HFPO TRIMER-BASED ALKYL TRIFLATE, A NOVEL BUILDING BLOCK FOR FLUOROUS CHEMISTRY. PREPARATION, REACTIONS AND ^{19}F gCOSY ANALYSIS

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Dedicated to Professor Oldřich Paleta on the occasion of his 70th birthday.

Triflate **4**, $CF_3(CF_2)_2O–CF(CF_3)CF_2O–CF(CF_3)CH_2–OTf$ ($R_{FO}CH_2OTf$), of the HFPO trimer-based alcohol **3** ($R_{FO}CH_2OH$) is a novel highly fluorinated building block for fluorous chemistry. In analogy to similar polyfluorinated triflates with methylene spacer, its reactivity is limited to strong and soft nucleophiles. Whereas reactions with cyanide anion, phenolate anion, enolate of diethyl malonate or lithium salt of benzaldehyde bis(phenylsulfanyl)acetal were unsuccessful, the corresponding imidazole **5**, iodide **6** or azide **7** were prepared in good yields. Reaction of imidazole **5** with (perfluorohexyl)methyl triflate (**9**) afforded highly fluorinated non-crystalline imidazolium salt **8**, $TfO^-R_{FO}CH_2–(C_3H_3N_2)^+–CH_2C_6F_{13}$-*n*, which could be employed as fluorous ionic liquid or intermediate for fluorous carbenes. Complete assignment of complex ^{19}F NMR spectra of all compounds employed was accomplished using ^{19}F gCOSY NMR method.

Keywords: Fluorous ligands; Polyethers; Polyfluorinated compounds; HFPO trimer; Triflates; Building blocks; ^{19}F COSY spectroscopy; Imidazolium salts.

Oligomers and telomers of hexafluoropropene-1,2-oxide (HFPO) are highly useful intermediates for industrial chemistry of polymers and inert liquids[1]. Among them, HFPO trimer **1**, $CF_3(CF_2)_2O–CF(CF_3)CF_2O–CF(CF_3)COF$ ($R_{FO}COF$) is probably the best compromise between the feasibility of preparation in a pure form and sufficient fluorophilicity. Its most useful transformation is

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decarboxylation leading to trifluorovinyl ether[2], the industrial monomer. Furthermore, the terminal acyl fluoride group can be easily transformed to the corresponding esters. However, they are much less stable than esters of non-fluorinated carboxylic acids[3] and this severely limits the scope of their applications in chemistry.

Polyfluorinated alcohols with non-fluorinated spacer of various lengths offer high variability in functionalization. Hence, several laboratories independently reported the reduction of HFPO trimer **1** or the ester **2** prepared from it to the corresponding alcohol **3** [4]. Its further reactions include the transformation to polymerizable methacrylates[4a], addition to fluoroalkenes[4b], or etherification[4c].

Among other possible transformations of polyfluorinated alcohols, acylation to the esters of sulfonic acids belongs to one of the most general approaches to polyfluoroalkylation reactions. Thus, polyfluorinated alcohols with a non-fluorinated three carbon chain have been transformed to the corresponding tosylates and used for the preparation of polyfluorinated amines[5]. We successfully employed triflate of polyfluorinated alcohol with a two carbon non-fluorinated spacer for the preparation of bis(polyfluoroalkylated) cyclopentadienes[6] and acetylenes[7], while the corresponding iodides were not sufficiently reactive. Fluoroalcohols with a one-carbon (i.e. methylene) spacer are rather acidic and hence they have to be transformed to the corresponding triflates to allow nucleophilic substitution[8]. These triflates react with alkoxides to form ethers[8a,8b], with inorganic iodides to the corresponding iodides[8c], or with tertiary amines to polyfluorinated ammonium salts[8d]. In the case of the reaction with alkoxides, unexpected attack on the sulfur atom of the triflic moiety was observed in some cases[8e]. In the search for novel fluorous ionic liquids we decided to synthesize triflate of the alcohol derived from the HFPO trimer and to perform a short study regarding the scope and limitations of its reactivity.

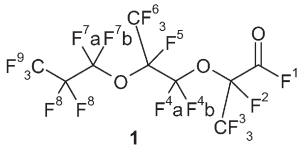
HFPO trimer contains two stereogenic centres and, consequently, consists of equimolar mixture of diastereomers. This, together with the presence of two CF_2 groups bearing two anisochronic fluorine atoms and large $^4J_{F\text{-}F}$ coupling constant values, results in highly complex ^{19}F NMR spectra which were not yet fully resolved. Similarly incomplete is the analysis of HFPO derivatives. Recently, advances in NMR instrumentation made ^{19}F COSY feasible, which was used for confirmation of the well known fact that $^4J_{F\text{-}F}$ coupling constants are generally larger than the $^3J_{F\text{-}F}$ ones[9]. We hence decided to employ ^{19}F gCOSY NMR for the full assignment of the NMR signals of the compounds synthesized including separate diastereomer description wherever possible.

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 (δ) are given in ppm, coupling constants(*J*) in Hz. Diastereomers are distinguished with upper case letters (**A**, **B**), anisochronic signals (strongly coupled AB systems) of non-equivalent fluorine atoms in CF_2 groups are marked with lower case letters (**a**, **b**). In some cases, ^{19}F gCOSY experiments were performed to allow full assignment of signals. FTIR spectra were determined on an FTIR Nicolet 6700 instrument in NaCl tablets. 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 in an oven-dried apparatuses. Perfluoro(2,5-dimethyl-3,6-dioxanonanoyl) fluoride (HFPO trimer **1**, $CF_3(CF_2)_2O–CF(CF_3)CF_2O–CF(CF_3)COF$), 2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptan-1-ol (1*H*,1*H*-perfluoroheptan-1-ol, n-$C_6F_{13}CH_2OH$) and trifluoromethanesulfonic anhydride (triflic anhydride) were purchased from Apollo Scientific, imidazole from Fluka. Acetone and acetonitrile were distilled over P_2O_5, dichloromethane and DMF over CaH_2, and toluene over Na. 1,2-Dibromo-1,1,2,2-tetrafluoroethane ($BrCF_2CF_2Br$) was distilled and dried over molecular sieves. 2,4,4,5,7,7,8,8,9,9,9-Undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonan-1-ol (**3**, $CF_3(CF_2)_2O–CF(CF_3)CF_2O–CF(CF_3)CH_2OH$) was prepared from HFPO trimer **1** via the corresponding methyl ester **2** according to ref.[4a], 2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl trifluoromethanesulfonate (**9**, n-$C_6F_{13}CH_2–OTf$) from the corresponding fluoroalcohol and trifluoromethanesulfonic anhydride according to ref.[8a]

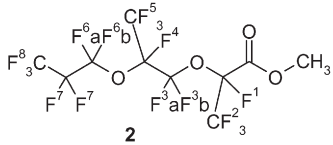
Perfluoro(2,5-dimethyl-3,6-dioxanonanoyl) Fluoride (HFPO Trimer **1**)[4a]



1

^{19}F NMR (282 MHz, THF-d_8): 26.6 s, 1 F (**F1A** or **F1B**); 26.7 s, 1 F (**F1A** or **F1B**); –78.8 dm, 1 F, $^{2}J_{F-F}$ = 145 (**F4aA**); –79.4 dm, 1 F, $^{2}J_{F-F}$ = 145 (**F4aB**); –80.7 m, 2 × 3 F (**F6A** and **F6B**); –81.8 dm, 2 × 1 F, $^{2}J_{F-F}$ = 145 (**F7aA** and **F7aB**); –82.2 dm, 2 × 1 F, $^{2}J_{F-F}$ = 145 (**F7bA** and **F7bB**); –82.2 t, 3 F, $^{4}J_{F-F}$ = 7 (**F9A** or **F9B**); –82.3 t, 3 F, $^{4}J_{F-F}$ = 7 (**F9A** or **F9B**); –82.8 m, 2 × 3 F (**F3A** and **F3B**); –85.5 dm, 1 F, $^{2}J_{F-F}$ = 145 (**F4bB**); –86.1 dm, 1 F, $^{2}J_{F-F}$ = 145 (**F4bA**); –130.2 s, 2 × 2 F (**F8A** and **F8B**); –131.2 dm, 1 F, $^{4}J_{F-F}$ = 21 (**F2B**); –131.3 dm, 1 F, $^{4}J_{F-F}$ = 21 (**F2A**); –145.4 t, 2 × 1 F, $^{4}J_{F-F}$ = 22 (**F5A** and **F5B**).

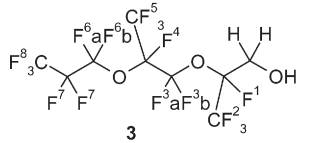
Methyl Perfluoro(2,5-dimethyl-3,6-dioxanonanoate) (**2**)[4a]



2

^{1}H NMR (300 MHz, acetone-d_6): 4.13 s, 3 H (C**H**$_3$). ^{19}F NMR (282 MHz, acetone-d_6): –78.6 dm, 1 F, $^2J_{F\text{-}F}$ = 145 (**F3aA**); –79.2 dm, 1 F, $^2J_{F\text{-}F}$ = 145 (**F3aB**); –79.8 m, 2 × 3 F (**F5A** and **F5B**); –80.9 dm, 2 × 1 F, $^2J_{F\text{-}F}$ = 145 (**F6aA** and **F6aB**); –81.1 t, 3 F, $^4J_{F\text{-}F}$ = 7 (**F8A** or **F8B**); –81.2 t, 3 F, $^4J_{F\text{-}F}$ = 7 (**F8A** or **F8B**); –81.3 dm, 2 × 1 F, $^2J_{F\text{-}F}$ = 145 (**F6bA** and **F6bB**); –82.2 m, 3 F (**F2A** or **F2B**); –82.2 m, 3 F (**F2A** or **F2B**); –84.4 dm, 1 F, $^2J_{F\text{-}F}$ = 145 (**F3bB**); –85.0 dm, 1 F, $^2J_{F\text{-}F}$ = 145 (**F3bA**); –129.3 s, 2 F (**F7A** or **F7B**); –129.3 s, 2 F (**F7A** or **F7B**); –131.1 dm, 1 F, $^4J_{F\text{-}F}$ = 23 (**F1B**); –131.1 dm, 1 F, $^4J_{F\text{-}F}$ = 23 (**F1A**); –144.8 t, 1 F, $^4J_{F\text{-}F}$ = 23 (**F4B**); –144.9 t, 1 F, $^4J_{F\text{-}F}$ = 23 (**F4A**).

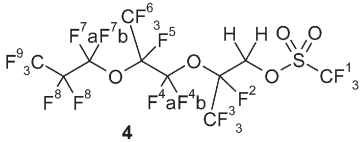
2,4,4,5,7,7,8,8,9,9,9-Undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonan-1-ol (**3**)[4a]



3

^{1}H NMR (300 MHz, acetone-d_6): 4.26 m, 2 H (C**H**$_2$); 5.36 bs, 1 H (O**H**). ^{19}F NMR (282 MHz, acetone-d_6): –78.6 dm, 1 F, $^2J_{F\text{-}F}$ = 145 (**F3aA**); –78.7 dm, 1 F, $^2J_{F\text{-}F}$ = 145 (**F3aB**); –79.9 m, 2 × 3 F (**F5A** and **F5B**); –80.8 dm, 2 × 1 F, $^2J_{F\text{-}F}$ = 145 (**F6aA** and **F6aB**); –81.1 dm, 1 F, $^2J_{F\text{-}F}$ = 145 (**F3bB**); –81.2 t, 3 F, $^4J_{F\text{-}F}$ = 7 (**F8A** or **F8B**); –81.2 t, 3 F, $^4J_{F\text{-}F}$ = 7 (**F8A** or **F8B**); –81.3 dm, 1 F, $^2J_{F\text{-}F}$ = 145 (**F3bA**); –81.4 dm, 2 × 1 F, $^2J_{F\text{-}F}$ = 145 (**F6bA** and **F6bB**); –82.0 m, 3 F (**F2A** or **F2B**); –82.1 m, 3 F (**F2A** or **F2B**); –129.4 s, 2 F (**F7A** or **F7B**); –129.4 s, 2 F (**F7A** or **F7B**); –134.4 dq, 1 F, $^4J_{F\text{-}F}$ = 24 (d), $^4J_{F\text{-}F}$ = $^3J_{H\text{-}F}$ = 12 (q) (**F1B**); –134.6 dq, 1 F, $^4J_{F\text{-}F}$ = 24 (d), $^4J_{F\text{-}F}$ = $^3J_{H\text{-}F}$ = 12 (q) (**F1A**); 144.8 t, 1 F, $^4J_{F\text{-}F}$ = 21 (**F4B**); –144.9 t, 1 F, $^4J_{F\text{-}F}$ = 21 (**F4A**).

2,4,4,5,7,7,8,8,9,9,9-Undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl Trifluoromethanesulfonate (**4**)

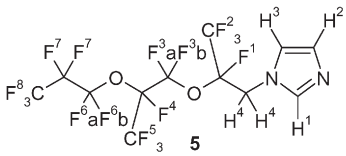


4

To an ice-cooled solution of fluoroalcohol **3** (15.26 g, 31.66 mmol) and pyridine (3.70 ml, 45.9 mmol) in absolute CH_2Cl_2 (50 ml), trifluoromethanesulfonic anhydride (7.63 ml, 45.4 mmol) was added dropwise while stirring vigorously. The mixture was stirred at 0 °C

for 2 h and then at room temperature overnight. Solid pyridinium trifluoromethanesulfonate was filtered off and the mixture was washed with cold water (3 × 40 ml). The organic phase was dried with anhydrous $MgSO_4$ and the solvent was evaporated to give a yellow oil, which on fractionation yielded 13.66 g (70.2%) of fluorotriflate **4** (colorless liquid, b.p. 80–82 °C/2.5 kPa). ^{1}H NMR (300 MHz, acetone-d_6): 5.57 m, 2 H (C**H**$_2$). ^{19}F NMR (282 MHz, acetone-d_6): –74.5 s, 3 F (**F1**); 79.3 dm, 1 F, $^2J_{F-F}$ = 145 (**F4aA**); –79.5 dm, 1 F, $^2J_{F-F}$ = 145 (**F4aB**); –79.7 m, 2 × 3 F (**F6A** and **F6B**); –80.5 dm, 1 F, $^2J_{F-F}$ = 145 (**F4bB**); –80.7 dm, 2 × 1 F, $^2J_{F-F}$ = 145 (**F7aA** and **F7aB**); –80.8 dm, 1 F, $^2J_{F-F}$ = 145 (**F4bA**); –81.2 t, 3 F, $^4J_{F-F}$ = 7 (**F9A** or **F9B**); –81.2 t, 3 F, $^4J_{F-F}$ = 7 (**F9A** or **F9B**); –81.4 dm, 2 × 1 F, $^2J_{F-F}$ = 145 (**F7bA** and **F7bB**); –81.8 d, 3 F, $^5J_{F-F}$ = 6 (**F3A** or **F3B**); –81.9 d, 3 F, $^5J_{F-F}$ = 6 (**F3A** or **F3B**); –129.3 s, 2 F (**F8A** or **F8B**); –129.3 s, 2 F (**F8A** or **F8B**); –135.5 dq, 1 F, $^4J_{F-F}$ = 23 (_), $^4J_{F-F}$ = $^3J_{H-F}$ = 12 (q) (**F2B**); –135.6 dq, 1 F, $^4J_{F-F}$ = 23 (_), $^4J_{F-F}$ = $^3J_{H-F}$ = 12 (q) (**F2A**); –144.4 t, 1 F, $^4J_{F-F}$ = 21 (**F5B**); –144.6 t, 1 F, $^4J_{F-F}$ = 21 (**F5A**). ^{13}C NMR (75 MHz, acetone-d_6): 69.0 d, 1 C, $^2J_{C-F}$ = 30 (CH_2); 100–126 m, 8C (C**F**, CF_2 and CF_3 groups); 118.6 q, 1 C, $^1J_{C-F}$ = 318 (CF_3SO$_2$O). MS (ESI), *m/z* (%): 545 [M – CF_3]$^+$, 55; 351 [M – CF(CF_3)$CH_2OSO_2CF_3$]$^+$, 50; 285 [M – $CF_2OCF(CF_3)CH_2OSO_2CF_3$]$^+$, 100. HRMS (FAB), *m/z*: calculated for $C_{10}H_2F_{20}NaO_5S$ [M + Na]$^+$ 636.91958, found 636.91882. IR: 1437 m, 1234 s, 1202 s, 1144 s, 609 m (C–S).

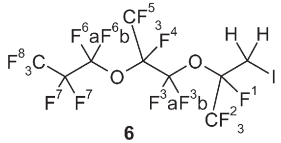
1-[2,4,4,5,7,7,8,8,9,9,9-Undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl]imidazole (**5**)



5

A flask was charged with imidazole (1.50 g, 23.5 mmol), fluoroalkyl triflate **4** (6.70 g, 10.9 mmol) and acetonitrile (40 ml). The mixture was refluxed for 8 h and then stirred at room temperature overnight. Acetonitrile was evaporated, the residue was dissolved in diethyl ether (100 ml) and washed with cold water (3 × 50 ml). The organic layer was dried with anhydrous $MgSO_4$ and the solvent was evaporated giving a brown oil. To remove traces of colored impurities, the crude product was dissolved in diethyl ether and stirred with charcoal overnight. Filtration and evaporation gave fluorinated imidazole **5** (5.80 g, 31.8%, colorless viscous oil). ^{1}H NMR (300 MHz, acetone-d_6): 5.21 m, 2 H (**H4**); 7.00 m, 1 H (**H2**); 7.21 m, 1 H (**H3**); 7.68 s, 1 H (**H1**). ^{19}F NMR (282 MHz, acetone-d_6): –77.9 dm, 1 F, $^2J_{F-F}$ = 145 (**F3aA**); –78.2 dm, 1 F, $^2J_{F-F}$ = 145 (**F3aB**); –79.5 m, 2 × 3 F (**F5A** and **F5B**); –80.4 dm, 1 F, $^2J_{F-F}$ = 145 (**F6aA** and **F6aB**); –80.6 dm, 1 F, $^2J_{F-F}$ = 145 (**F3bB**); –81.0 t, 3 F, $^4J_{F-F}$ = 6 (**F8A** or **F8B**); –81.0 t, 3 F, $^4J_{F-F}$ = 6 (**F8A** or **F8B**); –81.0 dm, 1 F, $^2J_{F-F}$ = 145 (**F3bA**); –81.3 dm, 2 × 1 F, $^2J_{F-F}$ = 145 (**F6bA** and **F6bB**); –81.6 d, 3 F, $^5J_{F-F}$ = 12 (**F2A** or **F2B**); –81.8 d, 3 F, $^5J_{F-F}$ = 12 (**F2A** or **F2B**); –129.1 s, 2 F (**F7A** or **F7B**); –129.2 s, 2 F (**F7A** or **F7B**); –134.7 dq, 1 F, $^4J_{F-F}$ = 20 (d), $^4J_{F-F}$ = $^3J_{H-F}$ = 12 (q) (**F1B**); –134.8 dq, 1 F, $^4J_{F-F}$ = 20 (d), $^4J_{F-F}$ = $^3J_{H-F}$ = 12 (q) (**F1A**); –144.2 t, 1 F, $^4J_{F-F}$ = 20 (**F4B**); –144.6 dt, 1 F, $^4J_{F-F}$ = 20 (t), $^3J_{F-F}$ = 9 (d) (**F4A**). ^{13}C NMR (75 MHz, acetone-d_6): 47.1 d, 1 C, $^2J_{C-F}$ = 21 (CH^4_2); 100–126 m, 8 C (C**F**, CF_2 and CF_3 groups); 121.3 s, 1 C (CH^2); 128.2 s, 1 C (CH^3); 138.8 s, 1 C (CH^1). MS (ESI), *m/z* (%): 533 [M + H]$^+$, 100. HRMS (ESI), *m/z*: calculated for $C_{12}H_6F_{17}N_2O_2$ [M + H]$^+$ 533.01523, found 533.01497. IR: 3124 w, 3005 w, 2968 w, 1695 w (C=N); 1507 w (C=C); 1239 s, 1198 s, 1157 s.

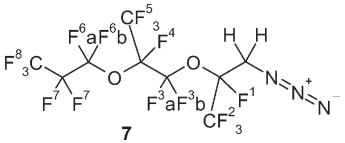
1,1,1,2,4,4,5,7,7,8,8,9,9,9-Tetradecafluoro-2-(iodomethyl)-5-(trifluoromethyl)-3,6-dioxanonane (**6**)



6

A flask was charged with acetone (20 ml), anhydrous NaI (12.42 g, 82.86 mmol) and triflate **4** (3.32 g, 5.40 mmol). The mixture was refluxed for 1 h and then stirred at room temperature overnight. The solvent was evaporated, the residue was dissolved in diethyl ether (50 ml) and rapidly washed with cold water (50 ml). The organic phase was dried with anhydrous Na_2SO_4 and the solvent was evaporated to afford a yellow oil. Distillation gave iodide **6** (2.43 g, 76.0%, b.p. 80–82 °C/2.5 kPa, colorless highly volatile oil). ^{1}H NMR (300 MHz, acetone-d_6): 4.05 m, 2 H (C**H**$_2$). ^{19}F NMR (282 MHz, acetone-d_6): –77.5 dm, 1 F, $^2J_{F-F}$ = 145 (**F3aA**); –78.0 dm, 1 F, $^2J_{F-F}$ = 145 (**F3aB**); –79.4 m, 3 F (**F5A** or **F5B**); –79.5 m, 3 F (**F5A** or **F5B**); –80.4 dm, 2 × 1 F, $^2J_{F-F}$ = 140 (**F6aA** and **F6aB**); –80.6 dm, 1 F, $^2J_{F-F}$ = 145 (**F3bB**); –80.9 dm, 1 F, $^2J_{F-F}$ = 145 (**F3bA**); –81.0 m, 6 F (**F2A**, **F2B**, **F8A** and **F8B**); –81.3 dm, 2 × 1 F, $^2J_{F-F}$ = 145 (**F6bA** and **F6bB**); –122.5 dq, 1 F, $^4J_{F-F}$ = $^3J_{H-F}$ = 21 (q), $^4J_{F-F}$ = 9 (d) (**F1B**); –122.9 dq, 1 F, $^4J_{F-F}$ = $^3J_{H-F}$ = 21 (q), $^4J_{F-F}$ = 9 (d) (**F1A**); –129.1 s, 2 F (**F7A** or **F7B**); –129.3 s, 2 F (**F7A** or **F7B**); –144.4 tm, 1 F, $^4J_{F-F}$ = 20 (**F4B**); –144.7 tm, 1 F, $^4J_{F-F}$ = 20 (**F4A**). ^{13}C NMR (75 MHz, acetone-d_6): 69.2 d, 1 C, $^2J_{C-F}$ = 30 (CH_2); 100–126 m, 8 C (C**F**, CF_2 and CF_3 groups). HRMS (EI), *m/z*: calculated for $C_9H_2F_{17}IO_2$ $[M]^+$ 591.88280, found 591.88187. IR: 1306 m, 1239 s, 1202 s, 1157 s.

2,4,4,5,7,7,8,8,9,9,9-Undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonylazide (**7**)



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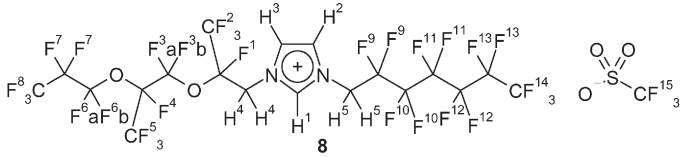
A flask was filled with fluoroalkyl triflate **4** (0.45 g, 0.74 mmol), NaN_3 (0.12 g, 1.85 mmol) and DMF (6 ml). The obtained two-phase (fluorous and DMF) mixture was heated while stirring to 50 °C for two days. DMF was removed by extraction of the reaction mixture with water. Organic phase was diluted with diethyl ether (50 ml), washed again with water (3 × 40 ml), dried with anhydrous Na_2SO_4 and the solvent was evaporated to give the target azide **7** (0.189 g, 50.5%, colorless oil). ^{1}H NMR (300 MHz, acetone-d_6): 4.41 m, 2 H (C**H**$_2$). ^{19}F NMR (282 MHz, acetone-d_6): –79.8 dm, 1 F, $^2J_{F-F}$ = 145 (**F3aA**); –80.0 dm, 1 F, $^2J_{F-F}$ = 145 (**F3aB**); –80.5 m, 2 × 3 F (**F5A** and **F5B**); –81.5 dm, 1 F, $^2J_{F-F}$ = 145 (**F3bB**); –81.6 dm, 2 × 1 F, $^2J_{F-F}$ = 145 (**F6aA** and **F6aB**); –81.9 dm, 1 F, $^2J_{F-F}$ = 145 (**F3bA**); –82.0 m, 2 × 3 F (**F8A** and **F8B**); –82.3 dm, 2 × 1 F, $^2J_{F-F}$ = 145 (**F6bA** and **F6bB**); –83.0 d, 1 F, $^5J_{F-F}$ = 6 (**F2A** or **F2B**); –83.1 d, 1 F, $^5J_{F-F}$ = 6 (**F2A** or **F2B**); –130.2 s, 2 F (**F7A** or **F7B**); –130.3 s, 2 F (**F7A** or **F7B**); –133.2 dq, 1 F, $^4J_{F-F}$ = 23 (d), $^4J_{F-F}$ = $^3J_{H-F}$ = 13 (q) (**F1B**); –133.3 dq, 1 F, $^4J_{F-F}$ = 23 (d), $^4J_{F-F}$ =

$^3J_{H-F}$ = 13 (q) (**F1A**); –145.6 tm, 1 F, $^4J_{F-F}$ = 22 (**F4B**); –145.7 tm, 1 F, $^4J_{F-F}$ = 21 (**F4A**). ^{13}C NMR (75 MHz, acetone-d_6): 80.8 d, 1 C, $^2J_{C-F}$ = 27 (CH_2); 100–126 m, 8 C (CF, CF_2 and CF_3 groups). MS (APCI), *m/z* (%): 480 $[M - N_2 + H]^+$, 8; 479 $[M - N_2]^+$, 100. HRMS (EI), *m/z*: calculated for $C_9H_2F_{17}N_3O_2$ $[M]^+$ 506.98755, found 506.98842. IR: 2117 m (N=N); 1238 s, 1201 s, 1159 m.

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 (**8**)



8

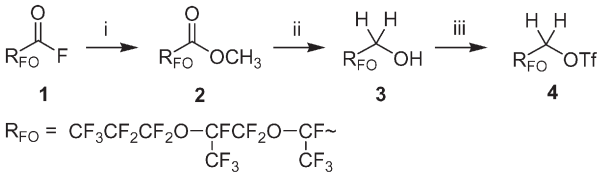
A flask was charged with fluoralkylated imidazole **5** (3.99 g, 7.49 mmol), fluoroalkyl triflate **9** (3.61 g, 7.49 mmol) and 10 ml of toluene. The reaction mixture was heated to 120 °C for 8 days while stirring. From the resulting two-phase mixture, toluene was evaporated and the residual solvents were removed by heating to 100 °C/1 Pa for two days, giving the target fluorous imidazolium triflate **8** (6.71 g, 88.2%, highly viscous yellow oil). ^{1}H NMR (300 MHz, acetone-d_6): 5.76 t, $^3J_{H-F}$ = 16.4, 2 H (**H**^{5}); 5.81 m, 2 H (**H4**); 8.21 m, 1 H (**H2**); 8.26 m, 1 H (**H3**); 9.84 s, 1 H (**H1**). ^{19}F NMR (282 MHz, acetone-d_6): –77.8 dm, 1 F, $^2J_{F-F}$ = 150 (**F3aA**); –78.0 dm, 1 F, $^2J_{F-F}$ = 150 (**F3aB**); –78.2 s, 2 × 3 F (**F15A** and **F15B**); –79.5 q, 3 F, $^4J_{F-F}$ = $^5J_{F-F}$ = 9 (**F5A** or **F5B**); –79.6 q, 3 F, $^4J_{F-F}$ = $^5J_{F-F}$ = 9 (**F5A** or **F5B**); –80.4 dm, 2 × 1 F, $^2J_{F-F}$ = 140 (**F6aA** and **F6aB**); –80.6 m, 2 × 3 F (**F14A** and **F14B**); –81.0 t, 3 F, $^4J_{F-F}$ = 7 (**F8A** or **F8B**); –81.1 dm, 1 F, $^2J_{F-F}$ = 150 (**F3bB**); –81.1 t, 3 F, $^4J_{F-F}$ = 7 (**F8A** or **F8B**); –81.3 d, 1 F, $^5J_{F-F}$ = 11 (**F2A** or **F2B**); –81.3 dm, 1 F, $^2J_{F-F}$ = 150 (**F3bA**); –81.4 dm, 2 × 1 F, $^2J_{F-F}$ = 140 (**F6bA** and **F6bB**); –81.5 d, 1 F, $^5J_{F-F}$ = 11 (**F2A** or **F2B**); –116.8 m, 2 × 2 F (**F9A** and **F9B**); –121.5 m, 2 × 2 F (**F11A** and **F11B**); –122.2 m, 2 × 2 F (**F10A** and **F10B**); –122.2 m, 2 × 2 F (**F12A** and **F12B**); –125.7 m, 2 × 2 F (**F13A** and **F13B**); –129.1 s, 2 F (**F7A** or **F7B**); –129.3 s, 2 F (**F7A** or **F7B**); –134.6 dq, 1 F, $^4J_{F-F}$ = $^3J_{H-F}$ = 22 (q), $^4J_{F-F}$ = 15 (d) (**F1B**); –135.2 dq, 1 F ,$^4J_{F-F}$ = $^3J_{H-F}$ = 22 (q), $^4J_{F-F}$ = 15 (d) (**F1A**); –144.0 tm, 2 × 1 F, $^4J_{F-F}$ = 21 (**F4A** and **F4B**). ^{13}C NMR (75 MHz, acetone-d_6): 48.8 t, 1 C, $^2J_{C-F}$ = 23 (CH^5_2); 49.6 d, 1 C, $^2J_{C-F}$ = 20 (CH^4_2); 100–126 m, 14 C (CF, CF_2 and CF_3 groups); 120.5 q, 1 C, $^1J_{C-F}$ = 317 (CF^{15}_3); 125.7 s, 1 C (CH^2); 125.8 s, 1 C (CH^3); 141.0 s, 1 C (CH^1). MS (ESI), *m/z* (%): 865 $[M - TfO^-]^+$, 100; 149 $[TfO]^-$, 100.

RESULTS AND DISCUSSION

*Preparation of HFPO Trimer-Based Triflate **4***

Esterification of HFPO trimer **1** (R_{FO}COF, 78% yield) followed by reduction of the ester **2** (R_{FO}COOMe, 75% yield) afforded polyfluorinated alcohol **3** ($R_{FO}CH_2OH$) according to the published data[4a].

Synthesis of the corresponding triflate **4** was accomplished according to the methodology employed for the preparation of triflates of fluorinated alcohols with methylene spacer[8a], i.e. by slowly adding triflic anhydride to the ice-cooled solution of fluoro alcohol **3** and pyridine in anhydrous dichloromethane. Purification of the mixture after standard aqueous work-up by fractional vacuum distillation afforded the target fluoroalkyl triflate as a colorless, slightly viscous liquid in 70% yield (Scheme 1). The triflate is remarkably stable and does not decompose on standing in water.



i MeOH, Et_2O, Na_2CO_3, $MgSO_4$, reflux/overnight, 78%; ii $NaBH_4$, MeOH, Et_2O, reflux/11 h, 75%; iii Tf_2O, pyridine, CH_2Cl_2, 0 °C/2h, then rt/overnight, 70%

SCHEME 1

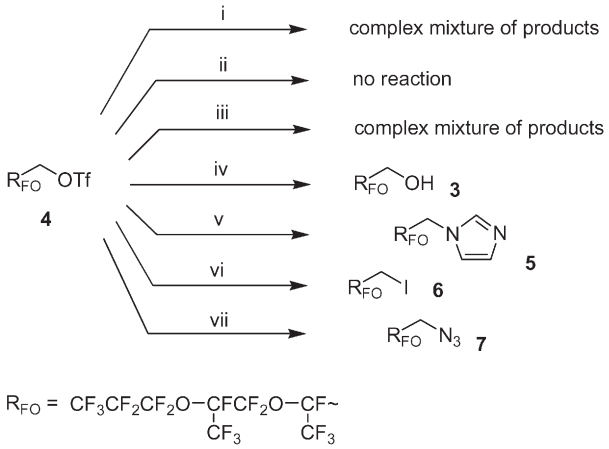
*Reactions of HFPO Trimer-Based Triflate **4***

The reactivity of polyfluoroalkylated triflates strikingly depends on the length of the non-fluorinated spacer between the perfluoroalkyl group and the triflate unit. Thus, trimethylene spacer leads to reactant with standard triflate reactivity and ethylene spacer limits the reactivity of the corresponding triflate only to a minor extent, allowing thus functionalization with most nucleophilic reagents[6a]. In contrast to this, polyfluoroalkylated triflates with methylene spacer exhibit highly limited reactivity[8]. Moreover, the substitution on the carbon atom can be accompanied by the attack of the nucleophile on the sulfur atom of the triflate moiety[8e]. To obtain the information how branching at the β-carbon and the change of the perfluoroalkyl chain for the perfluoropolyether one will influence the behaviour of the triflate, we performed a series of reactions of triflate **4** with various nucleophilic reagents.

We indeed found that the reactivity is lower compared to other triflates and limited to the most reactive nucleophiles. Thus, no reaction of triflate **4** was observed with KCN in MeCN at 70 °C or with sodium enolate of diethyl malonate in THF at 80 °C. Performing the reaction of KCN in DMF or DMPU at 120 °C lead to the formation of a complex mixture of products, in which individual components could not be identified. Similar negative results afforded the reaction of triflate **4** with lithium salt of benzaldehyde

bis(phenylsulfanyl)acetal. Reaction of triflate **4** with sodium phenolate in analogy to ref.[8a] afforded only polyfluorinated alcohol **3**, probably as a result of thiophilic attack of the phenoxide[8e].

On the other hand, reaction of triflate **4** with imidazole, a good nucleophile, in refluxing acetonitrile afforded the corresponding fluoroalkylated imidazole **5** in a moderate yield, where part of the product was lost in the course of purification procedure. Finkelstein reaction of triflate **4** with sodium iodide in acetone led to a good yield of fluorinated iodide **6** as the perspective intermediate for radical reactions. Finally, substitution of triflate **4** with another excellent nucleophile, sodium azide, in DMF at 50 °C yielded azide **7** as the precursor of the corresponding fluorinated amines (Scheme 2).



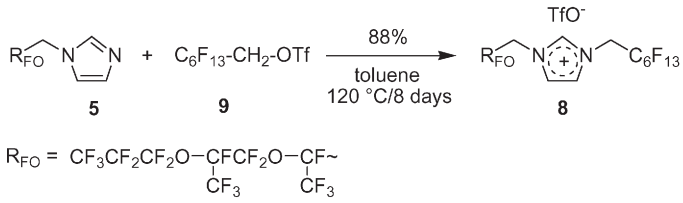
i KCN, MeCN, 70 °C or KCN, DMF, 120 °C or KCN, DMPU, 120 °C; ii diethyl malonate, NaH, THF, 80 °C; iii $PhCH(SPh)_2$, BuLi, THF, -78 °C to rt; iv PhOH, NaH, DMSO, 130 °C; v imidazole, MeCN, reflux/8 h, 32%; vi NaI, acetone, reflux/1 h, then rt/overnight, 76%; vii NaN_3, DMF, 50 °C/48 h, 50%

SCHEME 2

Preparation of Fluorous Imidazolium Salt ***8***

Appropriately 1,3-disubstituted imidazolium salts belong to the most common ionic liquids used. Several types of fluorous ionic liquids has been synthesized[11a], based on fluorinated heterocyclic cations[11b], ammonium salts[11c] or fluorinated anions[11c–11g]. Mono(polyfluoroalkylated) imidazolium salts are known and have been studied as solvents for metal ion extraction[12a], solvents for CO_2 [12b,12c], surfactants[12d], or solvents for Diels–Alder

reactions[12e]. These ionic liquids are in general insufficiently fluorinated to exert characteristic fluorous properties such as negligible miscibility with organic solvents. Bis(polyfluoroalkylated) imidazolium salts have been also prepared, but they are crystalline solids and hence can not be employed as room-temperature ionic liquids (RTILs)[13]. In contrast to long-chain perfluoroalkylated compounds which are in general crystalline, perfluorinated polyethers based on HFPO oligomers or telomers are liquids. This led us to the assumption that imidazolium salts bearing triflate **4** derived chain should not be crystalline. This was confirmed when we reacted fluoroimidazole **5** with (perfluoroalkyl)methyl triflate **9** and indeed obtained unsymmetrically polyfluoroalkylated imidazolium salt **8** as highly viscous liquid, the first known example of highly fluorous imdazole-based RTIL (Scheme 3).



SCHEME 3

Analysis of HFPO Trimer-Derived Compounds with ^{19}F gCOSY NMR

In HFPO trimer or its derivatives, the CF_2 group of the perfluoropropoxy fragment and CF groups have characteristic easily distinguishable signals (Fig. 1).

On the other hand, remaining signals, i.e. CF_3 and CF_2O groups, overlap in the region from –75 to –85 ppm, making especially the assignment of highly coupled anisochronic CF_2O groups in 1D ^{19}F NMR spectra impossible. Hence, all previously attempted assignments are either general and incomplete, or erroneous and generally omit the fact that the compounds consist of the mixtures of two diastereomers. This can be well documented on the published NMR assigments[4] of fluoroalcohol **3**. We therefore performed a series of ^{19}F gCOSY experiments, which allowed nearly complete assignment of all fluorine signals in HFPO trimer-derived compounds we worked with, viz. acyl fluoride **1**, ester **2**, alcohol **3**, triflate **4**, imidazole **5**, iodide **6**, azide **7** and imidazolium salt **8**. As the individual signal patterns are similar for all compounds, the assignment will be showed in detail only for the most complex case, imidazolium salt **8**.

We started the assignment with the description of the perfluorohexyl fragment of the (perfluorohexyl)methyl group. Apart of CF_3 group signal, all remaining CF_2 groups display signals in a narrow area between –115 and –130 ppm and are well resolved with the exception of two overlapping signals at –122.2 ppm. It is well known and documented that in perfluorinated compounds the $^4J_{F-F}$ coupling constant (~10 Hz) is characteristically larger than the $^3J_{F-F}$ one (<3 Hz)[9]. In analogy to ref.[9], two sets of interactions can be hence distinguished, the first among the even and the second among the odd fluorinated carbon atoms. The slice of gCOSY spectrum at –122.2 ppm reveals the $^4J_{F-F}$ coupling with the $C^{14}F_3$ group and allows thus to assign it unequivocally among other CF_3 groups of the perfluoropolyether chain. No other coupling can be recognized at this slice and hence the signal at –122.2 ppm of double integral intensity has to be assigned to both $C^{12}F_2$ and $C^{10}F_2$ groups. Correspondingly, the slice at –121.5 ppm shows the coupling with signals at –116.8 and –125.7 ppm. As the most upfield CF_2 group signal at –125.7 is known to belong to CF_3CF_2 moiety (i.e., to $C^{13}F_2$ group signal), the former has to be assigned to the C^9F_2 group signal (Fig. 2).

The assignment of signals of the perfluoropolyether moiety started from easily assesible upfield signals (see Fig. 1) of both CF groups and CF_2 group of the perfluoropropoxy unit, which was already performed earlier on other HFPO trimer derivatives[4]. Thus, the triplet at –144.0 ppm was assigned to the C^4F group as the signal common for both diastereomers. Closer inspection of gCOSY spectrum at the area around –135 ppm revealed that two signals of C^1F groups of the two diastereoisomers could be distinguished, viz. at –134.6 or –135.2 ppm. A slice of gCOSY spectrum at about –129 ppm did not show any coupling of the C^7F_2 group and hence the two signals at this area cannot be assigned as doublet of one CF_2 group, but as two singlets of two diastereoisomers (–129.1 or –129.3 ppm).

Slices at shifts of both CF signals, as well as the slice at the shift of the CF_2 group of the perfluoropropoxy group did not reveal any $^3J_{F-F}$ coupling in excellent agreement with observation made for perfluoroalkylated systems[9]. On the other hand, significant values of $^4J_{F-F}$ coupling constant in the slices at the shifts of the CF groups allowed to identify highly coupled signals of CF_2O groups. Thus, the slice at –144 ppm revealed the signal of the C^6F_2 group as two anisochronic F signals with strong geminal coupling exceeding 140 common for both diastereomers at –80.4 and –81.3 ppm. Similarly, the slices at –134.6 or –135.4 ppm revealed for both diastereomers two distinguished sets of anisochronic F signals with large geminal coupling and remarkably different shifts (–78.0 and –81.1 ppm, and –77.8

and –81.3 ppm, respectively). Final assignment of the three different CF_3 groups relied on coupling. Thus, the less coupled signals at –81.3 or –81.5 ppm were assigned to the two diastereomeric C^2F_3 groups (no $^4J_{F\text{-}F}$ coupling constant possible), whereas two triplets at –81.0 or –81.1 ppm to

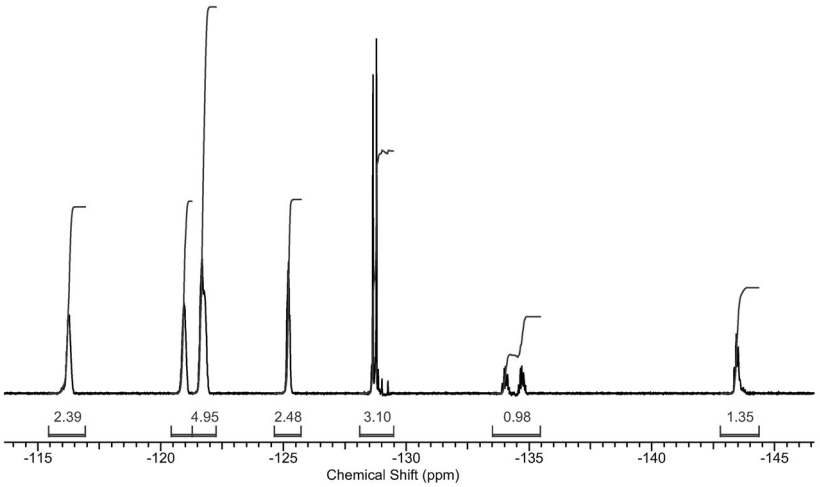


FIG. 1
Upfield part of the ^{19}F NMR spectrum of imidazolium salt **8**

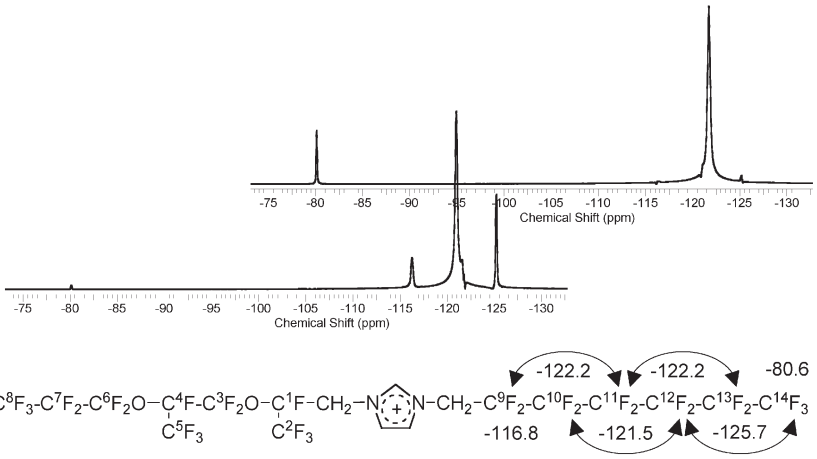


FIG. 2
Assignment of the signals of perfluorohexyl group of imidazolium salt **8**

the two diastereomeric C^8F_3 groups (characteristic signals of the perfluoropropyl group). Finally, the remaining two signals at –79.5 or –79.6 ppm with more complex coupling patterns were attributed to the two diastereomeric C^5F_3 groups (Fig. 3).

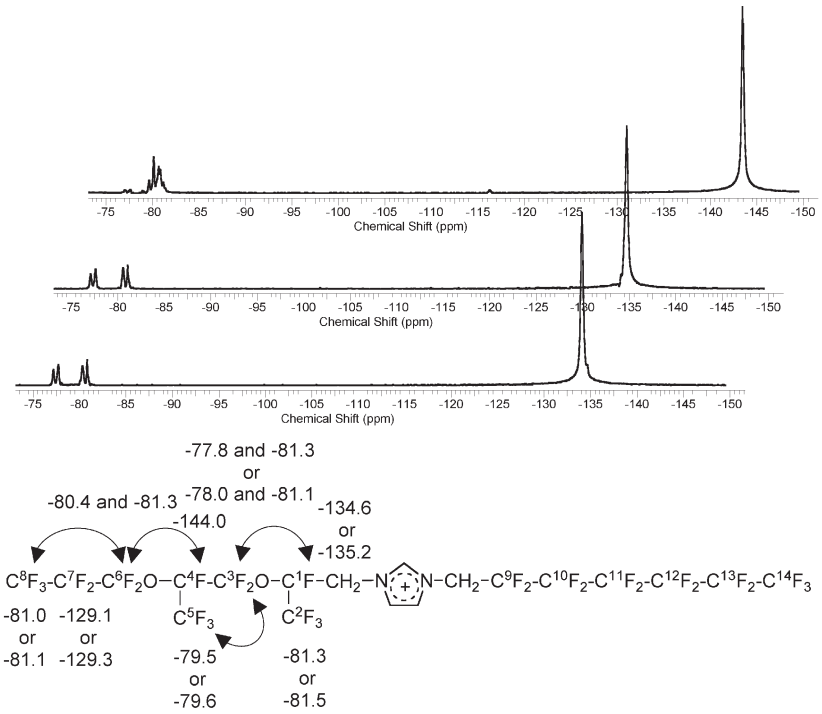


FIG. 3
Assignment of the signals of perfluoropolyether group of imidazolium salt **8**

CONCLUSIONS

We developed a new highly fluorinated building block based on HFPO trimer, which exerts low crystallinity. Although its reactivity is lower compared to the analogous perfluoroalkylated building blocks, it can be substituted with efficient nucleophiles as imidazole, azide or iodide. In contrast to known bis(polyfluoroalkylated) imidazolium salts, imidazolium salt based on this building block is not crystalline. For the first time, full ^{19}F NMR assignments of HPFO trimer-based compounds including the distinc-

tion between individual diastereomers were accomplished using ^{19}F gCOSY NMR spectroscopy.

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