Journal of Fluorine Chemistry 130 (2009) 966–973

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

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

Synthesis of bis(polyfluoroalkylated)imidazolium salts as key intermediates for fluorous NHC ligands

Martin Skalický [a], Markéta Rybáčková [a], Ondřej Kysilka [a], Magdalena Kvíčalová [b], Josef Cvačka [c], Jan Čejka [d], Jaroslav Kvíčala [a,*]

[a] Department of Organic Chemistry, Institute of Chemical Technology, Prague, Technická 5, 16628 Prague 6, Czech Republic
[b] Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Husinec-Řež 1001, 25068 Řež, Czech Republic
[c] Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, v.v.i., Flemingovo nám. 2, 16610 Prague 6, Czech Republic
[d] Department of Chemistry of Solid State, Institute of Chemical Technology, Prague, Technická 5, 16628 Prague 6, Czech Republic

ARTICLE INFO

Article history:
Received 22 January 2009
Received in revised form 20 July 2009
Accepted 22 July 2009
Available online 30 July 2009

Keywords:
Imidazolium
Fluorous
Fluorophilic
Triflate
Carbene
Mesityl
NHC ligand

ABSTRACT

1,3-Bis(polyfluoroalkyl)- and 1-mesityl-3-(polyfluoroalkyl)imidazolium salts differing in the length of a polyfluorinated chain and a non-fluorinated spacer were synthesized as key building blocks for fluorous NHC (*N*-heterocyclic carbene) ligands. A new approach using polyfluoroalkyl triflates instead of the corresponding iodides was employed allowing fine tailoring of fluorous properties, as well as of the electron density of the imidazolium ring. Using bis(polyfluoroalkylated)imidazolium salt, a fluorous analogue of the PEPPSI™ catalyst was synthesized and its structure confirmed by X-ray diffraction. The catalyst was employed in model Heck and Suzuki couplings with moderate yields, however, its recycle was not successful. Fluorophilicity of bis(polyfluoroalkylated)imidazolium salts was found to be surprisingly low compared with the analogous perfluoropolyether-based salts.

1. Introduction

Substituted imidazolium salts are frequently employed as ionic liquids [1,2] or as a part of biologically active compounds [3–5]. Moreover, they are precursors for the preparation of *N*-heterocyclic carbenes, which are a perspective class of compounds used in medicinal chemistry [6,7] or, even more importantly, as ligands in homogeneous catalysis [8,9]. Metal complexes derived from NHC ligands are stable to oxidation and heating to higher temperatures. 1,3-Disubstituted imidazol-2-ylidene complexes of transition metals have been successfully applied in reactions like Heck, Suzuki, Sonogashira, Kumada–Tamao–Corriu or Stille coupling [10]. The most commonly used NHC carbenes contain bulky groups like cyclohexyl, *o*-tolyl, mesityl, 2,6-diisopropylphenyl or adamantyl [11]. The *N*-substituents have a limited effect on the electronic density of the carbene carbon [12,13] and even carbenes with electron-withdrawing groups retain sufficient σ-donating ability to form complexes [14]. Fine tuning of NHC's properties hence relies mostly on steric bulk of the substituents surrounding the metal centers, which significantly improve their stability and activity.

Metal complexes with ligands containing fluorous tags exhibit special features like the possibility of using fluorous biphase catalysis or a recovery of the catalyst from the reaction mixture by means of fluorous solid phase extraction [15]. Surprisingly little is known about imidazolium salts bearing polyfluorinated chains. We recently published the synthesis of polyfluoroalkylated imidazolium salt substituted with branched fluorous polyether tails, which combined excellent fluorophilicity and ionic liquid properties [16]. In 2000, Xu et al. reported imidazolium salt **1** with linear fluorous chains and preparation of palladium NHC complex thereof [17]. Another fluorous imidazolium salt **2** was reported in 2001 and employed as an intermediate for a light fluorous Grubbs catalyst analogue [18] (Fig. 1).

In both cases, a perfluorohexyl chain with ethylene spacer was used and no discussion regarding the role of polyfluorinated ponytail was included. Several another imidazolium salts bearing one polyfluoroalkyl and one alkyl ponytail have been synthesized and employed, e.g. as ionic liquid/fluorocarbon emulsifiers [19]. In the last few years we oriented our research on the study of fluorous ligands [20–23]. This inevitably resulted in our aim in fluorous NHC ligands and the role of the length of the perfluorinated part of

* Corresponding author.
E-mail address: kvicalaj@vscht.cz (J. Kvíčala).

0022-1139/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2009.07.015

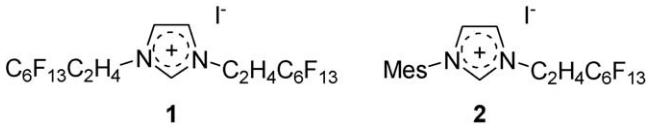


Fig. 1. Examples of published fluorous imidazolium salts.

the ponytails. We were also interested in the complexation properties–electron density relationship depending essentially on the length of the non-fluorinated spacer. As the first part of our research results we report here the synthesis of the key precursors of two classes of target fluorous NHC ligands, 1,3-bis(polyfluoroalkyl)- and 1-mesityl-3-(polyfluoroalkyl)imidazolium salts, together with preliminary results dealing with the preparation of fluorous PEPPSI™ catalyst and its applications in model Heck and Suzuki reactions.

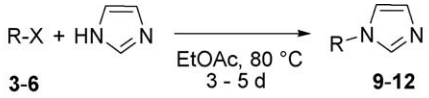
2. Results and discussion

2.1. 1-(Polyfluoroalkyl)imidazoles 9–12

The preparation of polyfluoroalkylated imidazoles was based on the reaction of imidazole with polyfluoroalkyl halide or triflate. In order to neutralize the acid formed, excess of imidazole was used. For imidazoles containing fluorous ponytail with the ethylene spacer, commercially available 2-(perfluoroalkyl)ethyl iodides **5**,**6** were used. Thus, (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazole **11** was obtained according to [17] and (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)imidazole **12** was prepared analogously, both in good yields (Scheme 1). However, polyfluoroalkyl iodides with methylene spacer are not commercially available and, moreover, their reactivity is significantly lower [24]. We hence employed instead of the iodides the corresponding polyfluoroalkyl triflates, 2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl triflate (**3**) and 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl triflate (**4**), prepared from commercially available polyfluorinated alcohols and trifluoromethanesulfonic anhydride according to [25,26] and obtained the corresponding 1-polyfluoroalkylated imidazoles **9** and **10** in excellent yields (Scheme 1).

2.2. 1,3-Bis(polyfluoroalkyl)imidazolium salts 13–22

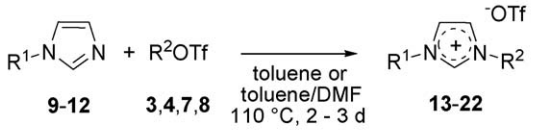
While the first alkylation proceeds smoothly at 80 °C, the second alkylation giving imidazolium salts requires reflux in toluene. Whereas we were able to reproduce [17] the reaction of fluoroimidazole **11** with 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl iodide (**5**) in an acceptable 45% yield, we were surprised that the same reaction using longer 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl iodide (**6**) as the alkylating reagent failed



Educt	Product	R	X	Yield (%)
3	**9**	$C_6F_{13}CH_2$	OTf	98.7
4	**10**	$C_8F_{17}CH_2$	OTf	96.8
5	**11**	$C_6F_{13}C_2H_4$	I	50.0[a]
6	**12**	$C_8F_{17}C_2H_4$	I	66.9

[a] [17]

Scheme 1.



Educts	Product	R^1	R^2	Yield (%)
9 **3**	**13**	$C_6F_{13}CH_2$	$C_6F_{13}CH_2$	44
9 **7**	**14**	$C_6F_{13}CH_2$	$C_6F_{13}CH_2CH_2$	87
9 **8**	**15**	$C_6F_{13}CH_2$	$C_8F_{17}CH_2CH_2$	93
10 **3**	**16**	$C_8F_{17}CH_2$	$C_6F_{13}CH_2$	74
10 **4**	**17**	$C_8F_{17}CH_2$	$C_8F_{17}CH_2$	46
10 **7**	**18**	$C_8F_{17}CH_2$	$C_6F_{13}CH_2CH_2$	65
10 **8**	**19**	$C_8F_{17}CH_2$	$C_8F_{17}CH_2CH_2$	58
11 **7**	**20**	$C_6F_{13}CH_2CH_2$	$C_6F_{13}CH_2CH_2$	90
11 **8**	**21**	$C_6F_{13}CH_2CH_2$	$C_8F_{17}CH_2CH_2$	98
12 **8**	**22**	$C_8F_{17}CH_2CH_2$	$C_8F_{17}CH_2CH_2$	90

Scheme 2.

completely. We therefore used the corresponding triflate, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl triflate (**8**), prepared from commercially available fluoroalcohol according to the procedure developed by us [27]. The second methylene spacer containing fluorous ponytails was attached similarly using the above mentioned triflates **3** and **4**. As a solvent, toluene was used in all cases except of the reactions of fluoroalkylated imidazole **10**, the solubility of which was not sufficient and hence a toluene/DMF mixture had to be used. The target 1,3-disubstituted imidazolium salts **13**–**22** were obtained in moderate to excellent yields (Scheme 2).

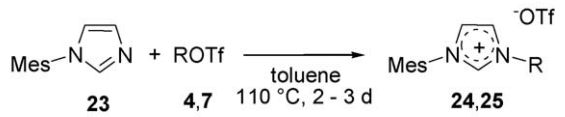
Melting point measurements of imidazolium salts **13**–**22** revealed two distinguished features: first, imidazolium salts **13**, **16**, **17** bearing only methylene spacers displayed significantly higher stability (they melt above 230 °C without decomposition compared to those with ethylene spacers which decompose above 150 °C); second, more symmetrical imidazolium salts **13**, **17** melted at slightly higher temperatures (245 °C and 251 °C, respectively) compared to non-symmetrical salt **16** (231 °C).

2.3. 1-Mesityl-3-(polyfluoroalkyl)imidazolium salts 24, 25

The title imidazolium salts bearing one mesityl and one polyfluoroalkyl substituent should display properties between the well-known 1,3-dimesitylimidazolium salts [28] and 1,3-bis(polyfluoroalkyl)imidazolium salts synthesized by us. Their synthesis paralleling published preparation [18] employed 1-mesitylimidazole (**23**) [29] and fluoroalkyl triflates **4** and **7**. The target unsymmetrical imidazolium salts **24**, **25** were obtained in good to excellent yields (Scheme 3).

2.4. Fluorophilicity measurements

We recently reported the synthesis and properties of imidazolium salts substituted with two polyfluorinated chains, at least one of which being based on perfluorinated polyethers [30]. We found that these salts behave as fluorous ionic liquids with excellent solubility in perfluorinated solvents and high fluorophilicities [31]. In contrast to this, bis(polyfluoroalkylated)imidazolium salts **13**–**25** showed rather limited solubility in perfluorinated solvents and, correspondingly, significantly lower values of



Educt	Product	R	Yield (%)
4	**24**	$C_8F_{17}CH_2$	85
7	**25**	$C_6F_{13}CH_2CH_2$	96

Scheme 3.

fluorous partition coefficients between perfluoro(methylcyclohexane) and toluene (Table 1).

Nevertheless, compared to mono(polyfluoroalkylated)imidazolium salts **24**, **25**, bis(polyfluoroalkylated)imidazolium salts can be regarded as fluorophilic, i.e. having fluorous partition coefficients larger than 1 and positive fluorophilicities. The length of perfluorinated segments and the number of CH_2-spacers in sidechains (**14**: 26 F and 3 CH_2; **17**: 34 F and 2 CH_2; **19**: 34 F and 3 CH_2) does not reflect the expected trend of fluorophilicity (i.e. **17**–**19** > **14**) probably due to experimental difficulties in the precise determination of partition coefficients of fluorous compounds which have rather low absolute solubility in the immiscible liquid phases.

Remarkable difference between the fluorophilicity of imidazolium salts containing perfluoroalkyl chains and those bearing perfluoropolyether segments can be attributed to relative rigidness of the perfluoroalkyl group compared to more flexible perfluoropolyether chain. Following that, central ionic part of fluorous imidazolium salts **13**–**25** containing only perfluoroalkylated segments remains exposed and hence highly fluorophobic in contrast to salts containing perfluoropolyether chain, which can probably shield the charged part of imidazolium salt from perfluorinated solvent.

2.5. Calculations of model polyfluorinated imidazolium salts

With the aim to find out how the electron density on the imidazolium ring can be influenced by substitution with polyfluoroalkyl groups we chose three model imidazolium salts, viz. 1,3-dimethylimidazolium triflate (**A**), 1,3-bis(2,2,3,3,3-pentafluoropropyl)imidazolium triflate (**B**) and 1,3-bis(3,3,4,4,4-pentafluorobutyl)imidazolium triflate (**C**) (Fig. 1). Comparison of mapped electrostatic potentials on the isoelectronic surfaces of these molecules clearly shows higher positive charge (cyan colour compared to green colour) on the site of the attack of base – hydrogen on ring C2 – for pentafluoroethylated systems **B** and **C**. On the other hand, the difference in the acidity of this hydrogen between molecules **B** and **C** differing in the non-fluorinated spacer length (methylene for **B** and ethylene for **C**) is less apparent.

Table 1
Fluorous partition coefficients of selected imidazolium salts in perfluoro(methylcyclohexane)/toluene mixture at 25 °C and their fluorophilicities.

Entry	Compound	P_i(FBS)	f_i
1	**25**	0.02	−4
2	**24**	0.4	−0.9
3	**17**	1.3	0.26
4	**19**	1.4	0.34
5	**14**	2.6	0.96

All calculations were performed with Gaussian 03W program suite [32] using DFT methods at the PBE1PBE/6-311+G(d,p) level of theory.

2.6. Fluorous PEPPSI^{TM} analogue 26

We prepared fluorous NHC ligand-based complex **26** by heating polyfluorinated imidazolium salt **1** with $PdCl_2$ and K_2CO_3 in an excess of 3-chloropyridine in analogy to the original PEPPSI^{TM} catalyst [33]. The product was isolated as an orange powder in a moderate yield after evaporation of 3-chloropyridine and precipitation of the crude product from dichloromethane solution with pentane (Scheme 4). Surprisingly, elemental analysis of the crystalline product **26** revealed that the product contains both chloride and iodide anions coordinated to the central palladium atom in a non-stoichiometric molar ratio of ca. 3:1.

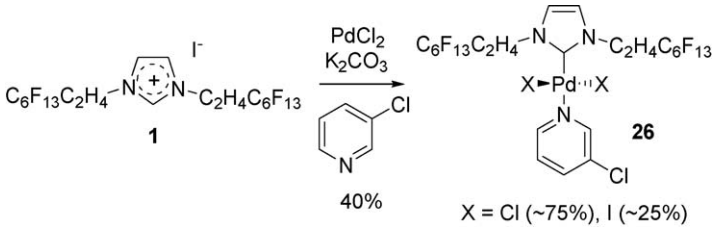
Orange crystals for X-ray diffraction were obtained by recrystallization from hexane/CH_2Cl_2 5:1 mixture. X-ray diffraction analysis confirmed the coordination of fluorous NHC carbene to the central palladium atom, as well as the non-stoichiometric content of chloride and iodide anions in the complex molecule (Fig. 2) [34].

In complex **26**, Pd–halogen bonds are oriented nearly perpendicularly to the imidazolylidene ring, whereas 3-chloropyridine ring approximately bisects the dihedral angle between both planes. The polyfluoroalkylated ponytails are arranged on the opposite sides of the imidazolylidene ring in agreement with the results of the computational studies (vide supra).

2.7. Model reactions of fluorous PEPPSI^{TM} analogue 26

PEPPSI^{TM} catalyst was successfully employed in many reactions catalyzed with transition metals, e.g. Negishi, Kumada or Suzuki–Miyaura coupling, yielding the corresponding products in excellent yields [36]. To compare the activity and recyclability of the complex **26** with the original PEPPSI^{TM} we performed two model reactions, i.e. Suzuki–Miyaura coupling of phenylboronic acid with 4-iodotoluene, and Heck reaction of 4-iodotoluene with oct-1-ene (Scheme 5).

Although fluorous catalyst **26** was active in both reactions, the yields of the corresponding reactions were moderate and inferior to that of the original PEPPSI^{TM} catalyst. We were not able to



Scheme 4.

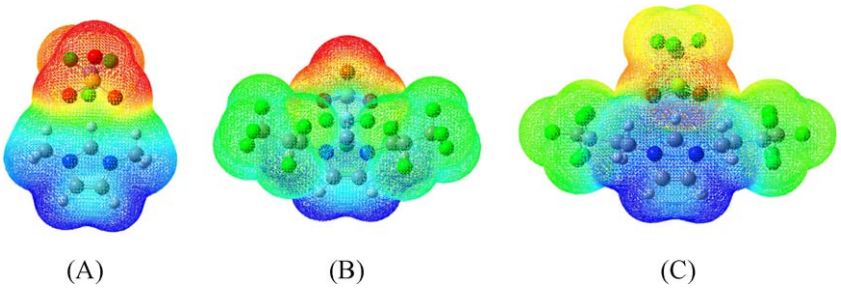


Fig. 2. Electrostatic potential mapped on isoelectronic surface for model imidazolium salts (red, negative charge; blue, positive charge).

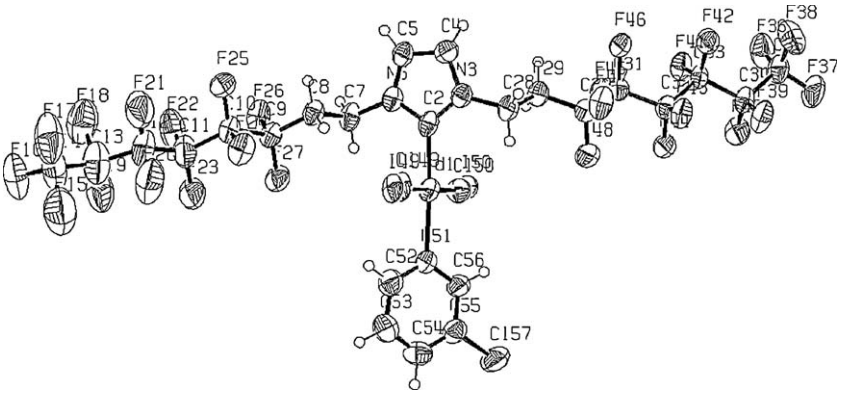
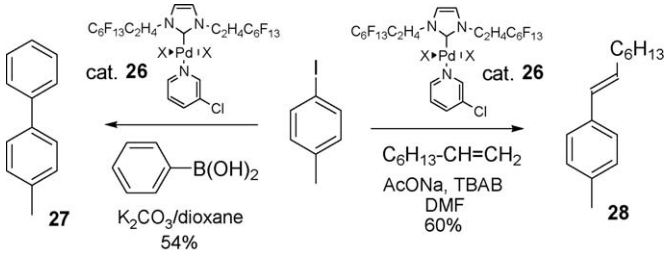


Fig. 3. ORTEP [35] plot (50% probability) of complex **26**.



Scheme 5.

recycle the catalyst using fluorous separation methods. However, this is not surprising as both complex **26** and the PEPPSI™ catalyst contain 3-chloropyridine as a throwaway ligand. Consequently, no information about possible recycle of this type of catalysts is available.

2.8. Pilot preparations of other complexes of fluorous NHC ligands

In recent preliminary experiments, we also synthesized a series of Ag and Cu complexes based on fluorous NHC ligands **13**–**22**, **24** and **25**, and confirmed their structure by NMR and MS experiments (Fig. 3). These results will be published in the following paper as soon as good quality crystals for X-ray analysis will be obtained (Fig. 4).

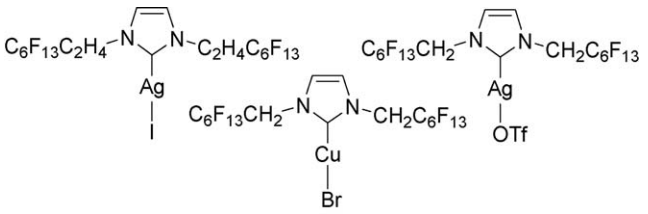


Fig. 4. Examples of fluorous NHC complexes recently synthesized in our laboratory.

3. Conclusions

We synthesized a series of fluorous imidazolium salts as the key intermediates for fluorous NHC ligands. Whereas shorter fluorinated ponytails with ethylene spacer could be attached to the central imidazole ring using commercial 2-(perfluoralkyl)ethyl iodides, polyfluoroalkyl triflates had to employed in other cases, i.e. when longer perfluorinated chain and/or methylene spacer were present. Based on bis(polyfluoroalkylated)imidazolium salt, fluorous analogue of PEPPSI™ catalyst was synthesized. Its catalytic activity in model Suzuki–Miyaura coupling and Heck reaction proved to be lower than that of the original PEPPSI™. Fluorophilicity of bis(polyfluoroalkylated)imidazolium salts was found to be substantially lower than that of the corresponding imidazolium salts containing polyfluoropolyether ponytails.

4. Experimental

Temperature data were uncorrected. NMR spectra were recorded with a Varian MercuryPlus spectrometer, ^{1}H NMR spectra at 299.97 MHz and ^{13}C NMR spectra at 75.43 MHz using residual deuterated solvent signals as the internal standards, ^{19}F NMR spectra at 282.22 MHz using CCl_3F as the internal standard. Chemical shifts are given in ppm, coupling constants in Hz. FTIR spectra were recorded with an FTIR Nicolet 6700 instrument. 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 argon atmosphere in an oven-dried apparatuses. Fluorous separations were accomplished using FluoroFlash® silica gel (40 μm grading, Fluorous Technologies, Inc.).

2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoroheptyl triflate (**3**), 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl triflate (**4**), 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl triflate (**7**) and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl triflate (**8**) were

prepared from commercially available alcohols and trifluoromethanesulfonic anhydride (triflic anhydride), all purchased from Apollo Scientific, following published procedures [25–27]. 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)imidazole (**11**) and 1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium iodide (**1**) were prepared according to [17], 1-mesitylimidazole (**23**) according to [29]. 1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-8-iodooctane (**5**) and 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iododecane (**6**) were kindly donated by Atochem. Imidazole was purchased from Fluka. Ethyl acetate and DMF were distilled from P_2O_5, toluene was stored over Na and distilled prior to use.

4.1. Preparation of polyfluorinated imidazoles—General procedure

Polyfluorinated triflate or iodide and imidazole were dissolved in dry EtOAc. Reaction was heated for specified time. After cooling to room temperature, organic phase was washed with water and combined water layers were extracted with EtOAc. Combined organic phases were dried with anhydrous magnesium sulfate, solvents were removed by rotary vacuum evaporator and crude product either recrystallized from hexane/EtOAc 20:1 mixture or purified by fluorous solid phase extraction (fluorophobic wash with MeOH/H_2O 4:1, fluorous wash with MeOH).

4.2. 1-(2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoroheptyl)imidazole (9)

A reaction mixture containing triflate **3** (1.00 g, 2 mmol, 1 equiv.) and imidazole (0.420 g, 6 mmol, 3 equiv.) in 30 ml of EtOAc was stirred for 3 d at 80 °C. After extraction (2× 30 ml of water, 10 ml of EtOAc) and recrystallization, 0.79 g of product **9** (98.7%, white crystals, m.p. 88.6–90.9 °C) was obtained. ^{1}H NMR ($CDCl_3$): δ 4.56 (t, 2H, $^3J_{HF}$ = 15.0 Hz), 6.96 (s, 1H), 7.10 (s, 1H), 7.51 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 46.5 (t, $^2J_{CF}$ = 24 Hz), 105–120 (m), 120.2; 130.0; 138.5. ^{19}F NMR ($CDCl_3$): δ −81.2 (bs, 3F), −117.8 (bs, 2F), −122.0 (bs, 2F), −123.0 (bs, 2F), −123.4 (bs, 2F), −126.4 (bs, 2F). MS (ESI), *m*/*z* (%): $[M+H]^+$ 401 (100). HRMS (ESI), calcd for $C_{10}H_6N_2F_{13}$ $[M+H]^+$, 401.0318; found 401.0318. IR (neat) ν 3129 (w), 3098 (w), 1517 (m), 1237 (s), 1211 (s), 1192 (s), 1151 (s).

4.3. 1-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl)imidazole (10)

A reaction mixture containing triflate **4** (3.00 g, 5.10 mmol, 1.0 equiv.) and imidazole (1.07 g, 15.3 mmol, 3 equiv.) in 100 ml of EtOAc was stirred for 3 d at 80 °C. After extraction (3× 30 ml of water, 20 ml of EtOAc) and recrystallization, 2.47 g of product **10** (96.8%, light brown crystals, m.p. 97.6–99.1 °C) was obtained. ^{1}H NMR ($CDCl_3$): δ 4.57 (t, 2H, $^3J_{HF}$ = 15.0 Hz), 7.01 (s, 1H), 7.15 (s, 1H), 7.56 (s 1H). ^{13}C NMR ($CDCl_3$): δ 45.7 (t, $^2J_{CF}$ = 23 Hz), 110–122 (m), 115.4, 125.7, 129.6. ^{19}F NMR ($CDCl_3$): δ −81.2 (t, 3F, $^3J_{FF}$ = 9 Hz), −118.0 (bs, 2F), −122.3 (bs, 6F), −123.4 (bs, 4F), −126.6 (bs, 2F). MS (ESI), *m*/*z* (%): $[M+H]^+$ 501 (100). HRMS (ESI), calcd for $C_{12}H_6F_{17}N_2$ $[M+H]^+$, 501.0254; found 501.0254. IR (neat) ν 3128 (w), 3099 (w), 1517 (m), 1229 (s), 1179 (s), 1160 (s).

4.4. 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)imidazole (12)

A reaction mixture containing 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iododecane (**6**, 500 mg, 0.871 mmol, 1.0 equiv.) and imidazole (148 mg, 2.18 mmol, 2.5 equiv.) in 40 ml of EtOAc was stirred for 5 d at 80 °C. After extraction (2× 30 ml of water, 20 ml of EtOAc) and purification by fluorous solid phase extraction, 300 mg of product **12** (66.9%, light brown crystals, m.p. 107.6–109.2 °C) was obtained. ^{1}H NMR ($CDCl_3$): δ 2.59 (m, 2H), 4.30 (t, 2H, $^3J_{HH}$ = 7.0 Hz), 6.94 (s, 1H), 7.10 (s, 1H), 7.53 (s 1H). ^{13}C NMR ($CDCl_3$): δ 33.0 (t, $^2J_{CF}$ = 22 Hz), 38.9, 104–119 (m), 118.5, 130.4, 137.1. ^{19}F NMR ($CDCl_3$): δ −80.9 (t, 3F, $^3J_{FF}$ = 10 Hz), −114.4 (bs, 2F), −121.8 (bs, 2F), −122.1 (bs, 4F), −122.9 (bs, 2F), −123.6 (bs, 2F), −126.3 (bs, 2F). MS (ESI), *m*/*z* (%): $[M+H]^+$ 515 (100). HRMS (ESI), calcd for $C_{13}H_7F_{17}N_2$ $[M+H]^+$, 515.0411; found 515.0409. IR (neat) ν 3199 (w), 3103 (w), 1513 (m), 1216 (s), 1195 (s), 1175 (s), 1199 (s).

4.5. Preparation of imidazolium salts—General procedure A

Polyfluoroalkylated imidazole and polyfluoroalkyl triflate were mixed in a Schlenk flask. Toluene was added and the mixture was stirred for specified time at 100 °C. After evaporating toluene on rotary vacuum evaporator (40 °C/2 h/2 kPa), the crude product was dissolved in a small amount of EtOAc and precipitated with 10-fold excess of hexane. Obtained crystals were decanted and washed with hexane. Traces of solvents were removed from the product by vacuum (r.t./2 h/100 Pa).

4.6. Preparation of imidazolium salts—General procedure B

Polyfluoroalkylated imidazole and polyfluoroalkyl triflate were mixed in a Schlenk flask. Toluene and DMF were added and the mixture was stirred for specified time at 100 °C. After evaporating bulk of solvents on a rotary vacuum evaporator (60 °C/2 h/2 kPa), a methanol/water mixture was added and the precipitate formed was filtered off. The crude product was dissolved in a small amount of EtOAc and precipitated with 10-fold excess of hexane. Obtained crystals were decanted and washed with hexane. Traces of solvents were removed from the product by vacuum (r.t./2 h/100 Pa).

4.7. 1,3-Bis(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)imidazolium triflate (13)

A mixture of fluoroimidazole **9** (2.80 g, 6.9 mmol, 1.0 equiv.) and triflate **3** (3.71 g, 7.7 mmol, 1.1 equiv.) in 100 ml of toluene was stirred for 72 h at 100 °C. Following the General procedure A (40 ml of EtOAc, 150 ml of hexane, washed with 20 ml of hexane) 2.76 g of product **13** (44.7%, grey powder, m.p. 244.5–246.1 °C) was obtained. ^{1}H NMR (aceton-d_6): δ 5.77 (t, 4H, $^3J_{HF}$ = 15.0 Hz), 8.25 (s, 2H), 9.85 (s, 1H). ^{13}C NMR (aceton-d_6): δ 49.6 (t, $^2J_{CF}$ = 22 Hz), 110–120 (m); 126.4, 142.1. ^{19}F NMR (aceton-d_6): δ −77.9 (s, 3F), −80.5 (bs, 6F), −116.5 (bs, 4F), −121.2 (bs, 4F), −122.1 (bs, 8F), −125.5 (bs, 4F). MS (ESI), *m*/*z* (%): 733 $[M-TfO^-]^+$ (100), 149 $[TfO]^-$ (100). HRMS (ESI), calcd for $C_{17}H_7F_{26}N_2$ $[M-TfO^-]^+$, 733.0189; found 733.0193. IR (neat) ν 3158 (w), 3043 (w), 3012 (w), 1576 (w), 1243 (s), 1214 (s), 1149 (s).

4.8. 1-(2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoroheptyl)-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium triflate (14)

A mixture of fluoroimidazole **9** (700 mg, 1.75 mmol, 1.0 equiv.) and triflate **7** (868 mg, 1.75 mmol, 1.0 equiv.) in 20 ml of toluene was stirred for 72 h at 100 °C. Following the General procedure A (3 ml of EtOAc, 30 ml of hexane, washed with 10 ml of hexane) 1.36 g of product **14** (86.7%, brown powder, 150 °C dec) was obtained. ^{1}H NMR (acetone-d_6): δ 3.22 (m, 2H), 5.00 (t, 2H, $^3J_{HH}$ = 7.1 Hz), 5.63 (t, 2H, $^3J_{HF}$ = 15.8 Hz), 8.09 (s, 1H), 8.18 (s, 1H), 9.66 (s, 1H). ^{13}C NMR (acetone-d_6): δ 31.9 (t, $^2J_{CF}$ = 20 Hz), 43.8, 49.1 (t, $^2J_{CF}$ = 26 Hz), 115–120 (m); 124.7; 126.0; 140.7. ^{19}F NMR (acetone-d_6): δ −78.0 (s, 3F), −80.6 (bs, 6F), −113.2 (bs, 2F), −116.5 (bs, 2F), −121.4 (bs, 4F), −122.2 (bs, 6F), −123.0 (bs, 2F), −125.7 (bs, 4F). MS (ESI), *m*/*z* (%): 747 $[M-TfO^-]^+$ (100), 149 $[TfO]^-$ (100). HRMS (ESI), calcd for $C_{18}H_9F_{26}N_2$ $[M-TfO^-]^+$, 747.0345; found 747.0350. IR (neat) ν 3154 (w), 3122 (w), 3070 (w), 1569 (w), 1240 (s), 1214 (s), 1150 (s).

*4.9. 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)imidazolium triflate (**15**)*

A mixture of fluoroimidazole **9** (230 mg, 0.57 mmol, 1.0 equiv.) and triflate **8** (350 mg, 0.57 mmol, 1.0 equiv.) in 20 ml of toluene was stirred for 72 h at 100 °C. Following the General procedure A (3 ml of EtOAc, 30 ml of hexane, washed with 10 ml of hexane) 531 mg of product **15** (92.7%, brown powder, 150 °C dec) was obtained. ^{1}H NMR (acetone-d_6): δ 3.21 (m, 2H), 5.00 (t, 2H, $^3J_{HH}$ = 7.1 Hz), 5.63 (t, 2H, $^3J_{HF}$ = 15.8 Hz), 8.09 (s, 1H), 8.19 (s, 1H), 9.65 (s, 1H). ^{13}C NMR (acetone-d_6): δ 32.4 (t, $^2J_{CF}$ = 20 Hz), 44.3, 49.7 (t, $^2J_{CF}$ = 23 Hz), 114–120 (m), 125.5, 126.6, 141.1. ^{19}F NMR (acetone-d_6): δ −78.1 (s, 3F), −80.6 (bs, 6F), −113.2 (bs, 2F), −116.5 (bs, 2F), −121.4 (bs, 8F), −122.2 (bs, 6F), −123.0 (bs, 2F), −125.6 (bs, 4F). MS (ESI), *m*/*z* (%): 847 [M−TfO$^-$]$^+$ (100), 149 [TfO]$^-$ (100). HRMS (ESI), calcd for $C_{20}H_9F_{30}N_2$ [M−TfO]$^+$, 847.0281; found 847.0286. IR (neat) ν 3154 (w), 3122 (w), 3070 (w), 1569 (w), 1243 (m), 1194 (s), 1179 (s), 1145 (s).

*4.10. 1-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl)-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)imidazolium triflate (**16**)*

A mixture of fluoroimidazole **10** (324 mg, 0.65 mmol, 1.0 equiv.) and triflate **3** (310 mg, 0.65 mmol, 1.0 equiv.) in 10 ml of toluene and 1 ml of DMF was stirred for 48 h at 100 °C. Following the General procedure B (8 ml of methanol with 2 ml of water, followed by 2 ml of EtOAc, 20 ml of hexane, washed with 5 ml of hexane) 468 mg of product **16** (73.6%, white powder, m.p. 229.5–232.3) was obtained. ^{1}H NMR (acetone-d_6): δ 5.71 (t, 4H, $^3J_{H-F}$ = 15.8 Hz), 8.21 (s, 2H), 9.81 (s, 1H). ^{13}C NMR (acetone-d_6): δ 50.1 (t, $^2J_{CF}$ = 22 Hz), 106–125 (m); 127.0, 142.9. ^{19}F NMR (acetone-d_6): δ −78.3 (s, 3F), −80.5 (bs, 6F), −116.5 (bs, 4F), −121.2 (bs, 8F), −122.2 (bs, 8F), −125.7 (bs, 4F). MS (ESI), *m*/*z* (%): 833 [M−TfO$^-$]$^+$ (100), 149 [TfO]$^-$ (100). HRMS (ESI), calcd for $C_{19}H_7F_{30}N_2$ [M−TfO]$^+$, 833.0125; found 833.0131. IR (neat) ν 3151 (w), 3127 (w), 3039 (w), 1574 (w), 1247 (s), 1197 (s), 1193 (s).

*4.11. 1,3-Bis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)imidazolium triflate (**17**)*

A mixture of fluoroimidazole **10** (300 mg, 0.60 mmol, 1.0 equiv.) and triflate **4** (350 mg, 0.60 mmol, 1.0 equiv.) in 10 ml of toluene and 1 ml of DMF was stirred for 48 h at 100 °C. Following the General procedure B (8 ml of methanol with 2 ml of water, followed by 2 ml of EtOAc, 20 ml of hexane, washed with 5 ml of hexane) 299 mg of product **17** (46.0%, white powder, m.p. 252.0–254.7 °C) was obtained. ^{1}H NMR (acetone-d_6): δ 5.72 (t, 4H, $^3J_{HF}$ = 14.4 Hz), 7.96 (s, 1H), 8.22 (s, 1H), 9.82 (s, 1H). ^{13}C NMR (acetone-d_6): δ 48.7 (t, $^3J_{CF}$ = 23 Hz), 110–120 (m), 125.6, 141.4. ^{19}F NMR (acetone-d_6): δ −78.1 (s, 3F), −80.5 (bs, 6F), −116.4 (bs, 4F), −121.2 (bs, 12F), −122.1 (bs, 8F), −125.6 (bs, 4F). MS (ESI), *m*/*z* (%): 933 [M−TfO$^-$]$^+$ (100), 149 [TfO]$^-$ (100). HRMS (ESI), calcd for $C_{21}H_7F_{34}N_2$ [M−TfO]$^+$, 933.0061; found 933.0067. IR (neat) ν 3135 (w), 3048 (w), 2986 (w), 1574 (w), 1231 (s), 1158 (s).

*4.12. 1-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl)-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium triflate (**18**)*

A mixture of fluoroimidazole **10** (300 mg, 0.60 mmol, 1.0 equiv.) and triflate **7** (298 mg, 0.60 mmol, 1.0 equiv.) in 10 ml of toluene and 1 ml of DMF was stirred for 48 h at 100 °C. Following the General procedure B (8 ml of methanol with 2 ml of water, followed by 2 ml of EtOAc, 20 ml of hexane, washed with 5 ml of hexane) 391 mg of product **18** (65.4%, white powder, 180 °C dec) was obtained. ^{1}H NMR (acetone-d_6): δ 3.19 (m, 2H), 4.97 (t, 2H, $^3J_{HH}$ = 7.0 Hz), 5.61 (t, 2H, $^3J_{HF}$ = 15.8 Hz), 8.05 (s, 1H), 8.17 (s, 1H), 9.64 (s, 1H). ^{13}C NMR (acetone-d_6): δ 30.9 (t, $^3J_{CF}$ = 21 Hz), 42.8, 48.2 (t, $^3J_{CF}$ = 21 Hz), 106–119 (m), 123.9, 125.0, 139.7. ^{19}F NMR (acetone-d_6): δ −78.2 (s, 3F), −80.6 (bs, 6F), −113.3 (bs, 2F), −116.5 (bs, 2F), −121.3 (bs, 8F), −122.1 (bs, 4F), −122.4 (bs, 2F), −123.0 (bs, 2F), −125.7 (bs, 4F). MS (ESI), *m*/*z* (%): 847 [M−TfO$^-$]$^+$ (100), 149 [TfO]$^-$ (100). HRMS (ESI), calcd for $C_{20}H_9F_{30}N_2$ [M−TfO]$^+$, 847.0281; found 847.0286. IR (neat) ν 3154 (w), 3122 (w), 3070 (w), 1571 (w), 1280 (s), 1224 (s), 1171 (s), 1154 (s).

*4.13. 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)-3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)imidazolium triflate (**19**)*

A mixture of fluoroimidazole **10** (300 mg, 0.60 mmol, 1.0 equiv.) and triflate **8** (358 mg, 0.60 mmol, 1.0 equiv.) in 10 ml of toluene and 1 ml of DMF was stirred for 48 h at 100 °C. Following the General procedure B (8 ml of methanol with 2 ml of water, followed by 2 ml of EtOAc, 20 ml of hexane, washed with 5 ml of hexane) 384 mg of product **19** (58.5%, white powder, 150 °C dec) was obtained. ^{1}H NMR (acetone-d_6): δ 3.19 (m, 2H), 4.97 (t, 2H, $^3J_{HH}$ = 7.0 Hz), 5.60 (t, 2H, $^3J_{HF}$ = 15.5 Hz), 8.05 (s, 1H), 8.16 (s, 1H), 9.63 (s, 1H). ^{13}C NMR (acetone-d_6): δ 32.5 (t, $^3J_{CF}$ = 21 Hz), 44.4, 49.7 (t, $^2J_{CF}$ = 23 Hz), 106–122 (m), 125.4, 126.7, 141.3. ^{19}F NMR (acetone-d_6): δ −78.2 (s, 3F), −80.7 (bs, 6F), −113.3 (bs, 2F), −116.5 (bs, 2F), −121.4 (bs, 12F), −122.2 (bs, 6F), −122.9 (bs, 2F), −125.7 (bs, 4F). MS (ESI), *m*/*z* (%): 947 [M−TfO$^-$]$^+$ (100), 149 [TfO]$^-$ (100). HRMS (ESI), calcd for $C_{22}H_9F_{34}N_2$ [M−TfO]$^+$, 947.0217; found 947.0224. IR (neat) ν 3154 (w), 3124 (w), 3069 (w), 1569 (w), 1263 (s), 1230 (s), 1155 (s).

*4.14. 1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium triflate (**20**)*

A mixture of fluoroimidazole **11** (576 mg, 1.18 mmol, 1.0 equiv.) and triflate **7** (490 mg, 1.18 mmol, 1.0 equiv.) in 20 ml of toluene was stirred for 48 h at 100 °C. Following the General procedure A (2 ml of EtOAc, 20 ml of hexane, washed with another 10 ml of hexane) 872 mg of product **20** (80.9%, light brown powder, 150 °C dec) was obtained. ^{1}H NMR (acetone-d_6): δ 3.11 (m, 4H), 4.85 (t, 4H, $^3J_{HH}$ = 7.0 Hz), 8.01 (s, 2H), 9.47 (s, 1H). ^{13}C NMR (acetone-d_6): δ 31.0 (t, $^2J_{CF}$ = 21 Hz), 42.2, 104–122 (m), 123.4, 138.1. ^{19}F NMR (acetone-d_6): δ −78.2 (s, 3F), −80.8 (t, 6F, $^4J_{FF}$ = 10 Hz), −113.4 (bs, 4F), −121.4 (bs, 4F), −122.4 (bs, 4F), −123.0 (bs, 4F), −125.8 (bs, 4F). MS (ESI), *m*/*z* (%): 761 [M−TfO$^-$]$^+$ (100), 149 [TfO]$^-$ (100). HRMS (ESI), calcd for $C_{19}H_{11}F_{26}N_2$ [M−TfO]$^+$, 761.0502; found 761.0504. IR (neat) ν 3149 (w), 3120 (w), 3070 (w), 1573 (m); 1347 (s), 1227 (s), 1178 (s), 1142 (s), 1124 (s).

*4.15. 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium triflate (**21**)*

A mixture of fluoroimidazole **11** (830 mg, 2.00 mmol, 1.0 equiv.) and triflate **8** (1.20 g, 2.00 mmol, 1.0 equiv.) in 30 ml of toluene was stirred for 48 h at 100 °C. Following the General procedure A (3 ml of EtOAc, 30 ml of hexane, washed with 10 ml of hexane) 1.98 g of product **21** (98.9%, grey powder, 170 °C dec) was obtained. ^{1}H NMR (acetone-d_6): δ 3.10 (m, 4H), 4.85 (t, 4H, $^3J_{HH}$ = 6.8 Hz), 8.00 (s, 2H), 9.46 (s, 1H). ^{13}C NMR (acetone-d_6): δ 32.9 (t, $^2J_{CF}$ = 20 Hz), 43.8, 107–126 (m), 125.0; 139.8. ^{19}F NMR (acetone-d_6): δ −79.7 (s, 3F), −82.5 (bs, 6F), −115.0 (bs, 4F), −122.8 (bs, 4F), −123.0 (bs, 4F), −124.0 (bs, 4F), −124.5 (bs, 4F), −127.5 (bs, 4F). MS (ESI), *m*/*z* (%): 861 [M−TfO$^-$]$^+$ (100), 149 [TfO]$^-$ (100). HRMS (ESI), calcd for $C_{21}H_{11}F_{30}N_2$ [M−TfO]$^+$, 861.0438; found 861.0443. IR (neat) ν 3153 (w), 3118 (w), 3070 (w), 1553 (w), 1248 (s), 1193 (s), 1176 (s), 1142 (s).

4.16. 1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)imidazolium triflate (22)

A mixture of fluoroimidazole **12** (100 mg, 0.2 mmol, 1.0 equiv.) and triflate **8** (120 mg, 0.2 mmol, 1.0 equiv.) in 10 ml of toluene was stirred for 30 h at 100 °C. Following the General procedure A (1 ml of EtOAc, 10 ml of hexane, washed with another 5 ml of hexane), 200 mg of product **22** (90.3%, grey powder, 150 °C dec) was obtained. ^{1}H NMR (acetone-d_6): δ 3.15 (m, 4H), 4.90 (t, 4H, $^3J_{HH}$ = 7.0 Hz), 8.02 (s, 2H), 9.51 (s, 1H). ^{13}C NMR (acetone-d_6): δ 32.7 (t, $^2J_{CF}$ = 20 Hz), 44.0, 108–122 (m), 125.1, 139.6. ^{19}F NMR (acetone-d_6): δ −78.0 (s, 3F), −80.6 (bs, 6F), −113.2 (bs, 4F), −121.0 (bs, 4F), −121.2 (bs, 8F), −122.1 (bs, 4F), −123.0 (bs, 4F), −125.9 (bs, 4F). MS (ESI), *m*/*z* (%): 961 $[M-TfO^-]^+$ (100), 149 $[TfO]^-$ (100). HRMS (ESI), calcd for $C_{23}H_{11}F_{34}N_2$ $[M-TfO^-]^+$, 961.0374; found 961.0377. IR (neat) ν 3154 (w), 3121 (w), 3073 (w), 1573 (w), 1251 (m), 1198 (s), 1178 (s), 1146 (s).

4.17. 1-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl)-3-mesitylimidazolium triflate (24)

A mixture of 1-mesitylimidazole (**23**, 345 mg, 1,85 mmol, 1.0 equiv.) and triflate **4** (1078 mg, 1.85 mmol, 1.0 equiv.) in 30 ml of dry toluene was stirred for 72 h at 100 °C. Following the General procedure A (7 ml of EtOAc, 30 ml of hexane, washed with 10 ml of hexane) 1.17 g of product **24** (81.8%, light pink crystals, m.p. 155.2–156.3) was obtained. ^{1}H NMR (acetone-d_6): δ 2.12 (s, 6H), 2.38 (s, 3H), 5.78 (t, 2H, $^3J_{HF}$ = 15.8 Hz), 7.18 (s, 2H), 8.11 (s, 1H), 8.38 (s, 1H), 9.70 (s, 1H). ^{13}C NMR (acetone-d_6): δ 16.5, 20.4, 48.6 (t, $^2J_{CF}$ = 23 Hz), 105–120 (m), 125.2, 125.7, 129.8, 131.2, 134.7, 140.1, 141.6. ^{19}F NMR (acetone-d_6): δ −77.9 (s, 3F), −80.5 (t, 3F, $^3J_{FF}$ = 10 Hz), −116.4 (bs, 2F), −121.1 (bs, 6F), −122.0 (bs, 4F), −125.6 (bs, 2F). MS (ESI), *m*/*z* (%): $[M-TfO^-]^+$ 619 (100); TfO^- 149 (100). HRMS (ESI), calcd for $C_{21}H_{16}F_{17}N_2$ $[M-TfO]^+$, 619.1037; found 619.1038. IR (neat) ν 3186 (w), 3118 (w), 3033 (w), 2986 (w), 1565 (w), 1554 (w), 1280 (s), 1296 (s), 1248 (s), 1214 (s), 1161 (s).

4.18. 1-Mesityl-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium triflate (25)

A mixture of 1-mesitylimidazole (**23**, 482 mg, 2.58 mmol, 1.0 equiv.) and triflate **7** (1.28 g, 2.58 mmol, 1.0 equiv.) in 30 ml of dry toluene was stirred for 72 h at 100 °C. 1.71 g of product **25** (96.8%, colorless oil) was obtained. ^{1}H NMR (acetone-d_6): δ 2.10 (s, 6H), 2.36 (s, 3H), 3.29 (m, 2H), 5.02 (t, 2H, $^3J_{HH}$ = 7.1 Hz), 7.15 (s, 2H), 7.93 (s, 1H), 8.31 (s, 1H), 9.48 (s, 1H) ^{13}C NMR (acetone-d_6): δ 16.6, 20.3, 31.0 (t, $^2J_{CF}$ = 21 Hz), 108–122 (m), 124.1, 124.6, 129.7, 131.5, 134.9, 138.3, 141.2 ^{19}F NMR (acetone-d_6): δ −77.9 (s, 3F), −80.5 (t, 3F, $^3J_{FF}$ = 10 Hz), −113.2 (bs, 2F), −121.3 (bs, 2F), −122.3 (bs, 2F), −122.9 (bs, 2F), −125.7 (bs, 2F). MS (ESI), *m*/*z* (%): 533 $[M-TfO^-]^+$ (100), 149 $[TfO]^-$ (100). HRMS (ESI), calcd for $C_{20}H_{18}F_{13}N_2$ $[M-TfO]^+$, 533.1257; found 533.1256. IR (neat) ν 3139 (w), 3101 (w), 1568 (w), 1553 (w), 1245 (s), 1225 (s), 1202 (s), 1162 (s), 1144 (s).

4.19. Measurements of fluorous partition coefficient—General procedure

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

4.20. Example of fluorous partition coefficient measurement: estimation of fluorophilicity of imidazolium salt 19

Using 10.05 mg of fluorous imidazolium salt **19**, 0.5 ml of toluene and 0.5 ml of perfluoro(methylcyclohexane) (PFMC), 0.13 mg and 0.09 mg of imidazolium salt **19** were obtained after equilibration from the 0.25 ml portions of the respective PFMC and toluene layers, which corresponds to P_i(FBS) = 1.4 and f_i = 0.34.

4.21. Dichloro[(1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-1,3-dihydroimidazol-2-ylidene](3-chloropyridine)palladium(II) (26)

In a Schlenk flask, 1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium iodide (**1**, 530 mg, 0.596 mmol, 1.1 equiv.), $PdCl_2$ (90 mg, 0.51 mmol, 1.0 equiv.) and K_2CO_3 (350 mg, 2.53 mmol, 5.0 equiv.) were mixed and 3-chloropyridine (2 ml) was added. The mixture was stirred for 48 h at 90 °C. After cooling to room temperature the reaction mixture was diluted with CH_2Cl_2 and passed through a short pad of silica covered with a pad of celite. CH_2Cl_2 was removed by rotary evaporator (30 °C/2 h/2 kPa) and 3-chloropyridine was removed by vacuum destilation (32 °C/400 Pa) for further reuse. After dissolving the solid in small amount of CH_2Cl_2 (0.5 ml), precipitation with pentane (5 ml), decanting and drying in vacuum (25 °C/12 h/100 Pa), 213 mg of complex **26** (39.9%, orange powder) was obtained. Crystals for X-ray diffraction were obtained by recrystallization (hexane/CH_2Cl_2 5:1). ^{1}H NMR ($CDCl_3$): δ 3.30 (m, 4H), 4.92 (m, 4H), 7.58 (s, 2H), 7.64 (m, 1H), 8.15 (m, 1H), 8.94 (m, 1H), 9.00 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 31.8 (t, $^2J_{CF}$ = 21 Hz), 43.8, 115–120 (m); 122.8; 125.0; 132.8; 138.1; 150.7; 151.8. ^{19}F NMR ($CDCl_3$): δ −80.5 (bs, 6F), −112.8 (bs, 4F), −121.2 (bs, 4F), −122.3 (bs, 4F), −122.8 (bs, 4F), −125.6 (bs, 4F). MS (ESI), *m*/*z* (%): 1166 $[C_{24}H_{14}Cl_2F_{26}IN_3NaPd]^-$ (100), 1072 $[C_{24}H_{14}Cl_3F_{26}N_3NaPd]^-$ (97).

4.22. Model Suzuki–Miyaura coupling catalyzed with complex 26

Phenylboronic acid (100 mg, 0.82 mmol, 1.2 equiv.) and 4-iodotoluene (149 mg, 0.68 mmol, 1.0 equiv.) were dissolved in dioxane (6 ml). K_2CO_3 (280 mg, 2.03 mmol, 3 equiv.) and complex **26** (15 mg, 10 μmol, 2%) were added and the reaction mixture was stirred at 80 °C overnight. After cooling to r.t. the reaction mixture was diluted with 15 ml of Et_2O and filtered through short pad of silica. After evaporating the solvents (40 °C/2 h/2 kPa), 4-methylbiphenyl (62 mg, 54%, white crystals) was isolated by column chromatography (eluent hexane/CH_2Cl_2 3:1), ^{1}H NMR spectrum of which was identical with the published values [37]

4.23. Model Heck reaction catalyzed with complex 26

4-Iodotoluene (300 mg, 1.37 mmol, 1.0 equiv.) and oct-1-ene (170 mg, 1.52 mmol, 1.1 equiv.) were dissolved in 15 ml of dry DMF. Complex **26** (28 mg, 0.03 mmol, 0.02 equiv.), *n*-Bu_4NBr (5 mg, 0.01 mmol, 0.01 equiv.) and AcONa (147 mg, 1.79 mmol, 1.3 equiv.) were added and the reaction mixture was heated to 120 °C for 48 h. After cooling to r.t., 50 ml of Et_2O was added and the organic layer was washed three times with 30 ml of water. After drying with anhydrous $MgSO_4$, filtration and evaporating the solvents (60 °C/2 h/1.5 kPa), 4-oct-1-enyltoluene (166 mg, 60%, colourless oil) was isolated by column chromatography (eluent hexane), ^{1}H NMR spectrum of which was identical with the published values [38].

Acknowledgements

We thank the Grant Agency of the Czech Republic (Grant No. 203/06/1511) and the Ministry of Education, Youth and Sports (Research Centre LC 06070, Research Projects Nos. 6046137301 and 6046137302) for financial support.

References

[1] T. Welton, Chem. Rev. 99 (1999) 2071–2083.
[2] J. Dupont, R.F. de Souza, P.A.Z. Suarez, Chem. Rev. 102 (2002) 3667–3692.
[3] P.J. Barnard, M.V. Baker, S.J. Berners-Price, D.A. Day, J. Inorg. Biochem. 98 (2004) 1642–1647.
[4] A. Casini, G. Mastrobuoni, M. Terenghi, C. Gabbiani, E. Monzani, G. Moneti, L. Casella, L. Messori, J. Biol. Inorg. Chem. 12 (2007) 1107–1117.
[5] C.D. Bedford, R.N. Harris III, R.A. Howd, D.A. Goff, G.A. Koolpe, M. Petesch, I. Koplovitz, W.E. Sultan, H.A. Musallam, J. Med. Chem. 32 (1989) 504–516.
[6] H. Miyachi, H. Kiyota, M. Segawa, Bioorg. Med. Chem. Lett. 9 (1999) 3003–3008.
[7] S. Ray, R. Mohan, J.K. Singh, M.K. Samantaray, M.M. Shaikh, D. Panda, P. Ghosh, J. Am. Chem. Soc. 129 (2007) 15042–15053.
[8] S.P. Nolan (Ed.), *N*-Heterocyclic Carbenes in Synthesis, Wiley–VCH, Weinheim, 2006.
[9] L. Cavallo, A. Correa, C. Costabile, H. Jacobsen, J. Organomet. Chem. 690 (2005) 5407–5413.
[10] A.C. Hiller, G.A. Grasa, M.S. Viciu, H.M. Lee, C. Yang, S.P. Nolan, J. Organomet. Chem. 653 (2002) 69–82.
[11] A.J. Arduengo, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361–363.
[12] R. Dorta, E.D. Stevens, N.M. Scott, C. Costabile, L. Cavallo, C.D. Hoff, S.P. Nolan, J. Am. Chem. Soc. 127 (2005) 2485–2495.
[13] A.R. Chianese, X. Li, M.C. Janzen, J.W. Faller, R.H. Crabtree, Organometallics 22 (2003) 1663–1667.
[14] C.J. O'Brien, E.A.B. Kantchev, G.A. Chass, N. Hadei, A.C. Hopkinson, M.G. Organ, D.H. Setiadi, T.-H. Tang, D.-C. Fang, Tetrahedron 61 (2005) 9723–9735.
[15] J.A. Gladysz, D.P. Curran, I.T. Horváth (Eds.), Handbook of Fluorous Chemistry, Wiley–VCH, Weinheim, 2004.
[16] O. Kysilka, M. Rybáčková, M. Skalický, M. Kvíčalová, J. Cvačka, J. Kvíčala, Collect. Czech. Chem. Commun. 73 (2008) 1799–1813.
[17] L. Xu, W. Chen, J.F. Bickley, A. Steiner, J. Xiao, J. Organomet. Chem. 598 (2000) 409–416.
[18] A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C.W. Lehmann, R. Mynott, F. Stelzer, O.R. Thiel, Chem. Eur. J. 7 (2001) 3236–3253.
[19] T.L. Merrigan, E.D. Bates, S.C. Dorman, J.H. Davies, Chem. Commun. (2000) 2051–2052.
[20] J. Kvíčala, T. Bříza, O. Paleta, J. Čermák, Collect. Czech. Chem. Commun. 67 (2002) 1345–1358.
[21] T. Bříza, J. Kvíčala, O. Paleta, J. Čermák, Tetrahedron 58 (2002) 3841–3846.
[22] J. Kvíčala, T. Bříza, O. Paleta, J. Čermák, Tetrahedron 58 (2002) 3847–3854.
[23] T. Bříza, J. Kvíčala, O. Paleta, Collect. Czech. Chem. Commun. 68 (2003) 1039–1045.
[24] T. Umemoto, Y. Gotoh, J. Fluorine Chem. 31 (1986) 231–236.
[25] D. Prescher, T. Thiele, R. Ruhmann, J. Fluorine Chem. 79 (1996) 145–148.
[26] J.L. Alvey, D. Rutherford, J.J. Juliette, J.A. Gladysz, J. Org. Chem. 63 (1998) 6302–6308.
[27] T. Bříza, J. Kvíčala, P. Mysík, O. Paleta, J. Čermák, Synlett (2001) 685–687.
[28] A.J. Arduengo, R. Krafczyk, R. Schmutzler, Tetrahedron 55 (1999) 14523–14534.
[29] M.G. Gardiner, W.A. Herrmann, C.P. Reisinger, J. Schwarz, M. Spiegler, J. Organomet. Chem. 572 (1999) 239–247.
[30] O. Kysilka, M. Rybáčková, M. Skalický, M. Kvíčalová, J. Cvačka, J. Kvíčala, J. Fluorine Chem. 130 (2009) 629–639.
[31] L.E. Kiss, I. Kövesdi, J. Rábai, J. Fluorine Chem. 108 (2001) 95–109.
[32] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision D.01, Gaussian, Inc., Wallingford, CT, 2004.
[33] C.J. O'Brien, E.A.B. Kantchev, C. Valente, N. Hadei, G.A. Chass, A. Lough, A.C. Hopkinson, M.G. Organ, Chem.-Eur. J. 12 (2006) 4743–4748.
[34] Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 734053 for Compound **26**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk, or URL: http://www.ccdc.cam.ac.uk).
[35] L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565.
[36] E.A.B. Kantchev, C.J. O'Brien, M.G. Organ, Aldrichim. Acta 39 (2006) 97–110.
[37] M.E. Mowery, P. DeShong, J. Org. Chem. 64 (1999) 3266–3270.
[38] Y. Fall, F. Berthiol, H. Doucet, M. Santelli, Synthesis (2007) 1683–1696.