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# Pentafluoroethyl(fluoro)phosphate ionic liquids: Synthesis and properties

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## Experimental Section

Reactions involving air-sensitive compounds were performed either in 100, 250, or 500 mL round-bottom flasks or in 20 or 60 mL glass tubes equipped with valves with PTFE stems (Rettberg, Göttingen) under argon using standard Schlenk-line techniques. $^{1}$H, $^{13}$C, $^{19}$F, and $^{31}$P NMR spectra were recorded at 25 °C in $(CD_3)_2CO$ or $CD_3CN$ on a Bruker Avance I 500 spectrometer equipped with a Prodigy Cryoprobe ($^{1}$H: 500.1 MHz, $^{13}$C: 125.7 MHz, $^{19}$F; 470.6 MHz, $^{31}$P: 202.5 MHz) or on a Bruker Avance Neo I 600 spectrometer ($^{1}$H: 600.2 MHz, $^{13}$C: 150.9 MHz, $^{19}$F: 564.7 MHz, $^{31}$P: 243.0 MHz). The $^{13}$C{$^{19}$F} NMR spectra were recorded on a Bruker Avance I 500 spectrometer equipped with a Prodigy Cryoprobe. The NMR signals were referenced against TMS ($^{1}$H and $^{13}$C), $CFCl_3$ with $\Xi(^{19}F)$ = 94.094011 MHz and 85% $H_3PO_4$ in $H_2O$ ($^{31}$P) with $\Xi(^{31}P)$ = 40.480742 MHz as external standards[1]. $^{1}$H and $^{13}$C chemical shifts were calibrated against the residual solvent signal and the solvent signal, respectively ($\delta(^{1}H)$: $(CD_2H)(CD_3)CO$ 2.05 ppm; $\delta(^{13}C)$: $(CD_3)_2CO$ 206.26 and 29.84 ppm).[2]

IR spectra were measured in the attenuated total reflection (ATR) mode in the region of 4000–400 cm$^{-1}$ with an apodized resolution of 2 cm$^{-1}$ with a Bruker Alpha II FT-IR spectrometer equipped with a monolithic diamond crystal ATR accessory. Raman spectra were recorded at room temperature with a MultiRAM FT-Raman spectrometer (Bruker) using the 1064 nm excitation line of a Nd/YAG laser on crystalline or liquid samples contained in melting point capillaries in the region of 3500–100 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. Elemental analyses (C, H, N) were performed with an Elementar Varion Micro Cube instrument. Viscosities and densities were measured with a rolling-ball viscometer Lovis 2000 ME combined with DMA 4100 M density meter (Anton Paar) at different angles and temperatures.

Thermal analyses were performed with a DSC 204 F1 Phoenix (Netzsch) in the temperature range of –175 to 550 °C with a heating rate of 10 K min$^{-1}$.

DTA measurements were performed with a STA 449 F3 Perseus (Netzsch), connected to an Alpha FT-IR spectrometer (Bruker) for the analysis of the gaseous decomposition products, in the temperature range of 30 to 500 °C with a heating rate of 10 K min$^{-1}$.

The isobaric heat capacity ($c_p$) measurements of [BMIm]**FAP$^{n}$** (n = 0–3) were performed at atmospheric pressure using a *NETZSCH DSC 204 F1* differential scanning calorimeter (DSC) between 273 and 448 K. Aluminum crucibles (25 µL) with lid were used for all measurements

which had been heated to 773 K before usage. A blank measurement (baseline correction) was conducted for each empty crucible. Sapphire (39.2 mg) was used as $c_p$ reference resulting in an uncertainty of ±5 %.[3] Sample masses between 39.1-40.9 mg were prepared using a *Sartorius M3P* micro balance. Each measurement was performed under a nitrogen flow of 20 ml·min$^{-1}$ at a heating rate of 10 K·min$^{-1}$ with an isothermal step of 20 min before and after heating.

The FT-IR spectra of the gaseous ARC high-temperature reaction products of [BMIm][$PF_6$] and [BMIm]**FAP$^3$** were acquired using a *Bruker VERTEX 80V* spectrometer equipped with a homebuilt stainless-steel gas cell (pathlength: 10 cm), a nitrogen-cooled mercury cadmium telluride (MCT) detector, and a KBr beamsplitter as well as KBr windows. The spectra were recorded at around 2 mbar sample pressure at room temperature with a resolution of 0.02 cm$^{-1}$ at a scan speed of 10 kHz. A total of 76 scans were accumulated for each spectrum.

Heat-Wait-Search (HWS) experiments of [BMIm]**FAP$^n$** (n = 0–3) were conducted with a *NETZSCH 254* Accelerating Rate Calorimeter (ARC) under near-adiabatic conditions. Each HWS process involved a heat step of 5 K at 2 K·min$^{-1}$, a waiting time of 30 min$^{-1}$, and a tracking time of 10 min with a detection threshold of 0.015 K·min$^{-1}$. All samples were placed in a fresh spherical vessel (Hastelloy C alloy) with a max. capacity of 7.5 mL and a wall thickness of 0.81 mm. The sample and vessel masses, heat capacities at 298 K, phi factor, and temperature ranges, are listed in Table S1.

Table S1: Experimental Conditions for ARC Experiments.

| sample | m(sample) [g] | m(bomb) [g] | $c_p$(298K) [J·g$^{-1}$·K$^{-1}$] | Φ factor [-] | temperature [°C] |
|---|---|---|---|---|---|
| [BMIm][$PF_6$] | 1.98 | 20.92 | 1.36 | 4.543 | 100-500 |
| [BMIm]**FAP$^1$** | 1.96 | 20.71 | 1.59 | 4.031 | 110-500 |
| [BMIm]**FAP$^2$** | 2.05 | 20.86 | 1.30 | 4.570 | 125-500 |
| [BMIm]**FAP$^3$** | 2.06 | 21.15 | 1.19 | 4.934 | 225-500 |

All electrochemical studies were performed on neat ILs under an argon atmosphere with a Metrohm PGSTAT30 potentiostat and a Microcell HC set-up with a Eurotherm temperature controller (rhd instruments). A 0.1 mL Pt-cell TSC-70 closed (rhd instruments) was applied and its cell body served as counter electrode, and it was equipped with a glassy carbon working electrode (surface area: 3.14 × 10$^{-2}$ cm$^2$). Specific conductivities ($\sigma$) were determined at different temperatures (20, 40 ,60, 70, and 80 °C) by impedance spectroscopy from 500 × 10$^3$ Hz to 800 Hz. The cell constant was determined on a 1413 µS cm$^{-1}$ conductivity

solution HI 70031 (HANNA instruments). Cyclic voltammetry was conducted at 20 °C with a scan rate of 50 mV $s^{-1}$ using the same set-up and an additional $Ag/Ag^+$ micro reference electrode (acetonitrile, rhd instruments).

The experimental FT-IR spectra were assigned based on harmonic IR frequency computations performed at the DFT/B3LYP/def2TZVPP level of theory[4-6] employing the *Gaussian16* computational chemistry software.[7] The computed frequencies were not scaled and were convolved with a Gaussian-shaped function ($\sigma$ = 6 $cm^{-1}$).

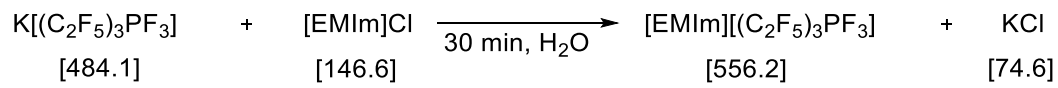
## Chemicals

All standard chemicals were obtained from commercial sources. Solvents were dried according to standard protocols and stored in flasks equipped with valves with PTFE stems (Rettberg, Göttingen) under an argon atmosphere. The phosphorane $(C_2F_5)_3PF_2$ was synthesized via electrochemical fluorination (ECF) of $(C_2H_5)_3P$.[8] Potassium-*mer*-tris(pentafluoroethyl)trifluorophosphate,[9,10] bis(pentafluoroethyl)phosphinic acid,[11-14] and pentafluoroethylphosphonic acid[11,14] were prepared according to literature methods. 1-Ethyl-3-methylimidazolium- and 1-butyl-3-methylimidazolium-hexafluorophosphate were purchased from Merck KGaA, Darmstadt, Germany.

# 1. Experimental

### 1.1 1-Ethyl-3-methylimidazolium fluorophosphates

#### 1.1.1 Synthesis of 1-ethyl-3-methylimidazolium *mer*-tris(pentafluoroethyl)trifluorophosphate ([EMIm]FAP$^3$)




Potassium [*mer*-tris(pentafluoroethyl)trifluorophosphate] (5.00 g, 10.3 mmol) was dissolved in water (20 mL) and a solution of [EMIm]Cl (1.51 g, 10.3 mmol) in water (20 mL) was added. After stirring for 30 minutes, the organic layer was removed and the aqueous layer was washed with $Et_2O$ (2 × 10 mL). The combined organic layers were thoroughly washed with bidistilled water (10 × 10 mL) until the residual aqueous phase remained clear after adding a solution of aqueous $AgNO_3$. All solvents were removed *in vacuo* and a viscous liquid remained.

**Yield**: 5.01 g (9.01 mmol, 87%) of a colorless liquid.

**$^1$H NMR** (500.1 MHz, 23 °C, $CD_3CN$): δ = 8.39 (s, 1H, C*H*), 7.34 (m, 1H, C*H*), 7.31 (m, 1H, C*H*), 4.17 (q, 2H, $^3J(^1H,^1H)$ = 7.22 Hz, C$H_2$), 3.82 (s, 3H, C$H_3$), 1.46 (t, 3H, $^3J(^1H,^1H)$ = 7.36 Hz, C$H_3$) ppm.

**$^{13}$C{$^1$H} NMR** (125.8 MHz, 23 °C, $CD_3CN$): δ = 136.6 (s, 1C, *C*H), 124.8 (s, 1C, *C*H), 123.1 (s, 1C, *C*H), 121.8 (qm, 2C, $^1J(^{19}F,^{13}C)$ = 280.4 Hz, *C*$F_3$), 121.2 (qm, 1C, $^2J(^{19}F,^{13}C)$ = 294.9 Hz, *C*$F_3$), 120.4 (m, 1C, *C*$F_2$), 118.9 (m, 2C, *C*$F_2$), 46.0 (s, 1C, *C*$H_2$), 36.9 (s, 1C, *C*$H_3$), 15.5 (s, 1C, *C*$H_3$) ppm.

**$^{13}$C{$^{19}$F} NMR** (125.8 MHz, 23 °C, $CD_3CN$): δ = 136.7 (dm, 1C, $^1J(^{13}C,^1H)$ = 220 Hz, *C*H), 124.8 (dm, 1C, $^1J(^{13}C,^1H)$ = 230.2 Hz, C*H*), 123.1 (dm, 1C, $^1J(^{13}C,^1H)$ = 207.2 Hz, C*H*), 121.7 (dm, 2C, $^2J(^{31}P,^{13}C)$ = 25.6 Hz, *C*$F_3$), 121.3 (d, 1C, $^2J(^{31}P,^{13}C)$ = 23.0 Hz, *C*$F_3$), 120.4 (d, 1C, $^1J(^{31}P,^{13}C)$ = 144.7 Hz, *C*$F_2$), 118.9 (d, 2C, $^1J(^{31}P,^{13}C)$ = 256.0 Hz, *C*$F_2$), 46.0 (tm, 1C, $^1J(^{13}C,^1H)$ = 145.7 Hz, *C*$H_2$), 36.9 (q, 1C, $^1J(^{13}C,^1H)$ = 143.8 Hz, *C*$H_2$), 15.0 (qt, 1C, $^1J(^{13}C,^1H$ = 129.0 Hz, *C*$H_3$), $^2J(^{13}C,^1H)$ = 3.76 Hz, *C*$H_3$) ppm.

**$^{19}$F NMR** (470.6 MHz, 23 °C, $CD_3CN$): δ = −44.8 (dm, 1F, $^1J(^{31}P,^{19}F)$ = 889.7 Hz, P*F*), −80.9 (m, 3F, C*F*$_3$), −83.6 (m, 6F, C*F*$_3$), −88.2 (dm, 2F, $^1J(^{31}P,^{19}F)$ = 902.0 Hz, P*F*), −116.3 (dm, 2F, $^2J(^{31}P,^{19}F)$ = 83.0 Hz, C*F*$_2$), −116.9 (dm, 4F, $^2J(^{31}P,^{19}F)$ = 97.8 Hz, C*F*$_2$) ppm.

**$^{31}P\{^{1}H\}$ NMR** (202.5 MHz, 23 °C, $CD_3CN$): δ = −147.9 (dtm, 1P, $^{1}J(^{31}P,^{19}F)$ = 902 Hz, $^{1}J(^{31}P,^{19}F)$ = 899.9 Hz) ppm.

**IR(ATR):** $\tilde{\nu}$ = 3179 (w, $\tilde{\nu}$(C–H)), 3128 (w, $\tilde{\nu}$(C–H)), 2997 (w, $\tilde{\nu}$(C–H)), 2976 (w, $\tilde{\nu}$(C–H)), 1598 (w), 1572 (w), 1473 (w), 1459 (w), 1433 (w), 1396 (w), 1359, (w), 1311 (m), 1296 (m), 1209 (s), 1183 (s), 1166 (s), 1126 (s), 1097 (s), 1070 (m), 1033 (vw), 963 (m), 807 (s), 760 (m), 743 (m), 717 (s), 637 (m), 615 (vs), 581 (m), 533 (m), 505 (w), 495 (m), 467 (w), 438 (m), 429 (m) $cm^{-1}$.

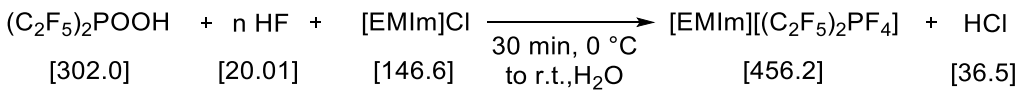
**Raman:** $\tilde{\nu}$ = 3187 (w, $\tilde{\nu}$(C–H)), 3120(w, $\tilde{\nu}$(C–H)), 2977 (s, $\tilde{\nu}$(C–H)), 2957 (s, $\tilde{\nu}$(C–H)), 2936 (s, $\tilde{\nu}$(C–H)), 2894 (w, $\tilde{\nu}$(C–H)), 2843 (w, $\tilde{\nu}$(C–H)), 2766 (w, $\tilde{\nu}$(C–H)), 2330 (w), 1572 (w), 1457 (w), 1422 (m), 1391 (w), 1337 (m), 1297 (w), 1252 (m), 1189 (m), 1112 (m), 1092 (m), 1026 (m), 962 (m), 744 (s), 725 (w), 703 (w), 637 (m), 600 (s), 542 (w), 432 (w) $cm^{-1}$.

**HRMS:** Calculated for $C_6F_{18}P^-$: 444.946 m/z, found: 444.943 m/z. Calculated for $C_6H_{11}N_2^+$: 111.092 m/z, found: 111.092 m/z.

**Elemental Analysis:** Calculated for [EMIm][*trans*-$(C_2F_5)_3PF_3$] (556.2 g·mol$^{-1}$): C, 25.91%; H, 1.99%; N, 5.04%; found: C, 26.43%; H, 2.17%; N, 6.13%.

**Refractive index** (25 °C): *n* = 1.37236.

### 1.1.2 Synthesis of 1-ethyl-3-methylimidazolium *trans*-bis(pentafluoroethyl)tetrafluorophosphate ([EMIm]FAP$^2$)




Bis(pentafluoroethyl)phosphinic acid (10 g, 5.60 mL, 33.1 mmol) was placed into a perfluoroalkoxy-copolymer (PFA) flask and cooled to 0 °C. Anhydrous HF (15.8 g, 17.1 mL, 790 mmol) was added and the mixture was stirred for 15 minutes. Crushed ice (50 g) and a solution of 1-ethyl-3-methylimidazolium chloride (4.62 g, 31.5 mmol) in water (20 mL) was added and stirred for 15 minutes while a colorless solid formed. The solid was filtered off and washed with water (10 × 10 mL) until pH of 7 of the washing phase.

**Yield**: 10.0 g (21.9 mmol, 70%) of a colorless solid.

**$^1$H NMR** (500.1 MHz, 23 °C, $CD_3CN$): $\delta$ = 8.38 (s, 1H, C*H*), 7.37 (m, 1H, C*H*), 7.31 (m, 1H, C*H*), 4.16 (q, 2H, $^3J(^1H,^1H)$ = 7.34 Hz, C$H_2$), 3.81 (s, 3H, C$H_3$), 1.45 (t, 3H, $^3J(^1H,^1H)$ = 7.34 Hz, C$H_3$) ppm.

**$^{13}$C{$^1$H} NMR** (125.8 MHz, 23 °C, $CD_3CN$): δ = 136.6 (s, 1C, C*H*), 124.7 (s, 1C, C*H*), 123.0 (s, 1C, C*H*), 121.5 (qm, 2C, $^1J(^{19}F,^{13}C)$ = 279.6 Hz, *C*$F_3$), 117.4 (m, 2C, *C*$F_2$), 45.9 (s, 1C, C$H_2$), 36.8 (s, 1C, C$H_3$), 15.5 (s, 1C, C$H_3$) ppm.

**$^{13}$C{$^{19}$F} NMR** (125.8 MHz, 23 °C, $CD_3CN$): δ = 135.5 (dm, 1C, $^1J(^{13}C,^1H)$ = 224.8 Hz, *C*H), 123.7 (dm, 1C, $^1J(^{13}C,^1H)$ = 206.2 Hz, *C*H), 121.9 (dm, 1C, $^1J(^{13}C,^1H)$ = 213.5 Hz, *C*H), 120.4 (d, 2C, $^2J(^{31}P,^{13}C)$ = 29.52 Hz, *C*$F_3$), 116.4 (d, 2C, $^1J(^{31}P,^{13}C)$ = 324.5 Hz, *C*$F_2$), 45.9 (tm, 1C, $^1J(^{13}C,^1H)$ = 142.5 Hz, C$H_2$), 36.8 (q, 1C, $^1J(^{13}C,^1H)$ = 144.7 Hz, C$H_3$), 15.5 (qt, 1C, $^1J(^{13}C,^1H)$ = 128.9 Hz, $^2J(^{13}C,^1H)$ = 3.74 Hz, *C*$H_3$) ppm.

**$^{19}$F NMR** (470.6 MHz, 23 °C, $CD_3CN$): δ = −72.8 (dquseptm, 4F, $^1J(^{31}P,^{19}F)$ = 915.9 Hz, $^3J(^{19}F,^{19}F)$ = 9.14 Hz, $^4J(^{19}F,^{19}F)$ = 7.39 Hz, P*F*), −83.5 (qum, 6F, $^4J(^{19}F,^{19}F)$ = 7.39 Hz, C*F*$_3$), −120.2 (dqum, 4F, $^2J(^{31}P,^{19}F)$ = 100.7 Hz, $^3J(^{19}F,^{19}F)$ = 9.11 Hz, C*F*$_2$) ppm.

**$^{31}$P{$^1$H} NMR** (202.5 MHz, 23 °C, $CD_3CN$): δ = −149.8 (ququm, 1P, $^1J(^{31}P,^{19}F)$ = 915.6 Hz, $^2J(^{31}P,^{19}F)$ = 100.9 Hz) ppm.

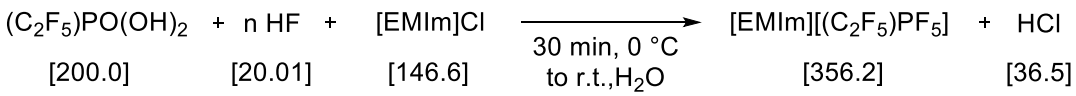
**IR(ATR):** $\tilde{\nu}$ = 3181 (w, $\tilde{\nu}$(C–H)), 3161 (w, $\tilde{\nu}$(C–H)), 3131 (w, $\tilde{\nu}$(C–H)), 3116 (w, $\tilde{\nu}$(C–H)), 3006 (s, $\tilde{\nu}$(C–H)), 2975 (s, $\tilde{\nu}$(C–H)), 2937 (m, $\tilde{\nu}$(C–H)), 2897 (m, $\tilde{\nu}$(C–H)), 2840 (s, $\tilde{\nu}$(C–H)), 1573 (m), 1459 (m), 1424 (m), 1389 (m), 1337 (m), 1254 (w), 1188 (m), 1146 (w), 1114 (m), 1096 (m), 1025 (m), 963 (m), 743 (s), 703 (w), 650 (s), 634 (w), 596 (m), 565 (w), 536 (w), 454 (w), 375 (m), 320 (m), 232 (m), 148 (w) $cm^{-1}$.

**Raman:** $\tilde{\nu}$ = 3181 (w, $\tilde{\nu}$(C–H)), 3163(w, $\tilde{\nu}$(C–H)), 3135 (w, $\tilde{\nu}$(C–H)), 3116 (w, $\tilde{\nu}$(C–H)), 3006 (m, $\tilde{\nu}$(C–H)), 2975 (s, $\tilde{\nu}$(C–H)), 2937 (m, $\tilde{\nu}$(C–H)), 2916 (m, $\tilde{\nu}$(C–H)), 2897 (m, $\tilde{\nu}$(C–H)), 2840 (w, $\tilde{\nu}$(C–H)), 2773 (m, $\tilde{\nu}$(C–H)), 2767 (w, $\tilde{\nu}$(C–H)), 2330 (w), 1573 (w), 1556 (w), 1515 (w), 1459 (m), 1433 (m), 1424 (m), 1389 (w), 1337 (m), 1303 (w), 1254 (w), 1210 (w), 1188 (w), 1172 (w), 1146 (w), 1114 (w), 1096 (m), 1033 (m), 1025 (m), 977 (w), 963 (m), 743 (s), 703 (m), 650 (s), 634 (w), 625 (w), 596 (m), 565 (w), 536 (w), 454 (w), 441 (w), 431 (w) $cm^{-1}$.

**HRMS:** Calculated for $C_4F_{14}P^-$: 344.952 m/z, found: 344.952 m/z. Calculated for $C_6H_{11}N_2^+$: 111.092 m/z, found: 111.092 m/z.

**Elemental Analysis:** Calculated for [EMIm][*trans*-$(C_2F_5)_2PF_4$] (456.2 g·mol$^{-1}$): C, 26.33%; H, 2.43%; N, 6.14%; found: C, 26.33%; H, 2.14%; N, 6.32%.

### 1.1.3 Synthesis of 1-ethyl-3-methylimidazolium pentafluoroethylpentafluorophosphate ([EMIm]FAP[1])




Pentafluoroethylphosphonic acid (11.6 g, 58.0 mmol) was placed in a perfluoroalkoxy-copolymer (PFA) flask and cooled to 0 °C. Anhydrous HF (23.2 g, 25.2 mL, 1.16 mol) was added and the mixture was stirred for 15 minutes. Crushed Ice (50 g) and a solution of ethylmethylimidazoliumchloride (8.93 g, 60.9 mmol) in water (20 mL) was added and stirred for 15 min while two phases formed. The IL was separated and washed with water (10 × 10 mL) until a pH of 7 of the washing phase.

**Yield:** 12.8 g (35.9 mmol), 62%) of a colorless liquid.

**$^{1}$H NMR** (500.1 MHz, 23 °C, $CD_3CN$): δ = 8.39 (s, 1H, C*H*), 7.37 (m, 1H, C*H*), 7.32 (m, 1H, C*H*), 4.16 (q, 2H, $^{3}J(^{1}H,^{1}H)$ = 7.34 Hz, $CH_2$), 3.82 (s, 3H, $CH_3$), 1.46 (t, 3H, $^{3}J(^{1}H,^{1}H)$ = 7.21 Hz, $CH_3$) ppm.

**$^{13}$C{$^{1}$H} NMR** (125.8 MHz, 23 °C, $CD_3CN$): δ = 136.6 (s, 1C, *C*H), 124.7 (s, 1C, *C*H), 123.0 (s, 1C, *C*H), 121.7 (qm, 1C, $^{1}J(^{19}F,^{13}C)$ = 278.9 Hz, $CF_3$), 117.9 (tdm, 1C, $^{1}J(^{31}P,^{13}C)$ = 321.6 Hz, $^{1}J(^{19}F,^{13}C)$ = 322.5 Hz, $CF_2$), 45.9 (s, 1C, $CH_2$), 36.8 (s, 1C, $CH_3$), 15.5 (s, 1C, $CH_3$) ppm.

**$^{13}$C{$^{19}$F} NMR** (125.8 MHz, 23 °C, $CD_3CN$): δ = 136.8 (dm, 1C, $^{1}J(^{13}C,^{1}H)$ = 221.0 Hz, *C*H), 124.7 (dm, 1C, $^{1}J(^{13}C,^{1}H)$ = 210.1 Hz, *C*H), 122.9 (dm, 1C, $^{1}J(^{13}C,^{1}H)$ = 205.6 Hz, *C*H), 121.7 (d, 1C, $^{2}J(^{31}P,^{13}C)$ = 28.22 Hz, $CF_3$), 117.9 (d, 1C, $^{1}J(^{31}P,^{13}C)$ = 321.6 Hz, $CF_2$), 45.9 (tm, 1C, $^{1}J(^{13}C,^{1}H)$ = 147.0 Hz, $CH_2$), 36.8 (q, 1C, $^{1}J(^{13}C,^{1}H)$ = 144.2 Hz, $CH_3$), 15.4 (qt, 1C, $^{1}J(^{13}C,^{1}H)$ = 128.9 Hz, $^{2}J(^{13}C,^{1}H)$ = 3.74 Hz, $CH_3$) ppm.

**$^{19}$F NMR** (470.6 MHz, 23 °C, $CD_3CN$): δ = −71.4 (ddm, 4F, $^{1}J(^{31}P,^{19}F)$ = 826.3 Hz, $^{2}J(^{19}F,^{19}F)$ = 47.20 Hz, P*F*), −74.7 (dp, 1F, $^{1}J(^{31}P,^{19}F)$ = 722.1 Hz, $^{2}J(^{19}F,^{19}F)$ = 47.14 Hz, P*F*), −83.7 (m, 3F, $CF_3$), −120.0 (dm, 2F, $^{2}J(^{31}P,^{19}F)$ = 89.7 Hz) =, $CF_2$) ppm.

**$^{31}$P{$^{1}$H} NMR** (202.5 MHz, 23 °C, $CD_3CN$): δ = −148.1 (dqutm, 1P, $^{1}J(^{31}P,^{19}F)$ = 826.4 Hz, $^{1}J(^{31}P,^{19}F)$ = 722.4 Hz, $^{2}J(^{31}P,^{19}F)$ = 89.9 Hz) ppm.

**IR(ATR):** $\tilde{\nu}$ = 3175 (w, $\tilde{\nu}$(C–H)), 3128 (w, $\tilde{\nu}$(C–H)), 2294 (w, $\tilde{\nu}$(C–H)), 1597 (w), 1574 (w), 1472 (w), 1458 (w), 1433 (w), 1395 (w), 1326 (w), 1269 (w), 1207 (w), 1190 (w), 1168 (w), 1147 (m), 1100 (w), 1086 (w), 1033 (w), 986 (w), 961 (w), 818 (w), 787 (s), 749 (w), 736 (m), 702 (w), 665 (m), 647 (w), 632 (w), 622 (w), 594 (w), 555 (w), 529 (m), 482 (w), 460 (w), 449 (w), 430 (w) $cm^{-1}$.

**Raman:** $\tilde{\nu}$ = 3197 (w, $\tilde{\nu}$(C–H)), 3183(w, $\tilde{\nu}$(C–H)), 3166 (w, $\tilde{\nu}$(C–H)), 3131 (w, $\tilde{\nu}$(C–H)), 3119 (w, $\tilde{\nu}$(C–H)), 3041 (w, $\tilde{\nu}$(C–H)), 3033 (w, $\tilde{\nu}$(C–H)), 2976 (s, $\tilde{\nu}$(C–H)), 2957 (w, $\tilde{\nu}$(C–H)), 2933 (w, $\tilde{\nu}$(C–H)), 2892 (w, $\tilde{\nu}$(C–H)), 2842 (w, $\tilde{\nu}$(C–H)), 2763 (w, $\tilde{\nu}$(C–H)), 2330 (w), 1573 (w), 1555 (w), 1544 (w), 1529 (w), 1508 (w), 1457 (w), 1424 (m), 1392 (w), 1362 (w), 1337 (w), 1254 (w), 1197 (w), 1183 (w) 1173 (w), 1165 (w), 1151 (w), 1112 (w), 1090 (w), 1026 (w) 983 (w) 962 (w) 740 (s), 703 (w), 667 (s), 567 (w), 558 (w), 463 (w), 441 (w) $cm^{-1}$.

**HRMS:** Calculated for $C_2F_{10}P^-$: 244.956 m/z, found: 244.958 m/z. Calculated for $C_6H_{11}N_2^+$: 111.092 m/z, found: 111.092 m/z.

**Elemental Analysis:** Calculated for [EMIm][$(C_2F_5)PF_5$] (356.2 $g \cdot mol^{-1}$): C, 26.98%; H, 3.11%; N, 7.87%; found: C, 27.30%; H, 3.26%; N, 7.92%.

**Refractive index** (25 °C): *n* = 1.37979.

### 1.1.4 Analytical Data of 1-ethyl-3-methylimidazolium hexafluorophosphate ([EMIm][$PF_6$])

**$^1$H NMR** (500.1 MHz, 23 °C, $CD_3CN$): δ = 8.39 (s, 1H, C*H*), 7.37 (m, 1H, C*H*), 7.32 (m, 1H, C*H*), 4.16 (q, 2H, $^3J(^1H,^1H)$ = 7.32 Hz, $CH_2$), 3.82 (s, 3H, $CH_3$), 1.46 (t, 3H, $^3J(^1H,^1H)$ = 7.36 Hz, $CH_3$) ppm.

**$^{13}C\{^1H\}$ NMR** (125.8 MHz, 23 °C, $CD_3CN$): δ = 136.6 (s, 1C, *C*H), 124.7 (s, 1C, *C*H), 123.0 (s, 1C, *C*H), 45.9 (s, 1C, $CH_2$), 36.8 (s, 1C, $CH_3$), 15.5 (s, 1C, $CH_3$) ppm.

**$^{13}C\{^{19}F\}$ NMR** (125.8 MHz, 23 °C, $CD_3CN$): δ = 136.7 (dm, 1C, $^1J(^{13}C,^1H)$ = 217.3 Hz, *C*H), 124.7 (dm, 1C, $^1J(^{13}C,^1H)$ = 202.2 Hz, *C*H), 123.0 (dm, 1C, $^1J(^{13}C,^1H)$ = 210.7 Hz, *C*H), 45.9 (tm, 1C, $^1J(^{13}C,^1H)$ = 146.9 Hz, $CH_2$), 36.8 (q, 1C, $^1J(^{13}C,^1H)$ = 144.2 Hz, $CH_3$), 15.5 (qt, 1C, $^1J(^{13}C,^1H)$ = 128.9 Hz, $^2J(^{13}C,^1H)$ = 3.67 Hz, $CH_3$) ppm.

**$^{19}F$ NMR** (470.6 MHz, 23 °C, $CD_3CN$): δ = −73.7 (d, 6F, $^1J(^{31}P,^{19}F)$ = 706.5 Hz) ppm.

**$^{31}P\{^1H\}$ NMR** (202.5 MHz, 23 °C, $CD_3CN$): δ = −144.6 (sept, 1P, $^1J(^{31}P,^{19}F)$ = 706.5 Hz) ppm.

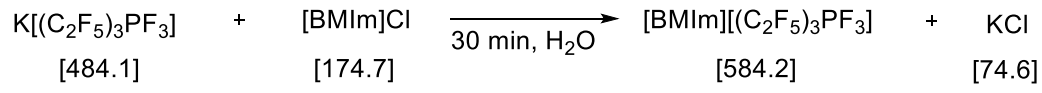
**IR(ATR):** $\tilde{\nu}$ = 3181 (w, $\tilde{\nu}$(C–H)), 3166 (w, $\tilde{\nu}$(C–H)), 3132 (w, $\tilde{\nu}$(C–H)), 2981 (w, $\tilde{\nu}$(C–H)), 1616 (w), 1595 (w), 1572 (w), 1559 (w), 1489 (w), 1473 (w), 1465 (w), 1452 (w), 1427 (w), 1396 (w), 1361 (w), 1335 (w), 1298 (w), 1209 (w), 1171 (s), 1134 (w), 1118 (w), 1086 (w), 1055 (w), 1034 (w), 1025 (w), 955 (w), 880 (w), 856 (w), 815 (s), 778 (w), 749 (w), 741 (w), 701 (w), 648 (m), 624 (m), 600 (w), 575 (w), 553 (s), 505 (w), 471 (w), 431 (w), 420 (w), 411 (w) $cm^{-1}$.

**Raman:** $\tilde{\nu}$ = 3296 (w, $\tilde{\nu}$(C–H)), 2998 (m, $\tilde{\nu}$(C–H)), 2963 (w, $\tilde{\nu}$(C–H)), 2950 (w, $\tilde{\nu}$(C–H)), 2902 (w, $\tilde{\nu}$(C–H)), 2792 (w, $\tilde{\nu}$(C–H)), 2779 (w, $\tilde{\nu}$(C–H)), 2758 (w, $\tilde{\nu}$(C–H)), 2057 (s), 2030 (w), 2013 (w), 1489 (w), 1465 (w), 1411 (w), 1394 (w), 1383 (w), 1315 (w), 1303 (w), 1215 (w), 1173 (w), 1136 (w), 1118 (w), 1084 (w), 1071 (w), 1027 (w), 1004 (w), 952 (w), 906 (w), 895 (w), 783 (w) $cm^{-1}$.

**HRMS:** Calculated for $F_6P^-$: 144.964 m/z, found: 144.965 m/z. Calculated for $C_6H_{11}N_2^+$: 111.092 m/z, found: 144.092 m/z.

## 1.2 1-Butyl-3-methylimidazolium fluorophosphates

### 1.2.1 Synthesis of 1-butyl-3-methylimidazolium *mer*-tris(pentafluoroethyl)trifluorophosphate ([BMIm]FAP$^3$)




Potassium [*mer*-(pentafluoroethyl)trifluorophosphate] (10.0 g, 20.7 mmol) was dissolved in water (20 mL) and a solution of [BMIm]Cl (3.79 g, 21.7 mmol) in water (20 mL) was added. After stirring for 30 minutes, the organic layer was removed and the aqueous layer was washed with $Et_2O$ (2 × 10 mL). The combined organic layers were thoroughly washed with bidistilled water (10 × 10 mL) until the residual aqueous phase remained clear after addition of a solution of aqueous $AgNO_3$. All volatiles were removed *in vacuo* to yield a colorless liquid.

**Yield**: 11.2 g (19.2 mmol, 93%) of a colorless liquid.

**$^1$H NMR** (500.1 MHz, 23 °C, $CD_3CN$): $\delta$ = 8.37 (s, 1H, C*H*), 7.35 (m, 1H, C*H*), 7.32 (m, 1H, C*H*), 4.11 (t, 2H, $^3J(^1H,^1H)$ = 7.35 Hz, C$H_2$), 3.81 (s, 3H, C$H_3$), 1.80 (m, 2H, C$H_2$), 1.33 (sext, 2H, $^3J(^1H,^1H)$ = 7.41 Hz, C$H_2$), 0.94 (t, 3H, $^3J(^1H,^1H)$ = 7.36 Hz, C$H_3$) ppm.

**$^{13}$C{$^1$H} NMR** (125.8 MHz, 23 °C, $CD_3CN$): $\delta$ = 136.8 (s, 1C, *C*H), 124.7 (s, 1C, *C*H), 123.3 (s, 1C, *C*H), 121.8 (m, 2C, C$F_3$), 121.1 (m, 1C, *C*$F_3$), 120.2 (m, 1C, *C*$F_2$), 118.7 (m, 2C, *C*$F_2$), 50.3 (s, 1C, *C*$H_2$), 36.9 (s, 1C, *C*$H_3$), 32.6 (s, 1C, *C*$H_2$), 20.0 (s, 1C, *C*$H_2$), 13.6 (s, 1C, *C*$H_3$) ppm.

**$^{13}$C{$^{19}$F} NMR** (125.8 MHz, 23 °C, $CD_3CN$): $\delta$ = 136.9 (d, 1C, $^1J(^{13}C,^1H)$ = 220.5 Hz, *C*H), 124.8 (dm, 1C, $^1J(^{13}C,^1H)$ = 170.6 Hz, *C*H), 123.3 (dm, 1C, $^1J(^{13}C,^1H)$ = 172.2 Hz *C*H), 121.5 (d, 2C, $^2J(^{31}P,^{13}C)$ = 25.9 Hz, *C*$F_3$), 121.1 (d, 1C, $^2J(^{31}P,^{13}C)$ = 22.7 Hz, *C*$F_3$), 120.2 (d, 1C, $^1J(^{31}P,^{13}C)$ = 145.0 Hz, *C*$F_2$), 118.7 (d, 2C, $^1J(^{31}P,^{13}C)$ = 225.8 Hz, *C*$F_2$), 50.4 (t, 1C, $^1J(^{13}C,^1H)$ = 143.8 Hz, *C*$H_2$), 36.8 (qm, 1C, $^1J(^{13}C,^1H)$ = 143.9 Hz, *C*$H_3$), 32.7 (tm, 1C, $^1J(^{13}C,^1H)$ = 128.2 Hz, *C*$H_2$), 20.0 (tm, 1C, $^1$J($^{13}$C,$^1$H) = 125.9 Hz, $^2J(^{13}C,^1H)$ = 4.08 Hz, *C*$H_2$), 13.7 (qm, 1C, $^1J(^{13}C,^1H)$ = 125.3 Hz, *C*$H_3$) ppm.

**$^{19}$F NMR** (470.6 MHz, 23 °C, $CD_3CN$): $\delta$ = −44.8 (dm, 1F, $^1J(^{31}P,^{19}F)$ = 889.6 Hz, P*F*), −80.9 (m, 3F, C*F*$_3$), −88.3 (dm, 2F, $^1J(^{31}P,^{19}F)$ = 902.2 Hz, P*F*), –116.3 (dm, 2F, $^2J(^{31}P,^{19}F)$ = 83.3 Hz, C*F*$_2$), –116.9 (dm, 4F, $^2J(^{31}P,^{19}F)$ = 97.9 Hz, C*F*$_2$) ppm.

**$^{31}P\{^{1}H\}$ NMR** (202.5 MHz, 23 °C, $CD_3CN$): $\delta$ = −147.9 (tdqut, 1P, $^{1}J(^{31}P,^{19}F)$ = 902.5 Hz, $^{1}J(^{31}P,^{19}F)$ = 888.8 Hz, $^{2}J(^{31}P,^{19}F)$ = 97.6 Hz, $^{2}J(^{31}P,^{19}F)$ = 83.6 Hz) ppm.

**IR(ATR):** $\tilde{\nu}$ = 3175 (w, $\tilde{\nu}$(C–H)), 3125 (w, $\tilde{\nu}$(C–H)), 2970 (w, $\tilde{\nu}$(C–H)), 2942 (w, $\tilde{\nu}$(C–H)), 2882 (w, $\tilde{\nu}$(C–H)), 1595 (w), 1568 (w), 1466 (w), 1432 (w), 1315 (s), 1280 (w), 1252 (m), 1205 (s), 1178 (s), 1168 (s), 1130 (s), 1068 (s), 974 (m), 965 (m), 861 (w), 838 (m), 791 (s), 762 (s), 739 (s), 701 (m), 675 (s), 653 (s), 622 (m), 593 (m), 572 (s), 521 (s), 491 (m), 473 (w), 438 (w), 426 (w) $cm^{-1}$.

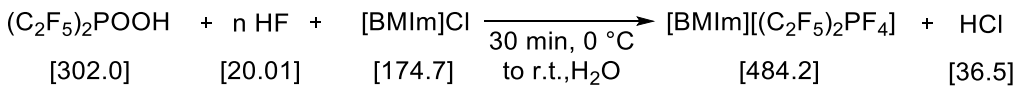
**Raman:** $\tilde{\nu}$ = 3188 (w, $\tilde{\nu}$(C–H)), 2975 (s, $\tilde{\nu}$(C–H)), 2945 (s, $\tilde{\nu}$(C–H)), 2920 (s, $\tilde{\nu}$(C–H)), 2881 (s, $\tilde{\nu}$(C–H)), 2840 (w, $\tilde{\nu}$(C–H)), 2329 (w), 2198 (s), 2050 (w), 1980 (m), 1573 (w), 1452 (m), 1419 (s), 1392 (m), 1338 (m), 1323 (m), 1176 (w), 1116 (m), 1087 (m), 1058 (w), 1026 (s), 979 (w), 908 (w), 862 (m), 848 (m), 827 (m), 740 (s), 680 (w), 657 (m), 636 (m), 595 (m), 580 (m), 536 (w), 522 (w), 499 (w), 430 (w) $cm^{-1}$.

**HRMS:** calculated for $C_8H_{15}N_2^+$: 139.123 m/z, found: 139.123 m/z; calculated for $C_6F_{18}P^-$: 444.945 m/z, found: 444.943 m/z.

**Elemental analysis:** calculated: C:28.78%, H: 2.59%, N: 4.80%. found: C: 28.97%, H: 2.56%, N: 5.09%.

**Refractive index** (25 °C): $n$ = 1.38002.

### 1.2.2 Synthesis of 1-butyl-3-methylimidazolium *trans*-bis(pentafluoroethyl)tetrafluorophosphate ([BMIm]FAP$^2$)




Bis(pentafluoroethyl)phosphinic acid (50.0 g, 166 mmol) was placed into a perfluoroalkoxy-copolymer (PFA) flask and cooled to 0 °C. Anhydrous HF (49.7 g, 51.2 mL, 2.48 mol) was added and the mixture was stirred for 15 minutes. Crushed ice (60 g) and a solution of 1-butyl-3-methylimidazolium chloride (30.4 g, 174 mmol) in water (50 mL) was added and the mixture was stirred for 15 min. The organic layer that had formed was separated and washed with bidistilled water (10 × 10 mL) until pH 7 of the washing phase.

**Yield**: 56.0 g (115.7 mmol, 70%) of a colorless liquid.

**$^1$H NMR** (500.1 MHz, 23 °C, $CD_3CN$): $\delta$ =8.37 (s, 1H), 7.35 (m, 1H, C*H*), 7.32 (m, 1H, C*H*), 4.11 (t, $^3J(^1H,^1H)$ = 7.29 Hz, C$H_2$), 3.81 (s, 3H, C$H_3$), 1.80 (m, 2H, C$H_2$), 1.33 (m, 2H, C$H_2$), 0.94.(t, 3H, $^3J(^1H,^1H)$ = 7.39 Hz, C$H_3$) ppm.

**$^{13}$C{$^1$H} NMR** (125.8 MHz, 23 °C, $CD_3CN$): $\delta$ = 136.8 (s, 1C, C*H*), 124.7 (s, 1C, C*H*), 123.3 (s, 1C, C*H*), 121.6 (qm, 2C, $^1J(^{19}F,^{13}C)$ = 282.4 Hz, *C*$F_3$), 117.4 (m, 2C, *C*$F_2$), 50.3 (s, 1C, *C*$H_2$), 36.9 (s, 1C, *C*$H_3$), 32.6 (s, 1C, *C*$H_2$), 20.0 (s, 1C, *C*$H_2$), 13.6 (s, 1C, *C*$H_3$) ppm.

**$^{13}$C{$^{19}$F} NMR** (125.8 MHz, 23 °C, $CD_3CN$): δ = 136.8 (dm, (2C, $^1J(^{13}C,^1H)$ = 223.4 Hz, *C*H), 124.8 (dm, 1C, $^1J(^{13}C,^1H)$ = 162.3 Hz, *C*H), 123.2 (dm, 1C, $^1J(^{13}C,^1H)$ = 172.7 Hz, *C*H), 121.5 (d, 2C, $^2J(^{31}P,^{13}C)$ = 29.52 Hz, *C*$F_3$), 117.4 (d, 2C, $^1J(^{31}P,^{13}C)$ = 324.4 Hz, *C*$F_2$), 50.3 (t, 1C, $^1J(^{13}C,^1H)$ = 141.3 Hz, *C*$H_2$), 36.8 (q, 1C, $^1J(^{13}C,^1H)$ = 144.5 Hz, *C*$H_3$), 32.6 (tm, 1C, $^1J(^{13}C,^1H)$ = 125.4 Hz, *C*$H_2$), 20.0 (tm, 1C, $^1J(^{13}C,^1H)$ = 126.0 Hz, *C*$H_2$), 13.6 (q, 1C, $^1J(^{13}C,^1H)$ = 125.3 Hz, *C*$H_3$) ppm.

**$^{19}$F NMR** (470.6 MHz, 23 °C, $CD_3CN$): δ = −72.8 (dquseptm, 4F, $^1J(^{31}P,^{19}F)$ = 915.9 Hz, $^3J(^{19}F,^{19}F)$ = 9.28 Hz, $^4J(^{19}F,^{19}F)$ = 7.39 Hz, P*F*), −83.5 (qum, 6F, $^4J(^{19}F,^{19}F)$ = 7.39 Hz, C*F*$_3$), −120.3 (dqum, 4F, $^2J(^{31}P,^{19}F)$ = 100.7 Hz, $^3J(^{19}F,^{19}F)$ = 9.16 Hz, C*F*$_2$) ppm.

**$^{31}$P{$^1$H} NMR** (202.5 MHz, 23 °C, $CD_3CN$): δ = −149.8 (ququm, 1P, $^1J(^{31}P,^{19}F)$ = 915.8 Hz, $^2J(^{31}P,^{19}F)$ = 100.7 Hz) ppm.

**IR(ATR):** $\tilde{\nu}$ = 3195 (w, $\tilde{\nu}$(C–H)), 3185 (w, $\tilde{\nu}$(C–H)), 3052 (w, $\tilde{\nu}$(C–H)), 3032 (w, $\tilde{\nu}$(C–H)), 2974 (s, $\tilde{\nu}$(C–H)), 2943 (s, $\tilde{\nu}$(C–H)), 2921 (s, $\tilde{\nu}$(C–H)), 2883 (s, $\tilde{\nu}$(C–H)), 2843 (s, $\tilde{\nu}$(C–H)), 2744 (w, $\tilde{\nu}$(C–H)), 2330 (w), 1569 (w), 1451 (m), 1433 (m), 1420 (m), 1392 (m), 1367 (m), 1339 (m), 1217 (w), 1205 (w), 1195 (w), 1187 (w), 1154 (w), 1145 (w), 1132 (w), 1116 (m), 1100 (w), 1093 (w), 1059 (w), 1026 (m), 979 (w), 909 (w), 885 (w), 826 (w), 743 (s), 652 (s), 633 (w), 623 (w), 595 (w), 566 (w), 456 (w) $cm^{-1}$.

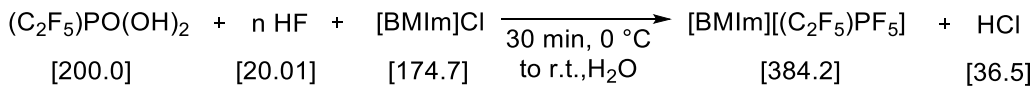
**Raman:** $\tilde{\nu}$ = 3195 (w, $\tilde{\nu}$(C–H)), 3185 (w, $\tilde{\nu}$(C–H)), 3163 (w, $\tilde{\nu}$(C–H)), 3064 (w, $\tilde{\nu}$(C–H)), 3052 (w, $\tilde{\nu}$(C–H)), 3032 (w, $\tilde{\nu}$(C–H)), 2974 (s, $\tilde{\nu}$(C–H)), 2943 (w, $\tilde{\nu}$(C–H)), 2921 (w, $\tilde{\nu}$(C–H)), 2883 (w, $\tilde{\nu}$(C–H)), 2843 (w, $\tilde{\nu}$(C–H)), 2330 (w),1569 (w), 1550 (w), 1451 (w), 1433 (w), 1420 (m), 1392 (w), 1367 (w), 1339 (w), 1217 (w), 1205 (w), 1195 (w), 1187 (w), 1173 (w), 1154 (w), 1145 (w), 1132 (w), 1116 (w), 1100 (w), 1093 (w), 1059 (w), 1026 (m), 979 (w), 909 (w), 909 (w), 885 (w), 826 (w), 807 (w), 743 (s), 652 (s), 633 (w), 623 (w), 595 (w), 566 (w), 536 (w), 456 (w) $cm^{-1}$.

**HRMS:** Calculated for $C_4F_{14}P^-$: 344.952 m/z, found: 344.951 m/z. Calculated for $C_8H_{15}N_2^+$: 139.123 m/z, found: 139.123 m/z.

**Elemental Analysis:** Calculated for [BMIm][*trans*-$(C_2F_5)_2PF_4$] (484.2 $g \cdot mol^{-1}$): C, 29.77%; H, 3.12%; N, 5.79%; found: C, 30.14%; H, 3.26%; N, 6.12%.

**Refractive index** (25 °C): $n$ = 1.37482.

### 1.2.3 Synthesis of 1-butyl-3-methylimidazolium pentafluoroethylpentafluorophosphate ([BMIm]FAP[1])




Pentafluoroethylphosphonic acid (32.3 g, 162 mmol) was placed into a perfluoroalkoxy-copolymer (PFA) flask and cooled to 0 °C. Anhydrous HF (64.6 g, 66.6 mL, 3.23 mol) was added and the mixture stirred for 15 minutes. Crushed ice (50 g) and a solution of 1-butyl-3-methylimidazolium chloride (29.6 g, 169 mmol) in water (50 mL) was added and the mixture was stirred for 15 minutes. The organic layer that had formed was separated and washed with bidistilled water (10 × 10 mL) until pH 7 of the washing phase.

**Yield:** 50.5 g (131 mmol, 81%) of a colorless liquid.

**$^{1}$H NMR** (500.1 MHz, 23 °C, $CD_3CN$): $\delta$ =8.37 (s, 1H, C*H*), 7.36 (m, 1H, C*H*), 7.33 (m, 1H, C*H*), 4.12 (t, $^{3}J(^{1}H,^{1}H)$ = 7.27 Hz, C$H_2$), 3.82 (s, 3H, C$H_3$), 1.81 (m, 2H, C$H_2$), 1.33 (m, 2H, C$H_2$), 0.94.(t, 3H, $^{3}J(^{1}H,^{1}H)$ = 7.36 Hz, C$H_3$) ppm.

**$^{13}$C{$^{1}$H} NMR** (125.8 MHz, 23 °C, $CD_3CN$): $\delta$ = 136.9 (s, 1C, *C*H), 124.8 (s, 1C, *C*H), 123.4 (s, 1C, *C*H), 121.9 (qum, 1C, $^{2}J(^{19}F,^{13}C)$ = 281.5 Hz, *C*$F_3$), 118.1 (dm, 1C, $^{1}J(^{31}P,^{13}C)$ = 321.8 Hz, *C*$F_2$), 50.5 (s, 1C, *C*$H_2$), 36.9 (s, 1C, *C*$H_3$), 32.7 (s, 1C, *C*$H_2$), 20.1 (s, 1C, *C*$H_2$), 13.7 (s, 1C, *C*$H_3$) ppm.

**$^{13}$C{$^{19}$F} NMR** (125.8 MHz, 23 °C, $CD_3CN$): δ = 136.9 (dm, 1C, $^{1}J(^{13}C,^{1}H)$ = 220.2 Hz, *C*H), 124.9 (dm, 1C, $^{1}J(^{13}C,^{1}H)$ = 175.2 Hz, *C*H), 123.3 (dm, 1C, $^{1}J(^{13}C,^{1}H)$ = 163.9 Hz, *C*H), 121.8 (d, 1C, $^{2}J(^{31}P,^{13}C)$ = 28.23 Hz, *C*$F_3$), 118.0 (d, 1C, $^{1}J(^{31}P,^{13}C)$ = 321.7 Hz, *C*$F_2$), 50.5 (t, 1C, $^{1}J(^{13}C,^{1}H)$ = 146.6 Hz, *C*$H_2$), 36.9 (q, 1C, $^{1}J(^{13}C,^{1}H)$ = 144.1 Hz, *C*$H_3$), 32.7 (tm, 1C, $^{1}J(^{13}C,^{1}H)$ = 130.2 Hz, *C*$H_2$), 20.1 (tm, 1C, $^{1}J(^{13}C,^{1}H)$ = 126.1 Hz, *C*$H_2$), 13.7 (q, 1C, $^{1}J(^{13}C,^{1}H)$ = 124.0 Hz, *C*$H_3$) ppm.

**$^{19}$F NMR** (470.6 MHz, 23 °C, $CD_3CN$): δ = −71.2 (ddm, 4F, $^{1}J(^{19}F,^{31}P)$ = 826.5 Hz, $^{2}J(^{19}F,^{19}F)$ = 45.2 Hz, P*F*), −74.4 (dqum, 1F, $^{1}J(^{31}P,^{19}F)$ = 722.0 Hz, $^{2}J(^{19}F,^{19}F)$ = 47.4 Hz, P*F*), –83.6 (m, 3F, C*F*$_3$), −120.2 (dm, 2F, $^{2}J(^{31}P,^{19}F)$ = 90.5 Hz, C*F*$_2$) ppm.

**$^{31}$P{$^{1}$H} NMR** (202.5 MHz, 23 °C, $CD_3CN$): δ = −149.7 (qudt, 1P, $^{1}J(^{31}P,^{19}F)$ = 827.0 Hz, $^{1}J(^{31}P,^{19}F)$ = 722.1 Hz, $^{2}J(^{31}P,^{19}F)$ = 89.9 Hz) ppm.

**IR(ATR):** $\tilde{\nu}$ = 3172 (w, $\tilde{\nu}$(C–H)), 3125 (w, $\tilde{\nu}$(C–H)), 2968 (w, $\tilde{\nu}$(C–H)), 2941 (w, $\tilde{\nu}$(C–H)), 2880 (w, $\tilde{\nu}$(C–H)) 1594 (w), 1573 (w), 1467 (w), 1433 (w), 1387 (w), 1325 (w), 1207 (w), 1190 (w), 1167 (w), 1147 (m), 1100 (w), 1086 (w), 986 (w), 818 (w), 788 (s), 751 (w), 736 (m), 698 (w), 665 (m), 622 (w), 594 (w), 555 (m), 529 (m), 482 (w), 460 (w), 449 (w) $cm^{-1}$.

**Raman:** $\tilde{\nu}$ = 2984 (w, $\tilde{\nu}$(C–H)), 3176 (w, $\tilde{\nu}$(C–H)), 3164 (w, $\tilde{\nu}$(C–H)), 3059 (w, $\tilde{\nu}$(C–H)), 3033 (w, $\tilde{\nu}$(C–H)), 3020 (w, $\tilde{\nu}$(C–H)), 2972 (s, $\tilde{\nu}$(C–H)), 2945 (w, $\tilde{\nu}$(C–H)), 2920 (w, $\tilde{\nu}$(C–H)), 2881 (w, $\tilde{\nu}$(C–H)), 2845 (w, $\tilde{\nu}$(C–H)), 2835 (w, $\tilde{\nu}$(C–H)), 2750 (w, $\tilde{\nu}$(C–H)), 2329 (w), 1569 (w), 1464 (w), 1449 (w), 1421 (s), 1391 (w), 1371 (w), 1362 (w), 1340 (w), 1315 (w), 1304 (w), 1184 (w), 1133 (w), 1118 (w), 1093 (w), 1056 (w), 1026 (s), 909 (w), 886 (w), 826 (w), 740 (s), 667 (s), 635 (w), 624 (w), 597 (w), 566 (w), 559 (w), 463 (w) $cm^{-1}$.

**HRMS:** Calculated for $C_2F_{10}P^-$: 244.958 m/z, found: 244.958 m/z. Calculated for $C_8H_{15}N_2^+$: 139.123 m/z, found: 139.123 m/z.

**Elemental Analysis:** Calculated for [BMIm][$(C_2F_5)PF_5$] (384.2 $g \cdot mol^{-1}$): C, 31.26%; H, 3.94%; N, 7.29%; found: C, 31.56%; H, 4.10%; N, 6.79%.

**Refractive index** (25 °C): *n* = 1.39150.

### 1.2.4 Analytical data of 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm][$PF_6$])

**$^1$H NMR** (500.1 MHz, 23 °C, $CD_3CN$): $\delta$ =8.38 (s, 1H, C*H*), 7.36 (m, 1H, C*H*), 7.33 (m, 1H, C*H*), 4.12 (t, $^3J(^1H,^1H)$ = 7.27 Hz, C$H_2$), 3.82 (s, 3H, C$H_3$), 1.80 (m, 2H, C$H_2$), 1.32 (m, 2H, C$H_2$), 0.93.(t, 3H, $^3J(^1H,^1H)$ = 7.39 Hz, C$H_3$) ppm.

**$^{13}$C{$^1$H} NMR** (125.8 MHz, 23 °C, $CD_3CN$): $\delta$ = 136.9 (s, 1C, *C*H), 124.7 (s, 1C, *C*H), 123.3 (s, 1C, *C*H), 50.3 (s, 1C, *C*$H_2$), 36.8 (s, 1C, *C*$H_3$), 32.6 (s, 1C, *C*$H_2$), 20.0 (s, 1C, *C*$H_2$), 13.7 (s, 1C, *C*$H_3$) ppm.

**$^{13}$C{$^{19}$F} NMR** (125.8 MHz, 23 °C, $CD_3CN$): δ = 136.9 (dm, 1C, $^1J(^{13}C,^1H)$ = 225.2 Hz, *C*H), 124.8 (dm, 1C, $^1J(^{13}C,^1H)$ = 179.7 Hz, *C*H), 123.2 (dm, 1C, $^1J(^{13}C,^1H)$ = 172.7 Hz, *C*H), 50.4 (tm, 1C, $^1J(^{13}C,^1H)$ = 143.6 Hz, *C*$H_2$), 36.9 (q, 1C, $^1J(^{13}C,^1H)$ = 143.9 Hz, *C*$H_3$), 32.7 (t, 1C, $^1J(^{13}C,^1H)$ = 128.4, *C*$H_2$), 20.0 (tm, 1C, $^1J(^{13}C,^1H)$ = 128.2 Hz, *C*$H_2$), 13.7 (q, 1C, $^1J(^{13}C,^1H)$ = 125.3 Hz, *C*$H_3$) ppm.

**$^{19}$F NMR** (470.6 MHz, 23 °C, $CD_3CN$): δ = −71.4 (d, 6F, $^1J(^{31}P,^{19}F)$ = 706.7 Hz) ppm.

**$^{31}$P{$^1$H} NMR** (202.5 MHz, 23 °C, $CD_3CN$): δ = −144.6 (sept, 1P, $^1J(^{31}P,^{19}F)$ = 706.8 Hz) ppm.

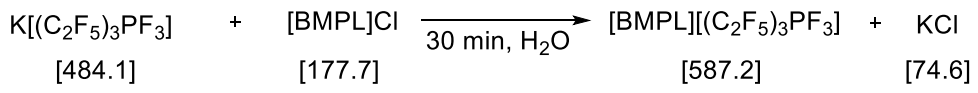
**IR(ATR):** $\tilde{\nu}$ = 3170 (w, $\tilde{\nu}$(C–H)), 3124 (w, $\tilde{\nu}$(C–H)), 2965 (w, $\tilde{\nu}$(C–H)), 2939 (w, $\tilde{\nu}$(C–H)), 2878 (w, $\tilde{\nu}$(C–H)), 1615 (w), 1575 (w), 1569 (w), 1467 (w), 1432 (w), 1387 (w), 1339 (w), 1167 (w), 1113 (w), 876 (w), 815 (s), 750 (w), 740 (w), 698 (w), 650 (w), 623 (w), 601 (w), 554 (s) $cm^{-1}$.

**Raman:** $\tilde{\nu}$ = 3181 (w, $\tilde{\nu}$(C–H)), 3130 (w, $\tilde{\nu}$(C–H)), 3114 (w, $\tilde{\nu}$(C–H)), 2971 (w, $\tilde{\nu}$(C–H)), 2942 (w, $\tilde{\nu}$(C–H)), 2918 (w, $\tilde{\nu}$(C–H)), 2879 (w, $\tilde{\nu}$(C–H)), 2841 (s, $\tilde{\nu}$(C–H)), 2740 (w, $\tilde{\nu}$(C–H)), 1569 (w), 1449 (w), 1421 (m), 1390 (w), 1341 (w), 1314 (w), 1283 (w), 1254 (w), 1213 (w), 1170 (w), 1117 (w), 1092 (w), 1057 (w), 1026 (m), 976 (w), 949 (w), 908 (w), 885 (w), 826 (w), 810 (w), 742 (s), 699 (w), 658 (w), 625 (w), 602 (w), 568 (w), 500 (w), 471 (w), 415 (w) $cm^{-1}$.

**HRMS:** Calculated for $F_6P^-$: 144.965 m/z, found: 144.965 m/z. Calculated for $C_8H_{15}N_2^+$: 139.123 m/z, found: 139.123 m/z.

### 1.3 1-Butyl-1-methylpyrrolidinium fluorophosphates

#### 1.3.1 Synthesis of 1-butyl-1-methylpyrrolidinium *mer*-tris(pentafluoroethyl)trifluorophosphate ([BMPL]FAP[3])




Potassium-[*mer-trans*-tris(pentafluoroethyl)trifluorophosphate] (5.00 g, 10.3 mmol) was dissolved in 20 mL water and a solution of [BMPL]Cl (1.92 g, 10.8 mmol) in water (20 mL) was added. After stirring for 30 Minutes the organic layer was removed and the aqueous layer was washed with $Et_2O$ (2 × 10 mL). The combined organic layers were thoroughly washed with bidistilled water (10 × 10 mL) until the residual aqueous phase remained clear after adding a solution of aqueous $AgNO_3$. All solvents were removed *in vacuo* and a colorless liquid remained.

**Yield**: 5.50 g (9.37 mmol, 91%) of a colorless liquid.

**$^{1}$H NMR** (500.1 MHz, 23 °C, $CD_3CN$): $\delta$ = 3.39 (m, 4H, C$H_2$), 3.21 (m, 2H, C$H_2$), 2.93 (s, 3H, C$H_3$), 2.15 (m, 4H, C$H_2$), 1.71 (m, 2H, C$H_2$), 1.37 (qt, 2H, $^{3}J(^{1}H,^{1}H)$ = 7.44 Hz, $^{3}J(^{1}H,^{1}H)$ = 7.43 Hz, C$H_2$), 0.97 (t, 3H, $^{3}J(^{1}H,^{1}H)$ = 7.38 Hz, C$H_3$) ppm.

**$^{13}$C{$^{1}$H} NMR** (125.8 MHz, 23 °C, $CD_3CN$): $\delta$ = 121.7 (qum, 2C, $^{1}J(^{19}F,^{13}C)$ = 283.1 Hz, C$F_3$), 121.4 (qum, 1C, $^{1}J(^{19}F,^{13}C)$ = 292.4 Hz, C$F_3$), 120.4 (m, 1C, *C*$F_2$), 118.8 (m, 2C, *C*$F_2$), 65.4 (t, 1C, $^{1}J(^{14}N,^{13}C)$ = 6.45 Hz, *C*$H_2$), 65.2 (t, 2C, $^{1}J(^{14}N,^{13}C)$ = 5.95 Hz, *C*$H_2$), 49.3 (t, 1C, $^{1}J(^{14}N,^{13}C)$ = 8.22 Hz, *C*$H_3$), 26.3 (s, 1C, *C*$H_2$), 22.4 (s, 2C, *C*$H_2$), 20.4 (t, 1C, $^{1}J(^{14}N,^{13}C)$ = 2.99 Hz, *C*$H_2$), 13.8 (s, 1C, *C*$H_3$) ppm

**$^{13}$C{$^{19}$F} NMR** (125.8 MHz, 23 °C, $CD_3CN$): δ = 121.6 (d, 2C, $^{2}J(^{31}P,^{13}C)$ = 25.6 Hz, *C*$F_3$), 121.2 (d, 1C, $^{2}J(^{31}P,^{13}C)$ = 23.0 Hz, *C*$F_3$), 120.3 (d, 1C, $^{1}J(^{31}P,^{13}C)$ = 144.9 Hz, *C*$F_2$), 118.8 (d, 2C, $^{1}J(^{31}P,^{13}C)$ = 255.9 Hz, *C*$F_2$), 65.4 (tm, 1C, $^{1}J(^{13}C,^{1}H)$ = 147.9 Hz, *C*$H_2$), 65.2 (tm, 2C, $^{1}J(^{13}C,^{1}H)$ = 141.8 Hz, *C*$H_2$), 49.3 (qm, 1C, $^{1}J(^{13}C,^{1}H)$ = 145.8 Hz, *C*$H_3$), 26.3 (tm, 1C, $^{1}J(^{13}C,^{1}H)$ = 128.4 Hz, *C*$H_2$), 22.4 (tm, 2C, $^{1}$J($^{13}$C,$^{1}$H) = 136.8 Hz, *C*$H_2$), 20.4 (tm, 1C, $^{1}$J($^{13}$C,$^{1}$H) = 128.5 Hz, *C*$H_2$), 13.8 (q, 1C, $^{1}J(^{13}C,^{1}H)$ = 125.5 Hz, *C*$H_3$) ppm.

**$^{19}$F NMR** (470.6 MHz, 23 °C, $CD_3CN$): δ = −44.8 (dm, 1F, $^1J(^{31}P,^{19}F)$ = 889.8 Hz, P*F*), −80.7 (m, 3F, C*F*$_3$), −82.6 (m, 6F, C*F*$_3$), −88.2 (dm, 2F, $^1J(^{31}P,^{19}F)$ = 902.0 Hz, P*F*), −116.3 (dm, 2F, $^2J(^{31}P,^{19}F)$ = 82.96 Hz, C*F*$_2$), −116.9 (dm, 4F, $^2J(^{31}P,^{19}F)$ = 97.83 Hz, C*F*$_2$) ppm.

**$^{31}$P{$^1$H} NMR** (202.5 MHz, 23 °C, $CD_3CN$): δ = −149.7 (dtm, 1P, $^1J(^{31}P,^{19}F)$ = 902.2 Hz, $^1J(^{31}P,^{19}F)$ = 888.8 Hz, C*H*$_3$) ppm.

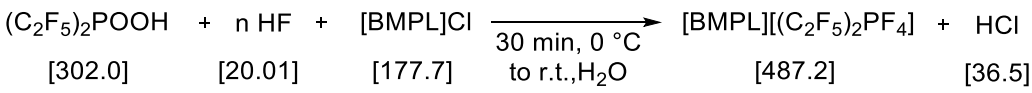
**IR(ATR):** $\tilde{\nu}$ = 2973 (w, $\tilde{\nu}$(C–H)), 2953 (w, $\tilde{\nu}$(C–H)), 2945 (w, $\tilde{\nu}$(C–H)), 2884 (w, $\tilde{\nu}$(C–H)), 1481 (w), 1467 (w), 1432 (w), 1312 (w), 1295 (w), 1209 (w), 1182 (m), 1133 (w), 1125 (w), 1098 (w), 1069 (w), 1004 (w), 973 (w), 962 (w), 928 (w), 909 (w), 891 (w), 807 (w), 760 (w), 750 (w), 743 (w), 717 (m), 636 (w), 616 (s), 581 (w), 532 (w), 506 (w), 496 (w), 467 (w), 439 (w), 429 (w), 422 (w) cm$^{-1}$.

**Raman:** $\tilde{\nu}$ = 3074 (w, $\tilde{\nu}$(C–H)), 3037 (w, $\tilde{\nu}$(C–H)), 2976 (s, $\tilde{\nu}$(C–H)), 2952 (w, $\tilde{\nu}$(C–H)), 2910 (w, $\tilde{\nu}$(C–H)), 2885 (w, $\tilde{\nu}$(C–H)), 2851 (w, $\tilde{\nu}$(C–H)), 2755 (w, $\tilde{\nu}$(C–H)), 2745 (w, $\tilde{\nu}$(C–H)), 2330 (w, $\tilde{\nu}$(C–H)), 1998 (w), 1502 (w), 1493 (w), 1460 (w), 1431 (w), 1319 (w), 1303 (w), 1242 (w), 1230 (w), 1222 (w), 1190 (w), 1187 (w), 1137 (w), 1124 (w), 1104 (w), 1062 (w), 1053 (w), 1037 (w), 1018 (w), 1004 (w), 965 (w), 926 (w), 905 (w), 828 (w), 821 (w), 800 (w), 768 (w), 744 (s), 725 (w), 636 (w), 602 (w), 542 (w), 433 (w), 428 (w) cm$^{-1}$.

**HRMS:** Calculated for $C_6F_{18}P^-$: 444.956 m/z, found: 344.944 m/z. Calculated for $C_9H_{20}N_1^+$: 142.159 m/z, found: 142.159 m/z.

**Elemental Analysis:** Berechnet für [BMPL][$(C_2F_5)_3PF_3$], $C_{15}H_{20}F_{18}NP$ (587.2 g·mol$^{-1}$): C, 30.73%; H, 3.27%; N, 2.39%; gefunden: C, 30.88%; H, 3.14%; N, 2.79%.

### 1.3.2 Synthesis of 1-butyl-1-methylpyrrolidinium *trans*-bis(pentafluoroethyl)tetrafluorophosphate ([BMPL]FAP$^2$)




Bis(pentafluoroethyl)phosphinic acid (10 g, 33.1 mmol) was placed into a perfluoroalkoxy-copolymer (PFA) flask and cooled to 0 °C. Anhydrous HF (9.94 g, 10.2 mL, 0.50 mol) was added and the mixture was stirred for 15 minutes. Crushed ice (40 g) and a solution of [BMPL]Cl (6.18 g, 34.8 mmol) in water (30 mL) was added and the mixture was stirred for 15 min while a colorless solid formed. The solid was filtered off and washed with water (10 × 10 mL) until pH of 7 of the washing phase.

**Yield**: 14.5 g (29.8 mmol, 90%) of a colorless solid.

**$^1$H NMR** (500.1 MHz, 23 °C, $CD_3CN$): $\delta$ = 3.39 (m, 4H, C$H_2$), 3.21 (m, 2H, C$H_2$), 2.93 (s, 3H, C$H_3$), 2.15 (m, 4H, C$H_2$), 1.71 (m, 2H, C$H_2$), 1.37 (qt, 2H, $^3J(^1H,^1H)$ = 12.37 Hz, $^3J(^1H,^1H)$ = 7.44 Hz, C$H_2$), 0.96 (t, 3H, $^3J(^1H,^1H)$ = 7.38 Hz, C$H_3$) ppm.

**$^{13}$C{$^1$H} NMR** (125.8 MHz, 23 °C, $CD_3CN$): δ = 121.7 (qum, 2C, $^1J(^{19}F,^{13}C)$ = 276.7 Hz, C$F_3$), 117.4 (m, 2C, $CF_2$), 65.4 (t, 1C, $^1J(^{14}N,^{13}C)$ = 6.68 Hz, $CH_2$), 65.3 (t, 2C, $^1J(^{14}N,^{13}C)$ = 6.00 Hz, $CH_2$), 49.3 (t, 1C, $^1J(^{14}N,^{13}C)$ = 4.13 Hz, $CH_3$), 26.3 (s, 1C, $CH_2$), 22.4 (s, 2C, $CH_2$), 20.4 (t, 1C, $^1J(^{14}N,^{13}C)$ = 1.55 Hz, $CH_2$), 13.8 (s, 1C, $CH_3$) ppm.

**$^{13}$C{$^{19}$F} NMR** (125.8 MHz, 23 °C, $CD_3CN$): δ = 121.6 (d, 2C, $^2J(^{31}P,^{13}C)$ = 29.51 Hz, $CF_3$), 117.5 (d, 2C, $^1J(^{31}P,^{13}C)$ = 324.5 Hz, $CF_2$), 65.4 (tm, 1C, $^1J(^{13}C,^1H)$ = 148.1 Hz, $CH_2$), 65.2 (tm, 2C, $^1J(^{13}C,^1H)$ = 142.2 Hz, $CH_2$), 49.3 (qm, 1C, $^1J(^{13}C,^1H)$ = 143.5 Hz, $CH_3$), 26.3 (tm, 1C, $^1J(^{13}C,^1H)$ = 128.6 Hz, $CH_2$), 22.4 (tm, 2C, $^1J(^{13}C,^1H)$ = 136.5 Hz, $CH_2$), 20.4 (tm, 1C, $^1J(^{13}C,^1H)$ = 126.8 Hz, $CH_2$), 12.6 (q, 1C, $^1J(^{13}C,^1H)$ = 125.4 Hz, $CH_3$) ppm.

**$^{19}$F NMR** (470.6 MHz, 23 °C, $CD_3CN$): δ = −72.8 (dquseptm, 4F, $^1J(^{31}P,^{19}F)$ = 916.1 Hz, $^3J(^{19}F,^{19}F)$ = 9.47 Hz, $^4J(^{19}F,^{19}F)$ = 7.37 Hz, P$F$), −83.5 (qum, 6F, $^4J(^{19}F,^{19}F)$ = 7.39 Hz, C$F_3$), −120.2 (dm, 4F, $^2J(^{31}P,^{19}F)$ = 100.9 Hz, $^3J(^{19}F,^{19}F)$ = 9.47 Hz, C$F_2$) ppm.

**$^{31}P\{^{1}H\}$ NMR** (202.5 MHz, 23 °C, $CD_3CN$): δ = −149.7 (ququm, 1P, $^{1}J(^{31}P,^{19}F)$ = 916.2 Hz, $^{2}J(^{31}P,^{19}F)$ = 100.9 Hz) ppm.

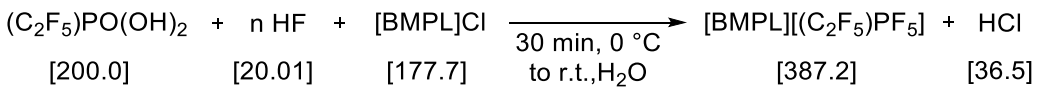
**IR(ATR):** $\tilde{\nu}$ = 3176 (w, $\tilde{\nu}$(C–H)), 2972 (w, $\tilde{\nu}$(C–H)), 2944 (w, $\tilde{\nu}$(C–H)), 2883 (w, $\tilde{\nu}$(C–H)), 1575 (w), 1568 (w), 1480 (w), 1467 (w), 1433 (w), 1325 (w), 1193 (s), 1164 (w), 1151 (w), 1143 (m), 1095 (m), 1018 (w), 995 (w), 977 (w), 930 (w), 807 (s), 754 (w), 742 (w), 697 (w), 642 (s), 629 (m), 594 (w), 574 (w), 567 (w), 531 (w), 500 (w), 486 (w), 455 (w), 429 (w), 419 (w) $cm^{-1}$.

**Raman:** $\tilde{\nu}$ = 2977 (s, $\tilde{\nu}$(C–H)), 2950 (w, $\tilde{\nu}$(C–H)), 2911 (w, $\tilde{\nu}$(C–H)), 2886 (w, $\tilde{\nu}$(C–H)), 2857 (w, $\tilde{\nu}$(C–H)), 2849 (w, $\tilde{\nu}$(C–H)), 2760 (w, $\tilde{\nu}$(C–H)), 2750 (w, $\tilde{\nu}$(C–H)), 1495 (w), 1459 (s), 1323 (w), 1234 (w), 1190 (w), 1144 (w), 1123 (w), 1101 (w), 1063 (w), 1052 (w), 1034 (w), 1021 (w), 1007 (w), 978 (w), 930 (w), 906 (w), 884 (w), 822 (w), 743 (s), 652 (s), 633 (w), 594 (w), 566 (w), 536 (w), 455 $cm^{-1}$.

**HRMS:** Calculated for $C_4F_{15}P^-$: 344.952 m/z, found: 344.951 m/z. Calculated for $C_9H_{20}N_1^+$: 142.159 m/z, found: 142.159 m/z.

**Elemental Analysis:** Calculated for [BMPL][$(C_2F_5)_2PF_4$] (487.2 $g \cdot mol^{-1}$): C, 32.05%; H, 4.14%; N, 2.87%; found: C, 32.40%; H, 4.19%; N, 3.04%.

### 1.3.3 Synthesis of 1-butyl-1-methylpyrrolidinium pentafluoroethylpentafluorophosphate ([BMPL]FAP[1])




Pentafluoroethylphosphonic acid (58.0 g, 290 mmol) was placed in a perfluoroalkoxy-copolymer flask and cooled to 0 °C. Anhydrous HF (87.0 g, 89.7 mL, 4.38 mol) was added and the mixture stirred for 15 minutes. Crushed ice (100 g) and a solution [BMPL]Cl (54.0 g, 304 mmol) in water (100 mL) was added and the mixture was stirred for 15 min while two phases formed. The organic layer that had formed was separated and washed with bidistilled water (10 × 10 mL) until pH 7 of the washing phase.

**Yield:** 80.4 g (208 mmol), 72%) of a colorless liquid.

**$^{1}$H NMR** (500.1 MHz, 23 °C, $CD_3CN$): $\delta$ = 3.40 (m, 4H, C$H_2$), 3.22 (m, 2H, C$H_2$), 2.93 (s, 3H, C$H_3$), 2.15 (m, 4H, C$H_2$), 1.72 (m, 2H, C$H_2$), 1.37 (m, 2H, C$H_2$), 0.96 (t, 3H, $^{3}J(^{1}H,^{1}H)$ = 7.39 Hz, C$H_3$) ppm.

**$^{13}$C{$^{1}$H} NMR** (125.8 MHz, 23 °C, $CD_3CN$): δ = 121.7 (qum, 1C, $^{1}J(^{19}F,^{13}C)$ = 282.0 Hz, *C*$F_3$), 117.5 (m, 1C, *C*$F_2$), 65.4 (t, 2C, $^{1}J(^{14}N,^{13}C)$ = 3.22 Hz, *C*$H_2$), 65.1 (t, 1C, $^{1}J(^{14}N,^{13}C)$ = 3.02 Hz, *C*$H_2$), 49.2 (t, 1C, $^{1}J(^{14}N,^{13}C)$ = 4.16 Hz, *C*$H_3$), 26.3 (s, 1C, *C*$H_2$), 22.4 (s, 2C, *C*$H_2$), 20.4 (t, 1C, $^{1}J(^{14}N,^{13}C)$ = 1.61 Hz, *C*$H_2$), 13.8 (s, 1C, *C*$H_3$) ppm.

**$^{13}$C{$^{19}$F} NMR** (125.8 MHz, 23 °C, $CD_3CN$): δ = 121.7 (d, 1C, $^{2}J(^{31}P,^{13}C)$ = 28.21 Hz, *C*$F_3$), 117.9 (d, 1C, $^{1}J(^{31}P,^{13}C)$ = 321.6 Hz, *C*$F_2$), 65.4 (tm, 1C, $^{1}J(^{13}C,^{1}H)$ = 148.3 Hz, *C*$H_2$), 65.1 (tm, 2C, $^{1}J(^{13}C,^{1}H)$ = 142.3 Hz, *C*$H_2$), 49.3 (qm, 1C, $^{1}J(^{13}C,^{1}H)$ = 144.0 Hz, *C*$H_3$), 26.3 (tm, 1C, $^{1}J(^{13}C,^{1}H)$ = 128.6 Hz, *C*$H_2$), 22.4 (tm, 1C, $^{1}$J($^{13}$C,$^{1}$H) = 136.6 Hz, *C*$H_2$), 20.4 (tm, 2C, $^{1}$J($^{13}$C,$^{1}$H) = 126.6 Hz, *C*$H_2$), 13.8 (q, 1C, $^{1}J(^{13}C,^{1}H)$ = 125.5 Hz, *C*$H_3$).

**$^{19}$F NMR** (470.6 MHz, 23 °C, $CD_3CN$): δ = −71.3 (ddm, 4F, $^{1}J(^{19}F,^{31}P)$ = 826.5 Hz, $^{2}J(^{19}F,^{19}F)$ = 47.3 Hz, P*F*), −74.6 (dqum, 1F, $^{1}J(^{31}P,^{19}F)$ = 722.5 Hz, $^{2}J(^{19}F,^{19}F)$ = 47.3 Hz, P*F*), 83.6 (m, 3F, C*F*$_3$), −120.0 (dqum, 2F, $^{2}J(^{31}P,^{19}F)$ = 89.6 Hz, $^{3}J(^{19}F,^{19}F)$ = 8.9 Hz, C*F*$_2$) ppm.

**$^{31}$P{$^{1}$H} NMR** (202.5 MHz, 23 °C, $CD_3CN$): δ = −149.7 (qudt, 1P, $^{1}J(^{31}P,^{19}F)$ = 826.5 Hz, $^{1}J(^{31}P,^{19}F)$ = 722.3 Hz, $^{2}J(^{31}P,^{19}F)$ = 89.9 Hz) ppm.

**IR(ATR):** $\tilde{\nu}$ = 2970 (w, $\tilde{\nu}$(C–H)), 2944 (w, $\tilde{\nu}$(C–H)), 2882 (w, $\tilde{\nu}$(C–H)), 1479 (w), 1467 (w), 1434 (w), 1347 (w), 1325 (w), 1207 (w), 1185 (w), 1147 (m), 1122 (w), 1100 (w), 1086 (w), 1002 (w), 985 (w), 929 (w), 820 (w), 788 (s), 737 (s), 664 (m), 634 (w), 622 (w), 594 (w), 555 (s), 528 (w), 460 (w) $cm^{-1}$.

**Raman:** $\tilde{\nu}$ = 2976 (s, $\tilde{\nu}$(C–H)), 2951 (w, $\tilde{\nu}$(C–H)), 2883 (w, $\tilde{\nu}$(C–H)), 2749 (w, $\tilde{\nu}$(C–H)), 2328 (w), 1496 (w), 1459 (m), 1323 (w), 1240 (w), 1183 (w), 1123 (w), 1061 (w), 1029 (w), 1021 (w), 1004 (w), 928 (w), 906 (w), 825 (w), 802 (w), 786 (w), 768 (w), 740 (s), 667 (m), 634 (w), 595 (w), 566 (w), 558 (w), 464 (w), 451 (w) $cm^{-1}$.

**HRMS:** Calculated for $C_2F_{10}P^-$: 244.958 m/z, found: 244.958 m/z. Calculated for $C_9H_{20}N^+$: 142.159 m/z, found: 142.159 m/z.

**Elemental Analysis:** Calculated for [BMPL][$(C_2F_5)PF_5$] (387.2 $g \cdot mol^{-1}$): C, 34.12%; H, 5.21%; N, 3.62%; found: C, 34.46%; H, 5.37%; N, 3.77%.

### 1.3.4 Analytical data of 1-butyl-1-methylpyrrolidinium hexafluorophosphate ([BMPL][$PF_6$])

**$^1$H NMR** (500.1 MHz, 23 °C, $CD_3CN$): $\delta$ = 3.40 (m, 4H, C$H_2$), 3.22 (m, 2H, C$H_2$), 2.93 (s, 3H, C$H_3$), 2.14 (m, 4H, C$H_2$), 1.72 (m, 2H, C$H_2$), 1.38 (qt, 2H, $^3J(^1H,^1H)$ = 12.37 Hz, $^3J(^1H,^1H)$ = 7.44 Hz, C$H_2$), 0.96 (t, 3H, $^3J(^1H,^1H)$ = 7.38 Hz, C$H_3$) ppm.

**$^{13}C\{^1H\}$ NMR** (125.8 MHz, 23 °C, $CD_3CN$): δ = 65.3 (t, 1C, $^1J(^{14}N,^{13}C)$ = 3.20 Hz, *C*$H_2$), 65.0 (t, 2C, $^1J(^{14}N,^{13}C)$ = 3.07 Hz, *C*$H_2$), 49.2 (t, 1C, $^1J(^{14}N,^{13}C)$ = 4.09 Hz, *C*$H_3$), 26.2 (s, 1C, *C*$H_2$), 22.3 (s, 2C, *C*$H_2$), 20.4 (t, 1C, $^1J(^{14}N,^{13}C)$ = 1.57 Hz, *C*$H_2$), 13.8 (s, 1C, *C*$H_3$) .

**$^{19}F$ NMR** (470.6 MHz, 23 °C, $CD_3CN$): δ = −72.8 (d, 6F, $^1J(^{31}P,^{19}F)$ = 706.7 Hz) ppm.

**$^{31}P\{^1H\}$ NMR** (202.5 MHz, 23 °C, $CD_3CN$): δ = −144.6 (sept, 1P, $^1J(^{31}P,^{19}F)$ = 706.7 Hz) ppm.

**IR(ATR):** $\tilde{\nu}$ = 2967 (s, $\tilde{\nu}$(C–H)), 2940 (w, $\tilde{\nu}$(C–H)), 2879 (w, $\tilde{\nu}$(C–H)), 1467 (w), 1434 (w), 1405 (w), 1305 (w), 1212 (w), 1181 (w), 1179 (w), 1121 (w), 1062 (w), 1031 (w), 1004 (w), 965 (w), 954 (w), 930 (w), 878 (w), 821 (s), n740 (w), 634 (w), 605 (w), 595 (w), 555 (s), 505 (w), 495 (w), 421 (w) $cm^{-1}$.

**Raman:** $\tilde{\nu}$ = 2973 (s, $\tilde{\nu}$(C–H)), 2994 (w, $\tilde{\nu}$(C–H)), 2880 (w, $\tilde{\nu}$(C–H)), 2749 (w, $\tilde{\nu}$(C–H)), 2738 (w, $\tilde{\nu}$(C–H)), 1459 (m), 1368 (w), 1353 (w), 1320 (w), 1285 (w), 1240 (w), 1190 (w), 1179 (w), 1123 (w), 1103 (w), 1063 (w), 1054 (w), 1032 (w), 1020 (w), 1006 (w), 967 (w), 954 (w), 905 (w), 823 (w), 742 (s), 627 (w), 586 (w), 569 (w), 491 (w), 471 (w), 448 (w), 421 (w), 408 (w) $cm^{-1}$.

**HRMS:** Calculated for $C_2F_{10}P^-$: 144.965 m/z, found: 144.964 m/z. Calculated for $C_9H_{20}N^+$: 142.159 m/z, found: 142.159 m/z.

## 2. NMR spectroscopic data

Table S2: Selected NMR spectroscopic data[a] of the perfluoroalkylfluorophosphate anions.

| Compound | $^{31}P$ | | $^{19}F$ | | | | | | $^{13}C$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $\delta$ | $^{1}J_{PF}$[b] *cis* / *trans* | $\delta$ (P–F)[b] *cis* / *trans* | $\delta$ (–$CF_2$–)[b] *cis* / *trans* | $\delta$ (–$CF_3$)[b] *cis* / *trans* | $^{1}J_{PF}$[b] *cis* / *trans* | $^{2}J_{PF}$[b] *cis* / *trans* | $^{3}J_{PF}$ *cis* / *trans* | $\delta$ (–$CF_2$–)[b] *cis* / *trans* | $\delta$ (–$CF_3$)[b] *cis* / *trans* |
| | [ppm] | [Hz] | [ppm] | | | [Hz] | | | [ppm] | |
| [EMIm]**FAP³** | –147.9 | 902.0<br>899.9 | –88.2<br>–44.8 | –116.3<br>–116.9 | –80.9<br>–83.6 | 902.0<br>889.7 | m[c] | m | 120.4<br>118.9 | 121.7<br>121.3 |
| [EMIm]**FAP²** | –149.8 | 915.6 | –72.8 | –120.2 | –83.5 | 915.9 | 100.7 | 7.44 | 116.4 | 120.4 |
| [EMIm]**FAP¹** | –148.1 | 826.8<br>727.8 | –71.4<br>–74.7 | –120.0 | –83.6 | 826.4<br>722.2 | 89.74 | 7.72 | 116.9 | 120.6 |
| [EMIm][$PF_6$] | –144.6 | 706.5 | –73.7 | - | - | 706.5 | - | - | - | - |
| [BMIm]**FAP³** | –147.9 | 902.5<br>888.8 | –88.3<br>–44.8 | –116.3<br>–116.9 | –80.9<br>–82.6 | 902.2<br>889.6 | m | m | 120.2<br>118.7 | 121.5<br>120.2 |
| [BMIm]**FAP²** | –149.8 | 915.8 | –72.8 | –120.3 | –83.5 | 915.9 | 100.7 | 7.39 | 116.3 | 120.4 |
| [BMIm]**FAP¹** | –149.7 | 827.0<br>722.1 | –71.2<br>–74.4 | –120.2 | –83.6 | 826.5<br>722.0 | 90.50 | m | 118.0 | 121.8 |
| [BMIm][$PF_6$] | –144.6 | 706.8 | –71.4 | - | - | 706.7 | - | - | - | - |
| [BMPL]**FAP³** | –147.9 | 902.2<br>888.8 | –88.2<br>–44.8 | –116.3<br>–116.9 | –82.6 | 902.0<br>889.8 | 97.83<br>82.96 | m | 119.2<br>117.7 | 120.5<br>120.1 |
| [BMPL]**FAP²** | –149.7 | 916.2 | –72.8 | –120.2 | –83.5 | 916.1 | 100.9 | 7.39 | 117.5 | 121.6 |
| [BMPL]**FAP¹** | –149.7 | 826.5<br>722.3 | –71.3 | –120.0 | –83.6 | 826.5<br>722.5 | 89.66 | 8.96 | 117.9 | 121.7 |
| [BMPL][$PF_6$] | –144.6 | 706.7 | –72.8 | - | - | 706.7 | - | - | - | - |

*a* Recorded in $CD_3CN$, *b* Only one value given in case of chemical equivalence, *c* m = multiplet.

**2.1 [EMIm]FAP[3]**

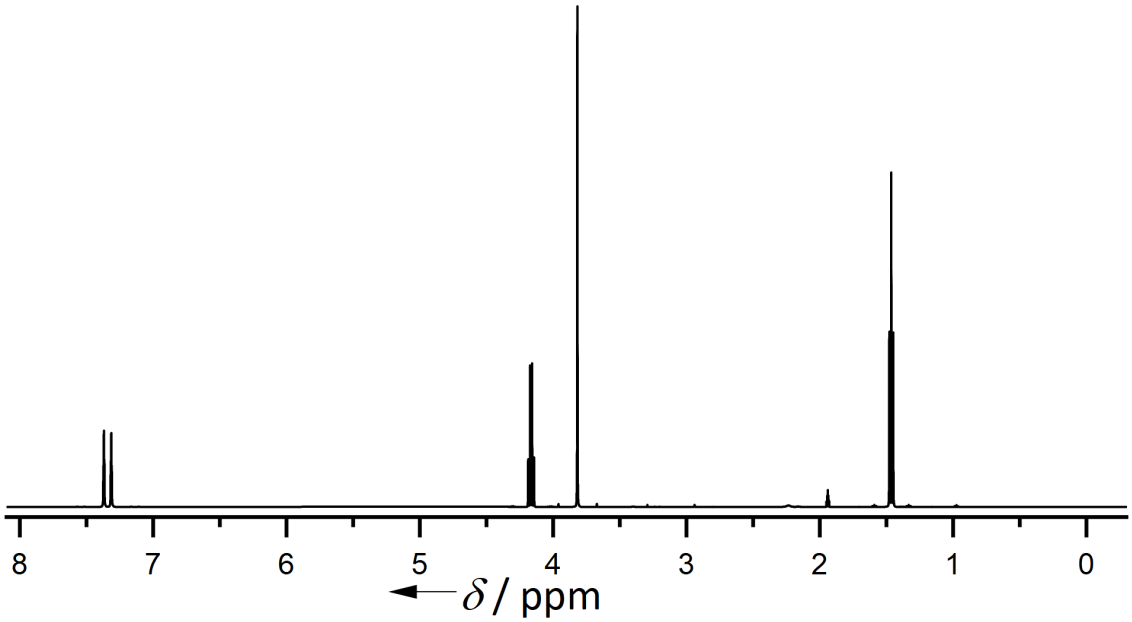



Figure 1: [1]H NMR of [EMIm]**FAP[3]**.

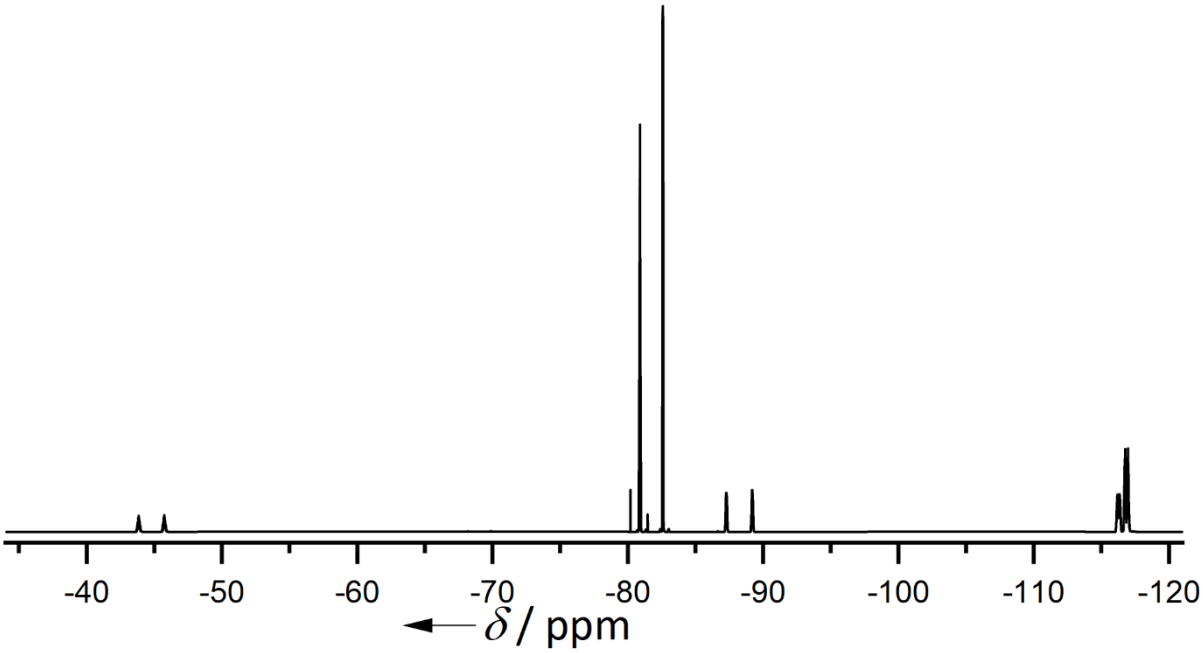



Figure 2: [19]F NMR of [EMIm]**FAP[3]**.

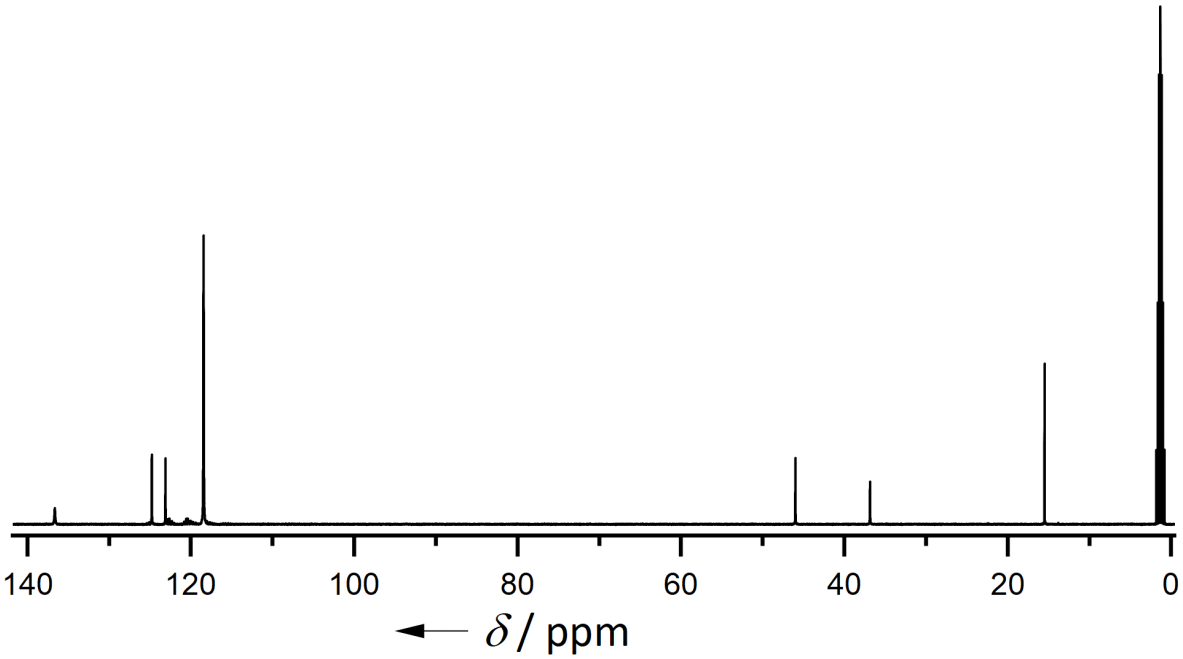



Figure 3: $^{13}C\{^{1}H\}$ NMR of [EMIm]**FAP**[3].

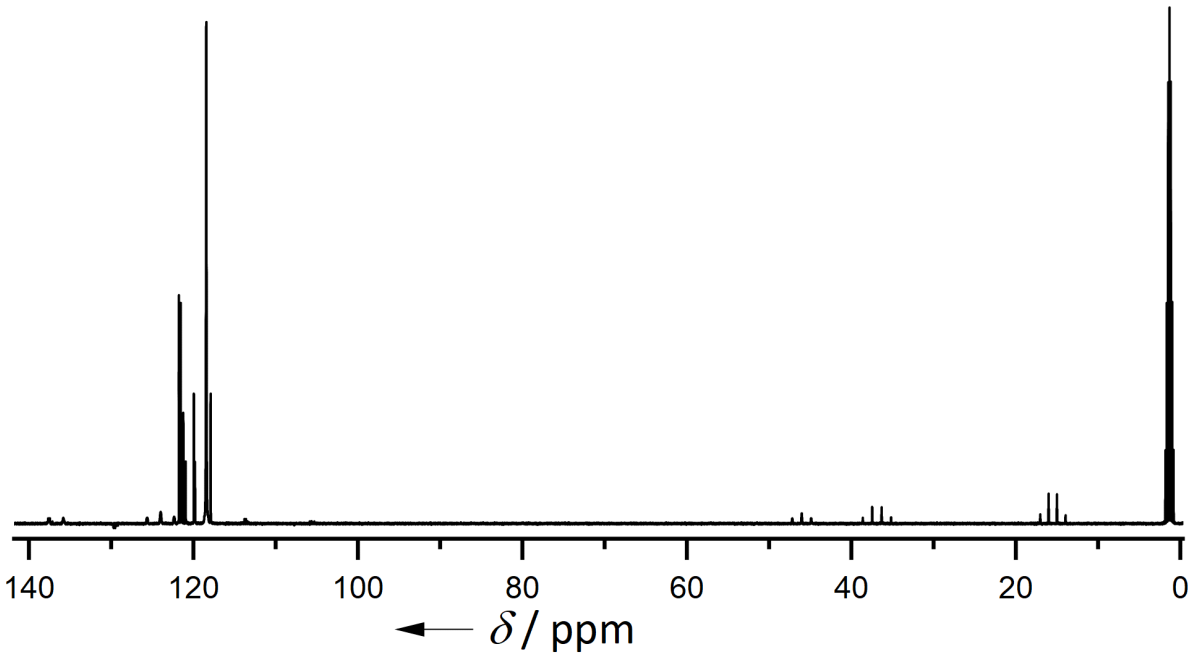



Figure 4: $^{13}C\{^{19}F\}$ NMR of [EMIm]**FAP**[3].

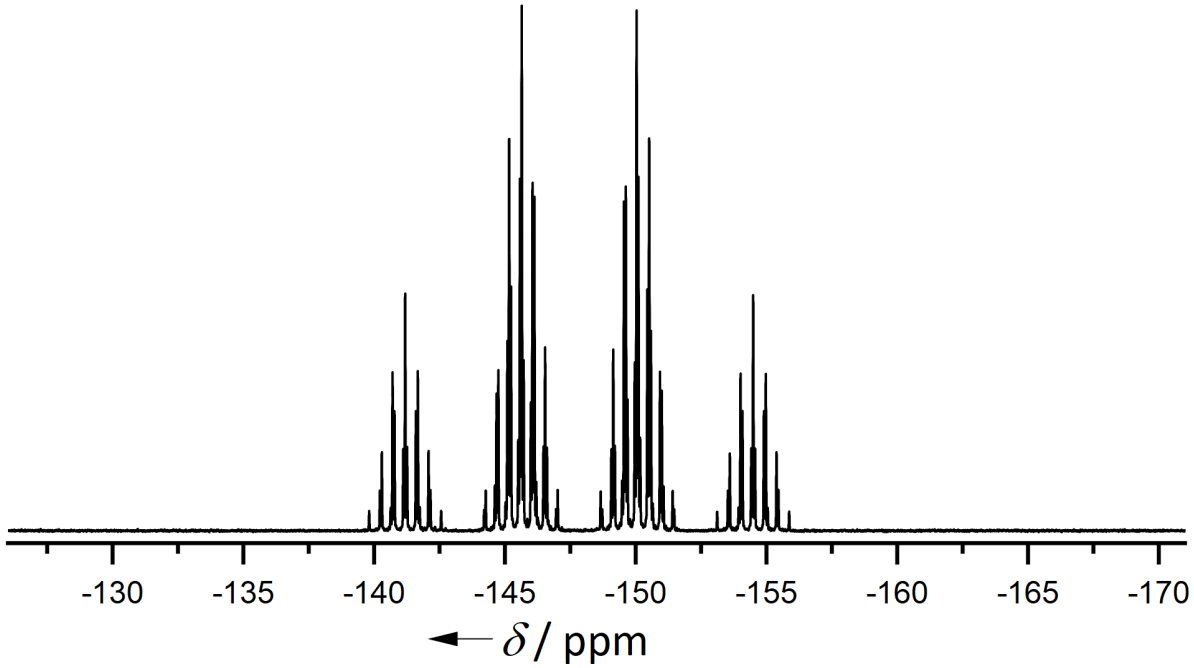



Figure 5: $^{31}P\{^{1}H\}$ NMR of [EMIm]**FAP$^{3}$**.

**2.2 [EMIm]FAP$^{2}$**

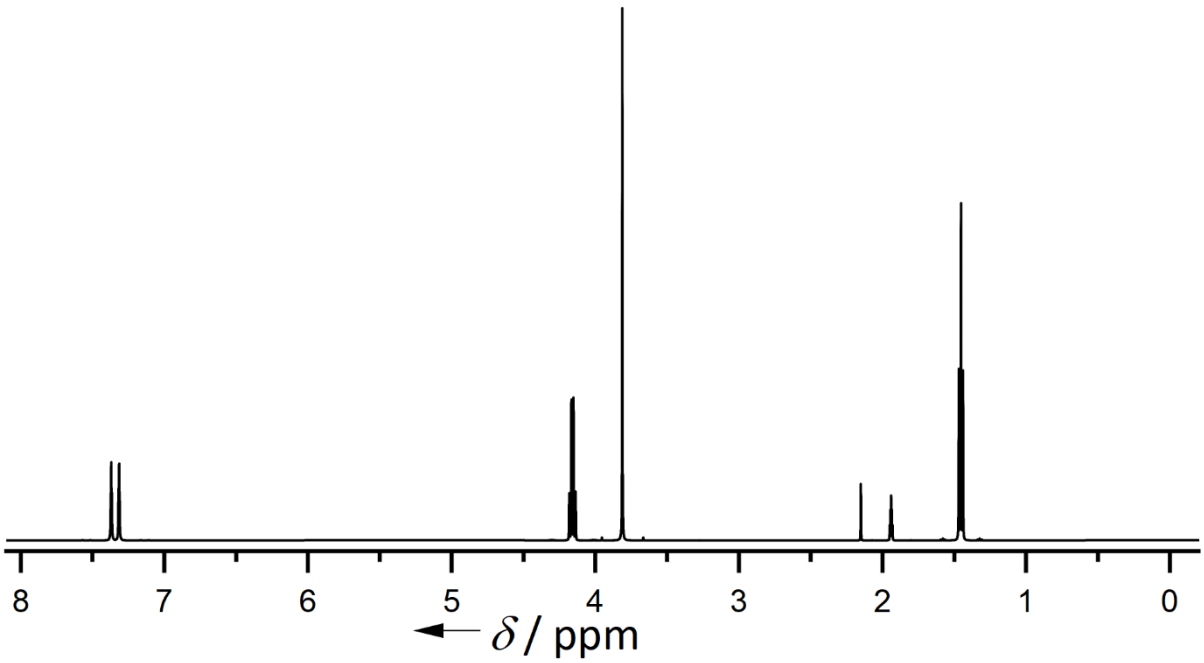



Figure 61: $^{1}H$ NMR of [EMIm]**FAP$^{2}$**.

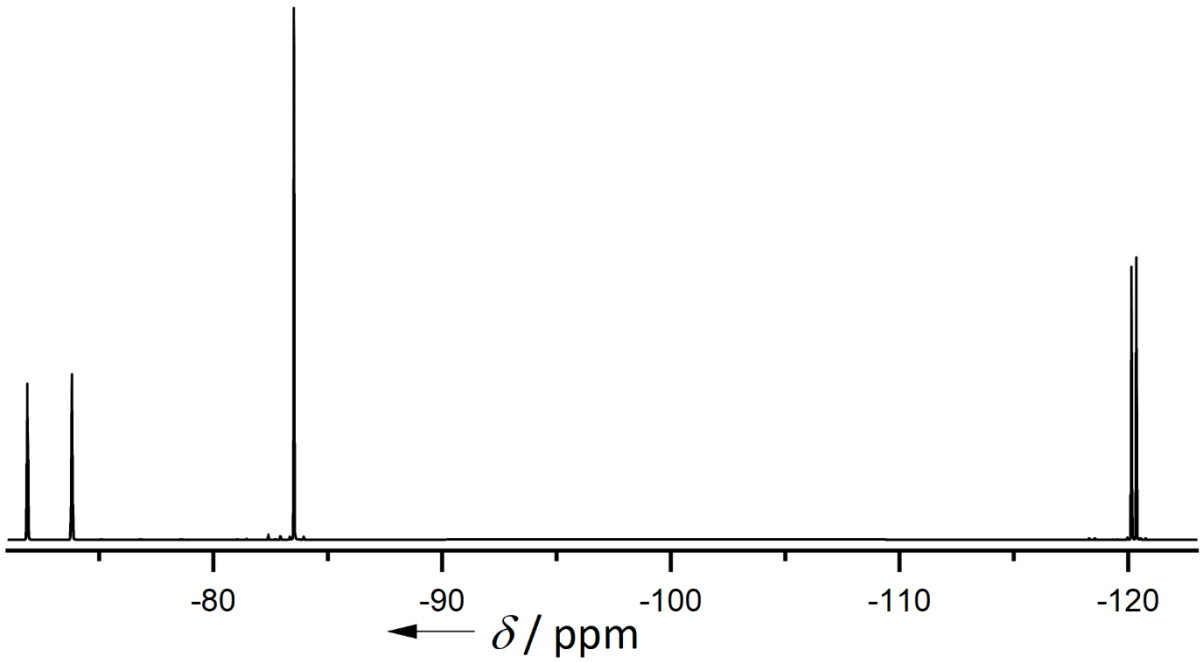



Figure 7: $^{19}$F NMR of [EMIm]**FAP$^2$**.

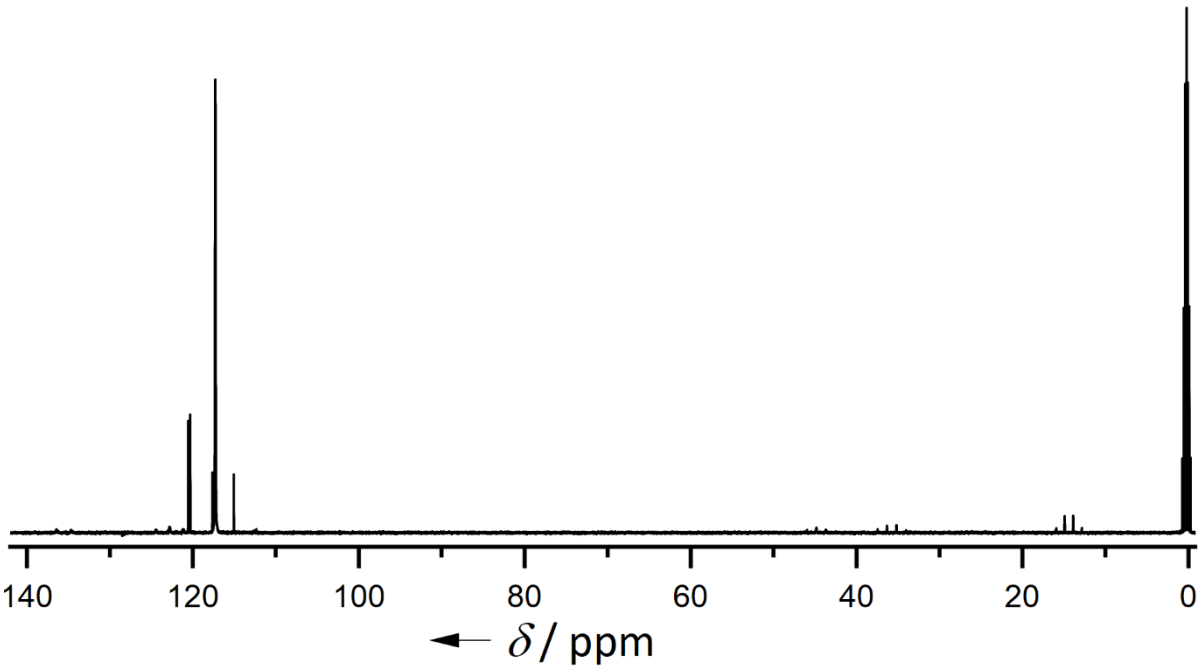



Figure 8: $^{13}$C{$^{19}$F} NMR of [EMIm]**FAP$^2$**.

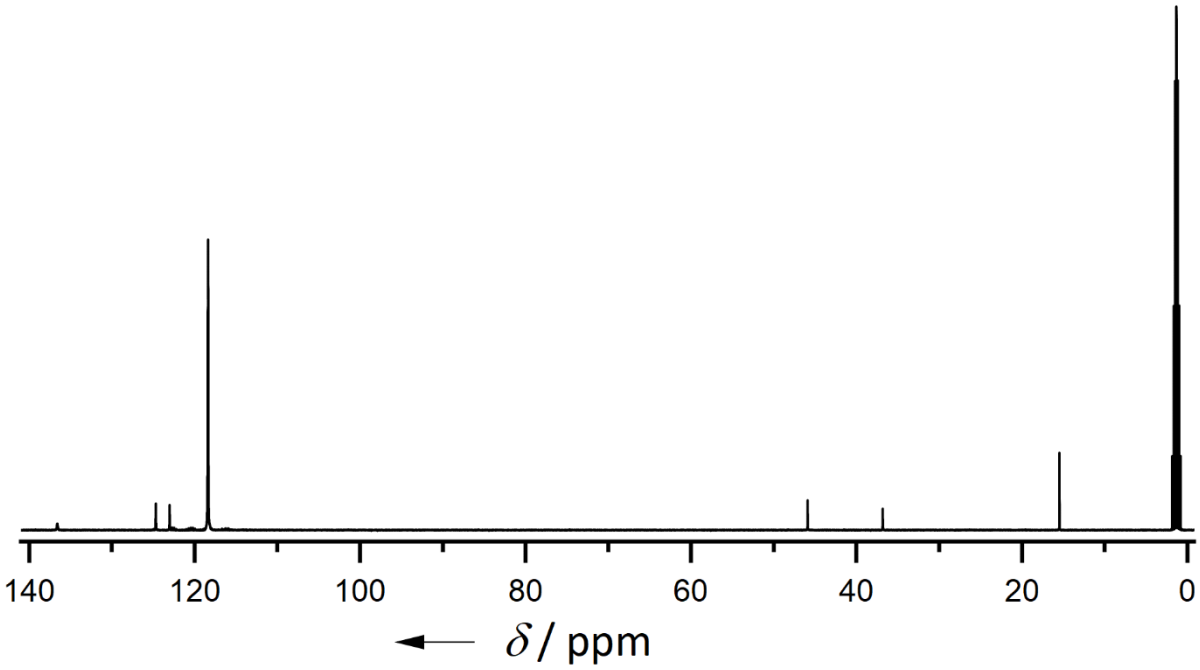



Figure 9: $^{13}C\{^{1}H\}$ NMR of [EMIm]**FAP²**.

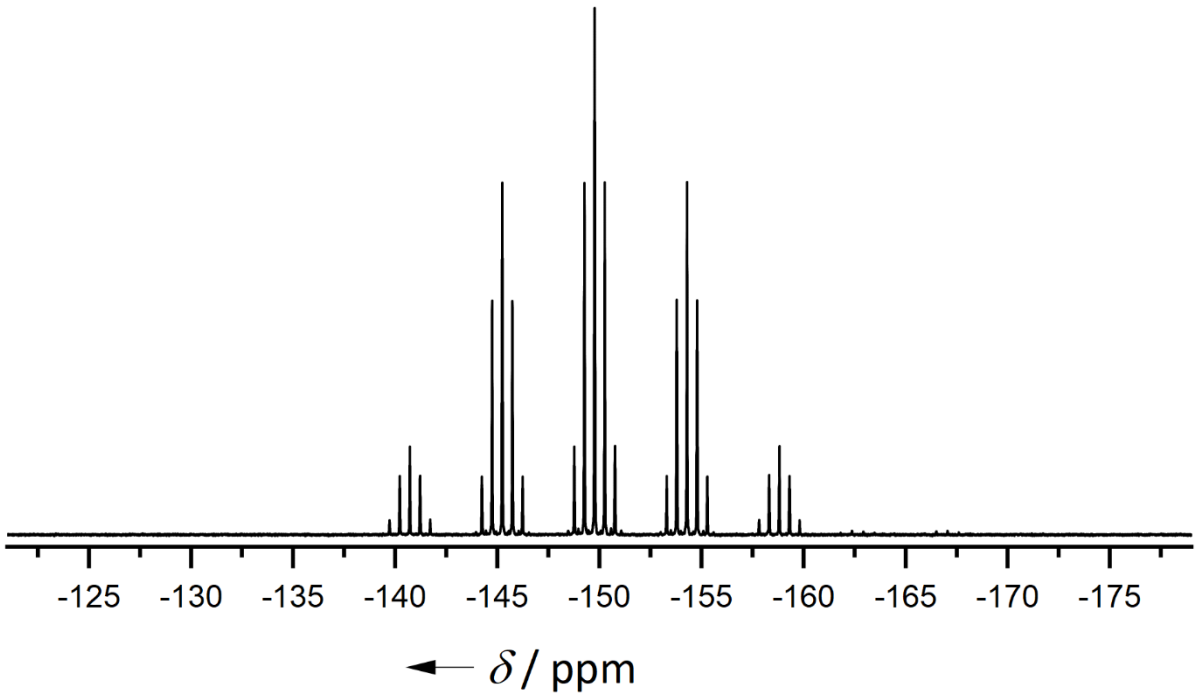



Figure 10: $^{31}P\{^{1}H\}$ NMR of [EMIm]**FAP²**.

**2.3 [EMIm]FAP[1]**

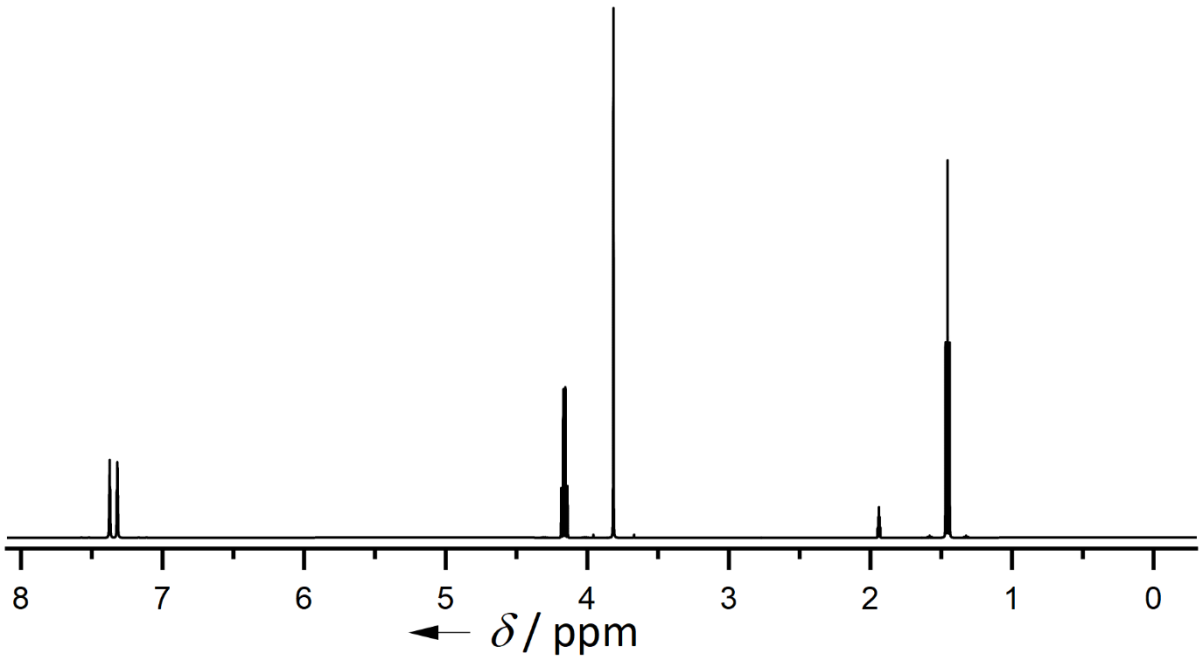



Figure 11: $^{1}$H NMR of [EMIm]**FAP[1]**.

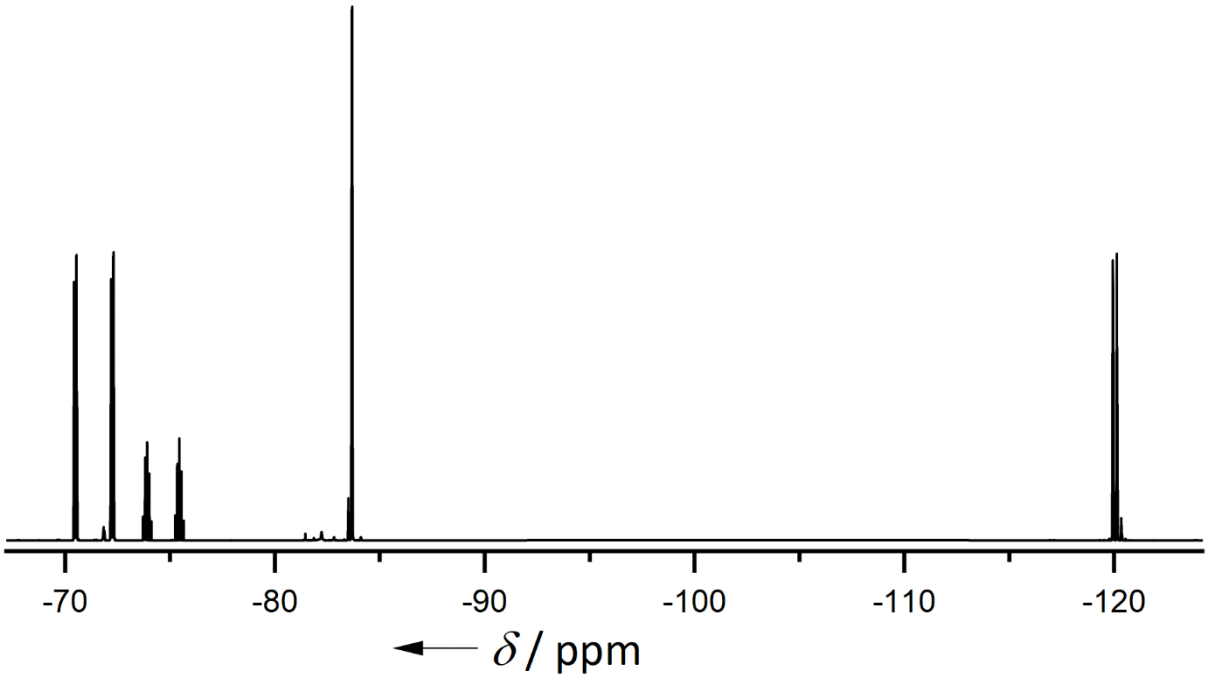



Figure 12: $^{19}$F NMR of [EMIm]**FAP[1]**.

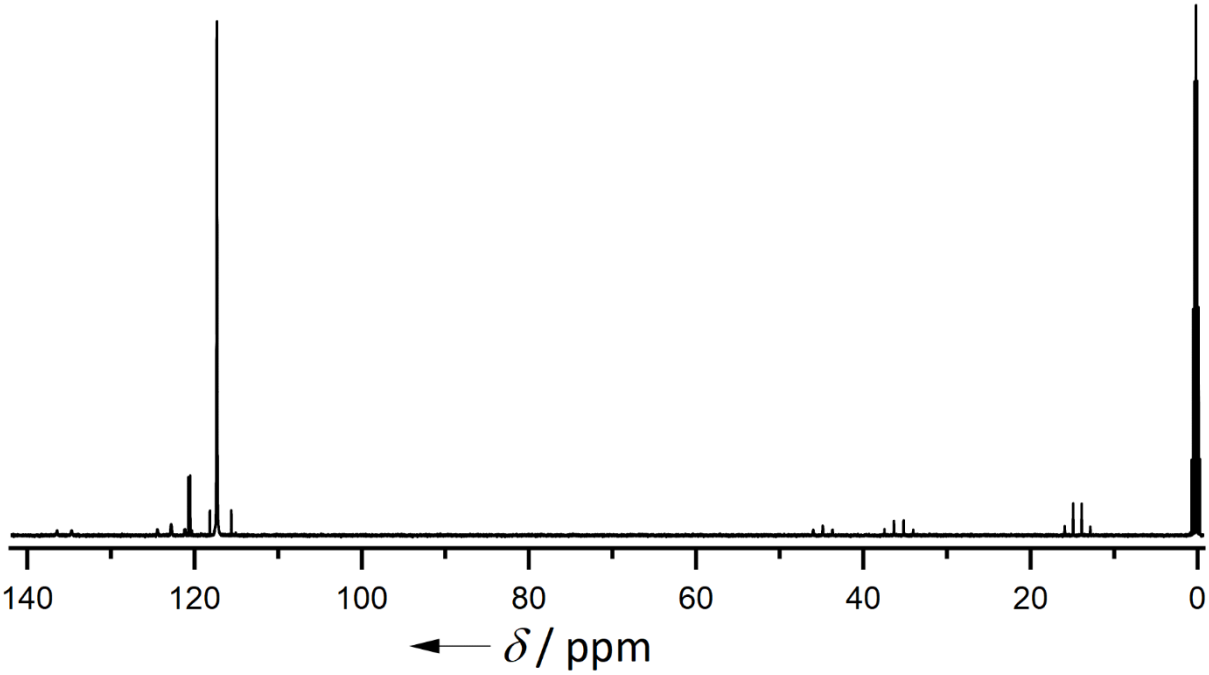



Figure 13: $^{13}C\{^{19}F\}$ NMR of [EMIm]**FAP**[1].

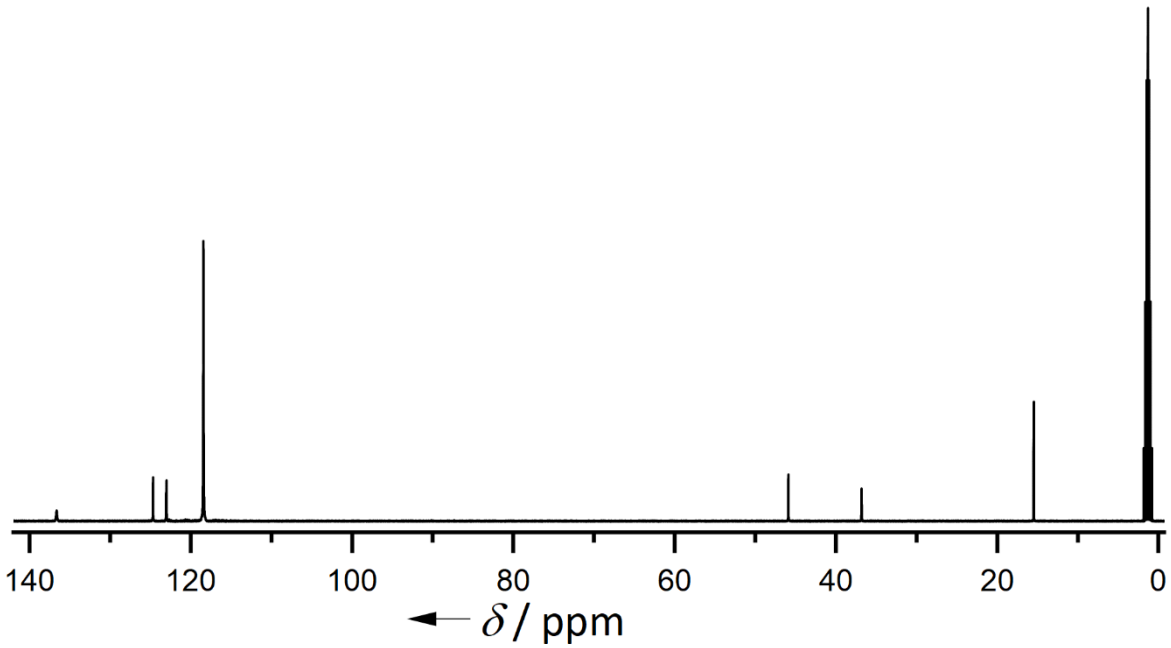



Figure 14: $^{13}C\{^{1}H\}$ NMR of [EMIm]**FAP**[1].

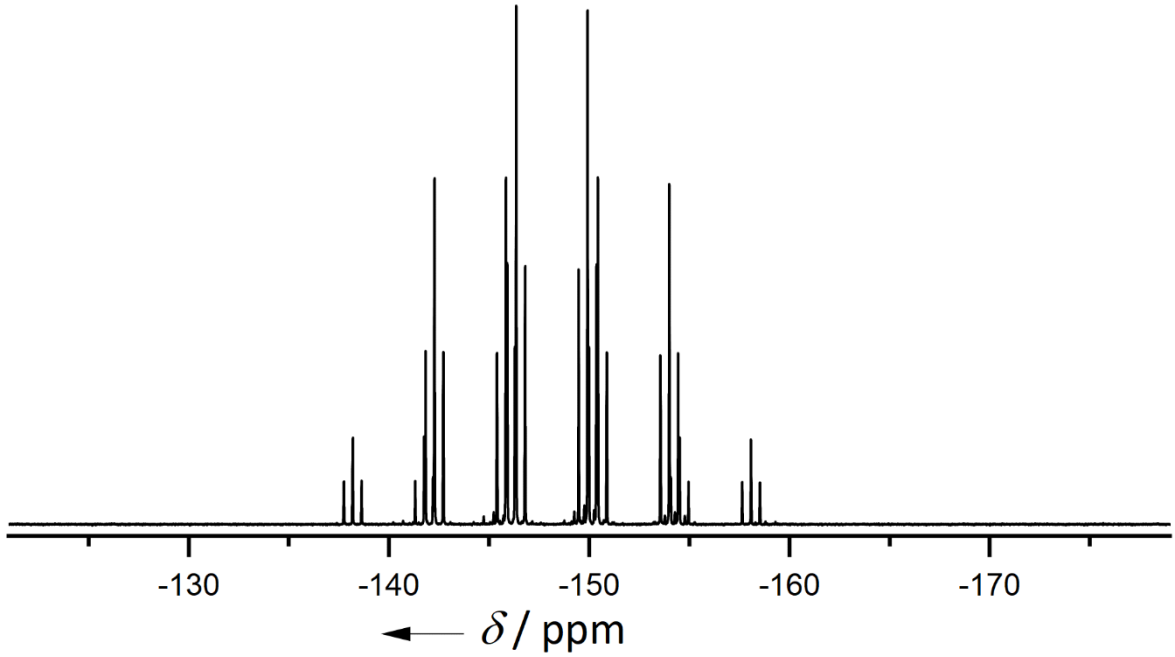



Figure 15: $^{31}P\{^{1}H\}$ NMR of [EMIm]**FAP**[1].

### 2.4 [EMIm][$PF_6$]

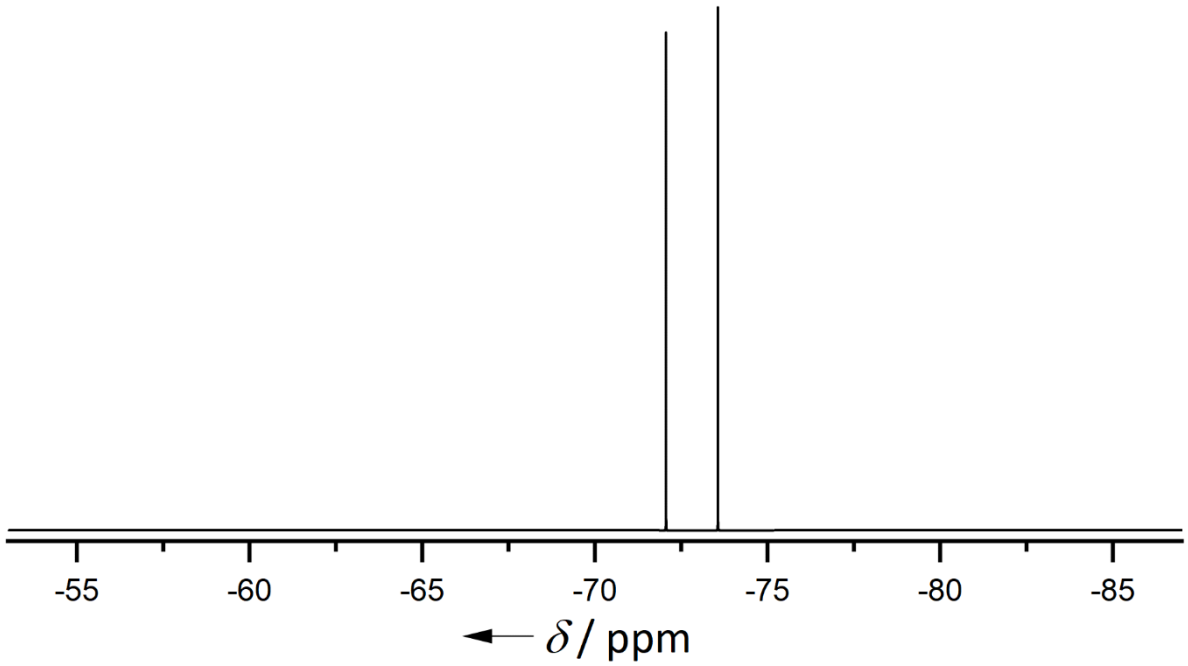



Figure 16: $^{19}F$ NMR of [EMIm][$PF_6$].

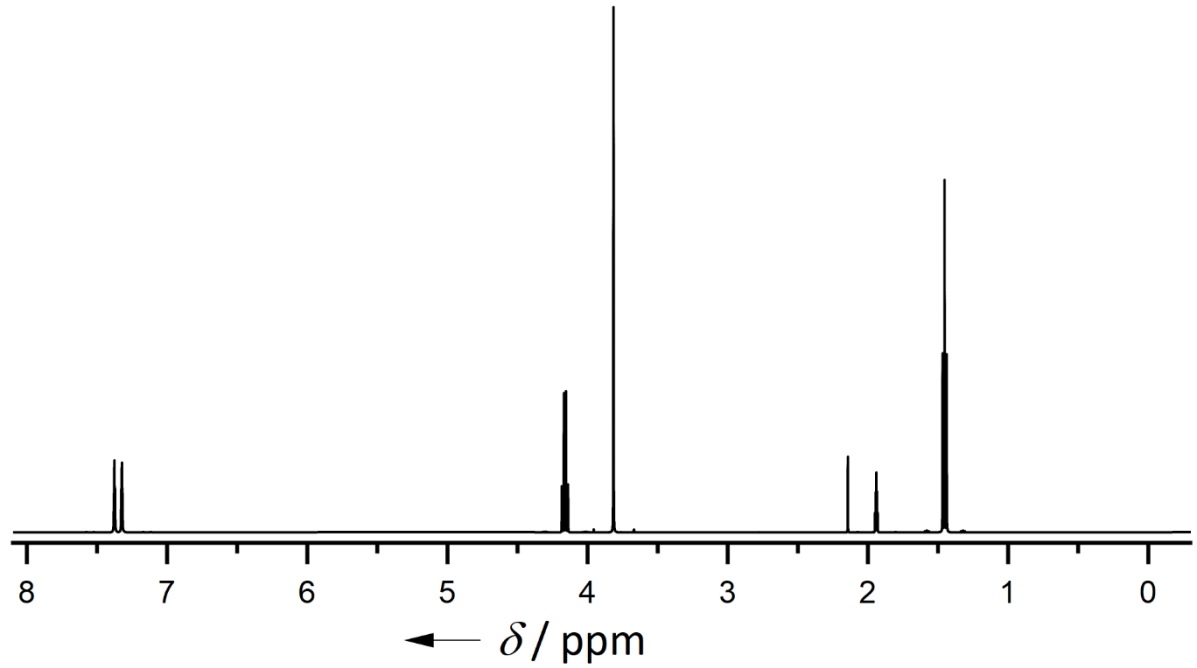



Figure 17: $^{1}H$ NMR of [EMIm][$PF_6$].

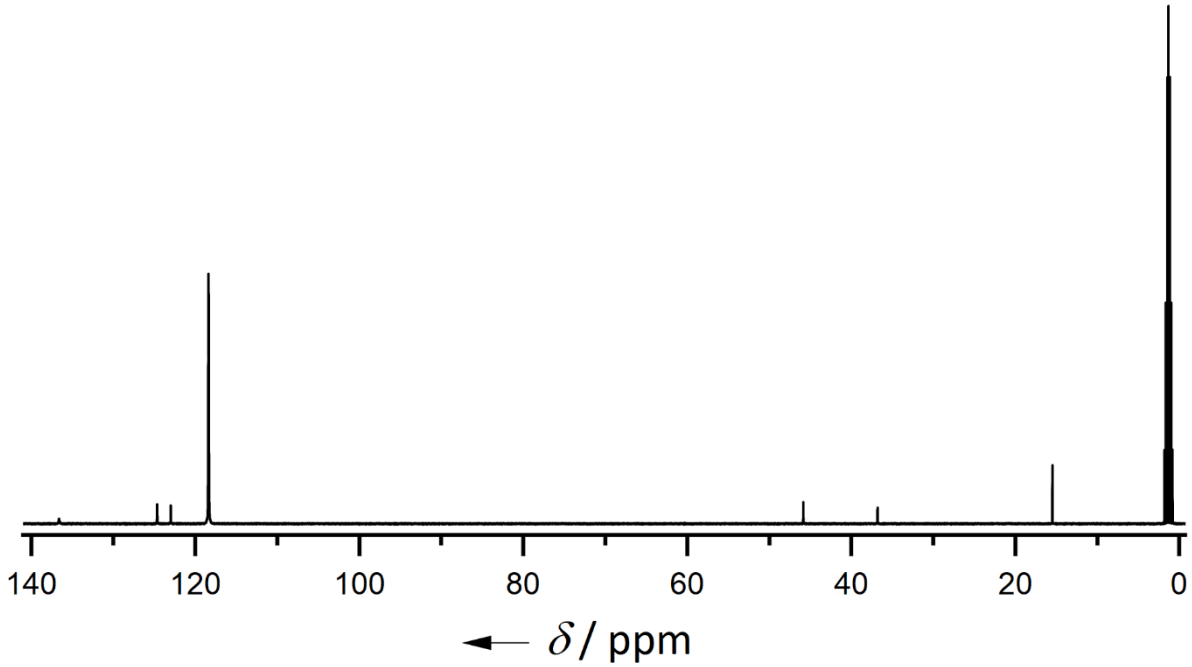



Figure 18: $^{13}C\{^{1}H\}$ NMR of [EMIm][$PF_6$].

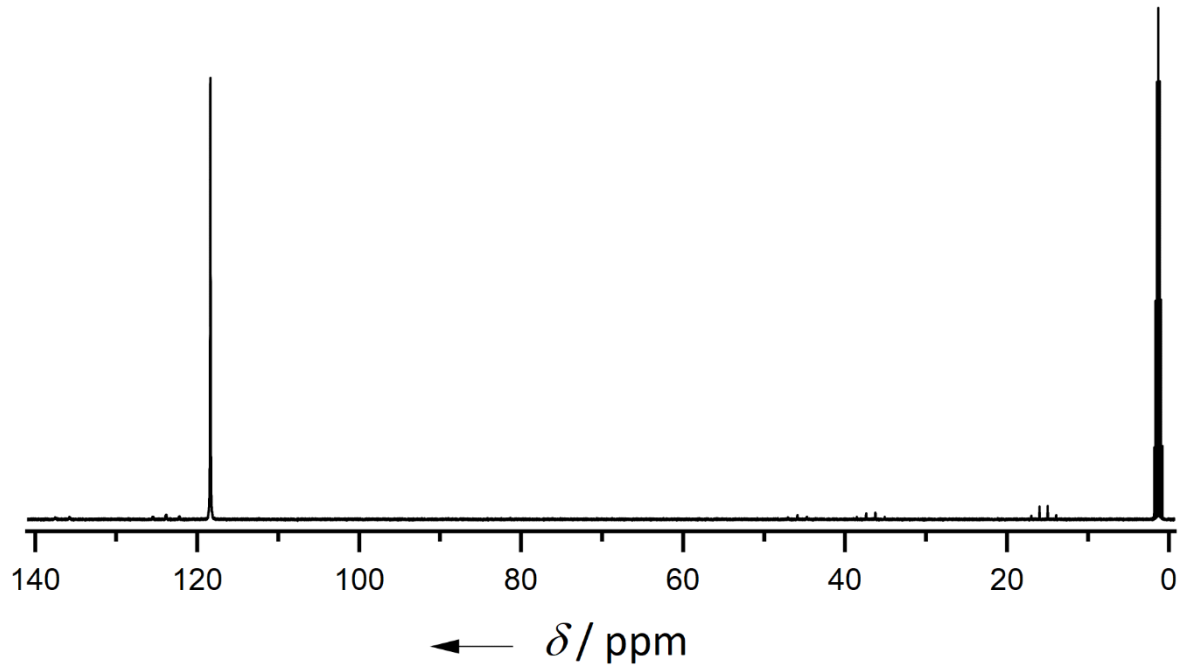



Figure 19: $^{13}C\{^{19}F\}$ NMR of [EMIm][$PF_6$].

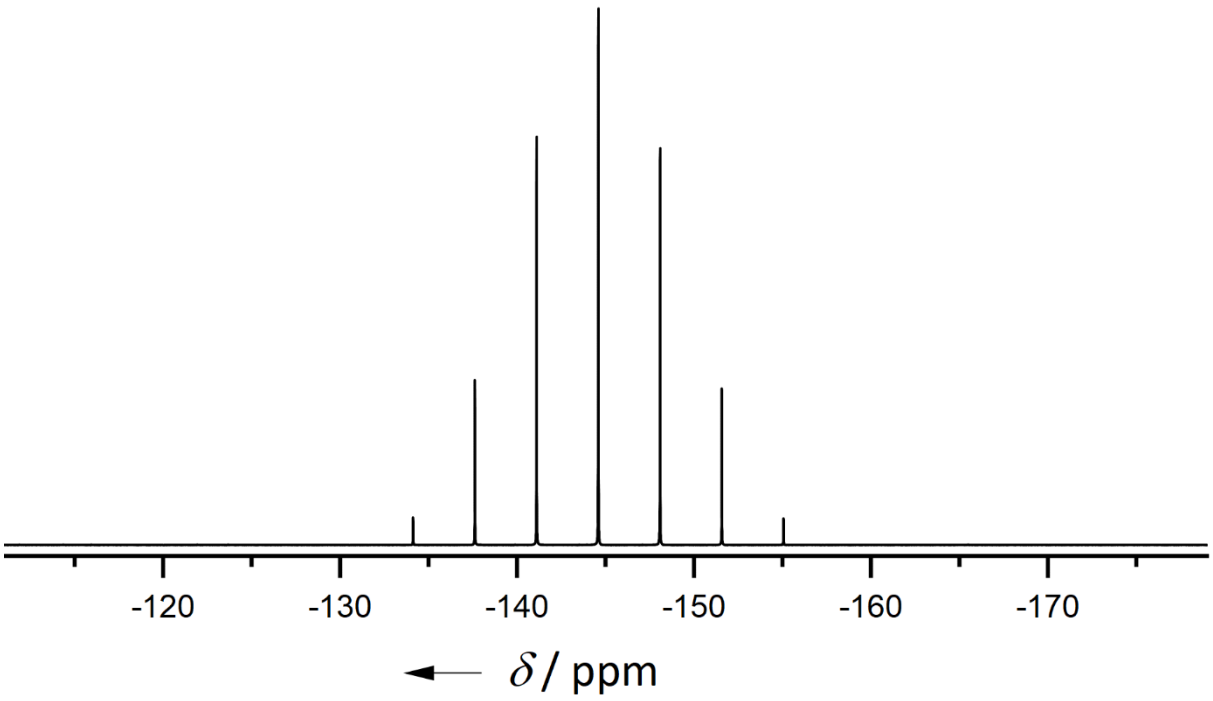



Figure 20: $^{31}P\{^{1}H\}$ NMR of [EMIm][$PF_6$].

**2.5 [BMIm]FAP$^3$**

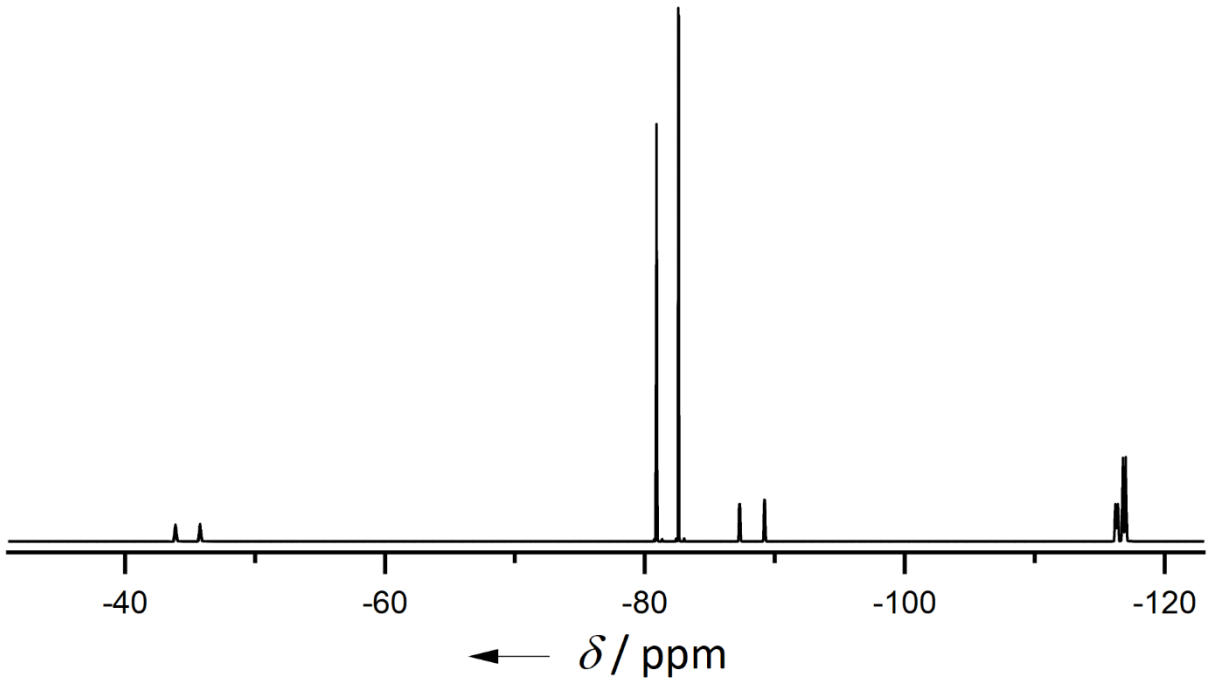



Figure 21: $^{19}$F NMR of [BMIm]**FAP$^3$**.

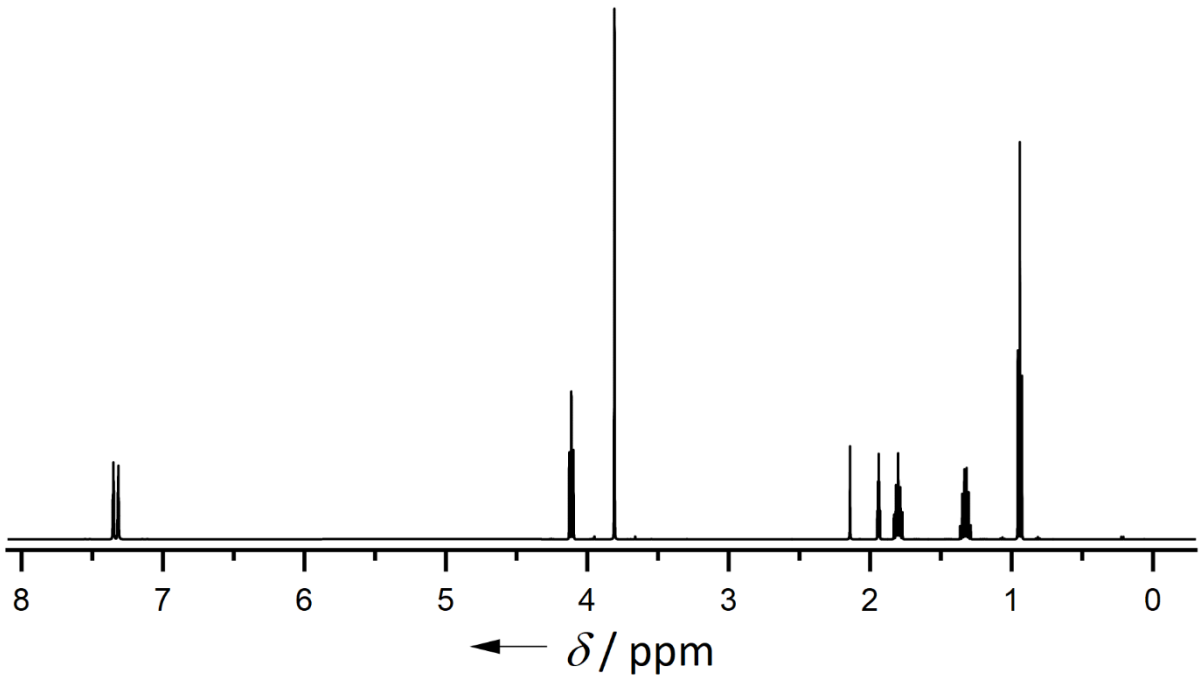



Figure 22: $^1$H NMR of [BMIm]**FAP$^3$**.

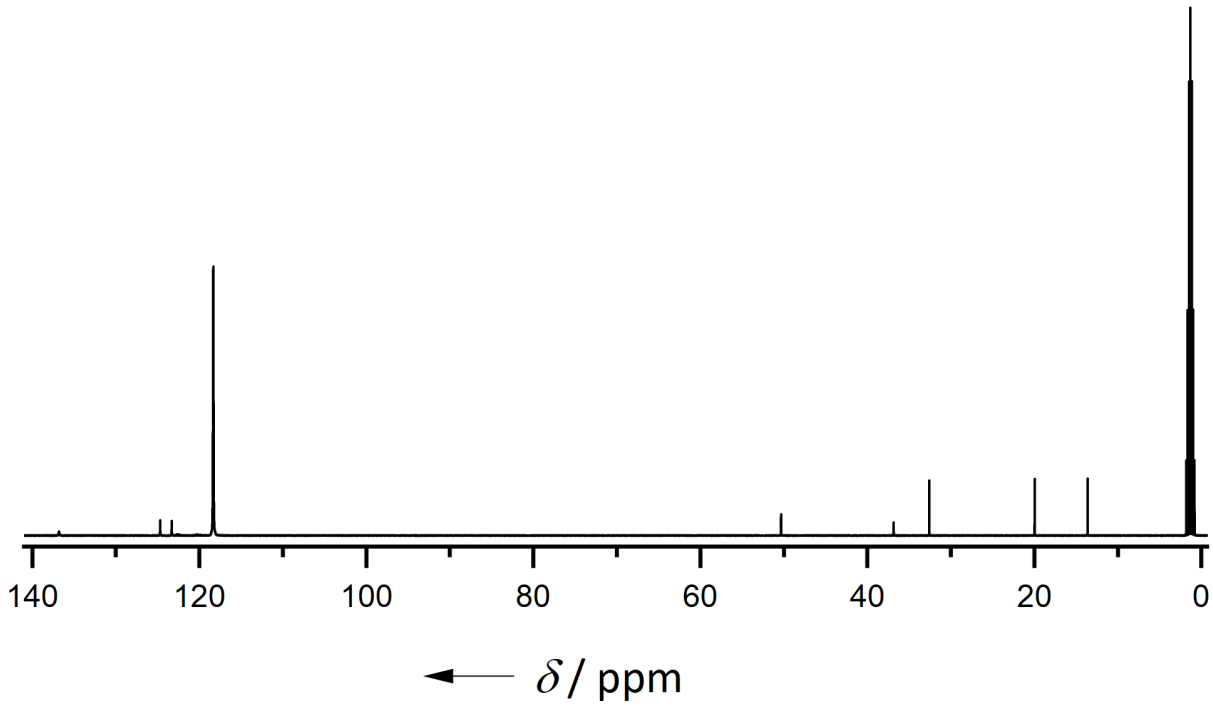



Figure 23: $^{13}C\{^{1}H\}$ NMR of [BMIm]**FAP$^{3}$**.

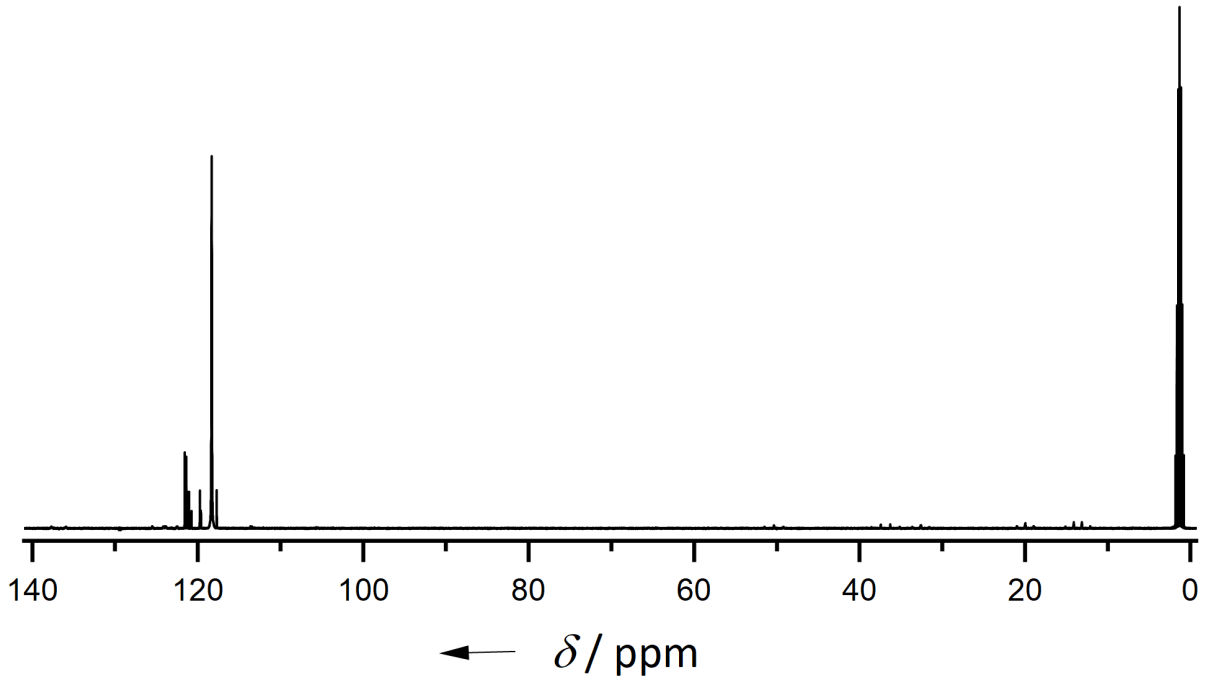



Figure 24: $^{13}C\{^{19}F\}$ NMR of [BMIm]**FAP$^{3}$**.

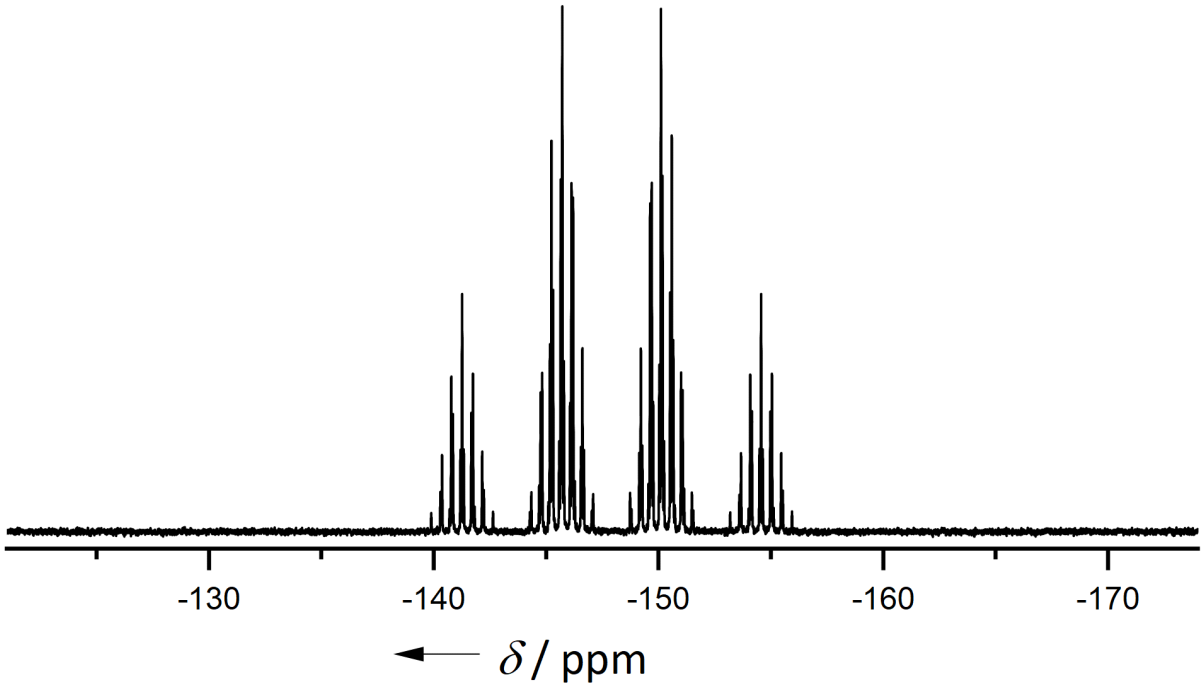



Figure 25: $^{31}P\{^{1}H\}$ NMR of [BMIm]**FAP$^{3}$**.

### 2.6 [BMIm]FAP$^{2}$

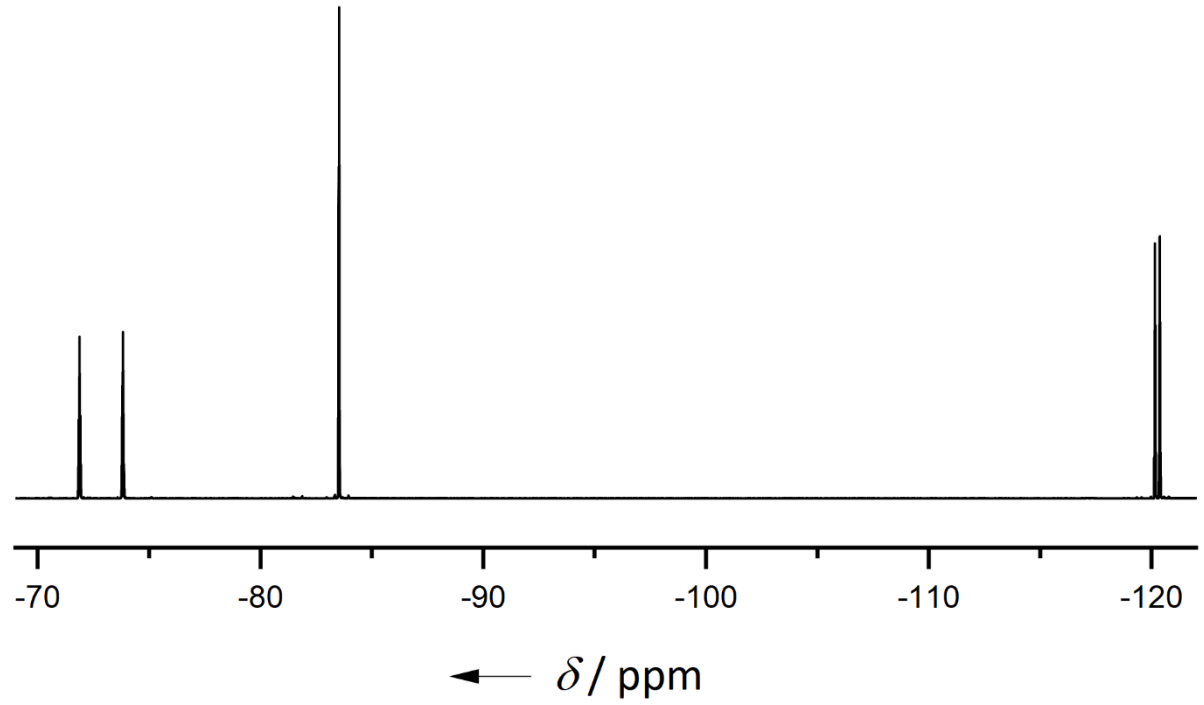



Figure 26: $^{19}F$ NMR of [BMIm]**FAP$^{2}$**.

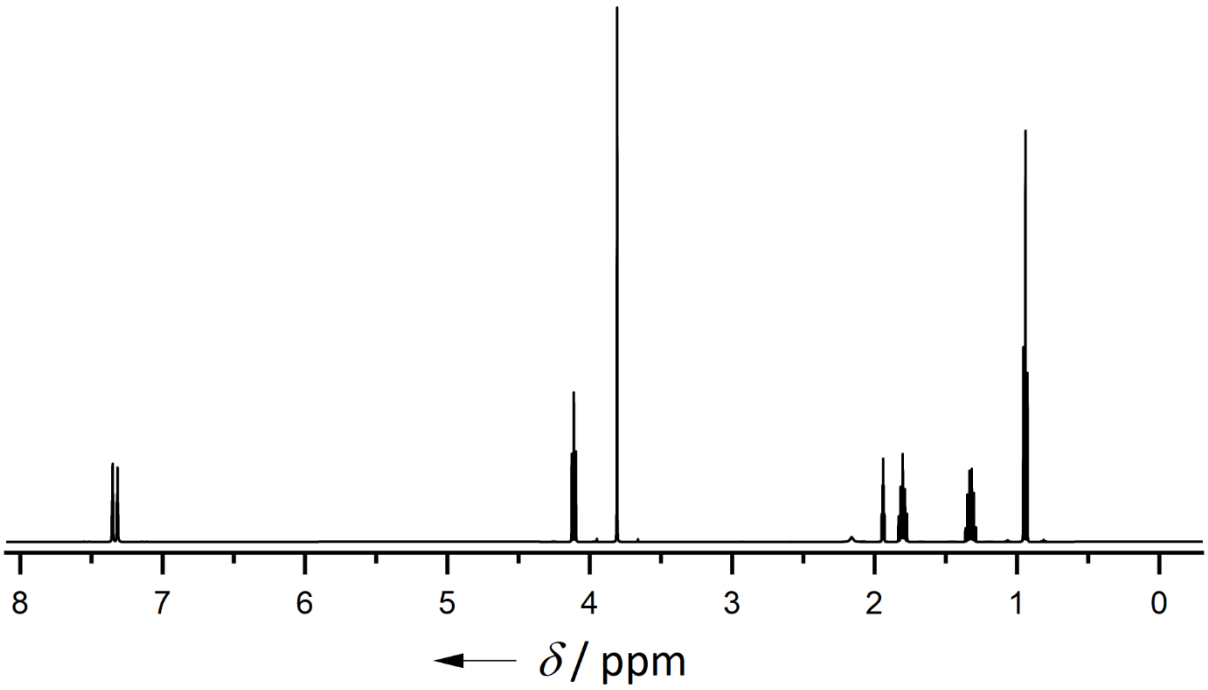



Figure 27: $^{1}H$ NMR of [EMIm]**FAP²**.

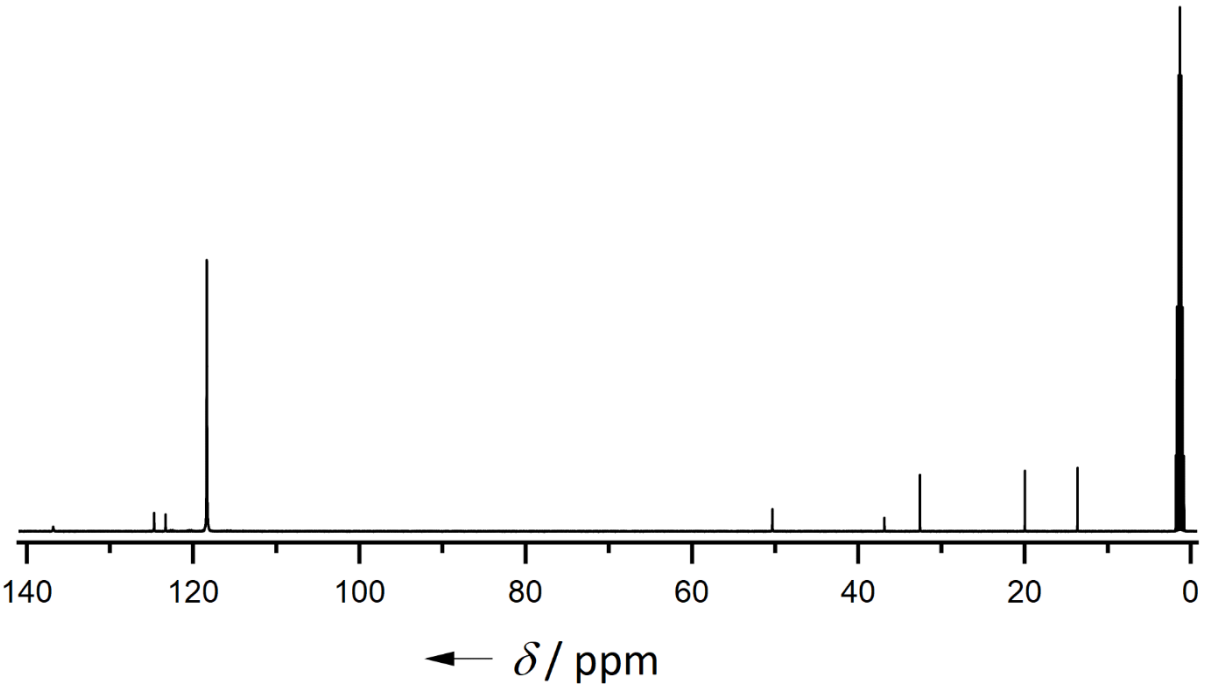



Figure 28: $^{13}C\{^{1}H\}$ NMR of [BMIm]**FAP²**.

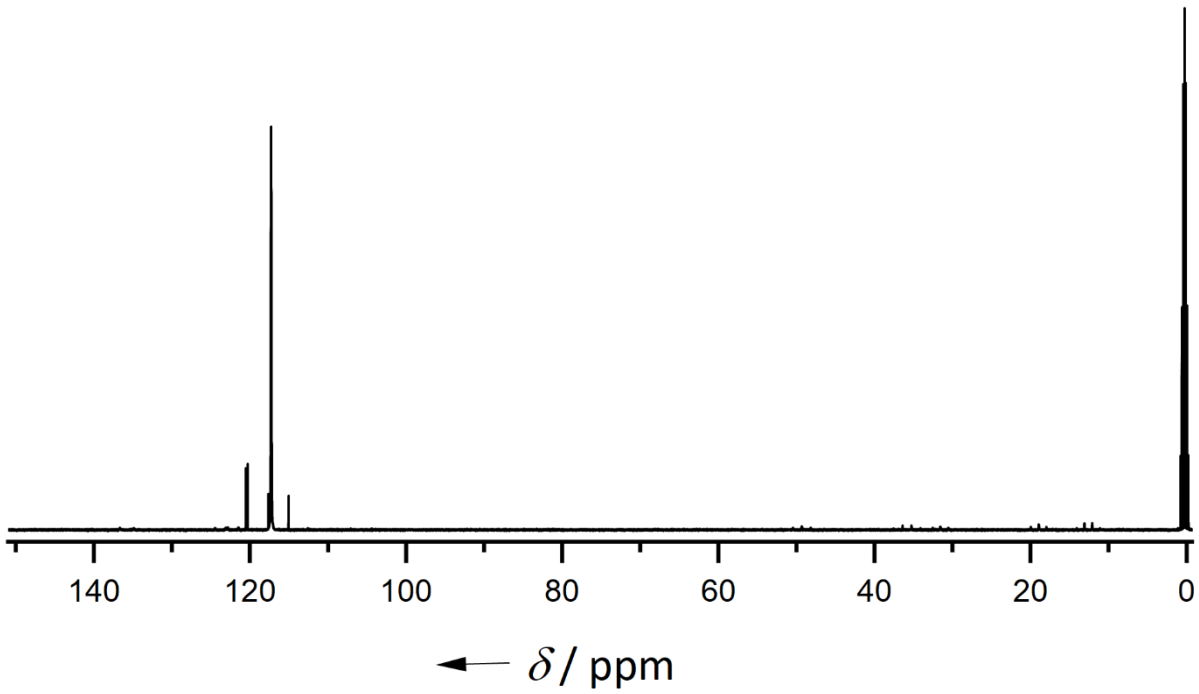



Figure 29: $^{13}C\{^{19}F\}$ NMR of [BMIm]**FAP²**.

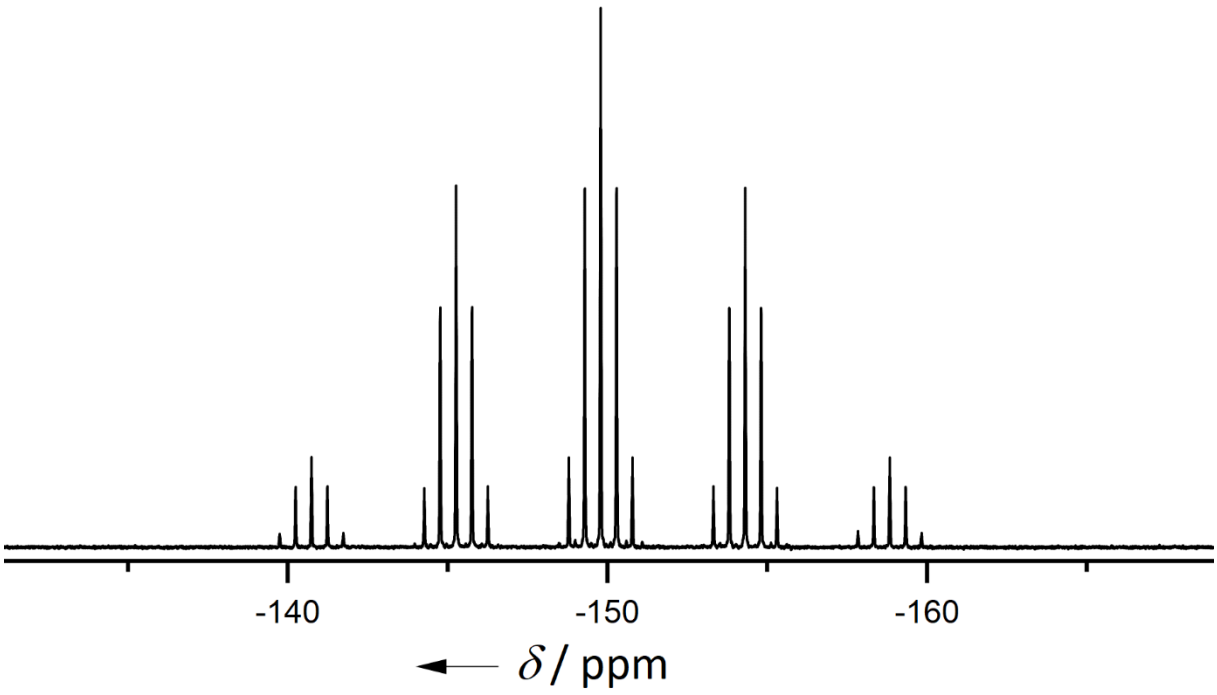



Figure 30: $^{31}P\{^{1}H\}$ NMR of [BMIm]**FAP²**.

**2.7 [BMIm]FAP[1]**

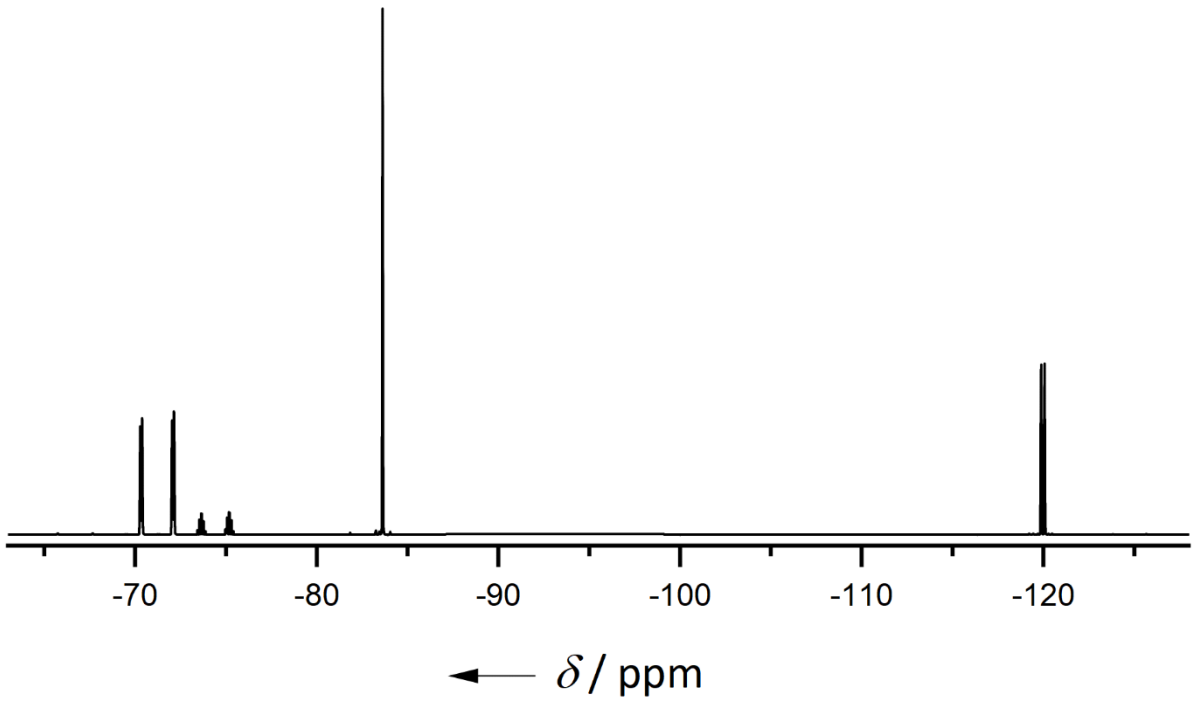



Figure 31: $^{19}$F NMR of [BMIm]**FAP[1]**.

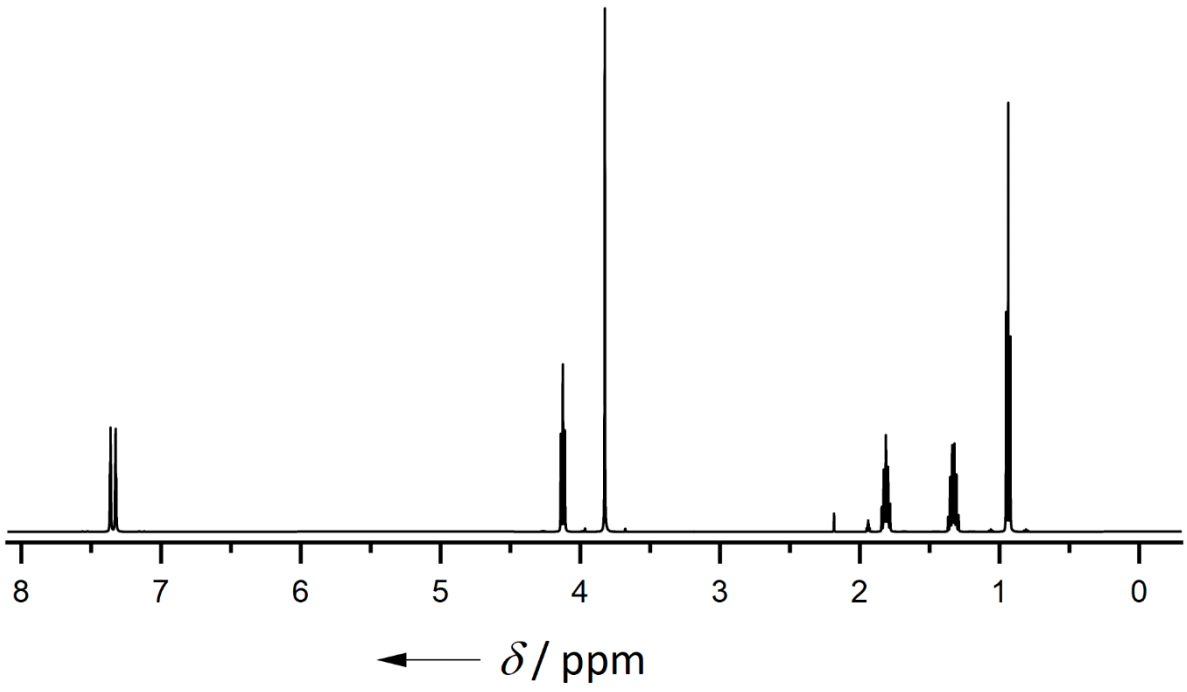



Figure 32: $^{1}$H NMR of [BMIm]**FAP[1]**.

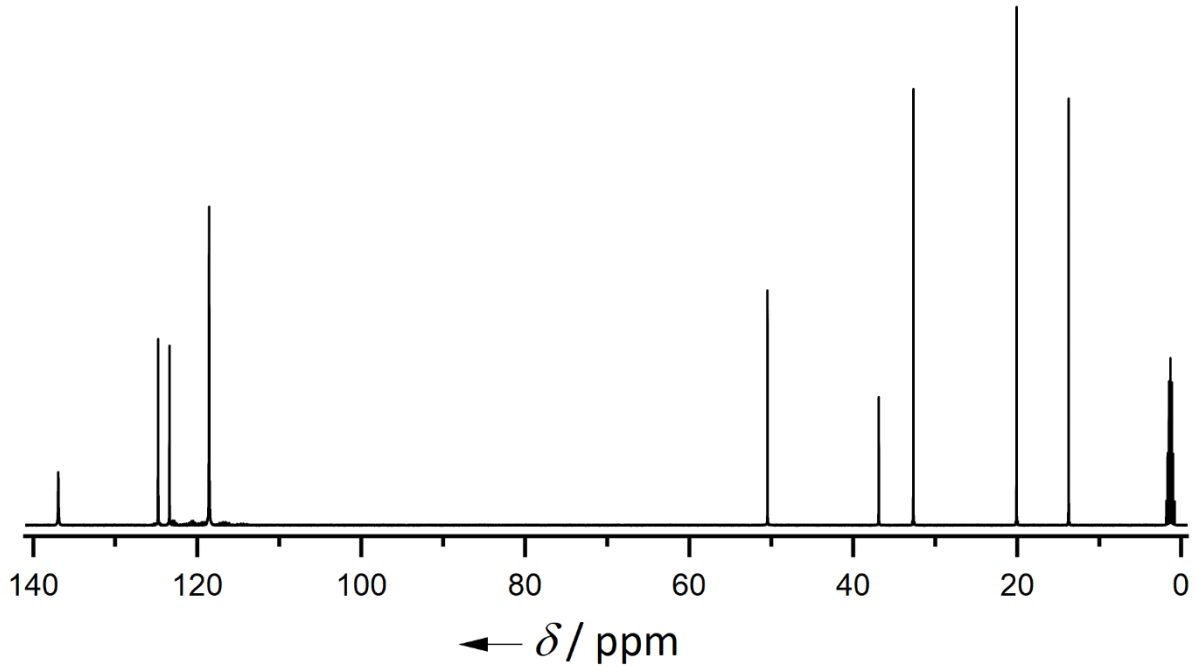



Figure 33: $^{13}C\{^{1}H\}$ NMR of [BMIm]**FAP**[1].

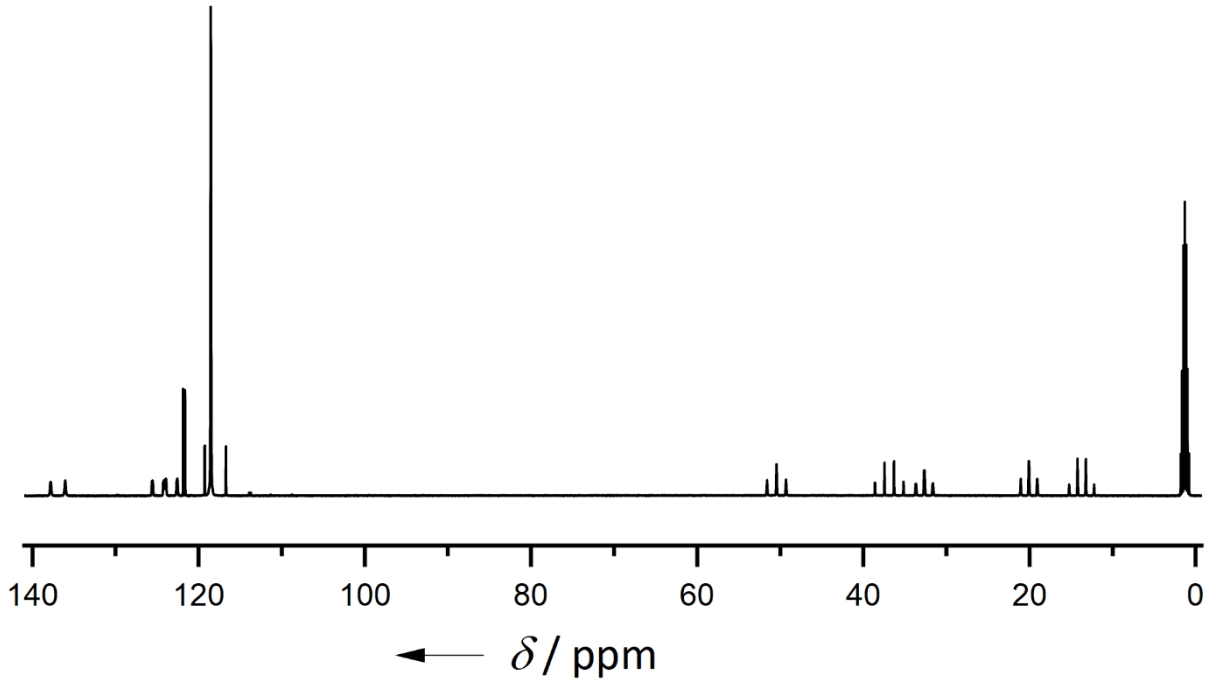



Figure 34: $^{13}C\{^{19}F\}$ NMR of [BMIm]**FAP**[1].

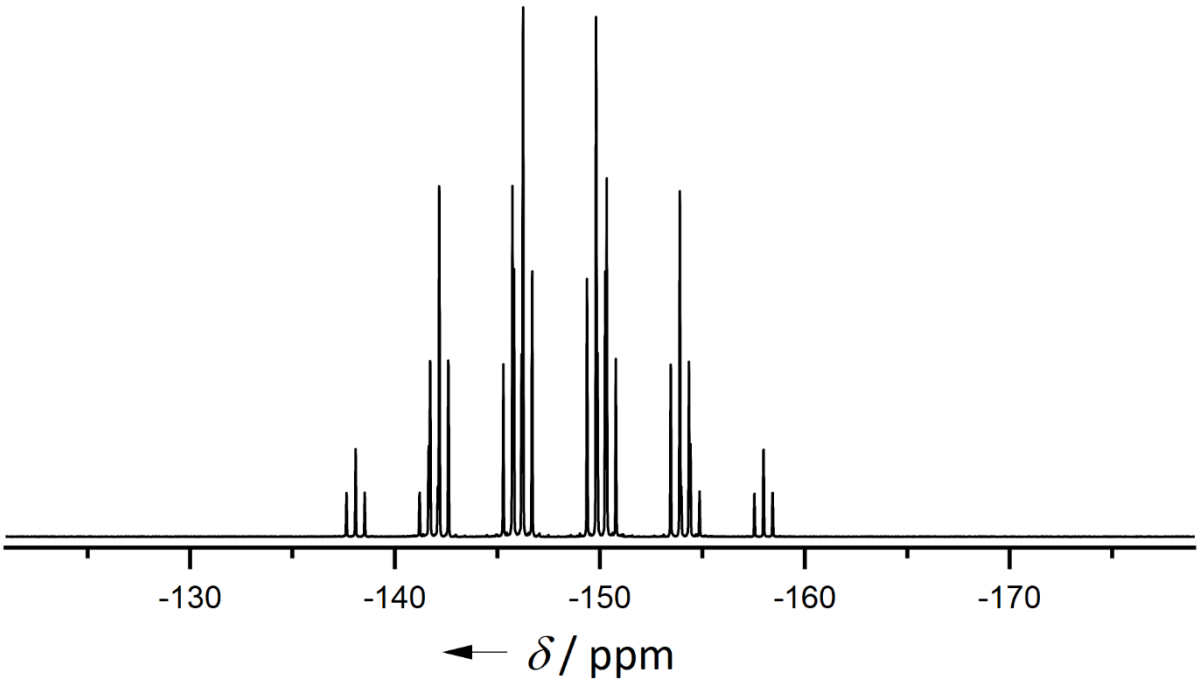



Figure 35: $^{31}P\{^{1}H\}$ NMR of [BMIm]**FAP$^{1}$**.

**2.8 [BMIm][$PF_6$]**

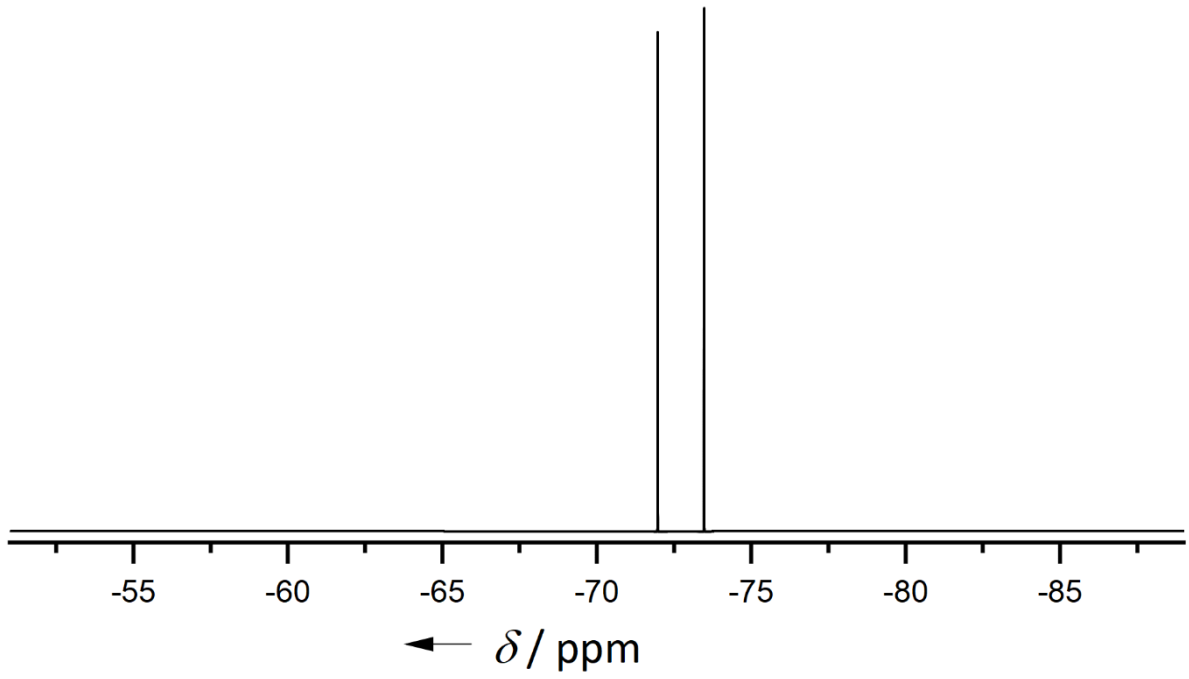



Figure 36: $^{19}F$ NMR of [BMIm][$PF_6$].

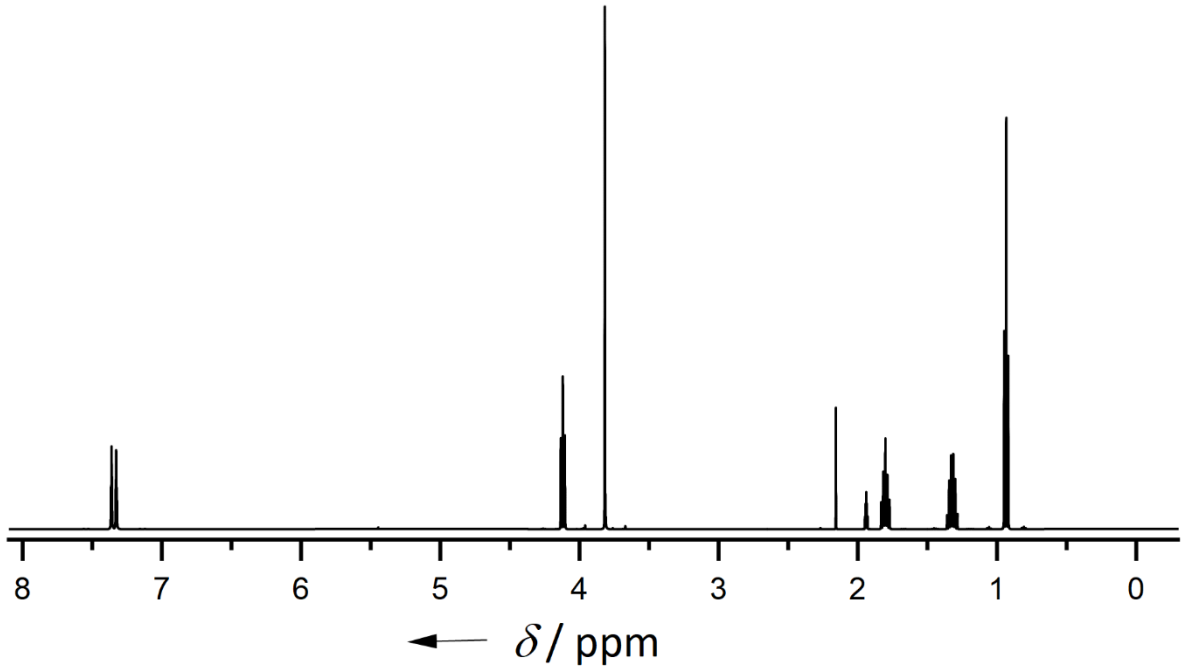



Figure 37: $^{1}H$ NMR of [BMIm][$PF_6$].

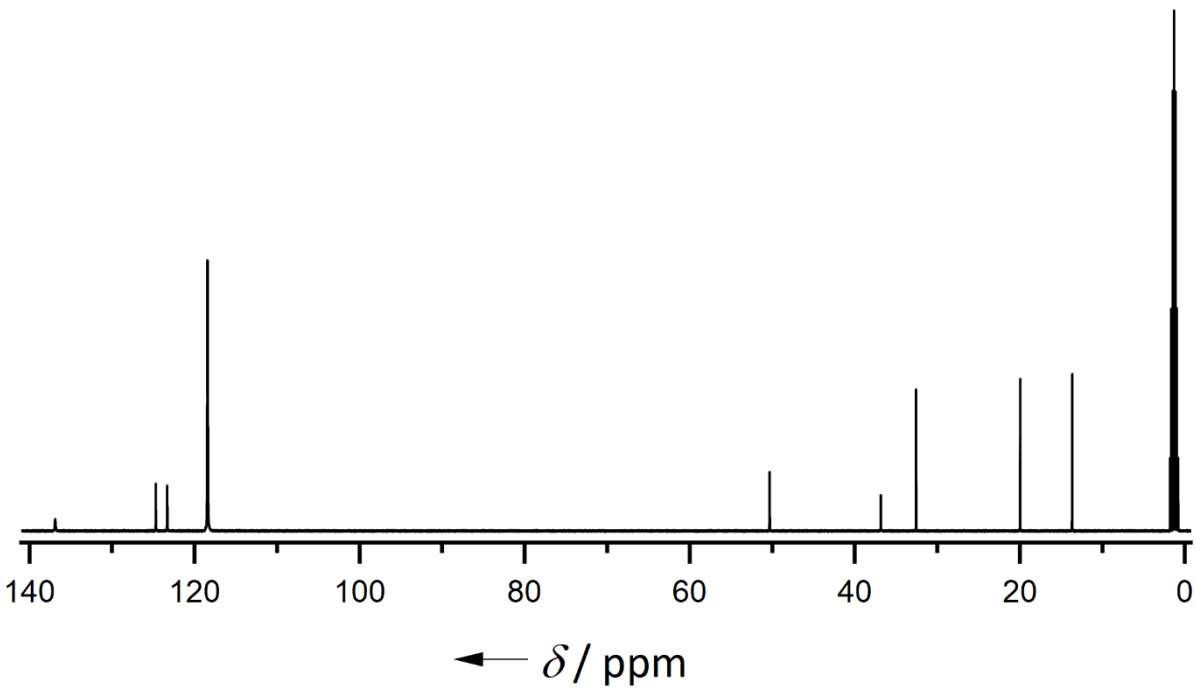



Figure 38: $^{13}C\{^{1}H\}$ NMR of [BMIm][$PF_6$].

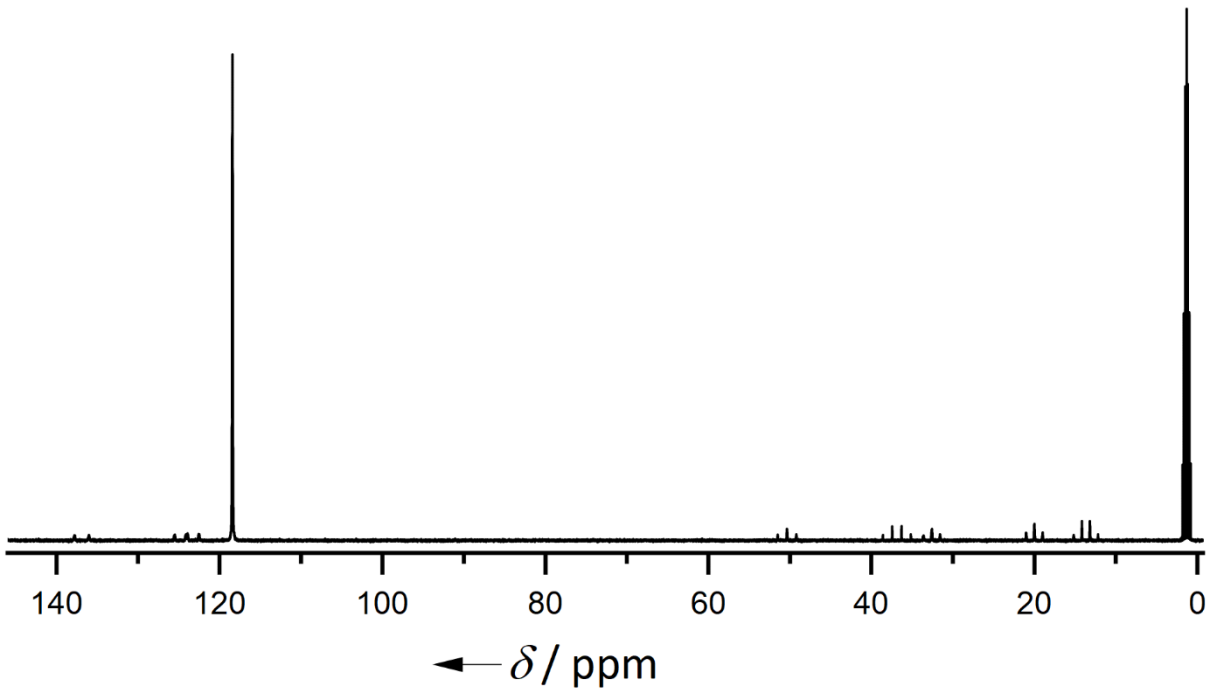



Figure 39: $^{13}C\{^{19}F\}$ NMR of [BMIm][$PF_6$].

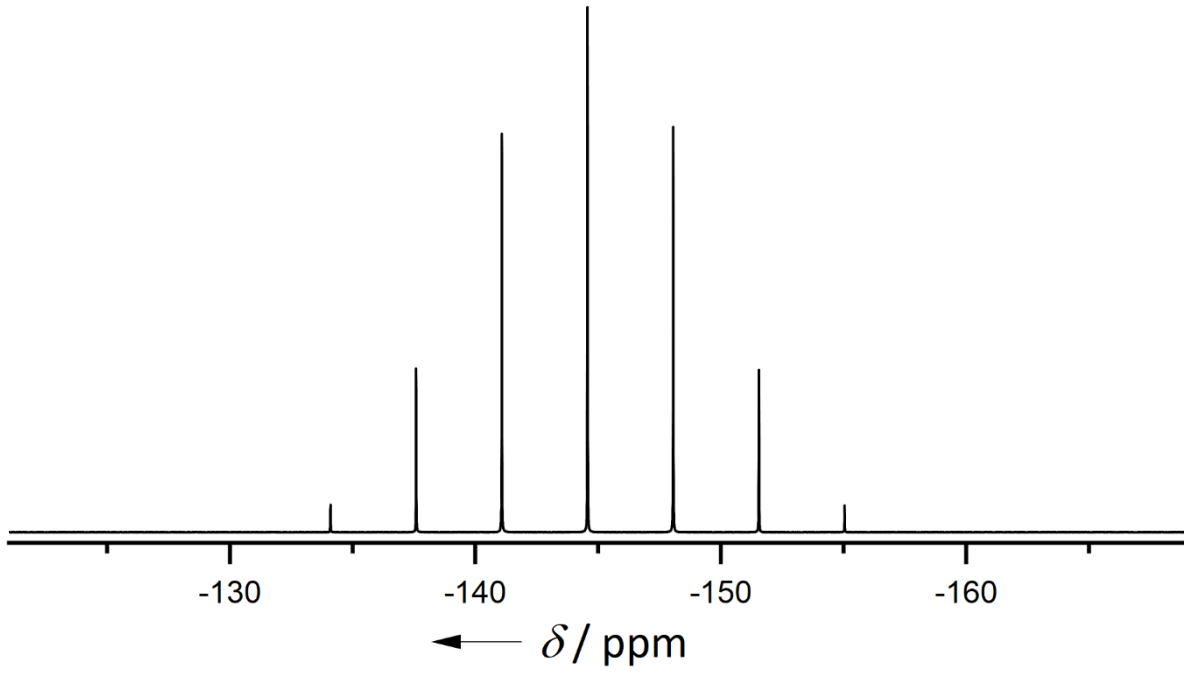



Figure 40: $^{31}P\{^{1}H\}$ NMR of [BMIm][$PF_6$].

**2.9 [BMPL]FAP$^3$**

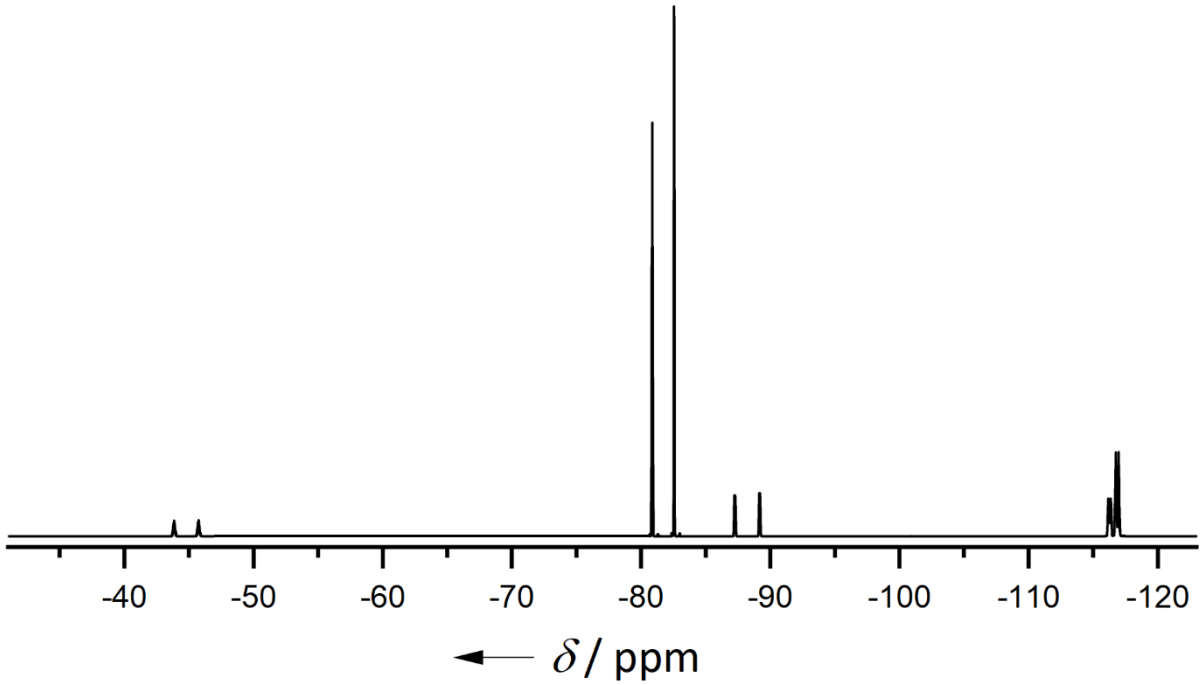



Figure 41: $^{19}$F NMR of [BMPL]**FAP$^3$**.

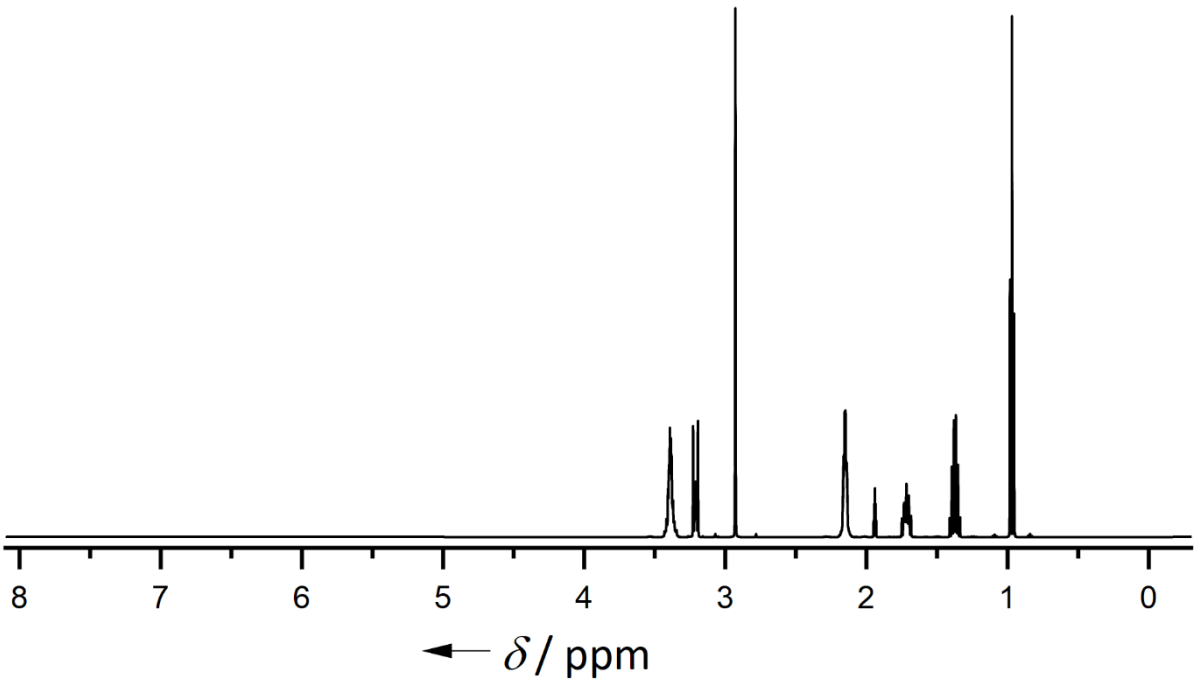



Figure 42: $^{1}$H NMR of [BMPL]**FAP$^3$**.

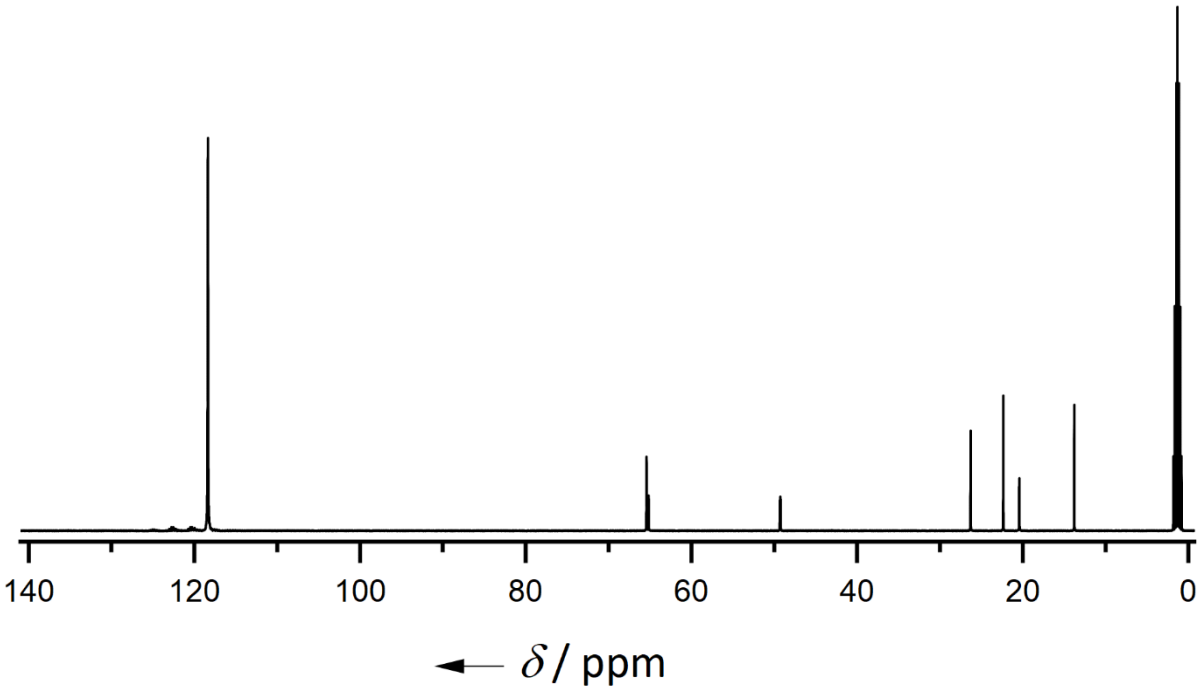



Figure 43: $^{13}C\{^{1}H\}$ NMR of [BMPL]**FAP$^{3}$**.

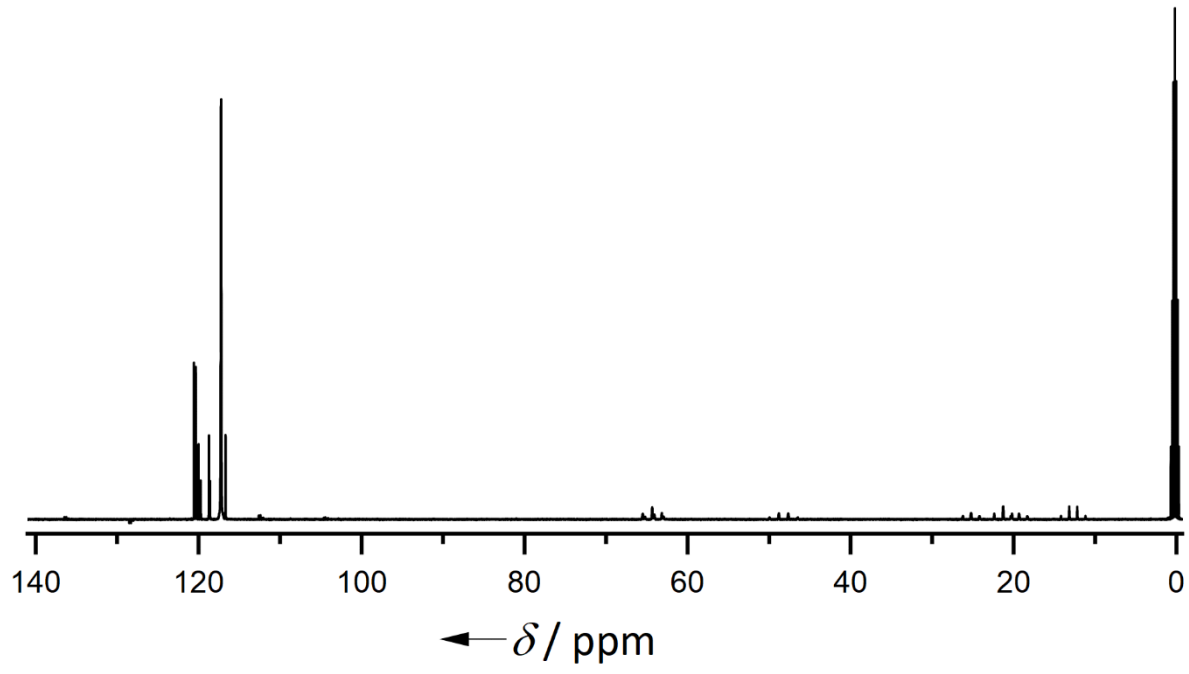



Figure 44: $^{13}C\{^{19}F\}$ NMR of [BMPL]**FAP$^{3}$**.

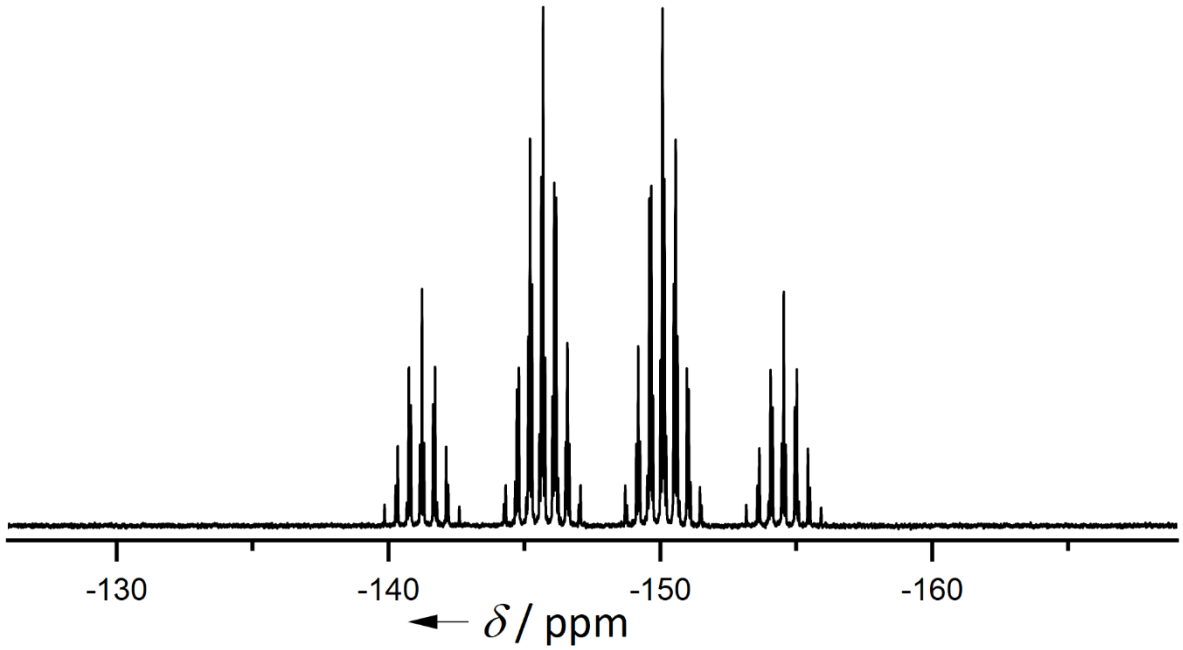



Figure 45: $^{31}P\{^{1}H\}$ NMR of [BMPL]**FAP$^{3}$**.

**2.10 [BMPL]FAP$^{2}$**

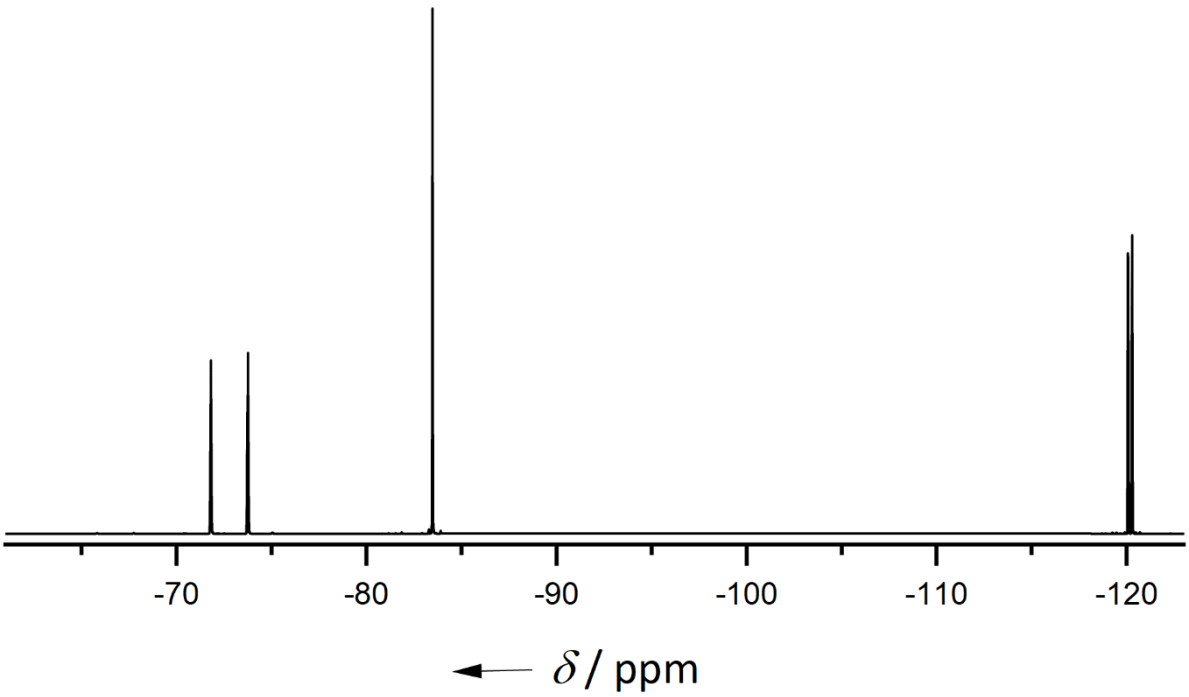



Figure 46: $^{19}F$ NMR of [BMPL]**FAP$^{2}$**.

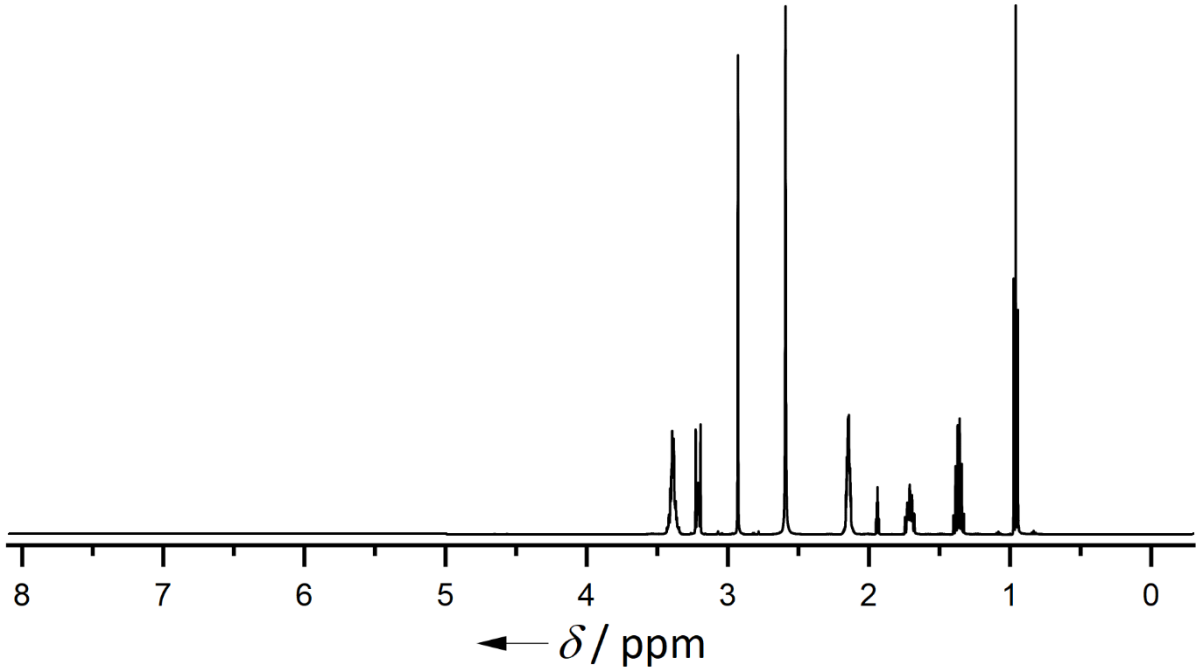



Figure 47: $^{1}$H NMR of [BMPL]**FAP$^{2}$**.

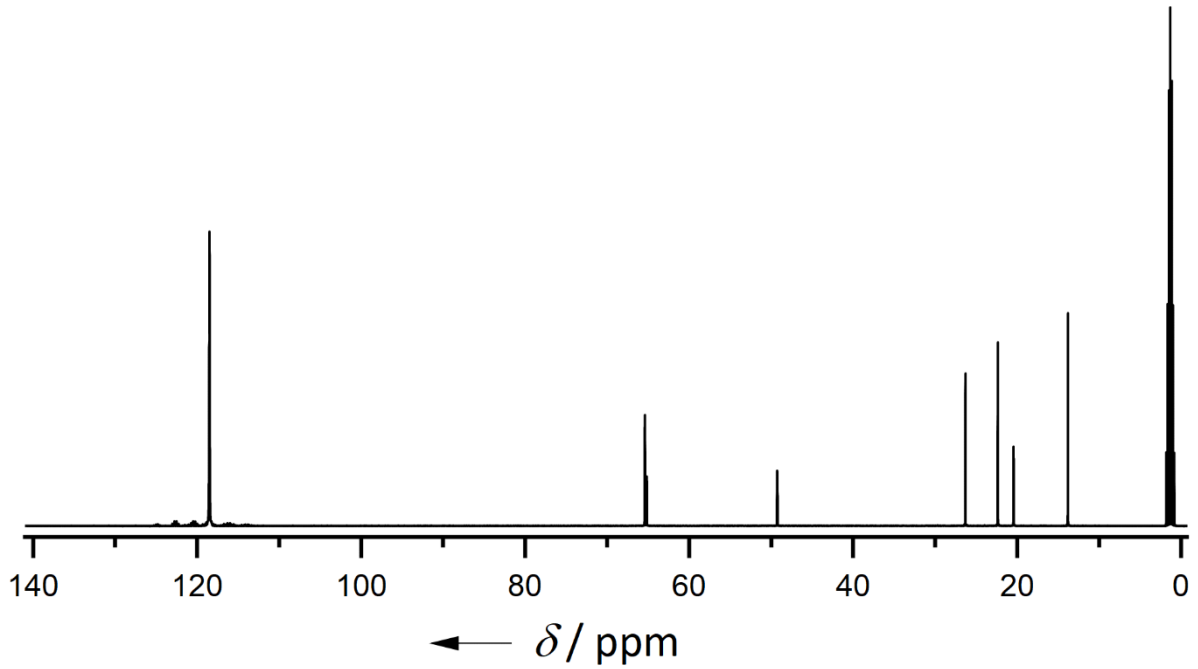



Figure 48: $^{13}$C{$^{1}$H} NMR of [BMPL]**FAP$^{2}$**.

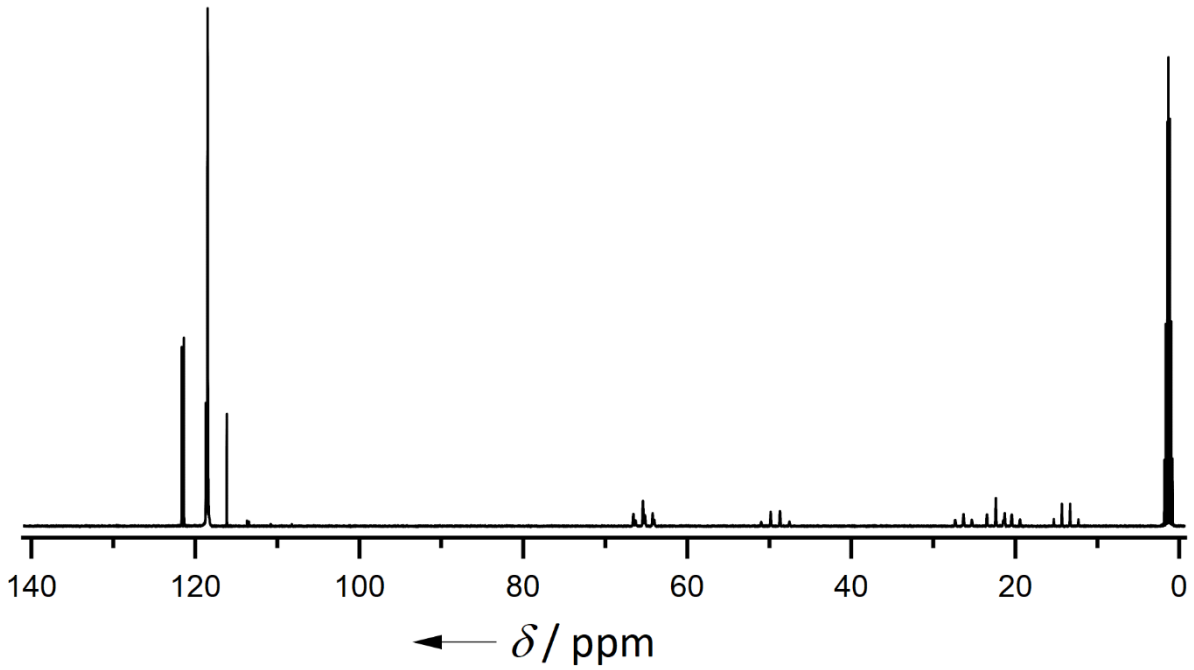



Figure 49: $^{13}C\{^{19}F\}$ NMR of [BMPL]**FAP²**.

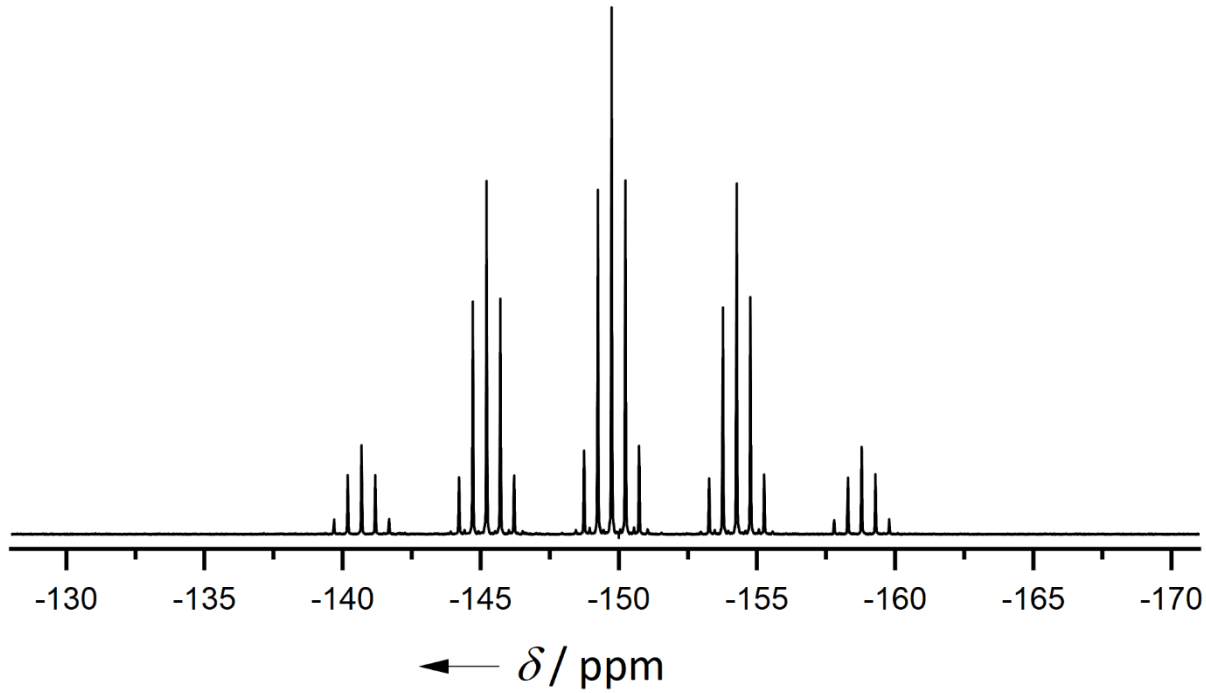



Figure 50: $^{31}P\{^{1}H\}$ NMR of [BMPL]**FAP²**.

**2.11 [BMPL]FAP[1]**

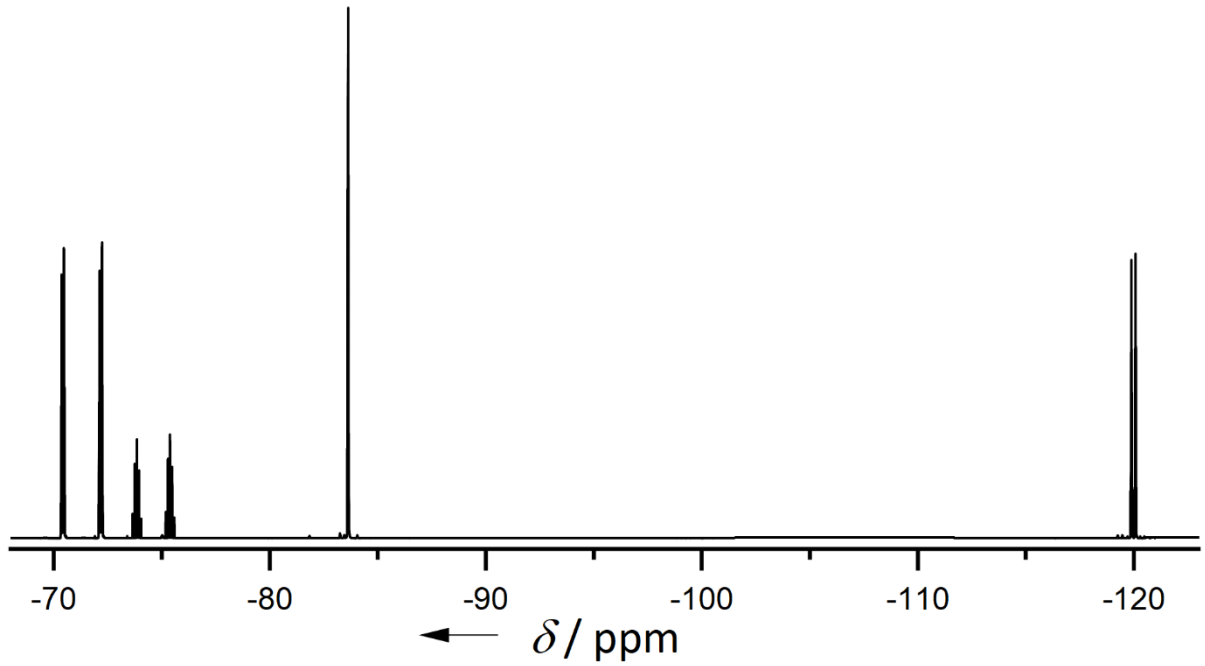



Figure 51: $^{19}$F NMR of [BMPL]**FAP[1]**.

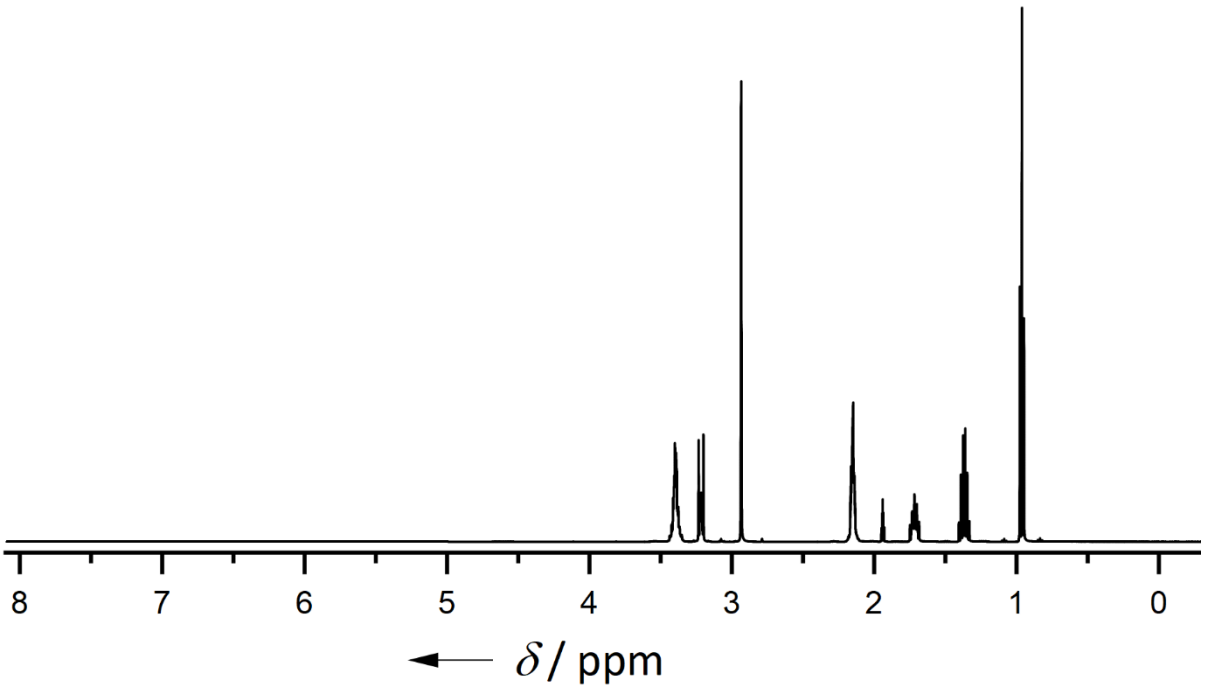



Figure 52: $^{1}$H NMR of [BMPL]**FAP[1]**.

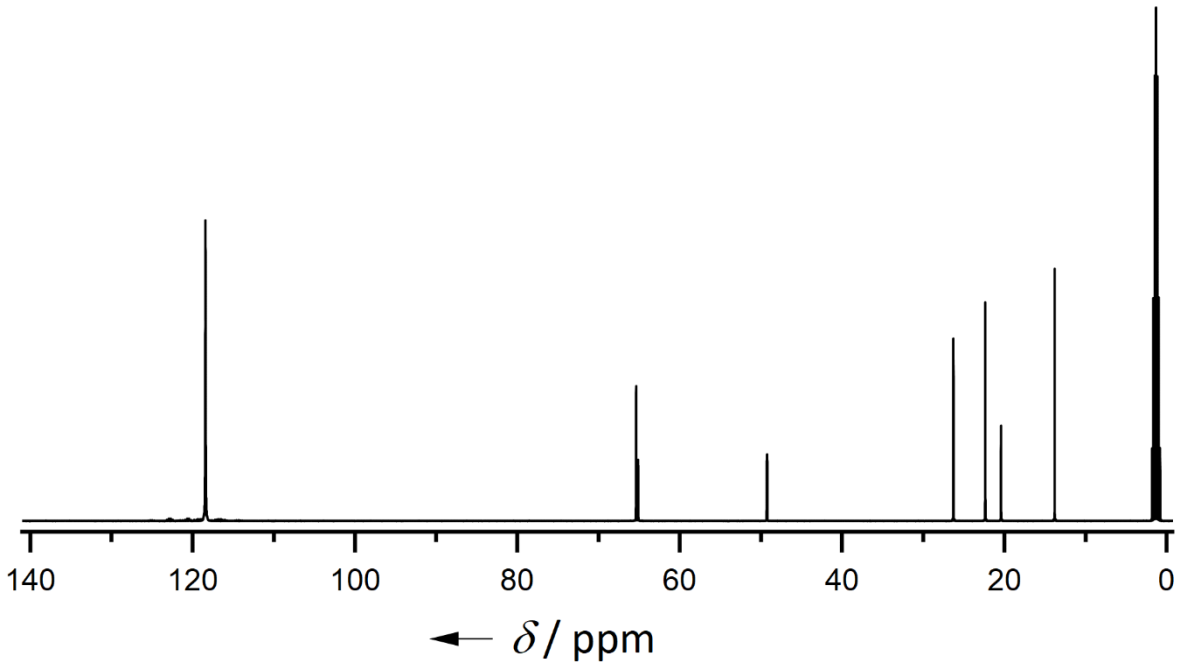



Figure 53: $^{13}C\{^{1}H\}$ NMR of [BMPL]**FAP$^{1}$**.

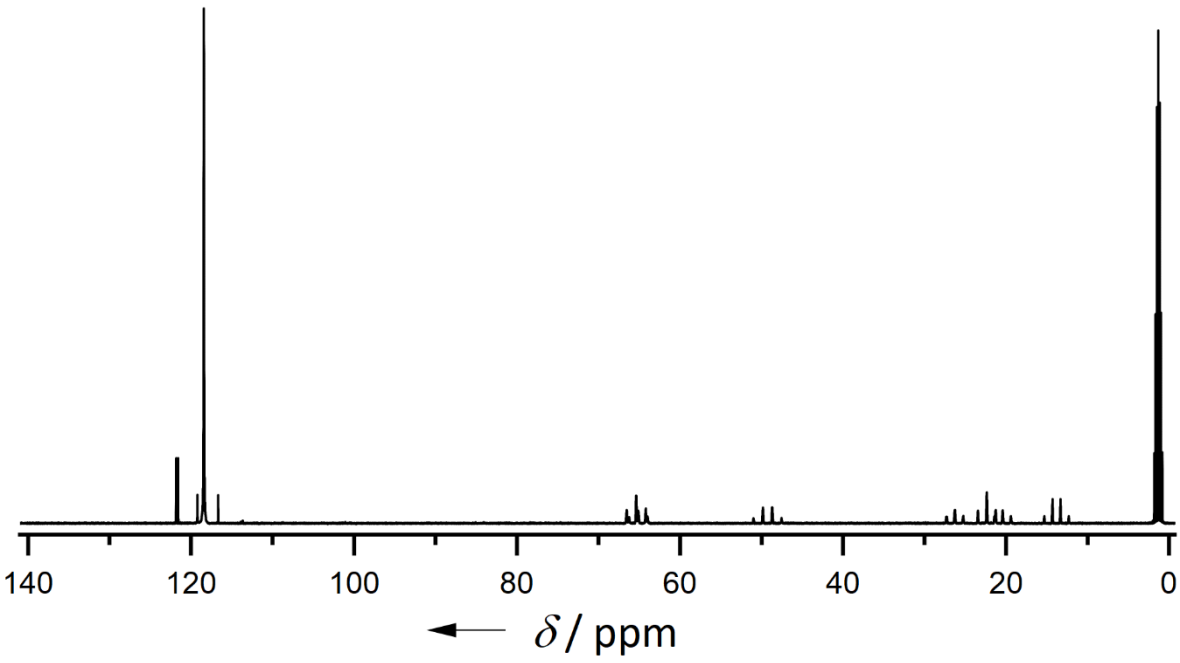



Figure 54: $^{13}C\{^{19}F\}$ NMR of [BMPL]**FAP$^{1}$**.

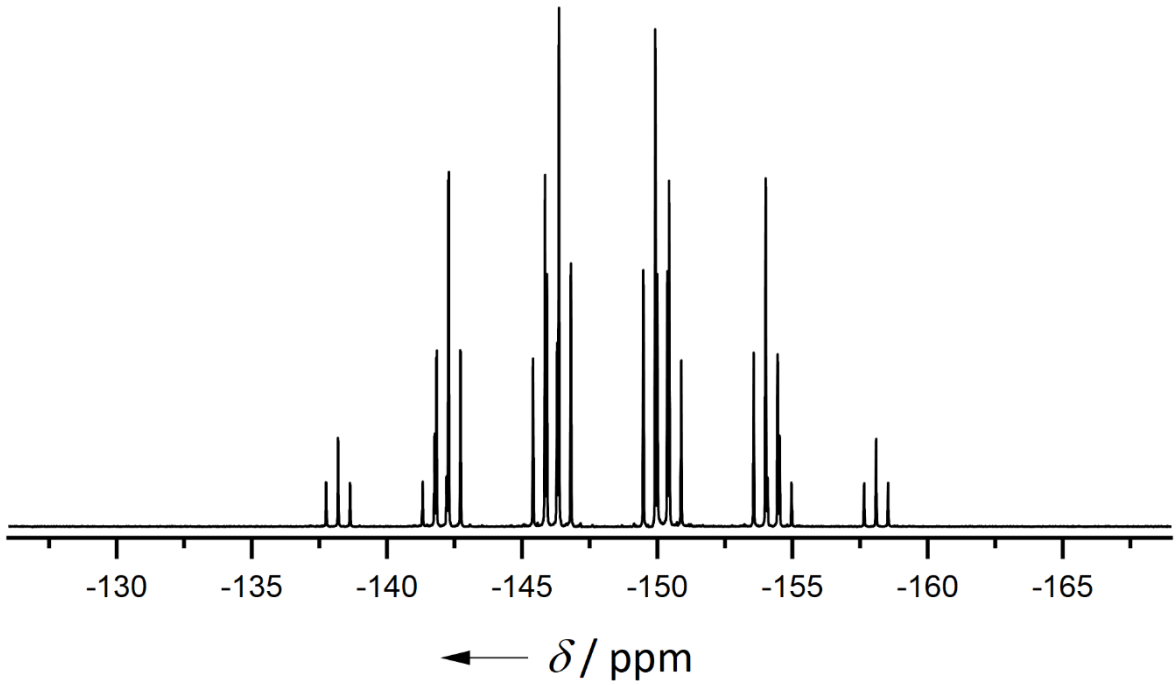



Figure 55: $^{31}P\{^{1}H\}$ NMR of [BMPL]**FAP**[1].

### 2.12 [BMPL][$PF_6$]

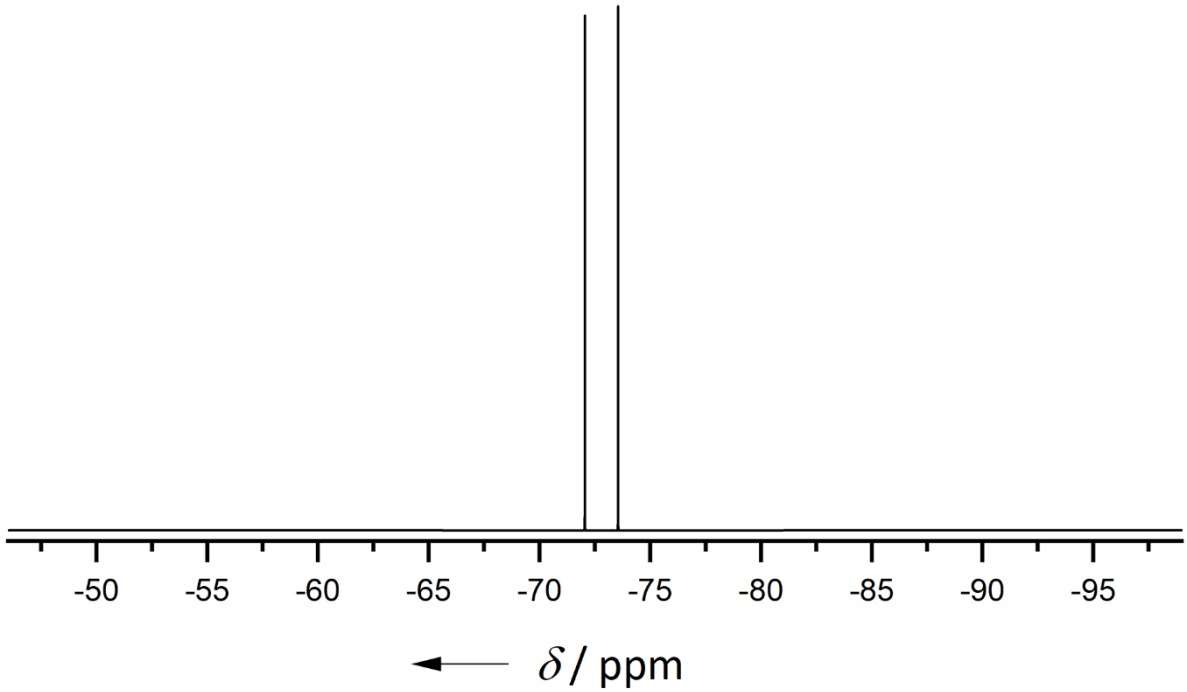



Figure 56: $^{19}F$ NMR of [BMPL][$PF_6$].

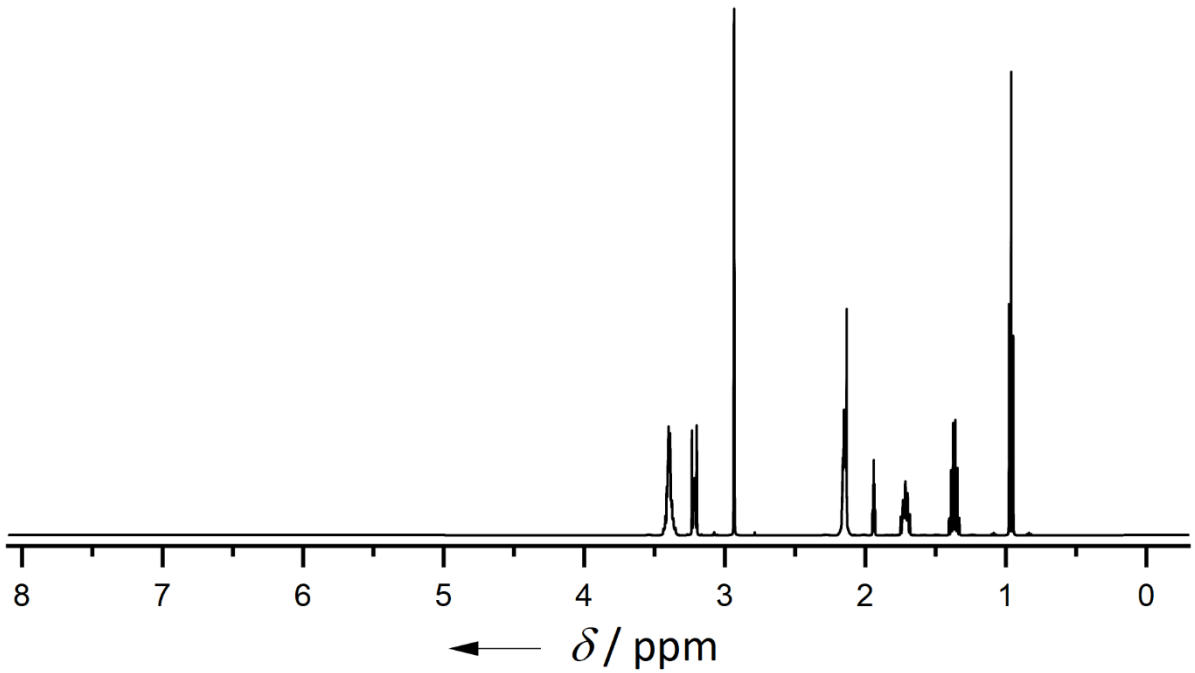



Figure 57: $^{1}H$ NMR of [BMPL][$PF_6$].

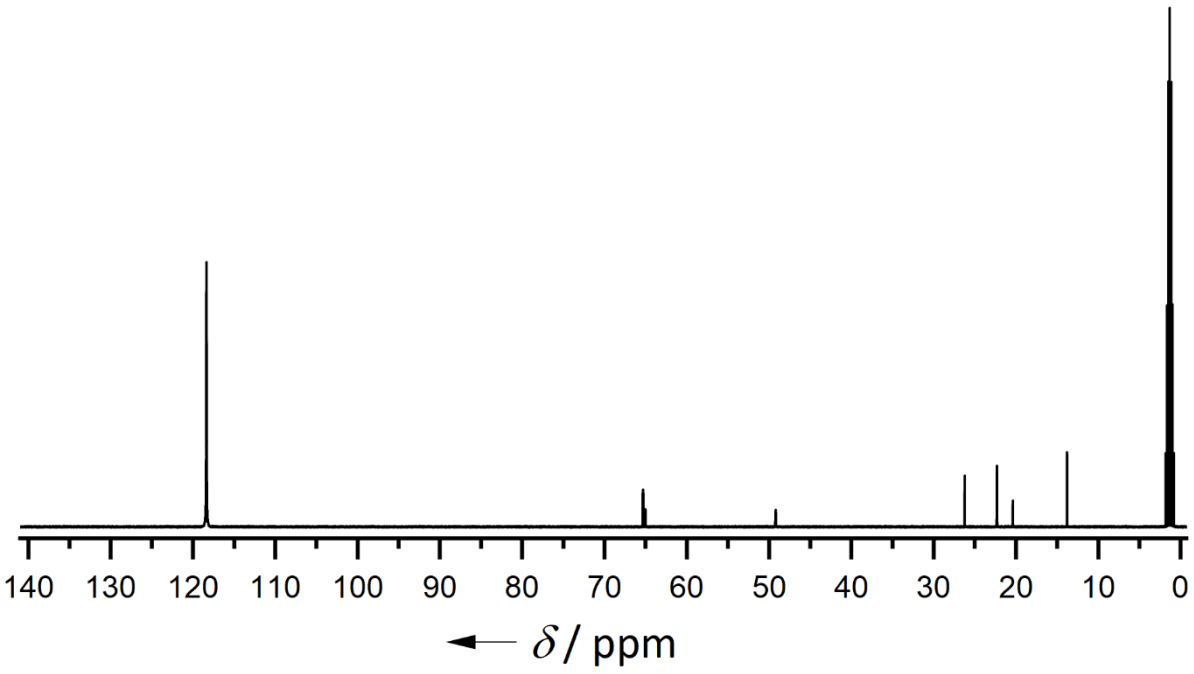



Figure 58: $^{13}C\{^{1}H\}$ NMR of [BMPL][$PF_6$].

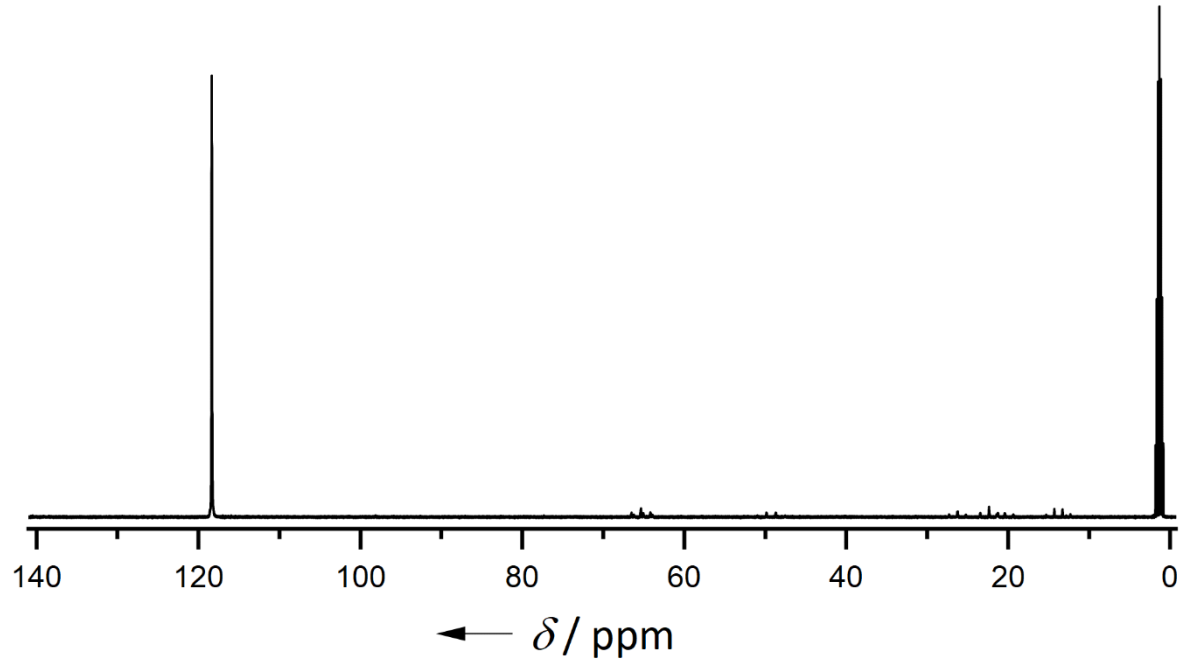



Figure 59: $^{13}C\{^{19}F\}$ NMR of [BMPL][$PF_6$].

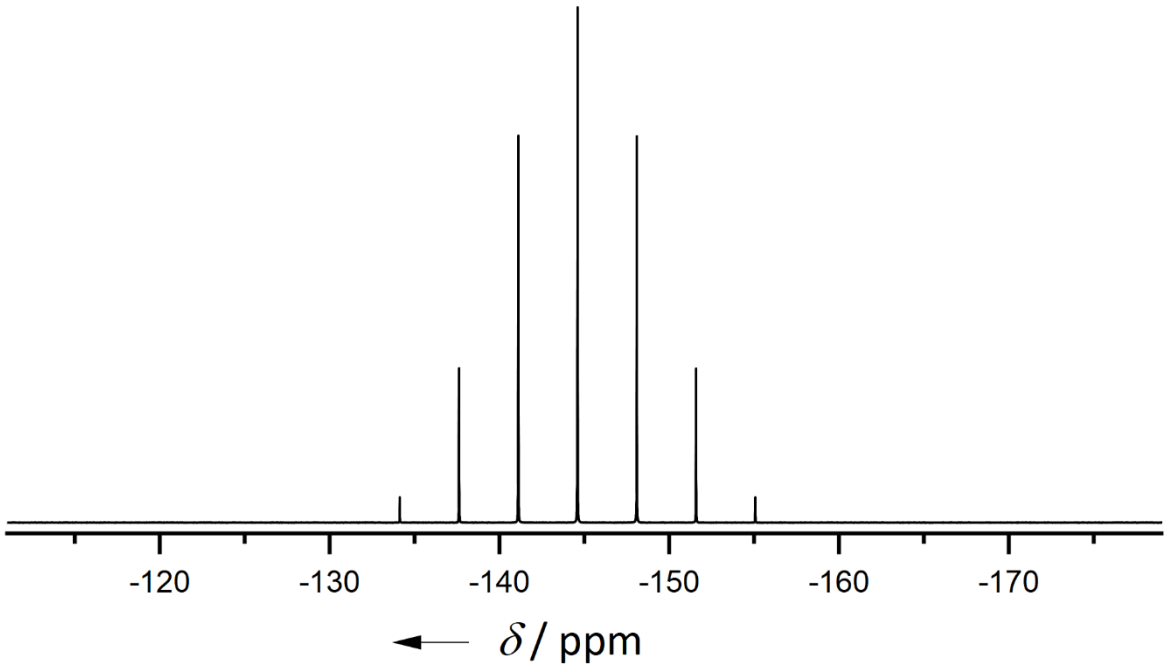



Figure 60: $^{31}P\{^{1}H\}$ NMR of [BMPL][$PF_6$].

# 3. Vibrational spectra

### 3.1 [EMIm]FAP$^3$

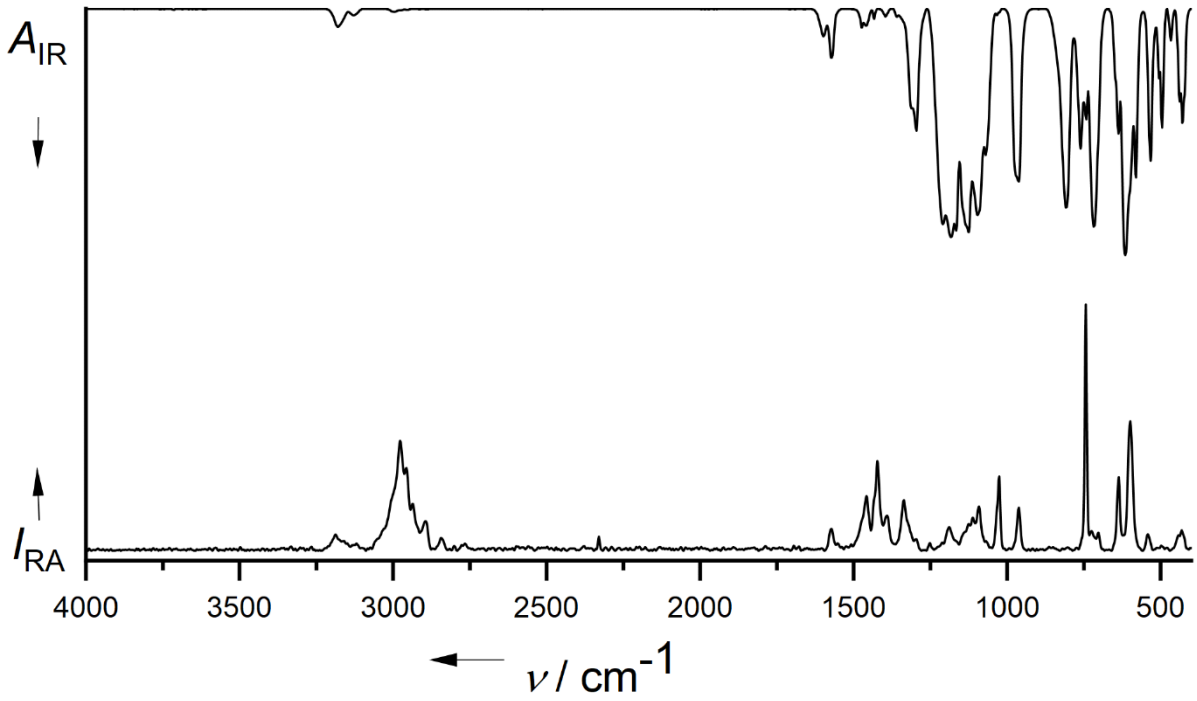



Figure 61: IR and Raman spectra of [EMIm]**FAP$^3$**.

### 3.2 [EMIm]FAP$^2$

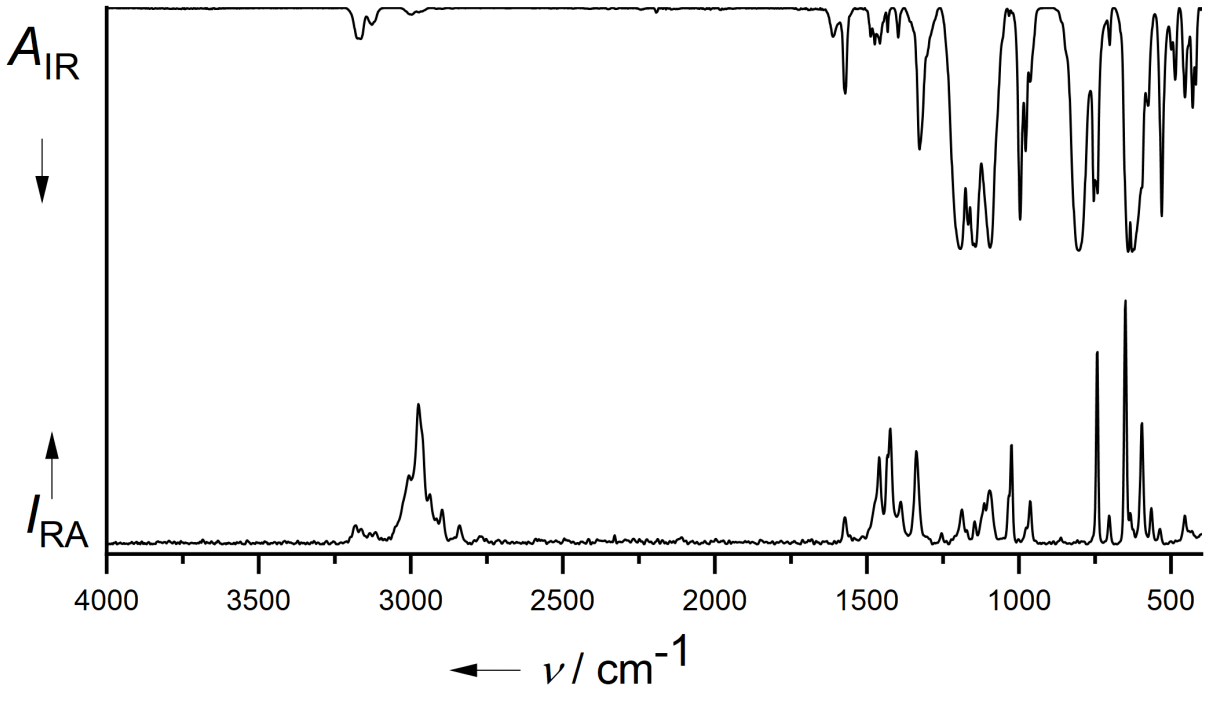



Figure 62: IR and Raman spectra of [EMIm]**FAP$^2$**.

### 3.3 [EMIm]FAP[1]

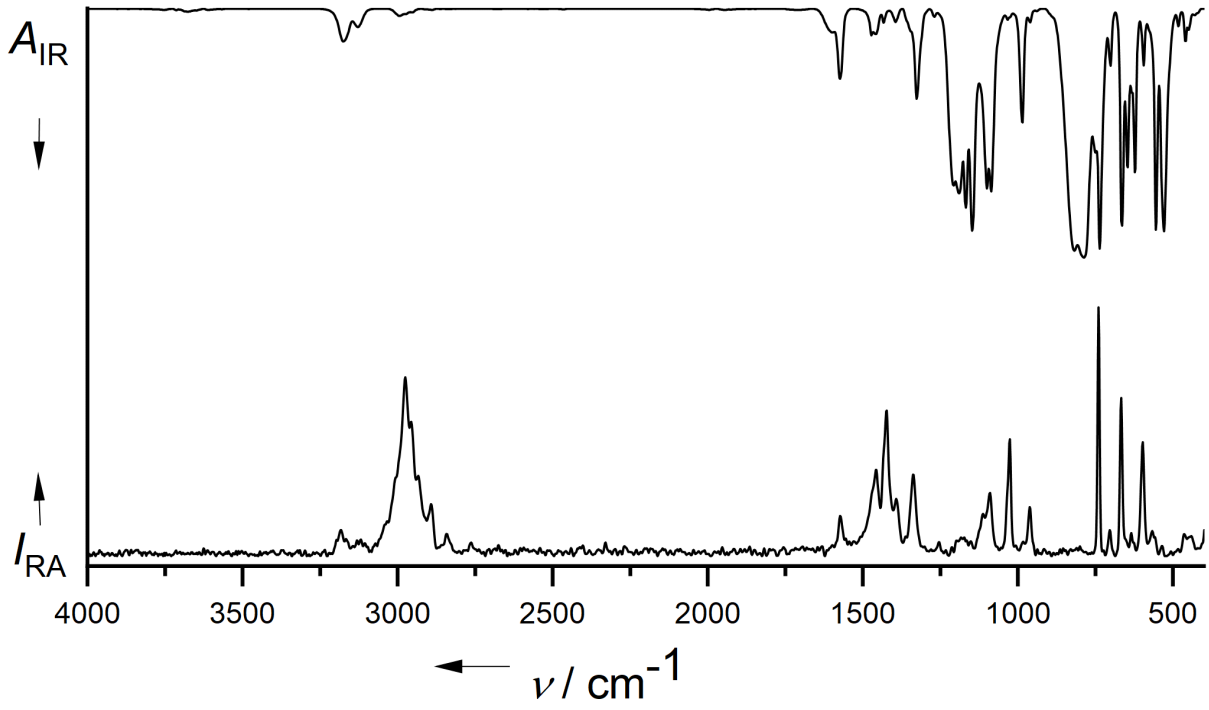



Figure 63: IR and Raman spectra of [EMIm]**FAP[1]**.

### 3.4 [EMIm][$PF_6$]

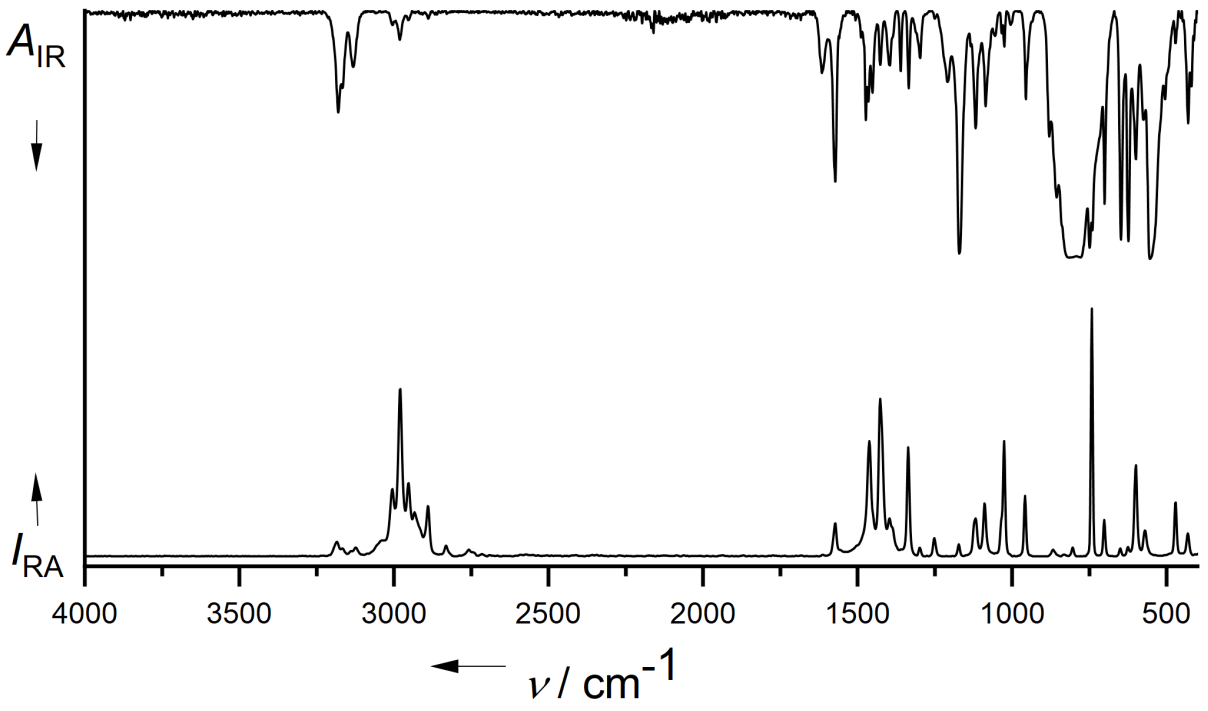



Figure 64: IR and Raman spectra of [EMIm][$PF_6$].

### 3.5 [BMIm]FAP$^3$

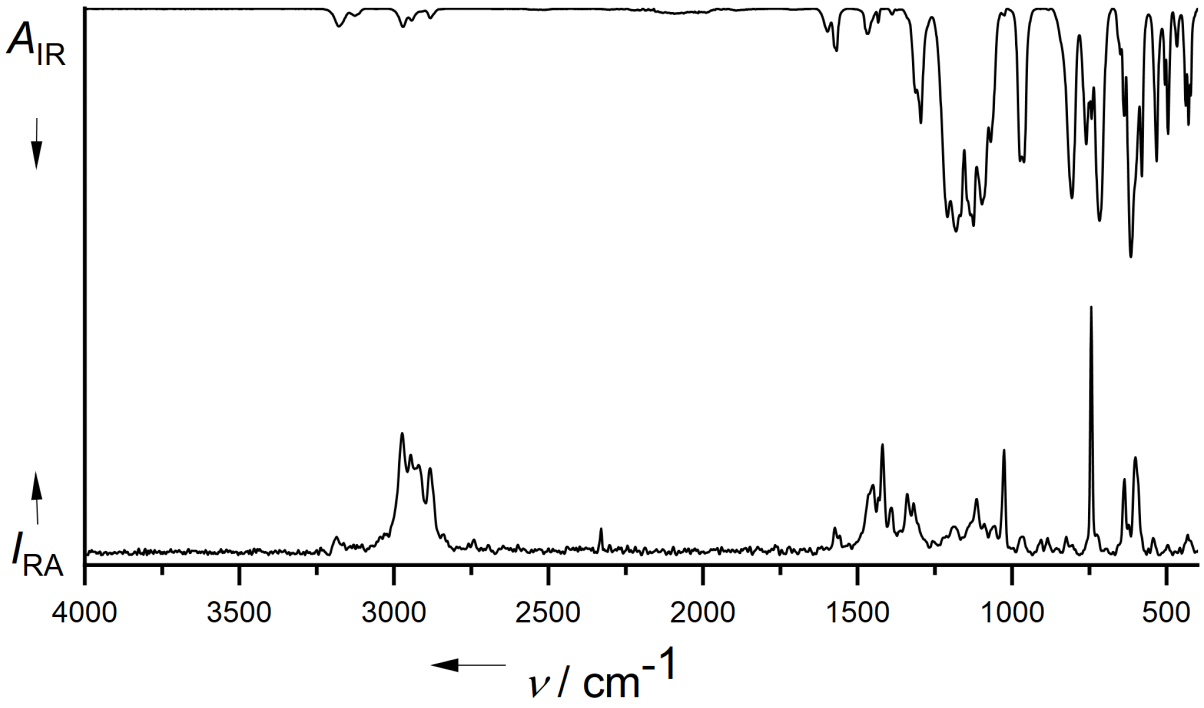



Figure 65: IR and Raman spectra of [BMIm]**FAP$^3$**.

### 3.6 [BMIm]FAP$^2$

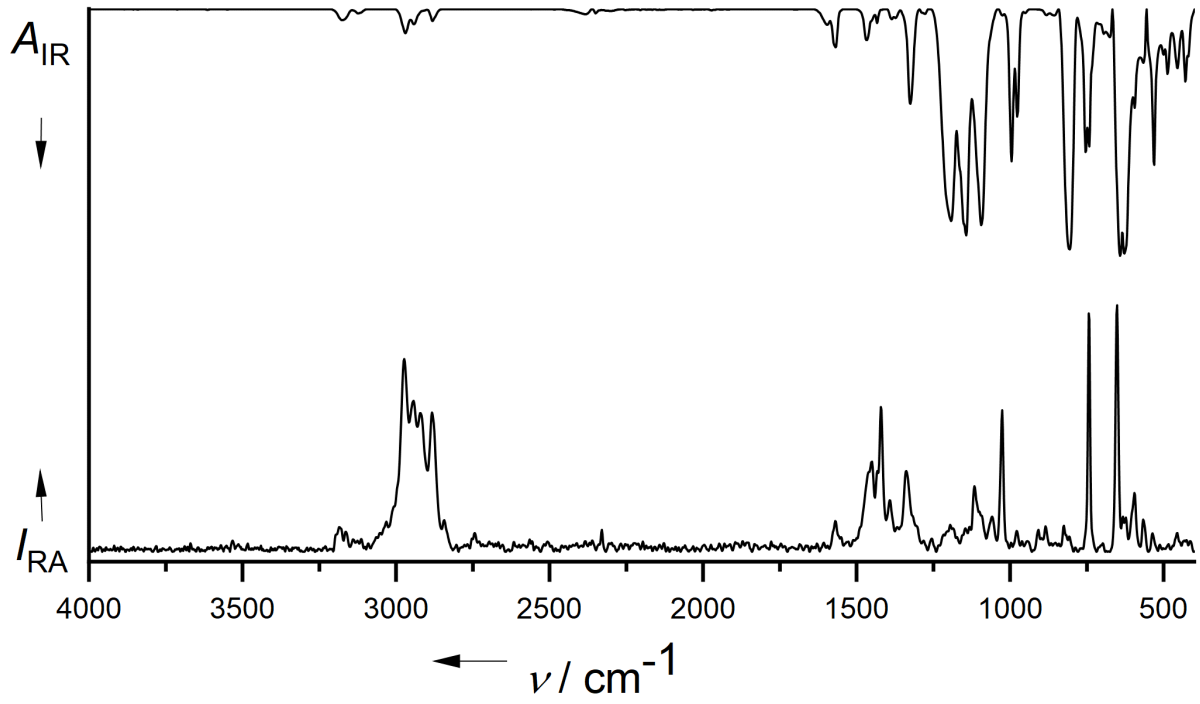



Figure 66: IR and Raman spectra of [BMIm]**FAP$^2$**.

### 3.7 [BMIm]FAP[1]

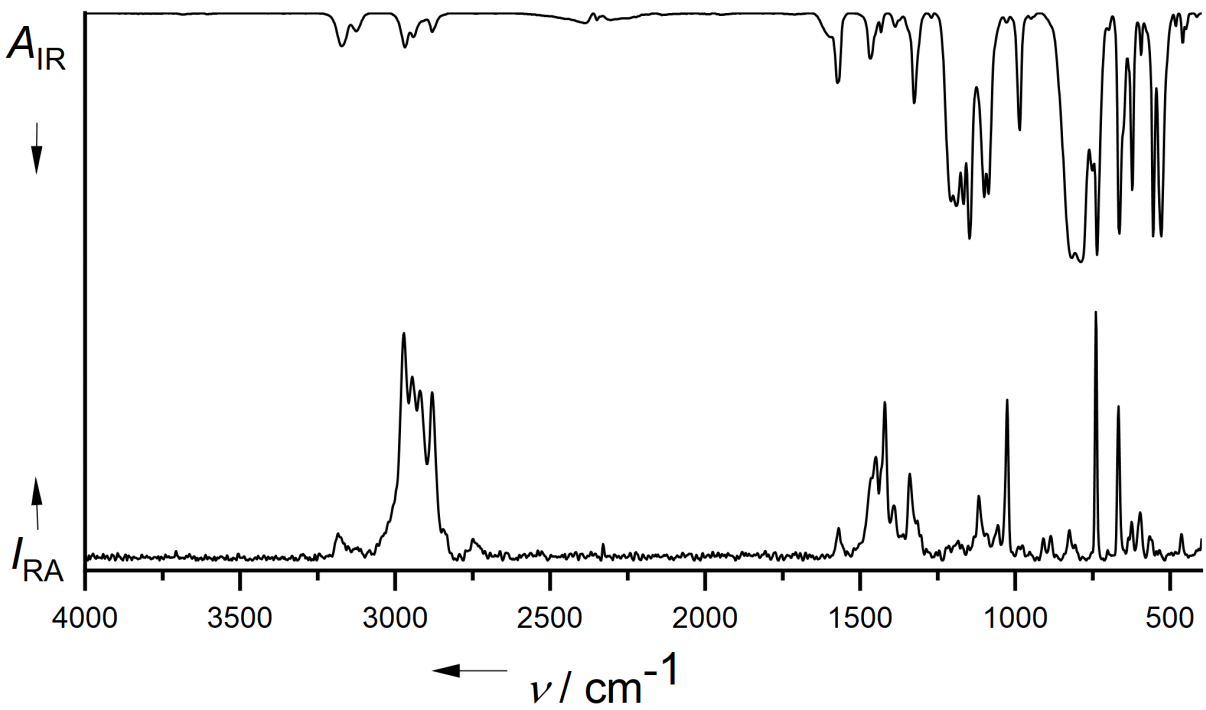



Figure 67: IR and Raman spectra of [BMIm]**FAP[1]**.

### 3.8 [BMIm][$PF_6$]

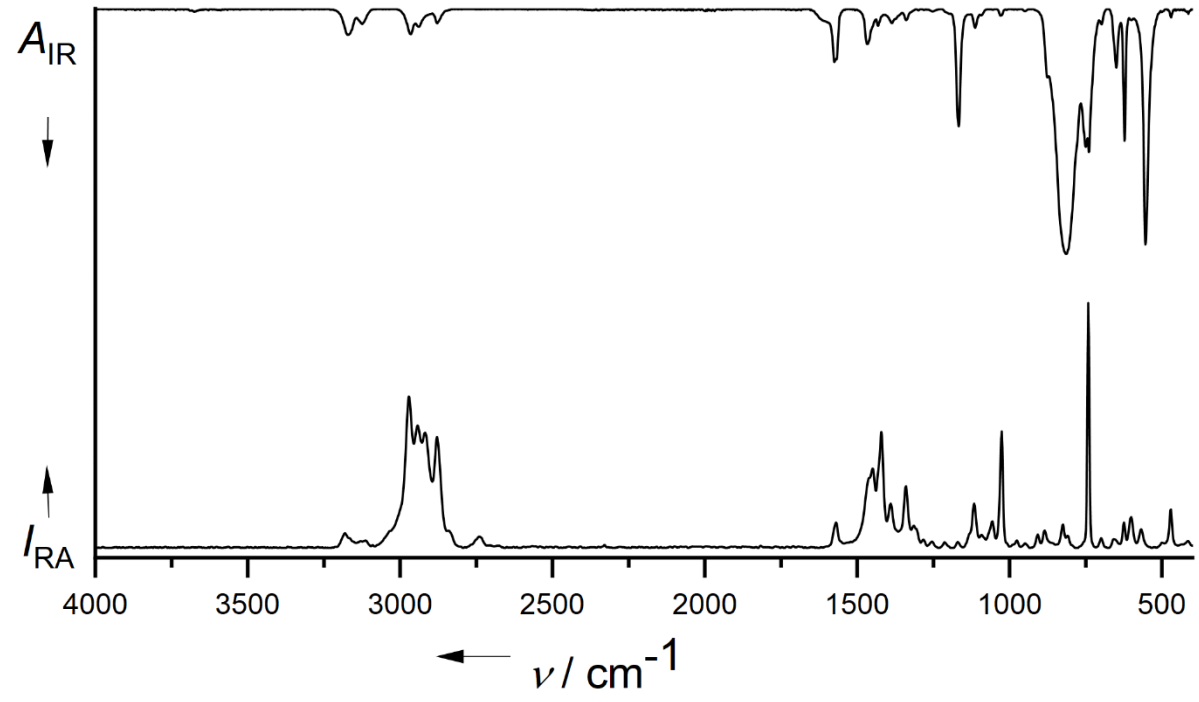



Figure 68: IR and Raman spectra of [BMIm][$PF_6$].

### 3.9 [BMPL]FAP$^3$

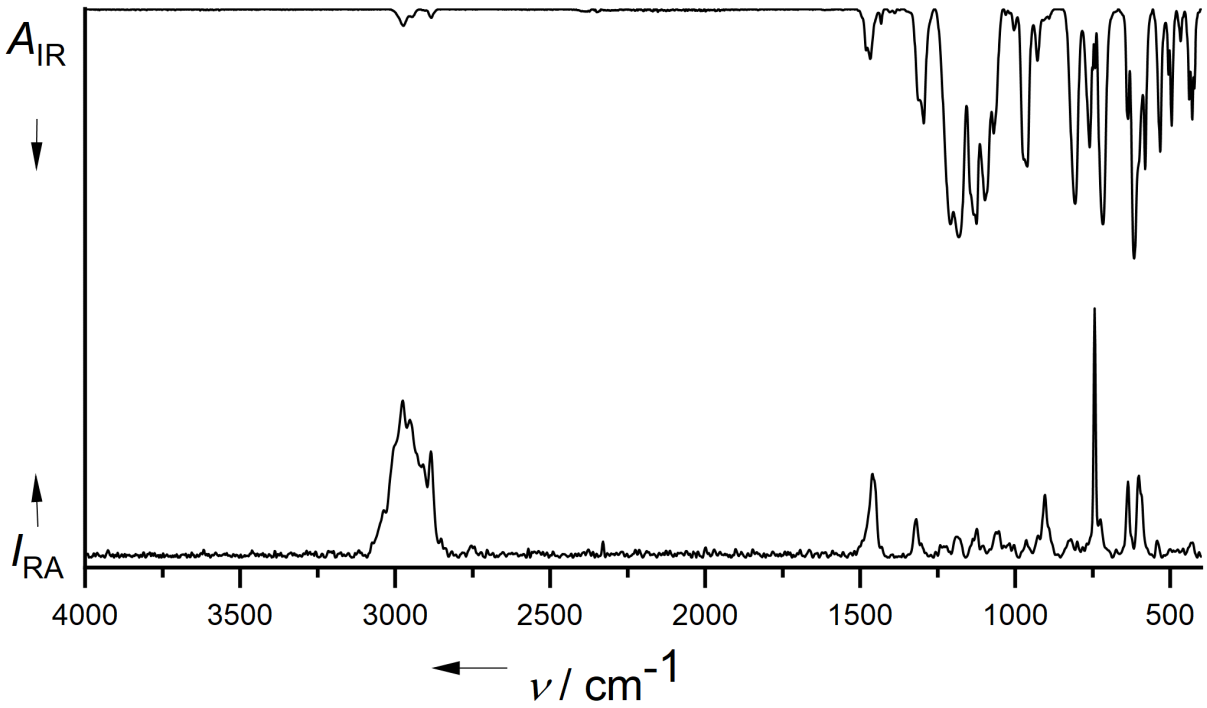



Figure 69: IR and Raman spectra of [BMPL]**FAP$^3$**.

### 3.10 [BMPL]FAP$^2$

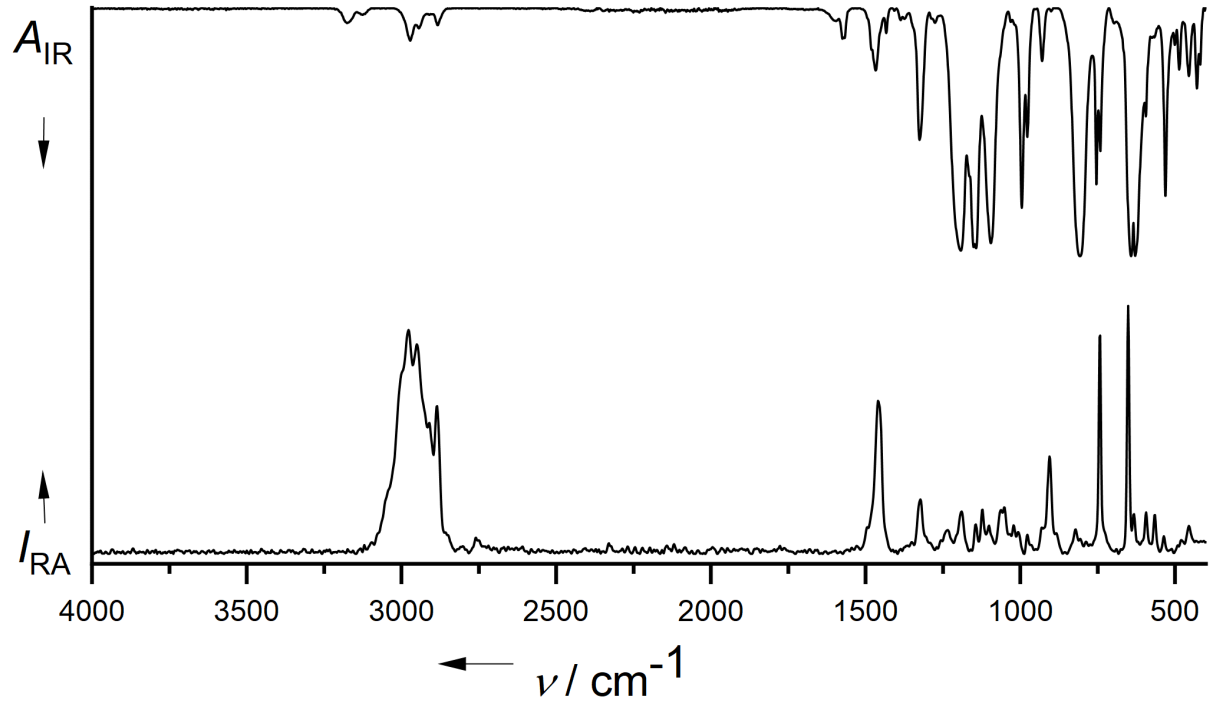



Figure 70: IR and Raman spectra of [BMPL]**FAP$^2$**.

### 3.11 [BMPL]FAP[1]

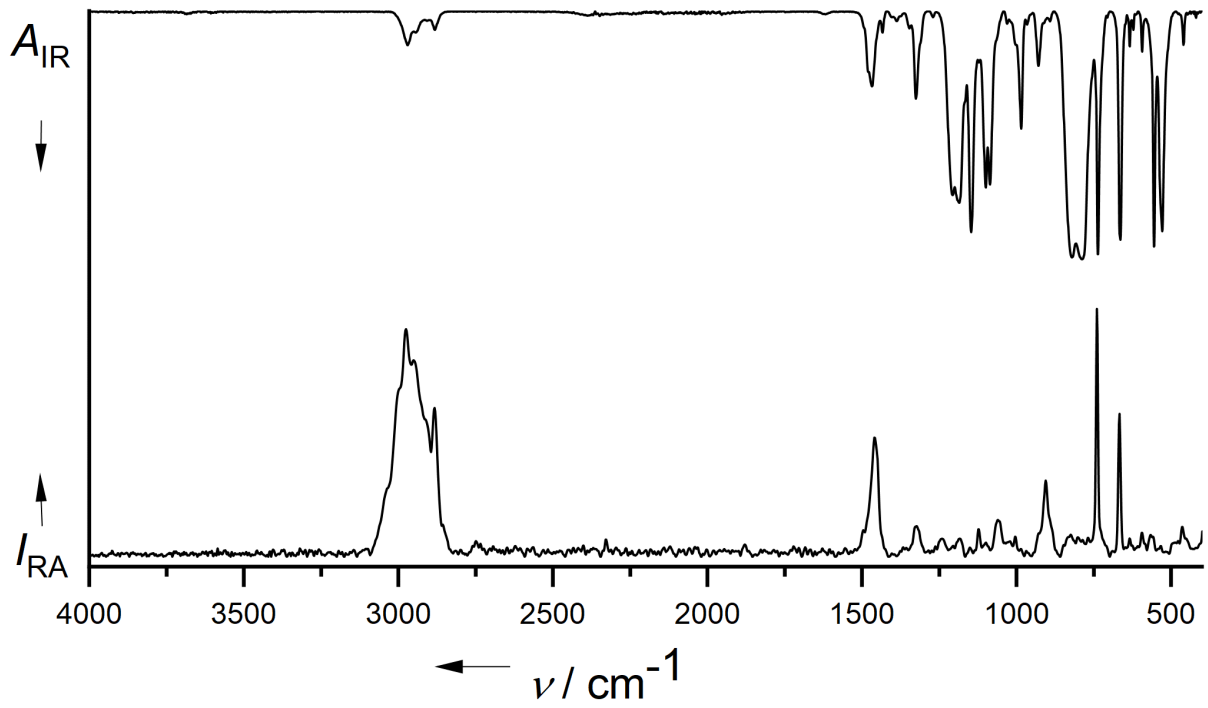



Figure 71: IR and Raman spectra of [BMPL]**FAP[1]**.

### 3.12 [BMPL][$PF_6$]

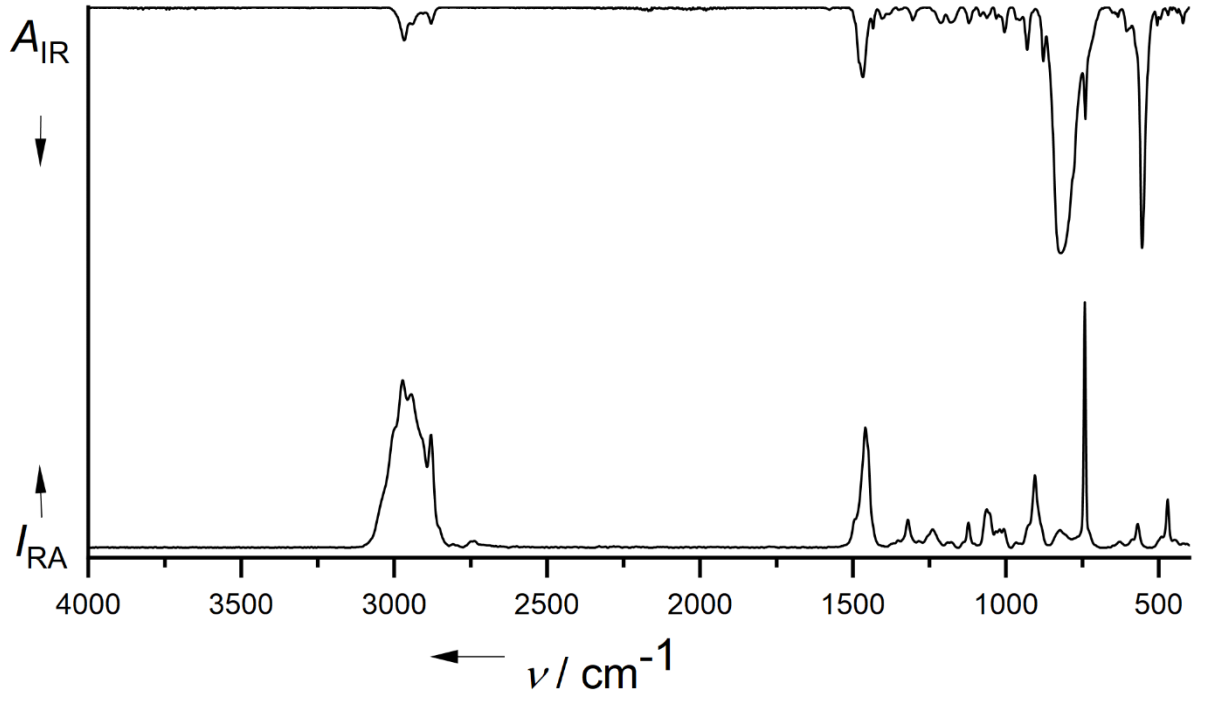



Figure 72: IR and Raman spectra of [BMPL][$PF_6$].

# 4. Thermal properties

## 4.1 DSC

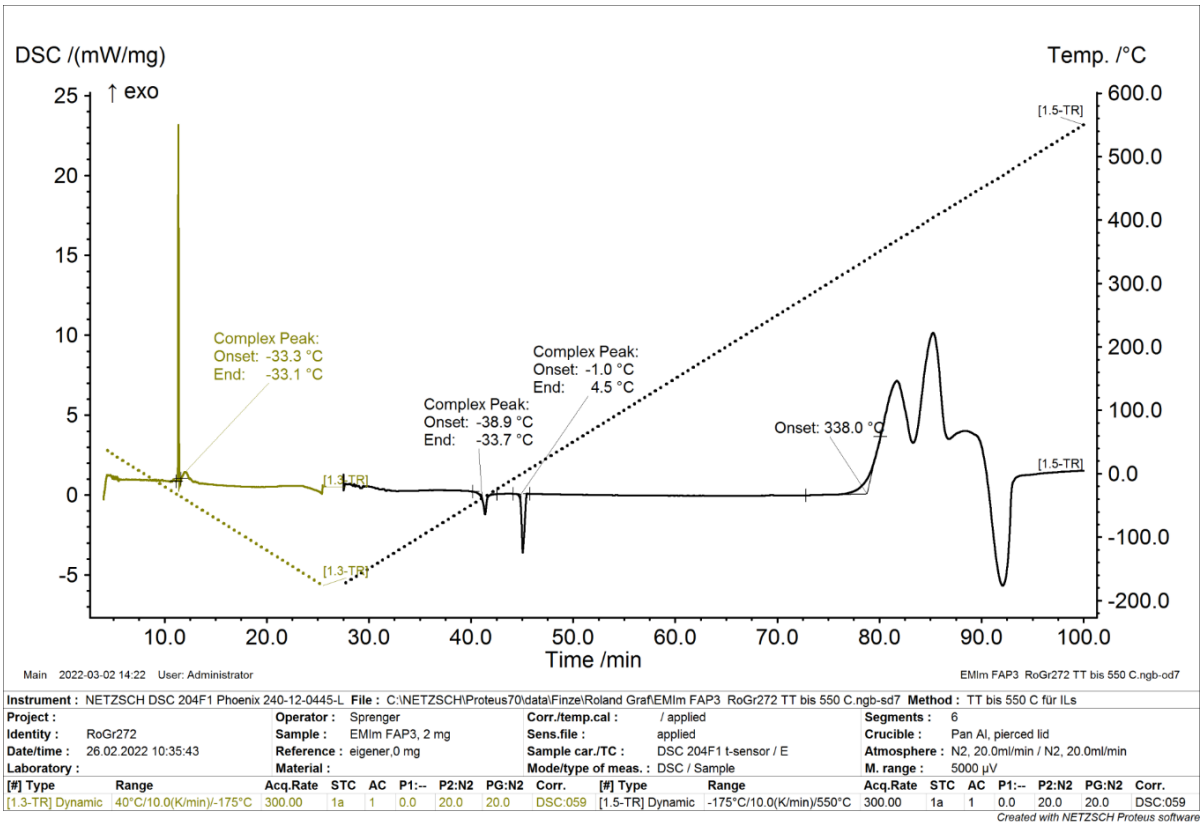



Figure 73: DSC curve of [EMIm]**FAP³**.

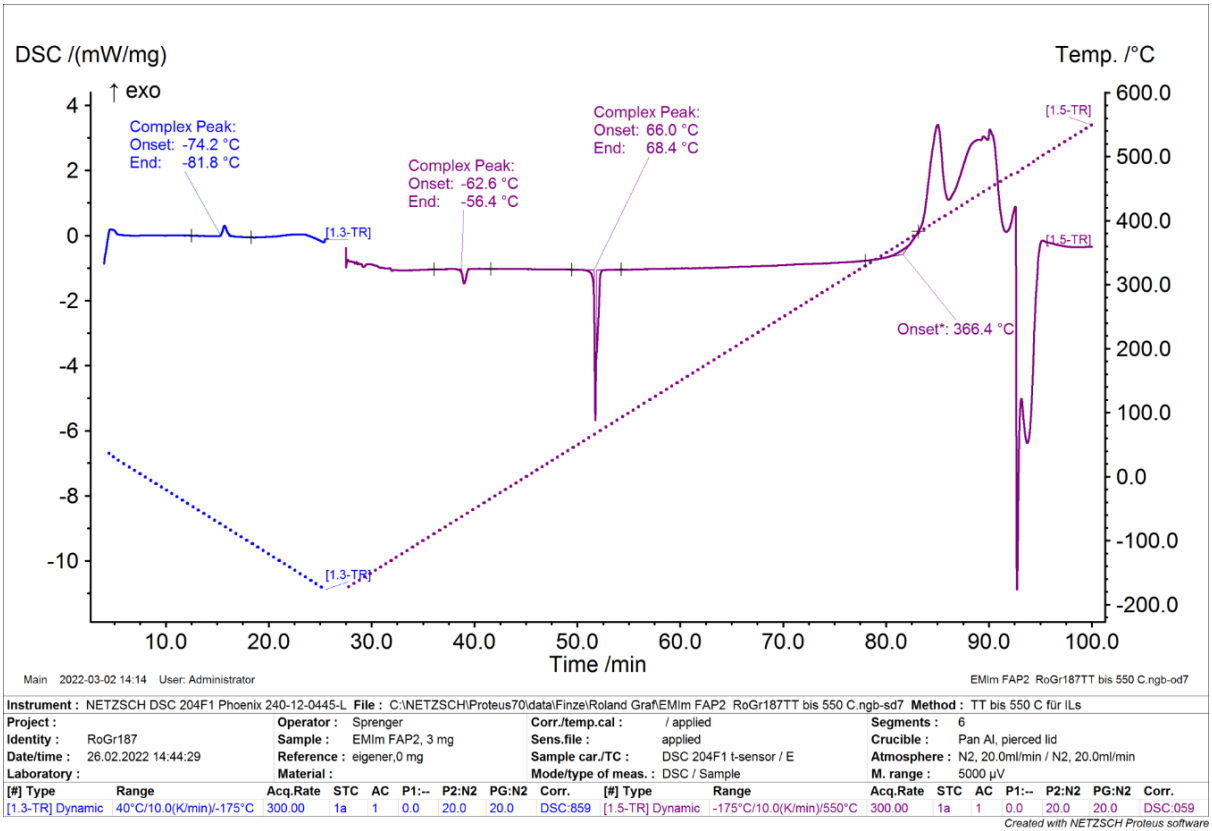



Figure 74: DSC curve of [EMIm]**FAP²**.

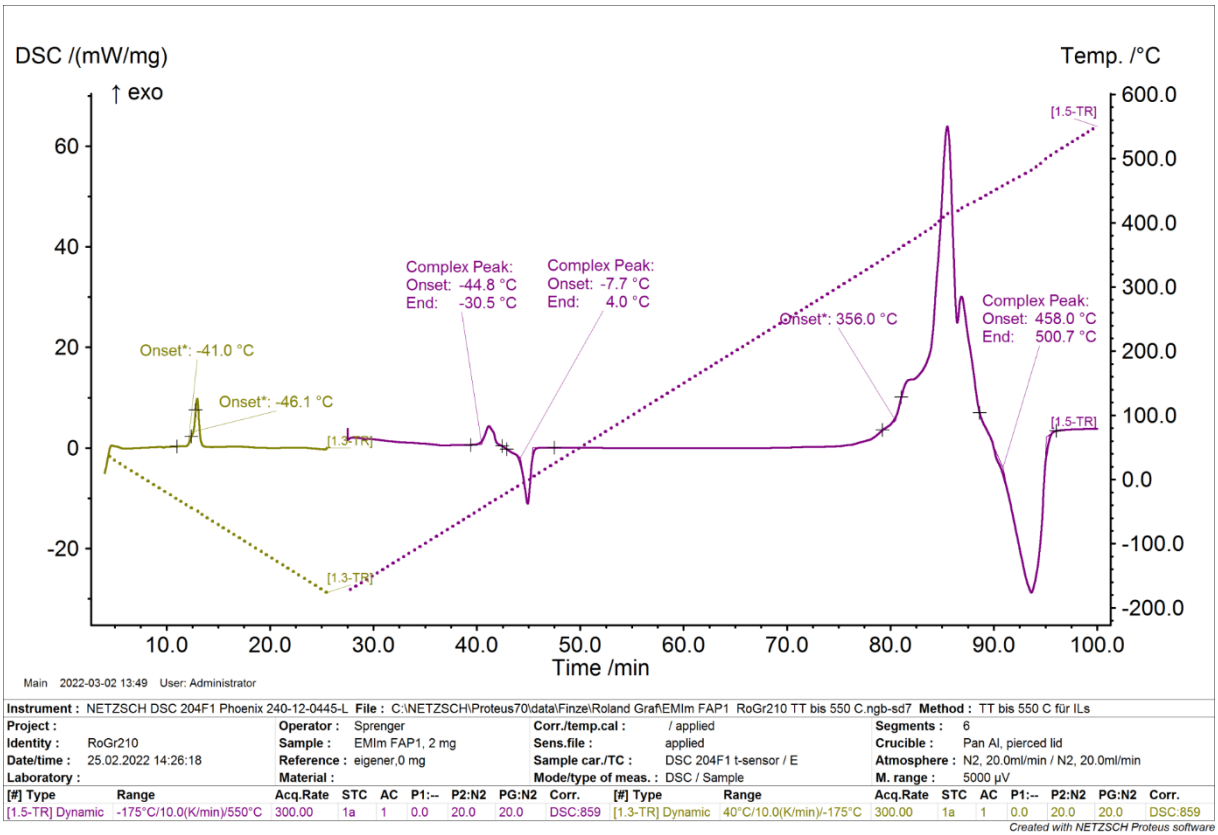
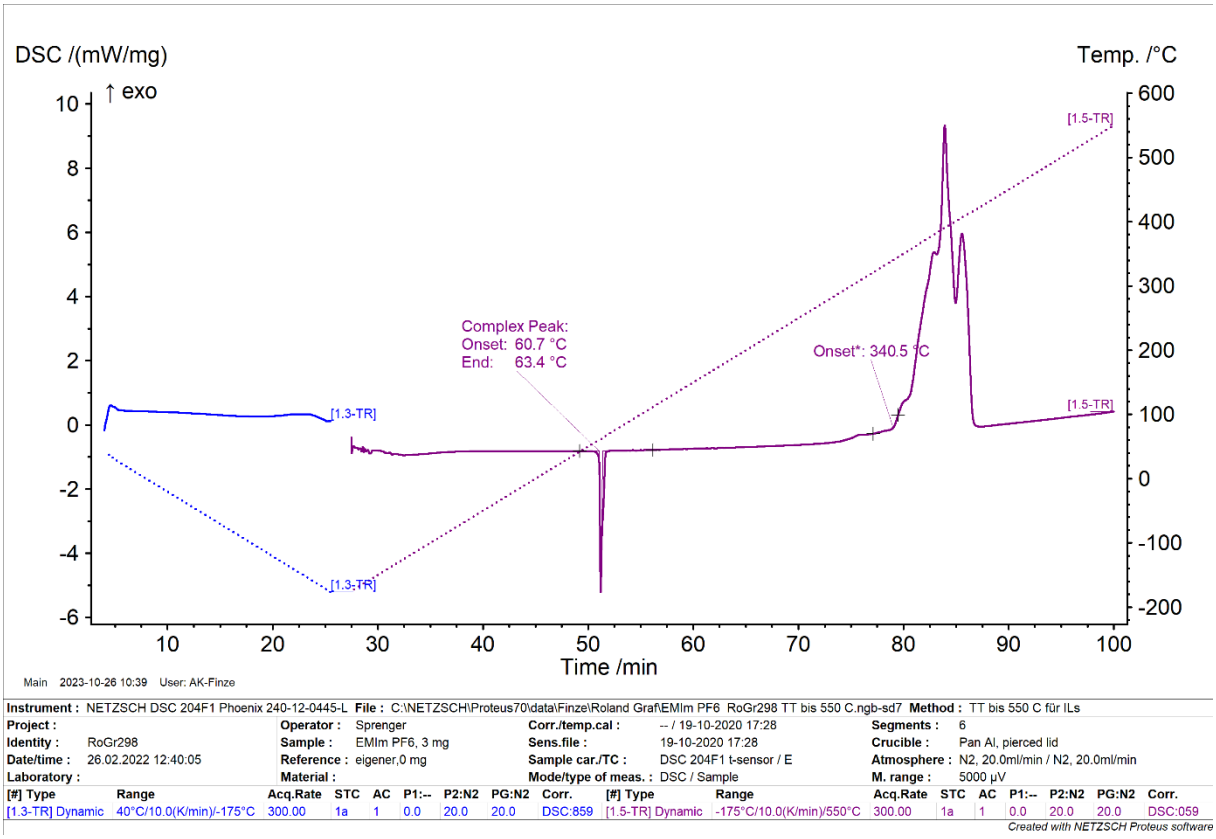



Figure 75: DSC curve of [EMIm]**FAP¹**.




| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Instrument :** | NETZSCH DSC 204F1 Phoenix 240-12-0445-L | **File :** | C:\NETZSCH\Proteus70\data\Finze\Roland Graf\EMIm PF6 RoGr298 TT bis 550 C.ngb-sd7 | **Method :** | TT bis 550 C für ILs | | | | | | | | | | | | | |
| **Project :** | | **Operator :** | Sprenger | **Corr./temp.cal :** | -- / 19-10-2020 17:28 | **Segments :** | 6 | | | | | | | | | | | |
| **Identity :** | RoGr298 | **Sample :** | EMIm PF6, 3 mg | **Sens.file :** | 19-10-2020 17:28 | **Crucible :** | Pan Al, pierced lid | | | | | | | | | | | |
| **Date/time :** | 26.02.2022 12:40:05 | **Reference :** | eigener,0 mg | **Sample car./TC :** | DSC 204F1 t-sensor / E | **Atmosphere :** | N2, 20.0ml/min / N2, 20.0ml/min | | | | | | | | | | | |
| **Laboratory :** | | **Material :** | | **Mode/type of meas. :** | DSC / Sample | **M. range :** | 5000 µV | | | | | | | | | | | |
| **[#] Type** | **Range** | **Acq.Rate** | **STC** | **AC** | **P1:--** | **P2:N2** | **PG:N2** | **Corr.** | **[#] Type** | **Range** | **Acq.Rate** | **STC** | **AC** | **P1:--** | **P2:N2** | **PG:N2** | **Corr.** | |
| [1.3-TR] Dynamic | 40°C/10.0(K/min)/-175°C | 300.00 | 1a | 1 | 0.0 | 20.0 | 20.0 | DSC:859 | [1.5-TR] Dynamic | -175°C/10.0(K/min)/550°C | 300.00 | 1a | 1 | 0.0 | 20.0 | 20.0 | DSC:059 | |

*Created with NETZSCH Proteus software*

Figure 76: DSC curve of [EMIm][$PF_6$].

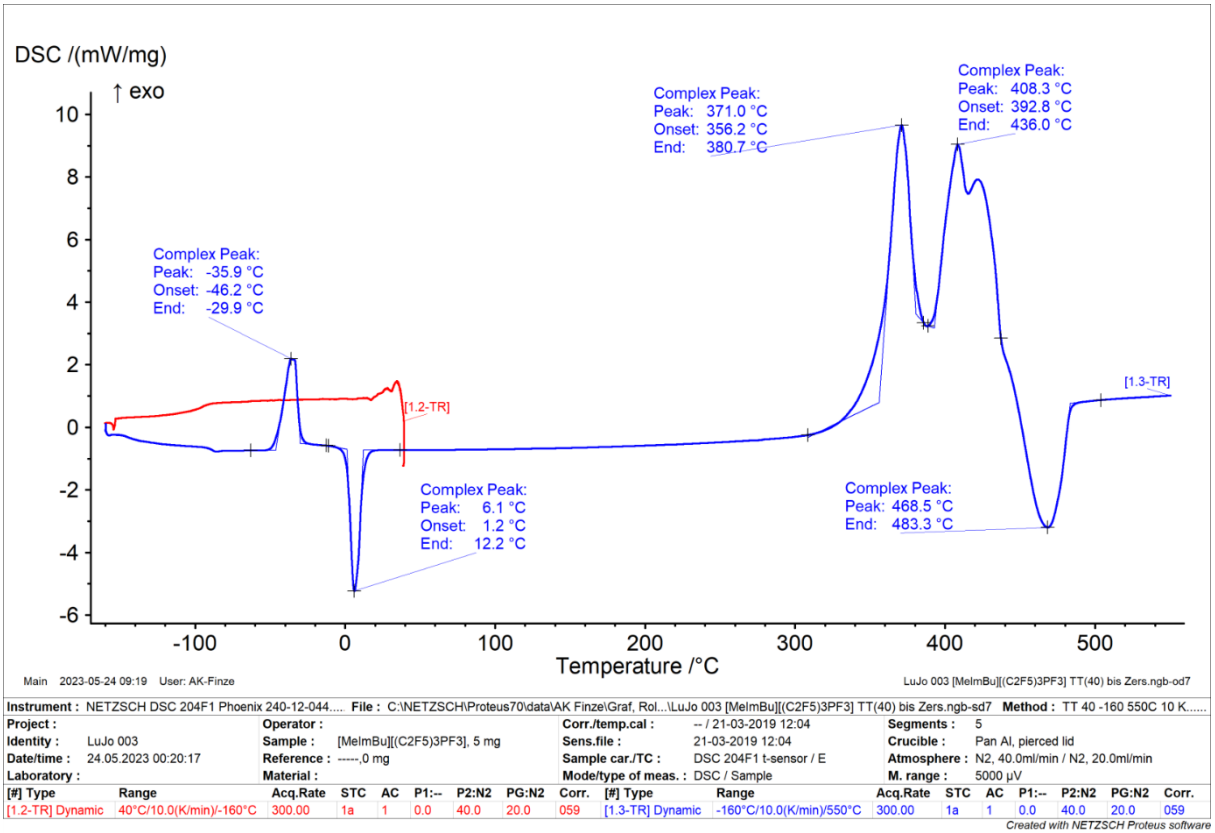



Figure 77: DSC curve of [BMIm]**FAP**[3].

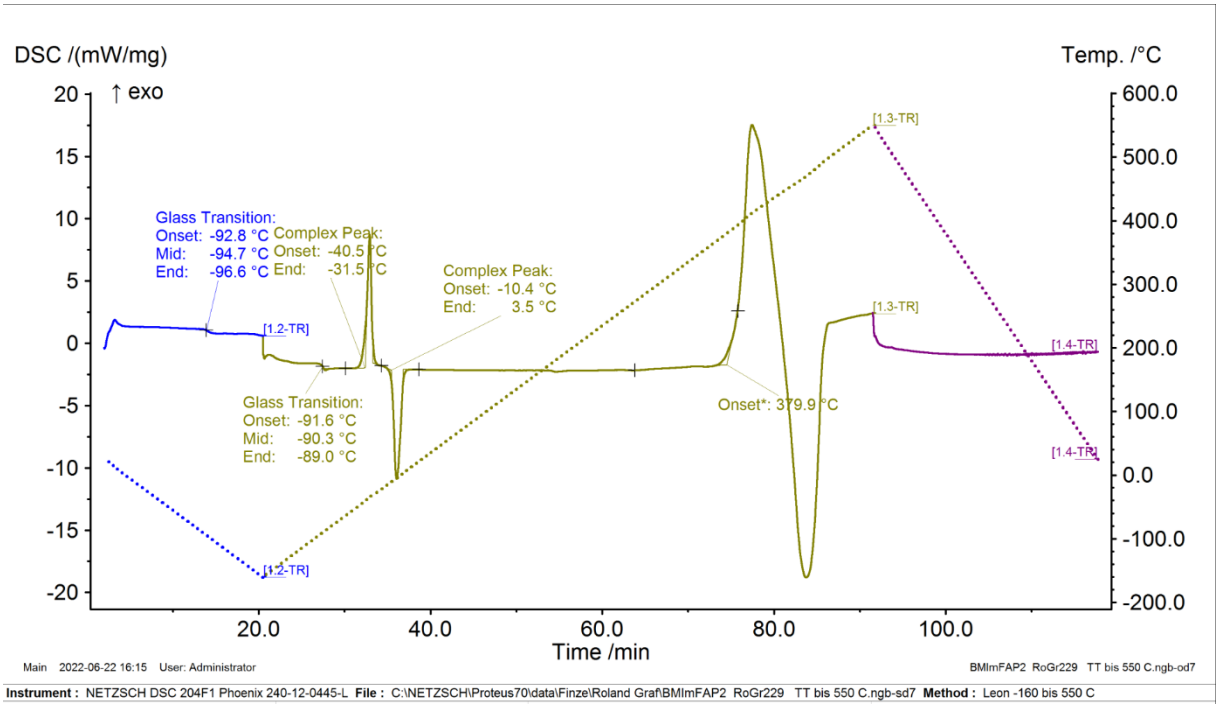



Figure 78: DSC curve of [BMIm]**FAP**[2].

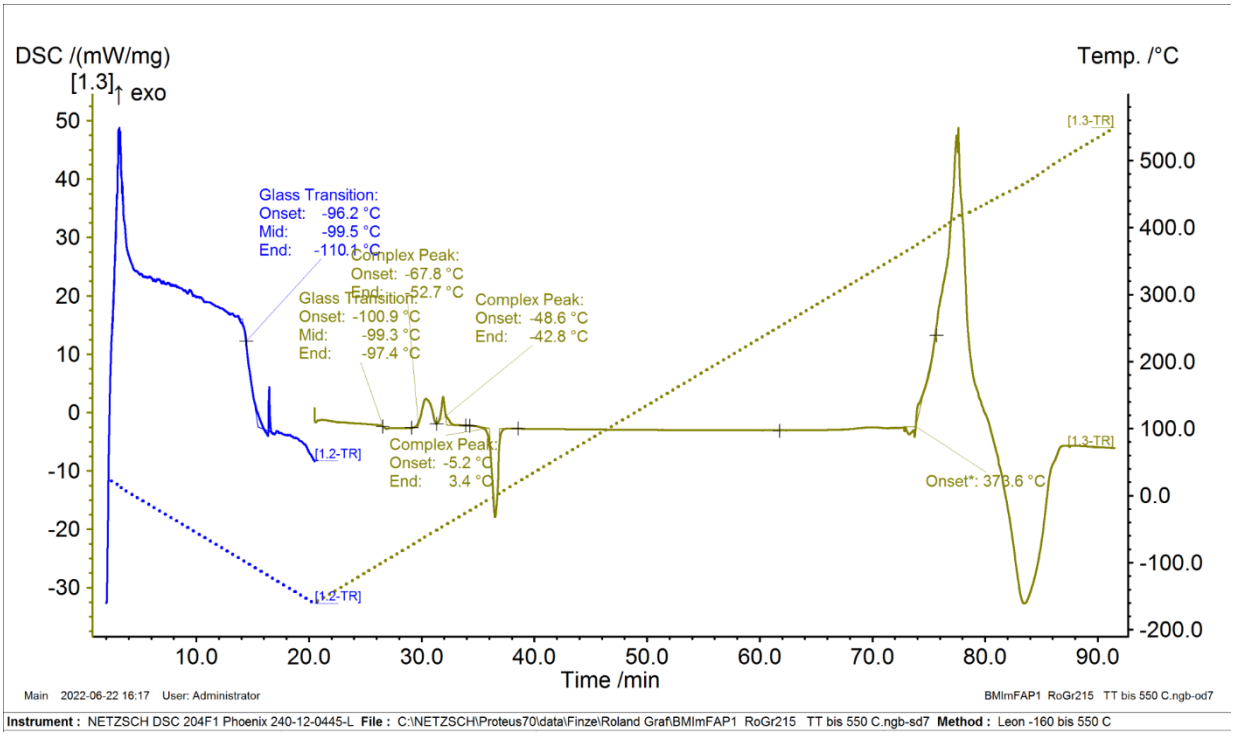



Figure 79: DSC curve of [BMIm]**FAP**[1].

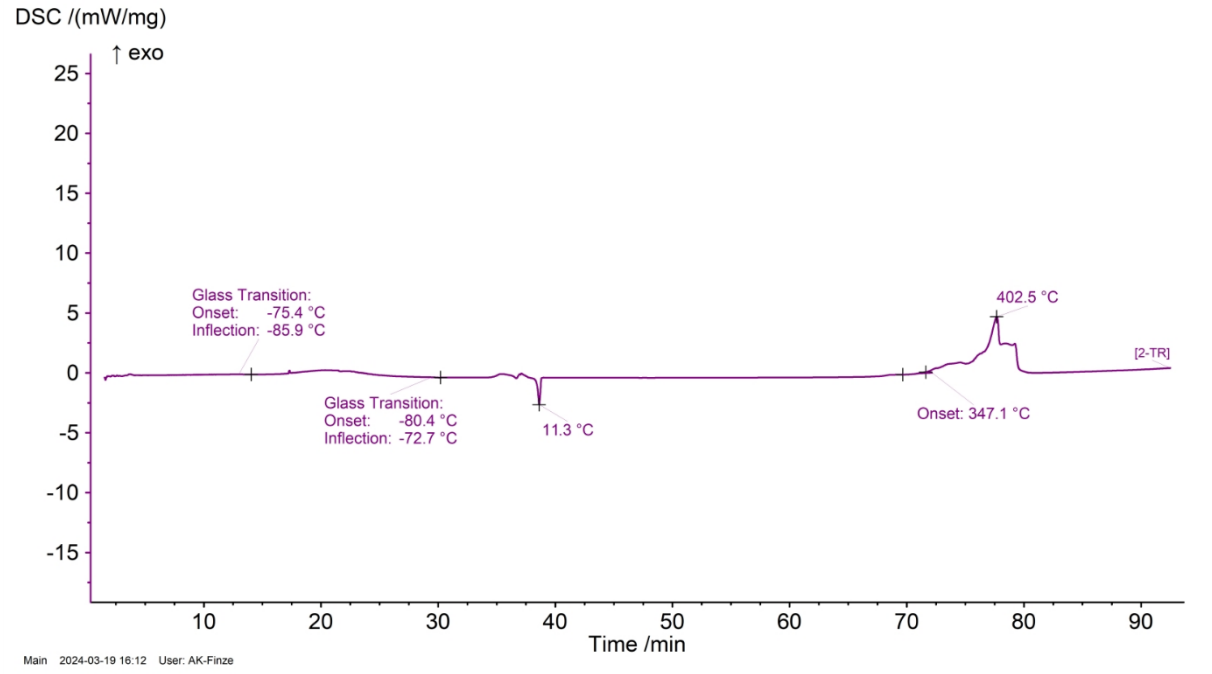



Figure 80: DSC curve of [BMIm][$PF_6$].

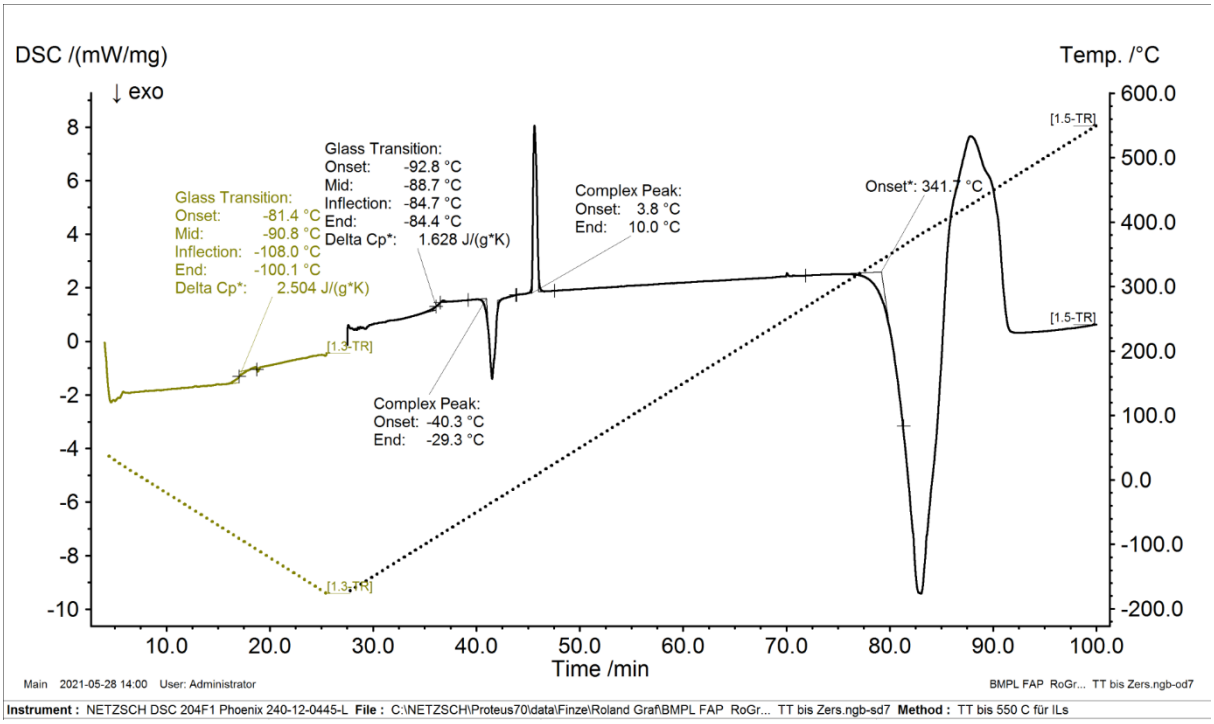



Figure 81: DSC curve of [BMPL]**FAP**$^{3}$.

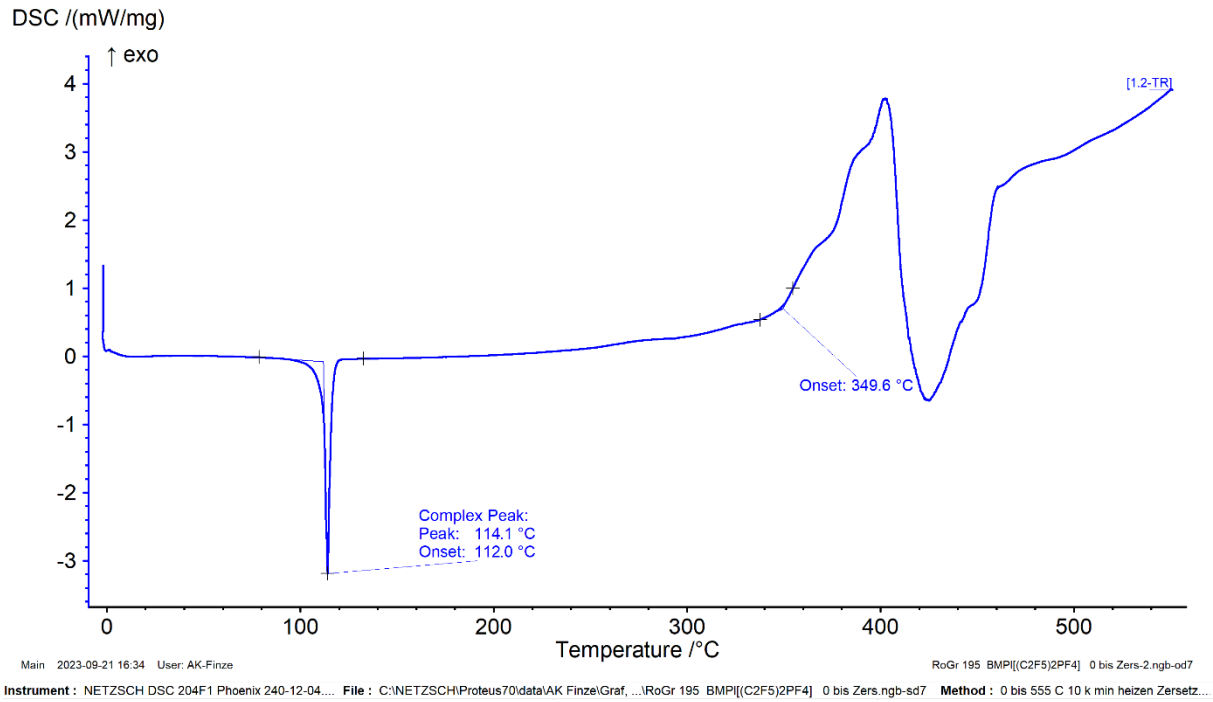



Figure 82: DSC curve of [BMPL]**FAP**$^{2}$.

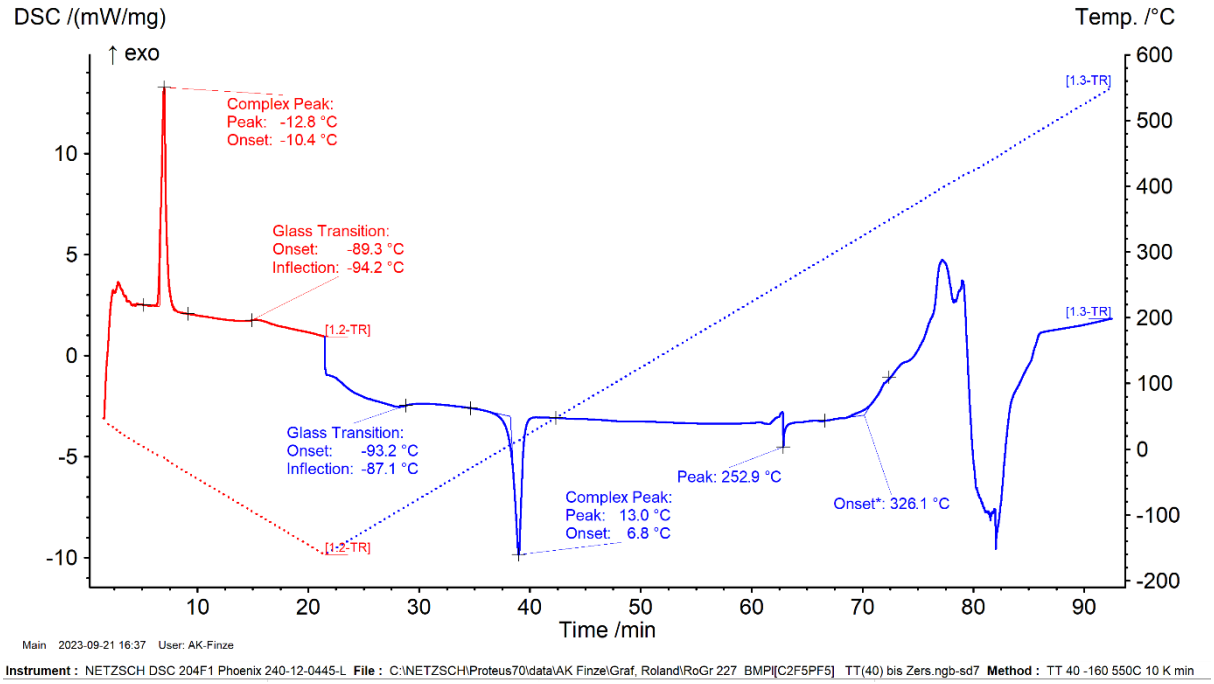



Figure 83: DSC curve of [BMPL]**FAP**[1].

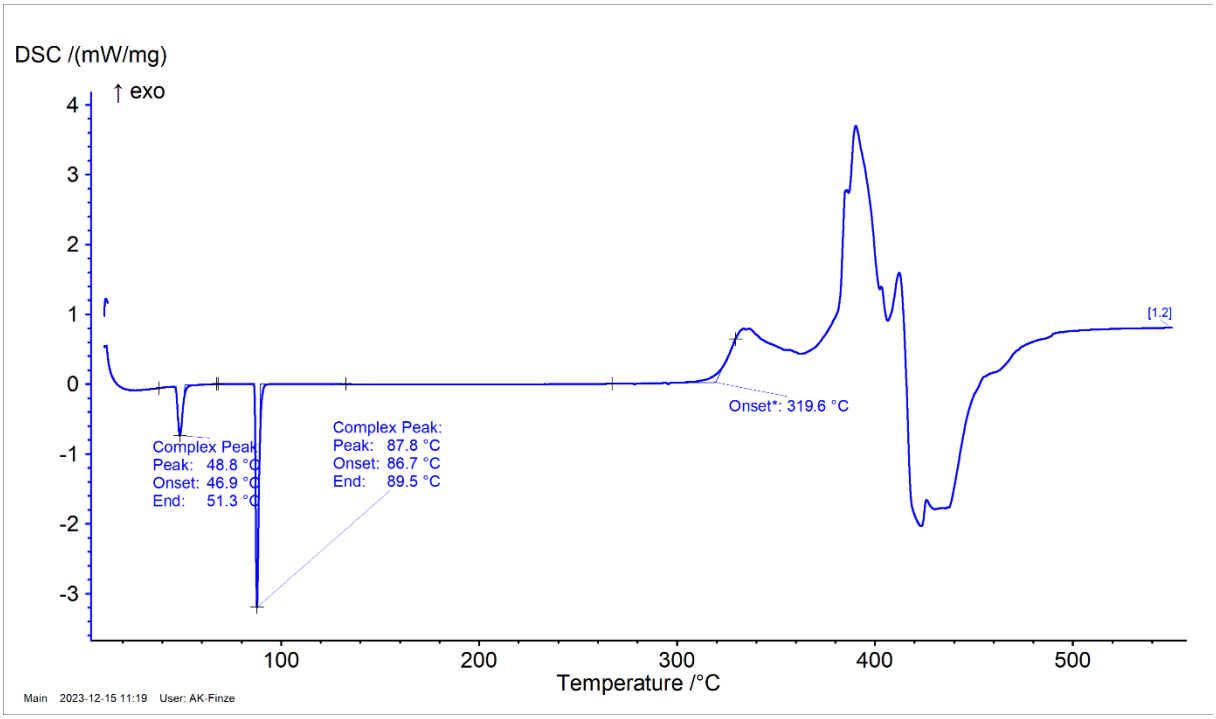



Figure 84: DSC curve of [BMPL][$PF_6$].

### 4.2 Heat capacities

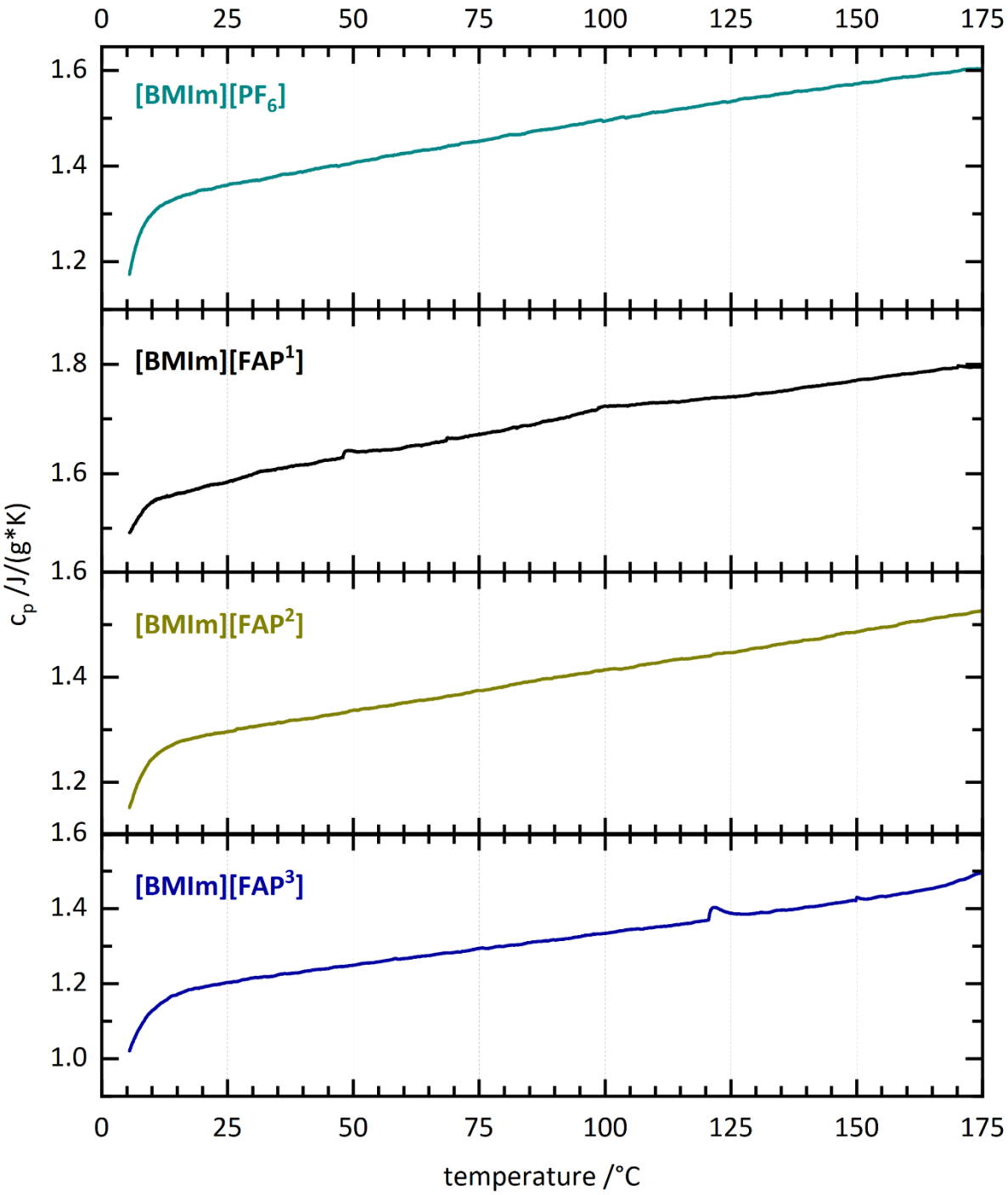



Figure 85: DSC heat capacity measurements of [BMIm] ILs.

### 4.3 ARC

#### 4.3.1 ARC heating data

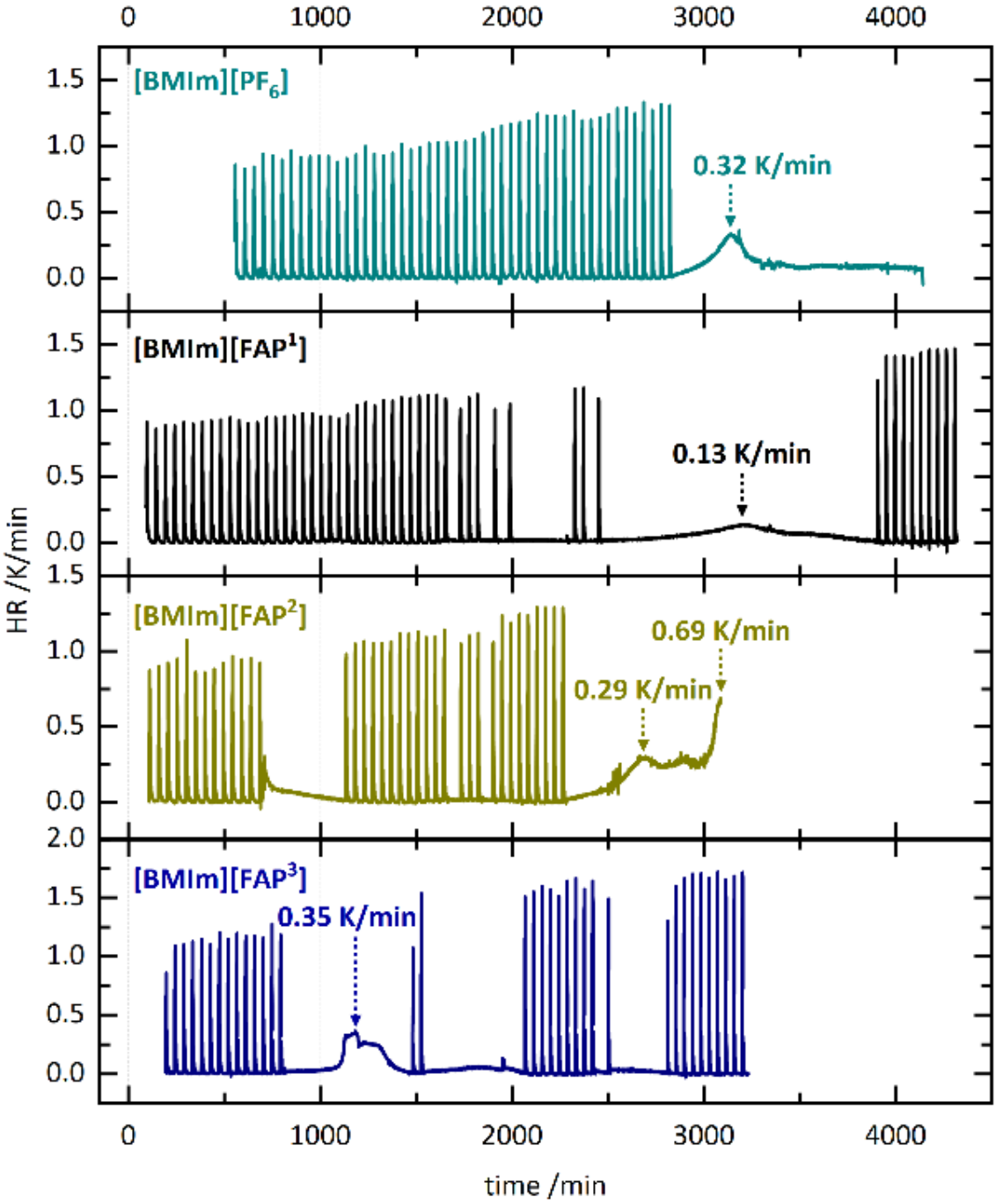



Figure 86: ARC self-heating rates of [BMIm][$PF_6$] and [BMIm]**FAP**$^n$ (n = 1,2,3) plotted against time.

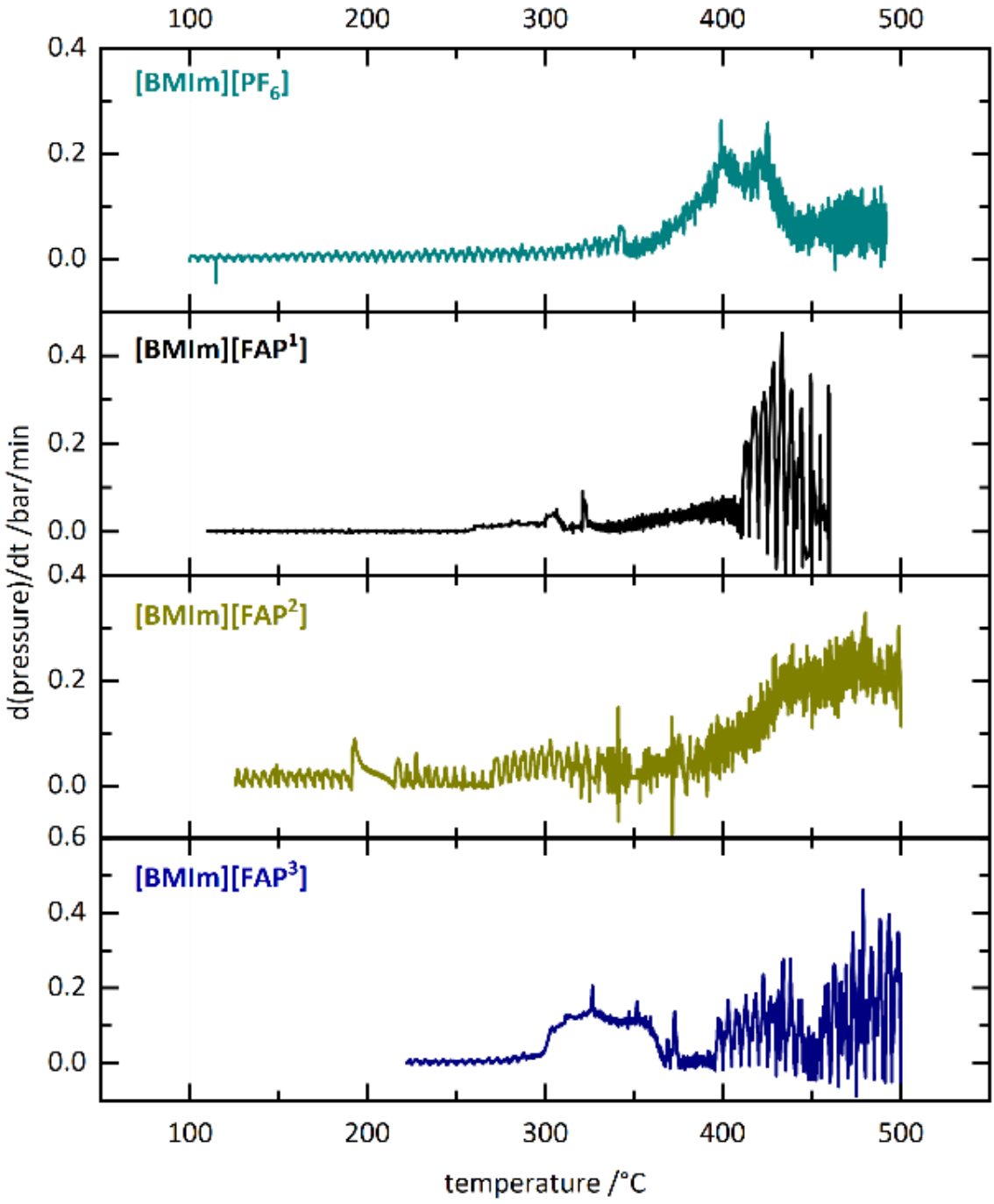



Figure 87: ARC pressure rise rates of [BMIm][$PF_6$] and [BMIm]**FAP$^n$** (n = 1,2,3) plotted against temperature.

### 4.3.2 ARC gas phase products

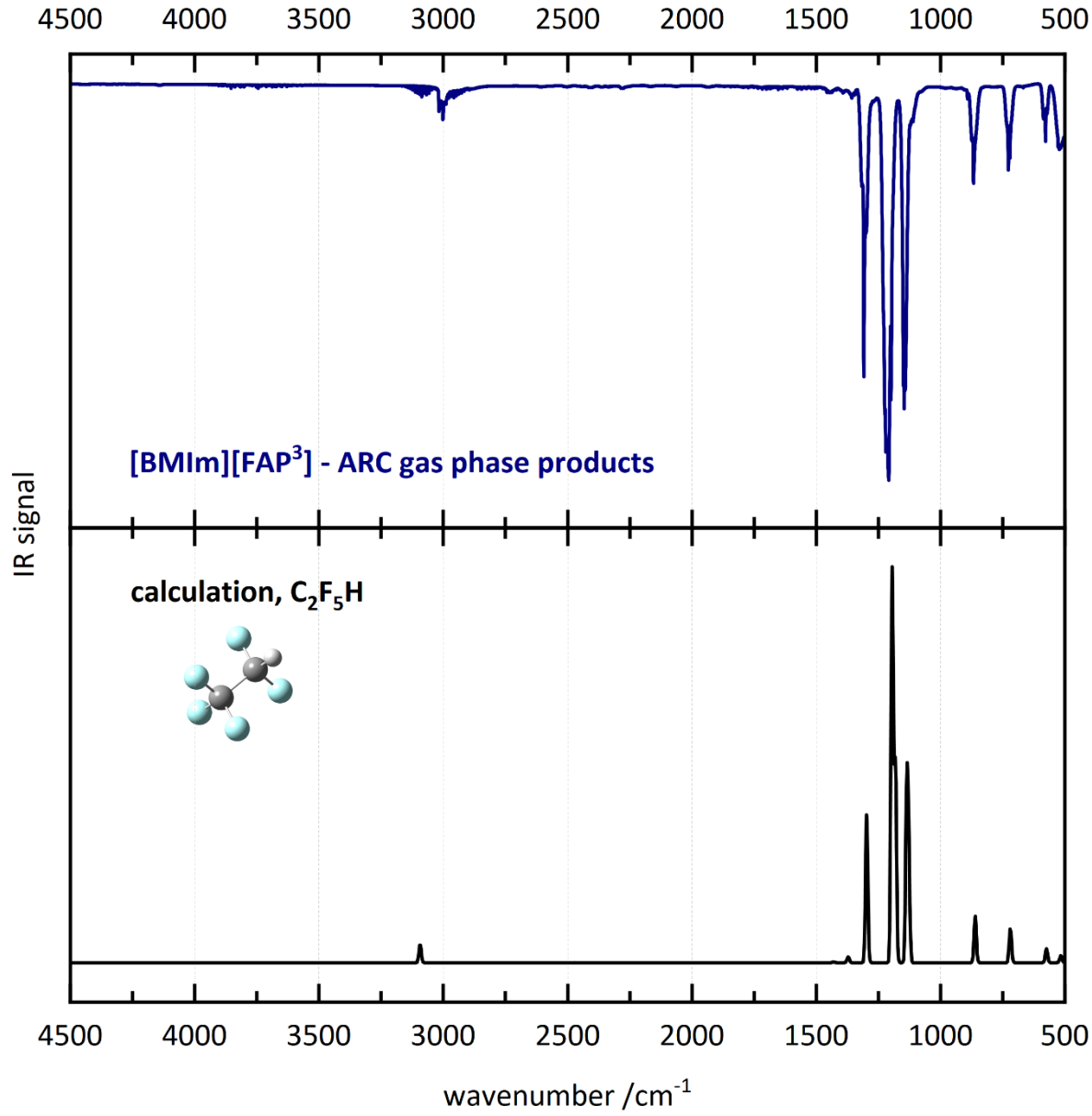



Figure 88: IR spectrum of [BMIm]**FAP³** gas phase products (1).

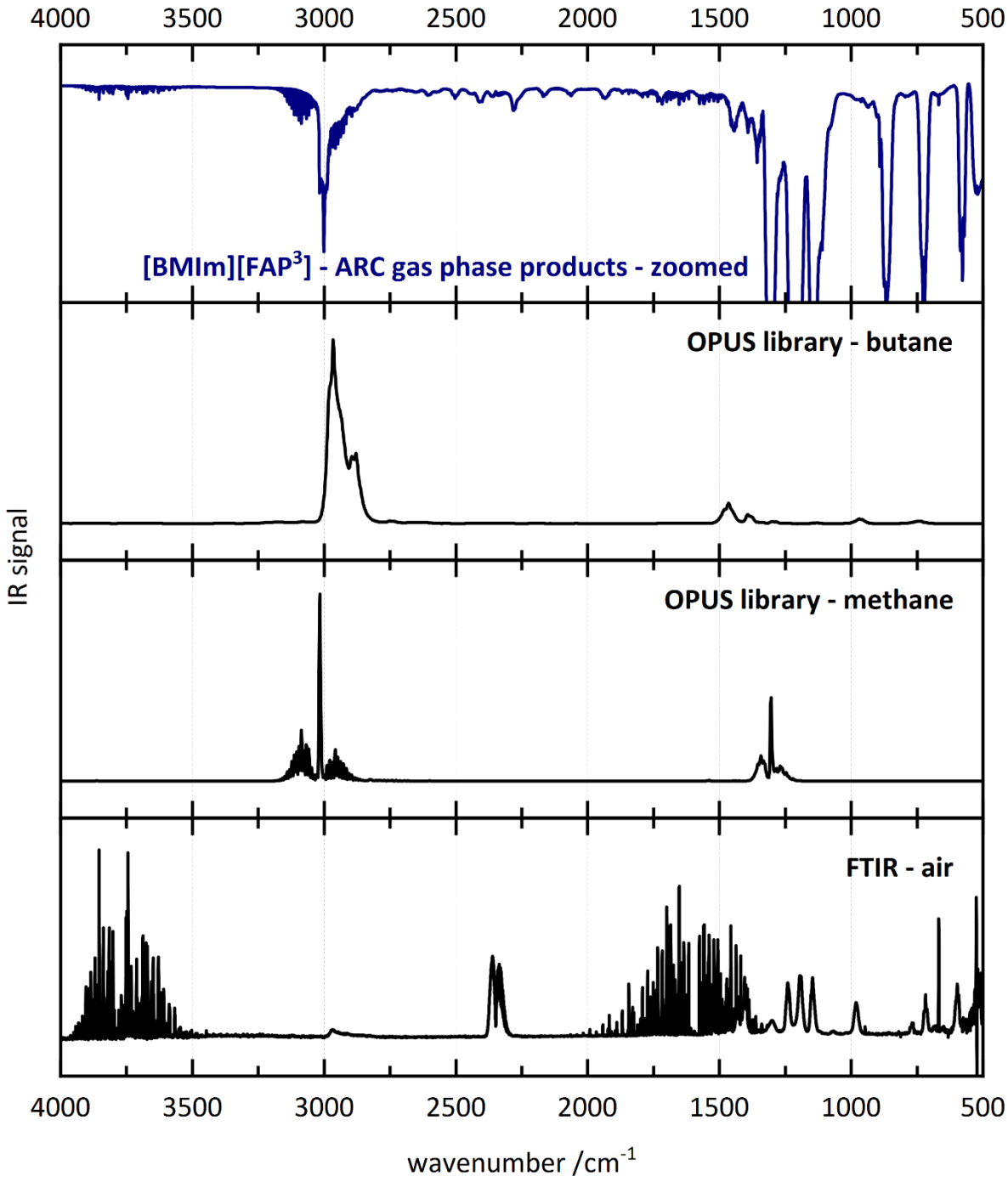



Figure 89: IR spectrum of [BMIm]**FAP³** gas phase products (2).

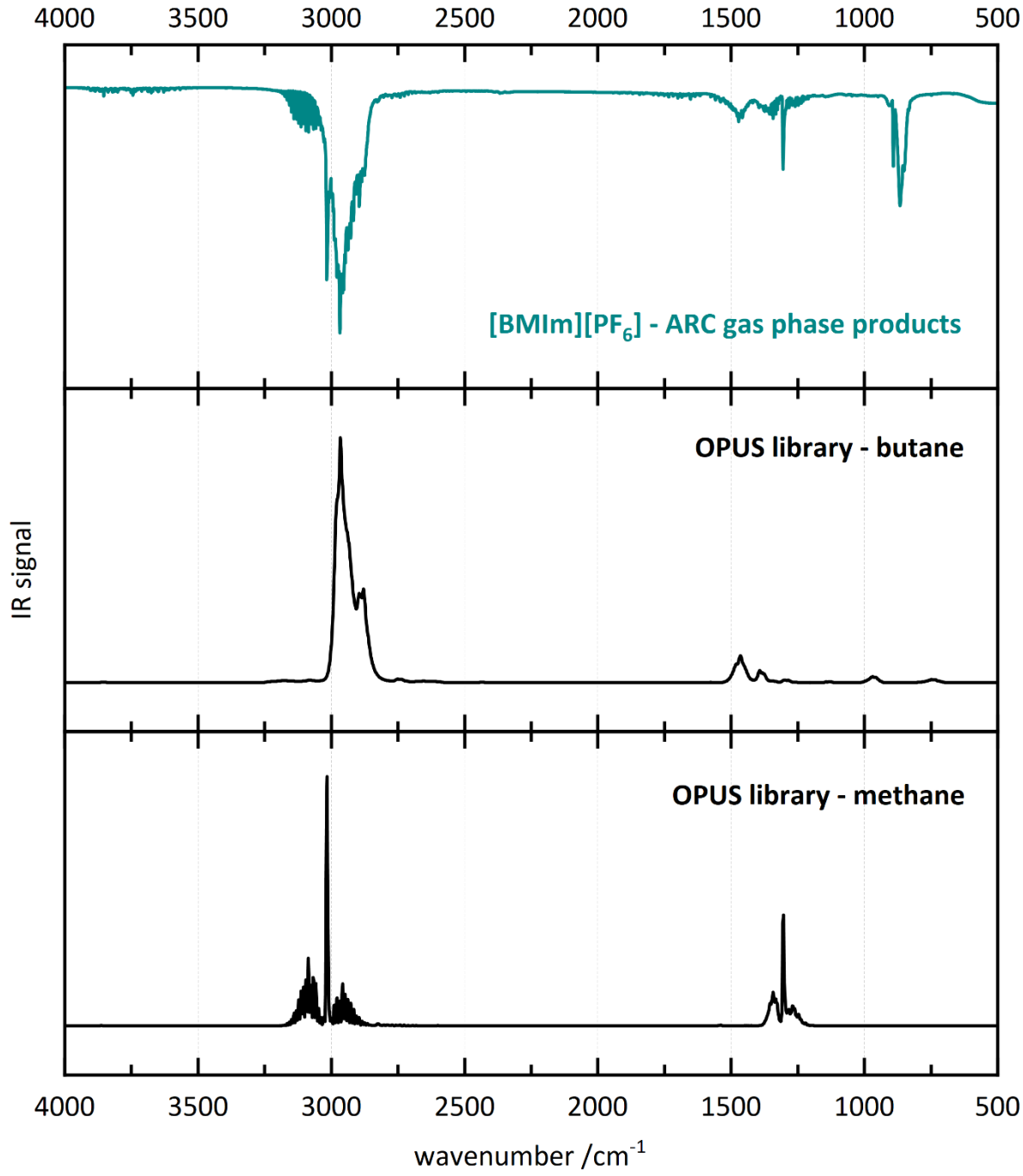



Figure 90: IR spectrum of [BMIm][$PF_6$] gas phase products.

# 5. Diffusion NMR

All diffusion (DOSY) NMR measurements were performed on a 14.1 T Bruker Avance III Spectrometer with a BCU 2 cooling unit using a BBFO probe equipped with a z-gradient (max. gradient strength of 50 G $cm^{-1}$). The ionic liquids were filled into coaxial insert tubes with the insert being filled with DMSO-$d_6$. No sample rotation was employed.

Each sample was measured at three different temperatures, 293.1 K, 313.1 K, 333.1 K, and 353.1 K, which were calibrated prior to the measurement series. $^{1}H$ and $^{19}F$ 90° pulses were calibrated for each sample and temperature. Furthermore, diffusion times Δ and durations of the bipolar gradient pulse δ were estimated based on the known viscosities and existing data in literature[15] and subsequently optimized for each sample prior to the experiment. The DOSY measurements were done using both the stimulated echo BPP-LED pulse (ledbpgp2s) sequence and the double stimulated echo pulse (dstebpgp3s) sequence. By comparison of the two datasets, convection effects could be excluded. Signals had decayed to below 10 % or, if possible, to below 5 % of the initial signal area. The analysis of the DOSY data was done using the Topspin T1/T2 module with the area option yielding the temperature dependent diffusion coefficients for each nucleus and thus for the different components of the ionic liquid.

# 6. Electrochemical and physical properties

Table S3: Selected electrochemical parameters of fluorophosphate RTILs in the temperature range of 293–353 K.

| Compound | *M* | density $\rho$ | | | | | | | | | dynamic viscosity $\eta$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 20 °C | 23 °C | 25 °C | 30 °C | 40 °C | 50 °C | 60 °C | 70 °C | 80 °C | 20 °C | 23 °C | 25 °C | 30 °C | 40 °C | 50 °C | 60 °C | 70 °C | 80 °C |
| | [g·mol$^{-1}$] | [g·mL$^{-1}$] | | | | | | | | | [mPa·s] | | | | | | | | |
| [EMIm]**FAP$^3$** | 556.2 | 1.71 | 1.71 | 1.71 | 1.70 | 1.69 | 1.68 | 1.67 | 1.66 | 1.64 | 75.7 | 67.1 | 61.3 | 49.5 | 34.1 | 24.8 | 18.8 | 14.7 | 11.2 |
| [EMIm]**FAP$^1$** | 356.2 | 1.57 | 1.57 | 1.56 | 1.56 | 1.55 | 1.54 | 1.53 | 1.52 | 1.51 | 43.7 | 40.0 | 37.4 | 31.7 | 23.9 | 18.2 | 14.6 | 12.0 | 9.9 |
| [BMIm]**FAP$^3$** | 584.2 | 1.63 | 1.62 | 1.62 | 1.61 | 1.60 | 1.59 | 1.58 | 1.57 | 1.56 | 91.9 | 80.2 | 72.8 | 57.9 | 39.3 | 27.8 | 20.5 | 15.8 | 12.5 |
| [BMIm]**FAP$^2$** | 484.2 | 1.54 | 1.54 | 1.54 | 1.53 | 1.52 | 1.51 | 1.50 | 1.49 | 1.48 | 64.7 | 57.6 | 52.9 | 43.1 | 29.6 | 21.4 | 16.0 | 12.5 | 9.8 |
| [BMIm]**FAP$^1$** | 384.2 | 1.47 | 1.47 | 1.47 | 1.46 | 1.45 | 1.44 | 1.43 | 1.42 | 1.41 | 69.5 | 62.0 | 57.0 | 46.9 | 32.6 | 23.8 | 18.0 | 13.9 | 11.1 |
| [BMIm][$PF_6$] | 284.2 | 1.37 | 1.37 | 1.37 | 1.36 | 1.36 | 1.35 | 1.34 | 1.33 | 1.32 | 389.8 | 321.1 | 284.4 | 207.8 | 123.2 | 77.4 | 51.4 | 36.0 | 26.3 |
| [BMPL]**FAP$^3$** | 587.2 | 1.59 | 1.59 | 1.58 | 1.58 | 1.57 | 1.56 | 1.55 | 1.54 | 1.53 | 287.5 | 239.0 | 210.1 | 157.5 | 94.9 | 60.8 | 39.8 | 28.3 | 20.9 |
| [BMPL]**FAP$^1$** | 387.2 | 1.42 | 1.42 | 1.42 | 1.41 | 1.40 | 1.39 | 1.39 | 1.38 | 1.37 | 122.8 | 110.0 | 100.6 | 83.8 | 57.8 | 41.6 | 30.8 | 23.6 | 18.6 |

Table S3: continued.

| Compound | concentration $c = \rho \cdot M^{-1}$ | | | | | | | | | specific conductivity $\sigma$ | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 20 °C | 23 °C | 25 °C | 30 °C | 40 °C | 50 °C | 60 °C | 70 °C | 80 °C | 20°C | 25°C | 30°C | 35°C | 40°C | 45°C | 50°C | 55°C | 60°C | 65°C | 70°C | 75°C | 80°C |
| | [mol·L$^{-1}$] | | | | | | | | | [mS·cm$^{-1}$] | | | | | | | | | | | | |
| [EMIm]**FAP$^{3}$** | 3.08 | 3.08 | 3.07 | 3.06 | 3.04 | 3.02 | 3.00 | 2.98 | 2.96 | 4.4 | 5.2 | 6.0 | 7.0 | 8.0 | 9.0 | 10.1 | 11.4 | 12.7 | 14.1 | 15.6 | 17.1 | 18.7 |
| [EMIm]**FAP$^{1}$** | 4.41 | 4.40 | 4.39 | 4.38 | 4.35 | 4.32 | 4.29 | 4.26 | 4.23 | 7.5 | 8.6 | 9.8 | 11.1 | 12.4 | 13.9 | 15.4 | 17.0 | 18.7 | 20.4 | 22.2 | 23.6 | 24.4 |
| [BMIm]**FAP$^{3}$** | 2.78 | 2.78 | 2.77 | 2.76 | 2.74 | 2.72 | 2.71 | 2.69 | 2.67 | 2.0 | 2.4 | 2.9 | 3.4 | 4.0 | 4.7 | 5.3 | 6.0 | 6.7 | 7.6 | 8.5 | 9.5 | 10.3 |
| [BMIm]**FAP$^{2}$** | 3.19 | 3.18 | 3.18 | 3.17 | 3.15 | 3.12 | 3.10 | 3.08 | 3.06 | 3.4 | 4.1 | 4.8 | 5.6 | 6.4 | 7.4 | 8.4 | 9.5 | 10.6 | 11.8 | 12.7 | 13.9 | 15.2 |
| [BMIm]**FAP$^{1}$** | 3.83 | 3.82 | 3.82 | 3.80 | 3.78 | 3.75 | 3.73 | 3.70 | 3.68 | 3.2 | 3.8 | 4.4 | 5.1 | 5.8 | 6.7 | 7.5 | 8.5 | 9.5 | 10.6 | 11.7 | 12.9 | 14.2 |
| [BMIm][$PF_6$] | 4.83 | 4.82 | 4.81 | 4.80 | 4.77 | 4.74 | 4.71 | 4.68 | 4.65 | 1.1 | 1.4 | 1.8 | 2.3 | 2.9 | 3.5 | 4.2 | 5.1 | 6.0 | 7.0 | 8.2 | 9.3 | 10.7 |
| [BMPL]**FAP$^{3}$** | 2.71 | 2.70 | 2.70 | 2.69 | 2.67 | 2.65 | 2.63 | 2.62 | 2.60 | 0.9 | 1.2 | 1.5 | 1.8 | 2.2 | 2.6 | 3.1 | 3.6 | 4.2 | 4.9 | 5.6 | 6.3 | 7.2 |
| [BMPL]**FAP$^{1}$** | 3.67 | 3.66 | 3.66 | 3.65 | 3.62 | 3.60 | 3.58 | 3.55 | 3.53 | 2.0 | 2.4 | 2.8 | 3.2 | 3.7 | 4.1 | 4.6 | 5.1 | 5.6 | 6.1 | 6.4 | 7.4 | 7.8 |

Table S3: continued.

| Compound | $D^+$ [b] | | | | $D^-$ [c] | | | | $\Lambda_{NMR}$ [d] | | | | $\Lambda_{imp}$ | | | | $I = \Lambda_{imp} \cdot \Lambda_{NMR}^{-1}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 20 °C | 40 °C | 60 °C | 80 °C | 20 °C | 40 °C | 60 °C | 80 °C | 20 °C | 40 °C | 60 °C | 80 °C | 20 °C | 40 °C | 60 °C | 80 °C | 20 °C | 40 °C | 60 °C | 80 °C |
| | [$10^{-11}$·m²·s$^{-1}$] | | | | [$10^{-11}$·m²·s$^{-1}$] | | | | [cm²·S·mol$^{-1}$] | | | | [cm²·S·mol$^{-1}$] | | | | [–] | | | |
| [EMIm]**FAP³** | 2.59 | 5.88 | 11.0 | 18.1 | 1.38 | 3.33 | 6.51 | 11.2 | 1.52 | 3.29 | 5.88 | 9.28 | 1.44 | 2.62 | 4.24 | 6.33 | 0.95 | 0.80 | 0.72 | 0.68 |
| [EMIm]**FAP¹** | 4.06 | 8.01 | 13.3 | 21.0 | 2.52 | 5.25 | 8.69 | 14.6 | 2.51 | 4.74 | 7.40 | 11.29 | 1.71 | 2.85 | 4.40 | 5.76 | 0.68 | 0.60 | 0.60 | 0.51 |
| [BMIm]**FAP³** | 1.55 | 3.95 | 7.75 | 13.6 | 1.13 | 2.96 | 5.96 | 10.5 | 1.02 | 2.47 | 4.61 | 7.64 | 0.72 | 1.46 | 2.49 | 3.86 | 0.70 | 0.59 | 0.54 | 0.51 |
| [BMIm]**FAP²** | 2.07 | 4.84 | 9.10 | 15.6 | 1.46 | 4.48 | 8.47 | 14.6 | 1.35 | 3.33 | 5.91 | 9.57 | 1.07 | 2.05 | 3.42 | 4.97 | 0.79 | 0.61 | 0.58 | 0.52 |
| [BMIm]**FAP¹** | 2.10 | 4.73 | 8.69 | 15.0 | 1.51 | 3.58 | 6.94 | 11.9 | 1.38 | 2.97 | 5.25 | 8.52 | 0.83 | 1.54 | 2.55 | 3.86 | 0.60 | 0.52 | 0.49 | 0.45 |
| [BMIm][$PF_6$] | 0.54 | 1.70 | 3.99 | 8.23 | 4.05 | 1.37 | 3.35 | 6.92 | 0.36 | 1.10 | 2.47 | 4.80 | 0.23 | 0.60 | 1.27 | 2.30 | 0.64 | 0.55 | 0.51 | 0.48 |
| [BMPL]**FAP³** | 0.48 | 1.54 | 3.57 | 7.16 | 0.46 | 1.47 | 3.39 | 6.76 | 0.36 | 1.08 | 2.34 | 4.41 | 0.34 | 0.82 | 1.60 | 2.76 | 0.96 | 0.76 | 0.69 | 0.62 |
| [BMPL]**FAP¹** | 1.20 | 2.78 | 5.35 | 9.70 | 0.98 | 2.38 | 4.66 | 8.56 | 0.83 | 1.84 | 3.36 | 5.79 | 0.55 | 1.01 | 1.57 | 2.21 | 0.65 | 0.55 | 0.47 | 0.38 |

[b] $D^+$ was determined by $^1$H NMR DOSY, mean value of all signals. [c] $D^-$ was determined by $^{19}$F NMR DOSY, mean value of all signals. [d] Calcd by: $\Lambda_{NMR} = (D^+ + D^-) \cdot N_A \cdot e^2 \cdot k_B^{-1} \cdot T^{-1}$.

Table S4: Parameters of the Vogel-Fulcher-Tammann (VFT) fits of the dynamic viscosity and specific conductivity of the fluorophosphate RTILs in the temperature range of 293–353 K.

| Compound | VFT parameters ($\eta$)[a] | | | VFT parameters ($\sigma$)[b] | |
|---|---|---|---|---|---|
| | $\eta_0$ [$10^{-3}$·mPa·s] | $k_\eta$ [K] | $T_0$ [K] | $\sigma_0$ [mS·cm$^{-1}$] | $k_\sigma$ [K] |
| [EMIm]**FAP³** | 161 ± 65 | 831 ± 121 | –115 ± 11 | 196 ± 55 | 331 ± 74 |
| [EMIm]**FAP¹** | 192 ± 80 | 856 ± 146 | –137 ± 15 | 1157 ± 91 | 955 ± 33 |
| [BMIm]**FAP³** | 198 ± 47 | 760 ± 66 | –103 ± 6 | 238 ± 43 | 467 ± 52 |
| [BMIm]**FAP²** | 78 ± 29 | 1090 ± 132 | –140 ± 11 | 934 ± 56 | 955 ± 25 |
| [BMIm]**FAP¹** | 66 ± 32 | 1084 ± 168 | –137 ± 13 | 408 ± 107 | 712 ± 89 |
| [BMIm][$PF_6$] | 107 ± 34 | 1000 ± 83 | –102 ± 6 | 1455 ± 191 | 931 ± 44 |
| [BMPL]**FAP³** | 85 ± 24 | 1022 ± 76 | –105 ± 5 | 112 ± 48 | 474 ± 130 |
| [BMPL]**FAP¹** | 26 ± 18 | 1741 ± 322 | –185 ± 21 | 773 ± 51 | 926 ± 23 |

[a] $R^2 \geq 99.98\%$. [b] $R^2 \geq 99.96\%$ except for [EMIm]**FAP³** and [BMPL]**FAP³** which is 99.8%.

# 7. X-Ray

Single Crystals of [EMIm]**FAP³**, [EMIm]**FAP²**, [EMIm]**FAP¹**, [BMIm]**FAP¹** and [EMIm][$PF_6$] were investigated with a XtaLAB Synergy, Dualflex, Hypix diffractometer using Cu-$K_\alpha$ radiation (micro-focus sealed X-Ray tube, $\lambda$ = 1.54184 Å).

All structures were solved by direct methods,[16] and refinements are based on full-matrix-least-squares calculations on $F^2$. All non-hydrogen atoms were refined anisotropically. The positions of all H atoms were located from electron density difference maps. In the final steps of the refinements, idealized bond lengths and angles were introduced for most of the H atoms.

All calculations were performed with the ShelXle graphical interface.[17] Molecular structure diagrams were drawn with the program Diamond 5.1.1.[18] Selected experimental details, crystal data and the CCDC numbers are collected in Table S5.

Table S5: Selected crystal data and experimental details for the structure determinations of perfluoroalkylfluorophosphates.

| **Compound** | [EMIm][*mer*-$(C_2F_5)_3PF_3$]} | [EMIm][*trans*-$(C_2F_5)_2PF_4$] | [EMIm][$(C_2F_5)PF_5$] | [BMIm][$(C_2F_5)PF_5$] | [EMIm][$PF_6$] |
|---|---|---|---|---|---|
| Sum formula | $C_{12}H_{11}F_{18}N_2P$ | $C_{10}H_{11}F_{14}N_2P$ | $C_8H_{11}F_{10}N_2P$ | $C_{10}H_{15}F_{10}N_2P$ | $C_6H_{11}F_6N_2P$ |
| Formula weight [g mol$^{-1}$] | 556.20 | 456.18 | 356.16 | 384.21 | 256.14 |
| Temperature [K] | 99.99(10) | 100.00(10) | 100.00(10) | 100.00(10) | 100.00(10) |
| colour | colorless | colorless | colorless | colorless | colorless |
| Crystal system | monoclinic | triclinic | monoclinic | monoclinic | monoclinic |
| Space group | *Ia* | *P*-1 | $P2_1/c$ | $P2_1/n$ | $P2_1/c$ |
| *a* [Å] | 16.9560(2) | 8.7017(2) | 9.4070(1) | 12.8239(2) | 8.6017(1) |
| *b* [Å] | 8.6506(1) | 12.7582(5) | 9.8575(1) | 8.3876(10) | 8.9823(1) |
| *c* [Å] | 14.9967(2) | 15.3820(4) | 14.6083(2) | 14.1448(2) | 13.4288(1) |
| $\alpha$ [°] | 90 | 71.555(2) | 90 | 90 | 90 |
| $\beta$ [°] | 119.598(2) | 87.074(2) | 96.374(1) | 90.1230(10) | 101.5750(10) |
| $\gamma$ [°] | 90 | 83.244(2) | 90 | 90 | 90 |
| Volume [Å$^3$] | 1912.67(5) | 1608.53(8) | 1346.25(3) | 1521.44(4) | 1016.45(2) |
| *Z* | 4 | 4 | 4 | 4 | 4 |
| $\rho_{ber}$ [Mg m$^{-3}$] | 1.932 | 1.884 | 1.757 | 1.677 | 1.674 |
| Absorption coefficient $\mu$ [mm$^{-1}$] | 2.987 | 0.301 | 2.951 | 2.660 | 3.064 |
| Absorption correction | Gaussian | Gaussian | Gaussian | Gaussian | Gaussian |
| *F*(000) [e] | 1096 | 904 | 712 | 776 | 520 |
| Device, radiation, wavelength | XtaLAB Synergy, Dualflex, HyPix, ($CuK_\alpha$ = 1.54184 Å) | XtaLAB Synergy, Dualflex, HyPix, ($CuK_\alpha$ = 1.54184 Å) | XtaLAB Synergy, Dualflex, HyPix, ($CuK_\alpha$ = 1.54184 Å) | XtaLAB Synergy, Dualflex, HyPix, ($CuK_\alpha$ = 1.54184 Å) | XtaLAB Synergy, Dualflex, HyPix, ($CuK_\alpha$ = 1.54184 Å) |
| Theta range for data collection [°] | 5.931 to 77.563 | 8.976 to 77.730 | 4.730 to 79.930 | 4.649 to 79.723 | 5.249 to 77.300 |
| Reflections collected / independent | 13266 / 3432 | 14126 / 6081 | 19775 / 2917 | 23281 / 3278 | 29850 / 2166 |
| Reflections with [$I > 2\sigma(I)$] | 3413 | 5645 | 2887 | 3176 | 2062 |
| *R*(int) | 0.0814 | 0.1784 | 0.0641 | 0.0670 | 0.0757 |
| Data / restraints / parameters | 3432 / 2 / 300 | 6081 / 0 / 494 | 2917 / 0 / 192 | 3278 / 126 / 248 | 2166 / 138 / 0 |
| $R_1$ [$I > 2\sigma(I)$][a] | 0.0527 | 0.1256 | 0.0504 | 0.0492 | 0.0324 |
| $wR_2$ (all data)[b] | 0.01370 | 0.2675 | 0.1600 | 0.1411 | 0.0845 |
| Goodness-of-fit $F^2$[c] | 1.085 | 1.097 | 1.097 | 1.085 | 1.076 |
| $\Delta\rho_{max}$ / $\Delta\rho_{min}$ [e Å$^{-3}$] | 0.708 / −0.430 | 1.540 / −1.214 | 0.435 / −0.385 | 0.416 / −0.508 | 0.244 / –0.408 |
| CCDC number | 2520839 | 2520840 | 2520841 | 2520843 | 2520842 |

# References


1 E. D. B. Robin K. Harris, Sonia M Cabral de Menezes, Robin Goodfellow, Pierre Granger, *Pure Appl. Chem.*, 2001, **73**, 1795–1818.

2 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.

3 T. L. Shaw, J. C. Carrol, *Int. J. Thermophys.*, 1998, **19**, 1671–1680.

4 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372–1377.

5 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100.

6 F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys. (PCCP)*, 2005, **7**, 3297–3305.

7 Gaussian 16 Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Blanesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian Inc.*, 2016.

8 N. V. Ignat'ev, J. Bader, K. Koppe, B. Hoge, H. Willner, *J. Fluorine Chem.*, 2015, **171**, 36–45.

9 N. V. Pavlenko, L. M. Yagupol'skii, *J. Gen. Chem. USSR*, 1989, **59**, 469–473.

10 M. Schmidt, A. Kühner, M. Jungnitz, F. Ott, N. Ignatyev, Merck Patent GmbH, DE10119278, 2002.

11 N. M. Ignatyev, D. Bejan, H. Willner, Merck Patent GmbH, WO2010012359, 2010.

12 N. Ignatyev, M. Weiden, U. Welz-Biermann, U. Heider, P. Sartori, A. Kucheryna, H. Willner, Merck Patent GmbH, WO2003087111, 2003.

13 U. Welz-Biermann, N. Ignatyev, M. Weiden, U. Heider, A. Kucheryna, H. Willner, P. Sartori, Merck Patent GmbH, WO2003087110, 2003.

14 N. V. Ignat'ev, D. Bejan, H. Willner, *Chim. Oggi – Chem. Today*, 2011, **29**, 42–45.

15 J. Landmann, J. A. P. Sprenger, P. T. Hennig, R. Bertermann, M. Grüne, F. Würthner, N. V. Ignat'ev, M. Finze, *Chem. Eur. J.*, 2018, **24**, 608–623.

16 G. Sheldrick, *Acta Crys. Sect. A*, 2008, **64**, 112–122.

17 C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.*, 2011, **44**, 1281–1284.

18 K. Brandenburg, *Diamond 5.1.1*, Crystal Impact GbR, Bonn, Germany, 2025.