Journal of Fluorine Chemistry 131 (2010) 1368–1376

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Greener fluorous chemistry: Convenient preparation of new types of 'CF_3-rich' secondary alkyl mesylates and their use for the synthesis of azides, amines, imidazoles and imidazolium salts

Anikó Nemes, László Tölgyesi, Andrea Bodor, József Rábai, Dénes Szabó *

Institute of Chemistry, Eötvös Loránd University, P.O. Box 32, H-1518, Budapest 112, Hungary

ARTICLE INFO

Article history:
Received 8 July 2010
Received in revised form 8 October 2010
Accepted 13 October 2010
Available online 20 October 2010

Keywords:
Alkylation
Fluorous secondary carbinols
Fluorous secondary mesylates
Fluorous imidazolium salts

ABSTRACT

2,2,2-Trifluoroethanol, 1,1,1,3,3,3-hexafluoro-2-propanol, and nonafluoro-*tert*-butyl alcohol were used as precursors for the preparation of the appropriate bis(polyfluoroalkoxymethyl)carbinols [$(R_{FH}OCH_2)_2$-CHOH, **1a–c**, R_{FH} = (a) CF_3CH_2, (b) $(CF_3)_2CH$, and (c) $(CF_3)_3C$] and the corresponding mesylates [$(R_{FH}OCH_2)_2CHOSO_2CH_3$, **2a–c**]. This novel design paradigm is introduced to eliminate the persistence and bioaccumulation problems of fluorous chemistry, which are associated with the use of longer linear perfluoroalkyl groups (e.g. $R_{fn} \geq$ *n*-C_8F_{17}, *n*-C_7F_{15}). Secondary mesylates **2a**,**b** and the primary tosylate [$(CF_3)_3COCH_2CH_2OTs$, **2d**] displayed acceptable reactivity towards azide and imidazole nucleophiles to allow the syntheses of novel fluorous azides, which on hydrogenolysis with H_2/Pd-C offered fluorous amines [$(R_{FH}OCH_2)_2CHNH_2$, **8a**,**b**], and 1-(polyfluoroalkyl)imidazoles (**5a**,**b**,**d**), respectively, while **2c** showed no reactivity due to steric hindrance. The reaction of **8a**,**b** with formaline, glyoxal and hydrochloric acid gave symmetrical 1,3-dialkylated imidazolium chlorides (**9a**,**b**), while **5a**,**b**,**d** were effectively alkylated using *n*-$C_8F_{17}(CH_2)_3I$, methyl iodide, 2-bromoethanol, and **2d** to yield the corresponding 1,3-dialkylimidazolium iodides, bromides, and tosylates (**7aa–ec**). Some physical properties of new compounds including mp, bp and solubility patterns were also analyzed; and the fluorophilicity values of **1a–c**, and **2a–c** were experimentally determined by GC and/or ^{19}F NMR spectroscopy.

1. Introduction

Sustainable fluorous chemistry [1] is an emerging paradigm, which calls for the elimination of the problems associated with the persistency of perfluoroalkanes and the bioaccumulation of compounds with longer perfluoroalkyl chains, such as $C_7F_{15}CO_2H$ or $C_8F_{17}SO_3H$ [2]. One obvious solution for these issues could be the replacement of volatile perfluoroalkanes and fluids with the more environmentally friendly polyfluoroalkyl-alkyl ethers (HFEs) [3] or by the introduction of novel fluorous ponytails, which are assembled from shorter perfluoroalkyl segments and expected to display higher degradability under environmental conditions [4].

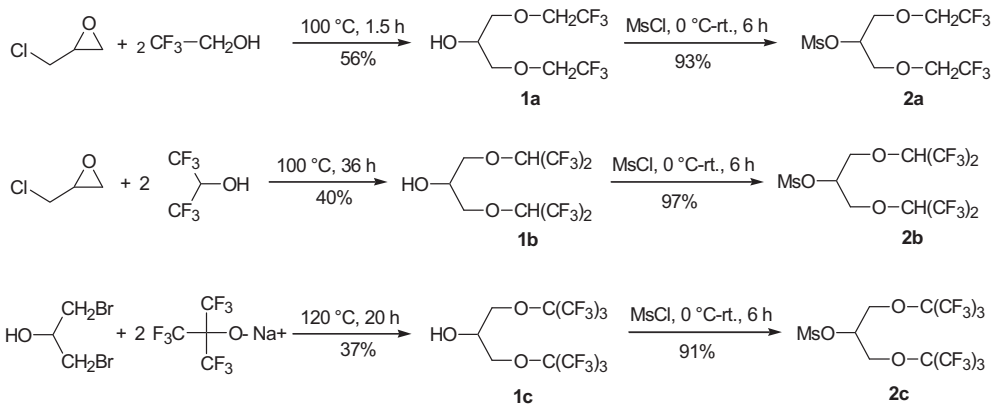
One family of fluorous compounds traces back to nonafluoro-*tert*-butyl alcohol as a final precursor [5]. Fluorophilic ethers (e.g. $(CF_3)_3CO(CH_2)_3R_{fn}$) [6], amines (e.g. $[(CF_3)_3CO(CH_2)_2]_xN_{3-x}$, x = 0–2) [7], alcohols (e.g. $[(CF_3)_3COCH_2]_3CCH_2OH$) [8], triflates (e.g. $[(CF_3)_3COCH_2]_3CCH_2OSO_2CF_3$) [9], second-generation (perfluoro-*tert*-butoxy)alkyl azodicarboxylates (e.g. $(CF_3)_3CO(CH_2)_3O_2CN{=}NCO_2(CH_2)_3OC(CF_3)_3$) [10], α,α-bis[(perfluoro-*tert*-butoxy)-methyl] substituted β-amino acids (e.g. $H_2NCH_2C[CH_2OC(CF_3)_3]_2CO_2H$) [11], spherical acetic acids (e.g. $[(CF_3)_3COCH_2]_3CCH_2OCH_2CO_2H$) [12], fluorous amphiphilic dendrimers [13], and other bulky structures [14] are based on this branched *F*-alcohol.

The above reagents are prototypes for a greener second generation of fluorous reagents bearing tags that are not expected to degrade in the environment to compounds that are highly persistent or that bioaccumulate in higher organisms [10]. Moreover, many of them display only a single ^{19}F NMR signal caused by the symmetry of the fluorinated spherical cone and consequently have high potential as ^{19}F MRI agents [8,9,11,12].

Other type of greener fluorous phase labels ($R_{FO}CH_2$) that could be a substitute for longer perfluoroalkyl ponytails are accessible by the reduction of HFPO based trimeric acid fluorides ($R_{FO}COF$) and consecutive activation of the formed $R_{FO}CH_2OH$ with Tf_2O, as described by Kvíčala et al. [15]. In analogy to similar polyfluorinated triflates with methylene spacer, the reactivity of $R_{FO}CH_2OTf$ is limited to strong and soft nucleophiles (imidazole, azide, and iodide). They have been used for the preparation of imidazolium

* Corresponding author. Tel.: +36 1 372 2500; fax: +36 1 372 2620.
E-mail address: szabod@elte.hu (D. Szabó).

0022-1139/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2010.10.001



Scheme 1. Synthesis of some 'CF_3-rich' isopropyl alcohols (**1a**–**c**) and mesylates (**2a**–**c**).

salt based room temperature ionic liquids; however those molecules display rather complex ^{19}F NMR patterns [16].

The present study is related to the synthesis of novel "CF_3-rich" and conformationally flexible fluorous reagents, and to reveal their reactivity depending on the steric hindrance caused by the increasing number of the CF_3-groups. Additionally our aim is to investigate the molecular structure–phase property correlations including melting and boiling points, volatility and fluorophilicity. We disclose here effective methods for the synthesis of fluorous secondary mesylates having structures of $[(CF_3)_{3-n}CH_n\text{-}O\text{-}CH_2]_2CH\text{-}OMs$ ($n = 0$–2) and demonstrate their ability for the alkylation of thioacetate, azide and imidazole nucleophiles.

In the literature there are many examples of alkylation of various C-, N-, O-, and S-nucleophiles with primary alkyl mesylates to afford the appropriate organic or fluorous products in excellent yields [17].

We chose here mesylates as leaving group of the fluorous secondary alkyl sulfonates (Scheme 1, **2a**–**c**) for atom economy, since they are the lightest one among sulfonates and halosulfates (MW: CH_3SO_3H (96.11) < FSO_3H (100.07) < $ClSO_3H$ (116.52) CF_3SO_3H (150.08) < $C_6H_5SO_3H$ (158.18) < $p\text{-}CH_3C_6H_4SO_3H$ (172.20) < $n\text{-}C_4F_9SO_2OH$ (300.10)). Their reactivity often matches that of tosylates [18].

We synthesized some novel fluorous azides, thioacetates, and 1-alkylimidazoles with branched tails as well (Scheme 2), then converted the latter compounds into unsymmetrical 1,3-disubstituted imidazolium salts (Scheme 3) or prepared the symmetrical ones with ring syntheses (Scheme 4), since imidazolium salts belong to a class of compounds receiving increasing interest both in basic and applied research [19].

2. Results and discussion

2.1. Synthesis

Bis(polyfluoroalkoxy)isopropyl alcohol intermediates are formed when polyfluorinated alcohols are treated with epichlorohydrin in the presence of KOH or pyridine [20]. Although compound **1a** has been used for some physico-chemical measurements [20a] or for the synthesis of new swallow-tailed liquid crystals [20b], and compound **1b** as an intermediate for the synthesis of fluorinated acrylate polymers [20c], they remained poorly characterized. We disclose here improved procedures for the synthesis of symmetrical 2° alcohols **1a**–**b** and our original method for **1c** (Scheme 1). The reaction of two equivalents of 2,2,2-trifluoroethanol or 1,1,1,3,3,3-hexafluoropropan-2-ol with one equivalent of epichlorohydrin in the presence of aqueous NaOH resulted in the formation of **1a** and **1b**, while with $(CF_3)_3COH$ failed to afford **1c**. Compound **1c** was prepared in moderate yield by reacting 1,3-dibromopropan-2-ol and sodium nonafluoro-*tert*-butoxide in dimethyl formamide. The latter salt can be prepared easily from the commercially available $(CF_3)_3COH$ by titration with aqueous NaOH. Then we prepared fluorous mesylates **2a**–**c**, *as new potential fluorous alkylating agents*, by the reaction of the precursor alcohols **1a**–**c** with methanesulfonyl chloride in dichloromethane in the presence of triethylamine (Scheme 1).

For testing the reactivity of 'CF_3-rich' mesylates **2a**–**c**, we selected *strong and soft* nucleophiles such as azide, thioacetate, and imidazole. We were also interested in the comparison of the substitution patterns with a similar alkylating agent, but having the leaving group in a primary position. Thus, 2-(perfluoro-*tert*-butoxy)ethyl tosylate (**2d**) was included here as a reference compound (Scheme 2), which has been introduced by us as a novel generation fluorous alkylating agent [7]. The results of these alkylation tests are summarized in Scheme 2.

First of all, it is a remarkable fact that reaction conditions and chemical yields are highly influenced by steric properties of these substrates. Thus mesylate **2c** did not react with any nucleophiles tested, even with the smallest azide-anion, perhaps due to its six bulky CF_3-groups which may cause considerable steric hindrance.

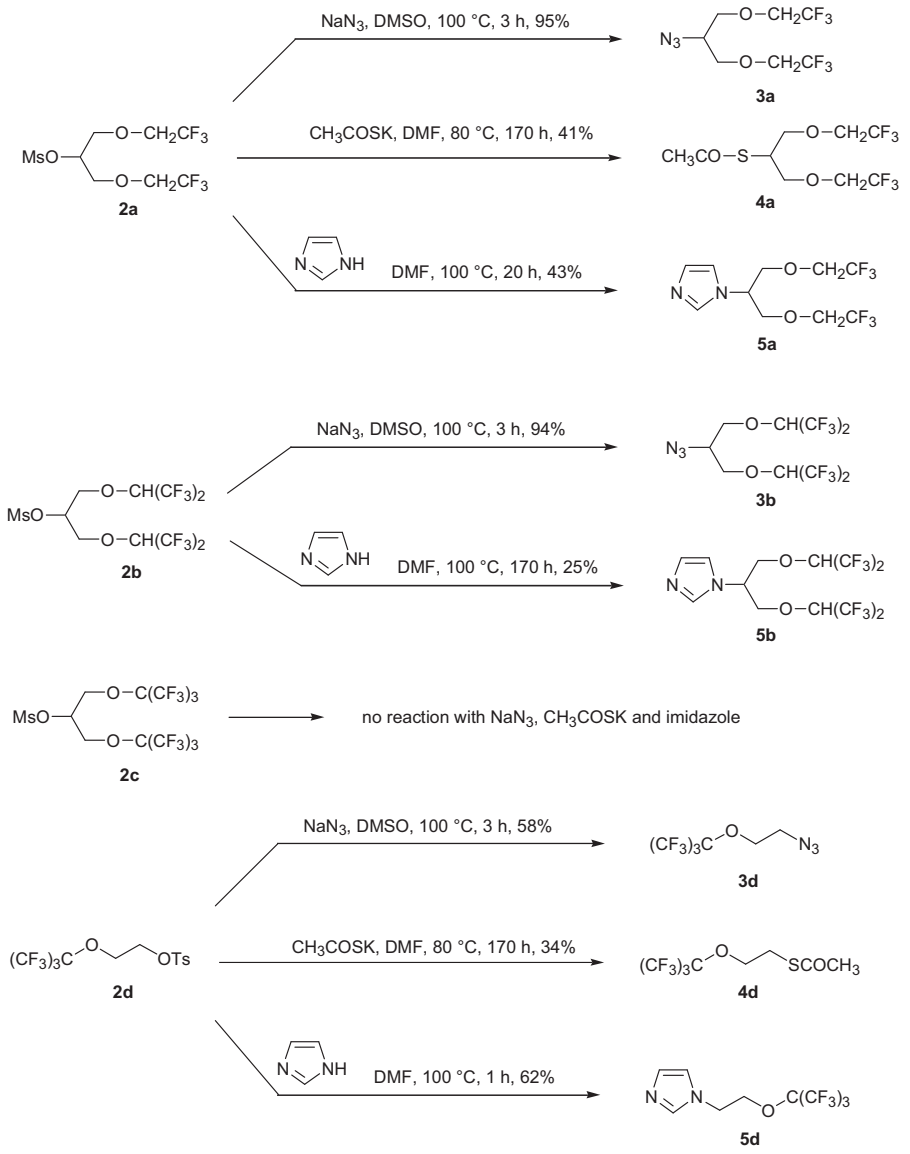
Therefore we tried to synthesize the corresponding $[(CF_3)_3COCH_2]_2CHOSO_2CF_3$, having a much better leaving group, from **1c** and Tf_2O, but its isolation in pure form failed due to quick decomposition even at 0 °C. However, the reactions of the other alkylating agents **2a**, **2b**, and **2d** with sodium azide afforded fluorous azides **3a**, **3b**, and **3d** in good to excellent isolated yields under same conditions (DMSO, 100 °C, and 3 h) (Scheme 2).

The reaction of thioacetate anion was successful with the primary (1°) tosylate **2d** and the least hindered secondary (2°) mesylate **2a** during one week reaction time with moderate yields, but the conversion of the more bulky mesylate **2b** into the corresponding thioacetate failed (Scheme 2).

For the *N*-alkylation of imidazole we applied this substrate in threefold excess to avoid the formation of 1,3-dialkylated imidazolium salts. While the reaction of the reference 1° tosylate **2d** gave the appropriate fluorous imidazole **5d** in relatively good yield (62%) within 1 h heating at 100 °C in DMF, those with the 2° mesylates **2a** or **2b** were rather sluggish and offered **5a** and **5b**, respectively, in 43 and 25% yields (Scheme 2).

We prepared a series of *N*,*N*′-dialkylimidazolium salts (**7a**, **a**–**d**; **7b**, **a**–**d**; **7d**, **a**–**d**; **7e**, **b**–**c**) by the reaction of 1-alkylimidazoles (**5a**–**b**,**d**–**e**) with one equivalent of a different alkylating agent (**6a**–**d**) (Scheme 3).

Reactants and reagents were loaded in a glass ampoule with acetonitrile, sealed and heated to 80 °C for 48 h. These reactions afforded the expected products only when the second alkyl groups (R^2) were primary. Thus we could apply this type of reaction with tosylate **2d** successfully, but with mesylates **2a**–**c** as alkylating



Scheme 2. Alkylation potential of 'CF_3-rich' mesylates/tosylate for strong and soft nucleophiles.

reagents failed completely. This is in contrary to the successful double alkylation of imidazole with 2-bromopropane [21].

3-(Perfluorooctyl)propyl iodide (**6a**), methyl iodide (**6b**), and 2-bromoethanol (**6c**) were used as further alkylating agents, while 1-[3-(perfluorooctyl)propyl]imidazole (**5e**) as another fluorous substrate (Scheme 3).

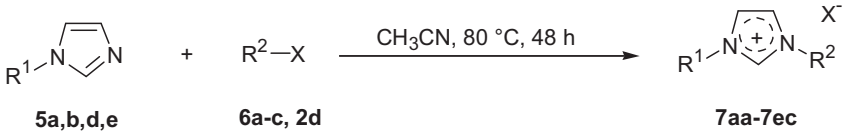
Since imidazolium salts with two 2° *N*-alkyl groups could not be prepared by direct alkylation with **2a** and **2b**, we introduced an alternative method for the synthesis of the symmetrical 1,3-dialkylimidazolium salts by a three components ring construction reaction in analogy to literature examples [22]. Starting azides **3a** and **3b** were converted into amines **8a** and **8b** by catalytic hydrogenation, which then reacted with CH_2O, glyoxal and hydrochloric acid in benzene solution to afford imidazolium chlorides **9a** and **9b** in good yields (Scheme 4).

2.2. Phase properties of selected compounds

We thought that the determination of fluorophilicity values ($f = \ln P_{CF_3C_6F_{11}/CH_3C_6H_5}$) for **1a–c** and **2a–c** could be a probe of their phase behaviour. Although we could not determine the equilibrium concentrations of **1a** or **2a** in the perfluoro(methylcyclohexane) phase by GC or ^{19}F NMR methods due their low fluorous solubility, the fluorophilicity values obtained for the other samples were in agreement with the expected trends [23]. Only the perfluoro-*tert*-butoxy-substituted analytes **1c** and **2c** are fluorophilic ($f = \ln P > 0$), while the fluorous partition coefficients are increasing by the number of the CF_3-groups for compounds in both series (Table 1).

It should also be commented that the volatility of these alcohols and mesylates steeply increases with the number of CF_3-groups and compensates for their higher molecular weights so that the boiling points are decreasing in the order of **1a** > **1b** > **1c** and **2a** > **2b** > **2c** (Table 1). The shielding effect of CF_3-groups on intermolecular attractive interactions could be responsible for this *volatility phenomenon*, which increases as the CF_3CH_2O- < $(CF_3)_2CHO-$ < $(CF_3)_3CO-$ structural fragments are in use. The chemical reactivity of **1a–c** and **2a–c** is also affected by the steric and electronic effects of these CF_3-rich fluorous building blocks (cf. Scheme 2).

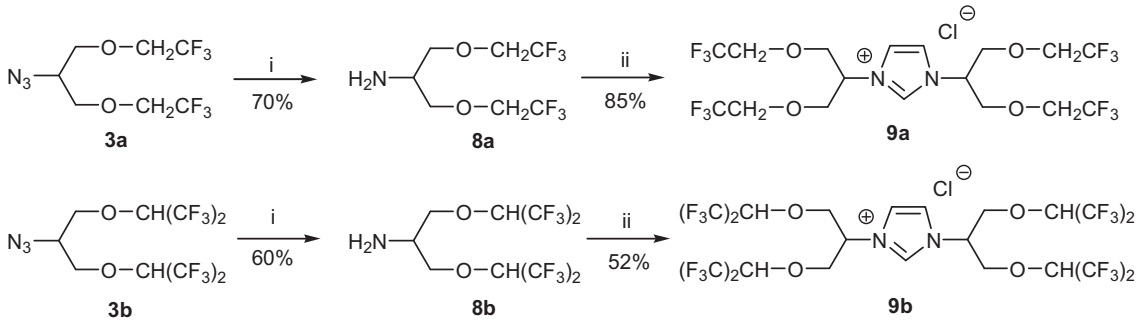
The solubility patterns and the state of matter (i.e. liquid or solid) of the compounds shown above can be analyzed qualitatively (cf. Schemes 3 and 4). Compounds with lower melting points display higher absolute solubilities in the solvents tested (cf.



5a,b,d,e **6a-c, 2d** **7aa-7ec**

N-alkyl-imidazole	R^1	R^2-X	Product	Yield (%)	Mp °C
5a	$CH(CH_2OCH_2CF_3)_2$	**6a** $C_8F_{17}(CH_2)_3I$	**7aa**	72	88-93
5a	$CH(CH_2OCH_2CF_3)_2$	**6b** CH_3I	**7ab**	80	oil
5a	$CH(CH_2OCH_2CF_3)_2$	**6c** $HOCH_2CH_2Br$	**7ac**	77	oil
5a	$CH(CH_2OCH_2CF_3)_2$	**2d** $(CF_3)_3COCH_2CH_2OTs$	**7ad**	83	98-105
5b	$CH[CH_2OCH(CF_3)_2]_2$	**6a** $C_8F_{17}(CH_2)_3I$	**7ba**	93	waxy solid
5b	$CH[CH_2OCH(CF_3)_2]_2$	**6b** CH_3I	**7bb**	81	waxy solid
5b	$CH[CH_2OCH(CF_3)_2]_2$	**6c** $HOCH_2CH_2Br$	**7bc**	67	waxy solid
5b	$CH[CH_2OCH(CF_3)_2]_2$	**2d** $(CF_3)_3COCH_2CH_2OTs$	**7bd**	77	96-99
5d	$CH_2CH_2OC(CF_3)_3$	**6a** $C_8F_{17}(CH_2)_3I$	**7da**	72	148.5-161
5d	$CH_2CH_2OC(CF_3)_3$	**6b** CH_3I	**7db**	97	123-132
5d	$CH_2CH_2OC(CF_3)_3$	**6c** $HOCH_2CH_2Br$	**7dc**	77	oil
5d	$CH_2CH_2OC(CF_3)_3$	**2d** $(CF_3)_3COCH_2CH_2OTs$	**7dd**	66	162-164
5e	$(CH_2)_3C_8F_{17}$	**6b** CH_3I	**7eb**	63	101-106
5e	$(CH_2)_3C_8F_{17}$	**6c** $HOCH_2CH_2Br$	**7ec**	56	waxy solid

Scheme 3. Synthesis of fluorous imidazolium salts by alkylation of *N*-alkylimidazoles.



i: H_2, Pd/C, EtOH, 280 kPa, 10 h; ii: H-CHO, benzene, 0 °C, 1 h then OHC-CHO, HCl, 100 °C, 24 h

Scheme 4. Synthesis of symmetrical 1,3-dialkylimidazolium salts by ring construction from 2° amines.

[23b]). Typical solubility patterns at room temperature are disclosed below.

Compounds **1a**–**c** and **2a**–**c** are practically insoluble in H_2O, but miscible with ether and CH_2Cl_2, and soluble in DMSO, $CDCl_3$, and toluene. Azides **3a**, **3b** and **3d** are miscible with ether and CH_2Cl_2, highly soluble in EtOH. Amines **8a** and **8b** are soluble in CH_3OH, CH_2Cl_2, $CHCl_3$, ether and toluene, but insoluble in water.

The crystalline imidazolium salts (**7aa**, **7ad**, **7bd**, **7da**, **7db**, **7dd** and **7eb**, Scheme 3) are easily soluble in CH_2Cl_2, $CHCl_3$, DMSO, methanol and ethyl acetate, while slightly soluble in ether and practically insoluble in water, hexane and *c*-$CF_3C_6F_{11}$. The lower melting ones show higher solubilities in CH_2Cl_2, $CHCl_3$, DMSO, and ethyl acetate, and moreover, they are soluble in ether and methanol, while insoluble in *n*-hexane and *c*-$CF_3C_6F_{11}$.

Table 1
Boiling points and fluorophilicity values of secondary fluorous alcohols and alkyl mesylates.

Compounds	MW	Bp (°C/kPa)	%*F*	$f = \ln P$
1a $(CF_3CH_2OCH_2)_2CH$-OH	256.15	93–96/2.67	44.50	n.d.
1b $((CF_3)_2CHOCH_2)_2CH$-OH	392.14	86–88/2.67	58.14	-0.45 ± 0.15
1c $((CF_3)_3COCH_2)_2CH$-OH	528.14	74–79/2.67	64.75	2.3 ± 0.05
2a $(CF_3CH_2OCH_2)_2CH$-OSO_2CH_3	334.24	138–140/0.07	34.10	n.d.
2b $((CF_3)_2CHOCH_2)_2CH$-OSO_2CH_3	470.23	112–114/0.07	48.48	-2.3 ± 0.3
2c $((CF_3)_3COCH_2)_2CH$-OSO_2CH_3	606.23	79–80/0.07	56.41	0.9 ± 0.1

n.d., not determined.

3. Conclusions

A series of 'CF_3-rich' secondary mesylates **2a–c** was synthesized and their reactivity compared with that of a primary fluorous tosylate [**2d**, $(CF_3)_3COCH_2CH_2OTs$]. All but **2c** of them could supplement the inventory of fluorous alkylating agents as proved by the synthesis of selected fluorous azides, thioacetates and *N*-alkyl-imidazoles. When such 'CF_3-rich' 1° and 2° fluorous alkoxyalkyl groups are incorporated in the molecules of 1,3-dialkylated imidazolium salts, their physical properties display larger diversity due to the conformational flexibility of these novel generation ponytails and symmetry factors opposed to the use of the classical ones [24]. The continuous move to the use of 'CF_3-rich' fluorous building blocks could facilitate the elimination of the environmental problems associated with the use of longer perfluoroalkyl groups.

4. Experimental

4.1. General description of materials and methods

CF_3CH_2OH, $(CF_3)_2CHOH$, $(CF_3)_3COH$ and *c*-$CF_3C_6F_{11}$ were purchased from Fluorochem, while $(CF_3)_3CONa$ [7a], **2d** [7a], **6a** [25], and $(BrCH_2)_2CHOH$ [26] were prepared as reported. The other reagents and solvents were Alfa-Aesar and Molar Chemicals, Ltd (Budapest) products. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker Avance 250 (250 MHz for ^{1}H) spectrometer using a 5 mm inverse ^{1}H/^{13}C/^{31}P/^{19}F probe head at 25 °C. Chemical shift values are in ppm relative to TMS (^{1}H, $\delta = 0$), $CDCl_3$ (^{13}C, $\delta = 77.0$) or CCl_3F (^{19}F, $\delta = 0$) on the δ scale. Coupling constants *J* were given in Hz. Oily and waxy samples in several cases caused line broadening in NMR spectra, therefore no exact coupling constants can be given. Agilent Technologies 6210A Time-of-Flight MS instrument equipped with a dual-nebulizer ESI source, operated in positive ion mode, was employed to acquire high resolution mass spectra. Melting points were determined on a Boetius micromelting point apparatus and are uncorrected. All reactions were monitored by GC (Hewlett-Packard 5890 Series II, PONA [cross-linked methylsilicone gum] 50 m × 0.2 mm × 0.5 μm column, H_2 carrier gas, FID detection) and/or using TLC Aluminium sheets (Silica gel 60 F_{254}, Merck KGaA, Darmstadt) with a CH_2Cl_2:methanol (9:1, v/v) eluent system. Fluorous partition coefficients (*P*) were determined by GC [7a] or by ^{19}F NMR as follows. In a 2 ml volumetric flask the given compound (30 mg) was extracted in a 1.00 ml to 1.00 ml mixture of pre-equilibrated *c*-$CF_3C_6F_{11}$ and toluene. The closed vessel was first immersed in a water bath (50 °C) for 30 min with frequent shaking, and then allowed to cool to 25 °C. After standing overnight at this temperature 50 ± 0.5 μl aliquots of the separated upper and lower phases were withdrawn and added to 20 ± 0.2 mg $C_6H_5CF_3$ in 100 μl $CDCl_3$, which served as an internal standard for NMR analysis (**1c**/^{19}F NMR, Table 1).

4.2. 1,3-Bis(2,2,2-trifluoroethoxy)propan-2-ol (1a)

To a stirred solution of sodium hydroxide (10.00 g, 0.25 mol) in water (120 ml) was added slowly 2,2,2-trifluoroethanol (21.8 ml, 30.0 g, 0.30 mol) at 0 °C. After stirring for 5 min epichlorohydrin (11.7 ml, 13.87 g, 0.15 mol) was added and the mixture was stirred at 100 °C for 1.5 h. The resulting solution was cooled to room temperature and the organic layer was separated. The aqueous phase was extracted with ether (2× 25 ml), the organic layers were combined, then washed with water (25 ml) and dried (Na_2SO_4). The solvent was removed under vacuum and the crude product was distilled to afford the title alcohol **1a**. Yield: 21.50 g (56%) colourless liquid, bp 93–96 °C/2.67 kPa (Lit. [20a,b] bp 86 °C/2.13 kPa, and 42–45 °C/1.20 kPa). ^{1}H NMR ($CDCl_3$): δ 2.64 (1H, s, OH), 3.65–3.76 (4H, m, CH_2-O), 3.90 (4H, q, $^3J_{HF} = 8.75$ Hz, CF_3-CH_2), 4.00 (1H, p, $^3J_{HH} = 5.50$ Hz, CH). ^{13}C NMR ($CDCl_3$): δ 69.2 (q, $^2J_{CF} = 34$ Hz, CH_2CF_3), 69.7 (CH), 73.4 (CH_2-O), 124.2 (q, $^1J_{CF} = 280$ Hz, CF_3). ^{19}F NMR ($CDCl_3$): δ −74.9 (6F, s, CF_3). ESI-HRMS: $m/z = 255.0461$; calcd. for $[C_7H_9F_6O_3]$ 255.0466.

4.3. 1,3-Bis[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]propan-2-ol (1b)

To a stirred solution of sodium hydroxide (10.61 g, 0.265 mol) in water (126 ml) was added slowly 1,1,1,3,3,3-hexafluoropropan-2-ol (33.5 ml, 53.50 g, 0.318 mol) at 0 °C. After stirring for 5 min epichlorohydrin (12.5 ml, 14.73 g, 0.16 mol) was added and the mixture was stirred at 100 °C for 36 h. After cooling to room temperature the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2× 100 ml), the organic phases were combined, then washed with water (25 ml) and dried (Na_2SO_4). The solvent was removed under vacuum and the crude product was distilled to afford the title alcohol **1b**. Yield: 25.33 g (41%), colourless liquid, bp 86–88 °C/2.67 kPa (Lit. [20c] bp 56.5–57 °C/0.67 kPa). ^{1}H NMR ($CDCl_3$): δ 2.47 (1H, d, $^3J_{HH} = 5.5$ Hz, OH), 3.995 (4H, m, CH_2O), 4.08 (1H, p, $^3J_{HH} = 5.5$ Hz, CHOH), 4.20 (2H, septet, $^3J_{HF} = 5.9$ Hz, $CH(CF_3)_2$). ^{13}C NMR ($CDCl_3$): δ 69.6 (CHOH), 74.9 (CH_2O), 77.2 (septet, $^2J_{CF} = 32$ Hz, $CH(CF_3)_2$), 121.7 (q, $^1J_{CF} = 282$ Hz, CF_3). ^{19}F NMR ($CDCl_3$): δ −74.5 (d, $^1J_{CF} = 5.9$ Hz, CF_3). ESI-HRMS: $m/z = 392.0265$; calcd. for $[C_9H_8F_{12}O_3]$ 392.0282.

4.4. 1,3-Bis[2,2,2-trifluoro-1,1-bis(trifluoromethyl)ethoxy]propan-2-ol (1c)

A stirred mixture of 1,3-dibromopropan-2-ol (0.84 g, 3.85 mmol) and sodium nonafluoro-*tert*-butoxide (2.40 g, 9.30 mmol) in dry DMF (10 ml) was heated at 120 °C under N_2 for 20 h. Water (20 ml) and ether (10 ml) was added, then the aqueous phase was separated and extracted with ether (2× 10 ml). The organic layers were combined, washed with water (3× 100 ml) and dried over Na_2SO_4. The solvent was removed under vacuum the crude product was distilled to afford the title alcohol **1c**. Yield: 0.75 g (37%), colourless liquid, bp 74–79 °C/2.67 kPa. ^{1}H NMR ($CDCl_3$): δ 2.40 (1H, s, OH), 4.00–4.20 (5H, overlapping signals, CH_2CHCH_2). ^{13}C NMR ($CDCl_3$): δ 68.8 (CH-OH), 69.0 (CH_2-O), 120.5 (q, $^1J_{CF} = 292$ Hz, CF_3). ^{19}F NMR ($CDCl_3$): δ −71.0 (s, CF_3). ESI-HRMS: $m/z = 528.0009$; calcd. for $[C_{11}H_6F_{18}O_3]$ 528.0030.

4.5. General procedure for the synthesis of mesylates 2a–c

To a solution of **1a** or **1b** (10.25 g or 15.68 g; 40 mmol) and triethylamine (6.41 ml, 4.65 g, 46 mmol) in anhydrous CH_2Cl_2 (150 ml) was added with stirring a solution of CH_3SO_2Cl (3.56 ml, 5.27 g, 46 mmol) in anhydrous CH_2Cl_2 (50 ml) at 0 °C. The suspension was warmed to room temperature and stirred for 4 h. Then ice-water (50 ml) was added and stirred for 1 h. Alcohol **1c** was reacted analogously on a 2.11 g (4.0 mmol) scale. The organic phase was separated, washed with water and dried (Na_2SO_4). The solvent was evaporated and the product was purified by distillation.

4.5.1. 1,3-Bis(2,2,2-trifluoroethoxy)propan-2-yl methanesulfonate (2a)

Yield: 12.42 g (93%) colourless liquid, bp 138–140 °C/66.7 Pa. ^{1}H NMR ($CDCl_3$): δ 3.08 (3H, s, SO_2CH_3), 3.9–4.0 (8H, m, CH_2OCH_2), 4.86 (1H, p, $^3J_{HH} = 4.8$ Hz, CH). ^{13}C NMR ($CDCl_3$): δ 38.6 (SO_2CH_3), 69.2 (q, $^2J_{CF} = 34$ Hz, CF_3CH_2), 71.6 (CH_2O), 79.2 (CH), 124.0 (q, $^1J_{CF} = 280$ Hz, CF_3). ^{19}F NMR ($CDCl_3$): δ −74.8 (t, $^3J_{HF} = 8.5$ Hz, CF_3). ESI-HRMS: $m/z = 334.0310$; calcd. for $[C_8H_{12}F_6O_5S]^+$ 334.0316.

*4.5.2. 1,3-Bis[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]propan-2-yl methanesulfonate (**2b**)*

Yield: 17.48 g (97%) colourless liquid, bp 112–114 °C/66.7 Pa. ^{1}H NMR ($CDCl_3$): δ 3.07 (3H, s, $SO_2C\underline{H}_3$), 4.14 (4H, d, $^3J_{HH}$ = 4.8 Hz, $C\underline{H}_2CH$), 4.19 (2H, septet, $^3J_{HF}$ = 5.8 Hz, $C\underline{H}(CF_3)_2$), 4.90 (1H, p, $^3J_{HF}$ = 4.8 Hz, $CHCH_2$). ^{13}C NMR ($CDCl_3$): δ 38.5 ($SO_2\underline{C}H_3$), 73.1 ($\underline{C}H$-OSO_2), 77.3 ($\underline{C}H_2O$), 77.1 (septet, $^2J_{CF}$ = 32 Hz, $\underline{C}H(CF_3)_2$), 121.5 (q, $^1J_{CF}$ = 284 Hz, $\underline{C}F_3$). ^{19}F NMR ($CDCl_3$): δ −74.4 (d, $^3J_{HF}$ = 5.8 Hz, $C\underline{F}_3$). ESI-HRMS: m/z = 470.0057; calcd. for $[C_{10}H_{10}F_{12}O_5S]^+$ 470.0061.

*4.5.3. 1,3-Bis[2,2,2-trifluoro-1,1-bis(trifluoromethyl)ethoxy]propan-2-yl methanesulfonate (**2c**)*

Yield: 2.20 g (91%) colourless liquid, bp 79–80 °C/66.7 Pa. ^{1}H NMR ($CDCl_3$): δ 3.07 (3H, s, $SO_2C\underline{H}_3$), 4.30 (4H, d, $^3J_{HH}$ = 5.0 Hz, $C\underline{H}_2$), 4.94 (1H, p, $^3J_{HH}$ = 5.0 Hz, $C\underline{H}$). ^{13}C NMR ($CDCl_3$): δ 38.4 ($SO_2\underline{C}H_3$), 67.4 ($\underline{C}H_2O$), 75.7 ($\underline{C}H$), 120.4 (q, $^1J_{CF}$ = 292 Hz, $\underline{C}F_3$). ^{19}F NMR ($CDCl_3$): δ −71.0 (s, $C\underline{F}_3$).

*4.6. General procedure for the synthesis of azides **3a**, **3b** and **3d***

To a solution of mesylate **2a**, **2b** or tosylate **2d** (30 mmol) in anhydrous DMSO (75 ml) was added sodium azide (4.10 g, 63 mmol) with stirring, and the mixture was heated to 100 °C and stirred for 3 h. Then it was poured into water (300 ml) and extracted with ether (3× 100 ml). The organic layers were combined, washed with water (3× 30 ml) and dried (Na_2SO_4). The solvent was evaporated at room temperature (CAUTION: *overheating of azides could lead to violent decompositions*) and the product obtained was used without further purification.

*4.6.1. 5-Azido-1,1,1,9,9,9-hexafluoro-3,7-dioxanonane (**3a**)*

Yield: 8.01 g (95%) pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 3.77–3.82 (5H, m, $C\underline{H}_2C\underline{H}C\underline{H}_2$), 3.89 (4H, q, $^3J_{HF}$ = 8.6 Hz, $CF_3C\underline{H}_2$). ^{13}C NMR ($CDCl_3$): δ 60.5 ($\underline{C}H$), 69.2 (q, $^2J_{CF}$ = 34 Hz, $CF_3\underline{C}H_2$), 71.9 ($\underline{C}H_2O$), 124.1 (q, $^1J_{CF}$ = 280 Hz, $\underline{C}F_3$). ^{19}F NMR ($CDCl_3$): δ −74.7 (t, $^3J_{HF}$ = 8.6 Hz, $C\underline{F}_3$).

*4.6.2. 5-Azido-1,1,1,9,9,9-hexafluoro-3,7-dioxa-2,8-bis(trifluoromethyl)nonane (**3b**)*

Yield: 11.8 g (94%) pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 3.83 (1H, p, $^3J_{HH}$ = 5.4 Hz, $C\underline{H}N_3$), 4.00 (4H, m, $^3J_{HH}$ = 5.4 Hz, $C\underline{H}_2O$), 4.14 (2H, septet, $^3J_{HF}$ = 5.8 Hz, $C\underline{H}(CF_3)_2$). ^{13}C NMR ($CDCl_3$): δ 59.9 ($\underline{C}HN_3$), 73.4 ($\underline{C}H_2O$), 77.1 (septet, $^2J_{CF}$ = 33 Hz, $\underline{C}H(CF_3)_2$), 121.5 (q, $^1J_{CF}$ = 284 Hz, $\underline{C}F_3$). ^{19}F NMR ($CDCl_3$): δ −74.5 (12F, d, $^3J_{HF}$ = 5.8 Hz, $C\underline{F}_3$).

*4.6.3. 5-Azido-1,1,1-trifluoro-2,2-bis(trifluoromethyl)-3-oxapentane (**3d**)*

Yield: 5.31 g (58%) pale yellow viscous oil. ^{1}H NMR ($CDCl_3$): δ 3.48 (2H, t, $^3J_{HH}$ = 4.8 Hz, $C\underline{H}_2N_3$), 4.20 (2H, t, $^3J_{HH}$ = 4.8 Hz, $C\underline{H}_2O$). ^{13}C NMR ($CDCl_3$): δ 50.7 ($\underline{C}H_2N_3$), 69.2 ($\underline{C}H_2O$), 120.6 (q, $^1J_{CF}$ = 292 Hz, $\underline{C}F_3$). ^{19}F NMR ($CDCl_3$): δ −71.0 (s, $C\underline{F}_3$).

*4.7. General procedure for the synthesis of thioacetates **4a** and **4d***

A stirred solution of mesylate **2a** or tosylate **2d** (20.10 g or 26.06 g; 60 mmol) and potassium thioacetate (7.50 g, 66 mmol) in anhydrous DMF (120 ml) was heated at 100 °C under N_2 for a week. The resulting brown gel was treated with water (120 ml), and then the organic phase was separated. The aqueous layer was extracted with ether (3× 100 ml) and the organic phase was washed with water (2× 30 ml), dried over Na_2SO_4 and evaporated. The residue was purified by distillation under reduced pressure.

*4.7.1. 1,3-Bis(2,2,2-trifluoroethoxy)propan-2-yl thioacetate (**4a**)*

Yield: 7.73 g (41%) yellow liquid, bp 88 °C/66.7 Pa. ^{1}H NMR ($CDCl_3$): δ 2.36 (3H, s, $C\underline{H}_3$), 3.75–3.96 (9H, m, $(C\underline{H}_2OC\underline{H}_2)_2C\underline{H}$). ^{13}C NMR ($CDCl_3$): δ 31.0 ($\underline{C}H_3$), 43.0 ($\underline{C}H$), 68.9 (q, $^2J_{CF}$ = 34 Hz, $\underline{C}H_2CF_3$), 71.0 ($\underline{C}H_2O$), 124.2 (q, $^1J_{CF}$ = 280 Hz, $\underline{C}F_3$), 194.9 ($\underline{C}O$). ^{19}F NMR ($CDCl_3$): δ −74.8 (t, $^3J_{HF}$ = 8.6 Hz, $C\underline{F}_3$).

*4.7.2. 5,5,5-Trifluoro-4,4-bis(trifluoromethyl)-3-oxapentan-1-yl thioacetate (**4d**)*

Yield: 6.90 g (34%) yellow liquid, bp 160–163 °C. ^{1}H NMR ($CDCl_3$): δ 2.36 (3H, s, $C\underline{H}_3$), 3.16 (2H, t, $^3J_{HH}$ = 6.4 Hz, $C\underline{H}_2S$), 4.10 (2H, t, $^3J_{HH}$ = 6.4 Hz, $C\underline{H}_2O$). ^{13}C NMR ($CDCl_3$): δ 28.9 (S-$\underline{C}H_2$), 30.8 ($\underline{C}H_3$), 68.5 ($\underline{C}H_2$-O), 120.6 (q, $^1J_{CF}$ = 295 Hz, $\underline{C}F_3$), 195.4 (CO). ^{19}F NMR ($CDCl_3$): δ −71.0 (s, $C\underline{F}_3$).

*4.8. General procedure for the synthesis of N-alkylimidazoles **5a**, **5b** and **5d***

A stirred solution of the alkylating agent (halide, toluenesulfonate, or methanesulfonate; 1 equiv.) and imidazole (3 equiv.) in CH_2Cl_2 was heated at 100 °C for 1–170 h. The reaction mixture was poured into 1 M NaOH (3.3 equiv.), extracted with CH_2Cl_2 (3×). The organic layers were combined, washed with water (3×), dried (Na_2SO_4) and evaporated. The residue was purified by vacuum distillation to afford the *N*-alkylimidazole.

*4.8.1. 1-(1,1,1,9,9,9-Hexafluoro-3,7-dioxanonan-5-yl)imidazole (**5a**)*

The reaction of mesylate **2a** (5.00 g, 15 mmol) and imidazole (3.08 g, 45 mmol) in DMF (8 ml) took place at 120 °C for 20 h to yield 1.97 g (43%) of **5a** as a colourless liquid, bp 115–117 °C/66.7 Pa. ^{1}H NMR ($CDCl_3$): δ 3.84 (4H, q, $^3J_{HF}$ = 8.6 Hz, $C\underline{H}_2$-CF_3), 3.97 (4H, t, $^3J_{HH}$ = 4.5 Hz, CH-$C\underline{H}_2$), 4.41 (1H, p, $^3J_{HH}$ = 5.0 Hz, $C\underline{H}$), 7.06 (2H, s, Im4,5), 7.59 (1H, s, Im2). ^{13}C NMR ($CDCl_3$): δ 57.2 (N-$\underline{C}H$), 69.1 (q, $^2J_{CF}$ = 35 Hz, $\underline{C}H_2CF_3$), 71.7 ($\underline{C}H_2CH$), 118.6 (Im5), 124.0 ($\underline{C}F_3$, q, $^1J_{CF}$ = 280 Hz), 129.9 (Im4), 137.2 (Im2). ^{19}F NMR ($CDCl_3$): δ −74.7 (t, $^3J_{HF}$ = 8.6 Hz, $C\underline{F}_3$). ESI-HRMS: m/z = 306.0803; calcd. for $[C_{10}H_{12}F_6N_2O_2]^+$ 306.0806.

*4.8.2. 1-[1,1,1,9,9,9-Hexafluoro-3,7-dioxa-2,8-bis(trifluoromethyl)nonan-5-yl]imidazole (**5b**)*

The reaction of mesylate **2b** (2.00 g, 4.26 mmol) and imidazole (0.87 g, 12.77 mmol) in DMF (3 ml) took place at 120 °C during 1 week to yield 0.47 g (25%) of **5b** as a colourless liquid, bp 115–132 °C/66.7 Pa. ^{1}H NMR ($CDCl_3$): δ 4.13–4.30 (6H, m, $C\underline{H}_2$-O-$C\underline{H}$), 4.56 (1H, p, $^3J_{HH}$ = 5.0 Hz, $C\underline{H}$), 7.04 (1H, s, Im4), 7.07 (1H, s, Im5), 7.57 (1H, s, Im2). ^{13}C NMR ($CDCl_3$): δ 56.6 (N-$\underline{C}H$), 73.1 ($\underline{C}H_2$), 76.8 (p, $^2J_{CF}$ = 33 Hz, $\underline{C}H(CF_3)_2$), 118.5 (Im5), 121.5 (q, $^1J_{CF}$ = 284 Hz, $\underline{C}F_3$), 129.9 (Im4), 136.9 (Im2). ^{19}F NMR ($CDCl_3$): δ −74.3 (6F, m, $^3J_{HF}$ = 6.5 Hz, $CH(C\underline{F}_3)_2$), −74.4 (6F, m, $^3J_{HF}$ = 6.5 Hz, $CH(C\underline{F}_3)_2$). ESI-HRMS: m/z = 442.0551; calcd. for $[C_{12}H_{10}F_{12}N_2O_2]^+$ 442.0554.

*4.8.3. 1-[5,5,5-Trifluoro-3-oxa-4,4-bis(trifluoromethyl)pentyl]imidazole (**5d**)*

The reaction of tosylate **2d** (13.03 g, 30 mmol) and imidazole (6.12 g, 90 mmol) in DMF (12.5 ml) took place at 100 °C during 1 h to yield 6.18 g (62%) of **5d** as a colourless liquid, which slowly crystallized upon standing, mp ~28 °C, bp 110 °C/66.7 Pa. ^{1}H NMR ($CDCl_3$): δ 4.18 (4H, s, $C\underline{H}_2$), 6.874 (1H, t, $^3J_{HH}$ = 1.3 Hz, Im4), 7.00 (1H, t, $^3J_{HH}$ = 1.0 Hz, Im5), 7.42 (1H, s, Im2). ^{13}C NMR ($CDCl_3$): δ 46.9 ($\underline{C}H_2N$), 69.3 ($\underline{C}H_2O$), 119.6 (Im5), 120.4 (q, $^1J_{CF}$ = 293 Hz, $\underline{C}F_3$), 130.1 (Im4), 137.7 (Im2). ^{19}F NMR ($CDCl_3$) −71.0 (s, $C\underline{F}_3$). ESI-HRMS: m/z = 330.0415; calcd. for $[C_9H_7F_9N_2O]^+$ 330.0423.

*4.8.4. 1-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecyl)imidazole (**5e**)*

The reaction of $C_8F_{17}(CH_2)_3I$ (5.88 g, 10 mmol) and imidazole (2.04 g, 30 mmol) in DMF (10 ml) took place at 100 °C during 5 h to yield 3.0 g (57%) of **5e** as white crystals, mp 47.5–53 °C/toluene (lit. [27] mp 48–50 °C).

^{1}H NMR ($CDCl_3$): δ 2.04 (4H, broad m, $C\underline{H}_2C\underline{H}_2$), 4.03 (2H, t, $^3J_{HH}$ = 6.5 Hz, $C\underline{H}_2$), 6.88 (1H, s, Im4), 7.11 (1H, s, Im5), 7.60 (1H, s, Im2). ^{19}F NMR ($CDCl_3$): δ −82.9 (3F, t, $^3J_{FF}$ = 10 Hz, CF_3), −114.9 (2F, broad m, $^3J_{FF}$ = 15 Hz, CF_2-4), −123.3 (6F, broad m, CF_2-6, 7, 8), −124.4 (4F, broad m, CF_2-5, 9), 127.9 (2F, broad m, CF_2-10).

4.9. General procedure for the synthesis of asymmetric imidazolium salts (cf. Scheme 3)

A solution of *N*-alkylimidazole (**5a**, **b**, **d**, **e**; 1 equiv.) and the alkylating agent (**6a–c**, **2d**; 1 equiv.) in anhydrous acetonitrile were heated at 80 °C for 48 h. When the product was crystallized from the solvent at room temperature it was filtered, and the crystals were washed with ether and dried. When the product is soluble in acetonitrile, the solvent was removed in vacuum, and then the crude product was washed with ether and dried.

4.9.1. 1-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecyl)-3-(1,1,1,9,9,9-hexafluoro-3,7-dioxanonan-5-yl)imidazolium iodide (7aa)

The reaction of **5a** (1.00 g, 3.27 mmol) and **6a** (1.92 g, 3.27 mmol) in acetonitrile (15 ml) afforded imidazolium salt **7aa**. Yield: 2.24 g (72%), mp 88–93 °C ^{1}H NMR (DMSO-d_6): δ 2.03–2.24 (4H, broad m, $C\underline{H}_2C\underline{H}_2N$), 3.98–4.18 (8H, m, $C\underline{H}_2OC\underline{H}_2$), 4.34 (2H, t, $^3J_{HH}$ = 6.3 Hz, $NC\underline{H}_2$), 4.96 (1H, p, $^3J_{HH}$ = 5.3 Hz, $C\underline{H}$), 7.88 (1H, s, Im4), 7.92 (1H, s, Im5), 9.31 (1H, s, Im2). ^{13}C NMR (DMSO-d_6): δ 21.2 ($\underline{C}H_2CH_2CF_3$), 27.2 ($\underline{C}H_2CF_2$), 48.2 ($\underline{C}H_2N$), 59.6 ($\underline{C}H$), 67.5 (q, $^2J_{CF}$ = 34 Hz, $\underline{C}H_2CF_3$), 69.8 ($\underline{C}H_2CH$), 120.8 (q, $^1J_{CF}$ = 227 Hz, $\underline{C}F_3$), 122.2 (Im5), 122.9 (Im4), 136.8 (Im2). ^{19}F NMR (DMSO-d_6): δ −74.1 (6F, t, $^3J_{HF}$ = 9.8 Hz, $CH(C\underline{F}_3)_2$), −81.6 (3F, t, $^3J_{FF}$ = 10.5 Hz, $CF_2C\underline{F}_3$), −114.3 (2F, t, $^3J_{FF}$ = 18.5 Hz, CF_2-4), −122.7 (6F, broad s, CF_2-6, 7, 8), −123.9 (4F, broad s, CF_2-5, 9), 126.9 (2F, s, CF_2-10). ESI-HRMS: m/z = 767.1001; calcd. for $[C_{21}H_{18}F_{23}N_2O_2]^+$ 767.0978.

4.9.2. 1-Methyl-3-(1,1,1,9,9,9-hexafluoro-3,7-dioxanonan-5-yl)imidazolium iodide (7ab)

The reaction of **5a** (0.32 g, 1.05 mmol) and **6b** (0.12 g, 1.05 mmol) in acetonitrile (1 ml) afforded the title imidazolium salt **7ab**. Yield: 1.06 g (80%) pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 3.94 (4H, m, $^3J_{HF}$ = 8.6 Hz $C\underline{H}_2CF_3$), 4.03 (3H, s, $C\underline{H}_3$-N), 4.15 (4H, d, $^3J_{HH}$ = 4.8 Hz, $C\underline{H}_2$-CH), 5.17 (1H, p, $^3J_{HH}$ = 4.8 Hz, $C\underline{H}$), 7.48 (1H, s, Im5), 7.61 (1H, s, Im4), 9.69 (1H, s, Im2). ^{13}C NMR ($CDCl_3$): δ 37.5 ($\underline{C}H_3$), 57.2 ($\underline{C}H$), 69.0 (q, $^2J_{CF}$ = 34 Hz, $\underline{C}H_2CF_3$), 70.5 ($\underline{C}H_2$), 122.6 (Im5), 123.6 (Im4), 124.0 (q, $^1J_{CF}$ = 280 Hz, $\underline{C}F_3$), 137.3 (Im2). ^{19}F NMR ($CDCl_3$): δ −74.6 (t, $^3J_{HF}$ = 8.6 Hz, $C\underline{F}_3$). ESI-HRMS: m/z = 321.1038; calcd. for $[C_{11}H_{15}F_6N_2O_2]^+$ 321.1039.

4.9.3. 1-(2-Hydroxyethyl)-3-(1,1,1,9,9,9-hexafluoro-3,7-dioxanonan-5-yl)imidazolium bromide (7ac)

The reaction of **5a** (1.00 g, 3.27 mmol) and **6c** (0.41 g, 3.27 mmol) in acetonitrile (4 ml) afforded imidazolium salt **7ac** as brownish liquid. Yield: 1.1 g (77%). ^{1}H NMR (DMSO-d_6): δ 4.00–4.20 (10H, overlapping signals, $C\underline{H}_2$), 4.27 (2H, t, $^3J_{HH}$ = 5.0 Hz, $C\underline{H}_2OH$), 5.03 (1H, m, $C\underline{H}$), 5.18 (1H, s, $O\underline{H}$), 7.85 (1H, Im5), 7.88 (1H, Im4), 9.34 (1H, Im2). ^{13}C NMR (DMSO-d_6): δ 52.1 ($\underline{C}H_2N$), 59.3 ($\underline{C}H_2OH$), 59.5 ($\underline{C}H$), 67.5 (q, $^2J_{CF}$ = 33 Hz, $\underline{C}H_2CF_3$), 70.0 ($\underline{C}H_2O$), 121.5 (Im5), 123.3 (Im4), 124.6 (q, $^1J_{CF}$ = 280 Hz, $\underline{C}F_3$), 136.9 (Im2). ^{19}F NMR (DMSO-d_6): δ −73.5 (t, $^3J_{HF}$ = 9.3 Hz, $C\underline{F}_3$). ESI-HRMS: m/z = 351.1143; calcd. for $[C_{12}H_{17}F_6N_2O]^+$ 351.1155.

4.9.4. 1-[5,5,5-Trifluoro-3-oxa-4,4-bis(trifluoromethyl)pentyl]-3-(1,1,1,9,9,9-hexafluoro-3,7-dioxanonan-5-yl)imidazolium 4-toluenesulfonate (7ad)

The reaction of **5a** (0.5 g, 1.63 mmol) and **2d** (0.71 g, 1.63 mmol) in acetonitrile (5 ml) afforded imidazolium salt **7ad**. Yield: 1.00 g (83%), mp 98–104.5 °C. ^{1}H NMR ($CDCl_3$): δ 2.32 (3H, s, $ArC\underline{H}_3$), 3.80 (4H, m, $^3J_{HF}$ = 9 Hz, $C\underline{H}_2CF_3$), 4.02 (4H, m, $^3J_{HH}$ = 4.5 Hz, $C\underline{H}_2CH$), 4.28 (2H, t, $^3J_{HH}$ = 4.5 Hz, $C\underline{H}_2N$), 4.66 (2H, t, $^3J_{HH}$ = 4.5 Hz, $C\underline{H}_2O$), 4.98 (1H, p, $^3J_{HH}$ = 4.5 Hz, $C\underline{H}$), 7.13 (2H, d, $^3J_{HH}$ = 8.1 Hz, m-Ar), 7.37 (1H, d, $^3J_{HH}$ = 1.3 Hz, Im5), 7.52 (1H, d, $^3J_{HH}$ = 1.5 Hz, Im4), 7.67 (2H, d, $^3J_{HH}$ = 8.1 Hz, o-Ar), 9.73 (1H, s, Im2). ^{13}C NMR ($CDCl_3$): δ 21.5 ($ArC\underline{H}_3$), 49.8 ($\underline{C}H_2N$), 60.3 ($\underline{C}HN$), 68.4 ($\underline{C}H_2OC(CF_3)_3$), 69.7 (q, $^2J_{CF}$ = 34 Hz, $\underline{C}H_2CF_3$), 126.0 (m-Ar), 129.1 (o-Ar), 138.4 (Im2), 140.1 (g-Ar), 143.9 (p-Ar). ^{19}F NMR ($CDCl_3$): δ −74.9 (6F, t, $^3J_{HF}$ = 9.0 Hz, $CH_2C\underline{F}_3$), −71.1 (9F, s, $C(C\underline{F}_3)_3$). ESI-HRMS: m/z = 569.0940; calcd. for $[C_{16}H_{16}F_{15}N_2O_3]^+$ 569.0921.

4.9.5. 1-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecyl)-3-[1,1,1,9,9,9-hexafluoro-3,7-dioxa-2,8-bis(trifluoromethyl)nonan-5-yl]imidazolium iodide (7ba)

The reaction of **5b** (0.77 g, 1.74 mmol) and **6a** (0.30 g, 2.26 mmol) in acetonitrile (3 ml) afforded imidazolium salt **7ba**. Yield: 1.67 g (93%) brown wax. ^{1}H NMR (DMSO-d_6): δ 2.00–2.15 (4H, broad s, $C\underline{H}_2C\underline{H}_2N$), 4.34 (4H, d, $^3J_{HH}$ = 5.8 Hz, $C\underline{H}_2CH$), 4.38 (2H, broad s, $CF_2C\underline{H}_2$), 5.10 (2H, p, $^3J_{HH}$ = 5.8 Hz, $C\underline{H}$-N), 5.60 (2H, p, $^3J_{HF}$ = 6.5 Hz, $C\underline{H}(CF_3)_2$), 7.94 (1H, s, Im5), 7.99 (1H, s, Im4), 9.43 (1H, s, Im2). ^{19}F NMR (DMSO-d_6): δ −74.2 (6F, m, $^3J_{HF}$ = 7.1 Hz, $CH(C\underline{F}_3)_2$), −74.6 (6F, m, $^3J_{HF}$ = 7.1 Hz, $CH(C\underline{F}_3)_2$), −81.4 (3F, t, $^3J_{FF}$ = 11 Hz, $C\underline{F}_3CF_2$), −114.4 (2F, t, $^3J_{FF}$ = 15 Hz, $C\underline{F}_2$-4), −122.7 (6F, broad s, $C\underline{F}_2$-6, 7, 8), −123.5 (2F, s, $C\underline{F}_2$-9), −124.1 (2F, s, $C\underline{F}_2$-5), −126.8 (2F, s, $C\underline{F}_2$-10). ESI-HRMS: m/z = 903.0773; calcd. for $[C_{23}H_{16}F_{29}N_2O_2]^+$ 703.0749.

4.9.6. 1-Methyl-3-[1,1,1,9,9,9-hexafluoro-3,7-dioxa-2,8-bis(trifluoromethyl)nonan-5-yl]imidazolium iodide (7bb)

The reaction of **5b** (1.00 g, 2.26 mmol) and **6b** (0.30 g, 2.26 mmol) in acetonitrile (3 ml) afforded imidazolium salt **7bb**. Yield: 1.07 g (81%) brown wax. ^{1}H NMR (DMSO-d_6): δ 3.90 (3H, s, $C\underline{H}_3$), 4.34 (4H, d, $^3J_{HH}$ = 5.8 Hz, $C\underline{H}_2$), 5.09 (1H, p, $^3J_{HH}$ = 5.8 Hz, $C\underline{H}$-N), 5.63 (2H, p, $^3J_{HF}$ = 6.5 Hz, $C\underline{H}(CF_3)_2$), 7.84 (2H, s, Im4, Im5), 9.31 (1H, s, Im2). ^{13}C NMR (DMSO-d_6): δ 36.3 ($\underline{C}H_3$), 59.2 ($\underline{C}H$-N), 71.7 ($\underline{C}H_2$), 74.3 (t, $^2J_{CF}$ = 32 Hz, $\underline{C}H(CF_3)_2$), 121.4 (Im5), 124.4 (Im4), 137.4 (Im2). ^{19}F NMR (DMSO-d_6): δ −73.8 (6F, m, $^3J_{HF}$ = 7.3 Hz, $CH(C\underline{F}_3)_2$), −74.2 (6F, m, $^3J_{HF}$ = 7.7 Hz, $CH(C\underline{F}_3)_2$). ESI-HRMS: m/z = 457.0798; calcd. for $[C_{13}H_{13}F_{12}N_2O_2]^+$ 457.0785.

4.9.7. 1-(2-Hydroxyethyl)-3-[1,1,1,9,9,9-hexafluoro-3,7-dioxa-2,8-bis(trifluoromethyl)nonan-5-yl]imidazolium bromide (7bc)

The reaction of *N*-alkylimidazole **5b** (1.00 g, 2.26 mmol) and **6c** (0.29 g, 2.26 mmol) in acetonitrile (3 ml) afforded imidazolium salt **7bc**. Yield: 0.87 g (67%) brown wax. ^{1}H NMR (DMSO-d_6): δ 3.71 (2H, t, $^3J_{HH}$ = not readable, $C\underline{H}_2$-O), 4,28 (2H, t, $^3J_{HH}$ = 5.0 Hz, $C\underline{H}_2$-N), 4.36 (4H, d, $^3J_{HH}$ = 5.8 Hz, $C\underline{H}_2CH$), 5.14 (1H, p, $^3J_{HH}$ = 5.8 Hz, $C\underline{H}$-N), 5.43 (1H, s, $O\underline{H}$), 5.70 (2H, p, $^3J_{HF}$ = 6.4 Hz, $C\underline{H}(CF_3)_2$), 7.88 (1H, s, Im5), 7.88 (1H, s, Im4), 9.37 (1H, s, Im2). ^{13}C NMR (DMSO-d_6): δ 52.1 ($\underline{C}H_2$-N), 59.2 ($\underline{C}H_2$-O), 59.6 ($\underline{C}H$), 71.7 ($\underline{C}H_2CH$), 74.3 (t, $^2J_{CF}$ = 32 Hz, $\underline{C}H(CF_3)_2$), 121.3 (Im5), 123.6 (Im4), 137.2 (Im2). ^{19}F NMR (DMSO-d_6): δ −73.8 (6F, m, $^3J_{HF}$ = 8.2 Hz, $CH(C\underline{F}_3)_2$), −74.1 (6F, m, $^3J_{HF}$ = 8.0 Hz, $CH(C\underline{F}_3)_2$). ESI-HRMS: m/z = 705.0669; calcd. for $[C_{18}H_{14}F_{21}N_2O_3]^+$ 705.0684.

4.9.8. 1-[5,5,5-Trifluoro-3-oxa-4,4-bis(trifluoromethyl)pentyl]-3-[1,1,1,9,9,9-hexafluoro-3,7-dioxa-2,8-bis(trifluoromethyl)nonan-5-yl]imidazolium 4-toluenesulfonate (7bd)

The reaction of **5b** (1.00 g, 2.26 mmol) and **2d** (0.98 g, 2.26 mmol) in acetonitrile (3.5 ml) afforded imidazolium salt **7bd**. Yield: 1.52 g (77%) mp 96–99 °C. ^{1}H NMR (DMSO-d_6): δ 2.27 (3H, s, $C\underline{H}_3$), 4.32 (4H, t, $^3J_{HH}$ = 4.3 Hz, $CHC\underline{H}_2O$), 4.45 (2H, s, $C\underline{H}_2N$), 4.62 (2H, t, $^3J_{HH}$ = 4.0 Hz, $CH_2C\underline{H}_2O$), 5.15 (1H, p, $^3J_{HH}$ = 4.0 Hz, $C\underline{H}$-N), 5.61 (2H, p, $^3J_{HF}$ = 6.0 Hz, $C\underline{H}(CF_3)_2$), 7.10 (2H, d, $^3J_{HH}$ = 8.0 Hz, m-Ar), 7.48 (2H, d, $^3J_{HH}$ = 8.0 Hz, o-Ar), 7.90 (1H, s, Im5), 7.94 (1H, s, Im4), 9.44 (1H, s, Im2). ^{13}C NMR (DMSO-d_6): δ (*missing signal*), 21.1

($\underline{C}H_3$), 49.2 ($\underline{C}H_2N$), 59.6 ($\underline{C}H$-N), 68.9 ($\underline{C}H_2OC(CF_3)_3$), 71.7 ($\underline{C}H(CF_3)_2$), 74.8 ($\underline{C}H_2CH$), 121.6 (Im5), 123.7 (Im4), 125.8 (m-Ar), 128.4 (o-Ar), 137.6 (Im2) 138.0 (g-Ar), 146.0 (p-Ar). ^{19}F NMR (DMSO-d_6): δ −70.9 (9F, s, C($\underline{C}F_3)_3$), −74.0 (6F, m, $^3J_{HF}$ = 7.6 Hz, CH($\underline{C}F_3)_2$), −74.3 (6F, m, $^3J_{HF}$ = 7.4 Hz, CH($\underline{C}F_3)_2$). ESI-HRMS: m/z = 705.0684; calcd. for $[C_{18}H_{14}F_{21}N_2O_3]^+$ 705.0699.

4.9.9. 1-[5,5,5-Trifluoro-3-oxa-4,4-bis(trifluoromethyl)pentyl]-3-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)imidazolium iodide (7da)

The reaction of *N*-alkylimidazole **5d** (1.00 g, 3.03 mmol) and **6a** (1.78 g, 3.03 mmol) in acetonitrile (15 ml) afforded imidazolium salt **7da**. Yield: 2.00 g (72%) white crystals, mp 148.5–161 °C. ^{1}H NMR (DMSO-d_6): δ 2.0–2.3 (4H, m, NC$\underline{H}_2$C$\underline{H}_2$CH$_2$), 4.35 (2H, t, $^3J_{HH}$ = 6.0 Hz, NC$\underline{H}_2$CH$_2$O), 4.48 (2H, t, $^3J_{HF}$ = 4.0 Hz, C$\underline{H}_2$CF$_2$), 4.57 (2H, t, $^3J_{HH}$ = 4.8 Hz, C$\underline{H}_2$OC(CF$_3$)$_3$), 7.83 (1H, s, Im4), 7.89 (1H, s, Im5), 9.26 (1H, s, Im2). ^{19}F NMR (DMSO-d_6): δ −71.5 (9F, s, C($\underline{C}F_3)_3$), −82.4 (3F, t, $^3J_{FF}$ = 11 Hz, $\underline{C}F_3$CF$_2$), −114.9 (2F, C$\underline{F}_2$-4), −122.9 (2F, s, C$\underline{F}_2$-6), −123.2 (4F, s, C$\underline{F}_2$-7, 8), −124.0 (2F, C$\underline{F}_2$-9), −124.4 (2F, C$\underline{F}_2$-5), −127.6 (2F, s, C$\underline{F}_2$-10). ESI-HRMS: m/z = 791.0613; calcd. for $[C_{20}H_{13}F_{26}N_2O]^+$ 791.0598.

4.9.10. 1-Methyl-3-[5,5,5-trifluoro-3-oxa-4,4-bis(trifluoromethyl)pentyl]imidazolium iodide (7db)

The reaction of **5d** (1.50 g, 4.55 mmol) and **6b** (0.65 g, 4.55 mmol) in acetonitrile (3 ml) afforded imidazolium salt **7db**. Yield: 2.08 g (97%) pale yellow solid, mp 123–132 °C. ^{1}H NMR ($CDCl_3$): δ 4.07 (3H, s, C$\underline{H}_3$), 4.46 (2H, t, $^3J_{HH}$ = 4.3 Hz, C$\underline{H}_2$O), 4.89 (2H, t, $^3J_{HH}$ = 4.8 Hz, C$\underline{H}_2$N), 7.55 (1H, s, Im4), 7.56 (1H, s, Im5), 9.87 (1H, s, Im2). ^{13}C NMR ($CDCl_3$): δ 37.7 ($\underline{C}H_3$), 50.0 ($\underline{C}H_2$N), 68.8 ($\underline{C}H_2$O), 120.3 (q, $^1J_{CF}$ = 293 Hz, $\underline{C}F_3$), 123.5 (Im4), 123.9 (Im5), 137.7 (Im2). ^{19}F NMR ($CDCl_3$): δ −70.9 (s, C$\underline{F}_3$). ESI-HRMS: m/z = 345.0663; calcd. for $[C_{10}H_{10}F_9N_2O]^+$ 345.0649.

4.9.11. 1-(2-Hydroxyethyl)-3-[5,5,5-trifluoro-3-oxa-4,4-bis(trifluoromethyl)pentyl]imidazolium bromide (7dc)

The reaction of **5d** (2.00 g, 6.06 mmol) and **6c** (0.76 g, 6.06 mmol) in acetonitrile (8 ml) afforded imidazolium salt **7dc**. Yield: 2.12 g (77%), pale yellow liquid. ^{1}H NMR ($CDCl_3$): δ 3.98 (2H, t, $^3J_{HH}$ = 4.5 Hz, C$\underline{H}_2$OH), 4.48 (4H, m, C$\underline{H}_2$N), 4.86 (2H, t, $^3J_{HH}$ = 4.5 Hz, C$\underline{H}_2$OC(CF$_3$)$_3$), 5.08 (1H, s, O$\underline{H}$), 7.45 (1H, s, Im5), 7.61 (1H, s, Im4), 9.81 (1H, s, Im2). ^{13}C NMR ($CDCl_3$): δ 50.0 ((CF$_3$)$_3$COCH$_2\underline{C}$H$_2$N), 53.1 (HOCH$_2\underline{C}$H$_2$N), 60.1 ($\underline{C}$H$_2$OH), 68.9 ($\underline{C}$H$_2$OC(CF$_3$)$_3$), 123.0 (Im4), 123.3 (Im5), 137.7 (Im2) (*missing signal for* $\underline{C}F_3$). ^{19}F NMR ($CDCl_3$): δ −71.9 (s, C$\underline{F}_3$). ESI-HRMS: m/z = 375.0755; calcd. for $[C_{11}H_{12}F_9N_2O_2]^+$ 375.0754.

4.9.12. 1,3-Bis[5,5,5-trifluoro-3-oxa-4,4-bis(trifluoromethyl)pentyl]imidazolium 4-toluenesulfonate (7dd)

The reaction of **5d** (1.486 g, 4.5 mmol) and **2d** (1.954 g, 4.5 mmol) in acetonitrile (10 ml) afforded imidazolium salt **7dd**. Yield: 2.26 g (66%) white crystals, mp 162–164 °C.

^{1}H NMR ($CDCl_3$–CD_3OD (10:1)): δ 2.36 (3H, s, Ar-C$\underline{H}_3$), 4.37 (4H, broad s, N-C$\underline{H}_2$), 4.65 (4H, broad s, O-C$\underline{H}_2$), 7.20 (2H, d, $^3J_{HH}$ = 10.0 Hz, m-Ar), 7.37 (1H, s, Im4), 7.38 (1H, s, Im5), 7.69 (2H, d, $^3J_{HH}$ = 10.0 Hz, o-Ar), 9.54 (1H, s, Im2). ^{13}C NMR ($CDCl_3$–CD_3OD (10:1)): δ 21.3 (Ar-$\underline{C}H_3$), 49.6 (N-$\underline{C}H_2$), 68.6 (O-$\underline{C}H_2$), 120.1 ($\underline{C}F_3$, q, $^1J_{CF}$ = 292 Hz), 123.1 (Im4,5), 125.7 (m-Ar), 129.0 (o-Ar), 138.2 (Im2), 140.4 (g-Ar), 142.4 (p-Ar). ^{19}F NMR ($CDCl_3$–CD_3OD (10:1)): δ −71.2 (s, C$\underline{F}_3$). ESI-HRMS: m/z = 593.0533 $[M^*]^+$; calcd. for $[C_{15}H_{11}F_{18}N_2O_2]^+$ 593.0535; ESI-MS: m/z = 171.0116; calcd. for $[C_7H_7O_3S]^-$ 171.0116.

4.9.13. 1-Methyl-3-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)imidazolium iodide (7eb)

The reaction of **5e** (1.00 g, 2.84 mmol) and **6b** (0.18 ml, 0.41 g, 2.84 mmol) in acetonitrile (3 ml) afforded imidazolium salt **7eb**. Yield: 1.19 g (63%) pale yellow solid, mp 101–106 °C. ^{1}H NMR (DMSO-d_6): δ 2.08 (2H, m, C$\underline{H}_2$), 2.49 (2H, t, $^3J_{HH}$ = 1.5 Hz, C$\underline{H}_2$), 3.85 (3H, s, C$\underline{H}_3$), 4.28 (2H, t, $^3J_{HH}$ = 7.0 Hz, C$\underline{H}_2$), 7.70 (1H, s, Im4), 7.78 (1H, s, Im5), 9.13 (1H, s, Im2). ^{13}C NMR (DMSO-d_6): δ (*missing signal* for $CF_2\underline{C}H_2$), 21.4 ($CH_2\underline{C}H_2CH_2$), 36.2 ($\underline{C}H_3$), 48.0 ($\underline{C}H_2$N), 122.6 (Im4), 124.1 (Im5), 137.2 (Im2). ^{19}F NMR (DMSO-d_6): δ −126.4 (2F), −123.5 (2F), −123.1 (2F), −122.3 (8F), −113.9 (2F, t, $^3J_{FF}$ = 15 Hz, CF_2), −80.9 (3F, t, $^3J_{FF}$ = 10 Hz, CF_3). ESI-HRMS: m/z = 543.0761; calcd. for $[C_{15}H_{12}F_{17}N_2]^+$ 543.0729.

4.9.14. 1-(2-Hydroxyethyl)-3-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)imidazolium iodide (7ec)

The reaction of *N*-alkylimidazole **5e** (0.24 g, 1.89 mmol) and **6c** (0.24 g, 1.89 mmol) in acetonitrile (6 ml) afforded imidazolium salt **7ec**. Yield: 0.70 g (56%) white waxy solid. ^{1}H NMR (DMSO-d_6): δ 2.0–2.3 (4H, m, N-C$\underline{H}_2$), 3.72 (2H, p, $^3J_{HH}$ = 4.5 Hz, C$\underline{H}_2$OH), 4.21 (2H, t, $^3J_{HH}$ = 5.0 Hz, C$\underline{H}_2$CH$_2$OH), 4.29 (2H, t, $^3J_{HH}$ = 7.0 Hz, C$\underline{H}_2$CH$_2$OC(CF$_3$)$_3$), 5.14 (1H, t, $^3J_{HH}$ = 5.0 Hz, C$\underline{H}_2$OC(CF$_3$)$_3$), 7.76 (1H, s, Im4), 7.82 (1H, s, Im5), 9.17 (1H, s, Im2). ^{13}C NMR (DMSO-d_6): δ 21.3 ($CH_2\underline{C}H_2CH_2$), 27.3 ($\underline{C}H_2$OH), 47.9 ($\underline{C}H_2$N), 52.1 ($\underline{C}H_2$N), 59.6 ($\underline{C}H_2CF_2$), 122.5 (Im4), 123.3 (Im5), 136.9 (Im2). ^{19}F NMR (DMSO-d_6): δ −126.8 (2F), −123.7 (4F), −122.6 (6F), −114.0 (2F), −81.5 (3F). ESI-HRMS: m/z = 573.0852; calcd. for $[C_{16}H_{14}F_{17}N_2O]^+$ 573.0835.

4.10. General procedure for the synthesis of secondary amines (Scheme 4)

To a solution of the secondary azides **3a** and **3b** (7.03 g or 10.45 g; 25 mmol) in a mixture of ethanol-chloroform (110 ml; 10:1, v/v) was added 10% Pd/C (130 mg, 0.5 mol%) and shaken in a Parr reaction bottle at 280 kPa hydrogen pressure for 10 h. The mixture was filtered and then evaporated. To the residue 1 M NaOH (40 ml) and ether (40 ml) was added and the aqueous layer separated and washed with ether (2× 25 ml). The organic phases were combined and dried over Na_2SO_4. The solvent was removed under vacuum, and then the crude product was distilled to afford the title 2° amines.

4.10.1. 1,1,1,9,9,9-Hexafluoro-3,7-dioxanonan-5-amine (8a)

Yield: 4.46 g (70%) colourless liquid, bp 85–86 °C/2.67 kPa. ^{1}H NMR ($CDCl_3$): δ 1.61 (2H, s, N$\underline{H}_2$), 3.18 (1H, p, $^3J_{HH}$ = 5.3 Hz, C$\underline{H}$), 3.60 (4H, m, $^3J_{HH}$ = 5.0 Hz, O-C$\underline{H}_2$), 3.85 (4H, q, $^3J_{HF}$ = 8.6 Hz, CF_3-C$\underline{H}_2$). ^{13}C NMR ($CDCl_3$): δ 51.1 (N-$\underline{C}$H), 69.0 (q, $^2J_{CF}$ = 34 Hz, CF_3-$\underline{C}H_2$), 74.7 (O-C$\underline{H}_2$), 124.3 (q, $^1J_{CF}$ = 280 Hz, $\underline{C}F_3$). ^{19}F NMR ($CDCl_3$): δ −74.7 (t, $^3J_{HF}$ = 8.6 Hz, C$\underline{F}_3$). ESI-HRMS: m/z = 255.0694; calcd. for $[C_7H_{11}F_6NO_2]^+$ 255.0701.

4.10.2. 1,1,1,9,9,9-Hexafluoro-3,7-dioxa-2,8-bis(trifluoromethyl)nonan-5-amine (8b)

Yield: 5.84 g (60%) colourless liquid, bp 128 °C/2.67 kPa. ^{1}H NMR ($CDCl_3$): δ 1.44 (2H, s, N$\underline{H}_2$), 3.25 (1H, p, $^3J_{HH}$ = 5.3 Hz, C$\underline{H}$NH$_2$), 3.87–3.89 (4H, m, C$\underline{H}_2$O), 4.11 (2H, septet, $^3J_{HF}$ = 5.9 Hz, C$\underline{H}$(CF$_3$)$_2$). ^{13}C NMR ($CDCl_3$): δ 51.0 ($\underline{C}$HNH$_2$), 76.5 ($\underline{C}$H$_2$O), 77.0 (septet), $^2J_{CF}$ = 33 Hz, $\underline{C}$H(CF$_3$)$_2$), 121.7 (q, $^1J_{CF}$ = 285 Hz, $\underline{C}F_3$). ^{19}F NMR ($CDCl_3$): δ −74.5 (12F, d, $^3J_{HF}$ = 5.9 Hz, CF_3). ESI-HRMS: m/z = 391.0442; calcd. for $[C_9H_9F_{12}NO_2]^+$ 391.0448.

4.11. General procedure for the synthesis of symmetrical imidazolium salts

To a stirred solution of **8a** or **8b** (10.2 g and 15.6 g, respectively, 40 mmol) in benzene (35 ml) was added 35% aqueous formaldehyde (0.56 ml, 20 mmol) at 0 °C. The mixture was stirred for 1 h at 20 °C, cooled with ice-bath until mixed with 37% hydrochloric acid (2.0 ml) and 40% aqueous glyoxal solution (0.34 ml, 20 mmol),

then heated at 100 °C for 24 h and evaporated to afford the title products.

4.11.1. 1,3-Bis(1,1,1,9,9,9-hexafluoro-3,7-dioxanonan-5-yl)imidazolium chloride (**9a**)

Yield: 8.89 g (77%) brownish liquid. ^{1}H NMR ($CDCl_3$): δ 3.92 (8H, m, $^{3}J_{HF}$ = 8.5 Hz, C$\underline{H}_2$CF$_3$), 4.13 (8H, d, $^{3}J_{HH}$ = 4.7 Hz, C$\underline{H}_2$O), 5.22 (2H, p, $^{3}J_{HH}$ = 5.0 Hz, C$\underline{H}$), 7.579 (1H, s, Im5), 7.582 (1H, s, Im4), 9.99 (1H, s, Im2). ^{13}C NMR ($CDCl_3$): δ 60.2 (C$\underline{H}$N), 68.8 (q, $^{2}J_{CF}$ = 35 Hz, $\underline{C}$H$_2$CF$_3$), 70.6 (C$\underline{H}_2$O), 121.9 (Im4,5), 124.0 (q, $^{1}J_{CF}$ = 280 Hz, $\underline{C}$F$_3$), 137.9 (Im2). ^{19}F NMR ($CDCl_3$): δ −74.8 (t, $^{3}J_{HF}$ = 8.5 Hz, CF$_3$). ESI-HRMS: m/z = 545.1310; calcd. for $[C_{17}H_{21}F_{12}N_2O_4]^+$ 545.1309.

4.11.2. 1,3-Bis[1,1,1,9,9,9-hexafluoro-3,7-dioxa-2,8-bis(trifluoromethyl)nonan-5-yl]imidazolium chloride (**9b**)

Yield: 8.88 g (52%) brownish liquid. ^{1}H NMR (DMSO-d_6): δ 4.32–4.49 (8H, m, C$\underline{H}_2$), 5.24 (2H, p, $^{3}J_{HH}$ = 3.5 Hz, C$\underline{H}$-N), 5.80 (4H, septet, $^{3}J_{HF}$ = 6.3 Hz, C$\underline{H}$(CF$_3$)$_2$), 8.12 (1H, s, Im5), 8.13 (1H, s, Im4), 9.82 (1H, s, Im2). ^{13}C NMR (DMSO-d_6): δ 59.8 (C$\underline{H}$N), 71.6 ($\underline{C}$H$_2$), 74.2 (m, $^{2}J_{CF}$ = 32 Hz, $\underline{C}$H(CF$_3$)$_2$), 121.7 (q, $^{1}J_{CF}$ = 283 Hz, $\underline{C}$F$_3$),121.9 (Im4,5), 137.6 (Im2). ^{19}F NMR (DMSO-d_6): δ −73.9 (d, $^{3}J_{HF}$ = 6.3 Hz, C$\underline{F}_3$).

Acknowledgments

These investigations were supported by the Hungarian Scientific Research Foundation (OTKAK 062191 "Sustainable fluorous chemistry"). The European Union and the European Social Fund have provided financial support to the project under the grant agreement no. TÁMOP 4.2.1./B-09/KMR-2010-0003. A. Bodor acknowledges the János Bolyai Research Scholarship of the Hungarian Academy of Sciences.

References

[1] I.T. Horváth, ACS Award for Creative Work in Fluorine Chemistry: Symposium in Honor of R.P. Hughes, 239th ACS National Meeting, March 21–25, 2010, San Francisco, CA, USA. http://abstracts.acs.org/chem/239nm/program/view.php?obj_id=5647&terms=.
[2] FLUOROS_International Symposium on Fluorinated Alkyl Organics in the Environment, August 18–20, 2005, Toronto, CANADA, Book of Abstracts (Ed.: Scott Mabury). http://www.chem.utoronto.ca/symposium/fluoros/abstractbook.htm.
[3] (a) 3M Novec Fluids: Product Description, 2005.
(b) J.A. Gladysz, in: P. Anastas (Ed.), Handbook of green chemistry. Volume 1: Homogeneous Catalysis; R. H. Crabtree, Volume Ed, Wiley/VCH, Weinheim, 2009, pp. 17–38;
(c) G. Malinverno, I. Colombo, M. Visca, Regul. Toxicol. Pharmacol. 41 (2005) 228–239.
[4] S. Dimitrov, V. Kamenska, J.D. Walker, W. Windlec, R. Purdy, M. Lewis, O. Mekenyan, SAR QSAR Environ. Res. 15 (2004) 69–82.
[5] (a) I.L. Knunyants, B.L. Dyatkin, Izv. Akad. Nauk SSSR Ser. Khim. 5 (1964) 923–925;
(b) F.J. Pavlik, US Patent 3,385,904 (1968).
[6] (a) J. Rábai, D. Szabó, E.K. Borbás, I. Kövesi, I. Kövesdi, A. Csámpai, Á. Gömöry, V.E. Pashinnik, Y.G. Shermolovich, J. Fluorine Chem. 114 (2002) 199–207;
(b) D. Szabó, A.-M. Bonto, I. Kövesdi, Á. Gömöry, J. Rábai, J. Fluorine Chem. 126 (2005) 641–652.
[7] (a) D. Szabó, J. Mohl, A.-M. Bálint, A. Bodor, J. Rábai, J. Fluorine Chem. 127 (2006) 1496–1504;
(b) D. Szabó, A. Nemes, I. Kövesdi, V. Farkas, M. Hollósi, J. Rábai, J. Fluorine Chem. 127 (2006) 1405–1414.
[8] Z.-X. Jiang, Y.B. Yu, Tetrahedron 63 (2007) 3982–3988.
[9] Z.-X. Jiang, Y.B. Yu, Synthesis (2008) 215–220.
[10] Q. Chu, C. Henry, D.P. Curran, Org. Lett. 10 (2008) 2453–2456.
[11] Z.-X. Jiang, Y.B. Yu, J. Org. Chem. 72 (2007) 1464–1467.
[12] Z.-X. Jiang, X. Liu, E.-K. Jeong, Y.B. Yu, Angew. Chem. Int. Ed. 48 (2009) 4755–4758.
[13] Z.-X. Jiang, Y.B. Yu, J. Org. Chem. 75 (2010) 2044–2049.
[14] Y. Yu, Z.-X. Yiang, WO Patent 2007/112100 (2007).
[15] O. Kysilka, M. Rybáčková, M. Skalický, M. Kvíčalová, J. Cvačka, J. Kvíčala, Collect. Czech. Chem. Commun. 73 (2008) 1799–1813.
[16] (a) O. Kysilka, M. Rybáčková, M. Skalický, M. Kvíčalová, J. Fluorine Chem. 130 (2009) 629–639;
(b) J. Kvíčala, M. Rybáčková, M. Skalický, O. Kysilka, CZ Patent 301543 (2010).
[17] (a) R.K. Crossland, K.L. Servis, J. Org. Chem. 35 (1970) 3195–3196;
(b) T. Bříza, V. Král, P. Martásek, R. Kaplánek, J. Fluorine Chem. 129 (2008) 235–247.
[18] P.J. Stang, M. Hanack, L.R. Subramanian, Synthesis (1982) 85–126.
[19] M. Skalický, M. Rybáčková, O. Kysilka, M. Kvíčalová, J. Cvačka, J. Čejka, J. Kvíčala, J. Fluorine Chem. 130 (2009) 966–973, and references cited therein.
[20] (a) M.L. Brey, P.J. Tarrant, J. Am. Chem. Soc. 79 (1957) 6533–6536;
(b) K.-T. Kang, S.K. Lee, C.W. Park, S.H. Cho, J.G. Lee, S.-K. Choi, Y.B. Kim, Bull. Korean Chem. Soc. 27 (2006) 1364–1370;
(c) L.G. Anello, R.F. Sweeney, (Allied Chemical Corp.) US Patent 3,409,602 (1968).
[21] S.V. Zyuba, S. Li, R.A. Bartsch, J. Heterocyclic Chem. 44 (2007) 223–225.
[22] L. Jafarpour, E.D. Stevens, S.P. Nolan, J. Organomet. Chem. 606 (2000) 49–54.
[23] (a) L.E. Kiss, I. Kövesdi, J. Rábai, J. Fluorine Chem. 108 (2001) 95–109;
(b) E. de Wolf, P. Ruelle, J. van den Broeke, B.-J. Deelman, G. van Koten, J. Phys. Chem. B 108 (2004) 1458–1466;
(c) J.A. Gladysz, C. Emnet, J. Rábai, in: J.A. Gladysz, D.P. Curran, I.T. Horvath (Eds.), Handbook of Fluorous Chemistry, Wiley/VCH, Weinheim, 2004, pp. 56–100.
[24] (a) I.T. Horváth, J. Rábai, Science 266 (1994) 72–75;
(b) I.T. Horváth, J. Rábai, (Exxon Research and Engineering Co., USA), EP 633062 (1995).
[25] J. Rábai, A. Abudurexiti, D. Szabó, in: J.A. Gladysz, D.P. Curran, I.T. Horváth (Eds.), Handbook of Fluorous Chemistry, Wiley/VCH, Weinheim, 2004, pp. 421–423.
[26] G. Braun, Org. Synth. Coll. Vol. II (1943) 308–309.
[27] W. Shen, L.-M. Wang, H. Tian, J. Tang, J.-J. Yu, J. Fluorine Chem. 130 (2009) 522–527.