

Thermolysis of Organofluoroborate Ionic Liquids to NHC-Organofluoroborates

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ABSTRACT

A range of dialkylimidazolium organotrifluoroborate ionic liquids were prepared by anion metathesis from newly available potassium organotrifluoroborate salts, and their physical properties were characterized by TGA, DSC, and STA. Thermal decomposition was subsequently investigated under vacuum with direct insertion mass spectrometry to determine whether thermolysis was a viable route to prepare N-heterocyclic carbene organofluoroborates, which are an important class of emerging compounds. Several key targets were identified, which highlighted the potential to short-cut complex synthetic methodologies otherwise required to access such molecules.

Introduction

NHC-trifluoroborates and NHC-organofluoroborates (i.e. NHC-BR_xF_{3-x}) are emerging as valuable new molecules with unique reactivity, which are impacting areas such as synthetic organic chemistry,^{1,2} polymer chemistry,³ photoelectrochemistry,⁴ and PET imaging.^{5,6} In many cases, NHC-BR_xF_{3-x} compounds are replacing expensive metal catalysts and their applications are rapidly growing as their chemistry is unraveled. NHC-BR_xF_{3-x} compounds can be prepared from free NHCs and BR_xF_{3-x}; however this method requires strong bases which limits the flexibility of the organic groups.⁷ Alternatively, NHC-boranes (i.e. NHC-BH₃) can be prepared from imidazolium salts and sodium borohydride,⁸ and aryl-substituted NHC-boranes can then be prepared by hydroboration to arynes,⁹ followed by fluorination to afford NHC-BRF₂.¹ Unfortunately, each step requires organic solvents, harmful reagents, industrially challenging work up procedures, and have low atom economies

Most ionic liquids decompose *via* mechanisms such as retro-S_N2 that yield starting materials or small molecules,^{10,11} however, thermolysis of imidazolium tetrafluoroborate (i.e. [C_nC₁Im][BF₄]) ionic liquids (ILs) under high vacuum has been shown to be a viable route to prepare high-value NHC-trifluoroborates (i.e. NHC-BF₃; SI, **Scheme S1a**).¹² Here, we prepare and characterize new organofluoroborate ILs (i.e. [C₄C₁Im][BR_xF_{4-x}]) from newly available potassium organotrifluoroborate (i.e. K[R-BF₃]) salts,¹³ and investigate their thermal behavior to understand whether they are suitable precursors for NHC-BR_xF_{3-x} synthesis (**Scheme S1b**). Electron ionization mass spectrometry (EI-MS) has previously been used to identify NHC-adducts from known fragmentation patterns (NHC-BF₃ → NHC-BF₂⁺; SI, **Scheme S1c**).¹⁴ We exploit this knowledge to identify vapour phase thermal decomposition (*T_d*) products from *in-situ* measurements with direct insertion mass spectrometry (DIMS). Heating ILs under reduced

pressure often leads to competitive vaporization and T_d , which can be monitored by MS signals of vaporized IL (i.e. neutral ion pairs, NIPs),¹⁵ NHC adducts,¹⁴ or S_N2 T_d products.¹⁶ Crucially, thermolysis can be a valuable synthetic short-cut to avoid numerous solvents and auxiliaries, but thermal behavior must first be fully understood to realize such possibilities.

Experimental

[C₄C₁Im][BR_xF_{4-x}] ILs were synthesized by anion metathesis from [C₄C₁Im]Cl in anhydrous DCM and characterized by NMR and HRMS. Relevant structures are shown in Figure 1 and Figure S1, and ILs are labelled IL1-11 according to Table 1. All ILs were analyzed by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and simultaneous thermal analysis (STA), and finally by DIMS (full details in the supporting information).

Results and Discussion

All ILs were first characterized by DSC, TGA, and STA to compare the effects of organo-groups on thermal properties (**Table 1**). Six of the seven [C₄C₁Im][BRF₃] ILs were found to be room temperature ILs by DSC. Butyl- (IL3) and cyclohexyl- (IL8) groups had the largest impacts by introducing melting points (T_m) that were 109.4 °C and 156.1 °C higher than the T_g of [C₄C₁Im][BF₄], respectively. Conversely, the single aromatic groups of IL5-7 only raised the glass transition (T_g) temperature by 22-28 °C, while the four phenyl groups of IL9 introduced a T_m 223.3 °C above the T_g of [C₄C₁Im][BF₄]. Except for [B(C₆H₅)]⁻ (i.e. IL-9), the organic groups compromised IL thermal stability by introducing exothermic T_d steps at significantly lower temperatures than those associated with endothermic [BF₄]⁻ T_d (SI, **Figure S26-36**). Hence, [C₄C₁Im][BRF₃] TGA T_d parameters were lower than those of [C₄C₁Im][BF₄], and the lowest

values were obtained for IL6 while the highest was obtained for IL5, which highlighted that strong electron withdrawing groups were detrimental to $[\text{RBF}_3]^-$ thermal stability. A dicationic analogue (IL11) had the highest stability as expected,¹⁷ and a hydroxyl-functionalized IL cation (IL10) also appeared to have higher stability than all $[\text{C}_4\text{C}_1\text{Im}][\text{BRF}_3]$ ILs. Isothermal TGA of allyl-functionalized $[\text{C}_4\text{C}_1\text{Im}][(\text{C}_3\text{H}_5)\text{BF}_3]$ highlighted that organo groups also had an impact on long-term thermal stability (SI, **Figure S37-39**). For example, the temperatures at which 1 % mass loss occurred over 10 hr ($T_{0.01/10}$) was 167 °C, which was 49 °C lower than the literature value for $[\text{C}_4\text{C}_1\text{Im}][\text{BF}_4]$.¹⁸ However, the activation energy (E_a) of T_d only decreased by 9.5 kJ mol⁻¹ from 108.4 kJ mol⁻¹ to 98.9 kJ mol⁻¹. In comparison, hydroxyl-functionalised IL10 had a relatively similar $T_{0.01/10}$ value of 166 °C (SI, **Figure S40-42**), but a significantly lower E_a of 85.1 kJ mol⁻¹, which was below the values of low thermal stability ILs.¹⁹ Therefore, functional groups compromised atmospheric pressure thermal stability, regardless of whether they were situation on the IL anion (i.e. $[(\text{C}_3\text{H}_5)\text{BF}_3]^-$) or cation (i.e. $[(\text{C}_2\text{OH})\text{C}_1\text{Im}]^+$).

Table 1. Atmospheric pressure phase transitions (T_m , T_g , T_{cc}) measured by DSC, thermal decompositions (T_{onset} , $T_{1\%}$) measured by TGA, number of steps in the TGA, STA signal for the initial thermal decomposition step.

IL	Cation	Anion	Temperature / °C				T_{onset}	$T_{1\%}$	No. Steps	Initial Step
			T_m	T_g	T_{cc}	T_{ss}				
1	[C ₄ C ₁ Im] ⁺	[BF ₄] ⁻		-94.2 ^a			429.7	367.5	1	endothermic
2	[C ₄ C ₁ Im] ⁺	[(CH ₃)BF ₃] ⁻		-95.3			299.9	195.0	2	exothermic
3	[C ₄ C ₁ Im] ⁺	[(C ₄ H ₉)BF ₃] ⁻	15.2	-79.1	-37.9		276.9	260.4	2-3	exothermic
4	[C ₄ C ₁ Im] ⁺	[(C ₃ H ₅)BF ₃] ⁻		-92.2			242.7	205.3	2	exothermic
5	[C ₄ C ₁ Im] ⁺	[(C ₆ H ₅)BF ₃] ⁻		-71.6			309.4	287.2	2	exothermic
6	[C ₄ C ₁ Im] ⁺	[(C ₆ H ₃ F ₂)BF ₃] ⁻		-69.9			233.8	198.7	2-3	exothermic
7	[C ₄ C ₁ Im] ⁺	[(C ₇ H ₆ OH)BF ₃] ⁻		-66.6			270.4	178.6	2-3	exothermic
8	[C ₄ C ₁ Im] ⁺	[(C ₆ H ₁₁)BF ₃] ⁻	61.9 ^b	-53.5 ^b	-13.1 ^b	26.3 ^b	316.1	267.9	2	exothermic
9	[C ₄ C ₁ Im] ⁺	[B(C ₆ H ₅) ₄] ⁻	129.1 ^c	-88.1 ^d			349.6	324.1	1	endothermic
10	[(C ₂ OH)C ₁ Im] ⁺	[BF ₄] ⁻		-87.8			360.5	265.0	1	endothermic
11	[C ₁₂ (C ₁ Im) ₂] ²⁺	2[BF ₄] ⁻	2.4	-49.7	-23.6		440.2	288.3	1	endothermic

^aLiterature value of -85.0 °C²⁰

^bResolved at 20°C/min

^cAmorphous m.p. of 129.1 °C from STA

^d T_g of the supercooled liquid; solid at R.T.

All ILs were next investigated by DIMS to probe their thermal behavior under vacuum (**Figure 1a-k**; SI, **Figure S43-53**). DIMS of the control **IL1** (**Figure 1a**) showed that both vaporization and T_d occurred simultaneously as m/z signals for NIPs (i.e. m/z 139 for [C₄C₁Im]⁺)^{21,22} and [C₄C₁Im]-BF₃ zwitterions (i.e. m/z 187 for [C₄C₁Im]-BF₂⁺)¹⁴ were observed. For dicationic **IL11**, no NHC-BF₃ adducts were observed and all T_d species were identified as alkyl-chain fragmentation

products (**Figure 1k**).²² This was supported by CH_2 -loss peaks observed in the MS and the presence of other imidazolium fragmentation products (i.e. m/z 82, 137).

All $[C_4C_1Im][BR_xF_{4-x}]$ ILs vaporized or decomposed (**Figure 1b-k**) far below **IL1** which had an onset of ≈ 300 °C. For **IL2** (**Figure 1b**), the m/z signal of $[C_4C_1Im]-BF_2^{+•}$ appeared around 125 °C and peaked at 250 °C before decreasing. This was ≈ 175 °C below **IL1** which suggested that $[C_4C_1Im]-BF_3$ was formed at low temperatures when fluorine was substituted for a methyl group. An additional fragmentation product $[C_4C_1Im]-B(CH_3)F^{+•}$ was also observed, albeit with very low intensity, which suggested that $[C_4C_1Im]-B(CH_3)F_2$ had formed through T_d of the IL. It was unclear whether $[C_4C_1Im]-BF_3$ was the major T_d product or whether $[C_4C_1Im]-BF_2^{+•}$ was the most stable fragmentation product and $[C_4C_1Im]-B(CH_3)F_2$ had formed but was not readily identified. Low MW $(CH_3)BF_2^{+•}$ was also identified in the IL vapour, which could have originated from either $[C_4C_1Im]-B(CH_3)F_2$ fragmentation or NIPs (i.e. $[(CH_3)BF_3]^+$).

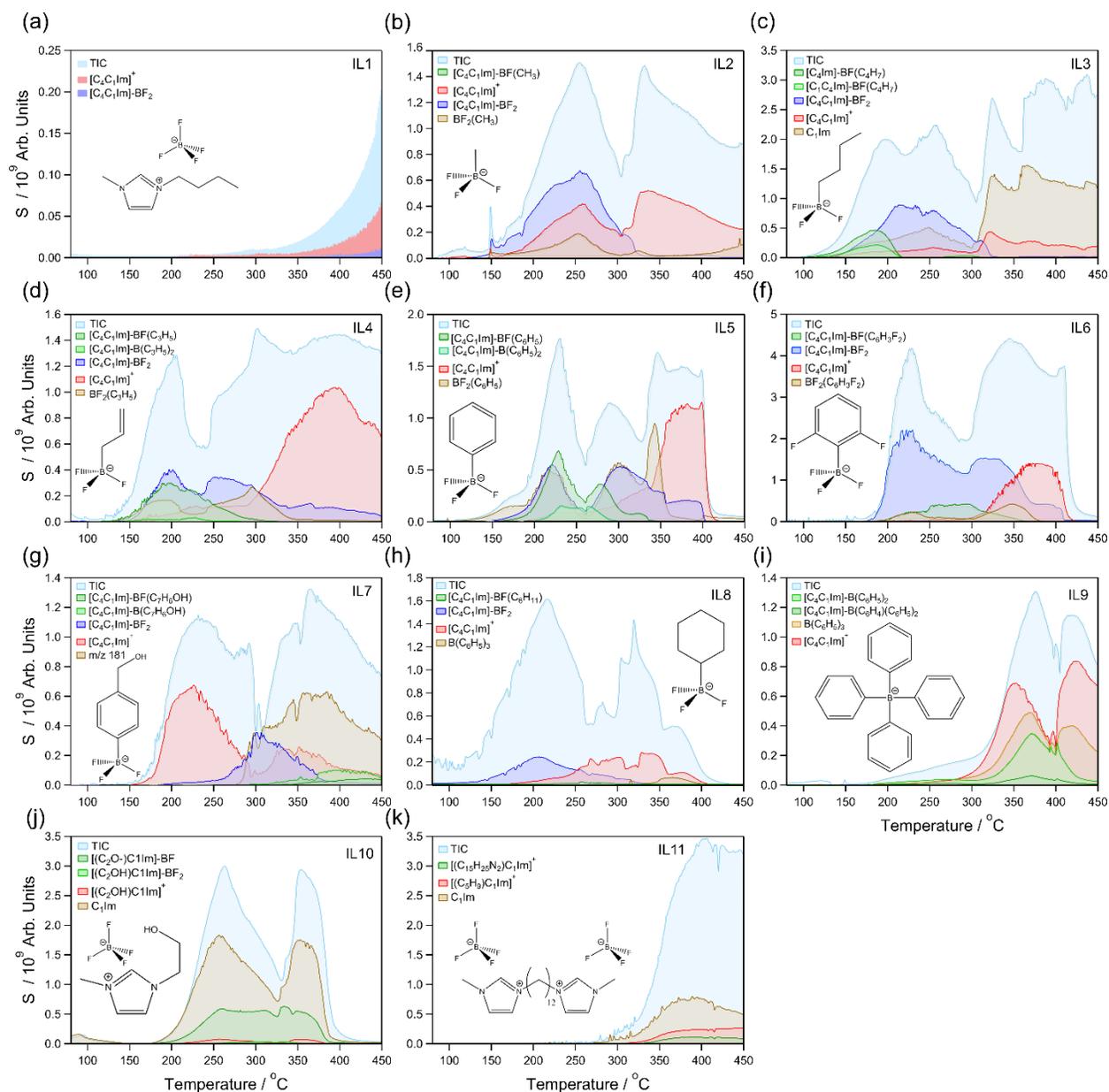


Figure 1. Total ion currents (blue) and selected m/z profiles for DIMS of $[C_4C_1Im][BF_4]$ (a), $[C_4C_1Im][BR_xF_{4-x}]$ where $x = 1$ or 4 (b-i) with anion structures only, $[(C_2OH)C_1Im][BF_4]$ (j), and $[C_{12}(C_1Im)_2][BF_4]_2$ at $10\text{ }^\circ\text{C}/\text{min}$.

The first two m/z signals from **IL3** appeared between $100\text{ }^\circ\text{C}$ and $225\text{ }^\circ\text{C}$ and were a result of T_d of the IL to $[C_4C_1Im]-BF_2(C_4H_9)$ (**Figure 1c**). A broad peak for $[C_4C_1Im]-BF_2^{2+}$ was observed from

118 °C to 325 °C, and this was subsequently followed by NIP signals from 325 °C to 450 °C. The high intensity of C₁Im relative to [C₄C₁Im]⁺ suggested that IL *T_d* was occurring *via* an S_N2 mechanism.¹⁶ DIMS of **IL4** (**Figure 1d**) supported the results from **IL3** by further confirming that the NHC-BRF₂ product was preferentially formed at low temperature between 125 °C to 300 °C. Interestingly, a disubstituted [C₄C₁Im]-BF(C₃H₅)₂^{+•} radical cation was also identified, which highlighted that additional *T_d* processes were occurring before formation of volatile NHC-BRF₂. The high intensity of [C₄C₁Im]⁺ at > 300 °C showed that the vapour was primarily composed of intact NIPs.

IL5 showed similar trends (**Figure 1e**) to those observed for **IL4**. Between 150-250 °C, *T_d* of [C₄C₁Im][(C₆H₅)BF₃] gave a mixture of [C₄C₁Im]-BF(C₆H₅)^{+•}, [C₄C₁Im]-B(C₆H₅)₂^{+•}, and [C₄C₁Im]-BF₂^{+•}. As the temperature increased to > 300 °C, [C₄C₁Im]-BF₂^{+•} was still present, but [C₄C₁Im]⁺ NIPs dominated the MS; BF₂(C₆H₅)^{+•} was present throughout heating. For **IL6**, the fluorinated phenyl-ring resulted in larger amounts of [C₄C₁Im]-BF₂^{+•} at low temperature (**Figure 1f**) compared to non-fluorinated analogue **IL5**. Although a relatively small amount of [C₄C₁Im]-BF(C₆H₃F₂)^{+•} was present in the vapour from 200 °C to 350 °C, no disubstituted [C₄C₁Im]-B(C₆H₃F₂)₂^{+•} was observed. Again, it was unclear whether the increased electron withdrawing properties of the organo-group were influencing *T_d* processes, or EI fragmentation processes.

Unlike all other ILs, **IL7** showed [C₄C₁Im]⁺ was present at relatively low temperature from 150 °C (**Figure 1g**). The *T_d* product [C₄C₁Im]-BF₃ was only produced at higher temperatures which peaked at 300 °C, then steadily decreased. Both [C₄C₁Im]-B(C₇H₆OH)^{+•} and [C₄C₁Im]-BF(C₇H₆OH)

⁺ were observed which indicated the presence of [C₄C₁Im]-BF₂(C₇H₆OH), albeit at very high temperatures (325 °C to 450 °C). An unidentified decomposition product was also observed (m/z 181) from 275 °C to 450 °C, which further highlighted the complexity of *T_d* when reactive functional groups were present. **IL8** gave a low intensity signal for [C₄C₁Im]-BF(C₆H₁₁)⁺ (**Figure 1h**) but had the lowest onset temperature for [C₄C₁Im]-BF₃ production, which was present in the 80 °C drying step before heating was started. The dehydrogenation product B(C₆H₅)₃⁺ was observed at high temperature (325 °C to 400°C). The tetraphenylborate anion in **IL9** gave a reasonably high vacuum *T_d* (**Figure 1i**), albeit with low levels of signal < 300 °C. The presence of [C₄C₁Im]-B(C₆H₅)₃ fragmentation products showed that NHC-BR₃ adducts could form through *T_d*. The fragmentation product B(C₆H₅)₃⁺ was observed throughout and could have originated from NIPs or [C₄C₁Im]-B(C₆H₅)₃.

The hydroxyl-functionalized cation of **IL10** produced only two major signals (**Figure 1j**), which suggested that the IL had relatively simple *T_d* behavior. The vapour was found to consist of C₁Im, an expected decomposition product from loss of -C₂OH, and [(C₂O-)C₁Im]-BF⁺ (**Figure 2f**) which was identified following EI fragmentation rules. Low levels of NIPs were present in the vapour and a low intensity signal for [(C₂OH)C₁Im]-BF₂ was observed. In total six key NHC-BR_xF_{3-x} targets were identified as potential high-value products (**Figure 2**), including the cyclic compound identified from **IL10**. We are currently undertaking subsequent steps involving the scale-up and isolation of such compounds in a bespoke set-up to optimize production.

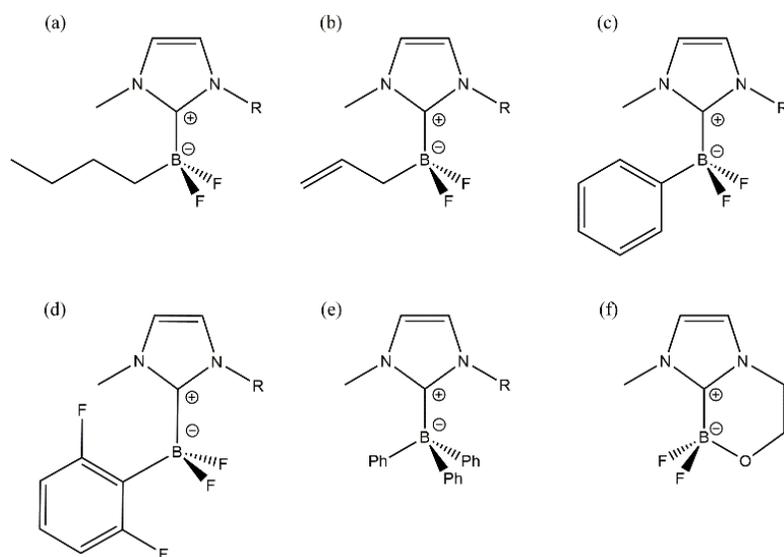


Figure 2. NHC- $\text{BR}_x\text{F}_{3-x}$ products identified as key targets from DIMS experiments.

Conclusions

A range of $[\text{C}_4\text{C}_1\text{Im}][\text{BR}_x\text{F}_{4-x}]$ ILs were prepared and thermally characterized. In all cases, organo-groups compromised thermal stabilities by introducing anion-led T_d steps far below $[\text{BF}_4]^-$ T_d . DIMS showed that vacuum thermolysis was a viable route to prepare high value NHC- $\text{BR}_x\text{F}_{3-x}$ compounds if the organic groups were thermally robust. In vacuum, all $[\text{C}_4\text{C}_1\text{Im}][\text{BR}_x\text{F}_{4-x}]$ ILs decomposed at lower temperatures than $[\text{C}_4\text{C}_1\text{Im}][\text{BF}_4]$, and mixtures of NIPs, NHC- $\text{BR}_x\text{F}_{3-x}$, and $\text{S}_{\text{N}}2$ T_d products were identified. Six $[\text{C}_4\text{C}_1\text{Im}][\text{BR}_x\text{F}_{4-x}]$ ILs were also identified as key precursors to novel NHC- $\text{BR}_x\text{F}_{3-x}$ compounds because NHC- $\text{BR}_x\text{F}_{3-x}$ was either produced at low temperatures or in high quantity. Although some ILs did not produce NHC- $\text{BR}_x\text{F}_{3-x}$, they may serve as ideal precursors to NHC- BF_3 compounds because of their potential to liberate NHC- BF_3 at low temperatures — likely because B-C bonds are significantly weaker than B-F bonds.³ Dicationic $[\text{C}_{12}(\text{C}_1\text{Im})_2][\text{BF}_4]_2$ decomposed by chain fragmentation, but hydroxyl-functionalised $[(\text{C}_2\text{OH})\text{C}_1\text{Im}][\text{BF}_4]$ produced significant quantities of a cyclic NHC- $\text{BR}_x\text{F}_{3-x}$ where the organic group was from the imidazolium alkyl-chain. By identifying key targets, we present the first steps

in realizing thermolysis as a viable short-cut to high value compounds that may bypass significant quantities of solvents, auxiliaries, and work-up procedures.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Experimental data including synthesis and characterization of ionic liquids, STA, TGA, DIMS, and TGA-MS data (PDF).

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Author Contributions

Experiments were performed by CJC, NDR, and AEJF. Data was interpreted by CJC and NDR and the manuscript was written by CJC. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

ILs, ionic liquids; PET, positron emission tomography; EI-MS, electron ionization mass spectrometry; T_d, thermal decomposition; DIMS, direct insertion mass spectrometry; NIPs, neutral ion pairs; DSC, differential scanning calorimetry; TGA, thermogravimetric analysis; STA, simultaneous thermal analysis; T_m, melting temperature; T_g, glass transition temperature; E_a, activation energy; T_{0.01/10}, temperature at which 1% mass is lost over 10 hours; T_{cc}, cold crystallization temperature; T_{ss}, solid-solid transition temperature; T_{onset}, onset of thermal decomposition; T_{1%}, 1% mass loss temperature;

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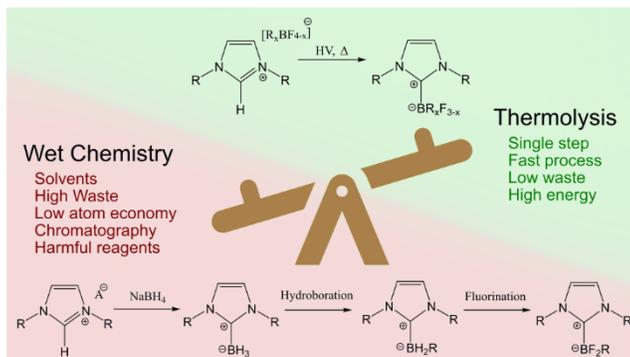
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SYNOPSIS. Organofluoroborates can be prepared by thermolysis of imidazolium organofluoroborate ionic liquids to avoid lengthy synthetic procedures and associated waste.