CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Accepted Article

Title: Fluorinated Unsymmetrical N,N'-Diaryl Imidazolium salts - new functionalized NHC ligand precursors

Authors: Sergey N. Osipov, Maria A. Zotova, Salekh M. Masoud, Artur K. Mailyan, Ivan V. Ananyev, Sergey E. Nefedov, Andrey F. Asachenko, and Maxim A. Topchiy

To be cited as: *Chem. Eur. J.* 10.1002/chem.201700624

Link to VoR: http://dx.doi.org/10.1002/chem.201700624

Supported by
ACES

WILEY-VCH

10.1002/chem.201700624

WILEY-VCH

Fluorinated Unsymmetrical *N,N'*-Diaryl Imidazolium salts - new functionalized NHC ligand precursors

Maxim A. Topchiy[a], Maria A. Zotova[a], Salekh M. Masoud[a], Artur K. Mailyan[a,b], Ivan V. Ananyev[a], Sergey E. Nefedov[c], Andrey F. Asachenko[a] and Sergey N. Osipov*[a]

Abstract: An efficient and scaled-up synthesis of the imidazol-2-ylidene-based unsymmetrical NHC precursors bearing sterically demanding hexafluoroisopropylalkoxy-group [$(CF_3)_2$(OR)C-] in *ortho*-position of *N*-aryl substituent was developed. The key step of the method involved transformation of Mes-substituted oxazolinium tetrafluoroborate salt *via* the reaction with the corresponding binucleophilic fluoroalkyl substituted aniline. The subsequent post-modification of the resulting hydroxyl-containing salt *via* simple *one step O*-alkylation protocol provided access to a new family of unsymmetrical fluorinated NHC precursors. The latter were further successfully utilized for the preparation of several novel metal complexes. The molecular structures of some NHC precursors and their metal complexes have been unambiguously characterized by single-crystal X-ray diffraction. A preliminary evaluation of catalytic activity of palladium complexes was performed on Buchwald-Hartwig amination reaction. As a result, two PEPPSI-type Pd-complexes have demonstrated promising activity in alkane solvents.

Introduction

N-Heterocyclic carbenes (NHCs) are important auxiliary ligands in coordination and organometallic chemistry[1] due to the unique electronic properties, namely high σ-basicity and low π-acidity, that often induce enhanced activity in metal-catalyzed processes,[2] such as C-C and C-N coupling reactions and olefin metathesis. Imidazolium-derived NHCs with bulky *N,N'*-diaryl substituents such as 1,3-dimesityl-2H-imidazol-2-ylidene (IMes) and 1,3-bis(2,6-diisopropylphenyl)-2H-imidazol-2-ylidene (IPr) are the most widely employed ligands in homogeneous catalysis. They represent the ideal platform from which an optimization of their electronic, steric, and asymmetric properties can be anticipated. For instance, the outstanding results have been recently obtained upon formal replacement of the 2,6-diisopropylphenyl (Dipp) nitrogen substituents by bulkier, flexible aryl groups[3] or by C2-symmetrical chiral aryl groups.[4]

[a] M.A. Topchiy, Dr. M.A. Zotova, S.M. Masoud, Dr. A.K. Mailyan, Dr. I.V. Ananyev, Dr. A.F. Asachenko, Prof. Dr. S.N. Osipov
A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences
Vavilov str. 28, 119991, Moscow, Russia
E-mail: osipov@ineos.ac.ru
[b] Department of Chemistry and Biochemistry
University of California, Santa Barbara, California 93106-9510
[c] Prof. S.E. Nefedov
N. S. Kurnakov Institute of General and Inorganic Chemistry,
119991 Moscow, Leninskij pr. 31, Russia

Supporting information for this article is given via a link at the end of the document.

In this context, the importance of unsymmetrical N-heterocyclic carbenes (uNHCs) as ligands in metal catalysis is doubtless, as desymmetrization allows for further fine-tuning. The introduction of functionality, chelation, chirality, and shielding effects can influence the catalyst stability, reactivity, and selectivity, thus motivating the exploration of new tailor-made systems.[5] Surprisingly, while a plenty of unsymmetrical saturated NHCs (i.e. imidazolin-2-ylidenes) have been prepared, their unsaturated analogues (i.e. imidazol-2-ylidenes) are still essentially limited to unhindered N-substituent moieties, obviously, due to a lack of synthetic procedures to access imidazolium salts bearing two different sterically demanding groups on the N-atoms.[6] As a consequence, only few examples of the corresponding metal complexes have been described up to date (Fig. 1). Therefore, given the above considerations, convenient methodologies allowing practical synthesis of unsymmetrical *N,N'*-disubstituted imidazolium salts bearing hindered aryl groups remain highly desirable.

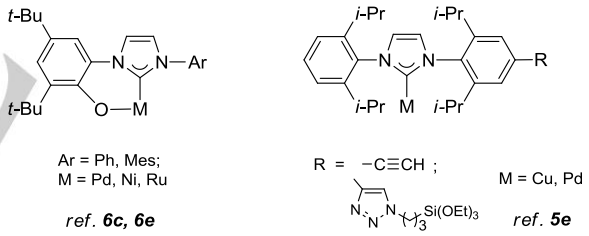


Figure 1. Unsymmetrically *N,N'*-diarylsubstituted imidazole-based NHC metal complexes.

On the other hand, fluorinated compounds have found widespread applications in the pharmaceutical[7] and medicinal chemistry[8] or crops[9] and material sciences.[10] Particular attention is focused on CF_3-containing compounds due to the unique properties of CF_3-group (*e.g.* high electronegativity, steric hindrance, hydrophobic character), which can dramatically alter the key physicochemical characteristics such as acidity/basicity of neighbouring groups, H-bonding ability, electron density distribution, or conformations to result in more desired properties, *e.g.* such as increased lipophilicity or chemical stability.[11]

In the field of metal catalysis, the steric and electronic impact of NHCs bearing *N*-fluoroaryl and *N*-fluoroalkyl groups on catalytic properties of the corresponding complexes has been studied mainly in metathesis and cross-coupling reactions.[12] Along with notable catalytic activity the main advantages were connected with remarkable stability and enhanced solubility in common solvents including supercritical CO_2[13] as well as the possibility

to utilize heavy fluorous separation techniques in the case of highly fluorinated *N*-alkyl chains.[14] One more advantage, found by Grubbs and co-workers, is a rate acceleration in RCM of diethyl diallylmalonate arising from a Ru···F interaction between one ring of a *N,N'*-bis(2,6-difluorophenyl)imidazol-2-ylidene and the metal center in the Grubbs II catalyst analogue.[15] This work has been further extended with studies of synthesis and catalytic activities of closely related saturated unsymmetrical analogues.[16]

To the best of our knowledge there are no examples of unsymmetrical *N,N'*-diaryl imidazole-based NHC ligands bearing fluorinated functional groups on one of the *N*-aryl moiety in the literature. Thus, taking into account all above reasons, the development of new effective methods for the preparation of such ligands, in particular sterically demanding ones, is of current interest.

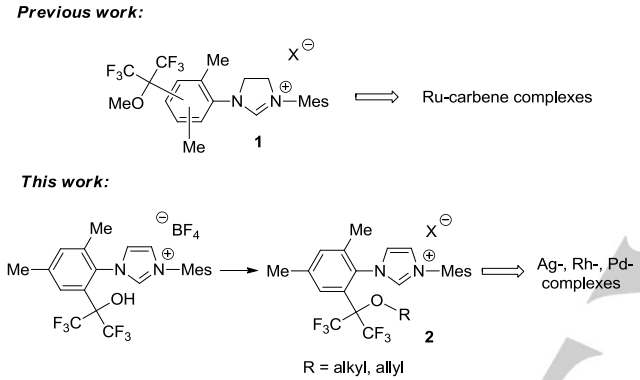
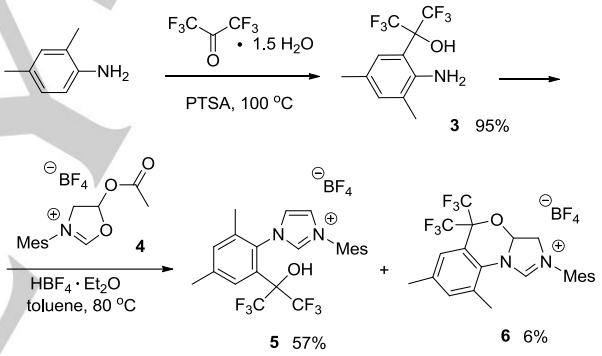


Figure 2. Synthesis of unsymmetrical CF_3-NHC metal complexes.

We have recently elaborated an access to unsymmetrical 1,3-bis(aryl)-4,5-dihydroimidazolium salts bearing the hexafluoroisopropylmethoxy group of *N*-aryl moiety (**1**, Fig. 2) and have demonstrated their further potential to be used as the precursors of the corresponding NHC ligands for the synthesis of new family of metathesis catalysts.[17] Now we wish to report on an efficient route to sterically demanding unsymmetrical 1,3-bis(aryl)-imidazolium salts comprising hexafluoroisopropylalkoxy-group [$(CF_3)_2$(OR)C-] in *ortho*-position of *N*-aryl substituent (**2**, Fig. 2) as well as their application for the preparation of new metal complexes. The combination of two bulky lipophilic CF_3-groups with anionic alkoxy group could generate a chelating ligand able to give rise to complexes with increased stability, steric rigidity and enhanced solubility in common organic solvents (or monomers).[18] In addition, the free OH-group would provide unique possibility for further functionalization of fluorinated NHC precursors opening the door to a new way to tune these ligands and subsequently reactivity of NHC-metal complexes. Here we also disclose the initial testing on catalytic activity of some Pd-complexes.

Results and Discussion

An access to unequally 1,3-diaryl-substituted NHCs is still limited to trivial substitution patterns. In fact, the preparation of their corresponding imidazolium salt precursors *via* quarternization of *N*-aryl substituted imidazoles are mainly restricted to simple aryl halides,[6d,f] hindered alkyl and aryl halides are more problematic and often impracticable. In 2006 Fürstner *et al*. developed an original approach based on heterocyclic interconversion of oxazolinium salts *via* the reaction with the corresponding arylamines.[19] However only two examples of *N*-Mes, *N*'-Dipp imidazolium salts were described. Since that time, surprisingly a few examples of unequally 1,3-diaryl-substituted imidazolium salts have been synthesized by this method and utilized for the preparation of the corresponding metal complexes.[5e, 20, 21] In the present work we for the first time investigated the reaction of binucleophilic fluorinated arylamine **3** with mesityl-substituted oxazolinium salt **4** and synthesized the new type of functionalized NHC precursors. The convenient method for the preparation of **3** has been previously developed by us from commercially available reagents [17] (Scheme 1).



Scheme 1. Synthesis of hydroxy-containing salt **5**.

Thus, we found that the reaction proceeds quite effectively in the presence of Brönsted acid to give a mixture of the expected hydroxyl-containing imidazolium salt **5** along with tricyclic product **6** in a ratio of 10:1 respectively (determined by ^{19}F NMR-analysis). The formation of salt **6** can be rationalized by the additional possibility for heterocyclization upon hydroxyl group under the reaction conditions. Fortunately, we succeeded to isolate the desired salt **5** in pure form by single crystallization from $CHCl_3$-ether solvent mixture. The procedure gives an acceptable yield (57 %) even on ten-gram scale. The compound **6** was obtained by fractional crystallization of mother liquor. The structures of **5** and **6** were fully characterized by standard physicochemical methods of analysis and, in addition, structure **5** was confirmed by single-crystal X-Ray diffraction study (Fig. 3).

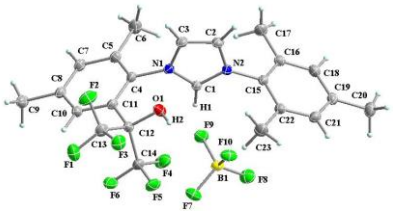
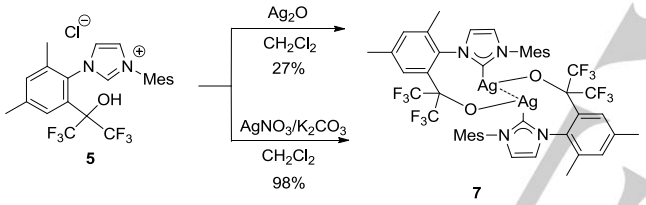


Figure 3. Molecular structure of salt **5**. Displacement ellipsoids are drawn at a 30 % probability level.

First, in order to check the ability of **5** to act as the corresponding NHC precursor, we performed its reaction with Ag_2O using the standard literature conditions. As a result, the light- and air-stable dimeric Ag(I) complex **7** has been isolated from the reaction mixture in low yield. Fortunately, the application of improved protocol, recently published by Gimeno and co-workers,[22] led to almost quantitative formation of **7** (Scheme 2). Its structure was fully confirmed by single-crystal X-Ray diffraction study (Fig. 4).

It should be noted that the similar non-fluorinated silver complexes with bidentate saturated (imidazoline-based) NHC ligands have been previously described by Hoveyda *et al*.[23]



Scheme 2. Preparation of binuclear complex **7**.

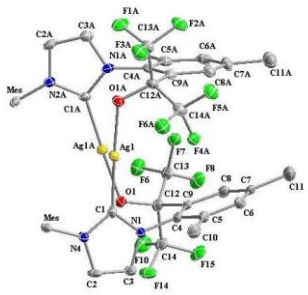
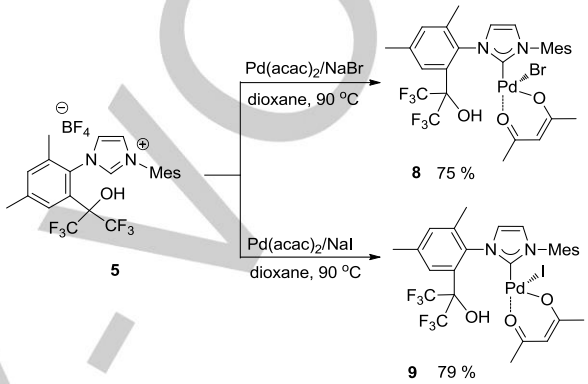


Figure 4. Structure of binuclear complex **7**. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms are omitted for clarity. *Selected bond lengths (for one of two independent molecules): Ag1…Ag1A 2.8858(7)Å, Ag1-O1A 2.077(4)Å, Ag1-C1 2.074(6)Å, Ag1A-O1 2.098(4)Å, Ag1A-C1A 2.065(6)Å; Ag1B…Ag1C 2.9135(8)Å, Ag1B-O1C 2.076(4)Å, Ag1C-O1B 2.103(4)Å, Ag1B-C1B 2.054(6)Å, Ag1C -C1C 2.080(6)Å.*

Then, we turned our attention to the synthesis of palladium (II) complexes bearing fluorinated bidentate NHC ligand. However our first attempt failed. Thus, the reaction of tetrafluoroborate salt **5** with palladium (II) acetylacetonate took place only under heating in dioxane to give a complicated mixture of products along with palladium black. This result can be rationalized by the possible formation of active Pd-cationic species under course of reaction. Therefore, we envisioned that the addition of halogen source could stabilize the palladium complex. Indeed, the addition of equimolar amounts of sodium bromide or iodide into the reaction mixture led to formation of OH-containing stable complexes **8** and **9** in good yields (Scheme 3).



Scheme 3. Synthesis of Pd(acac) complexes **8** and **9**.

The signal of carbene atom of **9** was unambiguously revealed by 2D NMR spectroscopy (see Supporting info). It was shifted into upper field (149.7 ppm) due to the influence of iodine atom, which is in the expected range for the similar Pd-complexes.[24] In addition, the structure of **9** was confirmed by single-crystal X-Ray analysis (Fig. 5).

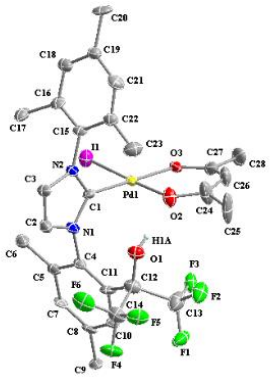


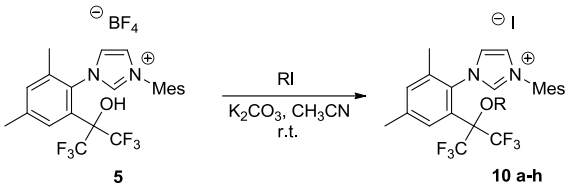
Figure 5. Molecular structure of complex **9**. Thermal ellipsoids are drawn at 30% probability. Hydrogen C-H atoms are omitted for clarity.

We have also made several attempts to perform intermolecular cyclization of **9** to get new complex with Pd-O covalent bond. The reactions were run under basic condition (Cs_2CO_3 or DBU) in anhydrous CH_3CN at 80 °C. However in all cases the starting Pd-complex **9** was recovered from the reaction mixture.

10.1002/chem.201700624

At the same time, the presence of free OH-group in imidazolium salt **5** prompted us to study the feasibility of its direct functionalization. Thus, the salt **5** was treated with three-fold excess of potassium carbonate in the presence of two equivalents of MeI at room temperature to afford the desired methoxy derivative **10a** in excellent yield (for X-ray structure of **10a** see Supporting Info, Fig. 6). These conditions proved to be optimal for other alkyl iodides (entrees 2-4, Table 1)

Table 1. Post-modification of imidazolium salt **5**.



5 **10 a-h**

Entry	RHal	Product	Yield[a], %
1	MeI	**10a**	92
2	EtI	**10b**	83
3	*n*-BuI	**10c**	74
4	ICH_2CO_2Et	**10d**	71
5	*i*-AmI	**10e**	69[b]
6	$PhCH_2Cl$	**10f**	56[c]
7	AllCl	**10g**	75[c]
8		**10h**	68[d,c]
9	*i*-PrI	**10i**	0[d]

[a] Isolated yield. [b] Reactions were conducted at 60°C, [c] in the presence of NaI, [d] Evolution of propylene was observed

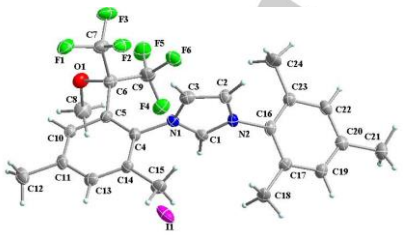
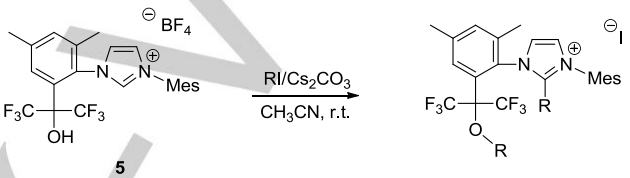


Figure 6. Structure of salt **10a**. Thermal ellipsoids are drawn at 30% probability.

The only exception was found for isopropyl iodide; the propylene gas evolution was observed during the reaction. In the case of allyl chloride (entry 7) the addition of sodium iodide was required for the successful formation of *O*-allylated product **10g**. The corresponding alkyl bromides were absolutely inactive under the studied conditions.

The simple synthetic procedure, facile isolation and purification of the final products (by single re-crystallization from toluene) render this method suitable for scale-up synthesis of new family of fluorinated unsymmetrical imidazolium salts **10** (see Experimental Section).

Interestingly, that the replacement of K_2CO_3 for more active Cs_2CO_3 leads to double alkylation product **11a** comprising alkyl groups upon oxygen of hexafluoroisopropoxy group and C2-carbon of imidazolium ring (Scheme 4). It was confirmed by the disappearance of characteristic proton signal at C2-imidazolium atom and the occurrence of two additional signals of methyl groups in ^{1}H NMR spectra of **11a**. The similar product **11b** was obtained when ethyl iodide was used as alkylating agent.



5

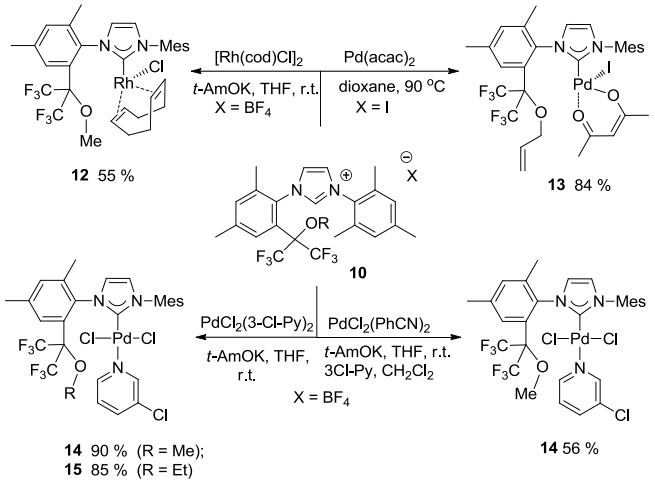
11a (R = Me, 87%);
11b (R = Et, 79%)

Scheme 4. Synthesis of double alkylated imidazolium salts.

Next, to evaluate the capability of imidazolium salts **10** to be utilized as the corresponding carbene precursors for the preparation of new NHC metal complexes, the free carbene species was generated from methoxy derivative **10a**. For this purpose, the latter has been initially transformed into tetrafluoroborate salt *via* modified literature procedure [25] (see Experimental Section). Then, the salt **10a** (BF_4^-) was deprotonated with *t*-AmOK in THF, the resulting solution was filtered out, THF was removed under reduced pressure and the residue was immediately re-dissolved in d_6-benzene for NMR analysis. Its ^{1}H NMR-spectra displays the disappearance of the low field C-2 proton at 9.57 ppm, which is consistent with the formation of the normal C-2 NHC. The ^{13}C NMR spectrum of the NHC displays a broad resonance at 220.1 ppm for the carbene center, which is in the expected range for aryl substituted imidazolylidenes.[26]

Inspired by this result, we synthesized several new metal complexes bearing unsymmetrical fluorinated NHC ligands (Scheme 5). Thus, complex **12** was obtained in acceptable yield (55%) by deprotonation of tetrafluoroborate salt **10a** with potassium *tert*-amylate in the presence of $[RhCl(cod)]_2$. In contrast, the preparation of complex **13** included the direct reaction of iodide salt **10g** with $Pd(acac)_2$ following the recent literature protocol.[27] Noteworthy, in our case the reaction proceeded very quickly; the full conversion of starting material was achieved in 20 min under heating in dioxane to give excellent yield of **13**.

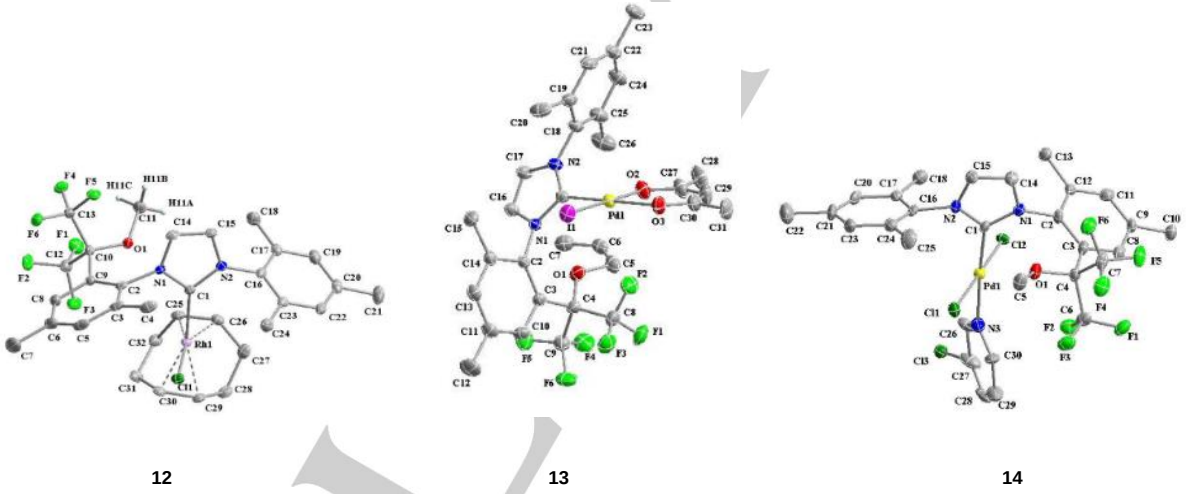
10.1002/chem.201700624



Scheme 5. Synthesis of $(CF_3)_2$(OR)C-containing complexes.

The complexes **14, 15** were obtained by one step procedure based on the usage of bis(3-chloropyridine)palladium dichloride complex $[PdCl_2(3\text{-chloropyridine})_2]$[28] as the palladium source. Its reaction with free carbenes generated *in situ* from **10a,b**, in the same manner as **12**, led to formation of desired complexes in excellent yields. In addition, *two-step* protocol can be also applied for the preparation of such pyridine containing complexes. Thus, methoxy derivative **14** was synthesized in moderate yield *via* the reaction of the corresponding free carbene with bis(benzonitrile)palladium(II) followed by the treatment of the intermediate complex with 3-chloropyridine (Scheme 5). The all complexes obtained proved to be air- and moisture-stable compounds and demonstrated remarkable solubility in common organic solvents including hexanes. The structures of **12**, **13** and **14** have been fully confirmed by single-crystal X-Ray diffraction studies (Fig. 7).

The structure of **14** was compared with known PEPPSI-IMes $[IMesPdCl_2(3\text{-Cl-Py})]$ complex.[29] The introduction of fluorinated group into Mes-substituent leads to changes of bond length values [Pd-Cl 2.356(2)Å, 2.339(2)Å; Pd-C1 1.954(8)Å; Pd-N3 2.099(8)Å in **14**; Pd-Cl 2.298(1)Å, 2.290(1)Å; Pd-C1 1.962(3)Å; Pd-N3 2.117(3)Å in PEPPSI-IMes] and angles Mes/C1N1N2 (81.1°, 71.8° in **14**; 76.8°, 72.4° in PEPPSI-IMes), C1N1N2/3-Cl-Py 61.2° and 62.6°; Cl1-Pd-Cl2/C1N1N2 25.2° and 23.5°; Cl1-Pd-Cl2/3-Cl-Py 45.5° and 50.5°, respectively (Table 2.).



12 **13** **14**

Figure 7. Molecular structures of complexes **12**, **13** and **14**. Thermal ellipsoids are drawn at 30% probability.

Noteworthy, rather short contacts between oxygen of $(CF_3)_2$(OR)C-group and imidazole atoms (O1…C1 2.949Å, O1…N1 2.577Å, O1…N2 3.666Å) were detected, probably due to steric and electronic factors (Table 3). Similar contacts were also found for all complexes obtained including **9** despite the presence of intramolecular hydrogen bond of OH-group with oxygen of C=O group of *acac* ligand (O…O 2.649Å). The only exception has been found in the case of salt **10a**, in which iodide anion has the contacts both with hydrogen of C1-H fragment (I…C 3.565Å) and with C2-H hydrogen of imidazole rings (I…C 3.695Å) belonged to two different cations. As a result in this case $(CF_3)_2$(OMe)C-group turns away from imidazole ring (see Supporting Info, Fig. S49).

Palladium-catalyzed cross-coupling reactions are widely employed for construction of new carbon-carbon and carbon-heteroatom bonds and have already gained an exclusive importance for the production of compounds in the pharmaceutical and fine chemical industries.[30] Keeping in mind the previous reports by M. Organ's and S. Nolan's research groups that PEPPSI (pyridine-enhanced pre-catalyst preparation, stabilization, and initiation) complexes with bulky NHC ligands are highly active and universal catalysts in many palladium-catalyzed cross-coupling processes,[31] including Buchwald-Hartwig reaction,[3d,32] we chose amination of bromobenzene by morpholine as a model reaction for the initial estimation of the catalytic activity of fluorinated PEPPSI-type catalysts **14** and **15**.

Reactions were conducted in standard solvent dimethoxyethane (DME) at 80°C as well as in heptane with 0.5 mol% catalyst loading; potassium *tert*-butoxide was used as a base. All reactions were performed in duplicate (Table 4).

Table 2. Selected geometric parameters of complexes obtained.

Com-plex	M-Hal, [Å]	M-C1, [Å]	C1-N, [Å]	Angle plane C_2N_2/sub-Mes[°]	Angle C_2N_2/-Mes [°]
5	-	-	1.324(2); 1.328(2)	86.2	83.7
9	2.5557 (7)	1.974 (6)	1.296(14); 1.403(14)	87.7	87.4
10a	-	-	1.309(8); 1.352(8)	87.5	67.5
12[a]	2.3753 (10) 2.4001 (9)	2.070 (3) 2.074 (4)	1.368(4); 1.369(4); 1.378(4); 1.362(4)	86.5; 74.8	72.2; 83.4
13	2.5742 (3)	1.971 (2)	1.356(3); 1.362(3)	82.2	68.9
14	2.356 (2); 2.339 (2)	1.954 (8)	1.363(10); 1.367(10)	81.1	71.8
PEPPSI-Mes[b]	2.298(1); 2.209(1)	1.962 (3)	1.352(5); 1.360(5)	-	76.8 72.4

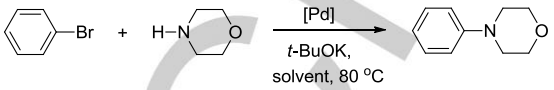
[a] two independent molecules; [b] see *ref.*29

Table 3. Contacts between oxygen of $(CF_3)_2$(OR)C-group and imidazole atoms.

Complex	C1, [Å]	N1, [Å]	N2, [Å]
5	3.085	2.566	3.627
9	3.051	2.753	3.644
10a	-	-	-
12[a]	3.121	2.642	3.804
13	3.218	2.617	3.856
14	2.949	2.557	3.666

Generally, the synthesized Pd-complexes demonstrated an expected activity in DME. Thus, despite structural similarity to symmetrical PEPPSI-IMes [*N,N*-bis(2,4,6-trimethylphenyl) imidazol-2-ylidene] the **14** and **15** exhibited higher catalytic activities in this model reaction. In addition, the remarkable solubility found for new complexes, induced by the influence of lipophilic fluorinated moiety, has allowed performing this reaction in heptane to afford the product even in better yields (entries 5, 6). The latter examples clearly show a potential of the catalysts obtained to function in alkane solvents, which are the most favorable for industrial application.[3g, 33]

Table 4. The catalytic activity of new Pd-complexes in Buchwald-Hartwig amination.



Entry	Catalyst	Solvent	Yield[a], %
1	PEPPSI-IMES	DME	32
2	14	DME	49
3	15	DME	51
4	PEPPSI-IMES	heptane	28
5	14	heptane	59
6	15	heptane	58

[a] isolated yield.

Conclusions

We developed an efficient and scaled-up synthesis of imidazole-based unsymmetrical NHC precursors bearing sterically demanding hexafluoroisopropylalkoxy [$(CF_3)_2$(OR)C-] group in *ortho*-position of *N*-aryl substituent. The method is based on heterocyclic interconversion of Mes-substituted oxazolinium tetrafluoroborate salt *via* the reaction with the corresponding fluoroalkyl substituted aniline. The subsequent post-modification of the resulting hydroxyl-containing salt lead to new family of fluorinated NHC precursors. The latter were further successfully utilized for the preparation of several novel metal complexes, which exhibited remarkable stability and solubility in common organic solvents including hexanes. An initial evaluation of catalytic activity of palladium complexes obtained was performed on Buchwald-Hartwig amination of bromobenzene with morpholine as a model reaction. As a result, two PEPPSI-type complexes revealed promising activity, approaching to the known active catalysts with bulky NHC ligands. The facile modification/functionalization of fluorinated NHC precursors *via* elaborated *O*-alkylation protocol would allow for further fine turning of these ligands and subsequently reactivity of NHC-metal complexes. In addition, the remarkable solubility of complexes would provide possibilities for the development of new catalytic procedures in industrially important alkane solvents. Studies of novel organometallic complexes of these ligands with a variety of metals, including Ru, Cu, Ni and W are in progress now.

Experimental Section

All solvents were freshly distilled from appropriate drying agents before use. All other reagents were recrystallized or distilled as necessary. Syntheses of metal complexes were performed under an argon atmosphere using standard Schlenk technique. Analytical TLC was performed with Merck silica gel 60 F254 plates. Visualization was accomplished by UV light (254 and 366 nm), spraying by $Ce(SO_4)_2$ solution in 5 % H_2SO_4 or $KMnO_4$ solution in water. Column chromatography was carried out using Merck silica gel 60 (230-400 mesh ASTM) and ethyl acetate/petroleum ether or ethyl acetate/CH_2Cl_2 as eluent. NMR spectra were recorded at room temperature on Bruker AV-300, AV-400, AV-600 spectrometers operating at 300 MHz, 400 MHz and 600 MHz for ^{1}H; 101 and 151 MHz for ^{13}C; 282 and 376 MHz and for ^{19}F (CF_3Cl as reference) and 121 MHz for ^{31}P (85% H_3PO_4 as reference). The chemical shifts are frequency referenced relative to the residual undeuterated solvent peaks. 2-(2-Amino-3,5-dimethylphenyl)-1,1,1,3,3,3-hexafluoro-propan-2-ol **3**[17], 5-acetoxy-3-mesityl-4,5-dihydrooxazol-3-ium tetrafluoroborate **4**[19] and $PdCl_2$(3-ClPy)$_2$[34] were synthesized according to the literature procedures. All crystals suitable for X-Ray experiments were obtained from the solvent mixture CH_2Cl_2/hexane (1:1) at -5° C.

Synthesis of 5. A mixture of oxazolium tetrafluoroborate **4** (9.85 g, 29.4 mmol) and fluorinated aniline **3** (12.6 g, 44.0 mmol) in 100 ml of dry toluene was stirred for 12 h at room temperature and then 6 ml of $HBF_4{\cdot}Et_2O$ was added. The resulting suspension was heated at 80 °C under stirring for 3 h, cooled to room temperature and evaporated to dryness in vacuum. The oily residue was stirred with 150 ml of diethyl ether until crystallization. Precipitate obtained was filtered, washed with minimal volume of $CHCl_3$ and dried in air to give 9.12 g (57 %) of beige powder (m.p. 231-233 °C (dec.). ^{1}H NMR (d_6-DMSO, *δ*, ppm) 9.57 (s, 1H, NC*H*-N), 8.86 (s, 1H, O*H*), 8.18 (s, 1H, NC*H*-C), 8.14 (s, 1H, NC*H*-C), 7.63 (s, 1H, H_{Ar}), 7.49 (s, 1H, H_{Ar}), 7.19 (s, 2H, H_{Ar}), 2.46 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.05 (s, 3H, CH_3). ^{13}C NMR (d_6-DMSO, *δ*, ppm) 141.3 (N*C*N), 140.6 (C_{arom}), 138.7 (C_{arom}), 138.4 (C_{arom}), 134.5 (C_{arom}), 134.1 (C_{arom}), 134.1 (C_{arom}), 130.9 (C_{arom}), 130.8 (C_{arom}), 129.4 (C_{arom}), 129.4 (C_{arom}), 126.9 (C_{arom}), 126.5 (C_{arom}), 126.1 (C_{arom}), 123.4 (C_{arom}), 122.6 (q, $^1J_{C,F}$ = 289 Hz, *C*F_3), 79.0 [m, *C*$(CF_3)_2$], 20.9 (*C*H_3), 20.6 (*C*H_3), 17.2 (*C*H_3), 17.2 (*C*H_3), 17.0 (*C*H_3). ^{19}F NMR (d_6-DMSO, δ, ppm) -72.45 (q, *J* = 7.6 Hz, C*F*$_3$), -73.12 (q, *J* = 7.7 Hz, C*F*$_3$), -148.23 (s, B*F*$_4$). Anal. Calcd for $C_{23}H_{23}BF_{10}N_2O$ (%): C, 50.76; H, 4.26; N, 5.15. Found: C, 50.64; H, 4.18; N, 5.08.

Anion exchange. In order to exchange BF_4 anion to Cl solution of 1.0 g of imidazolium tetrafluoroborate **5** was dissolved in 20 ml of methanol, filtered through a short pad (2 cm) of Amberlite® IRA-400(Cl). Ion exchange resin was washed with additional volume of methanol. Combined filtrate was concentrated in vacuum to give almost quantitative yield of chloride salt of **5**.

Imidazolinium tetrafluoroborate 6. Isolated as white crystals from mother liquor remaining after filtration of **5** (see procedure above). Yield 5 %, M.p. 200-202 °C (dec.). ^{1}H NMR (d_6-acetone, δ, ppm) 9.63 (s, 1H, NC*H*-N), 7.58 (s, 1H, H_{Ar}), 7.55 (s, 1H, H_{Ar}), 7.14 (s, 2H, H_{Ar}), 6.42 [d, $J_{H,H}$ = 6.2 Hz, 1H, N(O)C*H*], 5.14 (dd, $J_{H,H}$ = 14.7, 6.5 Hz, 1H, NCH_2), 4.69 (d, $J_{H,H}$ = 15.0 Hz, 1H, NCH_2), 2.61 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.34 (s, 6H, CH_3); ^{13}C NMR (d_6-acetone, δ, ppm) 159.0 (N*C*N), 142.1 (C_{arom}), 140.1 (C_{arom}), 136.6 (C_{arom}), 136.3 (C_{arom}), 133.1 (C_{arom}), 130.9 (C_{arom}), 130.2 (C_{arom}), 126.5 (C_{arom}), 123.1 (q, $^1J_{C,F}$ = 289 Hz, *C*F_3), 122.5 (q, $^1J_{C,F}$ = 286 Hz, *C*F_3), 117.8 (C_{arom}), 86.9 [N(O)*C*H], 79.6-78.5 [m, *C*$(CF_3)_2$], 58.1 (NCH_2), 21.2 (*C*H_3), 21.0 (*C*H_3), 17.5 (*C*H_3), 17.3 (*C*H_3), 17.1 (*C*H_3); ^{19}F NMR (d_6-acetone, δ, ppm) -72.35 (q, *J* = 8.6 Hz, C*F*$_3$), -76.45 (q, *J* = 8.6 Hz, C*F*$_3$), -151.47 (s, B*F*$_4$). Anal. Calcd for $C_{23}H_{23}BF_{10}N_2O$ (%): C, 50.76; H, 4.26; N, 5.15. Found: C, 50.68; H, 4.22; N, 5.04.

Silver complex 7. The mixture of 0.49 g (1 mmol) of imidazolium chloride **5**, 0.17 g (1 mmol) of silver nitrate and 0.69 g (5 mmol) of potassium carbonate in 30 ml of dichloromethane was stirred for 2 days, filtered through Celite and evaporated to dryness. Recrystallization of resulting solid from heptane afforded 0.50 g (98 %) of the product as white crystals. ^{1}H NMR (d_6-acetone, *δ*, ppm) 7.18 (s, 1H, H_{Im}), 7.17 (s, 1H, H_{Im}), 7.14 (s, 2H, H_{Ar}), 7.11 (s, 1H, H_{Ar}), 7.08 (s, 1H, H_{Ar}), 2.50 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 1.51 (s, 3H, CH_3). ^{13}C NMR (d_6-acetone, *δ*, ppm) 183.0 (dd, $^1J_{Ag(109),C}$ = 271.2 Hz, $^1J_{Ag(107),C}$ = 236.2 Hz, N*C*N), 139.6 (C_{arom}), 139.3 (C_{arom}), 138.4 (C_{arom}), 137.6 (C_{arom}), 137.0 (C_{arom}), 136.5 (C_{arom}), 135.7 (C_{arom}), 135.4 (C_{arom}), 132.5 (C_{arom}), 130.7 (C_{arom}), 130.1 (C_{arom}), 128.3 (C_{arom}), 128.0 (C_{arom}), 127.0 (q, $^1J_{C,F}$ = 296 Hz, *C*F_3), 126.8 (C_{arom}), 126.1 (qd, *J* = 293 Hz, 10 Hz, *C*F_3), 126.0 (C_{arom}), 121.4 (C_{arom}), 121.3 (C_{arom}), 88.8-87.8 [m, *C*$(CF_3)_2$], 21.4 (*C*H_3), 21.3 (*C*H_3), 18.8 (*C*H_3), 18.3 (*C*H_3), 17.7 (*C*H_3). ^{19}F NMR (d_6-acetone, *δ*, ppm): -71.90 (br. s, C*F*$_3$), -75.02 (q, *J* = 9.3 Hz, C*F*$_3$) Anal. Calcd for $C_{46}H_{44}Ag_2F_{12}N_4O_2$ (%): C, 48.95; H, 3.93; N, 4.96. Found: C, 50.14; H, 4.11; N, 5.02.

Synthesis of palladium complex 8. The mixture of 0.15 g (0.276 mmol) imidazolium tetrafluoroborate **5**, 0.0763 g (0.251 mmol, 0.91 eq) of $Pd(acac)_2$ and 0.085 g (0.827 mmol, 3 eq) of sodium bromide were dissolved in 5 ml of 1,4-dioxane. Reaction mixture was heated at 90°C until TLC showed full conversion of starting $Pd(acac)_2$ to product (4 h). After cooling to room temperature the reaction mixture was evaporated in vacuum, residue was dissolved in minimum amount of CH_2Cl_2 and purified by flash chromatography using hexanes-CH_2Cl_2 (1:1) mixture. Evaporation of resulting fractions yielded 0.140 g (75%) of pure product as yellowish solid (m.p. 123-125 °C). ^{1}H NMR ($CDCl_3$, *δ*, ppm) 7.47 (s, 1H, H_{Im}), 7.35 (s, 1H, H_{Im}), 7.12 (s, 1H, H_{Ar}), 7.09-6.93 (m, 4H, H_{Ar}, O*H*), 5.24 [s, 1H, C(O)C*H*], 2.47 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 1.90 [s, 3H, C(O)CH_3], 1.86 [s, 3H, C(O)CH_3]. ^{13}C NMR ($CDCl_3$, *δ*, ppm) 190.1 (*C*=O), 181.5 (*C*=O), 150.2 (N*C*N), 140.3 (C_{Ar}), 140.1 (C_{Ar}), 139.6 (C_{Ar}), 136.4 (C_{Im}), 135.5 (C_{Ar}), 134.9 (C_{Ar}), 134.8 (C_{Ar}), 134.7 (C_{Ar}), 130.0 (C_{Ar}), 129.2 (C_{Ar}), 127.5 (C_{Ar}), 127.3 (C_{Im}), 126.0 (d, *J* = 3 Hz, C_{Ar}), 124.3 (C_{Ar}), 123.5 (q, $^1J_{C,F}$ = 291 Hz, *C*F_3), 122.4 (q, $^1J_{C,F}$ = 287 Hz, *C*F_3), 101.0 [C(O)*C*H], 81.0-79.5 [m, *C*$(CF_3)_2$], 28.0 [C(O)*C*H_3], 25.4 [C(O)*C*H_3], 21.6 (*C*H_3), 21.3 (*C*H_3), 20.1 (*C*H_3), 19.4 (*C*H_3), 17.8 (*C*H_3). ^{19}F NMR ($CDCl_3$, *δ*, ppm) -69.60 (q, *J* = 8.7 Hz, C*F*$_3$), -76.16 (q, *J* = 8.4 Hz, C*F*$_3$). Anal. Calcd for $C_{28}H_{30}BrF_6N_2O_3Pd$ (%) C, 45.27; H, 4.07; N, 3.77. Found: C, 45.36; H, 4.19; N, 3.67.

Synthesis of palladium complex 9. The mixture of 0.15 g (0.276 mmol) of imidazolium tetrafluoroborate **5**, 0.0763 g (0.251 mmol) of $Pd(acac)_2$ and 0.1239 g (0.827 mmol) of sodium iodide were dissolved in 5 ml of 1,4-dioxane. Reaction mixture was heated at 90°C until TLC showed full conversion of starting $Pd(acac)_2$ to product (2 h). After cooling to room temperature the reaction mixture was evaporated in vacuum, residue was dissolved in minimum amount of CH_2Cl_2 and purified by flash chromatography using hexanes-CH_2Cl_2 (1:1) mixture. Evaporation of resulting fractions yielded 0.172 g (79%) of pure product as yellow solid (m.p. 127-129 °C). ^{1}H NMR ($CDCl_3$, *δ*, ppm) 7.47 (s, 1H, H_{Im}), 7.46 (s, 1H, O*H*), 7.33 (s, 1H, H_{Im}), 7.13 (s, 1H, H_{Ar}), 7.05 (s, 1H, H_{Ar}), 7.01 (s, 2H, H_{Ar}), 5.25 [s, 1H, C(O)C*H*], 2.47 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.25 (s, 6H, CH_3), 2.16 (s, 3H, CH_3), 1.93 [s, 3H, C(O)CH_3], 1.85 [s, 3H, C(O)CH_3]. ^{13}C NMR ($CDCl_3$, *δ*, ppm) 189.5 (*C*=O), 181.5 (*C*=O), 149.7 (N*C*N), 140.1 (C_{Ar}), 139.8 (C_{Ar}), 139.6 (C_{Ar}), 135.9 (C_{Im}), 135.6 (C_{Ar}), 134.9 (C_{Ar}), 134.9 (C_{Ar}), 134.8 (C_{Ar}), 130.0 (C_{Ar}), 129.3 (C_{Ar}), 127.6 (C_{Ar}), 127.4 (C_{Im}), 126.1 (NC_{Ar}), 124.6 (NC_{Ar}), 123.5 (q, $^1J_{C,F}$ = 291 Hz, *C*F_3), 122.4 (q, $^1J_{C,F}$ = 287 Hz, *C*F_3), 100.6 [C(O)*C*H], 80.2 [m, *C*$(CF_3)_2$], 28.1

[C(O)*C*H$_3$], 25.7 [C(O)*C*H$_3$], 21.6 (*C*H$_3$), 21.5 (*C*H$_3$), 21.3 (*C*H$_3$), 20.5 (*C*H$_3$), 18.0 (*C*H$_3$). ^{19}F NMR (CDCl$_3$, *δ*, ppm) -68.23 (s, C*F*$_3$), -75.05 (s C*F*$_3$). Anal. Calcd for $C_{28}H_{30}F_6IN_2O_3Pd$ (%) C, 42.58; H, 3.83; N, 3.55. Found: C, 42.39; H, 4.01; N, 3.61.

General procedure for *O*-aklylation of imidazolium salt 5. A mixture of 0.272 g (0.5 mmol) of imidazolium tetrafluoroborate **5**, 0.27 g (2 mmol) of anhydrous K_2CO_3 and 2 mmol of methyliodide was dissolved in 2 ml of CH_3CN. Reaction mixture was stirred until TLC analysis (acetone) showed absence of starting imidazolium salt (6 h). Reaction mixture was concentrated in vacuum, residue triturated in dichloromethane and filtered through Celite®. Resulting filtrate was evaporated to dryness. Crystallization from 2 ml of toluene afforded 0.275 g (92 %) of pure *O*-metylated imidazolium iodide **10a** as a white solid (m.p. 128-130 °C). ^{1}H NMR (CDCl$_3$, *δ*, ppm) 9.79 (s, 1H, NC*H*-N), 7.80 (s, 1H, NC*H*-C), 7.64 (s, 1H, NC*H*-C), 7.40 (s, 1H, *H*$_{Ar}$), 7.33 (s, 1H, *H*$_{Ar}$), 6.97 (s, 2H, *H*$_{Ar}$), 3.46 (s, 3H, OC*H*$_3$), 2.40 (s, 3H, C*H*$_3$), 2.28 (s, 3H, C*H*$_3$), 2.14 (s, 3H, C*H*$_3$), 2.07 (s, 3H, C*H*$_3$), 2.05 (s, 3H, C*H*$_3$). ^{13}C NMR (CDCl$_3$, *δ*, ppm) 142.1 (N*C*N), 141.6 (C$_{arom}$), 138.9 (C$_{arom}$), 138.4 (C$_{arom}$), 135.2 (C$_{arom}$), 134.2 (C$_{arom}$), 133.8 (C$_{arom}$), 130.1 (C$_{arom}$), 129.9 (C$_{arom}$), 129.6 (C$_{arom}$), 127.0 (C$_{arom}$), 125.0 (C$_{arom}$), 124.0 (C$_{arom}$), 122.0 (q, $^1J_{C,F}$ =292 Hz, *C*F$_3$), 121.7 (q, $^1J_{C,F}$ = 290 Hz, *C*F$_3$), 83.7 [m, $^2J_{C,F}$ = 28 Hz, *C*(CF$_3$)$_2$], 56.7 (O*C*H$_3$), 21.5 (CH$_3$), 21.1 (*C*H$_3$), 18.7 (*C*H$_3$), 18.1 (*C*H$_3$), 17.2 (*C*H$_3$). ^{19}F NMR (CDCl$_3$, *δ*, ppm) -66.80 (s, C*F*$_3$), -68.57 (s, C*F*$_3$). Anal. Calcd for $C_{24}H_{25}F_6IN_2O$ (%): C, 48.17; H, 4.21; N, 4.68. Found: C, 47.98; H, 4.26; N, 4.45.

Scaled-up synthesis of 10a. A mixture of 6.0 g (11.0 mmol) of imidazolium tetrafluoroborate **5**, 6.1 g (44.0 mmol) of anhydrous K_2CO_3 and methyliodide (6.26 g, 44.0 mmol) was suspended in 50 ml of CH_3CN. Reaction mixture was vigorously stirred at room temperature overnight. The solvent was removed under reduced pressure, and then the residue was triturated in dichloromethane (50 ml) and filtered out through Celite®. Resulting filtrate was evaporated to dryness. Crystallization from 25 ml of toluene gave 5.93 g (90 %) of analytically pure **10a**.

Synthesis of imidazolium tetrafluoroborate 10a. To the solution of imidazolium iodide **10a** (1.0 g, 1.67 mmol) in acetone (30 ml) sodium tetrafluoroborate (0.733 g, 6.68 mmol) solution in water (30 ml) was added. The resulting mixture was stirred for 10 min, concentrated in vacuum approx. to 30 ml and extracted with dichloromethane (3x20 ml). Organic extract was dried over $MgSO_4$ and evaporated to dryness to give 0.92 g (98%) of white solid (m.p. 103-105 °C). ^{1}H NMR (CDCl$_3$, *δ,* ppm) 8.77 (s, 1H, NC*H*-N), 7.65 (s, 1H, NC*H*-C), 7.52 (s, 1H, NC*H*-C), 7.47 (s, 1H, *H*$_{Ar}$), 7.39 (s, 1H, *H*$_{Ar}$), 7.03 (s, 2H, *H*$_{Ar}$), 3.48 (s, 3H, OC*H*$_3$), 2.46 (s, 3H, C*H*$_3$), 2.35 (s, 3H, C*H*$_3$), 2.25-1.91 (m, 9H, C*H*$_3$). ^{13}C NMR (CDCl$_3$, *δ*, ppm) 142.3 (N*C*N), 141.8 (C$_{arom}$), 139.1 (C$_{arom}$), 138.4 (C$_{arom}$), 135.3 (C$_{arom}$), 134.5 (C$_{arom}$), 134.1 (C$_{arom}$), 130.5 (C$_{arom}$), 130.2 (C$_{arom}$), 130.1 (C$_{arom}$), 129.7 (C$_{arom}$), 127.1 (C$_{arom}$), 125.2 (C$_{arom}$), 124.1 (C$_{arom}$), 122.3 (q, $^1J_{C,F}$ = 291 Hz, *C*F$_3$), 122.0 (q, $^1J_{C,F}$ = 290 Hz, *C*F$_3$), 84.0 [m, *C*(CF$_3$)$_2$], 56.4 (O*C*H$_3$), 21.6 (CH$_3$), 21.2 (*C*H$_3$), 17.9 (*C*H$_3$), 17.4 (CH$_3$), 17.2 (*C*H$_3$). ^{19}F NMR (CDCl$_3$, *δ*, ppm) -67.40 (s, C*F*$_3$), -70.55 (s, C*F*$_3$), -152.66 (m, B*F*$_4$). Anal. Calcd for $C_{24}H_{25}BF_{10}N_2O$ (%) C, 51.63; H, 4.51; N, 5.02. Found C, 51.73; H, 4.59; 5.15.

Imidazolium iodide 10b. Yield: 83% (m.p. 124-126 °C). ^{1}H NMR (CDCl$_3$, *δ*, ppm), 9.91 (s, 1H, NC*H*-N), 7.62 (s, 2H, *H*$_{Im}$), 7.50 (s, 1H, *H*$_{Ar}$), 7.34 (s, 1H, *H*$_{Ar}$), 6.98 (s, 2H, *H*$_{Ar}$), 3.76-3.54 (m, 2H, OC*H*$_2$), 2.42 (s, 3H, C*H*$_3$), 2.30 (s, 3H, C*H*$_3$), 2.16 (s, 3H, C*H*$_3$), 2.08 (s, 6H, C*H*$_3$), 1.26 (t, $^3J_{H,H}$ = 7.0 Hz, 3H, CH$_2$C*H*$_3$). ^{13}C NMR (CDCl$_3$, *δ*, ppm) 142.3 (N*C*N), 141.7 (C$_{arom}$), 139.4 (C$_{arom}$), 139.0 (C$_{arom}$), 135.4 (C$_{arom}$), 134.3 (C$_{arom}$), 133.8 (C$_{arom}$), 130.3 (C$_{arom}$), 130.2 (C$_{arom}$), 130.1 (C$_{arom}$), 129.9 (C$_{arom}$), 129.6 (C$_{arom}$), 126.9 (C$_{arom}$), 125.7 (C$_{arom}$), 122.1 (q, $^1J_{C,F}$ = 290 Hz, *C*F$_3$), 121.7 (q, $^1J_{C,F}$ = 289 Hz, *C*F$_3$), 83.8-82.6 [m, C(CF$_3$)$_2$], 63.6 (OCH$_2$), 21.6 (*C*H$_3$), 21.1 (*C*H$_3$), 18.8 (*C*H$_3$), 18.4 (*C*H$_3$), 17.4 (*C*H$_3$), 15.2 (CH$_2$*C*H$_3$). ^{19}F NMR (CDCl$_3$, *δ*, ppm) -67.52 (s, C*F*$_3$), -71.68 (s, C*F*$_3$). Anal. Calcd for $C_{25}H_{27}F_6IN_2O$ (%): C, 49.03; H, 4.44; N, 4.57. Found: C, 49.19; H, 4.31; N, 4.48.

Imidazolium tetrafluoroborate 10b. Using procedure described for compound **10a** (BF$_4$) the product **10b** was isolated as white solid (m.p. 97-99 °C) in 97% yield. ^{1}H NMR (CDCl$_3$, *δ*, ppm) 9.08 (s, 1H, NC*H*-N), 7.57 (s, 1H, NC*H*-C), 7.55 (s, 1H, NC*H*-C), 7.47 (s, 1H, *H*$_{Ar}$), 7.40 (s, 1H, *H*$_{Ar}$), 7.05 (s, 2H, *H*$_{Ar}$), 3.72 (m, 2H, OC*H*$_2$), 2.48 (s, 3H, C*H*$_3$), 2.36 (s, 3H, C*H*$_3$), 2.15 (s, 3H, C*H*$_3$), 2.13 (s, 3H, C*H*$_3$), 2.07 (s, 3H, C*H*$_3$), 1.31 (t, $^3J_{H,H}$ = 7.0 Hz, 3H, CH$_2$C*H*$_3$). ^{13}C NMR (CDCl$_3$, *δ*, ppm) 142.5, N*C*N, 142.0 (C$_{arom}$), 139.8 (C$_{arom}$), 139.1 (C$_{arom}$), 135.4 (C$_{arom}$), 134.6 (C$_{arom}$), 134.0 (C$_{arom}$), 130.4 (C$_{arom}$), 130.3 (C$_{arom}$), 130.1 (C$_{arom}$), 126.9 (C$_{arom}$), 125.8 (C$_{arom}$), 123.9 (C$_{arom}$), 122.3 (q, $^1J_{C,F}$ = 291 Hz, *C*F$_3$), 121.9 (q, $^1J_{C,F}$ = 288 Hz, *C*F$_3$), 83.3 [m, C(CF$_3$)$_2$], 63.7, (OCH$_2$), 21.7 (CH$_3$), 21.3 (*C*H$_3$), 18.0 (*C*H$_3$), 17.7 (CH$_3$), 17.4 (*C*H$_3$), 15.3(CH$_2$*C*H$_3$). ^{19}F NMR (CDCl$_3$, *δ*, ppm), *δ* -67.82 (s, C*F*$_3$), -71.92 (s, C*F*$_3$), -152.88 (d, *J* = 20 Hz, B*F*$_4$). Anal Calcd for $C_{25}H_{27}BF_{10}N_2O$ (%) C, 52.47; H, 4.76; N, 4.89. Found C, 52.62; H, 4.89; 4.75.

Imidazolium iodide 10c. Yield: 74% (m.p. 117-119 °C). ^{1}H NMR (CDCl$_3$, *δ*, ppm) 10.06 (s, 1H, NC*H*-N), 7.61 (s, 1H, NC*H*-C), 7.58 (s, 1H, NC*H*-C) 7.54 (s, 1H, *H*$_{Ar}$), 7.38 (s, 1H, *H*$_{Ar}$), 7.02 (s, 1H, *H*$_{Ar}$), 7.02 (s, 1H, *H*$_{Ar}$), 3.69-3.53 (m, 2H, OC*H*$_2$), 2.45 (s, 3H, C*H*$_3$), 2.33 (s, 3H, C*H*$_3$), 2.21 (s, 3H, C*H*$_3$), 2.13 (s, 3H, C*H*$_3$), 2.10 (s, 3H, C*H*$_3$), 1.68-1.60 (m, 2H, C*H*$_2$), 1.48-1.38 (m, 2H, C*H*$_2$), 0.92 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, C*H*$_3$). ^{13}C NMR (CDCl$_3$, *δ*, ppm) 142.4 (N*C*N), 141.8 (C$_{arom}$), 139.1 (C$_{arom}$), 135.5 (C$_{arom}$), 134.4 (C$_{arom}$), 133.9 (C$_{arom}$), 130.4 (C$_{arom}$), 130.3 (C$_{arom}$), 130.2 (C$_{arom}$), 130.1 (C$_{arom}$), 129.7 (C$_{arom}$), 126.8 (C$_{arom}$), 125.6 (C$_{arom}$), 124.0 (C$_{arom}$), 122.1 (q, $^1J_{C,F}$ = 291 Hz, *C*F$_3$), 121.7 (q, $^1J_{C,F}$ = 289 Hz, *C*F$_3$), 83.5-82.4 [m, *C*(CF$_3$)$_2$], 67.2 (OCH$_2$), 31.6 (CH$_2$), 21.6 (*C*H$_3$), 21.2 (*C*H$_3$), 19.0 (CH$_2$) 18.9 (*C*H$_3$), 18.5 (*C*H$_3$), 17.4 (*C*H$_3$), 13.8 (CH$_2$*C*H$_3$). ^{19}F NMR (CDCl$_3$, *δ*, ppm) -66.69 (s, C*F*$_3$), -70.82 (s, C*F*$_3$). Anal. Calcd for $C_{27}H_{31}F_6IN_2O$ (%): C, 50.64; H, 4.88; N, 4.37. Found: C, 50.26; H, 4.57; N, 4.30.

Imidazolium iodide 10d. Yield: 71% (m.p. 121-123 °C). ^{1}H NMR (CDCl$_3$, *δ*, ppm) 10.31 (s, 1H, NC*H*-N), 7.82 (s, 1H, NC*H*-C), 7.59 (s, 1H, NC*H*-C) 7.51 (s, 1H, *H*$_{Ar}$), 7.40 (s, 1H, *H*$_{Ar}$), 7.03 (s, 2H, *H*$_{Ar}$), 4.27 (dd, *J* = 66.9, 14.6 Hz, 2H, OC*H*$_2$CO), 4.25-4.20 (m, 2H, OC*H*$_2$CH$_3$), 2.43 (s, 3H, C*H*$_3$), 2.33 (s, 3H, C*H*$_3$), 2.20 (s, 3H, C*H*$_3$), 2.13 (s, 3H, C*H*$_3$), 2.11 (s, 3H, C*H*$_3$), 1.26 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, CH$_2$C*H*$_3$). ^{13}C NMR (CDCl$_3$, *δ*, ppm) 167.2 (*C*=O), 142.9 (N*C*N), 141.8 (C$_{arom}$), 139.9 (C$_{arom}$), 139.3 (C$_{arom}$), 135.9 (C$_{arom}$), 134.3 (C$_{arom}$), 133.9 (C$_{arom}$), 130.4 (C$_{arom}$), 130.3 (C$_{arom}$), 130.2 (C$_{arom}$), 129.7 (C$_{arom}$), 126.6 (C$_{arom}$), 124.8 (C$_{arom}$), 123.8 (C$_{arom}$), 122.0 (d, $^1J_{C,F}$ = 290 Hz, *C*F$_3$), 121.5 (d, $^1J_{C,F}$ = 289 Hz, *C*F$_3$), 83.5 [m, *C*(CF$_3$)$_2$], 64.6 (OCH$_2$CO), 61.9 (CH$_2$CH$_3$), 21.5 (CH$_3$), 21.2 (*C*H$_3$), 19.0 (*C*H$_3$), 18.5 (*C*H$_3$), 17.5 (*C*H$_3$), 14.2 (CH$_2$*C*H$_3$). ^{19}F NMR (CDCl$_3$, *δ*, ppm) -67.04 (s, C*F*$_3$), -71.42 (s, C*F*$_3$). Anal. Calcd for $C_{27}H_{29}F_6IN_2O_3$ (%) C, 48.37; H, 4.36; N, 4.18. Found: C, 48.31; H, 4.59; N, 4.20.

Imidazolium iodide 10e. Reaction was carried out at 60°C. Yield: 69% (m.p. 134-135 °C). ^{1}H NMR (CDCl$_3$, *δ*, ppm) δ 9.94 (s, 1H, NC*H*-N), 7.61 (s, 2H, NC*H*-C), 7.52 (s, 1H, *H*$_{Ar}$), 7.36 (s, 1H, *H*$_{Ar}$), 7.00 (s, 2H, *H*$_{Ar}$), 3.74-3.52 (m, 2H, OC*H*$_2$), 2.43 (s, 3H, C*H*$_3$), 2.31 (s, 3H, C*H*$_3$), 2.18 (s, 3H, C*H*$_3$), 2.10 (s, 3H, C*H*$_3$), 2.08 (s, 3H, C*H*$_3$), 1.79-1.69 [m, 1H, CH$_2$C*H*(CH$_3$)$_2$], 1.60-1.48 (m, 2H, CH$_2$C*H*$_2$CH), 0.88 (d, $^3J_{H,H}$ = 6.3 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, *δ*, ppm) δ 142.3 (N*C*N), 141.7 (C$_{arom}$), 139.4 (C$_{arom}$), 139.0 (C$_{arom}$), 135.4 (C$_{arom}$), 134.4 (C$_{arom}$), 133.8 (C$_{arom}$), 130.3 (C$_{arom}$), 130.2 (C$_{arom}$), 130.1 (C$_{arom}$), 130.1 (C$_{arom}$), 129.6 (C$_{arom}$), 126.9 (C$_{arom}$), 122.0 (q, $^1J_{C,F}$ = 291 Hz, *C*F$_3$), 121.7 (q, $^1J_{C,F}$ = 289 Hz, *C*F$_3$), 83.6-82.3 [m, *C*(CF$_3$)$_2$], 65.9 (OCH$_2$), 38.4 (CH$_2$CH$_2$CH), 24.6 [CH$_2$*C*H(CH$_3$)$_2$], 22.54 [CH(*C*H$_3$)$_2$], 22.47 [CH(*C*H$_3$)$_2$], 21.5 (*C*H$_3$), 21.1 (*C*H$_3$), 18.9 (*C*H$_3$), 18.4 (*C*H$_3$), 17.4 (*C*H$_3$). ^{19}F NMR (CDCl$_3$, *δ*, ppm) δ -

68.29 (s, CF_3), -71.47 (s, CF_3). Anal. Calcd for $C_{28}H_{33}F_6IN_2O$ (%) C, 51.39; H, 5.08; N, 4.28. Found: C, 51.25; H, 5.19; N, 4.32.

Imidazolium iodide 10f. 0.3 g (2 mmol) of NaI was added to a reaction mixture. Yield: 56%. ^{1}H NMR ($CDCl_3$, *δ*, ppm) 10.09 (s, 1H, NC*H*-N), 7.62 (s, 1H, NC*H*-C), 7.53 (s, 1H, NC*H*-C), 7.40-7.28 (m, 6H, H_{Ar}), 6.99 (s, 1H, H_{Ar}), 6.97 (s, 1H, H_{Ar}), 4.73 (q, *J* = 11.1 Hz, 2H, OCH_2), 2.34 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 1.99 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, *δ*, ppm) 142.4 (NCN), 141.7 (C_{arom}), 139.5 (C_{arom}), 139.2 (C_{arom}), 135.6 (C_{arom}), 135.4 (C_{arom}), 134.3 (C_{arom}), 133.9 (C_{arom}), 130.4 (C_{arom}), 130.3 (C_{arom}), 130.2 (C_{arom}), 130.1 (C_{arom}), 129.7 (C_{arom}), 128.7 (C_{arom}), 128.5 (C_{arom}), 127.7 (C_{arom}), 126.8 (C_{arom}), 125.3 (C_{arom}), 123.7 (C_{arom}), 122.1 (q, $^1J_{C,F}$ = 290 Hz, CF_3), 121.7 (q, $^1J_{C,F}$ = 289 Hz, CF_3), 84.2–83.0 [m, C(CF_3)$_2$], 69.1 (OCH_2), 21.4 (CH_3), 21.2 (CH_3), 19.0 (CH_3), 18.4 (CH_3), 17.3 (CH_3); ^{19}F NMR ($CDCl_3$, *δ*, ppm) -67.55 (s, CF_3), -71.24 (s, CF_3). Anal. Calcd for $C_{30}H_{29}F_6IN_2O$ (%): C, 53.42; H, 4.33; N, 4.15. Found: C, 53.36; H, 4.34; N, 4.09.

Imidazolium iodide 10g. 0.3 g (2 mmol) of NaI was added to a reaction mixture. Yield: 75% (m.p. 109-111 °C). ^{1}H NMR ($CDCl_3$, *δ*, ppm) 10.34 (s, 1H, NC*H*-N), 7.59 (s, 1H, NC*H*-C), 7.56 (s, 1H, NC*H*-C), 7.48 (s, 1H, H_{Ar}), 7.41 (s, 1H, H_{Ar}), 7.05 (m, 2H, H_{Ar}), 5.92 (m, 1H, CH_2CH=CH_2), 5.45 (d, *J* = 17.4 Hz, 1H, CH=CH_2), 5.28 (d, *J* = 10.5 Hz, 1H, CH=CH_2), 4.22 (m, 2H, OCH_2), 2.45 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.13 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, *δ*, ppm) 142.5 (NCN), 141.8 (C_{arom}), 139.7 (C_{arom}), 139.2 (C_{arom}), 135.6 (C_{arom}), 134.4 (C_{arom}), 133.8 (C_{arom}), 131.8 (*C*H=CH_2), 130.4 (C_{arom}), 130.3 (C_{arom}), 130.1 (C_{arom}), 129.7 (C_{arom}), 126.8 (C_{arom}), 125.4 (C_{arom}), 123.9 (C_{arom}), 122.1 (q, $^1J_{C,F}$ = 290 Hz, CF_3) , 121.8 (q, $^1J_{C,F}$ = 289 Hz, CF_3), 118.4 (CH=CH_2), 84.1-82.0 [m, C(CF_3)$_2$], 68.2 (OCH_2), 21.5 (CH_3), 21.2 (CH_3), 19.0 (CH_3), 18.5 (CH_3), 17.5 (CH_3). ^{19}F NMR (CDCl3, δ, ppm) -67.70 (s, CF_3), -71.48 (s, CF_3). Anal. Calcd for $C_{26}H_{27}F_6IN_2O$ (%): C, 50.01; H, 4.36; N, 4.49. Found: C, 49.86; H, 4.26; N, 4.37.

Imidazolium iodide 10h. 0.3 g (2 mmol) of NaI was added to a reaction mixture. Reaction was carried out at 60°C. Yield: 68% (m.p. 108-110°C). ^{1}H NMR ($CDCl_3$, *δ*, ppm) δ 10.05 (s, 1H, NC*H*-N), 7.59 (s, 2H, NC*H*-C), 7.56 (s, 1H, NC*H*-C), 7.56 (s, 1H, H_{Ar}), 7.36 (s, 1H, H_{Ar}), 7.00 (s, 2H, H_{Ar}), 5.09 (s, 1H, C=CH_2), 4.95 (s, 1H, C=CH_2), 4.08 (d, *J* = 12.0 Hz, 1H, OCH_2), 4.00 (d, *J* = 12.1 Hz, 1H, OCH_2), 2.40 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 1.75 [s, 3H, C(=CH_2)CH_3]. ^{13}C NMR ($CDCl_3$, *δ*, ppm) δ 142.4 (NCN), 141.7 (C_{arom}), 139.6 (C_{arom}), 139.1 (C_{arom}), 135.6 (C_{arom}), 134.4 (C_{arom}), 133.8 (C_{arom}), 130.3 (C_{arom}), 130.2 (C_{arom}), 130.12 (C_{arom}), 130.06 (*C*=CH_2), 129.6 (C_{arom}), 126.8 (C_{arom}), 125.2 (C_{arom}), 124.0 (C_{arom}), 121.7 (q, $^1J_{C,F}$ = 290 Hz, CF_3), 122.0 (q, $^1J_{C,F}$ = 290 Hz, CF_3), 113.1 (C=CH_2), 83.8-82.6 [m, C(CF_3)$_2$], 70.4 (OCH_2), 21.5 (CH_3), 21.2 (CH_3), 19.4 [C(=CH_2)CH_3], 18.9 (CH_3), 18.5 (CH_3), 17.4 (CH_3). ^{19}F NMR ($CDCl_3$, *δ*, ppm) δ -68.30 (s, CF_3), -71.41 (s, CF_3). Anal. Calcd for $C_{27}H_{29}F_6IN_2O$ (%) C, 50.79; H, 4.58; N, 4.39. Found: C, 50.63; H, 4.70; N, 4.19.

Synthesis of imidazolium salts 11a,b. A mixture of imidazolium tetrafluoroborate **5** (0.5 mmol), anhydrous Cs_2CO_3 (2 mmol) and MeI/or EtI (2 mmol) was dissolved in 2 ml of CH_3CN. The resulting suspension was stirred until TLC analysis (acetone) showed absence of starting imidazolium salt **5** (6 h). Reaction mixture was concentrated in vacuum, residue dissolved in dichloromethane and filtered through Celite plug. The filtrate was evaporated to dryness. Crystallization from 2 ml of toluene afforded doubly alkylated imidazolium iodides **11a,b** as a white solids. ***Data for* 11a**: ^{1}H NMR ($CDCl_3$, *δ*, ppm) 7.94 (s, 1H, H_{Im}), 7.88 (s, 1H, H_{Im}), 7.52 (s, 1H, H_{Ar}), 7.47 (s, 1H, H_{Ar}), 7.09 (s, 2H, H_{Ar}), 3.62 (s, 3H, OCH_3), 2.48 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.04 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, *δ*, ppm) 146.0 (NCN), 142.3 (C_{Ar}), 142.0 (C_{Ar}), 138.3 (C_{Ar}), 135.5 (C_{Ar}), 134.3 (C_{Ar}), 133.8 (C_{Ar}), 130.6 (C_{Ar}), 130.3 (C_{Ar}), 129.7 (C_{Im}), 129.6 (C_{Ar}), 129.4 (C_{Ar}), 126.2 (C_{Im}), 125.9 (C_{Ar}), 123.9 (C_{Ar}), 122.24 (q, $^1J_{C,F}$ = 292 Hz, CF_3), 122.17 (q, $^1J_{C,F}$ = 290 Hz, CF_3), 83.3 [p, $^2J_{C,F}$ = 29 Hz, C(CF_3)$_2$], 57.0 (OCH_3), 21.5 ($C_{Ar}H_3$), 21.1 ($C_{Ar}H_3$), 18.5 ($C_{Ar}H_3$), 18.0 ($C_{Ar}H_3$), 17.7 ($C_{Ar}H_3$), 10.8 ($C_{Im}H_3$). ^{19}F NMR ($CDCl_3$, *δ*, ppm) -66.92 (s, CF_3), -69.81 (s, CF_3). Anal. Calcd for $C_{25}H_{27}F_6IN_2O$ (%) C, 49.03; H, 4.44; N, 4.57. Found C, 49.13; H, 4.51; 4.65. ***Data for* 11b**: ^{1}H NMR ($CDCl_3$, *δ,* ppm) 7.88 (s, 1H, H_{Im}), 7.83 (s, 1H, H_{Im}), 7.60 (s, 1H, H_{Ar}), 7.47 (s, 1H, H_{Ar}), 7.092 (s, 1H, H_{Ar}), 7.085 (s, 1H, H_{Ar}), 3.86 (pent, *J* = 7.2 Hz, 1H, OCH_2), 3.71 (pent, *J* = 7.2 Hz, 1H, OCH_2), 2.56 (m, 2H, CCH_2), 2.49 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 1.31 (t, *J* = 6.9 Hz, 3H, OCH_2CH_3), 0.83 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, CCH_2CH_3). ^{13}C NMR ($CDCl_3$, *δ*, ppm) 149.5 (NCN), 142.5 (C_{Ar}), 142.1 (C_{Ar}), 138.6 (C_{Ar}), 135.6 (C_{Ar}), 134.3 (C_{Ar}), 133.7 (C_{Ar}), 130.6 (C_{Ar}), 130.5 (C_{Ar}), 130.3 (br. s, C_{Im}), 129.9 (C_{Ar}), 129.2 (C_{Ar}), 126.57 (C_{Im}), 126.55 (C_{Ar}), 124.5 (C_{Ar}), 122.3 (q, $^1J_{C,F}$ = 290 Hz, CF_3), 121.9 (q, $^1J_{C,F}$ = 289 Hz, CF_3), 83.2 [p, $^2J_{C,F}$ = 29 Hz, C(CF_3)$_2$], 64.4 (OCH_2), 21.6 (CH_3), 21.1 (CH_3), 19.2 (CCH_2), 18.7 (CH_3), 18.3 (CH_3), 17.5 (CH_3), 15.5 (CH_2CH_3), 9.3 (CH_2CH_3). ^{19}F NMR ($CDCl_3$, *δ*, ppm) -68.40 (s, CF_3), -69.62 (s, CF_3). Anal. Calcd for $C_{27}H_{31}F_6IN_2O$ (%) C, 50.64; H, 4.88; N, 4.37. Found C, 50.73; H, 4.94; 4.35.

Generation of free carbene. A Schlenk flask, equipped with magnetic stir bar, was charged with 70 mg (0.125 mmol, 1 eq) of imidazolium tetrafluoroborate **10a**, 5 ml of dry degassed THF and 0.09 ml of 1.7M KO*t*-Am in toluene. The reaction mixture was allowed to stir for 30 min at room temperature, and then THF was evaporated in vacuum. The solid residue was triturated with 1 ml of dry C_6D_6, filtered and transferred to a J Young NMR tube. ^{1}H NMR (C_6D_6, *δ*, ppm) 7.53 (s, 1H, H_{Ar}), 6.88-6.30 (m 4H, H_{Ar}, H_{Im}), 5.60 (br.s, 1H, H_{Ar}), 3.38 (s, 3H, OCH_3), 2.14 (s, 9H, CH_3), 2.00 (s, 3H, CH_3), 1.92 (s, 3H, CH_3). ^{13}C NMR (C_6D_6, *δ*, ppm) 220.1 (d, *J* = 3.9 Hz, NCN), 140.8 (C_{arom}), 139.6 (C_{arom}), 138.9 (C_{arom}), 138.1 (C_{arom}), 137.4 (C_{arom}), 134.2 (C_{arom}), 125.4 (C_{arom}), 123.5 (q, $^1J_{C,F}$ = 292 Hz, CF_3), 123.0 (q, $^1J_{C,F}$ = 289 Hz, CF_3), 122.9 (C_{arom}), 120.0 (C_{arom}), 86.2-84.3 [m, C(CF_3)$_2$], 56.2 (OCH_3), 30.1 (CH_3), 21.0 (CH_3), 18.8 (CH_3), 18.5 (CH_3), 18.2 (CH_3). ^{19}F NMR (C_6D_6, *δ*, ppm) -66.93 (s, CF_3), -69.96 (s, CF_3).

Synthesis of rhodium complex 12. A 20 ml Schlenk flask was charged with 0.102 g (0.18 mmol) of imidazolium tetrafluoroborate **10a** followed by 10 ml of dry THF. Resulting suspension was degassed with Ar, cooled to 0°C and 0.10 ml of 1.7M potassium *tert*-pentoxide solution in toluene was added. Reaction mixture was stirred at ambient temperature for 30 min and resulting cloudy solution was added to solution of 0.0375 g (0.08 mmol) of chloro(1,5-cycloocta-diene)rhodium(I) dimer. Obtained yellow solution was stirred overnight, and then opened to atmosphere; all volatiles were removed in vacuum. Residue was dissolved in minimal amount of CH_2Cl_2 and purified by flash chromatography using CH_2Cl_2 as eluent, followed by 5:1 CH_2Cl_2-acetone mixture to yield 60 mg (55%) of product as yellow solid. ^{1}H NMR ($CDCl_3$, *δ*, ppm) 7.36 (s, 1H, H_{Im}), 7.34 (s, 1H, H_{Im}), 7.06 (s, 1H, H_{Ar}), 7.02 (s, 1H, H_{Ar}), 6.99 (s, 1H, H_{Ar}), 6.94 (s, 1H, H_{Ar}), 4.69-4.55 (m, 1H, H_{Ar}), 4.34 (q, *J* = 7.2, 6.7 Hz, 1H, CH_2CH), 3.73-3.59 (m, 1H, CH_2CH), 3.49 (s, 3H, OCH_3), 3.25-3.14 (m, 1H, CH_2CH), 2.45 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 1.92-1.67 (m, 4H, CH_2CH_2), 1.63-1.35 (m, 4H, CH_2CH_2). ^{13}C NMR ($CDCl_3$, *δ*, ppm) 183.9 (d, $^1J_{Rh,C}$ = 53 Hz, NCN), 141.7 (C_{arom}), 138.7 (C_{arom}), 138.5 (C_{arom}), 138.2 (C_{arom}), 136.6 (C_{arom}), 134.4 (C_{arom}), 134.1 (C_{arom}), 129.8 (C_{arom}), 128.4 (C_{arom}), 127.2 (C_{arom}), 125.7 (C_{arom}), 124.0 (q, $^1J_{C,F}$ = 293 Hz, CF_3), 123.8 (d, *J* = 3.8 Hz, C_{arom}), 122.7 (C_{arom}), 122.5 (q, $^1J_{C,F}$ = 293 Hz, CF_3), 97.3 (d, $^1J_{Rh,C}$ = 7.9 Hz, CH_2CH), 95.1 (d, $^1J_{Rh,C}$ = 7.1 Hz, CH_2CH), 84.2 [m, $^2J_{C,F}$ = 27 Hz, C(CF_3)$_2$], 71.0 (d, $^1J_{C,F}$ = 15 Hz, CH_2CH), 66.1 (d, $^1J_{C,F}$ = 14 Hz, CH_2CH), 56.9 (OCH_3), 34.2 (CH_2), 31.3 (CH_2), 29.9 (CH_2), 27.1 (CH_2), 21.5 (CH_3), 21.3 (CH_3), 20.9 (CH_3), 20.2 (CH_3), 18.9 (CH_3). ^{19}F NMR ($CDCl_3$, *δ*, ppm)

-66.76 (s, CF_3), -67.56 (s, CF_3). HRMS *m/z* (ESI) calcd for $C_{32}H_{36}F_6N_2ORh$ $[M\text{-}Cl]^+$: 681.1787, found 681.1781.

Synthesis of palladium complex 13. The mixture of 0.2 g (0.32 mmol) of imidazolium iodide **10g** and 0.0883 g (0.29 mmol) of $Pd(acac)_2$ were dissolved in 5 ml of 1,4-dioxane. Reaction mixture was heated at 90°C until TLC showed full conversion of starting $Pd(acac)_2$ to product (30 min). After cooling to room temperature the reaction mixture was evaporated in vacuum, residue was dissolved in minimum amount of EtOAc. Purification by flash chromatography using 6:1 hexanes-EtOAc mixture yielded 0.202 g (84%) of product as yellow solid (m.p. 156-158 °C, dec.). ^{1}H NMR ($CDCl_3$, *δ*, ppm) 7.54 (s, 1H, H_{Im}), 7.26 (s, 1H, H_{Im}) 7.06 (s, 1H, H_{Ar}), 7.01 (s, 1H, H_{Ar}), 6.98 (s, 1H, H_{Ar}), 6.94 (s, 1H, H_{Ar}), 5.89-5.72 (m, 1H, CH=CH_2), 5.25 (d, *J* = 17.4 Hz, 1H, CH=CH_2), 5.16 (d, *J* = 10.5 Hz, 1H, CH=CH_2), 5.06 [s, 1H, C(O)CH], 4.48-4.17 (m, 2H, OCH_2), 2.41 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 1.78 [s, 3H, C(O)CH_3], 1.75 [s, 3H, C(O)CH_3]. ^{13}C NMR ($CDCl_3$, *δ*, ppm) 186.6 (*C*=O), 183.4 (*C*=O), 154.9, (N*C*N), 141.9 (C_{arom}), 139.6 (C_{arom}), 139.2 (C_{arom}), 136.2 (C_{arom}), 135.9 (C_{arom}), 135.7 (C_{arom}), 135.7 (C_{arom}), 135.5 (C_{arom}), 135.4 (C_{arom}), 134.8 (C_{arom}), 134.5 (C_{arom}), 133.2 (C_{arom}), 129.7 (C_{arom}), 129.0 (C_{arom}), 126.4 (C_{arom}), 126.1 (C_{arom}), 123.5, 122.8 (q, $^1J_{C,F}$ = 292 Hz, *C*F_3), 122.5 (q, $^1J_{C,F}$ = 291 Hz, *C*F_3), 117.3 (CH=*C*H2), 99.6 (*C*H=CH2), 98.9 (*C*H=CH2), 83.9 [m, $^2J_{C,F}$ = 30 Hz, *C*$(CF_3)_2$], 68.6 (O*C*H_2), 27.2 [C(O)*C*H_3], 27.0 [C(O)*C*H_3], 25.5 [C(O)*C*H_3], 25.1 [C(O)*C*H_3], 21.5 (*C*H_3), 21.2 (*C*H_3), 20.2 (*C*H_3), 19.3 (*C*H_3), 18.9 (*C*H_3). ^{19}F NMR ($CDCl_3$, *δ*, ppm) -67.23 (s, C*F*$_3$), -69.00 (s, C*F*$_3$). Anal. Calcd for $C_{31}H_{34}F_6IN_3OPd$ (%): C, 44.86; H, 4.13; N, 3.38. Found: C, 45.01; H, 3.99; N, 3.29.

Synthesis of palladium complex 14. *Method A.* A 20 ml Schlenk flask was charged with 0.286 g (0.51 mmol) of imidazolium tetrafluoroborate **10a** followed by 10 ml of dry THF. Resulting suspension was degassed with Ar, cooled to 0°C and 0.3 ml of 1.7M potassium *tert*-pentoxide solution in toluene was added. Reaction mixture was stirred at ambient temperature for 30 min and resulting cloudy solution was added to suspension of 0.198 g (0.49 mmol) of bis(3-chloropyridine)palladium chloride. Obtained red solution was stirred overnight, and then opened to atmosphere; all volatiles were removed in vacuum. Residue was dissolved in minimal amount of CH_2Cl_2 and purification by flash chromatography using CH_2Cl_2 as eluent yielded 0.35 g (90%) of yellow powder (m.p. 141-143 °C). ^{1}H NMR ($CDCl_3$, *δ*, ppm) 8.53 (d, $J_{H,H}$ = 2.3 Hz, 1H, H_{Py}), 8.45 (dd, $J_{H,H}$ = 5.6, 1.4 Hz, 1H, H_{Py}), 7.54 (ddd, $J_{H,H}$ = 8.2, 2.2, 1.4 Hz, 1H, H_{Py}), 7.48 (s, 1H, H_{Im}), 7.26 (s, 1H, H_{Im}), 7.10 – 7.00 (m, 5H, H_{Ar}, H_{Py}), 3.66 (s, 3H, OCH_3), 2.44 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.17 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, *δ*, ppm) 151.7 (NCN), 150.7 (C_{arom}), 149.7 (C_{arom}), 141.4 (C_{arom}), 139.2 (C_{arom}), 139.0 (C_{arom}), 137.4 (C_{arom}), 136.2 (C_{arom}), 135.7 (C_{arom}), 135.7 (C_{arom}), 135.2 (C_{arom}), 133.9 (C_{arom}), 132.0 (C_{arom}), 129.7 (C_{arom}), 129.6 (C_{arom}), 127.7 (C_{arom}), 126.6 (C_{arom}), 125.1 (C_{arom}), 124.4 (C_{arom}), 123.7 (q, $^1J_{C,F}$ = 294 Hz, *C*F_3), 123.2 (C_{arom}), 122.9 (q, $^1J_{C,F}$ = 293 Hz, *C*F_3), 83.6 [hept, $^2J_{C,F}$ = 28 Hz, *C*$(CF_3)_2$], 56.8 (O*C*H_3), 21.7 (*C*H_3), 21.3 (*C*H_3), 20.4 (*C*H_3), 19.6 (*C*H_3), 19.6 (*C*H_3). ^{19}F NMR ($CDCl_3$, *δ*, ppm) -66.34 (s, C*F*$_3$), -68.42 (s, C*F*$_3$). Anal. Calcd for $C_{29}H_{29}Cl_3F_6N_3OPd$ (%): C, 45.69; H, 3.83; N, 5.51. Found: C, 45.49; H, 3.93; N, 5.71. *Method B.* A 20 ml Schlenk flask was charged with 0.172 g (0.31 mmol) of imidazolium tetrafluoroborate **10a** followed by 10 ml of dry THF. Resulting suspension was degassed with Ar, cooled to 0°C and 0.17 ml of 1.7M potassium *tert*-pentoxide solution in toluene was added. Reaction mixture was stirred at ambient temperature for 30 min and resulting cloudy solution was added to solution of 0.0985 g (0.26 mmol) of bis(benzonitrile)palladium chloride. Obtained red solution was stirred overnight, all volatiles were removed in vacuum. Residue was dissolved in minimal amount of CH_2Cl_2 and purified by flash chromatography using CH_2Cl_2 as eluent. After purification palladium complex was dissolved in 5 ml of dichloromethane and 0.5 g (4.4 mmol) of 3-chloropyridine was added. Reaction mixture was stirred overnight; all volatiles were removed in vacuum, purification by flash chromatography using CH_2Cl_2 yielded 0.13 g (56%) of complex **14**.

Palladium complex 15. Obtained by analogy with **14** using method *A*. Yield: 85 % (m.p. 97-99 °C). ^{1}H NMR ($CDCl_3$, *δ*, ppm) 8.54 (d, $J_{H,H}$ = 2.3 Hz, 1H, H_{Py}), 8.46 (dd, $J_{H,H}$ = 5.6, 1.4 Hz, 1H, H_{Py}), 7.57-7.49 (m, 2H, H_{Py}, H_{Im}), 7.26 (s, 1H, H_{Im}), 7.10-7.01 (m, 5H, H_{Ar}, H_{Py}), 4.12 (m, 2H, CH_2CH$_3$), 2.45 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 1.09 (t, $^3J_{H,H}$ = 7.0 Hz, 3H, CH$_2$CH_3). ^{13}C NMR ($CDCl_3$, *δ*, ppm) 152.0 (NCN), 150.7 (C_{arom}), 149.7 (C_{arom}), 139.2 (C_{arom}), 139.0 (C_{arom}), 137.5 (C_{arom}), 136.2 (C_{arom}), 135.9 (C_{arom}), 135.8 (C_{arom}), 135.2 (C_{arom}), 133.9 (C_{arom}), 129.7 (C_{arom}), 129.6 (C_{arom}), 128.1 (C_{arom}), 126.9 (C_{arom}), 126.3 (C_{arom}), 124.4 (C_{arom}), 123.3, 123.2 (q, $^1J_{C,F}$ = 293 Hz, CF_3), 123.1 (q, $^1J_{C,F}$ = 293 Hz, CF_3), 64.7 (O*C*H$_2$), 21.6 (*C*H$_3$), 21.3 (*C*H$_3$), 20.5 (*C*H$_3$), 19.8 (*C*H$_3$), 19.7 (*C*H$_3$), 15.8 (CH$_2$*C*H$_3$). ^{19}F NMR ($CDCl_3$, *δ*, ppm) -65.25 (q, *J* = 6.5 Hz, C*F*$_3$), -69.55 (q, *J* = 7.2 Hz, C*F*$_3$). Anal. Calcd for $C_{30}H_{31}Cl_3F_6N_3OPd$ (%): C, 46.41; H, 4.02; N, 5.41. Found: C, 46.28; H, 3.95; N, 5.21.

Acknowledgements

This work was financially supported by the Russian Scientific Foundation (grant RSF № 16-13-10364).

Keywords: N-Heterocyclic carbenes • unsymmetrical imidazolium salts • fluorinated NHC ligands • metal catalysis

[1] a) S. Díez-González, RSC catalysis series N-Heterocyclic Carbenes, RSC Publishing, Cambridge, **2011**; for selected Reviews on NHCs as ligands in TM catalysis, see: b) D. Bézier, J.-B. Sortais, C. Darcel, *Adv. Synth. Catal*. **2013**, *355*, 19-33; c) C. Valente, S. Çalimsiz, K. H. Hoi, D. Mallik, M. Sayah, M. G. Organ, *Angew. Chem. Int. Ed*. **2012**, *51*, 3314-3332; *Angew. Chem.* **2012**, *124*, 3370-3388; d) G. C. Vougioukalakis, R H. Grubbs, *Chem. Rev*. **2010**, *110*, 1746-1787; e) G. C. Fortman, S. P. Nolan, *Chem. Soc. Rev.,* **2011**, *40*, 5151-5169; f) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev*. **2009**, *109*, 3612-3676; g) M.N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485-496.

[2] a) D. S. McGuinness, K. J. Cavell, *Organometallics* **1999**, *18*, 1596-1605; b) D. S. McGuinness, K. J. Cavell, *Organometallics* **2000**, *19*, 741-748; c) J. Schwarz, V. P. W. Böhm, M. G. Gardiner, M. Grosche, W A. Herrmann, W. Hieringer, G. Raudaschl-Sieber, *Chem. Eur. J.* **2000**, *6*, 1773-1780; d) M. H. Viciu, R. M. Kissling, E. D. Stevens, S. P. Nolan, *Org. Lett*. **2002**, *4*, 2229-2231; e) M. S. Viciu, R. F. Germaneau, S. P. Nolan, *Org. Lett*. **2002**, *4*, 4053-4056; f) W. A. Herrmann, *Angew. Chem Int. Ed.* **2002**, *41*, 1290-1309; *Angew. Chem.* **2002**, *114*, 1342-1363; g) E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Angew. Chem. Int. Ed.* **2007**, *46*, 2768-2813; *Angew. Chem.* **2007**, *119*, 2824-2870; h) S. Würtz, F. Glorius, *Acc. Chem. Res*. **2008**, *41*, 1523-1533; i) C. Samojłowicz, M. Bieniek, K. Grela, *Chem. Rev*. **2009**, *109*, 3708-3742; j) W. A. L. van Otterlo, C. B. de Koning, *Chem. Rev*. **2009**, *109*, 3743-3782; k) S. Monfette, D. E. Fogg, *Chem. Rev.* **2009**, *109*, 3783-3816; l) B. Alcaide, P. Almendros, A. Luna, *Chem. Rev*. **2009**, *109*, 3817-3858; m) Y. Zhang, V. Csar, G. Storch, N. Lugan, G. Lavigne, *Angew. Chem. Int. Ed*. **2014**, *53*, 6482-6486; *Angew. Chem.* **2014**, *126*, 6600-6604; n) D. Zhang, G. Zi, *Chem. Soc. Rev.*, **2015**, *44*, 1898-1921; o) A. Nasr, A. Winkler, M. Tamm, *Coord. Chem. Rev*. **2016**, *316*, 68-124.

[3] a) M. G. Organ, S. Çalimsiz, M. Sayah, K. H. Hoi, A. J. Lough, *Angew. Chem. Int. Ed*. **2009**, *48*, 2383-2387; *Angew. Chem.* **2009**, *121*, 2419-

2423; b) A. Chartoire, X. Frogneux, S. P. Nolan, *Adv. Synth. Catal*. **2012**, *354*, 1897-1901; c) S. Meiries, A. Chartoire, A. M. Z. Slawin, S. P. Nolan, *Organometallics* **2012**, *31*, 3402-3409; d) A. Chartoire, X. Frogneux, A. Boreux, A. M. Z. Slawin, S. P. Nolan, *Organometallics* **2012**, *31*, 6947-6951; e) A. Chartoire, M. Lesieur, L. Falivene, A. M. Z. Slawin, L. Cavallo, C. S. J. Cazin, S. P. Nolan, *Chem. Eur. J.* **2012**, *18*, 4517-4521; f) S. Meiries, G. Le Duc, A. Chartoire, A. Collado, K. Speck, K. S. A. Arachchige, A. M. Z. Slawin, S. P. Nolan, *Chem. Eur. J*. **2013**, *19*, 17358-17368; g) E. Marelli, A. Chartoire, G. Le Duc, S. P. Nolan, *ChemCatChem*, **2015**, *7*, 4021-4024; h) G. Liu, C. Liu, X. Zhao, J. Wang, *RSC Adv.*, **2016**, 44475-44479; i) A. Chartoire, C. Claver, M. Corpet, J. L Krinsky, J. Mayen, D. J. Nelson, S. P Nolan, I. Peñafiel, R. Woodward, R. E. Meadows, *Org. Process Res. Dev.*, **2016**, *20*, 551-557.

[4] a) A. Albright, R. E. Gawley, *J. Am. Chem. Soc*. **2011**, *133*, 19680-19683; b) C. T. Check, K. P. Jang, C. B. Schwamb, A. S. Wong, M. H. Wang, K. A. Scheidt, *Angew. Chem. Int. Ed*. **2015**, *54*, 4264-4268; *Angew. Chem.* **2015**, *127*, 4338-4342.

[5] a) J. Tornatzky, A. Kannenberg, S Blechert. *Dalton Trans*. **2012**, *41*, 8215-8225; b) S. Kress, S. Blechert, *Chem. Soc. Rev.,* **2012**, *41*, 4389-4408; c) P. Queval, C. Jahier, M. Rouen, I. Artur, J.-C. Legeay, L. Falivene, L. Toupet, C. Crévisy, L. Cavallo, O. Baslé, M. Mauduit, *Angew. Chem. Int. Ed*. **2013**, *52*, 14103-14107; *Angew. Chem.* **2013**, *125*, 14353-14357; d) C. Jahier-Diallo, M. S. T. Morin, P. Queval, M. Rouen, I. Artur, P. Querard, L. Toupet, C. Crévisy, O. Baslé, M. Mauduit, *Chem. Eur. J*. **2015**, *21*, 993-997; e) G. Price, A. R. Bogdan, A. L. Aguirre, T. Iwai, S. W. Djuric, M. G. Organ, *Catal. Sci. Technol.*, **2016**, *6*, 4733-4742.

[6] a) G. Xu, S. R. Gilbertson, *Org. Lett.*, **2005**, *7*, 4605-4608; b) K. Hirano, S. Urban, C. Wang, F. Glorius, *Org. Lett.*, **2009**, *11*, 1019-1022; c) Y. Kong, S. Xu, H. Song, B. Wang, *Organometallics* **2012**, *31*, 5527-5532; d) T. Lv, Z. Wang, J. You, J. Lan, G. Gao, *J. Org. Chem*., **2013**, *78*, 5723-5730; e) L. Dang, J. Guo, H. Song, B. Liu, B. Wang, *Dalton Trans*., **2014**, *43*, 17177-17183; f) S. Li, F. Yang, T. Lv, J. Lan, G. Gao, J. You, *Chem. Commun.,* **2014**, *50*, 3941-3943.

[7] a) H. Hiyama, *Organofluorine Compounds: Chemistry and Applications*; Springer: Berlin, **2000**; b) R. D. Chambers, *Fluorine in Organic Chemistry*; Blackwell Publishing Ltd.: Oxford, U.K., **2004**; c) P. Kirsch, *Modern Fluoroorganic Chemistry: Synthesis, Reactivity, Applications*; Wiley-VCH: 2-nd Ed., **2013**; d) K. Uneyama, *Organofluorine Chemistry*; Blackwell Publishing Ltd.: Oxford, U.K., **2006**; e) K. Müller, C. Faeh, F.Diederich, *Science* **2007**, *317*, 1881-1886; f) J. Wang, M. Sánchez-Roselló, J. L. Aceña, C. del Pozo, A. E. Sorochinsky, S. Fustero, V. A. Soloshonok, H. Liu, *Chem. Rev*. **2014**, *114*, 2432-2506.

[8] a) S. Purser, P. R. Moore, S. Swallow, V. Gouverneur, *Chem. Soc. Rev*. **2008**, *37*, 320-330; b) I. Ojima, Ed. *Fluorine in Medicinal Chemistry and Chemical Biology*; Wiley-Blackwell: Chichester, U.K., **2009**.

[9] a) R. E. Banks, B. E. Smart, J. C. Tatlow, *Organofluorine Chemistry: Principles and Commercial Applications*; Plenum Press: New York, **1994**. b) F. Giornal, S. Pazenok, L. Rodefeld, N. Lui, J.-P. Vors, F. R. Leroux, *J. Fluorine Chem*. **2013**, 152, 2-11.

[10] R. Berger, G. Resnati, P. Metrangolo, E. Weber, J. Hulliger, *Chem. Soc. Rev*. **2011**, *40*, 3496-3508.

[11] a) M. Schlosser, *Angew. Chem. Int. Ed.* **1998**, *37*, 1496-1513; *Angew. Chem.* **1998**, 110, 1538-1556; b) D. O'Hagan, *Chem. Soc. Rev*. **2008**, *37*, 308-319.

[12] a) S. Fustero, A. Simón-Fuentes, P. Barrio, G. Haufe, *Chem. Rev*., **2015**, *115*, 871-930; b) V. Kolaříková, O. Šimůnek, M. Rybáčková, J. Cvačka, A. Březinová, J. Kvíčala, *Dalton. Trans*., **2015**, *44*, 19663-19673.

[13] A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C. W. Lehmann, R. Mynott, F. Stelzer, O. R. Thiel, *Chem. Eur. J*. **2001**, *7*, 3236-3253.

[14] M. Skalický, V. Skalická, J. Paterová, M. Rybáčková, M. Kvíčalová, J. Cvačka, A. Březinová, J. Kvíčala, *Organometallics*, **2012**, *31*, 1524-1532.

[15] a) T. Ritter, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc*. **2006**, *128*, 11768-11769; b) D. R. Anderson, D. J. O'Leary, R. H. Grubbs, *Chem. Eur. J*. **2008**, *14*, 7536-7544.

[16] a) J. M. Berlin, K. Campbell, T. Ritter, T. W. Funk, A. Chlenov, R. H. Grubbs, *Org. Lett.* **2007**, *9*, 1339-1342; b) G. C. Vougioukalakis, R. H. Grubbs, *Organometallics* **2007**, *26*, 2469-2472; c) G. C. Vougioukalakis, R. H. Grubbs, *Chem. Eur. J.* **2008**, *14*, 7545-7556.

[17] S. M. Masoud, A. K. Mailyan, V. Dorcet, T. Roisnel, P. H. Dixneuf, C. Bruneau, S. N. Osipov, *Organometallics*, **2015**, *34*, 2305-2313.

[18] a) A. J. Arduengo, J. S. Dolphin, G. Gurău, W. J. Marshall, J. C. Nelson, V. A. Petrov, J. W. Runyon, *Angew. Chem. Int. Ed.* **2013**, *52*, 10871-10873; *Angew. Chem.* **2013**, *125*, 11071-11073; b) A. J. Arduengo, G. Gurau, S. P. Kelley, W. J. Marshall, J. W. Runyon, *Angew. Chem. Int. Ed*. **2013**, *52*, 5110-5114; *Angew. Chem*. **2013**, *125*, 5214-5218.

[19] A. Fürstner, M. Alcarazo, V. César, C. W. Lehmann, *Chem. Commun*., **2006**, 2176-2178.

[20] a) D. Katayev, Y.-X. Jia, A. K. Sharma, D. Banerjee, C. Besnard, R. B. Sunoj, E. P. Kündig, *Chem. Eur. J.* **2013**, *19*, 11916-11927; b) A. Schumacher, M. Bernasconi, A. Pfaltz, *Angew. Chem. Int. Ed*. **2013**, *52* 7422-7425; *Angew. Chem.*, **2013**, 125, 7570-7573; c) J. S. E. Ahlin, P. A. Donets, N. Cramer, *Angew. Chem. Int. Ed*., **2014**, *53*, 13229-13233; *Angew. Chem.*, **2014**, *126*, 13445-13449; d) M. J. Asay, S. P. Fisher, S. E. Lee, F. S. Tham, D. Borchardt, V. Lavallo, *Chem. Commun.,* **2015**, *51*, 5359-5362.

[21] T. Makino, H. Masu, K. Katagiri, R. Yamasaki, I. Azumaya, S. Saito, *Eur. J. Inorg. Chem.* **2008**, 4861-4865.

[22] R. Visbal, A. Laguna, M. C. Gimeno, *Chem. Commun.*, **2013**, *49*, 5642-5644.

[23] a) J. J. Van Veldhuizen, J. E. Campbell, R. E. Giudici, A. H. Hoveyda, *J. Am. Chem. Soc*. **2005**, *127*, 6877-6882; b) M. K. Brown, T. L. May, C. A Baxter, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2007**, *46*, 1097-1100; *Angew. Chem.* **2007**, 119, 1115-1118.

[24] a) W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus, *Chem. Eur. J.*, **1996**, 772-780; b) J. Mesnager, P. Lammel, E. Jeanneau, C. Pinel, *Applied Catalysis A: General* **2009**, *368*, 22-28.

[25] M. Iglesias, D. J. Beetstra, J. C. Knight, L.-L. Ooi, A. Stasch, S. Coles, L. Male, M. B. Hursthouse, K. J. Cavell, A. Dervisi, I. A. Fallis, *Organometallics*, **2008**, 27, 3279-3289.

[26] A. J. Arduengo III, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.*, **1992**, *114*, 5530-5534.

[27] S. Meiries, A. Chartoire, A. M. Z. Slawin, S. P. Nolan, *Organometallics* **2012**, *31*, 3402-3409.

[28] J. L. Krinsky, A. Martínez, C. Godard, S. Castillón, C. Claver, *Adv. Synth. Catal.*, **2014**, *356*, 460-474.

[29] J. Nasielski, N. Hadei, G. Achonduh, E. A. B. Kantchev, C. J. O'Brien, A. Lough, M. G. Organ, *Chem. Eur. J*. **2010**, *16*, 10844-10853.

[30] E.-I. Negishi, *Handbook of Organopalladium Chemistry for Organic Synthesis*, Wiley-VCH, New York, **2002**.

[31] a) C. Valente, S. Çalimsiz, K. H. Hoi, D. Mallik, M. Sayah, M. G. Organ, *Angew. Chem. Int. Ed*., **2012**, *51*, 3314-3332; *Angew. Chem.*, **2012**, 124, 3370-3388; b) B. Atwater, N. Chandrasoma, D. Mitchell, M. J. Rodriguez, M. Pompeo, R. D. J Froese, M. G. Organ, *Angew. Chem. Int. Ed.*, **2015**, *54*, 9502-9506; *Angew. Chem.*, **2015**, 127, 9638-9642.

[32] C. Valente, M. Pompeo, M. Sayah, M. G. Organ, *Org. Process Res. Dev.* **2014**, *18*, 180-190.

[33] C. Capello, U. Fischer, K. Hungerbuhler, *Green Chem*. **2007**, *9*, 927-934.

[34] A. Krogul, J. Skupińska, G. Litwinienko, *Journal of Molecular Catalysis A: Chemical* **2011**, *337*, 9-16.

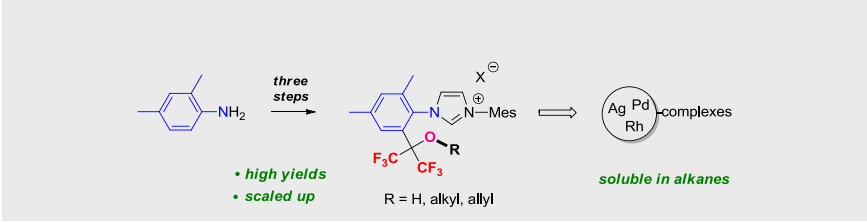
10.1002/chem.201700624

WILEY-VCH

Entry for the Table of Contents

Layout 1:

FULL PAPER



An efficient and scaled-up synthesis of the imidazole-based unsymmetrical NHC precursors bearing sterically demanding hexafluoroisopropylalkoxy-group [$(CF_3)_2$(OR)C-] in *ortho*-position of *N*-aryl substituent is reported. The method includes transformation of Mes-substituted oxazolinium tetrafluoroborate salt *via* the reaction with the corresponding binucleophilic fluorinated aniline and subsequent *O*-alkylation to access a new family of fluorinated NHC precursors.

*Maxim A. Topchiy, Maria A. Zotova, Salekh M. Masoud, Artur K. Mailyan, Ivan V. Ananyev, Sergey E. Nefedov, Andrey F. Asachenko, Sergey N. Osipov**

Page No. – Page No.

Fluorinated Unsymmetrical *N,N'*-Diaryl Imidazolium salts - new functionalized NHC ligand precursors