Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Thermal Stability of Dialkylimidazolium Tetrafluoroborate and Hexafluorophosphate Ionic Liquids: Ex Situ Bulk Heating to Complement In Situ Mass Spectrometry

Supplementary information

Furthe Experimental Details

Distillations:

The type K thermocouple was inserted into a glass blown inlet that was positioned above the surface of the liquid to provide vapor phase temperature measurements (see **Figure 1** of the main text). The still pot was subsequently wrapped with heating tape supported by PTFE tape as shown in **Figure S1**. The pot and tape were then wrapped in several layers of glass wool which was tightly bound with more PTFE tape. Temperature and pressure readings were recorded by a Picolog data logger connected to a local PC, to provide profiles for each distillation (e.g. **Figure S2** and **Figure S3**). Prior to distillation, a correlation between the wattage applied to the heating tape and the thermocouple temperature readings was made without any IL in the still pot. Likewise, calibration curves for the Pirani and Penning gauges were made (see **Figure S4** and **Figure S5**). During distillations the chosen temperature values were set according to the temperature calibration and the thermocouple and pressure gauge readings were recorded to provide the actual conditions of the experiments.

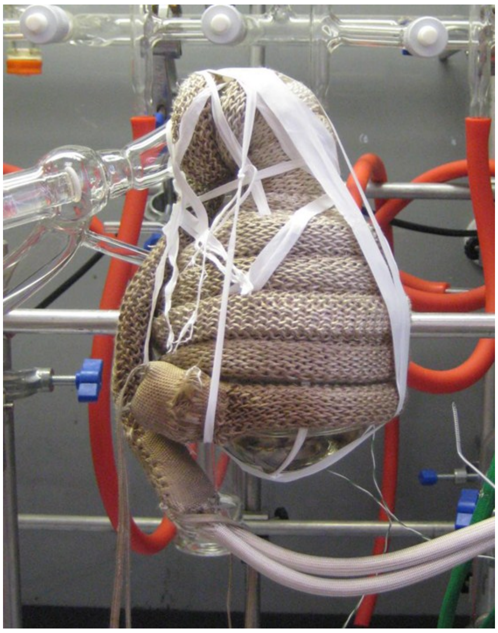


Figure S1 The heating tape around the distillation pot, supported with PTFE tape. The base was left uncovered and the entire pot was subsequently covered in several layers of glass wool.

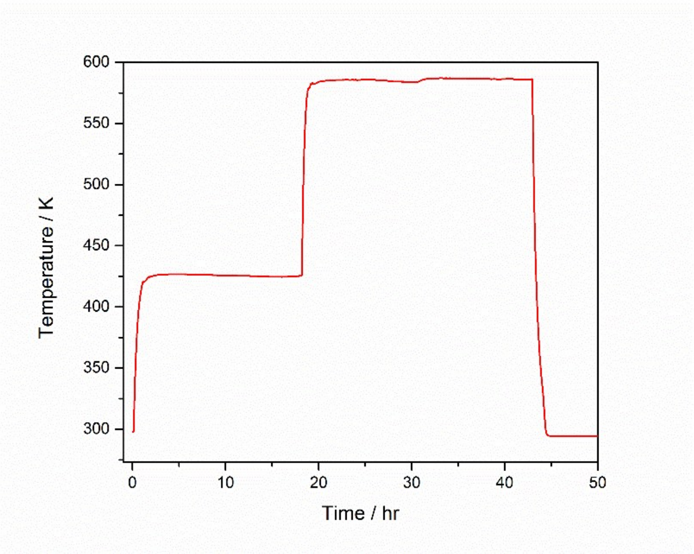


Figure S2 Temperature (K) versus time (hr) for the distillation of [C_2C_1Im][NTf_2].

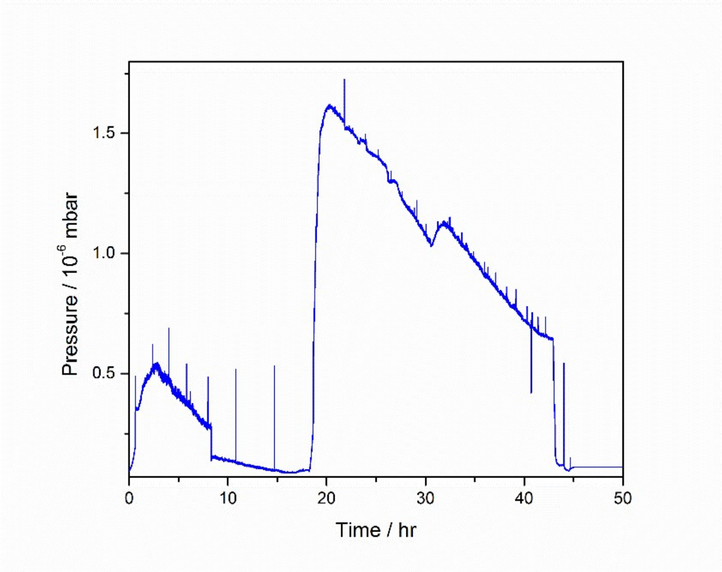


Figure S3 Pressure (mbar) versus time (hr) for the distillation of [C_2C_1Im][NTf_2]. Note: Pressure readings were taken approximately 1 hour after the distillation set-up had reached the desired temperature.

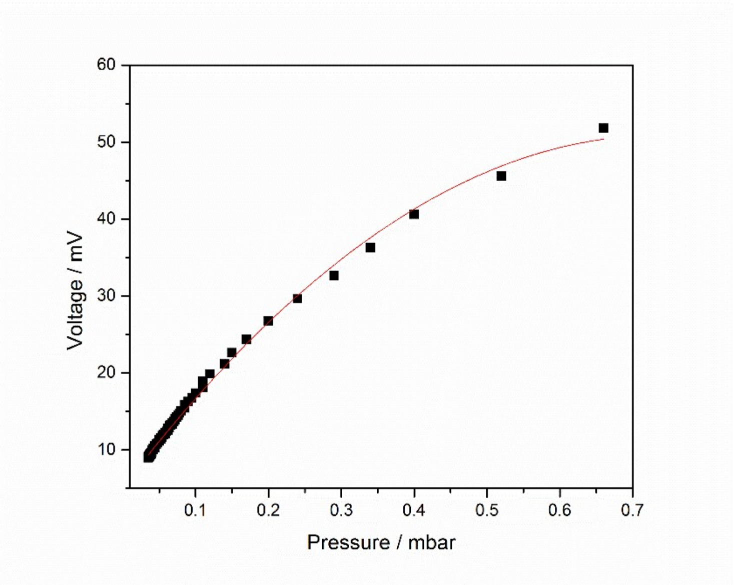


Figure S4 The Pirani gauge calibration curve with second degree polynomial fitting that was used to determine the pressure between the distillation set up and the diffusion pump.

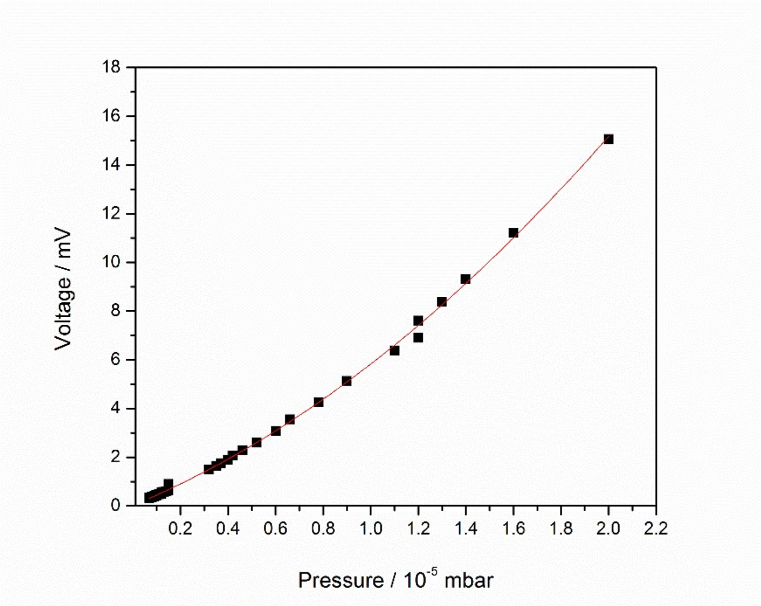


Figure S5 The Penning gauge calibration curve with second degree polynomial fitting that was used to determine the pressure on the head of the diffusion pump.

IL Synthesis:

Ionic liquids were made by salt metathesis using published procedures.[1,2] 1-Ethyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium chloride and 1-octyl-3-methylimidazolium chloride were purchased from Merck and used as received. Post anion metathesis, a DIONEX ICS-3000 ion chromatograph (flow rate = 0.25 mL/min, isocratic eluent: water, 60%; acetonitrile, 25%; 100 mM NaOH, 15%) fitted with an AS20 (2 x 250 mm) column and CG20 (2 x 50 mm) guard was used to determine the halide content of ionic liquids. All ionic liquids were found to contain < 10 ppm residual halides.

Other Data

To test the custom distillation glassware, bulk heating experiments were performed first with the thermally robust ionic liquid [C_2C_1Im][NTf_2], which successfully distilled as proven by ^{1}H NMR (**Figure S6**). Subsequently, the results of bulk heating experiments for [C_4C_1Im][BF_4] were tested for reproducibility by comparing two separate experiments at similar temperatures. The ^{1}H NMR of the distillates from experiments at 544 K and 543 K showed that the composition of ionic liquid to $C_4C_1(C_3N_2H_2)BF_3$ was identical for both experiments (**Figure S7**).

[C_2C_1Im][NTf_2]

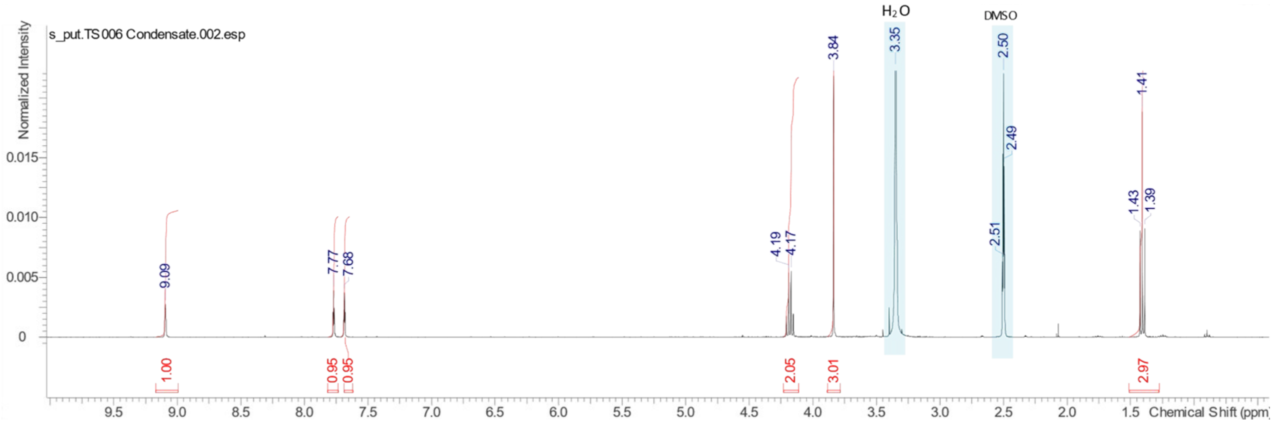


Figure S6 The ^{1}H NMR spectrum for condensed [C_2C_1Im][NTf_2] after distillation at 312 °C and 1.6 x 10^{-5} mbar.

Reproducibility:

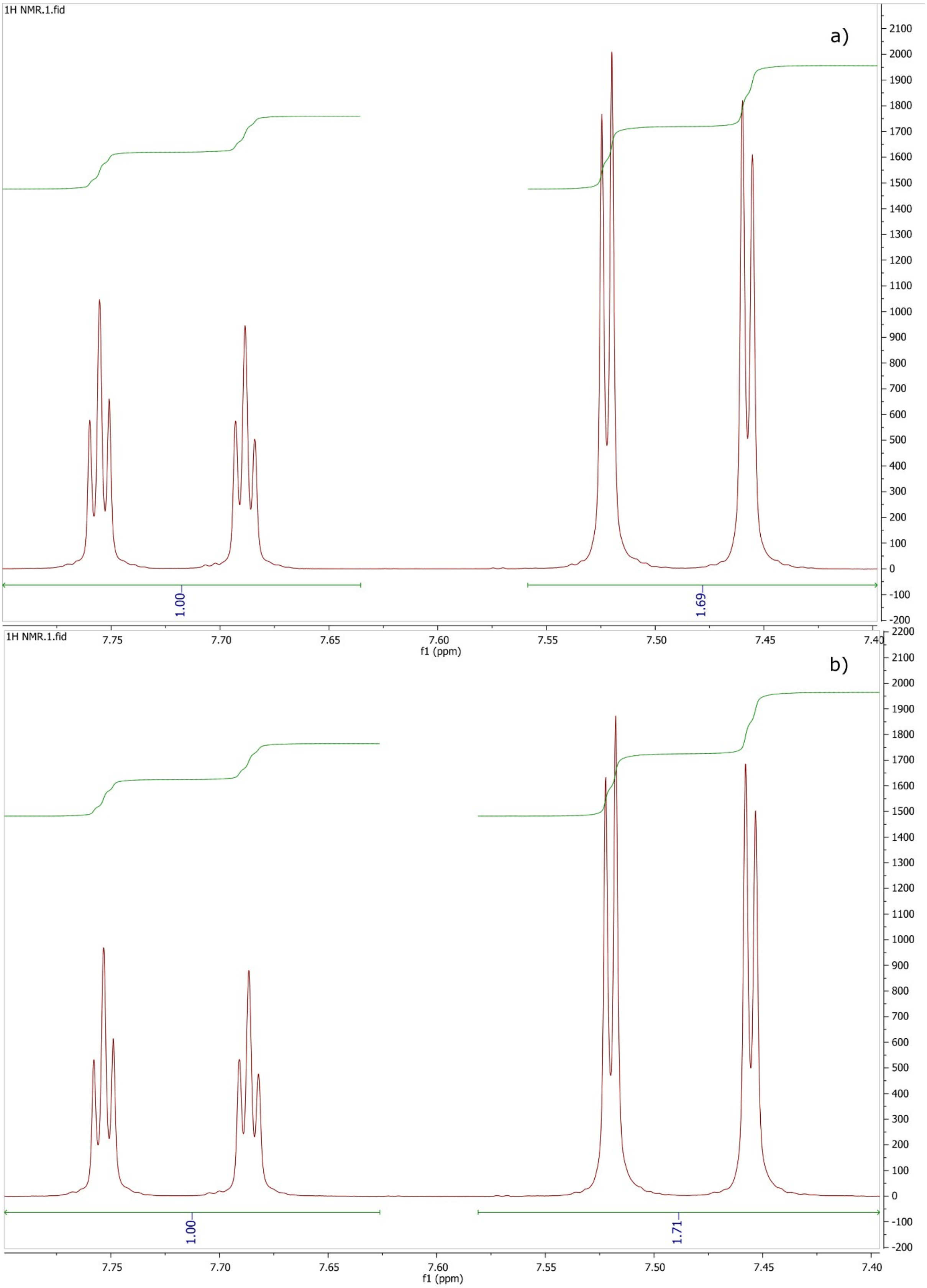


Figure S7 The ^{1}H NMR spectra of two $[C_4C_1Im][BF_4]$ bulk heating experiments in the custom distillation glassware at a) 544 K and b) 543 K, showing the integrals of the C^4-H and C^5-H protons of the ionic liquid (left) and $C_4C_1(C_3N_2H_2)BF_3$ product (right), normalized to the ionic liquid signals.

Purified $C_4C_1(C_3N_2H_2)PF_5$:

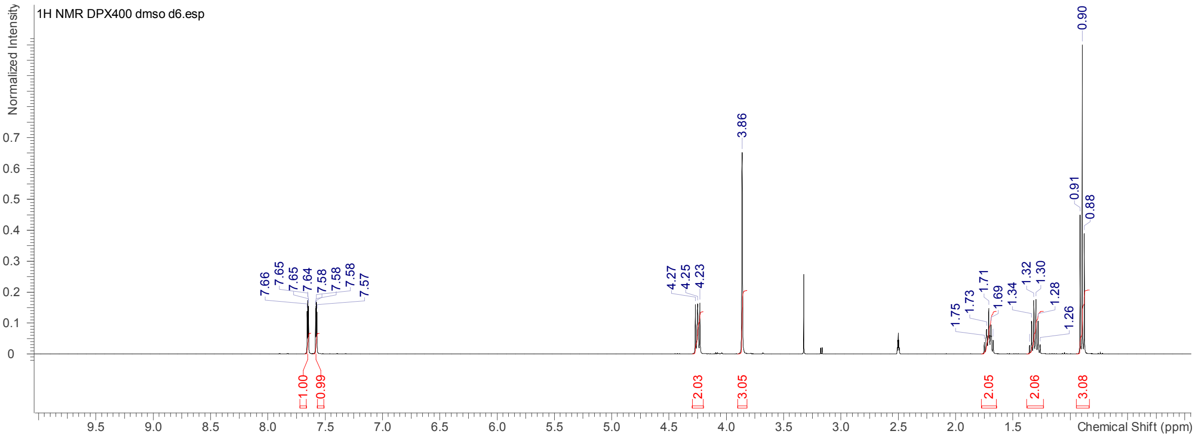


Figure S8 The ^{1}H NMR spectrum of $C_4C_1(C_3N_2H_2)PF_5$ in DMSO-*d6* after purification.

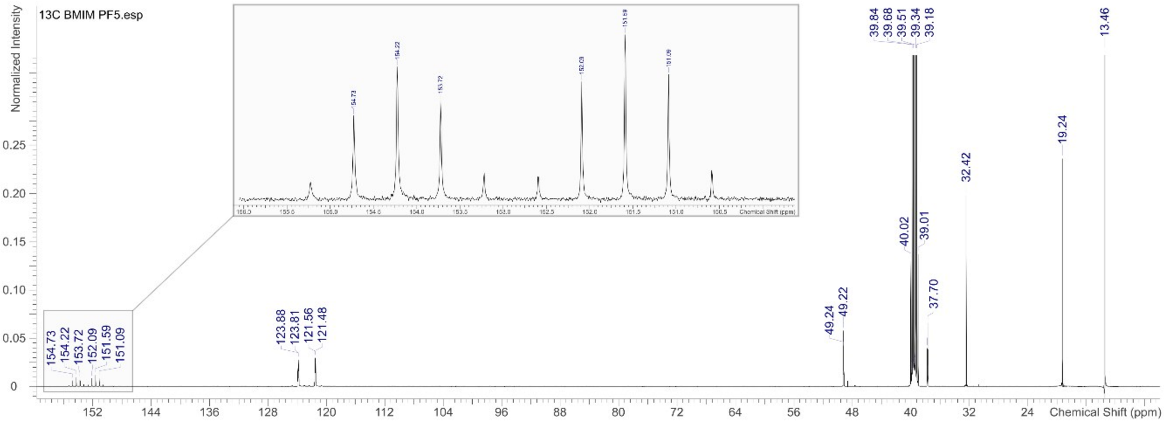


Figure S9 The ^{13}C NMR spectrum of $C_4C_1(C_3N_2H_2)PF_5$ in DMSO-*d6* after purification with an expansion of the C^2-carbon which has a doublet of quintet multiplicity from phosphorus, $^1J(PC)$ = *330.6 Hz, and* four *cis*-fluorine atoms, $^2J(F_{cis}C)$ = 62.7 Hz). Note: coupling to the single *trans*-fluorine is not observed, i.e. $^2J(F_{trans}C)$ = 0 Hz.

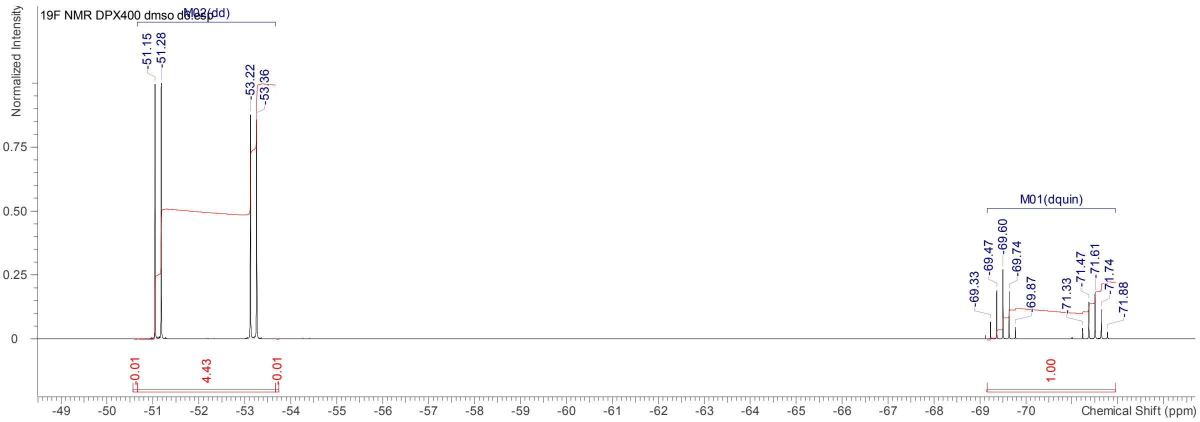


Figure S10 The ^{19}F NMR spectrum of $C_4C_1(C_3N_2H_2)PF_5$ in DMSO-*d6* after purification showing a doublet of doublets from the four equatorial fluorine atoms, $^1J(PF_{eq})$ = 782.0 *Hz* and $^2J(F_{ax}F_{eq})$ = 51.0 Hz, and a doublet of quintets from the single axial fluorine, $^1J(PF_{ax})$ = 755.0 *Hz* and $^2J(F_{eq}F_{ax})$ = 51.0 Hz.

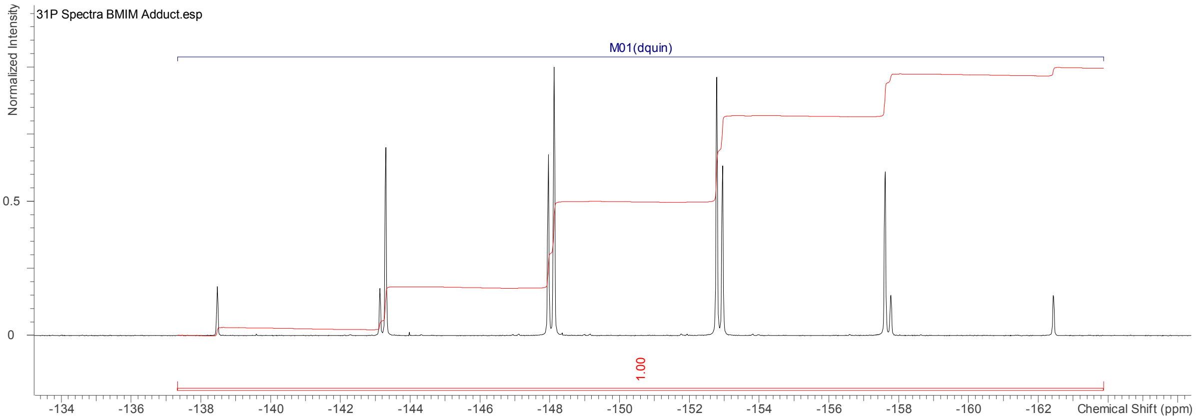


Figure S11 The ^{31}P NMR spectrum of $C_4C_1(C_3N_2H_2)PF_5$ in DMSO-*d6* after purification showing a doublet of quintets from axial and equatorial fluorine, $^1J(F_{ax}P)$ = 781.9 Hz and $^1J(F_{eq}P)$ = 755.1 Hz.

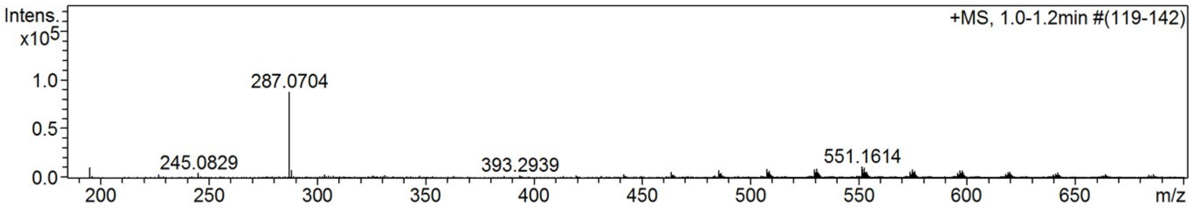


Figure S12 The ESI-MS spectrum of $C_4C_1(C_3N_2H_2)PF_5$ showing the $[M+Na]^+$ adduct at *m/z* 287.0704.

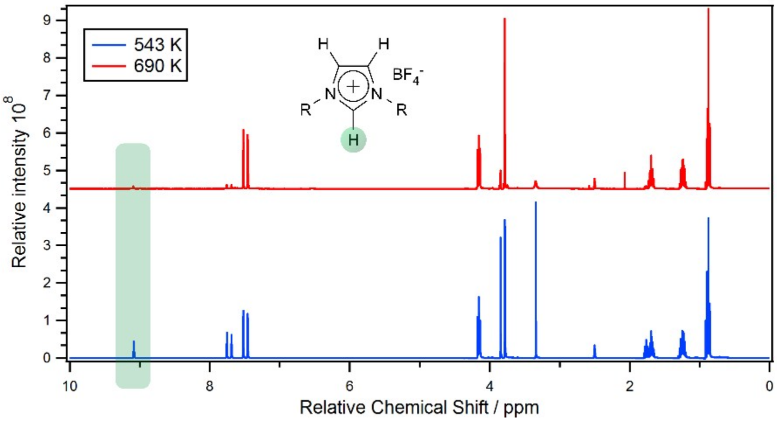
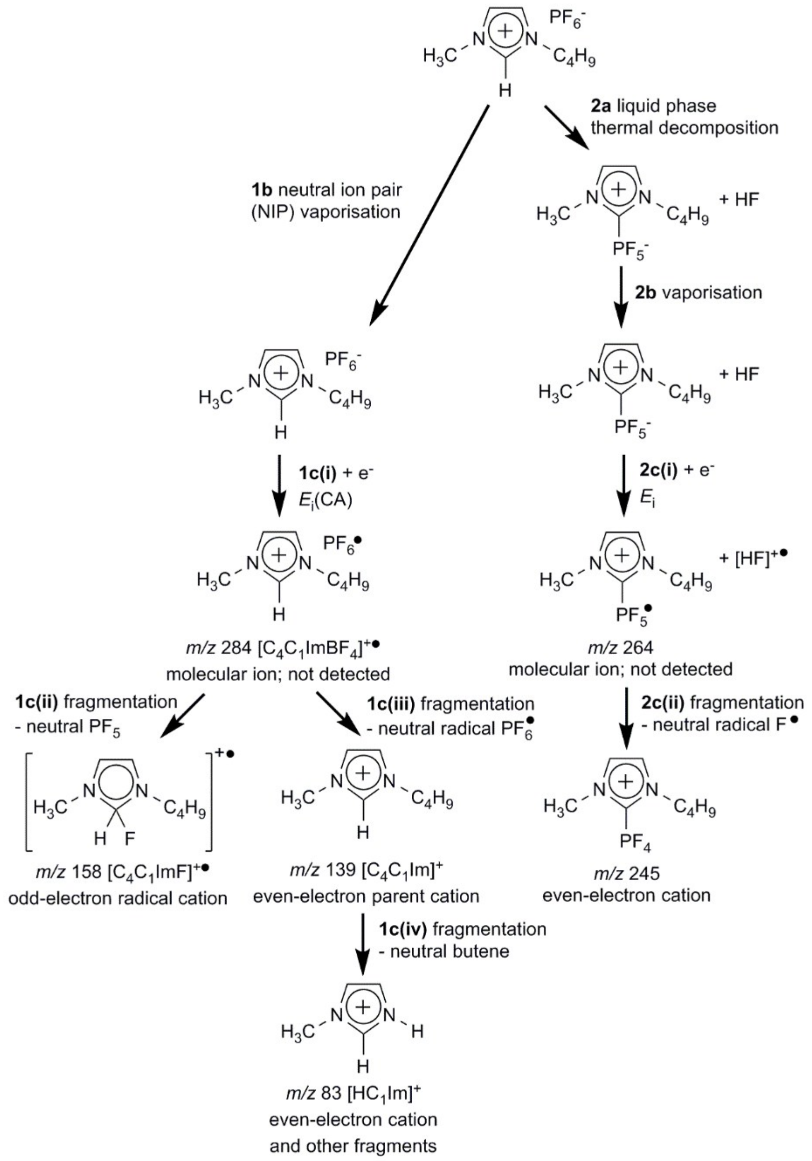


Figure S13 The full-scale ^{1}H NMR spectra of the distillates obtained from [C_4C_1Im][BF_4] distillations at 543 K and 690 K, showing the C^2-proton signal disappearing at as temperature increases, due to the formation of $C_4C_1(C_3N_2H_2)BF_3$.



Scheme S1 Analagous to Scheme 1: (a) Liquid phase TD, (b) vaporization, (c) electron ionization and fragmentation taking place in the vapor phase inside the mass spectrometer for $[C_4C_1Im][PF_6]$. Route 1 is for NIP vaporization, and route 2 is for liquid phase TD to form $C_4C_1(C_3N_2H_2)PF_5$ followed by vaporization.

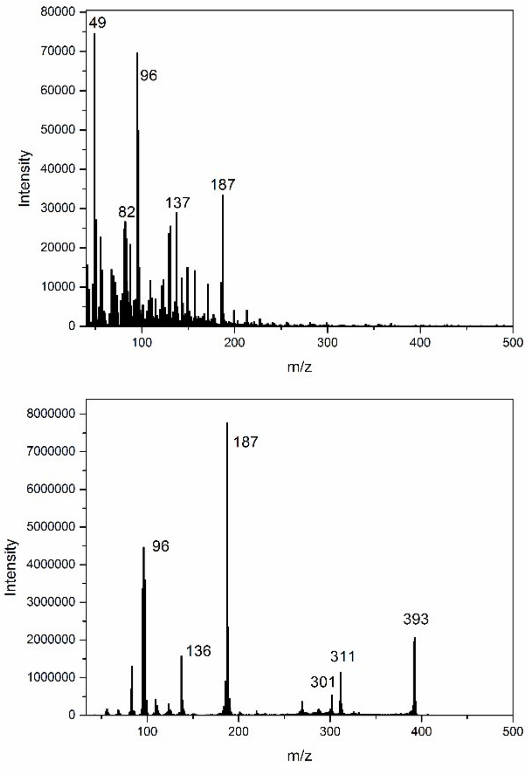


Figure S14 The positive mode MS of $C_4C_1(C3N_2H_2)BF_3$ at low temperature (314 K) and high temperature (436 K). The peak at m/z = 393 corresponds to a dimer of $C_4C_1(C3N_2H_2)BF_3$ minus one fluorine.

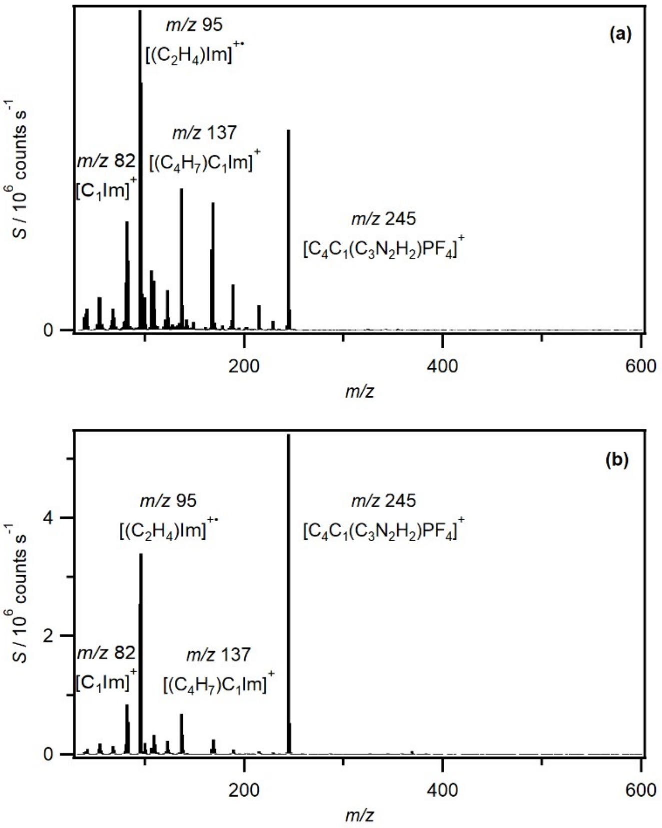


Figure S15 The positive mode MS of $C_4C_1(C3N_2H_2)PF_5$ at (a) low temperature (314 K) and (b) high temperature (436 K).

References

(1) Bonhôte, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, *Inorg. Chem.* **1996**, *35*, 1168–1178.

(2) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. a.; Rogers, R. D. *Green Chem.* **2001**, *3* (4), 156–164.