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Synthesis and properties of *N*,*N*′-dialkylimidazolium bis(nonafluorobutane-1-sulfonyl)imides: a new subfamily of ionic liquids

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Abstract—A series of *N*,*N*′-dialkylimidazolium bis(nonafluorobutane-1-sulfonyl)imides was synthesized in high yields by quaternization of imidazole derivatives with various readily available alkylating reagents, followed by anion exchange with highly stable and non-hygroscopic potassium bis(nonafluorobutane-1-sulfonyl)imide. The latter was obtained by an improved method starting from ammonium chloride and nonafluorobutane-1-sulfonyl fluoride. The quaternary imidazolium salts thus obtained constitute a new subfamily of thermally stable and remarkably hydrophobic ionic liquids with melting points in the range 0–40 °C and solubilities in water and organic solvents (aromatic hydrocarbons, dialkyl ethers) in the range of 0.5–1.5 wt%. The ionic liquids can be easily purified from ionic byproducts (e.g., halogenide salts) by aqueous extraction followed by thorough drying in a high vacuum without loss of yield. Due to the above features, these new ionic fluids may be considered as promising recyclable media in repeated catalytic processes.

1. Introduction

Low-melting salts containing lipophilic quaternary organic cations, ionic liquids, have attracted much interest in the area of electrochemistry as well as novel solvents and reaction media.[1] These fluids consisting of only ions were found to have no detectible equilibrium vapor pressure. In recognition of this remarkable property they were termed as environmentally benign or 'green' solvents.[1g] Many classical organic reactions were successfully modeled and often optimized in these media.

The first generation of ionic liquids comprised mainly the derivatives of inorganic halogen-ligated *ate*-complexes such as $BF_4^{\ominus}$, $PF_6^{\ominus}$ and $AlCl_4^{\ominus}$ as the anionic moieties. These anions, especially the latter two, are prone to releasing harmful and corrosive HF and HCl upon interaction with traces of moisture, which in turn imposes significant restrictions on applications of the corresponding ionic liquids. Moreover, uncontrolled halogenide content often affects and/or deteriorates transition metal catalysis.[1h] To circumvent these difficulties, other types of anions were introduced including *n*-alkyl sulfates, trifluoromethanesulfonates, bis(trifluoromethanesulfonyl)imides and tetraalkylborates. Alternative alkylating reagents, alkyl sulfates and sulfonates were employed in place of 'traditional' alkyl halogenides for synthesis of the *N*,*N*′-dialkylimidazolium moieties in order to completely eliminate the possibility of generating heavy halogenides ($Cl^{\ominus}$, $Br^{\ominus}$, $I^{\ominus}$). Special attention has been paid to ionic liquids containing *N*,*N*′-dialkylimidazolium cations combined with fluoroanions. As recently reviewed,[2] much diversity and availability of fluorine-containing anions ensure a broad range of properties and applications of the respective ionic liquids. Recently, *N*,*N*′-dialkylimidazolium bis(trifluoromethanesulfonyl)imides have received interest as remarkably thermo- and chemically stable ionic liquids.[2,3] In this respect, the anions combining high stability of bis(trifluoromethanesulfonyl)imide with much higher hydrophobicity due to higher fluorine content are of interest for design of novel ionic liquids as special solvent components for bi- and triphasic solvent systems. Herein, we report the synthesis and properties of *N*,*N*′-dialkylimidazolium bis(nonafluorobutane-1-sulfonyl)imides (**1** and **3**) and *N*,*N*′-dialkylimidazolium nonafluorobutane-1-sulfonates (**2**) as new series of ionic liquids (Fig. 1).

Keywords: Nonafluorobutane-1-sulfonyl fluoride; Dialkyl imidazolium; Bis(nonafluorobutane-1-sulfonyl)imide; Hydrophobicity; Ionic liquids.
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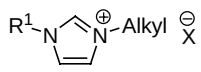


1–3

1: $R^1 = CH_3$, X = NNf_2
2: $R^1 = CH_3$, X = ONf
3: $R^1 = CH_3(CH_2)_2$, X = NNf_2
Nf:$CF_3(CF_2)_3SO_2$

Figure 1.

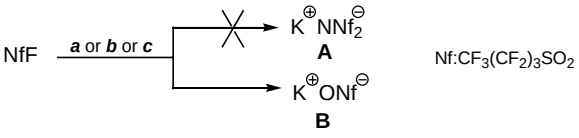
2. Results and discussion

Our approach towards the synthesis of compounds **1–3** is based on a two-step protocol, which comprises the quaternization of imidazole derivatives with various readily available alkylating reagents (alkyl bromides, chlorides, sulfates) followed by anion exchange with highly stable and non-hygroscopic potassium bis(nonafluorobutane-1-sulfonyl)imide (**A**) or potassium nonafluorobutane-1-sulfonate (**B**). We anticipated that the resulting salts **1–3** should be low-melting solids or even rt ionic liquids. They would be hydrophobic enough to make possible reduction of the residual halogenide content below detection limit by repeated extraction with deionized water without significant loss of yield at the purification step.

An inspection of available literature data showed that the potassium salt **A** could be synthesized directly from trifluoroacetamide or acetamide using the convenient and relatively inexpensive sulfonylating reagent, nonafluorobutane-1-sulfonyl fluoride (NfF),[4] in the presence of potassium carbonate.[5] As acetamide is widely available and cheap, it became a reactant of choice for the present study.

However, in our hands, no anticipated potassium imide **A** ($KNNf_2$) was obtained as a main reaction product (Scheme 1). Instead, potassium nonafluorobutane-1-sulfonate (KONf) (**B**) was isolated in reasonably good yield resulting from the reproduction of the literature procedure[5] (conditions **a**). The same results were obtained at rt employing either K_2CO_3 or more basic K_3PO_4 as an auxiliary base[6] in DMF as a solvent (modified conditions **b**).

A control experiment carried out with K_2CO_3 in the absence of acetamide (conditions **c**) revealed the same reaction



Scheme 1. a: $CH_3C(O)NH_2$, K_2CO_3 in THF 6 h at 65 °C, (62% yield);[7] **b**: $CH_3C(O)NH_2$, K_2CO_3 (73% yield) or K_3PO_4 (75% yield)[7] in DMF at rt; **c**: as in **b** employing K_2CO_3 but without $CH_3C(O)NH_2$, salt **B** (74% yield).

features (appearance, progress) resulting in a similar yield of KONf **B** as under conditions **b**. The identity of the main reaction product, KONf **B**[7] in all four protocols described above (see Scheme 1) was confirmed by FAB-MS analysis as well as by ^{19}F NMR measurements of the mixed samples indicating complete overlap of all the relevant signals (see Section 3).[8]

In the experiments with K_2CO_3, we noticed evolution of CO_2 gas during the reaction course and therefore inferred the following mechanism for the salt **B** formation (Scheme 2).

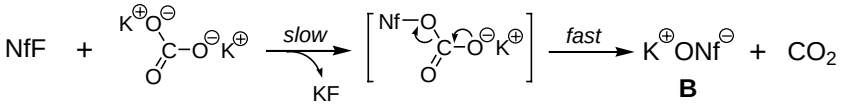
Presumably, acetamide remains mainly unreacted during the entire reaction course, and NfF interacts directly with K_2CO_3 owing to its affinity to anionic hard nucleophilic centers.[9] The lack of acetamide reactivity is attributed to the insufficient basicity of K_2CO_3 or K_3PO_4 failing to produce a sufficient equilibrial concentration of the reactive $CH_3C(O)NH^{\ominus}$ species for the desired *N*-sulfonylation to take place in favour of the direct interaction between NfF and K_2CO_3 (see Scheme 2).

To circumvent the difficulties caused by using K_2CO_3 we decided to develop a new protocol employing NH_4Cl instead of $CH_3C(O)NH_2$ and Et_3N,[10] which is fully compatible with NfF in MeCN as a reaction solvent.[11] This synthetic protocol proved to be successful and enabled us to obtain the intermediate triethylammonium salt $Et_3NH^{\oplus}NNf_2^{\ominus}$ (Scheme 3).

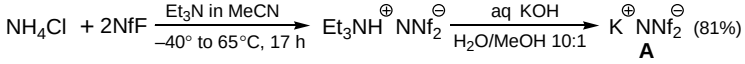
Subsequent treatment of the intermediate salt $Et_3NH^{\oplus}NNf_2^{\ominus}$ with aqueous KOH furnishes the desired pure potassium salt **A** as a white crystalline solid, which readily precipitates out of the aqueous solution[12] in good overall yield (see Section 3).

Both KONf and $KNNf_2$ were found to be thermally stable and non-hygroscopic salts.[13] They are poorly soluble in water, KONf somewhat better than $KNNf_2$. Remarkably, both salts show good solubilities in a number of organic solvents such as THF, MeCN, Me_2CO, AcOEt, DMSO, DMF, dioxane, 1,2-dimethoxyethane and alcohols although they are virtually insoluble in chlorohydrocarbon- and hydrocarbon solvents.

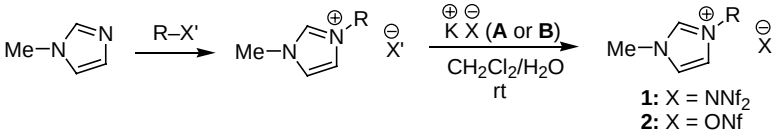
Having the requisite potassium salts **A** and **B** in hand, we established the synthesis of the target *N*-methyl-*N*′-alkyl imidazoliums **1** and **2** (Scheme 4). In a first step, an alkylation of *N*-methyl imidazole with a slight excess of RX′ was carried out upon heating without solvent



Scheme 2.



Scheme 3.



Scheme 4.

Table 1. Synthesis and properties of *N*-methyl-*N′*-alkyl imidazolium bis(nonafluorobutane-1-sulfonyl)imides **1** and nonaflates **2**

Entry	Reaction conditions			Product		Properties	
	RX' (equiv)	T (°C)	Time (h)	X	Salt 1 or 2 (yield, %)	Mp (°C)	Decomposition (°C)
1	$MeCH_2OSO_2Et$	rt[a]	17	NNf_2^-	**1a** (98)	<25[b] (31 °C)[15]	290
2	$Me(CH_2)_2Br$	70	4	NNf_2^-	**1b** (98)	<4[c]	300
3	$Me(CH_2)_3Cl$[17]	90	24	NNf_2^-	**1c** (>99)	<25[b]	320
4	$Me(CH_2)_4Br$	70	3	NNf_2^-	**1d** (97)	<25[b]	295
5	$Me_2CH(CH_2)_2Br$	70	5	NNf_2^-	**1e** (>99)	39–40	280
6	Me_2CHCH_2Br	70	17	NNf_2^-	**1f** (>99)	<4[c]	295
7	Me_2CHBr	70	24	NNf_2^-	**1g** (99)	28–29 °C	310
8	$MeCH_2CH(Me)Br$	70	24	NNf_2^-	**1h** (>99)	<4[c]	280
9	$Me(CH_2)_2Br$	70	4	ONf^-	**2a** (82)	33–34	285
10	$Me(CH_2)_3Cl$[17]	90	24	ONf^-	**2b** (82)	<25[b] (20 °C)[3]	295
11	Me_2CHBr	70	24	ONf^-	**2c** (81)	<25[b]	310
12	$MeCH_2CH(Me)Br$	70	24	ONf^-	**2d** (79)	42–43	280

[a] An appreciable exothermic effect was observed during the alkylation.
[b] Crystallizes in a fridge (+4 °C) and melts at rt again.
[c] Crystallizes in a deep freezer (−18 °C) and melts in a fridge (+4 °C) again.

(see Table 1) followed by removal of volatiles (if any) in high vacuum to give a nearly quantitative yield of the corresponding *N*-methyl-*N′*-alkyl imidazolium salts.[14]

The desired ionic fluids **1**, **2** were then produced by anion exchange with KX (**A** or **B**) in biphasic CH_2Cl_2/H_2O mixture followed by thorough washing of the organic phase with deionized water until a negative halogenide test with aqueous $AgNO_3$ was achieved. Removal of CH_2Cl_2 followed by thorough drying in high vacuum enabled us to obtain the ionic liquids **1**[15] and **2**[16] in high yields and purities. The alkylation reaction conditions, yields and properties of the *N*-methyl-*N′*-alkyl imidazolium salts **1** and **2** obtained are summarized in the Table 1.

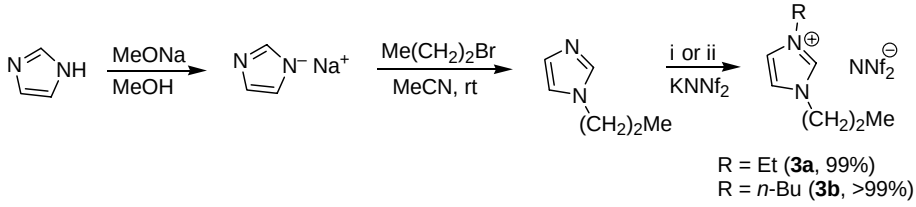
Unfortunately, among the few commercially available *N*-alkyl imidazoles, only *N*-methyl imidazole is offered at an affordable price. Hence, the ionic liquids obtained as described above are limited invariably to imidazolium derivatives comprising a *N*-methyl substituent.

To circumvent this limitation, we developed a one pot sequential alkylation protocol starting from parent imidazole. The protocol is exemplified by the synthesis of the products **3a**,**b** (Scheme 5).

Treatment of imidazole with MeONa in MeOH followed by removal of the solvent gave sodium imidazolide quantitatively. The first alkylation with *n*-propyl bromide was carried out in MeCN and enabled the introduction of only one propyl group with >95% selectivity. The second alkylation conducted after removal of MeCN in vacuum furnished the desirable unsymmetrical *N*,*N′*-dialkyl imidazolium moiety. This protocol culminated with anion exchange with $KNNf_2$ as described above resulting in the isolation of the anticipated products **3a**,**b** in high yields and at least 95% purity according to ^1H NMR spectroscopic data.

The imidazolium salts **1**–**3** are thermally stable (up to 300—320 °C), colourless or yellowish non-hygroscopic fluids or low-melting crystalline solids (Table 1). They neither change appearance nor gain weight upon exposure to atmospheric moisture for at least 1 week. The NNf_2-derivatives tend to melt at lower temperatures than their ONf-counterpart. Not surprisingly, symmetrical *N*,*N′*-dimethyl imidazolium bis(nonafluorobutane-1-sulfonyl)imide has a higher melting point (69 °C)[15] compared to the unsymmetrically substituted salts **1** and **3**.

In general, all NNf_2-derived ionic liquids presented in this work have interesting specific properties. We believe that the high content of perfluorobutyl groups in NNf_2-derived ionic liquids is accountable for their unique characteristics. Unlike conventional ionic liquids, which are often miscible with chlorohydrocarbon solvents, the salts **1** tend to form



Scheme 5. (i) $(EtO)_2SO_2$, 0 °C to rt, 17 h; (ii) $Me(CH_2)_3Br$, 70 °C, 3 h.

two-phase mixtures with chloroform. Thus, the salt **1h** forms a two-phase system upon mixing with $CDCl_3$, with the concentrations of **1h** in the upper and lower phases 3.5 and 45.5 wt%, respectively. The mixture turns homogeneous upon heating and separates to two-phases upon cooling down to rt.

The nature of the ionic liquids **1** is especially pronounced in their remarkably low solubilities in typical organic solvents (toluene, dialkyl ethers) and water. For example, the ionic liquid **1c** shows solubilities of 0.7 wt% in water, 0.3 wt% in toluene and 1.2 wt% in diisopropyl ether, that is, it is virtually immiscible with the above solvents. Specific solvation effects in the salts **1** make them truly orthogonal reaction media and should allow an easy recycling of these ionic liquids by extractive removal of organic products and inorganic salts with organic solvents and water, respectively. This feature may turn out to be useful in the design of new recoverable catalytic systems.[18]

3. Experimental

3.1. General

NMR spectra were recorded on Bruker 400 UltraShield instrument in $CDCl_3$ as a solvent unless stated otherwise. ^1H and ^{13}C chemical shifts are expressed as ppm downfield from $SiMe_4$ ($\delta=0$) used as an internal standard. ^{19}F chemical shifts are given in ppm upfield from $PhCF_3$ ($\delta=-63.7$ ppm)[19] used as an internal standard. ^{13}C signals of the $CF_3(CF_2)_3$ groups were not given due to very complicated and overlapping heteronuclear $^{13}C,^{19}F$ coupling patterns. ^{15}N NMR signals of the 1-isopropyl-3-methylimidazolium cation in the salt **1g** are obtained using insensitive nuclei enhanced by polarization (INEPT) technique with the chemical shifts expressed as ppm upfield from $MeNO_2$ ($\delta=0$) used as an external standard. Mass spectra were registered with Finnigan MAT 95XP (FAB-HRMS) and with Macromass Quattro micro™ API (ESI-MS) spectrometers. Decomposition temperatures of the salts **B**, **1** and **2** were determined with SDT 2960 Simultaneous DSC-TGA instrument. Microanalyses were performed with Euro Elemental Analyser. Melting points were determined using Büchi Melting Point B-540 apparatus and are uncorrected.

The syntheses of the potassium salts **A** and **B** were carried out under an atmosphere of argon in heat-gun dried reaction flasks. Solvents for syntheses were dried following standard procedures and freshly distilled prior to use: DMF (vacuum distillation from CaH_2), MeCN (distillation from CaH_2), THF (distillation from Na–K alloy/Ph_2CO). Solvents for extraction were distilled before use. Nonafluorobutane-1-sulfonyl fluoride was obtained from Bayer AG; it can also be purchased from commercial suppliers. *N*-Methyl imidazole (Fluka) was distilled and stored over BaO.

The alkylating reagents (see Table 1), purchased from Lancaster, Aldrich and Fluka were distilled before use.

K_2CO_3 (Fluka), $K_3PO_4\cdot H_2O$ (Riedel-de-Haen), NH_4Cl (Merck), $CH_3C(O)NH_2$ (Acros Organics) and imidazole (Lancaster) were dried in high vacuum before use. Et_3N (Riedel-de-Haen) was stored over KOH pellets.

3.1.1. Potassium bis(nonafluorobutane-1-sulfonyl)imide (A). NH_4Cl (13.9 g, 250 mmol) was placed into 1 L reaction flask equipped with efficient magnetic stirring bar and dried under high vacuum (hereafter HV) to remove traces of moisture before MeCN (125 mL) and NfF (166.9 g, 550 mmol) were added. The resulting two-phase suspension was cooled down to −40 °C, and Et_3N (127.6 g, 1250 mmol) pre-cooled with liquid nitrogen was quickly added to the reaction mixture upon vigorous stirring. After gradual warming up to ambient temperature, the resulting mixture was heated up to 65 °C and stirred at this temperature overnight. After cooling down to ambient temperature the bulk of MeCN was removed in vacuum. The residue was partitioned between CH_2Cl_2 (400 mL) and deionized water (200 mL). The organic layer was then thoroughly washed with deionized water (3×200 mL) until it showed a negative chloride test with aqueous $AgNO_3$. Volatiles were removed in vacuum to give the intermediate $Et_3NH^{\oplus}NNf_2^{\ominus}$ (165.85 g, 97% yield) as a tawny crystalline solid, mp 42–43 °C, ^1H NMR (400.23 MHz): δ 1.33 (9H, t, $^3J=7.3$ Hz, $3CH_2\mathit{CH}_3$), 3.18 (6H, br q, $^3J=7.3$ Hz, $3\mathit{CH}_2CH_3$), 7.19 (1H, br s, NH^+). ^{13}C NMR (100.65 MHz): δ 8.5 ($CH_2\mathit{CH}_3$), 47.2 (CH_2CH_3). ^{19}F NMR (376.59 MHz): δ −127.1 (4F, t*, $J=14.3$ Hz, $2CF_2$-3), −122.1 (4F, m_c, $2CF_2$-2), −113.9 (4F, t*, $J=14.3$ Hz, $2CF_2$-1), −81.9 (6F, tt, $J_1=10.0$ Hz, $J_2=2.3$ Hz, $2CF_3$); *further splitting due to the multiple $^{19}F,^{19}F$ couplings.

Without further purification, $Et_3NH^{\oplus}NNf_2^{\ominus}$ (165.9 g, 243 mmol) was dissolved in MeOH (30 mL) and added dropwise to the solution of KOH (27.0 g, 590 mmol) in water (300 mL) upon vigorous stirring. Instantaneous precipitation of the desired $KNNf_2$ **A** was observed. The reaction mixture was stirred overnight before filtering the precipitate. The crystalline residue was washed thoroughly with cold deionized water until neutral pH followed by drying on the sinter funnel and washing additionally with $CHCl_3$ (3×150 mL) to give the salt **A** (148.83 g, 81% yield) as a white crystalline solid, mp 340–341 °C (decomp.). **A**, ^{19}F NMR (376.59 MHz, DMSO-d_6): δ −128.2 (4F, t*, $J=13.9$ Hz, $2CF_2$-3), −123.5 (4F, m_c, $2CF_2$-2), −115.8 (4F, t*, $J=13.5$ Hz, $2CF_2$-1), −82.8 (6F, tt, $J_1=9.8$ Hz, $J_2=2.3$ Hz, $2CF_3$); *further splitting due to the multiple $^{19}F,^{19}F$ couplings. HRMS (FAB negative, Cs, 20 keV, direct, glycerin, *m/z*), found: 579.9083. Calcd ($C_8F_{18}NO_4S_2^-$): 579.8976. Anal. Calcd for $C_8F_{18}KNO_4S_2$: C, 15.52; F, 55.22; N, 2.26; S, 10.36. Found: C, 15.50; H, 0; N, 2.32; S, 10.60.

3.1.2. Attempts to prepare the potassium salt (A) by interaction of acetamide with NfF in the presence of K_2CO_3 or K_3PO_4: potassium nonafluorobutanesulfonate (B) (see Scheme 1).

a: according to the literature procedure:[5] The synthesis was attempted using $CH_3C(O)NH_2$ (0.827 g, 14.0 mmol), K_2CO_3 (5.00 g, 36.0 mmol), THF (15 mL) and NfF (2× 4.23 g, 2×14 mmol). After heating for the designated time (2×3 h) and removal of volatiles in vacuum, the mixed

solid residue was treated with Me_2CO (25 mL) and filtered; the insoluble precipitate on the sinter funnel was washed with Me_2CO, the combined filtrate was evaporated in vacuum, MeOH (10 mL) was added to the residue, and the resulting mixture was refluxed for a few minutes until the crystalline residue was completely dissolved. The resulting homogenous solution was diluted with $CHCl_3$. The crystalline precipitate was filtered off and dried to give 5.40 g of white crystalline solid, which was identified as potassium nonaflate **B** (62% yield).

b: room temperature modification employing DMF as a solvent: K_2CO_3 (81.8 g, 592 mmol) was dried at 200 °C in a HV for 3 h and transferred into 500 mL reaction flask equipped with efficient magnetic stirring bar. After flushing with dry argon and cooling, DMF (160 mL), dry CH_3-$C(O)NH_2$ (9.54 g, 161.5 mmol) and followed by NfF (103.4 g, 342 mmol) were consecutively added at rt. The reaction mixture was stirred for 40 h. During first 24 h, evolution of CO_2 was clearly observed. The isolation carried out as described above furnished 84.42 g of white crystalline solid, which was identified as potassium nonaflate **B** (73% yield). Likewise, the analogous reaction carried out with K_3PO_4 in place of K_2CO_3 afforded the salt **B** in 75% yield.

c: a reference experiment in DMF conducted in the absence of $CH_3C(O)NH_2$: The experiment was carried out with K_2CO_3 (3.24 g, 23.4 mmol), DMF (15 mL) and NfF (4.75 g, 15.7 mmol) as described above, the progress and appearance being identical. The workup and the isolation as described above resulted in the salt **B** (3.72 g, 74% yield) as a white crystalline solid, decomp. ca. 450 °C. **B**, ^{19}F NMR (376.59 MHz, DMSO-d_6): δ −128.1 (4F, t*, J=13.5 Hz, $2CF_2$-3), −123.8 (4F, m$_c$, $2CF_2$-2), −117.2 (4F, t*, J=13.5 Hz, $2CF_2$-1), −83.0 (6F, tt, J_1=9.8 Hz, J_2=2.9 Hz, $2CF_3$); *further splitting due to the multiple ^{19}F,^{19}F couplings. HRMS (FAB negative, Cs, 20 keV, direct, glycerin, *m/z*), found: 298.9449. Calcd ($C_4F_9O_3S^-$): 298.9419. Anal. Calcd for $C_4F_9KO_3S$: C, 14.21; F, 50.56; S, 9.48. Found: C, 14.48; H, 0; S, 9.75.

3.2. Synthesis of *N*-methyl-*N′*-alkyl imidazolium bis(nonafluorobutane-1-sulfonyl)imides (1) and nonaflates (2) (see Scheme 4): general procedure (GP1)

A mixture of *N*-methylimidazole (1.05 equiv) and the alkylating reagent R′X (1.1 equiv) was stirred under the conditions (temperature and time) specified in the Table 1. The volatiles were then removed in HV, the residue was dissolved in CH_2Cl_2 (typically 0.15–0.20 mmol/mL) and transferred into the separating funnel containing a suspension of the salt **A** or **B** (0.85–1 equiv) in water (typically 0.25–0.30 mmol/mL). The content of the funnel was vigorously shaken for 3–5 min so that no further precipitate was present in the resulting two-phase mixture. The organic layer was washed with dilute HCl (pH 1) and 3–4 times with deionized water so that the last aqueous layer after extraction should indicate pH 6–7 and give a negative halogenide test with aqueous $AgNO_3$. CH_2Cl_2 was removed in vacuum, and the residue was vigorously stirred for 15–17 h at 40–50 °C under HV to give the desired molten salt **1** or **2** in the designated yield (see Table 1).

3.2.1. 1-Ethyl-3-methylimidazolium bis(nonafluorobutane-1-sulfonyl)imide (1a). The title compound was prepared from *N*-methylimidazole (1.314 g, 16.0 mmol), $(EtO)_2SO_2$ (2.35 g, 15.2 mmol) and the salt **A** (9.00 g, 14.5 mmol) as described in GP1; yield 9.82 g (98%) as a clear viscous slightly yellowish liquid. **1a**, ^{1}H NMR (400.23 MHz, DMSO-d_6): δ 1.42 (3H, t, ^3J=7.3 Hz, CH_2CH_3), 3.85 (3H, s, NCH_3), 4.19 (2H, q, ^3J=7.3 Hz, NCH_2), 7.69 (1H, t, J=1.8 Hz) and 7.78 (1H, t, J=1.8 Hz) (both *CH*=*CH*), 9.11 (1H, br s, N–*CH*=N). ^{13}C NMR (100.65 MHz, DMSO-d_6): δ 15.1 (CH_2CH_3), 35.7 (NCH_3), 44.1 (NCH_2), 122.0 and 123.6 (both *CH*=*CH*), 136.3 (N–*CH*=N). ^{19}F NMR (376.59 MHz, DMSO-d_6): δ −128.1 (4F, t*, J=14 Hz, $2CF_2$-3), −123.4 (4F, m$_c$, $2CF_2$-2), −115.7 (4F, br t, J=14 Hz, $2CF_2$-1), −82.8 (6F, tt, J_1=9.7 Hz, J_2=2.5 Hz, $2CF_3$); *further splitting due to the multiple ^{19}F,^{19}F couplings. MS (ESI positive, ion energy 0.3 eV), *m/z* (%): 111.03 [$C_6H_{11}N_2^+$] (100) and lighter fragments. MS (ESI negative, ion energy 0.3 eV), *m/z* (%): 579.86 [$(C_4F_9SO_2)_2N^-$] (100), 296.95 [$C_4F_9SO_2N^-$] (24.3) and lighter fragments.

3.2.2. 1-Propyl-3-methylimidazolium bis(nonafluorobutane-1-sulfonyl)imide (1b). The title compound was prepared from *N*-methylimidazole (1.223 g, 14.9 mmol), $Me(CH_2)_2Br$ (1.93 g, 15.7 mmol) and the salt **A** (8.79 g, 14.2 mmol) as described in GP1; yield 9.85 g (98%) as a clear yellowish viscous liquid. **1b**, ^{1}H NMR (400.23 MHz, DMSO-d_6): δ 0.87 (3H, t, ^3J=7.4 Hz, CH_2CH_3), 1.81 (2H, sextet, ^3J=7.3 Hz, CH_2CH_3), 3.86 (3H, s, NCH_3), 4.13 (2H, t, ^3J=7.1 Hz, NCH_2), 7.70 (1H, t, J=1.8 Hz) and 7.76 (1H, t, J=1.8 Hz) (both *CH*=*CH*), 9.10 (1H, br s, N–*CH*=N). ^{13}C NMR (100.65 MHz, DMSO-d_6): δ 10.3 (CH_2CH_3), 22.9 (CH_2CH_3), 35.7 (NCH_3), 50.3 (NCH_2), 122.3 and 123.7 (both *CH*=*CH*), 136.6 (N–*CH*=N). ^{19}F NMR (376.59 MHz, DMSO-d_6): δ −128.1 (4F, t*, J=14 Hz, $2CF_2$-3), −123.3 (4F, m$_c$, $2CF_2$-2), −115.6 (4F, br t, J=14 Hz, $2CF_2$-1), −82.8 (6F, tt, J_1=9.7 Hz, J_2=2.5 Hz, $2CF_3$); *further splitting due to the multiple ^{19}F,^{19}F couplings. MS (ESI positive, ion energy 0.3 eV), *m/z* (%): 125 [$C_7H_{13}N_2^+$] (100) and lighter fragments. MS (ESI negative, ion energy 0.3 eV), *m/z* (%): 580 [$(C_4F_9SO_2)_2N^-$] (100) and lighter fragments.

3.2.3. 1-Butyl-3-methylimidazolium bis(nonafluorobutane-1-sulfonyl)imide (1c). The title compound was prepared from *N*-methylimidazole (1.20 g, 14.6 mmol), $Me(CH_2)_3Cl$ (1.42 g, 15.3 mmol) and the salt **A** (8.61 g, 13.9 mmol) as described in GP1; yield 9.96 g (>99%) as a clear yellowish viscous liquid. **1c**, ^{1}H NMR (400.23 MHz): δ 0.94 (3H, t, ^3J=7.4 Hz, CH_2CH_3), 1.36 (2H, sextet, ^3J=7.4 Hz, CH_2CH_3), 1.85 (2H, m$_c$, NCH_2CH_2), 3.93 (3H, s, NCH_3), 4.18 (2H, t, ^3J=7.6 Hz, NCH_2), 7.38 (1H, t, J=1.7 Hz) and 7.40 (1H, t, J=1.7 Hz) (both *CH*=*CH*), 8.71 (1H, br s, N–*CH*=N). ^{13}C NMR (100.65 MHz): δ 12.6 (CH_2CH_3), 19.0 (CH_2CH_3), 31.8 (NCH_2CH_2), 35.8 (NCH_3), 49.7 (NCH_2), 122.3 and 123.6 (both *CH*=*CH*), 135.7 (N–*CH*=N). ^{19}F NMR (376.59 MHz): δ −127.0 (4F, t*, J=14 Hz, $2CF_2$-3), −122.0 (4F, m$_c$, $2CF_2$-2), −113.8 (4F, br t, J=14 Hz, $2CF_2$-1), −82.0 (6F, tt, J_1=9.9 Hz, J_2=2.3 Hz, $2CF_3$); *further splitting due to the multiple ^{19}F,^{19}F couplings. MS (ESI positive, ion energy 0.3 eV), *m/z* (%): 139.1

$[C_8H_{15}N_2^+]$ (100) and lighter fragments. MS (ESI negative, ion energy 0.3 eV), *m/z* (%): 580.0 $[(C_4F_9SO_2)_2N^-]$ (100) and lighter fragments.

3.2.4. 1-Pentyl-3-methylimidazolium bis(nonafluorobutane-1-sulfonyl)imide (1d). The title compound was prepared from *N*-methylimidazole (1.172 g, 14.3 mmol), $Me(CH_2)_4Br$ (2.27 g, 15.0 mmol) and the salt **A** (8.42 g, 13.6 mmol) as described in GP1; yield 9.66 g (97%) as a clear yellowish viscous liquid. **1d**, ^{1}H NMR (400.23 MHz): δ 0.87 (3H, t, $^3J=7$ Hz, CH_2CH_3), 1.23–1.38 (4H, *m*, $CH_2CH_2CH_3$), 1.84 (2H, quintet, $^3J=7.5$ Hz, NCH_2CH_2), 3.91 (3H, s, NCH_3), 4.14 (2H, t, $^3J=7.6$ Hz, NCH_2), 7.32 (1H, t, $J=1.8$ Hz) and 7.33 (1H, t, $J=1.8$ Hz) (both *CH*=*CH*), 8.73 (1H, br s, N–*CH*=N). ^{13}C NMR (100.65 MHz): δ 13.4 (CH_2CH_3), 21.8 (CH_2CH_3), 28.0 and 29.7 (both CH_2) 36.0 (NCH_3), 50.0 (NCH_2), 122.2 and 123.7 (both *CH*=*CH*), 135.9 (N–*CH*=N). ^{19}F NMR (376.59 MHz): δ −127.1 (4F, t*, $J=14$ Hz, $2CF_2$-3), −122.2 (4F, m_c, $2CF_2$-2), −114.0 (4F, br t, $J=14$ Hz, $2CF_2$-1), −82.0 (6F, tt, $J_1=9.9$ Hz, $J_2=2$ Hz, $2CF_3$); *further splitting due to the multiple ^{19}F,^{19}F couplings. MS (ESI positive, ion energy 0.3 eV), *m/z* (%): 153.172 $[C_9H_{17}N_2^+]$ (100) and lighter fragments. MS (ESI negative, ion energy 0.3 eV), *m/z* (%): 579.951 $[(C_4F_9SO_2)_2N^-]$ (100) and lighter fragments.

3.2.5. 1-(3-Methyl-butyl)-3-methylimidazolium bis(nonafluorobutane-1-sulfonyl)imide (1e). The title compound was prepared from *N*-methylimidazole (1.223 g, 14.9 mmol), $Me_2CH(CH_2)_2Br$ (1.93 g, 15.7 mmol) and the salt **A** (8.42 g, 13.6 mmol) as described in GP1; yield 9.97 g (>99%) as a yellowish crystalline solid, mp 39–40 °C. **1e**, ^{1}H NMR (400.23 MHz, DMSO-d_6): δ 0.92 (6H, d, $^3J=6.7$ Hz, Me_2CH), 1.52 (1H, nonet, $^3J=6.7$ Hz, Me_2CH), 1.70 (2H, dt, $^3J_1=7.8$ Hz, $^3J_2=6.7$ Hz, NCH_2CH_2), 3.85 (3H, s, NCH_3), 4.18 (2H, t, $^3J=7.6$ Hz, NCH_2), 7.69 (1H, t, $J=1.8$ Hz) and 7.78 (1H, t, $J=1.8$ Hz) (both *CH*=*CH*), 9.12 (1H, br s, N–*CH*=N). ^{13}C NMR (100.65 MHz, DMSO-d_6): δ 21.9 (Me_2CH), 24.8 (Me_2CH), 35.7 (NCH_3), 38.2 (NCH_2CH_2), 47.2 (NCH_2), 122.3 and 123.6 (both *CH*=*CH*), 136.5 (N–*CH*=N). ^{19}F NMR (376.59 MHz, DMSO-d_6): δ −128.1 (4F, t*, $J=14$ Hz, $2CF_2$-3), −123.4 (4F, m_c, $2CF_2$-2), −115.7 (4F, br t, $J=14$ Hz, $2CF_2$-1), −82.8 (6F, tt, $J_1=9.8$ Hz, $J_2=2.6$ Hz, $2CF_3$); *further splitting due to the multiple ^{19}F,^{19}F couplings. MS (ESI positive, ion energy 0.3 eV), *m/z* (%): 153.2 $[C_9H_{17}N_2^+]$ (100) and lighter fragments. MS (ESI negative, ion energy 0.3 eV), *m/z* (%): 580.0 $[(C_4F_9SO_2)_2N^-]$ (100) and lighter fragments.

3.2.6. 1-Isobutyl-3-methylimidazolium bis(nonafluorobutane-1-sulfonyl)imide (1f). The title compound was prepared from *N*-methylimidazole (1.20 g, 14.6 mmol), Me_2CHCH_2Br (1.42 g, 15.3 mmol) and the salt **A** (8.61 g, 13.9 mmol) as described in GP1; yield 9.99 g (>99%) as a clear yellowish viscous liquid. **1f**, ^{1}H NMR (400.23 MHz): δ 0.94 (6H, d, $^3J=6.7$ Hz, Me_2CH), 2.15 (1H, nonet, $^3J=6.8$ Hz, Me_2CH), 3.95 (3H, s, NCH_3), 4.00 (2H, t, $^3J=7.4$ Hz, NCH_2), 7.39 (1H, t, $J=1.8$ Hz) and 7.41 (1H, t, $J=1.8$ Hz) (both *CH*=*CH*), 8.72 (1H, br s, N–*CH*=N). ^{13}C NMR (100.65 MHz): δ 18.6 (Me_2CH), 29.1 (Me_2CH), 35.8 (NCH_3), 56.7 (NCH_2), 122.7 and 123.6 (both *CH*=*CH*), 135.9 (N–*CH*=N). ^{19}F NMR (376.59 MHz): δ −127.0 (4F, t*, $J=14$ Hz, $2CF_2$-3), −122.0 (4F, m_c, $2CF_2$-2), −113.8 (4F, br t, $J=14$ Hz, $2CF_2$-1), −82.0 (6F, tt, $J_1=9.9$ Hz, $J_2=2.3$ Hz, $2CF_3$); *further splitting due to the multiple ^{19}F,^{19}F couplings. MS (ESI positive, ion energy 0.3 eV), *m/z* (%): 139.1 $[C_8H_{15}N_2^+]$ (100) and lighter fragments. MS (ESI negative, ion energy 0.3 eV), *m/z* (%): 580.0 $[(C_4F_9SO_2)_2N^-]$ (100) and lighter fragments.

3.2.7. 1-Isopropyl-3-methylimidazolium bis(nonafluorobutane-1-sulfonyl)imide (1g). The title compound was prepared from *N*-methylimidazole (1.22 g, 14.9 mmol), Me_2CHBr (1.93 g, 15.7 mmol) and the salt **A** (8.79 g, 14.2 mmol) as described in GP1; yield 9.87 g (99%) as a slightly yellowish deliquescent crystalline solid, mp 28–29 °C. **1g**, ^{1}H NMR (400.23 MHz, DMSO-d_6): δ 1.48 (6H, d, $^3J=6.7$ Hz, Me_2CH), 3.85 (3H, s, NCH_3), 4.63 (1H, heptet, $^3J=6.7$ Hz, $NCHMe_2$), 7.71 (1H, t, $J=1.8$ Hz) and 7.87 (1H, t, $J=1.8$ Hz) (both *CH*=*CH*), 9.17 (1H, br s, N–*CH*=N). ^{13}C NMR (100.65 MHz, DMSO-d_6): δ 22.3 (Me_2CH), 35.7 (NCH_3), 52.2 ($NCHMe_2$), 120.5 and 123.7 (both *CH*=*CH*), 135.4 (N–*CH*=N). ^{15}N NMR (40.57 MHz, DMSO-d_6): δ −183.6 and −210.4 (both endocyclic N). ^{19}F NMR (376.59 MHz, DMSO-d_6): δ −128.1 (4F, t*, $J=14$ Hz, $2CF_2$-3), −123.3 (4F, m_c, $2CF_2$-2), −115.6 (4F, br t, $J=14$ Hz, $2CF_2$-1), −82.8 (6F, tt, $J_1=9.8$ Hz, $J_2=2.6$ Hz, $2CF_3$); *further splitting due to the multiple ^{19}F,^{19}F couplings. MS (ESI positive, ion energy 0.3 eV), *m/z* (%): 125.114 $[C_7H_{13}N_2^+]$ (100) and lighter fragments. MS (ESI negative, ion energy 0.3 eV), *m/z* (%): 579.950 $[(C_4F_9SO_2)_2N^-]$ (100) and lighter fragments.

3.2.8. 1-*sec*-Butyl-3-methylimidazolium bis(nonafluorobutane-1-sulfonyl)imide (1h). The title compound was prepared from *N*-methylimidazole (1.20 g, 14.6 mmol), $MeCH_2CH(Me)Br$ (2.10 g, 15.3 mmol) and the salt **A** (7.25 g, 11.7 mmol) as described in GP1; yield 8.38 g (>99%) as a clear viscous tawny liquid. **1h**, ^{1}H NMR (400.23 MHz, DMSO-d_6): δ 0.78 (3H, t, $^3J=7.4$ Hz, CH_3CH_2), 1.47 (3H, d, $^3J=6.9$ Hz, CH_3CH), 1.80 (2H, m_c, CH_3CH_2), 3.86 (3H, s, NCH_3), 4.41 (1H, sextet, $^3J=6.9$ Hz, NCH), 7.73 (1H, t, $J=1.7$ Hz) and 7.86 (1H, t, $J=1.7$ Hz) (both *CH*=*CH*), 9.17 (1H, br s, N–*CH*=N). ^{13}C NMR (100.65 MHz, DMSO-d_6): δ 9.9 (CH_2CH_3), 20.2 (CH_3CHN), 29.1 (CH_2CH_3), 35.8 (NCH_3), 57.8 (NCH), 120.4 and 123.9 (both *CH*=*CH*), 135.7 (N–*CH*=N). ^{19}F NMR (376.59 MHz, DMSO-d_6): δ −128.1 (4F, t*, $J=14$ Hz, $2CF_2$-3), −123.4 (4F, m_c, $2CF_2$-2), −115.7 (4F, br t, $J=14$ Hz, $2CF_2$-1), −82.8 (6F, tt, $J_1=9.8$ Hz, $J_2=2.6$ Hz, $2CF_3$); *further splitting due to the multiple ^{19}F,^{19}F couplings. MS (ESI positive, ion energy 0.3 eV), *m/z* (%): 139.1 $[C_8H_{15}N_2^+]$ (100) and lighter fragments. MS (ESI negative, ion energy 0.3 eV), *m/z* (%): 580.0 $[(C_4F_9SO_2)_2N^-]$ (100) and lighter fragments.

3.2.9. 1-Propyl-3-methylimidazolium nonafluorobutanesulfonate (2a). The title compound was prepared from *N*-methylimidazole (2.044 g, 24.9 mmol), $Me(CH_2)_2Br$ (3.21 g, 26.1 mmol) and the salt **B** (8.00 g, 23.7 mmol) as described in GP1; yield 8.25 g (82%) as a slightly yellowish crystalline solid, mp 33–34 °C. **2a**, ^{1}H NMR (400.23 MHz): δ 0.94 (3H, t, $^3J=7.4$ Hz, CH_2CH_3), 1.90 (2H, sextet, $^3J=7.4$ Hz, CH_2CH_3), 3.96 (3H, s, NCH_3), 4.15 (2H, t,

^3J=7.4 Hz, NCH_2), 7.41 (1H, t, J=1.8 Hz) and 7.43 (1H, t, J=1.8 Hz) (both *CH*=*CH*), 9.09 (1H, br s, N–*CH*=N). ^{13}C NMR (100.65 MHz): δ 10.4 (CH_2CH_3), 23.4 (CH_2CH_3), 36.3 (NCH_3), 51.5 (NCH_2), 122.1 and 123.6 (both *CH*=*CH*), 136.9 (N–*CH*=N). ^{19}F NMR (376.59 MHz): δ −127.1 (2F, t*, J=14.2 Hz, 2CF_2-3), −122.7 (2F, m$_c$, 2CF_2-2), −115.9 (2F, t*, J=14.2 Hz, 2CF_2-1), −82.0 (3F, tt, J_1=9.9 Hz, J_2=2.7 Hz, 2CF_3); *further splitting due to the multiple ^{19}F,^{19}F couplings. MS (ESI positive, ion energy 0.3 eV), *m*/*z* (%): 125 [$C_7H_{13}N_2^+$] (100) and lighter fragments. MS (ESI negative, ion energy 0.3 eV), *m*/*z* (%): 298.9 [$C_4F_9SO_3^-$] (100) and lighter fragments.

3.2.10. 1-Butyl-3-methylimidazolium nonafluorobutanesulfonate (2b). The title compound was prepared from *N*-methylimidazole (2.04 g, 24.9 mmol), Me$(CH_2)_3$Cl (2.42 g, 26.1 mmol) and the salt **B** (8.00 g, 23.7 mmol) as described in GP1; yield 8.52 g (82%) as a clear yellow viscous liquid. **2b**, ^{1}H NMR (400.23 MHz): δ 0.94 (3H, t, ^3J=7.4 Hz, CH_2CH_3), 1.35 (2H, sextet, ^3J=7.5 Hz, CH_2CH_3), 1.85 (2H, m$_c$, NCH_2CH_2), 3.96 (3H, s, NCH_3), 4.19 (2H, t, ^3J=7.5 Hz, NCH_2), 7.37 (1H, t, J=1.8 Hz) and 7.41 (1H, t, J=1.8 Hz) (both *CH*=*CH*), 9.13 (1H, br s, N–*CH*=N). ^{13}C NMR (100.65 MHz): δ 13.1 (CH_2CH_3), 19.3 (CH_2CH_3), 31.9 (NCH_2CH_2), 36.2 (NCH_3), 49.8 (NCH_2), 122.2 and 123.6 (both *CH*=*CH*), 136.7 (N–*CH*=N). ^{19}F NMR (376.59 MHz): δ −127.1 (2F, t*, J=14 Hz, 2CF_2-3), −122.7 (2F, m$_c$, 2CF_2-2), −115.9 (2F, t*, J=14 Hz, 2CF_2-1), −82.0 (3F, tt, J_1=9.9 Hz, J_2=2.7 Hz, 2CF_3); *further splitting due to the multiple ^{19}F,^{19}F couplings. MS (ESI positive, ion energy 0.3 eV), *m*/*z* (%): 139.1 [$C_8H_{15}N_2^+$] (100) and lighter fragments. MS (ESI negative, ion energy 0.3 eV), *m*/*z* (%): 298.95 [$C_4F_9SO_3^-$] (100) and lighter fragments.

3.2.11. 1-Isopropyl-3-methylimidazolium nonafluorobutanesulfonate (2c). The title compound was prepared from *N*-methylimidazole (2.04 g, 24.9 mmol), Me_2CHBr (3.22 g, 26.2 mmol) and the salt **B** (8.00 g, 23.7 mmol) as described in GP1; yield 8.14 g (81%) as a clear yellowish viscous liquid. **2c**, ^{1}H NMR (400.23 MHz): δ 1.56 (6H, d, ^3J=6.7 Hz, Me_2CH), 3.97 (3H, s, NCH_3), 4.65 (1H, heptet, ^3J=6.7 Hz, N*CH*Me$_2$), 7.42 (1H, t, J=1.9 Hz) and 7.45 (1H, t, J=1.9 Hz) (both *CH*=*CH*), 9.12 (1H, br s, N–*CH*=N). ^{13}C NMR (100.65 MHz): δ 22.6 (Me_2CH), 36.1 (NCH_3), 53.3 (N*CH*Me$_2$), 120.2 and 123.7 (both *CH*=*CH*), 135.3 (N–*CH*=N). ^{19}F NMR (376.59 MHz): δ −127.1 (2F, t*, J=14.2 Hz, 2CF_2-3), −122.7 (2F, m$_c$, 2CF_2-2), −115.9 (2F, t*, J=14.2 Hz, 2CF_2-1), −82.0 (3F, tt, J_1=10.0 Hz, J_2=2.8 Hz, 2CF_3); *further splitting due to the multiple ^{19}F,^{19}F couplings. MS (ESI positive, ion energy 0.3 eV), *m*/*z* (%): 125 [$C_7H_{13}N_2^+$] (100) and lighter fragments. MS (ESI negative, ion energy 0.3 eV), *m*/*z* (%): 298.9 [$C_4F_9SO_3^-$] (100) and lighter fragments.

3.2.12. 1-*sec*-Butyl-3-methylimidazolium nonafluorobutanesulfonate (2d). The title compound was prepared from *N*-methylimidazole (2.04 g, 24.9 mmol), $MeCH_2$-CH(Me)Br (3.58 g, 26.1 mmol) and the salt **B** (6.74 g, 19.9 mmol) as described in GP1; yield 6.89 g (79%) as a tawny crystalline solid, mp 42–43 °C. **2d**, ^{1}H NMR (400.23 MHz): δ 0.87 (3H, t, ^3J=7.4 Hz, CH_3CH_2), 1.55 (3H, d, ^3J=6.9 Hz, CH_3CH), 1.86 (2H, quintet, ^3J=7.4 Hz, CH_3CH_2), 3.98 (3H, s, NCH_3), 4.41 (1H, sextet, ^3J=6.9 Hz, N*CH*), 7.41 (1H, t, J=1.8 Hz) and 7.46 (1H, t, J=1.8 Hz) (both *CH*=*CH*), 9.17 (1H, br s, N–*CH*=N). ^{13}C NMR (100.65 MHz): δ 9.9 (CH_2CH_3), 20.4 (CH_3CHN), 29.8 (CH_2CH_3), 36.2 (NCH_3), 59.1 (N*CH*), 120.2 and 123.8 (both *CH*=*CH*), 135.7 (N–*CH*=N). ^{19}F NMR (376.59 MHz): δ −127.1 (2F, t*, J=14.2 Hz, 2CF_2-3), −122.7 (2F, m$_c$, 2CF_2-2), −115.9 (2F, t*, J=14.2 Hz, 2CF_2-1), −82.0 (3F, tt, J_1=9.9 Hz, J_2=2.7 Hz, 2CF_3); *further splitting due to the multiple ^{19}F,^{19}F couplings. MS (ESI positive, ion energy 0.3 eV), *m*/*z* (%): 139 [$C_8H_{15}N_2^+$] (100) and lighter fragments. MS (ESI negative, ion energy 0.3 eV), *m*/*z* (%): 298.9 [$C_4F_9SO_3^-$] (100) and lighter fragments. HRMS (FAB negative, Cs, 20 keV, direct, glycerin, *m*/*z*), found: 298.9395. Calcd ($C_4F_9O_3S^-$): 298.9419.

3.3. Synthesis of *N*-propyl-*N*′-alkyl imidazolium bis-(nonafluorobutane-1-sulfonyl)imides (3) (see Scheme 5): general procedure (GP2)

Imidazole (1 equiv) was placed into the reaction flask and dried in HV (0.05 mbar, rt) to remove traces of moisture before adding a solution of MeONa (1.05 equiv) in MeOH (4.026 mmol/g, prepared from MeOH and Na). The reaction mixture was stirred for 15–20 min at rt, then MeOH was removed in vacuum followed by drying the residue in HV (0.05 mbar, rt) for 1 h. MeCN (0.5 mL per 1 mmol substrate) followed by the Me$(CH_2)_2$Br (1.0–1.1 equiv) were added to the resulting sodium imidazolide at 0 °C, and the reaction mixture was stirred for 5 h at 0 °C and 15 h at ambient temperature. After the completion of the first alkylation step (NMR-control), the volatiles were removed in vacuum followed by the addition of the second alkylating reagent. After the completion of the second alkylation step (NMR-control), the residue was combined with the salt **A** (0.95 equiv) in two-phase water/CH_2Cl_2 mixture and treated as described in GP1 furnishing the compounds **3a**,**b**.

3.3.1. 1-Propyl-3-ethylimidazolium bis(nonafluorobutane-1-sulfonyl)imide (3a). The title compound was prepared from imidazole (1.00 g, 14.7 mmol), MeONa (0.83 g, 15.4 mmol) in MeOH (10 mL), Me$(CH_2)_2$Br (1.80 g, 14.7 mmol) as a first alkylating reagent in MeCN (8 mL), $(EtO)_2SO_2$ (2.16 g, 14.0 mmol) as a second alkylating reagent employed at 0 °C to rt for 17 h, and the salt **A** (8.61 g, 13.9 mmol), as described in GP2; yield 9.90 g (99%) as a clear yellow viscous liquid. **3a**, ^{1}H NMR (400.23 MHz): δ 0.94 (3H, t, ^3J=7.4 Hz, $CH_2CH_2CH_3$), 1.52 (3H, t, ^3J=7.4 Hz, NCH_2CH_3), 1.89 (2H, sextet, ^3J=7.4 Hz, $CH_2CH_2CH_3$), 4.14 (2H, t, ^3J=7.4 Hz, NCH_2CH_2), 4.25 (2H, q, ^3J=7.4 Hz, NCH_2CH_3), 7.32 (1H, t, J=1.8 Hz) and 7.35 (1H, t, J=1.8 Hz) (both *CH*=*CH*), 8.82 (1H, br s, N–*CH*=N). ^{13}C NMR (100.65 MHz): δ 10.2 ($CH_2CH_2CH_3$), 15.0 ($CH_2CH_2CH_3$), 23.4 ($CH_2CH_2CH_3$), 45.2 (NCH_2CH_3), 51.5 (NCH_2CH_2), 121.9 and 122.3 (both *CH*=*CH*), 135.2 (N–*CH*=N). ^{19}F NMR (376.59 MHz): δ −127.1 (4F, t*, J=14 Hz, 2CF_2-3), −122.2 (4F, m$_c$, 2CF_2-2), −114.0 (4F, br t, J=14 Hz, 2CF_2-1), −81.9 (6F, tt, J_1=9.9 Hz, J_2=2.4 Hz, 2CF_3); *further splitting due to the multiple ^{19}F,^{19}F couplings. MS (ESI positive, ion energy 0.3 eV), *m*/*z* (%): 139.1 [$C_8H_{15}N_2^+$] (100) and lighter

fragments. MS (ESI negative, ion energy 0.3 eV), *m/z* (%): 580.0 [$(C_4F_9SO_2)_2N^-$] (100) and lighter fragments. HRMS (FAB negative, Cs, 20 keV, direct, glycerin, *m/z*), found: 579.8994. Calcd ($C_8F_{18}NO_4S_2^-$): 579.8976.

3.3.2. 1-Butyl-3-propylimidazolium bis(nonafluorobutane-1-sulfonyl)imide (3b). The title compound was prepared from imidazole (1.021 g, 15.0 mmol), MeONa (0.851 g, 15.8 mmol) in MeOH (10 mL), $Me(CH_2)_2Br$ (2.03 g, 16.5 mmol) as a first alkylating reagent in MeCN (7.5 mL), $Me(CH_2)_3Br$ (2.62 g, 19.1 mmol) as a second alkylating reagent employed for 3 h at 70 °C, and the salt **A** (8.30 g, 13.4 mmol), as described in GP2; yield 10.04 g (>99%) as a yellowish crystalline solid, mp 36–37 °C. **3b**, ^{1}H NMR (400.23 MHz): δ 0.936 and 0.940 (both 3H, t, ^3J=7.4 Hz, CH_2CH_3), 1.34 (2H, sextet, ^3J=7.4 Hz, CH_2CH_3 of *n*-C_4H_9), 1.83 (2H, m_c, NCH_2CH_2 of *n*-C_4H_9), 1.89 (2H, sextet, ^3J=7.4 Hz, NCH_2CH_2 of *n*-C_3H_7), 4.14 and 4.17 (both 2H, t, ^3J=7.4 Hz, NCH_2), 7.340 and 7.344 (both 1H, br s, *CH*=*CH*) 8.82 (1H, br s, N–*CH*=N). ^{13}C NMR (100.65 MHz): δ 10.2 and 13.0 (both CH_3), 19.2 and 23.4 (both CH_2CH_3), 32.0 (NCH_2CH_2 of *n*-C_4H_9), 49.9 and 51.5 (both NCH_2), 122.3 (both *CH*=*CH*), 135.5 (N–*CH*=N). ^{19}F NMR (376.59 MHz): δ −127.1 (4F, t*, J=14 Hz, $2CF_2$-3), −122.2 (4F, m_c, $2CF_2$-2), −114.0 (4F, br t, J=14 Hz, $2CF_2$-1), −81.9 (6F, tt, J_1=9.9 Hz, J_2=2.3 Hz, $2CF_3$); *further splitting due to the multiple ^{19}F,^{19}F couplings. MS (ESI positive, ion energy 0.3 eV), *m/z* (%): 167 [$C_{10}H_{19}N_2^+$] (100) and lighter fragments. MS (ESI negative, ion energy 0.3 eV), *m/z* (%): 580 [$(C_4F_9SO_2)_2N^-$] (100) and lighter fragments.

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4. NfF is available from many suppliers. It is produced in technical scale by the electrochemical fluorination of 2,5-dihydrothiophene 1,1-dioxide. According to ^{19}F NMR, our sample of NfF contains 7 mol% of side product, perfluorosulfolane: Bürger, H.; Heyder, F.; Pawelke, G.; Niederprüm, H. *J. Fluorine Chem.* **1979**, *13*, 251–260.
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6. pK_a[HCO_3^-]$_{aq}$=10.33, pK_a[HPO_4^{2-}]$_{aq}$=12.32, *Handbook of Chemistry and Physics* 81st ed., pp 8-44–8-45.
7. A careful analysis of the spectroscopic data of the products obtained under the conditions **a** and **b** showed that they consist of the salt **B** (60–70 mol%), $CH_3C(O)NNf^{\ominus}K^{\oplus}$ (25–40 mol%) and $KOSO_2(CF_2)_4H$ (up to 11 mol%, MS (ESI negative, ion energy 0.3 eV), *m/z* (%): 280.93 [$H(CF_2)_4SO_3]^-$). The latter salt may result from the nucleophilic ring opening of perfluorosulfolane, see Ref. 4 and Lyapkalo, I. M.; Webel, M.; Reissig, H.-U. *Eur. J. Org. Chem.* **2002**, 1015–1025. No desired $KNNf_2$ **A** is detected in either of the experiments. $CH_3C(O)NNf^{\ominus}K^{\oplus}$, ^{1}H NMR (400.23 MHz, DMSO-d_6): 1.81 (3H, s, CH_3). ^{19}F NMR (376.59 MHz, DMSO-d_6): δ −128.0 (2F, m_c, CF_2-3), −123.5 (2F, m_c, CF_2-2), −115.8 (2F, m_c, CF_2-1), −82.75 (3F, tt, J_1=9.8 Hz, J_2=2.9 Hz, CF_3). MS (ESI negative, ion energy 0.3 eV), *m/z* (%): 339.94 [$C_4F_9SO_2NC(O)CH_3]^-$.
8. In fact, microanalysis data given for $KNNf_2$ (see Ref. 5) are in a better consistency with the elemental composition of KONf!.
9. O-Sulfonylation of metal enolates or N-sulfonylation of lithium dialkylamides with NfF occurs instantaneously even at −78 °C, see: (a) Lyapkalo, I. M.; Webel, M.; Reissig, H.-U. *Synlett* **2001**, 1293–1295. (b) Lyapkalo, I. M.; Reissig, H.-U.; Schäfer, A.; Wagner, A. *Helv. Chim. Acta* **2002**, *85*, 4206–4215, respectively, whereas no evidences of $F^{\ominus}$ release were noticed upon activation of NfF with highly nucleophilic 4-(*N*,*N*-dimethylamino)pyridine.
10. Et_3N failed to produce the desired $NNf_2^{\ominus}$ ion when used as a base for sulfonylation of amides $RC(O)NH_2$ with NfF (see Ref. 5).
11. At the later stage of the optimization of $KNNf_2$ synthesis, we found out that a similar method was used for preparation of $LiNNf_2$ by heating of liquid NH_3 with NfF in access of Et_3N as an auxiliary base and solvent at 90 °C in autoclave: Conte, L.; Gambaretto, G. P.; Caporiccio, G.; Alessandrini, F.; Passerini, S. *J. Fluorine Chem.* **2004**, *125*, pp 243–252. Our protocol looks more convenient as it simplifies dosing of ammonia (in form of solid NH_4Cl) and is carried out at smoother conditions in normal laboratory glassware giving a better yield of the intermediate $Et_3NH^{\oplus}NNf_2^{\ominus}$.
12. The ^{19}F NMR spectrum contains no detectable signal of side product(s) that might result from perfluorosulfolane (cf. Ref. 7).
13. The samples of the salts neither change appearance nor gain in wait upon storage in open vial for a long period of time.
14. The reaction progress was monitored by ^{1}H NMR spectroscopy; in all the cases full conversion of the starting *N*-methyl imidazole was observed. Up to 15–18 mol% of *N*-methyl imidazolium bromide was detected by ^{1}H NMR as a side product resulting from HBr elimination from secondary bromides. It was easily removed from ionic liquid by aqueous extraction on the following anion exchange step. Although at higher temperature primary branched and secondary alkyl bromides react faster, a contribution of the E2 elimination pathway increases significantly.

15. First representatives of the salts **1**, *N*,*N*′-dimethyl- and *N*-methyl-*N*′-ethylimidazolium bis(nonafluorobutane-1-sulfonyl)imides were obtained earlier in a different way: Zhang, J.; Martin, G. R.; DesMarteau, D. D. *Chem. Commun.* **2003**, *18*, 2334–2335.
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