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Supplementary Information

A General Photocatalytic Hydrodefluorination and Defluoroalkylation of Electronically-Variable $ArCF_3$ by Changing Commercially-Available Arenethiolates

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1 General Information

Materials

All reactions were carried out in oven dried glassware under a nitrogen atmosphere. (purity ≥ 99.999%) unless otherwise mentioned. All solvents were purified and dried according to standard methods prior to use. Commercial reagents were purchased from Adamas-beta, TCI, Aladdin, Macklin, J&K Chemical, Innochem and Aldrich. Organic solutions were concentrated under reduced pressure on Yarong rotary evaporator of RE-2000B. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.2 ± 0.03 mm using UV light as a visualizing agent. Chromatographic purification of products was accomplished using forced-flow chromatography on silica gel (200-300 mesh). The LED lamps were purchased from Kessil (390 nm, 427 nm, 440 nm).

Instruments

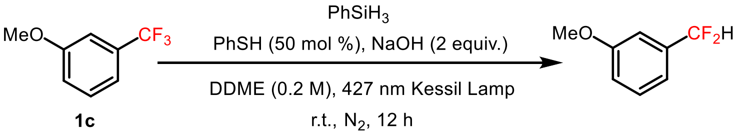
^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE NEO 600 MHz and Bruker AVANCE III 500 MHz. Chemical shifts (δ) were reported in parts per million relative to chloroform (7.26 ppm for ^{1}H NMR; 77.16 ppm for ^{13}C NMR). ^{19}F NMR chemical shifts were corrected by using (trifluoromethoxy)benzene as an internal standard (-58.30 ppm for ^{19}F NMR). Coupling constants were reported in Hertz. The following abbreviations are used to explain the multiplicities: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (b).

The HRMS analysis was obtained on the Waters G2-XS QTOF mass spectrometer. GC-MS measurements were conducted on an Agilent 8860/5977B. UV-Vis spectrum was measured by UV-2600i.

Figure S1. Reaction setup for hydrodefluorination and defluoroallylation of trifluoromethylarenes reaction using 427 nm Kessil Lamp.

2 Optimization of the Reaction Conditions

Table S1. Optimization of the reaction conditions.



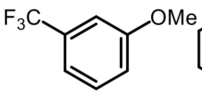
Entry	Deviation from the standard conditions[a]	Yield [%][b]
1	none	96
2	HCOONa instead of $PhSiH_3$	8
3	HCOOCs instead of $PhSiH_3$	8
4	Ph_2SiH_2 instead of $PhSiH_3$	79
5	Ph_3SiH instead of $PhSiH_3$	25
6	Et_3SiH instead of $PhSiH_3$	10
7	DME as solvent	66
8	THF as solvent	27
9	DMSO as solvent	10
10	Performed at 390 nm light	61
11	Performed at 440 nm light	88
12	*p*-Methoxybenzenethiol instead of PhSH	74
13	Cyclohexanethiol instead of PhSH	55

[a]Reaction conditions: **1g** (0.20 mmol, 1.0 equiv.), $PhSiH_3$ (1.2 mmol, 6.0 equiv.), PhSH (0.10 mmol, 0.5 equiv.) and NaOH (0.40 mmol, 2.0 equiv.) in DDME (1.0 mL, 0.2 M), irradiation with 427 nm Kessil Lamp at room temperature

under a nitrogen atmosphere for 12 h. ^{b}Yield determined by ^{19}F NMR using (trifluoromethoxy)benzene as an internal standard.

3 Preparation of Substrates

3.1 Preparation of Trifluoromethylarenes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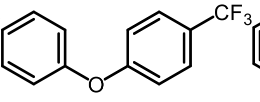
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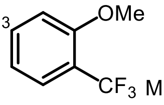
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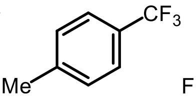
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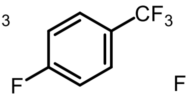
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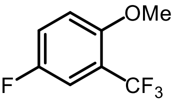
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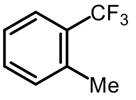
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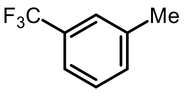
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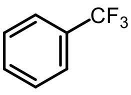
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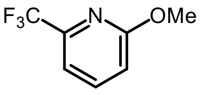
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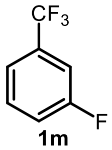
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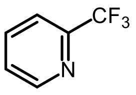
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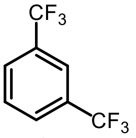
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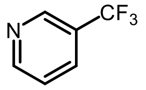
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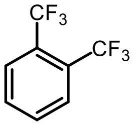
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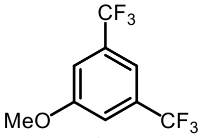
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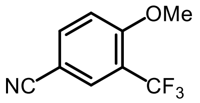
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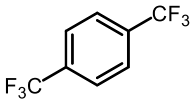
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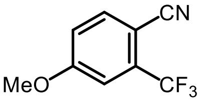
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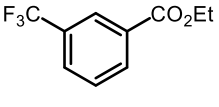
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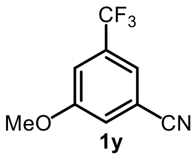
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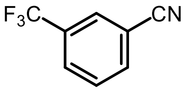
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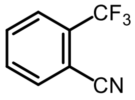
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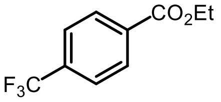
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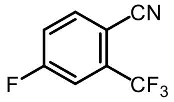
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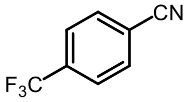
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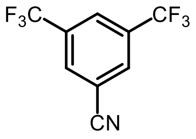
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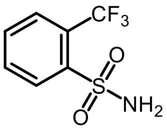
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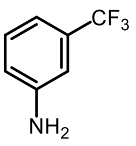
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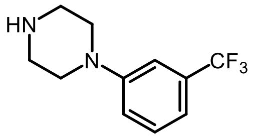
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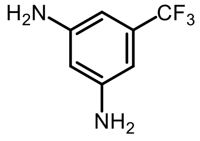
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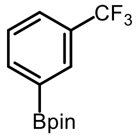
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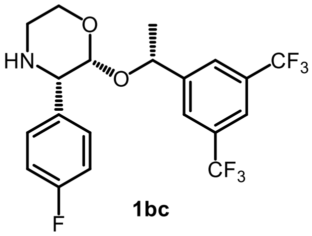
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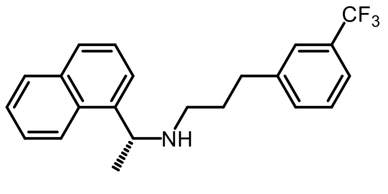
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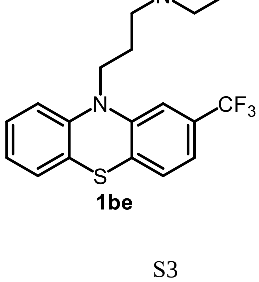
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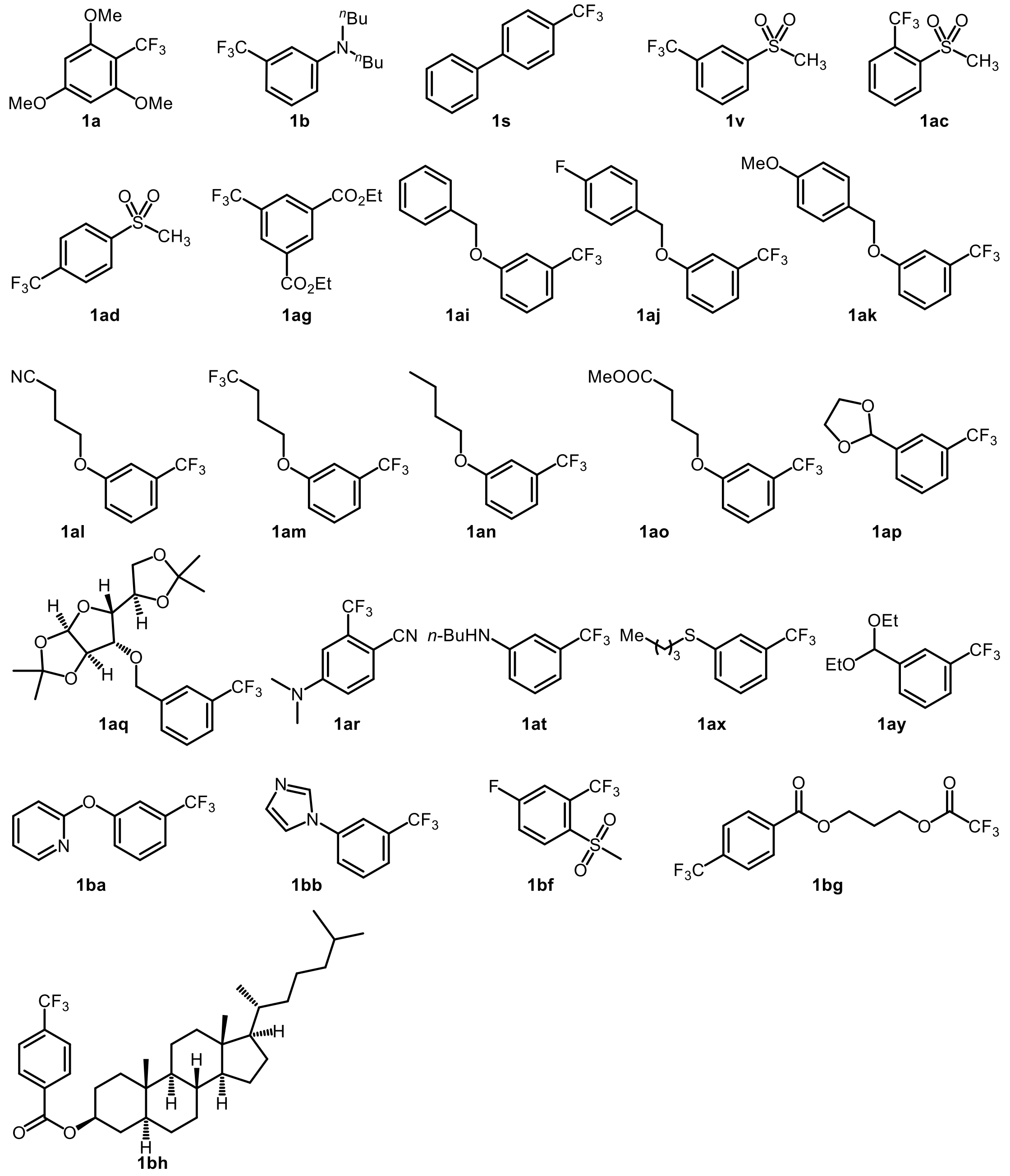
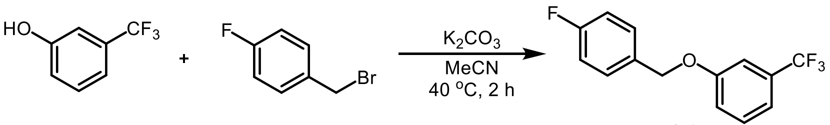
Scheme S1. Commercially Available Trifluoromethylarenes Substrates



Scheme S2. Preparation of Trifluoromethylarenes Substrates

Note: Substrates **1a**[1], **1b**[2], **1s**[3], **1v**[4], **1ac**[5], **1ad**[6], **1ag**[7], **1ai**[8], **1ak**[9], **1an**[10], **1ap**[11], **1ar**[12], **1at**[13], **1ax**[14], **1ay**[15], **1ba**[16], **1bb**[17], **1bf**[18] were prepared according to the literatures. Other substrates are prepared from commercially available compounds, which are described as follows.

Preparation of 1-((4-fluorobenzyl)oxy)-3-(trifluoromethyl)benzene (1aj)

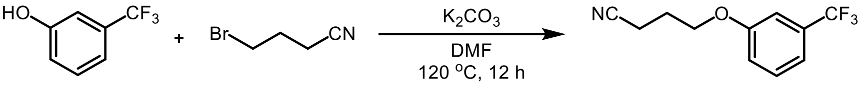


1aj

To a solution of 3-(trifluoromethyl)phenol (324 mg, 2.0 mmol, 1.0 equiv.) in acetonitrile (10 mL), 1-(bromomethyl)-4-fluorobenzene (274 μL, 2.2 mmol, 1.1 equiv.) and K_2CO_3 (415 mg, 3.0 mmol, 1.5 equiv.) were added under a nitrogen atmosphere. The mixture was stirred at 40 °C for 2 hours. After completion (monitored by TLC), the mixture was poured into water (20 mL), extracted with Et_2O (3 x 50 mL), combined organic layers were dried over anhydrous Na_2SO_4, filtered, concentrated *in vacuo* to give a residue. Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (100:1 (v/v)) as eluent afforded 1-((4-fluorobenzyl)oxy)-3-(trifluoromethyl)benzene **1aj** 465 mg as a colorless oil (86% yield).

R*f* = 0.4 (petroleum ether/EtOAc = 50:1). **NMR Spectroscopy**: **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.46 – 7.36 (m, 3H), 7.24 (s, 2H), 7.17 – 7.07 (m, 3H), 5.05 (s, 2H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 162.8 (d, *J* = 246.9 Hz), 158.8, 132.1 (d, *J* = 28.3 Hz), 130.2, 129.6, 129.5, 124.1 (q, *J* = 271.9 Hz), 118.4, 117.9 (q, *J* = 3.7 Hz), 115.8 (d, *J* = 21.6 Hz), 111.8, 69.8. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -62.72 (s, 3F), -113.72 – -113.77 (m, 1F).

Preparation of 4-(3-(trifluoromethyl)phenoxy)butanenitrile (1al)

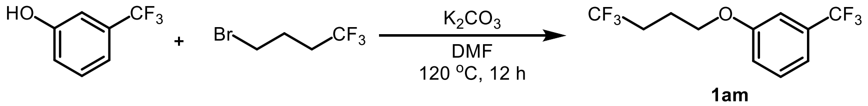


1al

To a solution of 3-(trifluoromethyl)phenol (1.6 g, 10 mmol, 1.0 equiv.) in dry DMF (20 mL), 4-bromobutyronitrile (2.2 g, 15 mmol, 1.5 equiv.) and K_2CO_3 (2.1g , 15 mmol, 1.5 equiv.) were added under a nitrogen atmosphere. The mixture was stirred at 120 °C for 12 hours. After completion (monitored by TLC), the reaction mixture was cooled to room temperature. The reaction mixture was activated of 20 % hydrochloric acid and diluted with water (20 mL) and extracted with ethyl ether (30 mL). The combined organic layers were washed with water (2 x 30 mL), dried over anhydrous Na_2SO_4, filtered, concentrated *in vacuo* to give a residue. Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded 4-(3-(trifluoromethyl)phenoxy)butanenitrile **1al** 1.8 g as a colorless oil (78% yield).

R*f* = 0.4 (petroleum ether/EtOAc = 10:1).**NMR Spectroscopy**: **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.43 – 7.31 (m, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.13 (s, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 4.10 (t, *J* = 5.8 Hz, 2H), 2.58 (t, *J* = 7.1 Hz, 2H), 2.14 (p, *J* = 6.2 Hz, 2H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 158.6, 131.9 (q, *J* = 32.1 Hz), 130.2, 124.0 (q, *J* = 272.4 Hz), 119.1, 117.9, 117.9 (q, J = 4.0 Hz), 111.3 (q, *J* = 3.5 Hz), 65.6, 25.3, 14.1. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -62.69 (s, 3F).

Preparation of 1-(4,4,4-trifluorobutoxy)-3-(trifluoromethyl)benzene (1am)

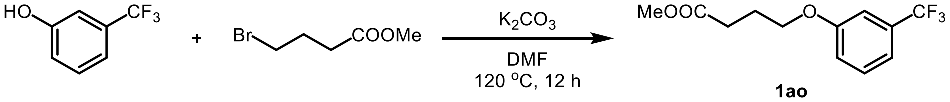


To a solution of 3-(trifluoromethyl)phenol (1.62 g, 10 mmol, 1.0 equiv.) in dry DMF (20 mL), 1-bromo-4,4,4-trifluorobutane (2.9 g, 15 mmol, 1.5 equiv.) and K$_2$CO$_3$ (2.07g , 15 mmol, 1.5 equiv.) were added under a nitrogen atmosphere. The mixture was stirred at 120 °C for 12 hours. After completion (monitored by TLC), the reaction mixture was cooled to room temperature. The reaction mixture was activated of 20 % hydrochloric acid and diluted with water (20 mL) and extracted with ethyl ether (30 mL). The combined organic layers were washed with water (2 * 30 mL), dried over anhydrous Na$_2$SO$_4$, filtered, concentrated *in vacuo* to give a residue. Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded 1-(4,4,4-Trifluorobutoxy)-3-(trifluoromethyl)benzene **1am** 2.2 g as a colorless oil (82% yield).

R*f* = 0.5 (petroleum ether/EtOAc = 50:1). **NMR Spectroscopy**: **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.44 – 7.36 (m, 1H), 7.24 – 7.21 (m, 1H), 7.15 – 7.11 (m, 1H), 7.10 – 7.03 (m, 1H), 4.06 (t, *J* = 6.0 Hz, 2H), 2.47 – 2.20 (m, 2H), 2.19 – 1.96 (m, 2H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 158.9, 132.1 (q, *J* = 32.2 Hz), 130.2, 127.2 (q, *J* = 275.9 Hz), 124.1 (q, *J* = 272.1 Hz), 118.0, 117.9 (q, *J* = 3.9 Hz), 111.4 (q, *J* = 3.4 Hz), 66.4, 30.8

(q, J = 29.2 Hz), 22.2 (q, J = 3.1 Hz). **^{19}F NMR (470 MHz, CDCl$_3$)** δ -62.80 (s, 3F), -66.40 (t, 3F, J = 10.8 Hz).

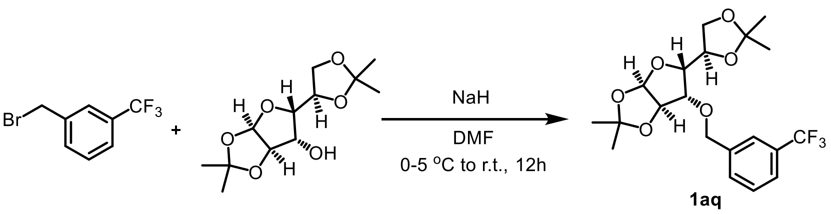
Preparation of methyl 4-(3-(trifluoromethyl)phenoxy)butanoate (1ao)



To a solution of 3-(trifluoromethyl)phenol (1.62 g, 10 mmol, 1.0 equiv.) in dry DMF (20 mL), methyl 4-bromobutanoate (1.9 mL, 15 mmol, 1.5 equiv.) and K_2CO_3 (2.07g , 15 mmol, 1.5 equiv.) were added under a nitrogen atmosphere. The mixture was stirred at 120 °C for 12 hours. The reaction mixture was cooled to room temperature. After completion (monitored by TLC), the reaction mixture was activated of 20 % hydrochloric acid and diluted with water (20 mL) and extracted with ethyl ether (30 mL). The combined organic layers were washed with water (2 x 30 mL), dried over anhydrous Na_2SO_4, filtered, concentrated *in vacuo* to give a residue. Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded **1ao** as a colorless oil.

R$_f$ = 0.4 (petroleum ether/EtOAc = 5:1). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, CDCl$_3$) δ 7.41 – 7.32 (m, 1H), 7.20 (d, J = 7.0 Hz, 1H), 7.11 (s, 1H), 7.05 (d, J = 6.7 Hz, 1H), 4.04 (t, J = 5.9 Hz, 2H), 3.70 (s, 3H), 2.54 (t, J = 7.1 Hz, 2H), 2.22 – 2.06 (m, 2H). **^{19}F NMR** (565 MHz, CDCl$_3$) δ -62.73 – -62.82 (m, 3F). **^{13}C NMR** (151 MHz, CDCl$_3$) δ 173.6, 159.0, 131.9 (q, J = 32.3 Hz), 130.1, 124.1 (q, J = 272.6 Hz), 118.0, 117.5, 111.3 (d, J = 3.8 Hz), 67.0, 51.7, 30.5, 24.6.

Preparation of (3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-((3-(trifluoromethyl)benzyl)oxy)tetrahydrofuro[2,3-*d*][1,3]dioxole (1aq)



Under a nitrogen atmosphere, to a solution of diacetone-D-glucose (1.3 g, 5.0 mmol, 1.0 equiv.) in dry DMF (10 mL) was added NaH (0.30 g, 60% in mineral oil, 7.5 mmol, 1.5 equiv.) in batches at 0°C, followed by stirring for half an hour at this temperature. Finally, benzyl bromide (1.1 mL, 7.5 mmol, 1.5 equiv.) was added to the reaction solution and stirred overnight at room temperature. After completion (monitored by TLC), the reaction was quenched by H_2O (15 mL) and extracted by ethyl ether (10 mL). The organic phase was washed with water (2 x 25 mL), dried over anhydrous Na_2SO_4, filtered, concentrated *in vacuo* to give a residue. Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded (3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-((3-(trifluoromethyl)benzyl)oxy)tetrahydrofuro[2,3-*d*][1,3]dioxole **1ai** 1.7 g as a colorless oil (80% yield).

R*f* = 0.4 (petroleum ether/EtOAc = 5:1). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.43 (m, 1H), 5.91 (d, *J* = 3.5 Hz, 1H), 4.76 (d, *J* = 12.3 Hz, 1H), 4.69 (d, *J* = 12.3 Hz, 1H), 4.62 (d, *J* = 3.5 Hz, 1H), 4.41 – 4.33 (m, 1H), 4.17 – 4.09 (m, 2H), 4.06 – 3.99 (m, 2H), 1.50 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H), 1.32 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.8, 130.8, 128.9, 124.8 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.2 Hz), 112.0, 109.3, 105.4, 82.6, 82.0, 81.5, 72.4, 71.5, 67.7, 26.9, 26.3, 25.3. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.57 (s, 3F).

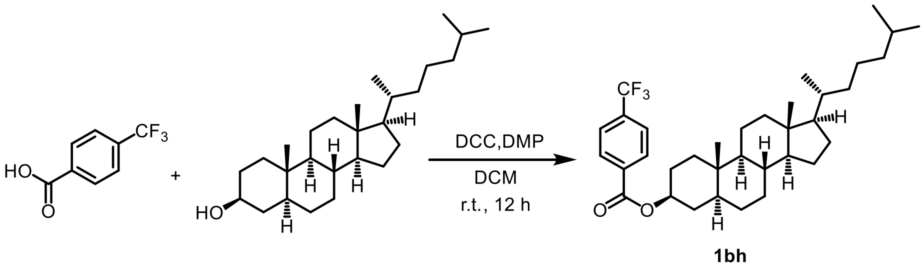
Preparation of 3-(2,2,2-trifluoroacetoxy)propyl 4-(trifluoromethyl)benzoate (1bj)

Under a nitrogen atmosphere, to a solution of 3-hydroxypropyl 4-(trifluoromethyl)benzoate (248 mg, 1.0 mmol, 1.0 equiv.) in dry DCM (6 mL) was added Et_3N (0.18 mL, 1.3 mmol, 1.3 equiv.), trifluoroacetic anhydride(0.18 mL, 1.3 mmol, 1.3 equiv.) at 0°C, followed by stirring for half an hour at this temperature.

Finally, stirred overnight at room temperature. After completion (monitored by TLC), the reaction was quenched by H_2O (15 mL) and extracted by ethyl ether (10 mL). The organic phase was washed with water (3 x 25 mL), dried over anhydrous Na_2SO_4, filtered, concentrated in *vacuo* to give a residue. Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (3:1 (v/v)) as eluent afforded 3-(2,2,2-trifluoroacetoxy)propyl 4-(trifluoromethyl)benzoate **1bj** 103 mg as a yellow oil (30% yield).

R_f = 0.2 (petroleum ether/EtOAc = 3:1). **NMR Spectroscopy**: **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.14 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 4.53 (t, *J* = 6.3 Hz, 2H), 4.48 (t, *J* = 6.2 Hz, 2H), 2.26 (p, *J* = 6.2 Hz, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 165.3, 157.6 (q, *J* = 42.5 Hz), 134.8 (q, *J* = 32.7 Hz), 133.2, 130.1, 125.6 (d, *J* = 3.8 Hz), 123.7 (q, *J* = 272.7 Hz), 114.6 (q, *J* = 285.3 Hz), 65.0, 61.6, 27.8. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -63.27 (s, 3F), -75.08 (s, 3F).

Preparation of (3*S*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(trifluoromethyl)benzoate (1bh)

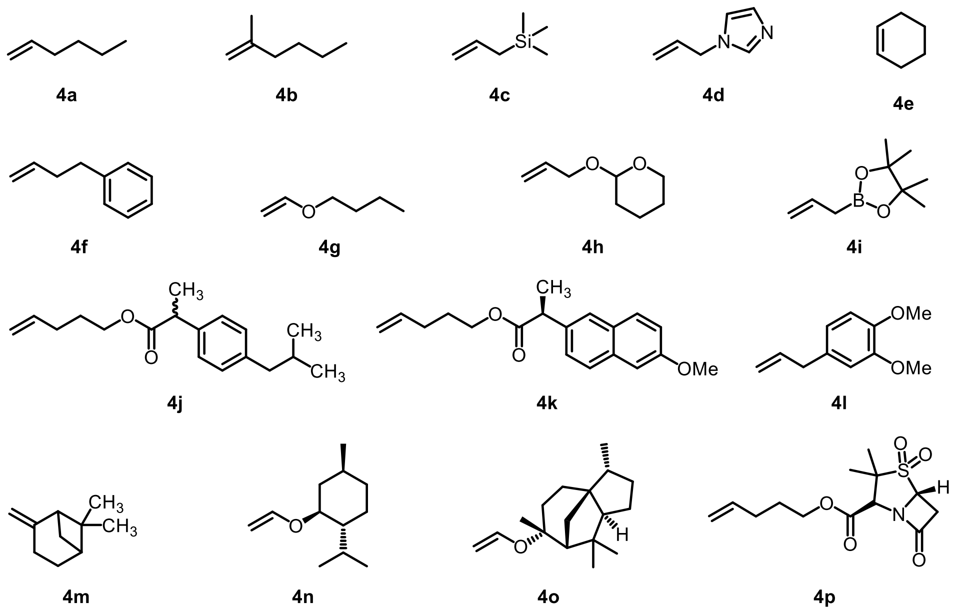


Under a nitrogen atmosphere, to a vigorously stirred solution of 4-(trifluoromethyl)benzoic acid (571 mg, 3.0 mmol, 1.0 equiv.), dihydrocholesterol (1.28 g, 3.3 mmol, 1.1 equiv.), 4-dimethylaminopyridine (41 mg, 0.3 mmol, 0.1 equiv.) in dry DCM (15 mL), added DCC (681 mg, 3.3 mmol, 1.1 equiv.), at room temperature, followed by stirring overnight at the same temperature. After completion (monitored by TLC), filter the solution, and wash with DCM and collect the filtrate, dried over anhydrous Na_2SO_4, filtered, concentrated in vacuo to give a residue. Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (30:1

(v/v)) as eluent afforded (3*S*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(trifluoromethyl)benzoate **1bh** 1.1 g as a white solid (68% yield).

R$_f$ = 0.3 (petroleum ether/EtOAc = 50:1). **NMR Spectroscopy**: **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.14 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 4.97 (tt, *J* = 11.0, 4.9 Hz, 1H), 2.06 – 1.89 (m, 2H), 1.89 – 1.76 (m, 2H), 1.76 – 1.70 (m, 1H), 1.72 – 1.63 (m, 2H), 1.61 – 1.44 (m, 4H), 1.43 – 1.19 (m, 10H), 1.19 – 1.05 (m, 6H), 1.05 – 0.96 (m, 3H), 0.96 – 0.82 (m, 12H), 0.75 – 0.53 (m, 4H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 165.0, 134.4 (q, *J* = 32.6 Hz), 134.3, 130.1, 125.4 (q, *J* = 3.9 Hz), 123.9 (q, *J* = 272.7 Hz), 75.3, 56.6, 56.5, 54.4, 44.9, 42.8, 40.2, 39.7, 36.9, 36.3, 36.0, 35.7, 34.2, 32.2, 28.8, 28.4, 28.2, 27.7, 24.4, 24.0, 23.0, 22.7, 21.4, 18.8, 12.4, 12.2. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -63.04 (s, 3F).

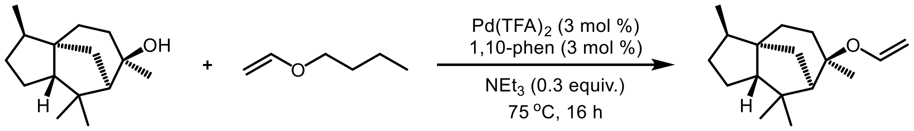
3.2 Preparation of Alkenes



Scheme S3. Alkenes

Note: Substrates **4a-4i, 4m** are commercially available. Substrates **4j**[19], **4k**[20], **4l**[21], **4n**[22], **4p**[23] were prepared according to the literatures.

Preparation of (3*R*, 3*aS*, 6*R*, 7*R*, 8*aS*) - 3,6,8,8-tetramethyl-6-(vinyloxy)octahydro-1H-3*a*,7-methanoazulene (4o)



4o

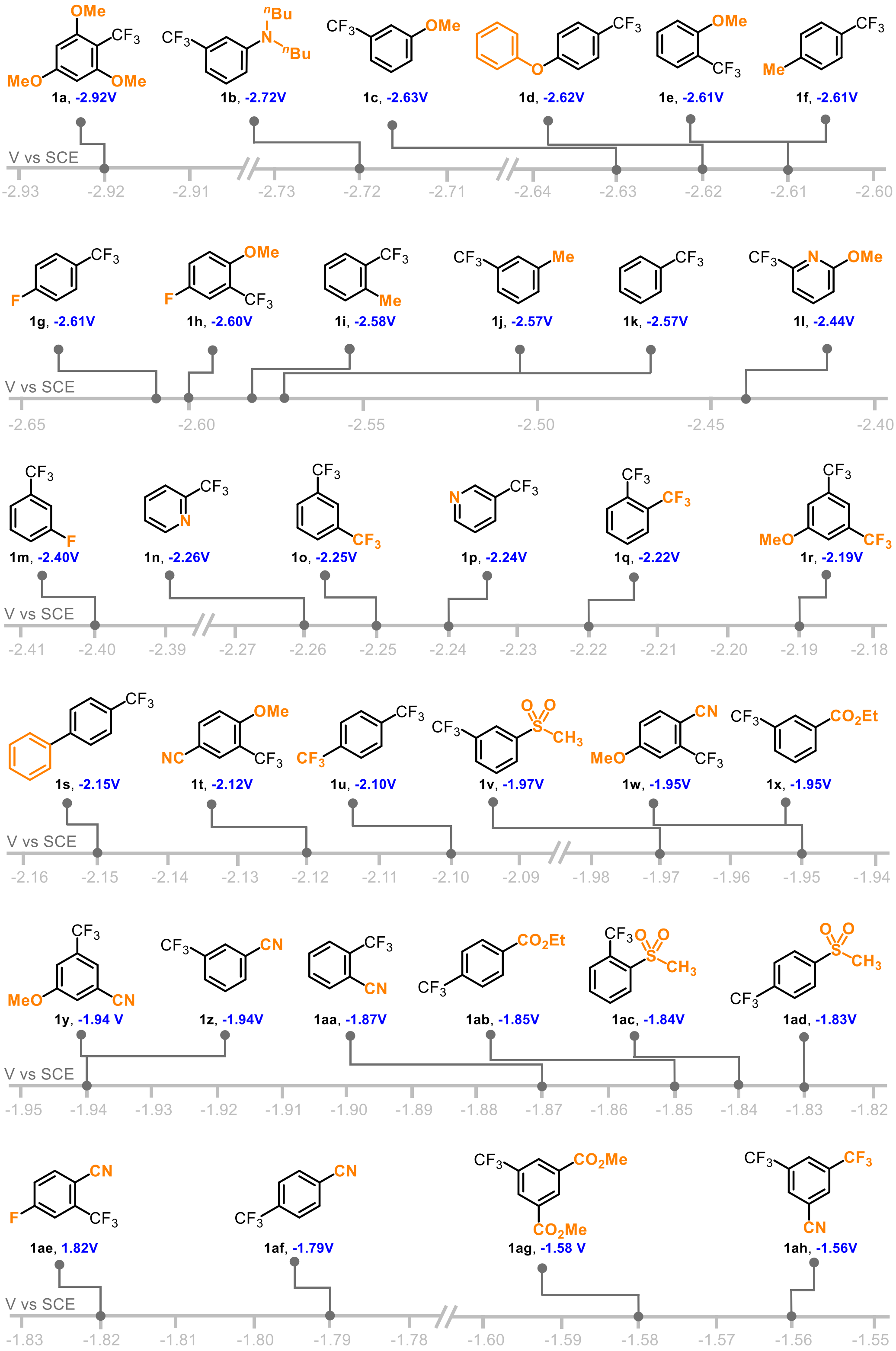
To an oven dried 60 mL Schlenk tube containing stir-bar a mixture of $Pd(TFA)_2$ (0.09 mmol, 30 mg) and 1,10-phenanthroline (0.09 mmol, 17.8 mg) in *n*-butyl vinyl ether (10.0 mL) was stirred at room temperature for 15 min. NEt_3 (0.9 mmol, 125 μL) and Cedrol (3.0 mmol, 469 mg) were added and the reaction mixture was heated at 75 °C under air atmosphere with continuous stirring. After 16 h, the reaction mixture was cooled and filtered through a pad of celite with EtOAc (15 mL). The filtrate was concentrated under reduced pressure and purification by column chromatography provided the vinyl ether as colorless liquid (506 mg, 68%).

R_f = 0.6 (petroleum ether). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 6.43 (dd, *J* = 13.8, 6.3 Hz, 1H), 4.31 (d, *J* = 13.8 Hz, 1H), 3.96 (d, *J* = 6.3 Hz, 1H), 1.92 (td, *J* = 13.0, 6.7 Hz, 1H), 1.86 (dt, *J* = 12.0, 6.0 Hz, 1H), 1.84 – 1.80 (m, 1H), 1.78 (t, *J* = 8.2 Hz, 1H), 1.74 (dd, *J* = 13.4, 5.6 Hz, 1H), 1.70 – 1.59 (m, 2H), 1.56 – 1.48 (m, 1H), 1.49 – 1.43 (m, 1H), 1.41 – 1.33 (m, 2H), 1.28 (s, 4H), 1.21 (s, 3H), 0.96 (s, 3H), 0.84 (dd, *J* = 8.8, 5.7 Hz, 4H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 145.8, 89.9, 81.6, 57.8, 56.9, 54.0, 43.5, 41.5, 41.3, 37.1, 33.0, 31.4, 28.8, 27.1, 26.1, 25.5, 15.7.

4 Cyclic Voltammetry Analysis

Cyclic Voltammetry Analysis of trifluoromethylarenes

CV measurement of trifluoromethylarenes. Cyclic voltammograms were recorded with a CHI760E potentiostat at room temperature in degassed DMF solution in the glovebox ([*n*-Bu_4NPF_6] = 0.1 M, [trifluoromethylarenes] = 5 mM. A Glass Carbon electrode was used as the working electrode and the auxiliary electrode was a Pt sheet. A SCE as reference electrode. The scan rate was 100 mV s^{-1} .



Scheme S4. CV data of trifluoromethylarenes

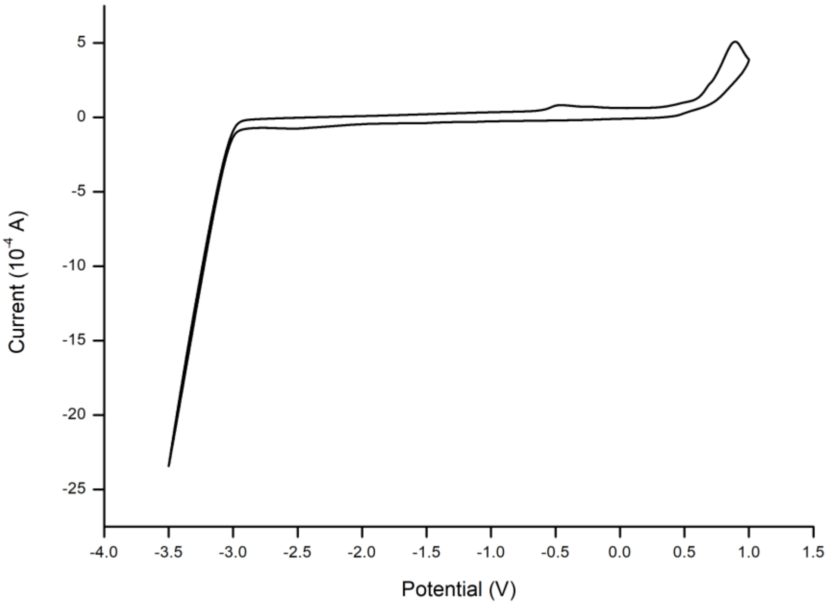


Figure S2. Blank control without substrate

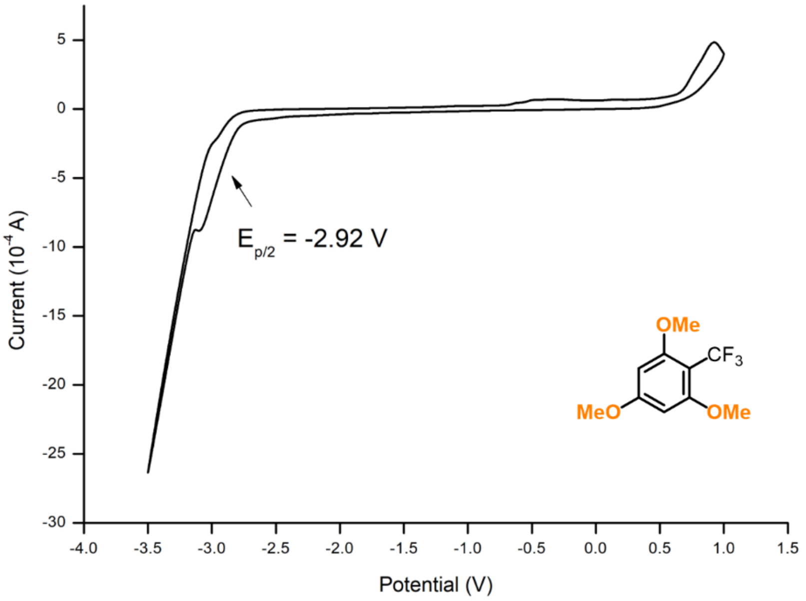


Figure S3. Cyclic Voltammogram of the **1a** in DMF. $E_{p/2}$ (**1a**/**1a**$^{\bullet-}$) = - 2.92 V vs SCE in DMF.

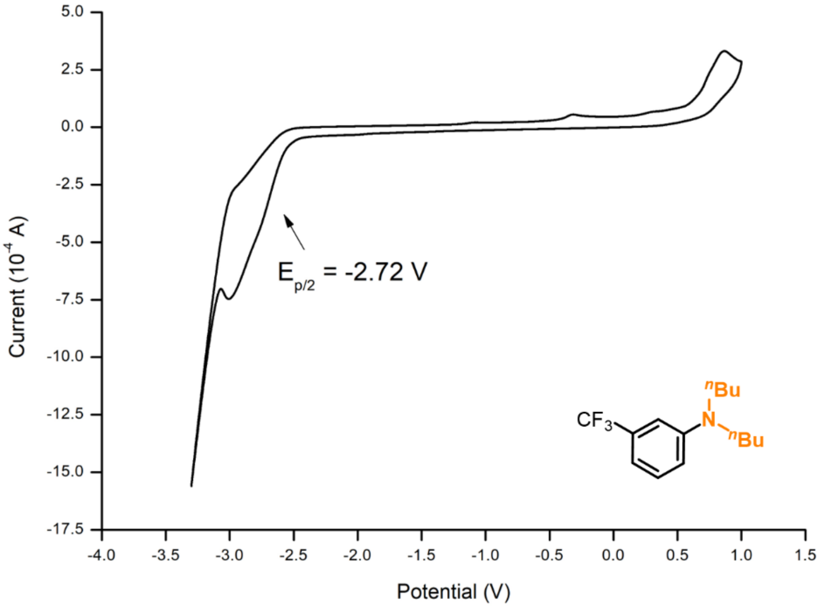


Figure S4. Cyclic Voltammogram of the **1b** in DMF. $E_{p/2}$ (**1b**/**1b**$^{\bullet -}$) = - 2.72 V vs SCE in DMF.

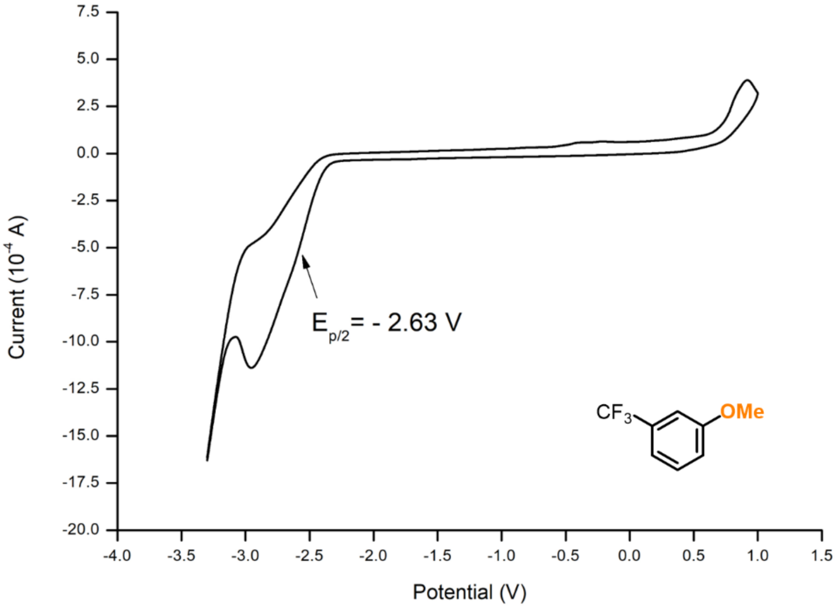


Figure S5. Cyclic Voltammogram of the **1c** in DMF. $E_{p/2}$ (**1c**/**1c**$^{\bullet -}$) = - 2.63 V vs SCE in DMF.

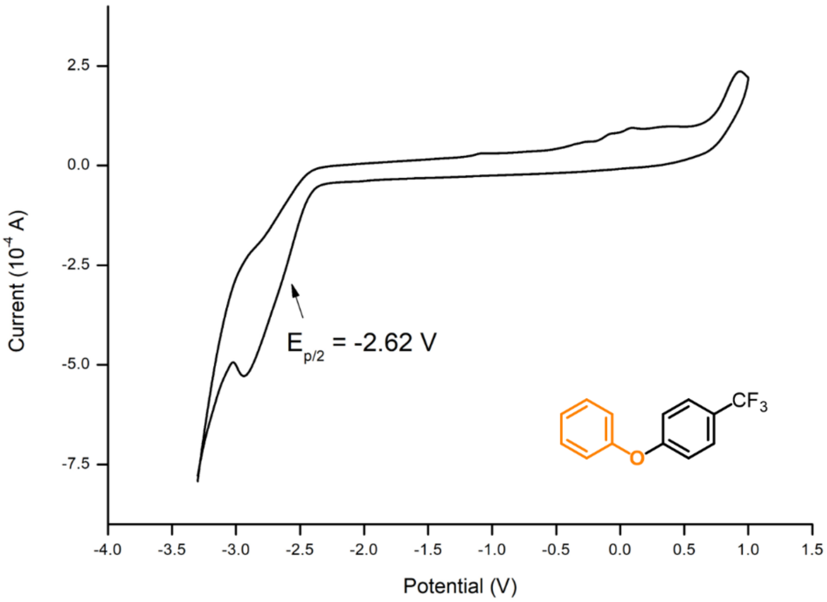


Figure S6. Cyclic Voltammogram of the **1d** in DMF. $E_{p/2}$ (**1d**/**1d**$^{\bullet -}$) = - 2.62 V vs SCE in DMF.

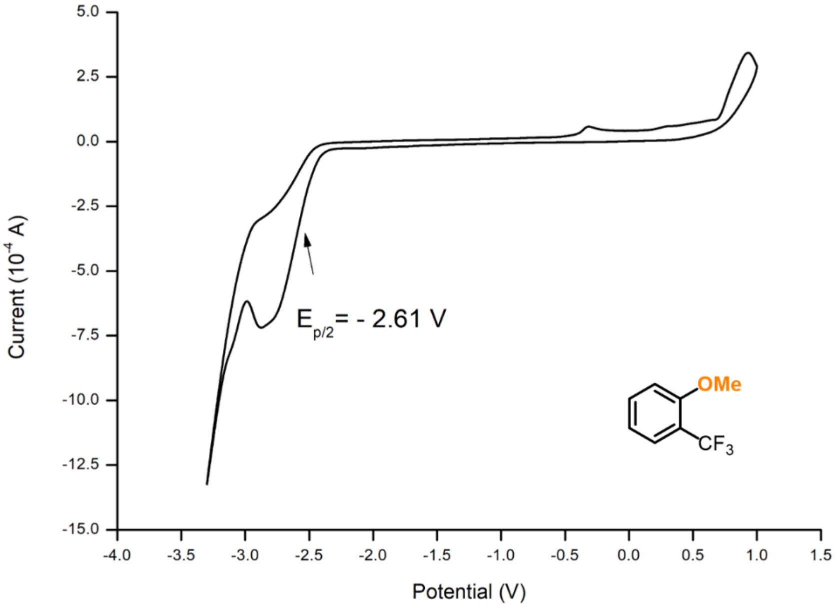


Figure S7. Cyclic Voltammogram of the **1e** in DMF. $E_{p/2}$ (**1e**/**1e**$^{\bullet -}$) = - 2.61 V vs SCE in DMF.

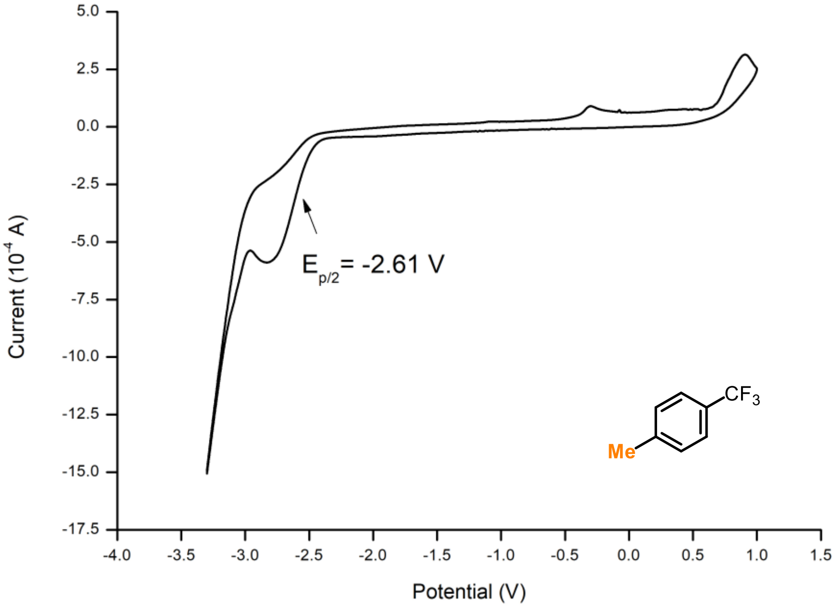


Figure S8. Cyclic Voltammogram of the **1f** in DMF. $E_{p/2}$ (**1f**/**1f**$^{\bullet -}$) = - 2.61 V vs SCE in DMF.

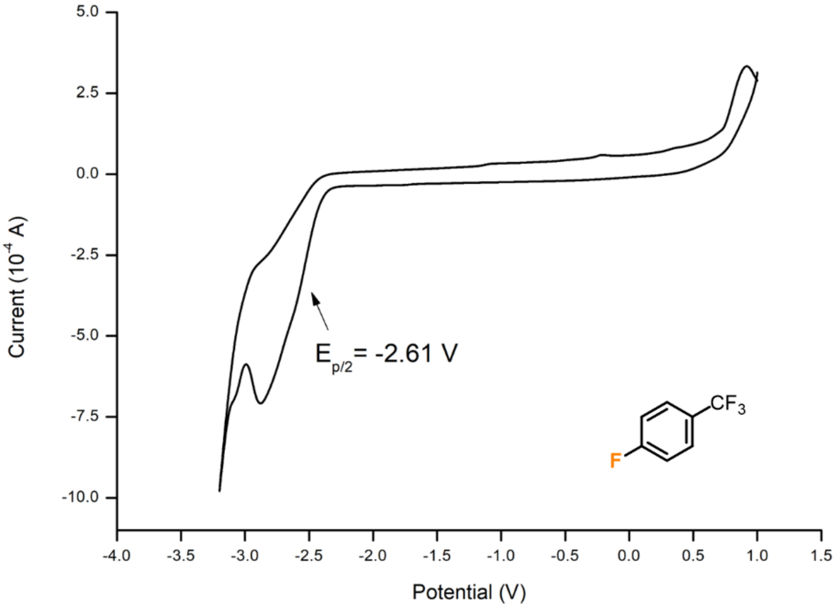


Figure S9. Cyclic Voltammogram of the **1g** in DMF. $E_{p/2}$ (**1g**/**1g**$^{\bullet -}$) = - 2.61 V vs SCE in DMF.

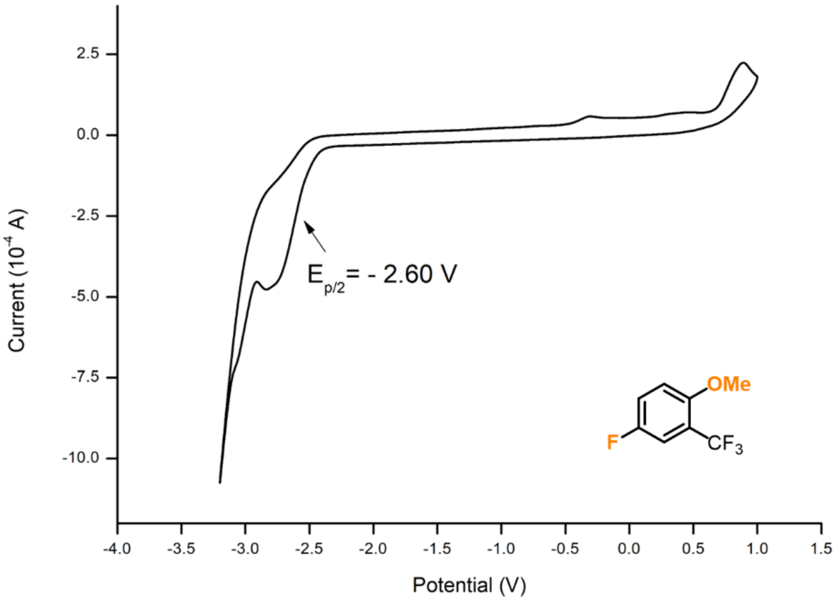


Figure S10. Cyclic Voltammogram of the **1h** in DMF. $E_{p/2}$ (**1h**/**1h**$^{\bullet -}$) = - 2.60 V vs SCE in DMF.

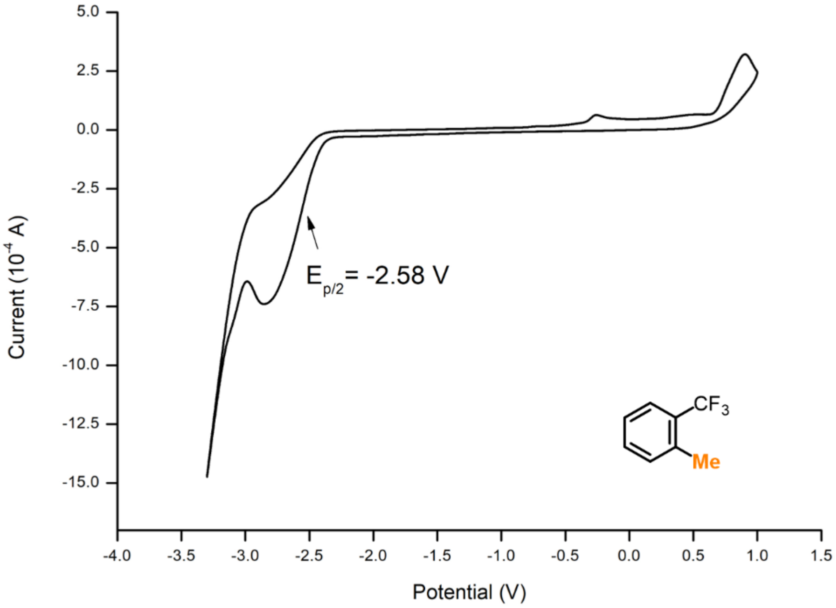


Figure S11. Cyclic Voltammogram of the **1i** in DMF. $E_{p/2}$ (**1i**/**1i**$^{\bullet -}$) = - 2.58 V vs SCE in DMF.

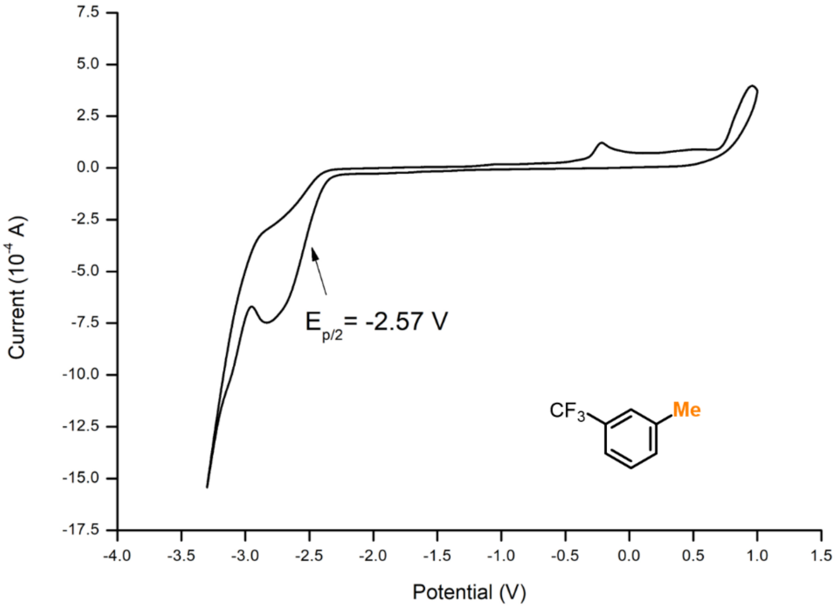


Figure S12. Cyclic Voltammogram of the **1j** in DMF. $E_{p/2}$ (**1j**/**1j**$^{\bullet -}$) = - 2.57 V vs SCE in DMF.

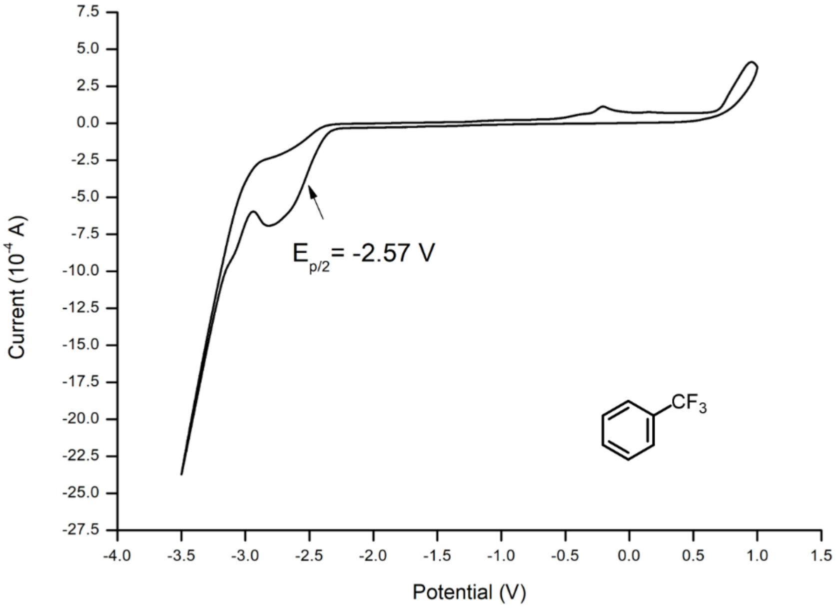


Figure S13. Cyclic Voltammogram of the **1k** in DMF. $E_{p/2}$ (**1k**/**1k**$^{\bullet -}$) = - 2.57 V vs SCE in DMF.

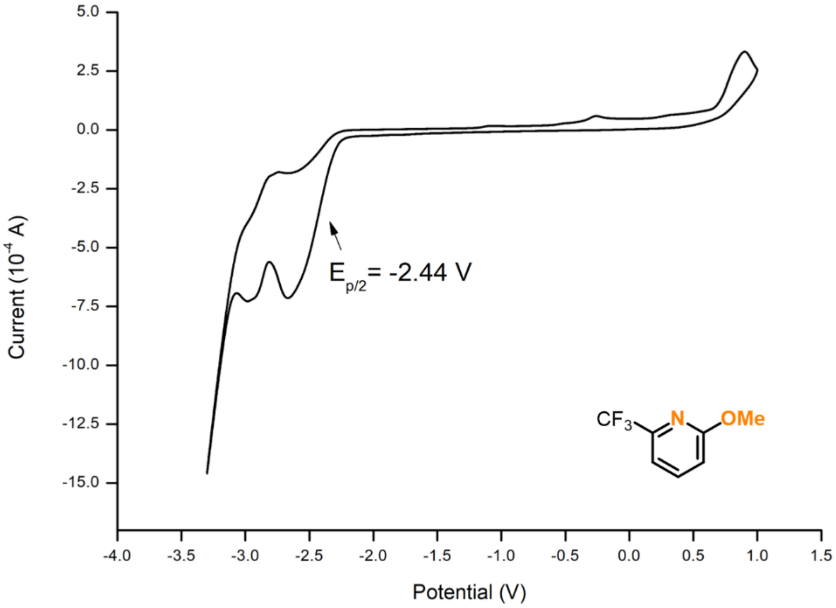


Figure S14. Cyclic Voltammogram of the **1l** in DMF. $E_{p/2}$ (**1l**/**1l**$^{\bullet -}$) = - 2.44 V vs SCE in DMF.

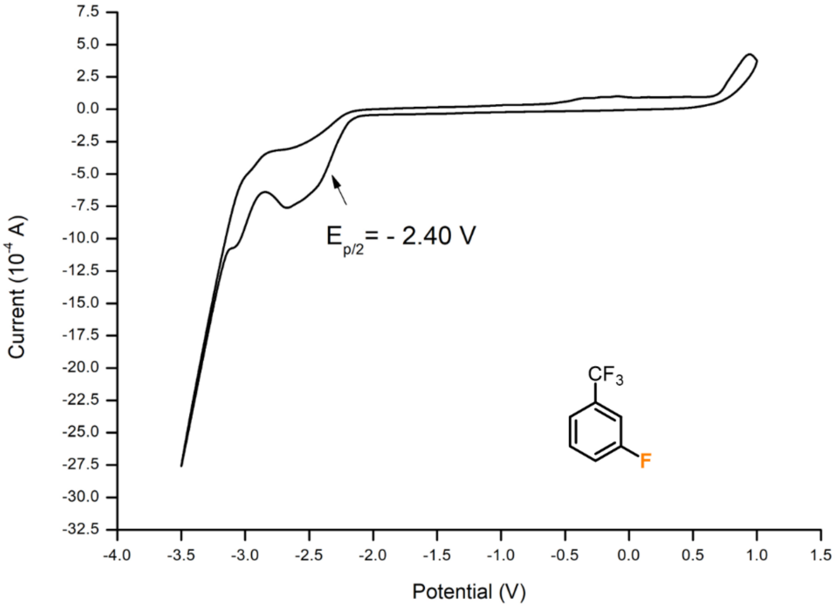


Figure S15. Cyclic Voltammogram of the **1m** in DMF. $E_{p/2}$ (**1m**/**1m**$^{\bullet -}$) = - 2.40 V vs SCE in DMF.

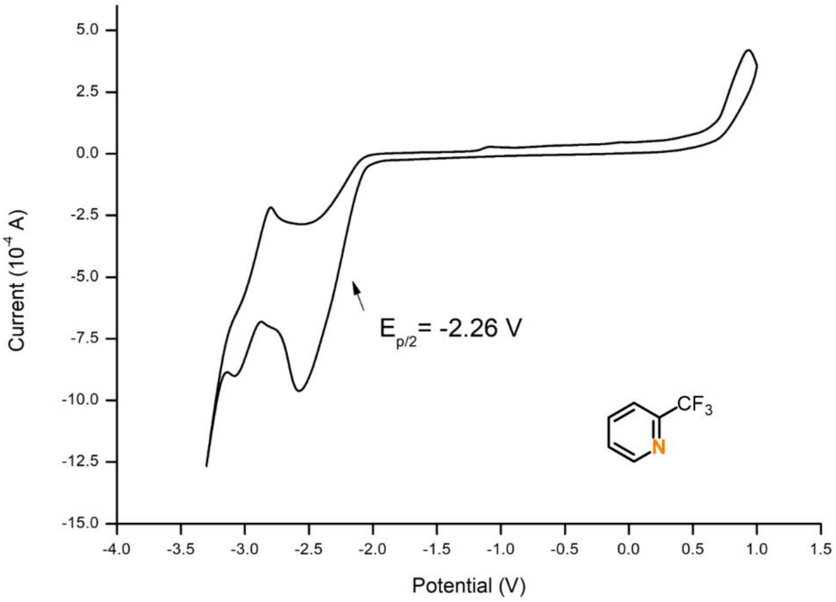


Figure S16. Cyclic Voltammogram of the **1n** in DMF. $E_{p/2}$ (**1n**/**1n$^{\bullet -}$**) = - 2.26 V vs SCE in DMF.

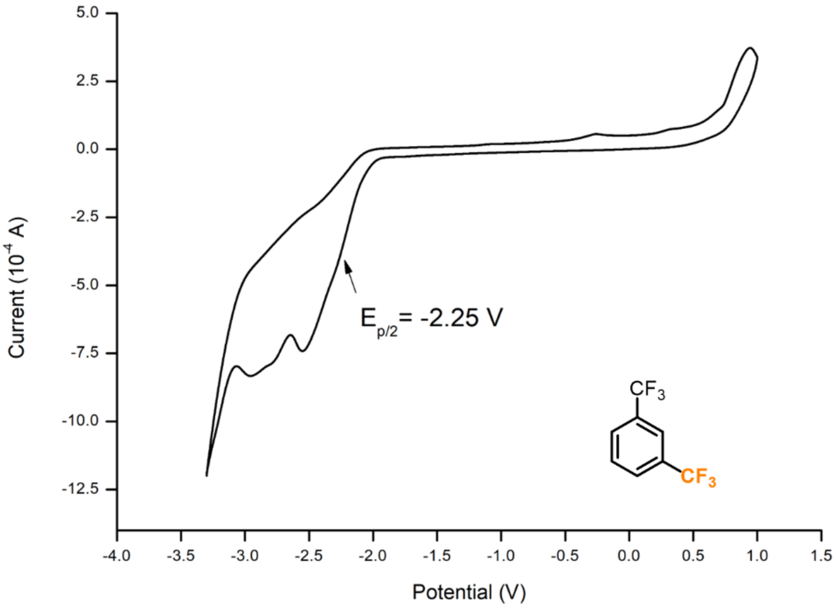


Figure S17. Cyclic Voltammogram of the **1o** in DMF. $E_{p/2}$ (**1o**/**1o$^{\bullet -}$**) = - 2.25 V vs SCE in DMF.

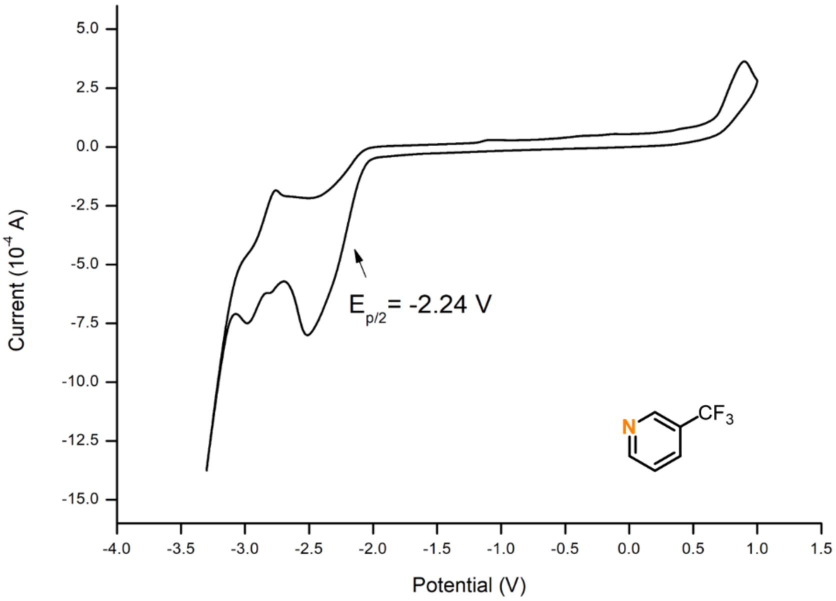


Figure S18. Cyclic Voltammogram of the **1p** in DMF. $E_{p/2}$ (**1p**/**1p**$^{\bullet -}$) = - 2.24 V vs SCE in DMF.

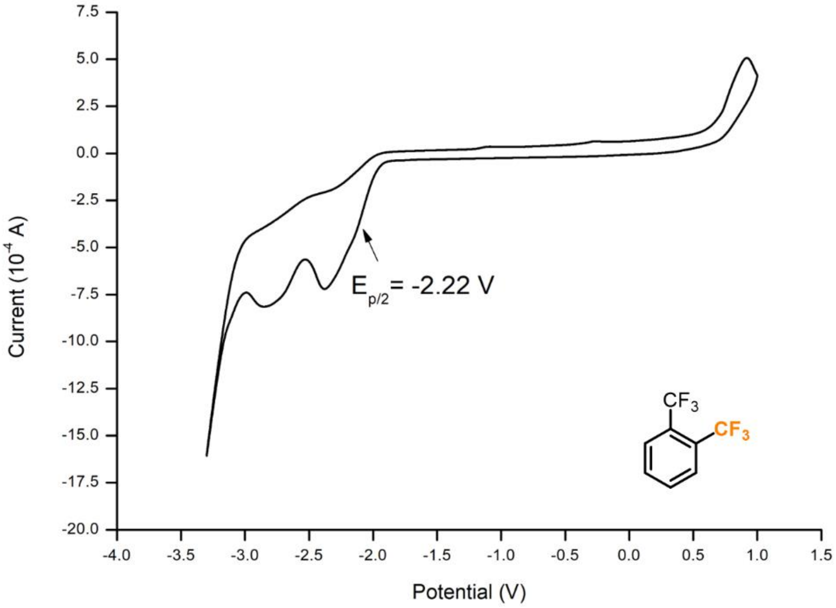


Figure S19. Cyclic Voltammogram of the **1q** in DMF. $E_{p/2}$ (**1q**/**1q**$^{\bullet -}$) = - 2.22 V vs SCE in DMF.

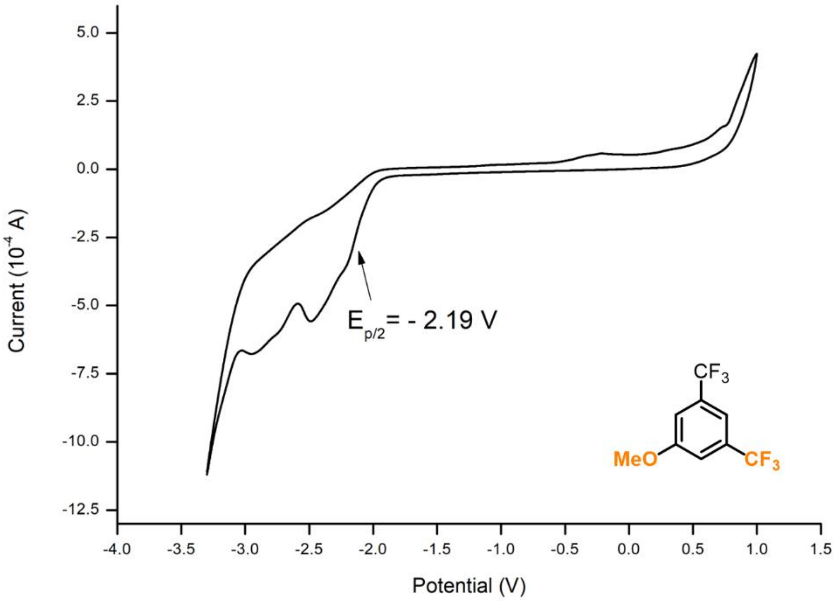


Figure S20. Cyclic Voltammogram of the **1r** in DMF. $E_{p/2}$ (**1r**/**1r**$^{\bullet -}$) = - 2.19 V vs SCE in DMF.

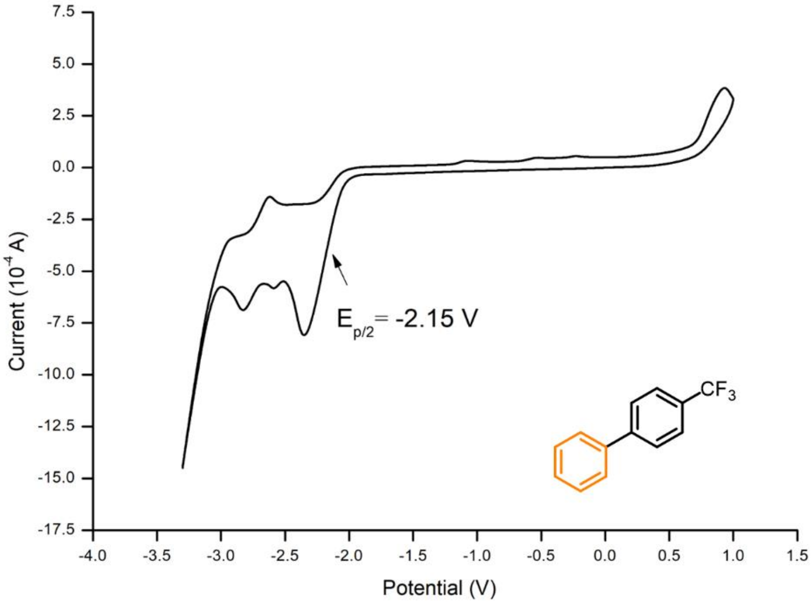


Figure S21. Cyclic Voltammogram of the **1s** in DMF. $E_{p/2}$ (**1s**/**1s**$^{\bullet -}$) = - 2.15 V vs SCE in DMF.

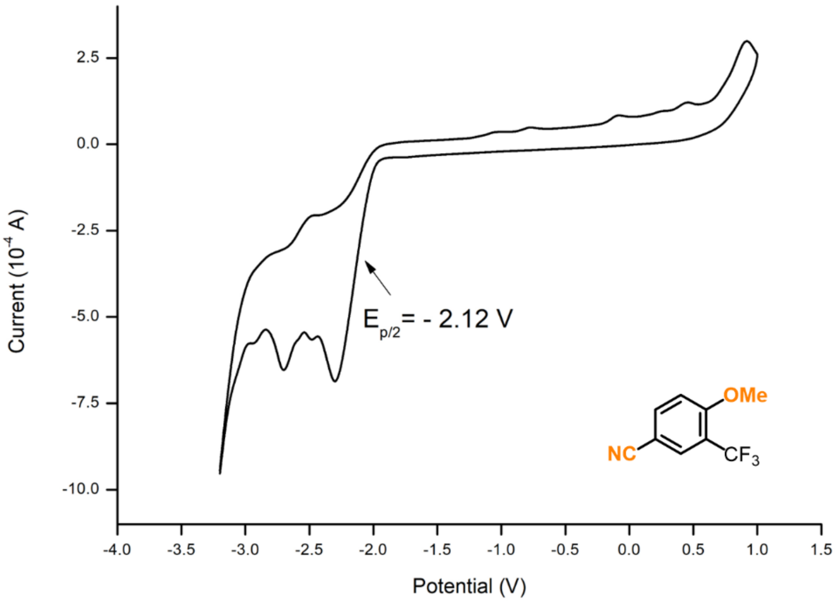


Figure S22. Cyclic Voltammogram of the **1t** in DMF. $E_{p/2}$ (**1t**/**1t**$^{\bullet -}$) = - 2.12 V vs SCE in DMF.

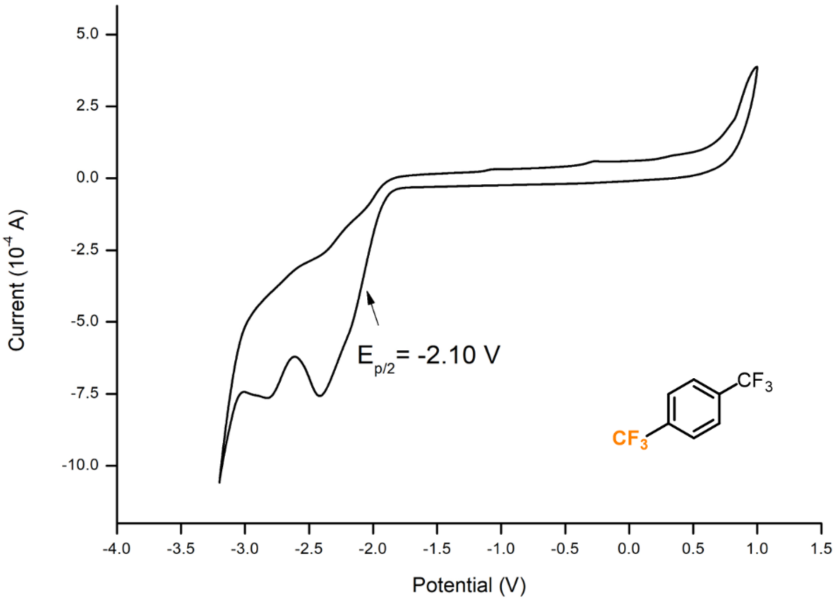


Figure S23. Cyclic Voltammogram of the **1u** in DMF. $E_{p/2}$ (**1u**/**1u**$^{\bullet -}$) = - 2.10 V vs SCE in DMF.

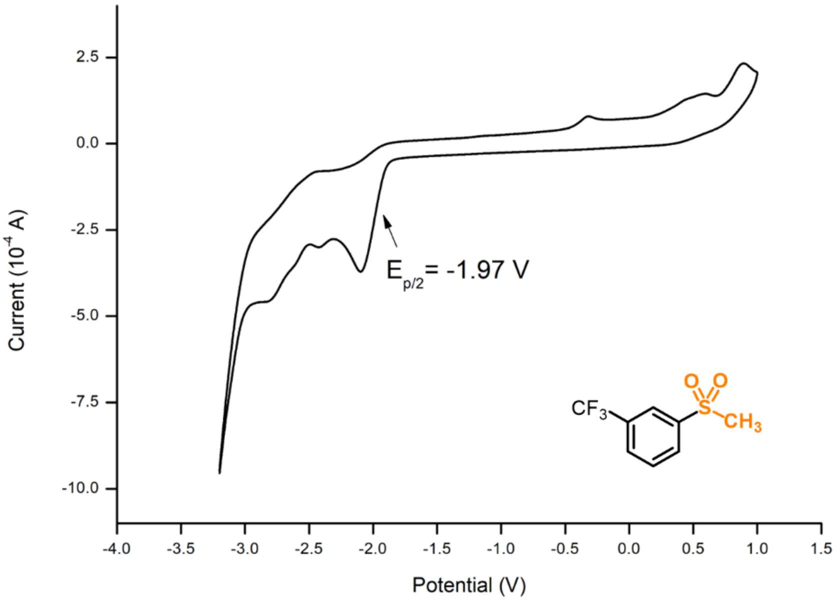


Figure S24. Cyclic Voltammogram of the **1v** in DMF. $E_{p/2}$ (**1v**/**1v**$^{\bullet -}$) = - 1.97 V vs SCE in DMF.

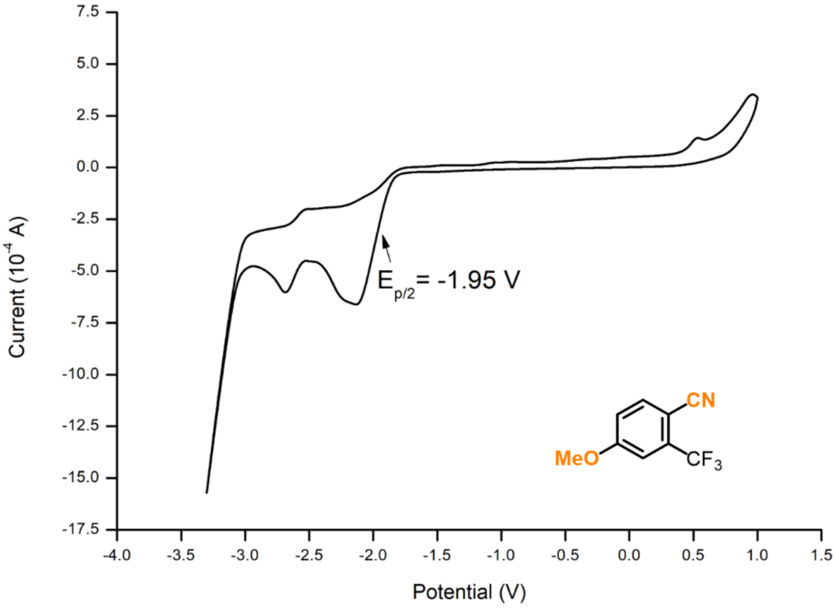


Figure S25. Cyclic Voltammogram of the **1w** in DMF. $E_{p/2}$ (**1w**/**1w**$^{\bullet -}$) = - 1.95 V vs SCE in DMF.

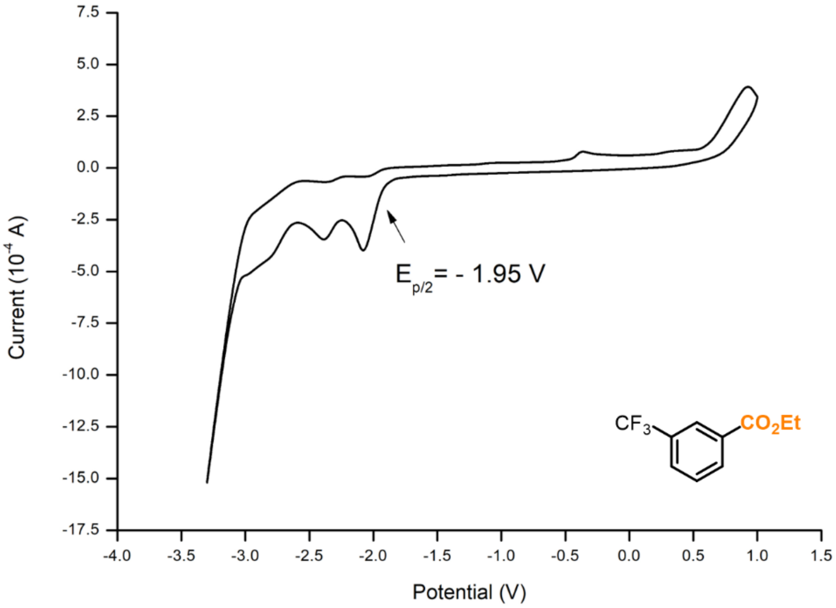


Figure S26. Cyclic Voltammogram of the **1x** in DMF. $E_{p/2}$ (**1x**/**1x**$^{\bullet-}$) = - 1.95 V vs SCE in DMF.

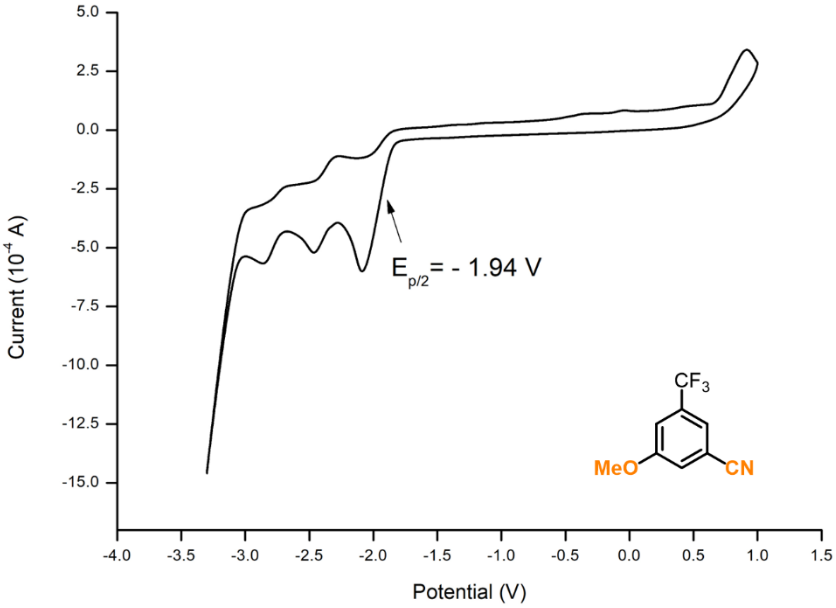


Figure S27. Cyclic Voltammogram of the **1y** in DMF. $E_{p/2}$ (**1y**/**1y**$^{\bullet-}$) = - 1.94 V vs SCE in DMF.

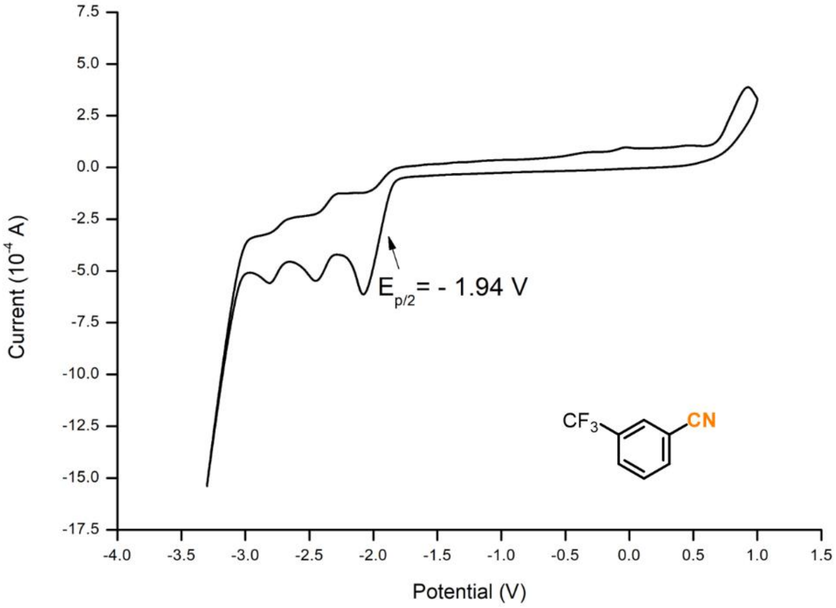


Figure S28. Cyclic Voltammogram of the **1z** in DMF. $E_{p/2}$ (**1z**/**1z**$^{\bullet -}$) = - 1.94 V vs SCE in DMF.

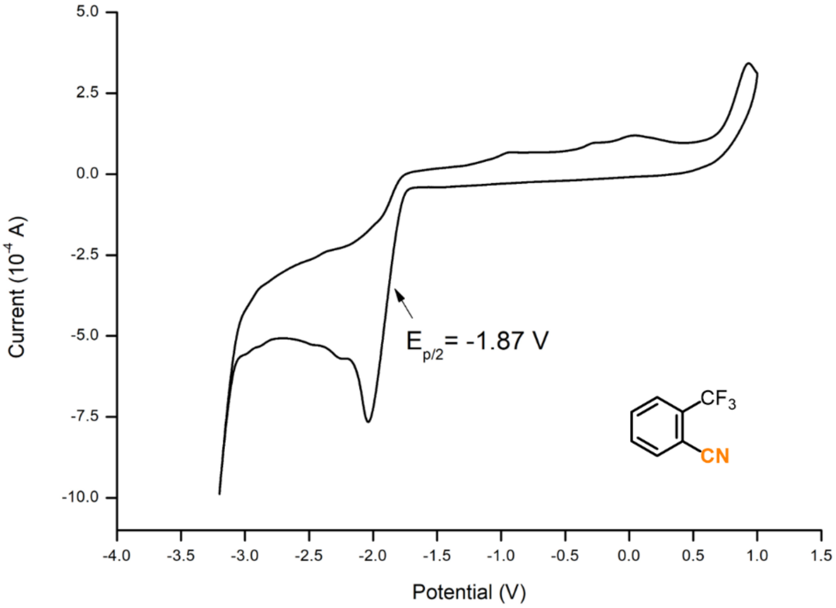


Figure S29. Cyclic Voltammogram of the **1aa** in DMF. $E_{p/2}$ (**1aa**/**1aa**$^{\bullet -}$) = - 1.87 V vs SCE in DMF.

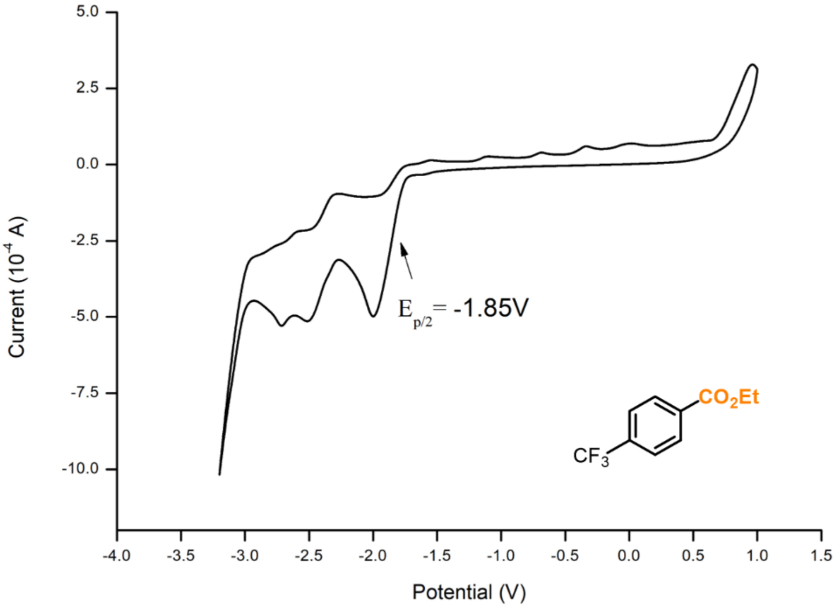


Figure S30. Cyclic Voltammogram of the **1ab** in DMF. $E_{p/2}$ (**1ab**/**1ab**$^{\bullet -}$) = - 1.85 V vs SCE in DMF.

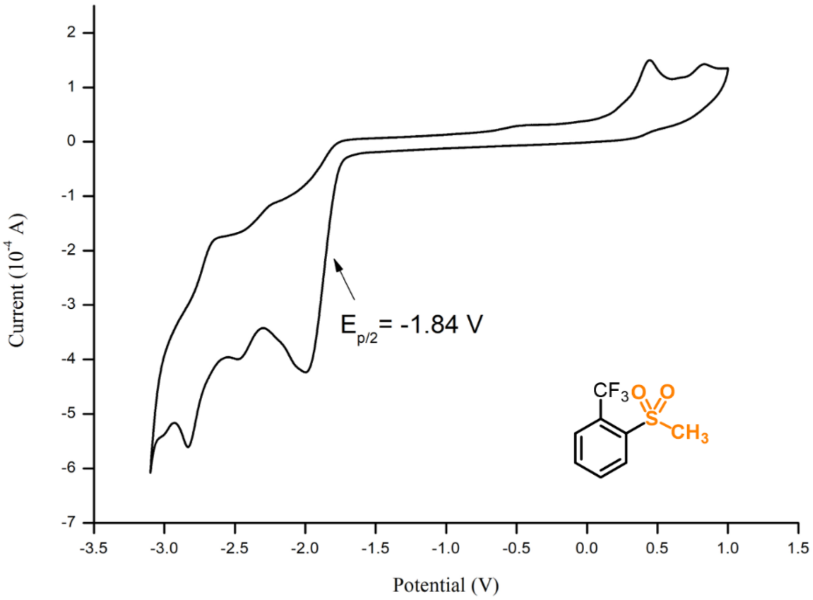


Figure S31. Cyclic Voltammogram of the **1ac** in DMF. $E_{p/2}$ (**1ac**/**1ac**$^{\bullet -}$) = - 1.84 V vs SCE in DMF.

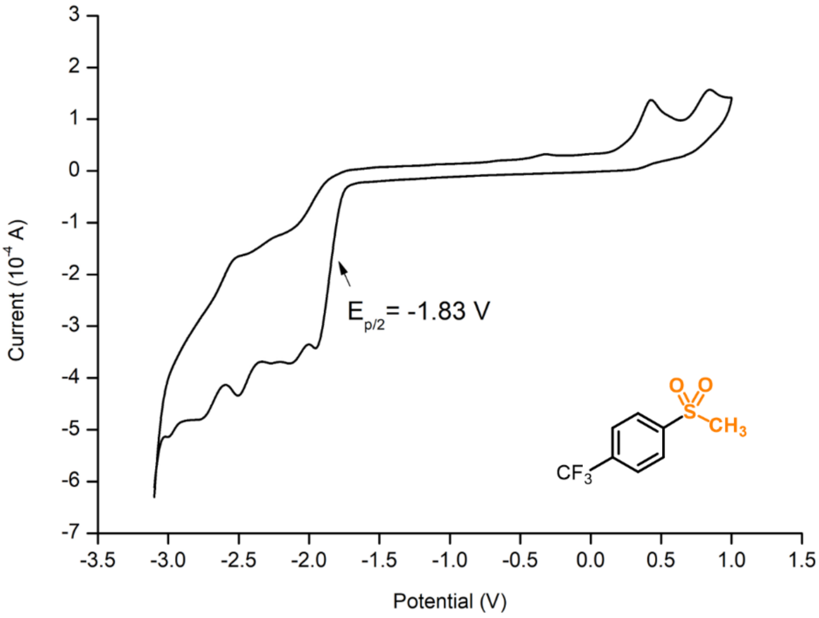


Figure S32. Cyclic Voltammogram of the **1ad** in DMF. $E_{p/2}$ (**1ad**/**1ad$^{\bullet -}$**) = - 1.83 V vs SCE in DMF.

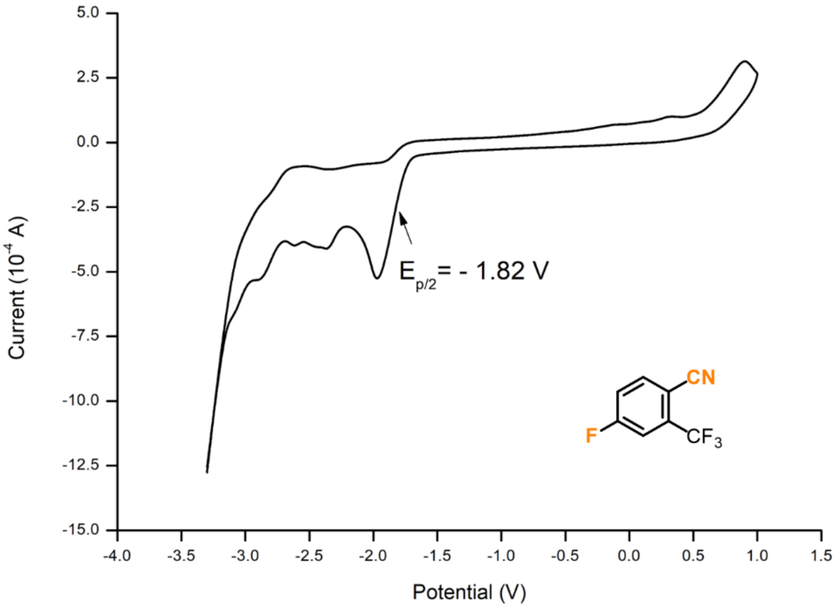


Figure S33. Cyclic Voltammogram of the **1ae** in DMF. $E_{p/2}$ (**1ae**/**1ae$^{\bullet -}$**) = - 1.82 V vs SCE in DMF.

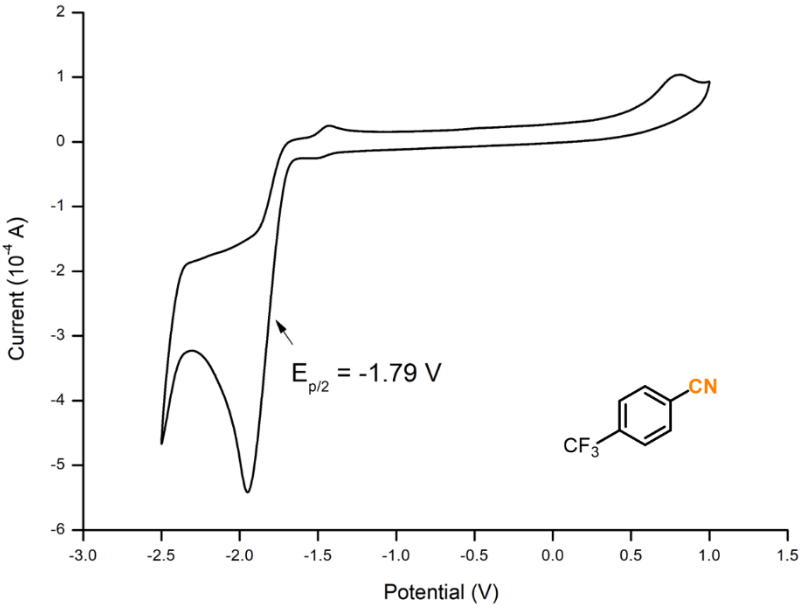


Figure S34. Cyclic Voltammogram of the **1af** in DMF. $E_{p/2}$ (**1af**/**1af**$^{\bullet -}$) = - 1.79 V vs SCE in DMF.

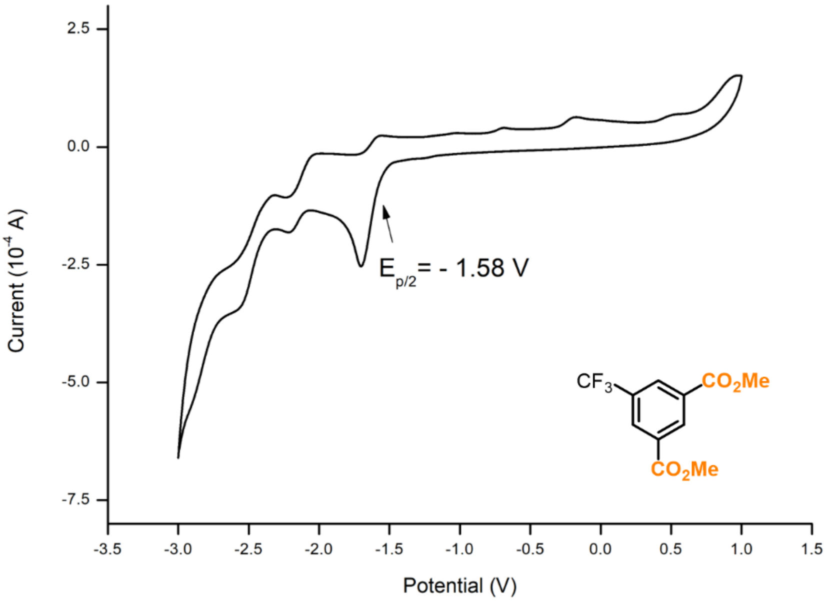


Figure S35. Cyclic Voltammogram of the **1ag** in DMF. $E_{p/2}$ (**1ag**/**1ag**$^{\bullet -}$) = - 1.58 V vs SCE in DMF.

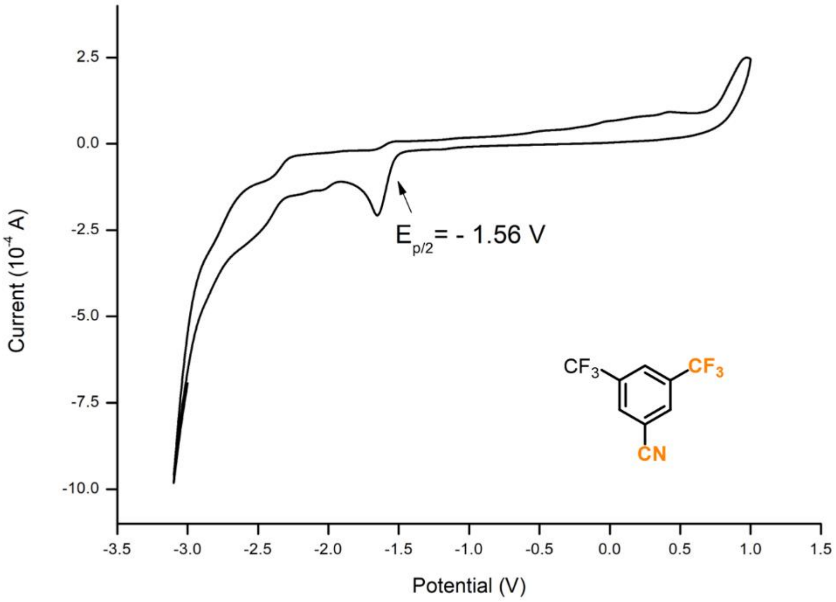


Figure S36. Cyclic Voltammogram of the **1ah** in DMF. $E_{p/2}$ (**1ah**/**1ah**$^{\bullet -}$) = - 1.56 V vs SCE in DMF.

Cyclic Voltammetry Analysis of thiophenol anion

CV measurement of trifluoromethylarenes. Cyclic voltammograms were recorded with a CHI760E potentiostat at room temperature in degassed DMF solution in the glovebox ([n-Bu_4NPF_6] = 0.1 M, [thiophenol anion] = 5 Mm (generated in situ by the deprotonation of the 2b with 2 equiv. NaOH). A Glass Carbon electrode was used as the working electrode and the auxiliary electrode was a Pt sheet. A SCE as reference electrode. The scan rate was 100 mV s^{-1} .

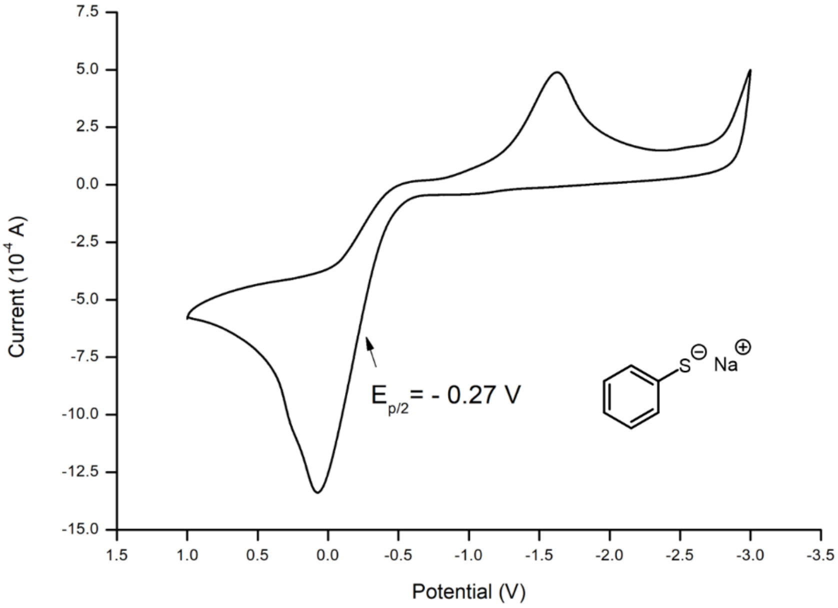


Figure S37. The cyclic voltammogram of the **2b** anions vs SCE in DMF.

With this data in hand, we calculated the redox potential of the excited **2b** anion employing the following equation:[24]

$$E_{p/2}(\mathbf{2b}^{\bullet}/\,\mathbf{2b}^{-\,*}) = E_{p/2}(\mathbf{2b}^{\bullet}/\,\mathbf{2b}^{-}) - E_{0\text{-}0}(\mathbf{2b}^{-*}/\,\mathbf{2b}^{-})$$

$$E_{p/2}(\mathbf{2b}^{\bullet}/\,\mathbf{2b}^{-}) = -0.27 \text{ V vs. SCE}$$

In the absence of vibrational structures, E0-0 can be roughly estimated from the absorption spectrum.[25] This corresponds to 390 nm, which translates into an $E_{0\text{-}0}(\mathbf{2b}^{-\,*}/\,\mathbf{2b}^{-})$ of 3.17 eV for the **2b** anion.

$$E_{p/2}(\mathbf{2b}^{\bullet}/\,\mathbf{2b}^{-\,*}) = E_{p/2}(\mathbf{2b}^{\bullet}/\,\mathbf{2b}^{-}) - E_{0\text{-}0}(\mathbf{2b}^{-*}/\,\mathbf{2b}^{-}) = -0.27 - 3.17 = -3.44 \text{ V}$$

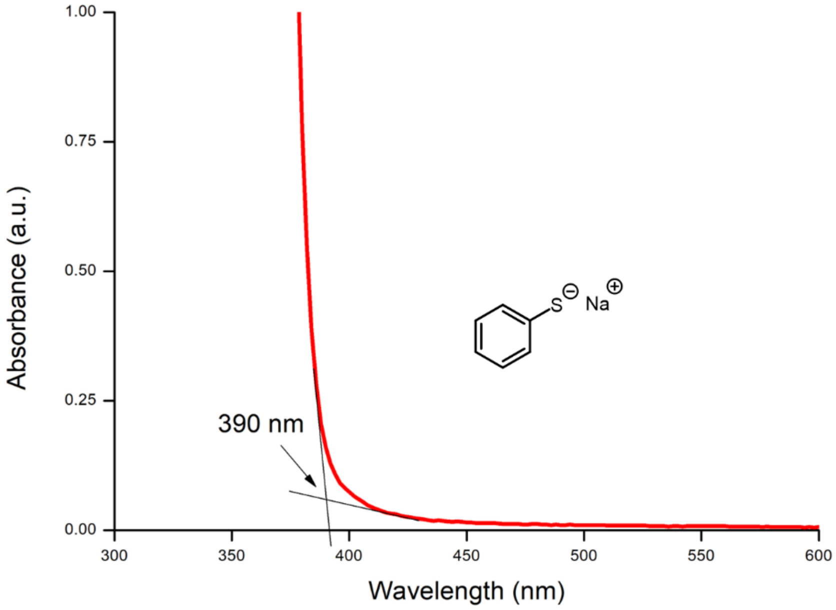


Figure S38. UV/vis absorption spectra of **2b** anion

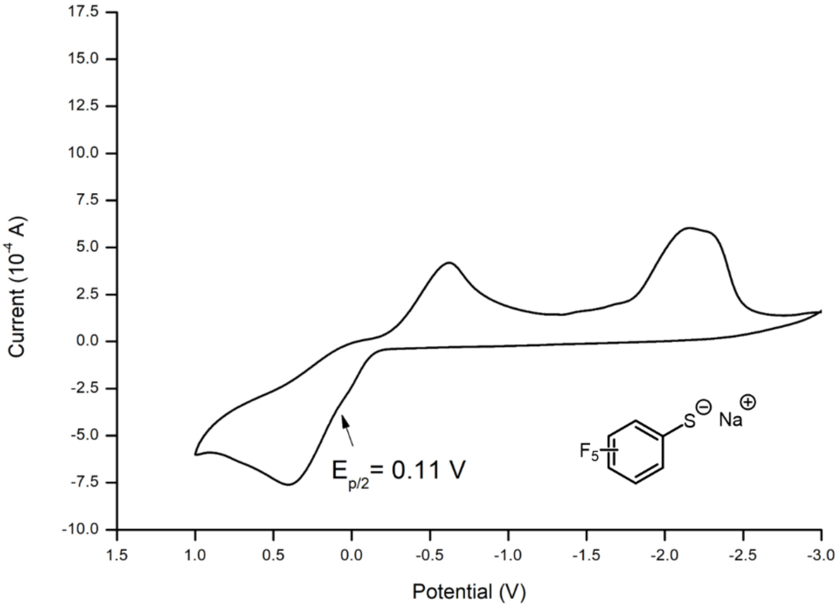


Figure S39. The cyclic voltammogram of the **2d** anions vs SCE in DMF.

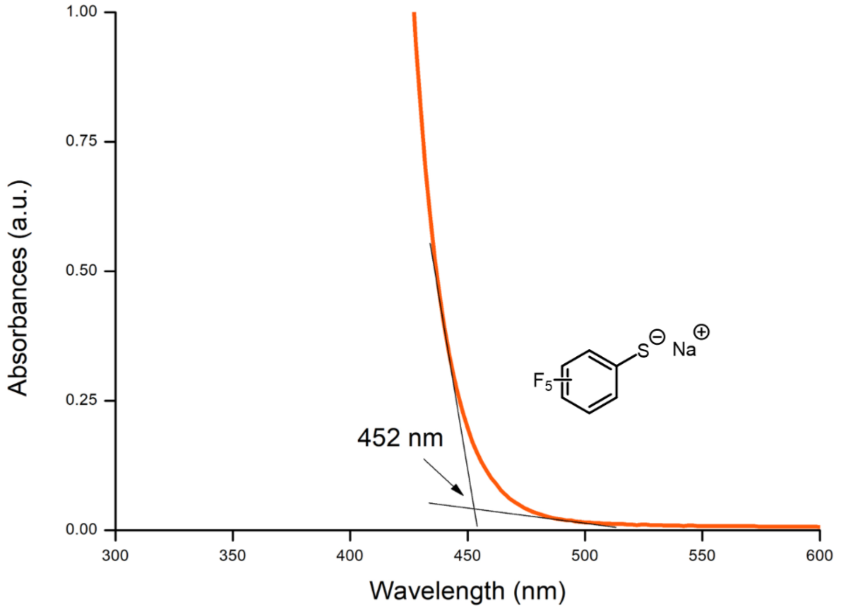
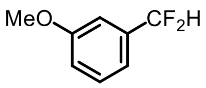


Figure S40. UV/vis absorption spectra of **2d** anion

$$E_{p/2}(\mathbf{2d}^{\bullet} / \mathbf{2d}^{-*}) = E_{p/2}(\mathbf{2d}^{\bullet} / \mathbf{2d}^{-}) - E_{0\text{-}0}(\mathbf{2d}^{-*} / \mathbf{2d}^{-}) = 0.11 - 2.74 = -2.63\ \text{V}$$

5 Experimental Procedures and Spectral Data

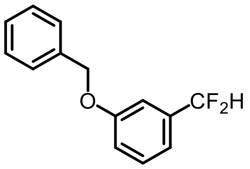
1-(Difluoromethyl)-3-methoxybenzene (3a)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in an 8.0 mL sealed vial tube. 1-methoxy-3-(trifluoromethyl)benzene (**1c**) (87 μL, 0.60 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Afford 1-(difluoromethyl)-3-methoxybenzene (**3a**). Due to the low boiling point of the product, NMR yield based on quantitative fluorine NMR is given, using (trifluoromethoxy)benzene as an internal standard yielded 96%. Product identity was confirmed by ^{19}F NMR. ^{19}F NMR (565 MHz, $CDCl_3$) δ -110.74 (d, *J* = 56.1 Hz, 2F).

Spectral data was consistent with literature.[25]

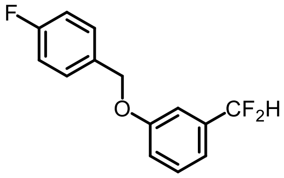
1-(Benzyloxy)-3-(difluoromethyl)benzene (3b)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 µL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 µL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-(benzyloxy)-3-(trifluoromethyl)benzene (**1ai**) (151 mg, 0.60 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (100:1 (v/v)), to afford 91 mg 1-(benzyloxy)-3-(difluoromethyl)benzene (**3b**) as a white solid (65% yield). Spectral data was consistent with literature.[25]

R_f = 0.2 (Petroleum ether/EtOAc = 100:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.44 (d, J = 7.3 Hz, 2H), 7.42 – 7.32 (m, 4H), 7.13 (s, 1H), 7.12 – 7.05 (m, 2H), 6.61 (t, J = 56.5 Hz, 1H), 5.10 (s, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 159.2 , 136.7 , 136.0 , 130.1 , 128.8 , 128.3 , 127.7 , 118.3 (t, J = 6.4 Hz), 117.5 , 114.7 (t, J = 239.1 Hz), 112.0 (t, J = 6.1 Hz), 70.4. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -110.75 (d, J = 56.5 Hz, 2F).

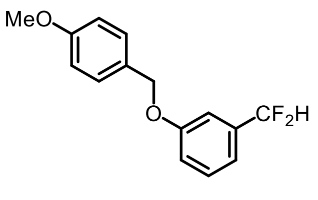
1-(Difluoromethyl)-3-((4-fluorobenzyl)oxy)benzene (3c)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-((4-fluorobenzyl)oxy)-3-(trifluoromethyl)benzene (**1aj**) (0.6 mmol, 162 mg, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (40:1 (v/v)), to afford 130 mg 1-(difluoromethyl)-3-((4-fluorobenzyl)oxy)benzene (**3c**) as a colorless liquid (86% yield).

R_f = 0.3 (Petroleum ether/EtOAc = 40:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.41 (dd, J = 8.2, 5.6 Hz, 2H), 7.39 – 7.34 (m, 1H), 7.14 – 7.03 (m, 5H), 6.62 (t, *J* = 56.5 Hz, 1H), 5.05 (s, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.7 (d, *J* = 246.8 Hz), 159.0, 136.0 (t, *J* = 21.9 Hz), 132.4, 130.1, 129.5 (d, *J* = 7.9 Hz), 118.4 (t, *J* = 6.2 Hz), 117.5, 115.7 (d, *J* = 21.6 Hz), 114.6 (t, *J* = 239.2 Hz), 111.8, 69.6. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -110.75 (d, 2F, *J* = 56.4 Hz), -113.88 – -113.97 (m, 1F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{11}F_3ONa^+$, 275.0654, found, 275.0661.

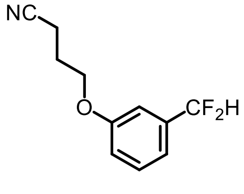
1-(Difluoromethyl)-3-((4-methoxybenzyl)oxy)benzene (3d)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-((4-methoxybenzyl)oxy)-3-(trifluoromethyl)benzene (**1ak**) (0.6 mmol, 170 mg, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (100:1 (v/v)), to afford 81 mg 1-(difluoromethyl)-3-((4-methoxybenzyl)oxy)benzene (**3d**) as a white solid (51% yield).

R*f* = 0.3 (Petroleum ether/EtOAc = 100:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.40 – 7.31 (m, 3H), 7.12 (s, 1H), 7.08 (dd, *J* = 14.0, 8.0 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.61 (t, *J* = 56.5 Hz, 1H), 5.01 (s, 2H), 3.82 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 159.7, 159.2, 135.9 (t, *J* = 26.2 Hz), 130.09, 129.5, 128.6, 118.1 (t, *J* = 6.3 Hz), 117.5, 114.7 (t, *J* = 241.6 Hz), 114.2, 111.8 (t, *J* = 6.2 Hz), 70.1, 55.5. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -110.67 (d, *J* = 56.5 Hz, 2F). HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{15}H_{15}F_2O_2^+$, 265.1035, found, 265.1035.

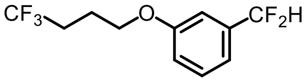
4-(3-(Difluoromethyl)phenoxy)butanenitrile (3e)



In a N$_2$ glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 4-(3-(trifluoromethyl)phenoxy)butanenitrile (**1al**) (138 mg, 0.60 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (5:1 (v/v)), to afford 103 mg 4-(3-(difluoromethyl)phenoxy)butanenitrile (**3e**) as a colorless liquid (81% yield).

R*f* = 0.2 (petroleum ether/EtOAc = 5:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.39-7.36 (m, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.04 (s, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.61 (t, *J* = 56.5 Hz, 1H), 4.12 (t, *J* = 5.7 Hz, 2H), 2.61 (t, *J* = 7.1 Hz, 2H), 2.21 – 2.13 (m, 2H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 158.7 , 136.1 , 130.2 , 119.2 , 118.6 (t, *J* = 6.2 Hz), 117.1 , 114.5(t, *J* = 239.3 Hz), 111.5 (t, *J* = 6.1 Hz), 65.6 , 25.6 , 14.4 . **^{19}F NMR (565 MHz, CDCl$_3$)** δ -110.85 (d, *J* = 56.5 Hz, 2F). HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{11}H_{11}F_2NONa^+$, 234.0701, found, 234.0710.

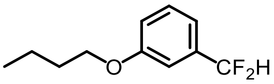
1-(Difluoromethyl)-3-(4,4,4-trifluorobutoxy)benzene (3f)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-(4,4,4-trifluorobutoxy)-3-(trifluoromethyl)benzene (**1am**) (163 mg, 0.60 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (20:1 (v/v)), to afford 127 mg 1-(difluoromethyl)-3-(4,4,4-trifluorobutoxy)benzene (**3f**) as a colorless liquid (83% yield).

R*f* = 0.5 (Petroleum ether: EtOAc = 20:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.38-7.35 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.03 (s, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.61 (t, *J* = 56.5 Hz, 1H), 4.06-4.04 (m, 2H), 2.40 – 2.24 (m, 2H), 2.15 – 1.97 (m, 2H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 159.0, 136.0 (t, *J* = 22.3 Hz), 130.1, 127.2 (q, *J* = 241.1 Hz), 118.4(t, *J* = 6.3 Hz), 117.1, 114.6 (t, *J* = 239.2 Hz), 111.4 (t, *J* = 6.2 Hz), 66.4, 30.9 (q, *J* = 29.1 Hz), 22.3 (q, *J* = 3.0 Hz). **^{19}F NMR (565 MHz, CDCl$_3$)** δ -66.33 (t, 3F, *J* = 10.8 Hz), -110.78 (d, *J* = 56.5 Hz, 2F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{12}F_5O^+$, 255.0803, found, 255.0802.

Butoxy-3-(difluoromethyl)benzene (3g)

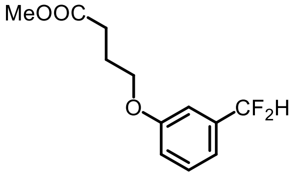


In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-butoxy-3-(trifluoromethyl)benzene (**1an**) (0.6 mmol, 131 mg, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether (40:1 (v/v)). The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate, to afford 131 mg butoxy-3-(difluoromethyl)benzene (**3g**) as a white solid (88% yield).

R*f* = 0.3 (Petroleum ether/EtOAc = 40:1). **NMR Spectroscopy: ^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.38 – 7.31 (m, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 7.03 (s, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.60 (t, *J* = 56.5 Hz, 1H), 3.99 (t, *J* = 6.5 Hz, 2H), 1.78 (dt, *J* = 14.4, 6.5 Hz, 2H), 1.49 (dt, *J* = 14.8, 7.5 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 159.5, 135.8 (t, *J* = 22.2 Hz), 123.0, 117.7 (t, *J* = 6.3 Hz), 117.2 (t, *J* = 1.8 Hz), 114.8 (t, *J* = 238.9 Hz), 111.4 (t, *J* = 6.1 Hz), 68.0, 31.4, 19.4, 14.0. **^{19}F NMR (470**

MHz, $CDCl_3$) δ -110.59 (d, *J* = 56.5 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{11}H_{14}F_2ONa^+$, 223.0905, found, 223.0913.

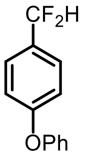
Methyl 4-(3-(difluoromethyl)phenoxy)butanoate (3h)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 µL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 µL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. Methyl 4-(3-(trifluoromethyl)phenoxy)butanoate (**1ao**) (157 mg, 0.60 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (20:1 (v/v)), to afford 73 mg methyl 4-(3-(difluoromethyl)phenoxy)butanoate (**3h**) as a yellow liquid (50% yield).

R_f = 0.2 (Petroleum ether: EtOAc = 20:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.36-7.33 (m, 1H) , 7.12 – 6.91 (m, 3H), 6.60 (t, *J* = 56.5 Hz, 1H), 4.04 (t, *J* = 6.0 Hz, 2H), 3.70 (s, 3H), 2.54 (t, *J* = 7.2 Hz, 2H), 2.17 – 2.09 (m, 2H).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.7 , 159.2 , 135.9 (t, *J* = 22.2 Hz), 130.0 , 118.0 (t, *J* = 6.3 Hz), 117.1 (t, *J* = 1.7 Hz), 114.7 (t, *J* = 239.0 Hz), 111.4 (t, *J* = 6.0 Hz), 67.0 , 51.8 , 30.6 , 24.7 . **^{19}F NMR (565 MHz, $CDCl_3$)** δ -110.69 (d, *J* = 56.5 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{12}H_{14}F_2O_3Na^+$, 267.0803, found, 267.0813.

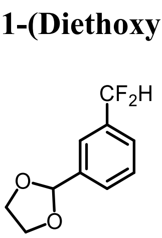
1-(Difluoromethyl)-4-phenoxybenzene (3i)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-phenoxy-4-(trifluoromethyl)benzene (**1d**) (143 mg, 0.60 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether, to afford 90 mg 1-(difluoromethyl)-4-phenoxybenzene (**3i**) as a colorless liquid (68% yield).

R_f = 0.2 (Petroleum ether). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.35 (m, 2H), 7.22 – 7.15 (m, 1H), 7.06 (d, *J* = 8.1 Hz, 4H), 6.64 (t, *J* = 56.6 Hz, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 159.8, 156.4, 130.1, 129.1 (t, *J* = 22.8 Hz), 127.5 (t, *J* = 6.0 Hz), 124.3, 119.8, 118.4, 114.8 (t, *J* = 238.1 Hz). **^{19}F NMR (565 MHz, $CDCl_3$)** δ -108.95 (d, *J* = 56.8 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{13}H_{10}F_2ONa^+$, 243.0592, found, 243.0589.

1-(Diethoxymethyl)-3-(difluoromethyl)benzene (3j)

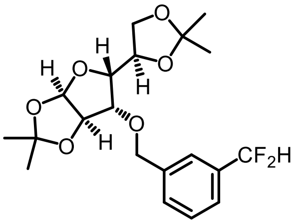


In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 2-(3-(trifluoromethyl)phenyl)-1,3-

dioxolane (**1ap**) (131 mg, 0.60 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (10:1 (v/v)), to afford 76 mg 1-(diethoxymethyl)-3-(difluoromethyl)benzene (**3j**) as a colorless liquid (63% yield).

R_f = 0.3 (Petroleum ether: EtOAc = 10:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.64 (s, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.50 – 7.45 (m, 1H), 6.66 (t, *J* = 56.4 Hz, 1H), 5.85 (s, 1H), 4.18 – 4.11 (m, 2H), 4.08 – 4.01 (m, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 139.0, 134.7 (t, *J* = 22.4 Hz), 129.0, 129.0, 126.4 (t, *J* = 5.3 Hz), 123.9 (t, *J* = 6.2 Hz), 114.7 (t, *J* = 239.2 Hz), 103.2, 65.5.**^{19}F NMR (565 MHz, $CDCl_3$)** δ -110.83 (d, *J* = 56.8 Hz, 2F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{10}H_{11}F_2O_2^+$, 201.0722, found, 201.0730.

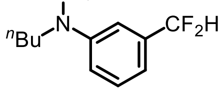
(3a*R*,5*R*,6*S*,6a*R*)-6-((3-(difluoromethyl)benzyl)oxy)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxole (3k)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. (3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-((3-(trifluoromethyl) benzyl) oxy)tetrahydrofuro [2,3-*d*][1,3]dioxole (**1aq**) (251 mg, 0.60 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (10:1 (v/v)), to afford 125 mg (3a*R*,5*R*,6*S*,6a*R*)-6-((3-(difluoromethyl)benzyl)oxy)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxole (**3k**) as a yellow liquid (52% yield).

R_f = 0.2 (Petroleum ether: EtOAc = 10:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.53 (s, 1H), 7.47 – 7.39 (m, 3H), 6.64 (t, *J* = 56.4 Hz, 1H), 6.02 – 5.83 (m, 1H), 4.80 – 4.65 (m, 2H), 4.64 – 4.55 (m, 1H), 4.38 (q, *J* = 6.5 Hz, 1H), 4.21 – 4.09 (m, 2H), 4.07 – 3.94 (m, 2H), 1.50 (s, 3H), 1.43 (s, 3H), 1.38 (s, 3H), 1.32 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 138.6, 134.8 (t, *J* = 22.5 Hz), 129.9, 128.9, 125.1 (t, *J* = 6.2 Hz), 124.7 (t, *J* = 6.0 Hz), 114.8 (t, *J* = 238.7 Hz), 112.0, 109.3, 105.4, 82.7, 82.0, 81.5, 72.5, 71.8, 67.7, 26.9, 26.4, 25.5. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -110.59 (dd, *J* = 56.6, 6.5 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{26}F_2O_6Na^+$, 423.1590, found, 423.1593.

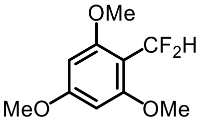
N, N-dibutyl-3-(difluoromethyl)aniline (3l)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added 4-methoxybenzenethiol (37 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. *N, N*-dibutyl-3-(trifluoromethyl)aniline (**1b**) (164 mg, 0.60 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (20:1 (v/v)), to afford 98 mg *N*, *N*-dibutyl-3-(difluoromethyl)aniline (**3l**) as a colorless liquid (64% yield).

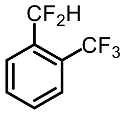
R_f = 0.3(Petroleum ether: EtOAc=20:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.28 – 7.22 (m, 1H), 6.78 – 6.68 (m, 3H), 6.57 (t, *J* = 56.8 Hz, 1H), 3.31 – 3.26 (m, 4H), 1.62 – 1.53 (m, 4H), 1.41 – 1.33 (m, 4H), 0.97 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 148.5, 135.5 (t, *J* = 21.6 Hz), 129.7, 115.6 (t, *J* = 238.7 Hz), 113.9, 112.2 (t, *J* = 6.1 Hz), 108.3 (t, *J* = 6.2 Hz), 50.9, 29.5, 20.5, 14.1. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -110.32 (d, *J* = 56.9 Hz, 2F). HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{15}H_{24}F_2N^+$, 256.1871, found, 256.1882.

2-(Difluoromethyl)-1,3,5-trimethoxybenzene (3m)



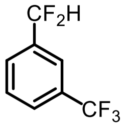
In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added 4-methoxybenzenethiol (37 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1,3,5-trimethoxy-2-(trifluoromethyl)benzene (**1a**) (142 mg, 0.60 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Afford 2-(difluoromethyl)-1,3,5-trimethoxybenzene (**3m**). Due to the low boiling point of the product, NMR yield based on quantitative fluorine NMR is given, using (Trifluoromethoxy)benzene as an internal standard yielded 86%. Product identity was confirmed by ^{19}F NMR. ^{19}F NMR (565 MHz, CDCl$_3$) δ -114.85 (d, *J* = 54.2 Hz, 2F). Spectral data was consistent with literature.[25]

1-(Difluoromethyl)-2-(trifluoromethyl)benzene (3n)



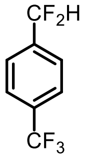
In a N_2 glovebox, to 4-fluorobenzenethiol (4.3 µL, 0.04 mmol, 0.4 equiv.) in dry DDME (1.0 mL) were added Na_2CO_3 (42 mg, 0.40 mmol, 4 equiv.) and phenylsilane (74 µL, 0.6 mmol, 6.0 equiv.) in a 2.0 mL sealed vial tube. 1,2-bis(trifluoromethyl)benzene (**1q**) (21 mg, 0.10 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Afford 1-(difluoromethyl)-2-(trifluoromethyl)benzene (**3n**). Due to the low boiling point of the product, NMR yield based on quantitative fluorine NMR is given, using (Trifluoromethoxy)benzene as an internal standard yielded 79%. Product identity was confirmed by ^{19}F NMR. ^{19}F NMR (565 MHz, $CDCl_3$) δ -111.27 (d, *J* = 54.4 Hz, 2F). Spectral data was consistent with literature.[25]

1-(Difluoromethyl)-3-(trifluoromethyl)benzene (3o)



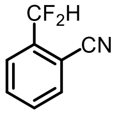
In a N_2 glovebox, to 4-fluorobenzenethiol (4.3 µL, 0.04 mmol, 0.4 equiv.) in dry DDME (1.0 mL) were added Na_2CO_3 (42 mg, 0.40 mmol, 4 equiv.) and phenylsilane (74 µL, 0.6 mmol, 6.0 equiv.) in a 2.0 mL sealed vial tube. 1,3-bis(trifluoromethyl)benzene (**1o**) (21 mg, 0.10 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Afford 1-(difluoromethyl)-3-(trifluoromethyl)benzene (**3o**). Due to the low boiling point of the product, NMR yield based on quantitative fluorine NMR is given, using (Trifluoromethoxy)benzene as an internal standard yielded 75%. Product identity was confirmed by ^{19}F NMR. ^{19}F NMR (565 MHz, $CDCl_3$) δ -112.01 (d, *J* = 55.6 Hz, 2F). Spectral data was consistent with literature.[25]

1-(Difluoromethyl)-4-(trifluoromethyl)benzene (3p)



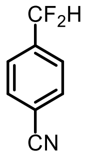
In a N_2 glovebox, to 4-fluorobenzenethiol (4.3 µL, 0.04 mmol, 0.4 equiv.) in dry DDME (1.0 mL) were added Na_2CO_3 (42 mg, 0.40 mmol, 4 equiv.) and phenylsilane (74 µL, 0.6 mmol, 6.0 equiv.) in a 2.0 mL sealed vial tube. 1,4-bis(trifluoromethyl)benzene (**1u** (21 mg, 0.10 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Due to the low boiling point of the product, NMR yield based on quantitative fluorine NMR is given, using (Trifluoromethoxy)benzene as an internal standard yielded 77%. Product identity was confirmed by ^{19}F NMR. ^{19}F NMR (565 MHz, $CDCl_3$) δ -112.56 (d, *J* = 55.5 Hz, 2F). Spectral data was consistent with literature.[25]

2-(Difluoromethyl)benzonitrile (3q)



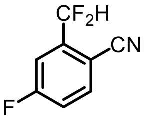
In a N_2 glovebox, to pentafluorobenzenethiol (2.7 µL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 µL, 0.20 mmol, 2 equiv.), PMP (72 µL, 0.4 mmol, 4 equiv.) and phenylsilane (74 µL, 0.60 mmol, 6.0 equiv.)in a 4.0 mL sealed vial tube. 2-(trifluoromethyl)benzonitrile (**1u**) (17 mg, 0.10 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Afford 2-(difluoromethyl)benzonitrile (**3q**). Due to the low boiling point of the product, NMR yield based on quantitative fluorine NMR is given, using (Trifluoromethoxy)benzene as an internal standard yielded 73%. Product identity was confirmed by ^{19}F NMR. ^{19}F NMR (565 MHz, $CDCl_3$) δ -112.80 (d, *J* = 54.4 Hz, 2F). Spectral data was consistent with literature.[25]

4-(Difluoromethyl)benzonitrile (3r)



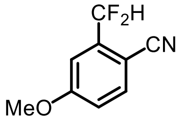
In a N_2 glovebox, to pentafluorobenzenethiol (2.7 µL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 µL, 0.20 mmol, 2 equiv.), PMP (72 µL, 0.4 mmol, 4 equiv.) and phenylsilane (74 µL, 0.60 mmol, 6.0 equiv.)in a 4.0 mL sealed vial tube. 4-(trifluoromethyl)benzonitrile (**1af**) (17 mg, 0.10 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Afford 4-(difluoromethyl)benzonitrile (**3u**). Due to the low boiling point of the product, NMR yield based on quantitative fluorine NMR is given, using (Trifluoromethoxy)benzene as an internal standard yielded 50%. Product identity was confirmed by ^{19}F NMR. ^{19}F NMR (565 MHz, $CDCl_3$) δ -113.13 (d, *J* = 55.5 Hz, 2F). Spectral data was consistent with literature.[25]

2-(Difluoromethyl)-4-fluorobenzonitrile (3s)



In a N_2 glovebox, to pentafluorobenzenethiol (2.7 µL, 0.02 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 µL, 0.20 mmol, 2 equiv.), PMP (72 µL, 0.4 mmol, 4 equiv.) and phenylsilane (74 µL, 0.60 mmol, 6.0 equiv.)in a 4.0 mL sealed vial tube. 4-fluoro-2-(trifluoromethyl)benzonitrile (**1ae**) (19 mg, 0.10 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Afford 2-(difluoromethyl)-4-fluorobenzonitrile (**3s**), Due to the low boiling point of the product, NMR yield based on quantitative fluorine NMR is given, using (Trifluoromethoxy)benzene as an internal standard yielded 95%. Product identity was confirmed by ^{19}F NMR. ^{19}F NMR (565 MHz, $CDCl_3$) δ -113.64 (d, *J* = 54.0 Hz, 2F). Spectral data was consistent with literature.[25]

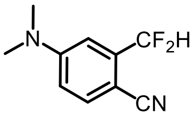
2-(Difluoromethyl)-4-methoxybenzonitrile (3t)



In a N_2 glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.)in a 4.0 mL sealed vial tube. 4-methoxy-2-(trifluoromethyl)benzonitrile (**1w**) (20 mg, 0.10 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (3:1 (v/v)), to afford 12 mg 2-(difluoromethyl)-4-methoxybenzonitrile (**3t**) as a white solid (63% yield). Spectral data was consistent with literature.[25]

R_f = 0.2 (petroleum ether/EtOAc = 3:1). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.68 (d, J = 8.5 Hz, 1H), 7.23 (s, 1H), 7.06 (d, J = 8.3 Hz, 1H), 6.89 (t, J = 54.7 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 163.3, 139.1 (t, J = 23.1 Hz), 135.2, 117.1, 116.3, 112.2 (t, J = 5.8 Hz), 112.1 (t, J = 240.45 Hz), 102.3, 56.1. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -112.51 (d, J = 54.6 Hz, 2F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_9H_8OF_2N^+$, 184.0568, found, 184.0570.

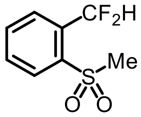
2-(Difluoromethyl)-4-(dimethylamino)benzonitrile (3u)



In a N_2 glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.) in a 4.0 mL sealed vial tube. 4-(dimethylamino)-2-(trifluoromethyl)benzonitrile (**1ar**) (21 mg, 0.10 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (10:1 (v/v)), to afford 9 mg 2-(difluoromethyl)-4-(dimethylamino)benzonitrile (**3u**) as a white solid (46% yield).

R$_f$ = 0.2 (petroleum ether/EtOAc = 10:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.53 (d, *J* = 8.7 Hz, 1H), 6.90 (s, 1H), 6.85 (t, *J* = 54.9 Hz, 1H), 6.71 (d, *J* = 8.5 Hz, 1H), 3.09 (s, 6H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 152.6, 138.1, 134.6, 117.8, 113.0, 112.8 (t, *J* = 240.0 Hz), 108.4 (t, *J* = 6.2 Hz), 95.3, 40.2.**^{19}F NMR (565 MHz, CDCl$_3$)** δ -112.52 (d, *J* = 55.0 Hz, 2F). HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{10}H_{11}F_2N_2^+$, 197.0885, found, 197.0891.

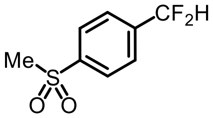
1-(Difluoromethyl)-2-(methylsulfonyl)benzene (3v)



In a N_2 glovebox, to pentafluorobenzenethiol (2.7 µL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 µL, 0.20 mmol, 2 equiv.), PMP (72 µL, 0.4 mmol, 4 equiv.) and phenylsilane (74 µL, 0.60 mmol, 6.0 equiv.)in a 4.0 mL sealed vial tube. 1-(methylsulfonyl)-2-(trifluoromethyl)benzene (**1ac**) (24 mg, 0.10 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (3:1 (v/v)), to afford 14 mg 1-(difluoromethyl)-2-(methylsulfonyl)benzene (**3v**) as a white solid (66% yield).

R$_f$ = 0.2 (petroleum ether/EtOAc = 3:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.13 (d, *J* = 7.9 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.79-7.77 (m , 1H), 7.73-7.70 (m, 1H), 7.64 (t, *J* = 55.2 Hz, 1H), 3.13 (s, 3H).**^{13}C NMR (151 MHz, CDCl$_3$)** δ 138.7 (t, *J* = 5.4 Hz), 134.4, 133.5 (t, *J* = 23.0 Hz), 131.5, 130.5, 126.9 (t, *J* = 8.6 Hz), 111.2 (t, *J* = 238.5 Hz), 45.8 (t, *J* = 2.4 Hz). **^{19}F NMR (565 MHz, CDCl$_3$)** δ -114.02 (d, *J* = 55.3 Hz, 2F). HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_8H_8F_2O_2SNa^+$, 229.0105, found, 229.0108.

1-(Difluoromethyl)-4-(methylsulfonyl)benzene (3w)

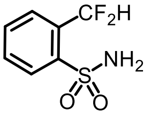


In a N_2 glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.)in a 4.0 mL sealed vial tube. 1-(methylsulfonyl)-4-(trifluoromethyl)benzene (**1ad**) (24 mg, 0.10 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (3:1 (v/v)), to afford 12 mg 1-(difluoromethyl)-4-(methylsulfonyl)benzene (**3w**) as a white solid (58% yield).

R$_f$ = 0.2 (petroleum ether/EtOAc = 3:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.05 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 6.73 (t, *J* = 55.8 Hz, 1H), 3.07 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 143.0, 139.7 (t, *J* = 22.8 Hz), 128.1, 126.9

(t, *J* = 6.0 Hz), 113.5 (t, *J* = 240.7 Hz), 44.5. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -112.85 (d, *J* = 55.9 Hz, 2F). Spectral data was consistent with literature.[25]

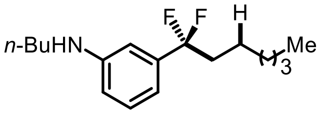
2-(Difluoromethyl)benzenesulfonamide (3x)



In a N_2 glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.)in a 4.0 mL sealed vial tube. 2-(trifluoromethyl)benzenesulfonamide (**1as**) (23 mg, 0.10 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (2:1 (v/v)), to afford 13 mg 2-(difluoromethyl)benzenesulfonamide (**3x**) as a white solid (65% yield).

R_f = 0.4 (petroleum ether/EtOAc = 2:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.11 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.78 – 7.68 (m, 1H), 7.69 – 7.63 (m, 1H), 7.51 (t, *J* = 55.4 Hz, 1H), 4.93 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 140.25, 133.20, 131.22, 128.86, 126.64, 123.20, 111.96 (t, *J* = 238.5 Hz). **^{19}F NMR (565 MHz, $CDCl_3$)** δ -115.33 (d, *J* = 55.2 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_7H_7F_2SNO_2Na^+$, 230.0058, found, 230.0068.

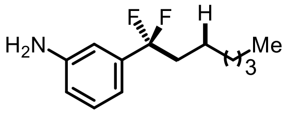
N-Butyl-3-(1,1-difluoroheptyl)aniline (5a)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added 4-methoxybenzenethiol (37 µL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 µL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. *N*-butyl-3-(trifluoromethyl)aniline (**1at**) (130 mg, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 µL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (10:1 (v/v)), to afford 133 mg *N*-butyl-3-(1,1-difluoroheptyl)aniline (**5a**) as a yellow liquid (78% yield).

R_f = 0.2 (petroleum ether/EtOAc = 10:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.22 – 7.16 (m, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 6.67 (s, 1H), 6.62 (dd, *J* = 8.1, 1.9 Hz, 1H), 3.73 (s, 1H), 3.13 (t, *J* = 7.1 Hz, 2H), 2.16 – 2.00 (m, 2H), 1.61 (dt, *J* = 20.1, 7.3 Hz, 2H), 1.49 – 1.38 (m, 4H), 1.34 – 1.21 (m, 6H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 148.6, 138.7 (t, *J* = 26.0 Hz), 129.4, 123.5 (t, *J* = 242.0 Hz), 113.8 (d, *J* = 6.4 Hz), 113.7, 109.2 (t, *J* = 6.2 Hz), 43.8, 39.2 (t, *J* = 27.4 Hz), 31.7, 31.6, 29.1, 22.7, 22.6, 20.4, 14.2, 14.0. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.49 (t, *J* = 16.4 Hz, 2F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{28}NF_2^+$, 284.2184, found, 284.2189.

3-(1,1-Difluoroheptyl)aniline (5b)

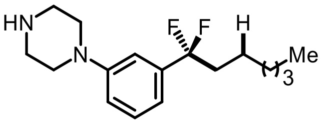


In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added 4-methoxybenzenethiol (37 µL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 µL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 3-(trifluoromethyl)aniline

(**1au**) (97 mg, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (5:1 (v/v)), to afford 72 mg 3-(1,1-difluoroheptyl)aniline (**5b**) as a yellow liquid (53% yield).

R_f = 0.2 (petroleum ether/EtOAc = 5:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.22 – 7.15 (m, 1H), 6.84 (d, J = 7.6 Hz, 1H), 6.77 (s, 1H), 6.71 (d, J = 7.4 Hz, 1H), 3.67 (s, 2H), 2.15 – 2.00 (m, 2H), 1.44 – 1.36 (m, 2H), 1.28 (m, 6H), 0.87 (t, J = 6.9 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 146.5, 138.9 (t, J = 26.3 Hz), 129.5, 123.3 (t, J = 242.1 Hz), 116.2, 115.3 (t, J = 6.2 Hz), 111.7 (t, J = 6.4 Hz), 39.2 (t, J = 27.4 Hz), 31.7, 29.1, 22.6, 22.6 (d, J = 4.6 Hz), 14.2. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -95.54 (t, J = 16.4 Hz, 2F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{20}F_2N^+$, 228.1558, found, 228.1560.

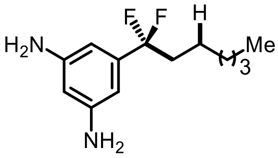
1-(3-(1,1-Difluoroheptyl)phenyl)piperazine (5c)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added 4-methoxybenzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-(3-(trifluoromethyl)phenyl)piperazine (**1av**) (138 mg, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of DCM and MeOH (10:1 (v/v)), to afford 100 mg 1-(3-(1,1-difluoroheptyl)phenyl)piperazine (**5c**) as a yellow liquid (56% yield).

R_f = 0.3 (DCM/MeOH = 10:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.28 (m , 1H), 6.99 (d, *J* = 16.9 Hz, 1H), 6.97 – 6.87 (m, 2H), 3.17 (s, 4H), 3.04 (s, 4H), 2.18 – 2.01 (m, 2H), 1.95 (s, 1H), 1.41 (s, 2H), 1.27 (d, *J* = 14.0 Hz, 6H), 0.86 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 151.9, 138.6 (t, *J* = 26.5 Hz), 129.3, 123.4 (t, *J* = 242.2 Hz), 117.0, 116.3 (t, *J* = 6.0 Hz), 112.6 (t, *J* = 6.4 Hz), 50.3, 46.2, 39.3 (t, *J* = 27.3 Hz), 31.7, 29.1, 22.6, 22.6 (t, *J* = 3.8 Hz), 14.1. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.43 (t, *J* = 16.3 Hz, 2F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{27}F_2N_2^+$, 297.2137, found, 297.2140.

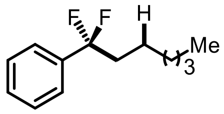
5-(1,1-Difluoroheptyl)benzene-1,3-diamine (5d)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added 4-methoxybenzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 5-(trifluoromethyl)benzene-1,3-diamine (**1aw**) (106 mg, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of DCM, to afford 93 mg 5-(1,1-difluoroheptyl)benzene-1,3-diamine (**5d**) as a yellow solid (64% yield).

R_f = 0.2 (DCM). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 6.19 (s, 2H), 6.04 (s, 1H), 3.65 (s, 4H), 2.11 – 1.96 (m, 2H), 1.40 (s, 2H), 1.27 (d, *J* = 8.7 Hz, 6H), 0.86 (t, *J* = 6.5 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 147.7, 140.1 (t, *J* = 29.0 Hz), 123.5 (t,*J* = 242.2 Hz), 102.8, 102.6, 39.1, 31.7, 29.1, 22.7, 22.6, 14.1. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.82 (t, *J* = 16.3 Hz, 2F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{21}N_2F_2^+$, 243.1667, found, 243.1676.

(1,1-Difluoroheptyl)benzene (5e)

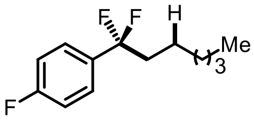


In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. (trifluoromethyl)benzene (**1k**) (74 μL, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether, to afford 105 mg (1,1-difluoroheptyl)benzene (**5e**) as a colorless liquid (82% yield).

R_f = 0.6 (petroleum ether). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.48 – 7.44 (m, 2H), 7.43 – 7.40 (m, 3H), 2.17 – 2.04 (m, 2H), 1.44 – 1.36 (m, 2H), 1.33 – 1.22 (m, 6H), 0.86 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 137.8 (t, *J* = 26.8 Hz), 129.7, 128.5, 125.1 (t, *J* = 6.2 Hz), 123.3 (t, *J* = 242.0 Hz), 39.3 (t, *J* = 27.4

Hz), 31.7, 29.1, 22.6, 22.5, 14.1. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -95.42 (t, *J* = 16.3 Hz, 2F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{19}F_2^+$, 213.1449, found, 213.1457.

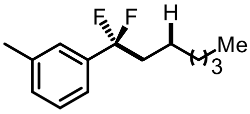
1-(1,1-Difluoroheptyl)-4-fluorobenzene (5f)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-fluoro-4-(trifluoromethyl)benzene (**1g**) (76 μL, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether, to afford 109 mg 1-(1,1-difluoroheptyl)-4-fluorobenzene (**5f**) as a colorless liquid (79% yield).

R_f = 0.6 (petroleum ether). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.48 – 7.39 (m, 2H), δ 7.14 – 7.05 (m, 2H), 2.16 – 2.03 (m, 2H), 1.43 – 1.35 (m, 2H), 1.33 – 1.22 (m, 6H), 0.87 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 163.5 (d, *J* = 248.6 Hz), 133.8 (t, *J* = 27.6 Hz), 127.3 (d, *J* = 6.4 Hz), 127.2 (d, *J* = 6.2 Hz), 123.0 (t, *J* = 242.4 Hz), 115.5 (d, *J* = 21.8 Hz), 39.3 (t, *J* = 27.5 Hz), 31.7, 29.0, 22.6, 22.6, 14.1. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -94.39 (t, *J* = 16.1 Hz, 2F), -111.80 (-111.74 – -111.85 (m) 1F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{18}F_3^+$, 231.1355, found, 231.1363.

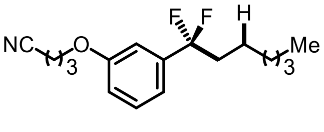
1-(1,1-Difluoroheptyl)-3-methylbenzene (5g)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-methyl-3-(trifluoromethyl)benzene (**1j**) (84 μL, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether, to afford 117 mg 1-(1,1-difluoroheptyl)-3-methylbenzene (**5g**) as a colorless liquid (86% yield).

R_f = 0.5 (petroleum ether). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.32 – 7.24 (m, 3H), 7.22 (d, J = 7.3 Hz, 1H), 2.40 (s, 3H), 2.17 – 2.03 (m, 2H), 1.46 – 1.37 (m, 2H), 1.35 – 1.24 (m, 6H), 0.87 (t, J = 6.9 Hz, 3H).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.3, 137.7 (t, J = 26.5 Hz), 130.4, 128.4, 125.7 (t, J = 6.1 Hz), 123.36 (t, J = 242.1 Hz), 122.2 (t, J = 6.4 Hz), 53.6, 39.3 (t, J = 27.4 Hz), 31.7, 29.1, 22.6, 21.6, 14.2.**^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.27 (t J = 16.5 Hz, 2F,). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{20}F_2Na^+$, 249.1425, found, 249.1434.

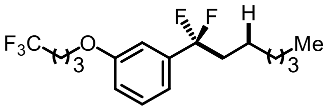
4-(3-(1,1-Difluoroheptyl)phenoxy)butanenitrile (5h)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 4-(3-(trifluoromethyl)phenoxy)butanenitrile (**1al**) (138 mg, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (10:1 (v/v)), to afford 128 mg 4-(3-(1,1-difluoroheptyl)phenoxy)butanenitrile (**5h**) as a colorless liquid (72% yield).

R$_f$ = 0.2 (petroleum ether/EtOAc = 10:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.37 – 7.29 (m, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.99 (s, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 4.10 (t, *J* = 5.6 Hz, 2H), 2.61 (t, *J* = 7.1 Hz, 2H), 2.19 – 2.13 (m, 2H), 2.14 – 2.04 (m, 2H), 1.46 – 1.36 (m, 2H), 1.34 – 1.20 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 158.5, 139.4 (t, *J* = 26.8 Hz), 129.8, 123.0 (t, *J* = 242.4 Hz), 119.2, 118.0 (t, *J* = 6.1 Hz), 115.6, 111.4 (t, *J* = 6.5 Hz), 65.6, 39.2 (t, *J* = 27.3 Hz), 31.7, 29.1, 25.6, 22.6, 22.6(t, *J* = 3.8 Hz), 14.4, 14.2. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -95.37 (t, *J* = 16.4 Hz, 2F). HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{17}H_{23}NOF_2Na^+$, 318.1640, found, 318.1642.

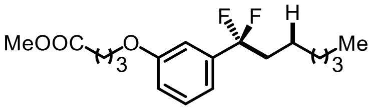
1-(1,1-Difluoroheptyl)-3-(4,4,4-trifluorobutoxy)benzene (5i)



In a N$_2$ glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-(4,4,4-trifluorobutoxy)-3-(trifluoromethyl)benzene (**1am**) (163 mg, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (50:1 (v/v)), to afford 154 mg 1-(1,1-difluoroheptyl)-3-(4,4,4-trifluorobutoxy)benzene (**5i**) as a colorless liquid (76% yield).

R_f = 0.3 (petroleum ether/EtOAc = 50:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.36 – 7.29 (m, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 16.3 Hz, 1H), 6.93 (dd, *J* = 8.2, 1.9 Hz, 1H), 4.04 (t, *J* = 5.9 Hz, 2H), 2.41 – 2.26 (m, 2H), 2.14 – 2.04 (m, 4H), 1.44 – 1.37 (m, 2H), 1.33 – 1.23 (m, 6H), 0.87 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.7, 139.3 (t, *J* = 26.9 Hz), 129.8, 126.3 (q, *J* = 241.1 Hz), 123.1 (t, *J* = 242.4 Hz), 117.8 (t, *J* = 6.2 Hz), 115.6, 111.4 (t, *J* = 6.4 Hz), 66.3, 39.2 (t, *J* = 27.3 Hz), 31.7, 30.9 (q, *J* = 29.1 Hz), 29.1, 22.6, 22.6 (d, *J* = 4.1 Hz), 22.3 (q, *J* = 5.4, 2.8 Hz), 14.1. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -66.33 (t, *J* = 10.9 Hz, 3F), -95.35 (t, *J* = 16.4 Hz, 2F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{24}F_5O^+$, 339.1742, found, 339.1755.

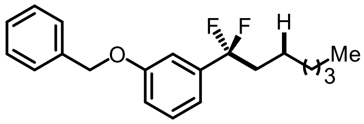
Methyl 4-(3-(1,1-difluoroheptyl)phenoxy)butanoate (5j)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. methyl 4-(3-(trifluoromethyl)phenoxy)butanoate (**1ao**) (157 mg, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (5:1 (v/v)), to afford 152 mg methyl 4-(3-(1,1-difluoroheptyl)phenoxy)butanoate (**5j**) as a colorless liquid (77% yield).

R_f = 0.3 (petroleum ether/EtOAc = 5:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.34 – 7.27 (m, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.97 (s, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 4.03 (t, *J* = 6.0 Hz, 2H), 3.69 (s, 3H), 2.54 (t, *J* = 7.3 Hz, 2H), 2.17 – 2.03 (m, 4H), 1.40 (dd, *J* = 15.6, 8.0 Hz, 2H), 1.33 – 1.21 (m, 6H), 0.87 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.7, 158.9, 139.2 (t, *J* = 26.7 Hz), 129.6, 123.1 (t, *J* = 242.2 Hz), 117.5 (t, *J* = 6.2 Hz), 115.7, 111.4 (t, *J* = 6.4 Hz), 67.0, 51.8, 39.2 (t, *J* = 27.3 Hz), 31.7, 30.6, 29.1, 24.7, 22.6, 22.6 (t, *J* = 3.5 Hz), 14.1. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.30 (t, *J* = 16.3 Hz, 2F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{26}O_3F_2Na^+$, 351.1742, found, 351.1745.

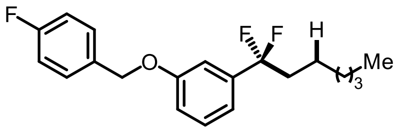
1-(Benzyloxy)-3-(1,1-difluoroheptyl)benzene (5k)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-(benzyloxy)-3-(trifluoromethyl)benzene (**1ai**) (151 mg, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (50:1 (v/v)), to afford 158 mg 1-(benzyloxy)-3-(1,1-difluoroheptyl)benzene (**5k**) as a colorless liquid (83% yield).

R_f = 0.3 (petroleum ether/EtOAc = 50:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.45 (d, *J* = 7.5 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.34 (dd, *J* = 14.0, 7.3 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 1H), 7.06 (t, *J* = 9.0 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 5.09 (s, 2H), 2.17 – 2.01 (m, 2H), 1.40 (dt, *J* = 15.5, 7.7 Hz, 2H), 1.33 – 1.24 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.9, 139.2 (t, *J* = 27.0 Hz), 136.8, 129.7, 128.8, 128.2, 127.7, 123.1 (t, *J* = 242.1 Hz), 117.7 (t, *J* = 6.1 Hz), 116.0, 111.9 (t, *J* = 6.3 Hz), 70.3, 39.2 (t, *J* = 27.3 Hz), 31.7, 29.1, 22.6, 22.6 (t, *J* = 3.6 Hz), 14.2. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.24 (t, *J* = 16.2 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{24}OF_2Na^+$, 341.1687, found, 341.1700.

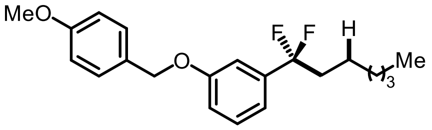
1-(1,1-Difluoroheptyl)-3-((4-fluorobenzyl)oxy)benzene (5l)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-(benzyloxy)-3-(trifluoromethyl)benzene (**1aj**) (162 mg, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (100:1 (v/v)), to afford 170 mg 1-(1,1-difluoroheptyl)-3-((4-fluorobenzyl)oxy)benzene (**5l**) as a colorless liquid (84% yield).

R_f = 0.2 (petroleum ether/EtOAc = 100:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.41 (dd, *J* = 8.1, 5.6 Hz, 2H), 7.36 – 7.30 (m, 1H), 7.11 – 7.04 (m, 4H), 7.00 (d, *J* = 8.0 Hz, 1H), 5.04 (s, 2H), 2.15 – 2.01 (m, 2H), 1.39 (dt, J = 15.6, 7.8 Hz, 2H), 1.32 – 1.17 (m, 6H), 0.87 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 161.8 (d, *J* = 246.5 Hz), 157.7, 138.3 (t, *J* = 26.8 Hz), 131.6, 128.75, 128.5 (d, *J* = 8.2 Hz), 122.1 (t, *J* = 242.3 Hz), 116.9 (t, *J* = 6.1 Hz), 115.1, 114.7 (d, *J* = 21.6 Hz), 110.9 (t, *J* = 5.9 Hz), 68.7, 38.2 (t, *J* = 27.3 Hz), 30.7, 28.1, 21.6, 21.6 (t, *J* = 4.1 Hz), 13.1. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.25 (t, *J* = 16.2 Hz, 2F), -113.97 – -114.06 (m, 1F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{24}F_3O^+$, 337.1774, found, 337.1772.

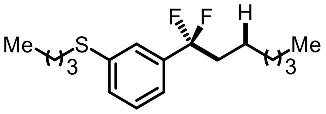
1-(1,1-Difluoroheptyl)-3-((4-methoxybenzyl)oxy)benzene (5m)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-((4-methoxybenzyl)oxy)-3-(trifluoromethyl)benzene (**1ak**) (169 mg, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (100:1 (v/v)), to afford 188 mg 1-(1,1-difluoroheptyl)-3-((4-methoxybenzyl)oxy)benzene (**5m**) as a white solid (90% yield).

R*f* = 0.2 (petroleum ether/EtOAc = 100:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.30 (m, 1H), 7.09 (s, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 2H), 5.02 (s, 2H), 3.83 (s, 3H), 2.19 – 2.02 (m, 2H), 1.47 – 1.36 (m, 2H), 1.35 – 1.21 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 159.7, 158.9, 139.2 (t, *J* = 26.8 Hz), 129.7, 129.4, 128.8, 123.1 (t, *J* = 242.4 Hz), 117.6 (t, *J* = 6.2 Hz), 116.1, 114.2, 111.9 (t, *J* = 6.4 Hz), 70.1, 55.4, 39.2 (t, *J* = 27.3 Hz), 31.7, 29.1, 22.6, 22.6 (t, *J* = 3.9 Hz), 14.1. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -95.24 (t, *J* = 16.3 Hz, 2F). HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{21}H_{26}O_2F_2Na^+$, 371.1793, found, 371.1807.

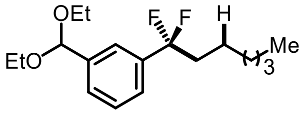
Butyl(3-(1,1-difluoroheptyl)phenyl)sulfane (5n)



In a N$_2$ glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. Butyl(3-(trifluoromethyl)phenyl)sulfane (**1ax**) (141 mg, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (100:1 (v/v)), to afford 123 mg butyl(3-(1,1-difluoroheptyl)phenyl)sulfane (**5n**) as a colorless liquid (68% yield).

R*f* = 0.3 (petroleum ether/EtOAc = 100:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.40 (s, 1H), 7.38 – 7.28 (m, 2H), 7.25 – 7.20 (m, 1H), 2.95 (t, *J* = 7.4 Hz, 2H), 2.18 – 1.99 (m, 2H), 1.70 – 1.58 (m, 2H), 1.51 – 1.44 (m, 2H), 1.41 (dt, *J* = 15.9, 8.0 Hz, 2H), 1.33 – 1.23 (m, 6H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 138.4 (t, *J* = 26.8 Hz), 137.9, 129.7, 128.9, 125.1 (t, *J* = 6.3 Hz), 123.0 (t, *J* = 242.5 Hz), 122.4 (t, *J* = 6.0 Hz), 39.2 (t, *J* = 27.2 Hz), 33.2, 31.7, 31.2, 29.0, 22.6, 22.6 (t, *J* = 3.9 Hz), 22.1, 14.1, 13.8. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -95.64 (t, *J* = 16.3 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{26}F_2SNa^+$, 323.1615, found, 323.1620.

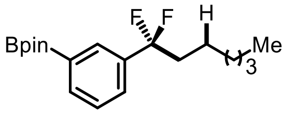
1-(Diethoxymethyl)-3-(1,1-difluoroheptyl)benzene (5o)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-(diethoxymethyl)-3-(trifluoromethyl)benzene (**1ay**) (149 mg, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (100:1 (v/v)), to afford 130 mg 1-(diethoxymethyl)-3-(1,1-difluoroheptyl)benzene (**5o**) as a colorless liquid (69% yield).

R_f = 0.3 (petroleum ether/EtOAc = 20:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.59 (s, 1H), 7.54 (d, *J* = 6.2 Hz, 1H), 7.44 – 7.38 (m, 2H), 5.54 (s, 1H), 3.62 (3.67 – 3.58 (m, 2H)), 3.59 – 3.51 (m, 2H), 2.19 – 2.03 (m, 2H), 1.50 – 1.36 (m, 2H), 1.35 – 1.28 (m, 6H), 1.25 (t, *J* = 7.1 Hz, 6H), 0.91 – 0.81 (m, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 139.7, 137.7 (t, *J* = 26.8 Hz), 128.4, 128.0, 125.0 (t, *J* = 6.2 Hz), 123.5 (t, *J* = 6.2 Hz), 123.2 (t, *J* = 242.3 Hz), 101.2, 61.2, 39.2 (t, *J* = 27.4 Hz), 31.7, 29.0, 22.6, 22.5, 15.3, 14.1. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -95.28 (t, *J* = 16.2 Hz, 2F). HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{18}H_{28}O_2F_2Na^+$, 337.1950, found, 337.1948.

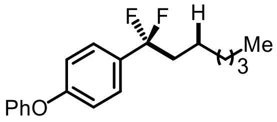
2-(3-(1,1-Difluoroheptyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5p)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 4,4,5,5-tetramethyl-2-(3-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (**1az**) (163 mg, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (20:1 (v/v)), to afford 87 mg 2-(3-(1,1-difluoroheptyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5p**) as a colorless liquid (43% yield).

R$_f$ = 0.3 (petroleum ether/EtOAc = 20:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.90 (s, 1H), 7.85 (d, *J* = 7.4 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.44 – 7.39 (m, 1H), 2.18 – 2.05 (m, 2H), 1.47 – 1.38 (m, 2H), 1.36 (s, 12H), 1.33 – 1.22 (m, 6H), 0.87 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 137.2 (t, *J* = 26.6 Hz), 136.1, 131.2 (t, *J* = 5.9 Hz), 127.9 (t, *J* = 6.3 Hz), 127.8, 123.4 (t, *J* = 242.1 Hz), 84.2, 39.3 (t, *J* = 27.3 Hz), 31.7, 29.1, 25.0, 22.6, 22.5 (t, *J* = 3.7 Hz), 14.1. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -95.51 (t, *J* = 16.3 Hz, 2F). HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{19}H_{29}O_2F_2BNa^+$, 361.2121, found, 361.2136.

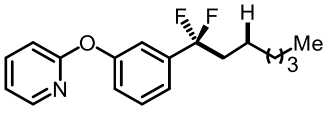
1-(1,1-Difluoroheptyl)-4-phenoxybenzene (5q)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-phenoxy-4-(trifluoromethyl)benzene (**1d**) (143 mg, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (100:1 (v/v)), to afford 144 mg 1-(1,1-difluoroheptyl)-4-phenoxybenzene (**5q**) as a colorless liquid (79% yield).

R_f = 0.2 (petroleum ether : EtOAc = 100:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.38-7.36 (m , 2H), 7.17-.14 (m , 1H), 7.03 (dd, *J* = 15.3, 8.1 Hz, 4H), 2.18 – 2.04 (m, 2H), 1.42 (dd, *J* = 15.3, 8.0 Hz, 2H), 1.30 (dd, *J* = 16.3, 9.7 Hz, 6H), 0.88 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.7, 156.6, 132.3 (t, *J* = 27.7 Hz), 130.0, 126.8 (t, *J* = 6.2 Hz), 124.0, 123.2 (t, *J* = 241.9 Hz), 119.6, 118.2, 39.2 (t, *J* = 27.5 Hz), 31.7, 291, 22.7, 22.6, 14.2. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -94.07 (t, *J* = 16.2 Hz, 2F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{23}F_2O^+$, 305.1711, found, 305.1718.

2-(3-(1,1-Difluoroheptyl)phenoxy)pyridine (5r)

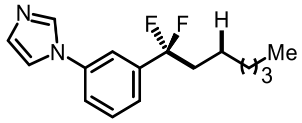


In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6

mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 2-(3-(trifluoromethyl)phenoxy)pyridine (**1ba**) (144 mg, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 µL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (10:1 (v/v)), to afford 112 mg 2-(3-(1,1-difluoroheptyl)phenoxy)pyridine (**5r**) as a colorless liquid (61% yield).

R_f = 0.2 (petroleum ether/EtOAc = 10:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.20 (d, *J* = 3.9 Hz, 1H), 7.75 – 7.67 (m, 1H), 7.48 – 7.40 (m, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.24 (s, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.05 – 6.99 (m, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 2.16 – 2.04 (m, 2H), 1.47 – 1.39 (m, 2H), 1.33 – 1.23 (m, 6H), 0.87 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 163.5, 154.4, 147.9, 139.7, 139.5 (t, *J* = 20.4 Hz), 129.8, 122.9 (t, *J* = 242.5 Hz), 122.3, 121.2 (t), 119.0, 118.1 (t), 111.9, 39.2 (t, *J* = 27.3 Hz), 31.7, 29.0, 22.6, 22.5 (t, *J* = 3.3 Hz), 14.1. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.47 (t, *J* = 16.3 Hz, 2F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{22}NOF_2^+$, 306.1664, found, 306.1672.

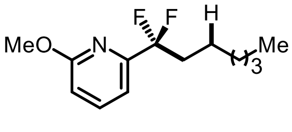
1-(3-(1,1-Difluoroheptyl)phenyl)-1H-imidazole (5s)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 µL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 µL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-(3-(trifluoromethyl)phenyl)-1H-imidazole (**1bb**) (127 mg, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 µL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (3:1 (v/v)), to afford 107 mg 1-(3-(1,1-difluoroheptyl)phenyl)-1H-imidazole (**5s**) as a colorless liquid (64% yield).

R*f* = 0.2 (petroleum ether/EtOAc = 3:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.09 (s, 1H), 7.59 – 7.54 (m, 1H), 7.53 – 7.45 (m, 3H), 7.33 (s, 1H), 7.27 (s, 1H), 2.22 – 2.05 (m, 2H), 1.49 – 1.39 (m, 2H), 1.38 – 1.21 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 140.1 (t, *J* = 27.6 Hz), 137.4, 135.5, 130.4, 129.8, 124.6 (t, *J* = 6.0 Hz), 122.8, 122.5 (t, *J* = 243.0 Hz), 118.5, 118.4 (t, *J* = 6.5 Hz), 39.1 (t, *J* = 26.9 Hz), 31.6, 29.0, 22.6, 22.5 (t, *J* = 3.8 Hz), 14.1. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -95.71 (t, *J* = 16.4 Hz, 2F). HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{16}H_{21}N_2F_2^+$: 279.1667, found: 279.1667.

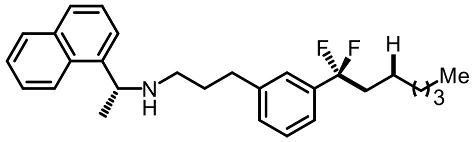
2-(1,1-Difluoroheptyl)-6-methoxypyridine (5t)



In a N$_2$ glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 2-methoxy-6-(trifluoromethyl)pyridine (**1l**) (106 mg, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (20:1 (v/v)), to afford 96 mg 2-(1,1-difluoroheptyl)-6-methoxypyridine (**5t**) as a yellow liquid (66% yield).

R*f* = 0.5 (petroleum ether : EtOAc = 20:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.27 (s, 1H), 7.63 (d, *J* = 8.5, 1.8 Hz, 1H), 6.76 (d, *J* = 8.6 Hz, 1H), 3.95 (d, *J* = 9.2 Hz, 3H), 2.15 – 2.06 (m, 2H), 1.44 – 1.38 (m, 2H), 1.32 – 1.29 (m, 2H), 1.28 (d, *J* = 9.8 Hz, 2H), 1.26 (s, 2H), 0.87 (t, *J* = 6.4 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 165.0, 144.4 (t, *J* = 7.1 Hz), 135.8 (t, *J* = 5.5 Hz), 126.5 (t, *J* = 27.9 Hz), 122.7 (t, *J* = 241.4 Hz), 110.8, 53.8, 39.1 (t, *J* = 27.3 Hz), 31.7, 29.0, 22.6, 22.6 (d, *J* = 4.1 Hz), 14.1. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -94.01 (t, *J* = 16.2 Hz, 2F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{20}F_2NO^+$: 244.1507, found: 244.1516.

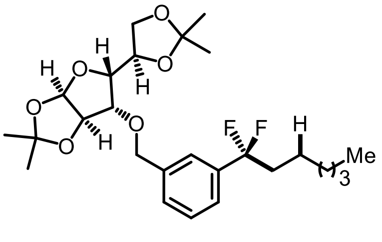
(R)-3-(3-(1,1-difluoroheptyl)phenyl)-*N*-(1-(naphthalen-1-yl)ethyl)propan-1-amine (5u)



In a N$_2$ glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 µL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 µL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. (*R*)-*N*-(1-(naphthalen-1-yl)ethyl)-3-(3-(trifluoromethyl)phenyl)propan-1-amine (**1bd**) (214 mg, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 µL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (3:1 (v/v)), to afford 81 mg (*R*)-3-(3-(1,1-difluoroheptyl)phenyl)-*N*-(1-(naphthalen-1-yl)ethyl)propan-1-amine (**5u**) as a yellow liquid (46% yield).

R*f* = 0.2 (petroleum ether/EtOAc = 3:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.18 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.65 (s, 1H), 7.52-7.47 (m, 3H), 7.30 – 7.22 (m, 3H), 7.18 (d, *J* = 7.0 Hz, 1H), 4.64 (s, 1H), 3.49 (s, 1H), 2.81 – 2.53 (m, 4H), 2.17 – 1.99 (m, 2H), 1.85 (s, 2H), 1.50 (d, *J* = 3.3 Hz, 3H), 1.42 – 1.33 (m, 2H), 1.32 – 1.20 (m, 6H), 0.86 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 142.7, 141.5, 137.8(t, *J* = 26.7 Hz), 134.2, 131.5, 129.7, 129.1, 128.4, 127.3, 125.9, 125.8, 125.4, 125.0 (t, *J* = 6.1 Hz), 124.9. (t, *J* = 241.4 Hz), 122.9 – 122.7 (m), 122.6 (t, *J* = 6.0 Hz), 123.4 – 121.6 (m), 53.9, 47.6, 39.3 (t, *J* = 27.5 Hz), 33.8, 32.2, 31.7, 29.1, 23.8, 22.6, 22.6, 14.1.**^{19}F NMR (565 MHz, CDCl$_3$)** δ -95.31 (t, *J* = 16.4 Hz, 2F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{36}F_2N^+$: 424.2810, found: 424.2820.

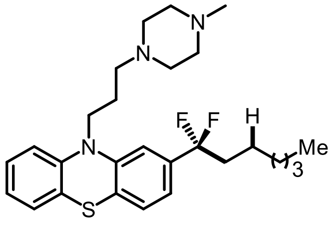
(3a*R*,5*R*,6*S*,6a*R*)-6-((3-(1,1-difluoroheptyl)benzyl)oxy)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxole (5v)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 µL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 µL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. (3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-((3-(trifluoromethyl)benzyl)oxy)tetrahydrofuro[2,3-*d*][1,3]dioxole (**1aq**) (251 mg, 0.60 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (372 µL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (5:1 (v/v)), to afford 189 mg (3a*R*,5*R*,6*S*,6a*R*)-6-((3-(1,1-difluoroheptyl)benzyl)oxy)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxole (**5v**) as a yellow liquid (65% yield).

R_f = 0.2 (petroleum ether : EtOAc = 5:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.46 (s, 1H), 7.42 – 7.36 (m, 3H), 5.91 (d, *J* = 3.7 Hz, 1H), 4.77 – 4.64 (m, 2H), 4.61 (d, *J* = 3.8 Hz, 1H), 4.41 – 4.36 (m, 1H), 4.22 – 4.08 (m, 2H), 4.07 – 3.97 (m, 2H), 2.10 (tt, *J* = 16.3, 8.0 Hz, 2H), 1.50 (s, 3H), 1.43 (s, 3H), 1.42 – 1.39 (m, 2H), 1.38 (s, 3H), 1.31 (s, 3H), 1.30 – 1.13 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.2, 137.9 (t, *J* = 26.7 Hz), 128.8, 128.6, 124.6 (t, *J* = 6.0 Hz), 124.1 (t, *J* = 6.1 Hz), 122.3 (t, *J* = 242.4 Hz), 111.9, 109.2, 105.4, 82.7, 82.0, 81.5, 72.5, 72.1, 67.6, 39.2 (t, *J* = 27.4 Hz), 31.6, 29.0, 26.9, 26.9, 26.3, 25.4, 22.6, 22.5, 14.1.**^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.40 (t, *J* = 16.2 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{26}H_{38}F_2O_6Na^+$: 507.2529, found: 507.2537.

2-(1,1-Difluoroheptyl)-10-(2-(4-methylpiperazin-1-yl)ethyl)-10H-phenothiazine (5w)

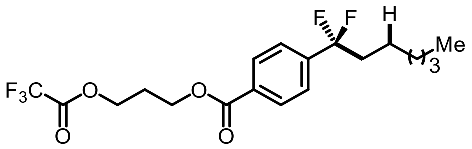


In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 10-(2-(4-methylpiperazin-1-yl)ethyl)-2-(trifluoromethyl)-10H-phenothiazine (**1be**) (236 mg, 0.60 mmol, 1.0 equiv.) and hex-

1-ene (**4a**) (372 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of DCM and MeOH (10:1 (v/v)), to afford 191 m*g* 2-(1,1-difluoroheptyl)-10-(2-(4-methylpiperazin-1-yl)ethyl)-10H-phenothia-zine (**5w**) as a yellow liquid (67% yield).

R_f = 0.2 (DCM/MeOH = 10:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.17 – 7.11 (m, 3H), 6.98 – 6.96 (m, 1H), 6.99-6.90 (m, 3H), 3.95 (t, *J* = 6.8 Hz, 2H), 2.49-2.26 (m, 13H), 2.11 – 2.03 (m, 2H), 1.94 (p, *J* = 6.9 Hz, 2H), 1.41 – 1.37 (m, 2H), 1.32 – 1.21 (m, 6H), 0.86 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 145.6, 145.0, 137.0 (t, *J* = 26.6 Hz), 127.6, 127.6, 127.4, 127.1, 126.5 (t, 240.6 Hz), 124.7, 122.9, 119.2 (t, *J* = 5.9 Hz), 115.9, 112.2 (t, *J* = 6.4 Hz), 55.6, 55.3, 53.4, 46.1, 45.5, 39.3 (t, *J* = 26.5 Hz), 31.7, 29.1, 24.5, 22.6, 14.2.**^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.11 (t, *J* = 15.9 Hz, 2F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{38}N_3F_2S^+$: 474.2749, found: 474.2761.

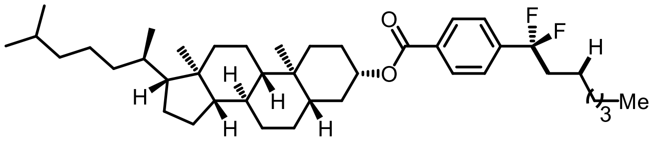
3-(2,2,2-Trifluoroacetoxy)propyl 4-(1,1-difluoroheptyl)benzoate (5x)



In a N_2 glovebox, to 4-fluorobenzenethiol (4.3 μL, 0.040 mmol, 0.4 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.) in a 4.0 mL sealed vial tube. 3-(2,2,2-trifluoroacetoxy)propyl 4-(trifluoromethyl)benzoate (**1bg**) (34 mg, 0.10 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (74 μL, 0.6 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (3:1 (v/v)), to afford 28 m*g* 3-(2,2,2-trifluoroacetoxy)propyl 4-(1,1-difluoroheptyl)benzoate (**5x**) as a yellow liquid (68% yield).

R*f* = 0.3 (petroleum ether/EtOAc = 3:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.08 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 4.54 (t, *J* = 6.2 Hz, 2H), 4.46 (t, *J* = 6.1 Hz, 2H), 2.29 – 2.22 (m, 2H), 2.17 – 2.06 (m, 2H), 1.39 (dt, *J* = 15.3, 7.5 Hz, 2H), 1.33 – 1.22 (m, 6H), 0.86 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 165.8, 157.6 (q, *J* = 42.6 Hz), 142.4 (t, *J* = 26.9 Hz), 131.1, 129.9, 125.4 (t, *J* = 6.2 Hz), 122.8 (t, *J* = 242.8 Hz), 114.6 (q, *J* = 287.3 Hz), 65.0, 61.3, 39.13 (t, *J* = 26.9 Hz), 31.6, 29.0, 27.9, 22.6, 22.5 (t, *J* = 3.9 Hz), 14.1. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -74.96 (s, 3F), -96.33 (t, *J* = 16.3 Hz, 2F). HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{19}H_{23}F_5O_4Na^+$: 433.1409, found: 433.1408.

(3*S*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[*a*]phenanthren-3-yl 4-(1,1-difluoroheptyl)benzoate (5y)

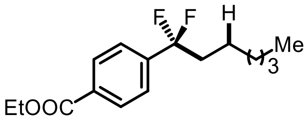


In a N_2 glovebox, to 4-fluorobenzenethiol (4.3 μL, 0.040 mmol, 0.4 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.)in a 4.0 mL sealed vial tube.. (3*S*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-

yl)hexadecahydro-1H-cyclopenta[*a*]phenanthren-3-yl 4-(trifluoromethyl)benzoate (**1bh**) (56 mg, 0.10 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (74 μL, 0.6 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether, to afford 29 mg (3*S*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[*a*]phenanthren-3-yl 4-(1,1-difluoroheptyl)benzoate (**5y**) as a white solid (46% yield).

R_f = 0.3 (petroleum ether). **NMR Spectroscopy:** δ 8.10 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 4.98 (dt, *J* = 11.5, 6.3 Hz, 1H), 2.30 – 2.05 (m, 2H), 1.99 (t, *J* = 15.9 Hz, 2H), 1.91 – 1.78 (m, 2H), 1.75 (d, *J* = 12.3 Hz, 2H), 1.62 – 1.48 (m, 6H), 1.45 – 1.20 (m, 22H), 1.15 – 1.08 (m, 3H), 1.02 – 0.99 (m, 2H), 0.96 – 0.80 (m, 15H), 0.66 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 165.6, 132.3, 129.8, 125.2 (t, *J* = 5.8 Hz), 122.1 (t, *J* = 242.4 Hz), 110.2, 74.9, 56.6, 56.4, 54.4, 44.9, 42.8, 40.1, 39.7, 36.9, 36.3, 36.0, 35.7, 35.7, 34.3, 32.2, 31.6, 29.9, 29.0, 28.8, 28.4, 28.2, 27.7, 24.4, 24.0, 23.0, 22.7, 22.6, 21.4, 18.8, 14.1, 12.5, 12.2. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -96.15 (t, *J* = 16.3 Hz, 2F). HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{41}H_{65}F_2O_2^+$: 627.4947, found: 627.4960.

Ethyl 4-(1,1-difluoroheptyl)benzoate (5z)

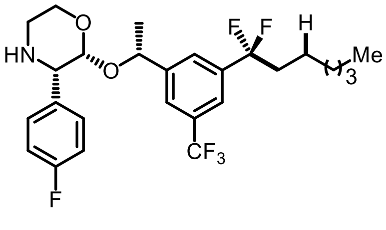


In a N_2 glovebox, to 4-fluorobenzenethiol (4.3 μL, 0.040 mmol, 0.4 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.)in a 4.0 mL sealed vial tube.

ethyl 4-(trifluoromethyl)benzoate (**1ab**) (22 mg, 0.10 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (74μL, 0.6 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (20:1 (v/v)), to afford 20 mg ethyl 4-(1,1-difluoroheptyl)benzoate (**5z**) as a yellow liquid (69% yield).

R$_f$ = 0.4 (petroleum ether/EtOAc = 20:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.16 – 2.05 (m, 2H), 1.43 – 1.35 (m, 5H), 1.33 – 1.20 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 166.1 , 142.0 (t, *J* = 26.7 Hz), 131.8 , 129.8 , 125.2 (t, *J* = 6.1 Hz), 122.9 (t, *J* = 242.9 Hz), 61.4 , 39.2 (t, *J* = 27.0 Hz), 31.7 , 29.0 , 22.6 , 22.5 (t, *J* = 3.9 Hz), 14.5 , 14.1 . **^{19}F NMR (565 MHz, CDCl$_3$)** δ -96.21 (t, *J* = 16.3 Hz, 2F). **HRMS (ESI):** HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{16}H_{23}F_2O_2^+$: 285.1661, found: 285.1663.

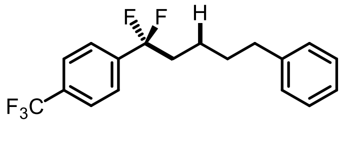
(2*R*, 3*S*)-2-((*R*)-1-(3-(1,1-Difluoroheptyl)-5-(trifluoromethyl)phenyl)ethoxy)-3-(4-fluorophenyl)morpholine(5aa)



In a N$_2$ glovebox, to 4-fluorobenzenethiol (8.6 μL, 0.080 mmol, 0.4 equiv.) in dry DDME (2.0 mL) were added Na_2CO_3 (85 mg, 0.80 mmol, 4 equiv.) and phenylsilane (148 μL, 1.2 mmol, 6.0 equiv.) in a 4.0 mL sealed vial tube. (2*R*, 3*S*)-2-[(1*R*)-1-[3,5-bis(trifluoromethyl)phenyl]ethoxy]-3-(4-fluorophenyl)morpholine 4-methylbenzenesulfonate (**1bc**) (122 mg, 0.20 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (149 μL, 1.2 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of DCM, to afford 32 mg (2*R*, 3*S*)-2-((*R*)-1-(3-(1,1-difluoroheptyl)-5-(trifluoromethyl)phenyl) ethoxy)-3-(4-fluorophenyl)morpholine (**5aa**) as a colorless liquid (32% yield).

R_f = 0.2 (DCM). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.70 (s, 1H), 7.63 (d, *J* = 9.5 Hz, 2H), 7.50 – 7.38 (m, 2H), 7.08 – 6.86 (m, 2H), 5.34 – 4.74 (m, 2H), 4.17 – 4.01 (m, 1H), 3.97 – 3.85 (m, 2H), 3.84 – 3.77 (m, 1H), 2.25 – 1.96 (m, 2H), 1.61 – 1.56 (m, 1H), 1.55 – 1.50 (m, 3H), 1.49 – 1.40 (m, 2H), 1.39 – 1.20 (m, 7H), 0.93 – 0.76 (m, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 164.2 (d, *J* = 250.5 Hz), 161.8, 143.8, 132.7, 131.6 (q, *J* = 33.3, 32.6 Hz), 128.7, 128.6, 127.3 (t, *J* = 6.0 Hz), 125.3, 123.7, (q, *J* = 272.7 Hz), 122.4 (t, *J* = 241.6 Hz), 122.0, 115.5, 115.4, 88.3, 73.4, 56.0, 53.6, 48.1, 39.0 (t, *J* = 27.0 Hz), 31.6, 28.9, 23.9, 22.6, 22.3, 14.1. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -62.59(s, 3F)., -95.75 (q, *J* = 164.2 Hz), -110.53(s, 1F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{26}H_{31}F_6NO_2Na^+$: 526.2151, found: 526.2172.

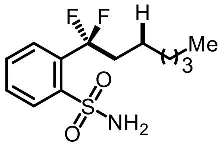
1-(1,1-Difluoro-5-phenylpentyl)-4-(trifluoromethyl)benzene (5ab)



In a N_2 glovebox, to 4-fluorobenzenethiol (4.3 μL, 0.040 mmol, 0.4 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.)in a 4.0 mL sealed vial tube. 1,4-bis(trifluoromethyl)benzene (**1u**) (21 mg, 0.10 mmol, 1.0 equiv.) and but-3-en-1-ylbenzene (**4f**) (79 mg, 0.6 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (50:1 (v/v)), to afford 14 mg 1-(1,1-difluoro-5-phenylpentyl)-4-(trifluoromethyl)benzene (**5ab**) as a colorless liquid (42% yield).

R*f* = 0.2 (petroleum ether/EtOAc = 50:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H),7.28-7.25 (m, 2H), 7.19-7.17 (m, 1H), 7.13 (d, *J* = 7.3 Hz, 2H), 2.59 (t, *J* = 7.7 Hz, 2H), 2.22 – 2.07 (m, 2H), 1.69 – 1.60 (m, 2H), 1.48 (dt, *J* = 15.6, 7.9 Hz, 2H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 142.1, 128.5, 128.5, 126.0, 125.7, 123.9 (q, *J* = 272.2 Hz), 122.5 (t, *J* = 243.1 Hz), 39.0 (t, *J* = 27.0 Hz), 35.7, 31.1, 29.9, 22.2 (t, *J* = 4.1 Hz), 14.3.**^{19}F NMR (565 MHz, CDCl$_3$)** δ -62.85 (s, 3F), -96.31 (t, *J* = 16.2 Hz, 2F).

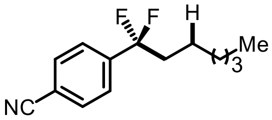
2-(1,1-Difluoroheptyl)benzenesulfonamide (5ac)



In a N$_2$ glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.) in a 4.0 mL sealed vial. 2-(trifluoromethyl)benzenesulfonamide (**1as**) (23 mg, 0.10 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (74 μL, 0.6 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (3:1 (v/v)), to afford 12 mg 2-(1,1-difluoroheptyl)benzenesulfonamide (**5ac**) as a white solid (40% yield).

R_f = 0.3 (petroleum ether/EtOAc = 3:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.23 (d, *J* = 7.9 Hz, 1H), 7.63 (s, 2H), 7.60 – 7.55 (m, 1H), 5.02 (s, 2H), 2.45-2.36 (m, 2H), 1.50 (dt, *J* = 15.5, 7.7 Hz, 2H), 1.35 – 1.28 (m, 2H), 1.27 (d, *J* = 3.2 Hz, 4H), 0.86 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 139.7 (t, *J* = 1.7 Hz), 135.6 (t, *J* = 27.0 Hz), 132.7 , 130.4 , 130.0 , 128.5 (t, *J* = 9.5 Hz), 124.6 (t, *J* = 243.7 Hz), 38.7 (t, *J* = 25.8 Hz), 31.7, 28.9 , 22.6 , 22.3 (t, *J* = 3.6 Hz), 14.16. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -91.07 (t, *J* = 18.3 Hz, 2F). HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{13}H_{19}F_2NO_2SNa^+$: 314.0997, found: 314.0995.

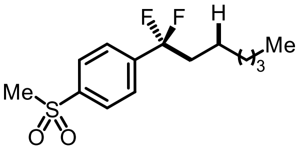
4-(1,1-Difluoroheptyl)benzonitrile (5ad)



In a N_2 glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.) in a 4.0 mL sealed vial. 4-(trifluoromethyl)benzonitrile (**1aa**) (17 mg, 0.10 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (74 μL, 0.6 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (20:1 (v/v)), to afford 16 mg 4-(1,1-difluoroheptyl)benzonitrile (**5ad**) as a colorless liquid (65% yield).

R_f = 0.4 (petroleum ether/EtOAc = 20:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 2.09 (tt, *J* = 16.4, 8.0 Hz, 2H), 1.46 – 1.35 (m, 2H), 1.34 – 1.17 (m, 6H), 0.86 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 142.24 (t, *J* = 27.2 Hz), 132.46, 126.06 (t, *J* = 6.2 Hz), 122.35 (t, *J* = 243.4 Hz), 118.26, 113.88, 39.01 (t, *J* = 26.8 Hz), 31.59, 28.94, 22.57, 22.40 (t, *J* = 3.9 Hz), 14.11. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -96.85 (t, *J* = 16.2 Hz, 2F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{18}F_2N^+$: 238.1402, found: 238.1414.

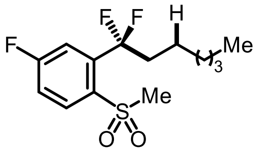
1-(1,1-Difluoroheptyl)-4-(methylsulfonyl)benzene (5ae)



In a N_2 glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.) in a 4.0 mL sealed vial. 1-(methylsulfonyl)-4-(trifluoromethyl)benzene (**1ad**) (22 mg, 0.10 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (74 μL, 0.6 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (5:1 (v/v)), to afford 20 mg 1-(1,1-difluoroheptyl)-4-(methylsulfonyl)benzene (**5ae**) as a white solid (70% yield).

R$_f$ = 0.2 (petroleum ether/EtOAc = 5:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 3.07 (s, 3H), 2.20 – 2.05 (m, 2H), 1.45 – 1.37 (m, 2H), 1.34 – 1.22 (m, 6H), 0.87 (t, *J* = 6.9 Hz, 3H).**^{13}C NMR (151 MHz, CDCl$_3$)** δ 143.2 (t, *J* = 27.3 Hz), 142.0, 127.8, 126.4 (t, *J* = 6.0 Hz), 122.4 (t, *J* = 243.3 Hz), 44.6, 39.1 (t, *J* = 26.9 Hz), 31.6, 29.0, 22.6, 22.4 (t, *J* = 3.4 Hz), 14.1. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -96.39 (t, *J* = 16.3 Hz, 2F). HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{14}H_{20}O_2F_2SNa^+$: 313.1044, found: 313.1052.

2-(1,1-Difluoroheptyl)-4-fluoro-1-(methylsulfonyl)benzene (5af)

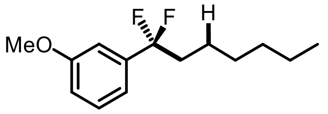


In a N$_2$ glovebox, to pentafluorobenzenethiol (2.7 µL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 µL, 0.20 mmol, 2 equiv.), PMP (72 µL, 0.4 mmol, 4 equiv.) and phenylsilane (74 µL, 0.60 mmol, 6.0 equiv.) in a 4.0 mL sealed vial. 4-fluoro-1-(methylsulfonyl)-2-(trifluoromethyl)benzene (**1bf**) (24 mg, 0.10 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (74 µL, 0.6 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (5:1 (v/v)), to afford 28 mg 2-(1,1-difluoroheptyl)-4-fluoro-1-(methylsulfonyl)benzene (**5af**) as a colorless liquid (90% yield).

R$_f$ = 0.2 (petroleum ether/EtOAc = 5:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.29 (dd, *J* = 8.9, 5.5 Hz, 1H), 7.37 (dd, *J* = 9.4, 2.6 Hz, 1H), 7.32 – 7.26 (m, 1H), 3.19 (s, 3H), 2.48 – 2.35 (m, 2H), 1.53 – 1.45 (m, 2H), 1.36 – 1.29 (m, 2H), 1.30

– 1.22 (m, 4H), 0.87 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 165.2 (d, *J* = 257.6 Hz), 140.9 (d, *J* = 8.1 Hz), 135.1 (d, *J* = 9.2 Hz), 134.6, 123.0 (t, *J* = 245.0 Hz), 117.3 (d, *J* = 21.2 Hz), 116.4 (dt, *J* = 21.0, 10.2 Hz), 46.0, 39.3 (t, *J* = 25.2 Hz), 31.7, 28.9, 22.6, 22.3, 14.2. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -90.4 (t, *J* = 18.0 Hz, 2F), -102.88 (s,1F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{19}O_2F_3SNa^+$: 331.0950, found: 331.0955.

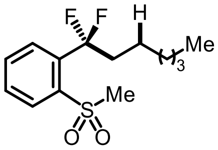
1-(1,1-Difluoroheptyl)-3-methoxybenzene (6a)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-methoxy-3-(trifluoromethyl)benzene (**1c**) (87 μL, 0.60 mmol, 1.0 equiv.) and 2-methylhex-1-ene (**4a**) (372 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether, to afford 134 mg 1-(1,1-difluoroheptyl)-3-methoxybenzene (**6a**) as a colorless liquid (92% yield).

R_f = 0.5 (petroleum ether). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.37 – 7.30 (m, 1H), 7.08 – 7.03 (m, 1H), 7.01 (s, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 3.84 (s, 3H), 2.18 – 2.02 (m, 2H), 1.46 – 1.37 (m, 2H), 1.34 – 1.23 (m, 6H), 0.87 (t, *J* = 11.1, 6.6 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 159.7, 139.2 (t, *J* = 26.8 Hz), 129.7, 123.1 (t, *J* = 242.2 Hz), 117.4 (t, *J* = 6.3 Hz), 115.2, 110.8 (t, *J* = 6.4 Hz), 55.5, 39.2 (t, *J* = 27.3 Hz), 31.7, 29.1, 22.6, 22.6 (t, J = 4.1 Hz), 14.1. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -95.29 (t, J = 16.2 Hz, 2F).HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{20}OF_2Na^+$: 265.1374, found: 265.1381.

1-(1,1-Difluoroheptyl)-2-(methylsulfonyl)benzene (6b)

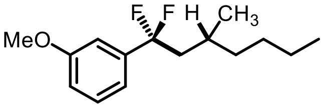


In a N_2 glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.) in a 4.0 mL sealed vial. 1-(methylsulfonyl)-2-(trifluoromethyl)benzene (**1ac**) (23 mg, 0.10 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (74 μL, 0.6 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (10:1 (v/v)), to afford 21 mg 1-(1,1-difluoroheptyl)-2-(methylsulfonyl)benzene (**6b**) as a colorless liquid (72% yield).

R_f = 0.3 (petroleum ether/EtOAc = 10:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.27 (d, J = 7.9 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.65 – 7.61 (m, 1H), 3.20 (s, 3H), 2.42 (ddd, J = 26.3, 17.8, 8.2 Hz, 2H), 1.53 – 1.46 (m, 2H), 1.34 – 1.29 (m, 2H), 1.29 – 1.24 (m, 4H), 0.86 (t, J = 6.8 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 138.6 , 137.6 , 133.6 , 131.8 , 130.6 , 128.5 (t, J = 9.7 Hz), 123.8 (t, J = 244.9 Hz), 45.9 (t, J = 5.9 Hz), 39.6 (t, J = 25.6 Hz), 31.7 , 28.9 , 22.6 , 22.4 (t, J = 3.5 Hz), 14.2 . **^{19}F NMR**

(565 MHz, CDCl$_3$) δ -89.92 (t, *J* = 18.0 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{20}F_2O_2SNa^+$: 313.1044, found: 313.1050.

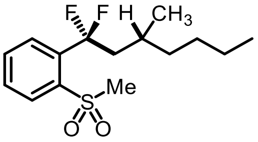
1-(1,1-Difluoro-3-methylheptyl)-3-methoxybenzene(6c)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-methoxy-3-(trifluoromethyl)benzene (**1c**) (87 μL, 0.60 mmol, 1.0 equiv.) and 2-methylhex-1-ene (**4b**) (423 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (5:1 (v/v)), to afford 117 mg 1-(1,1-difluoro-3-methylheptyl)-3-methoxybenzene (**6c**) as a colorless liquid (76% yield).

R_f = 0.4 (petroleum ether/EtOAc = 20:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.34-7.32 (m , 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 7.01 (s, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 3.84 (s, 3H), 2.14 (qd, *J* = 15.9, 4.3 Hz, 1H), 1.99 – 1.88 (m, 1H), 1.73 – 1.65 (m, 1H), 1.36 – 1.29 (m, 1H), 1.26 (d, *J* = 12.2 Hz, 3H), 1.19 (d, *J* = 7.3 Hz, 2H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.87 (t, *J* = 6.5 Hz, 3H) **^{13}C NMR (151 MHz, CDCl$_3$)** δ 159.7 , 139.6 (t, *J* = 26.7 Hz), 129.7 , 123.5 (t, *J* = 243.1 Hz), 117.4 (t, *J* = 6.2 Hz), 115.1 , 110.8 (t, *J* = 6.4 Hz), 55.42 , 45.79 (t, *J* = 26.1 Hz), 37.4 , 29.0, 28.0 (t, *J* = 2.4 Hz), 22.9 , 20.7 , 14.2 . **^{19}F NMR (565 MHz, CDCl$_3$)** δ -90.90 – -91.87 (m, 1F), -94.60 (dt, *J* = 243.4, 17.9 Hz, 1F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{23}F_2O^+$: 257.1711, found: 257.1726.

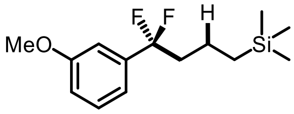
1-(1,1-Difluoro-3-methylheptyl)-2-(methylsulfonyl)benzene (6d)



In a N_2 glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.) in a 4.0 mL sealed vial. 1-(methylsulfonyl)-2-(trifluoromethyl)benzene (**1ac**) (23 mg, 0.10 mmol, 1.0 equiv.) and 2-methylhex-1-ene (**4b**) (85 μL, 0.6 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (5:1 (v/v)), to afford 25 mg 1-(1,1-difluoroheptyl)-2-(methylsulfonyl)benzene (**6d**) as a colorless liquid (81% yield).

R_f = 0.4 (petroleum ether/EtOAc = 5:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.26 (d, J = 7.9 Hz, 1H), 7.69 (d, J = 4.0 Hz, 2H), 7.62 (dt, J = 8.3, 4.3 Hz, 1H), 3.20 (s, 3H), 2.50 – 2.39 (m, 1H), 2.29 – 2.16 (m, 1H), 1.92 – 1.85 (m, 1H), 1.34 (d, J = 5.9 Hz, 1H), 1.29 – 1.19 (m, 5H), 0.99 (d, J = 6.6 Hz, 3H), 0.86 (t, J = 6.3 Hz, 3H).**^{13}C NMR (126 MHz, $CDCl_3$)** δ 138.4, 138.1 (t, J = 27.8 Hz), 133.7, 131.8, 130.6, 128.3 (t, J = 9.8 Hz), 124.1 (t, J = 242.6 Hz), 46.2 (d, J = 24.1 Hz), 45.9 (t, J = 5.6 Hz), 37.4, 29.0, 28.0, 22.9, 20.7, 14.2. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -87.75 – -89.60 (m, 2F). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{22}F_2O_2SNa^+$: 327.1201, found: 327.1208.

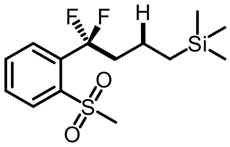
(4,4-Difluoro-4-(3-methoxyphenyl)butyl)trimethylsilane (6e)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 µL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 µL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-methoxy-3-(trifluoromethyl)benzene (**1c**) (87 µL, 0.60 mmol, 1.0 equiv.) and allyltrimethylsilane (**4c**) (477 µL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (20:1 (v/v)), to afford 149 mg (4,4-difluoro-4-(3-methoxyphenyl)butyl)trimethylsilane (**6e**) as a colorless liquid (91% yield).

R_f = 0.4 (petroleum ether/EtOAc = 20:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.37 – 7.30 (m, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.99 (s, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 3.84 (s, 3H), 2.21 – 2.04 (m, 2H), 1.51 – 1.41 (m, 2H), 0.54 – 0.46 (m, 2H), -0.03 (s, 9H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 159.7, 139.3 (t, *J* = 26.8 Hz), 129.7, 122.9 (t, *J* = 242.4 Hz), 117.4 (t, *J* = 6.2 Hz), 115.3, 110.7 (t, *J* = 6.4 Hz), 55.5, 42.9 (t, *J* = 27.0 Hz), 17.2 (t, *J* = 4.0 Hz), 16.6, -1.6. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.54 (t, *J* = 16.3 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{22}OF_2SiNa^+$: 295.1300, found: 295.1306.

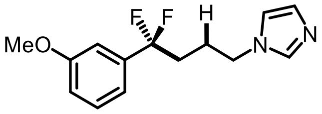
(4,4-Difluoro-4-(2-(methylsulfonyl)phenyl)butyl)trimethylsilane (6f)



In a N_2 glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.) in a 4.0 mL sealed vial. 1-(methylsulfonyl)-2-(trifluoromethyl)benzene (**1ac**) (23 mg, 0.10 mmol, 1.0 equiv.) and allyltrimethylsilane (**4c**) (95 μL, 0.6 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (3:1 (v/v)), to afford 26 mg (4,4-difluoro-4-(2-(methylsulfonyl)phenyl)butyl)trimethylsilane (**6f**) as a colorless liquid (81% yield).

R_f = 0.4 (petroleum ether/EtOAc = 3:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.26 (d, *J* = 7.9 Hz, 1H), 7.73 – 7.65 (m, 2H), 7.65 – 7.59 (m, 1H), 3.20 (s, 3H), 2.44 (ddd, *J* = 26.1, 17.9, 8.1 Hz, 2H), 1.63 – 1.46 (m, 2H), 0.60 – 0.45 (m, 2H), -0.03 (s, 9H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.6, 137.7 (t, *J* = 27.8 Hz), 133.6, 131.8, 130.6, 128.4 (t, *J* = 9.7 Hz), 123.6 (t, *J* = 244.5 Hz), 45.9 (t, *J* = 5.9 Hz), 43.2 (t, *J* = 25.3 Hz), 17.0 (t, *J* = 3.7 Hz), 16.5, -1.6. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -90.17 (t, *J* = 17.8 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{22}O_2F_2SSiNa^+$: 343.0970, found: 343.0979.

1-(4,4-Difluoro-4-(3-methoxyphenyl)butyl)-1H-pyrazole (6g)

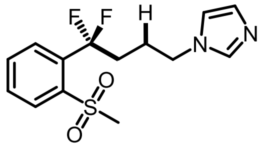


In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-methoxy-3-(trifluoromethyl)benzene

(**1c**) (348 μL, 2.4 mmol, 4.0 equiv.) and 1-allyl-1H-imidazole (**4d**) (65 μL, 0.6 mmol, 1.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of DCM and MeOH (20:1 (v/v)), to afford 157 mg 1-(4,4-difluoro-4-(3-methoxyphenyl)butyl)-1H-pyrazole (**6g**) as a colorless liquid (98% yield).

R_f = 0.2 (DCM/MeOH = 20:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.45 (s, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.07 (s, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.88 (s, 1H), 3.98 (t, *J* = 6.8 Hz, 2H), 3.82 (s, 3H), 2.13 – 2.03 (m, 2H), 1.98 (dd, *J* = 14.4, 7.1 Hz, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 159.9, 138.3(t, *J* = 26.5 Hz), 137.2, 130.0, 123.0, 122.5 (t, *J* = 243.2 Hz), 118.8, 117.2 (t, *J* = 6.2 Hz), 115.6, 110.7 (t, *J* = 6.5 Hz), 55.5, 46.3, 36.0 (t, *J* = 28.3 Hz), 24.5 (t, *J* = 3.5 Hz). **^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.81 (t, *J* = 16.0 Hz, 2F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{17}N_2OF_2^+$: 267.1303, found: 267.1314.

1-(4,4-Difluoro-4-(2-(methylsulfonyl)phenyl)butyl)-1H-pyrazole (6h)

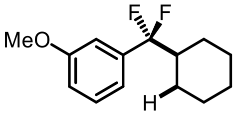


In a N_2 glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.) in a 4.0 mL sealed vial. 1-(methylsulfonyl)-2-(trifluoromethyl)benzene (**1ac**) (92 mg, 0.40 mmol, 4.0 equiv.) and 1-allyl-1H-imidazole (**4d**) (11 μL, 0.1 mmol, 1.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the

427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of DCM and MeOH (20:1 (v/v)), to afford 28 mg 1-(4,4-difluoro-4-(2-(methylsulfonyl)phenyl)butyl)-1H-pyrazole (**6h**) as a colorless liquid (88% yield).

R_f = 0.2 (DCM/MeOH = 50:1). **NMR Spectroscopy:^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.26 (d, *J* = 7.8 Hz, 1H), 7.76 – 7.61 (m, 3H), 7.48 (s, 1H), 7.06 (s, 1H), 6.93 (s, 1H), 4.02 (t, *J* = 7.2 Hz, 2H), 3.20 (s, 3H), 2.43 (ddd, *J* = 25.7, 17.7, 7.7 Hz, 2H), 2.14 – 2.04 (m, 2H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 138.5, 137.3, 136.8 (t, *J* = 27.3 Hz), 134.0, 132.1, 131.1, 129.8, 128.2 (t, *J* = 9.7 Hz), 123.0 (t, *J* = 245.1 Hz), 118.9, 46.4, 45.9 (t, *J* = 5.6 Hz), 36.7 (t, *J* = 26.1 Hz), 24.4. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -91.05 (t, *J* = 18.1 Hz, 2F). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{17}N_2O_2F_2S^+$: 315.0973, found: 315.0982.

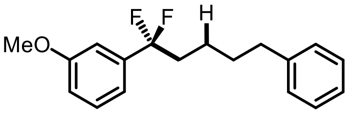
1-(Cyclohexyldifluoromethyl)-3-methoxybenzene (6i)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 3-(trifluoromethyl)anisole (**1c**) (87 μL, 0.60 mmol, 1.0 equiv.) and cyclohexene (**4e**) (304 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (50:1 (v/v)), to afford 75 mg 1-(cyclohexyldifluoromethyl)-3-methoxybenzene (**6i**) as a yellow liquid (52% yield).

R*f* = 0.5 (petroleum ether/EtOAc = 50:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.37 – 7.29 (m, 1H), 7.01 (d, *J* = 7.7 Hz, 1H), 6.98 – 6.91 (m, 2H), 3.83 (s, 3H), 2.05 – 1.89 (m, 1H), 1.85 – 1.73 (m, 4H), 1.66 (d, *J* = 12.0 Hz, 1H), 1.36 – 1.05 (m, 5H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 159.5, 138.4 (t, *J* = 27.1 Hz), 129.3, 124.0 (t, *J* = 245.1 Hz), 118.0 (t, *J* = 6.4 Hz), 114.9, 111.5 (t, *J* = 6.9 Hz), 55.5, 46.2 (t, *J* = 25.7 Hz), 26.1, 25.9 (t, *J* = 3.7 Hz), 25.8. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -103.20 (d, *J* = 13.8 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{18}F_2ONa^+$: 263.1218, found: 263.1218.

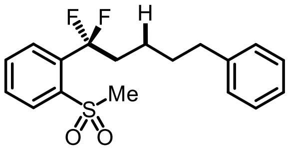
1-(1,1-Difluoro-5-phenylpentyl)-3-methoxybenzene(6k)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-methoxy-3-(trifluoromethyl)benzene (**1c**) (87 μL, 0.60 mmol, 1.0 equiv.) and but-3-en-1-ylbenzene (**4f**) (451 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether, to afford 157 mg 1-(1,1-difluoro-5-phenylpentyl)-3-methoxybenzene (**6k**) as a colorless liquid (90% yield).

R_f = 0.6 (petroleum ether). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.36 – 7.30 (m, 1H), 7.27 (d, J = 10.0 Hz, 2H), 7.20 – 7.15 (m, 1H), 7.14 (d, *J* = 7.5 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 11.7 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 3.82 (d, *J* = 11.8 Hz, 3H), 2.59 (t, *J* = 7.7 Hz, 2H), 2.24 – 2.06 (m, 2H), 1.68 – 1.58 (m, 2H), 1.56 – 1.43 (m, 2H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 159.7, 142.3, 139.1 (t, *J* = 26.7 Hz), 129.7, 128.5, 128.5, 125.9, 123.0 (t, *J* = 242.6 Hz), 117.4 (t, *J* = 6.3 Hz), 115.3 , 110.8 (t, *J* = 6.3 Hz), 55.5., 39.0 (t, *J* = 27.4 Hz), 35.8, 31.2, 22.4 **^{19}F NMR (565 MHz, CDCl$_3$)** δ -95.40 (t, *J* = 16.2 Hz, 2F). HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{18}H_{20}OF_2Na^+$: 313.1374, found: 313.1384.

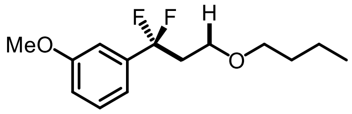
1-(1,1-Difluoro-5-phenylpentyl)-2-(methylsulfonyl)benzene (6l)



In a N$_2$ glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.) in a 4.0 mL sealed vial. 1-(methylsulfonyl)-2-(trifluoromethyl)benzene (**1ac**) (23 mg, 0.10 mmol, 1.0 equiv.) and 2-(allyloxy)tetrahydro-2H-pyran (**4f**) (90 μL, 0.6 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (3:1 (v/v)), to afford 26 mg 1-(1,1-difluoro-5-phenylpentyl)-2-(methylsulfonyl)benzene (**6l**) as a colorless liquid (76% yield).

R*f* = 0.5 (petroleum ether/EtOAc = 3:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.27 (d, *J* = 7.8 Hz, 1H), 7.73 – 7.58 (m, 3H), 7.29 – 7.23 (m, 2H), 7.16 (dd, *J* = 14.8, 7.4 Hz, 3H), 3.21 (s, 3H), 2.65 – 2.58 (m, 2H), 2.48 (ddd, *J* = 25.9, 17.8, 8.0 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.61 – 1.52 (m, 2H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 142.3, 138.7, 133.6, 131.9, 130.6, 128.6, 128.5, 123.7 (t, *J* = 246.3 Hz), 46.0, 39.3 (t, *J* = 25.6 Hz), 35.9, 31.0, 22.1. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -89.99 (t, *J* = 17.8 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{18}H_{20}O_2F_2SNa^+$: 361.1044, found: 361.1056.

1-(3-Butoxy-1,1-difluoropropyl)-3-methoxybenzene (6m)

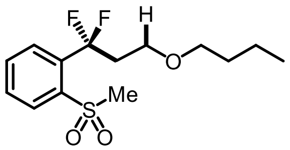


In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-methoxy-3-(trifluoromethyl)benzene (**1c**) (87 μL, 0.60 mmol, 1.0 equiv.) and 1-(vinyloxy)butane (**4g**) (388 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (3:1 (v/v)), to afford 140 mg 1-(3-butoxy-1,1-difluoropropyl)-3-methoxybenzene (**6m**) as a colorless liquid (90% yield).

R*f* = 0.2 (petroleum ether/EtOAc = 100:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.36 – 7.30 (m, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.00 (s, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 3.83 (s, 3H), 3.54 (t, *J* = 7.1 Hz, 2H), 3.36 (t, *J* = 6.6 Hz, 2H), 2.51 – 2.39 (m, 2H), 1.53 – 1.44 (m, 2H), 1.32 (dq, *J* = 14.6, 7.3 Hz, 2H), 0.94 – 0.85 (m, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 159.7, 138.7 (t, *J* = 26.3 Hz), 129.8, 122.1 (t, *J* = 242.5 Hz), 117.3

(t, J = 6.3 Hz), 115.5, 110.7 (t, J = 6.5 Hz), 71.1, 64.8 (t, J = 4.9 Hz), 55.5, 39.3 (t, J = 27.1 Hz), 31.9, 19.4, 14.0. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -94.04 (t, J = 16.4 Hz, 2F). HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{14}H_{20}O_2F_2Na^+$: 281.1324, found: 281.1327.

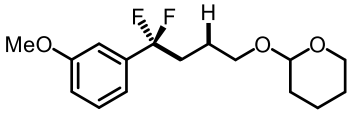
1-(3-Butoxy-1,1-difluoropropyl)-2-(methylsulfonyl)benzene (6n)



In a N_2 glovebox, to pentafluorobenzenethiol (2.7 µL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 µL, 0.20 mmol, 2 equiv.), PMP (72 µL, 0.4 mmol, 4 equiv.) and phenylsilane (74 µL, 0.60 mmol, 6.0 equiv.) in a 4.0 mL sealed vial. 1-(methylsulfonyl)-2-(trifluoromethyl)benzene (**1ac**) (23 mg, 0.10 mmol, 1.0 equiv.) and 1-(vinyloxy)butane (**4g**) (78 µL, 0.6 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (5:1 (v/v)), to afford 17 mg 1-(3-butoxy-1,1-difluoropropyl)-2-(methylsulfonyl)benzene (**6n**) as a white solid (55% yield).

R$_f$ = 0.3 (petroleum ether/EtOAc = 5:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.26 (d, J = 7.9 Hz, 1H), 7.77 – 7.67 (m, 2H), 7.66 – 7.61 (m, 1H), 3.59 (t, J = 6.5 Hz, 2H), 3.33 (t, J = 6.6 Hz, 2H), 3.19 (s, 3H), 2.86 – 2.69 (m, 2H), 1.49 – 1.39 (m, 2H), 1.35 – 1.22 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 138.6, 137.0 (t, J = 27.6 Hz), 133.6, 131.8, 130.7, 128.6 (t, J = 9.8 Hz), 123.0 (t, J = 244.9 Hz), 70.8, 64.6 (t, J = 4.6 Hz), 45.9 (t, J = 5.7 Hz), 39.5 (t, J = 25.3 Hz), 31.8, 19.4, 14.0. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -87.57 (t, *J* = 17.3 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{20}O_3F_2SNa^+$: 329.0993, found: 329.1003.

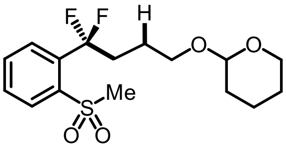
2-(4,4-Difluoro-4-(3-methoxyphenyl)butoxy)tetrahydro-2H-pyran (6o)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-methoxy-3-(trifluoromethyl)benzene (**1c**) (87 μL, 0.60 mmol, 1.0 equiv.) and 2-(allyloxy)tetrahydro-2H-pyran (**4h**) (454 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (15:1 (v/v)), to afford 106 mg 2-(4,4-difluoro-4-(3-methoxyphenyl)butoxy)tetrahydro-2H-pyran (**6o**) as a colorless liquid (59% yield).

R_f = 0.2 (petroleum ether/EtOAc = 15:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.35 – 7.30 (m, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.00 (s, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 4.54 (d, *J* = 3.2 Hz, 1H), 3.89 – 3.79 (m, 4H), 3.81 – 3.69 (m, 1H), 3.53 – 3.43 (m, 1H), 3.40 (dt, *J* = 9.6, 6.4 Hz, 1H), 2.22 (qd, *J* = 16.0, 7.6 Hz, 2H), 1.86 – 1.64 (m, 4H), 1.62 – 1.41 (m, 4H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 159.7, 138.9 (t, *J* = 26.0 Hz), 129.7, 123.0 (t, *J* = 242.5 Hz), 117.4 (t, *J* = 6.2 Hz), 115.3, 110.8 (t, *J* = 6.1 Hz), 98.9, 66.7, 62.4, 55.5, 36.1 (t, *J* = 28.1 Hz), 30.8, 25.6, 23.2 (t, *J* = 3.7 Hz), 19.7. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -95.50 (t, *J* = 16.3 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{20}O_3F_2SNa^+$: 323.1435, found: 323.1441.

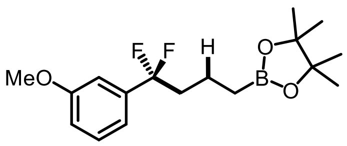
2-(4,4-Difluoro-4-(2-(methylsulfonyl)phenyl)butoxy)tetrahydro-2H-pyran (6p)



In a N_2 glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.) in a 4.0 mL sealed vial. 1-(methylsulfonyl)-2-(trifluoromethyl)benzene (**1ac**) (23 mg, 0.10 mmol, 1.0 equiv.) and 2-(allyloxy)tetrahydro-2H-pyran (**4h**) (91 μL, 0.6 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (3:1 (v/v)), to afford 19 mg 2-(4,4-difluoro-4-(2-(methylsulfonyl)phenyl)butoxy)tetrahydro-2H-pyran (**6p**) as a colorless liquid (55% yield).

R_f = 0.5 (petroleum ether/EtOAc = 3:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.27 (d, *J* = 7.9 Hz, 1H), 7.69 (s, 2H), 7.66 – 7.61 (m, 1H), 4.56 (s, 1H), 3.82 (t, *J* = 9.8 Hz, 1H), 3.76 (dt, *J* = 9.6, 6.6 Hz, 1H), 3.50 – 3.45 (m, 1H), 3.44 – 3.39 (m, 1H), 3.20 (s, 3H), 2.63 – 2.47 (m, 2H), 1.89 – 1.76 (m, 3H), 1.72 – 1.65 (m, 1H), 1.55 (dd, *J* = 10.0, 6.4 Hz, 2H), 1.50 (d, *J* = 5.3 Hz, 2H).**^{13}C NMR (126 MHz, $CDCl_3$)** δ 138.6 , 137.3 , 133.7 , 131.9 , 130.70 , 128.5 (t, *J* = 9.6 Hz), 123.6 (t, *J* = 244.4 Hz), 98.9 , 66.6 , 62.4 , 45.9 (t, *J* = 5.9 Hz), 36.6 (t, *J* = 25.9 Hz), 30.8 , 25.6 , 23.0 (t, *J* = 3.7 Hz), 19.7. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -90.08 (t, *J* = 17.9 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{16}H_{22}F_2O_4SNa^+$: 371.1099, found: 371.1103.

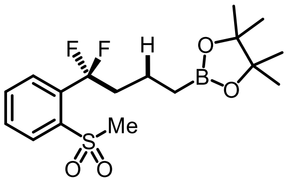
2-(4,4-Difluoro-4-(3-methoxyphenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6q)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-methoxy-3-(trifluoromethyl)benzene (**1c**) (87 μL, 0.60 mmol, 1.0 equiv.) and 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4i**) (563 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (3:1 (v/v)), to afford 157 mg 2-(4,4-difluoro-4-(3-methoxyphenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6q**) as a colorless liquid (80% yield).

R_f = 0.4 (petroleum ether/EtOAc = 10:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.35 – 7.29 (m, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 7.00 (s, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 3.83 (s, 3H), 2.21 – 2.07 (m, 2H), 1.59 – 1.48 (m, 2H), 1.23 (s, 12H), 0.79 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 159.7, 139.1 (t, *J* = 26.7 Hz), 129.6, 123.0 (t, *J* = 242.1 Hz), 117.5 (t, *J* = 6.1 Hz), 115.2, 110.8 (t, *J* = 6.4 Hz), 83.2, 55.5, 41.4 (t, *J* = 27.0 Hz), 24.9, 17.3 (t, *J* = 4.2 Hz). **^{19}F NMR (565 MHz, $CDCl_3$)** δ -94.86 (t, *J* = 16.3 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{25}O_3F_2BNa^+$: 349.1757, found: 349.1759.

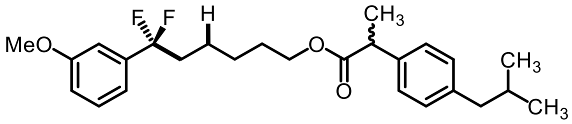
2-(4,4-Difluoro-4-(2-(methylsulfonyl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6r)



In a N_2 glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.) in a 4.0 mL sealed vial. 1-(methylsulfonyl)-2-(trifluoromethyl)benzene (**1ac**) (23 mg, 0.10 mmol, 1.0 equiv.) and 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4i**) (113 μL, 0.6 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (4:1 (v/v)), to afford 29 mg 2-(4,4-difluoro-4-(2-(methylsulfonyl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6p**) as a white solid (77% yield).

R_f = 0.3 (petroleum ether/EtOAc = 4:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.26 (d, *J* = 7.9 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.65 – 7.59 (m, 1H), 3.18 (d, *J* = 8.9 Hz, 3H), 2.52 – 2.35 (m, 2H), 1.68 – 1.59 (m, 2H), 1.22 (s, 12H), 0.81 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.7, 137.6 (t, *J* = 27.6 Hz), 133.6, 131.8, 130.5, 128.6 (t, *J* = 9.7 Hz), 123.6 (t, *J* = 243.8 Hz), 83.2, 45.9 (t, *J* = 5.8 Hz), 41.8 (t, *J* = 25.6 Hz), 25.0, 17.1. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -89.67 (t, *J* = 17.9 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{25}O_4F_2SBNa^+$: 397.1427, found: 397.1434.

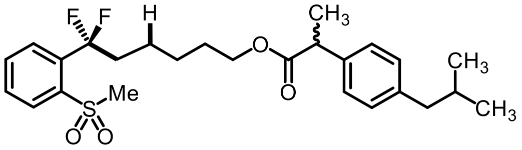
6,6-Difluoro-6-(3-methoxyphenyl)hexyl 2-(4-isobutylphenyl)propanoate (6s)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-methoxy-3-(trifluoromethyl)benzene (**1c**) (348 μL, 2.4 mmol, 4.0 equiv.) and pent-4-en-1-yl 2-(4-isobutylphenyl)propanoate (**4j**) (165 mg, 0.6 mmol, 1.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (4:1 (v/v)), to afford 161 mg 6,6-difluoro-6-(3-methoxyphenyl)hexyl 2-(4-isobutylphenyl)propanoate (**6s**) as a colorless liquid (62% yield).

R_f = 0.3 (petroleum ether/EtOAc = 10:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ7.35 – 7.30 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 7.7 Hz, 1H), 6.97 (s, 1H), 6.95 (dd, *J* = 8.3, 2.2 Hz, 1H), 4.10 – 3.96 (m, 2H), 3.83 (s, 3H), 3.66 (q, *J* = 7.1 Hz, 1H), 2.43 (d, *J* = 7.2 Hz, 2H), 2.14 – 1.96 (m, 2H), 1.83 (dp, *J* = 13.5, 6.8 Hz, 1H), 1.60 – 1.50 (m, 2H), 1.47 (d, *J* = 7.2 Hz, 3H), 1.44 – 1.34 (m, 2H), 1.31 – 1.21 (m, 2H), 0.89 (t, *J* = 5.3 Hz, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.9, 159.8, 140.7, 139.9 (t, *J* = 26.6 Hz), 138.0, 129.7, 129.4, 127.3, 122.9 (t, *J* = 242.6 Hz), 117.4 (t, *J* = 6.1 Hz), 117.4 (t, *J* = 6.1 Hz), 115.2, 110.8 (t, *J* = 6.4 Hz), 64.5, 55.5, 45.3, 45.2, 39.0 (t, *J* = 27.4 Hz), 30.3, 28.5, 25.6, 22.5, 22.3 (t, *J* = 4.0 Hz), 18.5. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.48 (t, *J* = 16.1 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{26}H_{34}O_3F_2Na^+$: 455.2368, found: 455.2379.

6,6-Difluoro-6-(2-(methylsulfonyl)phenyl)hexyl2-(4-isobutylphenyl) propanoate (6t)

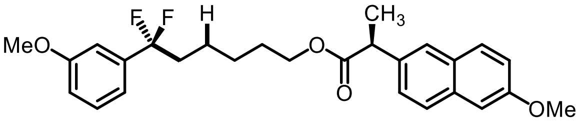


In a N_2 glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2.0 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (19 μL, 0.15 mmol, 1.5 equiv.) in a 4.0 mL sealed vial. 1-(methylsulfonyl)-2-(trifluoromethyl)benzene (**1ac**) (92 mg, 0.40 mmol, 4.0 equiv.) and pent-4-en-1-yl 2-(4-isobutylphenyl)propanoate (**4j**) (27 mg , 0.10 mmol, 1.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (2:1 (v/v)), to afford 28 mg 6,6-difluoro-6-(2-(methylsulfonyl)phenyl)hexyl2-(4-isobutylphenyl)propanoate (**6t**) as a colorless liquid (58% yield).

R_f = 0.3 (petroleum ether/EtOAc = 2:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.27 (d, *J* = 7.9 Hz, 1H), 7.71-7.69 (m , 1H), 7.64 (dd, *J* = 14.0, 7.0 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 4.03 (t, *J* = 6.4 Hz, 2H), 3.67 (q, *J* = 7.1 Hz, 1H), 3.20 (s, 3H), 2.42 (d, *J* = 7.2 Hz, 2H), 2.40 – 2.32 (m, 2H), 1.82 (td, *J* = 13.5, 6.7 Hz, 1H), 1.61 – 1.54 (m, 2H), 1.52 – 1.48 (m, 2H), 1.47 (d, *J* = 7.2 Hz, 3H), 1.32 – 1.25 (m, 2H), 0.88 (d, *J* = 6.6 Hz, 6H).**^{13}C NMR (126 MHz, $CDCl_3$)** δ 173.9, 139.6, 137.6 (t, *J* = 2.1 Hz), 137.0, 136.4, 132.7, 130.9, 129.7, 128.4, 127.4 (t, *J* = 9.7 Hz), 126.3, 122.5 (t, *J* = 244.5 Hz), 63.6, 44.9 (t, *J* = 5.8 Hz), 44.3, 44.2, 38.4 (t, *J* =

25.7 Hz), 29.3, 27.5, 24.5, 21.5, 21.0 (t, *J* = 3.6 Hz), 17.6. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -90.21 (t, *J* = 17.9 Hz, 2F). HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{26}H_{34}O_4F_2SNa^+$: 503.2038, found: 503.2043.

6,6-Difluoro-6-(3-methoxyphenyl)hexyl 2-(6-methoxynaphthalen-2-yl)propanoate (6u)

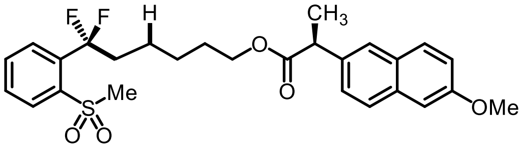


In a N$_2$ glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-methoxy-3-(trifluoromethyl)benzene (**1c**) (348 μL, 2.4 mmol, 4.0 equiv.) and pent-4-en-1-yl 2-(6-methoxynaphthalen-2-yl)propanoate (**4k**) (179 mg, 0.6 mmol, 1.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (10:1 (v/v)), to afford 151 mg 6,6-difluoro-6-(3-methoxyphenyl)hexyl 2-(6-methoxynaphthalen-2-yl)propanoate (**6u**) as a colorless liquid (55% yield).

R$_f$ = 0.3 (petroleum ether/EtOAc = 10:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.70 (d, *J* = 8.6 Hz, 2H), 7.66 (s, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.14 (d, *J* = 8.9 Hz, 1H), 7.12 (s, 1H), 7.02 – 6.91 (m, 3H), 4.09 – 4.00 (m, 2H), 3.91 (s, 3H), 3.86 – 3.80 (m, 4H), 2.09 – 1.82 (m, 2H), 1.59 – 1.51 (m, 5H), 1.40 – 1.32 (m, 2H), 1.27 – 1.18 (m, 2H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 174.8, 159.7, 157.8, 139.0 (t, *J* = 26.5 Hz), 135.9, 133.8, 129.5 (d, *J* = 46.1 Hz), 129.0, 127.2, 126.2

(d, J = 45.9 Hz), 122.9 (t, J = 242.4 Hz), 119.1, 117.3 (t, J = 6.1 Hz), 115.2, 110.8 (t, J = 6.4 Hz), 105.7, 64.6, 55.5, 55.4, 45.6, 38.9 (t, J = 27.4 Hz), 28.5, 25.6, 22.3 (t, J = 3.7 Hz), 18.5. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -95.40 (td, J = 16.1, 8.5 Hz, 2F). HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{27}H_{30}O_4F_2Na^+$: 479.2004, found: 479.2015.

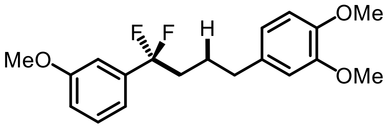
6,6-Difluoro-6-(2-(methylsulfonyl)phenyl)hexyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate (6v)



In a N_2 glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2.0 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (19 μL, 0.15 mmol, 1.5 equiv.) in a 4.0 mL sealed vial. 1-(methylsulfonyl)-2-(trifluoromethyl)benzene (**1ac**) (92 mg, 0.40 mmol, 4.0 equiv.) andpent-4-en-1-yl (S)-2-(6-methoxynaphthalen-2-yl)propanoate (**4k**) (30 mg, 0.10 mmol, 1.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (3:1 (v/v)), to afford 23 mg 6,6-difluoro-6-(2-(methylsulfonyl)phenyl)hexyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (**6v**) as a yellow liquid (46% yield).

R_f = 0.2 (petroleum ether/EtOAc = 3:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.73 – 7.59 (m, 3H), 7.49 (d, J = 6.8 Hz, 1H), 7.40 (dd, J = 8.4, 1.9 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.17 – 7.11 (m, 1H), 7.11 – 7.07 (m, 1H), 6.99 – 6.91 (m, 1H), 4.24 – 4.12 (m, 1H), 4.13 – 4.02 (m, 1H), 3.97 – 3.85 (m, 3H), 3.85 (q, J = 7.2 Hz, 1H), 3.13 (s, 1H), 2.77 – 2.61 (m, 1H), 2.22 – 1.97 (m, 1H), 1.81 – 1.70 (m, 1H), 1.69 – 1.61 (m, 2H), 1.61 – 1.52 (m, 3H), 1.43 – 1.30 (m, 2H), 1.26 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 174.8, 157.8, 146.9, 136.6 (t, *J* = 27.3 Hz), 135.9 (d, *J* = 2.8 Hz), 133.9, 131.5, 129.4, 129.3 (t, *J* = 244.6 Hz), 129.1, 127.8, 127.3, 126.3 (d, *J* = 6.8 Hz), 126.1 (d, *J* = 5.3 Hz), 124.4, 123.0, 119.2, 105.8, 64.5 (d, *J* = 11.1 Hz), 55.5, 45.7 (d, *J* = 3.5 Hz), 42.0 (td, *J* = 23.8, 23.2, 6.1 Hz), 39.7 (d, *J* = 8.3 Hz), 31.6 (d, *J* = 8.9 Hz), 29.9, 26.6 (d, *J* = 2.3 Hz), 18.4 (d, *J* = 5.3 Hz).**^{19}F NMR (565 MHz, CDCl$_3$)** δ -85.53 (q, *J* = 15.0, 14.1 Hz, 1F), -85.63 (t, *J* = 17.0 Hz, 1F). HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{27}H_{30}F_2O_5SNa^+$: 527.1674, found: 527.1685.

4-(4,4-Difluoro-4-(3-methoxyphenyl)butyl)-1,2-dimethoxybenzene (6w)

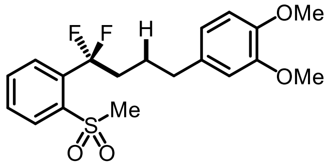


In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-methoxy-3-(trifluoromethyl)benzene (**1c**) (87 μL, 0.60 mmol, 1.0 equiv.) and 4-allyl-1,2-dimethoxybenzene (**4l**) (535 mg, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (10:1 (v/v)), to afford 127 mg 4-(4,4-difluoro-4-(3-methoxyphenyl)butyl)-1,2-dimethoxybenzene (**6w**) as a colorless liquid (63% yield).

R$_f$ = 0.3 (petroleum ether/EtOAc = 10:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.33 (dd, *J* = 19.3, 11.4 Hz, 1H), 7.01 (d, *J* = 7.7 Hz, 1H), 6.97 (s, 1H), 6.94

(d, *J* = 8.2 Hz, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 6.70 – 6.63 (m, 2H), 3.85 (s, 6H), 3.82 (s, 3H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.23 – 2.04 (m, 2H), 1.75 (dq, *J* = 15.6, 7.8 Hz, 2H).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 159.7, 149.0, 147.5, 139.0 (t, *J* = 26.9 Hz), 134.2, 129.7, 123.0 (t, *J* = 242.1 Hz), 120.4, 117.4 (t, *J* = 6.0 Hz), 115.3, 111.8, 111.4, 110.8 (t, *J* = 6.3 Hz), 56.0 (d, *J* = 16.4 Hz), 55.5, 38.5 (t, *J* = 27.5 Hz), 35.0, 24.4. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.22 (t, *J* = 16.2 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{22}O_3F_2Na^+$: 359.1429, found: 359.1432.

4-(4,4-Difluoro-4-(2-(methylsulfonyl)phenyl)butyl)-1,2-dimethoxybenzene (6x)

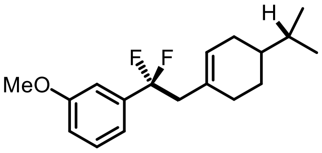


In a N_2 glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.) in a 4.0 mL sealed vial. 1-(methylsulfonyl)-2-(trifluoromethyl)benzene (**1ac**) (23 mg, 0.10 mmol, 1.0 equiv.) and 4-allyl-1,2-dimethoxybenzene (**4l**) (107 mg, 0.6 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (3:1 (v/v)), to afford 28 mg 4-(4,4-difluoro-4-(2-(methylsulfonyl)phenyl)butyl)-1,2-dimethoxybenzene (**6x**) as a colorless liquid (73% yield).

R_f = 0.4 (petroleum ether/EtOAc = 3:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.27 (d, *J* = 7.7 Hz, 1H), 7.71 – 7.61 (m, 3H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.70

(d, J = 8.2 Hz, 2H), 3.86 (d, J = 9.6 Hz, 6H), 3.21 (s, 3H), 2.59 (t, J = 7.8 Hz, 2H), 2.48 (ddd, J = 26.0, 17.6, 8.1 Hz, 2H), 1.83 (dt, J = 15.9, 8.0 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.1, 147.5, 134.4, 133.7, 131.9, 130.7, 128.5 (t, J = 9.5 Hz), 126.5 (t, J = 244.8 Hz) 120.3, 115.7, 111.8, 111.4, 110.2 (t, J = 30.1 Hz), 56.0 (d, J = 8.3 Hz), 45.9, 39.2 (t, J = 25.8 Hz), 35.0, 24.5.**^{19}F NMR (565 MHz, $CDCl_3$)** δ -89.93 (t, J = 17.6 Hz, 2F). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{22}F_2O_4SNa^+$: 407.1099, found: 407.1107.

1-(1,1-Difluoro-2-(4-isopropylcyclohex-1-en-1-yl)ethyl)-3-methoxybenzene (6y)

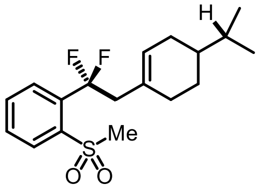


In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 1-methoxy-3-(trifluoromethyl)benzene (**1c**) (87 μL, 0.60 mmol, 1.0 equiv.) and 6,6-dimethyl-2-methylenebicyclo [3.1.1]heptane (**4m**) (476 μL, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (15:1 (v/v)), to afford 152 mg 1-(1,1-difluoro-2-(4-isopropylcyclohex-1-en-1-yl)ethyl)-3-methoxybenzene (**6y**) as a colorless liquid (86% yield).

R_f = 0.2 (petroleum ether/EtOAc = 15:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.34 – 7.28 (m, 1H), 7.02 (d, J = 7.5 Hz, 1H), 6.97 (s, 1H), 6.93 (d, J = 8.1 Hz, 1H), 5.46 (s, 1H), 3.83 (s, 3H), 2.81 – 2.66 (m, 2H), 2.10 – 1.83 (m, 3H), 1.69 (d,

J = 12.2 Hz, 2H), 1.49 – 1.36 (m, 1H), 1.29 – 1.02 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 159.6, 139.2 (t, *J* = 26.5 Hz), 129.8 (t, *J* = 3.3 Hz), 129.4, 128.3, 122.4 (t, *J* = 244.4 Hz), 117.6 (t, *J* = 6.1 Hz), 115.3, 110.8 (t, *J* = 6.3 Hz), 55.5, 47.4 (t, *J* = 27.5 Hz), 39.7, 32.3, 30.3, 29.3, 26.6, 20.1, 19.8. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -93.28 (dt, *J* = 240.8, 16.5 Hz, 1F), -93.96 (dt, *J* = 240.8, 16.8 Hz, 1F). HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{18}H_{24}OF_2H^+$: 295.1868, found: 295.1874.

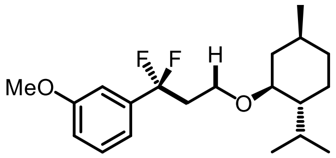
1-(1,1-Difluoro-2-(4-isopropylcyclohex-1-en-1-yl)ethyl)-2-(methylsulfonyl) benzene (6z)



In a N_2 glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.) in a 4.0 mL sealed vial. 1-(methylsulfonyl)-2-(trifluoromethyl)benzene (**1ac**) (23 mg, 0.10 mmol, 1.0 equiv.) and 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane (**4m**) (95 μL, 0.6 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (5:1 (v/v)), to afford 28 mg 1-(1,1-difluoro-2-(4-isopropylcyclohex-1-en-1-yl)ethyl)-2-(methylsulfonyl)benzene (**6z**) as a white solid (82% yield).

R$_f$ = 0.2 (petroleum ether/EtOAc = 5:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.29 – 8.22 (m, 1H), 7.70 – 7.64 (m, 1H), 7.64 – 7.60 (m, 2H), 5.52 (s, 1H), 3.21 (s, 3H), 3.15 – 3.01 (m, 2H), 1.98 (dd, J = 19.4, 7.0 Hz, 3H), 1.75 – 1.61 (m, 2H), 1.42 (dd, J = 13.3, 6.7 Hz, 1H), 1.24 – 1.15 (m, 1H), 1.15 – 1.04 (m, 1H), 0.86 (t, J = 7.0 Hz, 6H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 138.6, 137.2 (t, J = 27.5 Hz), 133.4, 131.6, 130.6, 129.7, 129.0, 128.9 (t, J = 9.6 Hz), 123.2 (t, J = 246.0 Hz), 47.0 (t, J = 25.6 Hz), 46.0 (t, J = 5.8 Hz), 39.8, 32.3, 30.6, 29.3, 26.6, 20.1, 19.8. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -87.28 (ddd, J = 245.4, 19.8, 15.4 Hz, 1F), -87.77 – -88.35 (m, 1F). HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{18}H_{24}O_2F_2SNa^+$: 365.1357, found: 365.1364.

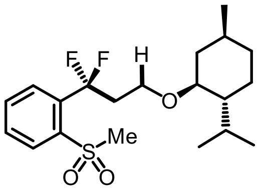
1-(1,1-difluoro-3-(((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl)oxy)propyl)-3-methoxybenzene (6aa)



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 3-(trifluoromethyl)anisole (**1c**) (87 μL, 0.60 mmol, 1.0 equiv.) and (1*R*,2*S*,4*S*)-1-isopropyl-4-methyl-2-(vinyloxy)cyclohexane (**4n**) (547 mg, 3.0 mmol, 5.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (20:1 (v/v)), to afford 147 mg 1-(1,1-difluoro-3-(((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl)oxy)propyl)-3-methoxybenzene (**6aa**) as a yellow liquid (72% yield).

R_f = 0.3 (petroleum ether/EtOAc = 20:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.34-7.31 (m , 1H), 7.06 (d, *J* = 6.4 Hz, 1H), 7.01 (s, 1H), 6.95 (d, *J* = 6.4 Hz, 1H), 3.83 (s, 3H), 3.73 (dd, *J* = 36.5, 11.4 Hz, 1H), 3.41 (t, *J* = 23.7 Hz, 1H), 2.99 (d, *J* = 10.0 Hz, 1H), 2.44 (d, *J* = 4.5 Hz, 2H), 2.17 – 1.96 (m, 2H), 1.70 – 1.52 (m, 2H), 1.29 (d, *J* = 30.6 Hz, 1H), 1.17 (d, *J* = 10.3 Hz, 1H), 1.00 – 0.93 (m, 1H), 0.90 (d, *J* = 5.5 Hz, 3H), 0.87 (d, *J* = 6.2 Hz, 3H), 0.84 – 0.78 (m, 2H), 0.74 (d, *J* = 6.0 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 159.7, 138.7 (t, *J* = 25.9 Hz), 129.7, 122.0 (t, *J* = 243.2 Hz), 117.3 (t, *J* = 6.0 Hz), 115.5, 110.6 (t, *J* = 6.1 Hz), 79.7, 62.4 (t, *J* = 4.6 Hz), 55.5, 48.3, 40.4, 39.8 (t, *J* = 26.8 Hz), 34.7, 31.6, 25.7, 23.5, 22.5, 21.1, 16.4. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -93.38 – -94.70 (m, 2F). HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{20}H_{30}F_2O_2Na^+$: 363.2106, found: 363.2118.

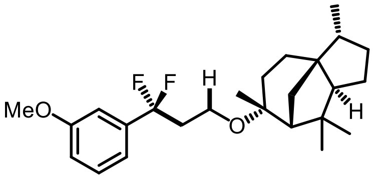
1-(1,1-difluoro-3-(((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl)oxy)propyl)-2-(methylsulfonyl)benzene (6ab)



In a N_2 glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.) in a 4.0 mL sealed vial. 1-(methylsulfonyl)-2-(trifluoromethyl)benzene (**1ac**) (23 mg, 0.10 mmol, 1.0 equiv.) and (1*R*,2*S*,4*S*)-1-isopropyl-4-methyl-2-(vinyloxy)cyclohexane (**4n**) (109 mg, 0.6 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (10:1 (v/v)), to afford 38 mg 1-(1,1-difluoro-3-(((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl)oxy)propyl)-2-(methylsulfonyl)benzene (**6ab**) as a colorless liquid (98% yield).

R$_f$ = 0.3 (petroleum ether/EtOAc = 10:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.25 (d, *J* = 7.9 Hz, 1H), 7.79 – 7.66 (m, 2H), 7.66 – 7.58 (m, 1H), 3.92 – 3.72 (m, 1H), 3.61 – 3.45 (m, 1H), 3.19 (s, 3H), 3.05 – 2.92 (m, 1H), 2.88 – 2.64 (m, 2H), 2.25 – 2.07 (m, 1H), 2.07 – 1.97 (m, 1H), 1.80 – 1.50 (m, 2H), 1.48 – 1.26 (m, 1H), 1.21 – 1.05 (m, 1H), 0.98 – 0.91 (m, 1H), 0.89 (d, *J* = 6.7 Hz, 3H), 0.85 (d, *J* = 7.1 Hz, 3H), 0.83 – 0.78 (m, 2H), 0.73 (d, *J* = 6.9 Hz, 3H).. **^{13}C NMR (151 MHz, CDCl$_3$)** δ 138.6, 137.1 (t, *J* = 27.3 Hz), 133.7, 131.8, 130.7, 128.6 (t, *J* = 9.8 Hz), 122.9 (t, *J* = 244.8 Hz), 79.6, 62.1 (t, *J* = 4.1 Hz), 48.3, 45.9 (t, *J* = 5.6 Hz), 40.4, 40.1 (d, *J* = 25.5 Hz), 34.7, 31.6, 25.6, 23.5, 22.5, 21.1, 16.4. ^{19}F NMR (565 MHz, CDCl$_3$) δ -87.25 – -88.91 (m, 2F). HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{20}H_{30}F_2O_3SNa^+$: 411.1776, found: 411.1719.

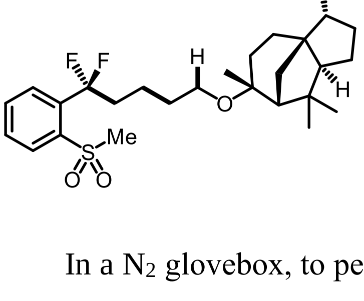
(3*R*, 3a*S*, 6*R*, 7*R*, 8a*S*)-6-(3,3-Difluoro-3-(3-methoxyphenyl)propoxy)-3,6,8,8-tetramethyloctahydro-1H-3a,7-methanoazulene (6ac)



In a N$_2$ glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (31 μL, 0.30 mmol, 0.5 equiv.) and phenylsilane (444 μL, 3.6 mmol, 6.0 equiv.) in a 8.0 mL sealed vial tube. 3-(trifluoromethyl)anisole (**1c**) (348 μL, 2.4 mmol, 4.0 equiv.) and (3*R*, 3a*S*, 6*R*, 7*R*, 8a*S*)-3,6,8,8-tetramethyl-6-(vinyloxy)octahydro-1H-3a,7-methanoazulene (**4o**) (149 mg, 0.6 mmol, 1.0 equiv.) were added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (20:1 (v/v)), to afford 198 mg (3*R*, 3a*S*, 6*R*, 7*R*, 8a*S*)-6-(3,3-difluoro-3-(3-methoxyphenyl)propoxy)-3,6,8,8-tetramethyloctahydro-1H-3a,7-methanoazulene (**6ac**) as a yellow liquid (81% yield).

R$_f$ = 0.5 (petroleum ether/EtOAc = 20:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.37 – 7.29 (m, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 7.01 (s, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 3.81 (d, *J* = 26.9 Hz, 3H), 3.54 – 3.44 (m, 2H), 2.40 (tt, *J* = 15.2, 7.8 Hz, 2H), 1.85 (dt, *J* = 11.6, 5.8 Hz, 1H), 1.75 (dd, *J* = 15.9, 6.4 Hz, 2H), 1.68 – 1.55 (m, 3H), 1.52 – 1.47 (m, 1H), 1.44 – 1.22 (m, 6H), 1.17 (d, *J* = 12.7 Hz, 6H), 0.92 (d, *J* = 10.7 Hz, 3H), 0.83 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 159.7, 138.9 (t, *J* = 26.2 Hz), 129.7, 122.2 (t, *J* = 242.1 Hz), 117.3 (t, *J* = 6.0 Hz), 115.5, 110.6 (t, *J* = 6.4 Hz), 78.8, 56.9, 56.3, 55.5, 54.6, 54.1, 43.4, 41.6, 41.3, 39.8 (t, *J* = 26.6 Hz), 37.2, 33.1, 31.4, 28.9, 27.0, 25.5, 24.7, 15.7. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -93.59 (dt, *J* = 246.4, 16.2 Hz, 1F), -94.61 (dt, *J* = 246.6, 17.0 Hz, 1F). HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{25}H_{36}O_2F_2Na^+$: 429.2576, found: 429.2575.

(3*R*, 3a*S*, 6*R*, 7*R*, 8a*S*)-6-(3,3-Difluoro-3-(2-(methylsulfonyl)phenyl)propoxy)-3,6,8,8-tetramethyloctahydro-1H-3a,7-methanoazulene (6ad)

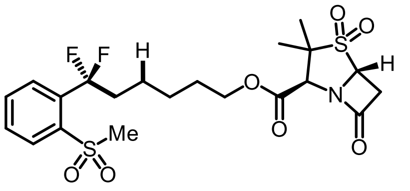


In a N$_2$ glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (74 μL, 0.60 mmol, 6.0 equiv.) in a 4.0 mL sealed vial. 1-(methylsulfonyl)-2-(trifluoromethyl)benzene (**1ac**) (23 mg, 0.10 mmol, 1.0 equiv.) and (3*R*, 3a*S*, 6*R*, 7*R*, 8a*S*)-3,6,8,8-tetramethyl-6-(vinyloxy)octahydro-1H-3a,7-

methanoazulene (**4o**) (149 mg, 0.6 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (10:1 (v/v)), to afford 36 mg (3*R*, 3a*S*, 6*R*, 7*R*, 8a*S*)-6-(3,3-difluoro-3-(2-(methylsulfonyl)phenyl) propoxy)-3,6,8,8-tetramethyloctahydro-1H-3*a*,7-methanoazulene (**6ad**) as a colorless liquid (78% yield).

R_f = 0.2 (petroleum ether/EtOAc = 10:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.25 (d, *J* = 7.9 Hz, 1H), 7.77 – 7.65 (m, 2H), 7.65 – 7.59 (m, 1H), 3.67 – 3.49 (m, 2H), 3.19 (s, 3H), 2.71 (tt, *J* = 17.8, 7.0 Hz, 2H), 1.90 – 1.80 (m, 1H), 1.81 – 1.66 (m, 3H), 1.67 – 1.60 (m, 2H), 1.60 – 1.52 (m, 2H), 1.53 – 1.45 (m, 1H), 1.44 – 1.35 (m, 1H), 1.35 – 1.30 (m, 1H), 1.28 – 1.21 (m, 2H), 1.16 (s, 3H), 1.13 (s, 3H), 0.92 (s, 3H), 0.81 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 138.6, 137.3, 133.6, 131.7, 130.7, 128.6 (t, *J* = 9.5 Hz), 123.1 (t, *J* = 244.6 Hz), 78.8, 56.9, 56.4, 54.4 (t, *J* = 4.8 Hz), 54.1, 46.0 (t, *J* = 5.8 Hz), 43.4, 41.6, 41.3, 40.5 (d, *J* = 24.2 Hz), 37.2, 33.1, 314, 29.0, 27.1, 25.5, 24.6, 15.7. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -88.14 (q, *J* = 17.0 Hz, 2F). HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{25}H_{36}O_2F_2Na^+$: 477.2245, found: 477.2256.

6,6-difluoro-6-(2-(methylsulfonyl)phenyl)hexyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (6af)

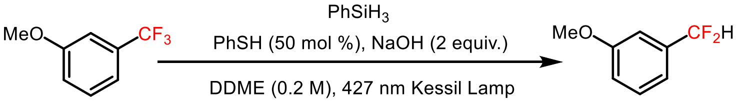


In a N$_2$ glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2.0 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and phenylsilane (19 μL, 0.15 mmol, 1.5 equiv.) in a 4.0 mL sealed vial. 1-(methylsulfonyl)-2-(trifluoromethyl)benzene (**1w**) (92 mg, 0.40 mmol, 4.0 equiv.) and pent-4-en-1-yl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (**4p**) (30 mg, 0.10 mmol, 1.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether (3:1 (v/v)). The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate, to afford 24 mg 6,6-difluoro-6-(2-(methylsulfonyl)phenyl)hexyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (**6af**) as a yellow solid (48% yield).

R_f = 0.2 (petroleum ether/EtOAc = 3:1). **NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.27 (d, *J* = 7.7 Hz, 1H), 7.76 – 7.62 (m, 3H), 4.62 (s, 1H), 4.37 (s, 1H), 4.19 (t, *J* = 5.8 Hz, 2H), 3.53 – 3.41 (m, 2H), 3.20 (s, 3H), 2.49 – 2.39 (m, 2H), 1.74 – 1.67 (m, 2H), 1.61 (s, 4H), 1.57 (s, 1H), 1.47 – 1.42 (m, 2H), 1.41 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 170.8 , 167.1 , 133.8 , 131. 9, 130.8 , 128.3 (t, *J* = 9.7 Hz), 123.4 (t, *J* = 245.0 Hz), 66.4 , 63.4 , 62.9 , 61.2 , 45.9 (t, *J* = 5.7 Hz), 39.4 (t, *J* = 25.8 Hz), 38.5, 29.8 , 28.2 , 25.5 , 21.88 (t, *J* = 3.4 Hz), 20.5 , 18.8 . **^{19}F NMR (565 MHz, $CDCl_3$)** δ -90.60 (t, 2F , *J* = 17.8 Hz). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{27}F_2NO_7S_2Na^+$: 530.1089, found: 530.1097.

6 Mechanistic Studies

6.1 UV-Vis Absorption Spectroscopic Measurements



1c

UV-Vis absorption spectra were measured in a 1 cm quartz cuvette using a UV-2600i spectrophotometer. Stock solutions of PhSH, NaOH, **1g** were prepared with the same concentration used in the reaction. NaOH was used in 2.0 equiv. to ensure generation of PhS^- under measurement condition. The solutions were prepared in the presence of air using DDME as solvent.

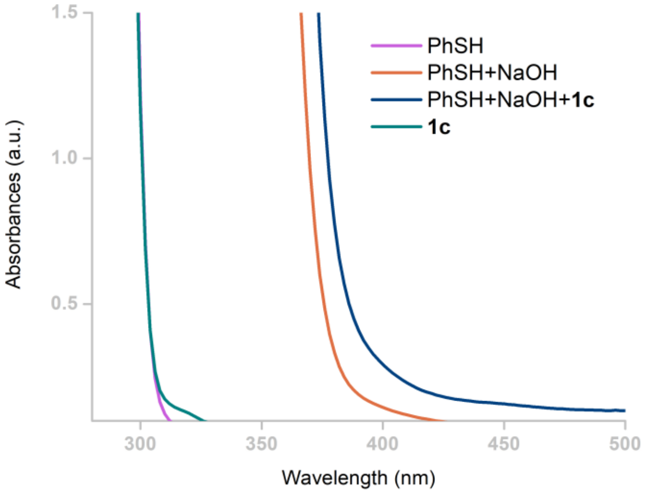
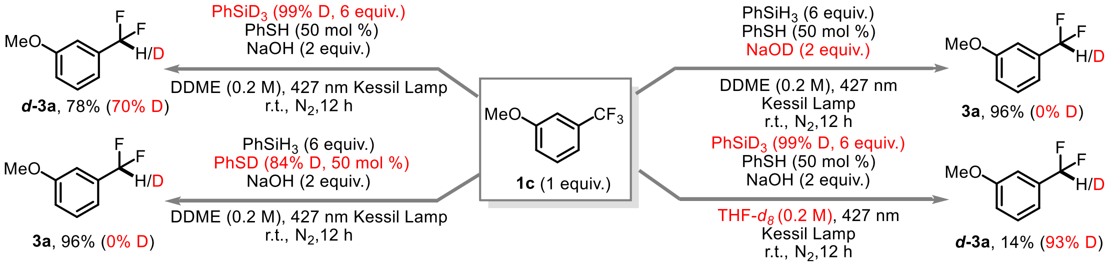


Figure S41. UV/vis absorption spectra of reductant, substrate, and the mixture of PhSH, NaOH and **1c**.

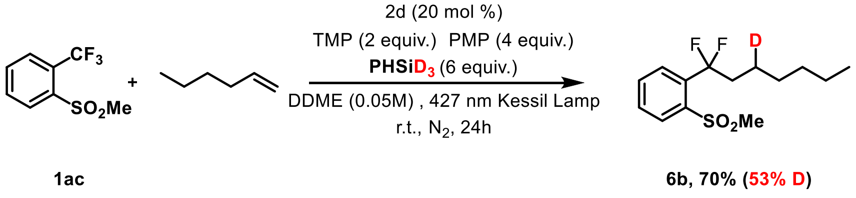
6.2 Deuteration experiment of Hydrodefluorination

The deuterium substitution experiment was carried out under the standard conditions of product **3a**, yield determined by ^{19}F NMR using (trifluoromethoxy)benzene as an internal standard, the substrate dosages for the four experimental groups were as follows:



Scheme S5. Deuteration experiment of Hydrodefluorination

In a N_2 glovebox, to pentafluorobenzenethiol (2.7 μL, 0.020 mmol, 0.2 equiv.) in dry DDME (2.0 mL) were added TMP (34 μL, 0.20 mmol, 2 equiv.), PMP (72 μL, 0.4 mmol, 4 equiv.) and $PhSiD_3$ (67 mg, 0.60 mmol, 6.0 equiv.) in a 4.0 mL sealed vial. 1-(methylsulfonyl)-2-(trifluoromethyl)benzene (**1ac**) (23 mg, 0.10 mmol, 1.0 equiv.) and hex-1-ene (**4a**) (74 μL, 0.6 mmol, 6.0 equiv.) were added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the reaction was diluted with diethyl ether and extracted with water, saturated ammonium chloride solution, and saturated sodium chloride solution, followed by reverse extraction of the mixed aqueous phase using diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate (10:1 (v/v)), to afford 20 mg **6b** and *d*-**6b** as a colorless liquid (70% yield).



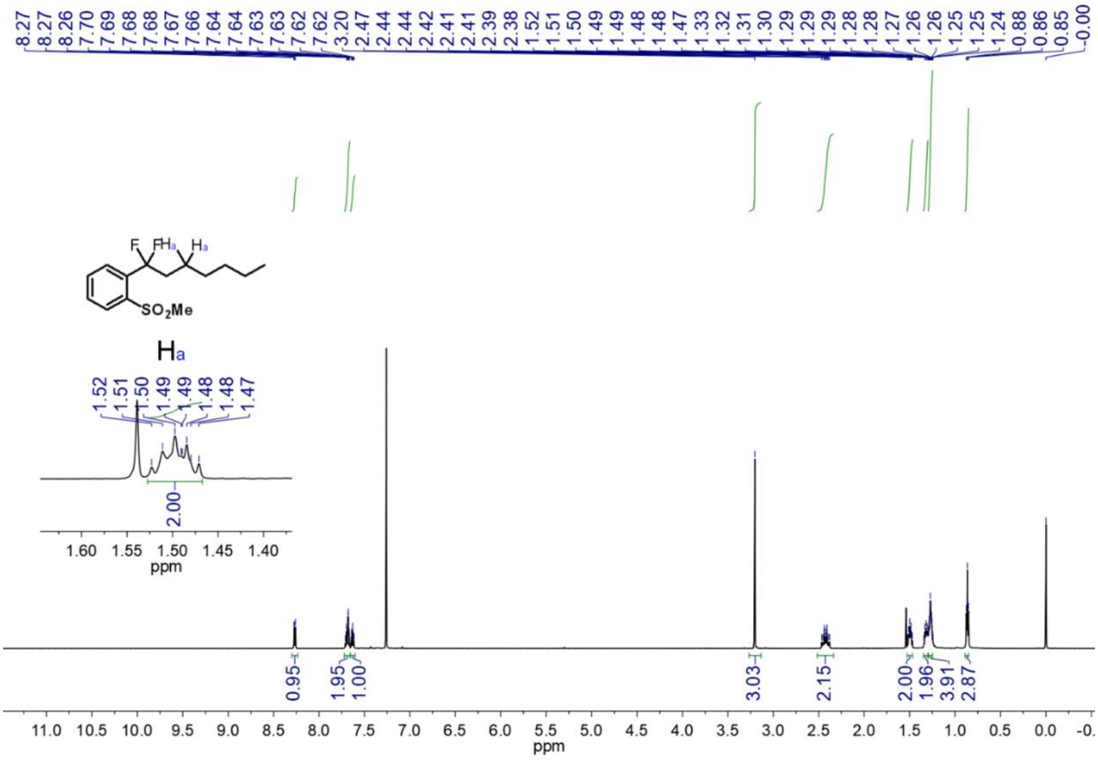


Figure S42. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6b**

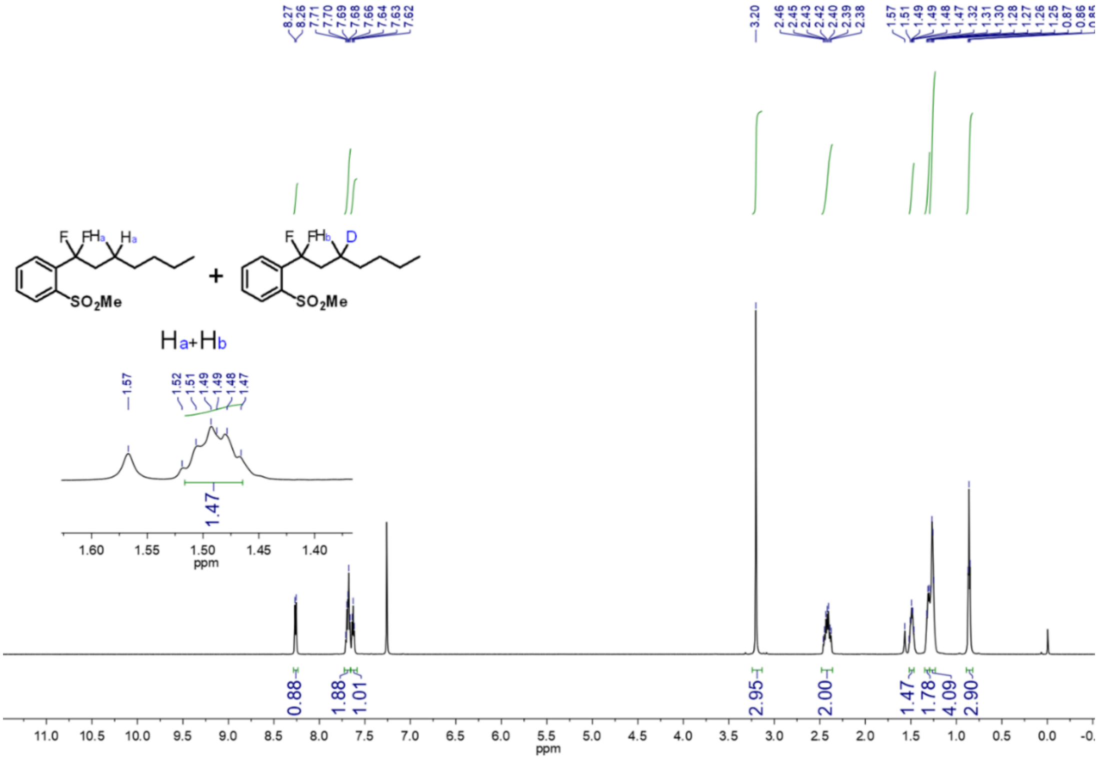
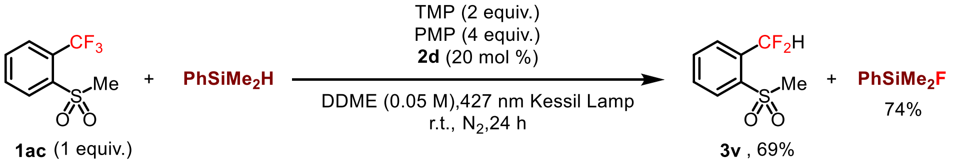


Figure S43. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6b** and ***d*-6b**

6.3 Silane reagents as fluorine scavengers for in situ generation of Si-F species



In a N_2 glovebox, to pentafluorobenzenethiol (1.4 μL, 0.010 mmol, 0.2 equiv.) in dry DDME (1.0 mL) were added TMP (17 μL, 0.10 mmol, 2 equiv.), PMP (36 μL, 0.2 mmol, 4 equiv.) and $PhSiMe_2H$ (41 μL, 0.30 mmol, 6.0 equiv.) in a 2.0 mL sealed vial tube. 1-(methylsulfonyl)-2-(trifluoromethyl)benzene (**1ac**) (11.2 mg, 0.05 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 24 h at room temperature under the 427 nm Kessil Lamp. Then, the crude residues were analyzed by ^{19}F NMR with $PhOCF_3$ as the internal standard and GC-MS. The ^{19}F NMR yield of **3v** were 69%, and $PhSiMe_2F$ trapped F^- were 74%, Spectral data was consistent with literature.[26] The $PhSiMe_2F$ was detected by GC-MS. MS (EI) m/z: 154.1.

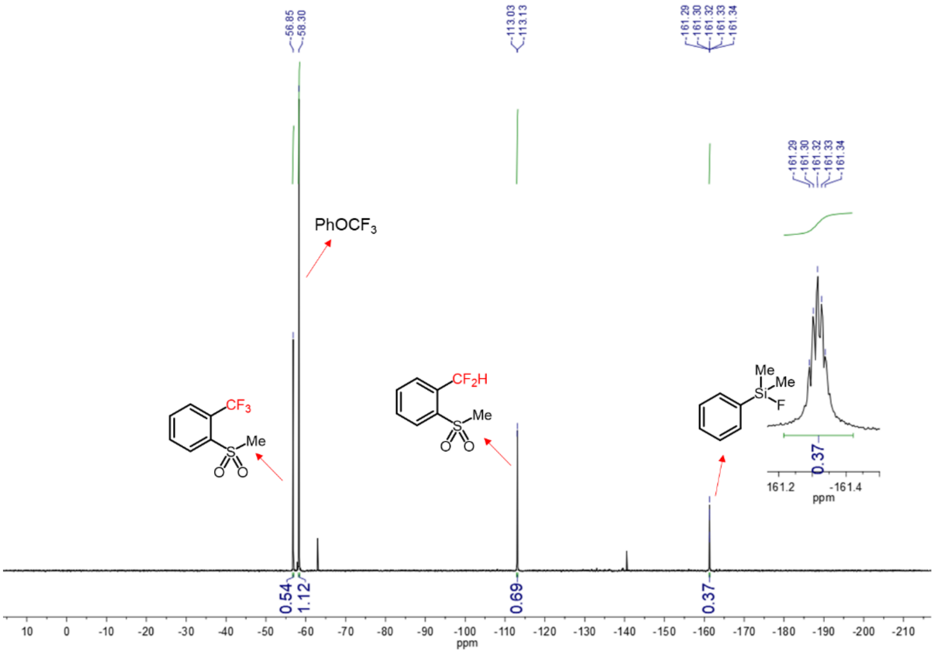


Figure S44. ^{19}F NMR Crude of the reaction

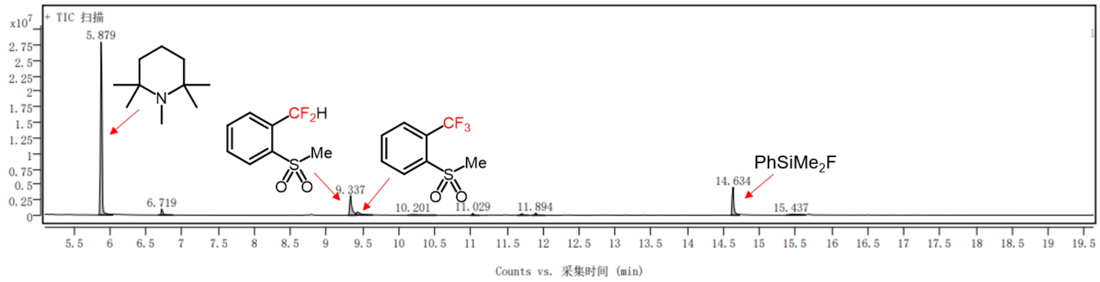


Figure S45. GC-MS of the reaction

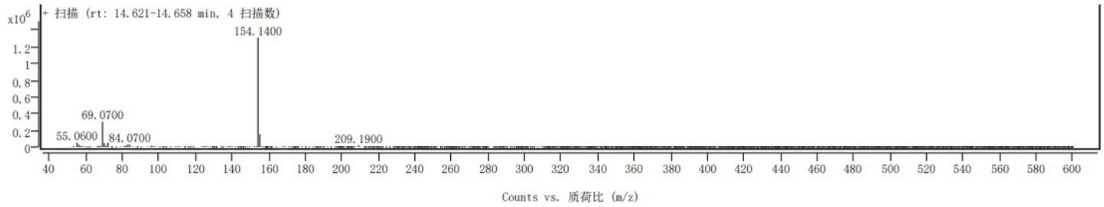
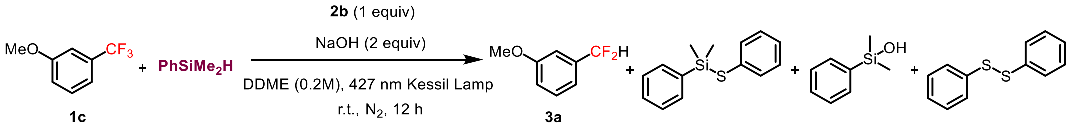


Figure S46. $PhSiMe_2F$ was detected by GC-MS.



In a N_2 glovebox, to NaOH (48 mg, 1.2 mmol, 2.0 equiv.) in dry DDME (3.0 mL) were added benzenethiol (62 µL, 0.60 mmol, 1.0 equiv.) and dimethylphenylsilane (552 µL, 3.6 mmol, 6.0 equiv.) in an 8.0 mL sealed vial tube. 1-methoxy-3-(trifluoromethyl)benzene (1c) (87 µL, 0.60 mmol, 1.0 equiv.) was added to the reaction and the resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the crude residues were analyzed by GC-MS and HRMS. The $PhSiMe_2OH$ was detected by GC-MS. MS (EI) m/z: 152. The PhSSPh was detected by GC-MS. MS (EI) m/z: 218.The $PhMe_2SiSPh$ was detected by HRMS.

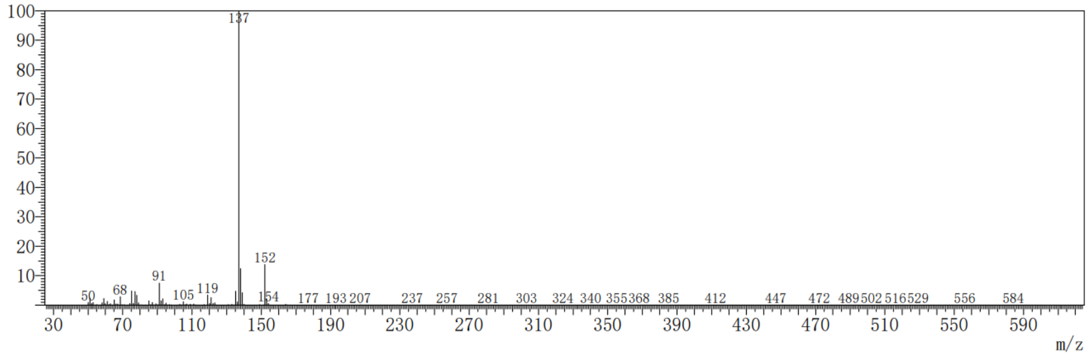


Figure S47. $PhSiMe_2OH$ was detected by GC-MS.

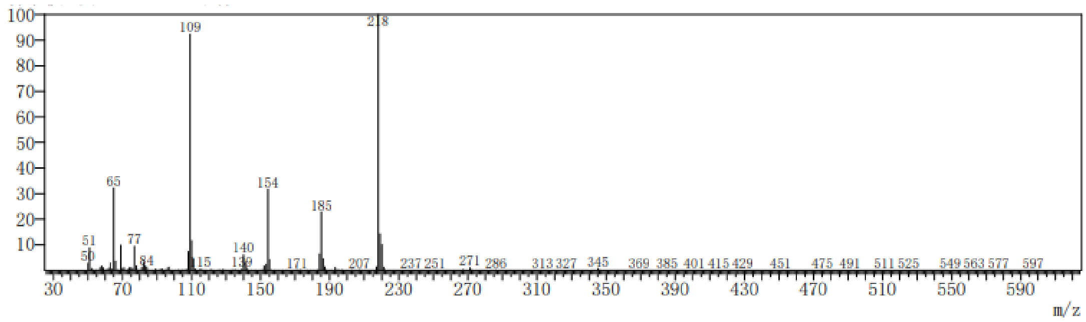
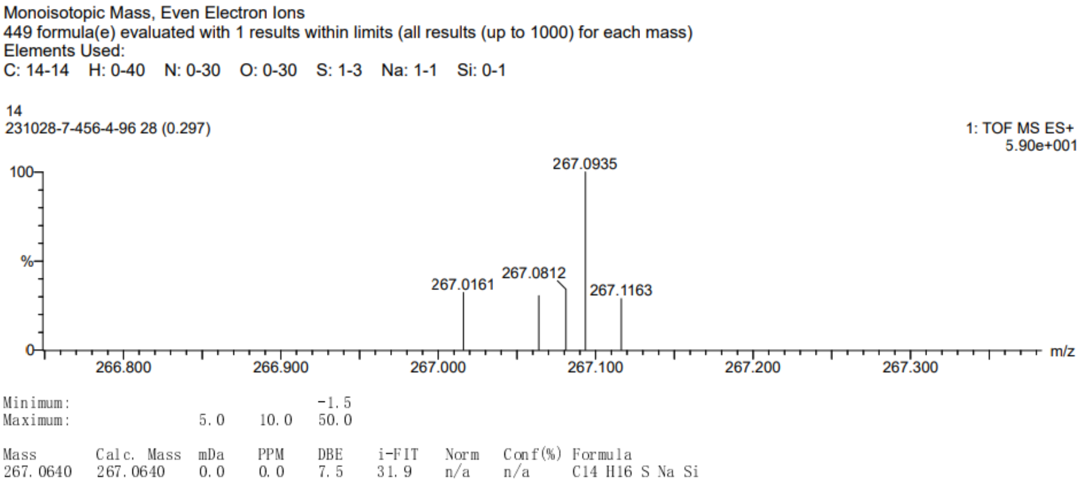


Figure S48. PhSSPh was detected by GC-MS.



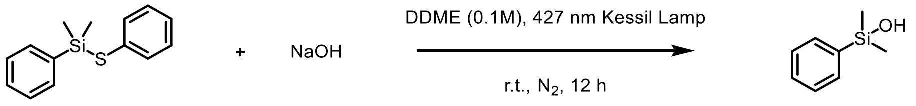
```
Monoisotopic Mass, Even Electron Ions
449 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 14-14    H: 0-40    N: 0-30    O: 0-30    S: 1-3    Na: 1-1    Si: 0-1

14
231028-7-456-4-96 28 (0.297)                                    1: TOF MS ES+
                                                                    5.90e+001

Minimum:                              -1.5
Maximum:              5.0     10.0    50.0

Mass      Calc. Mass  mDa    PPM    DBE    i-FIT   Norm   Conf(%)  Formula
267.0640  267.0640    0.0    0.0    7.5    31.9    n/a    n/a      C14 H16 S Na Si
```

Figure S49. $PhMe_2SiSPh$ was detected by HRMS.



In a N_2 glovebox, to NaOH (16 mg, 0.40 mmol, 4.0 equiv.) in dry DDME (1.0 mL) were added dimethyl(phenyl)(phenylthio)silane (24 mg, 0.10 mmol, 1.0 equiv.) in an 2.0 mL sealed vial tube. The resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the crude residues were analyzed by GC-MS. The $PhSiMe_2OH$ was detected by GC-MS. MS (EI) m/z: 152.

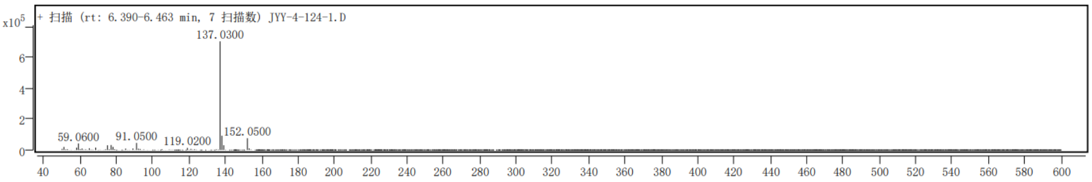
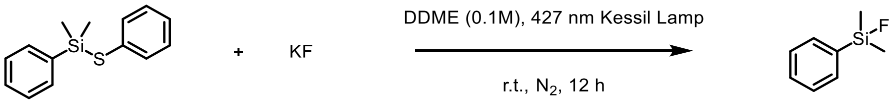


Figure S50. $PhSiMe_2OH$ was detected by GC-MS.



In a N_2 glovebox, to KF (23 mg, 0.40 mmol, 4.0 equiv.) in dry DDME (1.0 mL) were added dimethyl(phenyl)(phenylthio)silane (24 mg, 0.10 mmol, 1.0 equiv.) in an 2.0 mL sealed vial tube. The resulting mixture was stirred for 12 h at room temperature under the 427 nm Kessil Lamp. Then, the crude residues were analyzed by ^{19}F NMR. The $PhSiMe_2OH$ was detected by ^{19}F NMR.

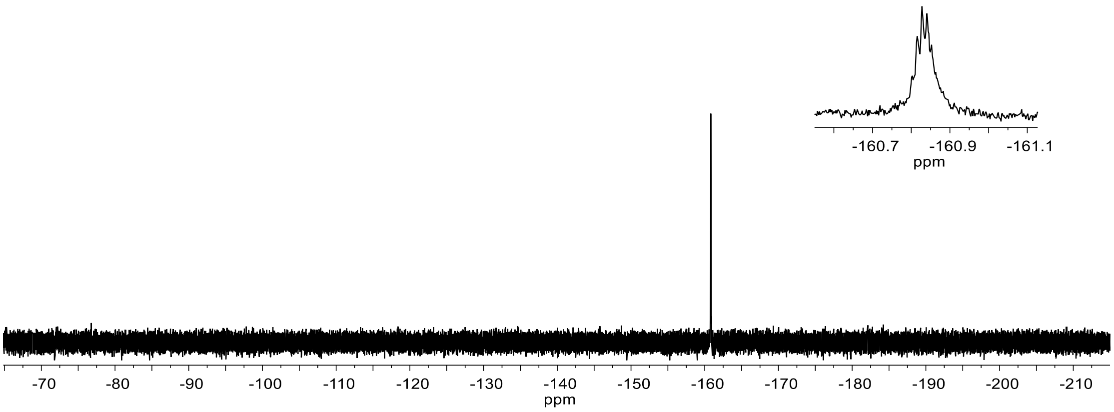


Figure S51. $PhSiMe_2F$ was detected by ^{19}F NMR

6.4 DFT Calculations

Computational Methods

Geometry optimizations in dimethoxyethane using the solvation model based on density (SMD) [27] and Grimme's D3 [28] dispersion were performed via the Gaussian 16 (Revision C 01) [29] package. The M06-2X [30] functional and the Truhlar and co-workers modified Def2-TZVP [31] basis sets with additional minimal augmentation (ma-Def2-TZVP)[32] were utilized. Frequency computations were used to verify the natures of all stationary points, and all located minima were confirmed with no imaginary frequency. The above optimizations [SMD(DMOE)-M06-2X-D3/ma-Def2-TZVP] were performed at 1 atm and 298.15 K. For comparisons, the gas-phase optimizations [M06-2X-D3/ma-Def2-TZVP] and [ωB97XD [33]/ma-Def2-TZVP] were also performed (see following text for the detailed comparisons).

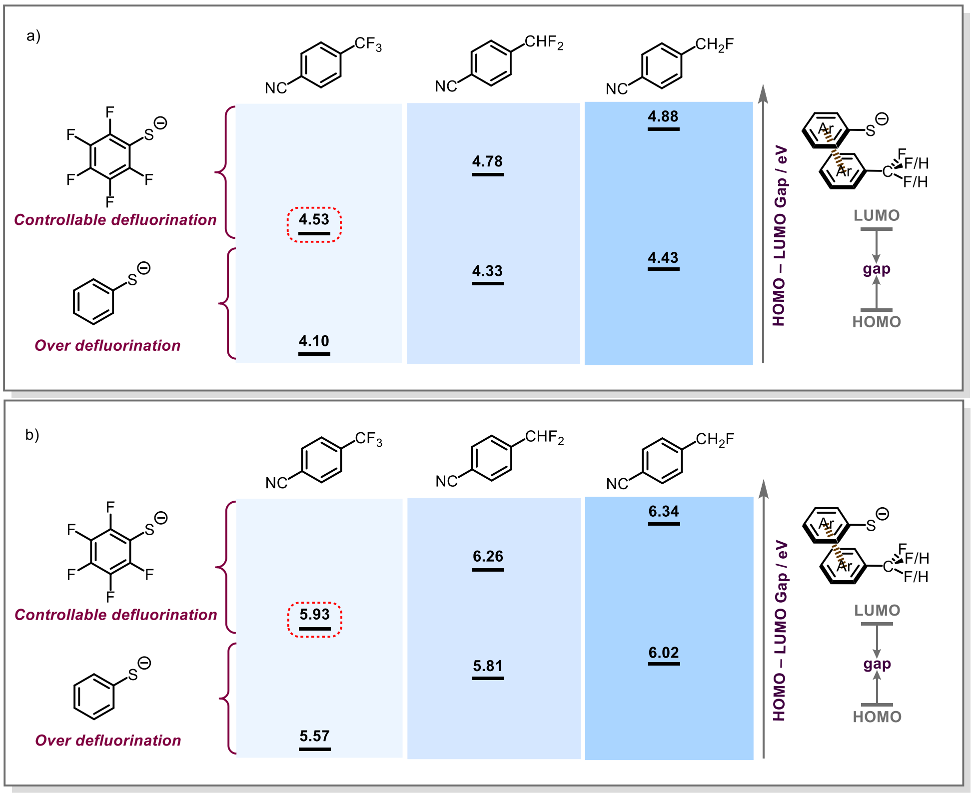
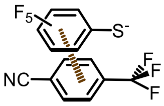


Figure S52. a) Computational results obtained from the [M06-2X-D3/ma-def2-TZVP] optimizations. b) Computational results obtained from the [ωB97XD/ ma-def2-TZVP] optimizations.

Table S2. Cartesian coordinates and absolute energies of the optimized structures.

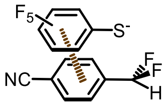
SMD(DME)-M06-2X-D3/ma-def2-TZVP:



el energy= -1779.79764856

C	-2.915206	-0.228790	-0.005164
C	-2.286096	-0.587411	-1.182877
C	-1.087131	-1.271133	-1.152489
C	-0.432874	-1.642650	0.031602
C	-1.094539	-1.222281	1.194621
C	-2.294430	-0.539969	1.190164
C	2.192542	0.862507	-0.023233
C	1.587825	1.154260	1.190270
C	0.327268	1.720913	1.196411

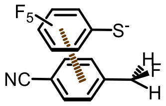
C	-0.324810	1.993692	-0.001787
C	0.288266	1.678508	-1.209793
C	1.548975	1.112423	-1.225343
H	2.090083	0.935968	2.122998
H	-0.164839	1.945667	2.134074
H	-0.234331	1.869816	-2.138343
S	1.048269	-2.531841	0.058988
C	3.597568	0.330058	-0.039345
F	3.853239	-0.424351	-1.110356
F	4.488992	1.344281	-0.071691
F	3.893653	-0.390840	1.044243
F	-0.543622	-1.576222	-2.338169
F	-2.845698	-0.264257	-2.353931
F	-4.078305	0.424528	-0.022508
F	-2.860923	-0.169478	2.343699
F	-0.557276	-1.476513	2.395022
H	2.020682	0.862718	-2.165952
C	-1.575646	2.599917	0.006696
N	-2.546118	3.129039	0.012172



el energy= -1680.53142387

C	2.649956	-0.379644	0.009343
C	1.989636	-0.645308	1.194303
C	0.731308	-1.213885	1.178469
C	0.048352	-1.558143	0.003524
C	0.743462	-1.228630	-1.168459
C	2.002042	-0.660840	-1.178828
C	-2.330432	1.151533	-0.004490
C	-1.682693	1.367163	-1.213611
C	-0.383805	1.837962	-1.217897
C	0.273870	2.093345	-0.018742
C	-0.379415	1.861157	1.186612
C	-1.679117	1.390098	1.197312
H	-2.186921	1.162469	-2.148682

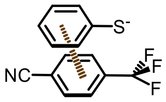
H	0.132962	2.003940	-2.154818
H	0.140472	2.046205	2.118225
S	-1.501661	-2.329359	-0.000409
C	-3.722464	0.591586	-0.005691
F	-4.435788	1.092784	-1.056248
F	-4.391798	0.963828	1.121966
F	0.160560	-1.433870	2.369953
F	2.576337	-0.345585	2.357961
F	3.872658	0.154177	0.012164
F	2.600963	-0.377430	-2.340359
F	0.184760	-1.463057	-2.362819
H	-2.179114	1.203813	2.138048
C	1.569190	2.595128	-0.025475
N	2.581091	3.040414	-0.030373
H	-3.736706	-0.496789	-0.070221



el energy= -1581.26807431

C	-2.831929	-0.263676	0.000258
C	-2.208498	-0.625244	-1.179180
C	-0.991729	-1.276862	-1.152229
C	-0.317825	-1.619357	0.028836
C	-0.977081	-1.200832	1.193403
C	-2.193736	-0.548182	1.192804
C	2.127036	0.853648	-0.014165
C	1.509627	1.214539	1.178462
C	0.269736	1.823841	1.163799
C	-0.369326	2.080152	-0.045996
C	0.253055	1.727533	-1.239594
C	1.493643	1.118656	-1.222419
H	1.992562	0.995950	2.123226
H	-0.223524	2.085249	2.091825
H	-0.252121	1.915150	-2.179022
S	1.185433	-2.475697	0.046432
C	3.471341	0.194981	0.005837

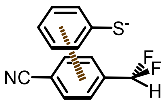
F	4.467751	1.187524	0.034711
F	-0.452980	-1.583571	-2.339456
F	-2.785865	-0.328747	-2.348561
F	-4.012882	0.357489	-0.012963
F	-2.755910	-0.174778	2.347451
F	-0.424219	-1.431319	2.391373
H	1.963486	0.824743	-2.153167
C	-1.616176	2.691707	-0.061798
N	-2.591362	3.212720	-0.073587
H	3.603928	-0.417994	0.895556
H	3.639298	-0.402823	-0.888321



el energy= -1283.54837400

C	-3.157334	0.455186	0.161183
C	-2.368928	0.852366	1.235797
C	-1.193124	1.559988	1.029523
C	-0.748162	1.907409	-0.261131
C	-1.566964	1.491613	-1.331256
C	-2.742893	0.786083	-1.125575
C	2.006464	-0.591185	0.096132
C	1.413891	-0.751748	-1.145073
C	0.173580	-1.356250	-1.224645
C	-0.467724	-1.805454	-0.075018
C	0.136779	-1.625319	1.164078
C	1.374221	-1.017931	1.255143
H	1.901997	-0.393010	-2.040092
H	-0.312867	-1.470990	-2.184053
H	-0.376582	-1.949340	2.059736
S	0.731767	2.795294	-0.521026
C	3.379814	0.004296	0.207716
H	1.839763	-0.873998	2.221479
C	-1.696310	-2.450530	-0.165397
N	-2.637313	-3.024791	-0.239908
H	-0.591309	1.859775	1.880073

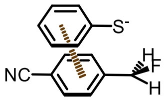
H	-2.672464	0.608313	2.248382
H	-4.069150	-0.106340	0.320254
H	-3.340945	0.485975	-1.979446
H	-1.260545	1.739708	-2.341121
F	3.487605	0.856774	1.232381
F	3.765321	0.646723	-0.895574
F	4.301585	-0.958683	0.427840



el energy= -1184.28269051

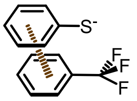
C	-3.164652	0.900108	-0.015034
C	-2.604636	1.155613	1.232590
C	-1.300880	1.617414	1.343166
C	-0.493443	1.849768	0.211948
C	-1.084591	1.579481	-1.037371
C	-2.388339	1.117240	-1.148457
C	1.658392	-1.115474	-0.091708
C	1.005208	-1.420183	-1.280275
C	-0.314341	-1.825800	-1.250436
C	-0.991430	-1.925828	-0.038834
C	-0.326529	-1.620480	1.143413
C	0.995487	-1.215867	1.121144
H	1.522155	-1.329539	-2.226961
H	-0.836265	-2.048651	-2.172089
H	-0.857457	-1.686545	2.084038
S	1.148171	2.437120	0.353092
C	3.067931	-0.605710	-0.154799
H	1.497470	-0.955389	2.042477
C	-2.318461	-2.337412	-0.006762
N	-3.357530	-2.712825	0.020679
H	-0.882297	1.810410	2.324310
H	-3.189756	0.993093	2.131405
H	-4.180051	0.534614	-0.101507
H	-2.801801	0.921261	-2.132100
H	-0.494943	1.740025	-1.932873

F	3.814361	-1.389782	-0.993319
F	3.668519	-0.679150	1.063870
H	3.127394	0.425099	-0.504019



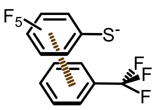
el energy= -1085.01882349

C	-2.914598	-0.320061	0.005408
C	-2.289390	-0.691815	-1.180647
C	-1.067099	-1.348117	-1.161599
C	-0.410350	-1.668200	0.043356
C	-1.067633	-1.281799	1.228409
C	-2.289927	-0.625508	1.210521
C	2.184559	0.903867	-0.019890
C	1.562921	1.254790	1.172722
C	0.326273	1.870472	1.157904
C	-0.306332	2.143591	-0.051388
C	0.324685	1.806174	-1.245119
C	1.561469	1.190711	-1.228701
H	2.038713	1.021451	2.117523
H	-0.172144	2.118852	2.086217
H	-0.174995	2.004555	-2.184713
S	1.126647	-2.502464	0.066815
C	3.522561	0.233475	-0.002827
F	4.529898	1.215880	-0.027014
H	2.035992	0.907216	-2.160321
C	-1.552897	2.757102	-0.067101
N	-2.521626	3.289324	-0.080705
H	-0.595594	-1.629510	-2.096395
H	-2.757554	-0.465957	-2.132725
H	-3.864732	0.198744	-0.009179
H	-2.758424	-0.346999	2.148389
H	-0.596410	-1.510568	2.177598
H	3.668182	-0.394985	-0.879634
H	3.667773	-0.350517	0.904260



el energy= -1199.28316314

C	-0.974939	0.760010	3.471715
C	-2.244981	0.937805	2.933444
C	-2.951223	-0.136218	2.408315
C	-2.424611	-1.441439	2.399874
C	-1.133735	-1.593271	2.944811
C	-0.427801	-0.520820	3.468469
H	-0.422677	1.597155	3.880197
H	-2.693662	1.925309	2.920827
H	-3.940056	0.025209	1.994539
H	-0.686410	-2.580704	2.949158
H	0.564409	-0.686277	3.874870
C	1.876801	-0.517713	0.450997
C	1.445039	-1.793085	0.098803
C	0.146453	-1.973421	-0.345783
C	-0.715516	-0.885008	-0.434377
C	-0.276966	0.382734	-0.084537
C	1.025530	0.572670	0.361716
H	2.119900	-2.636808	0.180076
H	-1.737923	-1.036010	-0.756365
H	-0.951019	1.227362	-0.145403
S	-3.316415	-2.794097	1.744787
C	3.280160	-0.358702	0.948163
F	3.604153	0.914351	1.202835
F	3.495931	-1.045258	2.084878
F	4.185798	-0.817620	0.064895
H	1.367188	1.559149	0.645488
H	-0.203729	-2.963611	-0.606932



el energy= -1695.53145677

C	-0.029040	-1.573583	0.992818
C	0.456171	-0.457952	1.648753

C	1.570399	0.202752	1.170014
C	2.271454	-0.190654	0.020862
C	1.724077	-1.311525	-0.618911
C	0.614371	-1.990975	-0.156588
C	-1.661162	1.029350	-0.544009
C	-0.764142	0.981408	-1.604147
C	0.243245	1.931154	-1.685862
C	0.349237	2.918358	-0.714397
C	-0.553110	2.960692	0.340937
C	-1.564619	2.014832	0.430227
H	-0.845722	0.203649	-2.353325
H	1.147454	3.647258	-0.773279
H	-0.463165	3.723732	1.103310
S	3.675667	0.635886	-0.560616
C	-2.768180	0.021859	-0.472793
F	-3.177694	-0.202207	0.782620
F	-3.858137	0.418729	-1.159061
F	-2.416201	-1.164714	-0.988224
H	-2.263692	2.036075	1.256328
H	0.957823	1.889103	-2.497193
F	1.982629	1.266609	1.872193
F	-0.166439	-0.021316	2.748540
F	-1.094842	-2.231691	1.457792
F	0.150632	-3.056078	-0.818417
F	2.284357	-1.778516	-1.742929

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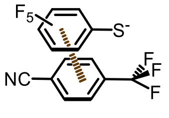
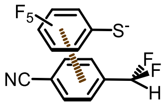


el energy= -1779.73308542

C	-2.882350	-0.234627	0.021583
C	-2.256822	-0.573721	-1.165904
C	-1.035746	-1.218030	-1.154641
C	-0.349162	-1.571557	0.022050
C	-1.020347	-1.188043	1.198221

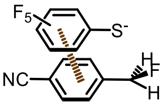
C	-2.241332	-0.543533	1.209041
C	2.136759	0.796405	-0.021758
C	1.519890	1.096956	1.182558
C	0.275895	1.696902	1.174999
C	-0.358066	2.002239	-0.025218
C	0.263620	1.664510	-1.223229
C	1.507609	1.064607	-1.227405
H	1.996805	0.835130	2.116380
H	-0.228208	1.916358	2.107313
H	-0.250278	1.858448	-2.155856
S	1.170607	-2.369375	0.022330
C	3.546208	0.274396	-0.021925
F	3.835079	-0.459346	-1.093306
F	4.414381	1.319439	-0.040044
F	3.845756	-0.430802	1.065624
F	-0.494633	-1.490939	-2.347220
F	-2.840878	-0.256702	-2.329747
F	-4.067677	0.381228	0.021495
F	-2.810195	-0.196799	2.371937
F	-0.463661	-1.430588	2.390195
H	1.974916	0.777520	-2.158655
C	-1.581109	2.660309	-0.027779
N	-2.511543	3.258173	-0.031058



el energy= -1680.46930686

C	2.387354	-0.387770	-0.220369
C	2.194752	-0.714782	1.110430
C	1.002981	-1.279516	1.526249
C	-0.068992	-1.560442	0.662080
C	0.175789	-1.200325	-0.673646
C	1.356005	-0.631736	-1.109653
C	-2.165018	1.111500	-0.320016
C	-1.464227	1.640845	-1.393872
C	-0.224815	2.216633	-1.186926

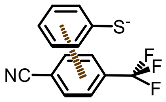
C	0.326279	2.263066	0.088707
C	-0.396514	1.749986	1.161057
C	-1.640091	1.180641	0.963272
H	-1.873896	1.571469	-2.391484
H	0.339306	2.610440	-2.021859
H	0.038496	1.771810	2.151694
S	-1.561814	-2.233681	1.196777
C	-3.443560	0.355219	-0.535795
F	-3.982661	0.652156	-1.753400
F	-4.370683	0.717701	0.395461
F	0.894889	-1.551498	2.830549
F	3.176398	-0.487625	1.990704
F	3.537626	0.150942	-0.638496
F	1.508811	-0.288530	-2.395646
F	-0.773600	-1.396240	-1.599565
H	-2.174886	0.733154	1.789060
C	1.582228	2.825457	0.288855
N	2.554858	3.327718	0.441584
H	-3.287311	-0.723531	-0.464996



el energy= -1581.20304587

C	-2.798605	-0.281391	0.009543
C	-2.161386	-0.625229	-1.169724
C	-0.928988	-1.248348	-1.143044
C	-0.248560	-1.580219	0.041361
C	-0.926786	-1.186490	1.207932
C	-2.159156	-0.562742	1.204052
C	2.085456	0.827411	-0.018223
C	1.459355	1.183790	1.169966
C	0.230939	1.814507	1.151499
C	-0.396785	2.104090	-0.056167
C	0.233727	1.748593	-1.244682
C	1.462173	1.118001	-1.225644
H	1.918784	0.924900	2.115375

H	-0.271350	2.060615	2.078551
H	-0.266546	1.943098	-2.184991
S	1.280442	-2.371223	0.060760
C	3.419937	0.147416	0.002199
F	4.434931	1.116194	-0.019648
F	-0.375200	-1.526649	-2.328275
F	-2.741609	-0.330032	-2.340716
F	-3.995558	0.311378	-0.004913
F	-2.737129	-0.205942	2.358914
F	-0.370838	-1.402118	2.405152
H	1.923691	0.807383	-2.154299
C	-1.624272	2.753629	-0.075390
N	-2.567557	3.330906	-0.092149
H	3.544097	-0.445986	0.905791
H	3.548525	-0.490743	-0.869714



el energy= -1283.47778006

C	-2.777150	0.551238	0.817143
C	-1.596545	1.163980	1.232872
C	-0.732843	1.743679	0.318995
C	-0.992176	1.730921	-1.069852
C	-2.198826	1.111781	-1.461280
C	-3.068195	0.543669	-0.543484
C	1.945711	-0.634446	0.424261
C	1.578923	-0.419404	-0.890029
C	0.380180	-0.949203	-1.346170
C	-0.434379	-1.684958	-0.503554
C	-0.055947	-1.875769	0.826362
C	1.129160	-1.354722	1.292297
H	2.170756	0.198377	-1.548712
H	0.060538	-0.732052	-2.356607
H	-0.716555	-2.417563	1.489635
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C	3.220560	-0.066893	0.971211

H	1.420811	-1.492067	2.325455
C	-1.608018	-2.263085	-0.974655
N	-2.491686	-2.812277	-1.347777
H	0.185629	2.208255	0.658885
H	-1.342742	1.186013	2.288005
H	-3.451542	0.096889	1.532305
H	-3.971137	0.059505	-0.898589
H	-2.430477	1.076383	-2.519402
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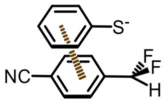

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C	-0.357686	-2.043293	-1.431120
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H	-0.829593	-2.424991	-2.327113
H	-1.046058	-1.455369	1.820016
S	1.244700	2.408047	1.028538
C	2.906895	-0.470938	-0.353249
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H	-1.047173	1.897294	2.699637

H	-3.304425	1.041404	2.214578
H	-3.965332	0.482622	-0.115517
H	-2.314019	0.823170	-1.942272
H	-0.065954	1.688508	-1.446720
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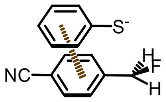

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C	-0.199680	2.116717	-0.477742
C	-1.186122	2.003853	-1.479461
C	-2.433352	1.451314	-1.226941
C	1.671202	-0.852877	0.198175
C	0.907555	-0.724606	-0.954056
C	-0.351680	-1.289101	-1.018599
C	-0.869203	-1.998511	0.058008
C	-0.088711	-2.147908	1.200201
C	1.169185	-1.582283	1.271016
H	1.274680	-0.118485	-1.772796
H	-0.959306	-1.151283	-1.902633
H	-0.485597	-2.698004	2.043848
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C	2.989334	-0.149497	0.316295
F	3.883124	-0.928841	1.056462
H	1.765840	-1.693606	2.166850
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N	-3.119729	-3.066202	-0.077472
H	0.162719	1.716271	1.597359
H	-2.043116	0.729552	2.047589
H	-3.735084	0.541772	0.234363
H	-3.156860	1.381213	-2.032722

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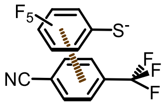

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C	1.743369	0.910426	0.175168
C	0.625872	1.431236	0.803749
C	-0.350635	2.089693	0.074942
C	-0.209257	2.210774	-1.305084
C	0.899361	1.697825	-1.938682
H	2.460940	0.348314	0.754148
H	0.494666	1.271301	1.865306
H	-0.991785	2.689234	-1.878589
S	0.560773	-1.952294	2.047332
C	3.094204	0.529960	-1.906356
F	2.772817	-0.154246	-3.013352
F	3.891361	1.546513	-2.311877
F	3.845324	-0.265417	-1.146037
F	0.587188	-1.948407	-0.977918
F	-1.251002	-0.969927	-2.627873
F	-3.557653	0.105698	-1.672667
F	-3.984534	0.152096	1.020207
F	-2.142926	-0.761775	2.706684
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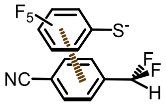

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C	-0.082593	-1.648724	-0.604474
C	0.963774	-1.373205	-1.500181
C	2.163761	-0.799330	-1.121497
C	-2.157471	1.158841	0.280632
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C	-0.349663	1.775411	-1.162950
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C	-0.257556	2.311643	1.169923
C	-1.494212	1.726012	1.356052
H	-2.079065	0.701117	-1.811445
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H	0.274668	2.731710	2.012950
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C	-3.446877	0.407764	0.460910
F	-4.392029	0.876385	-0.409844
F	-3.952992	0.588265	1.714050
F	-0.726509	-1.466317	1.673388
F	1.572208	-0.346585	2.397981
F	3.548512	0.088248	0.581546
F	3.119752	-0.573967	-2.030030
F	0.822618	-1.658623	-2.798017
H	-1.928970	1.680928	2.344030
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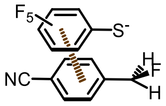

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C	-0.269898	-1.643949	0.022932
C	-0.931619	-1.241789	1.195438
C	-2.157063	-0.603247	1.201226
C	2.089807	0.855987	-0.010399
C	1.468532	1.230966	1.173172
C	0.249988	1.876162	1.151636
C	-0.375853	2.162557	-0.056218
C	0.247622	1.787482	-1.240717
C	1.466841	1.143313	-1.217031
H	1.925530	0.978809	2.121263
H	-0.244812	2.135442	2.078571
H	-0.249225	1.976732	-2.183368
S	1.251901	-2.452974	0.029486
C	3.413991	0.158500	0.015802
F	4.448056	1.112458	0.018203
F	-0.421937	-1.602165	-2.345676
F	-2.774364	-0.377267	-2.337211
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F	-2.722808	-0.241373	2.360085
F	-0.371596	-1.468505	2.388106
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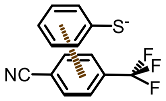

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C	-3.089199	0.569770	-0.520824
C	1.953860	-0.657844	0.449987
C	1.579054	-0.411648	-0.855769
C	0.397049	-0.952912	-1.333354
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C	-0.022272	-1.954553	0.803365
C	1.149133	-1.423313	1.288005
H	2.151296	0.242813	-1.496346
H	0.079646	-0.709456	-2.337831
H	-0.668732	-2.530448	1.451788
S	0.045683	2.419611	-2.297508
C	3.218563	-0.079001	1.016335
H	1.436406	-1.591126	2.317606
C	-1.563316	-2.317552	-1.009655
N	-2.441055	-2.875230	-1.401494
H	0.170894	2.278437	0.585123
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H	-3.414048	0.134617	1.566182
H	-3.998237	0.077266	-0.848789
H	-2.513484	1.096527	-2.514942
F	2.972754	0.772403	2.027590
F	3.946416	0.580159	0.113825
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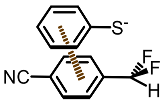

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C	-0.316387	2.018302	0.607360
C	-0.624421	1.619457	-0.708394

C	-1.852987	1.077572	-1.044169
C	1.439421	-1.089620	-0.285691
C	0.891078	-1.781923	-1.352580
C	-0.366793	-2.339444	-1.234908
C	-1.090861	-2.208392	-0.057121
C	-0.525354	-1.521841	1.010221
C	0.729162	-0.962749	0.899392
H	1.436538	-1.865044	-2.281939
H	-0.807294	-2.863213	-2.073546
H	-1.095310	-1.387195	1.918852
S	1.257730	2.612055	1.052917
C	2.768760	-0.395327	-0.384925
H	1.132827	-0.363751	1.705643
C	-2.360087	-2.760579	0.054257
N	-3.357918	-3.242860	0.135123
H	-1.154605	2.167959	2.573411
H	-3.345883	1.225487	1.976849
H	-3.811108	0.494783	-0.351384
H	-2.033801	0.767367	-2.068409
H	0.144706	1.722618	-1.465113
F	3.270783	-0.470146	-1.652249
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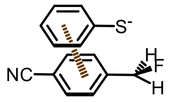

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C	-0.067123	2.148455	-1.241502
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C	-2.276678	1.269386	-1.807424
C	1.593769	-0.800492	0.254607
C	0.909195	-0.858636	-0.954549
C	-0.301577	-1.508402	-1.034235

C	-0.854715	-2.124103	0.083778
C	-0.155914	-2.079756	1.282359
C	1.058169	-1.425538	1.370304
H	1.297915	-0.326678	-1.814714
H	-0.847202	-1.509650	-1.967799
H	-0.578935	-2.550900	2.160808
S	1.506205	2.716928	-1.719317
C	2.856735	0.001925	0.323757
F	3.486950	-0.149696	1.556172
H	1.583104	-1.382030	2.314315
C	-2.081437	-2.767771	0.001522
N	-3.051383	-3.308246	-0.051505
H	0.308398	2.226152	0.868317
H	-1.852732	1.279750	1.539297
H	-3.536984	0.640688	-0.173853
H	-3.000221	1.004498	-2.572190
H	-0.823563	1.935941	-3.235014
H	2.632672	1.062201	0.157767
H	3.562604	-0.317075	-0.446856

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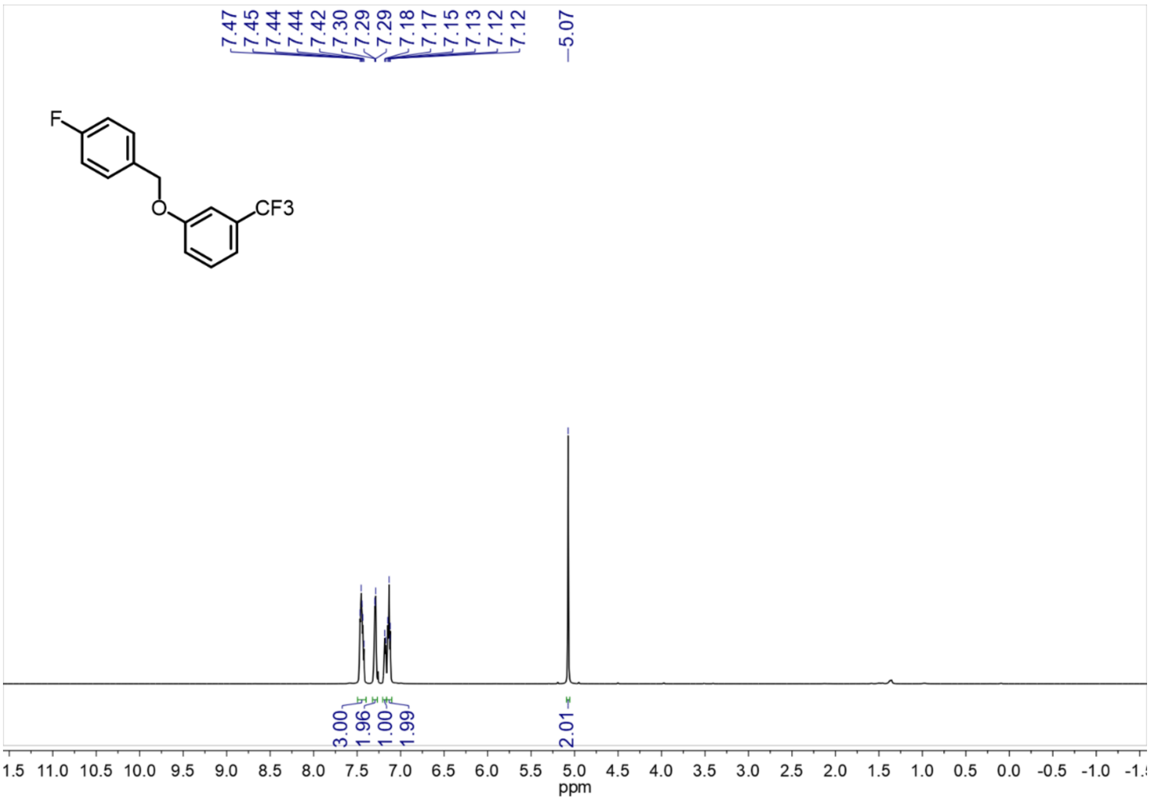
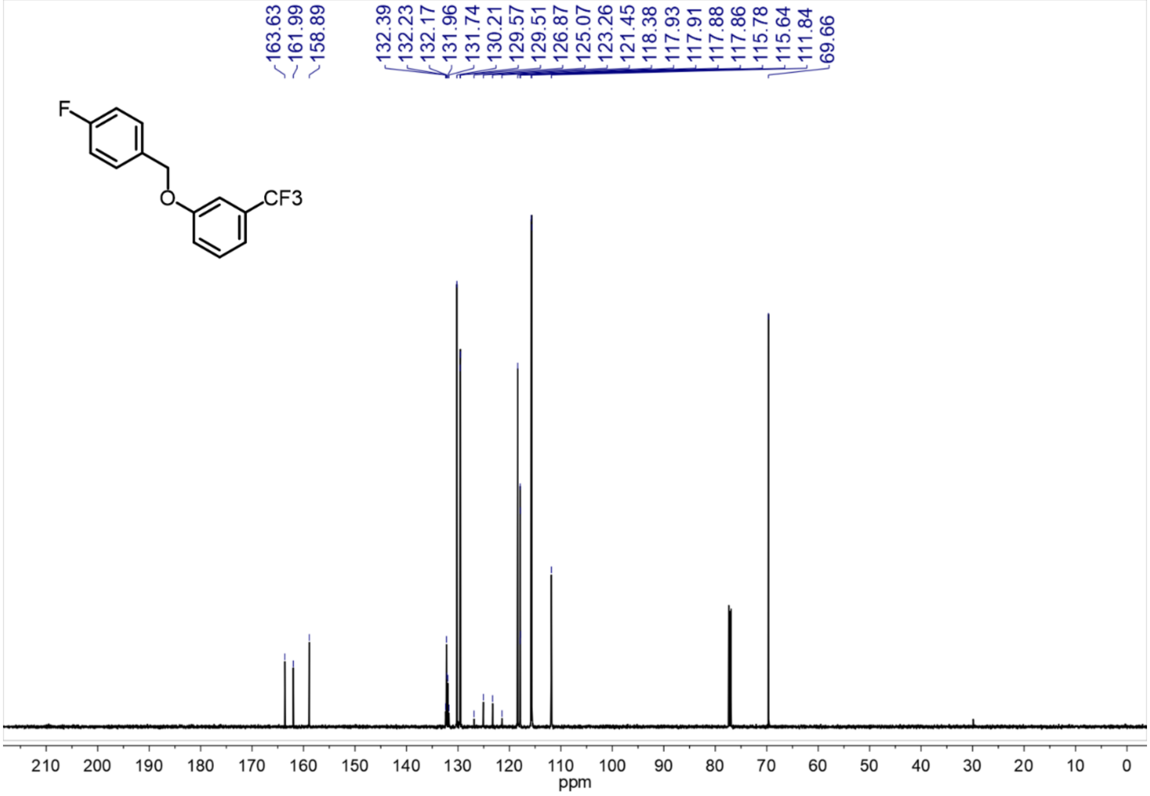
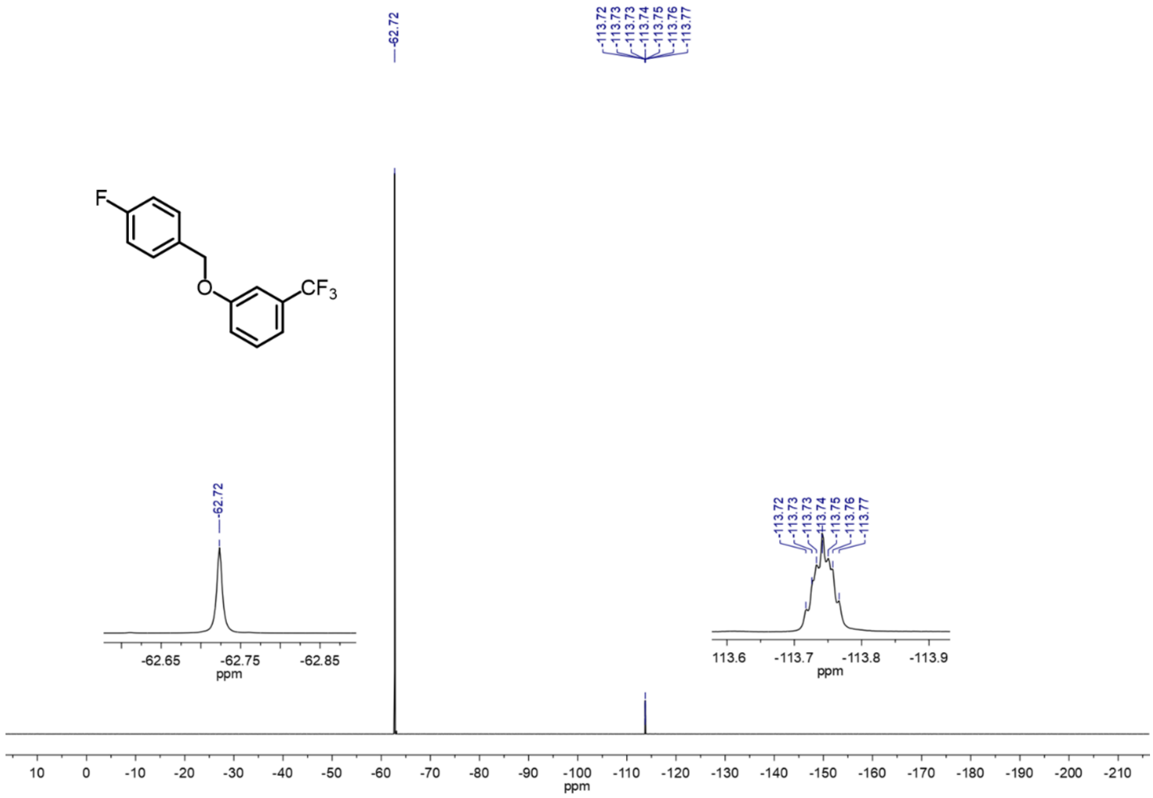
8 ^{1}H NMR, ^{19}F NMR and ^{13}C NMR Spectra



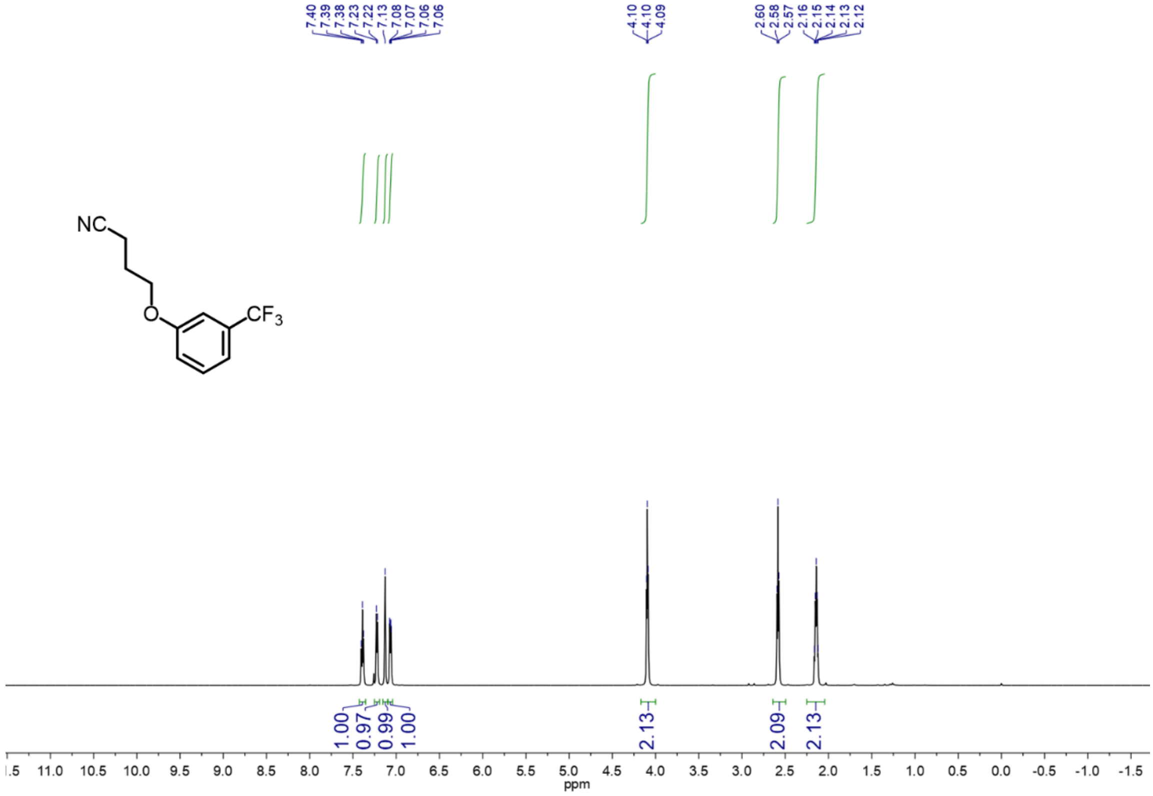
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **1aj**



^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **1aj**



^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **1aj**



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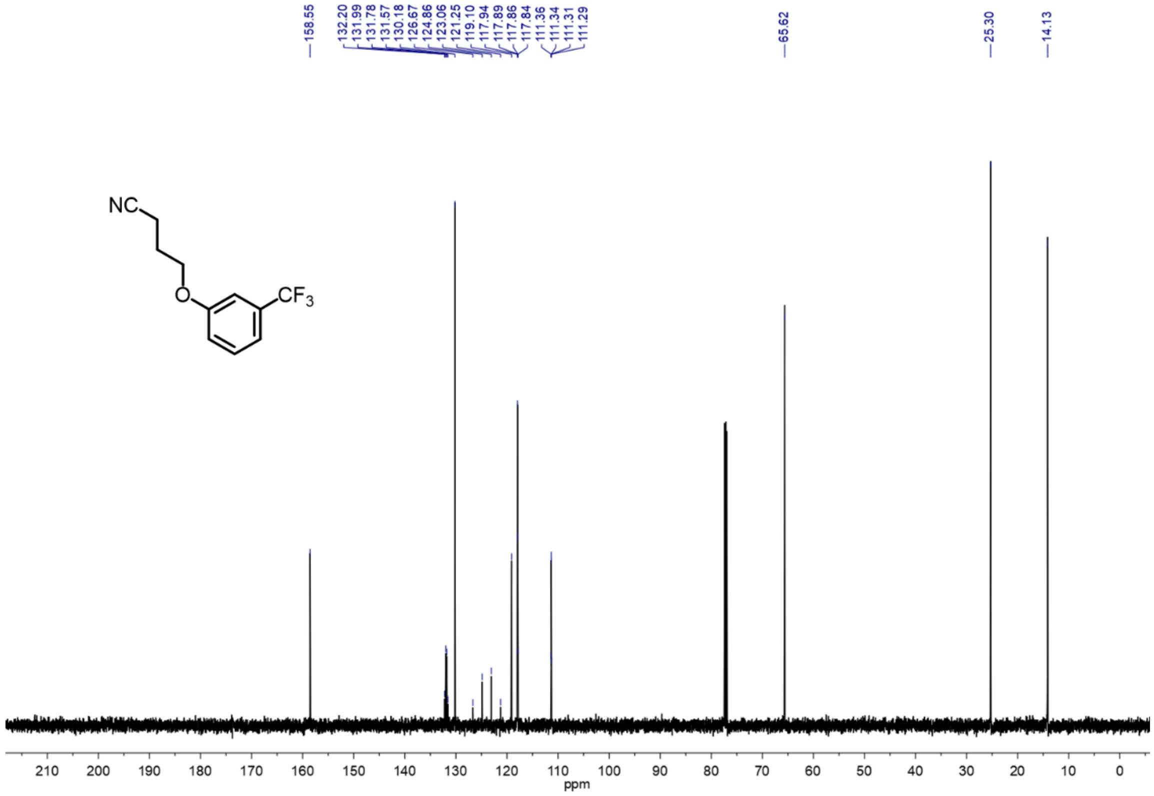

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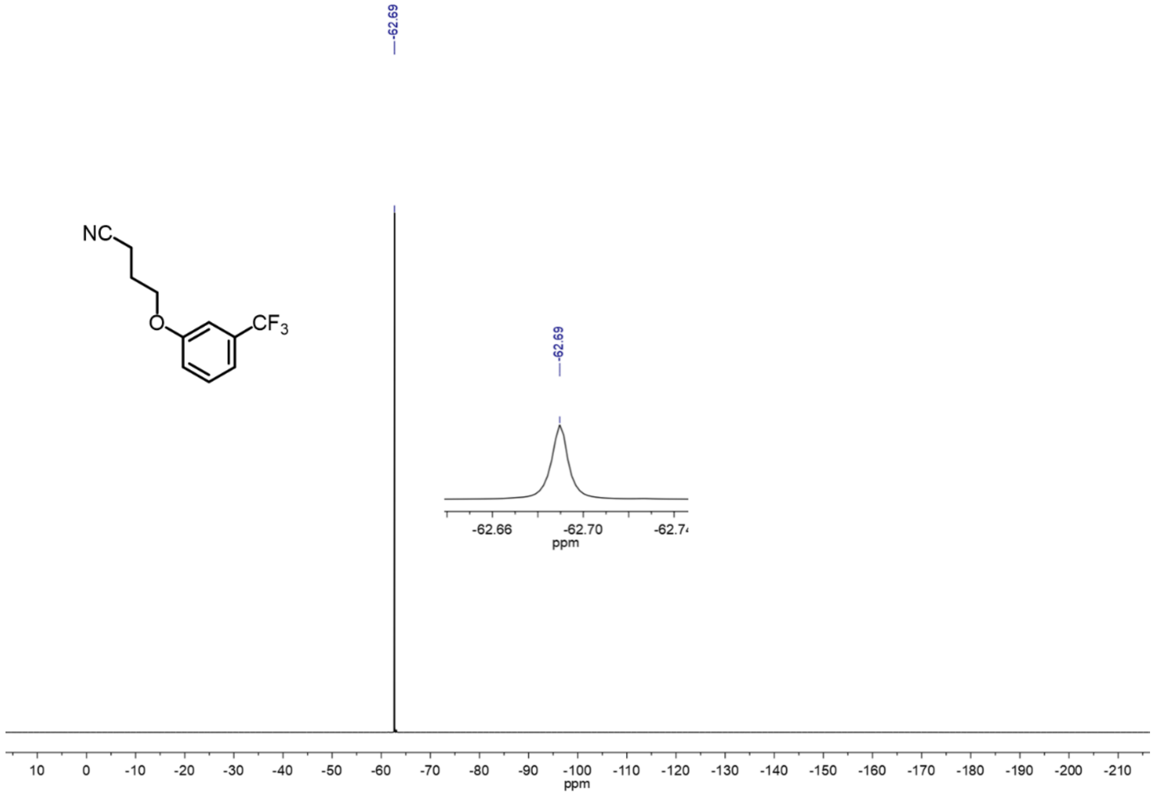

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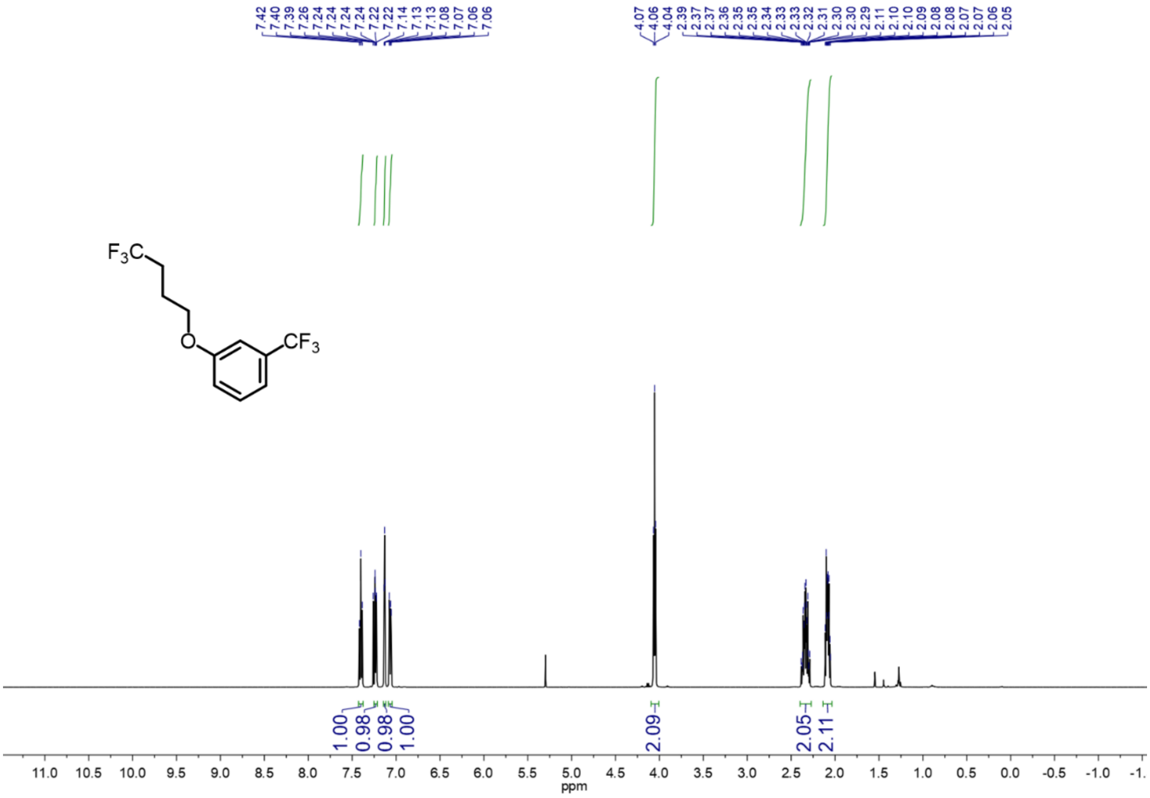

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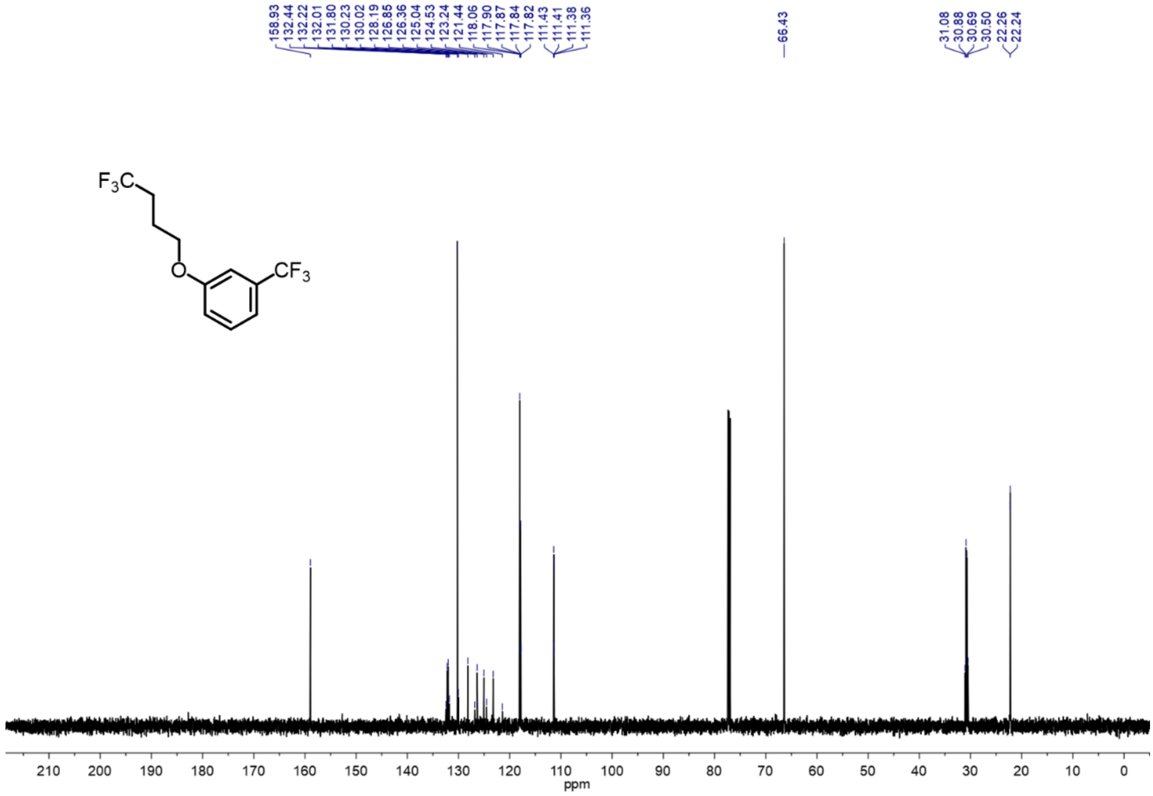
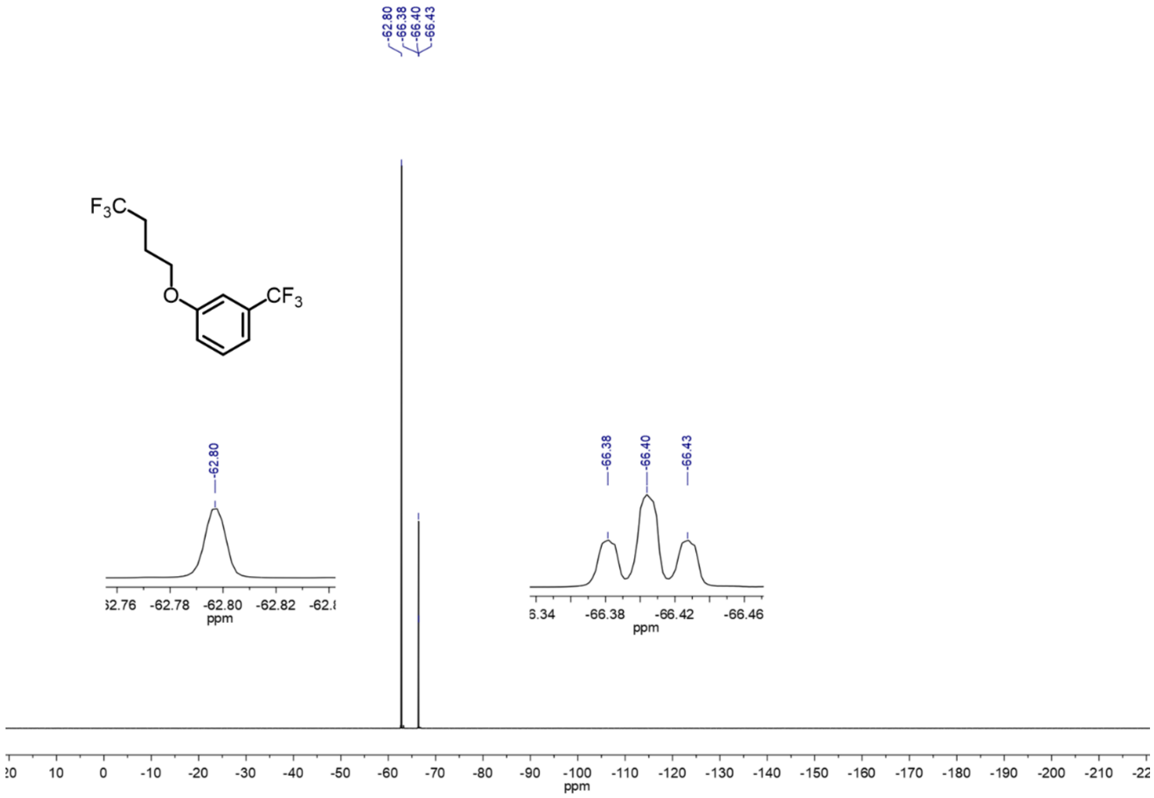


^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **1am**



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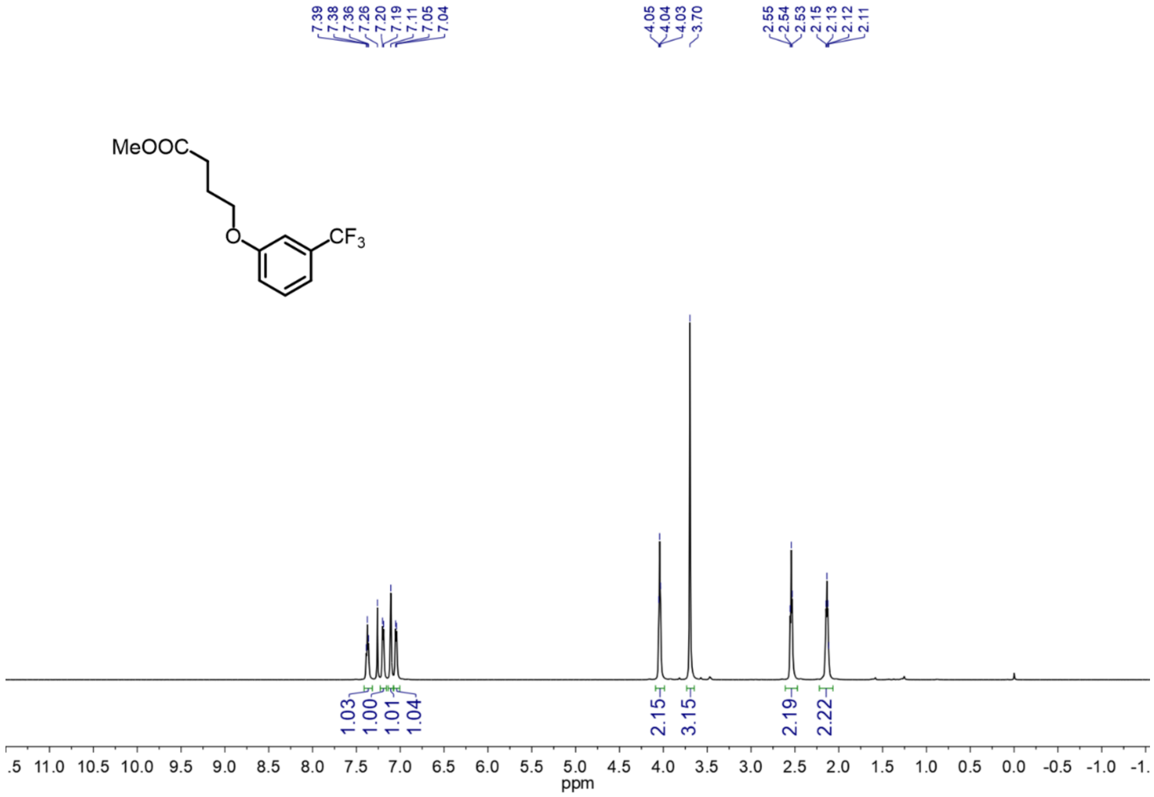

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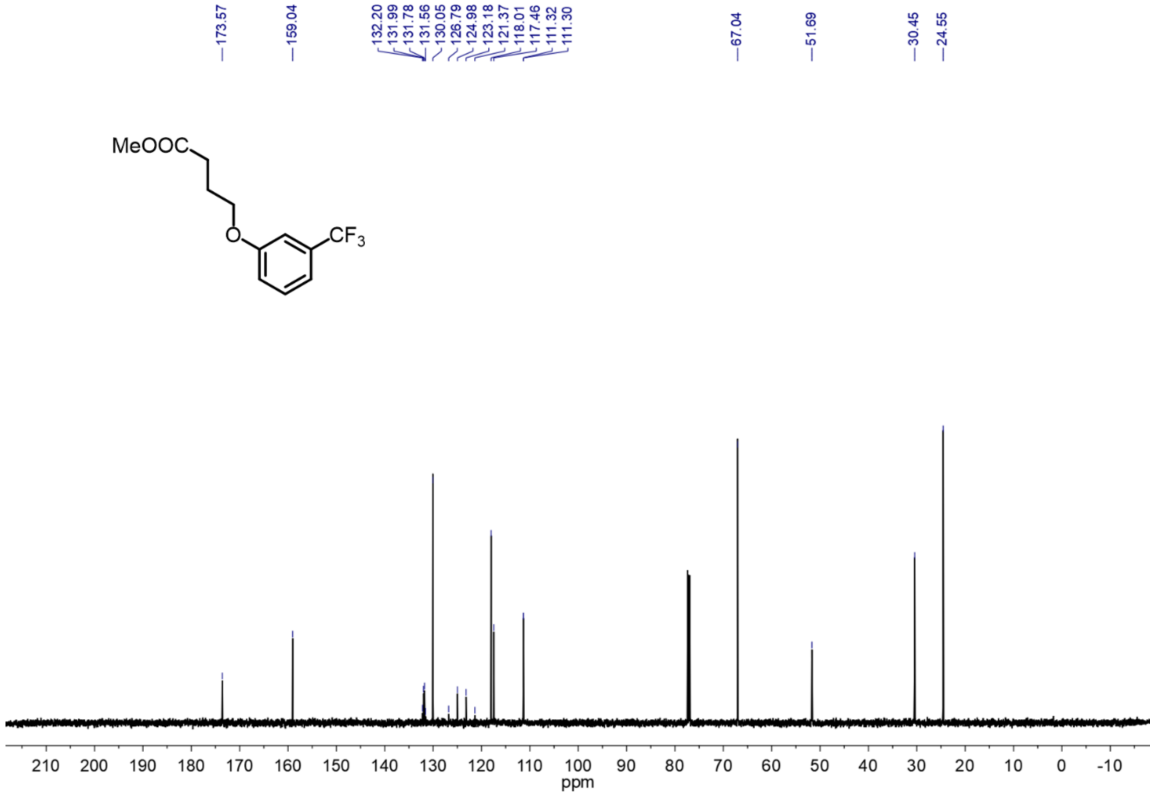
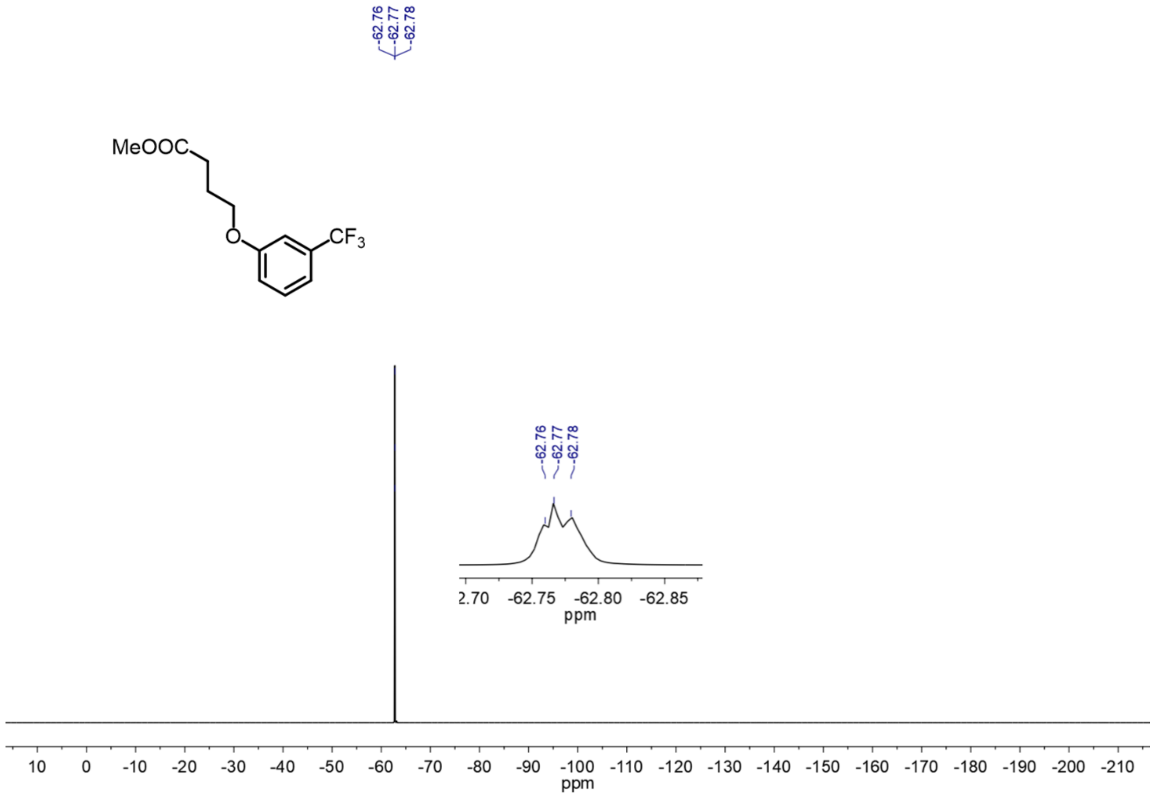
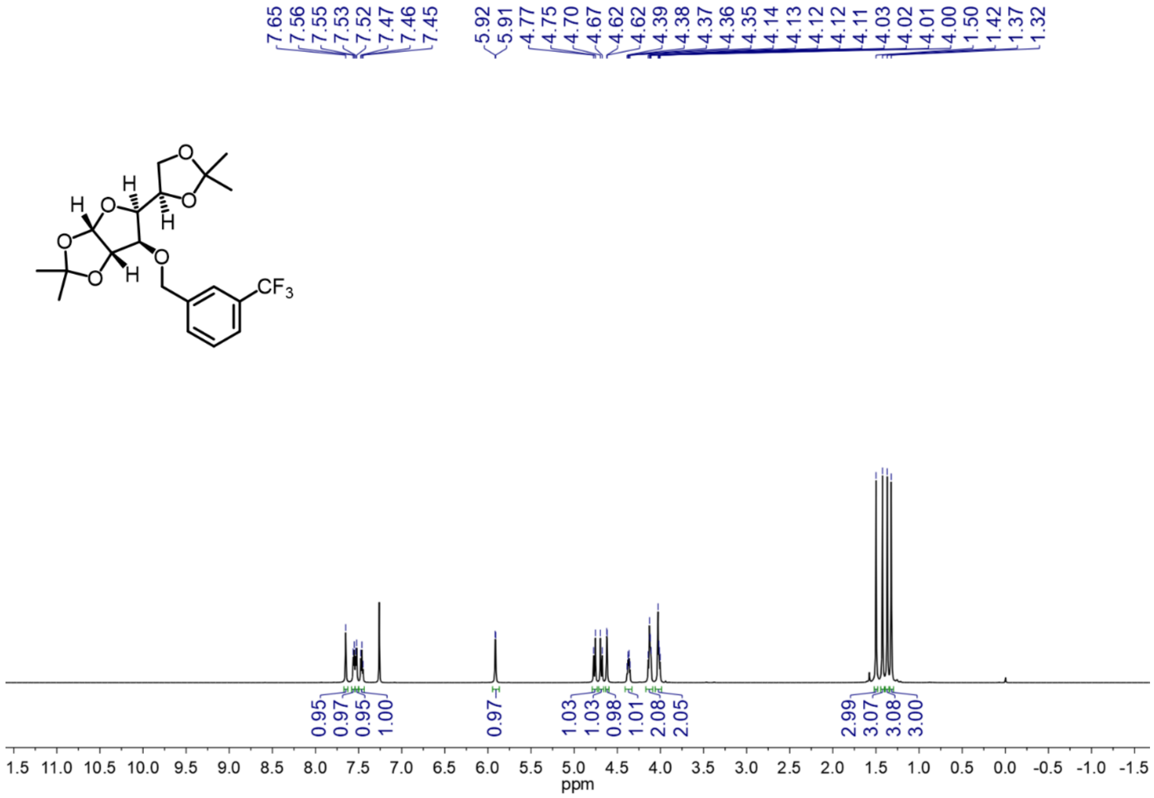


^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **1ao**



^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **1ao**



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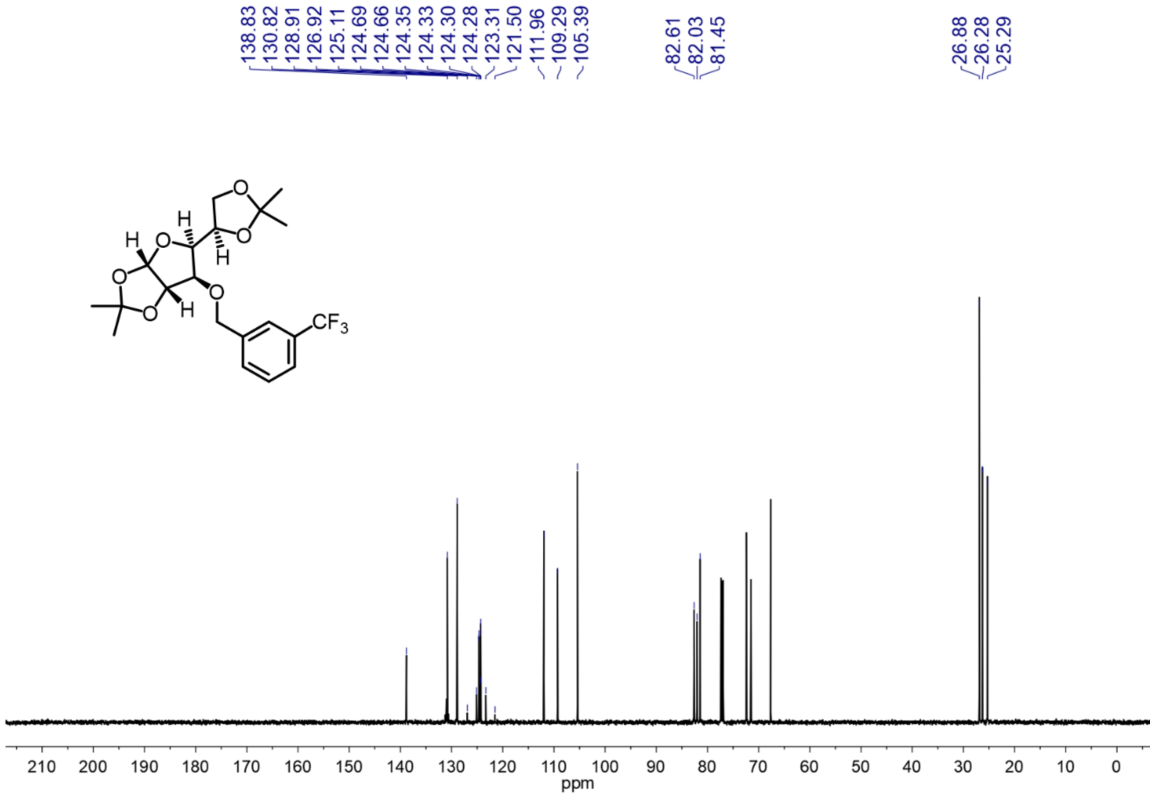

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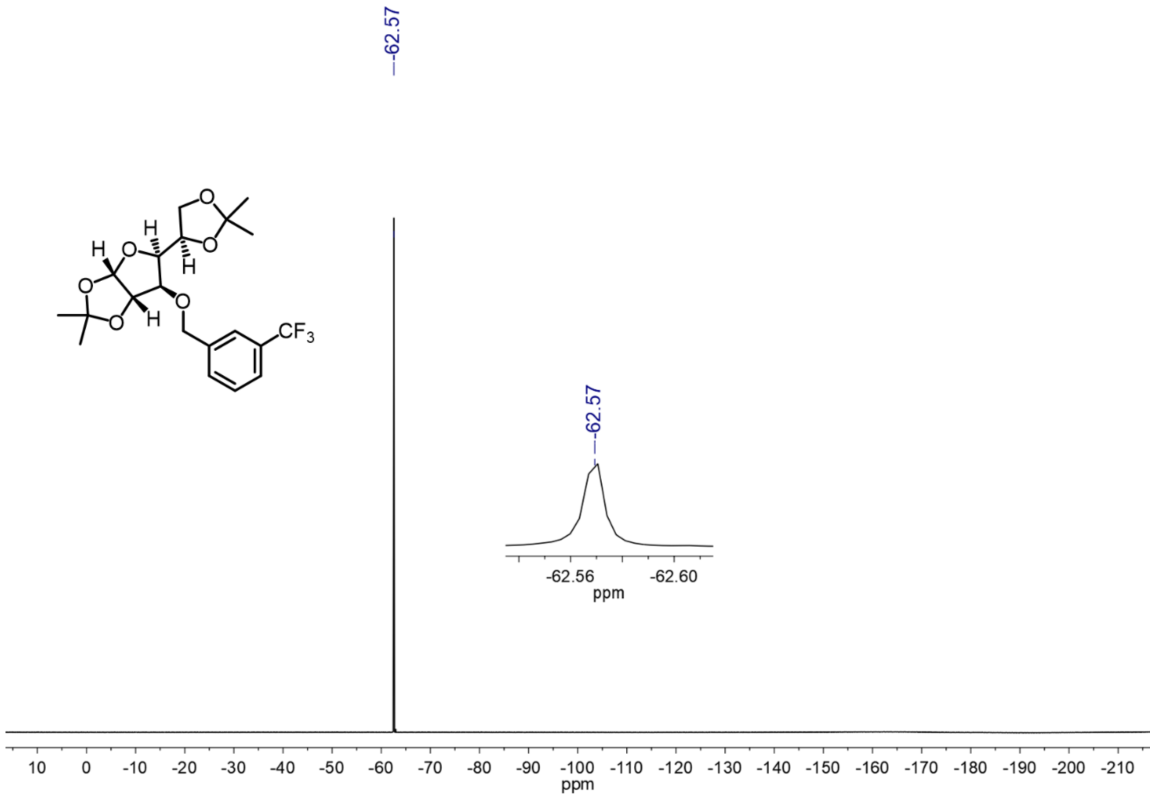

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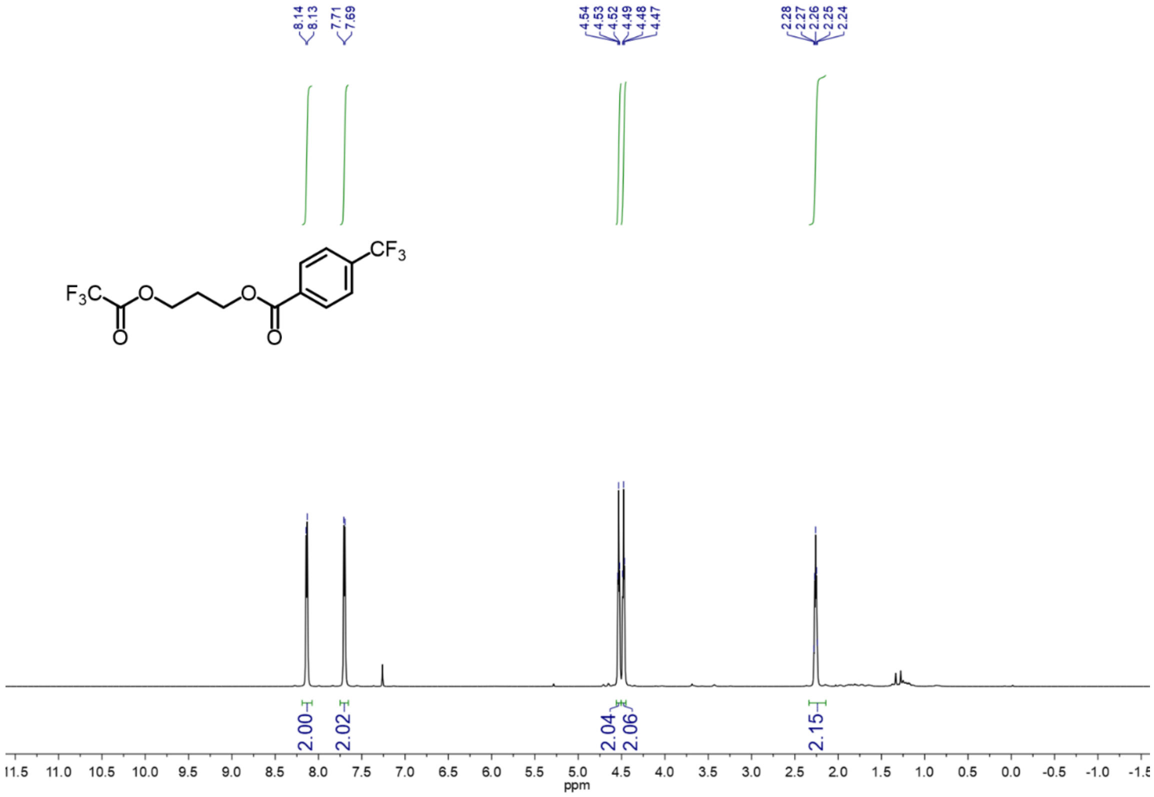

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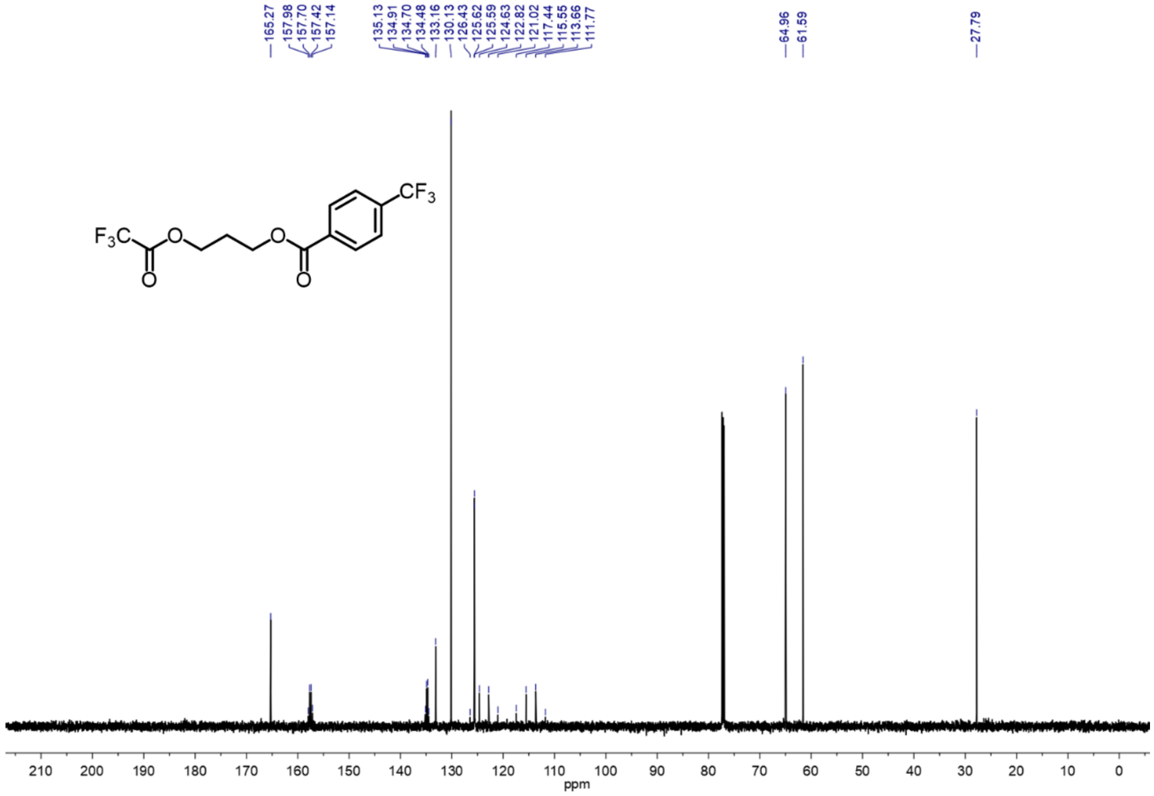
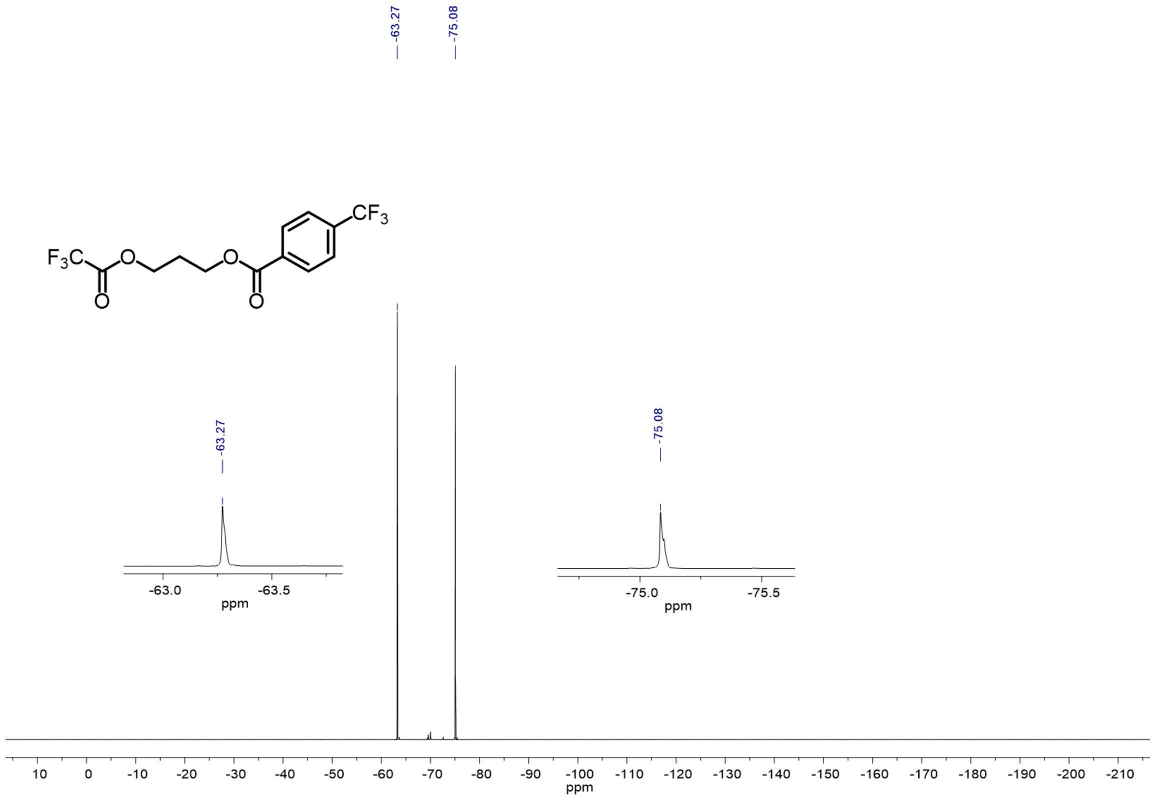


^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **1bg**



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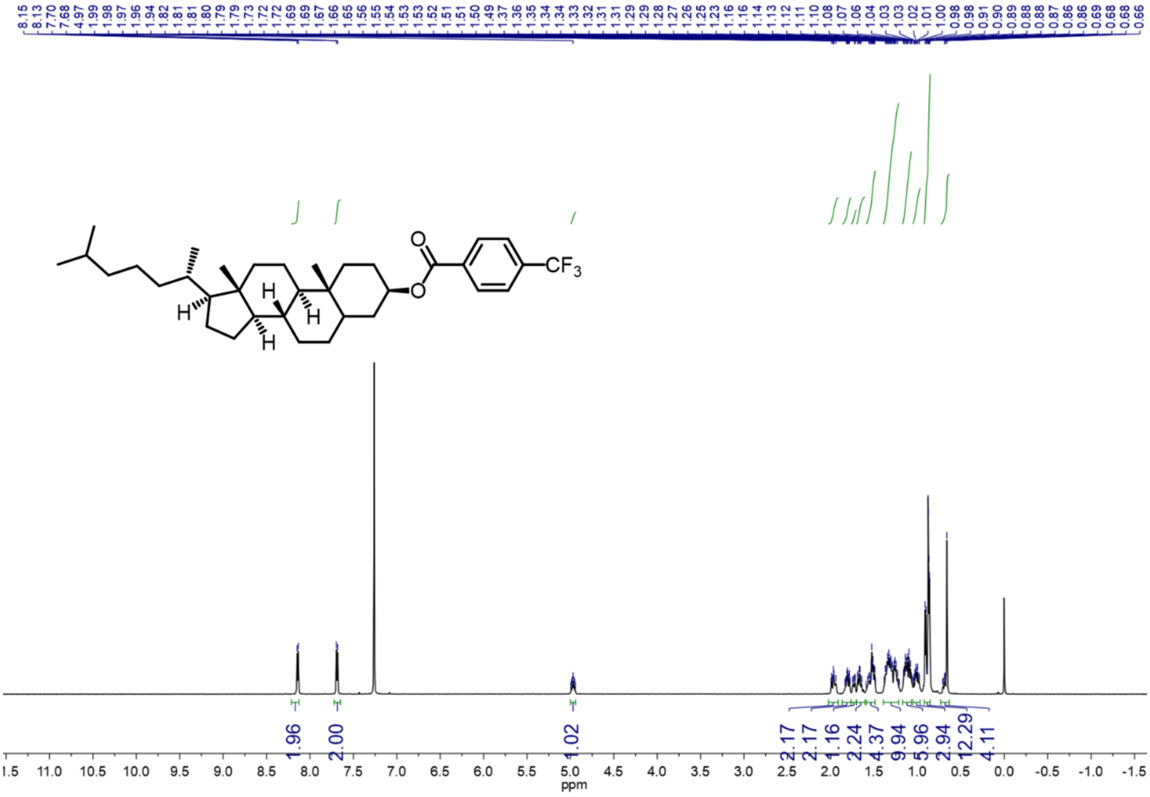

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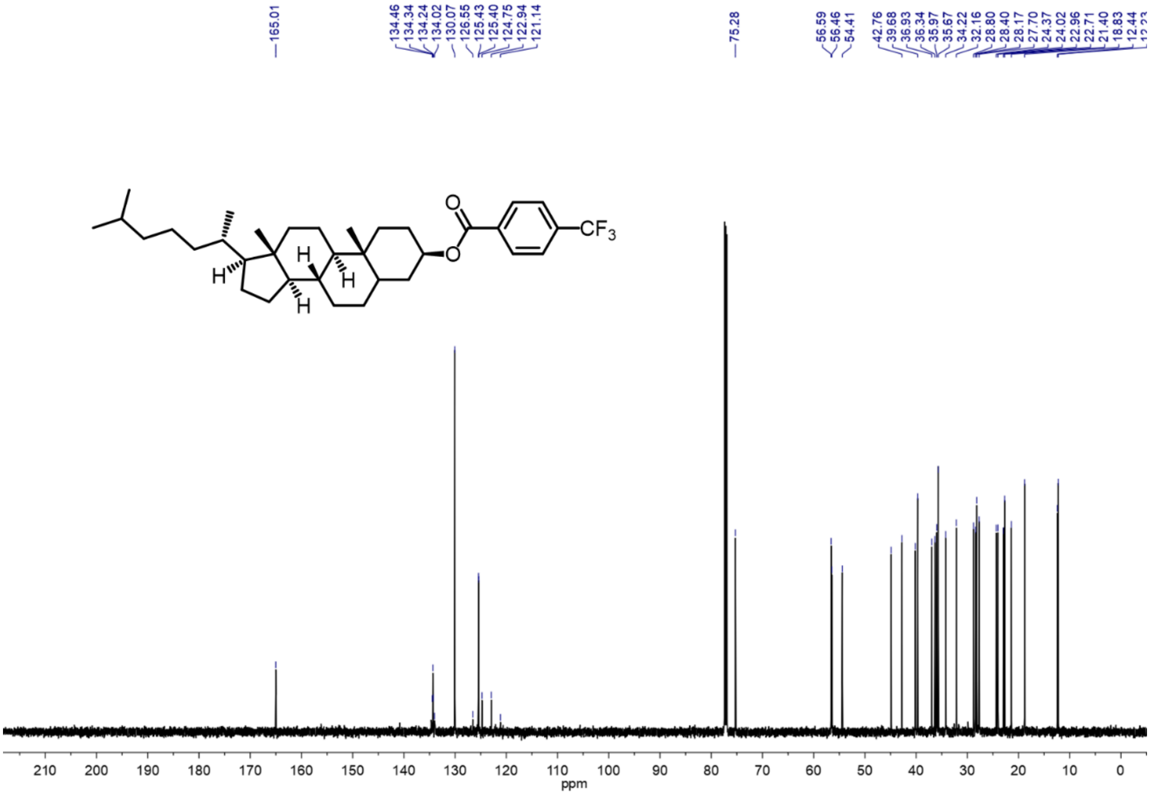

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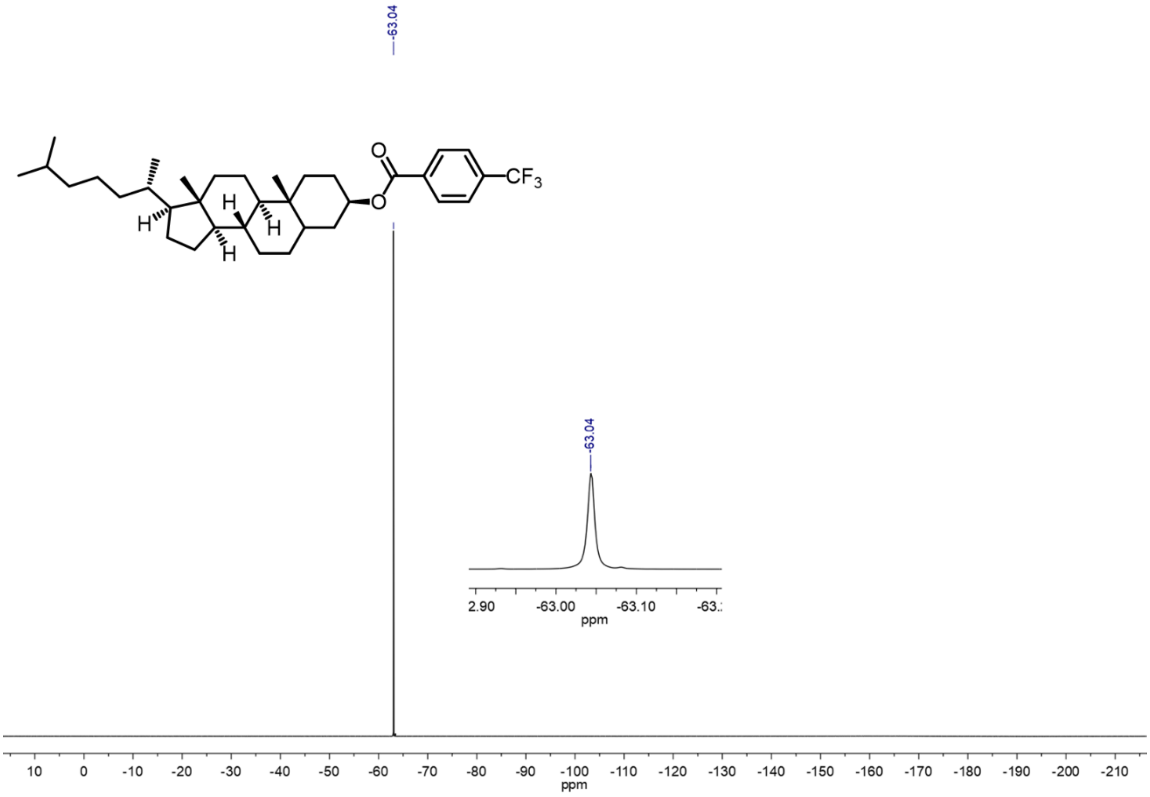

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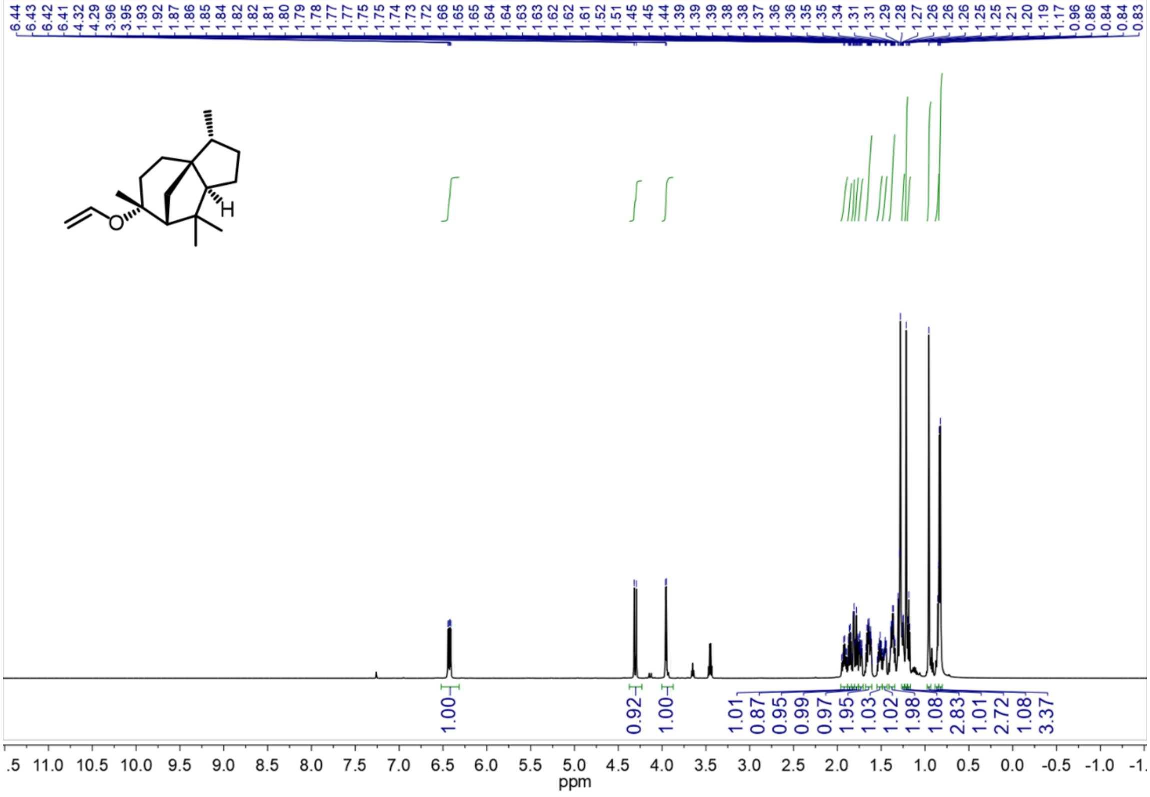
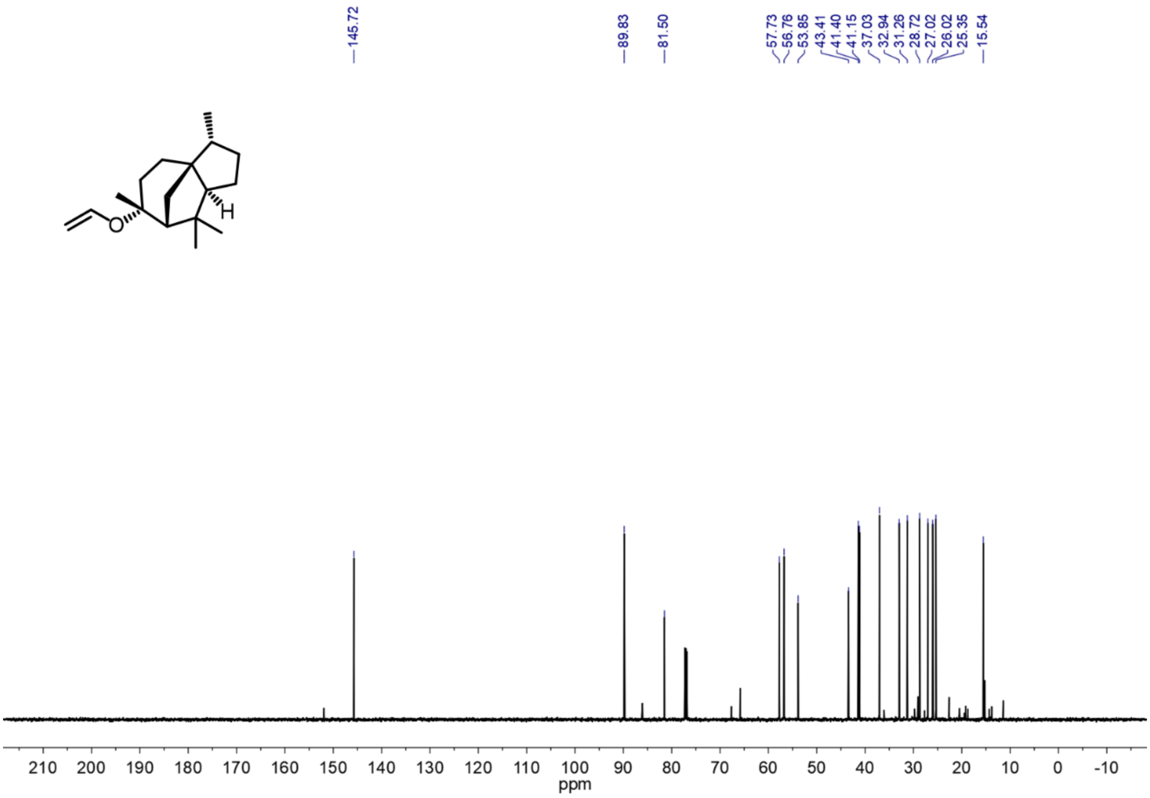


^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **4o**



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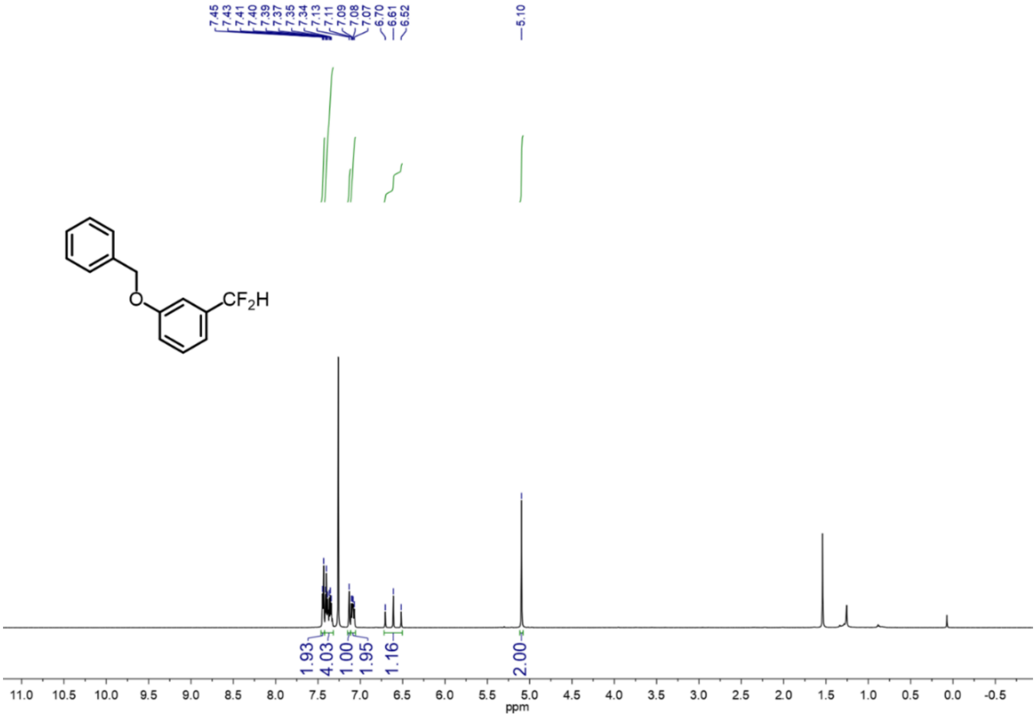
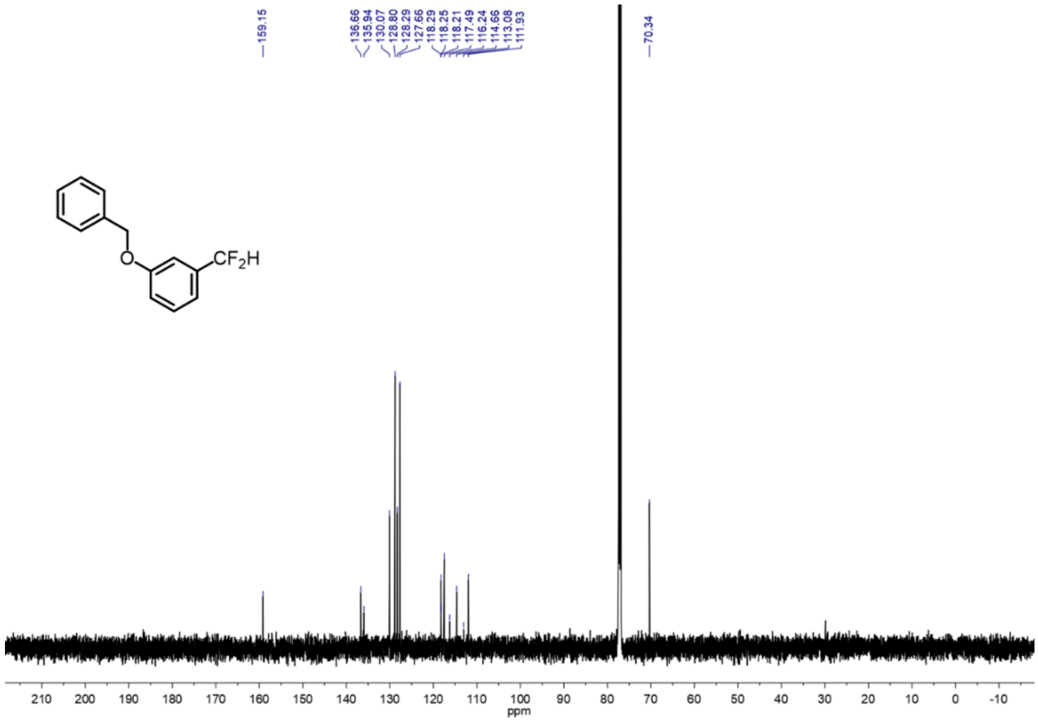


^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **3b**



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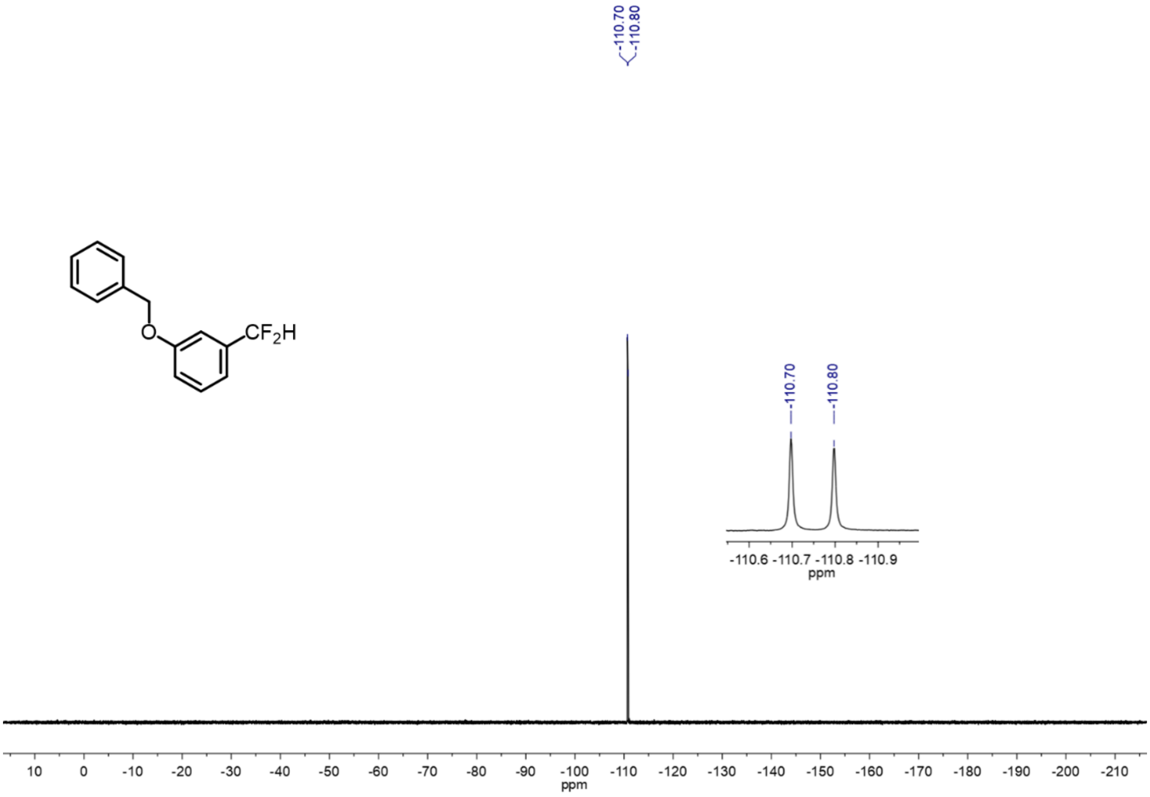
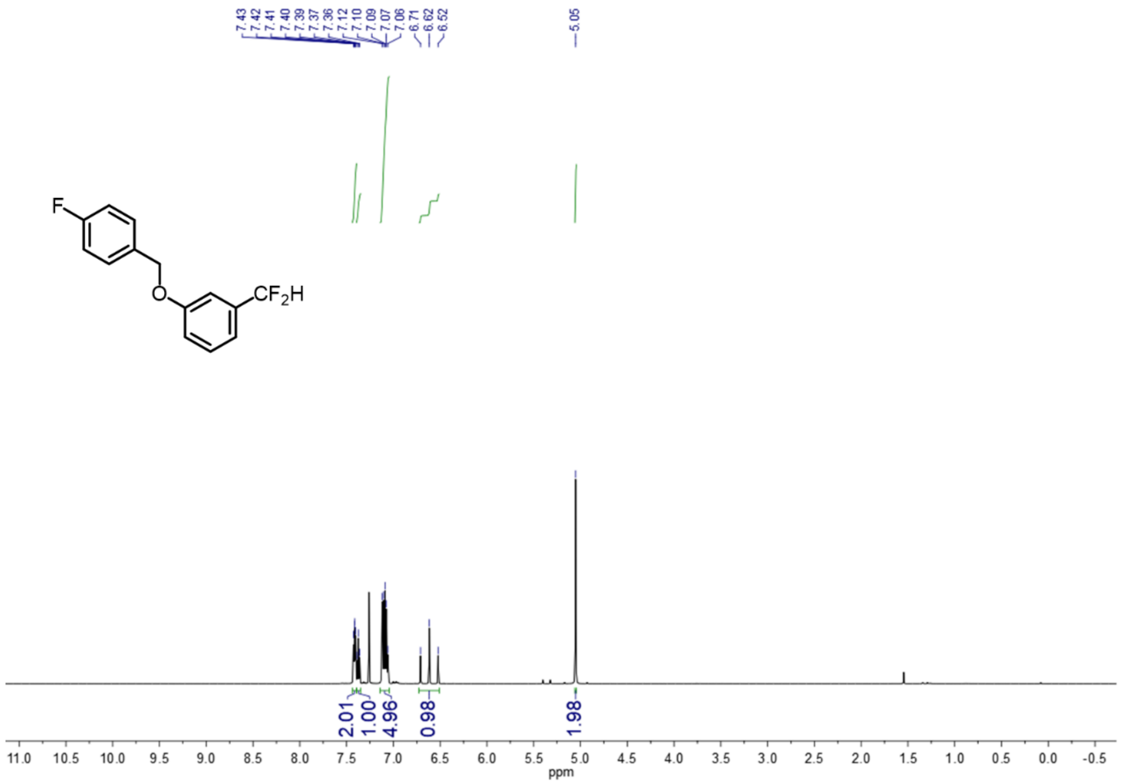


^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **3b**



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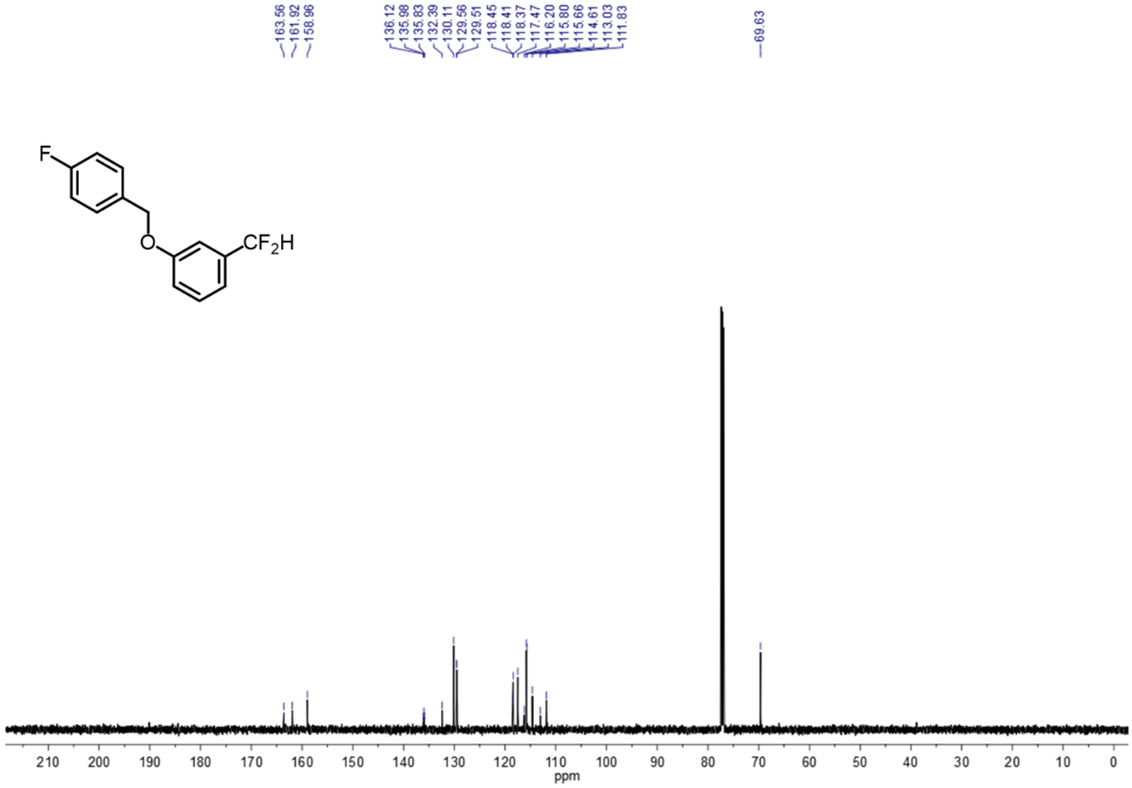

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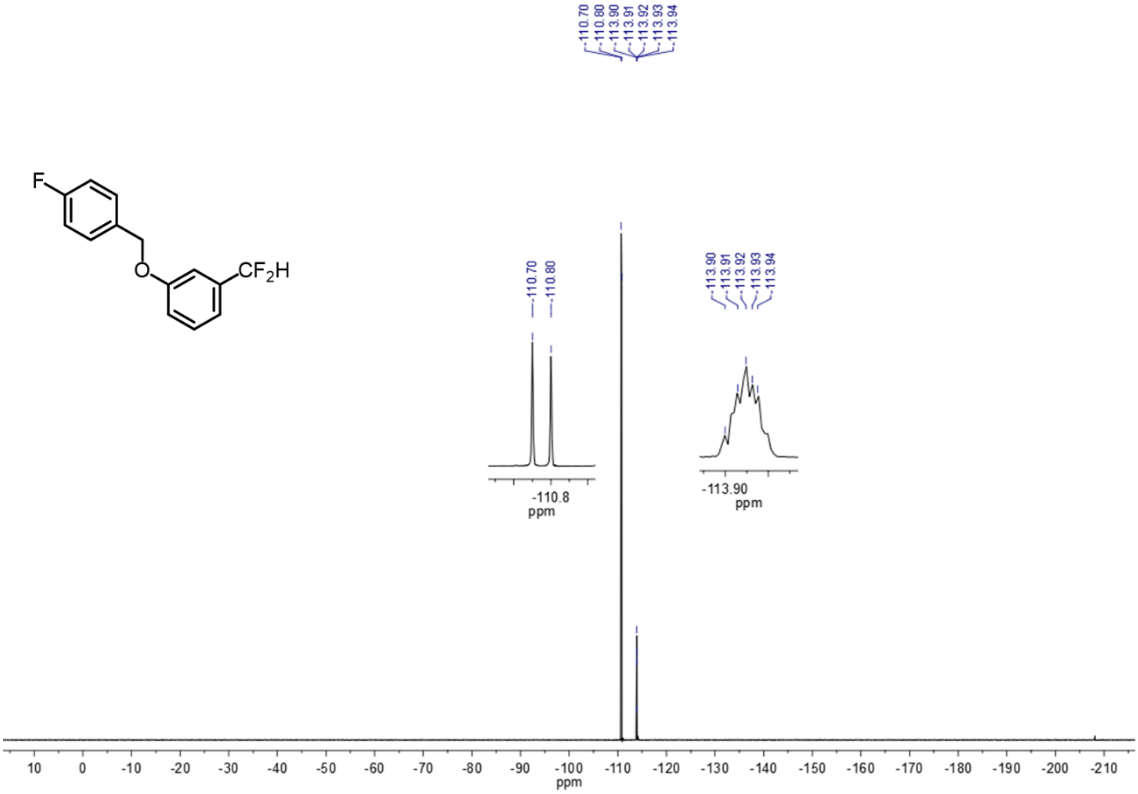

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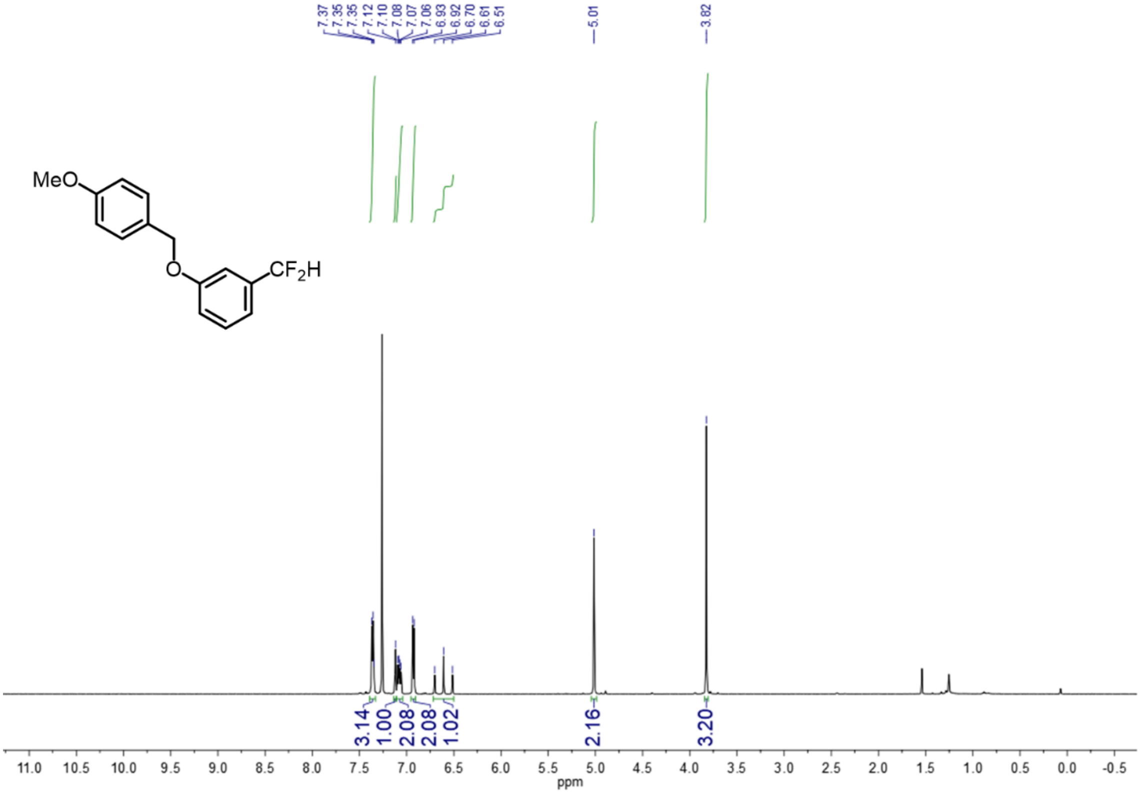

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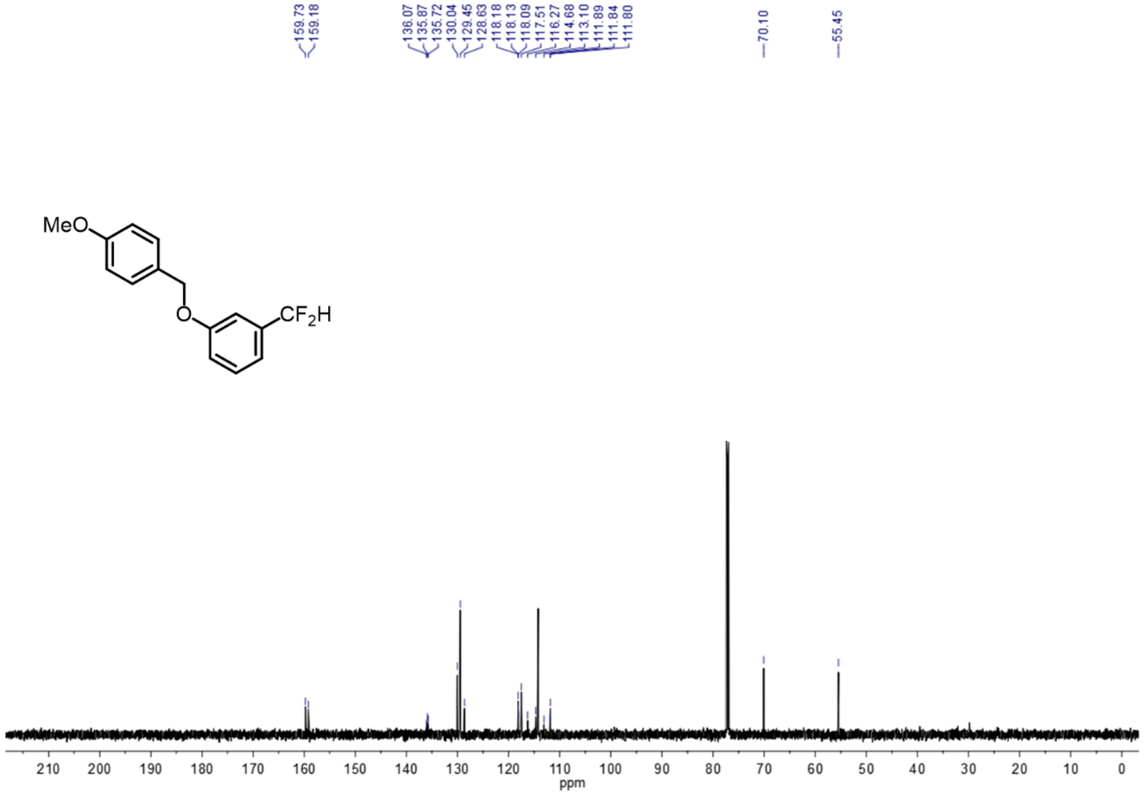
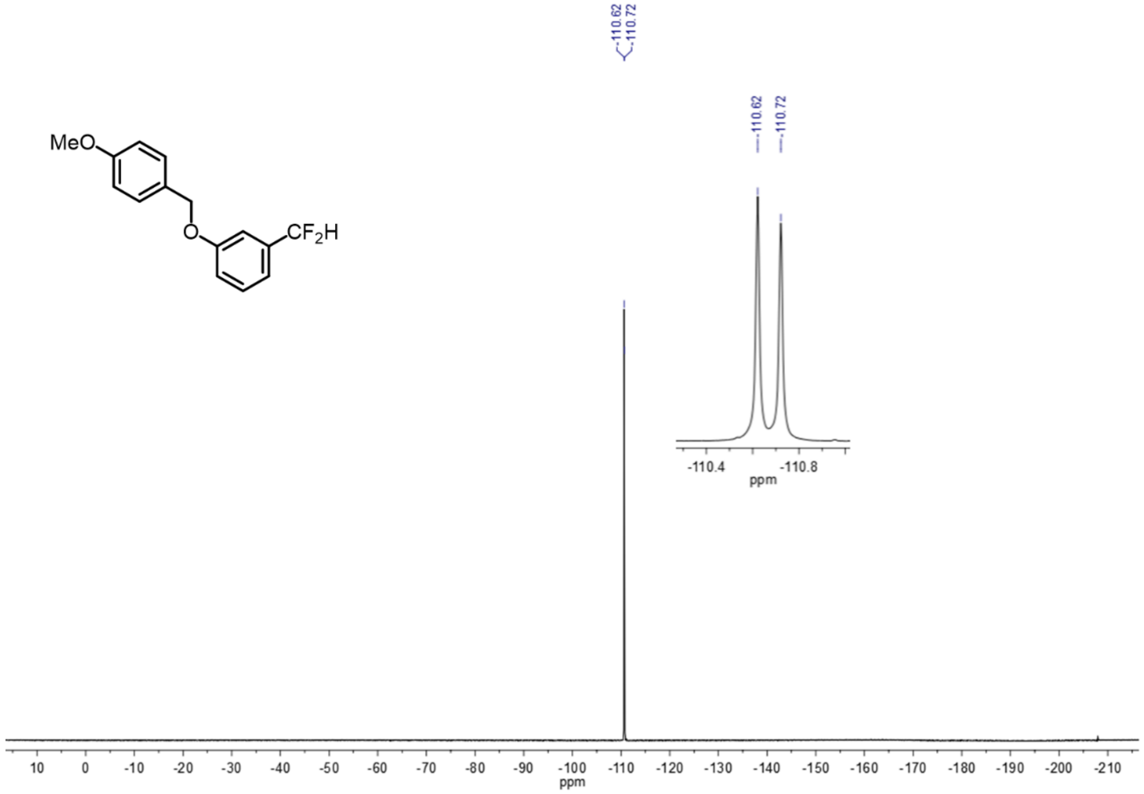


^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **3d**



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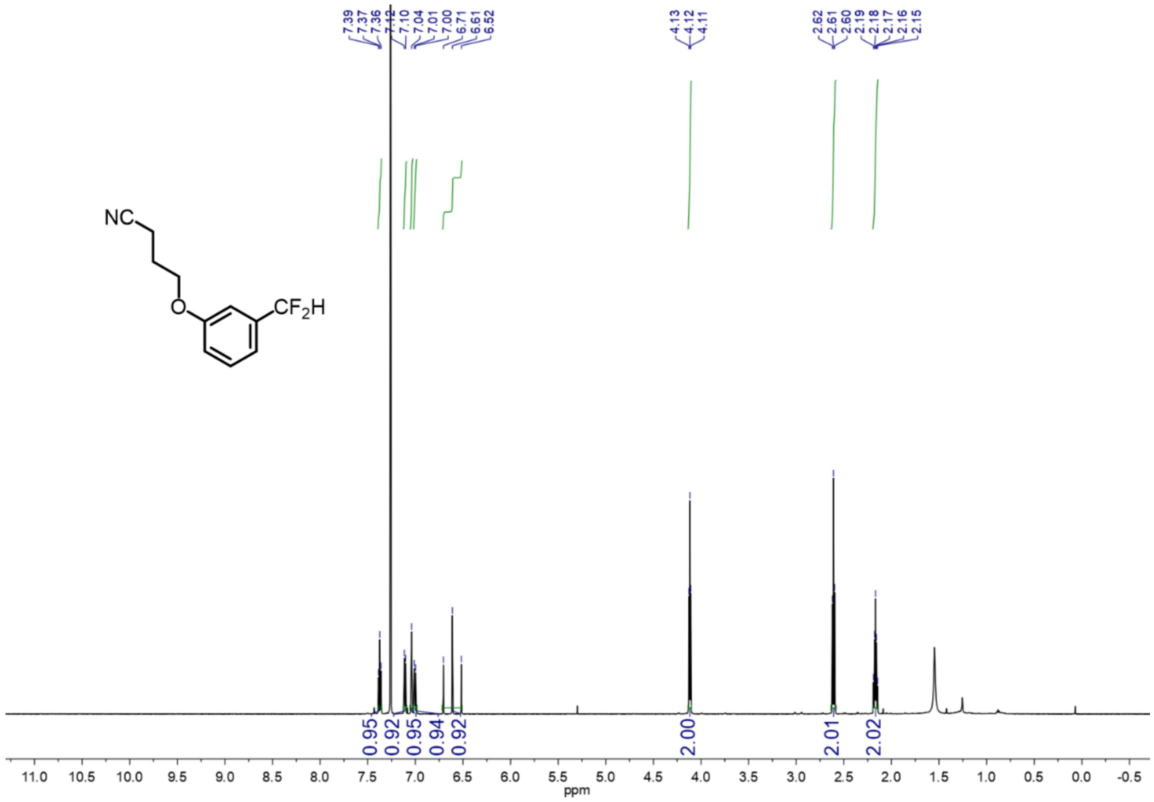

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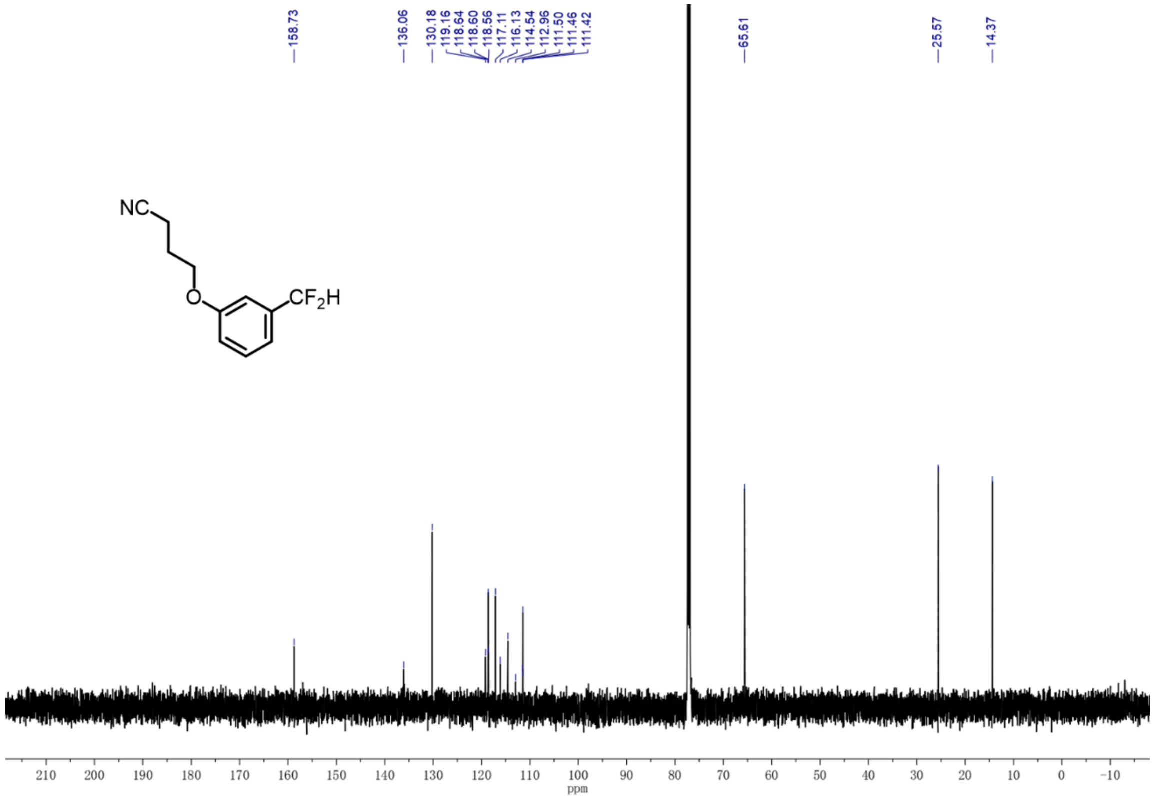

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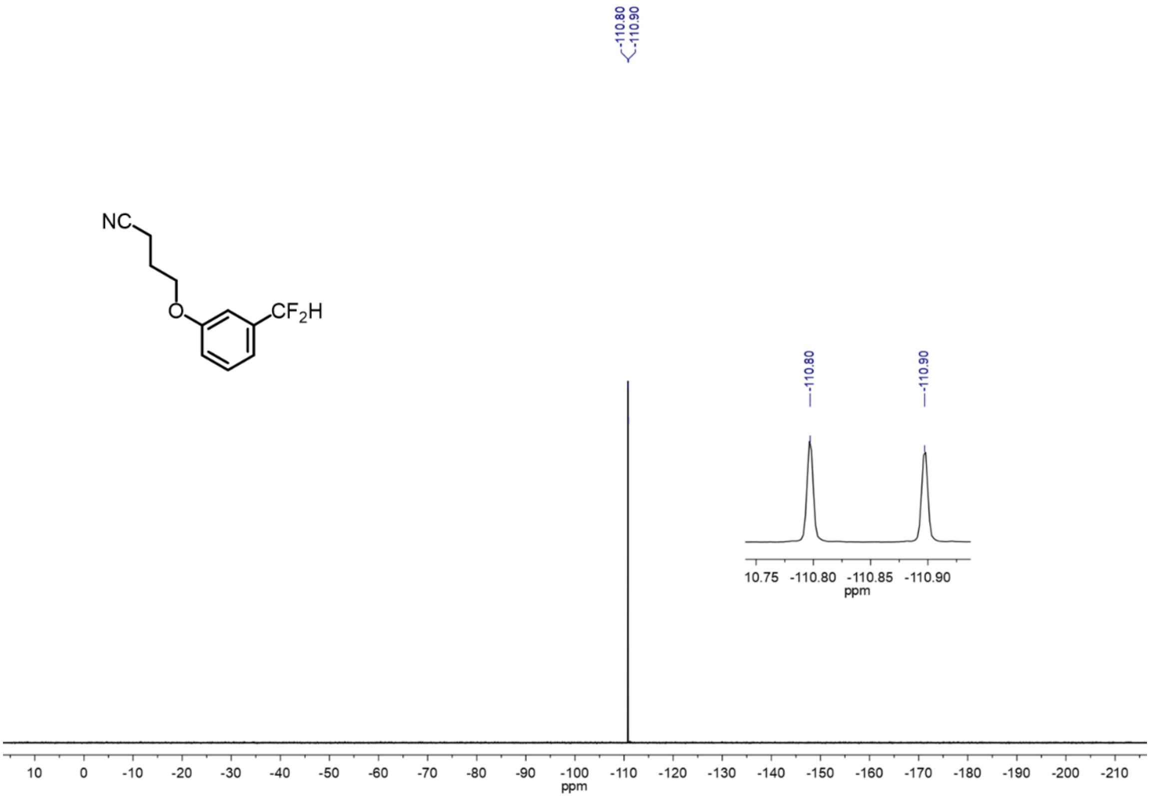

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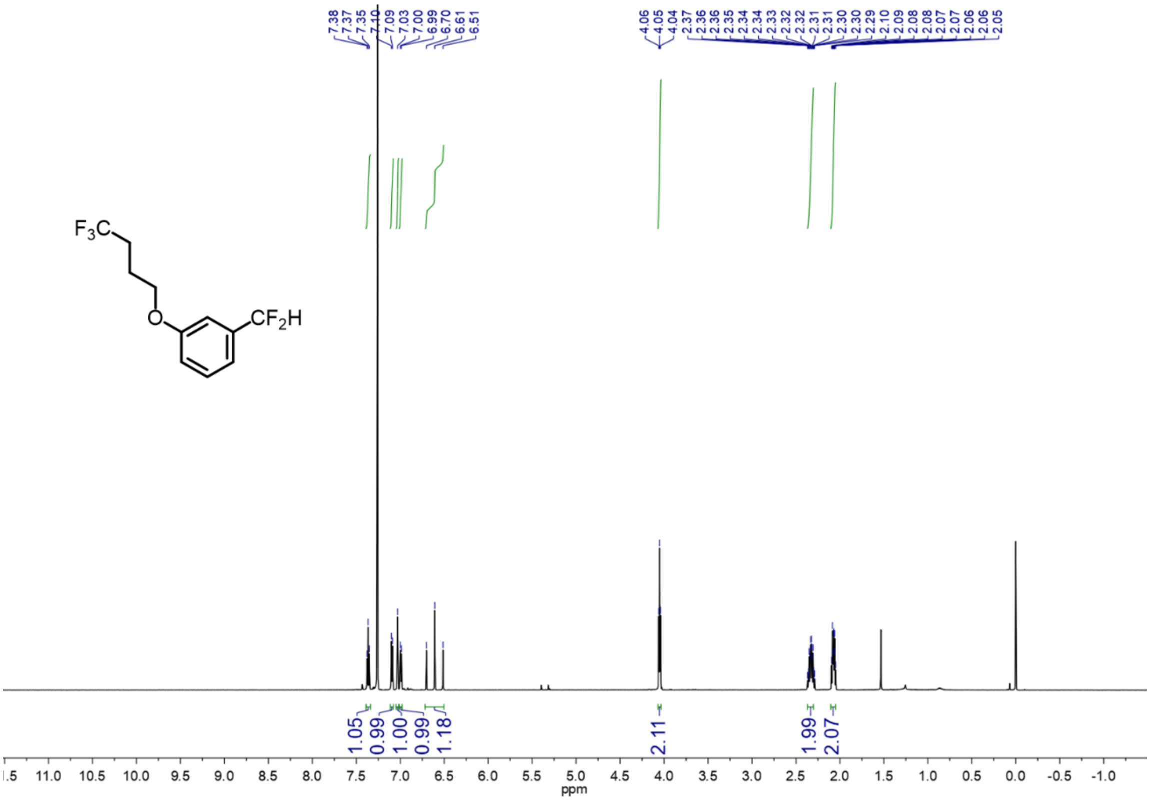

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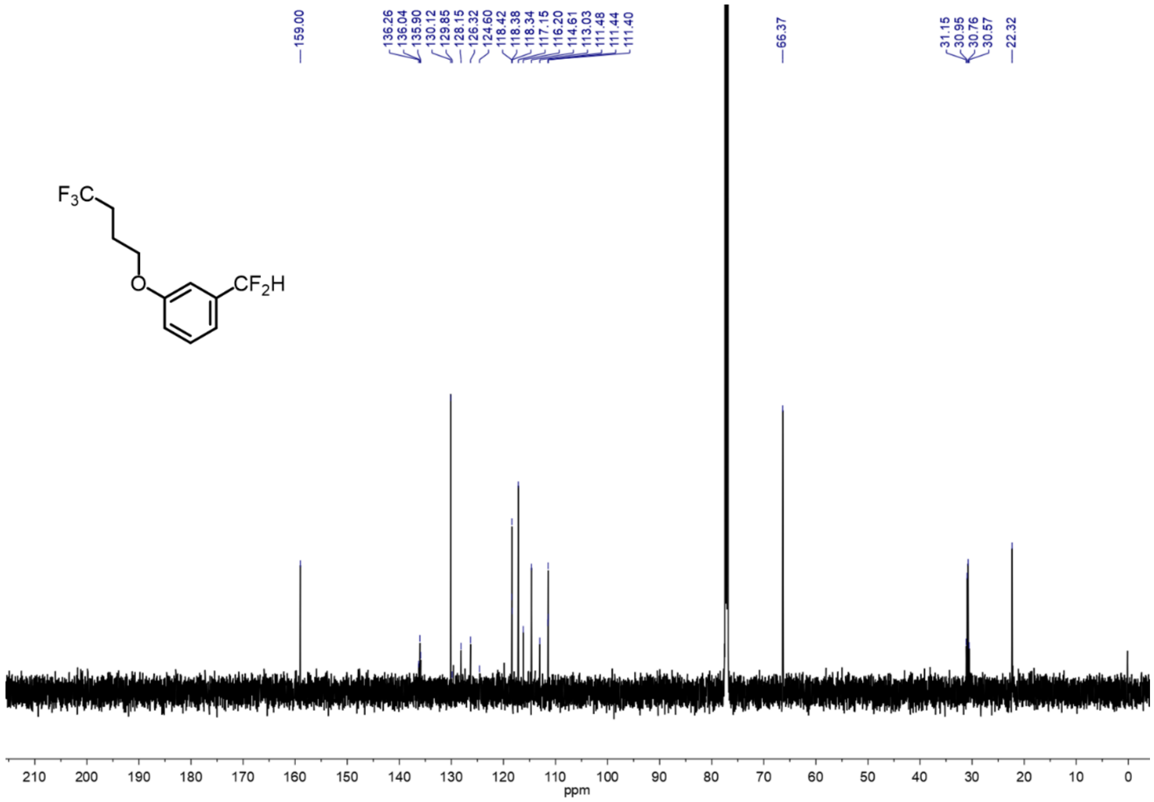

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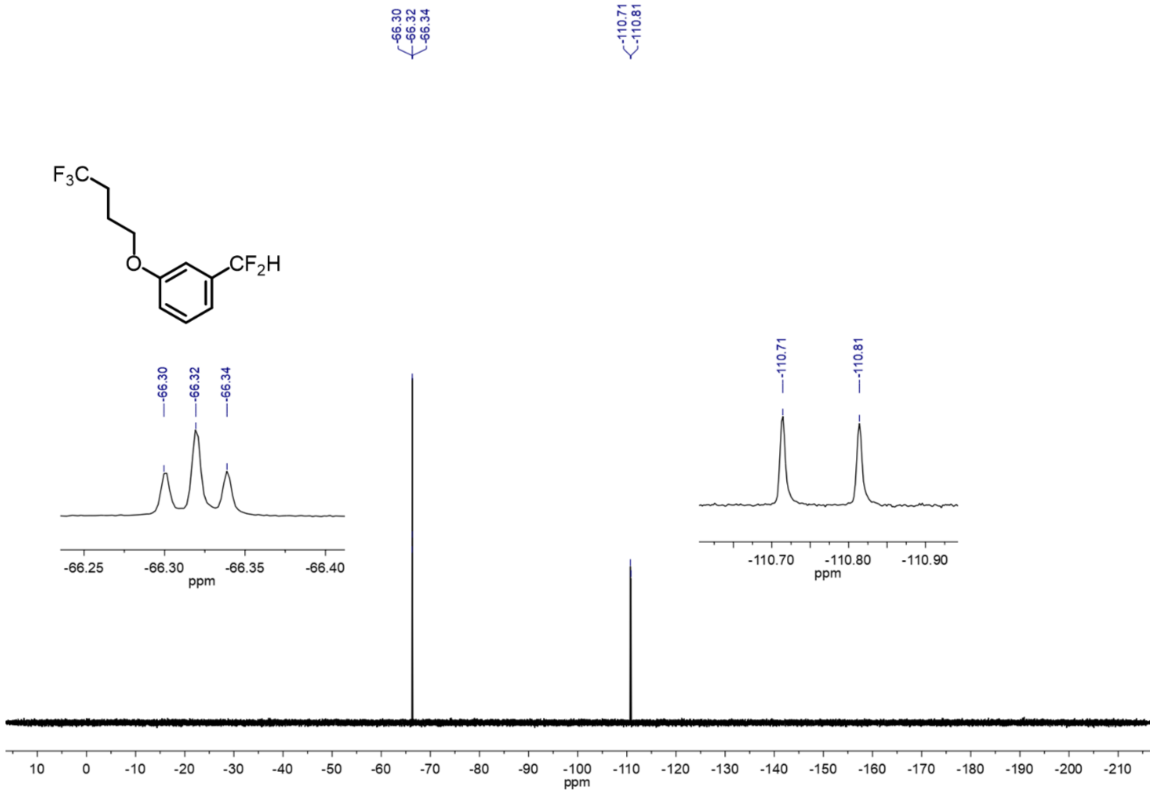

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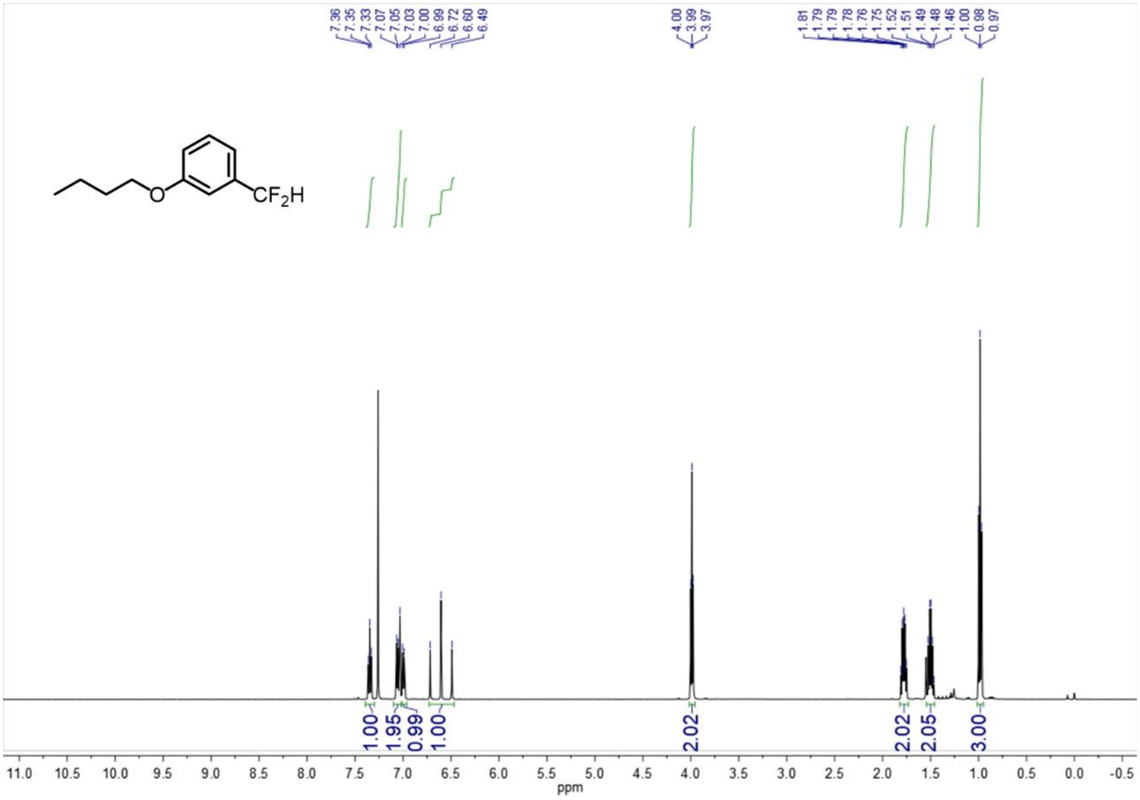

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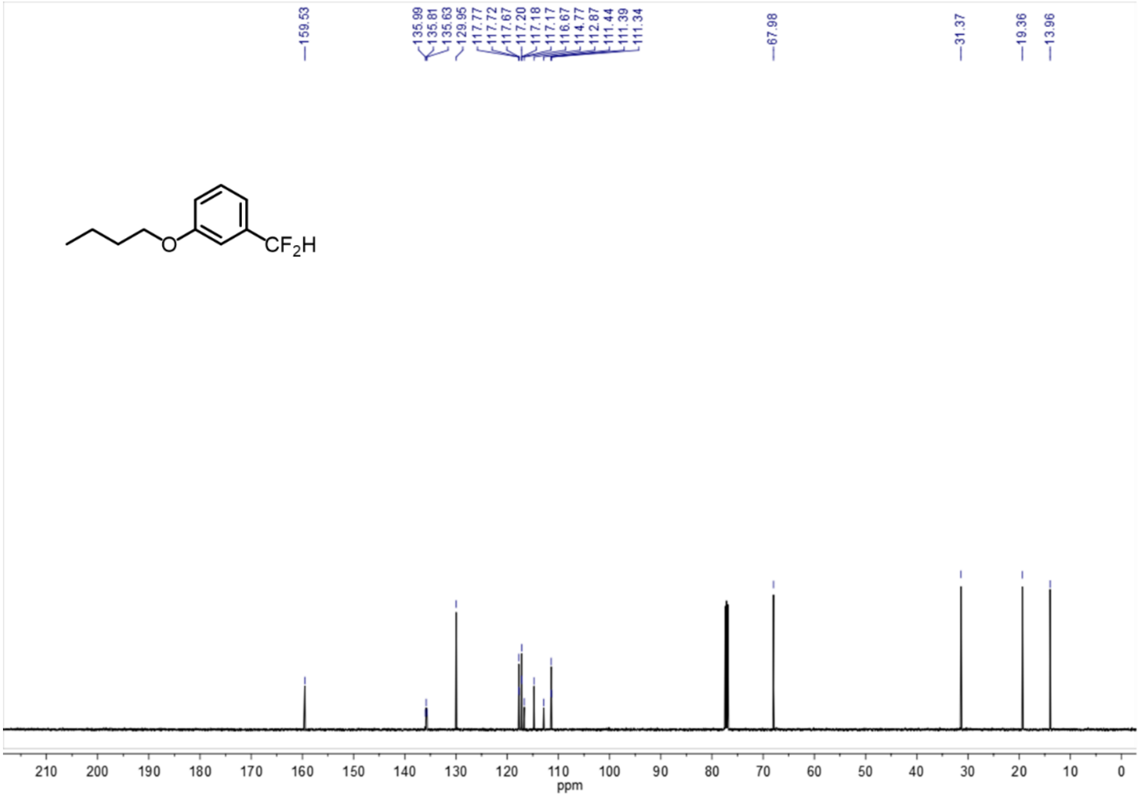

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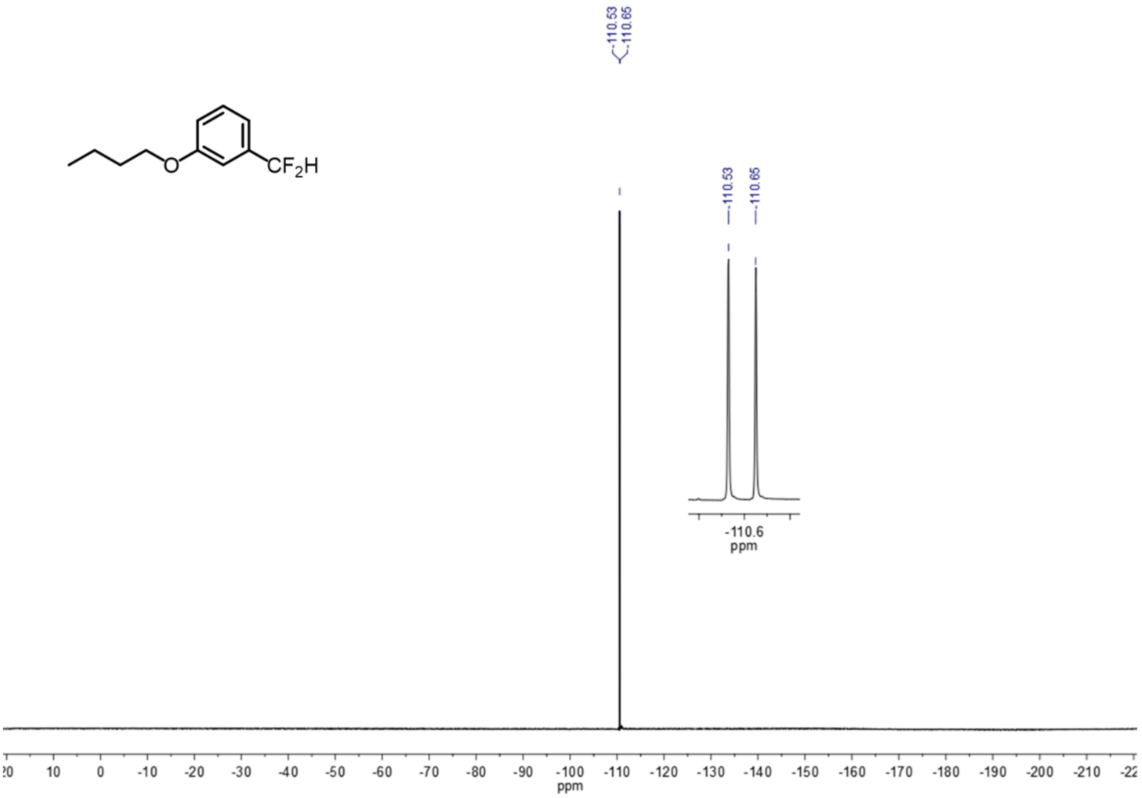

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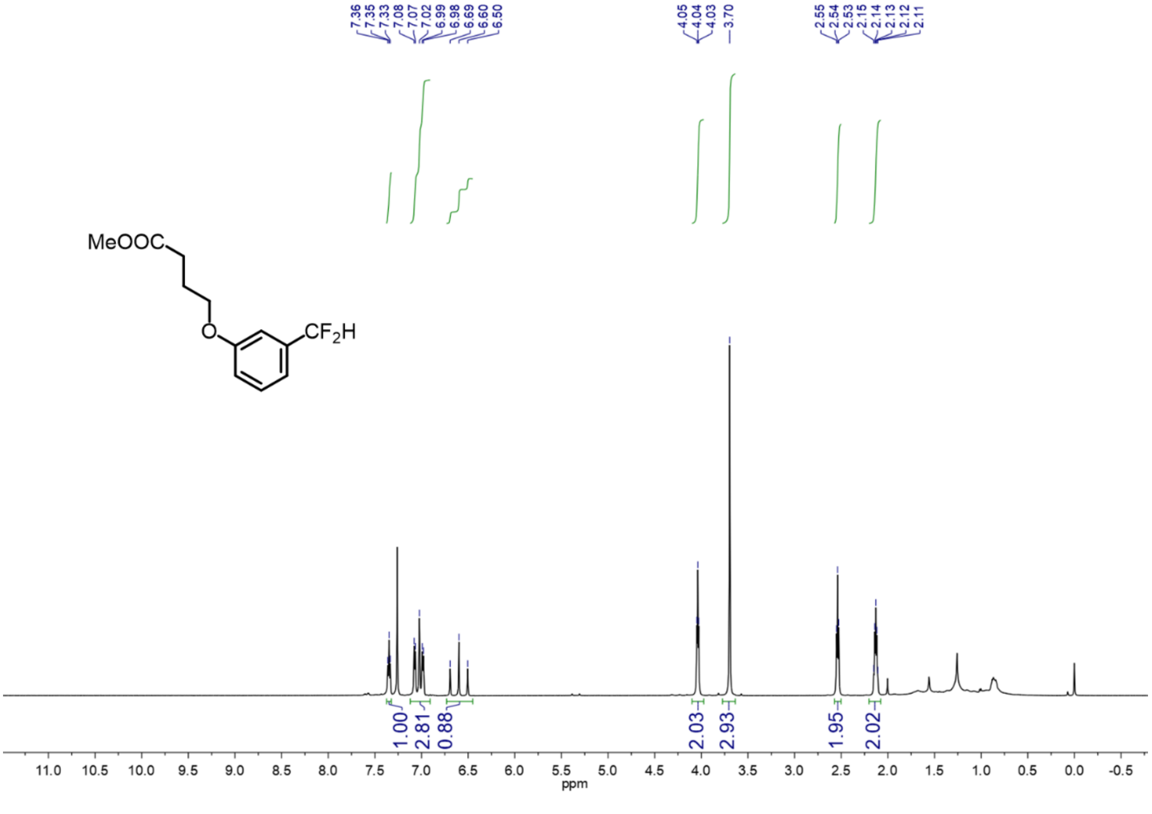

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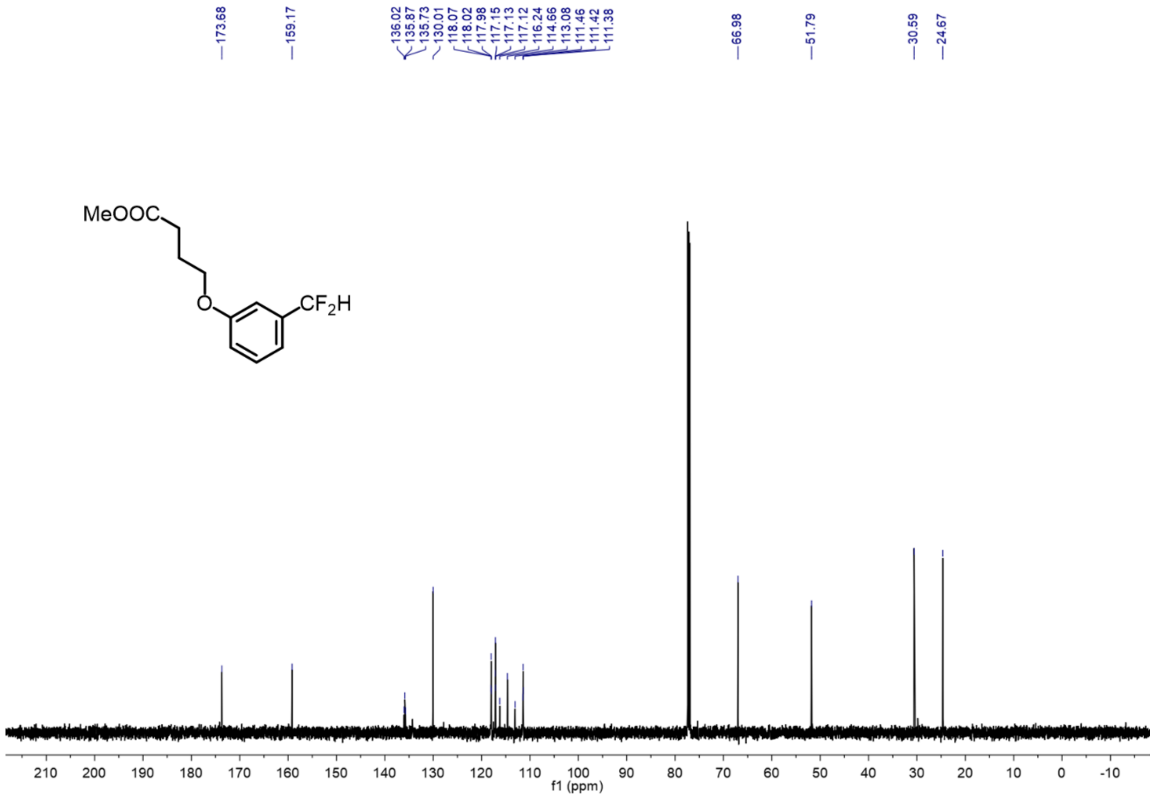

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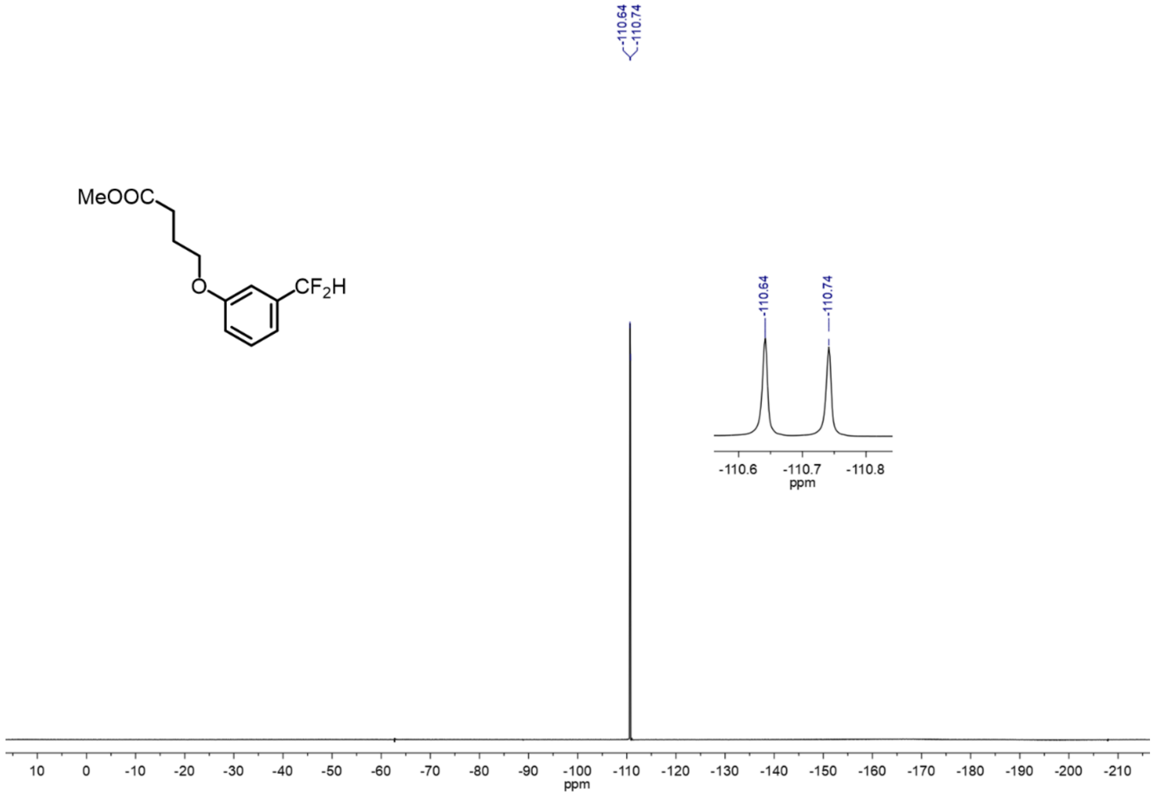

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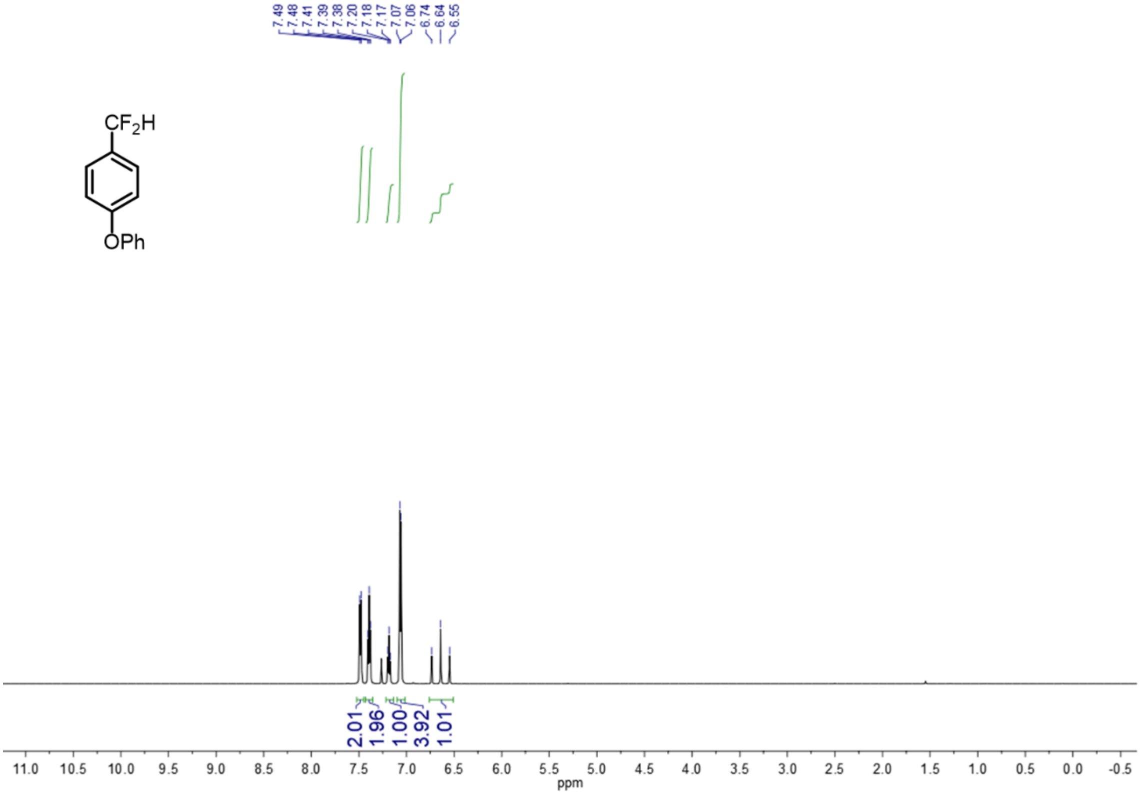

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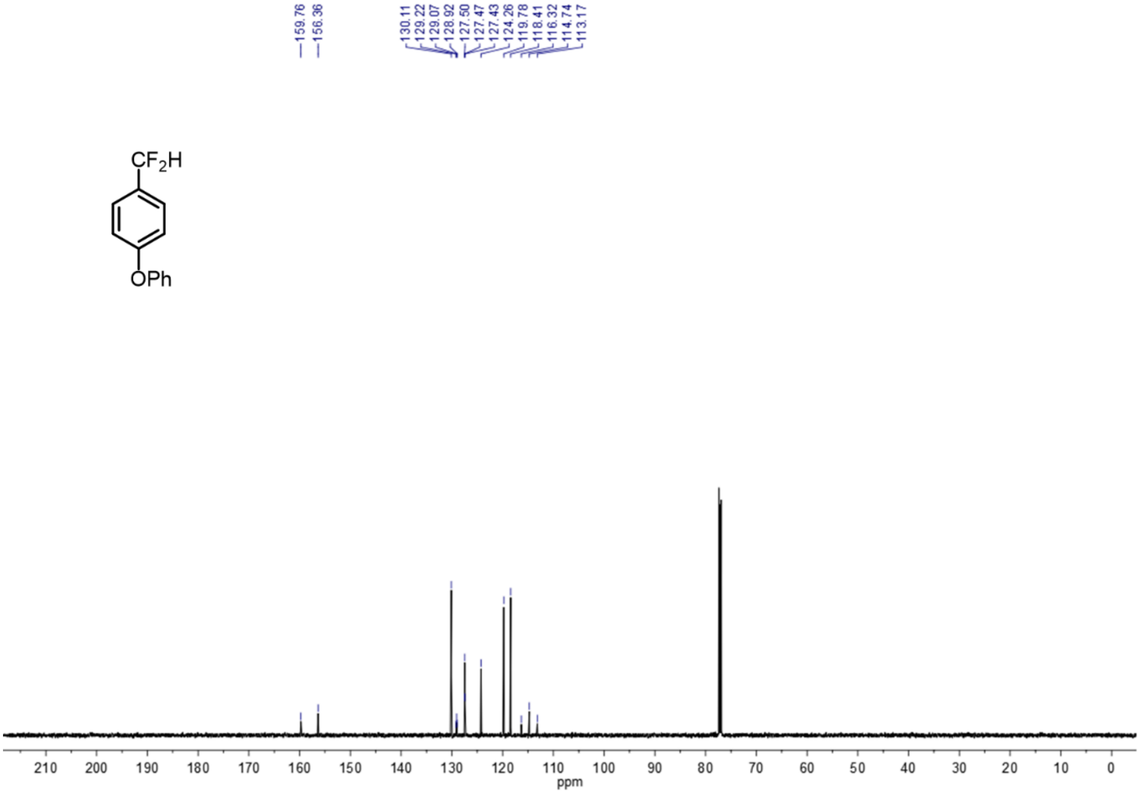

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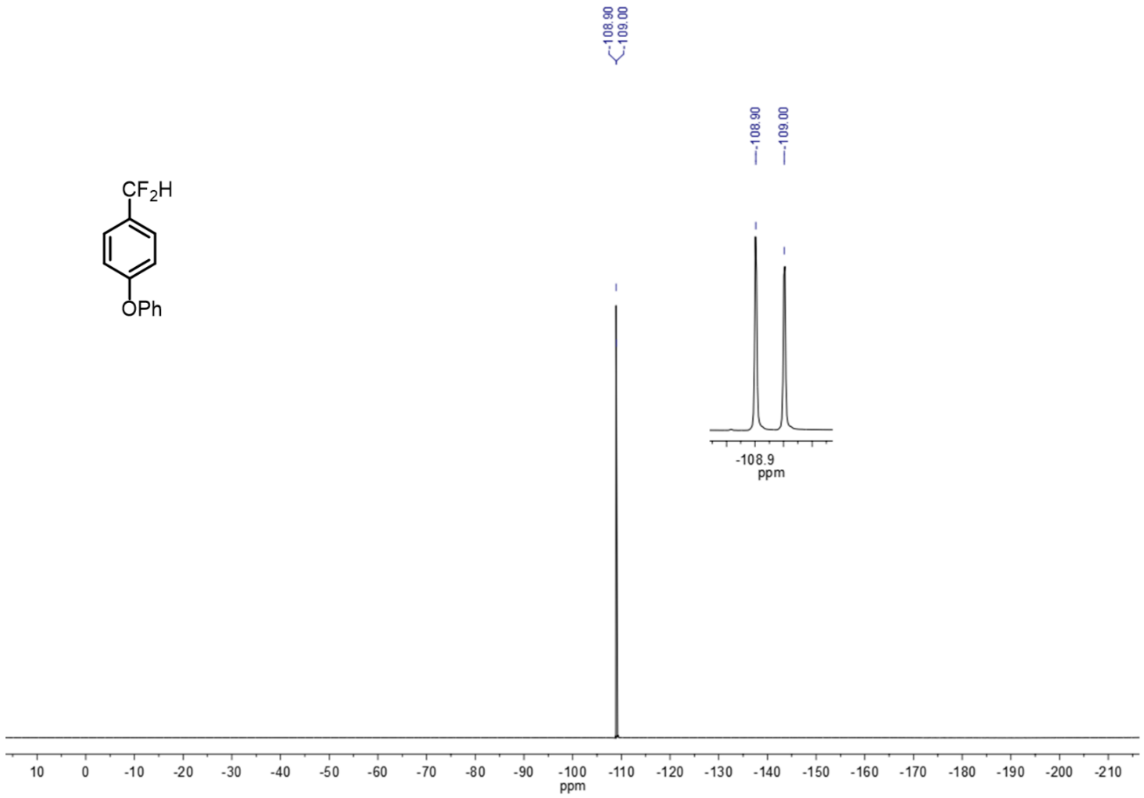

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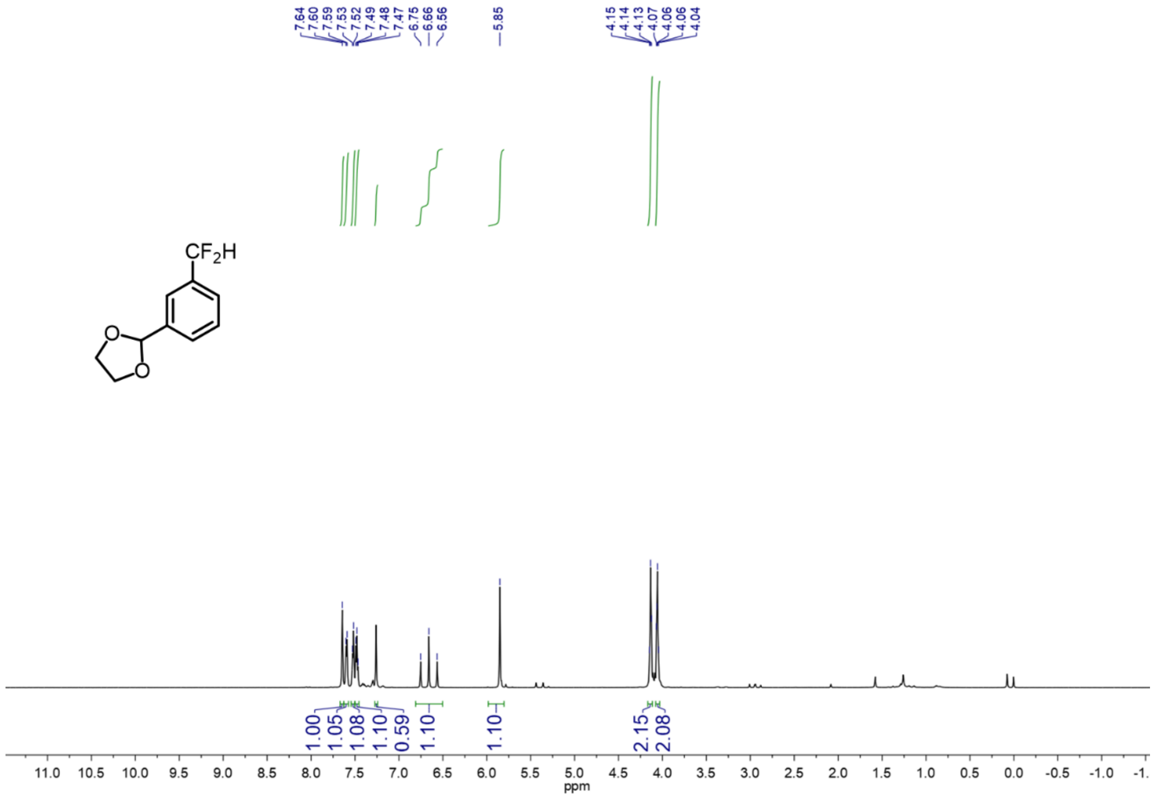

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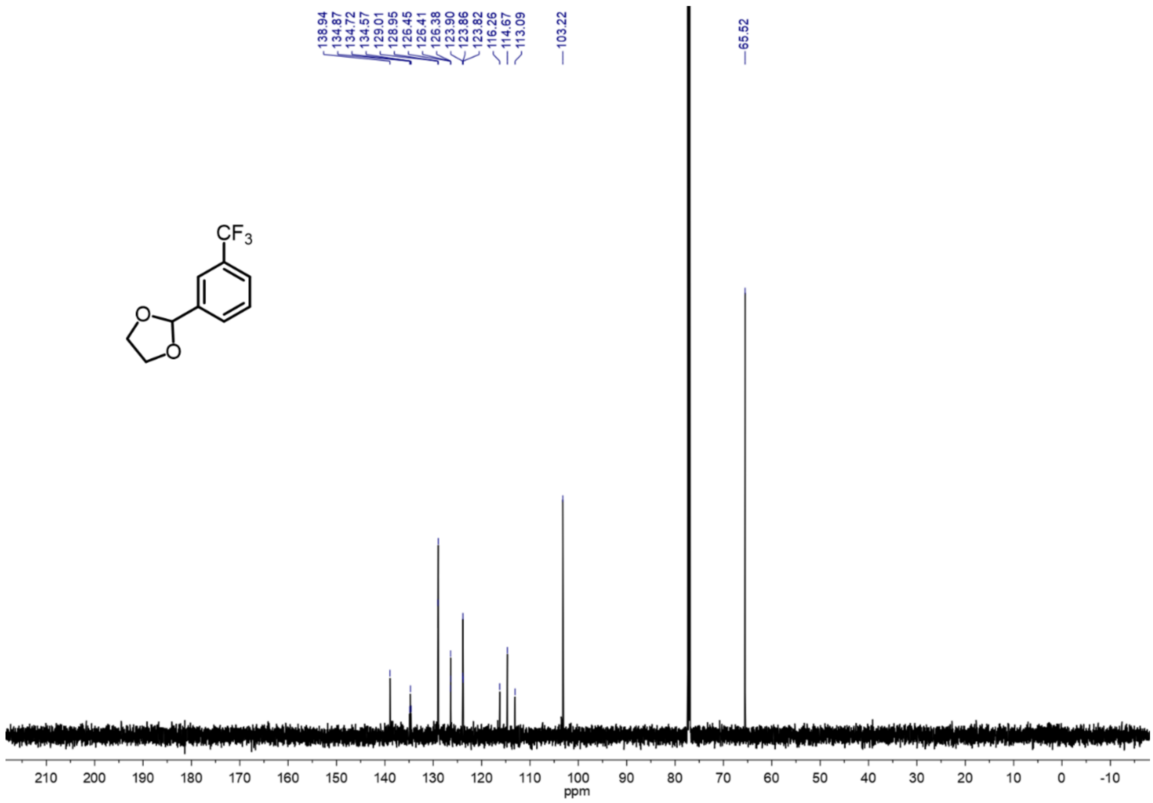

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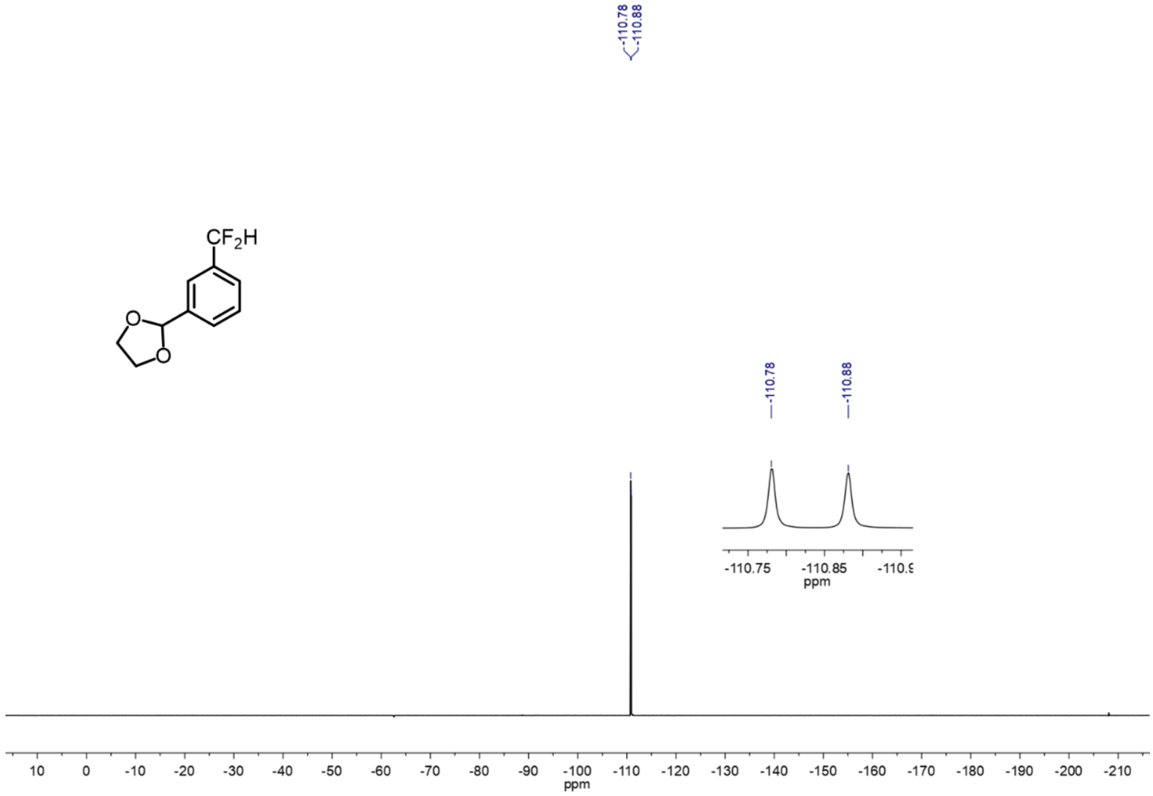

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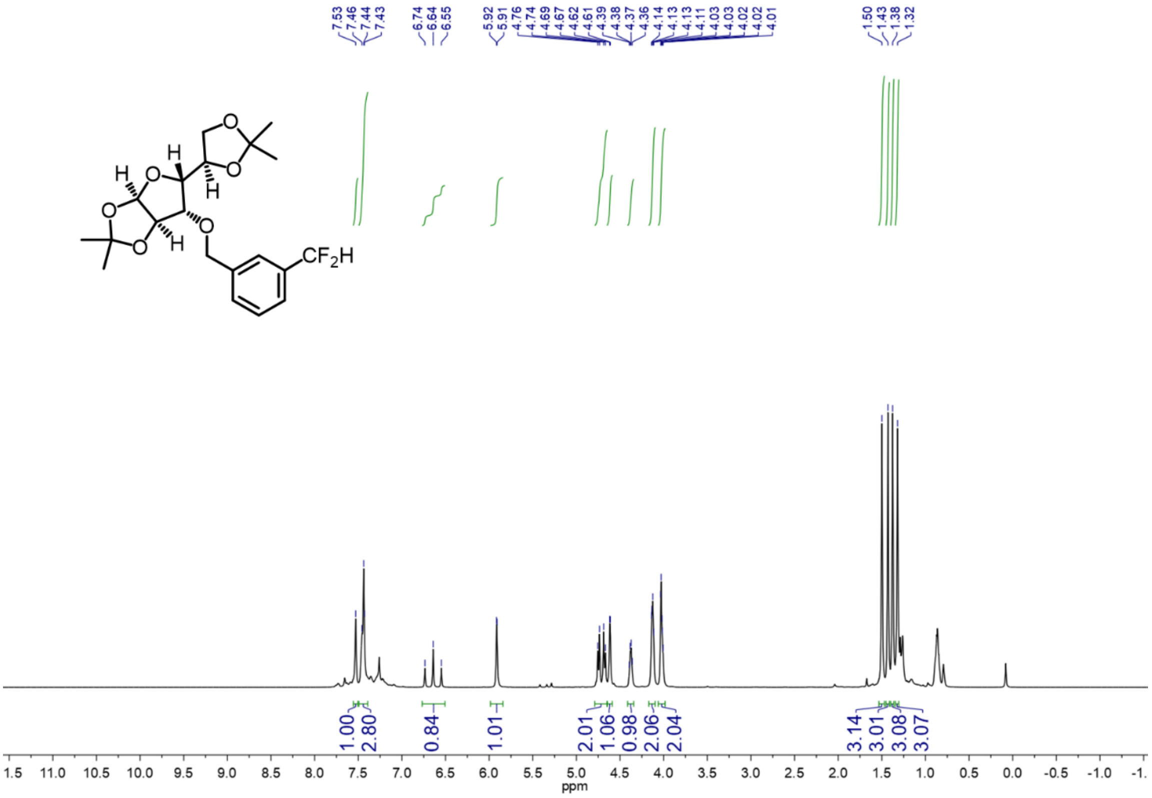

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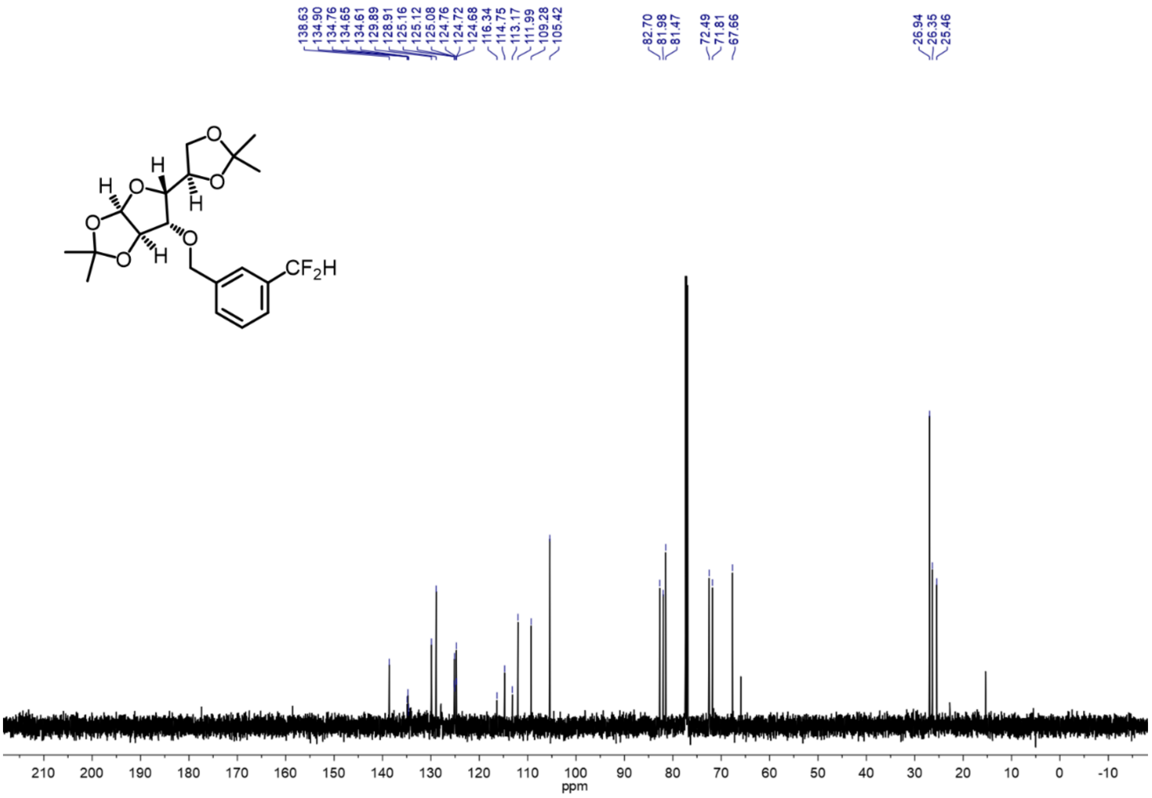

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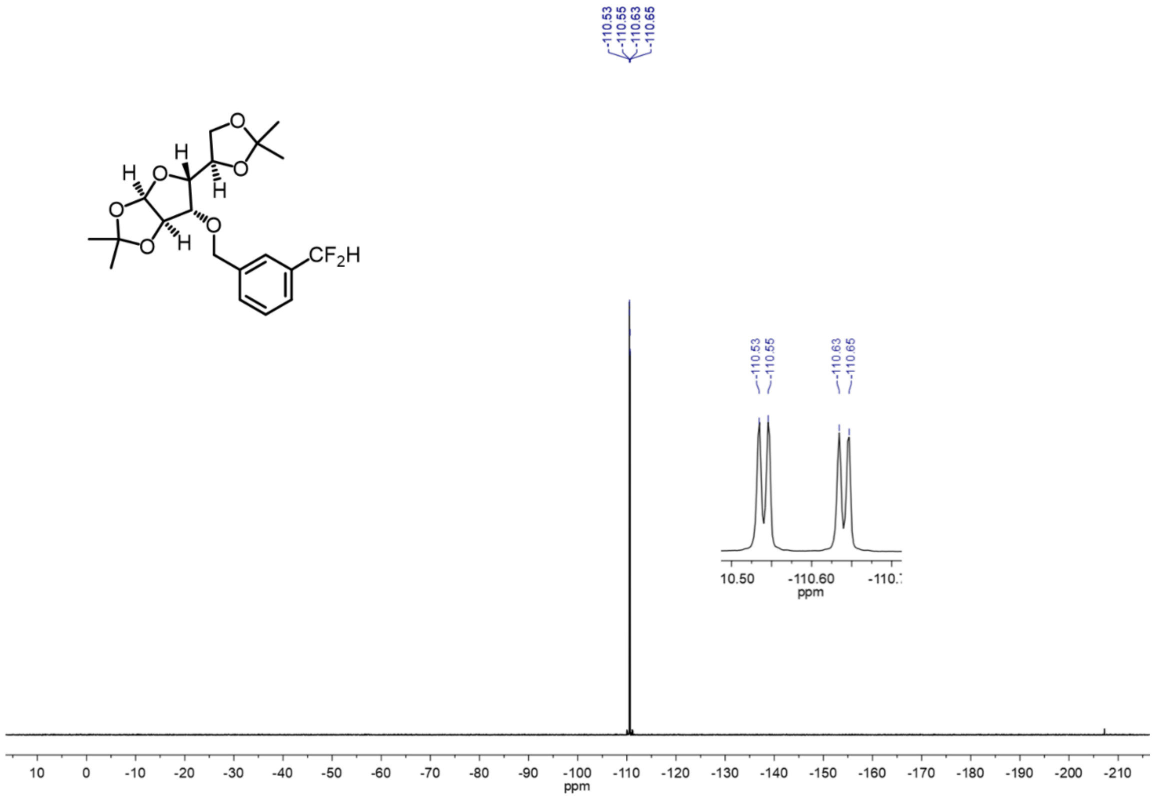

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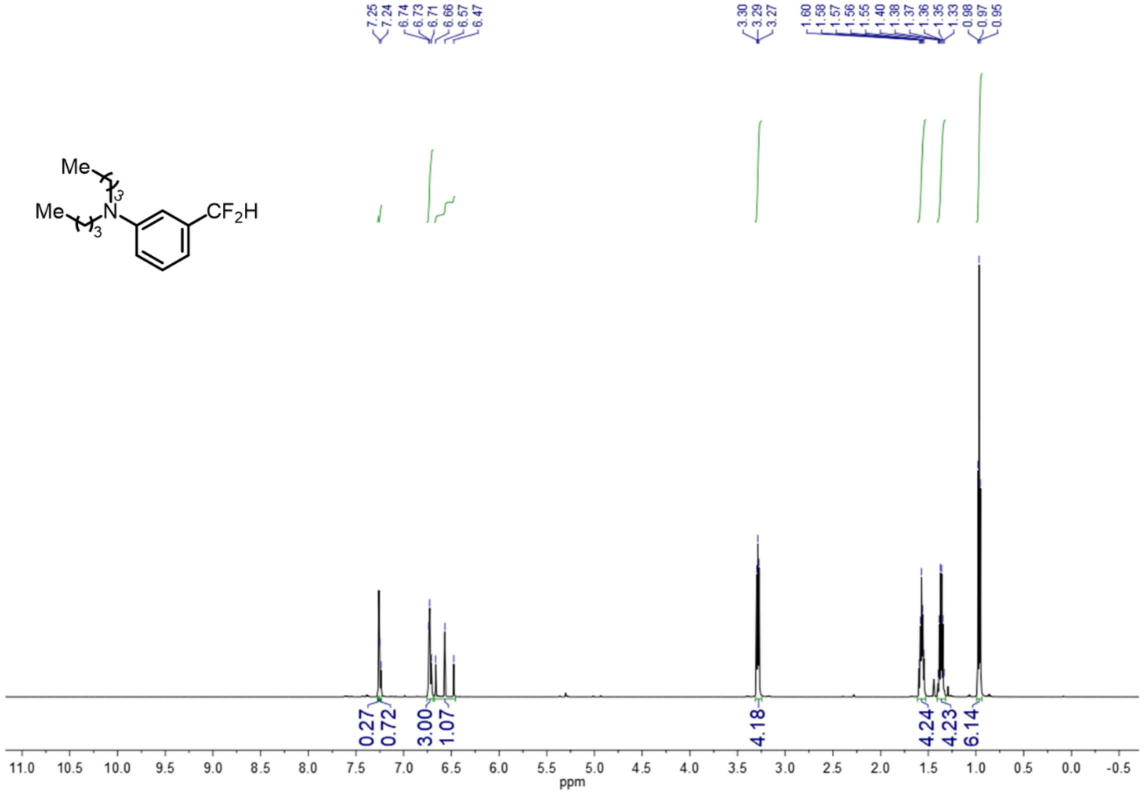

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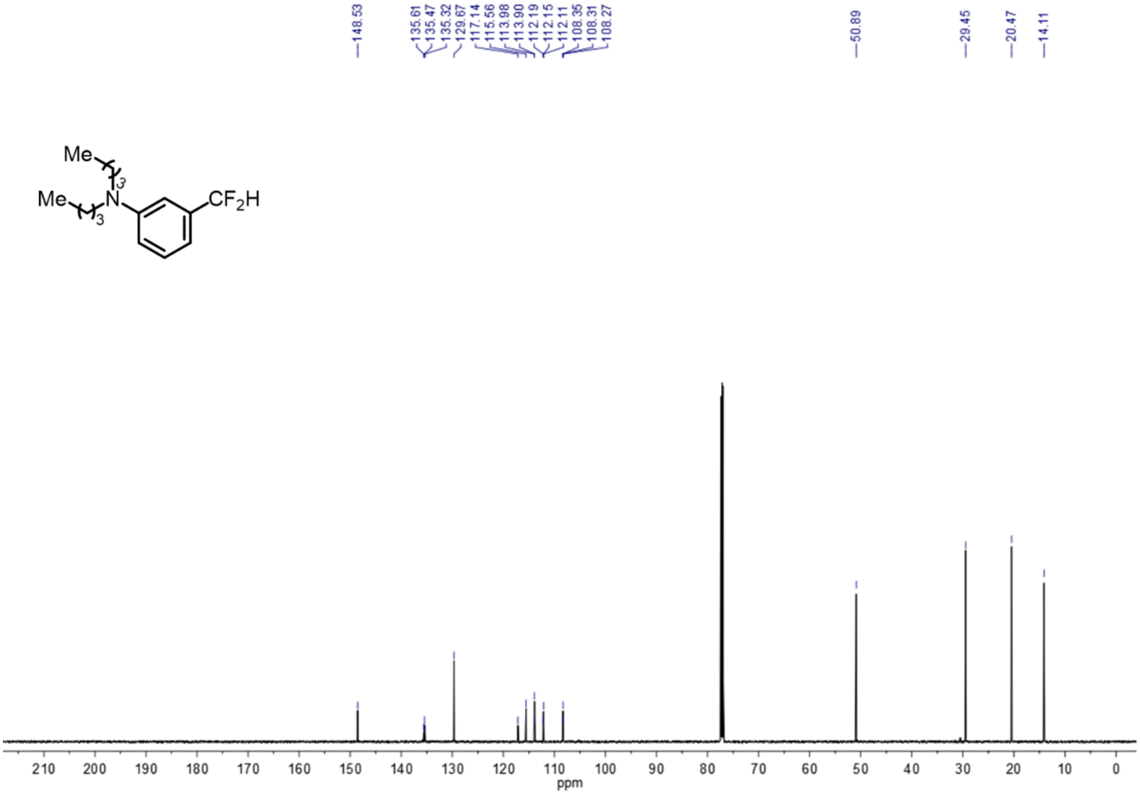
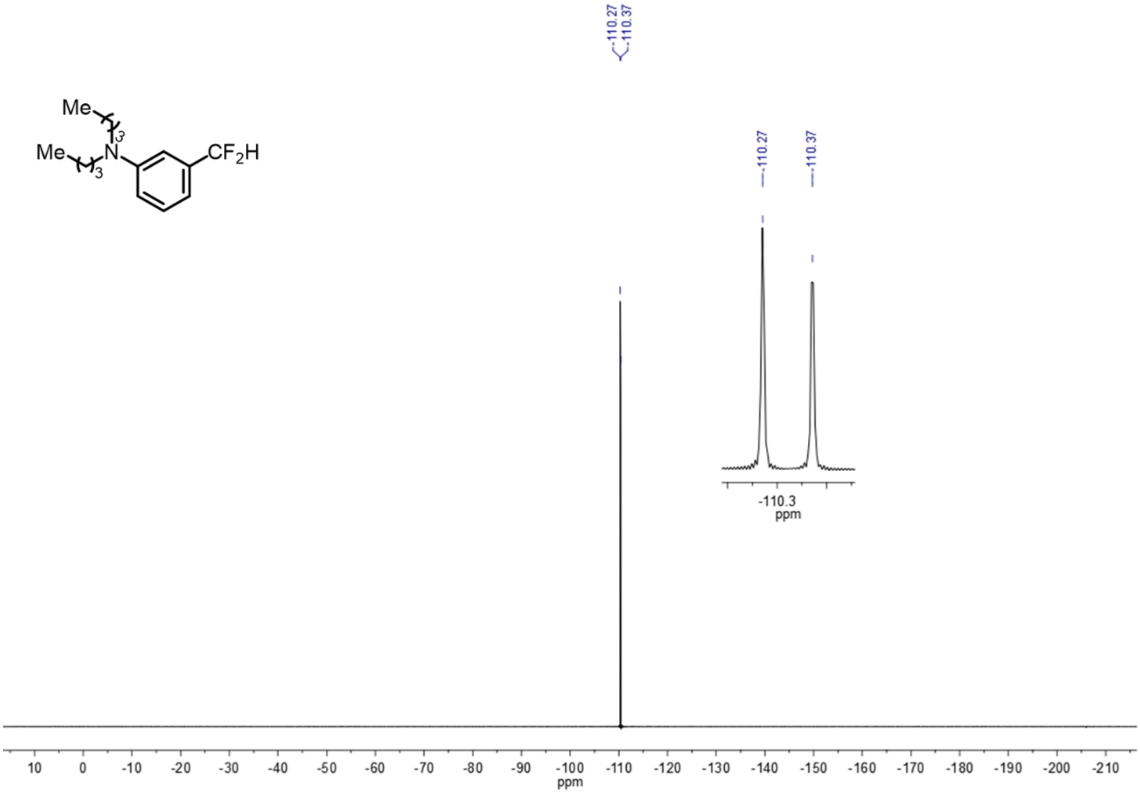
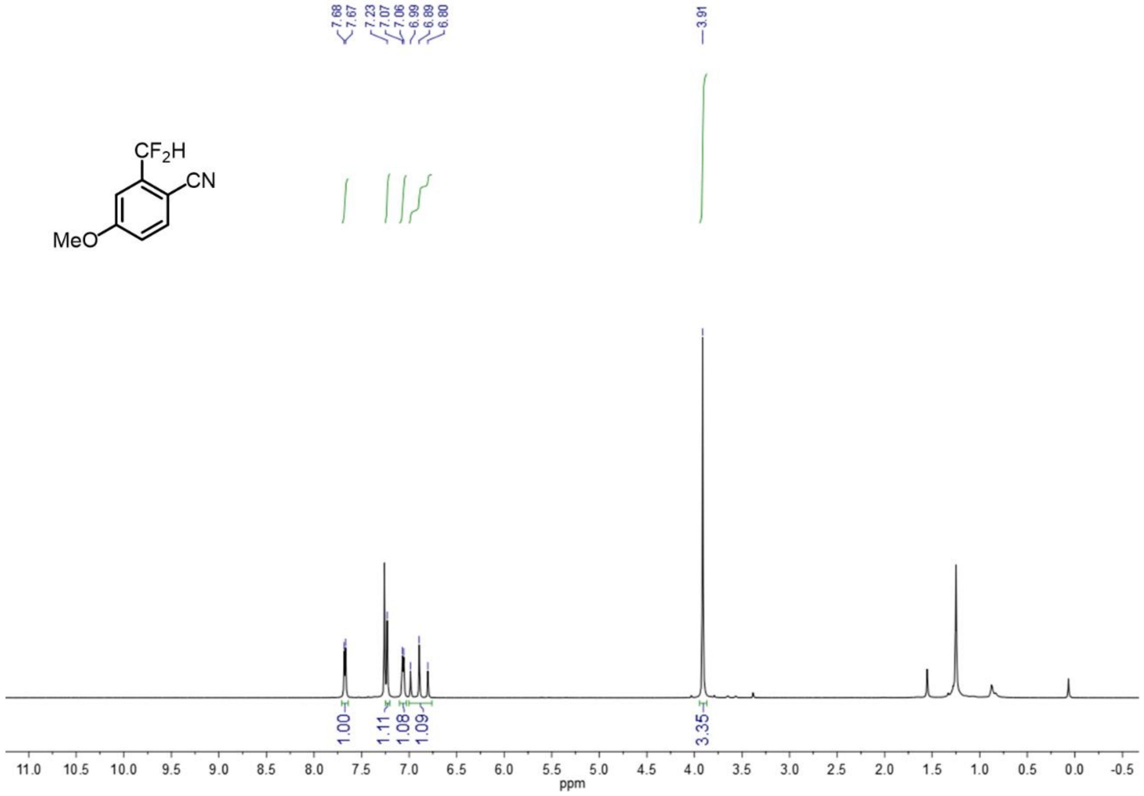


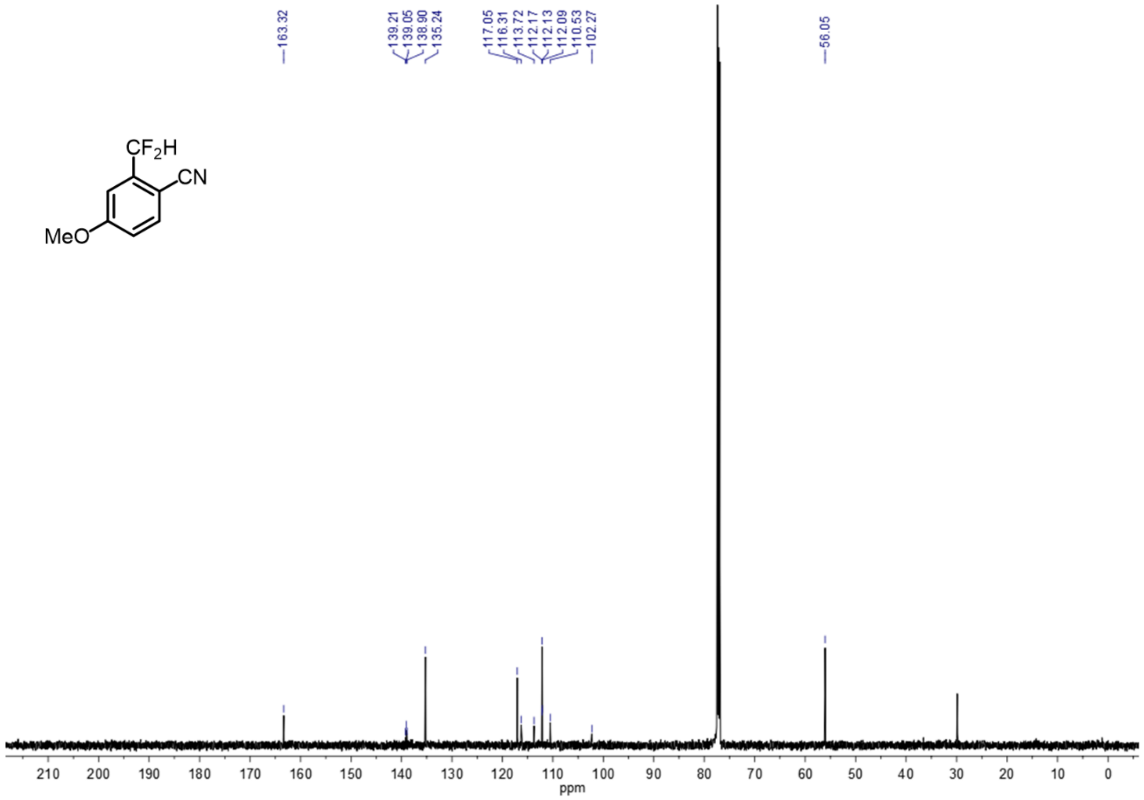
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **3l**



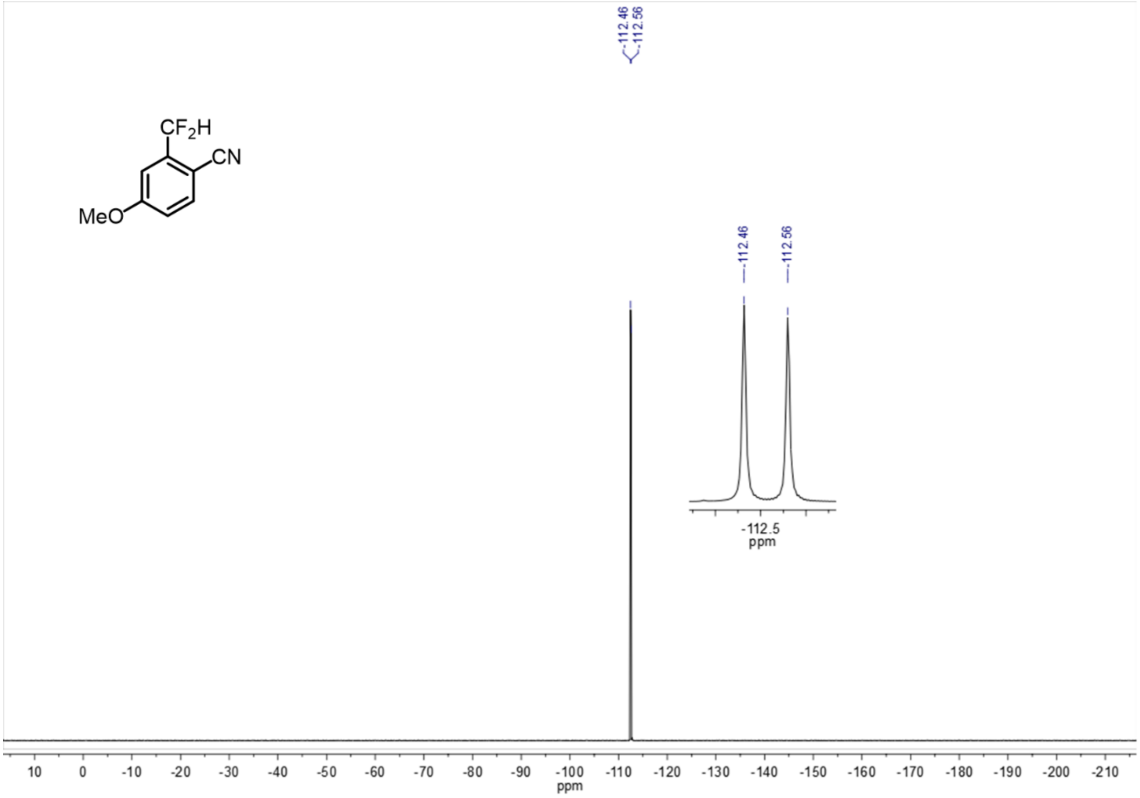
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **3l**



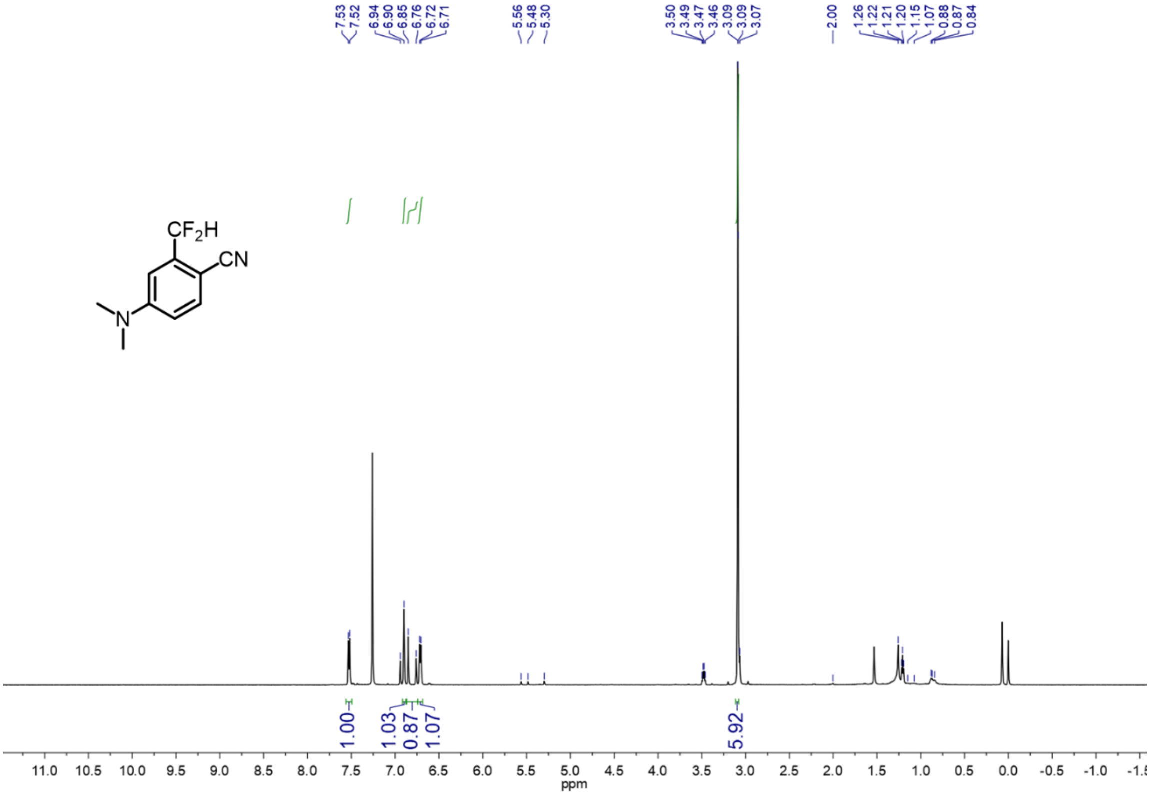
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **3t**



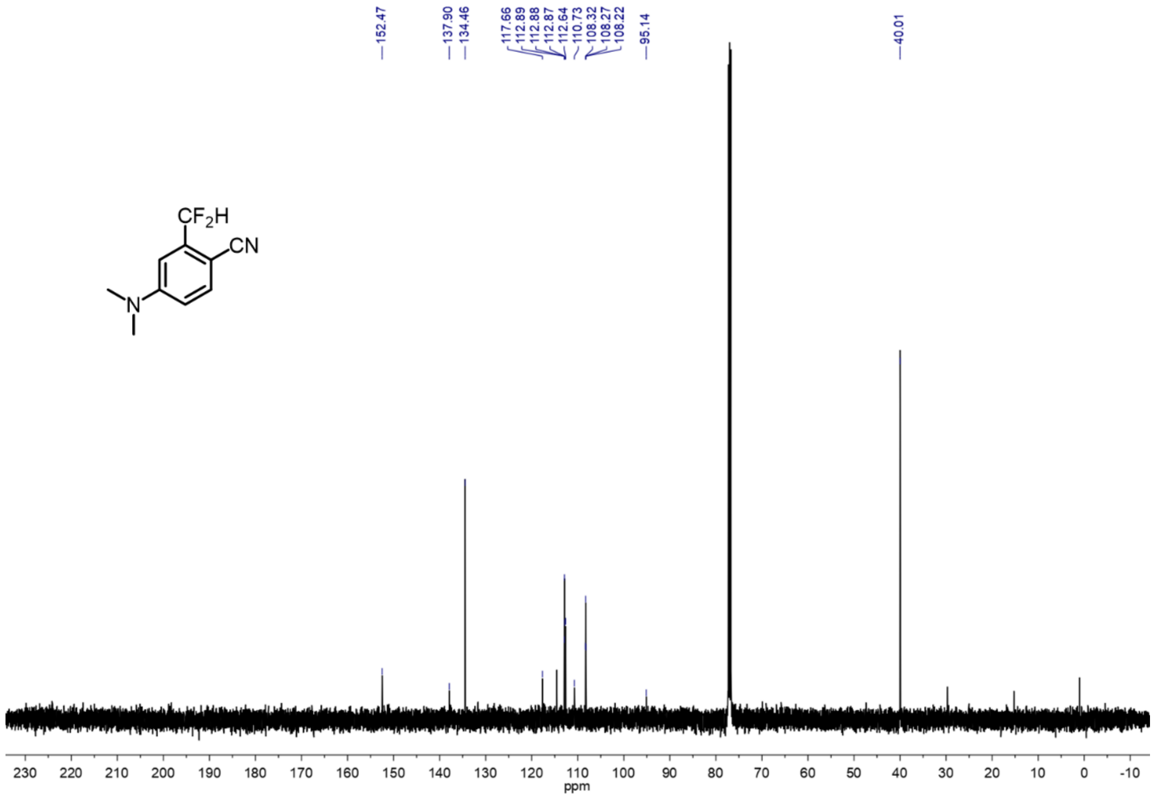
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **3t**



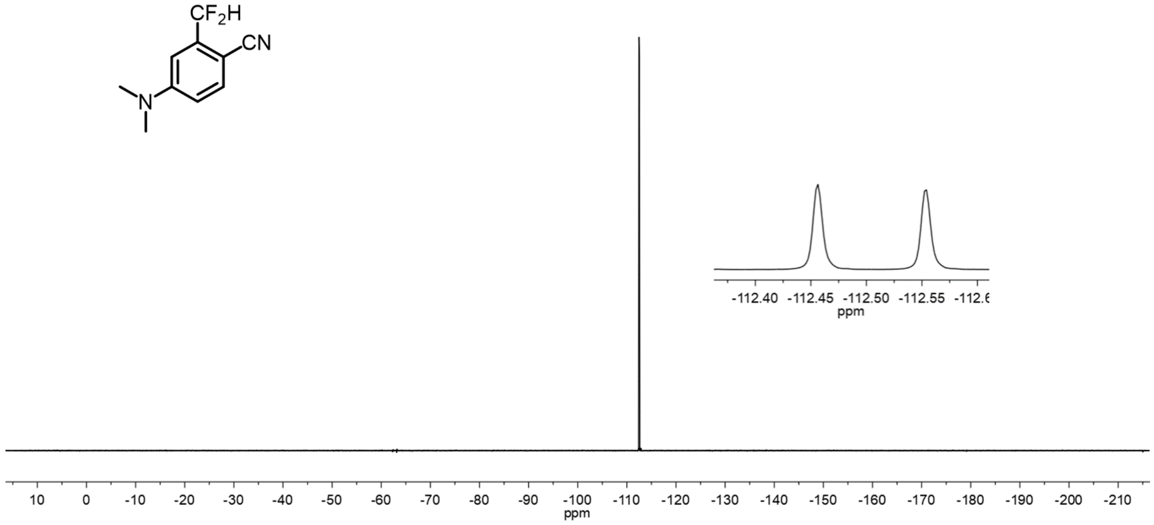
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **3t**



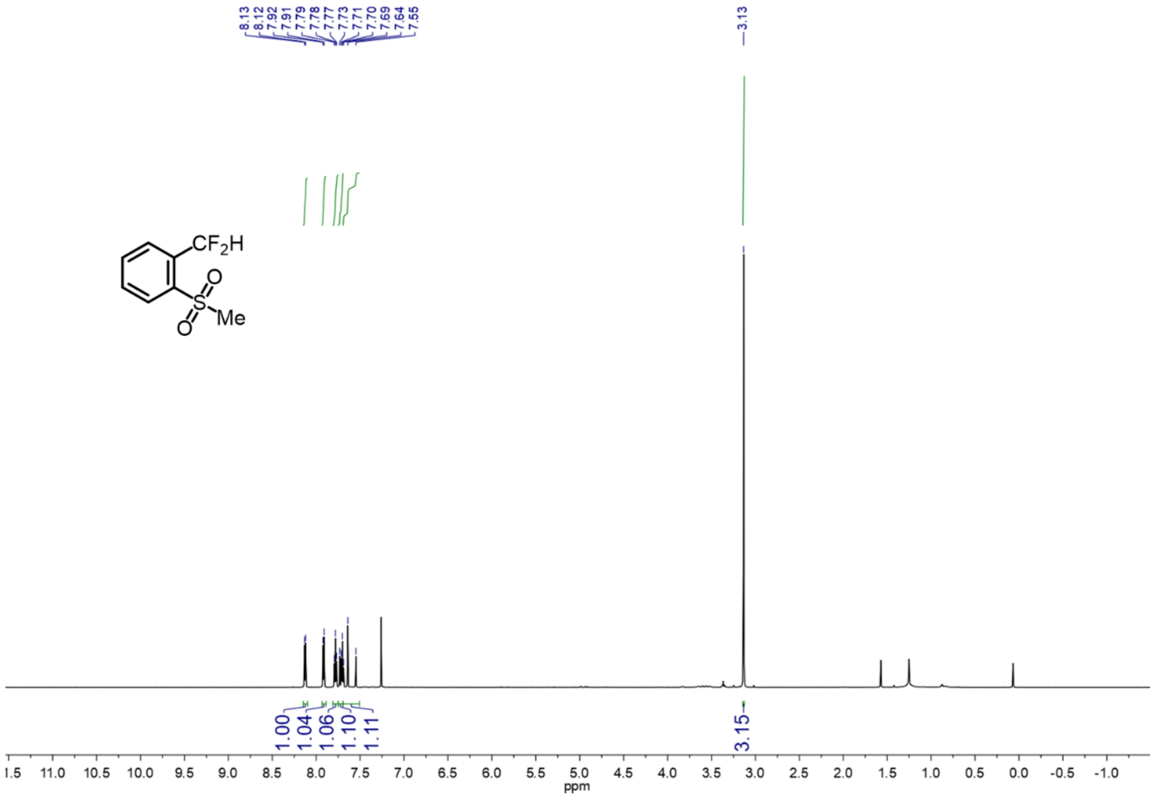
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **3u**



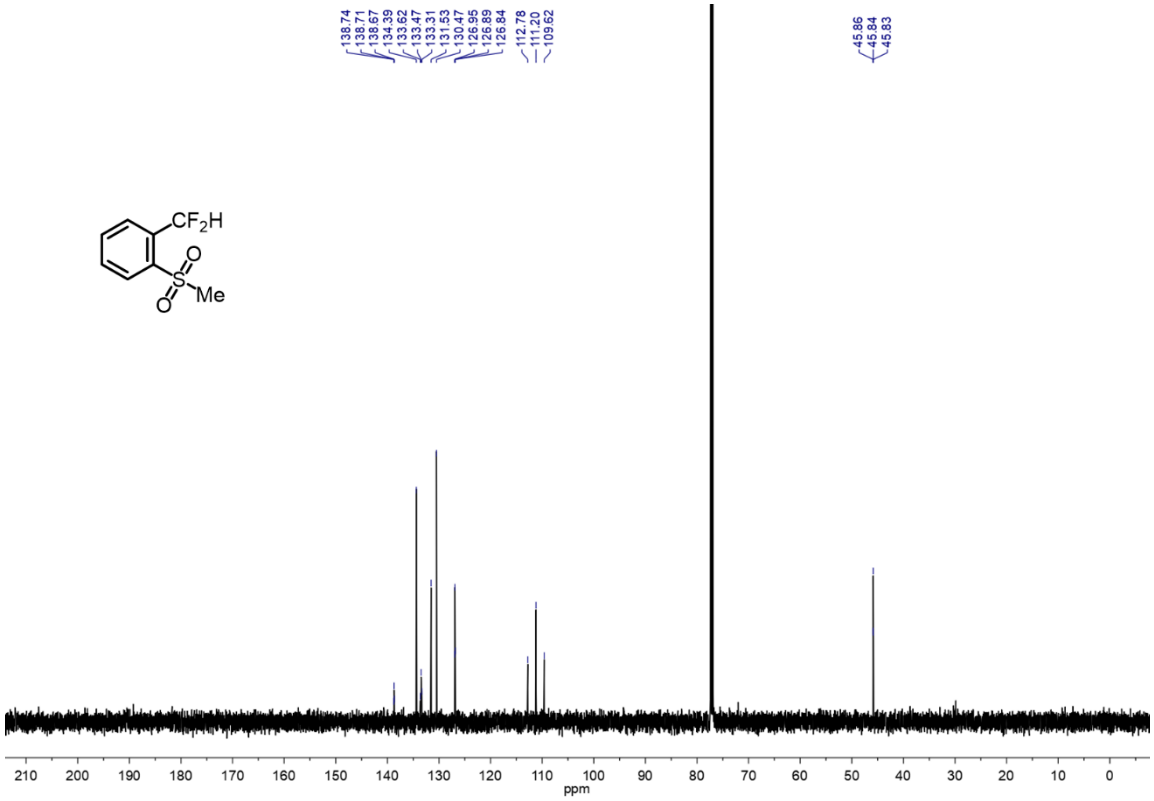
^{13}C NMR spectrum (126 MHz, $CDCl_3$, 23 ºC) of **3u**



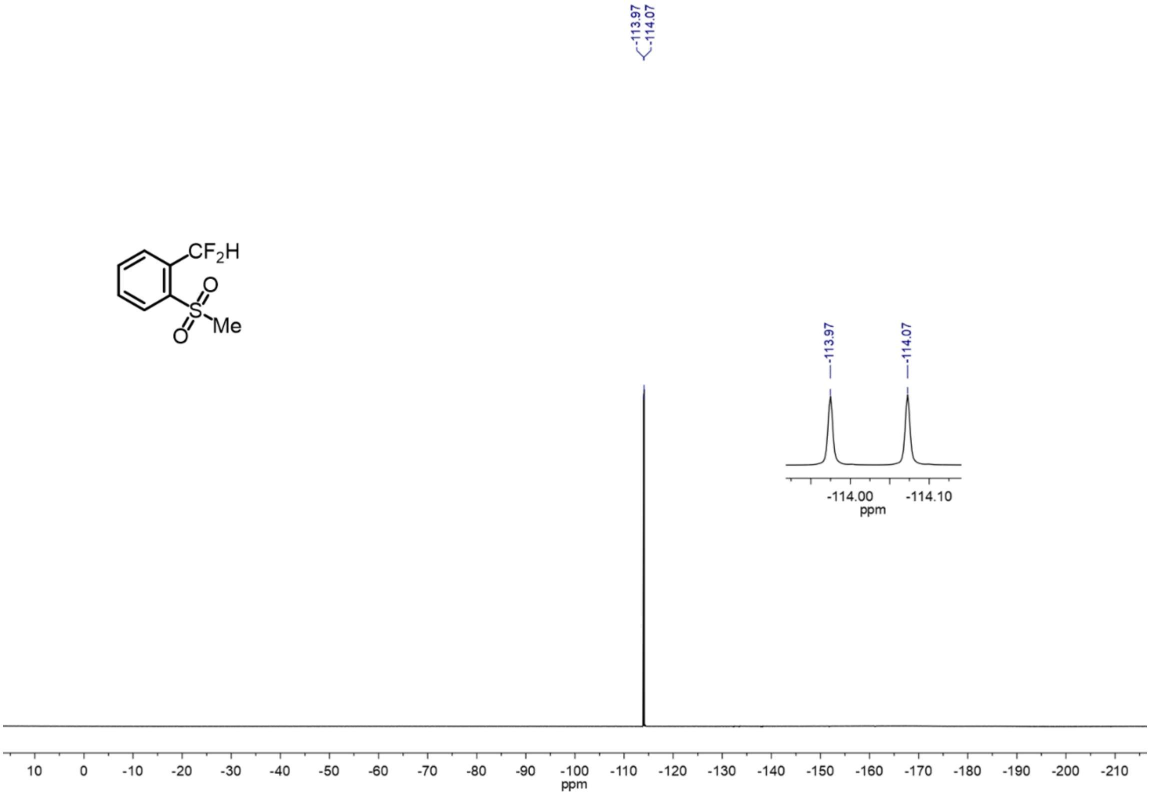
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **3u**



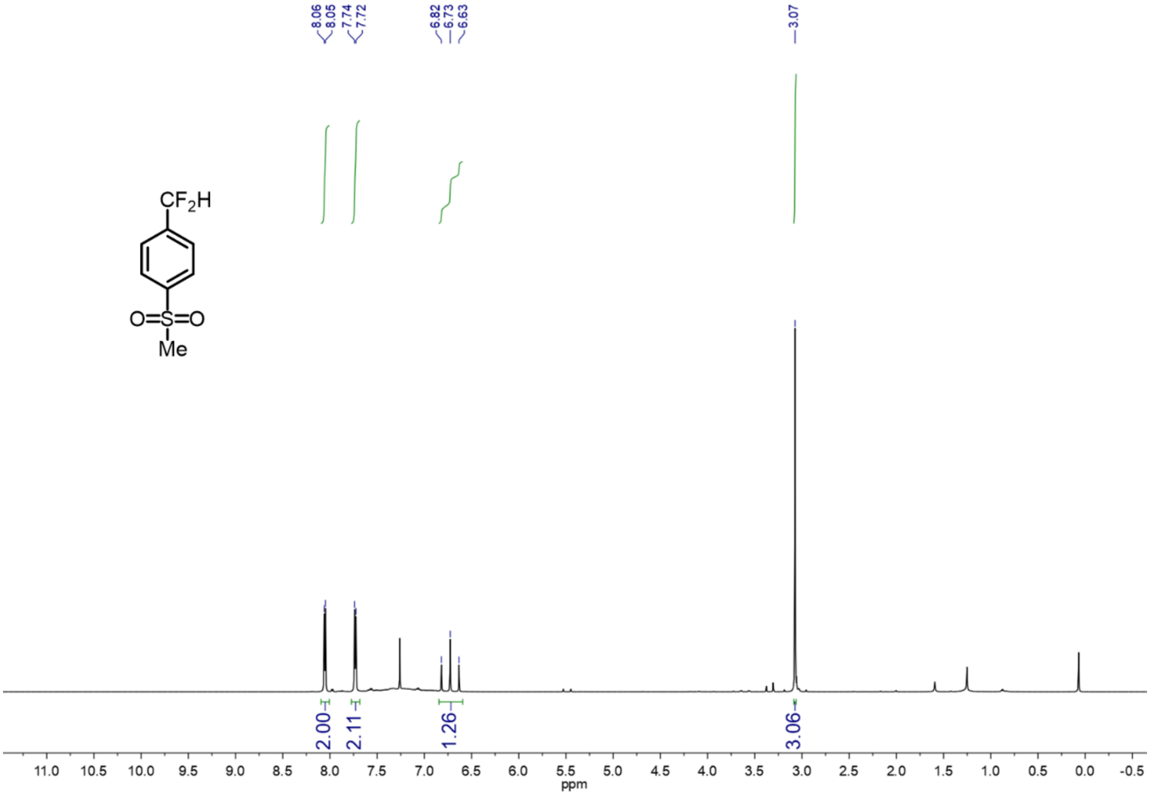
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **3v**



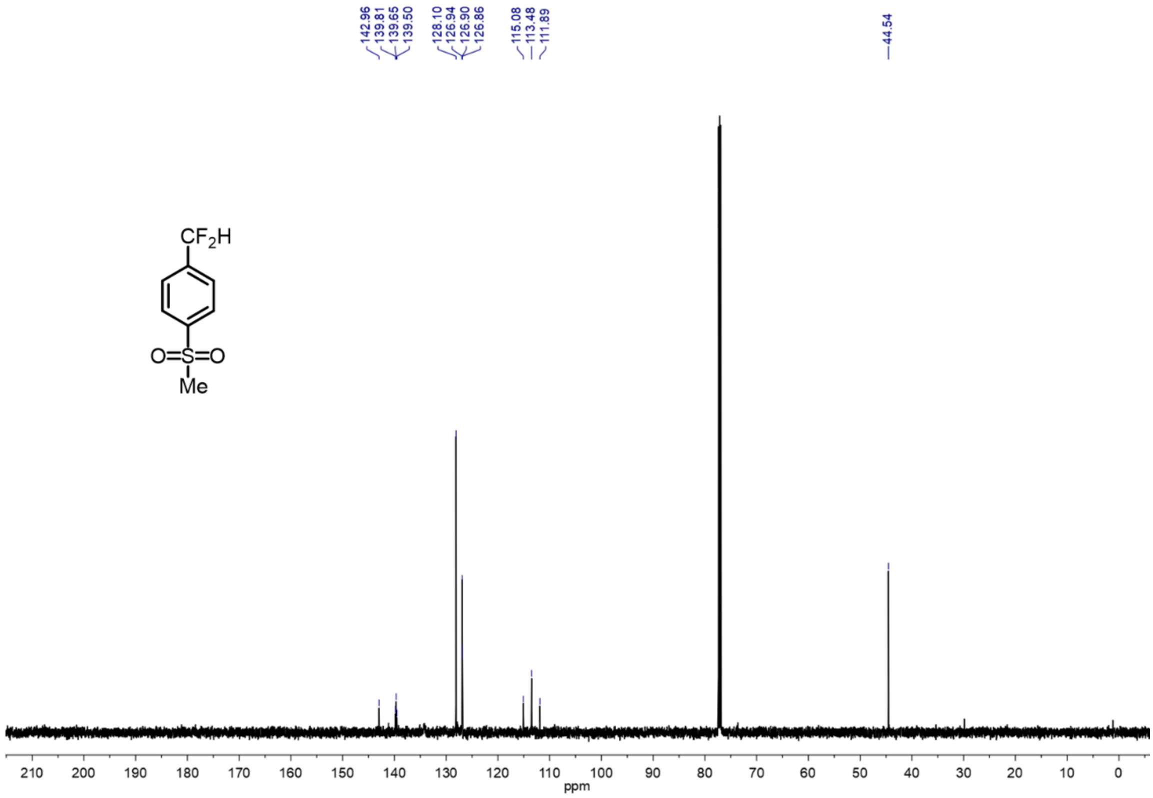
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **3v**



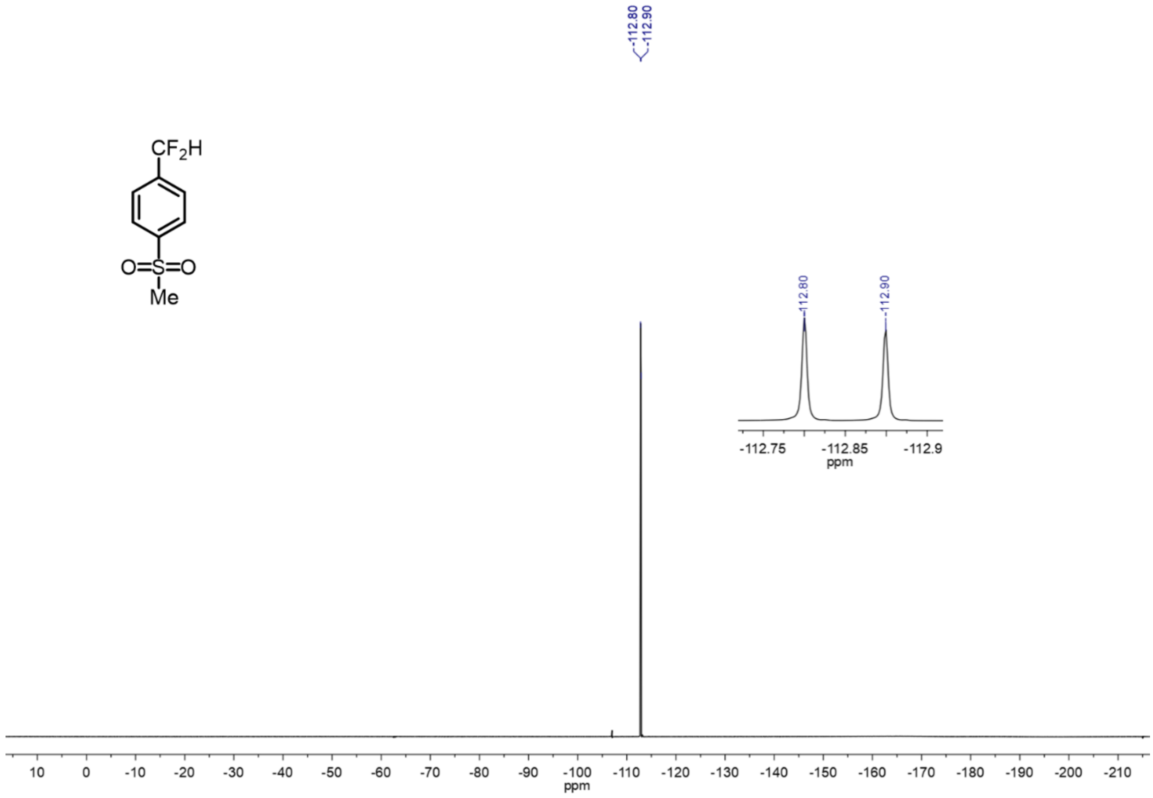
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **3v**



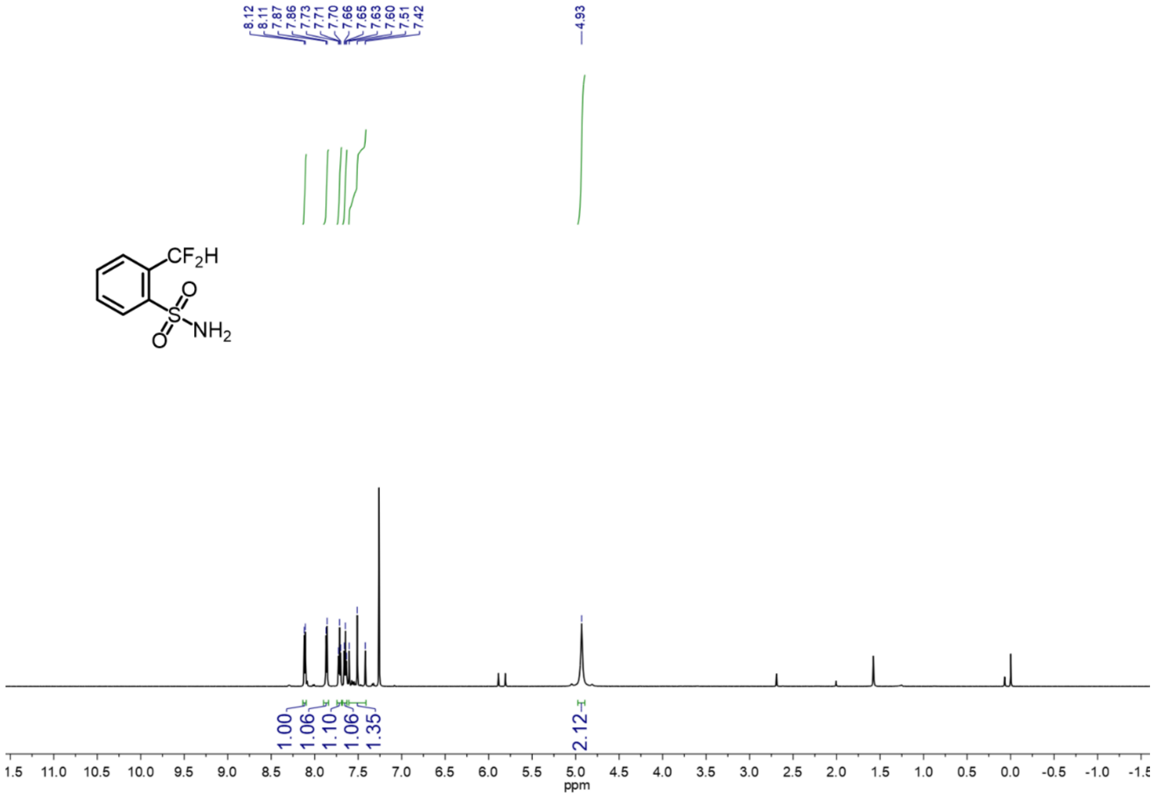
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **3w**



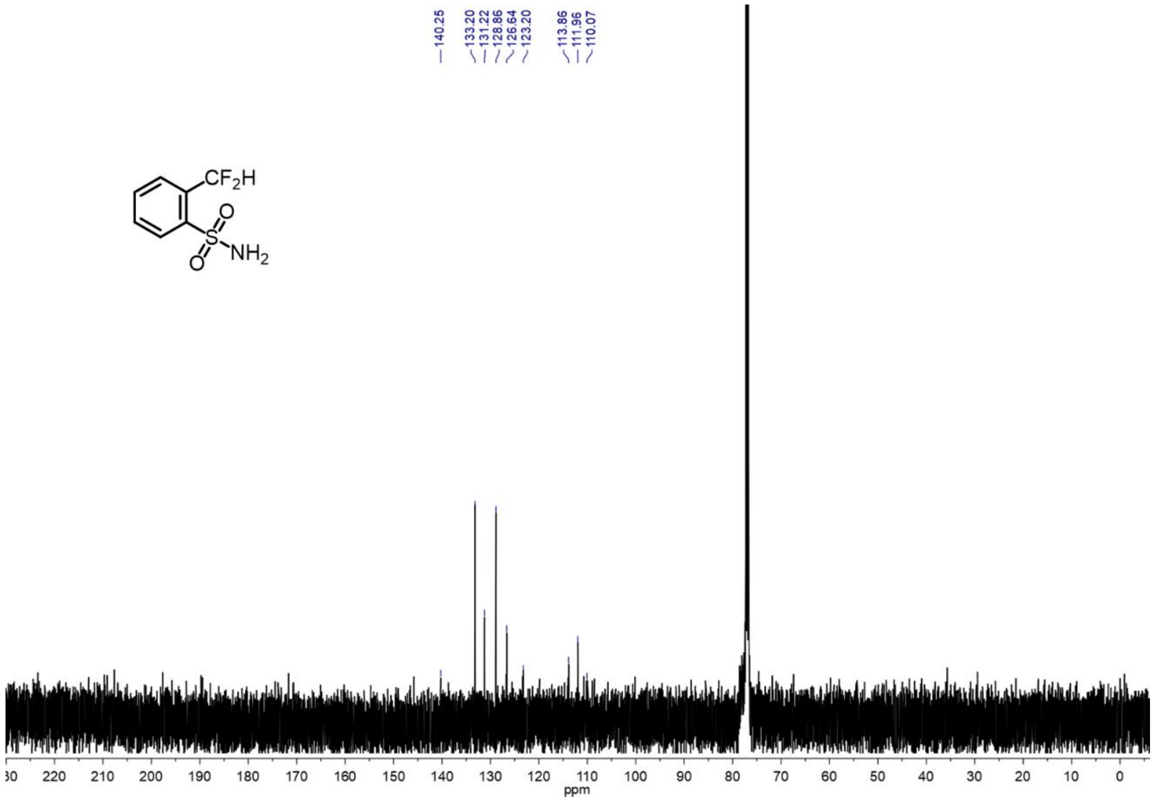
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **3w**



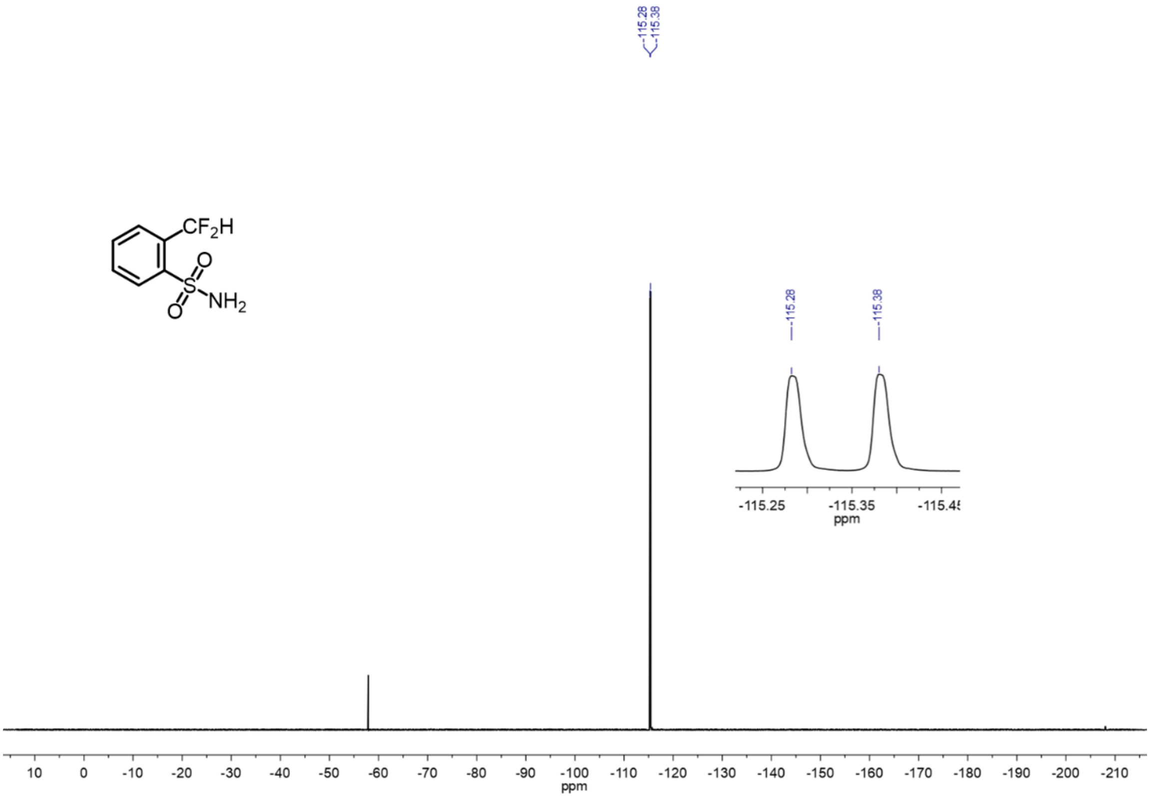
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **3w**



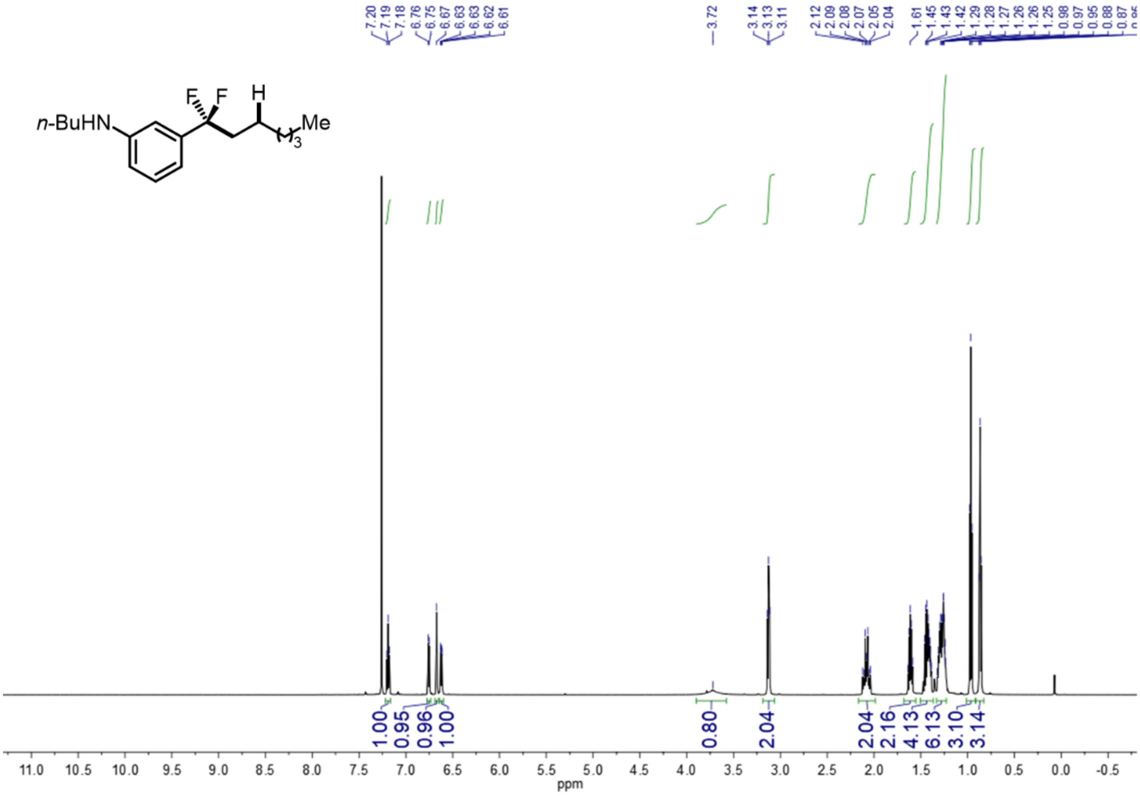
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **3x**



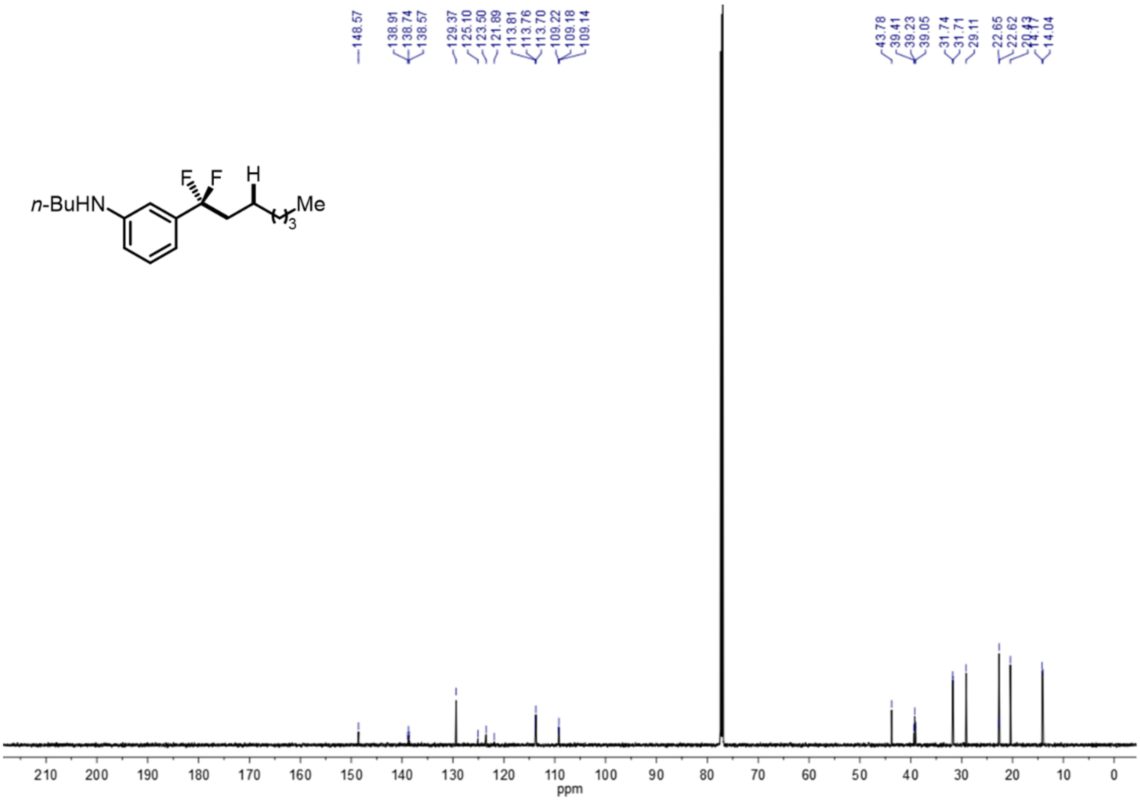
^{13}C NMR spectrum (126 MHz, CDCl$_3$, 23 ºC) of **3x**



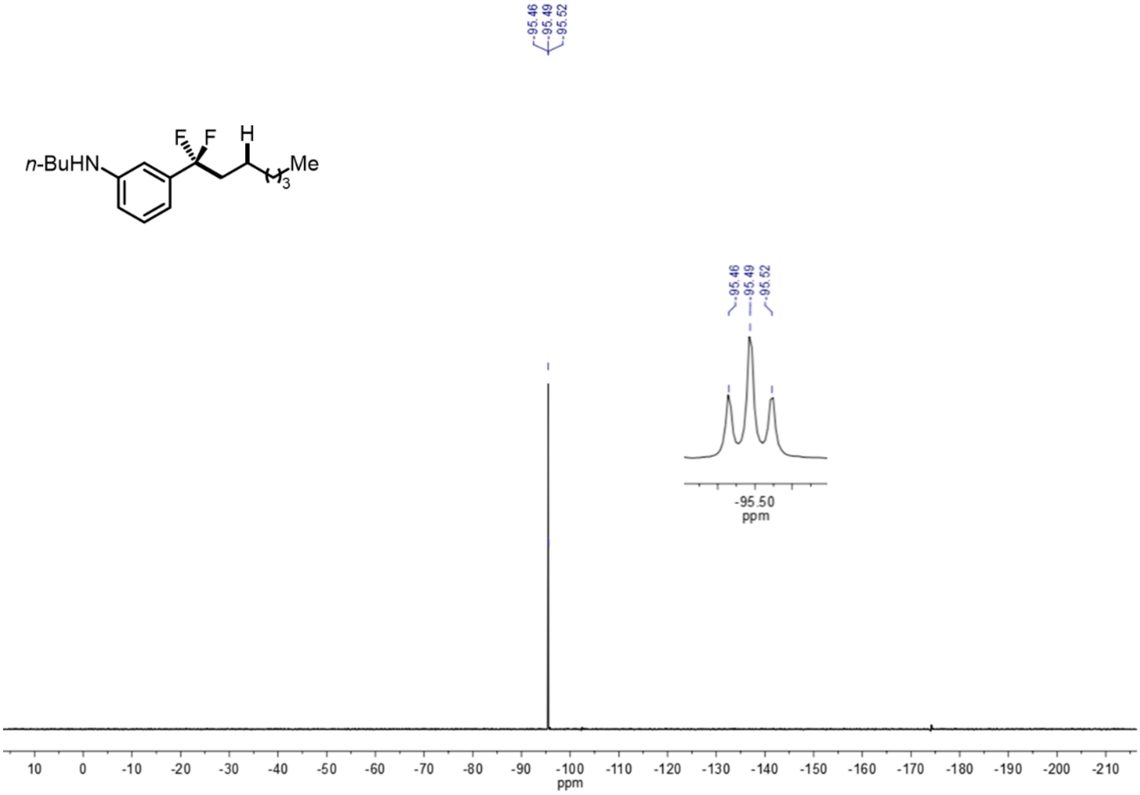
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **3x**



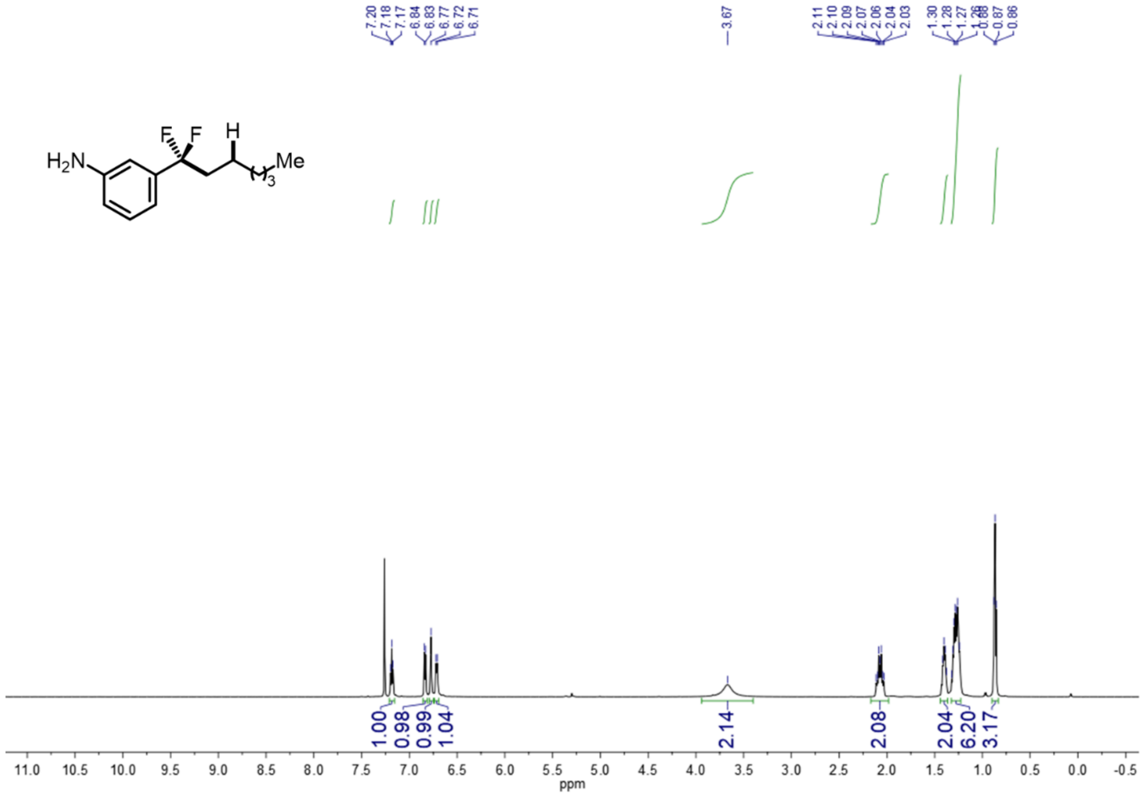
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5a**



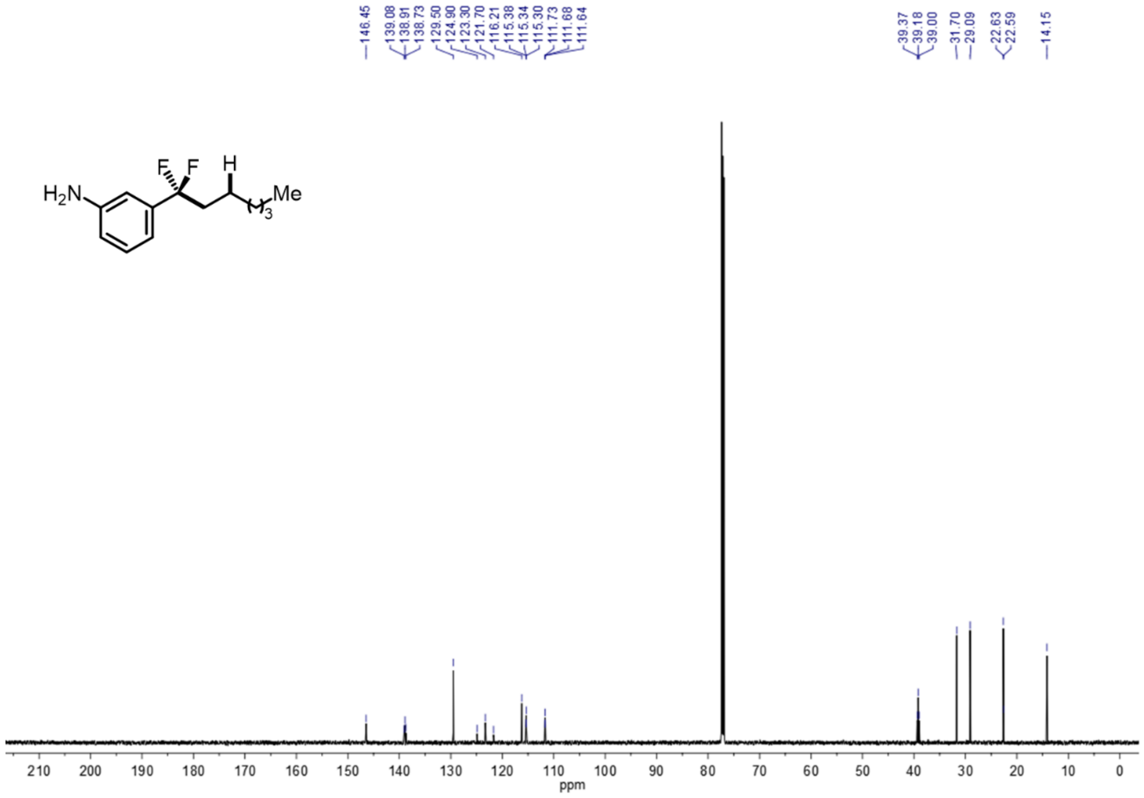
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5a**



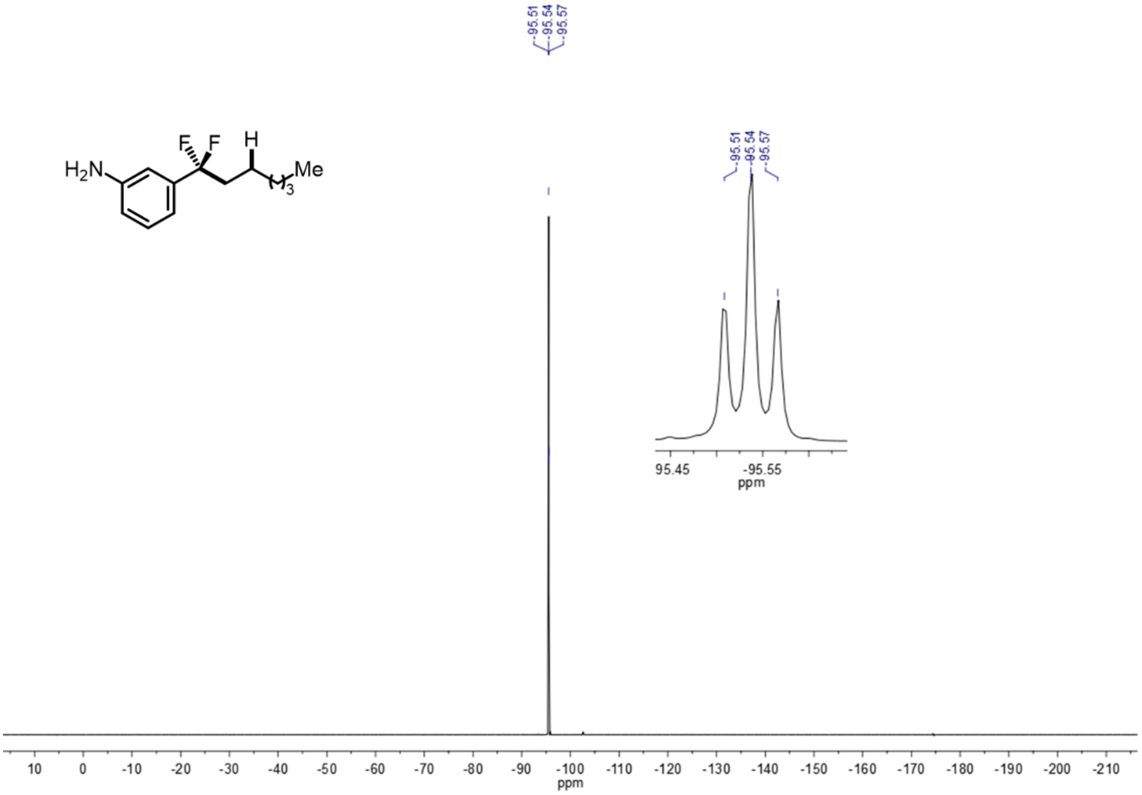
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5a**



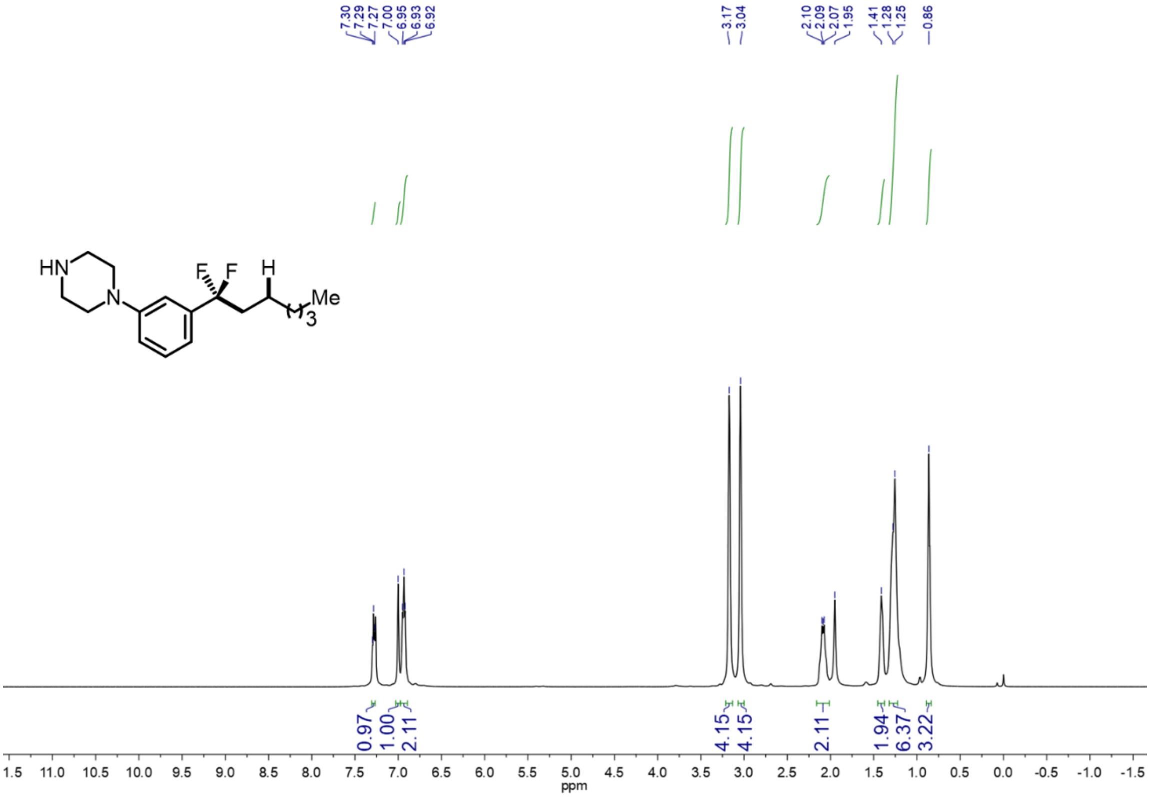
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5b**



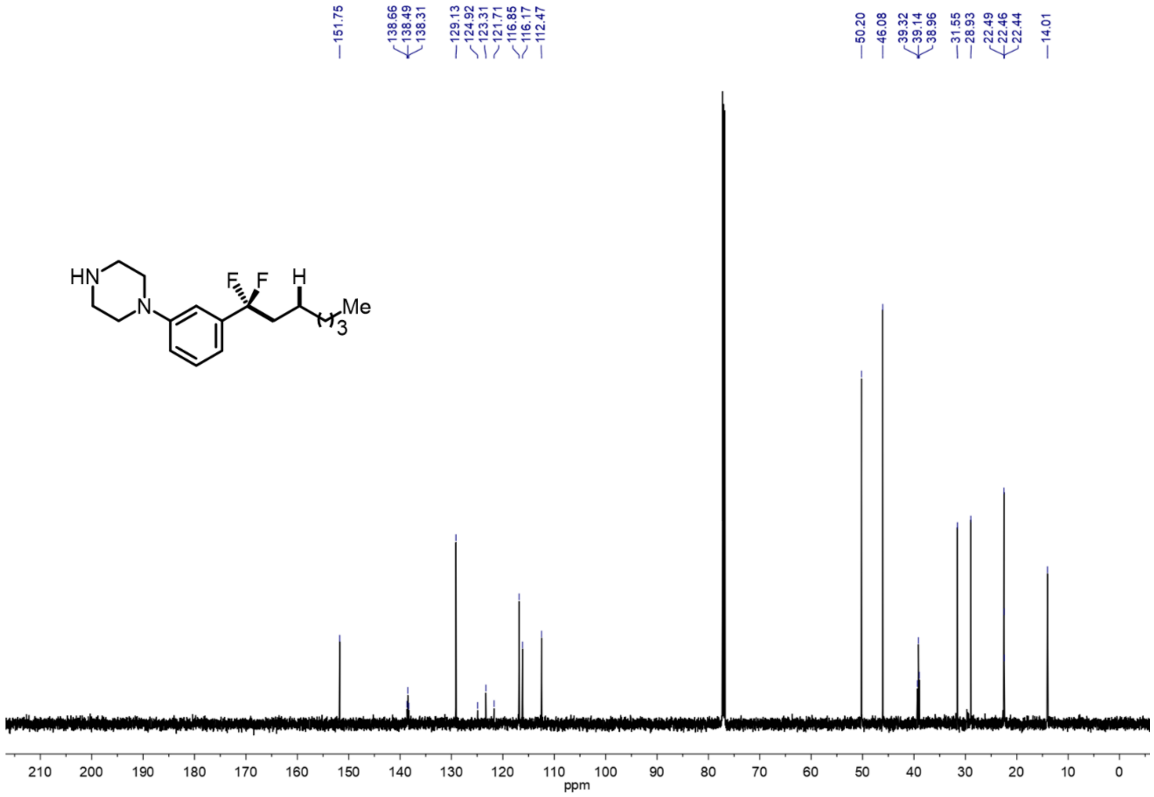
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5b**



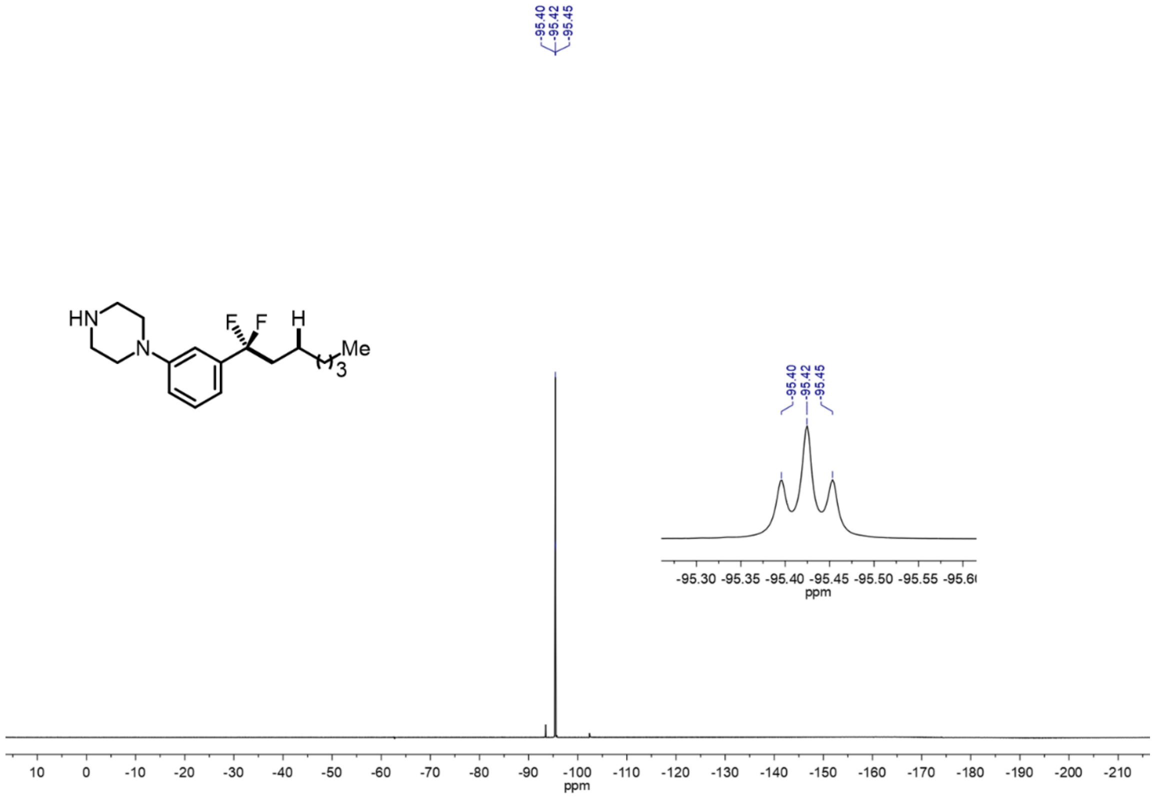
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5b**



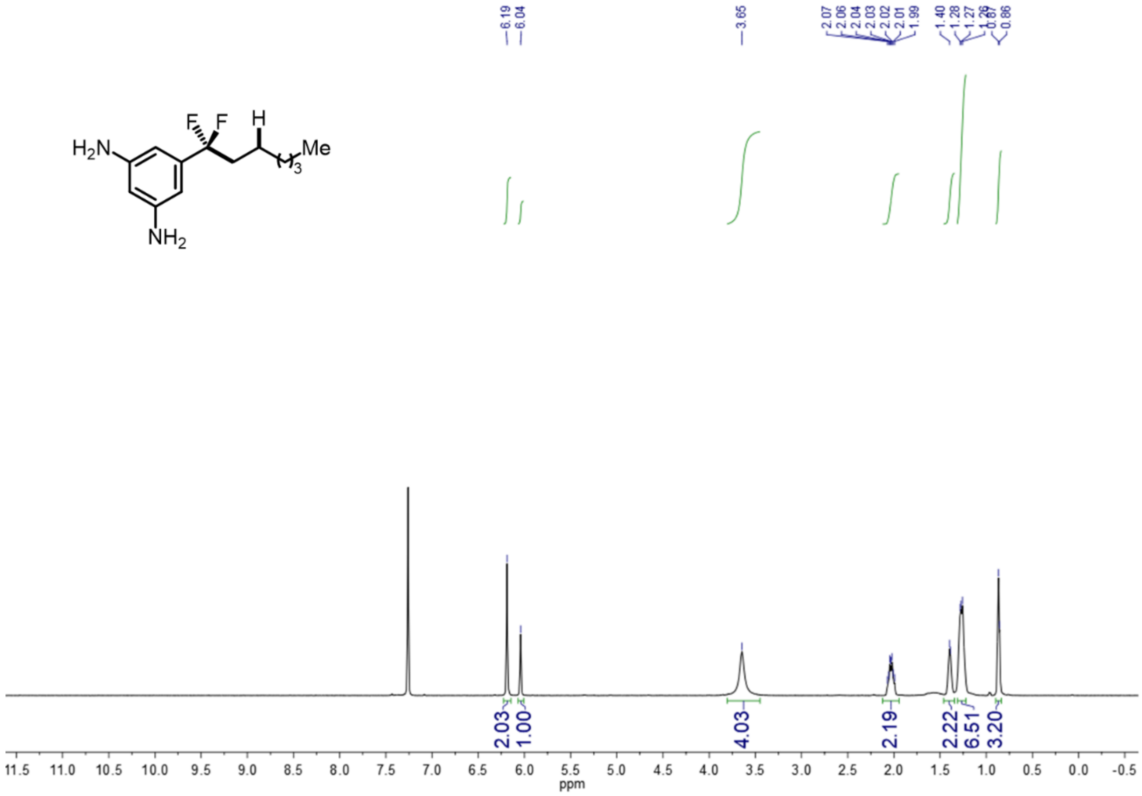
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5c**



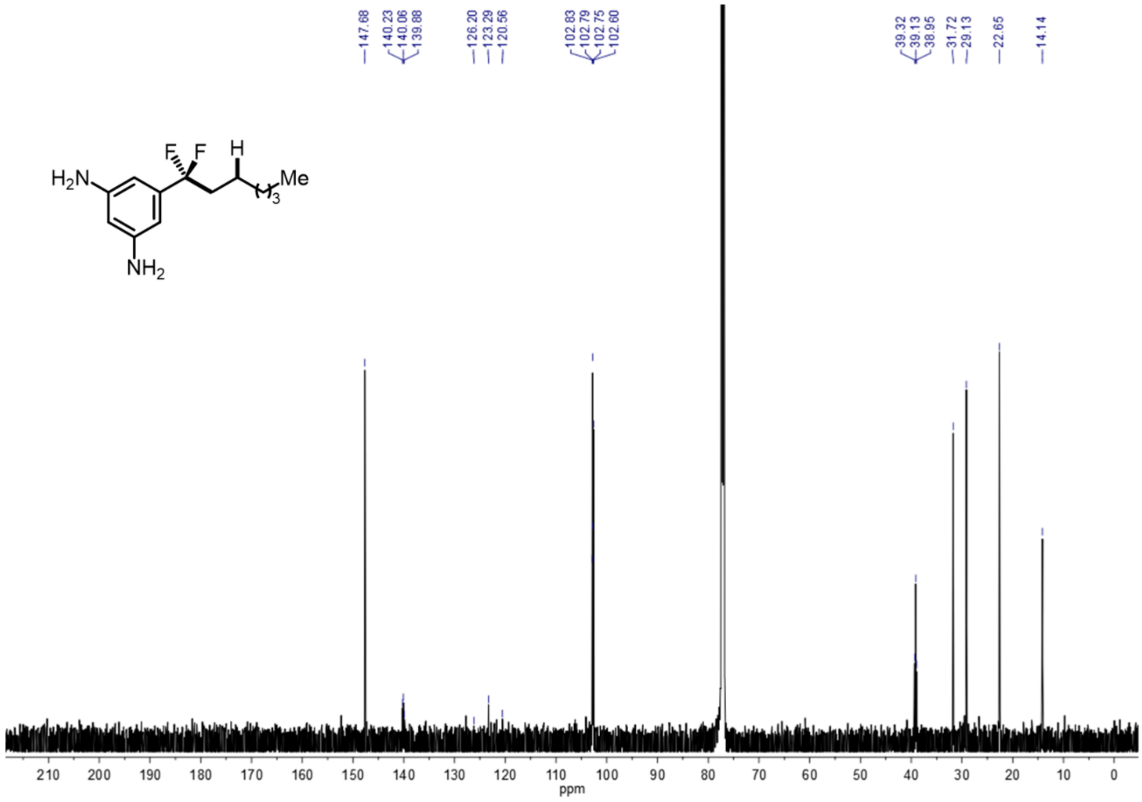
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5c**



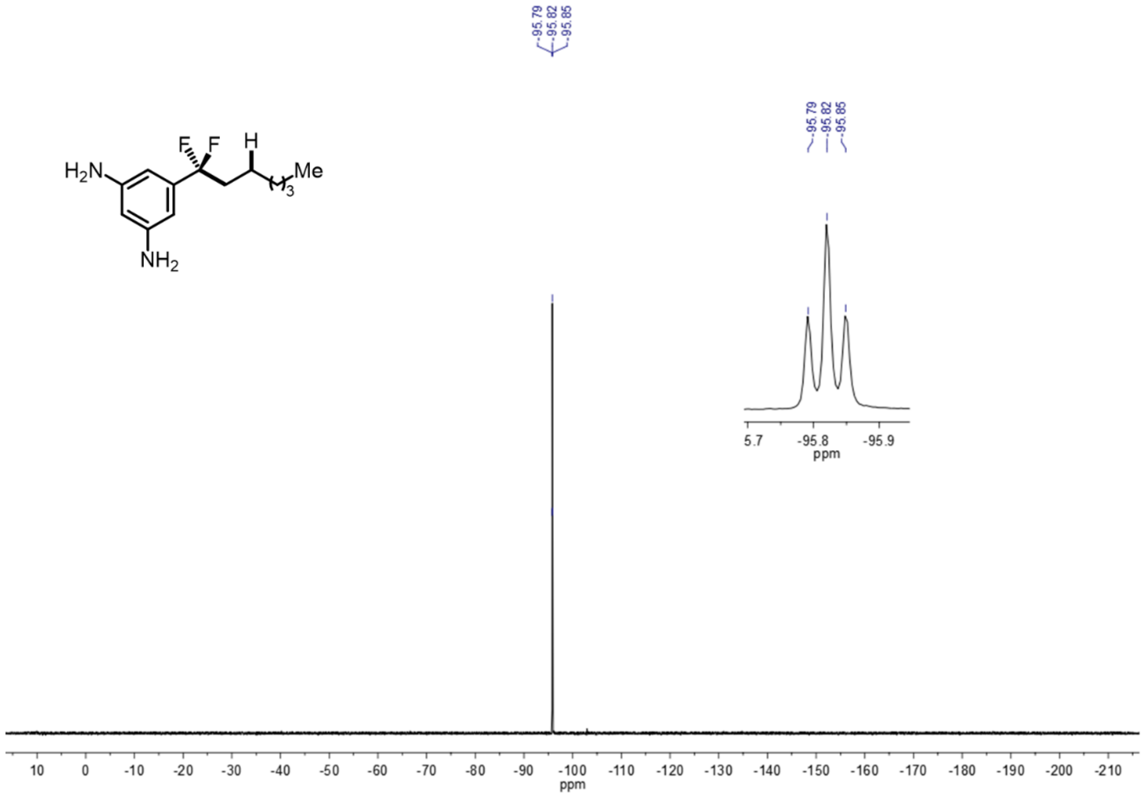
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5c**



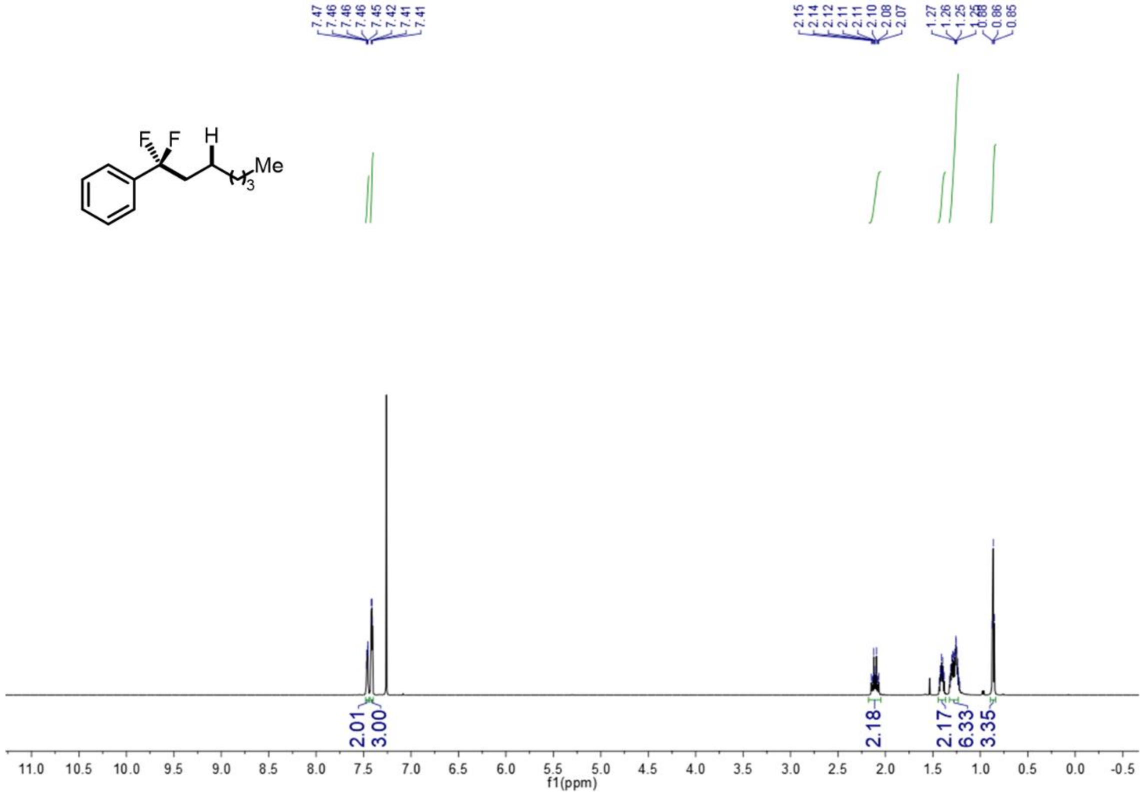
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5d**



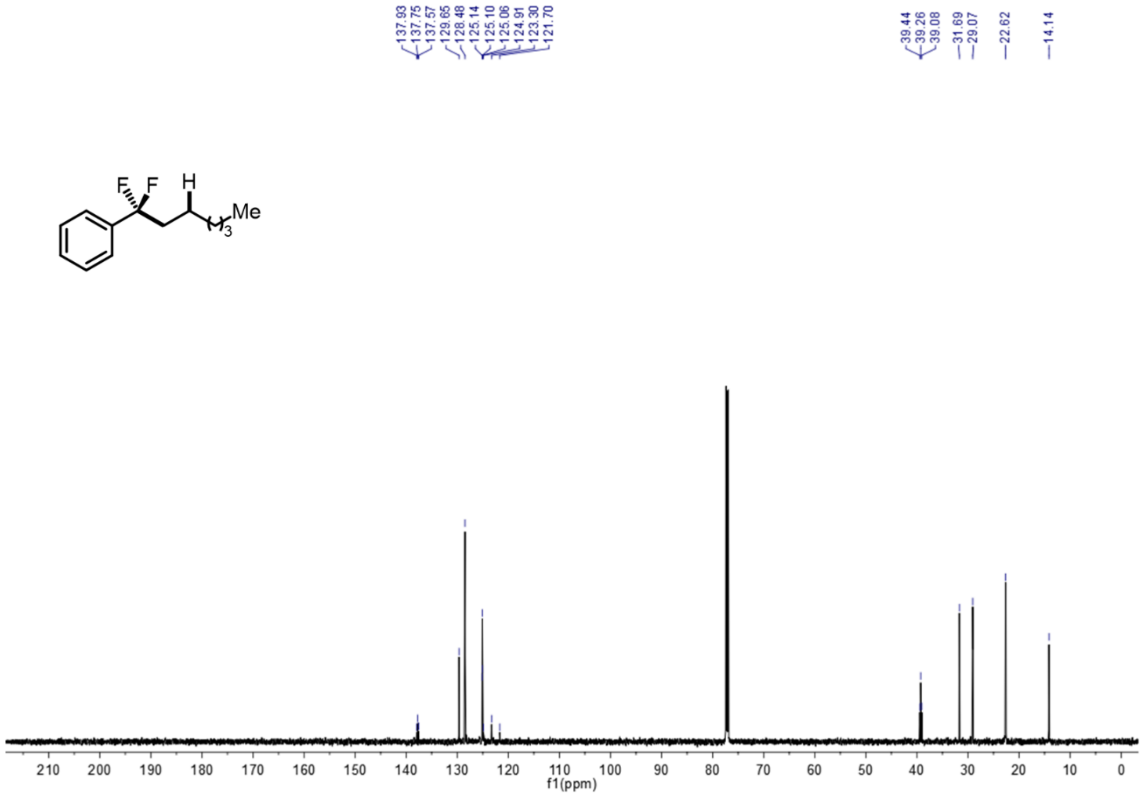
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5d**



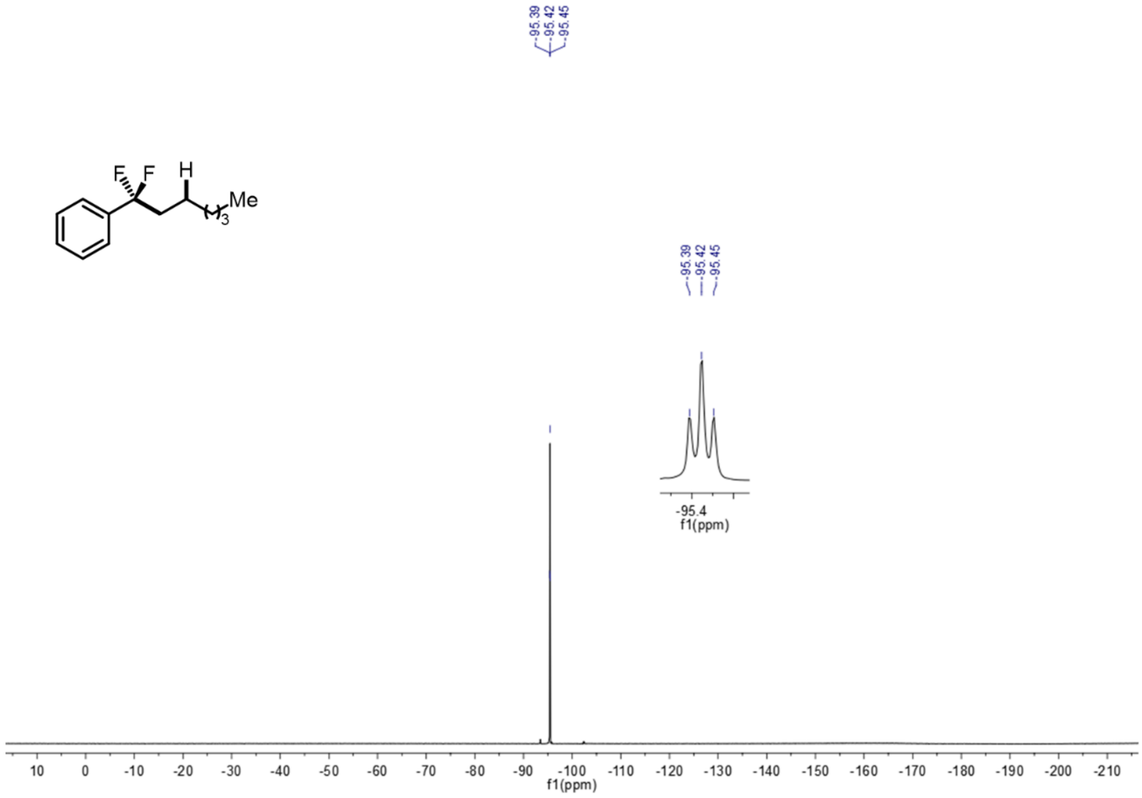
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5d**



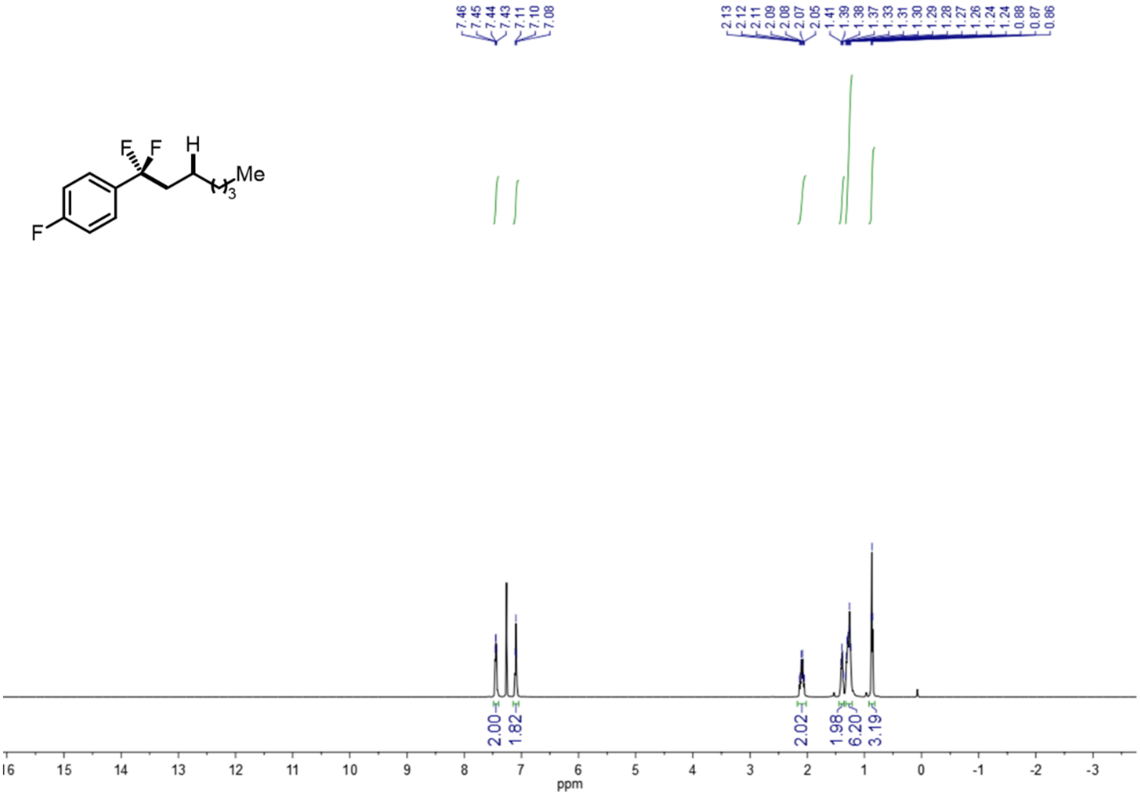
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5e**



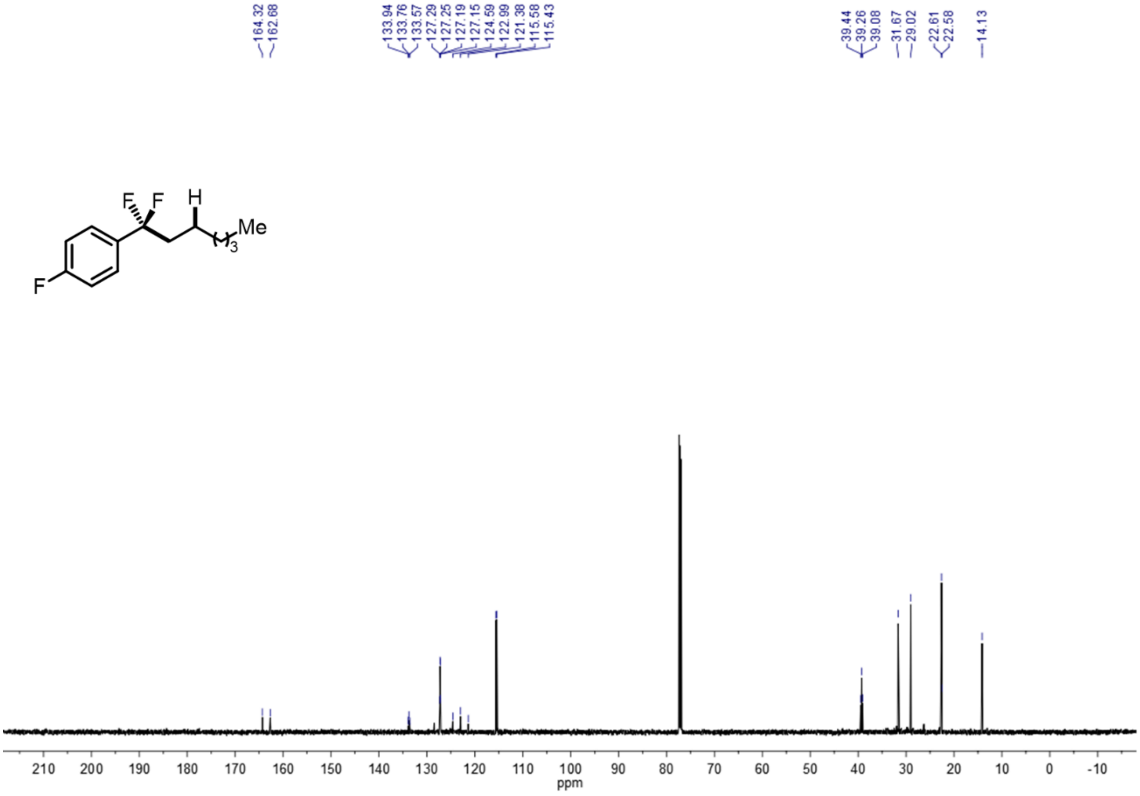
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5e**



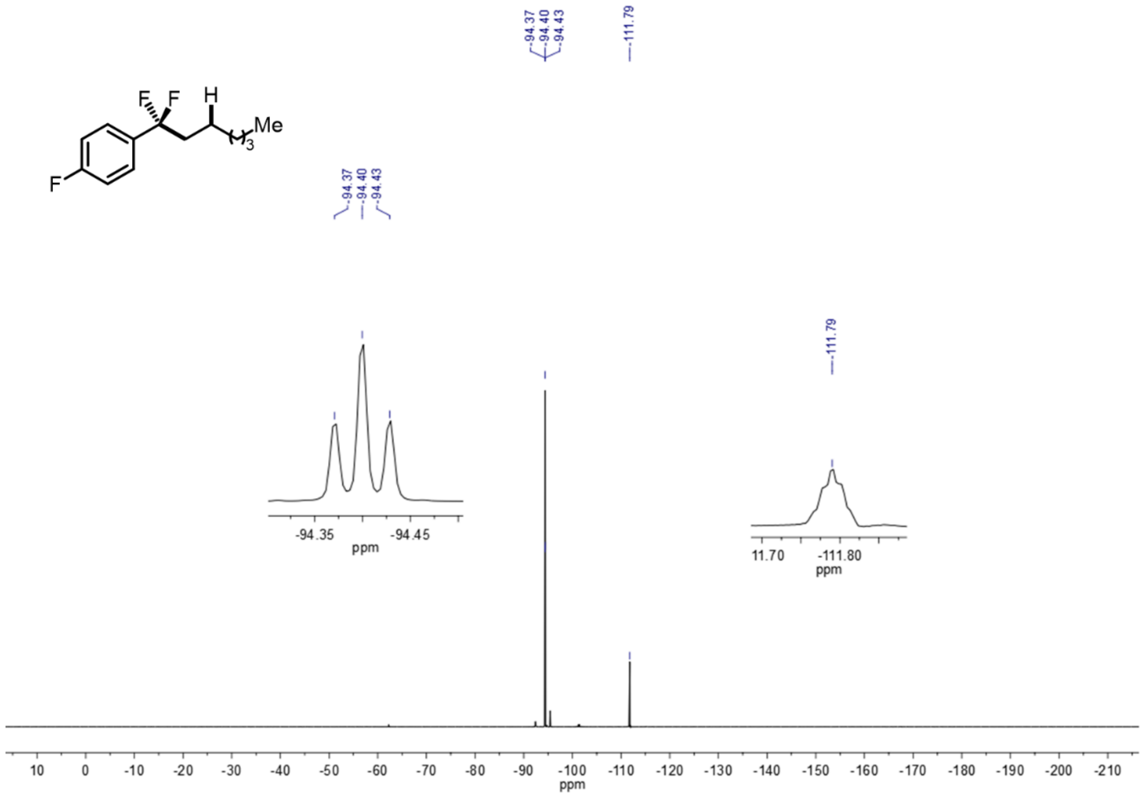
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5e**



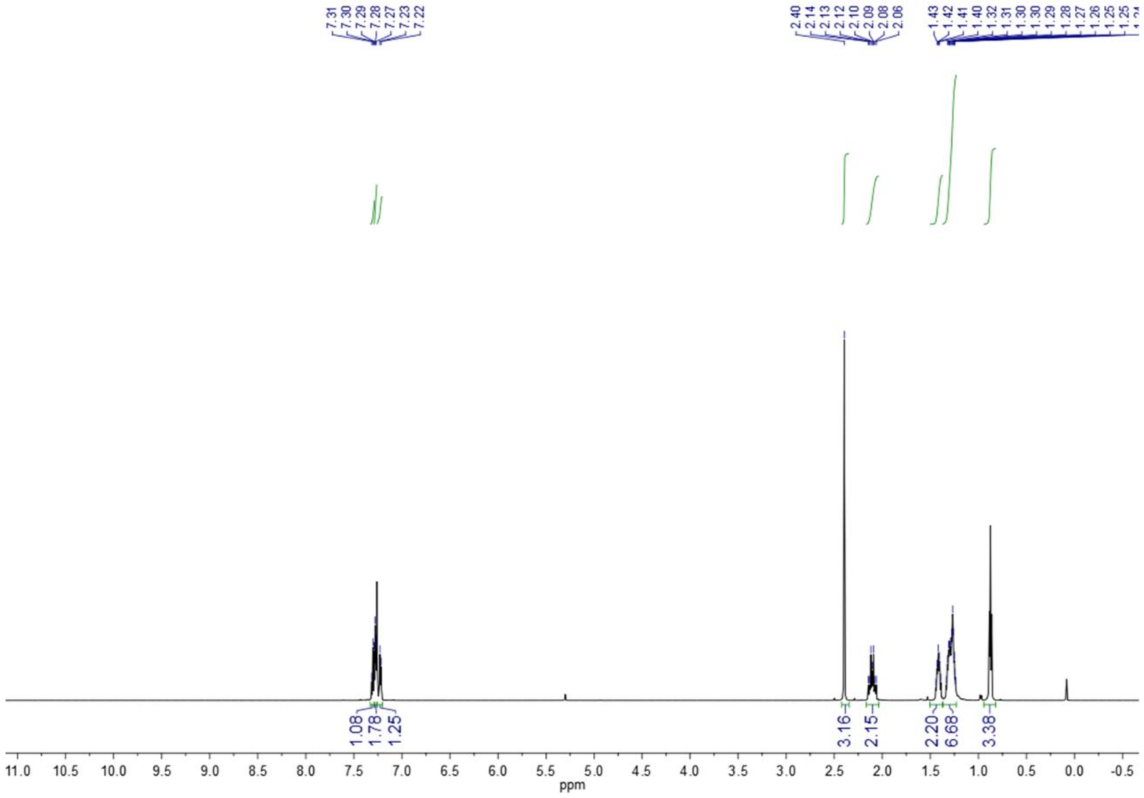
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5f**



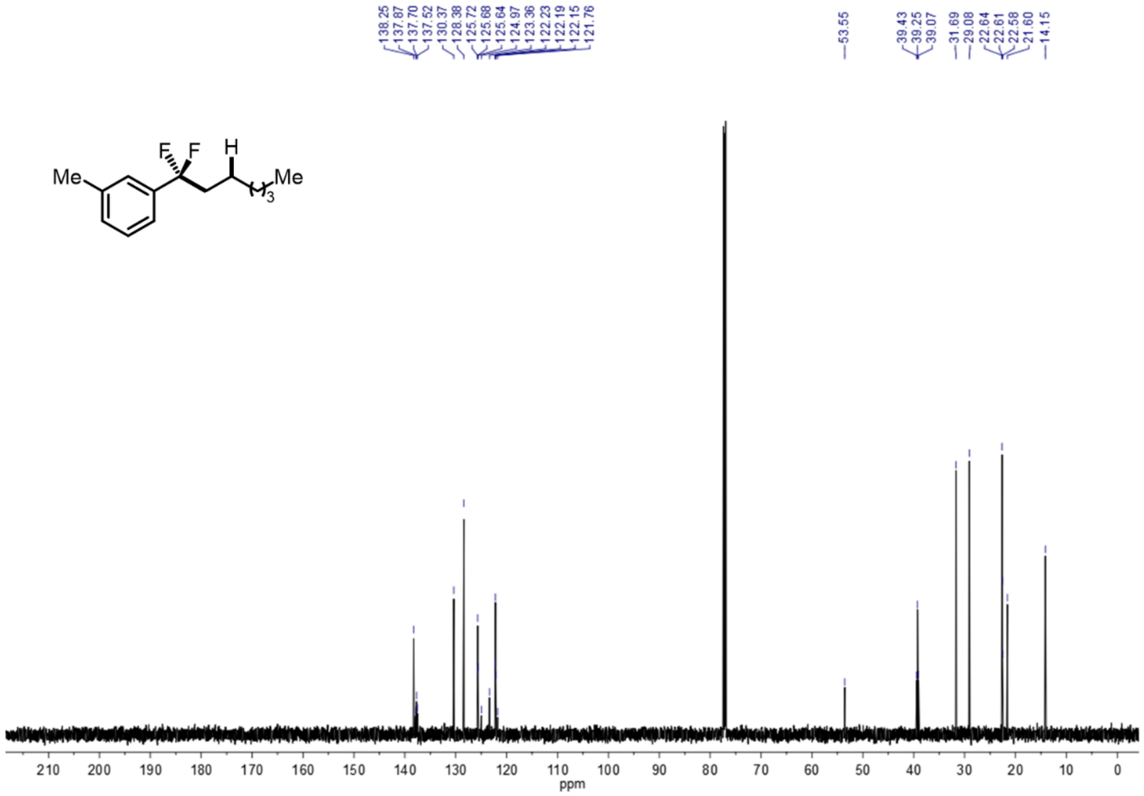
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5f**



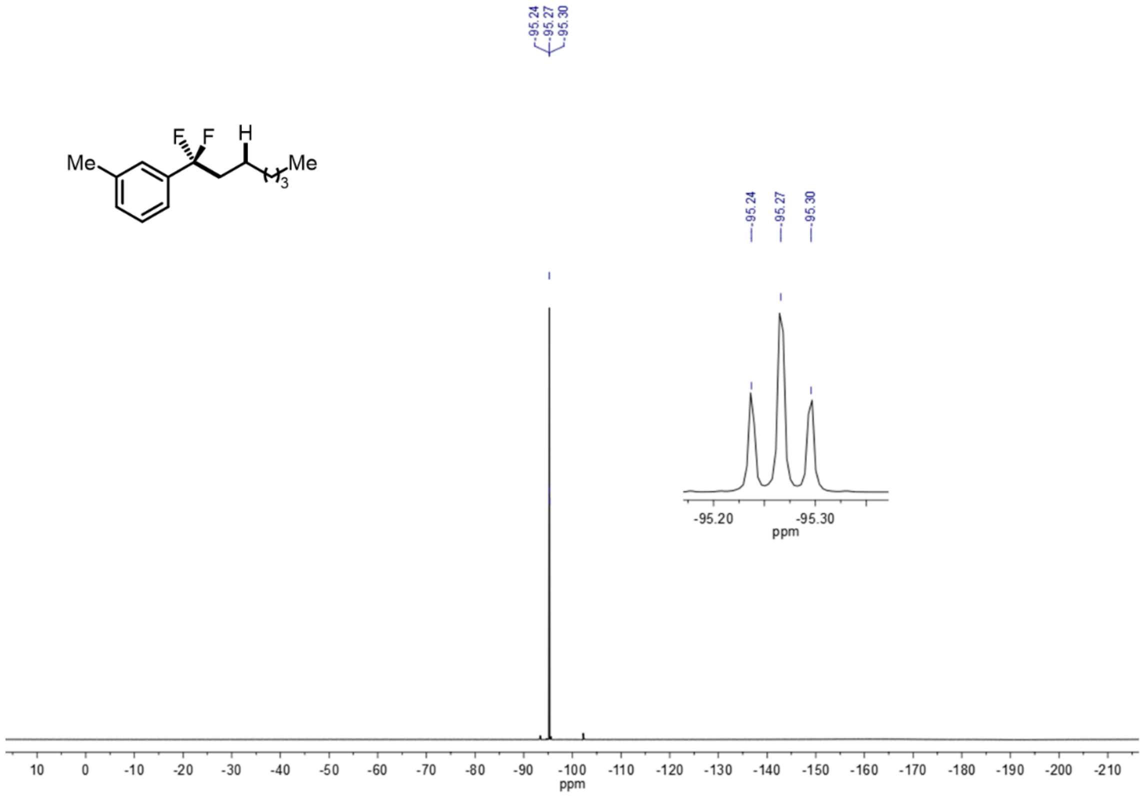
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5f**



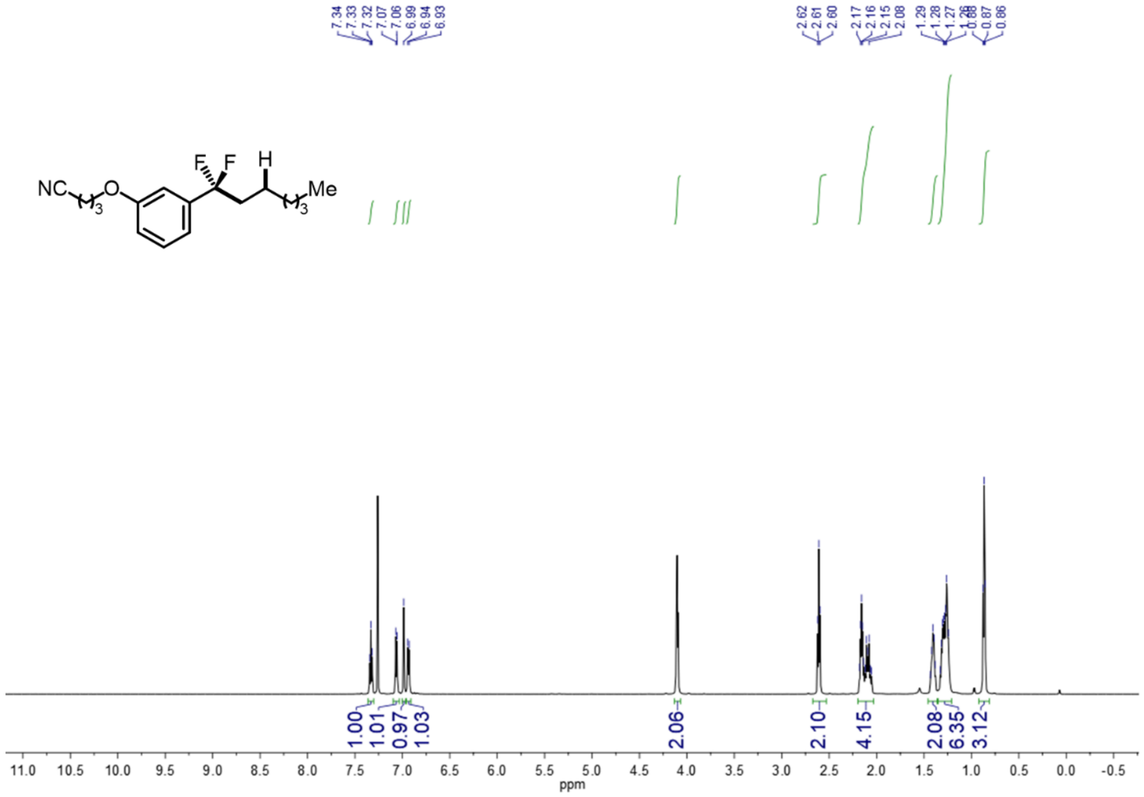
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5g**



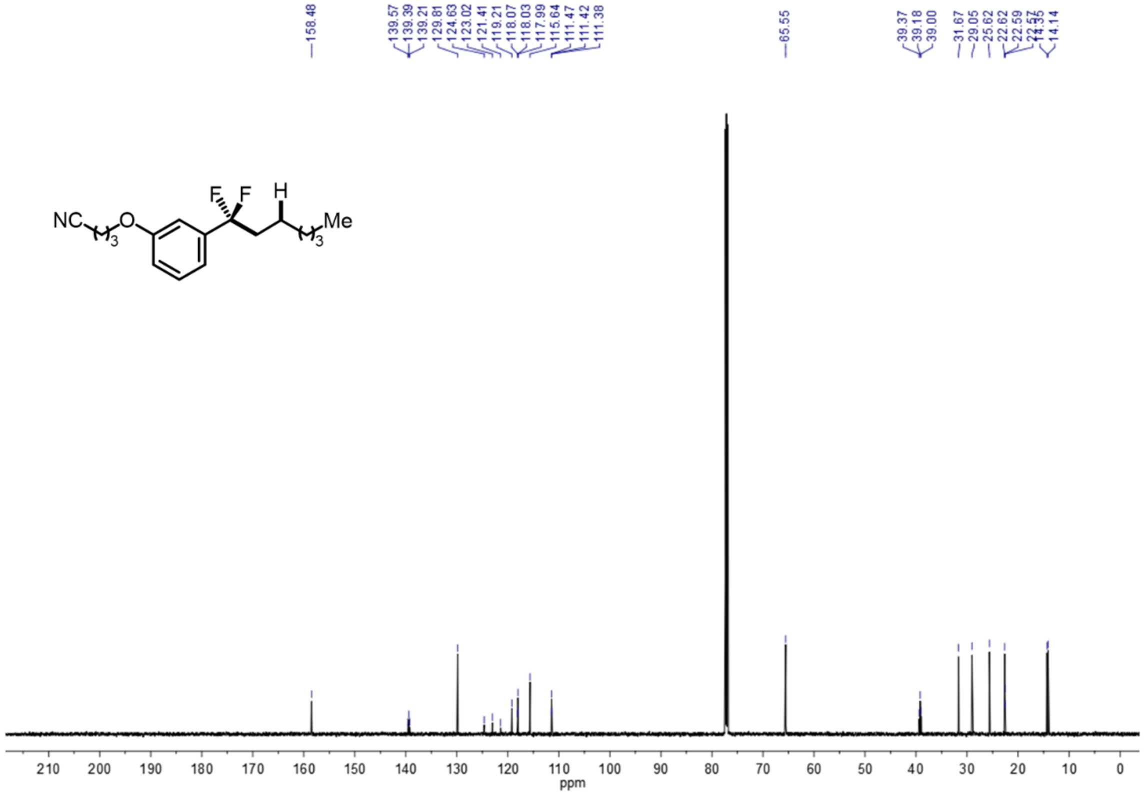
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5g**



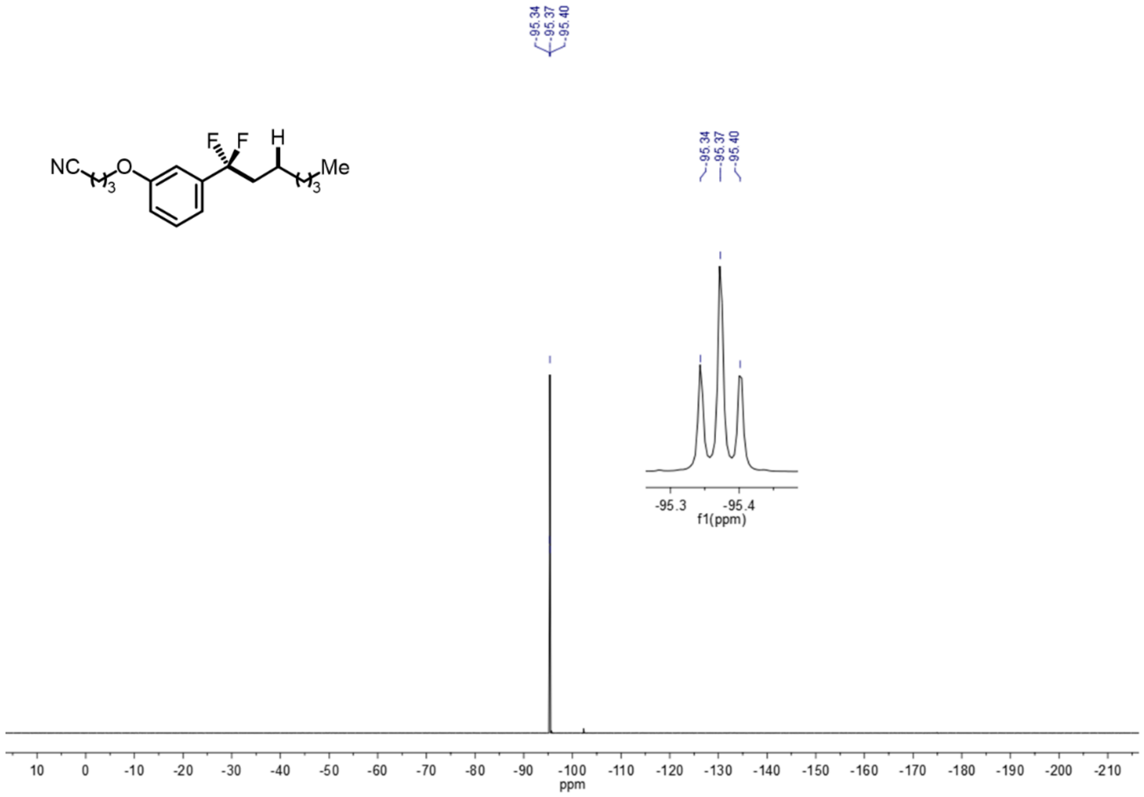
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5g**



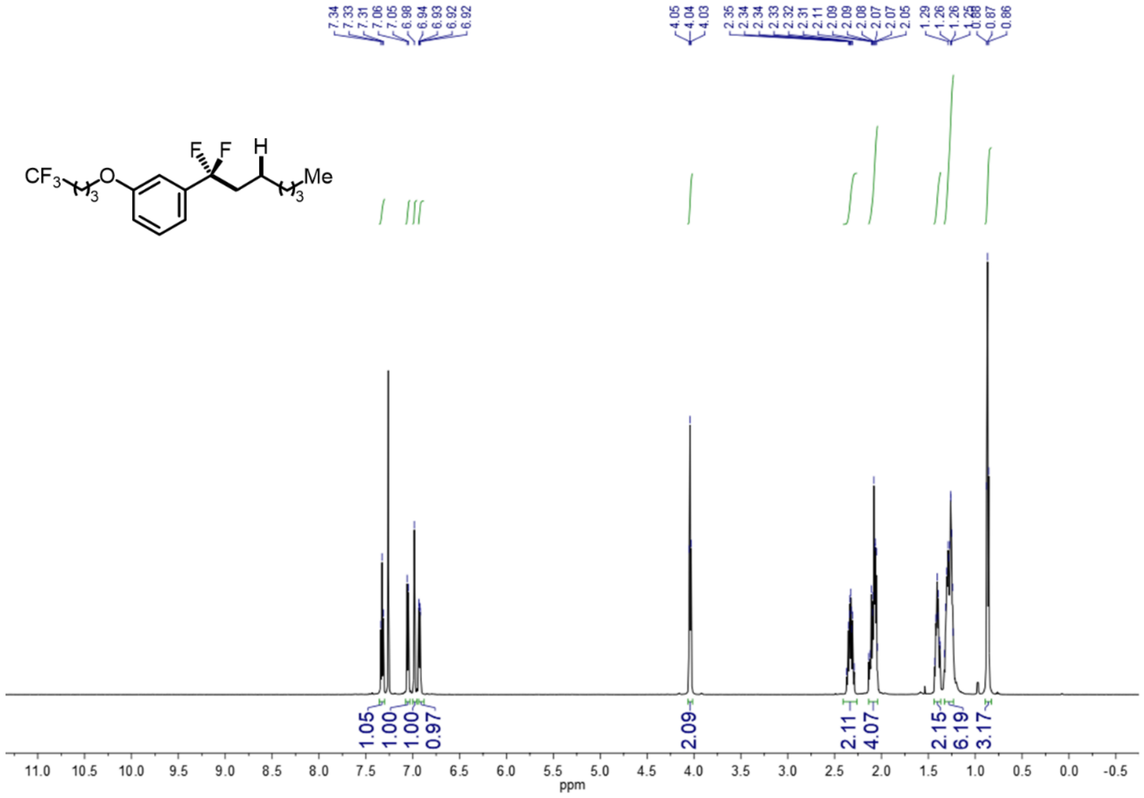
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5h**



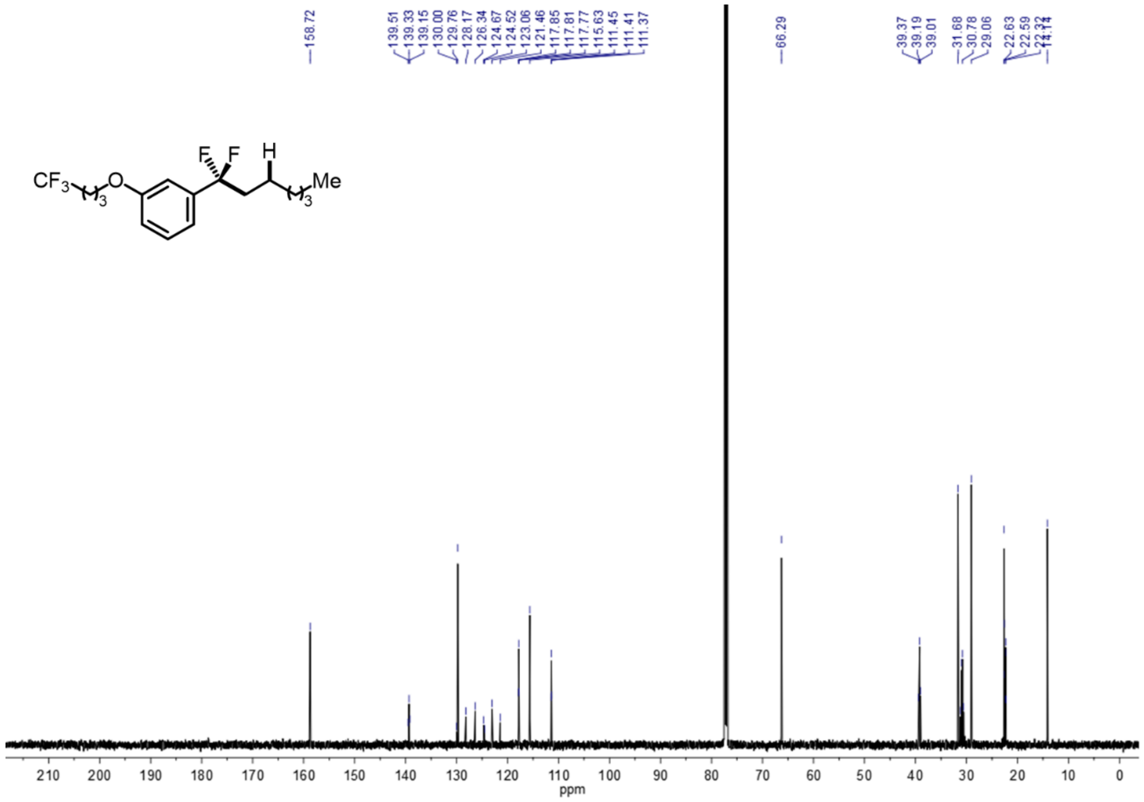
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5h**



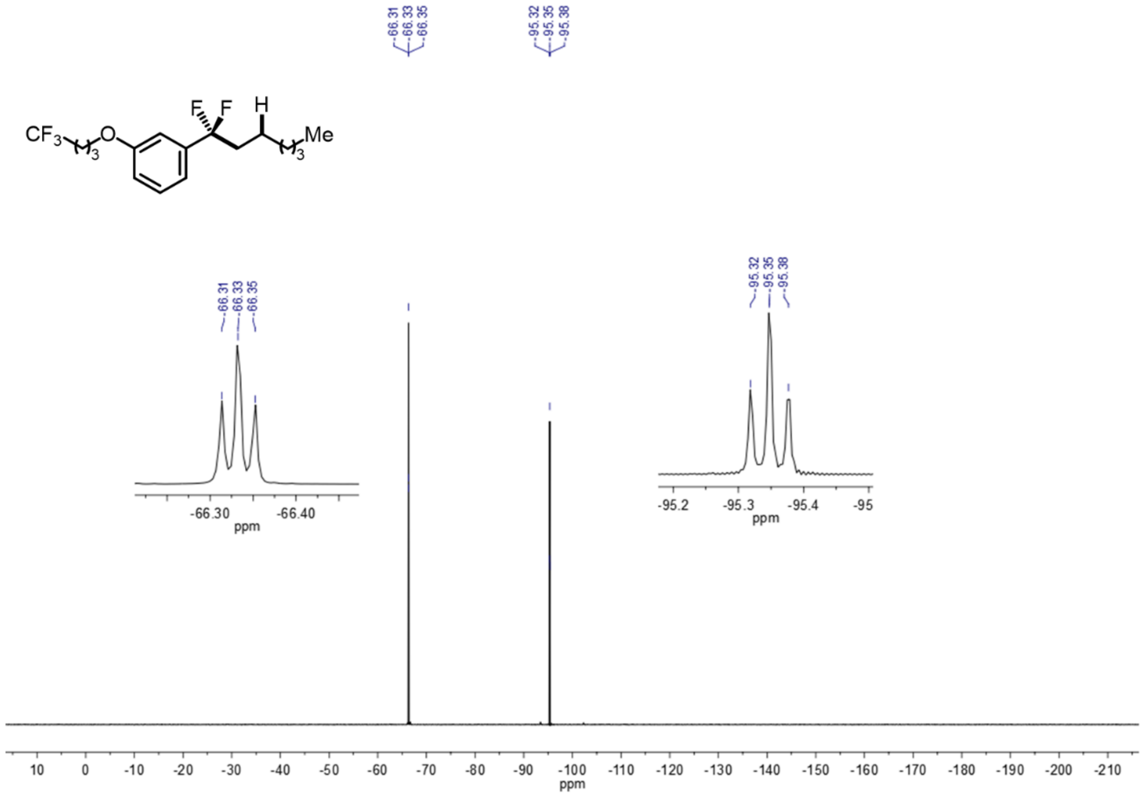
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5h**



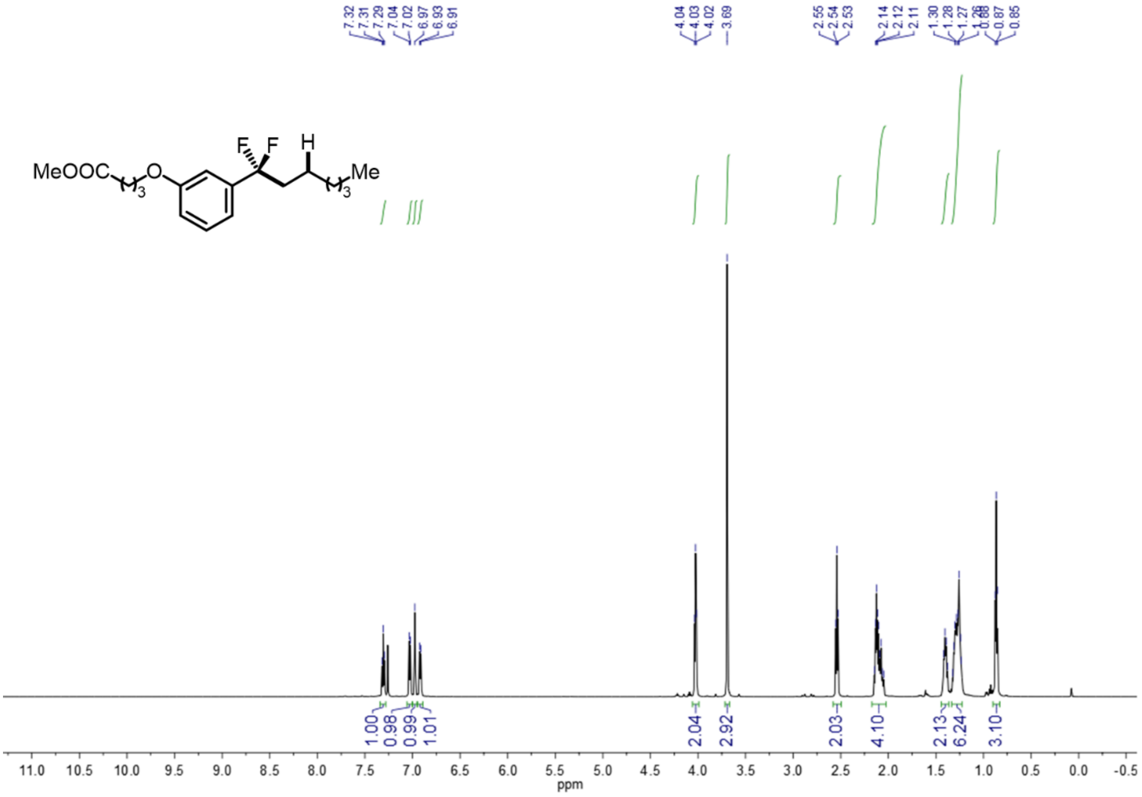
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5i**



^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5i**



^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5i**



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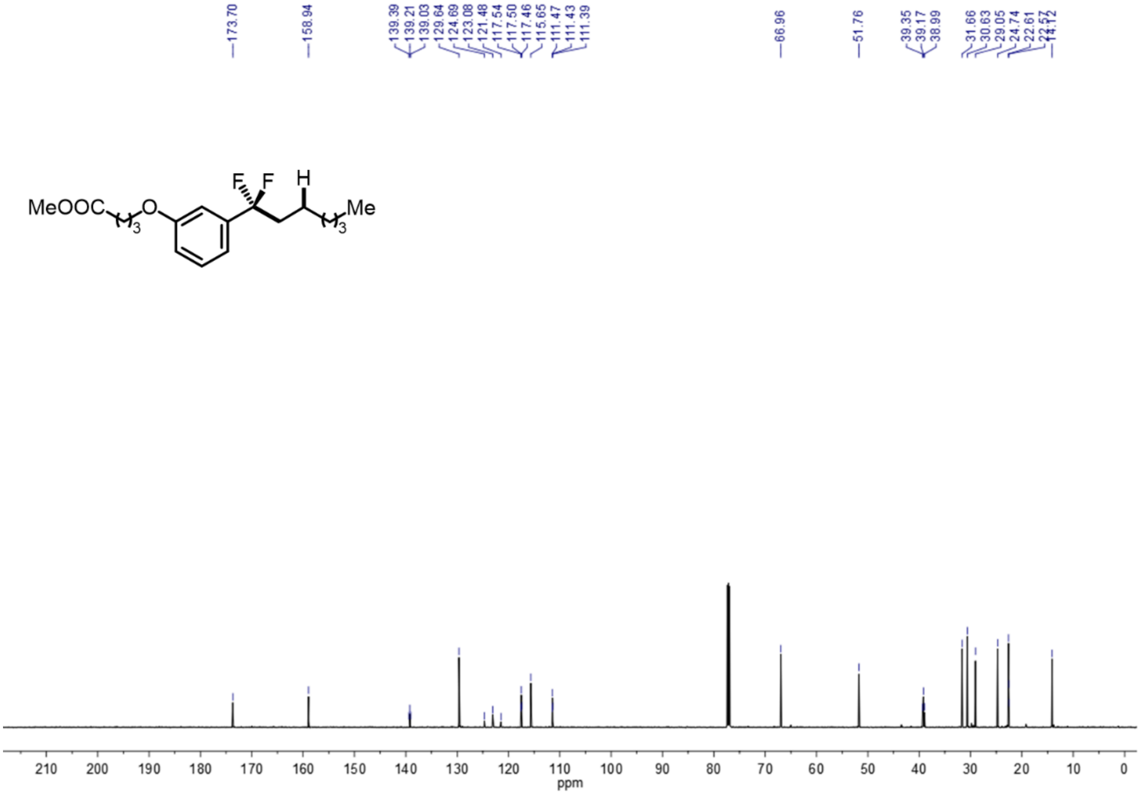
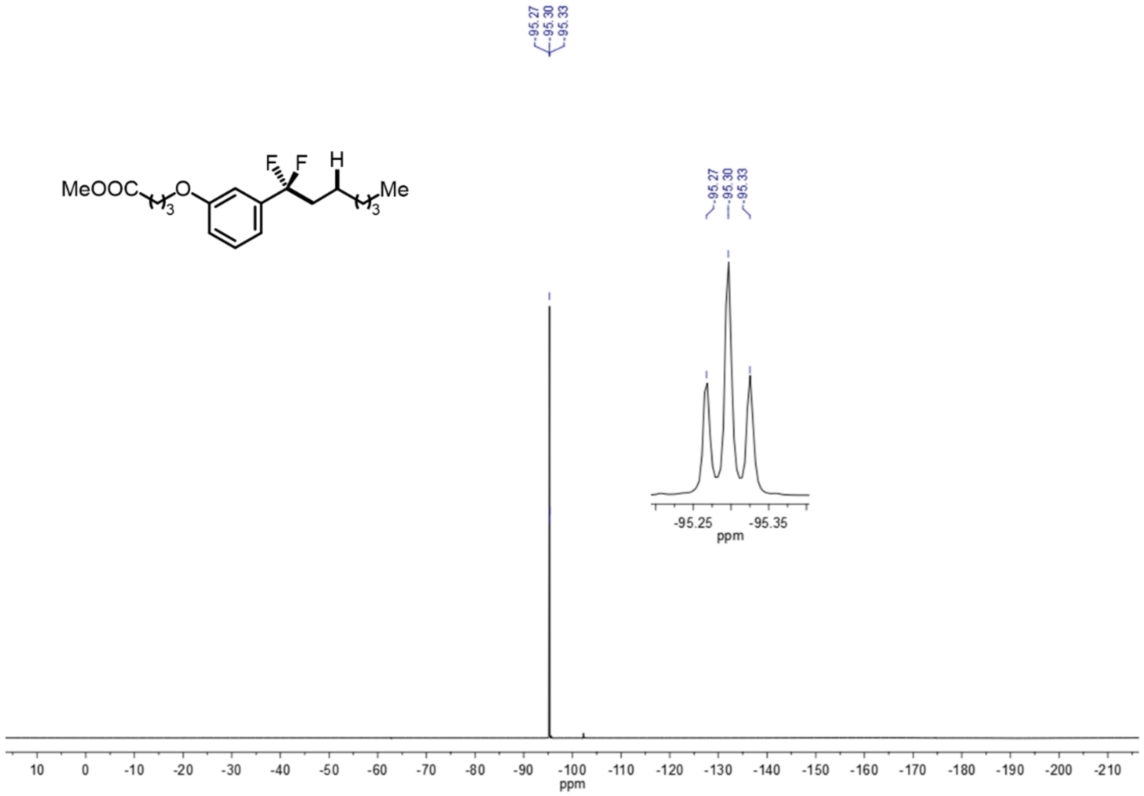
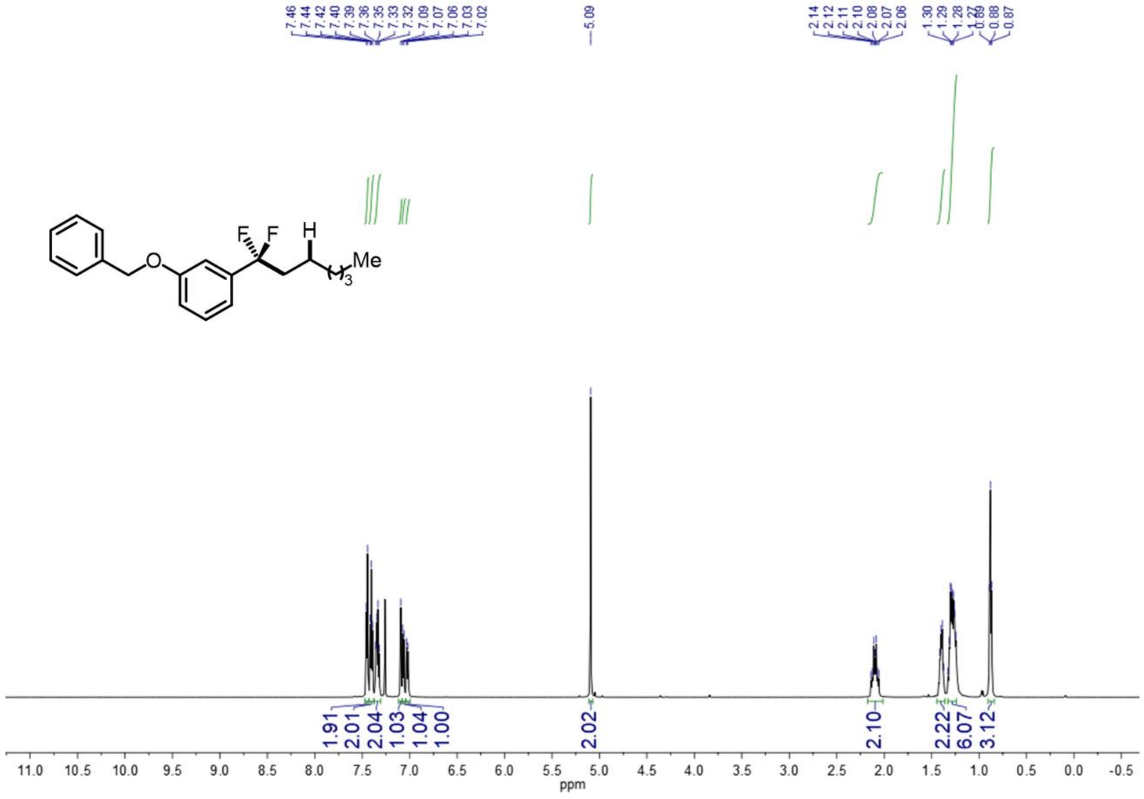


^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5j**



^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5j**



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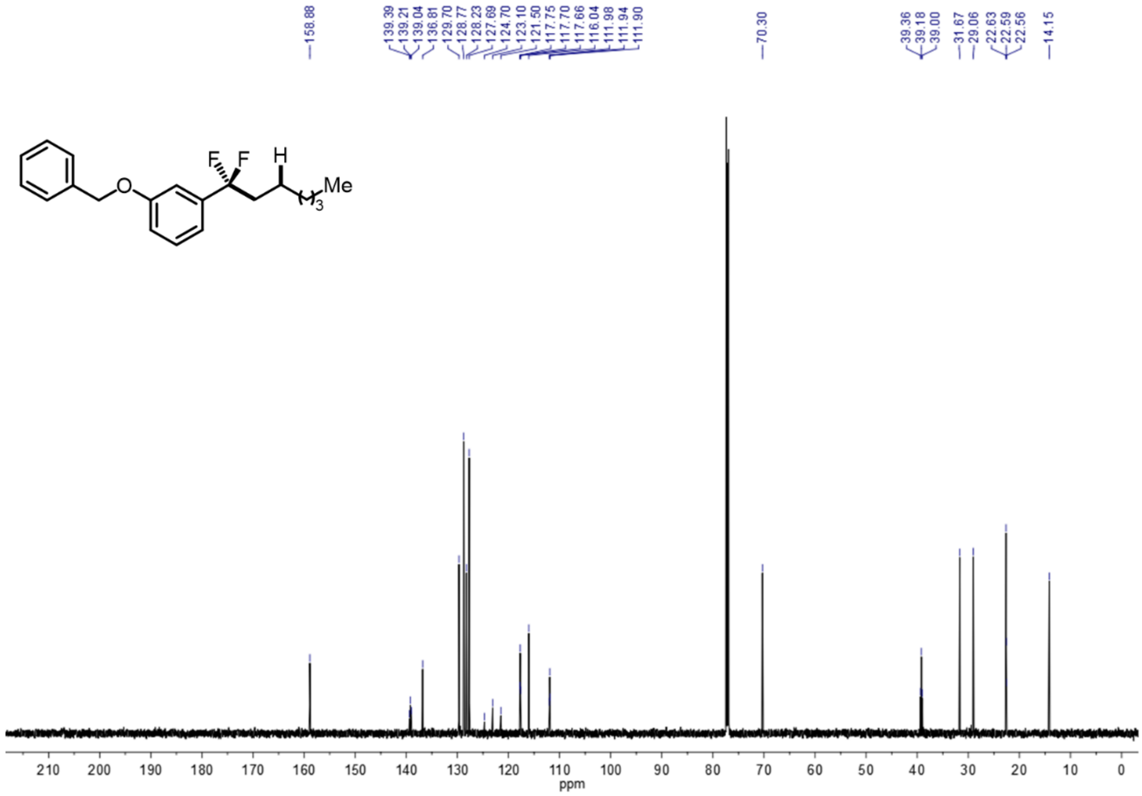
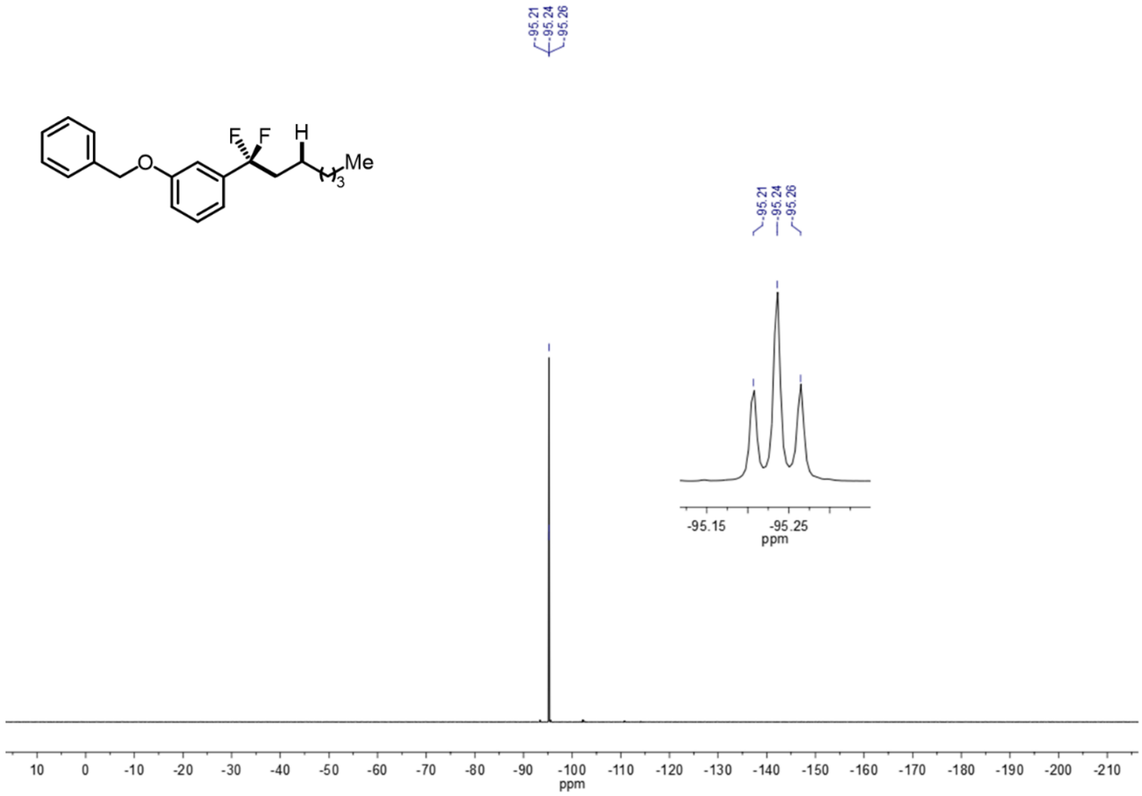
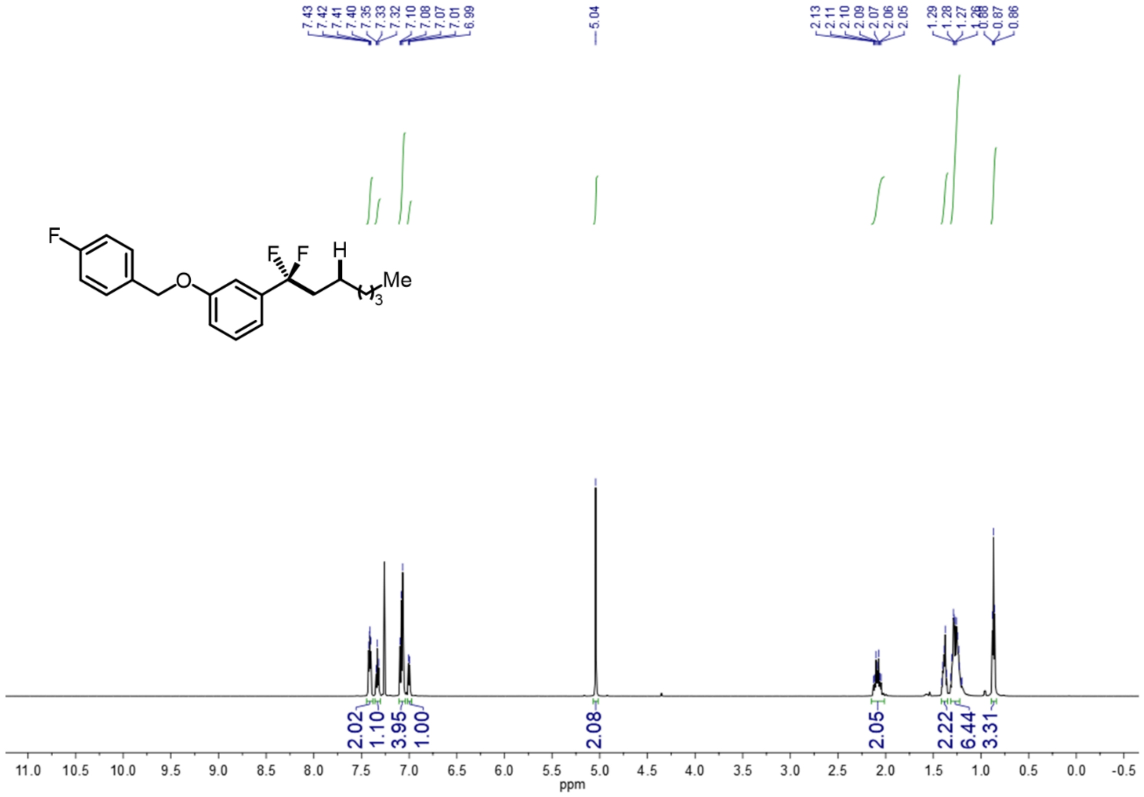


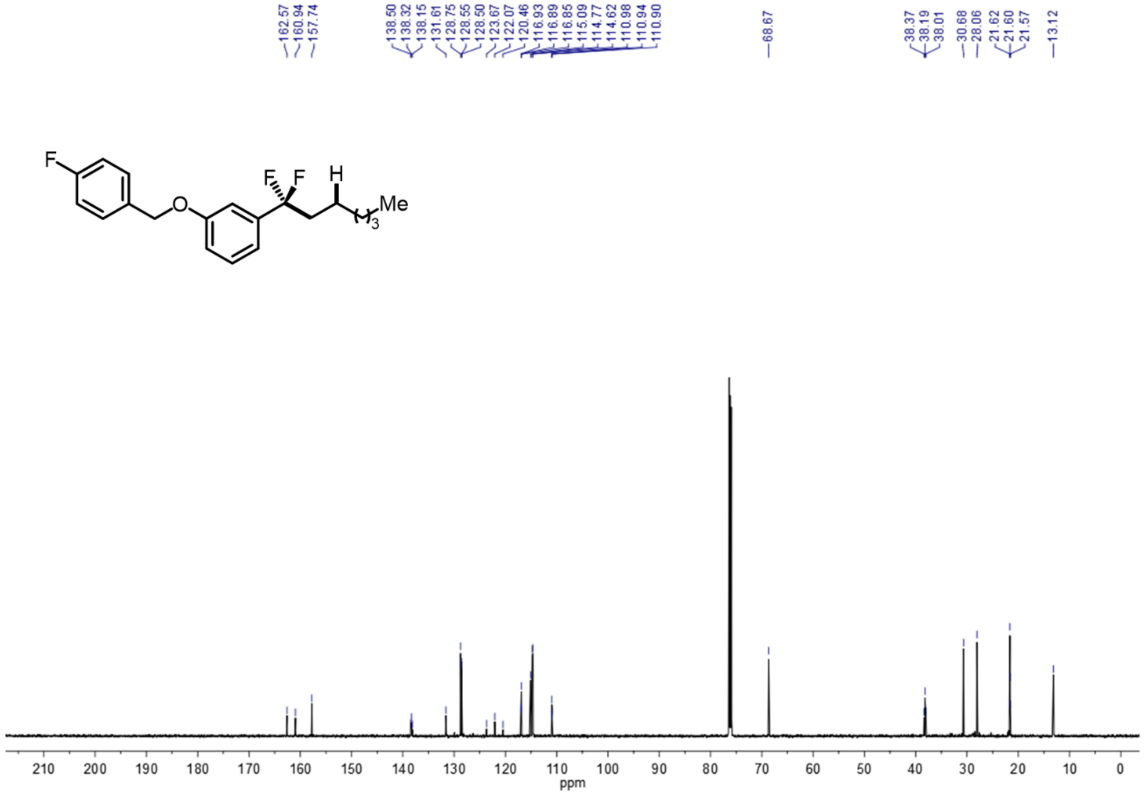
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5k**



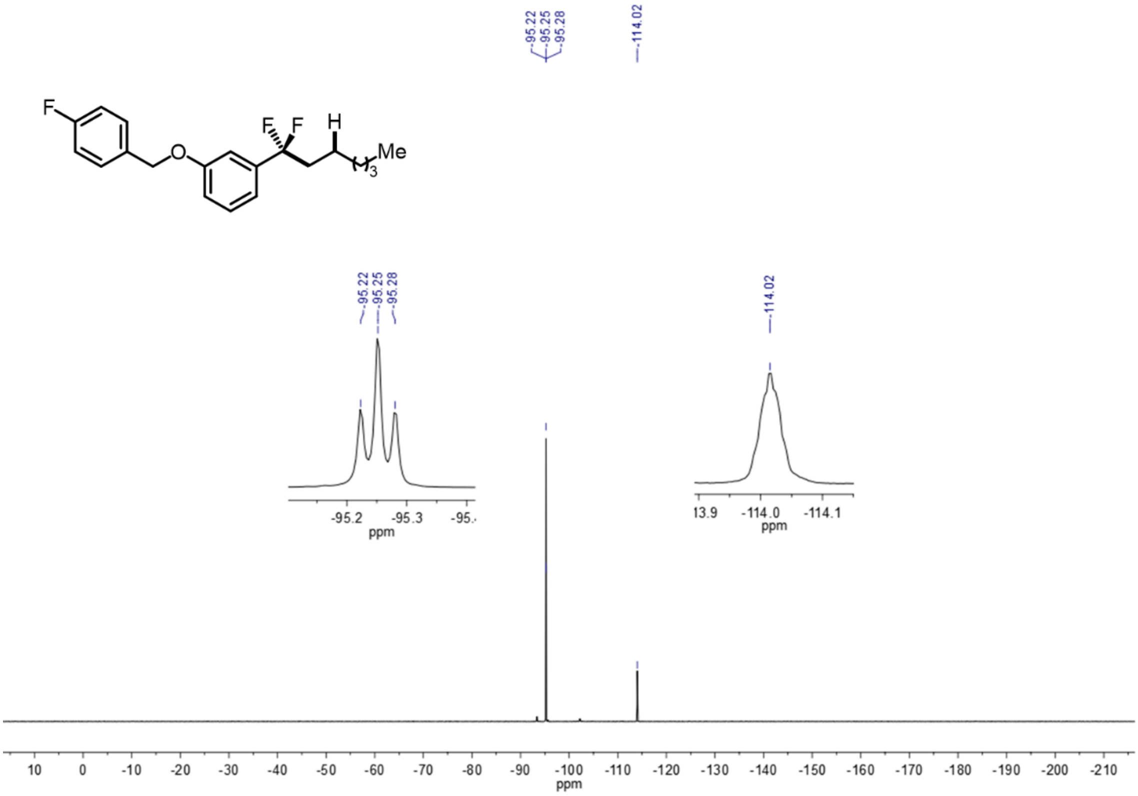
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5k**



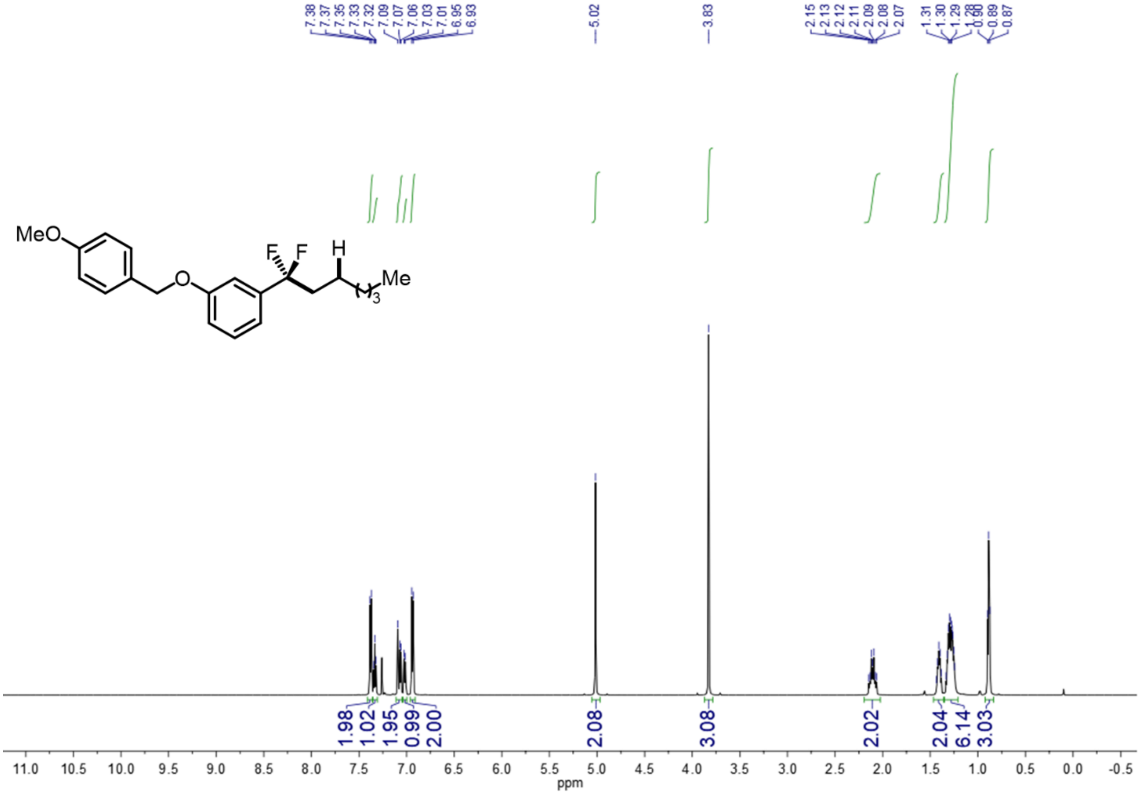
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5l**



^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5l**



^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5l**



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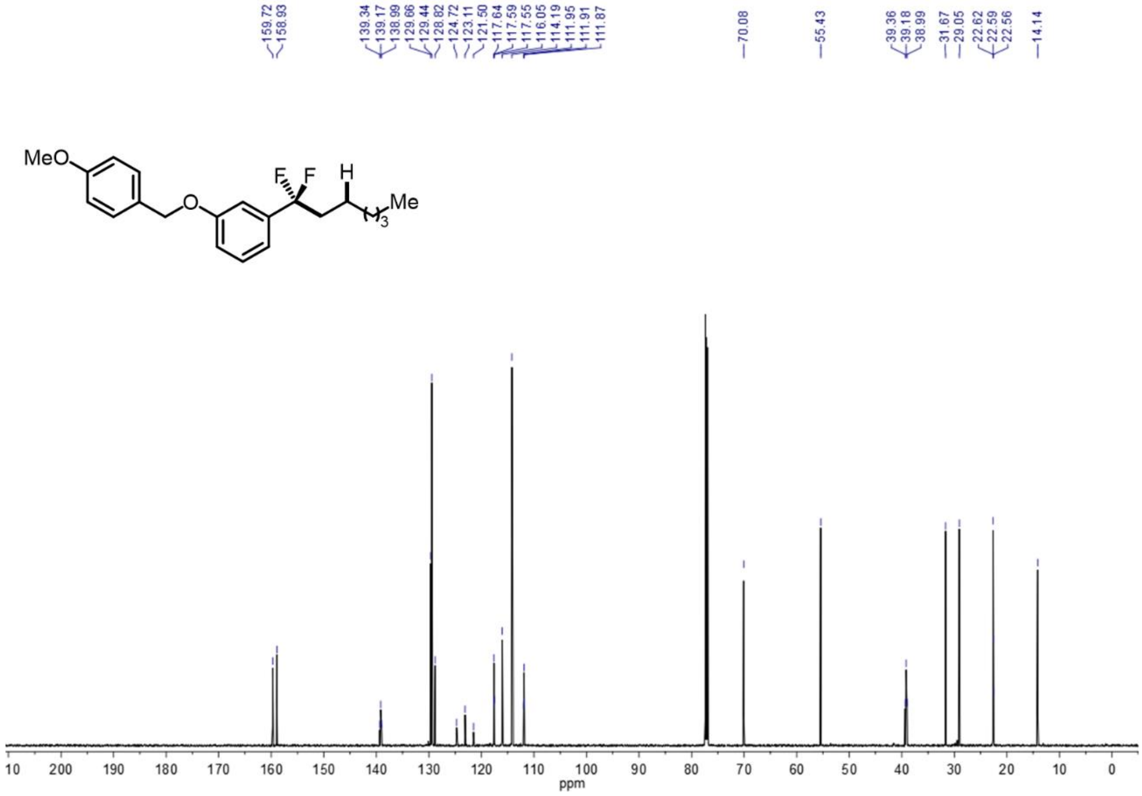
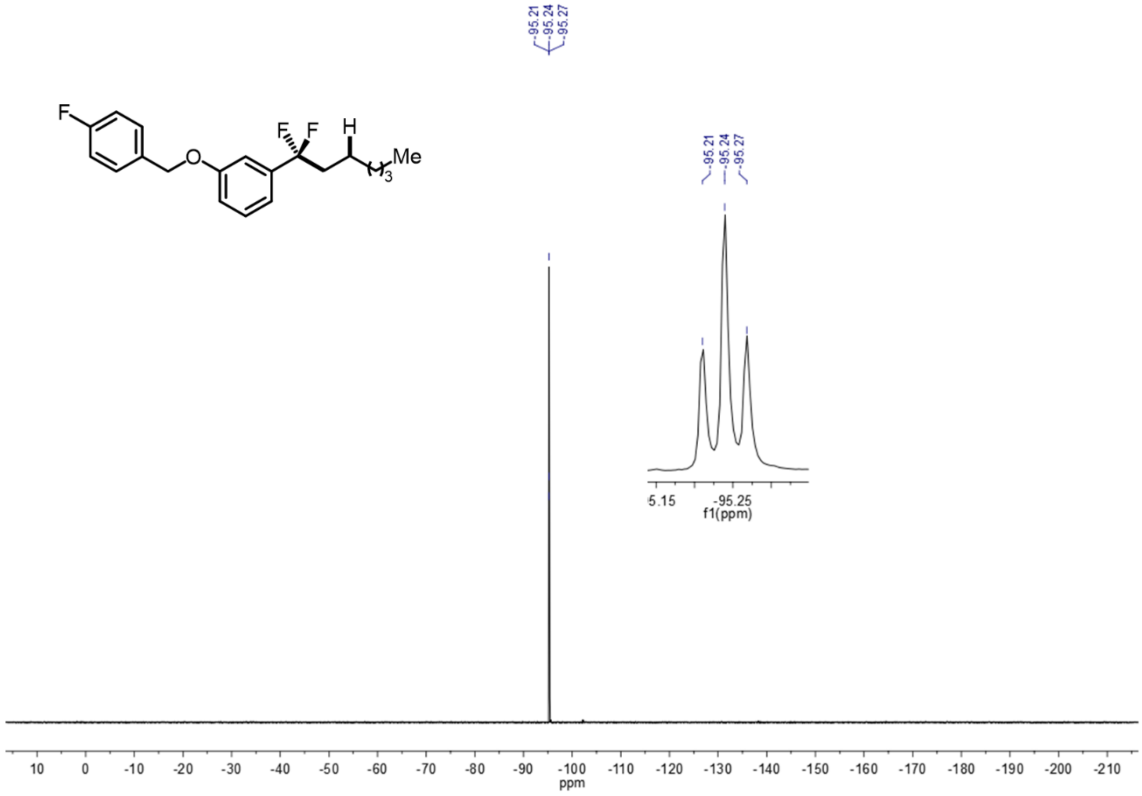


^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5m**



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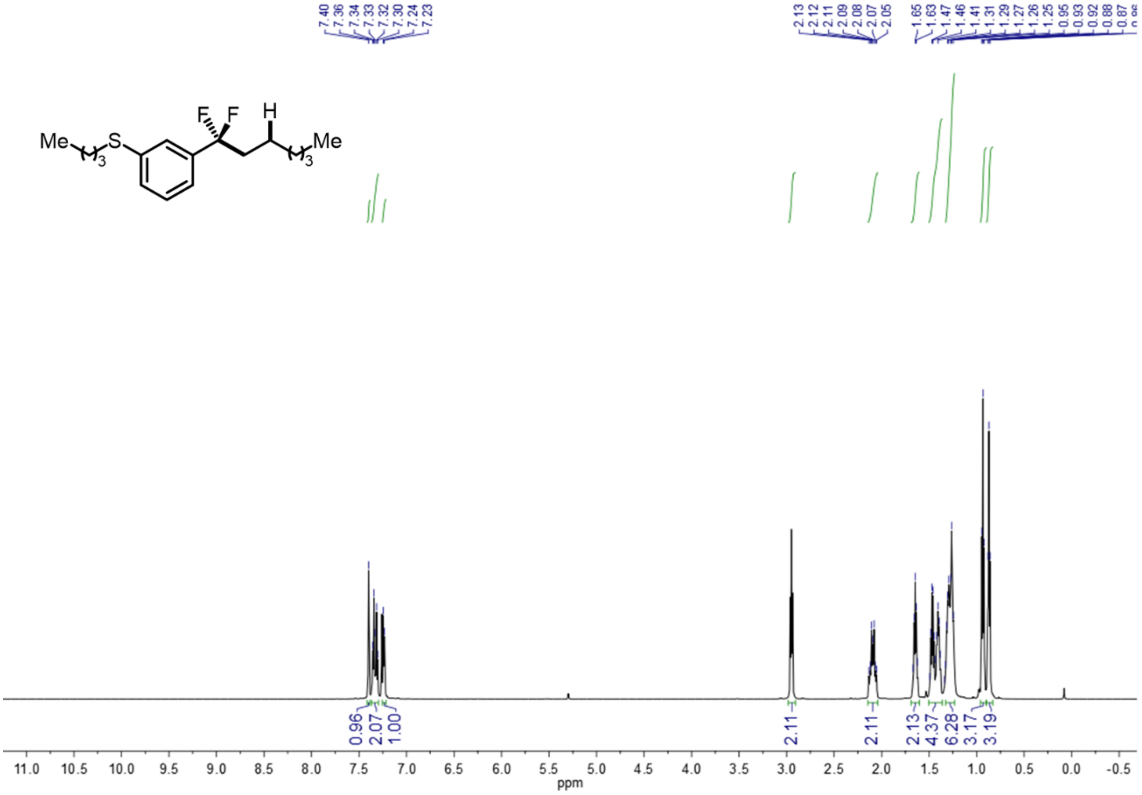

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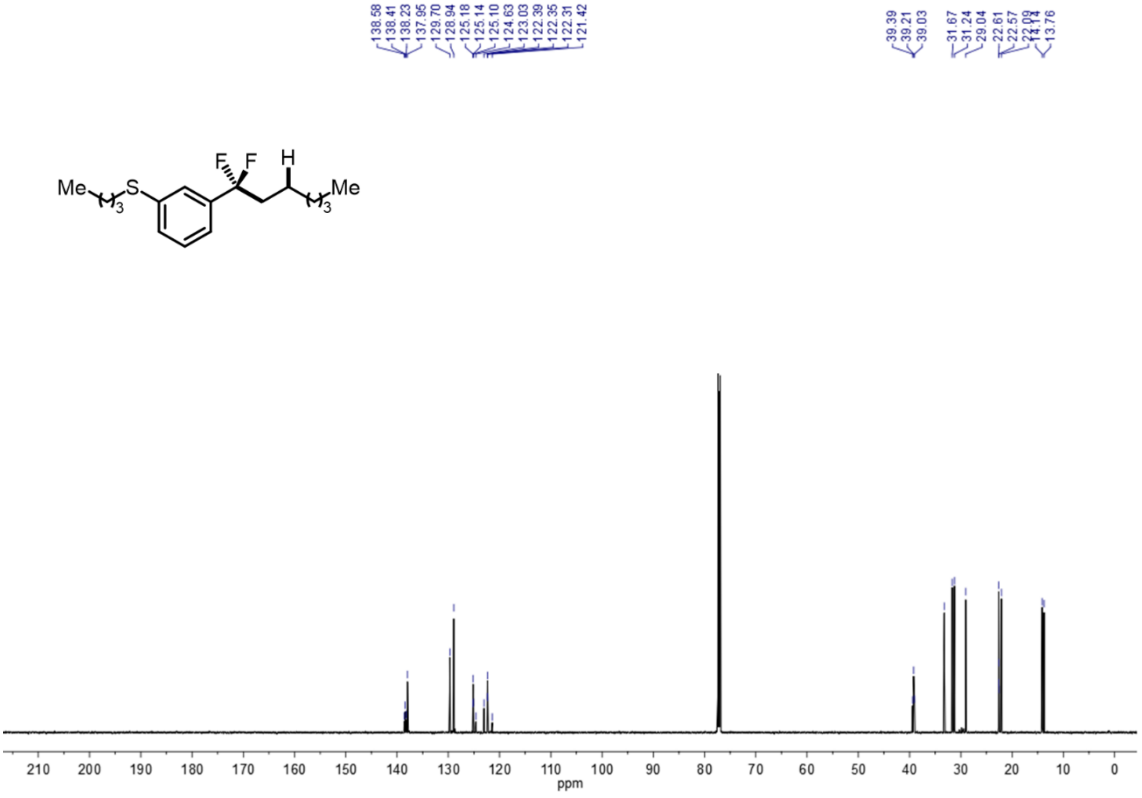

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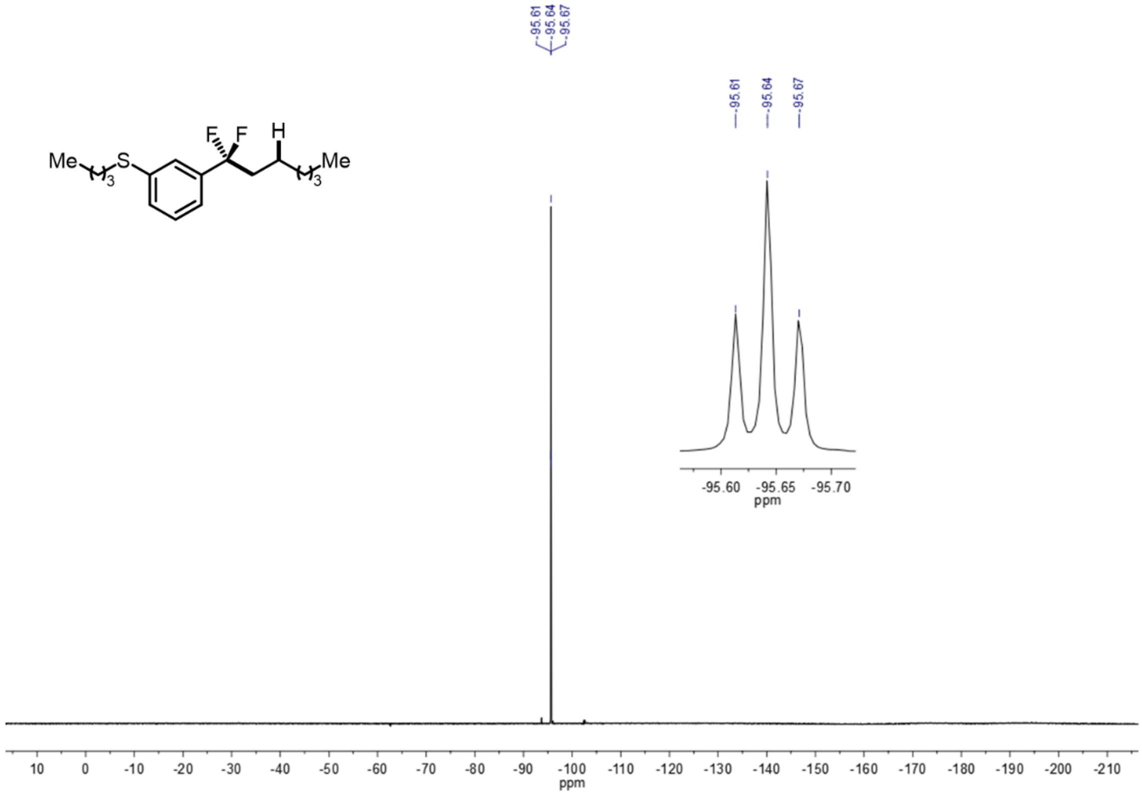
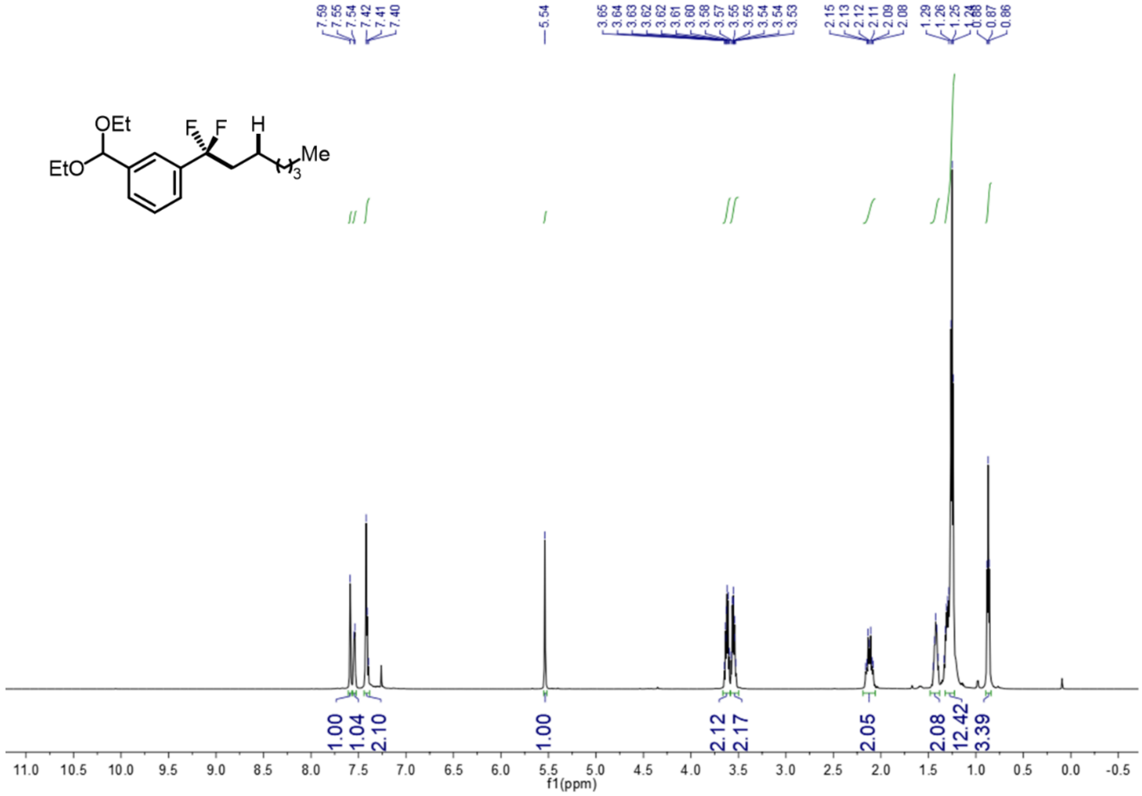


^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5n**



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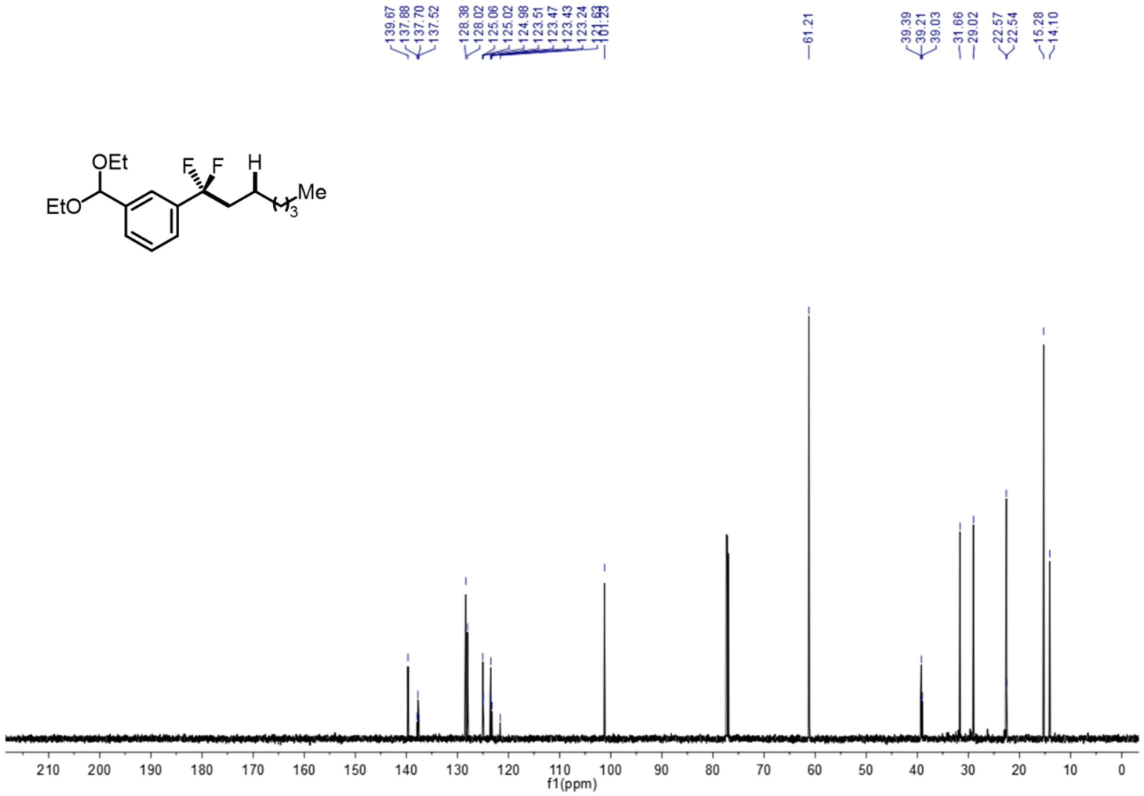
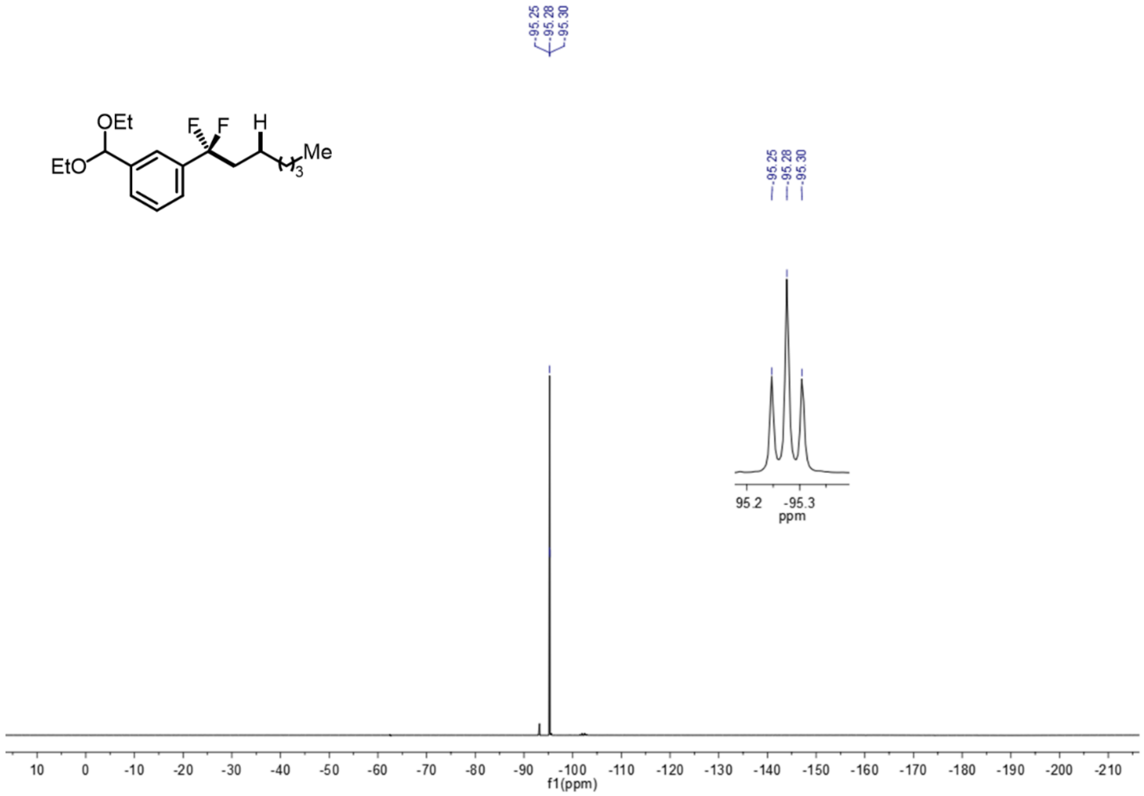
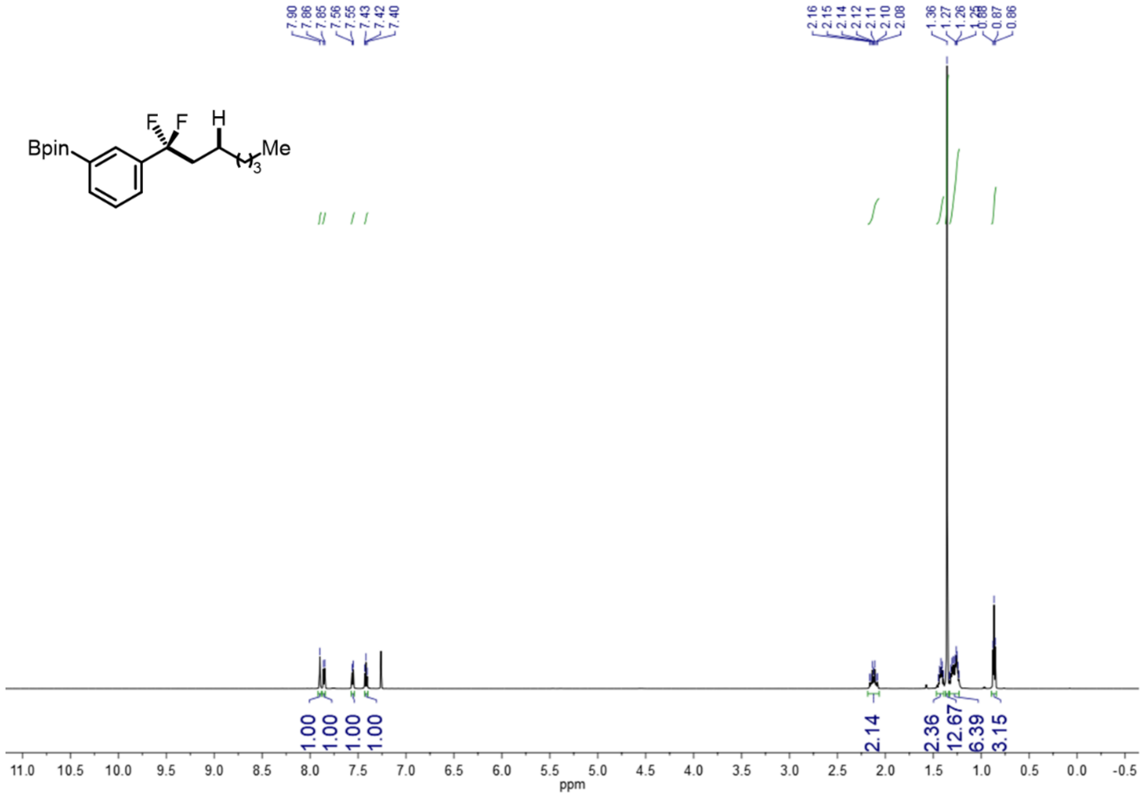


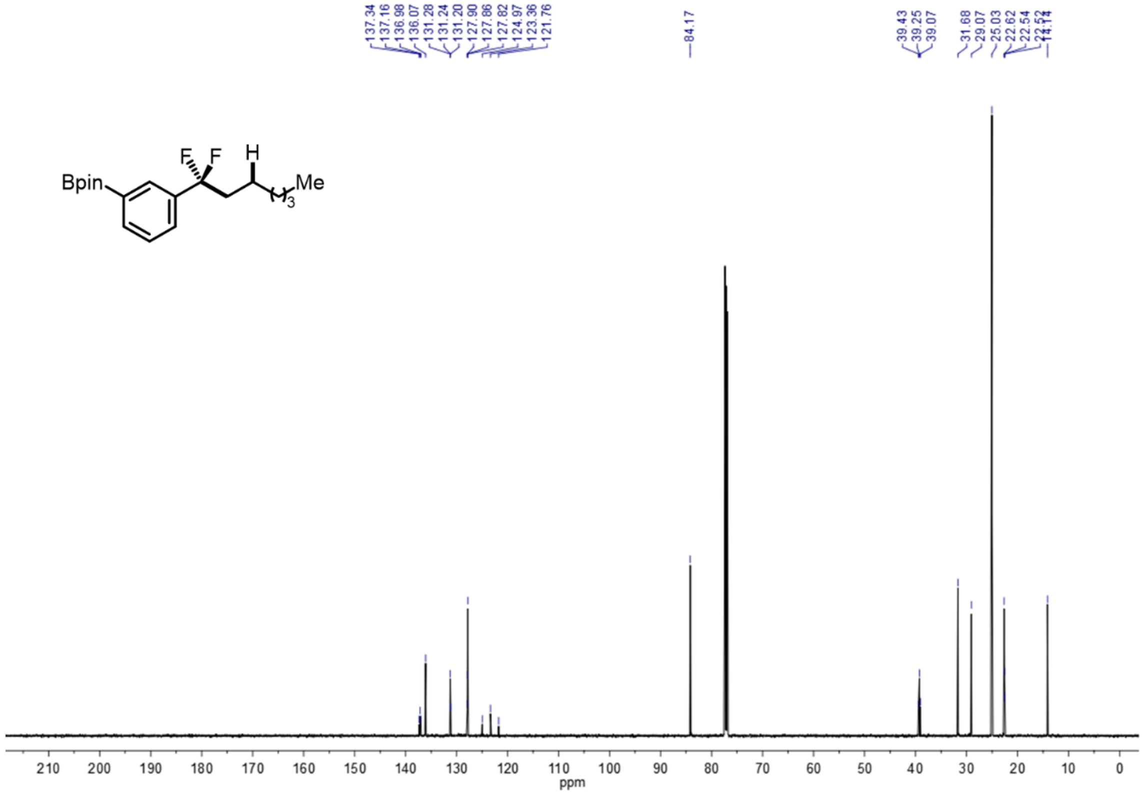
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5o**



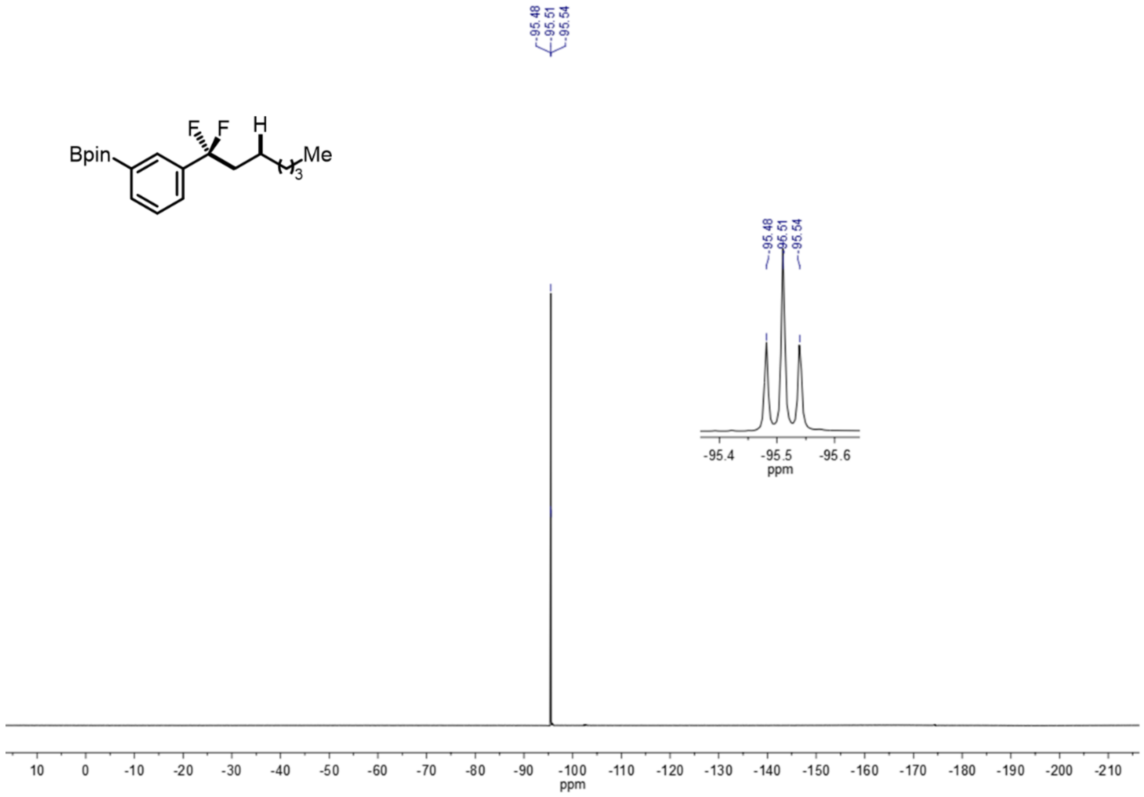
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5o**



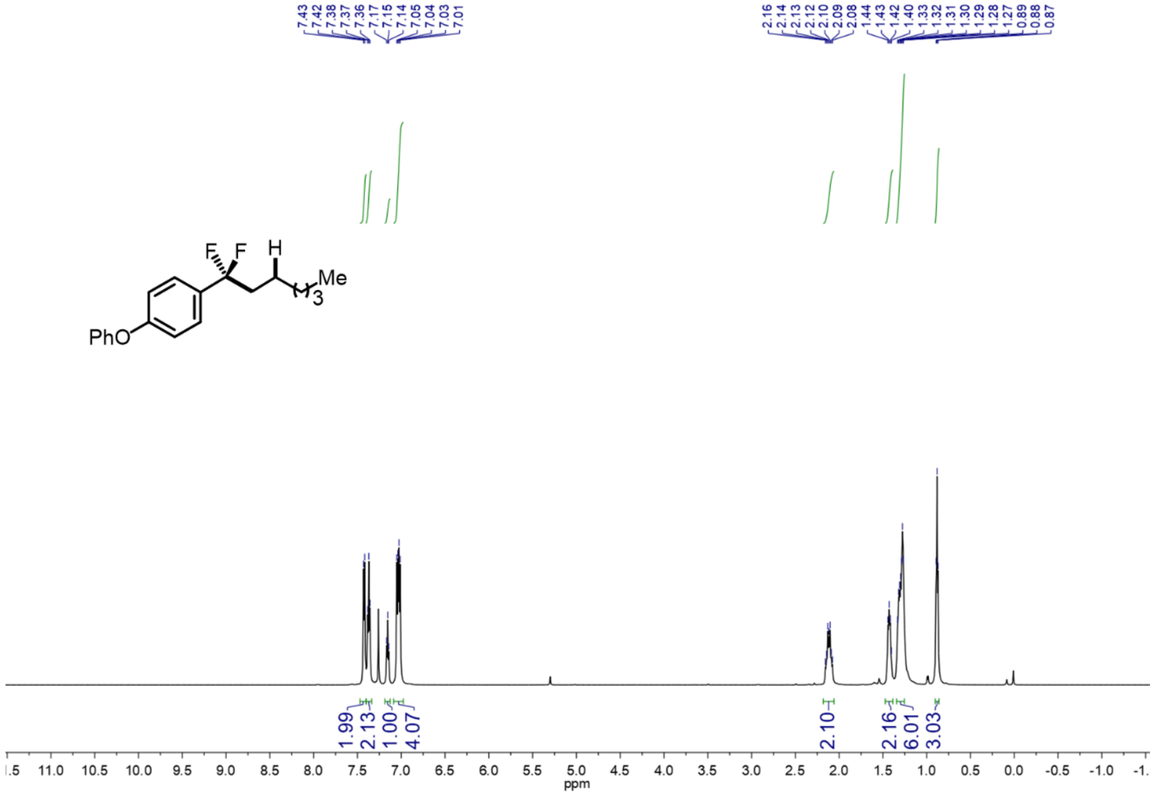
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5p**



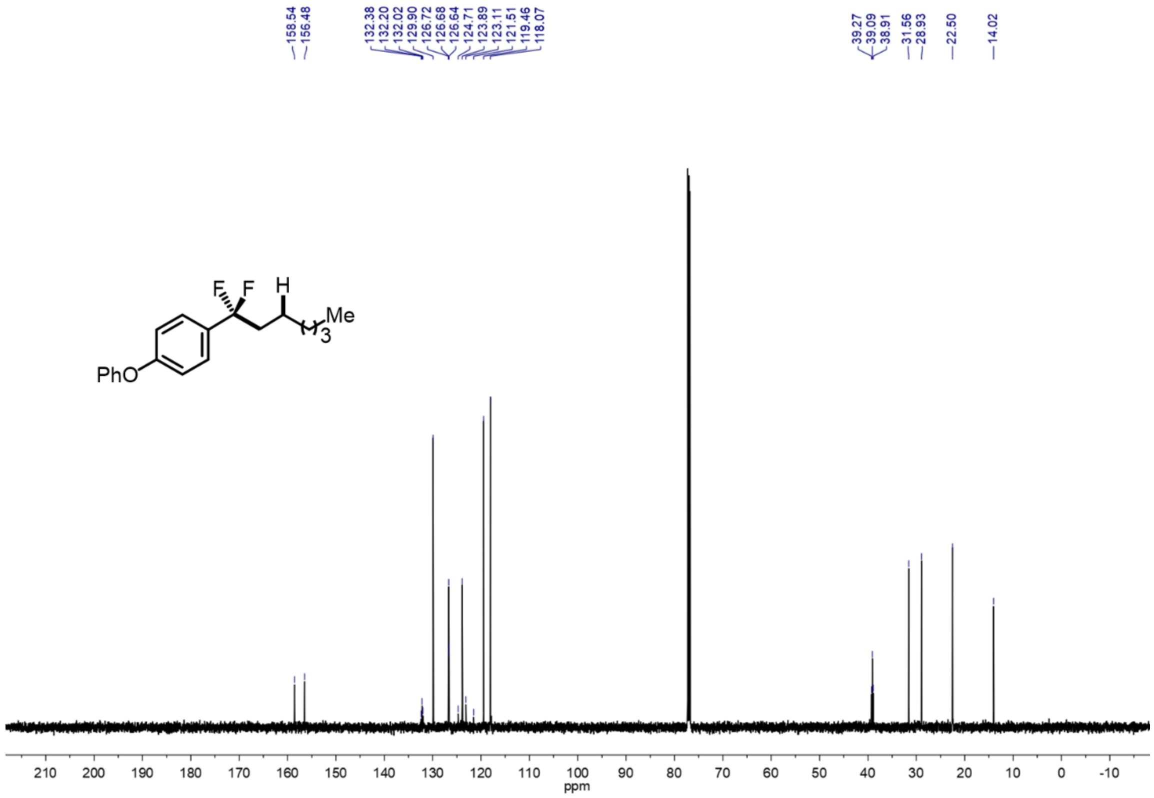
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5p**



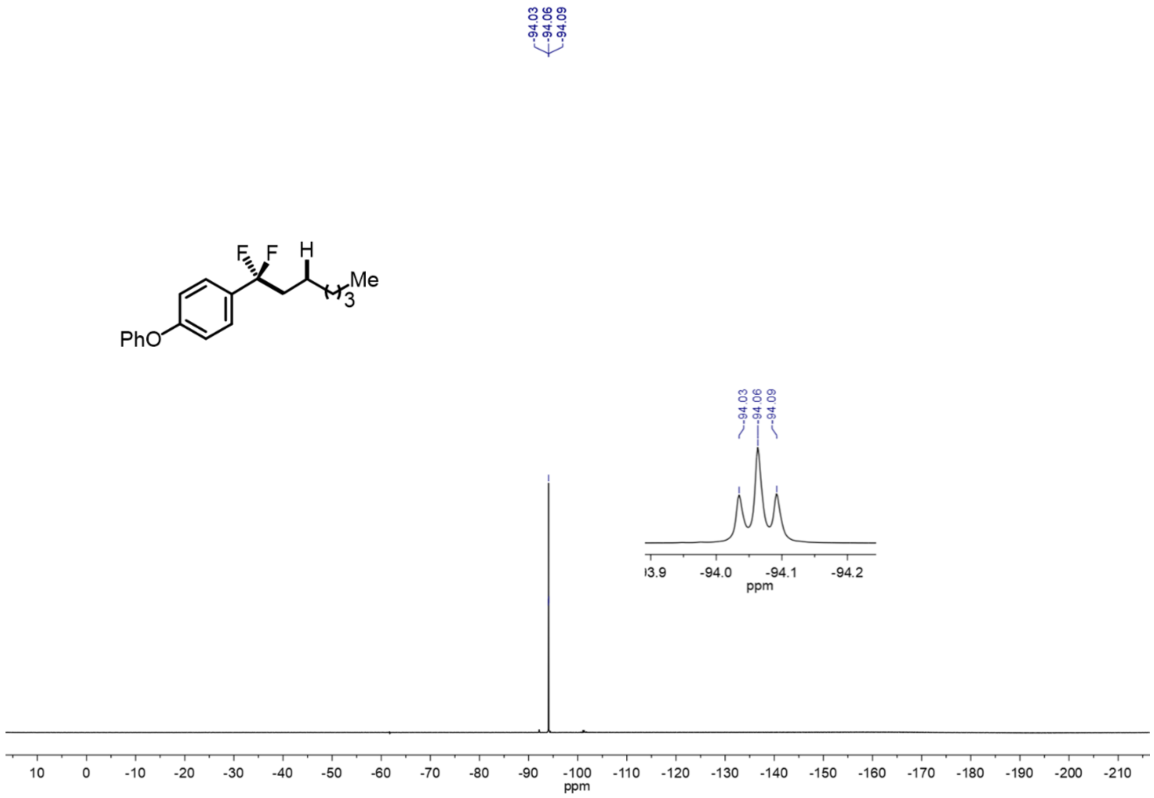
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5p**



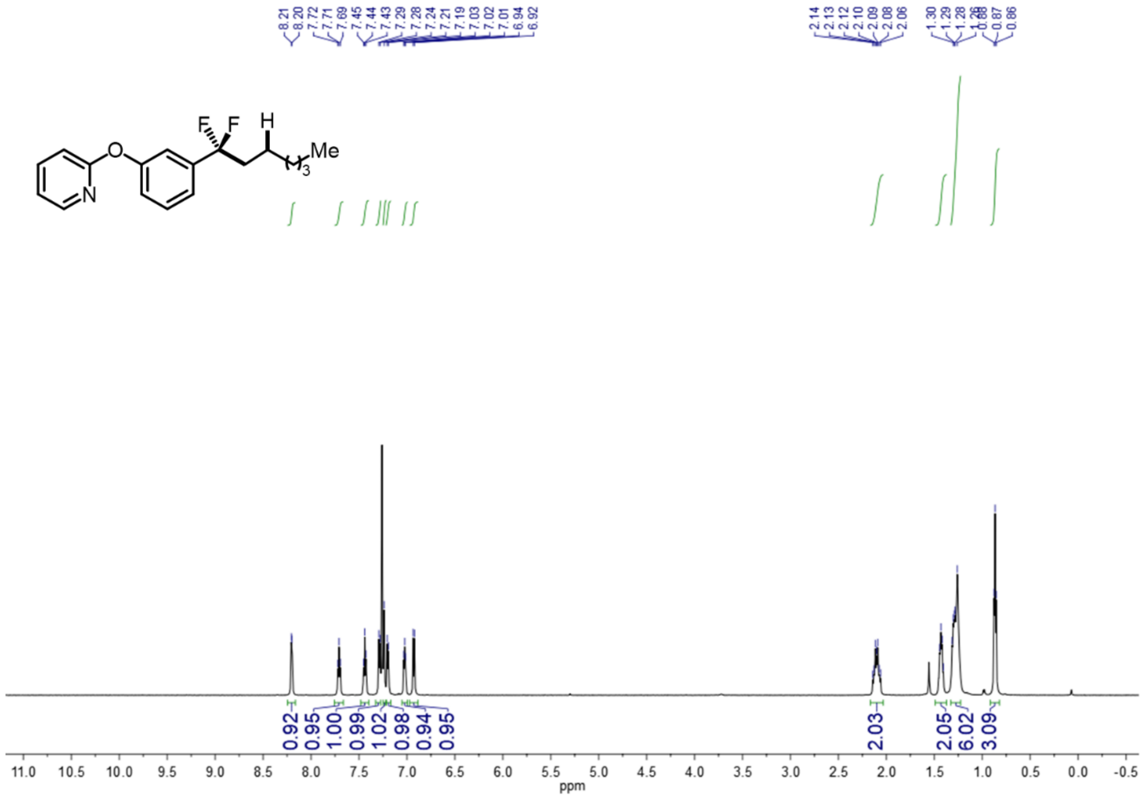
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5q**



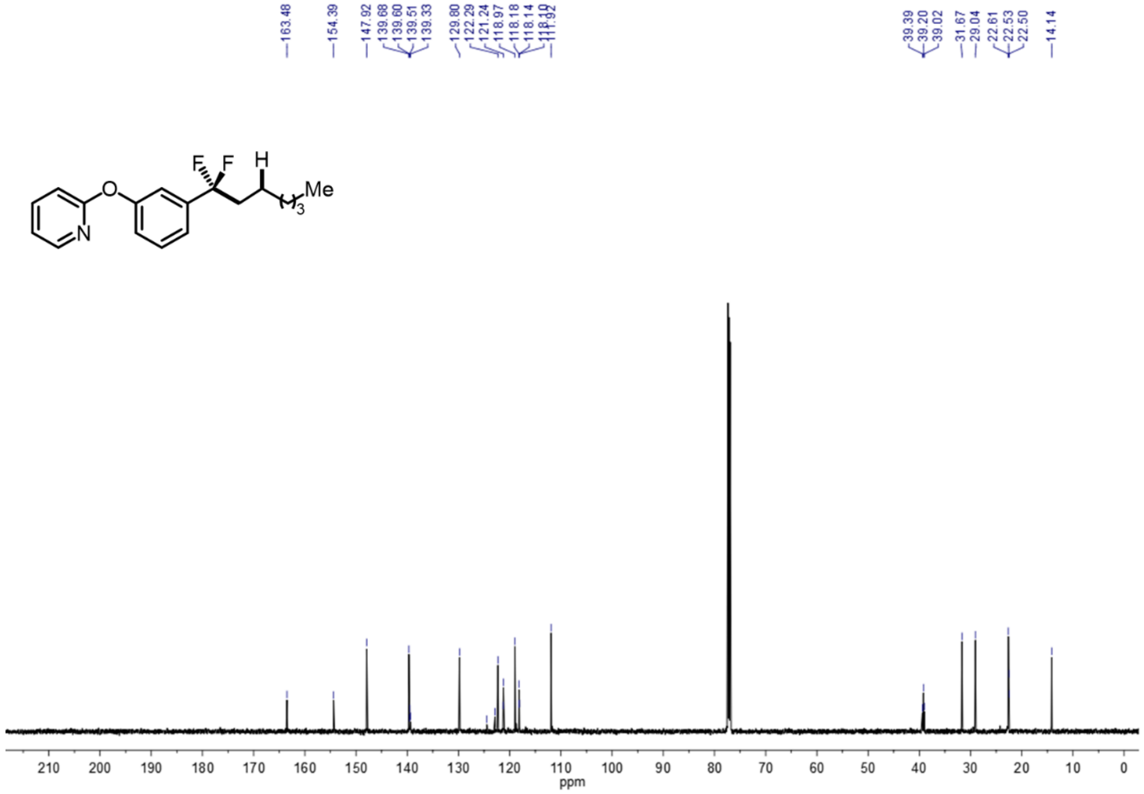
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5q**



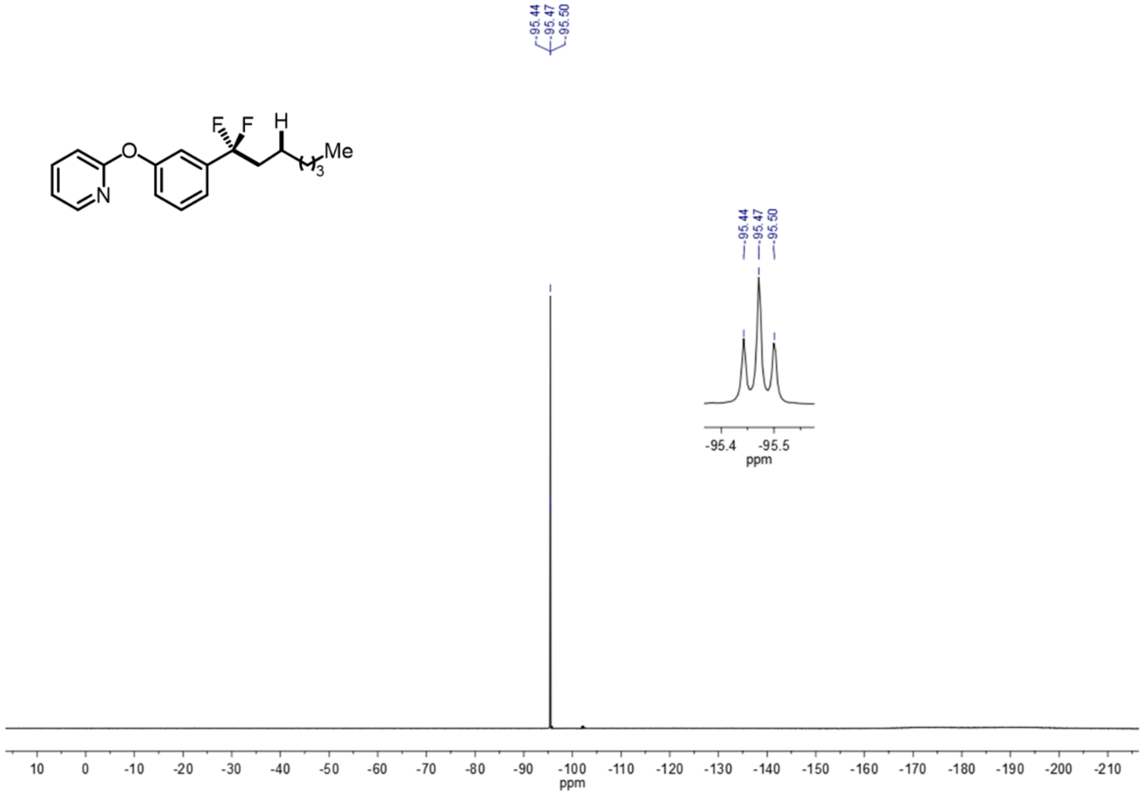
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5q**



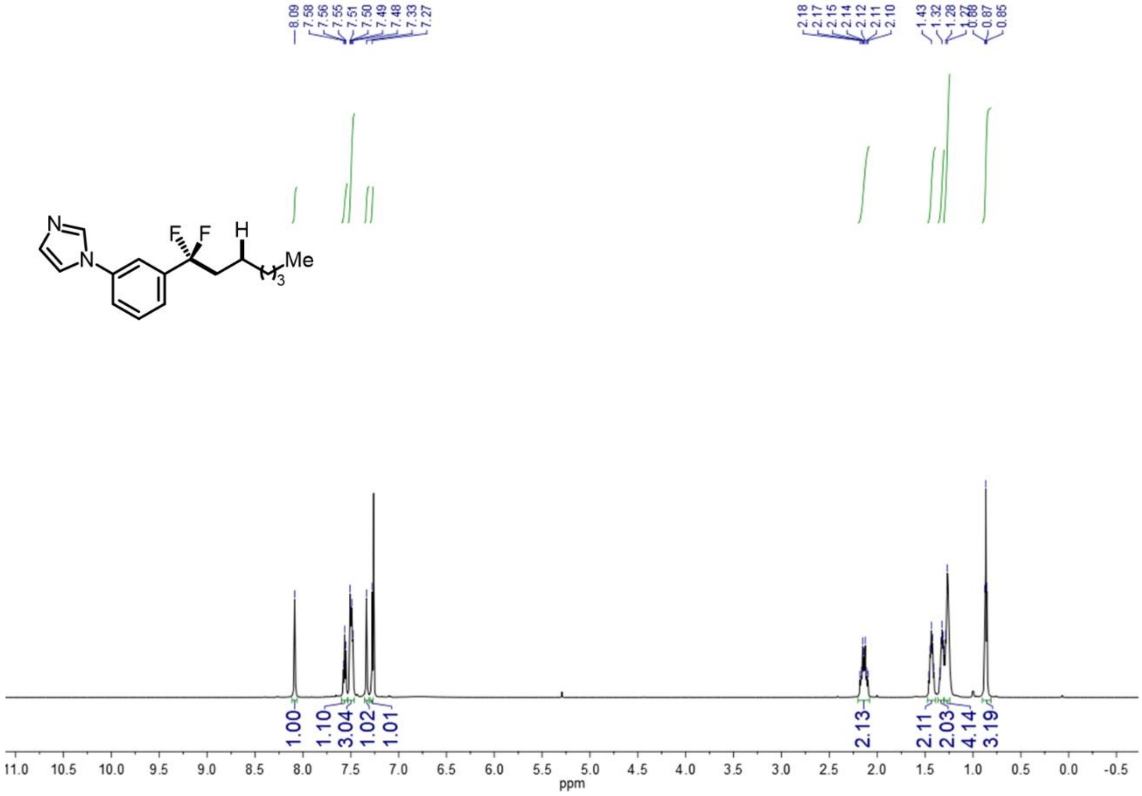
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5r**



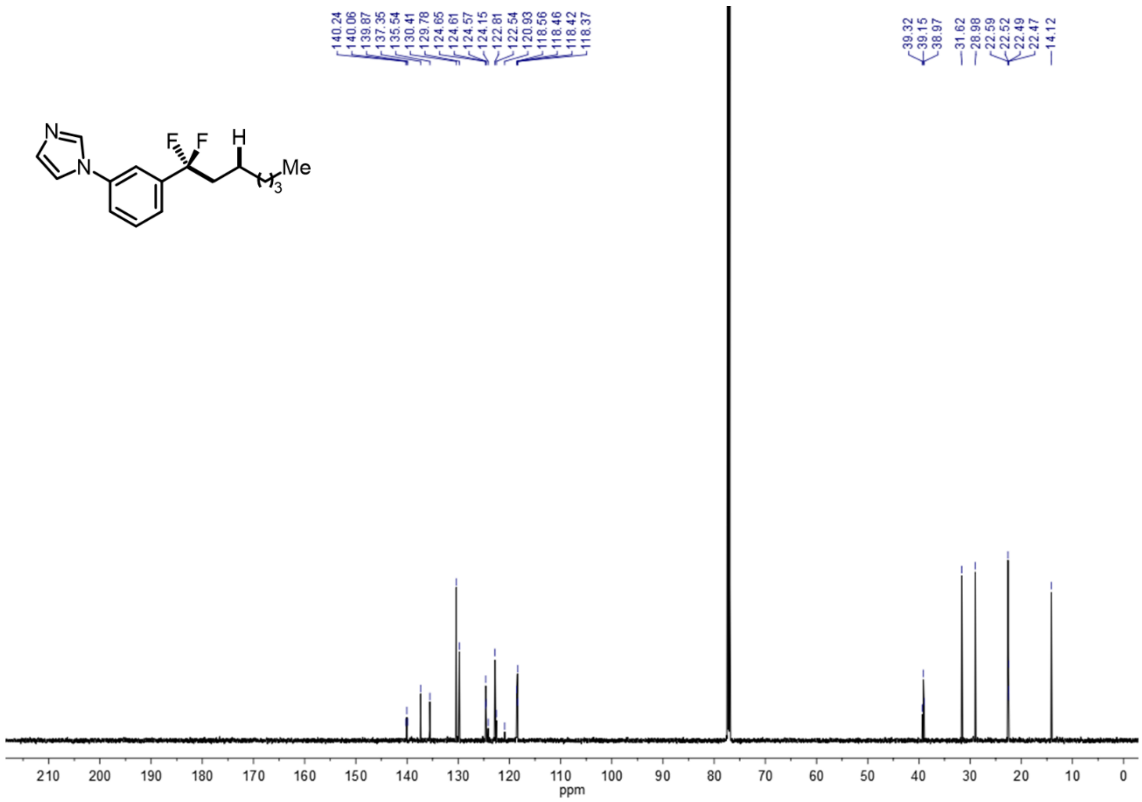
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5r**



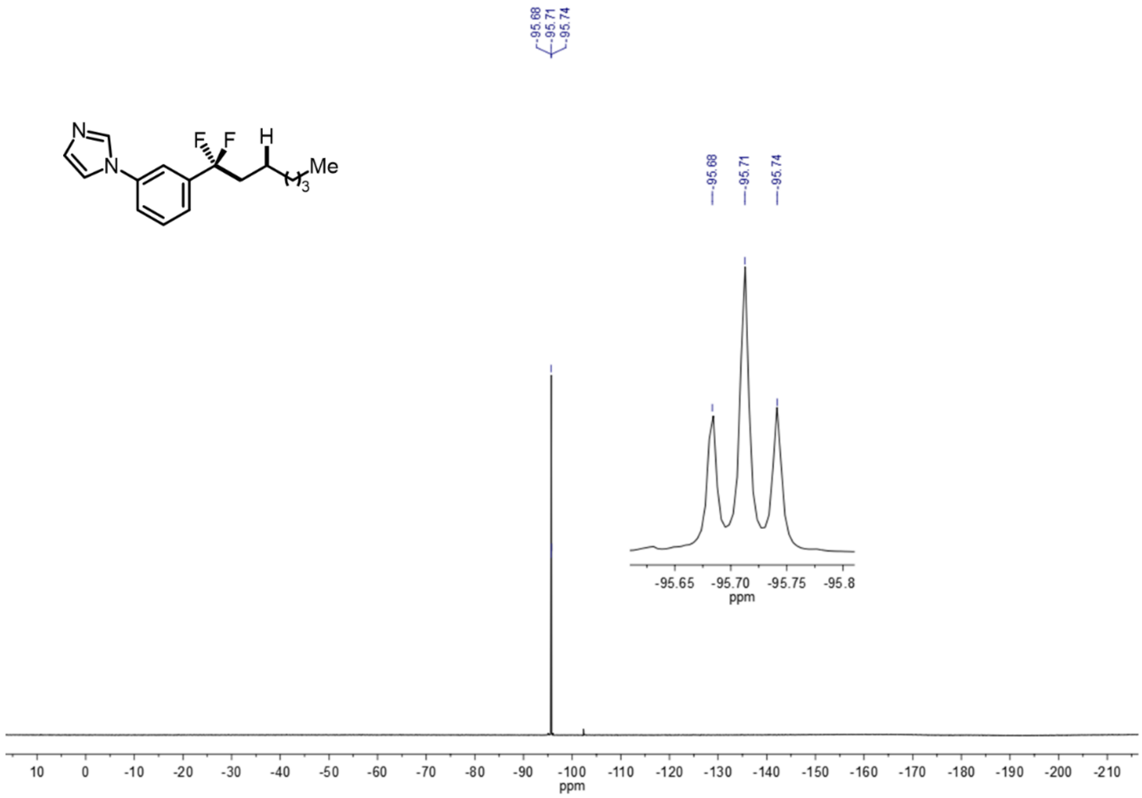
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5r**



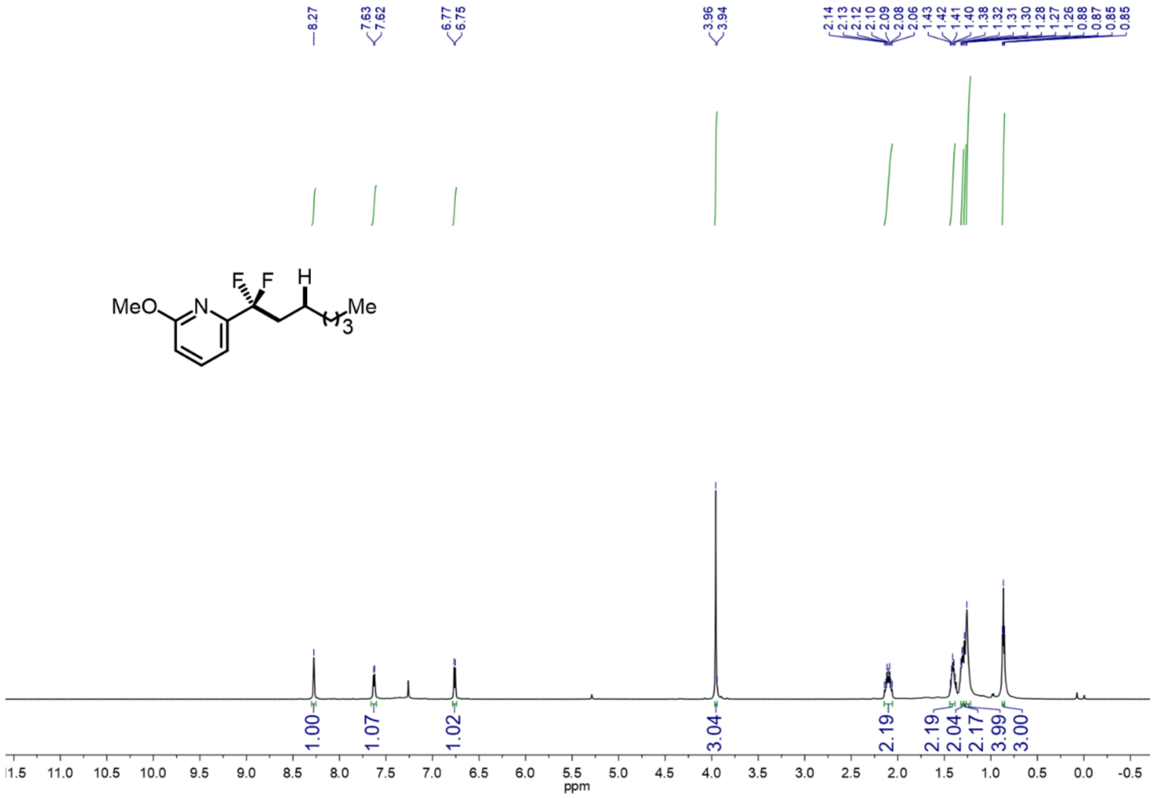
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5s**



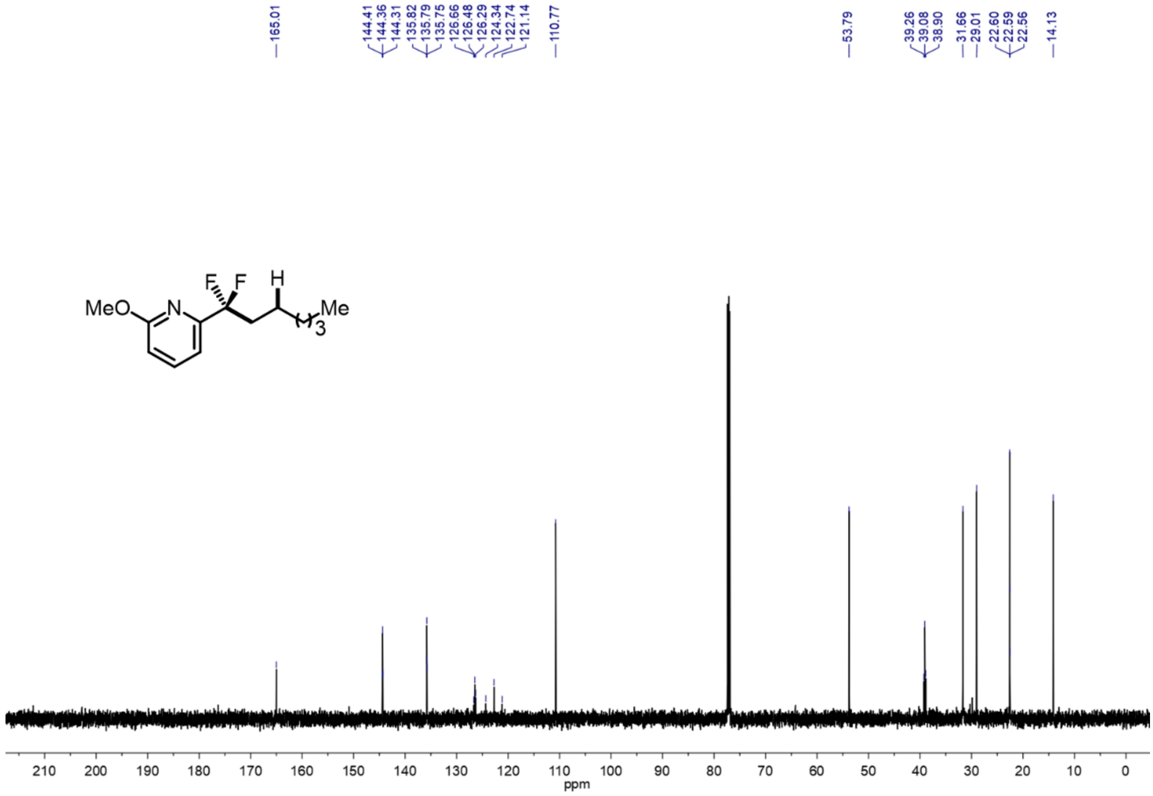
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5s**



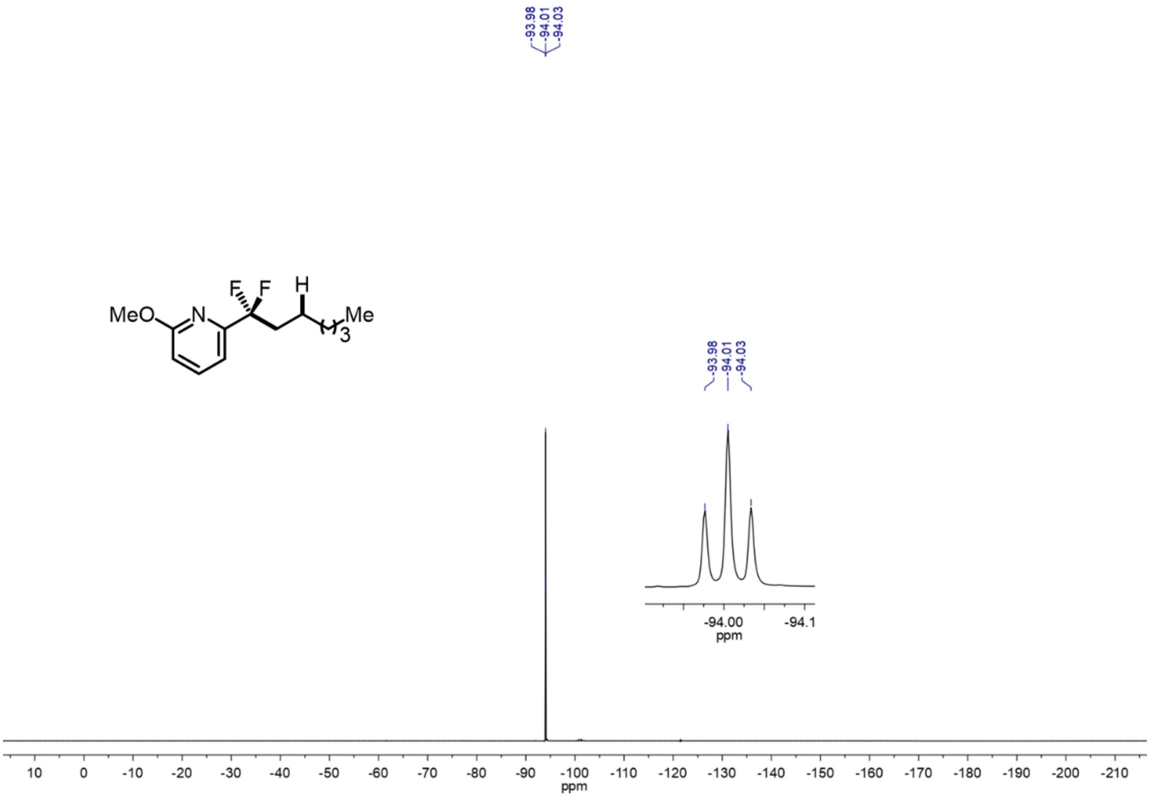
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5s**



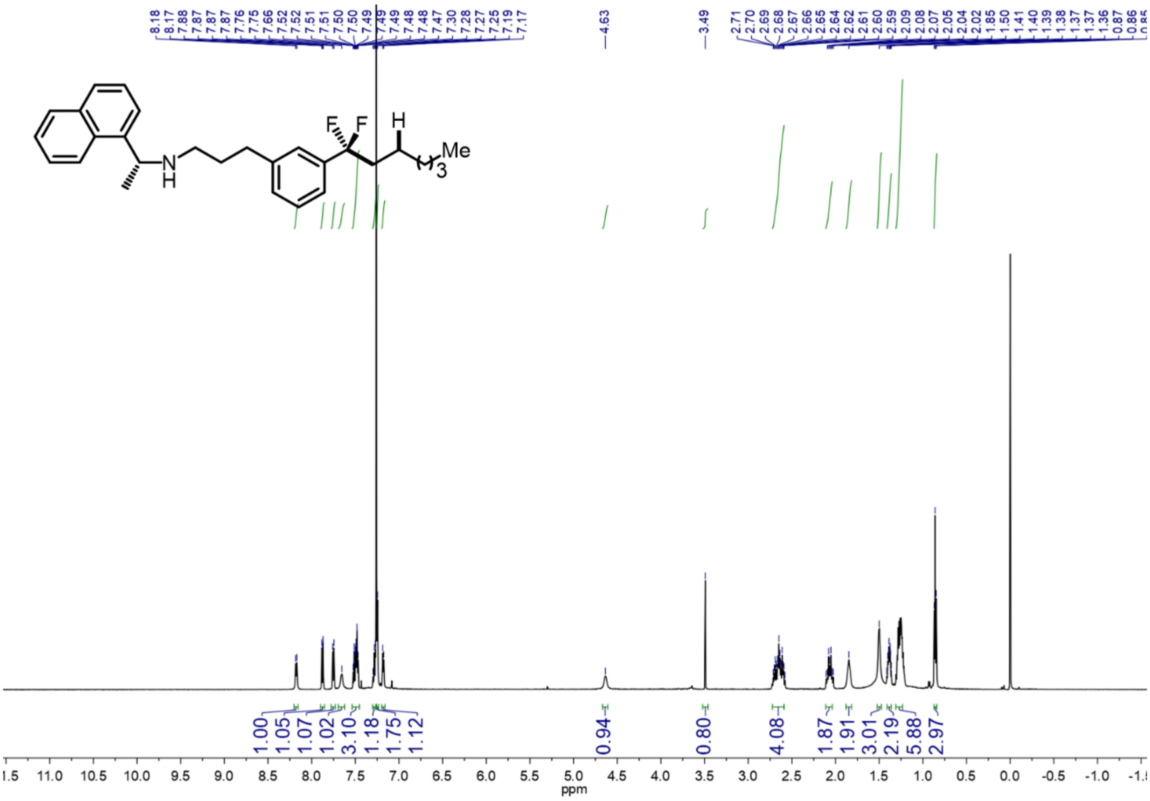
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5t**



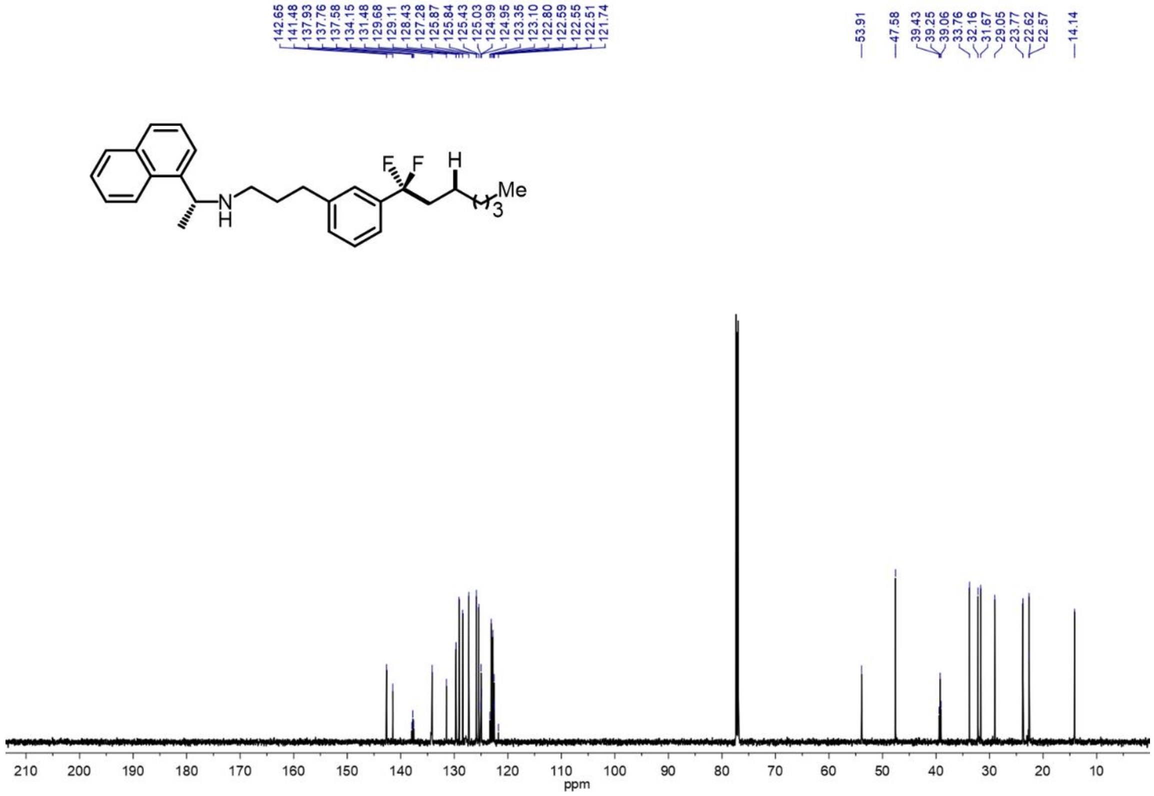
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5t**



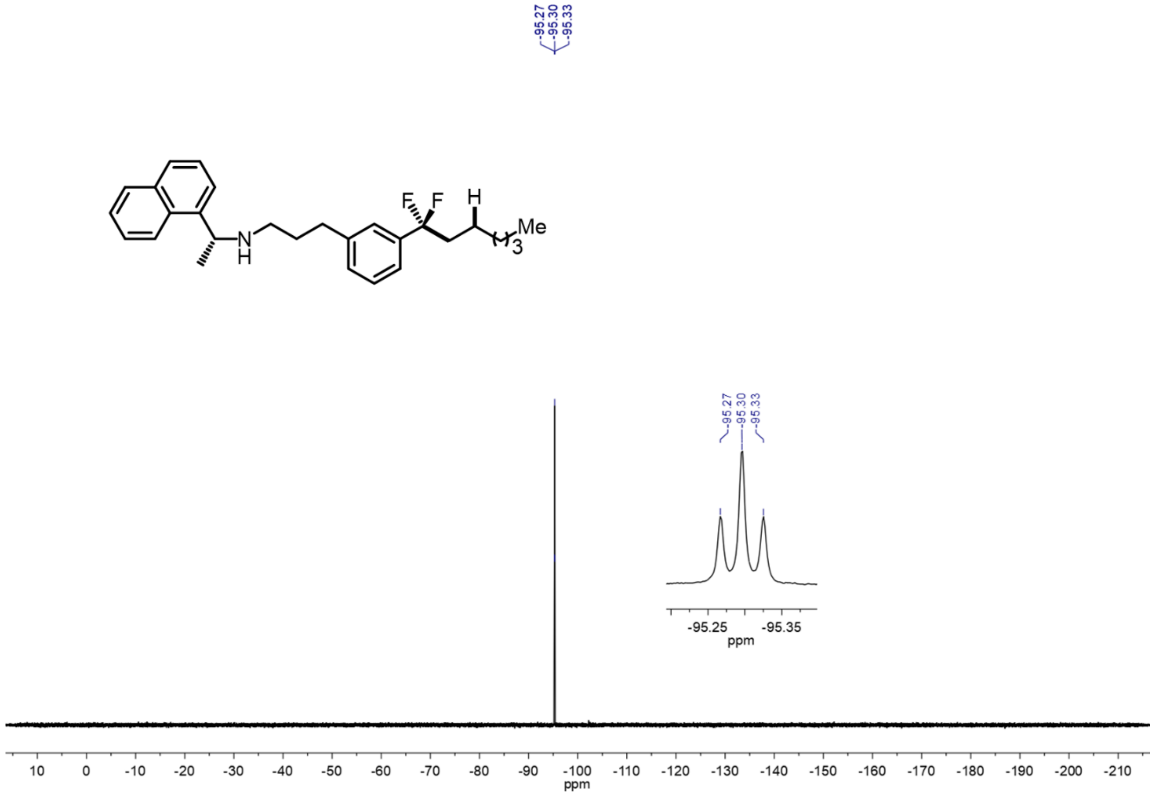
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5t**



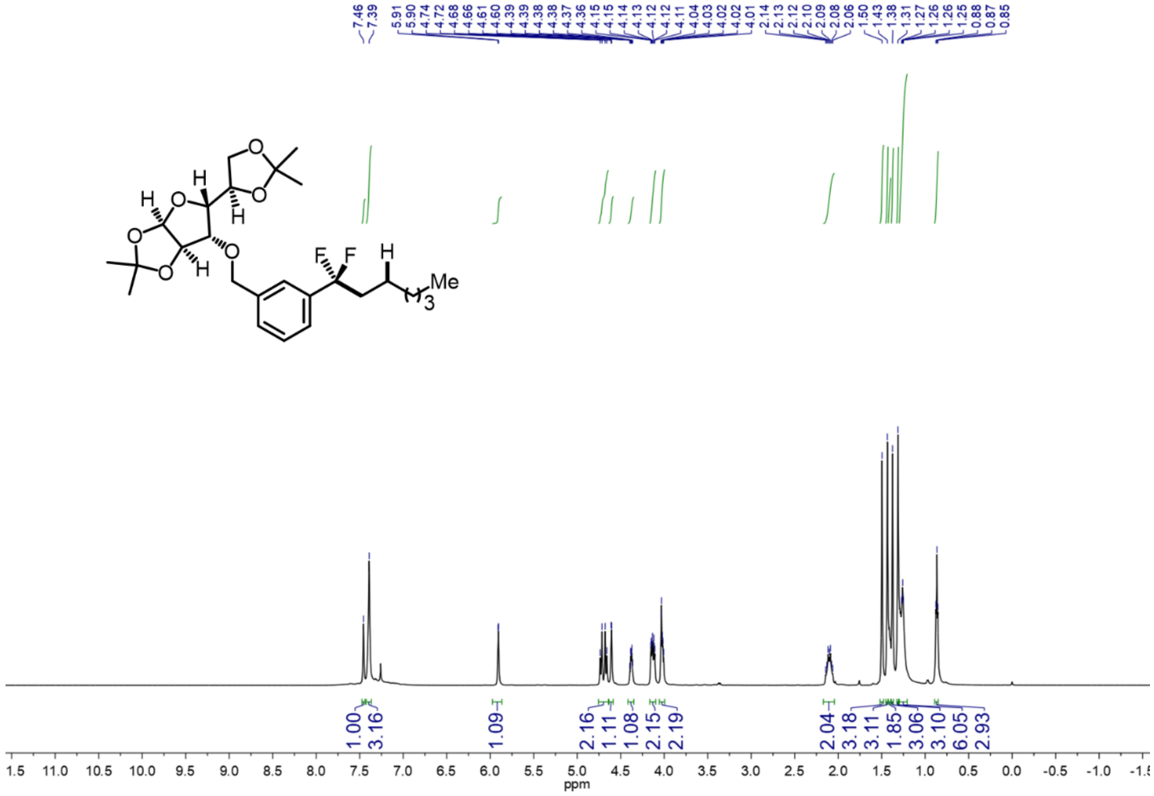
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5u**



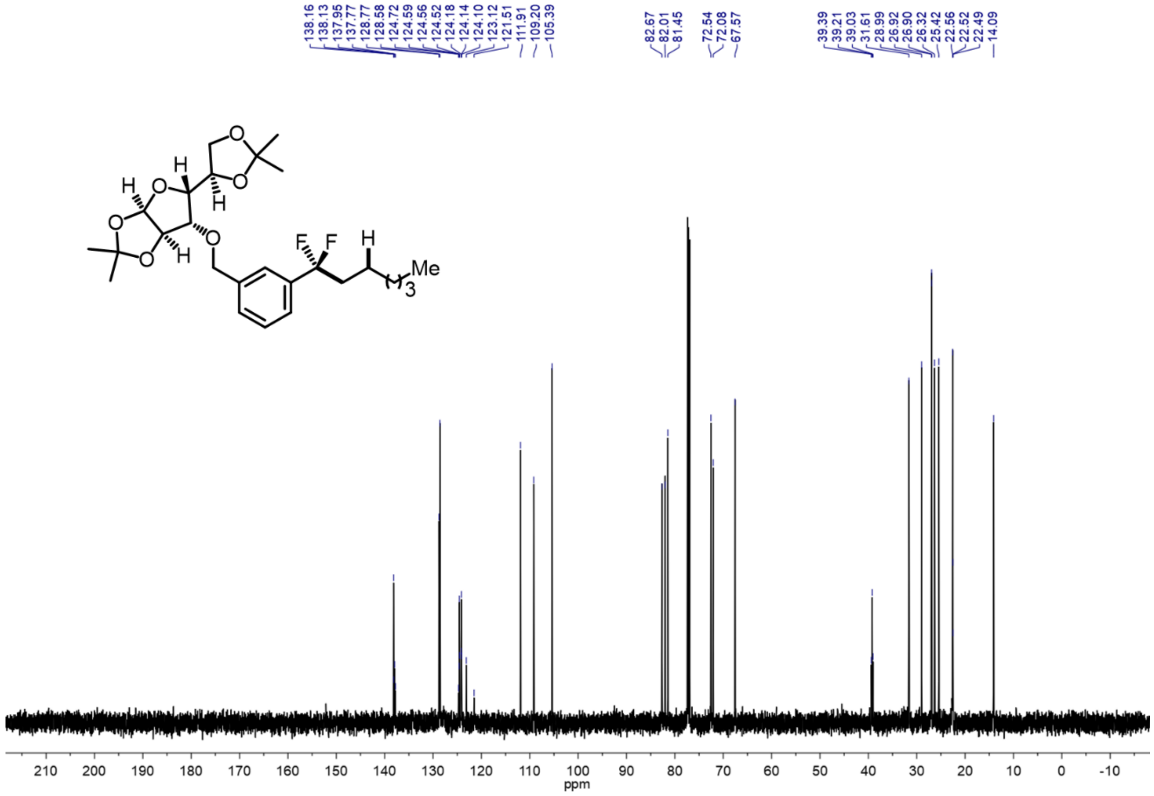
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5u**



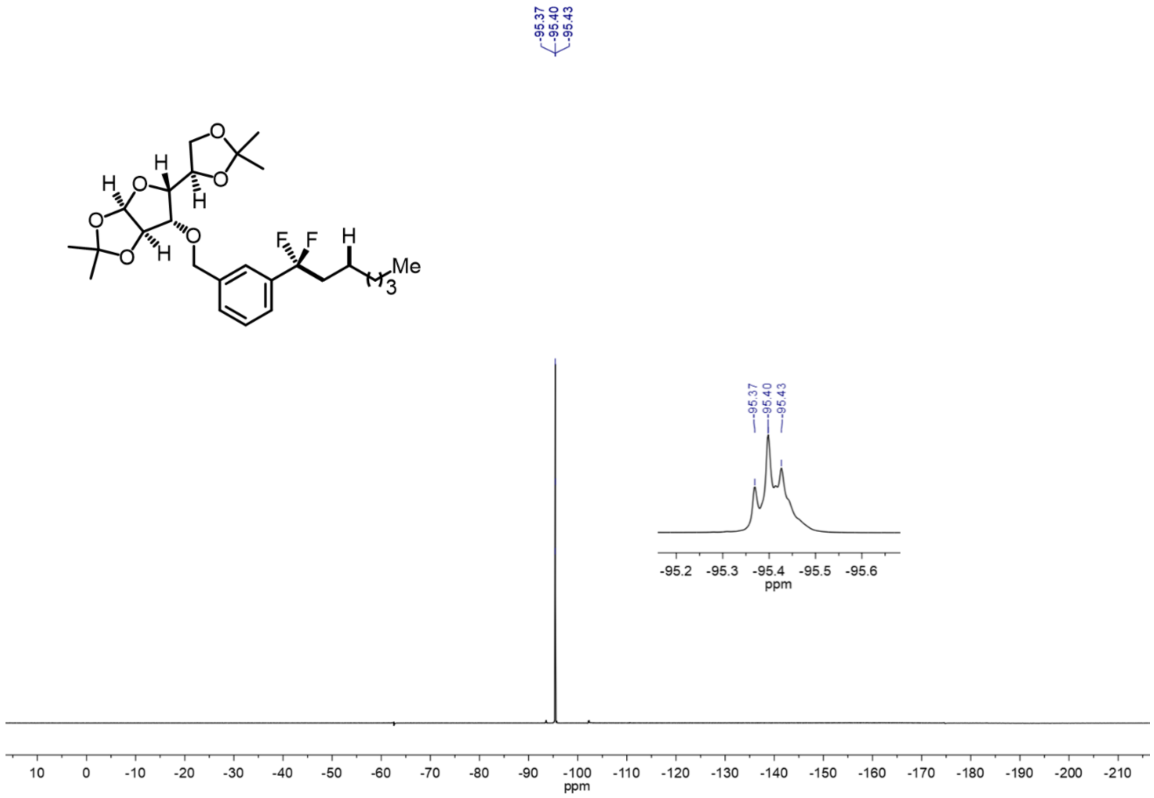
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5u**



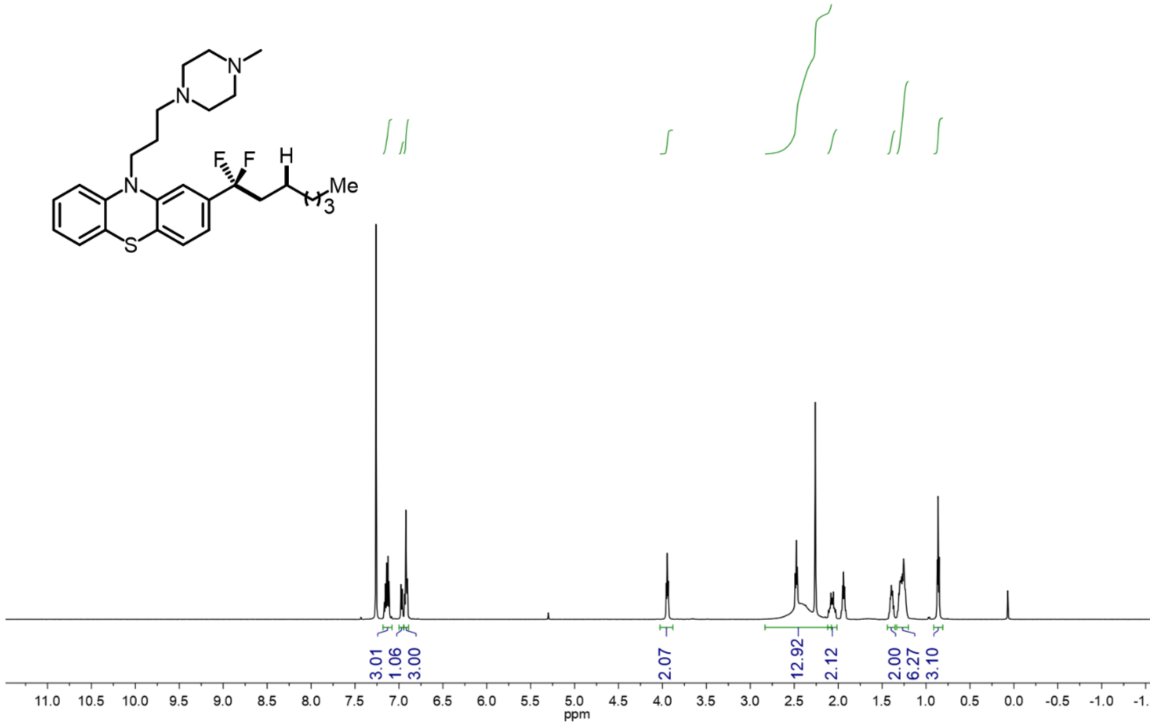
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5v**



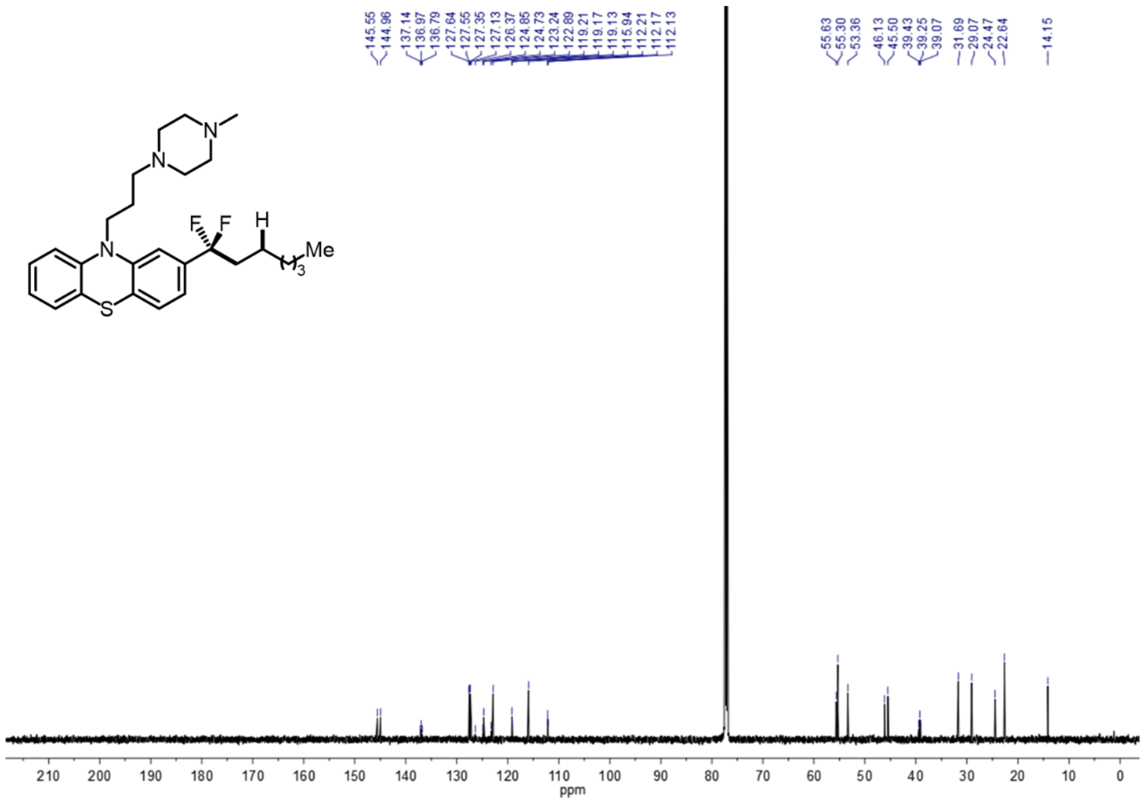
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5v**



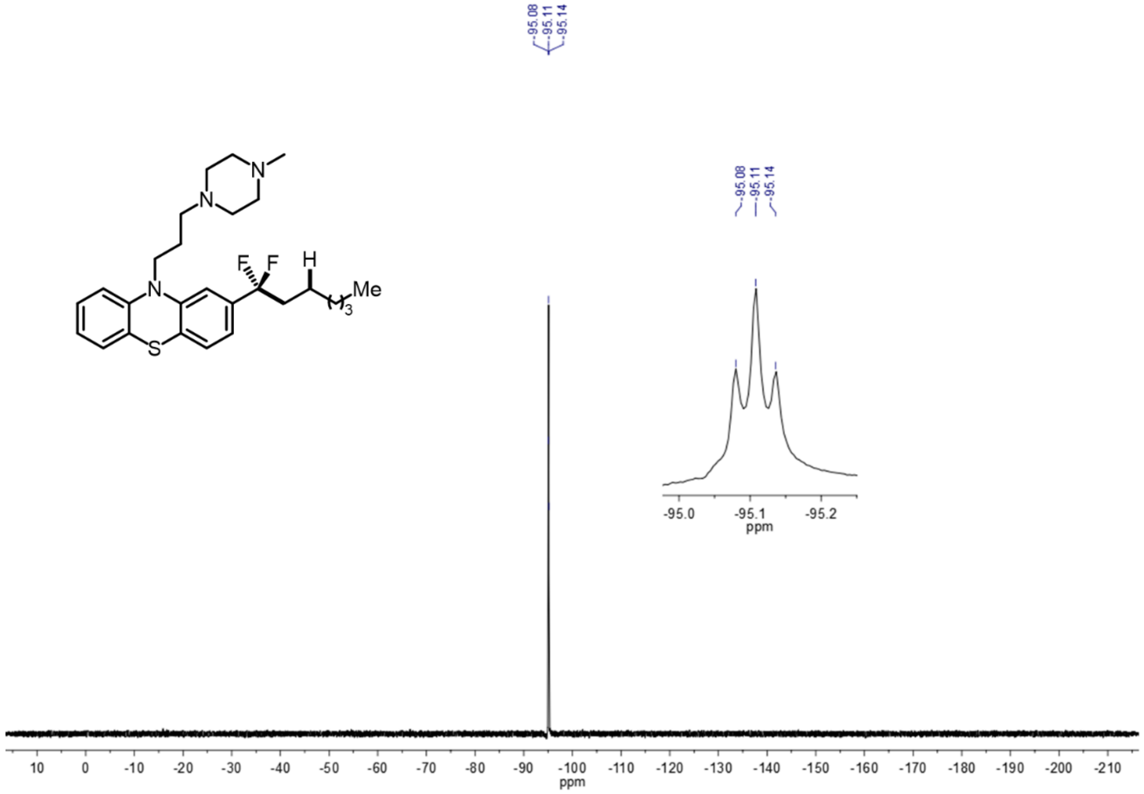
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5v**



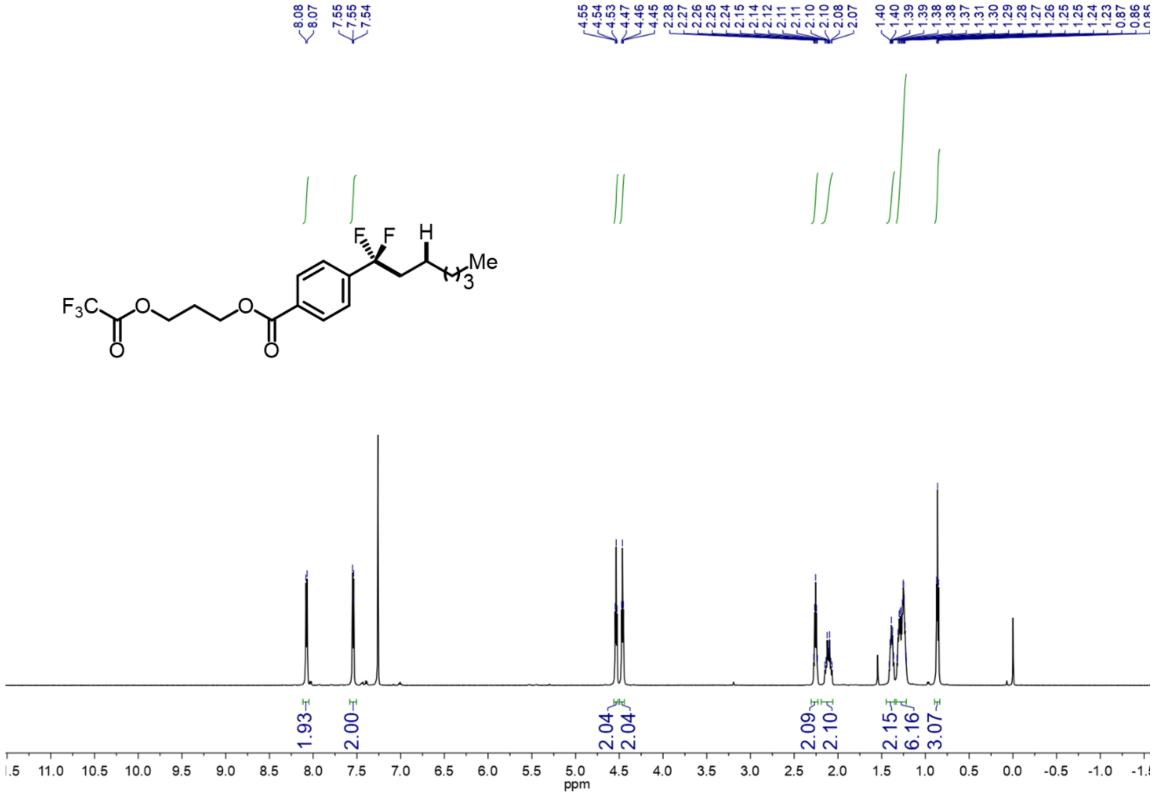
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5w**



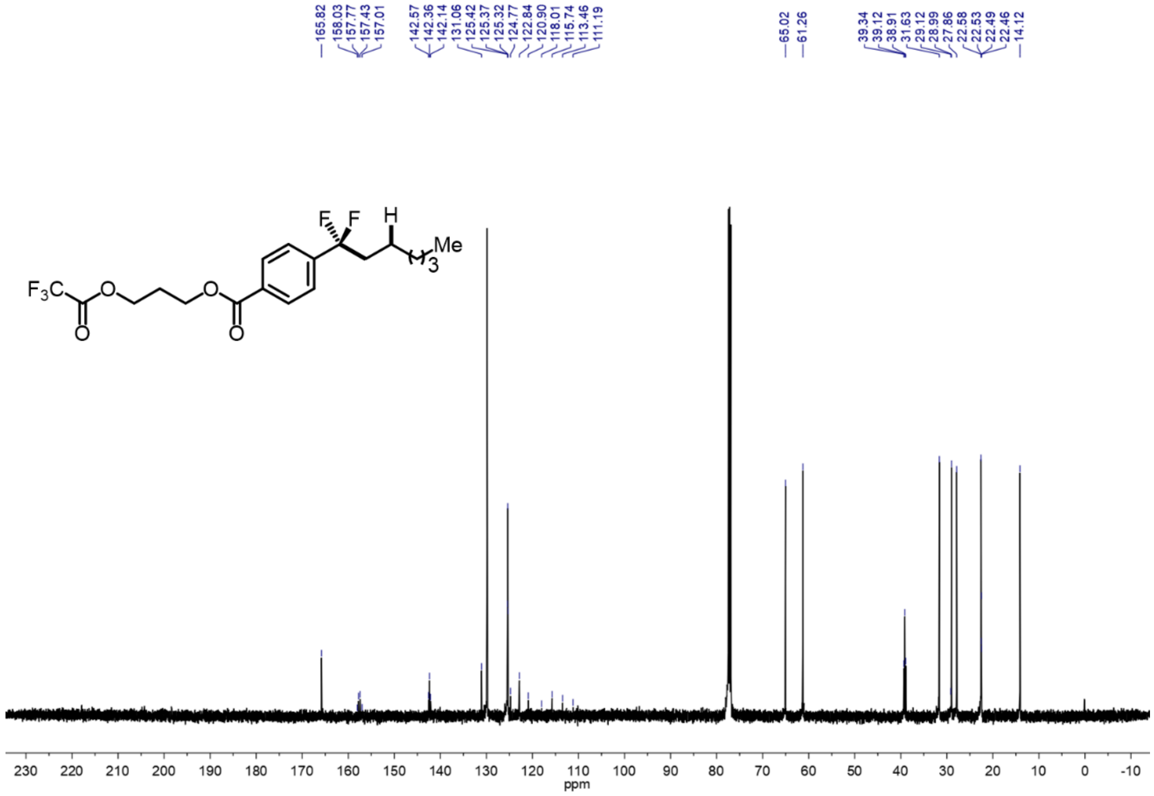
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5w**



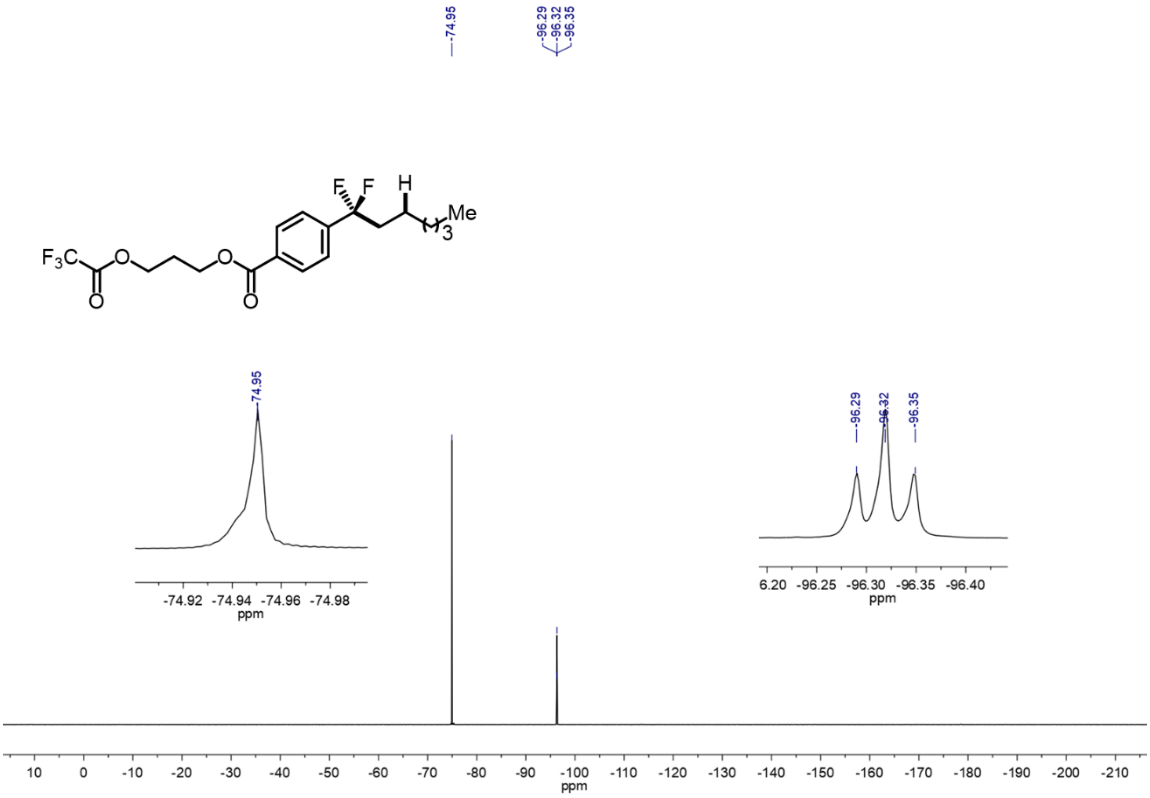
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5w**



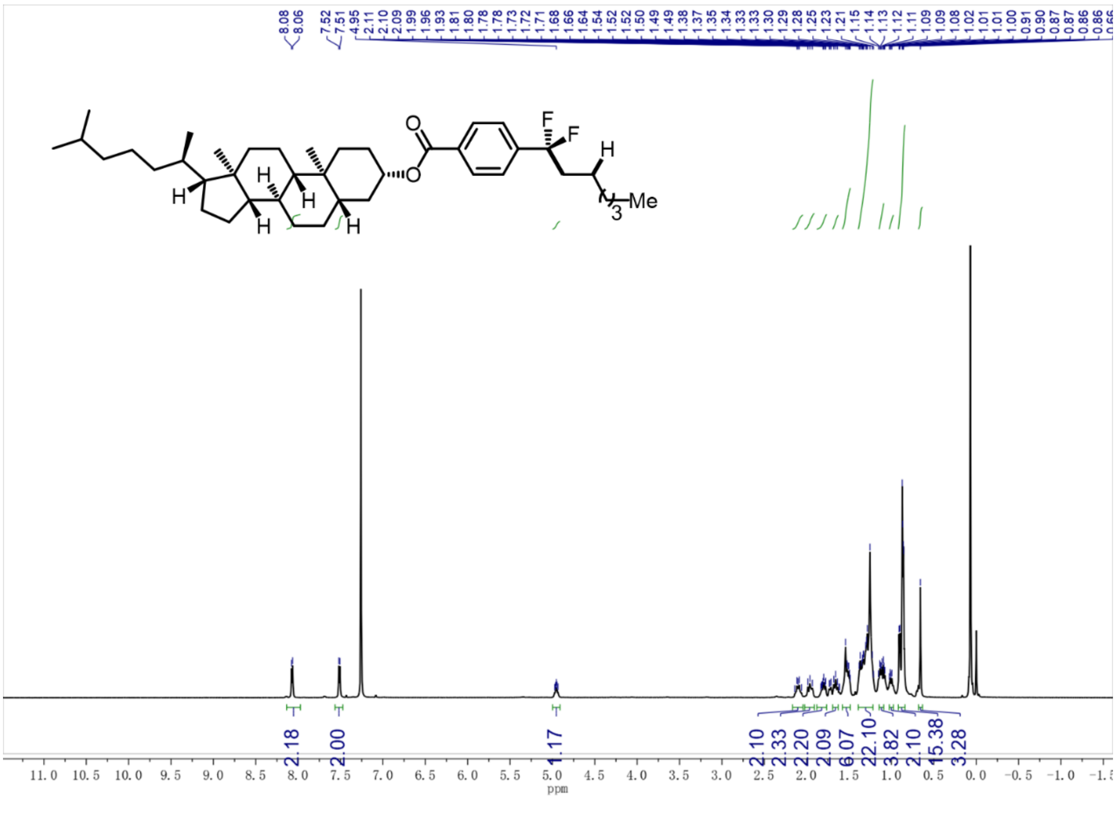
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5x**



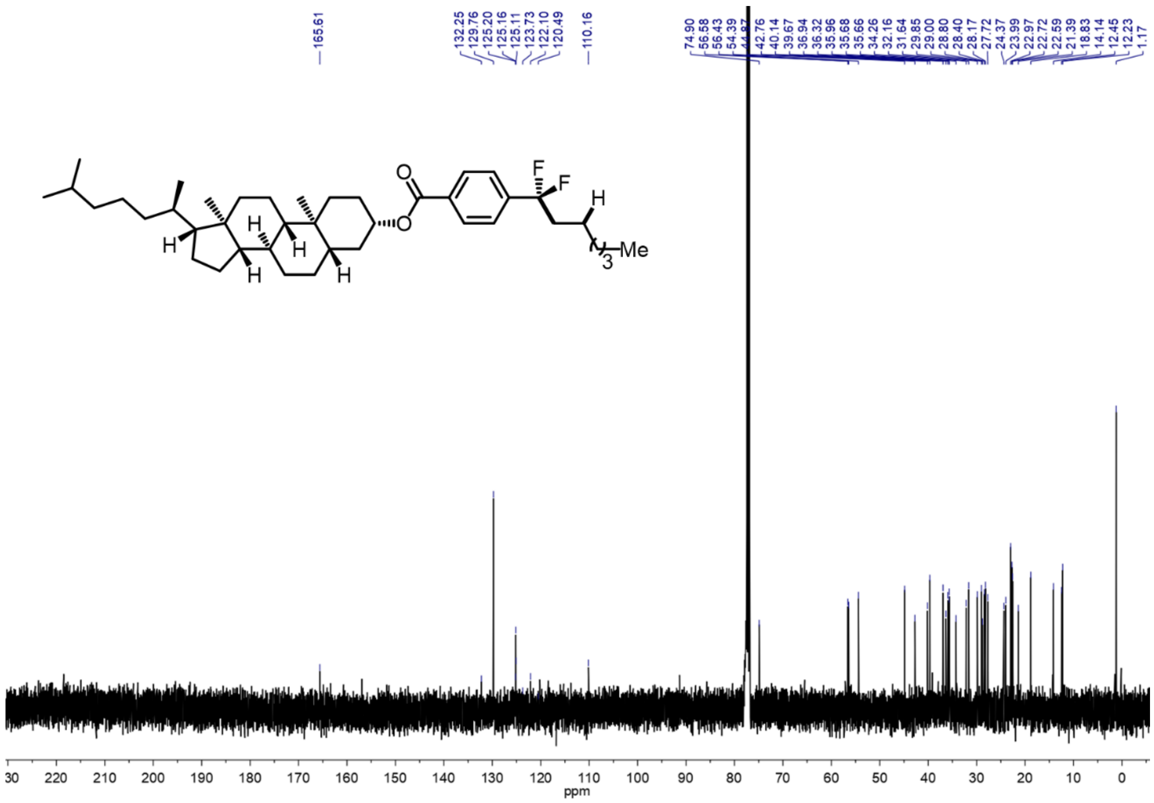
^{13}C NMR spectrum (126 MHz, CDCl$_3$, 23 ºC) of **5x**



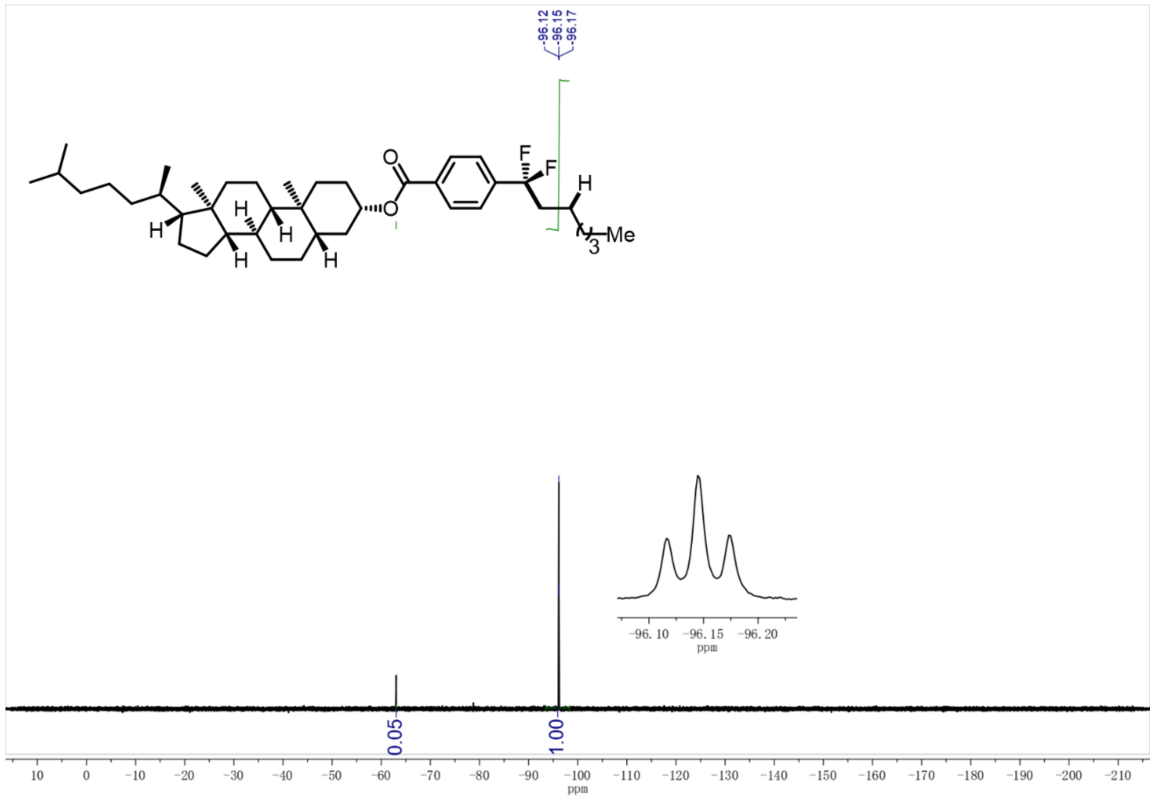
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5x**



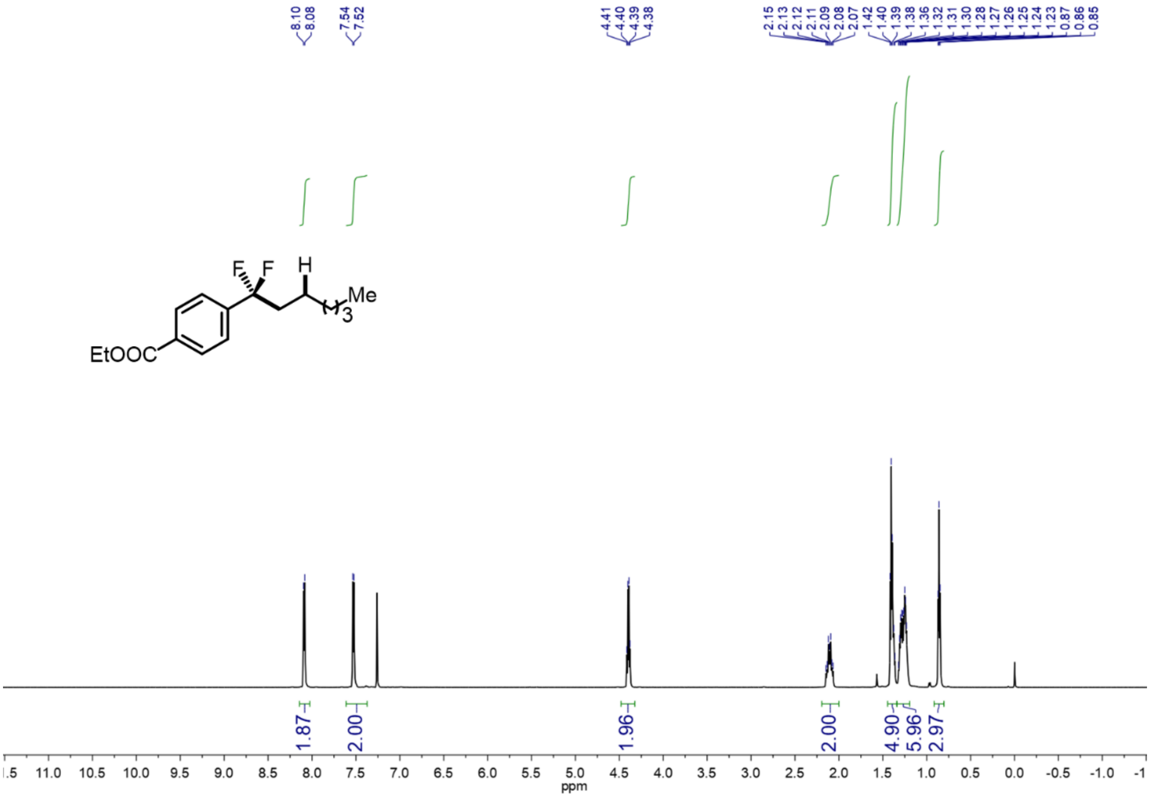
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5y**



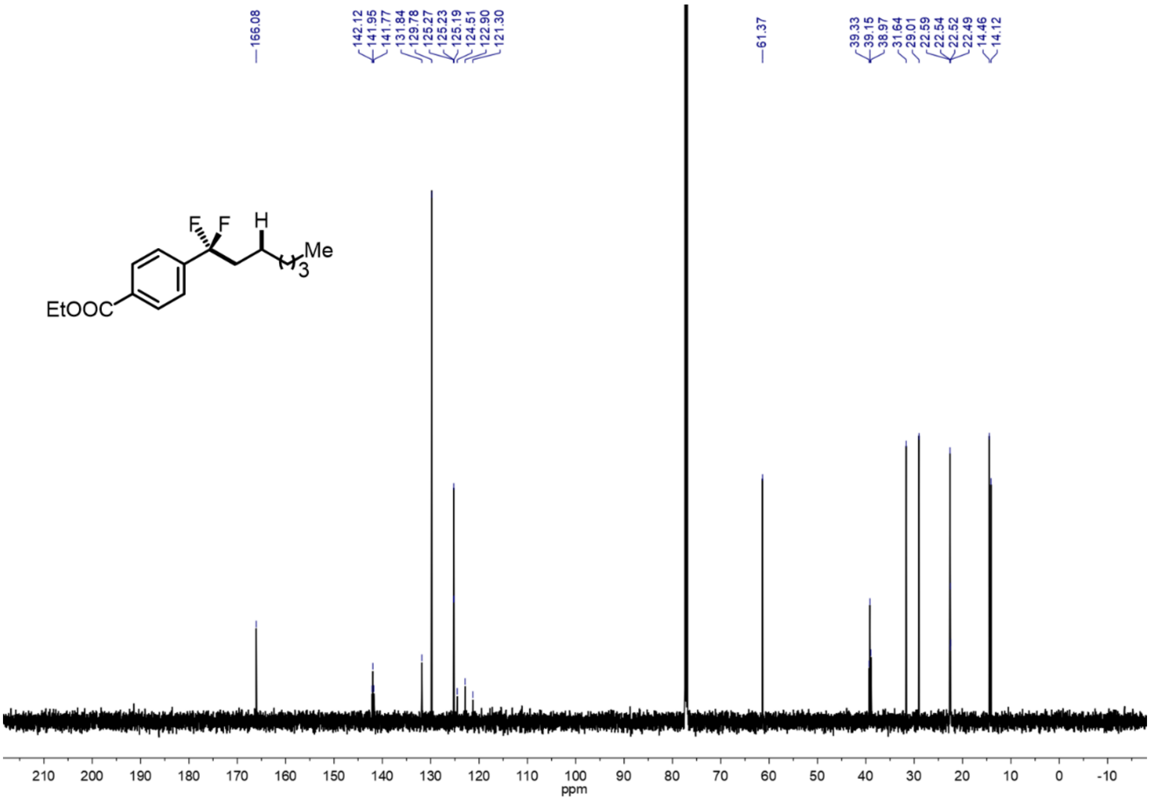
^{13}C NMR spectrum (126 MHz, CDCl$_3$, 23 ºC) of **5y**



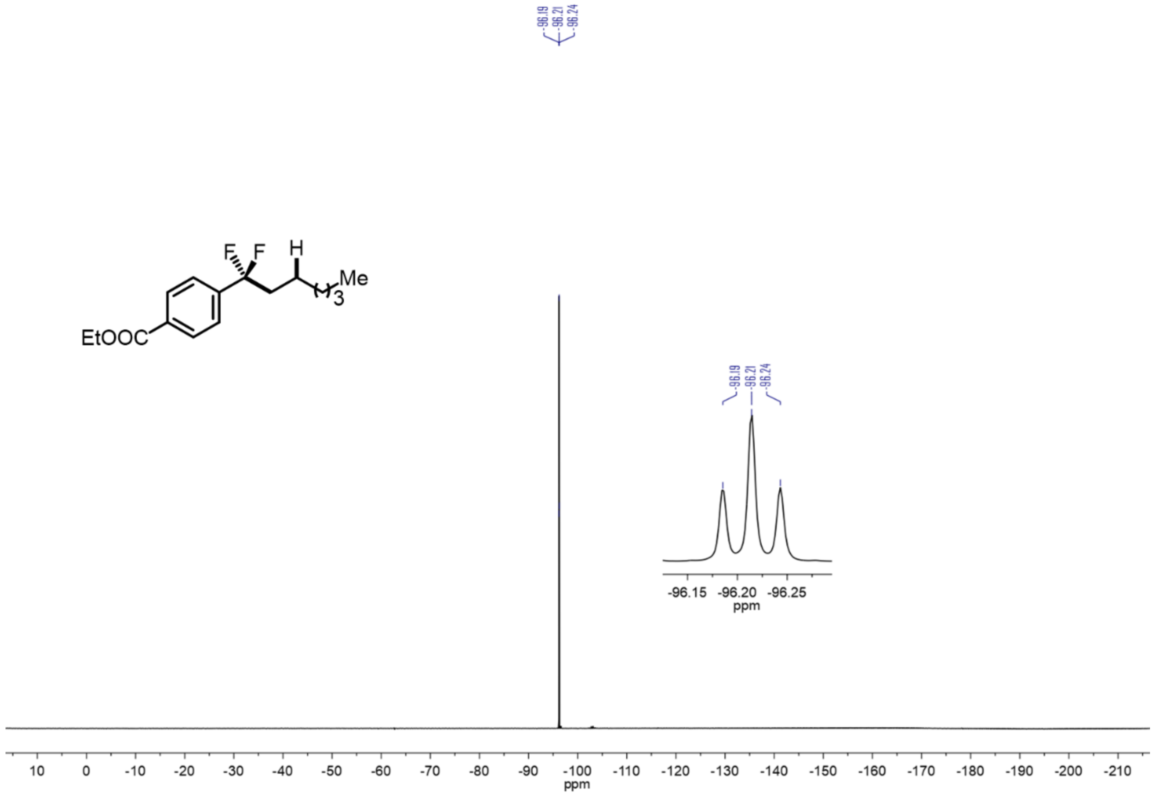
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5y**



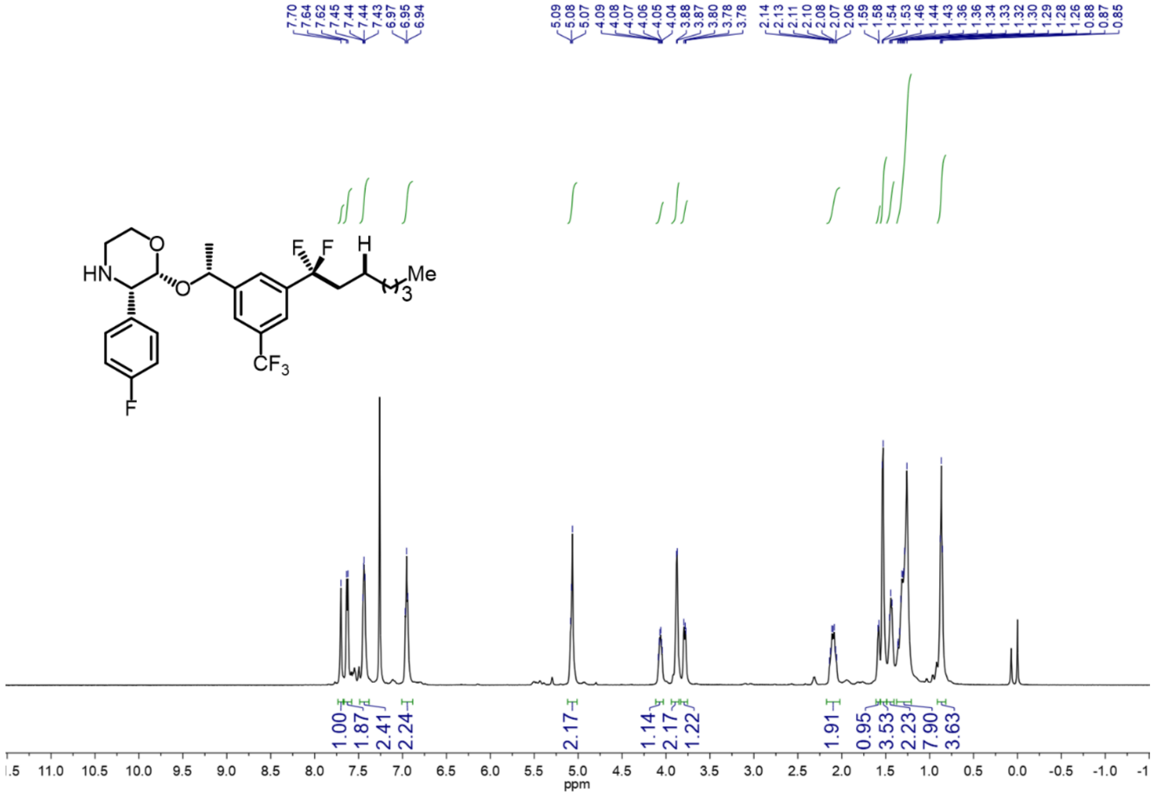
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5z**



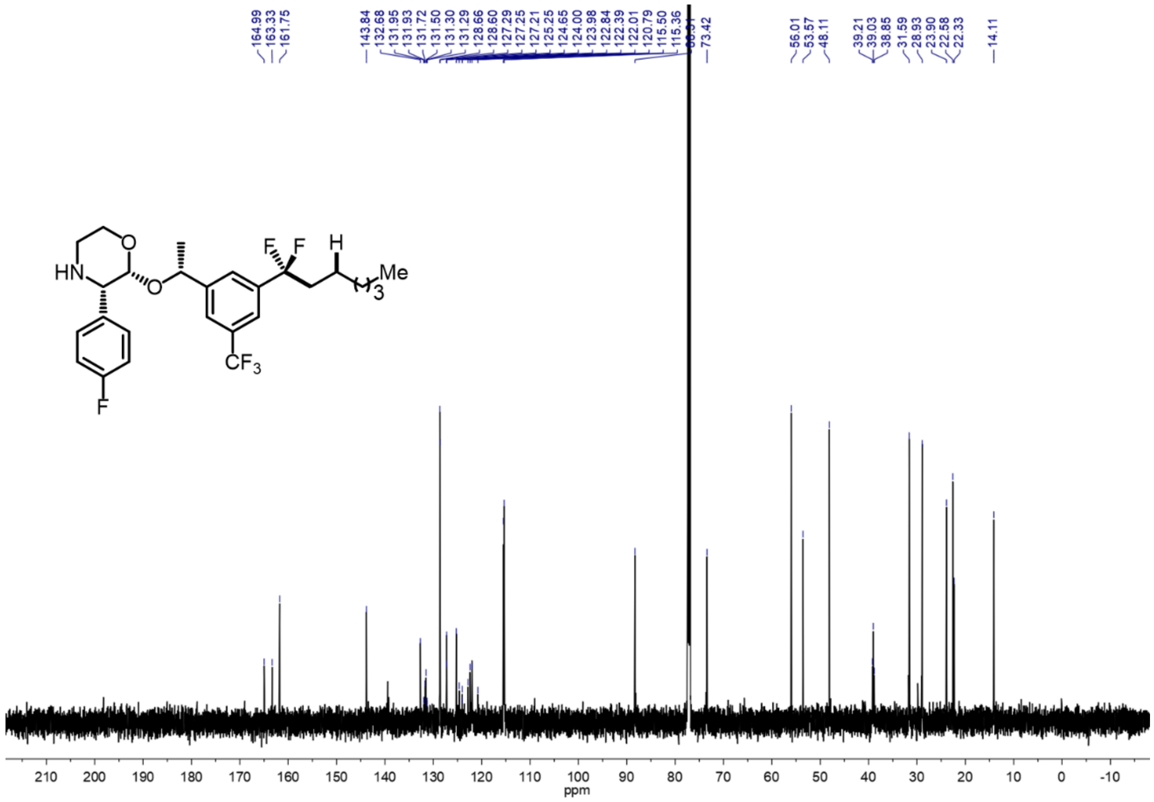
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5z**



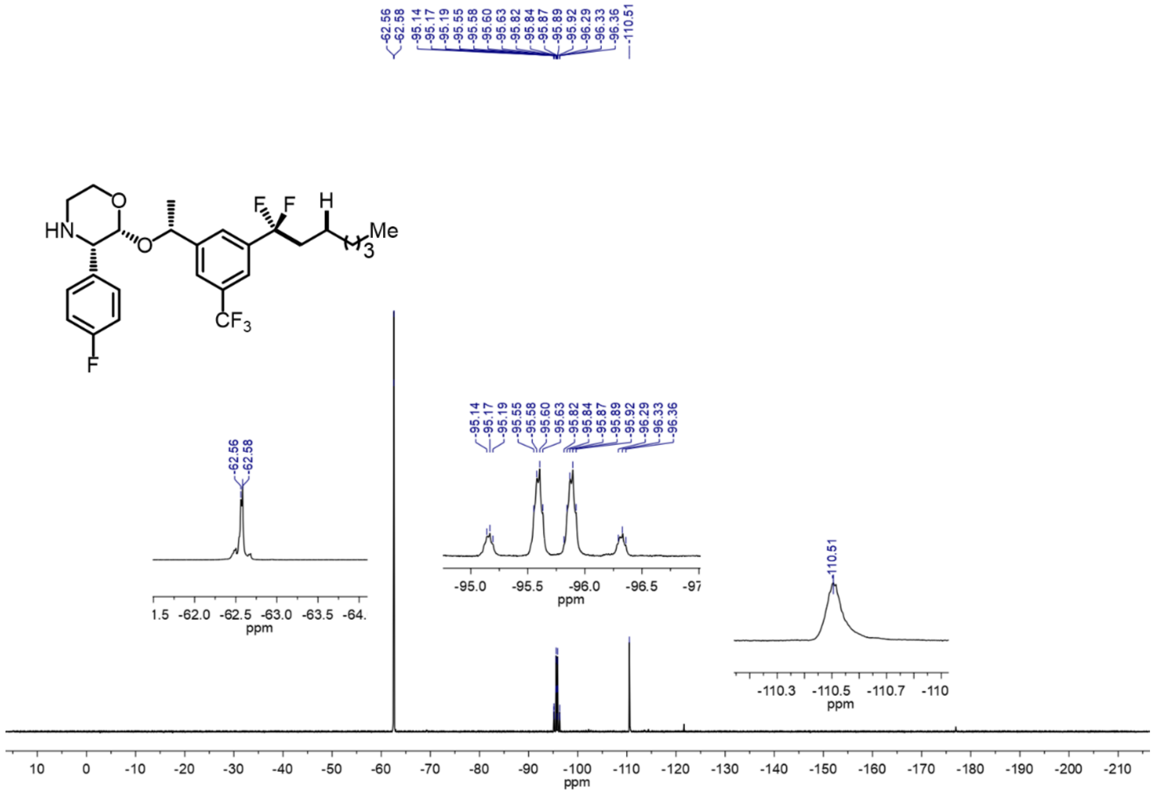
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5z**



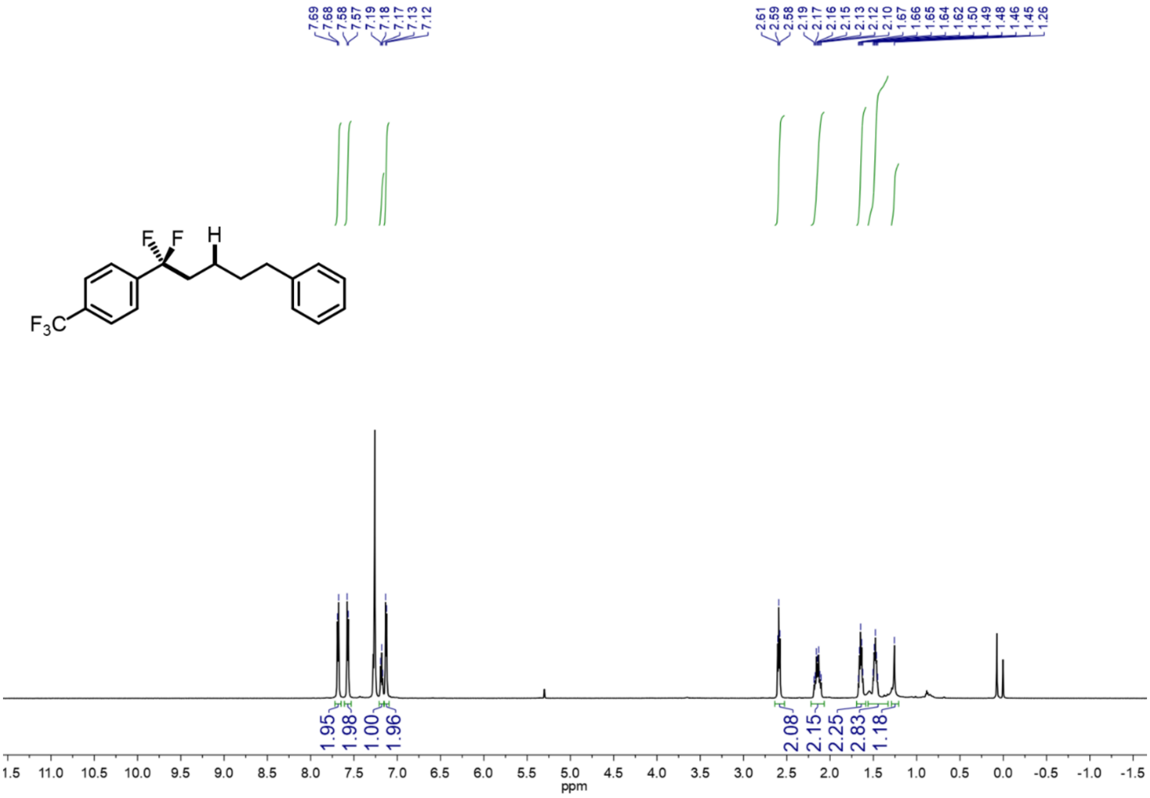
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5aa**



^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5aa**



^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5aa**



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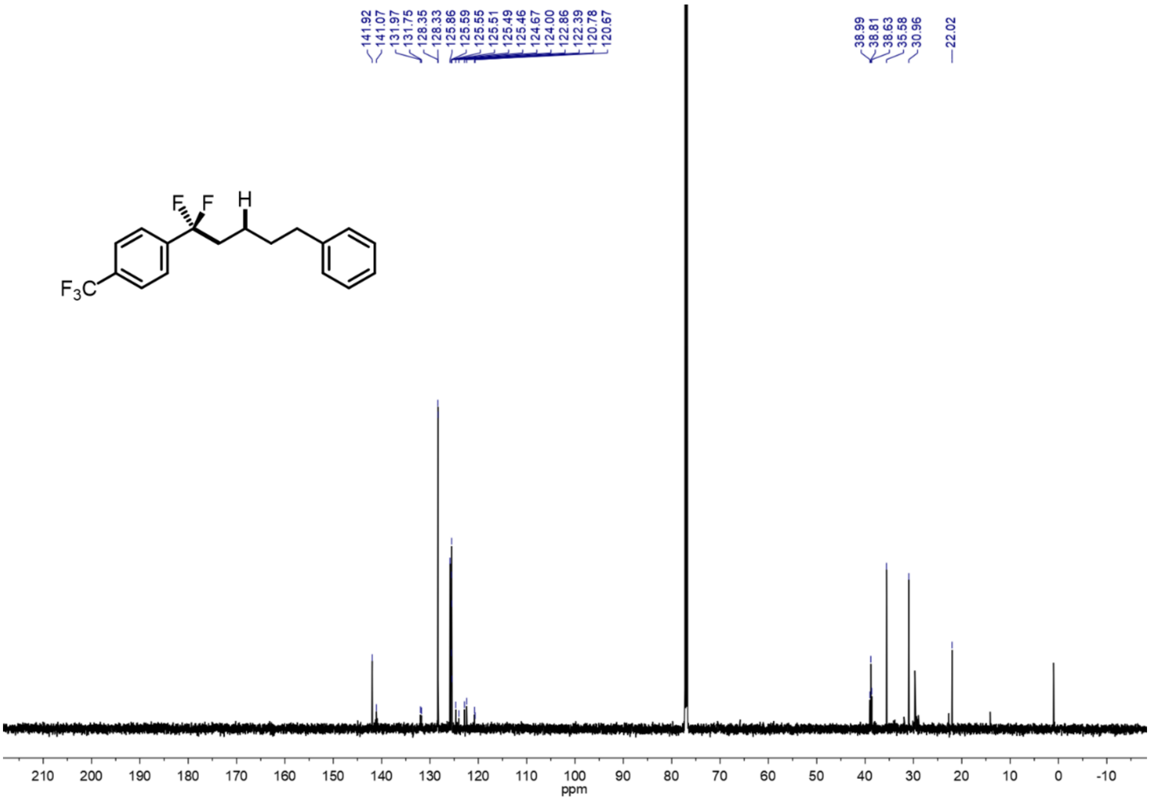
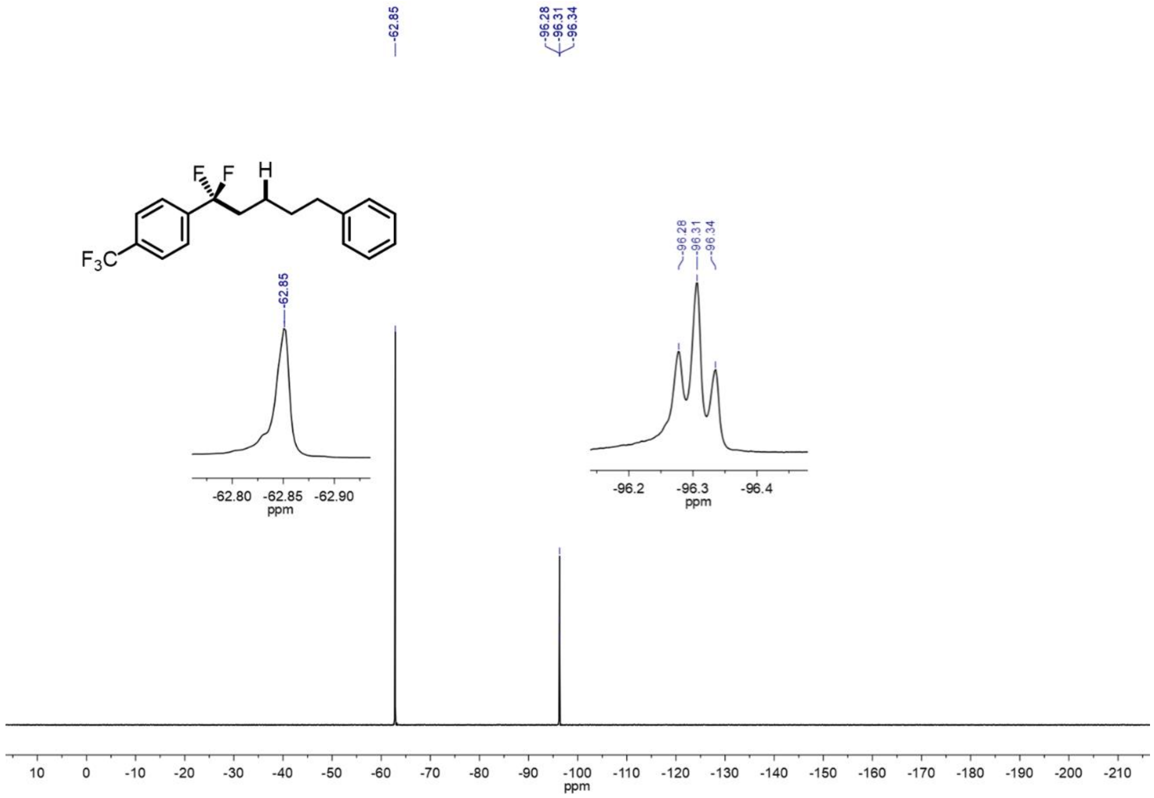
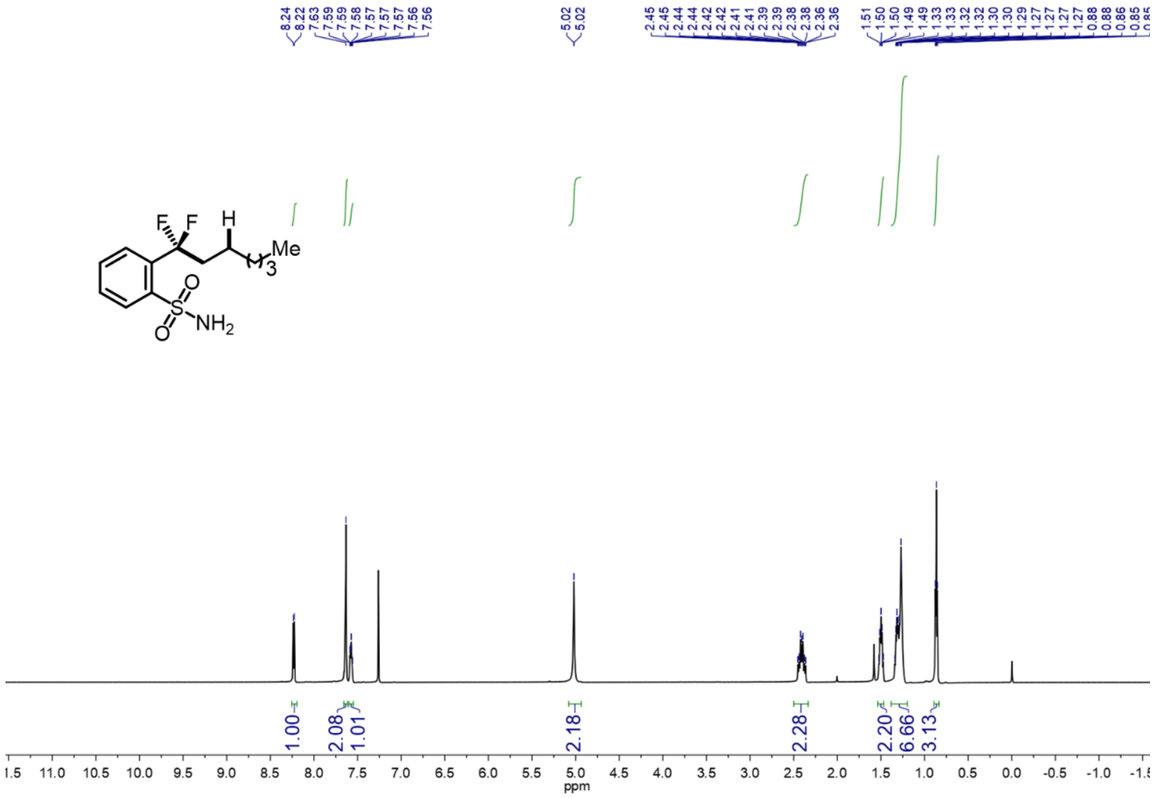


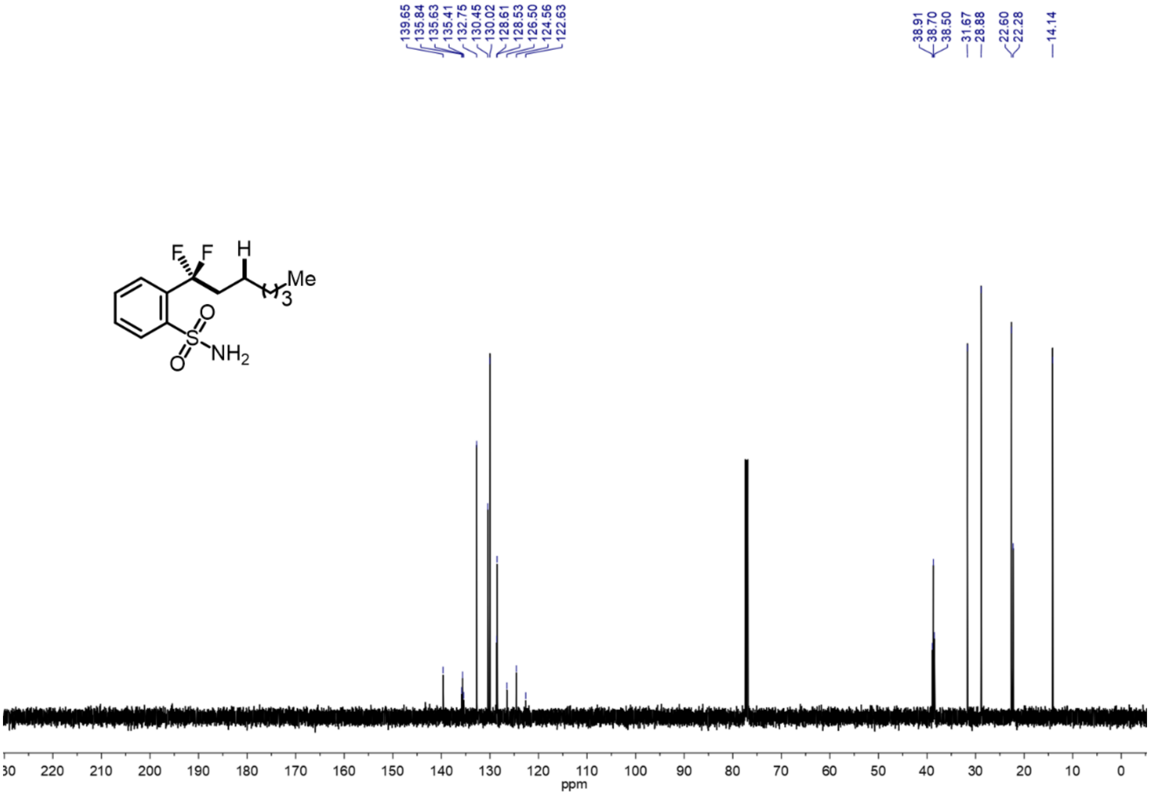
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5ab**



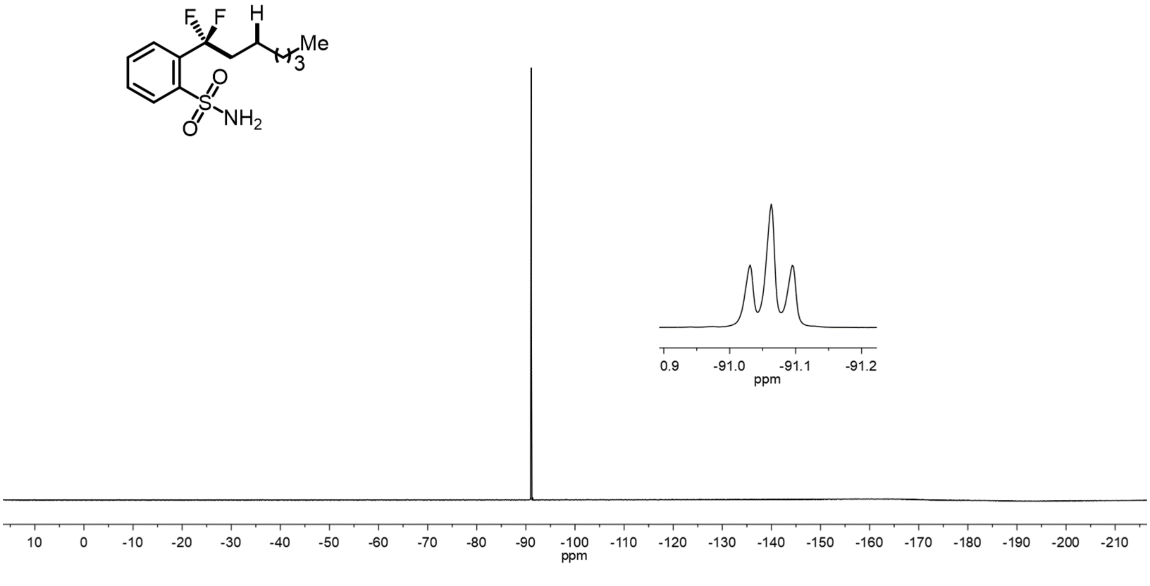
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5ab**



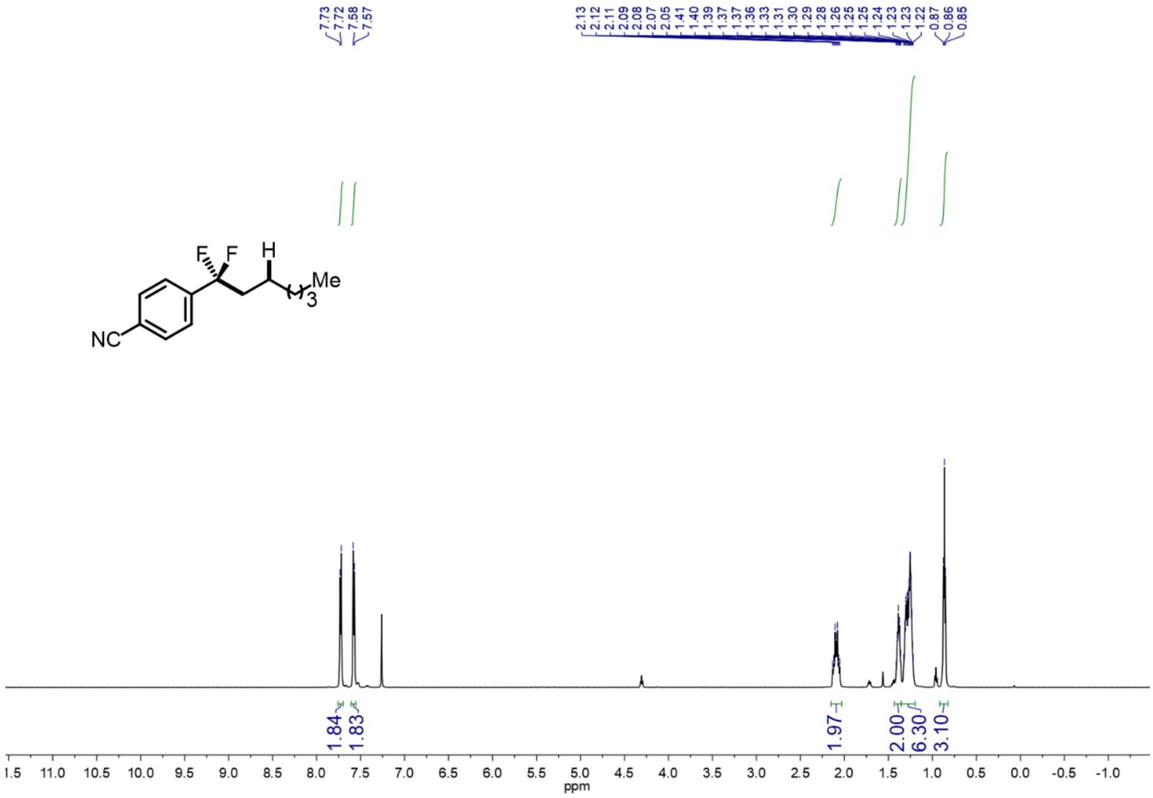
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5ac**



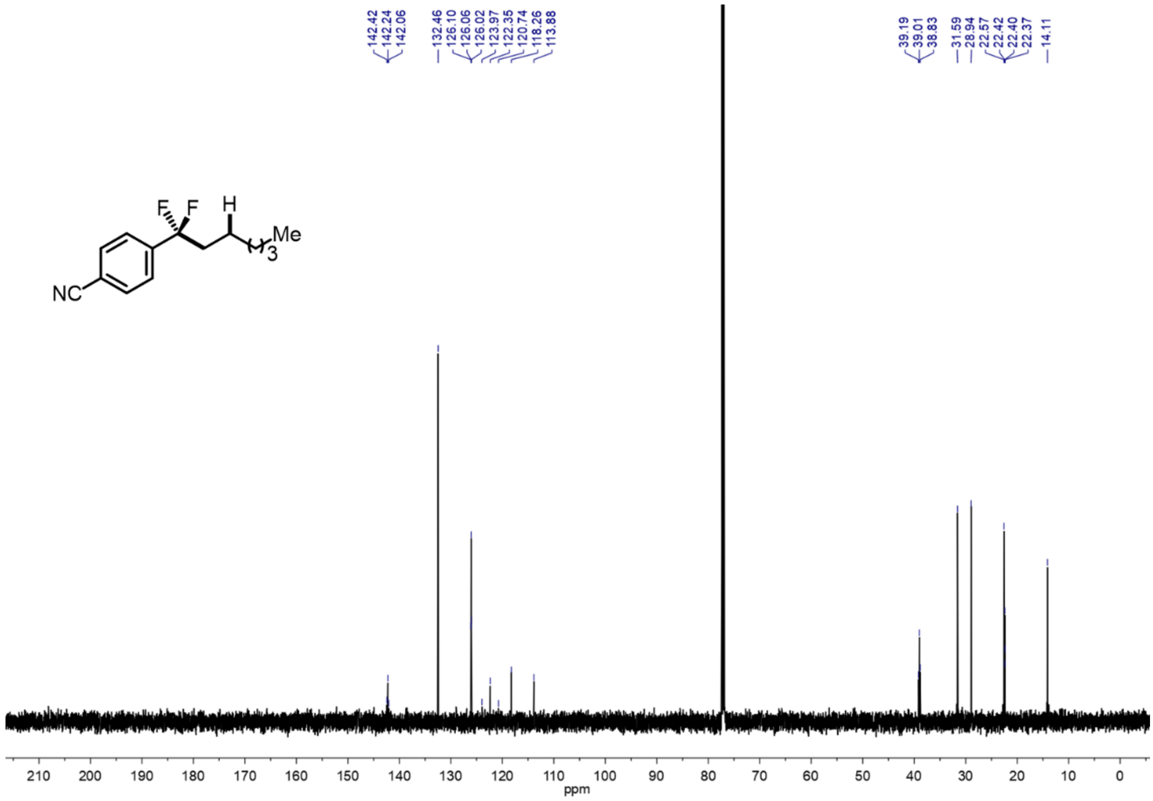
^{13}C NMR spectrum (126 MHz, CDCl$_3$, 23 ºC) of **5ac**



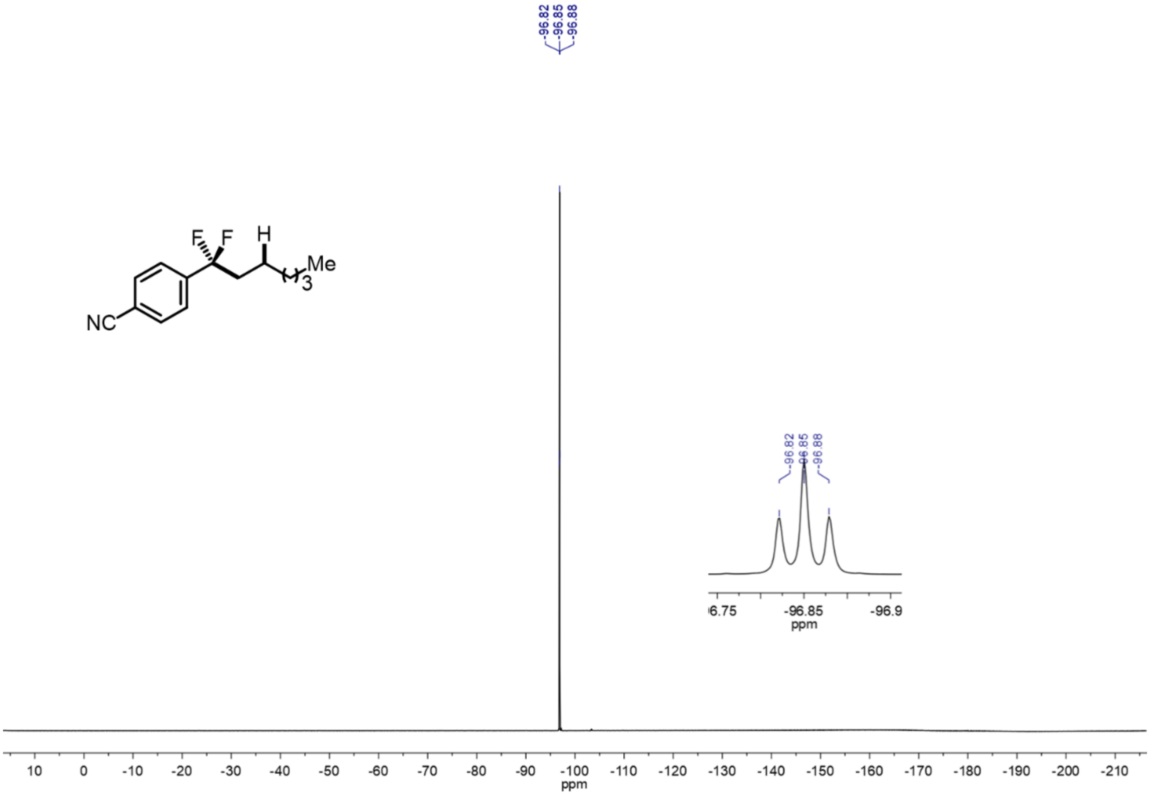
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5ac**



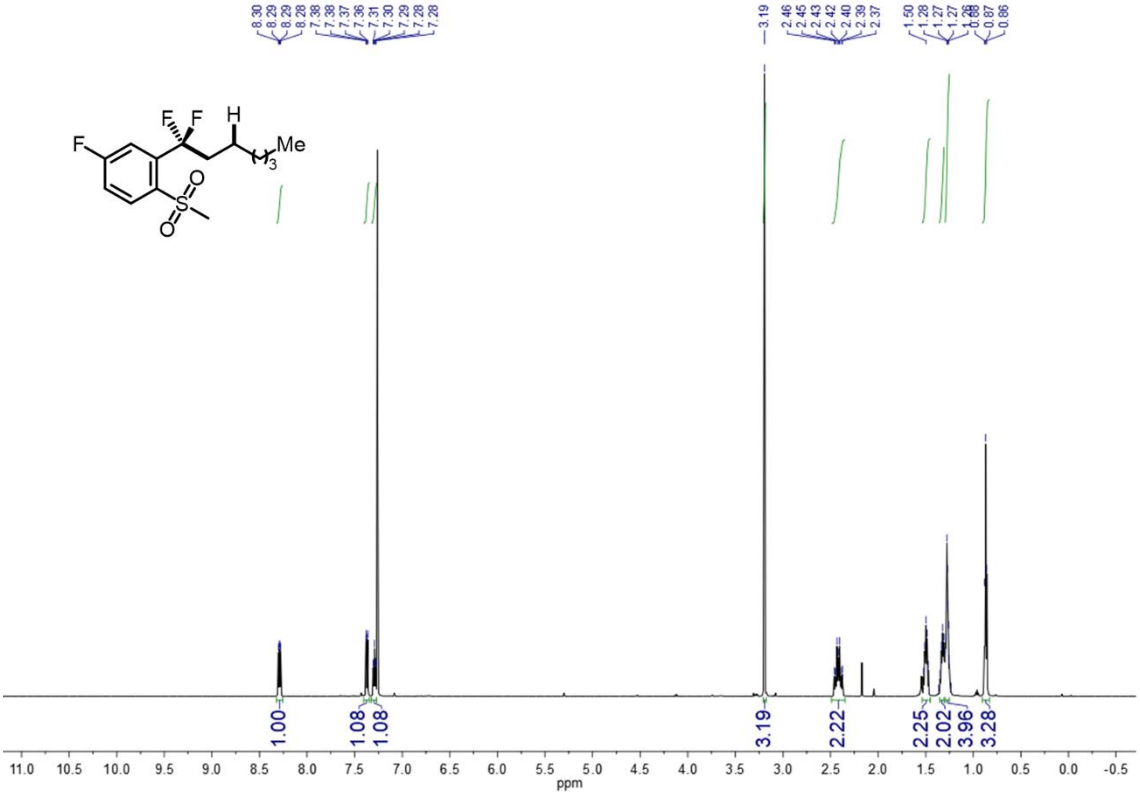
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5ad**



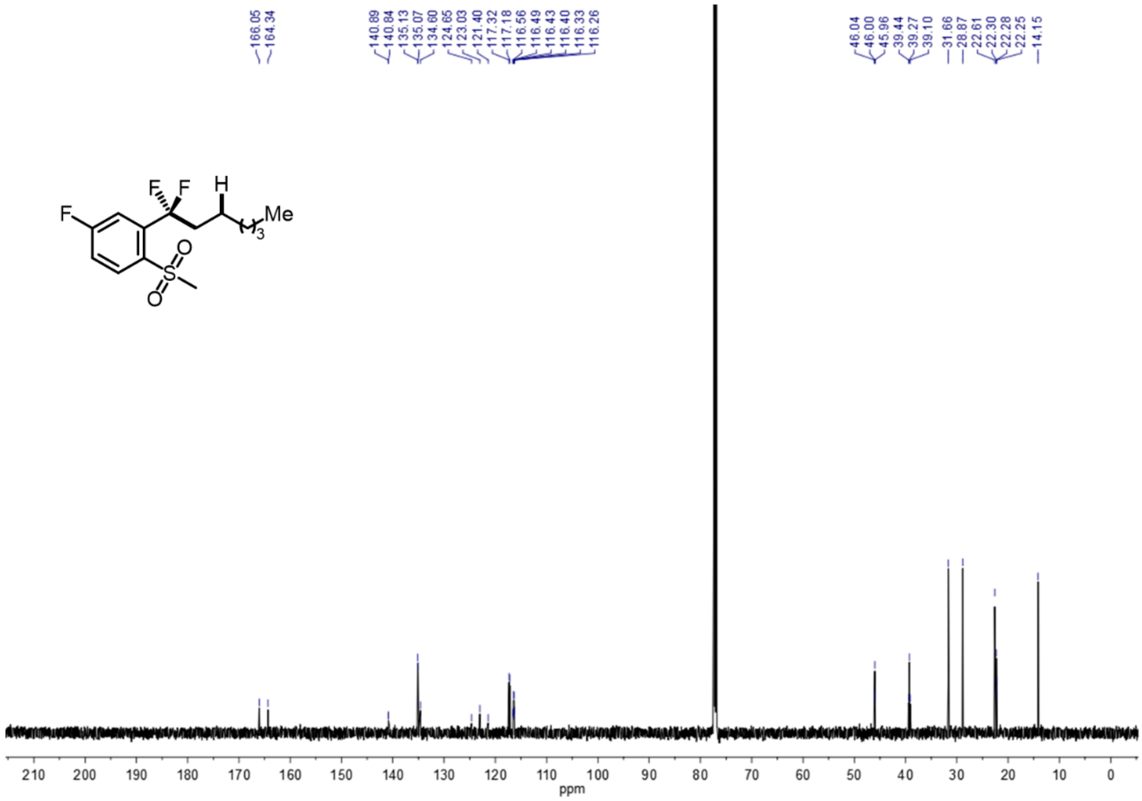
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5ad**



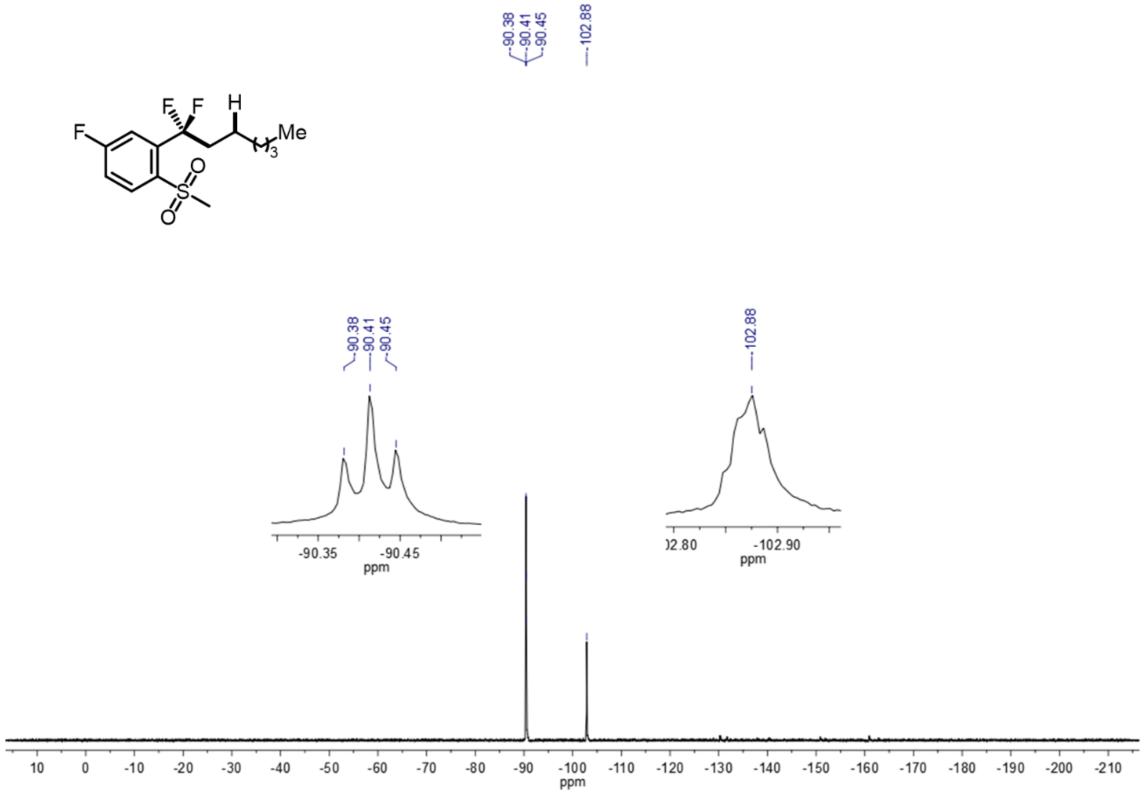
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5ad**



^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5ae**



^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5ae**



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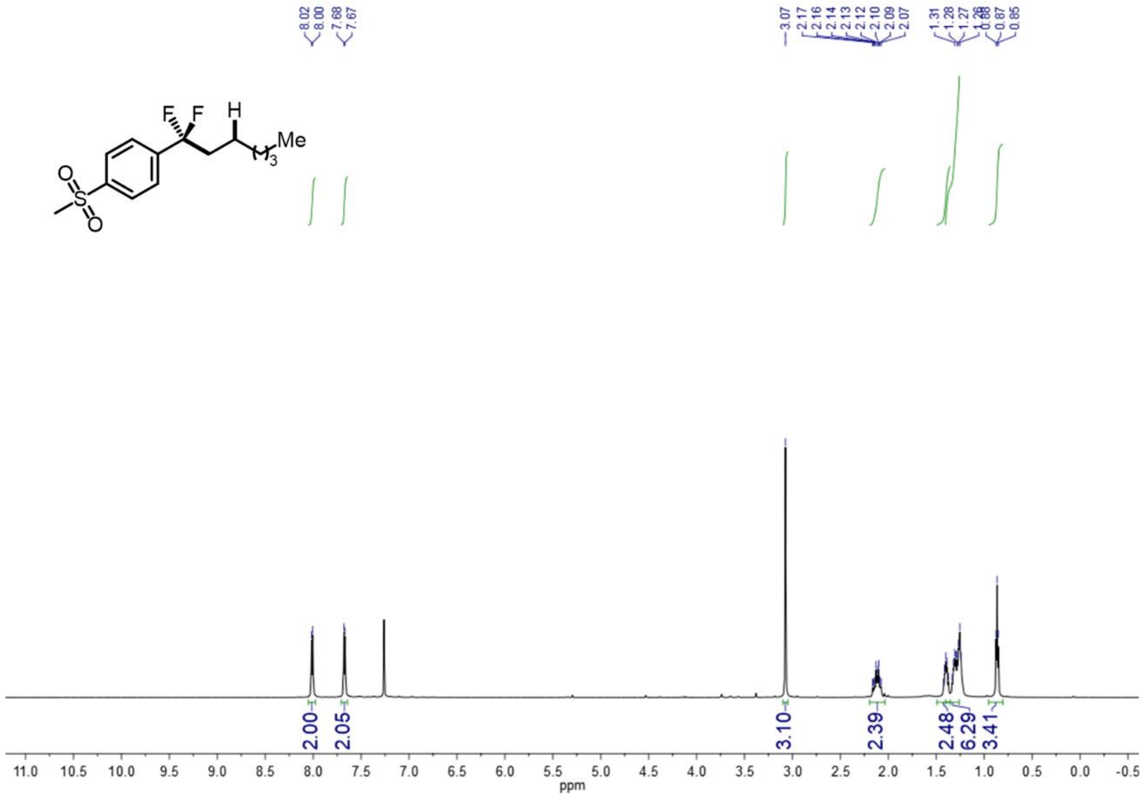
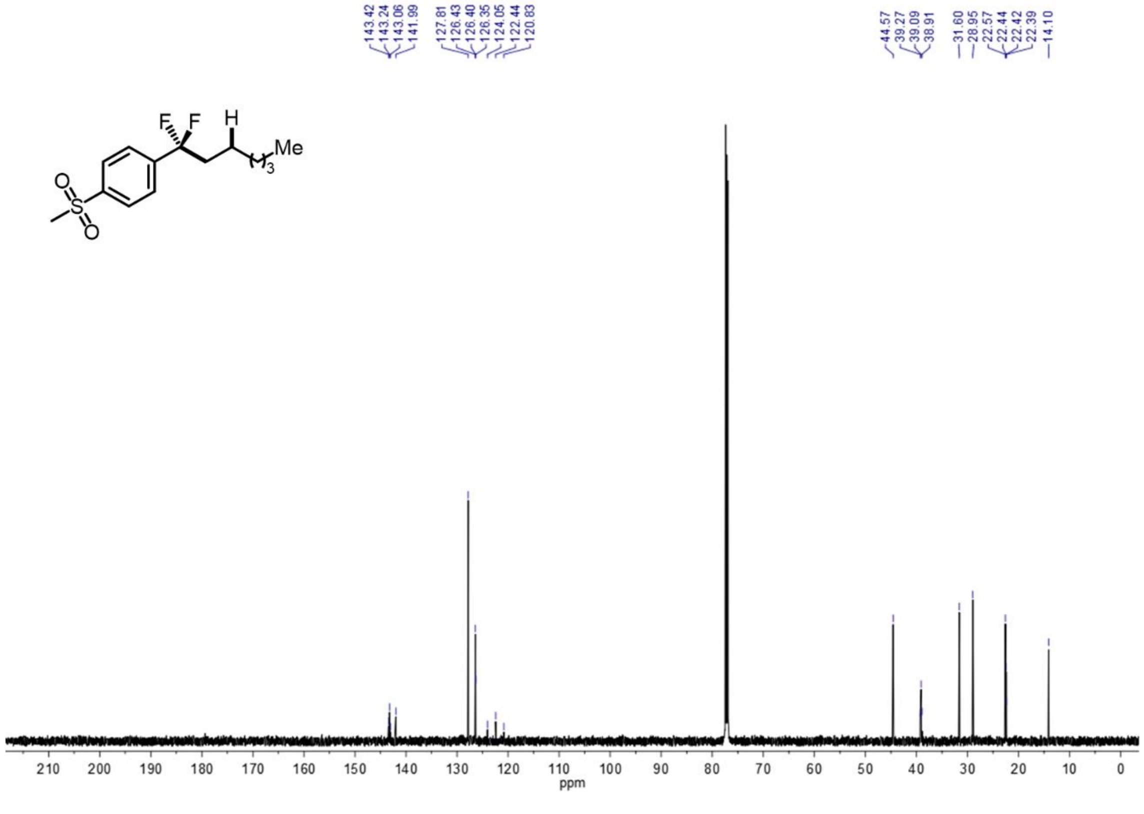
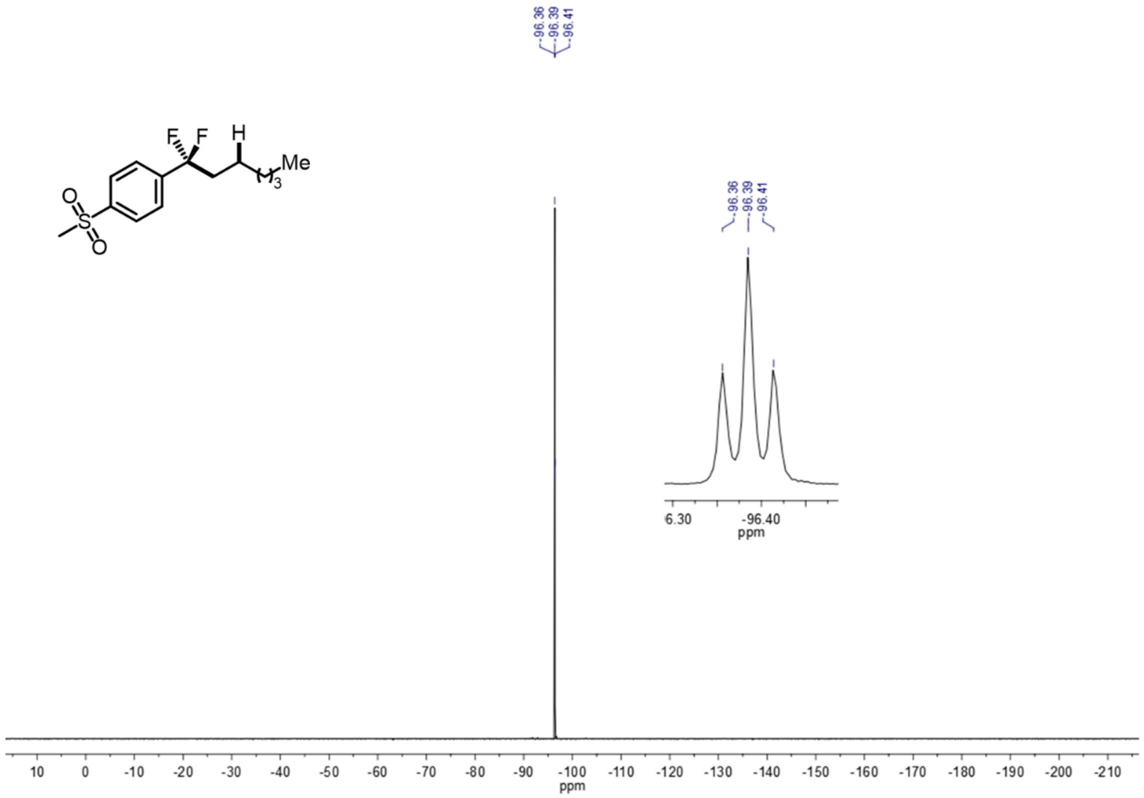


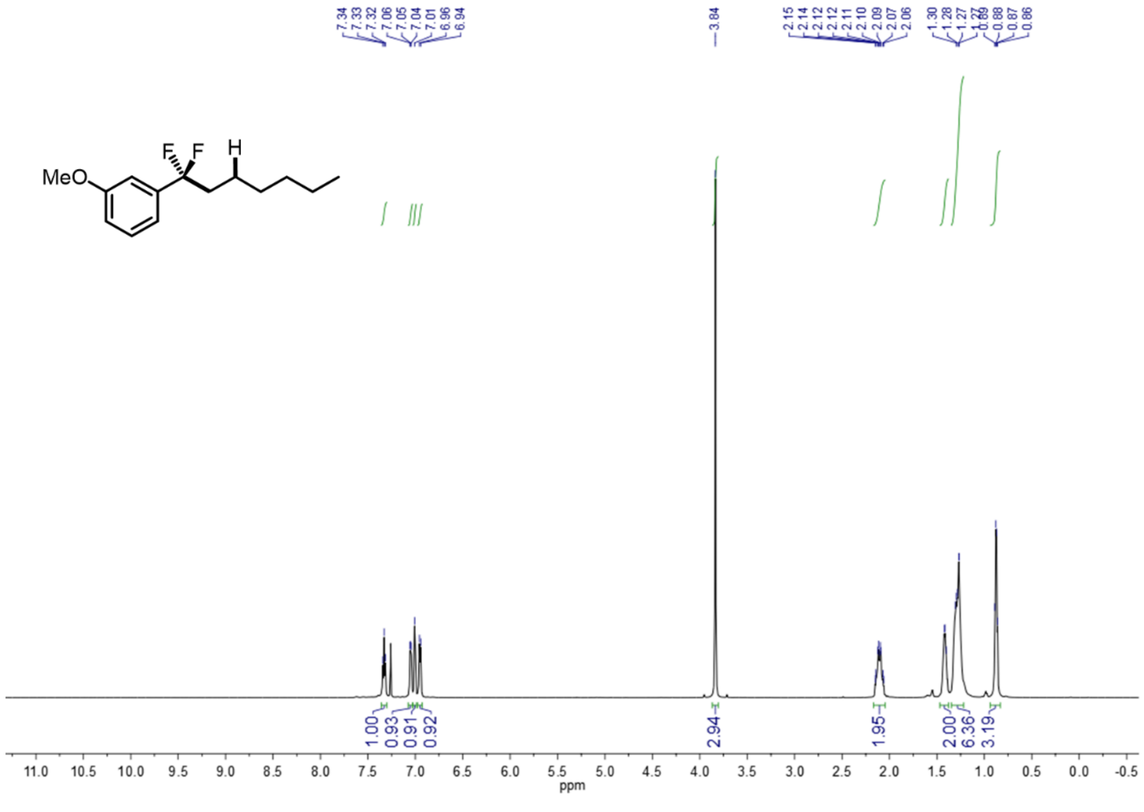
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **5af**



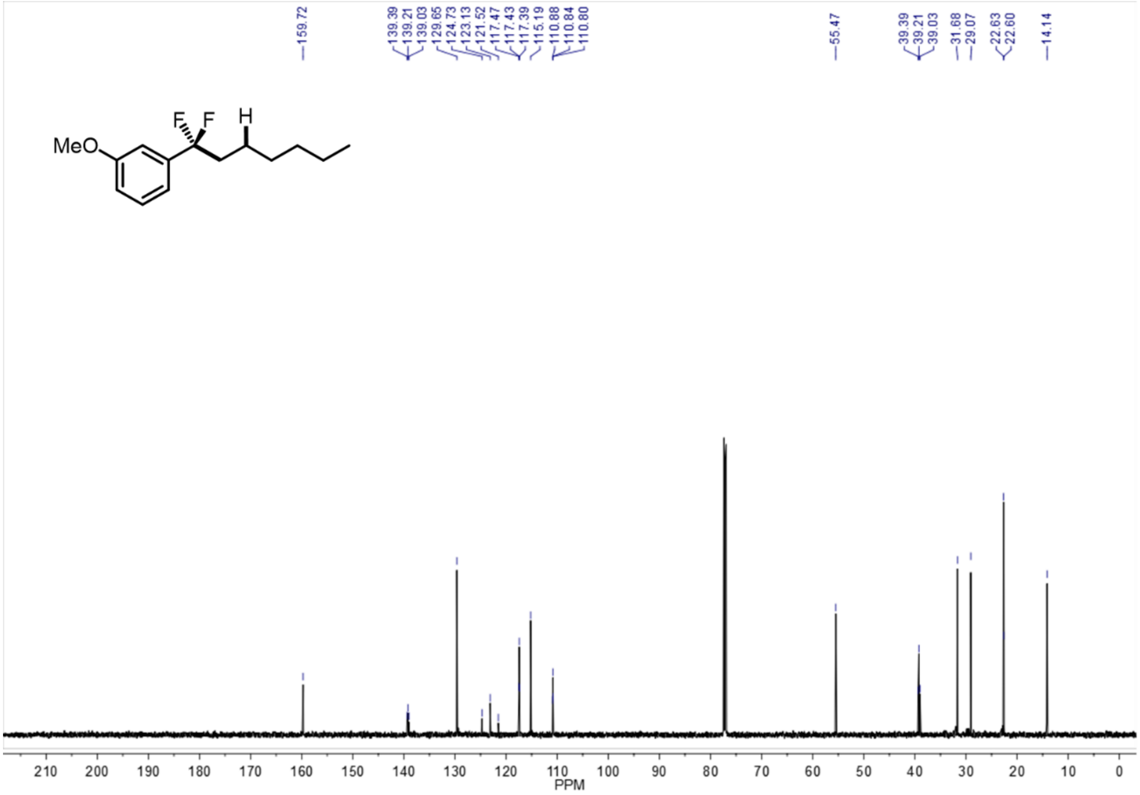
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **5af**



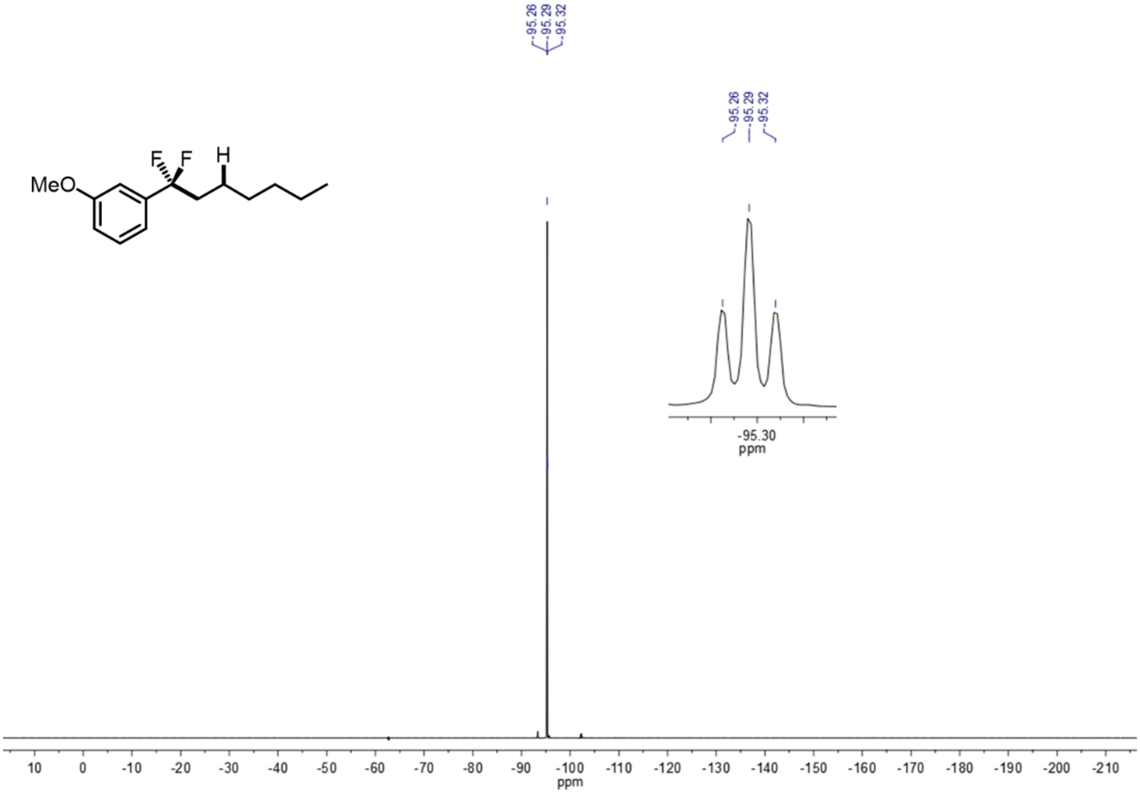
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **5af**



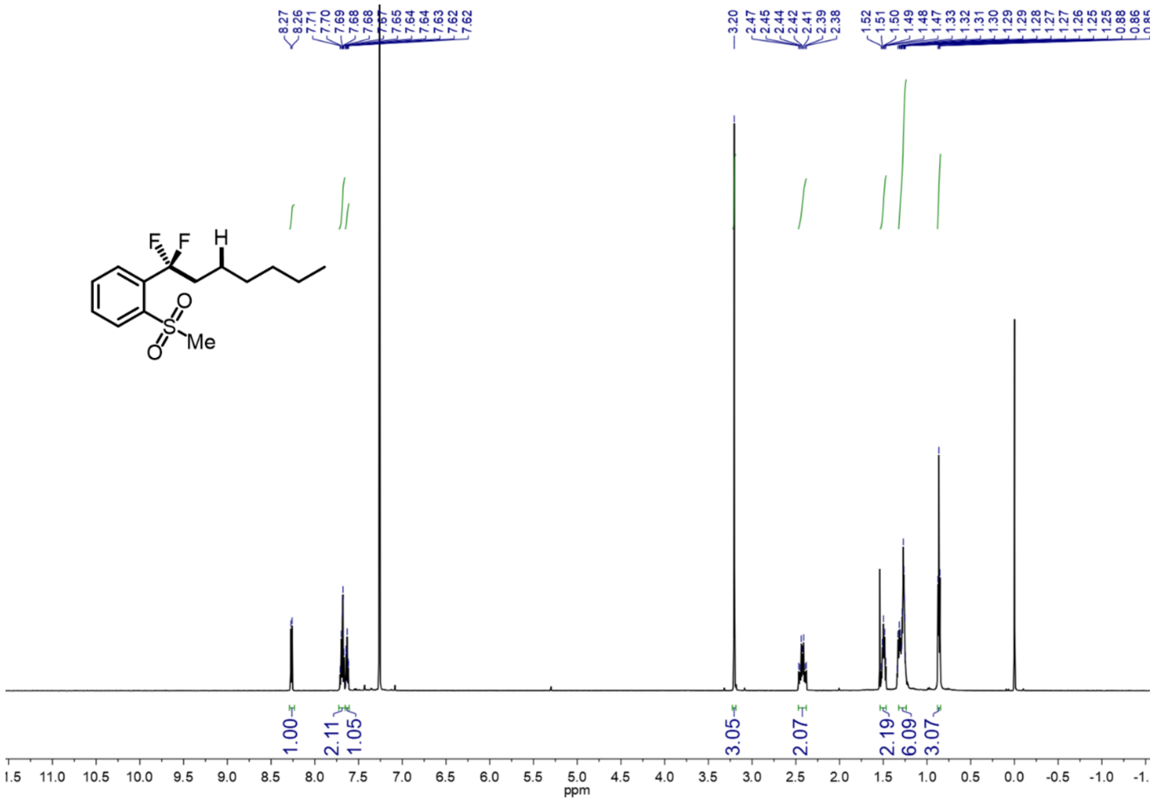
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6a**



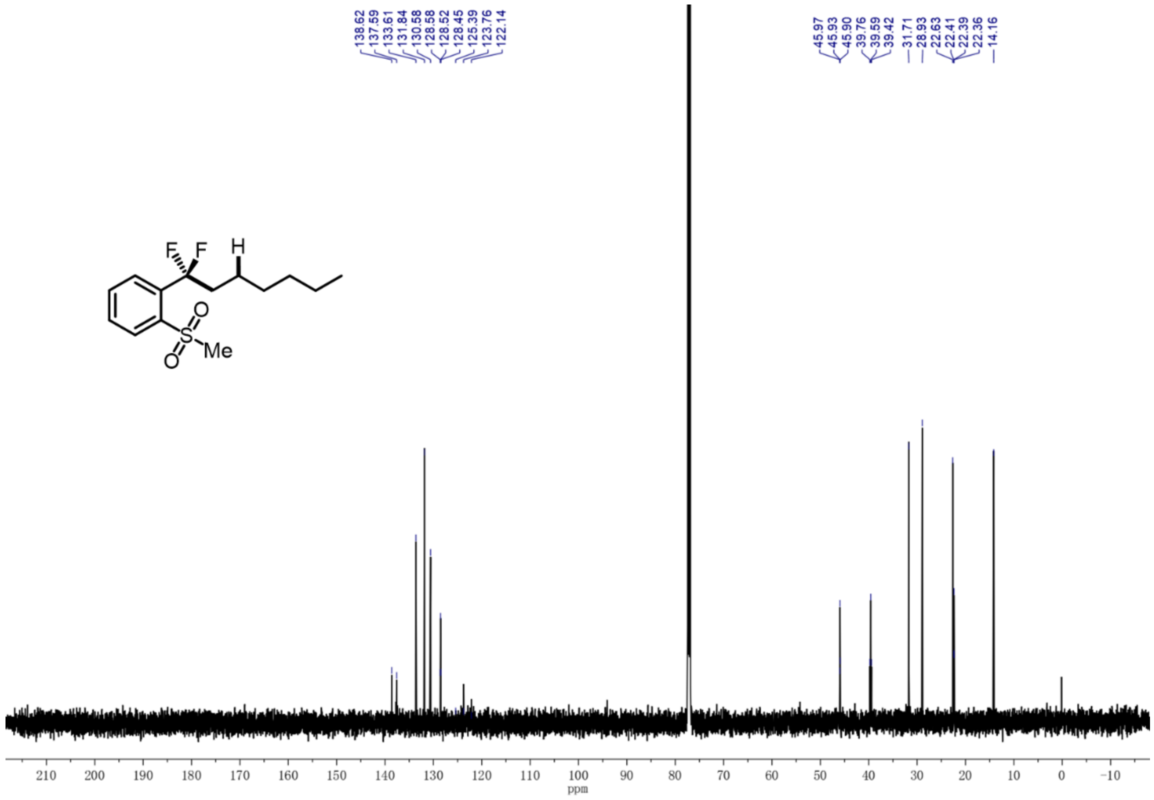
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6a**



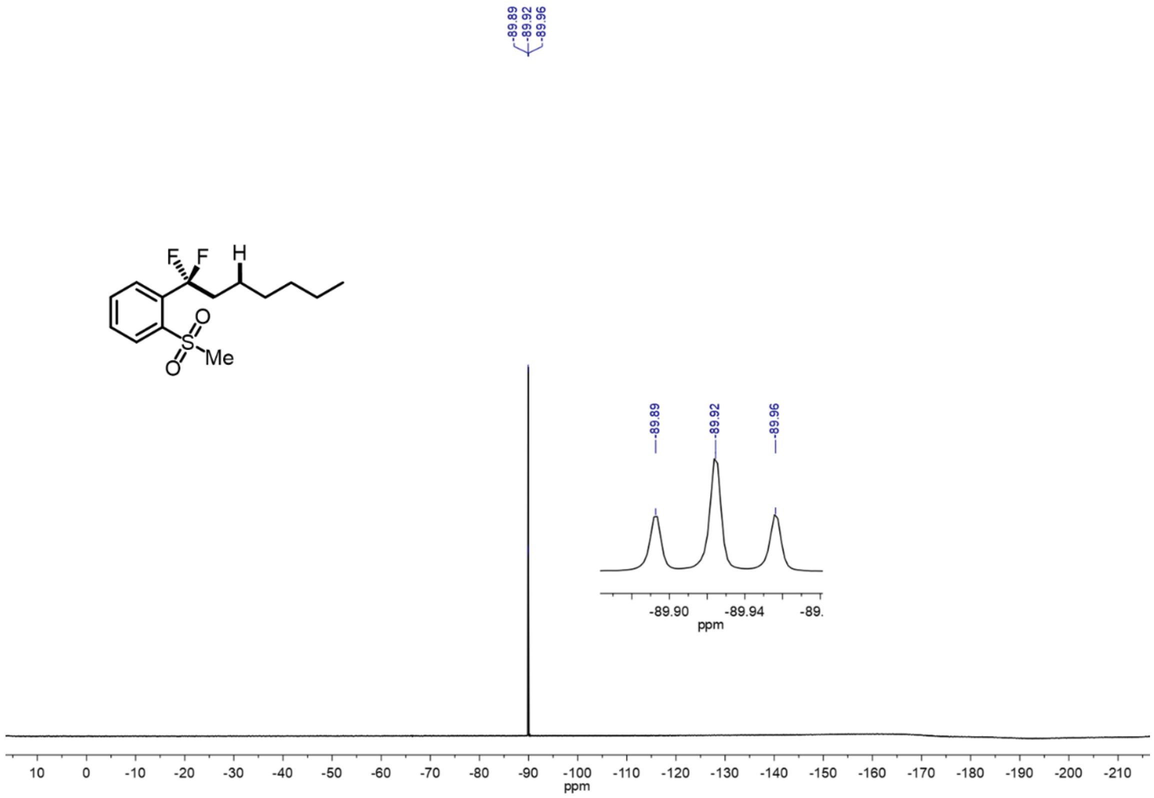
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6a**



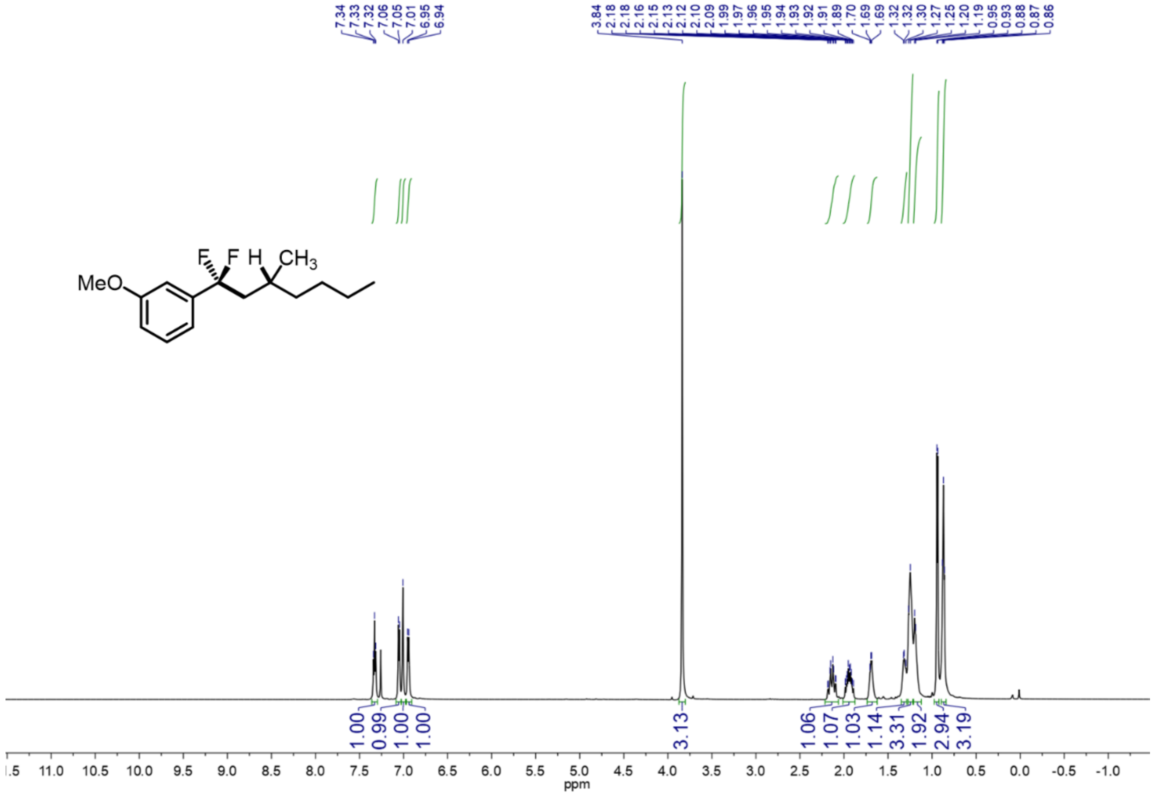
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6b**



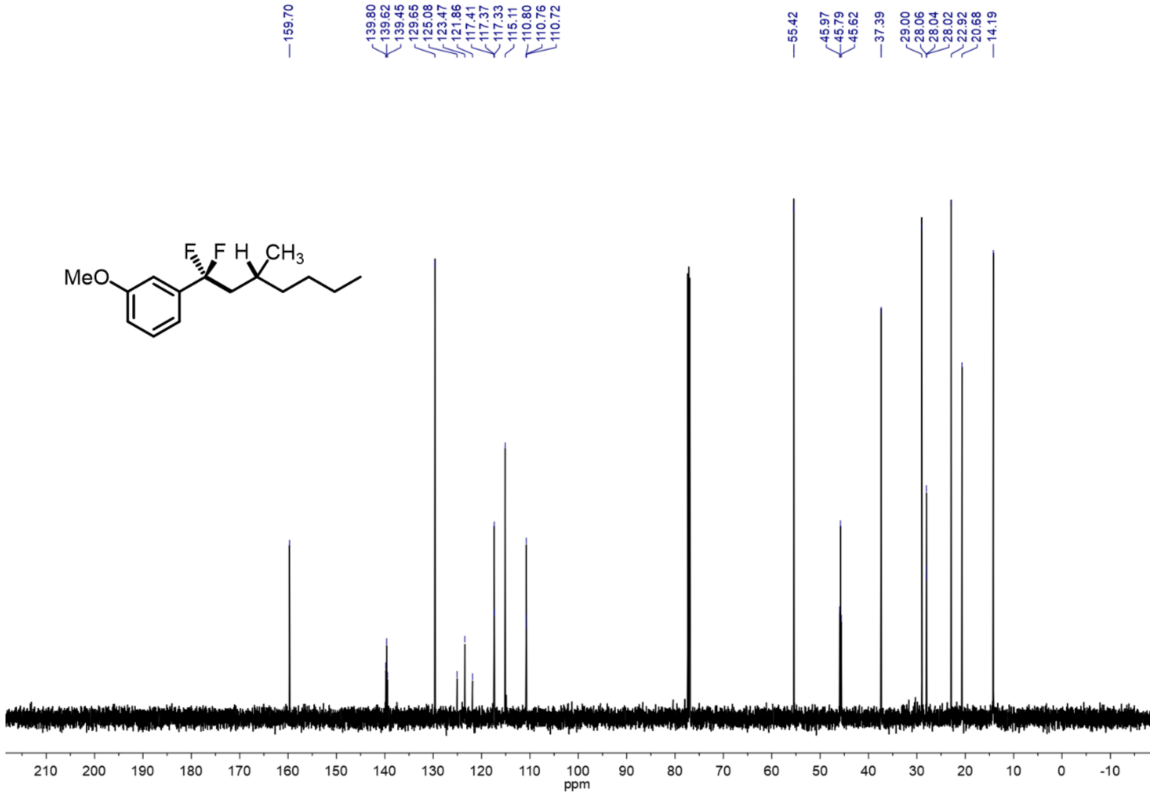
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6b**



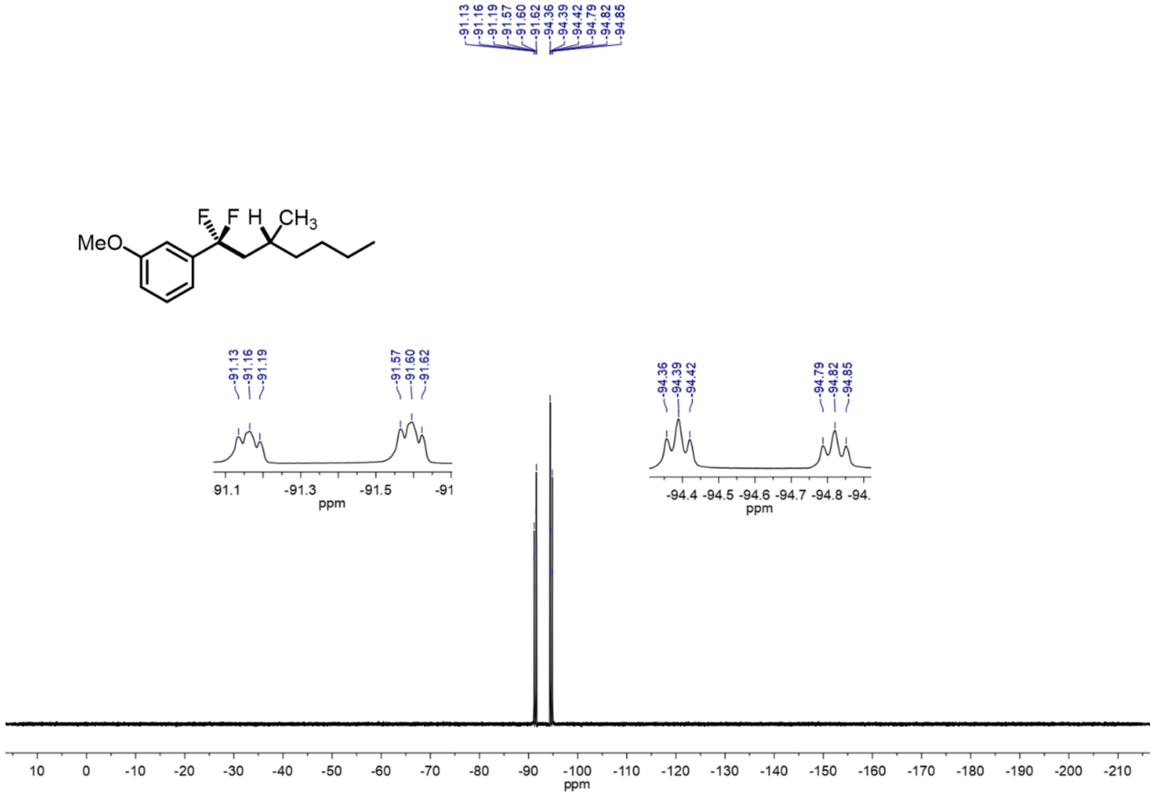
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6b**



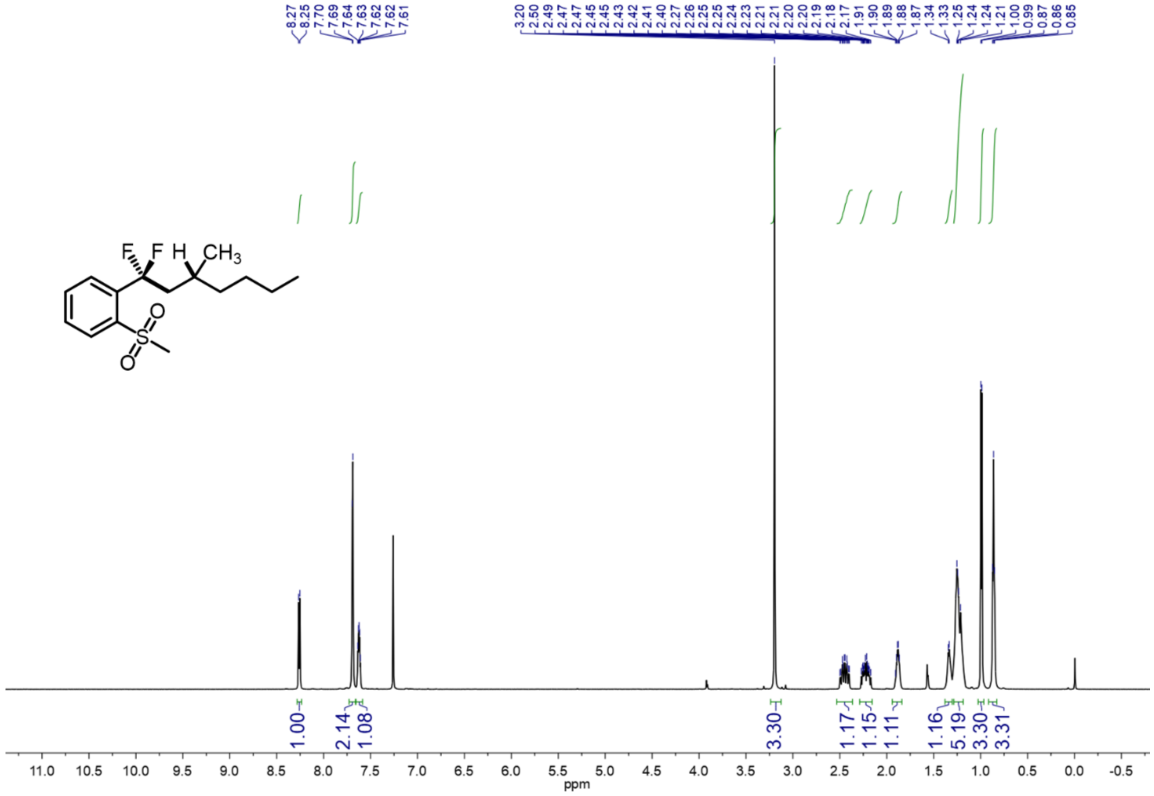
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6c**



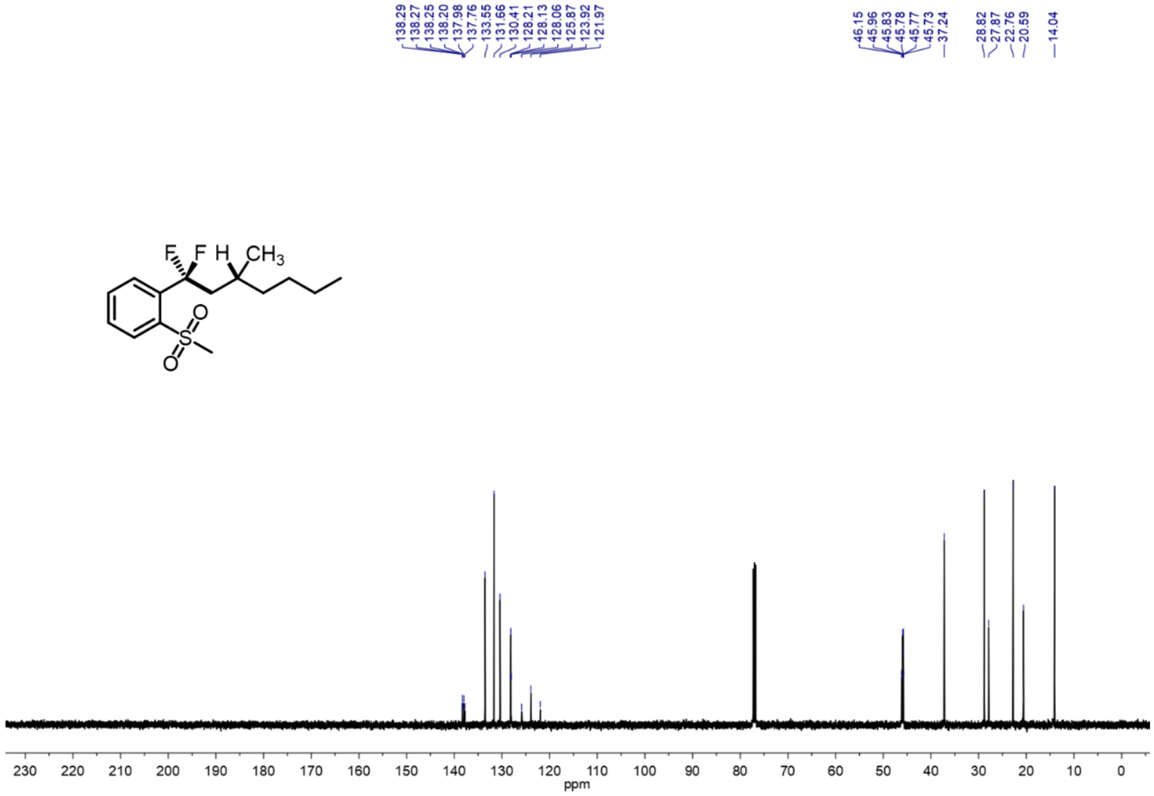
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6c**



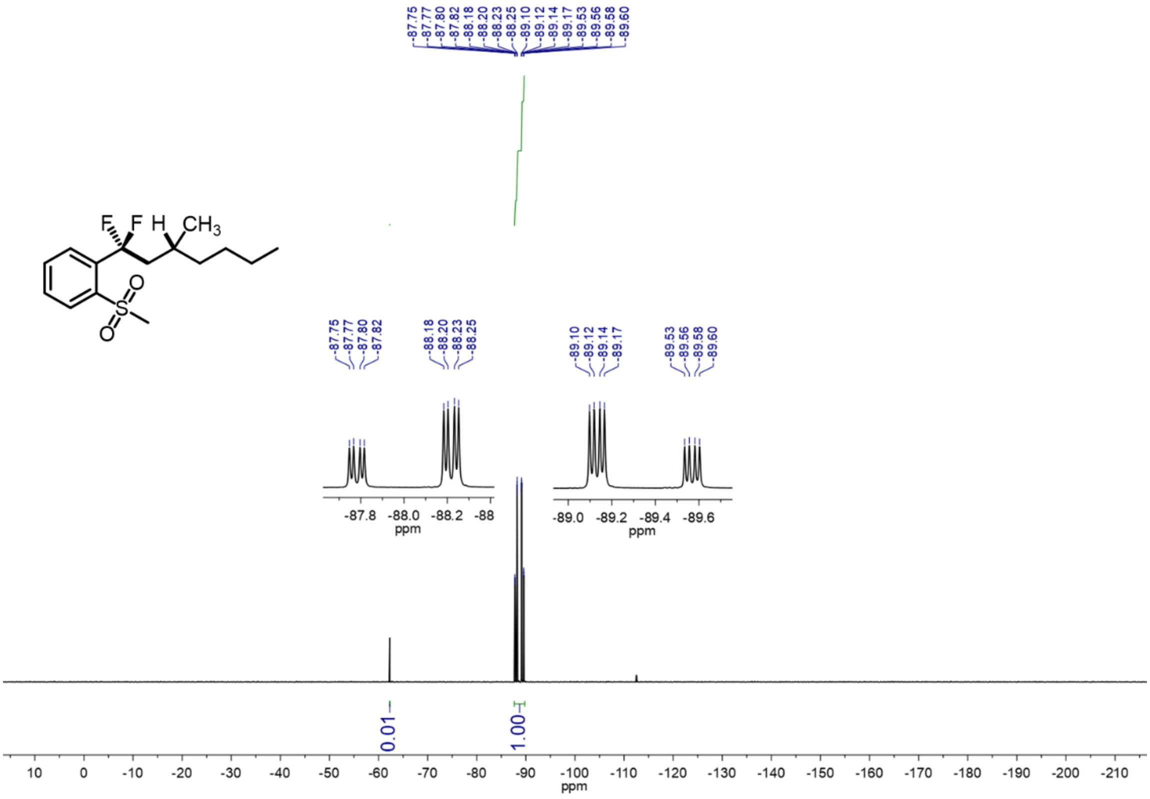
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6c**



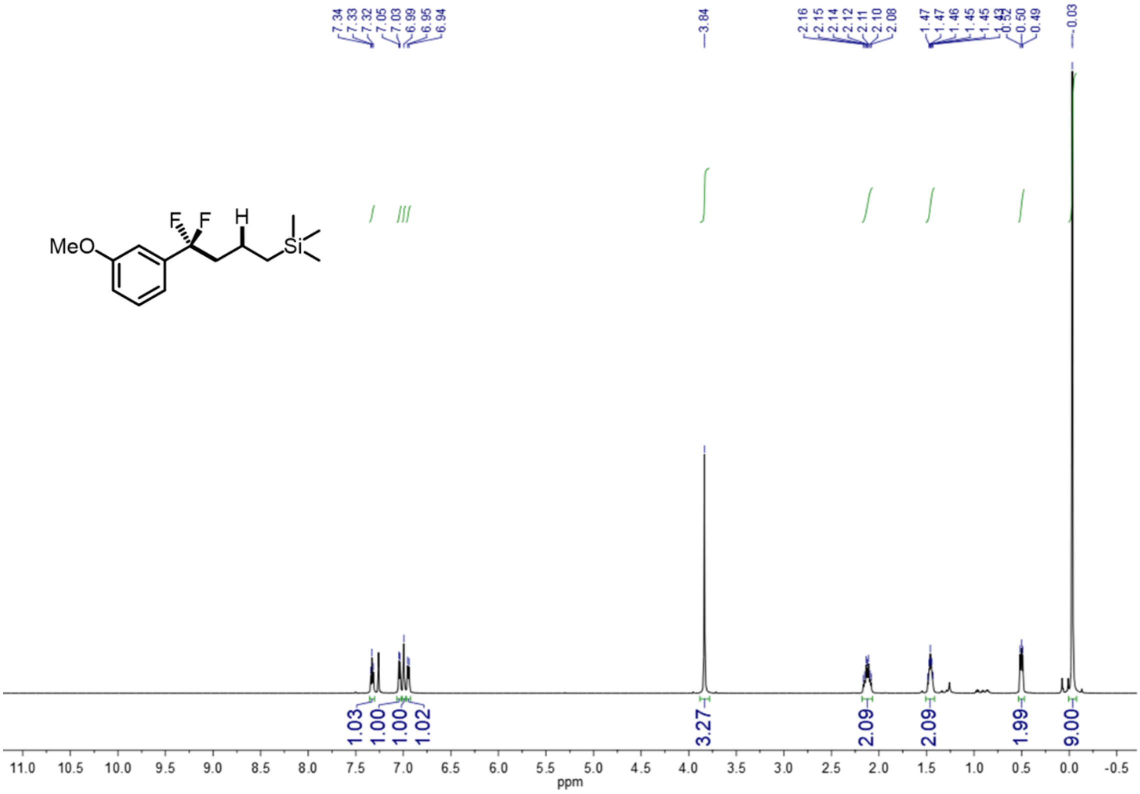
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6d**



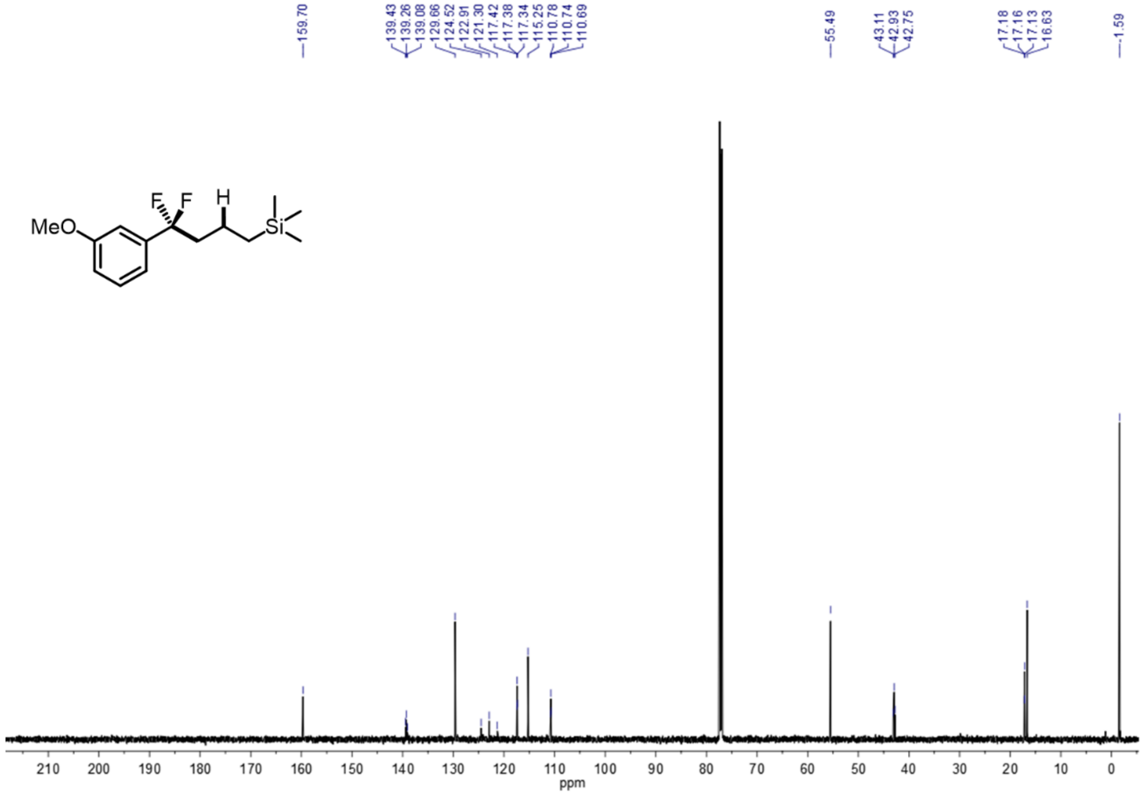
^{13}C NMR spectrum (126 MHz, CDCl$_3$, 23 ºC) of **6d**



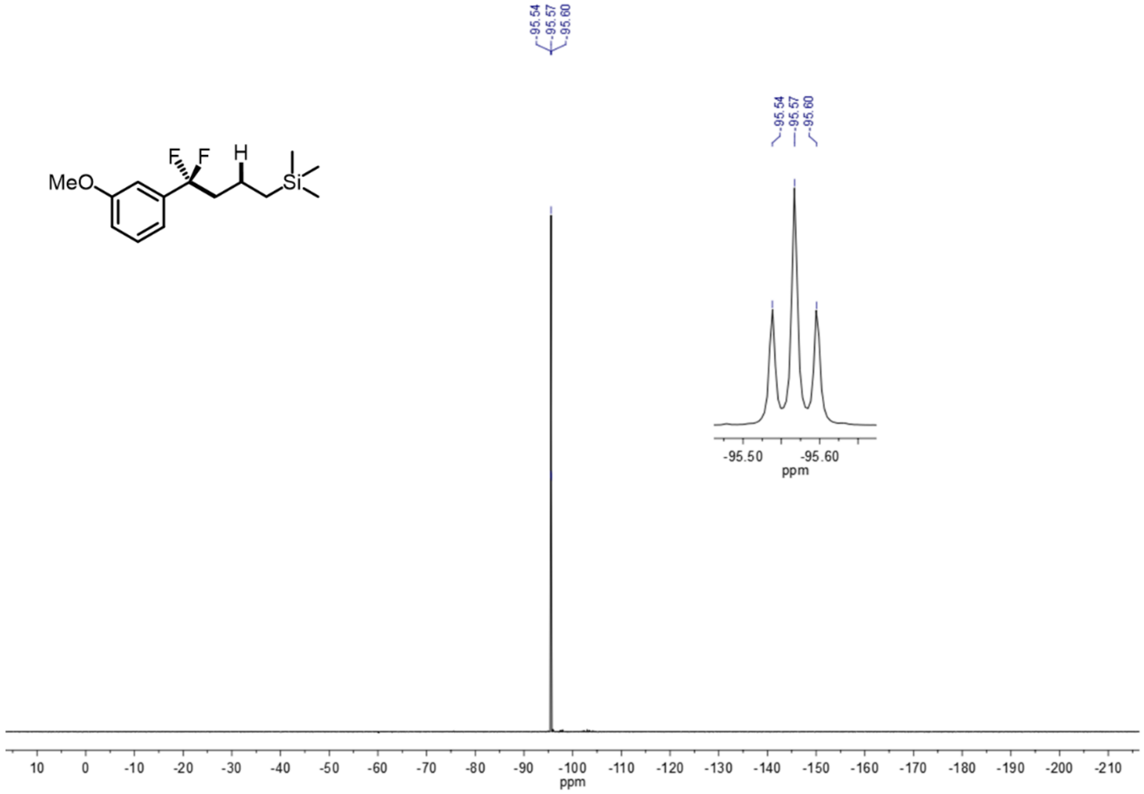
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6d**



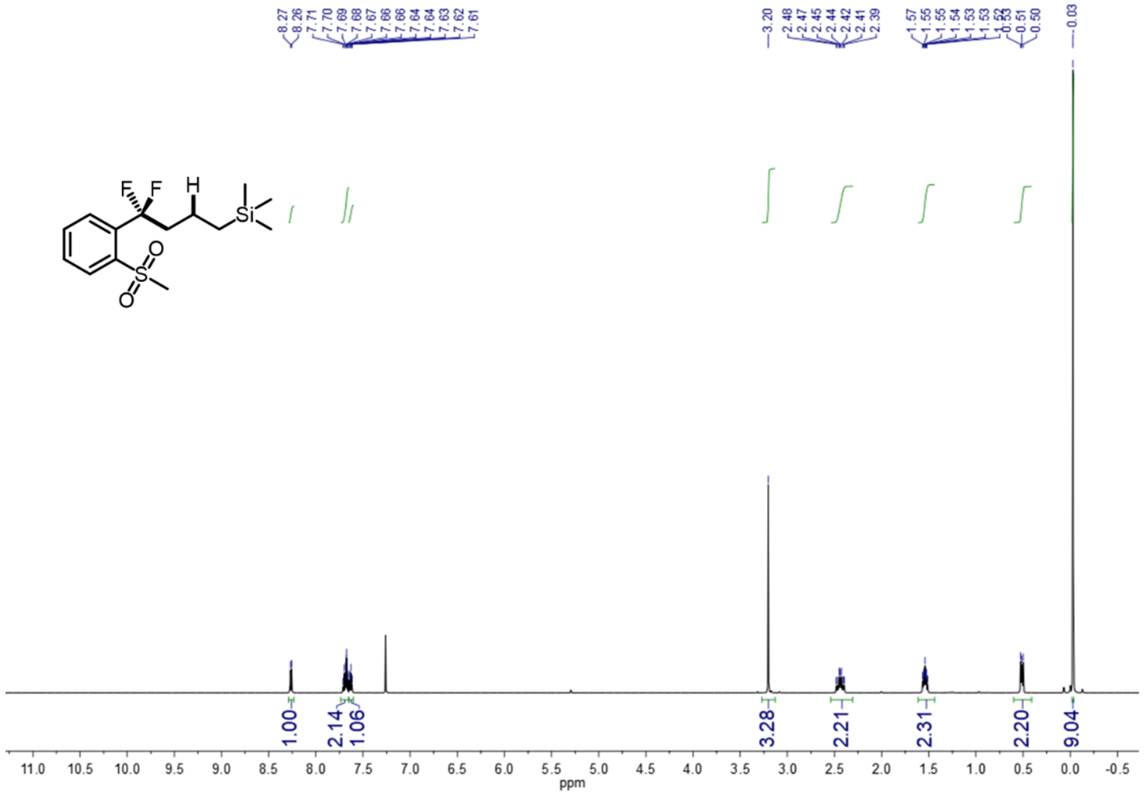
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6e**



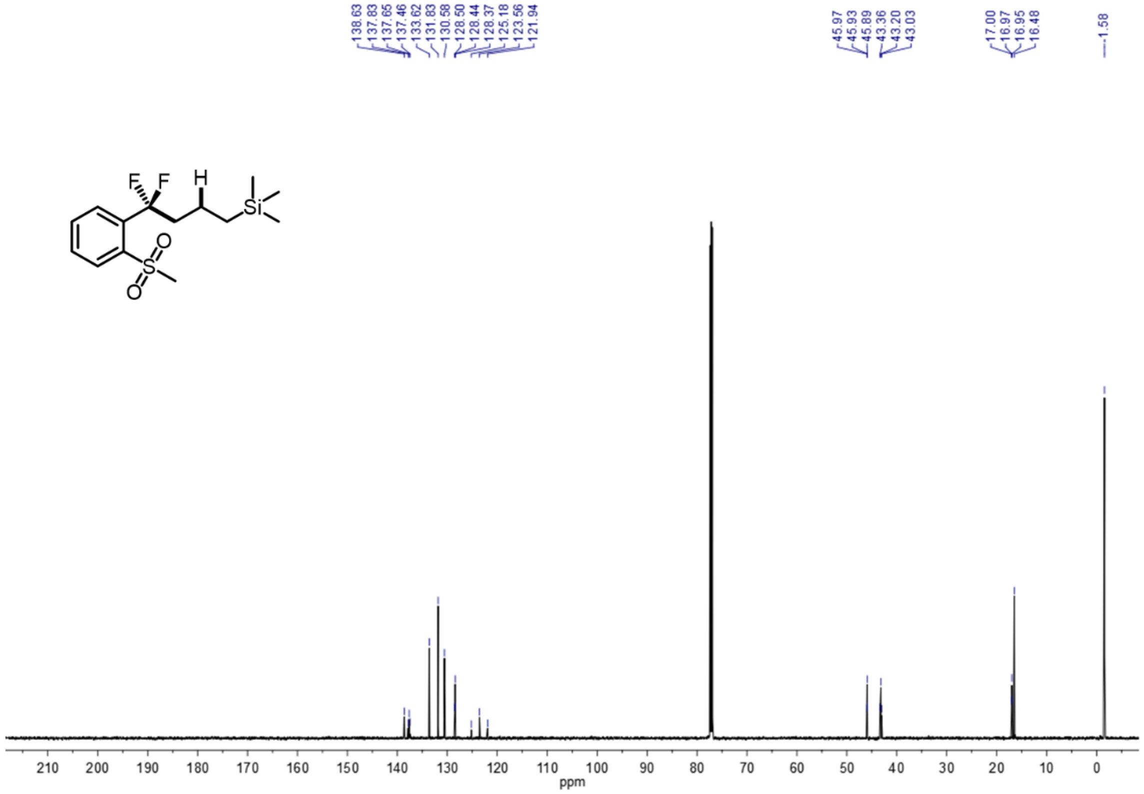
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6e**



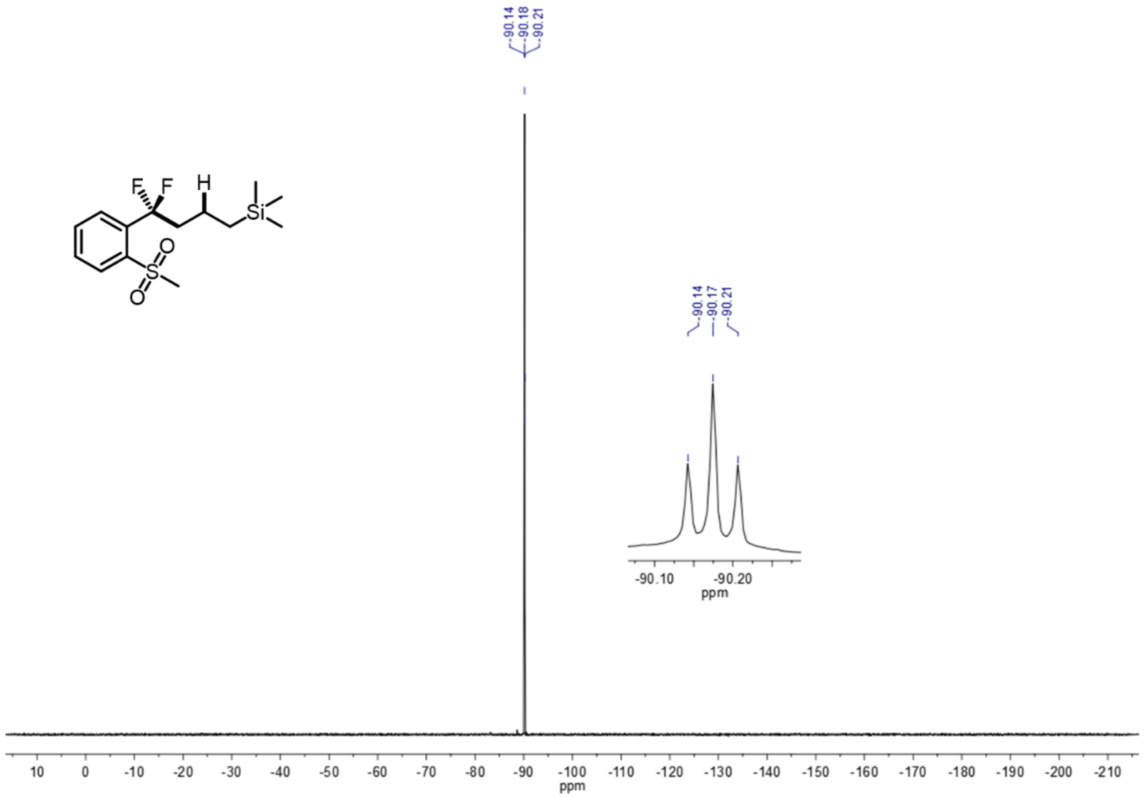
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6e**



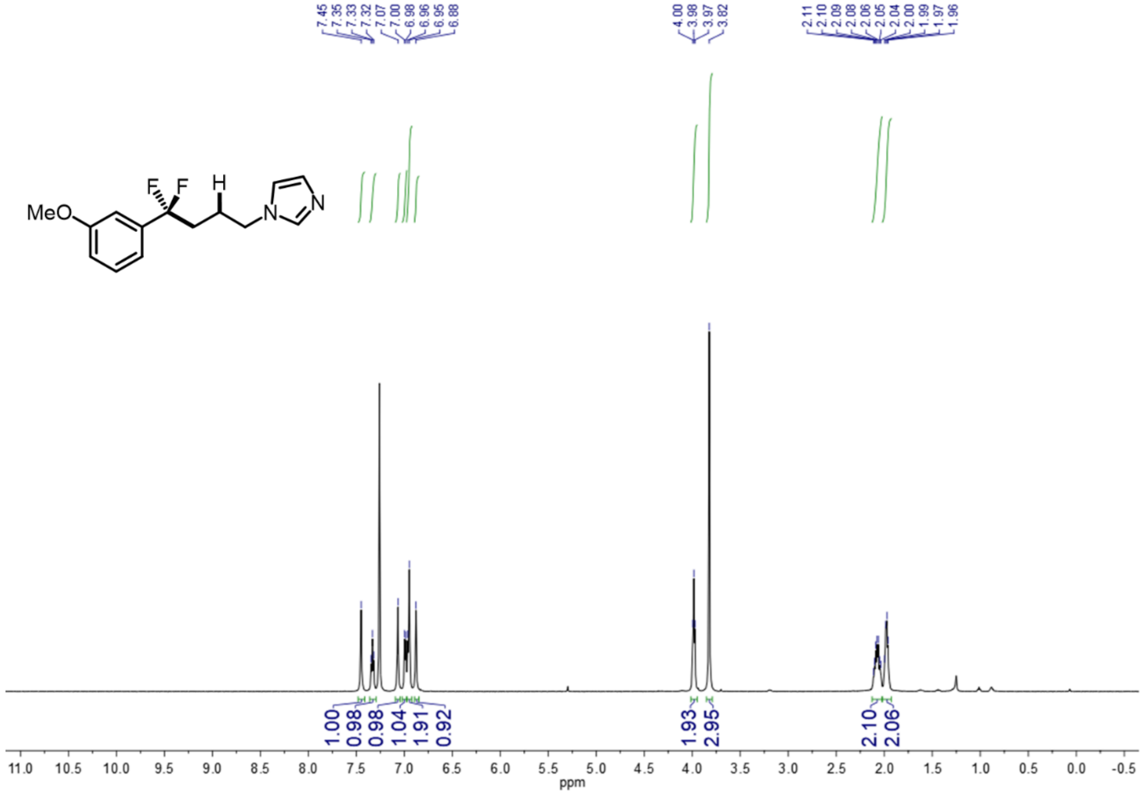
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **6f**



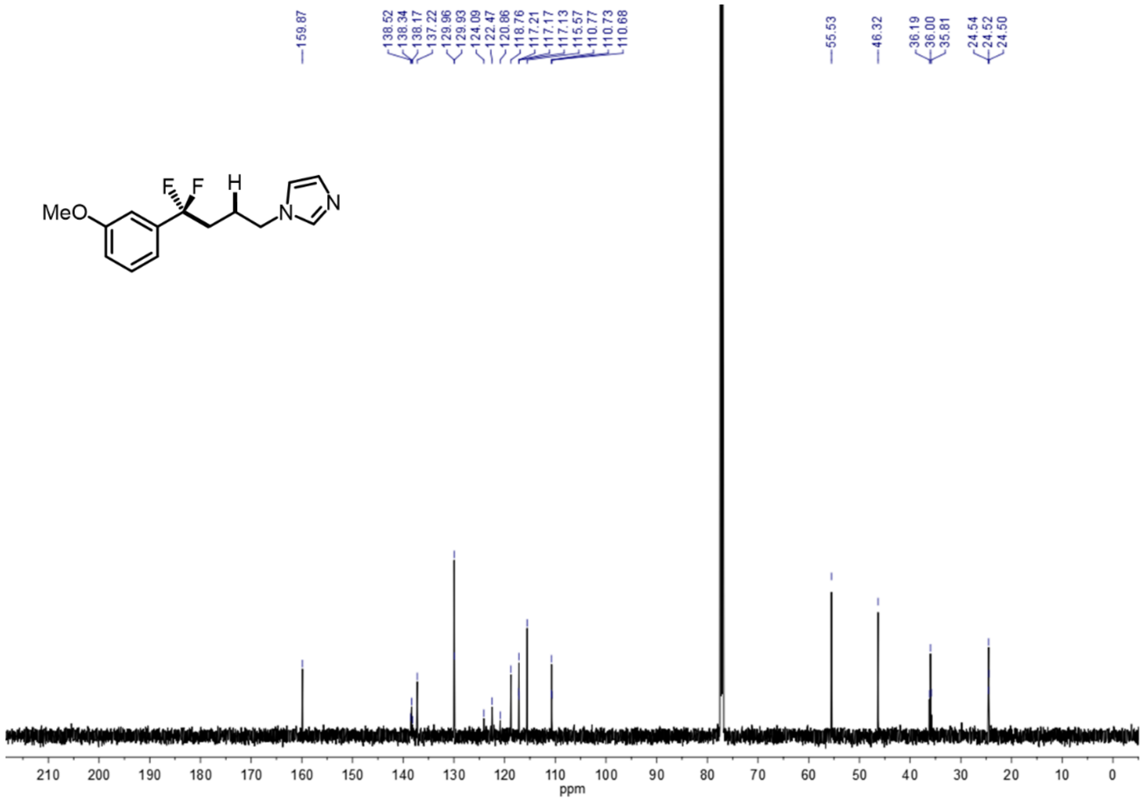
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **6f**



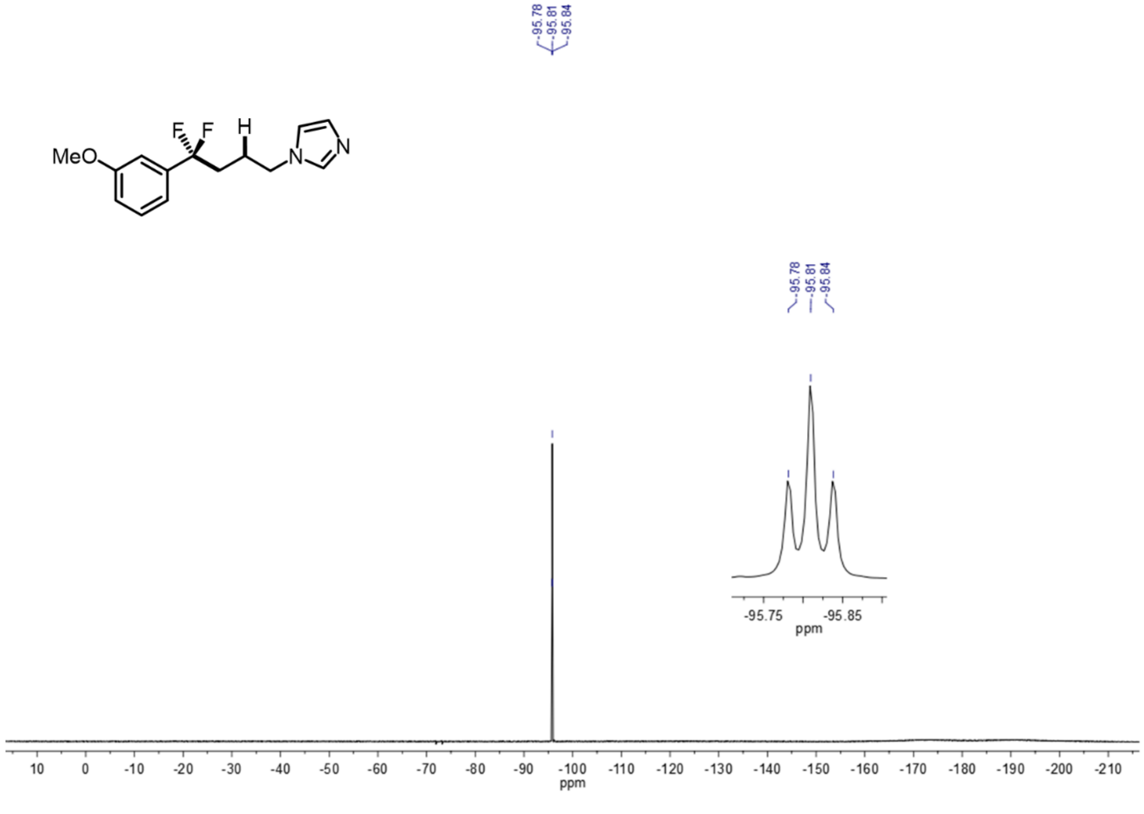
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6f**



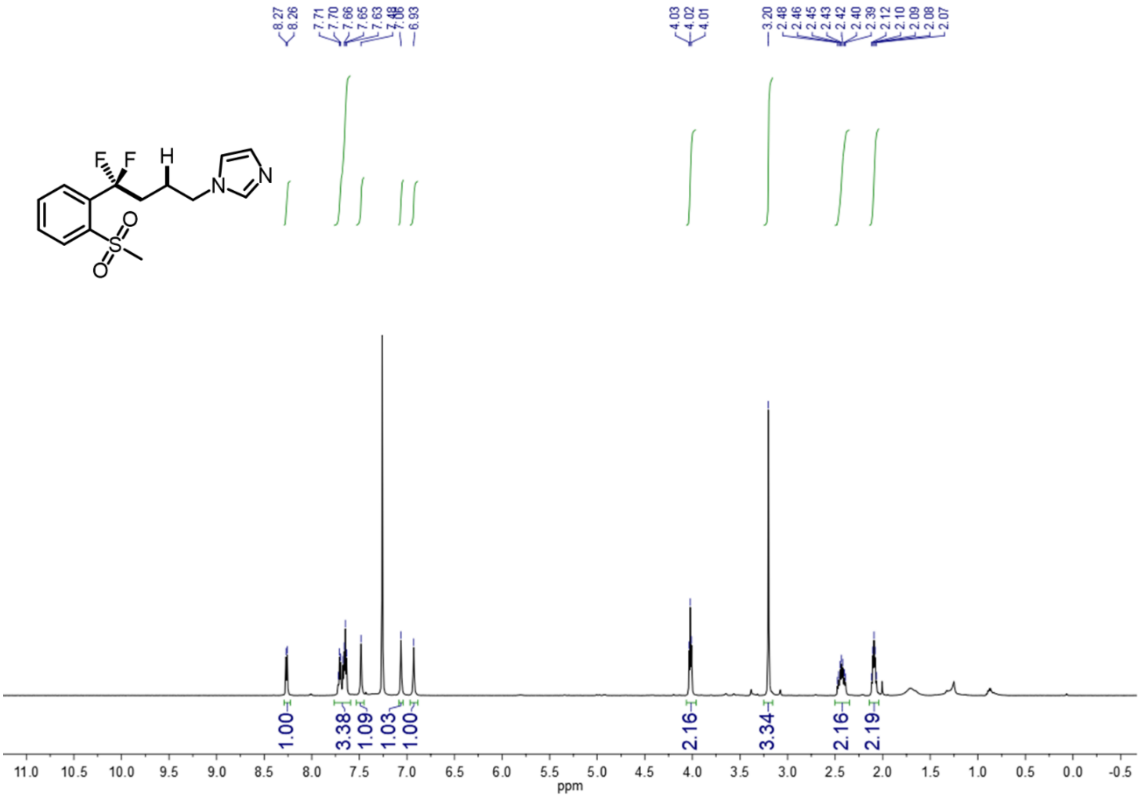
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6g**



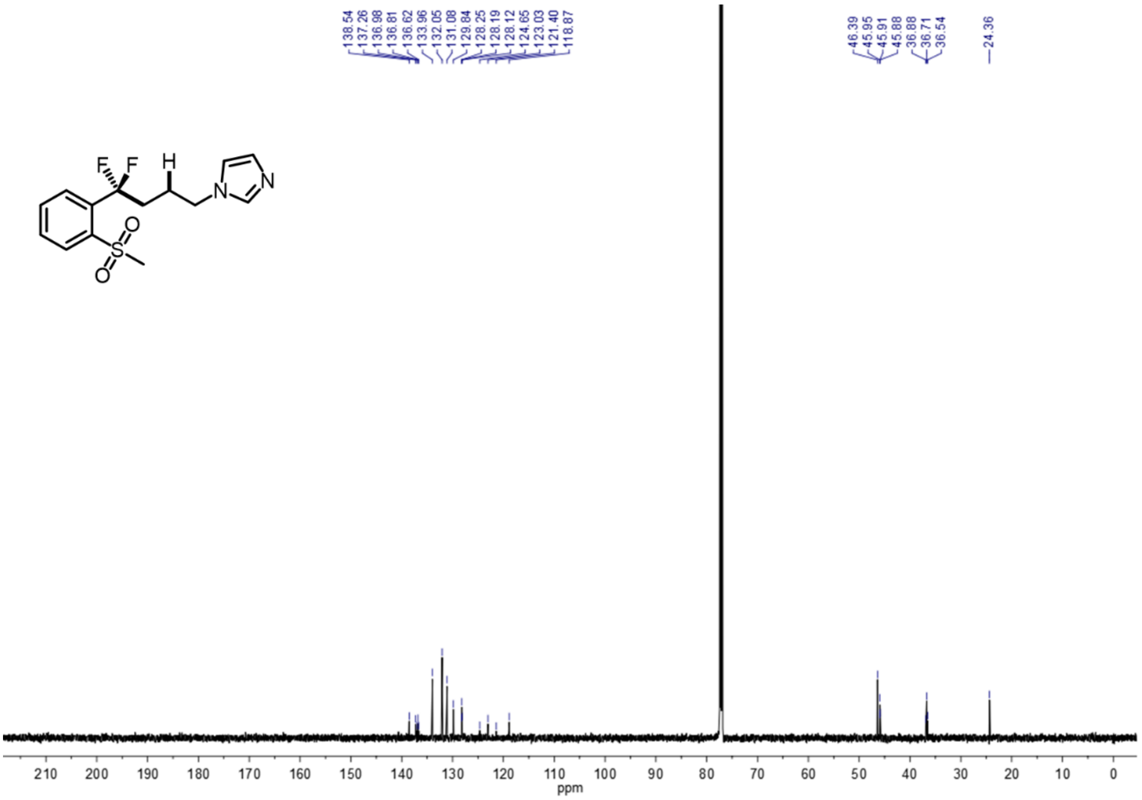
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6g**



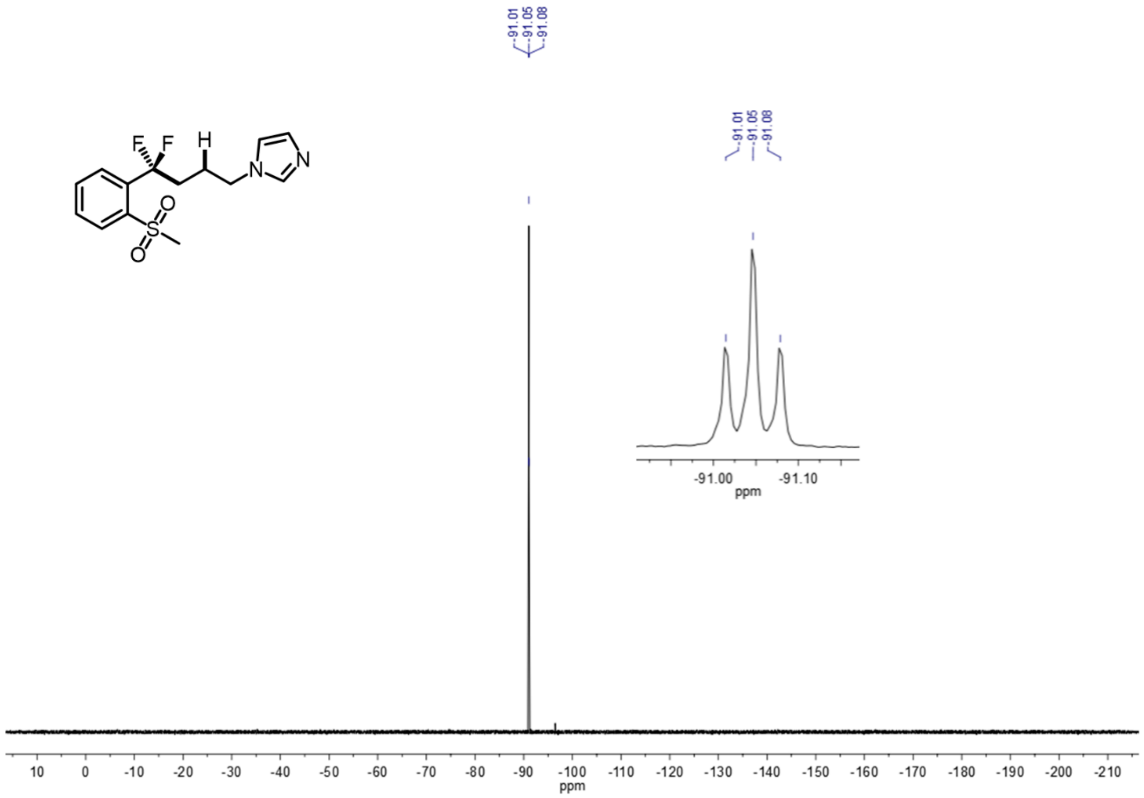
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6g**



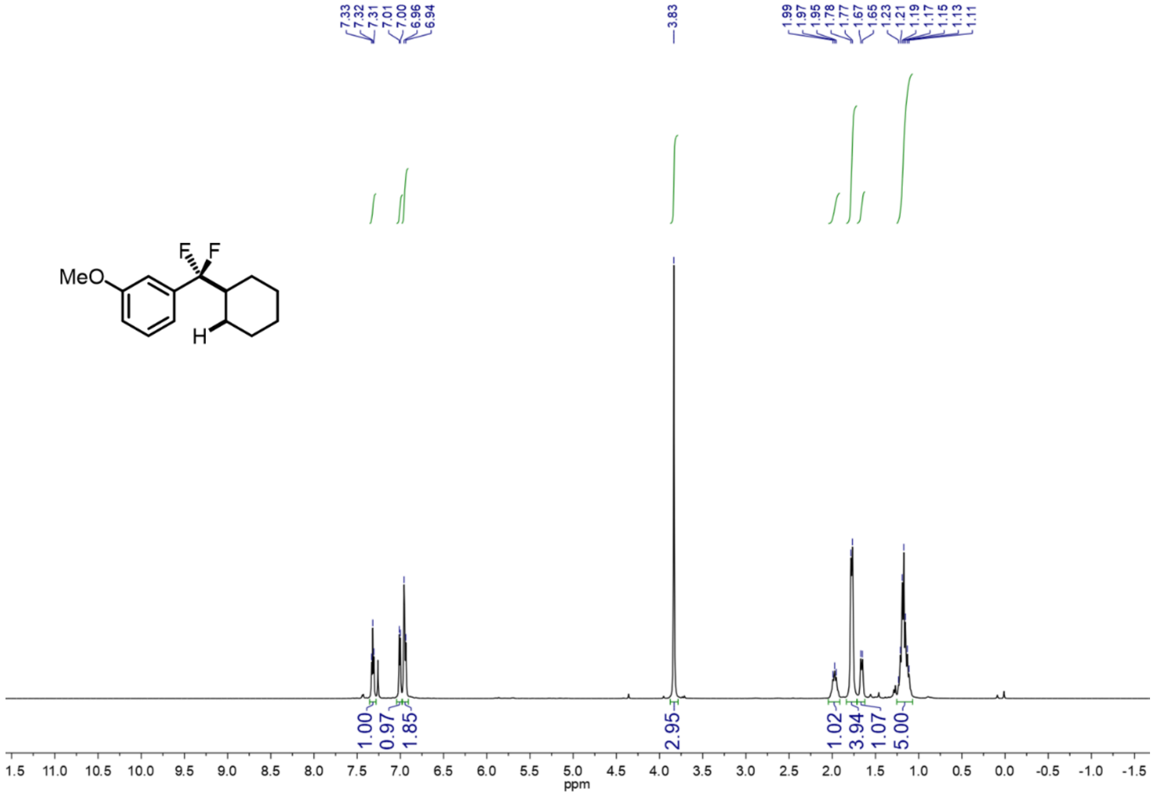
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6h**



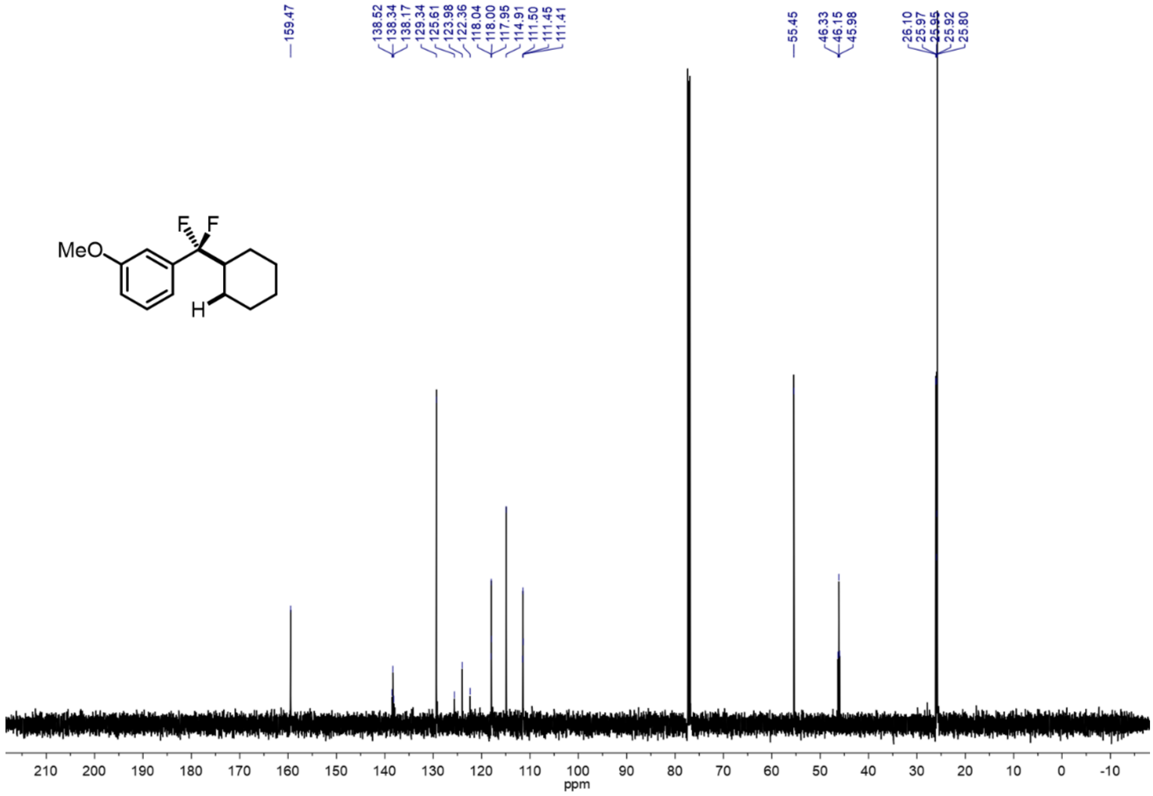
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6h**



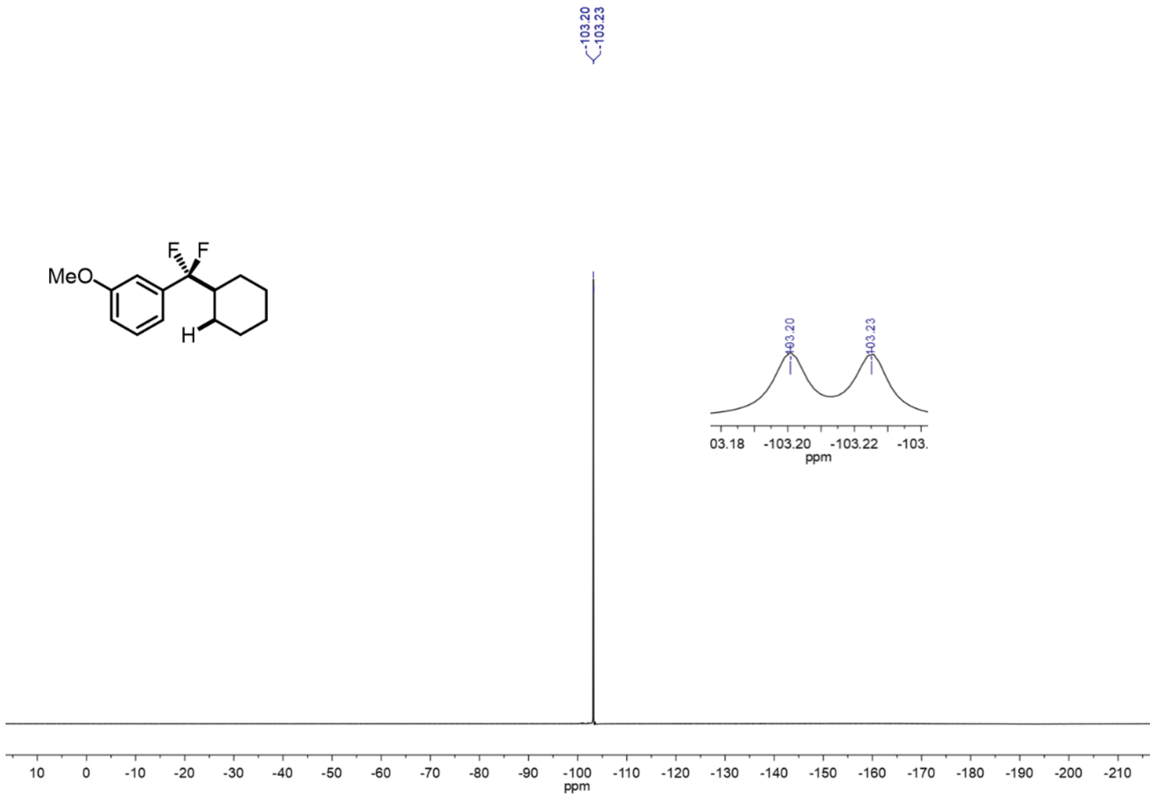
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6h**



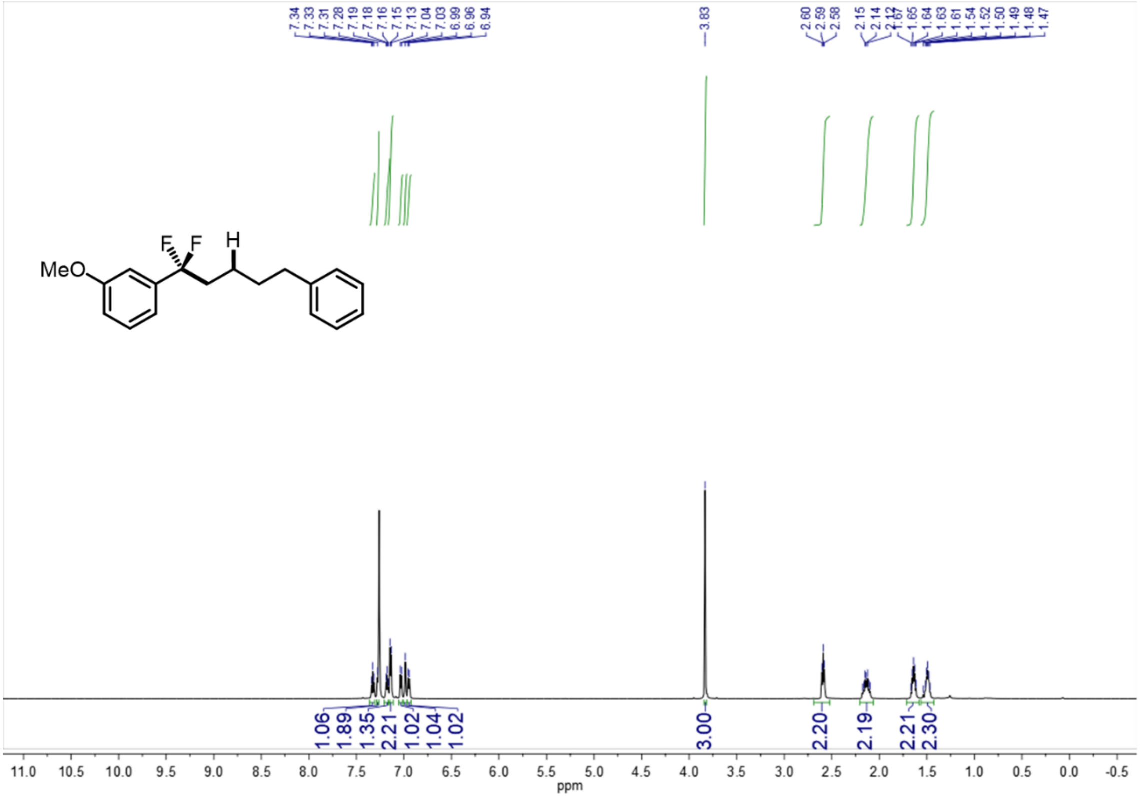
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6i**



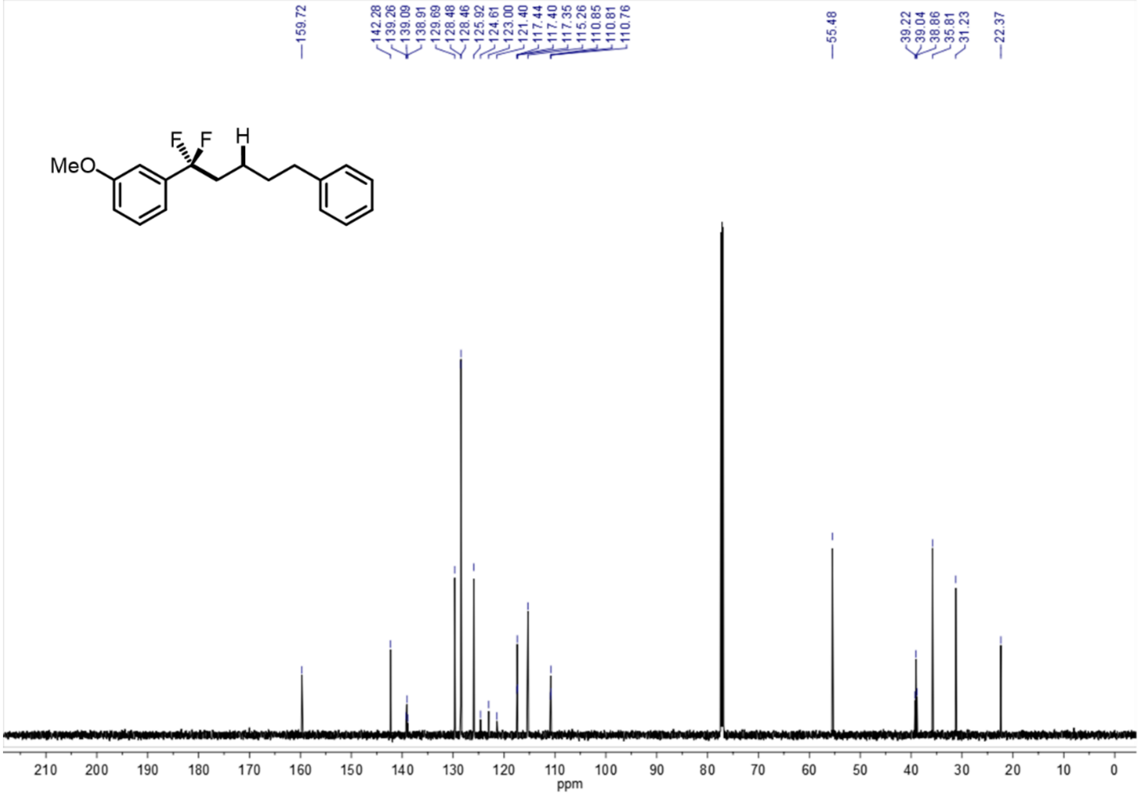
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6i**



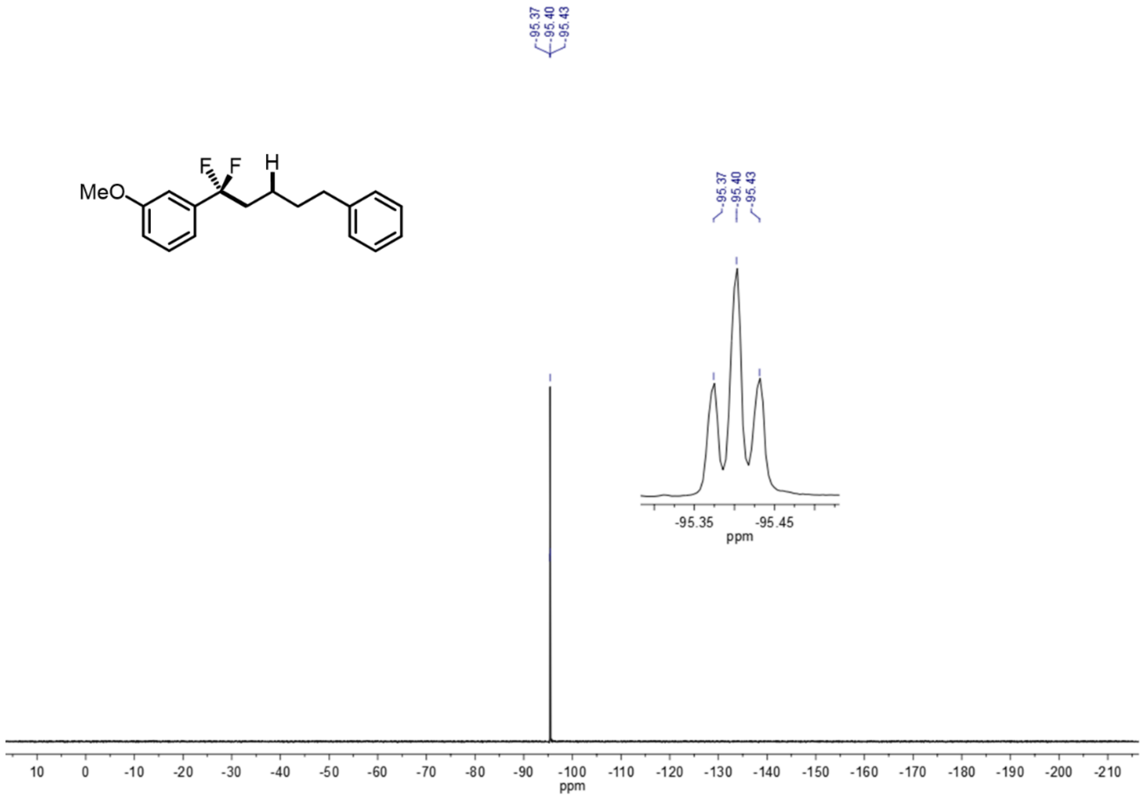
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6i**



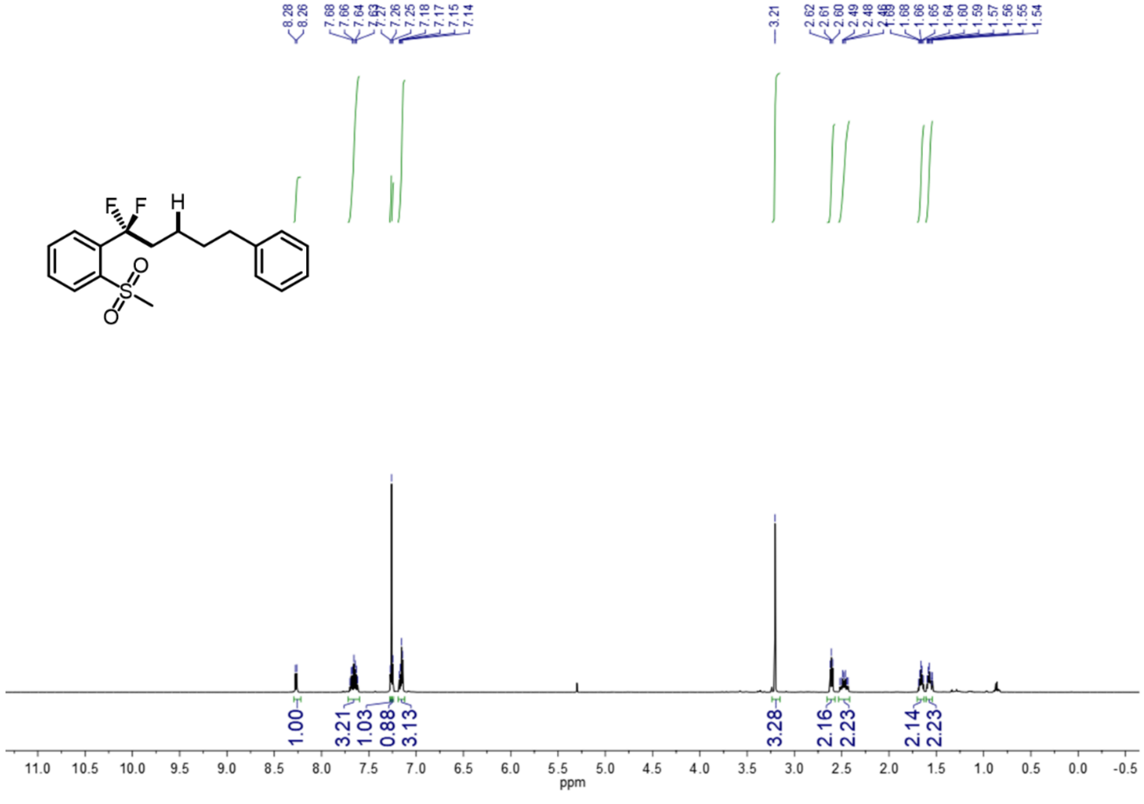
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6k**



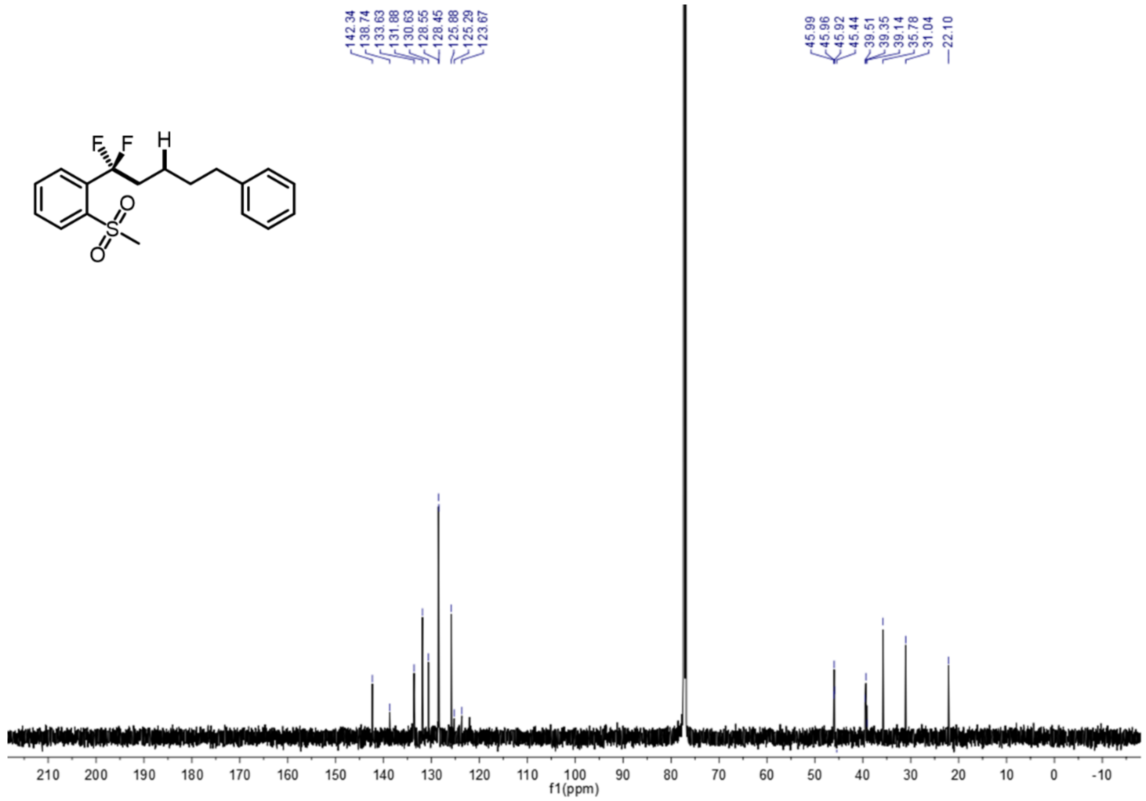
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6k**



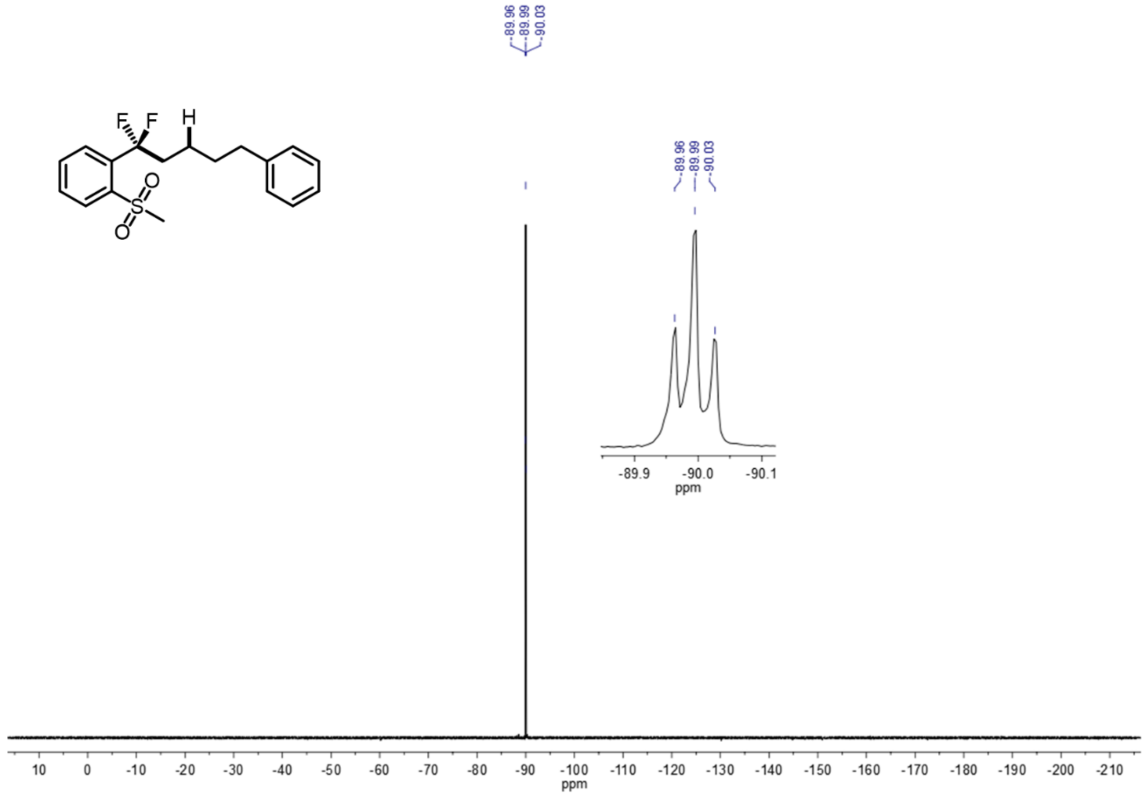
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **6k**



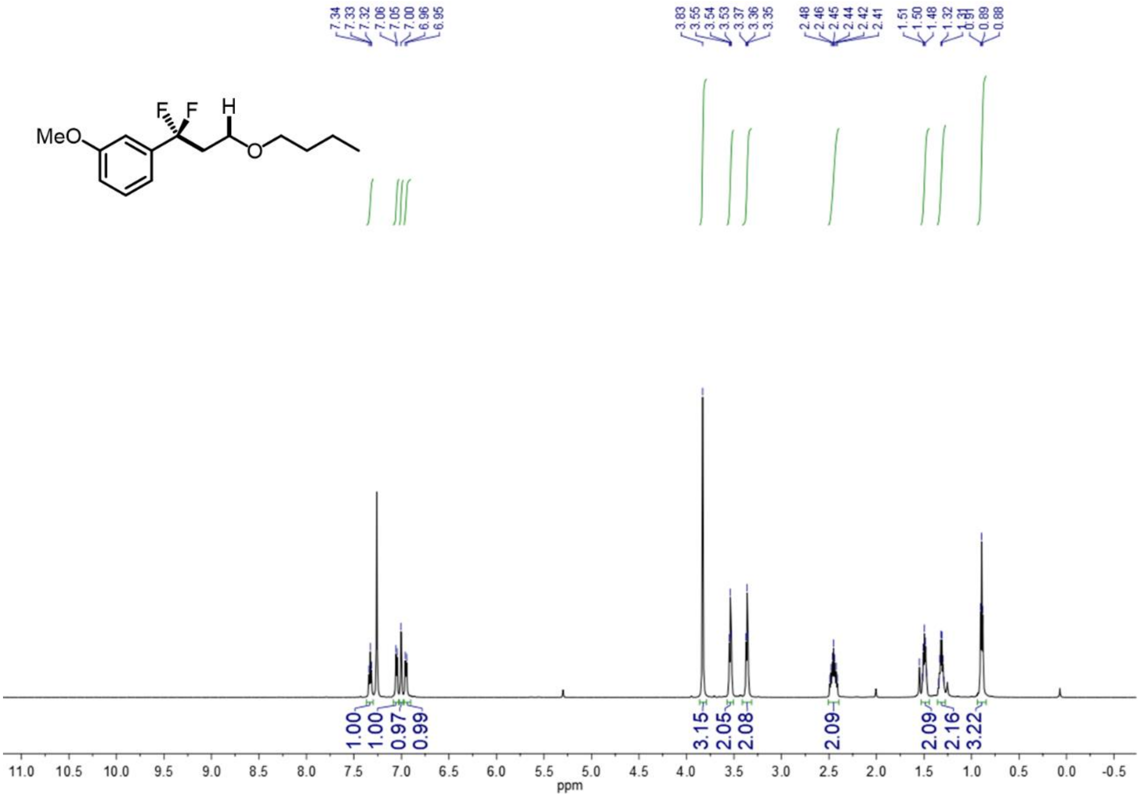
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **6l**



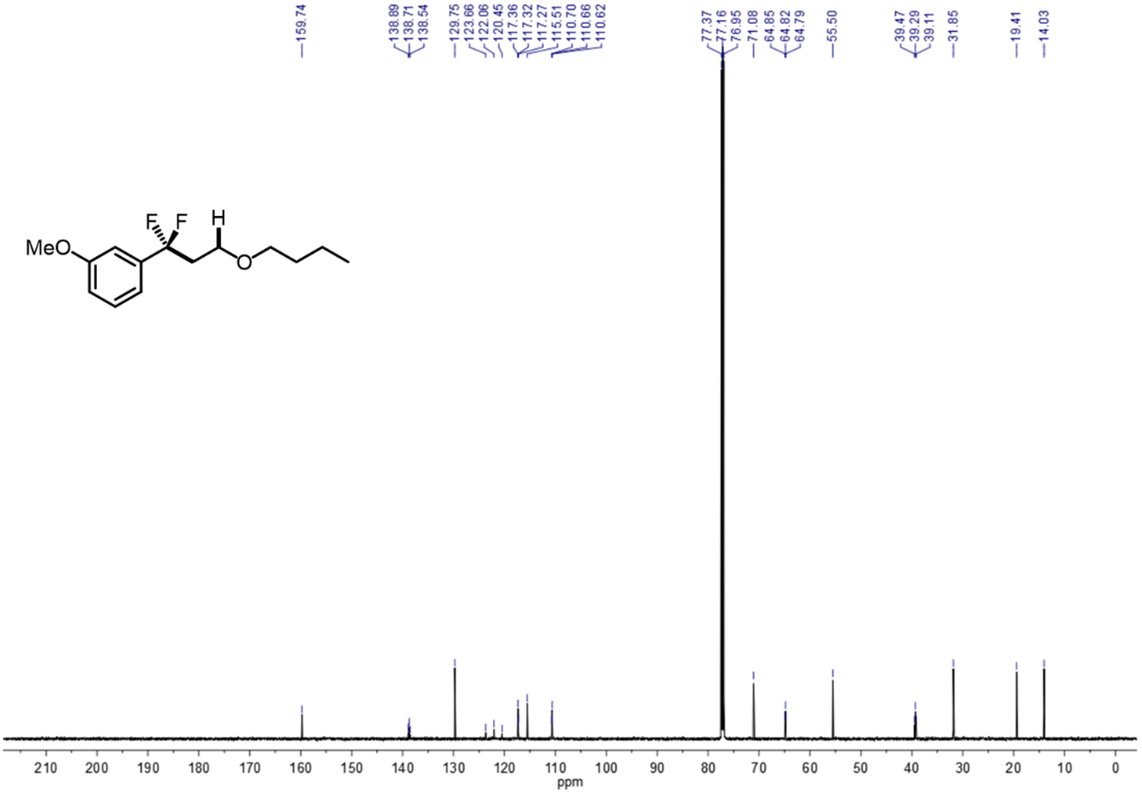
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6l**



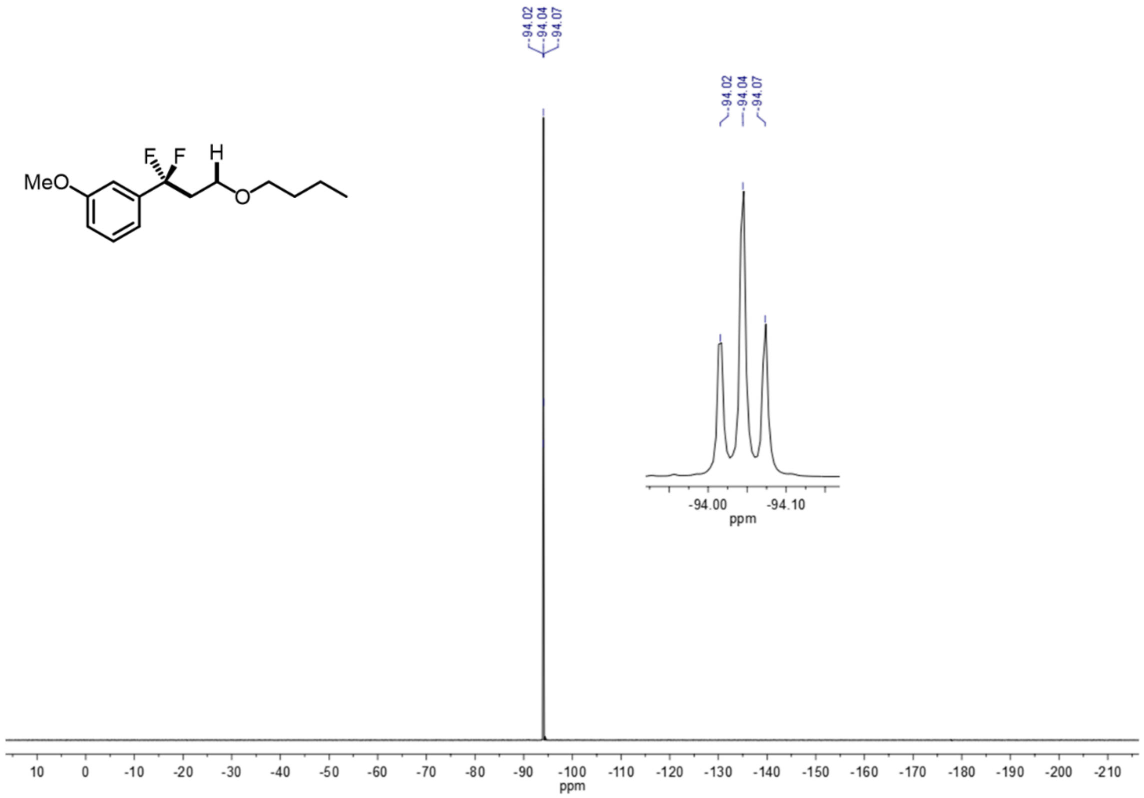
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6l**



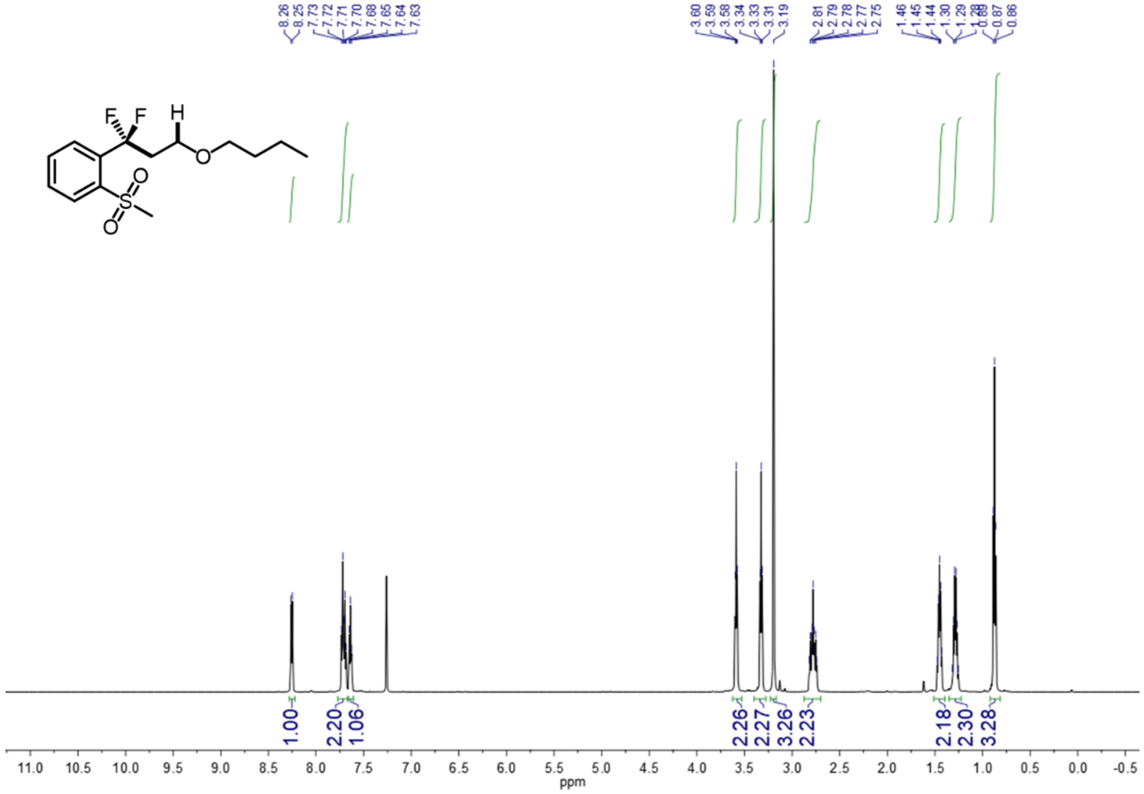
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6m**



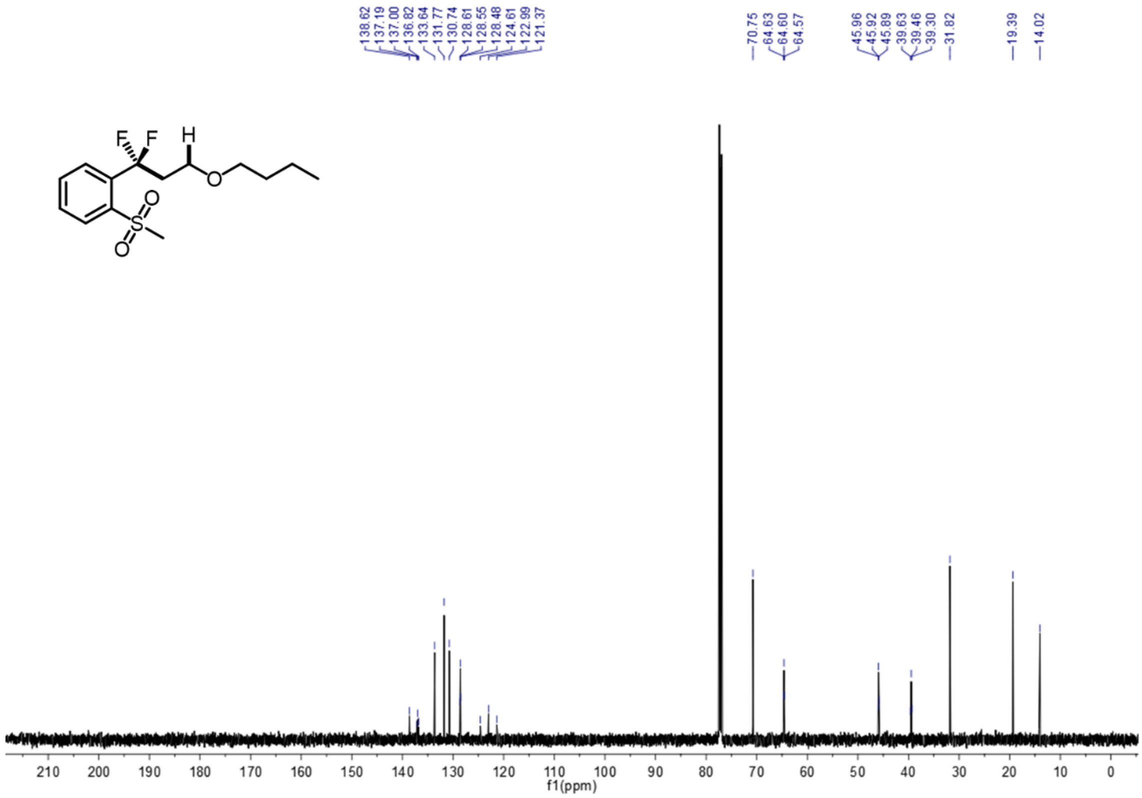
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6m**



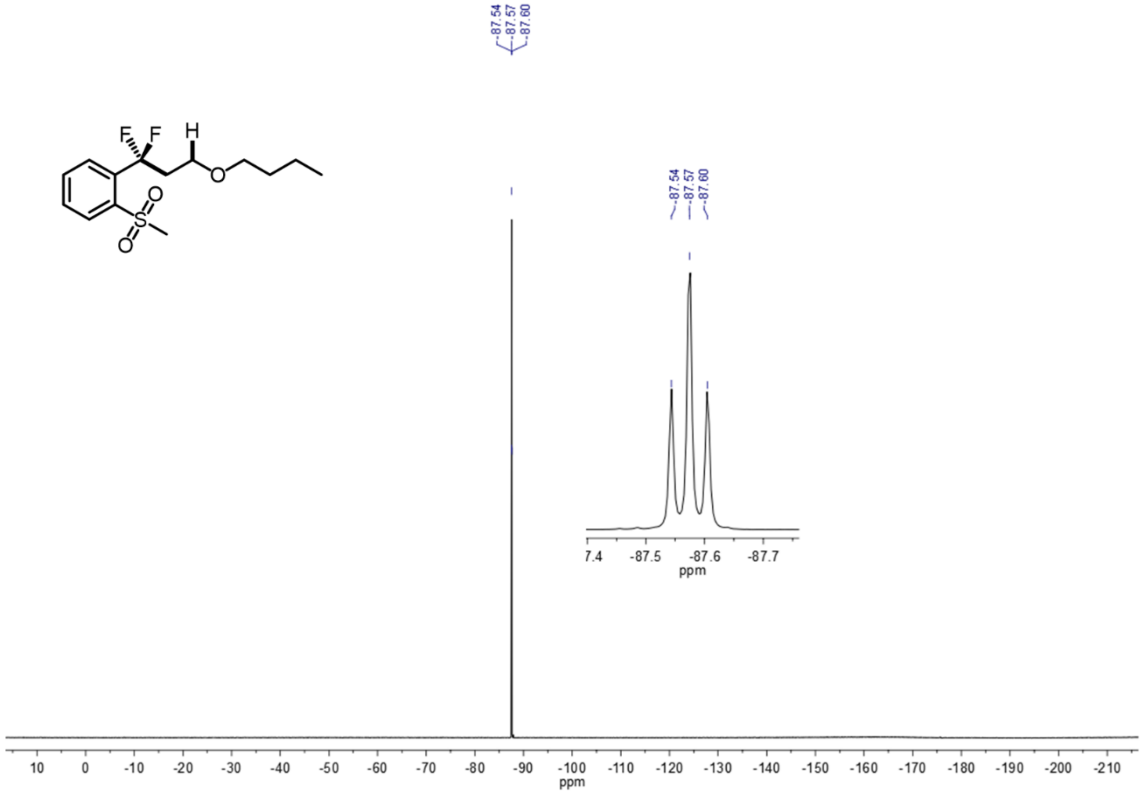
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6m**



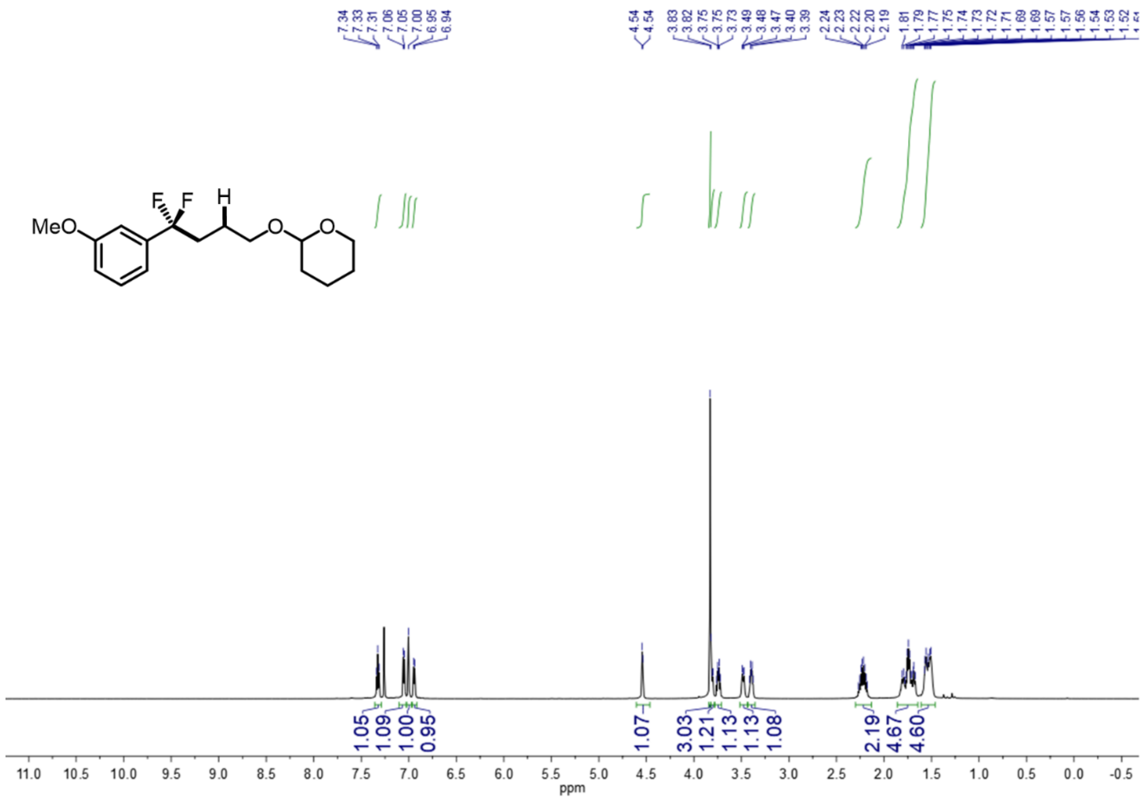
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6n**



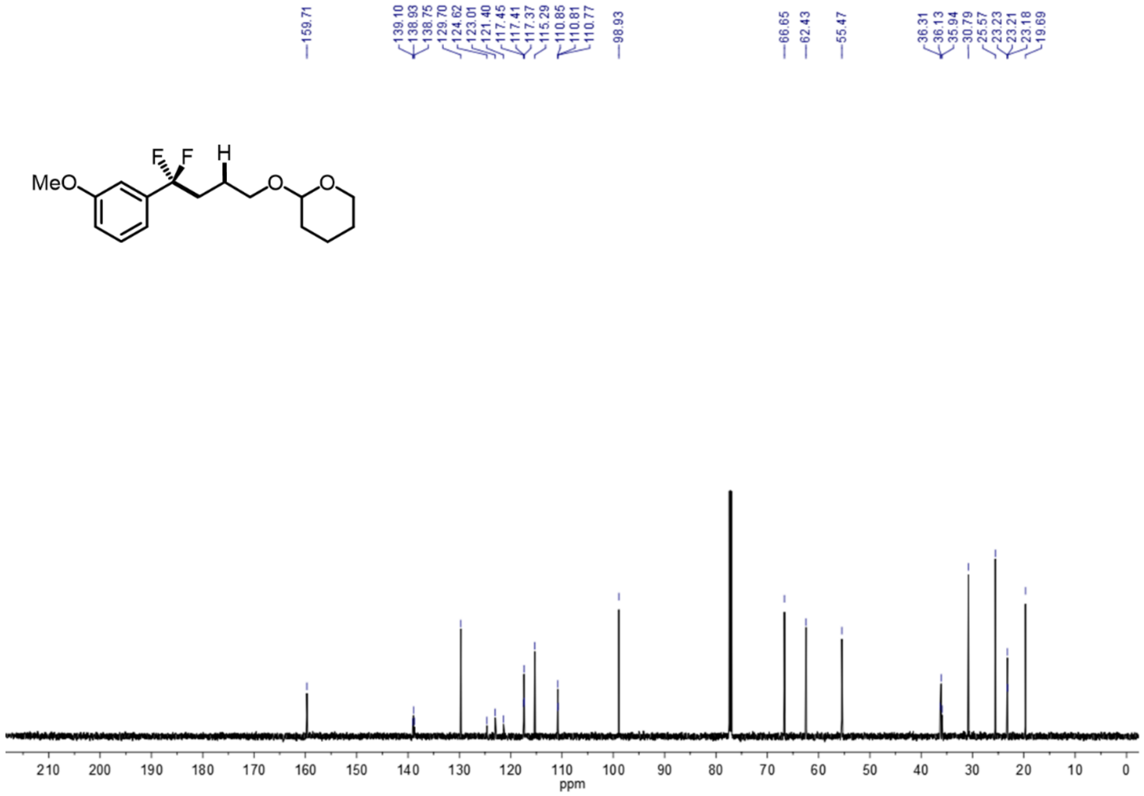
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6n**



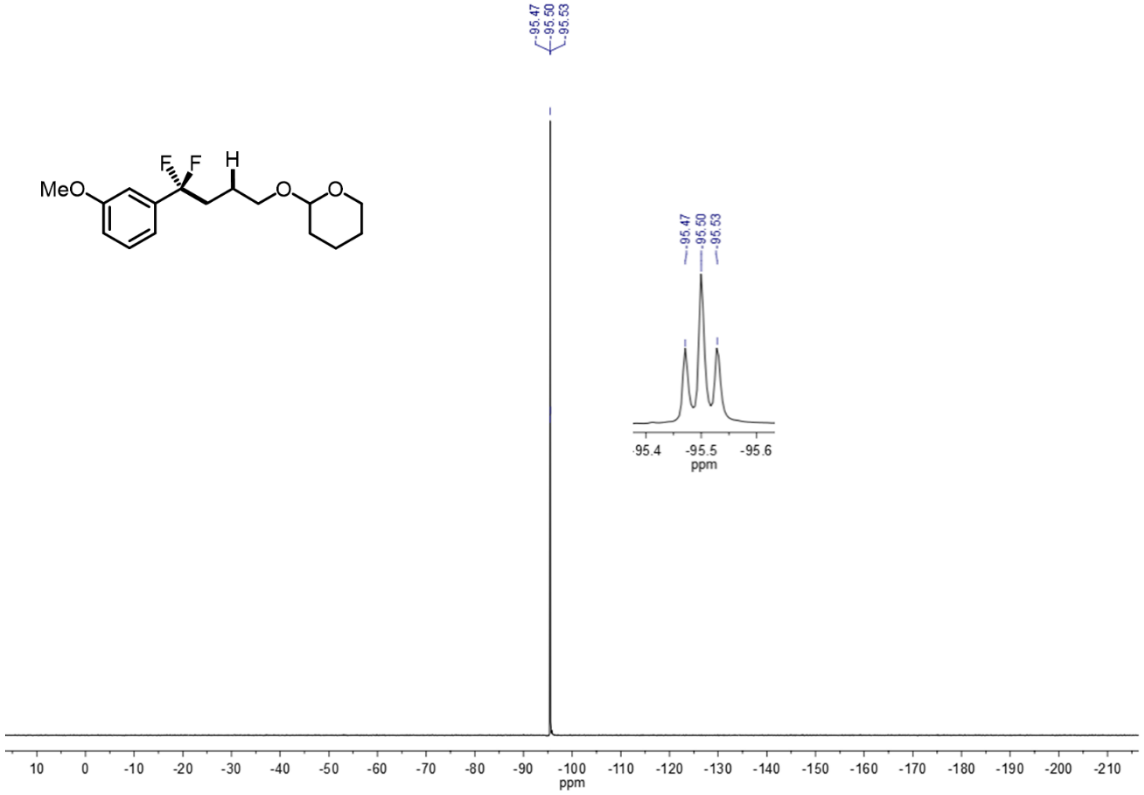
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6n**



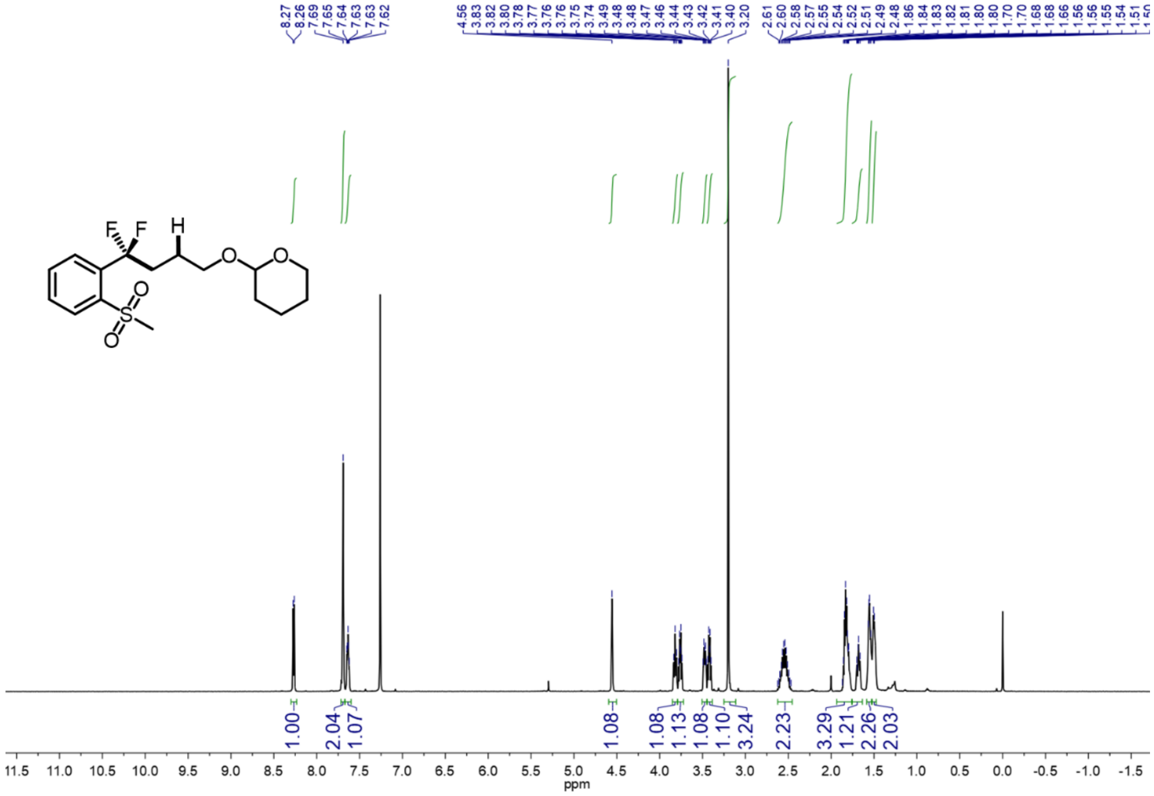
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **6o**



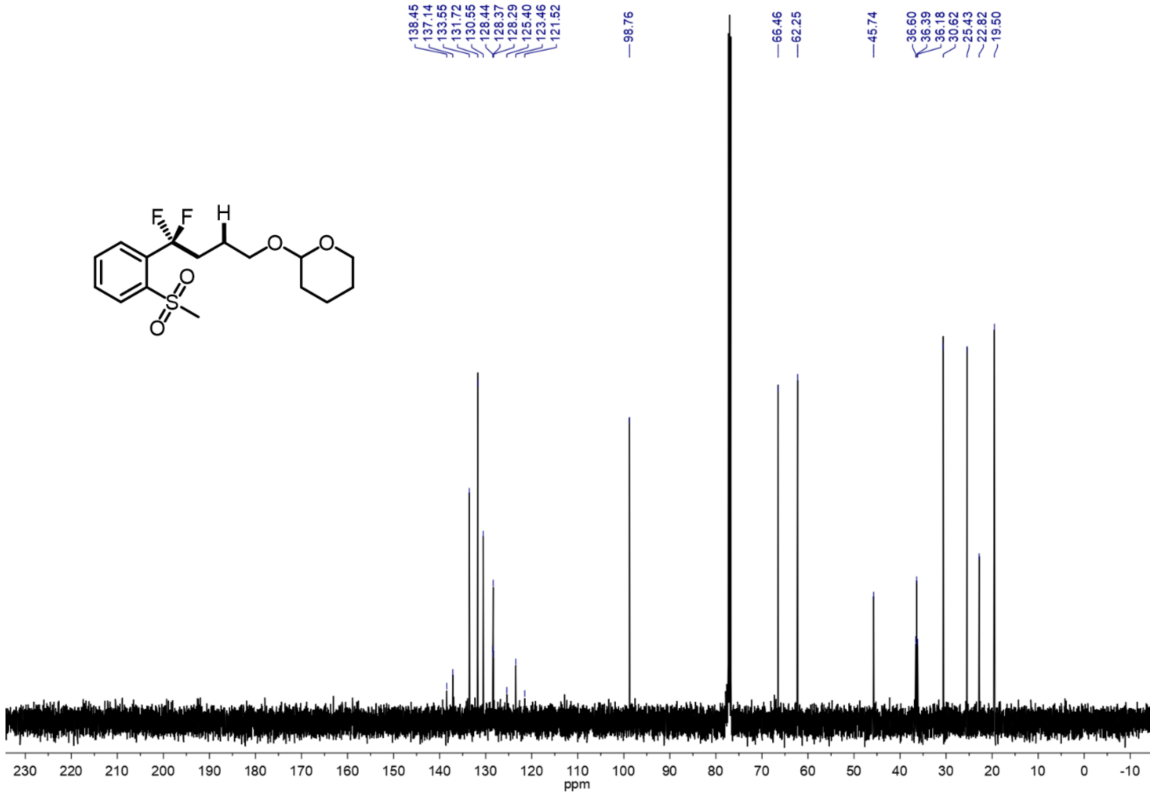
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **6o**



^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **6o**

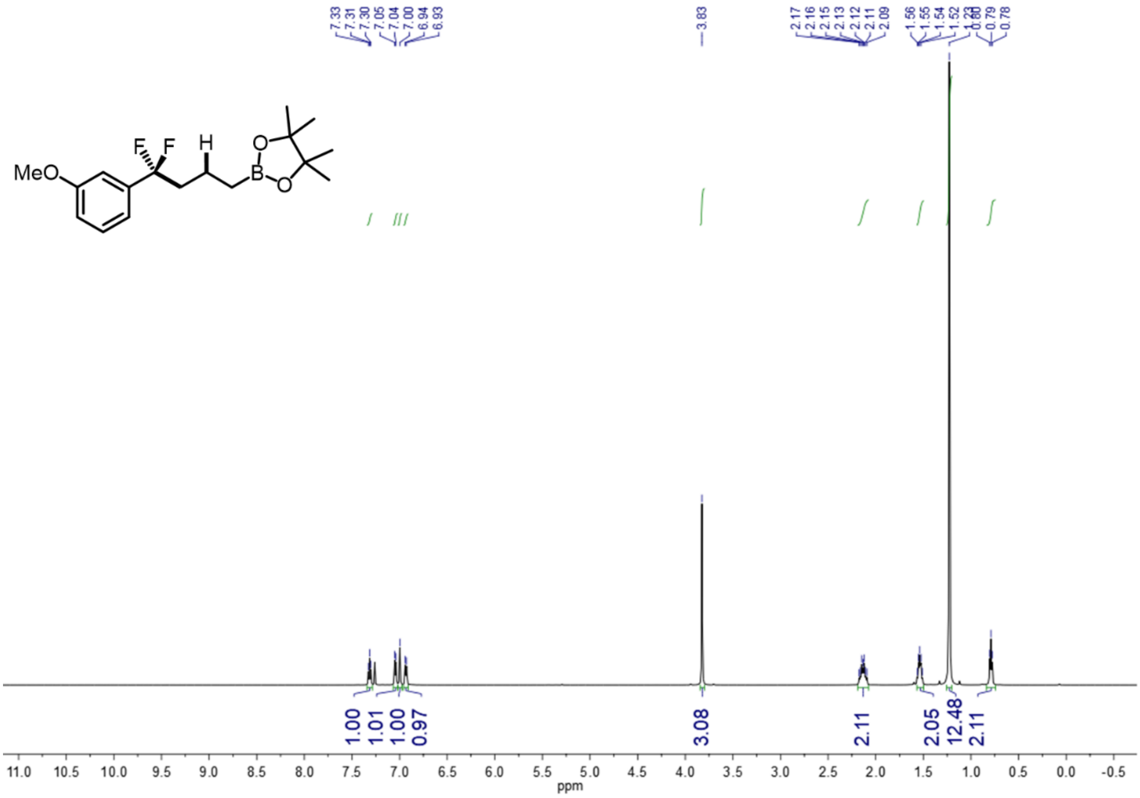


^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **6p**

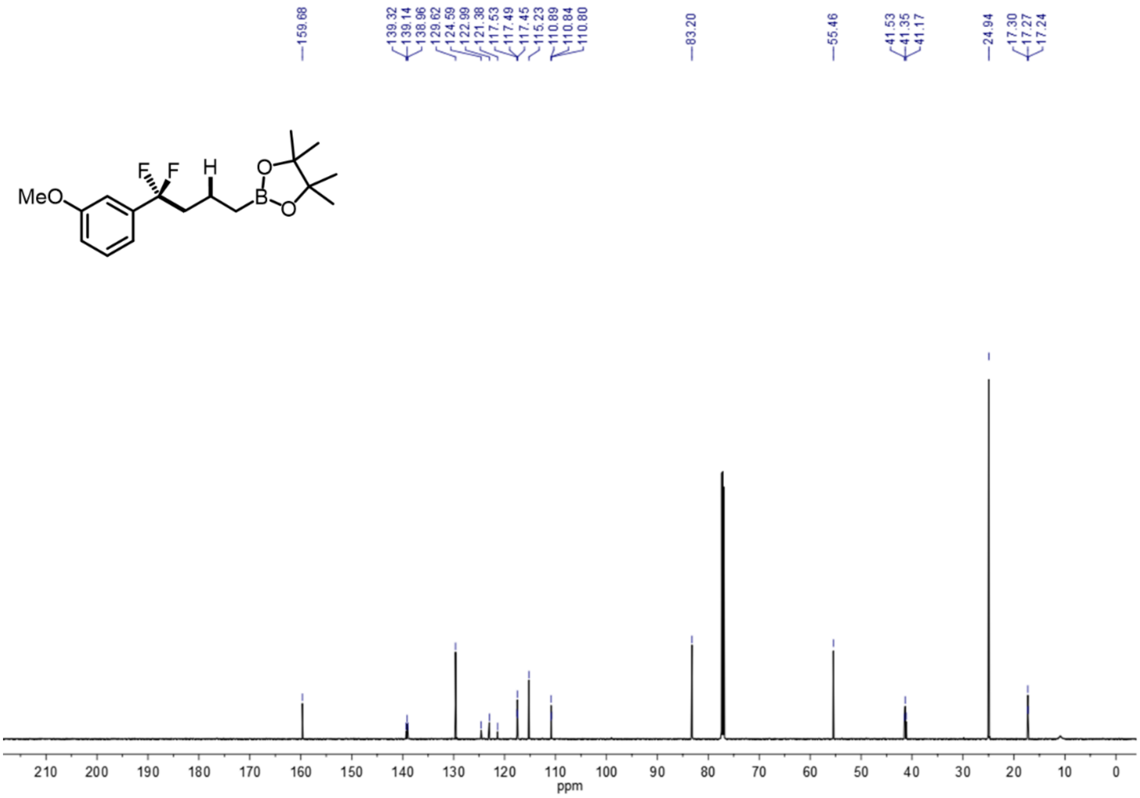


^{13}C NMR spectrum (126 MHz, CDCl$_3$, 23 ºC) of **6p**

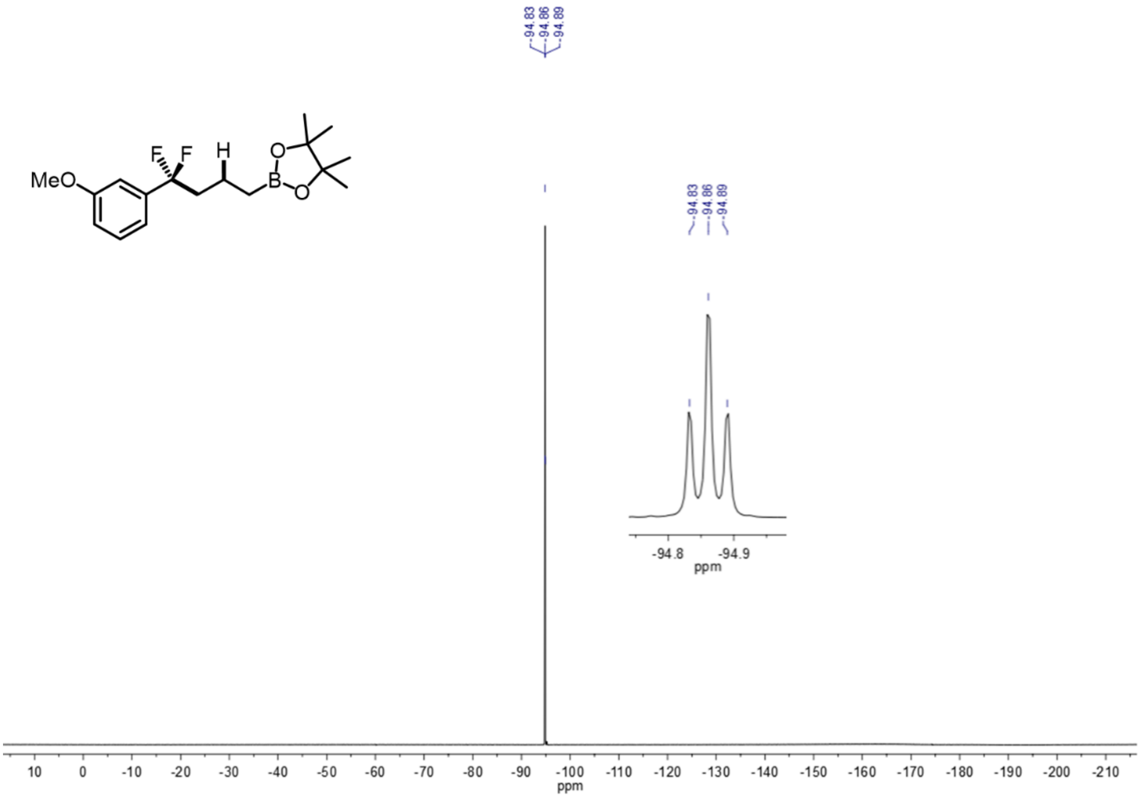
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6p**



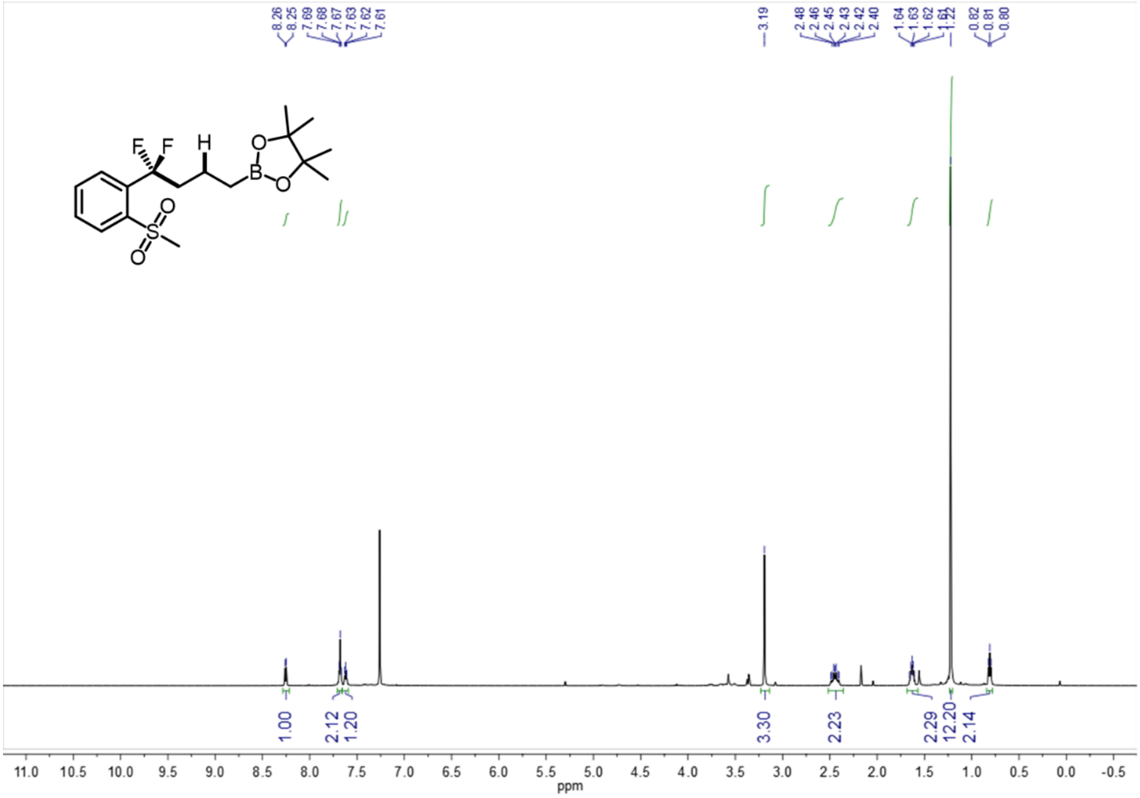
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6q**



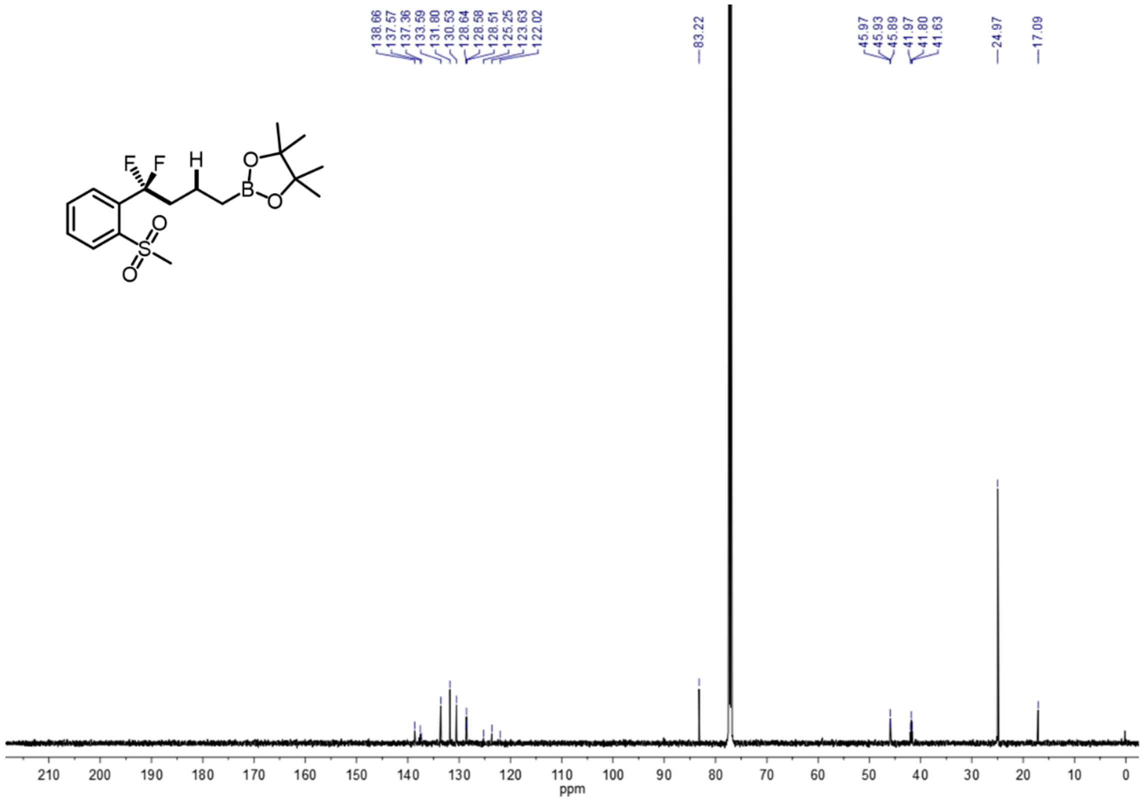
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6q**



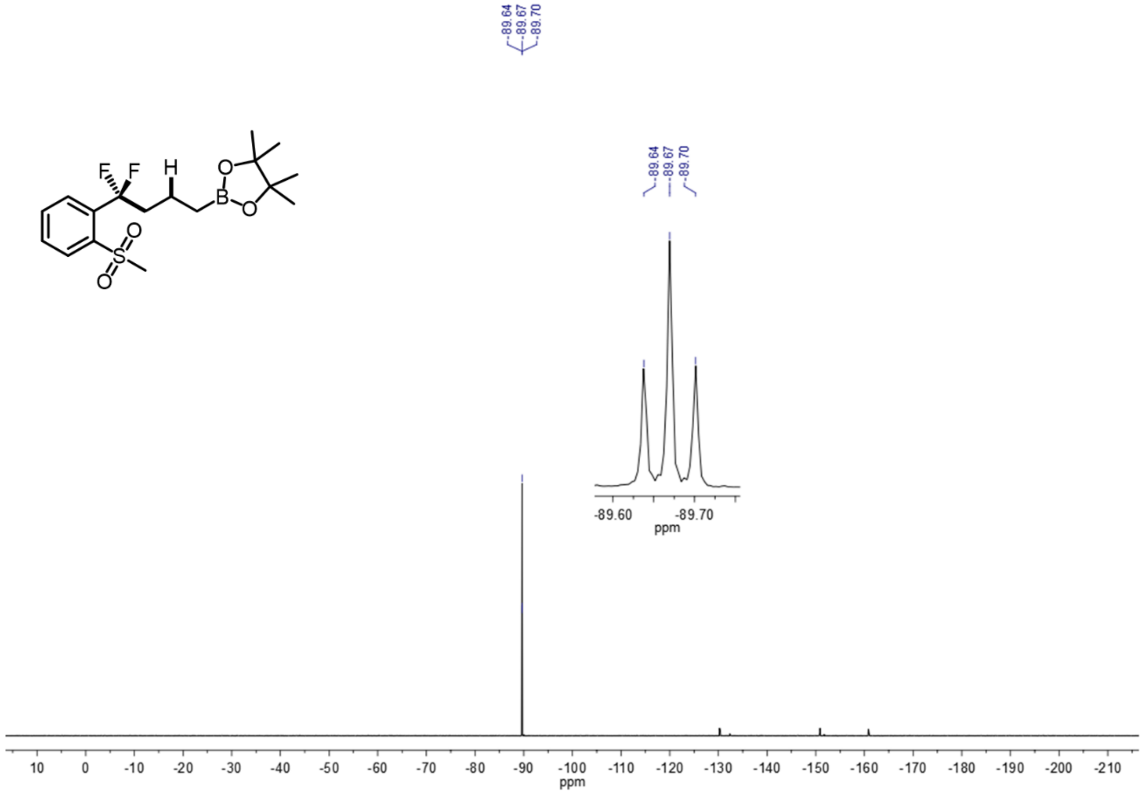
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **6q**



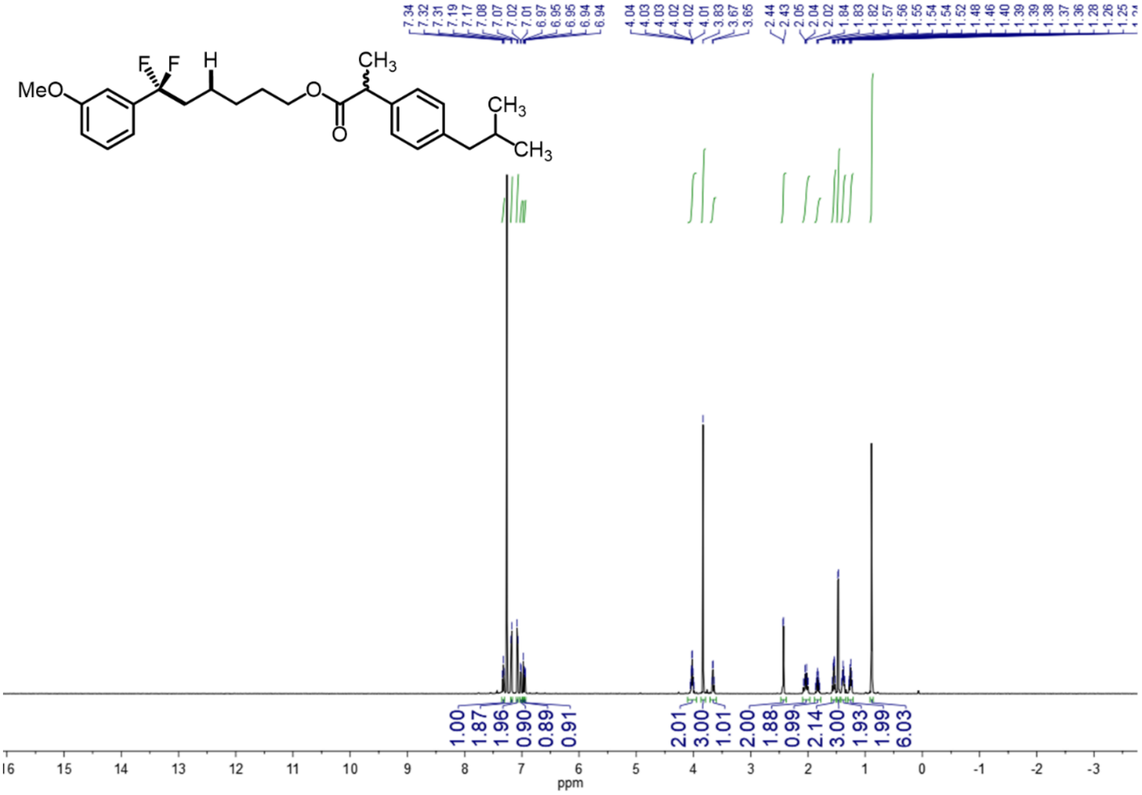
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **6r**



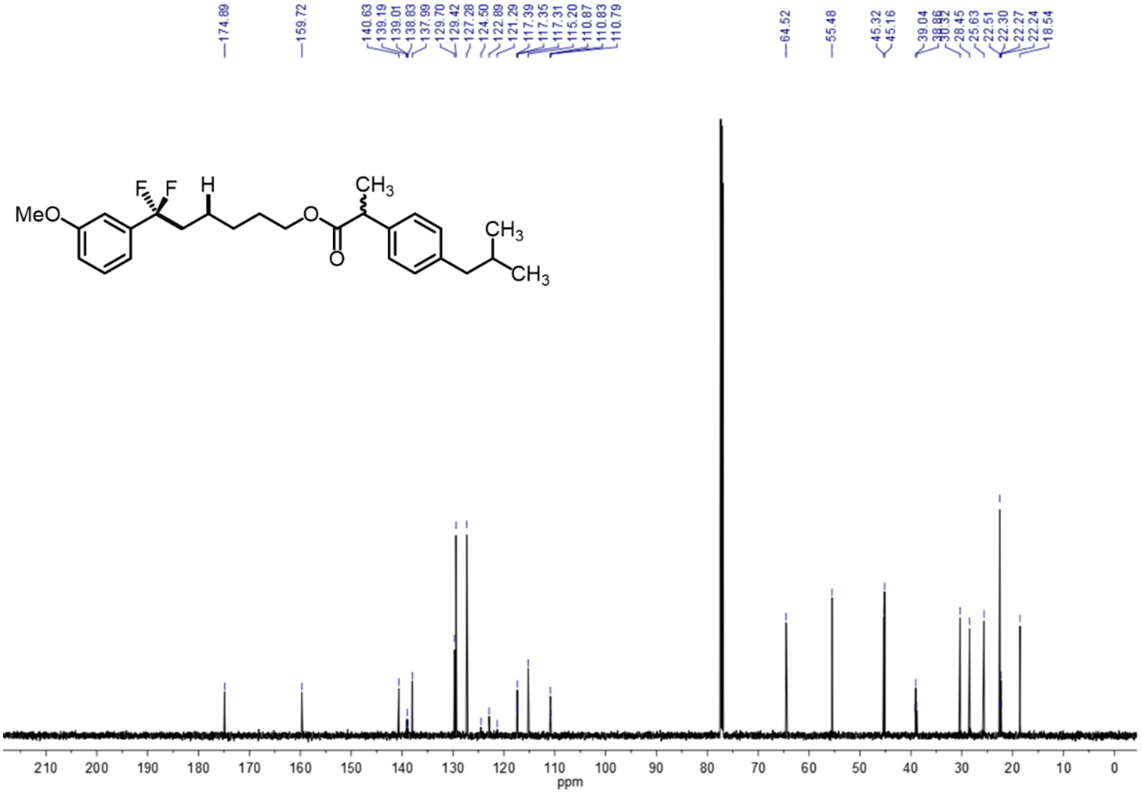
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6r**



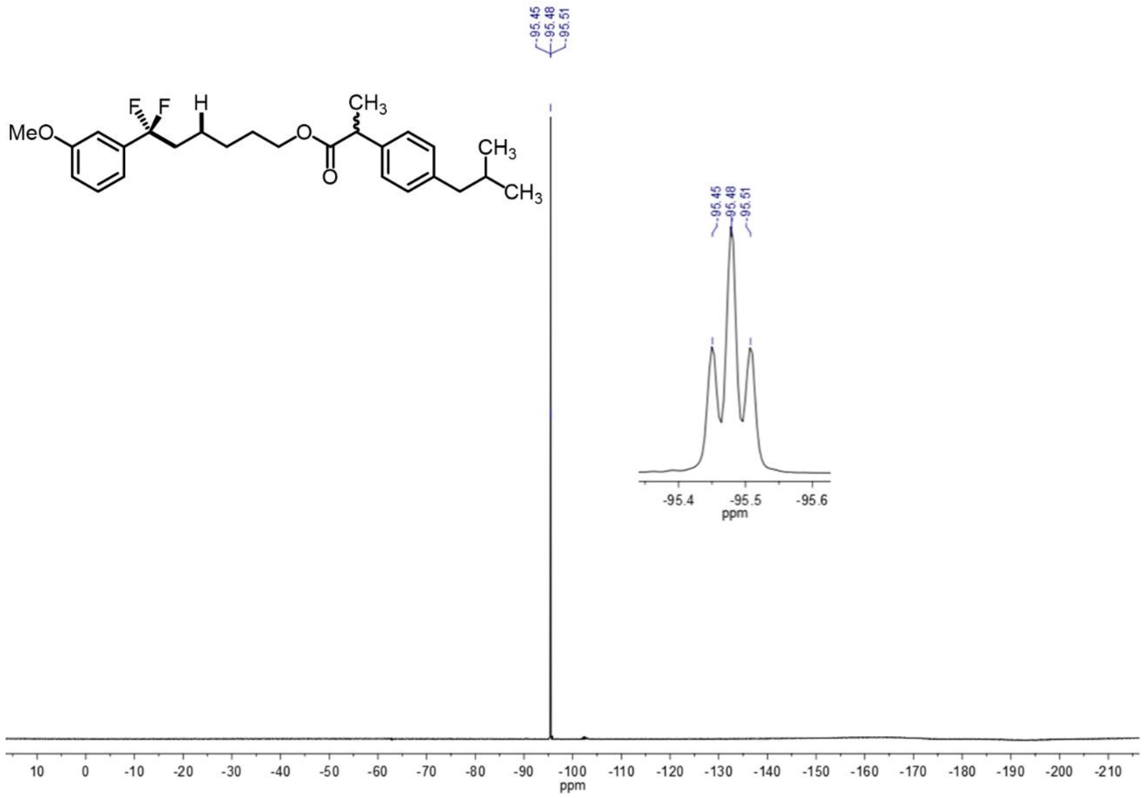
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6r**



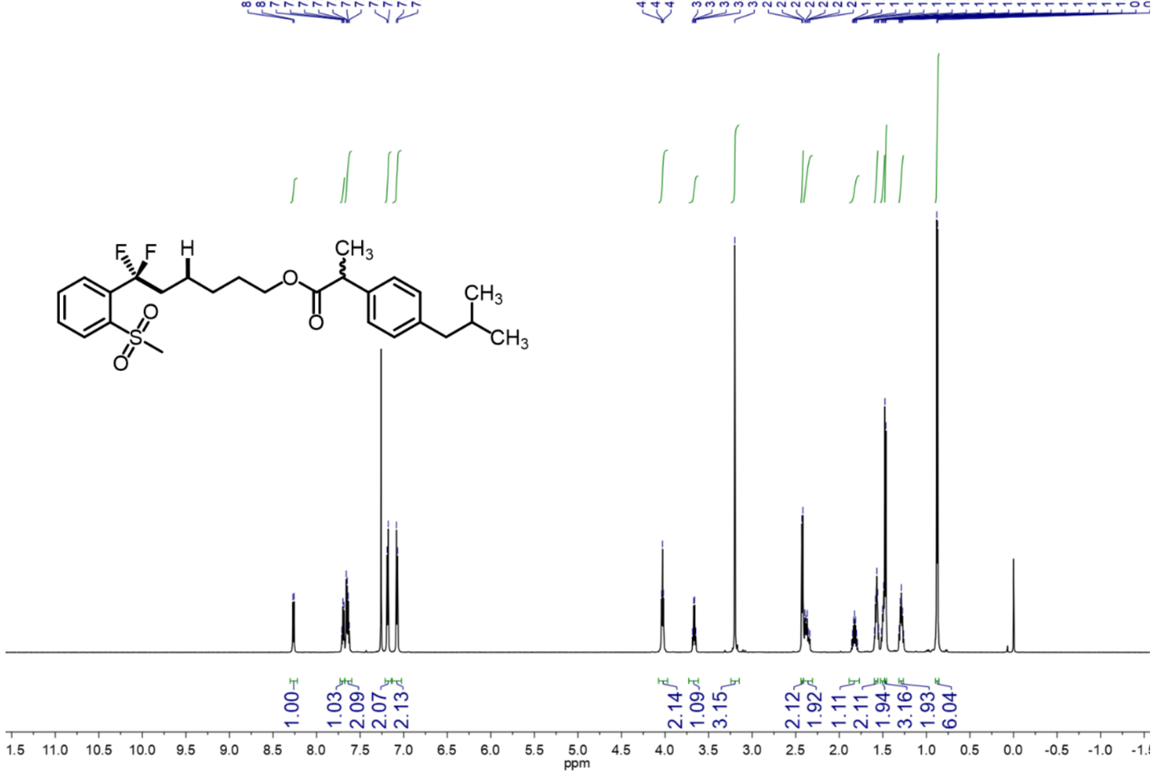
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6s**



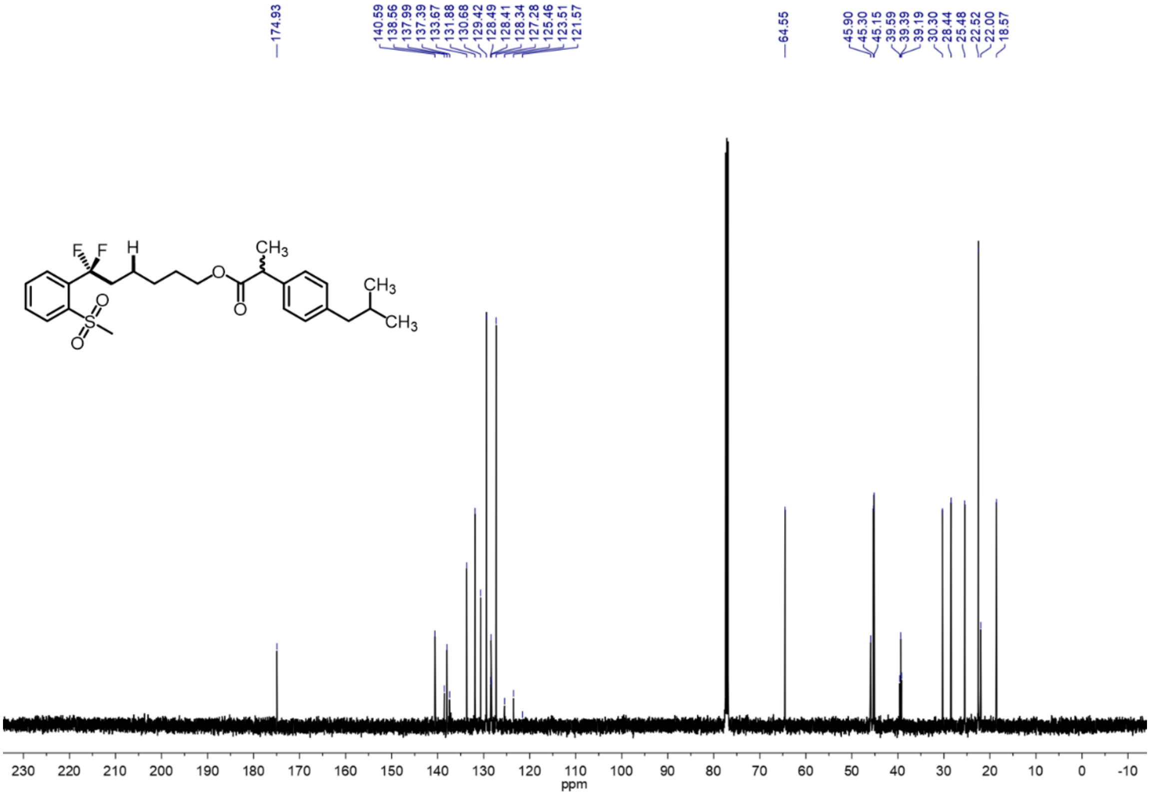
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6s**



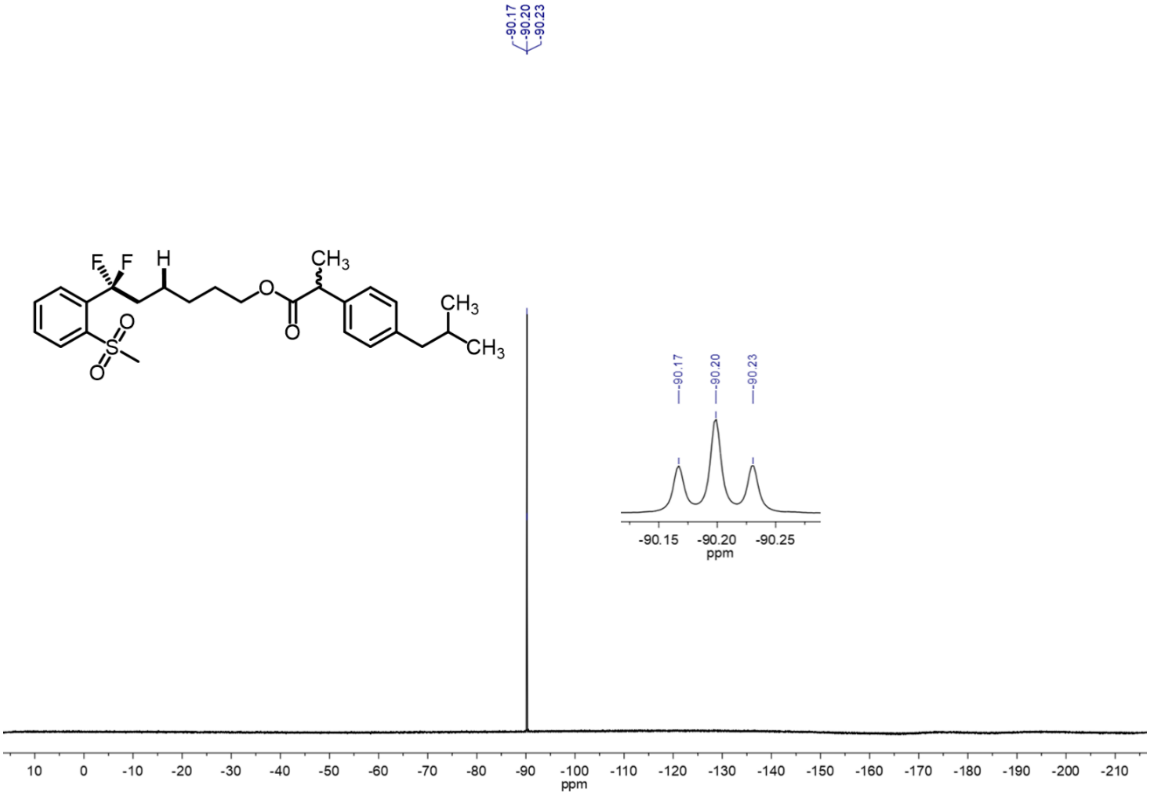
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6s**



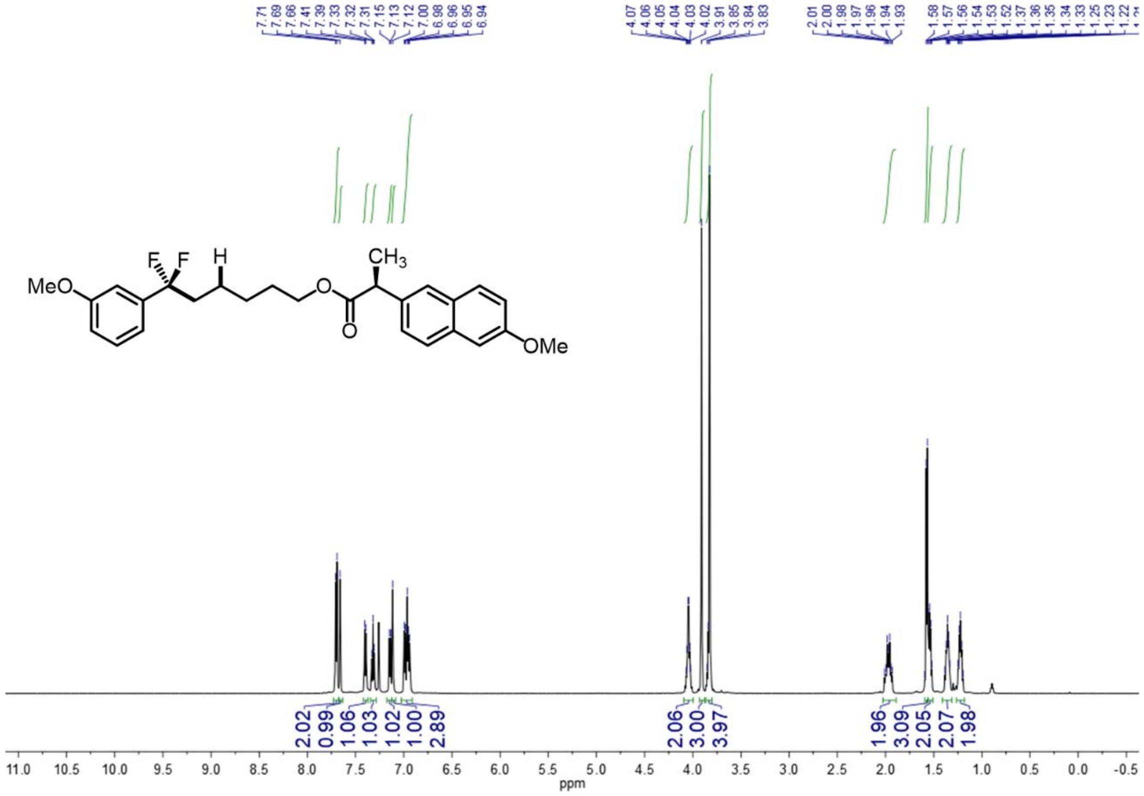
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6t**



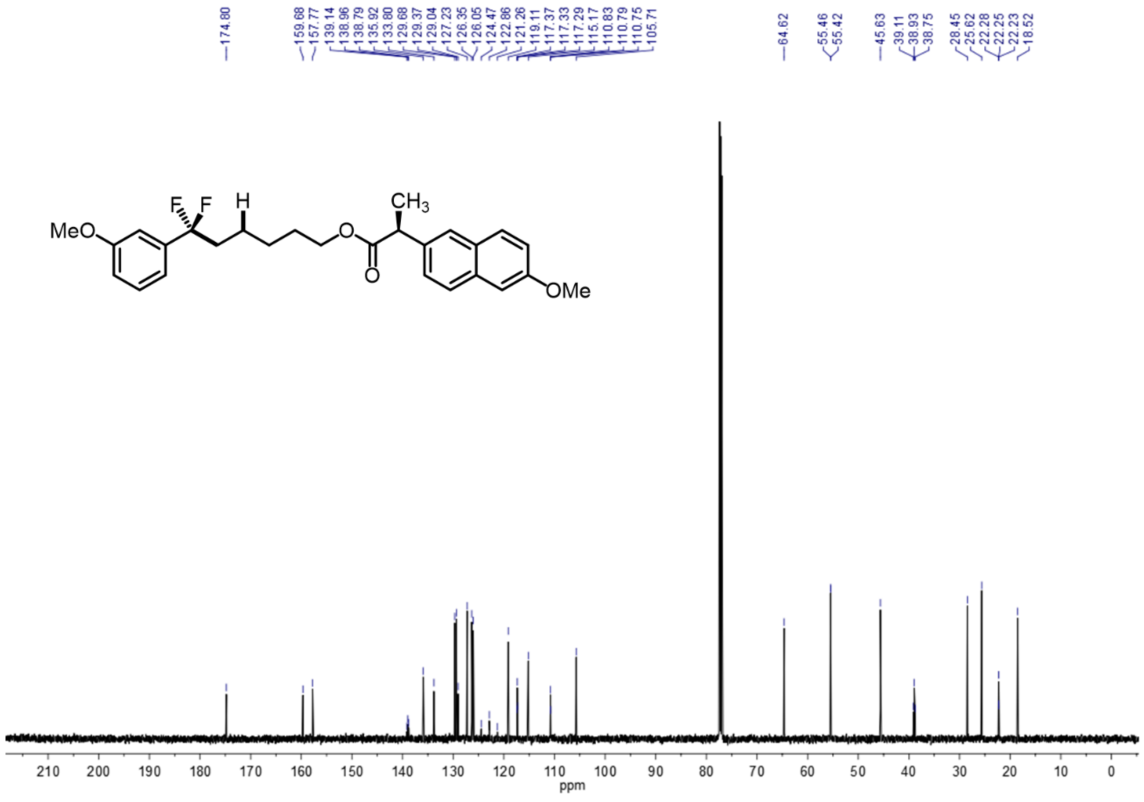
^{13}C NMR spectrum (126 MHz, CDCl$_3$, 23 ºC) of **6t**



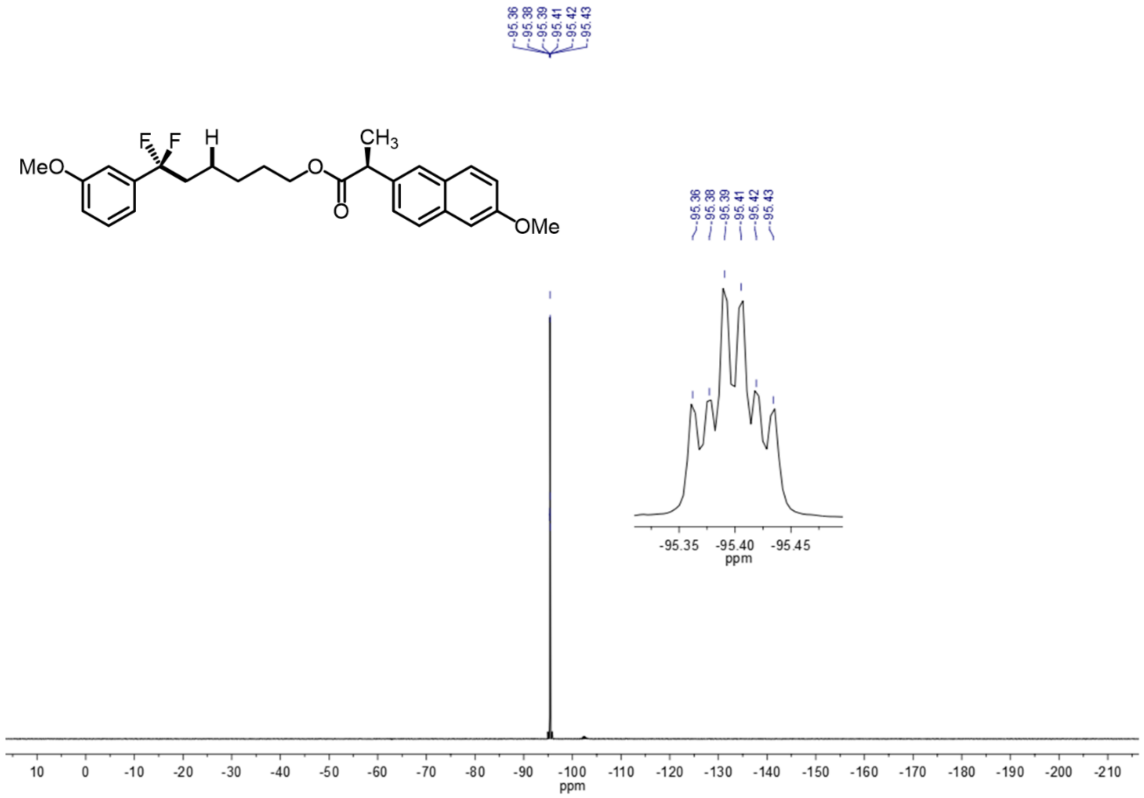
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6t**



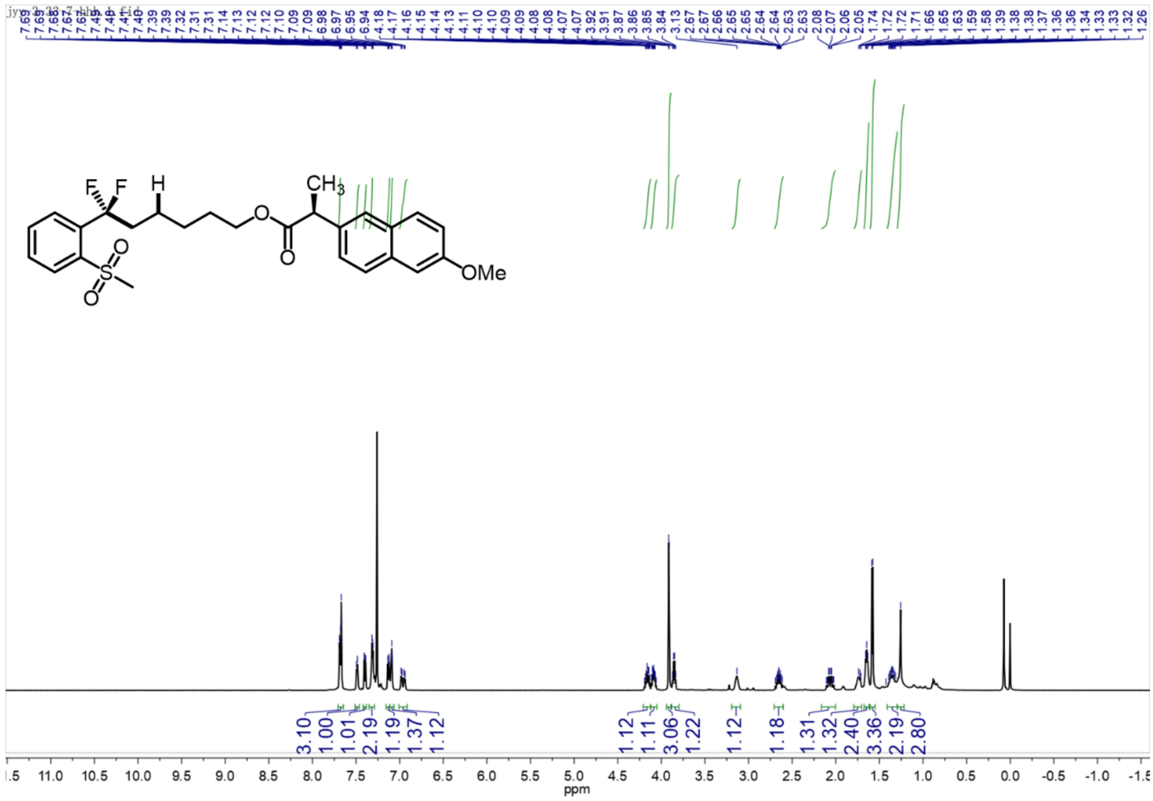
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6u**



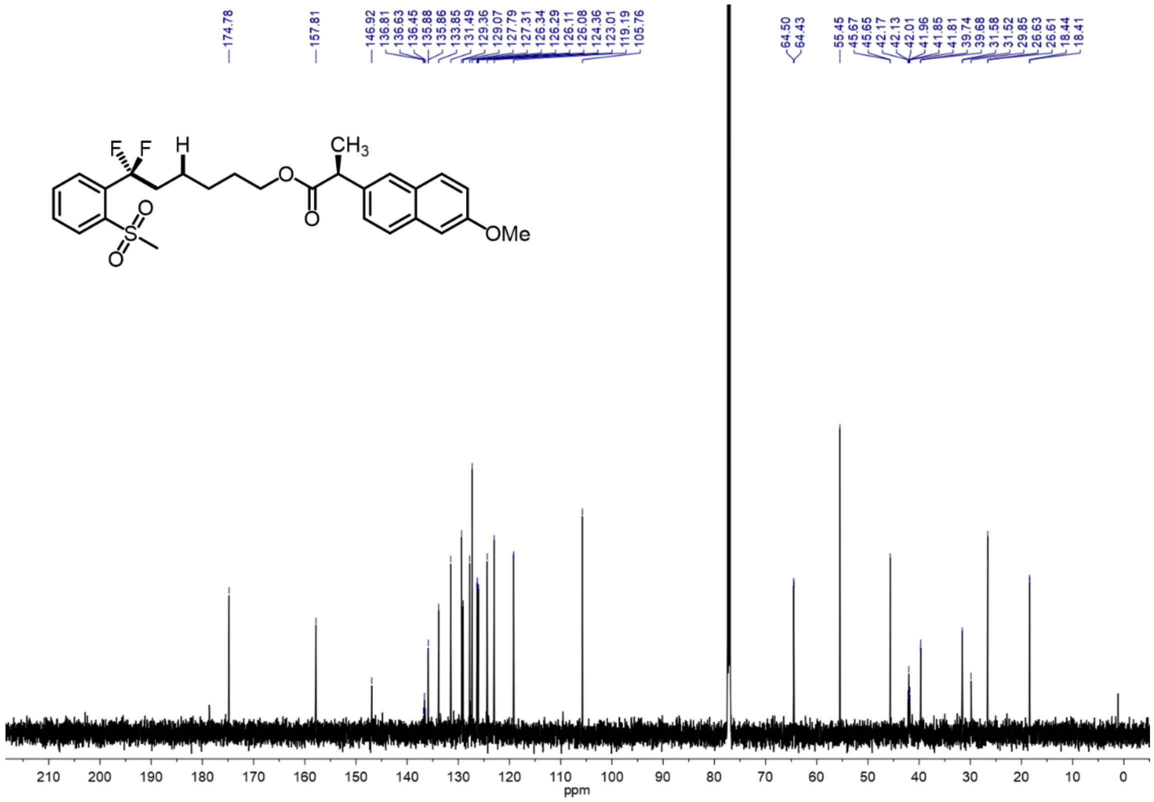
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6u**



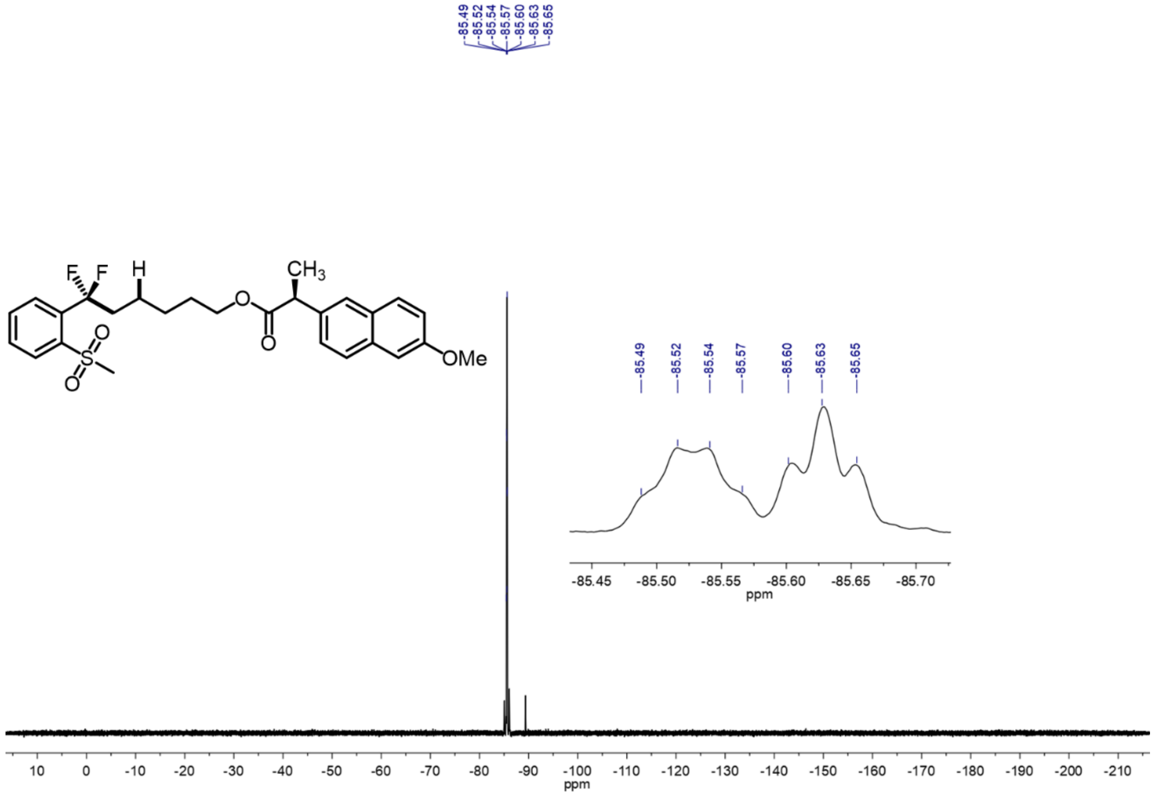
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6u**



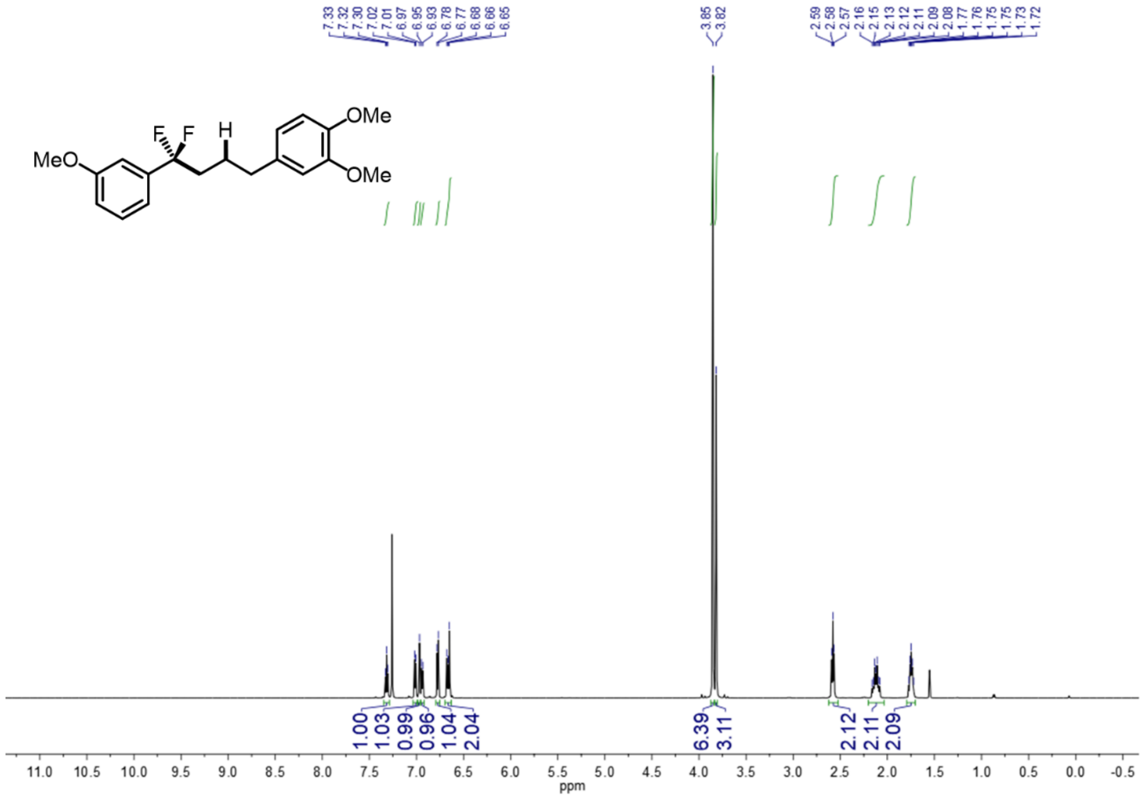
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6v**



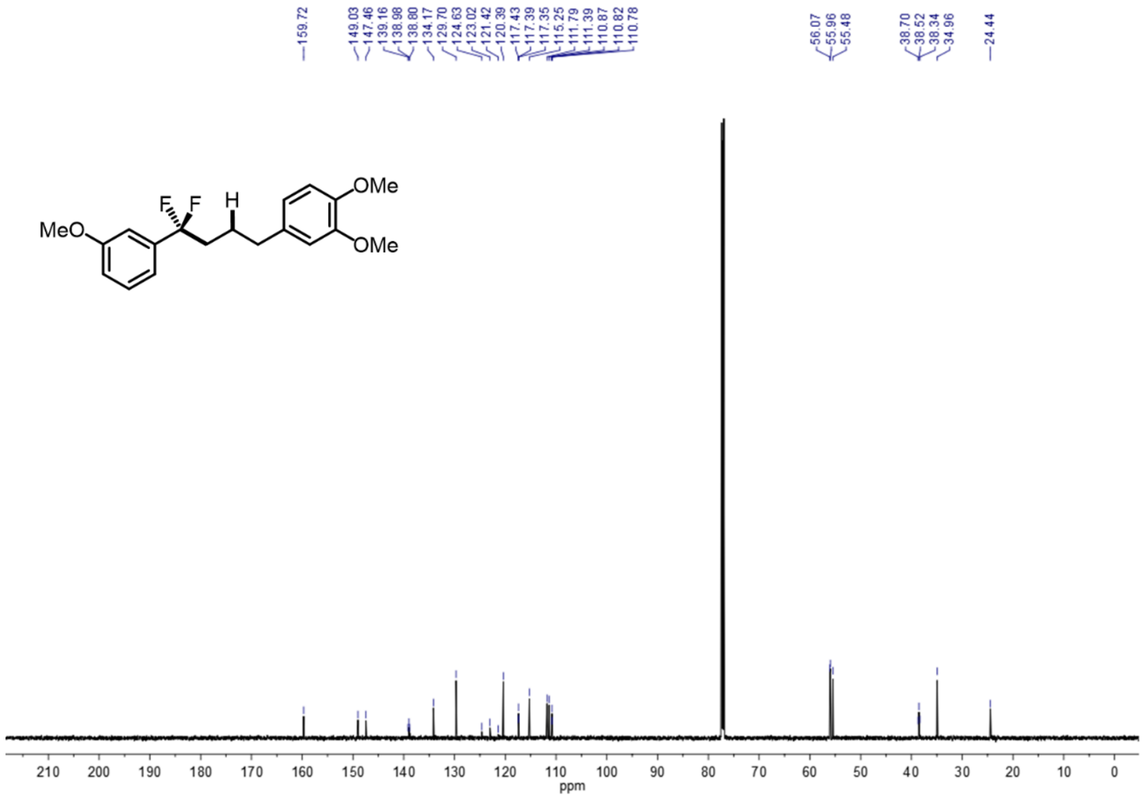
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6v**



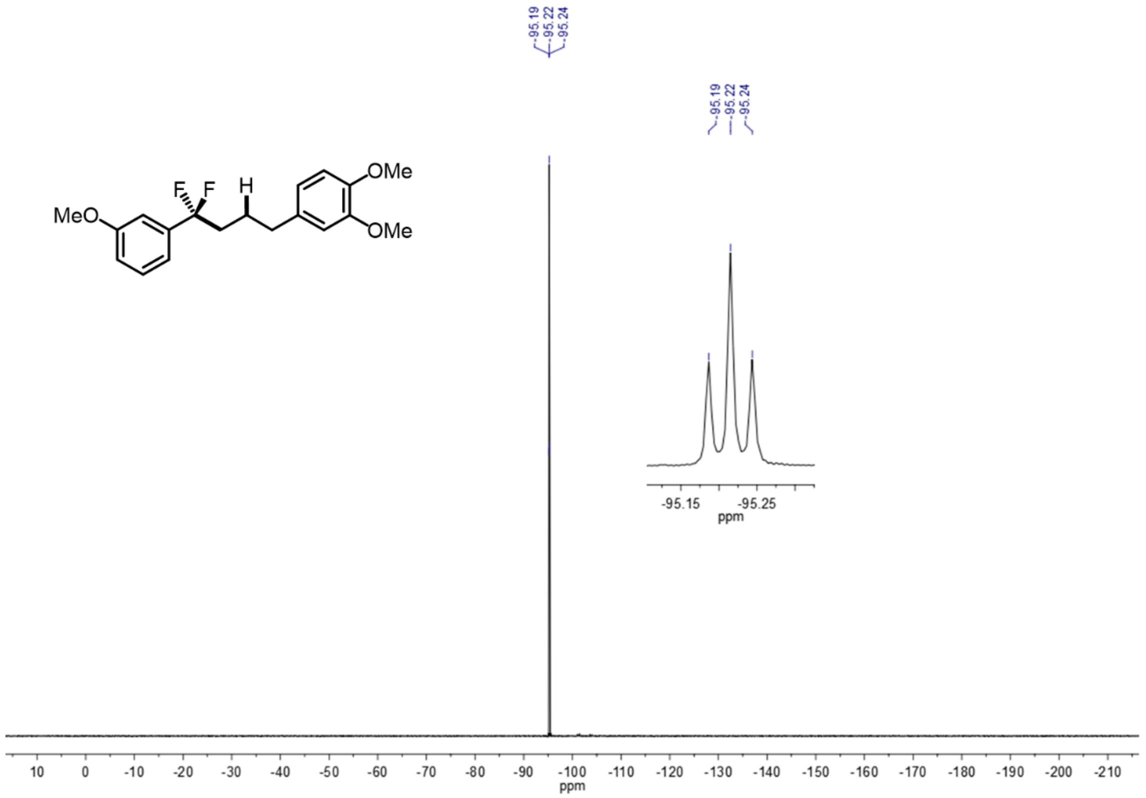
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6v**



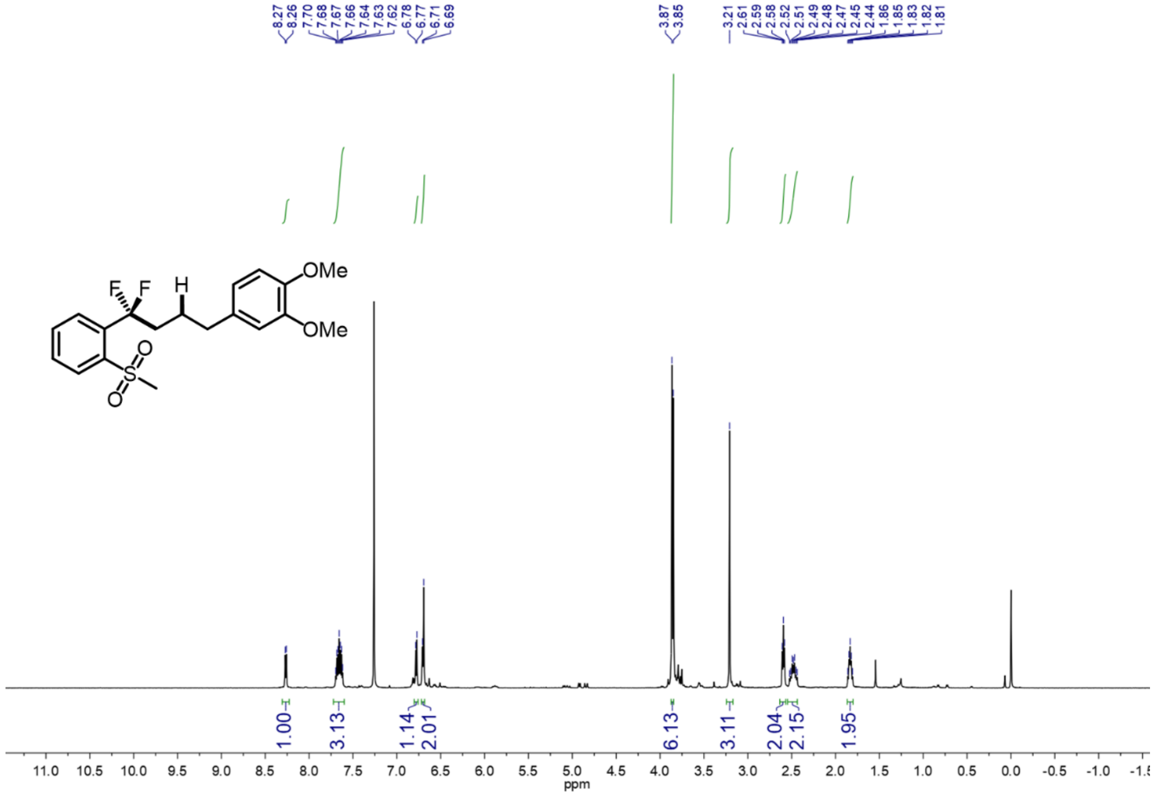
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6w**



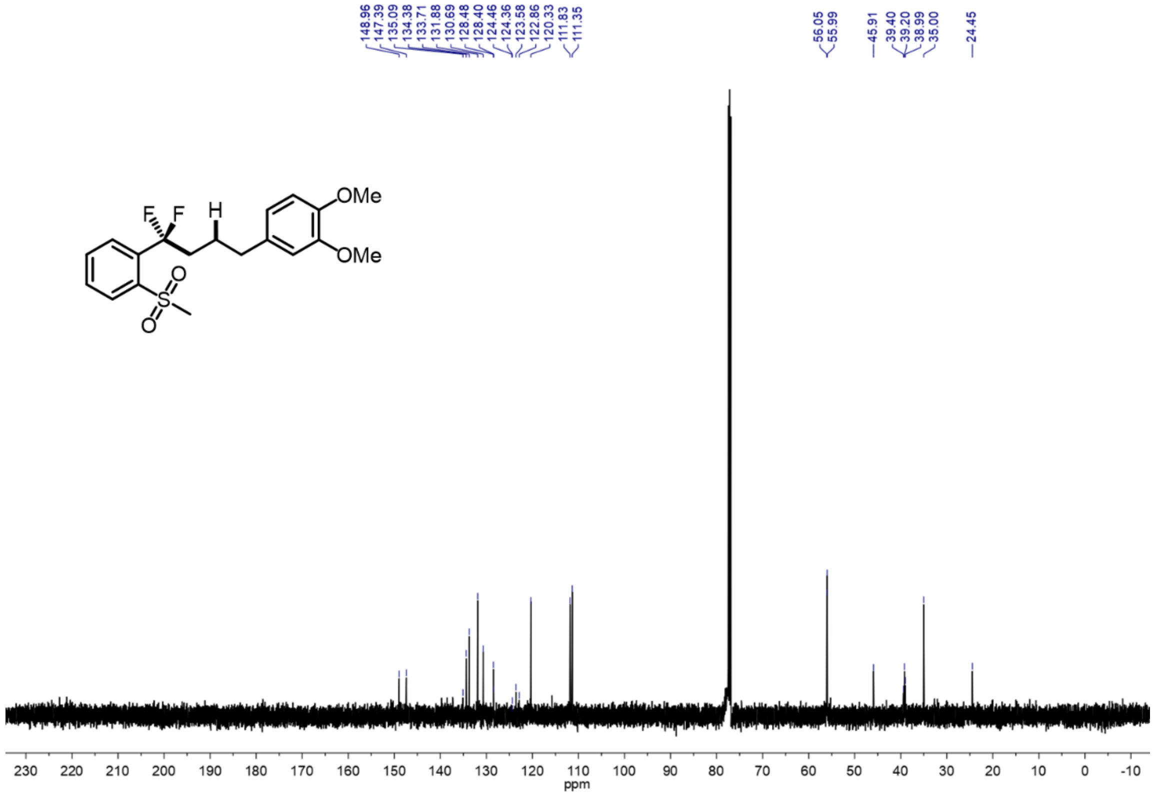
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6w**



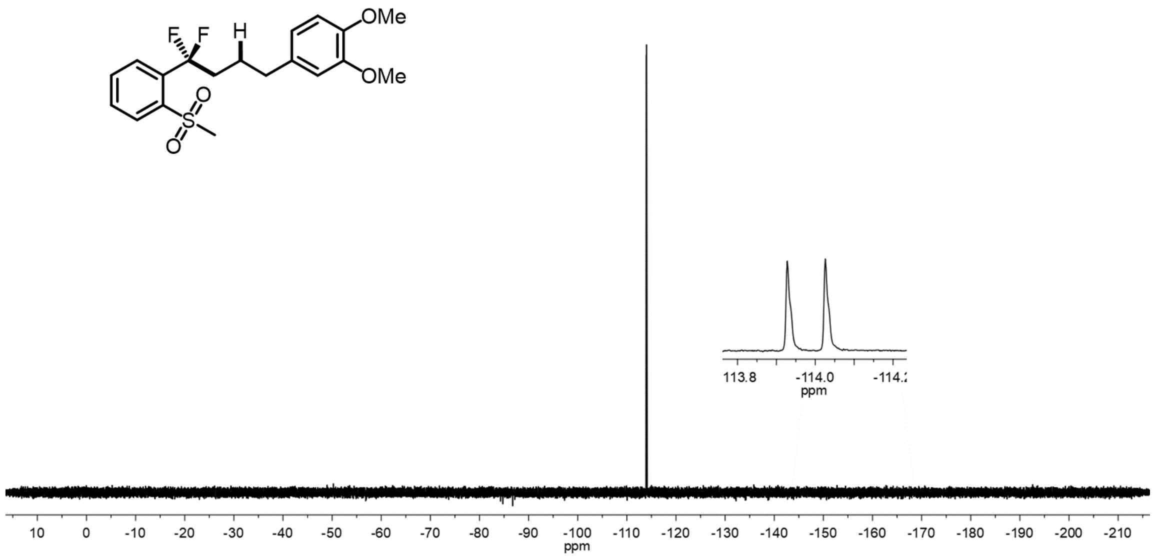
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6w**



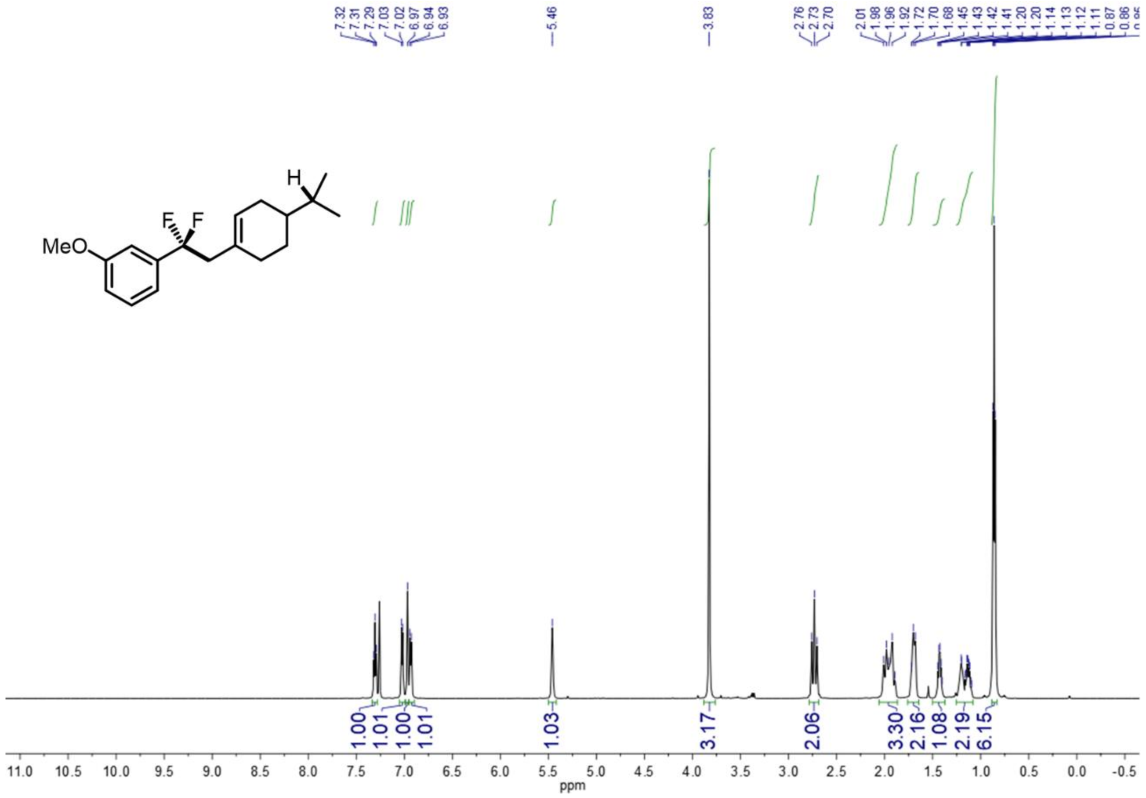
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6x**



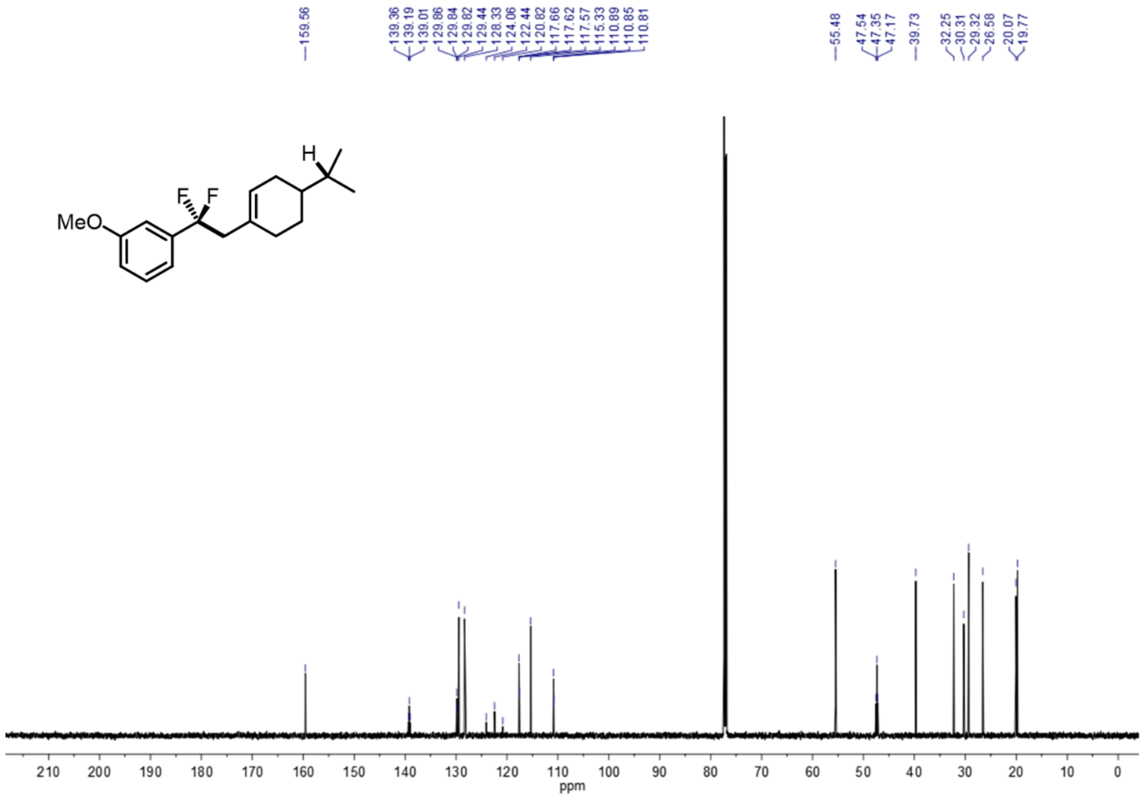
^{13}C NMR spectrum (126 MHz, $CDCl_3$, 23 ºC) of **6x**



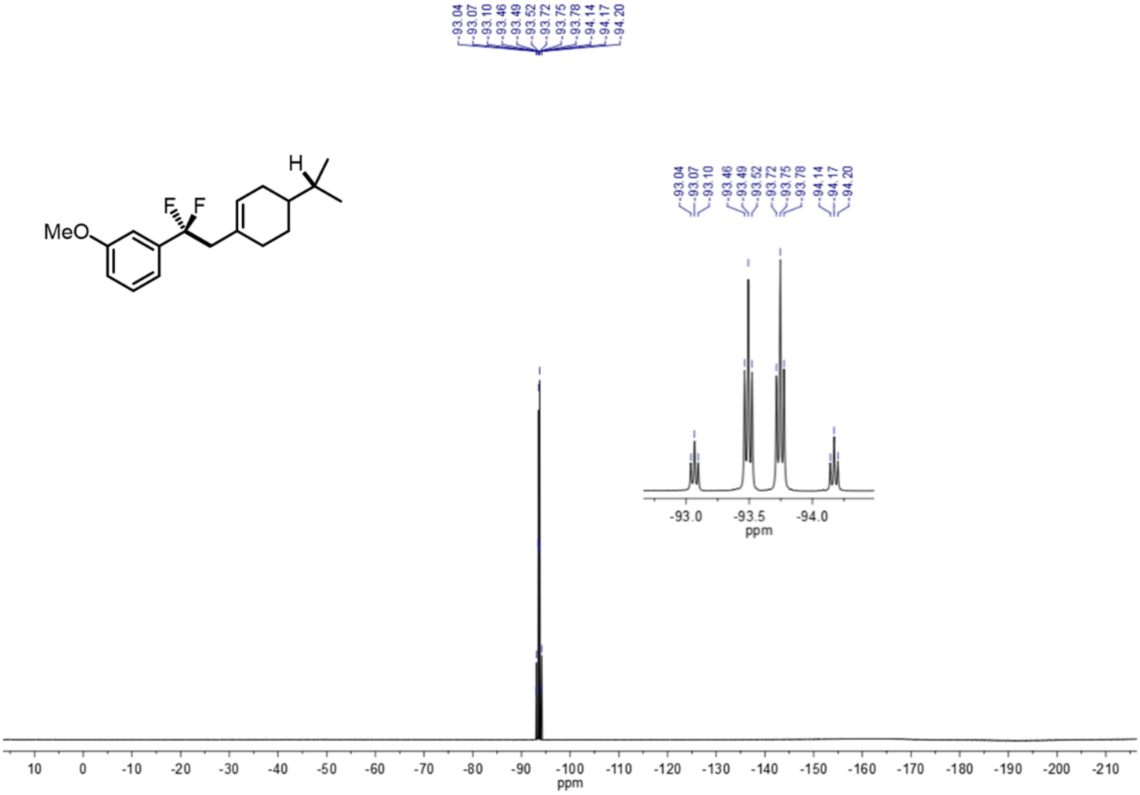
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **6x**



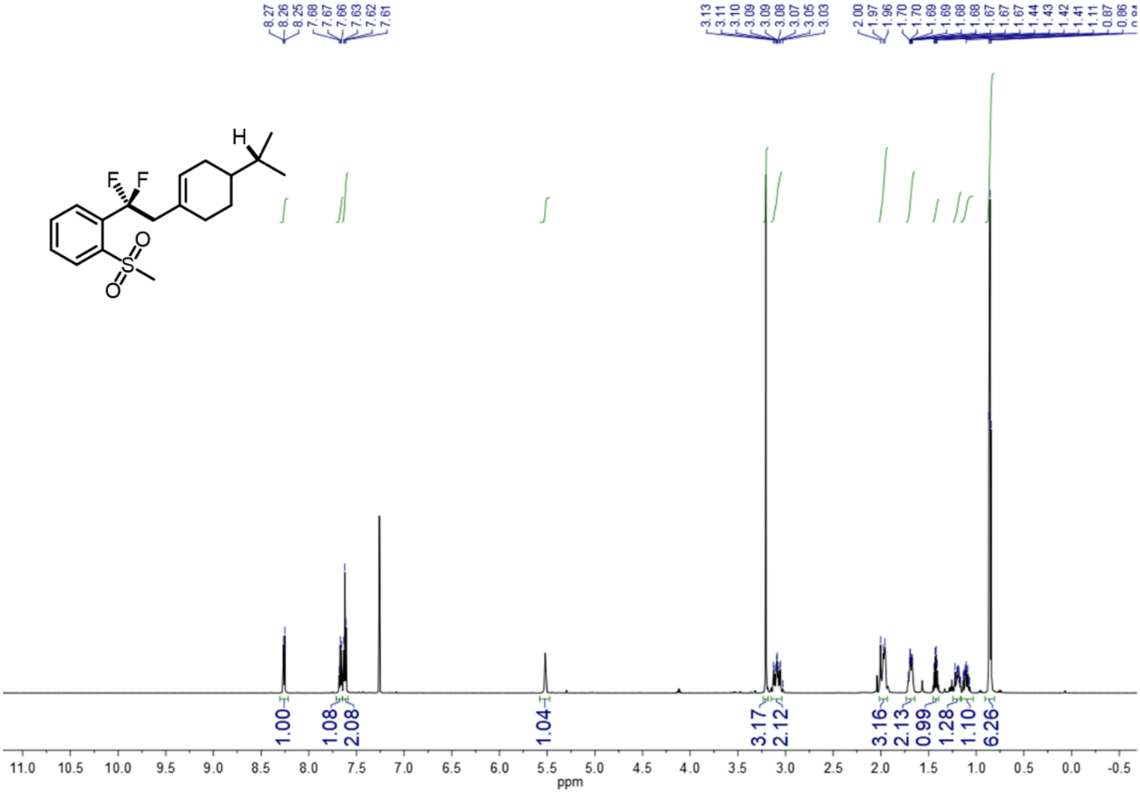
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6y**



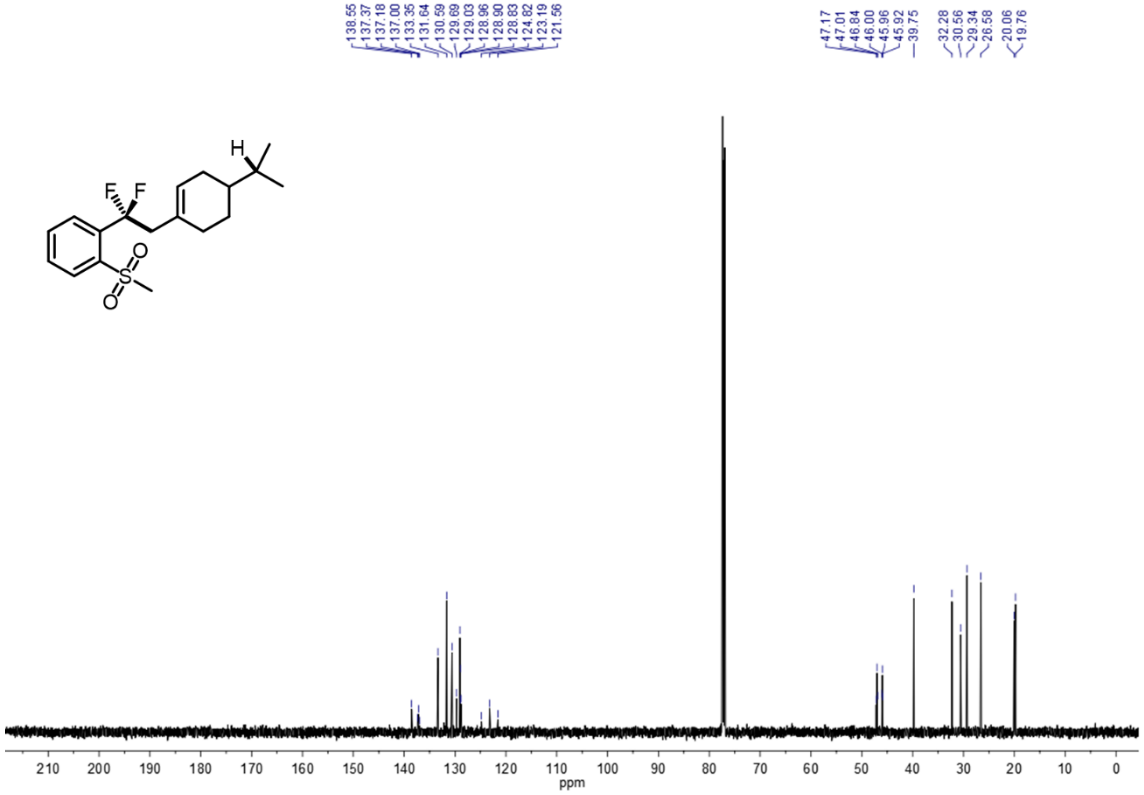
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6y**



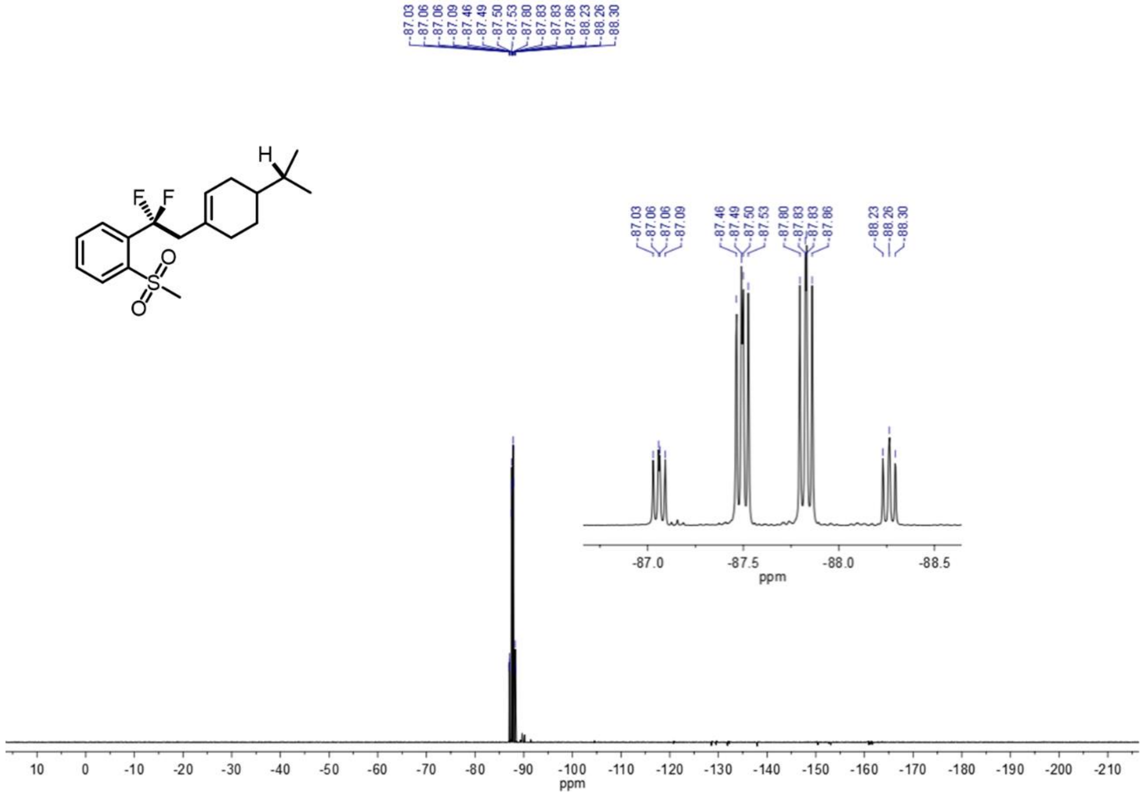
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6y**



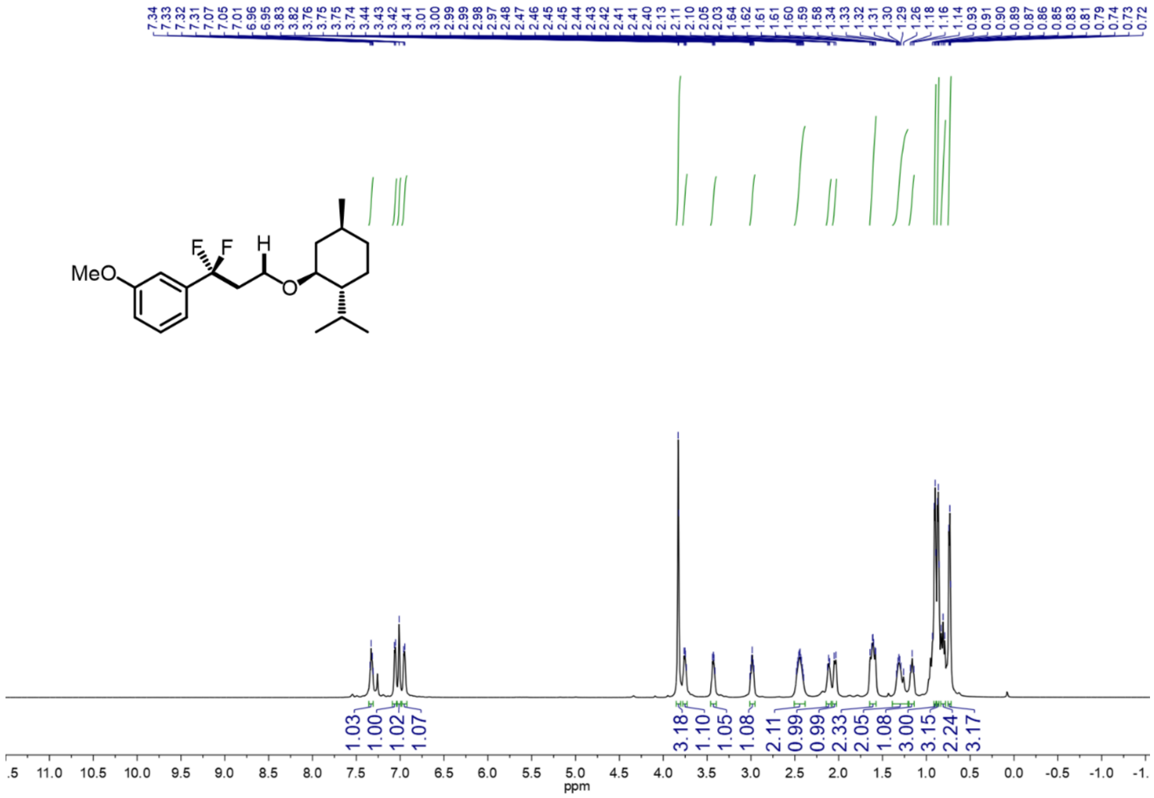
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6z**



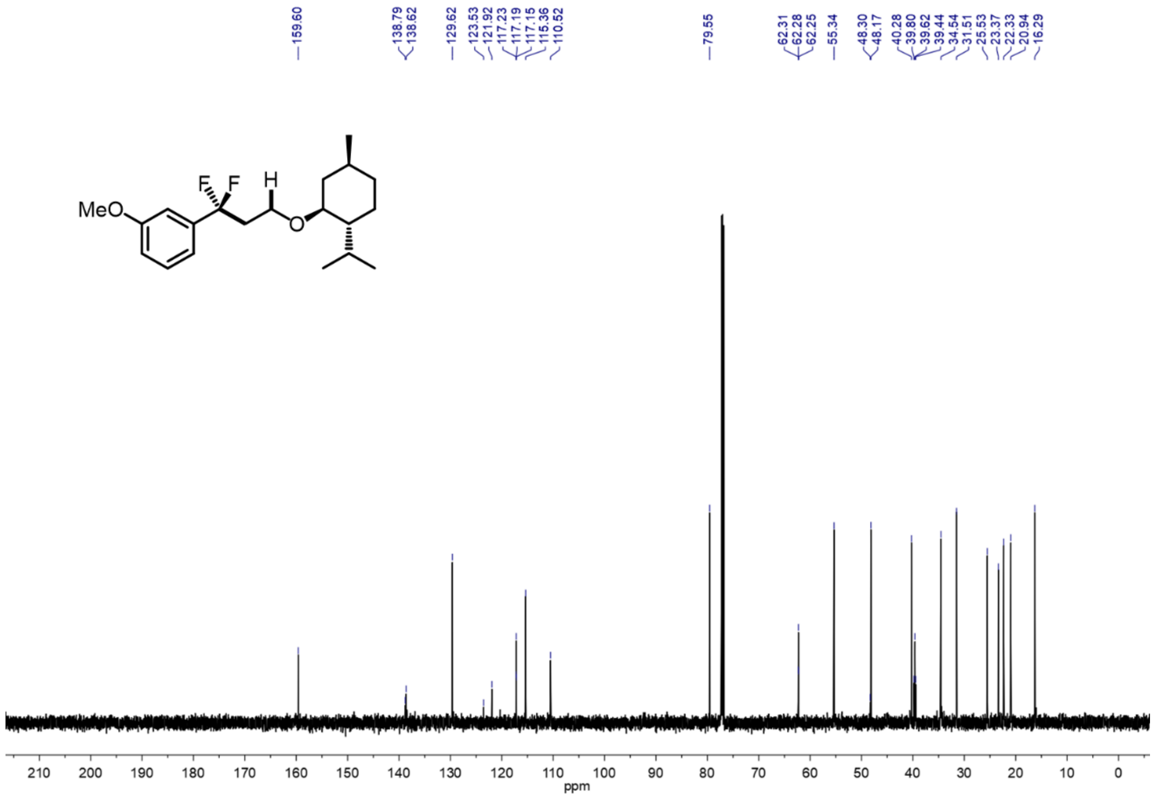
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6z**



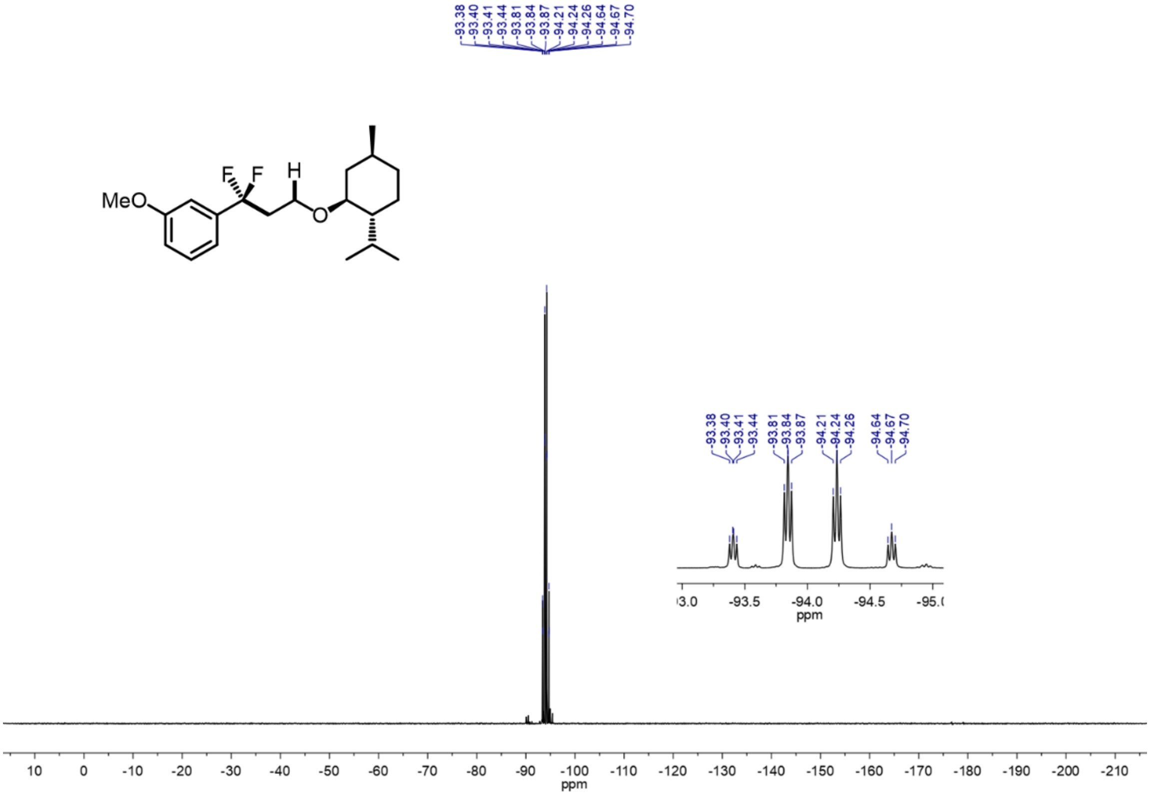
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6z**



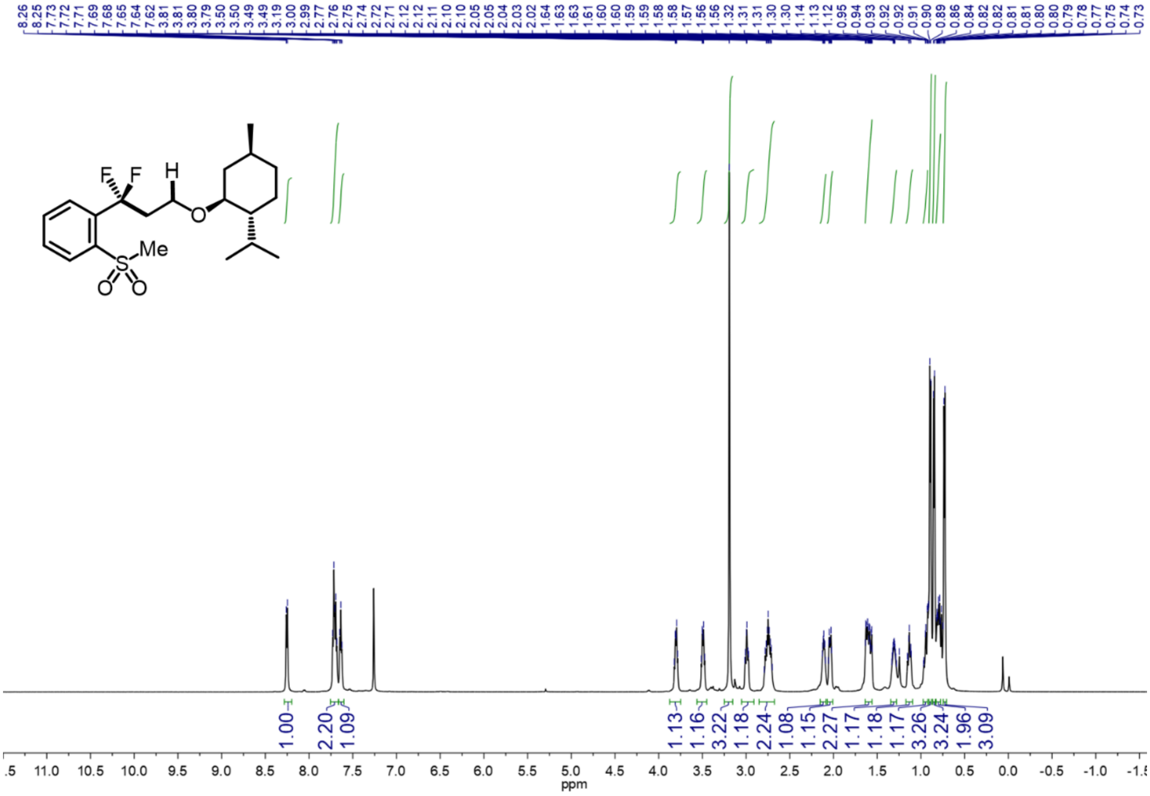
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6aa**



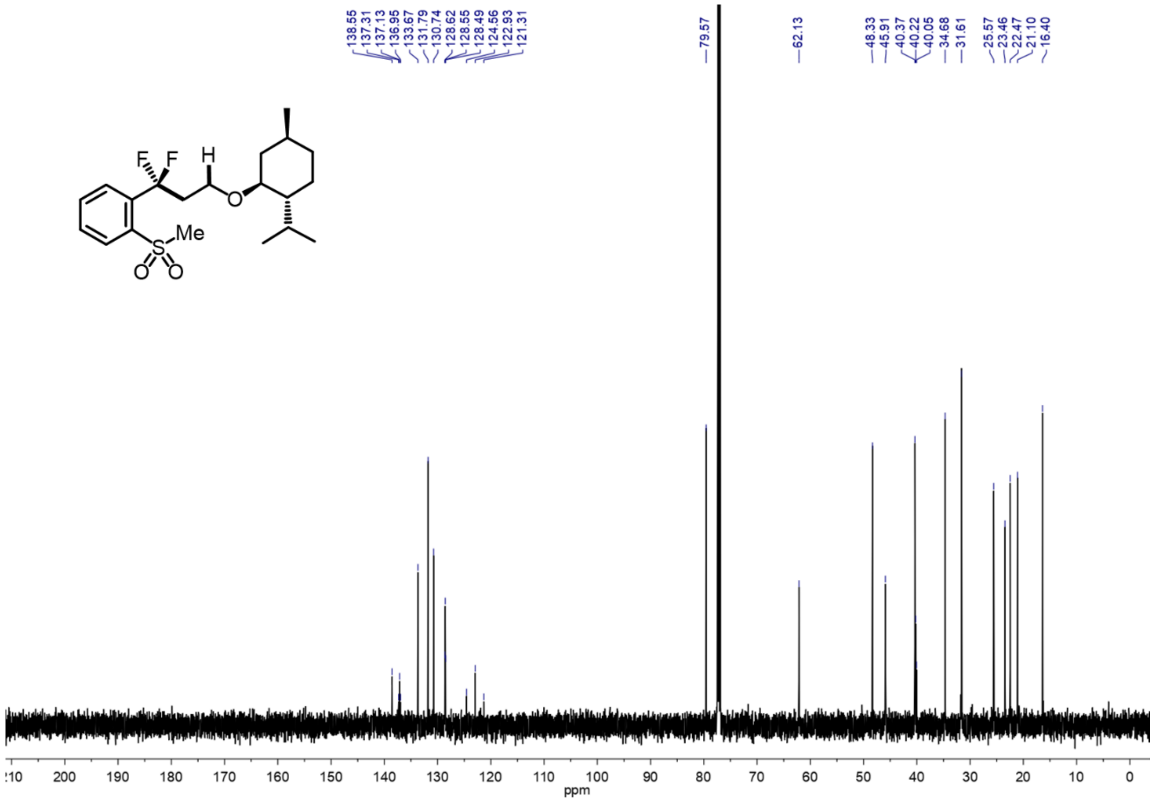
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6aa**



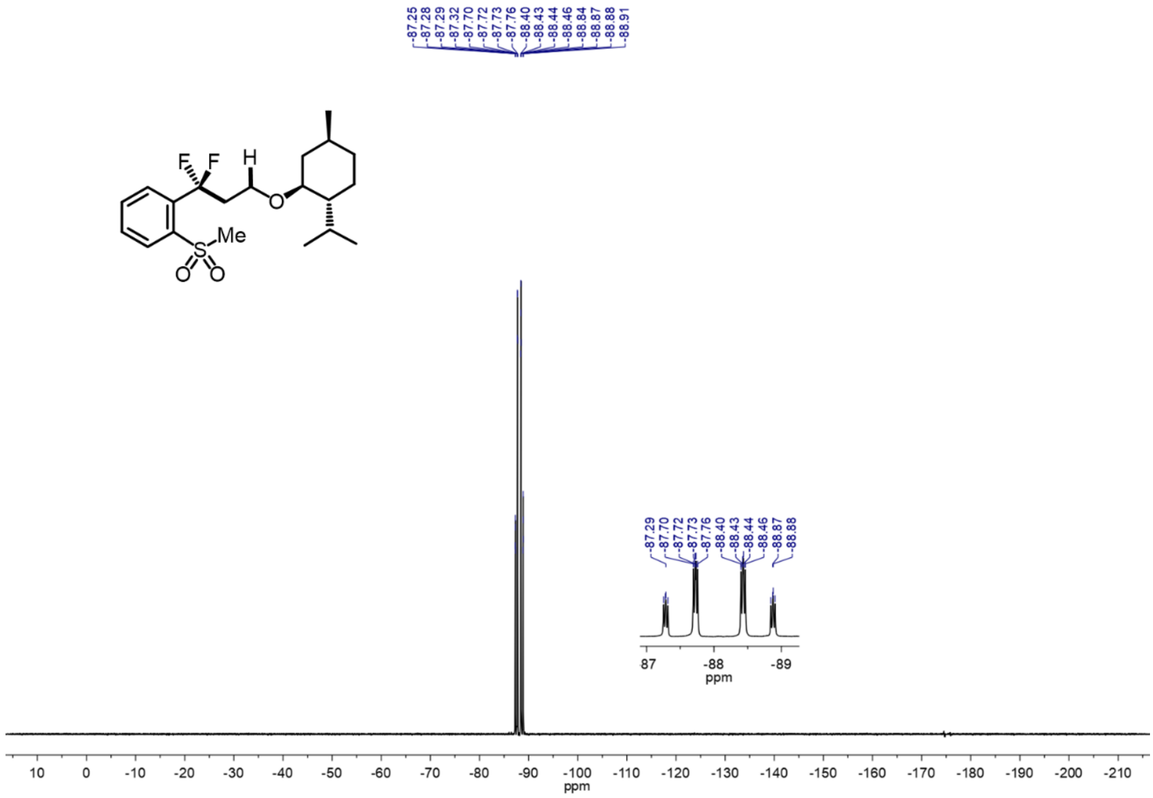
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6aa**



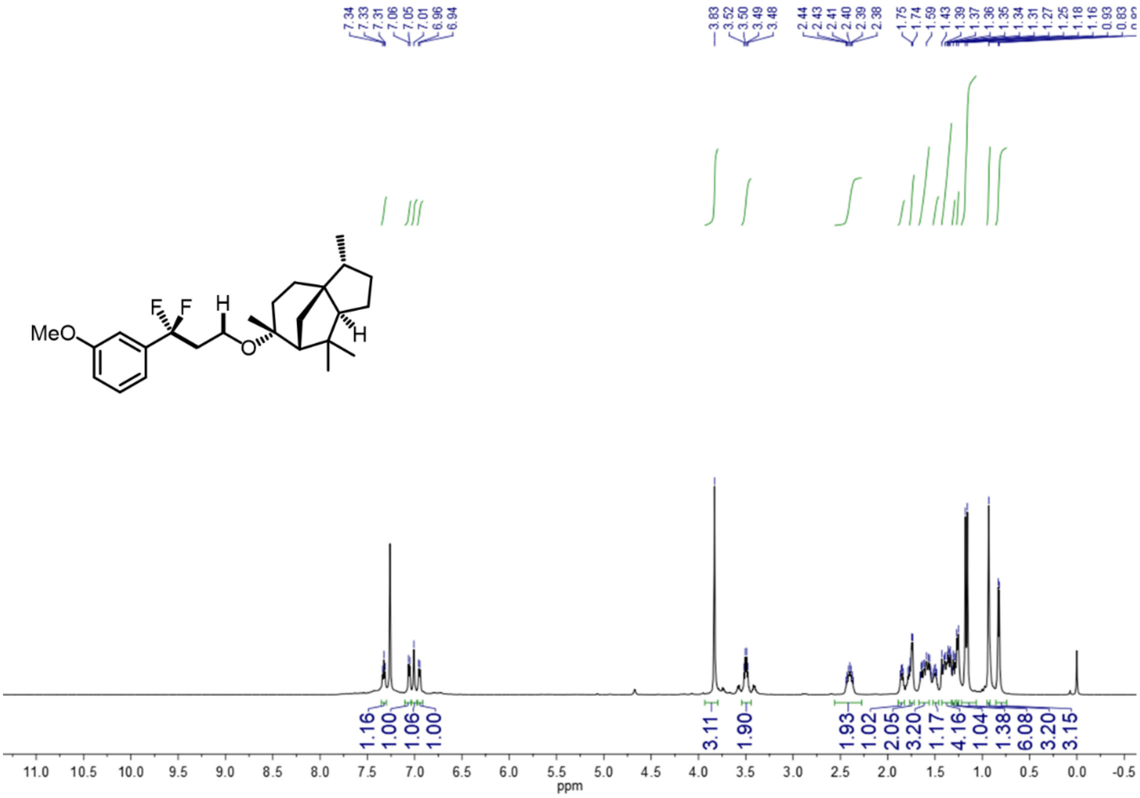
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6ab**



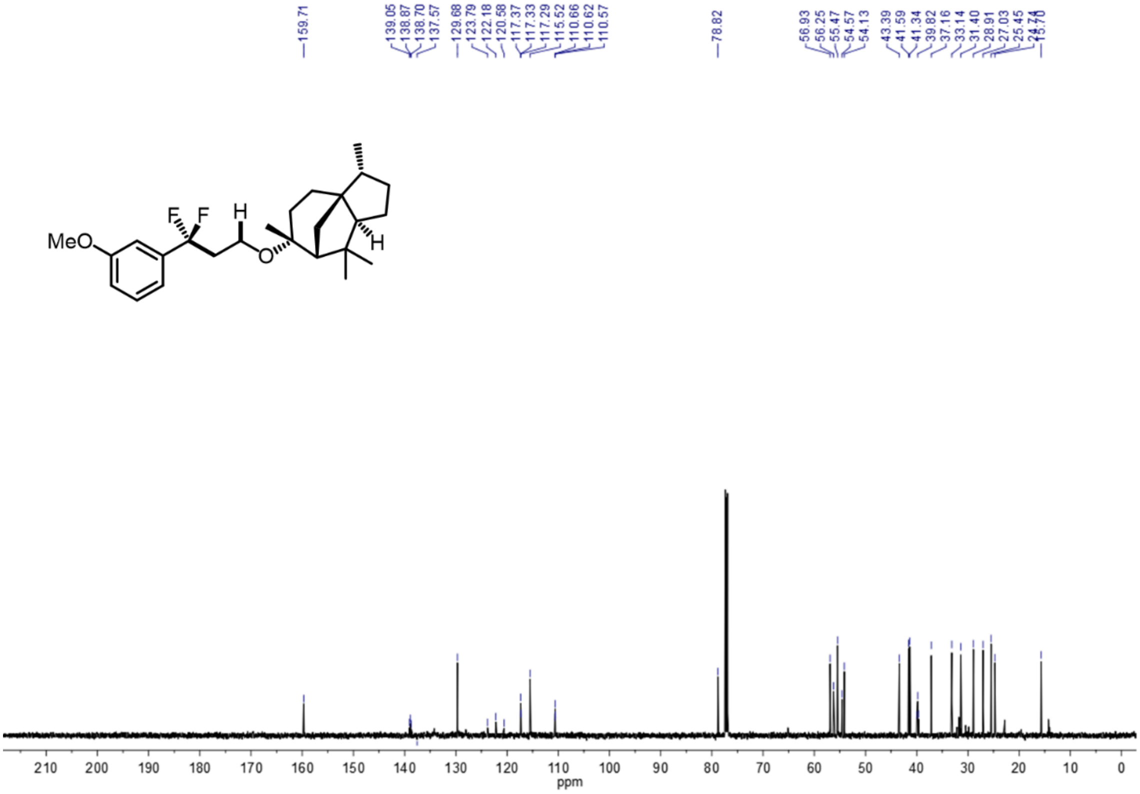
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6ab**



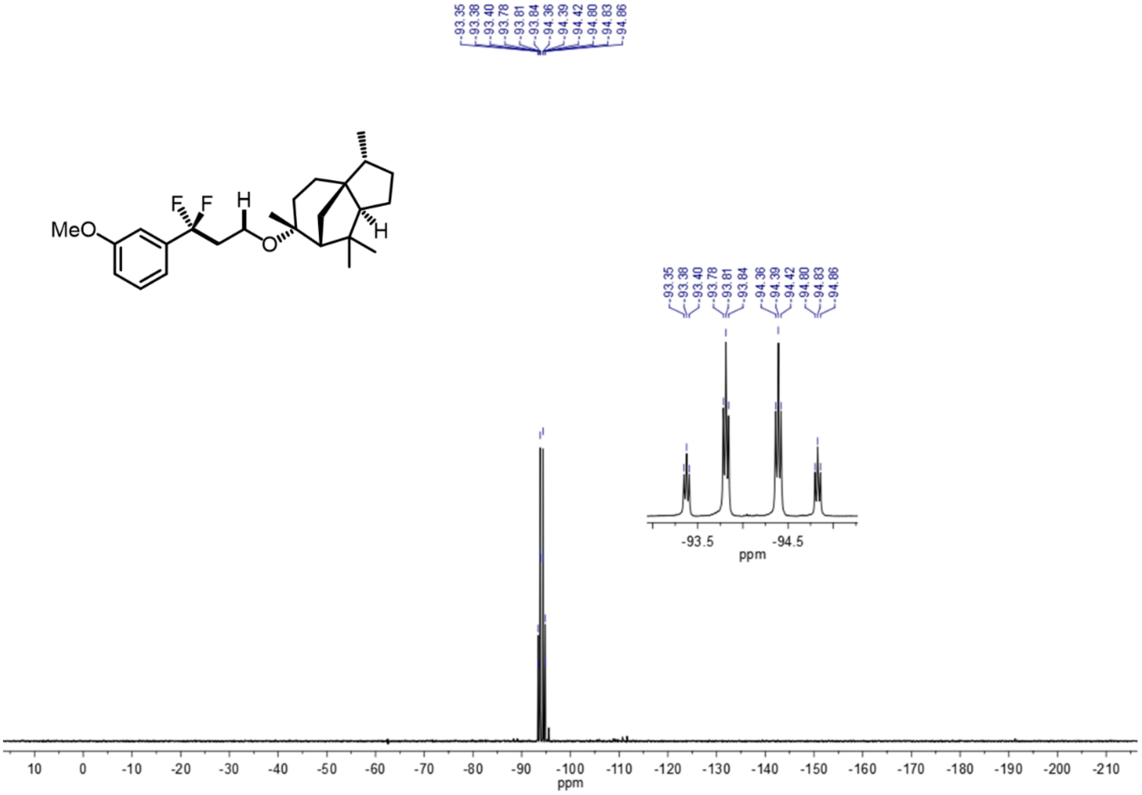
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6ab**



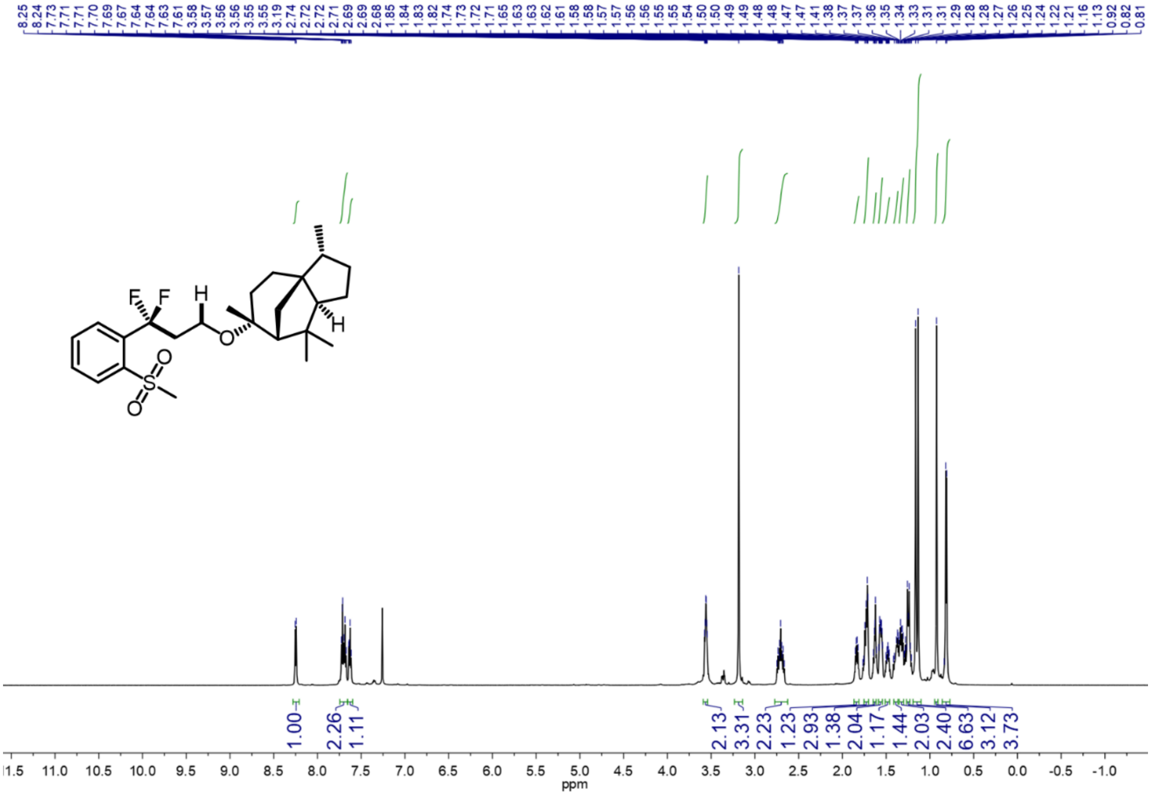
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6ac**



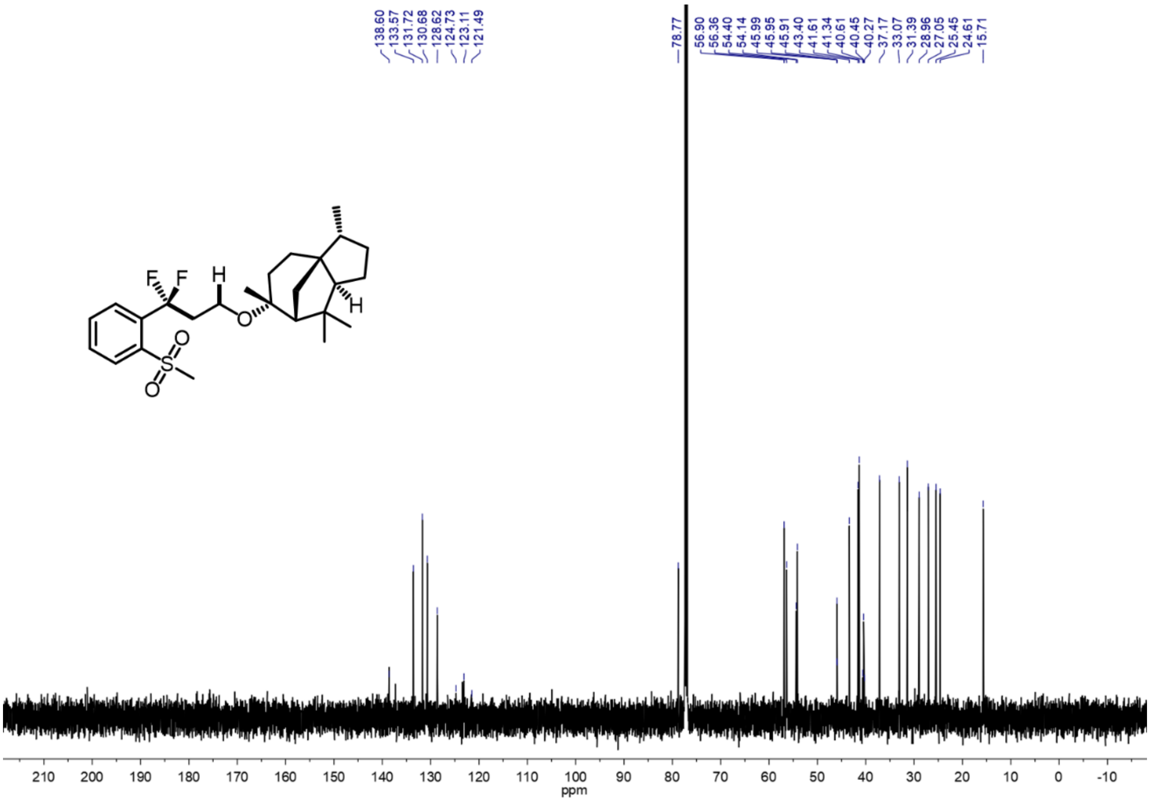
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6ac**



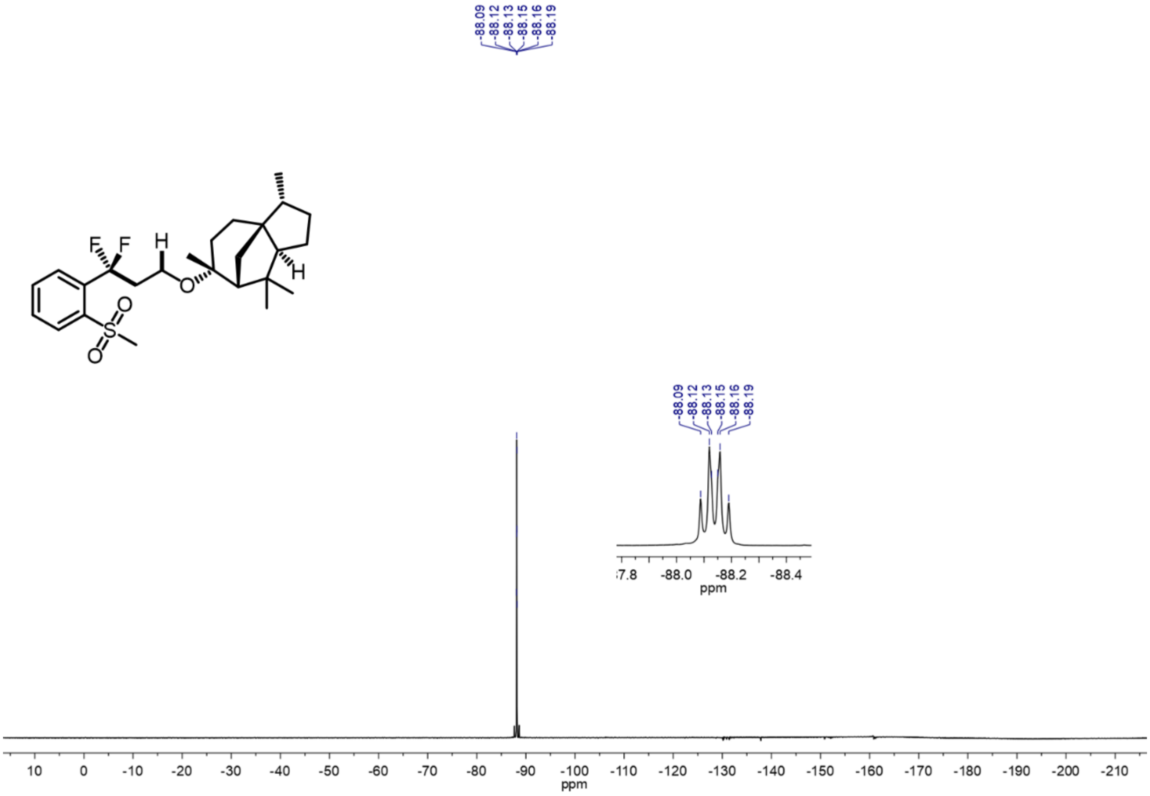
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6ac**



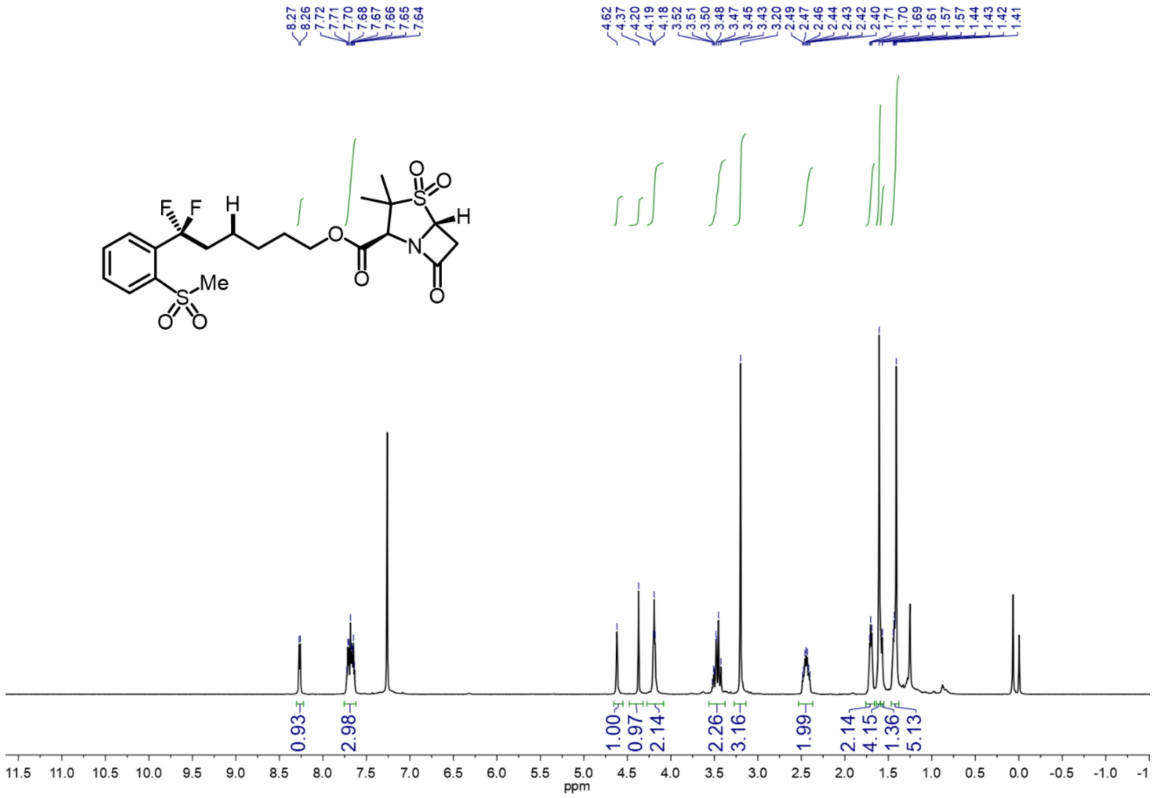
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6ad**



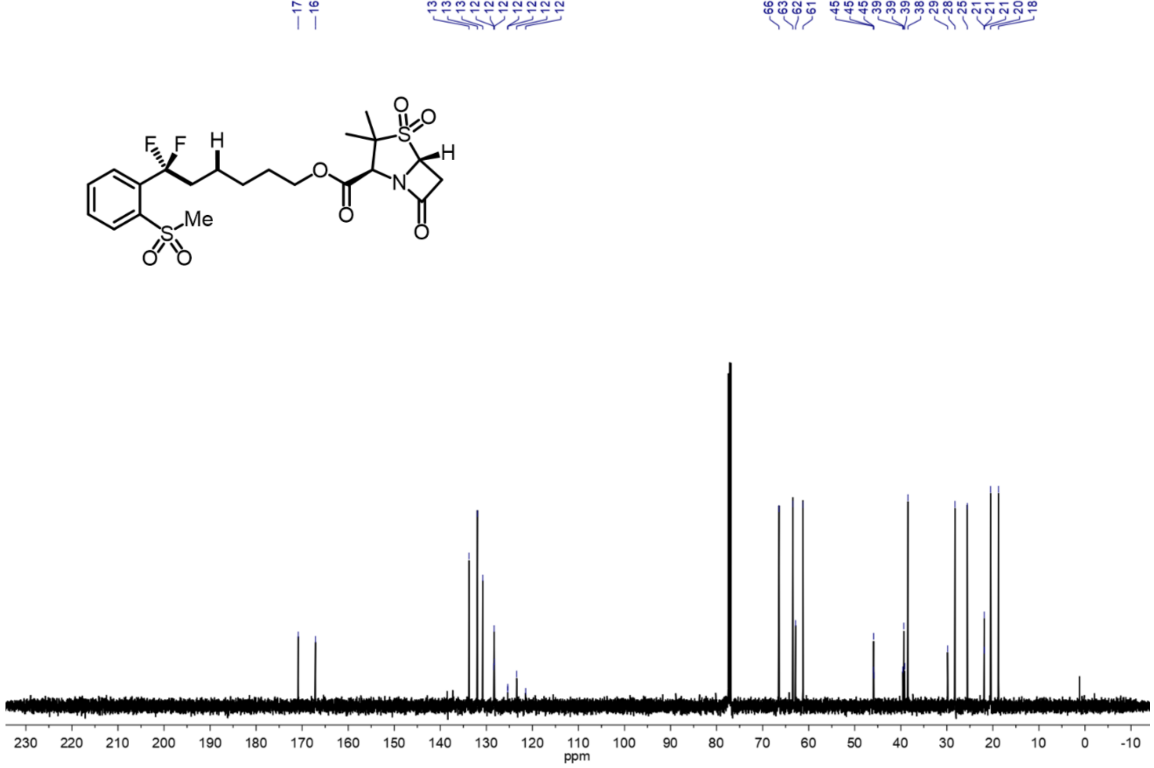
^{13}C NMR spectrum (151 MHz, CDCl$_3$, 23 ºC) of **6ad**



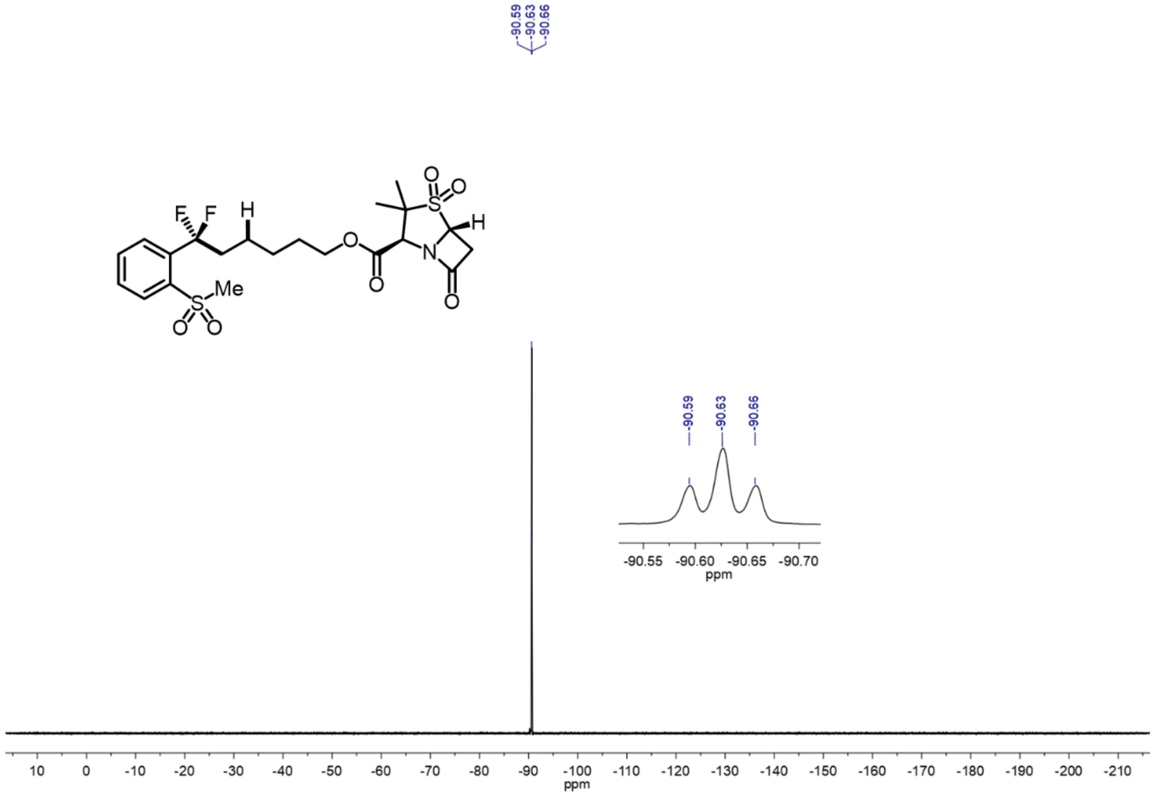
^{19}F NMR spectrum (565 MHz, CDCl$_3$, 23 ºC) of **6ad**



^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **6af**



^{13}C NMR spectrum (126 MHz, CDCl$_3$, 23 ºC) of **6af**



^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **6af**