

# Supporting Information

## Electrochemical *O*-Trifluoromethylation of Electron-deficient Phenols

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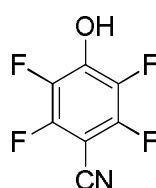
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## Synthesis of the starting materials

### General protocol A: Preparation of fluorinated phenols

Phenols **1b,g,h** were prepared based on literature protocol.<sup>1</sup> The corresponding fluorinated aromatic compound and KOH were dissolved in *tert*-butyl alcohol and heated to reflux for 3.5 h followed by evaporation of the solvent under reduced pressure. The residue was acidified with concentrated HCl and extracted with DCM (4 x 20 mL). The combined organic layers were washed with H<sub>2</sub>O and dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent gave the desired phenols **1b,g,h**. The products were used without further purification.

#### 2,3,5,6-Tetrafluoro-4-hydroxybenzonitril **1b**



**1b**

The preparation of **1b** was performed according to general protocol A with pentafluorobenzonitrile (2.0 g, 10.4 mmol), KOH (1.2 g, 21.5 mmol) and *tert*-butyl alcohol (20 mL). The product was obtained as a colorless solid.

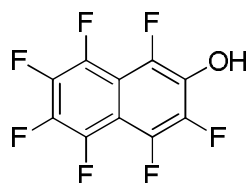
Yield: 1.63 g (82%)

<sup>13</sup>C{<sup>19</sup>F} NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  = 147.88 (s), 141.01 (s), 137.42 (s), 107.71 (s), 84.84 (s) ppm.

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>):  $\delta$  = -133.40 to -133.51 (m, 2 F, Ar-F), -159.62 to -159.74 (m, 2 F, Ar-F) ppm.

HRMS (MALDI): *m/z* [M]<sup>+</sup> calc.: 192.0022, found: 192.0031.

#### 1,3,4,5,6,7,8-Heptafluoro-naphthalen-2-ol **1g**



**1g**

**1g** was synthesized according to general protocol A with octafluoronaphthalene (0.5 g, 1.83 mmol), KOH (0.24 g, 4.28 mmol) and *tert*-butyl alcohol (5 mL). The product was obtained as a slightly yellow oil.

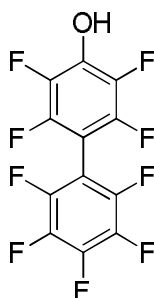
Yield: 0.49 g (99%)

$^{13}\text{C}\{^{19}\text{F}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 141.40 (s), 140.70 (s), 140.48 (s), 140.34 (s), 138.96 (s), 137.86 (s), 134.06 (s), 128.98 (s), 107.70 (s), 104.88 (s) ppm.

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -146.74 to -147.01 (m, 1 F, Ar-F), -148.02 to -148.35 (m, 3 F, Ar-F), -153.52 to -153.62 (m, 1H, Ar-F), -156.52 to -156.65 (m, 1 F, Ar-F), -158.50 to -158.60 (m, 1 F, Ar-F) ppm.

HRMS (MALDI):  $m/z$   $[\text{M}]^+$  calc.: 269.9910, found: 269.9915.

### 2,2',3,3',4',5,5',6,6'-Nonafluoro-[1,1'-biphenyl]-4-ol **1h**



**1h**

According to general protocol A, **1h** was prepared with decafluorobiphenyl (2.0 g, 6.02 mmol), KOH (0.77 g, 13.7 mmol) and *tert*-butyl alcohol (20 mL). Contrary to protocol A, the solvent was removed under reduced pressure after completion of the reaction. The residue was suspended in aq.  $\text{Na}_2\text{CO}_3$  solution and extracted with ethyl acetate (3 x 20 mL). The organic phases were extracted with  $\text{Na}_2\text{CO}_3$  solution (3 x 20 mL) and afterwards, the aqueous phases were acidified with hydrochloric acid. After extraction with DCM (3 x 20 mL), the organic phases were dried over  $\text{Na}_2\text{SO}_4$  and the solvent was removed under reduced pressure. Product **1h** was obtained as colorless solid.

Yield: 1.29 g (65%)

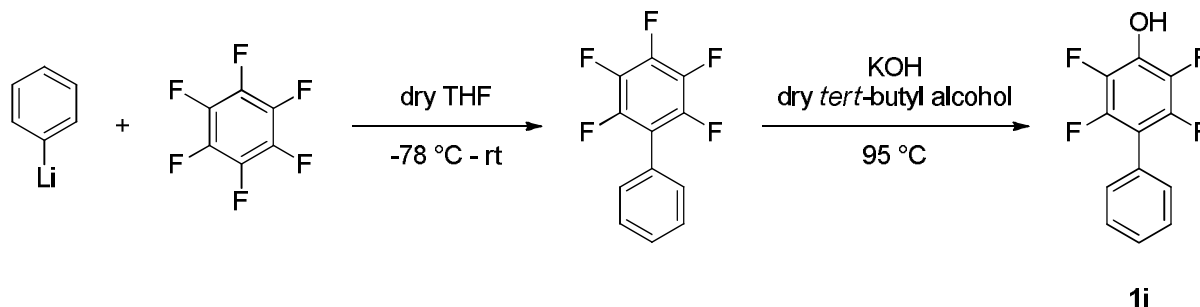
$^{13}\text{C}\{^{19}\text{F}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 144.99 (s), 144.54 (s), 143.44 (s), 142.27 (s), 137.91 (s), 137.35 (s), 102.58 (s), 96.21 (s) ppm.

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -137.61 to -137.69 (m, 2 F, Ar-F), -139.07 to -140.06 (m, 2 F, Ar-F), -151.21 (t,  $J$  = 22 Hz, 1H, Ar-F), -160.93 to -161.07 (m, 2 F, Ar-F), -161.93 to -162.04 (m, 2 F, Ar-F) ppm.

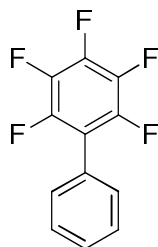
HRMS (MALDI):  $m/z$   $[\text{M}]^+$  calc.: 332.9912, found: 333.0423.

### 2,3,5,6-Tetrafluoro-[1,1'-biphenyl]-4-ol **1i**

The synthesis of compound **1i** was performed via a substitution reaction of phenyllithium with hexafluorobenzene followed by an introduction of the hydroxyl substituent by using potassium hydroxide.



### 2,3,4,5,6-Pentafluoro-1,1'-biphenyl



Hexafluorobenzene (0.35 ml, 3.0 mmol) was dissolved in dry THF (5 ml) and the solution was cooled to -78 °C. A 1.9 M solution of phenyllithium in dibutyl ether (1.4 ml, 2.7 mmol) was added. After stirring in the warming cooling bath for 23 h, the solvent was removed and the resulting crude product was purified by gradient sublimation at 125 °C for 1.5 h (ultra high vacuum). 2,3,4,5,6-pentafluoro-1,1'-biphenyl was obtained as a white solid.

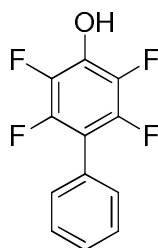
Yield: 0.18 g (27%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.50 - 7.41$  (m, 5 H, Ph-H) ppm.

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta = -143.2$  to  $-143.3$  (m, 2 F, Ar-F),  $-155.5$  to  $-155.7$  (m, 1 F, Ar-F),  $-162.2$  to  $-162.3$  (m, 2F, Ar-F) ppm.

The NMR shifts are in good agreement to those reported in literature.<sup>2</sup>

### 2,3,5,6-Tetrafluoro-[1,1'-biphenyl]-4-ol **1i**



To a solution of 2,3,4,5,6-pentafluoro-1,1'-biphenyl (0.18 g, 0.74 mmol) in dry *tert*-butyl alcohol (1 mL) potassium hydroxide (0.10 g, 1.7 mmol) was added. Afterwards the mixture was stirred for two hours at 95 °C followed by the addition of 1 M HCl<sub>aq</sub> (1 mL) to terminate the reaction. The combined organic layers were evaporated to dryness and the resulting crude product was purified by column chromatography on silica gel (eluent: dichloromethane). **1i** could be isolated as a colorless crystalline solid.

Isolated yield: 0.02 g (14%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.51 – 7.40 (m, 5 H, Ph-H), 5.66 (br, 1 H, OH) ppm.

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>):  $\delta$  = -145.1 to -145.2 (m, 2 F, Ar-F), -163.7 to -165.1 (m, 2 F, Ar-F) ppm.

The NMR data are comparable to those in literature.<sup>3</sup>

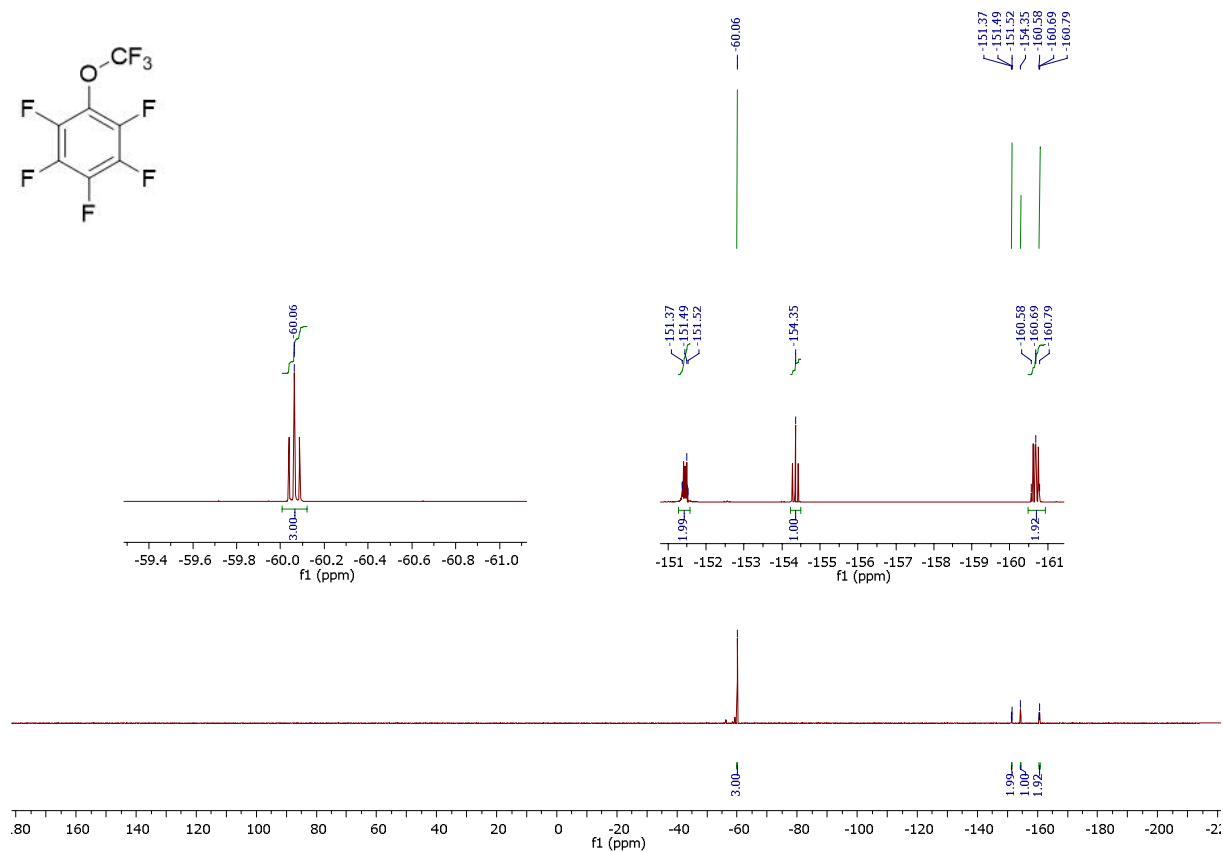
### General protocol B: Gram-scale electrolysis

In an undivided beaker-type cell equipped with a stir bar, phenol **1a,g** (6.80 mmol), NaSO<sub>2</sub>CF<sub>3</sub> (4.24 g, 27.2 mmol) and NaClO<sub>4</sub>\*H<sub>2</sub>O (2.81 g, 20.0 mmol) were dissolved in MeCN/H<sub>2</sub>O 4:1 (100 mL). After degassing the solution by purging with Ar for 5 min, the cell was equipped with two parallelly aligned graphite rods (electrode gap 1.5 cm) serving as anode and cathode. The electrolysis was performed under constant current conditions ( $j = 10 \text{ mA cm}^{-2}$ , active surface area 5.7 cm<sup>2</sup>, electric current 57 mA) until a charge of 8 *F* mol<sup>-1</sup> phenol **1a,g** was consumed. The purification procedure was according to the protocols given in the main text.

# NMR spectra

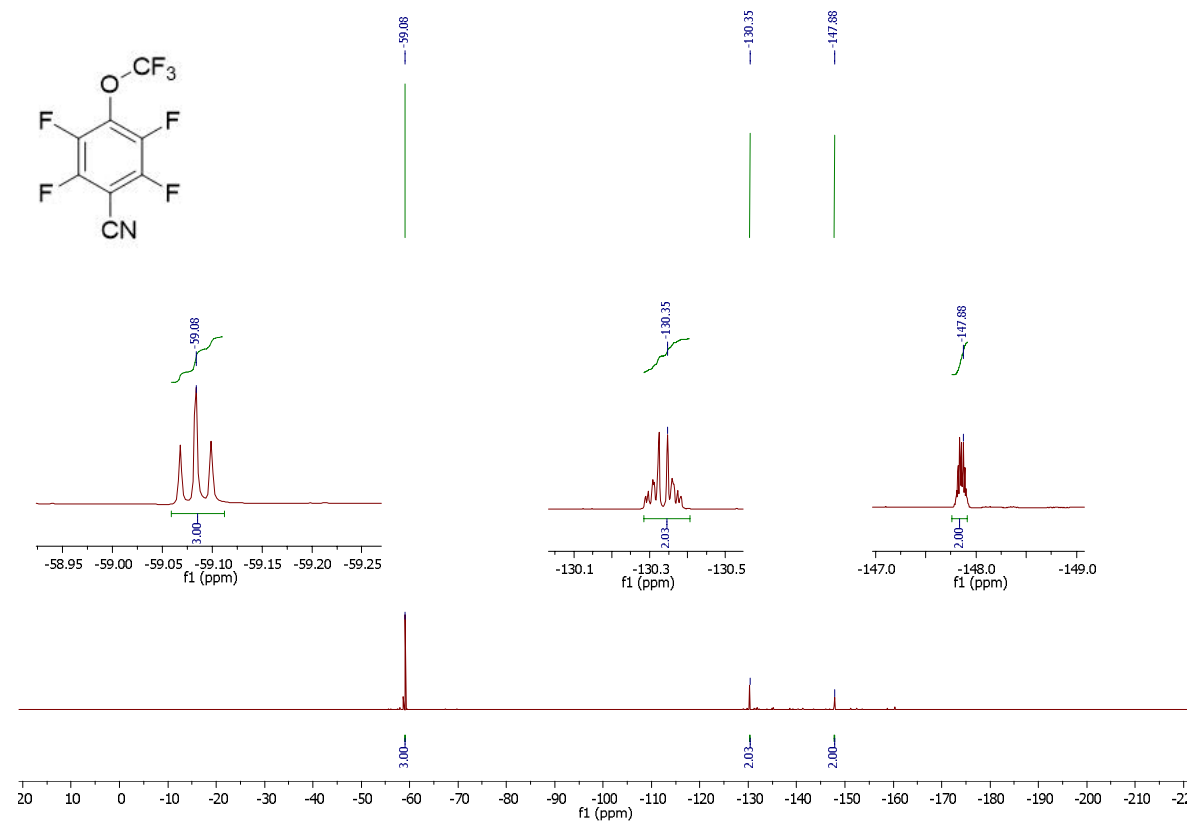
## Octafluoroanisole 3a

### $^{19}\text{F}$ NMR

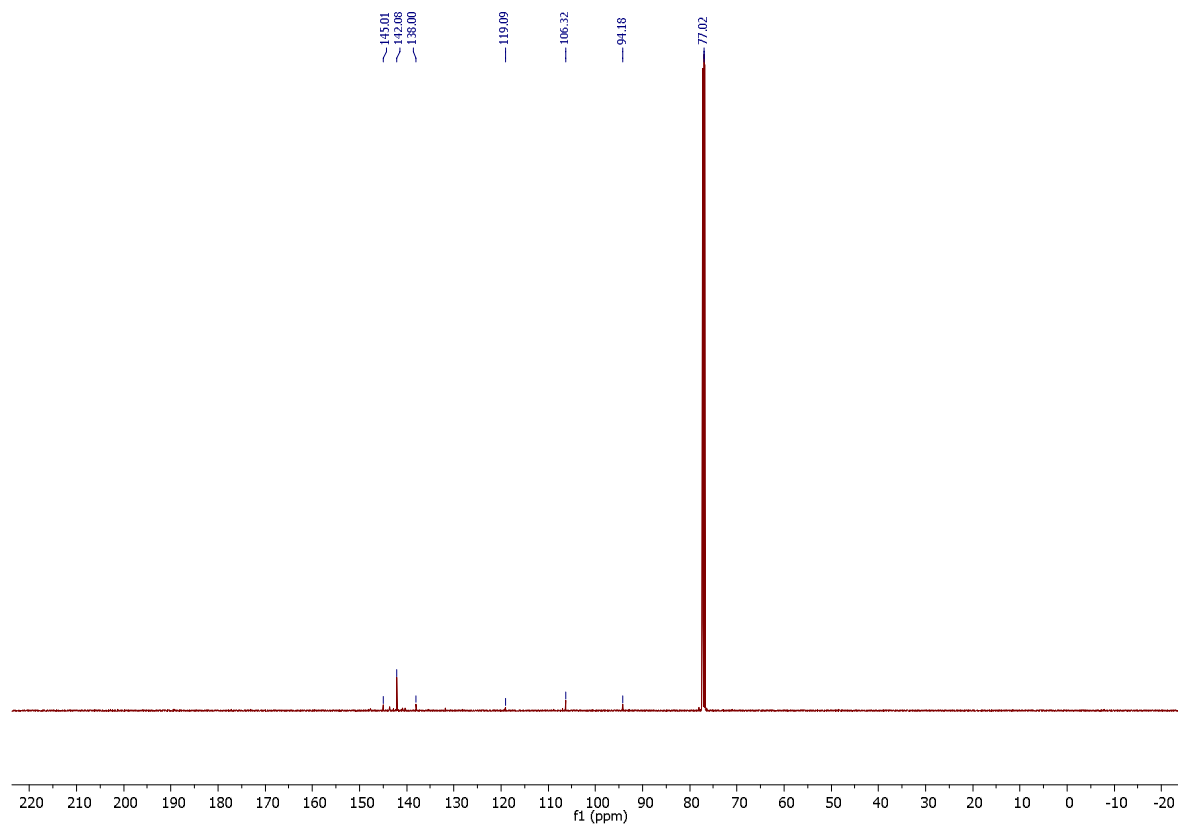


## 2,3,5,6-Tetrafluoro-4-(trifluoromethoxy)benzonitrile 3b

### $^{19}\text{F}$ NMR

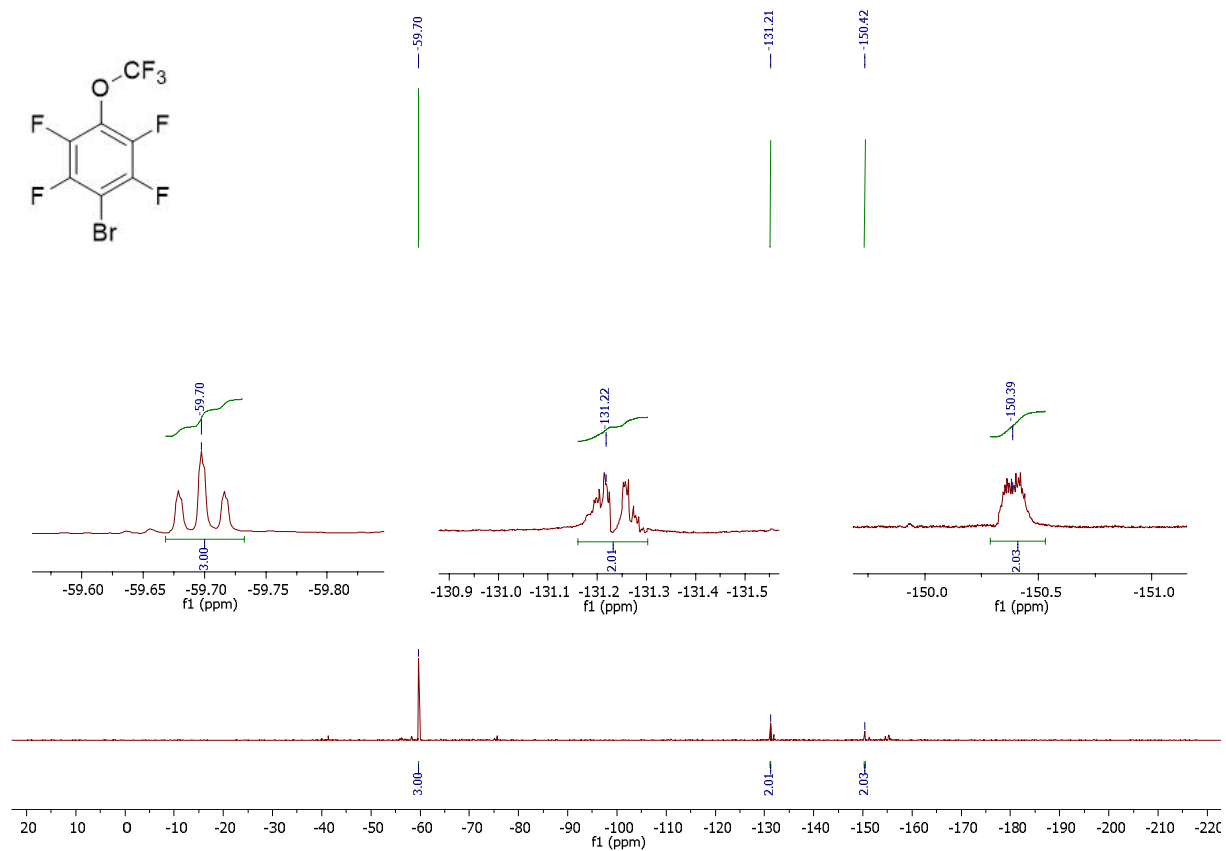


### $^{13}\text{C}\{^{19}\text{F}\}$ NMR



# 1-Bromo-2,3,5,6-tetrafluoro-4-(trifluoromethoxy)benzene 3c

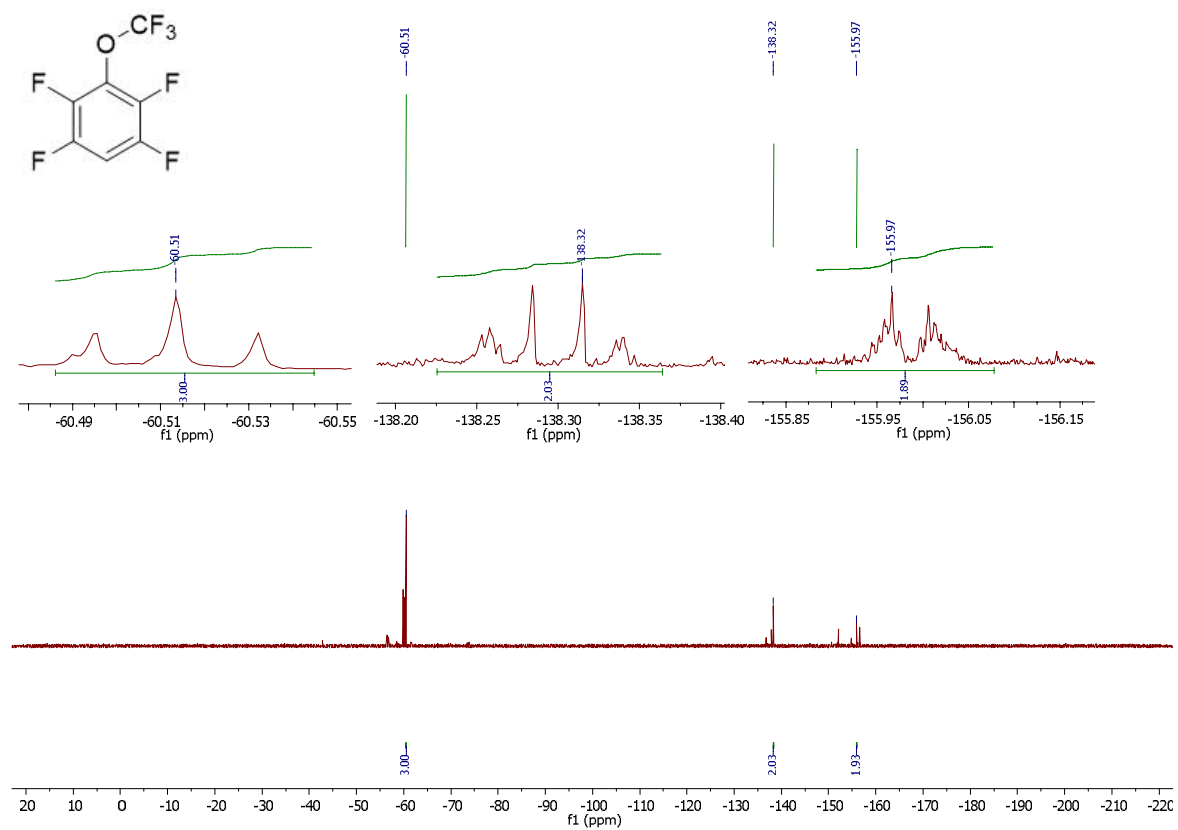
## $^{19}\text{F}$ NMR





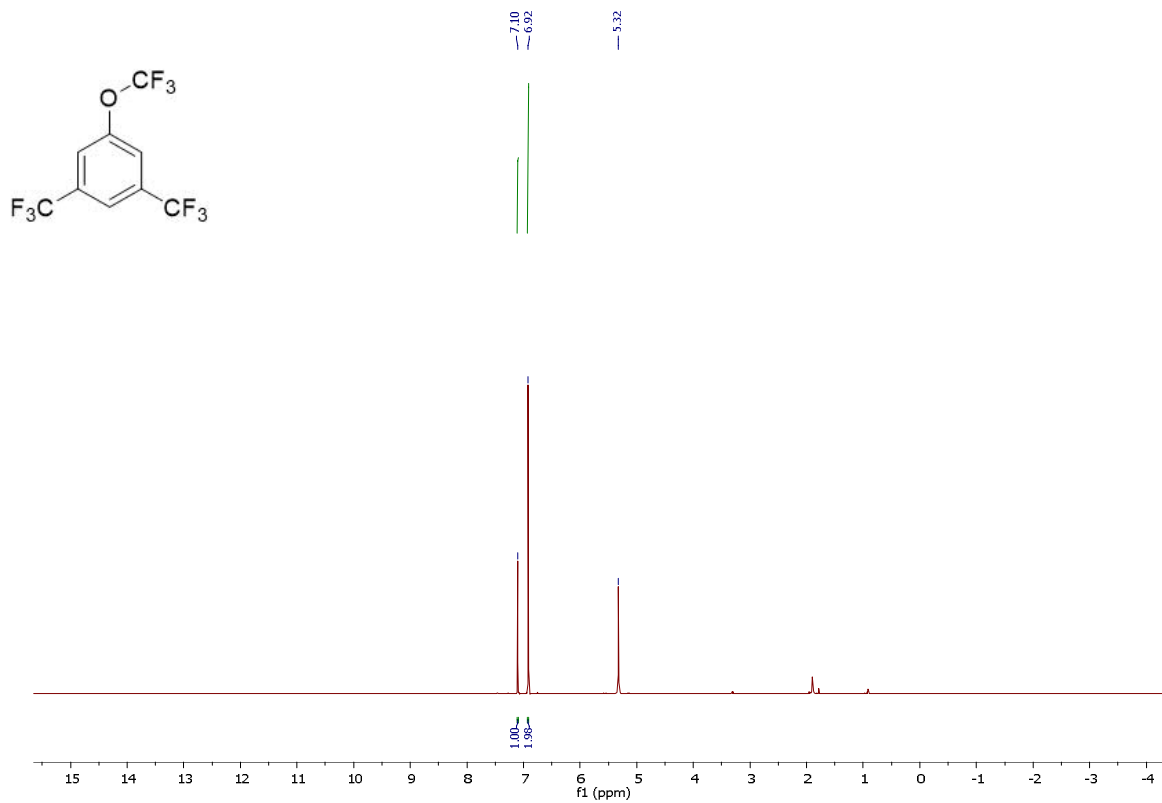
# 1,2,4,5-Tetrafluoro-3-(trifluoromethoxy)benzene 3d

## $^{19}\text{F}$ NMR

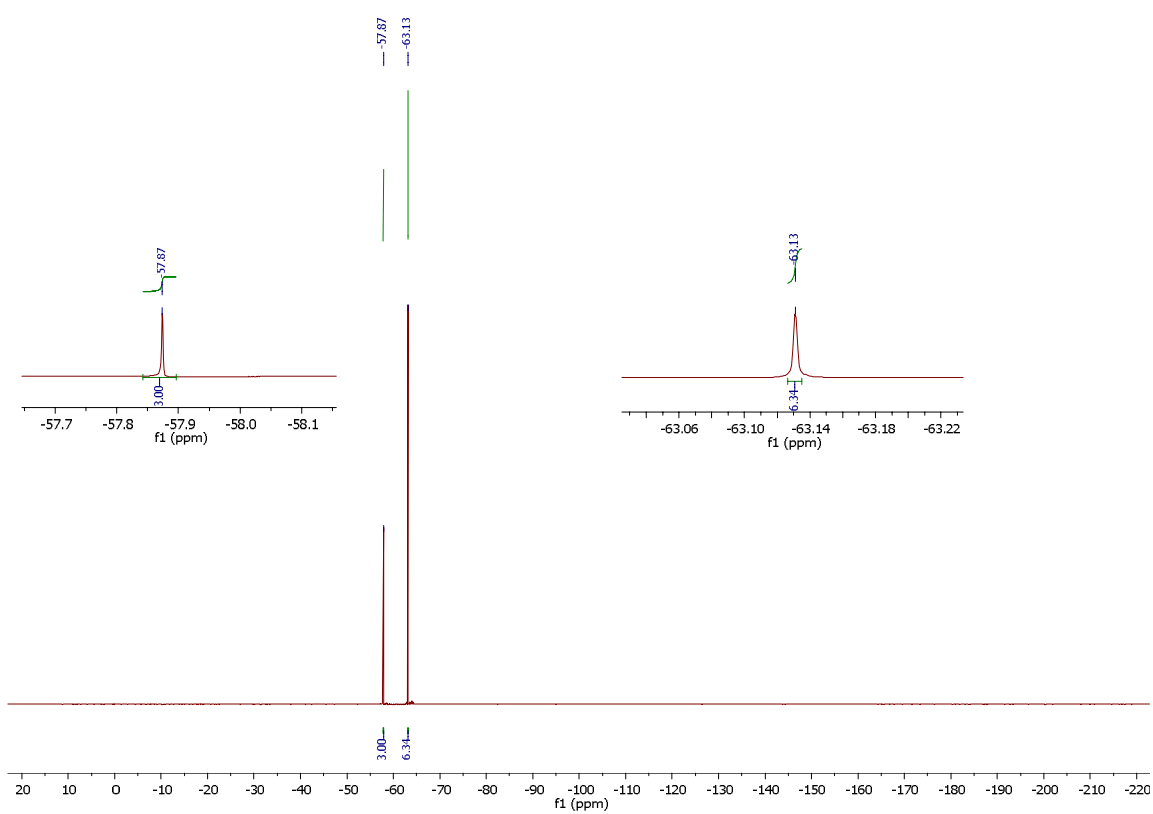


# 1-(Trifluoromethoxy)-3,5-bis(trifluoromethyl)benzene 3e

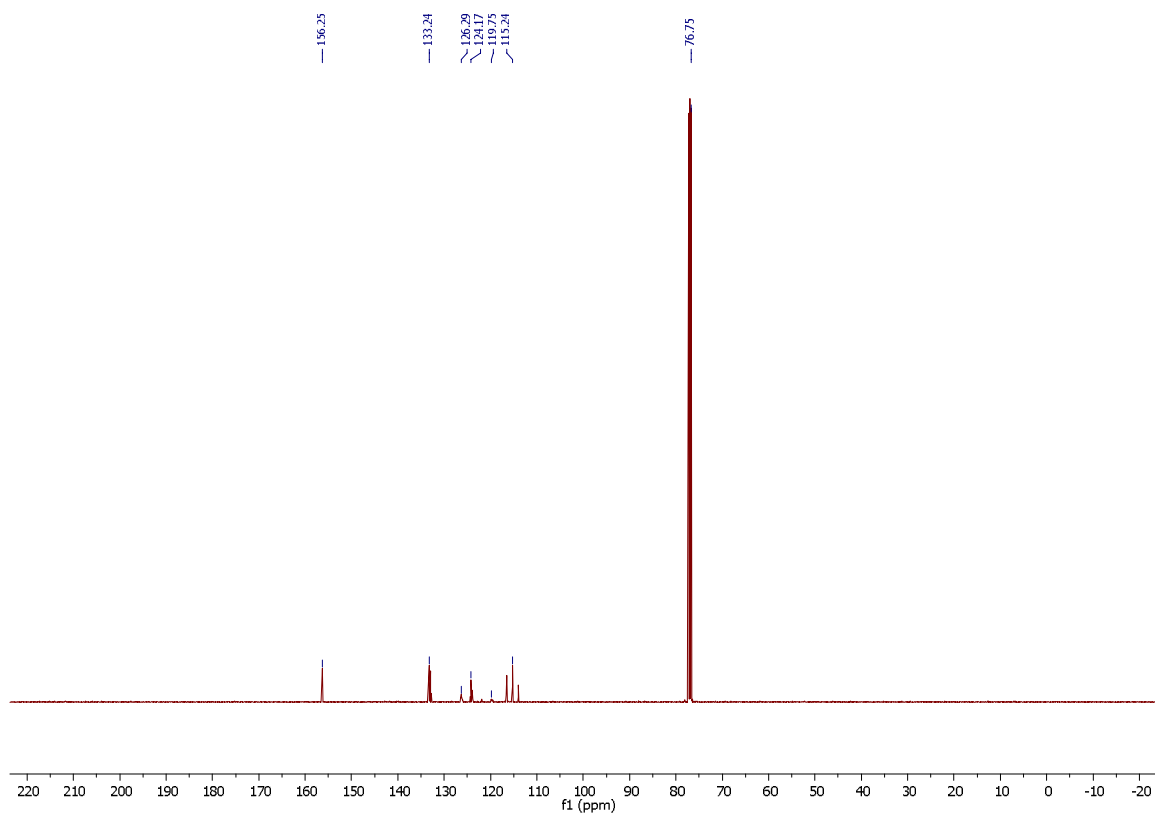
## $^1\text{H}$ NMR



## $^{19}\text{F}$ NMR

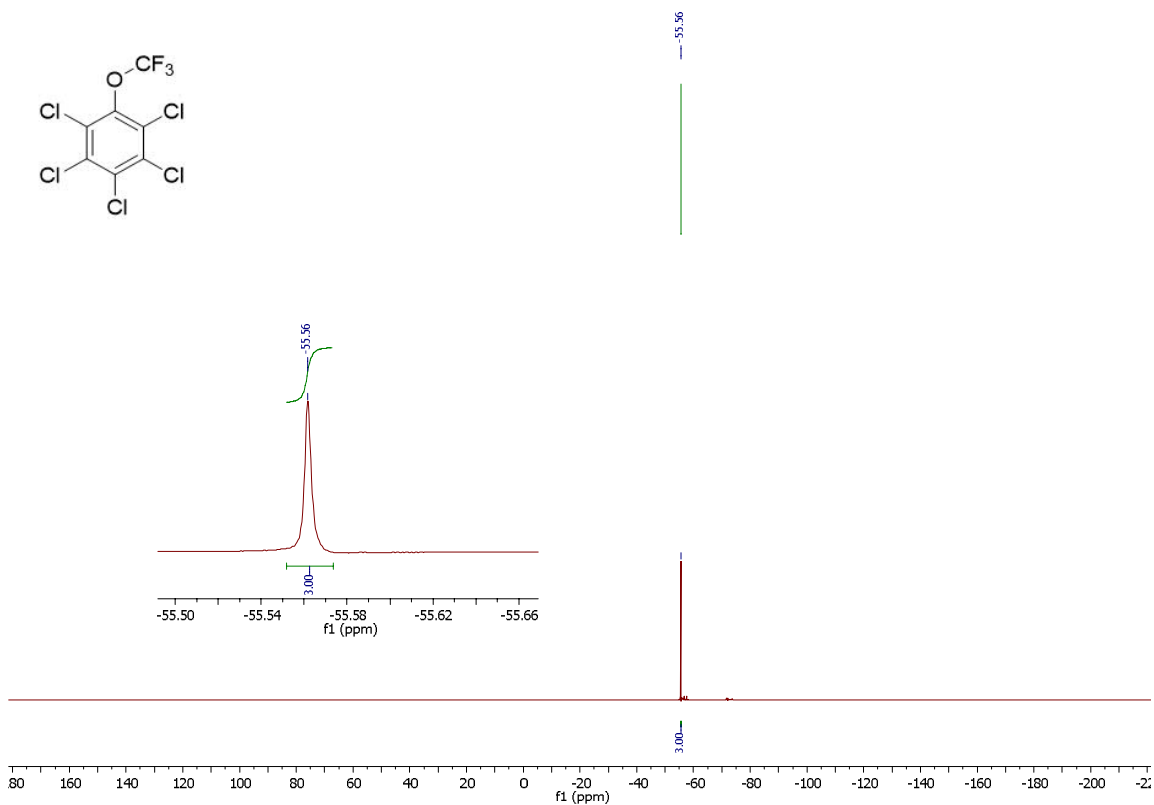


$^{13}\text{C}\{^{19}\text{F}\}$  NMR

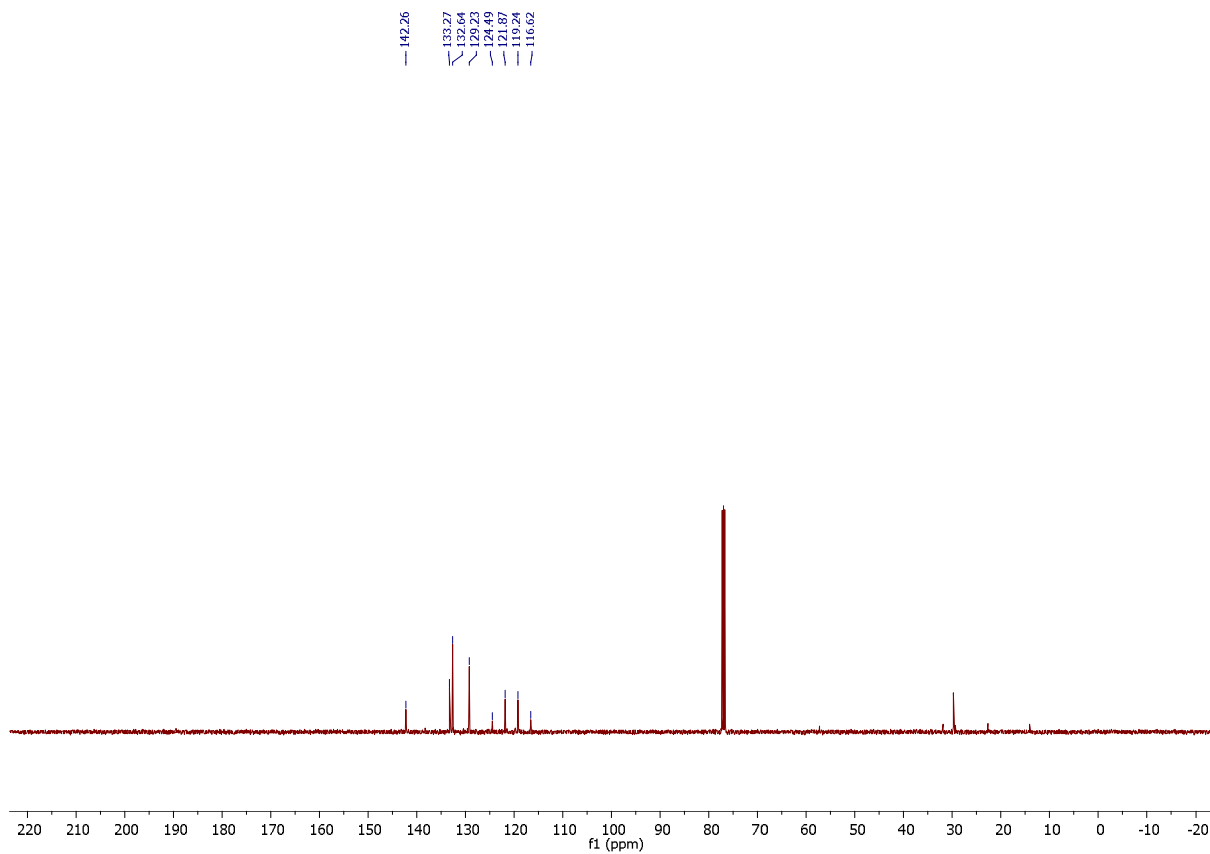


# 1,2,3,4,5-Pentachloro-6-(trifluoromethoxy)benzene 3f

## <sup>19</sup>F NMR

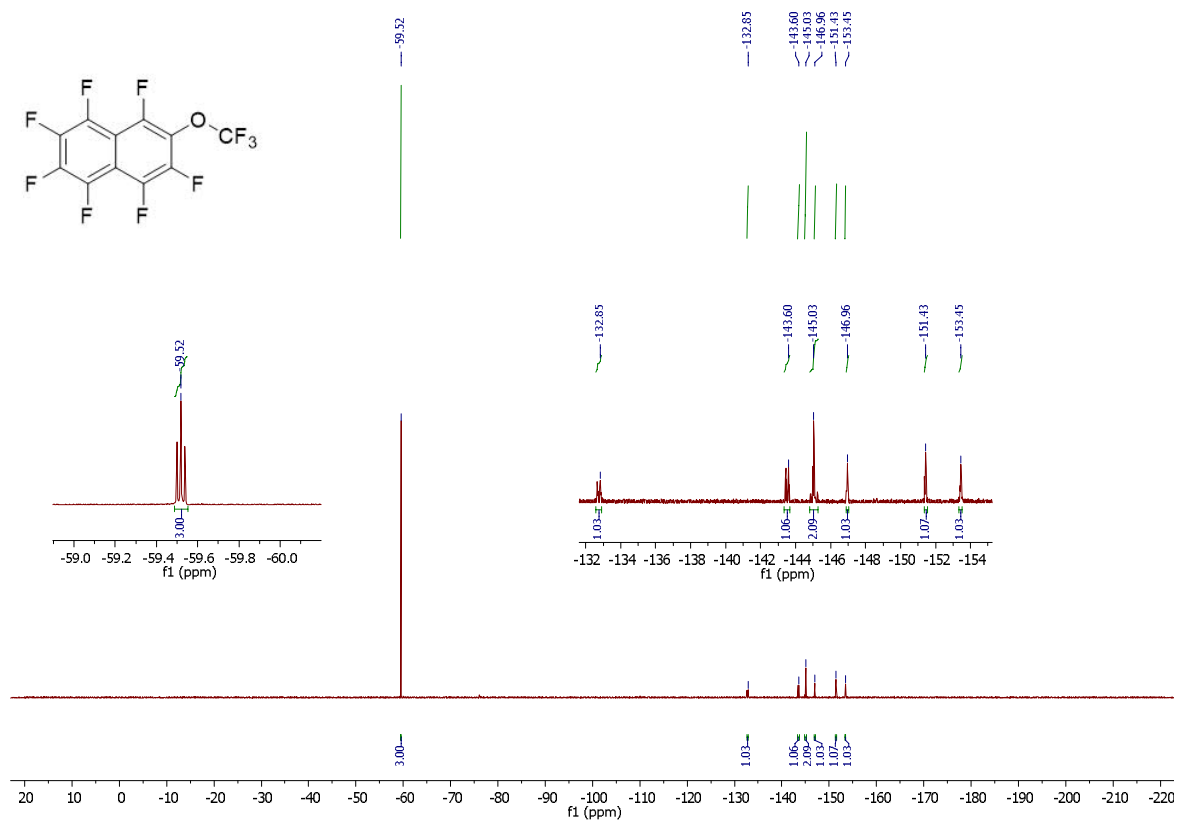


## <sup>13</sup>C NMR

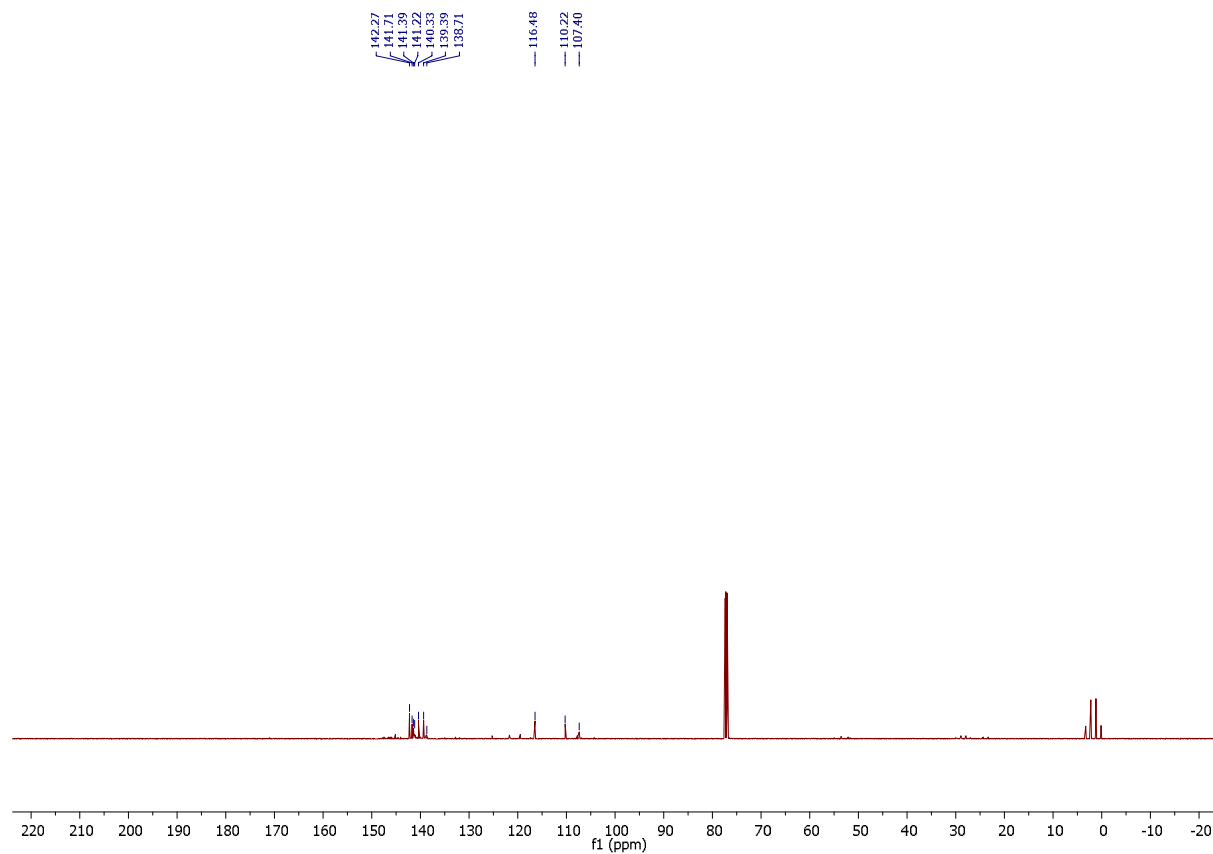


# 1,2,3,4,5,6,8-Heptafluoro-7-(trifluoromethoxy)naphthalene 3g

## $^{19}\text{F}$ NMR

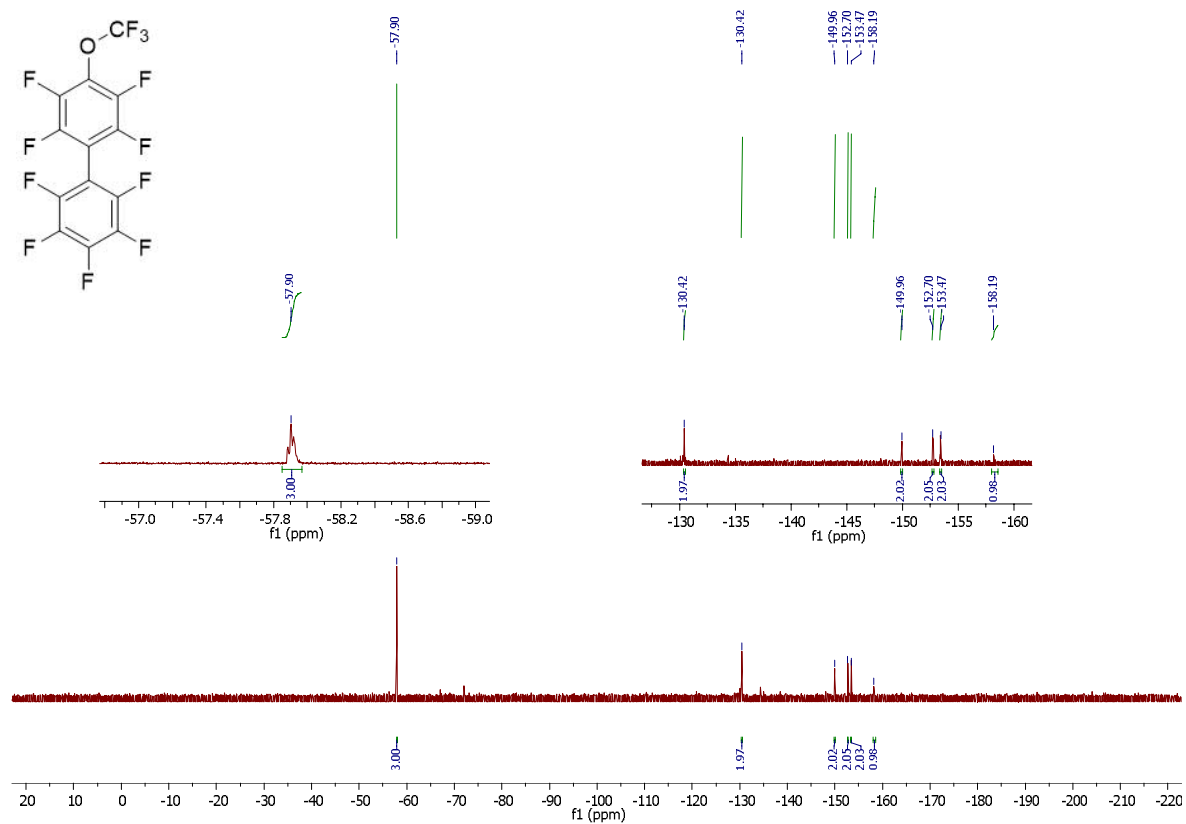


## $^{13}\text{C}\{^{19}\text{F}\}$ NMR

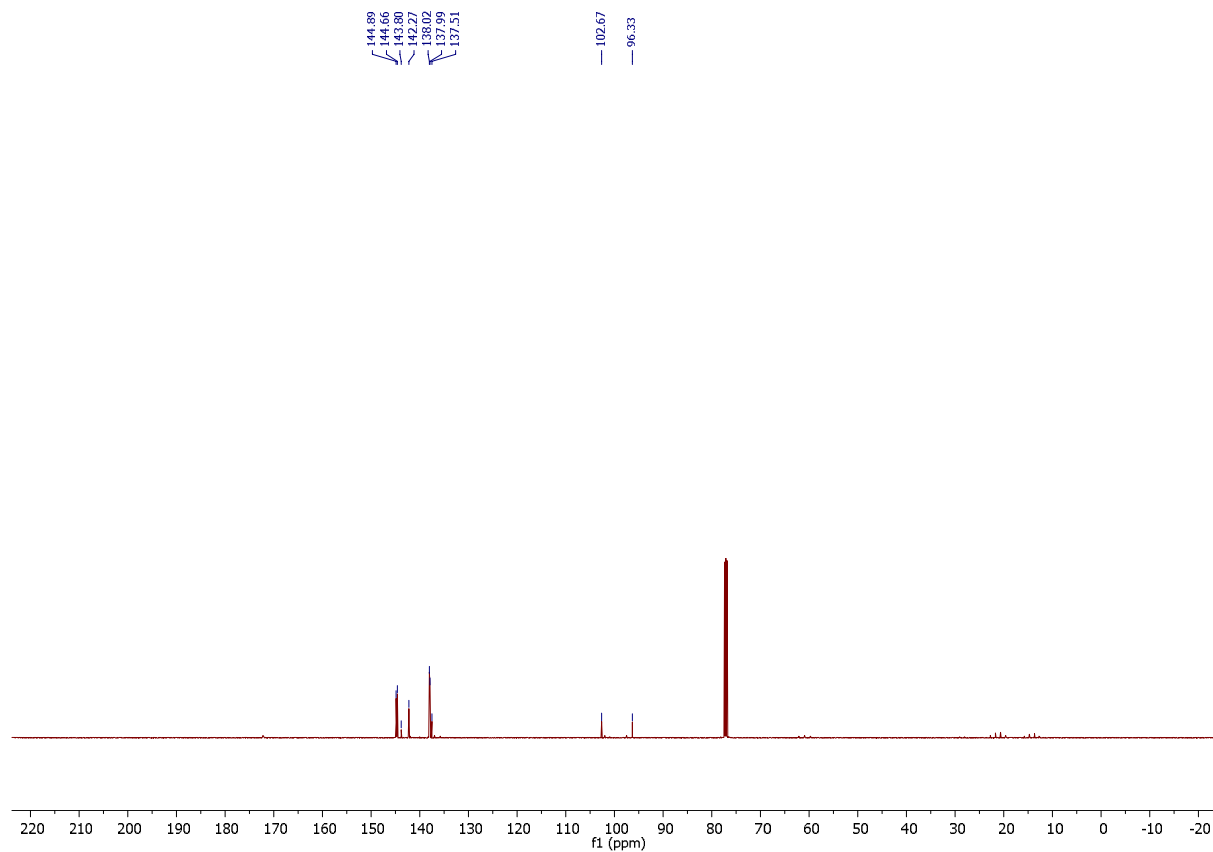


# 2,2',3,3',4,5,5',6,6'-Nonafluoro-4'-(trifluoromethoxy)-1,1'-biphenyl 3h

## $^{19}\text{F}$ NMR

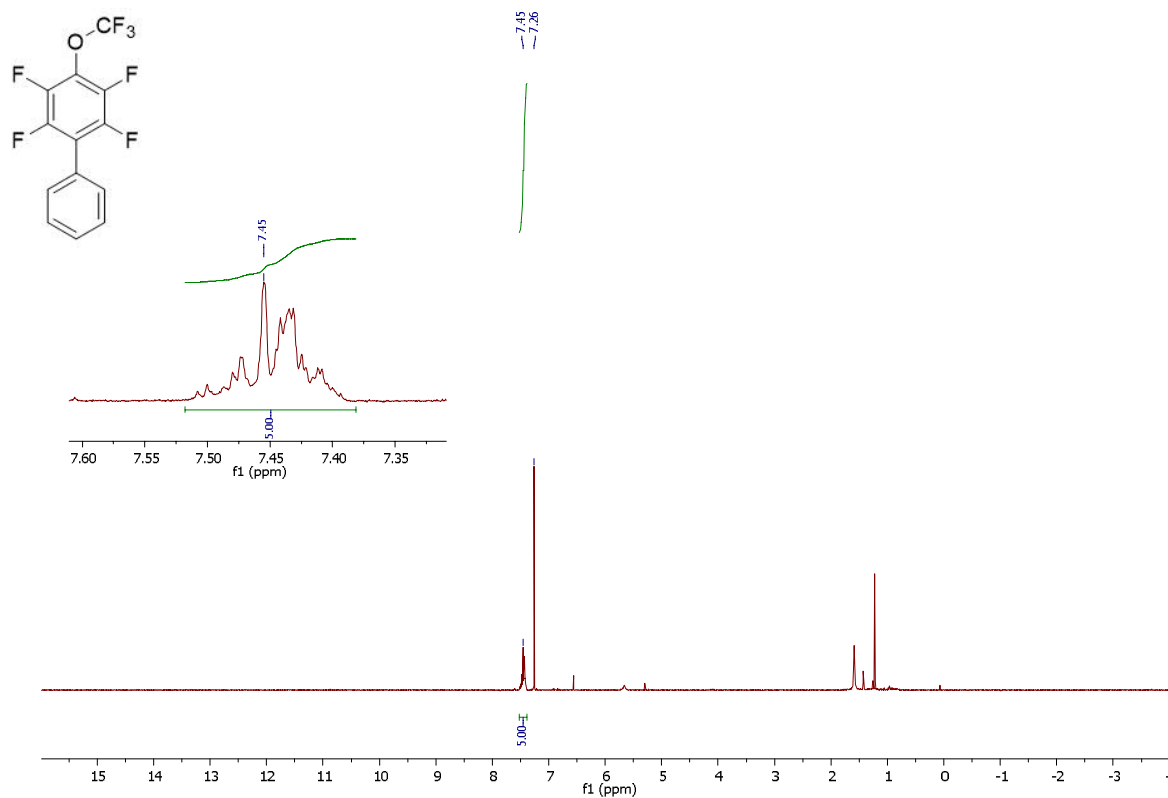


## $^{13}\text{C}\{^{19}\text{F}\}$ NMR

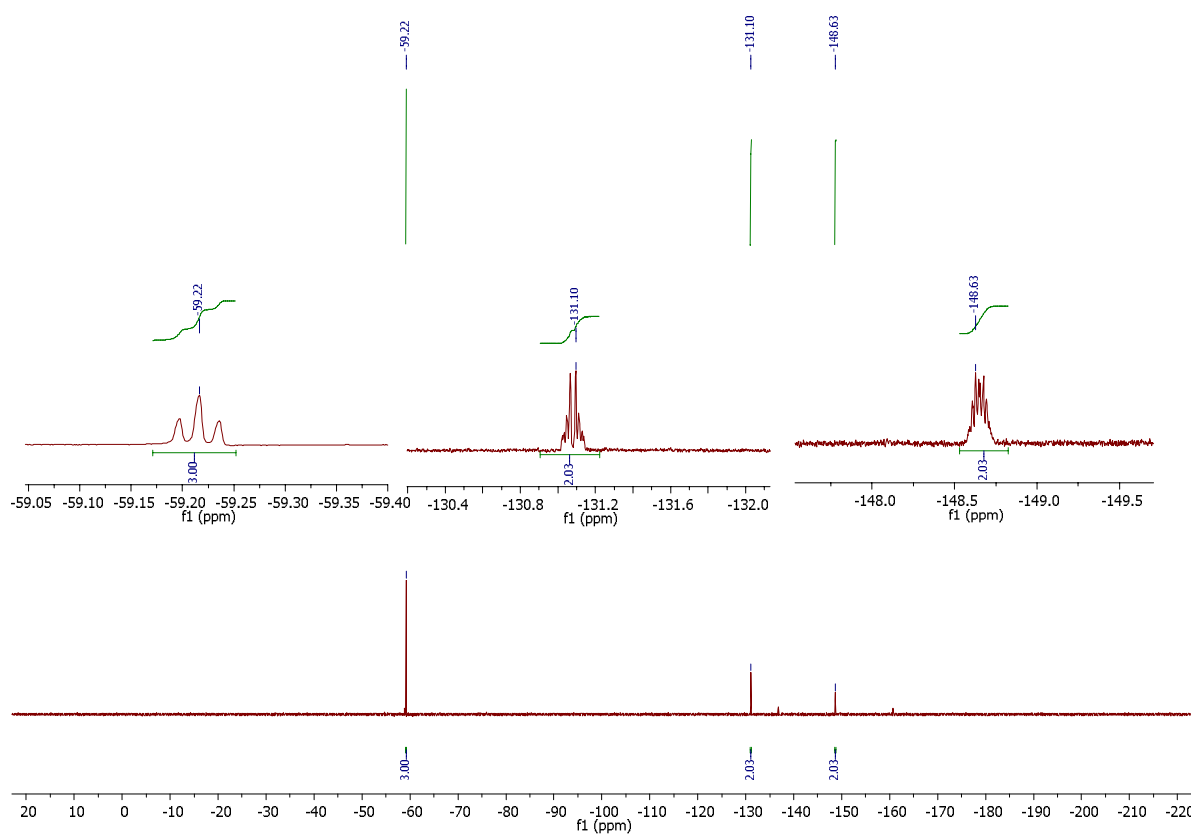


## 2,3,5,6-Tetrafluoro-4-(trifluoromethoxy)-1,1'-biphenyl 3i

### $^1\text{H}$ NMR



### $^{19}\text{F}$ NMR



## References

- <sup>1</sup> Karsch, M.; Lund, H.; Schulz, A.; Villinger, A.; Voss, K. *Eur. J. Inorg. Chem.* **2012**, 33, 5542-5553.
- <sup>2</sup> Fu, L.; You, J.; Nishihara, Y. *Chemical Communications* **2021**, 57, 3696-3699.
- <sup>3</sup> Allen, D. M.; Batsanov, A. S.; Brooke, G. M., Lockett, S. J. *J. Fluor. Chem.* **2000**, 108, 57-67.