Supplementary Information

Light-Induced Aryldifluoromethyl-sulfonylation/thioetherification of Alkenes Using Arenethiolate as Photoreductant and Sulfur Source

Jiayu Li, Zipeng Guo, Xiaofeng Zhang, Xiaoli Meng, Zhenyang Dai, Meiyun Gao, Shuo Guo,* and Pingping Tang

Table of Contents

1 General Information 4

2 Reaction Optimization Tables 5

2.1 Optimization of Bases (Table S1) 5

2.2 Optimization of Solvents (Table S2) 6

2.3 Optimization of Wavelength of Light (Table S3) 7

2.4 Optimization of the Amount of Arylthiols and Base (Table S4) 7

2.5 Optimization of Time and Amount of Solvent (Table S5) 8

2.6 Optimization of the Oxidation Step (Table S6) 8

2.7 Unsuccessful Substrates 9

3 Preparation of Substrates 9

3.1 Preparation of Alkenes 9

3.2 The Scope of Trifluoromethylarenes 11

3.3 The Scope of Arylthiols 15

4 Experimental Procedures and Spectral Data 16

4.1 General Procedure 16

4.2 Experimental Details and Characterization Data 17

5 Synthetic Applications 52

5.1 Gram-scale Reaction 52

5.2 Product Derivatizations 53

6 Mechanistic Studies 56

6.1 UV-Vis Absorption Spectroscopic Measurements 56

6.2 ^{19}F NMR Titration Experiments 58

6.3 Stern-Volmer Quenching Experiment 59

6.4 Light On/Off Experiment 62

6.5 DFT Calculations 63

6.6 Radical Clock Experiment 68

6.7 Detection of the Alkyl Radical Intermediate 70

7 NMR Spectra for New Compounds 74

8 X-Ray Crystallography Data of **5x** 167
9 References 169

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. The LED lamps were purchased from Kessil (370 nm, 390 nm, 427nm, 440 nm and 525 nm). The LED lamps of 365 nm (30 W) were purchased from Taobao (https://m.tb.cn/h.5avX9aS?tk=WwODdsSy18W).

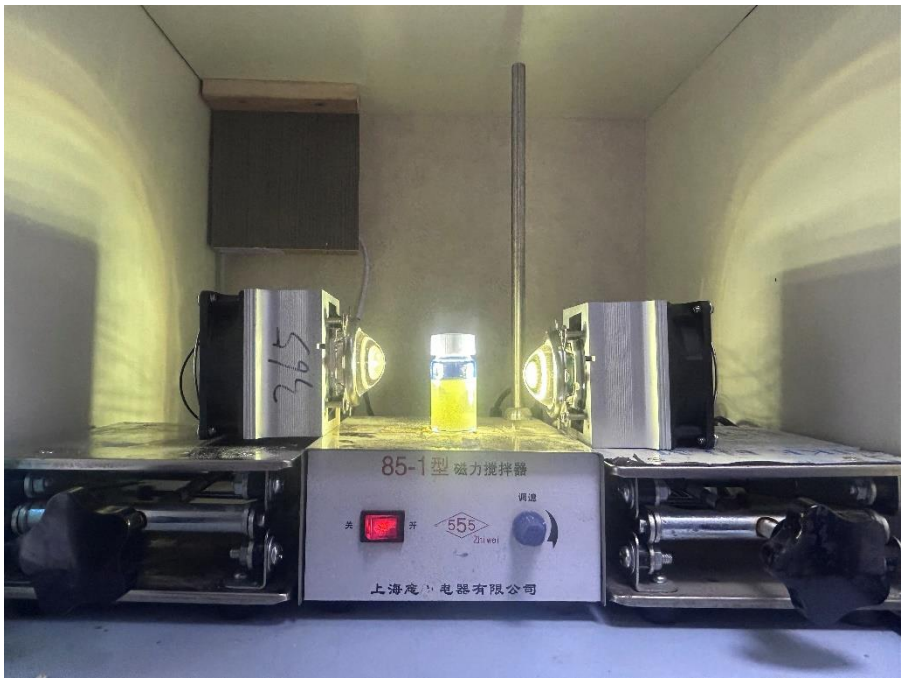


Figure S1. The photo reaction setup and 365 nm LED (30 W) lamps.

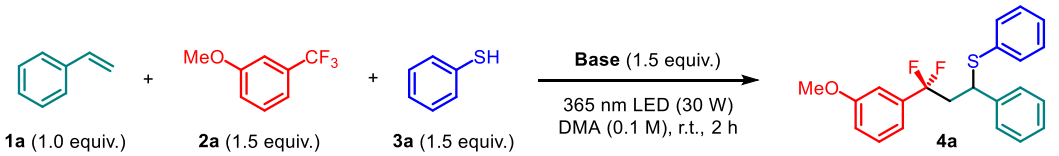
Instruments

^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded on Bruker AVIIIHD NEO 600 MHz. Chemical shifts (δ) were reported in parts per million relative to chloroform (7.26 ppm for ^{1}H NMR; 77.0 ppm for ^{13}C NMR) or acetone (2.05 ppm for ^{1}H NMR; 205.9

ppm and 30.6 ppm for ^{13}C NMR). ^{19}F NMR chemical shifts were corrected by using (trifluoromethoxy)benzene as an internal standard (-58.4 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. X-ray single crystal diffraction data were collected on a Bruker SMART APEX II. GC-MS measurements were conducted on an Agilent 8860/5977B. UV-Vis spectrum was measured by UV-2600i. Emission intensities were recorded on the HITACHI F-7000 spectrometer. Chromatographic purification of products was accomplished using forced-flow chromatography on silica gel (200-300 mesh).

2 Reaction Optimization Tables

2.1 Optimization of Bases (Table S1)



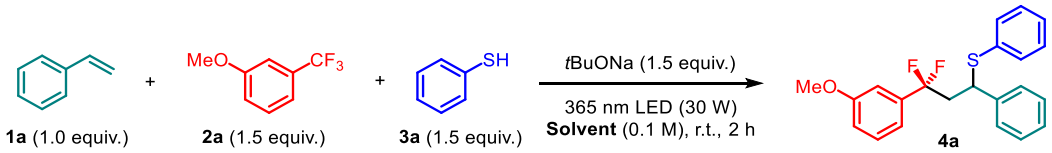
1a (1.0 equiv.) **2a** (1.5 equiv.) **3a** (1.5 equiv.) **4a**

Entry[a]	Base	Yield of **4a** (%)[b]
1	Cs_2CO_3	65
2	K_2CO_3	33
3	Na_2CO_3	N.D.
4	KOH	63
5	NaOH	89
6	*t*BuOLi	95
7	***t*BuONa**	**98**
8	*t*BuOK	84
9	KOMe	62
10	LiOMe	94
11	EtONa	92
12	EtOK	91
13	HCOONa	N.D.

14	HCOOCs	N.D.
15	CH_3COOCs	34
16	CH_3COOK	N.D.
17	CsF	12
18	KF	4
19	K_3PO_4	10
20	DBU (p*K*a=12.0)	71
21	TMG (p*K*a=12.7)	59
22	-	N.D.

[a]Reaction conditions: **1a** (0.10 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv.), **3a** (0.15 mmol, 1.5 equiv.) and base (0.15 mmol, 1.5 equiv.) in DMA (1.0 mL, 0.1 M), irradiation with 30 W 365 nm LED at room temperature under a nitrogen atmosphere for 2 h. [b]Yields were determined by ^{19}F NMR using (trifluoromethoxy)benzene as an internal standard.

2.2 Optimization of Solvents (Table S2)

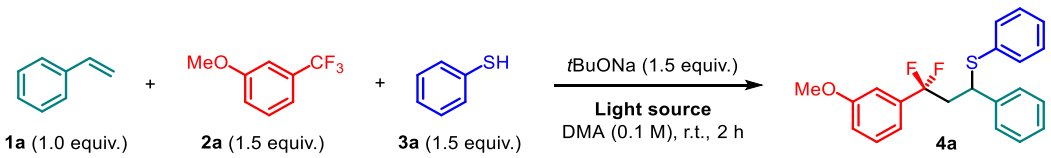


1a (1.0 equiv.) + **2a** (1.5 equiv.) + **3a** (1.5 equiv.) → **4a**

Entry[a]	Solvent	Yield of **4a** (%)[b]
1	DMF	72
2	**DMA**	**98**
3	DMSO	79
4	NMP	52
5	MeCN	18
6	DME	14
7	THF	N.D.
8	DCE	N.D.
9	MeOH	N.D.
10	toluene	N.D.
11	acetone	N.D.
12	1,4-dioxane	N.D.

[a]Reaction conditions: **1a** (0.10 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv.), **3a** (0.15 mmol, 1.5 equiv.) and *t*BuONa (0.15 mmol, 1.5 equiv.) in DMA (1.0 mL, 0.1 M), irradiation with 30 W 365 nm LED at room temperature under a nitrogen atmosphere for 2 h. [b]Yields were determined by ^{19}F NMR using (trifluoromethoxy)benzene as an internal standard.

2.3 Optimization of Wavelength of Light (Table S3)

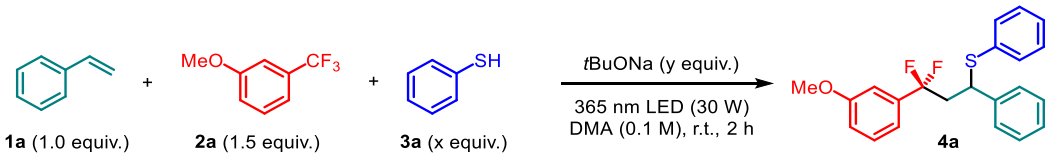


1a (1.0 equiv.) + **2a** (1.5 equiv.) + **3a** (1.5 equiv.) → **4a**

Entry[a]	Light source	Yield of **4a** (%)[b]
1	**365nm**	**98**
2	370nm	84
3	390nm	83
4	427nm	87
5	440nm	52
6	525nm	N.D.
7	CFL	N.D.
8	-	N.D.

[a]Reaction conditions: **1a** (0.10 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv.), **3a** (0.15 mmol, 1.5 equiv.) and *t*BuONa (0.15 mmol, 1.5 equiv.) in DMA (1.0 mL, 0.1 M), irradiation with light source at room temperature under a nitrogen atmosphere for 2 h. [b]Yields were determined by ^{19}F NMR using (trifluoromethoxy)benzene as an internal standard.

2.4 Optimization of the Amount of Arylthiols and Base (Table S4)

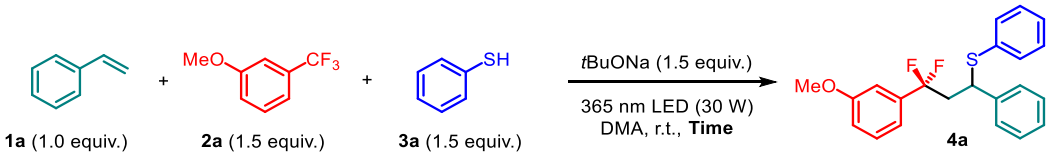


1a (1.0 equiv.) + **2a** (1.5 equiv.) + **3a** (x equiv.) → **4a**

Entry[a]	Amount of **3a** (x equiv.)	Amount of **base** (y equiv.)	Yield of **4a** (%)[b]
1	1.5	0.50	N.D.
2	1.5	1.00	29
3	1.5	1.25	73
4	**1.5**	**1.50**	**98**
5	1.5	1.75	68
6	1.5	2.00	20
7	1.5	3.00	1
8	1.0	1.50	N.D.
9	2.0	1.50	28
10	1.0	1.00	67
11	2.0	2.00	92

[a]Reaction conditions: **1a** (0.10 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv.), **3a** (x equiv.) and *t*BuONa (y equiv.) in DMA (1.0 mL, 0.1 M), irradiation with 30 W 365 nm LED at room temperature under a nitrogen atmosphere for 2 h. [b]Yields were determined by ^{19}F NMR using (trifluoromethoxy)benzene as an internal standard.

2.5 Optimization of Time and Amount of Solvent (Table S5)



1a (1.0 equiv.) **2a** (1.5 equiv.) **3a** (1.5 equiv.) **4a**

Entry[a]	Time (h)	Concentration	Yield of **4a** (%)[b]
1	0.5	0.1 M	53
2	1.0	0.1 M	78
3	**2.0**	**0.1 M**	**98**
4	3.0	0.1 M	91
5	2.0	0.025 M	64
6	2.0	0.05 M	82
7	2.0	0.2 M	87

[a]Reaction conditions: **1a** (0.10 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv.), **3a** (0.15 mmol, 1.5 equiv.) and *t*BuONa (0.15 mmol, 1.5 equiv.) in DMA (x M), irradiation with 30 W 365 nm LED at room temperature under a nitrogen atmosphere. [b]Yields were determined by ^{19}F NMR using (trifluoromethoxy)benzene as an internal standard.

2.6 Optimization of the Oxidation Step (Table S6)

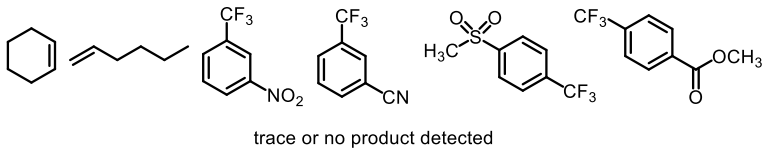
1a (1.0 equiv.) **2a** (1.5 equiv.) **3a** (1.5 equiv.) **5n**

Entry[a]	Conditions	Yield of **5n** (%)[b]
1	**dichloromethane**	**80**
2	**H_2O**	**62**
3	**H_2O/methanol (3:1)**	**81**
4	methanol	81
5	toluene	78
6	acetone	61
7	ethyl acetate	55
8	*i*propanol	49
9	*m*CPBA (1.0 equiv.)	37[c]

10	*m*CPBA (2.0 equiv.)		67[c]

[a]Reaction conditions: **1a** (0.10 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv.), **3a** (0.15 mmol, 1.5 equiv.) and *t*BuONa (0.15 mmol, 1.5 equiv.) in DMA (1.0 mL), irradiation with 30 W 365 nm LED at room temperature under a nitrogen atmosphere. After irradiation, remove DMA, then add solvent (2.0 ml, 0.05 M), *m*-CPBA (0.3 mmol, 3.0 equiv.), r.t. and 4 h. [b]Yields were determined by ^{19}F NMR using (trifluoromethoxy)benzene as an internal standard. [c]DCM (2.0 mL, 0.05M) was used as solvent.

2.7 Unsuccessful Substrates



trace or no product detected

Figure S2. Unsuccessful substrates.

3 Preparation of Substrates

3.1 Preparation of Alkenes

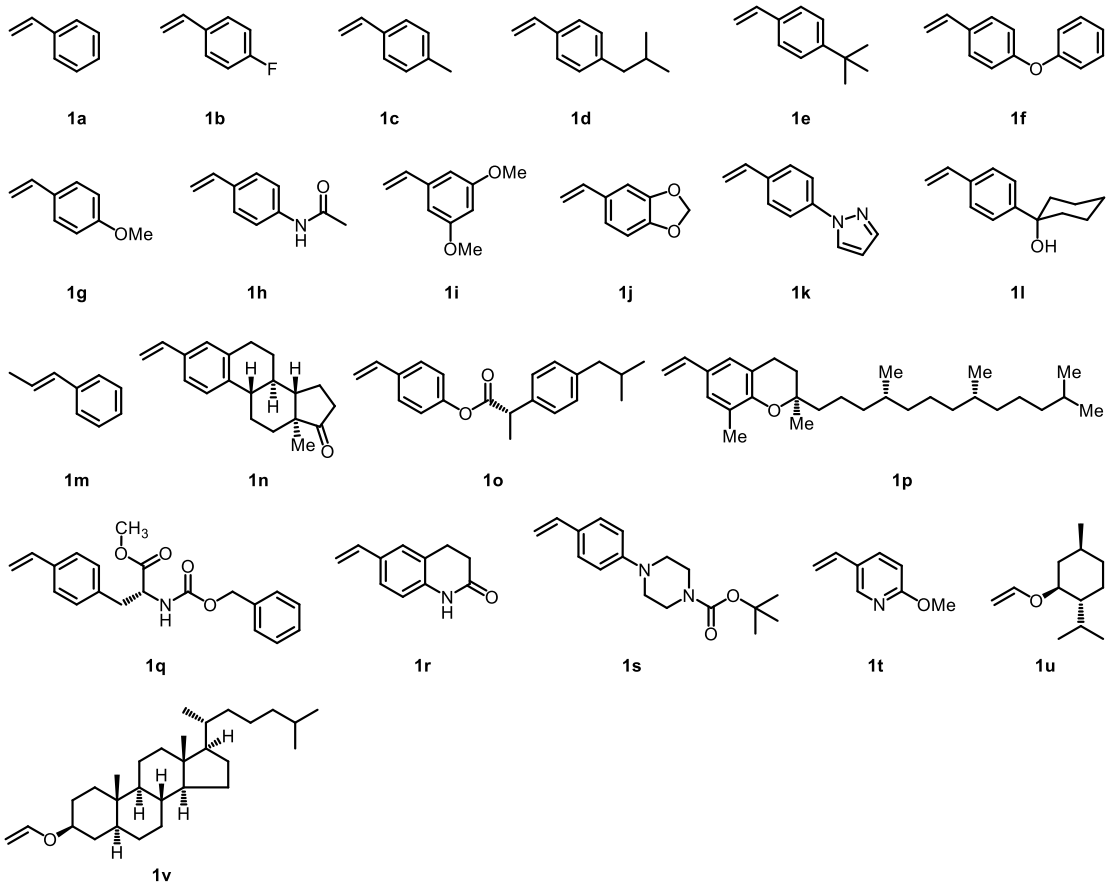
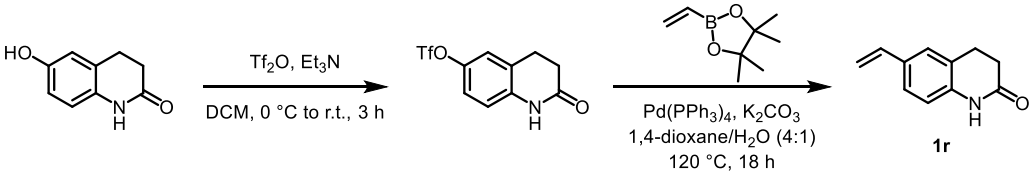


Figure S3. Scope of alkenes.

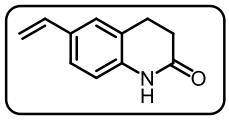
Note: Substrates **1a-1c**, **1e** and **1m** are commercially available. Substrates **1d**[1], **1f**[2], **1g**[3], **1h**[4], **1i**[5], **1j**[6], **1k**[7], **1l**[8], **1n**[9], **1o**[10], **1p**[11], **1q**[8], **1s**[12], **1t**[13], **1u**[14] and **1v**[15] were prepared according to the literatures. Other substrates are prepared from commercially available compounds, which are described in the following sections.

Synthesis of Compound 1r[16]



An oven-dried flask was charged with 6-hydroxy-2(1*H*)-3,4-dihydroquinolinone (326 mg, 2.0 mmol, 1.0 equiv.), DCM (10 mL), and Et_3N (0.56 mL, 2.4 mmol, 1.2 equiv.) cooled at 0 °C, then a solution of triflic anhydride (0.4 mL, 2.4 mmol, 1.2 equiv.) in CH_2Cl_2 (1 mL) was added dropwise. The reaction mixture was stirred at room temperature for 3 hours. The reaction was quenched by aqueous saturated NH_4Cl (10 mL) and extracted by DCM (3 x 10 mL). The combined organic phases 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 (1:1 (v/v)) as eluent afforded 2-oxo-1,2,3,4-tetrahydroquinolin-6-yl trifluoromethanesulfonate as a brown solid (396 mg, 82% yield).

2-Oxo-1,2,3,4-tetrahydroquinolin-6-yl trifluoromethanesulfonate (295 mg, 1.0 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (139 mg, 0.12 mmol, 12 mol%) and K_2CO_3 (414 mg, 3.0 mmol, 3.0 equiv.) were suspended under a nitrogen atmosphere. Add the 1,4-dioxane (8 mL) and H_2O (2 mL) to the mixture after continuous degassing for 5 minutes. Then, pinacol vinylboronate (0.22 mL, l.3 mmol, 1.3 equiv.) was added dropwise. The reaction mixture was stirred at 120 °C in an oil bath for 18 hours. The reaction mixture was cooled to room temperature, filtered and the solvent was removed under reduced pressure. Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (2:1 (v/v)) as eluent afforded 6-vinyl-3,4-dihydroquinolin-2(1*H*)-one **1r** as a yellow solid (150 mg, 87% yield).



NMR Spectroscopy: **^{1}H NMR** (600 MHz, acetone-d_6) δ 7.34 (s, 1H), 7.30 (d, J = 8.0 Hz, 1H), 6.94 (d, J = 8.1 Hz, 1H), 6.71 (dd, J = 17.5, 11.0 Hz, 1H), 5.73 (d, J = 17.6 Hz, 1H), 5.15 (d, J = 10.9 Hz, 1H), 2.98 (t, J = 7.3 Hz, 1H), 2.54 (t, J = 7.4 Hz, 1H). **^{13}C NMR** (151 MHz, acetone- d_6) δ 170.8, 138.5, 137.0, 132.5, 126.1, 125.8, 124.5, 115.7, 111.9, 30.9, 25.7.

3.2 The Scope of Trifluoromethylarenes

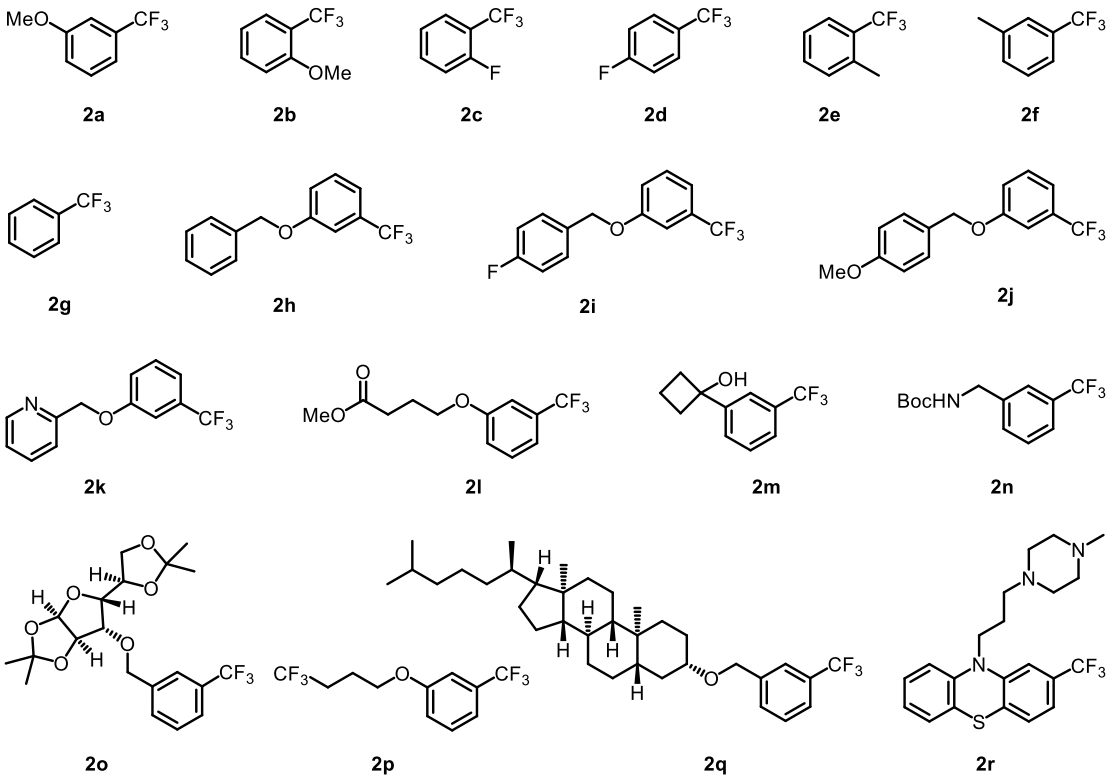
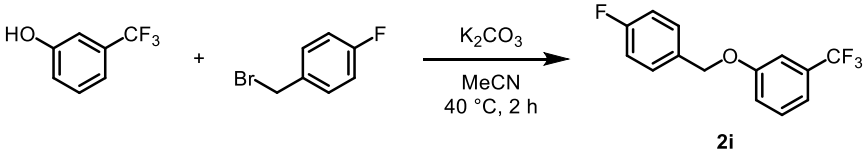


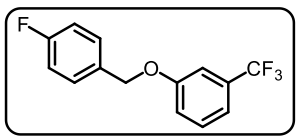
Figure S4. Scope of trifluoromethylarenes.

Note: Substrates **2a**-**2g** and **2r** are commercially available. Substrates **2h**[17], **2j**[18], **2k**[19], **2m**[20], and **2n**[21] were prepared according to the literatures. Other substrates are prepared from commercially available compounds, which are described as follows.

Synthesis of compound 2i[22]



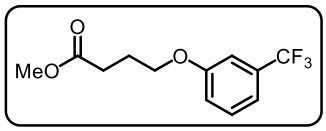
To a solution of 3-(trifluoromethyl)phenol (32.4 mg, 0.20 mmol, 1.0 equiv.) in acetonitrile (1 mL), 1-(bromomethyl)-4-fluorobenzene (27.5 μL, 0.22 mmol, 1.1 equiv.) and K_2CO_3 (41.5 mg, 0.30 mmol, 1.5 equiv.) were added under a nitrogen atmosphere. The mixture was stirred at 40 ℃ for 2 hours. After completion (monitored by TLC), the mixture was poured into water (2 mL), extracted with Et_2O (3 x 5 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 **2i** as a colorless oil (0.7 g, 86% yield).



NMR Spectroscopy: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 3H), 7.32 – 7.27 (m, 2H), 7.18 (d, *J* = 7.1 Hz, 1H), 7.16 – 7.10 (m, 2H), 5.07 (s, 2H).**^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.73 (s, 3F), -113.70 – -113.81 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.8 (d, *J* = 246.9 Hz), 158.9, 132.3, 132.1 (q, *J* = 32.6 Hz), 130.2, 129.6, 129.5, 126.0 (q, *J* = 272.5 Hz), 118.4, 117.9 (q, *J* = 3.5 Hz), 115.7 (d, *J* = 21.7 Hz), 111.8, 69.7.

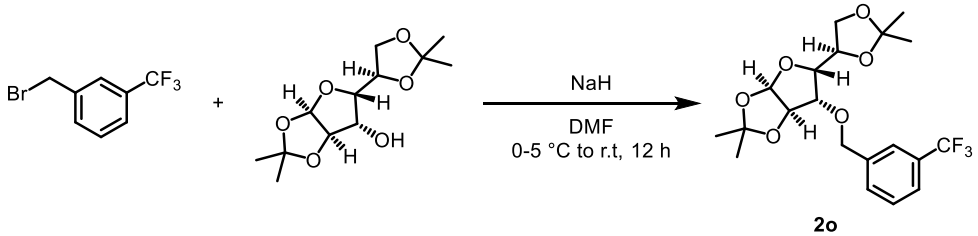
Synthesis of methyl 4-(3-(trifluoromethyl)phenoxy)butanoate (2l)[23]

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 ℃ 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 **2l** as a colorless oil (0.5 g, 64% yield).



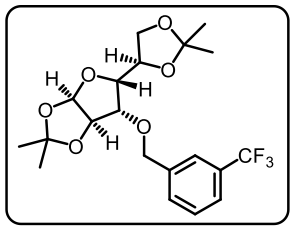
NMR Spectroscopy: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 1H), 7.20 (d, *J* = 7.0 Hz, 1H), 7.11 (s, 1H), 7.05 (d, *J* = 6.7 Hz, 1H), 4.04 (t, *J* = 5.9 Hz, 2H), 3.70 (s, 3H), 2.54 (t, *J* = 7.1 Hz, 2H), 2.22 – 2.06 (m, 2H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.73 – -62.82 (m, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.7, 159.1, 132.1 (q, *J* = 30.9 Hz), 130.1, 125.0 (q, *J* = 271.1 Hz), 119.0, 118.1, 117.6, 111.4, 67.1, 51.8, 30.5, 24.6.

Synthesis of Compound 2o



2o

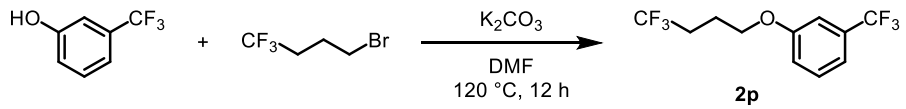
Under a nitrogen atmosphere, to a solution of diacetone-D-glucose (1.3 g, 5.0 mmol, 1.0 equiv.) in dry DMF (10 mL) was added NaH (0.30 g, 60% in mineral oil, 7.5 mmol, 1.5 equiv.) in batches at 0°C, followed by stirring for half an hour at this temperature. Finally, benzyl bromide (1.1 mL, 7.5 mmol, 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 **2o** as a white solid (1.7 g, 80% yield).



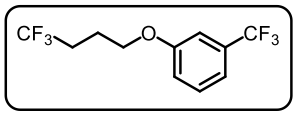
NMR Spectroscopy: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.43 (m, 1H), 5.91 (d, *J* = 3.5 Hz, 1H), 4.76 (d, *J* = 12.3 Hz, 1H), 4.69 (d, *J* = 12.3 Hz, 1H), 4.62 (d, *J* = 3.5 Hz, 1H), 4.41 – 4.33 (m, 1H), 4.17 – 4.09 (m, 2H), 4.06 – 3.99 (m, 2H), 1.50 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H), 1.32 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.57 (s, 3F). **^{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.

Synthesis of Compound 2p

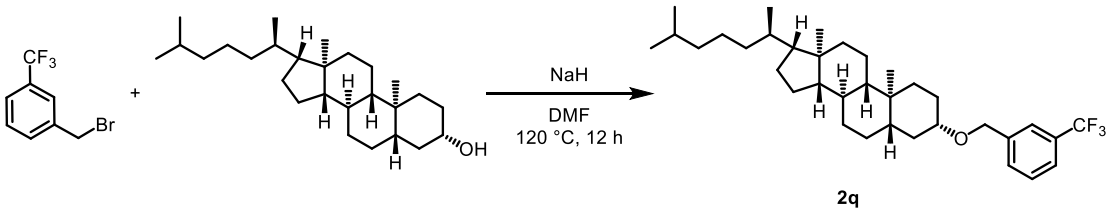


To a solution of 3-(trifluoromethyl)phenol (1.62 g, 10 mmol, 1.0 equiv.) in dry DMF (20 mL), 1-bromo-4,4,4-trifluorobutane (2.9 g, 15 mmol, 1.5 equiv.) and K_2CO_3 (2.07g , 15 mmol, 1.5 equiv.) were added under a nitrogen atmosphere. The mixture was stirred at 120 ℃ for 12 hours. After completion (monitored 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 **2p** as a colorless oil (2.2 g, 82% yield).

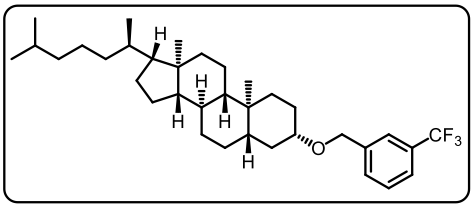


R_f = 0.5 (petroleum ether/EtOAc = 50:1). **NMR Spectroscopy**: **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.44 – 7.36 (m, 1H), 7.24 – 7.21 (m, 1H), 7.15 – 7.11 (m, 1H), 7.10 – 7.03 (m, 1H), 4.06 (t, J = 6.0 Hz, 2H), 2.47 – 2.20 (m, 2H), 2.19 – 1.96 (m, 2H). **^{19}F NMR (470 MHz, $CDCl_3$)** δ -62.80 (s, 3F), -66.40 (t, J = 10.8 Hz, 3F). **^{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).

Synthesis of Compound 2q



Under a nitrogen atmosphere, to a solution of dihydrocholesterol (1.9 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 the mixture was stirred at 120 ℃ for 12 hours. The reaction mixture was cooled to 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, and the solvent was removed *in vacuo*. Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (40:1 (v/v)) as eluent afforded **2q** as a white solid (464 mg, 17% yield).



NMR Spectroscopy: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.52 (s, 2H), 7.46 – 7.41 (m, 1H), 4.75 – 4.42 (m, 2H), 3.44 – 3.24 (m, 1H), 1.96 (d, *J* = 12.3 Hz, 1H), 1.91 (d, *J* = 12.2 Hz, 1H), 1.85 – 1.77 (m, 1H), 1.74 (d, *J* = 13.0 Hz, 1H), 1.67 (t, *J* = 14.1 Hz, 2H), 1.54 (s, 3H), 1.52 – 1.38 (m, 3H), 1.40 – 1.19 (m, 8H), 1.18 – 1.01 (m, 6H), 1.02 – 0.92 (m, 3H), 0.90 (d, *J* = 6.1 Hz, 3H), 0.86 (d, *J* = 3.8 Hz, 6H), 0.81 (s, 3H), 0.65 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.59 (s, 3F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.5, 130.8 (q, *J* = 32.3 Hz), 130.8, 128.9, 124.5 (q, *J* = 272.4 Hz), 124.3 (q, *J* = 3.5 Hz), 78.8, 69.3, 56.7, 56.5, 54.6, 45.0, 42.8, 40.2, 39.7, 37.2, 36.4, 36.0, 35.7, 35.0, 32.3, 29.0, 28.4, 28.4, 28.2, 24.4, 24.0, 23.0, 22.7, 21.4, 18.8, 12.5, 12.2.

3.3 The Scope of Arylthiols

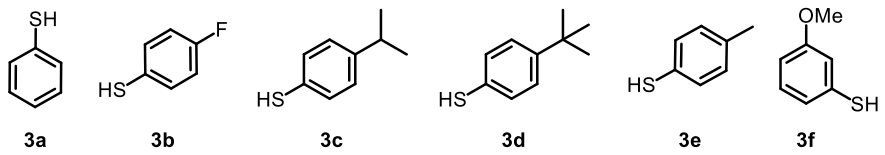


Figure S5. Scope of arylthiols.

Note: Substrates **3a-3f** are commercially available.

4 Experimental Procedures and Spectral Data

4.1 General Procedure

General Procedure A: **Aryldifluoromethyl-thioetherification of alkenes**

To a 20 mL oven dried screw-cap vial equipped with a magnetic stir bar was added *t*BuONa (1.8 mmol, 1.5 equiv.) in dry DMA (12 mL), followed by aryl thiols (1.8 mmol, 1.5 equiv.), trifluoromethyl aromatics (1.8 mmol, 1.5 equiv.) and alkenes (1.2 mmol, 1.0 equiv.) under a nitrogen atmosphere. The reaction mixture was stirred vigorously at room temperature and exposed to 30 W 365 nm LED for 2 hours. Then, the reaction was diluted with ethyl acetate (10 mL) and extracted with water (20 mL), saturated sodium chloride solution (2 x 30 mL), followed by reverse extraction of the mixed aqueous phase using ethyl acetate (30 mL). The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The crude mixture was purified by column chromatography on silica gel (200~300 mesh) to afford the title compounds.

General Procedure B: **Aryldifluoromethyl-sulfonylation of alkenes**

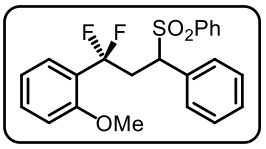
To a 20 mL oven dried screw-cap vial equipped with a magnetic stir bar was added *t*BuONa (1.8 mmol, 1.5 equiv.) in dry DMA (12 mL), followed by aryl thiols (1.8 mmol, 1.5 equiv.), trifluoromethyl aromatics (1.8 mmol, 1.5 equiv.) and alkenes (1.2 mmol, 1.0 equiv.) under a nitrogen atmosphere. The reaction mixture was stirred vigorously at room temperature and exposed to 30 W 365 nm LED for 2 hours. After the completion of the reaction, the resulting reaction mixture was concentrated *in vacuo* yielding the crude product which was used in the next step without further purification. Next, a 50 mL round bottomed flask charged with crude product in DCM (24 mL) was added 85 wt% 3-chloroperoxybenzoic acid (3.6 mmol, 3.0 equiv.). The reaction mixture was stirred for 4 hours at room temperature. After the completion of the reaction, the reaction was diluted with dichloromethane (10 mL) and extracted with saturated sodium bicarbonate solution (30 mL) until the solution was neutral, and water (2 x 30 mL).

Then the organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The crude mixture was purified by column chromatography on silica gel (200~300 mesh) to afford the title compounds.

4.2 Experimental Details and Characterization Data

1-(1,1-Difluoro-3-phenyl-3-(phenylsulfonyl)propyl)-2-methoxybenzene (5a)

General procedure B was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 1-methoxy-2-(trifluoromethyl)benzene (265 μL, 1.8 mmol, 1.5 equiv.), styrene (138 μL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded **5a** as a white solid (396 mg, 82% yield).

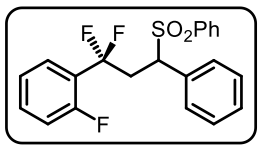


R_f = 0.3 (petroleum ether/ ethyl acetate 10:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.56 – 7.47 (m, 3H), 7.39 – 7.34 (m, 2H), 7.30 – 7.26 (m, 1H), 7.25 – 7.21 (m, 1H), 7.21 – 7.17 (m, 1H), 7.14 – 7.08 (m, 2H), 6.97 (d, *J* = 7.4 Hz, 2H), 6.87 – 6.81 (m, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 4.20 – 4.14 (m, 1H), 3.72 (s, 3H), 3.55 – 3.42 (m, 1H), 3.38 – 3.22 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -91.07 – -92.04 (m, 1F), -92.60 – -93.43 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.6, 136.9, 133.7, 131.8, 129.9, 129.1, 128.8, 128.7, 128.1, 126.5 (t, *J* = 8.8 Hz), 123.4 (t, *J* = 24.8 Hz), 121.1 (t, *J* = 245.1 Hz), 120.2, 119.5, 111.5, 67.03, 55.6, 35.2 (t, *J* = 27.4 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{22}H_{20}F_2O_3SNa^+$, 425.0993; found 425.0999.

1-(1,1-Difluoro-3-phenyl-3-(phenylsulfonyl)propyl)-2-fluorobenzene (5b)

General procedure B was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 1-fluoro-2-(trifluoromethyl)benzene (228 μL, 1.8 mmol, 1.5 equiv.), styrene (138 μL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded **5b** as a white solid

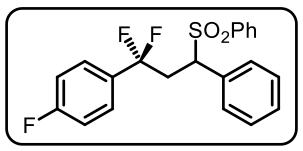
(337 mg, 72% yield).



R_f = 0.2 (petroleum ether/ ethyl acetate 10:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 1H), 7.52 – 7.48 (m, 2H), 7.39 – 7.34 (m, 2H), 7.34 – 7.28 (m, 1H), 7.28 – 7.23 (m, 1H), 7.22 – 7.16 (m, 1H), 7.15 – 7.09 (m, 2H), 7.07 – 7.02 (m, 1H), 7.01 (d, *J* = 7.4 Hz, 2H), 6.98 – 6.92 (m, 1H), 4.28 (dd, *J* = 11.2, 1.3 Hz, 1H), 3.46 – 3.35 (m, 1H), 3.28 – 3.15 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -91.37 – -92.32 (m, 1F), -93.53 – -94.39 (m, 1F), -113.87 – -114.32 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.5 (d, *J* = 251.6 Hz), 136.7, 133.9, 132.4 (d, *J* = 8.5 Hz), 131.7, 129.9, 129.2, 128.9 (d, *J* = 7.6 Hz), 128.4, 126.8 (t, *J* = 6.7 Hz), 124.1 (d, *J* = 3.4 Hz), 123.5 (t, *J* = 26.6 Hz), 123.4 (t, *J* = 26.7 Hz), 120.0 (t, *J* = 245.7 Hz), 116.5 (d, *J* = 21.1 Hz), 66.7, 36.1 (t, *J* = 27.8 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{21}H_{17}F_3O_2SNa^+$, 413.0794; found 413.0795.

1-(1,1-Difluoro-3-phenyl-3-(phenylsulfonyl)propyl)-4-fluorobenzene (5c)

General procedure B was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 1-fluoro-4-(trifluoromethyl)benzene (228 μL, 1.8 mmol, 1.5 equiv.), styrene (138 μL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded **5c** as a white solid (384 mg, 82% yield).

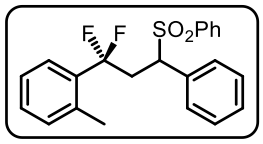


R_f = 0.30 (petroleum ether/ ethyl acetate 5:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 1H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.23 (m, 1H), 7.20 – 7.15 (m, 2H), 7.05 – 6.97 (m, 4H), 4.26 (d, *J* = 10.1 Hz, 1H), 3.42 – 3.21 (m, 1H), 3.17 – 2.93 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -91.73 – -92.55 (m, 1F), -92.69 – -93.70 (m, 1F), -110.75 – -111.42 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.7 (d, *J* = 249.8 Hz), 136.5, 133.9, 132.2 (t, *J* = 24.8 Hz), 131.9, 129.9, 129.2, 129.0, 128.9, 128.5, 127.2 (dd, *J* = 14.5, 6.2 Hz), 121.4 (t, *J* = 245.4 Hz),

115.7 (d, J = 22.1 Hz), 66.7, 37.3 (t, J = 28.6 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{21}H_{17}F_3O_2SNa^+$, 413.0794; found 413.0792.

1-(1,1-Difluoro-3-phenyl-3-(phenylsulfonyl)propyl)-2-methylbenzene (5d)

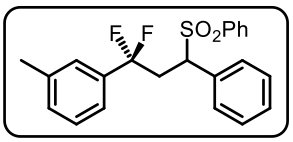
General procedure B was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), 1-methyl-2-(trifluoromethyl)benzene (246 µL, 1.8 mmol, 1.5 equiv.), styrene (138 µL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (3730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded **5d** as a white solid (371 mg, 80% yield).



$\mathbf{R_f}$ = 0.3 (petroleum ether/ ethyl acetate 10:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 1H), 7.48 (d, J = 7.4 Hz, 2H), 7.41 – 7.33 (m, 2H), 7.29 – 7.26 (m, 2H), 7.25 (s, 1H), 7.23 – 7.17 (m, 2H), 7.17 – 7.12 (m, 2H), 7.06 (d, J = 7.4 Hz, 2H), 4.31 (d, J = 11.0 Hz, 1H), 3.44 – 3.25 (m, 1H), 3.15 – 2.97 (m, 1H), 2.33 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -91.14 (ddd, J = 248.2, 21.4, 7.6 Hz, 1F), -92.93 (ddd, J = 248.4, 20.7, 12.9 Hz, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 136.7, 135.4, 134.1 (t, J = 24.0 Hz), 133.8, 132.2, 132.1, 130.2, 129.9, 129.2, 128.9, 128.9, 128.5, 125.9, 125.7 (t, J = 8.9 Hz), 122.5 (t, J = 246.2 Hz), 66.7, 36.5 (t, J = 27.8 Hz), 20.1. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{22}H_{20}F_2O_2SNa^+$, 409.1044; found 409.1053.

1-(1,1-Difluoro-3-phenyl-3-(phenylsulfonyl)propyl)-3-methylbenzene (5e)

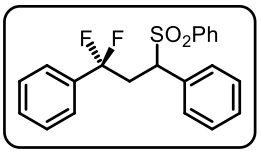
General procedure B was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), 1-methyl-3-(trifluoromethyl)benzene (251 µL, 1.8 mmol, 1.5 equiv.), styrene (138 µL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded **5e** as a white solid (357 mg, 77% yield).



R_f = 0.3 (petroleum ether/ ethyl acetate 10:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 1H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.39 – 7.31 (m, 2H), 7.25 – 7.21 (m, 2H), 7.21 – 7.15 (m, 3H), 7.15 – 7.08 (m, 2H), 7.05 (d, *J* = 7.4 Hz, 2H), 4.29 (d, *J* = 11.0 Hz, 1H), 3.40 – 3.20 (m, 1H), 3.14 – 2.90 (m, 1H), 2.32 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.68 (ddd, *J* = 244.7, 20.3, 8.2 Hz, 1F), -94.40 – -95.16 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.5, 136.7, 136.1 (t, *J* = 26.2 Hz), 133.9, 132.1, 131.0, 130.0, 129.2, 128.9, 128.8, 128.6, 128.4, 125.6 (t, *J* = 6.0 Hz), 122.0 (t, *J* = 6.0 Hz), 121.8 (t, *J* = 244.7 Hz), 66.8, 37.4 (t, *J* = 28.4 Hz), 21.5. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{22}H_{20}F_2O_2SNa^+$, 409.1044; found 409.1055.

(1,1-Difluoro-3-(phenylsulfonyl)propane-1,3-diyl)dibenzene (5f)

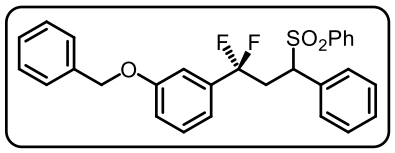
General procedure B was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), (trifluoromethyl)benzene (221 µL, 1.8 mmol, 1.5 equiv.), styrene (138 µL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded **5f** as a white solid (388 mg, 87% yield).



R_f = 0.3 (petroleum ether/ ethyl acetate 10:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 1H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.37 – 7.30 (m, 6H), 7.26 – 7.23 (m, 1H), 7.21 – 7.14 (m, 2H), 7.05 (d, *J* = 7.4 Hz, 2H), 4.29 (d, *J* = 9.9 Hz, 1H), 3.44 – 3.22 (m, 1H), 3.17 – 2.93 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.43 (ddd, *J* = 245.4, 20.4, 8.3 Hz, 1F), -95.21 (ddd, *J* = 245.3, 19.9, 13.6 Hz, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 136.7, 136.2 (t, *J* = 26.0 Hz), 133.9, 132.1, 130.3, 130.0, 129.2, 129.0, 128.8, 128.7, 128.5, 125.0 (t, *J* = 6.1 Hz), 121.7 (t, *J* = 245.2 Hz), 66.8, 37.4 (t, *J* = 28.3 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{21}H_{18}F_2O_2SNa^+$, 395.0888; found 395.0898.

1-(Benzyloxy)-3-(1,1-difluoro-3-phenyl-3-(phenylsulfonyl)propyl)benzene (5g)

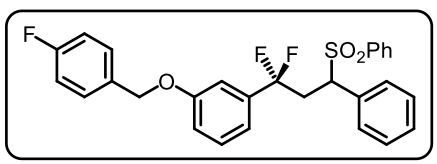
General procedure B was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 1-(benzyloxy)-3-(trifluoromethyl)benzene (454 mg, 1.8 mmol, 1.5 equiv.), styrene (138 μL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded **5g** as a white solid (407 mg, 71% yield).



R_f = 0.2 (petroleum ether/ ethyl acetate 10:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 1H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.44 – 7.38 (m, 4H), 7.38 – 7.31 (m, 3H), 7.29 – 7.23 (m, 2H), 7.21 – 7.15 (m, 2H), 7.03 (d, *J* = 7.4 Hz, 2H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.92 (m, 2H), 5.02 (s, 2H), 4.28 (d, *J* = 10.5 Hz, 1H), 3.39 – 3.22 (m, 1H), 3.13 – 2.91 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.53 (ddd, *J* = 244.5, 20.0, 8.7 Hz, 1F), -94.87 (ddd, *J* = 244.6, 18.8, 14.0 Hz, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.9, 137.6 (t, *J* = 26.2 Hz), 136.6, 133.9, 132.1, 130.0, 129.2, 128.9, 128.8, 128.8, 128.5, 128.3, 127.7, 121.5 (t, *J* = 245.6 Hz), 117.5 (d, *J* = 6.0 Hz), 116.8, 70.3, 66.8, 37.3 (t, *J* = 28.3 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{28}H_{24}F_2O_3SNa^+$, 501.1306; found 501.1317.

1-(1,1-Difluoro-3-phenyl-3-(phenylsulfonyl)propyl)-3-((4-fluorobenzyl)oxy)benzene (5h)

General procedure B was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 1-((4-fluorobenzyl)oxy)-3-(trifluoromethyl)benzene (486.4 mg, 1.8 mmol, 1.5 equiv.), styrene (138 μL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded **5h** as a white solid (524 mg, 88% yield).

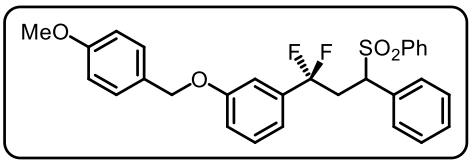


R_f = 0.30 (petroleum ether/ ethyl acetate 10:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 1H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.38 – 7.33 (m, 2H), 7.30 – 7.27 (m, 1H), 7.26 – 7.23 (m, 1H), 7.21 –

7.15 (m, 2H), 7.12 – 7.06 (m, 2H), 7.04 (d, J = 7.5 Hz, 2H), 6.97 (d, J = 8.2 Hz, 1H), 6.94 (d, J = 7.7 Hz, 1H), 6.92 (s, 1H), 4.97 (s, 2H), 4.29 (d, J = 10.3 Hz, 1H), 3.43 – 3.22 (m, 1H), 3.14 – 2.96 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.50 (ddd, J = 244.5, 20.2, 8.4 Hz, 1F), -94.89 (ddd, J = 244.7, 19.3, 13.4 Hz, 1F), -113.60 – -114.15 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.7 (d, J = 246.5 Hz), 158.8, 137.7 (t, J = 26.0 Hz), 136.6, 133.9, 132.2 (d, J = 42.6 Hz), 130.0, 129.9, 129.5, 129.5, 129.2, 128.9, 128.8, 128.4, 121.5 (t, J = 245.5 Hz), 117.6 (t, J = 6.0 Hz), 116.8, 115.7 (d, J = 21.6 Hz), 111.5, 69.6, 66.7, 37.3 (t, J = 28.3 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{28}H_{23}F_3O_3SNa^+$, 519.1212; found 519.1214.

1-(1,1-Difluoro-3-phenyl-3-(phenylsulfonyl)propyl)-3-((4-methoxybenzyl)oxy)benzene (5i)

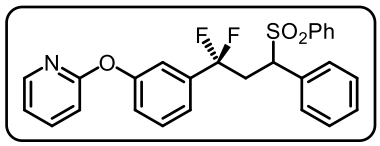
General procedure B was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 1-((4-methoxybenzyl)oxy)-3-(trifluoromethyl)benzene (508 mg, 1.8 mmol, 1.5 equiv.), styrene (138 μL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded **5i** as a white solid (500 mg, 82% yield).



R_f = 0.30 (petroleum ether/ ethyl acetate 10:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 1H), 7.46 (d, J = 7.7 Hz, 2H), 7.39 – 7.31 (m, 4H), 7.28 – 7.23 (m, 2H), 7.21 – 7.16 (m, 2H), 7.04 (d, J = 7.5 Hz, 2H), 6.97 (d, J = 7.4 Hz, 1H), 6.96 – 6.87 (m, 4H), 4.94 (s, 2H), 4.28 (d, J = 10.3 Hz, 1H), 3.83 (s, 3H), 3.36 – 3.24 (m, 1H), 3.09 – 2.97 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.42 (ddd, J = 244.6, 19.7, 7.9 Hz, 1F), -94.50 – -95.49 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.8, 159.0, 137.6 (t, J = 25.7 Hz), 136.7, 133.9, 132.1, 130.0, 129.9, 129.4, 129.2, 128.9, 128.8, 128.7, 128.5, 121.6 (t, J = 245.7 Hz), 117.4 (t, J = 6.1 Hz), 116.9, 114.3, 111.6 (t, J = 5.7 Hz), 70.1, 66.8, 55.5, 37.3 (t, J = 28.1 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{29}H_{26}F_2O_4SNa^+$, 531.1412; found 531.1419.

2-(3-(1,1-Difluoro-3-phenyl-3-(phenylsulfonyl)propyl)phenoxy)pyridine (5j)

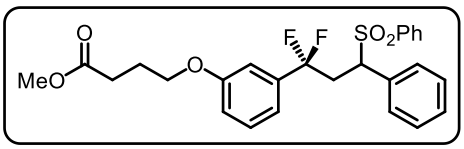
General procedure B was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), 2-(3-(trifluoromethyl)phenoxy)pyridine (430 mg, 1.8 mmol, 1.5 equiv.), styrene (138 µL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded **5j** as a white solid (374 mg, 67% yield).



$\mathbf{R_f}$ = 0.20 (petroleum ether/ ethyl acetate 10:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.22 – 8.16 (m, 1H), 7.75 – 7.67 (m, 1H), 7.57 – 7.51 (m, 1H), 7.50 – 7.45 (m, 2H), 7.40 – 7.33 (m, 3H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.20 – 7.13 (m, 4H), 7.05 – 7.01 (m, 1H), 7.06 (d, *J* = 7.3 Hz, 2H), 7.05 – 7.01 (m, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 4.32 (dd, *J* = 11.1, 1.7 Hz, 1H), 3.38 – 3.22 (m, 1H), 3.11 – 2.97 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.18 (ddd, *J* = 245.3, 20.2, 7.9 Hz, 1F), -95.24 (ddd, *J* = 245.7, 19.5, 13.5 Hz, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.3, 154.4, 147.8, 139.8, 137.8 (t, *J* = 26.5 Hz), 136.6, 133.9, 132.0, 130.1, 130.0, 129.2, 129.0, 128.8, 128.5, 123.02, 121.3 (t, *J* = 245.8 Hz), 121.1 (t, *J* = 5.8 Hz), 119.1, 118.1 (t, *J* = 6.2 Hz), 112.0, 66.6, 37.3 (t, *J* = 28.2 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{26}H_{21}F_2NO_3SNa^+$, 488.1102; found 488.1106.

Methyl-4-(3-(1,1-difluoro-3-phenyl-3-(phenylsulfonyl)propyl)phenoxy)butanoate (5k)

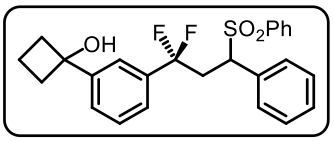
General procedure B was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), methyl 4-(3-(trifluoromethyl)phenoxy)butanoate (472 mg, 1.8 mmol, 1.5 equiv.), styrene (138 µL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (3:1 (v/v)) as eluent afforded **5k** as a white solid (363 mg, 62% yield).



R_f = 0.35 (petroleum ether/ ethyl acetate 3:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 1H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.21 – 7.15 (m, 2H), 7.04 (d, *J* = 7.0 Hz, 2H), 6.92 – 6.86 (m, 2H), 6.80 (s, 1H), 4.28 (d, *J* = 10.9 Hz, 1H), 3.95 (s, 2H), 3.69 (s, 3H), 3.36 – 3.23 (m, 1H), 3.12 – 2.96 (m, 1H), 2.52 (t, *J* = 6.5 Hz, 2H), 2.12 – 2.07 (m, 2H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.27 (ddd, *J* = 246.5, 17.7, 10.7 Hz, 1F), -94.00 – -94.70 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.7, 159.0, 137.6 (t, *J* = 25.7 Hz), 136.6, 133.9, 132.1, 129.9, 129.8, 129.2, 128.9, 128.8, 128.4, 121.5 (t, *J* = 245.5 Hz), 117.3 (t, *J* = 6.0 Hz), 116.4, 111.1, 66.9, 66.7, 51.8, 37.3 (t, *J* = 28.4 Hz), 30.6, 24.6. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{26}H_{26}F_2O_5SNa^+$, 511.1361; found 511.1366.

1-(3-(1,1-Difluoro-3-phenyl-3-(phenylsulfonyl)propyl)phenyl)cyclobutan-1-ol (5l)

General procedure B was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), 1-(3-(trifluoromethyl)-phenyl)cyclobutan-1-ol (389 mg, 1.8 mmol, 1.5 equiv.), styrene (138 µL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (3:1 (v/v)) as eluent afforded **5k** as a white solid (186 mg, 35% yield).

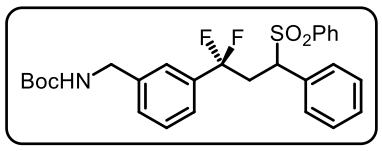


R_f = 0.30 (petroleum ether/ ethyl acetate 3:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 2H), 7.48 – 7.44 (m, 2H), 7.42 (s, 1H), 7.39 – 7.32 (m, 3H), 7.27 (s, 1H), 7.25 – 7.21 (m, 1H), 7.18 – 7.13 (m, 2H), 7.02 (d, *J* = 7.3 Hz, 2H), 4.29 (dd, *J* = 11.1, 1.7 Hz, 1H), 3.46 – 3.25 (m, 1H), 3.13 – 2.98 (m, 1H), 2.55 – 2.42 (m, 2H), 2.42 – 2.29 (m, 2H), 2.09 – 1.99 (m, 1H), 1.90 (s, 1H), 1.72 – 1.64 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -91.31 – -92.02 (m, 1F), -92.03 – -92.88 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.1, 136.5, 136.3 (t, *J* = 25.7 Hz), 133.9, 132.0, 130.0, 129.2, 128.9, 128.8, 128.8, 128.4, 126.9, 123.8 (t, *J* = 5.9 Hz), 121.8 (t, *J* = 245.3 Hz),

121.5 (t, J = 6.0 Hz), 76.9, 66.8, 37.5, 37.3, 37.1 (t, J = 6.5 Hz), 13.1. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{25}H_{24}F_2O_3SNa^+$, 465.1306; found 465.1315.

tert-Butyl-(3-(1,1-difluoro-3-phenyl-3-(phenylsulfonyl)propyl)benzyl)carbamate (5m)

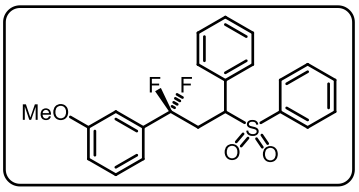
General procedure B was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), *tert*-butyl (3-(trifluoromethyl)benzyl)carbamate (495 mg, 1.8 mmol, 1.5 equiv.), styrene (138 µL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded **5m** as a white solid (427 mg, 71% yield).



$\mathbf{R_f}$ = 0.25 (petroleum ether/ ethyl acetate 10:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.25 – 7.19 (m, 8H), 7.18 (d, J = 7.0 Hz, 1H), 7.17 – 7.12 (m, 3H), 4.77 (s, 1H), 4.31 (dd, J = 9.3, 3.2 Hz, 1H), 4.29 – 4.21 (m, 2H), 2.95 – 2.83 (m, 1H), 2.83 – 2.71 (m, 1H), 1.47 (s, 9H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -93.19 (d, J = 7.9 Hz, 2F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.0, 140.7, 139.4, 137.1 (t, J = 24.7 Hz), 134.2, 133.0, 129.1, 128.9, 128.5, 128.0, 127.8, 127.5, 124.1 (t, J = 5.7 Hz), 121.9 (t, J = 245.7 Hz), 79.9 (t, J = 5.2 Hz), 47.6, 47.6, 44.9 (t, J = 27.5 Hz), 44.5, 28.5. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for : $C_{27}H_{29}F_2NO_4SNa^+$, 524.1678; found 524.1678.

1-(1,1-Difluoro-3-phenyl-3-(phenylsulfonyl)propyl)-3-methoxybenzene (5n)

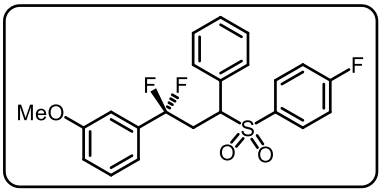
General procedure B was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 µL, 1.8 mmol, 1.5 equiv.), styrene (138 µL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded **5n** as a white solid (390 mg, 81% yield).



R_f = 0.30 (petroleum ether/ ethyl acetate 5:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 1H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.39 – 7.31 (m, 2H), 7.28 – 7.23 (m, 2H), 7.23 – 7.11 (m, 2H), 7.05 (d, *J* = 7.0 Hz, 2H), 6.91 (d, *J* = 7.5 Hz, 2H), 6.82 (s, 1H), 4.28 (d, *J* = 10.9 Hz, 1H), 3.77 (s, 3H), 3.39 – 3.21 (m, 1H), 3.13 – 2.94 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.24 (ddd, *J* = 244.2, 20.1, 8.4 Hz, 1F), -94.97 (ddd, *J* = 244.5, 19.2, 13.7 Hz, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.7, 137.5 (t, *J* = 26.2 Hz), 136.5, 133.9, 132.0, 130.0, 129.9, 129.2, 128.9, 128.8, 128.4, 121.5 (t, *J* = 245.6 Hz), 117.2 (t, *J* = 6.2 Hz), 116.0, 110.4 (t, *J* = 6.2 Hz), 66.7, 55.4, 37.3 (t, *J* = 28.4 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{22}H_{20}F_2O_3SNa^+$, 425.0993; found 425.0995.

1-(1,1-Difluoro-3-((4-fluorophenyl)sulfonyl)-3-phenylpropyl)-3-methoxybenzene (5o)

General procedure B was used with 4-fluorothiophenol (192 µL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 µL, 1.8 mmol, 1.5 equiv.), styrene (138 µL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded **5o** as a white solid (267 mg, 53% yield).

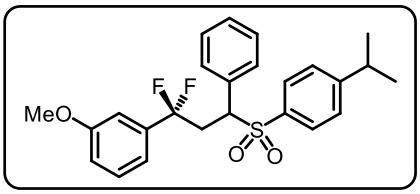


R_f = 0.50 (petroleum ether/ ethyl acetate 5:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.30 – 7.26 (m, 2H), 7.24 – 7.17 (m, 2H), 7.08 – 6.98 (m, 4H), 6.95 – 6.88 (m, 2H), 6.82 (s, 1H), 4.26 (d, *J* = 11.0 Hz, 1H), 3.78 (s, 3H), 3.38 – 3.24 (m, 1H), 3.11 – 2.97 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.34 (ddd, *J* = 244.7, 20.0, 8.1 Hz, 1F), -94.91 (ddd, *J* = 244.6, 18.9, 13.9 Hz, 1F), -102.92 – -103.07 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.0 (d, *J* = 257.0 Hz), 159.8, 137.5 (t, *J* = 25.8 Hz), 132.6, 132.0, 132.0, 129.9, 129.9, 129.1, 128.6, 121.5 (t, *J* = 245.3 Hz), 117.2 (t, *J* = 6.0 Hz), 116.2, 116.1 (d, *J* = 5.4 Hz), 110.5 (t, *J* = 5.7 Hz), 67.0, 55.5, 37.2 (t, *J* = 28.4 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for

$C_{22}H_{19}F_3O_3SNa^+$, 443.0899; found 443.0901.

1-(1,1-Difluoro-3-((4-isopropylphenyl)sulfonyl)-3-phenylpropyl)-3-methoxybenzene (5p)

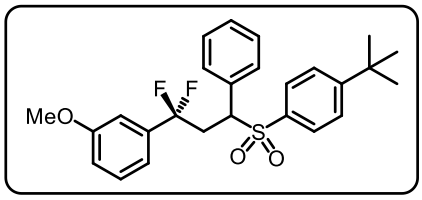
General procedure B was used with 4-isopropylbenzenethiol (280 µL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 µL, 1.8 mmol, 1.5 equiv.), styrene (138 µL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded **5p** as a white solid (432 mg, 81% yield).



R_f = 0.40 (petroleum ether/ ethyl acetate 5:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.27 (s, 1H), 7.26 – 7.23 (m, 1H), 7.22 – 7.14 (m, 4H), 7.04 (d, *J* = 7.5 Hz, 2H), 6.94 – 6.88 (m, 2H), 6.81 (s, 1H), 4.25 (d, *J* = 10.5 Hz, 1H), 3.77 (s, 3H), 3.35 – 3.20 (m, 1H), 3.13 – 2.98 (m, 1H), 2.96 – 2.87 (m, 1H), 1.24 – 1.20 (m, 6H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -91.98 (ddd, *J* = 244.6, 19.9, 8.3 Hz, 1F), -94.96 (ddd, *J* = 244.6, 19.2, 14.2 Hz, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.7, 155.7, 137.6 (t, *J* = 26.0 Hz), 133.8, 132.1, 130.0, 129.9, 129.3, 128.8, 128.3, 126.9, 121.6 (t, *J* = 245.5 Hz), 117.2 (t, *J* = 6.2 Hz), 116.0, 110.4 (t, *J* = 6.0 Hz), 66.8, 55.5, 37.3 (t, *J* = 28.5 Hz), 34.3, 23.7. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{25}H_{26}F_2O_3SNa^+$, 467.1463; found 467.1473.

1-(3-((4-(*tert*-Butyl)phenyl)sulfonyl)-1,1-difluoro-3-phenylpropyl)-3-methoxybenzene (5q)

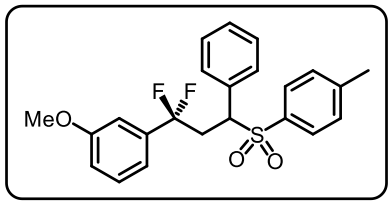
General procedure B was used with 4-(*tert*-butyl)benzenethiol (310 µL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 µL, 1.8 mmol, 1.5 equiv.), styrene (138 µL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded **5q** as a white solid (352 mg, 64% yield).



R_f = 0.30 (petroleum ether/ ethyl acetate 5:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 4H), 7.28 – 7.26 (m, 1H), 7.26 – 7.23 (m, 1H), 7.20 – 7.15 (m, 2H), 7.04 (d, *J* = 7.5 Hz, 2H), 6.93 – 6.88 (m, 2H), 6.82 (s, 1H), 4.25 (d, *J* = 10.7 Hz, 1H), 3.77 (s, 3H), 3.38 – 3.20 (m, 1H), 3.11 – 2.97 (m, 1H), 1.29 (s, 9H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -91.90 (ddd, *J* = 244.5, 19.7, 8.5 Hz, 1F), -94.91 (ddd, *J* = 244.6, 18.5, 14.5 Hz, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.7, 157.9, 137.6 (t, *J* = 25.8 Hz), 133.5, 132.1, 129.9, 129.9, 129.1, 128.8, 128.3, 125.8, 121.6 (t, *J* = 245.5 Hz), 117.2 (t, *J* = 6.0 Hz), 116.0, 110.4 (t, *J* = 5.0 Hz), 66.8, 55.5, 37.3 (t, *J* = 28.4 Hz), 35.3, 31.1. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{26}H_{28}F_2O_3SNa^+$, 481.1619; found 481.1625.

1-(1,1-Difluoro-3-phenyl-3-tosylpropyl)-3-methoxybenzene (5r)

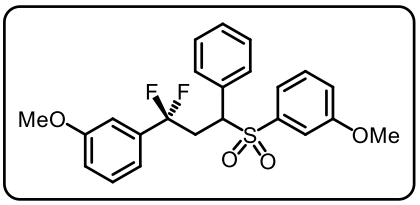
General procedure B was used with 4-methylbenzenethiol (223 mg, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 µL, 1.8 mmol, 1.5 equiv.), styrene (138 µL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded **5r** as a white solid (349 mg, 70% yield).



R_f = 0.30 (petroleum ether/ ethyl acetate 5:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.1 Hz, 2H), 7.28 (s, 1H), 7.25 (s, 1H), 7.22 – 7.17 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 7.5 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.81 (s, 1H), 4.24 (d, *J* = 11.0 Hz, 1H), 3.77 (s, 3H), 3.38 – 3.21 (m, 1H), 3.11 – 2.94 (m, 1H), 2.38 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.10 (ddd, *J* = 244.5, 19.9, 8.3 Hz, 1F), -95.00 (ddd, *J* = 244.5, 19.0, 14.1 Hz, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.7, 144.9, 137.5 (t, *J* = 26.0 Hz), 133.5, 132.1, 129.9, 129.8, 129.4, 129.1, 128.8, 128.3, 121.5 (t, *J* = 245.5 Hz), 117.1 (t, *J* = 5.9 Hz), 115.9, 110.4, 66.6, 55.4, 37.4 (t, *J* = 28.3 Hz), 21.6. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{23}H_{22}F_2O_3SNa^+$, 439.1150; found 439.1150.

1-(1,1-Difluoro-3-((3-methoxyphenyl)sulfonyl)-3-phenylpropyl)-3-methoxybenzene (5s)

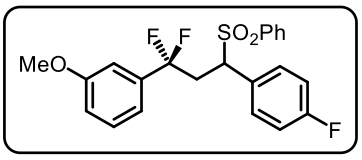
General procedure B was used with 3-methoxybenzenethiol (223 µL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 µL, 1.8 mmol, 1.5 equiv.), styrene (138 µL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded **5s** as a white solid (358 mg, 69% yield).



$\mathbf{R_f}$ = 0.50 (petroleum ether/ ethyl acetate 5:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 3H), 7.24 – 7.18 (m, 2H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.11 – 7.03 (m, 3H), 6.92 (d, *J* = 7.6 Hz, 2H), 6.82 (s, 2H), 4.27 (d, *J* = 11.0 Hz, 1H), 3.77 (s, 3H), 3.63 (s, 3H), 3.40 – 3.22 (m, 1H), 3.17 – 2.94 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.11 (ddd, *J* = 244.2, 19.8, 8.4 Hz, 1F), -95.02 (ddd, *J* = 244.6, 19.0, 14.1 Hz, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.7, 159.6, 137.5 (t, *J* = 26.1 Hz), 132.1, 130.0, 129.9, 128.9, 128.4, 121.5 (t, *J* = 245.2 Hz), 121.3, 121.0, 117.2 (t, *J* = 5.9 Hz), 116.0, 113.1, 110.4, 66.7, 55.6, 55.4, 37.2 (t, *J* = 28.4 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{23}H_{22}F_2O_4SNa^+$, 455.1099; found 455.1104.

1-(1,1-Difluoro-3-(4-fluorophenyl)-3-(phenylsulfonyl)propyl)-3-methoxybenzene (5t)

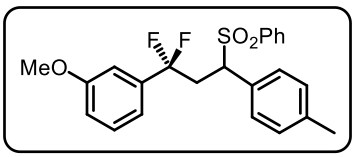
General procedure B was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 µL, 1.8 mmol, 1.5 equiv.), 1-fluoro-4-vinylbenzene (143 µL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded **5t** as a white solid (388 mg, 77% yield).



R$_f$ = 0.40 (petroleum ether/ ethyl acetate 5:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 1H), 7.48 (d, *J* = 7.4 Hz, 2H), 7.42 – 7.35 (m, 2H), 7.29 – 7.24 (m, 1H), 7.06 – 6.99 (m, 2H), 6.93 – 6.91 (m, 1H), 6.90 – 6.86 (m, 3H), 6.80 (s, 1H), 4.27 (d, *J* = 11.2 Hz, 1H), 3.77 (s, 3H), 3.39 – 3.18 (m, 1H), 3.07 – 2.87 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.10 – -92.75 (m 1F), -94.60 (ddd, *J* = 244.8, 18.4, 14.0 Hz, 1F), -112.15 – -112.26 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.0 (d, *J* = 257.0 Hz), 159.7, 137.5 (t, *J* = 25.8 Hz), 132.6, 132.0 (d, *J* = 9.4 Hz), 129.9, 129.9, 129.1, 128.6, 121.5 (t, *J* = 245.3 Hz), 117.2 (t, *J* = 6.0 Hz), 116.2, 116.1 (d, *J* = 5.4 Hz), 110.5 (t, *J* = 5.7 Hz), 67.0, 55.5, 37.2 (t, *J* = 28.4 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{22}H_{19}F_3O_3SNa^+$, 443.0899; found 443.0913.

1-(1,1-Difluoro-3-(phenylsulfonyl)-3-(*p*-tolyl)propyl)-3-methoxybenzene (5u)

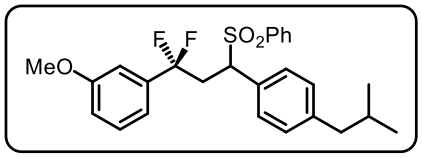
General procedure B was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 μL, 1.8 mmol, 1.5 equiv.), 1-methyl-4-vinylbenzene (158 μL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded **5u** as a white solid (265 mg, 53% yield).



R$_f$ = 0.30 (petroleum ether/ ethyl acetate 5:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 1H), 7.48 (d, *J* = 7.3 Hz, 2H), 7.41 – 7.33 (m, 2H), 7.30 – 7.26 (m, 1H), 7.00 (d, *J* = 7.6 Hz, 2H), 6.96 – 6.87 (m, 4H), 6.81 (s, 1H), 4.24 (d, *J* = 10.8 Hz, 1H), 3.77 (s, 3H), 3.34 – 3.18 (m, 1H), 3.12 – 2.92 (m, 1H), 2.30 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -91.87 (ddd, *J* = 244.3, 19.5, 8.0 Hz, 1F), -95.09 (ddd, *J* = 244.5, 18.9, 14.7 Hz, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.7, 138.9, 137.6 (t, *J* = 25.9 Hz), 136.7, 133.8, 129.8, 129.8, 129.2, 129.1, 128.8, 121.6 (t, *J* = 245.5 Hz), 117.2 (t, *J* = 6.0 Hz), 116.0, 110.4, 66.4, 55.4, 37.3 (t, *J* = 28.3 Hz), 21.6. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{23}H_{22}F_2O_3SNa^+$, 439.1150; found 439.1155.

1-(1,1-Difluoro-3-(4-isobutylphenyl)-3-(phenylsulfonyl)propyl)-3-methoxybenzene (5v)

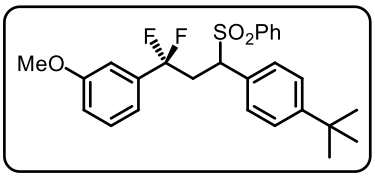
General procedure B was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 µL, 1.8 mmol, 1.5 equiv.), 1-methyl-4-vinylbenzene (218 µL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded **5v** as a white solid (440 mg, 80% yield).



R_f = 0.50 (petroleum ether/ ethyl acetate 5:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 1H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.36 – 7.29 (m, 2H), 7.28 – 7.23 (m, 1H), 6.98 – 6.88 (m, 6H), 6.83 (s, 1H), 4.25 (d, *J* = 10.9 Hz, 1H), 3.77 (s, 3H), 3.40 – 3.21 (m, 1H), 3.13 – 2.95 (m, 1H), 2.41 (d, *J* = 6.2 Hz, 2H), 1.88 – 1.71 (m, 1H), δ 0.87 (d, *J* = 6.5 Hz, 1H), 0.86 (d, *J* = 6.5 Hz, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.48 (ddd, *J* = 244.3, 19.7, 9.0 Hz, 1F), -94.07 – -94.84 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.8, 142.7, 137.7 (t, *J* = 26.1 Hz), 136.8, 133.7, 129.9, 129.7, 129.3, 129.3, 129.2, 128.7, 121.6 (t, *J* = 245.7 Hz), 117.3 (t, *J* = 5.9 Hz), 116.1, 110.5 (t, *J* = 6.3 Hz), 66.7, 55.5, 45.1, 37.2 (t, *J* = 28.7 Hz), 30.3, 22.4, 22.4. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{26}H_{28}F_2O_3SNa^+$, 481.1619; found 481.1624.

1-(3-(4-(*tert*-Butyl)phenyl)-1,1-difluoro-3-(phenylsulfonyl)propyl)-3-methoxybenzene (5w)

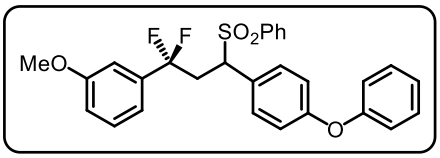
General procedure B was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 µL, 1.8 mmol, 1.5 equiv.), 1-(*tert*-butyl)-4-vinylbenzene (220 µL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded **5w** as a white solid (407 mg, 74% yield).



R_f = 0.30 (petroleum ether/ ethyl acetate 5:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 4H), 7.28 – 7.26 (m, 1H), 7.25 – 7.23 (m, 1H), 7.19 – 7.14 (m, 2H), 7.04 (d, *J* = 7.5 Hz, 2H), 6.93 – 6.88 (m, 2H), 6.82 (s, 1H), 4.25 (d, *J* = 10.7 Hz, 1H), 3.77 (s, 3H), 3.37 – 3.19 (m, 1H), 3.14 – 2.96 (m, 1H), 1.29 (s, 9H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -91.90 (ddd, *J* = 244.5, 19.7, 8.5 Hz, 1F), -94.91 (ddd, *J* = 244.6, 18.5, 14.5 Hz, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.7, 157.9, 137.6 (t, *J* = 25.8 Hz), 133.5, 132.1, 129.9, 129.9, 129.1, 128.8, 128.3, 125.8, 121.6 (t, *J* = 245.5 Hz), 117.2 (t, *J* = 6.0 Hz), 116.0, 110.4 (t, *J* = 5.0 Hz), 66.8, 55.5, 37.3 (t, *J* = 28.4 Hz), 35.3, 31.1. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{26}H_{28}F_2O_3SNa^+$, 481.1619; found 481.1624.

1-(1,1-Difluoro-3-(4-phenoxyphenyl)-3-(phenylsulfonyl)propyl)-3-methoxybenzene (5x)

General procedure B was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 µL, 1.8 mmol, 1.5 equiv.), 1-phenoxy-4-vinylbenzene (235 mg, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded **5x** as a white solid (480 mg, 81% yield).

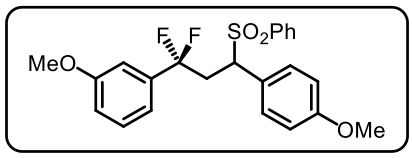


R_f = 0.30 (petroleum ether/ ethyl acetate 5:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 1H), 7.52 (d, *J* = 7.3 Hz, 2H), 7.44 – 7.38 (m, 2H), 7.38 – 7.33 (m, 2H), 7.29 – 7.26 (m, 1H), 7.17 – 7.10 (m, 1H), 7.01 – 6.94 (m, 4H), 6.94 – 6.89 (m, 2H), 6.83 – 6.77 (m, 3H), 4.26 (d, *J* = 9.7 Hz, 1H), 3.78 (s, 3H), 3.36 – 3.21 (m, 1H), 3.10 – 2.92 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.90 (ddd, *J* = 244.9, 19.2, 10.2 Hz, 1F), -93.93 (ddd, *J* = 244.9, 17.4, 14.3 Hz, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.8, 158.0, 156.8, 137.6 (t, *J* = 25.9 Hz), 136.8, 133.9, 131.4, 130.0, 129.9, 129.3, 128.9, 126.4, 123.9, 121.6 (t, *J* = 245.7 Hz), 119.3, 118.5,

117.3 (t, J = 6.2 Hz), 116.1, 110.5 (t, J = 6.2 Hz), 66.2, 55.5, 37.4 (t, J = 28.6 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{28}H_{24}F_2O_4SNa^+$, 517.1256; found 517.1266.

1-(1,1-Difluoro-3-(4-methoxyphenyl)-3-(phenylsulfonyl)propyl)-3-methoxybenzene (5y)

General procedure B was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 µL, 1.8 mmol, 1.5 equiv.), 1-methoxy-4-vinylbenzene (160 µL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded **5y** as a white solid (493 mg, 95% yield).

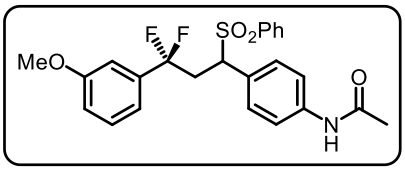


$\mathbf{R_f}$ = 0.30 (petroleum ether/ ethyl acetate 4:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.62 – 7.51 (m, 1H), 7.48 (d, J = 7.7 Hz, 2H), 7.43 – 7.35 (m, 2H), 7.28 (s, 1H), 6.96 (d, J = 8.4 Hz, 2H), 6.93 – 6.87 (m, 2H), 6.80 (s, 1H), 6.72 (d, J = 8.5 Hz, 2H), 4.22 (d, J = 11.0 Hz, 1H), 3.78 (s, 3H), 3.78 (s, 3H), 3.38 – 3.16 (m, 1H), 3.06 – 2.88 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.03 (ddd, J = 244.3, 19.6, 8.2 Hz, 1F), -94.98 (ddd, J = 244.2, 18.7, 14.5 Hz, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.1, 159.8, 137.7 (t, J = 25.6 Hz), 136.8, 133.8, 131.1, 129.9, 129.3, 128.9, 123.7, 121.6 (t, J = 245.8 Hz), 117.3 (t, J = 5.9 Hz), 116.0, 113.9, 110.5 (t, J = 6.3 Hz), 66.1, 55.5, 55.4, 37.3 (t, J = 28.1 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{23}H_{22}F_2O_4SNa^+$, 455.1099; found 455.1106.

***N*-(4-(3,3-Difluoro-3-(3-methoxyphenyl)-1-(phenylsulfonyl)propyl)phenyl)acetamide (5z)**

General procedure B was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 µL, 1.8 mmol, 1.5 equiv.), N-(4-vinylphenyl)acetamide (193 mg, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (1:1 (v/v)) as eluent afforded **5z** as a

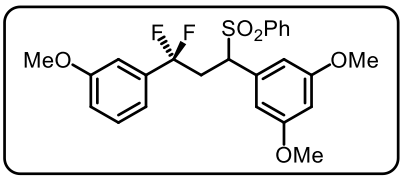
yellow solid (331 mg, 60% yield).



R_f = 0.30 (petroleum ether/ ethyl acetate 1:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.57 – 7.51 (m, 1H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.41 – 7.33 (m, 4H), 7.24 (d, *J* = 7.9 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.78 (s, 1H), 4.25 (d, *J* = 10.9 Hz, 1H), 3.74 (s, 3H), 3.29 – 3.12 (m, 1H), 3.06 – 2.89 (m, 1H), 2.10 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -91.56 (ddd, *J* = 244.3, 19.5, 7.4 Hz, 1F), -95.01 – -95.77 (m, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.9, 159.7, 139.0, 137.3 (t, *J* = 25.8 Hz), 136.4, 134.1, 130.5, 129.9, 129.0, 128.9, 126.8, 121.4 (t, *J* = 245.5 Hz), 119.3, 117.0 (t, *J* = 6.0 Hz), 115.9, 110.4 (t, *J* = 6.3 Hz), 66.1, 55.4, 37.4 (t, *J* = 28.4 Hz), 24.6, 14.3. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{24}H_{23}F_2NO_4SNa^+$, 482.1208; found 482.1215.

1-(3,3-Difluoro-3-(3-methoxyphenyl)-1-(phenylsulfonyl)propyl)-3,5-dimethoxy-benzene (**5aa**)

General procedure B was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 μL, 1.8 mmol, 1.5 equiv.), 1,3-dimethoxy-5-vinylbenzene (196 μL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (4:1 (v/v)) as eluent afforded **5aa** as a white solid (460 mg, 83% yield).

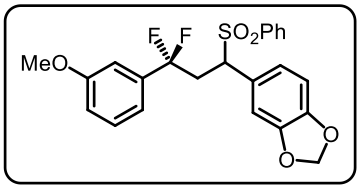


R_f = 0.20 (petroleum ether/ ethyl acetate 4:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.63 – 7.48 (m, 3H), 7.44 – 7.35 (m, 2H), 7.26 – 7.24 (m, 1H), 6.97 – 6.87 (m, 2H), 6.82 (s, 1H), 6.32 (s, 1H), 6.16 (s, 2H), 4.19 (d, *J* = 10.9 Hz, 1H), 3.77 (s, 3H), 3.65 (s, 6H), 3.36 – 3.16 (m, 1H), 3.08 – 2.90 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -93.23 (ddd, *J* = 244.6, 19.4, 9.9 Hz, 1F), -94.17 (ddd, *J* = 244.6, 18.2, 13.8 Hz, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.5, 159.7, 137.5 (t, *J* = 25.6 Hz), 136.6, 134.0, 133.9, 129.8, 129.2, 128.8, 121.5 (t, *J* = 245.5 Hz), 117.2 (t, *J* = 5.9 Hz),

116.0, 110.5 (t, J = 5.3 Hz), 108.0, 101.2, 66.8, 55.4, 37.4 (t, J = 28.6 Hz), 14.3. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{24}H_{24}F_2O_5SNa^+$, 485.1205; found 485.1205.

5-(3,3-Difluoro-3-(3-methoxyphenyl)-1-(phenylsulfonyl)propyl)benzo[d][1,3]dioxole (5ab)

General procedure B was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 µL, 1.8 mmol, 1.5 equiv.), 5-vinylbenzo[d][1,3]dioxole (152 µL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (4:1 (v/v)) as eluent afforded **5ab** as a yellow oil (375 mg, 70% yield).

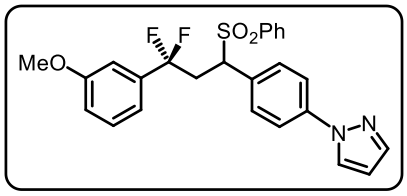


$\mathbf{R_f}$ = 0.30 (petroleum ether/ ethyl acetate 5:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.60 – 7.50 (m, 3H), 7.45 – 7.37 (m, 2H), 7.29 – 7.27 (m, 1H), 6.96 – 6.87 (m, 2H), 6.81 (s, 1H), 6.66 (s, 1H), 6.58 (d, J = 8.0 Hz, 1H), 6.41 (d, J = 7.8 Hz, 1H), 5.94 (d, J = 14.1 Hz, 2H), 4.19 (d, J = 10.2 Hz, 1H), 3.78 (s, 3H), 3.30 – 3.15 (m, 1H), 2.99 – 2.86 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.56 (ddd, J = 244.5, 19.5, 8.9 Hz, 1F), -94.80 (ddd, J = 244.7, 18.3, 14.2 Hz, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.7, 148.2, 147.8, 137.5 (t, J = 25.7 Hz), 136.7, 133.9, 129.9, 129.2, 128.9, 125.4, 124.3, 121.5 (t, J = 245.9 Hz), 117.2 (t, J = 6.0 Hz), 116.0, 110.5, 109.66, 108.1, 101.5, 66.4, 55.5, 37.5 (t, J = 28.2 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{23}H_{20}F_2O_5SNa^+$, 469.0892; found 469.0901.

1-(4-(3,3-Difluoro-3-(3-methoxyphenyl)-1-(phenylsulfonyl)propyl)phenyl)-1*H*-pyraz-ole (5ac)

General procedure B was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 µL, 1.8 mmol, 1.5 equiv.), 1-(4-vinylphenyl)-1*H*-pyrazole (204 mg, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (4:1 (v/v)) as

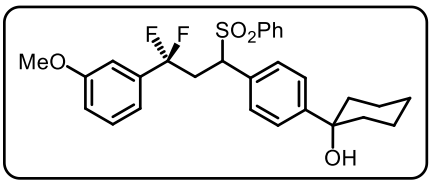
eluent afforded **5ac** as a yellow oil (410 mg, 73% yield).



R_f = 0.20 (petroleum ether/ ethyl acetate 4:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 1H), 7.72 (s, 1H), 7.58 – 7.50 (m, 5H), 7.42 – 7.34 (m, 2H), 7.30 – 7.26 (m, 1H), 7.14 (d, *J* = 8.3 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.82 (s, 1H), 6.48 (s, 1H), 4.31 (d, *J* = 11.0 Hz, 1H), 3.76 (s, 3H), 3.44 – 3.25 (m, 1H), 3.11 – 2.95 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.07 (ddd, *J* = 244.7, 19.7, 7.8 Hz, 1F), -94.97 (ddd, *J* = 244.7, 18.1, 14.3 Hz, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.8, 141.6, 140.5, 137.5 (t, *J* = 25.9 Hz), 136.5, 134.1, 131.0, 130.1, 130.0, 129.2, 129.0, 126.8, 121.5 (t, *J* = 245.7 Hz), 118.8, 117.2 (t, *J* = 6.0 Hz), 116.0, 110.5 (t, *J* = 6.1 Hz), 108.2, 66.2, 55.5, 37.4 (t, *J* = 28.4 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{25}H_{22}F_2N_2O_3SNa^+$, 491.1211; found 491.1223.

1-(4-(3,3-Difluoro-3-(3-methoxyphenyl)-1-(phenylsulfonyl)propyl)phenyl)cyclohexan-1-ol (5ad)

General procedure B was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 µL, 1.8 mmol, 1.5 equiv.), 1-(4-vinylphenyl)cyclohexan-1-ol (243 mg, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (4:1 (v/v)) as eluent afforded **5ad** as a yellow oil (450 mg, 75% yield).

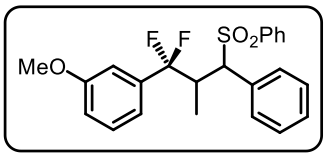


R_f = 0.20 (petroleum ether/ ethyl acetate 4:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 1H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.36 – 7.30 (m, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.21 (m, 1H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.93 – 6.85 (m, 2H), 6.76 (s, 1H), 4.27 (d, *J* = 10.5 Hz, 1H), 3.74 (s, 3H), 3.33 – 3.18 (m, 1H), 3.11 – 2.95 (m, 1H), 1.78 – 1.68 (m, 7H), 1.66 (s, 1H), 1.62 (s, 2H), 1.28 (s, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -93.16 (ddd, *J* = 244.8, 17.7, 12.0 Hz, 1F), -93.44 – -93.99 (m, 1F). **^{13}C**

NMR (151 MHz, $CDCl_3$) δ 159.6, 150.3, 137.5 (t, *J* = 25.9 Hz), 136.6, 133.8, 130.0, 129.8, 129.7, 129.13, 128.7, 124.7, 121.5 (t, *J* = 245.5 Hz), 117.2 (t, *J* = 6.0 Hz), 116.0, 110.4, 73.0, 66.4, 55.4, 38.9, 38.8, 37.3 (t, *J* = 28.7 Hz), 25.5, 22.2. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{28}H_{30}F_2O_4SNa^+$, 523.1725; found 523.1729.

1-(1,1-Difluoro-2-methyl-3-phenyl-3-(phenylsulfonyl)propyl)-3-methoxybenzenec (5ae)

General procedure B was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 μL, 1.8 mmol, 1.5 equiv.), (*E*)-prop-1-en-1-ylbenzene (156 μL, 1.2 mmol, 1.0 equiv.) and *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (4:1 (v/v)) as eluent afforded **5ae** with 1:1 d.r.[1] as a white solid (305 mg, 61% yield).



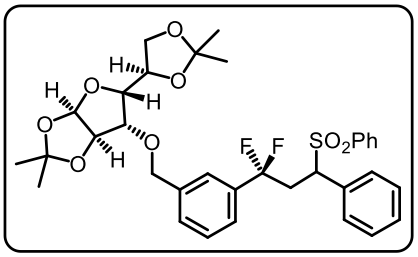
One of mixed isomers of 5ae R_f = 0.40 (petroleum ether/ ethyl acetate 5:1 (v/v)). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 3H), 7.25 – 7.19 (m, 3H), 7.13 – 7.08 (m, 1H), 7.08 – 6.94 (m, 4H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.78 (s, 1H), 4.32 (d, *J* = 8.7 Hz, 1H), 3.77 (s, 3H), 3.52 – 3.35 (m, 1H), 1.65 (d, *J* = 7.1 Hz, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -91.22 (dd, *J* = 243.6, 7.3 Hz, 1F), -104.11 (dd, *J* = 243.5, 18.0 Hz, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.6, 139.1, 137.3 (t, *J* = 25.3 Hz), 134.9, 133.1, 130.1, 129.6, 128.8, 128.4, 128.3, 123.4 (t, *J* = 247.7 Hz), 117.9 (t, *J* = 6.3 Hz), 115.6, 111.4 (t, *J* = 6.5 Hz), 71.6, 55.5, 44.7 (t, *J* = 25.1 Hz), 13.5. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{23}H_{22}F_2O_3SNa^+$, 439.1150; found 439.1148.

Compound (5af)

General procedure B was used with thiophenol (1.8 mmol, 184 μL, 1.5 equiv.), **2o** (753 mg, 1.8 mmol, 1.5 equiv.), styrene (138 μL, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification

[1] The diastereomeric ratio determined by ^{19}F NMR.

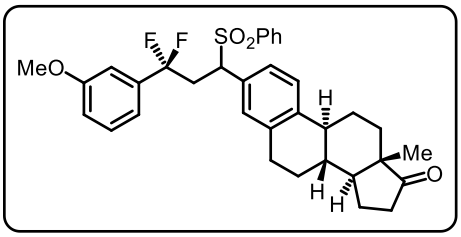
by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded **5af** with 1:1 d.r. as a colorless oil (271 mg, 35% yield).



The mixed isomers of 5af R_f = 0.20 (petroleum ether/ ethyl acetate 5:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 1H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.40 – 7.34 (m, 3H), 7.32 (s, 1H), 7.29 (s, 1H), 7.26 (d, *J* = 7.3 Hz, 1H), 7.22 – 7.16 (m, 2H), 7.05 (d, *J* = 7.5 Hz, 2H), 5.92 (d, *J* = 3.5 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.64 (s, 1H), 4.62 (s, 1H), 4.40 – 4.34 (m, 1H), 4.31 (dd, *J* = 10.6, 4.9 Hz, 1H), 4.22 – 4.08 (m, 2H), 4.08 – 3.95 (m, 2H), 3.44 – 3.25 (m, 1H), 3.16 – 2.96 (m, 1H), 1.52 (s, 3H), 1.45 (s, 3H), 1.37 (d, *J* = 3.5 Hz, 3H), 1.35 (s, 3H). **^{19}F NMR** δ -92.46 – -93.50 (m, 1F), -94.01 – -94.96 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.5, 136.7, 133.9, 132.2, 129.9, 129.4, 129.2, 129.0, 128.8, 128.5, 124.5 (t, *J* = 5.6 Hz), 124.1 (q, *J* = 6.1 Hz), 121.6 (t, *J* = 245.2 Hz), 112.0, 109.3 (d, *J* = 3.9 Hz), 105.5, 82.8, 82.2, 81.5, 72.5, 72.0, 67.7, 66.8, 37.3 (t, *J* = 26.7 Hz), 27.0, 26.4, 25.5. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{34}H_{38}F_2O_8SNa^+$, 667.2148; found 667.2156.

Compound (5ag)

General procedure B was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 μL, 1.8 mmol, 1.5 equiv.), **1n** (336 mg, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (3:1 (v/v)) as eluent afforded **5ag** with 1:1 d.r. as a white solid (604 mg, 87% yield).

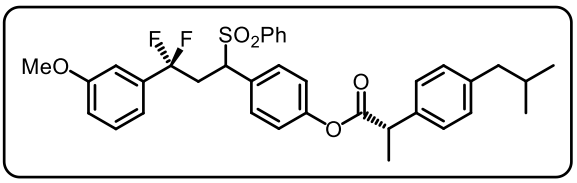


The mixed isomers of 5ag R_f = 0.30 (petroleum ether/ ethyl acetate 3:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.60 – 7.50 (m, 3H), 7.43 – 7.36 (m, 2H), 7.25 – 7.22 (m, 1H), 7.13 – 7.05 (m, 1H), 6.91 – 6.85 (m, 2H), 6.85 – 6.68 (m, 3H), 4.21 (d, *J* = 10.8 Hz, 1H), 3.75 (s, 3H), 3.24 – 3.09 (m, 1H), 3.06 – 2.91 (m, 1H), 2.81 – 2.73 (m,

1H), 2.73 – 2.63 (m, 1H), 2.51 (dd, J = 19.0, 8.7 Hz, 1H), 2.39 – 2.31 (m, 1H), 2.24 (t, J = 8.2 Hz, 1H), 2.20 – 2.10 (m, 1H), 2.09 – 2.02 (m, 1H), 2.01 – 1.91 (m, 2H), 1.67 – 1.58 (m, 1H), 1.58 – 1.44 (m, 4H), 1.44 – 1.32 (m, 1H), 0.93 (s, 1.5H), 0.92 (s, 1.5H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.64 – -93.39 (m, 1F), -93.43 – -94.28 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.7, 140.7, 140.6, 137.6 (t, J = 25.2 Hz), 136.9, 136.6, 136.5, 133.8, 130.7, 130.5, 130.3, 129.7, 129.3, 128.8, 127.4, 127.2, 125.4, 125.3, 121.5 (t, J = 249.4 Hz), 117.2 (t, J = 5.5 Hz), 116.0, 116.0, 110.3 (t, J = 10.0 Hz), 66.4, 55.4, 50.7, 48.0, 44.5, 44.4, 38.1, 38.1, 37.6 (t, J = 28.4 Hz), 37.5 (t, J = 28.8 Hz), 35.9, 35.3, 31.7, 29.2, 26.5, 25.7, 21.7, 21.7, 14.0. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{34}H_{36}F_2O_4SNa^+$, 601.2195; found 601.2209.

Compound (5ah)

General procedure B was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 μL, 1.8 mmol, 1.5 equiv.), **1o** (370 mg, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded **5ah** with 1:1 d.r. as a yellow oil (240 mg, 33% yield).

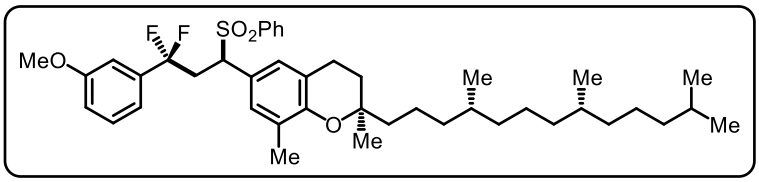


The mixed isomers of 5ah R_f = 0.50 (petroleum ether/ ethyl acetate 5:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 1H), 7.45 (d, J = 7.4 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.30 – 7.27 (m, 2H), 7.24 (s, 1H), 7.15 (d, J = 7.1 Hz, 2H), 7.01 (d, J = 7.7 Hz, 2H), 6.94 – 6.87 (m, 2H), 6.84 (d, J = 7.7 Hz, 2H), 6.81 (s, 1H), 4.25 (d, J = 11.0 Hz, 1H), 3.98 – 3.85 (m, 1H), 3.76 (s, 3H), 3.40 – 3.21 (m, 1H), 3.07 – 2.87 (m, 1H), 2.48 (d, J = 6.8 Hz, 2H), 1.92 – 1.80 (m, 1H), 1.60 (d, J = 6.6 Hz, 3H), 0.92 (d, J = 5.9 Hz, 6H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -91.94 – -92.72 (m, 1F), -94.60 – -95.40 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.9, 159.8, 151.4, 141.1, 137.5 (t, J = 26.1 Hz), 137.2, 136.4, 134.0, 130.8, 129.9, 129.7, 129.5, 129.2, 129.0, 127.3, 121.5 (t, J =245.4Hz), 117.2 (t, J = 5.6 Hz), 116.1, 110.4 (t, J = 5.3 Hz), 66.2, 55.5, 45.4, 45.2, 37.3 (t, J =

28.7 Hz), 30.3, 22.5, 18.6. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{35}H_{36}F_2O_5SNa^+$, 629.2144; found 629.2150.

Compound (5ai)

General procedure B was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 μL, 1.8 mmol, 1.5 equiv.), **1p** (495 mg, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by preparation of thin layer chromatography using petroleum ether and ethyl acetate (15:1 (v/v)) as eluent afforded **5ai** with 1:1 d.r. as a yellow oil (699 mg, 82% yield).

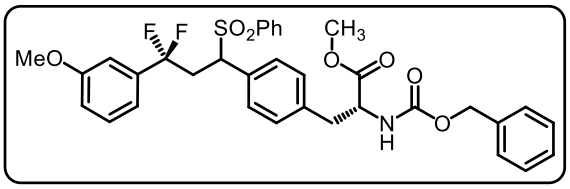


The mixed isomers of 5ai R_f = 0.30 (petroleum ether/ ethyl acetate 10:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.42 – 7.35 (m, 2H), 7.27 – 7.22 (m, 1H), 6.95 – 6.85 (m, 2H), 6.79 (s, 1H), 6.59 (s, 1H), 6.46 (s, 1H), 4.15 (d, *J* = 10.3 Hz, 1H), 3.77 (s, 3H), 3.30 – 3.14 (m, 1H), 3.07 – 2.90 (m, 1H), 2.65 – 2.54 (m, 1H), 2.54 – 2.42 (m, 1H), 2.03 (s, 3H), 1.79 – 1.67 (m, 2H), 1.59 – 1.56 (m, 1H), 1.55 – 1.52 (m, 1H), 1.39 – 1.23 (m, 16H), 1.18 – 1.07 (m, 6H), 0.91 – 0.86 (m, 12H). **^{19}F NMR** (565 MHz, $CDCl_3$) ^{19}F NMR (565 MHz, $CDCl_3$) δ -92.36 – -93.13 (m, 1F), -93.47 – -94.22 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.6, 152.8, 137.7 (t, *J* = 25.9 Hz), 137.1, 133.5, 129.8, 129.6, 129.4, 128.8, 128.6, 126.3, 121.7 (t, *J* = 245.4 Hz), 121.1, 120.3, 117.3 (t, *J* = 5.5 Hz), 115.9, 110.4 (t, *J* = 5.8 Hz), 76.5, 66.5, 55.4, 40.4, 40.3, 39.5, 37.7, 37.7, 37.6, 37.6, 37.5, 37.3 (t, *J* = 28.5 Hz), 33.0, 32.9, 31.2, 29.9, 28.1, 25.0, 24.6, 24.2, 24.2, 22.9, 22.8, 22.2, 21.1, 19.9, 19.8, 16.0. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{43}H_{60}F_2O_4SNa^+$, 733.4073; found 733.4082.

Compound (5aj)

General procedure B was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 3-

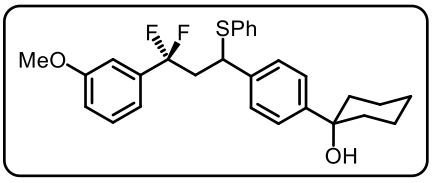
(trifluoromethyl)anisole (260 μL, 1.8 mmol, 1.5 equiv.), **1q** (407 mg, 1.2 mmol, 1.0 equiv.), *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) and 85 wt% *m*CPBA (730 mg, 3.6 mmol, 3.0 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (3:1 (v/v)) as eluent afforded **5aj** with 1:1 d.r. as a yellow white (551 mg, 74% yield).



The mixed isomers of 5aj R_f = 0.40 (petroleum ether/ ethyl acetate 3:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 1H), 7.44 – 7.29 (m, 10H), 7.00 – 6.85 (m, 6H), 6.81 (s, 1H), 5.20 – 5.04 (m, 3H), 4.62 (s, 1H), 4.23 (d, *J* = 10.8 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 1H), 3.69 (s, 2H), 3.38 – 3.23 (m, 1H), 3.16 – 2.90 (m, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -91.70 – -92.78 (m, 1F), -94.09 – -94.98 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.7, 159.7, 155.6, 137.5 (t, *J* = 25.7 Hz), 137.4 (t, *J* = 25.3 Hz), 136.8, 136.6, 136.4, 136.2, 133.9, 133.8, 131.0, 130.9, 130.1, 130.0, 129.8, 129.3, 129.3, 129.1, 129.1, 128.6, 128.3, 121.5 (t, *J* = 244.6 Hz), 117.2 (t, *J* = 5.6 Hz), 116.0, 116.0, 110.4, 67.2, 66.4, 55.4, 54.8, 54.7, 52.4, 52.3, 37.8, 37.7, 37.1 (t, *J* = 25.3 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{34}H_{33}F_2NO_7SNa^+$, 660.1838; found 660.1848.

1-(4-(3,3-Difluoro-3-(3-methoxyphenyl)-1-(phenylthio)propyl)phenyl)cyclohexan-1-ol (4b)

General procedure A was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 μL, 1.8 mmol, 1.5 equiv.), 1-(4-vinylphenyl)cyclohexan-1-ol (242 mg, 1.2 mmol, 1.0 equiv.) and *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded **4b** with as a colorless oil (528 mg, 94% yield).

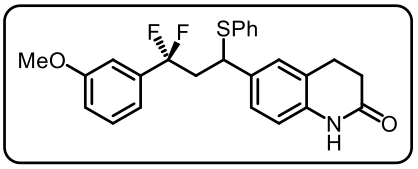


R_f = 0.30 (petroleum ether/ethyl acetate 5:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.22 (m, 6H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 7.1 Hz, 2H), 6.79 (s, 1H), 4.36 (dd, *J* = 9.6, 3.7 Hz,

1H), 3.77 (s, 3H), 2.98 – 2.86 (m, 1H), 2.85 – 2.73 (m, 1H), 1.87 – 1.73 (m, 7H), 1.70 – 1.62 (m, 2H), 1.60 (s, 1H), 1.37 – 1.25 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.45 – -93.03 (m, 1F), -93.03 – -93.61 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.6, 148.6, 138.8, 138.1 (t, *J* = 26.2 Hz), 134.4, 132.7, 129.6, 129.0, 127.8, 127.7, 124.8, 121.9 (t, *J* = 245.1 Hz), 117.4 (t, *J* = 6.4 Hz), 115.8, 110.5 (t, *J* = 5.6 Hz), 73.1, 55.4, 47.1, 44.8 (t, *J* = 27.5 Hz), 38.9, 38.9, 25.7, 22.3. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{28}H_{30}F_2O_2SNa^+$, 491.1827; found 491.1834.

6-(3,3-Difluoro-3-(3-methoxyphenyl)-1-(phenylthio)propyl)-3,4-dihydroquinolin-2(1*H*)-one (4c)

General procedure A was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 µL, 1.8 mmol, 1.5 equiv.), 6-vinyl-3,4-dihydroquinolin-2(1*H*)-one (208 mg, 1.2 mmol, 1.0 equiv.) and *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (1:1 (v/v)) as eluent afforded **4c** with as a yellow oil (379 mg, 72% yield).

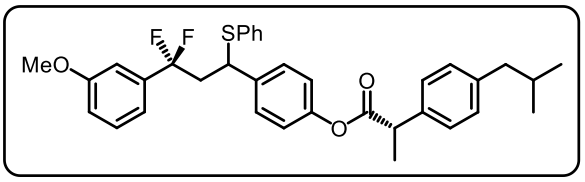


R_f = 0.30 (petroleum ether/ethyl acetate 1:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.15 (s, 1H), 7.25 (s, 1H), 7.23 (s, 5H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.94 (s, 1H), 6.92 – 6.86 (m, 2H), 6.78 (s, 1H), 6.69 (d, *J* = 8.1 Hz, 1H), 4.29 (dd, *J* = 9.8, 3.5 Hz, 1H), 3.76 (s, 3H), 2.93 – 2.80 (m, 3H), 2.80 – 2.69 (m, 1H), 2.66 – 2.55 (m, 2H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.39 – -93.10 (m, 1F), -93.13 – -93.87 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.2, 159.6, 138.0 (t, *J* = 26.4 Hz), 136.6, 135.2, 134.1, 132.8, 129.6, 129.0, 127.8, 127.5, 127.1, 123.6, 121.8 (t, *J* = 245.3 Hz), 117.3 (t, *J* = 6.0 Hz), 115.5, 115.5, 110.7, 55.4, 47.0, 44.7 (t, *J* = 27.1 Hz), 30.7, 25.4. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{25}H_{23}F_2NO_2SNa^+$, 462.1310; found 462.1313.

4-(3,3-Difluoro-3-(3-methoxyphenyl)-1-(phenylthio)propyl)phenyl (*S*)-2-(4-isobutyl-phenyl)propanoate (4d)

General procedure A was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), 3-

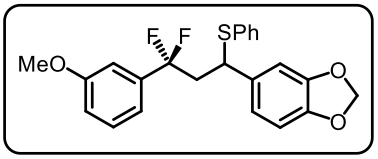
(trifluoromethyl)anisole (260 μL, 1.8 mmol, 1.5 equiv.), **1o** (370 mg, 1.2 mmol, 1.0 equiv.) and *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (20:1 (v/v)) as eluent afforded **4d** with 1:1 d.r. as a colorless oil (241 mg, 35% yield).



The mixed isomers of 4d $\mathbf{R_f}$ = 0.30 (petroleum ether/ethyl acetate 20:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.5 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.21 (s, 5H), 7.18 – 7.11 (m, 4H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 7.9 Hz, 3H), 6.82 (s, 1H), 4.30 (dd, *J* = 8.9, 3.9 Hz, 1H), 3.92 (q, *J* = 6.9 Hz, 1H), 3.76 (s, 3H), 2.91 – 2.68 (m, 2H), 2.49 (d, *J* = 7.1 Hz, 2H), 1.98 – 1.82 (m, 1H), 1.61 (d, *J* = 7.0 Hz, 3H), 0.93 (d, *J* = 6.5 Hz, 6H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -91.66 – -92.56 (m, 1F), -93.89 – -94.99 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.1, 159.7, 150.2, 141.0, 138.3, 138.0 (t, *J* = 21.0 Hz), 137.4, 133.9, 133.1, 129.8, 129.6, 129.0, 128.8, 127.9, 127.4, 121.8 (t, *J* = 245.1 Hz), 121.3, 117.3 (t, *J* = 6.2 Hz), 115.8, 110.6, 55.4, 47.1, 45.4, 45.2, 45.0 (t, *J* = 27.1 Hz), 30.3, 22.5, 18.6. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{35}H_{36}F_2O_3SNa^+$, 597.2245; found 597.2249.

5-(3,3-Difluoro-3-(3-methoxyphenyl)-1-(phenylthio)propyl)benzo[d][1,3]dio-xole (4e)

General procedure A was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 μL, 1.8 mmol, 1.5 equiv.), 5-vinylbenzo[d][1,3]dioxole (152 μL, 1.2 mmol, 1.0 equiv.) and *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded **4e** as a yellow oil (402 mg, 81% yield).

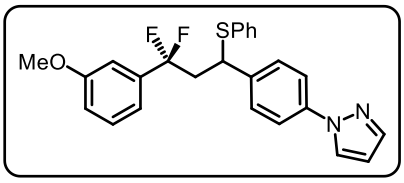


$\mathbf{R_f}$ = 0.50 (petroleum ether/ethyl acetate 5:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 1H), 7.24 (s, 5H), 6.96 – 6.88 (m, 2H), 6.83 (s, 1H), 6.76 (s, 1H), 6.68 – 6.57 (m, 2H), 5.93 (d, *J* = 4.7 Hz, 2H), 4.28 (d, *J* = 6.3 Hz, 1H), 3.78 (s, 3H), 2.96 – 2.60 (m, 2H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.23 (ddd,

J = 245.2, 17.0, 12.2 Hz, 1F), -93.91 – -94.75 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.7, 147.8, 146.9, 138.1 (t, *J* = 26.3 Hz), 134.5, 134.3, 132.8, 129.7, 129.0, 127.7, 121.8 (t, *J* = 245.1 Hz), 121.6, 117.4 (t, *J* = 6.1 Hz), 115.7, 110.6, 108.1, 108.0, 101.2, 55.4, 47.5, 45.0 (t, *J* = 27.3 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{23}H_{20}F_2O_3SNa^+$, 437.0993; found 437.1001.

1-(4-(3,3-Difluoro-3-(3-methoxyphenyl)-1-(phenylthio)propyl)phenyl)-1*H*-pyrazole (4f)

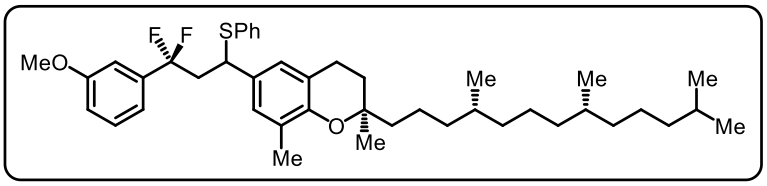
General procedure A was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 μL, 1.8 mmol, 1.5 equiv.), 1-(4-vinylphenyl)-1*H*-pyrazole (204 mg, 1.2 mmol, 1.0 equiv.) and *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded **4f** as a colorless oil (445 mg, 85% yield).



R_f = 0.20 (petroleum ether/ethyl acetate 10:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.95 – 7.84 (m, 1H), 7.71 (s, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.25 (s, 1H), 7.24 – 7.20 (m, 6H), 6.97 – 6.87 (m, 2H), 6.82 (s, 1H), 6.46 (s, 1H), 4.35 (dd, *J* = 9.6, 3.8 Hz, 1H), 3.76 (s, 3H), 2.94 – 2.73 (m, 2H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.03 (ddd, *J* = 245.2, 17.7, 11.1 Hz, 1F), -93.91 – -95.26 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.7, 141.2, 139.4, 139.1, 133.8, 133.2, 129.8, 129.1, 129.1, 128.0, 126.8, 121.8 (t, *J* = 244.4 Hz), 119.1, 117.4 (t, *J* = 6.2 Hz), 115.7, 110.7 (t, *J* = 5.7 Hz), 107.7, 55.5, 47.2, 44.8 (t, *J* = 27.1 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{25}H_{22}F_2N_2OSNa^+$, 459.1313; found 459.1326.

Compound (4g)

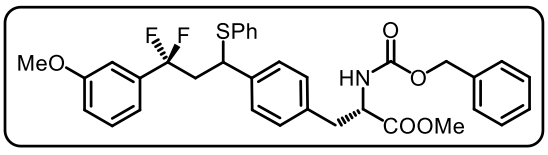
General procedure A was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 μL, 1.8 mmol, 1.5 equiv.), **1p** (495 mg, 1.2 mmol, 1.0 equiv.) and *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.). Purification by preparation of thin layer chromatography using petroleum ether and ethyl acetate (50:1 (v/v)) as eluent afforded **4g** with 1:1 d.r. as a colorless oil (684 mg, 84% yield).



The mixed isomers of 4g R_f = 0.30 (petroleum ether/ethyl acetate 50:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 6H), 6.91 – 6.84 (m, 2H), 6.78 (d, *J* = 11.9 Hz, 2H), 6.63 (s, 1H), 4.24 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.75 (s, 3H), 2.94 – 2.80 (m, 1H), 2.81 – 2.65 (m, 1H), 2.65 – 2.52 (m, 2H), 2.10 (s, 3H), 1.81 – 1.75 (m, 1H), 1.74 – 1.68 (m, 1H), 1.58 – 1.51 (m, 3H), 1.30 – 1.04 (m, 18H), 0.88 (d, *J* = 6.6 Hz, 8H), 0.86 (d, *J* = 6.7 Hz, 4H), 0.13 – 0.05 (m, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -91.71 – -92.72 (m, 1F), -92.94 – -94.20 (m, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.5, 151.5, 135.0, 132.4, 130.0, 129.4, 128.9, 127.8, 127.7, 127.4, 126.4, 126.4, 125.6, 120.3 (t, *J* = 213.9 Hz), 117.5 (t, *J* = 6.2 Hz), 115.6, 110.5 (t, *J* = 6.4 Hz), 76.2, 55.4, 46.9 (t, *J* = 3.1 Hz), 44.7 (t, *J* = 27.2 Hz), 44.6 (t, *J* = 27.3 Hz), 40.5, 40.4, 39.5, 37.7, 37.6, 37.5, 33.0, 32.9, 31.3, 28.1, 25.0, 24.6, 24.4, 24.3, 22.9, 22.8, 22.4, 21.2, 19.9, 19.8, 16.2. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{43}H_{60}F_2O_2SNa^+$, 701.4174; found 701.4180.

Compound (4h)

General procedure A was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 μL, 1.8 mmol, 1.5 equiv.), **1q** (407 mg, 1.2 mmol, 1.0 equiv.) and *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded **4h** with 1:1 d.r. as a white solid (581 mg, 80% yield).

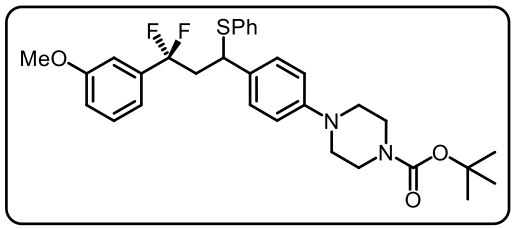


The mixed isomers of 4h R_f = 0.20 (petroleum ether/ethyl acetate 5:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 3H), 7.35 – 7.29 (m, 2H), 7.26 – 7.22 (m, 1H), 7.22 – 7.11 (m, 5H), 7.11 – 6.99 (m, 2H), 6.98 – 6.92 (m, 2H), 6.92 – 6.86 (m, 2H), 6.82 (s, 1H), 5.21 – 5.07 (m, 3H), 4.64 (dd, *J* = 13.1, 5.8 Hz, 1H), 4.27 (d, *J* = 8.0 Hz, 1H), 3.76 (s, 3H), 3.69 (d, *J* = 8.4 Hz, 2H), 3.06 (d, *J* = 5.4 Hz, 2H), 2.91 – 2.80 (m, 1H), 2.80 – 2.69

(m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -91.64 – -92.93 (m, 1F), -93.58 – -94.55 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.9, 159.7, 155.7, 139.7, 138.1 (t, *J* = 25.4 Hz), 136.4, 134.9, 134.8, 133.9, 133.8, 133.3, 133.2, 129.7, 129.3, 129.0, 128.7, 128.4, 128.3, 128.2, 127.9, 127.8, 121.8 (t, *J* = 245.1 Hz), 117.4 (t, *J* = 5.6 Hz), 115.8, 110.6, 67.2, 55.5, 54.9, 52.4, 47.3, 47.2, 44.8 (t, *J* = 21.0 Hz), 44.7 (t, *J* = 23.7 Hz), 38.0. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{34}H_{33}F_2NO_5SNa^+$, 628.1940; found 628.2086.

***tert* -Butyl -4-(4-(3,3-difluoro-3-(3-methoxyphenyl)-1-(phenylthio)propyl)phenyl)-piperazine-1-carboxylate (4i)**

General procedure A was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 µL, 1.8 mmol, 1.5 equiv.), *tert*-butyl 4-(4-vinylphenyl)piperazine-1-carboxylate (346 mg, 1.2 mmol, 1.0 equiv.) and *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded **4i** as a yellow oil (559 mg, 84% yield).

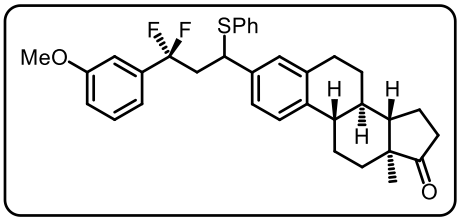


R_f = 0.30 (petroleum ether/ethyl acetate 5:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.25 (s, 1H), 7.22 (s, 5H), 7.10 (d, *J* = 7.3 Hz, 2H), 6.95 – 6.85 (m, 2H), 6.82 – 6.75 (m, 3H), 4.28 (d, *J* = 9.2 Hz, 1H), 3.77 (s, 3H), 3.57 (s, 4H), 3.11 (s, 4H), 2.92 – 2.78 (m, 1H), 2.78 – 2.65 (m, 1H), 1.49 (s, 9H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -90.98 – -92.49 (m, 1F), -93.95 – -95.17 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.7, 154.9, 150.5, 138.3 (t, *J* = 26.7 Hz), 134.6, 132.6, 131.9, 129.6, 129.0, 128.8, 127.5, 121.9 (t, *J* = 244.9 Hz), 117.4 (t, *J* = 6.0 Hz), 116.3, 115.8, 110.6 (t, *J* = 5.4 Hz), 80.0, 55.4, 49.3, 46.9, 44.8 (t, *J* = 26.6 Hz), 28.6. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{31}H_{36}F_2N_2O_3SNa^+$, 577.2307; found 577.2315.

Compound (4j)

General procedure A was used with thiophenol (184 µL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 µL, 1.8 mmol, 1.5 equiv.), **1n** (336 mg, 1.2 mmol, 1.0

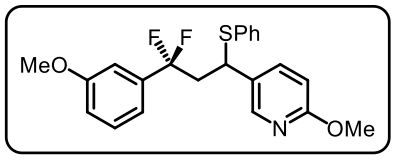
equiv.) and *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded **4j** with 1:1 d.r. as a white solid (531 mg, 81% yield).



The mixed isomers of 4j R_f = 0.10 (petroleum ether/ethyl acetate 10:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.24 (s, 6H), 7.18 – 7.12 (m, 1H), 7.03 – 6.96 (m, 1H), 6.92 – 6.83 (m, 3H), 6.76 (s, 1H), 4.29 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.75 (s, 3H), 2.94 – 2.85 (m, 1H), 2.85 – 2.78 (m, 2H), 2.78 – 2.67 (m, 1H), 2.51 (dd, *J* = 19.0, 8.7 Hz, 1H), 2.43 – 2.35 (m, 1H), 2.31 – 2.21 (m, 1H), 2.19 – 2.11 (m, 1H), 2.09 – 2.03 (m, 1H), 2.02 – 1.95 (m, 2H), 1.67 – 1.56 (m, 2H), 1.54 – 1.47 (m, 3H), 1.47 – 1.37 (m, 1H), 0.92 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.29 – -93.09 (m, 1F), -93.15 – -94.02 (m, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 220.9, 159.5, 139.0, 138.1 (t, *J* = 26.1 Hz), 137.6, 137.6, 136.5, 136.5, 134.7, 134.6, 132.3, 132.3, 129.5, 129.0, 128.4, 128.4, 127.5, 125.5, 125.4, 125.2, 125.1, 121.9 (t, *J* = 245.0 Hz), 117.3 (t, *J* = 6.1 Hz), 115.7, 110.4 (t, *J* = 6.5 Hz), 55.3, 50.6, 48.1, 46.8, 44.7 (t, *J* = 27.2 Hz), 44.6 (t, *J* = 27.3 Hz), 44.4, 38.1, 35.9, 31.7, 29.4, 26.6, 25.7, 21.7, 14.0. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{34}H_{36}F_2O_2SNa^+$, 569.2296; found 569.2305.

Compound (4k)

General procedure A was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 μL, 1.8 mmol, 1.5 equiv.), **1t** (162 mg, 1.2 mmol, 1.0 equiv.) and *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded **4k** as a colorless oil (395 mg, 82% yield).

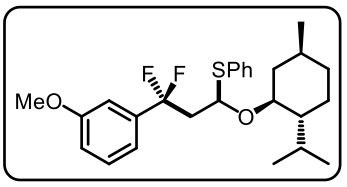


R_f = 0.30 (petroleum ether/ethyl acetate 10:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 1.7 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.29 – 7.26 (m, 1H), 7.22 (s, 5H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.79 (s, 1H), 6.62 (d, *J* = 8.6 Hz, 1H), 4.33 – 4.23 (m, 1H), 3.89 (s, 3H), 3.77 (s, 3H), 2.87 –

2.71 (m, 2H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -91.84 – -92.49 (m, 1F), -93.81 – -94.52 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.5, 159.7, 146.2, 137.9 (t, *J* = 25.9 Hz), 137.8, 133.5, 133.2, 129.8, 129.1, 128.9, 128.1, 121.8 (t, *J* = 245.2 Hz), 117.3 (t, *J* = 6.1 Hz), 115.8, 110.9, 110.6 (t, *J* = 6.2 Hz), 55.4, 53.6, 44.6, 44.5 (t, *J* = 27.2 Hz).

Compound (4l)

To a 20 mL oven dried screw-cap vial equipped with a magnetic stir bar was added *t*BuOLi (144 mg, 1.8 mmol, 1.5 equiv.) in dry DMA (18 mL), followed by thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (174 μL, 1.2 mmol, 1.0 equiv.) and **1u** (386 μL, 1.8 mmol, 1.5 equiv.) under a nitrogen atmosphere. The reaction mixture was stirred vigorously at room temperature and exposed to 30 W 365 nm LED for 2 hours. After reaction, purification by column chromatography on silica gel using petroleum ether and ethyl acetate (100:1 (v/v)) as eluent afforded **4l** as a colorless oil (224 mg, 50% yield).

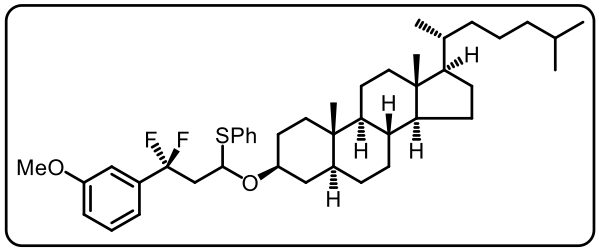


The mixed isomers of 4l R_f = 0.40 (petroleum ether/ethyl acetate 100:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 6.7 Hz, 2H), 7.32 – 7.26 (m, 4H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.96 – 6.90 (m, 2H), 5.18 (d, *J* = 5.8 Hz, 1H), 3.80 (s, 3H), 3.62 – 3.52 (m, 1H), 2.81 – 2.62 (m, 2H), 2.19 – 2.09 (m, 1H), 1.86 (d, *J* = 11.8 Hz, 1H), 1.60 (t, *J* = 12.9 Hz, 2H), 1.27 – 1.15 (m, 1H), 1.05 (t, *J* = 11.2 Hz, 1H), 1.00 – 0.89 (m, 1H), 0.86 (d, *J* = 5.3 Hz, 6H), 0.79 (d, *J* = 6.8 Hz, 3H), 0.78 – 0.75 (m, 1H), 0.67 – 0.55 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -90.65 – -91.43 (m, 1F), -94.29 – -95.16 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.6, 138.5 (t, *J* = 26.1 Hz), 133.8, 133.1, 129.5, 129.1, 127.6, 121.5 (t, *J* = 244.1 Hz), 117.7 (t, *J* = 6.1 Hz), 115.5, 110.9 (t, *J* = 5.9 Hz), 79.7, 75.6, 55.4, 48.1, 46.4 (t, *J* = 27.7 Hz), 38.8, 34.6, 31.5, 25.1, 23.1, 22.5, 21.3, 16.2.

Compound (4m)

To a 20 mL oven dried screw-cap vial equipped with a magnetic stir bar was added *t*BuOLi (144 mg, 1.8 mmol, 1.5 equiv.) in dry DMA (18 mL), followed by thiophenol

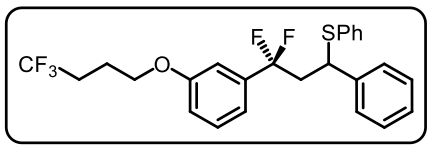
(184 μL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (174 μL, 1.2 mmol, 1.0 equiv.) and **1v** (746 mg, 1.8 mmol, 1.5 equiv.) under a nitrogen atmosphere. The reaction mixture was stirred vigorously at room temperature and exposed to 30 W 365 nm LED for 2 hours. After reaction, purification by column chromatography on silica gel using petroleum ether and ethyl acetate (100:1 (v/v)) as eluent afforded **4m** as a colorless oil (500 mg, 61% yield).



The mixed isomers of 4m R_f = 0.20 (petroleum ether/ethyl acetate 100:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.29 (s, 4H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.97 – 6.91 (m, 2H), 5.08 – 5.02 (m, 1H), 3.80 (s, 3H), 3.78 – 3.70 (m, 1H), 2.71 – 2.51 (m, 2Hz), 1.97 (d, *J* = 12.6 Hz, 1H), 1.86 – 1.73 (m, 2H), 1.75 – 1.59 (m, 3H), 1.61 – 1.38 (m, 5H), 1.40 – 1.29 (m, 5H), 1.29 – 1.18 (m, 5H), 1.18 – 1.05 (m, 6H), 1.05 – 0.94 (m, 4H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 2.5 Hz, 3H), 0.87 (d, *J* = 2.5 Hz, 3H), 0.77 (d, *J* = 4.9 Hz, 3H), 0.66 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -91.53 – -92.74 (m, 1F), -93.97 – -94.75 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.6, 138.6 (t, *J* = 26.4 Hz), 138.5 (t, *J* = 25.9 Hz), 134.3, 134.2, 132.3, 132.1, 129.6, 129.0, 128.0, 128.0, 121.5 (t, *J* = 244.5 Hz), 121.4 (t, *J* = 244.4 Hz), 117.7 (t, *J* = 5.7 Hz), 117.6 (t, *J* = 6.4 Hz), 115.5, 111.0 (t, *J* = 5.8 Hz), 79.9, 79.8, 76.5, 76.3, 56.6, 56.5, 55.4, 54.5, 54.4, 46.4 (t, *J* = 27.1 Hz), 46.3 (t, *J* = 27.4 Hz), 45.1, 44.8, 42.8, 40.2, 39.7, 37.2, 37.0, 36.3, 35.9, 35.8, 35.8, 35.7, 35.6, 35.5, 33.2, 32.3, 32.2, 29.0, 28.9, 28.3, 28.4, 28.2, 26.7, 24.4, 24.0, 23.0, 22.7, 21.4, 21.3, 18.8, 12.4, 12.3, 12.2.

Compound (4n)

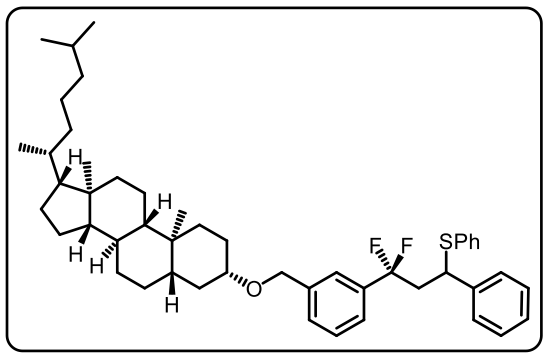
General procedure A was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), **2p** (290 mg, 1.8 mmol, 1.5 equiv.), styrene (138 μL, 1.2 mmol, 1.0 equiv.) and *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (100:1 (v/v)) as eluent afforded **4n** as a colorless oil (430 mg, 77% yield).



R_f = 0.40 (petroleum ether/ethyl acetate 100:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.20 (m, 7H), 7.20 – 7.16 (m, 3H), 6.95 – 6.87 (m, 2H), 6.81 (s, 1H), 4.33 (dd, *J* = 9.4, 4.1 Hz, 1H), 3.96 (t, *J* = 5.9 Hz, 2H), 2.96 – 2.83 (m, 1H), 2.83 – 2.70 (m, 1H), 2.38 – 2.24 (m, 2H), 2.09 – 1.99 (m, 2H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -66.27 (t, *J* = 10.7 Hz, 3F), -92.20 (ddd, *J* = 245.2, 18.0, 11.6 Hz, 1F), -94.11 – -94.69 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.7, 140.8, 138.3 (t, *J* = 26.3 Hz), 134.2, 132.9, 129.8, 129.0, 128.5, 128.0, 127.7, 127.5, 127.1 (q, *J* = 276.3 Hz), 121.8 (t, *J* = 244.9 Hz), 117.8 (t, *J* = 6.1 Hz), 116.1, 111.2 (t, *J* = 6.3 Hz), 66.2, 47.6, 44.9 (t, *J* = 27.2 Hz), 30.8 (q, *J* = 29.2 Hz), 22.3 (t, *J* = 2.9 Hz).

Compound (4o)

General procedure A was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), **2q** (984 mg, 1.8 mmol, 1.5 equiv.), styrene (138 μL, 1.2 mmol, 1.0 equiv.) and *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.). Purification by preparation of thin layer chromatography using petroleum ether and ethyl acetate (40:1 (v/v)) as eluent afforded **4o** with 1:1 d.r. as a colorless oil (284 mg, 32% yield).

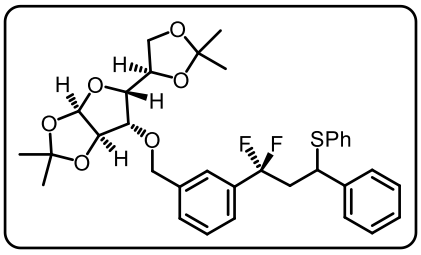


The mixed isomers of 4o R_f = 0.40 (petroleum ether/ethyl acetate 40:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 1H), 7.35 – 7.30 (m, 1H), 7.29 (s, 1H), 7.21 (s, 8H), 7.19 – 7.15 (m, 3H), 4.55 – 4.48 (m, 2H), 4.33 (dd, *J* = 8.7, 3.1 Hz, 1H), 3.37 – 3.26 (m, 1H), 2.94 – 2.82 (m, 1H), 2.82 – 2.70 (m, 1H), 1.97 (d, *J* = 12.3 Hz, 1H), 1.90 (d, *J* = 11.2 Hz, 1H), 1.85 – 1.76 (m, 1H), 1.74 (d, *J* = 12.8 Hz, 1H), 1.67 (s, 2H), 1.59 – 1.41 (m, 5H), 1.39 – 1.31 (m, 5H), 1.31 – 1.24 (m, 5H), 1.18 – 1.01 (m, 8H), 1.01 – 0.95 (m, 2H), 0.90 (d, *J* = 6.1 Hz, 3H), 0.87 (d, *J* = 4.6 Hz, 6H), 0.82 (s, 3H), 0.65 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -91.65 – -92.57 (m, 1F), -94.65 (ddd, *J* = 245.7, 35.3, 18.7 Hz, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.9,

139.9, 136.8 (t, J = 26.0 Hz), 134.2, 132.9, 129.0, 128.6, 128.5, 128.0, 127.7, 127.5, 124.1, 124.1, 124.1, 122.1 (t, J = 245.8 Hz), 78.6, 72.0, 69.5, 59.2, 56.7, 56.5, 54.6, 47.5, 45.0, 44.9 (t, J = 27.1 Hz), 42.8, 40.2, 39.7, 37.2, 36.3, 36.0, 35.9, 35.7, 35.0, 32.3, 29.0, 28.5, 28.4, 28.2, 24.4, 24.0, 23.0, 22.7, 21.4, 18.8, 12.5, 12.2. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{49}H_{66}F_2OSNa^+$, 763.4695; found 763.4717.

Compound (4p)

General procedure A was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), **2n** (1.8 mmol, 753 mg, 1.5 equiv.), styrene (138 μL, 1.2 mmol, 1.0 equiv.) and *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.). Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded **4p** with 1:1 d.r. as a colorless oil (485 mg, 66% yield).

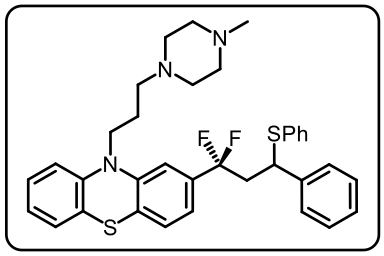


The mixed isomers of 4p R_f = 0.30 (petroleum ether/ethyl acetate 10:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 1H), 7.35 – 7.30 (m, 1H), 7.28 (s, 1H), 7.26 – 7.19 (m, 8H), 7.19 – 7.14 (m, 3H), 5.93 – 5.83 (m, 1H), 4.68 – 4.60 (m, 2H), 4.60 – 4.57 (m, 1H), 4.38 – 4.26 (m, 2H), 4.15 – 4.08 (m, 2H), 4.05 – 3.97 (m, 2H), 3.06 – 2.62 (m, 2H), 1.50 (s, 3H), 1.42 (d, J = 2.8 Hz, 3H), 1.35 (s, 3H), 1.32 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -92.24 – -93.10 (m, 1F), -93.61 – -94.39 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.5, 136.7, 133.9, 132.2, 129.9, 129.4, 129.2, 129.0, 128.8, 128.5, 124.5 (t, J = 5.6 Hz), 124.1 (t, J = 6.1 Hz), 121.6 (t, J = 245.2 Hz), 112.0, 109.3, 109.3, 105.5, 82.8, 82.2, 81.5, 72.5, 72.0, 72.0, 67.7, 66.8, 37.3 (t, J = 26.7 Hz), 27.0, 26.4, 25.5. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{34}H_{38}F_2O_6SNa^+$, 635.2249; found 635.2252.

Compound (4q)

General procedure A was used with thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), **2r** (733 mg, 1.8 mmol, 1.5 equiv.), styrene (138 μL, 1.2 mmol, 1.0 equiv.) and *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.). Purification by column chromatography on silica gel using

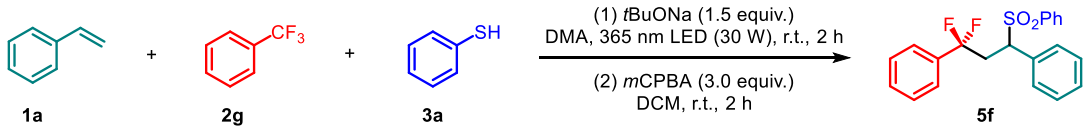
petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded **4q** as a white solid (296 mg, 41% yield).



R_f = 0.40 (petroleum ether/ethyl acetate 10:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.22 – 7.09 (m, 12H), 7.07 (d, *J* = 7.9 Hz, 1H), 6.96 – 6.92 (m, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 6.72 (s, 1H), 4.27 (dd, *J* = 9.4, 4.0 Hz, 1H), 3.83 (t, *J* = 6.8 Hz, 2H), 2.91 – 2.80 (m, 1H), 2.79 – 2.68 (m, 1H), 2.68 – 1.92 (m, 13H), 1.92 – 1.83 (m, 2H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -91.50 – -92.13 (m, 1F), -92.90 – -93.53 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 145.6, 144.8, 140.7, 134.1, 133.0, 129.0, 128.5, 128.0, 127.8, 127.6, 127.6, 127.5, 127.5, 127.3, 124.6, 123.0, 119.3 (t, *J* = 398.3 Hz), 116.0, 112.1 (t, *J* = 6.1 Hz), 55.7, 55.3, 53.5, 47.7, 46.2, 45.5, 44.9 (t, *J* = 27.6 Hz), 24.4. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{35}H_{37}F_2N_3S_2H^+$, 601.2470; found 602.2477.

5 Synthetic Applications

5.1 Gram-scale Reaction

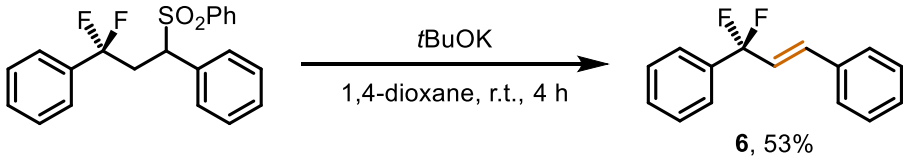


To a 250 mL oven dried screw-cap vial equipped with a magnetic stir bar was added *t*BuONa (1.44 g, 15 mmol, 1.5 equiv.) in dry DMA (100 mL), followed by thiophenol (1.5 mL, 15 mmol, 1.5 equiv.), benzotrifluoride (1.8 mL, 15 mmol, 1.5 equiv.) and styrene (1.1 mL, 10 mmol, 1.0 equiv.) under a nitrogen atmosphere. The reaction mixture was stirred vigorously at room temperature and exposed to 30 W 365 nm LED for 2 hours. After the completion of the reaction, the resulting reaction mixture was concentrated *in vacuo* yielding the crude product which was used in the next step without further purification. Next, a 500 mL round bottomed flask charged with crude

product in DCM (200 mL) was added 85 wt% 3-chloroperoxybenzoic acid (6.1 g, 30 mmol, 3.0 equiv.). The reaction mixture was stirred for 4 hours at room temperature. After the completion of the reaction, the reaction was diluted with dichloromethane (100 mL) and extracted with saturated sodium bicarbonate solution (60 mL) until the solution was neutral, and water (2 x 60 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed *in vacuo*. Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded **5f** as a white solid (3.39 g, 91% yield).

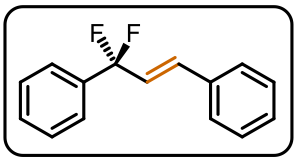
5.2 Product Derivatizations

(*E*)-(3,3-Difluoroprop-1-ene-1,3-diyl)dibenzene (6)



6, 53%

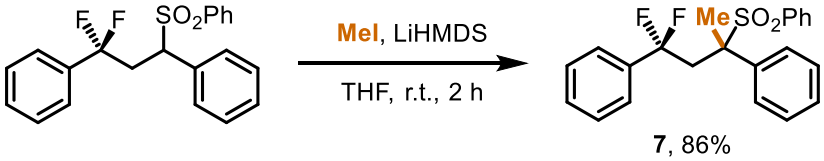
In a N_2 glovebox, to (1,1-difluoro-3-(phenylsulfonyl)propane-1,3-diyl)dibenzene (**5f**) (112 mg, 0.30 mmol, 1.0 equiv.) in 1,4-dioxane (3 mL) was added *t*BuOK (51 mg, 0.45 mmol, 1.5 equiv.). The reaction mixture was stirred at room temperature for 4 hours. The reaction was quenched by H_2O (4 mL) and extracted by diethyl ether (3 x 5 mL). The combined organic phase was dried over anhydrous sodium sulfate, filtered, and the solvent was removed *in vacuo*. Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (100:1 (v/v)) as eluent afforded **6** as a a colorless liquid (36.6 mg, 53% yield).



R_f =0.5 (petroleum ether). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 2H), 7.49 – 7.44 (m, 3H), 7.42 (d, J = 7.4 Hz, 2H), 7.39 – 7.29 (m, 3H), 6.84 (d, J = 16.1 Hz, 1H), 6.51 – 6.41 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -90.72 (d, J = 9.6 Hz, 2F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.9, 145.2, 138.3, 135.0, 133.0, 130.7, 129.1,

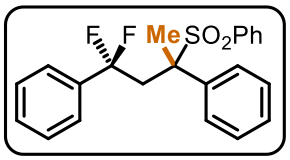
128.8, 128.7, 128.6, 122.3. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{15}H_{12}F_2Na^+$, 253.0799; found 253.0800.

(1,1-Difluoro-3-(phenylsulfonyl)butane-1,3-diyl)dibenzene (7)



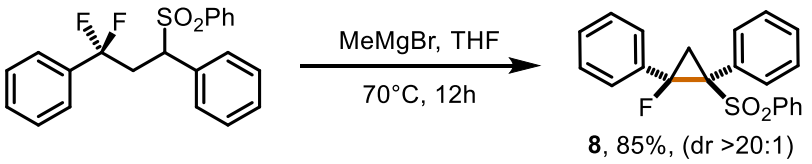
7, 86%

To a 25 mL oven dried round bottomed flask equipped with a magnetic stir bar was added (1,1-difluoro-3-(phenylsulfonyl)propane-1,3-diyl)dibenzene (**5f**) (372 mg, 1 mmol, 1.0 equiv.) in dry THF (10 mL) under a nitrogen atomsphere and cooled to 0 °C, then LiHMDS (1.00 M in THF, 2.0 mL) was added dropwise. After 15 minutes, a solution of methyl iodide (187 µL, 3 mmol, 3.0 equiv.) in dry THF (2 mL) was added. The mixture was stirred at room temperature for 2 hours. The reaction was quenched by saturated aqueous NH_4Cl (10 mL) and extracted by EtOAc (3 x 10 mL). The combined organic phase was dried over anhydrous sodium sulfate, filtered, and the solvent was removed *in vacuo*. Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded **7** as a white solid (322 mg, 86% yield).



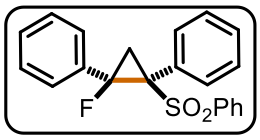
R_f =0.2 (petroleum ether/EtOAc 10:1 (v/v). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 6.5 Hz, 1H), 7.34 (s, 5H), 7.31 (d, *J* = 7.2 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 3H), 7.24 – 7.15 (m, 4H), 3.62 – 3.52 (m, 1H), 3.20 – 3.09 (m, 1H), 1.93 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -87.62 (ddd, *J* = 243.8, 26.2, 9.4 Hz, 1F), -94.07 (ddd, *J* = 243.7, 22.0, 6.2 Hz, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.0 (t, *J* = 25.9 Hz), 134.9, 134.0, 133.7, 130.7, 130.0, 128.7, 128.6, 128.6, 128.3, 127.9, 124.7 (t, *J* = 6.3 Hz), 122.3 (t, *J* = 249.3 Hz), 68.3, 41.2 (t, *J* = 26.5 Hz), 19.7. **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{22}H_{20}F_2O_2SNa^+$, 409.1044; found 409.1051.

((1*R*,2*S*)-1-Fluoro-2-(phenylsulfonyl)cyclopropane-1,2-diyl)dibenzene (8)



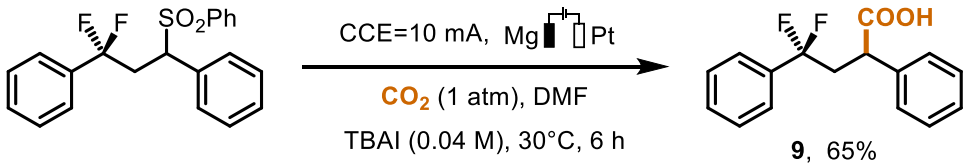
8, 85%, (dr >20:1)

To a 10 mL Schlenk tube with a magnetic stir bar was added (1,1-difluoro-3-(phenylsulfonyl)propane-1,3-diyl)dibenzene (**5f**) (224 mg, 0.6 mmol, 1.0 equiv.), THF (4 mL) and methyl magnesium bromide (358 mg, 3 mmol, 5.0 equiv.) under a nitrogen atmosphere. The reaction mixture was stirred at 70℃ for 12 hours. Upon cooling at room temperature, the reaction was quenched with H_2O (5 mL) and extracted with Et_2O (3 x 5 mL). The combined organic phase was dried over anhydrous sodium sulfate, filtered, and the solvent was removed *in vacuo*. Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 (v/v)) as eluent afforded **8** as a white solid (180 mg, 85% yield).



R_f =0.3 (petroleum ether/EtOAc 10:1 (v/v). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (s, 2H), 7.48 (s, 4H), 7.32 (s, 2H), 7.28 – 7.19 (m, 5H), 7.11 (d, J = 7.2 Hz, 2H), 2.98 – 2.88 (m, 1H), 2.20 – 2.08 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -143.26 – -143.40 (m, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 137.9, 133.6, 130.6, 130.1, 130.1, 129.8, 129.8, 129.3, 129.2, 128.4, 128.3, 83.5 (d, J = 226.4 Hz), 56.7 (d, J = 15.7 Hz), 29.9, 22.0 (d, J = 10.6 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{21}H_{17}FO_2SNa^+$, 375.0825; found 375.0830.

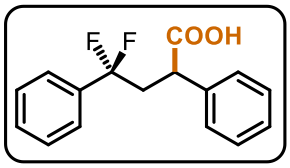
4,4-Difluoro-2,4-diphenylbutanoic acid (9)



9, 65%

To an undivided cell equipped with a magnesium anode (1 cm x 1 cm) and a platinum cathode (1 cm x 1 cm) were added a stirring bar, TBAI (443 mg, 1.2 mmol, 1.2 equiv.) and (1,1-difluoro-3-(phenylsulfonyl)propane-1,3-diyl)dibenzene (**5f**) (372 mg, 1 mmol, 1.0 equiv.). All of the starting materials were dissolved in anhydrous DMF (12.5 mL) under a CO_2 atmosphere. The reaction mixture under 10 mA of constant current was

applied for 6 hours at 30 °C. During the electrolysis, CO_2 was supplied by a balloon. After electrolysis, the reaction mixture was acidified with 1 M HCl (40 mL) and extracted with brine (2 x 40 mL). The aqueous phase was extracted with EtOAc (60 mL). The combined organic phase was dried over anhydrous sodium sulfate, filtered, and the solvent was removed *in vacuo*. Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1 (v/v)) as eluent afforded **9** as a white solid (179 mg, 65% yield).



R_f =0.3 (petroleum ether/EtOAc 5:1 (v/v). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 6.2 Hz, 2H), 7.42 – 7.34 (m, 3H), 7.30 (dd, *J* = 20.5, 15.4 Hz, 5H), 3.95 (d, *J* = 6.6 Hz, 1H), 3.17 (td, *J* = 23.9, 13.8 Hz, 1H), 2.66 – 2.35 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -95.74 (ddd, *J* = 246.3, 19.8, 12.7 Hz, 1F), -96.38 (ddd, *J* = 246.4, 19.7, 12.2 Hz, 1F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 178.4, 137.8, 136.7 (t, *J* = 26.2 Hz), 130.2, 129.1, 128.6, 128.0, 127.9, 125.1 (t, *J* = 6.0 Hz), 122.0 (t, *J* = 243.6 Hz), 45.7, 42.6 (t, *J* = 27.6 Hz). **HRMS (ESI)** (m/z): $[M+Na]^+$ calcd for $C_{16}H_{14}F_2O_2Na^+$, 299.0854; found 299.0856.

6 Mechanistic Studies

6.1 UV-Vis Absorption Spectroscopic Measurements

UV-Vis absorption spectra were measured in a 1 cm quartz cuvette using a UV-2600i spectrophotometer. The association constant for three components was determined by UV-Vis measurements in DMA. The absorbance of a constant concentration of **3a** (0.15 M) with *t*BuONa (0.15 M), and an increasing volume of **1a** or **2a** was recorded. The absorption spectra shown in Figures S6 and S7.

2.0 mL **3a** anion solution (freshly prepared in situ by the deprotonation of **3a** with *t*BuONa) in cuvettes were added **1a** (0 μL, 2.30 μL, 4.30 μL and 8.30 μL) and to prepare four samples. The results were depicted as follows:

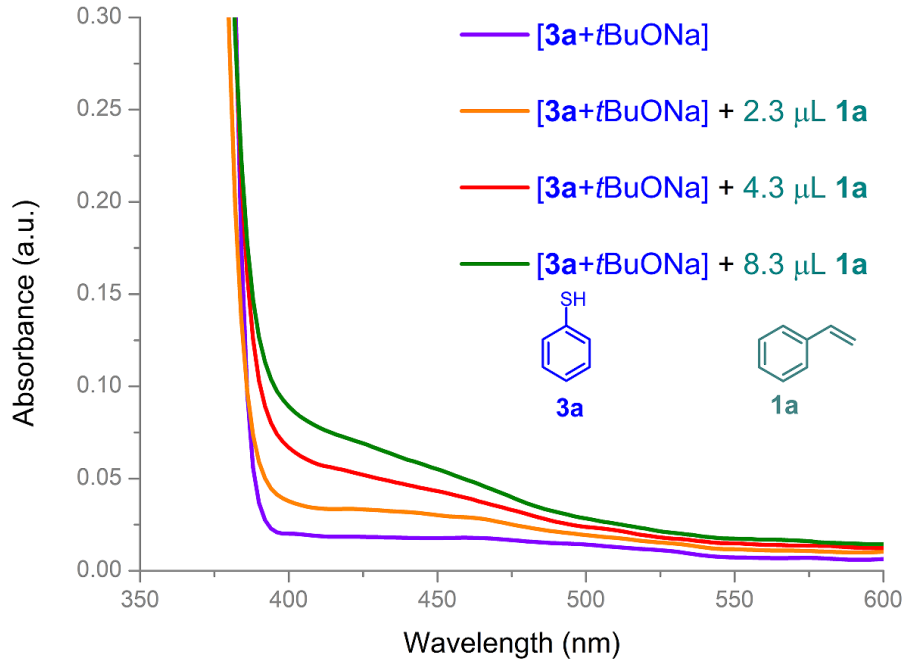


Figure S6. UV-Vis absorption spectra of **3a** (0.15 M in DMA) and *t*BuONa (0.15 M in DMA) in combination with increasing concentration of **1a**.

2.0 mL **3a** anion solution (freshly prepared in situ by the deprotonation of **3a** with *t*BuONa) in cuvettes were added **2a** (0 μL, 4.40 μL, 6.40 μL and 14.4 μL) and to prepare four samples. The results were depicted as follows:

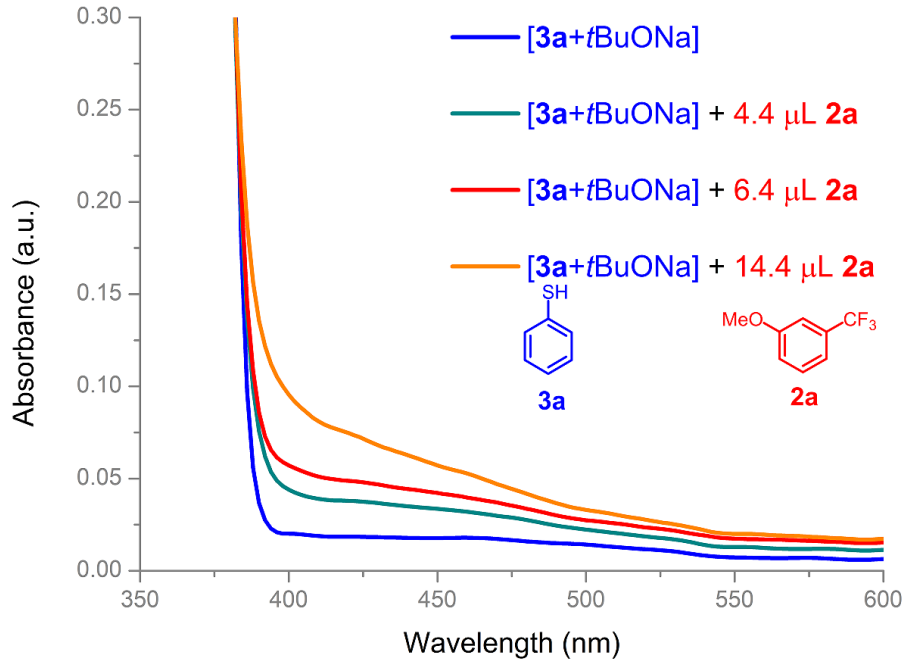


Figure S7. UV-Vis absorption spectra of **3a** (0.15 M in DMA) and *t*BuONa (0.15 M in DMA) in combination with increasing concentration of **2a**.

6.2 ^{19}F NMR Titration Experiments

^{19}F NMR titrations were performed by the preparation of the mixture of **1p**, **3a** and *t*BuONa and the mixture of **2a**, **3a** and *t*BuONa, respectively. (Trifluoromethoxy)benzene was used as an internal standard. The total volume of the mixture was 1.0 mL, and the amount of **1p** or **2a** was kept constant at 0.15 mmol (0.15 M), while the amount of **3a** anion (freshly prepared *in situ* by the deprotonation of **3a** with *t*BuONa) was varied from 0 to 0.75 mmol (0~0.75 M). The addition of **3a** anion to the solution of **1p** resulted in a further upfield shift (Figure S8). Similar upfield shift occurs when proportionable **3a** anion was added into the solution of **2a** (Figure S9).

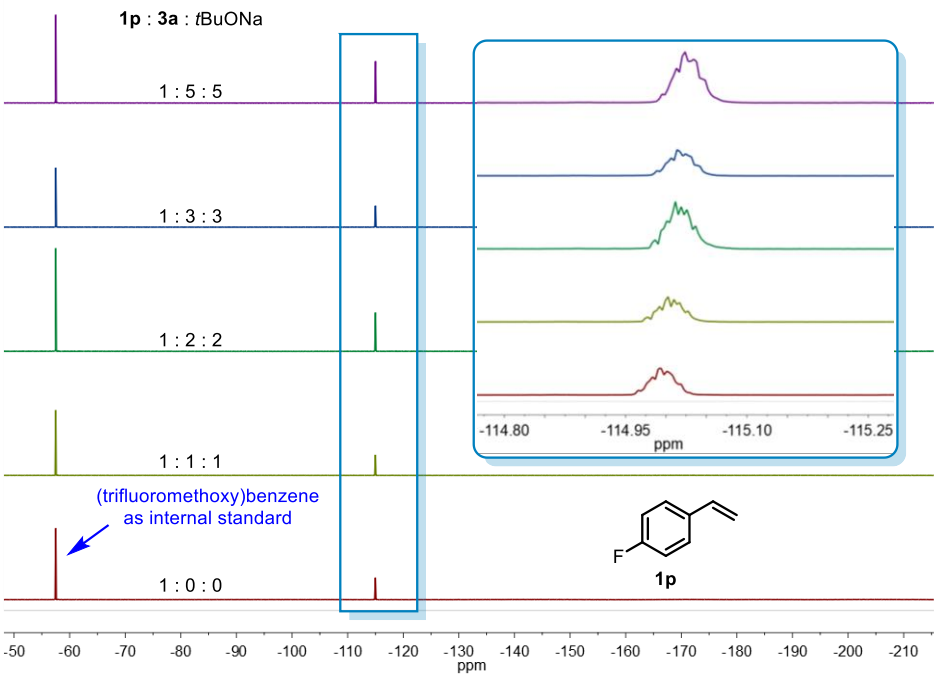


Figure S8. ^{19}F NMR spectrum of **1x** with adding **3a** anion (565 MHz, $CDCl_3$).

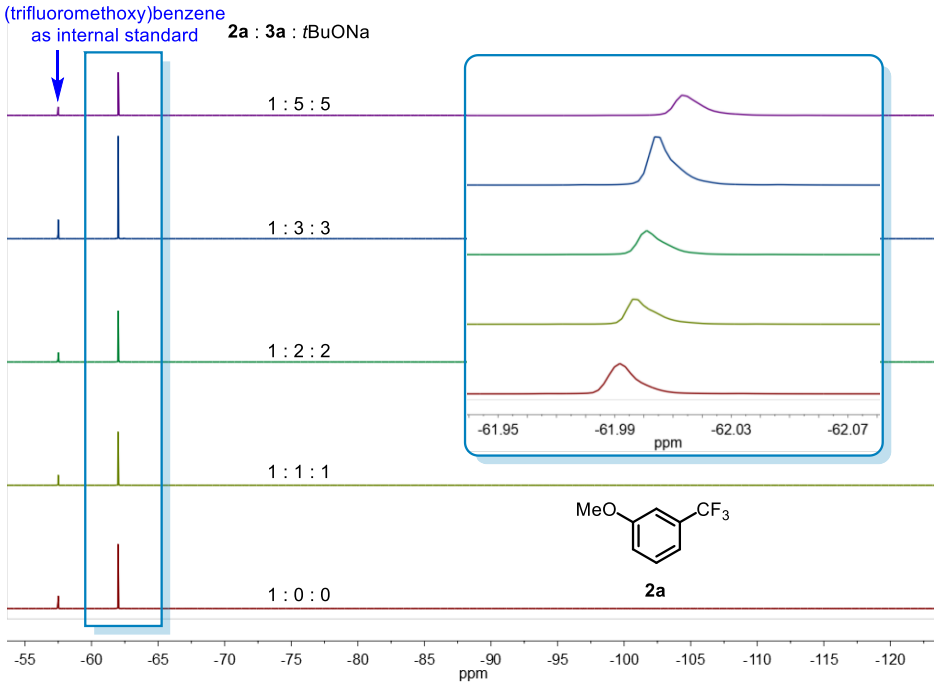


Figure S9. ^{19}F NMR spectrum of **2a** with adding **3a** anion (565 MHz, $CDCl_3$).

6.3 Stern-Volmer Quenching Experiment

Stern-Volmer fluorescence quenching experiments were collected on a HITACHI F-7000 spectrofluorometer at 25 °C. Parameters: data interval = 0.2 nm, scan rate = 1200 nm/min, Averaging time = 0.5 sec. The samples were measured in N-buliv quartz

cuvettes (chamber volume = 3.50 mL, H×W×D = 45.0 mm × 12.5 mm × 12.5 mm). The excitation wavelength was fixed at 375 nm, the emission light was acquired from 400 nm to 600 nm. Preparing solution of **3a** anion (0.15 M, freshly prepared in situ by the deprotonation of **3a** with *t*BuONa) with dry DMA, solution of **1a** (1.70 mg in volumetric flask of 5 mL with dry DMA, 3.2 mM) and solution of **2a** (3.0 mg in volumetric flask of 5 mL with dry DMA, 3.4 mM).

2.0 mL **3a** anion solution in cuvettes were added **1a** solution (0 μL, 4.0 μL, 6.0 μL, 9.0 μL, 10.0 μL) and to prepare five samples **3a** anion, **3a** anion+**1a** (8.5 μM), **3a** anion+**1a** (17.0 μM), **3a** anion+**1a** (25.5 μM), **3a** anion+**1a** (34.0 μM). The results were depicted as follows:

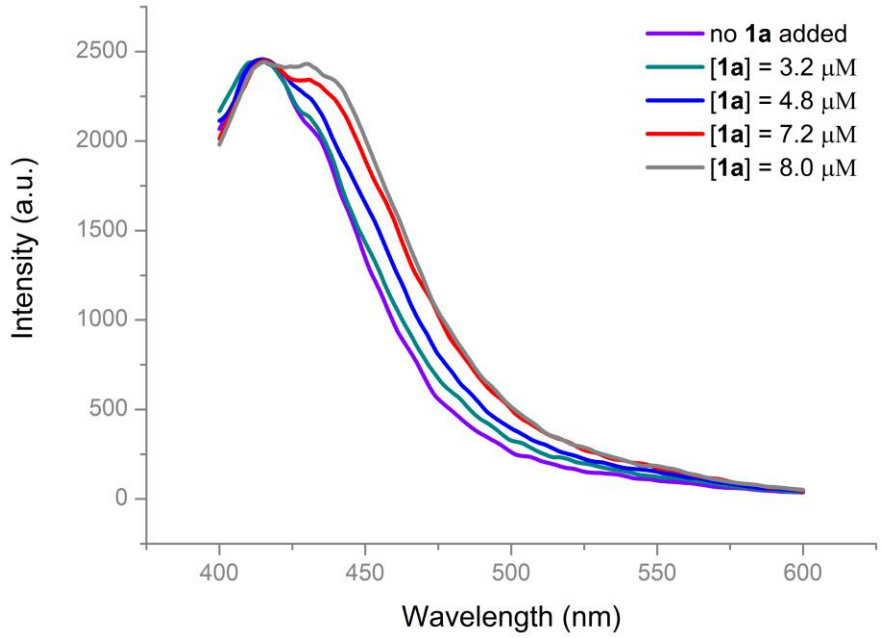


Figure S10. Quenching of the **3a** anion emission (0.15 M in DMA) in the presence of increasing amounts of **1a**.

2.0 mL **3a** anion solution in cuvettes were added **2a** solution (0 μL, 5.0 μL, 10.0 μL, 15.0 μL, 20.0 μL) and to prepare five samples **3a** anion, **3a** anion+**2a** (8.5 μM), **3a** anion+**2a** (17.0 μM), **3a** anion+**2a** (25.5 μM), **3a** anion+**2a** (34.0 μM). The results were depicted as follows:

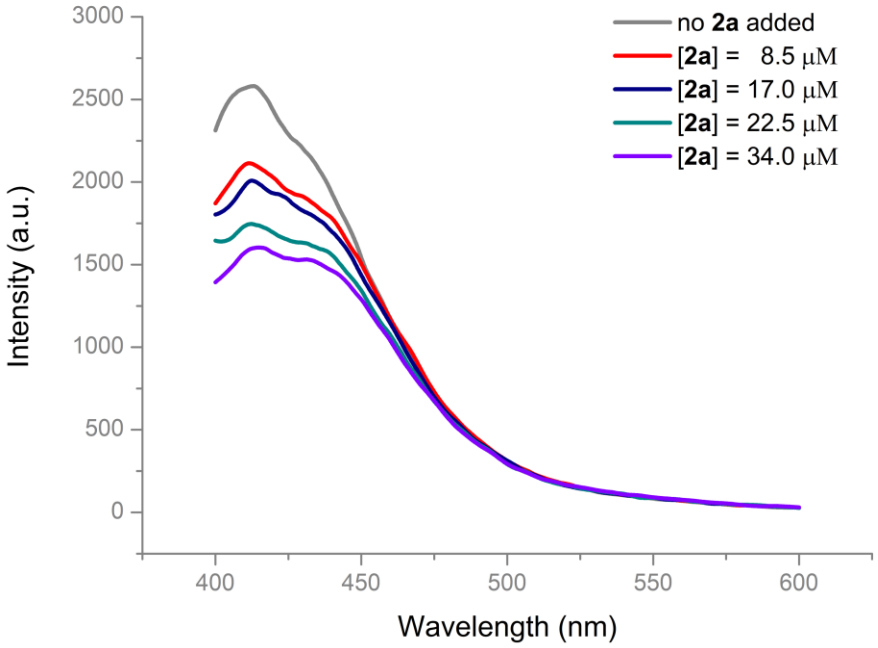


Figure S11. Quenching of the **3a** anion emission (0.15 M in DMA) in the presence of increasing amounts of **2a**.

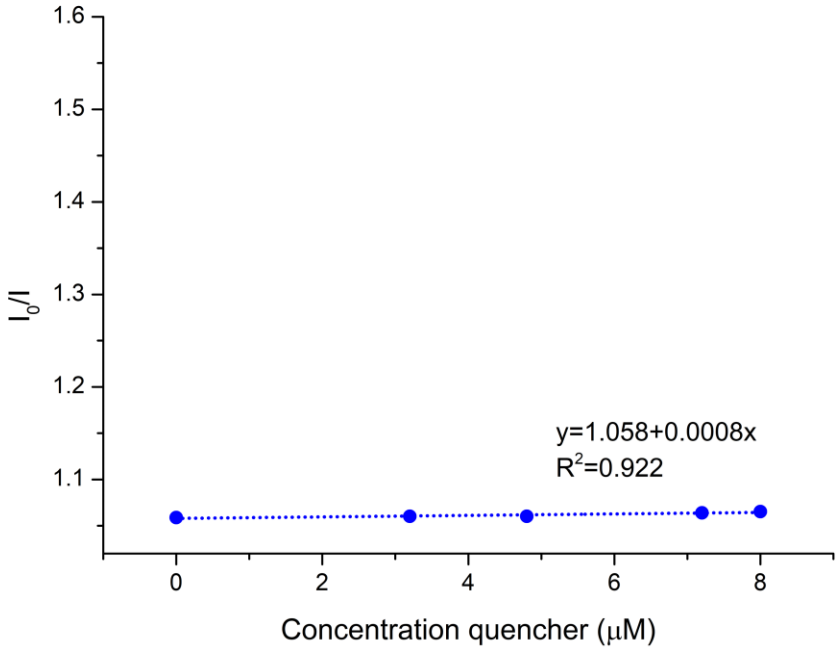


Figure S12. Stern-Volmer quenching plot of substrate **1a**.

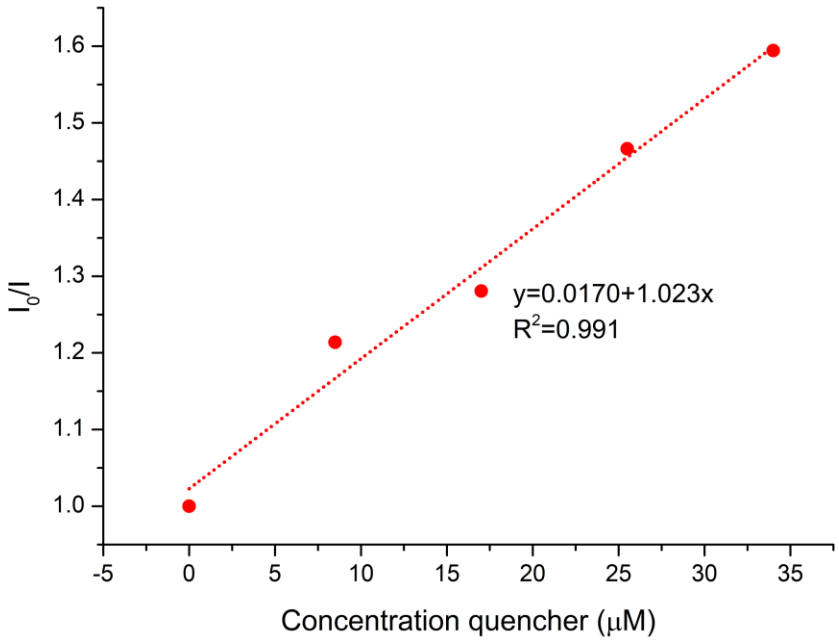


Figure S13. Stern-Volmer quenching plot of substrate **2a**.

6.4 Light On/Off Experiment

Several standard reactions according to General Procedure A were parallelly set up on a 0.20 mmol scale and irradiated with 2 x 30 W (365 nm) LEDs at a distance of 4 cm and/or in the absence of light. Every ten minutes, one reaction was worked up and analyzed by ^{19}F NMR to determine the yield of the corresponding product using trifluoromethoxy)benzene as an internal standard (Figure S14). The corresponding results revealed that light is a necessary component of the reaction.

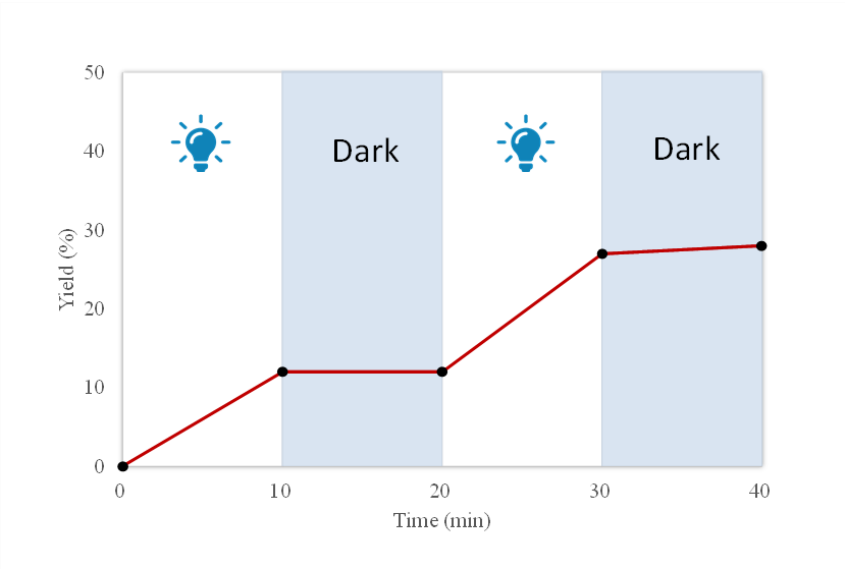


Figure S14. Line chart of light On/Off experiment.

6.5 DFT Calculations

Computational details

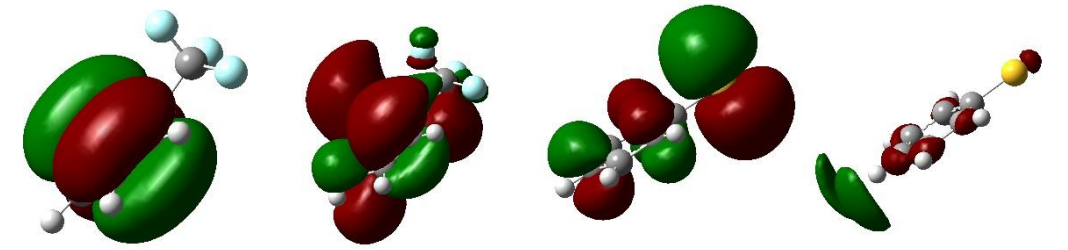
All geometry optimizations were performed with the Gaussian 16 at the M06-2X level of theory. Harmonic vibrational frequency calculations were performed for all of the stationary points to confirm them as a local minima or transition structures. The solvent effects were considered by an SMD solvation model in *N, N*-dimethylacetamide solvent. All Gibbs energies reported throughout the text are in kcal mol^{-1}.

The molecular orbital diagram was conducted at M06-2X-D3 level of theory in *N, N*-dimethylacetamide solvent.

DFT calculations of EDA between $PhCF_3$ and PhS^- (or styrene and PhS^-)

DFT calculations are preformed to illuminate the formation of EDA II ($PhCF_3$ and PhS^-) or EDA III (styrene and PhS^-). The energy gap of benzotrifluoride (**2g**) between HOMO (-8.6 eV) and LUMO (0.2 eV) was calculated to be 8.8 eV. The energy gap of thiophenol (**3a**) anion between HOMO (-5.3 eV) and LUMO (0.4 eV) was calculated to be 5.7 eV. The energy gap of stryene (**1a**) between HOMO (-7.7 eV) and LUMO (0.4 eV) was calculated to be 8.1 eV. The high energy gap led to the difficulty in absorbing the visible light for these three compounds. By comparison, the EDA II between **2g** and **3a** anion displayed a reduced HOMO-LUMO gap with 5.1 eV (HOMO

-5.0 eV, LUMO -0.1 eV). The reduced HOMO-LUMO gap might arise from the electron donation from HOMO of **3a** anion to the LUMO of **2g**. Since **1a** may also interact with **3a** anion, the possibility of the formation of EDA III between **1a** and **3a** anion was also calculated. A reduced HOMO-LUMO gap was obtained with 4.9 eV (HOMO -5.1 eV, LUMO -0.2 eV. Consequently, both of the reduced HOMO-LUMO gaps suggest the formation of EDA II complex and EDA III complex, which is consistent with the experiment data (see Figure S15 and Figure S16).

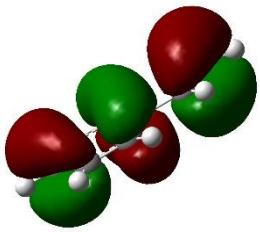


HOMO (-8.6 eV) **2g**

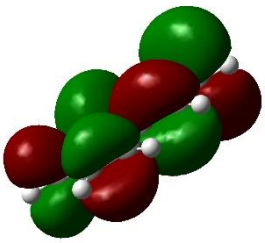
LUMO (-0.2 eV) **2g**

HOMO (-5.3 eV) **3a** anion

LUMO (0.4 eV) **3a** anion

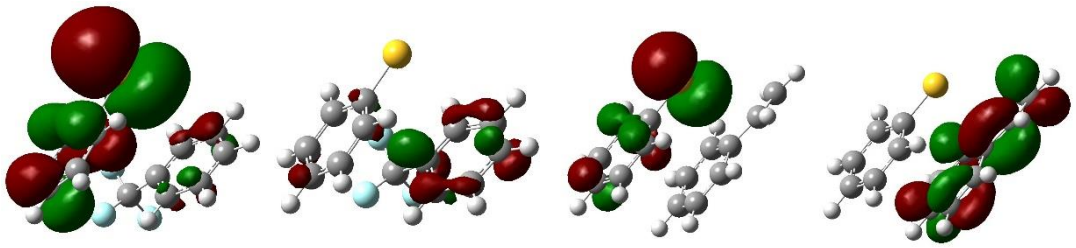


HOMO (-7.7 eV) **1a**



LUMO (0.4 eV) **1a**

Figure S15: The HOMO and LUMO energy of **2g**, **3a** anion and **1a**.



HOMO (-5.1 eV) **EDA II**

LUMO (-0.2 eV) **EDA II**

HOMO (-5.0 eV) **EDA III**

LUMO (-0.1 eV) **EDA III**

Figure S16: The HOMO and LUMO energy possible EDA.

DFT calculations of Gibbs free energy

As shown in Scheme 5e, **1a**, **3a** anion were used as model substrate. Thermodynamically, the relationship between EDA II and EDA III in the system is studied by Gibbs free energy.

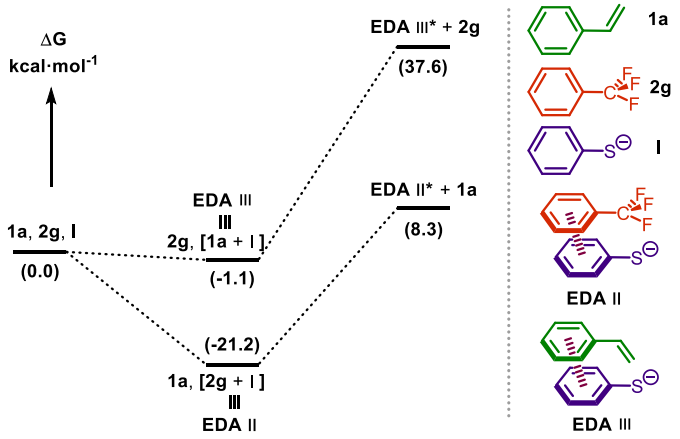


Figure 17. Computed relative free energies for complex EDA II and EDA III.

DFT calculation Electronic Energy, Gibbs free energy, and frequencies (Table S7)

Compounds	*Electronic Energy (EE)*[a]	*Gibbs free energy*[b]	*IF*[c]
1a	-309.625052685	-309.522161	-
2g	-529.095377161	-529.014179	-
I	-575.269278777	-575.202542	-
EDA II	-1104.41976420	-1104.250567	-
EDA III	-884.914665882	-884.726454	-
EDA II*	-1104.36857578	-1104.203487	-
EDA III*	*-884.851079067*	*-884.664784*	-

[a]The electronic energy calculated by M06-2X-D3 in solvent. [b]The Gibbs energy calculated by M06-2X-D3 in solvent. [c]The M06-2X-D3 calculated imaginary frequencies for the transition states.

Geometries for all the optimized compounds

1a

C	-2.25012700	0.26504100	0.00000000
C	-1.34820400	1.32540400	0.00000000
C	0.01618500	1.08484600	0.00000000
C	0.50925700	-0.22394600	0.00000000
C	-0.40608400	-1.27819700	0.00000000
C	-1.77406100	-1.03868300	0.00000000
H	-3.31570700	0.45733300	0.00000000
H	-1.71272100	2.34526000	0.00000000
H	0.70232000	1.92278500	0.00000100
H	-0.03584600	-2.29719900	0.00000000
H	-2.46659900	-1.87129800	-0.00000100
C	1.94902000	-0.53572700	0.00000000
H	2.18301700	-1.59681600	0.00000200
C	2.95029200	0.33950400	-0.00000100
H	3.97813600	-0.00090200	0.00000000
H	2.78974000	1.41138400	-0.00000200

2g

C	0.03022600	-0.00004400	-0.14718600
C	-0.65614400	-1.19230800	-0.07055100
C	-2.03695000	-1.19965500	-0.00559100
C	-2.73257100	-0.00001200	0.03416600
C	-2.03678900	1.19972500	-0.00564500
C	-0.65611400	1.19241400	-0.07052600
H	-0.11820200	-2.12787100	-0.12212500
H	-3.81400900	0.00011200	0.08854600
H	-2.57573400	2.13815200	0.02902900
C	1.44372400	-0.00004000	0.01053600
F	1.90019200	1.04133700	-0.54226100
F	1.65182700	-0.00032700	1.26582800
F	1.90013300	-1.04107000	-0.54284900
H	-0.11807500	2.12789400	-0.12220300
H	-2.57564000	-2.13822000	0.02907400

3a anion

C	1.56586200	1.19118100	0.00006000
C	0.17926600	1.17546000	-0.00042300
C	-0.59439000	-0.00002600	-0.00034500
C	0.17924200	-1.17549200	-0.00023100
C	1.56591800	-1.19113200	-0.00000300
C	2.27924500	-0.00000500	00024200
H	2.08947900	2.14075800	0.00038700
H	-0.33432400	2.12956800	-0.00032100
H	-0.33422000	-2.12966100	-0.00049300
H	2.08944600	-2.14076200	0.00014000
H	3.36208800	0.00005700	0.00085300
S	-2.37020800	0.00000800	0.00022700

EDA II

C	2.73662200	0.51796800	1.28406600
C	2.14548300	-0.62794700	1.80160200
C	1.47451900	-1.50662500	0.96832200
C	1.30511400	-1.27085800	-0.40458500
C	1.96203100	-0.13666600	-0.89497300
C	2.67588100	0.72341800	-0.08565300
H	3.30055300	1.18766000	1.92133700
H	2.22638300	-0.85451200	2.85885100
H	1.02594100	-2.39192300	1.40352500
H	1.94850400	0.03124700	-1.96026100
H	3.08166200	1.63442700	-0.51034200
C	-1.09234500	0.61177800	0.02269900
C	-1.94862700	-0.08594000	-0.80023600
C	-2.82875800	-1.01047700	-0.27195200
C	-2.89043300	-1.19749200	1.10119900
C	-2.04830500	-0.46886700	1.93130400
C	-1.18113200	0.46027600	1.38747700
H	-1.89729300	0.05894500	-1.86984100

H -3.58234300 -1.91442700 1.52575900
H -2.09294600 -0.61041500 3.00397600
S 0.44754900 -2.41339800 -1.45398600
C -0.40936500 1.74425800 -0.50123900
F 0.52676400 2.07105000 0.28674900
F 0.03035300 1.42563900 -1.64576000
F -1.28230000 2.66696300 -0.58080500
H -0.54799700 1.04439600 2.03955400
H -3.50070800 -1.56086100 -0.91862500

EDA III

C -0.12960000 -2.57645800 -0.13121000
C -1.04605600 -2.31457800 0.88234400
C -1.93299100 -1.25410800 0.76961800
C -1.91864700 -0.42802500 -0.35780100
C -0.96196100 -0.67191200 -1.34391300
C -0.07987500 -1.73857700 -1.23772700
H 0.55969000 -3.40715900 -0.04273100
H -1.07595300 -2.94628100 1.76182800
H -2.64147400 -1.06791000 1.56781100
H -0.90138100 -0.00005600 -2.19321000
H 0.64571100 -1.91687100 -2.02234600
C -2.88957500 0.65997200 -0.56294800
H -2.67692000 1.30296700 -1.41147500
C -3.99529200 0.87434900 0.14563200
H -4.65970700 1.69271100 -0.10262700
H -4.27579500 0.25586100 0.99058300
C 3.04663700 0.24283000 -0.97526000
C 2.03400300 1.18259100 -0.86772400
C 1.18869700 1.28262600 0.25516300
C 1.50069800 0.38881300 1.29300700
C 2.50334000 -0.56502800 1.20176400
C 3.29423100 -0.64722700 0.06300900
H 3.65003300 0.20565000 -1.87573200
H 1.87352900 1.86068900 -1.69743300
H 0.90637600 0.42066100 2.19850400
H 2.67720700 -1.24047900 2.03237100
H 4.08126300 -1.38696300 -0.01546400
S -0.11526400 2.47597400 0.37538800

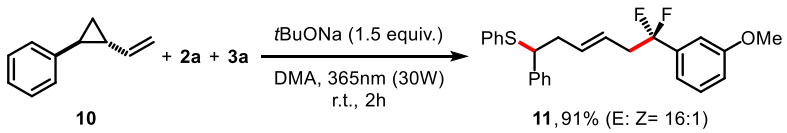
EDA II*

C 3.80477200 -0.17902600 0.57485600
C 3.07717700 -1.37518200 0.75918600
C 1.93170700 -1.61880300 0.04805900
C 1.36306500 -0.63523900 -0.81915600
C 2.21280000 0.46592900 -1.13855100
C 3.33711700 0.72696600 -0.40851300
H 4.70933700 0.01829000 1.13459800
H 3.44528600 -2.12775400 1.45014600
H 1.38001200 -2.53340600 0.23527200
H 1.90459500 1.16650700 -1.90242200
H 3.94309700 1.59566600 -0.64720900
C -1.11084700 0.13183500 0.01940700
C -2.23218300 0.83324900 -0.60973000
C -3.44417100 0.24232600 -0.68186400
C -3.72520600 -0.93907800 0.05379600
C -2.73189200 -1.46179900 0.90672600
C -1.50448100 -0.88995600 0.99708200
H -2.01249700 1.78611300 -1.06693900
H -4.69426700 -1.41295000 -0.02227800
H -2.98222200 -2.31086600 1.53101300
S -0.23611200 -0.71899300 -1.42282200
C -0.25761300 1.11258000 0.58240300
F 0.67228400 0.51398500 1.19298400
F 0.16741100 1.84586400 -0.35794300
F -0.97738900 1.79725100 1.37927400
H -0.75420800 -1.27917000 1.67101900
H -4.24355900 0.70473200 -1.24908900

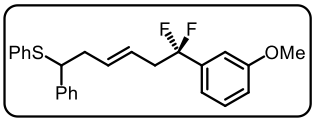
EDA III*

C	-0.02322300	2.08257600	-0.82571700
C	-0.39464600	0.98534300	-1.58833000
C	-1.34496000	0.05698400	-1.12954400
C	-2.07472300	0.33883400	0.12876400
C	-1.72307000	1.55487300	0.82998100
C	-0.70029000	2.35024700	0.39435800
H	0.73987300	2.76703500	-1.17474000
H	0.04134000	0.84582500	-2.57033200
H	-1.79434200	-0.59936700	-1.86318200
H	-2.31070200	1.83237000	1.69813100
H	-0.45183300	3.24635800	0.95268700
C	-3.21345300	-0.43368200	0.47919100
H	-3.70082700	-0.14074800	1.40659200
C	-3.66628800	-1.55904900	-0.15322800
H	-4.51427900	-2.10165700	0.24354500
H	-3.24936900	-1.91718400	-1.08604900
C	3.16882700	0.06019400	1.26013500
C	1.82913400	-0.26508900	1.36288000
C	1.08716400	-0.78069300	0.28472900
C	1.80377000	-0.96312200	-0.91469000
C	3.14371700	-0.63434800	-1.03490800
C	3.84201500	-0.12258500	0.05372000
H	3.69404000	0.45271500	2.12303800
H	1.32190100	-0.08808900	2.30523300
H	1.29369600	-1.38608600	-1.77177100
H	3.65478100	-0.79390600	-1.97759100
H	4.88948500	0.13639300	-0.03714600
S	-0.62610100	-1.14228500	0.42922200

6.6 Radical Clock Experiment

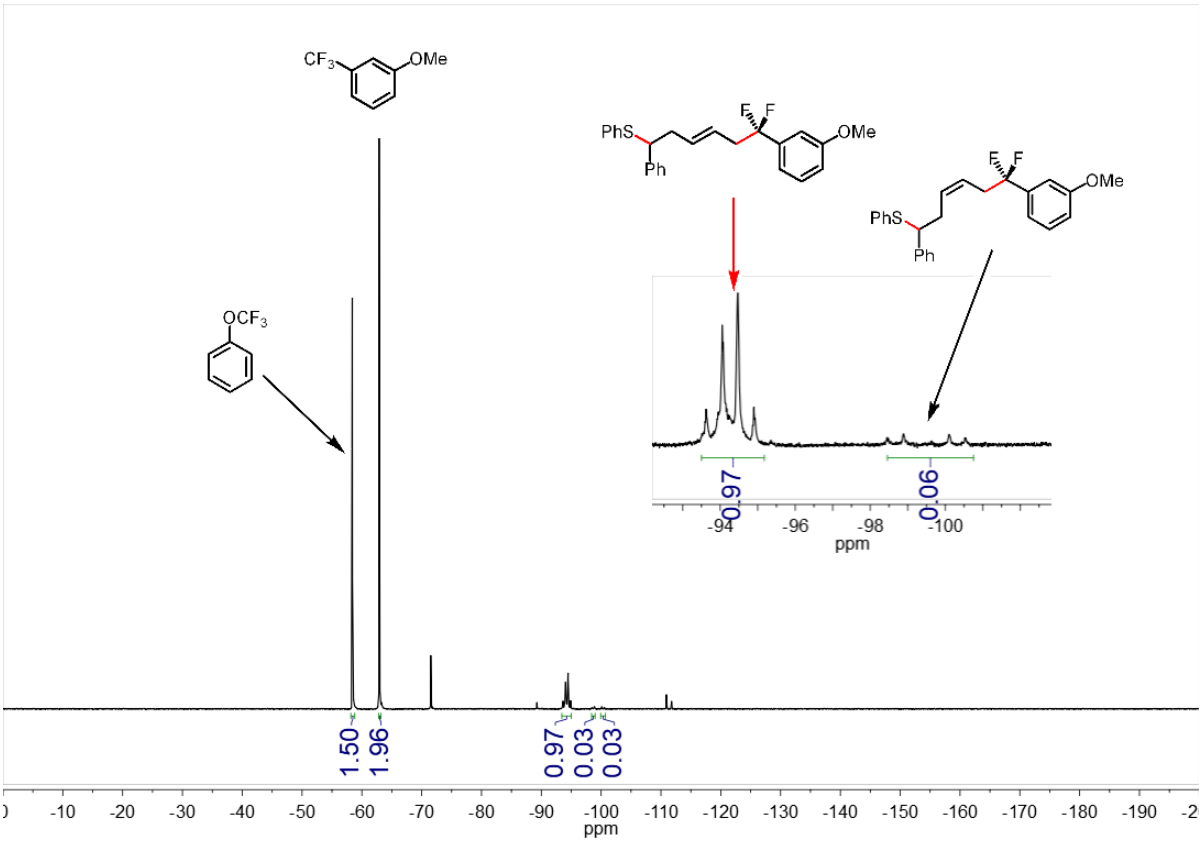


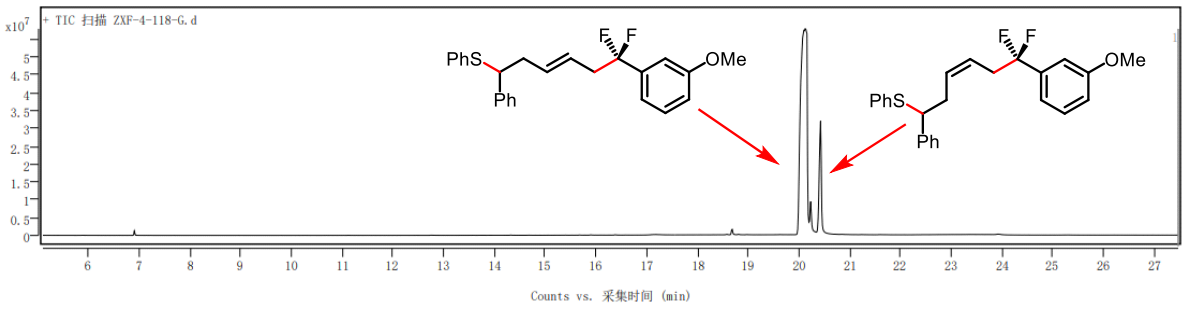
To a 20 mL oven dried screw-cap vial equipped with a magnetic stir bar was added *t*BuONa (173 mg, 1.8 mmol, 1.5 equiv.) in dry DMA (12 mL), followed by thiophenol (184 μL, 1.8 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (260 μL, 1.8 mmol, 1.5 equiv.) and **10** (173 mg, 0.6 mmol, 1.0 equiv.) under a nitrogen atmosphere. The reaction mixture was stirred vigorously at room temperature and exposed to 30 W 365 nm LED for 2 hours. Then, the reaction was diluted with ethyl acetate (10 mL) and extracted with water (20 mL), saturated sodium chloride solution (2 x 30 mL), followed by reverse extraction of the mixed aqueous phase using ethyl acetate (30 mL). The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. Purification by column chromatography on silica gel using petroleum ether and ethyl acetate (20:1 (v/v)) as eluent afforded **11** with E:Z=16:1 as a colorless oil (448 mg, 91% yield).

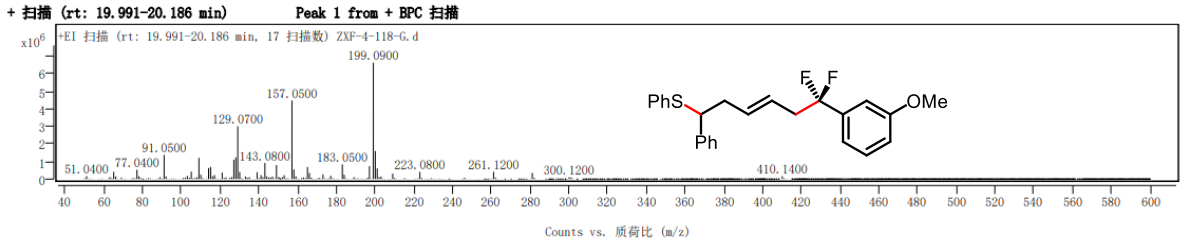


R_f = 0.30 (petroleum ether/ ethyl acetate 20:1 (v/v)). **NMR Spectroscopy**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 1H), 7.25 – 7.11 (m, 11H), 6.95 – 6.92 (m, 2H), 5.49 – 5.41 (m, 1H), 5.39 – 5.32 (m, 1H), 4.09 (t, *J*

= 7.3 Hz, 1H), 3.81 (s, 3H), 2.81 – 2.70 (m, 2H), 2.67 – 2.57 (m, 2H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -94.47 (dt, *J* = 242.7, 15.4 Hz, 1F), -95.31 (dt, *J* = 242.7, 16.1 Hz, 1F).







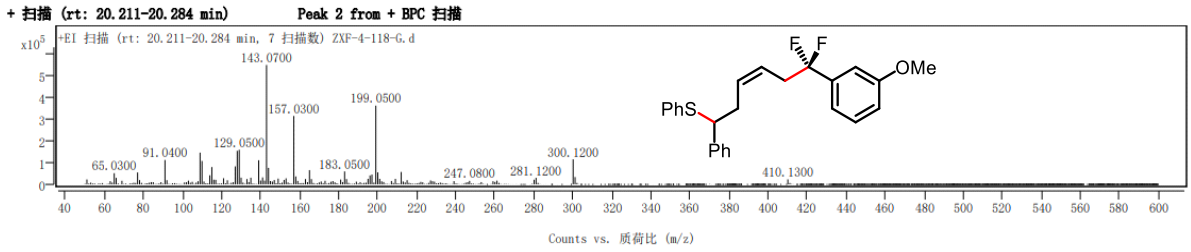
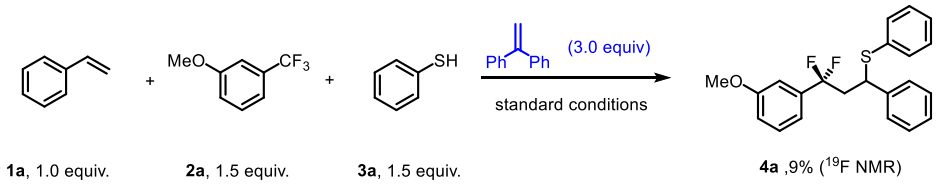


Figure 18. Detection of **11** by ^{19}F NMR and GC-MS.

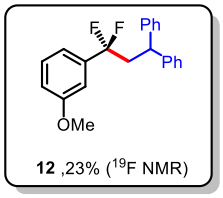
6.7 Detection of the Alkyl Radical Intermediate

Radical trapping experiment with 1,1-Diphenylethylene



1a, 1.0 equiv. **2a**, 1.5 equiv. **3a**, 1.5 equiv. **4a** ,9% (^{19}F NMR)

1,1-Diphenylethylene-radical adduct:



12 ,23% (^{19}F NMR)

To a 2.0 mL oven dried screw-cap vial equipped with a magnetic stir bar was charged with *t*BuONa (14.5 mg, 0.15 mmol, 1.5 equiv.) in dry DMA (1.00 mL), followed by thiophenol (15.5 μL, 0.15 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (22.0 μL, 0.15 mmol, 1.5 equiv.), styrene (11.5 μL, 0.10 mmol, 1.0 equiv.) and 1,1-diphenylethylene (53.0 μL, 0.30 mmol, 2.0 equiv.) under a nitrogen atmosphere. The reaction mixture was stirred vigorously at room temperature and exposed to 30 W 365 nm LED for 2 hours. The crude ^{19}F NMR of the obtained materials showed yield of desired product and some reactive radical intermediates with (trifluoromethoxy)benzene as an internal standard.

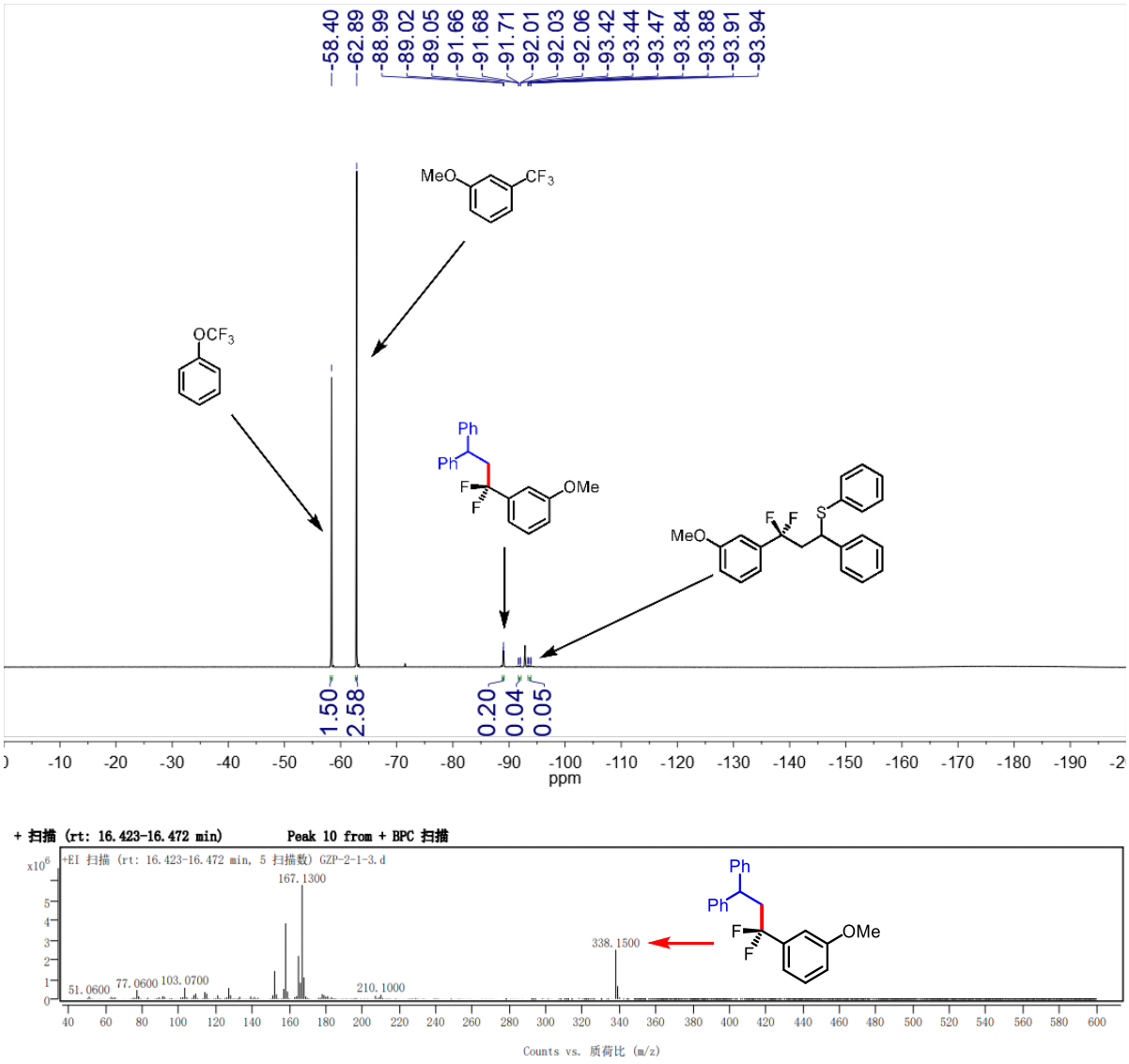
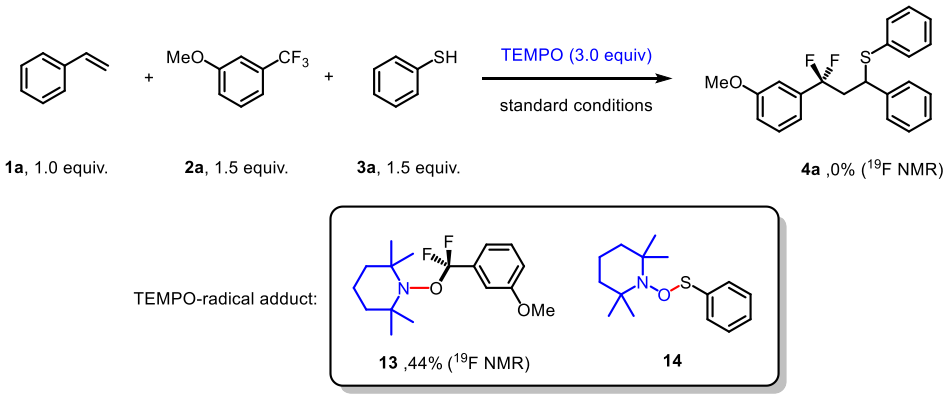


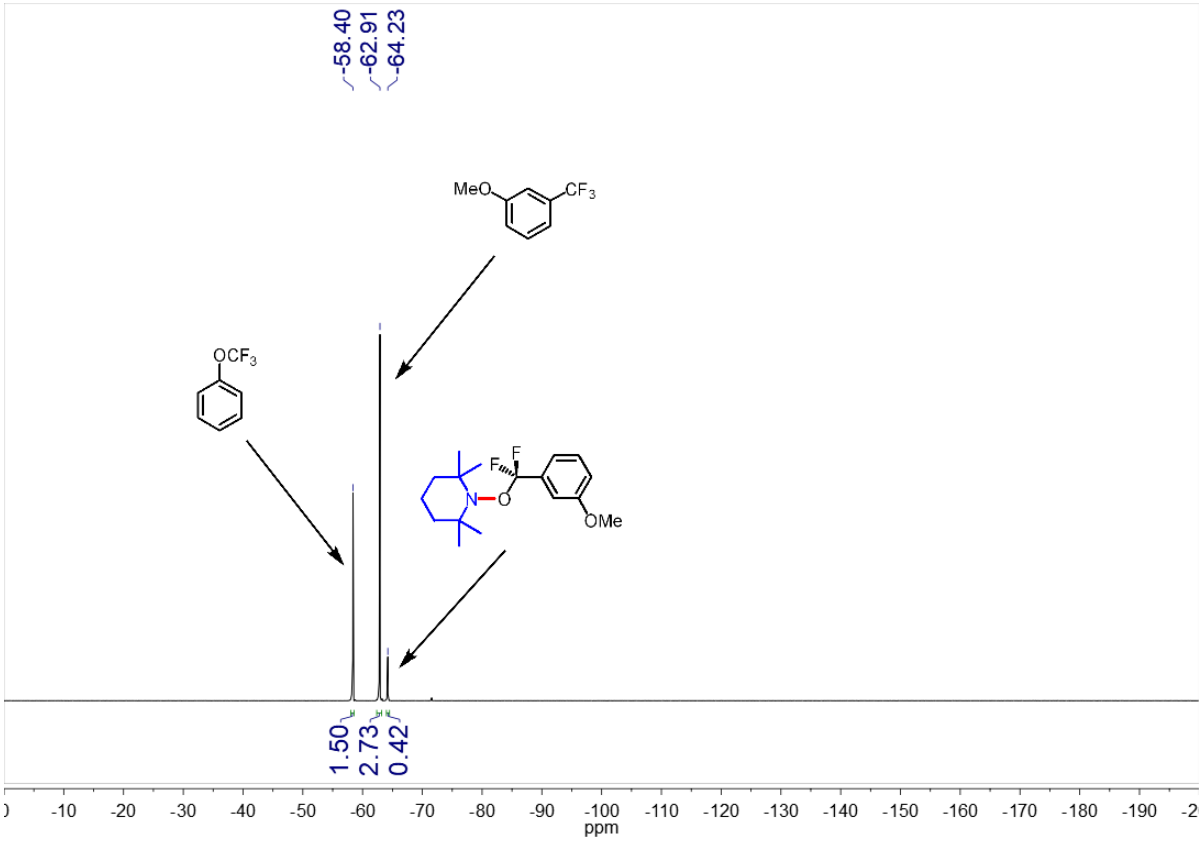
Figure 19. Detection of compounds **12** by ^{19}F NMR and GC-MS.

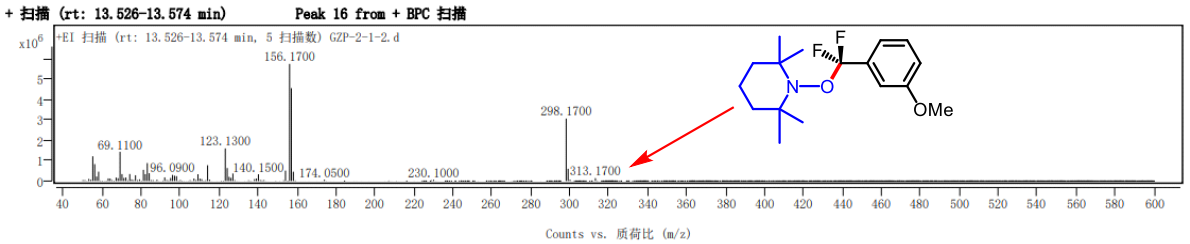
Radical trapping experiment with TEMPO



To a 2.0 mL oven dried screw-cap vial equipped with a magnetic stir bar was charged with *t*BuONa (14.5 mg, 0.15 mmol, 1.5 equiv.) in dry DMA (1.00 mL), followed by thiophenol

(15.5 μL, 0.15 mmol, 1.5 equiv.), 3-(trifluoromethyl)anisole (22.0 μL, 0.15 mmol, 1.5 equiv.), styrene (11.5 μL, 0.10 mmol, 1.0 equiv.) and 2,2,6,6-Tetramethylpiperidinooxy (TEMPO) (46.9 mg, 0.30 mmol, 3.0 equiv.) under a nitrogen atmosphere. The reaction mixture was stirred vigorously at room temperature and exposed to 30 W 365 nm LED for 2 hours. The crude ^{19}F NMR of the obtained materials showed some reactive radical intermediates with (trifluoromethoxy)benzene as an internal standard. GC-MS showed trapping of the reactive radical intermediates by TEMPO.





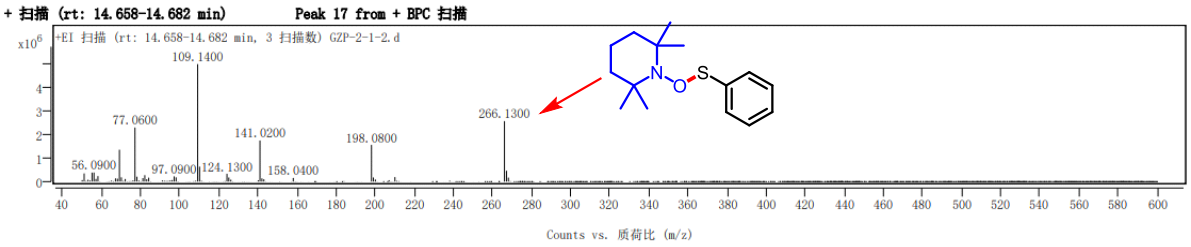
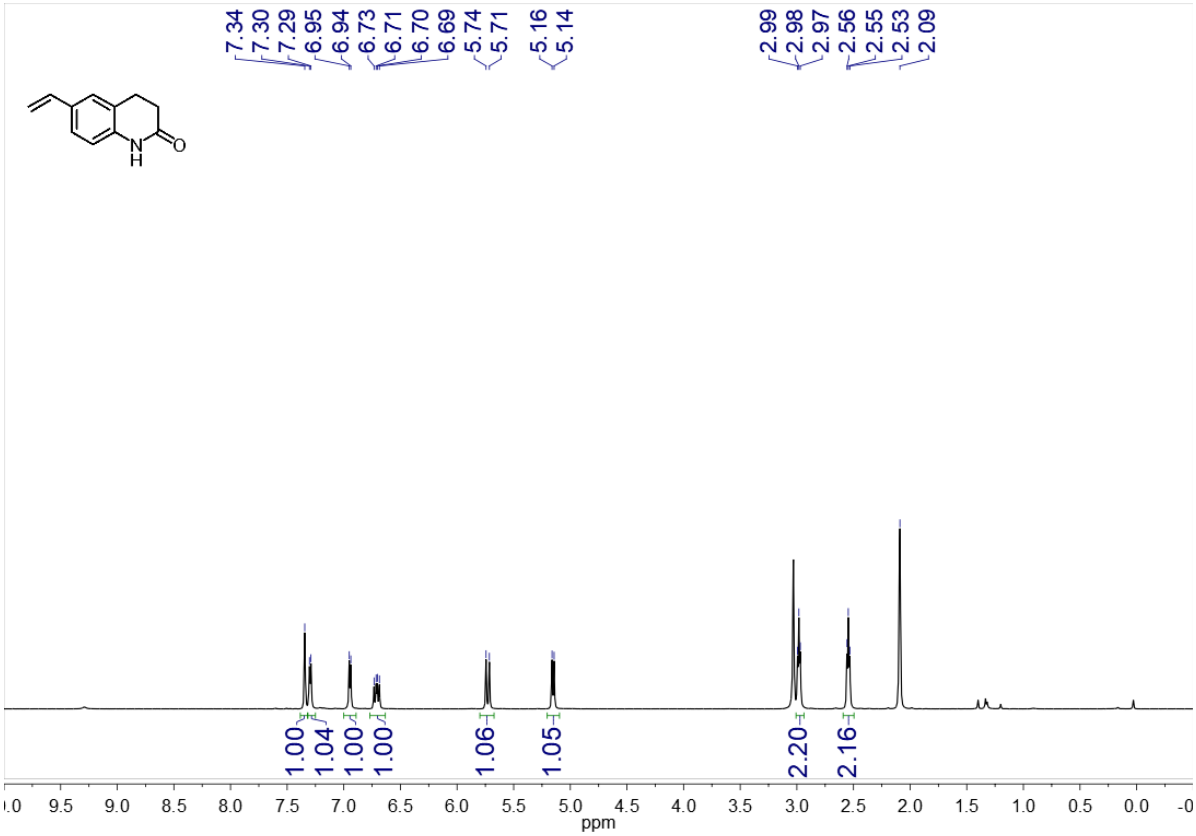
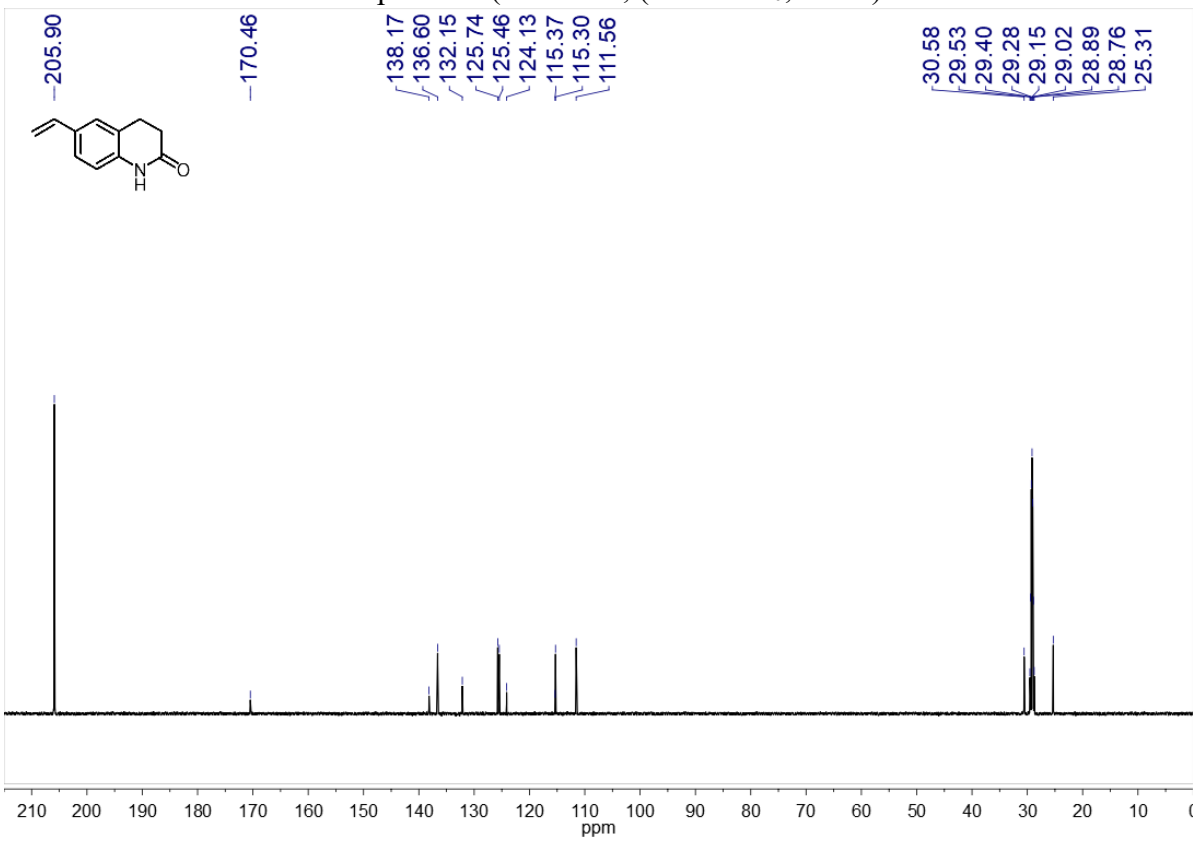


Figure S20. Detection of compounds **13** and **14** by ^{19}F NMR and GC-MS.

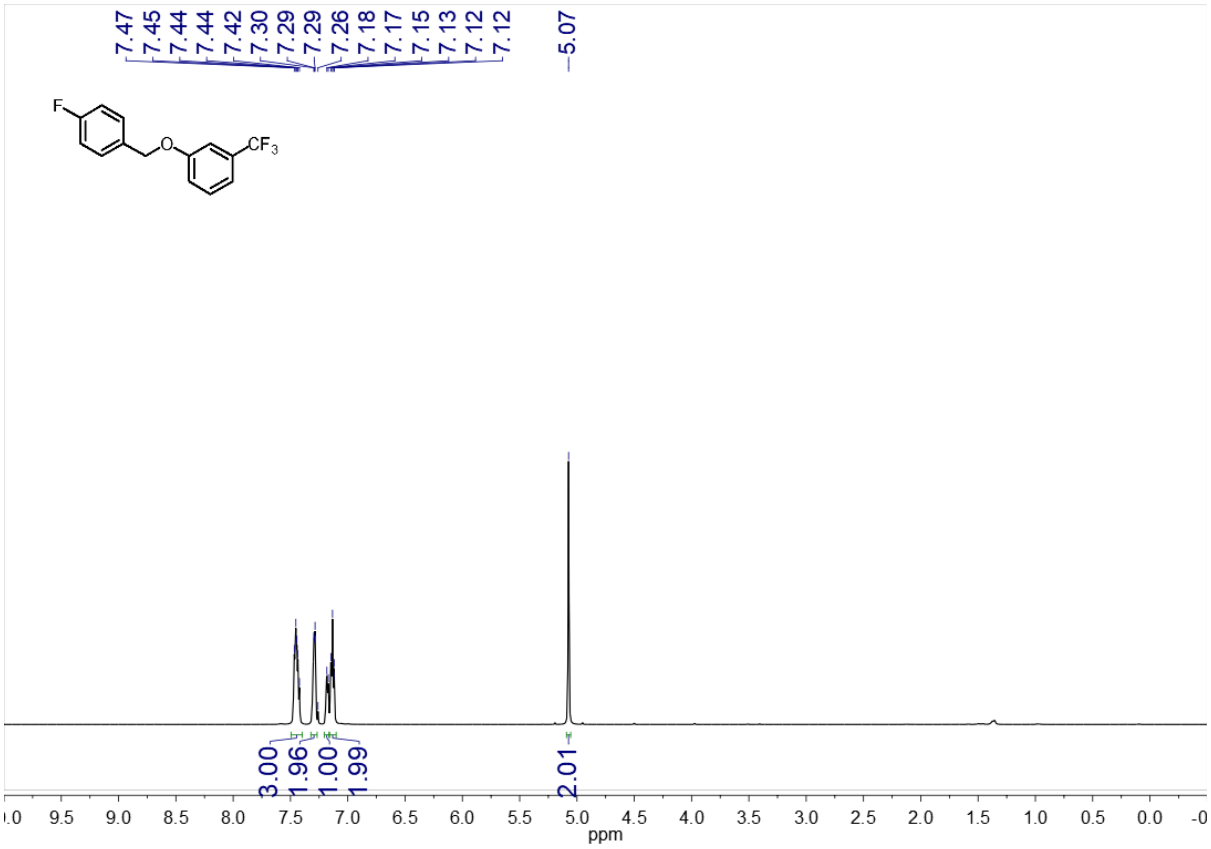
7 NMR Spectra for New Compounds



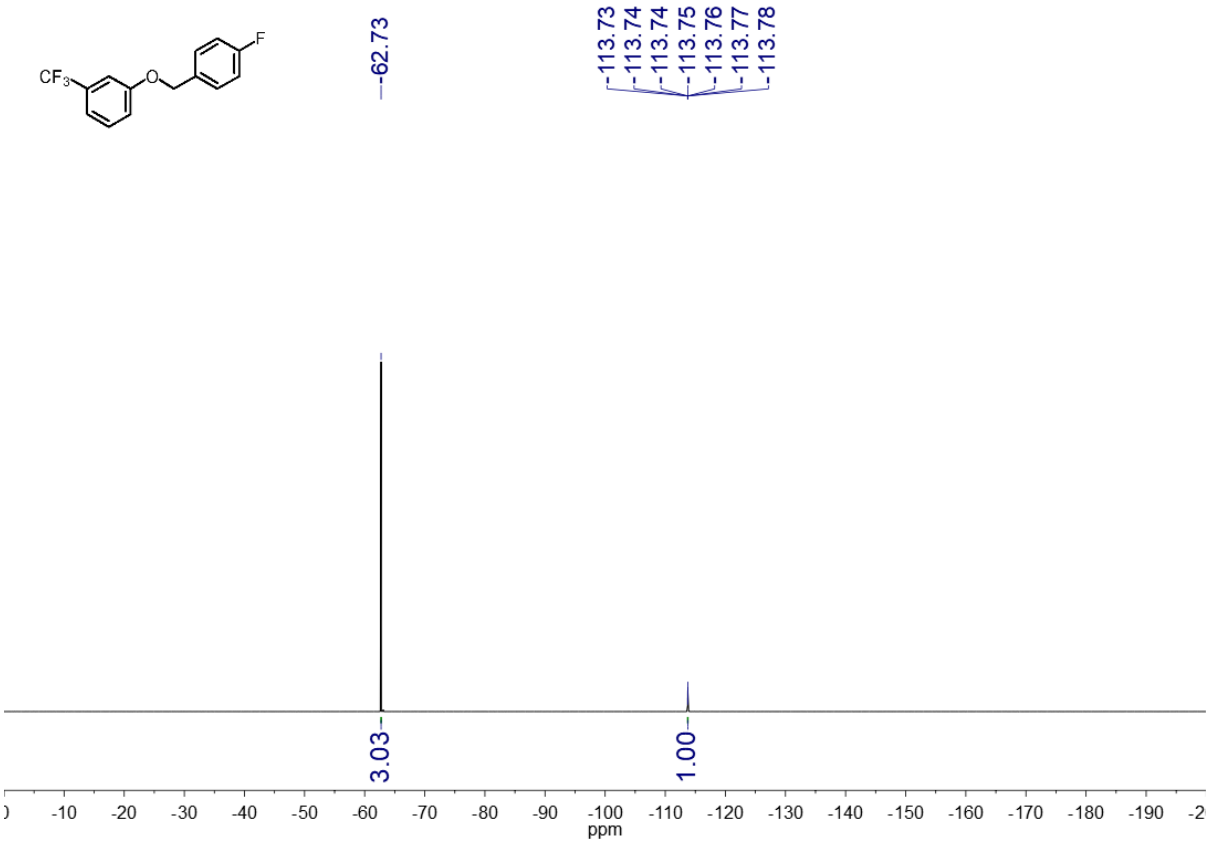
^{1}H NMR spectrum (600 MHz, (acetone-d_6, 23 ºC) of **1r**



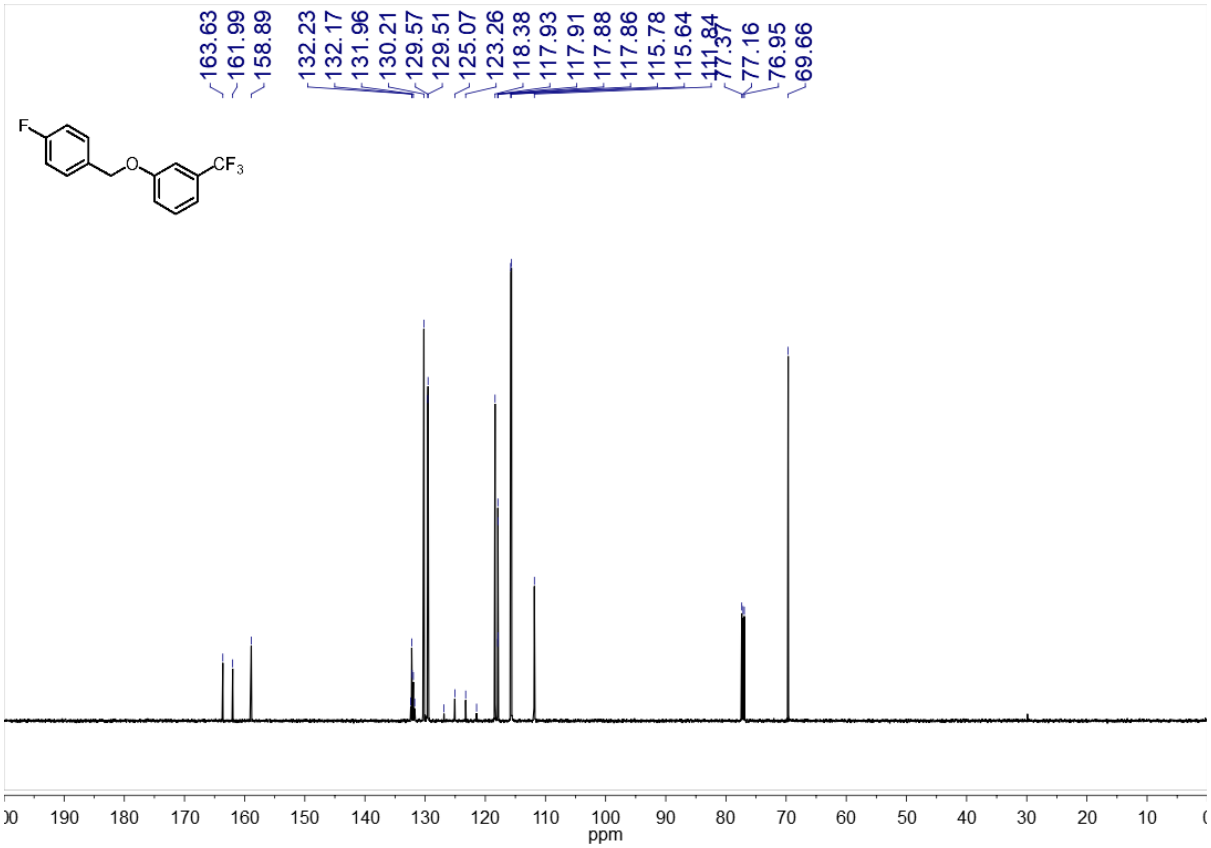
^{13}C NMR spectrum (565 MHz, acetone-d_6, 23 ºC) of **1r**



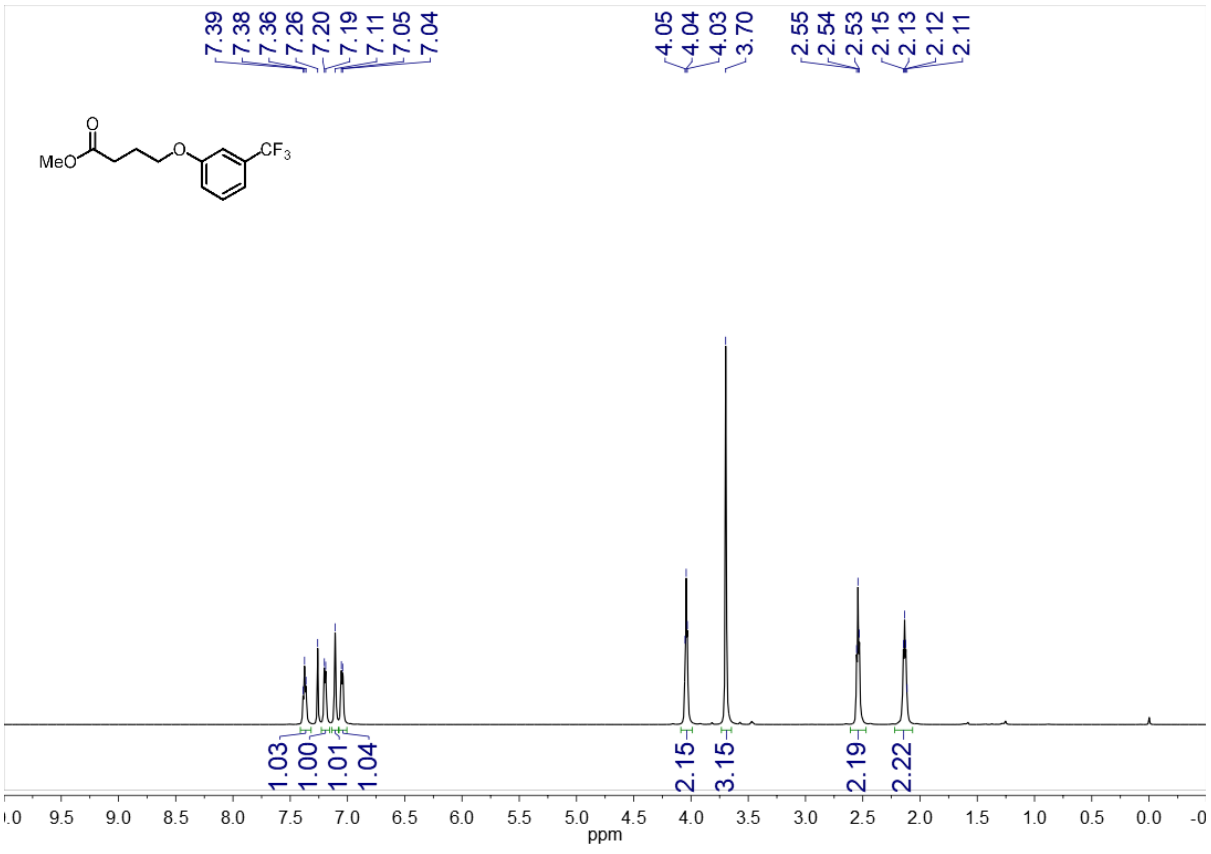
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **2i**



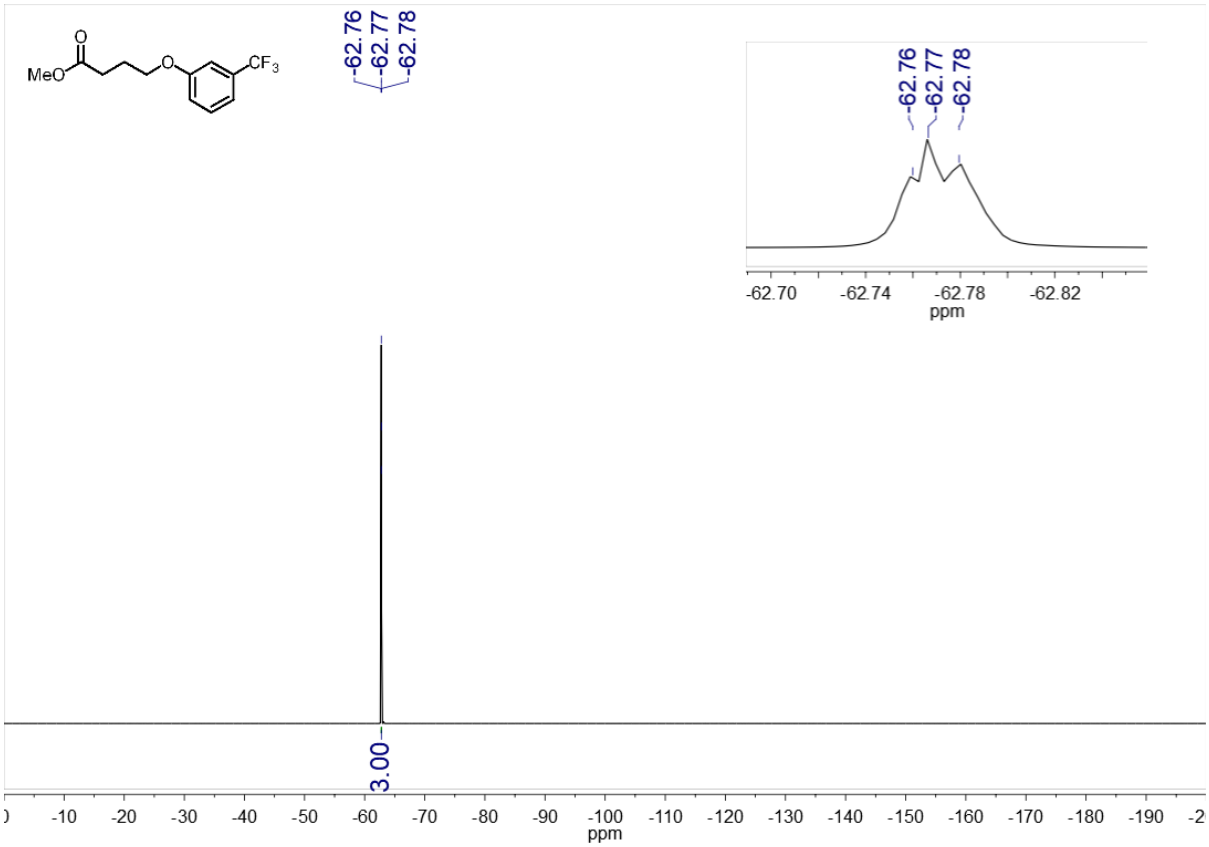
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **2i**



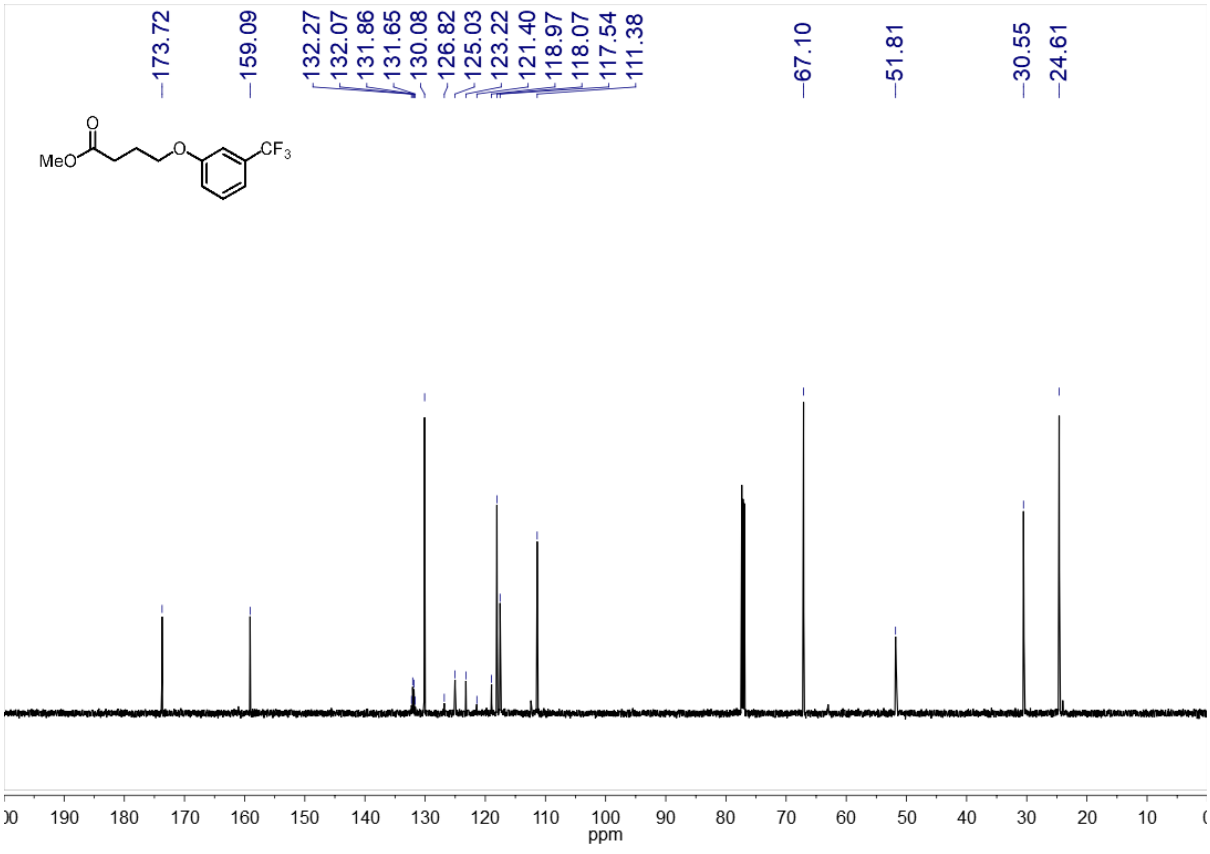
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **2i**



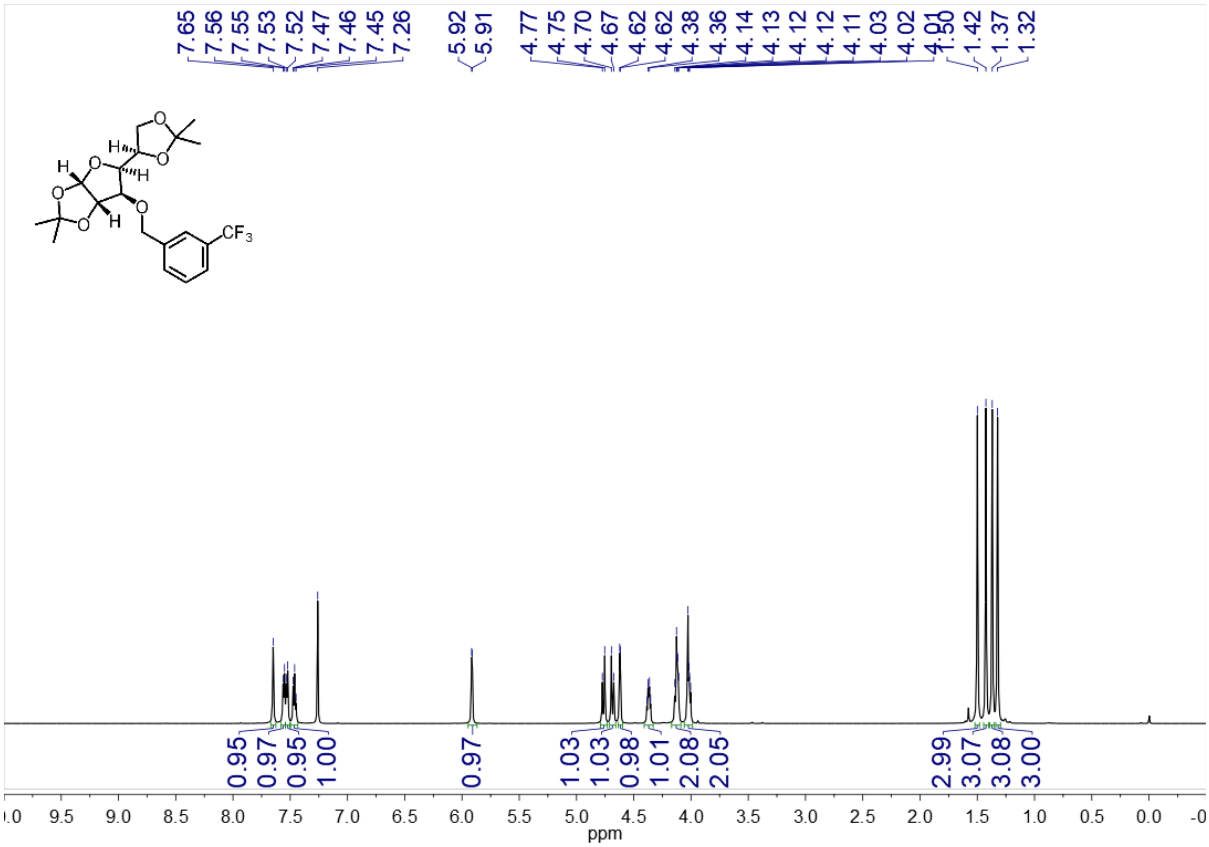
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **2l**



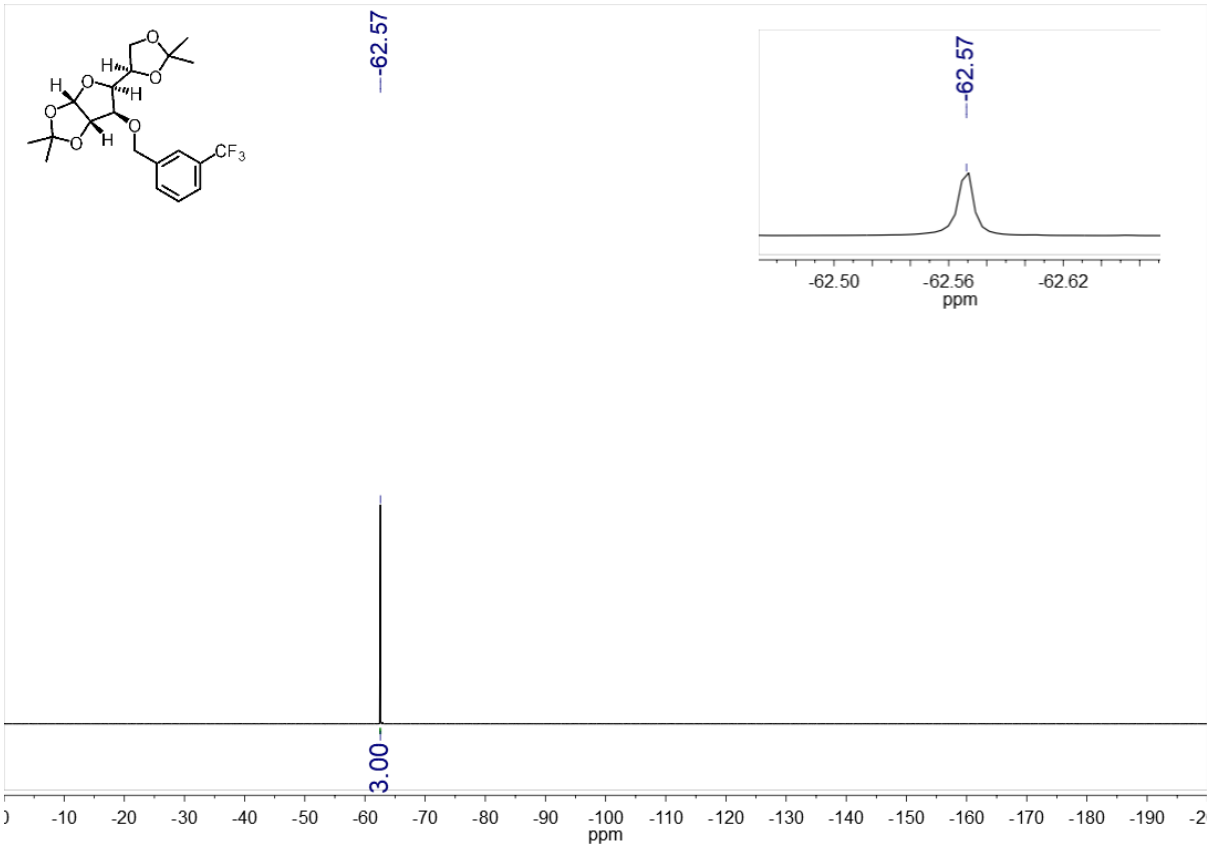
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **2l**



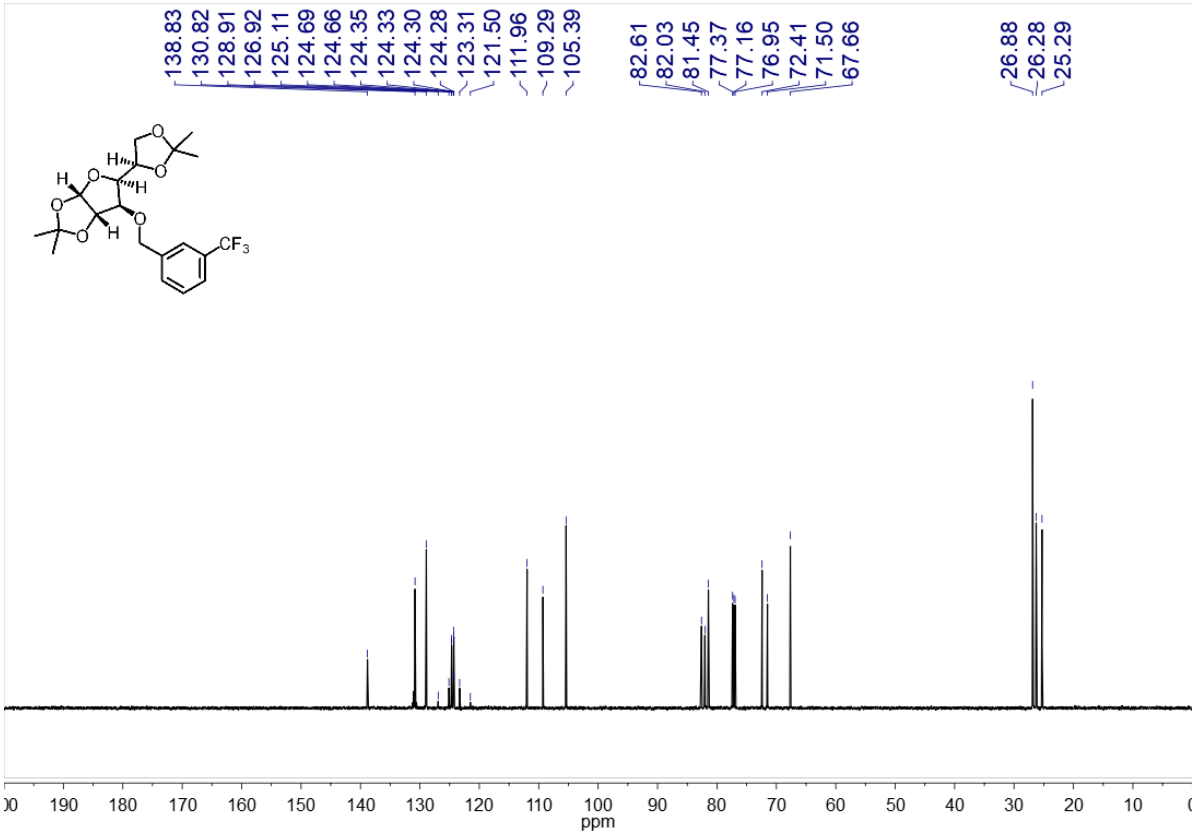
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **2l**



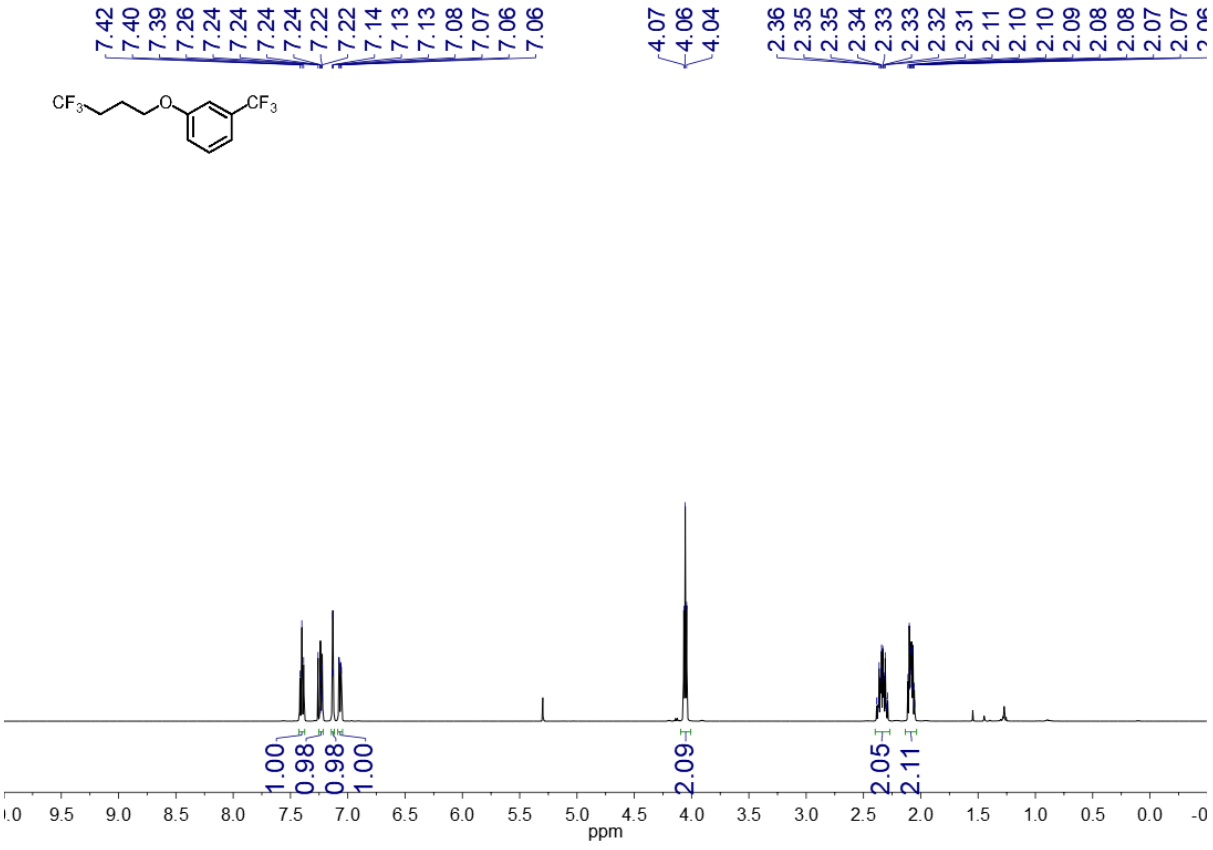
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **2o**



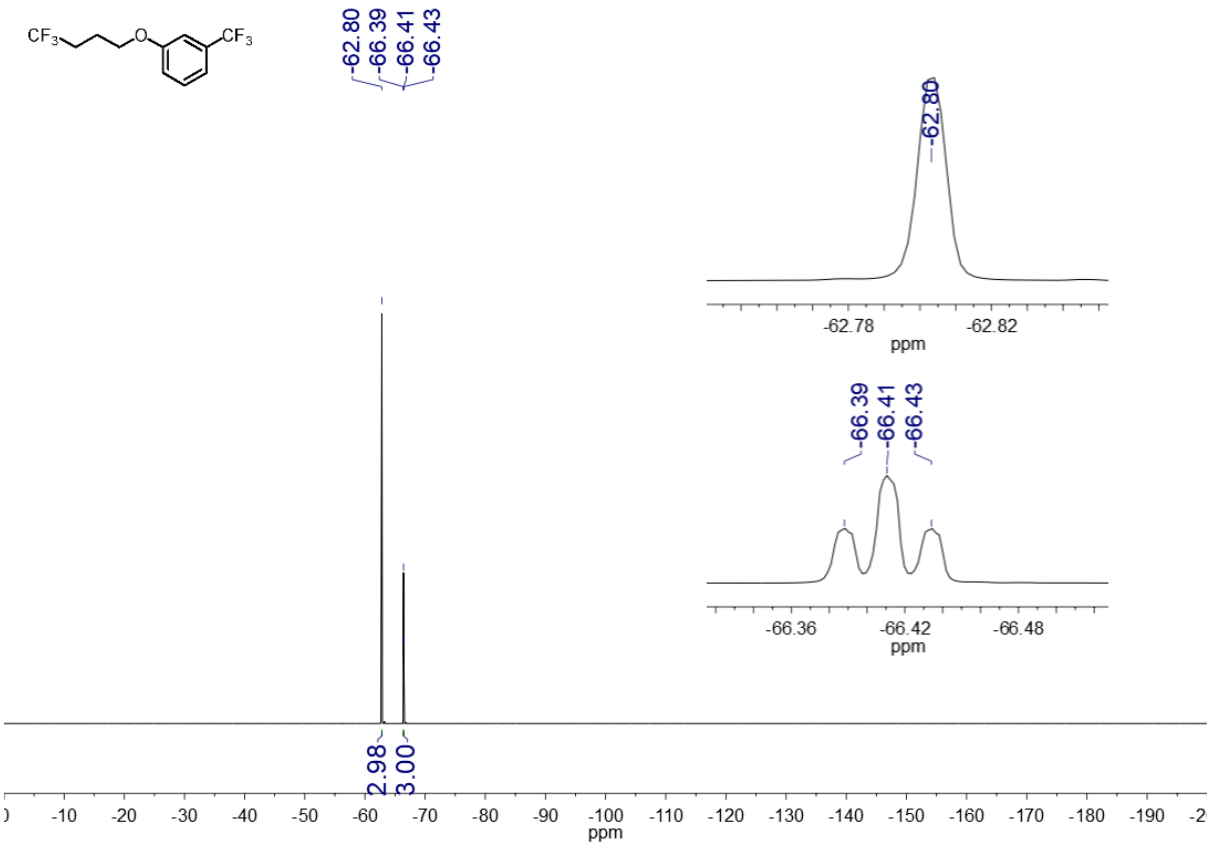
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **2o**



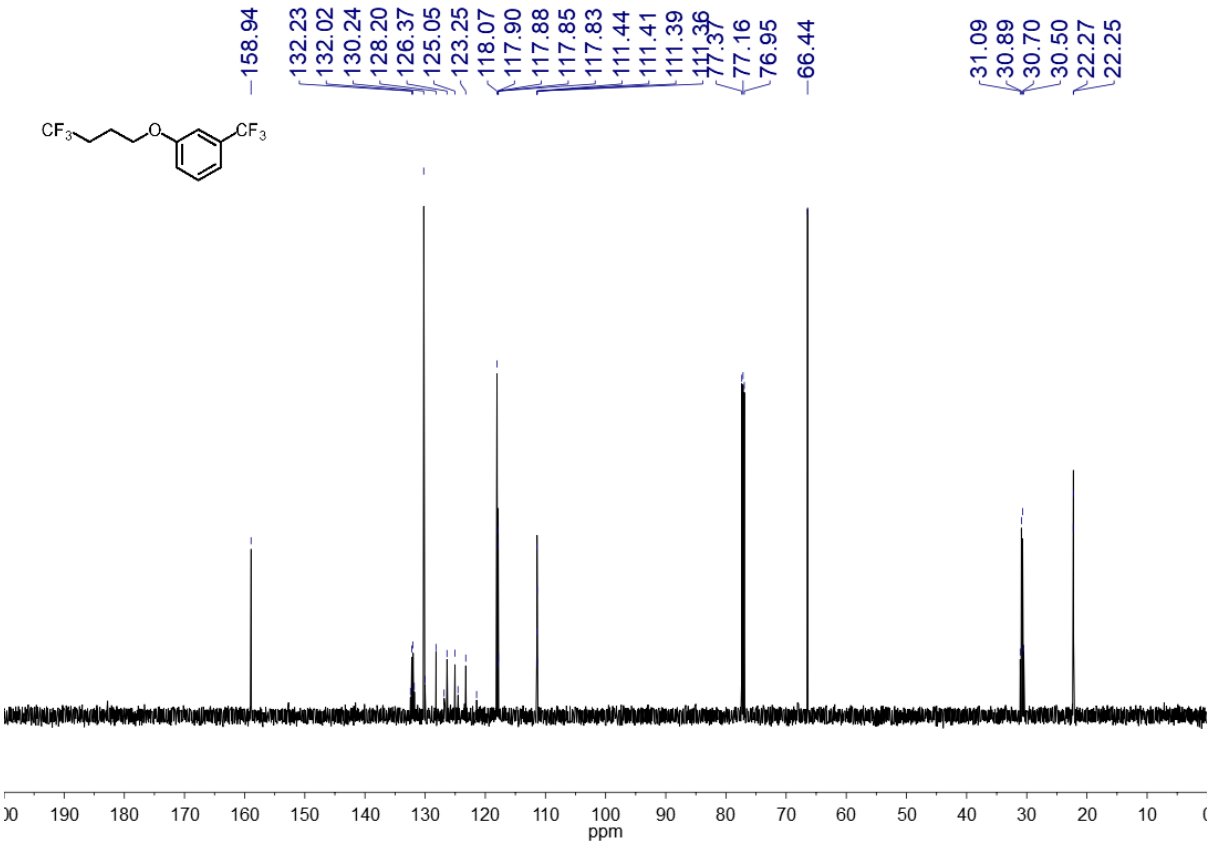
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **2o**



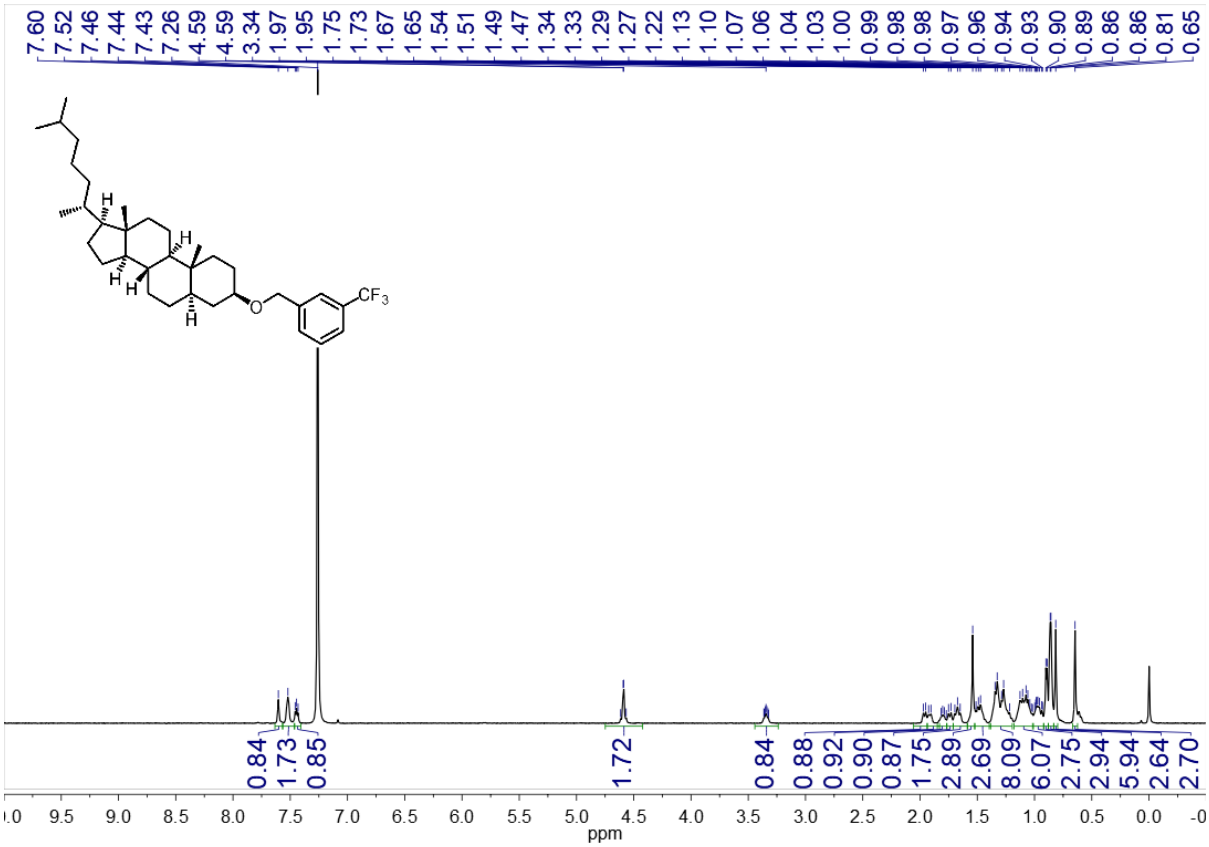
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **2p**



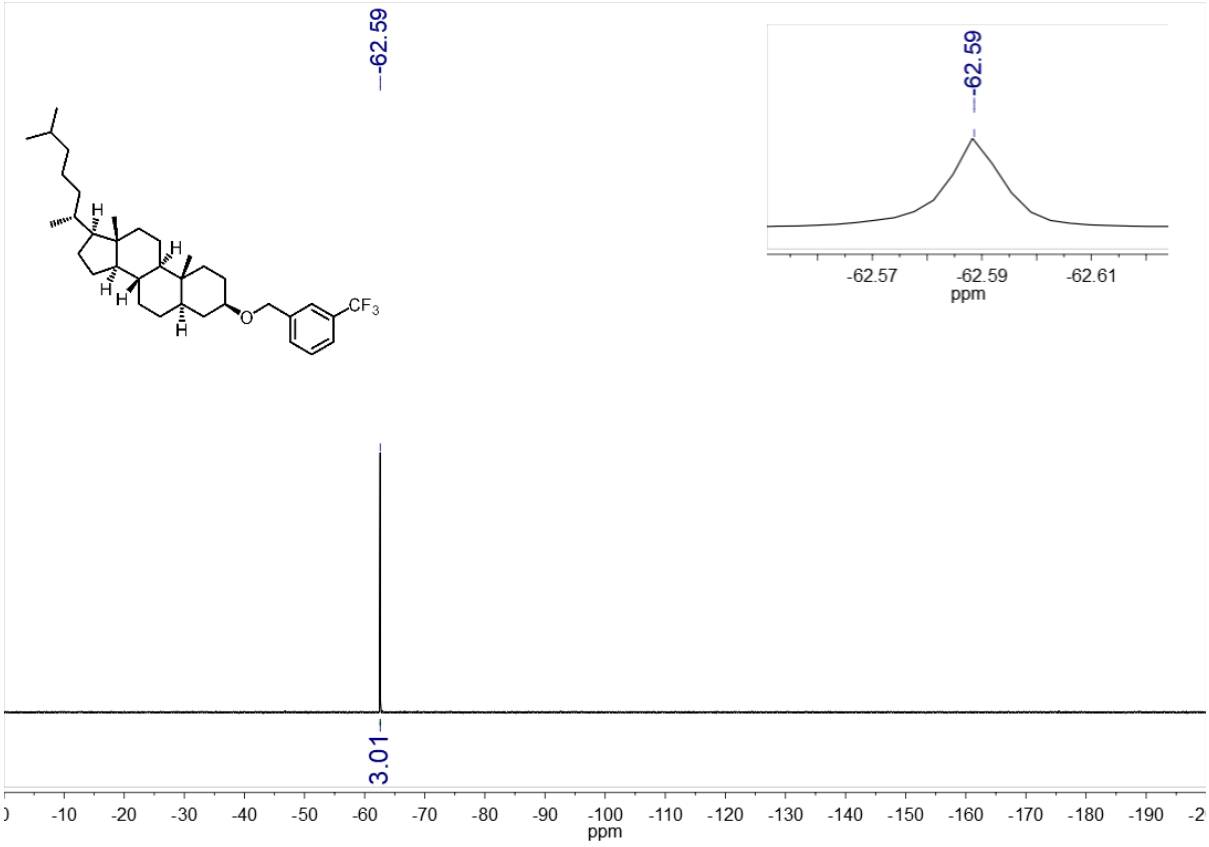
^{19}F NMR spectrum (470 MHz, $CDCl_3$, 23 ºC) of **2p**



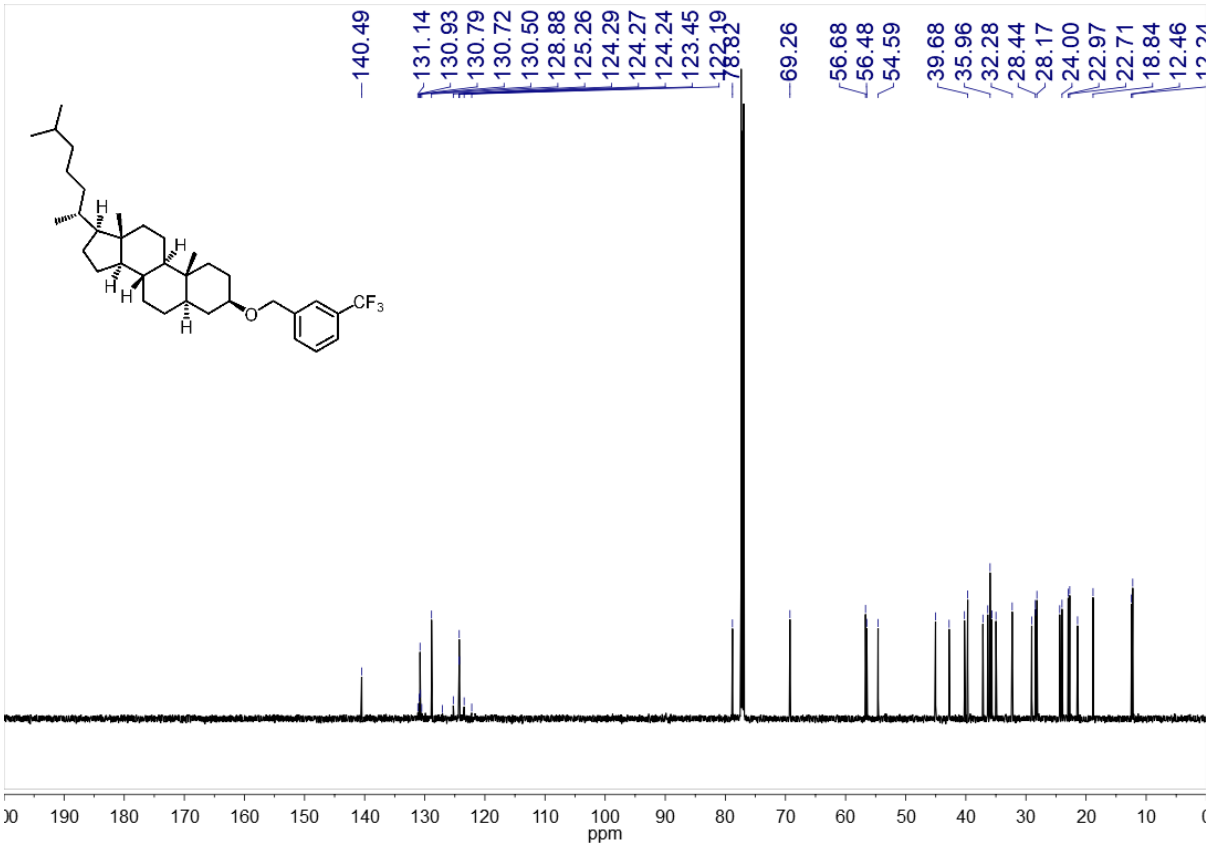
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **2p**



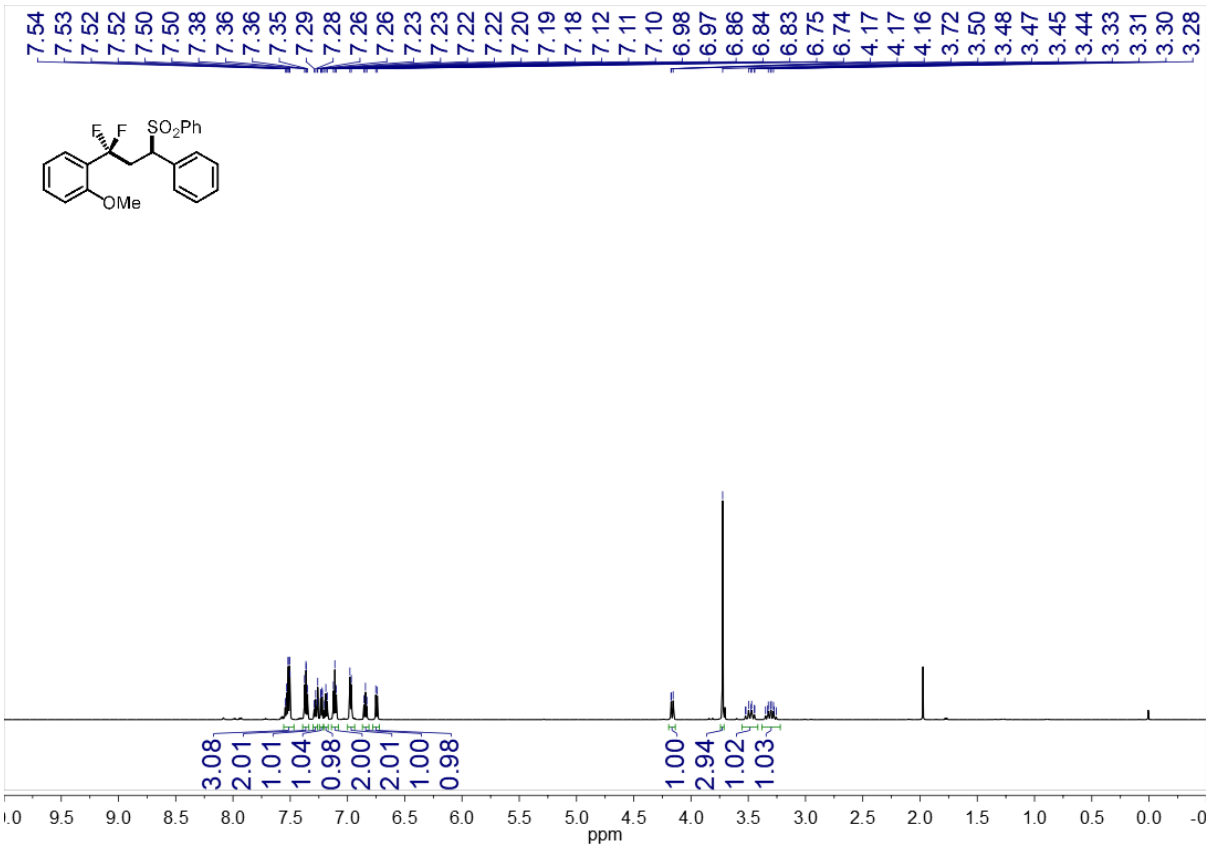
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **2q**



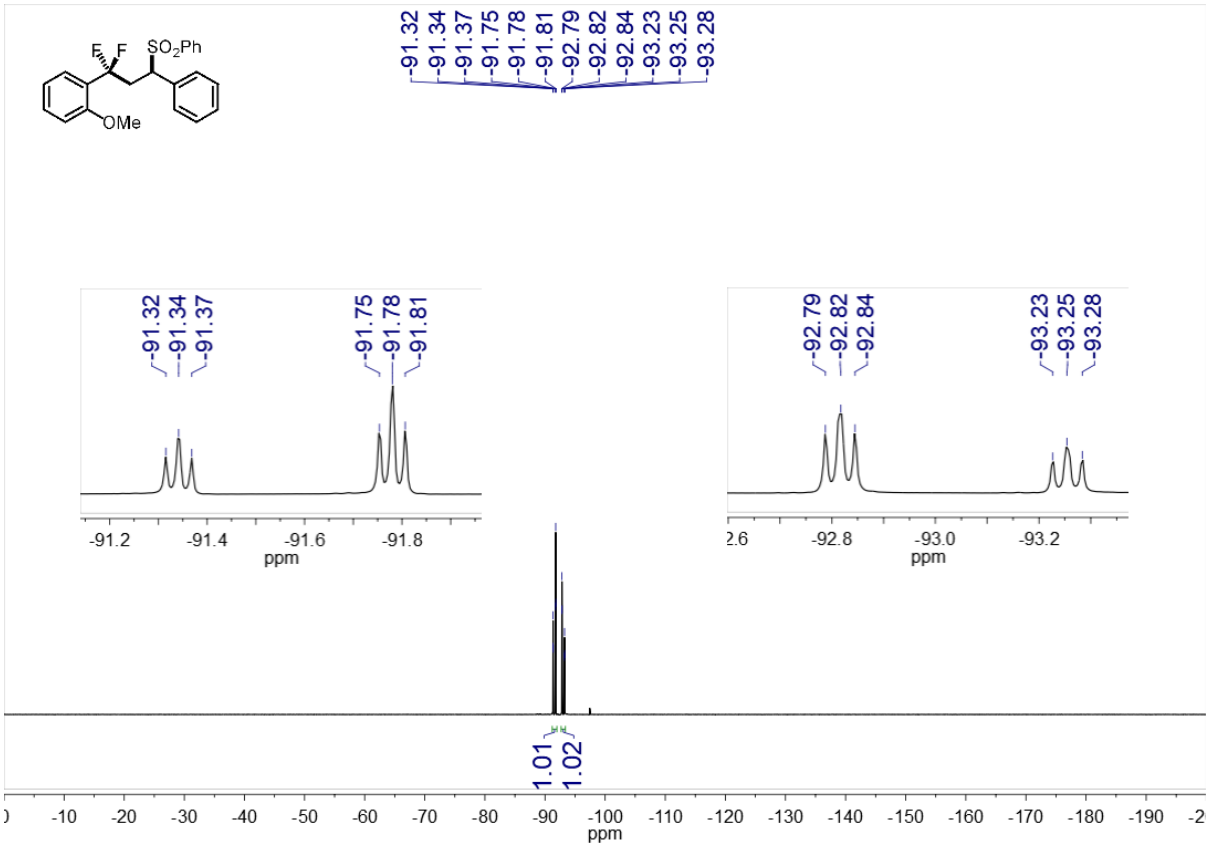
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **2q**



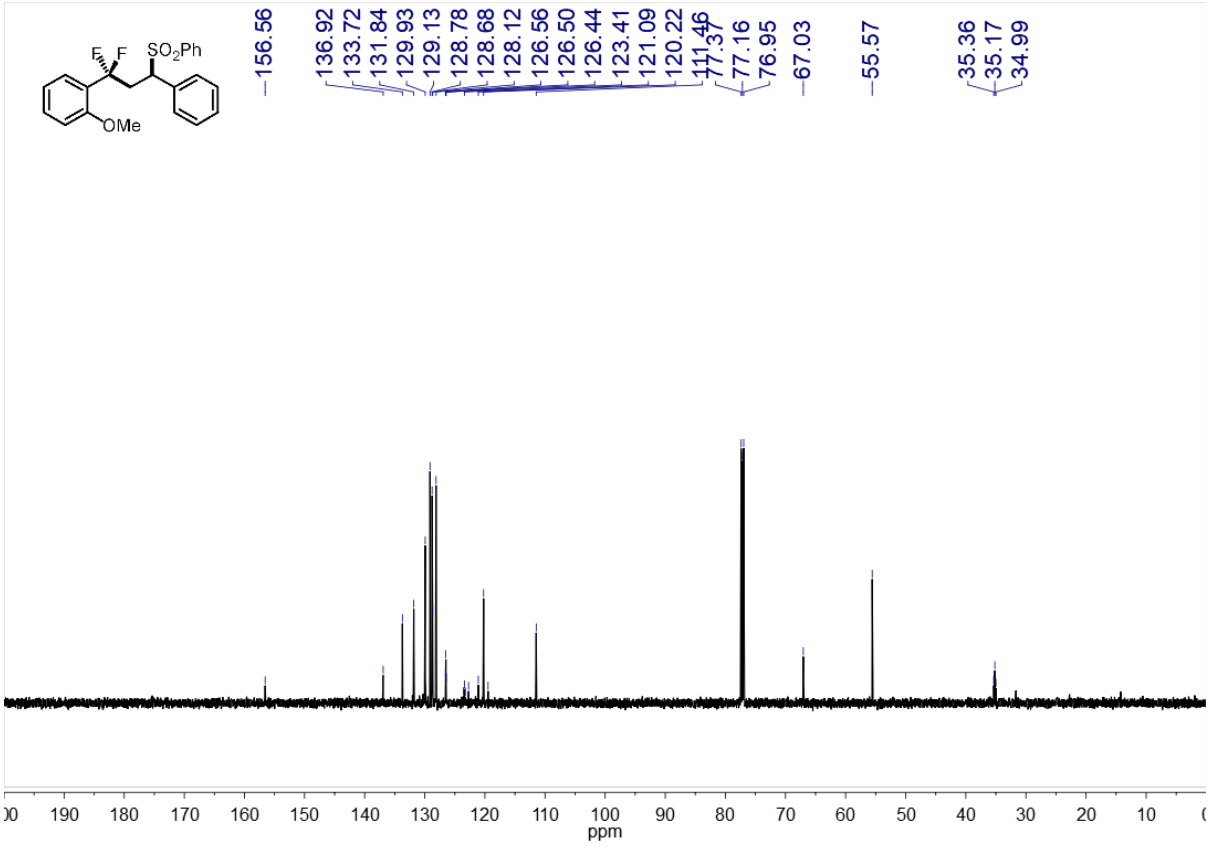
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **2q**



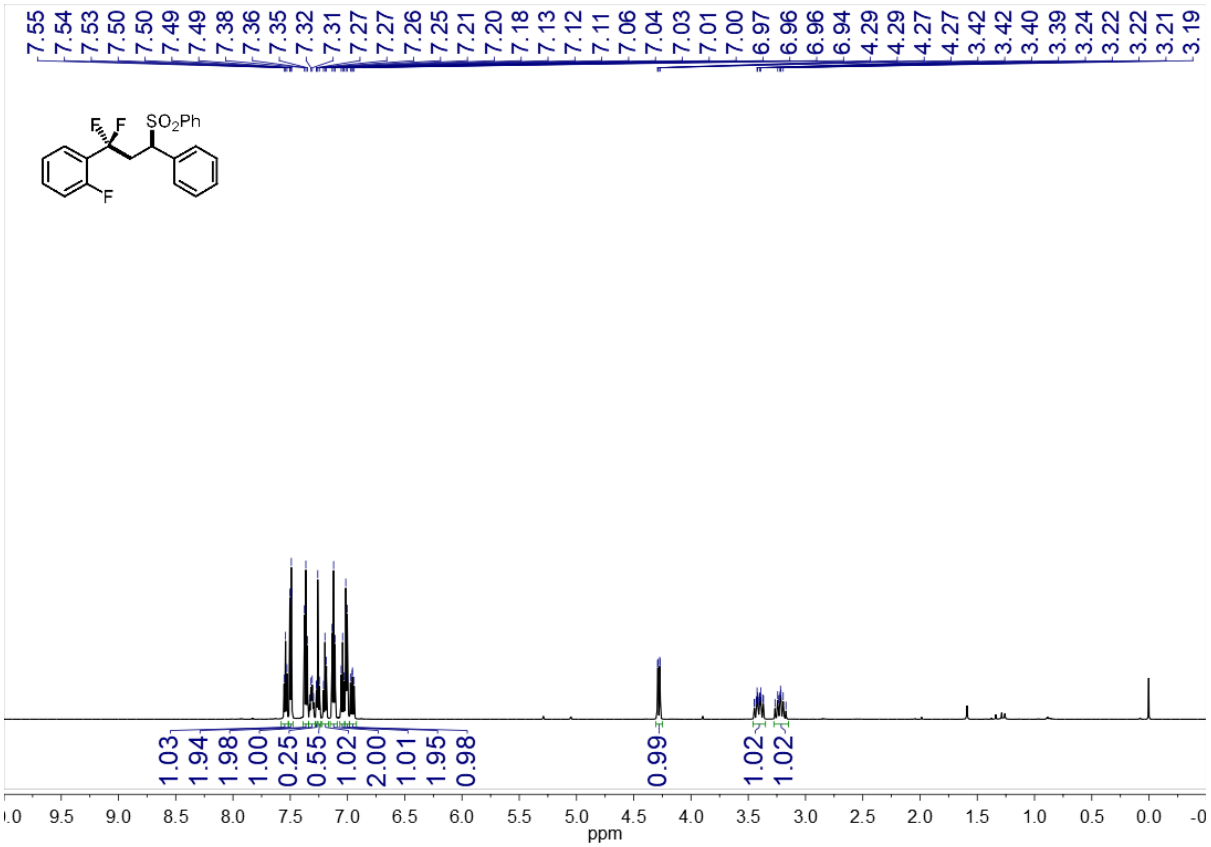
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5a**



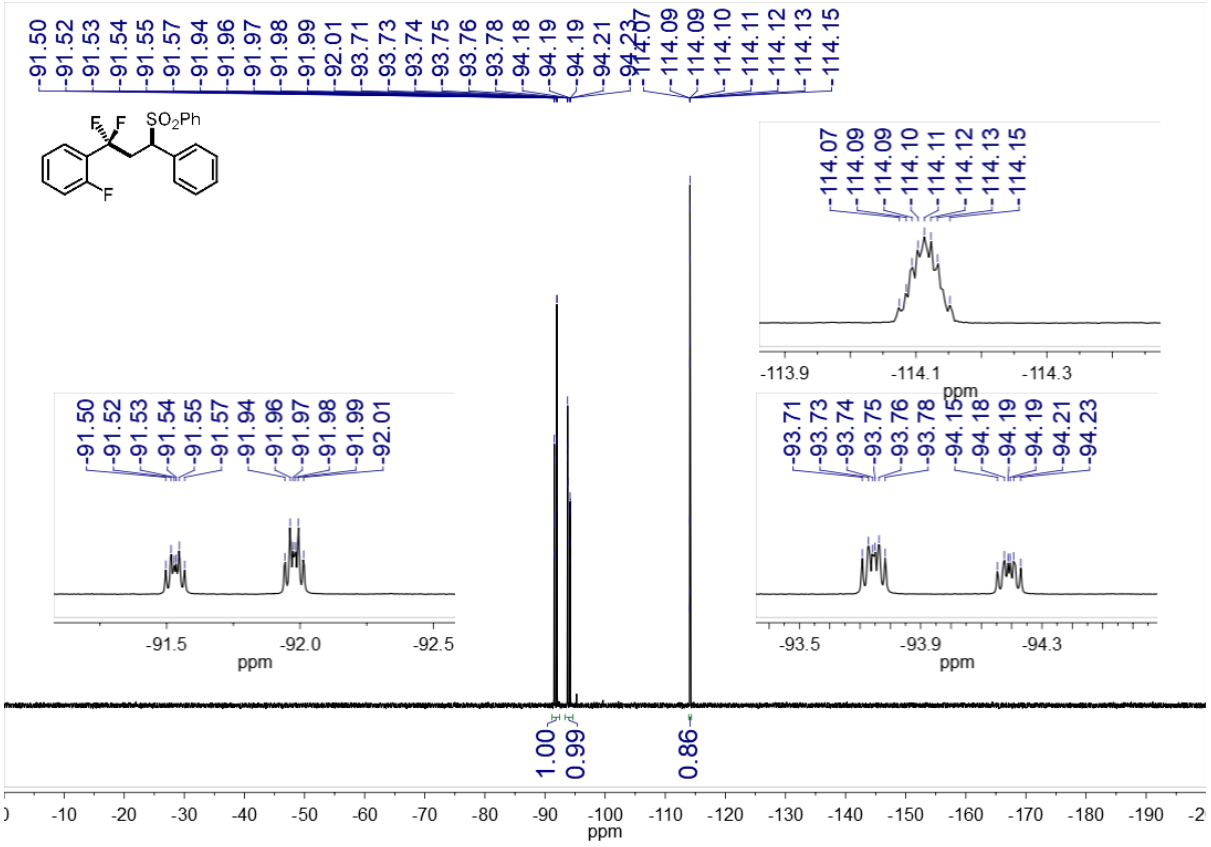
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5a**



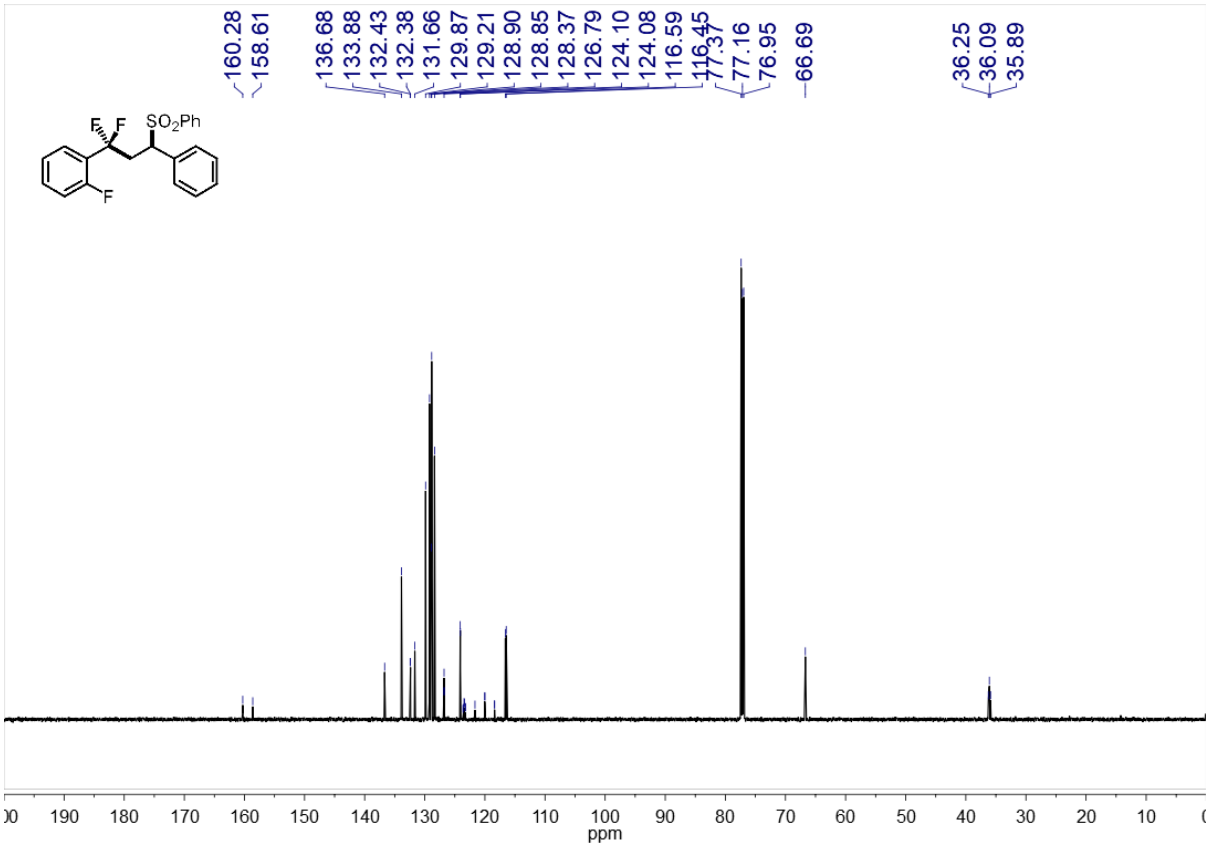
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5a**



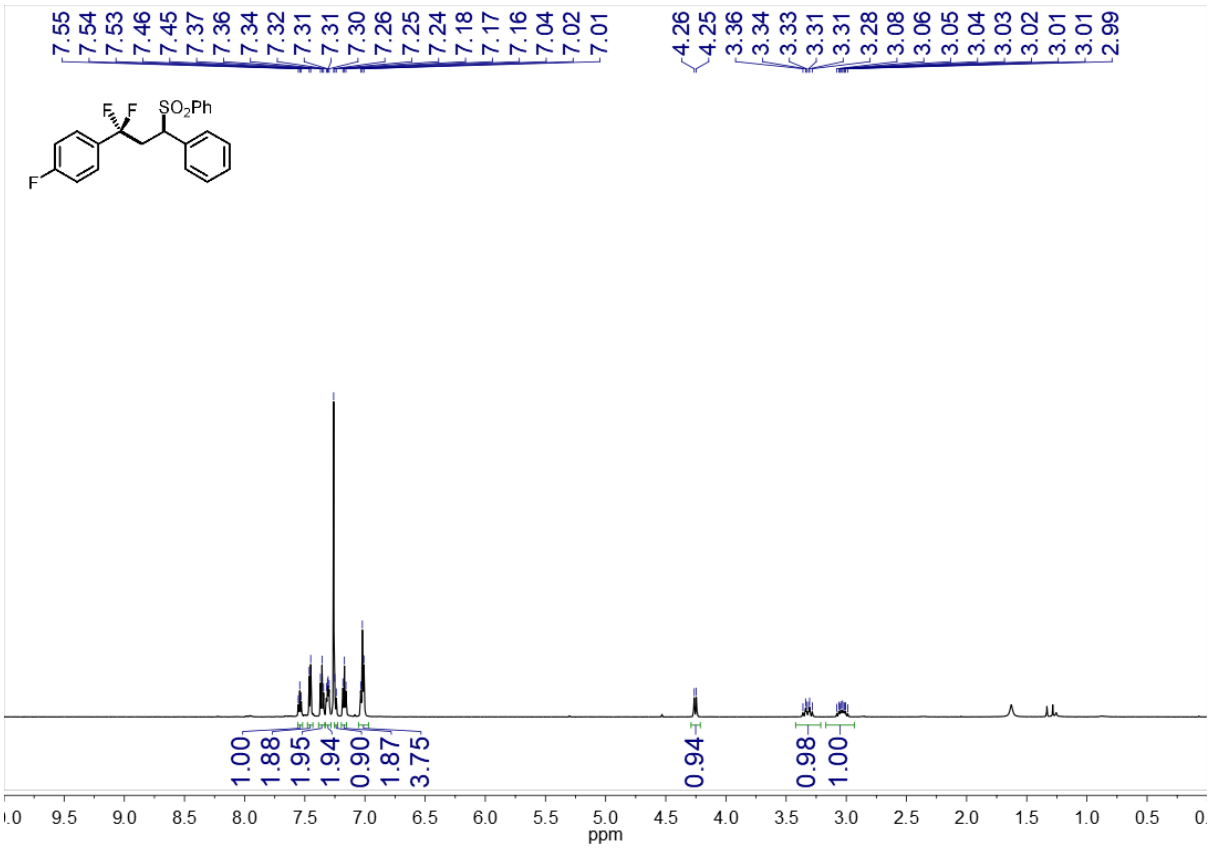
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5b**



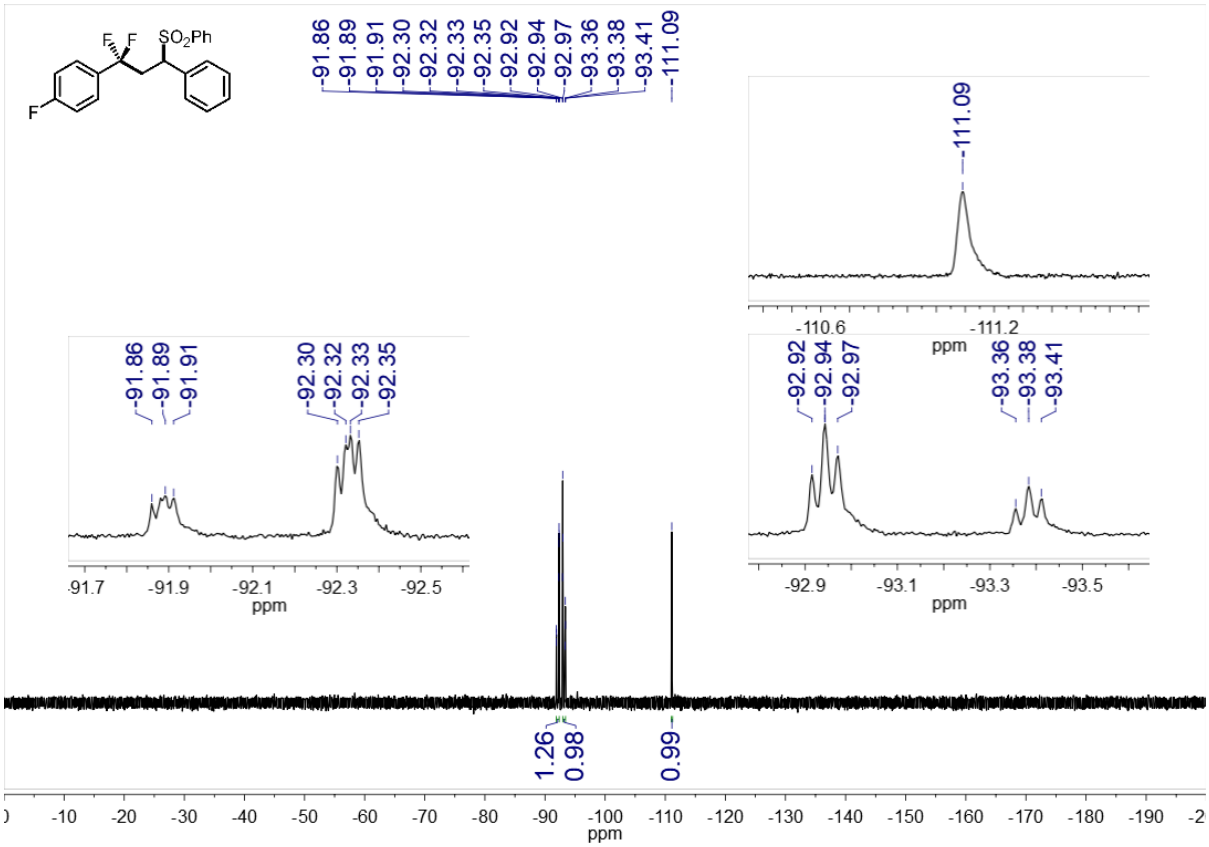
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5b**



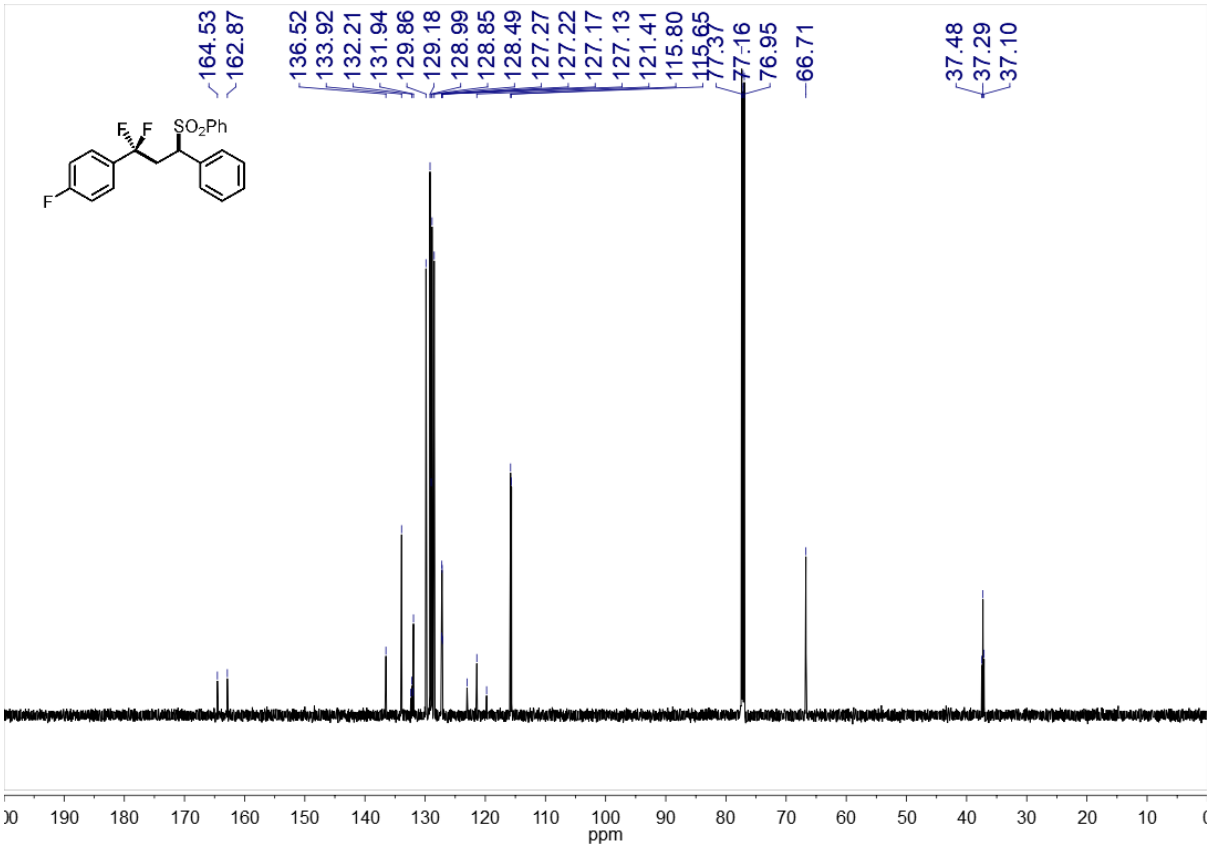
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5b**



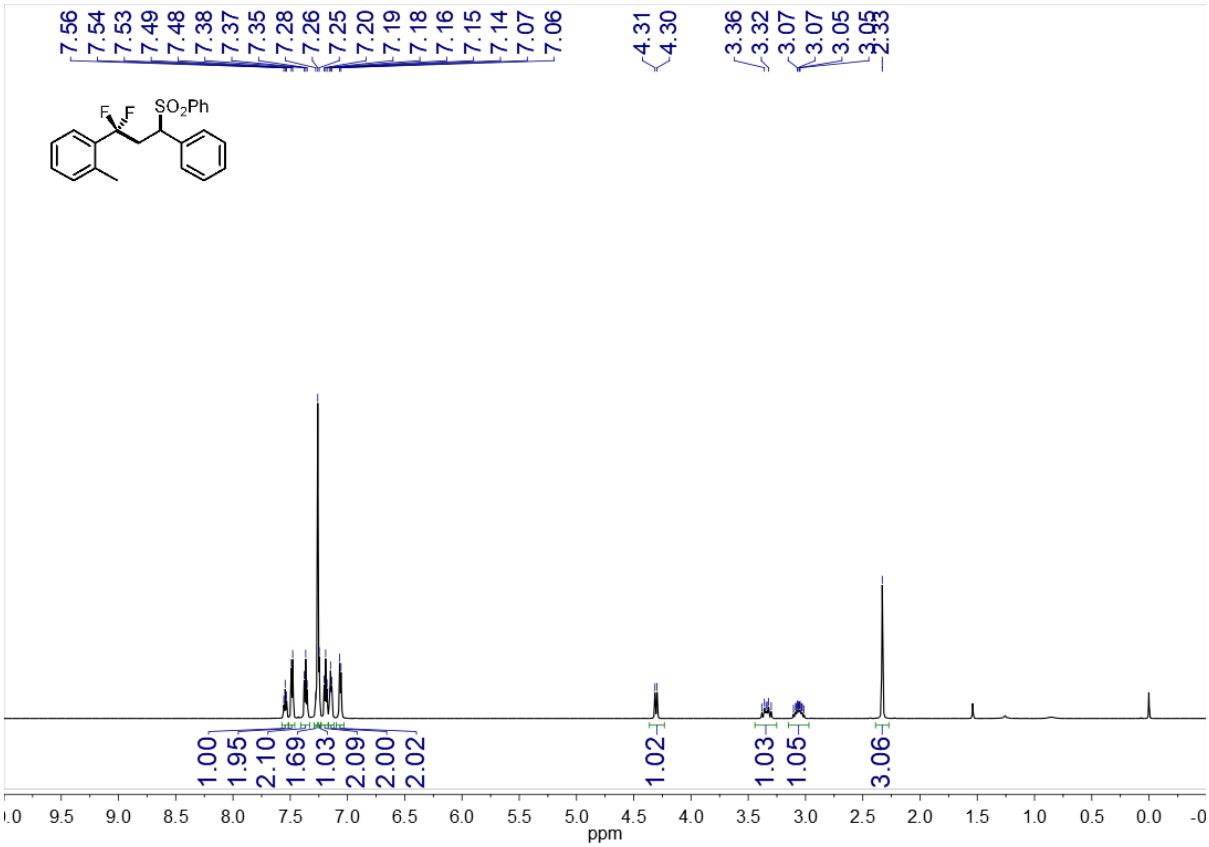
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5c**



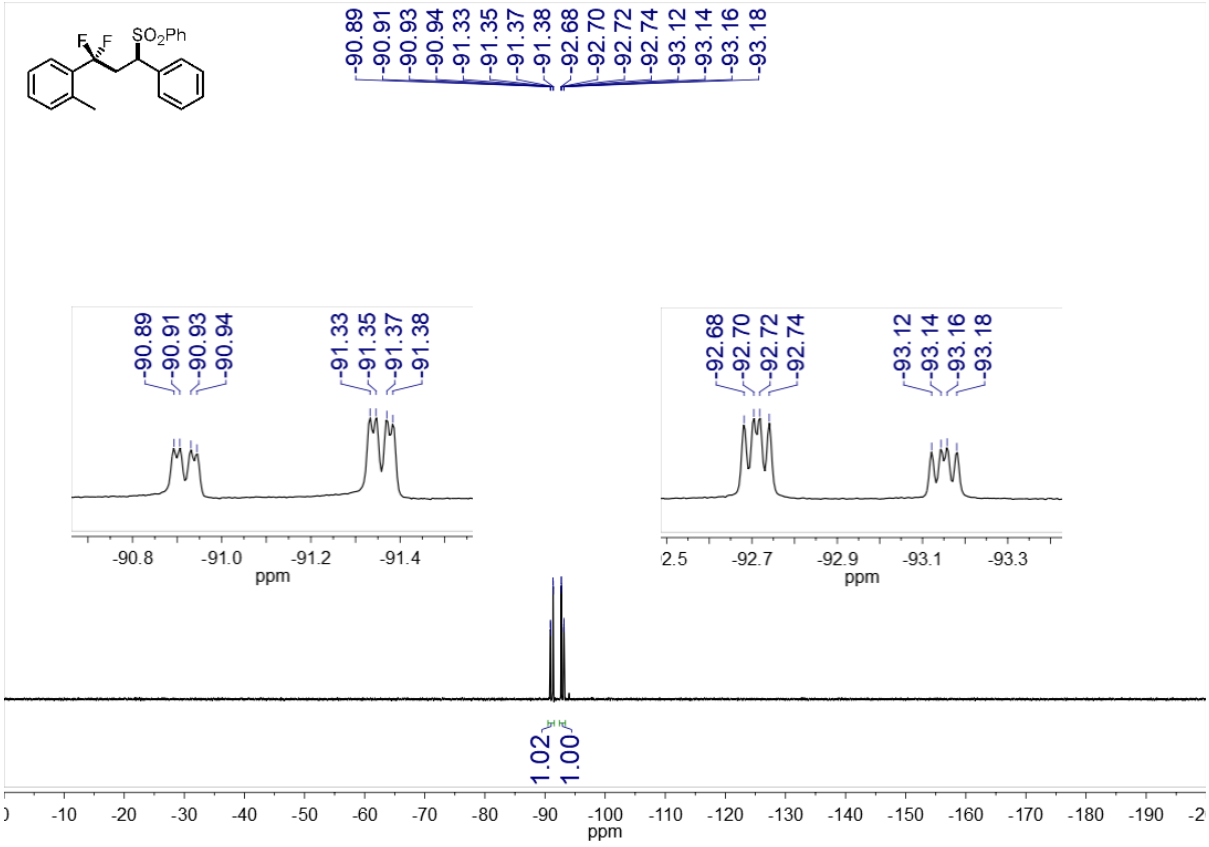
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5c**



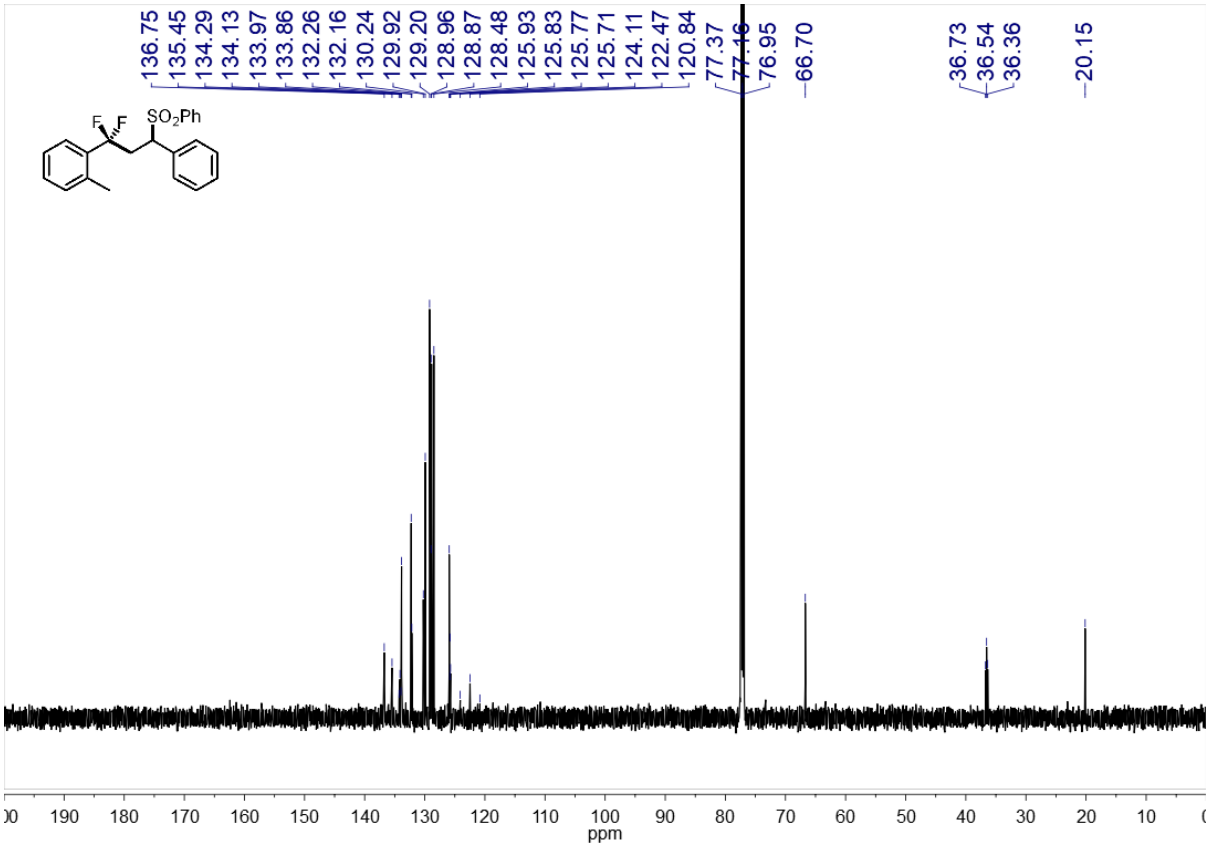
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5c**



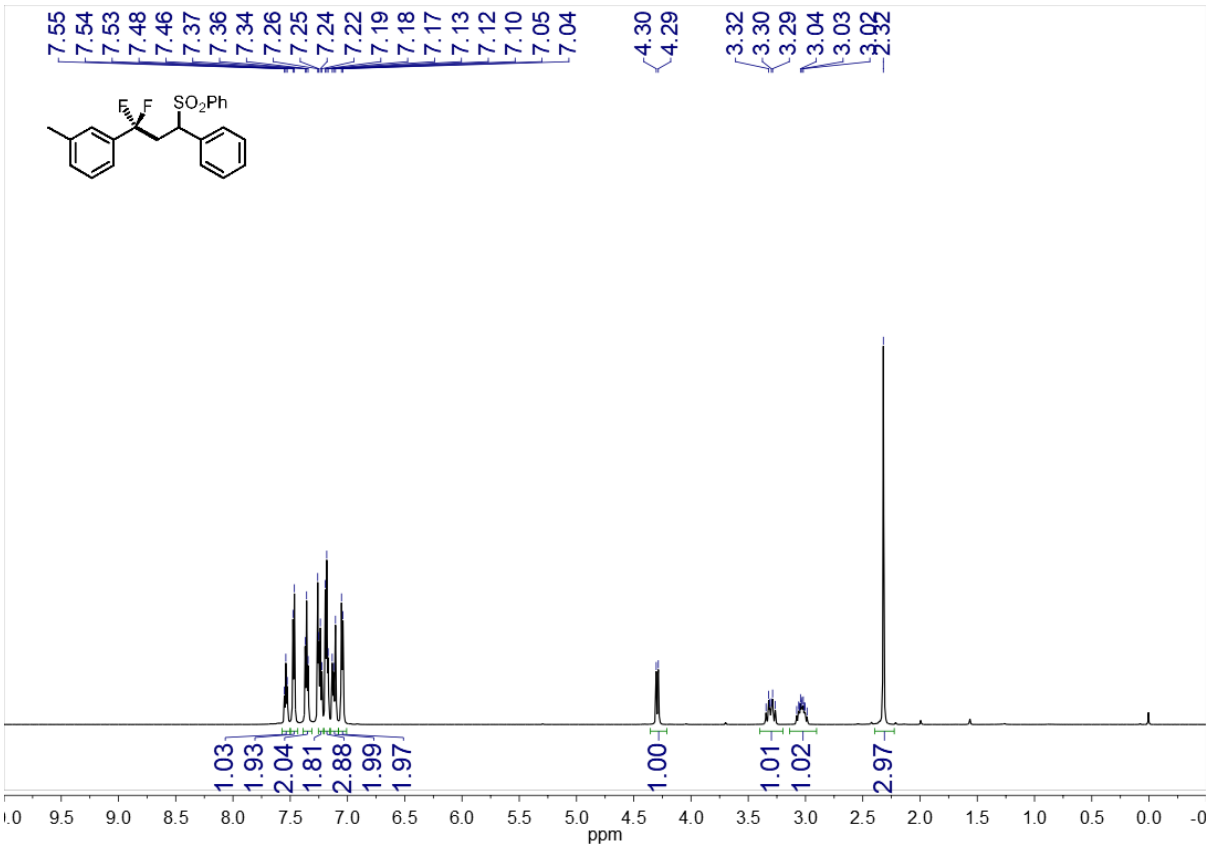
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5d**



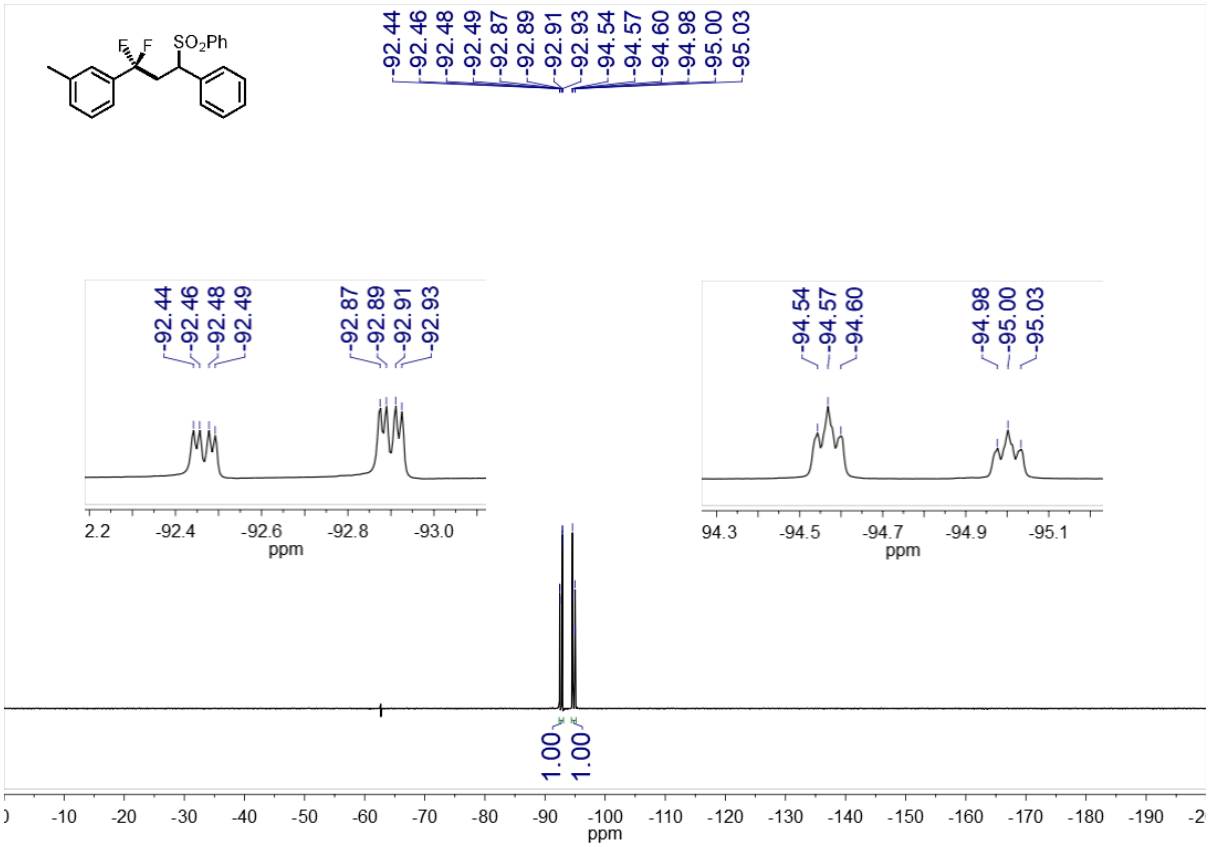
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5d**



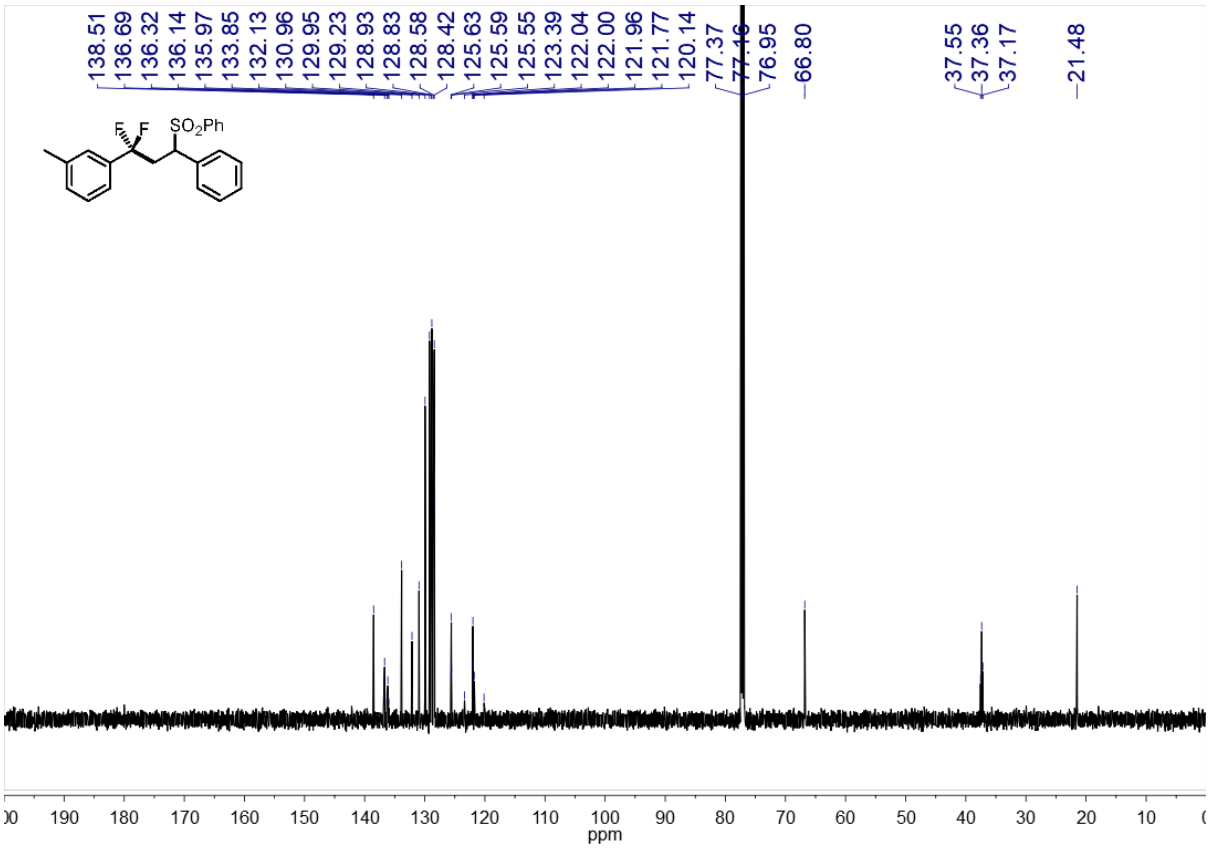
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5d**



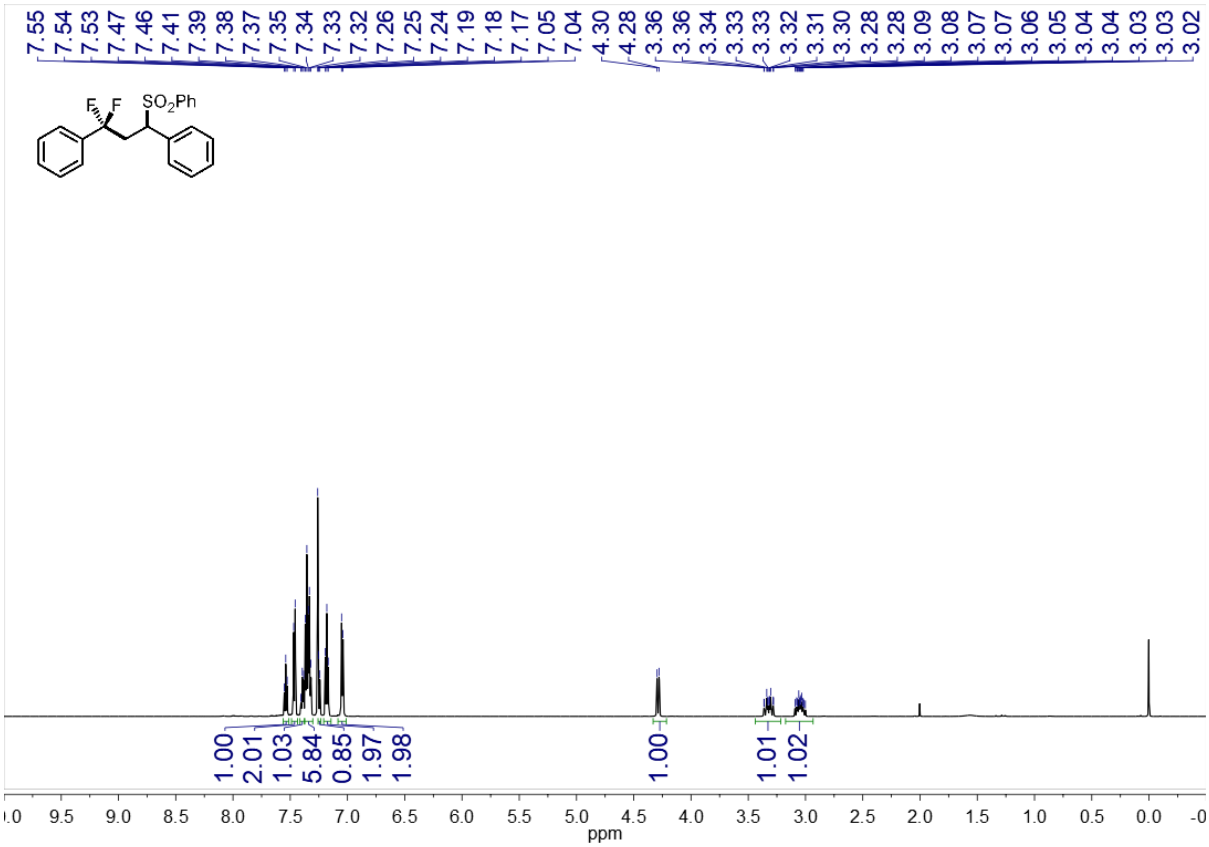
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5e**



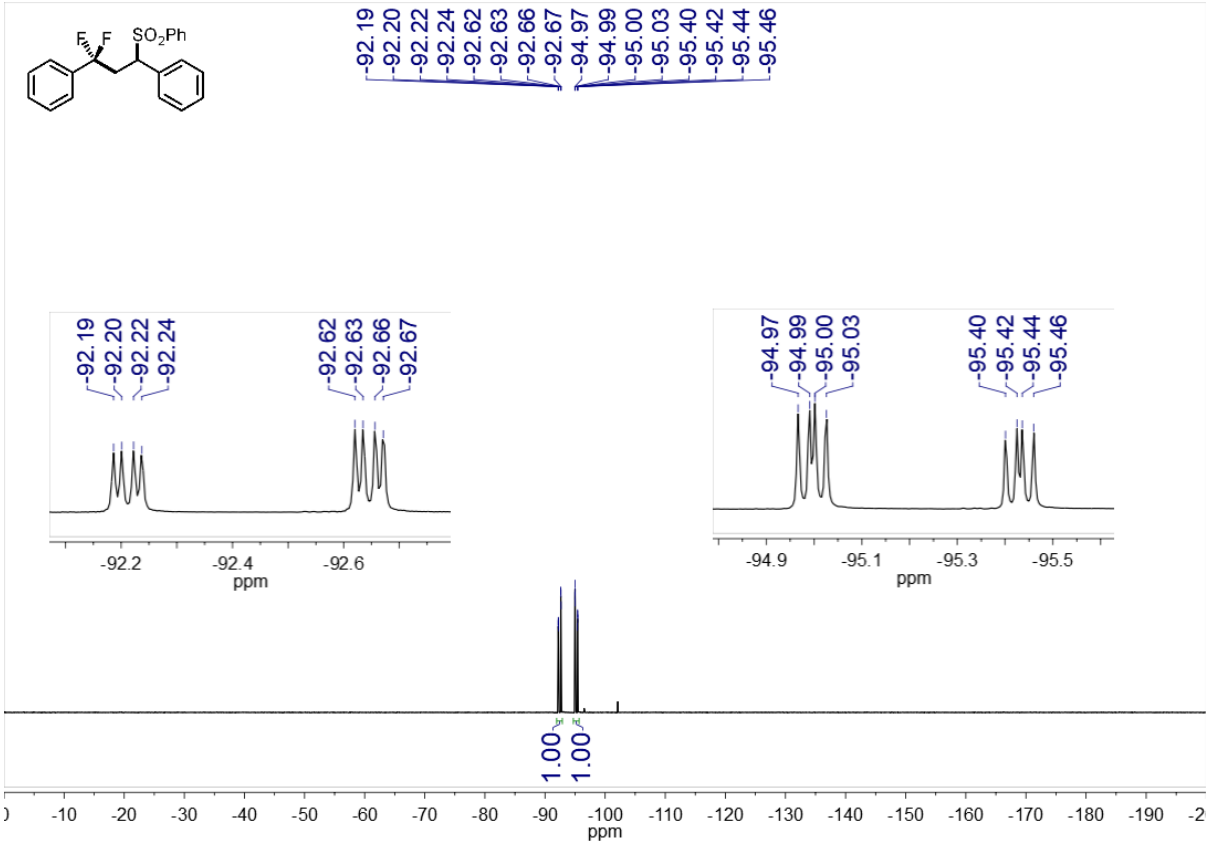
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5e**



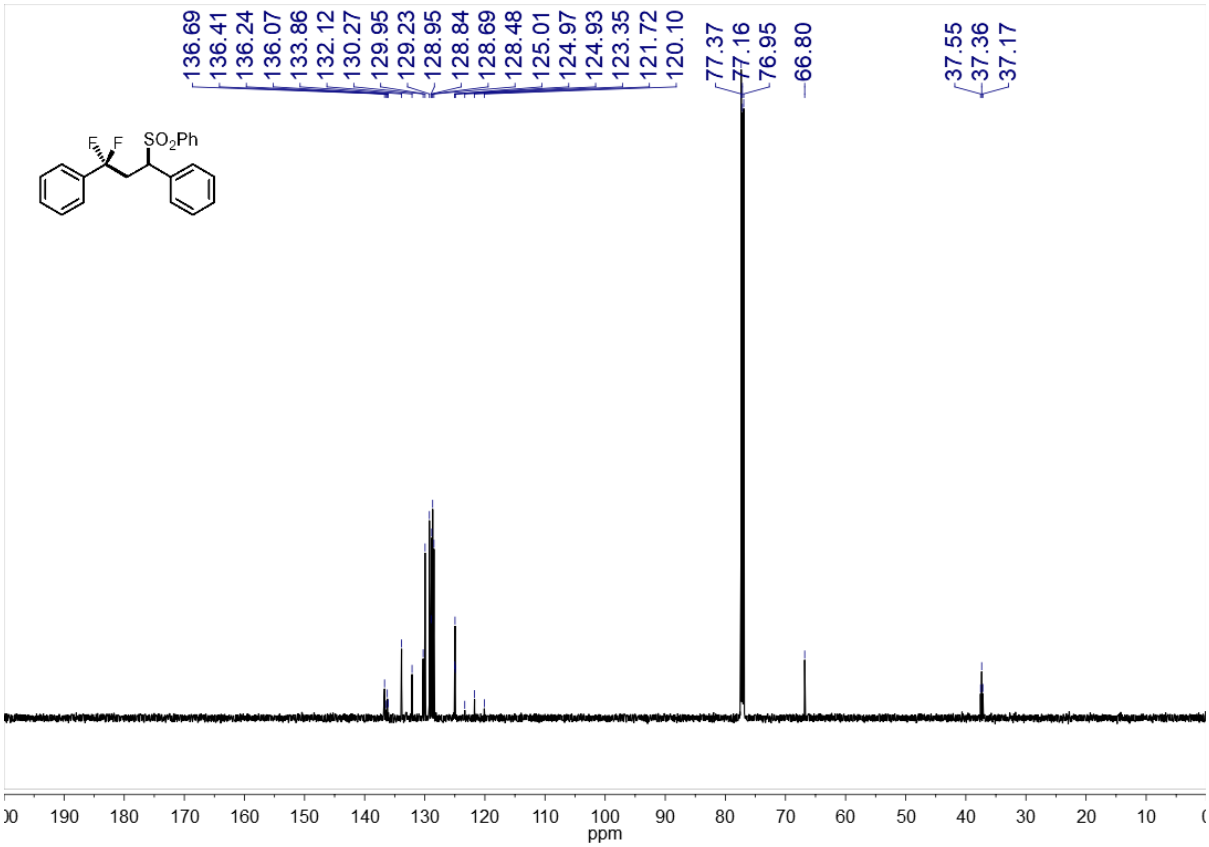
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5e**



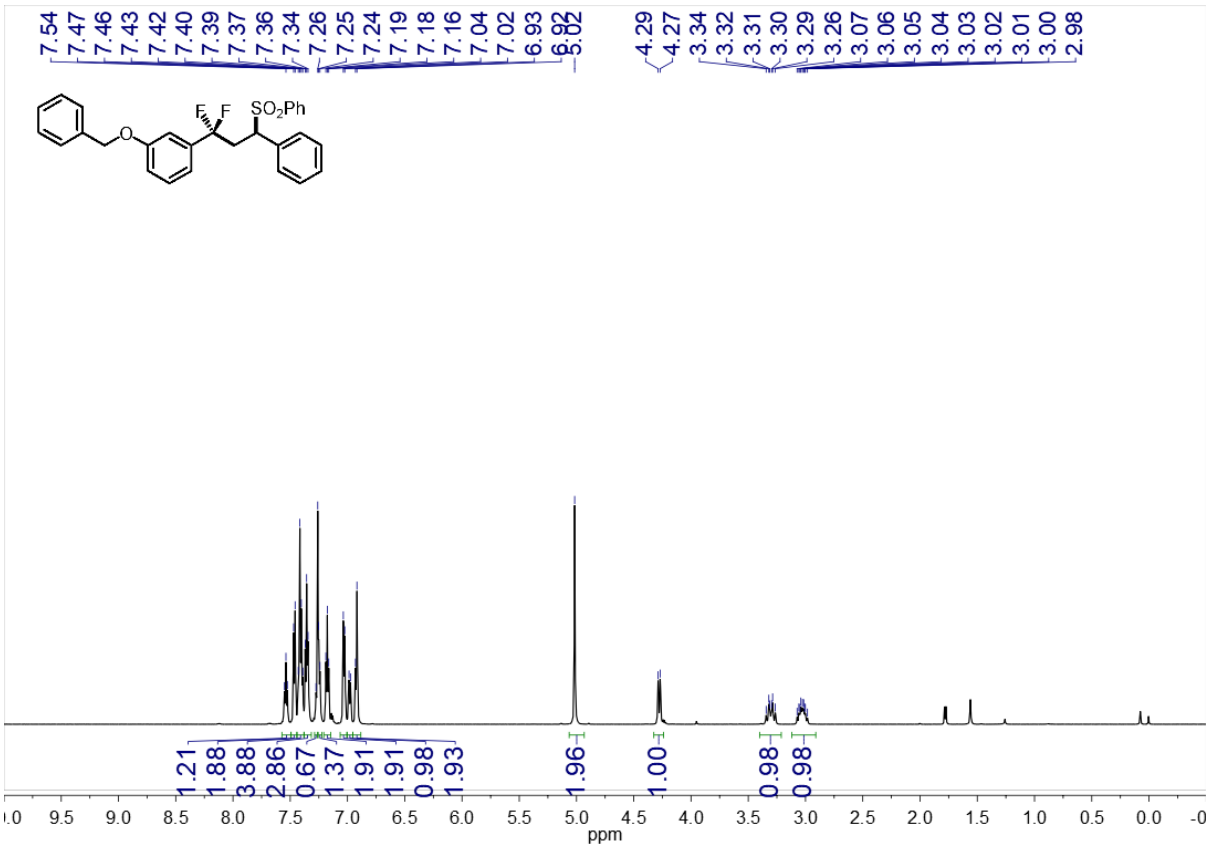
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5f**



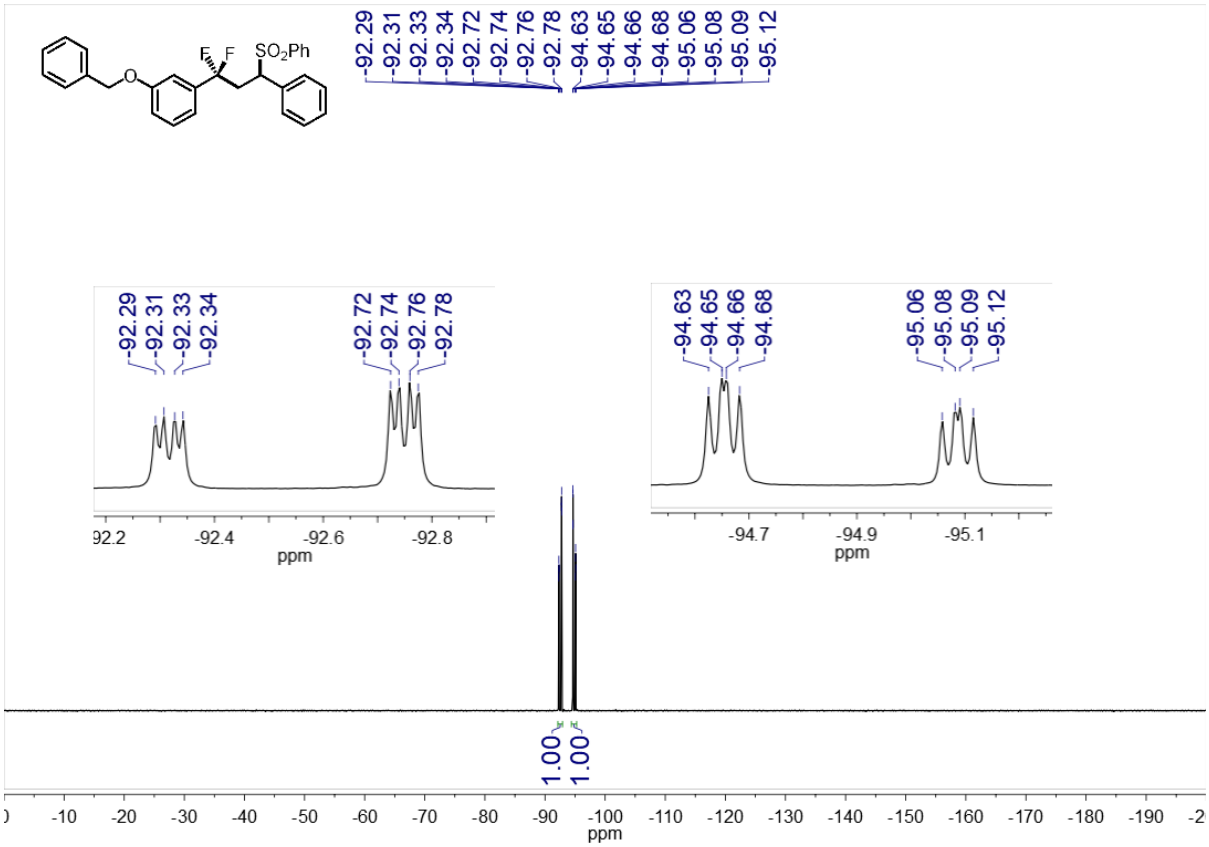
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5f**



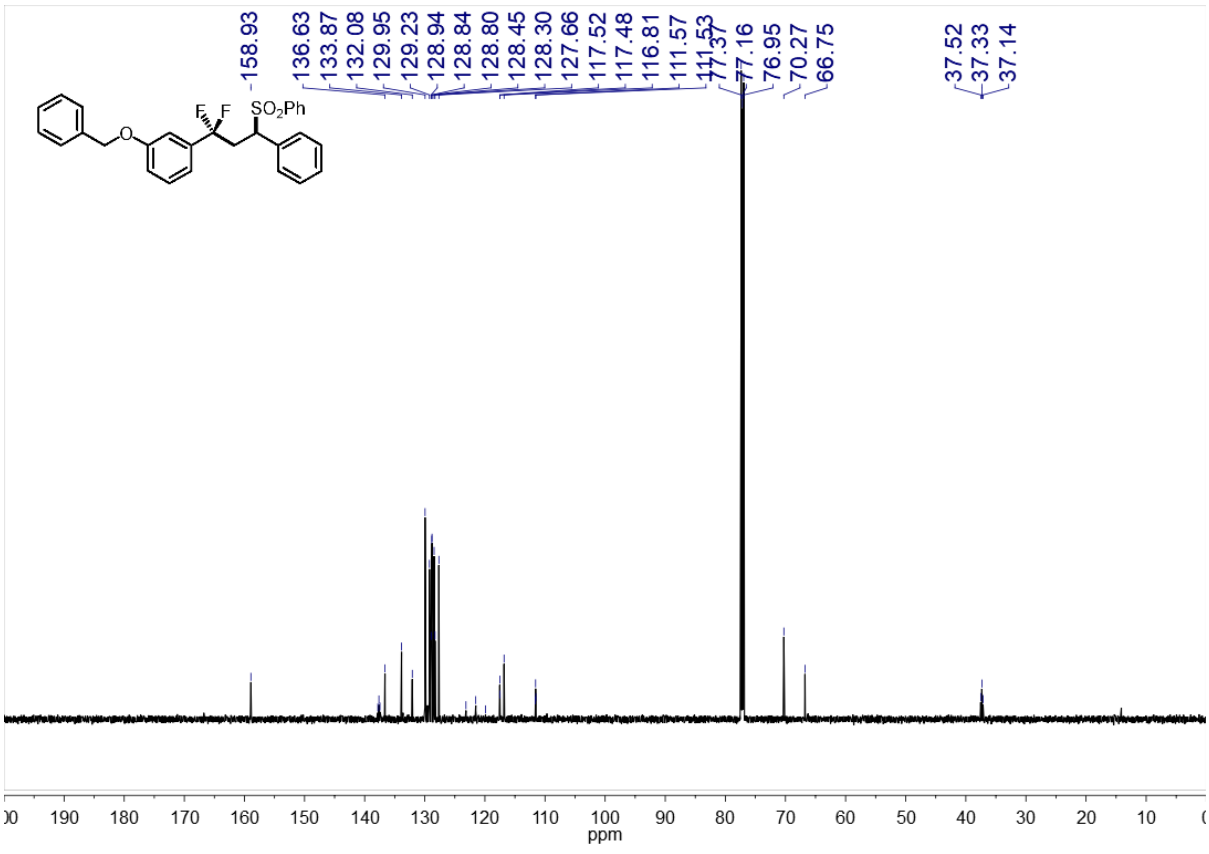
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5f**



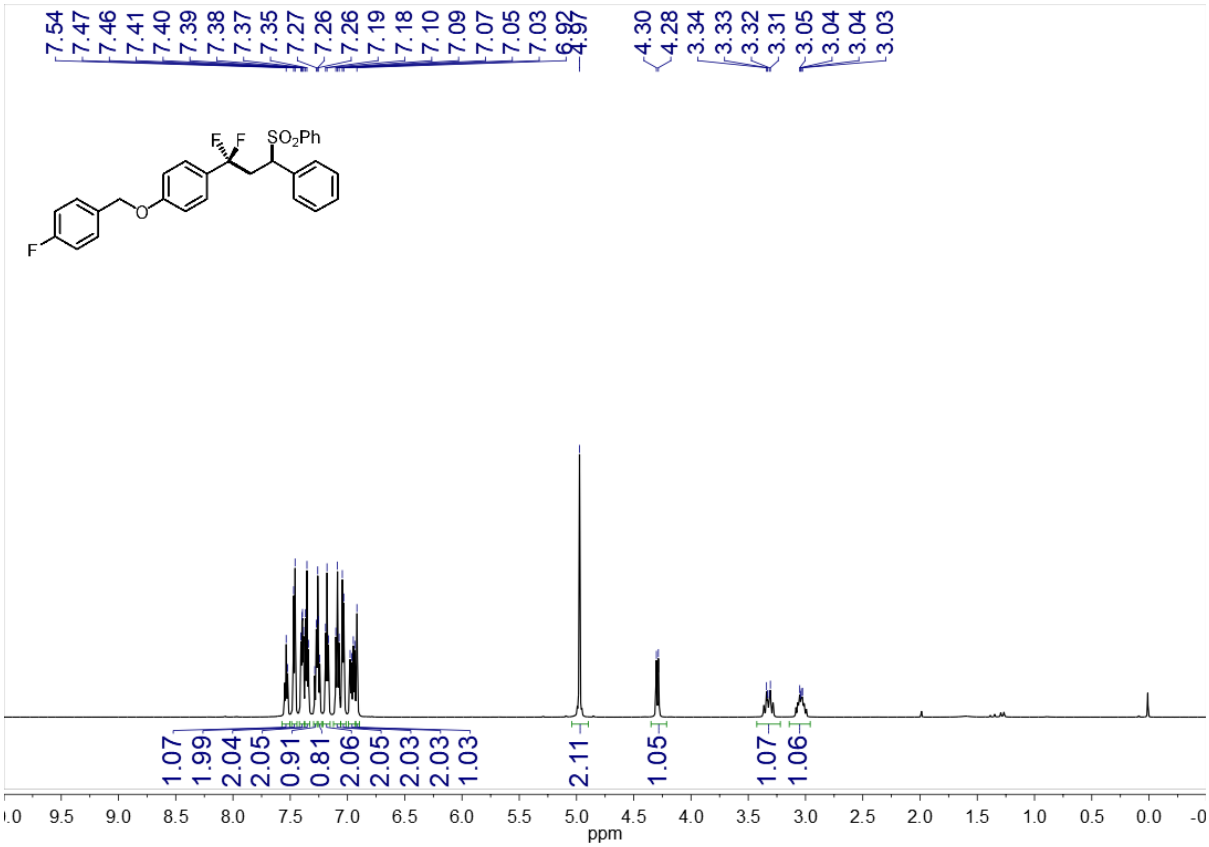
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5g**



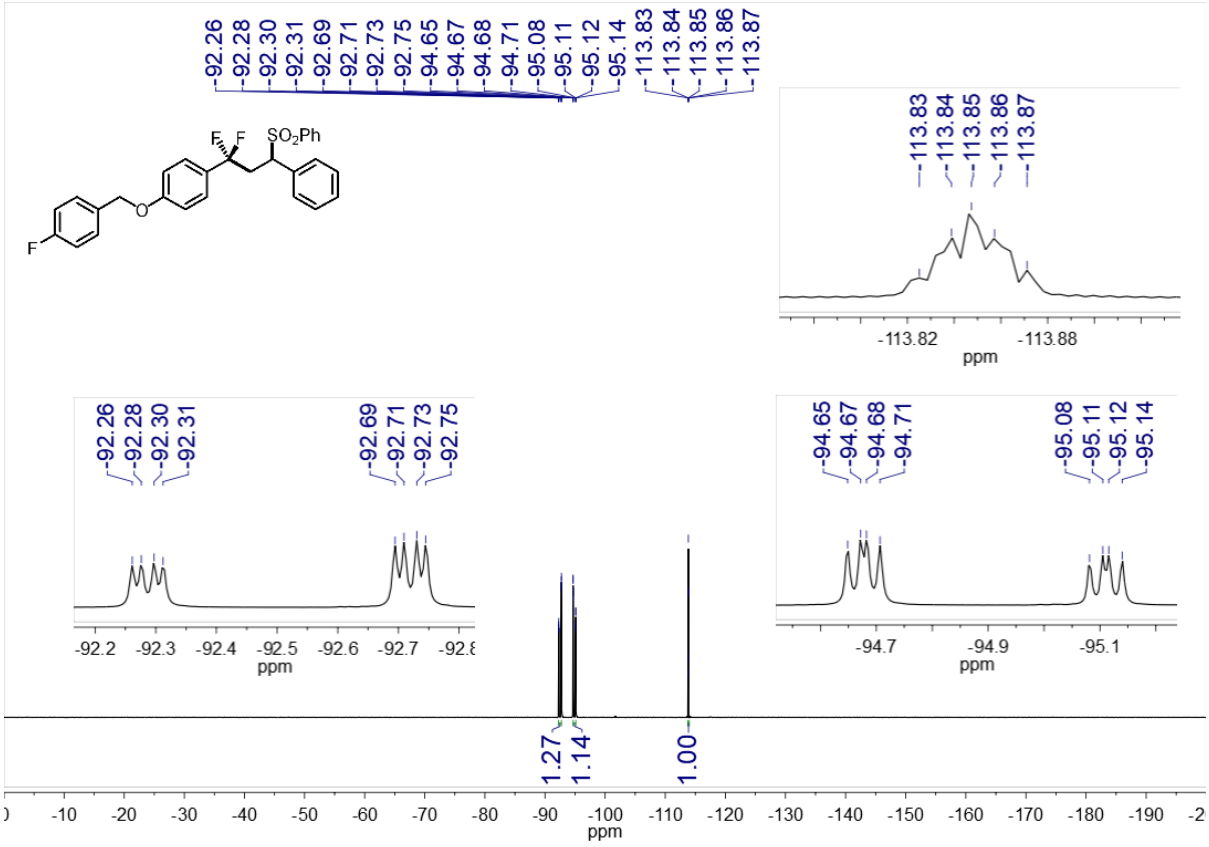
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5g**



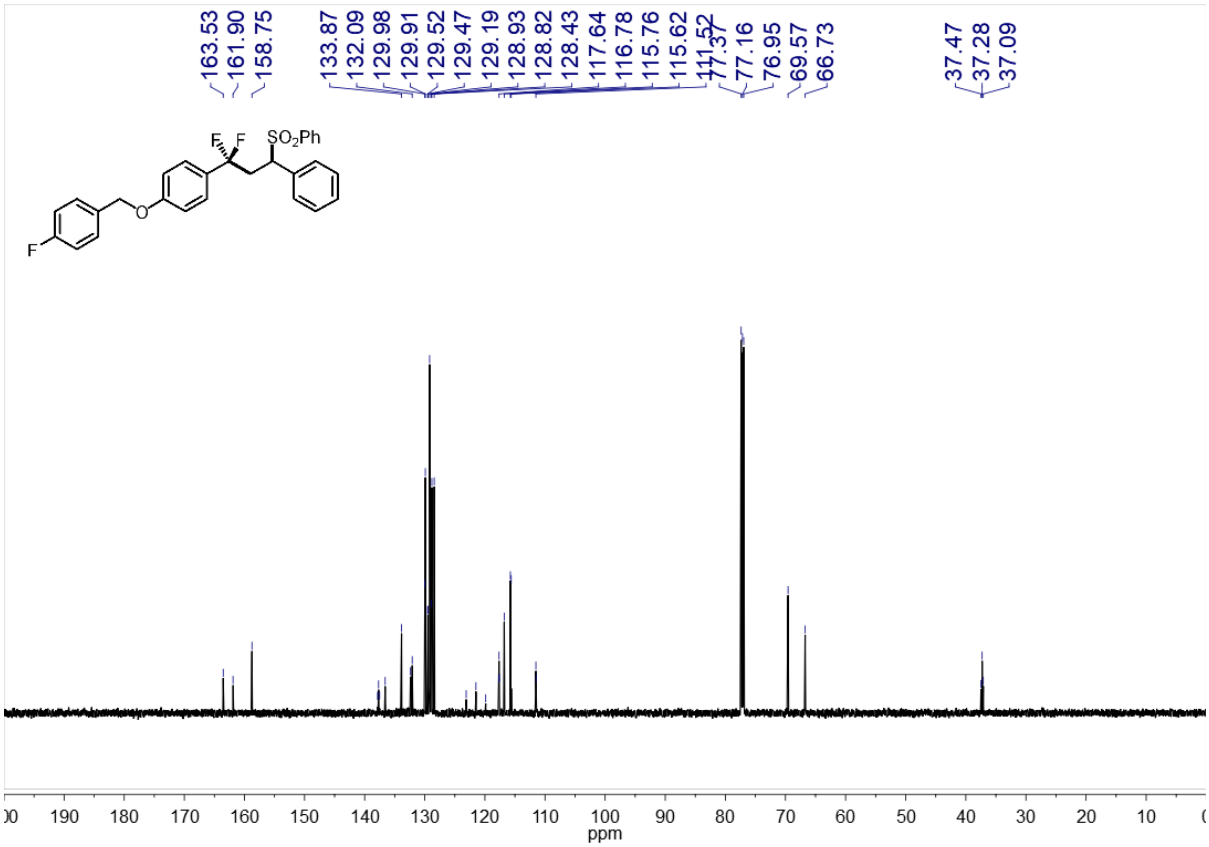
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5g**



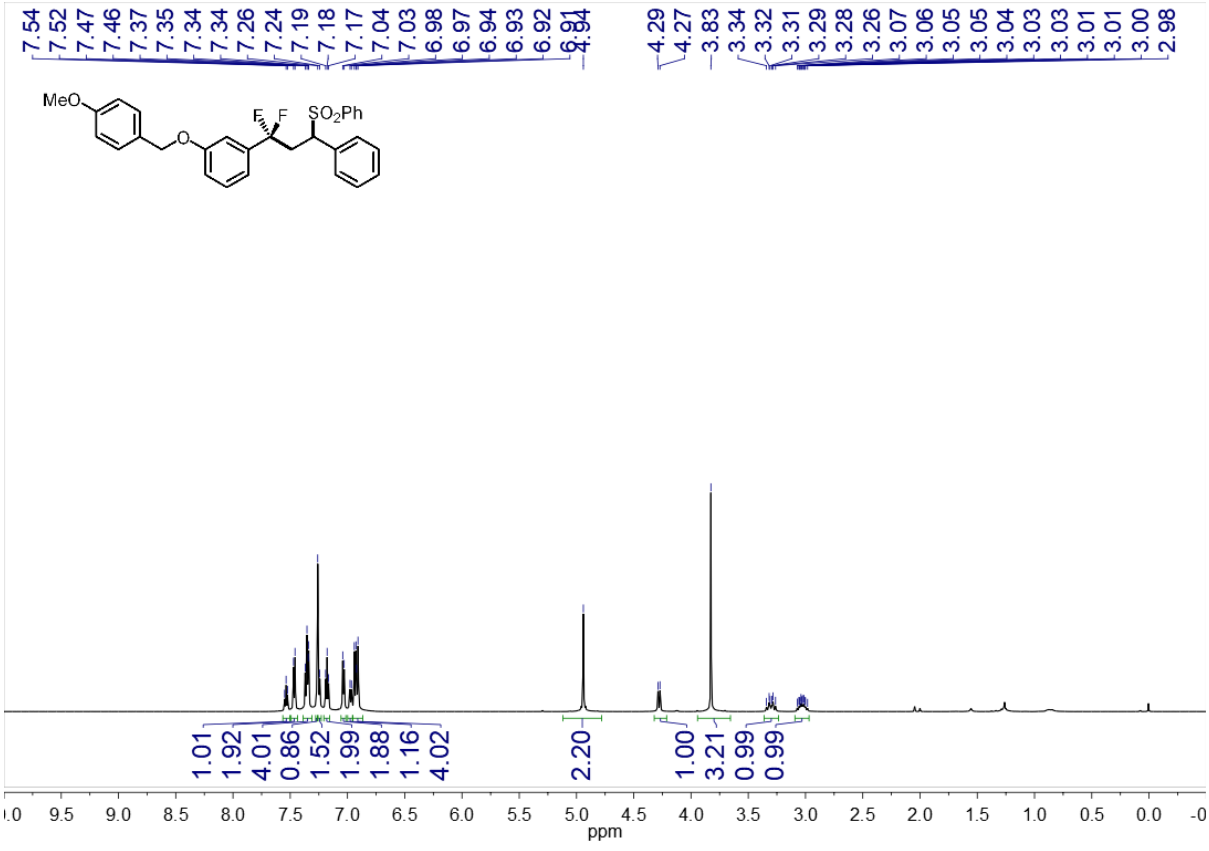
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5h**



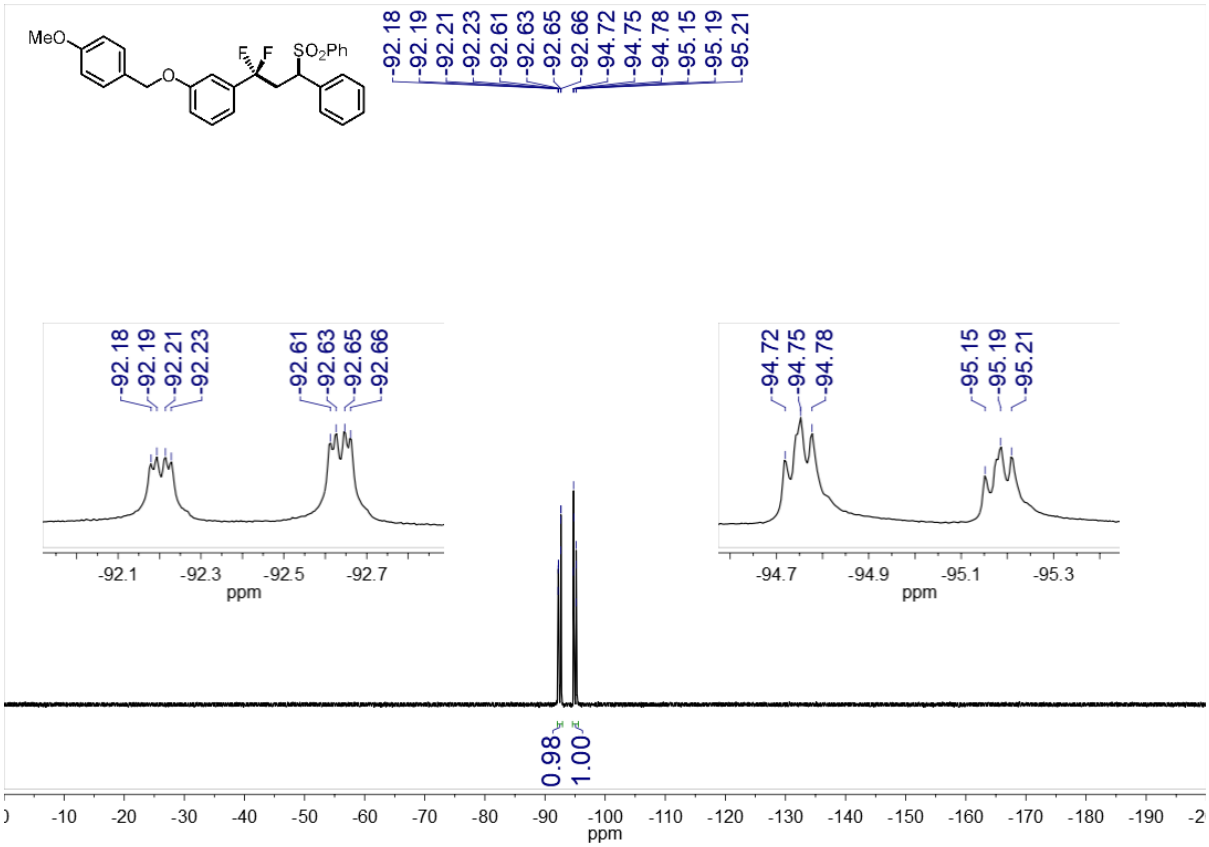
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5h**



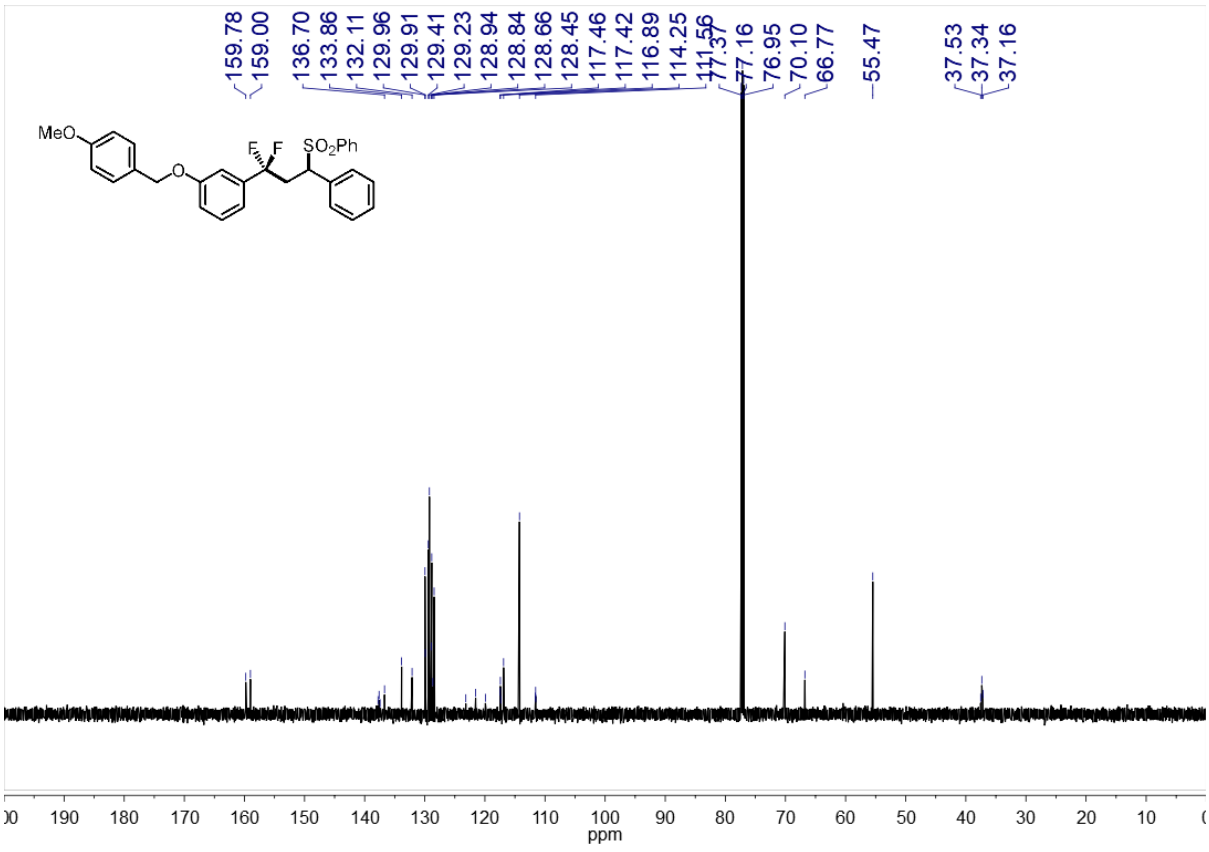
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5h**



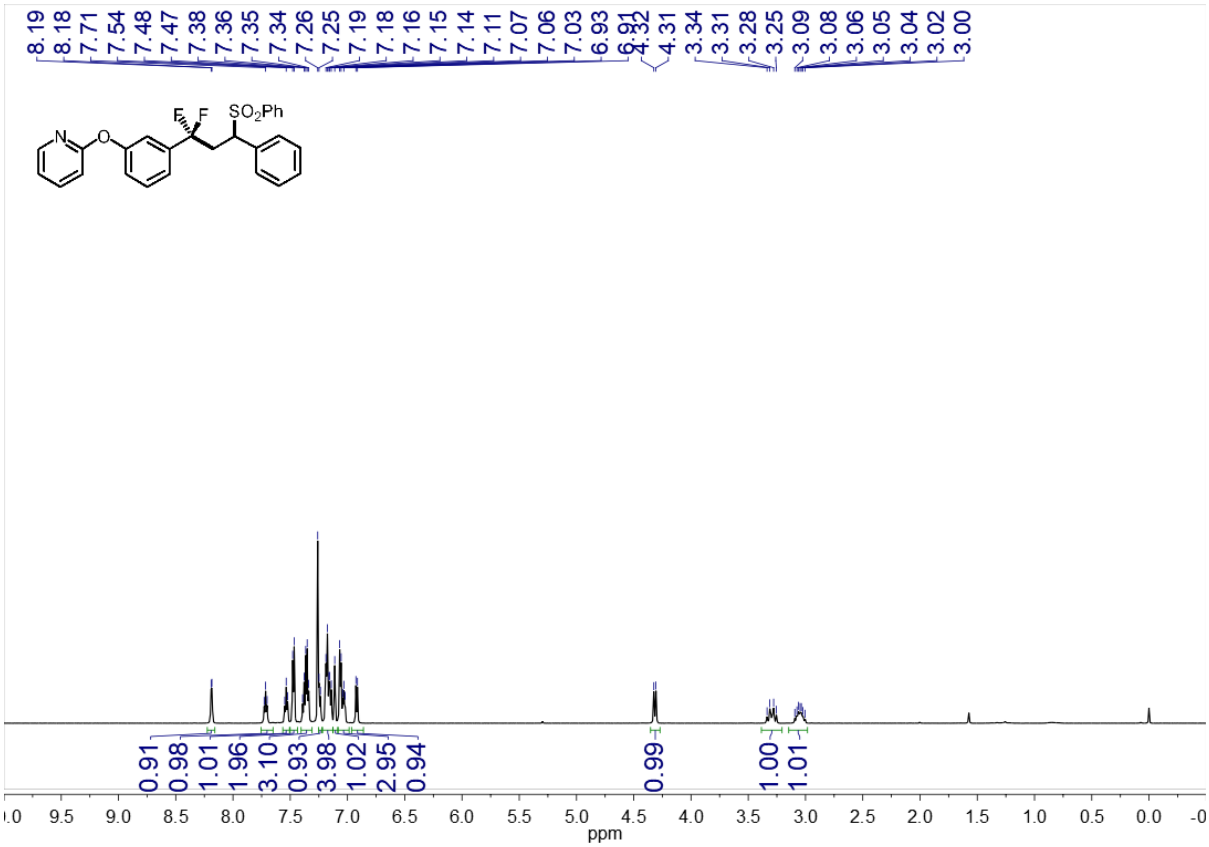
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5i**



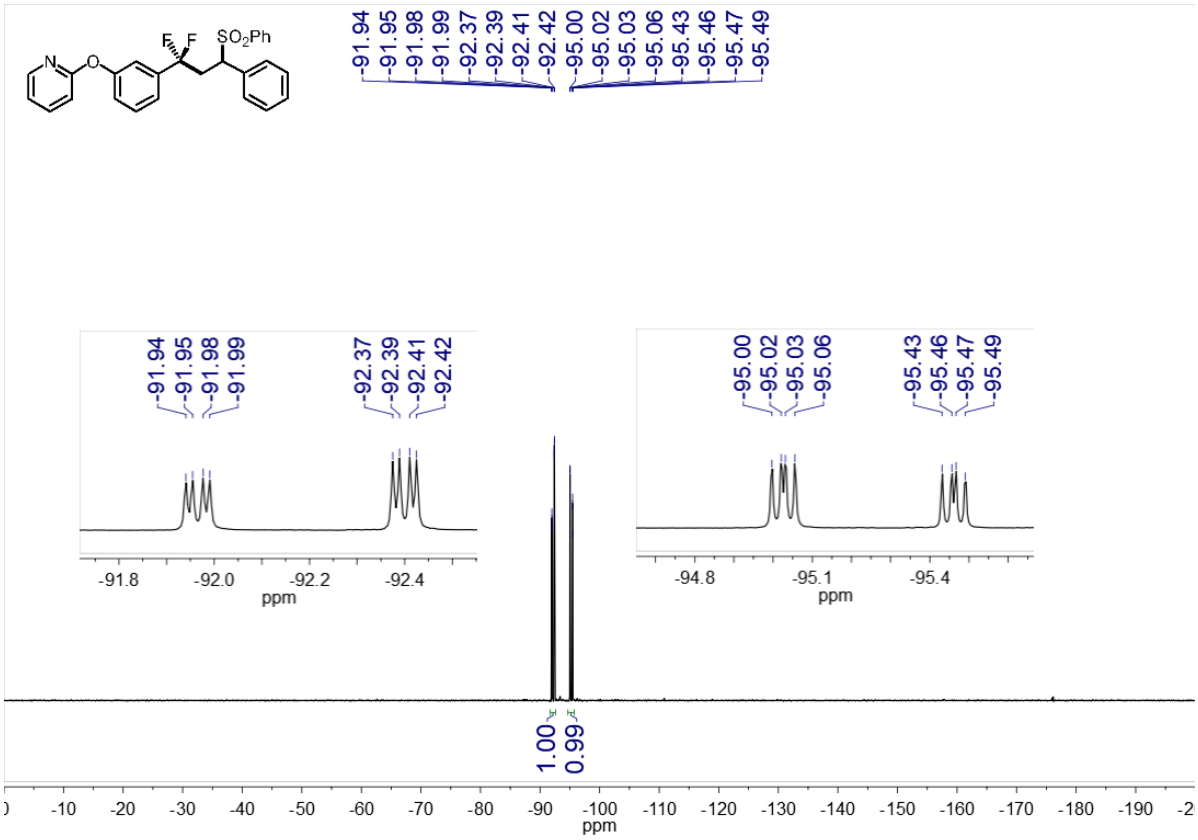
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5i**



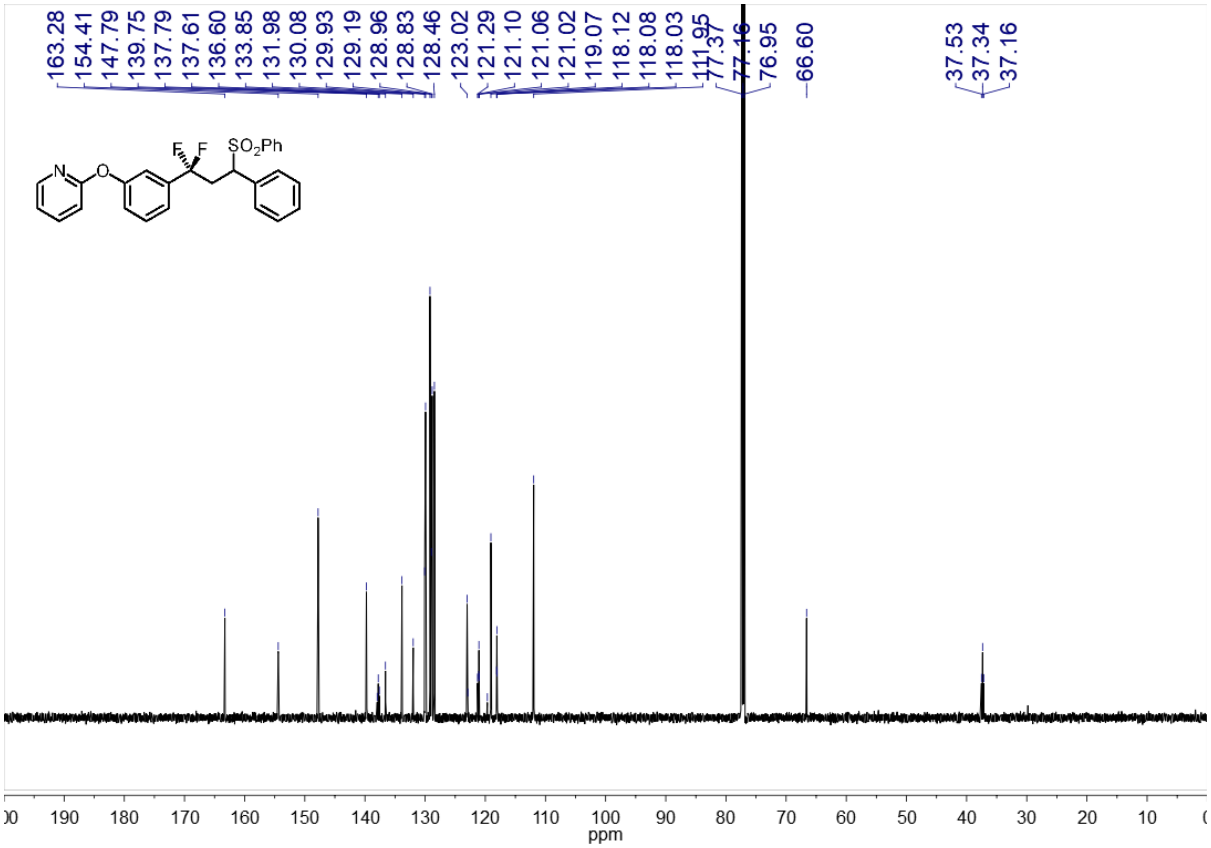
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5i**



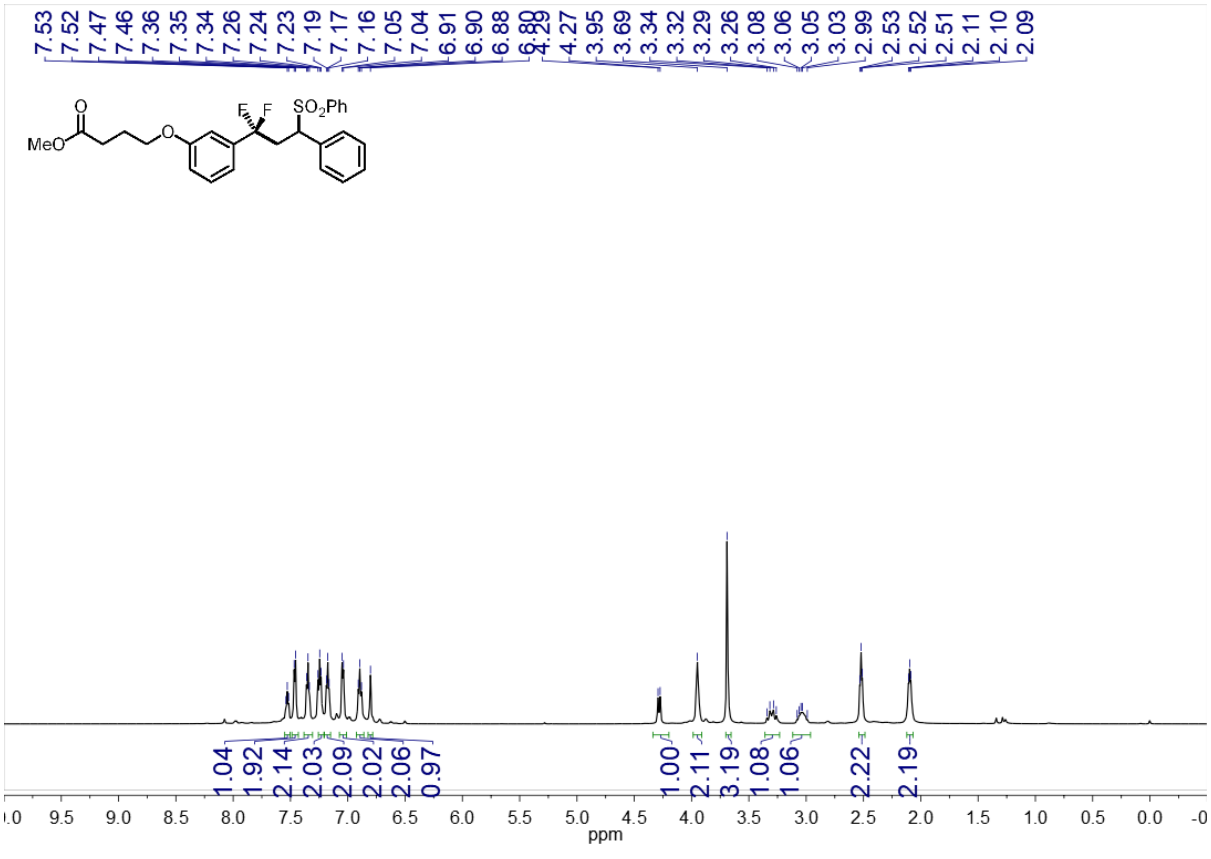
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5j**



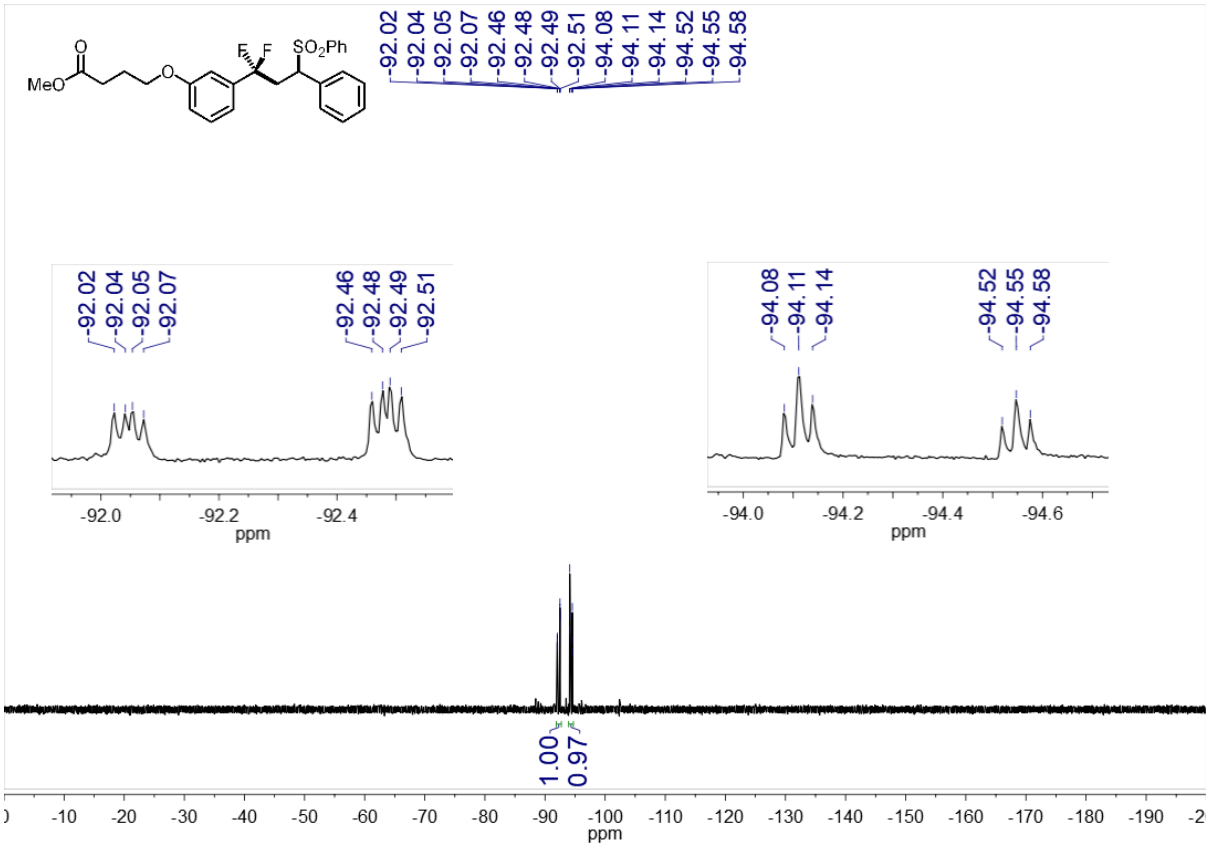
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5j**



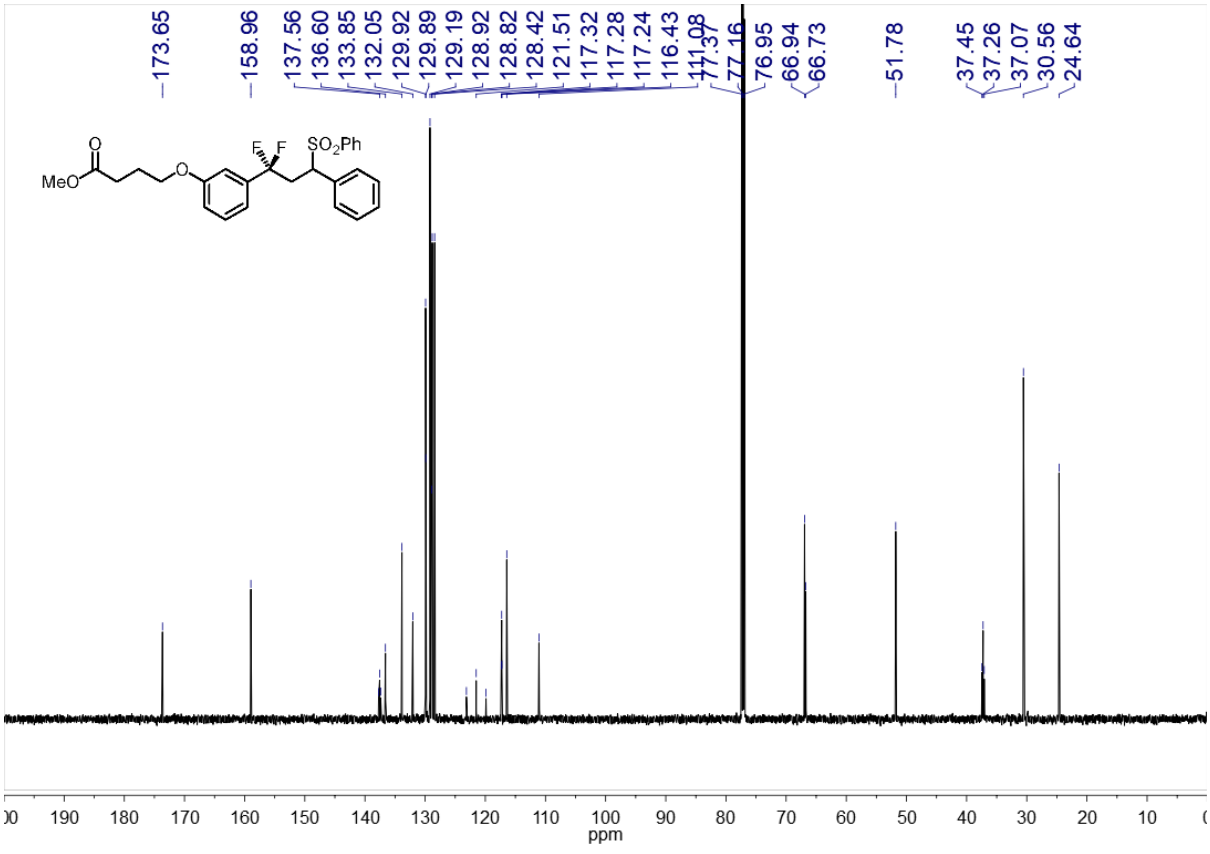
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5j**



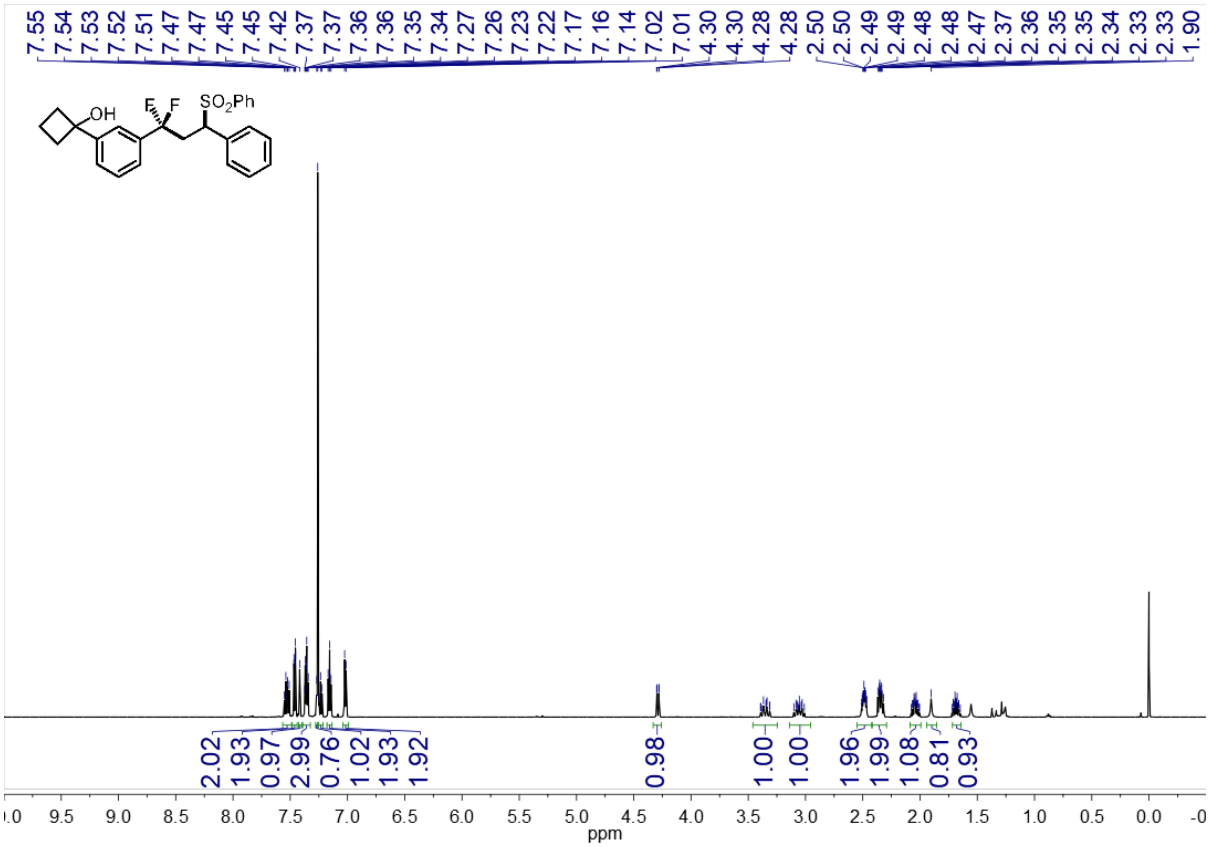
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5k**



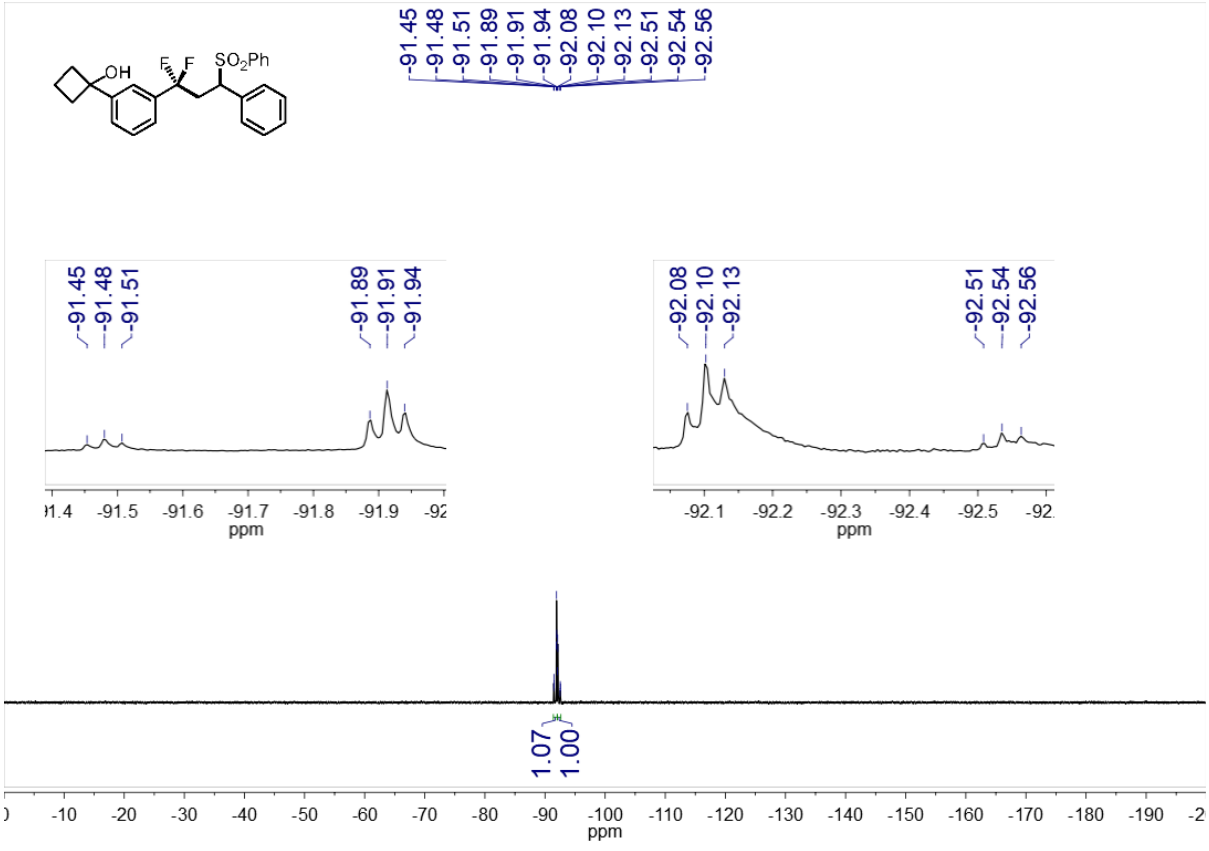
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5k**



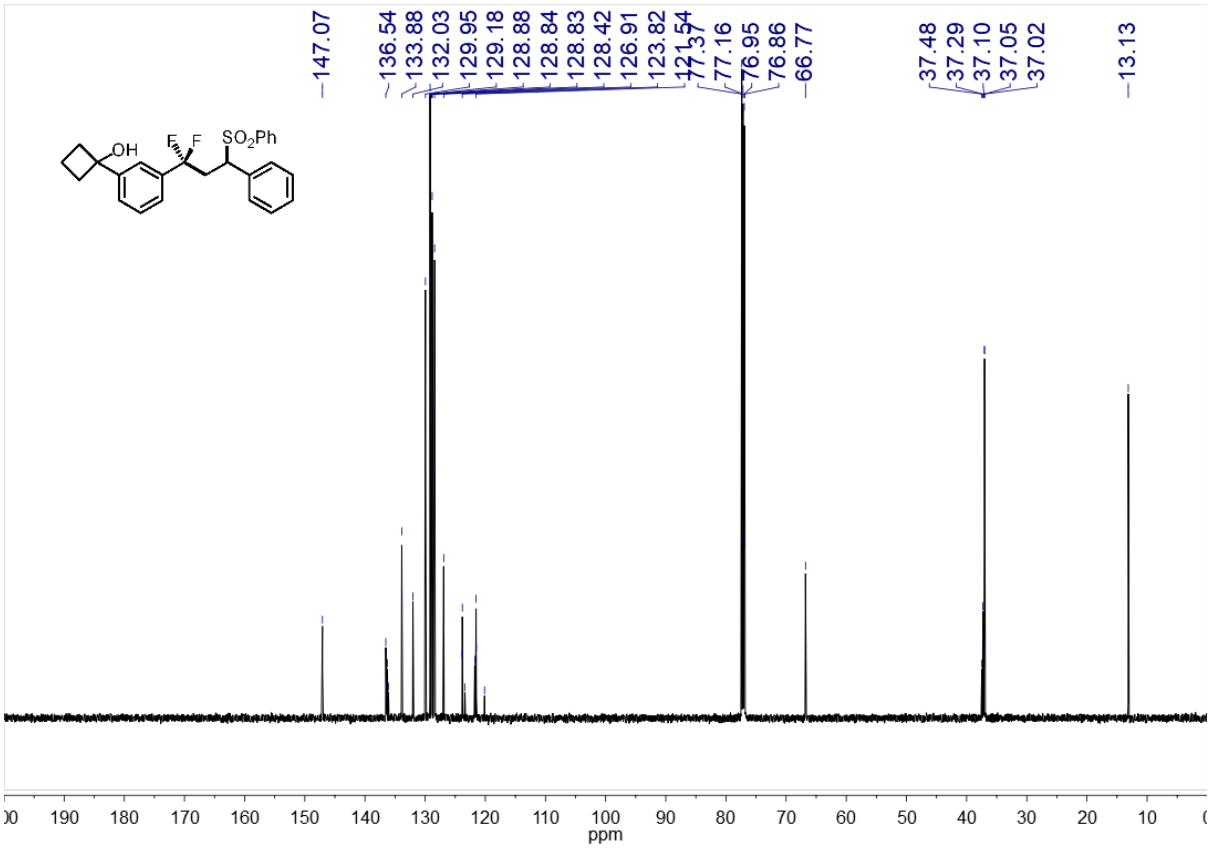
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5k**



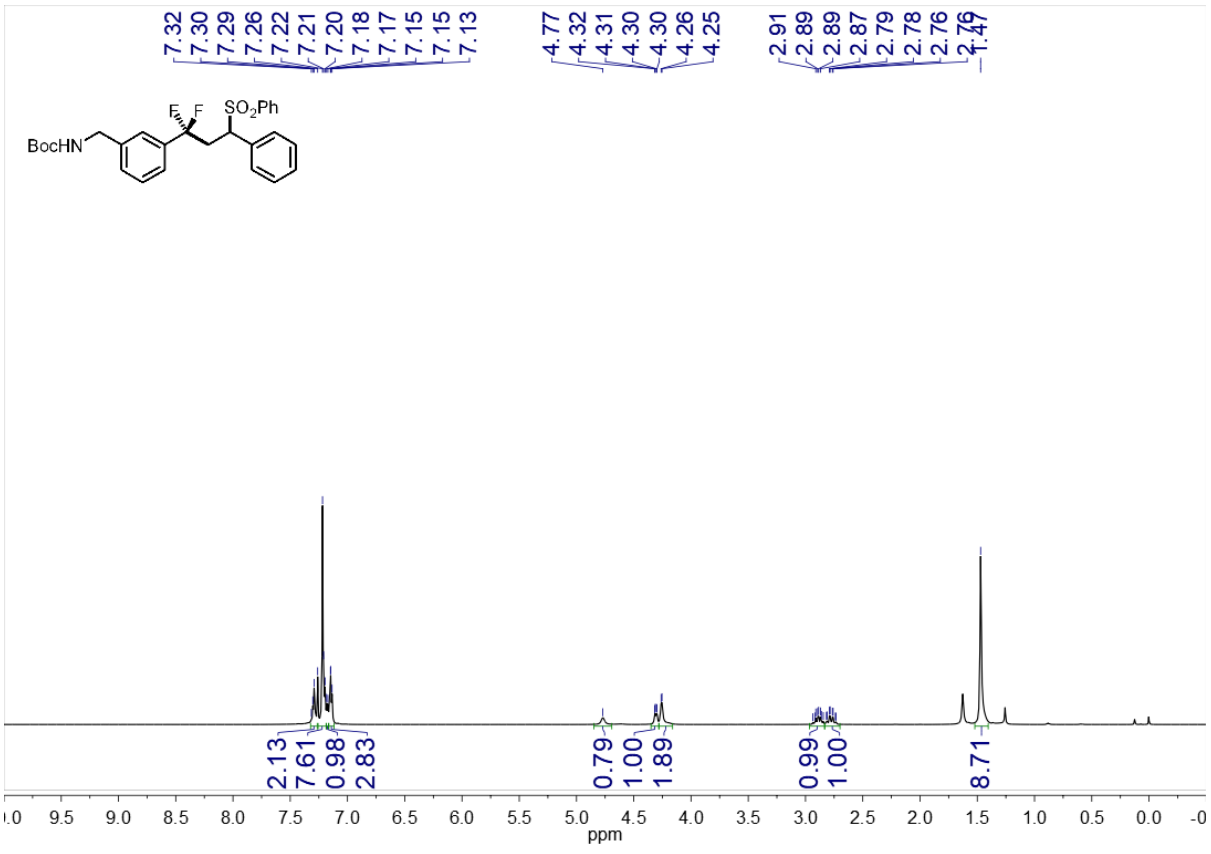
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5l**



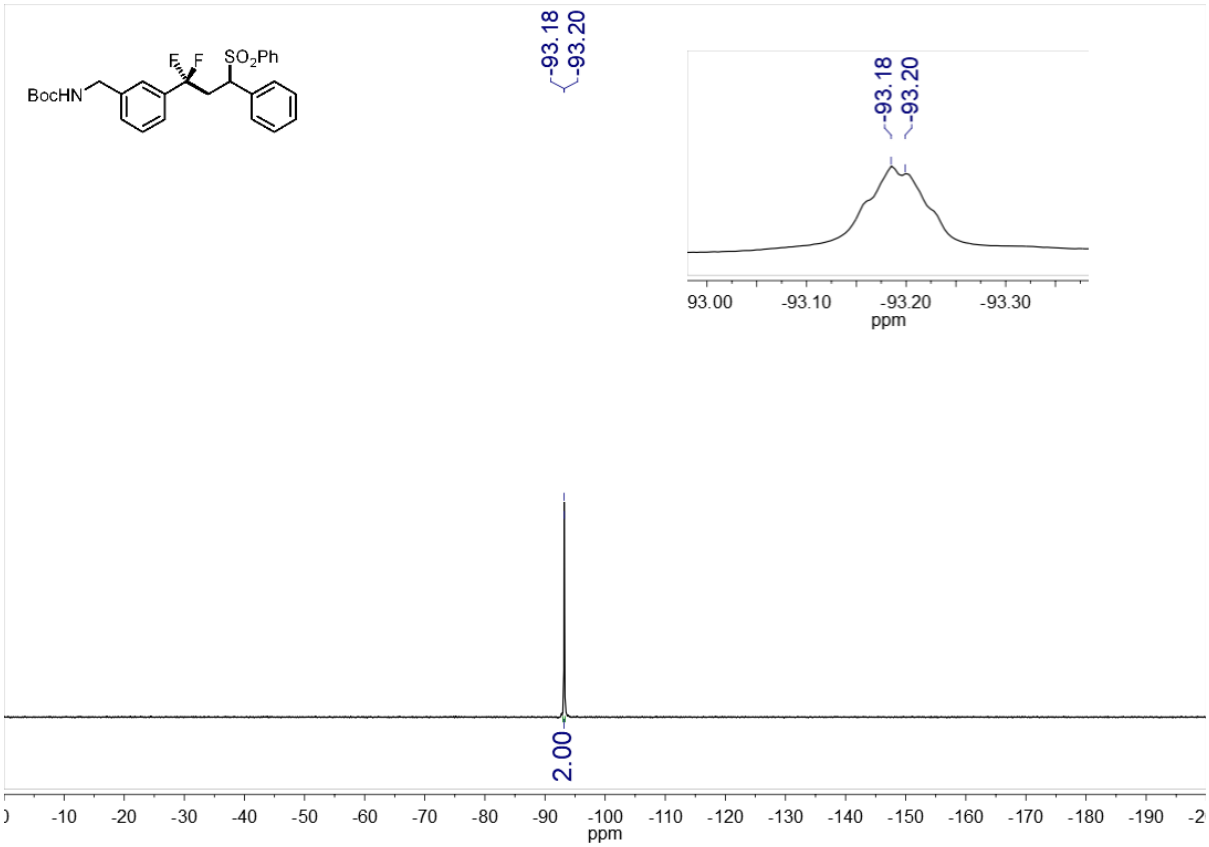
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5l**



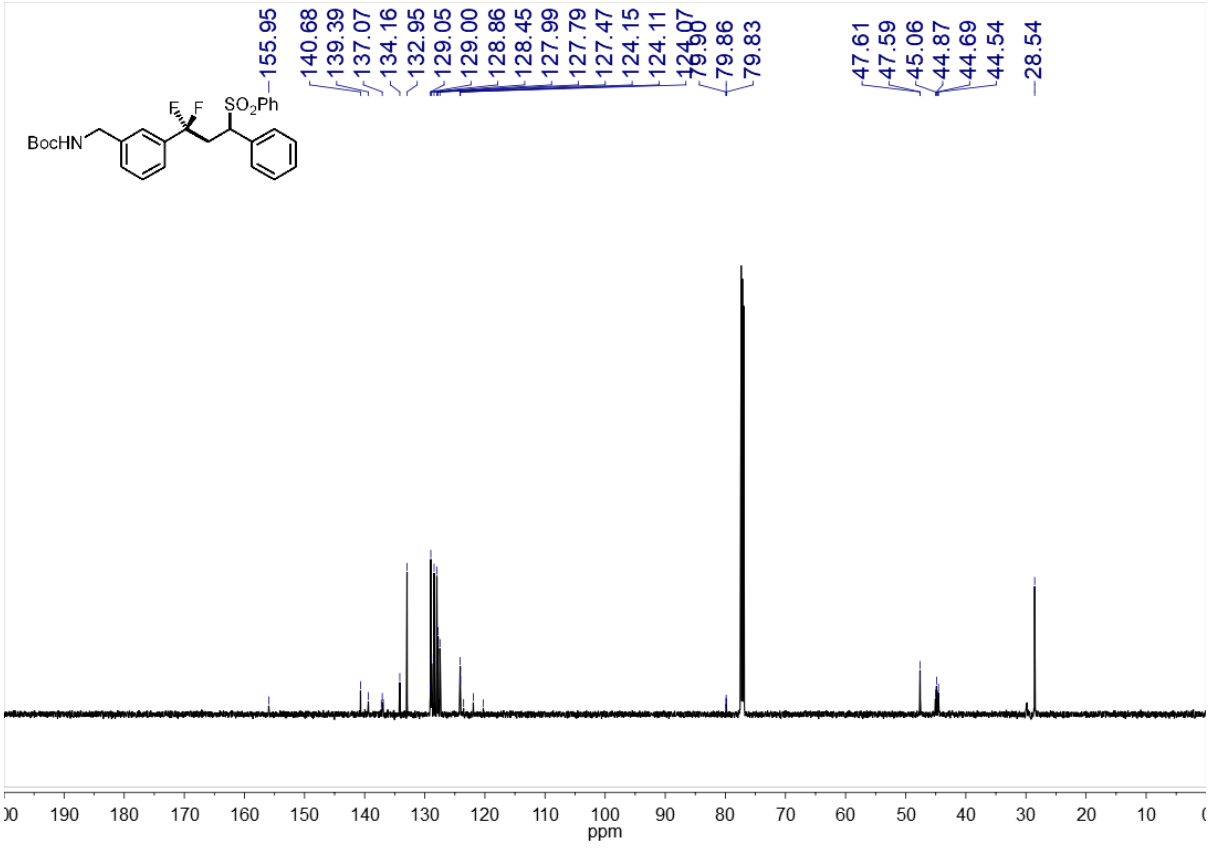
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5l**



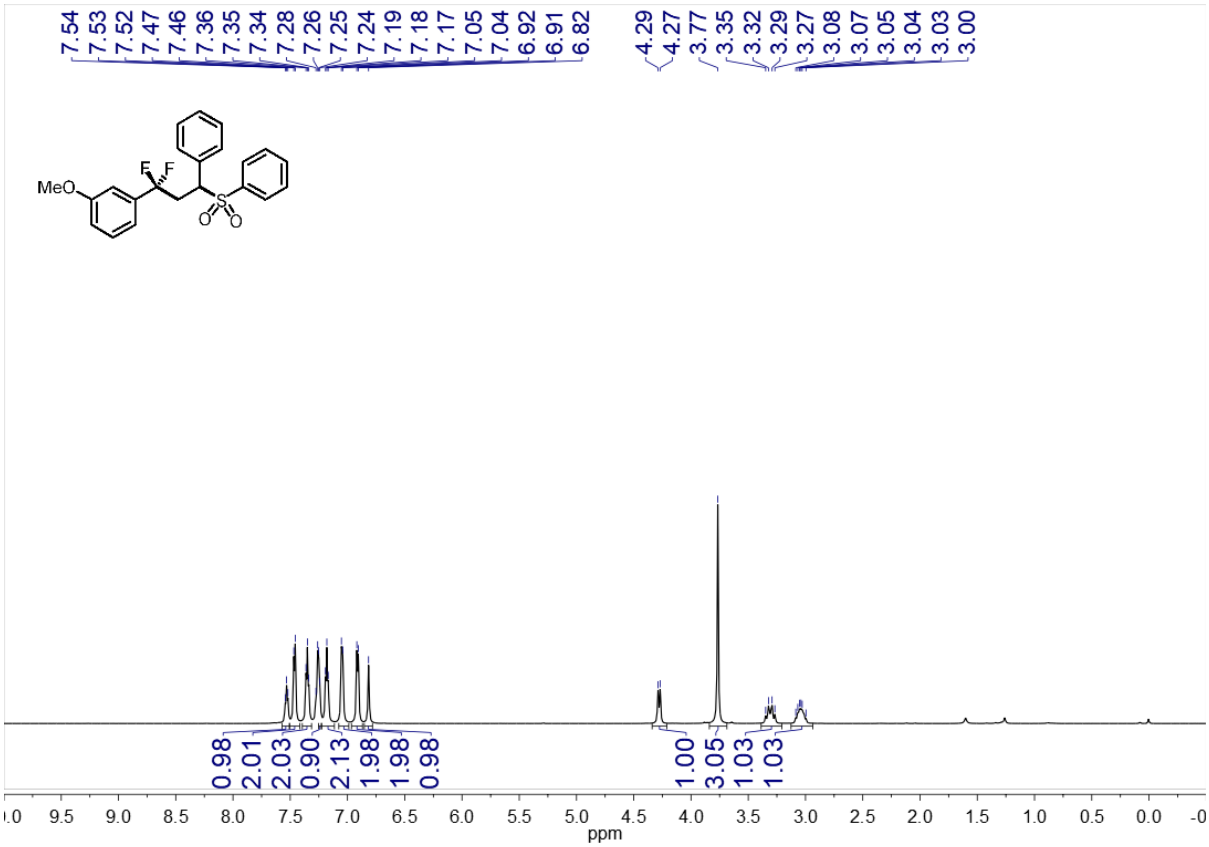
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5m**



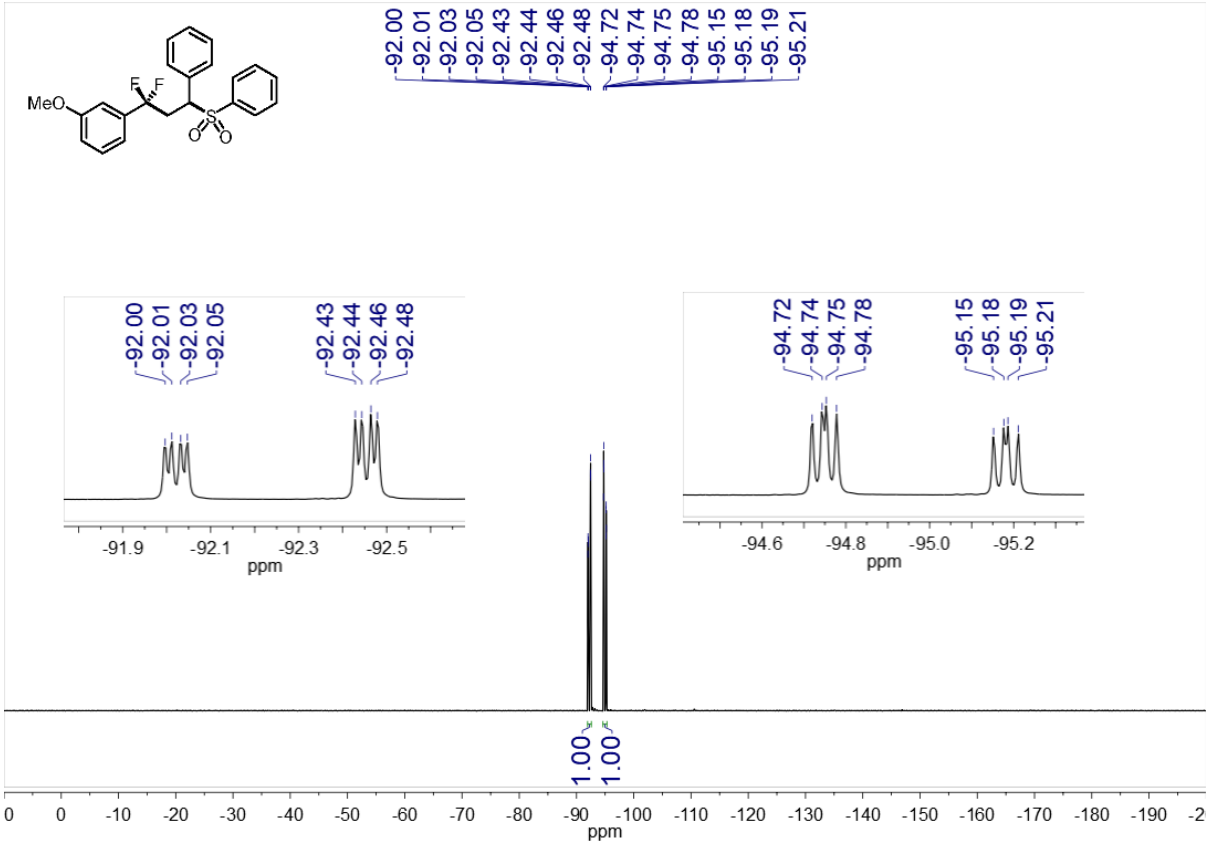
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5m**



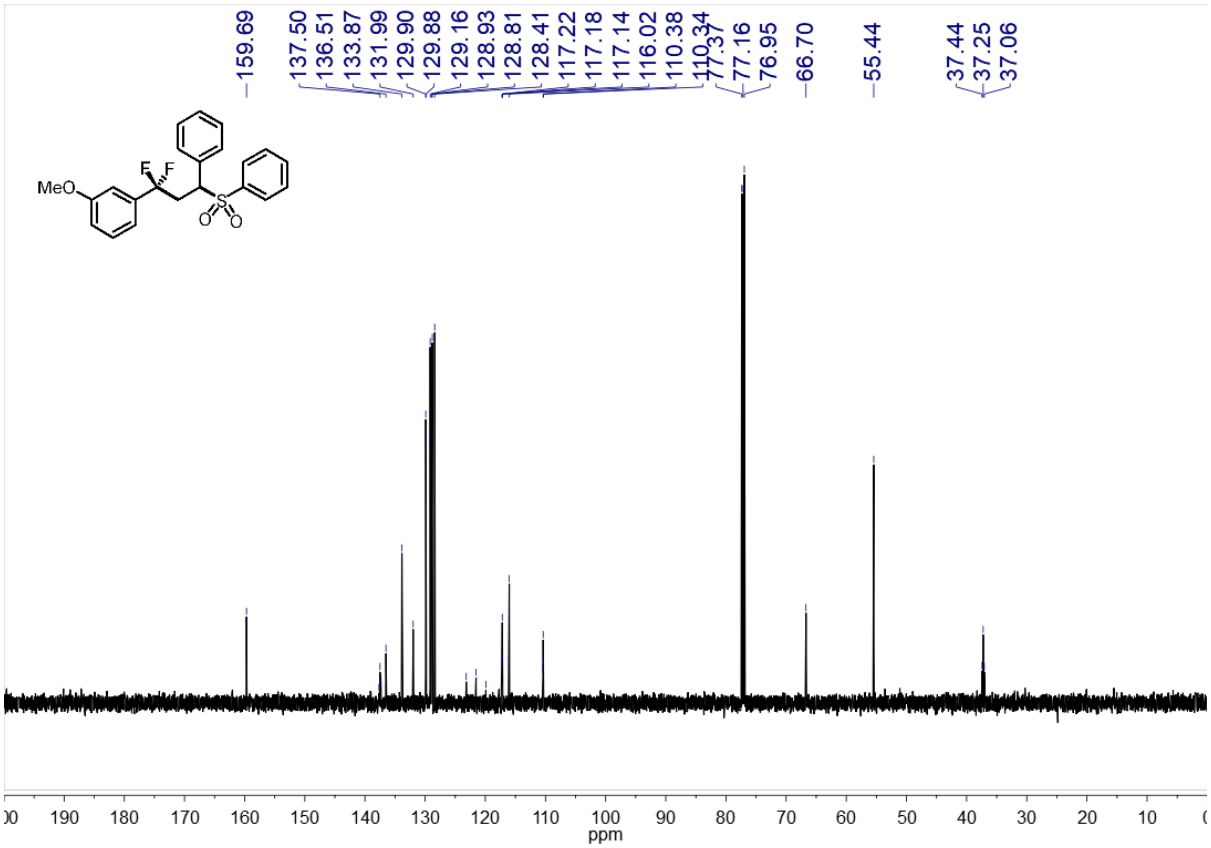
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5m**



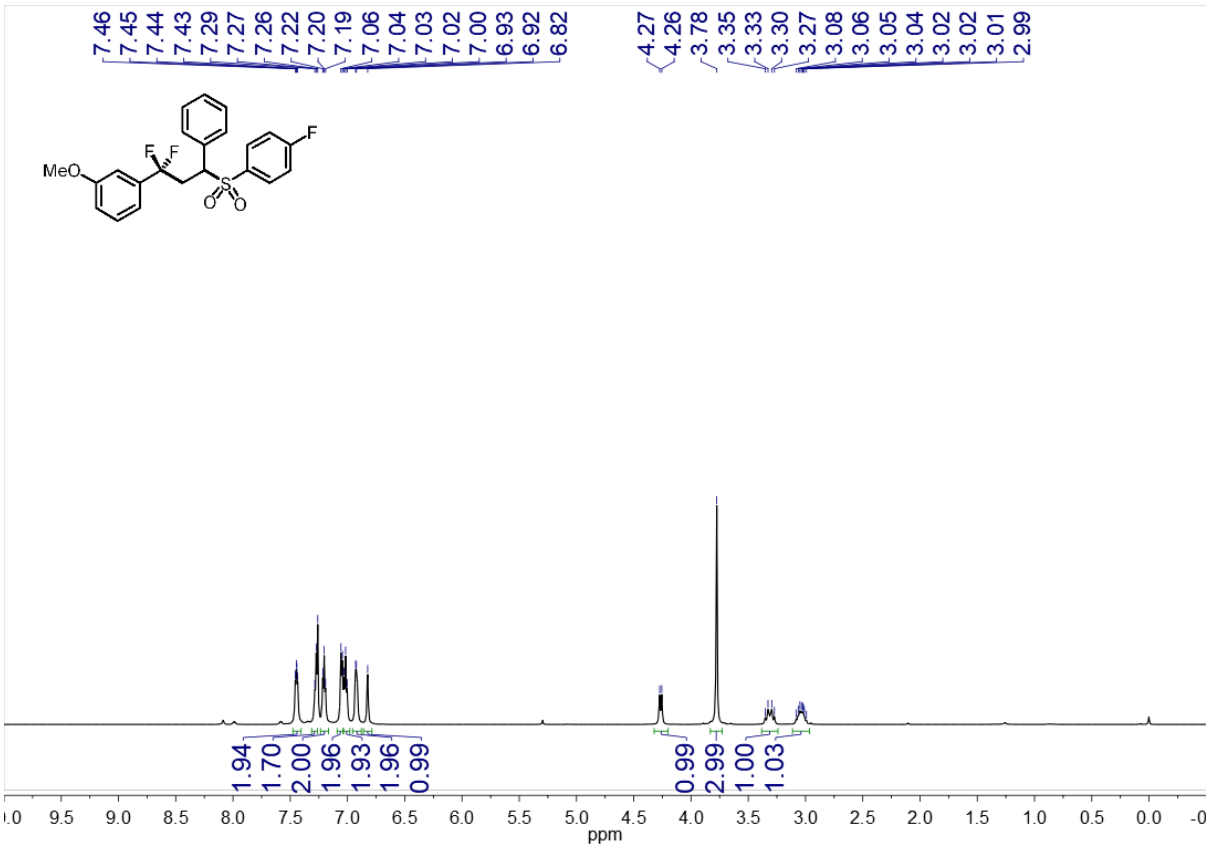
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5n**



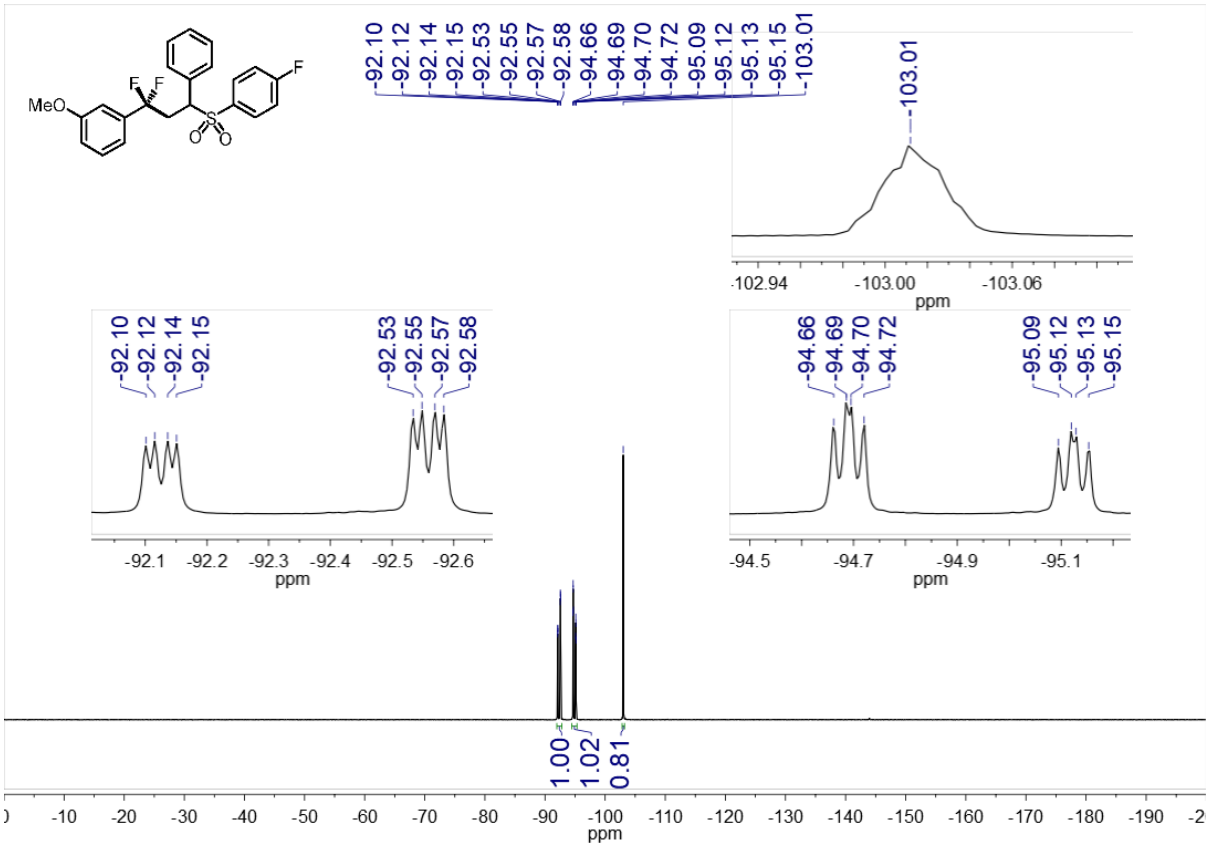
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5n**



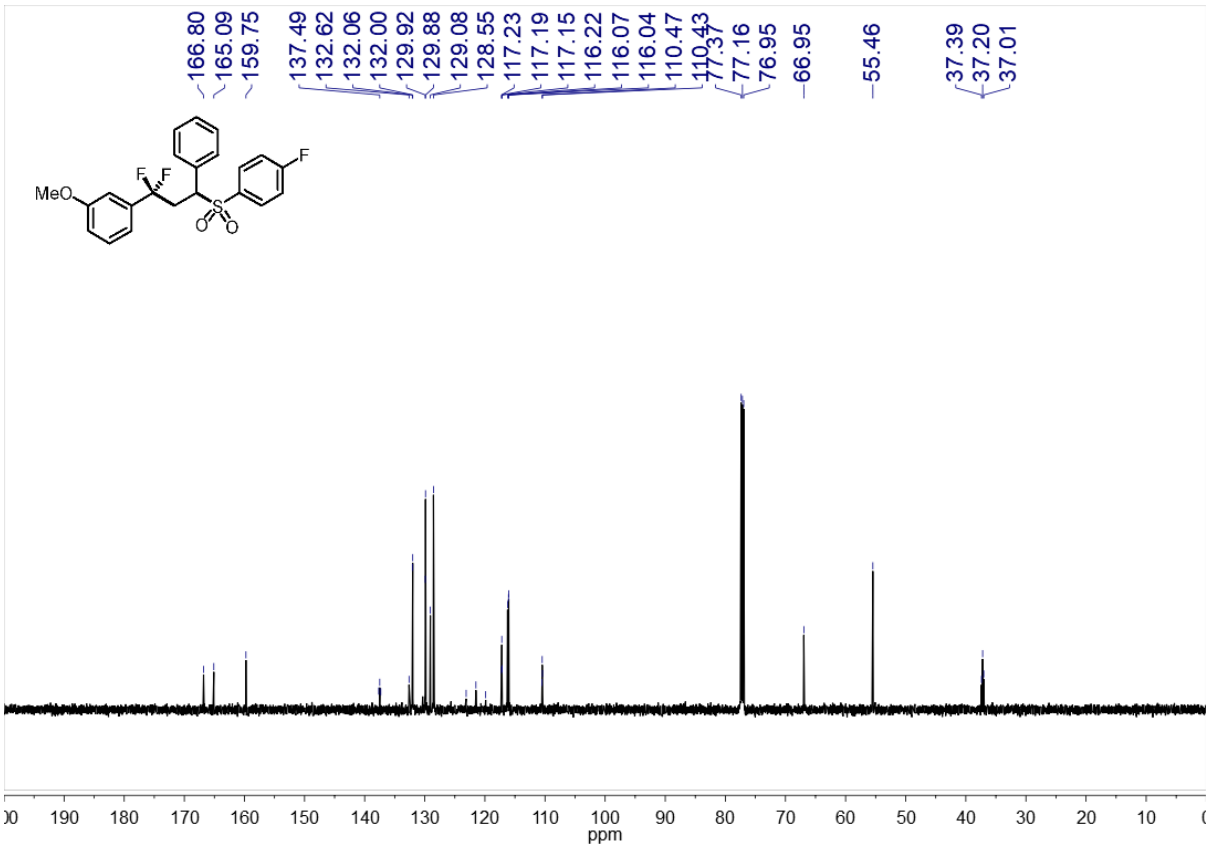
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5n**



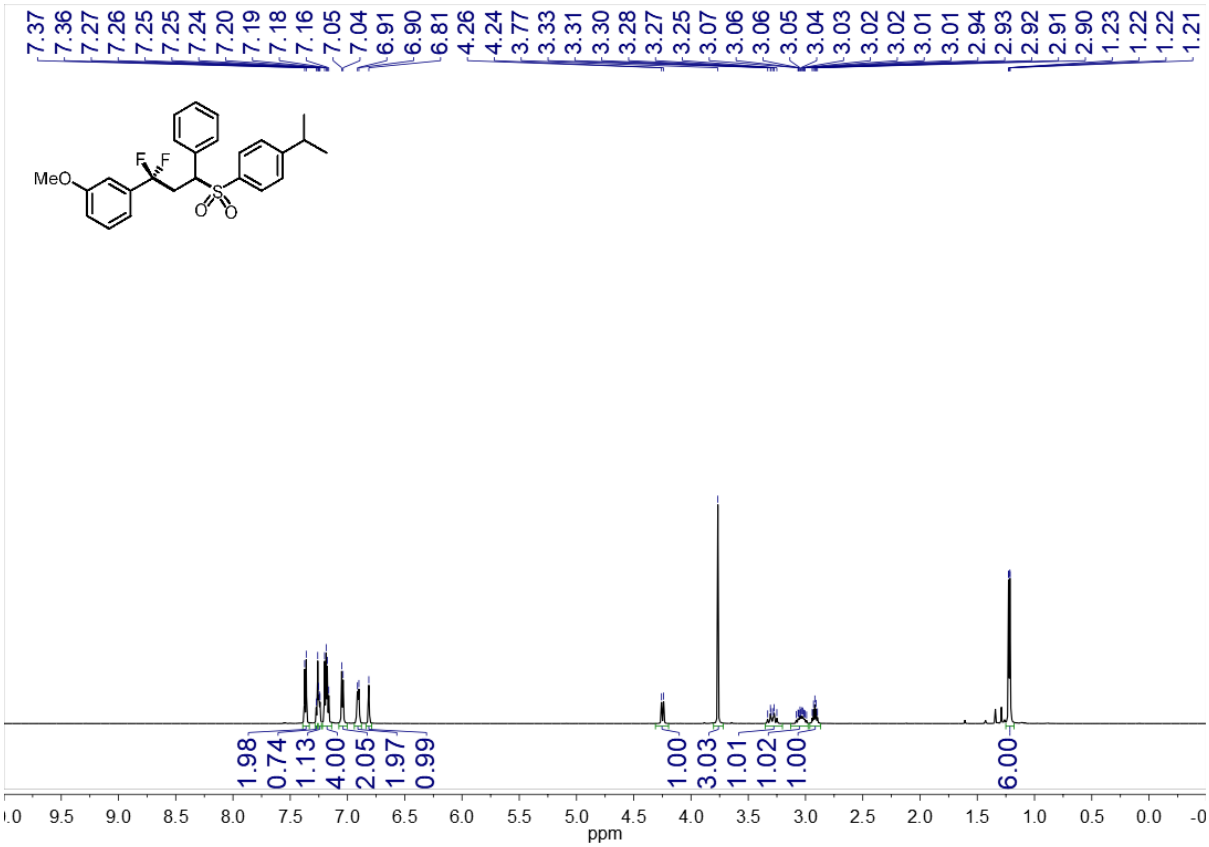
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5o**



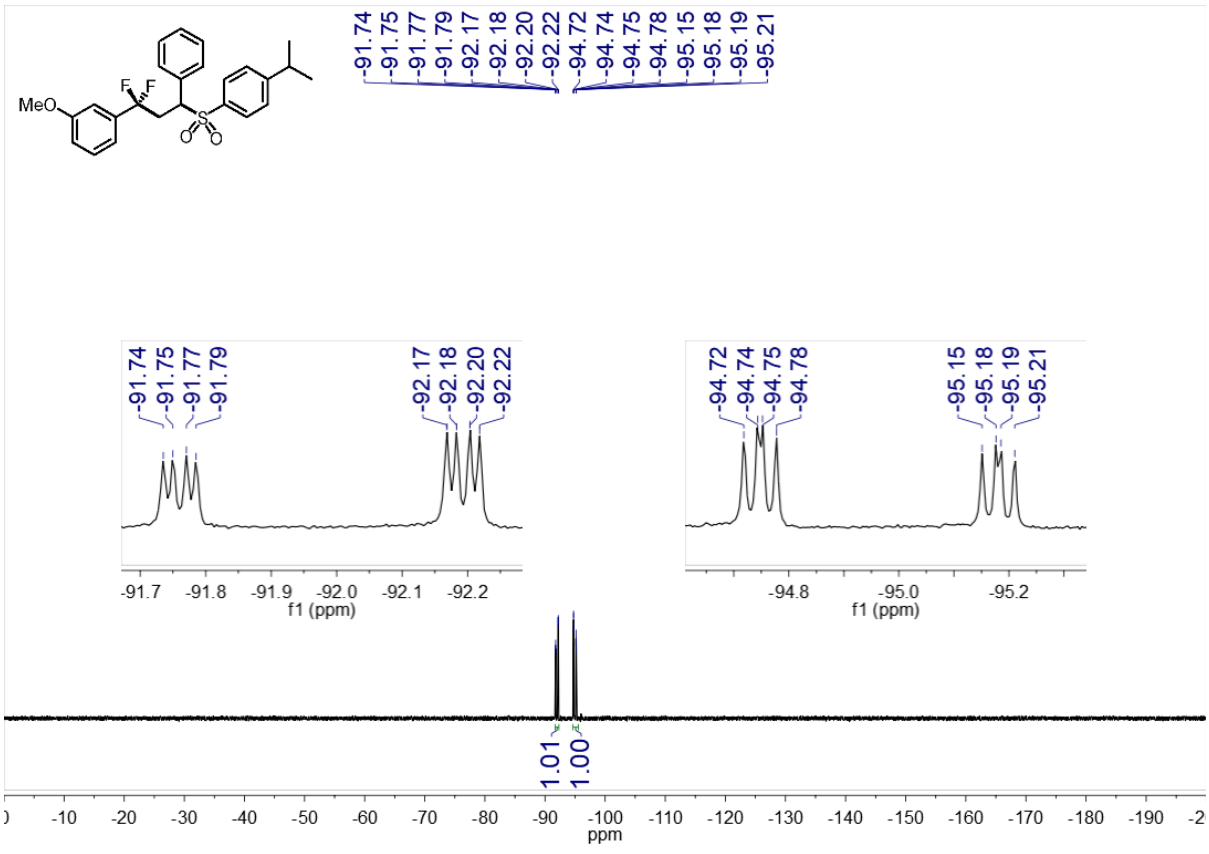
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5o**



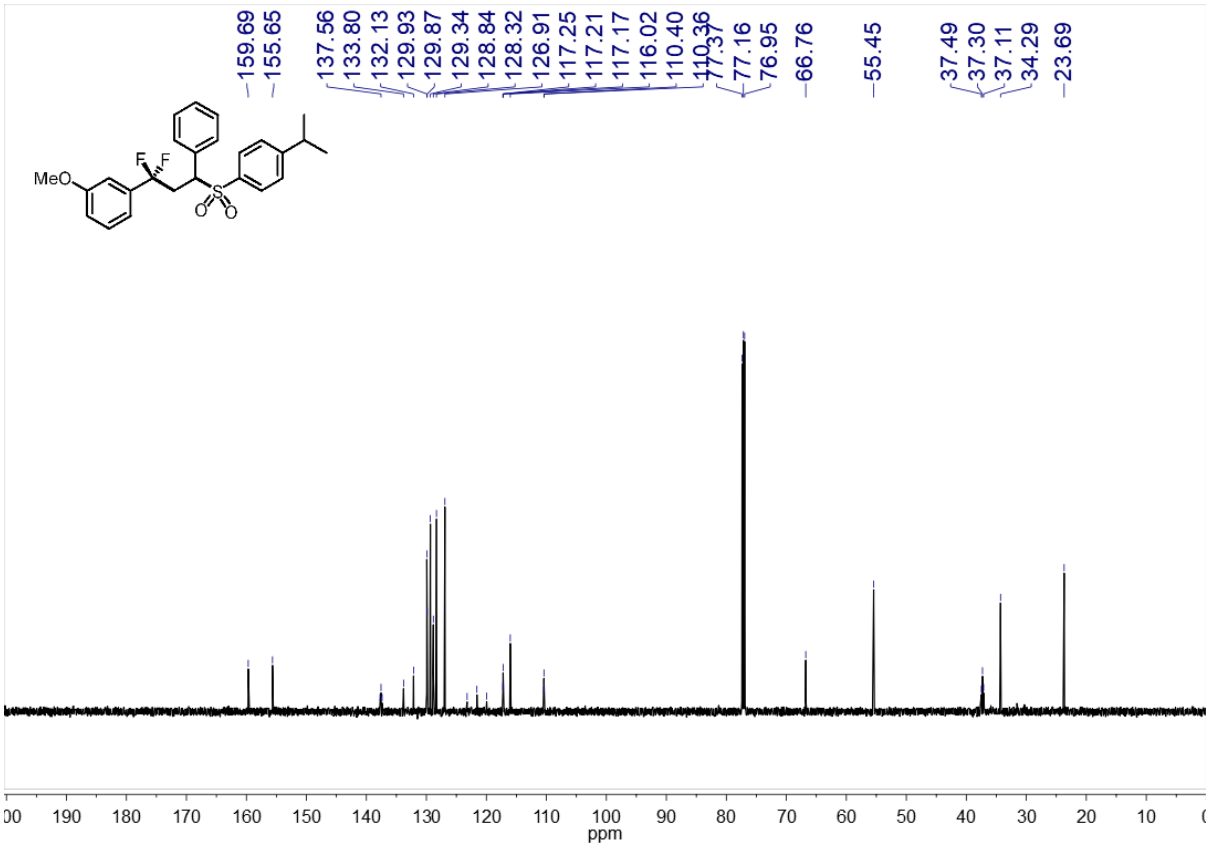
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5o**



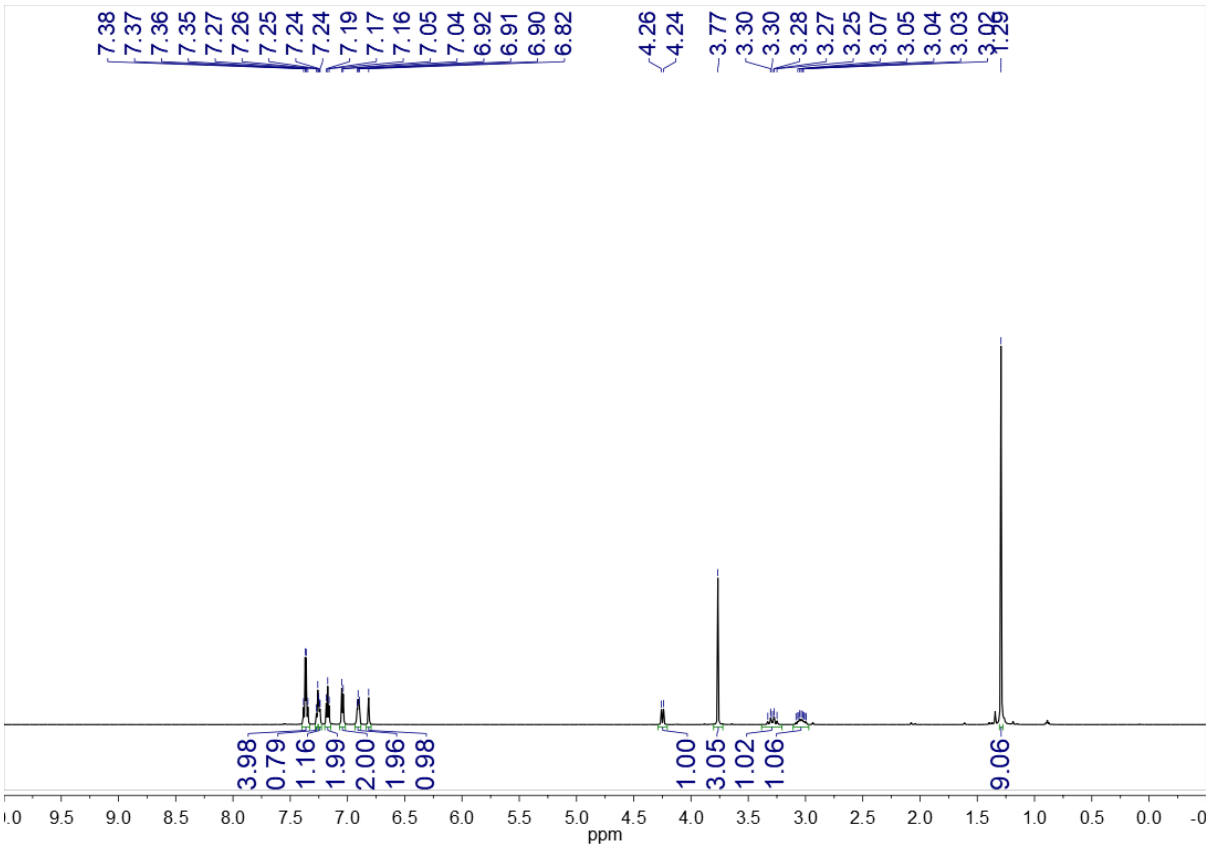
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5p**



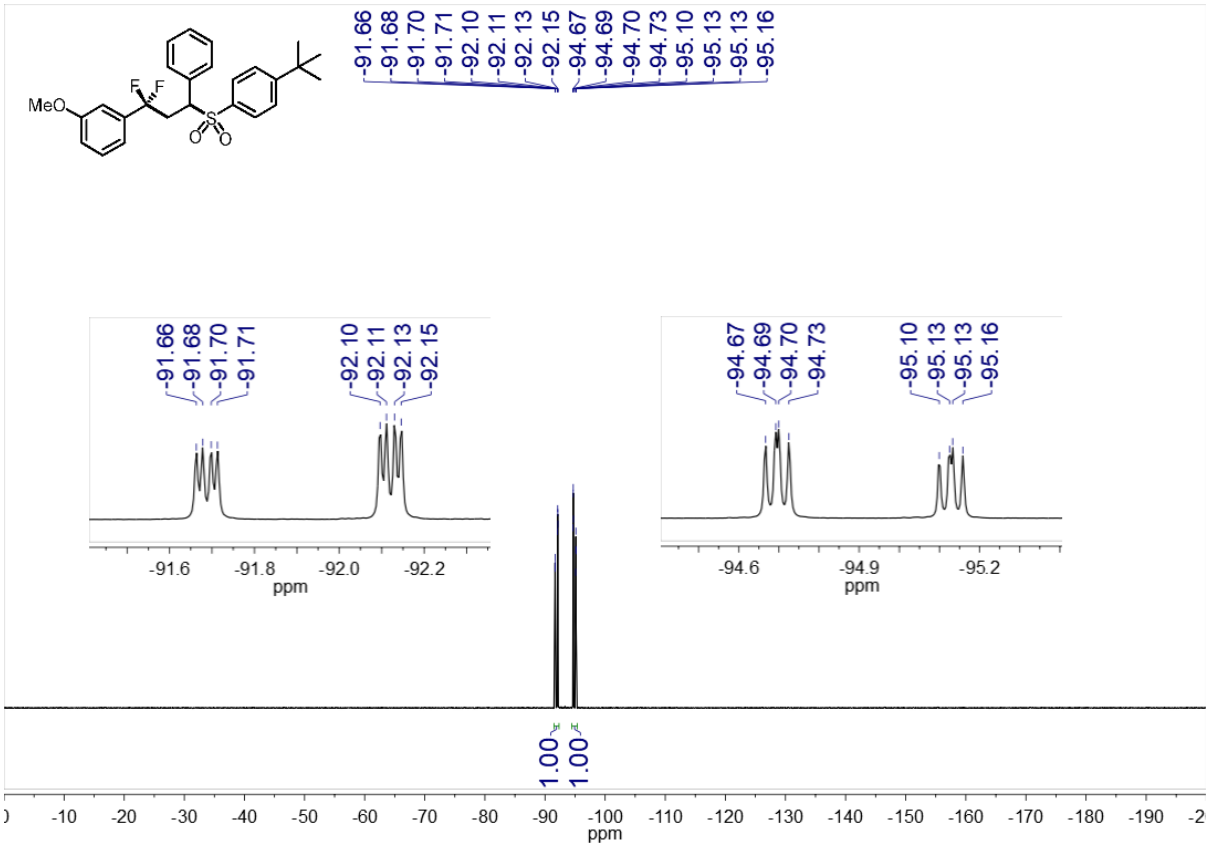
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5p**



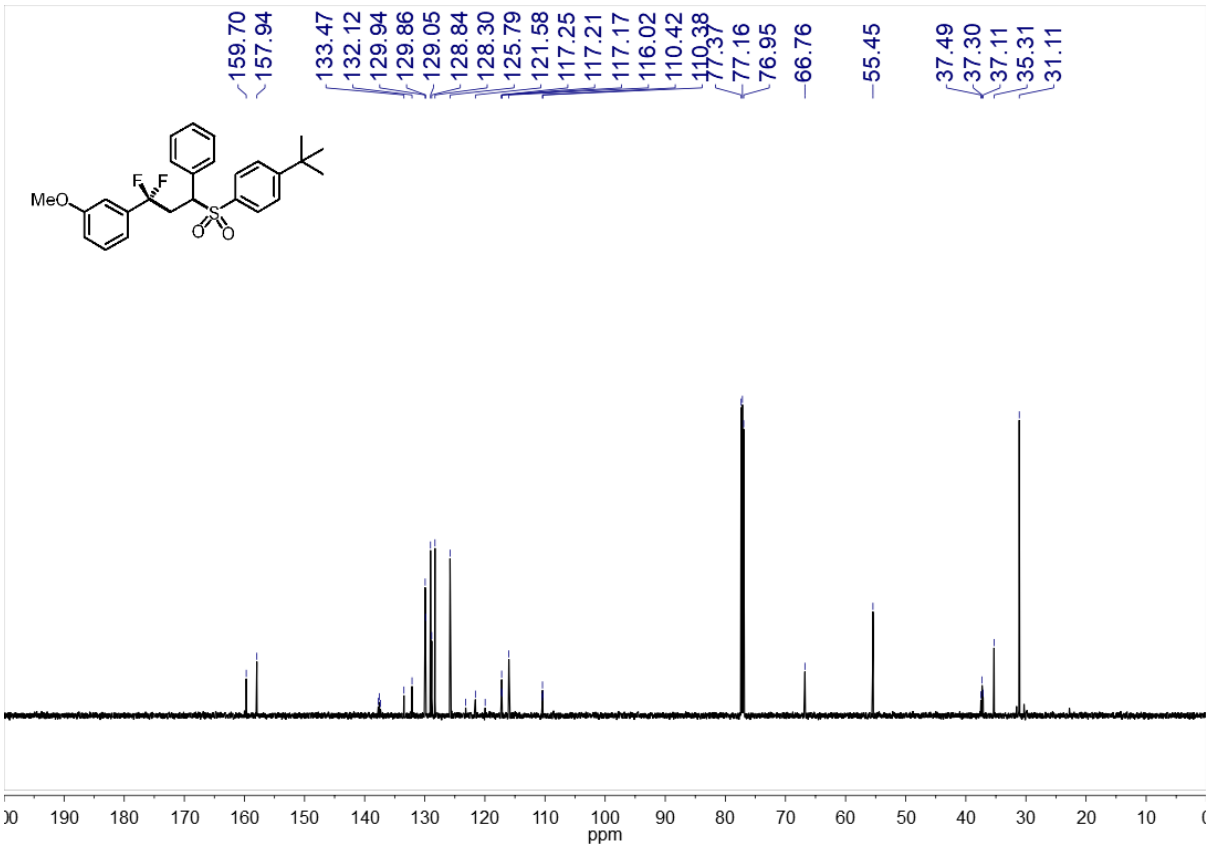
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5p**



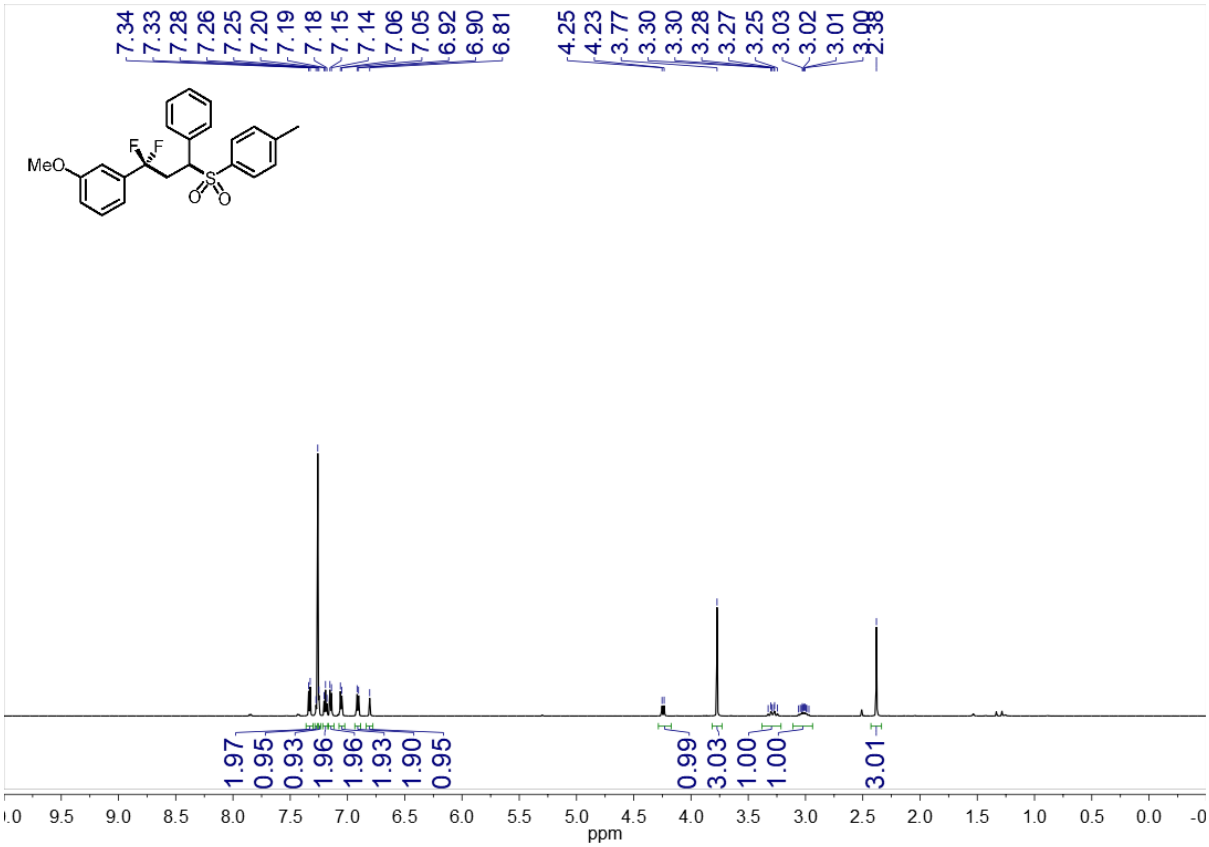
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5q**



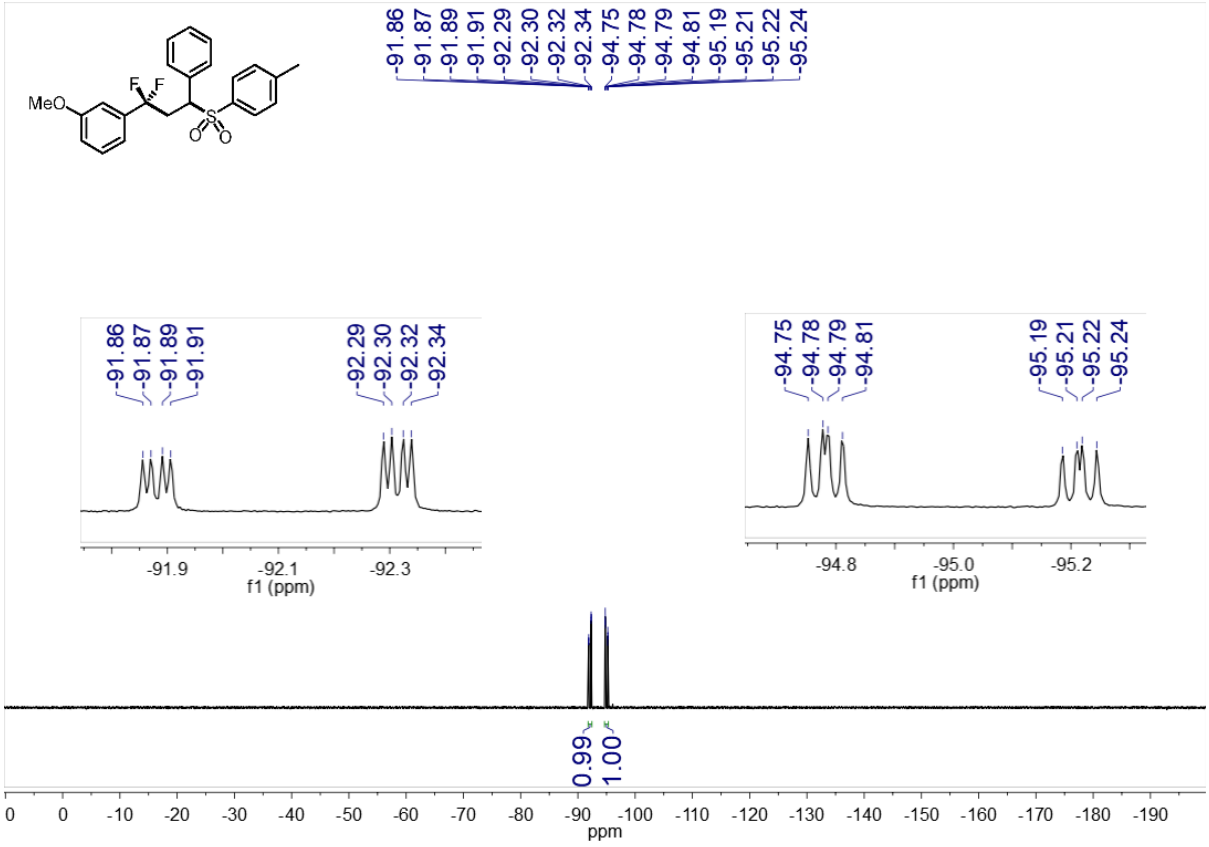
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5q**



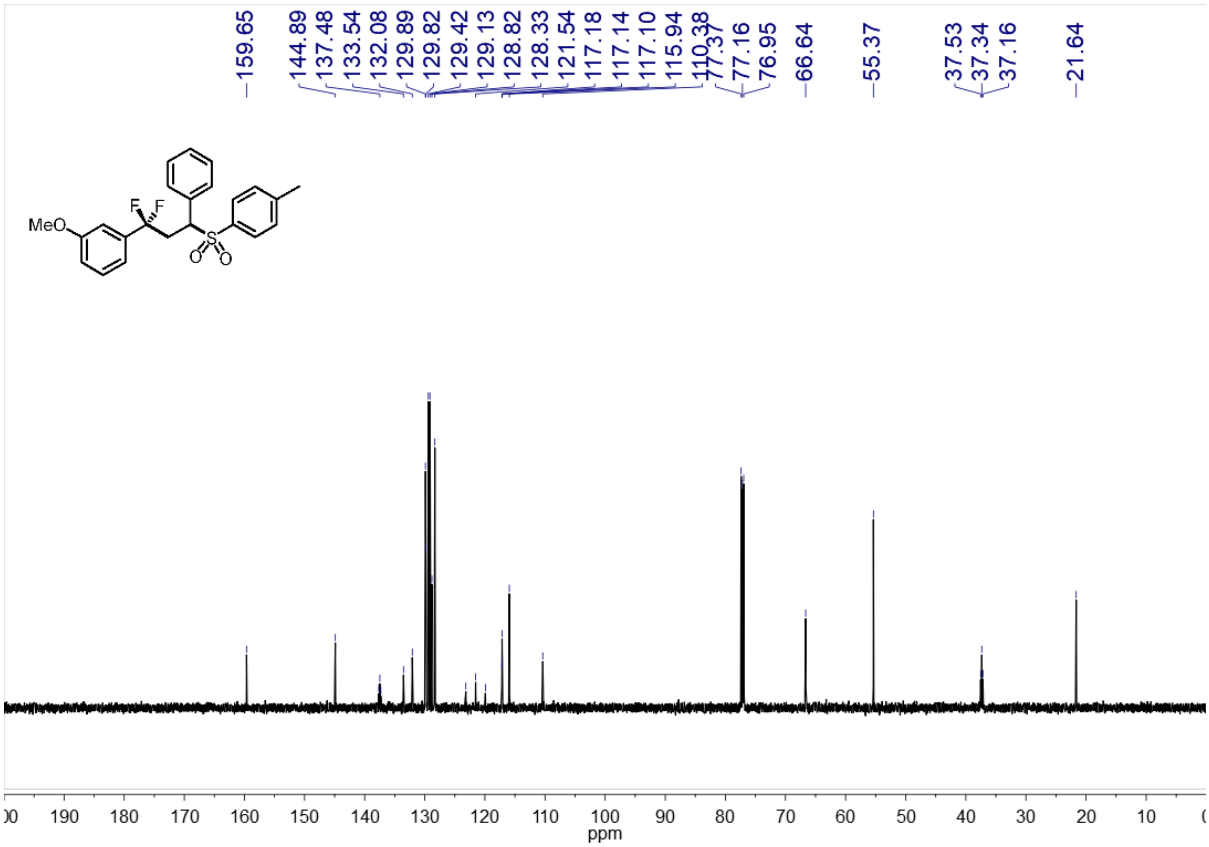
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5q**



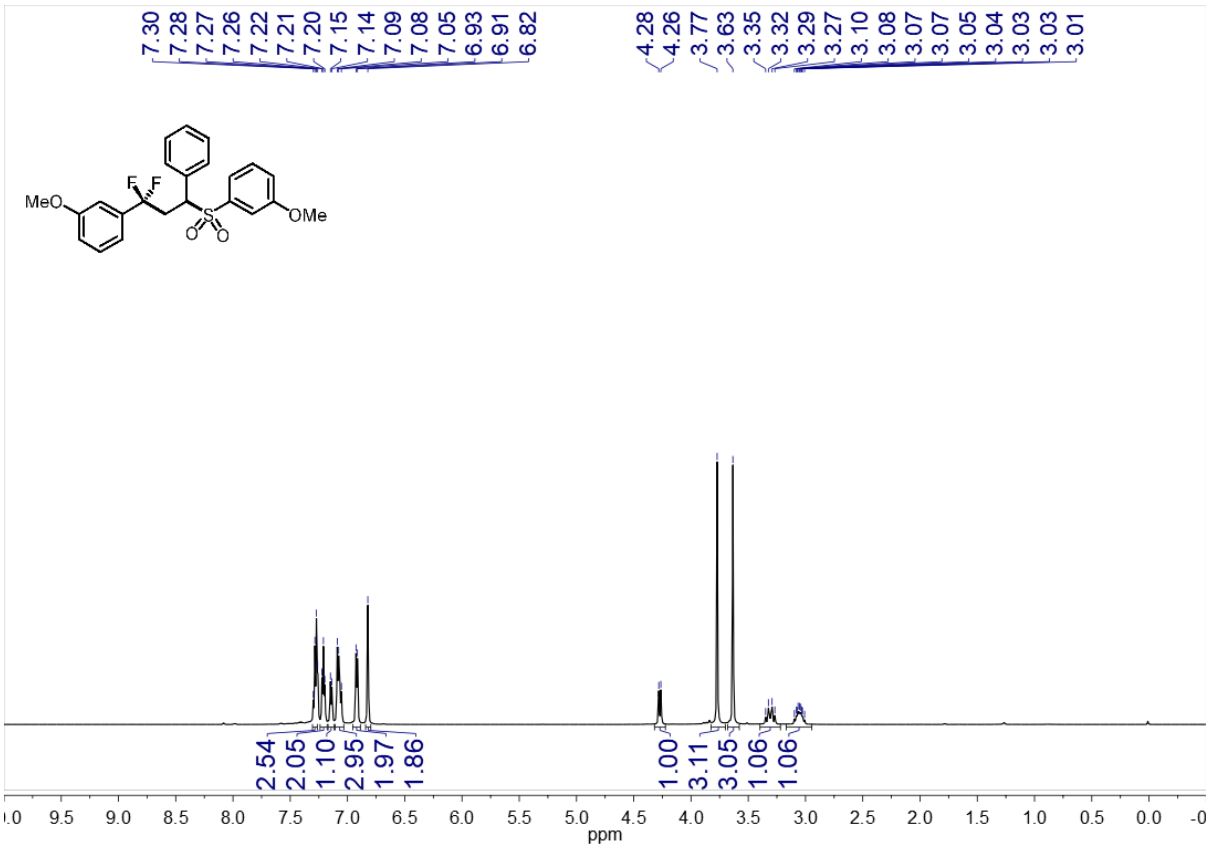
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5r**



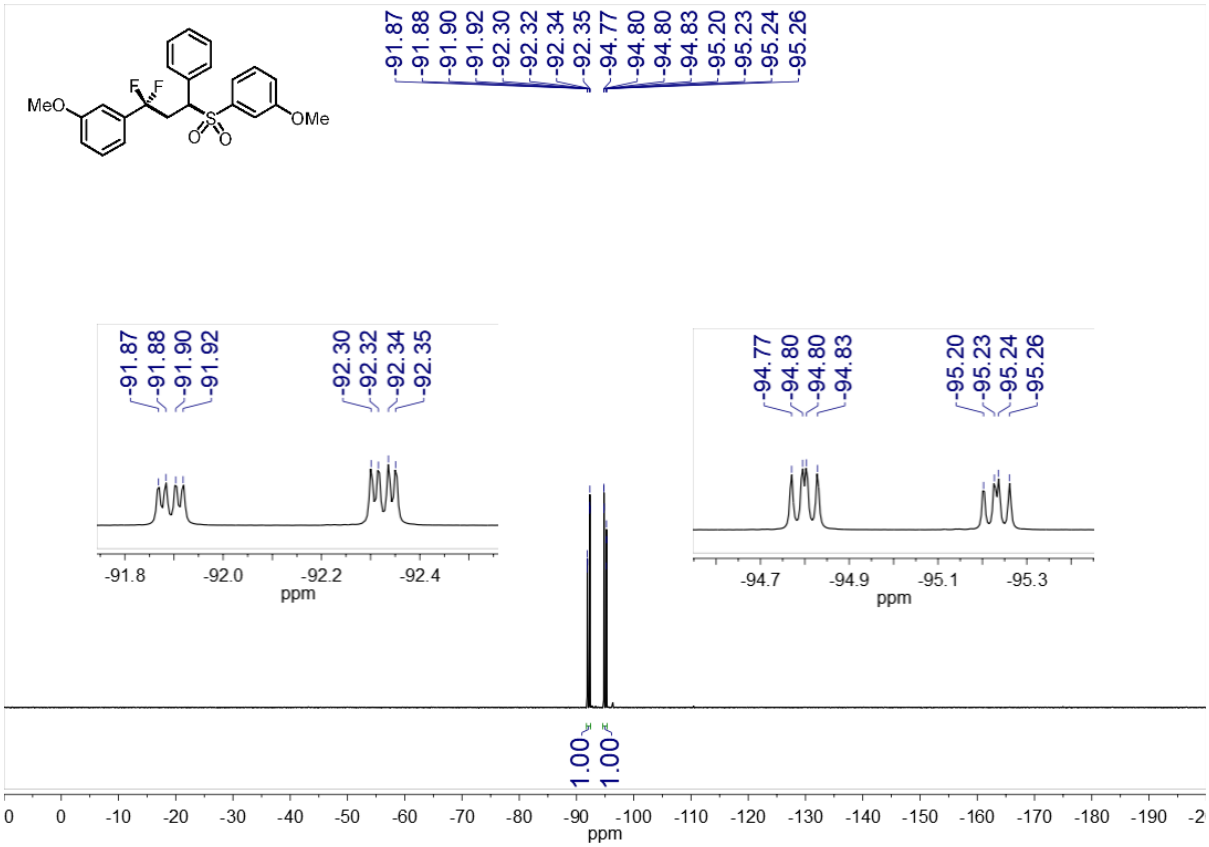
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5r**



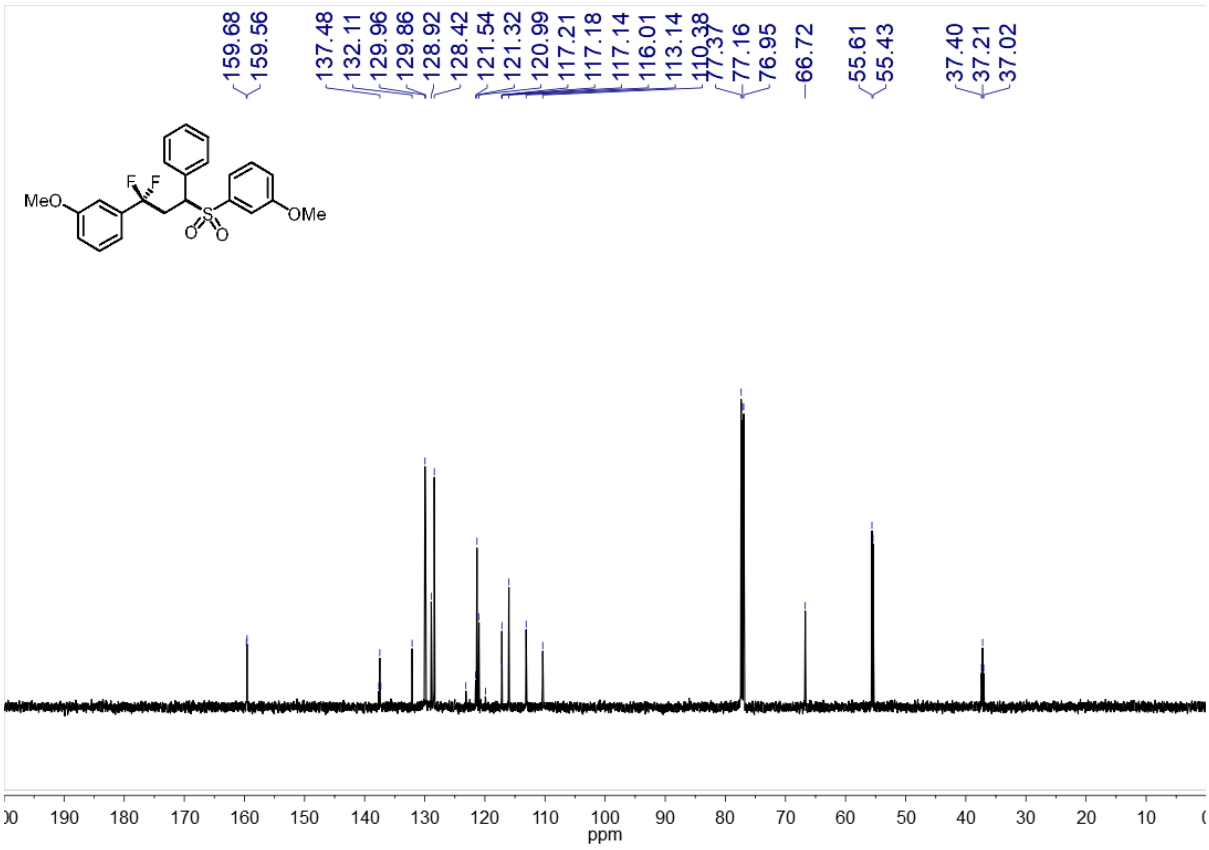
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5r**



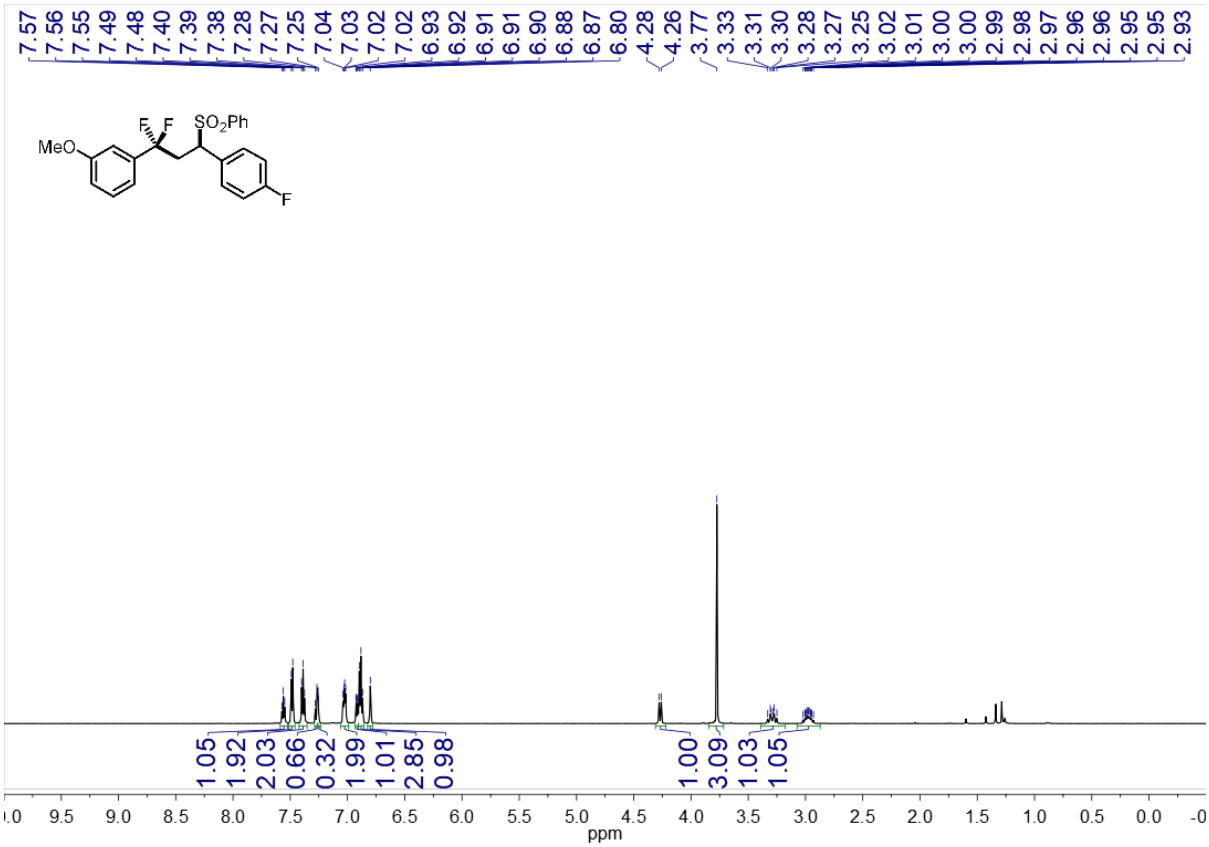
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5s**



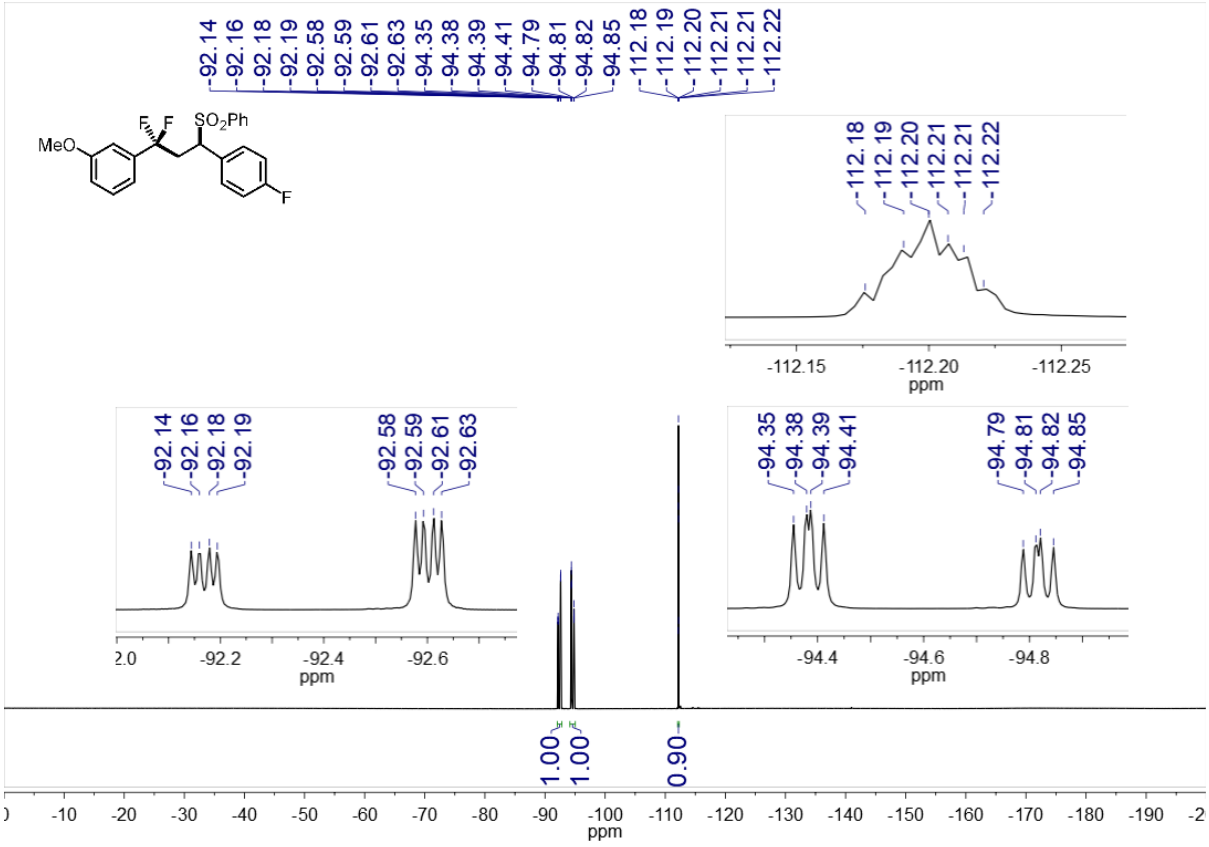
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5s**



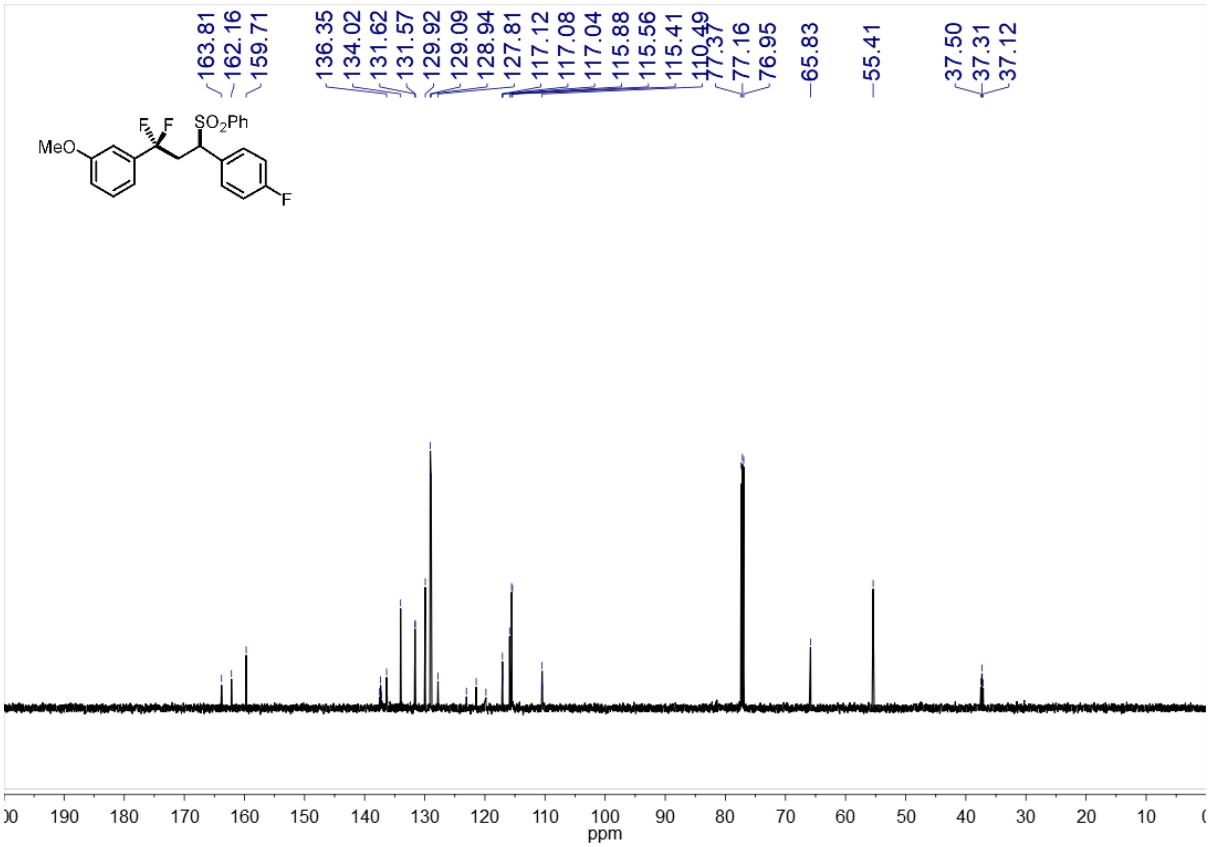
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5s**



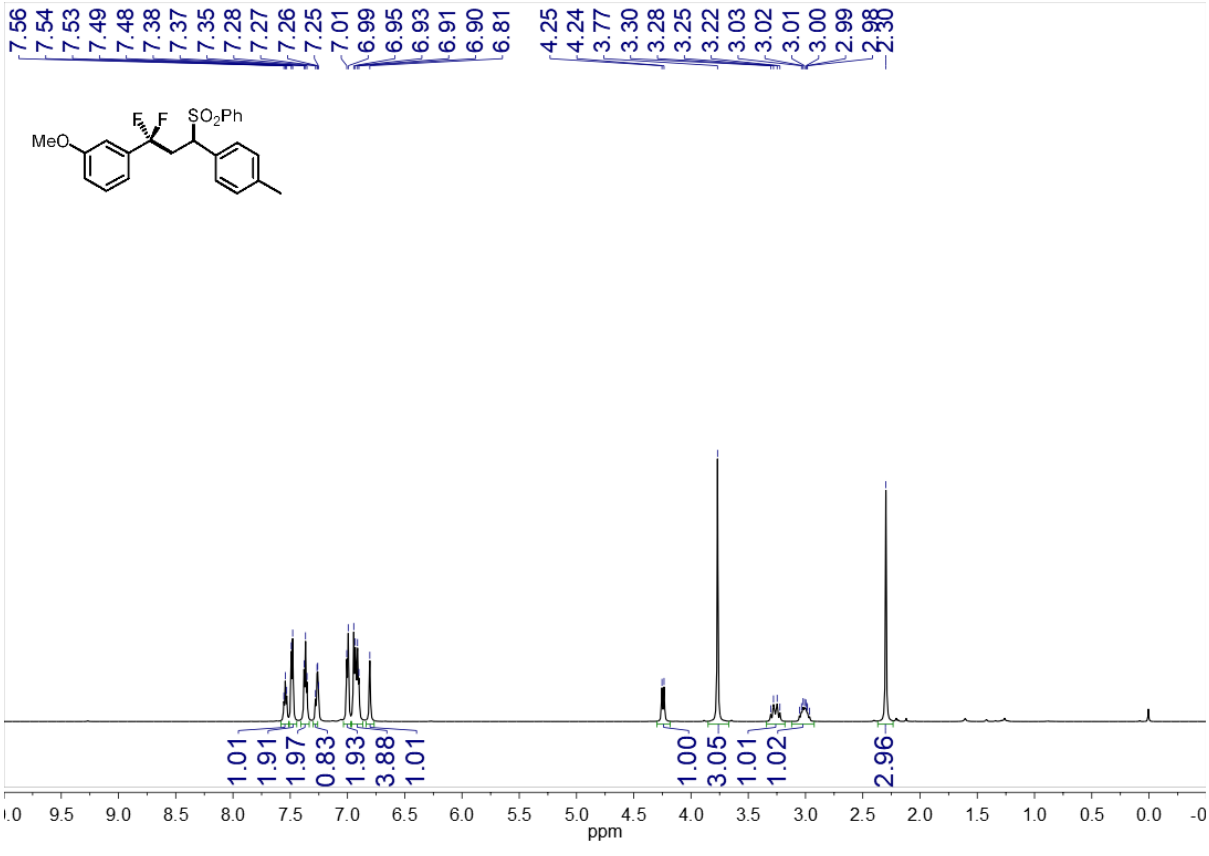
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5t**



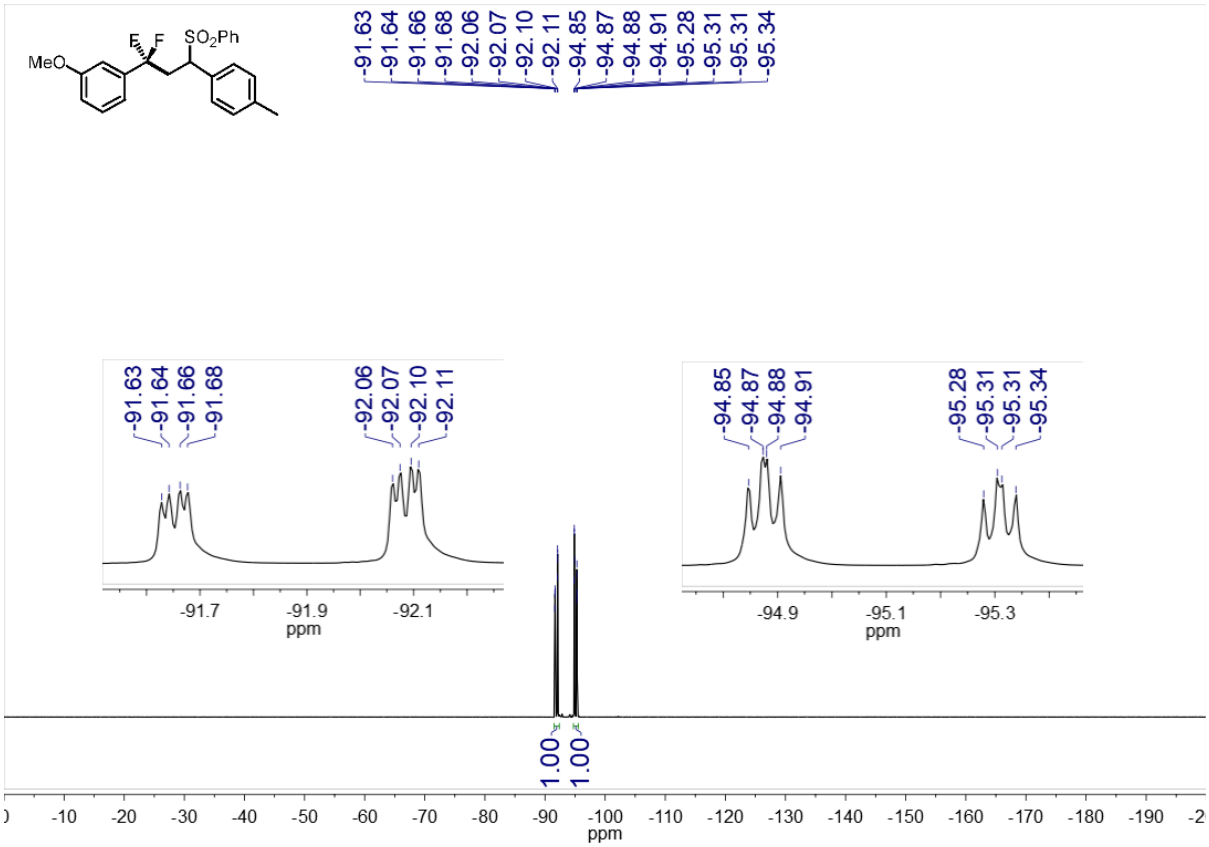
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5t**



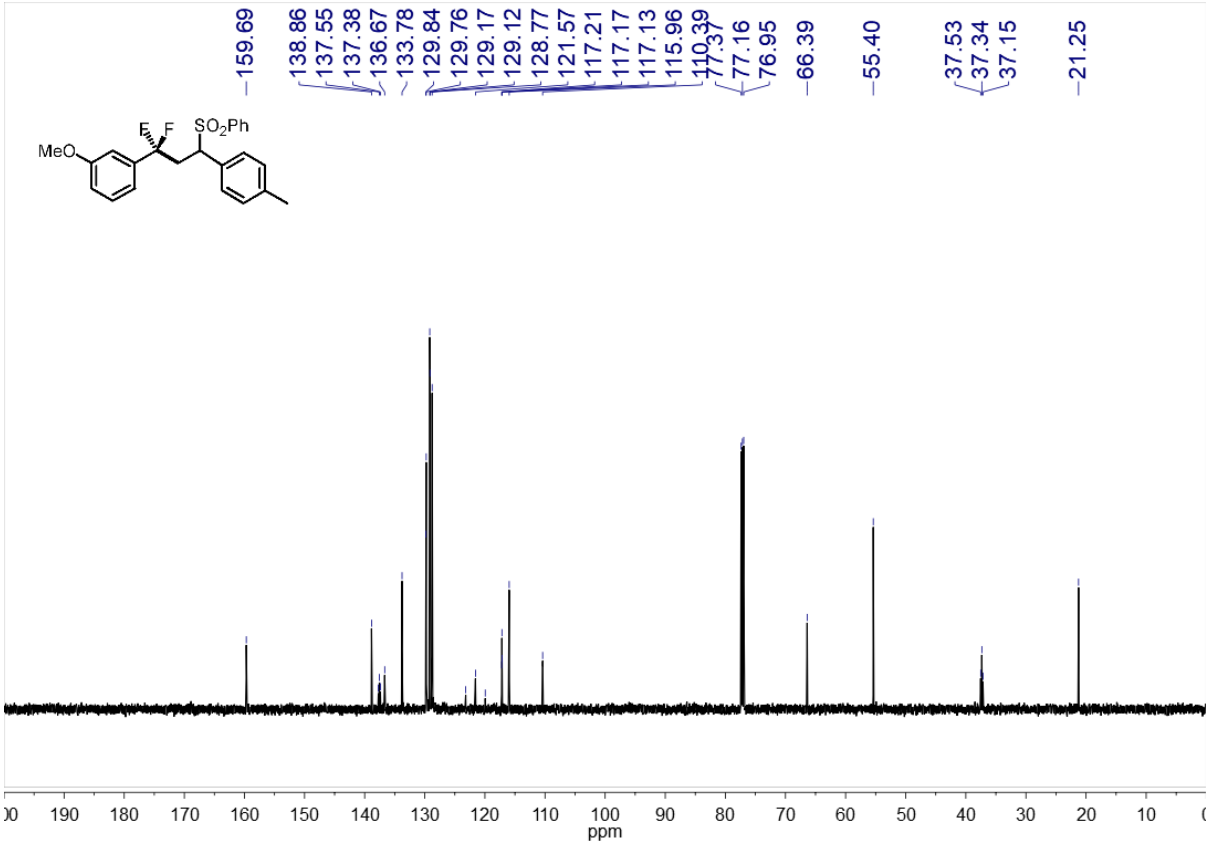
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5t**



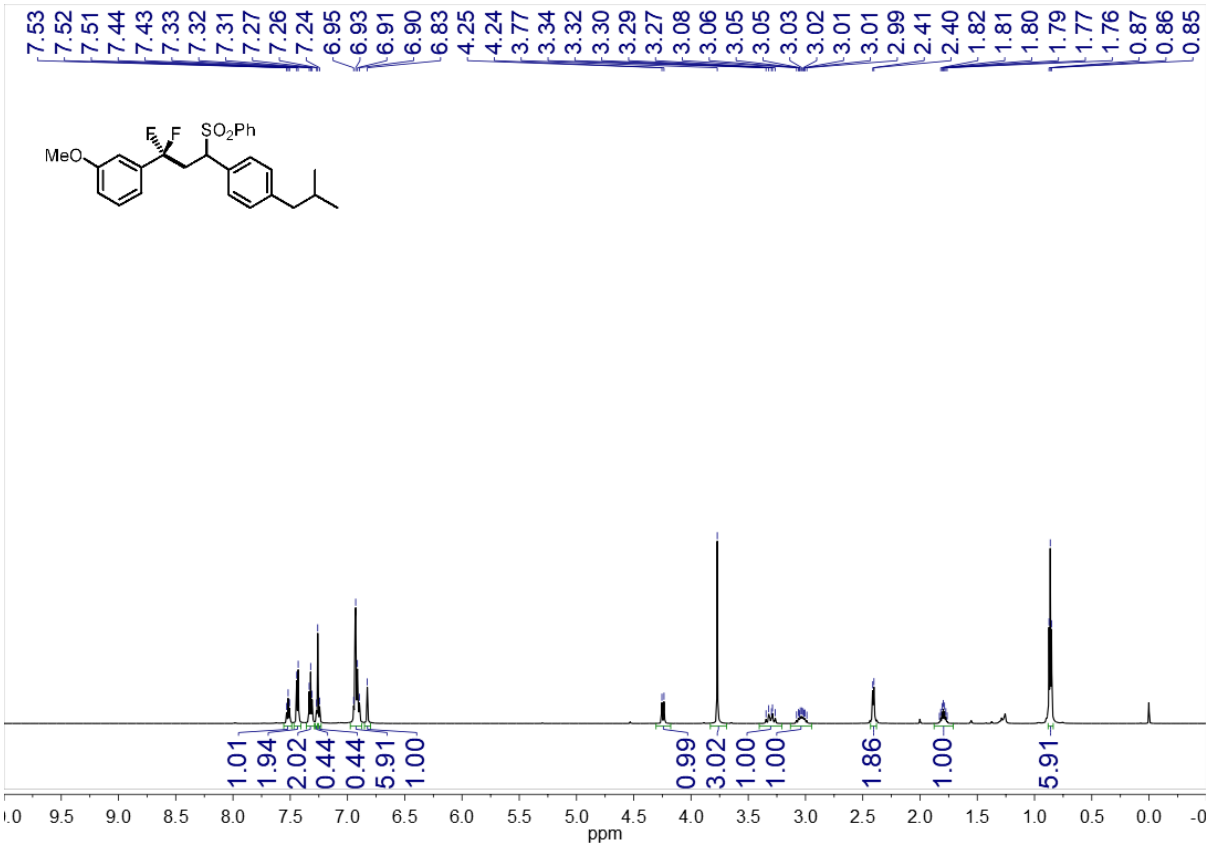
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5u**



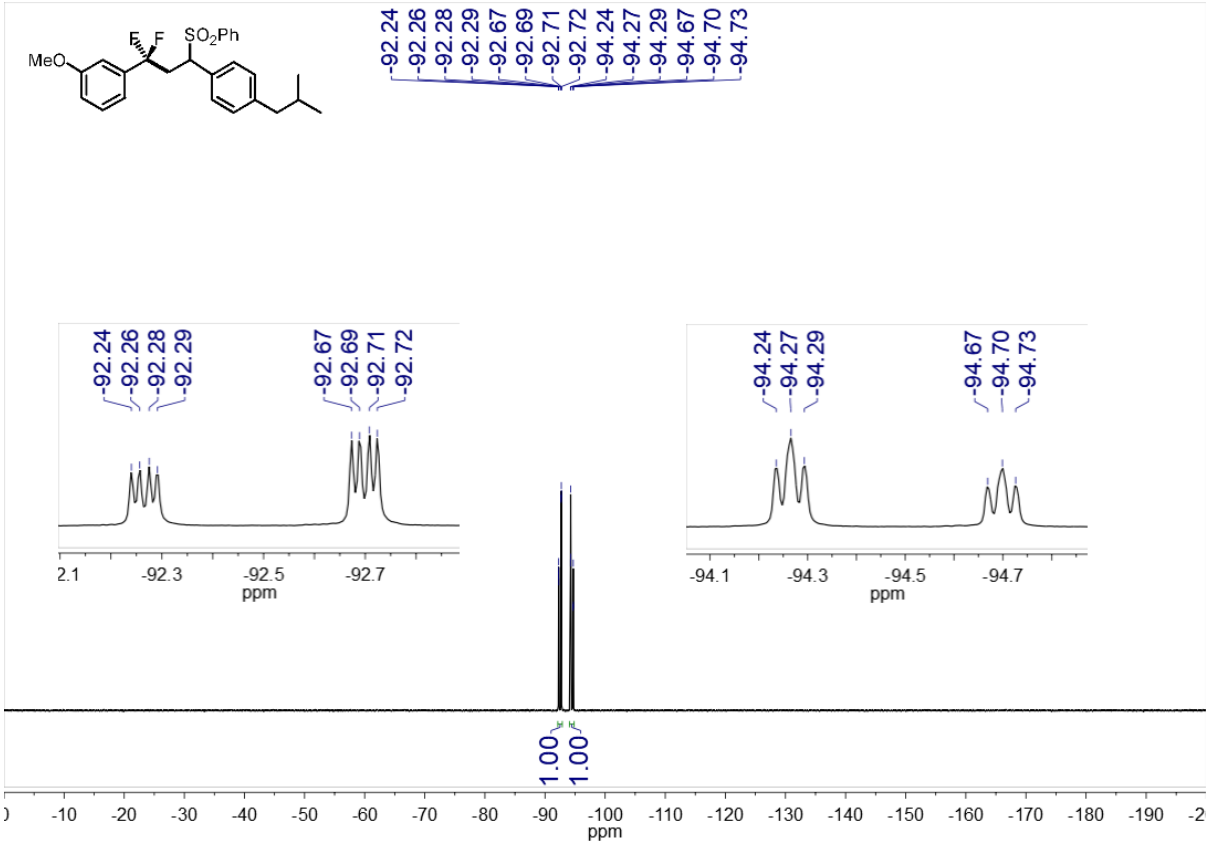
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5u**



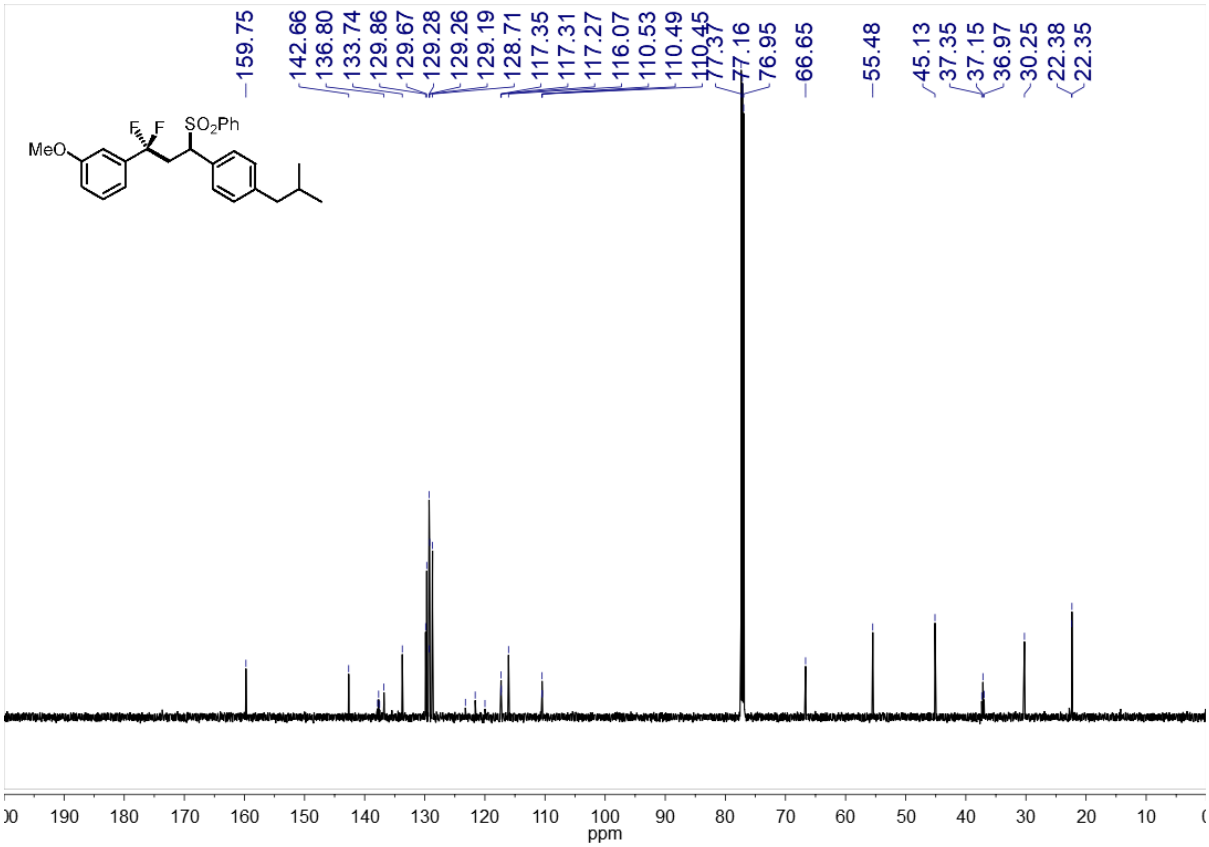
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5u**



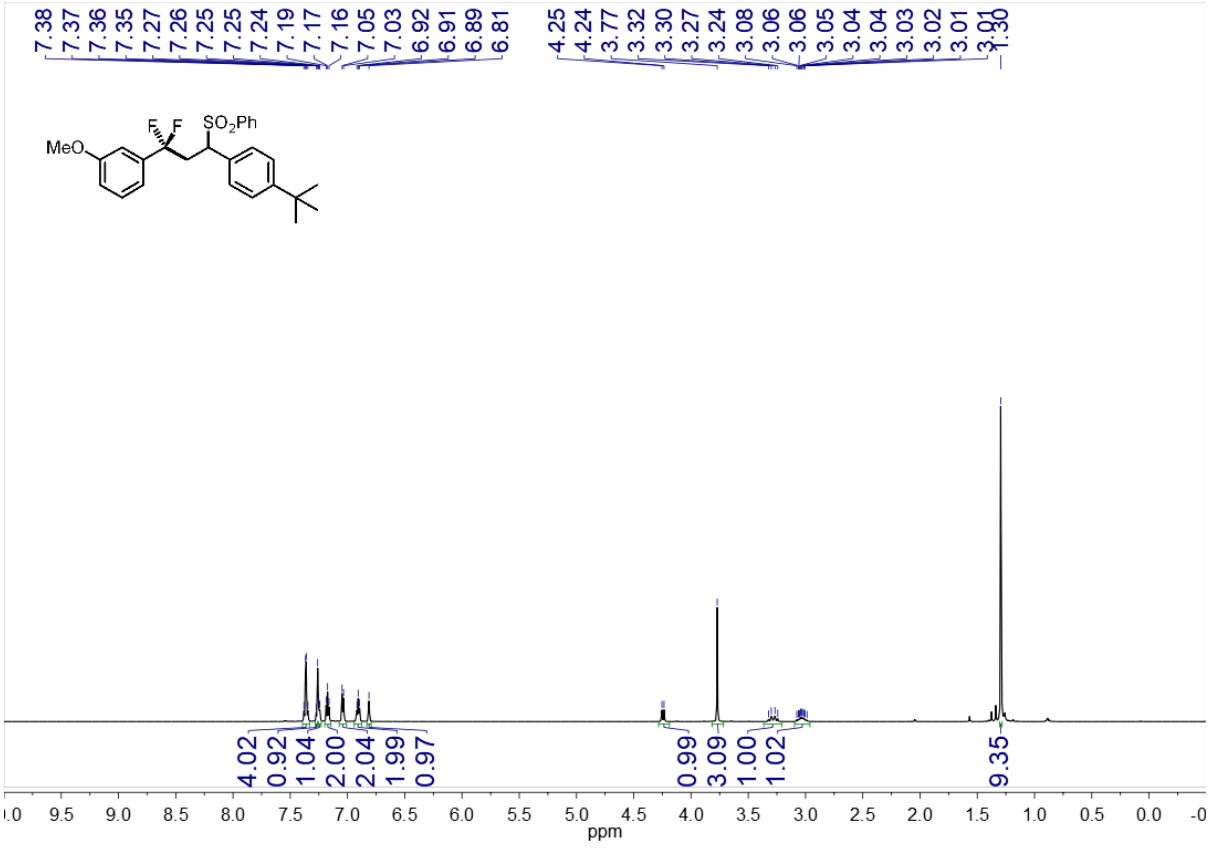
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5v**



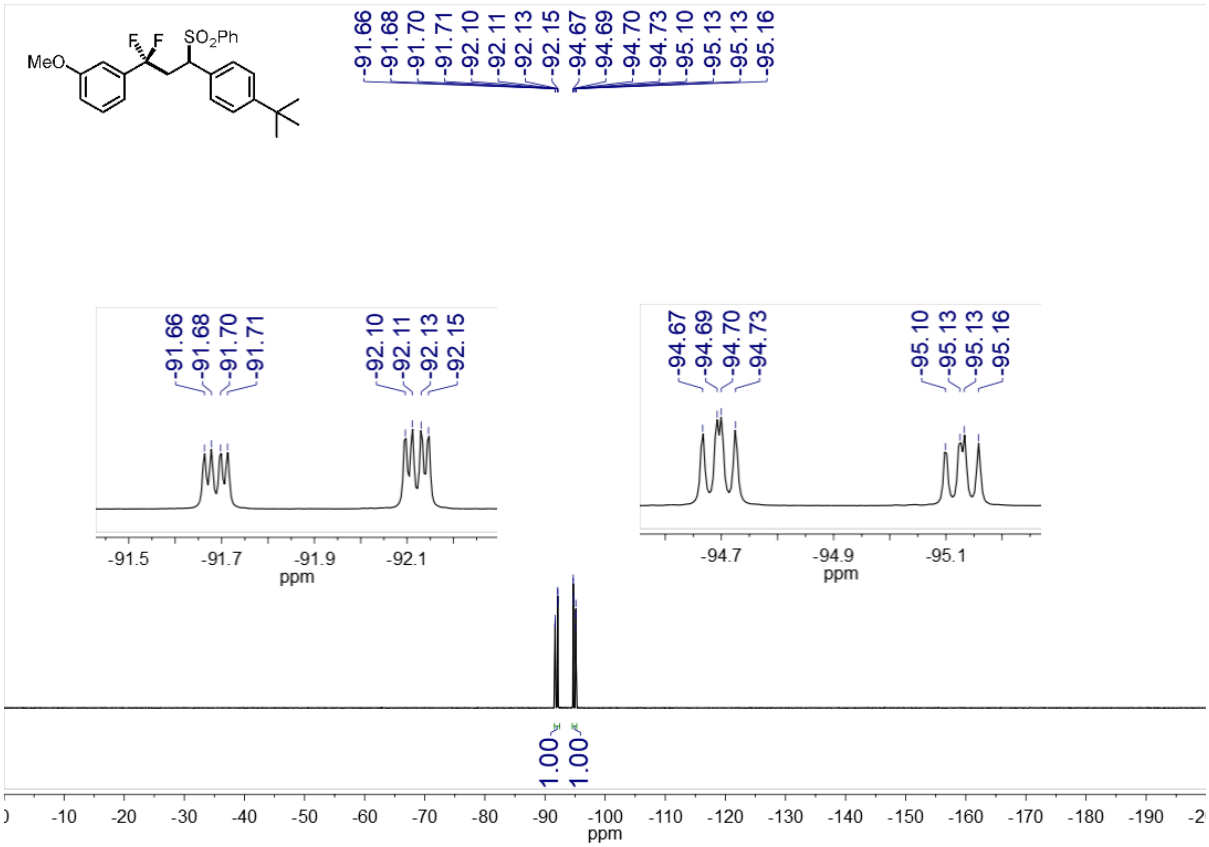
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5v**



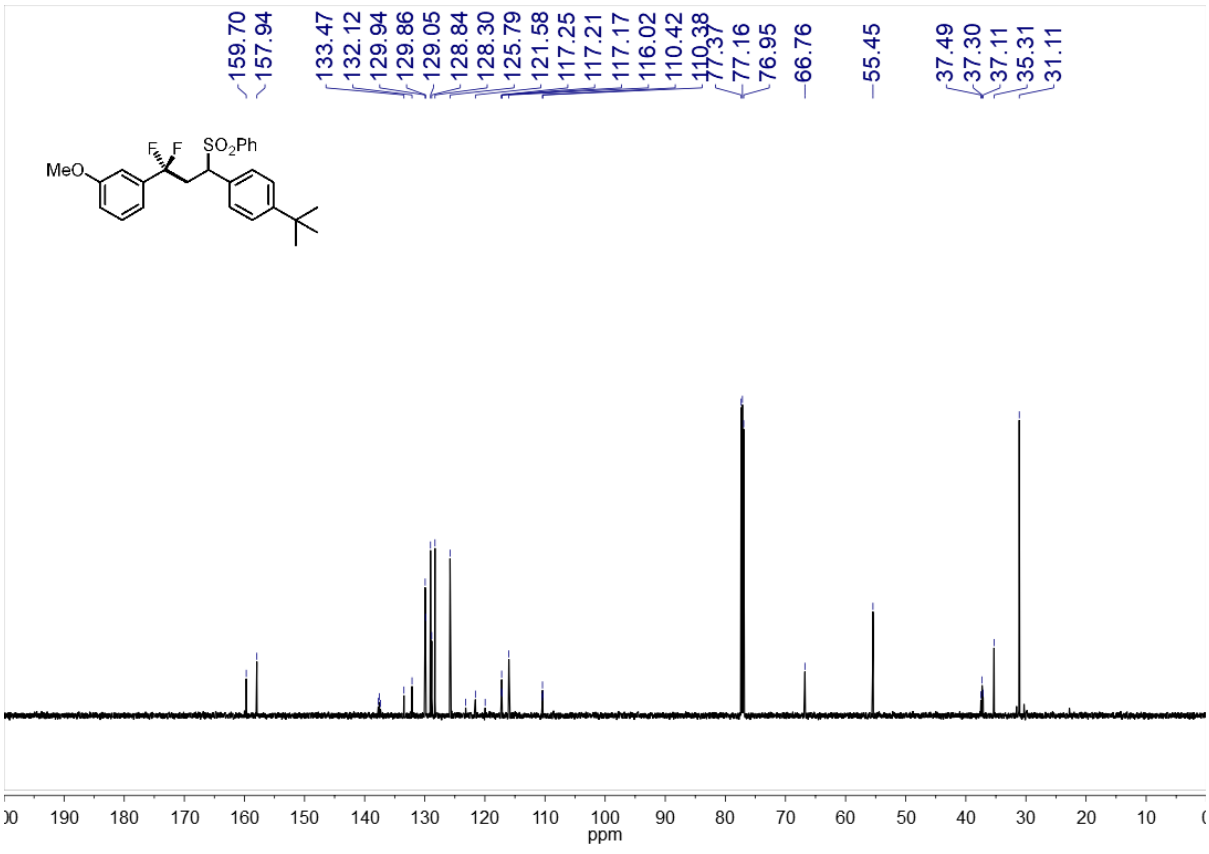
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5v**



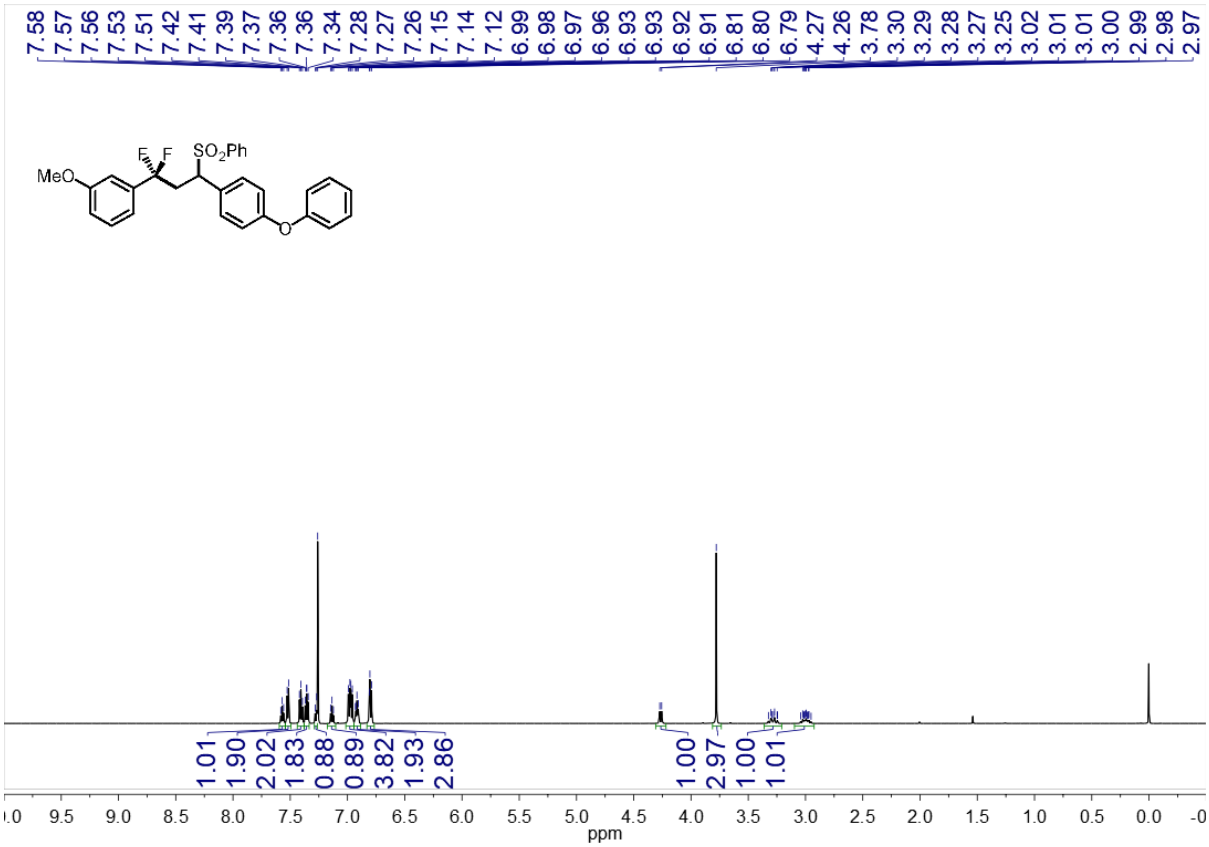
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5w**



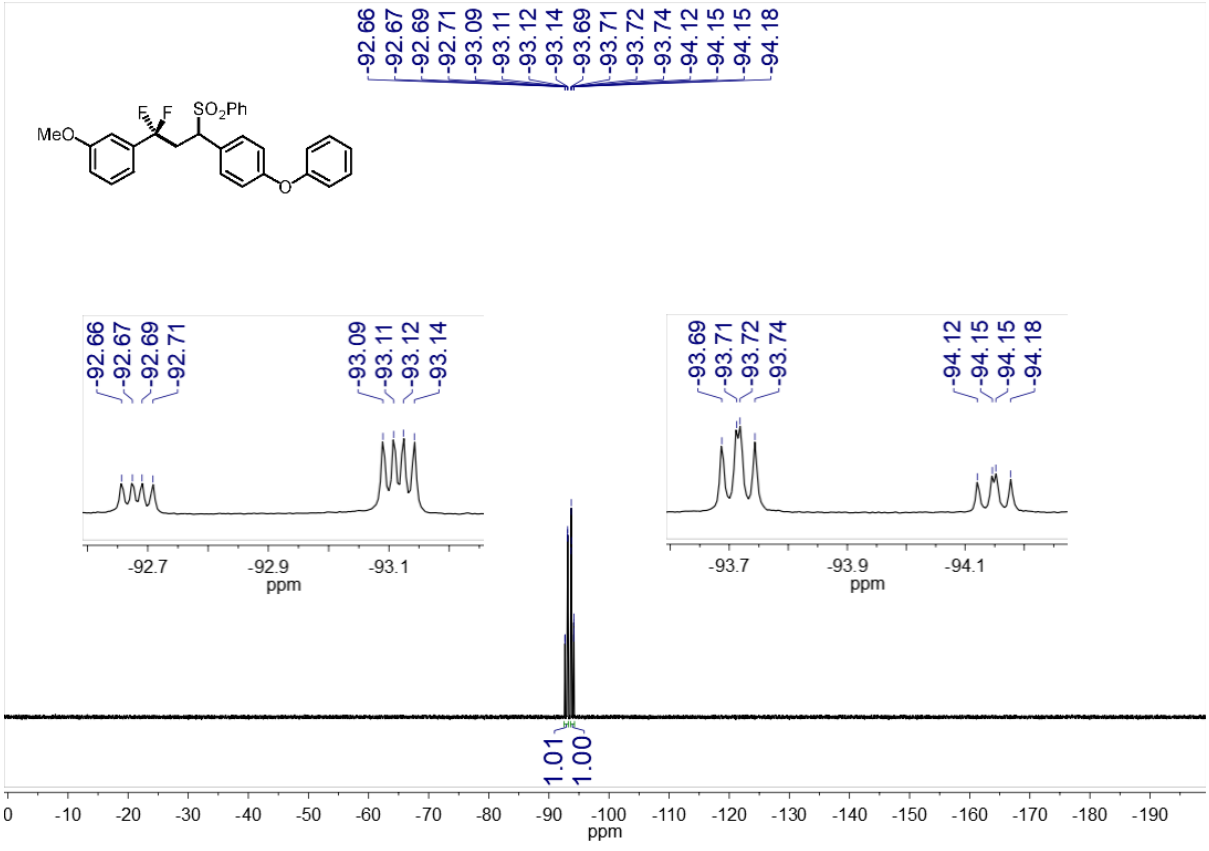
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5w**



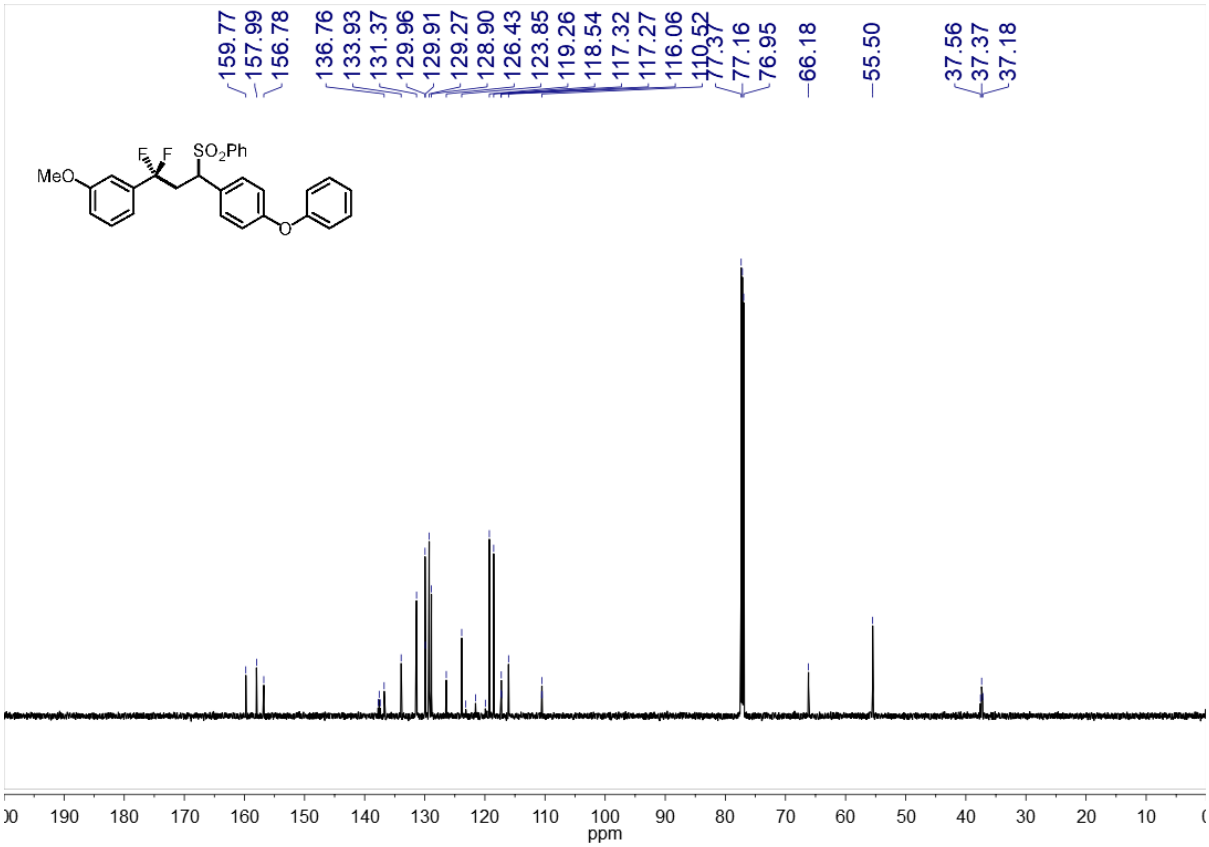
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5w**



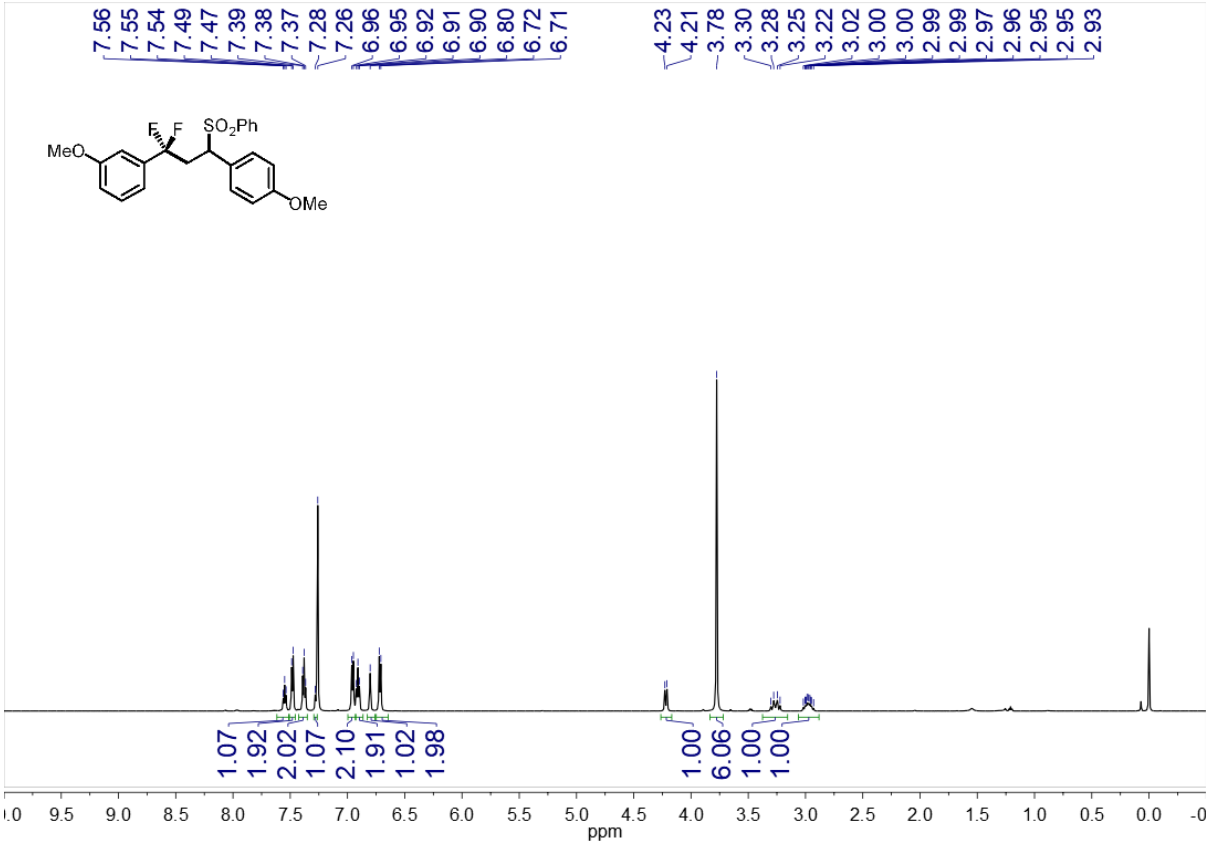
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5x**



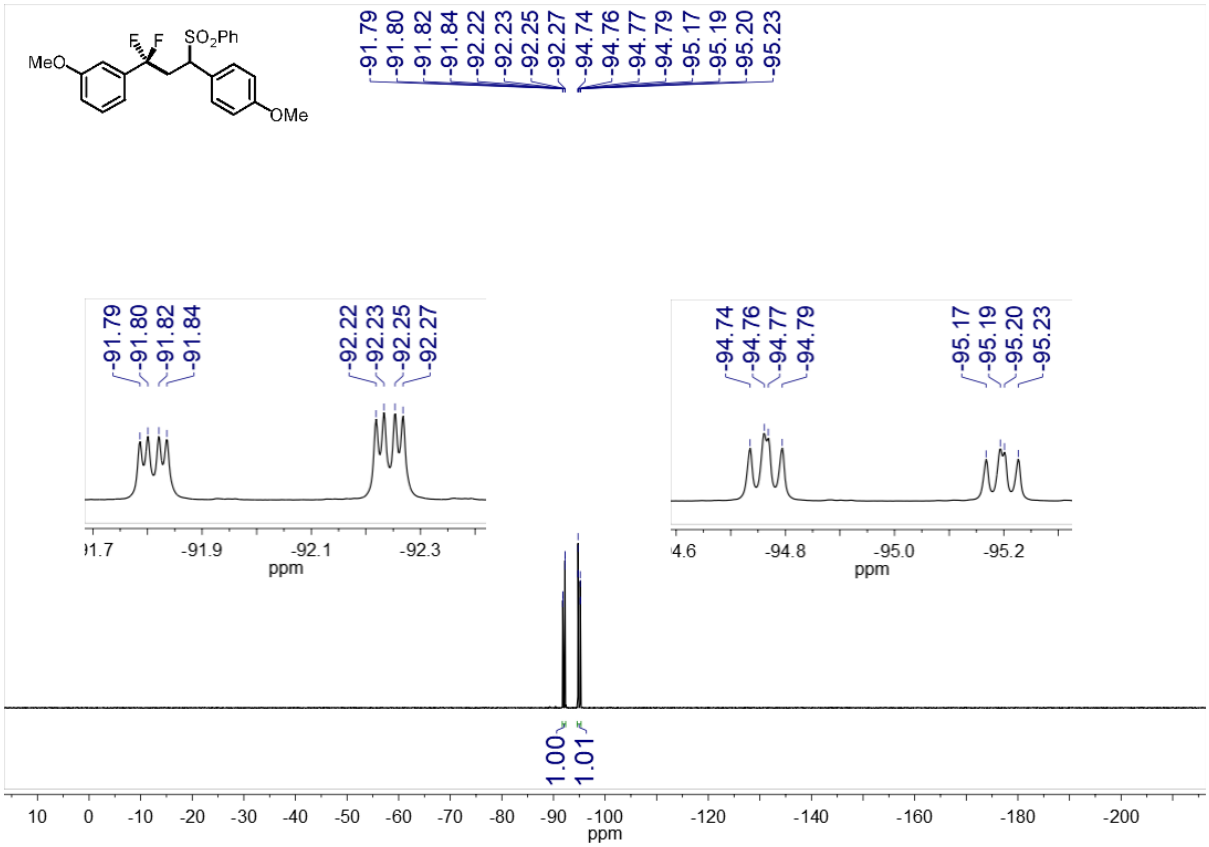
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5x**



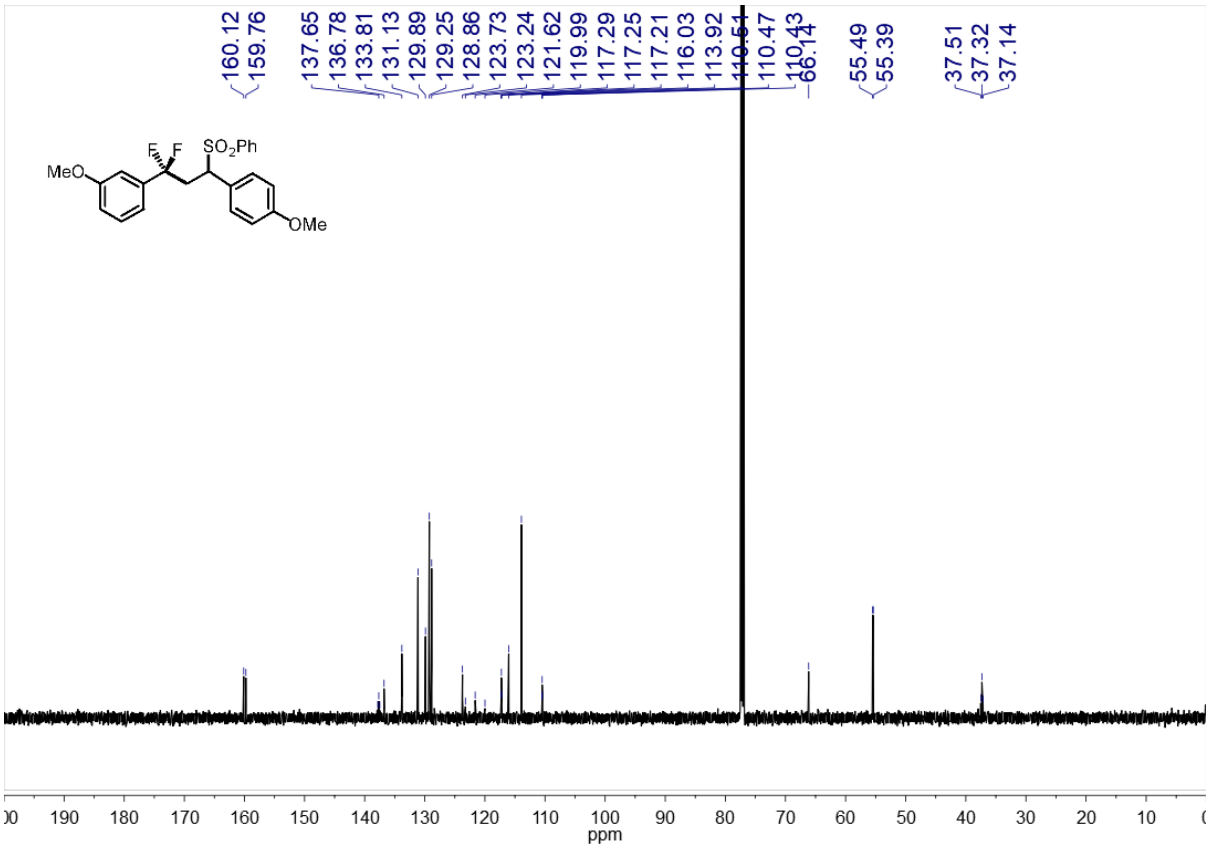
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5x**



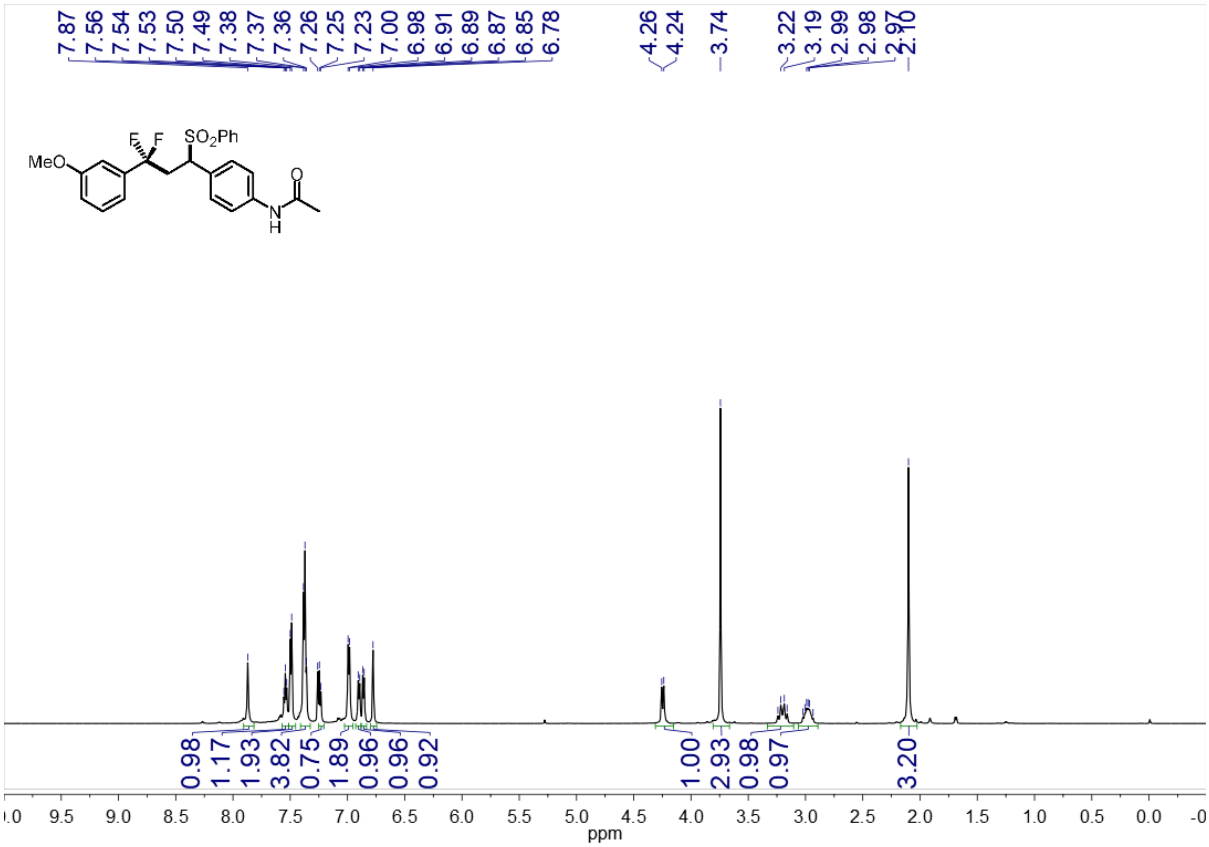
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5y**



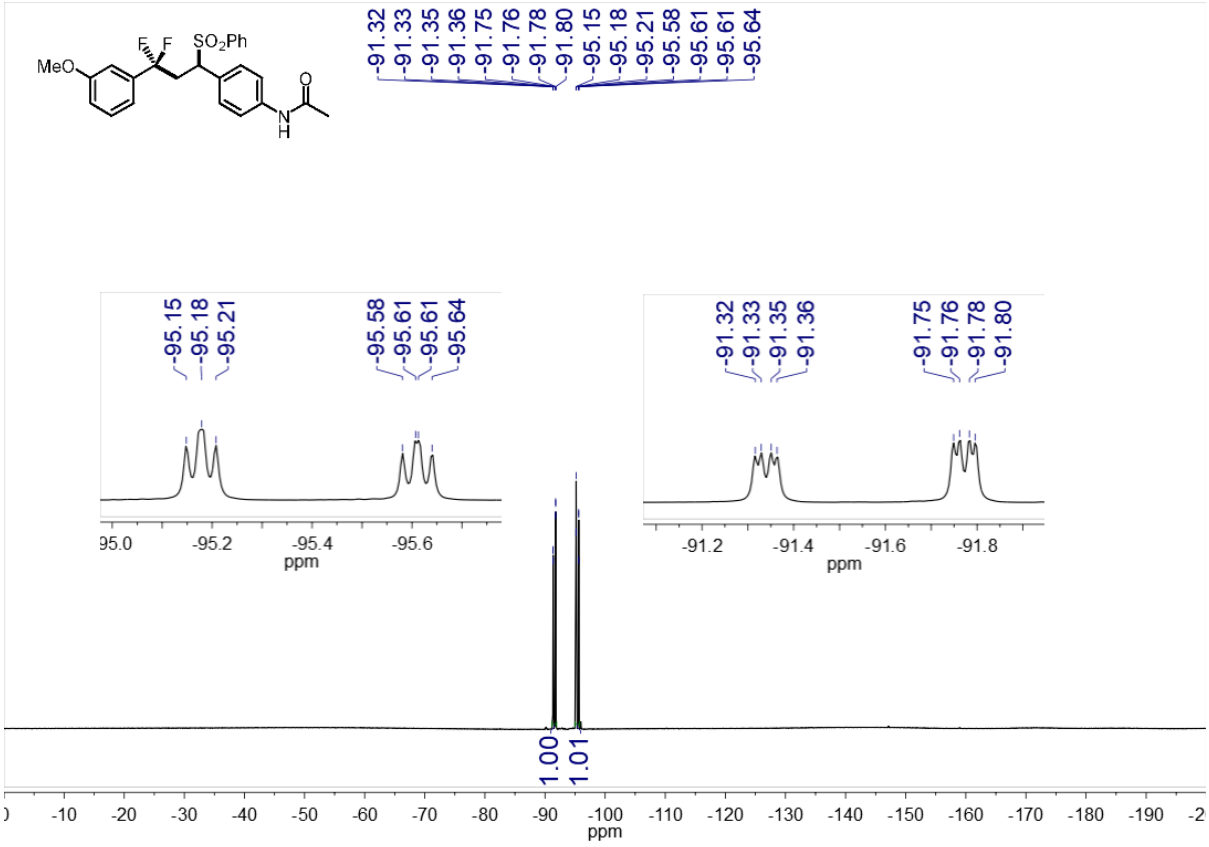
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5y**



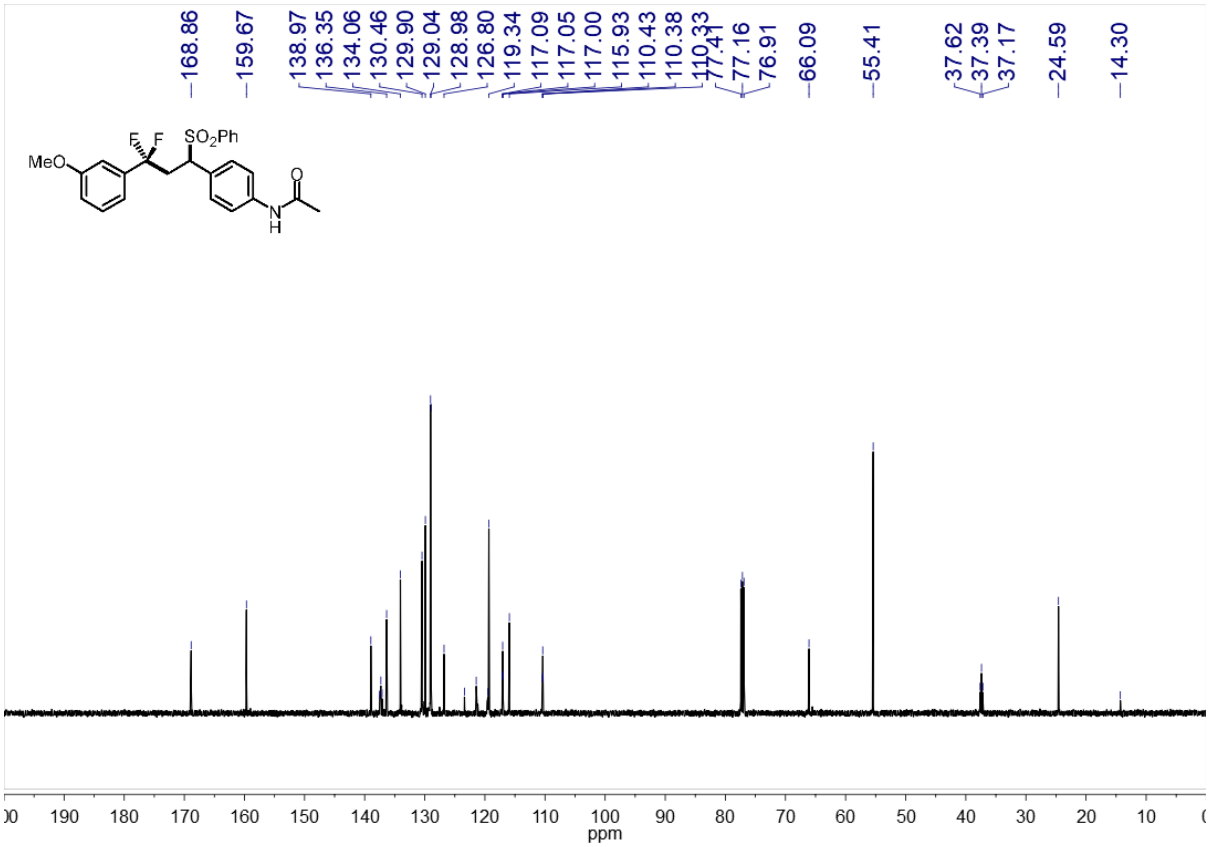
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5y**



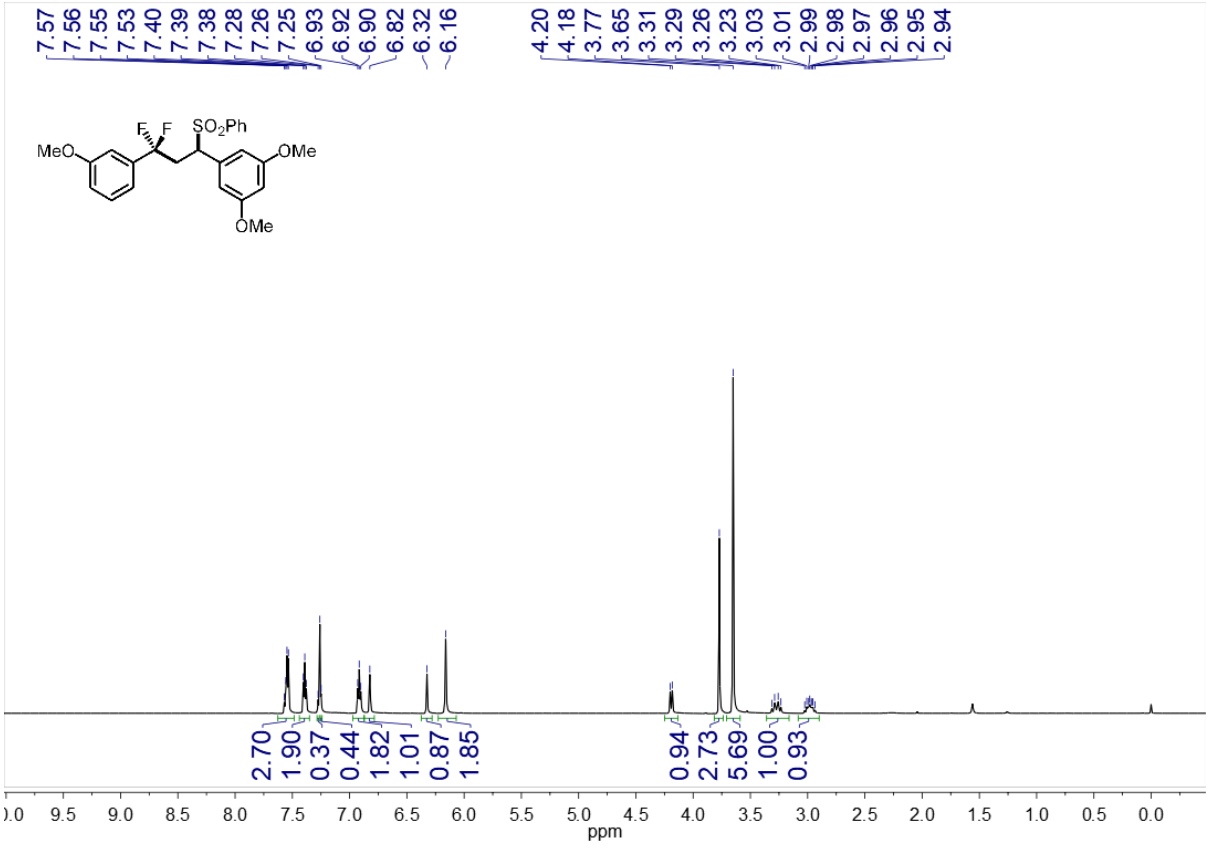
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5z**



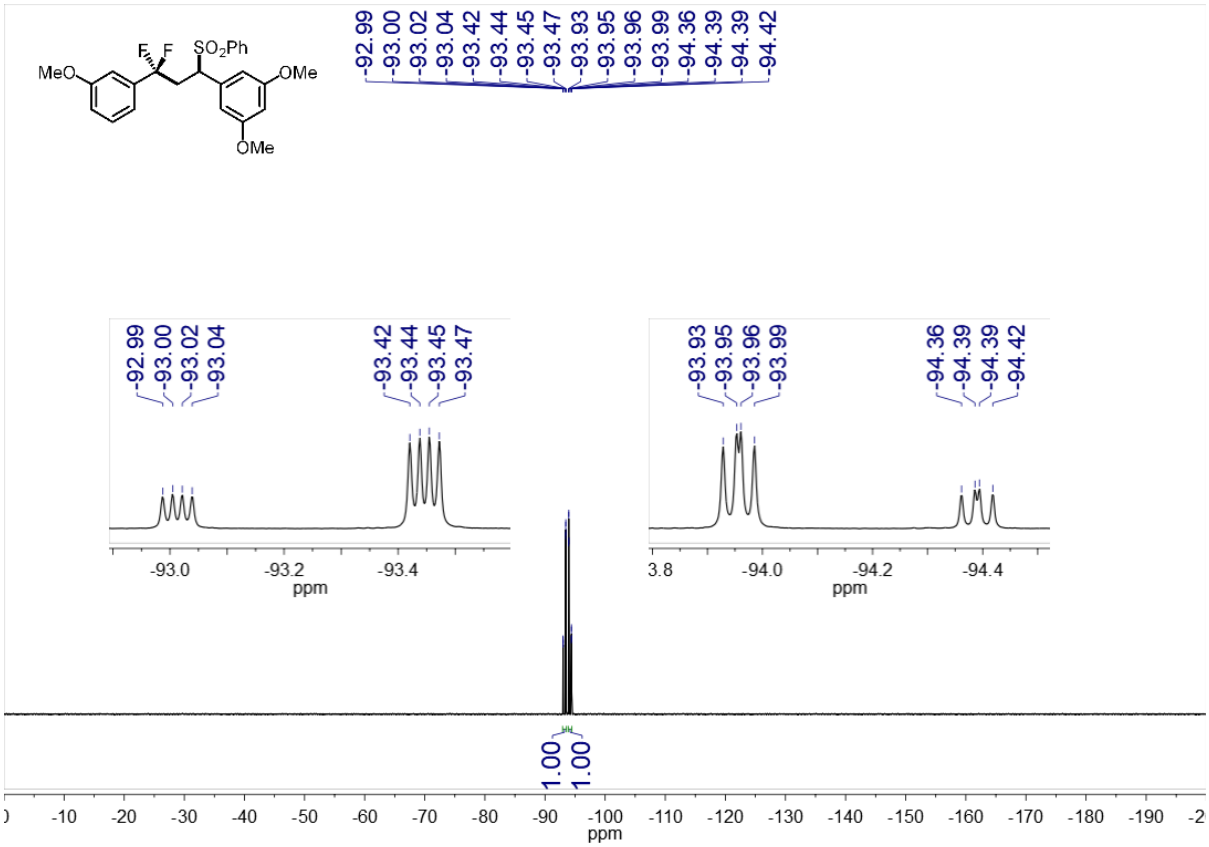
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5z**



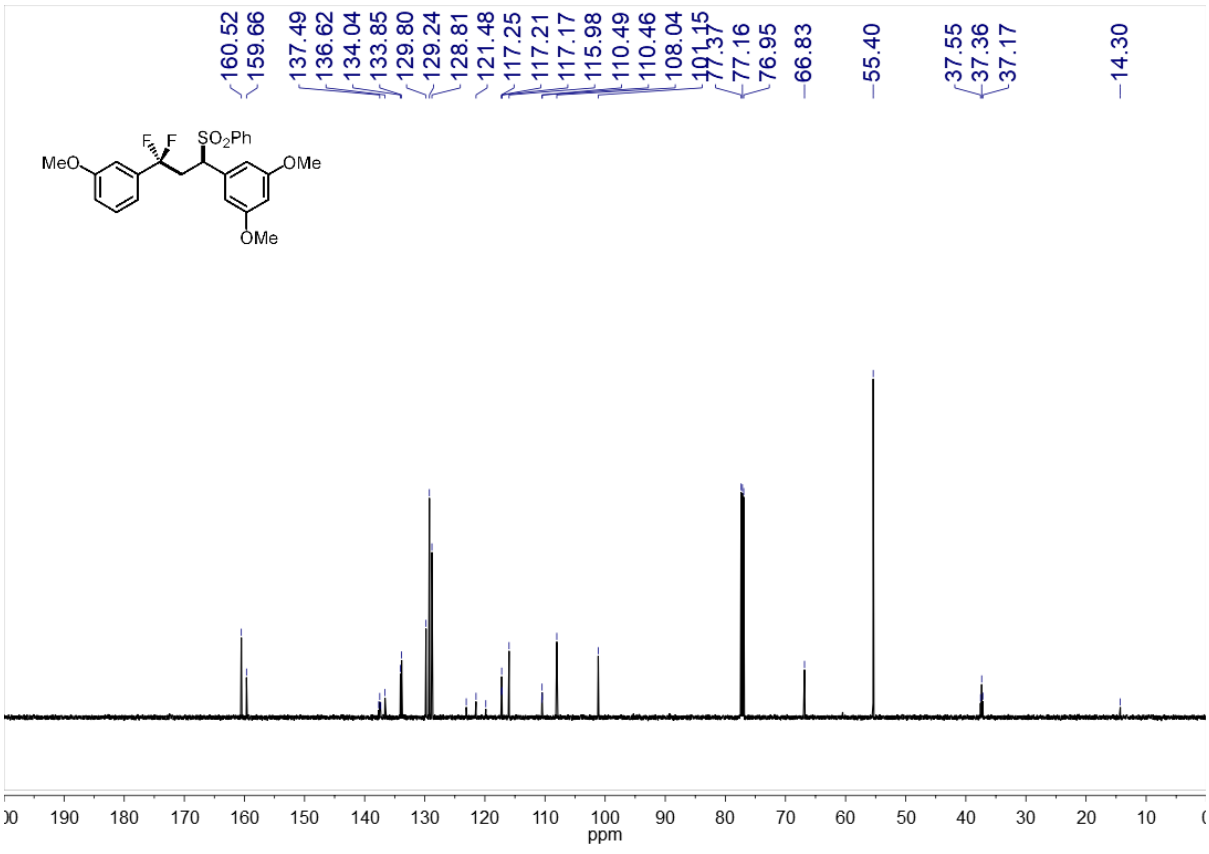
^{13}C NMR spectrum (126 MHz, $CDCl_3$, 23 ºC) of **5z**



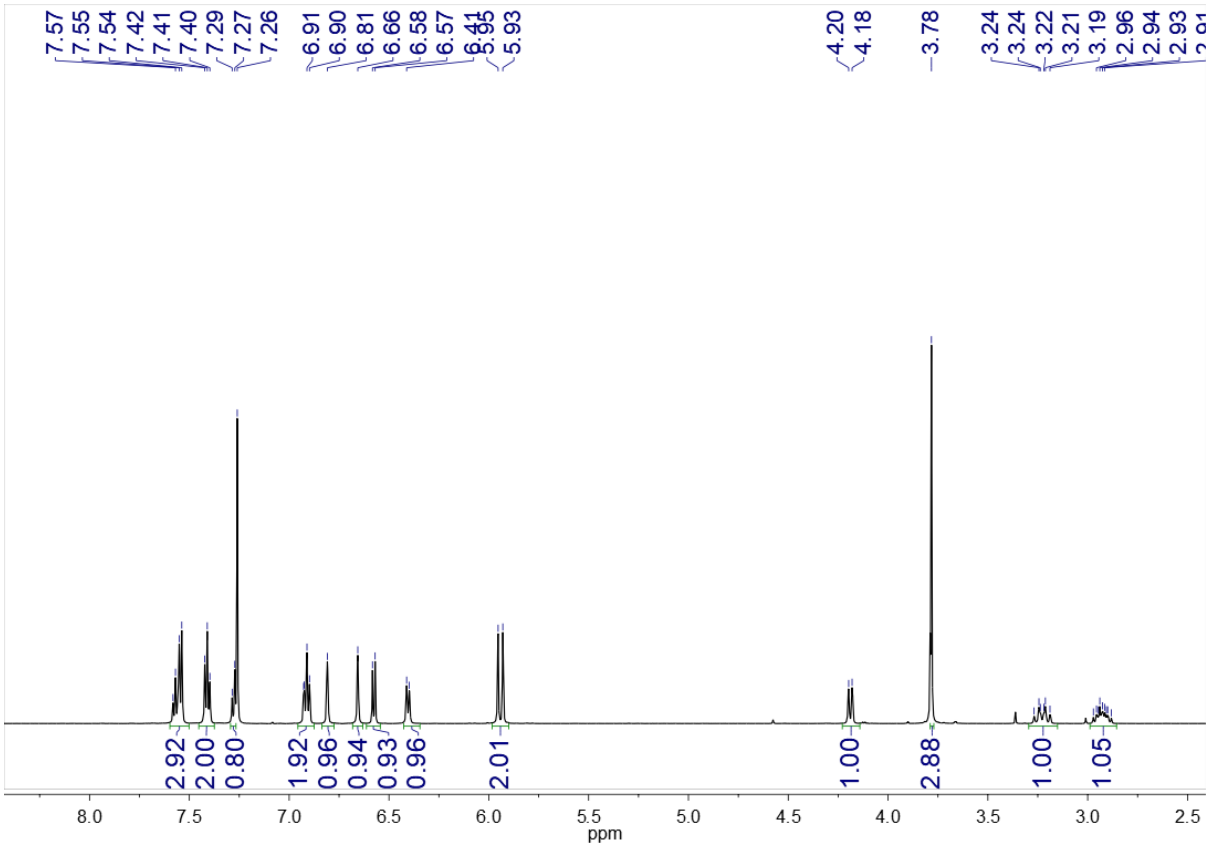
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5aa**



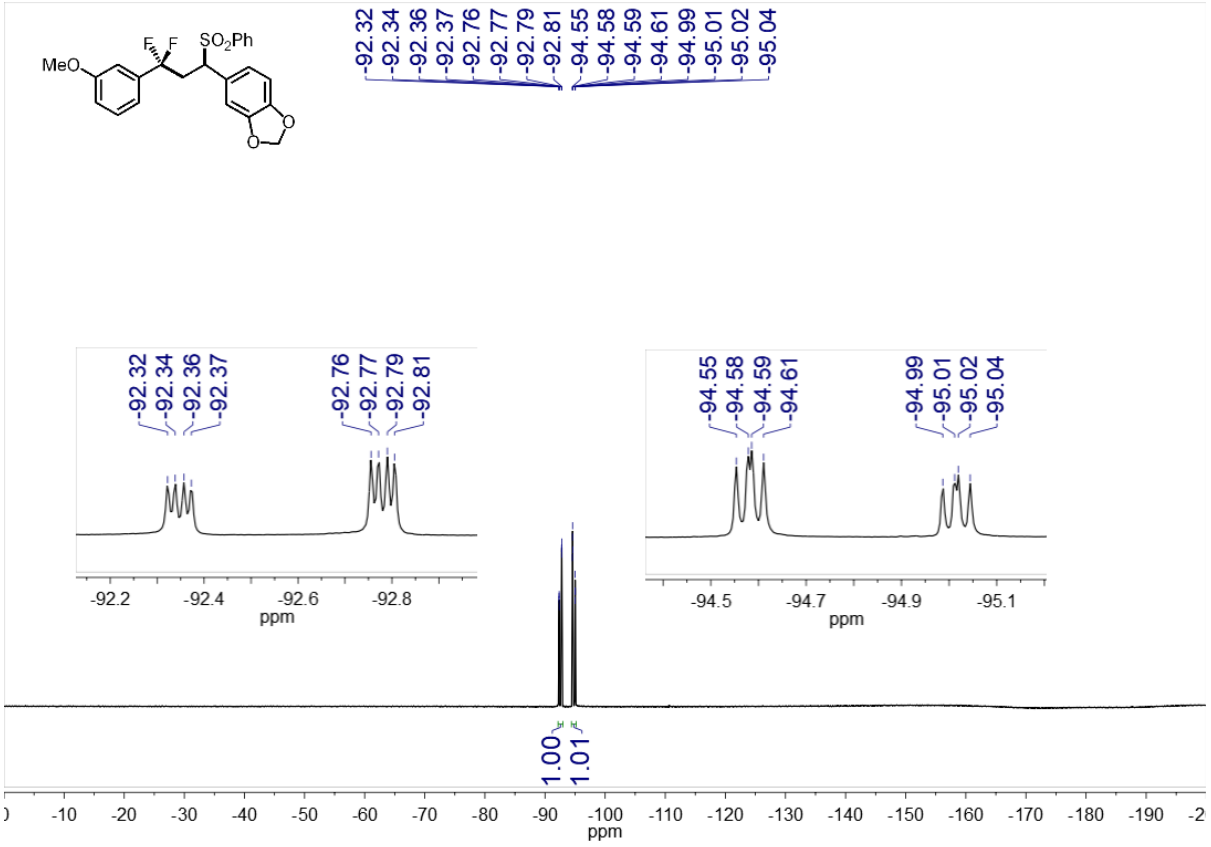
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5aa**



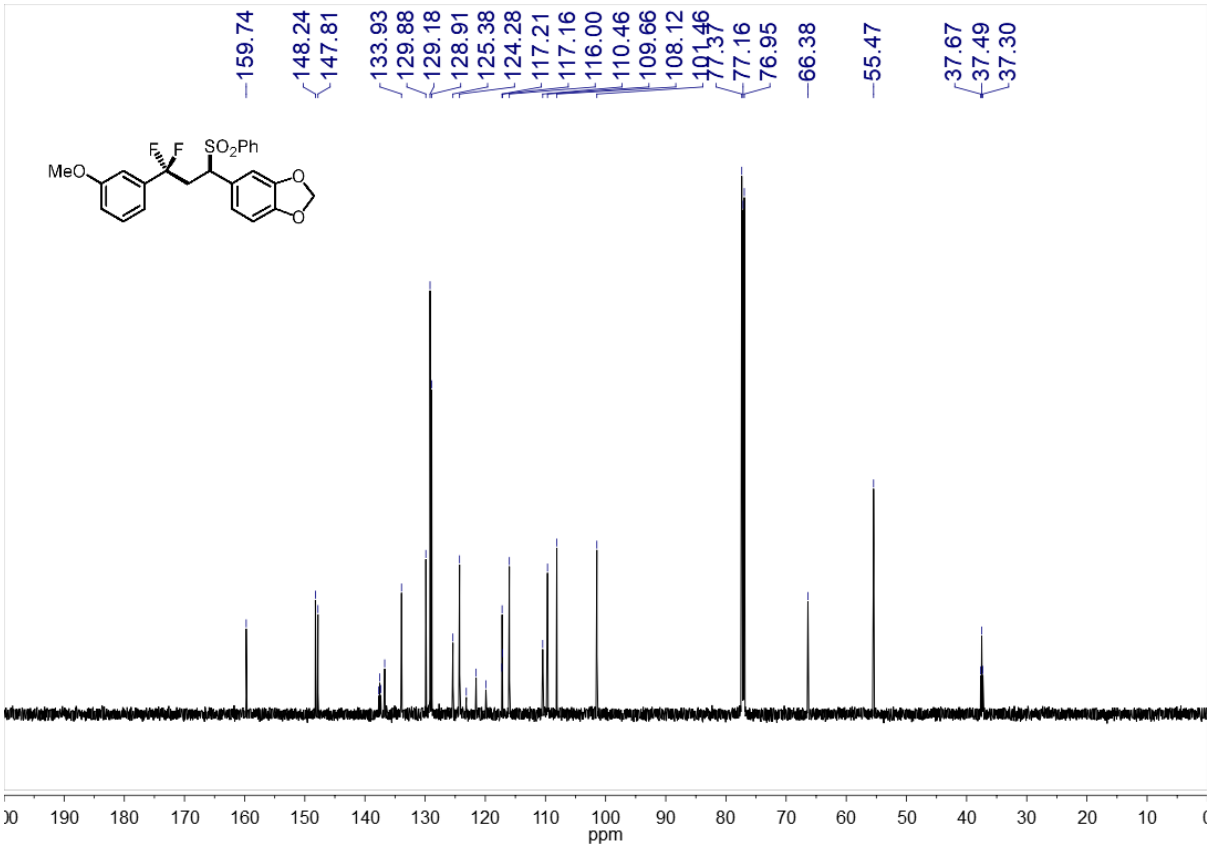
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5aa**



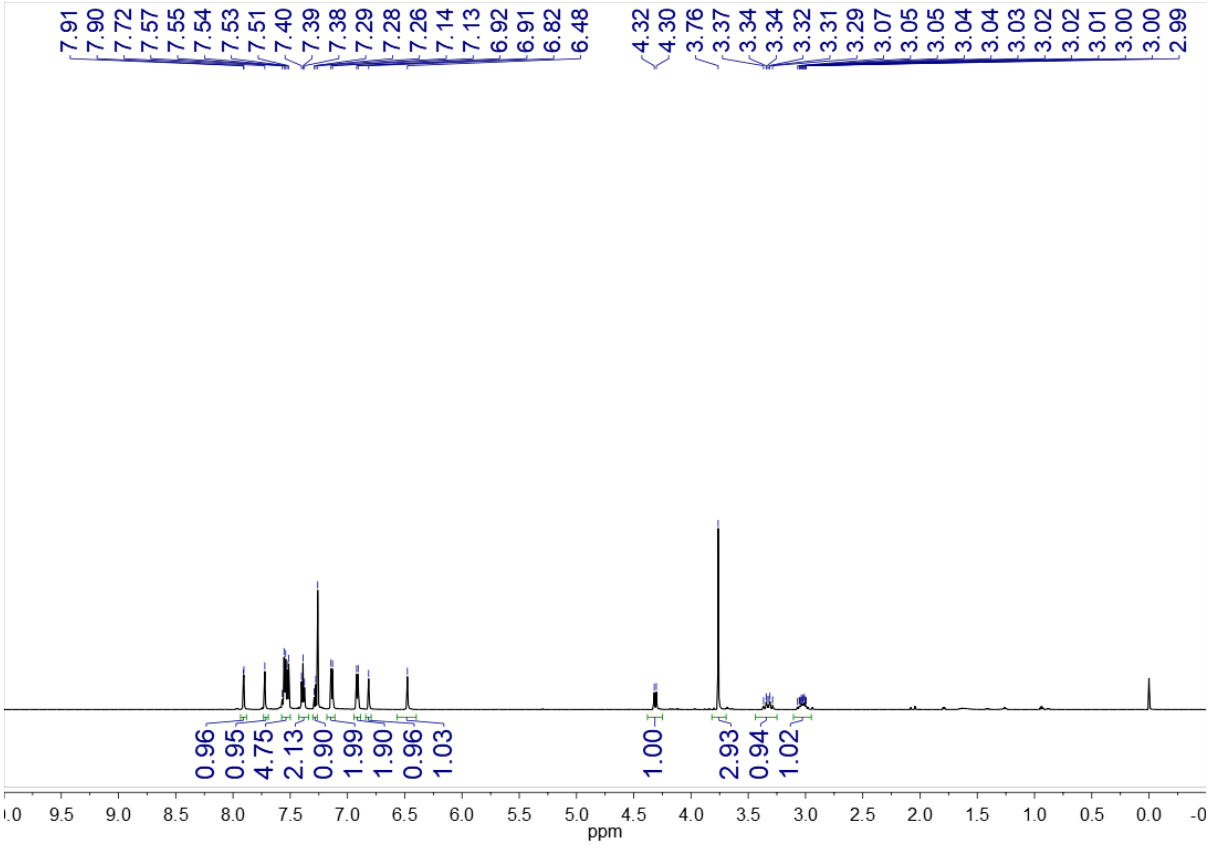
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5ab**



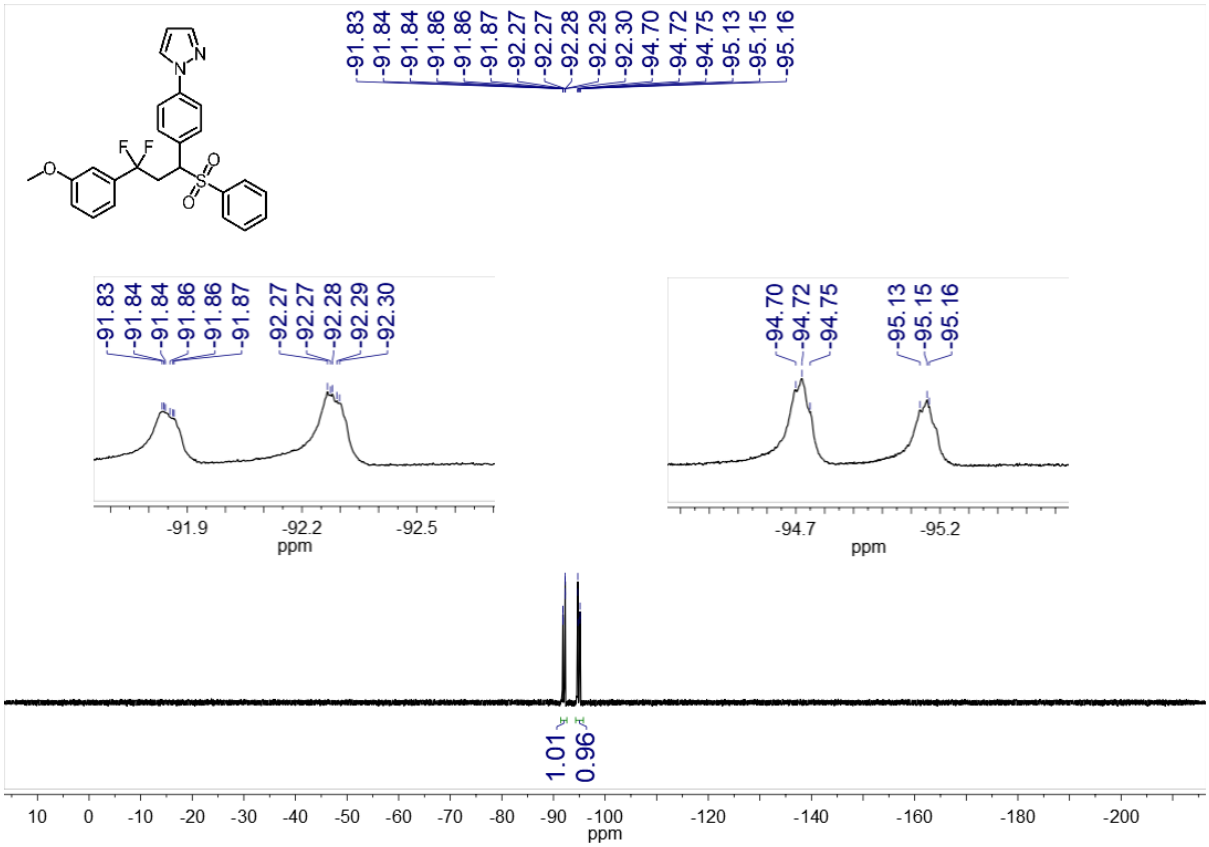
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5ab**



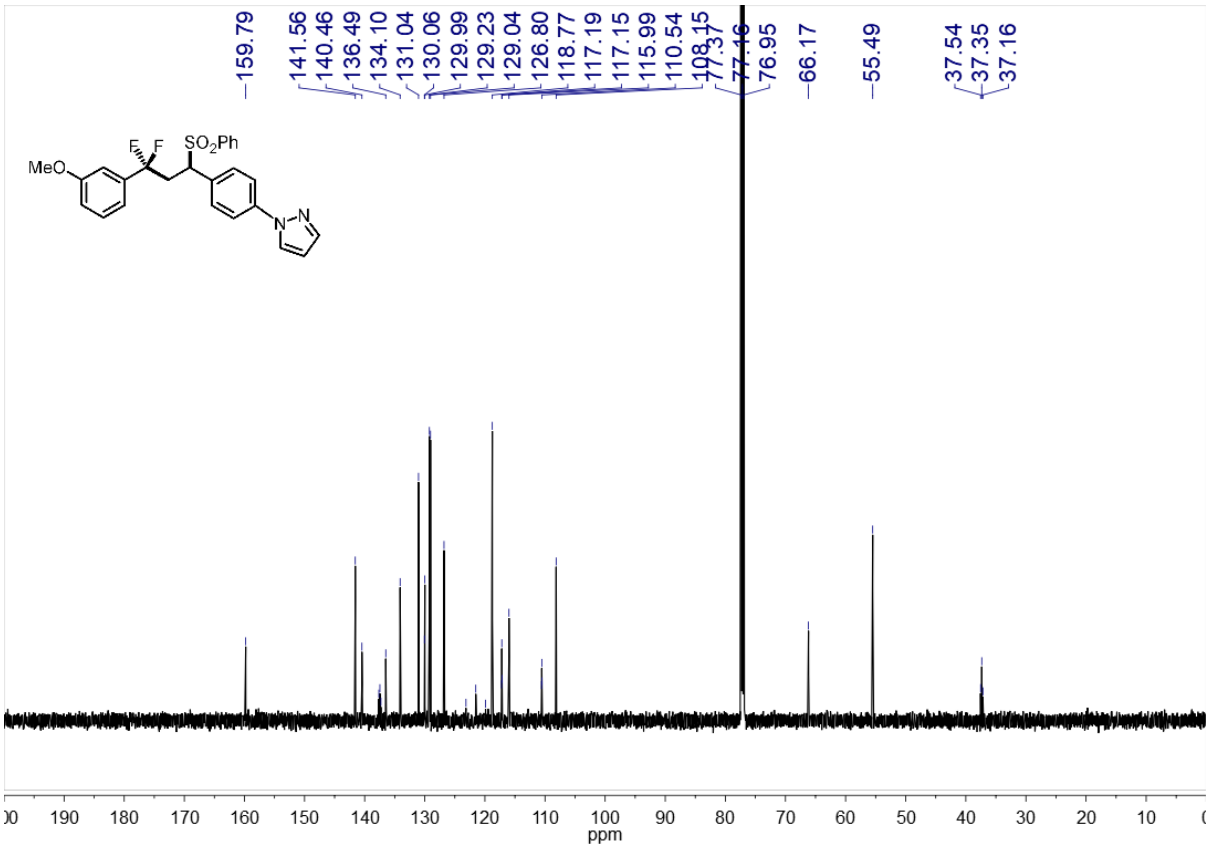
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5ab**



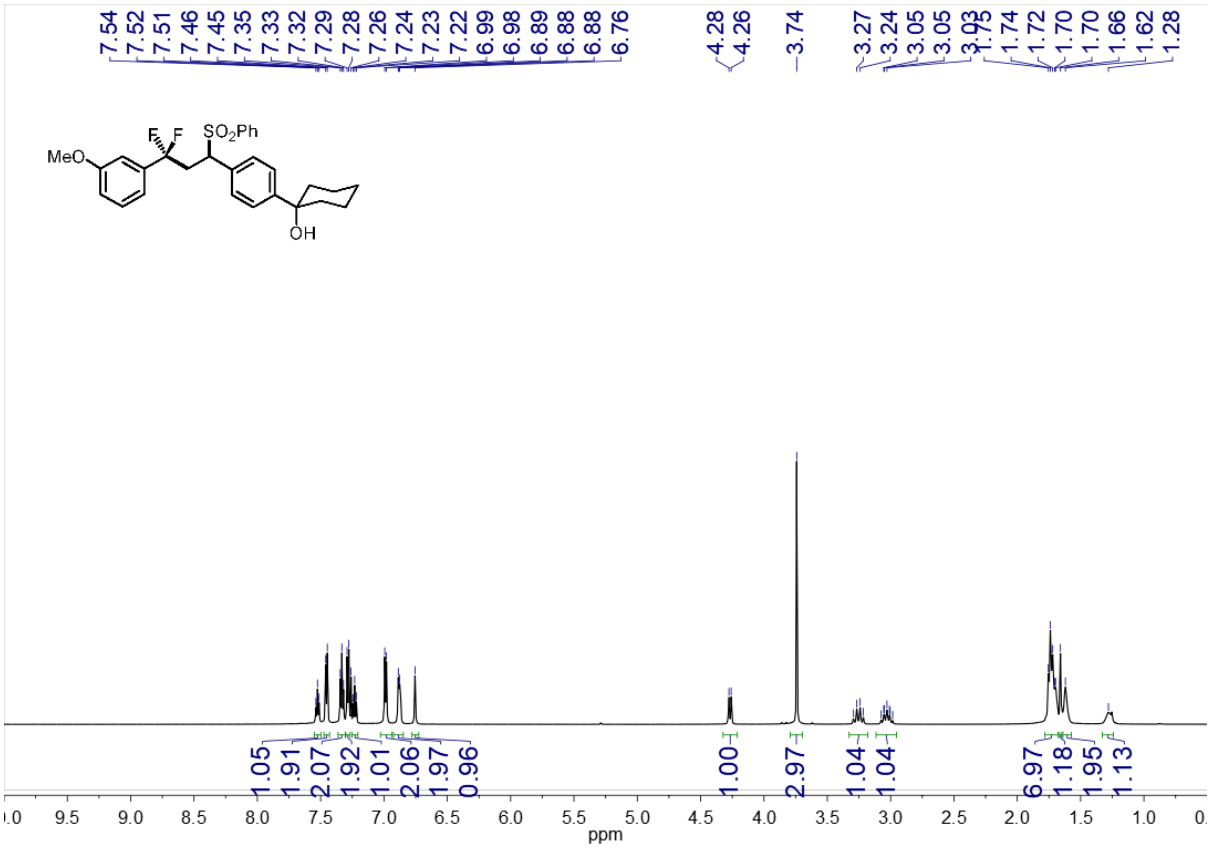
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5ac**



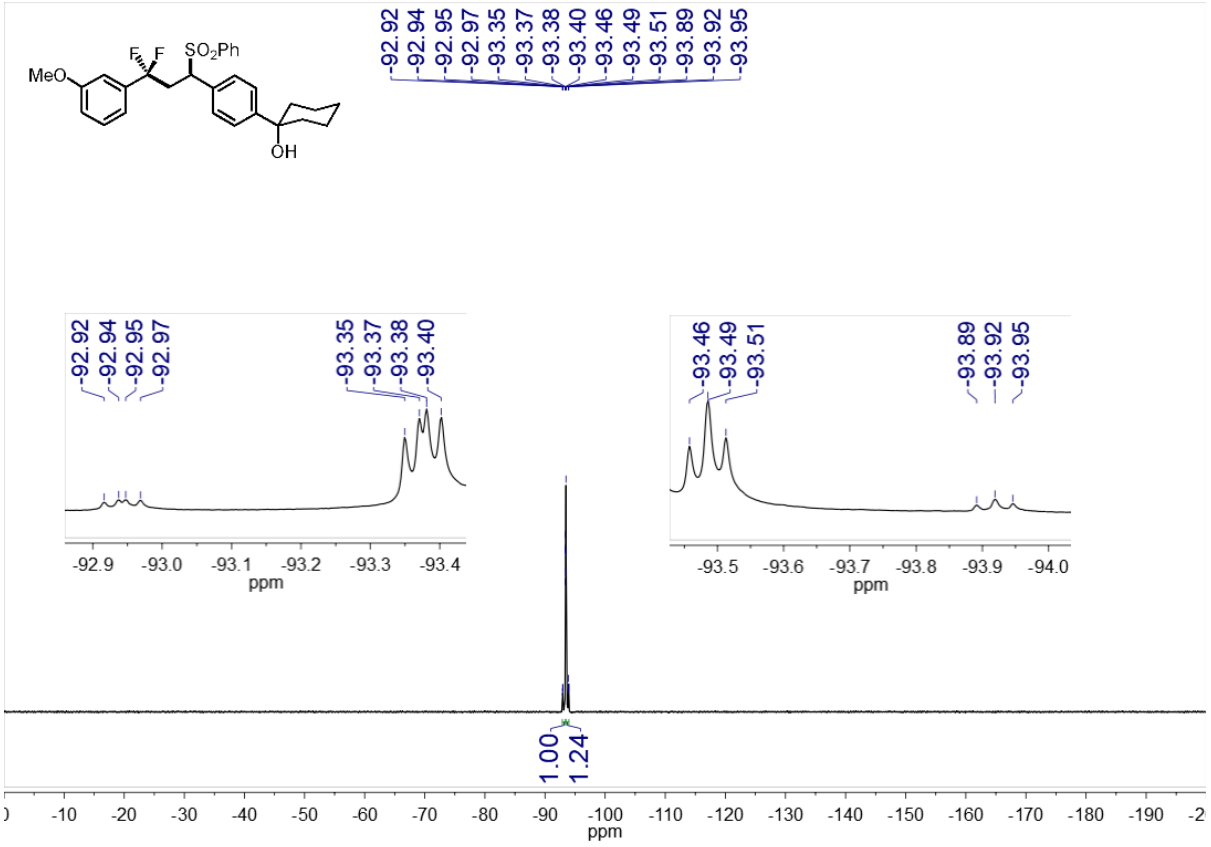
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5ac**



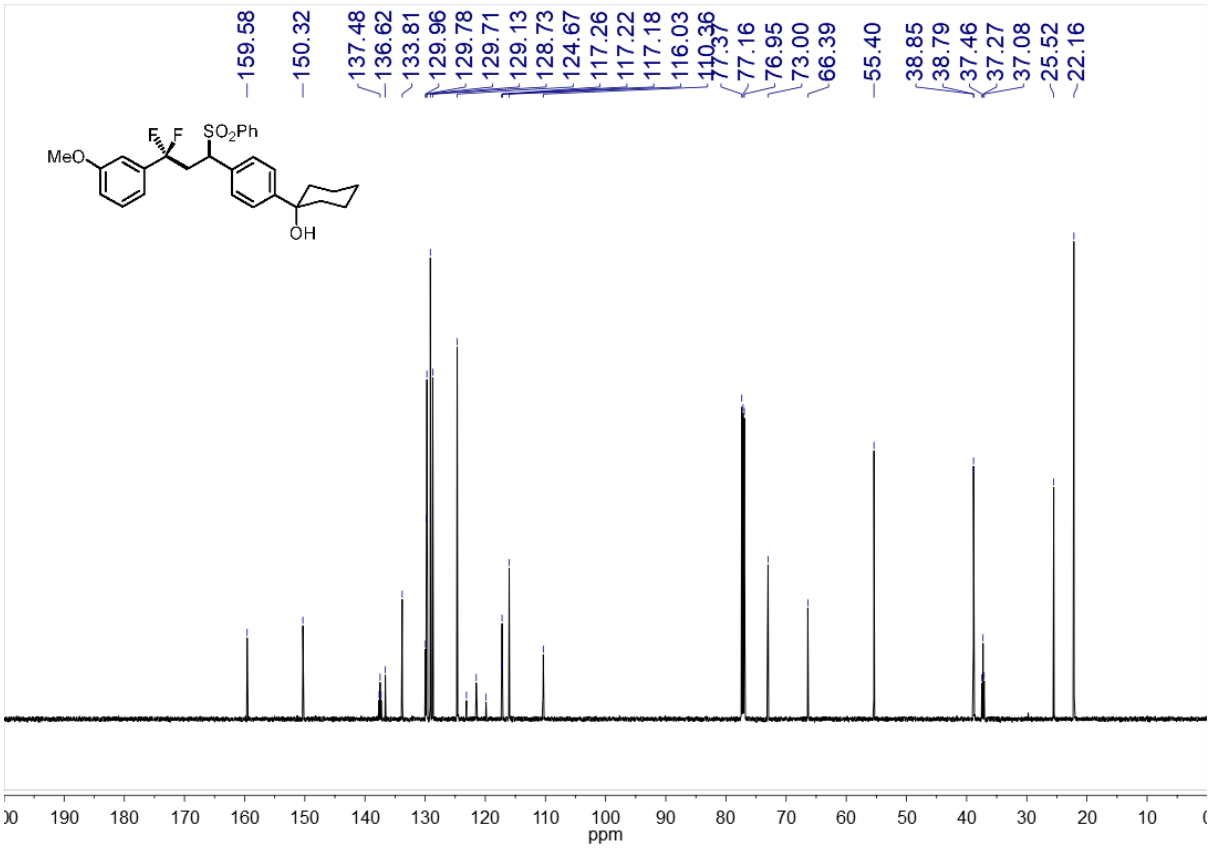
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5ac**



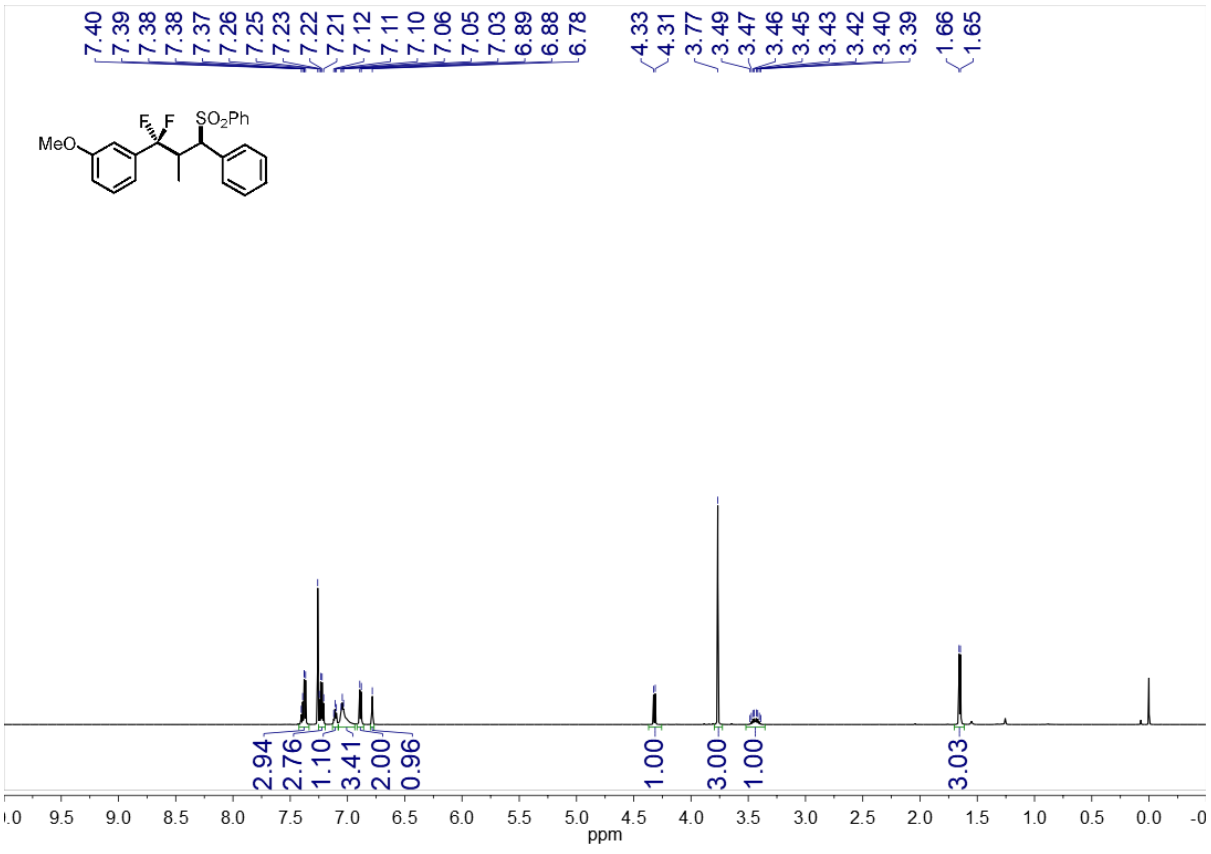
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5ad**



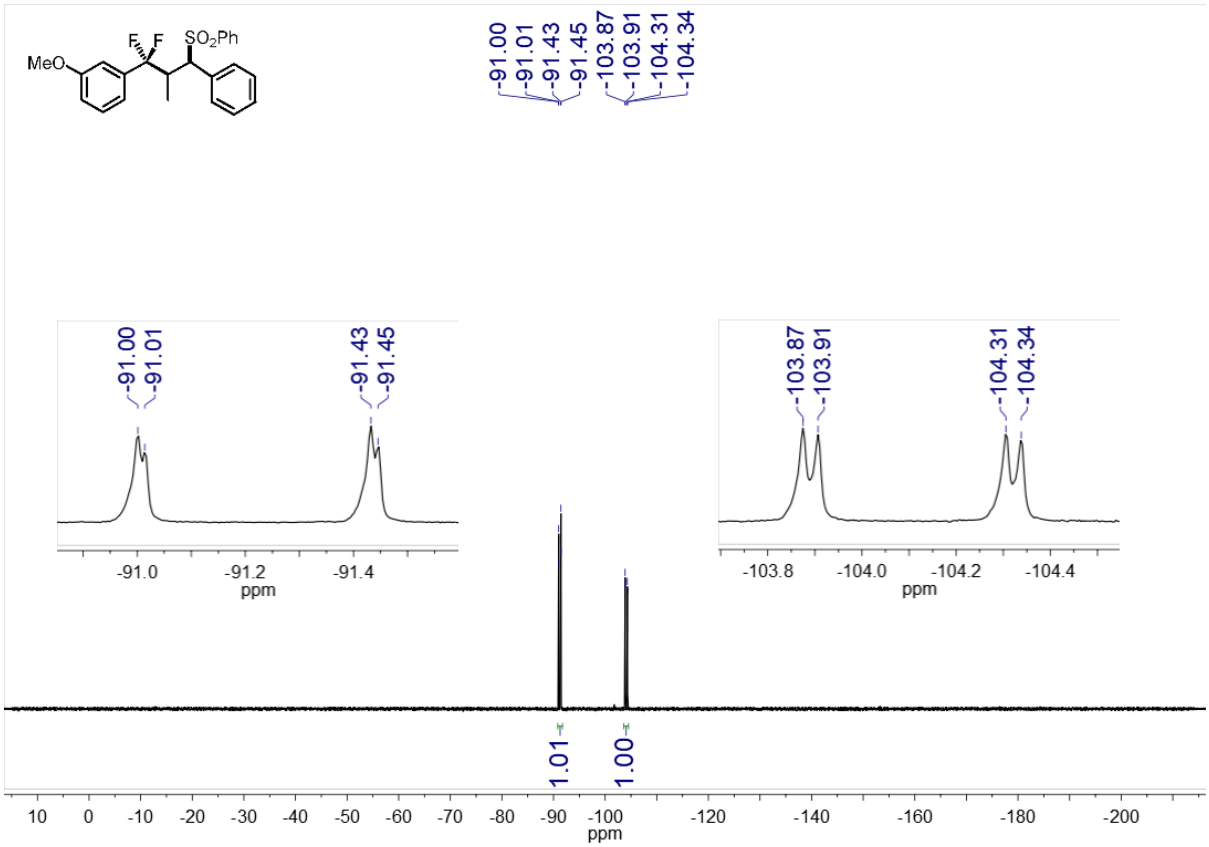
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5ad**



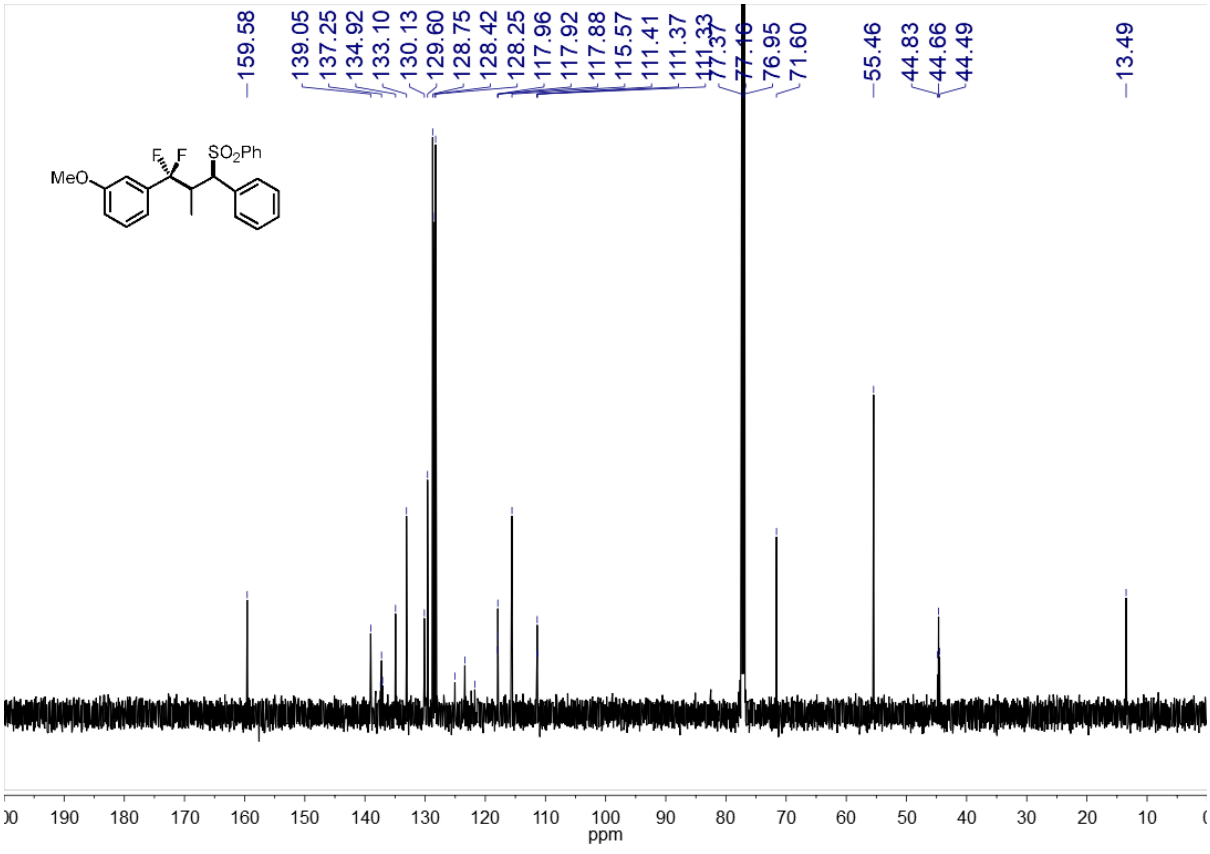
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5ad**



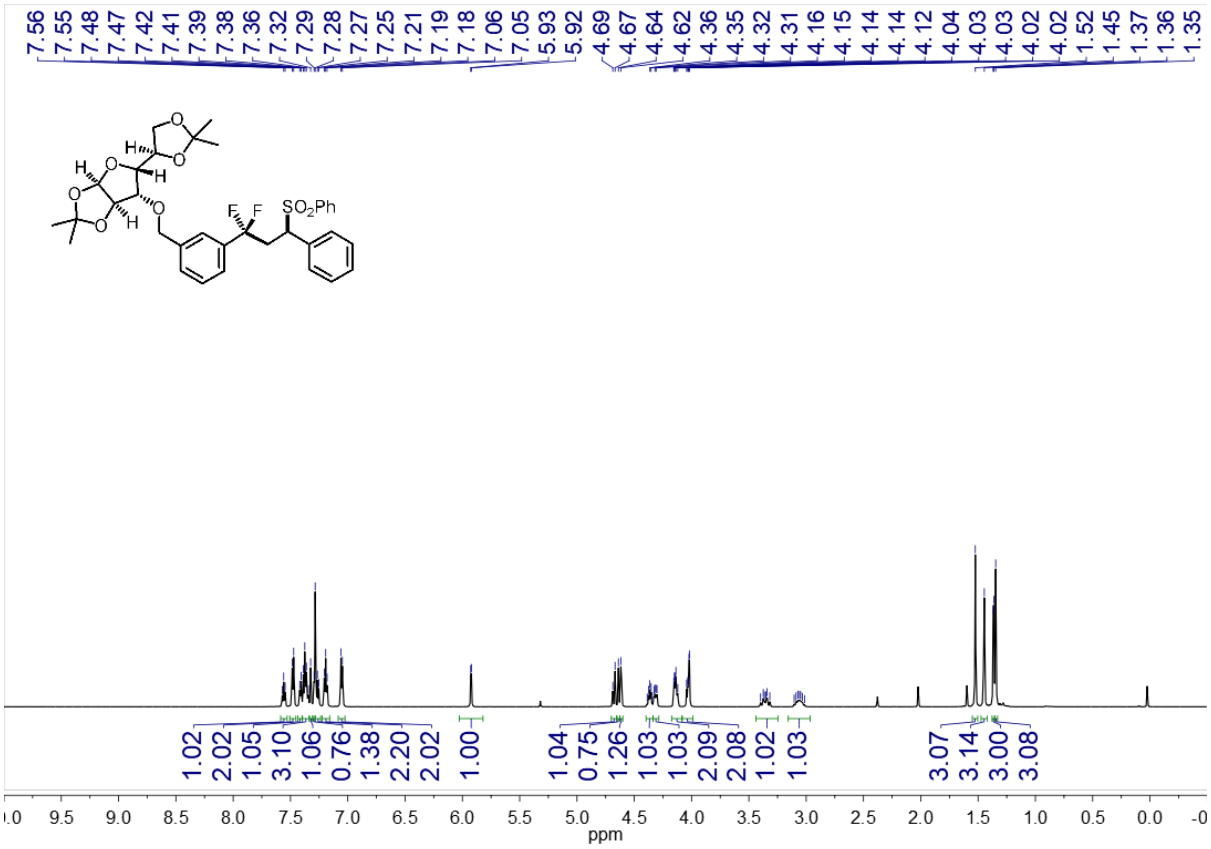
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5ae**



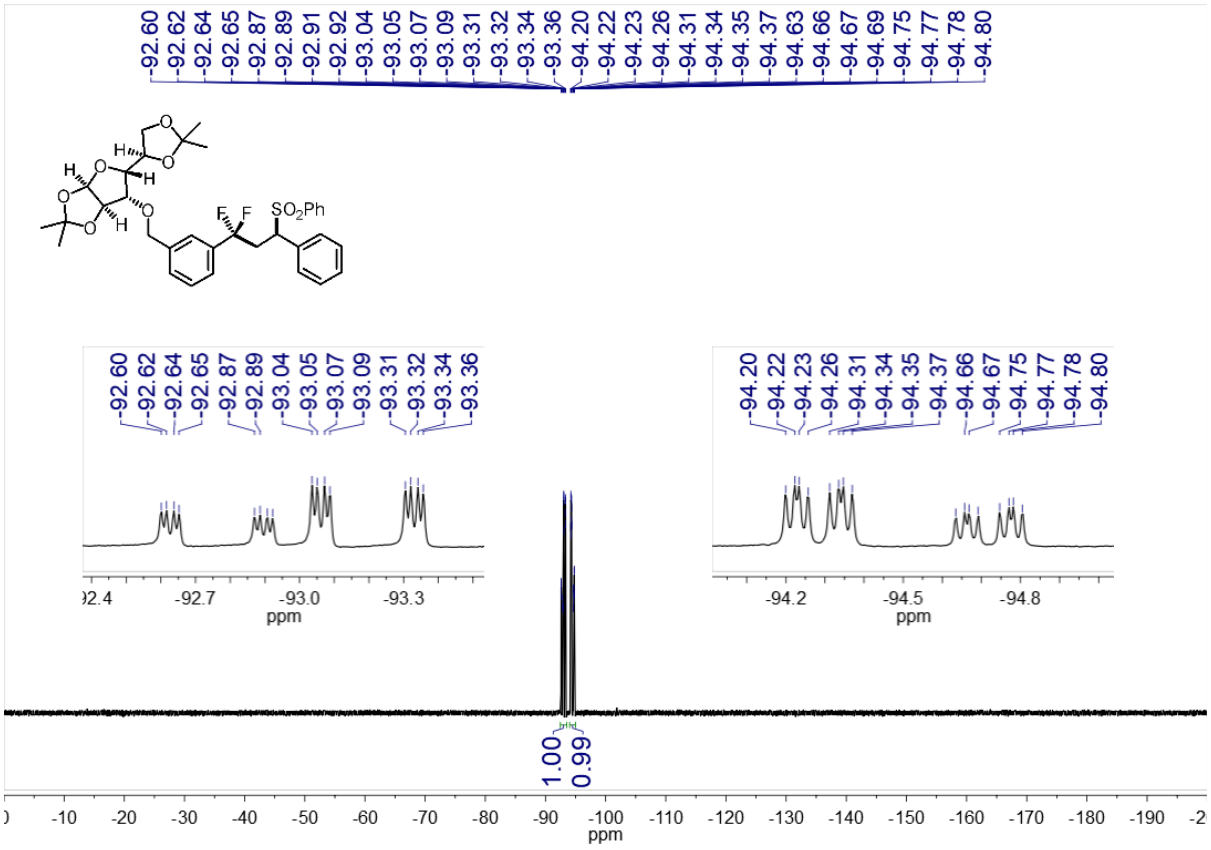
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5ae**



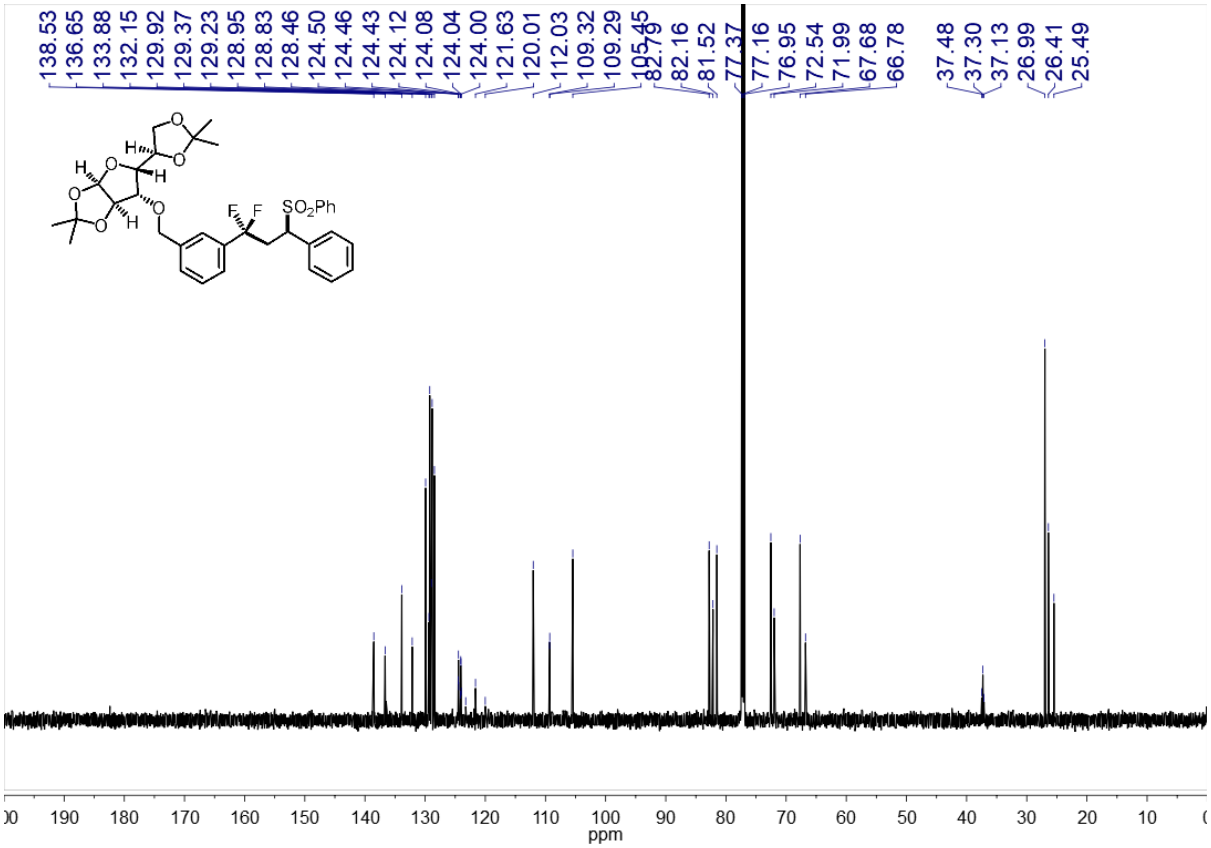
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5ae**



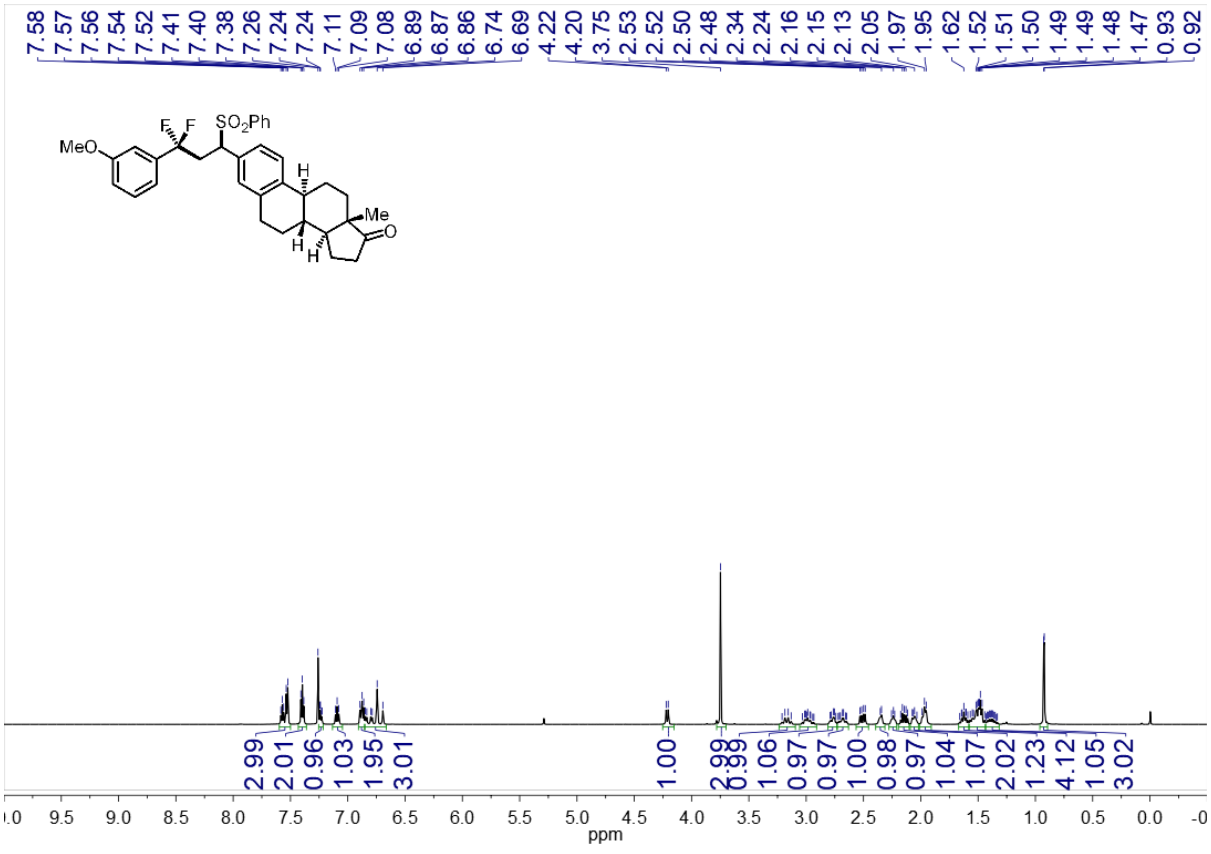
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5af**



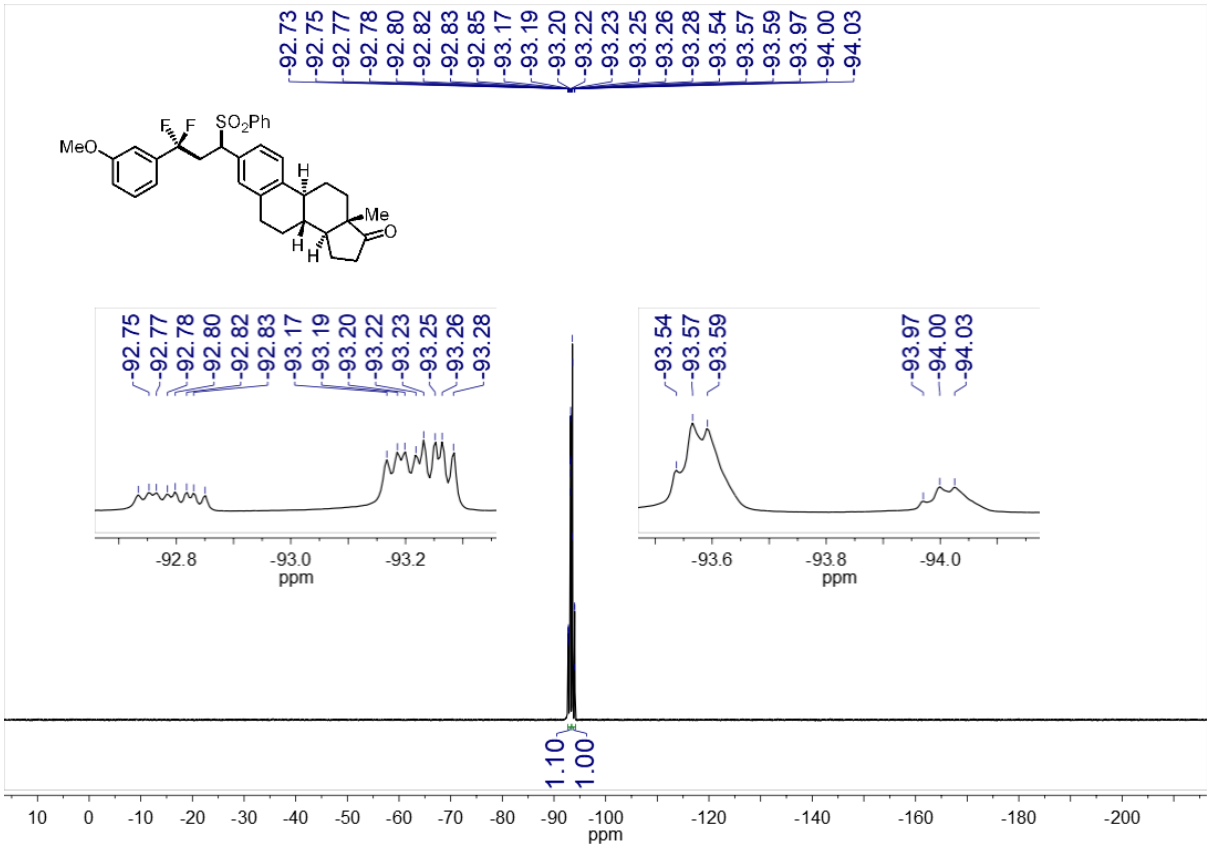
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5af**



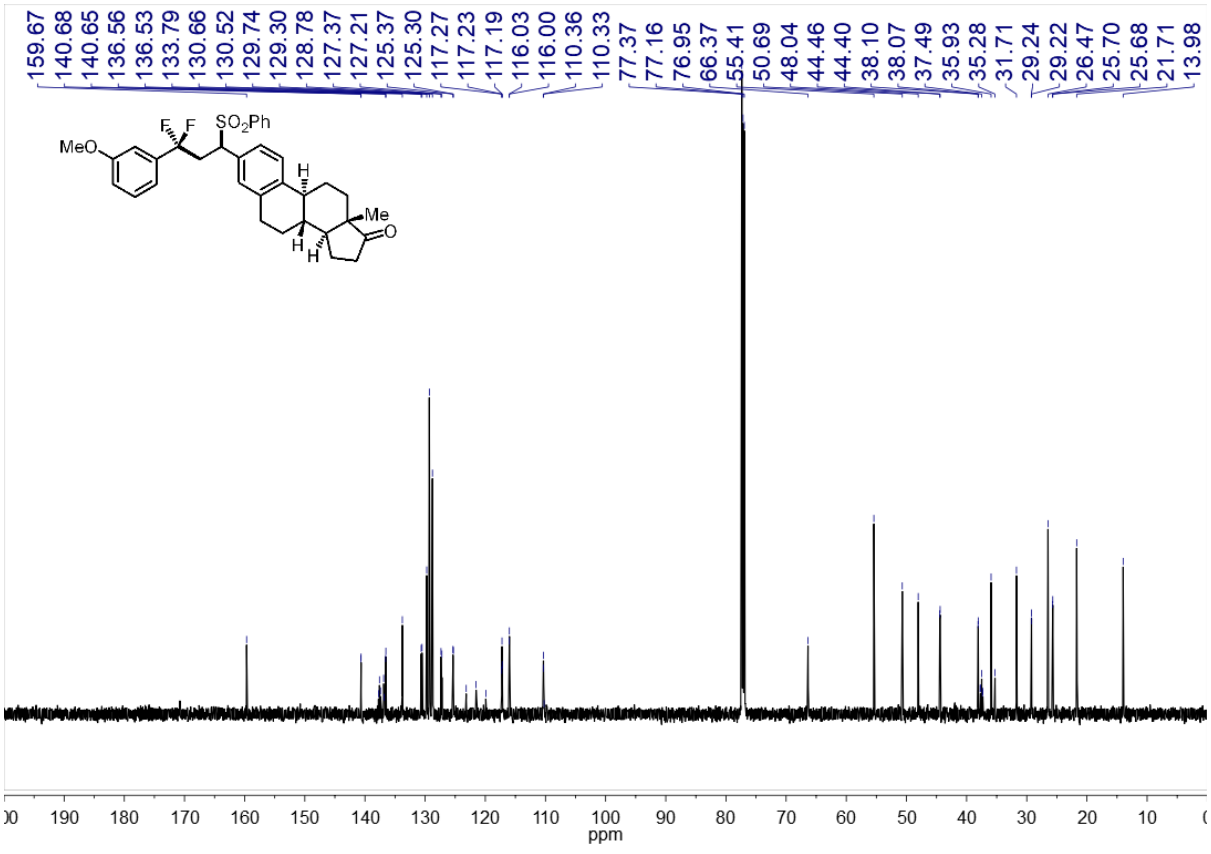
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5af**



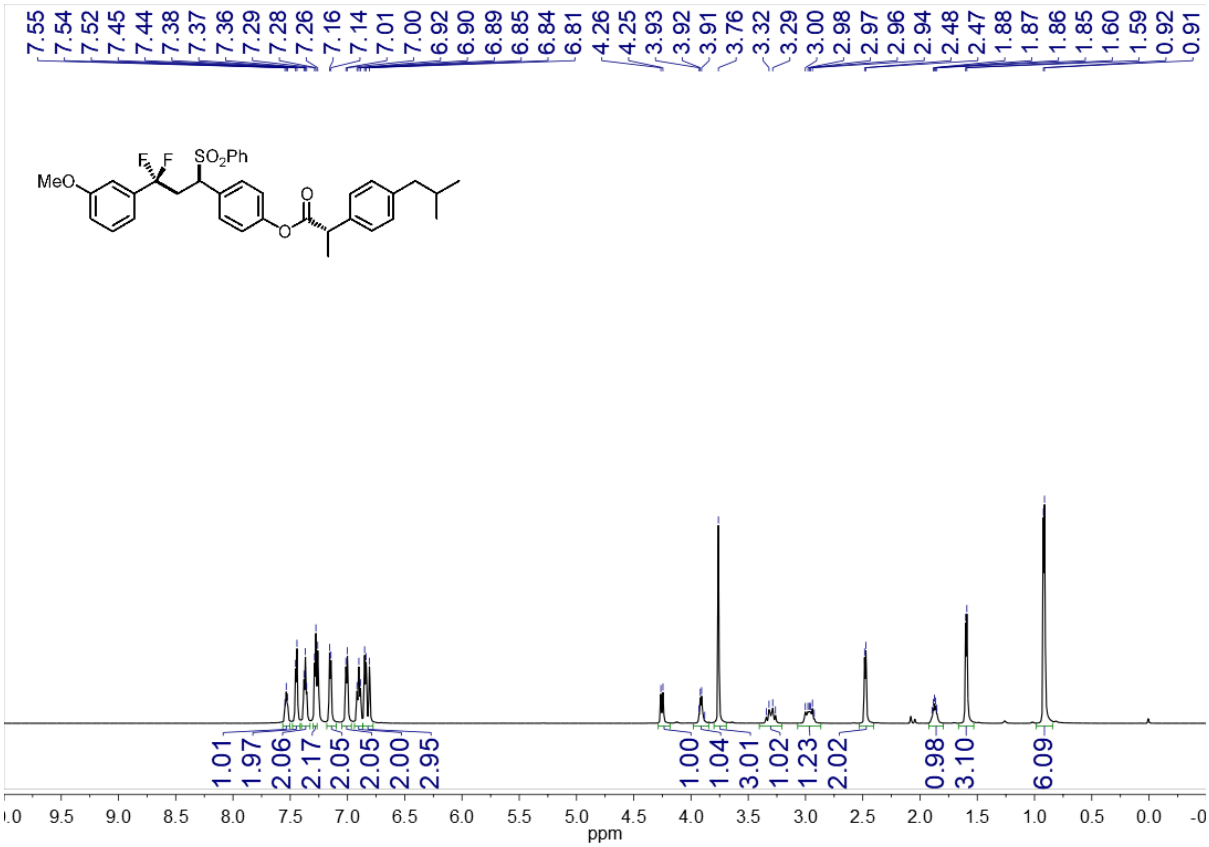
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5ag**



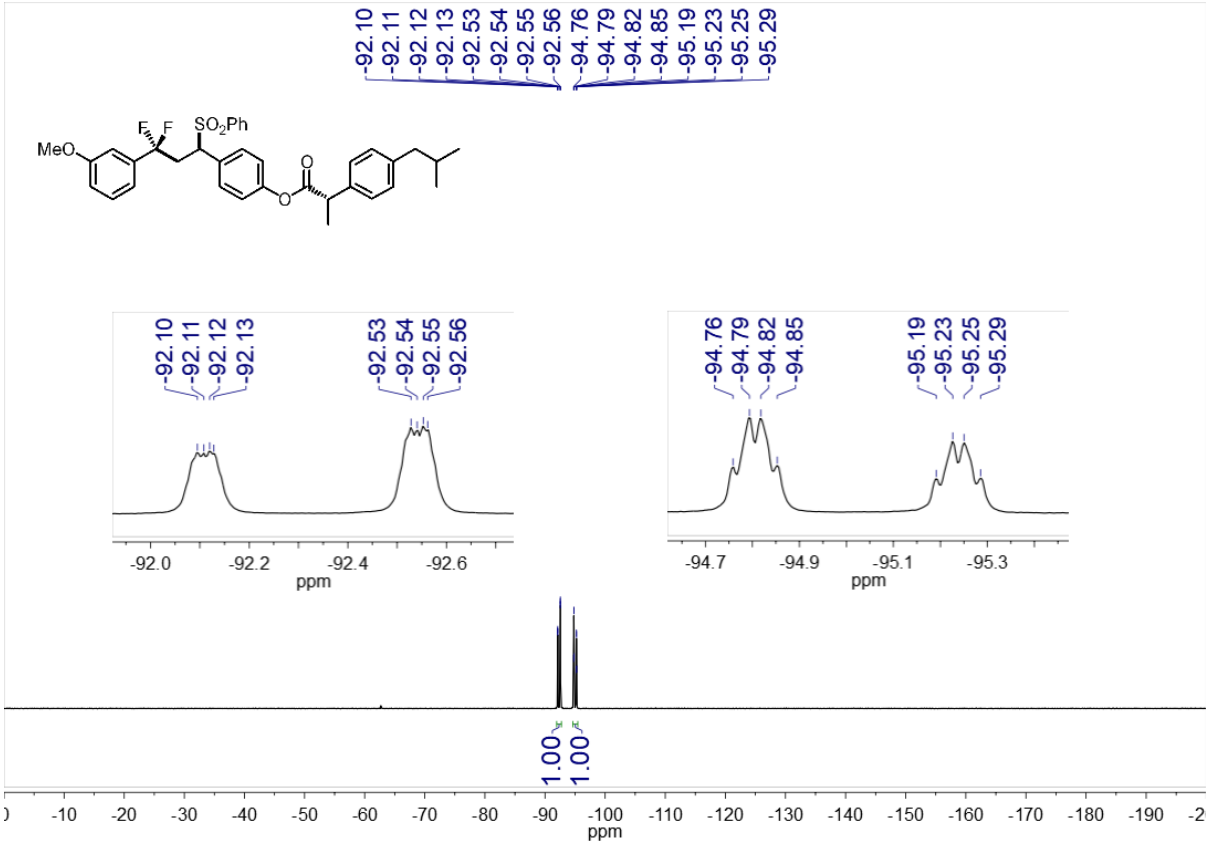
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5ag**



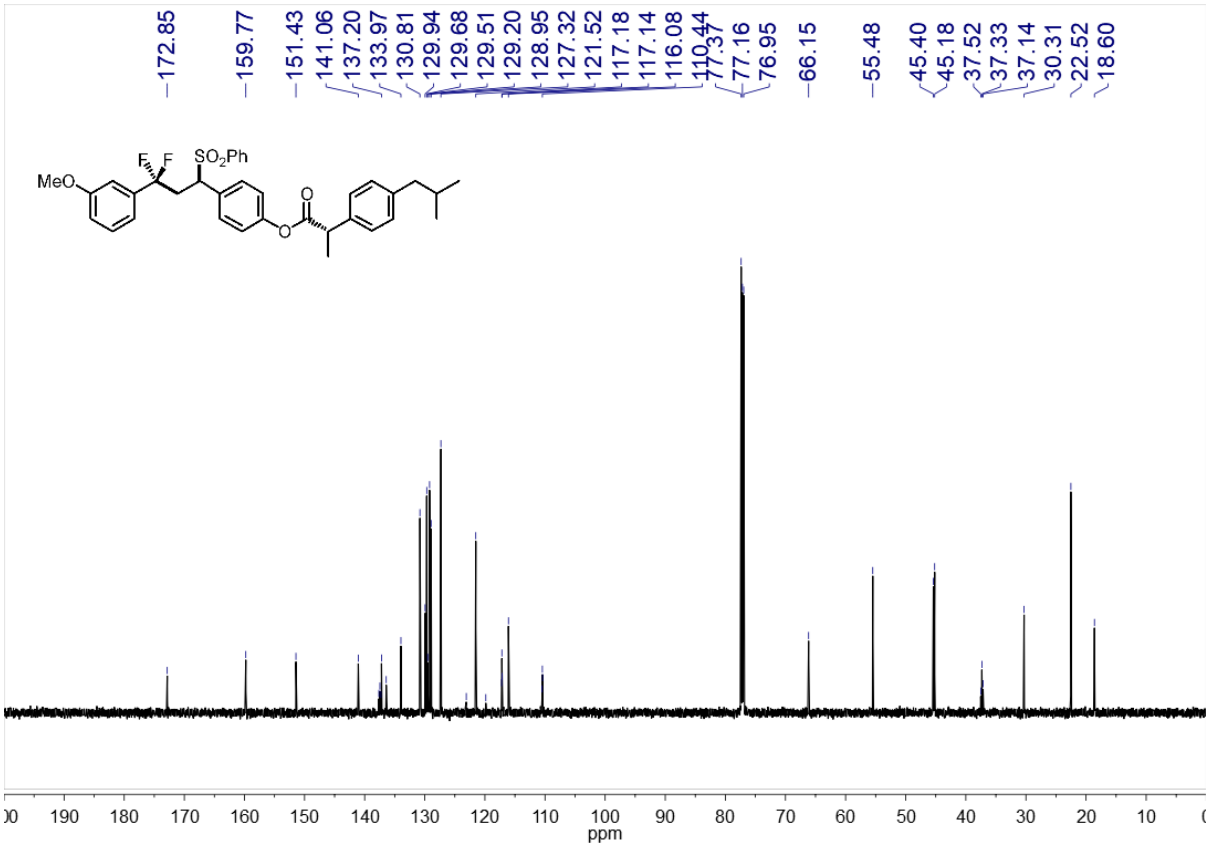
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5ag**



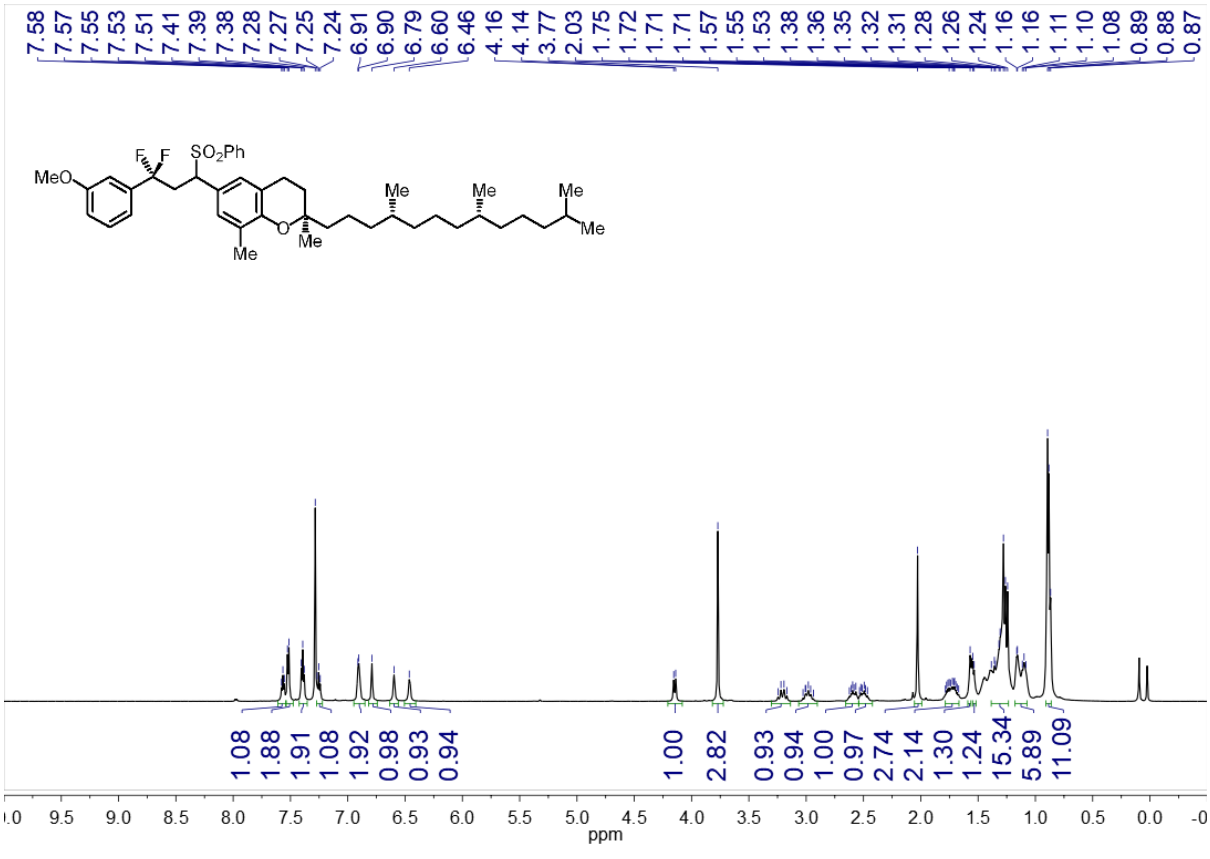
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5ah**



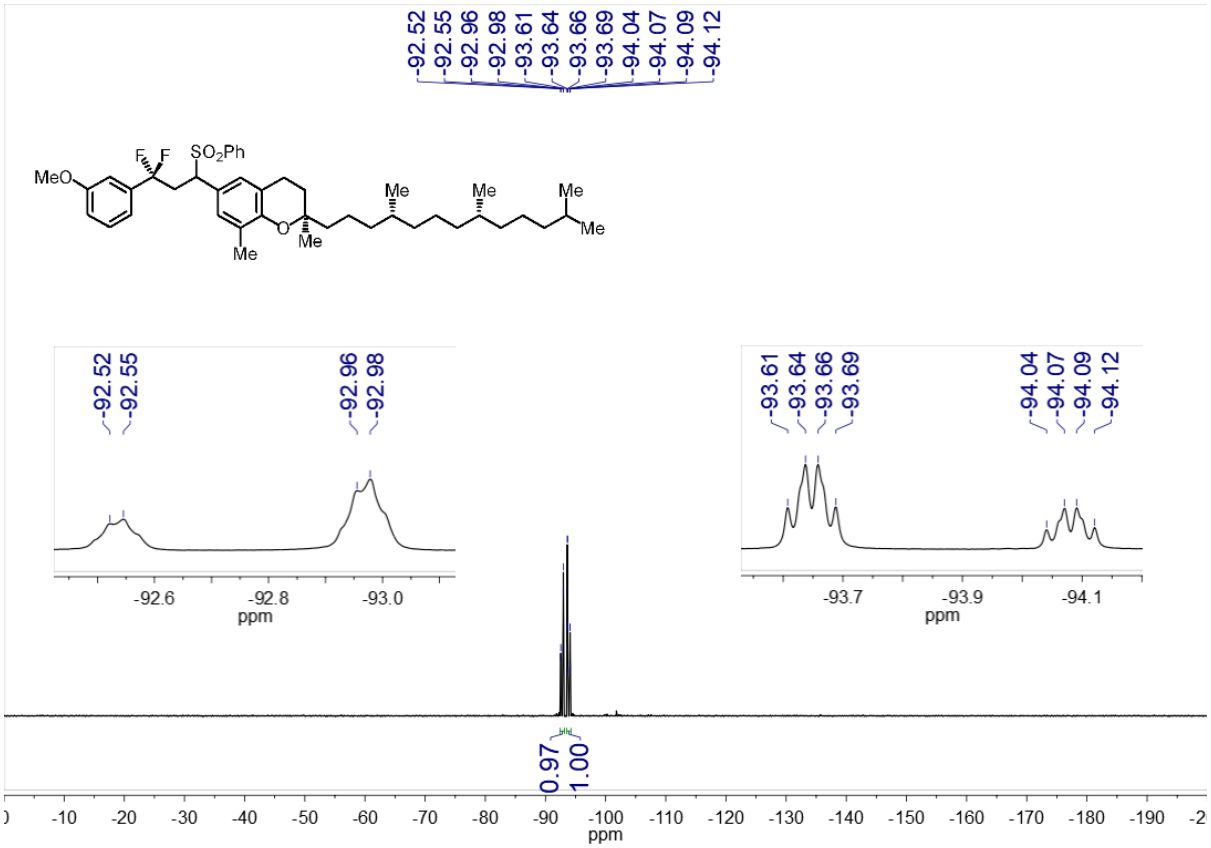
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5ah**



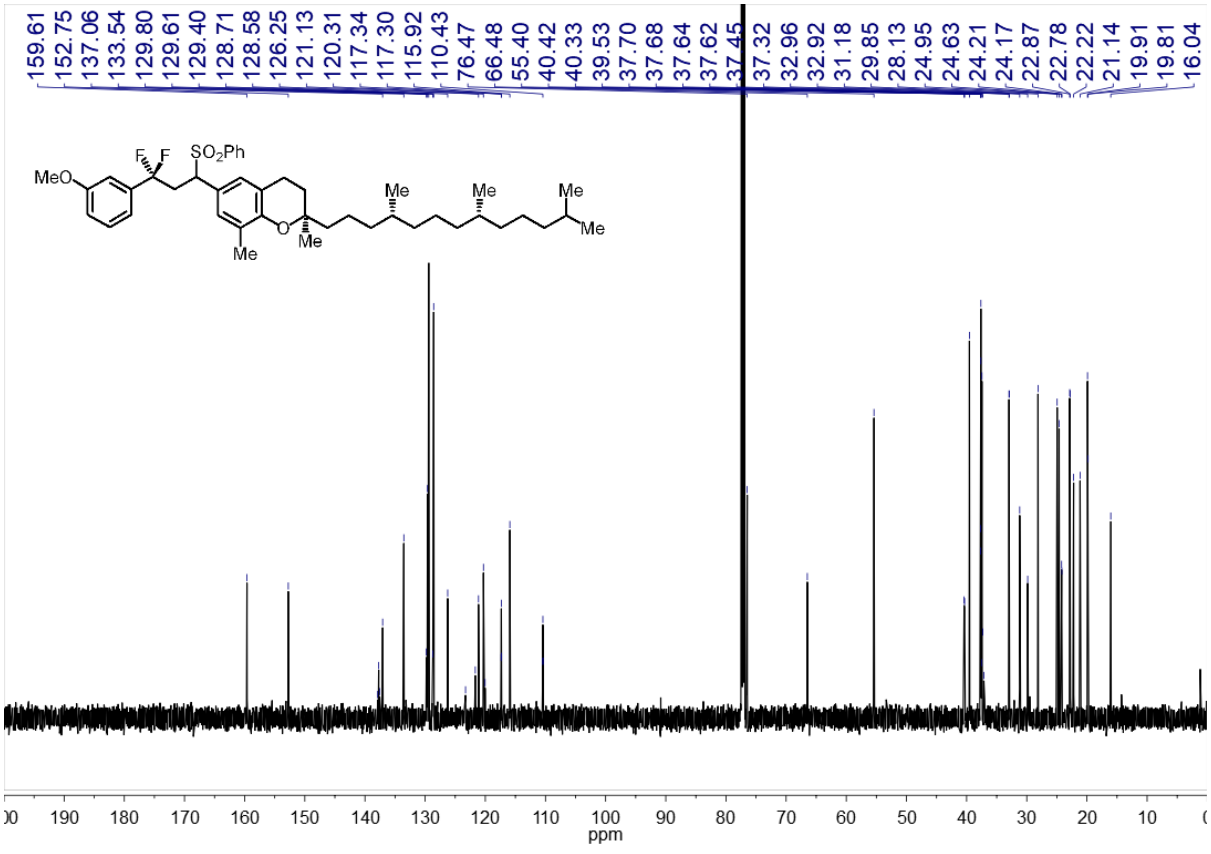
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5ah**



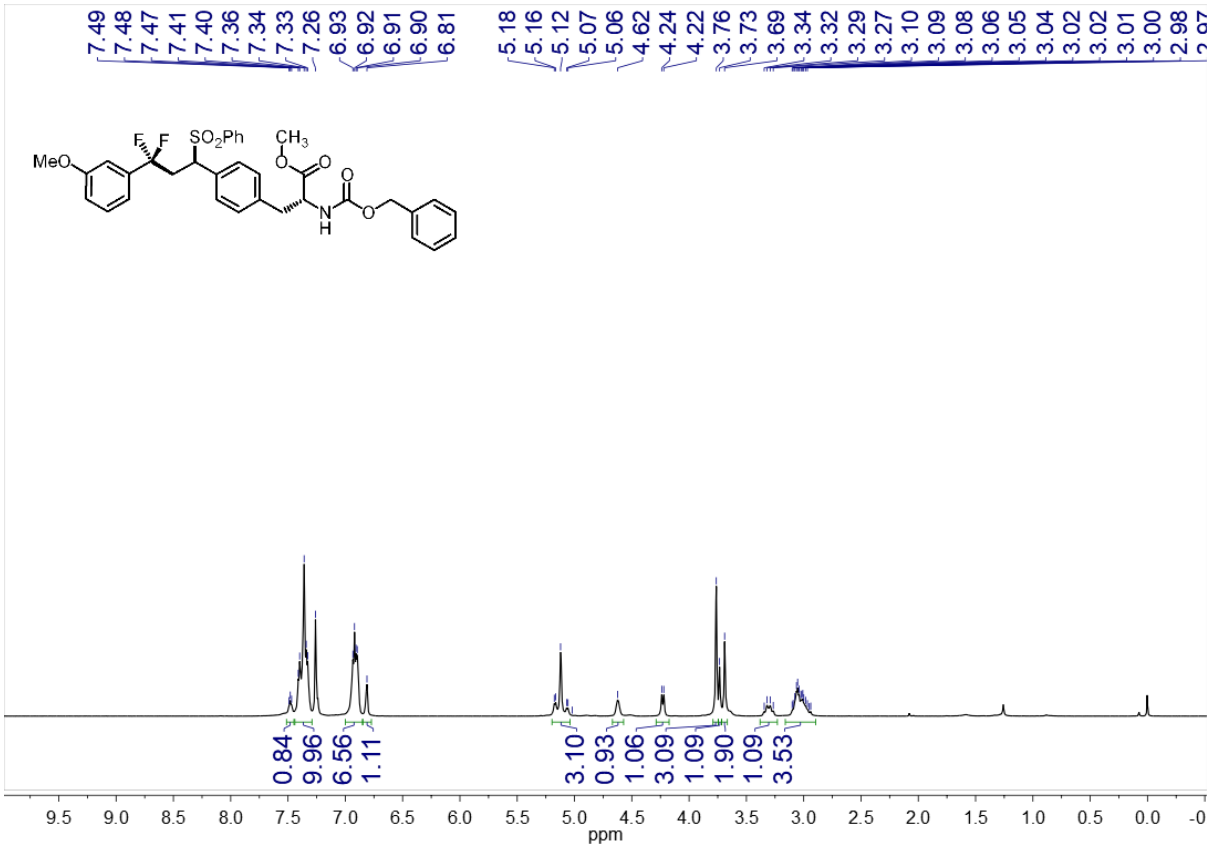
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5ai**



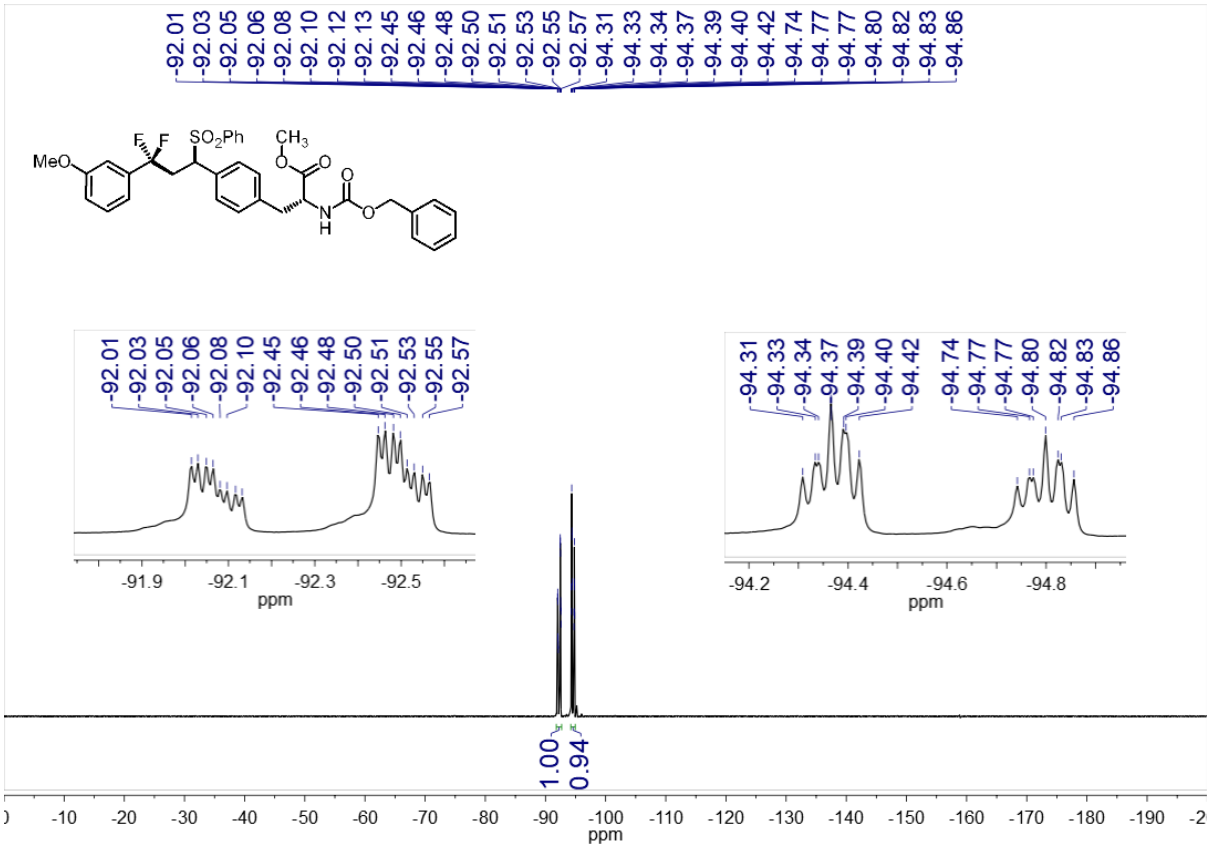
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5ai**



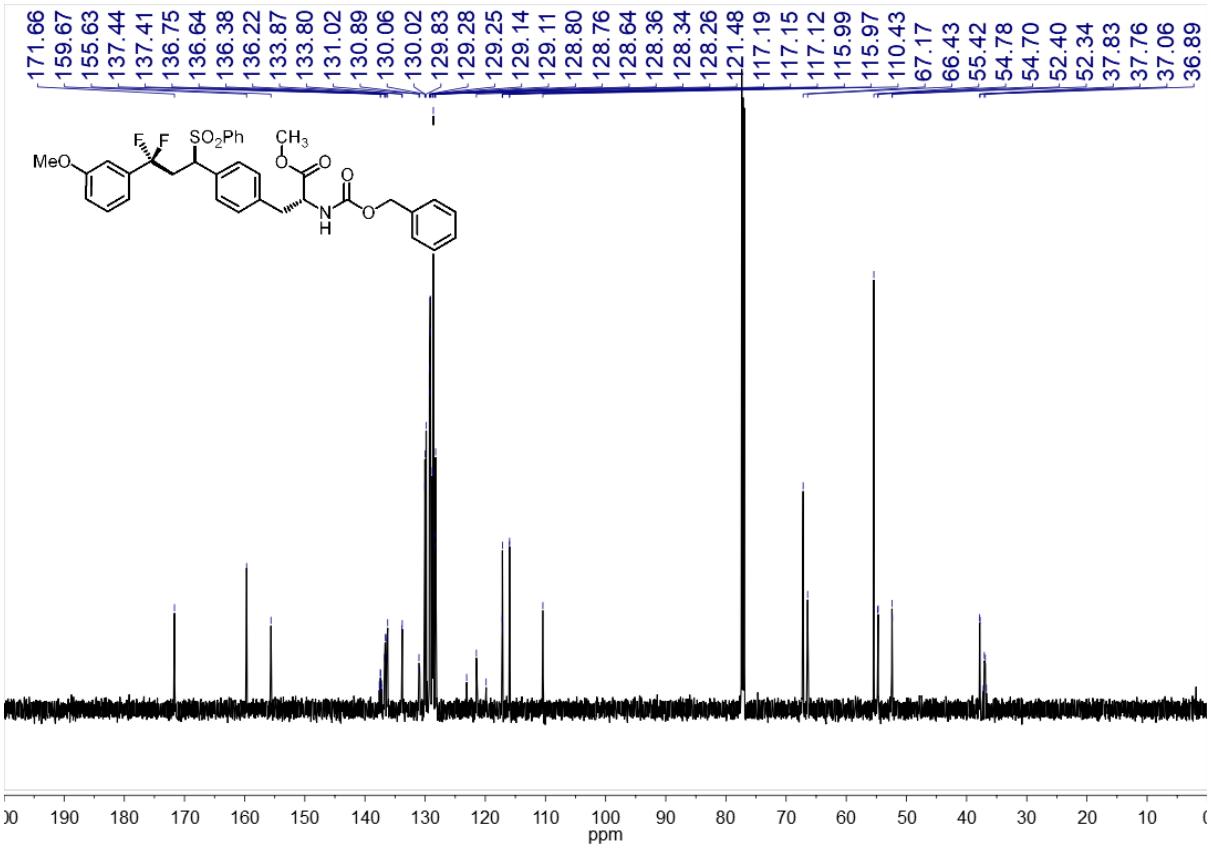
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5ai**



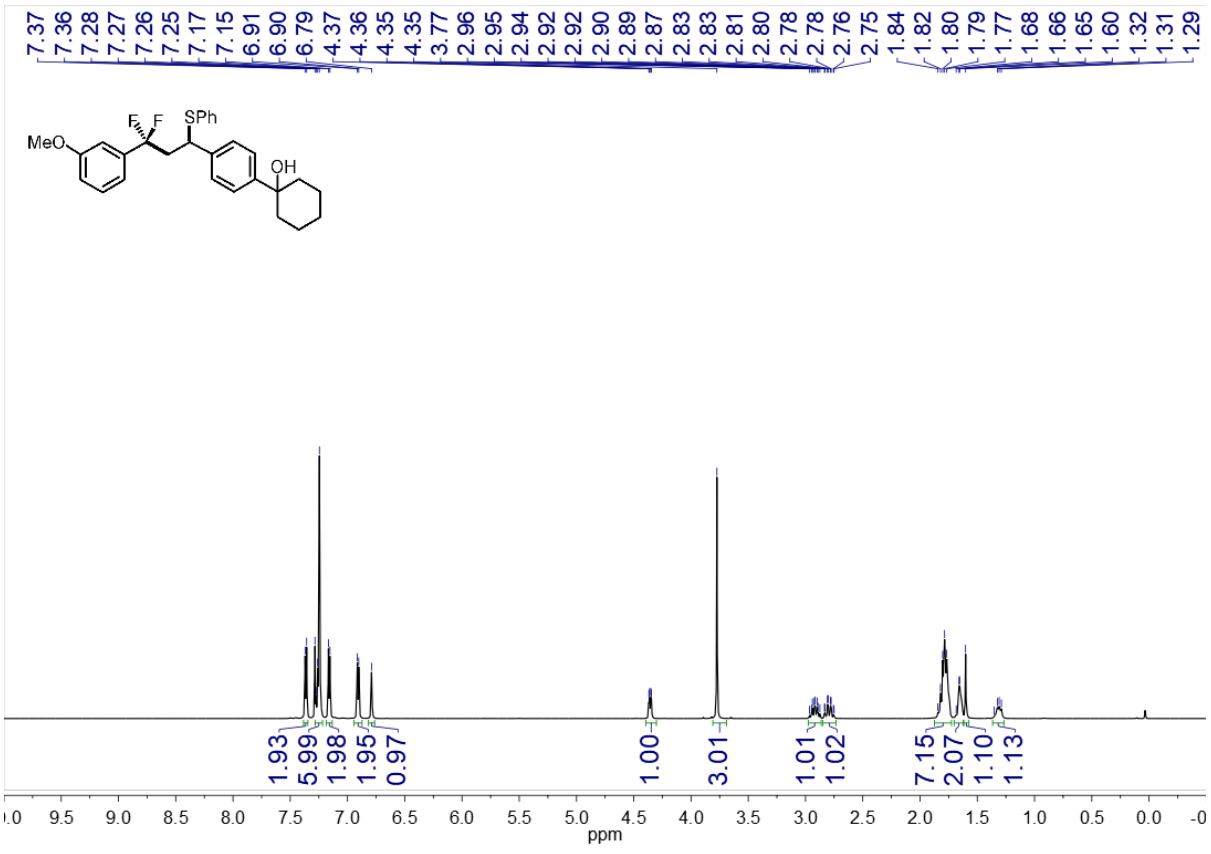
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **5aj**



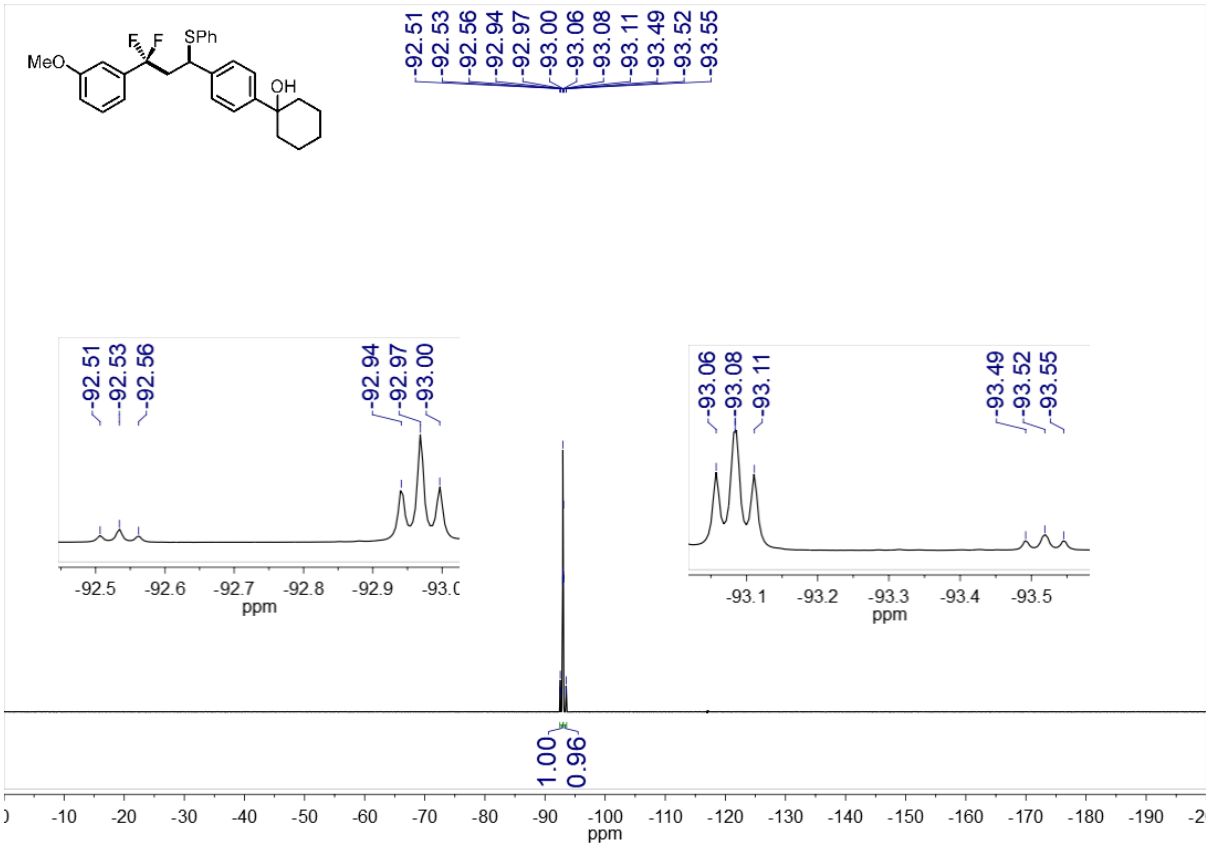
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **5aj**



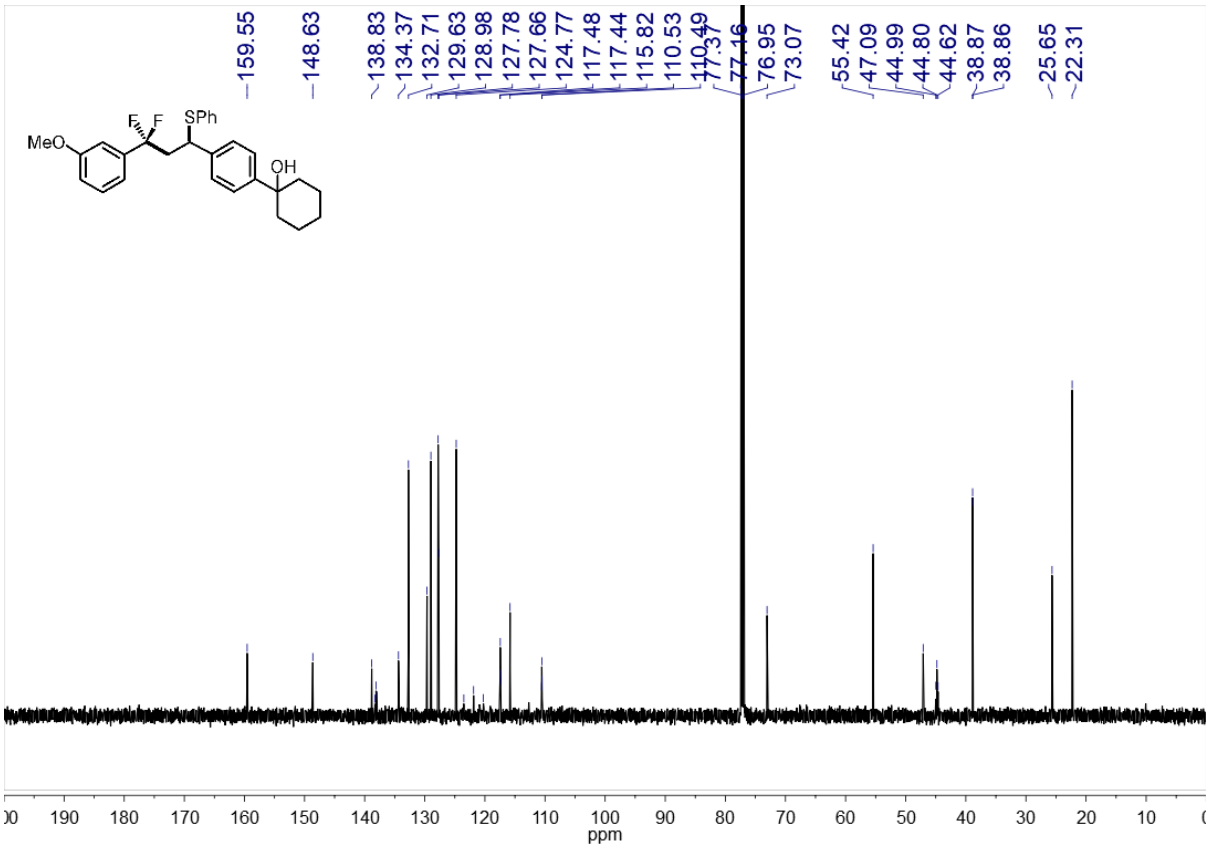
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **5aj**



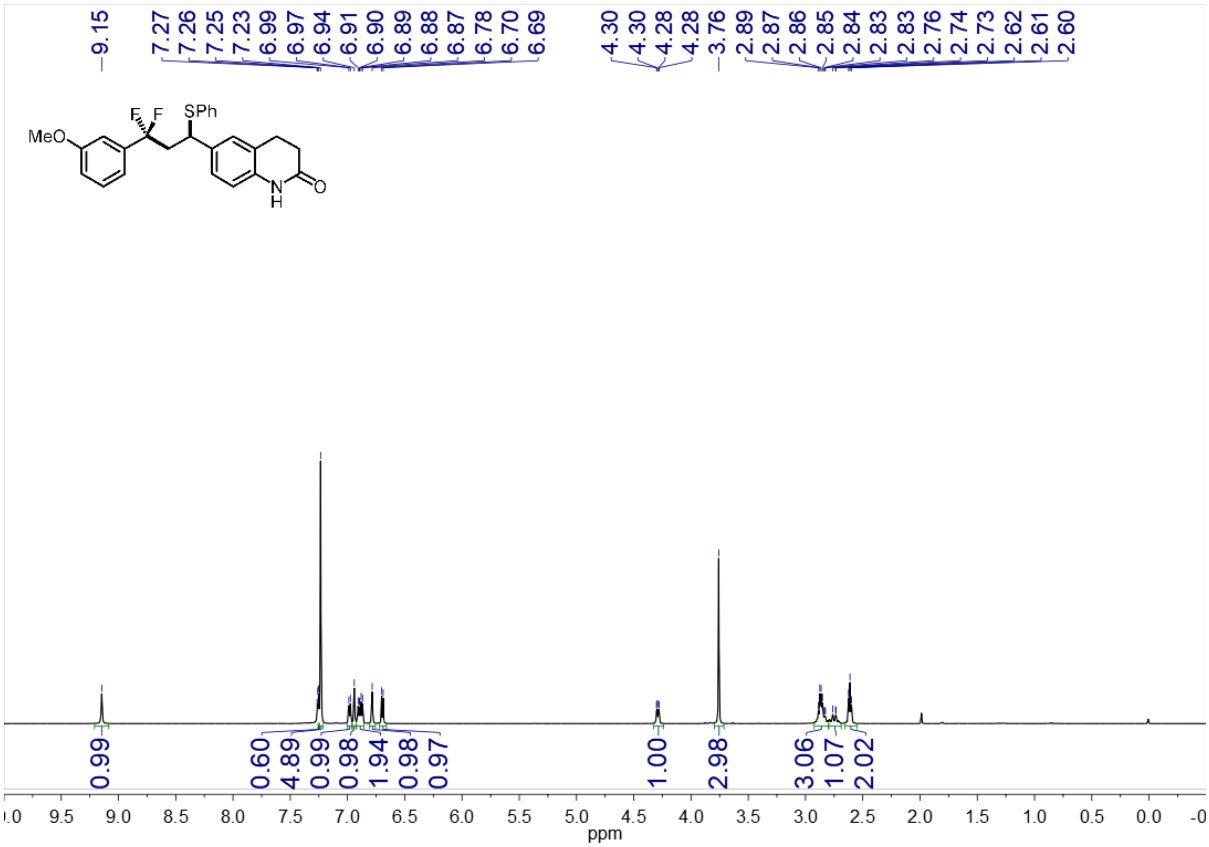
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **4b**



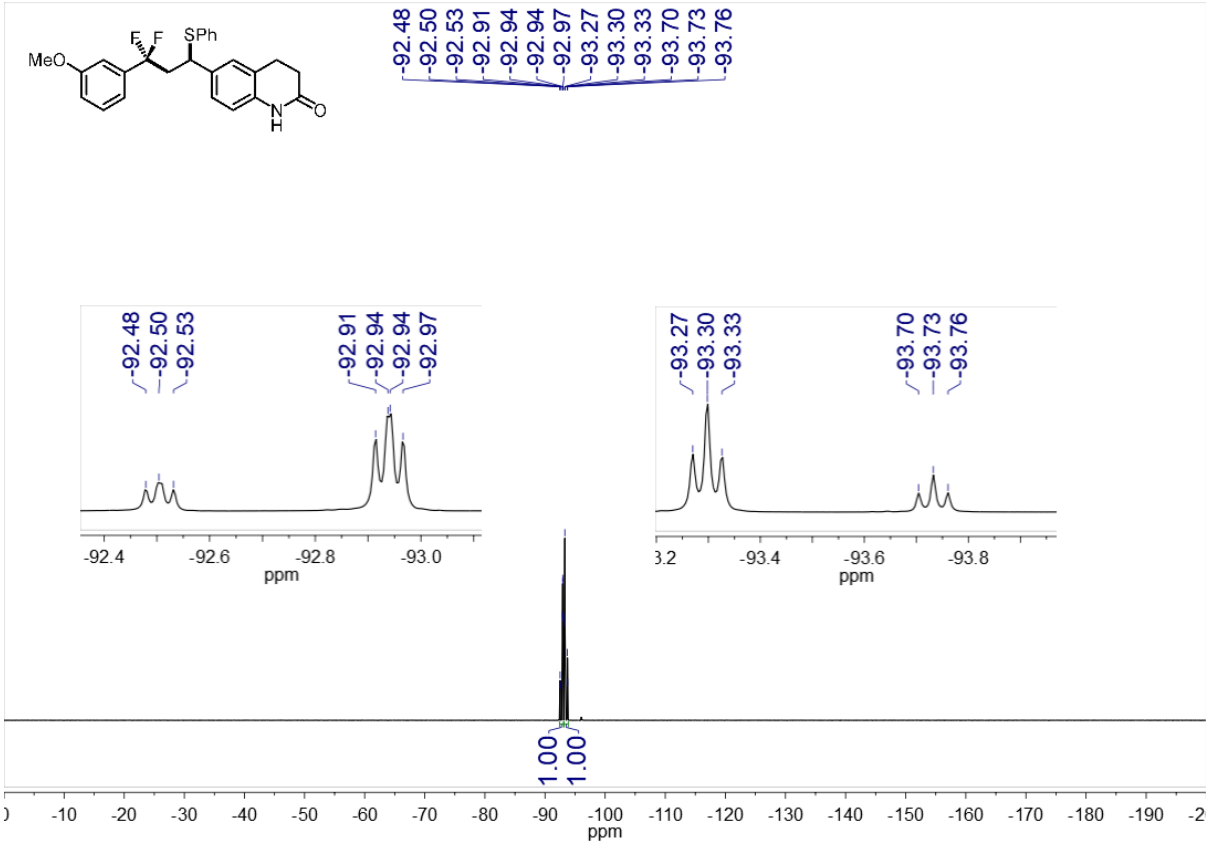
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **4b**



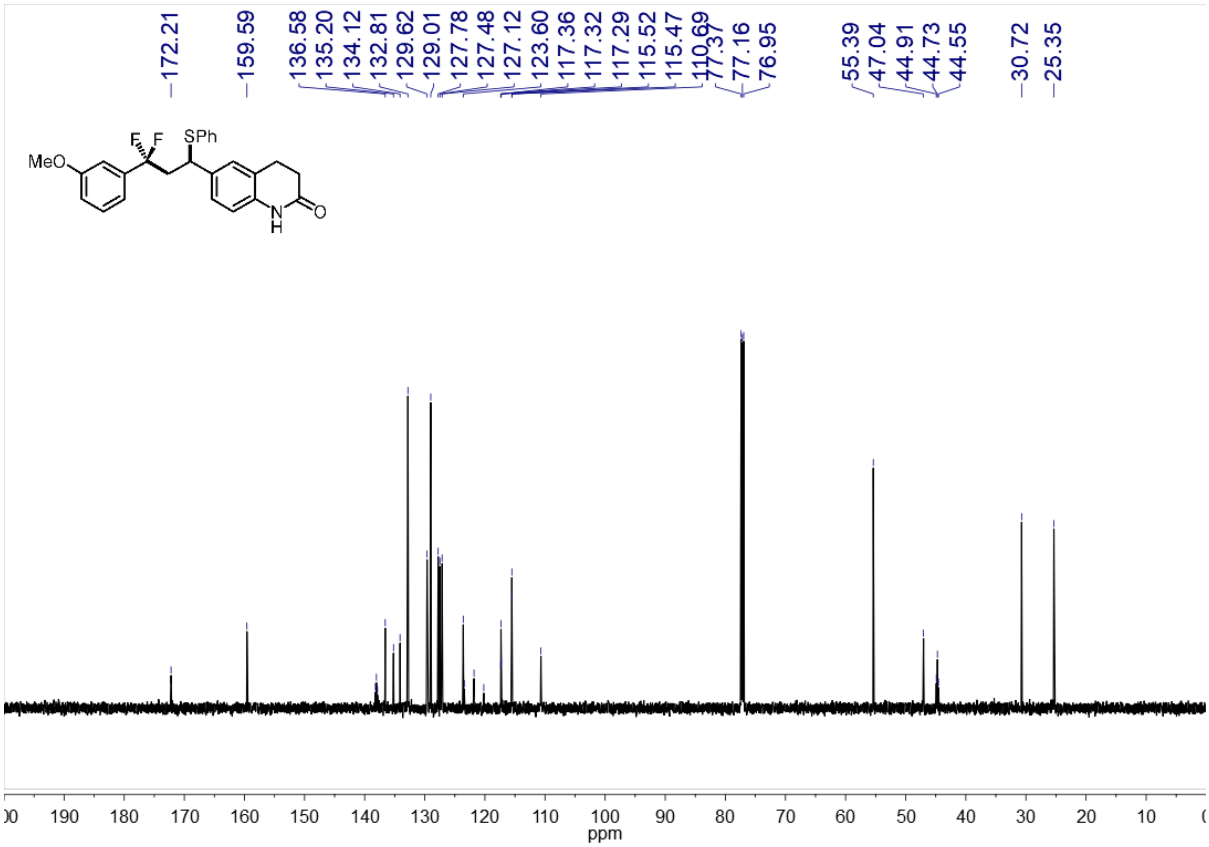
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **4b**



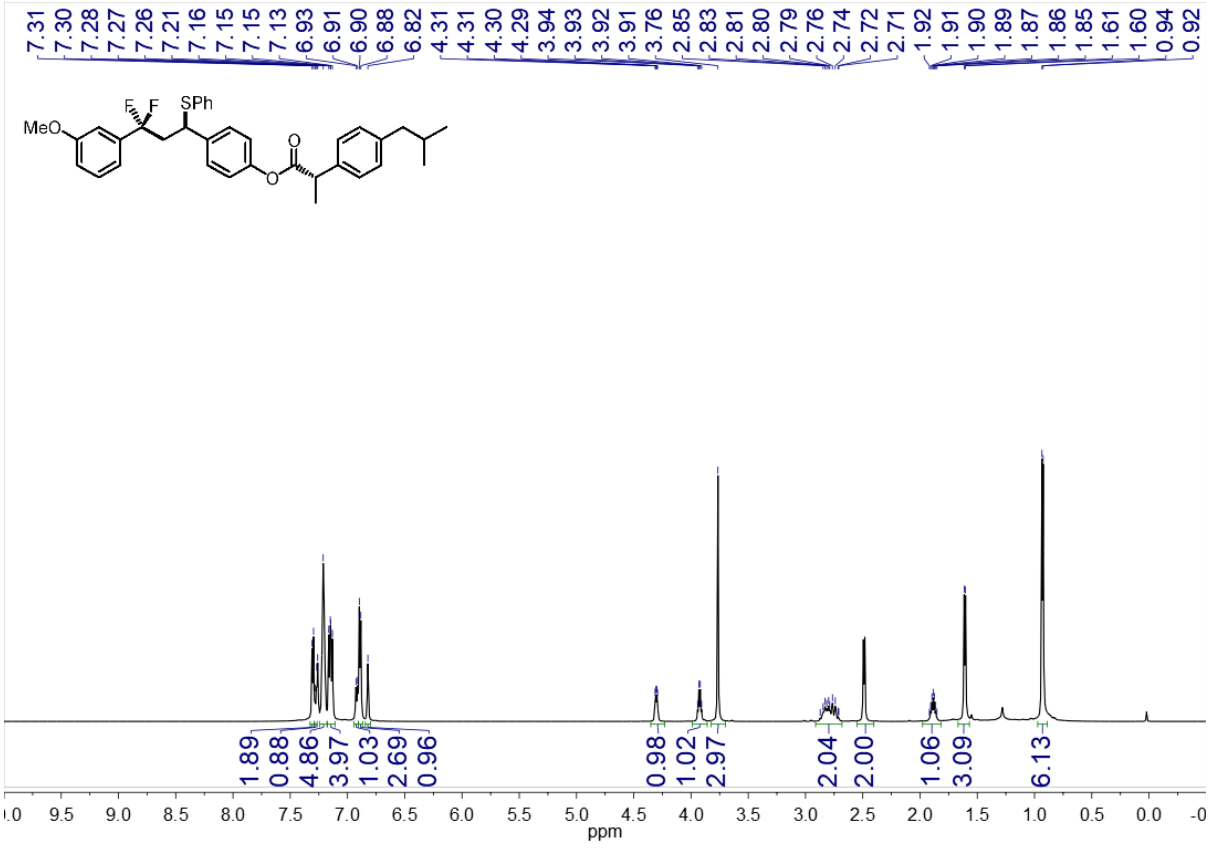
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **4c**



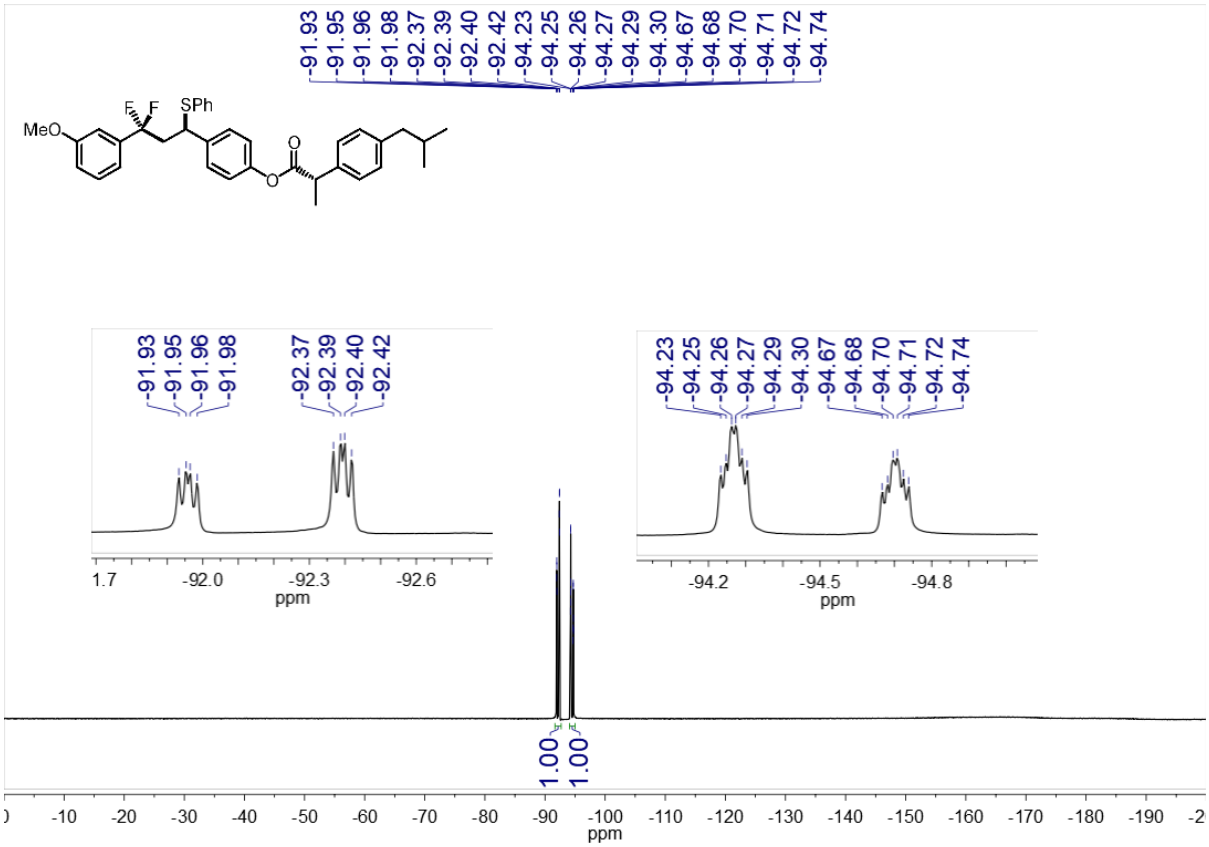
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **4c**



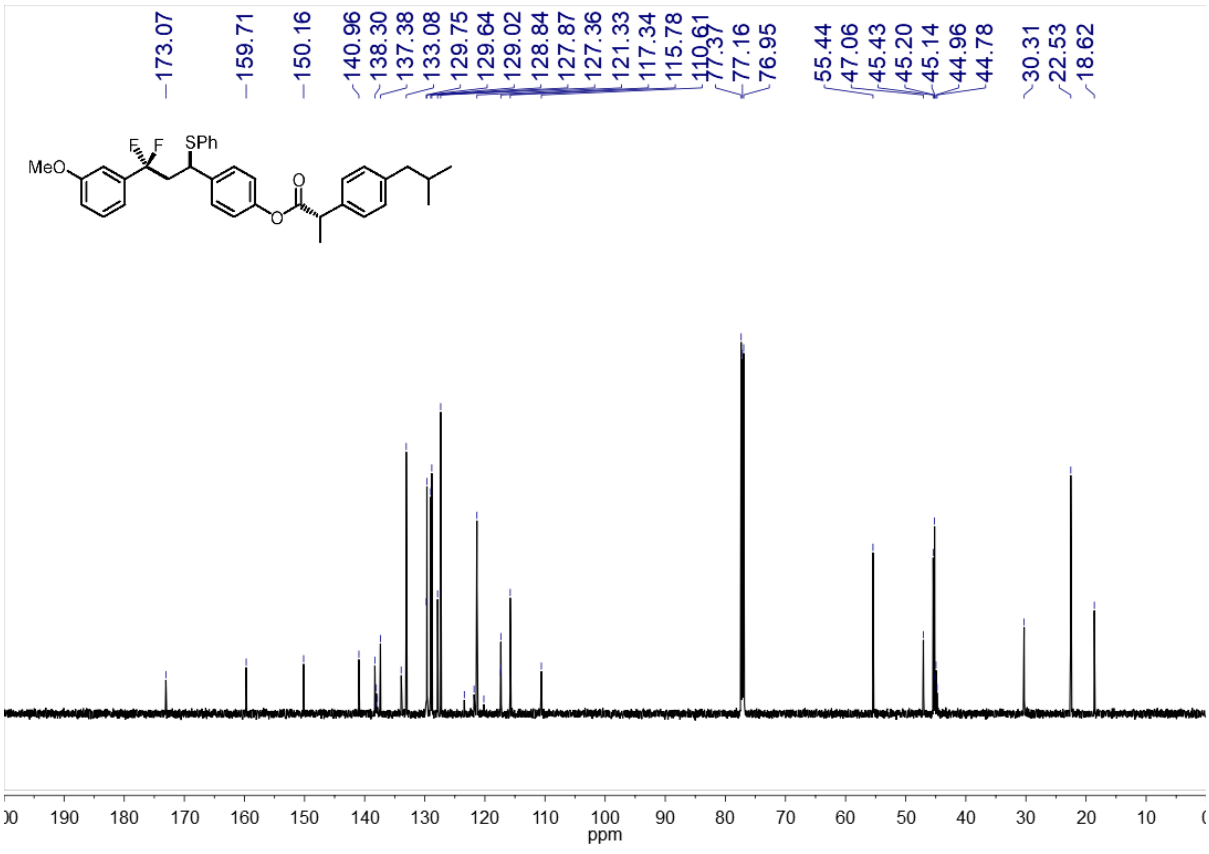
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **4c**



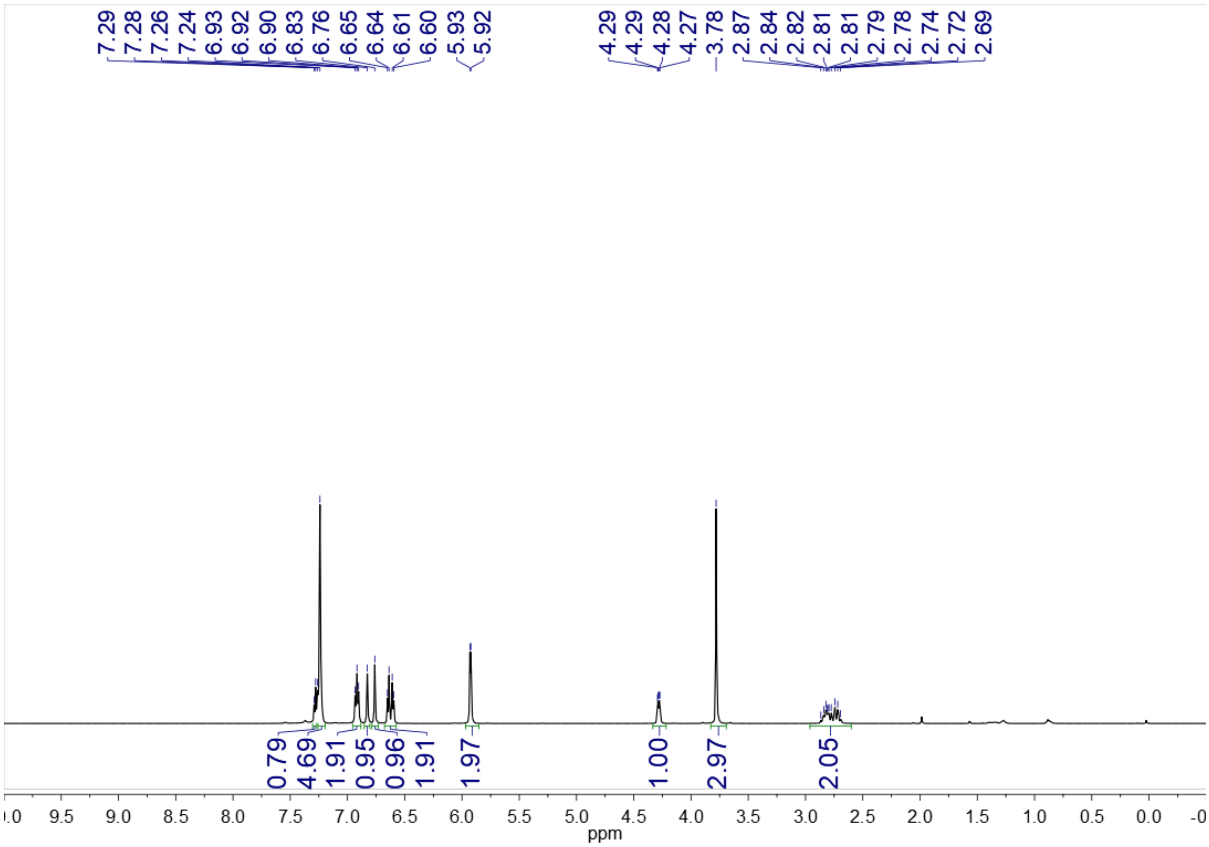
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **4d**



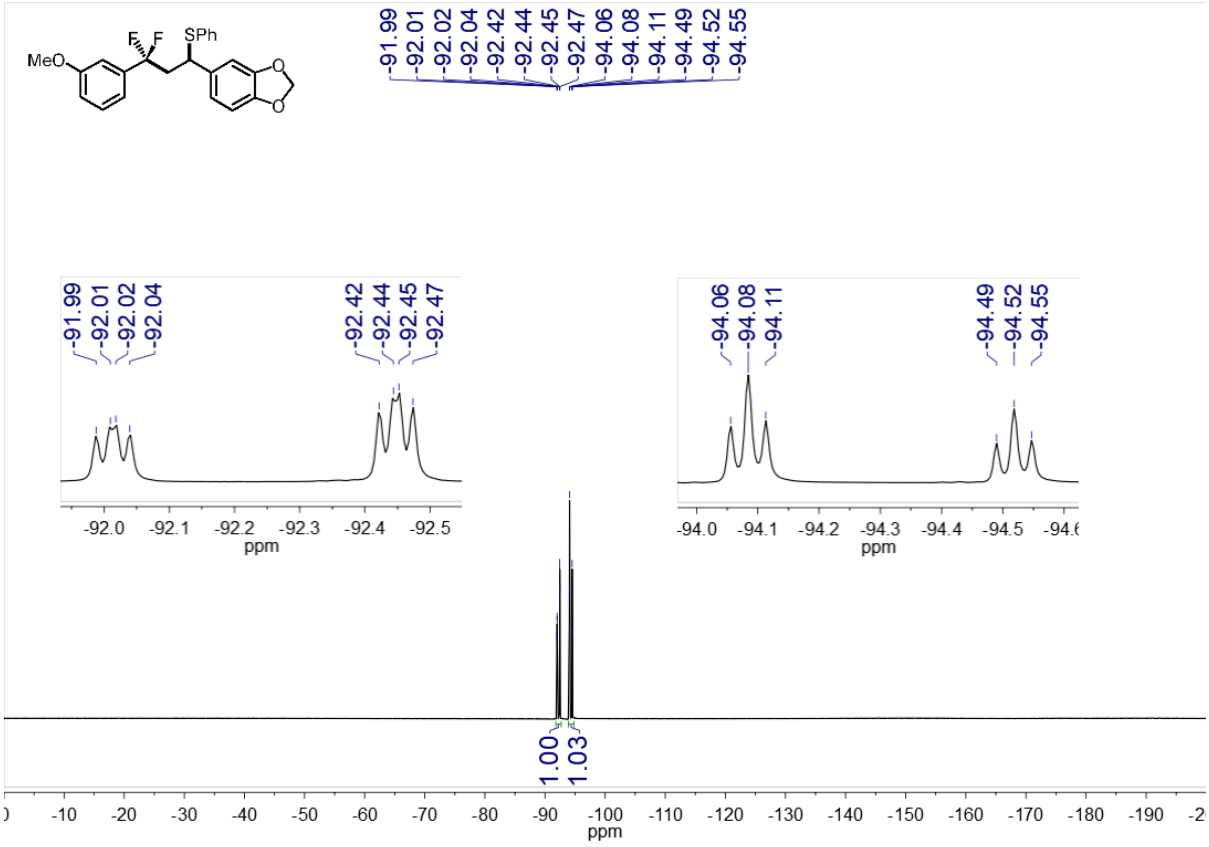
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **4d**



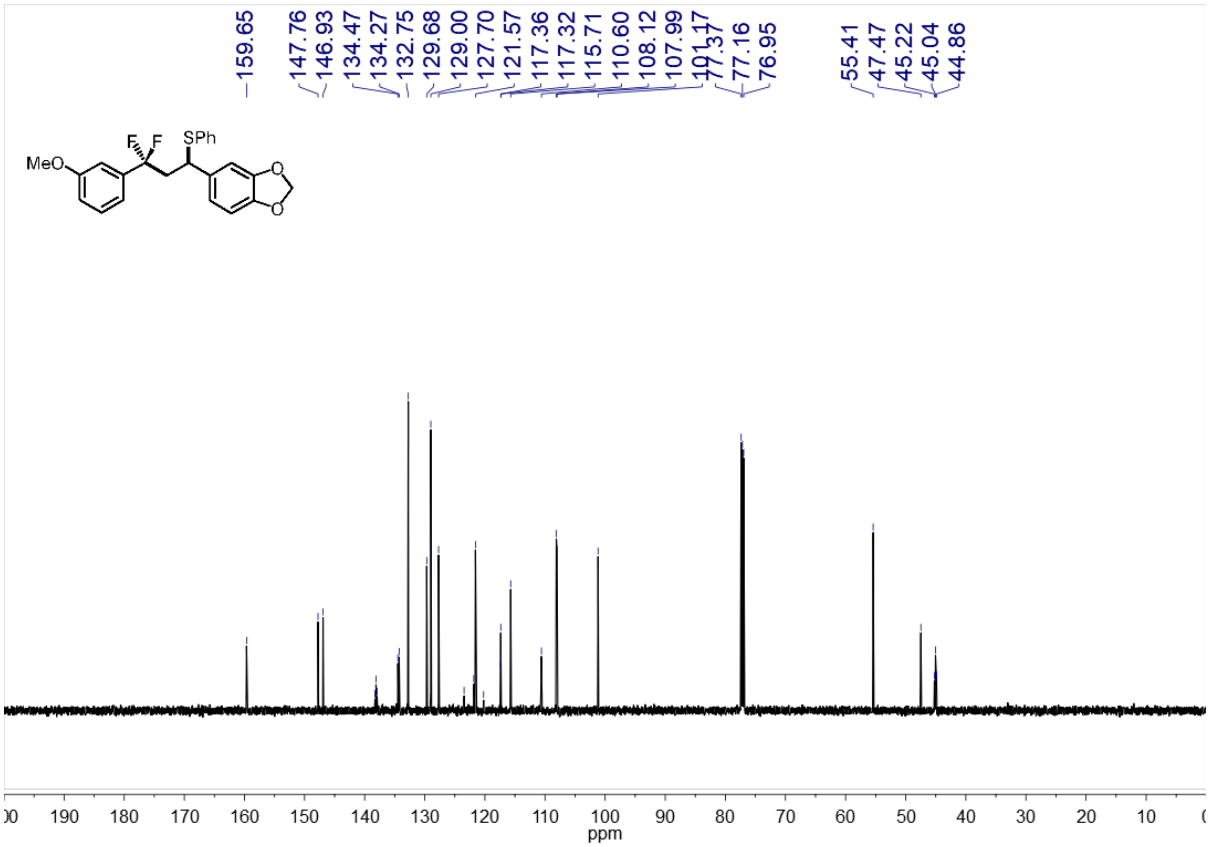
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **4d**



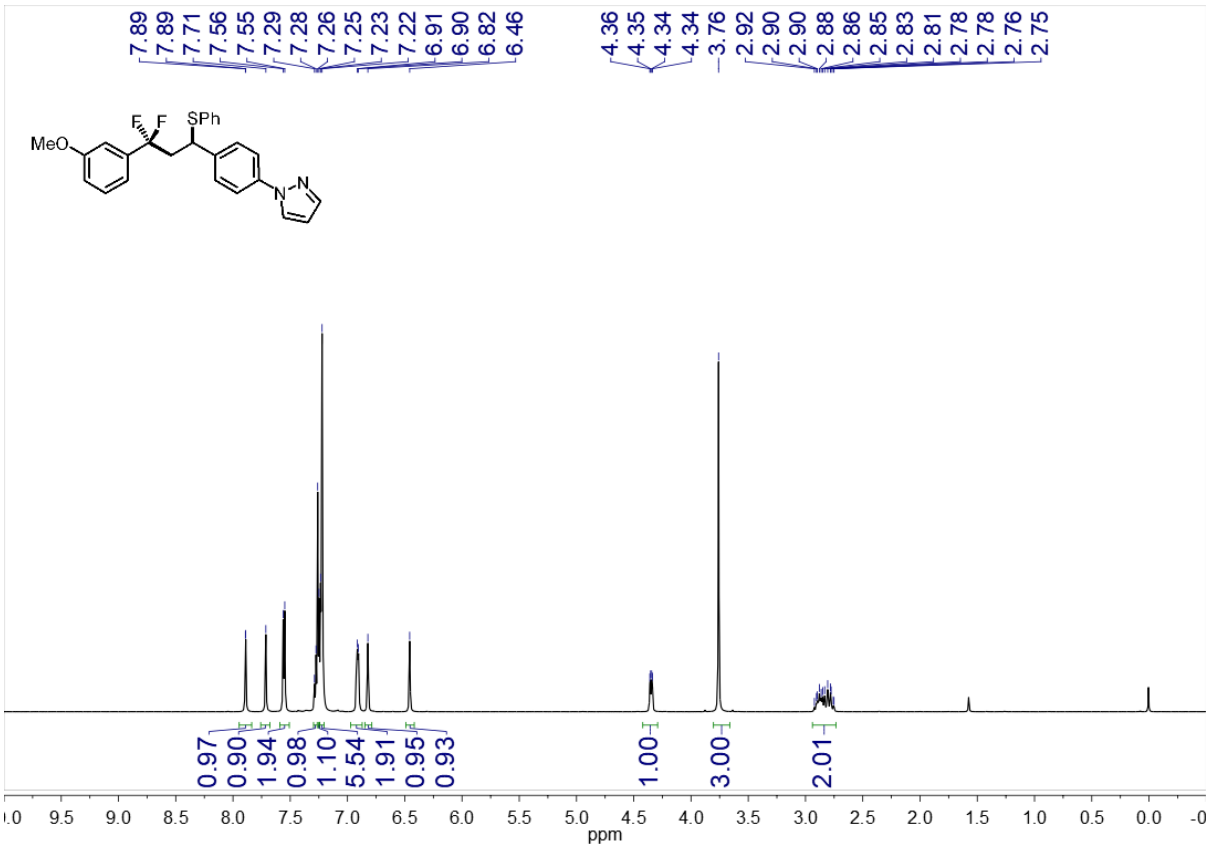
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **4e**



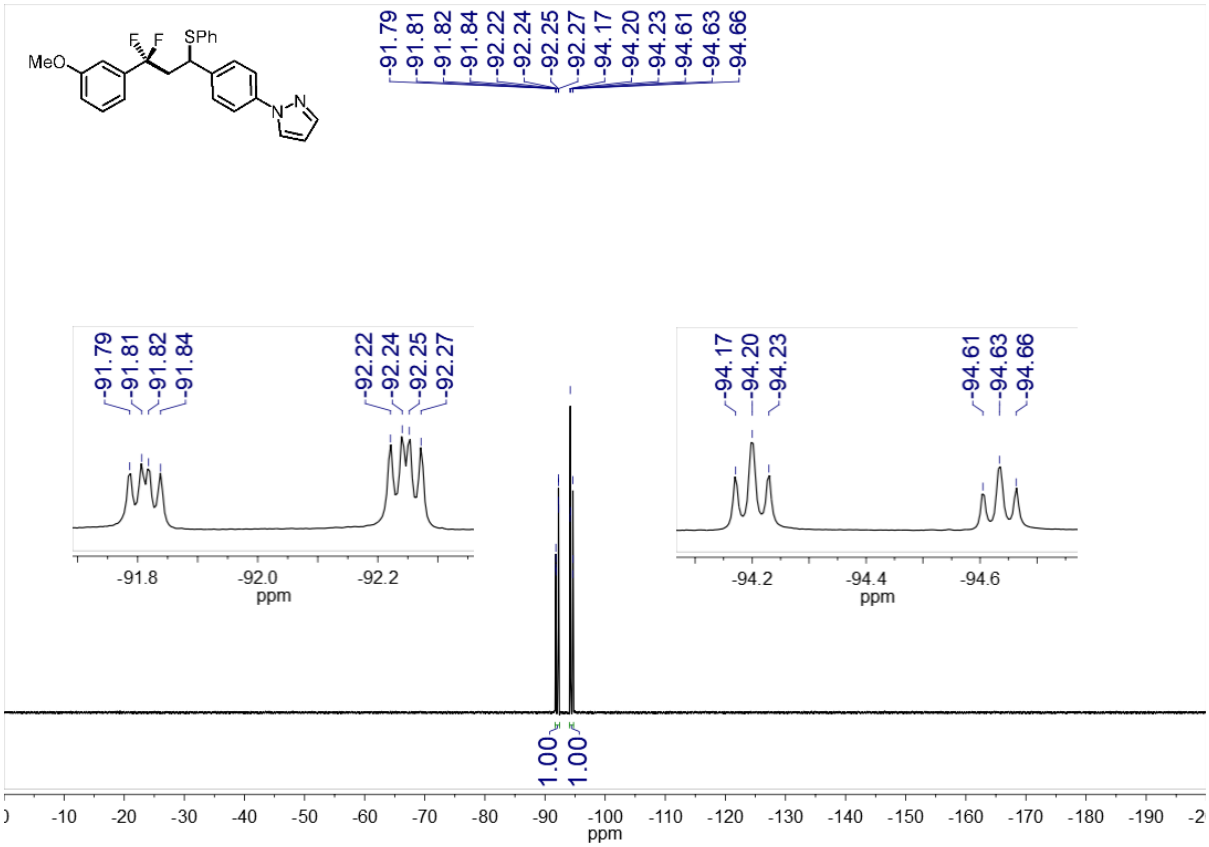
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **4e**



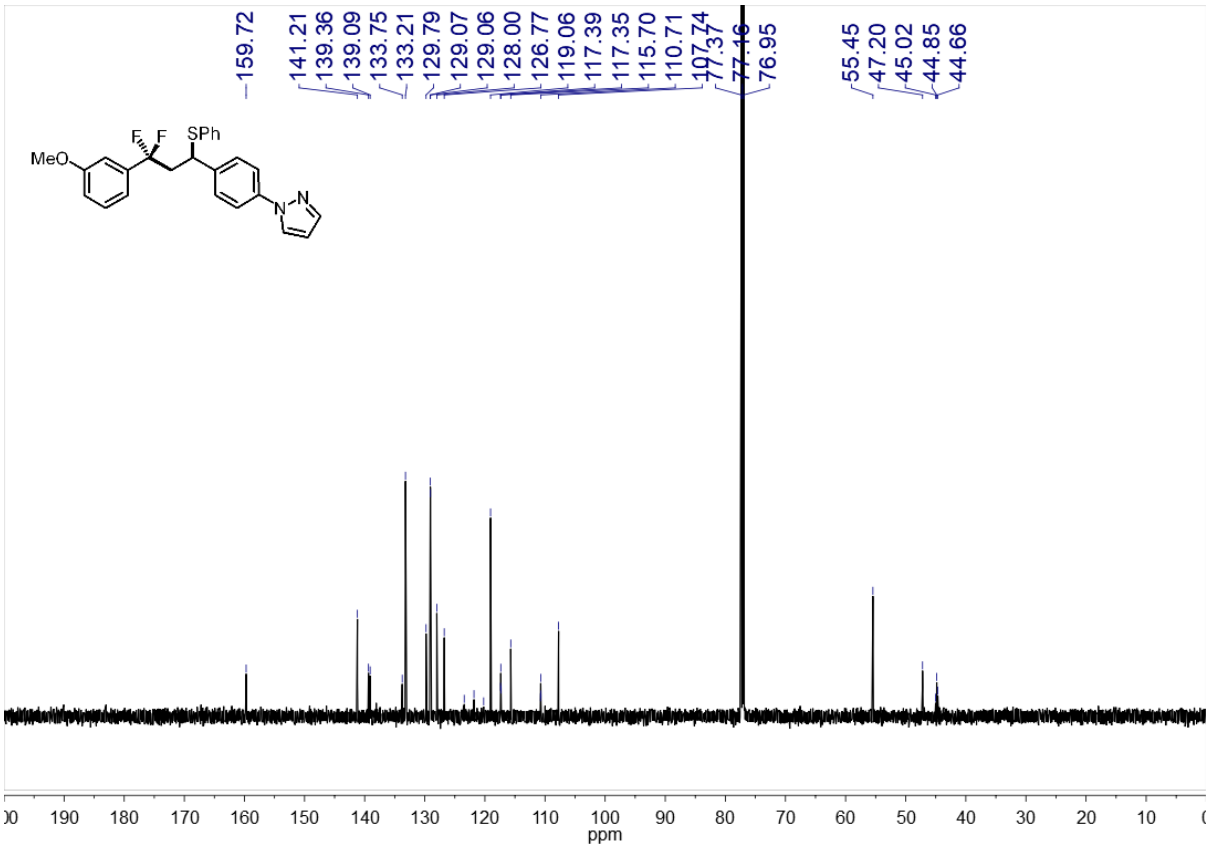
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **4e**



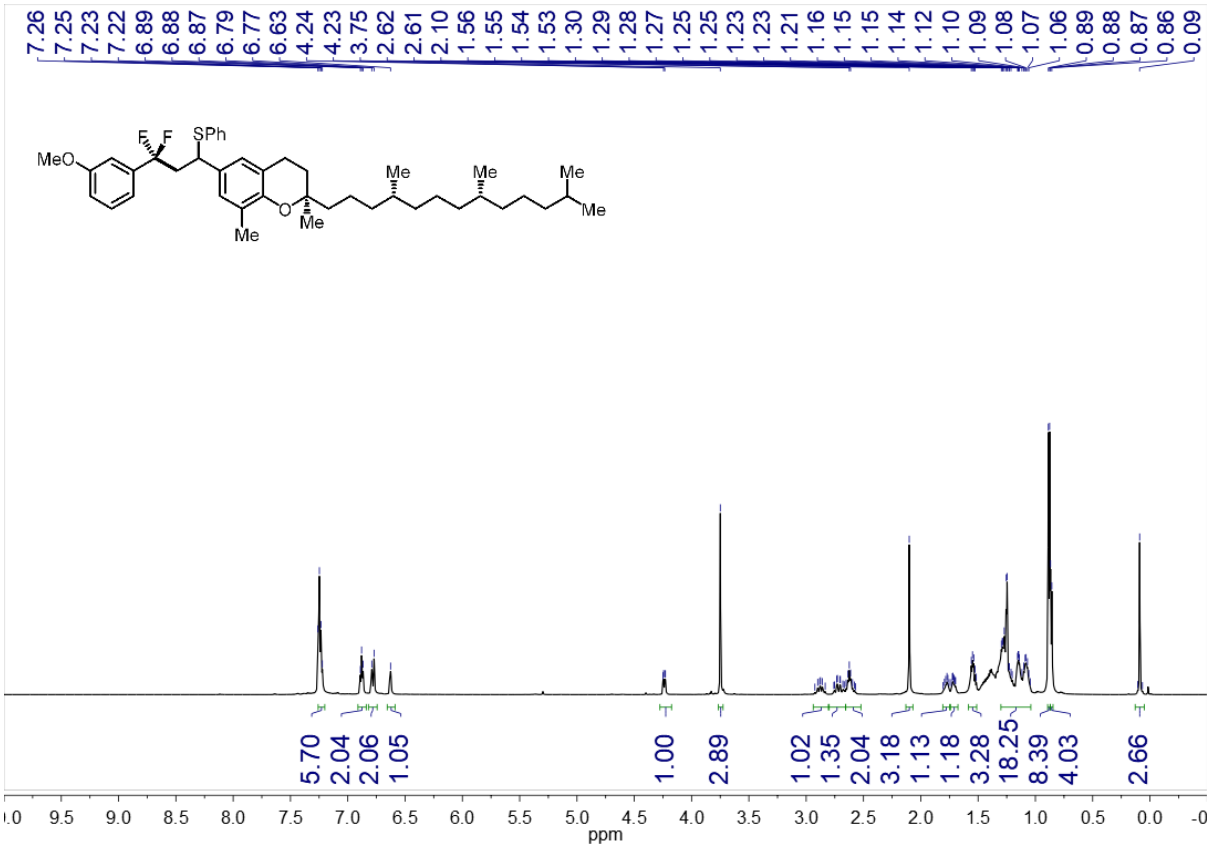
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **4f**



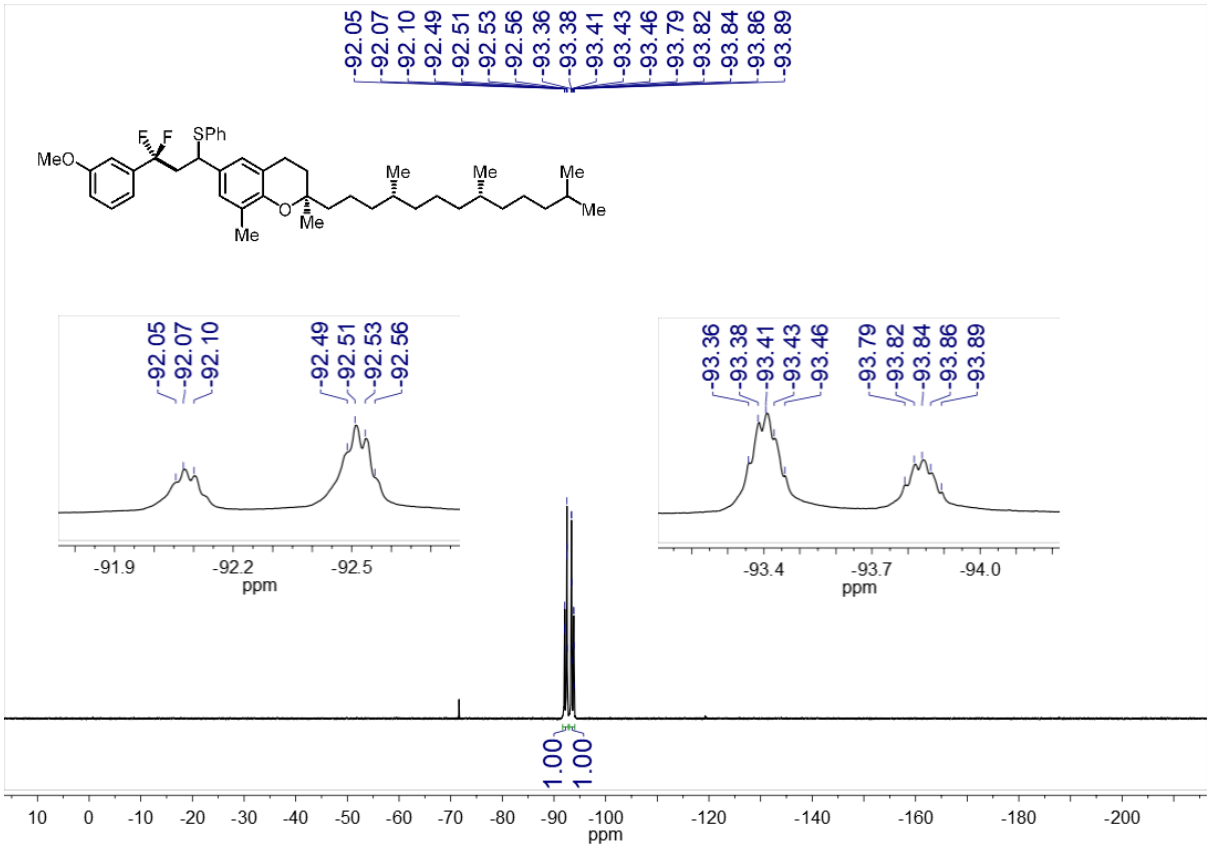
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **4f**



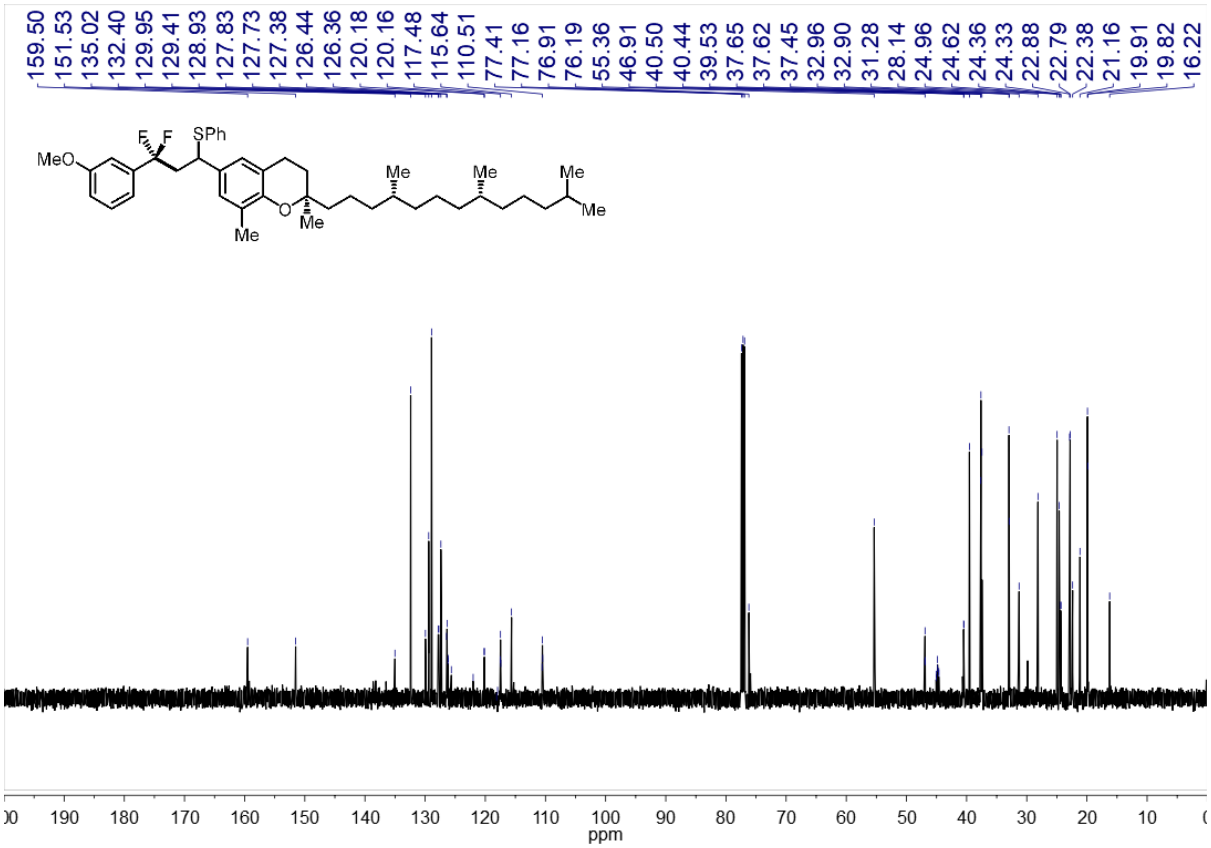
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **4f**



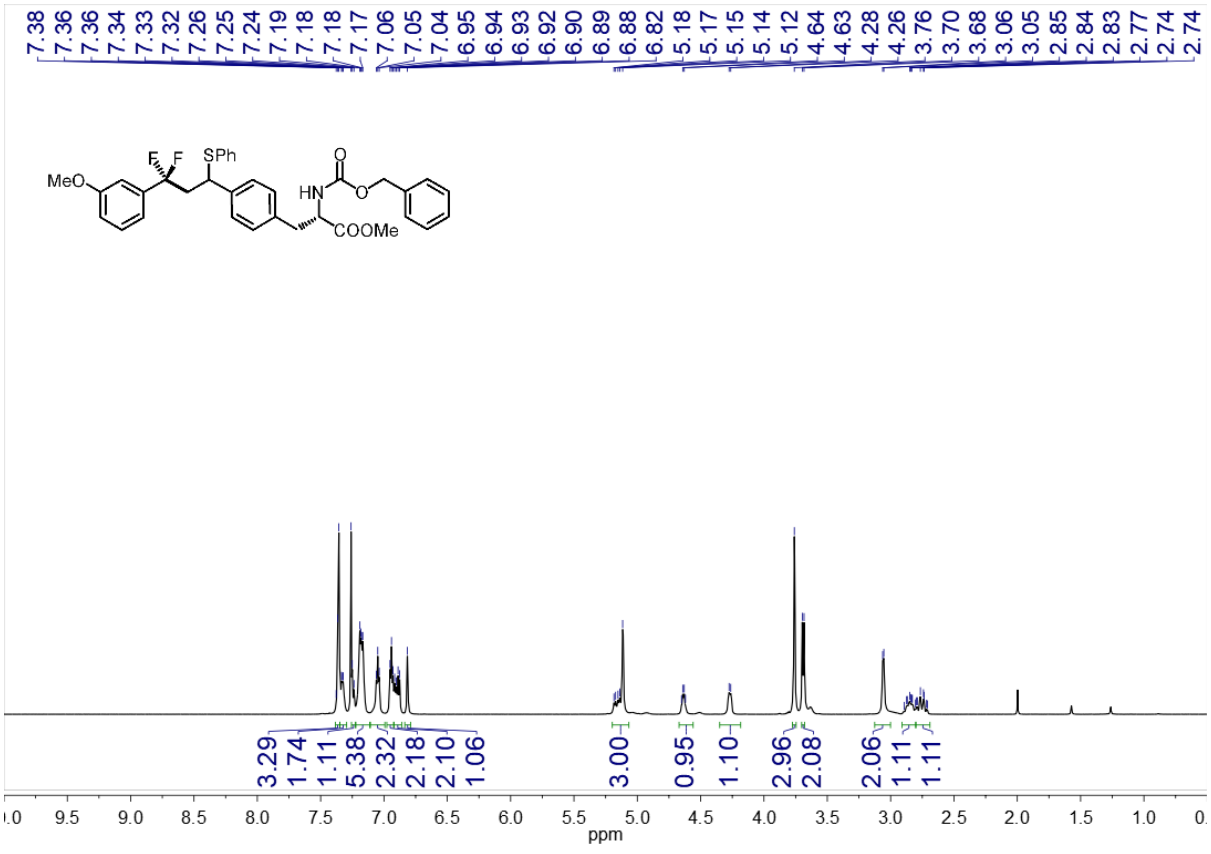
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **4g**



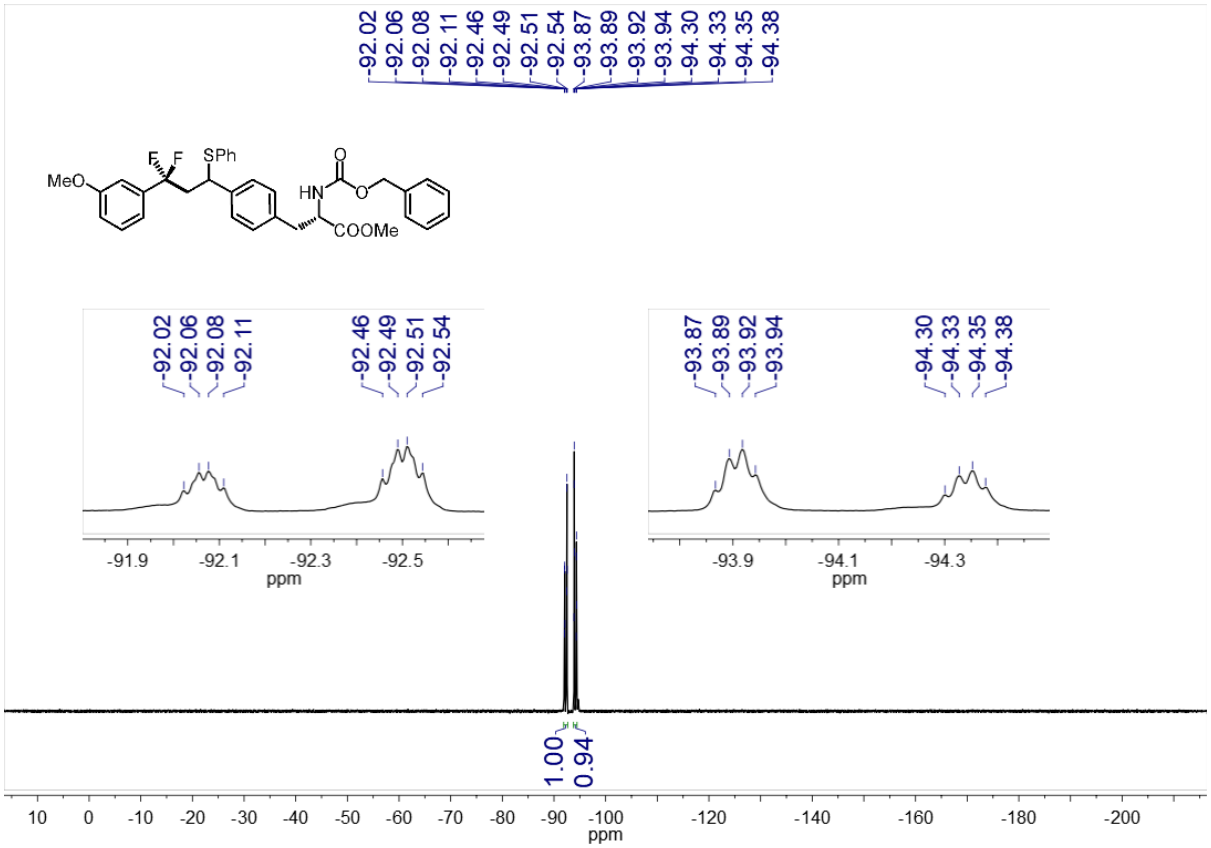
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **4g**



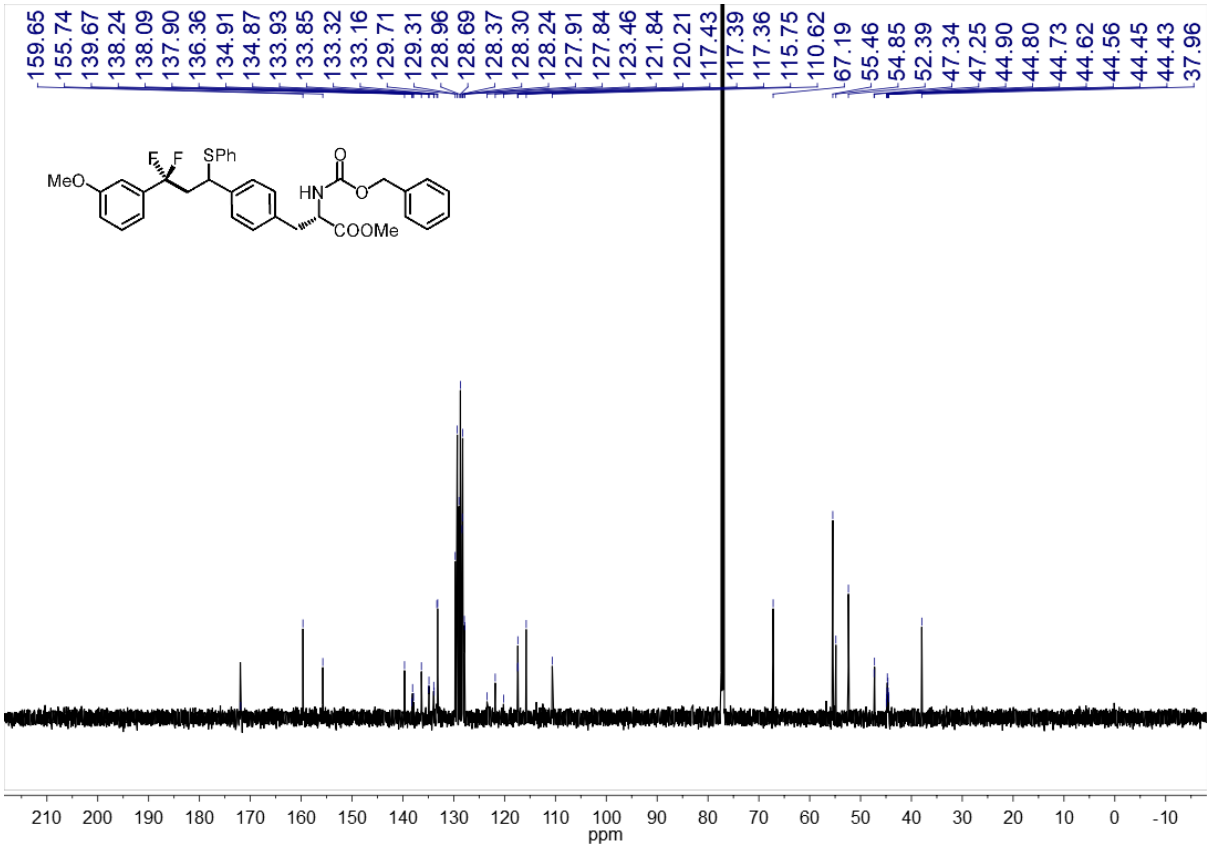
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **4g**



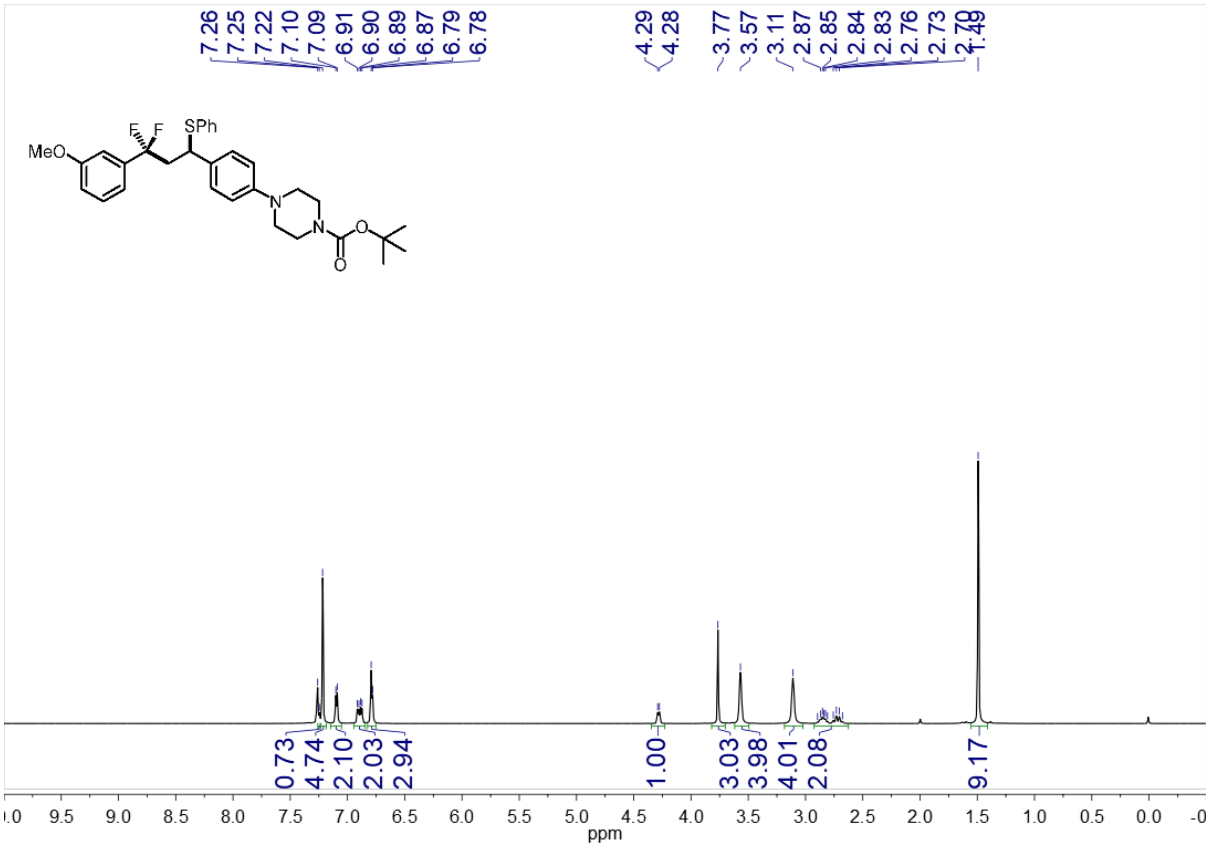
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **4h**



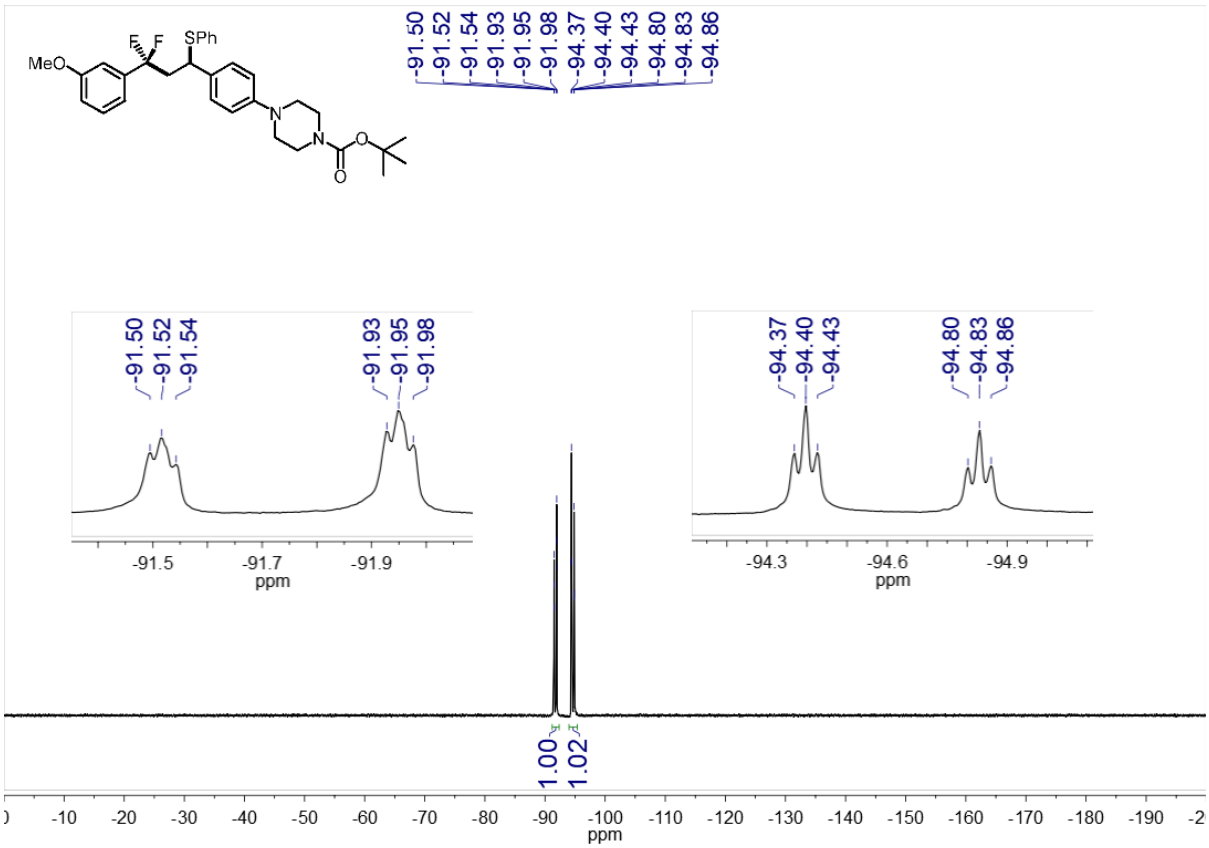
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **4h**



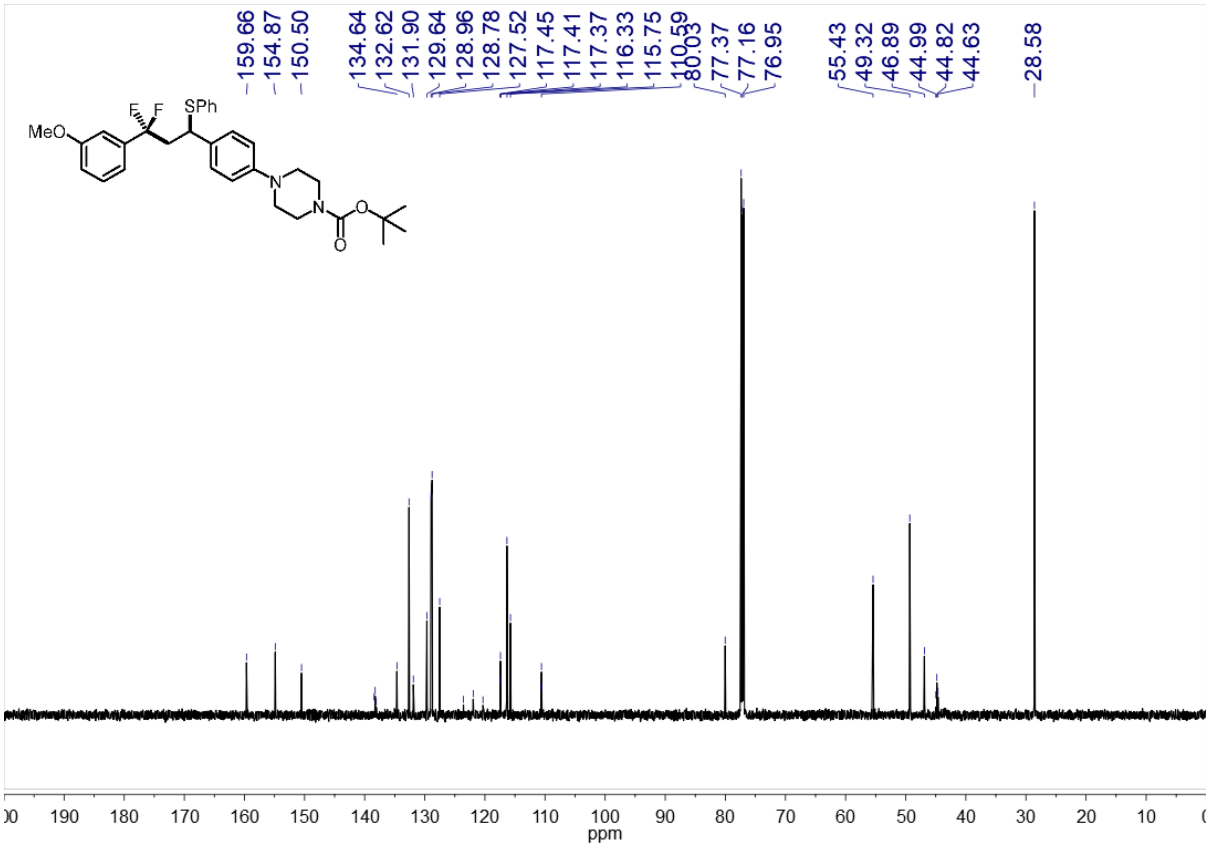
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **4h**



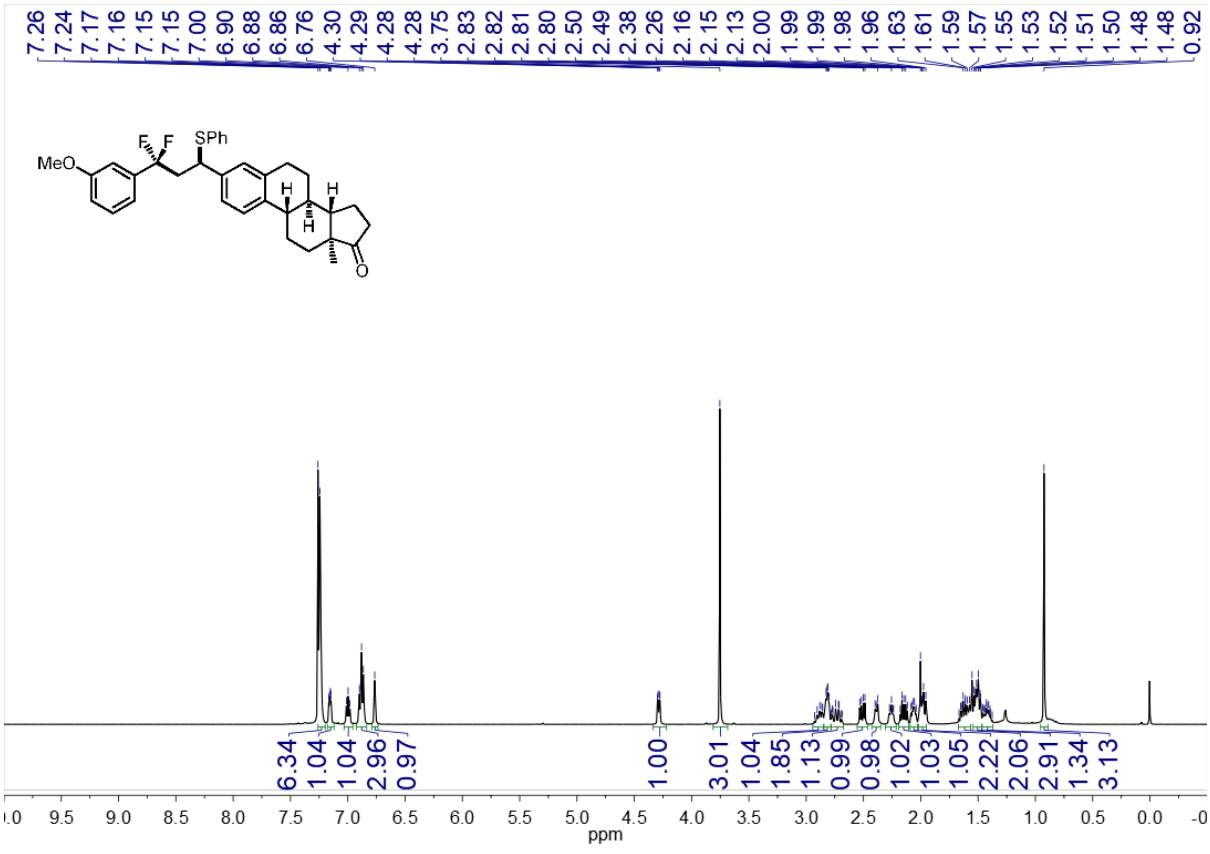
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **4i**



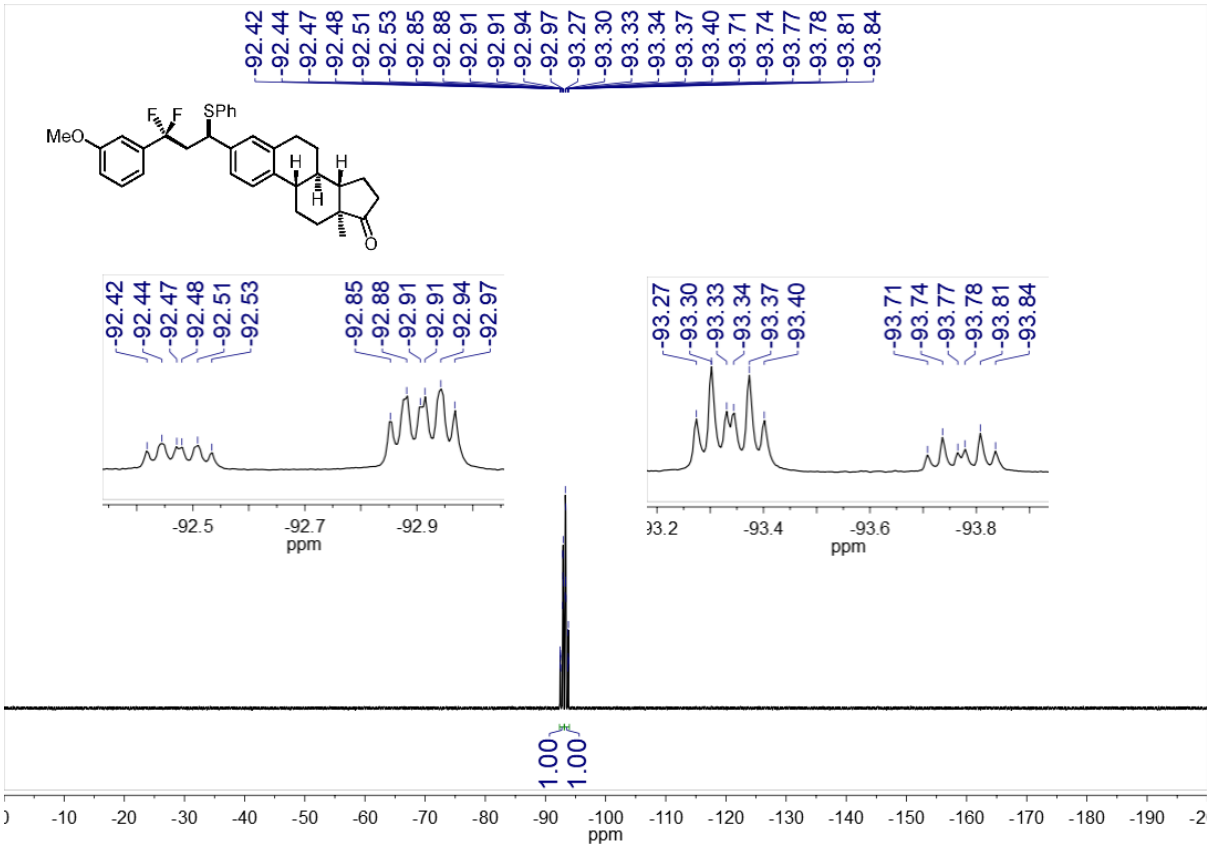
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **4i**



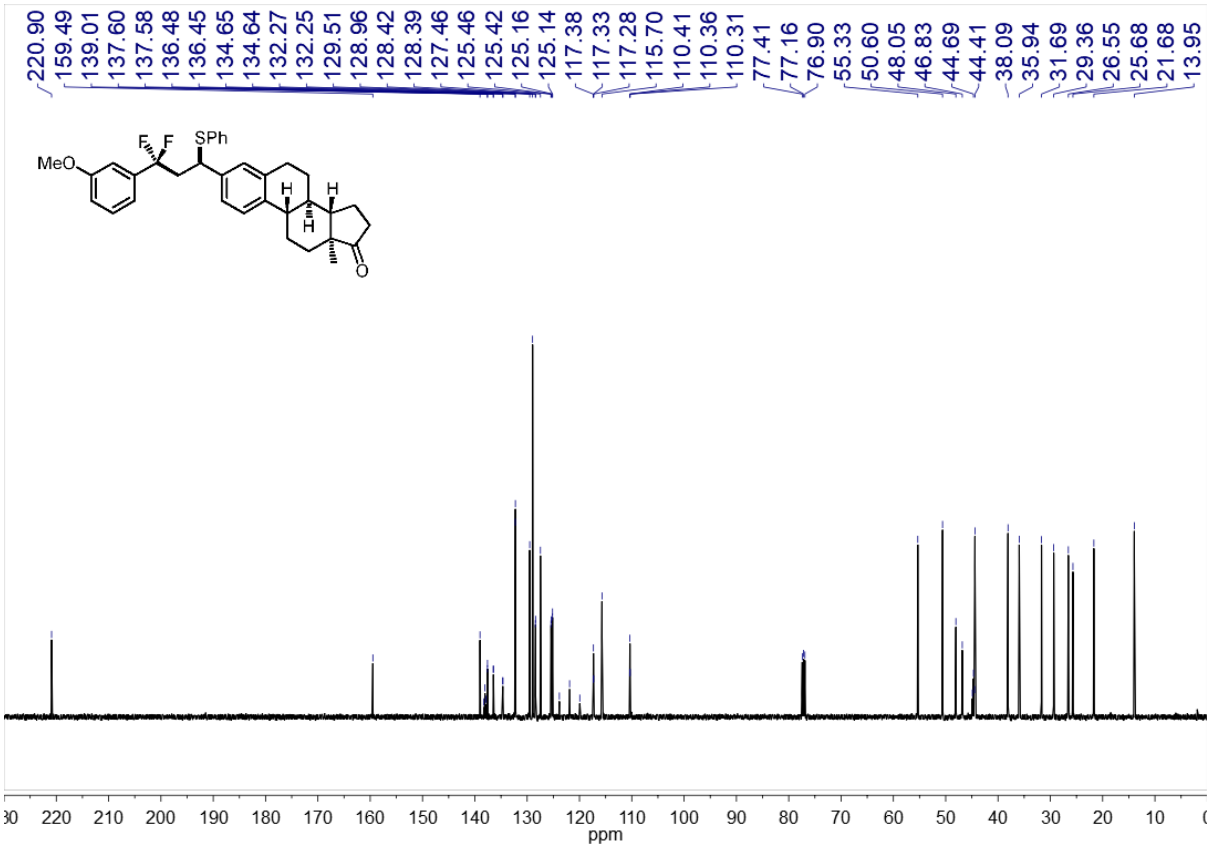
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **4i**



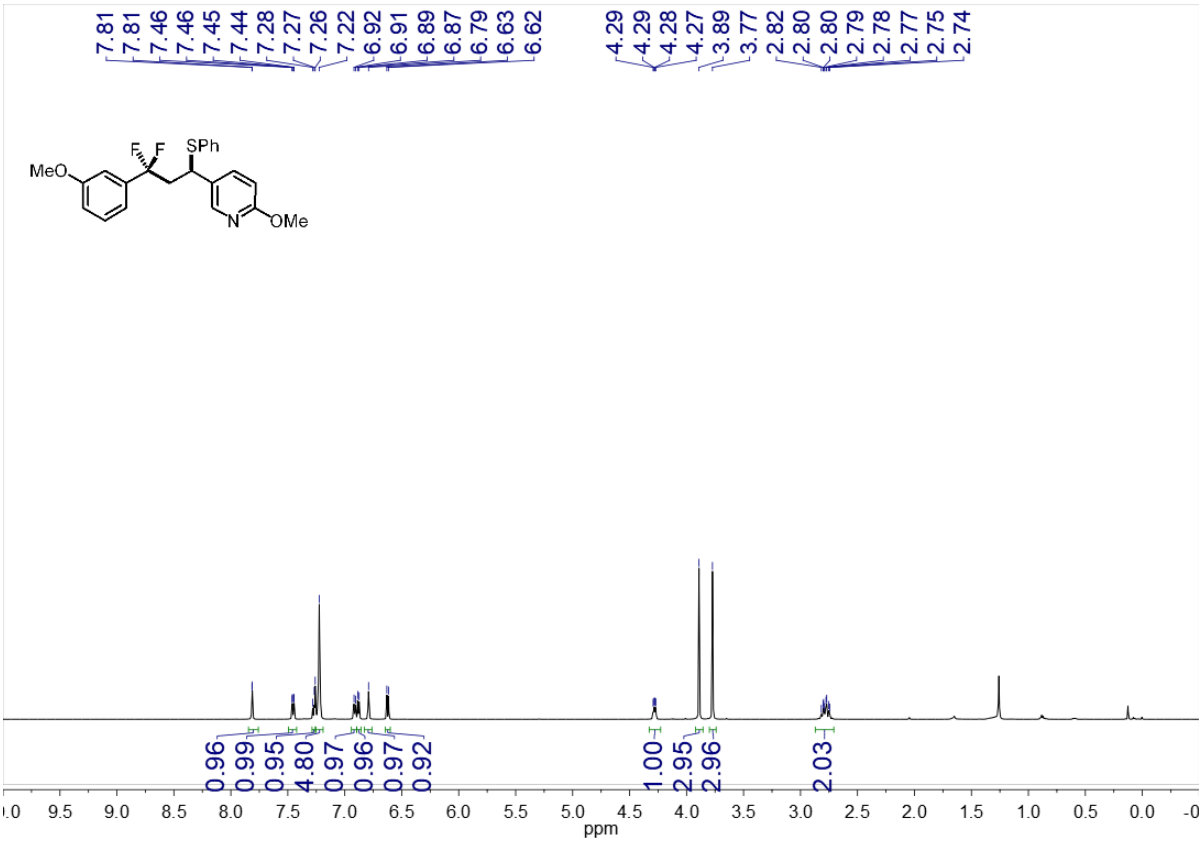
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **4j**



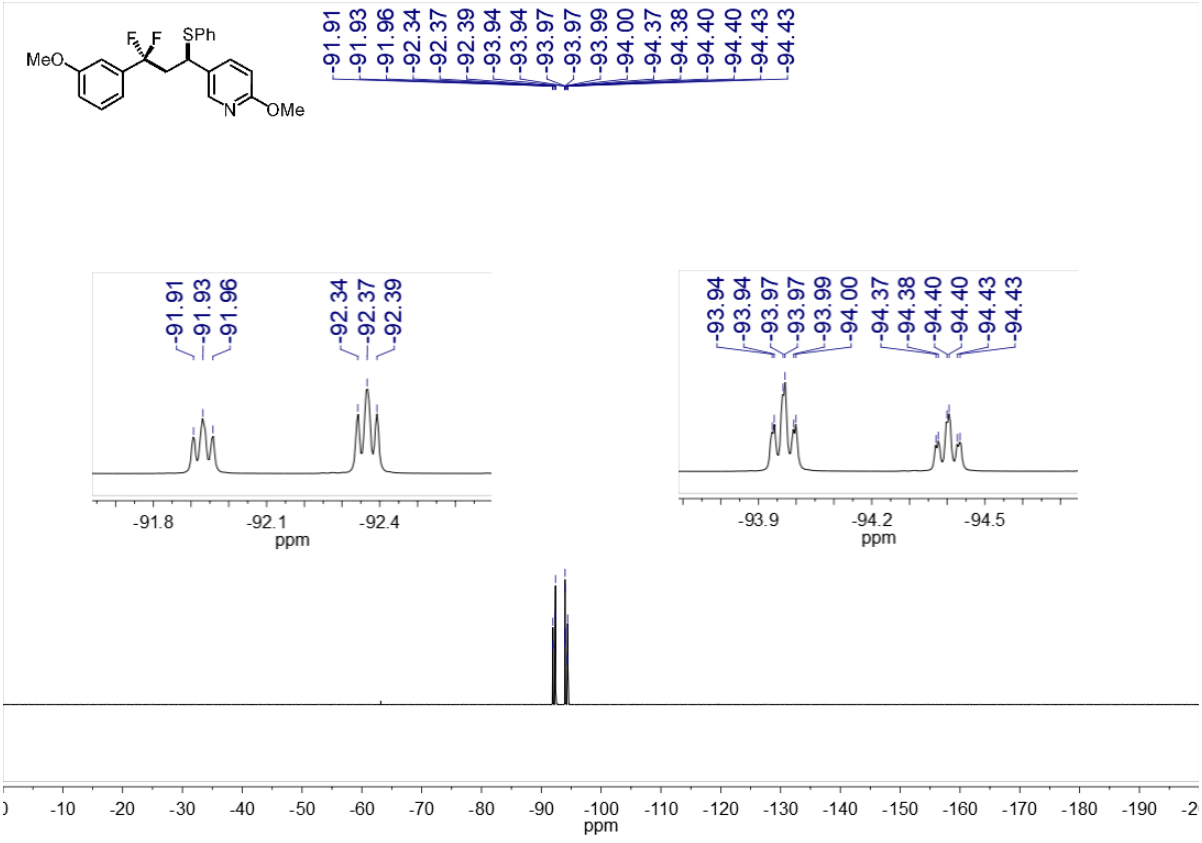
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **4j**



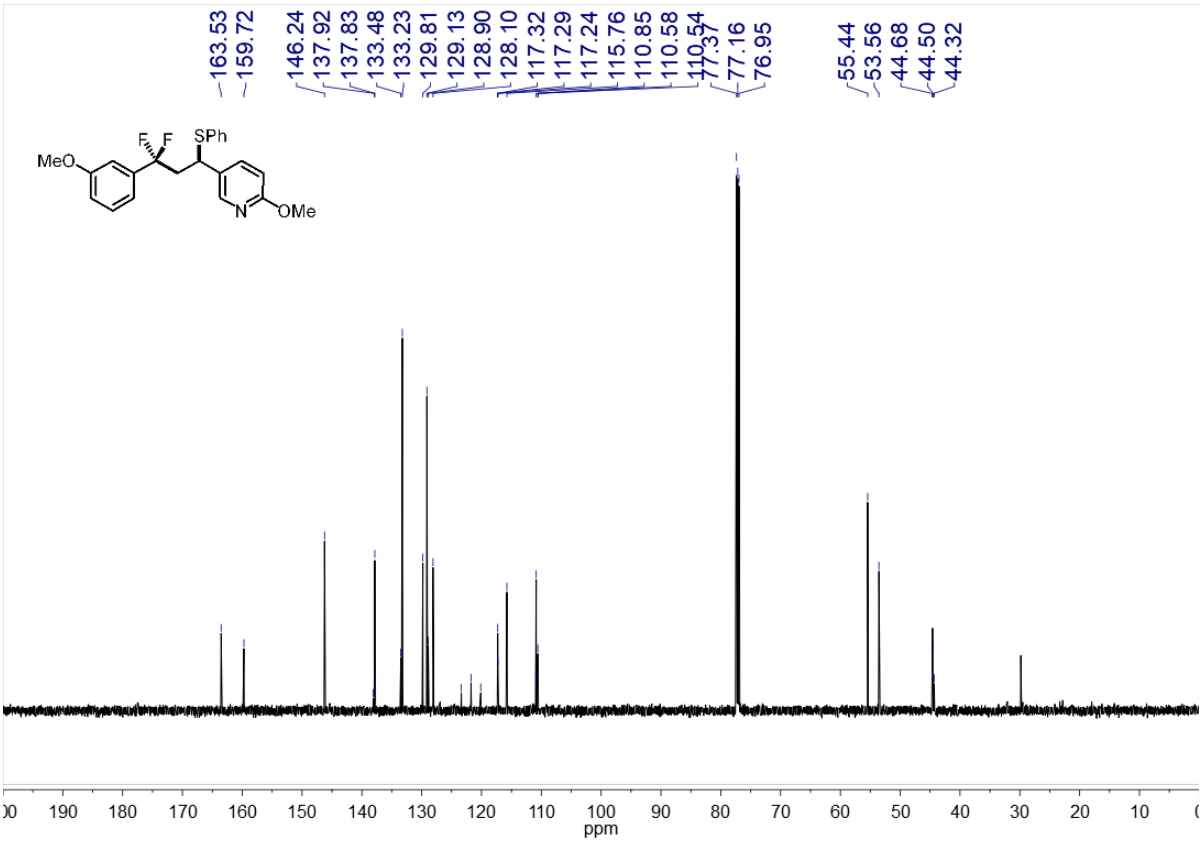
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **4j**



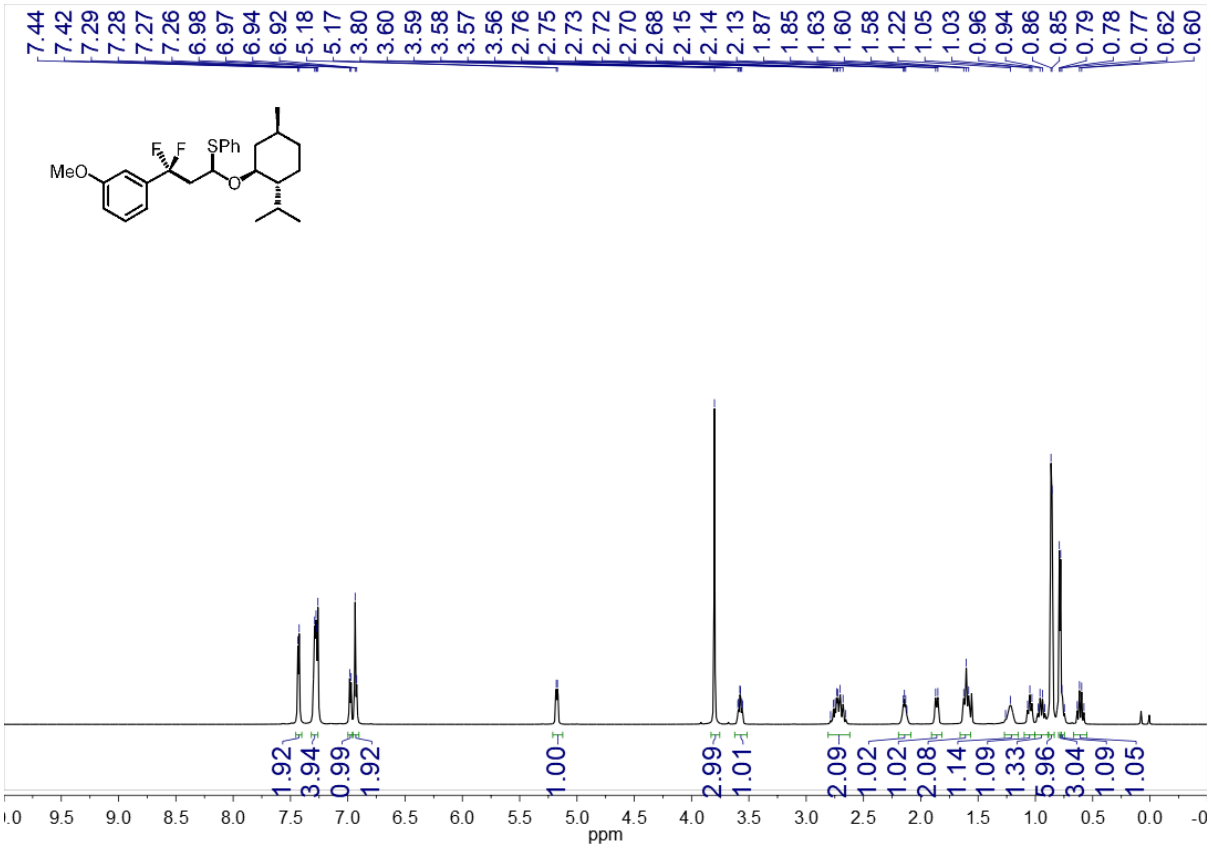
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **4k**



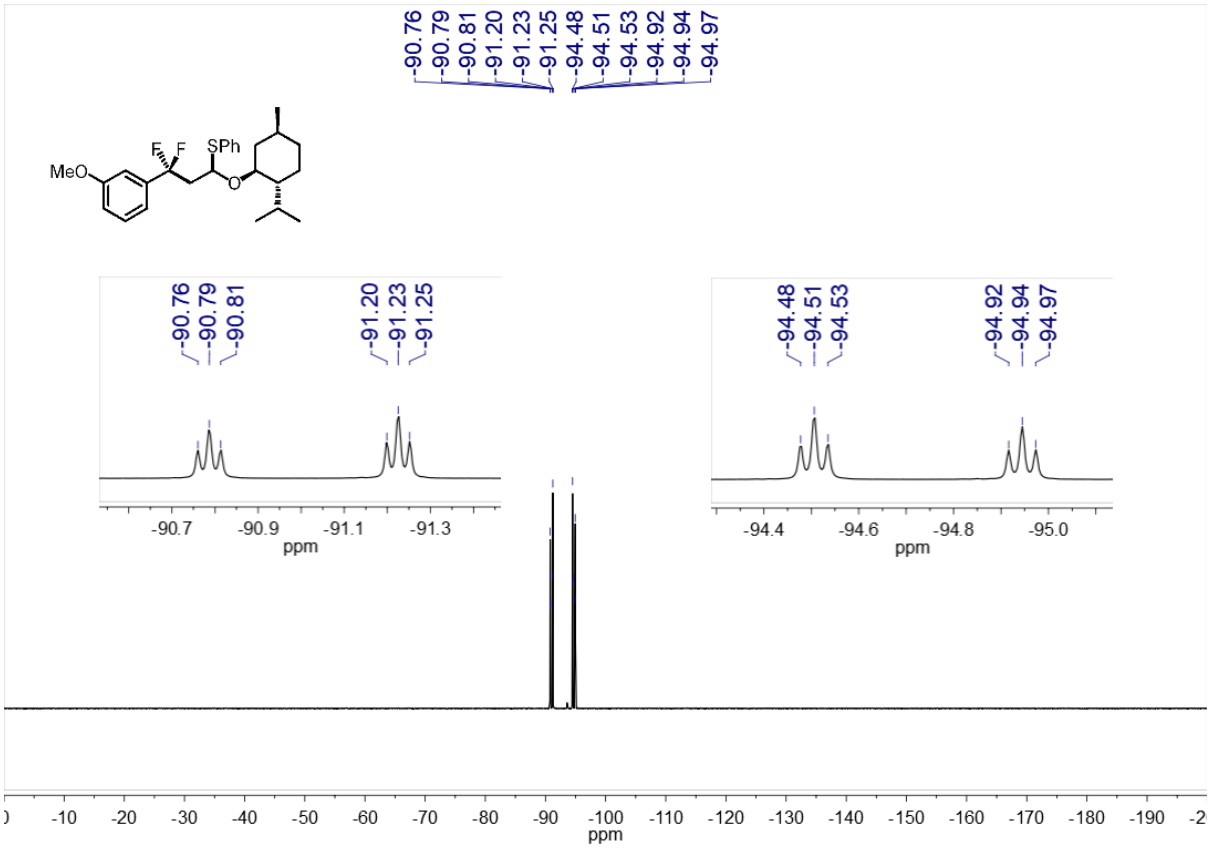
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **4k**



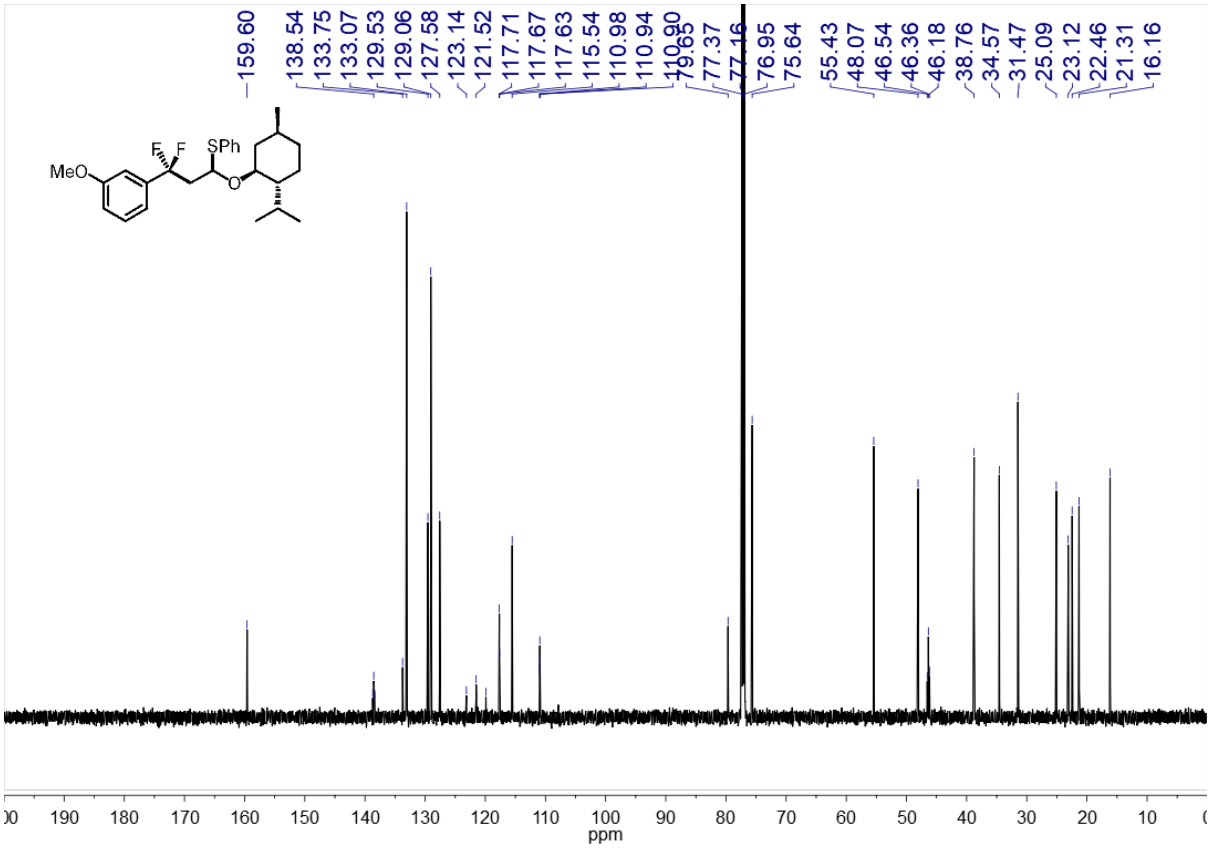
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **4k**



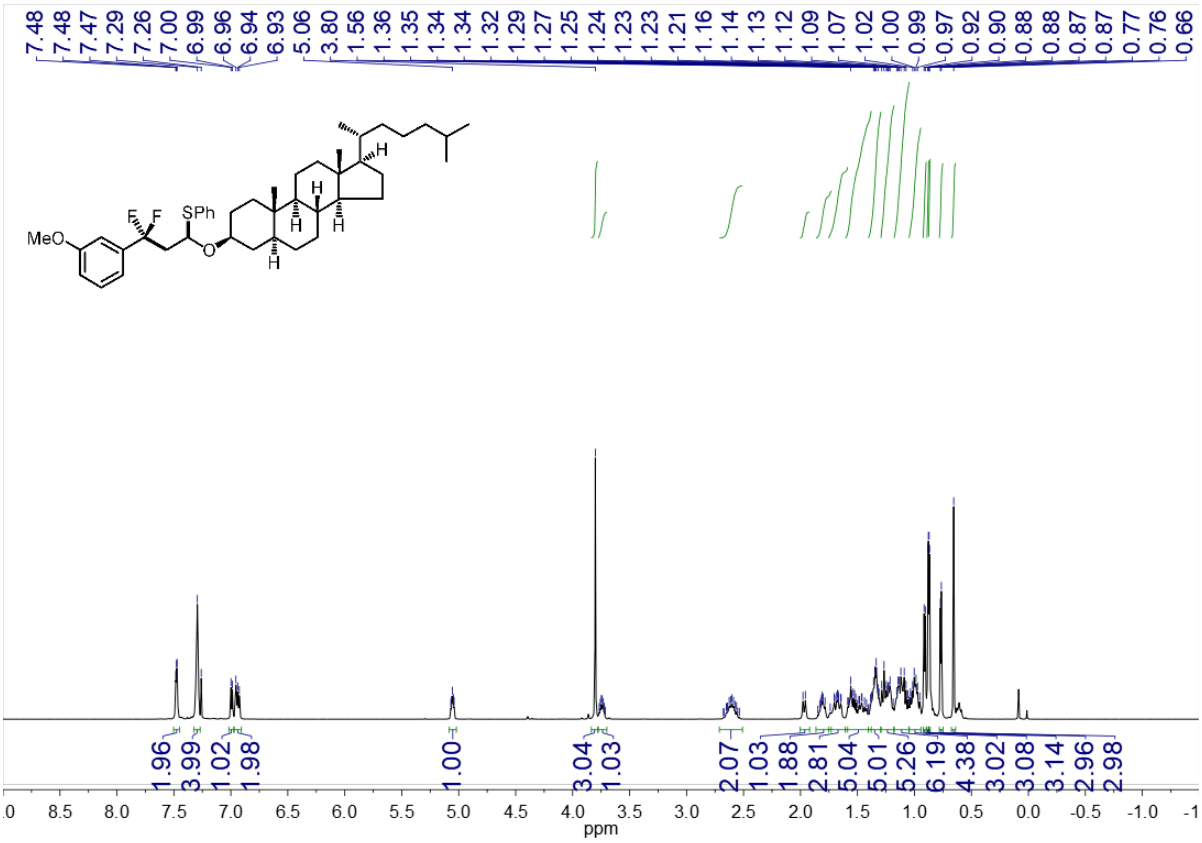
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **4l**



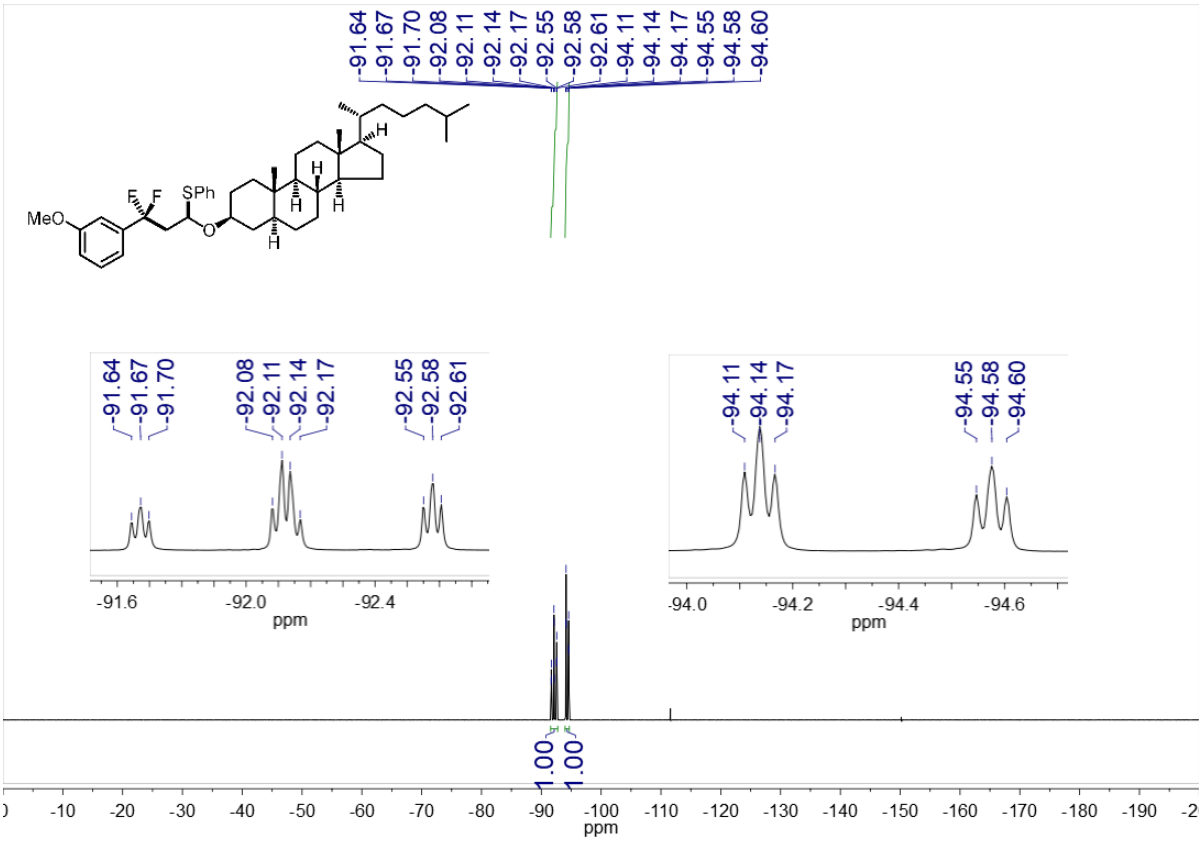
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **4l**



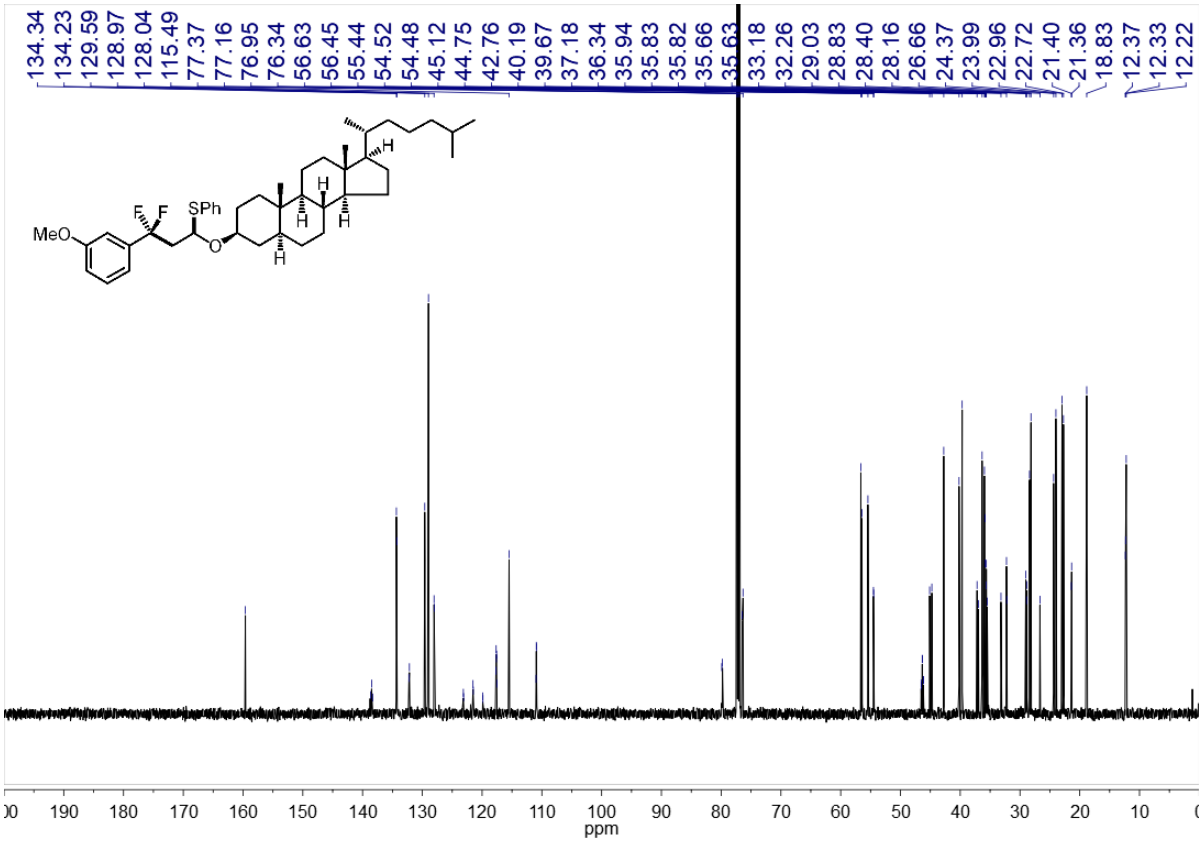
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **4l**



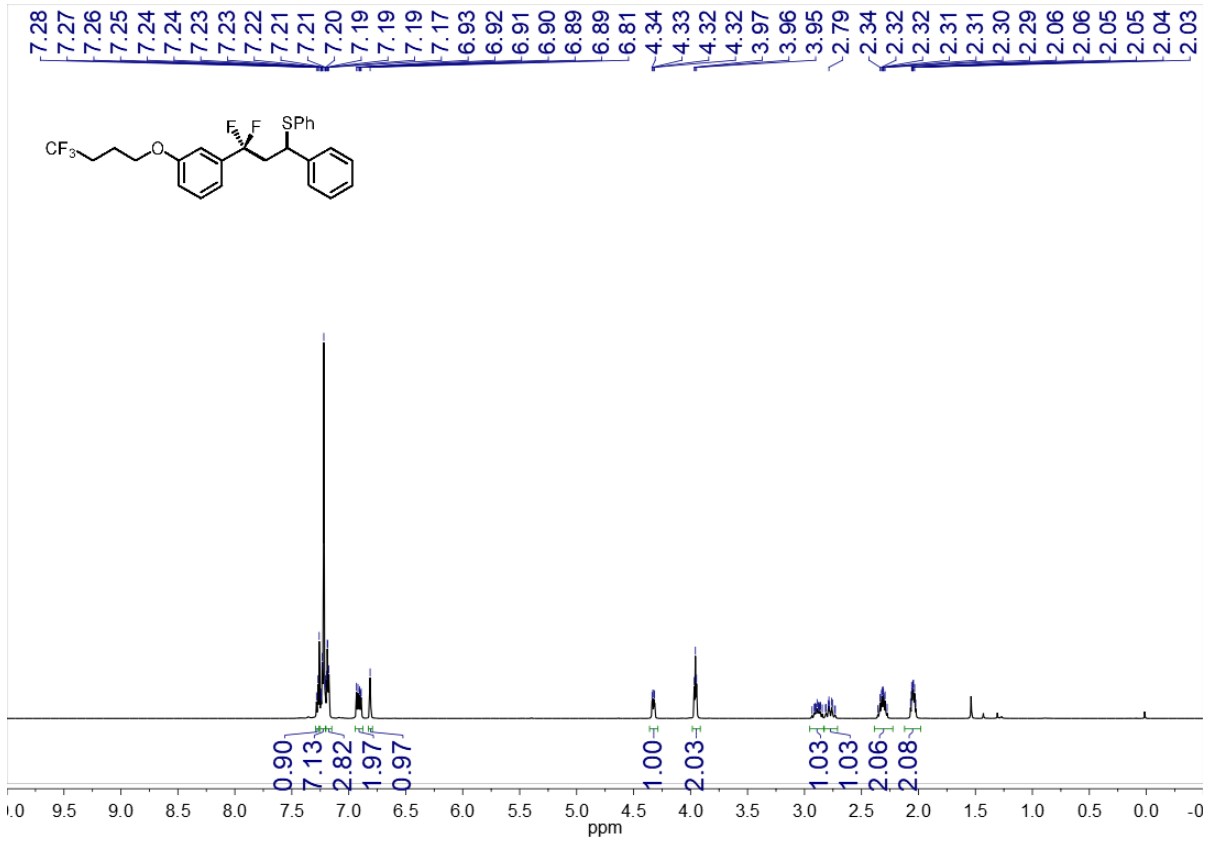
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **4m**



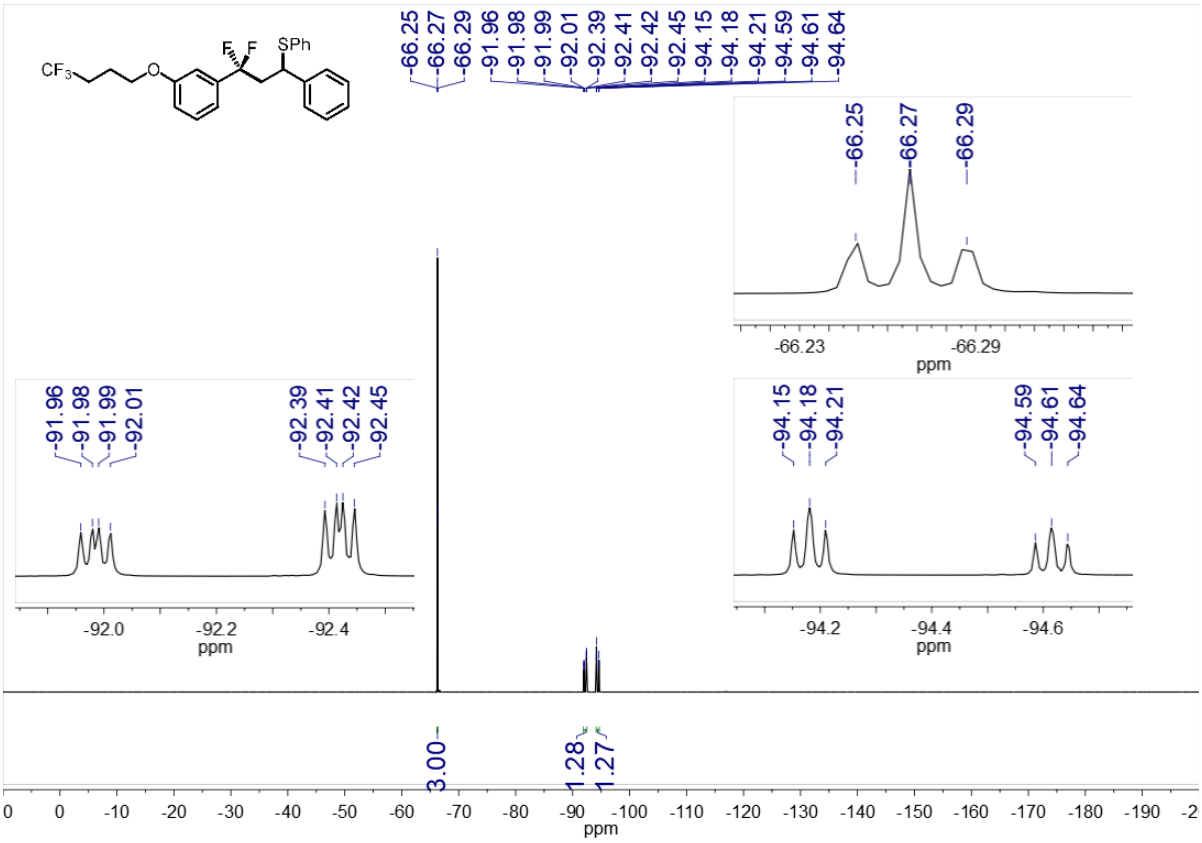
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **4m**



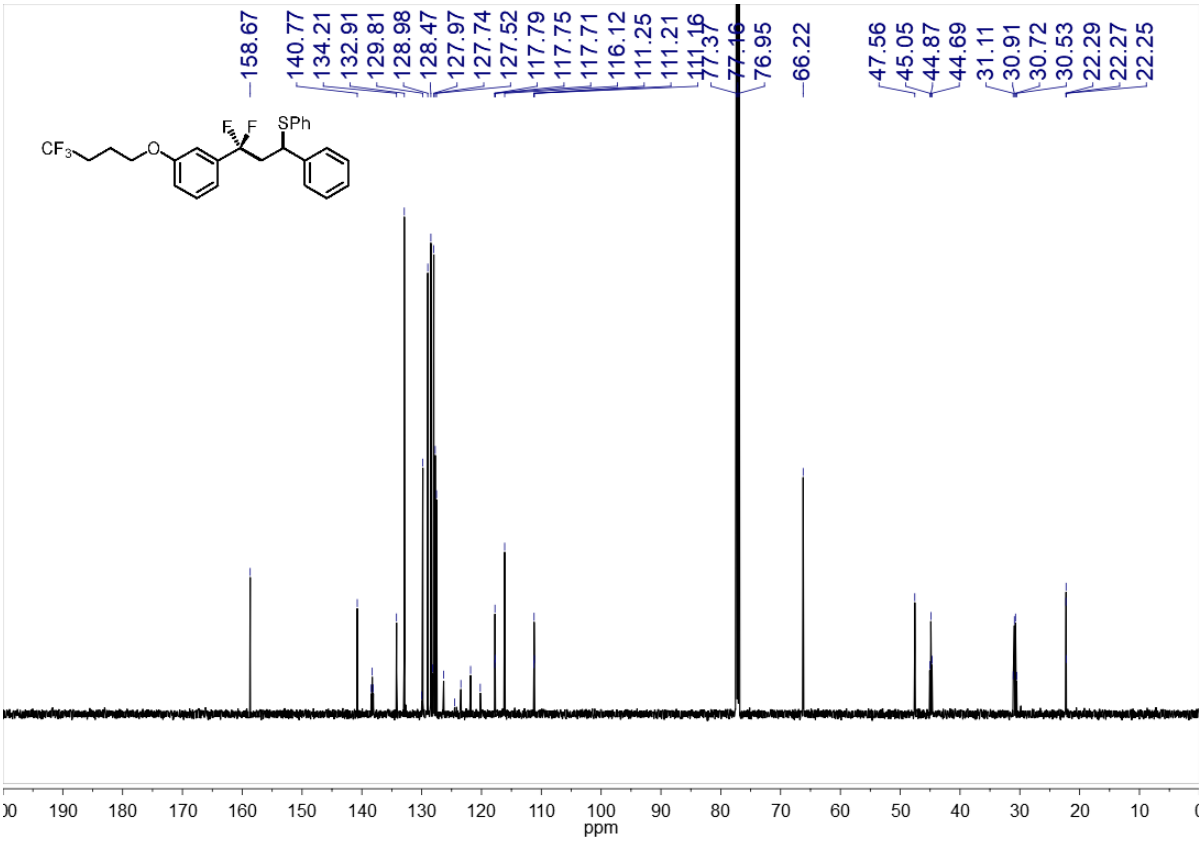
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **4m**



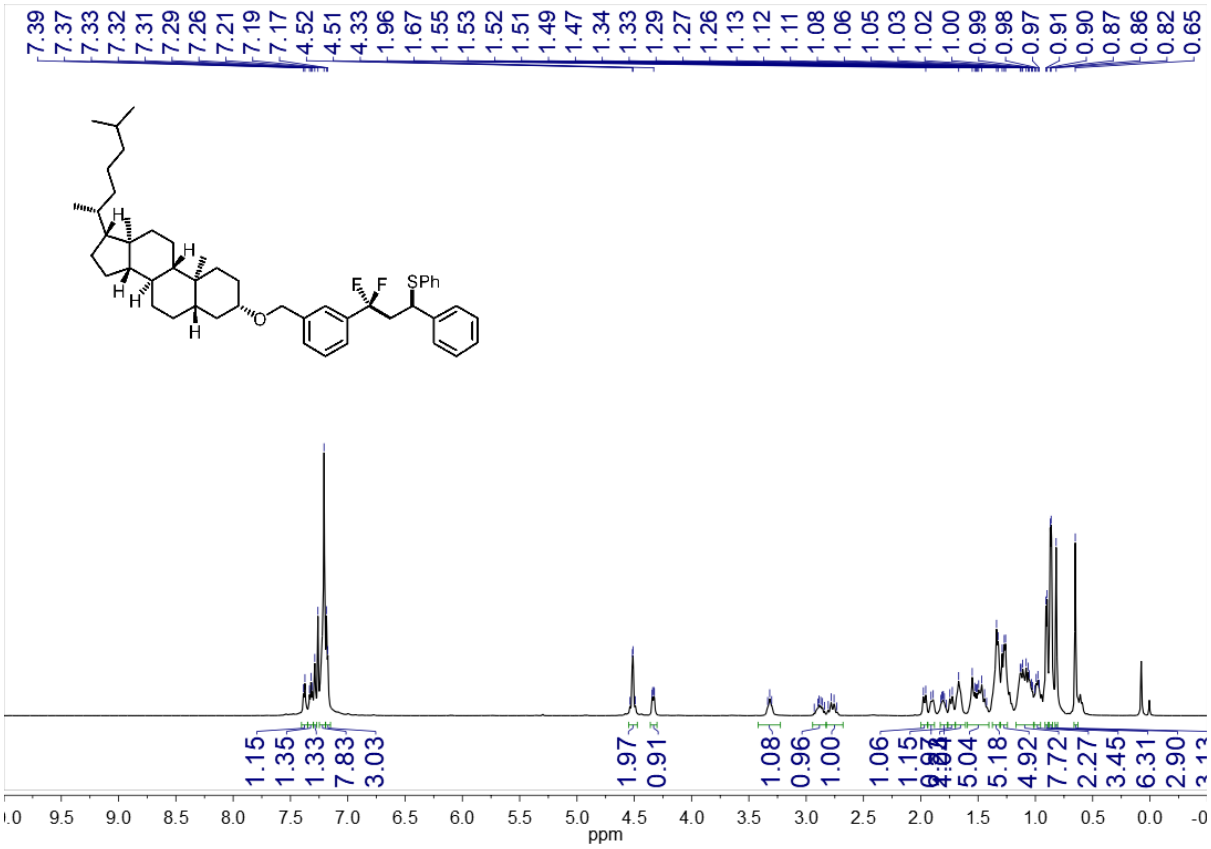
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **4n**



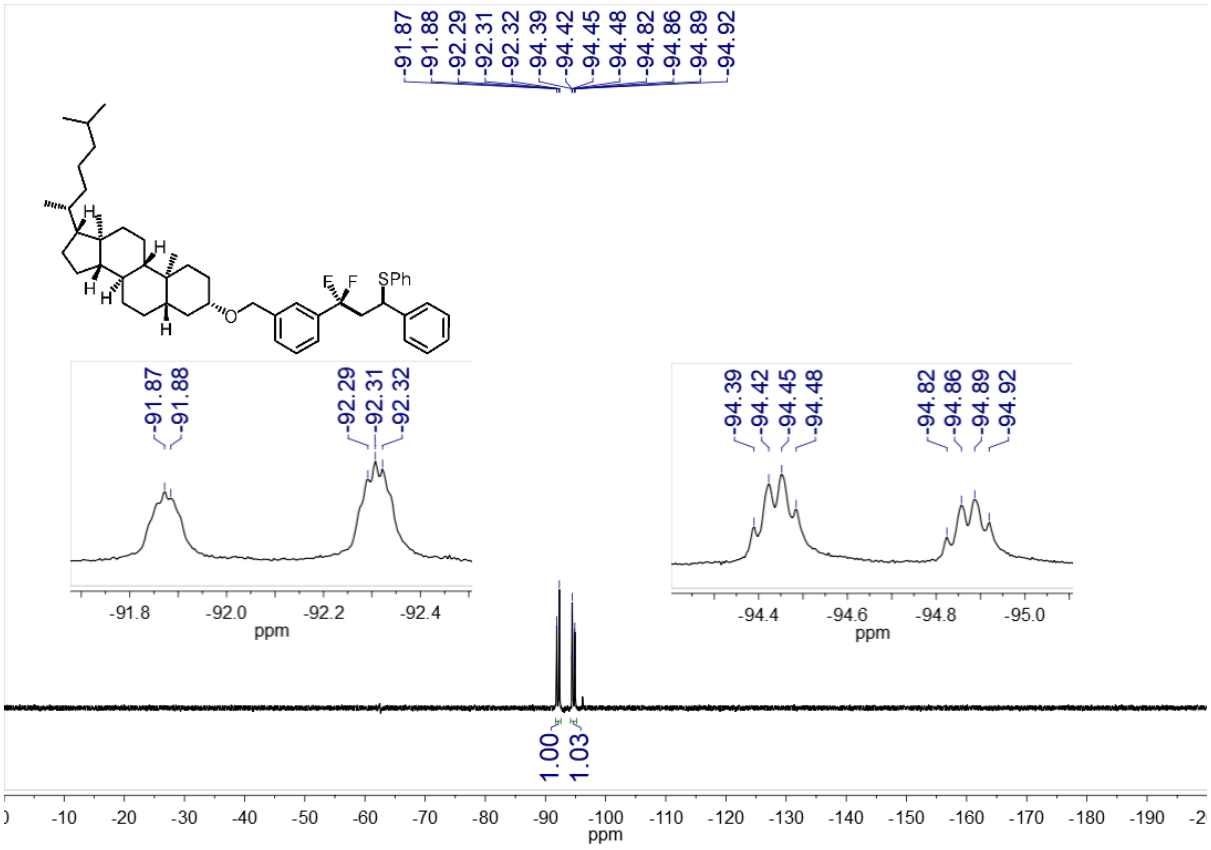
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **4n**



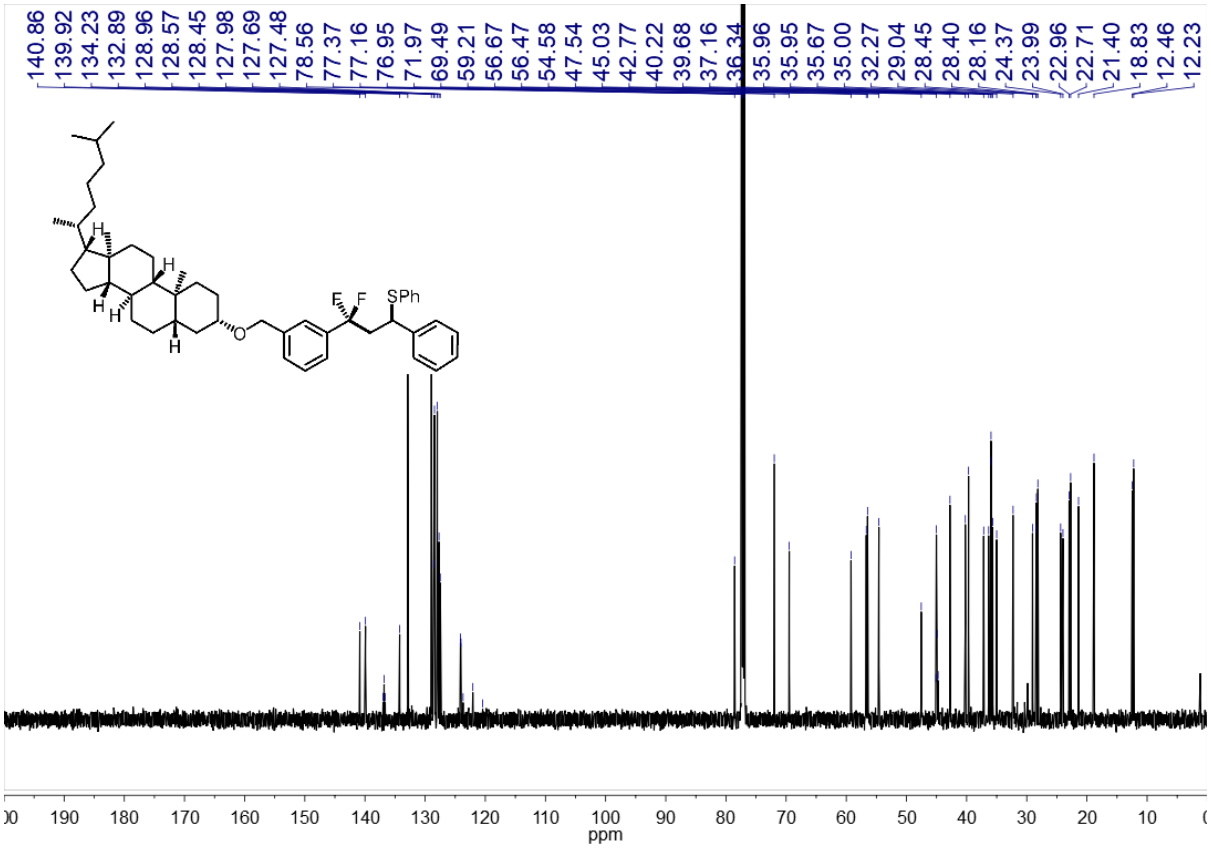
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **4n**



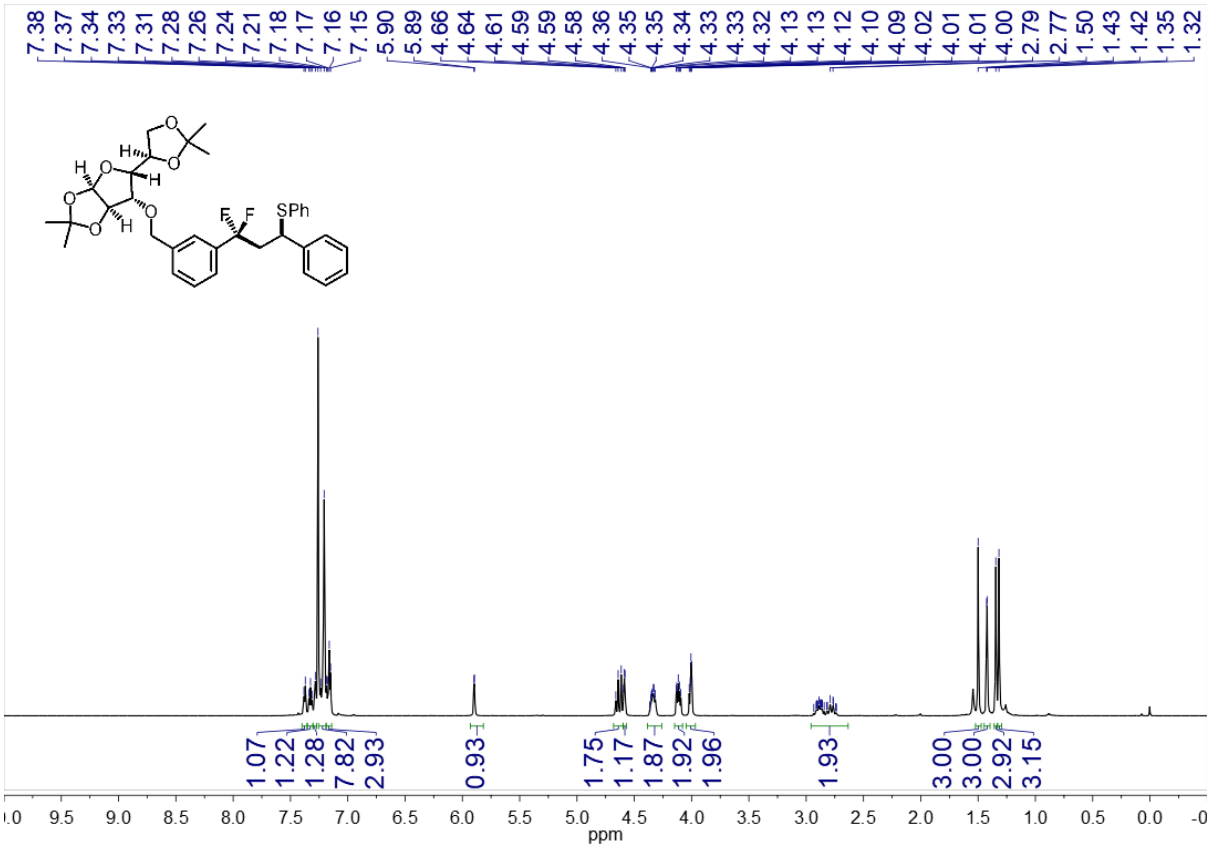
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **4o**



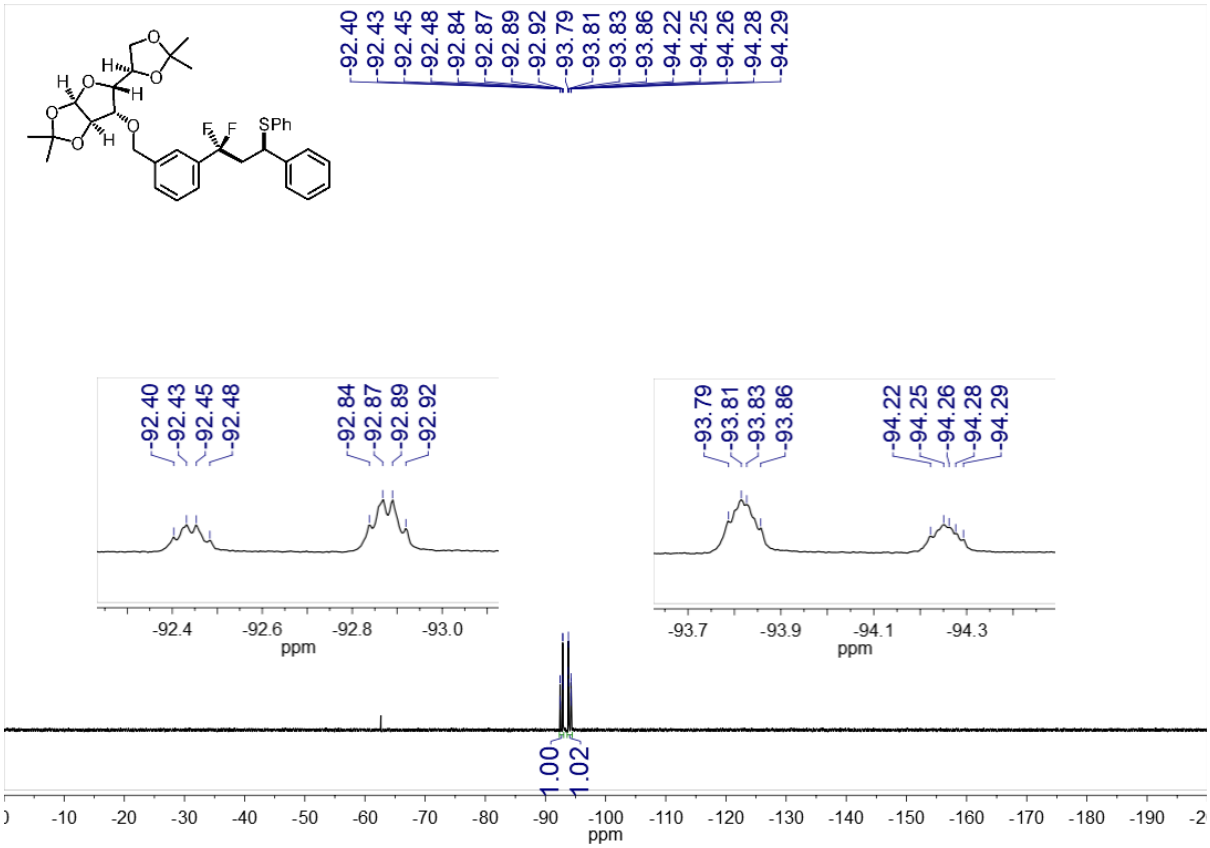
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **4o**



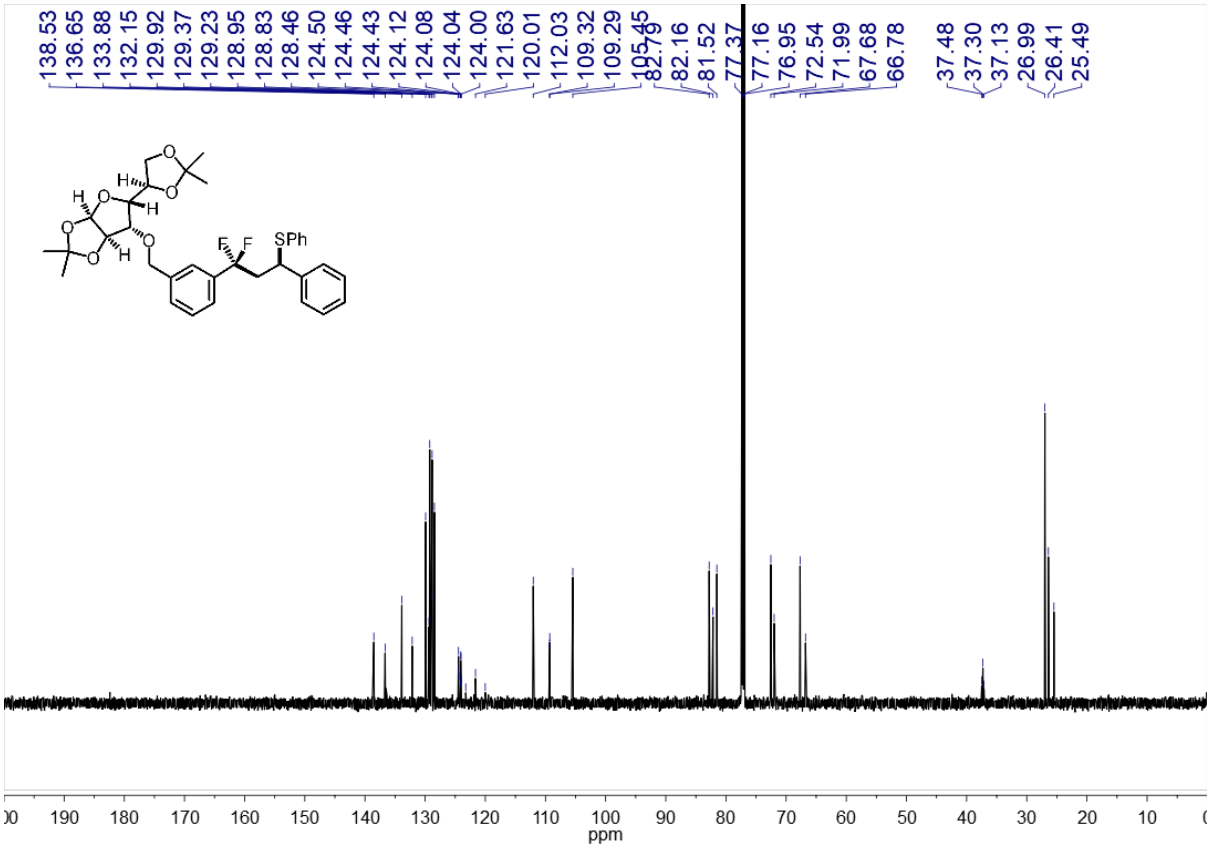
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **4o**



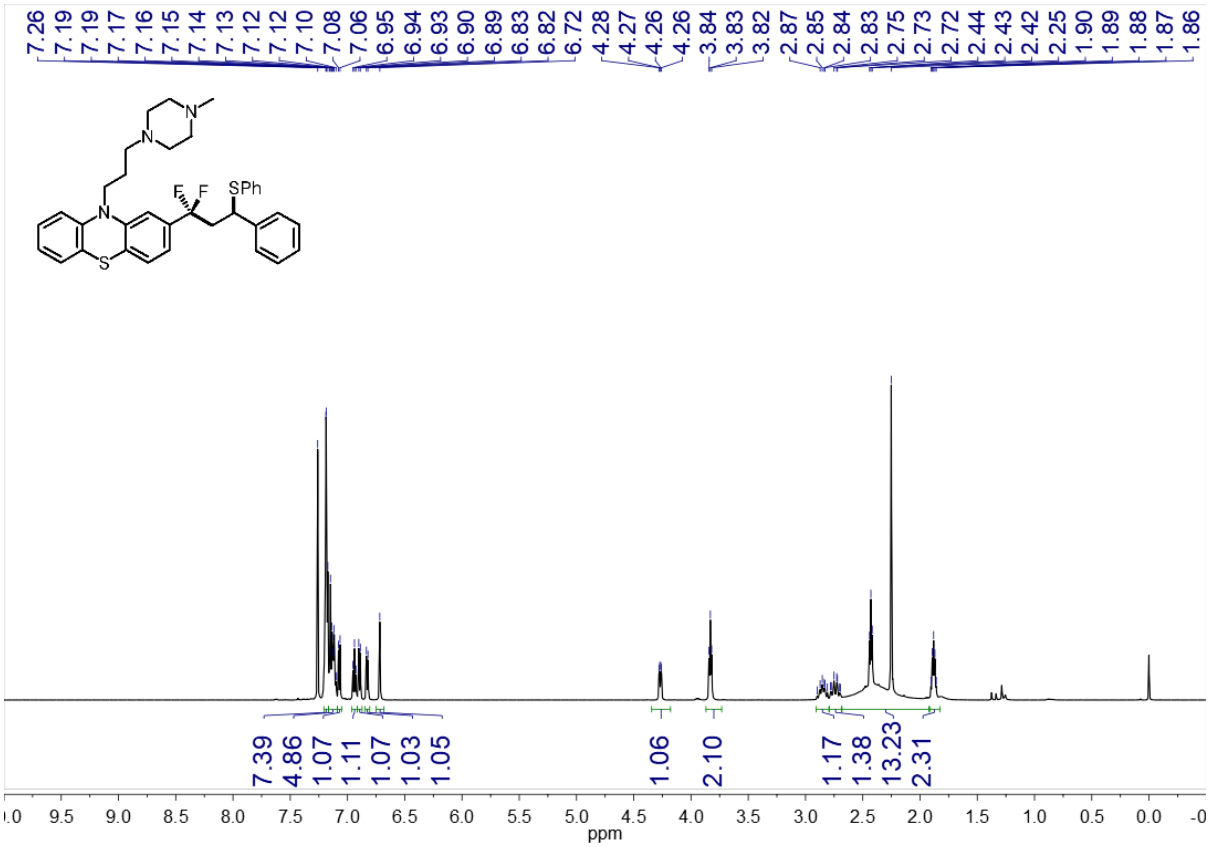
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **4p**



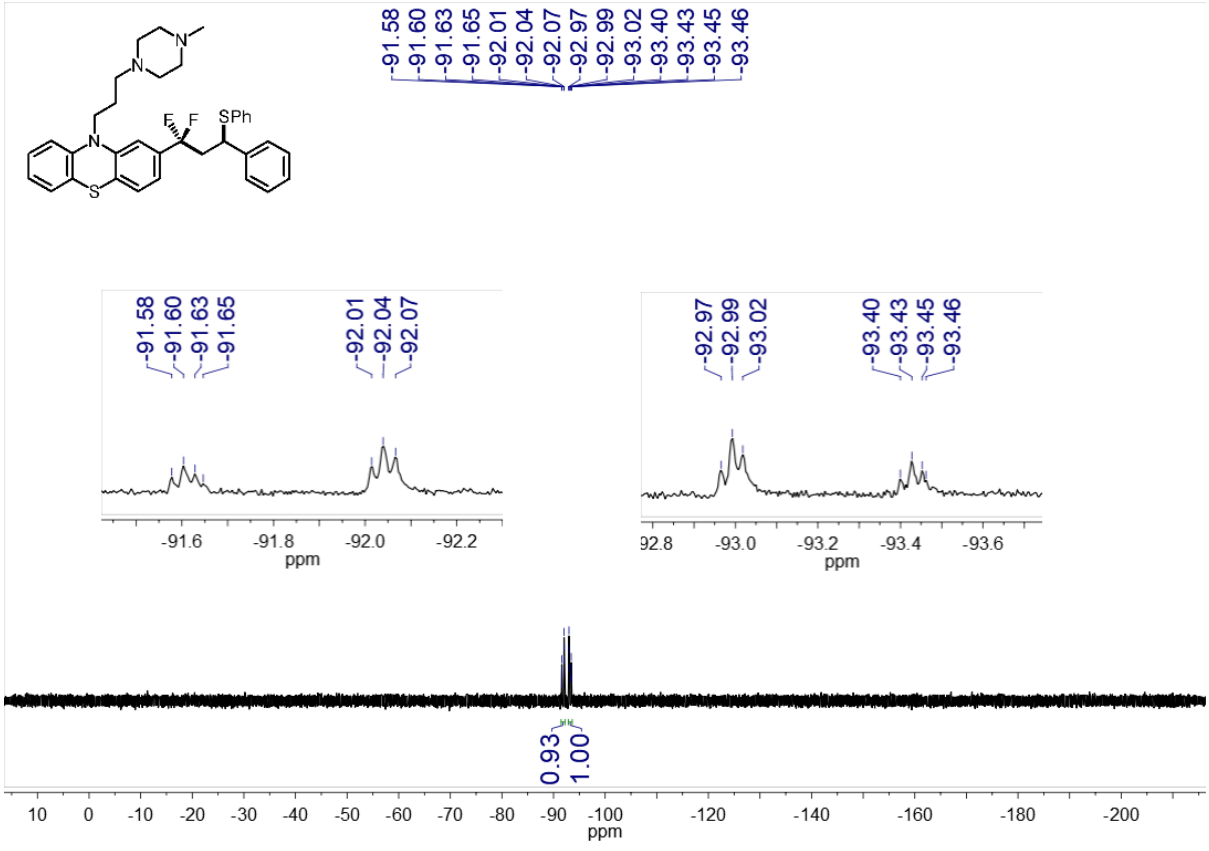
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **4p**



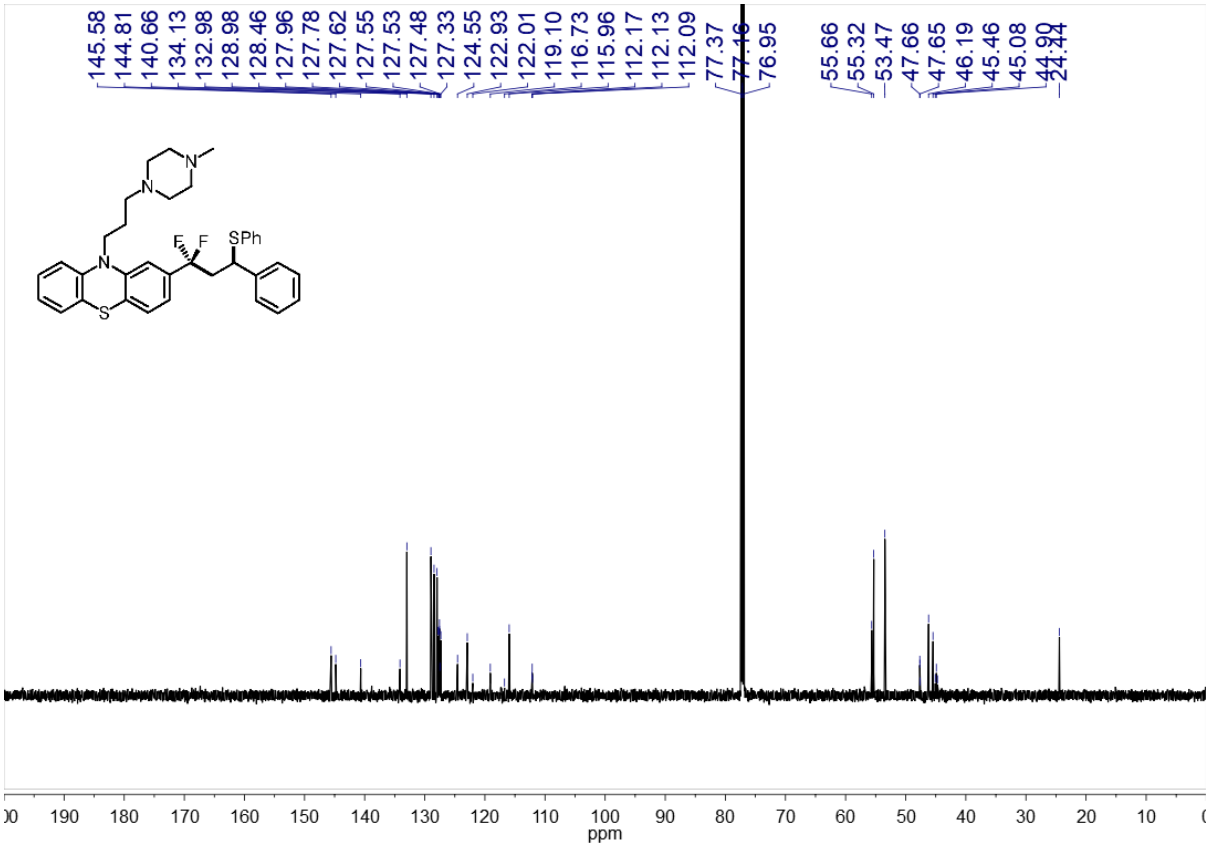
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **4p**



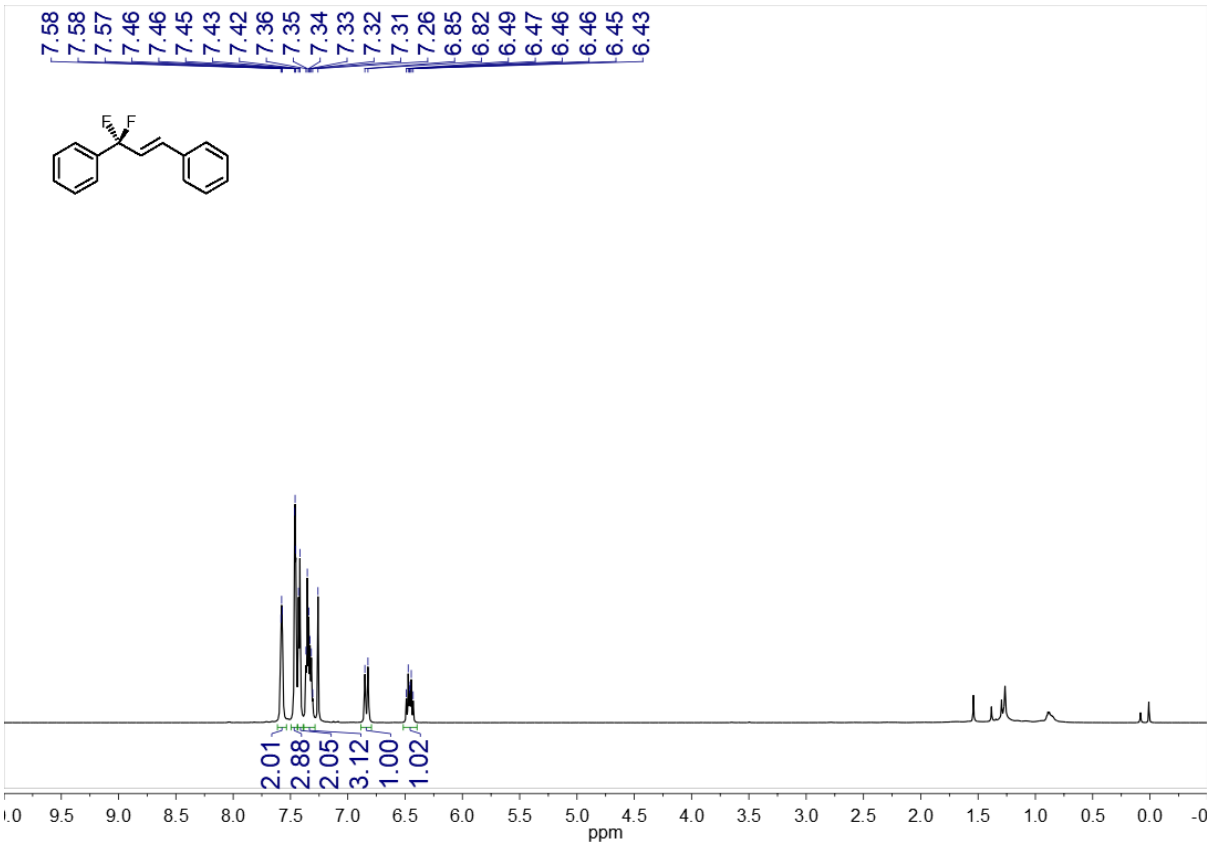
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **4q**



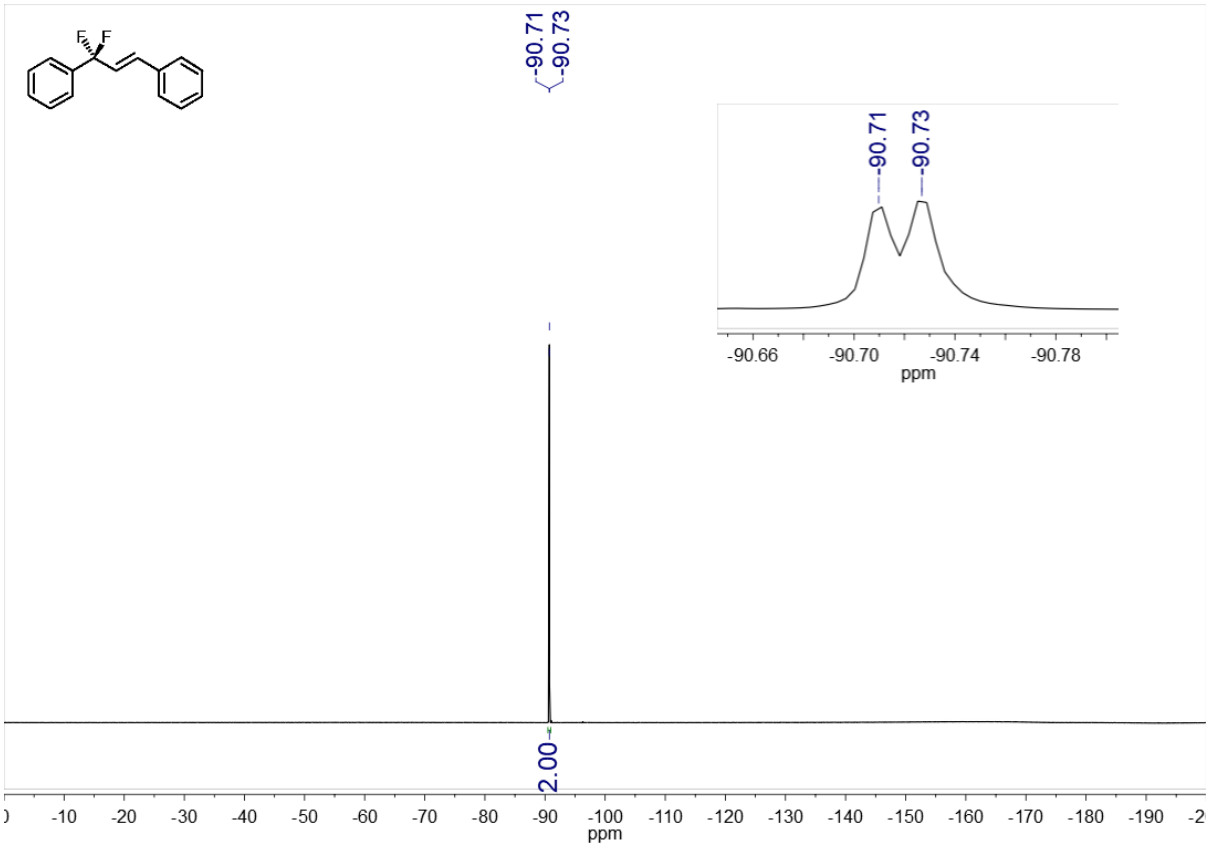
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **4q**



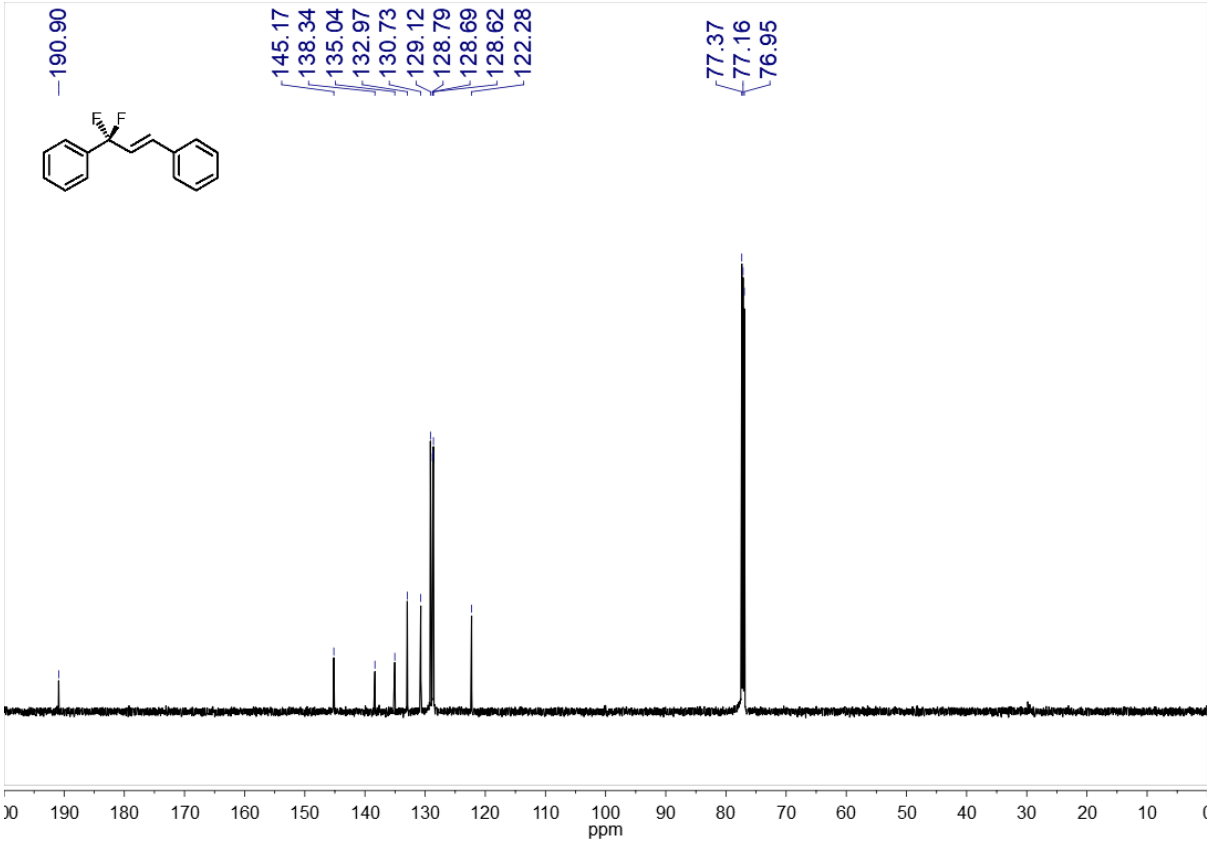
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **4q**



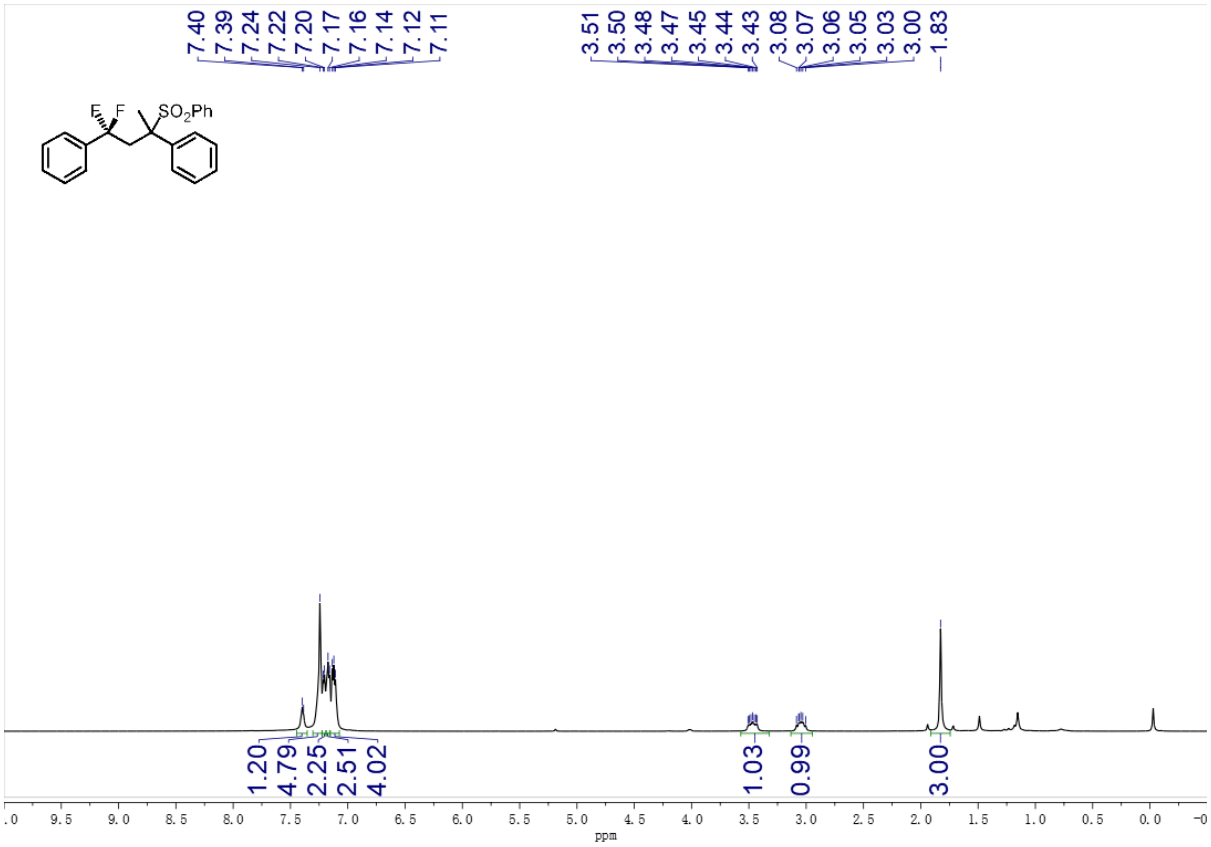
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **6**



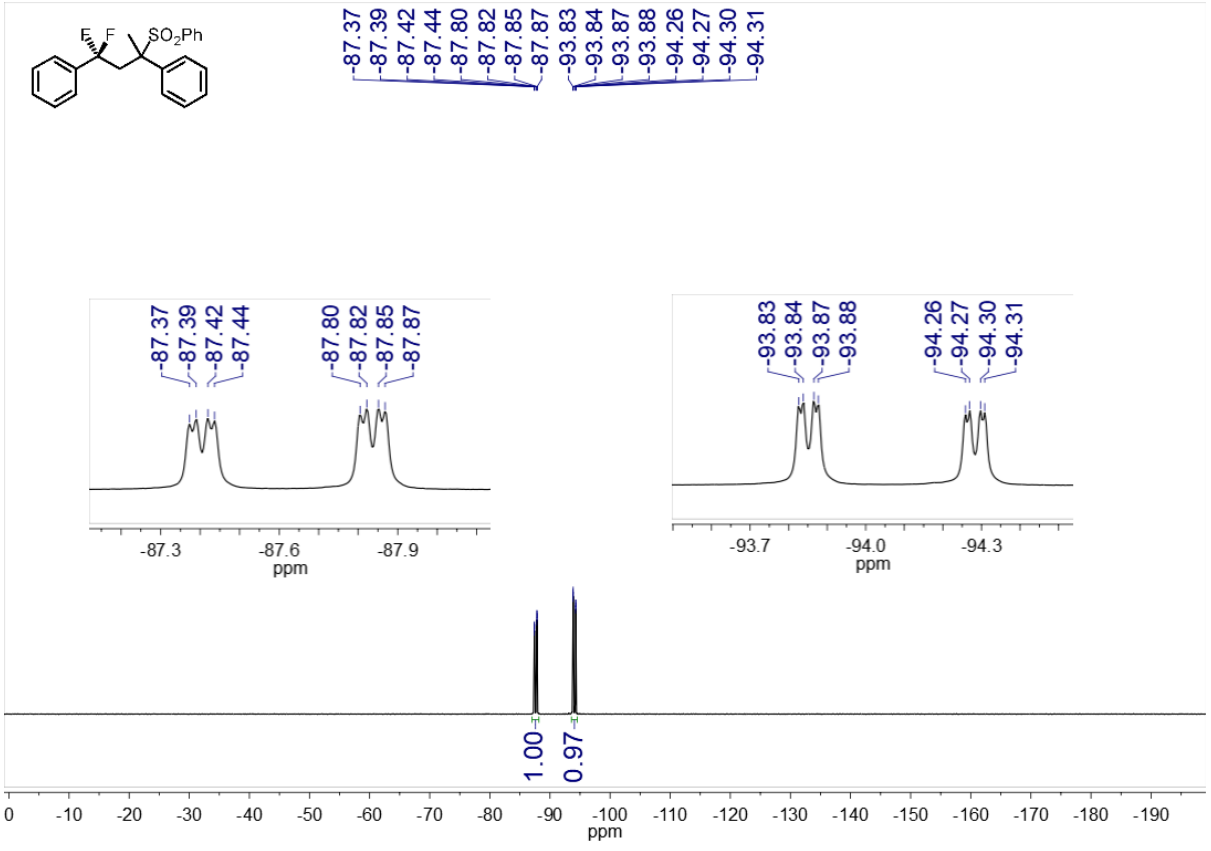
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **6**



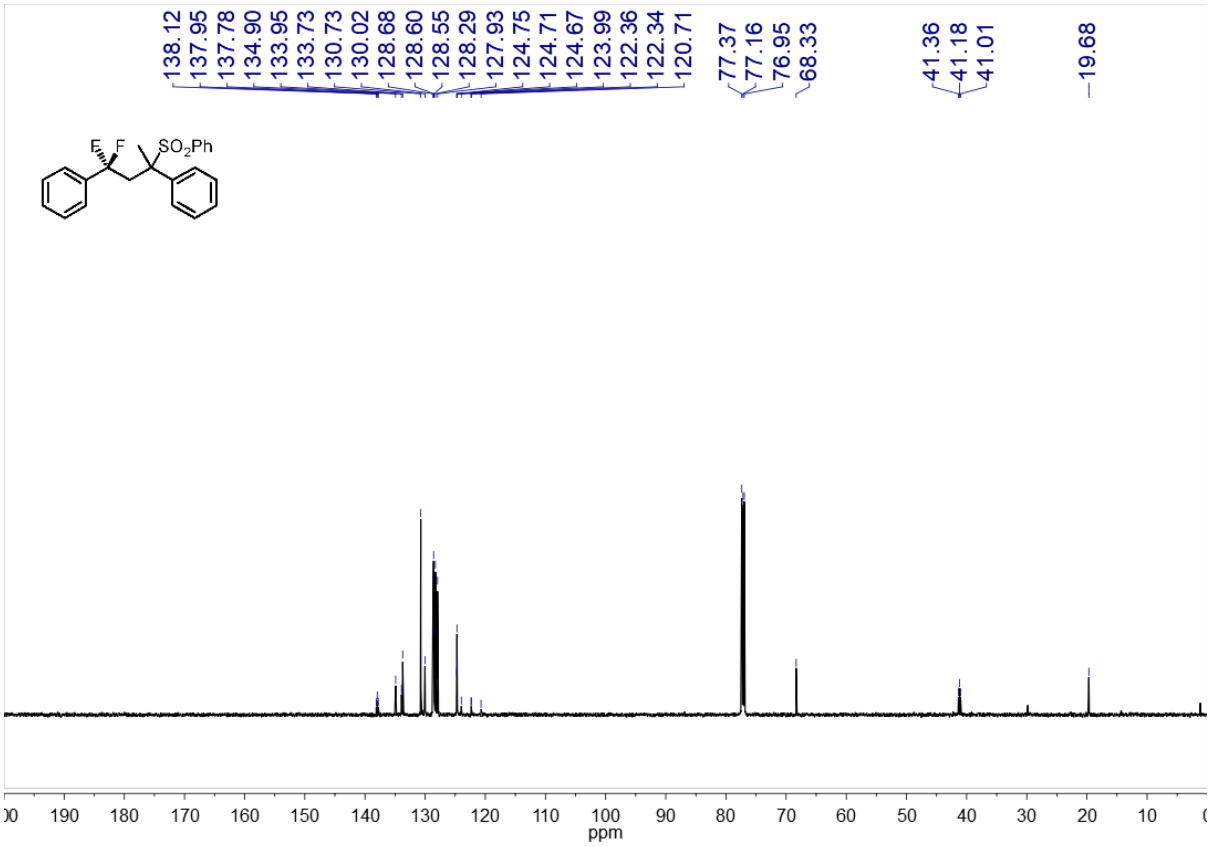
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **6**



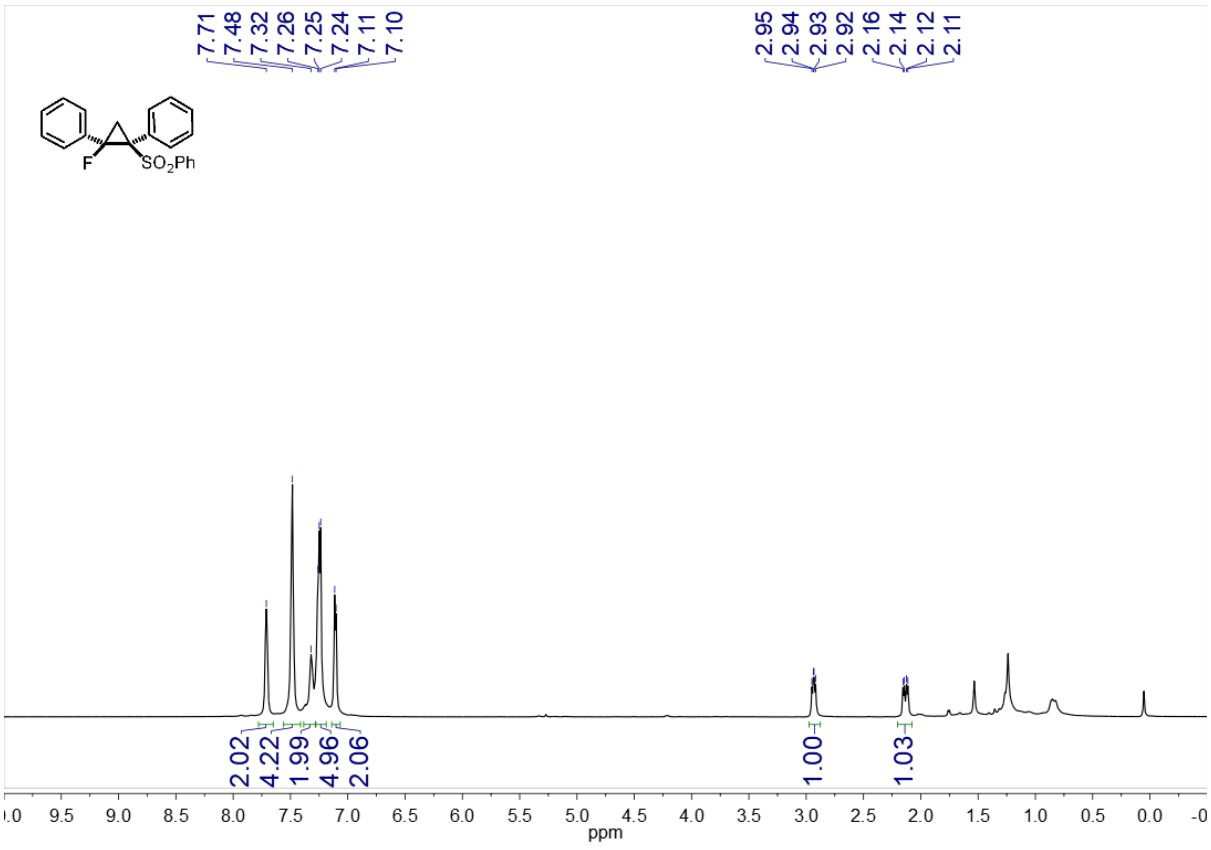
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **7**



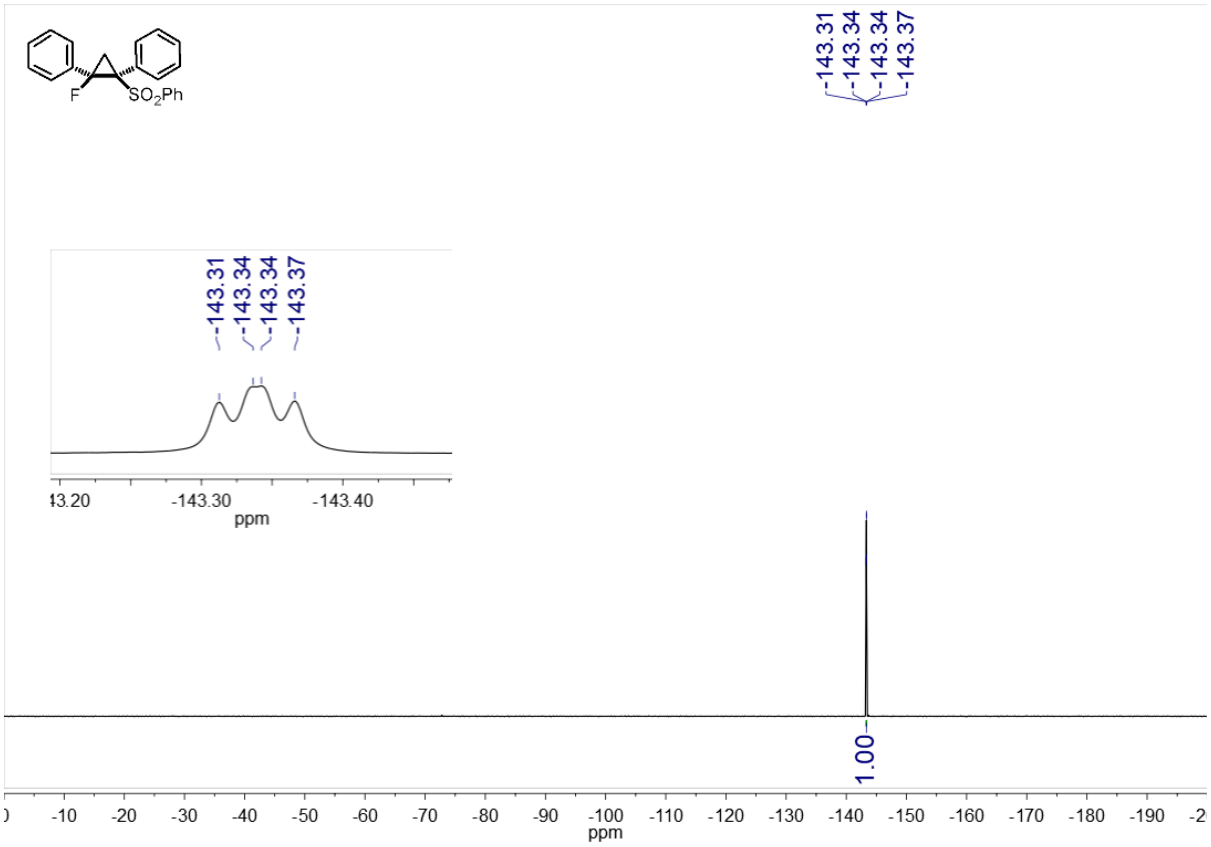
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **7**



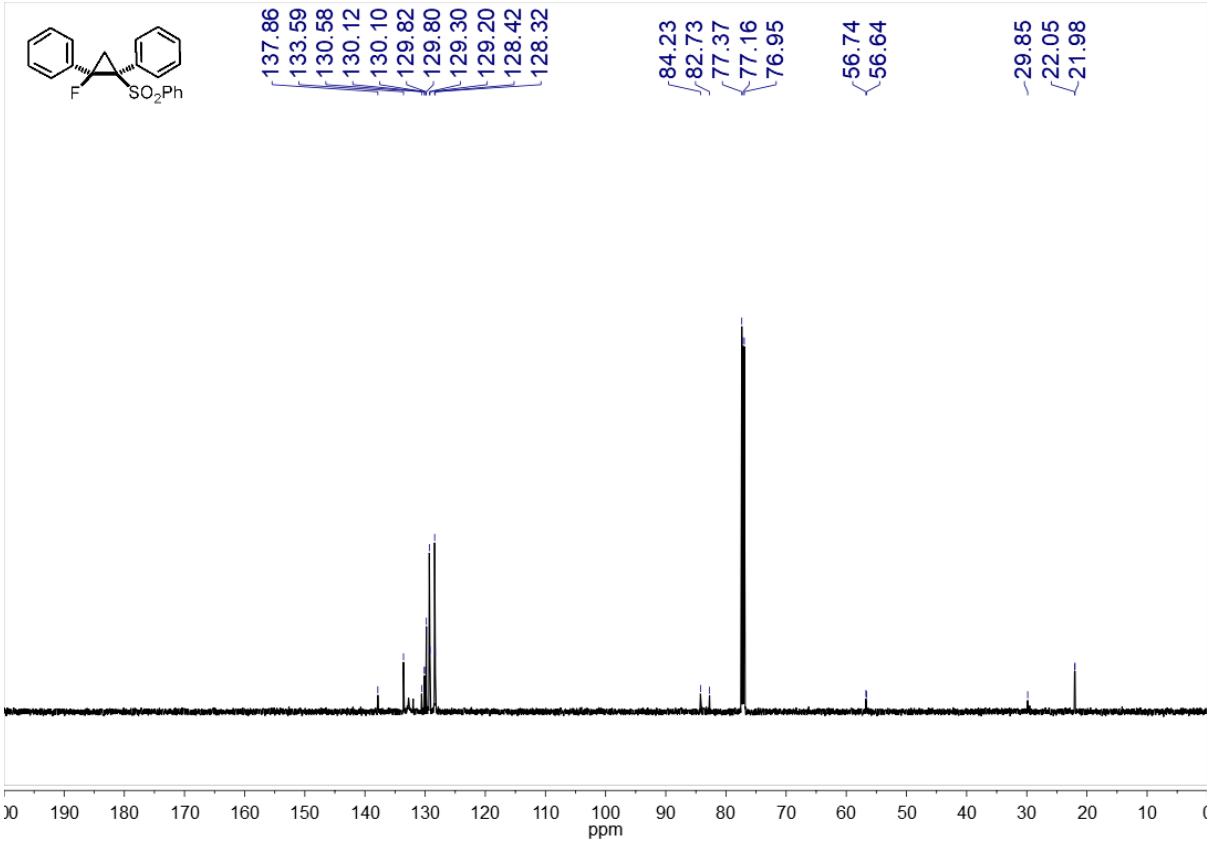
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **7**



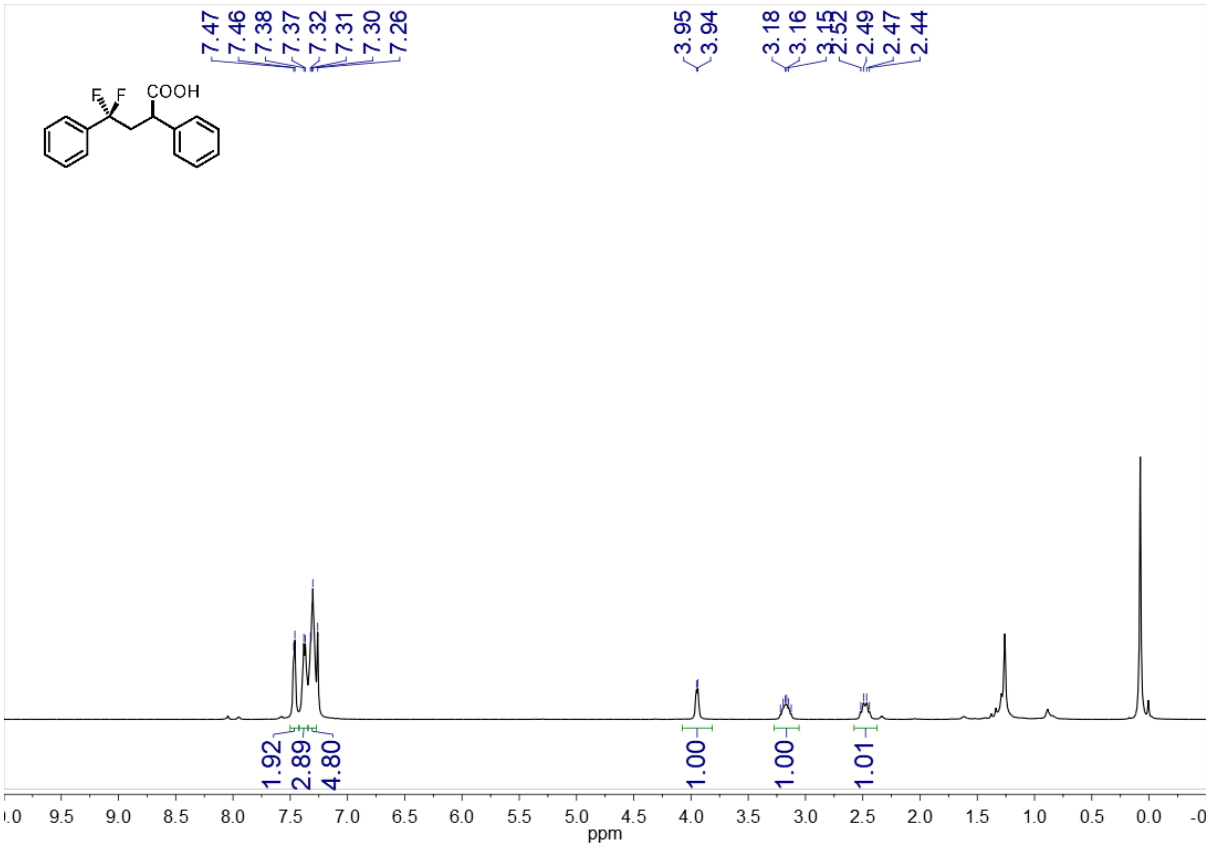
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **8**



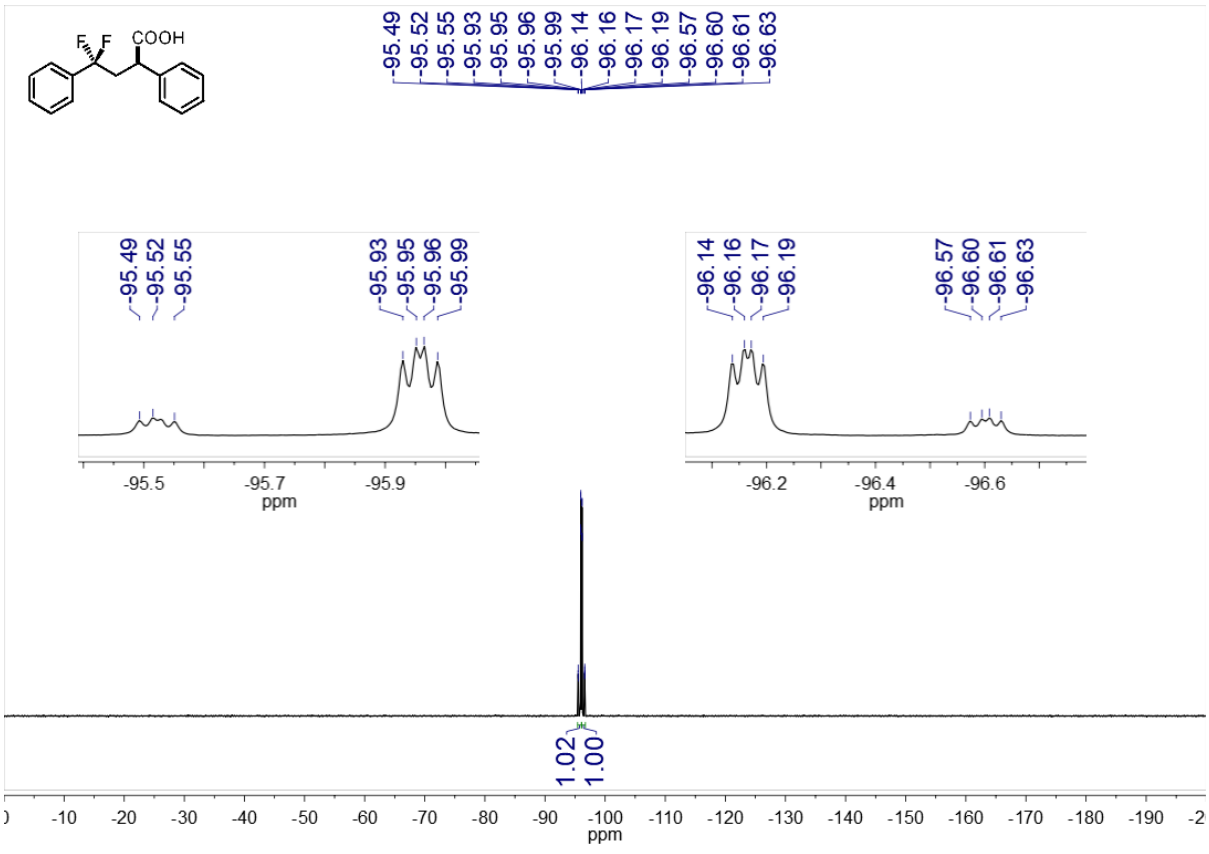
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **8**



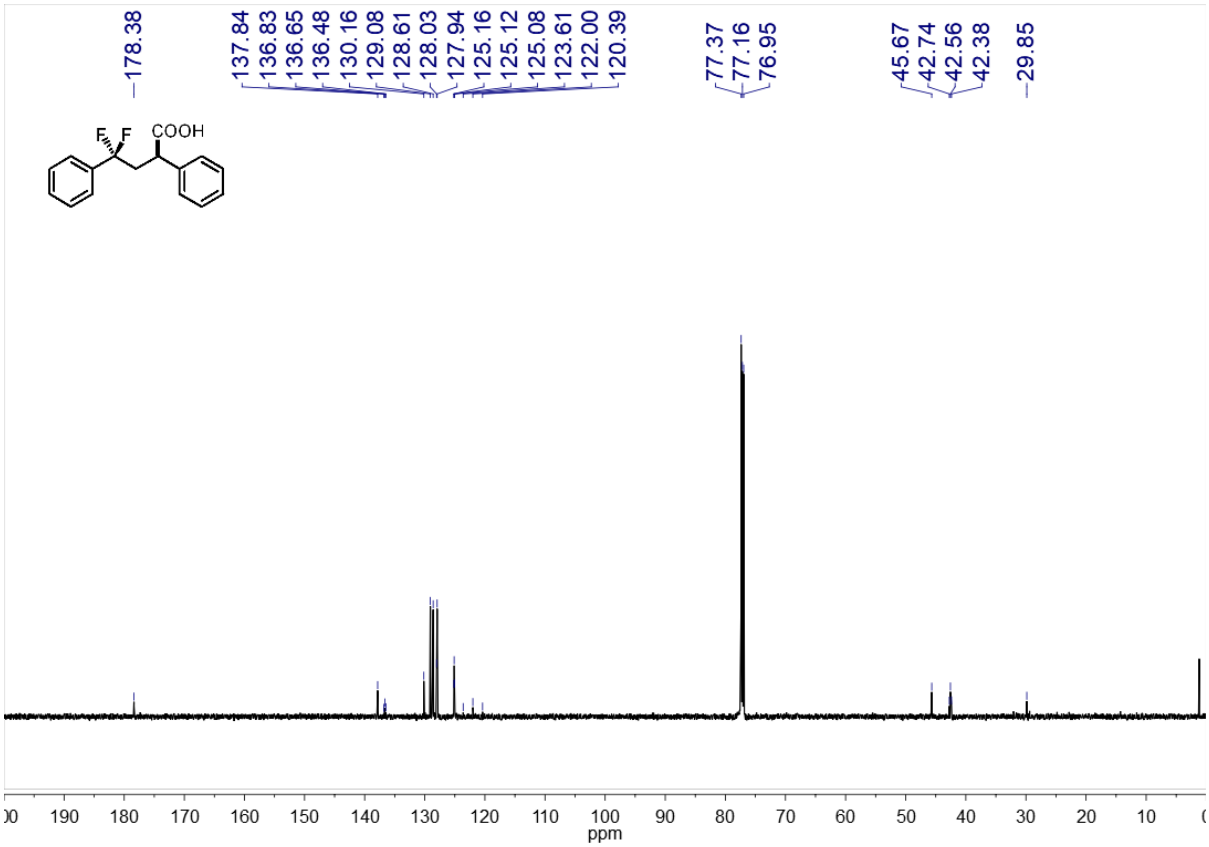
^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **8**



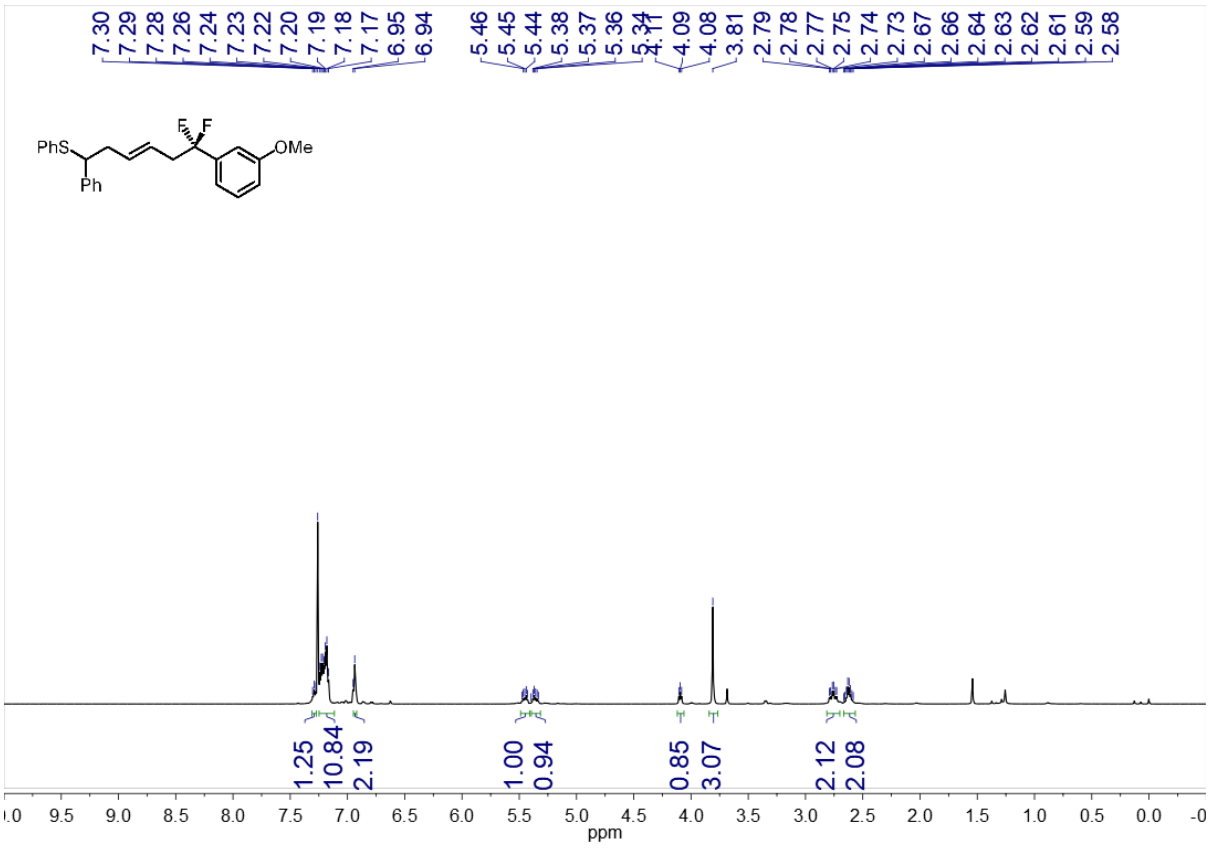
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **9**



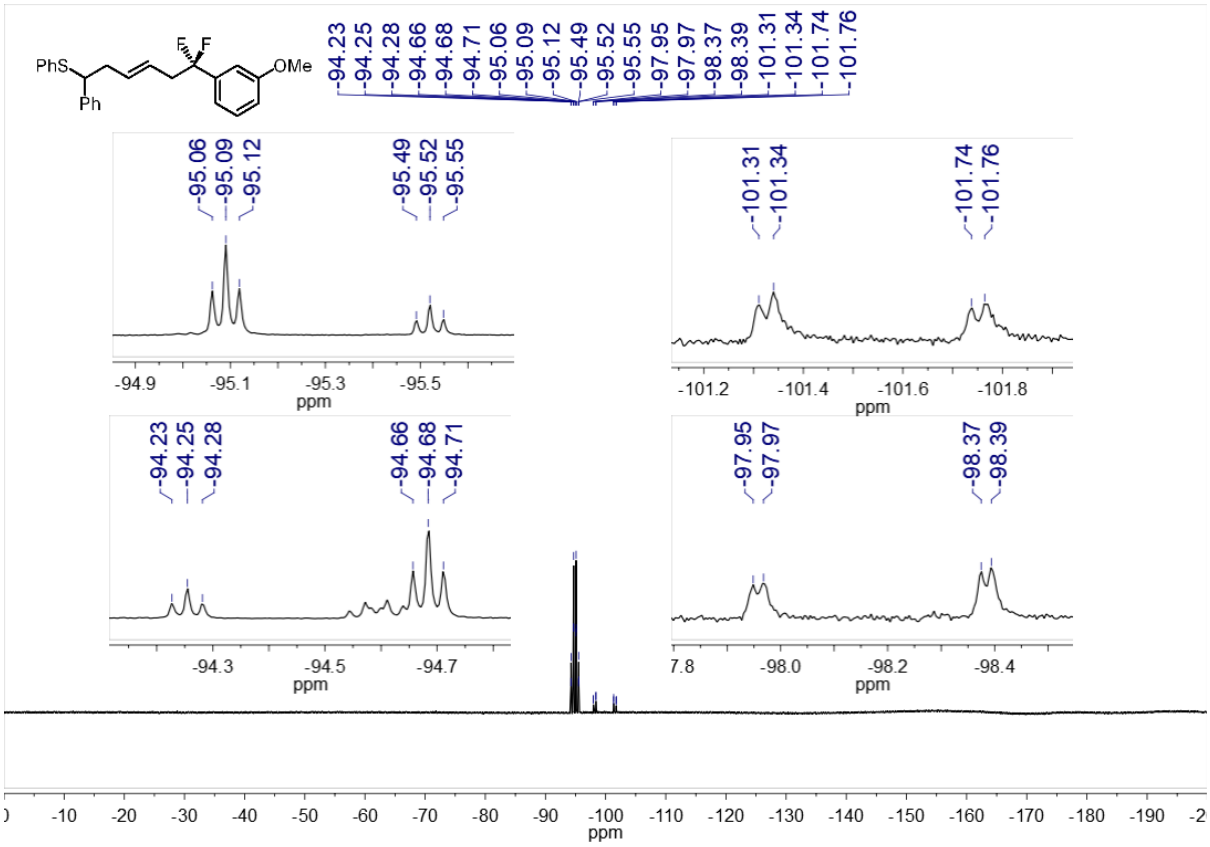
^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **9**



^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **9**



^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **11**



^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **11**

8 X-Ray Crystallography Data of 5x

The suitable crystals were selected on a PANalytical B.V diffractometer. The crystals were ke pt at 296.15 K during data collection. Using Olex2[2], the structures were solved with the ShelX T[3] structure solution program using Intrinsic Phasing and refined with the ShelXL[4] refinement package using Least Squares minimisation.

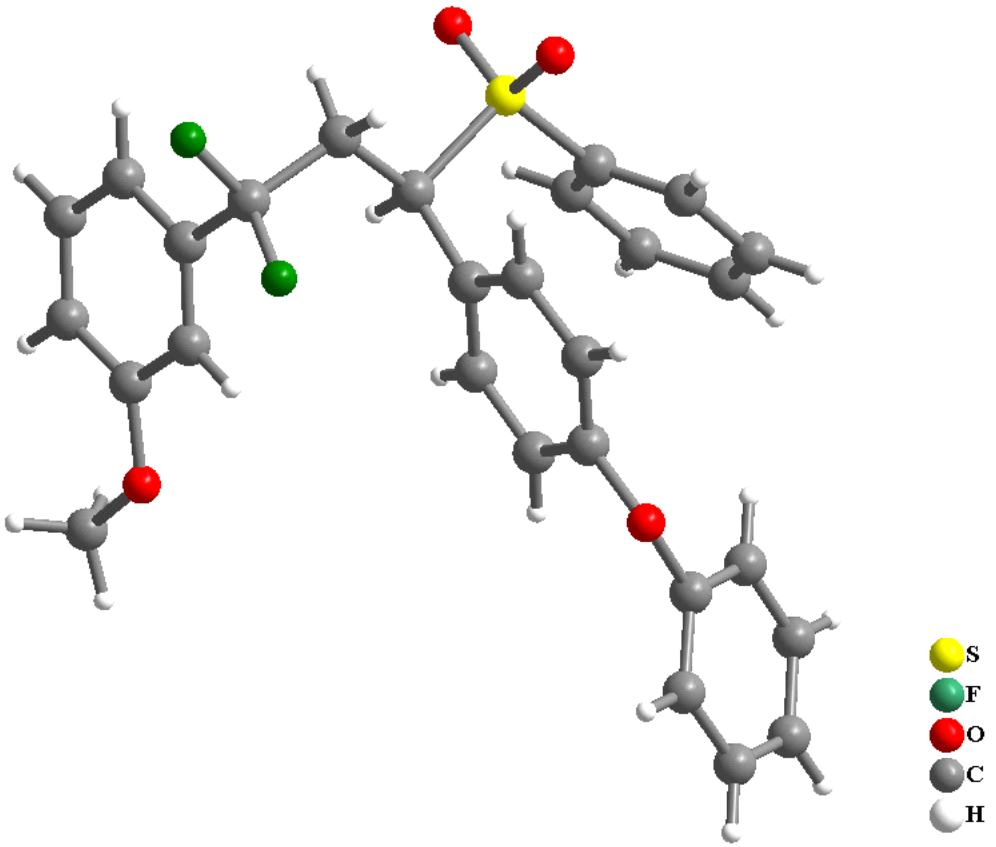
Single-crystals suitable for X-ray diffraction analysis were grown from the recrystallization in chloroform and methanol (1/1, v/v) at 2-8 ℃.

X-Ray crystallography data of 5x (CCDC 2266205)

[2] O.V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard & H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341.

[3] Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

[4] Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.



Formula	$C_{28}H_{24}F_2O_4S$	μ(mm^{-1})	0.180
Formula weight	494.53	F (000)	1032
Temperature (K)	296.15	Reflns collected	23539
Crystal system	Monoclinic	Independent reflns	6091
Space group	P2(1)/c	R_{int}	0.0281
a (Å)	15.0930(6)	Thetarange (°)	2.796-56.628
b (Å)	8.0955(3)	Params/restraints/data	128/0/1698
c (Å)	20.7666(7)	$R_1[I > 2\sigma(I)]$	0.0443
D_c (g/cm^3)	1.975	wR_2(all data)	0.1329
Volume/ ($Å^3$)	2448.56(16)	GOF on F^2	1.042
Z	4	ρ_{max}/ρ_{min}, e $Å^{-3}$	0.31/-0.27

$^{a}R1 = ||F_o|-|F_c||/|F_o|$; $^{b}wR2 = [w(F_o^2-F_c^2)^2]/[w(F_o^2)^2]^{1/2}$

9 References

[1] M. D. Greenhalgh, S. P. Thomas, *J. Am. Chem. Soc.* **2012**, *134*, 11900-11903.

[2] T. W. Butcher, E. J. McClain, T. G. Hamilton, T. M. Perrone, K. M. Kroner, G. C. Donohoe, N. G. Akhmedov, J. L. Petersen, B. V. Popp, *Org. Lett.* **2016**, *18*, 6428-6431.

[3] C. Wan, R. J. Song, J. H. Li, *Org. Lett.* **2019**, *21*, 2800-2803.

[4] J. Shen, J. Li, M. Chen, Y. Chen, *Org. Chem. Front.* **2023**, *10*, 1166-1172.

[5] J. Manigrasso, I. Chillon, V. Genna, P. Vidossich, S. Somarowthu, A. M. Pyle, M. De Vivo, M. Marcia, *Nat. Commun.* **2022**, *13*, 2837-2851.

[6] J. J. Molloy, C. P. Seath, M. J. West, C. McLaughlin, N. J. Fazakerley, A. R. Kennedy, D. J. Nelson, A. J. B. Watson, *J. Am. Chem. Soc.* **2018**, *140*, 126-130.

[7] N. L. Frye, A. Bhunia, A. Studer, *Org. Lett.* **2020**, *22*, 4456-4460.

[8] B. N. Bhawal, J. C. Reisenbauer, C. Ehinger, B. Morandi, *J. Am. Chem. Soc.* **2020**, *142*, 10914-10920.

[9] C. Y. Huang, A. G. Doyle, *J. Am. Chem. Soc.* **2012**, *134*, 9541-9544.

[10] J. Liu, S. Wu, J. Yu, C. Lu, Z. Wu, X. Wu, X. S. Xue, C. Zhu, *Angew. Chem. Int. Ed.* **2020**, *59*, 8195-8202.

[11] G. S. Lee, D. Kim, S. H. Hong, *Nat. Commun.* **2021**, *12*, 991-1002.

[12] P. Picconi, P. Prabaharan, J. L. Auer, S. Sandiford, F. Cascio, M. Chowdhury, C. Hind, M. E. Wand, J. M. Sutton, K. M. Rahman, *Bioorg. Med. Chem.* **2017**, *25*, 3971-3979.

[13] H. Cao, H. Jiang, H. Feng, J. M. C. Kwan, X. Liu, J. Wu, *J. Am. Chem. Soc.* **2018**, *140*, 16360-16367.

[14] M. S. Martin Bosch, *J. Org. Chem.* **2003**, *68*, 5225-5227.

[15] Q. Wang, Y. Qu, H. Tian, Y. Liu, H. Song, Q. Wang, *Chem. Eur. J.* **2019**, *25*, 8686-8690.

[16] M. P. John Esposito, Y. B. Kang, *U.S. Patent WO2021151062,* July 29, **2021**.

[17] R. Y. Yang, X. Gao, K. Gong, J. Wang, X. Zeng, M. Wang, J. Han, B. Xu, *Org. Lett.* **2022**, *24*, 164-168.

[18] R. A. Escobar, J. W. Johannes, *Chem. Eur. J.* **2020**, *26*, 5168-5173.

[19] S. Ni, M. Hribersek, S. K. Baddigam, F. J. L. Ingner, A. Orthaber, P. J. Gates, L. T.

Pilarski, *Angew. Chem. Int. Ed.* **2021**, *60*, 6660-6666.

[20] Y. Miki, N. Tomita, K. Ban, H. Sajiki, Y. Sawama, *Adv. Synth. Catal.* **2021**, *363*, 3481-3484.

[21] L. Zhou, W. Lu, *Org. Lett.* **2014**, *16*, 508-511.

[22] J. Z. Wu, V. Jean Michel; H. Chen, J. L. Song, *U.S. Patent US20090326059,* December 31, **2019**.

[23] S. M. Park, J. U. Lee; D. H. Lee, *K.R. Patent KR2022066701,* November 16, **2020**.