Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplemental Information

A new oligo(hexafluoropropylene oxide)-*b*-oligo(ethylene oxide) block co-oligomeric surfactant obtained by radical reactions

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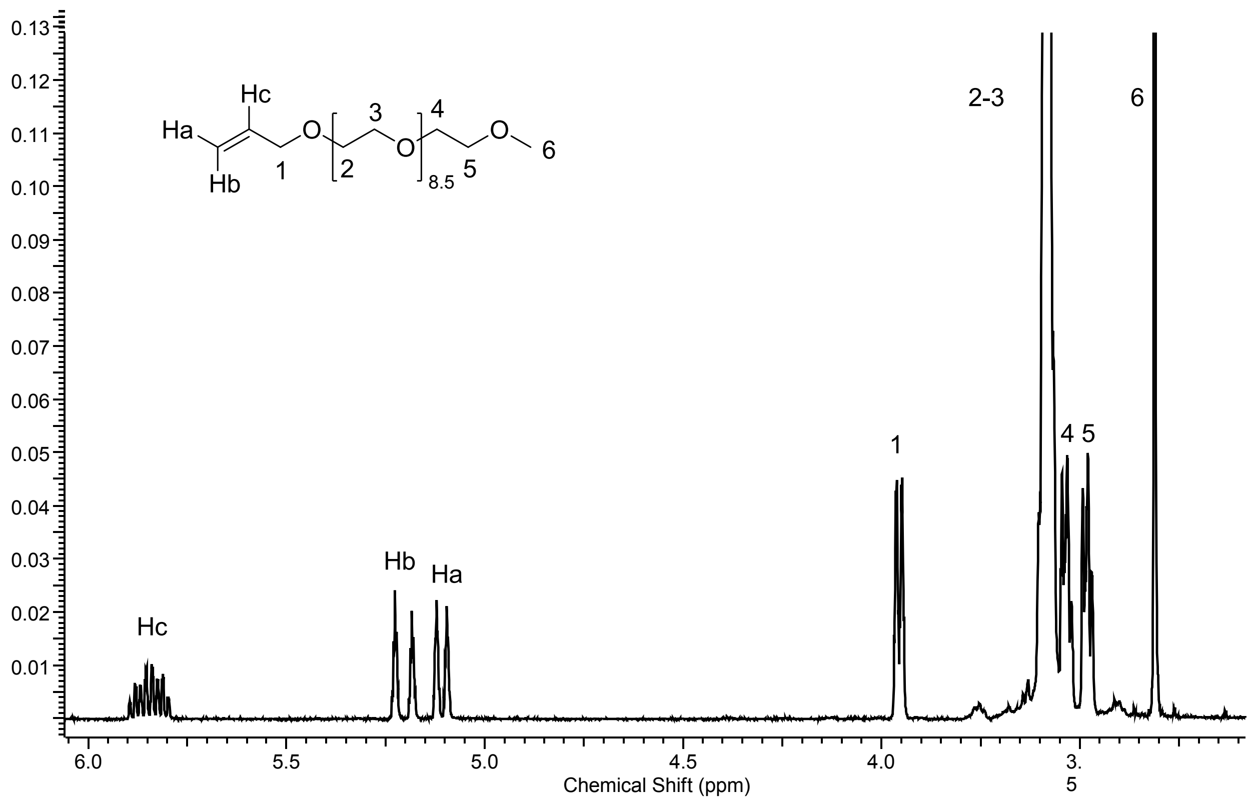


Figure S1: ^{1}H-NMR spectrum of Allyl-PEG-OCH$_3$.

^{1}H NMR (400 MHz, C_6D_6, 25°C) δ = 5.85 (ddt, CH$_a$H$_b$=C$\underline{H_c}$CH$_2$-, $^3J_{HcHb(trans)}$=17.34 Hz, $^3J_{HcHa(cis)}$=10.36 Hz, $^3J_{HcH(CH2)}$=5.81 Hz, 1H), 5.20 (ddt, CH$_a\underline{H_b}$=CH$_c$CH$_2$-, $^2J_{HbHa}$=1.77 Hz, $^3J_{HbHc(trans)}$=17.18 Hz, $^4J_{HbH(CH2)}$=1.77 Hz, 1H), 5.11 (dm, C$\underline{H_a}$H$_b$=CH$_c$CH$_2$-,$^3J_{HaHc(cis)}$=10.36 Hz, 1H), 3.96 (dm, CH$_a$H$_b$=CH$_c$C$\underline{H_2}$O-, $^3J_{H(CH2)Hc}$=5.56 Hz, 2H), 3.53 (t, -OC$\underline{H_2}$CH$_2$OCH3, $^3J_{HH}$=5.5 Hz, 2H), 3.55-3.61 (m,- CH$_2$O-, 19 X 2H), 3.31 (s, -OCH$_3$, $^4J_{HH}$=0.72 Hz, 3H), 3.48 (t, -C$\underline{H_2}$OCH$_3$, $^3J_{HH}$=5.5 Hz, 2H).

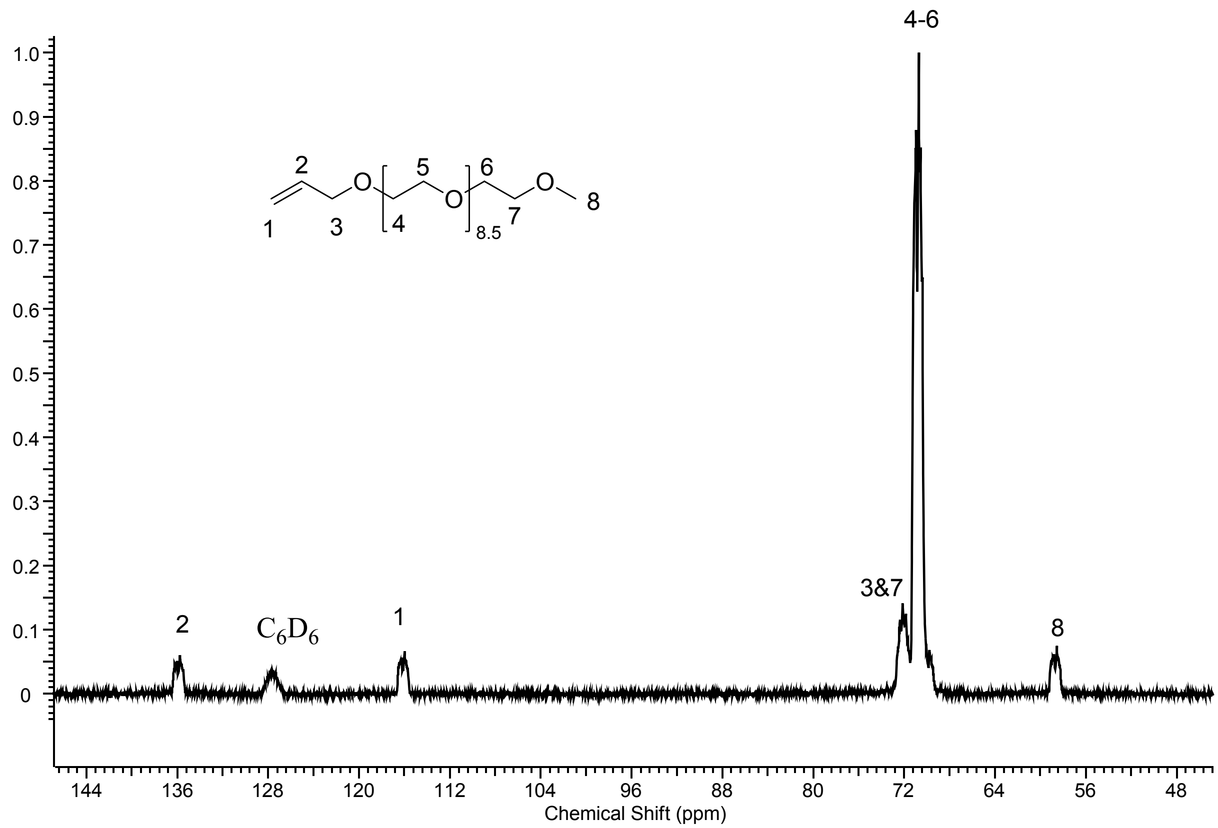


Figure S2: ^{13}C-NMR spectrum of Allyl-PEG-OCH$_3$.

^{13}C NMR (101 MHz, C_6D_6, 25°C) δ = 135.97 (s, 1C, –CH=), 116.0 (s, 1C, =CH$_2$), 72.07 (s, 1C, C̲H$_2$-allyl), 72.07 (s, 1C, C̲H$_2$–CH$_2$–OMe), 70.74 (s, 19 X 1C, -C̲H$_2$–O), 58.65 (s, 1C, C̲H$_3$).

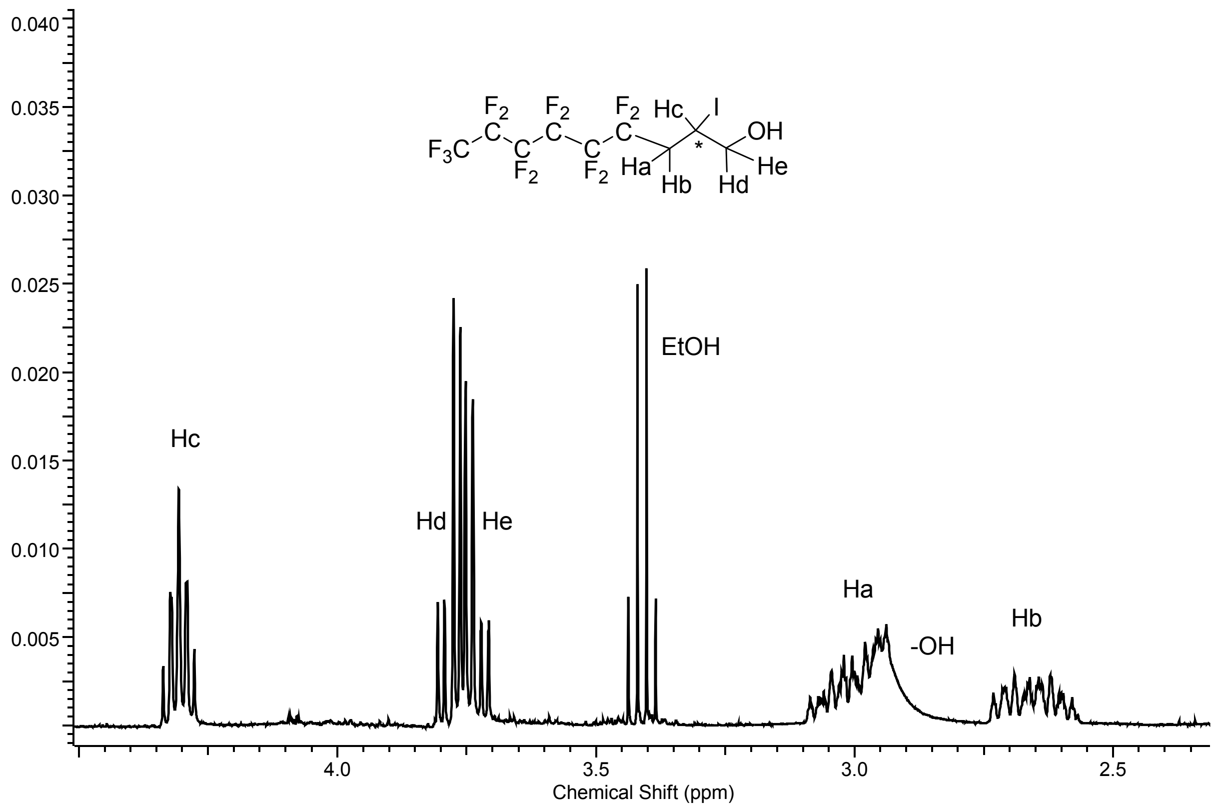


Figure S3: ^{1}H-NMR spectrum of $C_6F_{13}CH_2CHICH_2OH$ initiated by TBPPI.

^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 4.31 (quin, $-CH_2C\underline{H}ICH_2OH$, $^3J_{HH}$=6.57 Hz, 1H), 3.80, 3.74 ($-CH_2CHIC\underline{H_a}H_bOH$, $^2J_{HaHb}$=12.13 Hz, 1H), 3.78, 3.73(d, $-CH_2CHICH_a\underline{H_b}OH$, $^2J_{HbHa}$=12.13 Hz, 1H) 3.01 (m, $-CF_2C\underline{H_a}H_bCHI-$, 1H), 2.65 (m, $-CF_2CH_a\underline{H_b}CHI-$, 1H), 2.95($-CH_2O\underline{H}$, 1H).

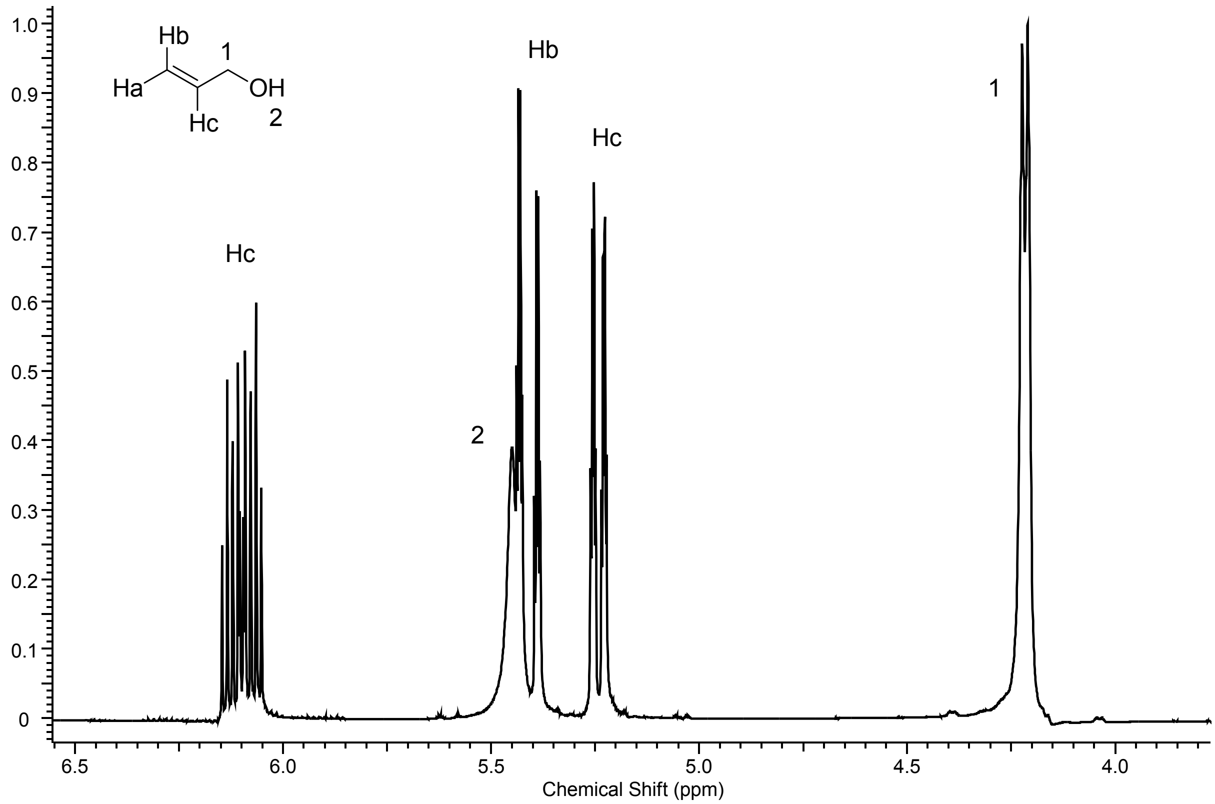


Figure S4. ^{1}H-NMR spectrum of allyl alcohol (CH_2=$CHCH_2OH$).

^{1}H NMR (400 MHz, Neat, 25°C) δ = 6.10 (ddt, CH_aH_b=$C\underline{H_c}CH_2$-, $^3J_{HcHb(trans)}$=16.84 Hz, $^3J_{HcHa(cis)}$=10.61 Hz, $^3J_{HcH(CH2)}$=5.05 Hz, 1H), 5.44 (broad, -O$\underline{H}$, 1H), 4.22 (dt, CH_aH_b=$CH_cC\underline{H_2}O$-, $^3J_{H(CH2)Hc}$=5.31 Hz, $^4J_{H(CH2)H(a+b)}$ = 1.52 Hz, 2H), 5.41 (ddt, $CH_a\underline{H_b}$=CH_cCH_2-, $^2J_{HbHa}$=1.77 Hz, $^3J_{HbHc(trans)}$=17.20 Hz, $^4J_{HbH(CH2)}$=1.77 Hz, 1H), 5.24 (ddt, $C\underline{H_a}H_b$=CH_cCH_2-,$^2J_{HaHb}$=1.52, $^3J_{HaHc(cis)}$=10.54 Hz, $^4J_{HaH(CH2)}$=1.52, 1H).

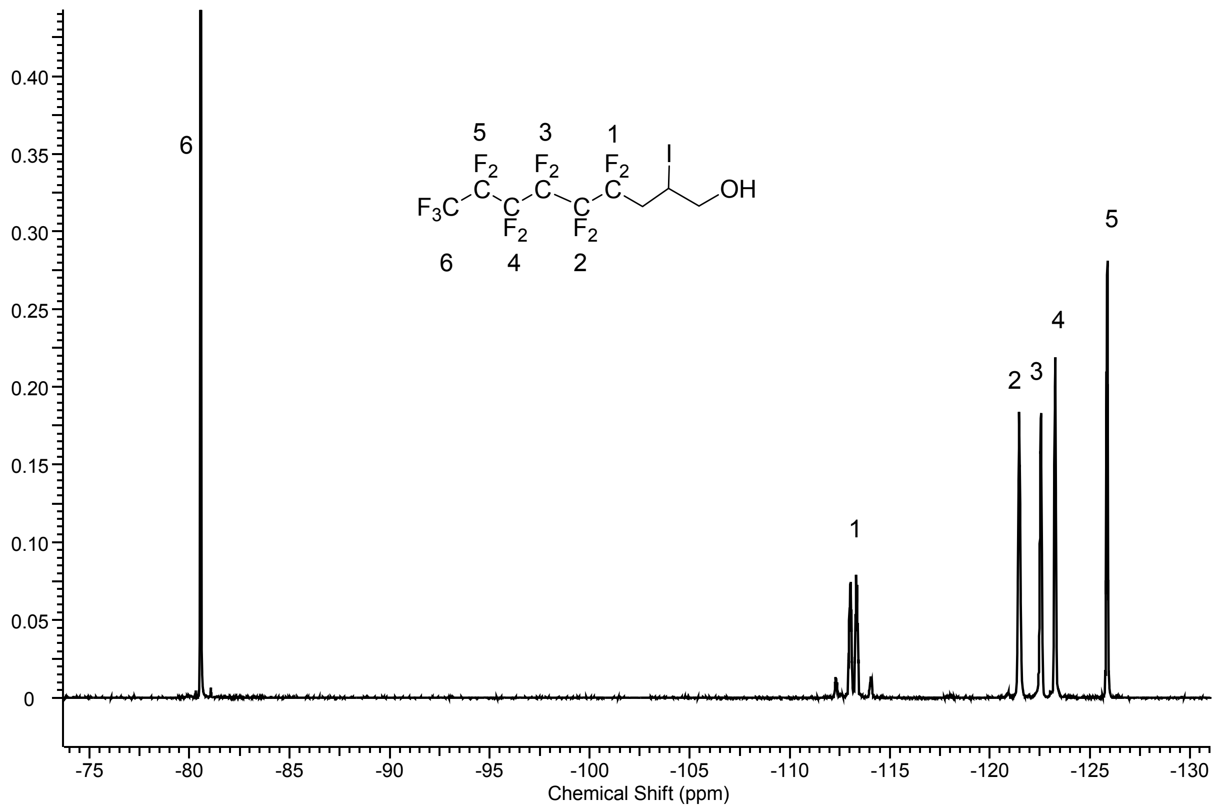


Figure S5: ^{19}F-NMR spectrum of $C_6F_{13}CH_2CHICH_2OH$ initiated by TBPPI.

^{19}F NMR (376.41 MHz, $CDCl_3$, 25°C): δ = -81.06 (CF3-, $^3J_{FF}$=10.33, $^4J_{FF}$=2.30 Hz, 3F), -126.36(m, $CF_3CF_2(CF_2)_4CH_2$-, 2F), -123.77(m, -$CF_2(CF_2)_3CH_2$-, 2F), -123.05 (m, -$CF_2(CF_2)_2CH_2$-, 2F), -121.97(m, -$CF_2CF_2CH_2$-, 2F), -113.17, -114.20 (dm, $^2J_{FF}$ =144.68 Hz, 2F).

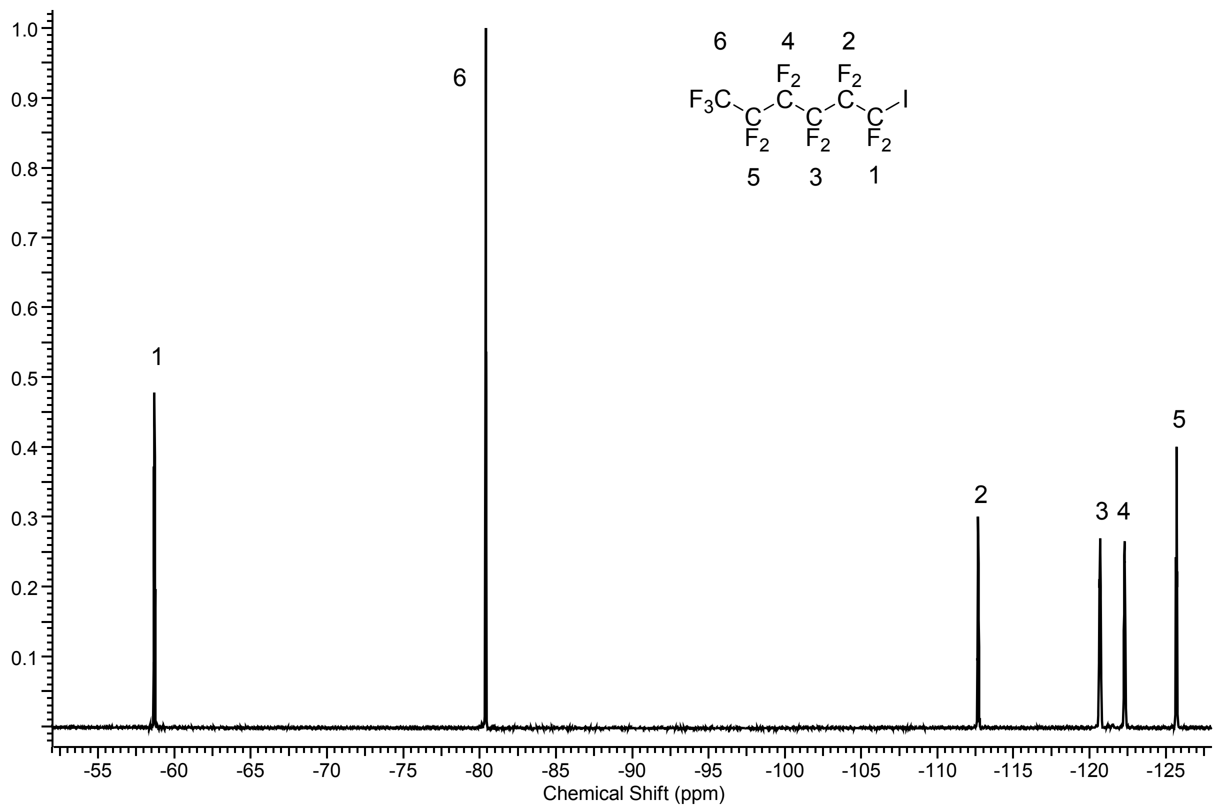


Figure S6: ^{19}F-NMR spectrum of 1-iodo-perfluorohexane ($C_6F_{13}I$).

^{19}F NMR (376.41 MHz, neat, 25°C): δ = -59.19(m, CF2I, 2F), -80.19(tm, C$\underline{F}_3$-, $^3J_{FF}$ =9.4 Hz, 3F), -126.19(m, $CF_3C\underline{F}_2(CF_2)_4I$, 2F), -122.79(m, -$C\underline{F}_2(CF_2)_3I$, 2F), -121.17 (m, -$C\underline{F}_2(CF_2)_2I$, 2F), -113.17(m, -$C\underline{F}_2CF_2I$, 2F)

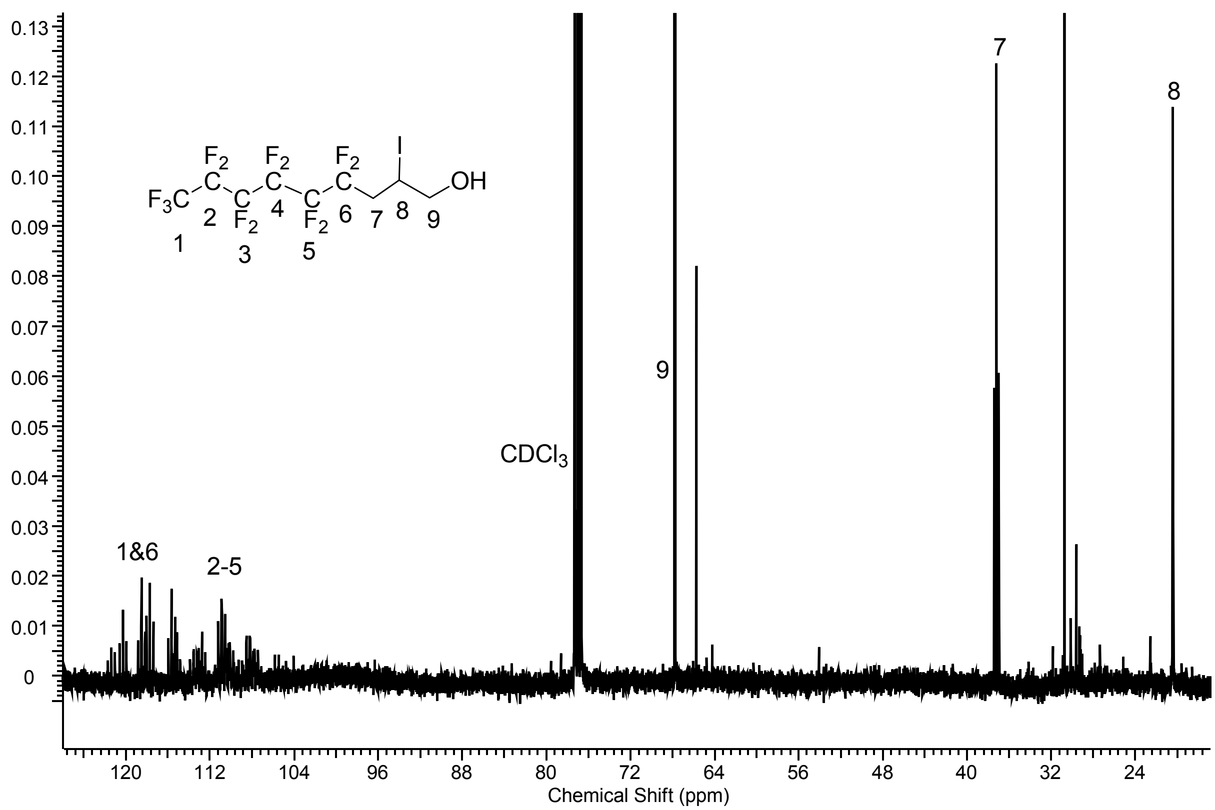


Figure S7: ^{13}C-NMR spectrum of $C_6F_{13}CH_2CHICH_2OH$ initiated by TBPPI.

^{13}C NMR (101 MHz, $CDCl_3$, 25°C) δ = 118.49 (qt, <u>C</u>F_3CF_2- $^1J_{CF}$=288.34 Hz, $^2J_{CF}$= 33.66 Hz), 117.70 (tt, -CF_2<u>C</u>F_2CH_2-, $^1J_{CF}$=257.61 Hz, $^2J_{CF}$ = 32.20 Hz), 110.87 (m, -CF_2<u>C</u>F_2CF_2-, 4C), 67.78 (s, -<u>C</u>H_2OH, 1C), 37.18 (t, -CF_2<u>C</u>H_2CHI-, $^2J_{CF}$ = 20.49 Hz, 1C), 20.4 (s, -CH_2<u>C</u>HICH_2OH, 1C).

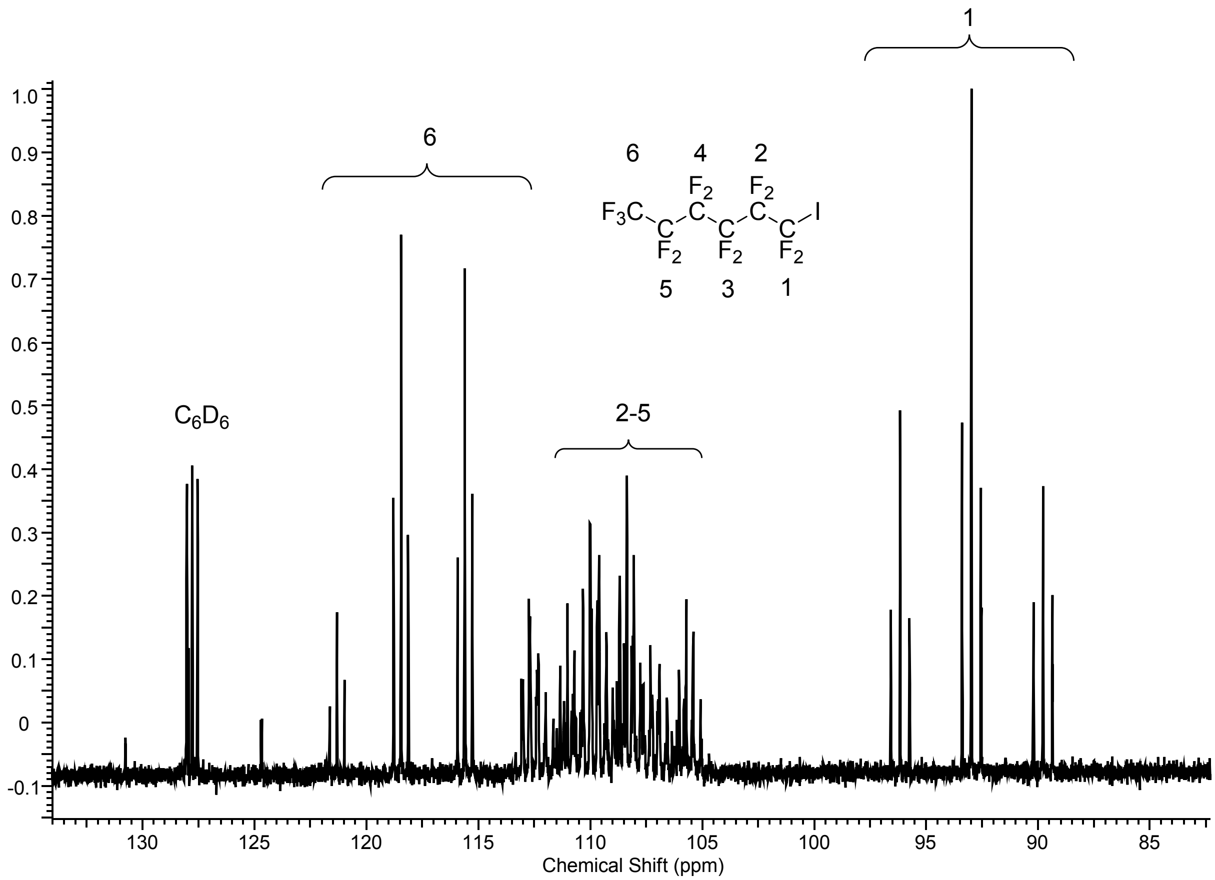


Figure S8: ^{13}C-NMR spectrum of 1-iodo-perfluorohexane ($C_6F_{13}I$).

^{13}C NMR (101 MHz, C_6D_6 capillary, 25°C) δ = 117.03 (qt, $\underline{C}F_3$CF2-, $^{1}J_{CF}$ = 287.61 Hz, $^{2}J_{CF}$ = 32.93 Hz, 1C), 110.01 (tquin, -$CF_2\underline{C}F_2CF_2$-, $^{1}J_{CF}$ = 275.17 Hz, $^{2}J_{CF}$ = 32.93 Hz, 1C), 109.82(tsext, $CF_3\underline{C}F_2CF_2$-, $^{1}J_{CF}$ = 277.37 Hz, $^{2}J_{CF}$ = 33.67 Hz, 1C), 108.49 (tquin, -$CF_2\underline{C}F_2CF_2$-, $^{1}J_{CF}$ = 270.78 Hz, $^{2}J_{CF}$ = 33.66 Hz, 1C), 108.36 (tquin, -$CF_2\underline{C}F_2CF_2$-, $^{1}J_{CF}$ = 265.66 Hz, $^{2}J_{CF}$ = 32.20 Hz, 1C), 92.97 (tt, $I\underline{C}F_2CF_2$-, $^{1}J_{CF}$ = 320.54 Hz, $^{2}J_{CF}$ = 42.45 Hz, 1C).

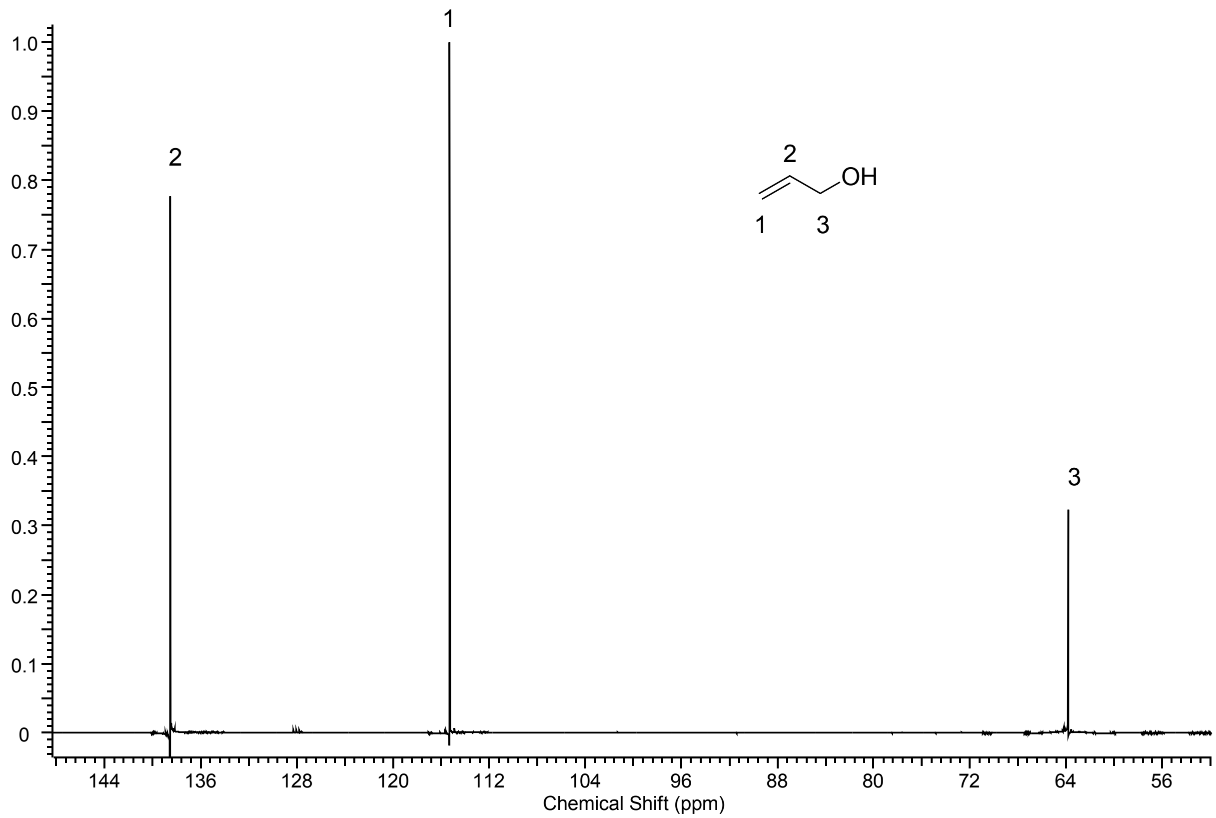


Figure S9: ^{13}C-NMR spectrum of allyl alcohol (CH_2=$CHCH_2OH$).

^{13}C NMR (101 MHz, C_6D_6, 25°C) δ = 138.53 (s, CH_2=$\underline{C}H_2CH_2OH$, 1C), 115.26 (s, $\underline{C}H_2$=CH_2CH_2OH, 1C), 63.8(s, CH_2=$CH_2\underline{C}H_2OH$, 1C)

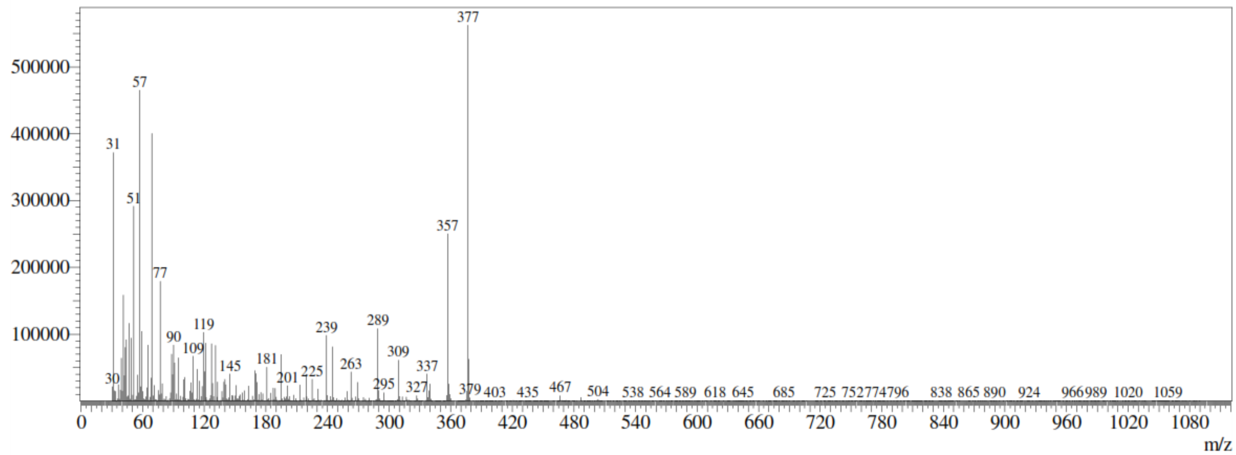


Figure S10: Electron Impact (EI) Quadrople Mass Spectrum of $C_6F_{13}CH_2CHICH_2OH$.

504 m/z = $C_6F_{13}CH_2CHICH_2OH$

377 m/z = $C_6F_{13}CH_2CHICH_2OH$ -iodide

357 m/z = $C_6F_{13}CH_2CHICH_2OH$ -iodide -HF

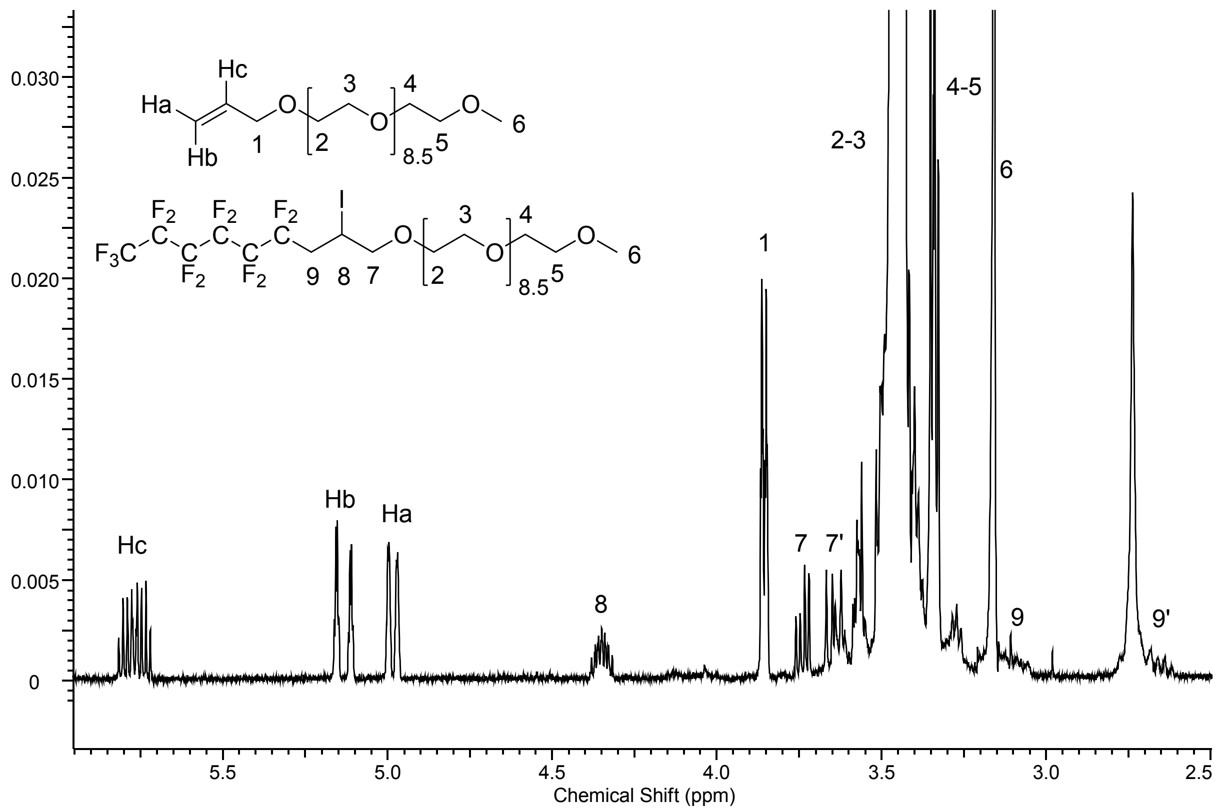


Figure S11: ^{1}H-NMR spectrum of $C_6F_{13}CH_2CHICH_2O(CH_2CH_2O)_{9.5}CH_3$ (37.4% purity).

1H NMR (400 MHz, $CDCl_3$, 25 °C): 4.35 (m, -$CH_2C\underline{H}ICH_2OH$, 1H), 3.80, 3.74 (-$CH_2CHIC\underline{H}_aH_bO$-, $^2J_{HaHb}$=10.86 Hz, 1H), 3.65, 3.64(d, -$CH_2CHICH_a\underline{H}_eOH$, $^2J_{HbHa}$=10.86 Hz, 1H) 3.16 (s, -OCH_3, $^4J_{HH}$=0.72 Hz, 3H), 3.35 (t, -$OC\underline{H}_2CH_2OCH3$, $^3J_{HH}$=5.3 Hz, 2H), 3.33 (t, -$C\underline{H}_2OCH_3$, $^3J_{HH}$=6.3 Hz, 2H), 3.5-3.4 (m, -CH_2O-, 19 X 2H), 3.14-3.03 (m, -$CF_2C\underline{H}_aH_bCHI$-, 1H), 2.70-2.59 (m, $CF_2CH_a\underline{H}_bCHI$-, 1H).

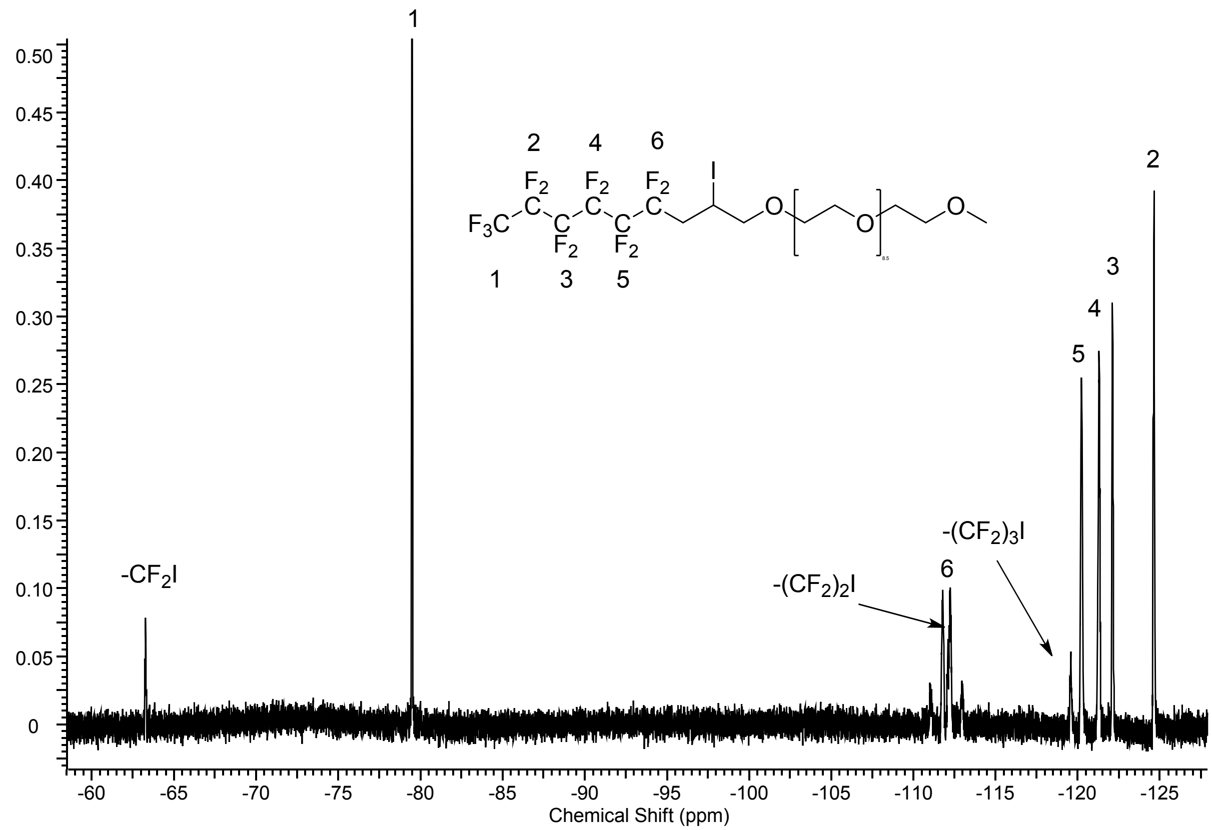


Figure S12: ^{19}F-NMR spectrum of $C_6F_{13}CH_2CHICH_2O(CH_2CH_2O)_{9.5}CH_3$

^{19}F NMR (376.41 MHz, DMSO capillary, 25°C): δ = -80 (t, $C\underline{F}_3$-, $^3J_{FF}$ =9.4 Hz, 3F), -112.24 (d, -$CF_aF_bCH_2$- , $^2J_{FaFb}$=273.06 Hz, 1F),-112.83 (d, -$CF_aF_bCH_2$- , $^2J_{FbFa}$=273.06 Hz, 1F), 2F), -120.73 (m, -$C\underline{F}_2CF_2CH_2$-, 2F), -121.78(m, -$C\underline{F}_2(CF_2)_2CH_2$-, 2F), -122.62 (m, $C\underline{F}_2(CF_2)_3CH_2$-, 2F), -125.15 (s, $CF_3C\underline{F}_2(CF_2)_4CH_2$-); *impurity*: -63.78(m, CF_2I, 2F), -112.59(m, -$C\underline{F}_2CF_2I$, -120.08 (m, -$(CF_2)_2I$, 2F).

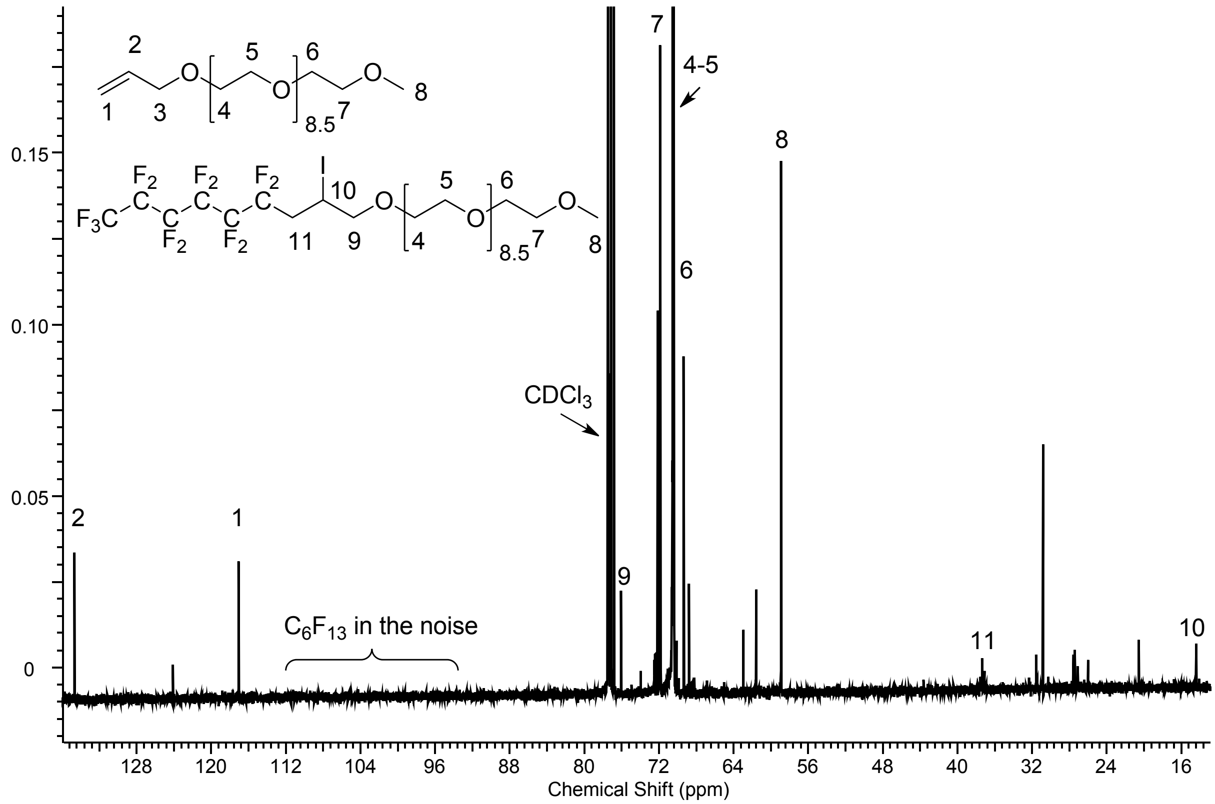
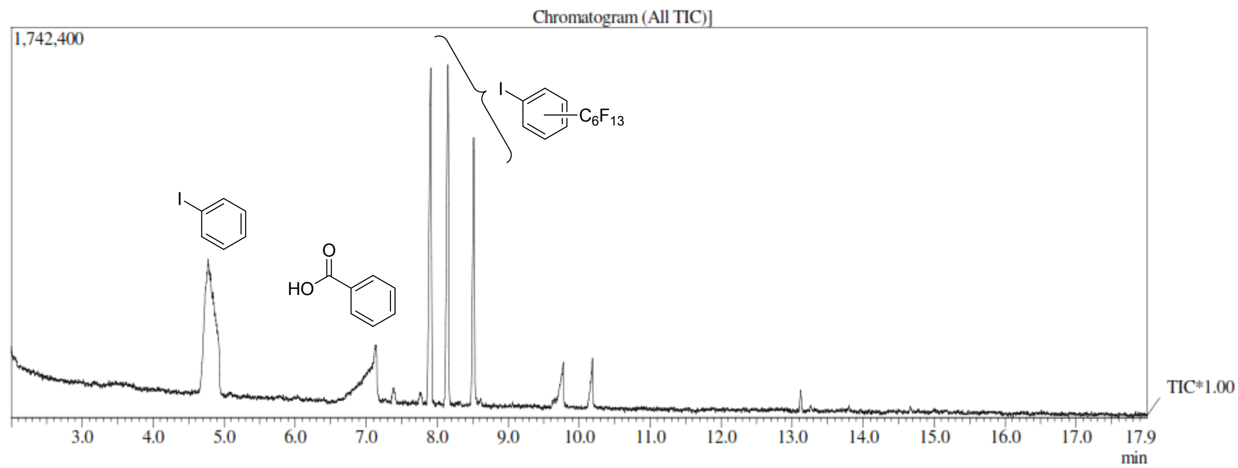


Figure S13: ^{13}C-NMR spectrum of $C_6F_{13}CH_2CHICH_2O(CH_2CH_2O)_{9.5}CH_3$

^{13}C NMR (101 MHz, CDCl3 capillary, 25°C) δ = 76.05 (s, -CHI$\underline{C}H_2$O-, 1C), 71.85 (s, -$\underline{C}H_2$OMe, 1C), 70.47 (s, -O$\underline{C}H_2$-, 19 X 1C), 70.40 (s, -O$\underline{C}H_2CH_2$OMe), 58.92 (s, -O$\underline{C}H_3$, 1C), 14.39 (s, -$CH_2\underline{C}HICH_2$O-, 1C), 37.34 (t, $^2J_{CF}$ = 20.83 Hz,-$CF_2\underline{C}H_2$CHI-, 1C), Impurities: 134.67 (s, 1C, –CH=), 117.05 (s, 1C, =CH_2), 70.60 (s, 1C, $\underline{C}H_2$-allyl).

(A)



(B)

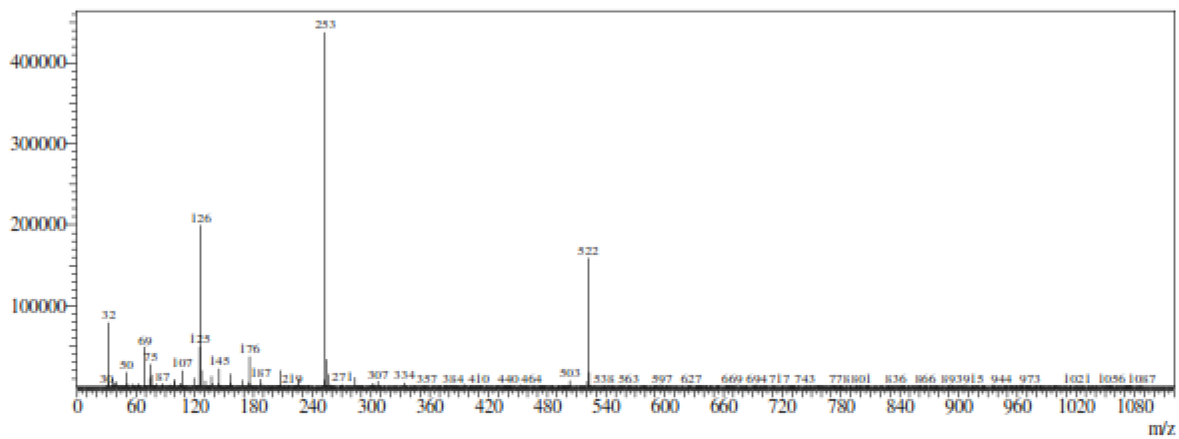


Figure S14. Gas Chromatography/mass spectrometry of the reaction of $C_6F_{13}I$ with BPO. (A) Chromatograpy of products, (B) Mass Spectrum of $C_6F_{13}PhI$ where 126, 253, and 522 m/z are $PhCF_2$+, $IPhCF_2$+, and $C_6F_{13}PhI$, respectively.

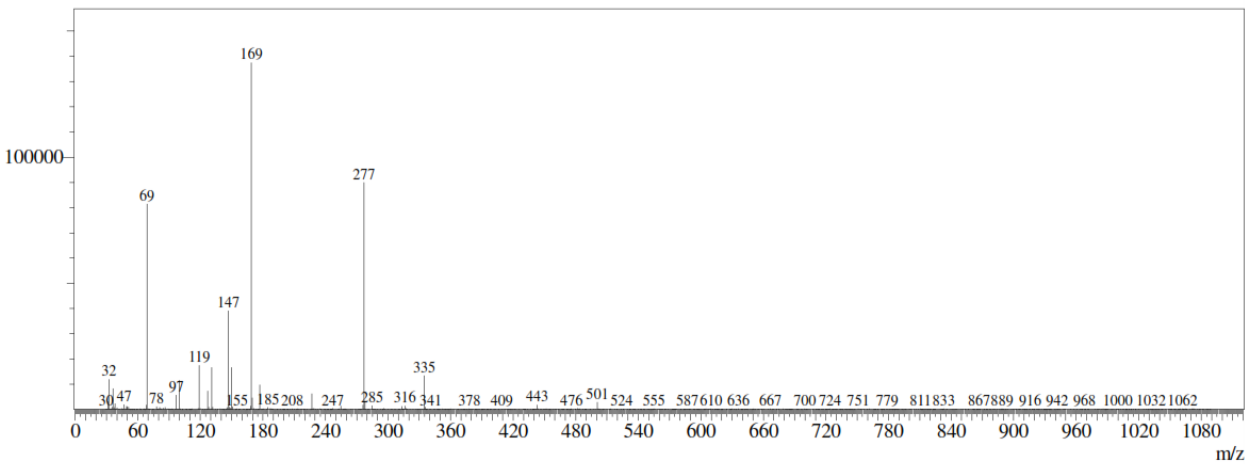


Figure S15: Electron Impact (EI) Quadrople Mass Spectrum of 1-iodo-2-oligo(hexafluoropropylene oxide)perfluoropropane ($F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2I$).

335 m/z = $CF_3CF_2CF_2OCF(CF_3)CF_2+$

277 m/z = $+CF(CF_3)CF_2I$

169 m/z/= $CF_3CF_2CF_2+$

69 m/z = CF_3+

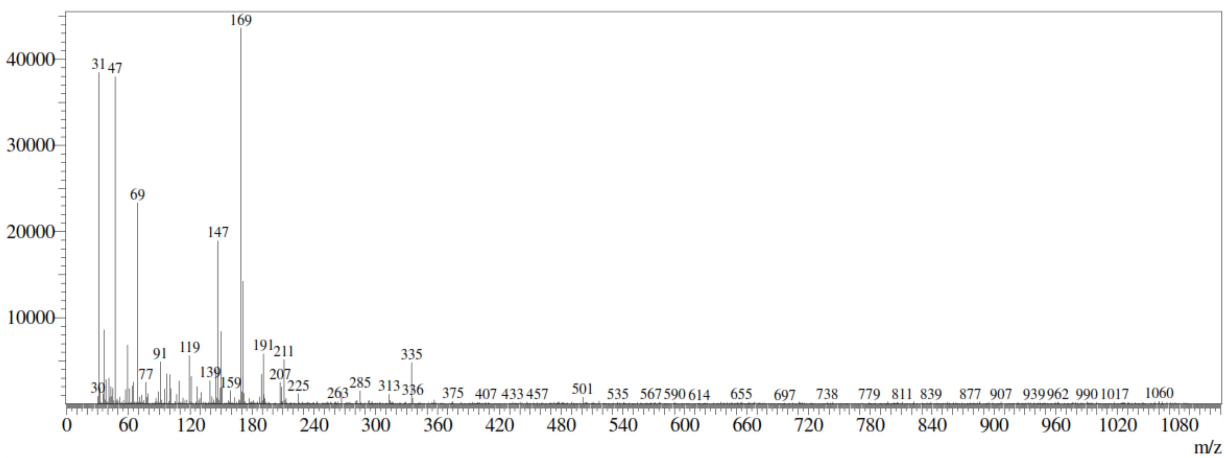


Figure S16: Electron Impact (EI) Quadrople Mass Spectrum of $F[CF(CF_3)CF_2O]_{8.9}CFCF_3CF_2CH_2CHICH_2OH$.

31m/z = $+CH_2OH$; 207 m/z = $+CF(CF_3)CF_2CH_2CHICH_2OH$ -HI

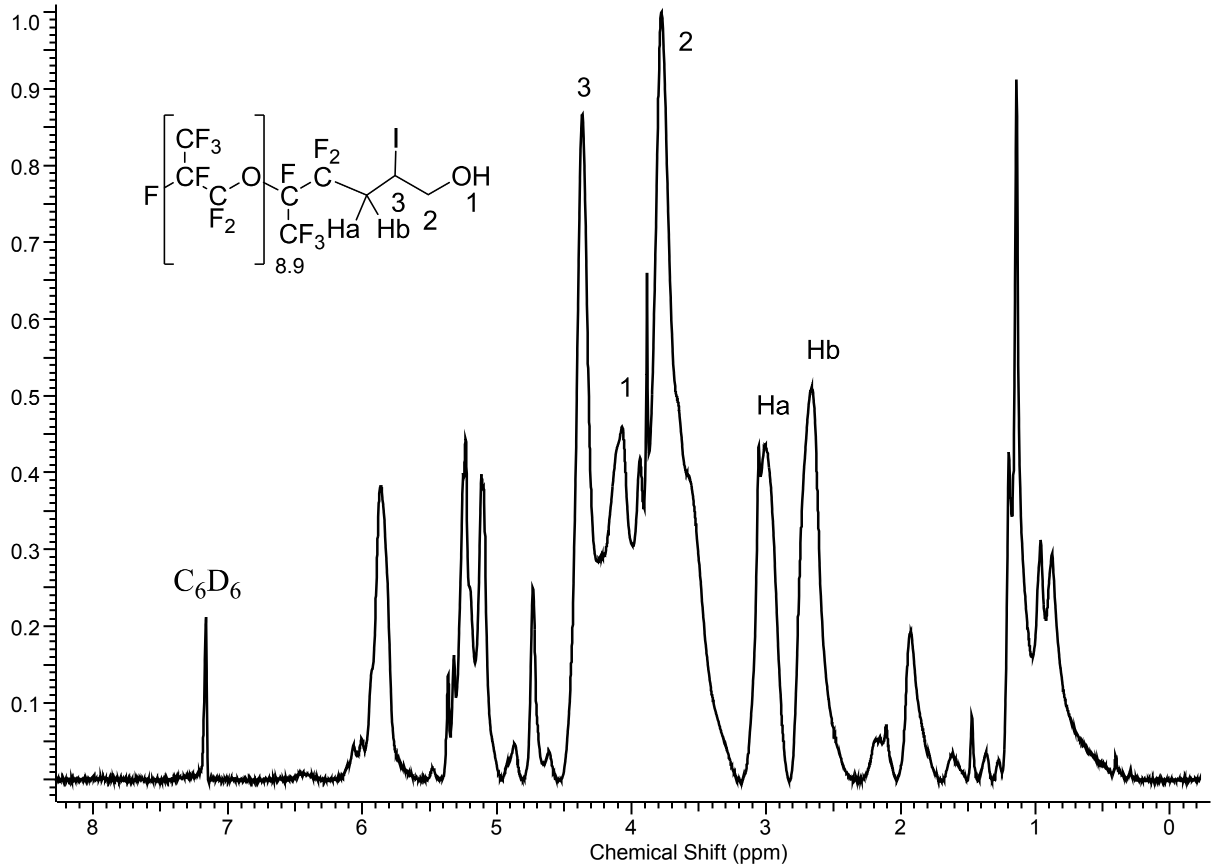


Figure S17: ^{1}H-NMR spectrum of F[CF(CF$_3$)CF$_2$O]$_{9.68}$CFCF$_3$CF$_2$CH$_2$CHICH$_2$OH initiated by TBPPI.

(TBPPI): ^{1}H NMR (400 MHz, C_6D_6 capillary, 25°C): δ = 4.4 (s, -CH$_2$C*H̲*ICH$_2$OH, 1H), 4.21(s,-CH$_2$O*H̲*, 1H), 3.81 (-CH$_2$CHIC*H̲$_2$*OH,2H), 2.98 (m, -CF$_2$C*H̲$_a$*H$_b$CHI-, 1H), 2.72 (m, -CF$_2$CH$_a$*H̲$_b$*CHI-, 1H).

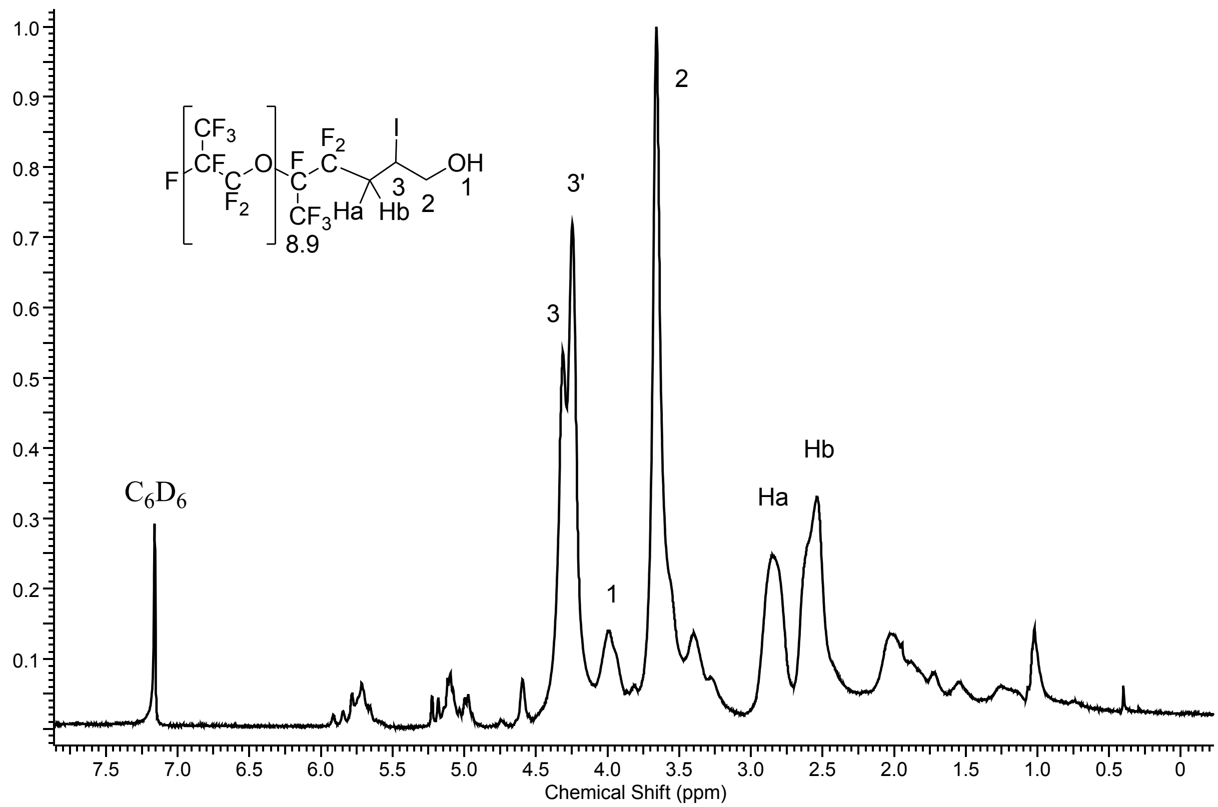


Figure S18: ^{1}H-NMR spectrum of $F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2CH_2CHICH_2OH$ initiated by AIBN.

(AIBN): ^{1}H NMR (400 MHz, C_6D_6 capillary, 25°C): δ = 4.31, 4.25 (s, $-CH_2C\underline{H}ICH_2OH$, 1H), 3.99(s,-$CH_2O\underline{H}$, 1H), 3.66 ($-CH_2CHIC\underline{H_2}OH$,2H), 2.84 (m, $-CF_2C\underline{H_a}H_bCHI-$, 1H), 2.54 (m, $-CF_2CH_a\underline{H_b}CHI-$, 1H).

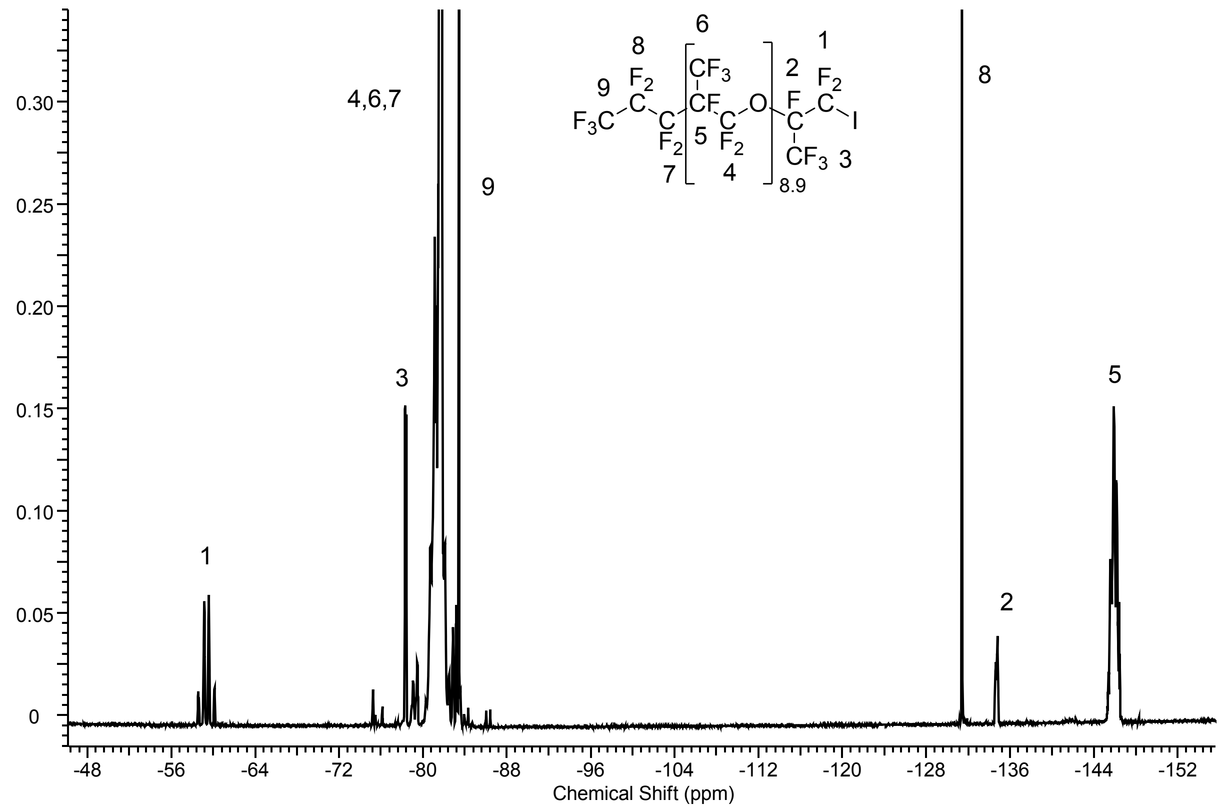


Figure S19: ^{19}F-NMR spectrum of 1-iodo-2-oligo(hexafluoropropylene oxide)perfluoropropane($F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2I$).

^{19}F NMR (376.41 MHz, C_6D_6, 25°C): δ = -59.68, -60.64(s, $-CF_aF_bI$, $^2J_{FF}$ =212.25 Hz, 2F), -79.15 (d, -$CF(C\underline{F}_3)CF_2I$, $^3J_{FF}$= 51.63Hz, 3F), -79 to -84 (-$[CF(C\underline{F}_3)C\underline{F}_2O]$-), -82.54 ($CF_3CF_2C\underline{F}_2O$-, 2F), -84.25 (s, $C\underline{F}_3CF_2CF_2O$- , 3F), -132.21 (s, $CF_3C\underline{F}_2CF_2$-, 2F), -135.51(s, -$C\underline{F}(CF_3)CF_2I$, 1F), -146.72 (m, -$[C\underline{F}(CF_3)CF_2O]$-, 8.9 x 1F).

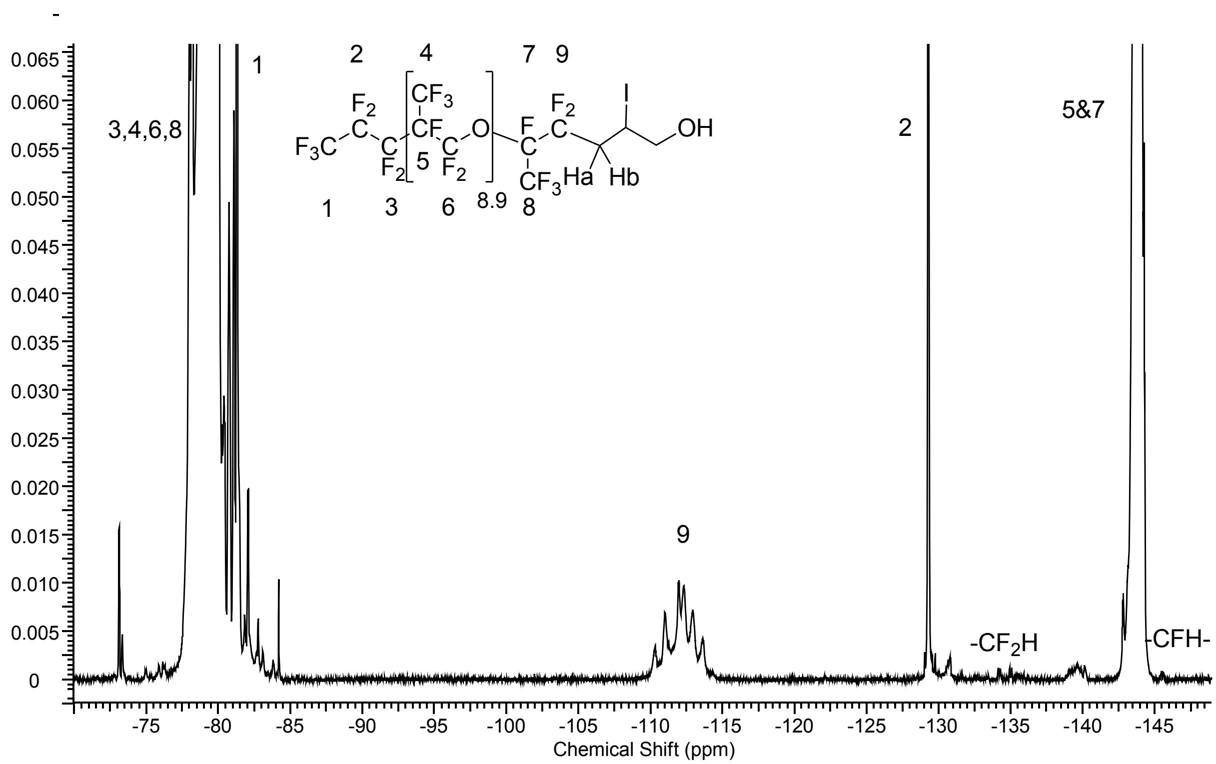


Figure S20: ^{19}F-NMR spectrum of F[CF(CF$_3$)CF$_2$O]$_{8.9}$CF(CF$_3$)CF$_2$CH$_2$CHICH$_2$OH initiated by TBPPI.

^{19}F NMR (376.41 MHz, C_6D_6, 25°C): δ = -80 to -85 (m, CF(C$\underline{F}_3$)C$\underline{F}_2$O-), -80.15 (s, C$\underline{F}_3$CF$_2$CF$_2$O- , 3F), -81.80 (s, CF$_3$CF$_2$C$\underline{F}_2$O-, 2F), -110.92 ($^2J_{FF}$ = 262.73Hz), -112.54 ($^2J_{FF}$ = 237.49Hz), -113.99 ($^2J_{FF}$ = 261.58Hz), -129.80 (s, CF$_3$C$\underline{F}_2$CF$_2$-, 2F), -146.80 (m, -C$\underline{F}$(CF$_3$)CF$_2$-, 8.9 x 1F).

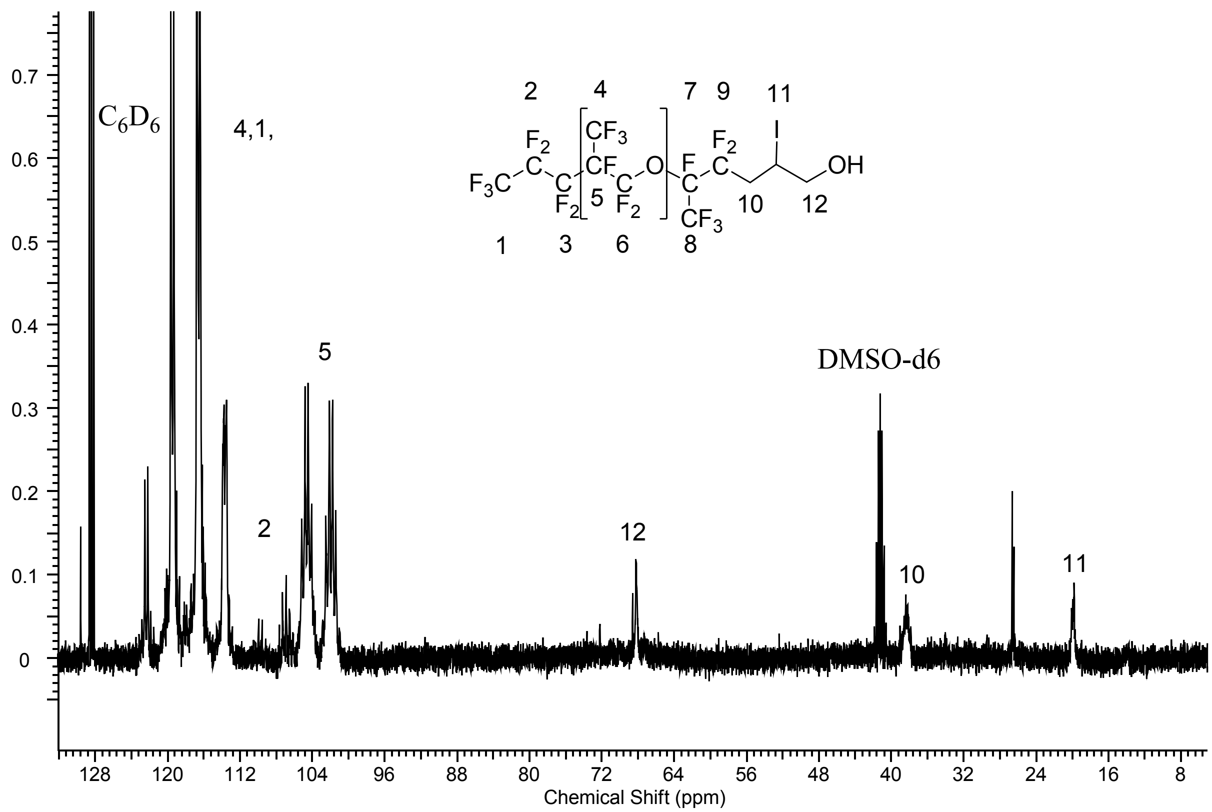


Figure S21: ^{13}C-NMR spectrum of $F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2CH_2CHICH_2OH$ initiated by TBPPI.

^{13}C NMR (101 MHz, DMSO/C_6D_6 capillary, 25°C) δ = 118.0 (qd, $^1J_{CF}$ =290.9, $^2J_{CF}$ = 28.2 Hz –OCF(<u>C</u>F3)CF2-), 117.6 (qt, $^1J_{CF}$ = 286.15 Hz, $^2J_{CF}$ = 32.93 Hz, <u>C</u>$F_3CF_2CF_2$O-, 1C), 117.5 (qd, $^1J_{CF}$ =286.15, $^2J_{CF}$ = 34.40 Hz, CF_3CF_2<u>C</u>F_2O, 1C), 114.7 (td,$^1J_{CF}$ = 285.74, $^2J_{CF}$ = 31.26Hz,-OCF(CF_3)<u>C</u>F_2-, 8.9 x 1C), 105.2 (tsext, $^1J_{CF}$= 267.03 Hz, $^2J_{CF}$ = 36.68 Hz, CF_3<u>C</u>F_2CF_2O-, 1C), 101.8(dsext, $^1J_{CF}$ = 270.7, $^2J_{CF}$ =36.7 Hz, –O<u>C</u>F(CF_3)CF_2-), 66.32 (s, -CH_2CHI<u>C</u>H_2OH, 1C), 36.52(m, -CF_2<u>C</u>H_2CHICH_2OH, 1C), 18.09, 17.90(s, -CH_2<u>C</u>$HICH_2$OH, 1C).

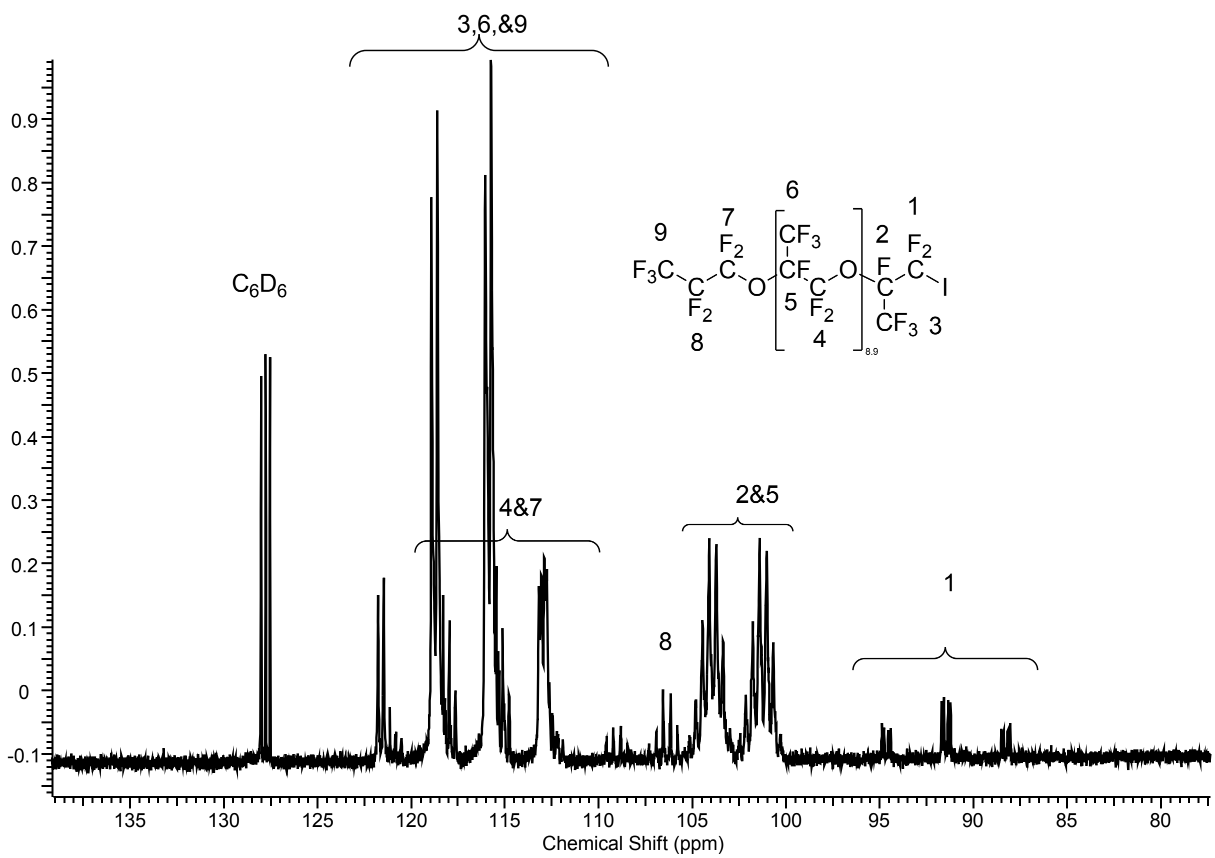
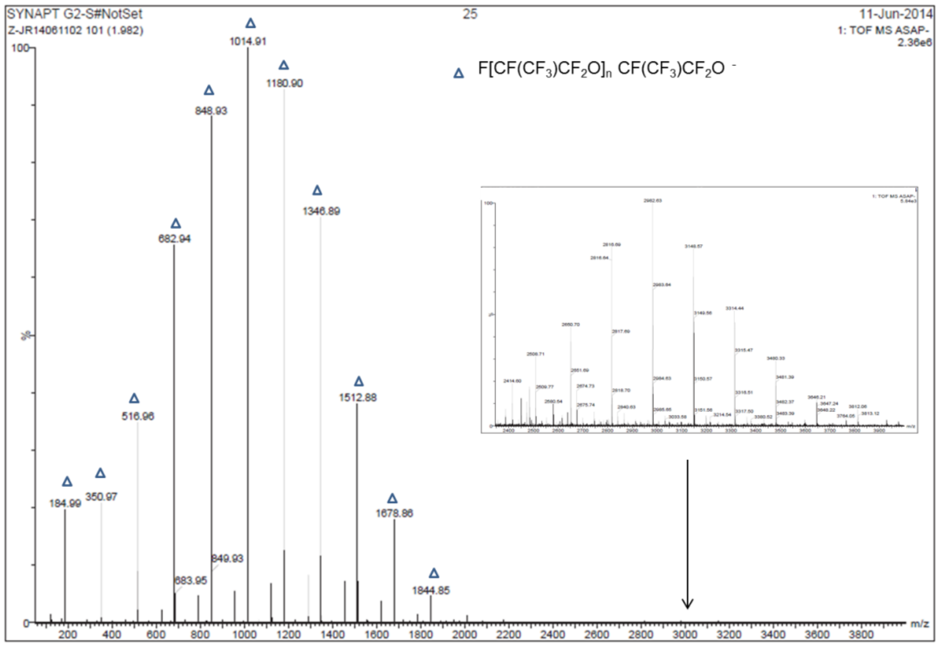


Figure S22: ^{13}C-NMR spectrum of 1-iodo-2-oligo(hexafluoropropylene oxide)perfluoropropane($F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2I$).

^{13}C NMR (101 MHz, C_6D_6 capillary, 25°C): δ = 117.3 (qd, $^1J_{CF}$ =288.3 Hz, $^2J_{CF}$ = 30.7 Hz –$OCF(\underline{C}F_3)CF_2$-, 8.9 x 1C), 116.86 (qt, $^1J_{CF}$ = 286.15 Hz, $^2J_{CF}$ = 32.93 Hz, $\underline{C}F_3CF_2CF_2O$-, 1C), 116.2(qd, $^1J_{CF}$ =285.4 Hz, $^2J_{CF}$ = 30.0 Hz, –$OCF(\underline{C}F_3)CF_2I$, 1C), 115.8 (td, $^1J_{CF}$ =287.6, $^2J_{CF}$ = 28.5 Hz, -$OCF(CF_3)\underline{C}F_2O$-, 8.9 x 1C), 115.35 (qd, $^1J_{CF}$ =286.15, $^2J_{CF}$ = 34.40 Hz, $CF_3CF_2\underline{C}F_2O$, 1C), 106.3 (tsex, $^1J_{CF}$=270.1, $^2J_{CF}$=40.83 Hz,$CF_3\underline{C}F_2CF_2O$-, 1C), 102.75 (dsext, $^1J_{CF}$ = 269.3, $^2J_{CF}$ =37.3 Hz, –$O\underline{C}F(CF_3)CF_2$-), 102.65 (dsext, $^1J_{CF}$ = 270.78, $^2J_{CF}$ =39.52 Hz, –$O\underline{C}F(CF_3)CF_2I$, 1C), 91.5 (td, $^1J_{CF}$ = 319.95 Hz, $^2J_{CF}$ = 33.93 Hz, –$OC^*F(CF_3)\underline{C}F_2I$), 91.3 (td, $^1J_{CF}$ = 320.71 Hz, $^2J_{CF}$ = 36.41 Hz, –$OC^*F(CF_3)\underline{C}F_2I$).

A)



B)

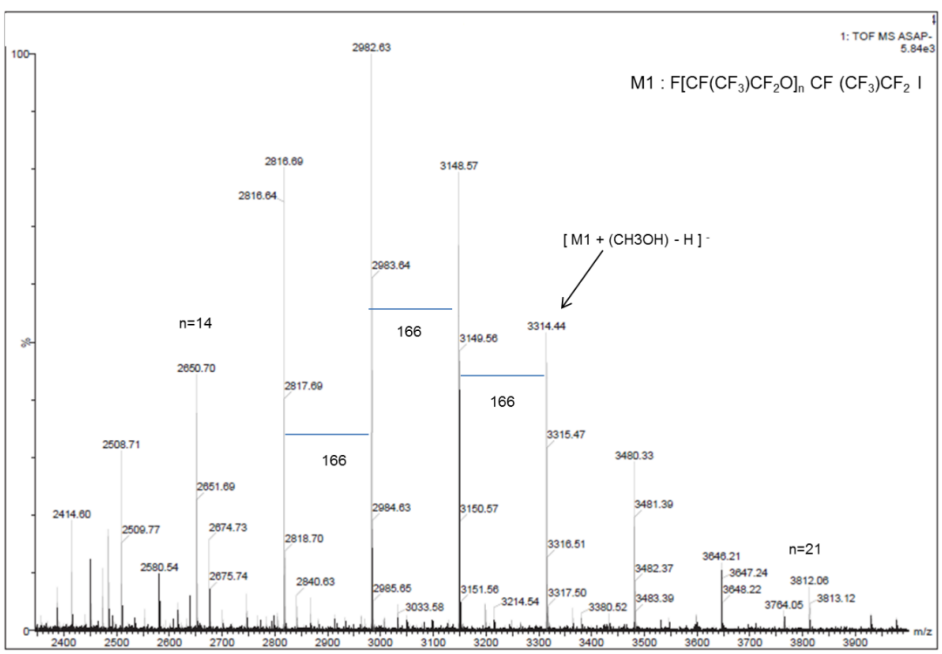


Figure S23: Negative Mode, Atmospheric pressure Solids Analysis Probe (ASAP) mass spectrum (MS) of 1-iodo-2-oligo(hexafluoropropylene oxide) perfluoropropane ($F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2I$). The expansion (Figure B) is the minor distribution of heavier homologues of oligo(HFPO) iodide centered around 2982 m/z (average n = 16).

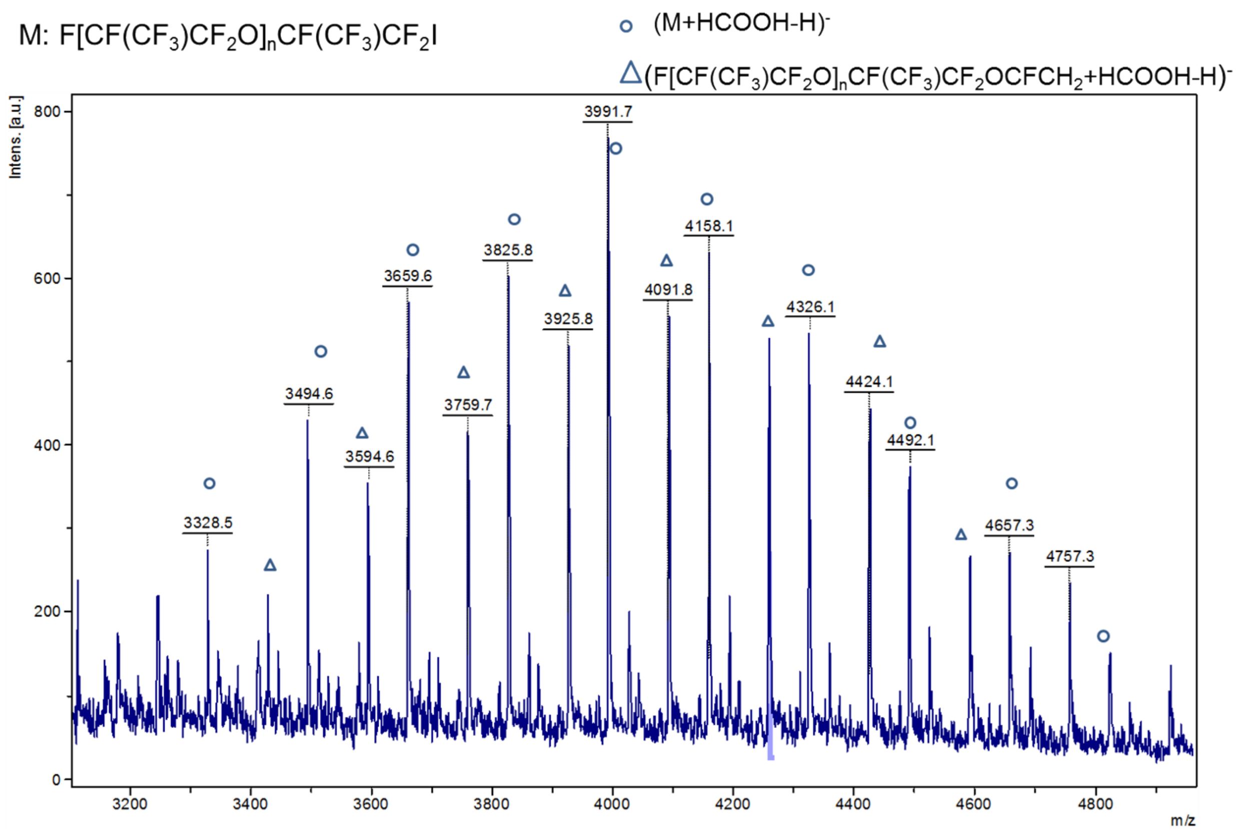


Figure S24: Matrix assisted laser desorption ionization-time-of-flight mass spectrum (MALDI-TOF-MS) of 1-iodo-2-oligo(hexafluoropropylene oxide) perfluoropropane ($F[CF(CF_3)CF_2O]_{8.9}$-$CF(CF_3)CF_2I$).

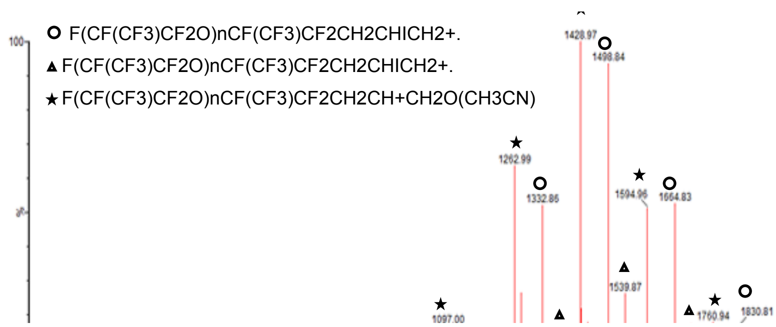


Figure S25: Atmospheric pressure Solids Analysis Probe (ASAP) *Mass Spectrum (MS)* of $F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2CH_2CHICH_2OH$ initiated by TBPPI.

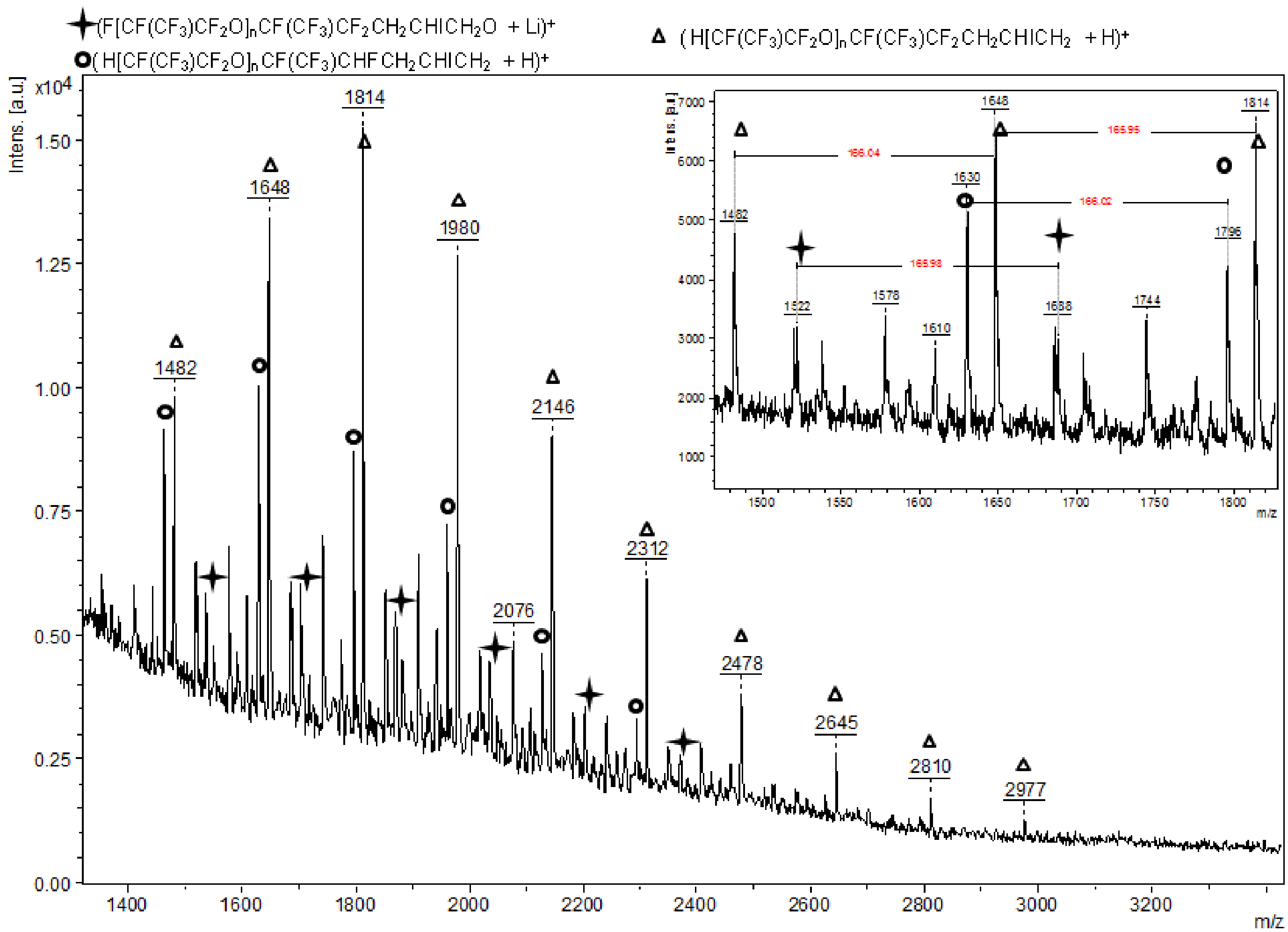


Figure S26. Matrix assisted laser desorption ionization (Positive ion mode)-time of flight-mass spectrum of $F[C(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2CH_2CHICH_2OH$ (using as matrix trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) and LiCl as the cationizing agent).

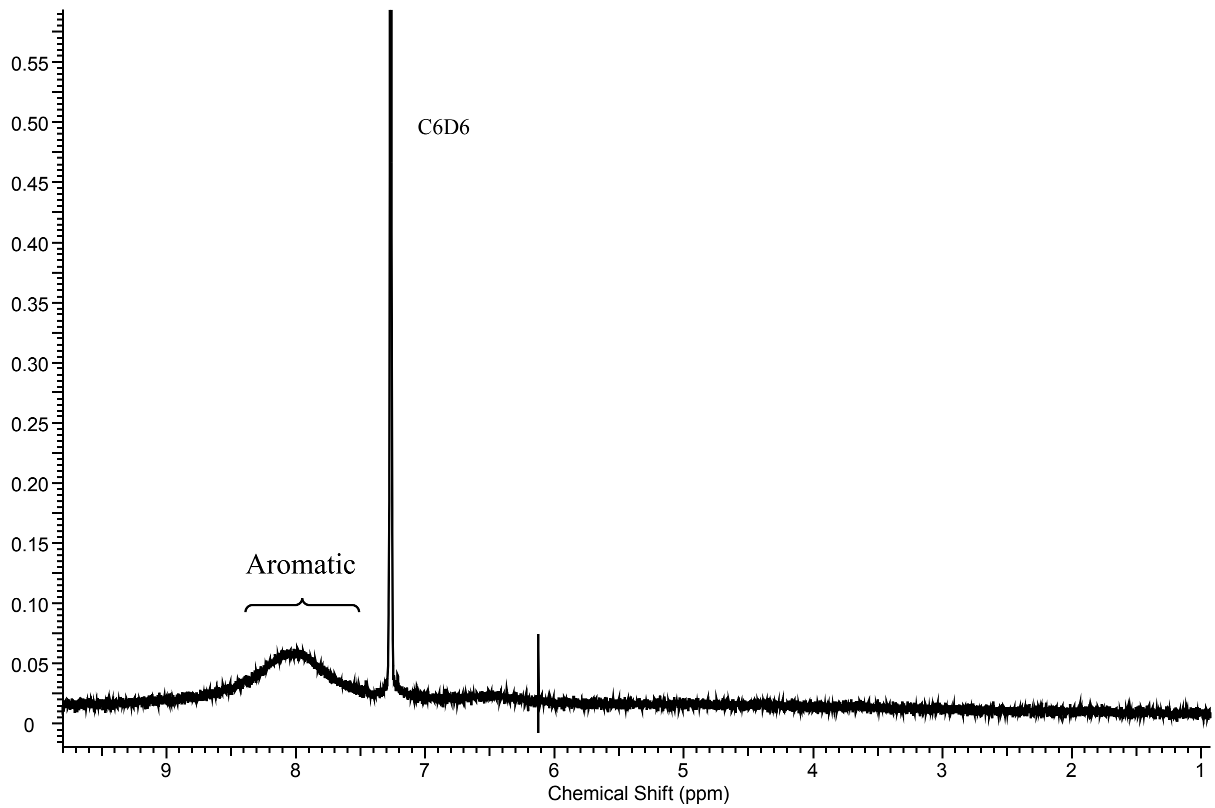


Figure S27: ^{1}H-NMR spectrum of the reaction of 1-iodo-2-oligo(hexafluoropropylene oxide)perfluoropropane($F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2I$)with benzoyl peroxide initiated by BPO.

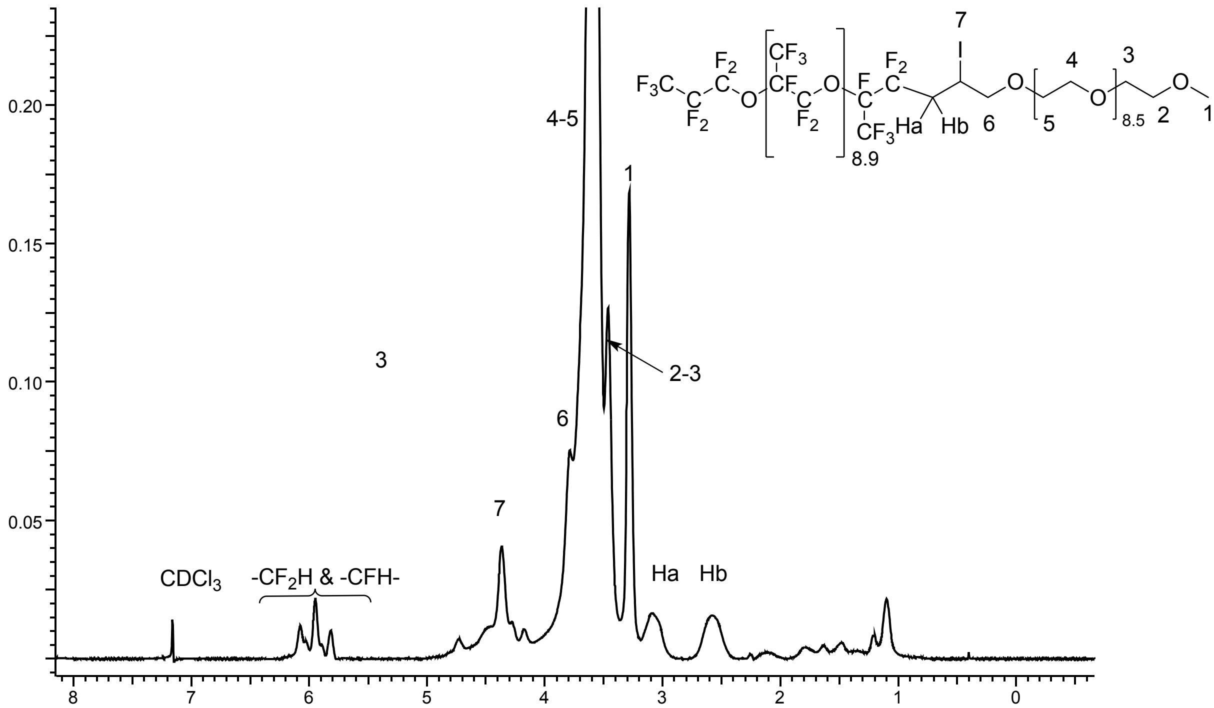


Figure S28: ¹H-NMR spectrum of $F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2CH_2CHICH_2O(CH_2CH_2O)_{8.5}CH_3$ initiated by AIBN.

1H NMR (400 MHz, $CDCl_3$ capillary, 25 ºC): δ= 4.36 (b, -C*H*I-, 1H), 3.79 (b, -CHICH_2O, 2H), 3.59 (b, -CH_2O, 19 x 1H), 3.46 (b, -CH_2CH_2OCH_3, 4H), 3.28 (s, CH_3O-, 3H), 3.09 (vb, -CF_2C$H_a$$H_b$CHI-, 1H), 2.58 (vb CF_2C$H_a$$H_b$CHI-, 1H).

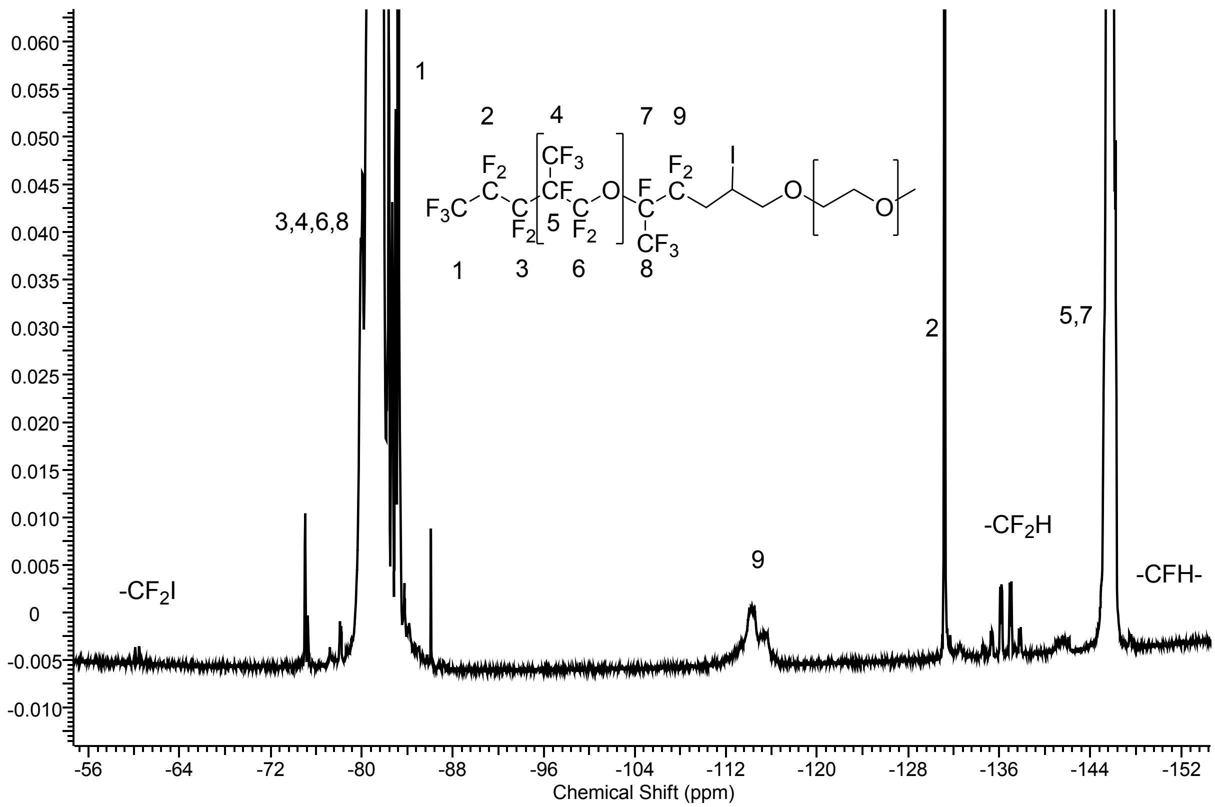


Figure S29: ^{19}F-NMR spectrum of $F[C(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2CH_2CHICH_2O(CH_2CH_2O)_{9.5}CH_3$ initiated by BPO.

^{19}F NMR (376.41 MHz, C_6D_6, 25°C): δ = -80 to -84 (CF(C$\underline{F}_3$)C$\underline{F}_2$O-), -84.04 (C$\underline{F}_3$$CF_2CF_2$O- , 3F), -82.37 ($CF_3CF_2C\underline{F}_2$O-, 2F), -112 to -117.5 (b, -CF(CF3)C$\underline{F}_2$$CH_2$CHI-, 2F), -132.03 (s, CF_3C$\underline{F}_2$$CF_2$-, 2F), -146.54 (m, -C$\underline{F}$($CF_3$)$CF_2$-, 8.9 x 1F).

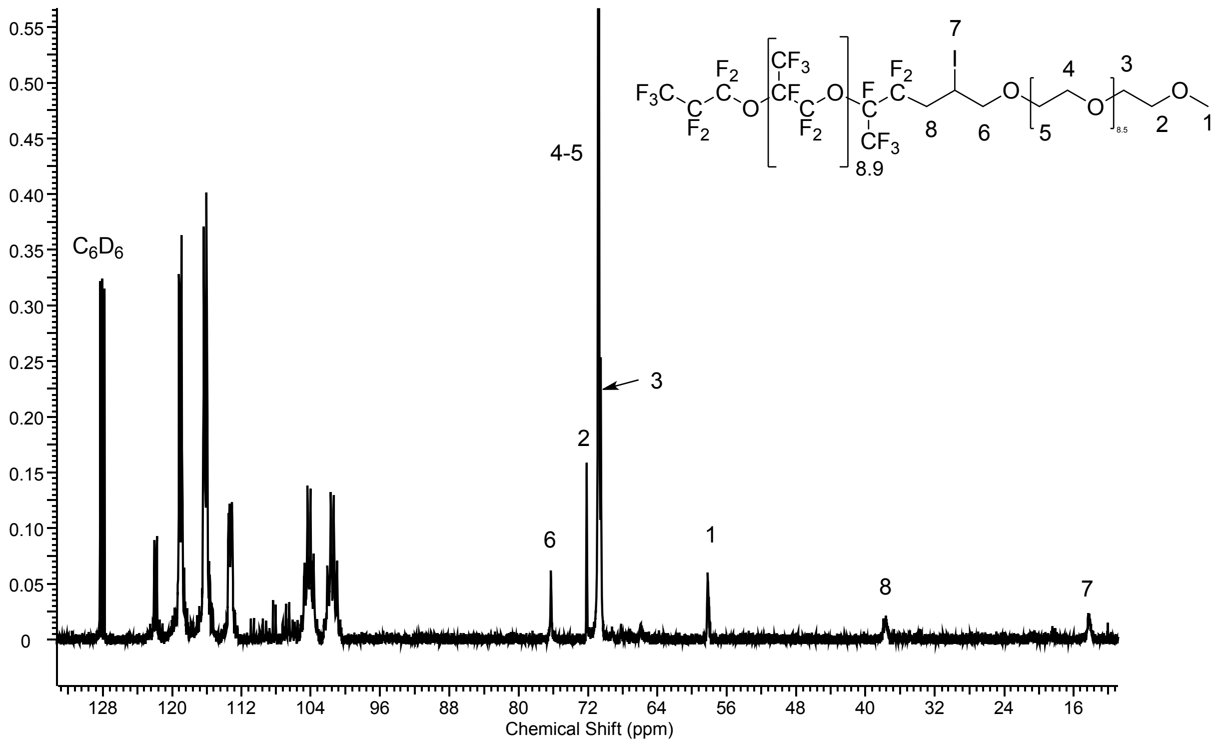


Figure S30: ^{13}C-NMR spectrum of F[CF(CF_3)CF_2O]$_{8.9}$CF(CF_3)$CF_2CH_2CHICH_2O(CH_2CH_2O)_{9.5}CH_3$ initiated by AIBN.

^{13}C NMR (101 MHz, C_6D_6, 25°C) δ = 118.0 (qd, $^1J_{CF}$ =290.9, $^2J_{CF}$ = 28.2 Hz –OCF(<u>C</u>F3)CF2-), 117.6 (qt, $^1J_{CF}$ = 286.15 Hz, $^2J_{CF}$ = 32.93 Hz, <u>C</u>$F_3CF_2CF_2$O-, 1C), 117.5 (qd, $^1J_{CF}$ =286.15, $^2J_{CF}$ = 34.40 Hz, CF_3CF_2<u>C</u>F_2O, 1C), 114.7 (td,$^1J_{CF}$ = 285.74, $^2J_{CF}$ = 31.26Hz,-OCF(CF_3)<u>C</u>F_2-, 8.9 x 1C), 105.2 (tsext, $^1J_{CF}$= 267.03 Hz, $^2J_{CF}$ = 36.68 Hz, CF_3<u>C</u>F_2CF_2O-, 1C), 101.8 (dsext, $^1J_{CF}$ = 270.7, $^2J_{CF}$ =36.7 Hz, –O<u>C</u>F(CF_3)CF_2-), 76.27 (s, -CH_2CHI<u>C</u>H_2O-, 1C), 72.17 (s, <u>C</u>H_2–CH_2–OMe, 2C), 70.79 (s, 19 X 1C, -<u>C</u>H_2–O), 70.54 (s, -CH_2<u>C</u>H_2OMe, 1C) 58.65 (s, 1C, <u>C</u>H_3), 37.65(m, -CF_2<u>C</u>H_2CHICH_2O-, 1C), 14.30(s, -CH_2<u>C</u>HICH_2O-, 1C).

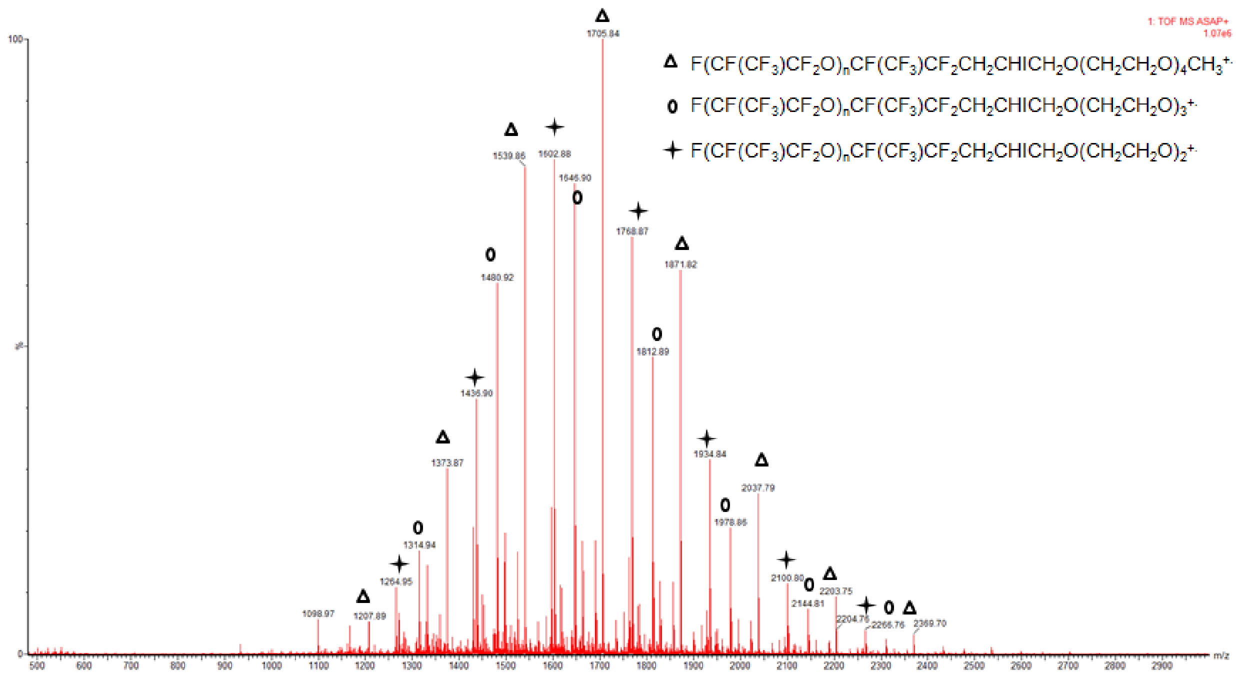


Figure S31: Atmospheric pressure Solids Analysis Probe (ASAP) Mass Spectrum (MS) of $F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2CH_2CHICH_2O(CH_2CH_2O)_{9.5}CH_3$ initiated by BPO.

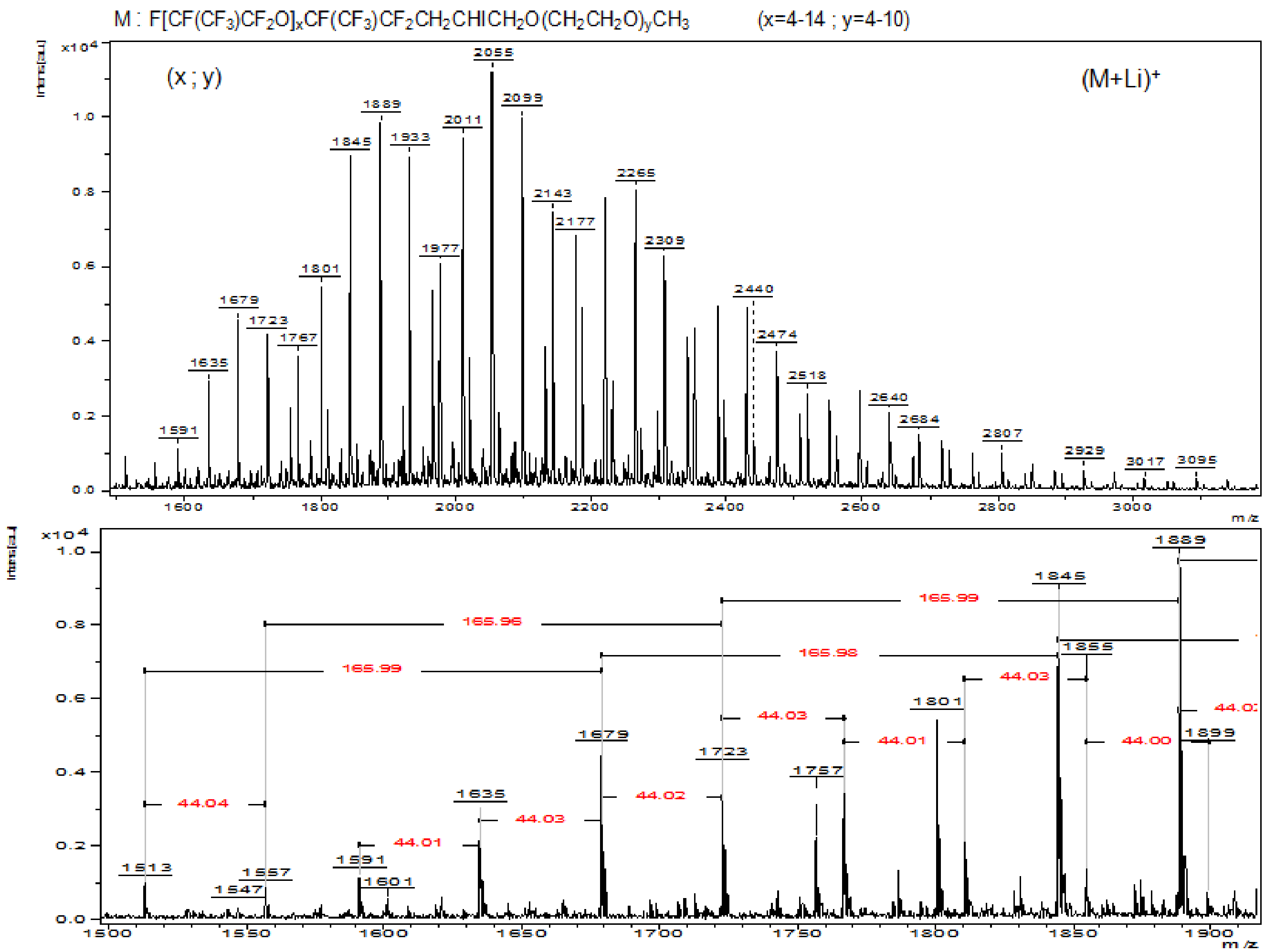


Figure S32: Matrix assisted laser desorption ionization-time-of-flight mass spectrum (MALDI-TOF-MS) of $F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2CH_2CHICH_2O(CH_2CH_2O)_{9.5}CH_3$ initiated by BPO. The adduct $(M+Li)^+$ at 1889 is x=7 and y=8. The expansion *m/z* between 1500 and 1900 displays 166 m/z-repeat unit for HFPO $[CF(CF_3)CF_2O]$ and 44 m/z-repeat unit of ethylene oxide (CH_2CH_2O).

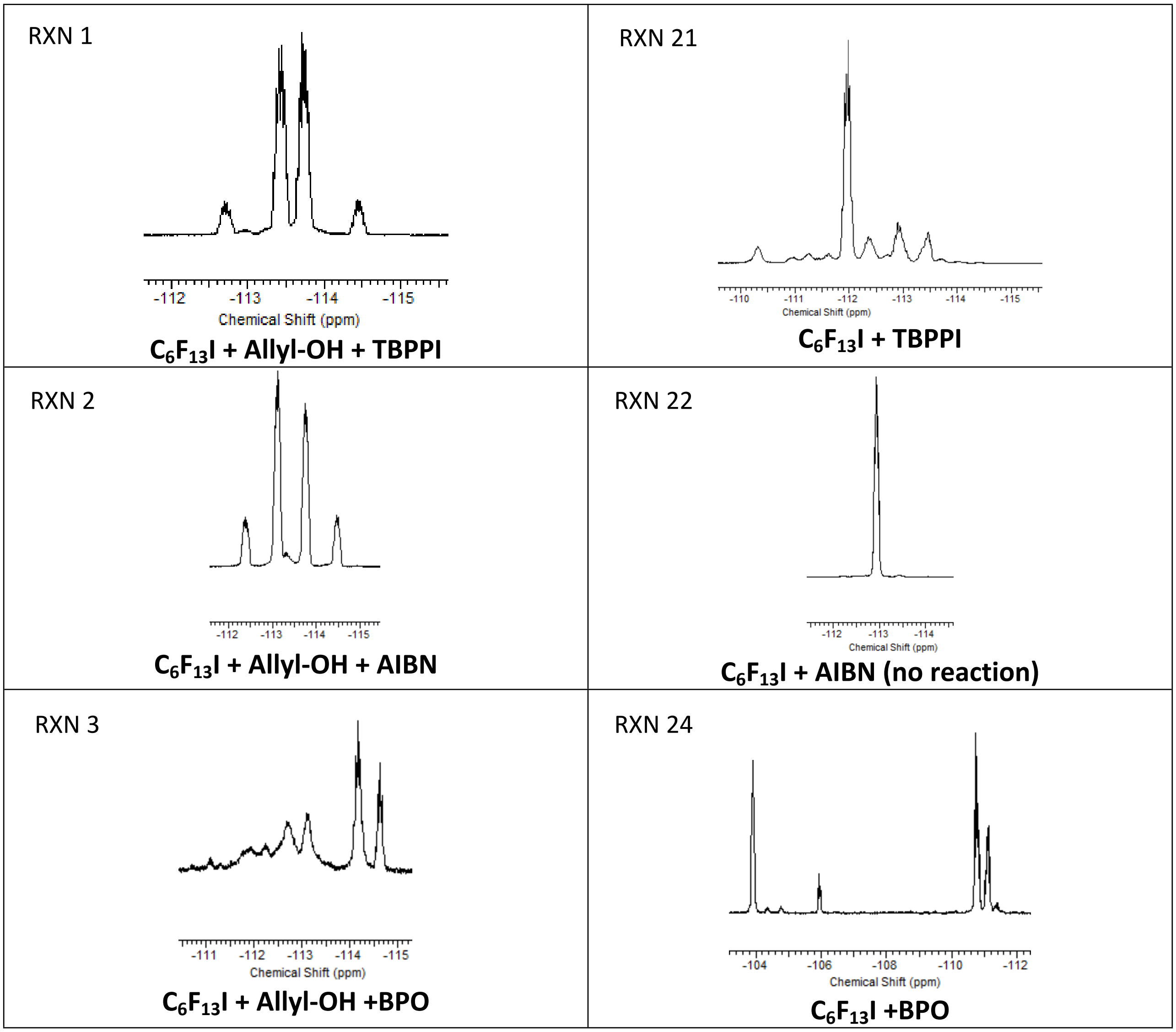


Figure S33. Comparison of the ^{19}F-NMR expansions of the reaction $C_6F_{13}I$ with the initiator (TBPPi, AIBN, BPO) and initiator with allyl alcohol.

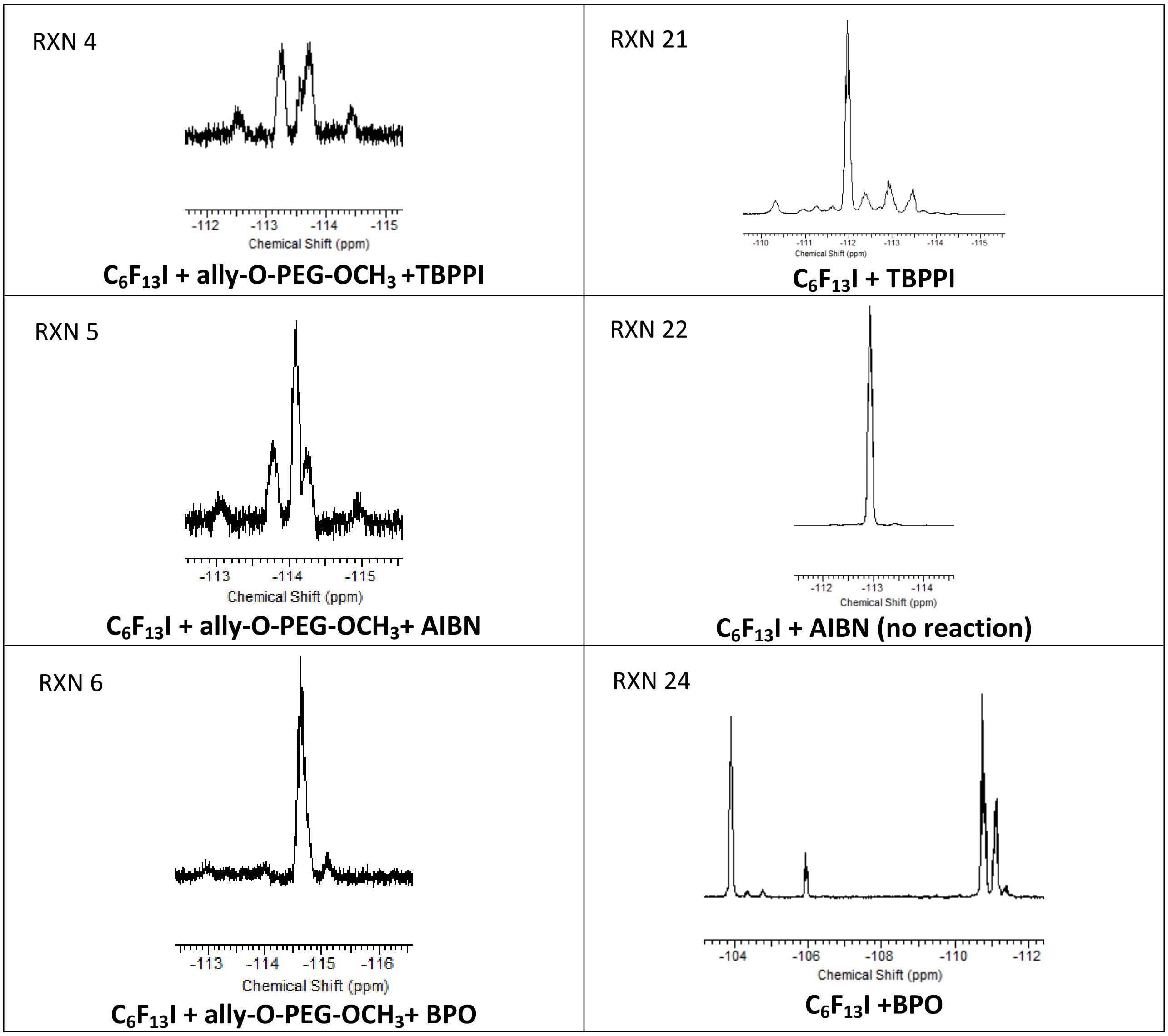


Figure S34. Comparison of the ^{19}F-NMR expansions of the reaction of $C_6F_{13}I$ with the initiator (TBPPi, AIBN, BPO) and initiator with ally-O-PEG-OCH_3.

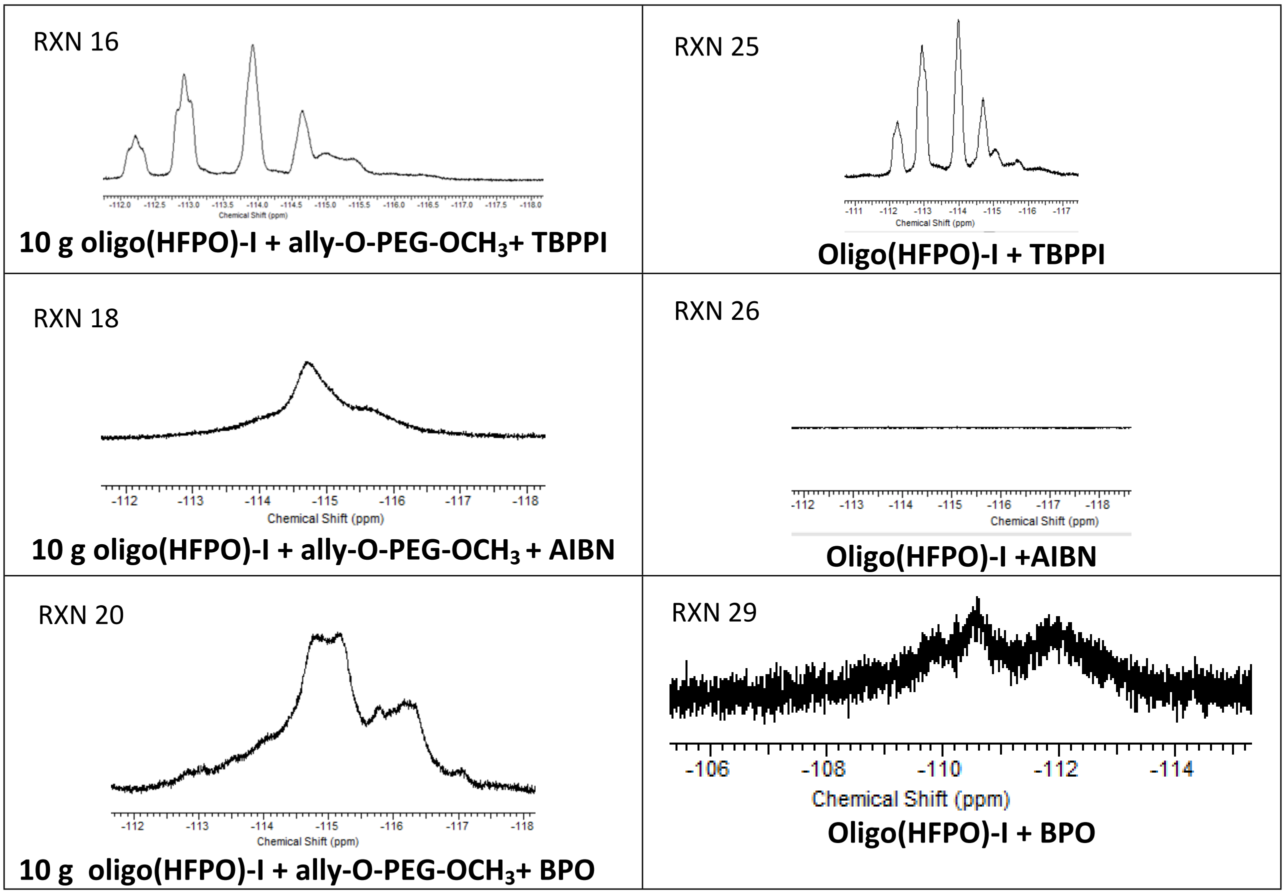


Figure S35. Comparison of the ^{19}F-NMR expansions of the reaction of oligo(HFPO)-CF(CF_3)CF_2I with the initiator (TBPPi, AIBN, BPO) and initiator with ally-O-PEG-OCH_3.

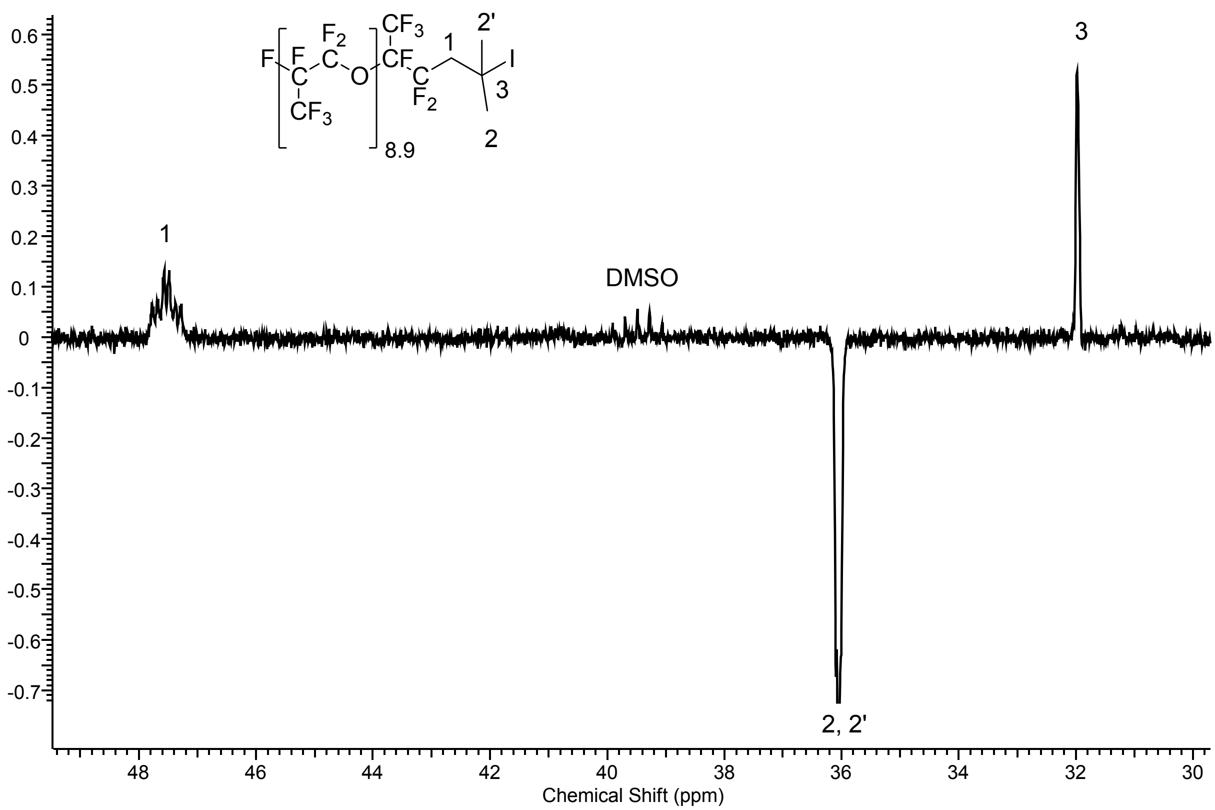


Figure S36: ^{13}C-NMR spectrum , Attached Proton Test (APT), of 1-iodo-2-methyl-3-[2-(poly(hexafluoro-propylene oxide) perfluoropropyl]-propane. A side reaction of 1-iodo-2-oligo(hexafluoropropylene oxide)perfluoropropane (F[CF(CF_3)CF_2O]$_{8.9}$CF(CF_3)CF_2I) with TBPPI.

^{13}C NMR (101 MHz, C_6D_6, 25°C) δ = 47.51 (td, $^2J_{CF}$ = 19.0 Hz, $^3JF_{CF}$ = 8.1 Hz, -CF(CF_3)CF_2<u>*C*</u>H_2C-(CH_3)$_2$I, 1C), 36.06 (s, -CF(CF_3)$CF_2$$CH_2$C($CH_3$)$_2$I, 2C), 31.98 (s, , -CF($CF_3$)$CF_2$$CH_2$<u>*C*</u>($CH_3$)I, 1C).

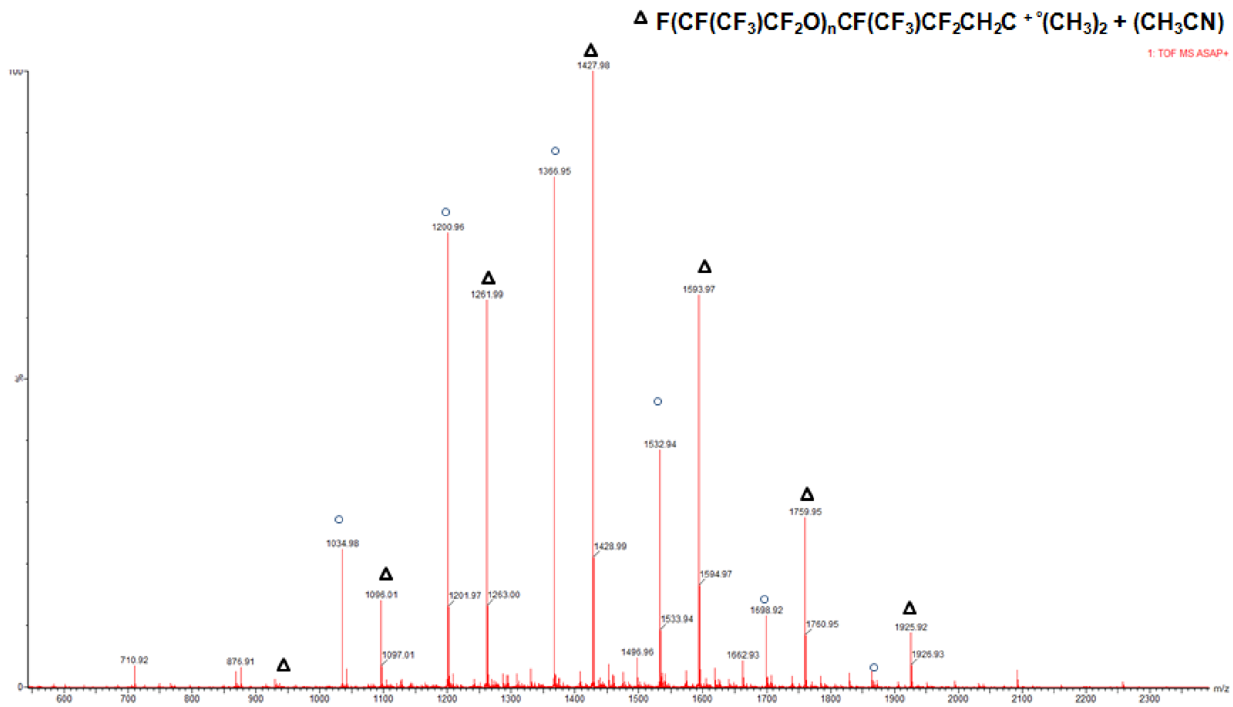


Figure S37: Atmospheric pressure Solids Analysis Probe (ASAP) Mass Spectrum (MS) of 1-iodo-2-methyl-3-[2-(poly(hexafluoropropylene oxide)perfluoropropyl]-propane, side reaction of 1-iodo-2-oligo(hexafluoropropylene oxide)perfluoropropane ($F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2I$) with TBPPI.

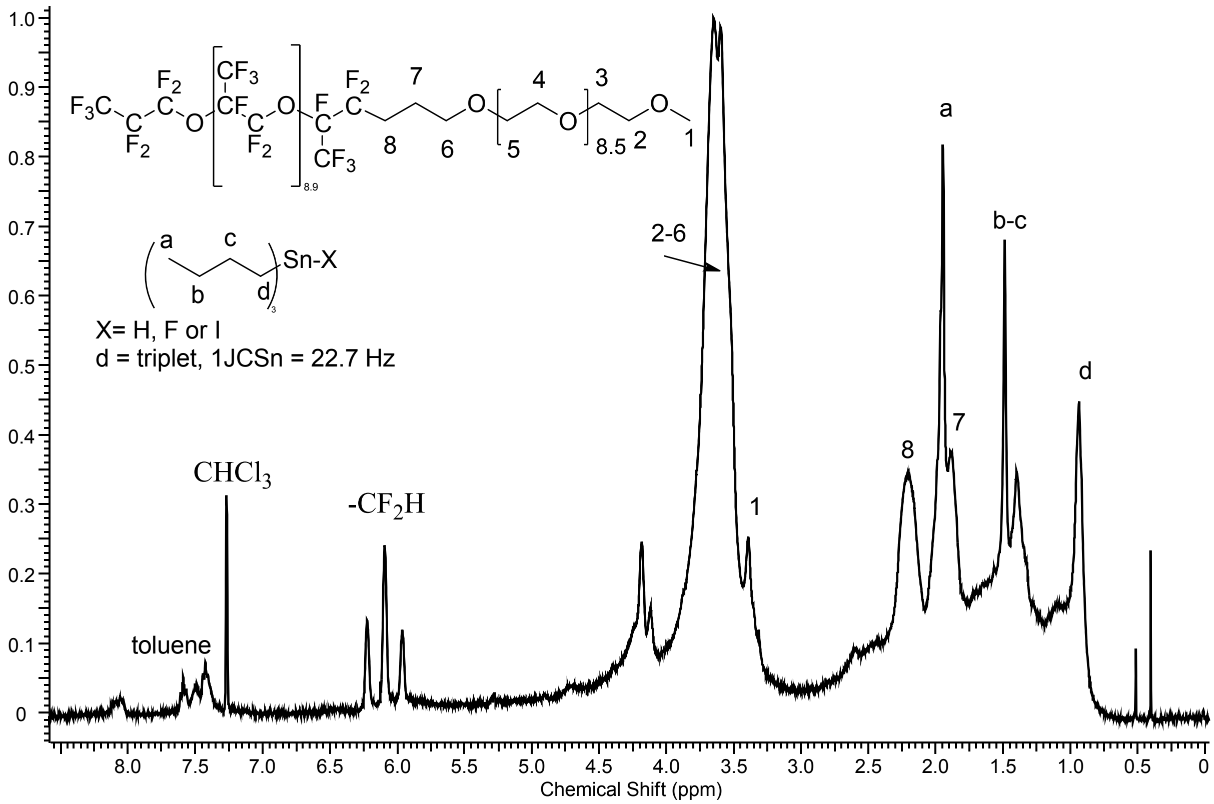


Figure S38: ^{1}H-NMR spectrum of F[CF(CF$_3$)CF$_2$O]$_{8.9}$CF(CF$_3$)CF$_2$CH$_2$CH$_2$CH$_2$O(CH$_2$CH$_2$O)$_{9.5}$CH$_3$.

^{1}H NMR (400 MHz, CDCl$_3$ capillary, 25 ^{o}C): δ= 3.59 (b, -C*H*$_2$O, 23 x 1H), 3.40 (s, C*H*$_3$O-, 3H), 2.20 (b, -CF$_2$C*H*$_2$CH$_2$-, 1H), 1.89 (b, -CF$_2$CH$_2$*C*H$_2$-, 1H).

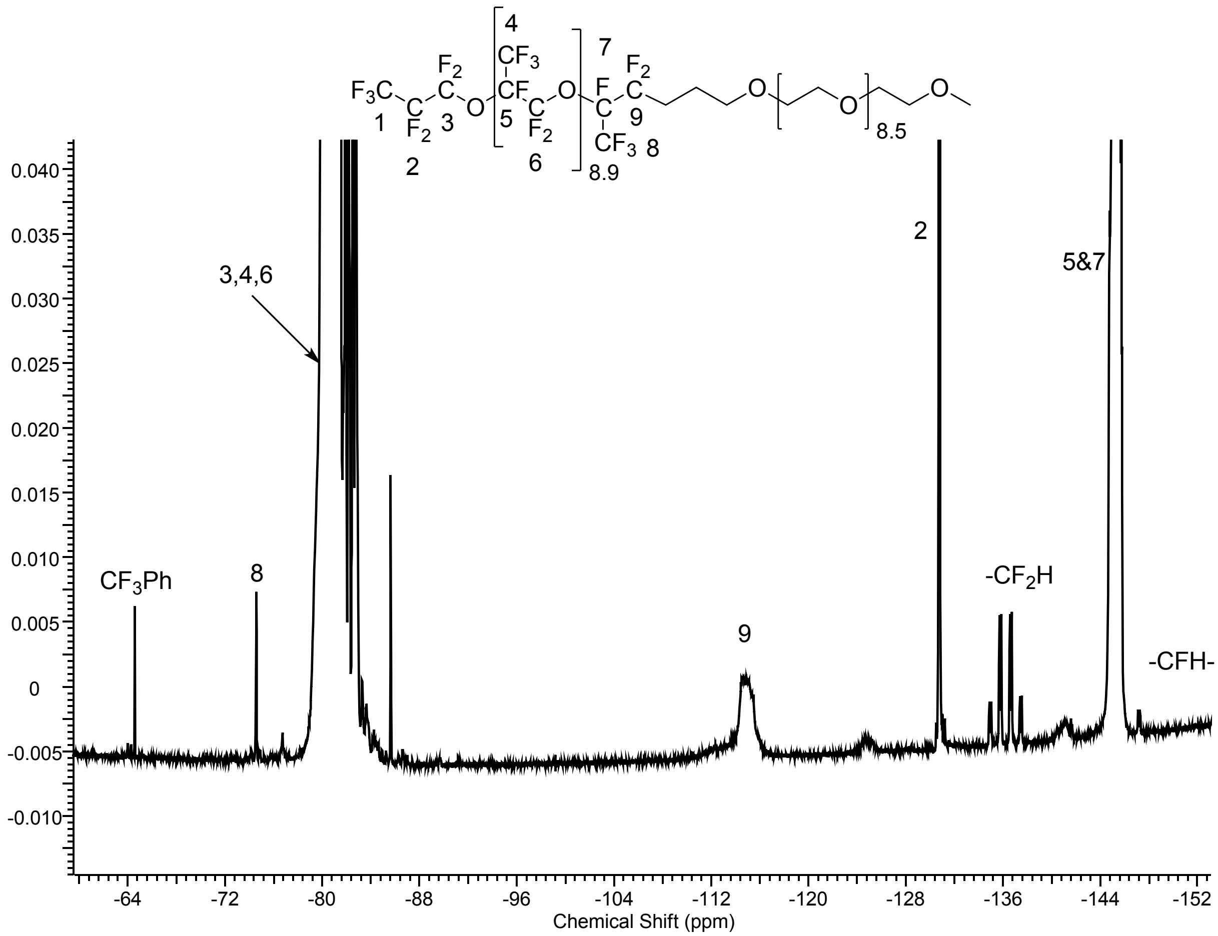


Figure S39: [19]F-NMR spectrum of $F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2CH_2CH_2CH_2O(CH_2CH_2O)_{9.5}CH_3$.

[19]F NMR (376.41 MHz, C_6D_6, 25°C): δ = -80 to -84 (CF(C$\underline{F}_3$)C$\underline{F}_2$O-), -84.04 (C$\underline{F}_3$CF$_2$CF$_2$O- , 3F), -82.37 (CF$_3$CF$_2$C$\underline{F}_2$O-, 2F), -112 to -118 (b, -CF(CF3)C$\underline{F}_2$CH$_2$CH$_2$-, 2F), -131.56 (s, CF$_3$C$\underline{F}_2$CF$_2$-, 2F), -146.05 (m, -C$\underline{F}$(CF$_3$)CF$_2$-, 9.9 x 1F).

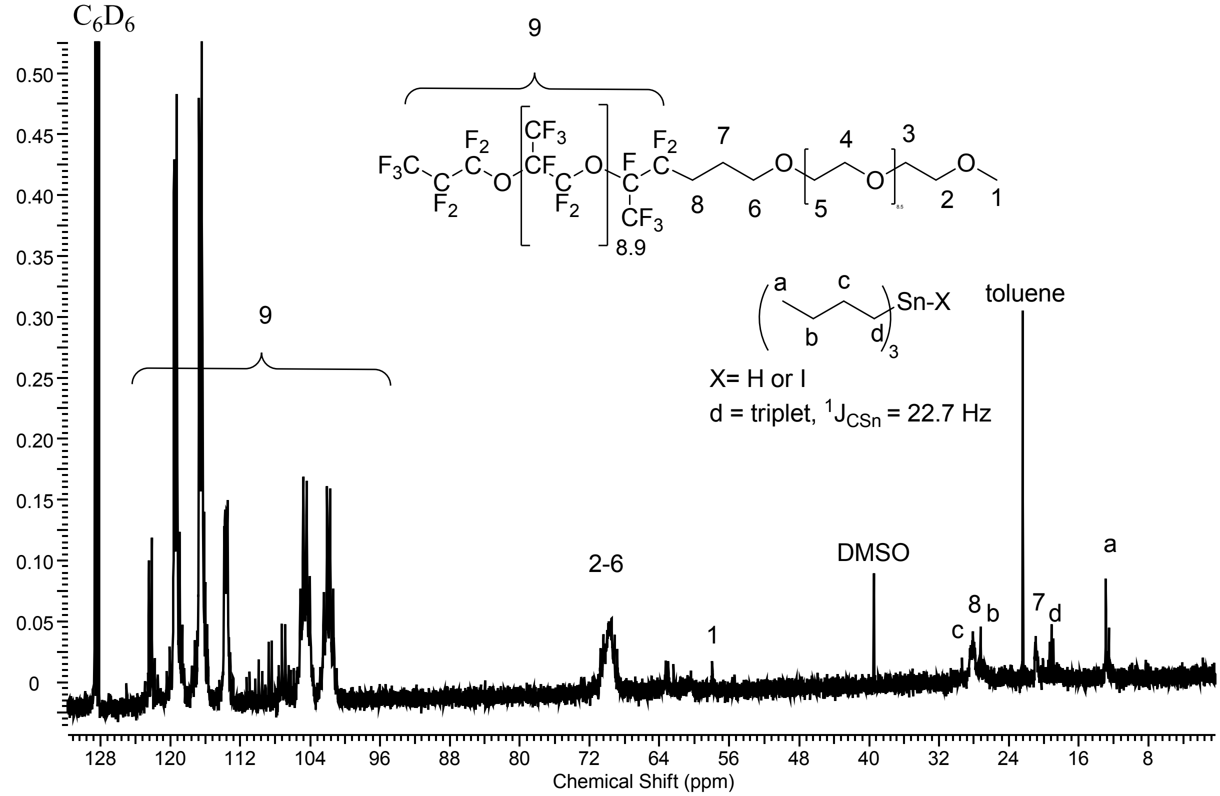


Figure S40: ^{13}C-NMR spectrum of $F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2CH_2CH_2CH_2O(CH_2CH_2O)_{9.5}CH_3$

^{13}C NMR (101 MHz, C_6D_6, 25°C) δ = 118.0 (qd, $^1J_{CF}$ =290.9, $^2J_{CF}$ = 28.2 Hz, –OCF($\underline{C}$F3)CF2-), 117.6 (qt, $^1J_{CF}$ = 286.15 Hz, $^2J_{CF}$ = 32.93 Hz, $\underline{C}F_3CF_2CF_2O$-, 1C), 117.5 (qd, $^1J_{CF}$ =286.15, $^2J_{CF}$ = 34.40 Hz, $CF_3CF_2\underline{C}F_2O$, 1C), 114.7 (td,$^1J_{CF}$ = 285.74, $^2J_{CF}$ = 31.26Hz,-OCF(CF_3)$\underline{C}F_2$-, 8.9 x 1C), 105.2 (tsext, $^1J_{CF}$= 267.03 Hz, $^2J_{CF}$ = 36.68 Hz, $CF_3\underline{C}F_2CF_2O$-, 1C), 101.8 (dsext, $^1J_{CF}$ = 270.7, $^2J_{CF}$ =36.7 Hz, –O$\underline{C}$F(CF_3)CF_2-), 69.42 (bs, -CH_2O-, 21 X 1C), 57.59 (s, $\underline{C}H_3$,1C), 27.80(m, -$CF_2\underline{C}H_2CH_2CH_2O$-, 1C), 20.55 (s, -$CH_2\underline{C}H_2CH_2O$-, 1C). Impurities (tributyl-Sn-X): 28.98 (s, $CH_3CH_2\underline{C}H_2CH_2$-Sn, 3C), 26.90 (s, $CH_3\underline{C}H_2CH_2CH_2$-Sn, 3C), 18.76 (t, $CH_3CH_2CH_2\underline{C}H_2$-Sn, $^1J_{CSn}$ = 20.49 Hz, 3C), 12.53 (s, $\underline{C}H_3CH_2CH_2CH_2$-Sn, 3C)

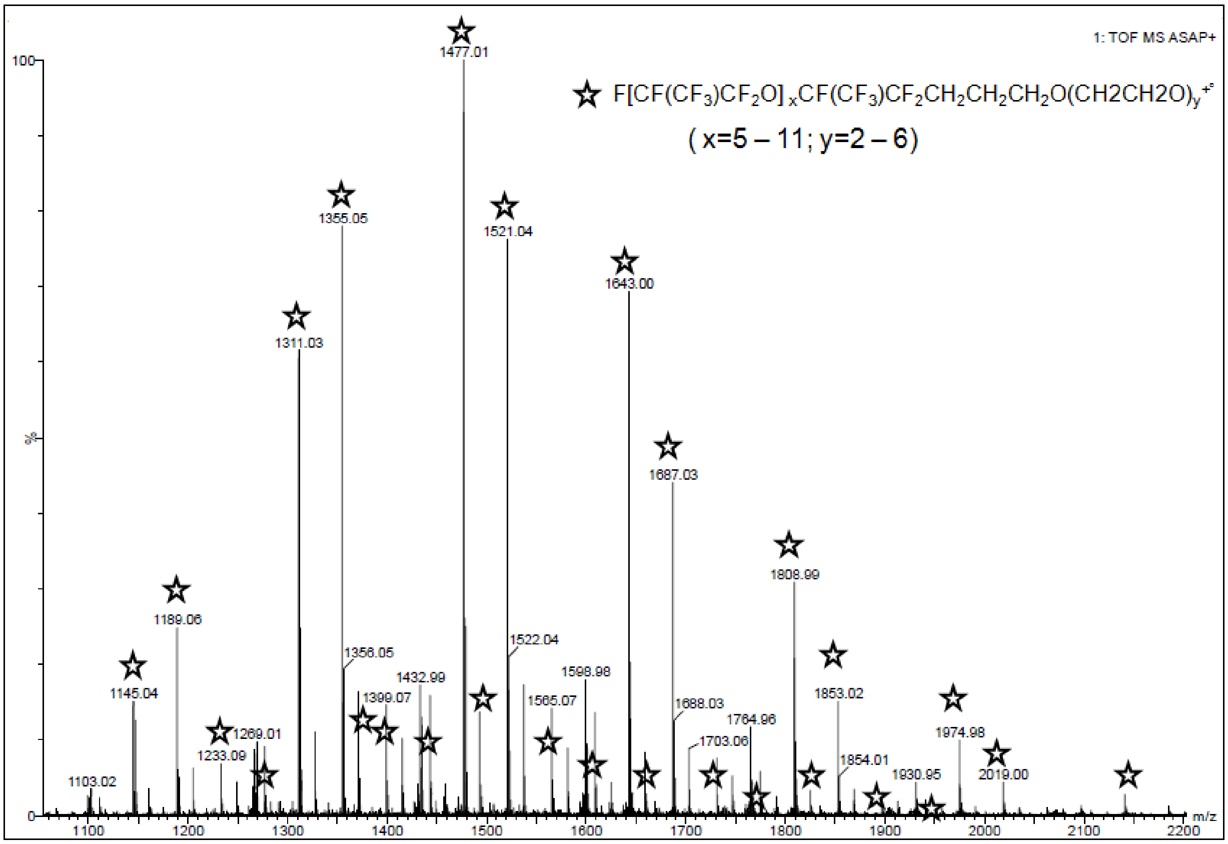


Figure S41. Positive mode atmospheric pressure solids analysis probe (ASAP) mass spectrum (MS) of oligo(HFPO)-$CH_2CH_2CH_2$-oligo(PEG)

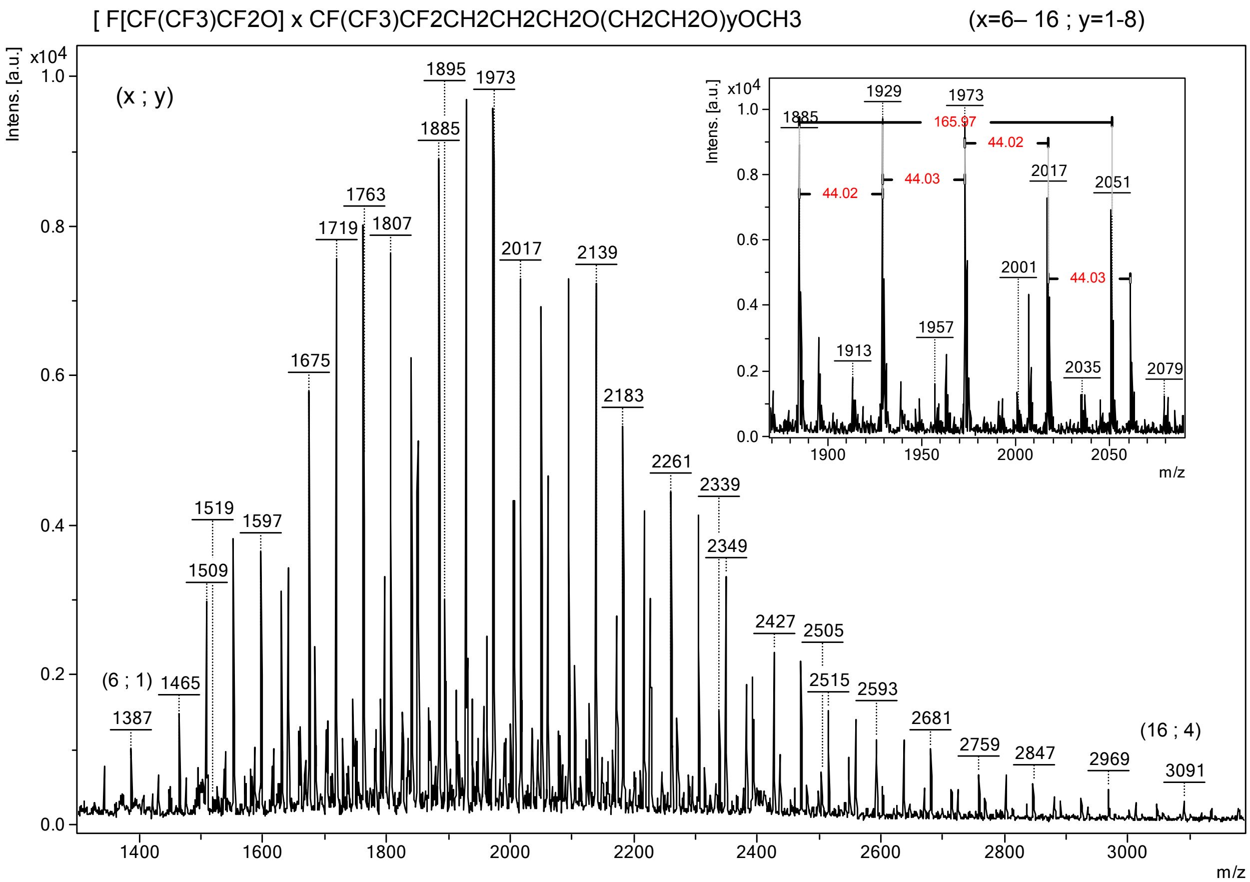


Figure S42. Positive ion mode MALDI-TOF-MS spectrum of oligo(HFPO)-$CH_2CH_2CH_2$-oligo(PEG) (using as matrix DCTB and LiCl as the cationizing agent), 1807 m/z is x =8 and y = 5. The insert expansion *m/z* between 1850 and 2100 displays 166 m/z-repeat unit for HFPO [CF(CF_3)CF_2O] and 44 m/z-repeat unit of ethylene oxide (CH_2CH_2O).

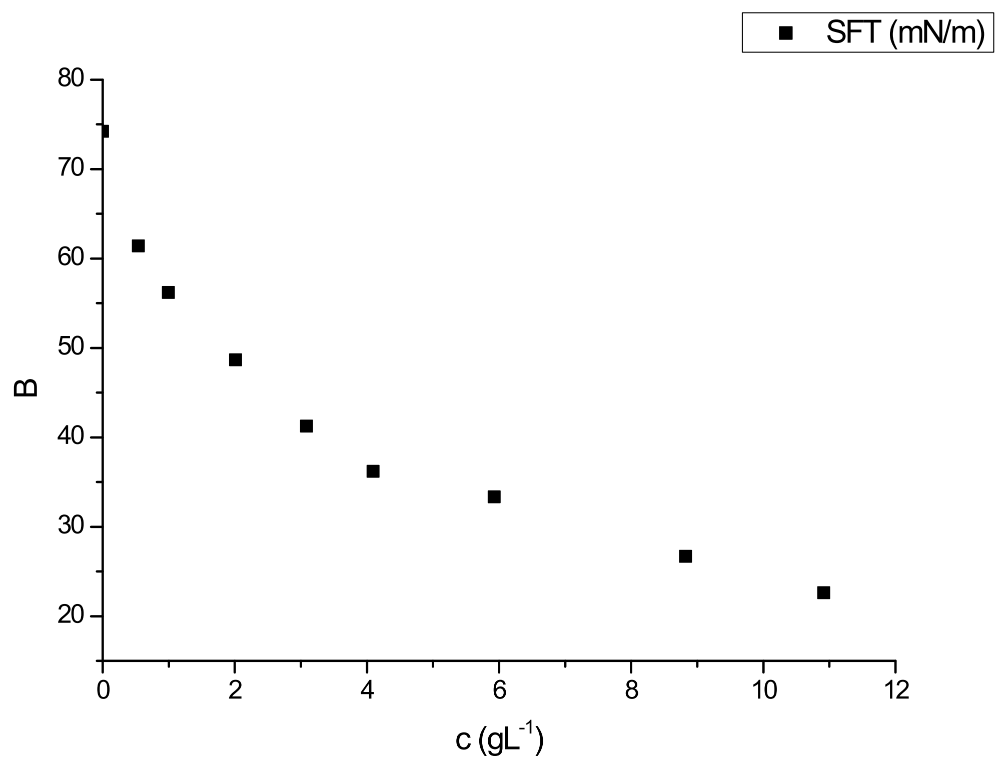


Figure S43: Surface Tension measurement of ammonium perfluorooctanoate ($C_7F_{15}C(O)O^-$ NH_4^+), CMC = 3.77 g/L.

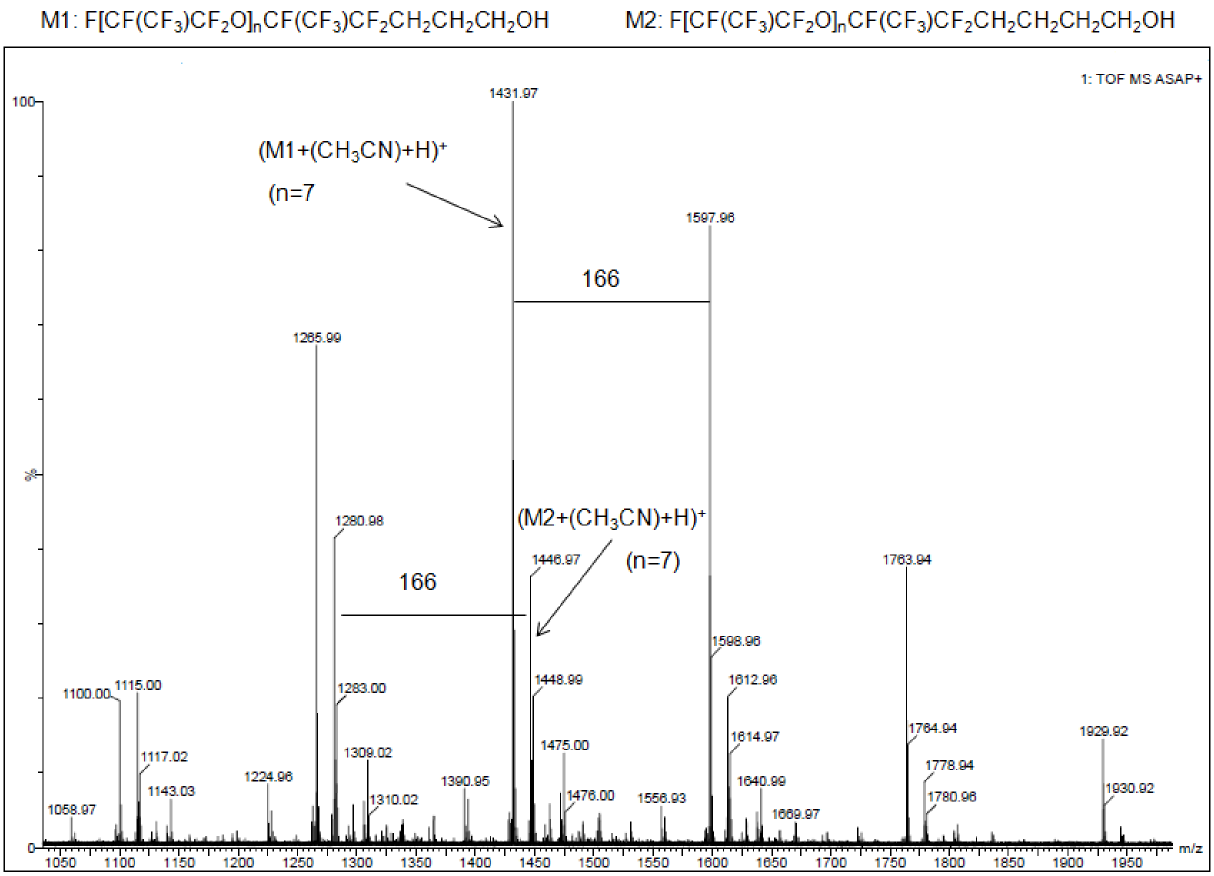


Figure S44: Positive mode atmospheric pressure solids analysis probe (ASAP)-time-of-flight-mass spectrum (MS) of oligo(HFPO)-$CH_2CH_2CH_2OH$, in trifluorotoluene.

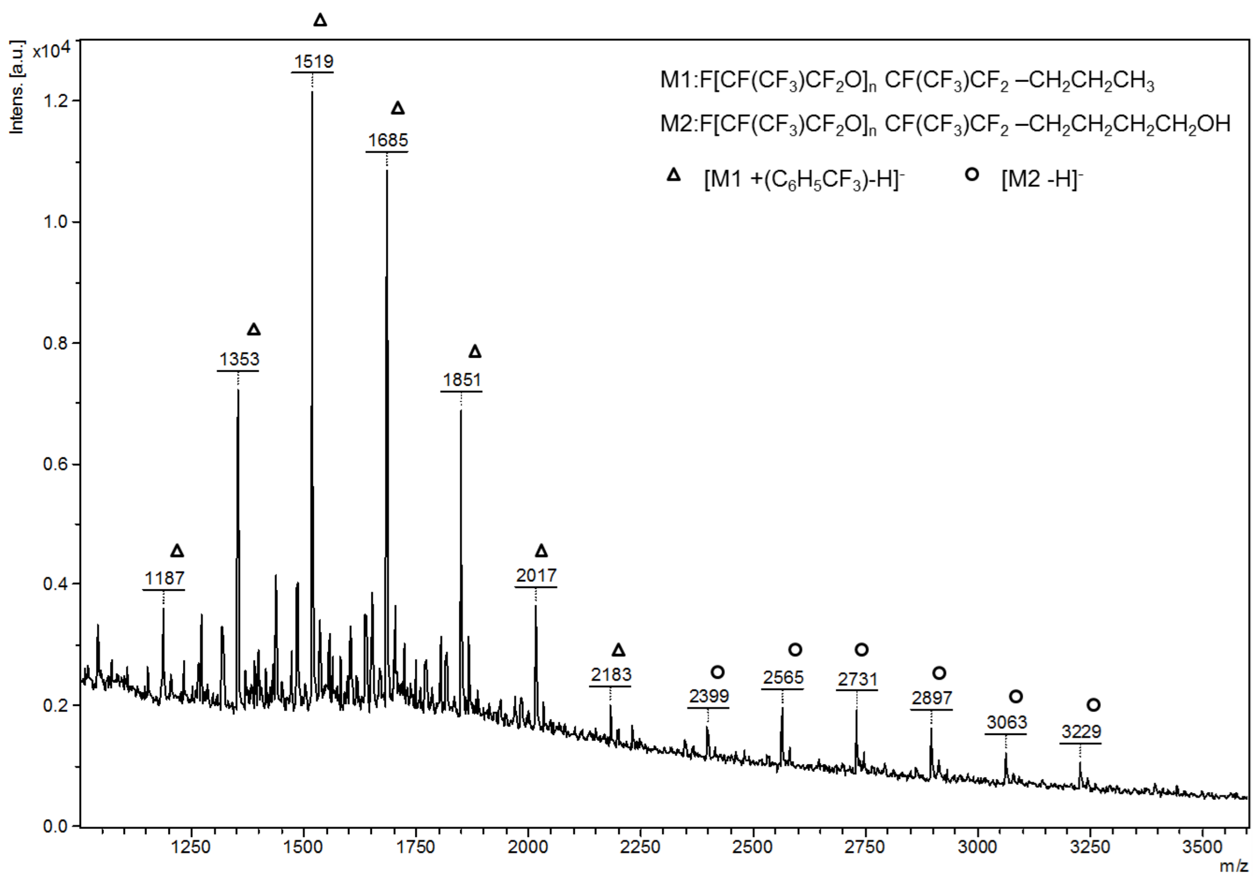


Figure S45: Negative ion mode MALDI-TOF-MS spectrum of oligo(HFPO)$CH_2CH_2CH_2OH$, in trifluorotoluene (using as matrix DCTB and LiCl as the cationizing agent).