, 4H), 2.08-1.99 (m, 1H), 1.37-1.17 (m, 8H), 0.86 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.4, 154.2 (dd, *J* = 290.7, 288.3 Hz), 140.5, 140.4, 132.2, 128.9, 128.7 (t, *J* = 3.0 Hz), 127.5, 127.3, 127.1, 90.7 (dd, *J* = 19.6, 15.0 Hz), 48.0, 33.8, 32.1, 32.0, 31.5 (t, *J* = 2.0 Hz), 26.2, 22.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.91 (d, *J* = 41.0 Hz, 1F), -90.04 (d, *J* = 41.0 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{23}H_{27}F_2O$ 357.2030; Found 357.2027.

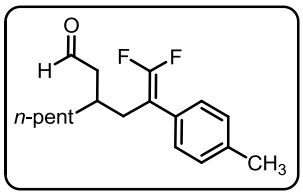
3-(3,3-difluoro-2-phenylallyl)octanal (3b):



R_f: 0.6 (petroleum ether/ethyl acetate 20:1). Colorless oil (35 mg, 62% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), δ 7. 39-7.35 (m, 2H), 7.31-7.26 (m, 3H), 2.51-2.32 (m, 4H), 2.0-1.94 (m, 1H), 1.34-1.20 (m, 8H), 0.85 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR**

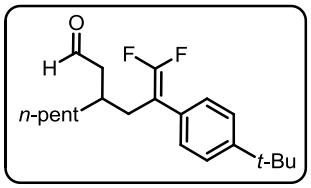
(101 MHz, $CDCl_3$) δ 202.5, 154.1 (t, *J* = 289 Hz), 133.3, 128.7, 128.3 (t, *J* = 2.9 Hz), 127.6, 91.0 (t, *J* = 17.4 Hz), 48.0, 33.8, 32.2, 31.9, 31.4 (t, *J* = 2.2 Hz), 26.1, 22.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.61 (s, 2F) **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}F_2O$ 281.1717; Found 281.1715.

3-(3,3-difluoro-2-*p*-tolylallyl)octanal (3c):



R_f: 0.61 (petroleum ether/ethyl acetate 20:1). Colorless oil (40 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.18 (s, 4H), 2.49-2.44 (m, 1H), 2.38-2.31 (m, 6H), 1.99-1.94 (m, 1H), 1.33-1.20 (m, 8H), 0.86 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.6, 154.1 (dd, *J* = 290.0, 287.2 Hz), 137.4, 130.2, 129.4, 128.2 (t, *J* = 3.0 Hz), 90.7 (dd, *J* = 19.9, 14.8 Hz), 48.0, 33.9, 32.3, 32.0, 31.4 (t, *J* = 2.4 Hz), 26.2, 22.6, 21.2, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.95 (d, *J* = 43.1 Hz, 1F), -91.10 (d, *J* = 43.1 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{18}H_{25}F_2O$ 295.1873; Found 295.1869.

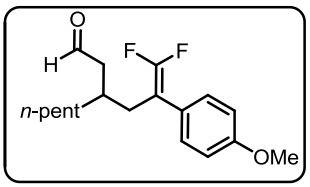
3-(2-(4-tert-butylphenyl)-3,3-difluoroallyl)octanal (3d):



R_f: 0.7 (petroleum ether/ethyl acetate 20:1). Colorless oil (44 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.50-2.32 (m, 4H), 2.02-1.99 (m, 1H), 1.32 (s, 9H), 1.27-1.20 (m, 8H), 0.85 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.7, 154.2 (t, *J* = 288.8 Hz), 150.5, 130.2, 127.9 (t, *J* = 3.0 Hz), 125.6, 90.7 (t, *J* = 17.2 Hz), 48.0, 34.6, 33.8, 32.1, 32.0, 31.5 (t, *J* = 2.4 Hz), 26.1, 22.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.72 (s, 2F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{21}H_{31}F_2O$ 337.2343; Found 337.2339.

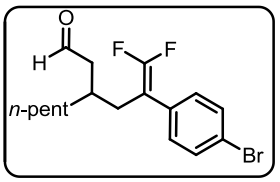
3-(3,3-difluoro-2-(4-methoxyphenyl)allyl)octanal (3e):

R_f: 0.62 (petroleum ether/ethyl acetate 20:1). Colorless oil (44 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 8.0 Hz,



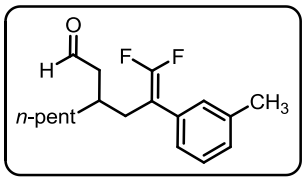
2H), 3.82 (s, 3H), 2.47-2.31 (m, 4H), 2.00-1.94 (m, 1H), 1.33-1.21 (m, 8H), 0.86 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.6, 156.5 (t, *J* = 288.0 Hz), 129.4 (t, *J* = 3.1 Hz), 125.3, 114.1, 90.4 (dd, *J* = 19.5, 15.4 Hz), 55.4, 48.0, 33.8, 32.3, 32.0, 31.4 (t, *J* = 2.1 Hz), 26.2, 22.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.46 (d, *J* = 44.5 Hz, 1F), -91.59 (d, *J* = 44.4 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{18}H_{25}F_2O_2$ 311.1823; Found 311.1822.

3-(2-(4-bromophenyl)-3,3-difluoroallyl)octanal (3f):



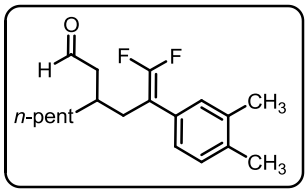
R_f: 0.64 (petroleum ether/ethyl acetate 20:1). Colorless oil (55 mg, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 2.46-2.33 (m, 4H), 1.96-1.91 (m, 1H), 1.32-1.20 (m, 8H), 0.85 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.1, 154.1 (dd, *J* = 291.3, 288.4 Hz), 132.2 (t, *J* = 3.0 Hz), 131.9, 130.0 (t, *J* = 3.1 Hz), 121.6, 90.3 (dd, *J* = 20.7, 14.6 Hz), 48.0, 33.7, 32.1, 32.0, 31.3 (t, *J* = 2.4 Hz), 26.1, 22.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.53 (d, *J* = 40.0 Hz, 1F), -89.67 (d, *J* = 39.9 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{17}H_{22}BrF_2O$ 359.0822; Found 359.0820.

3-(3,3-difluoro-2-*m*-tolylallyl)octanal (3g):



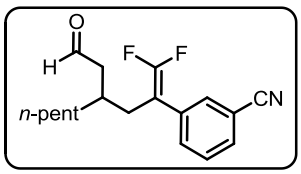
R_f: 0.61 (petroleum ether/ethyl acetate 20:1). Colorless oil (39 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.30-7.26 (m, 1H), 7.13-7.11 (m, 3H), 2.53-2.49 (m, 1H), 2.42-2.34 (m, 6H), 2.02-1.97 (m, 1H), 1.36-1.23 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.6, 154.1 (dd, *J* = 290.9, 286.8 Hz), 138.3, 133.2 (t, *J* = 3.0 Hz), 129.0 (t, *J* = 2.9 Hz), 128.5, 128.4, 125.4 (t, *J* = 2.9 Hz), 91.0 (dd, *J* = 20.8, 14.0 Hz), 48.0, 33.8, 32.3, 32.0, 31.4 (t, *J* = 2.3 Hz), 26.1, 22.6, 21.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.60 (d, *J* = 42.3 Hz, 1F), -90.83 (d, *J* = 42.4 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{18}H_{25}F_2O$ 295.1873; Found 295.1870.

3-(2-(3,4-dimethylphenyl)-3,3-difluoroallyl)octanal (3h):



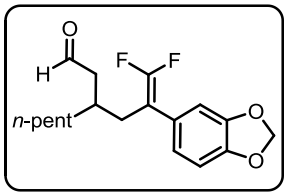
R_f: 0.61 (petroleum ether/ethyl acetate 20:1). Colorless oil (41 mg, 67% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.13 (d, *J* = 7.7 Hz, 1H), 7.07 (s, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 2.49-2.44 (m, 1H), 2.37-2.31 (m, 3H), 2.27 (s, 3H), 2.26 (s, 3H), 2.00-1.95 (m, 1H), 1.34-1.21 (m, 8H), 0.86 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.7, 154.08 (dd, *J* = 290.4, 286.5 Hz), 136.8, 136.0, 130.6 (t, *J* = 3.03 Hz), 129.9, 129.5 (t, *J* = 2.9 Hz), 125.7 (t, *J* = 2.9 Hz), 90.8 (dd, *J* = 20.8, 13.8 Hz), 48.0, 33.8, 32.3, 32.0, 31.4 (t, *J* = 2.2 Hz), 26.1, 22.6, 19.9, 19.5, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.96 (d, *J* = 43.5 Hz, 1F), -91.27 (d, *J* = 43.5 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{19}H_{27}F_2O$ 309.2030; Found 309.2018.

3-(1,1-difluoro-4-(2-oxoethyl)non-1-en-2-yl)benzonitrile (3i):



R_f: 0.5 (petroleum ether/ethyl acetate 20:1). Colorless oil (40 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.69 (t, *J* = 1.7 Hz, 1H), 7.62-7.56 (m, 3H), 7.51-7.47 (m, 1H), 2.44-2.30 (m, 4H), 1.96-1.88 (m, 1H), 1.33-1.18 (m, 8H), 0.85 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.8, 154.5 (dd, *J* = 293.3, 289.1 Hz), 134.8 (t, *J* = 4.1 Hz), 132.7 (t, *J* = 3.2 Hz), 131.9 (t, *J* = 3.4 Hz), 131.1, 129.6, 118.5, 113.1, 89.9 (dd, *J* = 23.1, 12.5 Hz), 47.9, 33.6, 31.9, 31.1 (t, *J* = 1.9 Hz), 26.1, 22.6, 14.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -87.87 (d, *J* = 36.7 Hz, 1F), -88.45 (d, *J* = 36.9 Hz, 1F). **HRMS (ESI)** m/z: $[M+H^+]$ calcd for $C_{18}H_{22}F_2NO$ 306.1669; Found 306.1665.

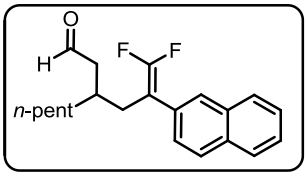
3-(2-(benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)octanal (3j):



R_f: 0.56 (petroleum ether/ethyl acetate 20:1). Colorless oil (45 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 6.81-6.74 (m, 3H), 5.97 (s, 2H), 2.43-2.38 (m, 1H), 2.33-2.29 (m, 3H), 1.99-1.95 (m, 1H), 1.33-1.21 (m, 8H), 0.86 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.4, 154.1 (dd, *J* = 290.3,

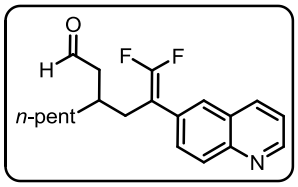
286.6 Hz), 147.9, 147.0, 126.8 (t, *J* = 3.03 Hz), 121.9 (t, *J* = 3.0 Hz), 108.8 (t, *J* = 3.2 Hz), 108.5, 101.3, 90.7 (dd, *J* = 22.0, 13.7 Hz), 48.0, 33.8, 32.5, 32.0, 31.3 (t, *J* = 2.2 Hz), 26.2, 22.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.75 (d, *J* = 43.3 Hz, 1F), -91.19 (d, *J* = 43.4 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{18}H_{23}F_2O_3$ 325.1615; Found 325.1608.

3-(3,3-difluoro-2-(naphthalen-2-yl)allyl)octanal (3k):



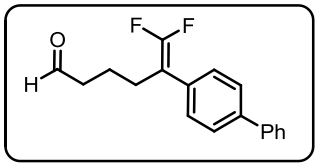
R_f: 0.6 (petroleum ether/ethyl acetate 20:1). Colorless oil (33 mg, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.86-7.78 (m, 4H), 7.51-7.42 (m, 3H), 2.62-2.47 (m, 2H), 2.36-2.35 (m, 2H), 2.03-2.00 (m, 1H), 1.38-1.24 (m, 8H), 0.84 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 154.4 (dd, *J* = 291.5, 287.6 Hz), 133.4, 132.6, 130.7 (t, *J* = 3.0 Hz), 128.4, 128.0, 127.7, 127.5 (t, *J* = 3.1 Hz), 126.5, 126.4, 126.0 (t, *J* = 3.0 Hz), 91.1 (dd, *J* = 21.1, 13.6 Hz), 48.0, 33.8, 32.3, 31.9, 31.5 (t, *J* = 2.3 Hz), 26.2, 22.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.93 (d, *J* = 40.9 Hz, 1F), -90.19 (d, *J* = 40.9 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{21}H_{25}F_2O$ 331.1873; Found 331.1868.

3-(3,3-difluoro-2-(quinolin-6-yl)allyl)octanal (3l):



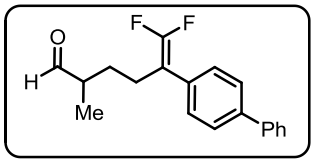
R_f: 0.52 (petroleum ether/ethyl acetate 20:1). Colorless oil (29 mg, 44% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 8.89 (s, 1H), 8.11 (d, *J* = 7.8 Hz, 2H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 2.61-2.51 (m, 2H), 2.40-2.39 (m, 2H), 2.04-1.98 (m, 1H), 1.37-1.19 (m, 8H), 0.82 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.9, 154.7 (dd, *J* = 293.1, 289.1 Hz), 150.1, 147.2, 135.1, 129.9, 129.3, 127.9, 127.7, 127.3, 126.5 (t, *J* = 4.3 Hz), 88.7 (dd, *J* = 23.2, 13.4 Hz), 48.0, 33.7, 32.0, 31.9, 31.3 (t, *J* = 2.1 Hz), 26.2, 22.6, 14.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -87.88 (d, *J* = 37.4 Hz, 1F), -88.63 (d, *J* = 37.5 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{24}F_2NO$ 332.1826; Found 332.1818.

5-(biphenyl-4-yl)-6,6-difluorohex-5-enal (3m):



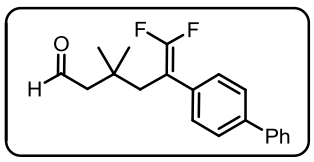
R_f: 0.6 (petroleum ether/ethyl acetate 20:1). Colorless oil (30 mg, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.60 (d, *J* = 8.1 Hz, 4H), 7.47-7.34 (m, 5H), 2.53-2.45 (m, 4H), 1.80-1.72 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.9, 153.9 (t, *J* = 289.5 Hz), 140.5, 140.3, 132.1, 128.9, 128.6 (t, *J* = 3.3 Hz), 127.5, 127.3, 127.1, 91.5 (dd, *J* = 18.2, 16.6 Hz), 43.0, 26.9, 20.3 (t, *J* = 2.5 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.31 (d, *J* = 41.8 Hz, 1F), -90.42 (d, *J* = 41.8 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}F_2O$ 287.1247; Found 287.1240.

5-(biphenyl-4-yl)-6,6-difluoro-2-methylhex-5-enal (3n):



R_f: 0.6 (petroleum ether/ethyl acetate 20:1). Colorless oil (25.9 mg, 43% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.61 (d, *J* = 1.6 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 4H), 7.48-7.35 (m, 5H), 2.54-2.49 (m, 2H), 2.43-2.34 (m, 1H), 1.91-1.82 (m, 1H), 1.52-1.43 (m, 1H), 1.13 (d, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.4, 153.8 (t, *J* = 290.8 Hz), 140.5, 140.3, 132.1, 128.9, 128.6 (t, *J* = 3.3 Hz), 127.5, 127.3, 127.1, 91.6 (dd, *J* = 18.9, 16.0 Hz), 45.7, 28.6 (t, *J* = 2.5 Hz), 25.1, 13.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.31 (d, *J* = 41.9 Hz, 1F), -90.41 (d, *J* = 42.0 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}F_2O$ 301.1404; Found 301.1401.

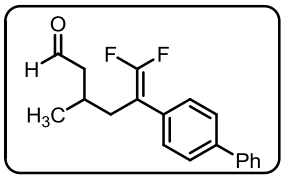
5-(biphenyl-4-yl)-6,6-difluoro-3,3-dimethylhex-5-enal (3o):



R_f: 0.6 (petroleum ether/ethyl acetate 20:1). Colorless oil (43 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.70 (t, *J* = 2.2 Hz, 1H), 7.61-7.58 (m, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.39-7.33 (m, 3H), 2.54 (s, 2H), 2.21 (d, *J* = 2.3 Hz, 2H), 1.00 (s, 6H): **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.7, 154.7 (dd, *J* = 291.3, 288.5 Hz), 140.4, 140.2, 133.8 (dd, *J* = 4.3. 3.0 Hz), 128.95, 128.90, 127.6, 127.3, 127.1, 90.0 (dd, *J* = 21.2, 13.8 Hz), 54.7, 39.9, 35.4 (t, *J* = 2.4 Hz), 27.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -88.33 (d, *J* = 38.3 Hz, 1F), -90.64 (d, *J* = 38.3 Hz, 1F); **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}F_2O$

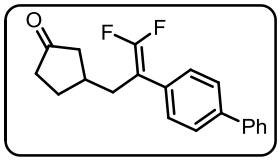
315.1560; Found 315.1550

5-(biphenyl-4-yl)-6,6-difluoro-3-methylhex-5-enal (3p):



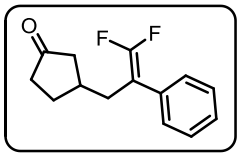
R_f: 0.6 (petroleum ether/ethyl acetate 20:1). Colorless oil (40 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.70 (t, *J* = 1.8 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 4H), 7.47-7.34 (m, 5H), 2.53-2.35 (m, 3H), 2.32-2.25 (m, 1H), 2.19-2.11 (m, 1H), 0.99 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.1, 154.3 (dd, *J* = 291.6, 287.5 Hz), 140.5, 140.4, 132.2 (t, *J* = 3.5 Hz), 128.9, 128.7 (t, *J* = 3.2 Hz), 127.6, 127.4, 127.1, 90.6 (dd, *J* = 21.4, 13.5 Hz), 50.4, 34.5, 26.7 (t, *J* = 2.3 Hz), 19.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.92 (d, *J* = 41.1 Hz, 1F), -90.21 (d, *J* = 41.0 Hz, 1F); **HRMS (ESI)** m/z: [M+H$^+$] Calcd for $C_{19}H_{19}F_2O$ 301.1404; Found 301.1409.

3-(2-(biphenyl-4-yl)-3,3-difluoroallyl)cyclopentanone (5a):



R_f: 0.35 (petroleum ether/ethyl acetate 20:1). Colorless oil (46.8 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 4H), 7.47-7.43 (m, 2H), 7.40-7.30 (m, 3H), 2.59 (d, *J* = 7.1 Hz, 2H), 2.36-2.21 (m, 3H), 2.16-2.06 (m, 2H), 1.87 (dd, *J* = 17.3, 9.3 Hz, 1H), 1.64-1.59 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 218.7, 154.2 (dd, *J* = 290.8, 287.9 Hz), 140.57, 140.53, 132.2 (dd, *J* = 3.0 Hz), 128.9, 128.7 (t, *J* = 3.0 Hz), 127.6, 127.4, 127.1, 90.9 (dd, *J* = 20.8, 14.5 Hz), 44.7, 38.4, 35.6 (t, *J* = 2.2 Hz), 33.3, 29.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.48 (d, *J* = 42.1 Hz, 1F), -90.66 (d, *J* = 42.1 Hz, 1F); **HRMS (ESI)** m/z: [M+H]$^+$ Calcd for $C_{20}H_{19}F_2O$ 313.1404; Found 313.1401.

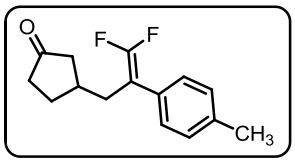
3-(3,3-difluoro-2-phenylallyl)cyclopentanone (5b):



R_f: 0.35 (petroleum ether/ethyl acetate 20:1). Colorless oil (32 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39-7.35 (m, 2H), 7.31-7.27 (m, 3H), 2.56-2.53 (m, 2H), 2.32-2.04 (m, 5H), 1.87-1.80 (m, 1H), 1.59-1.52 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 218.7, 154.1,

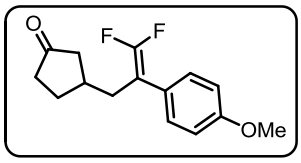
133.3 (d, *J* = 2.0 Hz), 128.7, 128.3 (t, *J* = 2.9 Hz), 127.7, 91.2 (dd, *J* = 19.6, 16.0 Hz), 44.7, 38.4, 35.5 (t, *J* = 2.5 Hz), 33.4, 29.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.12 (d, *J* = 42.9 Hz, 1F), -91.25 (d, *J* = 42.9 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{14}H_{15}F_2O$ 237.1091; Found 237.1084.

3-(3,3-difluoro-2-*p*-tolylallyl)cyclopentanone (5c):



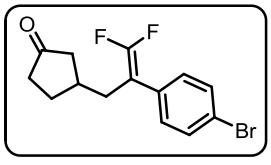
R_f: 0.35 (petroleum ether/ethyl acetate 20:1). Colorless oil (34 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.9 Hz, 2H), 7.17 (d, *J* = 8.9 Hz, 2H), 2.54-2.51 (m, 2H), 2.35 (s, 3H), 2.31-2.25 (m, 2H), 2.22-2.15 (m, 1H), 2.13-2.03 (m, 2H), 1.86-1.79 (m, 1H), 1.58-1.51 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 218.7, 154.0 (t, *J* = 288.4 Hz), 137.5, 130.3, 129.4, 128.2 (t, *J* = 2.9 Hz), 91.0 (t, *J* = 17.8 Hz), 44.7, 38.4, 35.5 (t, *J* = 2.5 Hz), 33.4, 29.0, 21.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.59 (s, 2F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{15}H_{17}F_2O$ 251.1247; Found 251.1241.

3-(3,3-difluoro-2-(4-methoxyphenyl)allyl)cyclopentanone (5d):



R_f: 0.36 (petroleum ether/ethyl acetate 20:1). Colorless oil (37 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 2.52-2.49 (m, 2H), 2.31-2.03 (m, 5H), 1.86-1.79 (m, 1H), 1.60-1.51 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 218.7, 159.0, 154.0 (t, *J* = 288.0), 129.4 (t, *J* = 3.0 Hz), 125.4 (d, *J* = 1.6 Hz), 114.2, 90.6 (dd, *J* = 19.3, 16.6 Hz), 55.4, 44.7, 38.4, 35.5 (t, *J* = 2.4 Hz), 33.4, 29.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -92.01 (d, *J* = 45.2 Hz, 1F), -92.12 (d, *J* = 45.3 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{15}H_{17}F_2O_2$ 267.1197; Found 267.1187.

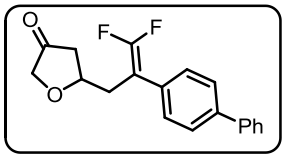
3-(2-(4-bromophenyl)-3,3-difluoroallyl)cyclopentanone (5e):



R_f: 0.37 (petroleum ether/ethyl acetate 20:1). Colorless oil (39 mg, 63% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51-7.48 (m, 2H), 7.19-7.17 (m, 2H), 2.53-2.50 (m, 2H), 2.31-2.25 (m, 2H),

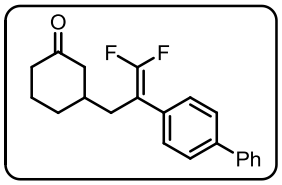
2.20-2.02 (m, 3H), 1.86-1.79 (m, 1H), 1.58-1.50 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 218.3, 154.0 (dd, *J* = 291.3, 288.1 Hz), 132.3 (dd, *J* = 3.9, 2.8 Hz), 131.9, 129.9 (t, *J* = 3.1 Hz), 121.7, 90.5 (dd, *J* = 22.1, 14.2 Hz), 44.6, 38.3, 35.5 (t, *J* = 2.4 Hz), 33.2, 29.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.01 (d, *J* = 40.8 Hz, 1F), -90.23 (d, *J* = 40.8 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}BrF_2O$ 315.0196; Found 315.0190.

5-(2-(biphenyl-4-yl)-3,3-difluoroallyl)dihydrofuran-3(2H)-one (5f):



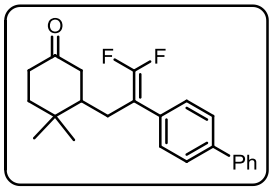
R_f: 0.32 (petroleum ether/ethyl acetate 20:1). Colorless oil (38 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.59 (m, 4H), 7.47-7.41 (m, 4H), 7.38-7.34 (m, 1H), 4.31-4.26 (m, 1H), 4.07-4.00 (m, 1H), 3.72 (dd, *J* = 9.0, 4.1 Hz, 1H), 2.87-2.80 (m, 1H), 2.73-2.66 (m, 1H), 2.47 (dd, *J* = 7.8, 6.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 215.1, 154.5 (dd, *J* = 290.8, 288.8 Hz), 140.59, 140.57, 131.5 (t, *J* = 3.6 Hz), 129.0 (t, *J* = 3.1 Hz), 128.9, 127.6, 127.3, 127.1 88.6 (dd, *J* = 21.2, 16.3 Hz), 77.3, 64.4, 36.8, 29.3 (d, *J* = 2.0 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -88.7 (d, *J* = 38.7 Hz, 1F), -89.5 (d, *J* = 38.6 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{19}H_{17}F_2O_2$ 315.1197; Found 315.1190.

3-(2-(biphenyl-4-yl)-3,3-difluoroallyl)cyclohexanone (5g):



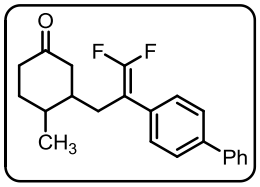
R_f: 0.35 (petroleum ether/ethyl acetate 20:1). Colorless oil (46 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62-7.58 (m, 4H), 7.47-7.43 (m, 2H), 7.39-7.34 (m, 3H), 2.55-2.41 (m, 3H), 2.37-2.31 (m, 1H), 2.29-2.20 (m, 1H), 2.09-1.99 (m, 2H), 1.93-1.80 (m, 2H), 1.63-1.52 (m, 1H), 1.44-1.34 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.0, 154.2 (dd, *J* = 291.6, 287.2 Hz), 140.5, 140.4, 132.1 (t, *J* = 3.0 Hz), 128.9, 128.6 (t, *J* = 3.1 Hz), 127.5, 127.3, 127.1, 90.1 (dd, *J* = 21.6, 13.7 Hz), 47.6, 41.3, 37.1 (t, *J* = 2.4 Hz), 34.5, 30.9, 25.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.91 (d, *J* = 41.4 Hz, 1F), -90.22 (d, *J* = 41.4 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{21}H_{21}F_2O$ 327.1560; Found 327.1552.

3-(2-(biphenyl-4-yl)-3,3-difluoroallyl)-4,4-dimethylcyclohexanone (5h):



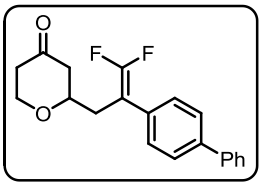
R_f: 0.35 (petroleum ether/ethyl acetate 20:1). Colorless oil (46 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.58 (m, 4H), 7.46-7.43 (m, 2H), 7.37-7.34 (m, 3H), 2.73-2.66 (m, 1H), 2.44-2.33 (m, 2H), 2.27-2.21 (m, 2H), 2.13-2.06 (m, 1H), 1.72-1.66 (m, 1H), 1.56-1.50 (m, 2H), 1.10 (s, 3H), 1.06 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.2, 153.2 (dd, *J* = 291.4, 287.0 Hz), 140.5, 140.4, 131.8 (t, *J* = 3.7 Hz), 128.9, 128.6 (t, *J* = 3.1 Hz), 127.6, 127.4, 127.1, 90.3 (dd, J = 21.6, 13.4 Hz), 44.1, 42.4, 40.2, 38.2, 32.8, 28.9, 28.7, 19.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.87 (d, *J* = 42.0 Hz, 1F), -90.39 (d, *J* = 42.0 Hz, 1F); **HRMS (ESI)** m/z: [M+H$^+$] Calcd for $C_{23}H_{25}F_2O$ 355.1873; Found 355.1868.

3-(2-(biphenyl-4-yl)-3,3-difluoroallyl)-4-methylcyclohexanone (5i):



R_f: 0.35 (petroleum ether/ethyl acetate 20:1).Colorless oil (42 mg, 62% yield), A mixture of two inseparable diastereomers (dr = 14:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.58 (m, 4H), 7.47-7.43 (m, 2H), 7.38-7.34 (m, 3H), 2.85-2.78 (m, 1H), 2.44 (dd, *J* = 14.4, 4.1 Hz, 1H), 2.34-2.26 (m, 3H), 2.04-1.95 (m, 2H), 1.70-1.59 (m, 1H), 1.55-1.35 (m, 2H), 1.07 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.2, 154.2 (dd, J = 291.2, 287.6 Hz) 140.5, 140.4, 132.0 (t, *J* = 3.0 Hz), 128.9, 128.6 (t, *J* = 3.1 Hz), 127.6, 127.4, 127.1, 90.1 (dd, *J* = 20.8, 14.1 Hz), 45.4, 42.3 (t, *J* = 1.9 Hz), 40.9, 35.7, 34.0, 32.3, 19.0 ; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.02 (d, *J* = 41.9 Hz, 1F), -90.20 (d, *J* = 41.7 Hz, 1F); **HRMS (ESI)** m/z: [M+H]$^+$ Calcd for $C_{22}H_{23}F_2O$ 341.1717; Found 341.1709.

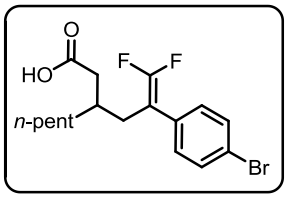
2-(2-(biphenyl-4-yl)-3,3-difluoroallyl)dihydro-2H-pyran-4(3H)-one (5j):



R_f: 0.32 (petroleum ether/ethyl acetate 20:1). Colorless oil (39 mg, 59% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 4H), 7.47-7.34 (m, 5H), 4.30-4.25 (m, 1H), 3.64-3.53 (m, 2H), 2.89-2.82 (m, 1H), 2.65-2.54 (m, 2H), 2.45-2.40 (m, 1H),

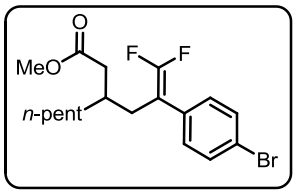
2.35-2.27 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.3, 154.6 (dd, *J* = 291.1, 288.7 Hz), 140.59, 140.51, 132.0 (t, *J* = 2.7 Hz), 128.9, 128.7 (t, *J* = 3.1 Hz), 127.6, 127.4, 127.1, 88.6 (dd, *J* = 20.7, 16.3 Hz), 75.8 (t, *J* = 2.9 Hz), 66.5, 47.8, 42.1, 34.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.04 (d, *J* = 38.8 Hz, 1F), -89.17 (d, *J* = 38.8 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}F_2O_2$ 329.1353; Found 329.1348.

3-(2-(4-bromophenyl)-3,3-difluoroallyl)octanoic acid (6):



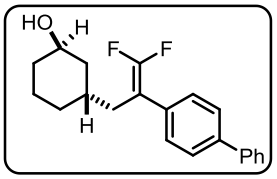
R_f: 0.5 (petroleum ether/ethyl acetate 3:1). Colorless oil (57 mg, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 2.42 (d, *J* = 7.1 Hz, 2H), 2.33-2.22 (m, 2H), 1.87-1.81 (m, 1H), 1.33-1.19 (m, 8H), 0.85 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.8, 154.1 (dd, *J* = 291.5, 288.3 Hz), 132.3 (t, *J* = 3.03 Hz), 131.8, 130.0 (t, *J* = 3.1 Hz), 121.5, 90.3 (dd, *J* = 21.5, 13.8 Hz), 38.1, 33.3, 33.2, 31.98, 31.90, 26.0, 22.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.54 (d, *J* = 40.2 Hz, 1F), -89.73 (d, *J* = 40.2 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{17}H_{22}BrF_2O_2$ 375.0771; Found 375.0768.

methyl 3-(2-(4-bromophenyl)-3,3-difluoroallyl)octanoate (7):



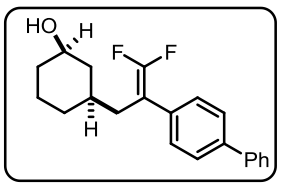
R_f: 0.7 (petroleum ether/ethyl acetate 10:1). Colorless oil (54 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 3.63 (s, 3H), 2.39 (d, *J* = 6.2 Hz, 2H), 2.29-2.17 (m, 2H), 1.84-1.80 (m, 1H), 1.25-1.19 (m, 8H), 0.85 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.4, 154.1 (dd, *J* = 290.9, 288.1 Hz), 132.4 (t, *J* = 3.0 Hz), 131.8, 130.0 (t, *J* = 3.1 Hz), 121.4, 90. (dd, *J* = 21.3, 14.0 Hz), 51.5, 38.2, 33.4, 33.3 (t, *J* = 2.2 Hz), 32.0, 31.9, 26.0, 22.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ δ -89.73 (d, *J* = 40.5 Hz, 1F), -89.90 (d, *J* = 40.5 Hz, 1F). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{18}H_{24}BrF_2O_2$ 389.0928; Found 389.0925.

***trans*-3-(2-(biphenyl-4-yl)-3,3-difluoroallyl)cyclohexanol (8):**



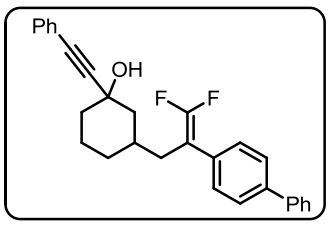
R_f: 0.3 (petroleum ether/ethyl acetate 5:1). Colorless oil (54.3 mg, 55% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63-7.59 (m, 4H), 7.47-7.34 (m, 5H), 3.52-3.45 (m, 1H), 2.44-2.33 (m, 2H), 2.04-1.92 (m, 2H), 1.78-1.66 (m, 2H), 1.47-1.36 (m, 1H), 1.31-1.08 (m, 2H), 0.99-0.82 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.2 (dd, *J* = 291.0, 286.7 Hz), 140.6, 140.1, 132.8 (t, *J* = 4.04 Hz), 128.9, 128.6 (t, *J* = 3.2 Hz), 127.5, 127.2, 127.1, 90.6 (dd, *J* = 22.0, 12.8 Hz), 70.6, 42.0, 35.7, 34.8, 34.7 (t, *J* = 2.3 Hz), 31.8, 23.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.22 (d, *J* = 42.3 Hz, 1F), -90.76 (d, *J* = 42.3 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}F_2O$ 329.1717; Found 329.1710.

***cis*-3-(2-(biphenyl-4-yl)-3,3-difluoroallyl)cyclohexanol (8'):**



R_f: 0.45 (petroleum ether/ethyl acetate 5:1). Colorless oil (19.7 mg, 20% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.57 (m, 4H), 7.46-7.33 (m, 5H), 4.06 (s, 1H), 2.35 (d, *J* = 7.2 Hz, 2H), 1.81-1.53 (m, 5H), 1.38-1.26 (m, 3H), 1.08-0.99 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.2 (dd, *J* = 291.0, 286.5 Hz), 140.7, 140.1, 132.8 (t, *J* = 3.03 Hz), 128.9, 128.7 (t, *J* = 3.2 Hz), 127.5, 127.2, 127.1, 90.7 (dd, *J* = 21.9, 12.7 Hz), 66.7, 39.3, 34.3, 33.3, 31.7, 30.1 (t, *J* = 2.1 Hz), 19.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.54 (d, *J* = 43.0 Hz, 1F), -90.96 (d, *J* = 42.9 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}F_2O$ 329.1717; Found 329.1710.

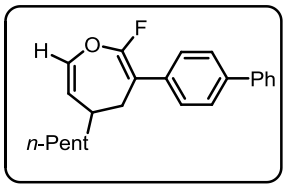
3-(2-(biphenyl-4-yl)-3,3-difluoroallyl)-1-(phenylethynyl)cyclohexanol (9):



R_f: 0.54 (petroleum ether/ethyl acetate 5:1). Colorless oil (51.3 mg, 60% yield, dr >20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59-7.56 (m, 4H), 7.47-7.35 (m, 5H), 7.20-7.13 (m, 3H), 7.09-7.05 (m, 2H), 2.48-2.2.36 (m, 2H), 2.18-2.15 (m, 1H), 2.07-2.05 (m, 1H), 1.87-1.75 (m, 2H), 1.59-1.44 (m, 2H), 1.32-1.26 (m, 1H), 1.00-0.91 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.1 (dd, *J* = 290.1, 287.1 Hz), 140.5, 140.0, 132.7 (t, *J* = 3.03 Hz), 131.6, 128.9, 128.2, 127.5,

127.1, 127.0, 122.6, 91.8, 90.5 (dd, *J* = 21.2, 14.0 Hz), 85.4, 70.0, 46.1, 40.0, 34.3, 33.9 (t, *J* = 2.0 Hz), 31.9, 23.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.67 (d, *J* = 43.0 Hz, 1F), -90.87 (d, *J* = 43.0 Hz, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{29}H_{27}F_2O$ 429.2030; Found 429.2024.

3-(biphenyl-4-yl)-2-fluoro-5-pentyl-4,5-dihydrooxepine (10):

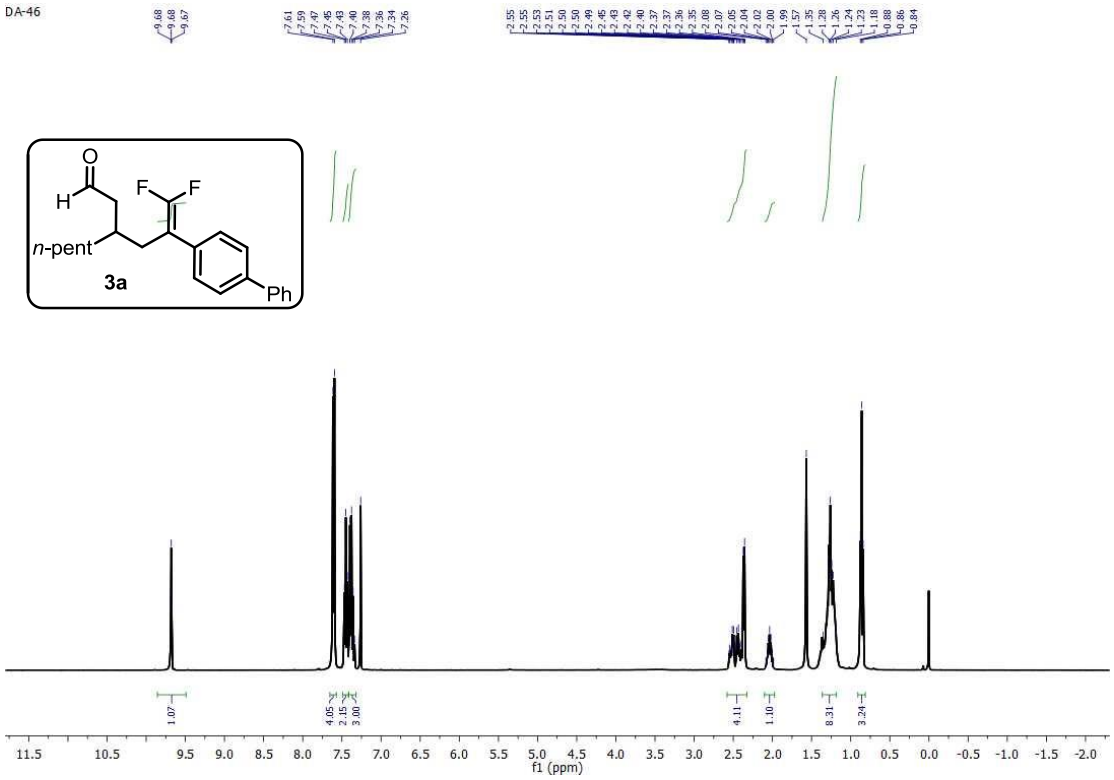


R_f: 0.7 (petroleum ether/ethyl acetate 20:1). Colorless oil (30 mg, 44% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62-7.57 (m, 4H), 7.46-7.40 (m, 4H), 7.36-7.33 (m, 1H), 6.34 (dd, *J* = 7.2, 2.0 Hz, 1H), 4.95 (dd, *J* = 7.1, 3.1 Hz, 1H), 2.67-2.56 (m, 2H), 2.48-2.47 (m, 1H), 1.46-1.27 (m, 8H), 0.87 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.9 (d, *J* = 268.1 Hz), 140.9, 139.6, 139.4, 136.6 (d, *J* = 3.8 Hz), 128.9, 128.3 (d, *J* = 4.1 Hz), 127.3, 127.1, 127.0, 116.2 (d, *J* = 1.9 Hz), 96.5 (d, *J* = 26.2 Hz), 36.6, 36.3 (d, *J* = 2.1 Hz), 33.4 (d, *J* = 3.9 Hz), 32.0, 26.6, 22.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -82.17 (S, 1F); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{23}H_{26}FO$ 337.1968; Found 337.1962.

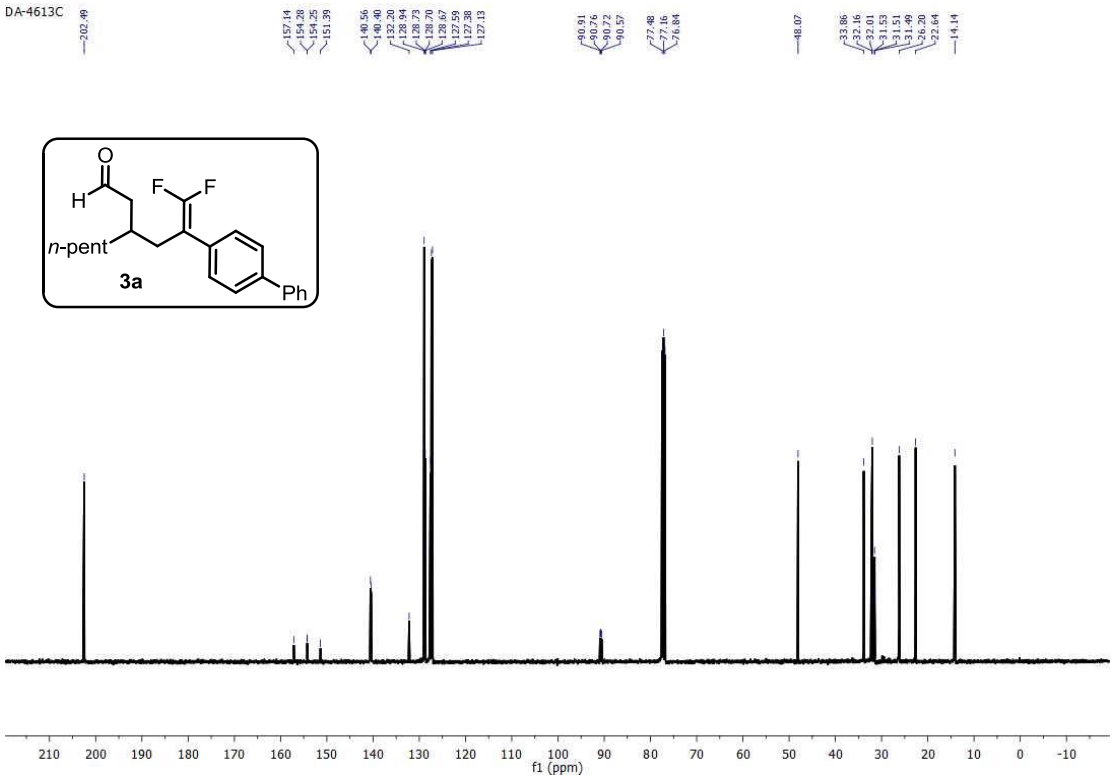
Reference

1. (a) Ichitsuka, T.; Fujita, T.; Arita, T.; Ichikawa, J. *Angew. Chem., Int. Ed.* **2014**, *53*, 7564. (b) Trost, B. M.; Debien, L. *J. Am. Chem. Soc.*, **2015**, *137*, 11606.
2. Jiang, H.; Studer, A. *Angew. Chem. Int. Ed.* **2017**, *56*, 12273.

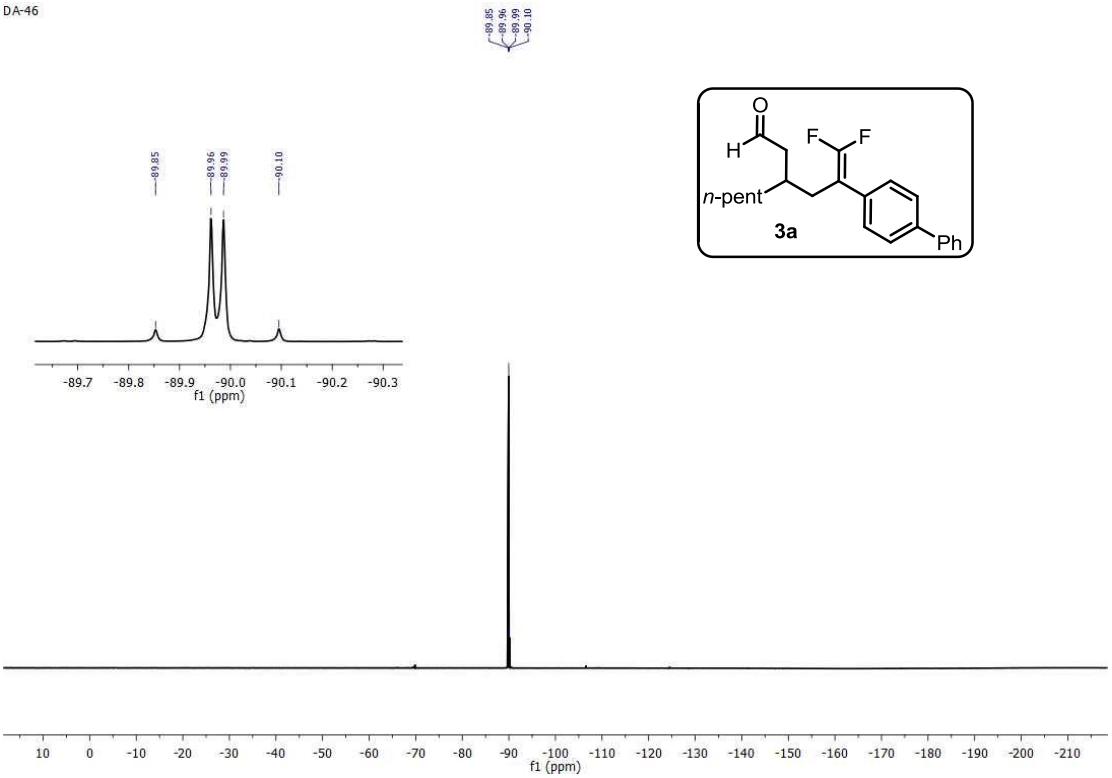
^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra



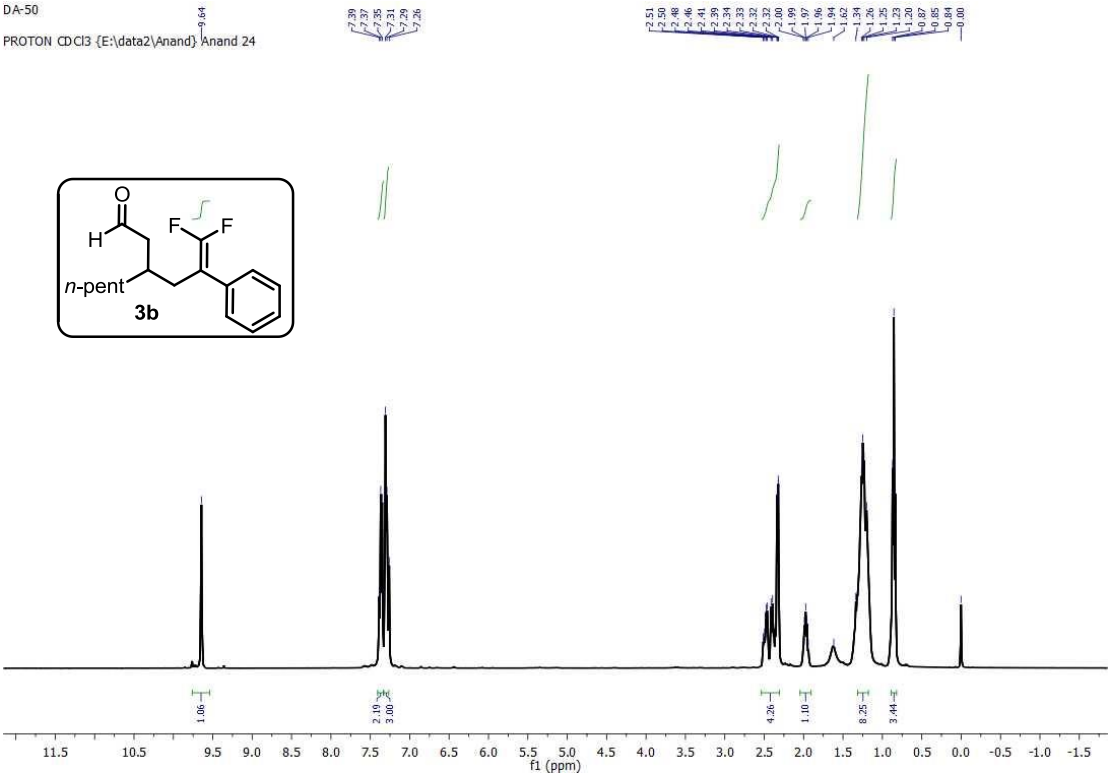
^{1}H NMR (400 MHz, $CDCl_3$)



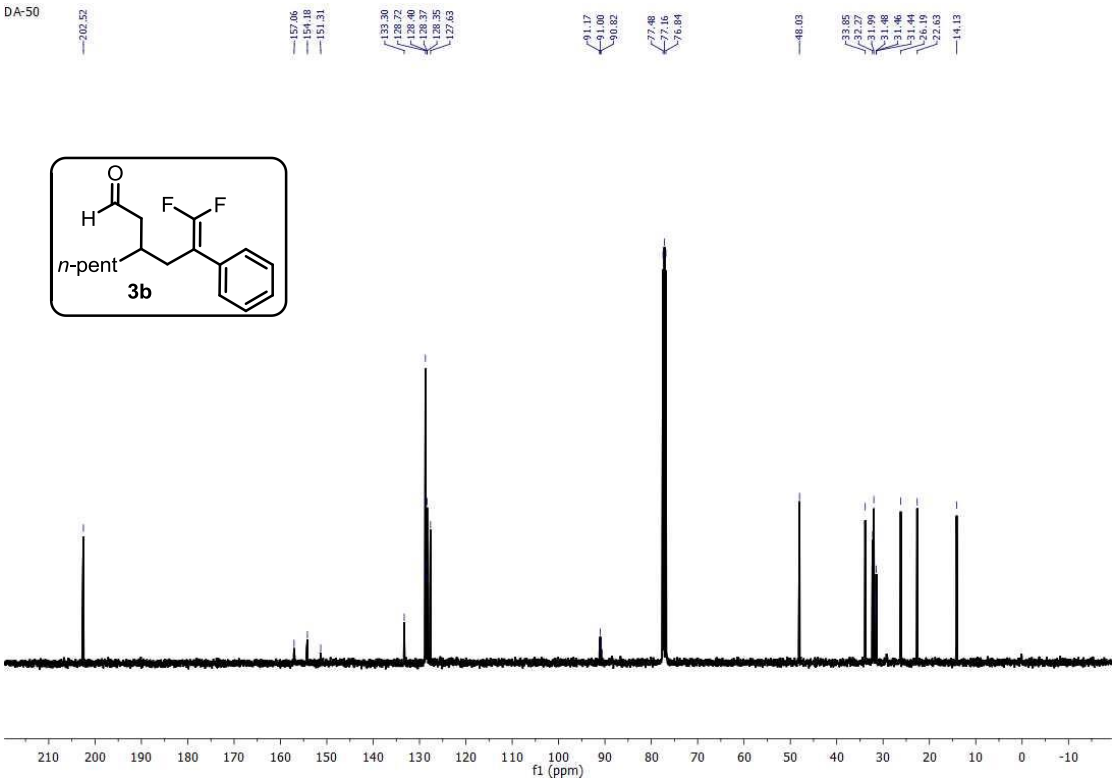
^{13}C NMR (101 MHz, $CDCl_3$)



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

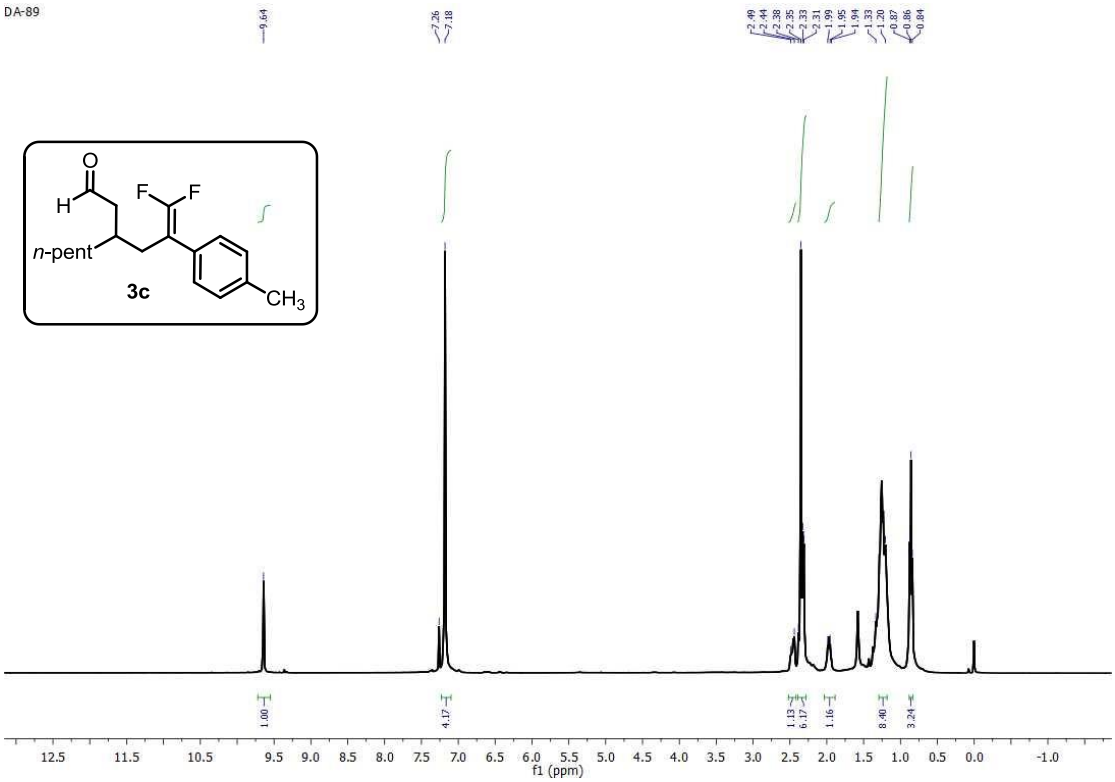


^{1}H NMR (400 MHz, $CDCl_3$)

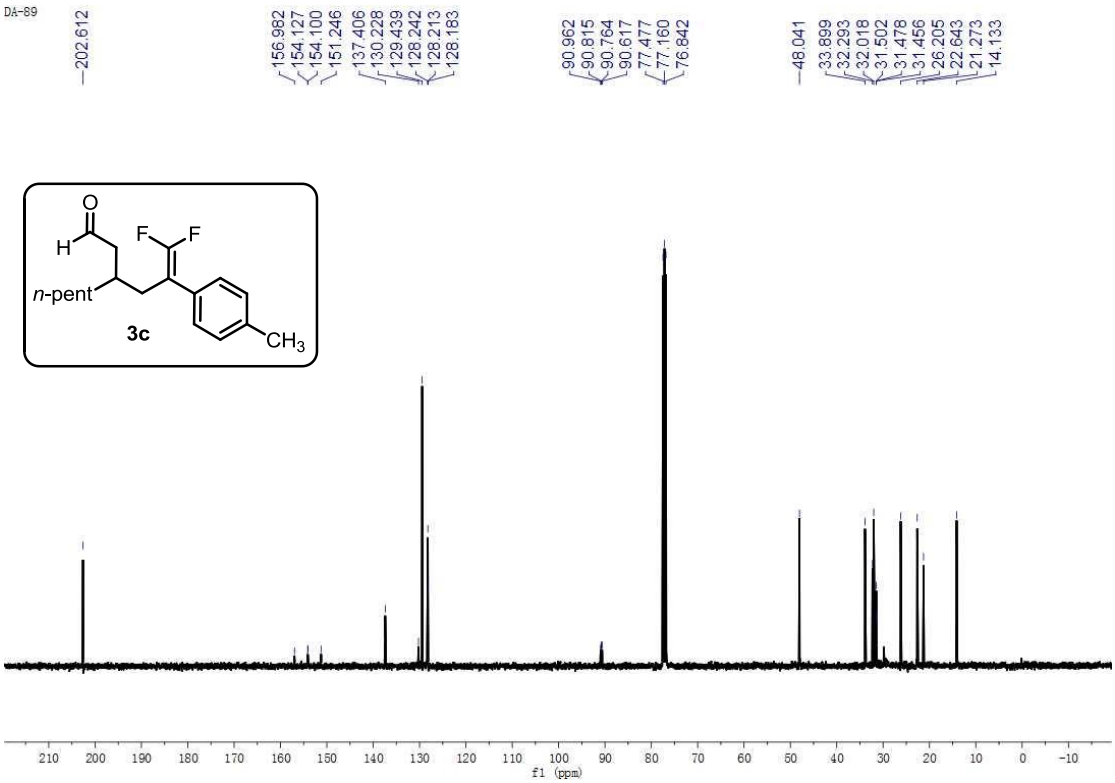


^{13}C NMR (101 MHz, $CDCl_3$)

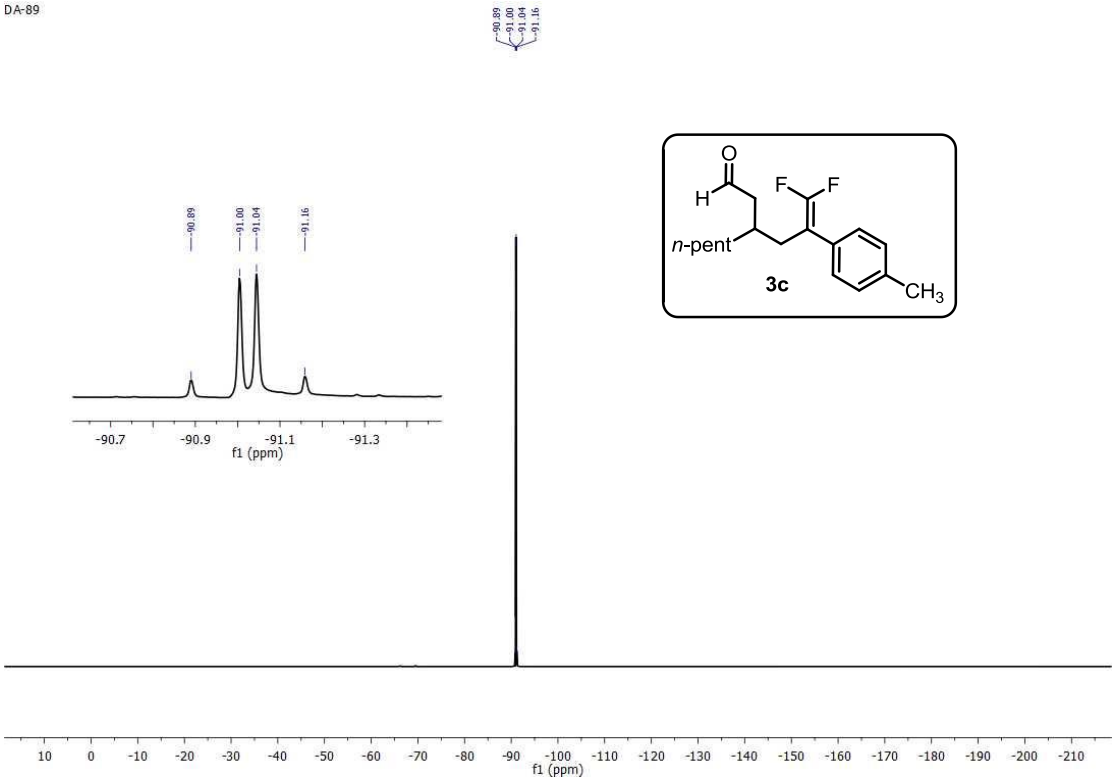
^{19}F NMR (376 MHz, $CDCl_3$)



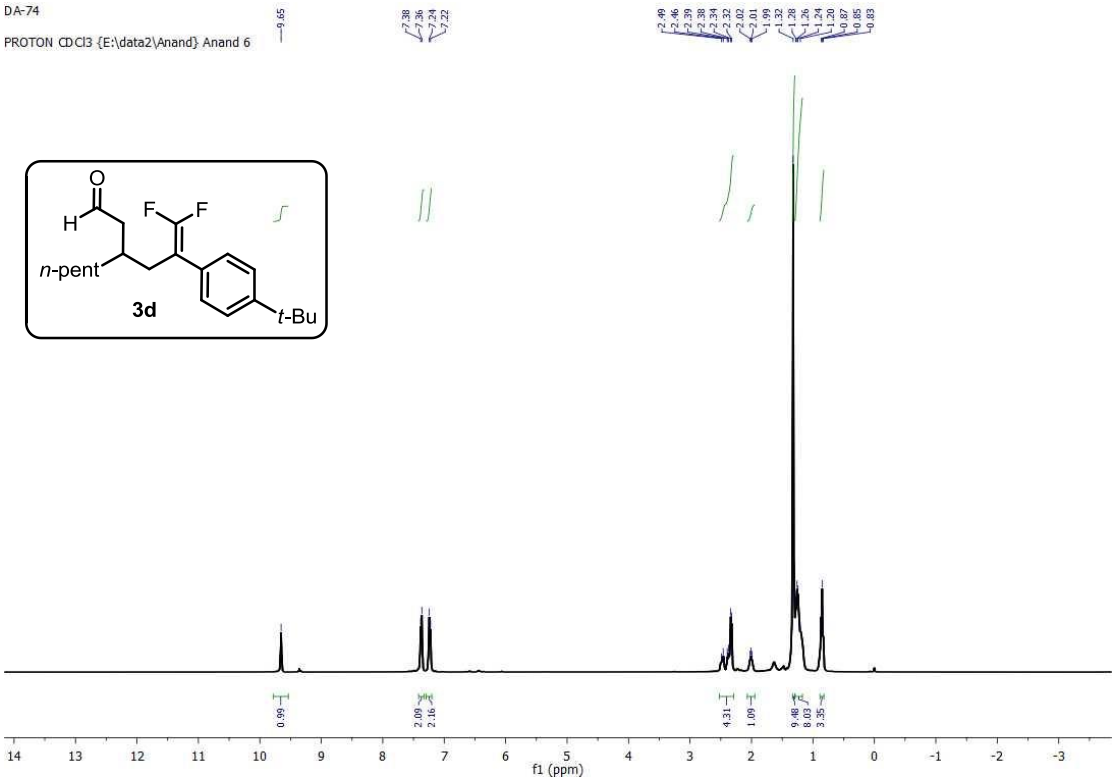
^{1}H NMR (400 MHz, $CDCl_3$)



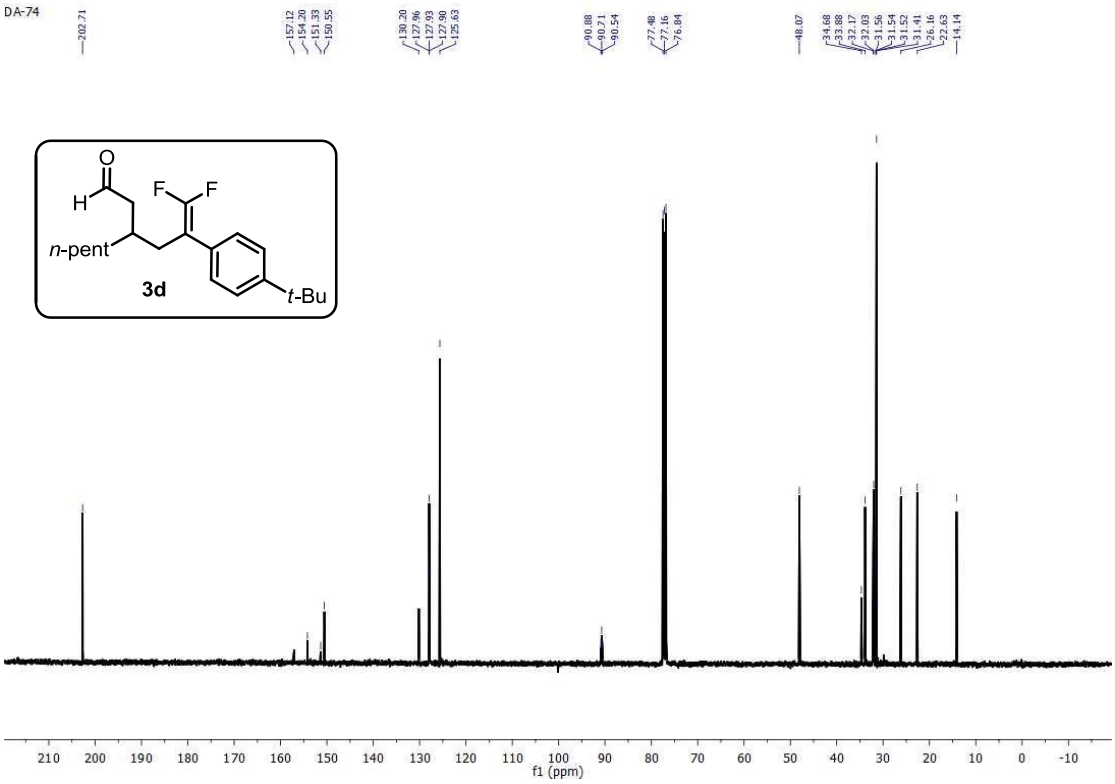
^{13}C NMR (101 MHz, $CDCl_3$)



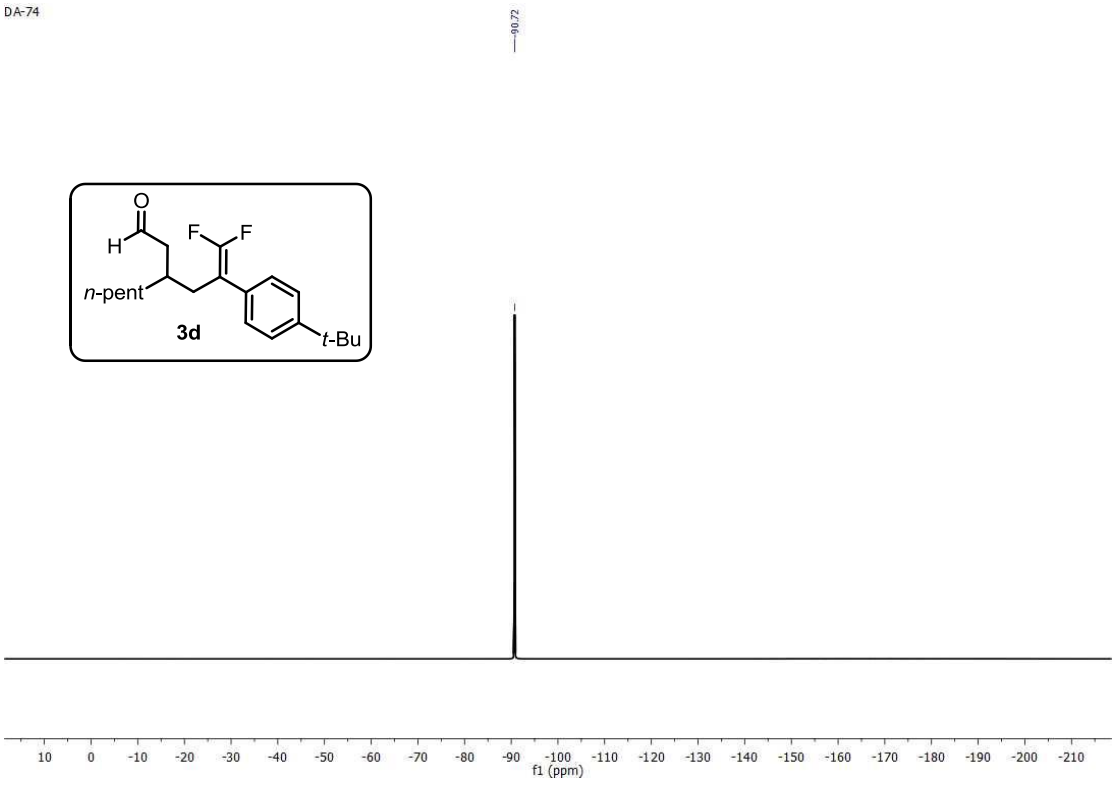
^{19}F NMR (376 MHz, $CDCl_3$)



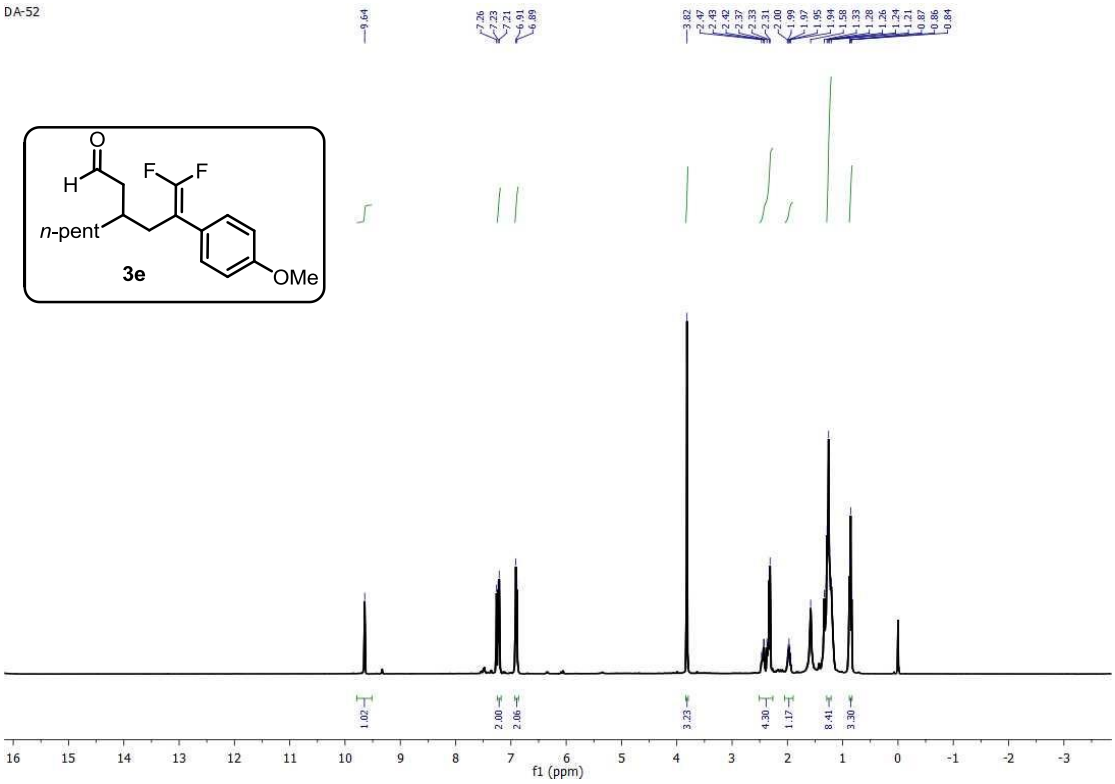
^{1}H NMR (400 MHz, $CDCl_3$)



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



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



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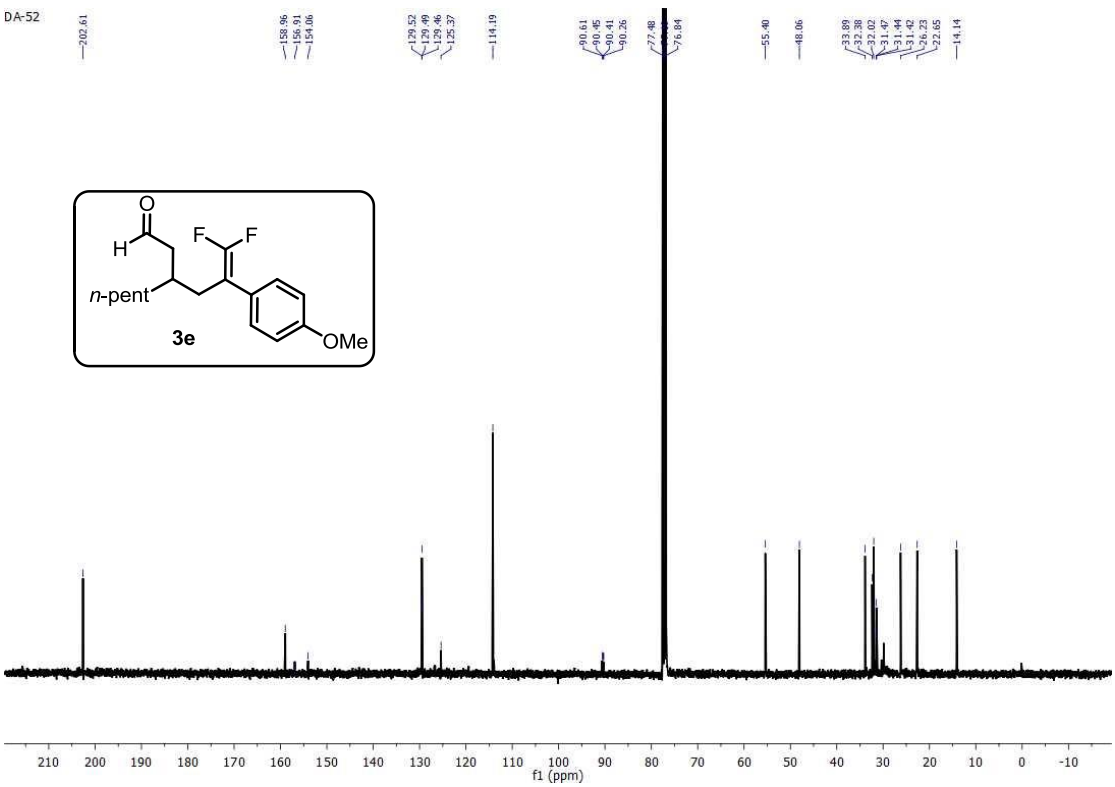

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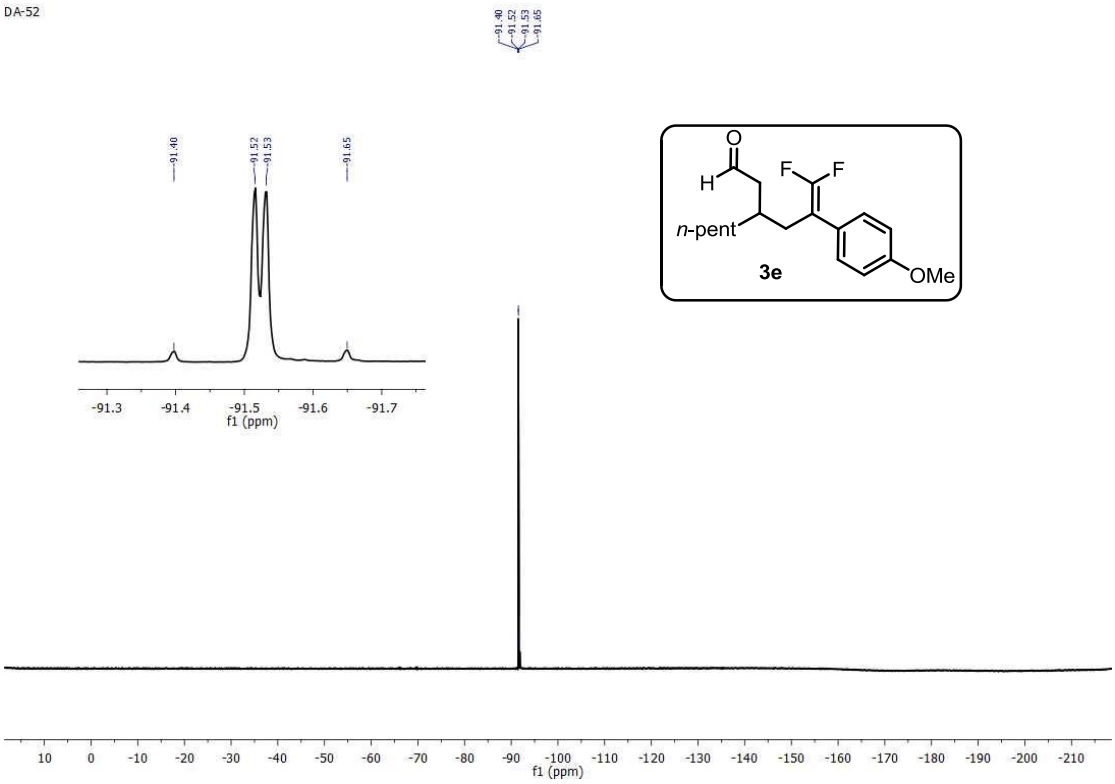

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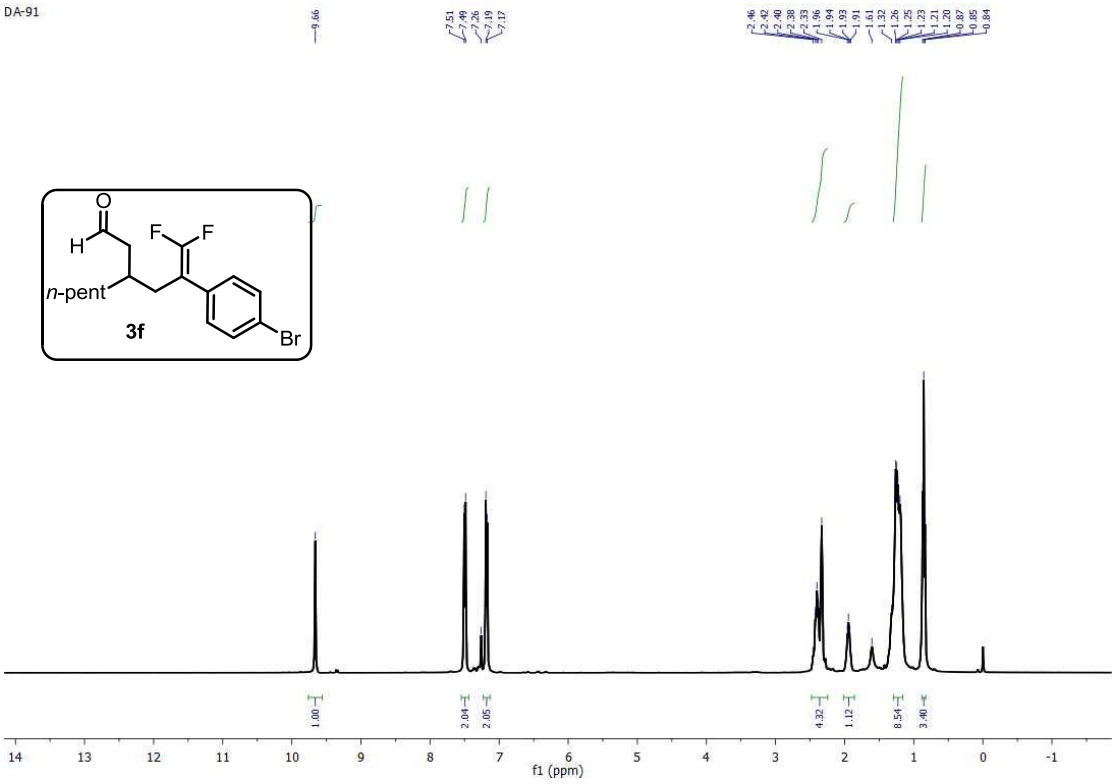

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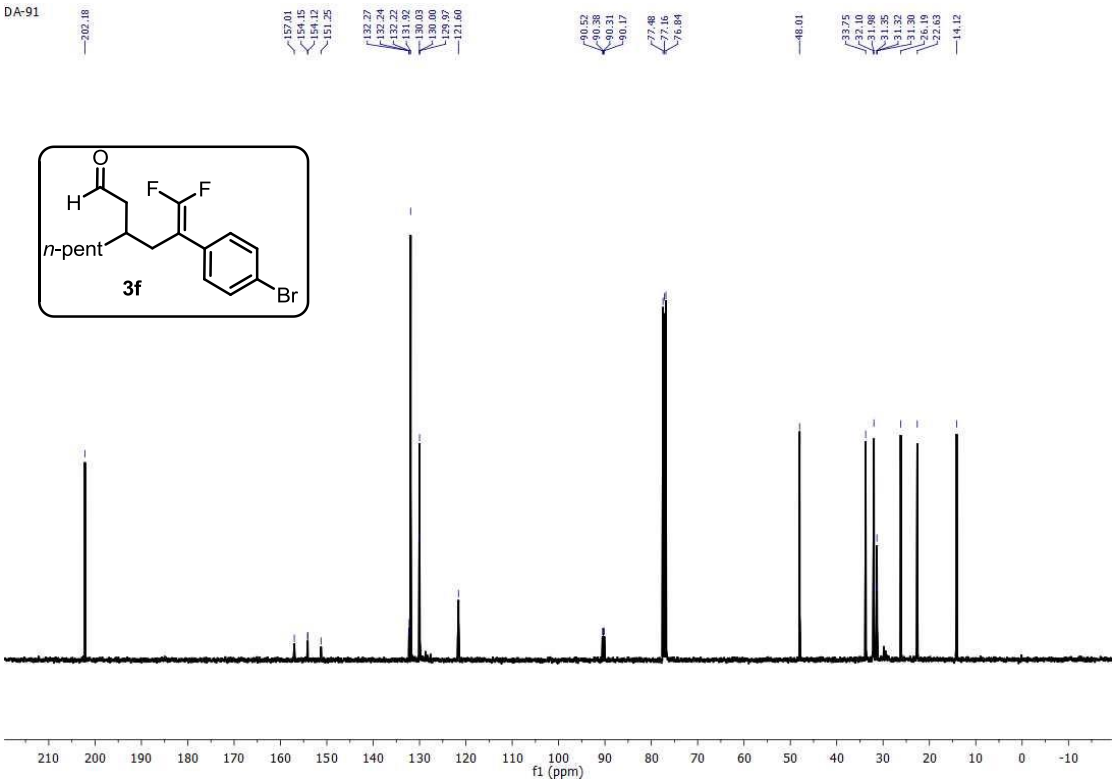

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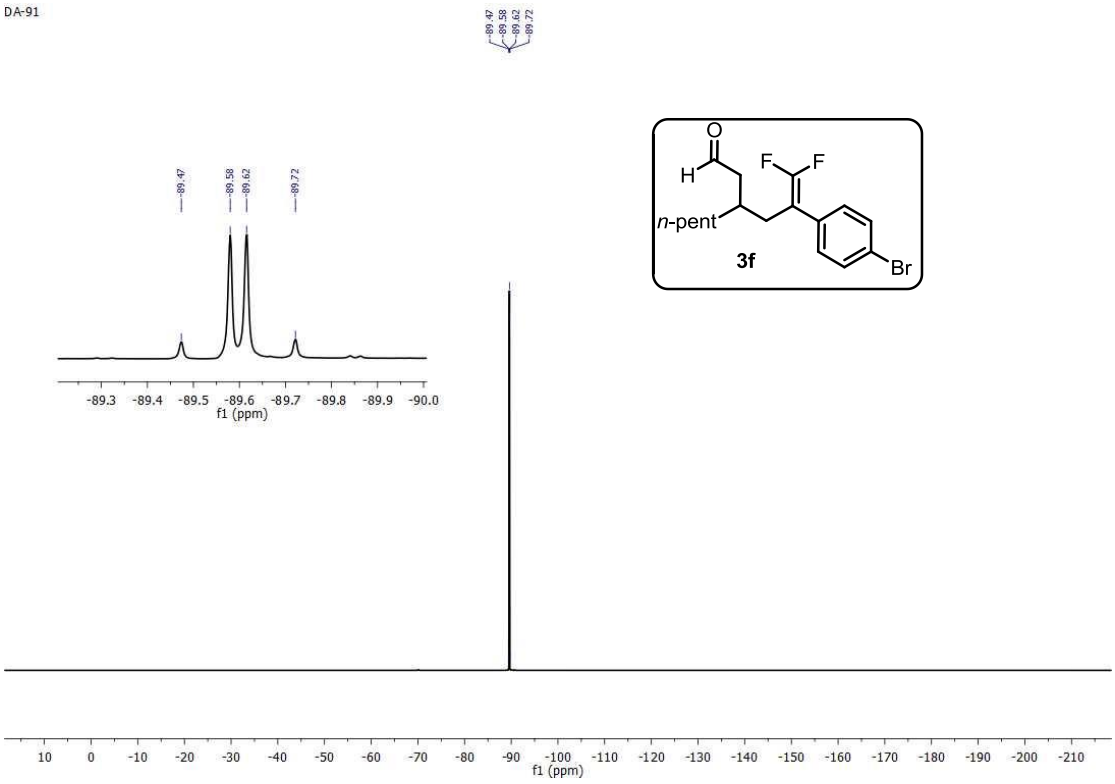

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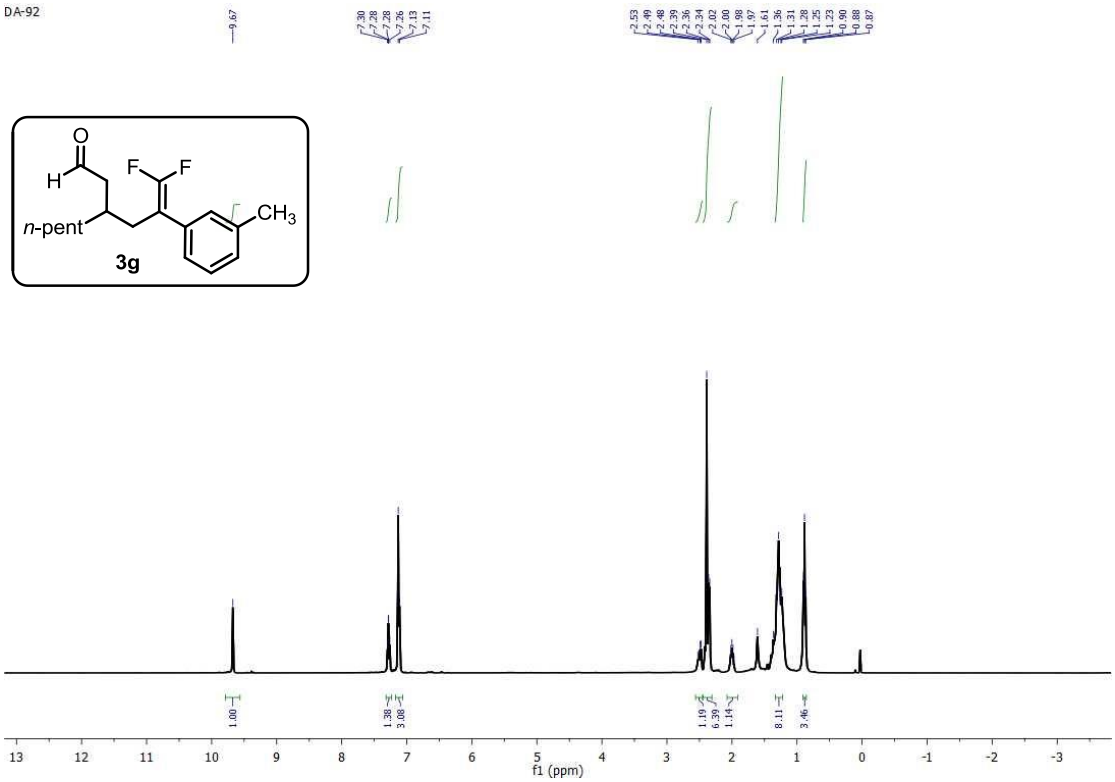

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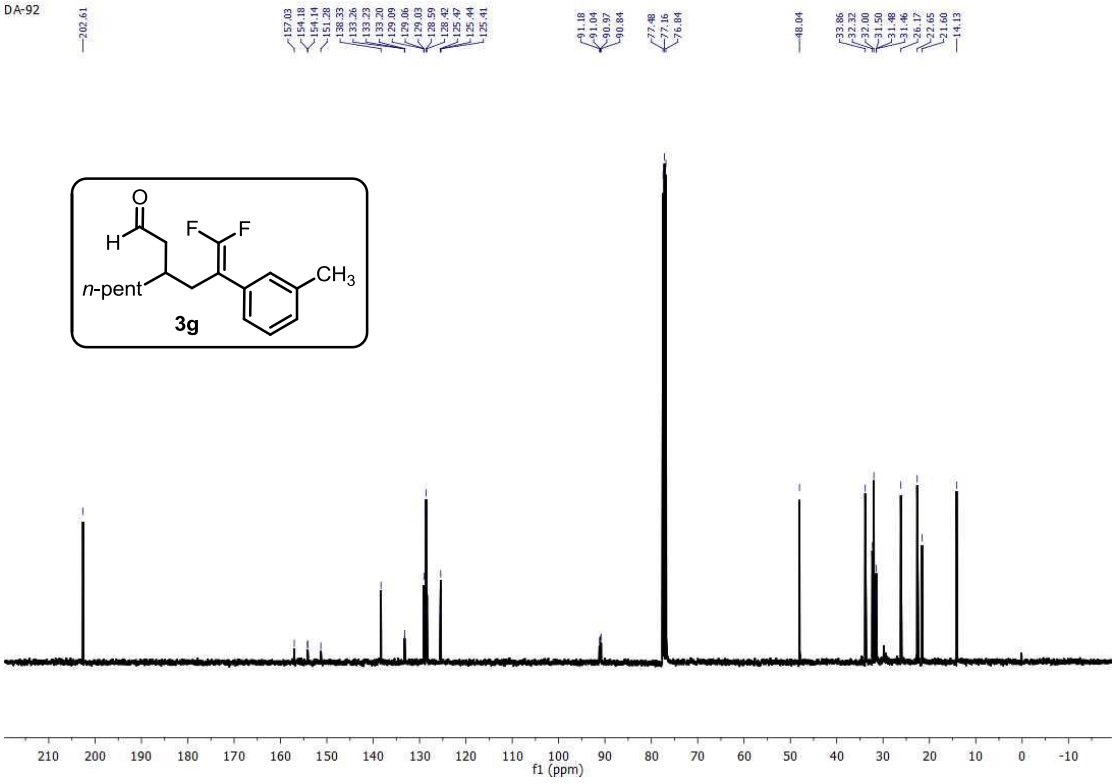

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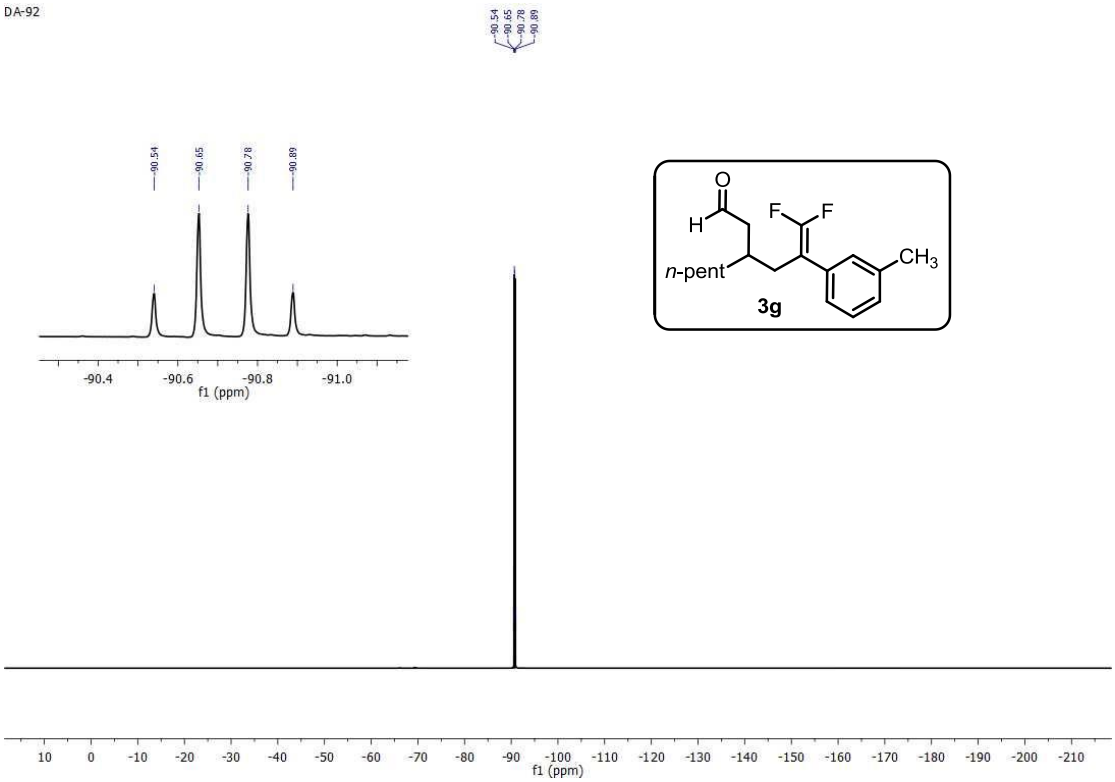

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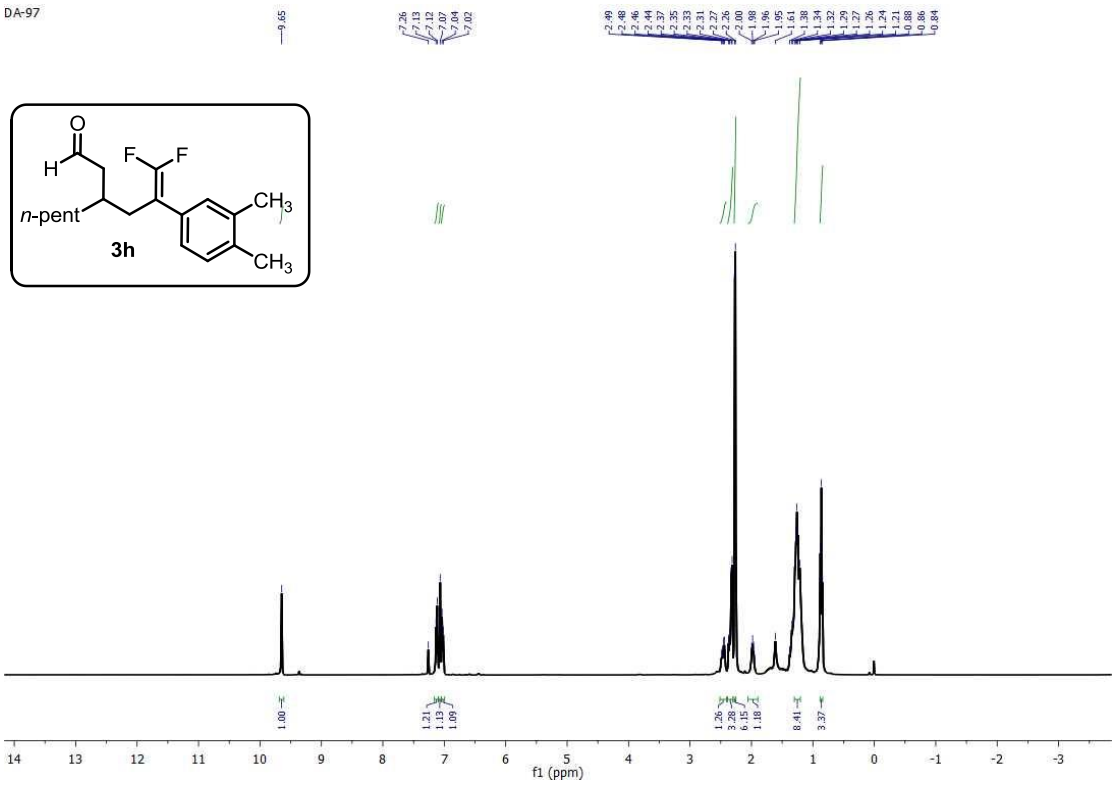

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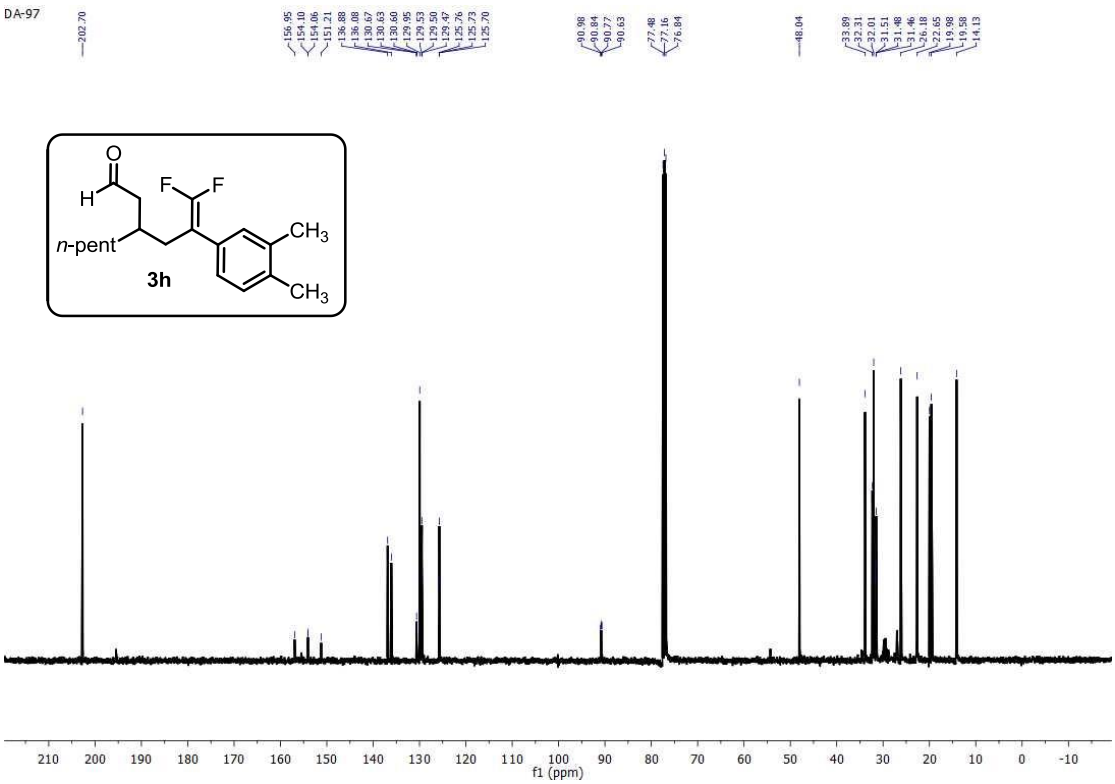

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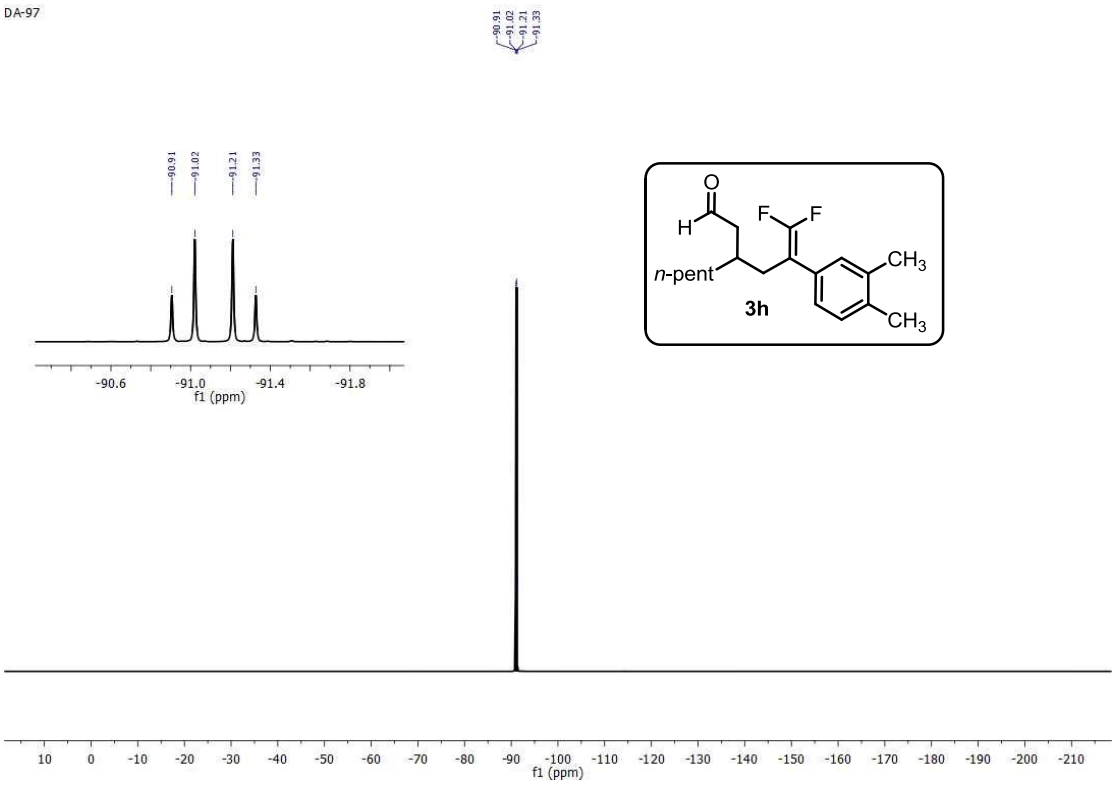

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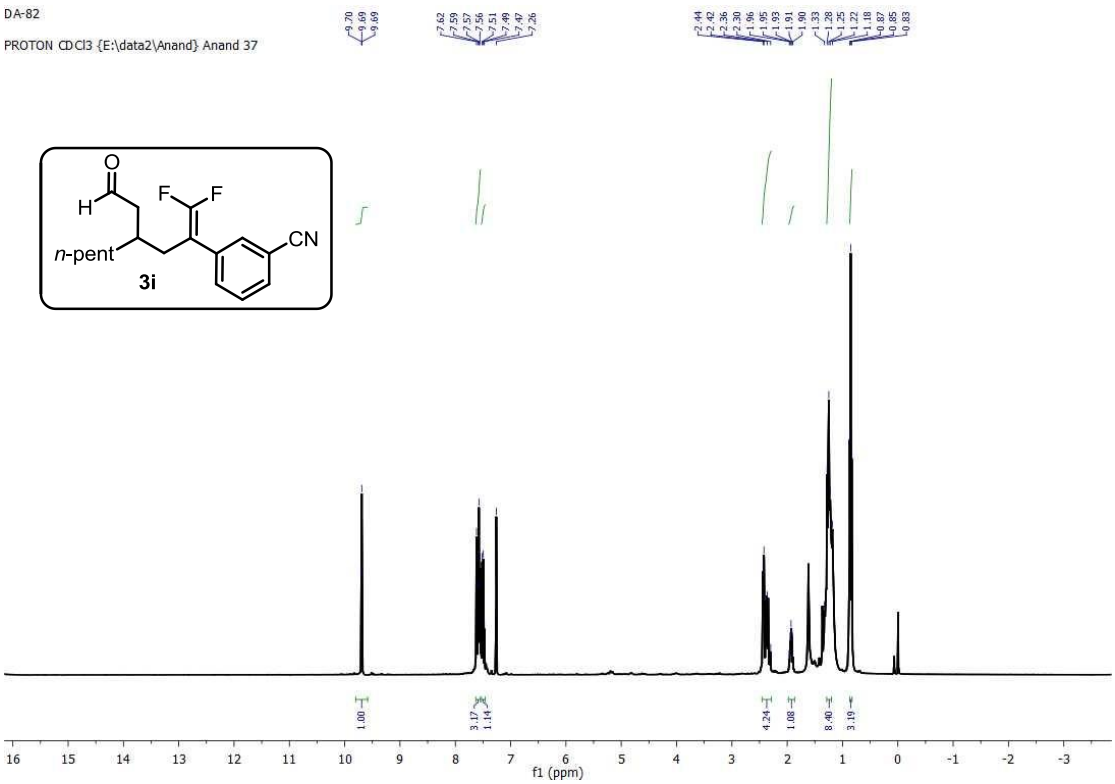

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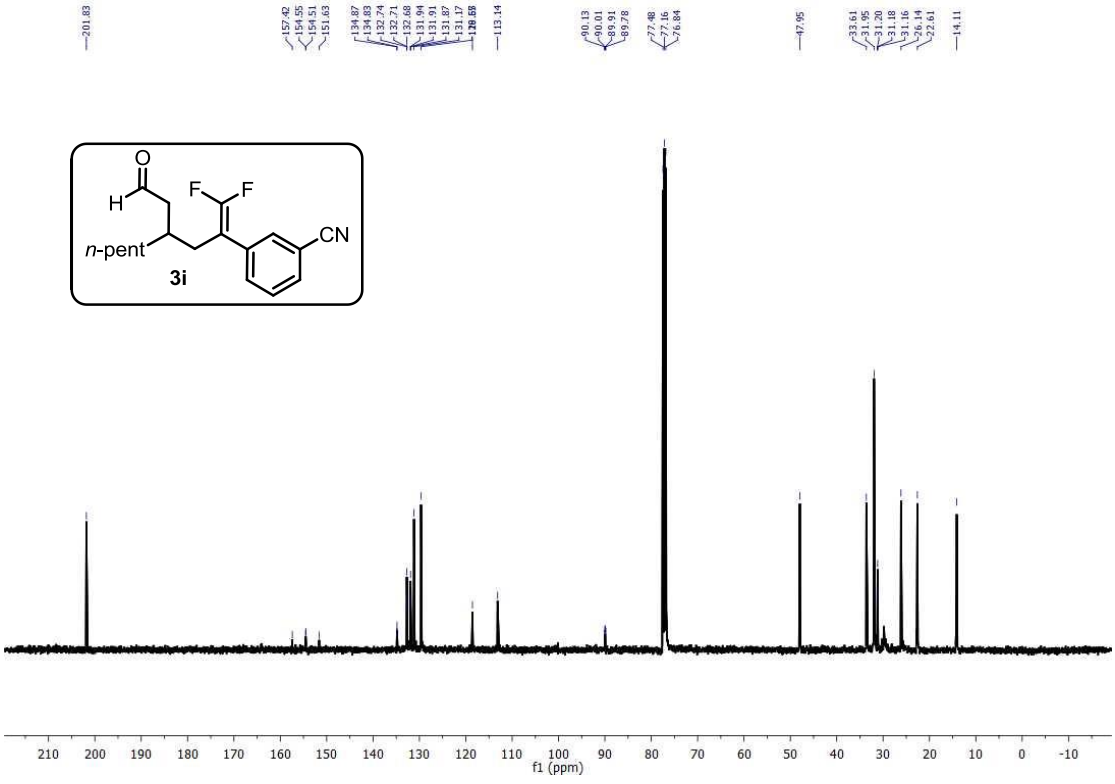

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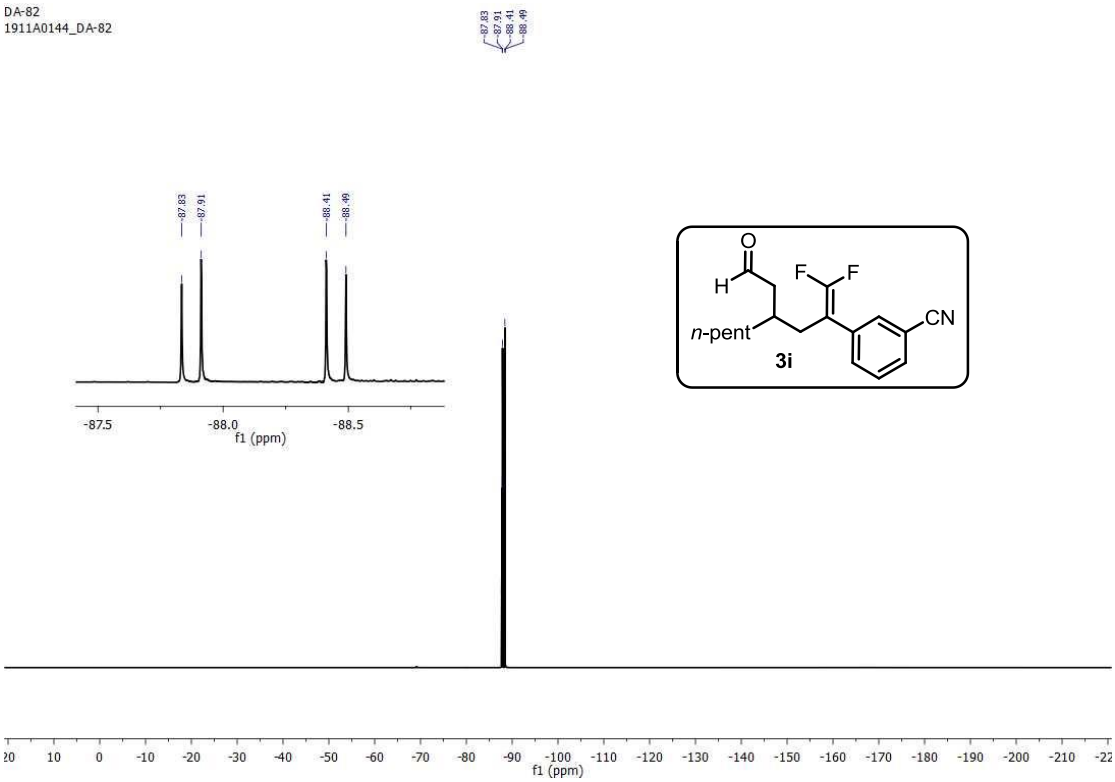

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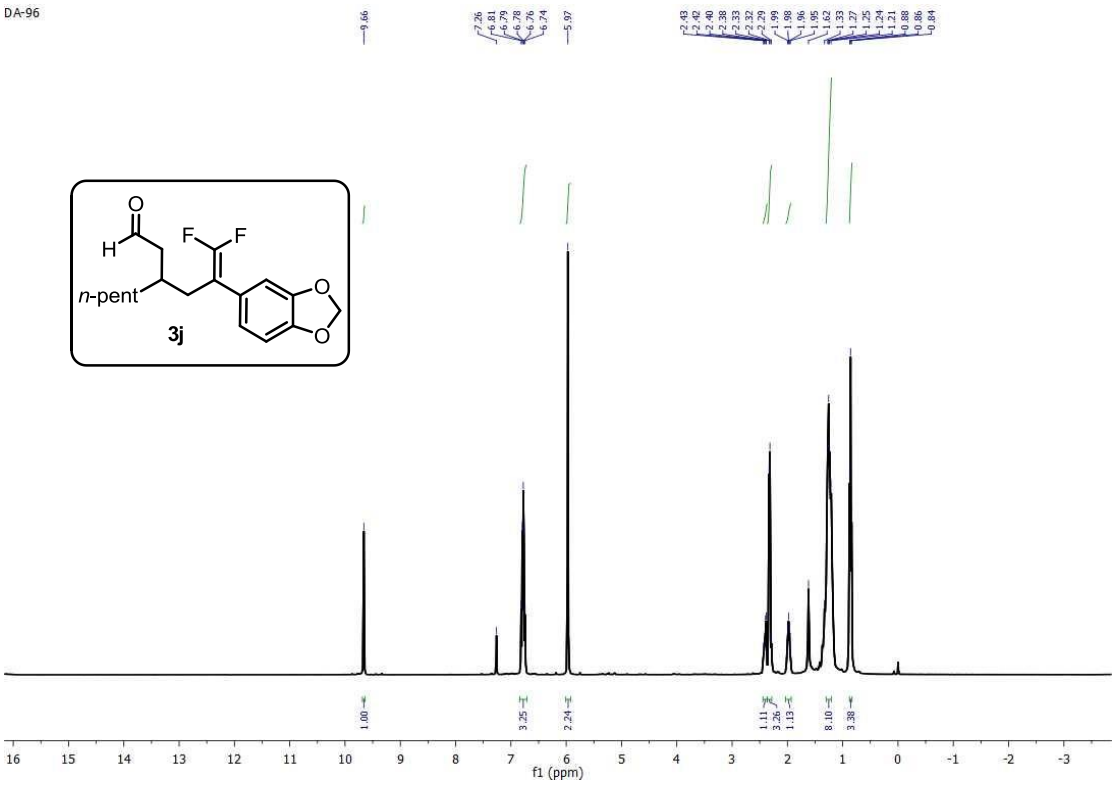

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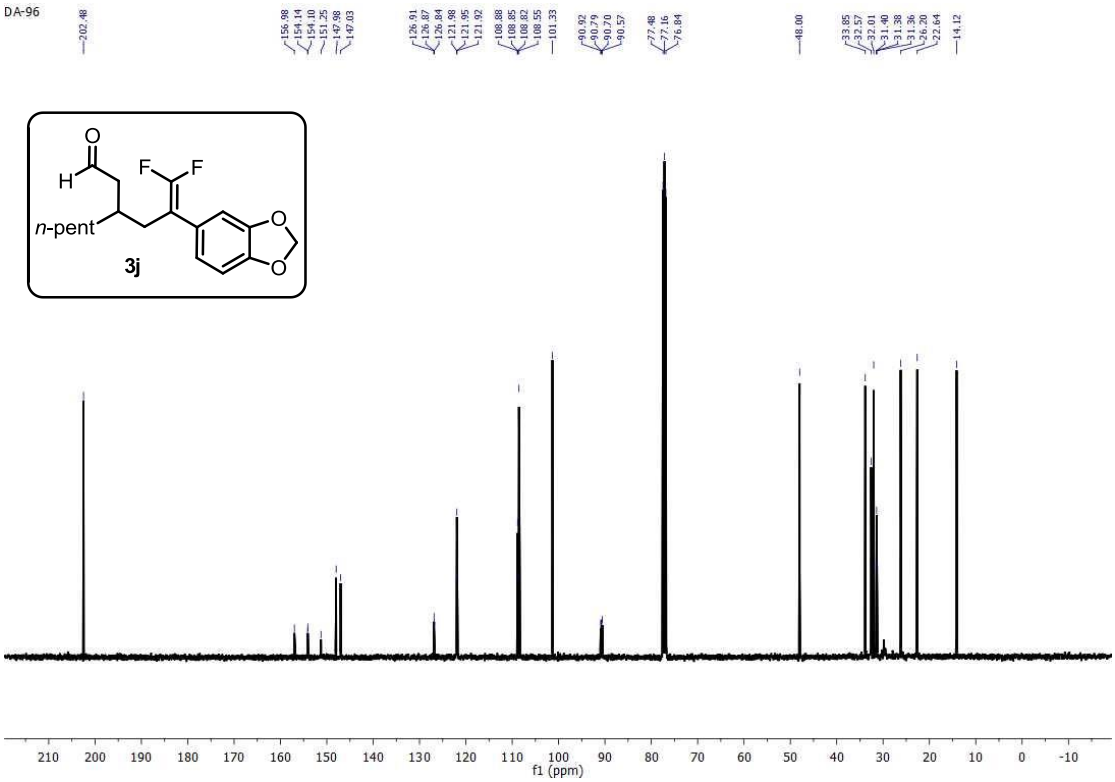

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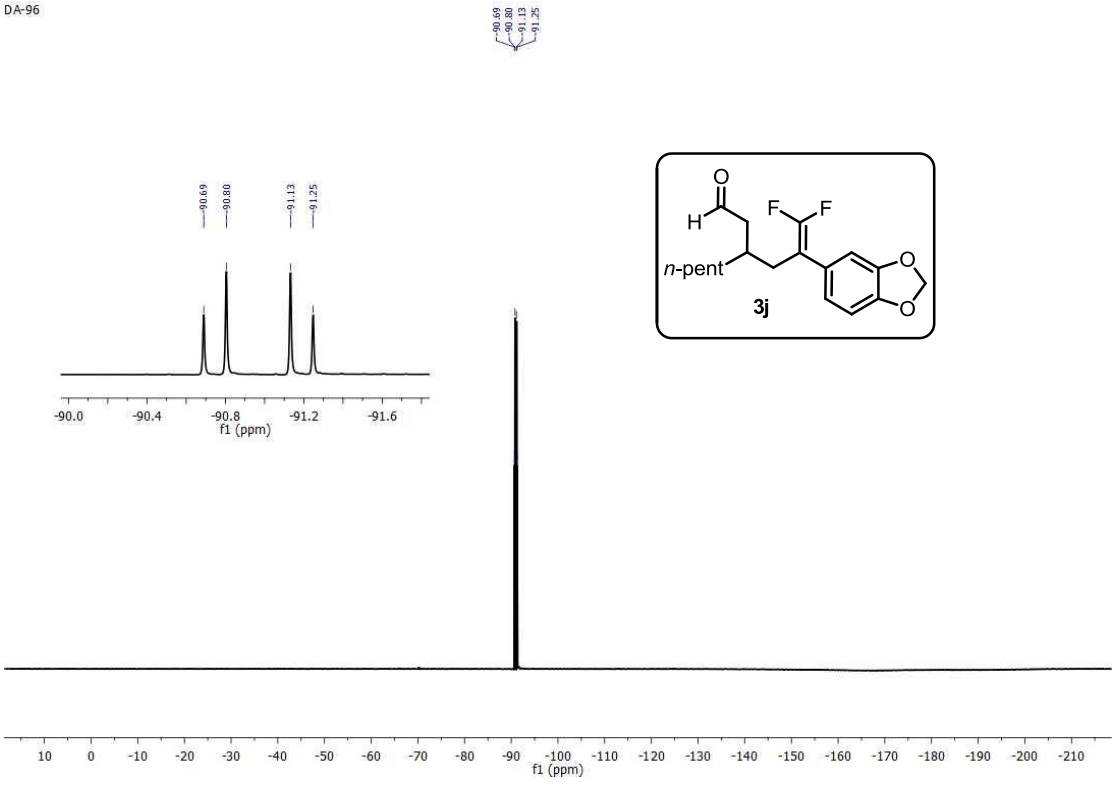

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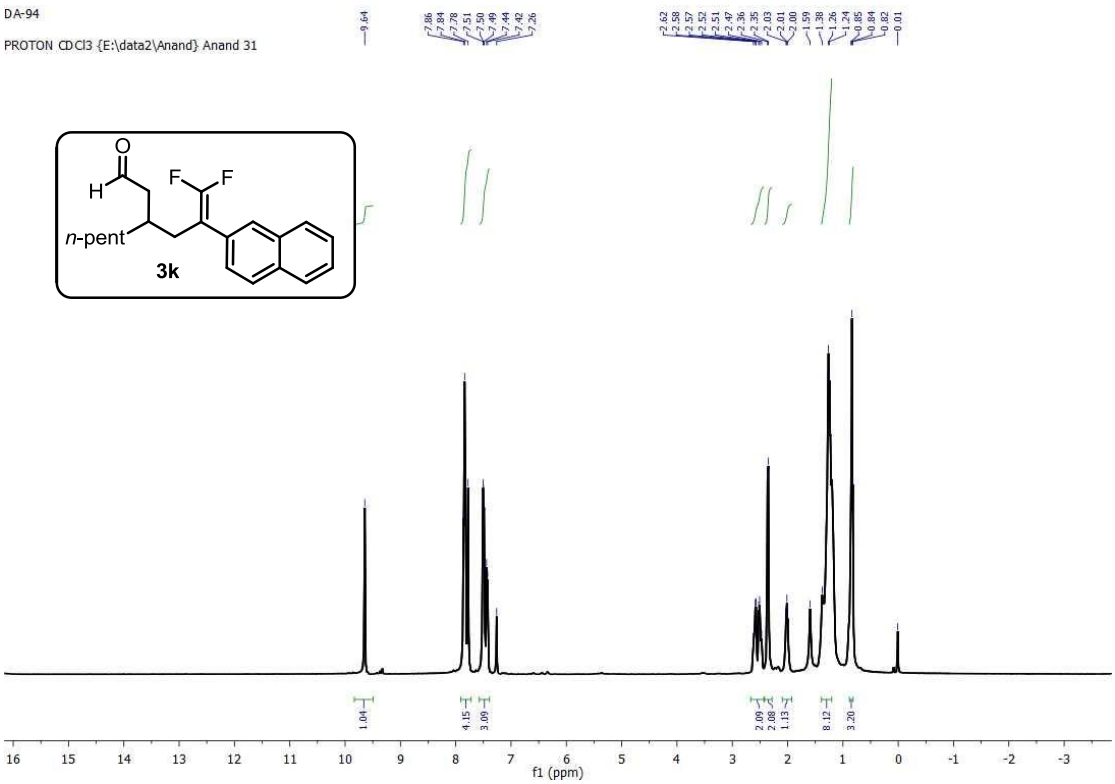

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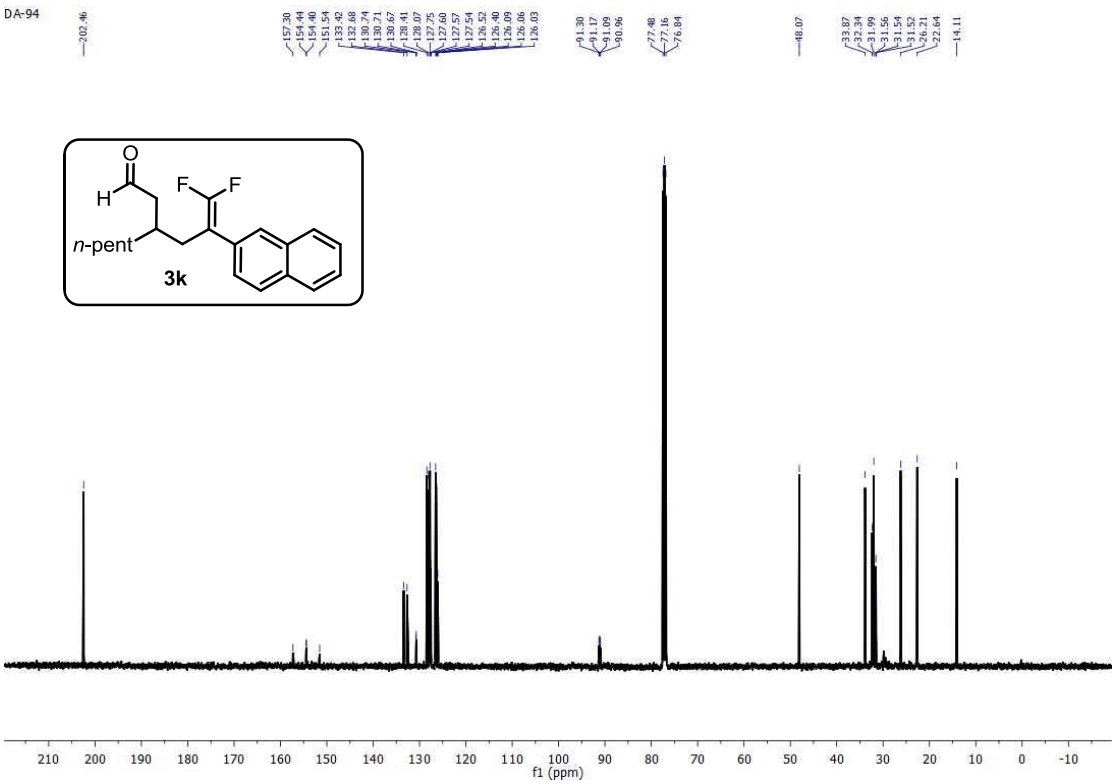

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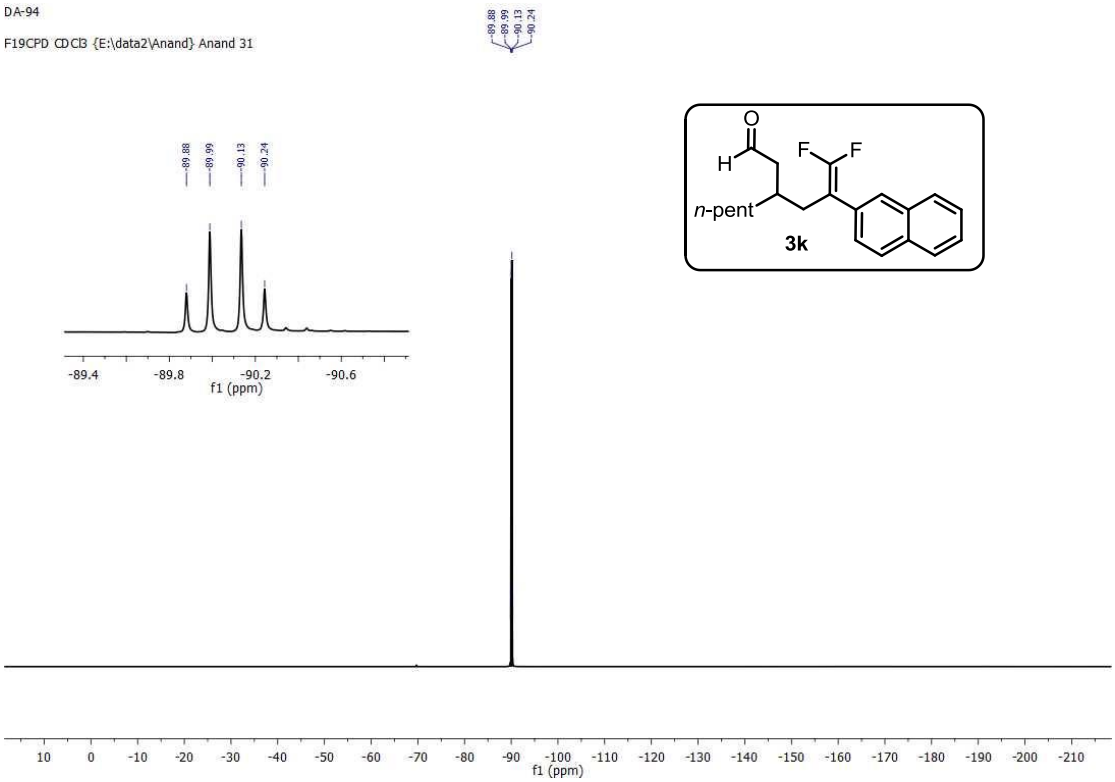

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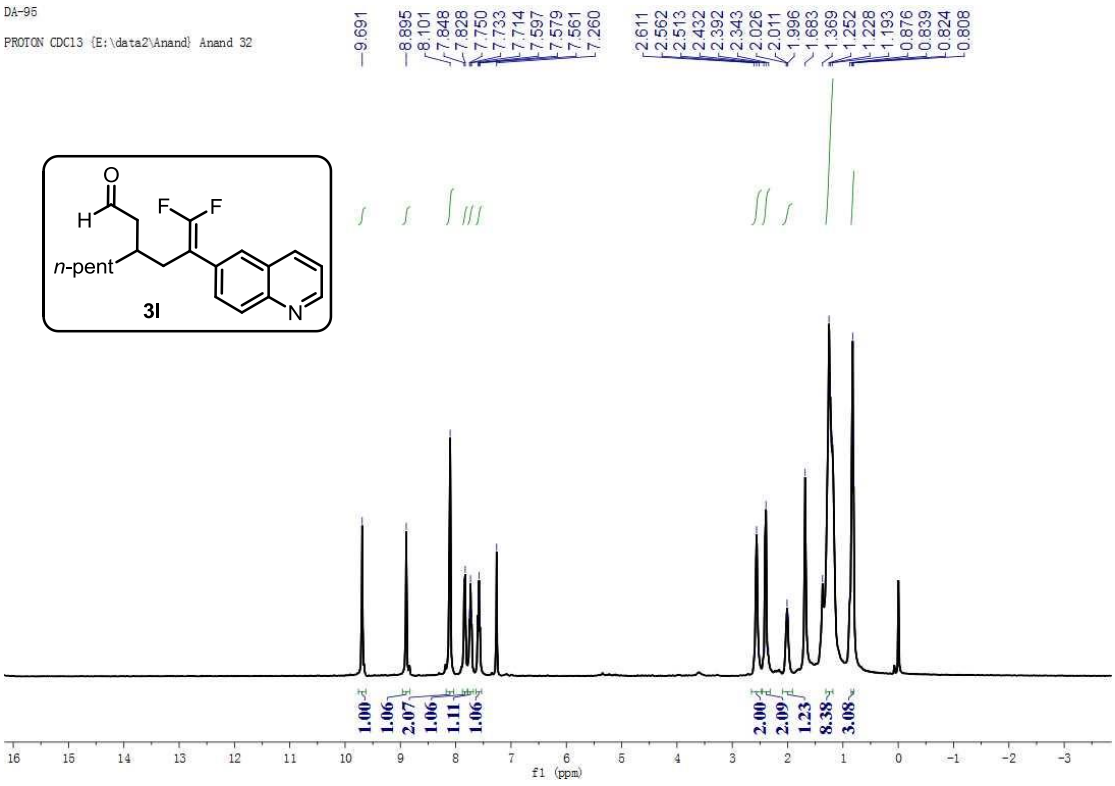

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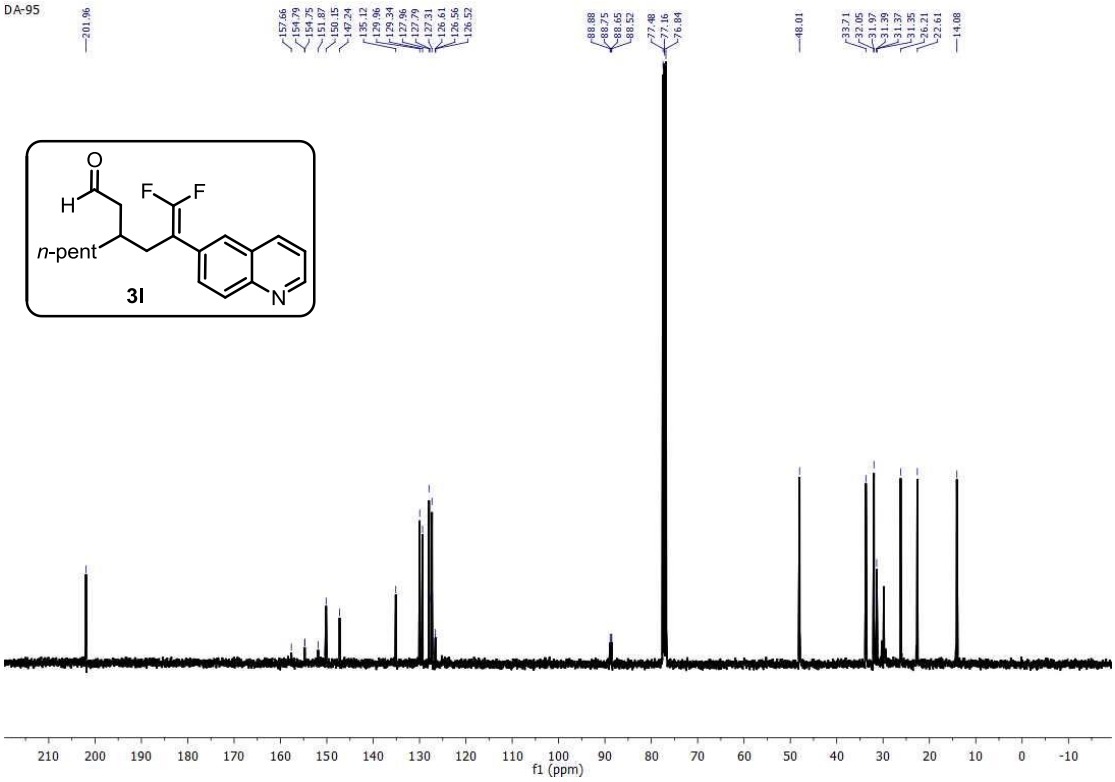

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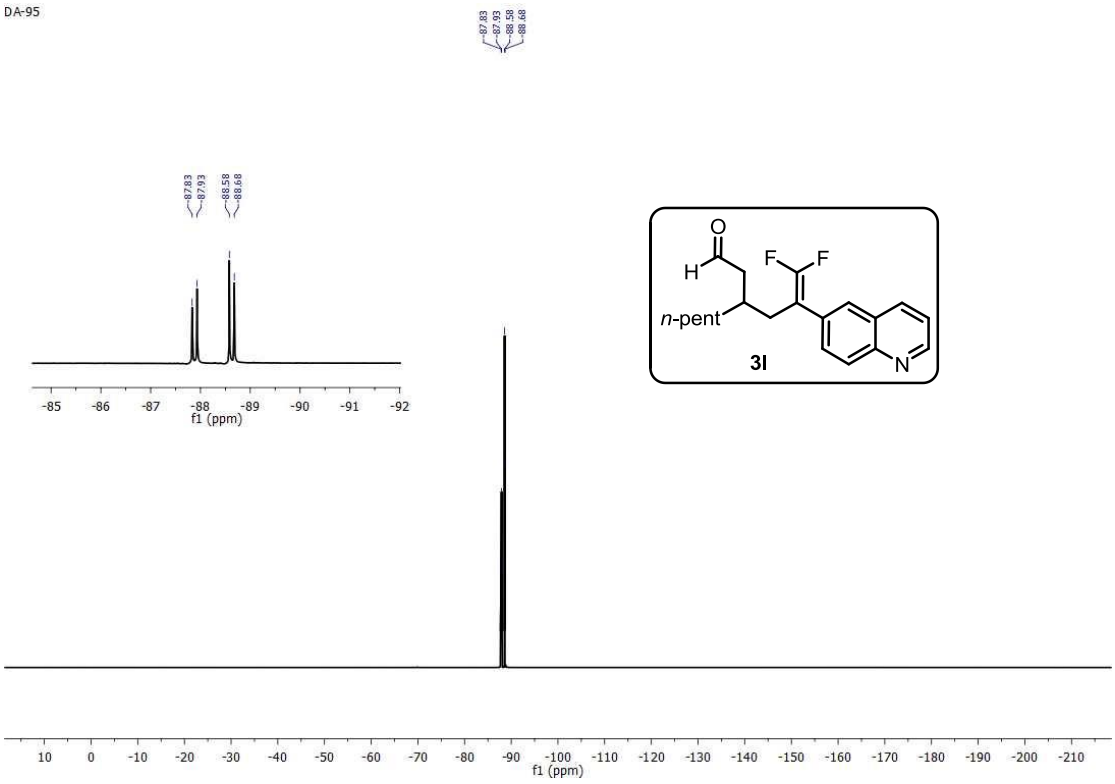

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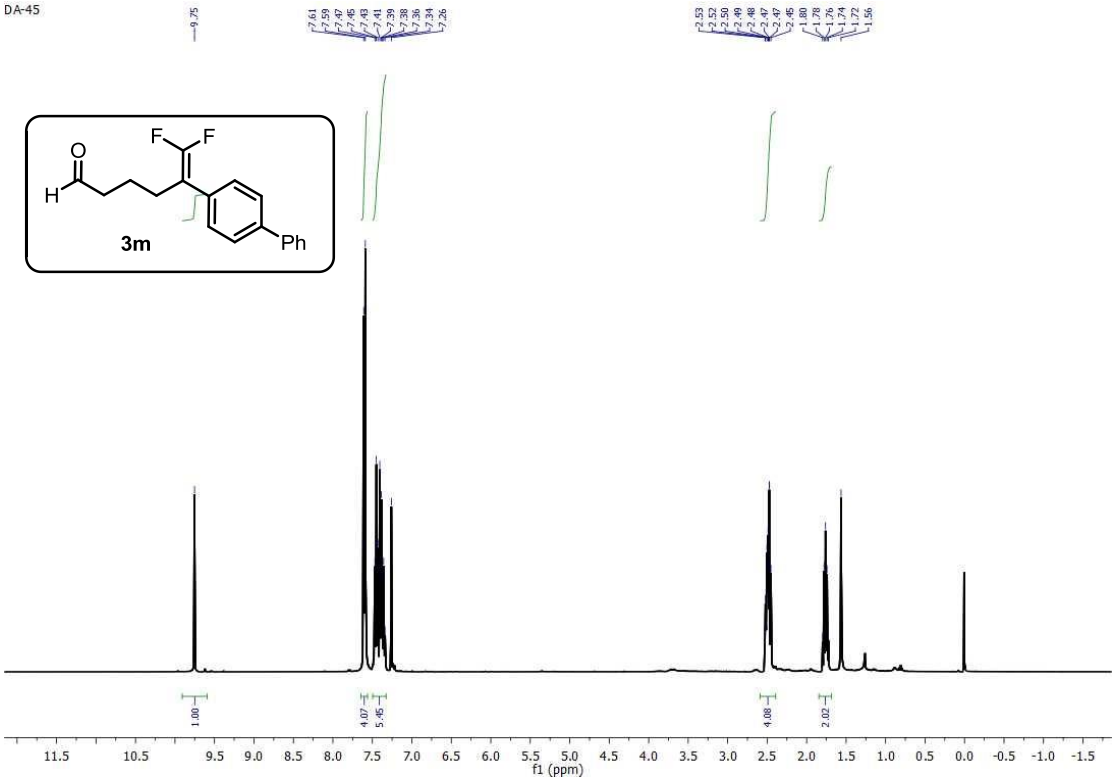

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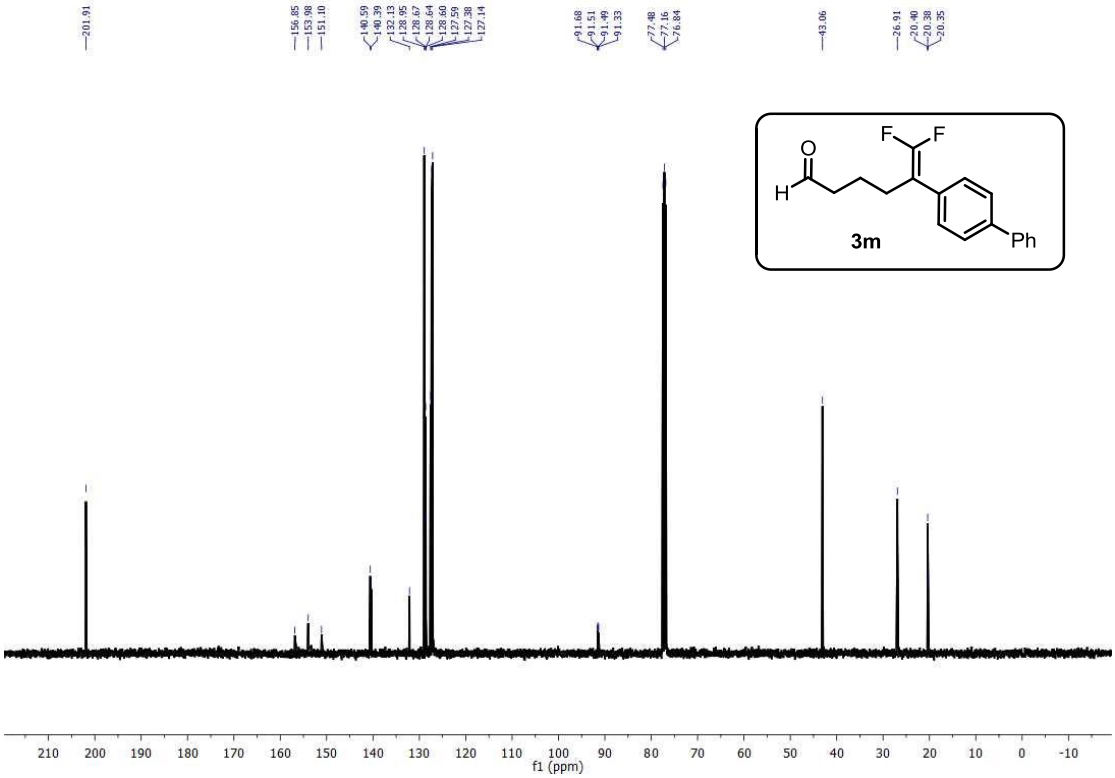

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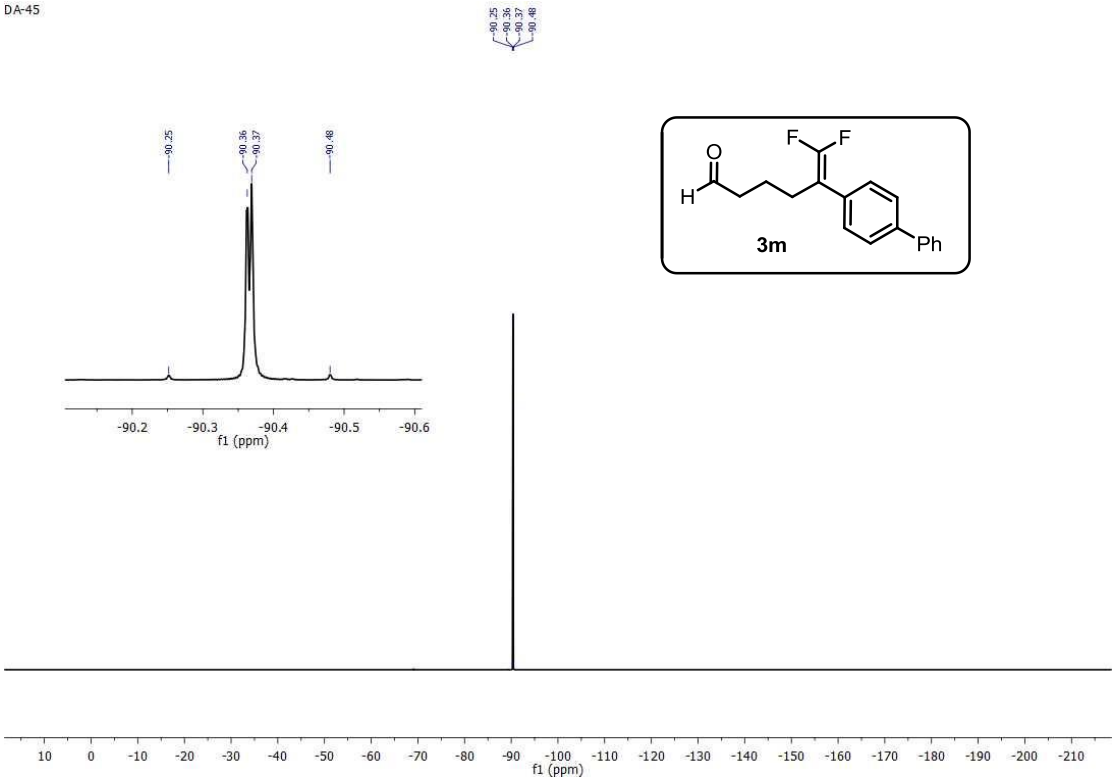

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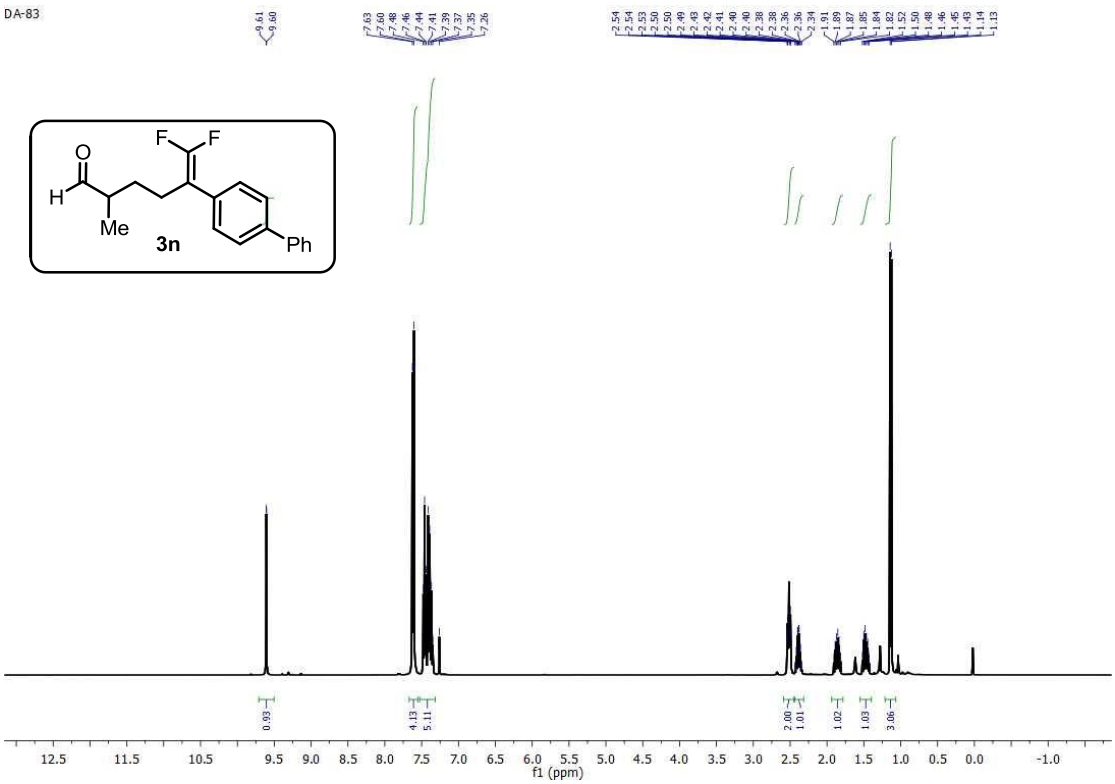

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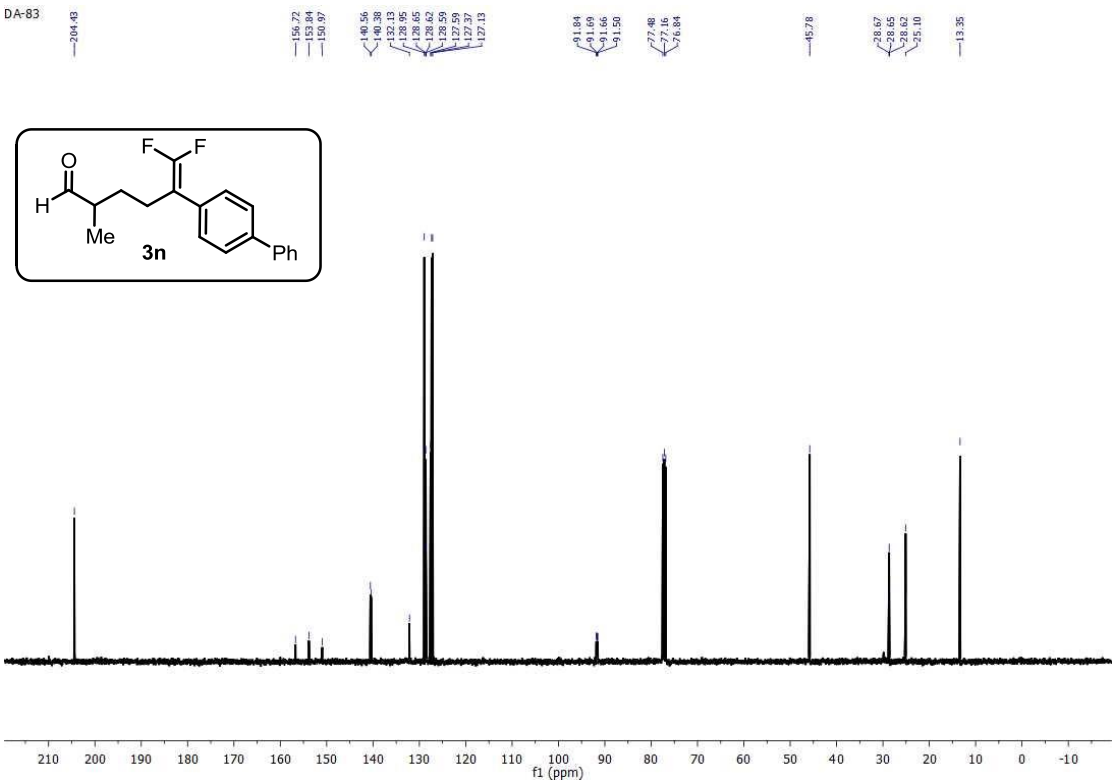

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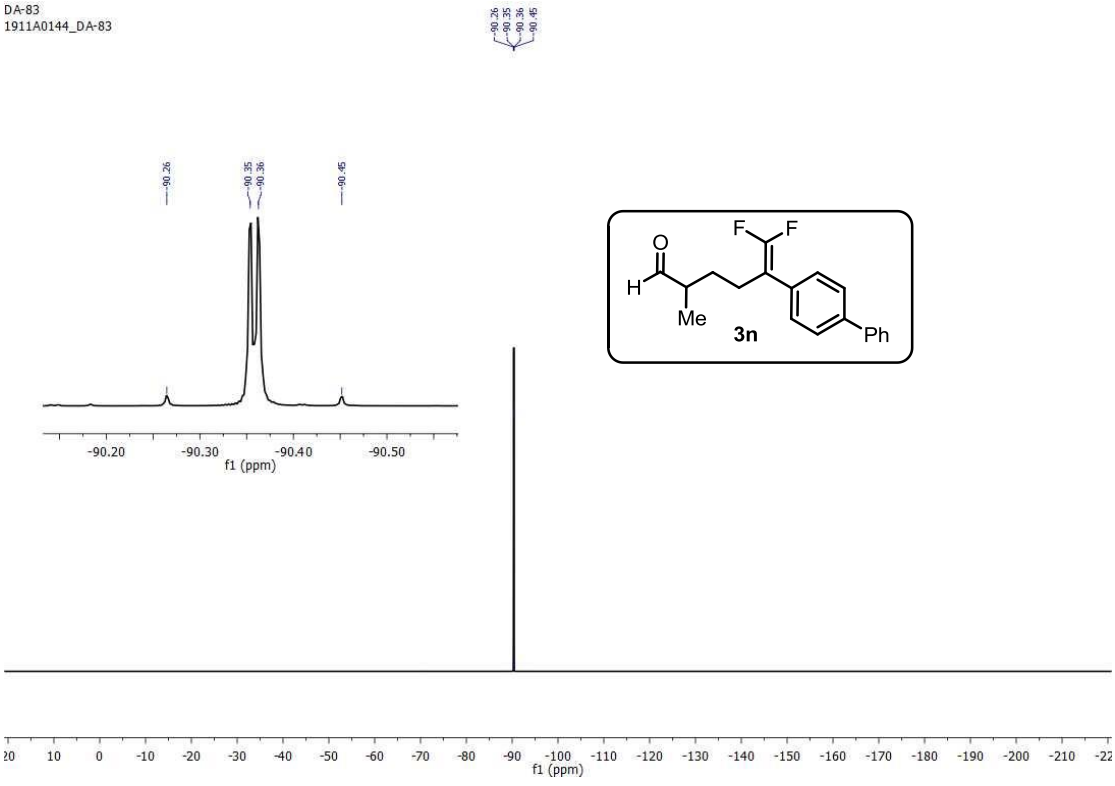

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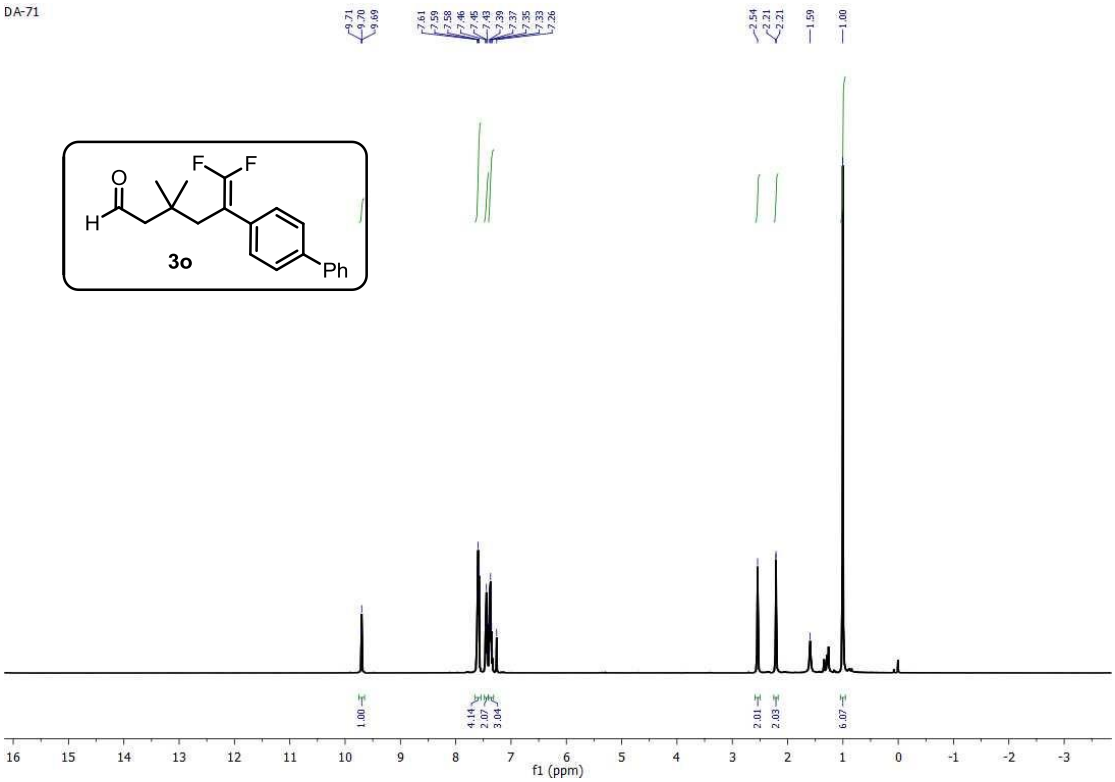

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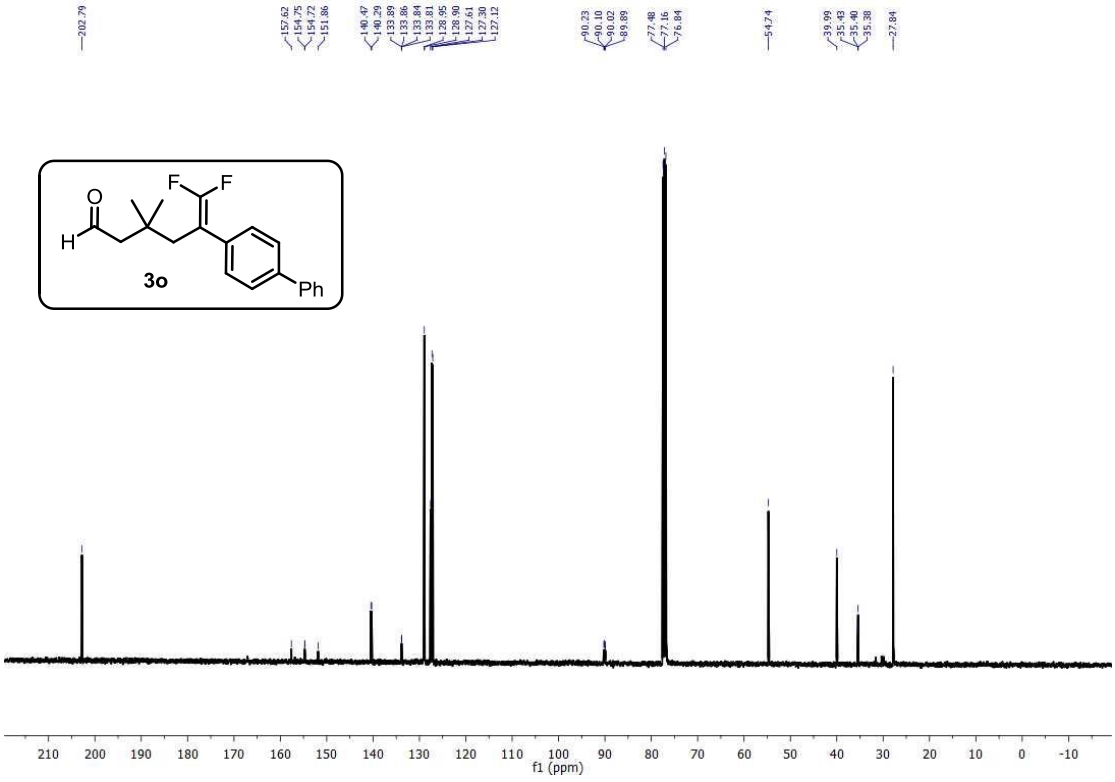

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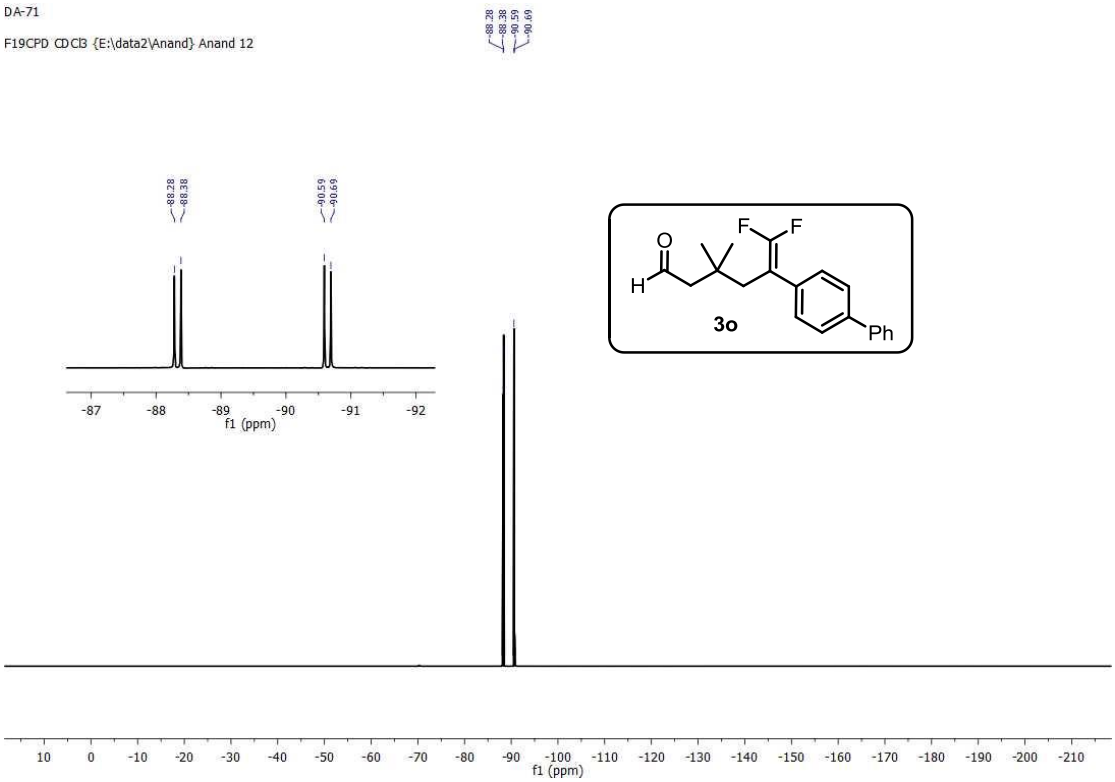

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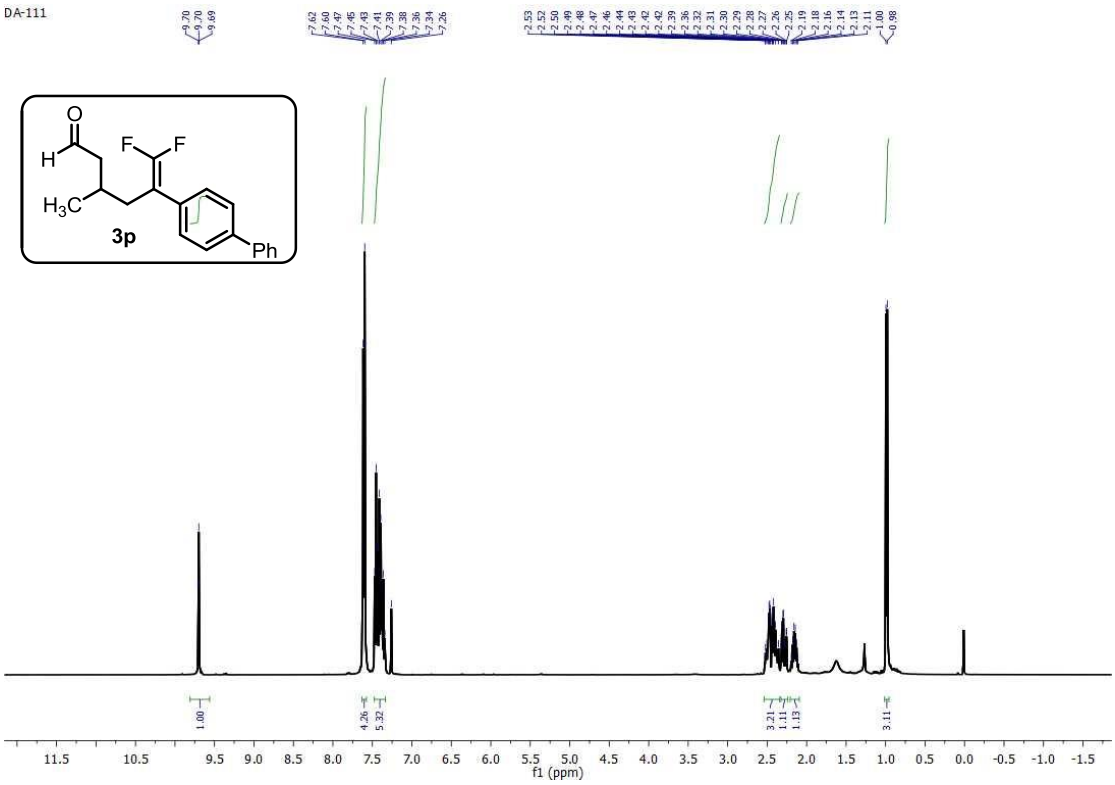

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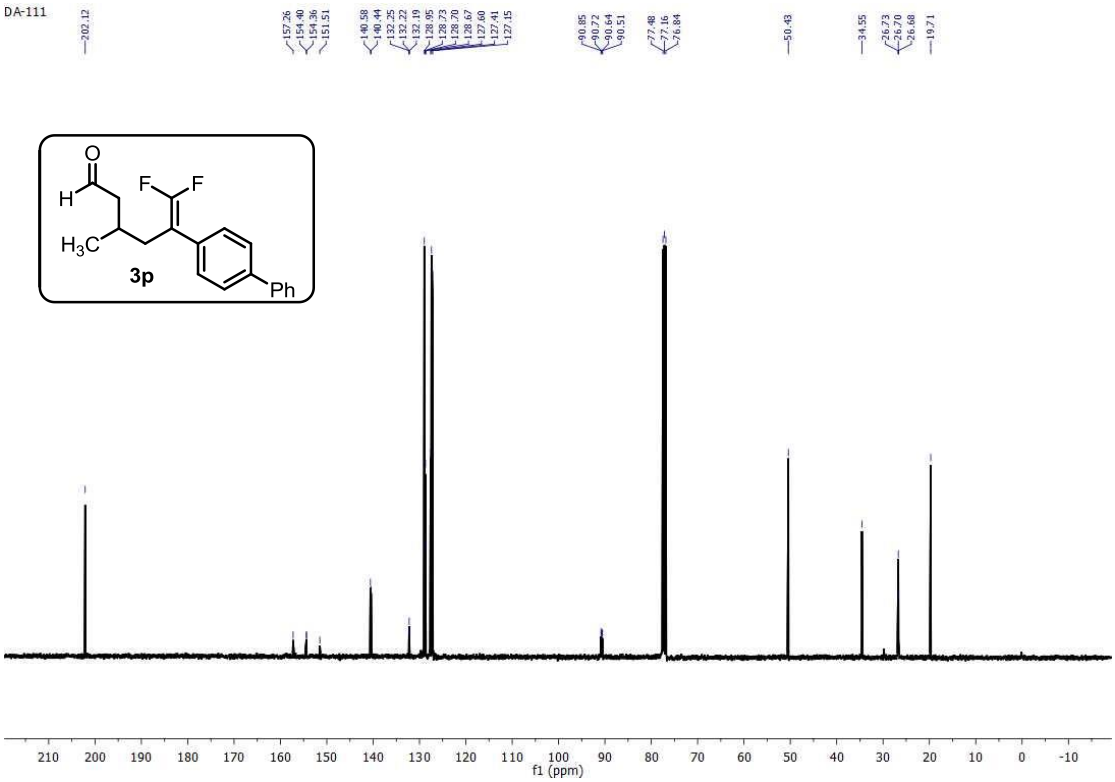

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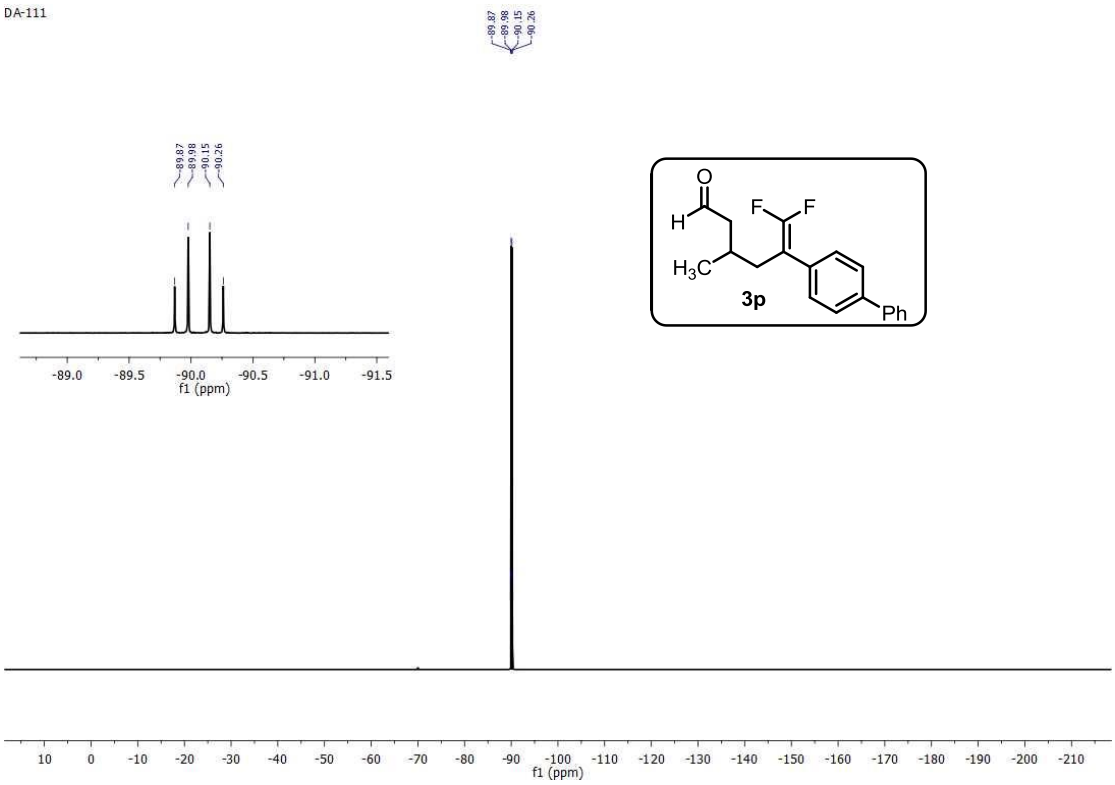

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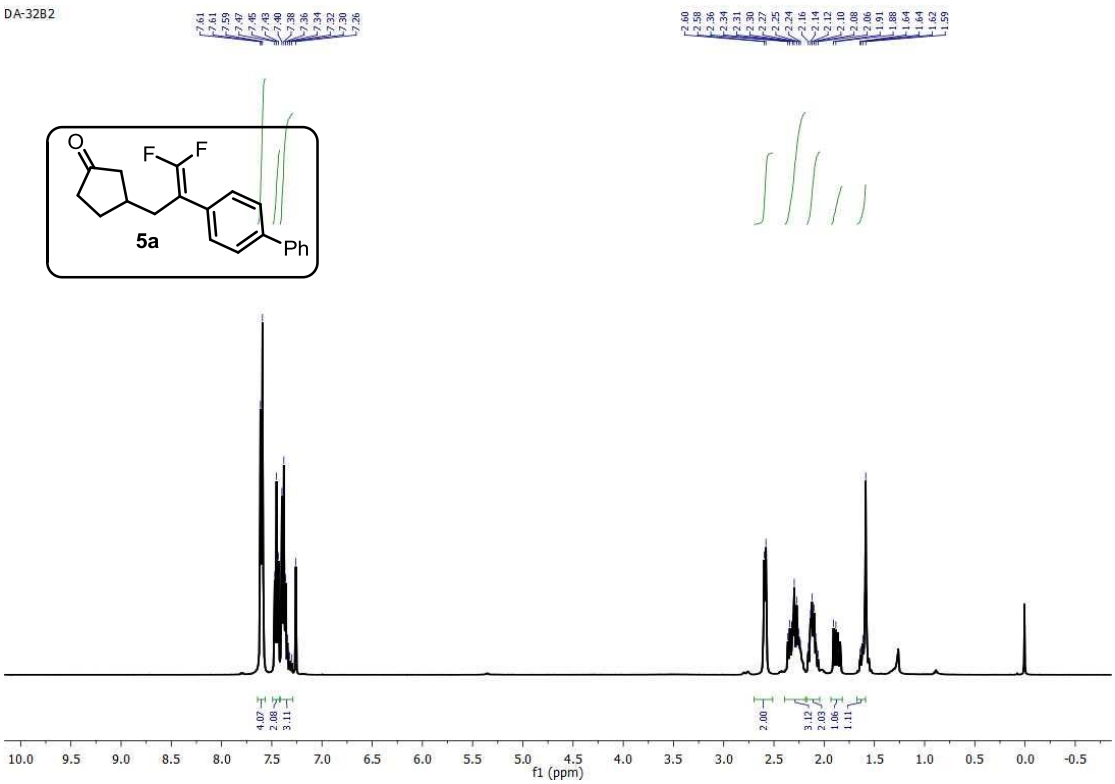

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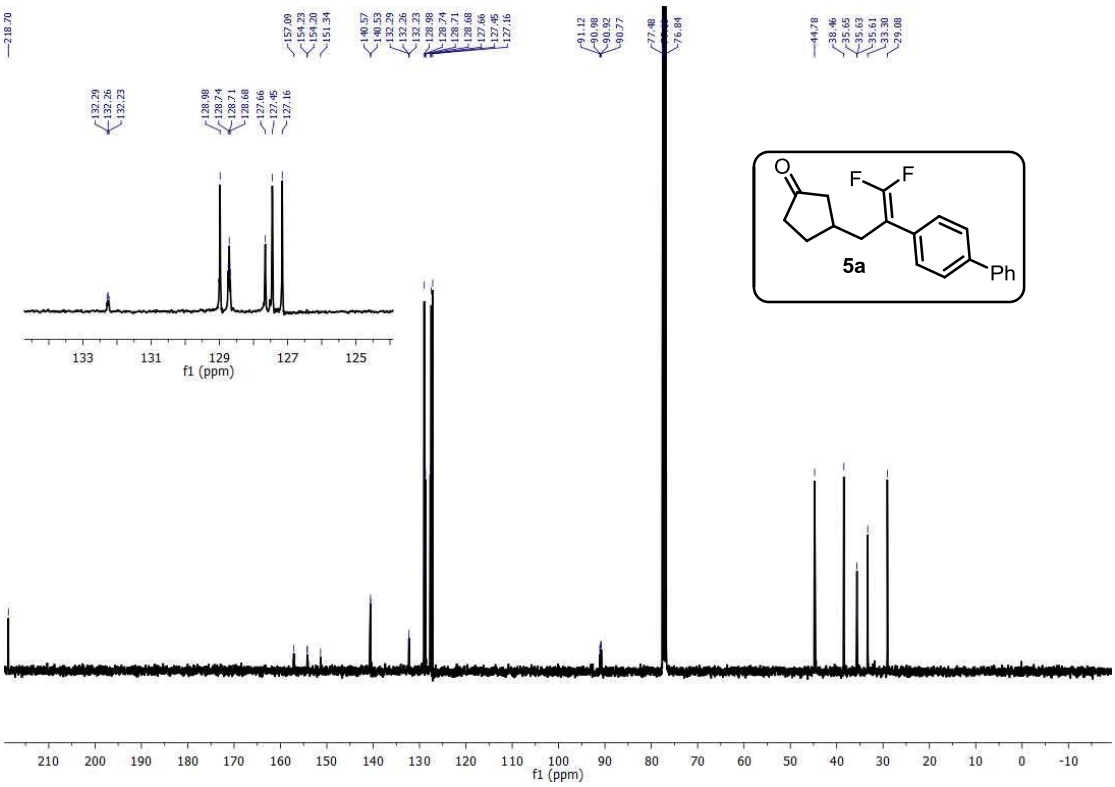

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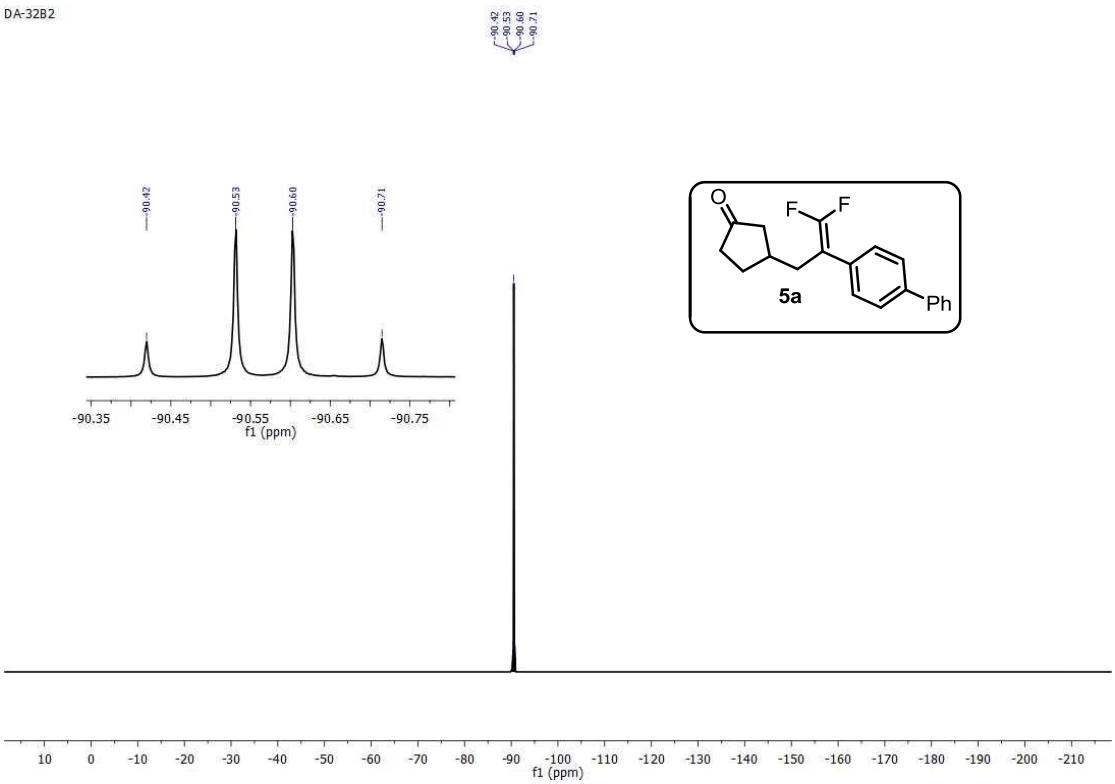

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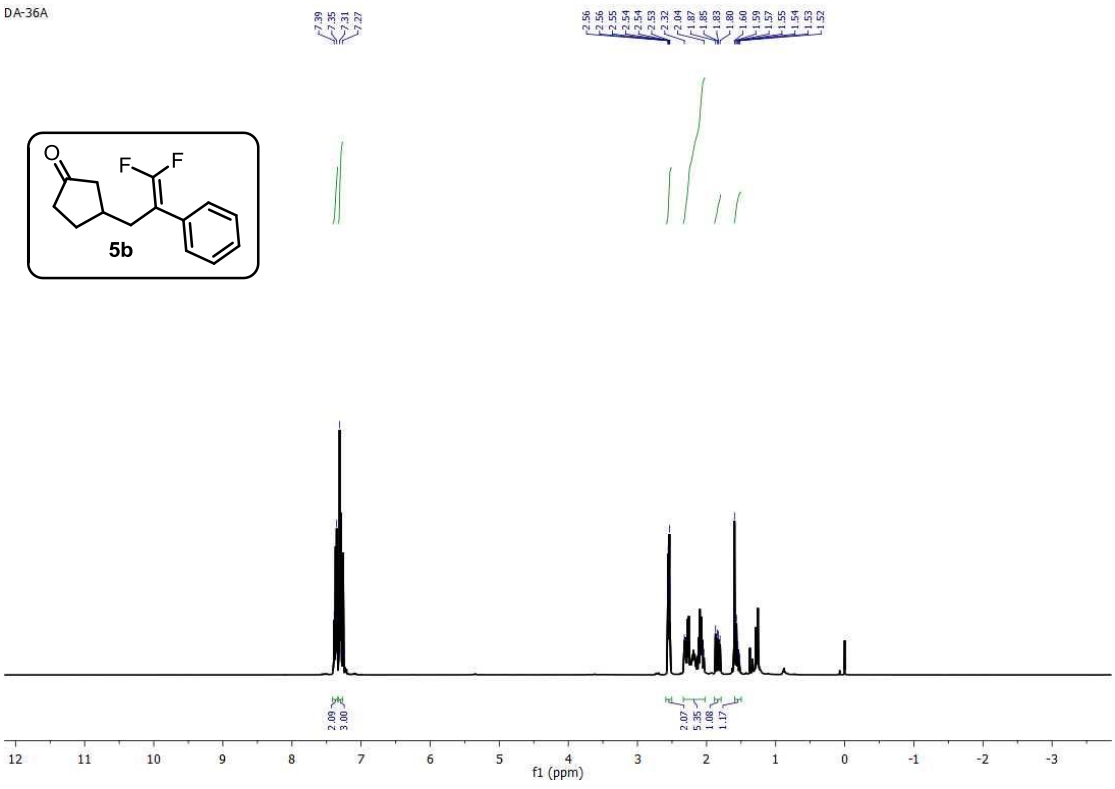

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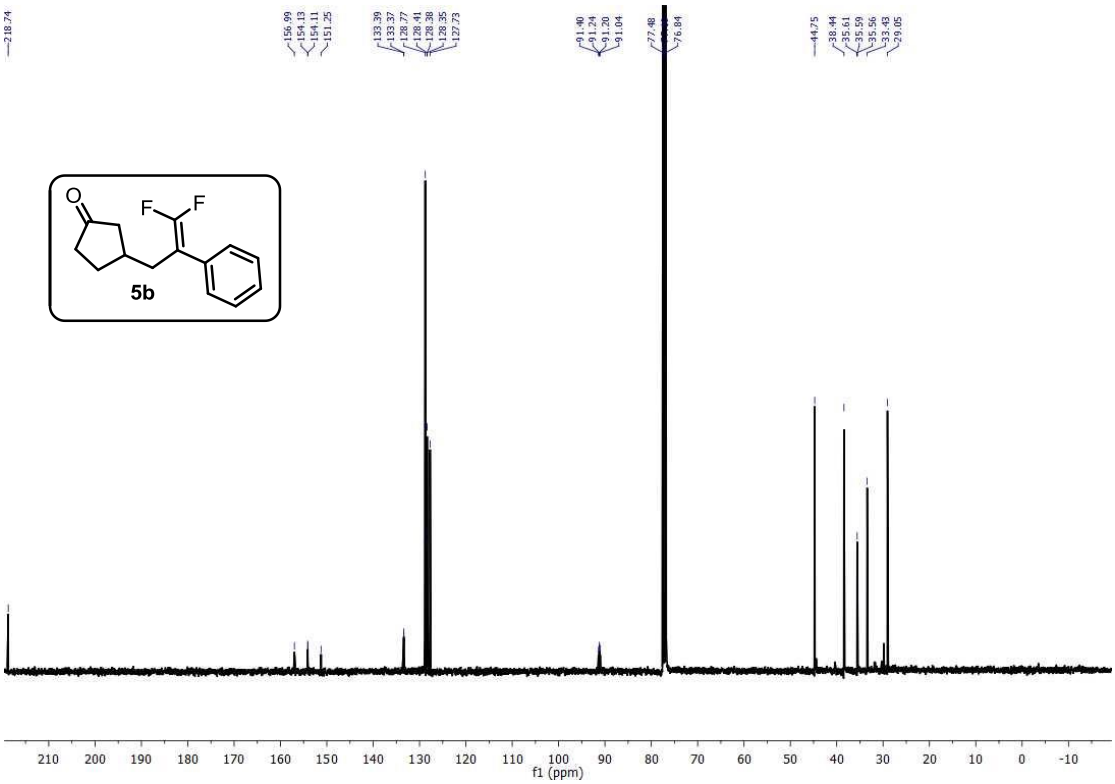

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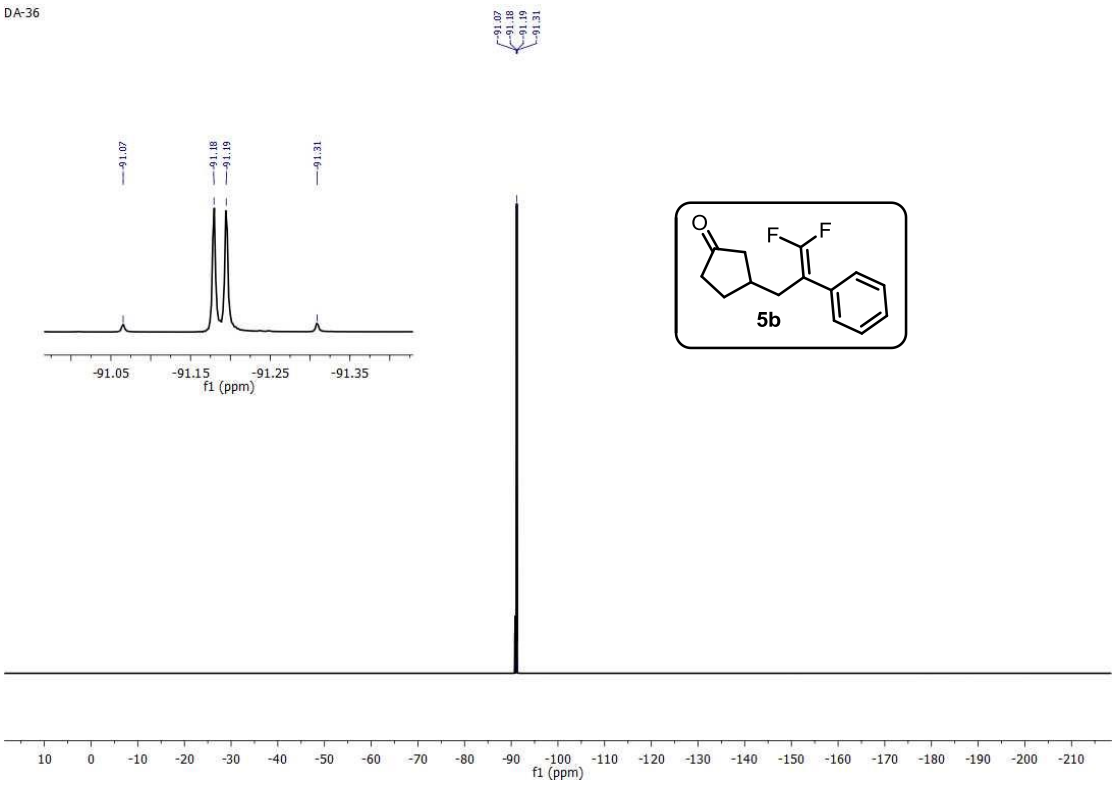

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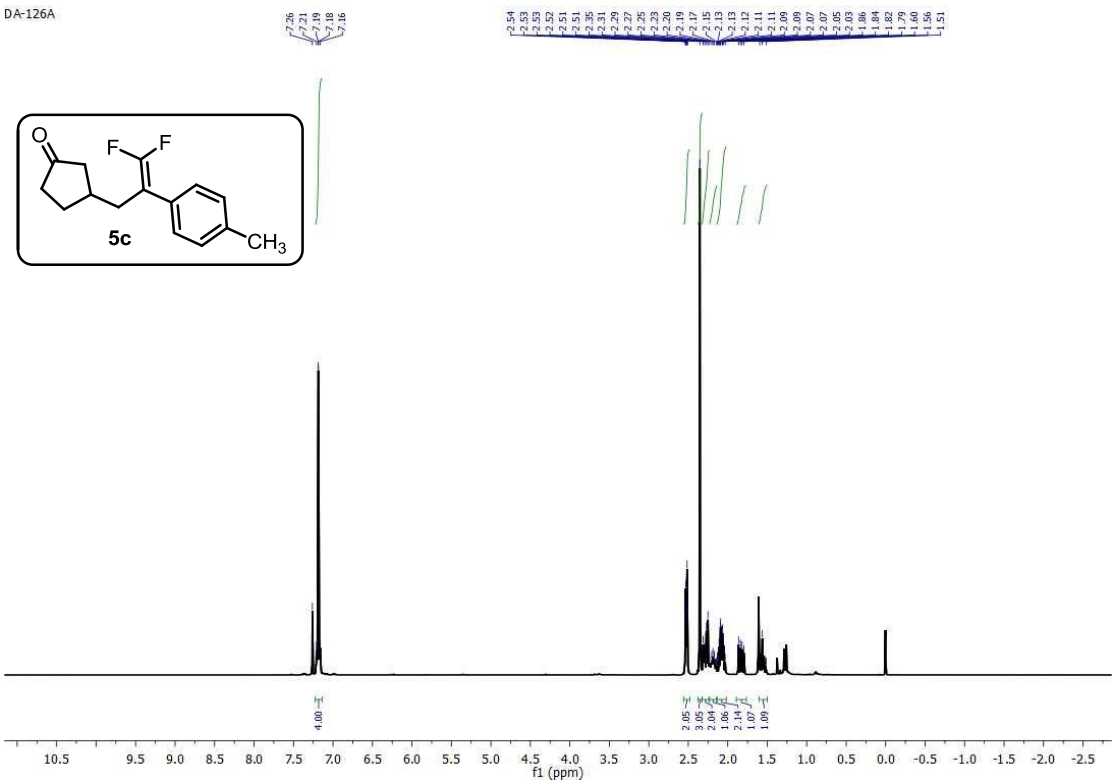

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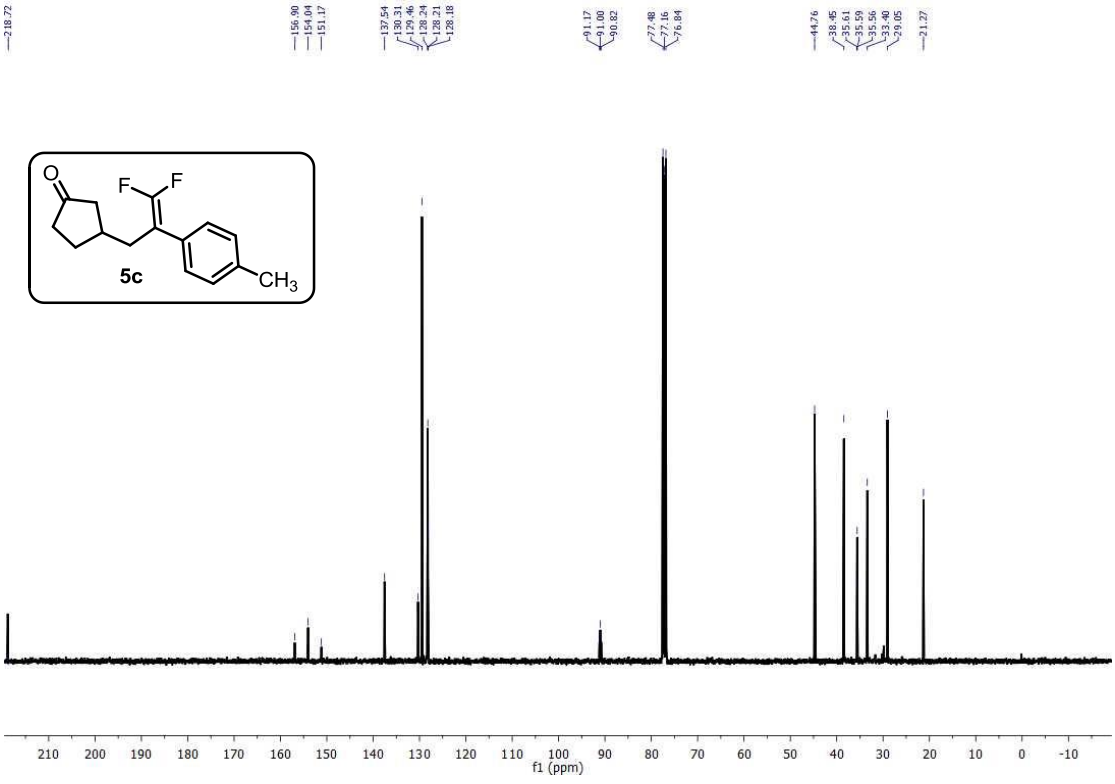

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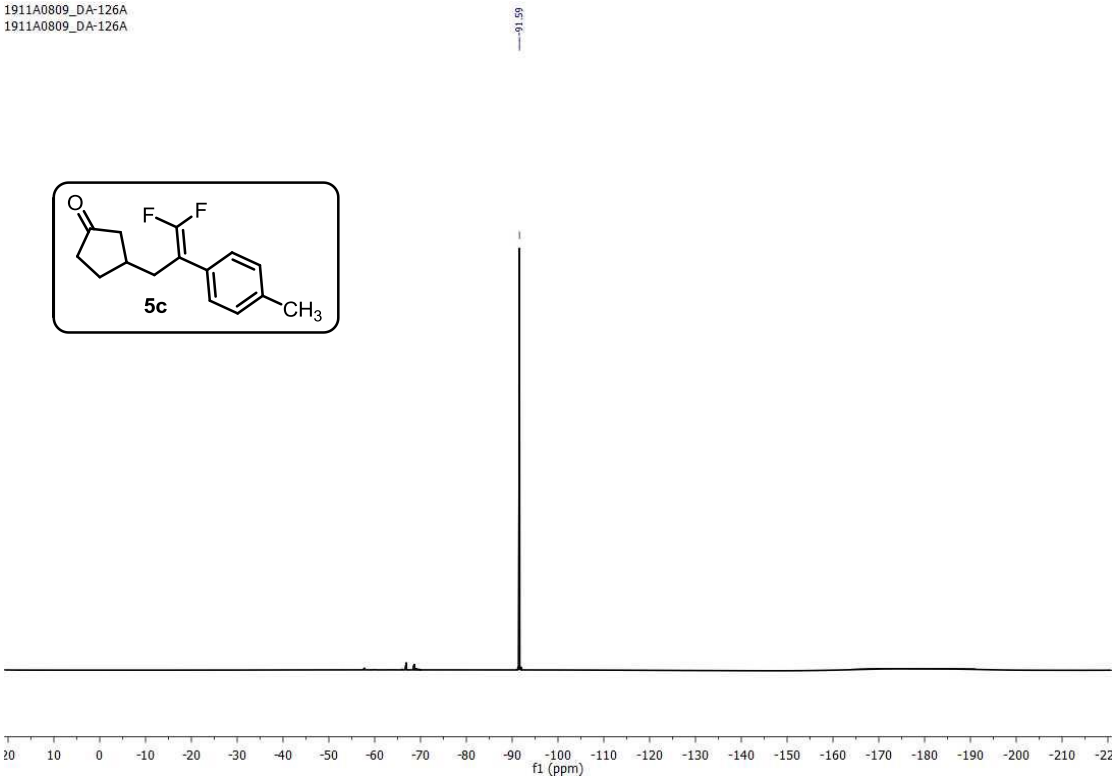
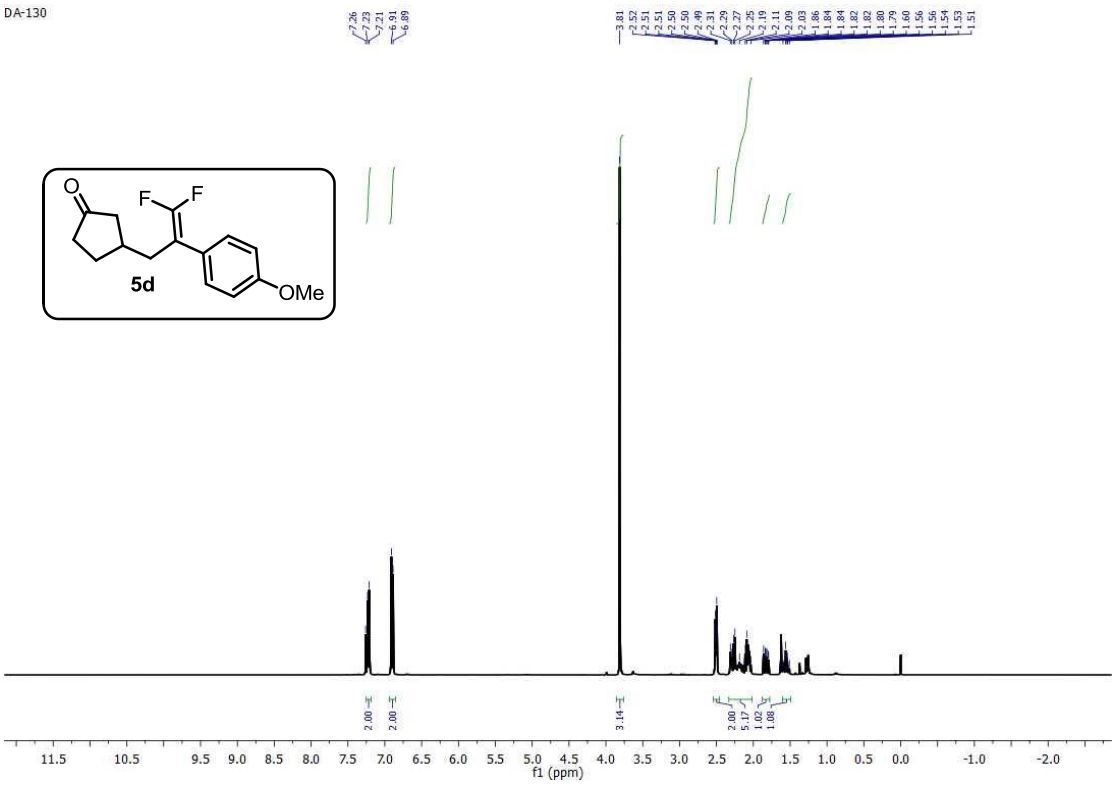


^{19}F NMR (376 MHz, $CDCl_3$)



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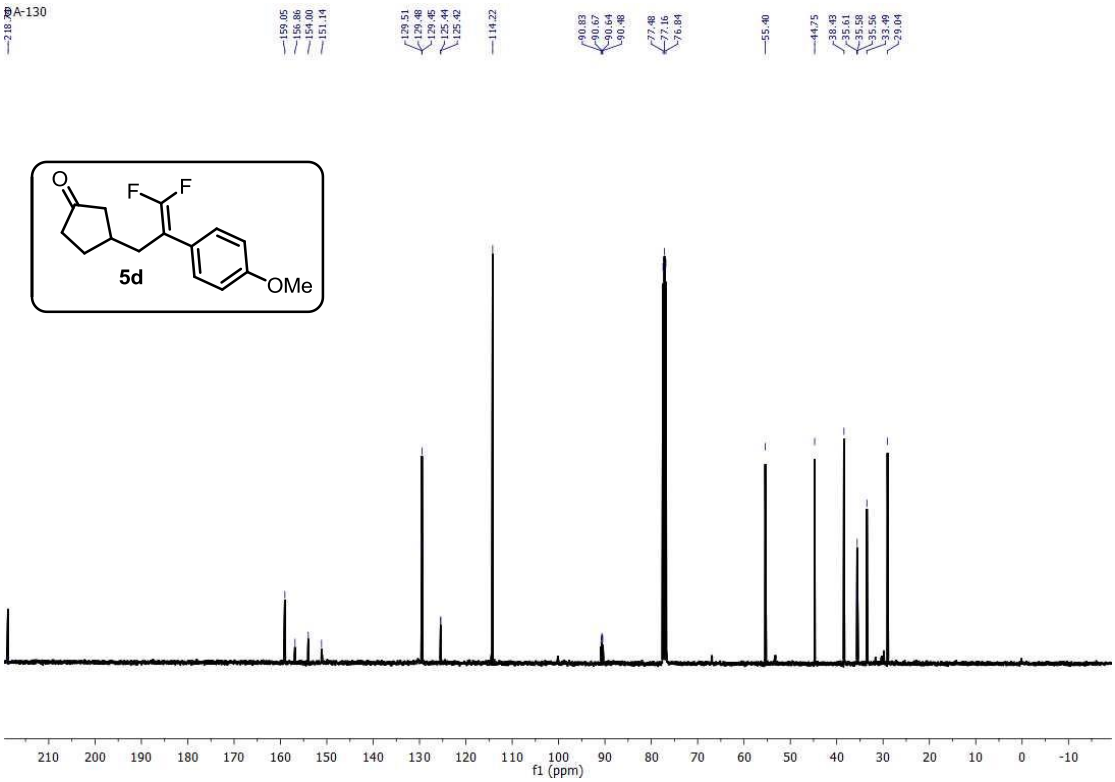

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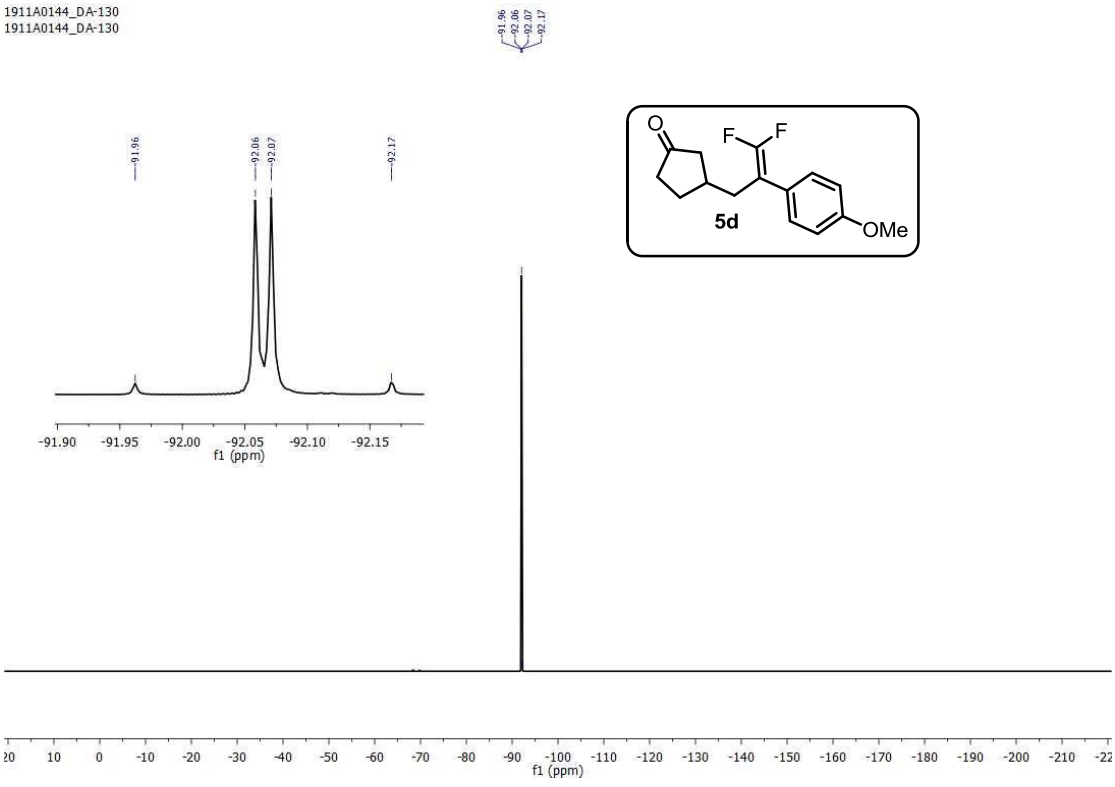
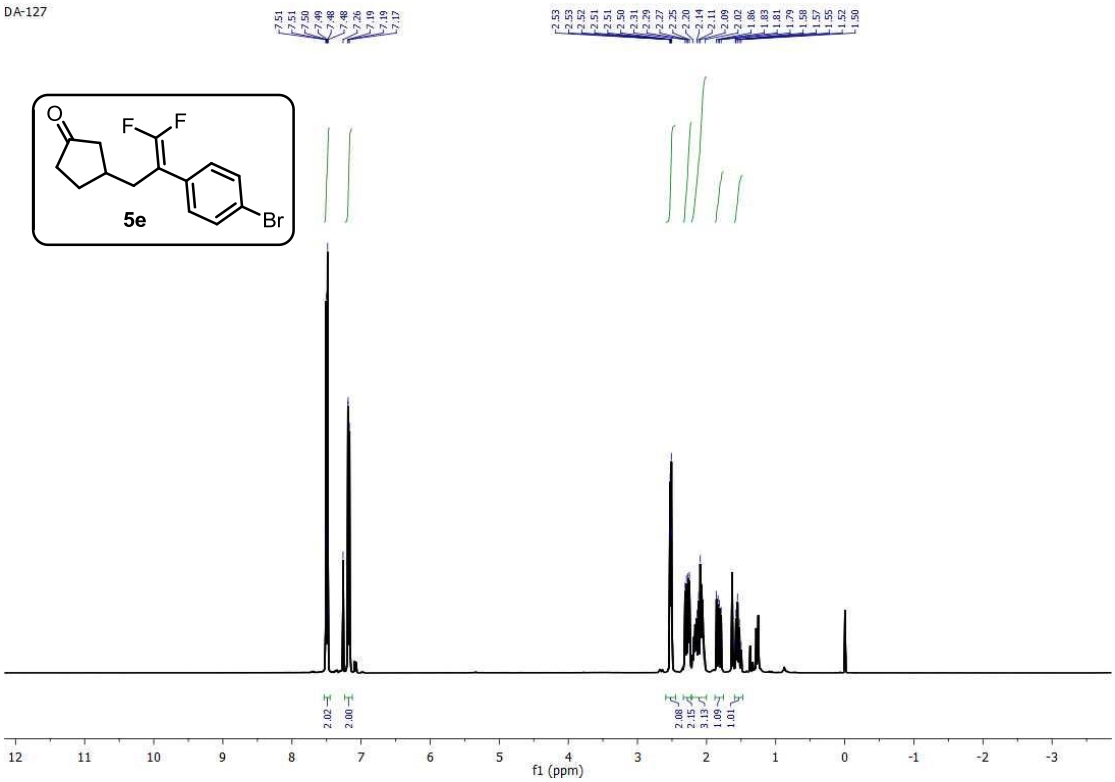


^{19}F NMR (376 MHz, $CDCl_3$)



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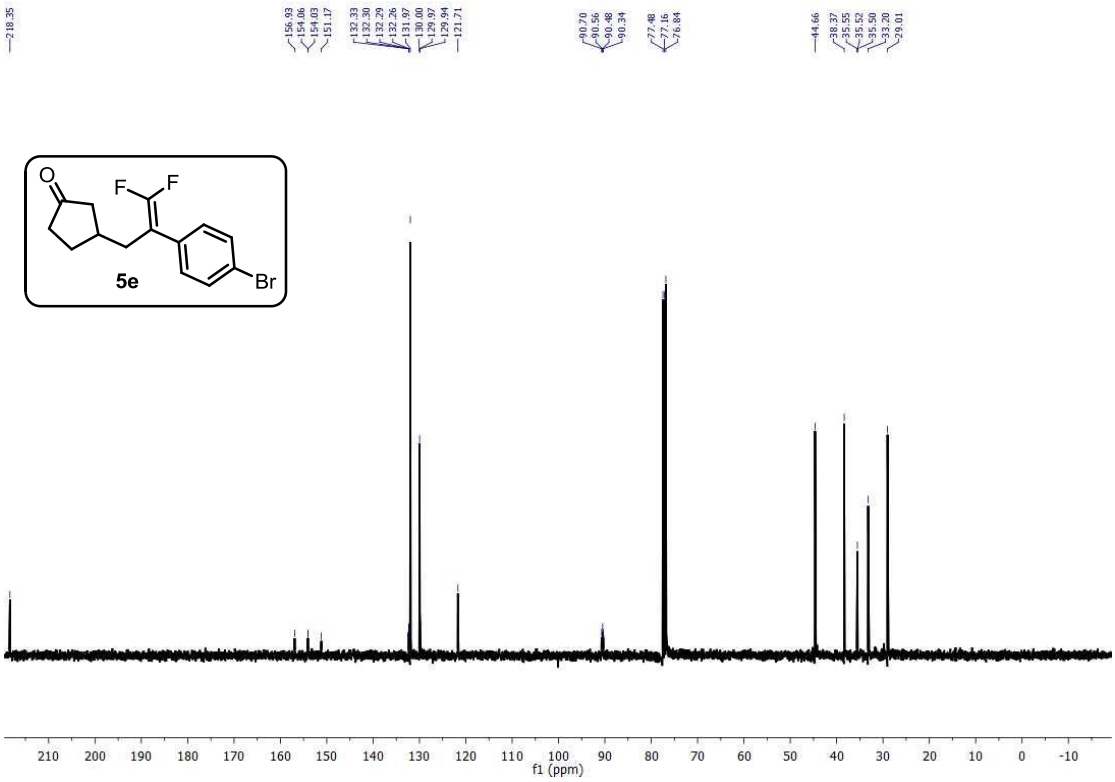

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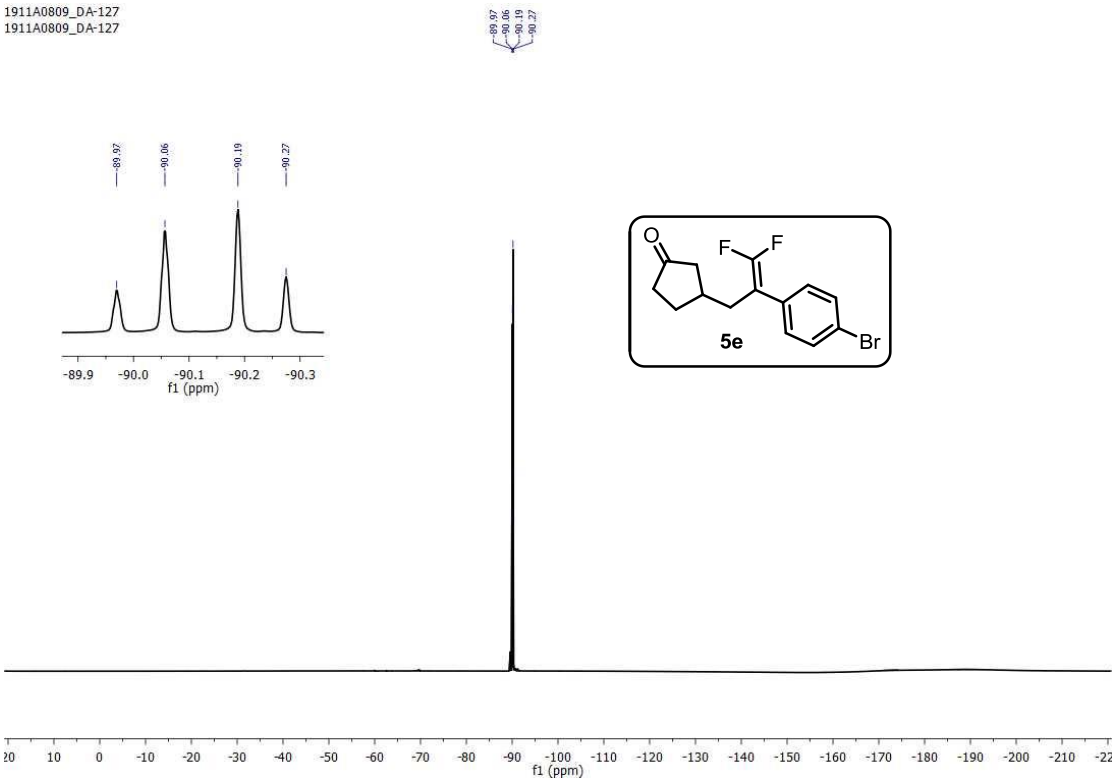
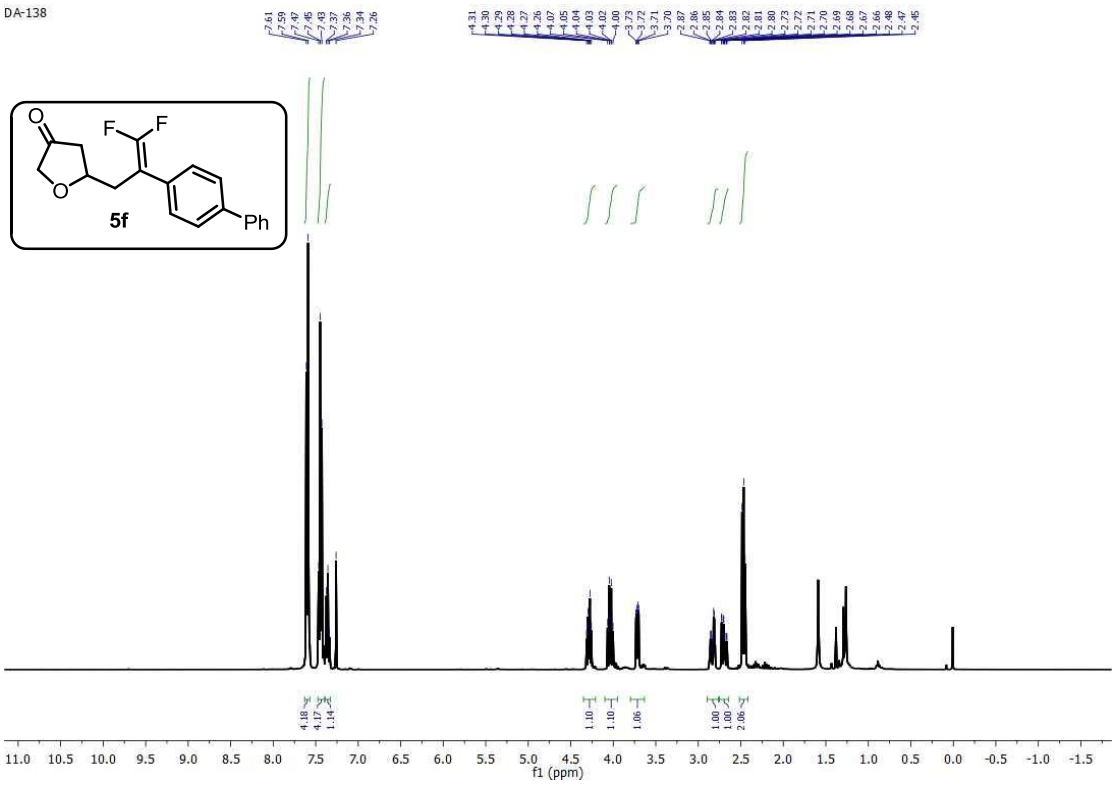
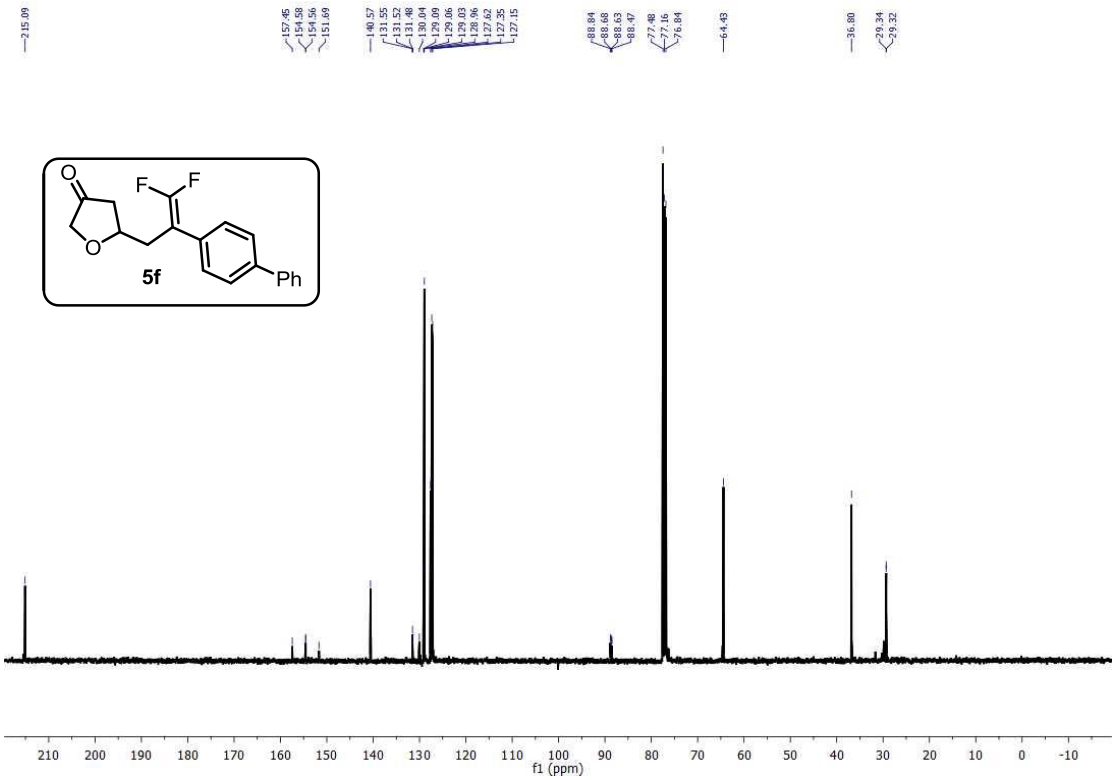


^{19}F NMR (376 MHz, $CDCl_3$)

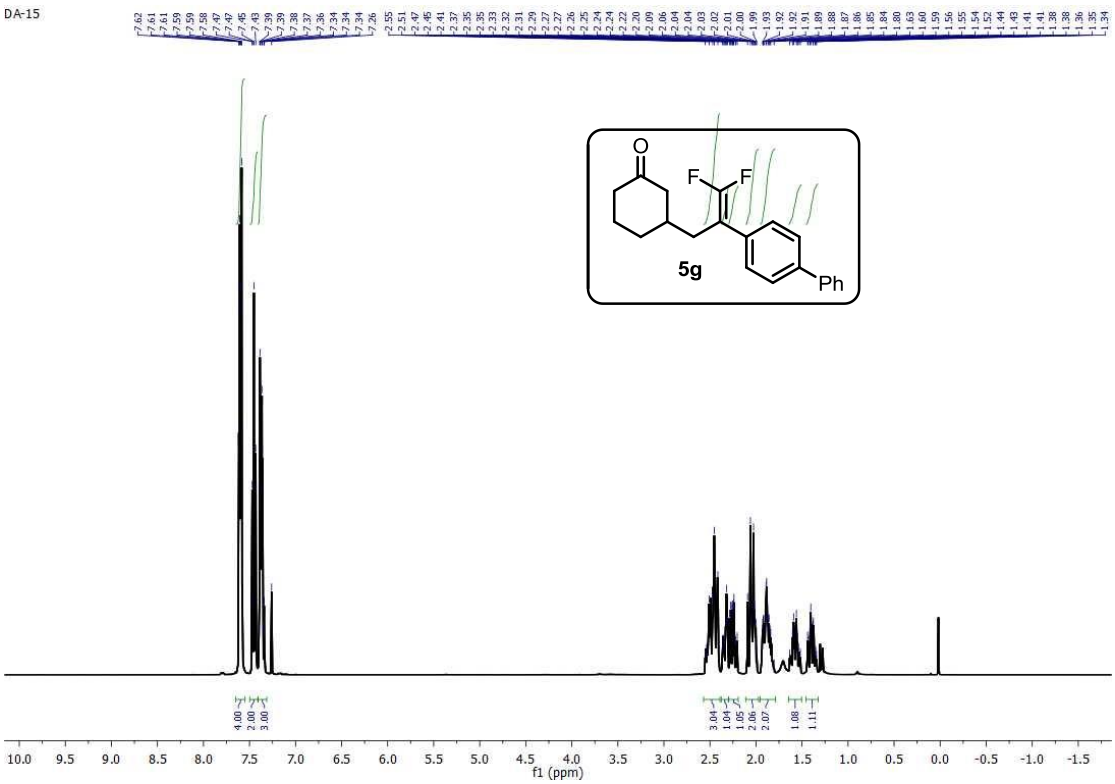


^{1}H NMR (400 MHz, $CDCl_3$)

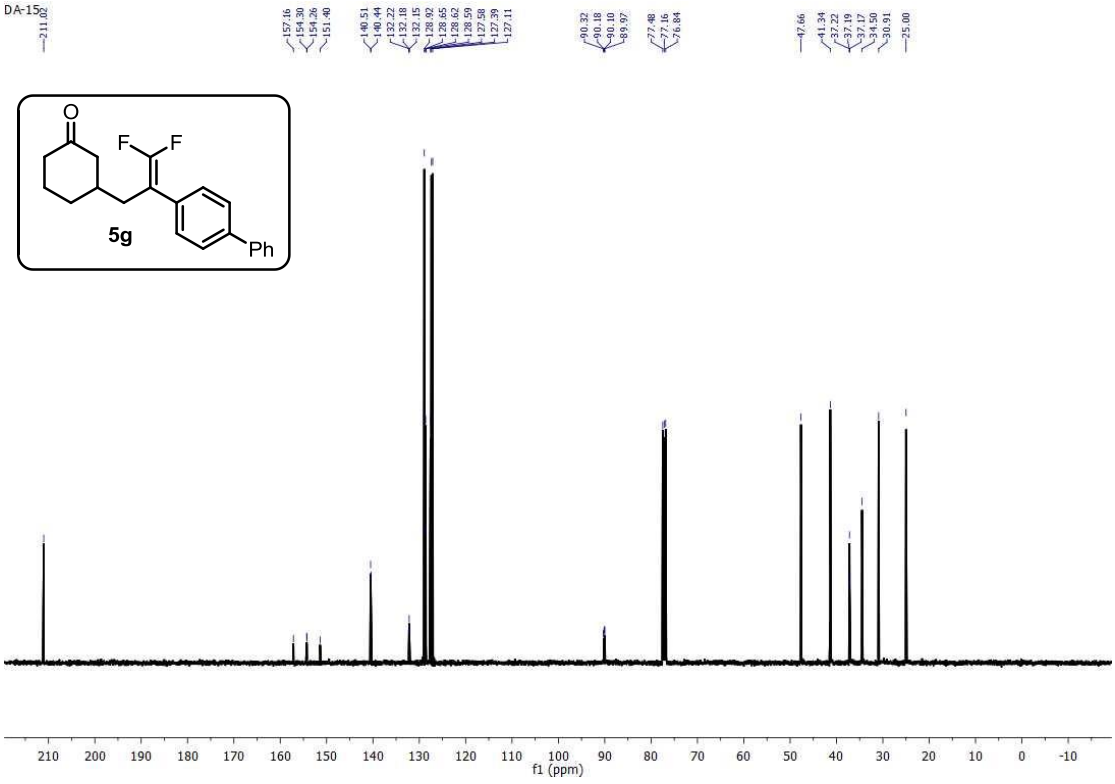


^{13}C NMR (101 MHz, $CDCl_3$)

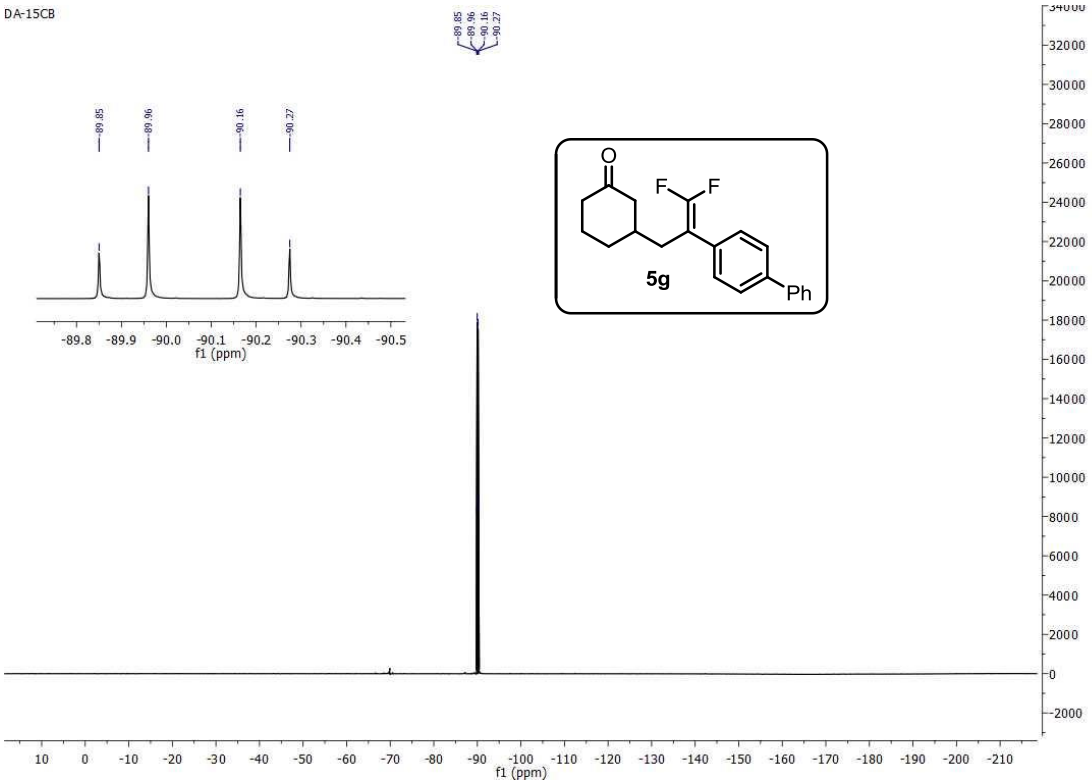
^{19}F NMR (376 MHz, $CDCl_3$)



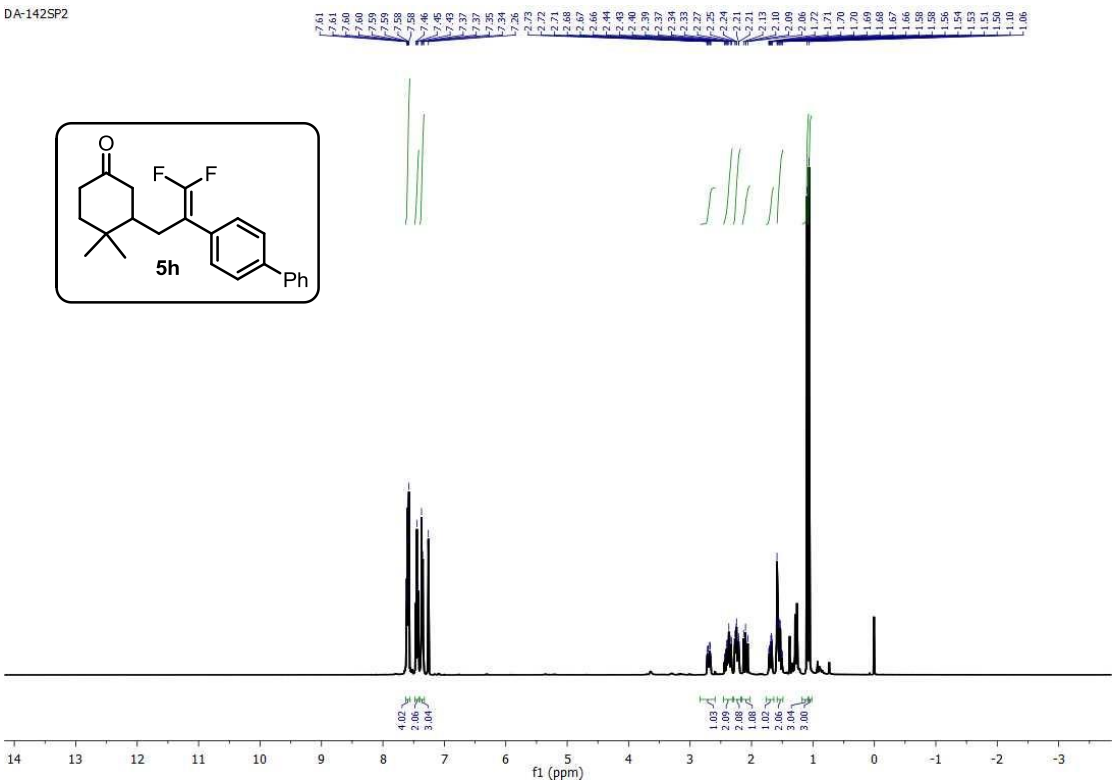
^{1}H NMR (400 MHz, $CDCl_3$)



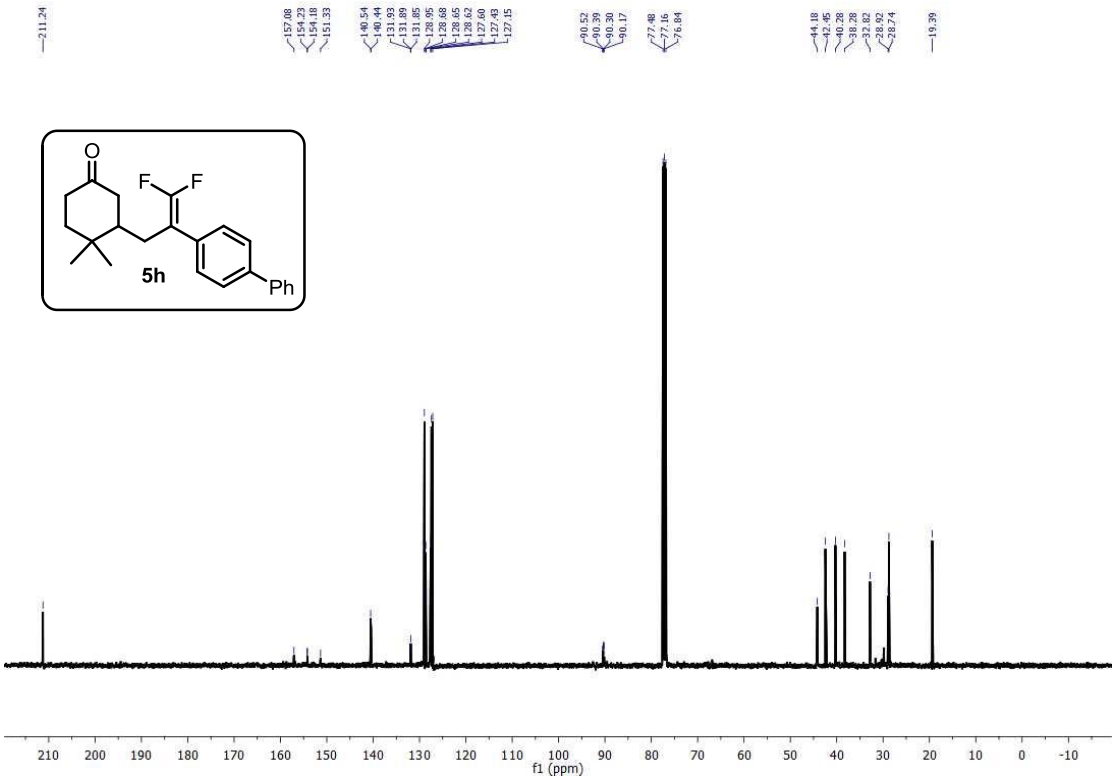
^{13}C NMR (101 MHz, $CDCl_3$)



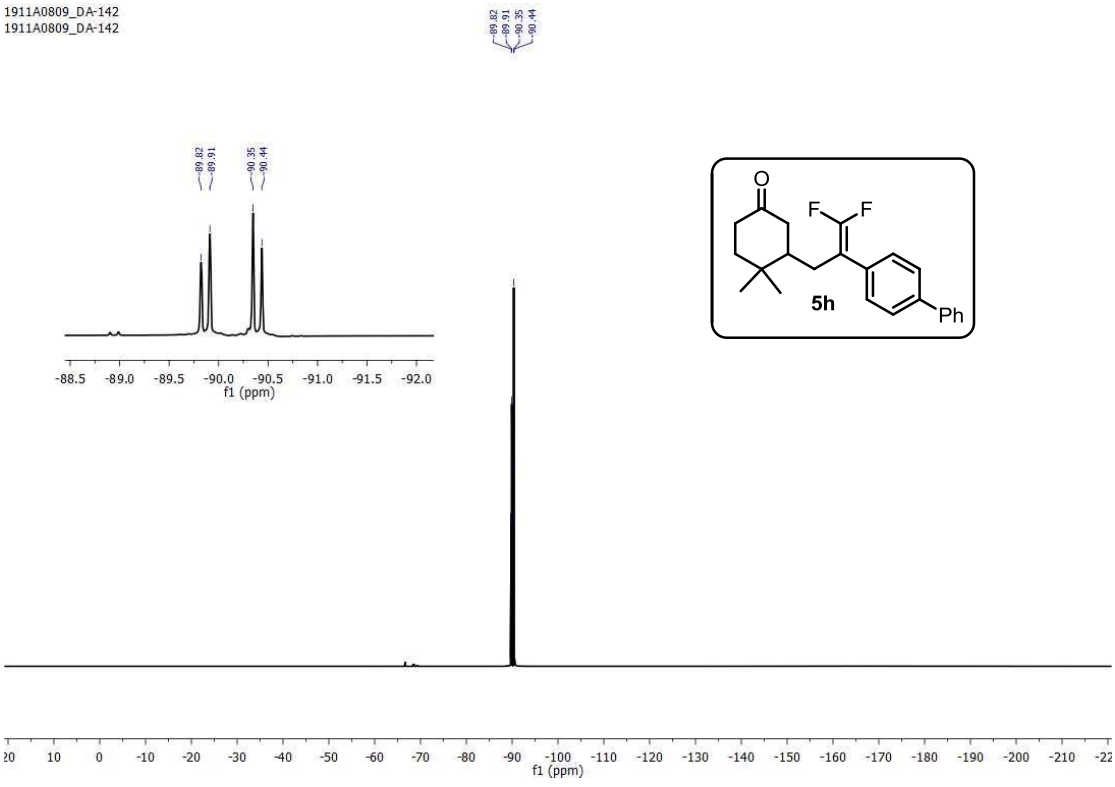
^{19}F NMR (376 MHz, $CDCl_3$)



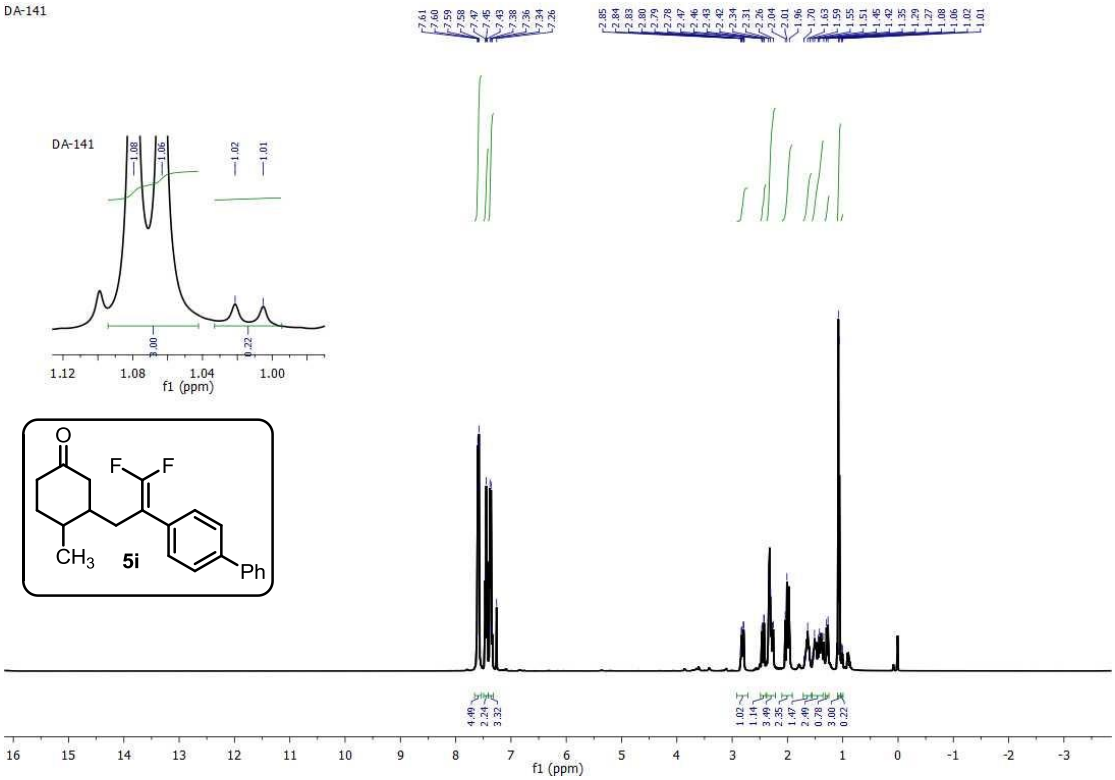
^{1}H NMR (400 MHz, $CDCl_3$)



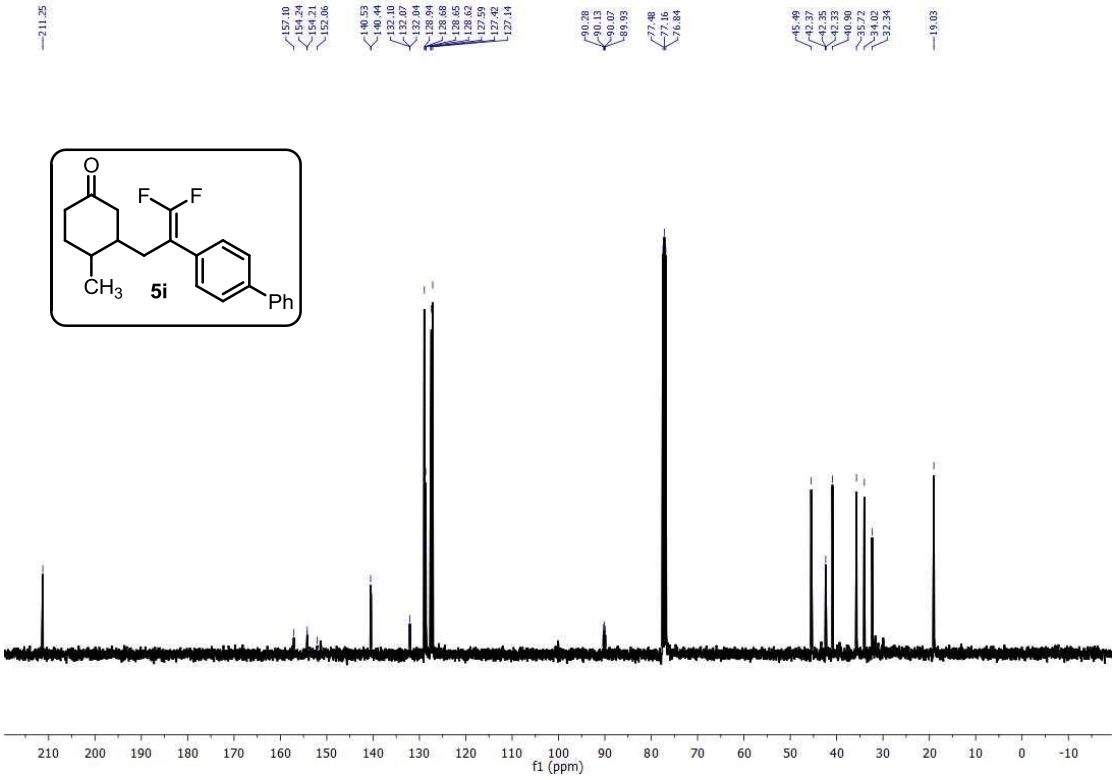
^{13}C NMR (101 MHz, $CDCl_3$)



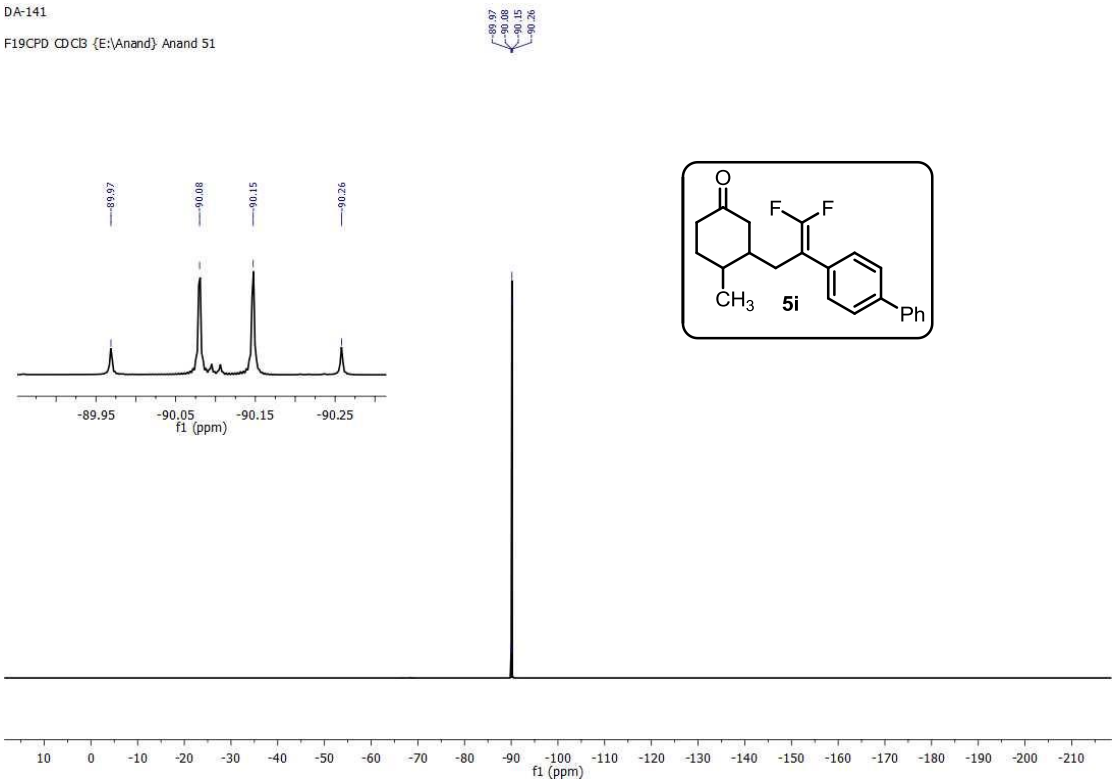
^{19}F NMR (376 MHz, $CDCl_3$)



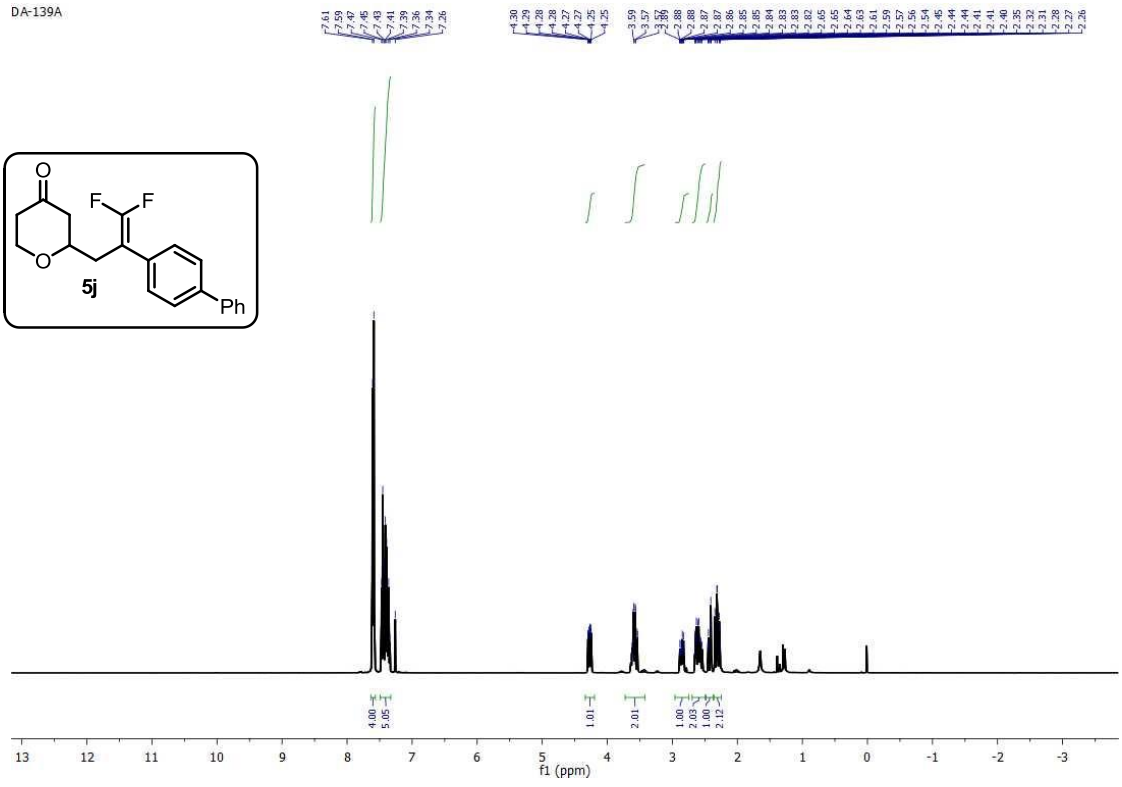
^{1}H NMR (400 MHz, $CDCl_3$)



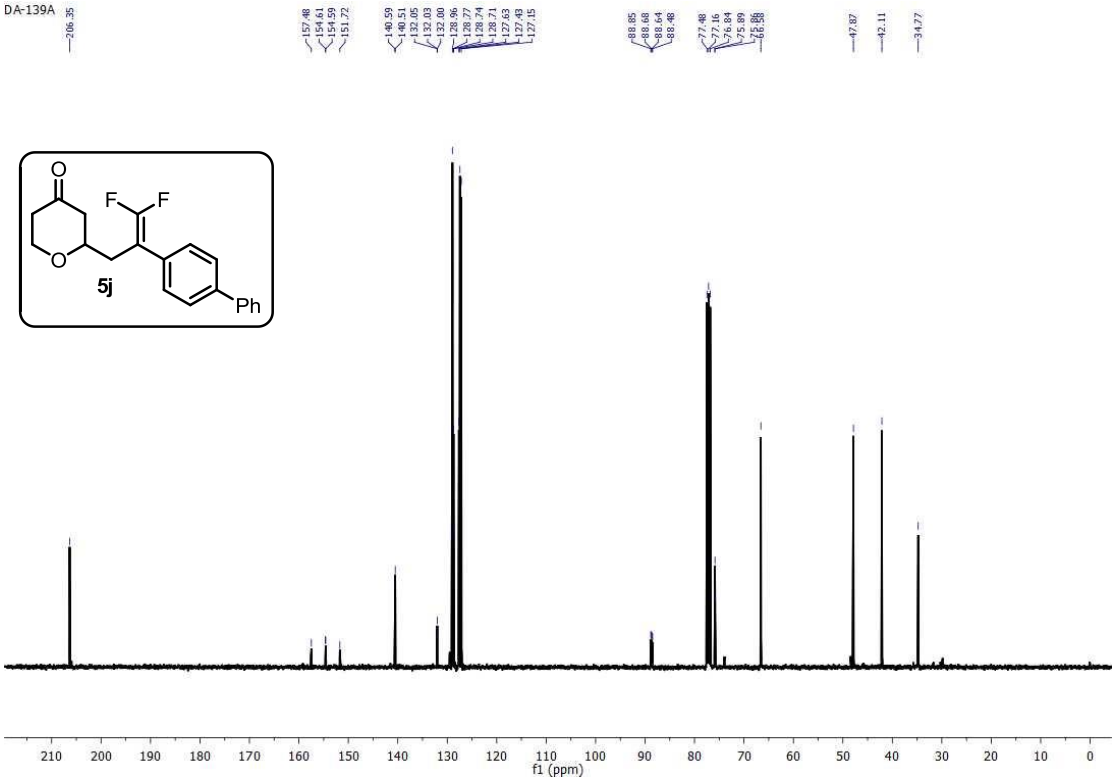
^{13}C NMR (101 MHz, $CDCl_3$)



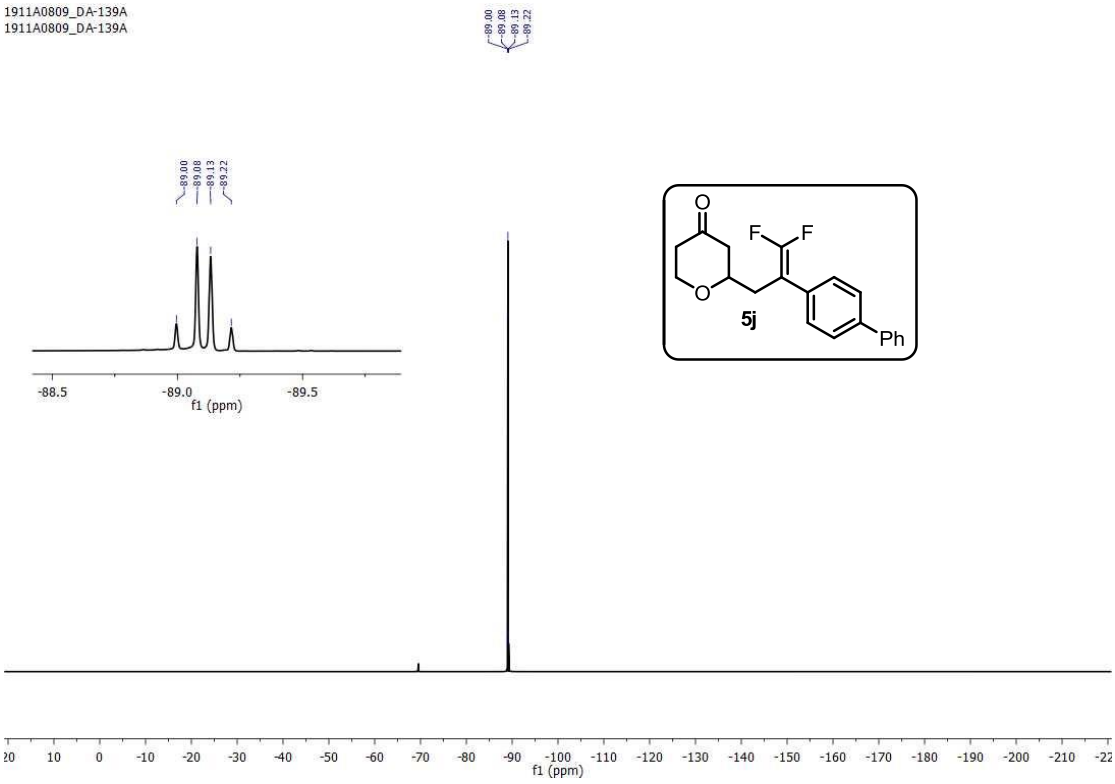
^{19}F NMR (376 MHz, $CDCl_3$)



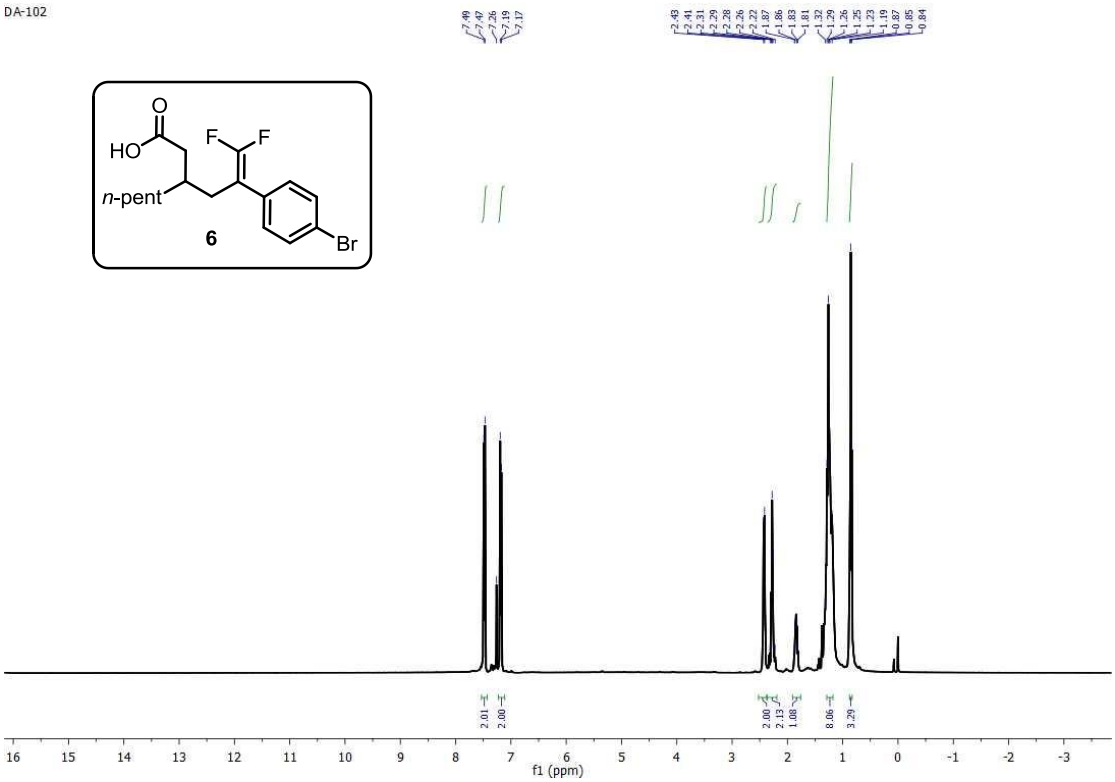
^{1}H NMR (400 MHz, $CDCl_3$)



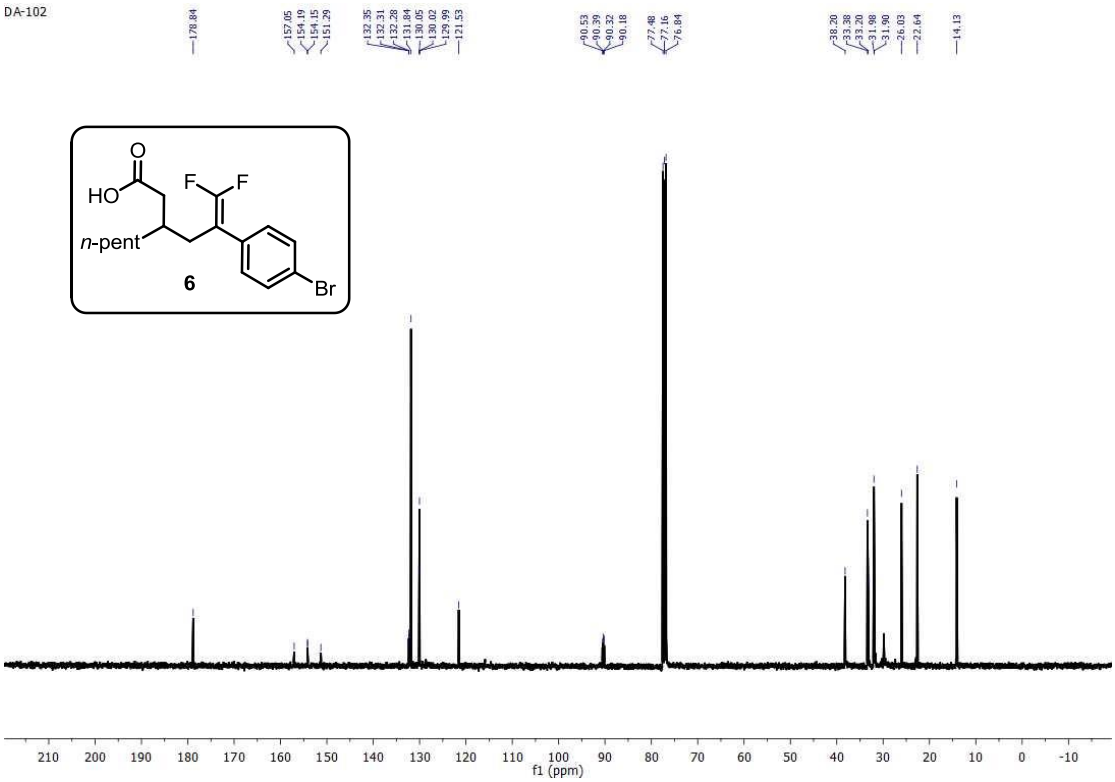
^{13}C NMR (101 MHz, $CDCl_3$)



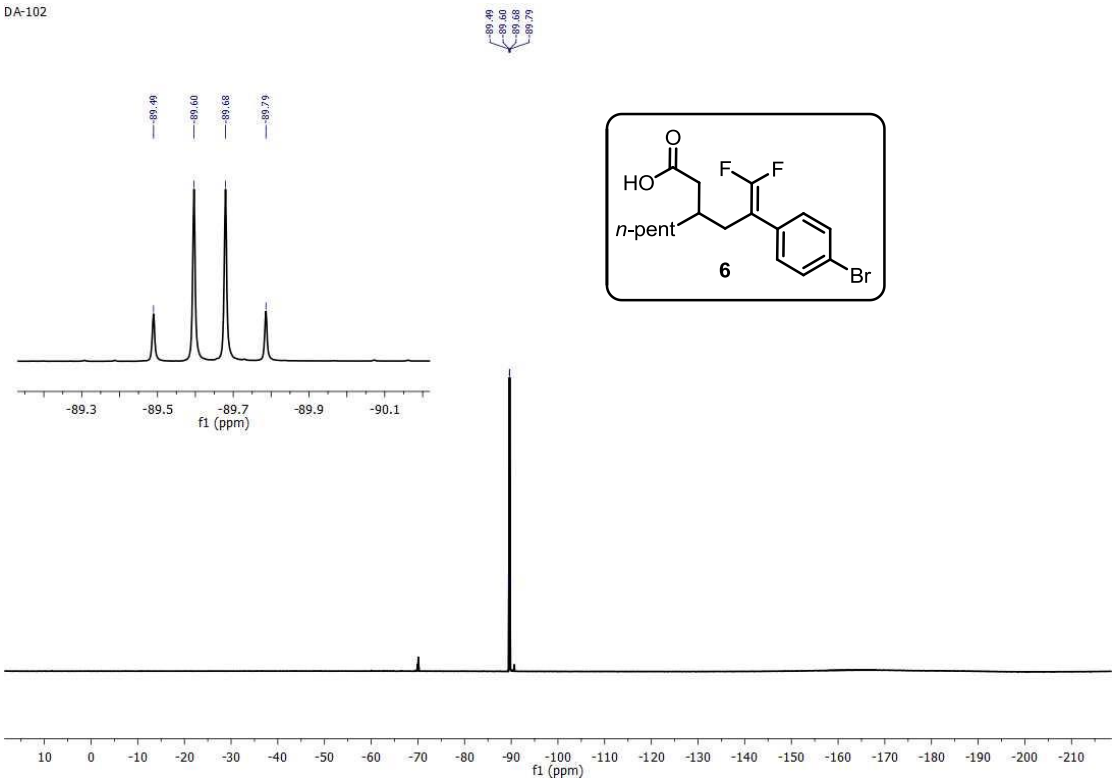
^{19}F NMR (376 MHz, $CDCl_3$)



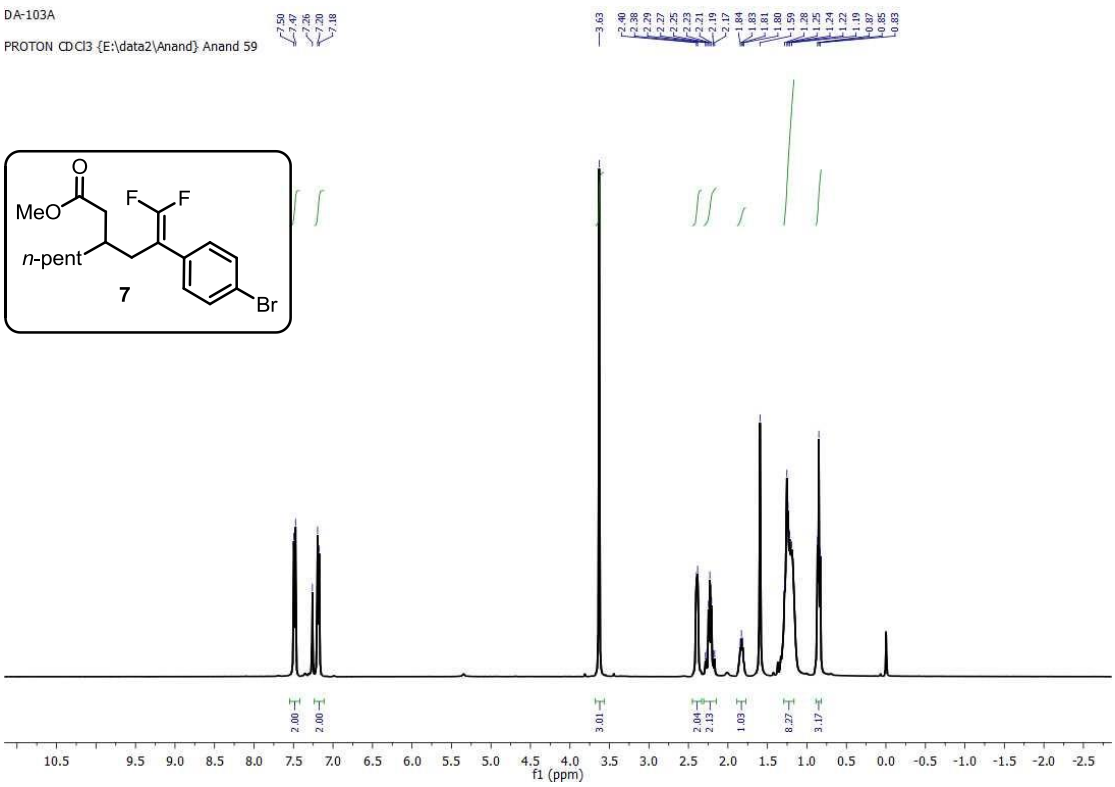
^{1}H NMR (400 MHz, $CDCl_3$)



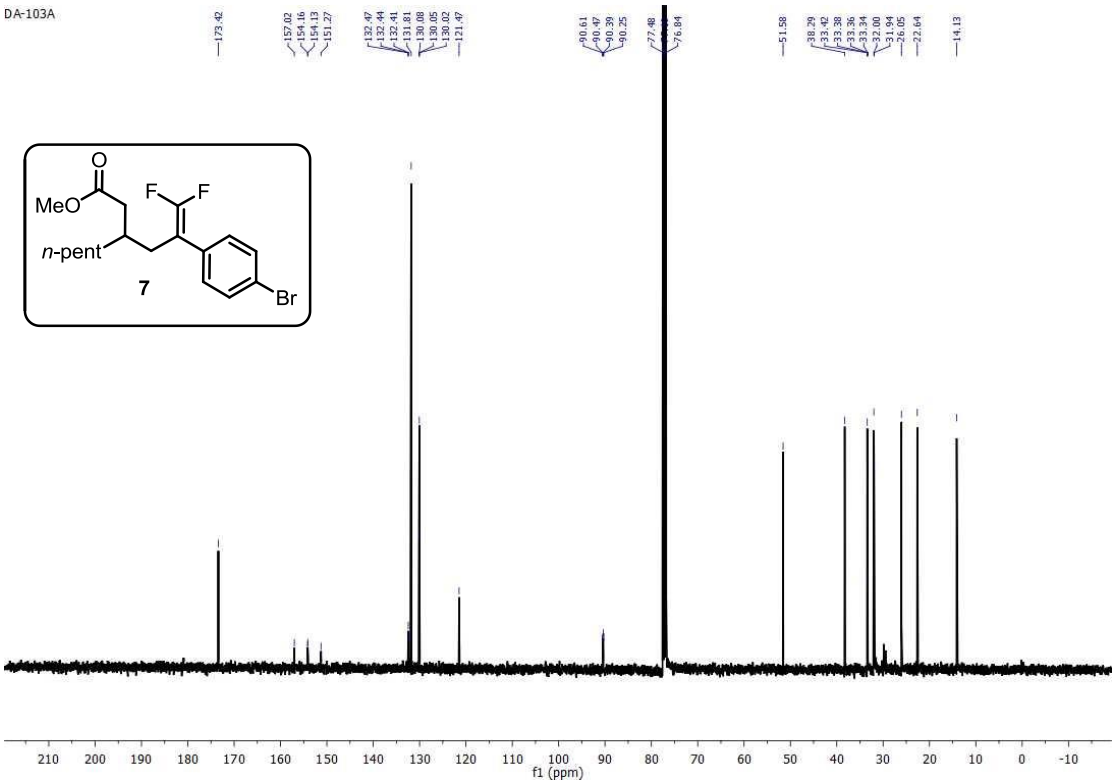
^{13}C NMR (101 MHz, $CDCl_3$)



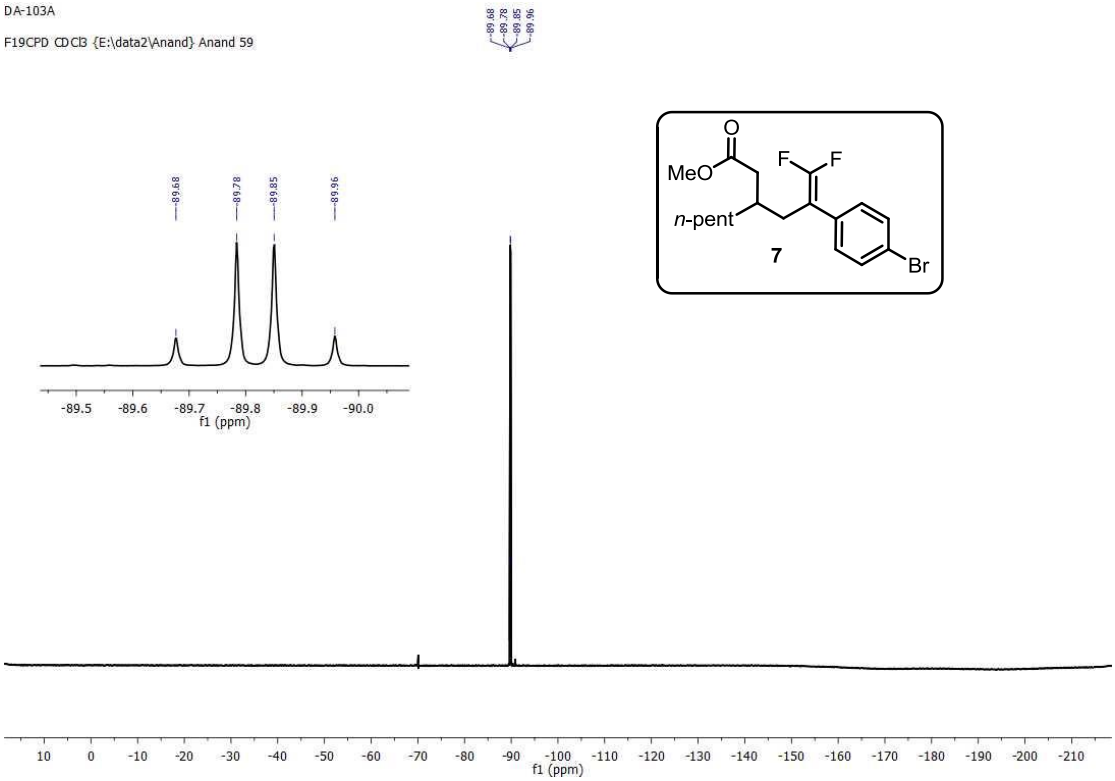
^{19}F NMR (376 MHz, $CDCl_3$)



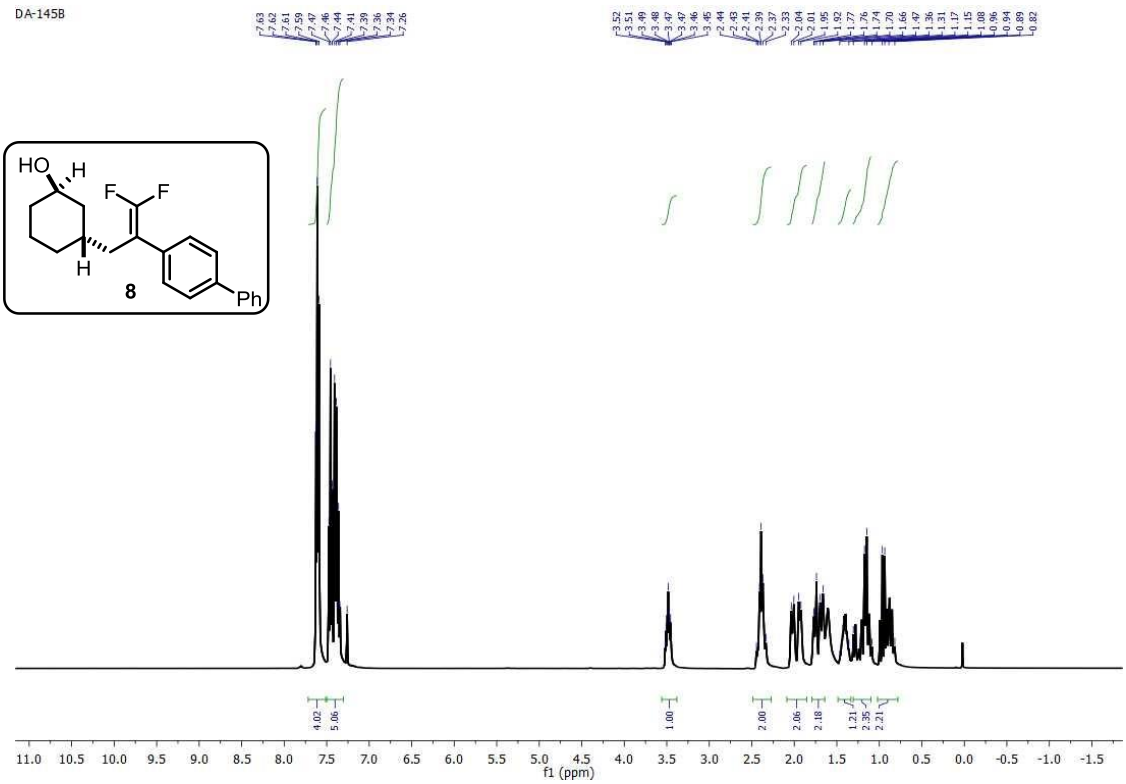
^{1}H NMR (400 MHz, $CDCl_3$)



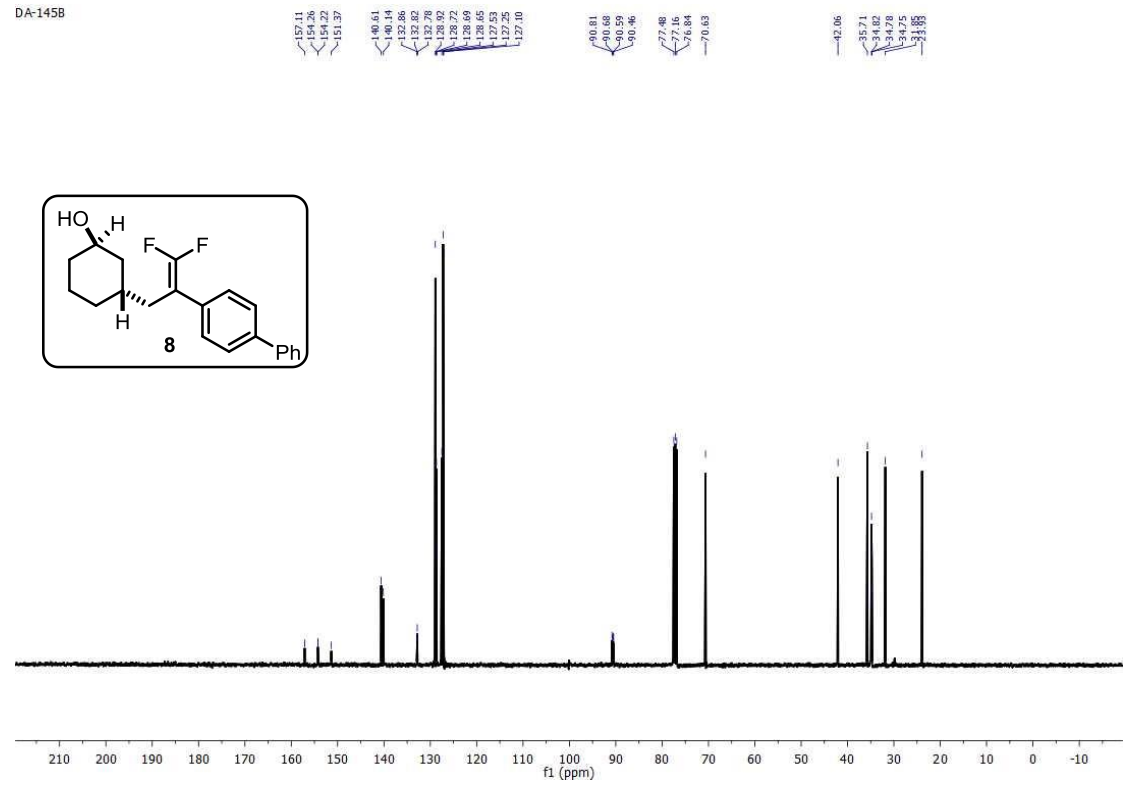
^{13}C NMR (101 MHz, $CDCl_3$)



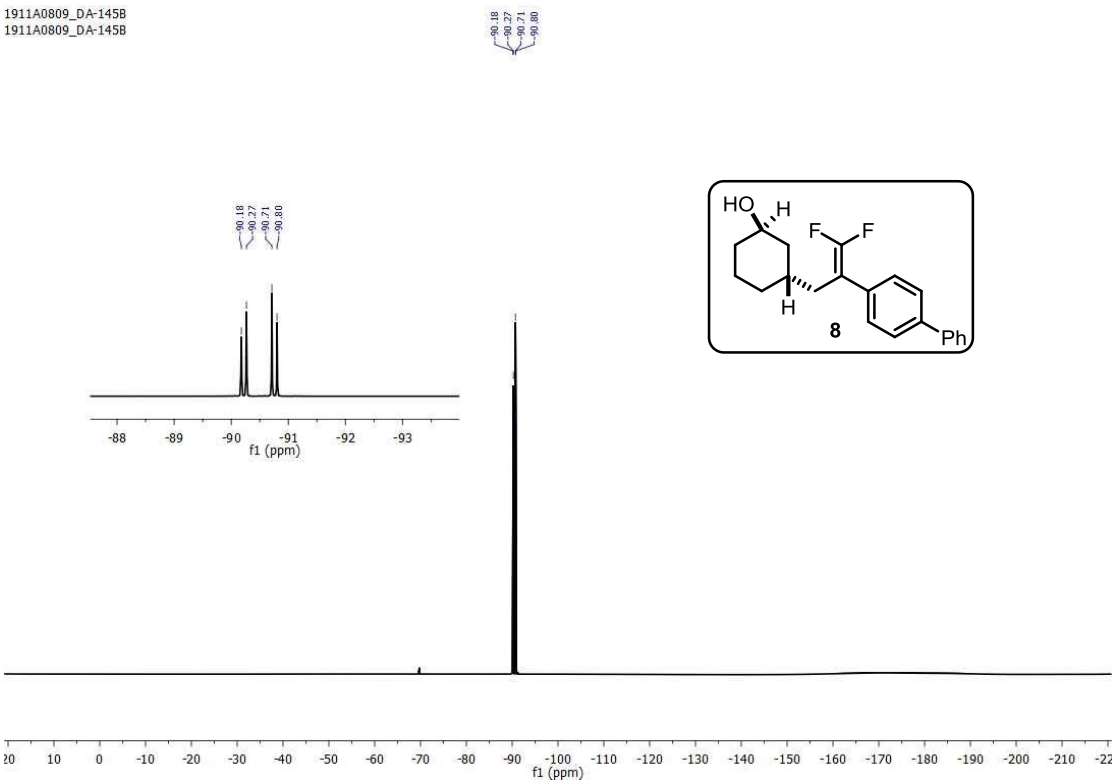
^{19}F NMR (376 MHz, $CDCl_3$)



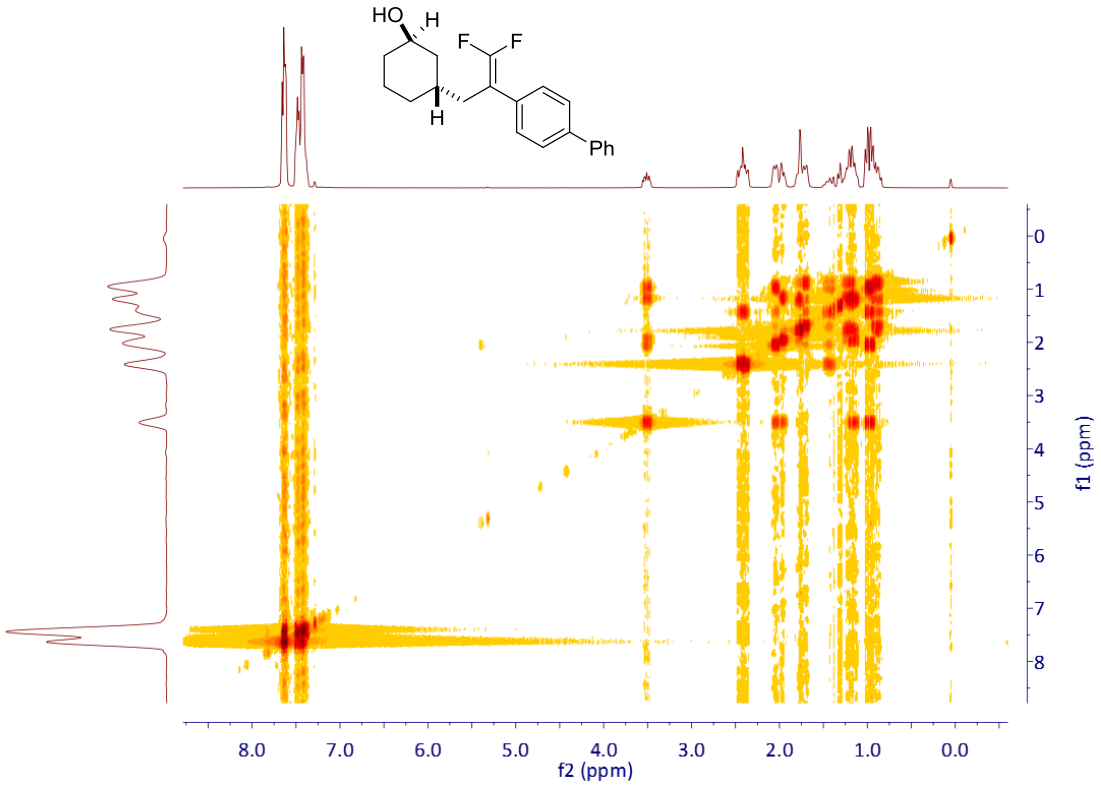
^{1}H NMR (400 MHz, $CDCl_3$)



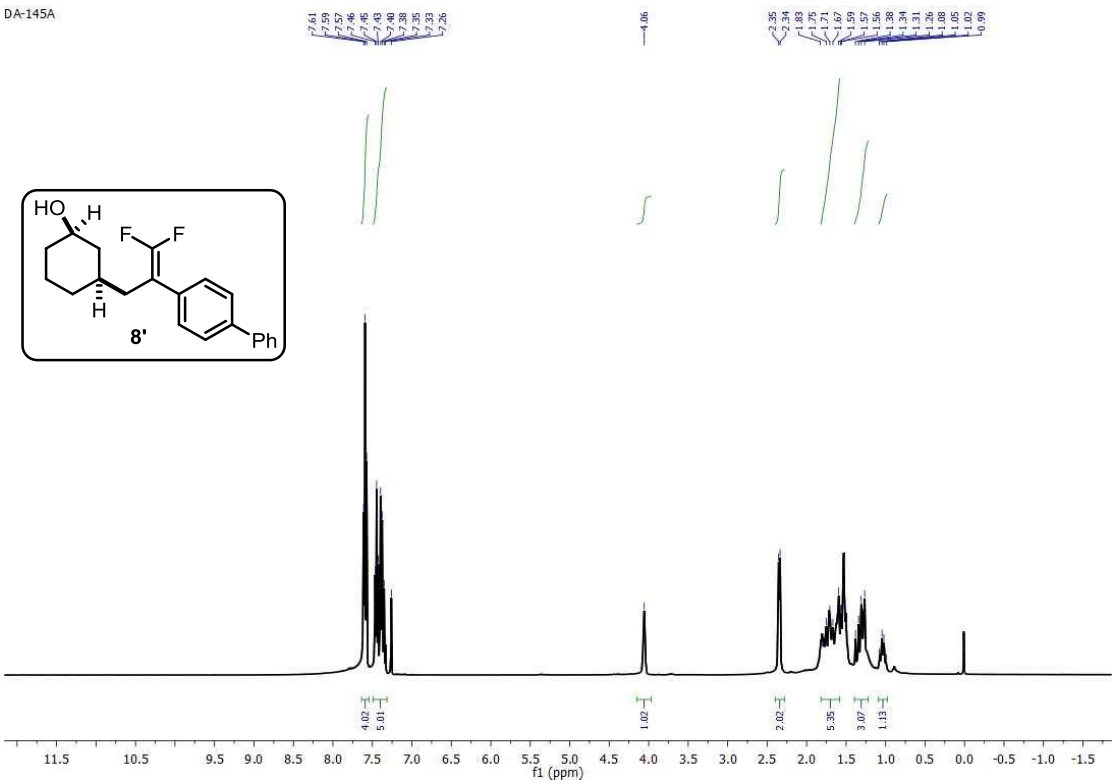
^{13}C NMR (400 MHz, $CDCl_3$)



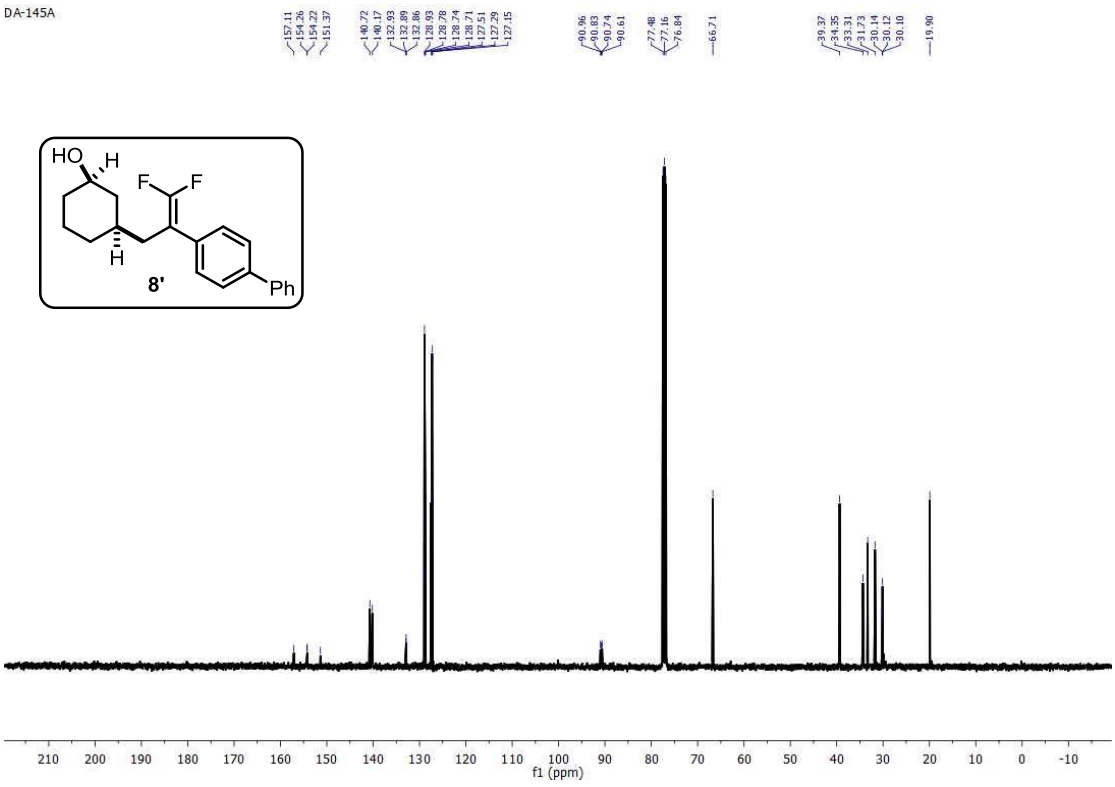
^{19}F NMR (376 MHz, $CDCl_3$)



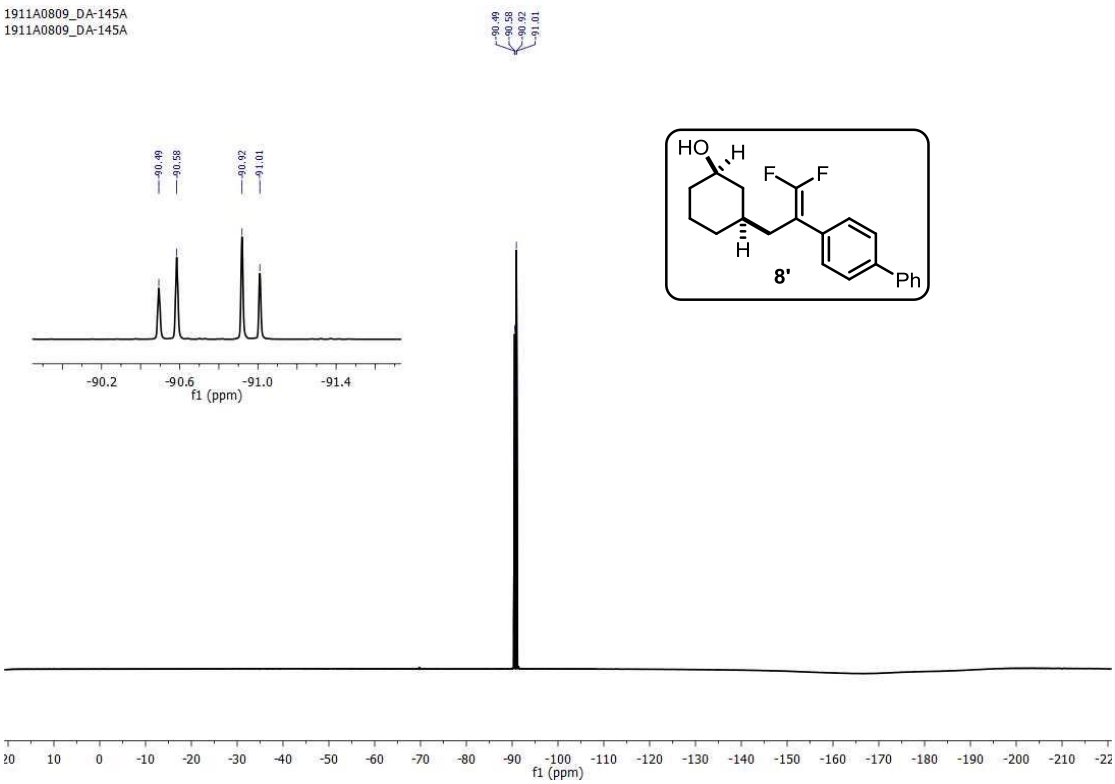
COSY of **8** (400 MHz, $CDCl_3$)



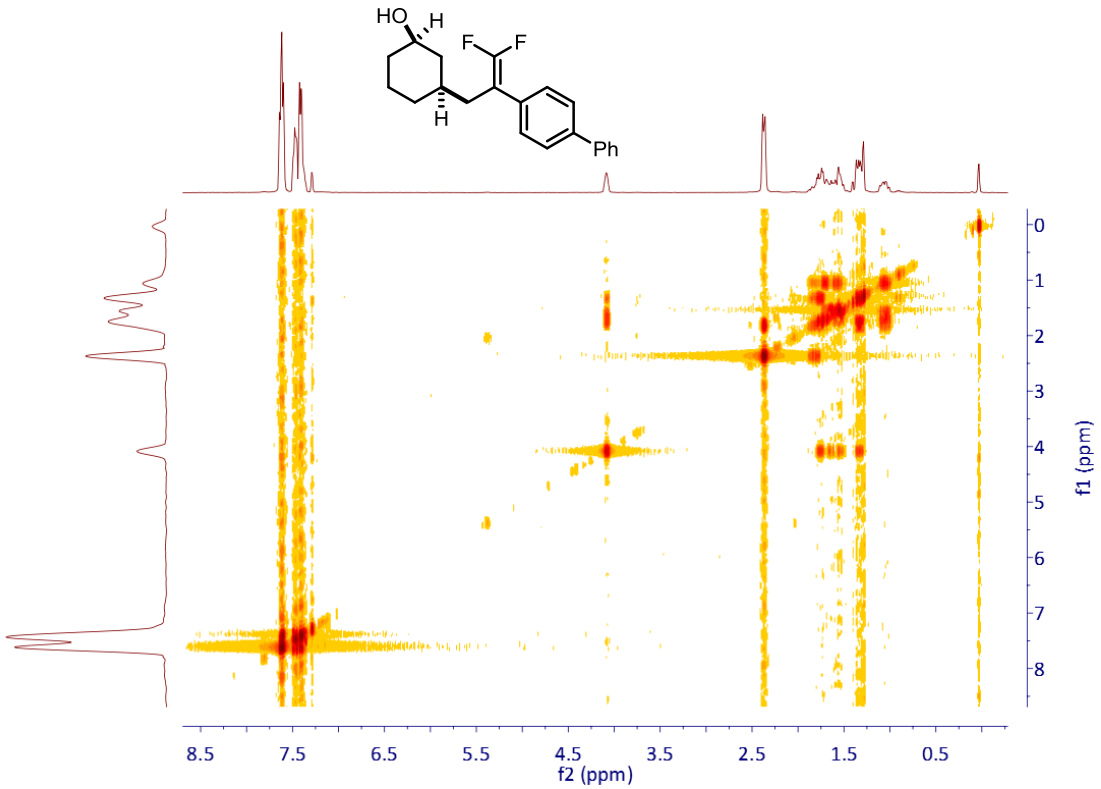
^{1}H NMR (400 MHz, $CDCl_3$)



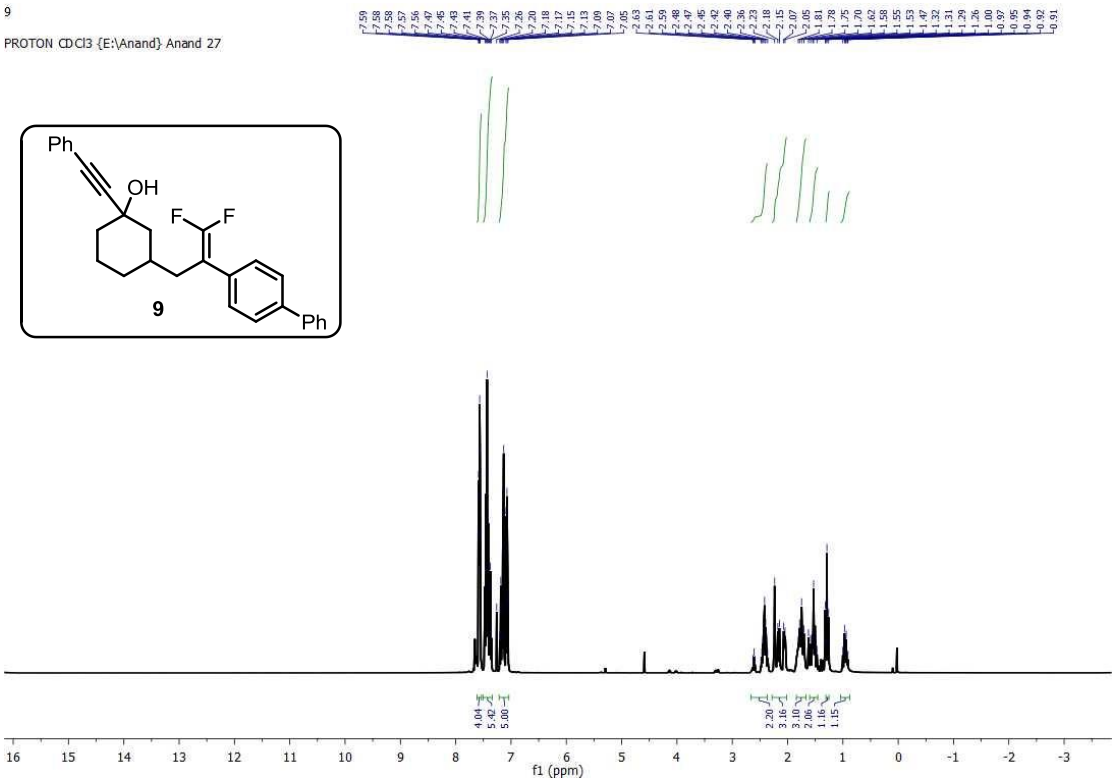
^{13}C NMR (400 MHz, $CDCl_3$)



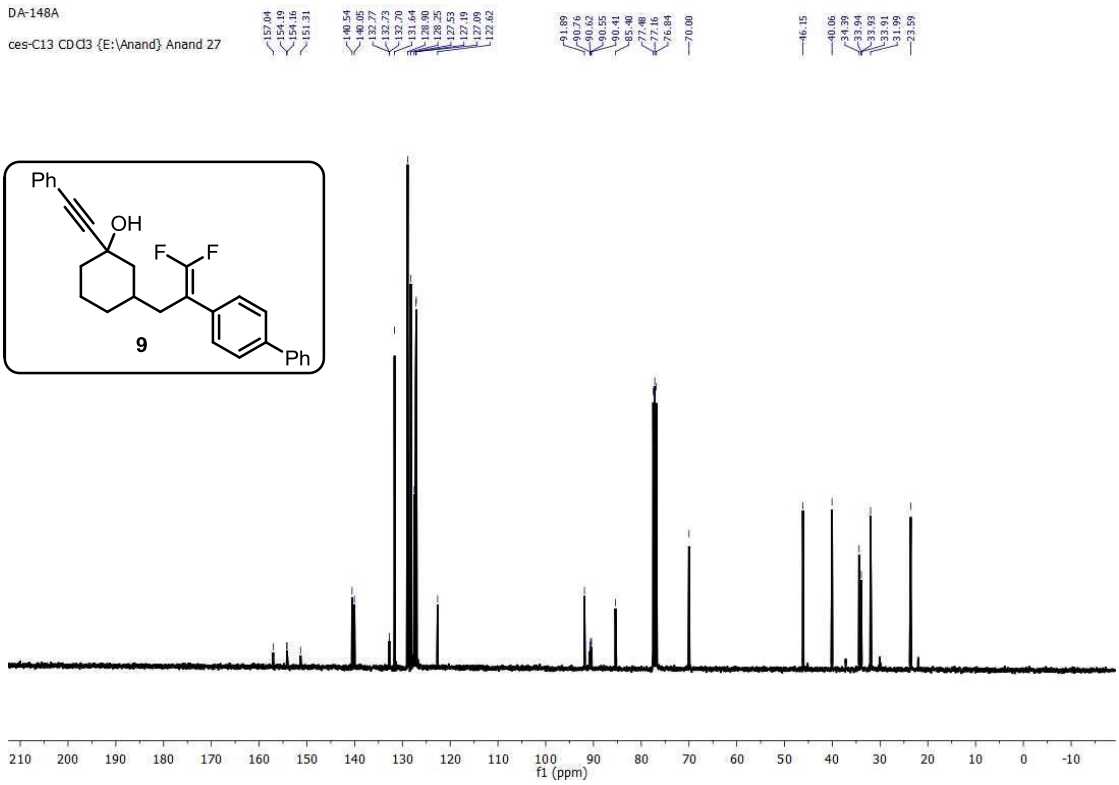
^{19}F NMR (376 MHz, $CDCl_3$)



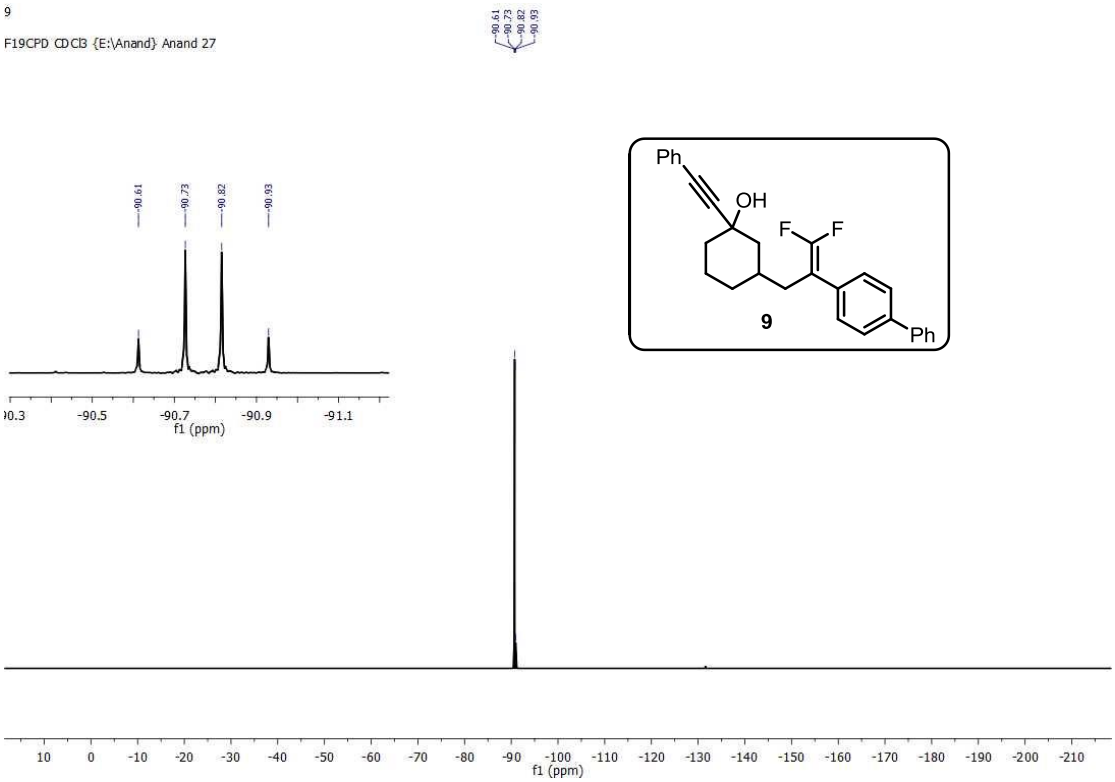
COSY of **8'** (400 MHz, $CDCl_3$)



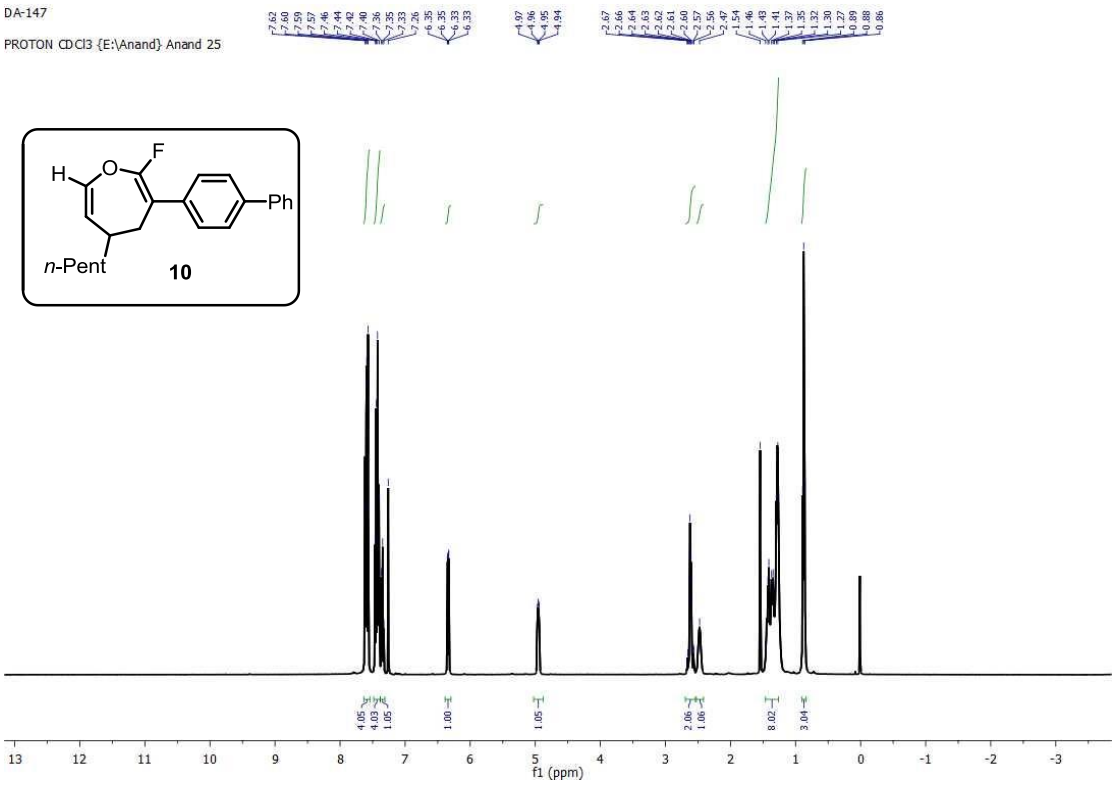
^{1}H NMR (400 MHz, $CDCl_3$)



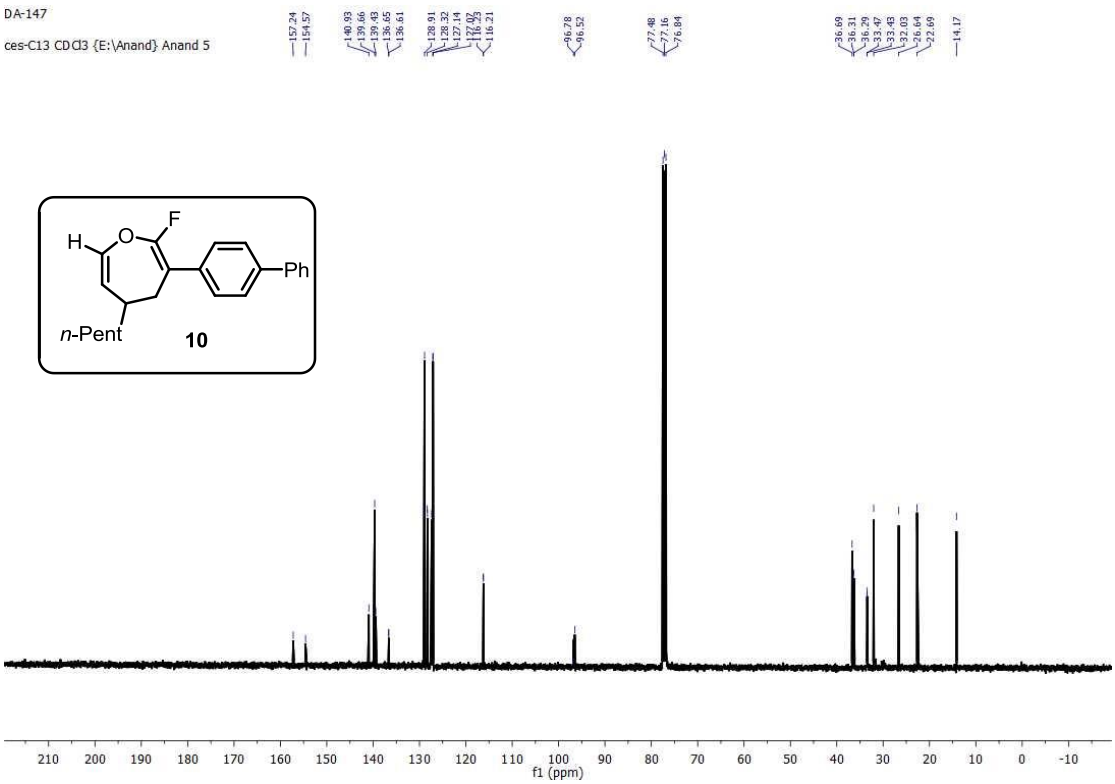
^{13}C NMR (400 MHz, $CDCl_3$)



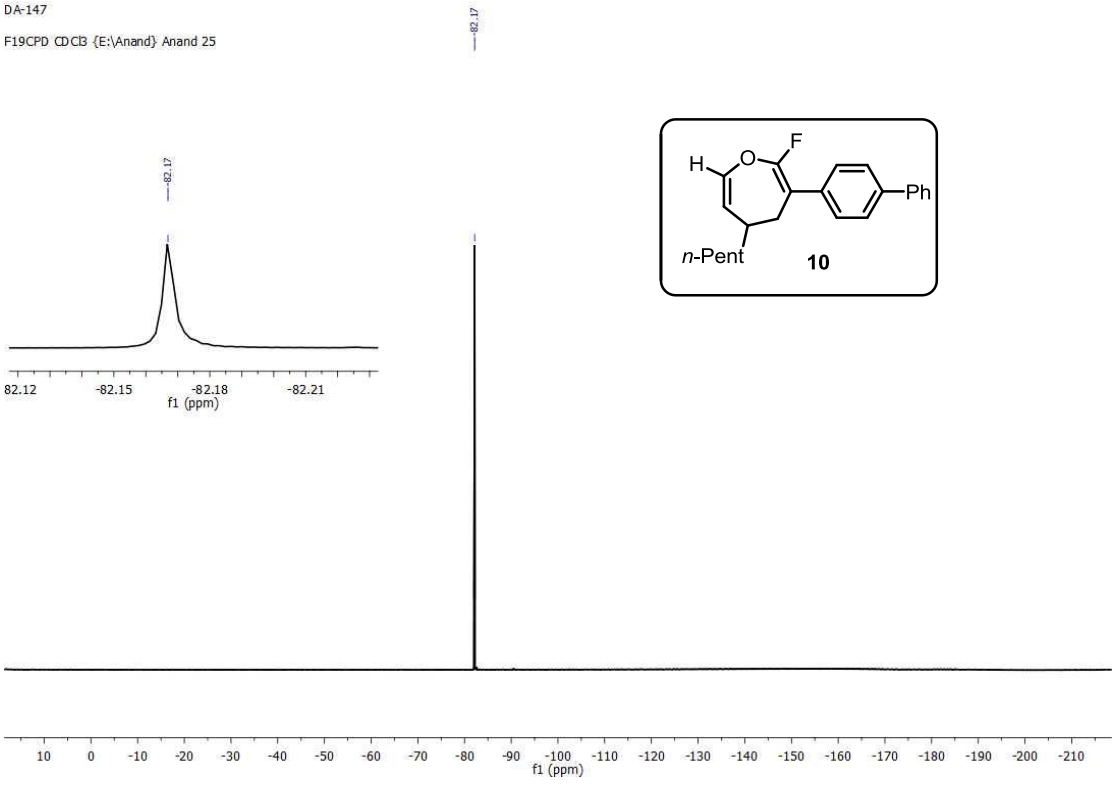
^{19}F NMR (376 MHz, $CDCl_3$)



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



^{13}C NMR (400 MHz, $CDCl_3$)



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