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Fluorous imidazolium room-temperature ionic liquids based on HFPO trimer

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ABSTRACT

Imidazole substituted with a polyfluoropolyether chain based on HFPO trimer combined with various polyfluoroalkyl triflates produced novel highly fluorous ionic liquids. Their metathesis with four different anions generated a final set of 20 fluorous ionic liquids of waxy or viscous liquid character, which are all soluble in perfluorinated solvents. Two model reactions using selected ionic liquid, the opening of a THF ring with benzoyl chloride under Friedel–Crafts conditions and substitution of benzyl chloride with sodium azide, led to decomposition of the ionic liquid. However, Diels–Alder reaction of 2,3-dimethylbuta-1,3-diene with dimethyl acetylenedicarboxylate in a fluorous ionic liquid resulted in a reasonable enhancing of the reaction rate with smooth recycle of the fluorous solvent. The fluorophilicity of these fluorous ionic liquids ranges from more than 10 for water, toluene or dichloromethane to less than 0.2 for acetonitrile or methanol.

1. Introduction

Ionic liquids are a class of organic compounds which displays two characteristic features: first, they are composed only of ions, and second, they are liquids below 100 °C. If the ionic liquids are liquid at room temperature, they are called room-temperature ionic liquids (RTILs). Due to their unique properties they found applications in many areas of chemistry, e.g. as solvents for synthesis and catalysis, biocatalysis, electrochemistry, as thermal fluids, in liquid–liquid extractions, etc. Their synthesis, properties and applications have been thoroughly reviewed [1–9]. Among numerous types of ionic liquids, 1,3-disubstituted imidazolium salts attract most attention mainly due to low price, easy synthesis and low crystallinity [1–4].

Various ionic liquids containing long perfluorinated chain have been reported based on various types of heterocyclic cationic core, e.g. pyridinium, pyrimidinium, triazolium, pyrrolidium or other ring type [10,11]. An alternative approach employs polyfluoroalkylated ammonium salts [10]. Also, several types of ionic liquids bearing polyfluoroalkylated anions have been synthesized and applied for recycling of polyfluoroalkylated homogeneous catalysts [12,13] or as solvents for enzymatic or catalytic reactions [14,15]. Recently, a new type of highly fluorinated ionic liquids and its electrochemical applications have been reported but no details were given about its synthesis and fluorous properties [16].

Nevertheless, in analogy to non-fluorinated ionic liquids most attention has been devoted to polyfluoroalkylated imidazolium salts, which were studied as surfactants for ionic liquids [17], solvents for metal ion extraction [18] or Diels–Alder reactions [19], or ionic liquid/CO_2 biphase systems for homogeneous catalysis [20,21]. However, all of the published polyfluoroalkylated imidazolium-based ionic liquids do not have a sufficient fluorine content to be soluble in perfluorinated solvents. The sole example of (polyfluoroalkylated) imidazolium salt was synthesized but it is a high temperature-melting solid [22].

In the course of the last few years we oriented our research was oriented towards the study of cyclopentadiene-based fluorous ligands [23–26] but found out that for multiple-polyfluoroalkylated cyclopentadienes their complexation ability ceases [27]. Looking for other fluorous ligands substituting commonly used phosphines we started to investigate the area of fluorous imidazolylidene carbenes (NHC ligands). We recently submitted a paper regarding the synthesis and properties of a series of bis(polyfluoroalkylated) imidazolium salts [28], and this together with our previous experience in the synthesis of chloropolyfluoropolyethers [29] initiated our interest in the preparation of imidazolium salts in which the polyfluoroalkyl group would be substituted by a perfluoropolyether chain. In this paper we report the synthesis of

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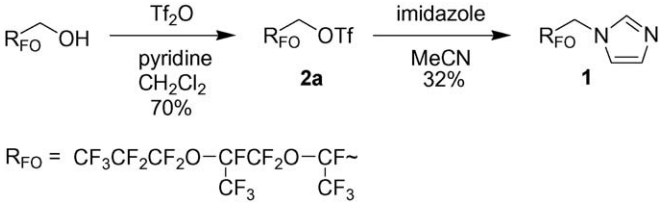
a novel class of highly fluorinated ionic liquids (including several metathetic reactions), which have either a waxy or a viscous oil character, with a reasonable solubility in perfluorinated solvents.

2. Results and discussion

2.1. Synthesis

In contrast to the compounds bearing long perfluorinated chains which tend to crystallize starting with C_6F_{13} chains, perfluorinated polyethers are liquids over a wide range of molecular weights. For the incorporation of the perfluoropolyether segment in the imidazole ring, the simple transformation to the amide was not chosen due to the high sensitivity of the polyfluorinated acyl group to hydrolysis [30]. We also avoided the simple addition of imidazole on commercially available, and industrially extensively used perfluorovinylether, because the CF_2-CHF group formed by this reaction is highly prone to HF elimination [31,32]. Following our positive experience with the modification of imidazole ring by triflates of polyfluorinated alcohols [28], we employed for the synthesis triflate **2a** of a commercially available alcohol based on hexafluoropropene-1,2-oxide (HFPO) trimer. This novel fluorinated building block displayed limited reactivity but afforded the key intermediate, fluorinated imidazole **1** to be obtained, in an acceptable yield [33] (Scheme 1).



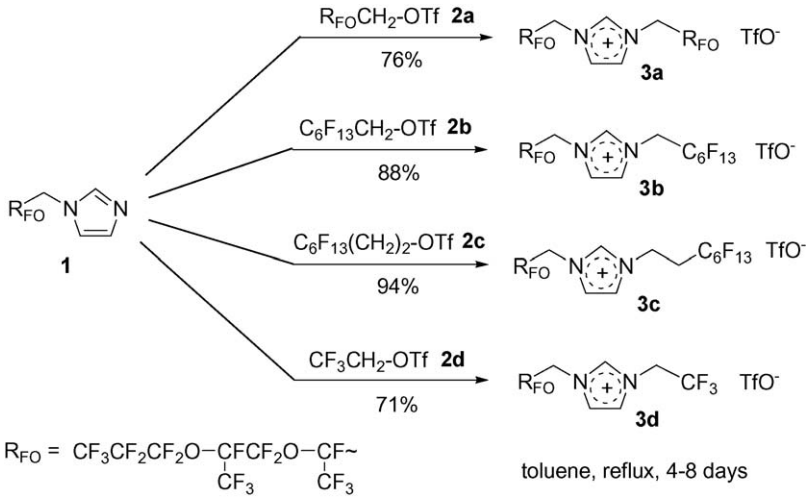
Scheme 1.

In a preliminary experiment, we found that polyfluoroalkoxylated imidazole **1** can be reacted with polyfluoroalkylated triflate **2b** to produce the corresponding fluorinated imidazolium salt **3b**, which have a waxy consistence [33] in contrast to the crystalline bis(polyfluoroalkylated) imidazolium salts with high melting points [28]. To understand better the behaviour of this novel class of compounds, we proceeded to react fluoroimidazole **1** with other three fluoroalkylated triflates **2a**, **2c** and **2d** and obtained the corresponding imidazolium salts **3a**, **3c** and **3d** in good yields (Scheme 2). Attempts to substitute the triflate **3c** with analogous commercially available, but less reactive iodide **4**, resulted even on prolonged heating to reflux in only minimal conversion to the target imidazolium iodide. While imidazolium salts **3b**, **3c** bearing long perfluorinated chain have waxy consistence, imidazolium salts **3a** and **3d** are highly viscous oils and hence represent a first example of fluorous RTIL's (room-temperature ionic liquids).

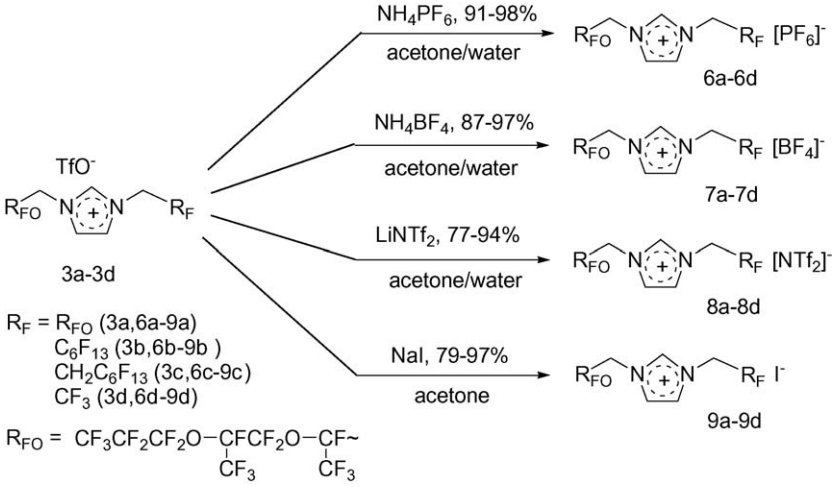
Detailed inspection of the NMR spectra disclosed that in some experiments (especially in the case of the preparation of bis(polyfluoroalkoxylated) imidazolium salt **3a**) a side product was formed, which could be isolated as a white sublimate from the crude reaction mixture by prolonged heating in vacuum. Its structure corresponds to the triflate salt **5** of polyfluoroalkoxylated imidazole **1**. As its fluorophilicity is remarkably lower than that of the disubstituted imidazolium salts **3**, it is virtually insoluble in perfluorinated solvents. Moreover, its solubility in common dipolar aprotic solvents such as acetone or acetonitrile is also significantly lower. It could hence be removed from the crude reaction mixtures as an insoluble solid by trituration with dipolar aprotic or perfluorinated solvents. The side-product **5** is probably formed by the thiophilic attack of fluoroimidazole **1** at the sulfur atom of the triflates **2**, a side-reaction which is characteristic for triflates of polyfluorinated alcohols with methylene spacer [34], followed by the hydrolysis of the intermediary imidazolide of triflic acid.

2.2. Metathesis of polyfluoroalkylated imidazolium triflates 3

To improve the properties of imidazolium-based ionic liquids, namely, decrease the melting point, metathetic reactions with appropriate non-nucleophilic fluorinated counteranions such as hexafluorophosphate, tetrafluoroborate or bis(trifluoromethanesulfonyl)amide anion are a frequently employed procedure. On the other hand, for some experiments ionic liquids bearing a reactive iodide anion are required. We therefore performed metatheses of the four synthesized bis(polyfluoroalkylated) imidazolium triflates **3a**–**3d** with the four above mentioned anions. For the three fluorinated anions, the simple mixing with 5- to 20-fold excess of the corresponding ammonium or lithium salt in aqueous acetone was used, while for the iodide anion stirring with sodium iodide in anhydrous acetone (Finkelstein conditions) was preferred (Scheme 3). The completeness of the metathesis was confirmed by the absence of the triflate signal in ^{19}F NMR spectra. The corresponding imidazolium salts **6**–**9** were obtained in good to excellent yields (Table 1).



Scheme 2.



Scheme 3.

2.3. Model reactions in fluorous ionic liquids

Many reactions proceed with better yields or with better separation of products in ionic liquids. Among them, we chose three characteristic reactions and tested whether they can be performed in our fluorous ionic liquids. The respective reactions were the nucleophilic substitution of benzyl chloride with sodium azide [35], opening of the tetrahydrofuran ring with benzoyl chloride under Friedel–Crafts conditions [36], and the Diels–Alder reaction of 2,3-dimethylbuta-1,3-diene (DMB) with dimethyl acetylenedicarboxylate (DMAD) [37].

Substitution of benzyl chloride with sodium azide was performed in three parallel experiments for 100 h at 40 °C, in the fluorous ionic liquid **3a**, in DMF, and without solvent. Whereas no reaction was detected without solvent, more than 99% conversion was achieved in DMF. On the other hand, we observed limited conversion (about 22%) in the ionic liquid **3a**, thus this solvent being inferior to DMF. Moreover, significant decomposition (about 40% according to NMR) of the ionic liquid into a complex mixture of products occurred, probably due to attack of the imidazolium ring by the azide anion.

For the second reaction, an ionic liquid bearing the iodide anion is required and we hence employed the fluorous ionic liquid **9a**. According to the standard procedure [36], imidazolium iodide **9a** was stirred first with aluminum trichloride at room temperature for 5 h, followed by the addition of THF and benzoyl chloride. After 12 h of continuous stirring at room temperature, only traces of the product, 4-iodobutyl benzoate, were detected in the crude reaction mixture by NMR. However, the ionic liquid **9a** was completely decomposed into the complex mixture of products.

The Diels–Alder reaction was again performed in three parallel experiments for 2 h at 80 °C, in the fluorous ionic liquid **3a**, in THF and without solvent. The conversion of the starting compounds into the final product was estimated from the ^{1}H NMR spectrum of the crude product. Thus, the reaction without solvent provided a 61% conversion to the final product while the reaction in THF reached a 65% conversion. However, the reaction was nearly completed (> 99% conversion) in the fluorous ionic liquid, although even at 80 °C the reaction mixture was not looking homogeneous. After cooling, the product was separated from the fluorous ionic liquid as an upper layer containing less then 1% of the fluorous ionic liquid. The bottom layer, consisting exclusively of the ionic liquid **3a**, was reused in a replicate experiment, under identical conditions, and the same result, i.e. complete conversion into the final product, that was easily separated with no decomposition of the ionic liquid **3a**.

Table 1
Results of metatheses of imidazolium salts **3a**–**3d**.

Label	R^1	R^2	Anion	Yield (%)
6a	$C_2F_5[CF_2OCF(CF_3)]_2CH_2$	$C_2F_5[CF_2OCF(CF_3)]_2CH_2$	$[PF_6]^-$	91
6b	$C_2F_5[CF_2OCF(CF_3)]_2CH_2$	$C_6F_{13}CH_2$	$[PF_6]^-$	96
6c	$C_2F_5[CF_2OCF(CF_3)]_2CH_2$	$C_6F_{13}CH_2CH_2$	$[PF_6]^-$	98
6d	$C_2F_5[CF_2OCF(CF_3)]_2CH_2$	CF_3CH_2	$[PF_6]^-$	93
7a	$C_2F_5[CF_2OCF(CF_3)]_2CH_2$	$C_2F_5[CF_2OCF(CF_3)]_2CH_2$	$[BF_4]^-$	90
7b	$C_2F_5[CF_2OCF(CF_3)]_2CH_2$	$C_6F_{13}CH_2$	$[BF_4]^-$	87
7c	$C_2F_5[CF_2OCF(CF_3)]_2CH_2$	$C_6F_{13}CH_2CH_2$	$[BF_4]^-$	97
7d	$C_2F_5[CF_2OCF(CF_3)]_2CH_2$	CF_3CH_2	$[BF_4]^-$	87
8a	$C_2F_5[CF_2OCF(CF_3)]_2CH_2$	$C_2F_5[CF_2OCF(CF_3)]_2CH_2$	$[NTf_2]^-$	77
8b	$C_2F_5[CF_2OCF(CF_3)]_2CH_2$	$C_6F_{13}CH_2$	$[NTf_2]^-$	94
8c	$C_2F_5[CF_2OCF(CF_3)]_2CH_2$	$C_6F_{13}CH_2CH_2$	$[NTf_2]^-$	93
8d	$C_2F_5[CF_2OCF(CF_3)]_2CH_2$	CF_3CH_2	$[NTf_2]^-$	85
9a	$C_2F_5[CF_2OCF(CF_3)]_2CH_2$	$C_2F_5[CF_2OCF(CF_3)]_2CH_2$	I^-	87
9b	$C_2F_5[CF_2OCF(CF_3)]_2CH_2$	$C_6F_{13}CH_2$	I^-	97
9c	$C_2F_5[CF_2OCF(CF_3)]_2CH_2$	$C_6F_{13}CH_2CH_2$	I^-	79
9d	$C_2F_5[CF_2OCF(CF_3)]_2CH_2$	CF_3CH_2	I^-	87

2.4. Solubility and fluorous partition coefficients of bis(polyfluoroalkylated) imidazolium salts 3

Fluorous imidazolium salts **3** and **6**–**9** display unique solubility patterns. They are highly soluble in polar protic or aprotic solvents such as methanol, acetone, acetonitrile and diethyl ether, and moderately soluble in non-polar fluorinated compounds such as 1,2-dibromotetrafluoroethane (FC114B2) or perfluoro(methylcyclohexane). On the other hand, they are virtually insoluble both in non-fluorinated solvents of lower polarity (toluene, dichloromethane) and in water. Interestingly, their solubility in perfluorinated solvents is at least an order of magnitude higher than that of bis(polyfluoroalkylated) imidazolium salts with two perfluorinated chains and reaches more than 50 mg/ml. We measured the fluorous partition coefficients P_i(FBS) [38] of fluorous ionic liquid

Table 2
Fluorous partition coefficients of imidazolium salt **3c** between perfluoro(methylcyclohexane) and various solvents at 25 °C.

Entry	Solvent	P_i (FBS)
1	Toluene	49.1
2	Dichloromethane	10.7
3	Tetrahydrofuran	2.05
4	Acetonitrile	0.047
5	Methanol	0.11
6	Water	36.5

Table 3
Fluorous partition coefficients of imidazolium salts **3a**–**3d** in perfluoro(methylcyclohexane)/toluene mixture at 25 °C and their fluorophilicities.

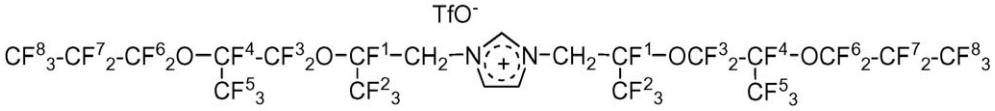
Entry	Compound	P_i (FBS)	f_i
1	**3a**	88.2	4.48
2	**3b**	94.1	4.54
3	**3c**	49.1	3.89
4	**3d**	11.5	2.45

3c between perfluoro(methylcyclohexane) and various solvents at 25 °C, which correspond to the above mentioned solubility pattern (Table 2). Thus, fluorous partition coefficients are larger than 10 for water, toluene and dichloromethane (Entries 6, 1 and 2) and on the other hand lower than 0.2 for methanol and acetonitrile (Entries 4 and 5). Fluorous ionic liquids **3** and **6**–**9** can thus be characterized as lipophobic and hydrophobic amphiphiles. We could not measure the fluorous partition coefficients for pentane, hexane and diethylether as they mix with perfluoro(methylcyclohexane).

To clarify the role of various fluorinated side-chains, we also compared fluorophilicities (natural logarithms of fluorous partition coefficients for perfluoro(methylcyclohexane)/toluene mixtures [38]) of the imidazolium salts **3a**–**3d** (Table 3). From these results it can be seen that enlarging the non-fluorinated spacer lowers a little the fluorophilicity (Entries 2 and 3), substitution of the perfluorohexyl chain for the polyether chain with eight fluorinated carbons has negligible effect (Entries 1 and 2) and substitution of perfluorohexyl group by trifluoromethyl significantly diminishes the fluorophilicity (as well as the solubility in the perfluorinated solvent to about 20 mg/ml) (Entries 2 and 4).

3. Conclusions

Using a novel polyfluorinated building block based on HFPO trimer, we synthesized a series of 20 fluorous ionic liquids containing an imidazolium core, which have either a waxy or viscous liquid character. These liquids exhibit unique solubility and fluorophilicity patterns with high solubility in perfluorinated and dipolar aprotic solvents but negligible in toluene and water.



These ionic liquids are decomposed by reactive nucleophiles limiting thus their synthetic value as solvents, however, they accelerate Diels–Alder-type reactions and are easy to separate and recycle.

4. Experimental

Temperature data were uncorrected. NMR spectra were recorded with a Varian MercuryPlus spectrometer, ^{1}H NMR spectra at 299.97 MHz and ^{13}C NMR spectra at 75.43 MHz using residual deuterated solvent signals as the internal standards, ^{19}F NMR spectra at 282.22 MHz using CCl_3F as the internal standard. Chemical shifts are given in ppm, coupling constants in Hz. Anisochronic signals (strongly coupled AB systems) of non-equivalent fluorine atoms in CF_2- groups are marked with lower case letters (**a**,**b**), diastereomer signals with upper case letter (**A**,**B**). In some cases, ^{19}F gCOSY experiments were performed in some cases to allow full assignment of signals. In the case of the ^{19}F NMR spectra, signals are given separately for the *erythro*/*threo* configuration of the polyether chain wherever possible. Mass spectra (ESI, APCI) were measured with a LCQ Fleet (Finnigan) instrument, HRMS spectra (ESI, APCI, FAB) with a LTQ Orbitrap XL (Thermo Fisher Scientific) or ZAB-EQ (VG Analytical) instruments.

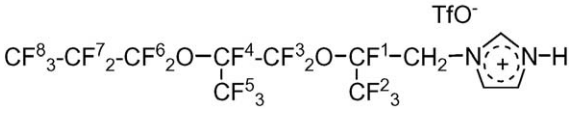
All reactions were performed in dry inert atmosphere (Ar) in an oven-dried flasks. 1-[2,4,4,5,7,7,8,8,9,9,9-Undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazole (**1**, R_FOCH_2Im), 2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl trifluoromethanesulfonate (**2a**, R_FOCH_2OTf) and 1-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-3-[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazolium trifluoromethanesulfonate (**3b**, $R_FOCH_2Im^+CH_2C_6F_{13}$-*n* $^-$OTf) were prepared according to [33] from perfluoro(2,5-dimethyl-3,6-dioxanonanoyl) fluoride (HFPO trimer, $CF_3(CF_2)_2O$-$CF(CF_3)CF_2O$-$CF(CF_3)$COF)). 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl trifluormethanesulfonate (**2c**, *n*-$C_6F_{13}(CH_2)_2$OTf) was synthesized according to [39] and 2,2,2-trifluoroethyl trifluoromethanesulfonate (**2d**, CF_3CH_2OTf) according to [40] from the respective fluoroalcohols and trifluoromethanesulfonic anhydride. 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoroctan-1-ol (1*H*,1*H*,2*H*,2*H*-perfluorooctan-1-ol, *n*-$C_6F_{13}(CH_2)_2$OH) and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-iodooctane (**4**, 1*H*,1*H*,2*H*,2*H*-perfluorooctyl iodide, *n*-$C_6F_{13}(CH_2)_2$I) were kindly donated by Atochem. Perfluoro(2,5-dimethyl-3,6-dioxanonanoyl) fluoride (HFPO trimer, $CF_3(CF_2)_2O$-$CF(CF_3)CF_2O$-$CF(CF_3)$COF, R_FOCOF), 2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptan-1-ol (1*H*,1*H*-perfluoroheptan-1-ol, *n*–$C_6F_{13}CH_2$OH) and trifluoromethanesulfonic anhydride (triflic anhydride) were purchased from Apollo Scientific, imidazole from Fluka, 2,2,2-trifluoroethanol, ammonium hexafluorophosphate, ammonium tetrafluoroborate and lithium-bis(trifluoromethylsulfonyl)imide from Sigma-Aldrich. Acetone and acetonitrile were distilled over P_2O_5, dichloromethane and DMF over CaH_2, pyridine over KOH, THF over sodium benzophenone ketyl and toluene over Na. 1,2-Dibromo-1,1,2,2-tetrafluoroethane (FC114B2, $BrCF_2CF_2Br$) was distilled and dried over molecular sieves.

4.1. 1,3-Bis[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazolium trifluoromethanesulfonate (3a)

A flask was loaded with fluoroalkylimidazole **1** (5.19 g, 9.8 mmol), fluoroalkyl triflate **2a** (5.99 g, 9.8 mmol) and toluene (10 ml). The mixture was heated to 120 °C for 4 days under continous stirring. After cooling to r.t., toluene was removed using a rotary vacuum evaporator (50 °C/2 h/2 kPa) and the residue was heated in vacuo (70 °C/48 h/10 Pa) to obtain the product **3a** (8.45 g, 75.6%) as a light yellow highly viscous oil. ^{1}H NMR (299.97 MHz, acetone-d_6) δ 5.66 m, 4H (C**H**$_2$); 8.19 m, 2H (C**H**=CH); 9.87 m; 1H (N–C**H**=N). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −77.3 dm, 2F, $^2J_{F\text{-}F}$ = 155 Hz (**F^{3}a**); −78.4 s, 6F (**F^9**); −79.5 m, 6F (**F^5**); −80.4 dm, 2F, $^2J_{F\text{-}F}$ = 140 Hz (**F^{6}a**); −80.6 dm, 2F, $^2J_{F\text{-}F}$ = 140 Hz (**F^{6}b**); −81.2 m, 6F (**F^8**); −81.3 m, 6F (**F^2**); −81.6 dm, 6F, $^2J_{F\text{-}F}$ = 155 Hz (**F^{3}b**); −129.3 m, 4F (**F^7**); −134.8 m, 2F (**F^1**); −144.2 m, 2F (**F^4**). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 49. 6 d, 2C, $^2J_{C\text{-}F}$ = 20.1 Hz (**C**H$_2$); 100–126 m, 16C (**C**F, **C**F$_2$ and **C**F$_3$ groups); 120.3 q, 1C, $^1J_{C\text{-}F}$ = 316.8 Hz (**C**F$_3$SO$_2$O); 125.9s, 2C (C**H**=CH); 141.2s, (N–C**H**=N). MS (ESI), *m*/*z* (%): 997 [M−TfO$^-$]$^+$, 100; 149 [TfO]$^-$, 100.

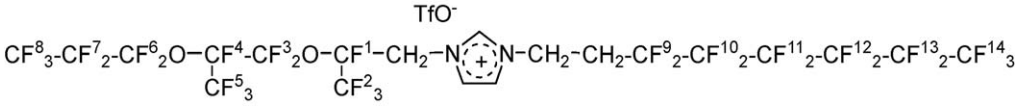
During heating under vacuum, 1,26 g (18.9%) of white crystallinic sublimate (s.p. 154–156 °C) was obtained, which was identified as 1-[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluor-

omethyl)-3,6-dioxanonyl]imidazolium trifluoromethanesulfonate (**5**).



^{1}H NMR (299.97 MHz, acetone-d_6) δ 5.60 m, 2H (C**H$_2$**); 7.96 m, 1H (C**H**=CH); 8.03 m, 1H (CH=C**H**); 9.45 s, 1H (N–C**H**=N). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −77.4 m, 1F (**F^{3}a**); −78.8s, 3F (**F^9**); −79.5 m, 3F (**F^5**); −80.5 m, 1F (**F^{6}a**); −80.2 m, 1F (**F^{6}b**); −81.3 m, 3F (**F^8**); −81.3 m, 3F (**F^2**); −81.7 m, 3F (**F^{3}b**); −129.4 m, 2F (**F^7**); −134.8 m (**F^1**); −144.2 m, 1F (**F^4**). MS (ESI), *m/z* (%): 533 [M−TfO$^-$]$^+$, 100. ^{13}C NMR spectrum could not be recorded due to a low solubility of salt **5** in common NMR solvents.

4.2. 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)-3-[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazolium trifluoromethanesulfonate (3c)

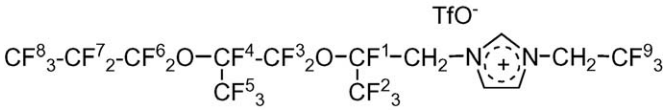


A flask was loaded with fluoroalkylimidazole **1** (0.45 g, 0.90 mmol), fluoroalkyl triflate **2c** (0.42 g, 0.90 mmol) and toluene (10 ml). The mixture was heated to 100 °C for 6 days under continuous stirring. After cooling to r.t., toluene was removed using a rotary vacuum evaporator (50 °C/2 h/2 kPa). The residue was dissolved in FC114B2 (10 ml), washed with deionized water (3 × 10 ml) and the organic layer was separated. Removal of the solvent using a rotary vacuum evaporator (50 °C/2 h/2 kPa) followed by heating of the residue in vacuo (70 °C/12 h/10 Pa) yielded product **3c** (0.822 g, 94.5%) as a light brown wax. ^{1}H NMR (299.97 MHz, acetone-d_6) δ 3.19 tt, 2H, $^3J_{H\text{-}F}$ = 19.0 Hz, $^3J_{H\text{-}H}$ = 6.7 Hz (CF_2-C**H$_2$**); 5.04 t, 2H, $^3J_{H\text{-}H}$ = 6.7 Hz (CF_2-CH_2-C**H$_2$**); 5.70 d, 2H, $^3J_{H\text{-}F}$ = 19.0 Hz (CF–C**H$_2$**); 8.05 m, 1H, (C**H**=CH); 8.21 m, 1H (CH=C**H**); 9.69s, 1H (N–C**H**=N). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −77.8 dm, 1F, $^2J_{F\text{-}F}$ = 145 Hz (**F^{3}a**); −78.0 s, 6F (C**F$_3$**SO$_2$O); −79.4 q, 6F, $^4J_{F\text{-}F}$ = $^5J_{F\text{-}F}$ = 10 Hz (**F^5**); −79.5 q, 3F, $^4J_{F\text{-}F}$ = $^5J_{F\text{-}F}$ = 10 Hz (**F^{5}A** or **F^{5}B**); −80.4 dm, 1F, $^2J_{F\text{-}F}$ = 145 Hz (**F^{6}a**); −80.6 t, 3F, $^4J_{F\text{-}F}$ = 10 Hz (**F^{14}A** or **F^{14}B**); −80.7 t, 3F, $^4J_{F\text{-}F}$ = 10 Hz (**F^{14}A** or **F^{14}B**); −80.8 dm, 1F, $^2J_{F\text{-}F}$ = 145 Hz (**F^{3}b**); −81.0 t, 3F, $^4J_{F\text{-}F}$ = 6 Hz (**F^{8}A** or **F^{8}B**); −81.1 t, 3F, $^4J_{F\text{-}F}$ = 6 Hz (**F^{8}A** or **F^{8}B**); −81.3 d, 3F, $^5J_{F\text{-}F}$ = 13 Hz (**F^{2}A** or **F^{2}B**); −81.3 dm, 1F, $^2J_{F\text{-}F}$ = 145 Hz (**F^{6}b**); −81.4 d, 3F, $^5J_{F\text{-}F}$ = 13 Hz (**F^{2}A** or **F^{2}B**); −113.4 m, 4F (**F^9**); −121.4 m, 4F (**F^{11}**); −122.4 m, 4F (**F^{10}**); −123.1 m, 4F (**F^{12}**); −125.7 m, 4F (**F^{13}**); (129.1 s, 2F (**F^{7}A** or **F^{7}B**); −129.2 s, 2F (**F^{7}A** or **F^{7}B**); −134.5 dq, 1F, $^4J_{F\text{-}F}$ = $^3J_{H\text{-}F}$ = 22 Hz (q), $^4J_{F\text{-}F}$ = 15 Hz (d) (**F^{1}A**); −134.9 dq, 1F, $^4J_{F\text{-}F}$ = $^3J_{H\text{-}F}$ = 22 Hz (q), $^4J_{F\text{-}F}$ = 15 Hz (d) (**F^{1}B**); −144.0 tm, 1F, $^4J_{F\text{-}F}$ = 21 Hz (**F^{4}A**); −144.1 m, 1F (**F^{4}B**). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 30.9 t, 1C, $^3J_{C\text{-}F}$ = 20.7 Hz (CF_2C**H$_2$**); 42.9 t, 1C, $^4J_{C\text{-}F}$ = 4.8 Hz (CF_2CH_2C**H$_2$**,); 49.2 d, 1C, $^2J_{C\text{-}F}$ = 21.0 Hz (CFC**H$_2$**); 100–140 m 14C (**C**F, **C**F$_2$ and **C**F$_3$ groups); 120.5 q, 1C, $^1J_{C\text{-}F}$ = 316.8 (**C**F$_3$SO$_2$O); 123.9 s, 1C (C**H**=CH); 124.9 s, 1C (CH=C**H**); 139.6 s, 1C, (N–C**H**=N). MS (ESI), *m/z* (%): 997 [M−TfO$^-$]$^+$, 100; 149 [TfO]$^-$, 100. HRMS (EI), *m/z* (%): calcd. for $C_{20}H_9F_{30}N_2O_2$ [M]$^+$, 879,01794; found 879,01742.

4.3. Attempted preparation of 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-3-[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazolium iodide

A flask was loaded with fluoroalkylimidazole **1** (0.45 g, 0.90 mmol), fluoroalkyl iodide **4** (0.42 g, 0.90 mmol) and toluene (10 ml). The mixture was heated to 110 °C for 7 days under continuous stirring. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy indicated that less then 5% conversion to the target imidazolium iodide was achieved.

4.4. 1-(2,2,2-Trifluoroethyl)-3-[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazolium trifluoromethanesulfonate (3d)

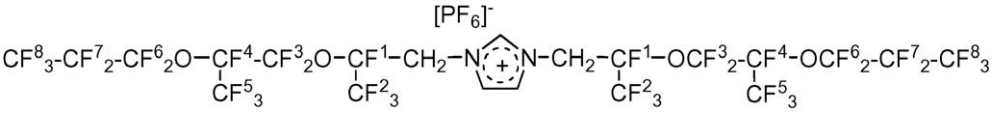


A glass ampoule equipped with a magnetic stirrer was loaded with toluene (20 ml), fluoroalkylimidazole **1** (3.22 g, 6.3 mmol) and fluoroalkyl triflate **2d** (1.53 g, 6.6 mmol), sealed and heated to 100 °C for 6 days while stirring. After cooling, toluene was removed from the reaction mixture using a rotary vacuum evaporator (70 °C/12 h/2 kPa). The crude product was triturated three times with acetone (5 ml) to remove small amount of the side product **5** as insoluble solid. By heating in vacuo (80 °C/70 h/10 Pa), the residual solvent was removed and **3d** (3.28 g, 70.8%) was obtained as a highly viscous light yellow oil. ^{1}H NMR (299.97 MHz, acetone-d_6) δ 5.62 q, 2H, $^3J_{H\text{-}F}$ = 8.7 Hz (CF_3-C**H$_2$**); 5.77 m, 2H (CF–C**H$_2$**); 8.20 m, 1H (C**H**=CH); 8.22 m, 1H (CH=C**H**); 9.80 s, 1H (N–C**H**=N). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −71.5 t, 6F, $^3J_{H\text{-}F}$ = 8 Hz (**F^9**); −77.9 dm, 1F, $^2J_{F\text{-}F}$ = 150 Hz (**F^{3}aB**); −78.0 s, 6F (C**F$_3$**SO$_2$O); −78.2 dm, 1F, $^2J_{F\text{-}F}$ = 150 Hz (**F^{3}aA**); −79.4 q, 3F, $^4J_{F\text{-}F}$ = $^5J_{F\text{-}F}$ = 8 Hz (**F^{5}A** or **F^{5}B**); −79.5 q, 3F, $^4J_{F\text{-}F}$ = $^5J_{F\text{-}F}$ = 9 Hz (**F^{5}A** or **F^{5}B**); −80.4 dm, 1F, $^2J_{F\text{-}F}$ = 150 Hz (**F^6**); −80.9 dm, 1F, $^2J_{F\text{-}F}$ = 140 Hz (**F^{3}bB**); −81.0 dm, 1F, $^2J_{F\text{-}F}$ = 140 Hz (**F^{3}bA**); −81.0 t, 3F, $^4J_{F\text{-}F}$ = 6 Hz (**F^{8}A** or **F^{8}B**); −81.1 t, 3F, $^4J_{F\text{-}F}$ = 6 Hz (**F^{8}A** or **F^{8}B**); −81.3 d, 3F, $^5J_{F\text{-}F}$ = 13 Hz (**F^{2}A** or **F^{2}B**); −81.3 dm, 3F, $^2J_{F\text{-}F}$ = 150 Hz (**F^{6}bB**); −81.5 dm, 1F, $^2J_{F\text{-}F}$ = 150 Hz (**F^{6}bA**); −81.5 d, 3F, $^5J_{F\text{-}F}$ = 13 Hz (**F^{2}A** or **F^{2}B**); −129.1 s, 2F (**F^{7}A** or **F^{7}B**); −129.3 s, 2F (**F^{7}A** or **F^{7}B**); −134.5 dq, 1F, $^4J_{F\text{-}F}$ = $^3J_{H\text{-}F}$ = 22 Hz (q), $^4J_{F\text{-}F}$ = 15 Hz (d) (**F^{1}B**); −135.0 dq, 1F, $^4J_{F\text{-}F}$ = $^3J_{H\text{-}F}$ = 22 Hz (q), $^4J_{F\text{-}F}$ = 15 Hz (d) (**F^{1}A**); −144.0 tm, 1F, $^4J_{F\text{-}F}$ = 22 Hz (**F^{4}A** or **F^{4}B**); −144.1 m, 1F (**F^{4}A** or **F^{4}B**). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 49.8 q, 1C, $^2J_{C\text{-}F}$ = 37.1 Hz (CF_3C**H$_2$**); 49.4 d, 1C, $^2J_{C\text{-}F}$ = 20.6 Hz (CFC**H$_2$**); 100–126 m, 8C (**C**F, **C**F$_2$ and **C**F$_3$ groups); 120.3 q, 1C, $^1J_{C\text{-}F}$ = 316.8 (**C**F$_3$SO$_2$O); 125.1 s, 1C (CH=C**H**); 125.8 s, 1C (C**H**=CH); 140.9 s, (N–C**H**=N). MS (ESI), *m/z* (%): 615 [M−TfO$^-$]$^+$, 100; 149 [TfO]$^-$, 100.

4.5. Preparation of bis(polyfluoroalkyl)imidazolium hexafluorophosphates 6: general procedure

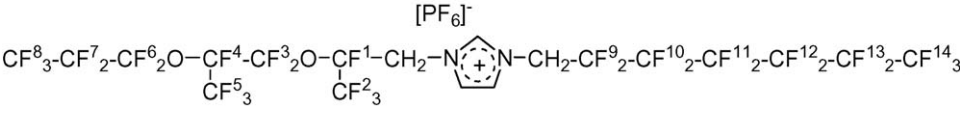
Bis(polyfluoroalkylated) imidazolium trifluoromethanesulfonate **3** (about 0.1 mmol) was dissolved in a 3:1 acetone/deionized water mixture (15 ml). NH_4PF_6 (about 10 to 20-fold excess) was added and the mixture was stirred for 5 h at r.t. Acetone was removed using a rotary vacuum evaporator (40 °C/1 h/2 kPa) and the residue was dissolved in the 1:1 1,2-dibromotetrafluoroethane (CFC 114B2)/deionized water mixture (100 ml). The separated organic phase was washed with deionized water (5 × 50 ml) and dried over anhydrous $MgSO_4$. Removal of the solvent using a rotary vacuum evaporator (40 °C/1 h/2 kPa) followed by heating the residue in vacuo (75 °C/12 h/10 Pa) yielded the target hexafluorophosphate salt **6**.

*4.6. 1,3-Bis[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazolium hexafluorophosphate (**6a**)*



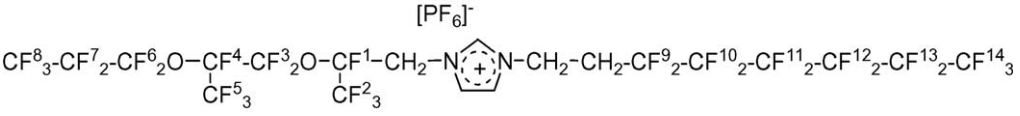
From the metathesis of 111 mg (0.11 mmol) of fluoroimidazolium triflate **3a** and 247 mg (1.65 mmol) of NH_4PF_6, 114 mg (91%) of product **6a** was obtained according to the general procedure. ^{1}H NMR (299.97 MHz, acetone-d_6) δ 5.82 m, 4H (C**H**$_2$); 8.22 m, 2H (C**H**=CH); 9.88 m, 1H, (N–C**H**=N). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −71.5 d, 12F, $^1J_{P\text{-}F}$ = 707 Hz (P**F$_6$**); −77.3 dm, 2F, $^2J_{F\text{-}F}$ = 155 Hz (**F^{3}a**); −79.5 m, 6F (**F^5**); −80.4 dm, 2F, $^2J_{F\text{-}F}$ = 140 Hz (**F^{6}a**); −80.6 dm, 2F, $^2J_{F\text{-}F}$ = 140 Hz (**F^{6}b**); −81.2 m, 6F (**F^8**); −81.3 m, 6F (**F^2**); −81.6 dm, 2F, $^2J_{F\text{-}F}$ = 155 Hz (**F^{3}b**); −129.3 m, 4F (**F^7**); −134.8 m, 2F (**F^1**); −144.2 m, 2F (**F^4**). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 49.6 d, 2C $^2J_{C\text{-}F}$ = 20.1 Hz (**C**H$_2$); 100–126 m, 16C (**C**F, **C**F$_2$ and **C**F$_3$ groups); 125.9 s, 2C (C**H**=CH); 141.2 s, 1C (N–C**H**=N). MS (ESI), *m/z* (%): 997 [M−PF$_6^-$]$^+$, 100; 145 [PF$_6$]$^-$, 100.

*4.7. 1-(2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoroheptyl)-3-[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazolium hexafluorophosphate (**6b**)*



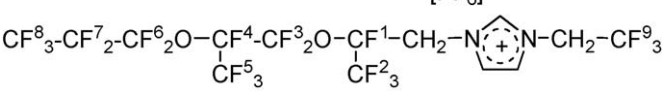
From the metathesis of 127 mg (0.12 mmol) of fluoroimidazolium triflate **3b** and 226 mg (2.16 mmol) of NH_4PF_6, 116 mg (96%) of product **6b** was obtained according to the general procedure. ^{1}H NMR (299.97 MHz, acetone-d_6) δ 5.68–5.88 m, 4H (C**H**$_2$); 8.20 m, 1H (C**H**=CH); 8.25 m, 1H (C**H**=CH); 9.80 s, 1H (N–C**H**=N). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −71.4 d, 12F, $^1J_{P\text{-}F}$ = 707 Hz (P**F$_6$**); −77.8 dm, 1F, $^2J_{F\text{-}F}$ = 150 Hz (**F^{3}aA**); −78.0 dm, 1F, $^2J_{F\text{-}F}$ = 150 Hz (**F^{3}aB**); −78.2 s, 6F (**F^{15}**); −79.5 q, 3F, $^4J_{F\text{-}F}$ = $^5J_{F\text{-}F}$ = 9 Hz (**F^{5}A** or **F^{5}B**); −79.6 q, 3F, $^4J_{F\text{-}F}$ = $^5J_{F\text{-}F}$ = 9 Hz (**F^{5}A** or **F^{5}B**); −80.4 dm, 2F, $^2J_{F\text{-}F}$ = 140 Hz (**F^{6}a**); −80.6 m, 6F, (**F^{14}**); −81.0 t, 3F, $^4J_{F\text{-}F}$ = 7 Hz (**F^{8}A** or **F^{8}B**); −81.1 dm, 1F, $^2J_{F\text{-}F}$ = 150 Hz (**F^{3}bB**); −81.0 t, 3F, $^4J_{F\text{-}F}$ = 7 Hz (**F^{8}A** or **F^{8}B**); −81.3 d, 1F, $^5J_{F\text{-}F}$ = 11 Hz (**F^{2}A** or **F^{2}B**); −81.3 dm, 1F, $^2J_{F\text{-}F}$ = 150 Hz (**F^{3}bA**); −81.4 dm, 2F, $^2J_{F\text{-}F}$ = 140 Hz (**F^{6}b**); −81.5 d, 3F, $^5J_{F\text{-}F}$ = 11 Hz (**F^{2}A** or **F^{2}B**); −116.7 m, 4F (**F^9**); −121.4 m, 4F (**F^{11}**); −122.1 m, 4F (**F^{10}**); 122.2 m, 4F (**F^{12}**); 125.7 m, 2F (**F^{13}**); −129.1 s, 2F (**F^{7}A** or **F^{7}B**); −129.3 s, 2F (**F^{7}A** or **F^{7}B**); −134.5 dq, 1F, $^4J_{F\text{-}F}$ = $^3J_{H\text{-}F}$ = 22 Hz (q), $^4J_{F\text{-}F}$ = 15 Hz (d) (**F^{1}B**); −135.2 dq, 1F, $^4J_{F\text{-}F}$ = $^3J_{H\text{-}F}$ = 22 Hz (q), $^4J_{F\text{-}F}$ = 15 Hz (d) (**F^{1}B**); −143.9 tm, 2F, $^4J_{F\text{-}F}$ = 21 Hz (**F^4**). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 48.8 t, 1C, $^2J_{C\text{-}F}$ = 23 Hz (CF$_2$-**C**H$_2$); 49.6 d, 1C, $^2J_{C\text{-}F}$ = 20 Hz (CF–CH$_2$); 100–126 m, 14C (**C**F, **C**F$_2$ and **C**F$_3$ groups); 125.7 s, 1C (C**H**=CH); 125.8 s, 1C (C**H**=CH); 141.0 s, 1C (N–C**H**=N). MS (ESI), *m/z* (%): 865 [M−PF$_6^-$]$^+$, 100; 145 [PF$_6$]$^-$, 100.

*4.8. 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)-3-[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazolium hexafluorophosphate (**6c**)*



From the metathesis of 82 mg (0.08 mmol) of fluoroimidazolium triflate **3c** and 195 mg (1.75 mmol) of NH_4PF_6, 80 mg (98%) of product **6c** was obtained according to the general procedure. ^{1}H NMR (299.97 MHz, acetone-d_6) δ 3.21 tt, $^3J_{H\text{-}F}$ = 18.7 Hz, $^3J_{H\text{-}H}$ = 6.70 Hz (CF$_2$-C**H**$_2$-CH$_2$); 5.07 t, 2H, $^3J_{H\text{-}H}$ = 6.70 Hz (CF$_2$-CH$_2$-C**H**$_2$); 5.72 d, 2H, $^3J_{H\text{-}F}$ = 19.5 Hz (CF–C**H**$_2$); 8.11 m, 1H, (C**H**=CH); 8.27 m, 1H (C**H**=CH); 9.78 m, 1H (N–C**H**=N). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −71.4 d, 12F, $^1J_{P\text{-}F}$ = 707 Hz (P**F$_6$**); −77.8 dm, 2F, $^2J_{F\text{-}F}$ = 145 Hz (**F^{3}a**); −79.4 q, 3F, $^4J_{F\text{-}F}$ = $^5J_{F\text{-}F}$ = 10 Hz (**F^{5}A** or **F^{5}B**); −79.5 q, 3F, $^4J_{F\text{-}F}$ = $^5J_{F\text{-}F}$ = 10 Hz (**F^{5}A** or **F^{5}B**); −80.4 dm, 2F, $^2J_{F\text{-}F}$ = 145 Hz (**F^6**); −80.6 t, 3F, $^4J_{F\text{-}F}$ = 10 Hz (**F^{14}A** or **F^{14}B**); −80.7 t, 3F, $^4J_{F\text{-}F}$ = 10 Hz (**F^{14}A** or **F^{14}B**); −80.8 dm, 2F, $^2J_{F\text{-}F}$ = 145 Hz (**F^{3}b**); −81.0 t, 3F, $^4J_{F\text{-}F}$ = 6 Hz (**F^{8}A** or **F^{8}B**); −81.1 t, 3F, $^4J_{F\text{-}F}$ = 6 Hz (**F^{8}A** or **F^{8}B**); −81.3 d, 3F, $^5J_{F\text{-}F}$ = 13 Hz (**F^{2}A** or **F^{2}B**); −81.3 dm, 2F, $^2J_{F\text{-}F}$ = 145 Hz (**F^{6}b**); −81.4 d, 3F, $^5J_{F\text{-}F}$ = 13 Hz (**F^{2}A** or **F^{2}B**); −113.5 m, 4F (**F^9**); −121.4 m, 4F (**F^{11}**); −122.4 m, 4F (**F^{10}**); −123.1 m, 4F (**F^{12}**); −125.7 m, 4F (**F^{13}**); −129.1 s, 2F (**F^{7}A** or **F^{7}B**); −129.2 s, 2F (**F^{7}A** or **F^{7}B**); −134.5 dq, 1F, $^4J_{F\text{-}F}$ = $^3J_{H\text{-}F}$ = 22 Hz (q), $^4J_{F\text{-}F}$ = 15 Hz (d) (**F^{1}B**); −134.9 dq, 1F, $^4J_{F\text{-}F}$ = $^3J_{H\text{-}F}$ = 22 Hz (q), $^4J_{F\text{-}F}$ = 15 Hz (d) (**F^{1}B**); −144.0 tm, 1F, $^4J_{F\text{-}F}$ = 21 Hz (**F^{4}A**); −144.1 m, 1F (**F^{4}B**). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 30.9 t, 1C, $^3J_{C\text{-}F}$ = 20.7 Hz (CF$_2$-**C**H$_2$-CH$_2$); 42.9 t, 1C, $^4J_{C\text{-}F}$ = 4.8 Hz (CF$_2$-CH$_2$-**C**H$_2$); 49.2 d, 1C, $^2J_{C\text{-}F}$ = 21.0 Hz (CF–CH$_2$); 100 - 140 m, 14C (**C**F, **C**F$_2$ and **C**F$_3$ groups); 123.9 s, 1C, (C**H**=CH); 124.9 s, 1C, (C**H**=CH); 139.6 s, (N–C**H**=N). MS (ESI), *m/z* (%): 879 [M−PF$_6^-$]$^+$, 100; 145 [PF$_6$]$^-$, 100.

*4.9. 1-(2,2,2-Trifluoroethyl)-3-[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazolium hexafluorophosphate (**6d**)*



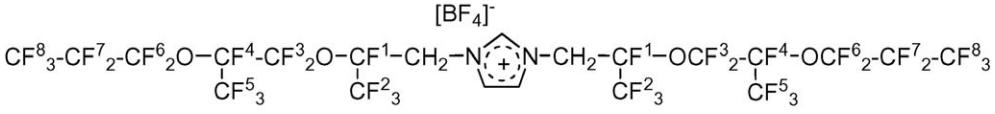
From the metathesis of 163 mg (0.21 mmol) of fluoroimidazolium triflate **3d** and 784 mg (2.73 mmol) of NH_4PF_6, 148 mg (93%) of product **6d** was obtained according to the general procedure. ^{1}H NMR (299.97 MHz, acetone-d_6) δ 5.57 q, 2H, $^3J_{H\text{-}F}$ = 8.6 Hz (CF$_3$-C**H**$_2$); 5.76 m, 2H, (CF–C**H**$_2$); 8.16 m, 1H (C**H**=CH); 8.20 m, 1H (C**H**=CH); 9.70 m, 1H (N–C**H**=N). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −71.4 d, 12F, $^1J_{P\text{-}F}$ = 707 Hz (P**F$_6$**); −71.5 t, 6F $^3J_{F\text{-}H}$ = 8 Hz (**F^9**); −77.9 dm, 1F, $^2J_{F\text{-}F}$ = 150 Hz (**F^{3}aB**); −78.2 dm, 1F, $^2J_{F\text{-}F}$ = 150 Hz (**F^{3}aA**); −79.4 q, 3F, $^4J_{F\text{-}F}$ = $^5J_{F\text{-}F}$ = 8 Hz (**F^{5}A** or **F^{5}B**); −79.5 q, 3F, $^4J_{F\text{-}F}$ = $^5J_{F\text{-}F}$ = 9 Hz (**F^{5}A** or **F^{5}B**); −80.4 dm, 2F, $^2J_{F\text{-}F}$ = 150 Hz (**F^{6}a**); −80.9 dm, 1F, $^2J_{F\text{-}F}$ = 140 Hz (**F^{3}bB**); −81.0 dm, 1F, $^2J_{F\text{-}F}$ = 140 Hz (**F^{3}bA**); −81.0 t, 3F, $^4J_{F\text{-}F}$ = 6 Hz (**F^{8}A** or **F^{8}B**); −81.1 t, 3F, $^4J_{F\text{-}F}$ = 6 Hz (**F^{8}A** or **F^{8}B**); −81.3 d, 3F, $^5J_{F\text{-}F}$ = 13 Hz (**F^{2}A** or **F^{2}B**); −81.3 dm, 3F,

$^{2}J_{F-F}$ = 150 Hz (**F⁶bB**); −81.5 dm, 1F, $^{2}J_{F-F}$ = 150 Hz (**F⁶bA**); −81.5 d, 3F, $^{5}J_{F-F}$ = 13 Hz (**F²A** or **F²B**); −129.2 s, 2F (**F⁷A** or **F⁷B**); −129.3 s, 2F (**F⁷A** or **F⁷B**); −134.6 dq, 1F, $^{4}J_{F-F}$ = $^{3}J_{H-F}$ = 22 Hz (q), $^{4}J_{F-F}$ = 15 Hz (d) (**F¹B**); −135.0 dq, 1F, $^{4}J_{F-F}$ = $^{3}J_{H-F}$ = 22 Hz (q), $^{4}J_{F-F}$ = 15 Hz (d) (**F¹A**); −144.0 tm, 1F, $^{4}J_{F-F}$ = 22 Hz (**F⁴A** or **F⁴B**); −144.1 m, 1F (**F⁴A** or **F⁴B**). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 49.8 q, $^{2}J_{C-F}$ = 37.1 Hz (CF_3-CH_2); 49.4 d, $^{2}J_{C-F}$ = 20.6 Hz (CF–CH_2); 100–126 m, 8C (**C**F, **C**F_2 and **C**F_3 groups); 125.1 s (C**H**=CH); 125.8 s, (C**H**=CH); 140.9 s, (N–C**H**=N). MS (ESI), *m/z* (%): 615 [M−PF_6^-]$^+$, 100; 145 [PF_6^-]$^-$, 100.

4.10. Preparation of bis(polyfluoroalkylimidazolium) tetrafluoroborates 7: general procedure

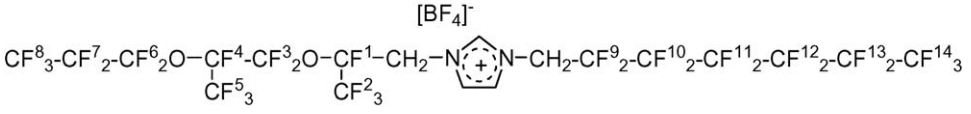
Bis(polyfluoroalkylated) imidazolium trifluoromethanesulfonate **3** (about 0.1 mmol) was dissolved in a 3:1 acetone/deionized water mixture (15 ml). NH_4BF_4 (about 10 to 20-fold excess) was added and the mixture was stirred for 5 h at r.t. Acetone was then removed using a rotary vacuum evaporator (40 °C/1 h/2 kPa) and the residue was dissolved in the 1:1 1,2-dibromotetrafluoroethane (CFC 114B2)/deionized water mixture (100 ml). The separated organic phase was washed with deionized water (5 × 50 ml) and dried over anhydrous $MgSO_4$. Removal of the solvent using a rotary vacuum evaporator (40 °C/1 h/2 kPa) followed by heating the residue in vacuo (75 °C/12 h/10 Pa) yielded the target tetrafluoroborate salt **7**.

4.11. 1,3-Bis[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis (trifluoromethyl)-3,6-dioxanonyl]imidazolium tetrafluoroborate (7a)



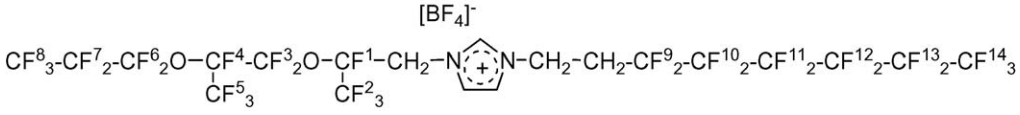
From the metathesis of 180 mg (0.16 mmol) of fluoroimidazolium triflate **3a** and 197 mg (1.89 mmol) of NH_4BF_4, 190 mg (90%) of product **7a** was obtained according to the general procedure. ^{1}H NMR (299.97 MHz, acetone-d_6) δ 6.02 m, 4H (C**H**$_2$); 8.21 m, 2H (C**H**=CH); 10.41 m, 1H, (N–C**H**=N). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −77.3 dm, 2F, $^{2}J_{F-F}$ = 155 Hz (**F³a**); −79.5 m, 6F (**F⁵**); −80.4 dm, 2F, $^{2}J_{F-F}$ = 140 Hz (**F⁶a**); −80.6 dm, 2F, $^{2}J_{F-F}$ = 140 Hz (**F⁶b**); −81.2 m, 6F (**F⁸**); −81.3 m, 6F (**F²**); −81.6 dm, 2F, $^{2}J_{F-F}$ = 155 Hz (**F³b**); −129.3 m, 4F (**F⁷**); −134.8 m, 2F (**F¹**); −144.2 m, 2F (**F⁴**); −150.2 s, 8F (^{10}B**F**$_4$); −150,3 s, 8F (^{11}B**F**$_4$). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 49.6 d, 2C $^{2}J_{C-F}$ = 20.1 Hz (**C**H_2); 100–126 m, 16C (**C**F, **C**F_2 and **C**F_3 groups); 125.9 s, 2C (C**H**=CH); 141.2 s, 1C (N–C**H**=N). MS (ESI), *m/z* (%): 997 [M−BF_4^-]$^+$, 100; 87 [BF_4]$^-$, 100.

4.12. 1-(2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoroheptyl)-3-[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazolium tetrafluoroborate (7b)



From the metathesis of 115 mg (0.11 mmol) of fluoroimidazolium triflate **3b** and 164 mg (1.57 mmol) of NH_4BF_4, 92 mg (87%) of product **7b** was obtained according to the general procedure. ^{1}H NMR (299.97 MHz, acetone-d_6) δ 5.88 m, 2H (CF_2-C**H**$_2$); 5,95 m, 2H (CF–C**H**$_2$); 8.20 m, 1H (C**H**=CH); 8.25 m, 1H (C**H**=CH); 10.17 s, 1H (N–C**H**=N). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −77.8 dm, 1F, $^{2}J_{F-F}$ = 150 Hz (**F³aA**); −78.0 dm, 1F, $^{2}J_{F-F}$ = 150 Hz (**F³aB**); −79.5 q, 3F, $^{4}J_{F-F}$ = $^{5}J_{F-F}$ = 9 Hz (**F⁵A** or **F⁵B**); −79.6 q, 3F, $^{4}J_{F-F}$ = $^{5}J_{F-F}$ = 9 Hz (**F⁵A** or **F⁵B**); −80.4 dm, 2F, $^{2}J_{F-F}$ = 140 Hz (**F⁶a**); −80.6 m, 6F, (**F¹⁴**); −81.0 t, 3F, $^{4}J_{F-F}$ = 7 Hz (**F⁸A** or **F⁸B**); −81.1 dm, 1F, $^{2}J_{F-F}$ = 150 Hz (**F³bB**); −81.0 t, 3F, $^{4}J_{F-F}$ = 7 Hz (**F⁸A** or **F⁸B**); −81.3 d, 3F, $^{5}J_{F-F}$ = 11 Hz (**F²A** or **F²B**); −81.3 dm, 1F, $^{2}J_{F-F}$ = 150 Hz (**F³bA**); −81.4 dm, 2F, $^{2}J_{F-F}$ = 140 Hz (**F⁶b**); −81.5 d, 3F, $^{5}J_{F-F}$ = 11 Hz (**F²A** or **F²B**); −116.4 t, 2F, $^{3}J_{F-H}$ = 15 Hz (**F⁹A** or **F⁹B**); −116.8 m, 2F (**F⁹A** or **F⁹B**); −121.5 m, 4F (**F¹¹**); −122.1 m, 4F (**F¹⁰**); 122.3 m, 4F (**F¹²**); 125.7 m, 4F (**F¹³**); −129.2 s, 2F (**F⁷A** or **F⁷B**); −129.3 s, 2F (**F⁷A** or **F⁷B**); −134.5 dq, 1F, $^{4}J_{F-F}$ = $^{3}J_{H-F}$ = 22 Hz (q), $^{4}J_{F-F}$ = 15 Hz (d) (**F¹B**); −135.2 dq, 1F, $^{4}J_{F-F}$ = $^{3}J_{H-F}$ = 22 Hz (q), $^{4}J_{F-F}$ = 15 Hz (d) (**F¹A**); −144.0 tm, 2F, $^{4}J_{F-F}$ = 21 Hz (**F⁴**); −150.0 s, 8F (^{10}B**F**$_4$); −150.1 s, 4F (^{11}B**F**$_4$). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 48.8 t, 1C, $^{2}J_{C-F}$ = 23 Hz (CF_2-CH_2); 49.6 d, 1C, $^{2}J_{C-F}$ = 20 Hz (CF–CH_2); 100–126 m, 14C (**C**F, **C**F_2 and **C**F_3 groups); 125.7 s, 1C (C**H**=CH); 125.8 s, 1C (C**H**=CH); 141.0 s, 1C (N–C**H**=N). MS (ESI), *m/z* (%): 865 [M−BF_4^-]$^+$, 100; 87 [BF_4]$^-$, 100.

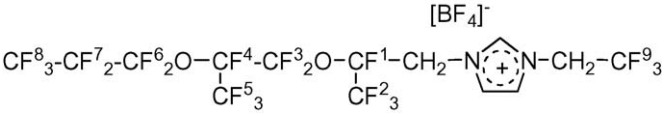
4.13. 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)-3-[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazolium tetrafluoroborate (7c)



From the metathesis of 150 mg (0.15 mmol) of fluoroimidazolium triflate **3c** and 183 mg (1.74 mmol) of NH_4BF_4, 137 mg (97%) of product **7c** was obtained according to the general procedure. ^{1}H NMR (299.97 MHz, acetone-d_6) δ 3.19 tt, $^{3}J_{H-F}$ = 19.1 Hz, $^{3}J_{H-H}$ = 6.8 Hz (CF_2-C**H**$_2$-CH_2); 5.02 t, 2H, $^{3}J_{H-H}$ = 5.6 Hz (CF_2-CH_2-C**H**$_2$); 5.70 d, 2H, $^{3}J_{H-F}$ = 19.5 Hz (CF–C**H**$_2$); 8.05 m, 1H, (C**H**=CH); 8.21 m, 1H (C**H**=CH); 9.69 m, 1H (N–C**H**=N). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −77.8 dm, 2F, $^{2}J_{F-F}$ = 145 Hz (**F³a**); −79.4 q, 3F, $^{4}J_{F-F}$ = $^{5}J_{F-F}$ = 10 Hz (**F⁵A** or **F⁵B**); −79.5 q, 3F, $^{4}J_{F-F}$ = $^{5}J_{F-F}$ = 10 Hz (**F⁵A** or **F⁵B**); −80.4 dm, 2F, $^{2}J_{F-F}$ = 145 Hz (**F⁶**); −80.6 t, 3F, $^{4}J_{F-F}$ = 10 Hz (**F¹⁴A** or **F¹⁴B**); −80.7 t, 3F, $^{4}J_{F-F}$ = 10 Hz (**F¹⁴A** or **F¹⁴B**); −80.8 dm, 2F, $^{2}J_{F-F}$ = 145 Hz (**F³b**); −81.0 t, 3F, $^{4}J_{F-F}$ = 6 Hz (**F⁸A** or **F⁸B**); −81.1 t, 3F, $^{4}J_{F-F}$ = 6 Hz (**F⁸A** or **F⁸B**); −81.3 d, 3F, $^{5}J_{F-F}$ = 13 Hz (**F²A** or **F²B**); −81.3 dm, 2F, $^{2}J_{F-F}$ = 145 Hz (**F⁶b**); −81.4 d, 3F, $^{5}J_{F-F}$ = 13 Hz (**F²A** or **F²B**); −113.5 m, 4F (**F⁹**); −121.4 m, 4F (**F¹¹**); −122.4 m, 4F (**F¹⁰**); −123.1 m, 4F (**F¹²**); −125.7 m, 4F (**F¹³**); −129.1 s, 2F (**F⁷A** or **F⁷B**); −129.2 s, 2F (**F⁷A** or **F⁷B**); −134.5 dq, 1F, $^{4}J_{F-F}$ = $^{3}J_{H-F}$ = 22 Hz (q), $^{4}J_{F-F}$ = 15 Hz (d) (**F¹B**); −134.9 dq, 1F, $^{4}J_{F-F}$ = $^{3}J_{H-F}$ = 22 Hz (q), $^{4}J_{F-F}$ = 15 Hz (d) (**F¹B**); −144.0 tm, 1F, $^{4}J_{F-}$

$_F$ = 21 Hz (**F⁴A**); −144.1 m, 1F (**F⁴B**); −150.3 s, 8F (^{10}B**F₄**); −150.4 s, 8F (^{11}B**F₄**). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 30.9 t, 1C, $^3J_{C-F}$ = 20.7 Hz (CF_2-**C**H_2-CH_2); 42.9 t, 1C, $^4J_{C-F}$ = 4.8 Hz (CF_2-CH_2-**C**H_2); 49.2 d, 1C, $^2J_{C-F}$ = 21.0 Hz (CF–CH_2); 100 - 140 m, 14C (**C**F, **C**F_2 and **C**F_3 groups); 123.9 s, 1C, (C**H**=CH); 124.9 s, 1C, (C**H**=CH); 139.6 s, (N–C**H**=N). MS (ESI), *m/z* (%): 879 [M−BF_4^-]$^+$, 100; 87 [BF_4]$^-$, 100.

4.14. 1-(2,2,2-Trifluoroethyl)-3-[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazolium tetrafluoroborate (7d)

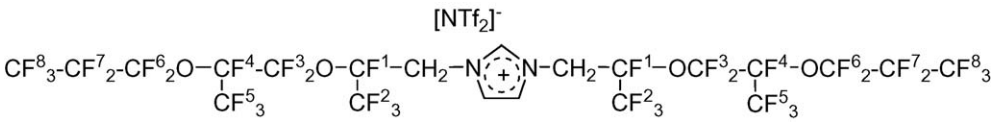


From the metathesis of 122 mg (0.16 mmol) of fluoroimidazolium triflate **3d** and 284 mg (2.71 mmol) of NH_4BF_4, 95 mg (87%) of product **7c** was obtained according to the general procedure. ^{1}H NMR (299.97 MHz, acetone-d_6) δ 5.60 q, 2H, $^3J_{H-F}$ = 8.5 Hz (CF_3-C**H**$_2$); 5.79 m, 2H, (CF–C**H**$_2$); 8.18 m, 1H (C**H**=CH); 8.20 m, 1H (C**H**=CH); 9.79 m, 1H (N–C**H**=N). ^{19}F NMR (282.23 MHz, acetone-d_6) −71.5 t, 6F, $^3J_{F-H}$ = 8 Hz (**F⁹**); −77.9 dm, 1F, $^2J_{F-F}$ = 150 Hz (**F³aB**); −78.2 dm, 1F, $^2J_{F-F}$ = 150 Hz (**F³aA**); −79.4 q, 3F, $^4J_{F-F}$ = $^5J_{F-F}$ = 8 Hz (**F⁵A** or **F⁵B**); −79.5 q, 3F, $^4J_{F-F}$ = $^5J_{F-F}$ = 9 Hz (**F⁵A** or **F⁵B**); −80.4 dm, 2F, $^2J_{F-F}$ = 150 Hz (**F⁶a**); −80.9 dm, 1F, $^2J_{F-F}$ = 140 Hz (**F³bB**); −81.0 dm, 1F, $^2J_{F-F}$ = 140 Hz (**F³bA**); −81.0 t, 3F, $^4J_{F-F}$ = 6 Hz (**F⁸A** or **F⁸B**); −81.1 t, 3F, $^4J_{F-F}$ = 6 Hz (**F⁸A** or **F⁸B**); −81.3 d, 3F, $^5J_{F-F}$ = 13 Hz (**F²A** or **F²B**); −81.3 dm, 3F, $^2J_{F-F}$ = 150 Hz (**F⁶bB**); −81.5 dm, 1F, $^2J_{F-F}$ = 150 Hz (**F⁶bA**); −81.5 d, 3F, $^5J_{F-F}$ = 13 Hz (**F²A** or **F²B**); −129.2 s, 2F (**F⁷A** or **F⁷B**); −129.3 s, 2F (**F⁷A** or **F⁷B**); −134.6 dq, 1F, $^4J_{F-F}$ = $^3J_{H-F}$ = 22 Hz (q), $^4J_{F-F}$ = 15 Hz (d) (**F¹B**); −135.0 dq, 1F, $^4J_{F-F}$ = $^3J_{H-F}$ = 22 Hz (q), $^4J_{F-F}$ = 15 Hz (d) (**F¹A**); −144.0 tm, 1F, $^4J_{F-F}$ = 22 Hz (**F⁴A** or **F⁴B**); −144.1 m, 1F (**F⁴A** or **F⁴B**); −150.3 s, 8F (^{10}B**F₄**); −150.4 s, 8F (^{11}B**F₄**). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 49.8 q, $^2J_{C-F}$ = 37.1 Hz (CF_3-**C**H_2); 49.4 d, $^2J_{C-F}$ = 20.6 Hz (CF–CH_2); 100–126 m, 8C (**C**F, **C**F_2 and **C**F_3 groups); 125.1 s (C**H**=CH); 125.8 s, (C**H**=CH); 140.9 s, (N–C**H**=N). MS (ESI), *m/z* (%): 615 [M−BF_4^-]$^+$, 100; 87 [BF_4^-]$^-$, 100.

4.15. Preparation of bis(polyfluoroalkyl)imidazolium bis(trifluoromethanesulfonyl)amides 8: general procedure

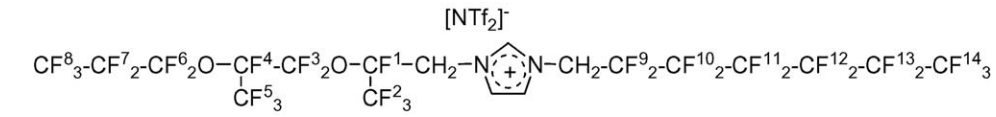
Bis(polyfluoroalkylated) imidazolium trifluoromethanesulfonate **3** (about 0.1 mmol) was dissolved in a 3:1 acetone/deionized water mixture (15 ml). Lithium bis(trifluoromethanesulfonyl)amide (about 10 to 20 fold excess) was added and the mixture was stirred for 5 h at r.t. Acetone was removed using a rotary vacuum evaporator (40 °C/1 h/2 kPa) and the residue was dissolved in the 1:1 1,2-dibromotetrafluoroethane (CFC 114B2)/deionized water mixture (100 ml). The separated organic phase was washed with deionized water (5 × 50 ml) and dried over anhydrous $MgSO_4$. Removal of the solvent uisng a rotary vacuum evaporator (40 °C/1 h/2 kPa) followed by heating the residue in vacuo (75 °C/12 h/10 Pa) yielded the target bis(trifluoromethanesulfonyl)amide salt **8**.

4.16. 1,3-Bis[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazolium bis(trifluoromethanesulfonyl)amide (8a)



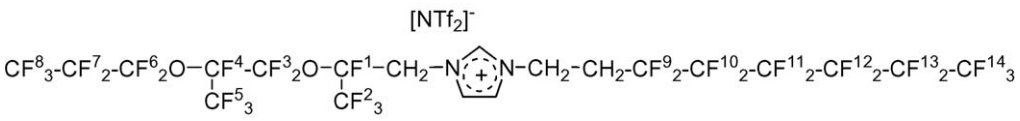
From the metathesis of 110 mg (0.09 mmol) of fluoroimidazolium triflate **3a** and 386 mg (1.34 mmol) of $LiNTf_2$, 88 mg (77%) of product **8a** was obtained according to the general procedure. ^{1}H NMR (299.97 MHz, acetone-d_6) δ 5.82 m, 4H (C**H**$_2$); 8.22 m, 2H (C**H**=CH); 9.88 m, 1H, (N–C**H**=N). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −77.3 dm, 2F, $^2J_{F-F}$ = 155 Hz (**F³a**); −79,1 s, 12F (CF_3SO_2); (79.5 m, 6F (**F⁵**); −80.4 dm, 2F, $^2J_{F-F}$ = 140 Hz (**F⁶a**); −80.6 dm, 2F, $^2J_{F-F}$ = 140 Hz (**F⁶b**); −81.2 m, 6F (**F⁸**); −81.3 m, 6F (**F²**); −81.6 dm, 2F, $^2J_{F-F}$ = 155 Hz (**F³b**); −129.3 m, 4F (**F⁷**); −134.8 m, 2F (**F¹**); −144.2 m, 2F (**F⁴**). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 49.6 d, 2C $^2J_{C-F}$ = 20.1 Hz (**C**H_2); 100–126 m, 16C (**C**F, **C**F_2 and **C**F_3 groups); 120.4 q, $^1J_{C-F}$ = 316.8 (**C**F_3SO_2); 125.9 s, 2C (C**H**=CH); 141.2 s, 1C (N–C**H**=N). MS (ESI), *m/z* (%): 997 [M−NTf_2^-]$^+$, 100; 280 [NTf_2]$^-$, 100.

4.17. 1-(2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoroheptyl)-3-[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazolium bis(trifluoromethanesulfonyl)amide (8b)



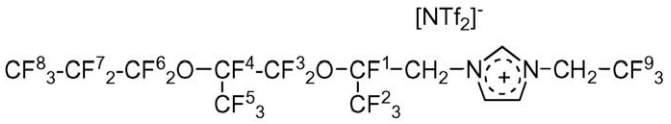
From the metathesis of 199 mg (0.20 mmol) of fluoroimidazolium triflate **3b** and 845 mg (2.94 mmol) of $LiNTf_2$, 215 mg (94%) of product **8b** was obtained according to the general procedure. ^{1}H NMR (299.97 MHz, acetone-d_6) δ 5.72–5.90 m, 4H (C**H**$_2$); 8.23 m, 1H (C**H**=CH); 8.28 m, 1H (C**H**=CH); 9.84 s, 1H (N–C**H**=N). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −77.8 dm, 1F, $^2J_{F-F}$ = 150 Hz (**F³aA**); −78.0 dm, 1F, $^2J_{F-F}$ = 150 Hz (**F³aB**); −79.0 s, 12F (CF_3SO_2); (79.5 q, 3F, $^4J_{F-F}$ = $^5J_{F-F}$ = 9 Hz (**F⁵A** or **F⁵B**); −79.6 q, 3F, $^4J_{F-F}$ = $^5J_{F-F}$ = 9 Hz (**F⁵A** or **F⁵B**); −80.4 dm, 2F, $^2J_{F-F}$ = 140 Hz (**F⁶a**); −80.6 m, 6F, (**F¹⁴**); −81.0 t, 3F, $^4J_{F-F}$ = 7 Hz (**F⁸A** or **F⁸B**); −81.1 dm, 1F, $^2J_{F-F}$ = 150 Hz (**F³bB**); −81.1 t, 3F, $^4J_{F-F}$ = 7 Hz (**F⁸A** or **F⁸B**); −81.3 d, 3F, $^5J_{F-F}$ = 11 Hz (**F²A** or **F²B**); −81.3 dm, 1F, $^2J_{F-F}$ = 150 Hz (**F³bA**); −81.4 dm, 2F, $^2J_{F-F}$ = 140 Hz (**F⁶b**); −81.5 d, 3F, $^5J_{F-F}$ = 11 Hz (**F²A** or **F²B**); −116.7 t, 4F, $^3J_{F-H}$ = 15 Hz (**F⁹**); −121.4 m, 4F (**F¹¹**); −122.1 m, 4F (**F¹⁰**); 122.2 m, 4F (**F¹²**); 125.7 m, 4F (**F¹³**); −129.1 s, 2F (**F⁷A** or **F⁷B**); −129.3 s, 2F (**F⁷A** or **F⁷B**); −134.5 dq, 1F, $^4J_{F-F}$ = $^3J_{H-F}$ = 22 Hz (q), $^4J_{F-F}$ = 15 Hz (d) (**F¹B**); −135.2 dq, 1F, $^4J_{F-F}$ = $^3J_{H-F}$ = 22 Hz (q), $^4J_{F-F}$ = 15 Hz (d) (**F¹A**); −143.9 tm, 2F, $^4J_{F-F}$ = 21 Hz (**F⁴**). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 48.8 t, 1C, $^2J_{C-F}$ = 23 Hz (CF_2-**C**H_2); 49.6 d, 1C, $^2J_{C-F}$ = 20 Hz (CF–CH_2); 100–126 m, 14C (**C**F, **C**F_2 and **C**F_3 groups); 120.5 q, $^1J_{C-F}$ = 317 Hz (**C**F_3SO_2); 125.7 s, 1C (C**H**=CH); 125.8 s, 1C (C**H**=CH); 141.0 s, 1C (N–C**H**=N). MS (ESI), *m/z* (%): 865 [M−NTf_2^-]$^+$, 100; 280 [NTf_2]$^-$, 100.

*4.18. 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)-3-[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazolium bis(trifluoromethanesulfonyl)amide (**8c**)*



From the metathesis of 67 mg (0.07 mmol) of fluoroimidazolium triflate **3c** and 187 mg (0.70 mmol) of $LiNTf_2$, 75 mg (93%) of product **8c** was obtained according to the general procedure. ^1H NMR (299.97 MHz, acetone-d_6) δ 3.07 tt, $^3J_{H\text{-}F}$ = 18.7 Hz, $^3J_{H\text{-}H}$ = 6.7 Hz (CF_2-C**H$_2$**-CH_2); 4.93 t, 2H, $^3J_{H\text{-}H}$ = 6.7 Hz (CF_2-CH_2-C**H$_2$**); 5.63 m, 2H (CF–C**H$_2$**); 7.97 m, 1H, (C**H**=CH); 8.13 m, 1H (C**H**=CH); 9.57 m, 1H (N–C**H**=N). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −77.8 dm, 2F, $^2J_{F\text{-}F}$ = 145 Hz (**F^{3}a**); (−78.9 s, 12F (**CF$_3$**SO_2); −79.4 q, 3F, $^4J_{F\text{-}F}$ = $^5J_{F\text{-}F}$ = 10 Hz (**F^{5}A** or **F^{5}B**); (−79.5 q, 3F, $^4J_{F\text{-}F}$ = $^5J_{F\text{-}F}$ = 10 Hz (**F^{5}A** or **F^{5}B**); −80.4 dm, 2F, $^2J_{F\text{-}F}$ = 145 Hz (**F^6**); −80.6 t, 3F, $^4J_{F\text{-}F}$ = 10 Hz (**F^{14}A** or **F^{14}B**); −80.7 t, 3F, $^4J_{F\text{-}F}$ = 10 Hz (**F^{14}A** or **F^{14}B**); −80.8 dm, 2F, $^2J_{F\text{-}F}$ = 145 Hz (**F^{3}b**); −81.0 t, 3F, $^4J_{F\text{-}F}$ = 6 Hz (**F^{8}A** or **F^{8}B**); −81.1 t, 3F, $^4J_{F\text{-}F}$ = 6 Hz (**F^{8}A** or **F^{8}B**); −81.3 d, 3F, $^5J_{F\text{-}F}$ = 13 Hz (**F^{2}A** or **F^{2}B**); −81.3 dm, 2F, $^2J_{F\text{-}F}$ = 145 Hz (**F^{6}b**); −81.4 d, 3F, $^5J_{F\text{-}F}$ = 13 Hz (**F^{2}A** or **F^{2}B**); −113.5 m, 4F (**F^9**); −121.4 m, 4F (**F^{11}**); −122.4 m, 4F (**F^{10}**); −123.1 m, 4F (**F^{12}**); −125.7 m, 4F (**F^{13}**); −129.1 s, 2F (**F^{7}A** or **F^{7}B**); −129.2 s, 2F (**F^{7}A** or **F^{7}B**); −134.5 dq, 1F, $^4J_{F\text{-}F}$ = $^3J_{H\text{-}F}$ = 22 Hz (q), $^4J_{F\text{-}F}$ = 15 Hz (d) (**F^{1}B**); −134.9 dq, 1F, $^4J_{F\text{-}F}$ = $^3J_{H\text{-}F}$ = 22 Hz (q), $^4J_{F\text{-}F}$ = 15 Hz (d) (**F^{1}A**); −144.0 tm, 1F, $^4J_{F\text{-}F}$ = 21 Hz (**F^{4}A**); −144.1 m, 1F (**F^{4}B**). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 30.9 t, 1C, $^3J_{C\text{-}F}$ = 20.7 Hz (CF_2-**C**H_2-CH_2); 42.9 t, 1C, $^4J_{C\text{-}F}$ = 4.8 Hz (CF_2-CH_2-**C**H_2); 49.2 d, 1C, $^2J_{C\text{-}F}$ = 21.0 Hz (CF–CH_2); 100 - 140 m, 14C (**C**F, **C**F_2 and **C**F_3 groups); 123.9 s, 1C, (C**H**=CH); 124.9 s, 1C, (C**H**=CH); 139.6 s, (N–C**H**=N). MS (ESI), *m/z* (%): 879 [M−NTf_2^-]$^+$, 100; 87 [NTf_2]$^-$, 100.

*4.19. 1-(2,2,2-Trifluoroethyl)-3-[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazolium tetrafluoroborate bis(trifluoromethanesulfonyl)amide (**8d**)*

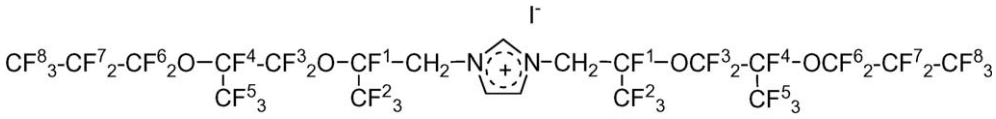


From the metathesis of 230 mg (0.30 mmol) of fluoroimidazolium triflate **3d** and 1.04 g (3.61 mmol) of $LiNTf_2$, 228 mg (85%) of product **8d** was obtained according to the general procedure. ^1H NMR (299.97 MHz, acetone-d_6) δ 5.61 q, 2H, $^3J_{H\text{-}F}$ = 8.5 Hz (CF_3-C**H$_2$**); 5.76 m, 2H, (C**H$_2$**); 8.21 m, 1H (C**H**=CH); 8.22 m, 1H (C**H**=CH); 9.78 s, 1H (N–C**H**=N). ^{19}F NMR (282.23 MHz, acetone-d_6) −71.5 t, 6F, $^3J_{F\text{-}H}$ = 8 Hz (**F^9**); −77.9 dm, 1F, $^2J_{F\text{-}F}$ = 150 Hz (**F^{3}aB**); −78.2 dm, 1F, $^2J_{F\text{-}F}$ = 150 Hz (**F^{3}aA**); −79.0 s, 12F (**CF$_3$**SO_2); −79.4 q, 3F, $^4J_{F\text{-}F}$ = $^5J_{F\text{-}F}$ = 8 Hz (**F^{5}A** or **F^{5}B**); −79.5 q, 3F, $^4J_{F\text{-}F}$ = $^5J_{F\text{-}F}$ = 9 Hz (**F^{5}A** or **F^{5}B**); −80.4 dm, 2F, $^2J_{F\text{-}F}$ = 150 Hz (**F^{6}a**); −80.9 dm, 1F, $^2J_{F\text{-}F}$ = 140 Hz (**F^{3}bB**); −81.0 dm, 1F, $^2J_{F\text{-}F}$ = 140 Hz (**F^{3}bA**); −81.0 t, 3F, $^4J_{F\text{-}F}$ = 6 Hz (**F^{8}A** or **F^{8}B**); −81.1 t, 3F, $^4J_{F\text{-}F}$ = 6 Hz (**F^{8}A** or **F^{8}B**); −81.3 d, 3F, $^5J_{F\text{-}F}$ = 13 Hz (**F^{2}A** or **F^{2}B**); −81.3 dm, 3F, $^2J_{F\text{-}F}$ = 150 Hz (**F^{6}bB**); −81.5 dm, 1F, $^2J_{F\text{-}F}$ = 150 Hz (**F^{6}bA**); −81.5 d, 3F, $^5J_{F\text{-}F}$ = 13 Hz (**F^{2}A** or **F^{2}B**); −129.2 s, 2F (**F^{7}A** or **F^{7}B**); −129.3 s, 2F (**F^{7}A** or **F^{7}B**); −134.6 dq, 1F, $^4J_{F\text{-}F}$ = $^3J_{H\text{-}F}$ = 22 Hz (q), $^4J_{F\text{-}F}$ = 15 Hz (d) (**F^{1}B**); −135.0 dq, 1F, $^4J_{F\text{-}F}$ = $^3J_{H\text{-}F}$ = 22 Hz (q), $^4J_{F\text{-}F}$ = 15 Hz (d) (**F^{1}A**); −144.0 tm, 1F, $^4J_{F\text{-}F}$ = 22 Hz (**F^{4}A** or **F^{4}B**); −144.1 m, 1F (**F^{4}A** or **F^{4}B**). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 49.8 q, $^2J_{C\text{-}F}$ = 37.1 Hz (CF_3-**C**H_2); 49.4 d, $^2J_{C\text{-}F}$ = 20.6 Hz (CF–CH_2); 100–126 m, 8C (**C**F, **C**F_2 and **C**F_3 groups); 120.3 q, $^1J_{C\text{-}F}$ = 316.8 (CF_3SO_2); 125.1 s (C**H**=CH); 125.8 s, (C**H**=CH); 140.9 s, (N–C**H**=N). MS (ESI), *m/z* (%): 615 [M−NTf_2^-]$^+$, 100; 280 [NTf_2^-]$^-$, 100.

*4.20. Preparation of bis(polyfluoroalkyl)imidazolium iodides **9**: general procedure*

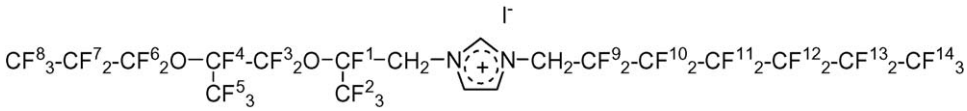
Bis(polyfluoroalkylated) imidazolium trifluoromethanesulfonate **3** (about 0.1 mmol) was dissolved in acetone (10 ml). Sodium iodide (5 to 10 fold excess) was added and the mixture was stirred for 5 h at r.t. Precipitated sodium triflate was filtered off, while acetone was removed using a rotary vacuum evaporator (40 °C/1 h/2 kPa) and the residue was dissolved in the 2:1 diethyl ether/deionized water mixture (150 ml). The separated organic phase was washed with deionized water (4 × 100 ml) and dried over anhydrous $MgSO_4$. Removal of the solvent using a rotary vacuum evaporator (40 °C/1 h/2 kPa) followed by heating the residue in vacuo (75 °C/12 h/10 Pa) yielded the target iodide **9**.

*4.21. 1,3-Bis[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazolium iodide (**9a**)*



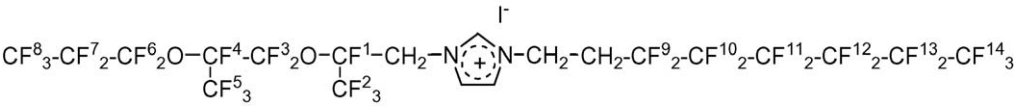
From the metathesis of 159 mg (0.14 mmol) of fluoroimidazolium triflate **3a** and 104 mg (0.70 mmol) of NaI, 139 mg (87%) of product **9a** was obtained according to the general procedure. ^1H NMR (299.97 MHz, acetone-d_6) δ 6.02 m, 4H (C**H$_2$**); 8.25 m, 2H (C**H**=CH); 10.45 m, 1H, (N–C**H**=N). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −77.3 dm, 2F, $^2J_{F\text{-}F}$ = 155 Hz (**F^{3}a**); −79.5 m, 6F (**F^5**); −80.4 dm, 2F, $^2J_{F\text{-}F}$ = 140 Hz (**F^{6}a**); −80.6 dm, 2F, $^2J_{F\text{-}F}$ = 140 Hz (**F^{6}b**); −81.2 m, 6F (**F^8**); −81.3 m, 6F (**F^2**); −81.6 dm, 2F, $^2J_{F\text{-}F}$ = 155 Hz (**F^{3}b**); −129.3 m, 4F (**F^7**); −134.8 m, 2F (**F^1**); −144.2 m, 2F (**F^4**). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 49.6 d, 2C $^2J_{C\text{-}F}$ = 20.1 Hz (**C**H_2); 100–126 m, 16C (**C**F, **C**F_2 and **C**F_3 groups); 120.4 q, 125.9 s, 2C (C**H**=CH); 141.2 s, 1C (N–C**H**=N). MS (ESI), *m/z* (%): 997 [M−I^-]$^+$, 100; 127 [I]$^-$, 100.

*4.22. 1-(2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoroheptyl)-3-[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazolium iodide (**9b**)*



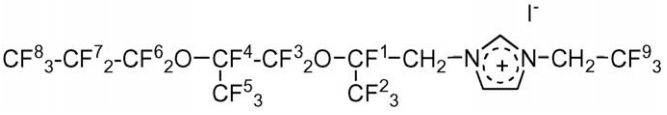
From the metathesis of 190 mg (0.18 mmol) of fluoroimidazolium triflate **3b** and 169 mg (1.12 mmol) of NaI, 175 mg (97%) of product9**b** was obtained according to the general procedure. ^{1}H NMR (299.97 MHz, acetone-d_6) δ 6.00 m, 2H (CF_2-C**H$_2$**); 6.07 m, 2H (CF–C**H$_2$**); 8.22 m, 1H (C**H**=CH); 8.29 m, 1H (C**H**=CH); 10,60 s, 1H (N–C**H**=N). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −77.8 dm, 1F, $^2J_{F-F}$ = 150 Hz (**F^{3}aA**); −78.0 dm, 1F, $^2J_{F-F}$ = 150 Hz (**F^{3}aB**); −79.5 q, 3F, $^4J_{F-F}$ = $^5J_{F-F}$ = 9 Hz (**F^{5}A** or **F^{5}B**); −79.6 q, 3F, $^4J_{F-F}$ = $^5J_{F-F}$ = 9 Hz (**F^{5}A** or **F^{5}B**); −80.4 dm, 2F, $^2J_{F-F}$ = 140 Hz (**F^{6}a**); −80.6 m, 6F, (**F^{14}**); −81.0 t, 3F, $^4J_{F-F}$ = 7 Hz (**F^{8}A** or **F^{8}B**); −81.1 dm, 1F, $^2J_{F-F}$ = 150 Hz (**F^{3}bB**); −81.1 t, 3F, $^4J_{F-F}$ = 7 Hz (**F^{8}A** or **F^{8}B**); −81.3 d, 3F, $^5J_{F-F}$ = 11 Hz (**F^{2}A** or **F^{2}B**); −81.3 dm, 1F, $^2J_{F-F}$ = 150 Hz (**F^{3}bA**); −81.4 dm, 2F, $^2J_{F-F}$ = 140 Hz (**F^{6}b**); −81.5 d, 3F, $^5J_{F-F}$ = 11 Hz (**F^{2}A** or **F^{2}B**); −116.7 t, 4F, $^3J_{H-H}$ = 15 Hz (**F^9**); −121.4 m, 4F (**F^{11}**); −122.1 m, 4F (**F^{10}**); 122.2 m, 4F (**F^{12}**); 125.7 m, 4F (**F^{13}**); −129.1 s, 2F (**F^{7}A** or **F^{7}B**); −129.3 s, 2F (**F^{7}A** or **F^{7}B**); −134.5 dq, 1F, $^4J_{F-F}$ = $^3J_{H-F}$ = 22 Hz (q), $^4J_{F-F}$ = 15 Hz (d) (**F^{1}B**); −135.2 dq, 1F, $^4J_{F-F}$ = $^3J_{H-F}$ = 22 Hz (q), $^4J_{F-F}$ = 15 Hz (d) (**F^{1}A**); −143.9 tm, 2F, $^4J_{F-F}$ = 21 Hz (**F^4**). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 48.8 t, 1C, $^2J_{C-F}$ = 23 Hz (CF_2-**C**H_2); 49.6 d, 1C, $^2J_{C-F}$ = 20 Hz (CF–CH_2); 100–126 m, 14C (**C**F, **C**F_2 and **C**F_3 groups); 125.7 s, 1C (C**H**=CH); 125.8 s, 1C (C**H**=CH); 141.0 s, 1C (N–C**H**=N). MS (ESI), *m/z* (%): 865 $[M-I^-]^+$, 100; 127 $[I]^-$, 100.

*4.23. 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)-3-[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazolium iodide (**9c**)*



From the metathesis of 41 mg (0.04 mmol) of fluoroimidazolium triflate **3c** and 30 mg (0.20 mmol) of NaI, 32 mg (79%) of product9**c** was obtained according to the general procedure. ^{1}H NMR (299.97 MHz, acetone-d_6) δ 3.25 tt, $^3J_{H-F}$ = 19.4 Hz, $^3J_{H-H}$ = 6.7 Hz (CF_2-C**H$_2$**-CH_2); 5.07 t, 2H, $^3J_{H-H}$ = 7.3 Hz (CF_2-CH_2-C**H$_2$**); 5.85 m, 2H (CF–C**H$_2$**); 8.09 m, 1H, (C**H**=CH); 8.30 m, 1H (C**H**=CH); 10.10 m, 1H (N–C**H**=N). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −77.8 dm, 2F, $^2J_{F-F}$ = 145 Hz (**F^{3}a**); −79.4 q, 3F, $^4J_{F-F}$ = $^5J_{F-F}$ = 10 Hz (**F^{5}A** or **F^{5}B**); −79.5 q, 3F, $^4J_{F-F}$ = $^5J_{F-F}$ = 10 Hz (**F^{5}A** or **F^{5}B**); −80.4 dm, 2F, $^2J_{F-F}$ = 145 Hz (**F^6**); −80.6 t, 3F, $^4J_{F-F}$ = 10 Hz (**F^{14}A** or **F^{14}B**); −80.7 t, 3F, $^4J_{F-F}$ = 10 Hz (**F^{14}A** or **F^{14}B**); −80.8 dm, 2F, $^2J_{F-F}$ = 145 Hz (**F^{3}b**); −81.0 t, 3F, $^4J_{F-F}$ = 6 Hz (**F^{8}A** or **F^{8}B**); −81.1 t, 3F, $^4J_{F-F}$ = 6 Hz (**F^{8}A** or **F^{8}B**); −81.3 d, 3F, $^5J_{F-F}$ = 13 Hz (**F^{2}A** or **F^{2}B**); −81.3 dm, 2F, $^2J_{F-F}$ = 145 Hz (**F^{6}b**); −81.4 d, 3F, $^5J_{F-F}$ = 13 Hz (**F^{2}A** or **F^{2}B**); −113.5 m, 4F (**F^9**); −121.4 m, 4F (**F^{11}**); −122.4 m, 4F (**F^{10}**); −123.1 m, 4F (**F^{12}**); −125.7 m, 4F (**F^{13}**); −129.1 s, 2F (**F^{7}A** or **F^{7}B**); −129.2 s, 2F (**F^{7}A** or **F^{7}B**); −134.5 dq, 1F, $^4J_{F-F}$ = $^3J_{H-F}$ = 22 Hz (q), $^4J_{F-F}$ = 15 Hz (d) (**F^{1}B**); −134.9 dq, 1F, $^4J_{F-F}$ = $^3J_{H-F}$ = 22 Hz (q), $^4J_{F-F}$ = 15 Hz (d) (**F^{1}A**); −144.0 tm, 1F, $^4J_{F-F}$ = 21 Hz (**F^{4}A**); −144.1 m, 1F (**F^{4}B**). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 31.1 t, $^3J_{C-F}$ = 20.7 Hz (CF_2-**C**H_2-CH_2); 42.9 t, $^4J_{C-F}$ = 4.8 Hz (CF_2-CH_2-**C**H_2); 49.4 d, $^2J_{C-F}$ = 21.0 Hz (CF–CH_2); 100(140 m, 14C (**C**F, **C**F_2 and **C**F_3 groups); 123.9 s, (C**H**=CH); 125.0 s (C**H**=CH); 139.7 s, (N–C**H**=N). MS (ESI), *m/z* (%): 879 $[M-I^-]^+$, 100; 127 $[I]^-$, 100.

*4.24. 1-(2,2,2-Trifluoroethyl)-3-[2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazolium iodide (**9d**)*



From the metathesis of 174 mg (0.23 mmol) of fluoroimidazolium triflate **3d** and 159 mg (1.4 mmol) of NaI, 150 mg (87%) of product **9d** was obtained according to the general procedure. ^{1}H NMR (299.97 MHz, acetone-d_6) δ 5.96 q, 2H, $^3J_{H-F}$ = 8.5 Hz (CF_3-C**H$_2$**); 6.03 m, 2H, (CF_2-C**H$_2$**); 8.20 m, 1H (C**H**=CH); 8.21 m, 1H (C**H**=CH); 10.78 m, 1H (N–C**H**=N). ^{19}F NMR (282.23 MHz, acetone-d_6) −71.5 t, 6F, $^3J_{F-H}$ = 8 Hz (**F^9**); −77.9 dm, 1F, $^2J_{F-F}$ = 150 Hz (**F^{3}aB**); −78.2 dm, 1F, $^2J_{F-F}$ = 150 Hz (**F^{3}aA**); −79.4 q, 3F, $^4J_{F-F}$ = $^5J_{F-F}$ = 8 Hz (**F^{5}A** or **F^{5}B**); −79.5 q, 3F, $^4J_{F-F}$ = $^5J_{F-F}$ = 9 Hz (**F^{5}A** or **F^{5}B**); −80.4 dm, 2F, $^2J_{F-F}$ = 150 Hz (**F^{6}a**); −80.9 dm, 1F, $^2J_{F-F}$ = 140 Hz (**F^{3}bB**); −81.0 dm, 1F, $^2J_{F-F}$ = 140 Hz (**F^{3}bA**); −81.0 t, 3F, $^4J_{F-F}$ = 6 Hz (**F^{8}A** or **F^{8}B**); −81.1 t, 3F, $^4J_{F-F}$ = 6 Hz (**F^{8}A** or **F^{8}B**); −81.3 d, 3F, $^5J_{F-F}$ = 13 Hz (**F^{2}A** or **F^{2}B**); −81.3 dm, 3F, $^2J_{F-F}$ = 150 Hz (**F^{6}bB**); −81.5 dm, 1F, $^2J_{F-F}$ = 150 Hz (**F^{6}bA**); −81.5 d, 3F, $^5J_{F-F}$ = 13 Hz (**F^{2}A** or **F^{2}B**); −129.2 s, 2F (**F^{7}A** or **F^{7}B**); −129.3 s, 2F (**F^{7}A** or **F^{7}B**); −134.6 dq, 1F, $^4J_{F-F}$ = $^3J_{H-F}$ = 22 Hz (q), $^4J_{F-F}$ = 15 Hz (d) (**F^{1}B**); −135.0 dq, 1F, $^4J_{F-F}$ = $^3J_{H-F}$ = 22 Hz (q), $^4J_{F-F}$ = 15 Hz (d) (**F^{1}A**); −144.0 tm, 1F, $^4J_{F-F}$ = 22 Hz (**F^{4}A** or **F^{4}B**); −144.1 m, 1F (**F^{4}A** or **F^{4}B**). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 49.8 q, $^2J_{C-F}$ = 37.1 Hz (CF_3-**C**H_2); 49.4 d, $^2J_{C-F}$ = 20.6 Hz (CF–CH_2); 100–126 m, 8C (**C**F, **C**F_2 and **C**F_3 groups); 125.1 s (C**H**=CH); 125.8 s, (C**H**=CH); 140.9 s, (N–C**H**=N). MS (ESI), *m/z* (%): 615 $[M-8I^-]^+$, 100; 147 $[I]^-$, 100.

4.25. Model reaction 1: attempted nucleophilic substitution of benzyl chloride with sodium azide in fluorous ionic liquid

A flask was loaded with fluoroalkoxylated imidazolium triflate **3a** (0.70 g, 0.61 mmol), NaN_3 (1.04 g, 16.0 mmol) and benzyl chloride (1.33 g, 10.5 mmol). The heterogeneous mixture was stirred for 4 days at 40 °C. After cooling with ice-water mixture, the upper organic layer was separated and analyzed by ^{1}H NMR, showing 22% conversion of benzyl chloride to benzyl azide without any other products formed. The bottom fluorous layer was dissolved in diethyl ether (25 ml) and washed with water (3 × 20 ml). From the organic layer, the solvent was removed using a rotary vacuum evaporator (40 °C/1 h/2 kPa) followed by heating the residue in vacuo (75 °C/12 h/10 Pa). Analysis of the residue by ^{1}H and ^{19}F NMR spectroscopy indicated a partial degradation (about 40%) of the ionic liquid **3a** into a complex mixture containing fluoroalkoxylated imidazole **1** together with other non-identified side products.

4.26. Model reaction 2: attempted reaction of tetrahydrofuran with benzoyl chloride in fluorous ionic liquid

A flask was loaded with fluoroalkoxylated imidazolium triflate **3a** (0.56 g, 0.5 mmol) and anhydrous $AlCl_3$ (0.13 g, 1.0 mmol) and the mixture was stirred for 5 h at r.t. THF (60 mg, 0.9 mmol) was added followed after 15 min by dropwise addition of benzoyl chloride (0.12 g, 0.9 mmol). The reaction mixture was stirred overnight at r.t., then water (20 ml) was added and the mixture was extracted with chloroform (3 × 20 ml). The organic layer was dried over anhydrous $MgSO_4$ and chloroform was removed using a rotary vacuum evaporator (40 °C/1 h/2 kPa). Analysis of the residue by ^{1}H NMR showed only traces of the targeted product in a complex mixture of side-products.

4.27. Model reaction 3: Diels–Alder reaction of 2,3-dimethylbuta-1,3-diene (DMB) with dimethyl acetylenedicarboxylate (DMAD) in a fluorous ionic liquid

A flask was loaded with ionic liquid **3a** (0.61 g, 0.6 mmol), DMB (0.13 g, 1.6 mmol) and DMAD (0.22 g, 1.5 mmol). The flask was

sealed and the heterogeneous mixture was stirred for 2 h at 80 °C. After cooling the mixture with a ice/water mixture, the upper organic layer was separated and checked by ^{1}H NMR showing no presence of DMAD. The bottom fluorous layer was washed with hexane (1 ml), and then the organic layers were combined. The solvents were removed using a rotary vacuum evaporator (40 °C/1 h/2 kPa) obtaining 0.32 g (94%) of dimethyl 4,5-dimethylcyclohexa-1,4-diene-1,2-dicarboxylate (**10**). The bottom fluorous layer was washed again with hexane (5 × 1 ml) and traces of solvent were removed by vacuum (150 °C/10 h/10 Pa). Control by ^{1}H and ^{19}F NMR spectroscopy indicated no decomposition of the ionic liquid **3a**. In the recycling experiment, to the imidazolium salt **3a** were added again DMB (0.13 g, 1.6 mmol) and DMAD (0.22 g, 1.5 mmol). After sealing, heating for 2 h at 80 °C and analogous work-up 0.33 g (98%) of diester **10** was obtained. Analogous repurification of the fluorous layer produced 0.56 g (95%) of imidazolium salt **3a** with unchanged ^{1}H and ^{19}F NMR spectra.

4.28. Control experiment 3a: Diels–Alder reaction of 2,3-dimethylbuta-1,3-diene (DMB) with dimethyl acetylenedicarboxylate (DMAD) without solvent

A flask was loaded with DMB (0.13 g, 1.6 mmol) and DMAD (0.22 g, 1.5 mmol). The flask was sealed and the mixture was stirred for 2 h at 80 °C. After cooling the reaction mixture with an ice/water mixture, the products were analyzed by ^{1}H NMR spectroscopy indicating 61% conversion of DMAD to cyclic diester **10**.

4.29. Control experiment 3b: Diels–Alder reaction of 2,3-dimethylbuta-1,3-diene (DMB) with dimethyl acetylenedicarboxylate (DMAD) in THF

A flask was charged with THF (1 ml), DMB (0.13 g, 1.6 mmol) and DMAD (0.22 g, 1.5 mmol). The flask was sealed and the mixture was stirred for 2 h at 80 °C. After cooling the reaction mixture with ice/water mixture, the mixture was analyzed with ^{1}H NMR spectroscopy indicating 65% conversion of DMAD to cyclic diester **10**.

4.30. Measurements of fluorous partition coefficient: general procedure

A 1.5 ml vial equipped with a magnetic stirbar was loaded with a known quantity of fluorous compound (10–40 mg), perfluorinated solvent (0.5 ml) and a non-fluorinated solvent (0.5 ml). The mixture was stirred while thermostatted at 25 °C for 1 h, then the stirring was stopped. After 0.5 h of standing at 25 °C 0.25 ml of each layer was removed, evaporated (40 °C/1 h/2 kPa) and weighed precisely.

4.31. Example of fluorous partition coefficient measurement: estimation of fluorophilicity of imidazolium salt 6b

Using 12.13 mg of fluoroalkoxylated imidazolium ionic liquid **6b**, 0.5 ml of toluene and 0.5 ml of perfluoro(methylcyclohexane) (PFMC), 5.40 mg and 0.11 mg of imidazolium salt **6b** were obtained after equilibration from the 0.25 ml portions of the respective PFMC and toluene layers, which corresponds to P_i(FBS) = 49.1 and f_i = 3.89.

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