Supporting information for:

Highly Fluorinated Phosphonium Ionic Liquids: Novel Media for the Generation of Superhydrophobic Coatings

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Experimental Section

The 2,4,4'-trimethylpentyl phosphine was generously donated by Cytec Corporation. Silver p-toluenesulfonate AgOTs (Aldrich), TMS-OTf, $AgBF_4$, $AgPF_6$ (Alfa Aesar), $LiNTf_2$ (Fluka), $AgNO_3$ (EMD), *1H,1H,2H*-perfluorodec-1-ene, *1H*,*1H*,*2H*,*2H*-perfluorooctyliodide (Fluorous Technologies Inc.) and VAZO 67, 2,2'-azobis(2-methylbutanenitrile) (Dupont) were used as received without further purification. The purity of all reagents was assessed by multinuclear NMR spectroscopy (^1H, $^{19}F\{^1H\}$, $^{31}P\{^1H\}$), and they were stored in a nitrogen-filled MBraun Labmaster 130 glove box. Solvents were obtained from Caledon Laboratories and dried using an Innovative Technologies Inc. Solvent Purification System. The dried solvents were collected under vacuum and stored under a nitrogen or argon atmosphere in Strauss flasks, or stored in the drybox over 4Å molecular sieves. Deuterated chloroform was dried with CaH_2, vacuum distilled and stored over 4Å molecular sieves in the glove box. Solution ^1H, $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra were recorded on a Varian INOVA 400 MHz spectrometer unless otherwise noted (^1H; 400.09 MHz, ^{31}P; 161.82 MHz, ^{19}F; 376.15 MHz). All samples for ^1H NMR spectroscopy were referenced to the residual protons in the solvent relative to $(CH_3)_4Si$ (δ (ppm); chloroform-*d* 7.26; acetone-d_6 2.05). Phosphorus-31 and ^{19}F NMR chemical shifts were reported relative to external standards (85% H_3PO_4; 0.00 ppm and $CF_3(C_6H_5)$; -63.9 ppm, relative to $CFCl_3$; 0.00 ppm). Mass spectrometry measurements were recorded in positive and negative ion modes using an electrospray ionization Micromass LCT spectrometer. Elemental analyses were performed by

Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada and Columbia Analytical Services Inc., Tucson, Arizona, USA.

The decomposition temperatures were determined using Thermal Gravimetric Analysis (TGA) on a TGA/SDTA 851e Mettler Toledo instrument for **[1][A]** or on a Q600 SDT TA Instrument for **[2][X]**. A 0.005-0.010 g sample was heated at a rate of 10 °C/min over a temperature range of 100°C-600°C. Isothermal heating experiments were conducted using a 0.005 - 0.010 g sample of the PIL heated at 120°C for 5 h for **[1][A]** and at 180°C for 10h for **[2][Br]** and the percent mass loss was determined using Thermal Gravimetric Analysis. Melting and glass transition points were determined using Differential Scanning Calorimetry (DSC) on a DSC 822^e Mettler Toledo instrument for **[1][A]** or on a Q20 DSC TA instrument for **[2][X]**. For **[1][A]** a 0.005 g – 0.010 g sample was cooled to -70 °C where the temperature was sustained for 15 minutes, followed by heating to 500 °C at 10 °C/min. For **[2][X]** a 0.005 g – 0.010 g sample was cooled -90 °C and then heated to 200 °C at 10 °C/min, cooled to -90 at 10 °C/min and finally reheated to 200 °C at 10 °C/min. The glass transition temperatures were taken from the final heat cycle. All thermal analysis experiments were conducted in a $N_{2\,(g)}$ atmosphere.

The HFPILs were tested for their water content by Karl Fischer titration, on a 684 KF Coulometer by Metrohm. The samples were first dried *in vacuo* for 3 h at 100 °C, transferred to a glove box, where they were weighed out (0.02 g), and dissolved in dry CH_2Cl_2. The water content of the CH_2Cl_2 was determined, and was subtracted from the value obtained for each ionic liquid. The microsyringe was cleaned and dried between each titration.

To prepare the superhydrophobic surfaces, a copper plate (15 mm x 15 mm x 2 mm) was cleaned using a polishing wheel (4000 grit sand paper) and then washed with acetone and EtOH and dried under stream of $N_{2\,(g)}$. A silver coating was deposited on the surface by immersing the

copper plate in a 0.01 M $AgNO_3$ solution for 2 min. The plate was dried under a stream of $N_{2\,(g)}$ and re-immersed in the $AgNO_3$ for 5 min, dried, re-immersed for a further 5 min and then dried. The Ag-coated copper plate was then dip coated (50 times) into a solution of **[1][A]** in acetone (8.15 mmol·L^{-1}) and for **[2][X]** the substrate was immersed in solution of acetone (8.15 mmol·L^{-1}) for 15 min. It is important to note here that **[1][A]** and **[2][X]** are also soluble at room temperature in trifluorotoluene, methyl ethyl ketone and likely other fluorous solvents at elevated temperatures. Scanning electron microscope images of the surfaces were obtained using a Hitachi S-4500 instrument, operated at an electron beam voltage of 5 kV or the LEO/Zeiss 1540XB FIB/SEM CrossBeam operated at an electron beam voltage of 1 kV. Water contact angles were measured on a Ramé-Hart Instrument Co. goniometer with DROPimage software or on a FTA 1000 Drop Shape Instrument, B Frame with FTA Video Drop Shape Software. Using an automated dispensing system, a minimum of 3 static 4-6 μL droplets of ultrapure water (Aldrich) were deposited in different areas upon the surface. The contact angles were measured on the left and right side of each drop on at least 3 identical substrates resulting in a minimum of 18 angles per ionic liquid coating, which were reported as the average.

The UV stability experiment was carried out by placing neat **[1][I]** (0.374 g) in a glass vial and exposing it to broad spectrum UV light (Ace Glass, medium pressure, quartz, mercury-vapour immersion lamp) for 12 h. The sample exhibited no change in mass and an alloquot was analyzed by NMR spectroscopy, which revealed no detectable decomposition or reactivity.

Synthesis of $C(CH_3)_3CH_2CH(CH_3)CH_2P((CH_2)_2(CF_2)_7CF_3)_2$.[S1] A (15 mL) pressure tube was charged with *1H,1H,2H*-perfluorodec-1-ene (23.8 mmol), 2,4,4'-trimethylpentyl phosphine, 40 wt % in toluene, (11.9 mmol) and VAZO 67 (0.95 mmol, 8 mol %) under nitrogen and stirred at 80 °C for 2h. Further addition of VAZO 67 was added every 2 h (3 × 8 mol %), after which,

the solution was stirred at 80°C for 17 h. Excess fluorous olefin, and diethyldimethyl-succinonitrile were removed *via* sublimation from the oil (60 °C; -20 °C cold finger). The remaining brown liquid was distilled (0.05 mmHg, 140 °C) to give a colourless viscous liquid (8.67 g, 8.35 mmol, 70%). ^{1}H NMR (399.76 MHz, $CDCl_3$) δ (ppm); 2.23-2.08 (m, 4H, PCH_2CH_2), 1.67-1.57 (m, 5H, PCH_2CH_2 and $(CH_3)_3CH_aH_bCHCH_3$)), 1.51-1.45 (ddd, 1H, $(CH_3)_3CH_aH_bCHCH_3$), ^{2}J= 14.0 Hz, ^{3}J= 3.2 Hz), 1.39-1.31 (m, 2H, $(CH_3)_3CH_aH_bCHCH_3CH_2P$)), 1.20-1.14 (ddd, 1H, $(CH_3)_3CH_aH_bCHCH_3$), ^{2}J= 14.0 Hz, ^{3}J= 1.2 Hz), 1.07-1.05 (d, 3H, $(CH_3)_3CH_aH_bCHCH_3$), J=6.8 Hz), 0.89 (s, 9H $(CH_3)_3CH_aH_bCHCH_3$)); ^{19}F{^{1}H} NMR (376.15 MHz, $CDCl_3$) δ (ppm); -86.6 (m, 6F), -120.6 (m, 4F), -127.6 (m, 12F), -128.5 (m, 4F), -129.1 (m, 4F), -131.9 (m, 4F); ^{31}P{^{1}H} NMR (161.83 MHz, $CDCl_3$) δ (ppm); -31.5 (s). MS (ESI); m/z^+ (%): 1037.1 (100) [M^+].

Synthesis of [1][I]. A 100 mL round bottom schlenk flask was charged with $RP[(CH_2)_2Rf_8]_2$ **(**R = 2,4,4'-trimethylpentyl) (2.663 g, 2.570 mmol), $I(CH_2)_2Rf_6$ (2.432 g, 5.131 mmol) and DMF (5 mL). The solution was heated to 120 °C and stirred for 6 h under a flow of nitrogen. The DMF was removed in vacuo (0.05 mmHg, 100 °C). The resulting liquid was dissolved in a minimal amount of acetone and extracted with 1:5 *n*-pentane:toluene mixture and placed at -30 °C to promote separation of product. Excess solvent was decanted and the residual volatiles were removed in vacuo resulting in a clear yellow glassy liquid (3.566 g, 2.358 mmol, 92 %). ^{1}H NMR (399.76 MHz, Acetone-d_6) δ (ppm); 3.45-3.38 (m, 6H, PCH_2CH_2), 3.23-3.18 (dd, 2H, $(CH_3)_3CH_aH_bCHCH_3CH_2P$), ^{2}J= 13.6 Hz, ^{3}J = 6.4), 3.11-2.96 (m, 6H, PCH_2CH_2), 2.47-2.40 (m, 1H, $(CH_3)_3CH_aH_bCHCH_3$)), 1.63-1.59 (dd, 1H, $(CH_3)_3CH_aH_bCHCH_3$), ^{2}J= 14.0 Hz, ^{3}J= 2.4 Hz), 1.49-1.44 (dd, 1H, $(CH_3)_3CH_aH_bCHCH_3$), ^{2}J= 14.0 Hz, ^{3}J= 8.4 Hz), 1.33-1.31 (d, 3H, $(CH_3)_3CH_aH_bCHCH_3$), J= 6.8Hz), 0.97 (s, 9H, $(CH_3)_3CH_aH_bCHCH_3$)); ^{19}F{^{1}H} NMR (376.15

MHz, Acetone-d_6) δ (ppm); -82.2 (m, 9F), -115.4 (m, 6F), -122.9 (m, 14F), -123.8 (m, 12F), -127.3 (m, 6F); $^{31}P\{^1H\}$ NMR (161.83 MHz, Acetone-d_6) δ (ppm); 40.3 (s). MS (ESI); m/z^+ (%): 1385.0 (100) [M^+ -I], 2897.4 (20) [M_2I^+], 3151.6 (10) [$M_3I_2^+$].

General Procedure for anion exchange reactions for [1][BF_4] [1][PF_6] and [1][OTs]. A vial wrapped in aluminum foil was charged with the desired silver salt ($AgBF_4$, $AgPF_6$ or AgOTs, 2.49 mmol) in trifluorotoluene (5 mL). The phosphonium iodide (1.66 mmol) in trifluorotoluene (40 mL) was heated to dissolve (80 °C), added to the silver salt mixture and stirred for 5 days. The resulting suspension was centrifuged, the supernatant was passed through a celite column and the volites were removed *in vacuo*, yielding the desired phosphonium salt as a yellow viscous liquid. **[1][BF_4]**; 0.73g, 0.50 mmol, 75%; MS (ESI); $m/z^{+/-}$ (%): 1384.8 (100) [M^+ -BF_4], 2857.1 (2) [$M_2BF_4^+$], 1557.4 (100) [$M(BF_4)_2^-$], 3029.9 (15) [$M_2(BF_4)_3^-$]; Anal. Calcd. (Found) C, 29.35 (29.39); H, 1.99 (1.76); **[1][PF_6]**; 1.58 g, 1.04 mmol, 74%; MS (ESI); $m/z^{+/-}$ (%): 1387.3 (100) [M^+ -PF_6], 2913.2 (35) [$M_2PF_6^+$], 1674.2 (100) [MPF_6^-], 3205.3 (10) [$M_2(PF_6)_3^-$]; Anal. Calcd. (Found) C, 28.23 (29.16); H, 1.91 (1.79); **[1][OTs]**; 2.09 g, 1.34 mmol, 98%; MS (ESI); $m/z^{+/-}$ (%): 1384.9 (100) [M^+ -OTs], 2941.1 (38) [M_2OTs^+], 1726.9 (100) [$MOTs_2^-$], 3284.1 (18) [$M_2OTs_3^-$]; Anal. Calcd. (Found) C, 33.16 (33.31); H, 2.33 (2.58).

Synthesis of [1][OTf]. Compound **[1][I]** (0.2 g, 0.132 mmol) and trifluorotoluene (4 mL) and were heated (80 °C) until monophasic. Trimethylsilyltriflate (0.044 g, 0.198 mmol) in trifluorotoluene (1 mL) was added and the solution was stirred at RT for 18 h, at which time the volatiles were removed *in vacuo*, resulting in viscous yellow liquid (0.15g, 0.10 mmol, 75%). MS (ESI); $m/z^{+/-}$ (%): 1384.9 (100) [M^+ -OTf], 2919.5 (5) [M_2OTf^+], 1683.0 (100) [$MOTf_2^-$], 3217.8 (35) [$M_2OTf_3^-$]; Anal. Calcd. (Found) C, 28.94 (29.16); H, 1.91 (2.15).

Synthesis of [1][NTf$_2$]. Compound **[1][I]** (0.65 g, 0.43 mmol) and acetone (4 mL) and were heated (80 °C) until monophasic. Lithium bistriflimide (0.19 g, 0.65 mmol) in acetone (1 mL) was added and the solution was stirred at RT for 48 h. The solvent was removed *in vacuo* and the resulting yellow liquid was dissolved in trifluorotoluene and filtered. The filtrate was extracted with H_2O (20 mL x 4) and each aqueous layer was titrated with 10% $AgNO_3$ solution to confirm the removal of LiI. The organic fraction was dried with $MgSO_4$ and the volatiles were removed *in vacuo* producing a yellow waxy solid (0.55 g, 0.33 mmol, 76%). **[1][NTf$_2$]:** MS (ESI); $m/z^{+/-}$ (%): 1387.4 (100) [M^+ -(NTf_2)], 3048.3 (35) [$M_2(NTf_2)^+$], 1944.2 (70) [$M(NTf_2)_2^-$], 3610.8 (15) [$M_2(NTf_2)_3^-$].

Note: The $^{31}P\{^1H\}$ NMR spectra for the anion exchange products were identical to the phosphonium iodide (40.3 ppm). The anion exchange ^1H NMR and $^{19}F\{^1H\}$ NMR spectra were identical, given the nature of the alkyl and fluorous alkyl chains with the obvious variations for the specific anion.

General **[1][A]**: ^1H NMR (399.76 MHz, Acetone-d_6) δ (ppm); 3.30-3.23 (m, 6H, PCH_2CH$_2$), 3.08-2.94 (m, 8H, PCH$_2$CH_2, (CH$_3$)$_3$CH$_a$H$_b$CHCH$_3$CH_2P)), 2.45-2.34 (m, 1H, (CH$_3$)$_3$CH$_a$H$_b$CHCH$_3$)), 1.56-1.45 (m, 2H, (CH$_3$)$_3$CH_aH_bCHCH$_3$), 1.31 (d, 3H, (CH$_3$)$_3$CH$_a$H$_b$CHCH_3), J= 8.0 Hz), 0.96 (s, 9H, (CH_3)$_3$CH$_a$H$_b$CHCH$_3$)).

General **[1][A]**: $^{19}F\{^1H\}$ NMR (376.15 MHz, Acetone-d_6) δ (ppm); -81.6 (t, 9F, $^3J_{F\text{-}F}$ = 9.9 Hz), -115.5 (m, 6F), -122.5 (m, 14F), -123.6 (m, 12F), -127.1 (m, 6F).

[1][BF$_4$]: $^{19}F\{^1H\}$ NMR (376.15 MHz, Acetone-d_6) δ (ppm); -149.2 (s, 4F, $^1J_{B\text{-}F}$=19.5 Hz)

[1][PF$_6$]: $^{19}F\{^1H\}$ NMR (376.15 MHz, Acetone-d_6) δ (ppm); -72.8 (d, 6F, $^1J_{P\text{-}F}$=708.3 Hz); $^{31}P\{^1H\}$ NMR (161.83 MHz, Acetone-d_6) δ (ppm); -142.8 (sept, 6F, $^1J_{P\text{-}F}$= 708.2 Hz)

[1][OTs]: ^1H NMR (399.76 MHz, Acetone-d_6) δ (ppm); 7.67 (d, 2H), 7.12 (d, 2H), 2.31 (s, 3H).

[1][OTf]: $^{19}F\{^{1}H\}$ NMR (376.15 MHz, Acetone-d_6) δ (ppm); -79.5 (s, 3F).

[1][NTf$_2$]: $^{19}F\{^{1}H\}$ NMR (376.15 MHz, Acetone-d_6) δ (ppm); -80.5 (s, 6F).

Synthesis of $Rf_6(CH_2)_2P(O)(O^iPr)_2$.[S2]

Alterations to the referenced procedure include substituting $P(OEt)_3$ with $P(O^iPr)_3$, the reaction time was reduced to from 16 h to 8 h and the product was purified by distillation instead of column chromatography ($Rf_6(CH_2)_2P(O)(O^iPr)_2$ bp 138 °C, 0. 5 mmHg).

Yield; 11.29 g, 22.75 mmol, 56%; ^{1}H NMR (400.09 MHz, $CDCl_3$) δ (ppm); 4.74-4.66 (sept, 2H, $^{3}J_{H-H}$ = 6.4 Hz), 2.40-2.24 (m, 2H, CH_2CF$_2$), 1.95-1.86 (m, 2H, CH_2P), 1.30 (d, 12H, CH(CH_3)$_2$); $^{31}P\{^{1}H\}$ NMR (161.96 MHz, $CDCl_3$) δ (ppm); 26.6 (s); $^{19}F\{^{1}H\}$ NMR (376.15 MHz, $CDCl_3$) δ (ppm); -80.7 (m, 3F), -115.2 (m, 2F), -121.8 (m, 2F), -122.8 (m, 2F), -123.3 (m, 2F), -126.1 (m, 2F).

Synthesis of $Rf_6(CH_2)_2PH_2$. [S2]

Alterations to the referenced procedure include substituting $Rf_6(CH_2)_2P(O)(OEt)_2$ for $Rf_6(CH_2)_2P(O)(O^iPr)_2$, the reaction time was reduced from 16 h to 10 min.

Yield; 9.79 g, 25.76 mmol, 62%; ^{1}H NMR (399.8 MHz, $CDCl_3$) δ (ppm); 3.04 (dt, 2H, $^{1}J_{H-P}$ = 194.8 Hz, PH_2), 2.36-2.22 (m, 2H, CH_2CF$_2$), 1.79 – 1.70 (m, 2H, PCH_2); $^{31}P\{^{1}H\}$ NMR (161.96 MHz, $CDCl_3$) δ (ppm); -133.8 (s); $^{19}F\{^{1}H\}$ NMR (376.15 MHz, $CDCl_3$) δ (ppm); -80.9 (t, 3F, $^{3}J_{F-F}$ = 10.5), -115.1 (m, 2F), -122.0 (m, 2F), -123.0 (m, 2F), -123.6 (m, 2F), -126.2 (m, 2F).

Synthesis of $P[(CH_2)_2Rf_6]_3$. [S1]

Alterations to the referenced procedure include the use of a 20% excess of the fluorous olefin instead of a 25% excess, instead of $PhPH_2$, the primary phosphine used was $Rf_6(CH_2)_2PH_2$, the AIBN was substituted for VAZO 67 and the temperature was increased to 90 °C. After the final addition of VAZO 67, the reaction was allowed to stir for only 3 h instead of 7 h. The diethyldimethyl-succinonitrile was removed by sublimation (-20 °C cold finger, 0.5 mmHg, 60 °C oil bath) and the oil was distilled

$[Rf_6(CH_2)_2]_3P$ bp 130 °C, 0. 5 mmHg).

Yield; 16.55 g, 86.06 mmol, 60 %; ^{1}H NMR (400.09 MHz, $CDCl_3$) δ (ppm); 2.28-2.13 (m, 2H, C*H*$_2$CF$_2$), 1.78-1.71 (m, 2H, PC*H*$_2$); ^{31}P{^{1}H} NMR (161.96 MHz, $CDCl_3$/$C_7H_5F_3$) δ (ppm); -24.6 (s); ^{19}F{^{1}H} NMR (376.15 MHz, $CDCl_3$) δ (ppm); -80.9 (m, 3F), -114.9 (m, 2F), -122.0 (m, 2F), -122.9 (m, 2F), -123.4 (m, 2F), -126.2 (m, 2F).

Synthesis of $CH_3(CO)S(CH_2)_{12}Br$. [S3]

Alterations to the referenced procedure include the substitution of 2-(12-Bromododecyl)-1,4-dimethoxybenzene for 1,12-dibromododecane, the product was extracted in CH_2Cl_2 and H_2O instead of toluene and H_2O and the product was purified by column chromatography (10:1 hexane: ethyl acetate).

Yield; 6.30 g, 19.43 mmol, 79%; ^{1}H NMR (400.09 MHz, $CDCl_3$) δ (ppm); 3.41 (t, 2H, $^3J_{H\text{-}H}$ = 6.8 Hz, BrC*H*$_2$), 2.86 (t, 2H, $^3J_{H\text{-}H}$ = 7.4 Hz, SC*H*$_2$), 2.32 (s, 3H, C*H*$_3$CO), 1.85 (quintet, 2H, $^3J_{H\text{-}H}$ = 7.2 Hz, BrCH$_2$C*H*$_2$), 1.56 (quintet, 2H, $^3J_{H\text{-}H}$ = 6.8 Hz, SCH$_2$C*H*$_2$), 1.46-1.26 (m, 16H, CH_2).

Synthesis of $HS(CH_2)_{12}Br$. Workentin, J. ElectroAnal. Chem. 2007, 218.

Alternations to the referenced procedure include the substitution of S-12-(2,5-dihydroxyphenyl)dodecyl ethanethioate with $CH_3(CO)S(CH_2)_{12}Br$ and K_2CO_3 for concentrated HCl, the reaction time was reduced from 12 h to 5 h and the product was purified by sublimation (-20°C cold finger, 0.5mmHg, 70°C oil bath).

Yield; 3.47 g, 12.32 mmol, 89%; ^{1}H NMR (400.09 MHz, $CDCl_3$) δ (ppm); 3.40 (t, 2H, $^3J_{H\text{-}H}$ = 7.2 Hz, BrC*H*$_2$), 2.51 (dt, 2H, $^3J_{H\text{-}H}$ = 7.2 Hz, HSC*H*$_2$), 1.84 (quintet, 2H, $^3J_{H\text{-}H}$ = 7.2 Hz, BrCH$_2$C*H*$_2$), 1.60 (quintet, 2H, $^3J_{H\text{-}H}$ = 7.2 Hz, HSCH$_2$C*H*$_2$), 1.44-1.26 (m, 17H, CH_2 and SH t, $^3J_{H\text{-}H}$ = 7.6 Hz). 13C NMR (100.60 MHz, $CDCl_3$) δ (ppm); 45.14, 34.01, 32.80, 32.61, 29.45, 29.03, 28.85, 28.72, 28.33, 28.14, 26.84, 24.62.

Synthesis of [2][Br]. A pressure tube was charged with 1-bromo-12-mercaptododecane (2.62 g, 9.33

mmol) in DMF (15 mL) and $P[(CH_2)_2Rf_6]_3$ (5.00 g, 4.66 mmol) in trifluorotoluene (15 mL) under nitrogen and heated at 130 °C for 24 h. The solvent was removed in vacuo at 100 °C and the impurities were removed by sublimation (110 °C; -20 °C cold finger) and the liquid was further purified by dissolving in a minimal amount of trifluorotoluene and extracted with 1:1 n-pentane:toluene mixture. Excess solvent was decanted and the residual volatiles were removed in vacuo resulting in a clear dark orange viscous liquid (3.71 g, 2.74 mmol, 59 %). ^{1}H NMR (599.69 MHz, Acetone-d_6) δ (ppm); 3.45-3.39 (m, 6H, CH_2CF$_2$), 3.25-3.20 (m, 2H, PCH_2CH$_2$CH$_2$), 3.07-2.99 (m, 6H, PCH_2CH$_2$CF$_2$), 2.50 (dt, 2H, $^{3}J_{H\text{-}H}$ = 7.8 Hz, HSCH_2), 1.87-1.83 (m, 2H, PCH$_2$CH$_2$CH_2), 1.66 (t, 1H, $^{3}J_{H\text{-}H}$ = 7.8 Hz, *H*S), 1.59-1.53 (m, 4H, CH$_2$), 1.44-1.37 (m, 4H, CH$_2$), 1.32-1.29 (m, 10H, CH$_2$). ^{19}F{^{1}H} NMR (376.15 MHz, Acetone-d_6) δ (ppm); -81.2 (s, 9F), -114.4 (m, 6F), -121.9 (m, 6F), -122.8 (m, 12F), -126.3 (m, 6F); ^{31}P{^{1}H} NMR (161.83 MHz, Acetone-d_6) δ (ppm); 40.1 (s); MS (ESI); $m/z^{+/-}$ (%): 1271.1 (100) [M^+ - Br], 2623.0 (15) [M_2Br^+], 3974.0 (1) [$M_3Br_2^+$], 1430.6 (100) [MBr_2^-], 2782.3 (12) [$M_2Br_3^-$], 4133.9 (2) [$M_3Br_4^-$]; FT-IR (cm^{-1}(ranked intensity)); 456(20), 530(6), 566(13), 605(19), 707(7), 736(11), 780(15), 810(12), 846(17), 913(18), 951(14), 1020(16), 1071(8), 1259(3), 1317(5), 1365(4), 1438(9), 1717(21), 2462(22), 2858(2), 2929(1).

Synthesis of [2][NTf$_2$]. Lithium bistriflimide (0.65 g, 2.26 mmol) in acetone (5 mL) was added dropwise to **[2][Br]** (1.53 g, 1.13 mmol) in acetone (25 mL) under nitrogen and was stirred for 44 h. The solvent was removed *in vacuo* and the salt was re-dissolved in trifluorotoluene (25 mL), filtered and then transferred to a Schlenk tube. The solution was extracted with degassed H_2O (3 × 60 mL) and then dried with $MgSO_4$, filtered and the solvent was removed *in vacuo*. The impurities were removed by sublimation (110 °C; -20 °C cold finger) and the liquid was further purified by dissolving in a minimal amount of trifluorotoluene and extracted with Et_2O. The residual solvent and water was removed *in vacuo* at 90 °C for 36 h yielding a brown liquid (0.82 g, 0.53 mmol, 47 %). ^{1}H NMR (599.69 MHz,

Acetone-d_6) δ (ppm); 3.27-3.23 (m, 6H, CH_2CF$_2$), 3.07-2.93 (m, 8H, PCH_2CH$_2$CH$_2$, PCH_2CH$_2$CF$_2$), 2.50 (dt, 2H, $^3J_{H\text{-}H}$ = 7.8 Hz, HSCH_2), 1.96-1.89 (m, 2H, PCH$_2$CH$_2$CH_2), 1.63 (t, 1H, $^3J_{H\text{-}H}$ = 7.8 Hz, *H*S), 1.60-1.54 (m, 4H, CH$_2$), 1.41-1.36 (m, 4H, CH$_2$), 1.32-1.28 (m, 10H, CH$_2$). ^{19}F{^{1}H} NMR (376.15 MHz, Acetone-d_6) δ (ppm); -79.5 (s, 6F), -81.2 (s, 9F), -114.7 (m, 6F), -121.9 (m, 6F), -123.0 (m, 12F), -126.3 (m, 6F); ^{31}P{^{1}H} NMR (161.83 MHz, Acetone-d_6) δ (ppm); 41.3 (s); MS (ESI); $m/z^{+/-}$ (%): 1273.9 (100) [M^+ -(NTf$_2$)], 2821.6 (10) [M_2(NTf$_2$)$^+$], 1833.0 (65) [M(NTf$_2$)$_2^-$]. FT-IR (cm^{-1}(ranked intensity)); 513(12), 531(16), 571(9), 618(5), 652(10), 708(7), 741(8), 790(14), 810(13), 847(17), 913(19), 952(15), 1100(6), 1244(2), 1348(3), 1441(18), 2386(21), 2859(11), 2981(1). Anal. Calcd. (Found) C, 29.39 (30.14); H, 2.39 (2.10).

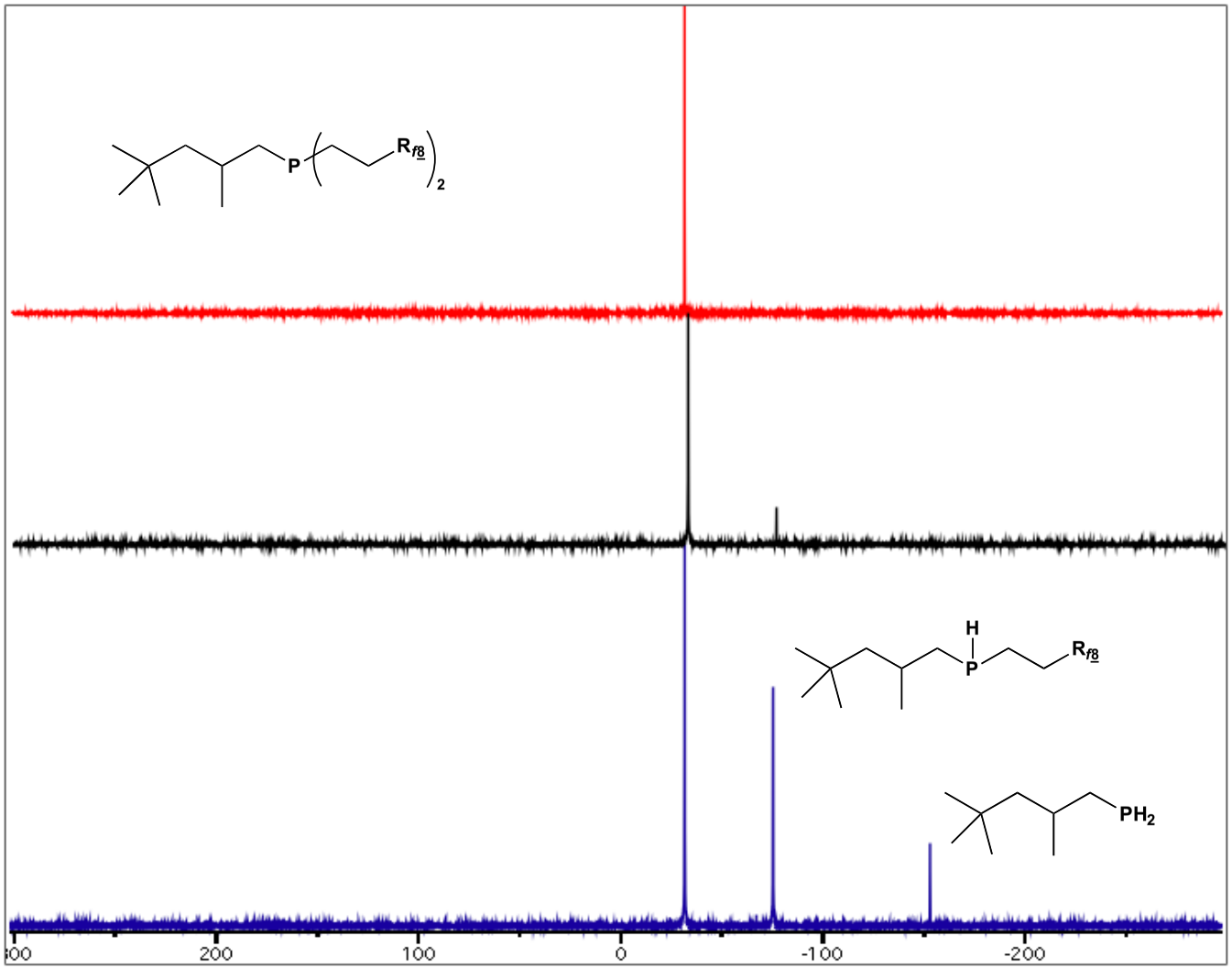

Figure S-1: $^{31}P\{^{1}H\}$ NMR spectrum indicating the transition from the primary phosphine to the fluorinated tertiary phosphine.

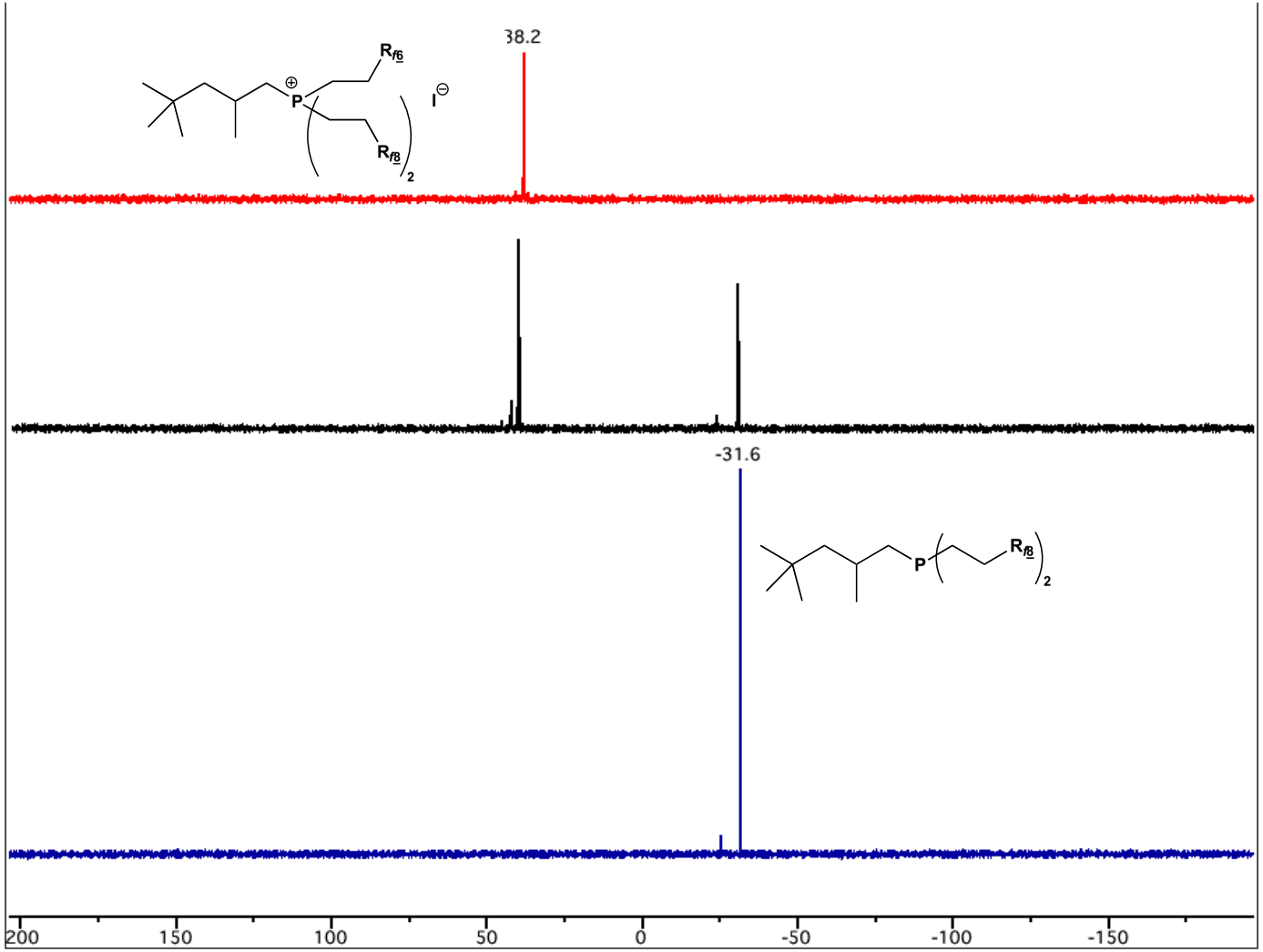

Figure S-2: $^{31}P\{^{1}H\}$ NMR spectrum demonstrating the conversion of the phosphine to the phosphonium salt **[1][I]**.

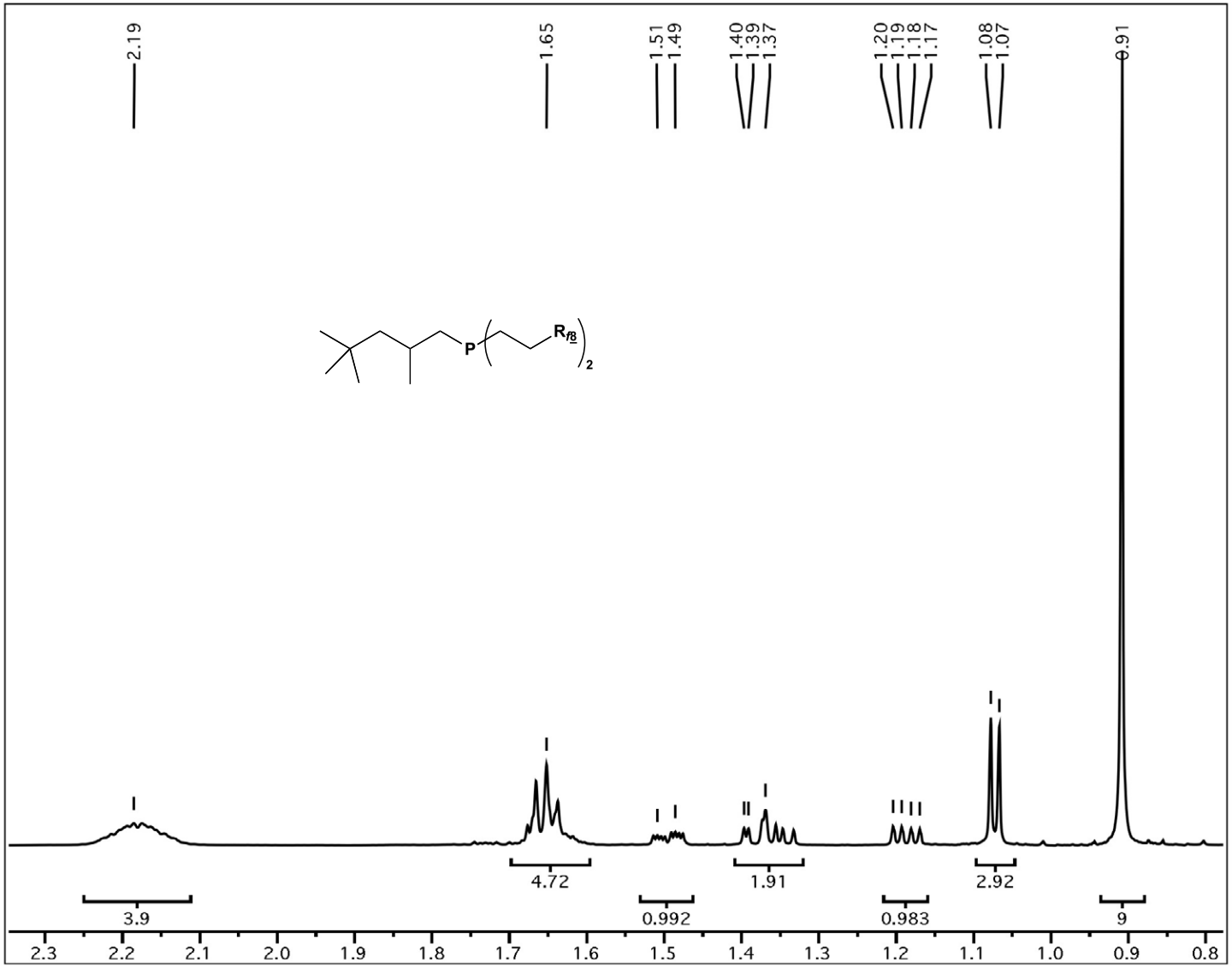

Figure S-3: ^{1}H NMR spectrum of the fluorinated tertiary phosphine.

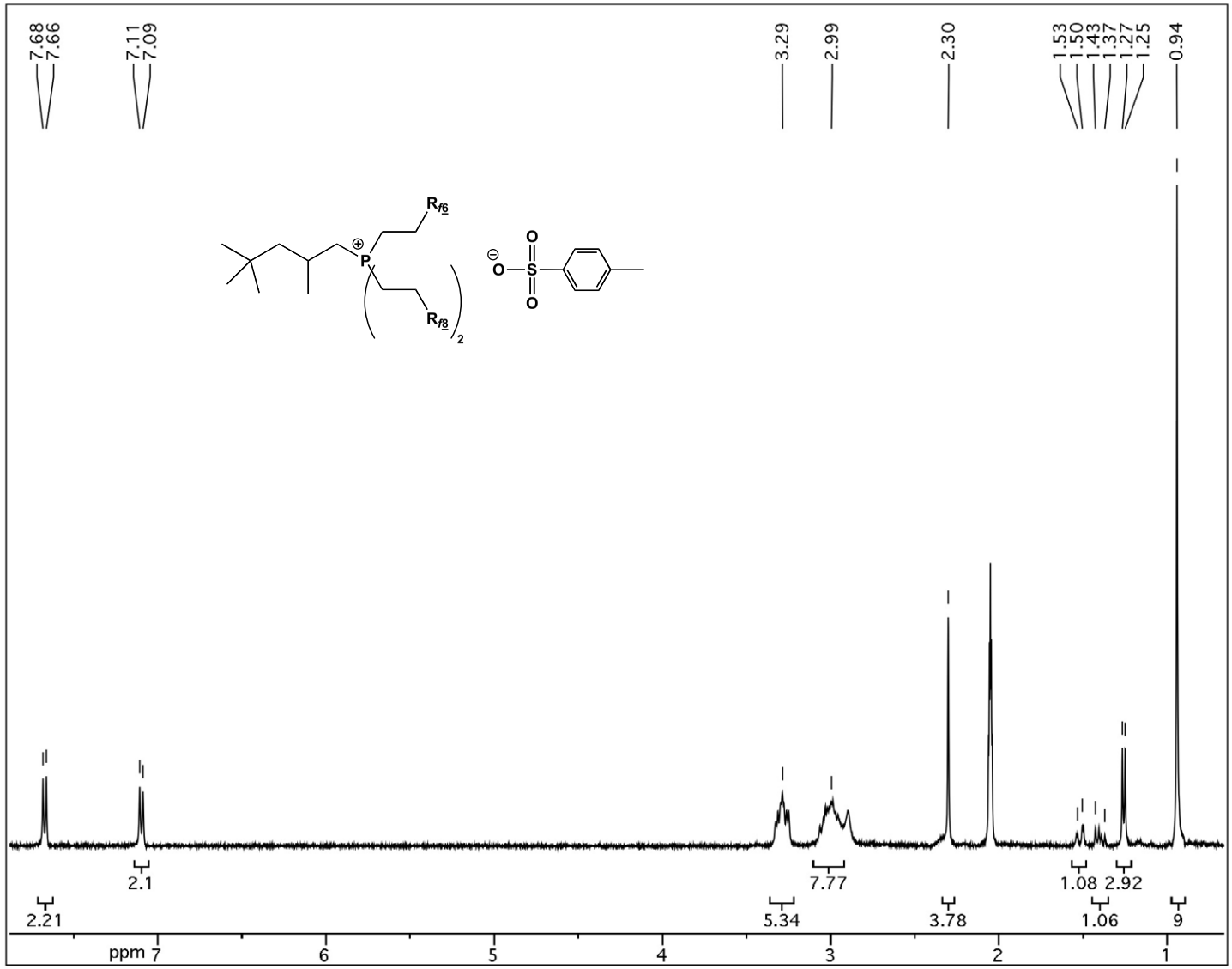

Figure S-4: ^{1}H NMR spectrum of **[1][OTs]**

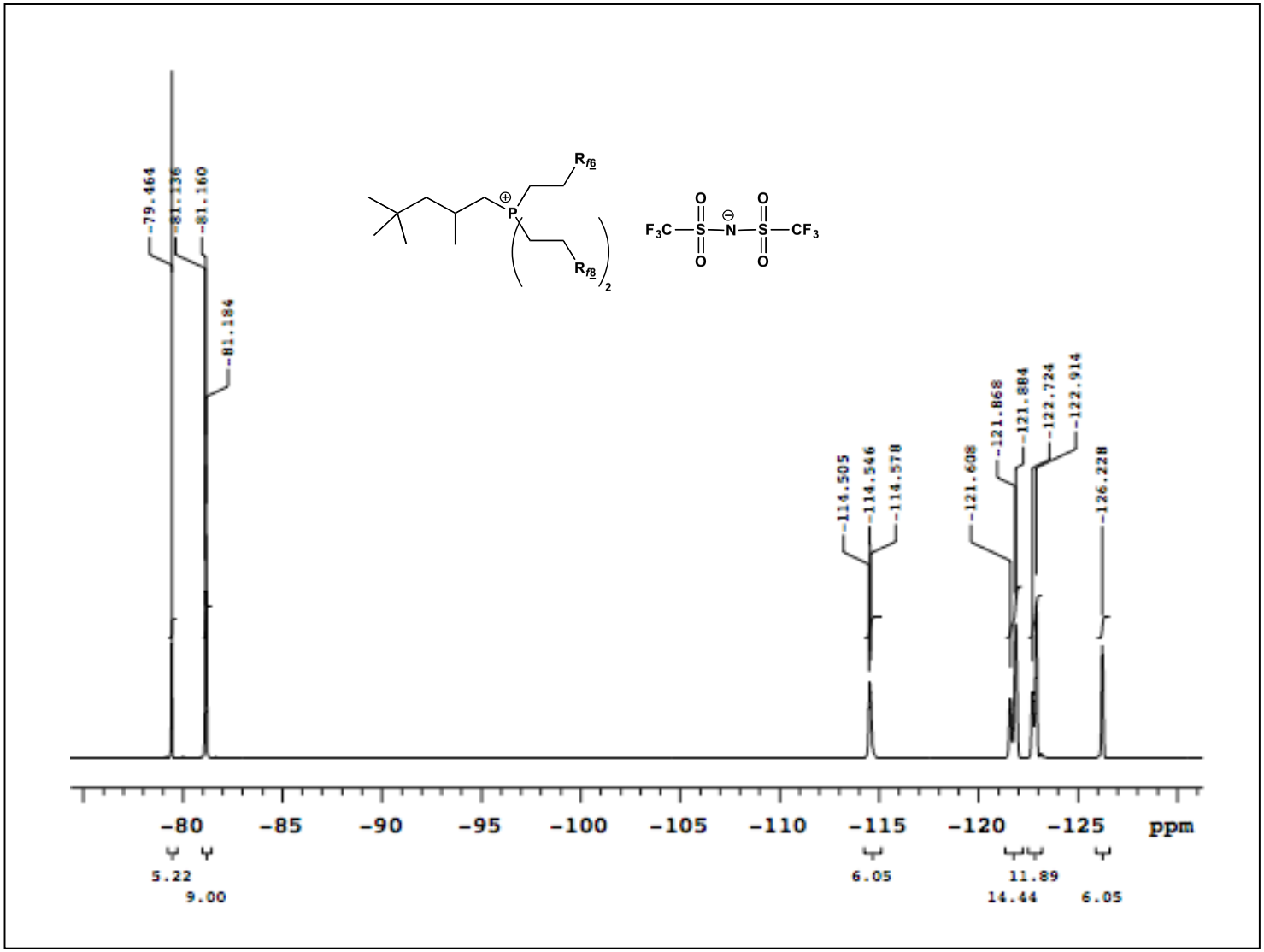

Figure S-5: $^{19}F\{^{1}H\}$ NMR spectrum of **[1][NTf$_2$]**

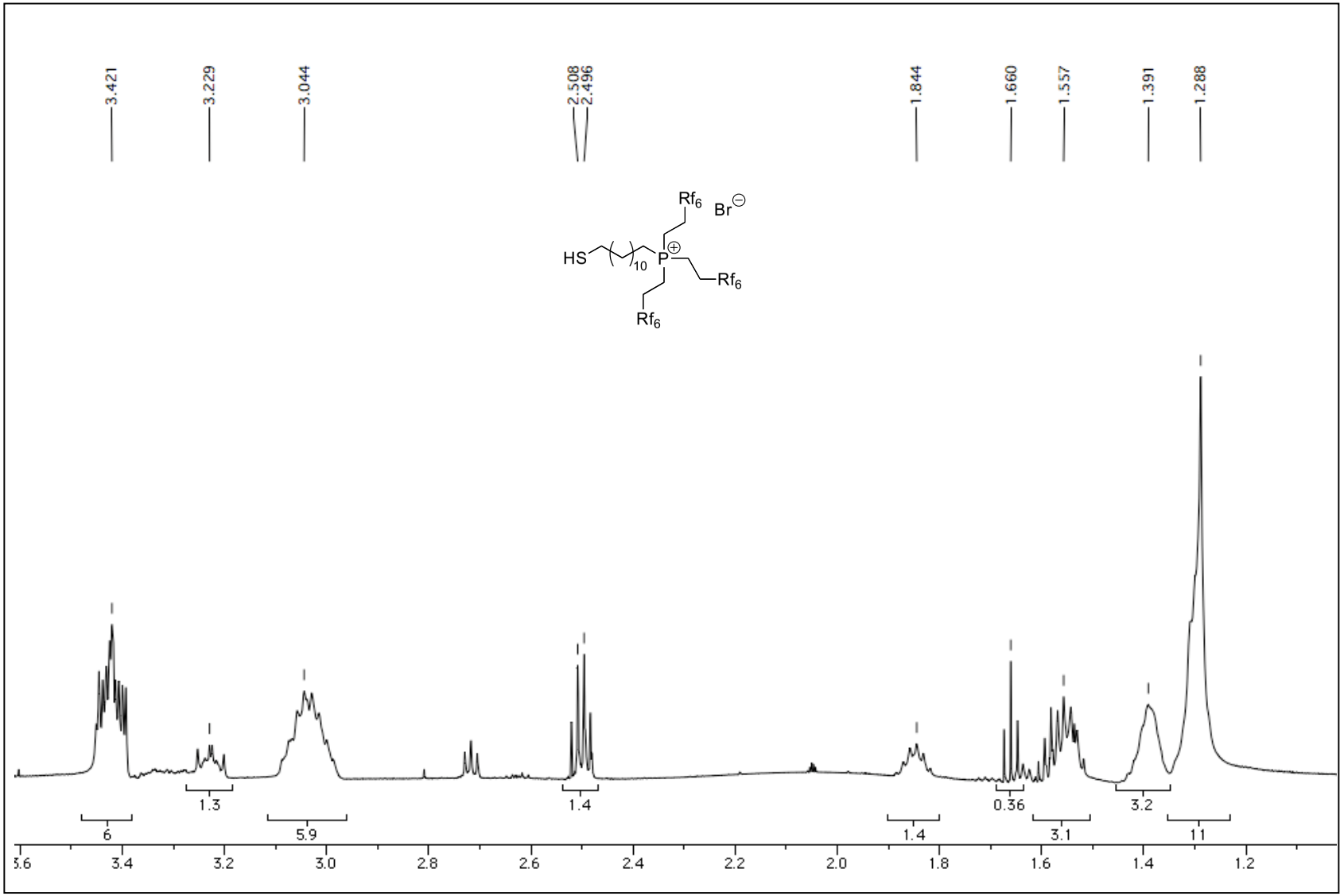

Figure S-6: ^{1}H NMR spectrum of **[2][Br]**

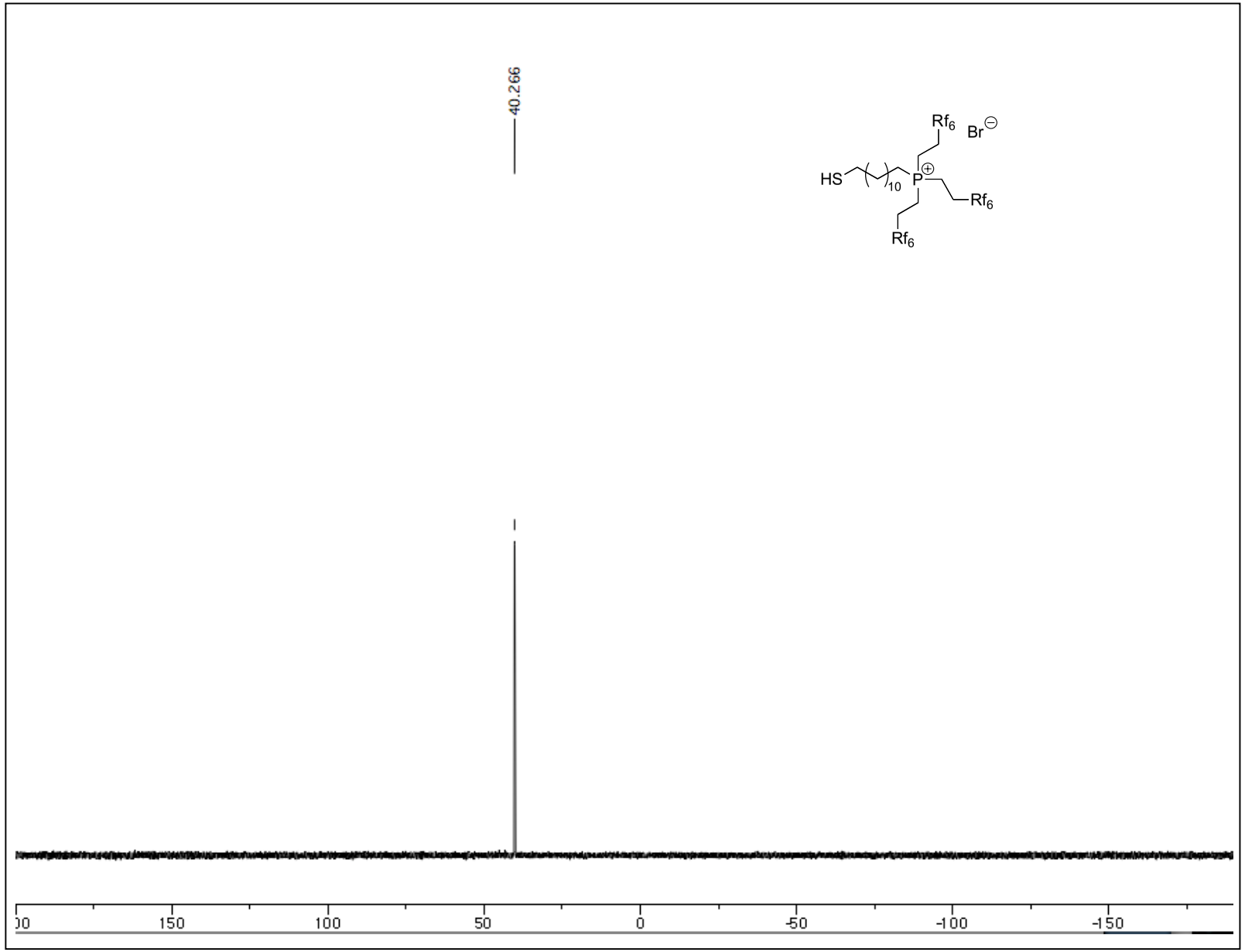

Figure S-7: $^{31}P\{^{1}H\}$ NMR Spectrum of **[2][Br]**

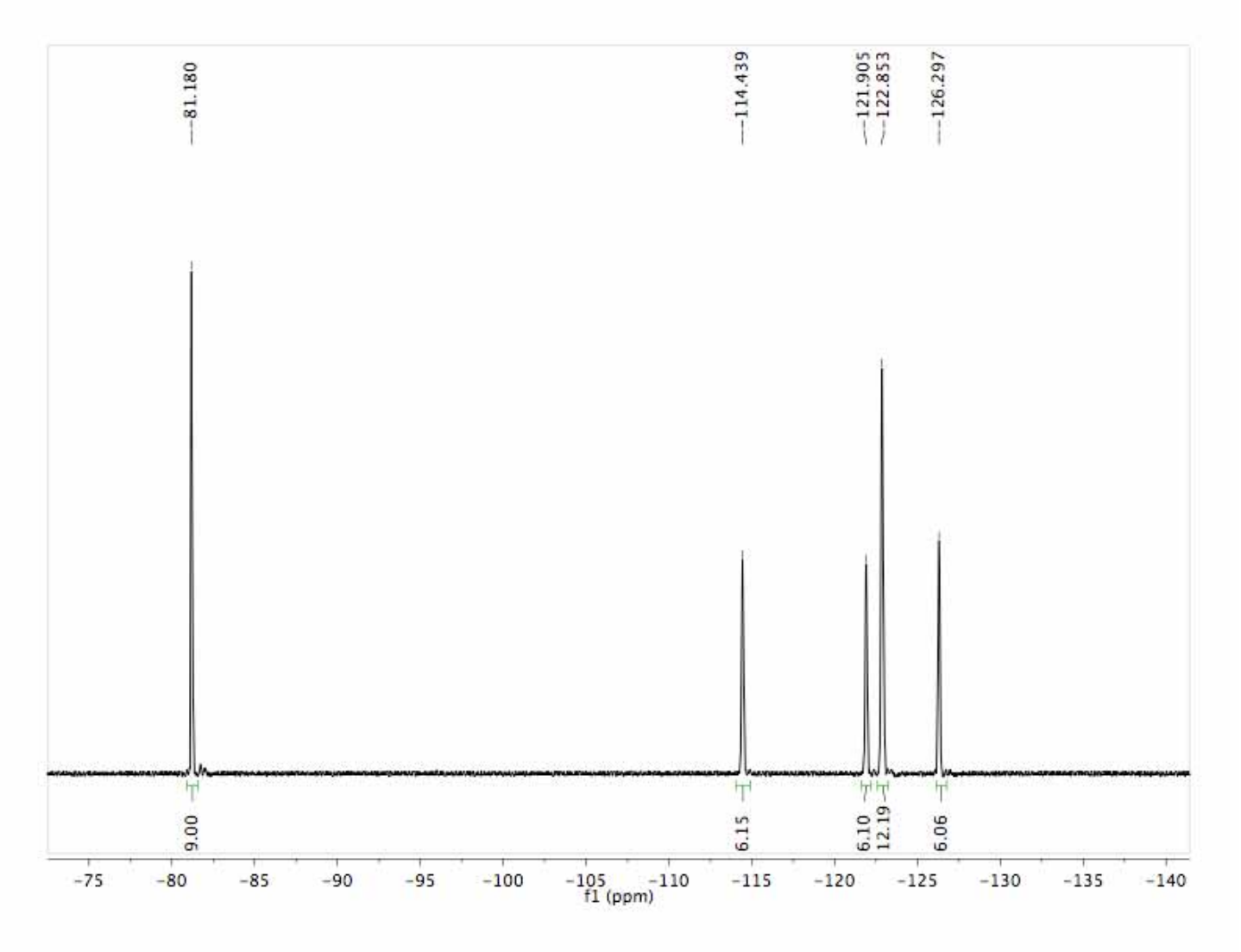

Figure S-8: $^{19}F\{^{1}H\}$ NMR Spectrum of **[2][Br]**

Table S-1: Water Content in **[1][A]** determined by Karl Fischer titration (mM).

Sample [A]	Average Water Content (mM)
$[BF_4]$	0.556
$[NTf_2]$	0
[OTf]	0.779
[I]	0
[OTs]	1.019
$[PF_6]$	0

Thermal Stability of PILs under Dynamic Heating Experiments:

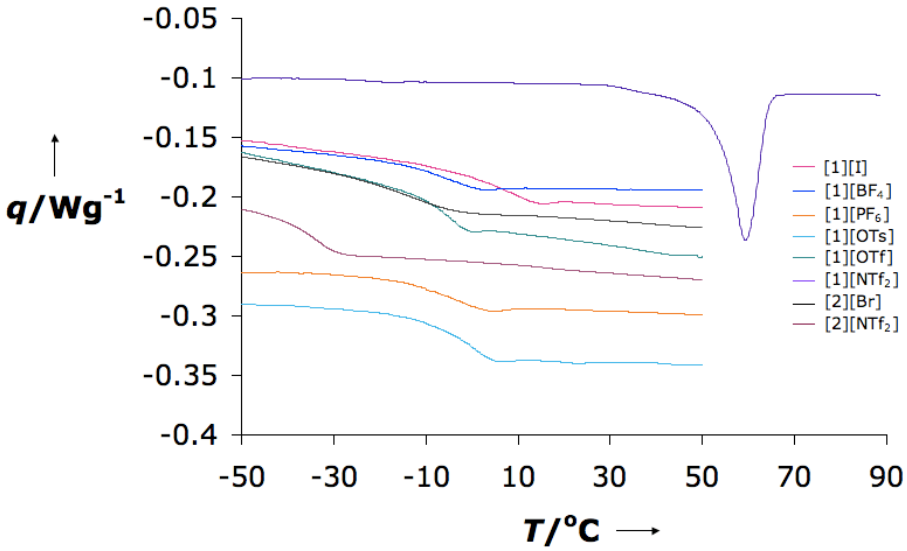

Figure S-9: DSC heat ramp analysis for **[1][A]** and **[2][X]**

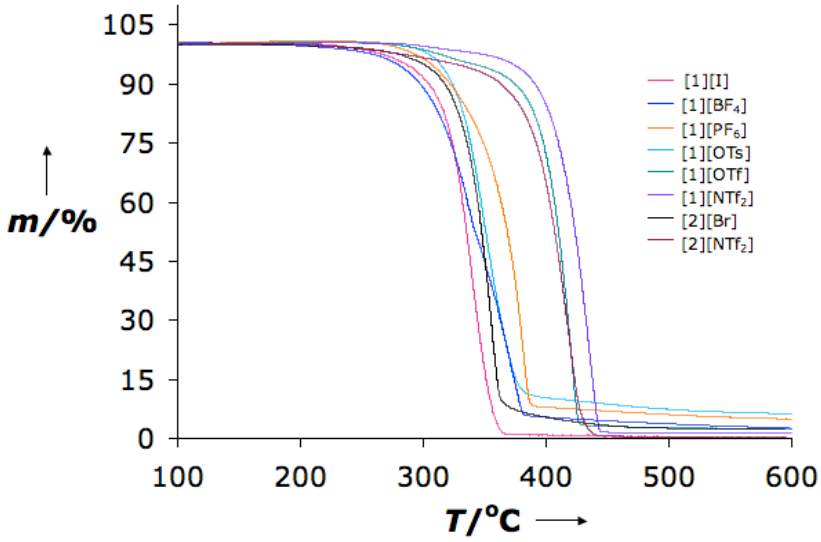

Figure S-10: TGA heat ramp analysis for **[1][A]** and **[2][X]**

Thermal Stability of PILs under Isothermal Heating Experiments:

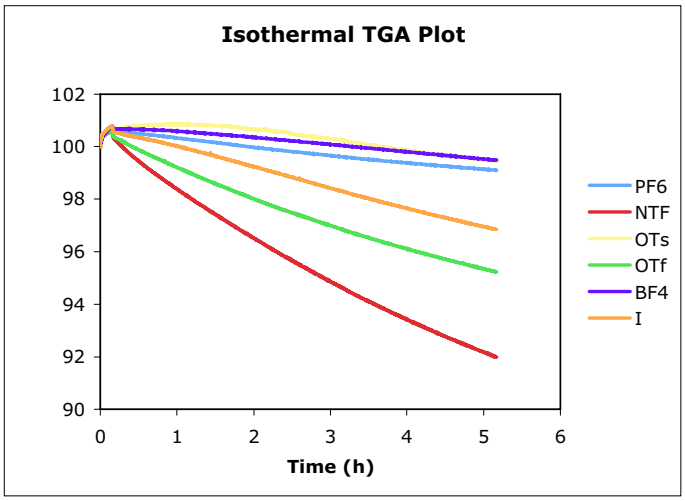

Figure S-11: Isothermal TGA Plot for **[1][A]**

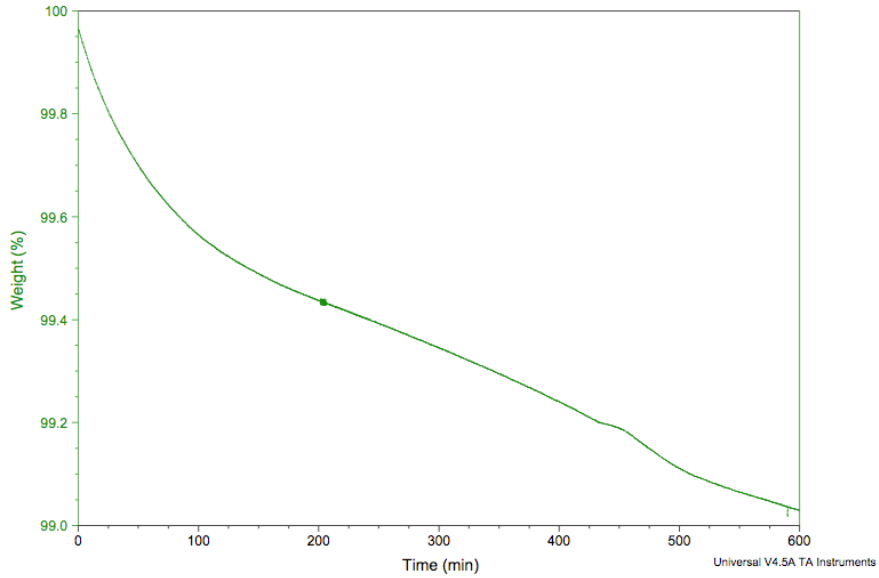

Figure S-12: Isothermal TGA Plot for **[2][Br]**

Thermal Stability Check Determined using Differential Scanning Calorimetry for [1][A]:

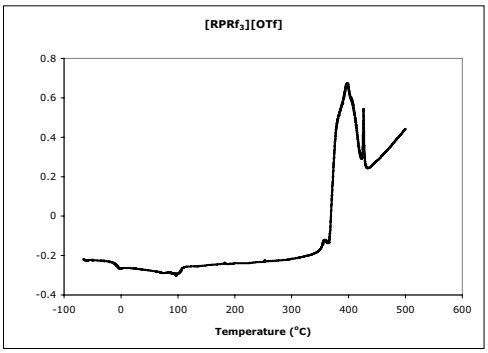

Figure S-13: Thermal stability of **[1][OTf]** determined by DSC

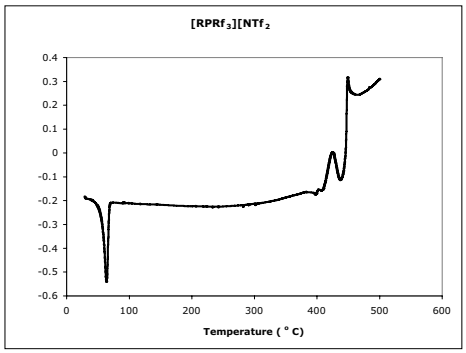

Figure S-14: Thermal stability of **[1][NTf_2]** determined by DSC

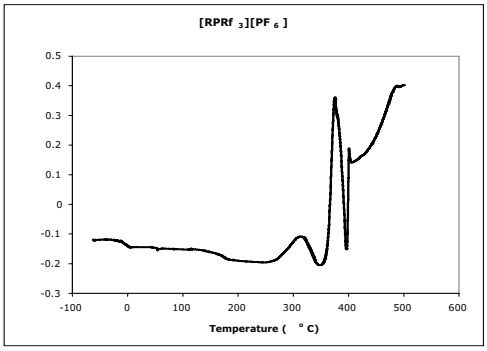

Figure S-15: Thermal stability of **[1][PF_6]** determined by DSC

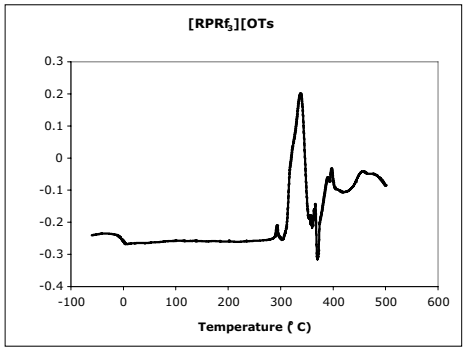

Figure S-16: Thermal stability of **[1][OTs]** determined by DSC

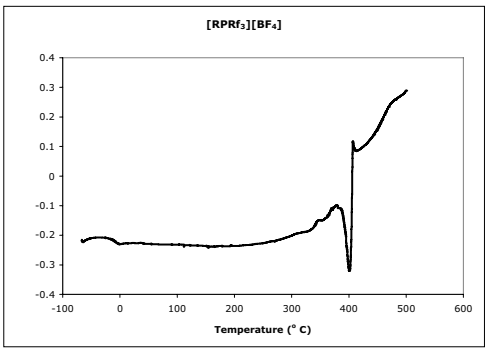

Figure S-17: Thermal stability of **[1][BF_4]** determined by DSC

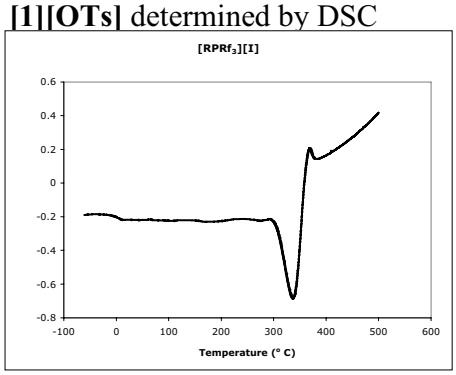

Figure S-18: Thermal stability of **[1][I]** determined by DSC

References:

In addition to the references mentioned in the experimental details, further citations regarding fluorinated ionic liquids are listed below (S4 to S6), which may be of interest to the reader but where not essential to the body of the manuscript herein.

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[S3] M. Shamsipur, S. H. Kazemi, A. Alizadeh, M. F. Mousavi, M. S. Workentin, *J. Electroanal. Chem.* **2007**, *610*, 218.

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[S7] A. Vidiš, G. Laurenczy, E. Küsters, G. Sedelmeier, P. J. Dyson, *J. Phys. Org. Chem.* **2007**, *20*, 109.