

## Electronic Supporting Information for:

# Synthetic Access to an Elusive High-Temperature Polymeric-based Perfluoroisopropenyl Ether Precursor for Radical Copolymerization

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## A. General Considerations

### A.1. Materials

All reagents were used as received unless otherwise stated. Diethyl ether, diglyme, hexane, acetonitrile, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and dimethylformamide were dried over activated 3 Å mole sieves (Sigma-Aldrich) for 48 hours. Anhydrous hexanes and tetrahydrofuran were dried by reflux over Na/benzophenone, followed by distillation under dry nitrogen. Perfluorohexane (Synquest) was pretreated with phenyl lithium to ensure the removal of residual C<sub>6</sub>F<sub>13</sub>H and then distilled. Prior to use, all solvents were degassed by 3 cycles of freeze-pump-thaw, and stored under nitrogen. Poly(hexafluoropropylene oxide) primary iodide (MW = 1824 g/mol) received as clear, pink oil and methyl ester (MW = 1250 g/mol) received as clear, colourless oil were kindly offered by DuPont (Wilmington, USA). Prior to usage, each oil was degassed *in vacuo* (1-4 Torr) at 60 °C for at least 30 min, yielding a clear and colourless oil that was stored under nitrogen. Also provided Deuterated benzene and hexafluorobenzene used for NMR spectroscopy was purchased from (Sigma-Aldrich).

The phenyl lithium concentration was standardized (1.9M in dibutyl ether, Sigma-Aldrich) by triplicate titration with N-benzylbenzamide in THF at 0 °C to a blue endpoint as demonstrated by Burchat et al.<sup>1</sup>

### A.2. Glassware

All glassware was inspected and found to be free of etching and defects. Glassware was then washed thoroughly with soap, rinsed with deionized water and acetone, and placed in a drying oven at 150 °C for at least 4 hours prior to usage.

### A.3. Methods of Analysis

*Gas Chromatography (GC) Mass Spectrometry (MS):* Total product mixtures were analyzed for composition by a GC/MS. A standard analysis was conducted by removing 1-3 drop aliquots of the lower fluoruous layers by syringe and diluted with 1.5mL of dichloromethane and 5-10 drops of a methoxyperfluorobutane cosolvent (3M's Novec™ HFE-7100) in a GC vial. These samples were run on an Agilent Technologies 6890N GC fitted with an Agilent Technologies 7638B series injector and coupled to an Agilent Technologies 5975B inert mass spectrometer detector (MSD) with electron impact (EI) at 70eV as the mode of ionization. The GC was equipped with a Zebron ZB-5ms column, 20 m x 0.18 mm id, 0.18 μm df. The detector and the injector temperatures were 200 °C and 280 °C, respectively. The temperature program started from 50 °C with a 2 minute hold then the heating rate was 25 °C/min until reaching 250 °C and holding at 250 °C for 2 minutes. The total pressure 108 kPa, total flow was 25.9 mL/min, column flow 0.74 mL/min, purge flow 3mL/min, linear velocity 38.2 cm/s and a split injection of 30:1.

*Nuclear Magnetic Resonance (NMR) spectroscopy:* The structure of the products was determined by NMR spectroscopy at room temperature (25 °C) on a Bruker ASCEND III 400 MHz and a Bruker Avance II 600 MHz "QNP" 600" as required to generate NMR data. The experimental conditions were accomplished using TopSpin 3.5 operating at 400.13 (<sup>1</sup>H), 376.50 (<sup>19</sup>F), 100.61 (<sup>13</sup>C) MHz. Flip angle 30° for <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F-NMR); acquisition time 4.08 s (<sup>1</sup>H), 1.279 s (<sup>19</sup>F), 1.36 s (<sup>13</sup>C); pulse

delay 2 ( $^1\text{H}$ ), 4 s ( $^{19}\text{F}$  and  $^{13}\text{C}$ ); scans 16 ( $^1\text{H}$ ), 16 ( $^{19}\text{F}$ ), 1024 ( $^{13}\text{C}$ ); and pulse width of 4.57 ( $^1\text{H}$ ), 14.6 ( $^{19}\text{F}$ ), and 3.3 ( $^{13}\text{C}$ )  $\mu\text{s}$ . The letters s, d, t, q, and sext stand for singlet, doublet, triplet, quartet, and sextet, respectively.

*Matrix Assisted Laser Desorption Ionization-Time-Of-Flight mass spectrometry (MALDI-TOF-MS):* Experiments were determined with a Bruker Autoflex III with a positive ionization method for compounds containing a higher content of hydrocarbons and a negative ionization method for compounds higher in fluorocarbon content. For sample preparation, materials were diluted in 1 mL of 20 g/L perfluorocinnamic acid in a 50/50 solvent mixture of HFE-7100 and methanol. 1  $\mu\text{l}$  of this dilute sample was spotted onto the target plate, and treated with 1  $\mu\text{l}$  of 10 mg/mL LiCl/MeOH and dried. Calibration of the experiments due to target plate imperfections were done by comparison to a secondary standard of oligo(HFPO)-methyl alcohol (2000 g/mol) on adjacent target spots.

## B. Preparation and Characterization of Compounds

### B.1. Oligo(hexafluoropropylene oxide) primary iodide [1a]

$\delta^{13}\text{C}$  NMR (101MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ): 117.23 (qd,  $^1J_{\text{CF}} = 291.989$  Hz,  $^2J_{\text{CF}} = 30.62$  Hz,  $-\text{CF}(\text{CF}_3)\text{CF}_2\text{I}$ ), 116.68 (qd,  $^1J_{\text{CF}} = 286.13$  Hz,  $^2J_{\text{CF}} = 32.90$  Hz,  $-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}-$ ), 115.87 (td,  $^1J_{\text{CF}} = 287.986$  Hz,  $^2J_{\text{CF}} = 30.875$  Hz,  $-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}-$ ), 106.34 (tsext,  $^1J_{\text{CF}} = 265.437$  Hz,  $^2J_{\text{CF}} = 38.81$  Hz,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}-$ ), 102.52 (dsext,  $^1J_{\text{CF}} = 265.8$  Hz,  $^2J_{\text{CF}} = 35.6$  Hz,  $-\text{OCF}(\text{CF}_3)\text{CF}_2-$ ), 92.86 (td,  $^1J_{\text{CF}} = 320.62$  Hz,  $^2J_{\text{CF}} = 35.1$  Hz,  $\text{CF}(\text{CF}_3)\text{CF}_2\text{I}$ ), 91.27 (td,  $^1J_{\text{CF}} = 320.72$  Hz,  $^2J_{\text{CF}} = 35.767$  Hz,  $\text{CF}(\text{CF}_3)\text{CF}_2\text{I}$ )

$\delta^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ ): -59.0957 (dd,  $-\text{CF}(\text{CF}_3)\text{CF}_a\text{F}_b\text{I}$ , 12F), -60.08 (d,  $-\text{CF}(\text{CF}_3)\text{CF}_a\text{F}_b\text{I}$ , 1F), -75.40 (s,  $\text{CF}(\text{CF}_3)\text{CF}_2\text{I}$ , 3F), -83.60 (s,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}-$ , 3F), -131.58 (s,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}-$ , 2F), -134.95 (m,  $-\text{CF}(\text{CF}_3)\text{CF}_2\text{I}$ , 1F), -146.22 (m,  $-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}-$ , n=8.21 F)

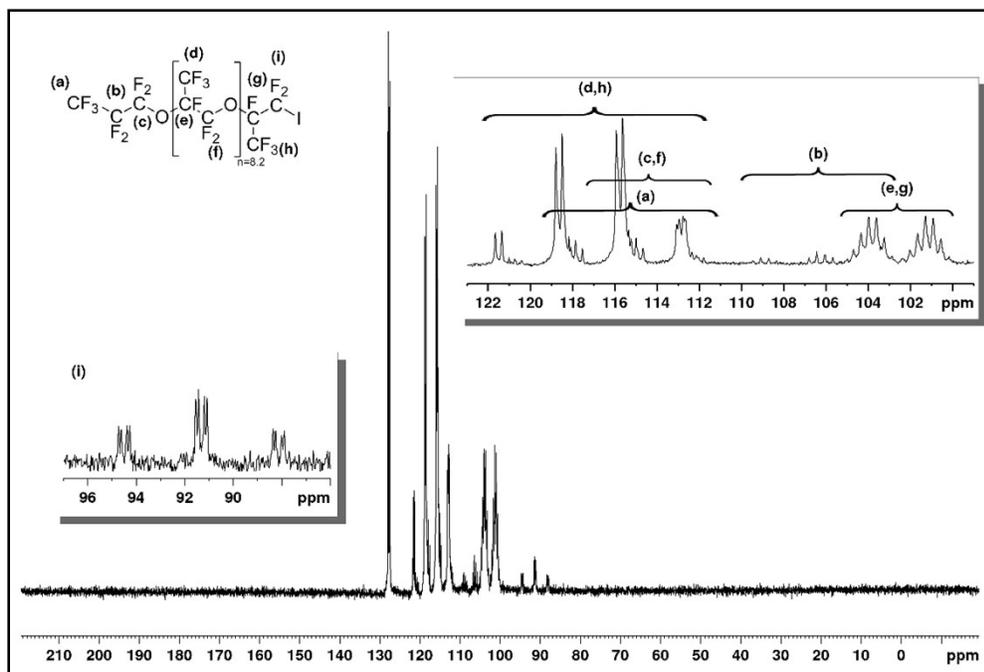


Figure 1:  $^{13}\text{C}$  NMR spectrum (101MHz,  $\text{C}_6\text{D}_6$ ) of oligo(HFPO) primary iodide

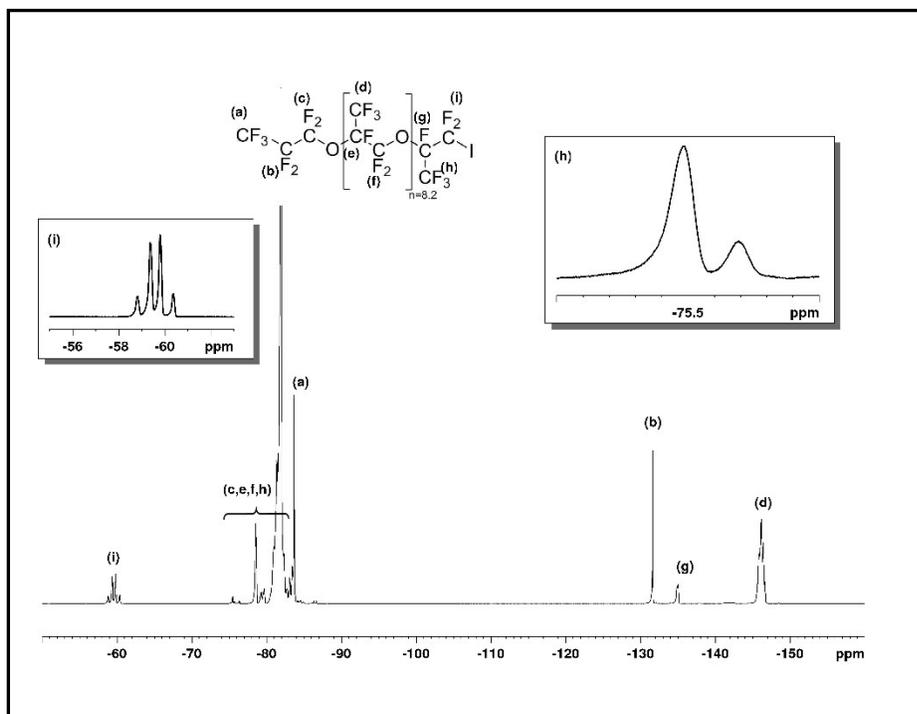


Figure 2:  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{C}_6\text{D}_6$ ) of oligo(HFPO) primary iodide

## B.2. Oligo(hexafluoropropylene oxide) primary bromide [1c]

An oven-dried 250 mL 3-neck round bottom flask was equipped with a stirbar, reflux condenser, gas adapter, a glass stopper and assembled before cooling under N<sub>2</sub>. To this was added 20.0g of oligo(HFPO) primary iodide, 6.279g of *N*-bromosuccinimide, and 75 mL of 2H-perfluoro-5-methyl-3,6-dioxanonane and set to stir. Benzoyl peroxide was added slowly in 1.23g portions three times at 45 minutes intervals. After each addition, the mixture was heated to 75°C. An aliquot was sampled at two-hour intervals and analyzed by GC/MS until completion. After cooling to room temperature, the cloudy, white fluoruous product mixture was filtered using Whatman #1 filter paper by suction filtration. The fluorinated solvent was collected as a cloudy, colourless distillate by vacuum distillation at 100 °C (5 Torr). The product mixture was washed three times with 50 mL of saturated aqueous sodium bicarbonate, three times with 50 mL glacial acetic acid, and then three times with 50 mL of diethyl ether in a 125 mL separatory funnel. The resulting liquid was transferred to a 50mL single-neck round-bottomed flask by pipette, and remaining volatiles were removed *in vacuo* (2 Torr) at 85°C for 4 hours to yield 12.5g (65%) of oligo(HFPO) primary bromide as a clear, colorless oil.

$\delta^{13}\text{C}$  NMR (101MHz, neat, 25 °C): 117.26 (qd,  $^1J_{\text{CF}} = 288.51$  Hz,  $^2J_{\text{CF}} = 31.03$  Hz, -CF(CF<sub>3</sub>)CF<sub>2</sub>Br), 116.68 (qd,  $^1J_{\text{CF}} = 286.13$  Hz,  $^2J_{\text{CF}} = 32.90$  Hz, -CF(CF<sub>3</sub>)CF<sub>2</sub>O-), 115.87 (td,  $^1J_{\text{CF}} = 287.986$  Hz,  $^2J_{\text{CF}} = 30.875$  Hz, -CF(CF<sub>3</sub>)CF<sub>2</sub>O-), 114.06 (td,  $^1J_{\text{CF}} = 314.00$  Hz,  $^2J_{\text{CF}} = 36.11$ , -CF(CF<sub>3</sub>)CF<sub>2</sub>Br), 106.32 (tsext,  $^1J_{\text{CF}} = 268.326$  Hz,  $^2J_{\text{CF}} = 38.107$  Hz, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>O-), 102.46 (dsext,  $^1J_{\text{CF}} = 271.436$  Hz,  $^2J_{\text{CF}} = 34.32$  Hz, -OCF(CF<sub>3</sub>)CF<sub>2</sub>-)

$\delta^{19}\text{F}$  NMR (376 MHz, neat): -65.49 (b, -CF(CF<sub>3</sub>)CF<sub>2</sub>Br, 2F), -79.81 (s, CF(CF<sub>3</sub>)CF<sub>2</sub>Br, 3F), -82(m, -CF(CF<sub>3</sub>)CF<sub>2</sub>O-), -83.60 (s, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>O-, 3F), -131.74 (s, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>O-, 2F), -139.42 (m, -CF(CF<sub>3</sub>)CF<sub>2</sub>Br, 1F), -146.22 (m, -CF(CF<sub>3</sub>)CF<sub>2</sub>O-, n=8.36 F)

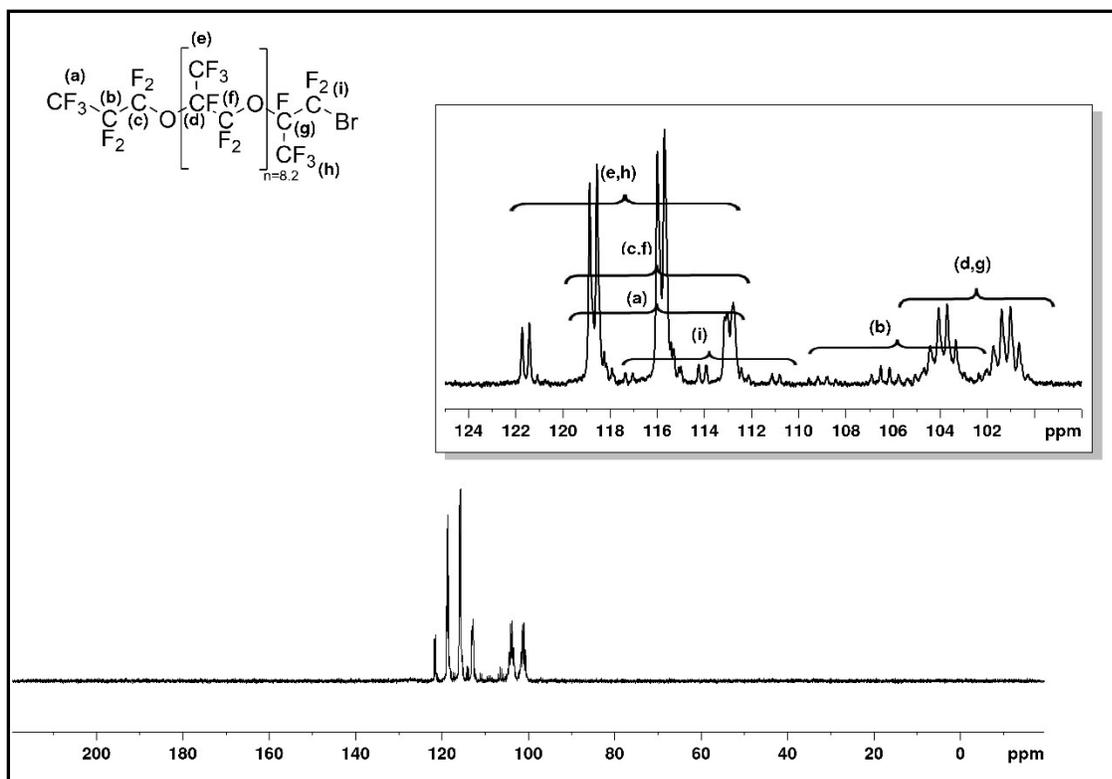


Figure 3:  $^{13}\text{C}$  NMR spectrum (101MHz, Neat) of oligo(HFPO) primary bromide

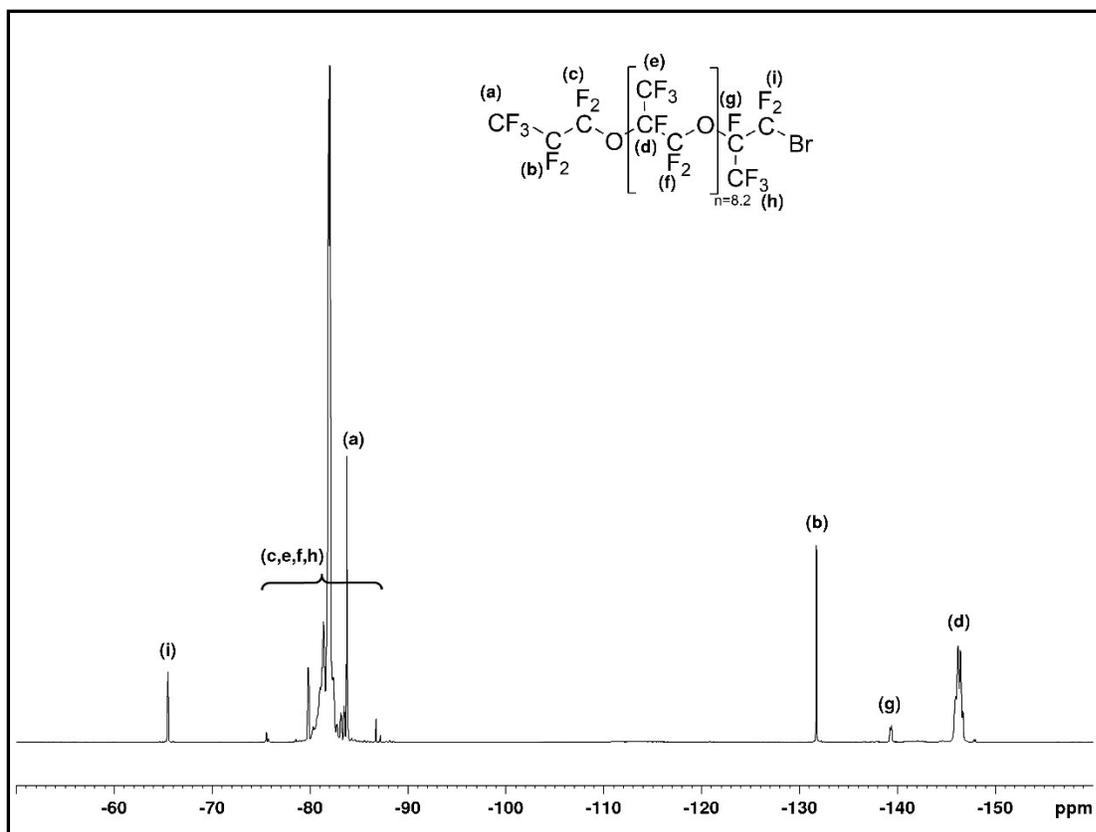


Figure 4: <sup>19</sup>F NMR spectrum (376 MHz, neat) of oligo(HFPO) primary bromide

### B.3. Oligo(hexafluoropropylene oxide) perfluoroisopropenyl ether [1b]

A 50mL three-necked round-bottomed flask with a magnetic stir bar was removed from the drying oven and quickly fitted with an elbow stopcock gas inlet adaptor, glass stopper, and rubber septum. All glass-glass joints were sealed with Dow Corning® high-vacuum grease. The system was immediately connected to nitrogen gas via a Schlenk line and allowed to purge while cooling for 15 minutes. The flask was then charged with freshly ordered phenyl lithium solution of recently determined titre in dibutyl ether (3.41 mL, 6.16 mmol, 1.80 M) by syringe. The phenyl lithium was dried *in vacuo* (2 Torr) to give a tan powder after 1 hour. The flask was slowly back-filled with nitrogen, and the contents were diluted and agitated in 3mL of scrupulously anhydrous hexanes to a cloudy white solution. The solution was then cooled to -78 °C with stirring in an insulated bath of dry ice/acetone.

A second 50mL three-necked round-bottomed flask with a magnetic stir bar was fitted as above, and then purged with nitrogen while cooling to room temperature. 1.00 molar equivalents of previously degassed oligo(hexafluoropropylene oxide) primary iodide (10.0 g, 6.16 mmol) was added by weighed syringe. This oil was diluted in 5 mL of anhydrous perfluorohexane while stirring, and then cooled to -78 °C in an insulated dry ice/acetone bath. After cooling for 45 min, the fluoros solution was transferred by syringe to the flask containing phenyl lithium in hexanes, using an additional 2mL perfluorohexane rinse to facilitate quantitative transfer.

The reaction mixture in the insulated dry ice/acetone bath was allowed to slowly warm to room temperature with continuous stirring over 3-4 hours, followed by quenching with 0.5 mL of deionized water. The solvent was removed *in vacuo* at room temperature in an oil bath. The remaining oligo(HFPO) product was washed 3 times with glacial acetic acid, 3 times with ice cold diethyl ether and then isolated under vacuum to afford a clear, light yellow oil of oligo(HFPO) perfluoroisopropenyl ether (7.5 g, 82% isolated yield).

IR:  $\nu_{\max}/\text{cm}^{-1}$  1765 (C=CF<sub>2</sub> str.), 1377 (C=CF<sub>2</sub> asym str.), 1306, 1233s (C-F str), 1178b (C-F asym str.), 1126 (C-O stretch), 1026 (=CF<sub>2</sub> sym str.), 981 (C-O scissoring), 807 (-CF<sub>3</sub> str), 746, 651

$\delta$  <sup>13</sup>C NMR (100MHz, C<sub>6</sub>D<sub>6</sub>, C<sub>6</sub>F<sub>6</sub>, 25 °C): 102.52 (dsext, <sup>1</sup>J<sub>CF</sub> = 265.8 Hz, <sup>2</sup>J<sub>CF</sub> = 35.6 Hz, -OCF(CF<sub>3</sub>)CF<sub>2</sub>-), 106.34 (tsext, <sup>1</sup>J<sub>CF</sub> = 265.437 Hz, <sup>2</sup>J<sub>CF</sub> = 38.81 Hz, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>O-), 115.87 (td, <sup>1</sup>J<sub>CF</sub>=287.986 Hz, <sup>2</sup>J<sub>CF</sub> = 30.875 Hz, -CF(CF<sub>3</sub>)CF<sub>2</sub>O-), 117.73 (qd, <sup>1</sup>J<sub>CF</sub>=286.13 Hz, <sup>2</sup>J<sub>CF</sub> = 32.90 Hz, -CF(CF<sub>3</sub>)CF<sub>2</sub>O-), 157.57 (t, <sup>1</sup>J<sub>CF</sub> = 301.445 Hz, -OC(CF<sub>3</sub>)=CF<sub>2</sub>)

$\delta$  <sup>19</sup>F NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): -66.50 (dd, -C(CF<sub>3</sub>)=CF<sub>a</sub>F<sub>b</sub>, 3F), -80 (m, -CF(CF<sub>3</sub>)CF<sub>2</sub>O-), -82.41 (s, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>O-, 3F), -84.42 (s, -OC(CF<sub>3</sub>)=CF<sub>a</sub>F<sub>b</sub>, 1F), -88.40 (m, -OC(CF<sub>3</sub>)=CF<sub>a</sub>F<sub>b</sub>, 1F), -130.32 (s, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>O-, 2F), -144.83 (m, -CF(CF<sub>3</sub>)CF<sub>2</sub>O-, n=8.59 F)

Maldi-TOF (Li+) = 1485.390, 1651.248, 1817.471, 1983.517, 2149.560, 2315.606, 2481.648, 2647.687, 2813.722, 2979.756, 3145.777, 3311.800

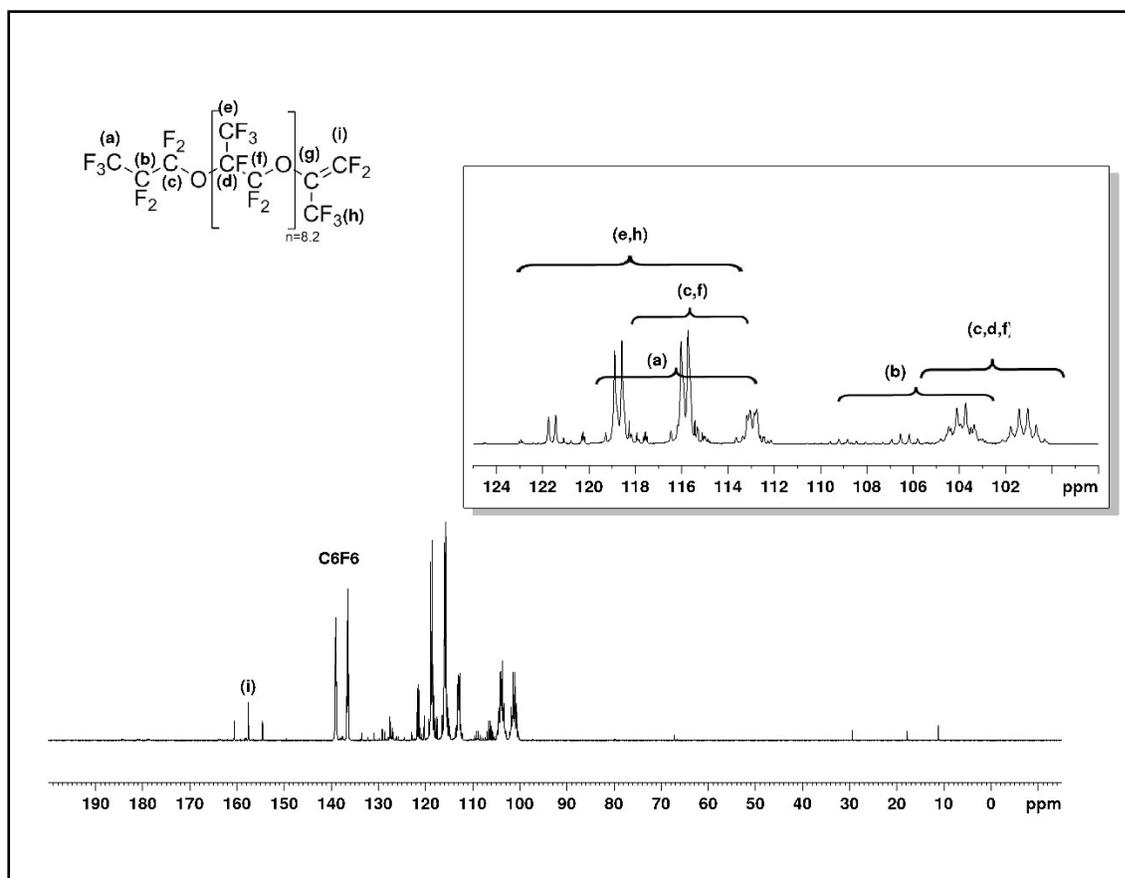


Figure 5:  $^{13}\text{C}$  NMR spectrum (100MHz,  $\text{C}_6\text{F}_6$ ) of oligo(HFPO) perfluoroisopropenyl ether

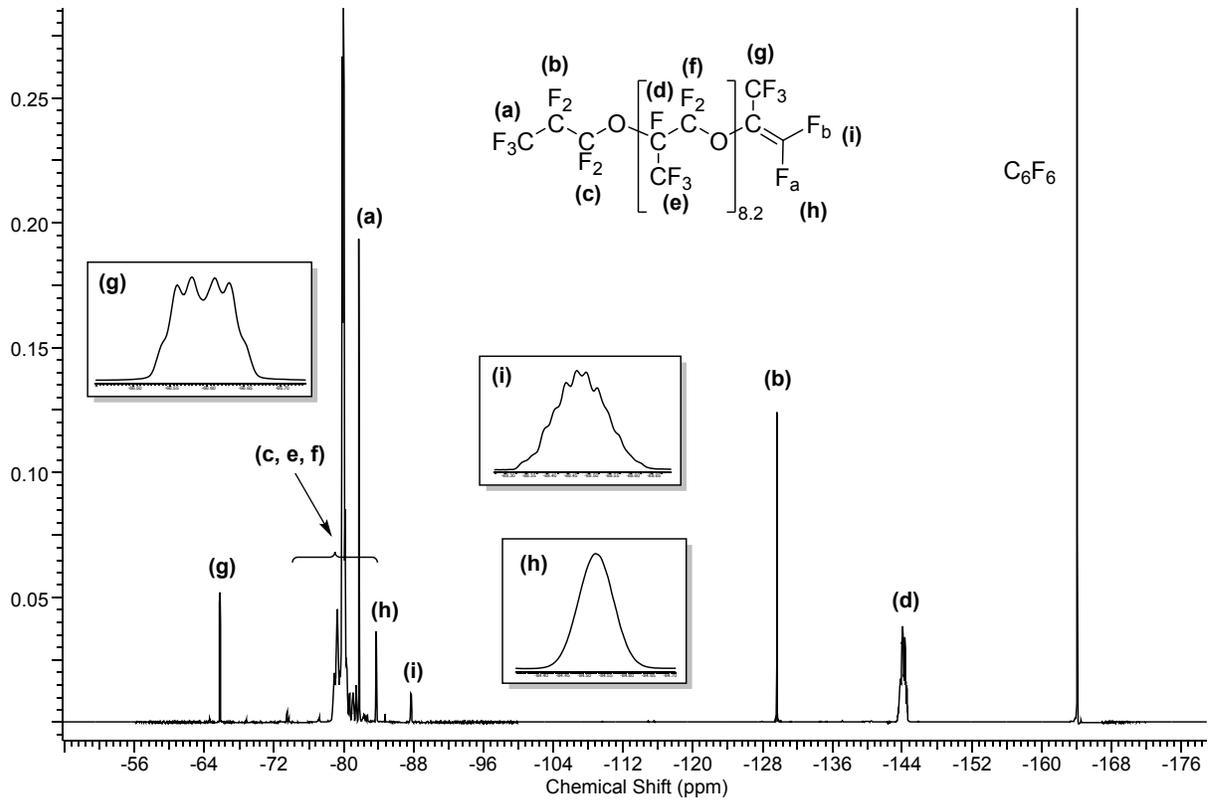


Figure 6: <sup>19</sup>F NMR spectrum (376 MHz, C<sub>6</sub>F<sub>6</sub>) of oligo(HFPO) perfluoroisopropenyl ether

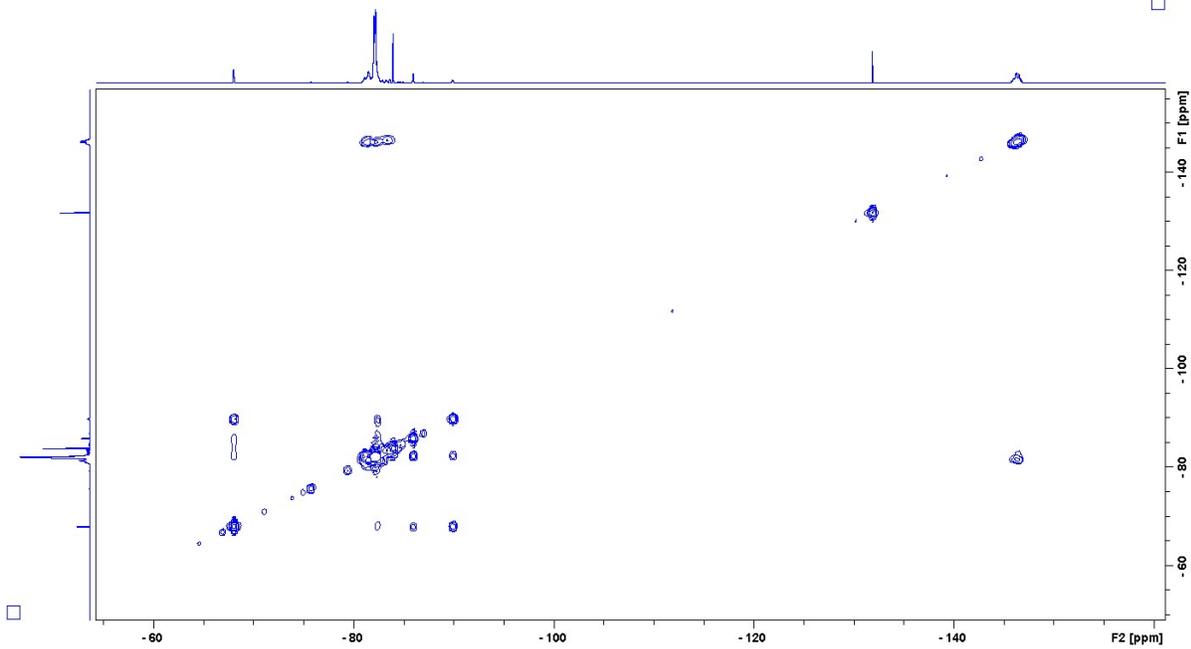


Figure 7: <sup>19</sup>F-<sup>19</sup>F COSY spectrum (376 MHz, C<sub>6</sub>F<sub>6</sub>) of oligo(HFPO) perfluoroisopropenyl ether

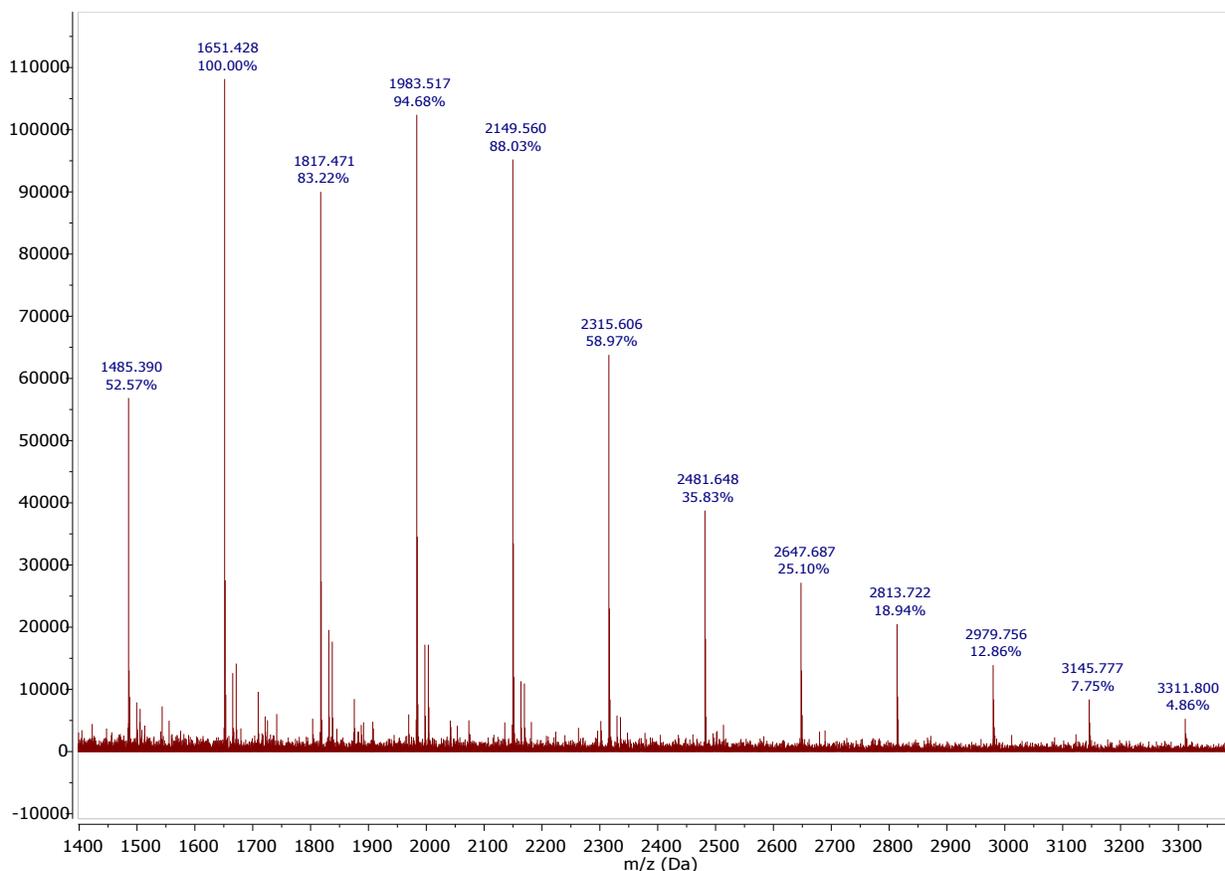


Figure 8: MALDI-TOF Spectrum (Li+) of oligo(HFPO) perfluoroisopropenyl ether

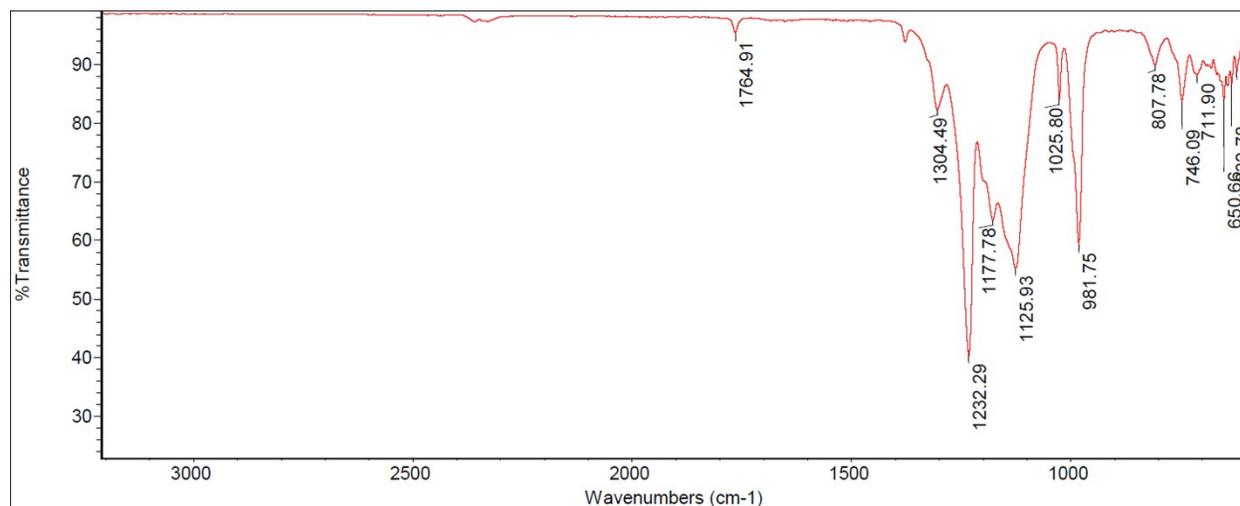


Figure 9: FTIR Spectrum of oligo(HFPO) perfluoroisopropenyl ether

#### B.4. Oligo(hexafluoropropylene oxide) perfluoroisopropenyl ester [1i]

Poly(hexafluoropropylene oxide) acid fluoride (1250 g/mol) was kindly offered by DuPont (Wilmington, USA) and received as a clear, colourless oil, and stored under pure nitrogen in a Vacuum Atmospheres HE-493 glovebox. In the glovebox, a 50 mL three-necked round-bottomed flask with a magnetic stir bar, elbow stopcock gas inlet adaptor, and glass stoppers

was charged with acid fluoride (2.00 g, 1.60 mmol). All joints were sealed with Dow Corning® high-vacuum grease, and the flask was transferred to a fume hood and placed under N<sub>2</sub> purge where it was fitted with an addition funnel.

A second 50mL three-necked round-bottomed flask with a magnetic stir bar was fitted as above, and then purged with nitrogen while cooling to room temperature. To 5 mL of anhydrous THF was added 1.0 equivalent of dry 1,1,1,3,3,3-hexafluoro-2-propanol (0.269 g, 1.60 mmol, degassed and stored under nitrogen) by weighed syringe. While stirring, 2.0 equivalents of n-BuLi (2.00 mL, 3.2 mmol, 1.60 M in hexanes) was added dropwise at 20 °C by syringe, and stirred for 30min to form Lithium 1,1,1,3,3-pentafluoro-2-propenolate. This enolate solution was then transferred by syringe to the addition funnel, and added slowly dropwise over 30 min at 20 °C to the stirring acid fluoride. After stirring for 4 hours, the solution is quenched with aqueous sodium bicarbonate. The remaining oil is washed twice with glacial acetic acid and then ice cold diethyl ether. The resulting pale, tan oil was then isolated *in vacuo* 1.868g (82% yield).

$\delta$  <sup>13</sup>C NMR (101 MHz, neat, 25 °C): 102.44 (dq, <sup>1</sup>J<sub>CF</sub> = 265.8 Hz, <sup>2</sup>J<sub>CF</sub> = 35.6 Hz, -OCF(CF<sub>3</sub>)CF<sub>2</sub>-), 106.23 (tsext, <sup>1</sup>J<sub>CF</sub> = 265.437 Hz, <sup>2</sup>J<sub>CF</sub> = 38.81 Hz, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>O-), 115.87 (td, <sup>1</sup>J<sub>CF</sub>=287.986 Hz, <sup>2</sup>J<sub>CF</sub> = 30.875 Hz, -CF(CF<sub>3</sub>)CF<sub>2</sub>O-), 117.06 (qd, <sup>1</sup>J<sub>CF</sub>=287.83 Hz, <sup>2</sup>J<sub>CF</sub> = 30.985 Hz, -CF(CF<sub>3</sub>)CF<sub>2</sub>O-), 155.53 (t, <sup>1</sup>J = 299.43 Hz, -OC(CF<sub>3</sub>)=CF<sub>2</sub>), 161.68 (d, <sup>2</sup>J<sub>CF</sub> = 34.657 Hz, -CF(CF<sub>3</sub>)C(O)-OC(CF<sub>3</sub>)=CF<sub>2</sub>)

$\delta$  <sup>19</sup>F NMR (376 MHz, neat, 25 °C): -69.0 (dd, <sup>3</sup>J<sub>FF</sub> = 20.10 Hz, <sup>3</sup>J<sub>FF</sub> = 4.32 Hz, -OC(CF<sub>3</sub>)=CF<sub>a</sub>F<sub>b</sub>, 3F), -80 (b m, -CF(CF<sub>3</sub>)CF<sub>2</sub>O-), -82.41 (s, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>O-, 3F), -84.48 (d, <sup>2</sup>J<sub>FF</sub> = 19.61 Hz, -OC(CF<sub>3</sub>)=CF<sub>a</sub>F<sub>b</sub>, 1F), -84.78 (d, <sup>2</sup>J<sub>FF</sub> = 19.435 Hz, -OC(CF<sub>3</sub>)=CF<sub>a</sub>F<sub>b</sub>, 1F), -131.84 (s, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>O-, 2F), -133.32 (s, -CF(CF<sub>3</sub>)C(O)O-, 1F), -144.83 (m, -CF(CF<sub>3</sub>)CF<sub>2</sub>O-, n=4.37 F)

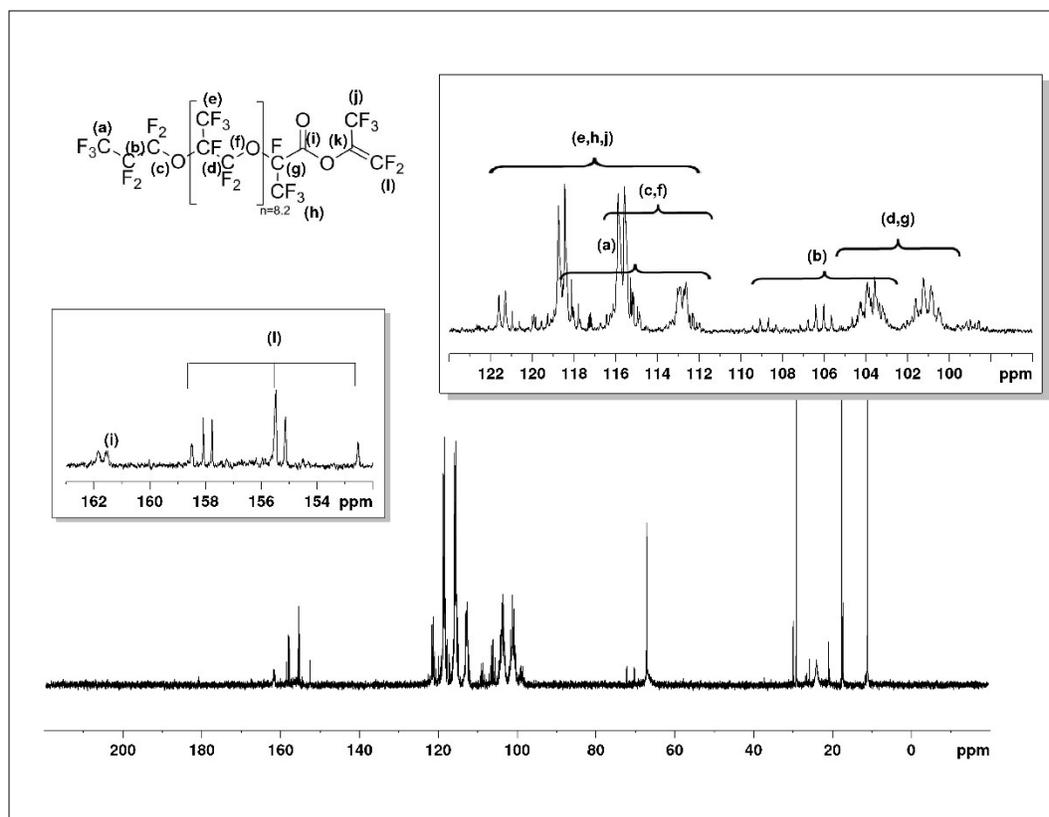


Figure 10:  $^{13}\text{C}$  NMR spectrum (101 MHz, neat) of oligo(HFPO)-perfluoroisopropenyl ester

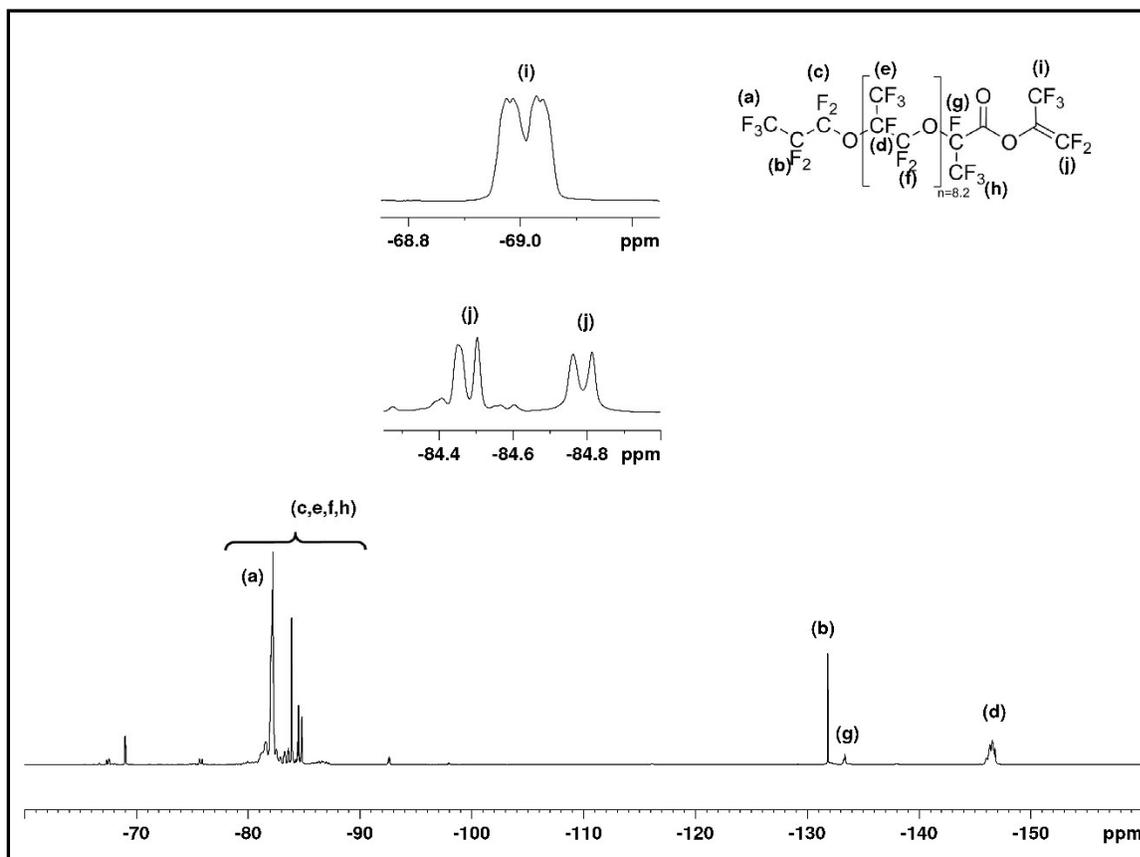


Figure 11:  $^{19}\text{F}$  NMR spectrum (376 MHz, neat) of oligo(HFPO)-perfluoroisopropenyl ester

### B.5. Oligo(hexafluoropropylene oxide) primary hydrogen end-cap [1d]

A 50 mL three-necked round-bottomed flask with a magnetic stir bar, water-cooled condenser with nitrogen gas purge, glass thermometer and glass stopper was charged with oligo(hexafluoropropylene oxide) primary iodide (5.0 g, 3.08 mmol, 1624 g/mol), followed by 1.2 equivalents of tris(trimethylsilyl)silane (0.919 g, 3.69 mmol) and 20 mL of glacial acetic acid. The mixture was heated in a mineral oil bath to 90 °C and fed with 0.3 g of benzoyl peroxide initiator at 30 min intervals. Reaction completion was achieved within 90 min (by GC-MS sampling). The lower fluororous layer was washed twice with glacial acetic acid and then ice-cold diethyl ether. The resulting clear, colourless oil was then isolated under vacuum (4.0 g, 87% isolated yield).

$\delta$   $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , TMS, 25 °C): 5.74 (t,  $^{24}J_{\text{HF}} = 52.43$  Hz,  $\text{CF}(\text{CF}_3)\text{CF}_2\text{H}$ )

$\delta$   $^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{F}_6$ ,  $\text{C}_6\text{D}_6$ , 25 °C): 102.52 (dq,  $^1J_{\text{CF}} = 265.8$ ,  $^2J_{\text{CF}} = 35.6$  Hz,  $-\text{OCF}(\text{CF}_3)\text{CF}_2^-$ ), 102.80 (dsext,  $^1J_{\text{CF}} = 265.74$  Hz,  $^2J_{\text{CF}} = 35.60$  Hz,  $-\text{OCF}(\text{CF}_3)\text{CF}_2\text{H}$ ), 106.34 (tsext,  $^1J_{\text{CF}} = 265.437$  Hz,  $^2J_{\text{CF}} = 38.81$  Hz,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}$ ), 107.88 (td,  $^1J_{\text{CF}} = 255.22$  Hz,  $^2J_{\text{CF}} = 34.00$  Hz,  $-\text{CF}(\text{CF}_3)\text{CF}_2\text{H}$ ), 115.87 (td,  $^1J_{\text{CF}} = 287.986$  Hz,  $^2J_{\text{CF}} = 30.875$  Hz,  $-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}$ ), 116.68 (qd,  $^1J_{\text{CF}} = 286.13$  Hz,  $^2J_{\text{CF}} = 32.90$  Hz,  $-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}$ ), 117.23 (qd,  $^1J_{\text{CF}} = 291.989$  Hz,  $^2J_{\text{CF}} = 30.62$  Hz,  $-\text{CF}(\text{CF}_3)\text{CF}_2\text{H}$ ), 117.76 (qd,  $^1J_{\text{CF}} = 286.31$  Hz,  $^2J_{\text{CF}} = 30.877$  Hz,  $-\text{OCF}(\text{CF}_3)\text{CF}_2$ )

$\delta$   $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , 25 °C): -81.46 (s,  $-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}-$ ), -82.12 ( $-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}-$ ), -83.08 ( $-\text{CF}(\text{CF}_3)\text{CF}_a\text{F}_b\text{H}$ ), -83.91 (t,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}-$ , 3F), -131.83 (s,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}-$ , 2F), -136.41 (dd,  $^2J_{\text{FF}}=310.438$  Hz,  $^2J_{\text{HF}}=52.35$  Hz,  $-\text{CF}(\text{CF}_3)\text{CF}_a\text{F}_b\text{H}$ , 1F), -137.95 (dd,  $^2J_{\text{FF}}=310.108$  Hz,  $^2J_{\text{HF}}=52.768$  Hz  $-\text{CF}(\text{CF}_3)\text{CF}_a\text{F}_b\text{H}$  1F), -146.37 (m,  $-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}-$ ,  $n=9.36$  F)

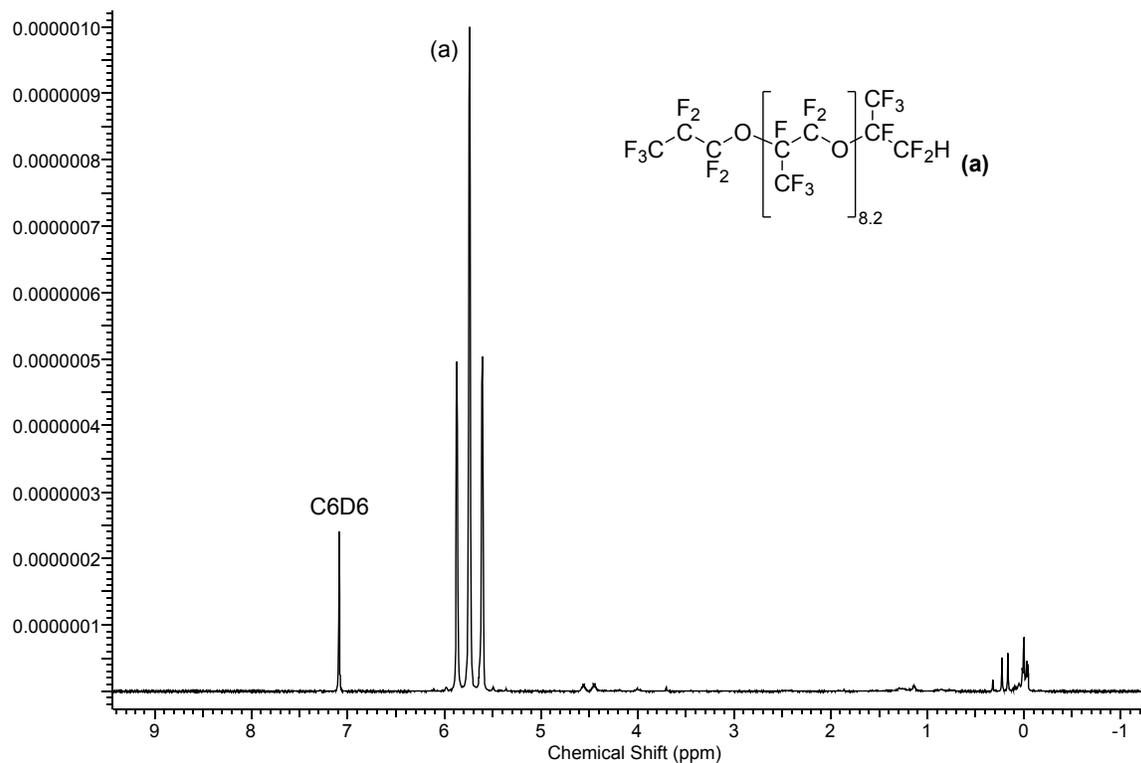


Figure 9:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_6\text{D}_6$ ) of oligo(HFPO) primary hydrogen endcap

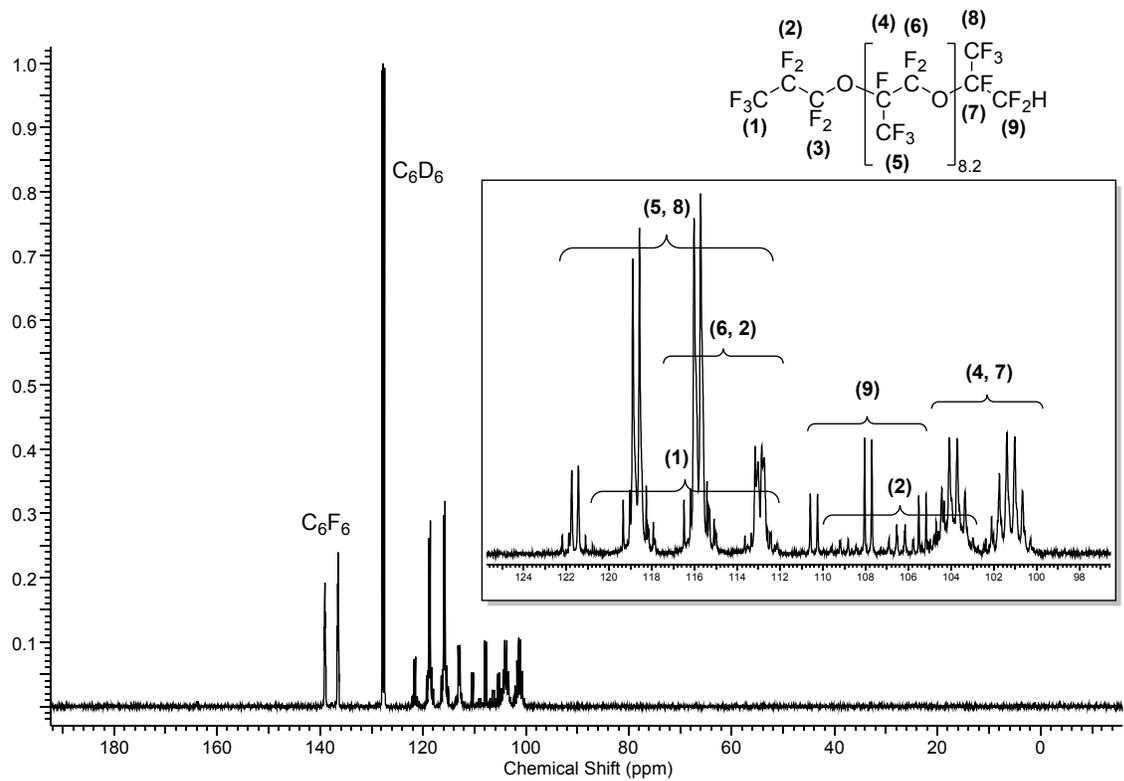


Figure 12:  $^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{C}_6\text{F}_6$ ,  $\text{C}_6\text{D}_6$ ) of oligo(HFPO) primary hydrogen endcap

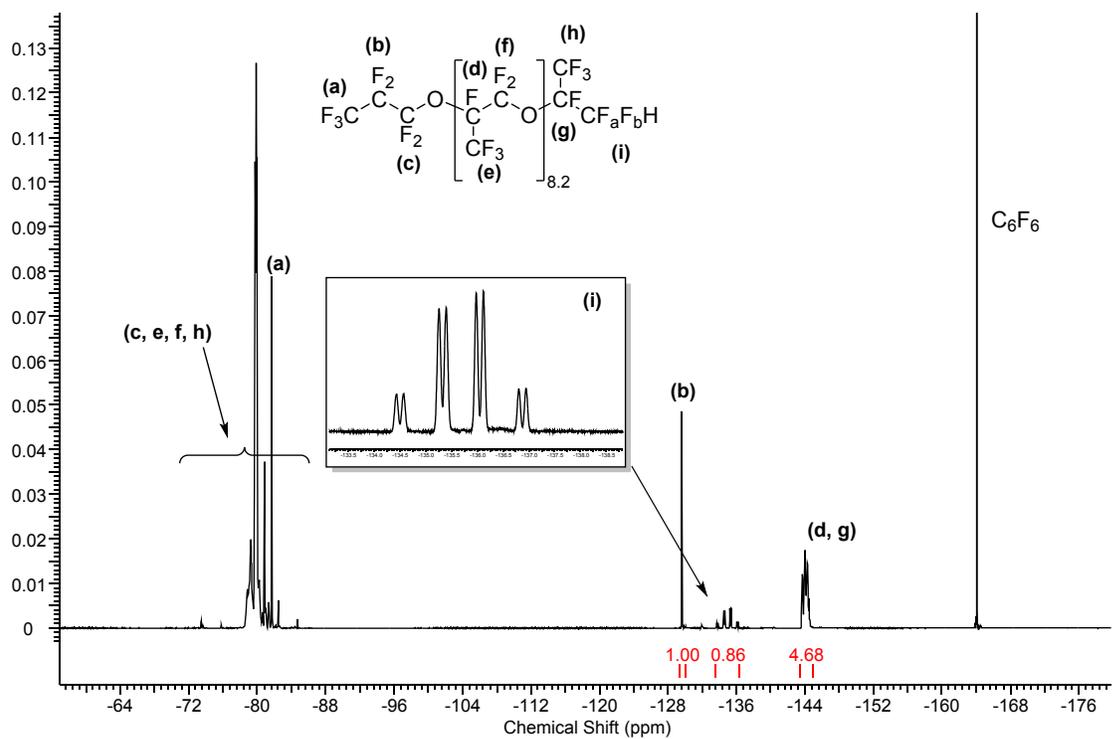


Figure 11:  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{C}_6\text{F}_6$ ) of oligo(HFPO) primary hydrogen endcap

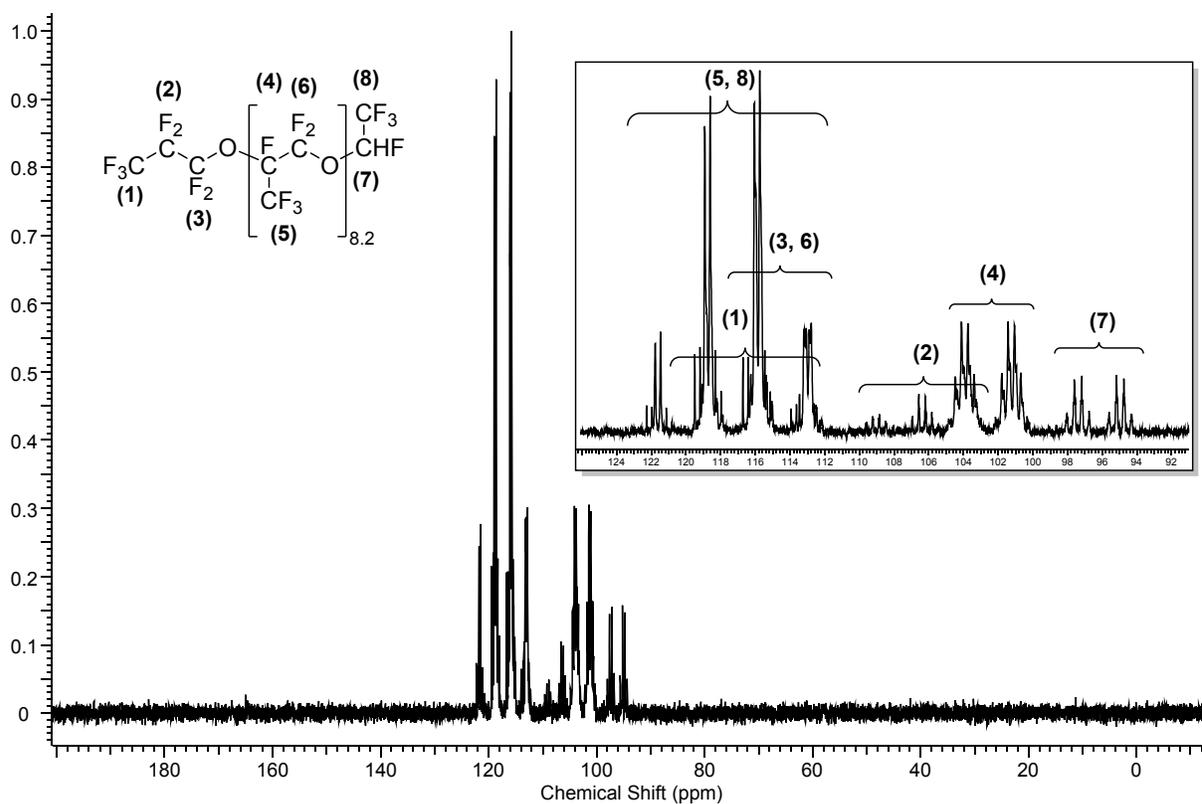
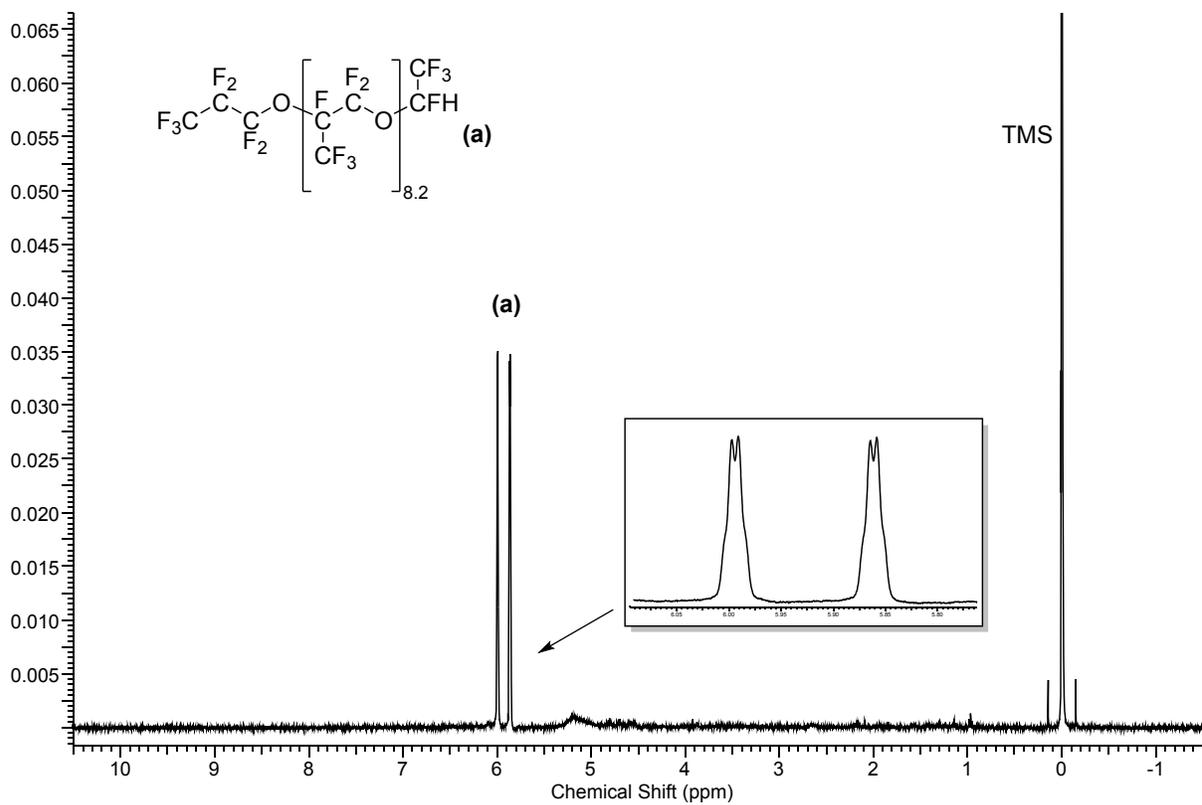
### B.6. Oligo(hexafluoropropylene oxide) secondary hydrogen end-cap [1e]

A 250 mL three-necked round-bottomed flask with a magnetic stir bar, water-cooled condenser with nitrogen gas purge, glass thermometer and glass stopper was charged with oligo(hexafluoropropylene oxide) secondary iodide (40.842 g, 0.025 mol, 1627.12 g/mol) and 100 ml of glacial acetic acid and heated to 55 °C under nitrogen purge to degas. This was followed by a slow addition of 1.2 equivalents of tributyltin hydride (9.325 g, 0.032 mmol) at which the system spontaneously warmed to 100 °C. This was allowed to cool to 75 °C before feeding the reaction with 7.87 g of benzoyl peroxide initiator. The reaction was cooled and washed three times with 40 mL of glacial acetic acid, three times with 30 mL of diethyl ether and then volatiles removed via rotary evaporator. The resulting oil was then distilled under reduced pressure from 90°C to 210°C to yield a clear, pale yellow oil. (19.829 g, 50% isolated yield).

$\delta$  <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C): 5.80 (dq, <sup>21</sup>J<sub>HF</sub> = 53.109 Hz, <sup>32</sup>J<sub>HF</sub> = 1.108 Hz, -OCF(CF<sub>3</sub>)H)

$\delta$  <sup>13</sup>C NMR (101 MHz, neat, 25 °C): 96.18 (dq, <sup>1</sup>J<sub>CF</sub> = 244.71 Hz, <sup>2</sup>J<sub>CF</sub> = 43.02-97 Hz, OCF(CF<sub>3</sub>)H), 102.58 (dq, <sup>1</sup>J<sub>CF</sub> = 269.986 Hz, <sup>2</sup>J<sub>CF</sub> = 36.22 Hz, -OCF(CF<sub>3</sub>)CF<sub>2</sub>-), 106.34 (tsext, <sup>1</sup>J<sub>CF</sub> = 267.876, <sup>2</sup>J<sub>CF</sub> = 37.10 Hz, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>O), 115.77 (td, <sup>1</sup>J<sub>CF</sub> = 285.74, <sup>2</sup>J<sub>CF</sub> = 31.326 Hz, -OCF(CF<sub>3</sub>)CF<sub>2</sub>-), 117.38 (qd, <sup>1</sup>J<sub>CF</sub> = 288.04 Hz, <sup>2</sup>J<sub>CF</sub> = 30.877 Hz, -OCF(CF<sub>3</sub>)CF<sub>2</sub>-), 117.95 (qd, <sup>1</sup>J<sub>CF</sub> = 279.768 Hz, <sup>2</sup>J<sub>CF</sub> = 31.03 Hz, -OCF(CF<sub>3</sub>)CF<sub>2</sub>H)

$\delta$  <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 25 °C): -82.11 (s, -CF(CF<sub>3</sub>)CF<sub>2</sub>O-), -83.45 (s, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>O, 3F), -131.78 (s, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>O, 2F), -146 (m, -CF(CF<sub>3</sub>)CF<sub>2</sub>O-, n = 7.35 F), 147.97 (d, <sup>1</sup>J<sub>HF</sub> = 53.216 Hz, <sup>3</sup>J<sub>FF</sub> = 4.876 Hz, -OCF(CF<sub>3</sub>)H, 1F)



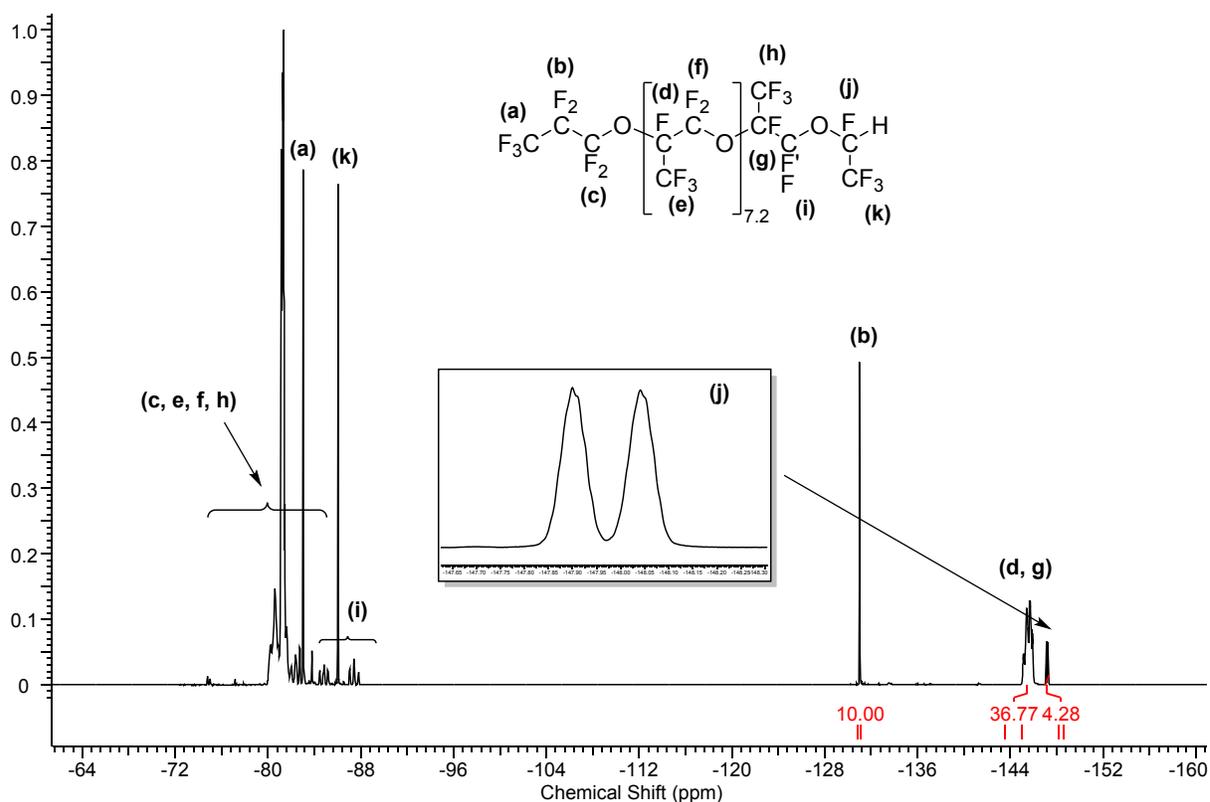
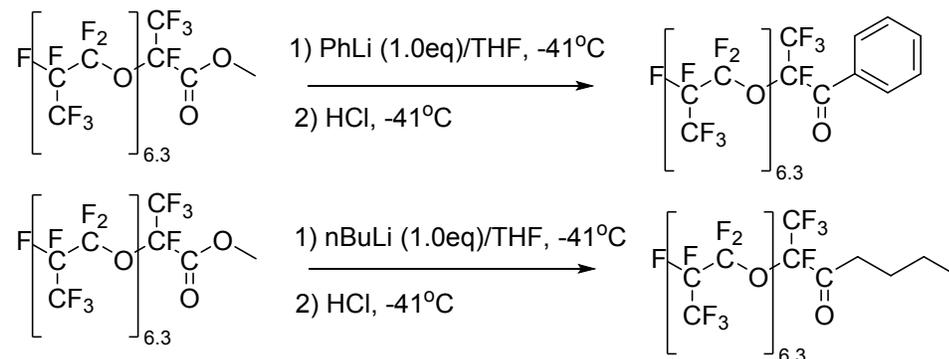


Figure 15:  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{CDCl}_3$ ) of oligo(HFPO) secondary hydrogen end-cap

### B.7. Oligo(hexafluoropropylene oxide) butyl ketone [S1] and phenyl ketone [1g]

To identify butyl and phenyl ketone by-products identified in Scheme 3, model compounds were synthesized in excellent yield from the oligo(hexafluoropropylene oxide) methyl ester using the corresponding alkyl lithium in accordance with Chen et al.<sup>2</sup> The oligo(HFPO) substrates have not yet been reported or characterized.



An oven dried 50 mL three-necked round-bottomed flask with a magnetic stir bar equipped with an elbow stopcock gas inlet adaptor, glass stopper, and rubber septum was assembled under nitrogen purge and allowed to cool for 15 minutes. All glass-glass joints were sealed with Dow Corning® high-vacuum grease.

Precisely 1.00 equivalent of previously degassed oligo(hexafluoropropylene oxide) methyl ester (2.00 g, 1.64 mmol, MW = 1220 g/mol) was added by weighed syringe, followed by 10 mL of anhydrous THF. The system was cooled to -41 °C in a bath of dry ice in acetonitrile. After cooling for 45 min, precisely 1.0 equivalents of the alkyl lithium of recently determined titre (PhLi: 0.91 mL, 1.64 mmol, 1.80 M in dibutyl ether; nBuLi: 1.02 mL, 1.64 mmol, 1.60 M in hexanes) was added slowly dropwise by syringe. After addition, the mixture was stirred for 10 min at -41°C, then quenched immediately with 2 mL of 2 M HCl<sub>(aq)</sub>. Volatiles were stripped off by rotary evaporator, and the remaining oil was washed twice with glacial acetic acid and then ice-cold diethyl ether. The resulting pale, tan oil was then isolated *in vacuo*.

#### B.7.a. Characterization of oligo(HFPO)-butyl ketone [S1]

Yield: 0.96g (48% - 67% Purity by 19F)

$\delta$  <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>F<sub>6</sub>, C<sub>6</sub>D<sub>6</sub>, 25 °C): 2.71 (m, -C(O)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, 2H), 1.59 (p, <sup>3</sup>J<sub>H</sub> = 7.436 Hz, -C(O)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, 2H), (sext, <sup>3</sup>J<sub>H</sub> = 7.439 Hz, -C(O)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, 2H), (t, <sup>3</sup>J<sub>H</sub> = 7.34 Hz, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, 3H)

$\delta$  <sup>13</sup>C NMR (101 MHz, C<sub>6</sub>F<sub>6</sub>, C<sub>6</sub>D<sub>6</sub>, 25 °C): 102.61 (dq, <sup>1</sup>J<sub>CF</sub> = 265.8, <sup>2</sup>J<sub>CF</sub> = 35.6 Hz, -OCF(CF<sub>3</sub>)CF<sub>2</sub>-), 106.34 (tsext, <sup>1</sup>J<sub>CF</sub> = 265.437, <sup>2</sup>J<sub>CF</sub> = 38.81 Hz, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>O), 115.84 (qt, <sup>1</sup>J<sub>CF</sub> = 287.986, <sup>2</sup>J<sub>CF</sub> = 30.875 Hz, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>O-), 117.35 (qd, <sup>1</sup>J<sub>CF</sub> = 287.985, <sup>2</sup>J<sub>CF</sub> = 30.83 Hz, -OCF(CF<sub>3</sub>)CF<sub>2</sub>-), 194.10 (d, <sup>2</sup>J<sub>CF</sub> = 31.00.99 Hz, -CF(CF<sub>3</sub>)C(O)CH<sub>2</sub>-); oligo(HFPO)-Methyl Ester 158.82 (d, <sup>2</sup>J<sub>CF</sub> = 33.04 Hz, -CF(CF<sub>3</sub>)C(O)OCH<sub>3</sub>), 52.64 (s, -CF(CF<sub>3</sub>)C(O)OCH<sub>3</sub>)

$\delta$  <sup>19</sup>F NMR (376 MHz, C<sub>6</sub>F<sub>6</sub>, 25 °C): -82.11 (s, CF(CF<sub>3</sub>)CF<sub>2</sub>O), -83.77 (s, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>O, 3F), -131.68 (s, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>O, 2F), -146.27 (m, -CF(CF<sub>3</sub>)CF<sub>2</sub>O-, 1F); oligo(HFPO)-Methyl Ester -133.35 (s, -CF(CF<sub>3</sub>)C(O)Me, 1F)

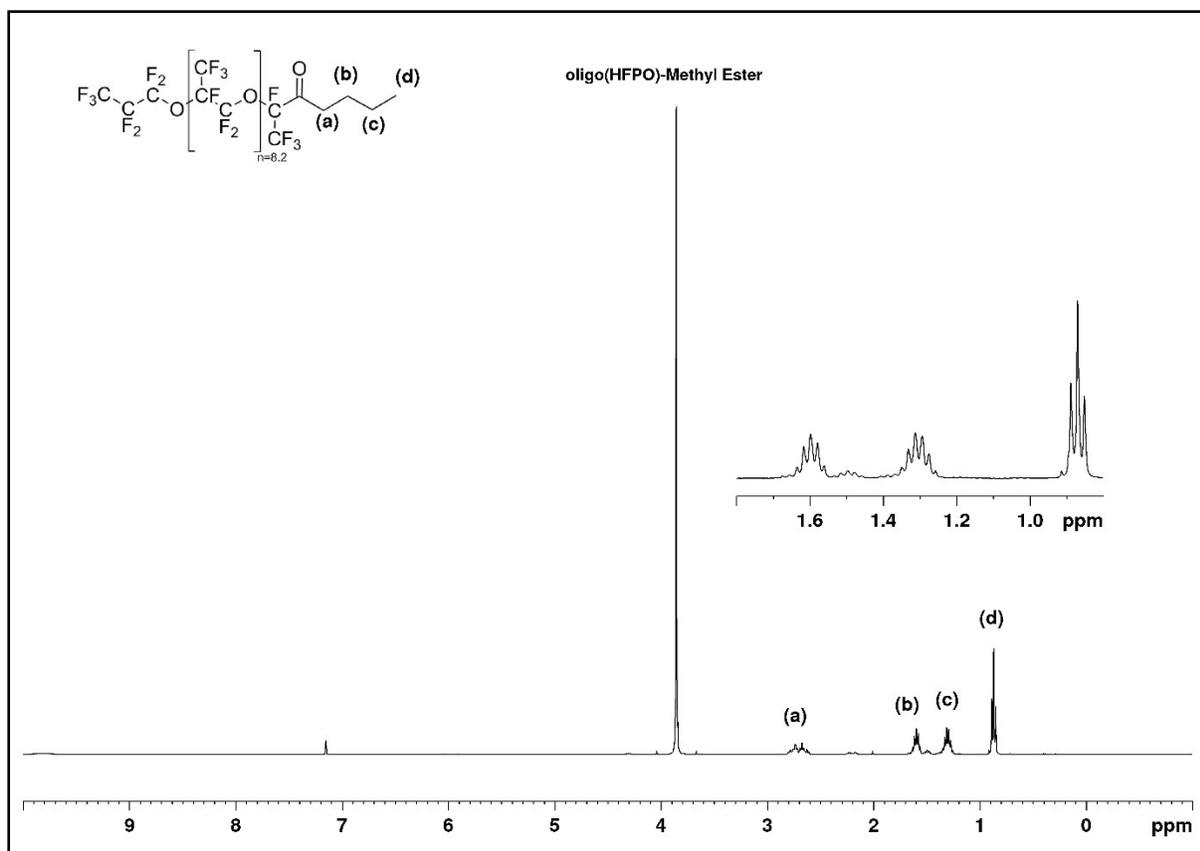


Figure 16: <sup>1</sup>H NMR spectrum (400 MHz, C<sub>6</sub>F<sub>6</sub>, C<sub>6</sub>D<sub>6</sub>) of oligo(HFPO) butyl ketone

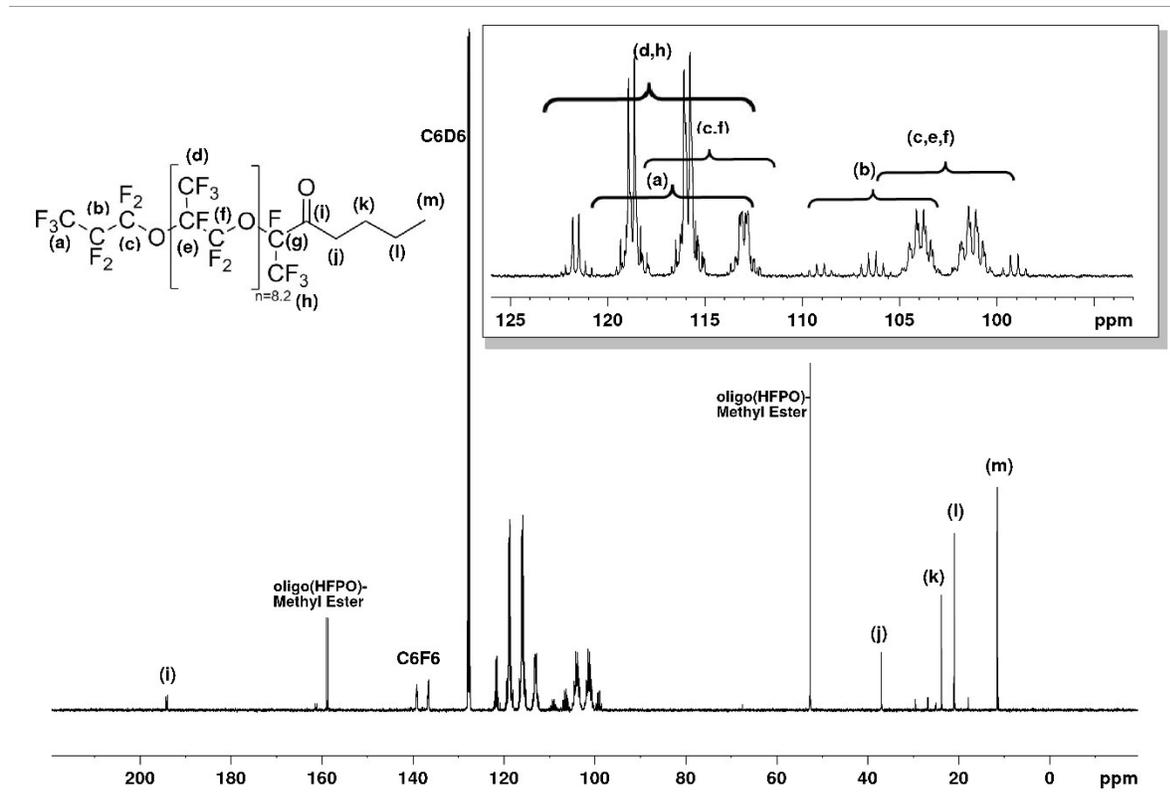


Figure 17:  $^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{C}_6\text{F}_6$ ,  $\text{C}_6\text{D}_6$ ) of oligo(HFPO) butyl ketone

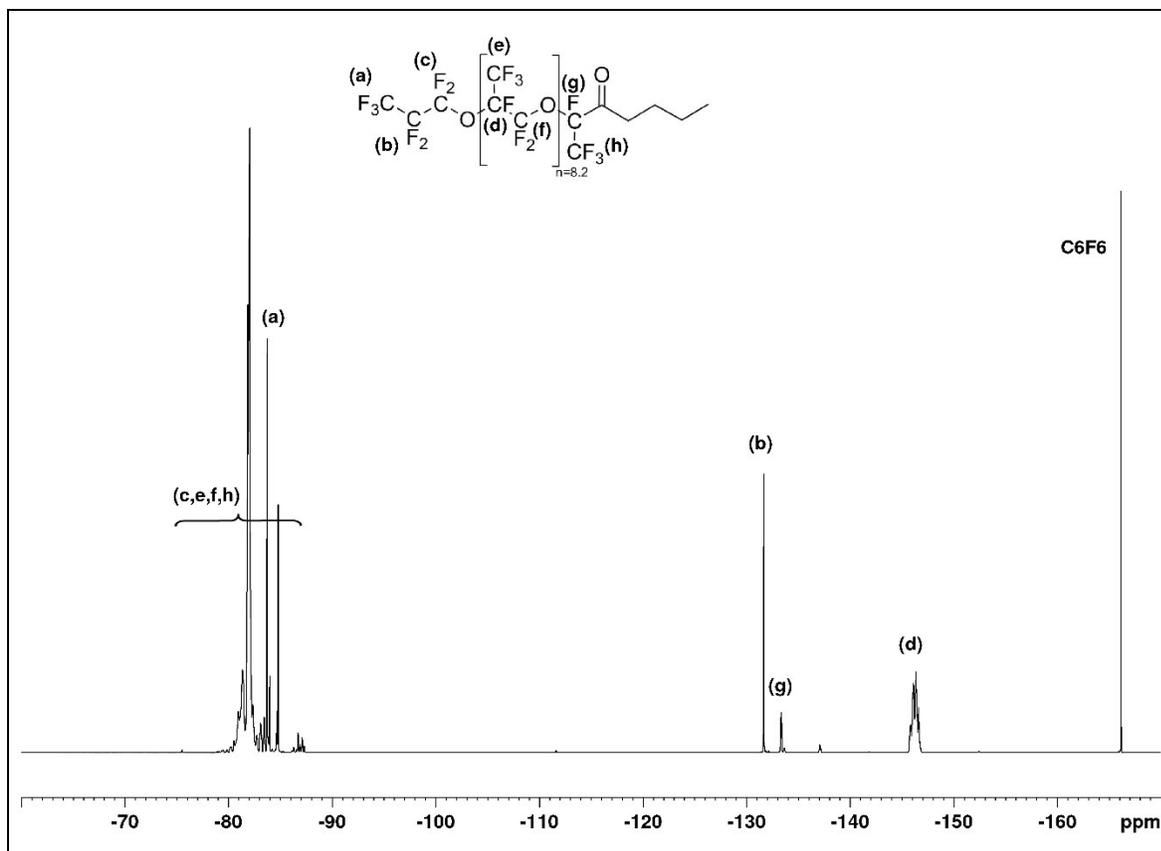


Figure 18:  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{C}_6\text{F}_6$ ) of oligo(HFPO) butyl ketone

#### B.7.b. Characterization of oligo(hexafluoropropylene oxide) phenyl ketone [1g]

Yield: 1.1g (52% Yield - 72% pure by  $^{19}\text{F}$  NMR)

$\delta$   $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{F}_6$ ,  $\text{C}_6\text{D}_6$ ): 7.85 (d, *o*-Ph, 2H), 7.38 (t, *m*-Ph, 1H), 7.23 (t, *p*-Ph, 2H)

$\delta$   $^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{F}_6$ ,  $\text{C}_6\text{D}_6$ ): 102.61 (dq,  $^1J_{\text{CF}} = 265.8$ ,  $^2J_{\text{CF}} = 35.6$  Hz,  $-\text{OCF}(\text{CF}_3)\text{CF}_2-$ ), 106.34 (tsex,  $^1J_{\text{CF}} = 265.437$ ,  $^2J_{\text{CF}} = 38.81$  Hz,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}$ ), 115.84 (qt,  $^1J_{\text{CF}} = 287.986$ ,  $^2J_{\text{CF}} = 30.875$  Hz,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}$ ), 117.35 (qd,  $^1J_{\text{CF}} = 287.85$ ,  $^2J_{\text{CF}} = 30.83$  Hz,  $-\text{OCF}(\text{CF}_3)\text{CF}_2-$ ), 127.77 (s,  $-\text{CF}(\text{CF}_3)\text{C}(\text{O})(\text{o-Ph})$ ), 129.29 (d,  $^3J_{\text{CF}} = 7.0696$  Hz,  $\text{CF}(\text{CF}_3)\text{C}(\text{O})(\text{m-Ph})$ ) 132.03(s,  $\text{CF}(\text{CF}_3)\text{C}(\text{O})(\text{p-Ph})$ ), 133.81(s,  $\text{CF}(\text{CF}_3)\text{C}(\text{O})(\text{ipso-Ph})$ ), 184.30 (d,  $^2J_{\text{CF}} = 28.63$  Hz,  $-\text{CF}(\text{CF}_3)\text{C}(\text{O})\text{Ph}$ ); oligo(HFPO)-Methyl Ester 158.82 (d,  $^2J_{\text{CF}} = 33.04$  Hz,  $-\text{CF}(\text{CF}_3)\text{C}(\text{O})\text{OCH}_3$ ), 52.64 (s,  $-\text{CF}(\text{CF}_3)\text{C}(\text{O})\text{OCH}_3$ )

$\delta$   $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{F}_6$ ,  $\text{C}_6\text{D}_6$ , 25 °C): -82.11 (s,  $-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}$ -), -83.77 (s,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}$ -, 3F), -129.92 (s,  $-\text{CF}(\text{CF}_3)\text{C}(\text{O})\text{Ph}$ , 1H), -131.64 (s,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}$ -, 2F), -133.30(s,  $\text{CF}(\text{CF}_3)\text{C}(\text{O})\text{OMe}$  146.27 (m,  $-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}$ -, 1F)

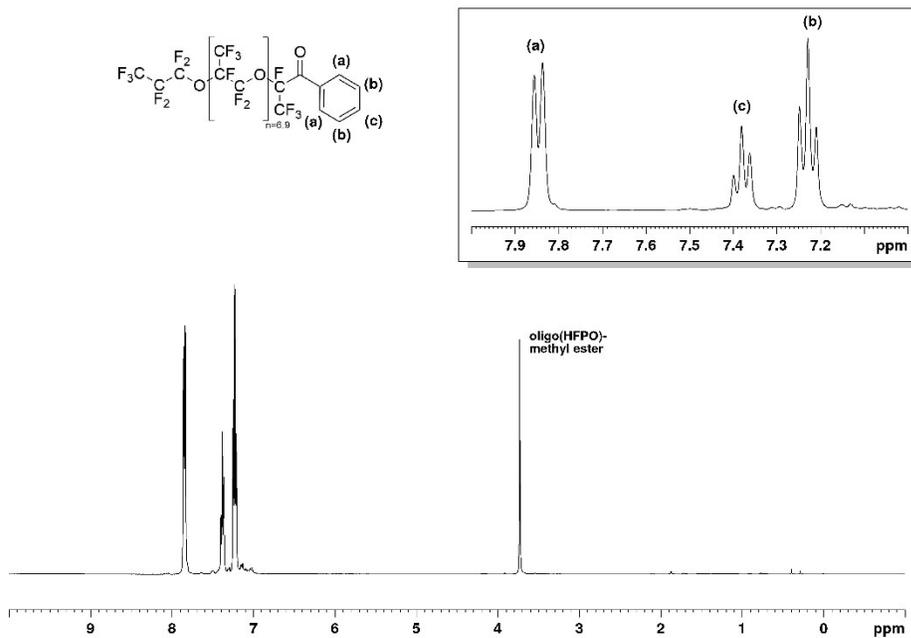


Figure 19:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_6\text{F}_6$ ,  $\text{C}_6\text{D}_6$ ) of oligo(HFPO) phenyl ketone

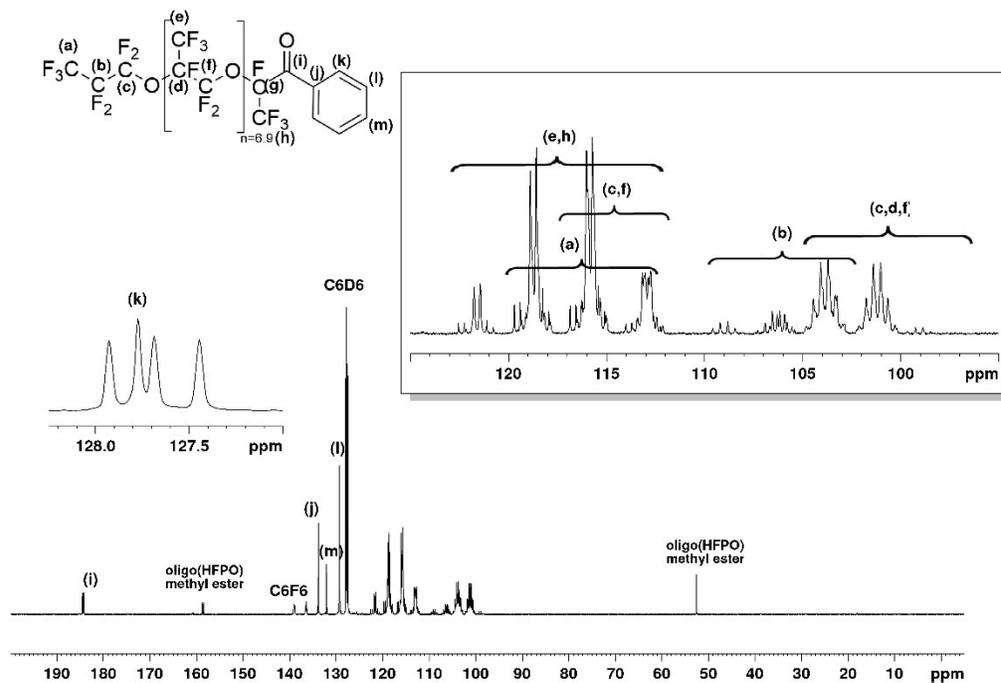


Figure 20:  $^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{C}_6\text{F}_6$ ,  $\text{C}_6\text{D}_6$ ) of oligo(HFPO) phenyl ketone

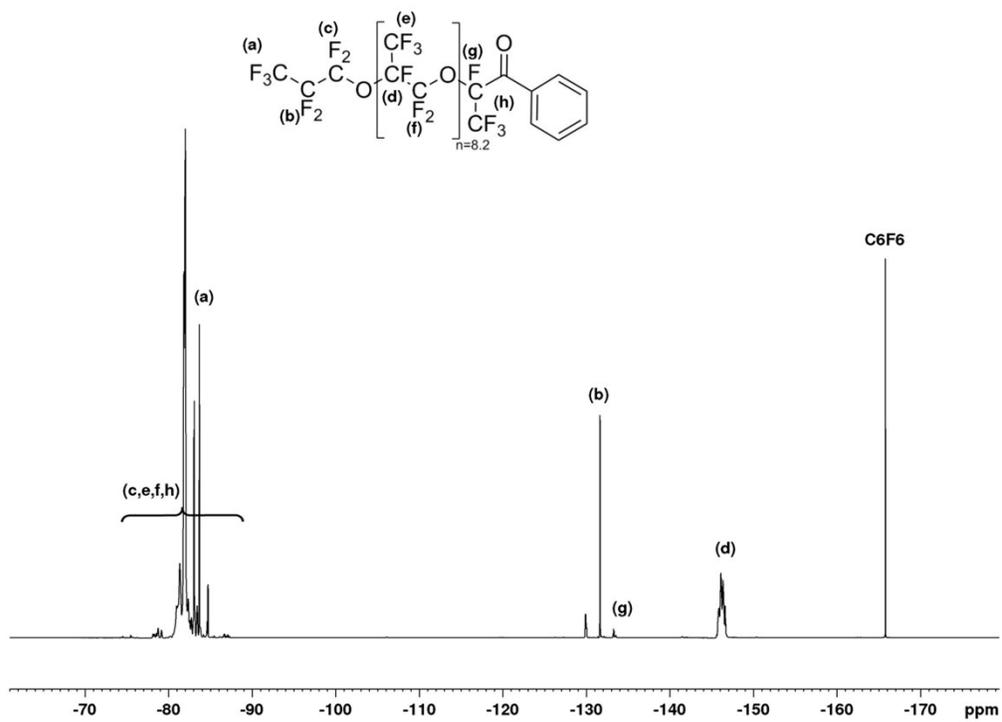


Figure 21:  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{C}_6\text{F}_6$ ,  $\text{C}_6\text{D}_6$ ) of oligo(HFPO) phenyl ketone

## B.8 Hexafluoropropylene (HFP) [S2]

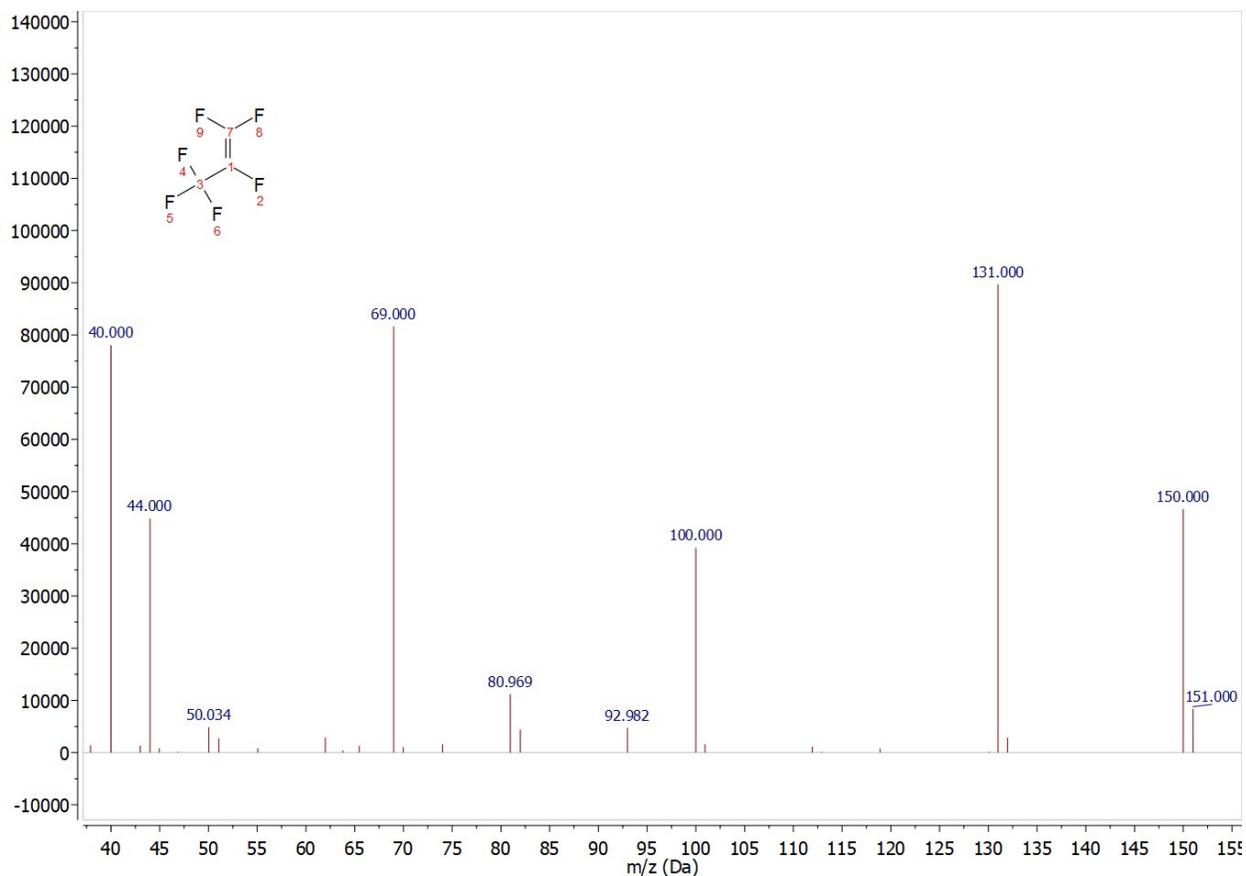


Figure 22: Experimental Electron Impact/Mass Spectrum (EI/MS) of Hexafluoropropylene

EI/MS: m/z 150 ( $M^+$ , 6.04%), 131.00 (11.61, M - F), 100.00 (5.08, M - CF<sub>2</sub>), 92.98 (0.62), 80.97 (1.45), 69.00 (10.26, CF<sub>3</sub>), 44.00 (5.39), 40 (8.52)

## B.9 Benzophenone (Ph<sub>2</sub>C(O)) [S3]

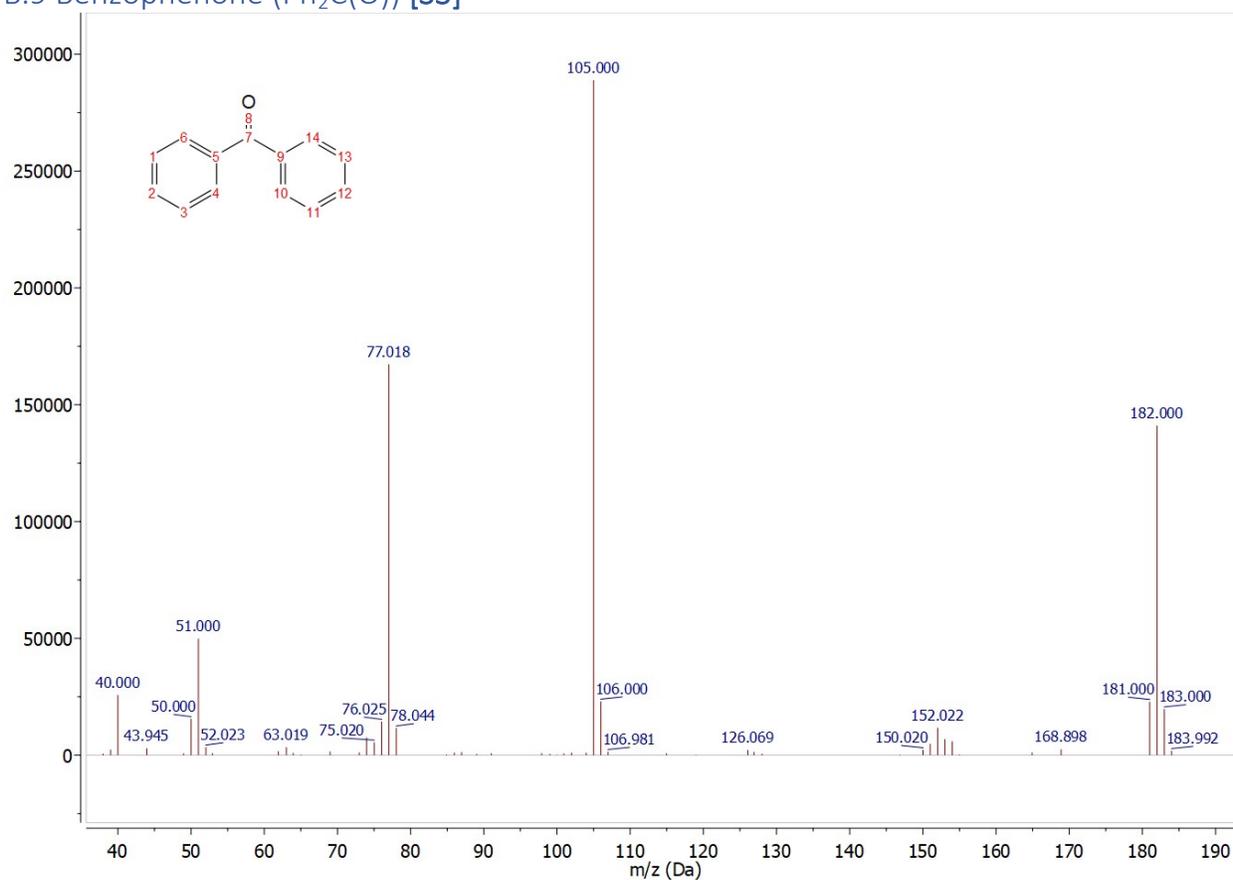


Figure 23: Experimental EI/MS of Benzophenone

EI/MS: 182.00 (M<sup>+</sup>, 49.17), 181.00 (M – H, 7.56), 169.00 (0.60), 152.00 (3.79), 126.10 (0.72), 106.00 (8.19), 105.00 (M – Ph), 98.00 (0.60), 78.10 (4.23), 77.00 (57.42), 76.10 (5.10), 75.10 (1.58), 74.00 (2.46), 63.00 (1.13), 52.00 (1.19), 51.00 (16.77), 50.00 (5.06), 40.00 (7.70)

## B.10 1,1,1,3,3-pentafluoro-2-phenyl-propyl-2-ene [S4]

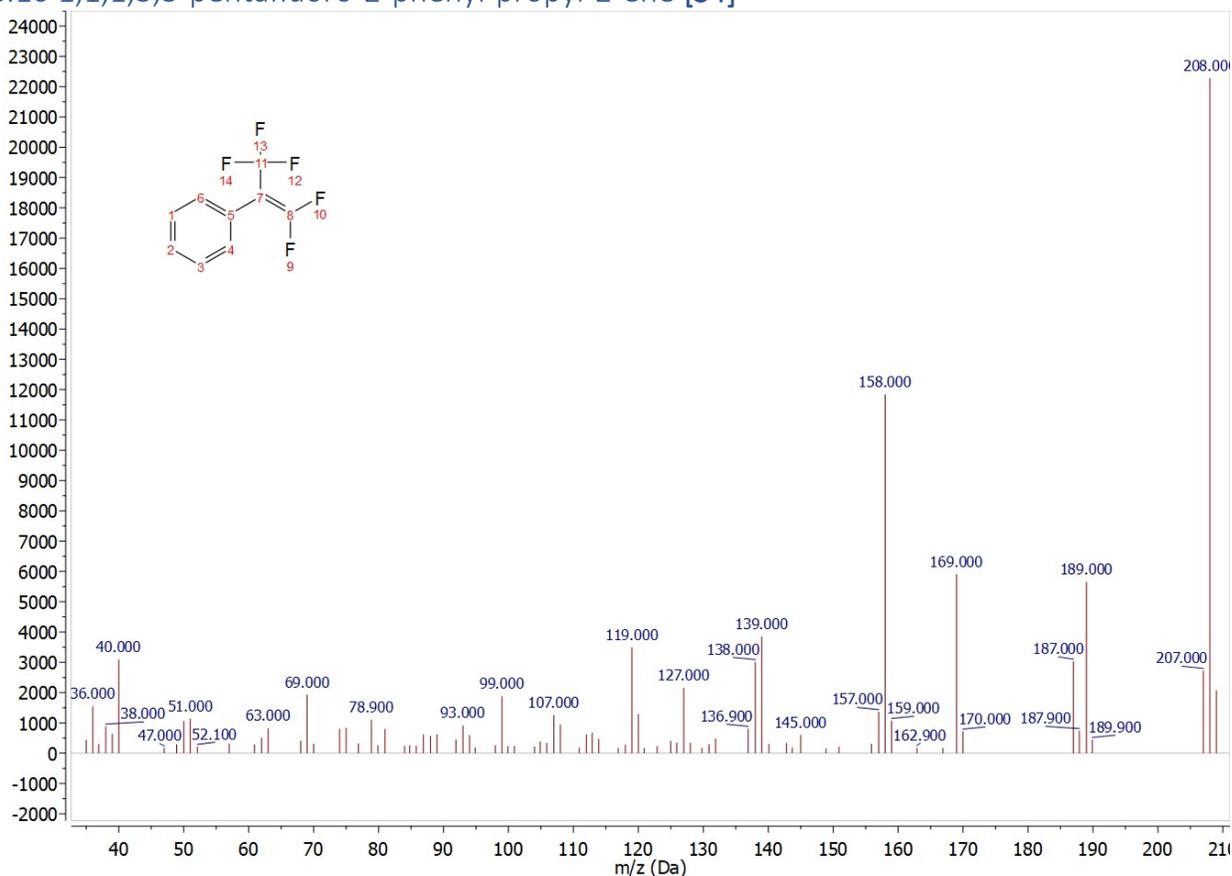


Figure 24: Experiment EI/MS of Phenyl Perfluoroisopropylene (Relative abundance omitted for clarity)

EI/MS: 208.979 ( $M^+ + 1$ , 9.33), 208.00 ( $M^+$ , 100), 207.00 (12.23), 189.900 (2.01), 189.00 (25.36), 187.00 (13.60), 187.90 (3.32), 170.00 (3.25), 169.00 (26.52), 166.90 (0.76), 162.90 (0.77), 159.00 (4.82), 158.00 (53.17), 157.00 (6.14), 150.90 (0.95), 145.00 (2.72), 140.10 (1.37), 139.00 (17.29), 138.00 (13.55), 136.90 (3.64), 131.90 (2.19), 130.90 (1.30), 129.80 (0.81), 128.00 (1.53), 127.00 (9.68), 125.90 (1.56), 125.00 (1.84), 122.90 (1.03), 120.90 (0.75), 120.00 (5.79), 119.00 (15.69), 118.00 (1.28), 116.90 (0.79), 113.90 (2.09), 112.90 (3.02), 112.00 (2.80), 110.90 (0.84), 108.00 (4.26), 107.00 (5.63), 105.90 (1.52), 104.90 (1.73), 104.00 (0.98), 100.90 (1.07), 99.90 (1.05), 99.00 (8.45), 98.00 (1.18), 94.90 (.083), 94.00 (2.68), 93.00 (4.10), 91.90 (2.03), 89.00 (2.82), 88.00 (2.54), 86.90 (2.7), 85.80 (1.14), 84.80 (1.18), 84.00 (1.09), 81.00 (3.58), 79.90 (1.20), 78.90 (4.94), 76.90 (1.45), 75.00 (3.77), 74.00 (3.61), 70.00 (1.40), 69.00 (8.68), 68.00 (1.84), 63.00 (3.70), 62.00 (2.28), 60.90 (1.31), 52.10 (0.97), 51.00 (5.10), 50.00 (4.76), 48.90 (1.30), 47.00 (0.79), 40.00 (13.88)

## References

<sup>1</sup> Bruchat, A. F., Chong, J. M., Nielsen, Nathan., *J. Organomet. Chem.*, **1997**, 542(2), 281-283

<sup>2</sup> Chen, L. S., Chen, Grace J., Tamborski, C., *J. Fluor. Chem.*, **1981**, 18(2), 117-129