Charles University

Faculty of Science

Department of Organic and Nuclear Chemistry

Roman A. Kunetskiy

1,3-Dialkyl-4,5-dimethylimidazol-2-ylidene Amines as a New Class of Strong Electron Donors in Design and Synthesis of Organosuperbases and Stable Cations

PhD Thesis

Supervisors: Ullrich Jahn, PhD and Ilya M. Lyapkalo, PhD

Institute of Organic Chemistry and Biochemistry,

Academy of Sciences of the Czech Republic, v.v.i.

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Syntéza organosuperbazí a stabilních kationtů na bázi 1,3-dialkyl-4,5-dimethylimidazol-2-ylidenaminů jako nového druhu silných elektron-donorů

Dizertační práce

Školitelé: Ullrich Jahn, PhD a Ilya M. Lyapkalo, PhD

Ústav organické chemie a biochemie,
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V Praze .....

Roman A. Kunetskiy

Памяти Ильи Михайловича Ляпкало посвящается…

Dedicated to the memory of Ilya M. Lyapkalo…

Abstract

Simple and efficient method for the introduction of the new strong electron donor 1,3-dialkyl-4,5-dimethylimidazol-2-ylidene amino group (IMAM) in different organic molecules using 2-fluoroimidazolium or 2-chloroimidazolium salts was developed. According to this method, three new families of phase transfer catalysts and two new families of stable phosphorus-free organic superbases (SBs) were synthesized and studied. Selected phase transfer catalysts showed very high stability towards hydrolysis under different drastic basic conditions. Very high basicity of prepared SBs in solution as well as in the gas phase was studied and found to be caused by aromatization and steric strain release upon protonation. A new efficient method for amination of 1,3-dialkylimidazol-2-ylidenes as well as tris(dimethylamino)phosphine by *tert*-butyl azide was developed. The basicity of new highly sterically hindered 1,3-di-*tert*-butyl-4,5-dimethylimidazol-2-ylidene was estimated, pK_{BH+}(DMSO) = 24.8.

Abstrakt

Byla vyvinuta jednoduchá a efektivní metoda pro zavedení nové silně elektron-donorní 1,3-dialkyl-4,5-dimethylimidazol-2-yliden aminové skupiny (IMAM) do různých organických molekul za použití 2-fluorimidazoliových nebo 2-chlorimidazoliových solí. Touto metodou byly syntetizovány a studovány tři nové druhy katalyzátorů fázového přenosu a dva nové druhy stabilních nefosforných organických superbazí (SB). Vybrané katalyzátory fázového přenosu se ukázaly velice stabilní vůči hydrolýze za různých silně bazických podmínek. Byla studována velmi vysoká bazicita připravených SB v roztoku či v plynné fázi a bylo zjištěno, že je způsobena aromatizací a uvolněním sterického napětí po protonaci. Byla vyvinuta nová efektivní metoda pro aminaci 1,3-dialkylimidazol-2-ylidenů a tris(dimethylamino)fosfinu *terc*-butylazidem. Byla určena bazicita nových vysoce stericky bráněných 1,3-di-*terc*-butyl-4,5-dimethylimidazol-2-ylidenů, pK_{BH}^{+}(DMSO) = 24.8.

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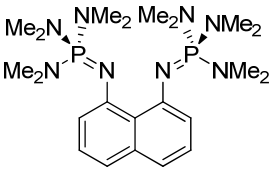
1. Introduction: Superbases and Delocalized Lipophilic Cations

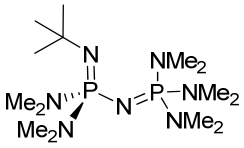
1.1. Definition and Application

Neutral organic superbases[1,2*] (SBs) and delocalized lipophilic cations[3,4,5,6] (DLCs) are important objects of study in modern organic chemistry. For the last 20 years, due to the activities of groups of Schwesinger,[7,8,9] Verkade,[10,11,12] Tan,[6,13] Ishikawa,[14,15] Leito,[16,17,18] Teplý,[19,20] Kolomeitsev,[18,21,22] and many others,[23,24,25,26,27] a significant amount of new compounds from both families was designed, synthesized and/or studied. The efficiency of these substances first of all as catalysts and activators in modern organic synthesis was demonstrated.



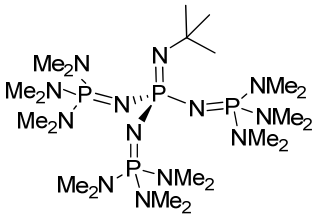
i1

One of the strongest `proton sponge`
pK_{BH+} = 29.9 (MeCN)[27]



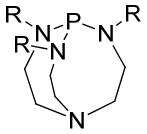
i2

Schwesinger's P_2 base,
very strong organic base,
efficient organocatalyst,
pK_{BH+} = 33.5 (MeCN)[8]



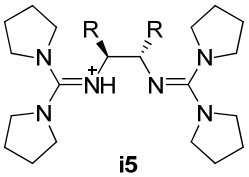
i3

Schwesinger's P_4 base,
one of the strongest neutral bases,
efficient organocatalyst,
pK_{BH+} = 30.2 (DMSO)[8]



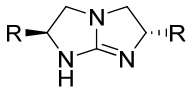
i4

Verkade's base,
efficient organocatalyst and
important ligand for
transition metals catalysis,
pK_{BH+} (R = *i*Pr) = 33.6 (MeCN)[12]



i5

Chiral organocatalyst
for Pudovik reaction
(up to 94% *ee*)



i6

Chiral organocatalysts
for many Michael reactions
(up to 97% *ee*)

Figure 1.1. Some remarkable examples of superbases: **i1-i6**.[2,8,10,13,27]

* Superbases are organic bases stronger than DMAN (1,8-bis(dimethylamino)naphthalene, proton sponge) having pK_{BH+} > 18.2 (in MeCN) or > 7.47 (in DMSO), GB > 239 kcal mol^{-1}, PA > 245.3 kcal mol^{-1}.

Particularly, superbases of various designs have found significant applications in chiral[2,13] and achiral[10, 28 , 29 , 30] homogeneous organocatalysis and as ligands[11, 31] in metal catalysis (Figure 1.1). Compared to ionic bases absence of a coordinating metal ion plays key role in their specific reativity.[1]

Commercially available superbases such as DBN, DBU, TMG and P_1-phosphazene bases (Figure 1.2) were entered a long time ago into the tool kit of modern organic synthesis as strong Brønsted bases, which are used catalytically or stochiometrically.[1]

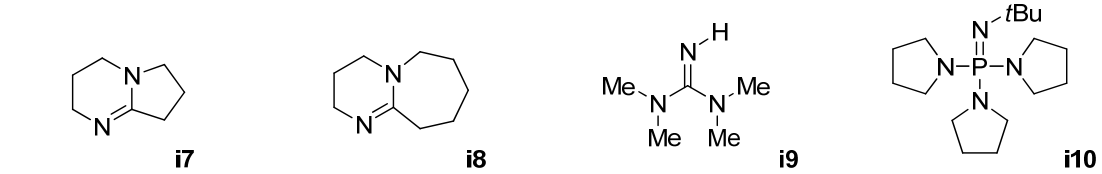
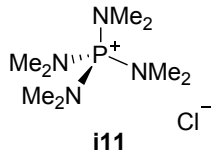


Figure 1.2. Some simple commercially available superbases as Brønsted bases.[1,16]

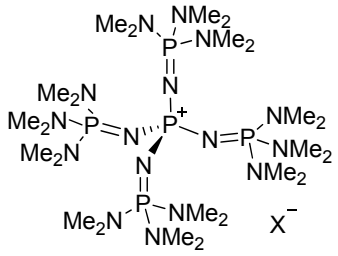
On the other hand, delocalized lipophilic cations have found significant use in chiral[6] and achiral[32,33,34] phase transfer catalysis (PTC), frequently as carriers of OH^-, $OAlk^-$ or F^- anions to the organic phase (Figure 1.3), often applied under drastic conditions (i.e. elevated temperatures, highly basic and/or nucleophilic media), where long lifetimes even in such conditions are required to maintain their activity.[4] The level of cation stabilization defines the "level of freedom" of the anion and also influences the contribution of a DLC to a transition state of the reaction that can modulate the reactivity and the selectivity.[5]

Those special properties of DLCs make them efficient reagents and catalysts in two important industrial processes, namely anionic polymerization[35,36,37] and the Halex process.[32] The latter is the nucleophilic replacement of halogen atom in organic halogenides by fluorine, using usually organic chlorides as staring materials and alkaline metal fluorides as sources of fluoride ion.



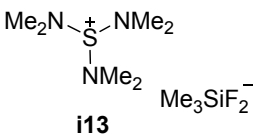
i11

P_1-cation:
Efficient PTC in Halex process



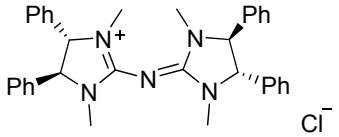
i12

P_5-cation:
One of the most stable organic cations
efficient PTC in some polymerization processes



i13

TASF
Activator of silyl enol ethers and
allyltrifluorosilanes



i14

Chiral PTC
for some Michael reactions (up to 97% *ee*)

Figure 1.3. Some remarkable examples of delocalized lipophilic cations: **i11-i14**.[4,6,38]

DLCs found application in medicinal chemistry and biochemistry as well. Since time of the first selective staining of mitochondria with Janus green dye, research of mitochondria in living cells and mitochondria targeted agents was inseparably linked with DLCs.[39] Two important features of DLCs, namely lipophilicity and a positive charge, allows these substances to pass easily through the internal mitochondrial membrane and to concentrate inside because of a significant negative membrane potential inherent only to living mitochondria. Thus the concentration of DLC in a cell becomes approximately 5-10 times higher inside the mitochondria than outside, and approximately 100-500 times higher than outside of a cell.[39] Therefore, most classical fluorescence probes for mitochondria either belong to DLC subset (e.g. Rhodamine 123 and DASPEI, Figure 1.4) or produce them *in vivo*.[40]

Recently a growing interest to the DLCs subset was caused by demonstration of the ability of some compounds to selectively target mitochondria of carcinoma cells resulting in their selective killing.[41,42,43] The selectivity was caused by a hyperpolarization of the mitochondria inner membrane in the tumor compared to normal cells. For example, recently Leder demonstrated an efficient inhibition of proliferation of many mammary epithelial, *neu-*

overexpressing cells, as well as a variety of human breast cancer cell lines using DLC **i17** (Figure 1.4).[44]

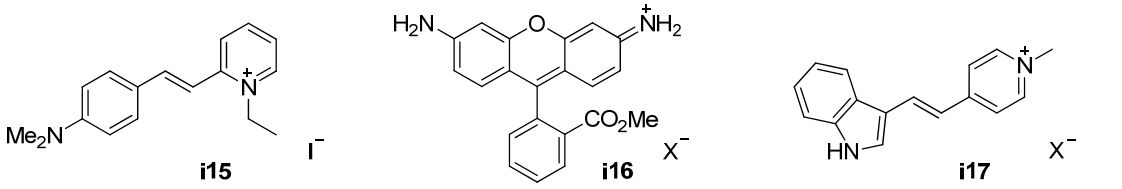


Figure 1.4. Some important mitochondria targeting molecules.

Thus, the design, synthesis and investigation of new classes of superbases and delocalized lipophilic cations is a general current problem for modern chemistry.

1.2. General Principles of Design of DLCs and SBs

Generally, similar principles in design of superbases and delocalized lipophilic cations may be easily explained as a result of a fundamental connection between both classes. Protonated forms of most neutral superbases correspond to highly stabilized DLCs. Thus, the protonated forms of superbases may be considered as a sub-family of DLCs. However, in contrast to other type of DLCs, SBH^+s contain relatively acidic protons.

The most important parameter characterizing both DLCs and SBH^+s is the level of delocalization and stabilization of a positive charge in their molecules. Generally, the increase of positive charge stabilization in a DLC leads to a decrease of its electrophilicity, increase of lipophilicity and increase of freedom of the counterion. These parameters are very important for the purposes of using the DLCs as PTCs or as mitochondria targeting molecules (see Chapter 1.1). In SBH^+ the increase of stabilization of a positive charge leads to an increase of basicity and nucleophilicity of the conjugate base.

Basicity level of bases, i.e. their ability to accept a proton can be defined by the following parameters: gas-phase basicity (GB), proton affinity (PA) and pK_{BH+}.* The two

* Gas phase basicity, **GB** = $-\Delta G°$ for the following reaction in the gas phase: $B + H^+ \rightarrow BH^+$;
Proton affinity, **PA** = $-\Delta H°$ for the following reaction in the gas phase: $B + H^+ \rightarrow BH^+$;
Basicity in solution, $\mathbf{pK_{BH+}} = -\log K_{BH}+$, where $K_{BH}+ = a_B.a_{H+}/a_{BH+}$; B – base, *a* – activity.

former are frequently used for the description of basicity in the gas-phase and the latter one is common for basicity in solution, for SBs often in MeCN,[1,8] THF,[1,18] or DMSO.[1,45]

Achievement of an optimal level of delocalization and stabilization of a positive charge in DLC and proper level of basicity and nucleophilicity of SB is the main but not the sole goal in the design of new compounds. It is also important that DLCs, SBs, and also SBH^+s would possess sufficient thermal stability, stability towards hydrolysis and oxidation. Designed molecules also should not be toxic or sources of toxins after decomposition in the environment.

Most DLCs and conjugate protonated forms of superbases, SBH^+s, can be presented schematically in the form of $G^i_nX^+$ or $G^i_nX^+$-NHR, where G^1, G^2 … G^i – electron donating groups; n – their number; X – atom, usually C, P or S; and R = H, alkyl or aryl group. The choice of X-atom, G^i groups, their numbers and their donicity evidently allows to modulate level of delocalization and stabilization of a positive charge in a target molecule of DLC or SBH^+. The donicity route for selected donor groups G^i often applied in design of DLCs and SBs is given in Figure 1.5.

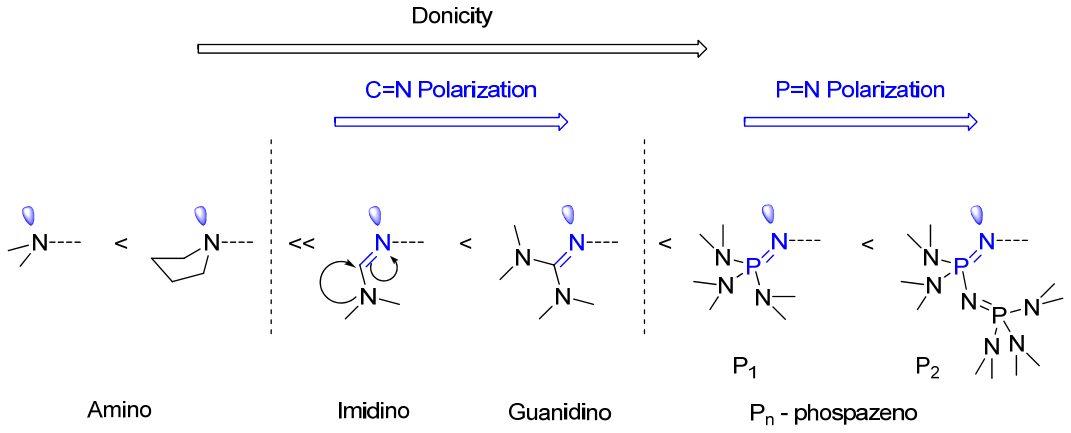


Figure 1.5. General donicity trend of useful nitrogen electron donor groups.

In design of SBs with general structure $G^i_nX{=}NR$, it is necessary to choose an R group. The nucleophilicity of SB decreases significantly with increasing of bulkiness of R in a sequence of R = Me, Et, *i*Pr, *t*Bu, *t*Oct ~ CEt_3, *t*Hept, however basicity changes usually slightly (Figure 1.6).[8,9]

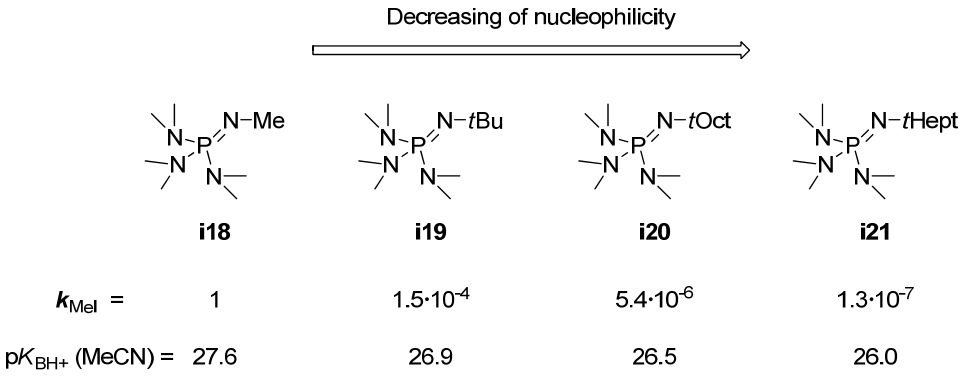


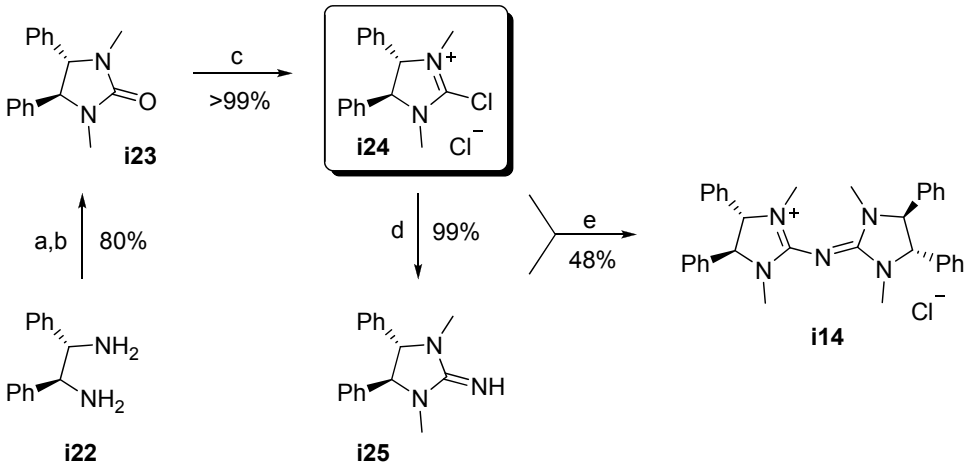
Figure 1.6. Nucleophilicity trend *vs*. basicity trend of similar phosphazene P_1(dma) bases with varying R substituents. k_{MeI} – relative constant of methylation with MeI in PhCl / EtCN (1:1).[9]

Two independent research directions in design, synthesis and use of DLCs and SBs can be marked out in modern chemistry:

(a) DLCs and SBs as effective chiral catalysts for chirality induction.

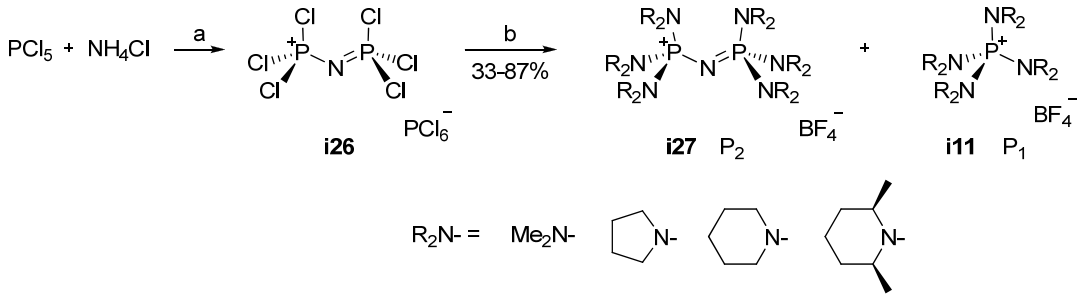
(b) DLCs and SBs as reagents and catalysts in achiral synthesis.

As example of (a), Tan offered important chiral PTC **i14** and provided a five-stage method for its synthesis starting from chiral diphenylethylenediamine (**i22**).[6] Key step of the method included nucleophilic substitution of Cl in chloroimidazolinium salt **i24** with related guanidine **i25** (Scheme 1.1). The high efficiency of new DLC **i14** / Cs_2CO_3 as catalyst system was demonstrated in enantioselective Michael additions of *tert*-butyl glycinate-benzophenone Schiff base to various chalcones.



Scheme 1.1. Synthesis of **i14**: (a) Triphosgene, Et_3N, CH_2Cl_2; (b) MeI, NaH, THF; (c) $(COCl)_2$, toluene, reflux 24 h; (d) NH_3, MeCN, sealed tube, reflux; (e) Et_3N, MeCN, recrystallization.

As example of (b), Schwesinger developed an elegant two-stage protocol for preparation of P_2^+ cations (Scheme 1.2).[8,46] In reaction conditions, active PCl_6^- anion of perchlorodiphosphazenium salt **i26** led to one equivalent of P_1^+ cation **i11**, which was easily separated from target product P_2^+ **i27** by recrystallization. The high stability of P_2^+ cations towards hydrolysis under drastic basic conditions as well as high "nakedness" of fluorine in $P_2(dma)^+F^-$ were demonstrated.[4,5]



Scheme 1.2. Schwesinger's method for synthesis of P_2^+ **i27**: (a) NaCl, $POCl_3$; (b) R_2NH, PhCl, r.t. to reflux. Overall yields are given.

In the first case (a) electrophilicity of chiral DLCs should not be too high but also should not be too week as it allows the DLC to play a key role in the transition state,

effectively transferring the chirality and providing sufficient TOF and TON values. The same is true for chiral superbases in respect to their basicity and nucleophilicity. Thus, chiral DLCs and SBs often represent electrophiles and bases of moderate power respectively. In contrast, in the second case (b), achiral DLCs and SBs often represent slightly electrophilic, highly stabilized DLCs and powerful SBs respectively.

It is obvious that different requirements for properties of DLCs and SBs mean also different preferences in a choice of X-atom and G^i groups in their design. In design of chiral DLCs and SBs less powerful electron donor G^i groups are used and/or in smaller number in comparison with design of achiral ones. As X-atom in the first case C-atom is more often preferred and in the second case – P and S atoms (Figure 1.1 and 1.3).

1.3. Drawbacks and Limitations of Classical Design of Highly Stabilized DLCs and Powerful SBs

In design of highly stabilized DLCs and powerful SBs two families of strong electron donor groups – phosphazenes and guanidines – are frequently used. Limitations in synthesis and use of such DLCs and SBs are closely connected with shortcomings of indicated electron donors and methods for their introduction into the desired molecule. Drawbacks can be divided on specific and general for both families.

While phosphazene groups are the strongest electron donors, their price is high, access of corresponding building blocks (e.g. $(Me_2N)_3P{=}NH$) is difficult, intermediates are toxic. The products containing phosphazene groups are possible sources of traces of toxic compounds (e.g. HMPA) arising from partial decomposition.[18]

In contrast, building blocks corresponding to guanidine electron donors are more accessible and less expensive (e.g. TMG). Compared to phosphazenes, guanidine groups are presumably less toxic.[18] However, guanidines considerably concede on electron donicity even to simplest phosphazenes (P_1(dma) group).

One of the common shortcomings for both families is associated with a nature of their high donicity. Being connected to a selected cation they introduce an extended conjugation chain and considerable delocalization of a positive charge that leads to cation stabilization, but expansion of conjugation length by introducing larger number of donor groups or by increasing their power (for example, by replacing of P_1 with P_2) considerably increases the molecular weight of a target molecule as well as its cost. Besides, in the case of

Schwesinger's phosphazene bases further elongation of a conjugation chain by moving from P_4 to P_7 fragments according to a homologation principle leads to insignificant growth of basicity – "saturation" effect (Figure 1.7).[8] Analogous effect was also demonstrated for polyguanides.[47]

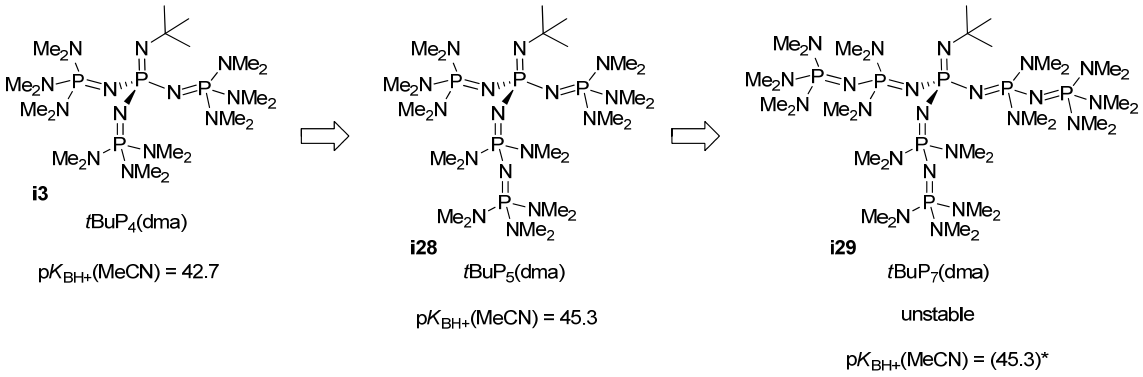


Figure 1.7. Homologation principle in design of Schwesinger's P_5, P_7 bases. * Estimated value.

Moreover, in contrast to P_4 and P_5 bases, attempts to prepare P_7 by analogous deprotonation of P_7H^+ with KNH_2 / NH_3 were unsuccessful and starting salt P_7H^+ was found to be very sensitive to acid hydrolysis.[8]

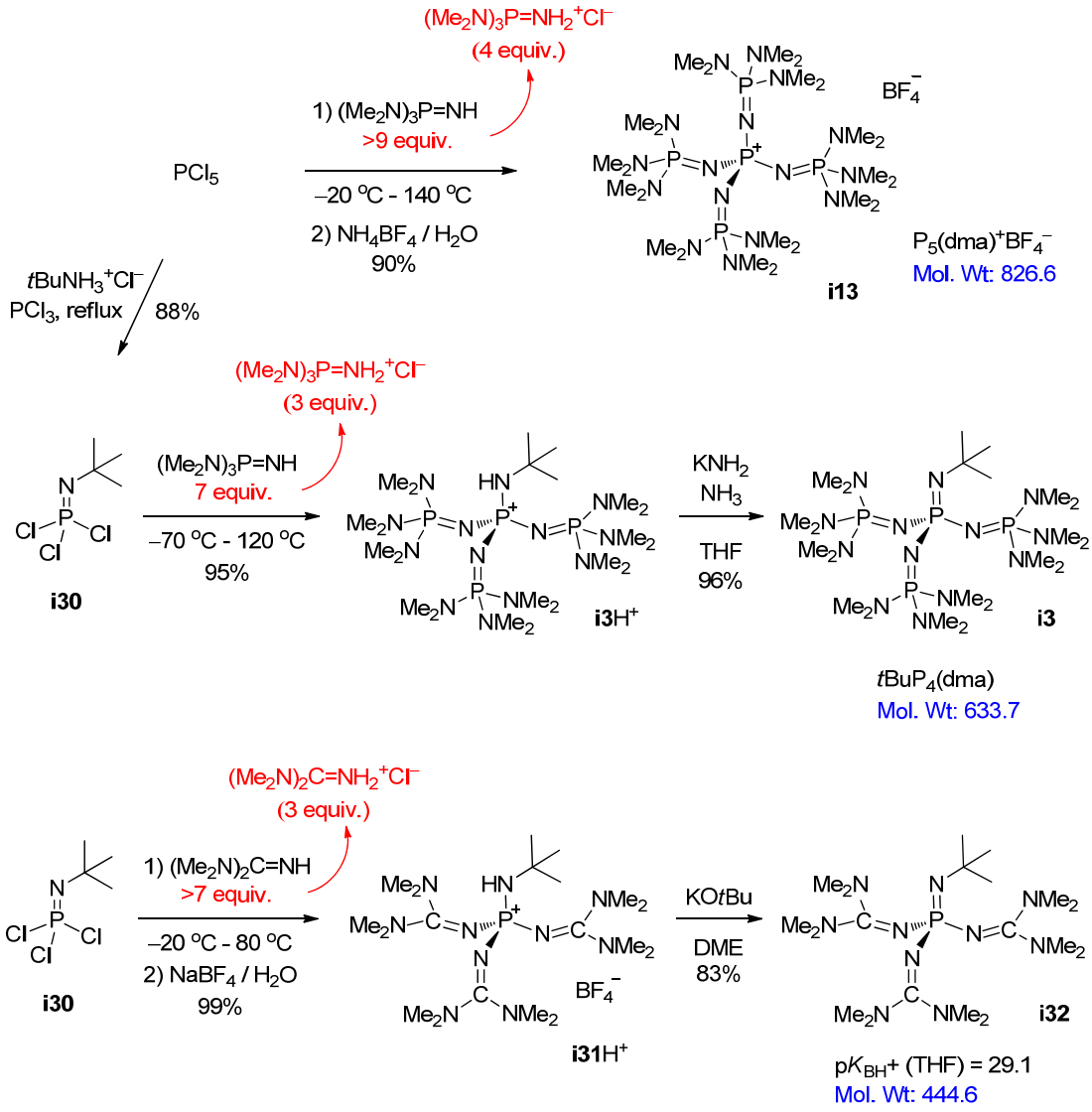
Thus, the increase of conjugation length using homologation principle also has its limit.

Other common shortcoming is associated with general approach for introducing phosphazene and guanidine groups into the desired molecule. Frequently, the reaction of nucleophilic substitution of Hal in $XHal_n$ with, for example, $(Me_2N)_3P{=}NH$ or TMG is used. This leads to a necessity of using at least two-fold excess of nucleophile since half of it is consumed on linkage of HHal emitted in the course of reaction.

Both mentioned shortcomings of guanidine and phosphazene groups in design are demonstrated on example of synthesis of $P_5(dma)^+$ cation **i13**, P_4(dma) base **i3**, and Kolomeitsev's P_1(tmg) **i32** (Scheme 1.3).

Recently Kolomeitsev offered an alternative to P_4 bases by replacing the phosphazene groups by tetramethylguanidine units (Scheme 1.3).[18] Indeed, this new family is considered to be less toxic, in particular it is not a source of toxic HMPA. However, Kolomeitsev relied on the same principles as for phosphazenes. The substitution of phosphazene by TMG units led to significant reduction of basicity in comparison to original phosphazenes. For example,

Kolomeitsev's base $(tmg)_3P{=}NPh$ has pK_{BH+} (THF) = 24.3, analogous Schwesinger's base $[(pyrr)_3P{=}N\text{-}]_3P{=}NPh$ has pK_{BH+} (THF) = 28.1.[18]



Scheme 1.3. Synthesis of Schwesinger's $P_5(dma)^+$ cation, $P_4(dma)$ base and Kolomeitsev's $P_1(tmg)$ base.

Thus, search of alternatives to the phosphazenes, which will show similar level of high donicity / basicity and will not have the specified above disadvantages, is still remaining an actual area of research.

1.4. Our Design

One of the ways to overcome stated above problems in design and synthesis of highly stabilized DLCs and powerful SBs is the search for new classes of strong electron donors and methods for their introduction.

One such class are *pseudo*-aromatic imines (Figure 1.8). Their donicity should be larger compared to simple acyclic or saturated analogues because of increased polarization of $C=N_{exo}$ bond caused by partial aromatization of the molecule. This fact fundamentally separates this family from amidines, guanidines and phosphazenes, in which polarization of C=N or P=N bonds does not lead to aromatization of the molecules.

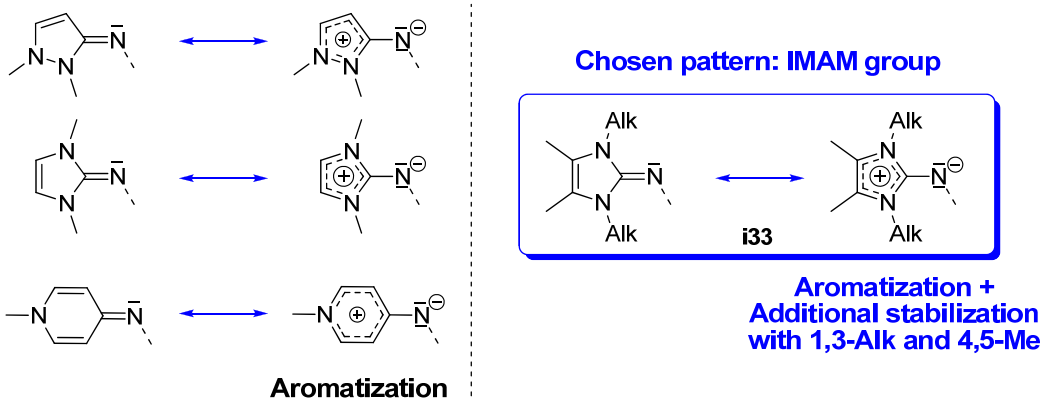


Figure 1.8. *Pseudo*-aromatic imine donor patterns and chosen imidazol-2-ylidene amino patern **i33** (IMAM).

Among other patterns, the imidazol-2-ylidene amine motif was chosen as a first class of *pseudo*-aromatic imines for the realization of such a concept. Among the known patterns the 1,3-dialkyl-4,5-dimethylimidazol-2-ylidene amino subset **i33** (IMAM) was preferred because of its optimum topology for the achievement of a maximum of donicity, basicity and lipophilicity (Figure 1.8). Moreover, the methyl groups at the 4,5-positions in **i33** are believed to be essential to protect from possible side reactions during the preparation of target molecules.[48,49]

Many compounds containing 1,3-dialkylimidazol-2-ylidene amino group connected to Ti,[50,51] Mo,[52,53] W,[52,53,54] Re[55] and rare earth metals (Sc, Y, Lu, Gd)[56,57,58] were synthesized and investigated. However, only a few compounds, in which those groups are connected to C

or P, are known (Figure 1.9). The compounds were synthesized using simple nucleophilic substitution reaction between **i34**-Y and **i35**-Y and corresponding C-Hal, C-OTs or P-Hal electrophiles; a set of metal complexes of **i36**,**i37**,**i39** and **i40** with Pd, Rh, Cu, Mo were also described (see references, Figure 1.9).

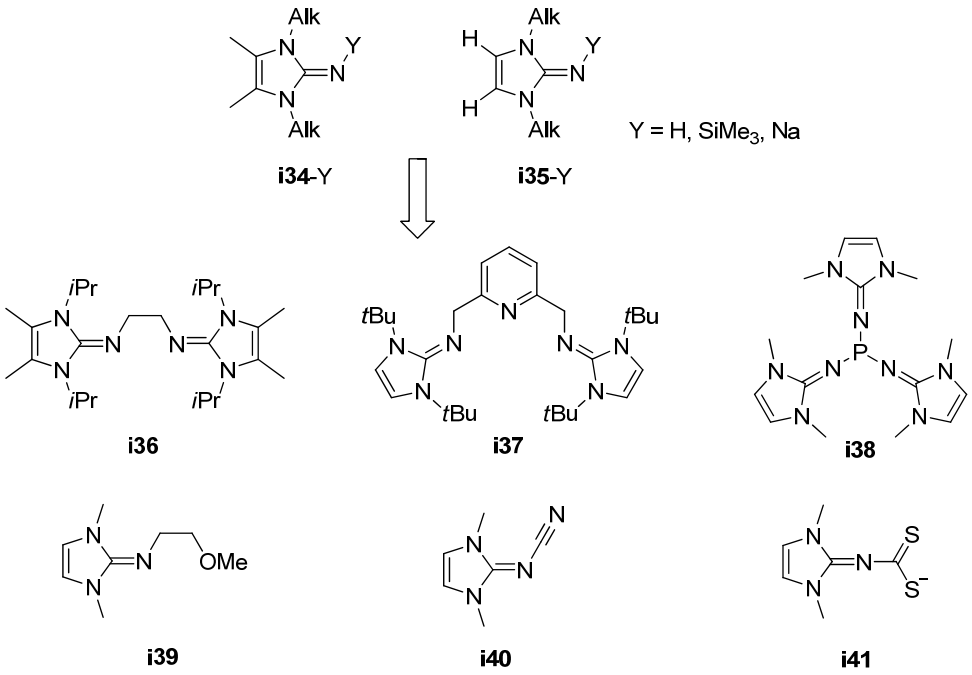
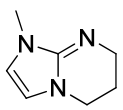


Figure 1.9. Examples of known compounds, containing 1,3-dialkylimidazol-2-ylidene amino group, **i36-i41**.[59,60,61,62,63,64]

Examination of the literature data revealed that only one base, 1-methyl-1,5,6,7-tetrahydroimidazo[1,2-*a*]pyrimidine (**ImPyr**, Figure 1.10) containing fragment related to IMAM was described, for which a reliable experimental pK_{BH+} = 24.55 in acetonitrile was determined.[7] This base **ImPyr** was also investigated computationally.[65]



ImPyr **i42**

pK_{BH+} = 24.55

Figure 1.10. One reported base containing IMAM motif.

Aims of the Work

- Development of an effective method for introduction of 1,3-dialkyl-4,5-dimethylimidazol-2-ylidene amino group (IMAM) in an organic molecule (Figure 1.11).

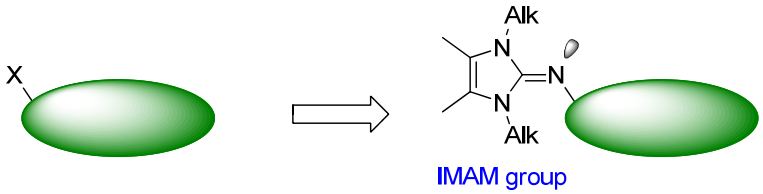


Figure 1.11. Introduction of a new strong electron donor IMAM group.

- Synthesis of new families of phase transfer catalysts (PTC) – highly stable delocalized lipophilic cations (DLCs) based on IMAM group and an estimation of the stability of the products under various drastic basic conditions.

As three new classes of PTCs, containing IMAM group are offered bis(1,3-dialkyl-4,5-dimethylimidazol-2-ylidene)ammonium salts $\mathbf{1}^+$ (further BIMA), tris(dimethylamino)(1,3-dialkyl-4,5-dimethylimidazol-2-ylidene amino)phosphonium salts $\mathbf{2}^+$ (further PIMA) and bis(dimethylamino)(1,3-dialkyl-4,5-dimethylimidazol-2-ylidene amino)methyl salts $\mathbf{3}^+$ (further TIMA) (Figure 1.12).

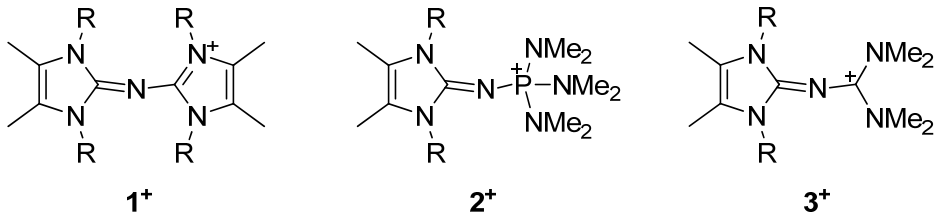
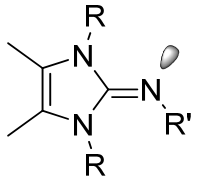


Figure 1.12. New DLCs: BIMA, PIMA and TIMA designed for PTC applications in strongly basic media at high temperature, R = Alk.

In the cations $\mathbf{1}^+$, $\mathbf{2}^+$, $\mathbf{3}^+$ IMAM group additionally stabilize three different types of already quite stable cations - 2-imidazolium, triaminophosphonium and bis(dimethylamino)methyl cation, respectively.

- Synthesis of new classes of powerful superbases including one IMAM group, an estimation and determination of the basicity of such superbases and the factors influencing it.

The most simple of such possible superbases are *N*-alkyl- and *N*-aryl-1,3-dialkyl-4,5-dimethylimidazol-2-ylidene amine bases (further IMAM bases) of general structure shown in Figure 1.13.



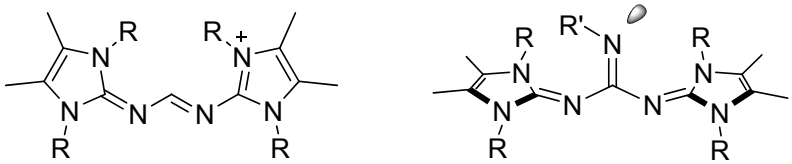
4

Figure 1.13. IMAM bases **4**, R = Alk, R' = H, Alk or Ar.

Investigation of basicity of such bases and also the effects responsible for their basicity would allow to directly study the level and the nature of donicity of new imidazol-2-ylidene amino group and to estimate aromatization role in such *pseudo*-aromatic imine pattern.

- Synthesis of new classes of DLCs and powerful superbases including two 1,3-dialkyl-4,5-dimethylimidazol-2-ylidene amino (IMAM) groups, an estimation and determination of the basicity of such superbases.

As simple structures containing two IMAM groups *N,N′*-bis(1,3-dialkyl-4,5-dimethylimidazol-2-ylidene)formamidinium cations $\mathbf{5}^+$ (further BIF cations) and *N,N′*-bis(1,3-dialkyl-4,5-dimethylimidazol-2-ylidene)guanidines **6** (further BIG bases) of general structures shown in Figure 1.14 are offered.



$\mathbf{5}^+$ **6**

Figure 1.14. BIF cations $\mathbf{5}^+$ and BIG bases **6**, R = Alk, R' = H or Alk.

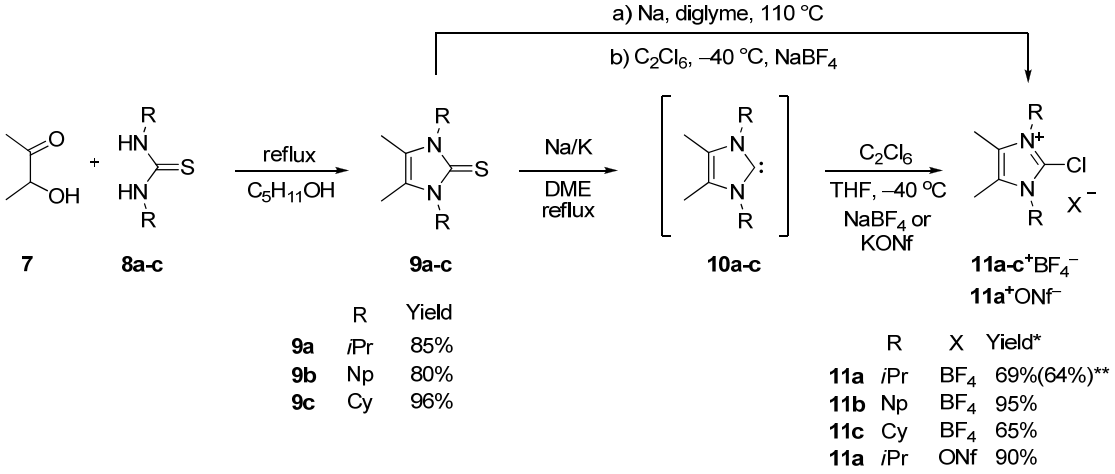
Results and Discussions

2. Bis(*N,N′*-dialkylimidazol-2-ylidene)ammonium (BIMA) and Related Phosphonium (PIMA) and Guanidinium (TIMA) Cations

2.1. General Approach for the Synthesis of BIMAs, PIMAs and TIMAs

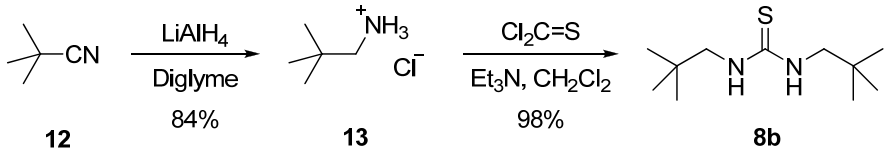
2.1.1. Synthesis of intermediates and the first generation protocol

The first step for the synthesis of BIMAs $\mathbf{1}^+$, PIMAs $\mathbf{2}^+$ and TIMAs $\mathbf{3}^+$ was the condensation of thioureas **8a-c** (R = *i*Pr, Np, Cy) with 3-hydroxybutan-2-one **7** by refluxing in amyl alcohol at least for 6 h with distillation of formed water using a Dean-Stark head (Scheme 2.1). Imidazole-2-thiones **9a-c** were isolated in good yields. The isolation of imidazole-2-thiones **9** was simplified in comparison with original literature protocol.[66]



Scheme 2.1. Synthesis of 2-chloroimidazolium salts $\mathbf{11a\text{-}c}^+$. * Isolated yields are reported over two steps starting from **9**. ** Yield of $\mathbf{9a}^+BF_4^-$ for *one-pot* K-free protocol.

Commercially unavailable thiourea **8b**[67] was prepared from neopentylamine[68] in good yield according to a general method[69] for the synthesis of thioureas (Scheme 2.2).

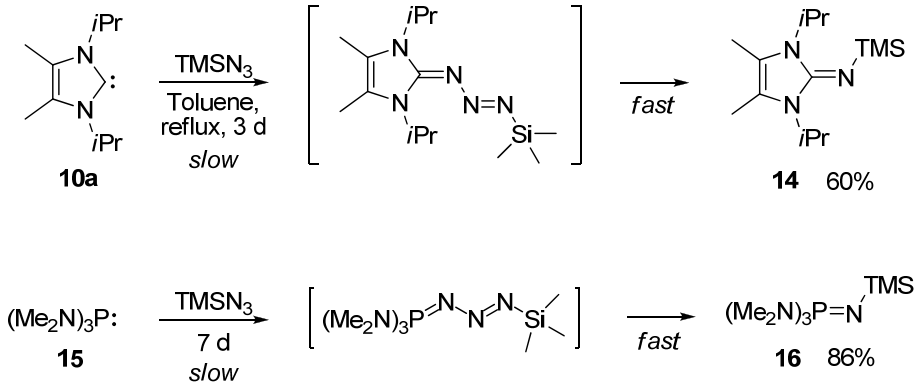


Scheme 2.2. Synthesis of *N,N'*-dineopentylthiourea **8b**.

The next step consisted of reduction of imidazole-2-thiones **9a-c** to the corresponding NHCs **10a-c** (Scheme 2.1).[66,70] The literature procedure was not always well reproduced since low conversion of **9** to **10** was observed. Reduction of **9** with K/Na alloy in refluxing DME instead of using K in refluxing THF was reproducible and high yields (>85%) of the target compounds **10** were achieved (Scheme 2.1). Obtained NHCs **10a-c** were stored as solutions in dry hexane at ambient temperature under argon and were used within several weeks.

2-Chloroimidazolium salts **11a**$^{+}$ONf^{-} and **11a-c**$^{+}$$BF_4^{-}$ were synthesized by electrophilic chlorination of NHCs **10a-c** with hexachloroethane in THF at –40 ºC in good yields (Scheme 2.1).[75,71] In contrast to 2-fluoroimidazolium,[72,73] 2-bromoimidazolium[74,75] and 2-iodoimidazolium cations,[76] 2-chloroimidazolium cations **11**$^{+}$ were chosen owing to their availability, stability and *a priori* reactivity in S_NAr reactions.

Later, a significantly modified and simplified one-pot protocol was also developed and used, enabling the access to key chloroimidazolium **11a**$^{+}$$BF_4^{-}$ from **9a** in multigram amounts. Heating of **9a** with sodium in diglyme at 110 °C for 24 h, followed by quenching of the intermediate NHC with hexachloroethane gave **11a**$^{+}$$BF_4^{-}$ in 64% yield using neither potassium nor reflux conditions (Scheme 2.1).

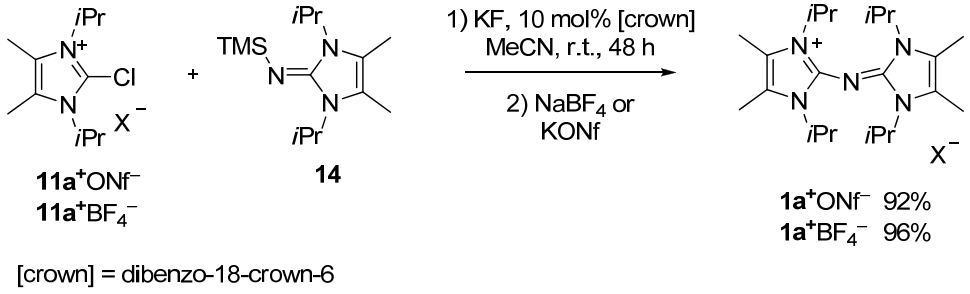


Scheme 2.3. Synthesis of nucleophiles **14** and **16**.

Compound **14** was synthesized according to the literature in good yield as a moisture sensitive oil (Scheme 2.3).[51] Silylphosphazene **16** was obtained using a modified literature protocol that allowed to practically avoid the formation of by products and improve the yield significantly. $TMSN_3$ and hexamethylphosphorous triamide **15** were reacted for a week at ambient temperature, followed by distillation of target silylphosphazene **16** in vacuo in good yield (Scheme 2.3). In contrast, in original protocol, the reaction was carried out with heating and a considerable amount of higher phosphazene derivatives were formed.[77,78]

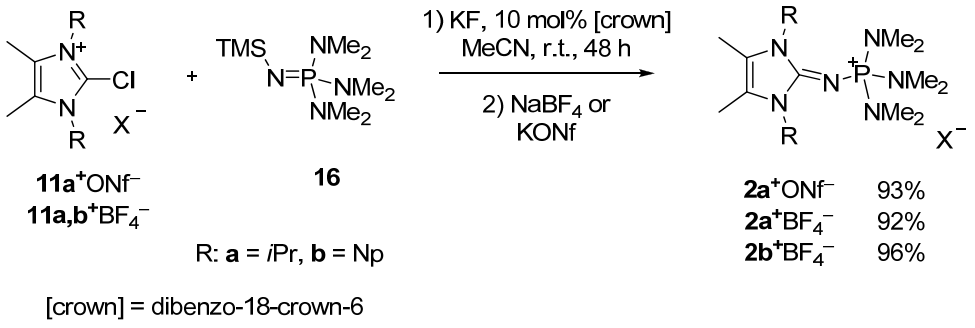
The last step for the preparation of BIMA $\mathbf{1}^+$ was conducted by coupling of $\mathbf{11a}^+ONf^-$ and $\mathbf{11a}^+BF_4^-$ with **14** in acetonitrile in the presence of an excess of dry KF and 10 mol% of dibenzo-18-crown-6 at ambient temperature providing the target BIMA salts $\mathbf{1a}^+ONf^-$ and $\mathbf{1a}^+BF_4^-$ in high yields (Scheme 2.4).

KF played dual role as an activator at the silicon atom and as a scavenger of liberating TMSCl, which is known to give saline adducts with compounds of type **14** that might take out a half of **14** from the reaction.[79]



Scheme 2.4. Synthesis of BIMA $\mathbf{1a}^+ONf^-$ and $\mathbf{1a}^+BF_4^-$ according to the first generation approach.

Synthesis of PIMAs $\mathbf{2}^+$ was carried out by reaction between $\mathbf{11a,b}^+$ and trimethylsilylphosphazene **16** in acetonitrile in the presence of an excess of dry KF and 10 mol% of dibenzo-18-crown-6. The reaction gave the desired PIMAs $\mathbf{2a}^+ONf^-$, $\mathbf{2a}^+BF_4^-$ and $\mathbf{2b}^+BF_4^-$ after 2 days at room temperature in high yield (Scheme 2.5).



11a$^+$ONf$^-$
11a,b$^+$$BF_4^-$

16

2a$^+$ONf$^-$ 93%
2a$^+$$BF_4^-$ 92%
2b$^+$$BF_4^-$ 96%

Scheme 2.5. Synthesis of PIMAs **2a**$^+$ONf$^-$, **2a**$^+$$BF_4^-$ and **2b**$^+$$BF_4^-$ according to the first generation approach.

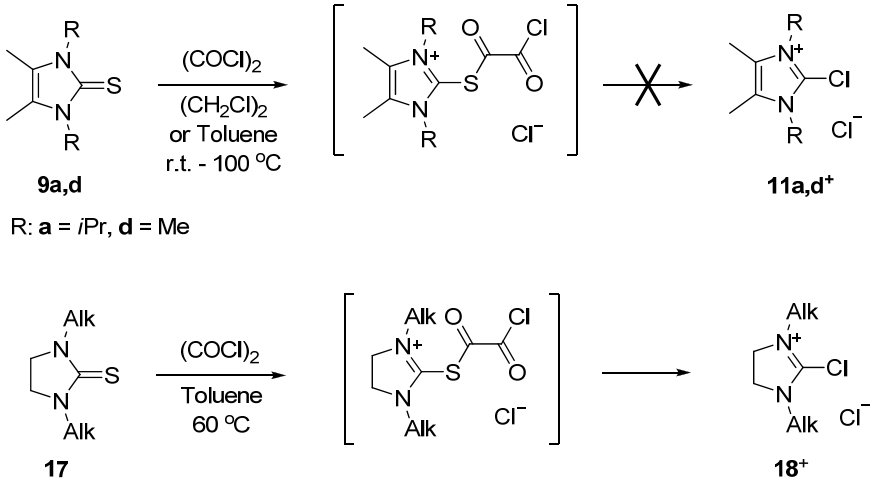
BIMA **1a**$^+$ONf$^-$ and PIMA **2a**$^+$ONf$^-$ were checked with respect to their stability under drastic basic conditions. Both compounds were heated in DMSO-d6 in NMR tubes in the presence of 5 equiv. of KOH (50% aq.) for 5 h at temperature 120–130 °C. From the analysis of the reaction mixtures by ^{1}H NMR the extent of hydrolytic degradation of compounds **1a**$^+$ONf$^-$ and **2a**$^+$ONf$^-$ was found not to exceeded 15% and 25%, respectively. Such unexpected high stability prompted development of the more efficient protocol for BIMA **1**$^+$ and PIMA **2**$^+$ syntheses and further studying of their high stability under different drastic basic conditions.

2.1.2. The second generation protocol

Attempts to improve provided method for BIMA and PIMA synthesis, i.e. the first generation protocol, were undertaken remaining within the same general model of their synthesis. It was important to try to reduce the number of stages for preparation of 2-chloroimidazolium salts **11**$^+$ or to find other possible electrophiles. Moreover alternatives to nucleophiles **14** and **16** (Scheme 2.3) were desirable since their preparation required considerable reaction time (3-7 days) and handling of toxic $TMSN_3$.

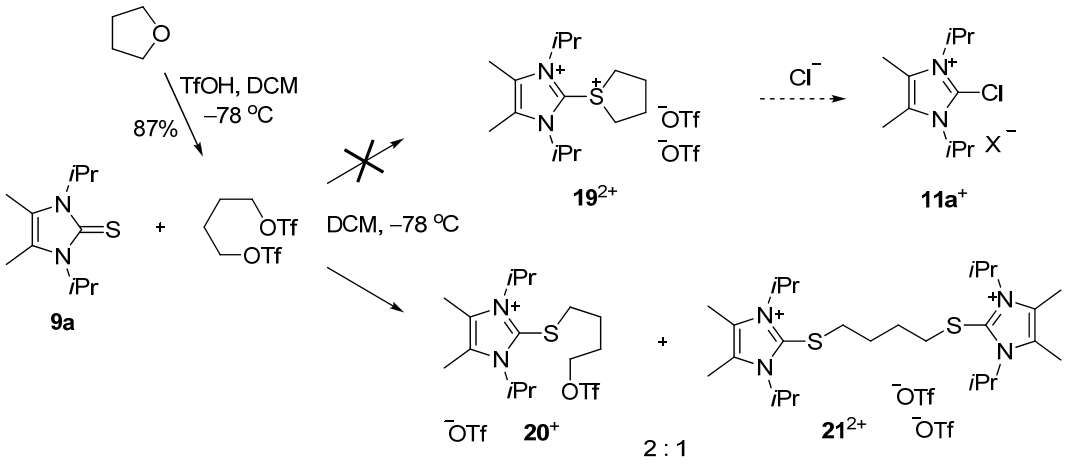
All attempts to synthesize **11a**,**d**$^+$ directly from imidazole-2-thiones **9a**,**d** using common nucleophilic chlorination reagents such as $(COCl)_2$, $SOCl_2$, PCl_5 in $POCl_3$, and $(EtO)_2ClPO$ were unsuccessful. After mixing at ambient temperature an intermediate was observed, which was assumed to be the product of substitution of one chlorine atom of the chlorination reagent by the sulphur of **9**. Increasing the temperature resulted either in a mixture of products or in

products in which the methyls in 4,5 position of imidazolium ring were affected. It is necessary to note that $(COCl)_2$ is a common reagent for transformation of cyclic thioureas **17** to 2-chloroimidazoline cations **18**$^+$, saturated analogues of **11**$^+$ (Scheme 2.6).[15]



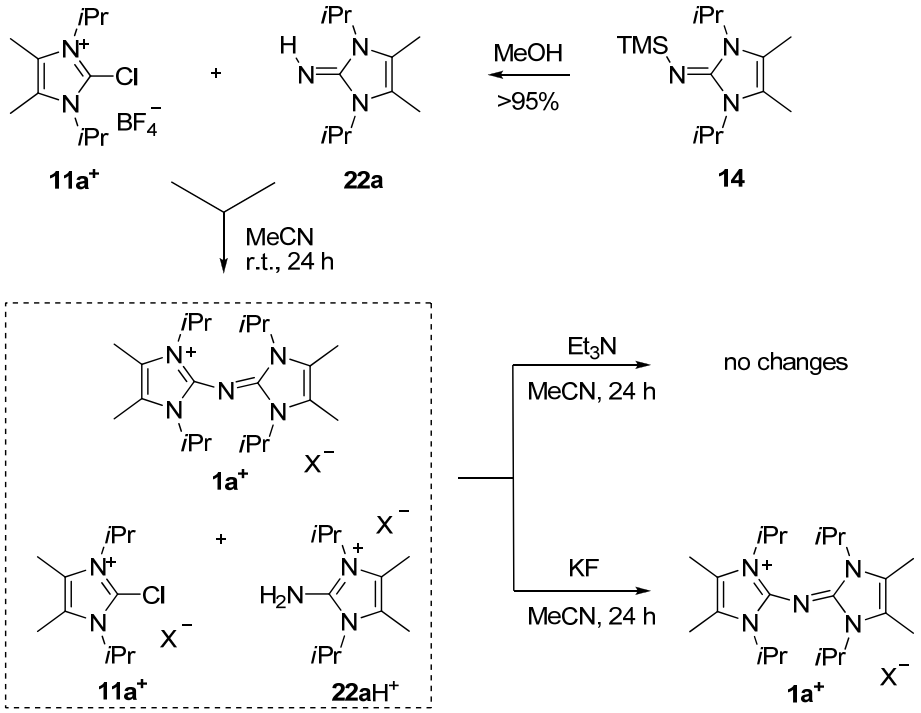
Scheme 2.6. Chlorination of thioureas **17** *vs*. imidazole-2-thiones **9** using oxalyl chloride.

1,4-Butaneditriflate[80] easily prepared from THF and TfOH was also tried as imidazole-2-thione activator for further substitution of tetrahydrothiophene in dicationic intermediate **19**$^{2+}$ by chloride anion (Scheme 2.7). No target dicationic intermediate **19**$^{2+}$ was observed, but a statistic mixture of products of mono- and disubstitution of 1,4-butaneditriflate (**20**$^+$ and **21**$^{2+}$) formed after full conversion of **9a**.



Scheme 2.7. Attempted synthesis of 2-chloroimidazolium salt **11a**$^+$ using 1,4-butaneditriflate.

Compound **22a**,[48] the product of methanolysis of **14**, reacted with **11a**$^+BF_4^-$ giving a mixture of BIMA **1a**$^+$, **11a**$^+$ and **22a**H$^+$ in a ratio 1:1:1 within one day. Addition of an excess of Et_3N followed by stirring for one day more did not improve the conversion to product **1a**$^+$ (Scheme 2.8). KF proved to be suitable to achieve full conversion toward BIMA **1a**$^+$ and within 24 h gave BIMA **1a**$^+$ as a sole product almost quantitatively.

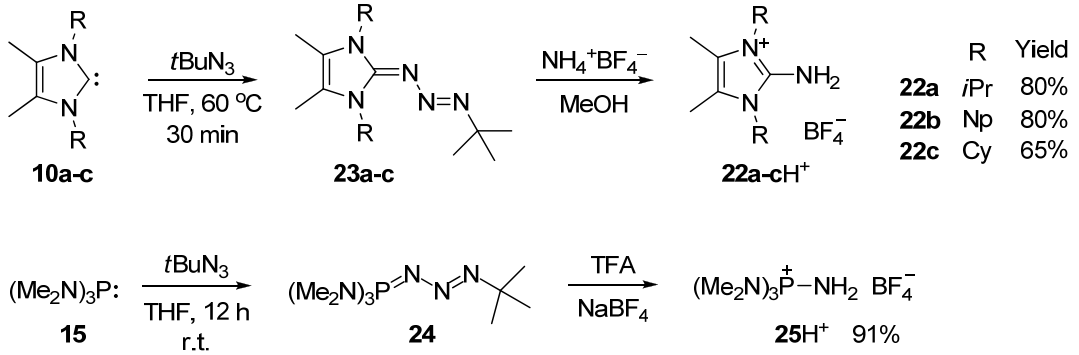


Scheme 2.8. Reaction of 2-chloroimidazolium **11a**$^+$ with imidazol-2-ylidene amine **22a**.

The crown ether was not used on this step, thus reacting **11a**$^+X^-$ and forming **1a**$^+X^-$ acted themselves as effective PTCs during the reaction. This way for the synthesis of BIMA cation **1a**$^+$ was more attractive than that used earlier, since it did not require working with hydrolytically labile silyl derivatives (see Scheme 2.4). Advantages of this procedure are more evidenced especially if one considers the fact that instead of **22** their salts **22**H$^+$ can be used in the presence of excess KF.

A new convenient way for the preparation of salts **22**H$^+$ and their phosphorous analogue **25**H$^+$ consisted of reaction of NHCs **10** or phosphine **15** with *tert*-butyl azide and subsequent decomposition of the intermediate triazenes **23** and **24**[81] to compounds **22**H$^+$ or **25**H$^+$ by

careful addition of acids under mild conditions; isobutylene and nitrogen were released in the course of reaction (Scheme 2.9).[82]



Scheme 2.9. Amination of carbenes **10a-c** and phosphorous triamide **15** with *tert*-butyl azide.

The formation of stable triazene intermediates **23a-c** and **24** was always observed in ^{1}H NMR spectra of the reaction mixture. In a separate experiment **23a** was isolated in almost quantitative yield in form of colorless crystals and its structure was confirmed by single-crystal X-ray diffraction (Figure 2.1).

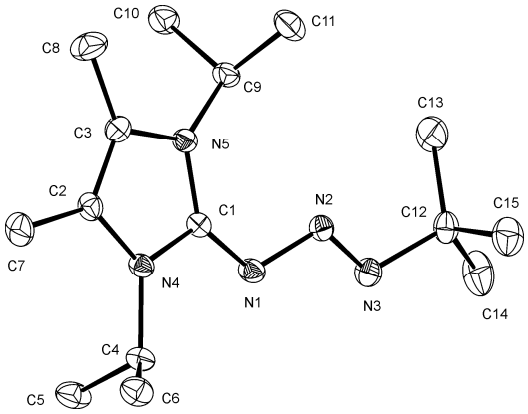
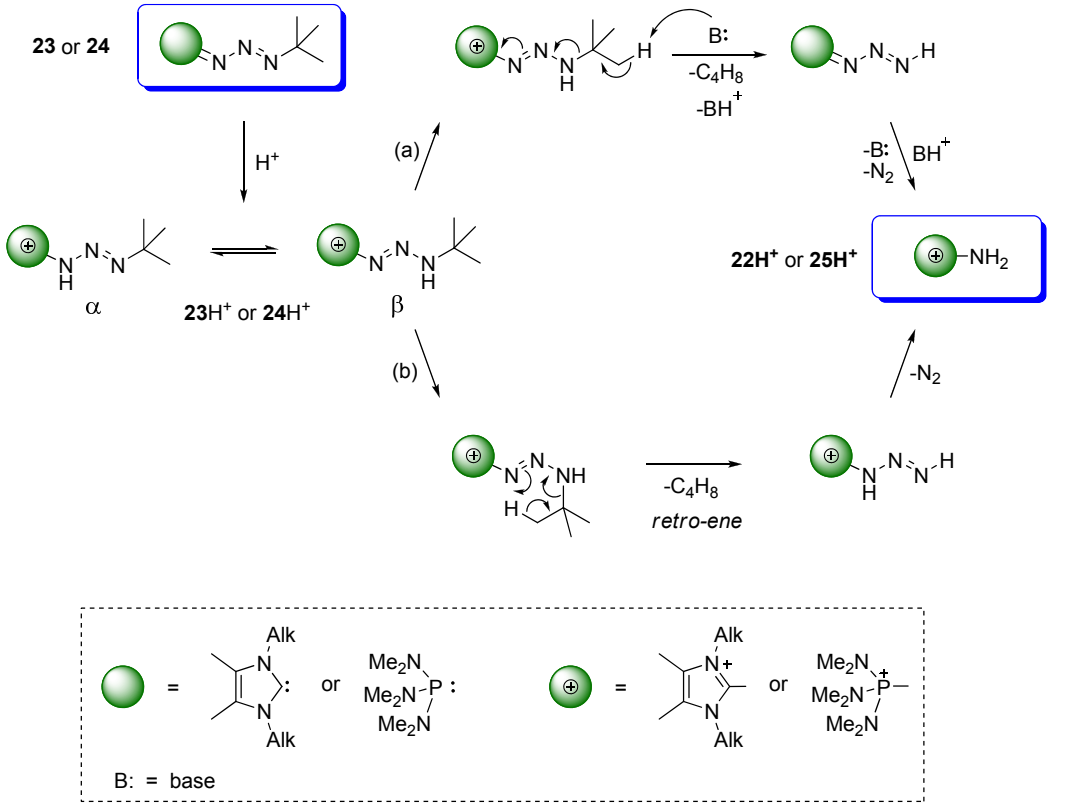


Figure 2.1. X-ray crystal structure of the triazene **23a**. The displacement ellipsoids are drawn on 30% probability level. Hydrogen atoms are omitted for clarity. Selected bonds distances [Å] and angles [°]: N(1)-C(1) 1.3411(16), N(4)-C(1) 1.3638(15), N(5)-C(1) 1.3618(16), N(4)-C(2) 1.3951(16), C(2)-C(3) 1.3537 (18), N(5)-C(3) 1.4115(17), N(1)-N(2) 1.3617(15), N(2)-N(3) 1.2517(16), N(3)-C(12) 1.4856(18).

The X-ray data proved the expected *E* configuration of triazene **23a**. Four atoms N(1)-N(2)-N(3)-C(12) are located in one plane. The torsion angle of N(5)-C(1)-N(1)-N(2) amounts to 22.7 ° that may be caused by steric repulsion between electron pairs of N(1), N(2) and *i*Pr group of imidazole ring.

It must be noted that *t*BuN$_3$ is a reagent, which can be synthesized in quantitative yield in multigram-scale from *tert*-butanol with sodium azide in diluted aq. sulfuric acid,[83] it does not require distillation for its isolation. For ease of handling it is recommended to work with 50% solutions in, for example, toluene.*

Two possible pathways for fragmentation of **23** or **24** by acidic treatment are offered: (a) an intermolecular way and (b) an intramolecular retro-ene way (Scheme 2.10).



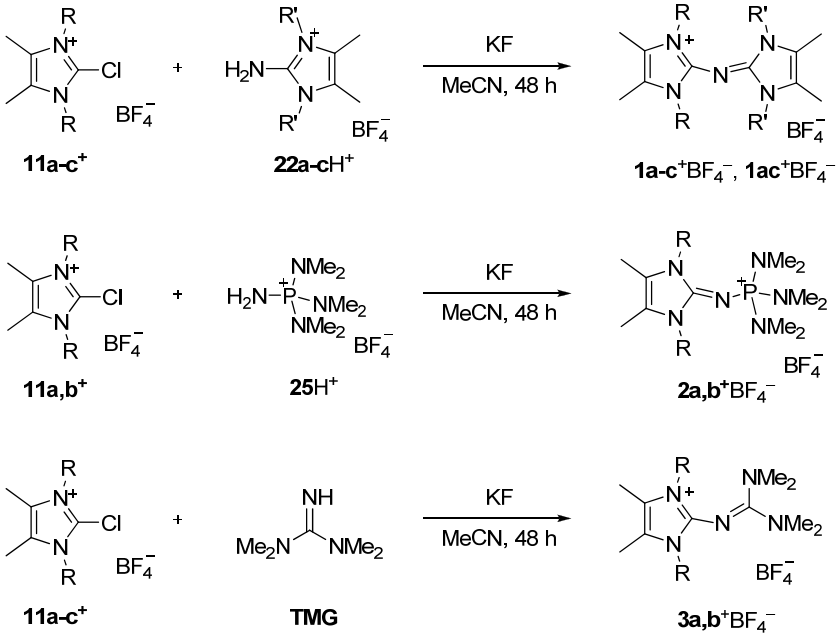
Scheme 2.10. Possible mechanisms of mild acidic decomposition of trazenes **23** and **24** to **22**H$^+$ and **25**H$^+$.

* Even pure *t*BuN$_3$ is considered to be quite stable reagent: no explosions or exothermic decompositions were observed while few years of handling and intensive use of the reagent in our group. Use of solution in hydrocarbons should improve the safety even more.

Both pathways start from protonation of triazene **23** or **24** and both are proposed to occur from β tautomer of **23**H^+ or **24**H^+ (Scheme 2.10). In case of pathway (a) triazene **23** or **24** may play a role of the base B: (Scheme 2.10).

Developed method for the synthesis of **22**H^+ and **25**H^+ required significantly shorter reaction time and milder conditions in comparison with previously used method for preparation of related silyl derivatives **14** and **16** (Scheme 2.3).

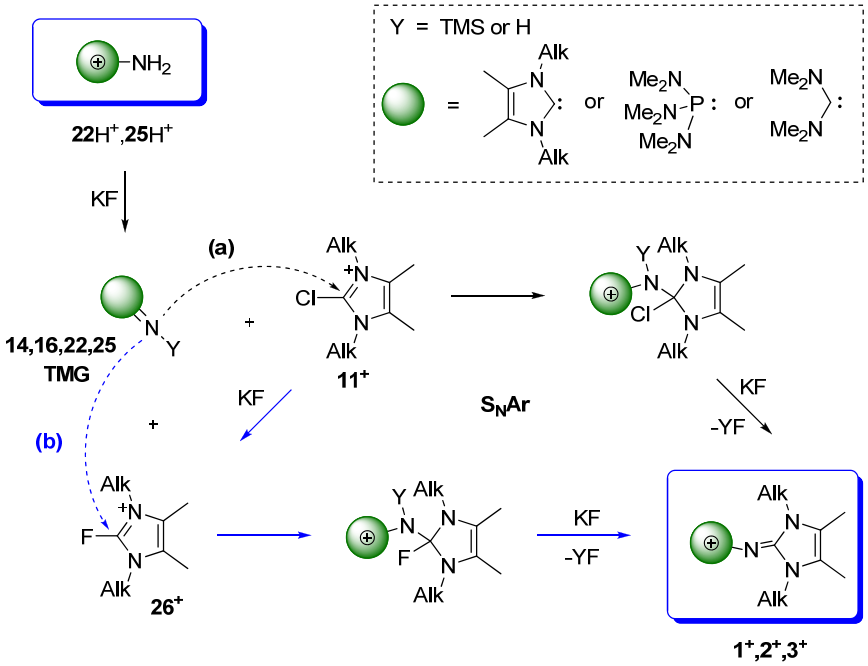
Compounds **22a-c**$H^+BF_4^-$ and **25**$H^+BF_4^-$ reacted with 2-chloroimidazolium salts **11a-c**$^+BF_4^-$ in acetonitrile in the presence of excess KF giving the target BIMA **1a-c**$^+BF_4^-$ and PIMA **2a**,**b**$^+BF_4^-$ after 48 hours in good to high yields (Scheme 2.11). Using a combination of **11c**$^+BF_4^-$ with **22a**$H^+BF_4^-$ asymmetrically substituted BIMA **1ac**$^+$ was prepared in good yield. TIMAs **3a**,**b**$^+BF_4^-$ were prepared similarly by combination of 2-chloroimidazolium salts **11a**,**b**$^+BF_4^-$ with TMG in the presence of excess KF in high yields.



	R	R'	Yield
1a	*i*Pr	*i*Pr	78%
1b*	Np	Np	84%
1c	Cy	Cy	87%
1ac	Cy	*i*Pr	71%
2a	*i*Pr		95%
2b*	Np		91%
3a	*i*Pr		91%
3b	Np		89%

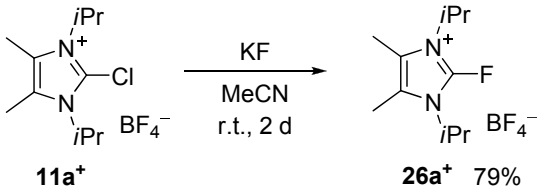
Scheme 2.11. Synthesis of BIMA **1**$^+$, PIMA **2**$^+$ and TIMA **3**$^+$ according to the second generation protocol. * For preparation of compounds **1b**$^+$ and **2b**$^+$ heating at 60 °C was applied.

Two possible pathways, a direct pathway (a) and pathway (b) through 2-fluoroimidazolium cation **26**$^+$ (Scheme 2.12) may account for the formation of **1**$^+$, **2**$^+$ and **3**$^+$.



Scheme 2.12. Two possible pathways of formation **1-3**$^{+}$.

The possibility of pathway (a) was demonstrated earlier (Scheme 2.8). In this case KF acted exclusively as a base to reach full conversion. Possibility of the pathway (b) was demonstrated in separate experiment by isolation of 2-fluoroimidazolium salt **26a**$^{+}BF_4^{-}$ in good yield from reaction of corresponding 2-chloroimidazolium salt **11a**$^{+}BF_4^{-}$ with KF without addition of nucleophile (Scheme 2.13). 2-Fluoroimidazolium cation **26a**$^{+}$ was described earlier; however it was synthesized only by electrophilic fluorination of the corresponding NHC **10a** using SF_4 and SO_2F_2.[72,73]



Scheme 2.13. Preparation of 2-fluoroimidazolium salt **26a**$^{+}BF_4^{-}$ from 2-chloroimidazolium salt **11a**$^{+}BF_4^{-}$.

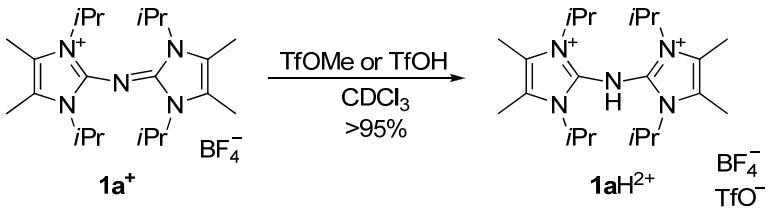
However, 2-fluoroimidazolium cations **26**$^+$ were never observed in the ^{1}H NMR spectra of reaction mixtures in the course of the syntheses of **1-3**$^+$ (Scheme 2.11). This might be associated with the higher reactivity of **26**$^+$ in comparison with **11**$^+$.

2.1.3. Features of BIMAs, PIMAs and TIMAs

BIMA **1**$^+$, PIMA **2**$^+$ and TIMA **3**$^+$ tetrafluoroborate salts are stable crystalline non-hygroscopic solids readily soluble in chlorinated hydrocarbons, alcohols and polar non-protic organic solvents.

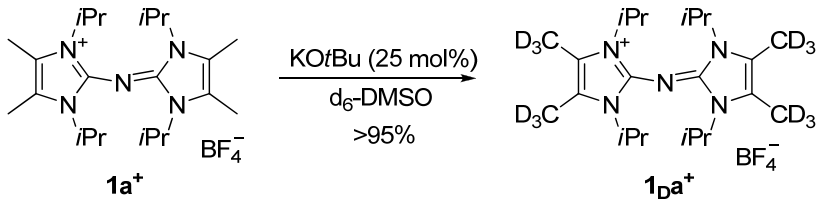
Atempt to methylate central nitrogen of **1a**$^+$ with TfOMe was unsuccessful; instead *N*-protonation leading to stable symmetrical dication **1a**H^{2+} took place. The failure argued for considerable steric crowding created around the C-2,N,C-2' fragment by four isopropyl groups. Similar results were observed earlier in reactions of sterically hindered 2,6-di-*tert*-butylpyridine derivatives with $MeOSO_2F$.[84,85]

The dication **1a**H^{2+} was generated independently by treatment of **1a**$^+$ with TfOH (Scheme 2.14).



Scheme 2.14. Protonation of **1a**$^+$ to **1a**H^{2+}.

BIMA **1a**$^+$ in DMSO-d6 in presence of catalytic amount of KO*t*Bu at room temperature was subjected to fast H-D exchange on methyl groups in 4,5 positions gave after one day partially deuterated BIMA **1$_D$a**$^+$ (Scheme 2.15). Deuterium exchange of **1a**$^+$ was not observed within several days if CD_3OD was used instead of DMSO-d6.



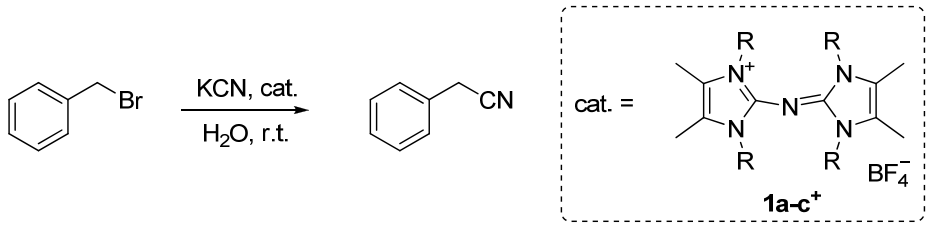
Scheme 2.15. Proton-deuterium exchange in BIMA **1a**$^{+}$.

2.2. BIMAs and Related Cations as potentially useful PTCs for applications under Drastic Basic Conditions

2.2.1. PTC activity of BIMA 1^{+}BF$_4^{-}$

For potential application of prepared salts **1-3**$^{+}$ as PTCs under drastic basic conditions, at first, it was desirable to know their catalytic activities under mild conditions using one of PTC activity tests.

In such experiment, 4 mol % of compounds **1a-c**$^{+}$BF$_4^{-}$ were added to a two phase mixture of BnBr / aq. KCN followed by stirring at room temperature (Scheme 2.16). All tested BIMAs **1a-c** showed similarly good PTC activity. The conversions of BnBr to BnCN in those experiments were compared with blank experiment data (Table 2.1).



Scheme 2.16. PTC by BIMAs **1a-c**$^{+}$.

Table 2.1. Catalytic activity of BIMAs **1**.

Entry	Catalyst[a]	Time, h	Conversion[b], %	Yield[c], %
1	–	3	<5	–
2	**1a**$^+BF_4^-$	3	>99	80 (95)[d]
3	**1b**$^+BF_4^-$	3	>99	77 (83)[d]
4	**1c**$^+BF_4^-$	3	>99	84

[a] 4 mol % of BIMA **1** was used. [b] Conversion to $PhCH_2CN$ by GC MS. [c] Yield of $PhCH_2CN$ by GC MS using *n*-dodecane as a reference. [d] Isolated yield of $PhCH_2CN$.

2.2.2. Estimation of stability of 1-3$^+BF_4^-$ (conditions A and B)

For potential application of prepared salts **1-3**$^+$ as PTCs under drastic basic conditions, at second, it was desirable to estimate their stability towards hydrolysis in such conditions.[4]

In the first case (Table 2.2, **A**) selected compounds were refluxed in a biphasic mixture of PhCl / KOH (50% aq.), in the second case (Table 2.2, **B**) selected compounds were refluxed in 1 M solution of KOH in ethylene glycol. In both cases decomposition was monitored by ^{1}H NMR of the reaction mixtures and conversion of the starting material was estimated either relative to the internal standard (dibenzo-18-crown-6) or without a standard in the case if a clear decomposing pattern was observed. Half-life times ($t_{1/2}$) for compounds **1**$^+$, **2**$^+$, **3**$^+$ are compiled in Table 2.2.

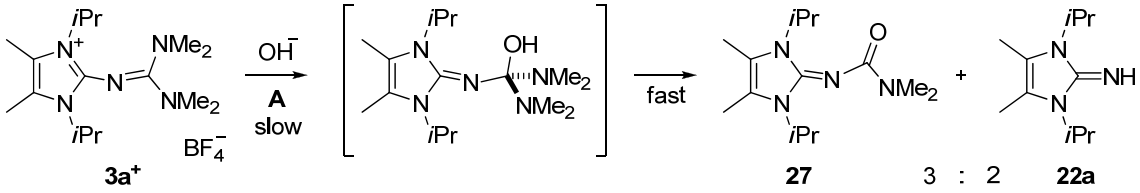
For comparison highly stable $P_5^+BF_4^-$ (see Figure 1.3) was prepared according to the literature protocol[4] and the stability of this salt was also determined under the same conditions (Table 2.2).

Table 2.2. Half-life times of **1-3**$^+$ in strongly basic media.[a]

Entry	Compound	Conditions	Reaction time (h)	Conversion (%)	$t_{½}$ (h)
1	**1a**$^+BF_4^-$	**A**	24	42	31
2	**1b**$^+BF_4^-$	**A**	48	traces[b]	stable
3	**1c**$^+BF_4^-$	**A**	21	33	36
4	**2a**$^+BF_4^-$	**A**	30	20	94
5	**2b**$^+BF_4^-$	**A**	48	traces[b]	stable
6	**3a**$^+BF_4^-$	**A**	16	18	58[c]
7	$P_5^+BF_4^-$	**A**	48	traces[b]	stable
8	**1b**$^+BF_4^-$	**B**	24	<5	>650
9	**2b**$^+BF_4^-$	**B**	24	<5	>650
10	$P_5^+BF_4^-$	**B**	24	<5	>650

[a] Conditions **A**: vigorously stirred biphasic mixture of PhCl / 50% aqueous KOH, reflux (115 °C inner temperature, 145 °C oil bath temperature). Conditions **B**: 1 M solution of KOH in ethylene glycol, reflux. [b] Limit of detection by NMR technique. [c] At room temperature.

Cation **3a**$^+$ turned out to be least stable (Table 2.2, Entry 6). It was cleaved slowly by 50% aq. KOH with loss of one Me_2N group already at room temperature (Scheme 2.17).

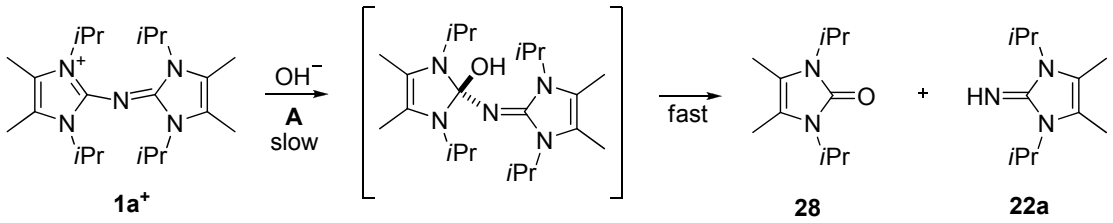


Scheme 2.17. Decomposition of **3a**$^+$ in conditions **A**.

The $(Me_2N)_2C{=}N$ group in organic cations is hydrolytically unstable in aqueous alkali solutions, especially at high temperatures, but it was found to be quite stable towards fluoride anion in aprotic media and used in design of PTCs for Halex process.[32] This fact illustrates that the stability sequence towards OH^- and F^- anions in general are not the same and compounds of type **3**$^+$ can still be useful as PTCs transferring fluoride anion.

BIMA **1a**,**c**$^+$ and PIMA **2a**$^+$ displayed much higher resistance to OH^-. The half-life times were in the range of 30 to 95 h under condition **A** (Table 2.2, Entries 1, 3 and 4).

In the case of BIMA **1a**$^+BF_4^-$ mass spectrometric analysis (ESI-MS) as well as ^1H NMR spectra of the reaction mixture revealed that the major pathway of decomposition was cleavage of the central C–N bond after addition of OH^- to the C2 atom of one of the imidazole units (Scheme 2.18). At the same time, degradation by Hoffman mechanism (β-elimination) or by nucleophilic attack of hydroxide anion on substituents at nitrogen atoms in 1,3-positions of imidazolium rings was not observed.[4]



Scheme 2.18. Decomposition of **1a**$^+$ under condition **A**.

The N-neopentyl substituted cations **1b**$^+$ and **2b**$^+$ and the P_5-phosphazenium cation turned out to be most stable in the series studied. They did not show distinct signs of decompositions in refluxing biphasic mixture of PhCl with 50% aq. KOH (Table 2.2, entries 2, 5 and 7). Prolonged reflux of **1b**$^+$, **2b**$^+$ and $P_5^+BF_4^-$ in 1 M KOH ethylene glycol solution led to insignificant decomposition (Table 2.2, Entries 8–10).

Thus BIMA **1**$^+$ and PIMA **2**$^+$ are potentially useful as new classes of PTCs for drastic basic conditions.

2.2.3. Estimation of stability of 1a,b$^+Cl^-$ (conditions C)

Two representative examples BIMA **1a**$^+$ and **1b**$^+$ were checked for their stability also in the form of chlorides in strongly basic conditions **C**: reflux in biphasic mixture of PhCl / NaOH (50% aq.) at bath temperature 100 °C, because for many known PTCs in form of chlorides half-life times were determined in such conditions (Figure 2.2).[4] The degree of degradation was estimated similarly as described above. Half-life times were found to be ~40 min and ~10 h for BIMA **1a**$^+Cl^-$ and **1b**$^+Cl^-$ respectively (Figure 2.2).

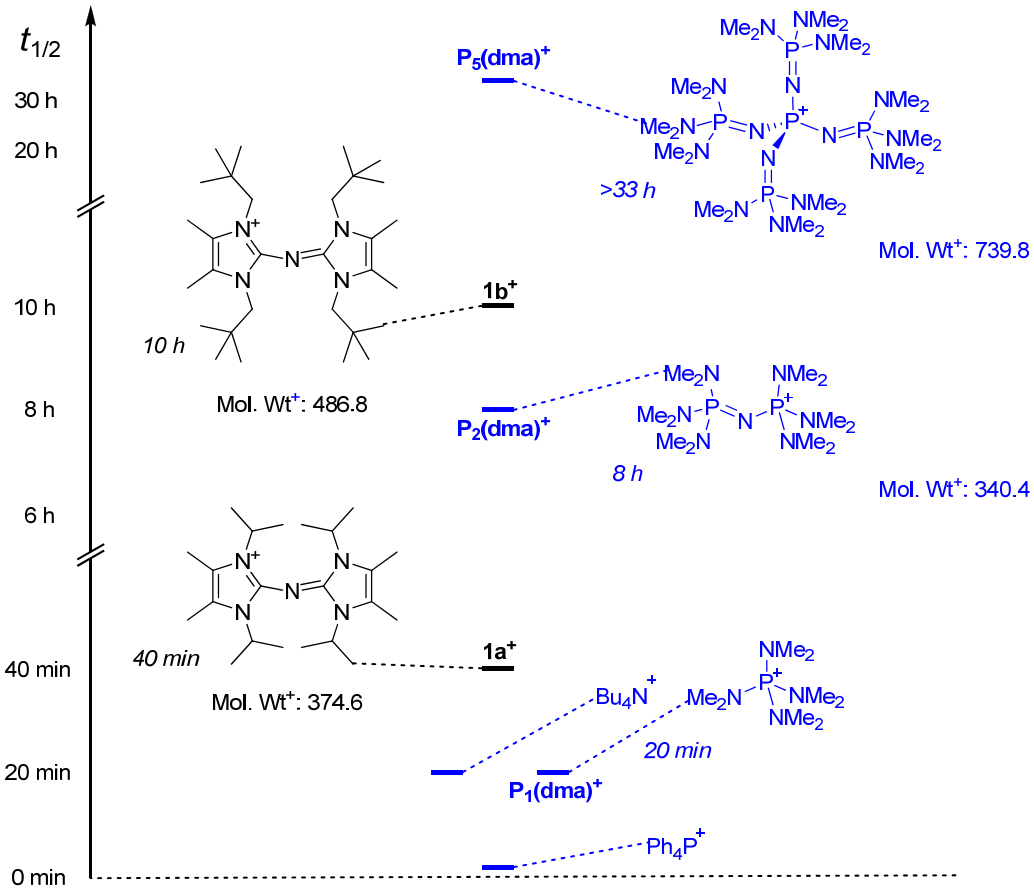


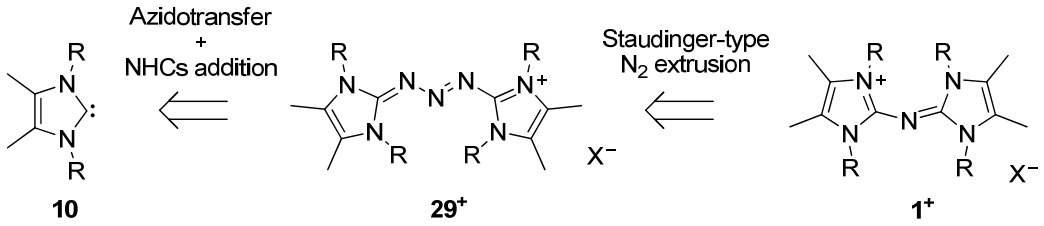
Figure 2.2. Comparison of half-life times of BIMAs **1a**,**b**$^+$Cl$^-$ (in black) and some known PTCs data (in blue)[4] in a vigorously stirred biphasic mixture of PhCl / 50% aqueous NaOH, bath temperature 100 ºC.

BIMA **1a**$^+$ cation was found to be two times more stable than Bu_4N^+ and $P_1(dma)^+$ while BIMA **1b**$^+$ cation was close to $P_2(dma)^+$ and turned out to be only several times less stable than $P_5(dma)^+$ (Figure 2.2).

The general decrease of cations **1a**$^+$ and **1b**$^+$ stability under conditions **C** (~40 min and ~10 h, respectively) relative to conditions **A** (~31 h and >650 h, respectively) was observed. It might be associated with more hydrophilic chlorides used as counterions to **1a**$^+$ and **1b**$^+$ for conditions **C** in contrast to tetrafluoroborates used for conditions **A** and **B**. The substitution of BF_4^- by Cl^- resulted in higher concentration of chloride anion in aqueous phase and consequently, in higher equilibrium concentration of hydroxide anion in organic phase. The latter led to increased rates of decomposition of the investigated cations.

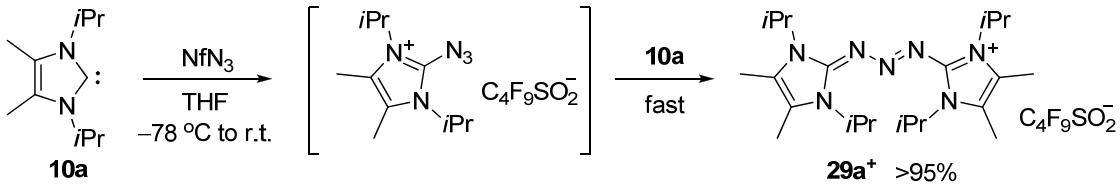
2.3. Synthesis of BIMA by Alternative Synthetic Pathways

An alternative synthetic pathway to symmetric BIMAs $\mathbf{1}^+$ consisted of three main steps: Synthesis of NHCs **10**, azide transfer reaction with formation of triazene $\mathbf{29}^+$ and Staudinger-type nitrogen extrusion to $\mathbf{1}^+$ (Scheme 2.19).



Scheme 2.19. Alternative general approach for synthesis of symmetrical BIMA $\mathbf{1}^+$ cations.

Reaction of two equivalents of NHC **10a** and one equivalent of nonaflyl azide[86] in THF at -78 °C resulted in the formation of symmetrically substituted bis(imidazol-2-ylidene)triazenyl cation $\mathbf{29a}^+$ with nonafluorobutanesulfinate (Nf^-) counterion in high yield as a dark orange oil. The reaction is considered to proceed via the intermediate formation of 2-azidoimidazolium cation, which was however not detected in the course of reaction (Scheme 2.20).

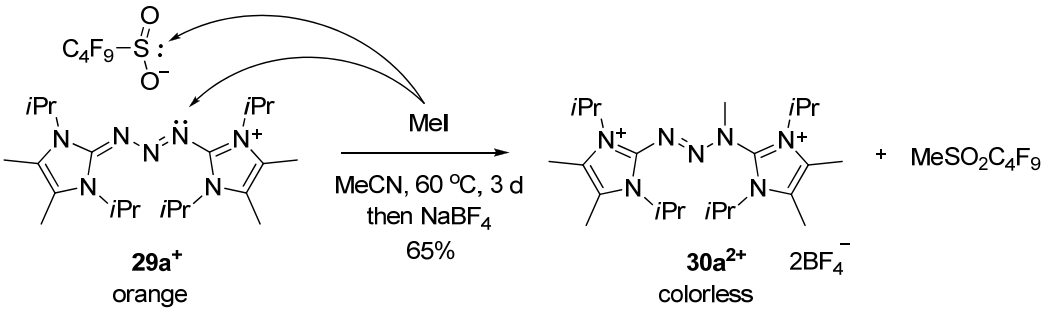


Scheme 2.20. Synthesis of bis(imidazol-2-ylidene)triazenyl nonafluorosulfinate $\mathbf{29a}^+Nf^-$ starting from nonaflyl azide.

Since nonafluorosulfinate anion was known to be to some extent nucleophilic,[87] its replacement by inert and thermally stable anion was attempted before realization of the thermal extrusion of nitrogen by Staudinger type reaction.

Replacement of Nf^- by chloride anion by treatment the solution of **29a**$^+Nf^-$ in dichloromethane with a solution of chlorine in CCl_4 at –78 °C was found as too harsh and resulted in a mixture of chlorinated products.

Attempted replacement of nonafluorosulfinate anion by iodide through heating of **29a**$^+Nf^-$ in acetonitrile with an excess of methyl iodide led to methylation of the triazene group providing colorless dication **30a**$^{2+}$, which was isolated as the bis(tetrafluoroborate) salt (Scheme 2.22). The structure of **30a**$^{2+}$ was confirmed by X-Ray analysis (Figure 2.3).



Scheme 2.22. Anion exchange with subsequent formation of methylated product **30a**$^{2+}$.

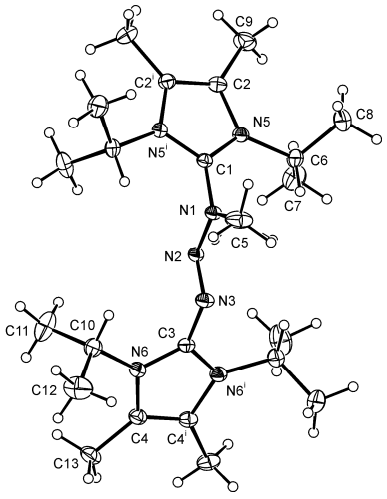
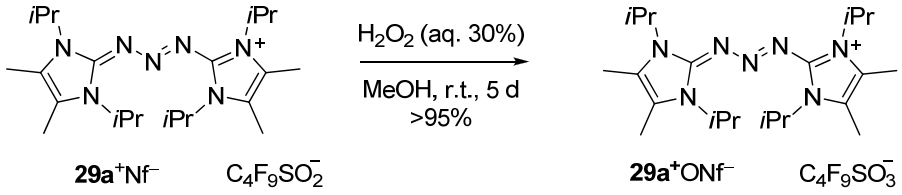


Figure 2.3. X-ray crystal structure the dication **30a**$^{2+}(BF_4^-)_2$ with atom numbering schema. The half of the molecule is generated via mirror operation. The displacement ellipsoids are drawn at 30% probability level. Anions are omitted for clarity.

As can be seen from Figure 2.3 planes of two imidazolium rings in **30a**$^{2+}$ are orthogonal to plane N1-N2-N3 that is in agreement with lack of color after methylation of **29a**$^+$.

The oxidation of the nonafluorosulfinate anion to nonaflate by reaction with 30% aqueous hydrogen peroxide in methanol at room temperature according to the literature[88] was optimal (Scheme 2.23). Evaporation of the solvent and careful drying with a small amount of diglyme in high vacuum gave bis(imidazol-2-ylidene)triazenyl nonaflate **29a**$^+$ONf$^-$ in quantitative yield as a dark orange oil.



Scheme 2.23. Oxidation of nonafluorosulfinate to nonaflate anion in **29a**$^+$.

Triazenyl nonaflate **29a**$^+$ONf$^-$ was subjected to pyrolysis in different solvents at various temperatures. Sulfolane and NMP were chosen as high boiling solvents. However, heating at temperatures 170 °C or 195 °C led to slow decomposition of starting **29a**$^+$. The desired cation **1a**$^+$ was not detected in the reaction mixture. This is probably associated with the weak nucleophilicity of nitrogen in triazene fragment of **29a**$^+$, the weak electrophilicity of the C-2 atom of the imidazolium ring and the high steric congestion of the possible Staudinger intermediate.

2.4. Selected Solid State Structures

The solid state structures of the salts **1a**$^+$OTs$^-$ and **1b**$^+$I$^-$ were characterized by X-ray crystal structure analysis. In both cations N1 is close to sp^2-hybridization. The steric repulsion between *i*Pr or Np groups results in significant deviation from planarity with 74° and 53° dihedral angle between two imidazolium rings in **1a**$^+$ and **1b**$^+$ correspondingly. In both cations *i*Pr and Np substituents are spatially arranged to provide an efficient steric protection of C1/C4 centres from nucleophilic attack by OH$^-$.

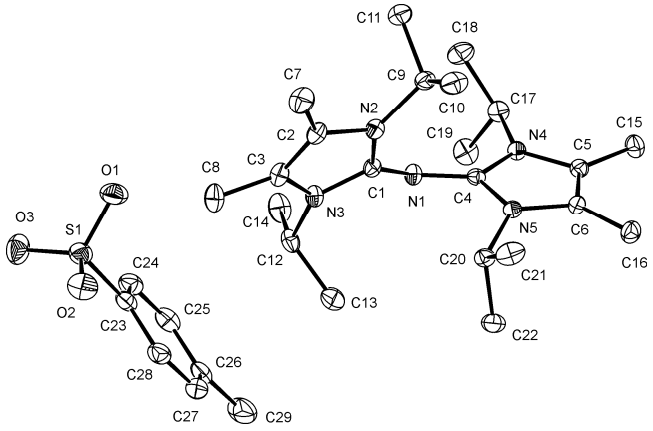


Figure 2.4. X-ray crystal structure of the BIMA salt **1a**$^{+}$OTs^{-}. The displacement ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bonds distances [Å] and angles [°]: N(1)-C(1) 1.332 (2), N(1)-C(4) 1.331 (2), N(2)-C(1) 1.360 (2), N(2)-C(2) 1.410 (3), C(2)-C(3) 1.351 (3), N(3)-C(3) 1.403 (2), N(3)-C(1) 1.357 (2), N(4)-C(4) 1.355 (2), N(4)-C(5) 1.403 (2), C(5)-C(6) 1.345 (3), N(5)-C(6) 1.413 (2); C(4)-N(1)-C(1) 124.96 (13); dihedral angle between the two imidazolium rings 73.96(11).

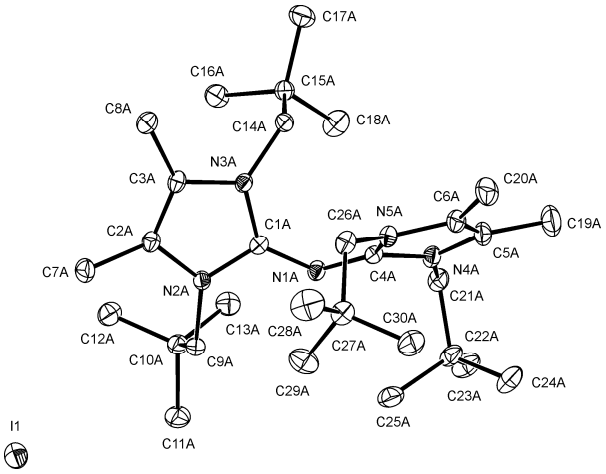


Figure 2.5. X-ray crystal structure of the BIMA salt **1b**$^{+}$I^{-}. The displacement ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bonds distances [Å] and angles [°]: N(1A)-C(1A) 1.333(3), N(1A)-C(4A) 1.336(3), N(2A)-C(1A) 1.355(3), N(2A)-C(2A) 1.412(3), C(2A)-C(3A) 1.343 (3), N(3A)-C(3A) 1.408(3), N(3A)-C(1A) 1.364(3), N(4A)-C(4A) 1.359 (3), N(4A)-C(5A) 1.407(3), C(5A)-C(6A) 1.345(4), C(1A)-N(1A)-C(4A) 122.8(2); dihedral angle between the two imidazolium rings 52.9(2).

2.5. Dynamic Processes in NMR Spectra of BIMAs

Slow dynamic processes on the NMR timescale were observed for solutions of salt **1b**$^{+}BF_4^{-}$ (Figures 2.7 and 2.8). The broadening and non-equivalence of CH_2CMe_3 groups was observed in the ^1H NMR spectrum at 25 °C. In CD_3OD at –33 °C, the ^1H signals of two non-equivalent CH_2 groups were split to *AB* systems, additionally two non-equivalent CMe_3 and Me were observed. Both ^1H NMR and ^{13}C NMR spectra at low temperature were in good agreement with *pseudo*-C_2 symmetry of **1b**$^{+}$ (Figure 2.6). At 100 °C in DMSO-d6 the proton signals within each group become equivalent and appeared as typical singlets.

The activation barrier of observed temperature dependent dynamic process, $\Delta G^{\neq} = 14.6$ kcal mol^{-1} (298 K) was determined in collaboration with Dr. David Šaman. The process was believed to be a slow rotation of the Me_3CCH_2 groups about CH_2–N bonds associated with slow rotation of the imidazolium rings about exo-cyclic C-2,N / N,C-2' bonds.

In contrast to **1b**$^{+}$, no slow dynamic processes were observed for the cation **1a**$^{+}$, and its NMR spectra remained unchanged to –20 °C.

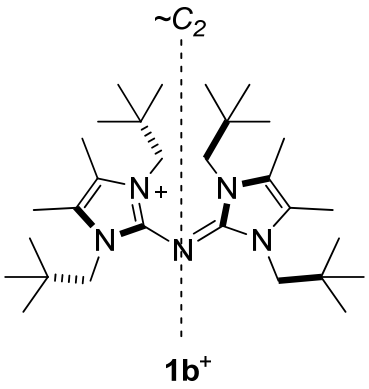


Figure 2.6. BIMA **1b**$^{+}$ *pseudo*-symmetry.

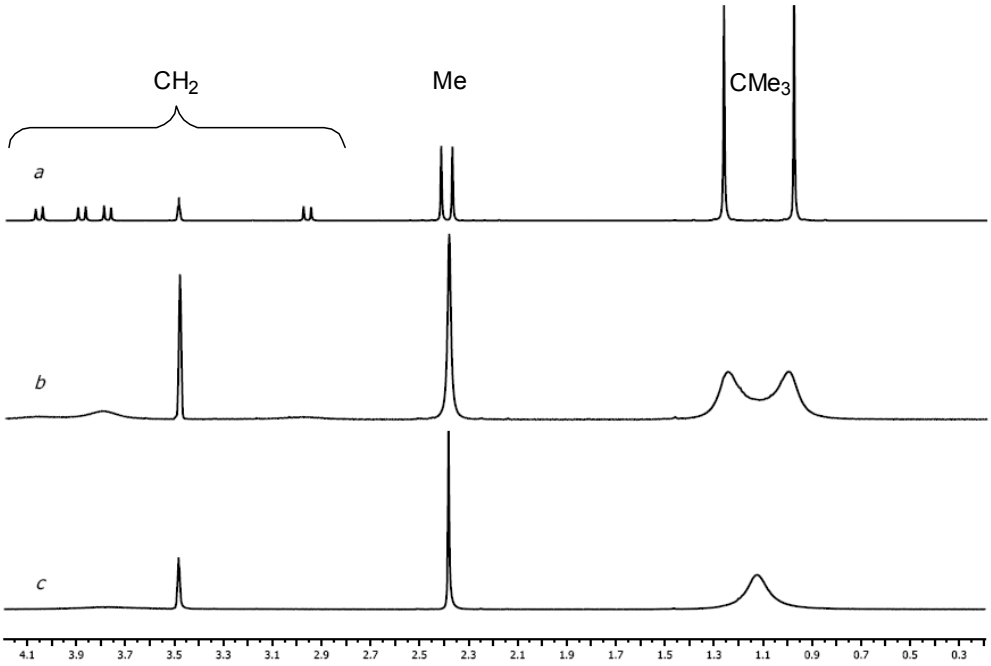


Figure 2.7. Temperature dependent ^{1}H NMR spectra of the cation **1b**$^{+}$ measured in CD_3OD at 240 K (*a*), 298 K (*b*) and 313 K (*c*).

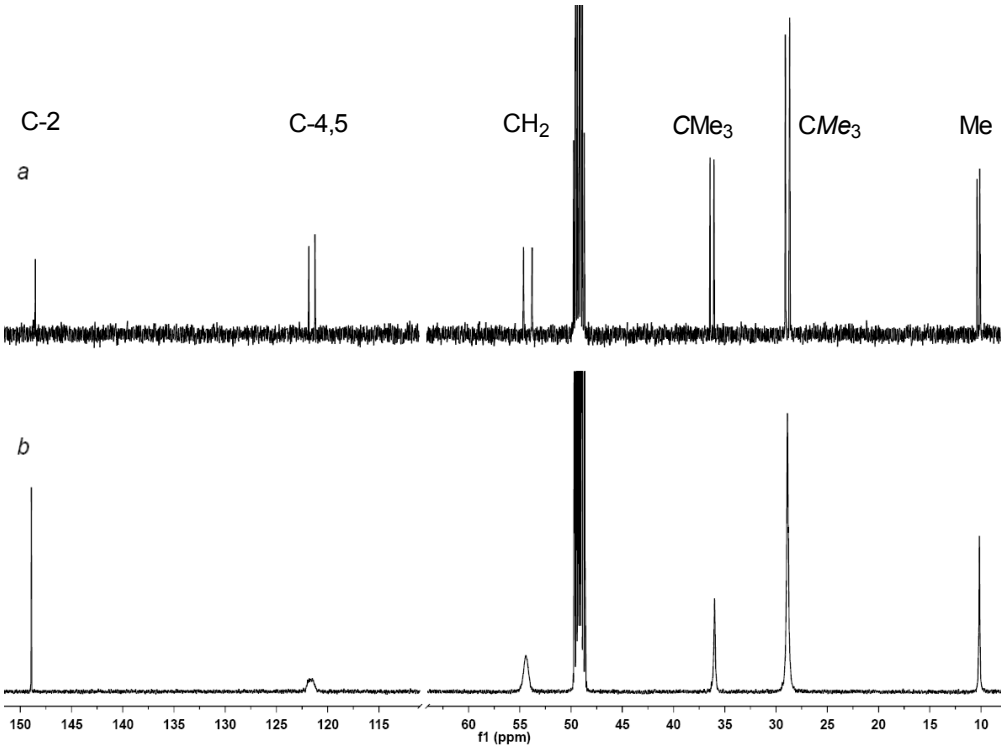
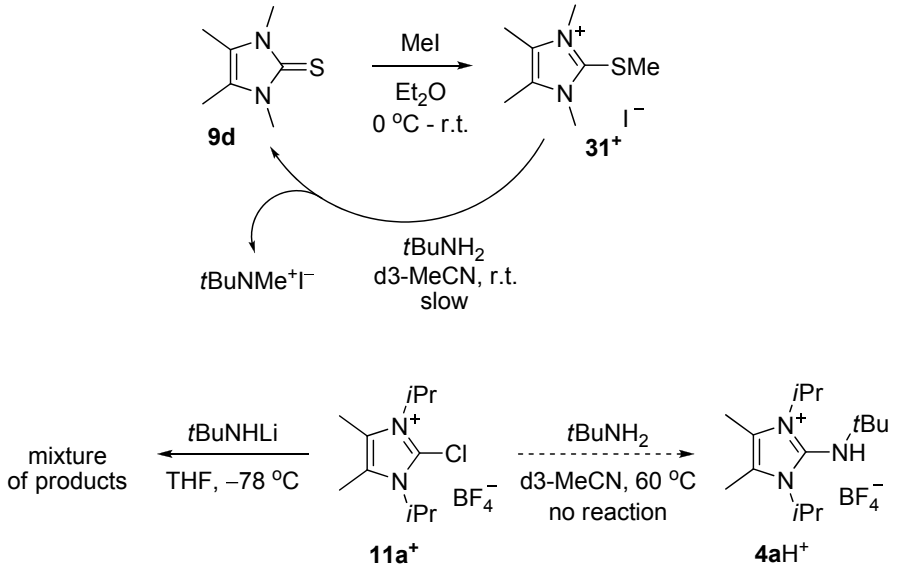


Figure 2.8. Temperature dependent ^{13}C NMR spectra of the cation **1b**$^{+}$ measured in CD_3OD at 240 K (*a*) and 300 K (*b*).

3. 1,3-Dialkyl-4,5-dimethylimidazol-2-ylidene Amine (IMAM) Bases

3.1. First Attempts to IMAM Bases Synthesis

The synthesis of the protonated forms of *N*-*tert*-butyl-substituted imidazol-2-ylidene amine bases **4**H$^+$ was first attempted by reaction of *tert*-butyl amine with two different 2-X-imidazolium cations **31**$^+$ and **11a**$^+$ (Scheme 3.1). Neither more accessible 2-methylthioimidazolium salt **31**$^+$I$^-$, nor more electrophilic 2-chloroimidazolium salt **11a**$^+$BF$_4^-$ gave the target products **4**H$^+$. In the case of salt **31**$^+$I$^-$ [89] synthesized from tetramethylimidazole-2-thione **9d**[66] by reaction with methyl iodide a slow methylation of *tert*-butyl amine and re-formation of the corresponding imidazole-2-thione **9d** was observed. No reaction between 2-chloroimidazolium salt **11a**$^+$BF$_4^-$ and *tert*-butyl amine was detected at 60 °C, while the reaction with hard nucleophilic *t*BuNHLi (2 equiv.) at –78 °C led to mixture of unidentified products (Scheme 3.1).

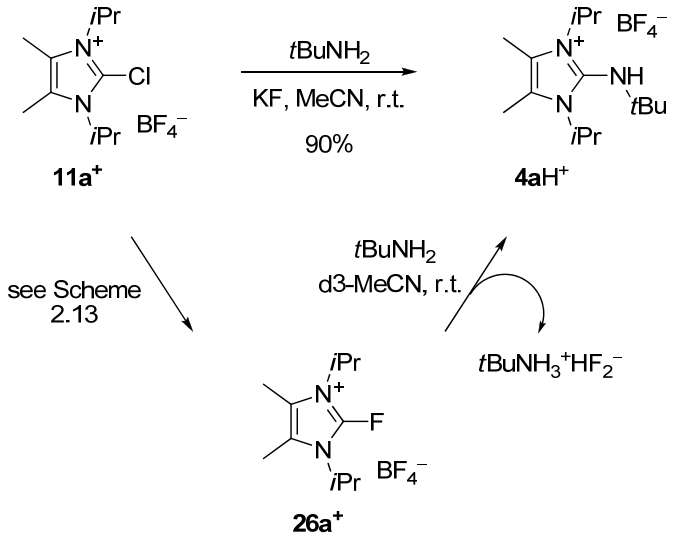


Scheme 3.1. Attempted substitution reactions of X in 2-X-imidazolium cations with *t*BuNH$_2$.

The imidazolation technique used previously in synthesis of BIMAs (see Chapter 2) turned out to be effective also for imidazolation of primary amines. The reaction of 2-chloroimidazolium salt **11a**$^+$BF$_4^-$ with excess *t*BuNH$_2$ in the presence of an excess KF gave

product **4a**$H^+BF_4^-$ in high yield within two days (Scheme 3.2). This confirms the assumption that KF acts not only as a base scavenging protons and allowing thus to achieve the full conversion, but also as an activator converting 2-chloroimidazolium cation $\mathbf{11}^+$ to the more electrophilic 2-fluoroimidazolium cation $\mathbf{26}^+$ (see Schemes 2.12 and 2.13), which reacts even with primary amines. When the reaction was monitored before complete conversion, both $\mathbf{11a}^+$ and $\mathbf{26a}^+$ were observed in the reaction mixture along with the formed product. Thus substitution of chloride by fluoride and imidazolation of *tert*-butyl amine by 2-fluoroimidazolium cation $\mathbf{26}^+$ progresses with comparable rates. Imidazolation of *tert*-butyl amine in contrast to imidazolation of 2-aminoimidazolium cations **22**H^+ proceeds exclusively by pathway (b) (see Scheme 2.12).

Such reactivity was completely confirmed by the reaction of 2-fluoroimidazolium salt **26a**$^+BF_4^-$ with *tert*-butyl amine to 2-aminoimidazolium salt **4a**H^+ in the absence of KF at ambient temperature (Scheme 3.2).



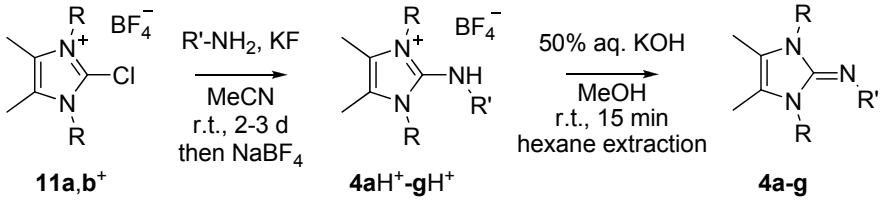
Scheme 3.2. Reactivity of 2-chloro- and 2-fluoroimidazolium salts towards *tert*-butyl amine.

3.2. Synthesis and Properties of IMAM Bases

The 4-5 steps protocol for the synthesis of IMAM bases **4** commenced with preparation of chloroimidazolium cations $\mathbf{11}^+$ as described in Chapter 2.1.1.

The IMAM salts **4a-g**$H^+BF_4^-$ were synthesized by KF-mediated coupling of 2-chloroimidazolium salts **11a**,**b**$^+BF_4^-$ with the corresponding primary amines in acetonitrile in good yields. A wide range of primary amines with different sterics and electron donicity was used in this reaction. Emphasis was placed on the most sterically hindered and electron donating alkyl amines (e. g. tertiary alkyl amines) to achieve high basicity along with relatively low nucleophilicity of the formed bases.

The IMAM bases **4a-g** were liberated in high yields from the corresponding salts by using a 1:1 v/v mixture of 50% aq. KOH and methanol (Scheme 3.4).



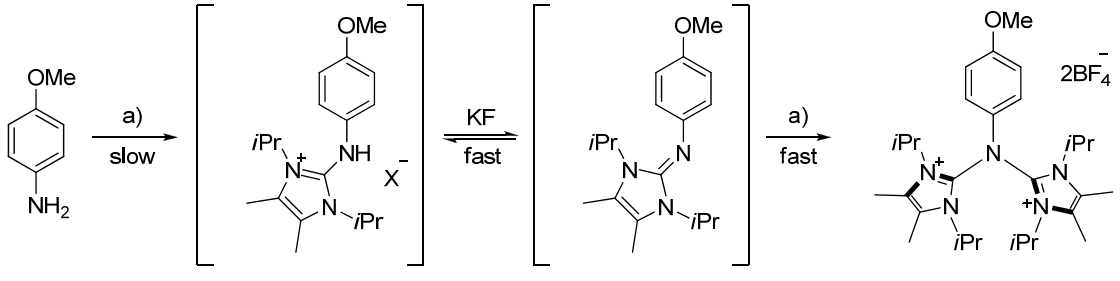
11a,**b**$^+$ **4a**H^+-**g**H^+ **4a-g**

a: R = *i*Pr
b: R = Np

	R	R'	Yield*
4a	*i*Pr	*t*Bu	68%
4b	*i*Pr	CMe_2CH_2tBu	65%
4c	*i*Pr	*i*Pr	76%
4d	*i*Pr	CH_2tBu	70%
4e	*i*Pr	Me	81%
4f	CH_2tBu	*t*Bu	68%
4g	*i*Pr	Et	69%

Scheme 3.4. Synthesis of bases **4a-g** from **11**$^+$. * Isolated yields are given for two steps starting from **11**$^+$ for bases **4a-g**.

With *p*-anisidine a fast double imidazolation resulting in the dicationic salt **32**$^{2+}(BF_4^-)_2$ was observed (Scheme 3.5).



4hH^+ **4h** **32** 82%

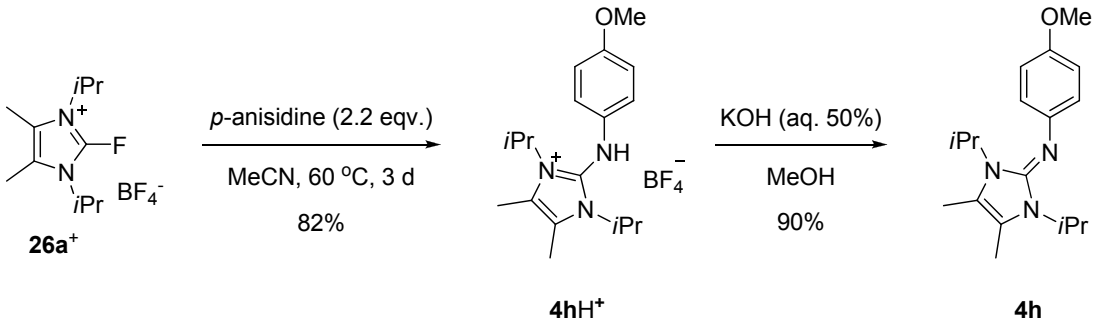
active nucleophile

Scheme 3.5. KF-mediated formation of dication **32**$^{2+}$. a) **11a**$^+$, KF, MeCN, 60 °C, 3 days.

That a similar process was not observed in *N*-alkyl substituted products **4a-g** might be associated with the lower acidity of **4a-g**H^+ resulting in smaller equilibrium concentration of free bases **4** in the reaction mixture. This result can be traced to the much higher acidity of **4h**H^+ in comparison with **4a-g**H^+, which resulted in a significant quasi-equilibrium concentration of corresponding base **4h** under the basic reaction conditions and fast second imidazolation to dication $\mathbf{32}^{2+}$.

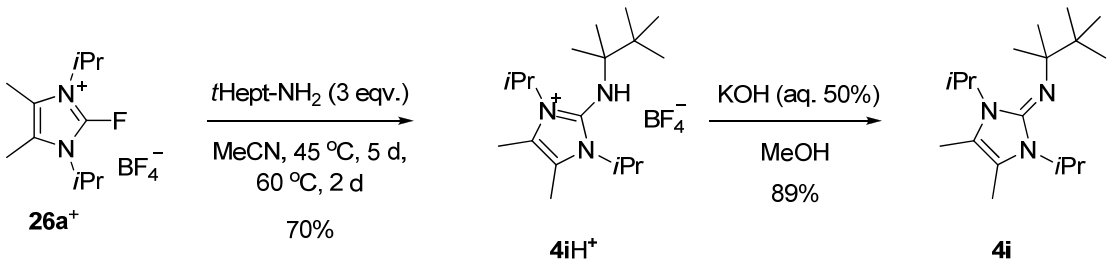
Attempts to stop the reaction after the first imidazolation of *p*-anisidine by using 2-fluoroimidazolium salt $\mathbf{26a}^+$ and weaker bases such as triethylamine led to a mixture of **4h**H^+ and $\mathbf{32}^{2+}$ in a ratio of ~3:1.

Salt **4h**$H^+BF_4^-$ was selectively prepared by using of *p*-anisidine as reagent and base. Excess of *p*-anisidine was easily separated from a crude product by washing with ether. Deprotonation of salt **4h**$H^+BF_4^-$ gave the desired base **4h** in good overall yield (Scheme 3.7).



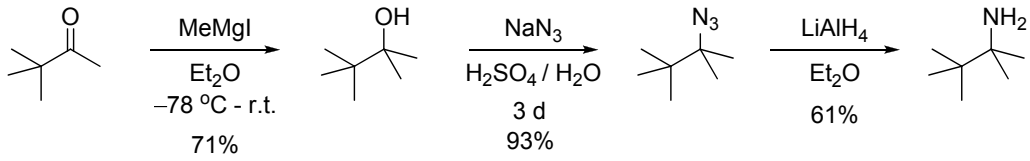
Scheme 3.7. Synthesis of IMAM base **4h**.

A similar indirect method was also used for the synthesis of salt **4i**$H^+BF_4^-$ and base **4i**, because a considerably better yield was achieved (Scheme 3.8).



Scheme 3.8. Synthesis of IMAM base **4i**.

tert-Heptyl amine[90] was prepared in 3 steps in moderate overall yield starting from methyl *tert*-butyl ketone via *tert*-heptanol (triptanol)[91] and *tert*-heptylazide (Scheme 3.9). The latter was prepared analogously to *tert*-butyl azide,[83] but with continuous stirring for 3 days. This approach was found to be better alternative to the known procedure via *tert*-heptyl formamide formation.[92]

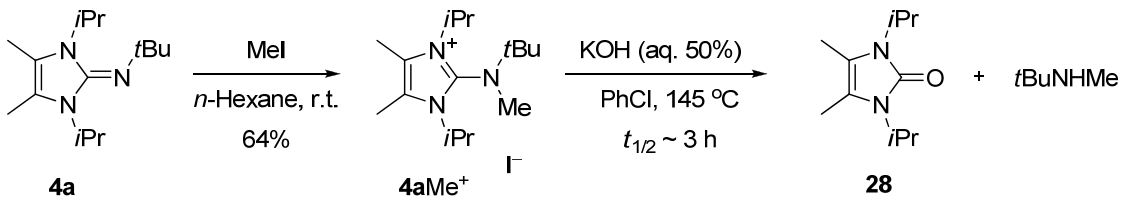


Scheme 3.9. Preparation of *tert*-heptyl amine from pinacolone.

Unsubstituted IMAM base **22a** was synthesized from corresponding *N*-TMS derivative as shown in Scheme 2.8 (Chapter 2.1.2).

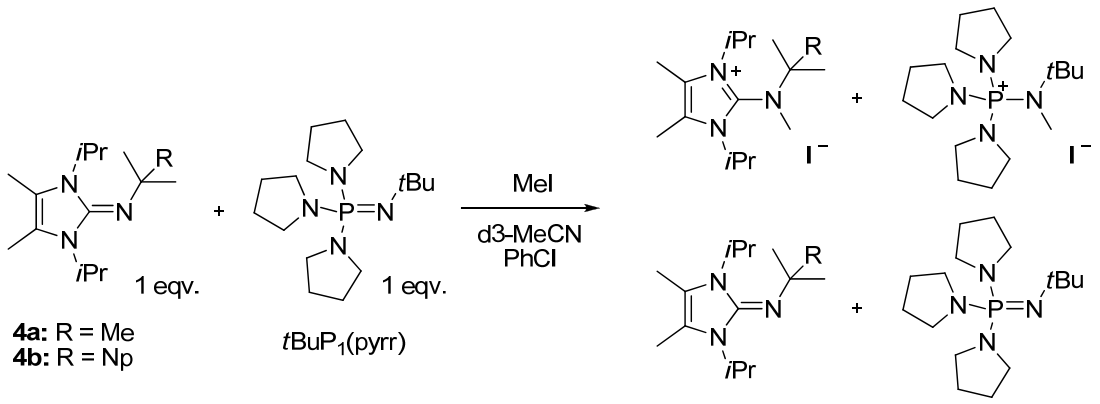
IMAM bases are stable liquids (**4a**-**g**) or crystalline solids (**4h**,**i**). They can be stored as hexane stock solutions at 5 °C over BaO for several months. IMAM bases are readily miscible with common aprotic organic solvents including hydrocarbons. Highly hydgophobic base **4a** was found to be soluble in D_2O, where it exists in fully ionized form **4a**D^+OD^- according to ^{13}C NMR (see Chapter 3.6). It is quite stable towards hydrolysis, and no changes were observed after heating at 100 °C in D_2O for one hour. The most basic compounds were found to be sensitive to atmospheric moisture and CO_2, giving protonated forms on air rapidly (probably as the bicarbonate salts).

Product **4a**Me^+I^- prepared from **4a** and methyl iodide was found to be reasonably stable towards hydrolysis even under drastic alkaline conditions **A** (see Chapter 2.2.2) showing a half-life time of ~3 h (Scheme 3.10).



Scheme 3.10. Hydrolysis of **1a**Me^+ under drastic basic conditions.

The nucleophilities of bases **4a** and **4b** were estimated by comparison with known *t*BuP$_1$(pyrr) by a NMR competition experiment. Equimolar mixtures of **4a**/*t*BuP$_1$(pyrr) or **4b**/*t*BuP$_1$(pyrr) and methyl iodide in MeCN-d$_3$ were monitored by ^{1}H NMR spectroscopy at room temperature. After completion of methylation the ratios of all four compounds were determined (Scheme 3.11). Thus, nucleophilicity of **4a** and **4b** towards methylation by methyl iodide was found to be ~ 60 and ~ 5 times higher than of *t*BuP$_1$(pyrr) respectively.

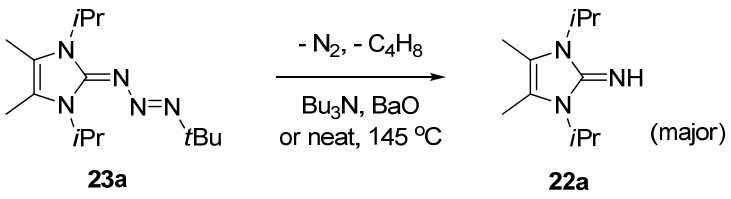


Scheme 3.11. Comparison of the nucleophilicity of IMAM bases **4a**,**b** relative to P$_1$ base.

3.3. Synthesis of IMAM Bases Using Alternative Approaches

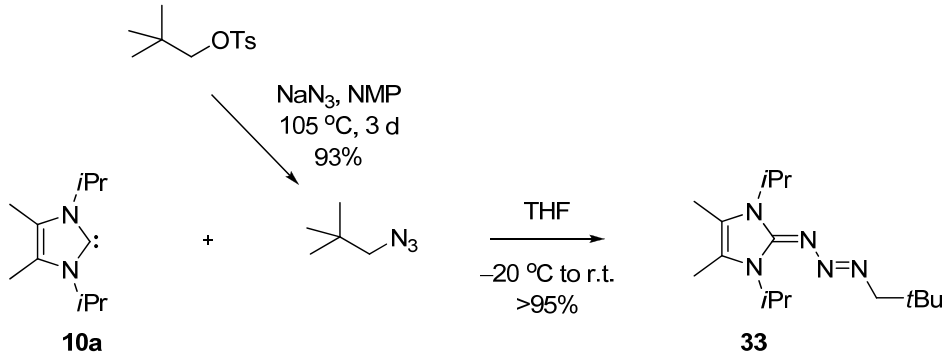
Recently Bielawski and Khramov showed the possibility of Staudinger type decomposition of two triazenes with formation of IMAM base analogues with benzyl and aryl *N*-substituents in high yield after pyrolysis in different solvents.[93,94]

Attempts to perform similar Staudinger-type reactions for synthesis of bases **4** from *N*-alkyl-substituted triazene precursors **23** were unsuccessful. Thermolysis *t*Bu-substituted triazene **23a** neat or in solution in the presence of bases led invariably to extrusion of isobutene and nitrogen yielding **22a** as was established by NMR spectra (Scheme 3.12).



Scheme 3.12. Attempted pyrolysis of *tert*-butyl-substituted triazene **23a**.

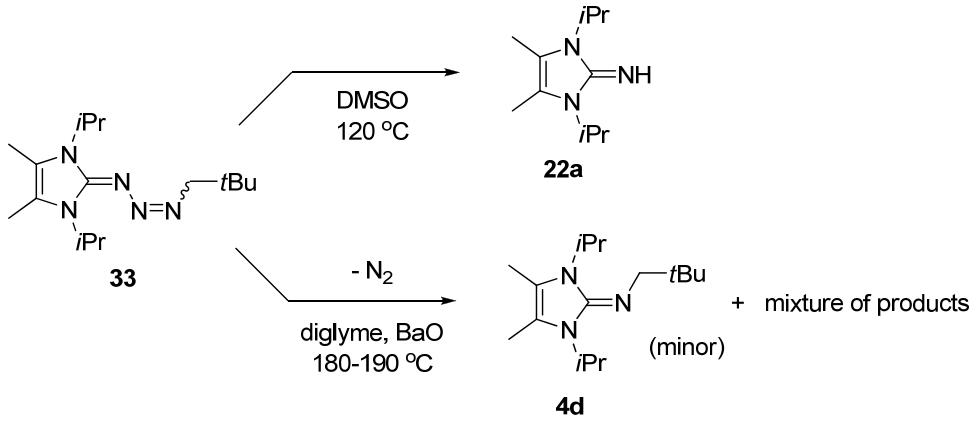
Neopentyl-substituted triazene **33** was isolated in excellent yield by reaction of imidazol-2-ylidene **10a** with neopentyl azide[95,96] prepared in high yield from neopentyl tosylate[97] (Scheme 3.13).



10a **33**

Scheme 3.13. Preparation of neopentyl-substituted triazene **33**.

However, thermolysis of triazene **33** in DMSO at 120 °C within several hours ($t_{1/2}$ ~ 40 min) also gave the product **22a** as revealed by the NMR spectra of the reaction mixture (Scheme 3.14). Since traces of water were able to catalyze the degradation, thermolysis of triazene **33** was carried out also in dry diglyme in the presence of barium oxide. Although slower consumption of the initial triazene was observed, a mixture of several compounds resulted, the target product **4d** was found only in insignificant quantity.

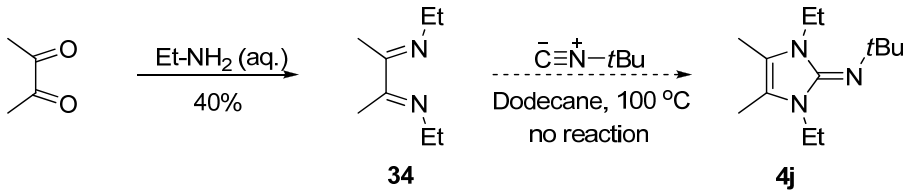


Scheme 3.14. Attempts of Staudinger type synthesis of IMAM base **4d**.

The failure of Staudinger-type reactions or their very low yields for *N*-alkyl substituted triazenes can be explained by a considerably higher steric hindrance at the N-3 atom in

triazenes with *tert*-butyl and neopentyl groups in comparison with triazenes with phenyl and benzyl groups described by Bielawski and Khramov.

A second alternative pathway potentially suitable for the synthesis of IMAM bases by a two-step procedure from accessible compounds consisted of [4+1] cycloaddition of *tert*-butyl isonitrile to diimine **34** (Scheme 3.15). Diimine **34** was prepared from the diketone and ethylamine in moderate yield. *tert*-Butyl isonitrile was prepared from *tert*-butylformamide[98] according to Casanova's protocol in low yield.[99,100] After heating of an equimolar mixture of diimine **34** and *tert*-butyl isonitrile in dodecane at 100–105 °C overnight no changes in the reaction mixture was observed.

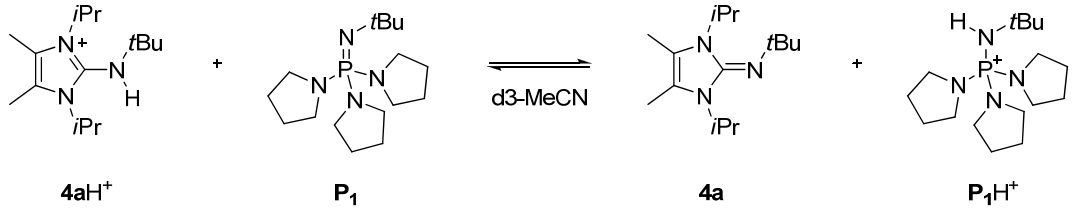


34 **4j**

Scheme 3.15. Attempted synthesis of IMAM base **4j** by [4+1] cycloaddition of isonitrile.

3.4. Basicity Estimation of IMAM Bases

pK_{BH+} value of IMAM base **4a** was estimated by ability of base *t*BuP$_1$(pyrr) with known pK_{BH+} to deprotonate IMAM salt **4a**H$^+$BF$_4^-$ according to the following reaction (Scheme 3.16).



4aH$^+$ **P$_1$** **4a** **P$_1$**H$^+$

Scheme 3.16. Experiment of the basicity comparison of IMAM base **4a** *vs.* *t*BuP$_1$(pyrr) base.

For equilibrium conditions the pK_{BH+} for compound **4a** can be calculated using simple formula shown on the Eq. 3.1, where [**4a**H$^+$], [**4a**], [**P$_1$**], [**P$_1$**H$^+$] – relative concentrations of **4a**H$^+$, **4a**, P$_1$, P$_1$H$^+$, respectively.

$$p\mathit{K}_{BH+}{}^{MeCN}\,(\mathbf{4a}) \approx p\mathit{K}_{BH+}{}^{MeCN}\,(\mathbf{P_1}) + \lg([\mathbf{4a}H^+]([\mathbf{P_1}]_o - [\mathbf{4a}])\,/\,[\mathbf{4a}]^2)$$

$$[\mathbf{P_1}]_o = [\mathbf{P_1}] + [\mathbf{P_1}H^+] \qquad \textbf{(Eq. 3.1)}$$

Equilibrium relative concentrations of **4a** and **4a**H^+ were defined from ^{13}C NMR spectra of the reaction mixture as follows. It was found that the differences, Δ, between the chemical shifts of C2 and C4,5 carbon atoms in ^{13}C NMR spectra for IMAM salt **4a**$H^+BF_4^-$ while deprotonation correlated linearly ($R^2 = 0.99$) with the degree of the deprotonation according to Eq. 3.2, where $[\mathbf{4a}H^+]_o = [\mathbf{4a}] + [\mathbf{4a}H^+]$ and Δ = δ(C2) – δ(C4,5), ppm.

$$[\mathbf{4a}]/[\mathbf{4a}H^+]_o \approx 0.0704\Delta - 1.13 \qquad \textbf{(Eq. 3.2)}$$

Thus, the Δ value of imidazolium signals after reaching equilibrium (Scheme 3.16) allowed the calculation of the relative concentrations of **4a** and **4a**H^+ in the reaction mixture.

The ratio between $[\mathbf{4a}H^+]_o$ and $[\mathbf{P_1}]_o$ may be defined from the starting molar loadings or from the ^1H NMR spectrum. It is necessary to note that proton exchange between phospazene base *t*BuP_1(pyrr) and its protonated form is fast in the time scales of ^1H NMR and ^{13}C NMR and average signals are visible only. The same is true for IMAM base **4a** and salt **4a**H^+ as well.

After insertion of the obtained values into Eq. 3.1, the $p\mathit{K}_{BH+}$ for base **4a** amounted ~ 30.5 (*c.f.* precisely determined value, Chapter 3.5). This means that IMAM base **4a** is two orders of magnitude more basic than *t*BuP_1(pyrr) and six orders more basic than DBU!

It was supposed that aromatization and steric strain release upon protonation play significant role in high basicity of **4a**.

This unexpected high basicity of **4a** prompted a more accurate determination of the basicity for majority of the synthesized IMAM bases **4** and exploration of the factors responsible for their basicity.

3.5. Basicity Determination of IMAM Bases

The $p\mathit{K}_{BH+}$ values for eleven examples of IMAM bases **4a-f**,**h**,**i**,**k**,**l** and **22a** were determined in MeCN solution in collaboration with Leito's group (University of Tartu,

Estonia), see Table 1, Experimental Part. The basicities were measured using photometrical titrations with references dyes with known pK_a and were corrected, in particular, by taking into account the contribution of ion pair formation. The uncertainties of the pK_{BH+} values are estimated to be ± 0.15 pK_{BH+} units. The determined pK_{BH+} values are plotted in Figure 3.1. For comparison, pK_{BH+} values of some known bases are also added.

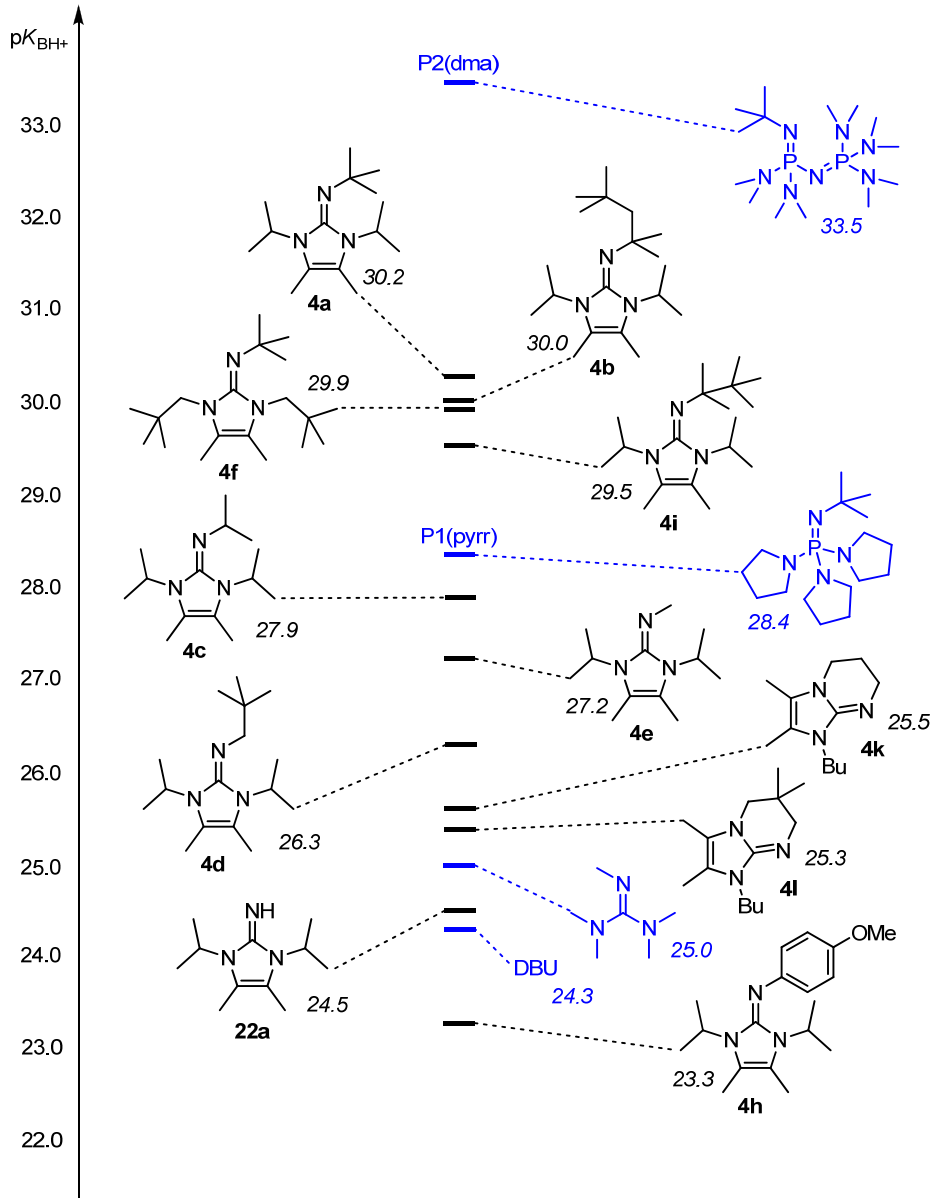
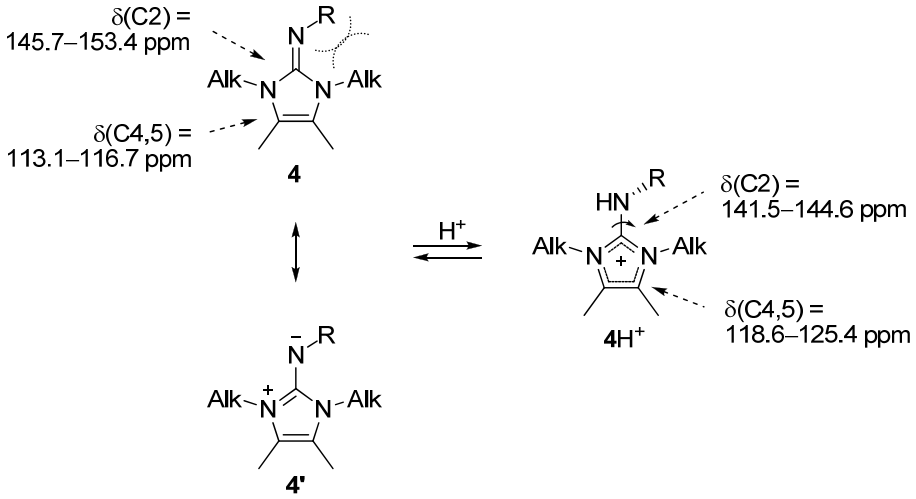


Figure 3.1. Measured pK_{BH+} of IMAM bases **4** (black) in comparison with known pK_{BH+} of phosphazene, guanidine and amidine bases (blue) in MeCN. Basicity of the bases increases from bottom to top. * Bases **4k**,**l** were prepared by S. Polyakova.[101]

The compounds **4** having *tert*-alkyl substituent at the imine nitrogen atom were found to be stronger than *t*BuP$_1$(pyrr) base (Figure 3.1). Some variability of the substituents in 1,3-position was possible without diminishing the basicity significantly (**4a** *vs* **4f**). Increase of the bulkiness of the substituent at the imine nitrogen in the route *t*Bu – *t*Oct – *t*Hept led to insignificant decrease of basicity (**4a** *vs* **4b**, **4i)**. However, as the bulkiness of the substituent decreases in the route *t*Bu – *i*Pr – Me – H, the basicity becomes lower (**4a** > **4c** > **4e** > **22a**).

In contrast to the gas phase where **4a** and **4i** have almost equal basicity (see Experimental part, Table 1), in MeCN solution **4a** is slightly stronger than **4i**, what can be explained by better stabilization by solvation of cation **4a**H$^+$ compared to bulkier **4i**H$^+$. Compound **4h** with aromatic imino substituent displayed the weakest basicity among all bases **4**. Bicyclic compounds **4k**,**l** displayed a significantly lower basicity than monocyclic bases, but still a higher than **22a** and literature known **ImPyr** (Figure 1.10). One pK_{BH+} unit difference in basicity of **4k** and **ImPyr** allows to estimate the contribution of two donor methyl groups in basicity of IMAM bases in the solution.

3.6. NMR Spectra of IMAM Bases and their Basicity in Solution



Scheme 3.17. Aromatization of **4** upon protonation and ^{13}C NMR chemical shifts ranges for selected atoms of bases **4** and salts **4**H$^+$. The chemical shifts for **4**, **22a** are measured in C_6D_6, for **4**H$^+$, **22a**H$^+$ in $CDCl_3$.

The chemical shifts of the central C2 and carbon atoms C4,5 for bases **4**, **22a** and their protonated forms in ^{13}C NMR are given on Scheme 3.17. For the bases and salts Δ = δ(C2) –

δ(C4,5) amounted 29.6–40.3 ppm and 13.3–24.7 ppm, respectively, can be used to describe the level of aromaticity of their imidazolium rings. The smaller the value of Δ in base **4**, the larger is the contribution of aromatic resonance structure **4'**. The smaller the value of Δ in protonated form **4**H$^+$, the more aromatic this form is.

In the salts **4**H$^+$ the Δ parameter increases in the following order: **4a**H$^+$ (R' = *t*Bu, 17.3 ppm) < **4c**H$^+$ (R' = *i*Pr, 19.5 ppm) < **4e**H$^+$ (R' = Me, 21.6 ppm) < **22a**H$^+$ (R' = H, 23.4 ppm). The Δ values of the free bases **4** increase in the same order: **4a** (R' = *t*Bu, 30.1 ppm) < **4c** (R' = *i*Pr, 32.6 ppm) < **4e** (R' = Me, 35.9 ppm) < **22a** (R' = H, 40.1 ppm). Thus, the Δ value is the lowest for the most sterically hindered compounds and highest for the least sterically hindered compounds. In stated above route from **22a** to **4a** increases steric repulsion between the substituent on N-*exo* and *i*Pr substituents on N-1 or N-3. Consequently, the double bond character of base **4** decreases and the contribution of the aromatic imidazolium amide resonance structure **4'** rises that lead to growth of basicity of IMAM base **4**. On the other hand, increase of the steric repusion in the protonated from in the similar route from **22a**H$^+$ to **4a**H$^+$ lead to smaller interaction of N-*exo* electron pair with imidazolium ring, growth of aromaticity of **4**H$^+$ and decrease of **4**H$^+$ acidity.

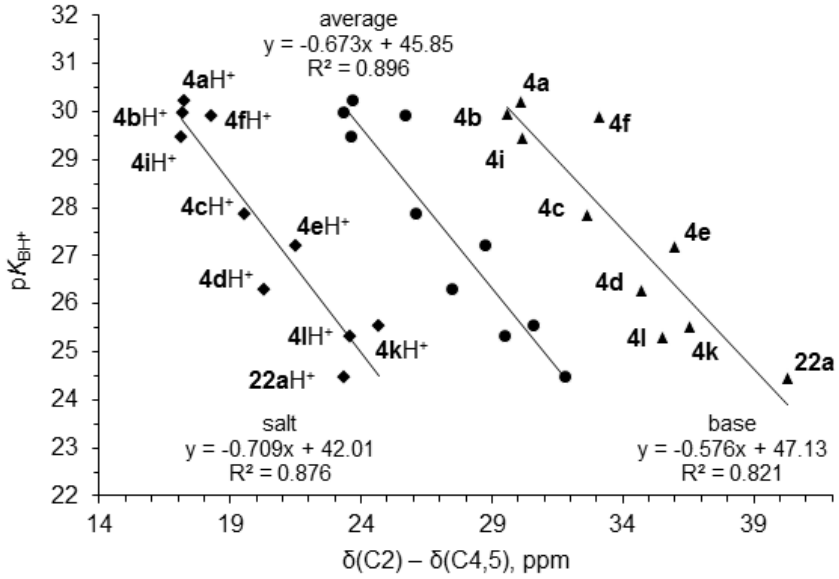


Figure 3.2. pK_{BH+} values (in MeCN) *vs*. ^{13}C NMR chemical shift differences for bases **4a-f**,**i**,**k**,**l** and **22a** and corresponding salts.

When chemical shift differences Δ for bases **4** and salts **4**H$^+$ were plotted against the measured pK_{BH+} a reasonable linear correlations were found (Figure 3.2, right and left). The correlation was even better for average chemical shift differences Δ for **4** and **4**H$^+$ (Figure 3.2, middle). The linear correlation was only valid, if the substituents on N-*exo* had a similar electronic nature, and thus does not hold for **4h** with aromatic imino substituent.

Found trends and correlation supports the idea that synergetic effect of aromatization and steric strain release play important role in high basicity of IMAM bases **4** in solution. Compounds **4k**,**l** were found to be five orders of magnitude weaker bases than monocyclic base **4a**, because the additional rigid six-membered ring precludes free C=N rotation and significant steric strain release upon protonation.

3.7. Basicity in the Gas Phase and Factors Influencing It

A computational study of compounds **4a-f**,**h**,**i**,**k**,**l** and **22a** was performed by Leito's group and included calculation of GB and ΔNICS(1)* values in the gas phase (see Table 1, Experimental Part). The latter characterizes the level of aromatization of the imidazole ring of IMAM bases on protonation and was important for estimation of the contribution of aromatization to their basicity in the gas phase. [102] The more negative ΔNICS(1) values indicates the higher increase of aromaticity.

Calculated GBs almost linearly correlated with measured pK_{BH+} in MeCN (Figure 3.3), observed slight deviations can be explained by difference in solvation of IMAM bases.

* The term ΔNICS(1) here denotes the difference between NICS(1) values of protonated and neutral form of IMIM base. NICS(1) is the average value between the values calculated 1 Å above and below the mass-centre of the ring.

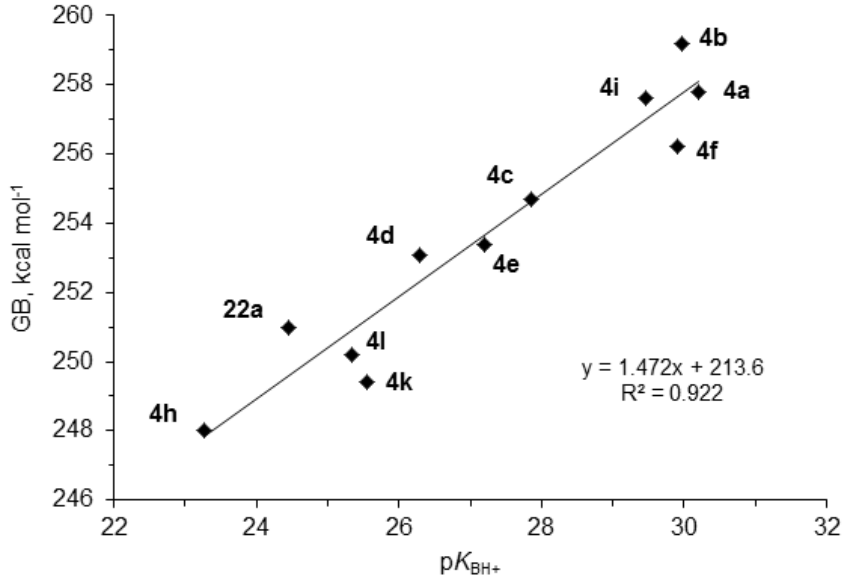


Figure 3.3. Correlation of the gas phase basicities and measured MeCN pK_{BH+} of IMAM bases.

A rough linear correlation was also found between measured MeCN pK_{BH+} values and calculated ΔNICS(1) values for **4** in the gas phase (Figure 3.4).

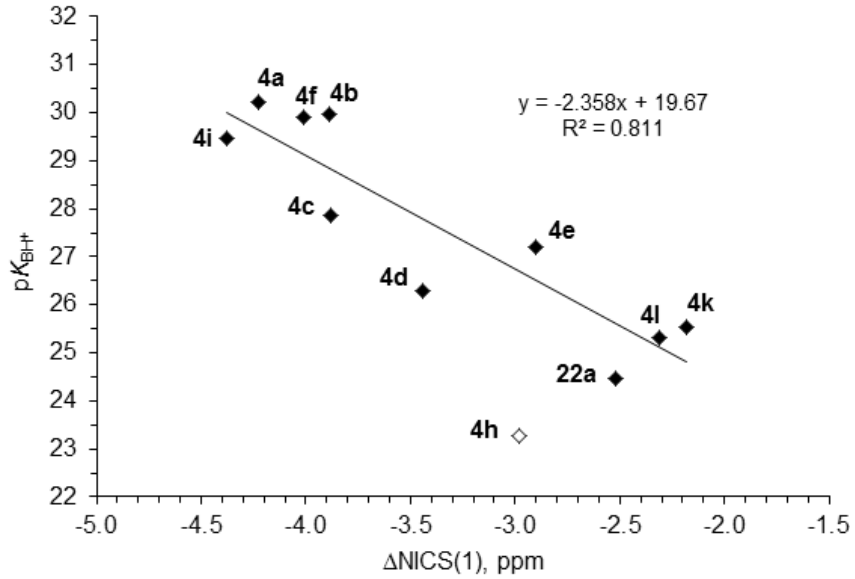


Figure 3.4. Correlation between ΔNICS(1) values and measured MeCN pK_{BH+} values of IMAM bases, **4h** has been excluded from linear fitting.

As evidenced, all studied bases **4** and **22a** showed significant increase of aromaticity on protonation in the gas phase, their ΔNICS(1) values were in the range of –2.18 – (–4.38). Thus, prepared compounds **4** are the first class of strong bases where aromatization upon protonation contribute to its high basicity.[103,104]

To estimate and compare the individual role of aromatization, steric strain release and other factors in highly basic nature of **4**, GB of compounds **A**, **B**, **C** and **D** were calculated and compared with each other and **4a**,**e** (Figure 3.5). Comparison of basicities in solution between **4** and literature known cyclic guanidines,[105,106] and imidazol-2-ylidene amines[48,107] was supposed difficult, since no experimental pK_{BH+} values were reported for them.

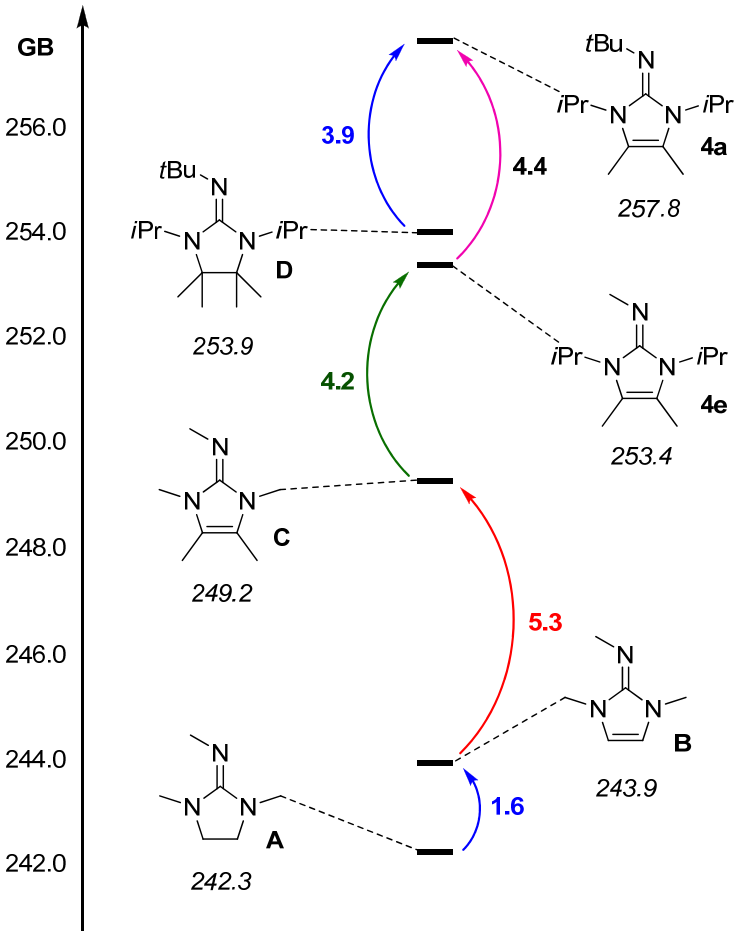


Figure 3.5. Calculated gas phase basicities (kcal mol^{-1}) for imidazol-2-ylidene amines and their saturated analogues.

As can be seen, individual role of aromatization upon protonation (blue arrows, Figure 3.5) to some extent can be estimated comparing **A** with **B** and **D** with **4a**. In the first case, increase of basicity by aromatization factor was 1.6 kcal mol^{-1}, however in the second case it was grown to 3.9 kcal mol^{-1}, what can be explained by existence of synergetic effect of aromatization and steric strain release on protonation. Evidently, for pair **D**-**4a** steric strain release is more significant than for pair **A**-**B**.

Substitution of 4,5-hydrogen atoms in **B** with two donor methyl groups (**C**) allows to gain 5.3 kcal mol^{-1} of GB (red arow).

Substitution of 1,3-methyl groups in **C** with two more electron donor and bulkier *i*Pr groups (**1e**) results in increase of GB additionally on 4.2 kcal mol^{-1} (green arrow).

Eventually, substitution of methyl group in **1e** with bulky *t*Bu (**1a**) allows to gain additionally 4.4 kcal mol^{-1} (magenta arrow), partly by increase of steric strain release effect. Thus, high basicity nature of compounds **4** in the gas phase is considered to be a result of a comparable contribution of such factors as donor effect of two methyls in 4,5-position, donor effect of 1,3-dialkyl substituents, aromatization and steric strain release on protonation. Many those factors have synergetic action.

It should be noted, that the contributions of the discussed factors in the gas phase may differ from those in solution dramatically.

3.8. Selected Solid State Structures

The solid state structures of the salts **4a**$H^+BF_4^-$ (Figure 3.5), **4i**$H^+BF_4^-$ (Figure 3.6), **4h**$H^+BF_4^-$ (Figure 3.7) as well as the free base **4h** (Figure 3.8) were characterized by X-ray crystal structure analysis. The imidazole rings for all three structures **4a**H^+, **4h**H^+ and **4h** are planar. *Exo*-nitrogen atoms (N4) for salts **4a**H^+, **4h**H^+ are located in the plane of the imidazolium rings, while for base **4h** a very slight deviation (6.7 °) from planarity was observed. The bond lengths between N1(3)–C2, N1(3)–C5(4) and C4–C5 in salts **4a**H^+ and **4h**H^+ are close to each other. The average N1(3)–C2–N4–C14 torsion angle is close to orthogonal with 88.0° for salt **4a**H^+ and approximately 70.0° for salt **4h**H^+. On deprotonation of the salt **4h**H^+ the bonds N1(3)–C2 and N1(3)–C5(4) became elongated in **4h** by 0.010-0.036 Å, while the C4–C5 and C2–N4 bond were shortened by 0.013 Å and 0.064 Å. The average N1(3)–C2–N4–C14 torsion angle (34.8°) for base **4h** indicates a significant deviation of the C–N double bond from the planar geometry.

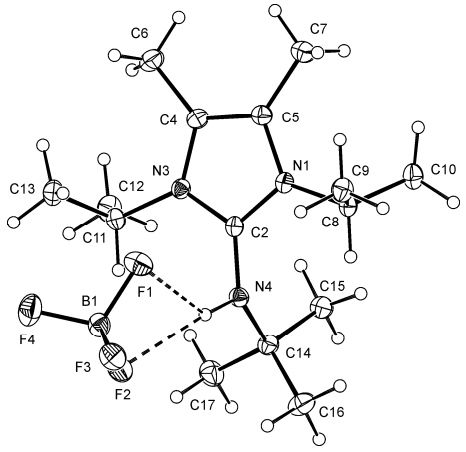


Figure 3.5. X-ray crystal structure of the salt **4a**$H^+BF_4^-$. The displacement ellipsoids are drawn on 30% probability level. Selected bonds distances [Å] and angles [°]: N4–C2 1.367(2), N1–C2 1.351(2), N3–C2 1.348(2), N1–C5 1.395(2), N3–C4 1.397(2), C4–C5 1.352(2); N1–C2–N4 123.55(15), N3–C2–N4 128.58(15), N1–C2–N3 107.73(13), C2–N4–C14 124.53(13); average N1(3)–C2–N4–C14 torsion angle: 88.0.

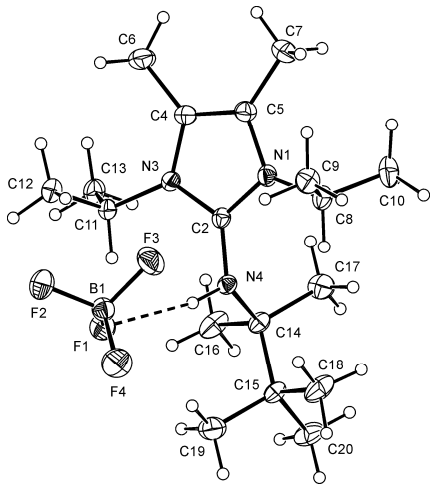


Figure 3.6. X-ray crystal structure of the salt **4i**$H^+BF_4^-$. The displacement ellipsoids are drawn on 30% probability level. Selected bonds distances [Å] and angles [°]: N1-C2 1.354(2), N1-C5 1.395(2), N3-C2 1.352(2), N3-C4 1.396(2), N4-C2 1.373(2), N4-C14 1.513(2), C4-C5 1.349(2); N1-C2-N3 107.6(1), C2-N4-C14 121.4(1); average N1(3)–C2–N4–C14 torsion angle: 88.5.

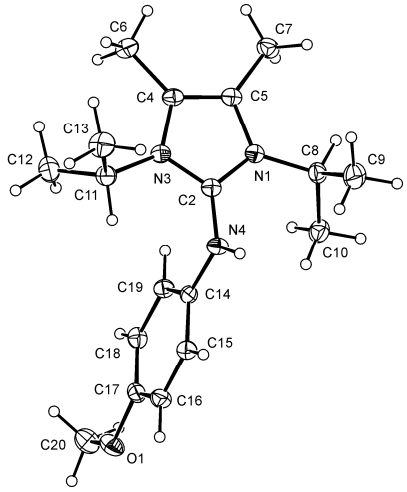


Figure 3.7. X-ray crystal structure of the salt **4h**$H^+BF_4^-$. The displacement ellipsoids are drawn on 30% probability level. Distorted counterion (BF_4^-) is omitted for clarity. Selected bonds distances [Å] and angles [°]: N4–C2 1.372(2), N1–C2 1.341(2), N3–C2 1.346(2), N1–C5 1.386(2), N3–C4 1.391(2), C4–C5 1.354(3); N1–C2–N4 125.82(17), N3–C2–N4 125.79(17), N1–C2–N3 108.37(15), C2–N4–C14 122.00(14); average N1(3)–C2–N4–C14 torsion angle: 70.0.

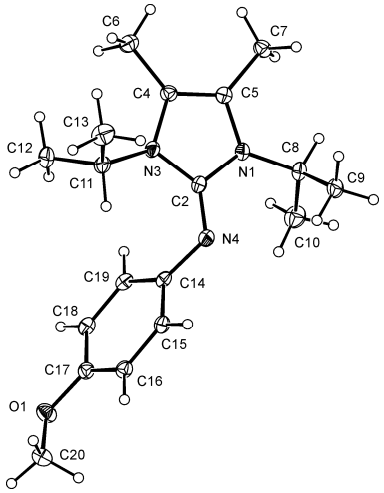
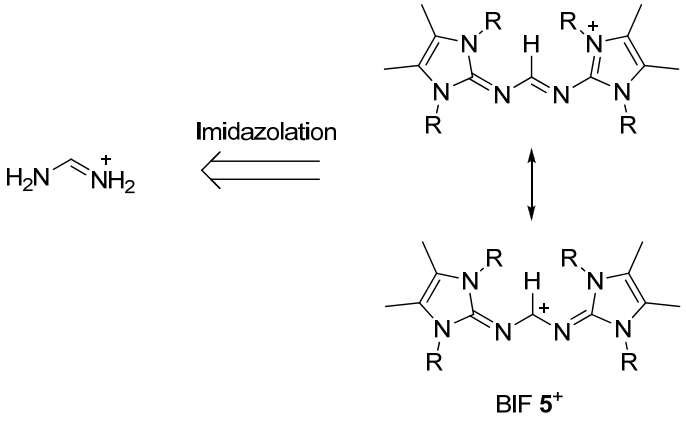


Figure 3.8. X-ray crystal structure of the base **4h**. The displacement ellipsoids are drawn on 30% probability level. Selected bonds distances [Å] and angles [°]: N4–C2 1.308(2), N1–C2 1.370(2), N3–C2 1.382(2), N1–C5 1.396(2), N3–C4 1.414(2), C4–C5 1.341(2); N1–C2–N4 123.01(12), N3–C2–N4 131.14(12), N1–C2–N3 105.63(11), C2–N4–C14 123.12(11); average N1(3)–C2–N4–C14 torsion angle: 34.8.

4. Imidazolation of Amidinium and Guanidinium Salts. BIG Bases

4.1. Imidazolation of Formamidinium Salts

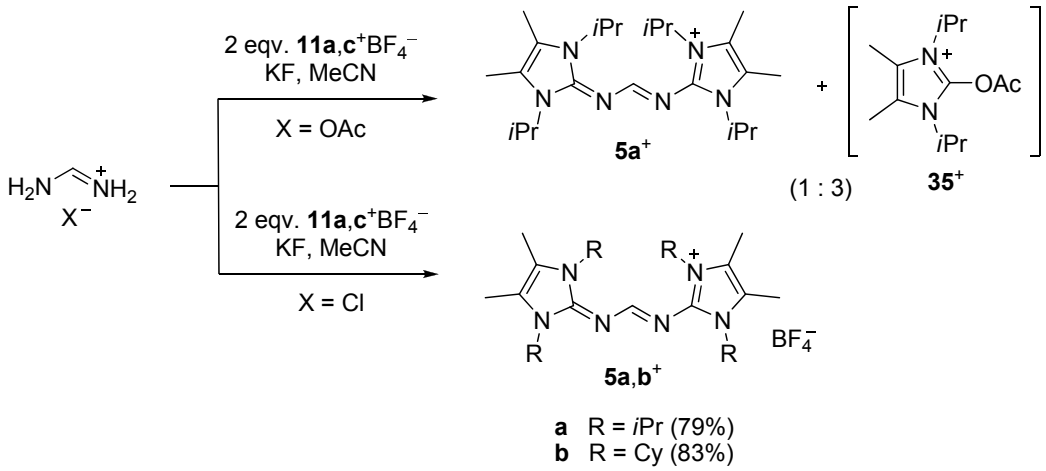
N,N'-Bis(imidazol-2-ylidene)formamidinium cation (BIF) $\mathbf{5}^+$ containing two donor imidazol-2-ylidene amino groups can be considered to be one of the most stabilized and least electrophilic cations of X_2CH^+ type. Compounds $\mathbf{5}^+$ were envisaged to be accessed from formamidinium salts (Scheme 4.1).



Scheme 4.1. Synthetic pathway toward BIF cations $\mathbf{5}^+$.

Formamidinium acetate was prepared in moderate yield by reflux of ammonium acetate in trimethylorthoformate.[108] Imidazolation of the salt after 1 day at ambient temperature resulted in a mixture of a desired product $\mathbf{5a}^+$ and product of imidazolation of an acetate anion $\mathbf{35}^+$ in a ratio ~1:3 (Scheme 4.2).

Therefore, formamidinium chloride was used, which was obtained from formamidinium acetate by reaction with HCl in MeOH. Imidazolation of formamidinium chloride with $\mathbf{11a}^+BF_4^-$ within 1 day yielded BIF salt $\mathbf{5a}^+BF_4^-$ in 79% yield (Scheme 4.2). The corresponding tetra-cyclohexyl derivative BIF $\mathbf{5b}^+BF_4^-$ was prepared similarly in 83% yield.



Scheme 4.2. Imidazolation of formamidinium salts with formation of BIF cations $\mathbf{5}^+$.

During recrystallization of crude $\mathbf{5a}^+BF_4^-$ from EtOAc an unexpected two step precipitation was observed. A minor crystalline material precipitating first was composed of a 1:1:1 adduct of $\mathbf{5a}^+BF_4^-$, its protonated dication $\mathbf{5a}H^{2+}(BF_4^-)_2$ and one molecule of solvent as revealed by single X-ray diffraction analysis (Figure 4.1). Probably during the isolation of $\mathbf{5a}^+BF_4^-$ partial protonation of the relatively basic exo-cyclic nitrogen atom took place followed by co-crystallization. The major pure $\mathbf{5a}^+BF_4^-$ precipitated from the mother liquid by addition of Et_2O.

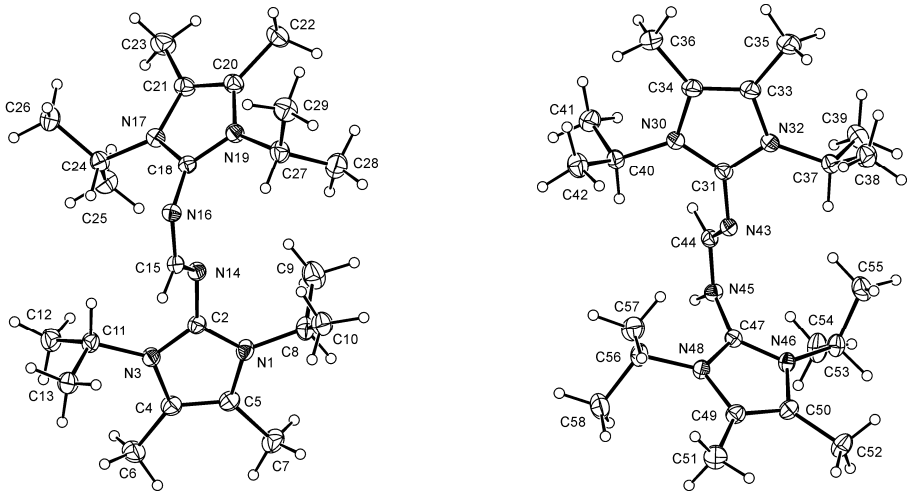
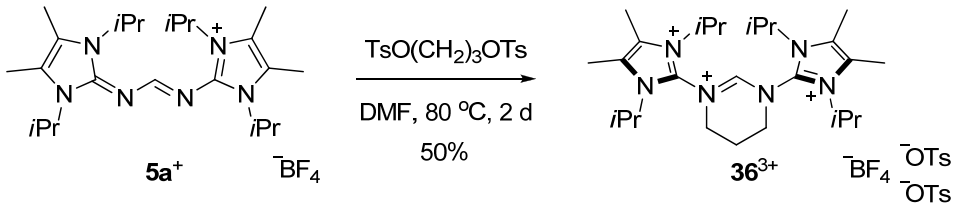


Figure 4.1. Two fragments in cell unit of X-ray diffraction crystal structure of inclusion complex $\mathbf{5a}^+\cdot\mathbf{5a}H^{2+}$: BIF $\mathbf{5a}^+$ (left) and $\mathbf{5a}H^{2+}$ (right). Counterions (BF_4^-) and molecule of

EtOAc were omitted for clarity. The displacement ellipsoids are drawn on 30% probability level.

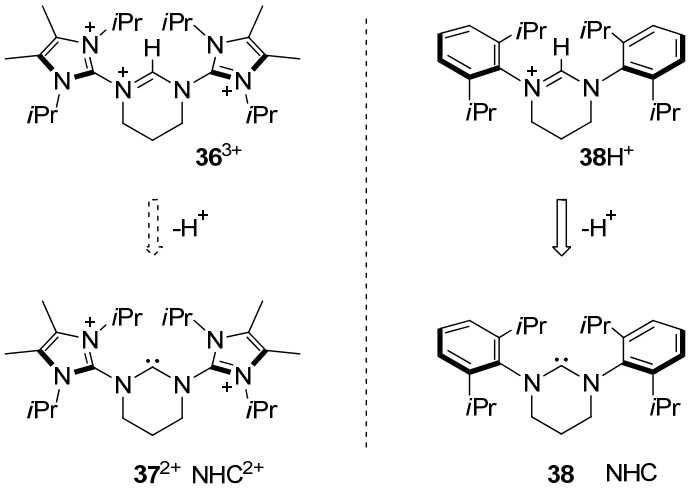
Prepared novel family of DLCs $\mathbf{5}^+$ might be potentially interesting as ligands for metal complex catalysis, because they are related to known neural *N*-aryl-*N*′-imidazol-2-ylidenformamidines, which were used as ligands for Pd^{2+} and Ti^{4+} complexes.[109]

BIF $\mathbf{5a}^+BF_4^-$ can be further *N*-alkylated even twice. Warming a mixture of the salt with 1,3-propylene ditosylate[110] in DMF during 2 days led to complete *N,N*′-dialkylation with formation of trication $\mathbf{36}^{3+}BF_4^-(OTs^-)_2$, which was isolated from the reaction mixture by filtration under argon in 50% yield in the form of a colorless powder, which was very sensitive to hydrolysis by atmospheric moisture (Scheme 4.3).



Scheme 4.3. Double alkylation of BIF cation $\mathbf{5a}^+$ with formation of $\mathbf{36}^{3+}$.

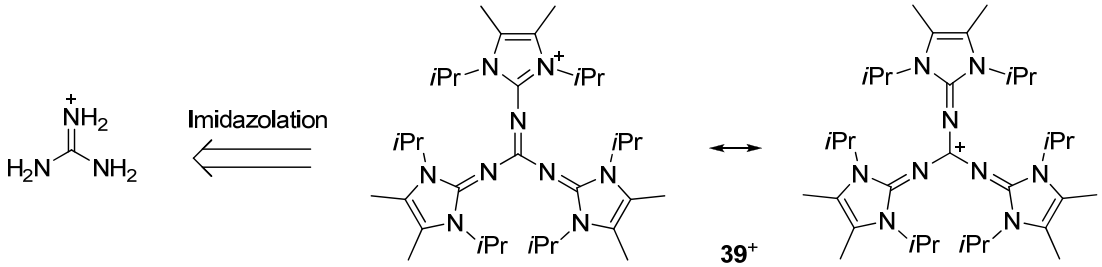
Such trications are potential precursors for new doubly positive charged carbenes NHC^{2+}, such as $\mathbf{37}^{2+}$, analogues to known six-membered NHC, [111] for example **38** (Scheme 4.4), which were successfully applied as ligands for metal complex catalysis.[112] Several attempts to prepare carbene $\mathbf{37}^{2+}$ from trication $\mathbf{36}^{3+}$ using KO*t*Bu / THF or $KNTMS_2$ / toluene as bases resulted in mixtures of unidentified compounds.



Scheme 4.4. Trication $\mathbf{36}^{3+}$ as potential source of carbene $\mathbf{37}^{2+}$.

4.2. Imidazolation of Guanidinium Salts. BIG Bases

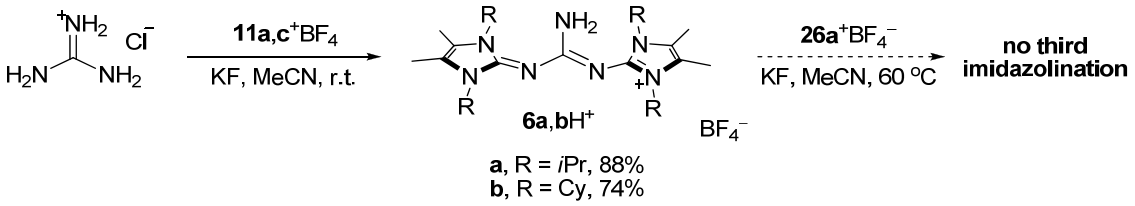
The *N,N′,N″*-tris(imidazol-2-ylidene amino)methyl cation $\mathbf{39}^{+}$ is considered to be one of the most stable and least electrophilic cations of the X_3C^+ type. Guanidinium salt was chosen as a starting compound (Scheme 4.5).



Scheme 4.5. General approach to the synthesis of cation $\mathbf{39}^{+}$.

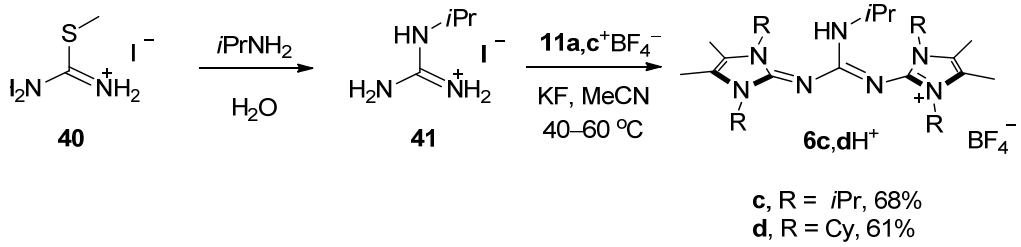
It was found that imidazolation stopped at the stage of *N,N′*-bis(imidazol-2-ylidene)guanidinium (BIG) cation $\mathbf{6}H^+$ (Scheme 4.6). It was further shown that $\mathbf{6a}H^+$ did not react with very active 2-fluoroimidazolium salt $\mathbf{26a}^+BF_4^-$ even at 60 ºC in the presence of KF. The impossibility of third imidazolation of the unsubstituted nitrogen in BIG $\mathbf{6a}H^+$ in the absence of an obvious steric hindrance at this center was interpreted as the sign of a very small equilibrium concentration of the active nucleophile in the reaction - deprotonated form **6a** - probably because of its high basicity.

For studying of cations **6**H$^+$ as sources of new *N,N′*-bis(imidazol-2-ylidene)guanidinium bases **6** (further BIG bases), two *N*-unsubstituted salts **6a**,**b**H$^+$BF$_4^-$ were prepared from guanidinium chloride and two equivalents of chloroimidazolium **11**$^+$ tetrafluoroborate, using the standard imidazolation conditions (Scheme 4.6).



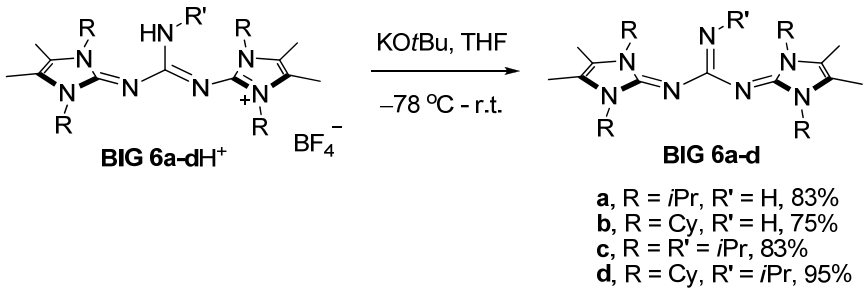
Scheme 4.6. Imidazolation of guanidinium chloride with formation of BIG salts **6a**,**b**H$^+$.

Two of *N*-isopropyl substituted salts **6c**,**d**H$^+$BF$_4^-$ were synthesized using similar imidazolation conditions from *i*Pr-substituted guanidinium iodide **41** (Scheme 4.7). The starting guanidinium salt **41** was prepared from **40** using slightly modified literature procedure.[113,114] Imidazolation of **41** proceeded more slowly in comparison with unsubstituted guanidinium chloride and required warming.



Scheme 4.7. Synthesis of alkyl substituted BIG salts **6c**,**d**H$^+$BF$_4^-$. Yields over two steps are given.

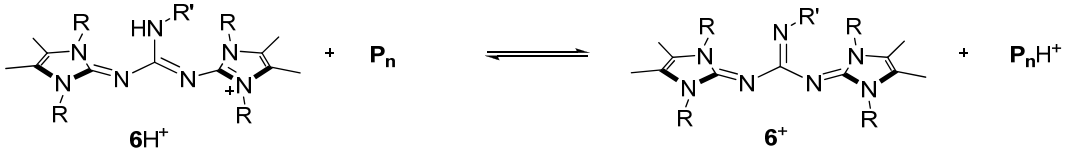
BIG bases **6a-d** were liberated from **6a-d**H$^+$BF$_4^-$ in good to high yields using 1 M KO*t*Bu in THF (Scheme 4.8). Prepared BIG bases **6a-d** are stable slowly crystallizing viscous oils, which can be stored as hexane or hexane-toluene solutions under inert atmosphere.



Scheme 4.8. Liberation of BIG bases **6a-d** from corresponding salts **6a-d**$H^+BF_4^-$.

4.3. Estimation of Basicity of Some BIG Bases

The pK_{BH+}^{MeCN} of several BIG bases **6** were estimated using *t*BuP$_1$(pyrr) and *t*BuP$_2$(dma) as reference bases with known pK_{BH+} by their ability to deprotonate salts **6**$H^+BF_4^-$ according to the following equilibria (Scheme 4.9).



Scheme 4.9. Proton transfer equilibrium between BIG bases **6** and *t*BuP$_1$(pyrr) and *t*BuP$_2$(dma) bases (**P$_n$**).

At equilibrium the pK_{BH+} values of BIG **6** can be calculated using Eq. 4.1, where [**P$_n$**H^+], [**P$_n$**], [**6**H^+], [**6**] – relative equilibrium concentrations of **P$_n$**H^+, **P$_n$**, **6**H^+, **6**, respectively.

$$pK_{BH+}^{Solv.}(\mathbf{6}) \approx pK_{BH+}^{Solv.}(\mathbf{P_n}) + \lg([\mathbf{P_n}]([\mathbf{6}H^+]_o - [\mathbf{P_n}H^+])/[\mathbf{P_n}H^+]^2)$$

$$[\mathbf{6}H^+]_o = [\mathbf{6}H^+] + [\mathbf{6}] \qquad \textbf{(Eq. 4.1)}$$

Relative concentrations of P_n and P_nH^+ can be determined from ^{31}P NMR spectra of the reaction mixture as follows.

It was shown that the chemical shift of a phosphorus signal for a mixture of *t*BuP$_1$(pyrr) / *t*BuP$_1$(pyrr)H$^+$ in ^{31}P NMR depended almost linearly ($R^2 > 0.99$) on the protonation degree of *t*BuP$_1$(pyrr).

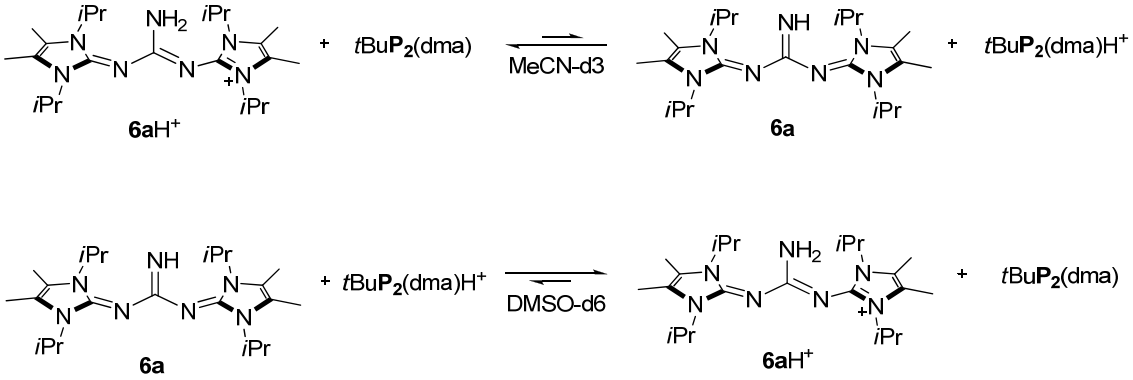
The correlation of $^2J_{P\text{-}P}$ for the mixture of *t*BuP$_2$(dma) / *t*BuP$_2$(dma)H$^+$ *vs.* protonation degree of *t*BuP$_2$(dma) was also considered as linear. Thus the linear equation was derived (Eq. 4.2),* in which $[\mathbf{P_2}]_o = [\mathbf{P_2}] + [\mathbf{P_2}H^+]$.

$$[\mathbf{P_2}H^+] / [\mathbf{P_2}]_o \approx 0.03 J_{P\text{-}P}\,(\mathbf{P_2}) - 1.07 \qquad \textbf{(Eq. 4.2)}$$

The obtained equilibrium chemical shift value δ for P$_1$ or $^2J_{P\text{-}P}$ coupling constant for P$_2$ allows to define equilibrium concentrations of the corresponding $\mathbf{P_n}$ and $\mathbf{P_n}H^+$ in the reaction mixture. The relative concentration $[\mathbf{6}H^+]_o$ can be determined from the initial loadings. Knowledge of those three relative concentrations allows to estimate the pK_{BH+} of the corresponding BIG base **6** using Eq. 4.1.

The first attempt of the estimation using approximately equimolar mixture of BIG salt **6a**H$^+$BF$_4^-$ and *t*BuP$_1$(pyrr) was unsuccessful since deprotonation was not observed. This indicated a pK_{BH+}^{MeCN} (BIG **6a**) >> 28.4.

Significantly stronger base *t*BuP$_2$(dma) was mixed with BIG **6a**H$^+$BF$_4^-$ in a ratio close to equimolar (Scheme 4.10).



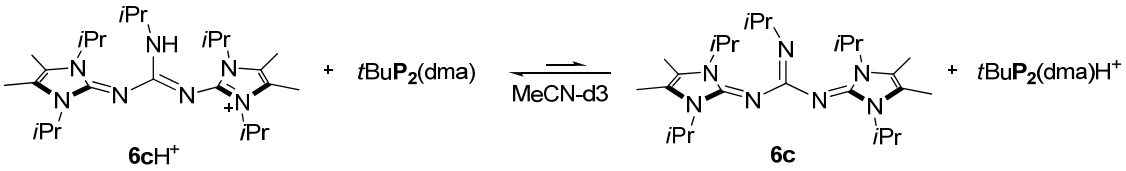
Scheme 4.10. BIG base **6a** *vs.* *t*BuP$_2$(dma) indirect and direct NMR experiments.

* In particular in ^{1}H NMR and ^{31}P NMR proton exchange between phospazene bases and their protonated forms is fast on the NMR time scale and an average signals are visible only. The same is true for BIG bases as well.

The $^{2}J_{P\text{-}P}$ coupling constant for *t*BuP$_2$(dma) / *t*BuP$_2$(dma)H$^+$ mixture was obtained from ^{31}P NMR spectra and relative concentrations of both forms were calculated. Insertion to Eq. 4.1 gave the value of pK_{BH+}^{MeCN} ~ 34.5, thus BIG base **6a** was found to be approximately 10 times stronger than *t*BuP$_2$(dma).

In a reversed experiment freshly isolated BIG base **6a** and P$_2$(dma)H$^+$OMs$^-$ salt were mixed in almost equimolar ratio in DMSO-d6 (Scheme 4.10). In contrast to previous experiments DMSO-d6 was used instead of MeCN-d3 to avoid any possibility of chemical interaction of BIG **6a** with the solvent. BIG **6a** was found to be also approximately 10 times stronger than *t*BuP$_2$(dma).

The basicity of alkyl substituted BIG base **6c** was estimated to see how *N*-alkyl group introduction affected the basicity of this class of compounds (Scheme 4.11). Similarly to the previous experiments pK_{BH+}^{MeCN} of BIG **6c** was found to be ~ 35.0. This value was only half an order of magnitude higher than that of BIG **6a** (R' = H, Scheme 4.8). However, the difference in basicity for *i*Pr-substituted IMAM base **4c** and H-substituted IMAM base **22a** was ~3.4 orders. Such disparity is possibly associated with a higher contribution of steric strain release factor to basicity of IMAM bases compared to BIG bases.



Scheme 4.11. BIG base **6c** *vs.* *t*BuP$_2$(dma) indirect NMR experiment.

NMR spectra (^{1}H NMR and ^{31}P NMR) of the reaction mixtures were identical approximately after 15 min from the start and after 1 day showing that equilibrium was reached very quickly and the values obtained for the first spectrum corresponded to the equilibrium.

4.4. Determination of Basicity of Some BIG Bases

The pK_{BH+} values for two examples of BIG bases **6a**,**d** were estimated in collaboration with Leito's group (University of Tartu, Estonia) by measuring their ion pair basicities pK_{ip} in THF solution. The basicities were obtained using photometrical titrations with references

dyes.[115,116] The determined pK_{ip} values and known pK_{ip} values for some phosphazene bases are plotted in Figure 5.3.

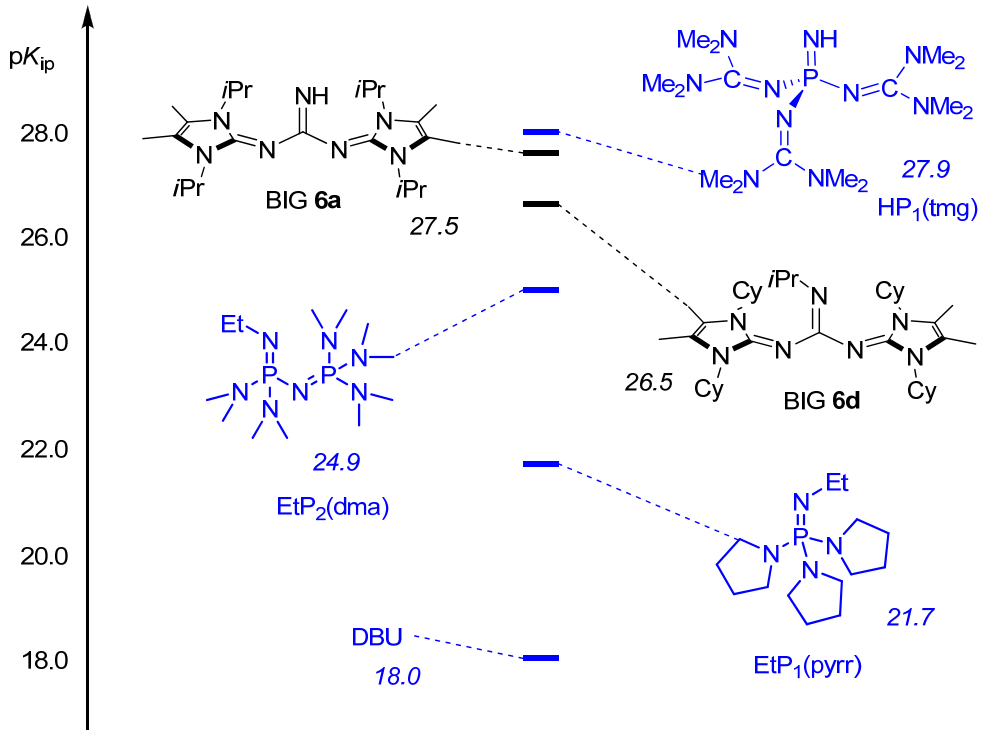
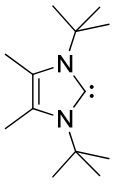


Figure 5.3. Comparison of pK_{ip} of **6a**,**d** (black) with earlier described pK_{ip} values for some known bases (blue) in THF.

As evidenced from the figure, BIG bases **6a**,**d** were indeed more stronger than P_1 and P_2 phosphazene bases,[115,116] and only slightly weaker than Kolomeitsev's base HP_1(tmg).[18]

5. 1,3-Di-*tert*-butyl-4,5-dimethylimidazol-2-ylidene: Nucleophilic Properties and Basicity Estimation

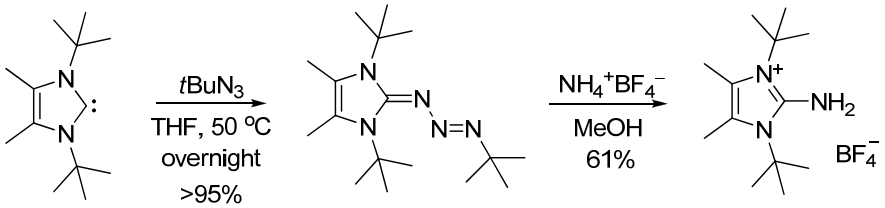
Recently, a convenient general method for the synthesis of previously inaccessible 1,3-di-*tert*-alkyl-4,5-dimethylimidazol-2-ylidenes (NHCs) was developed. [117] Among the synthesized compounds 1,3-di-*tert*-butyl-4,5-dimethylimidazol-2-ylidene was found to be one of the most sterically hindered imidazol-2-ylidene known to date (Figure 5.1).



NHC **10i**

Figure 5.1. The first example of new class of 1,3-di-*tert*-alkyl-4,5-dimethylimidazol-2-ylidenes.

It was necessary to characterize NHC **10i** with respect to its nucleophilic properties by amination with *tert*-butyl azide. Moreover, amination product could be useful as a source of new imidazol-2-ylidene amine as a ligand for series of complexes with transition metals, effective catalysts, in particular for alkyne metathesis.[52]



10i **23i** **22i**$^+$

Scheme 5.1. Amination of **10i** with *tert*-butyl azide.

How expected, **10i** was found to be less reactive towards *tert*-butyl azide addition than 1,3-isopropyl- and 1,3-neopentyl-substituted analogues **10a**,**b**. It required warming at 50 °C for 16 h for achievement of full conversion to **23i** (Scheme 5.1).[53,54]

Crystalline triazene **23i** was isolated in a yield of >95% and was characterized by ^{1}H and ^{13}C NMR. Triazene **23i** quickly decomposed under mild acidic conditions yielding the corresponding 2-aminoimidazolium salt **22i**$^{+}BF_4^{-}$ in moderate yield over two stages.

For estimation of the basicity of **10i** an approach similar to that applied by Alder[118] was used. The method consisted of mixing NHC with equimolar quantities of an indicator in DMSO-d6. The indicator should be an acidic hydrocarbon with known p*K*a, which is close to the pK_{BH+} of investigated carbene. After equilibrium (Scheme 5.2) relative concentrations of all four components were estimated from ^{1}H NMR spectra, and pK_{BH+} value of investigated NHC was calculated using Eq. 5.1, where [**10**]$_o$ = [**10**] + [**10**H^{+}].

Scheme 5.2. Equillibrium between carbene **10** and CH acid (Ind-H).

$$pK_{BH+}\,(\mathbf{10}) \approx pK_a\,(\text{Ind-H}) + \log([\text{Ind}^-]^2 / [\text{Ind-H}]\,([\mathbf{10}]_o - [\text{Ind}^-])) \qquad \textbf{(Eq. 5.1)}$$

The important difference of this approach compared to that used earlier for the estimation of the basicity of IMAM and BIG bases (Chapter 3.4 and 4.3) consisted of the fact that the proton exchange between many hydrocarbons and their deprotonated forms occurs slowly enough on the time scale of ^{1}H NMR so both forms are easily distinguished in the reaction mixture. This considerably simplifies determination of their relative concentration. It is necessary to note that proton exchange between NHC **10** and **10**H^{+} is significant faster and the average signal is only observed in ^{1}H NMR spectra. However their equilibrium concentrations formally do not enter to Eq 5.1.

At the beginning fluorene (pK_a 22.6 in DMSO)[45] was used as the indicator (Figure 5.2). However the equilibrium was completely shifted to the right showing that pK_{BH+} of **10i** is appreciable above 22.6 in DMSO.

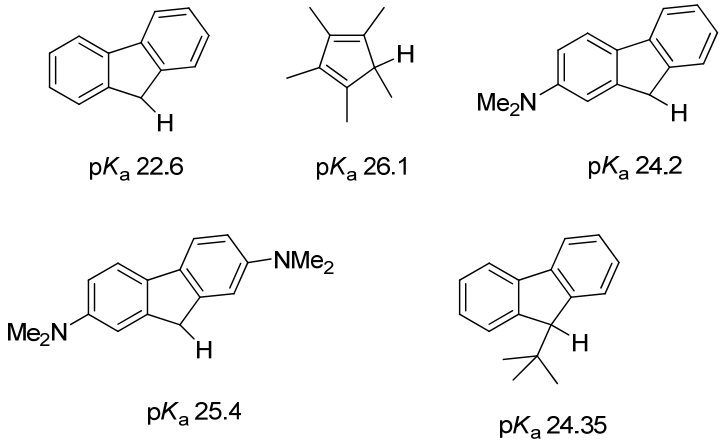


Figure 5.2. Indicators (Ind-H) used for estimation of basicity of NHC **10i** with their acidities in DMSO.

Four weak C-H acids were chosen then: 1,2,3,4,5-pentamethylcyclopentadiene (pK_a 26.1),[45] 9-*tert*-butylfluorene (pK_a 24.35),[119] 2-(dimethylamino)fluorene (pK_a 24.2)[120] and 2,7-bis(dimethylamino)fluorene (pK_a 25.4).[120] The last three indicators are commercially inaccessible and were synthesized using described procedures. 2-(Dimethylamino)fluorene and 2,7-bis(dimethylamino)fluorene[120] were synthesized by methylation of corresponding 2-aminofluorene and 2,7-diaminofluorene using trimethylphosphate.[121] 9-*tert*-Butylfluorene was synthesized by reduction of 9-*tert*-butylfluoren-9-ol,[122] where the latter was prepared with low yield by reaction of fluorenone with *tert*-butyllithium in benzene.[123]

The three indicators Cp*-H, 9-*tert*-butylfluorene and 2-(dimethylamino)fluorene showed good results and an average value of pK_{BH+} for NHC **10i** was calculated to 24.8 in DMSO. 2,7-Bis(dimethylamino)fluorene was not applicable because of its low solubility in the reaction mixture. Comparison values described for other NHCs showed that **10i** is the most basic imidazol-2-ylidene NHC known to date (Figure 5.3).

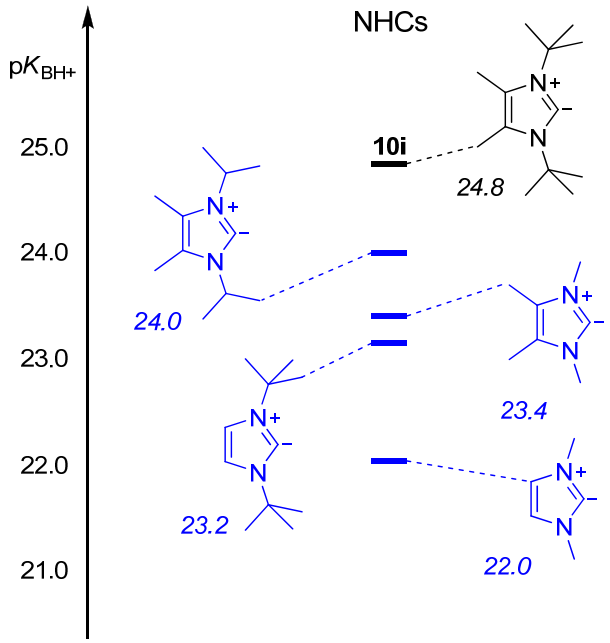


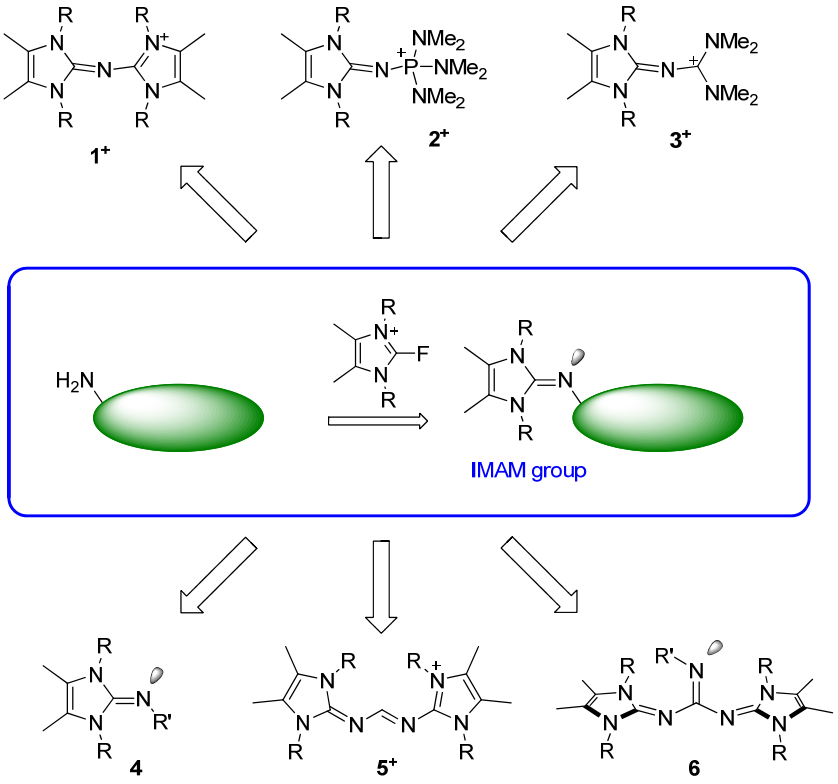
Figure 5.3. Comparison of estimated basicity value pK_{BH+} of **10i** (in black) with earlier described pK_{BH+} values for its analogues (in blue) in DMSO.[124]

The higher basicity of NHC **10i** relative to its closest analogues (Figure 5.3) can be explained by additional stabilization of the positive charge in the imidazolium ring by two donor methyls in 4,5-positions and/or reduced solvation of C-2 anionic centre caused by a larger congestion of this centre due to transferring of steric effects of 4,5-methyl groups by *t*Bu groups onto C-2.

The used approach is only estimation. For precise measurements of basicity it is necessary to consider also formation of ion pairs ([NHC-H···Ind]) and dimers ([NHC-H-NHC]$^+$) which is a much more difficult technical problem. It was shown for the closest analogue of **10i**, 1,3-di-*tert*-butylimidazol-2-ylidene (Figure 5.3), that corrections for the formation of dimers are negligibly small, while corrections for the formation of ion pairs for this carbene led to smaller value of pK_{BH+} of 22.7 in comparison with the estimated pK_{BH+} value of 23.2.[125] Obviously, the error between two values was no more than half an order of magnitude.

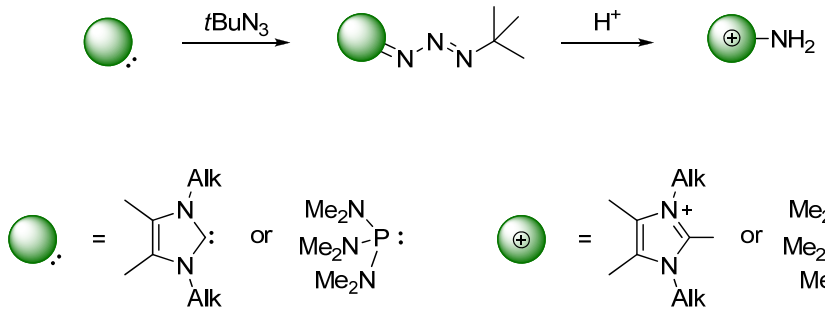
Summary

- Simple and efficient method for imidazolation of a series of nitrogen nucleophiles - monosubstituted amines, formamidine, guanidines, 2-aminoimidazolium cations and aminophosphonium cation was developed. This protocol allowed to introduce easily new strong electron donor 1,3-dialkyl-4,5-dimethylimidazol-2-ylidene amino group (IMAM) in different organic molecules using 2-fluoroimidazolium salts or 2-chloroimidazolium salts / KF in MeCN.



- A series of novel stable phase transfer catalysts (PTC) $\mathbf{1}^+$, $\mathbf{2}^+$, $\mathbf{3}^+$, containing a strong electron donor IMAM group were designed and efficiently synthesized. Salts $\mathbf{1}^+BF_4^-$ showed very good PTC activity. Cations $\mathbf{1}^+$ and $\mathbf{2}^+$ have demonstrated high resistance in different drastic basic conditions. High stability of the cations was caused by efficient stabilization of the positive charge by strong electron donor IMAM group and by efficient steric protection of C-2 centres in their molecules.

- A series of novel stable phosphorus-free organosuperbases **4** (IMAM bases) containing a strong electron donor IMAM group were designed and efficiently synthesized. Their high basicity, moderate nucleophilicity and good stability towards hydrolysis was estimated and/or determined. Bases with *N*-*tert*-alkyl imino substituents were found to be more stronger than *t*BuP_1(pyrr) phosphazene base. In collaboration with Leito's group it was demonstrated that protonation of superbases **4** in the gas phase and in solution was associated with significant increase of aromaticity (calculated ΔNICS(1) for gas phase and measured ^{13}C NMR shifts for solution).
- A series of novel stable DLCs $\mathbf{5}^+$ (BIF cations) containing two strong electron donor IMAM group were designed and efficiently synthesized. Their double alkylation ability was demonstrated.
- A series of novel stable phosphorus-free organosuperbases **6** (BIG bases) containing two strong electron donor IMAM groups were designed and efficiently synthesized. For few examples extremely high basicity was estimated and determined. Tested bases were found to be stronger than P_2(dma) phosphazene bases.
- A new efficient method for amination of 1,3-dialkylimidazol-2-ylidenes (NHC) as well as of tris(dimethylamino)phosphine by *tert*-butyl azide was developed.



- The basicity of new highly sterically hindered 1,3-di-*tert*-butyl-4,5-dimethylimidazol-2-ylidene (NHC) was estimated in DMSO using three different reference CH acids and found to be highest among known imidazol-2-ylidenes, $pK_{BH+} \sim 24.8$. The high basicity was caused by electron donor effect of two methyl groups in 4,5-positions and/or reduced solvation of sterically hindered C-2 anionic centre of the NHC.

Experimental Part

1. General Remarks

NMR spectra were recorded in $CDCl_3$ on a *Bruker Avance 400* spectrometer (400 MHz for ^1H, 100.6 MHz for ^{13}C) at 300 K unless stated otherwise. Temperature-dependent NMR spectra were recorded on a *Bruker Avance 500* spectrometer (500 MHz for ^1H, 125.7 MHz for ^{13}C). Chemical shifts (δ) are given in ppm. ^1H (400 MHz) referenced to internal standard $SiMe_4$ ($\delta = 0$ ppm) if not otherwise specified; ^{13}C (100.6 MHz) referenced to d-solvent signals;[126] ^{31}P (162 MHz) referenced to internal standard $(MeO)_3PO$ ($\delta = 3.0$ ppm in $CDCl_3$ or 3.5 ppm in DMSO-d6); ^{19}F NMR (376.5 MHz) referenced to internal standard $PhCF_3$ ($\delta = -63.7$ ppm), the signals of BF_4 anion of the imidazolium salts appeared at –155±0.5 ppm as two singlets due to $^{10}BF_4$ and $^{11}BF_4$ (1:4 ratio), the former 0.06 ppm downfield from the latter. Multiplicities of signals are described as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, oct = octet, m = multiplet, br = broad. Coupling constants (*J*) are given in Hz.

IR spectra were recorded on a *Bruker Alpha* spectrometer equipped with an ATR device as a neat compound and in hexane solution using a *Bruker Equinox 55* instrument.

ESI mass spectra were recorded using a *Thermo Scientific LCQ Fleet* mass spectrometer. High-resolution mass spectra (HRMS) were obtained with ESI or APCI instruments on a *LTQ Orbitrap XL* instrument.

GC MS spectra were recorded on an *Agilent 7890A* gas chromatograph coupled with a 5975C quadrupole mass-selective electron impact (EI) detector (70 eV).

Elemental analyses were carried out using a *PE 2400 Series II* CHN analyzer.

Melting points were determined using a *Wagner & Munz PolyTherm A* apparatus.

All common inorganic and organic acids, alkali bases, PhCl, $CyNH_2$, *i*$PrNH_2$, aq. $MeNH_2$, aq. $EtNH_2$, *t*$BuNH_2$, *t*$OctNH_2$, *p*-anisidine, 3-hydroxybutan-2-one, *N*,*N*′-dimethylthiourea, *N*,*N*′-diisopropylthiourea, *N*,*N*′-dicyclohexylthiourea, pentan-1-ol, butan-2-ol, NMP, dodecane, tributylamine, *tert*-butanol, 1,3-propanediol, *neo*-pentanol, *t*BuCN, thiophosgene, C_2Cl_6, 25% aq. NH_3, 40% aq. HBF_4, TFA, NfF, $BF_3{\bullet}Et_2O$, Et_3SiH, H_2O_2, $POCl_3$, PCl_3, $(COCl)_2$, TMG, $P(NMe_2)_3$, TMSCl, MeI, ethylene glycol, TfOMe, TfOH, P_2O_5, CaH_2, $NaBF_4$, $LiAlH_4$, KI, NH_4Cl, Na_3PO_4, $MgSO_4$, BaO, NaN_3 were used as purchased from commercial suppliers.

Solvents were dried by standard procedures: THF, Et_2O and DME were distilled over Na with Ph_2CO added; diglyme was freshly distilled in vacuum over Na; toluene was freshly distilled over Na; MeCN was freshly distilled over CaH_2; hexane was distilled over P_2O_5; DMF was freshly distilled in vacuum over CaH_2; sulfolane was distilled in high vacuum over P_2O_5. All other common solvents were used without additional purification.

Commercially available "dry" KF (*ca*. 20 g) was placed in a mortar and maintained in an oven at 200 °C for 12 h. Then, whilst still hot, it was thoroughly ground into a fine powder using a hot pestle (thick leather gloves!). Thus pre-dried KF was used for further activation to serve as heterogeneous base in the synthesis of the target compounds.

Et_3N was dried and stored over KOH pellets. TMG was freshly distilled in vacuum over BaO. NH_4BF_4 was prepared by careful neutralization of aq. NH_3 with aq. HBF_4 followed by removal of water at reduced pressure and drying in high vacuum.

All reactions were carried out with magnetic stirring under positive argon or nitrogen atmosphere using the standard technique with vacuum – inert gas manifold, unless stated otherwise. All reactions including Na, K or metal organic reagents were carried out in *vacuo* – heat-gun dried glassware equipped with magnetic stirring bars (for Na/K alloy only glass-coated stirring bars, no Teflon!) under an atmosphere of dry argon or nitrogen.

Organic solutions were dried with $MgSO_4$, BaO or KOH pellets.

2. Preparation of Known Compounds

tert-Butyl azide,[83] nonaflyl azide,[86] $P_5^+BF_4^-$,[4] neopentylamine,[68] *N*,*N*′-dineopentylthiourea,[69] 1,3-propylene ditosylate,[110] 1,4-butylene ditriflate,[80] *N,N*-dimethyl-9*H*-fluoren-2-amine,[121] N^2,N^2,N^7,N^7-tetramethyl-9*H*-fluorene-2,7-diamine,[121] 9-*tert*-butyl-9*H*-fluoren-9-ol,[123] 9-*tert*-butyl-9*H*-fluorene,[122] neopentyl tosylate,[97] 1,3,4,5-tetramethyl-1*H*-imidazole-2(3*H*)-thione (**9d**),[66] 1,3,4,5-tetramethyl-2-(methylthio)-1*H*-imidazolium iodide (**31**),[89] *N*-(1,3-diisopropyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylidene)-1,1,1-trimethylsilanamine (**14**),[51] 1,3-diisopropyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-imine (**22a**)[48] were prepared according to the literature procedures.

3. Experimental Procedures

***N,N′*-Dialkyl-4,5-dimethyl-1*H*-imidazole-2(3*H*)-thiones (9). General procedure (GP1)**: *N,N′*-Dialkylthiourea **8** (100 mmol), 3-hydroxybutanone **7** (9.69 g, 110 mmol) and *n*-pentanol (65 mL) were placed in a 250 mL reaction flask equipped with a magnetic stirring bar, Dean-Stark head and reflux condenser. The reaction mixture was refluxed in an oil bath until no more water was produced indicating full conversion (at least 6 h). The work up is given at the individual compounds.

***N,N′*-Dialkyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylidenes (10). General procedure (GP2)**: Na (1.61 g, 70 mmol) and K (5.47 g, 140 mmol) were sequentially placed into an argon flushed reaction flask equipped with a three-way tap. It was then connected to a vacuum pump, and the Na-K eutectic was formed by cautiously melting the metals with a heat-gun under reduced pressure while gently swirling the flask. The reaction flask was filled with argon and allowed to cool to ambient temperature. A glass-coated magnetic stirring bar was placed into the reaction flask, and a solution of **9** (70 mmol) in 1,2-dimethoxyethane (150 mL) was cautiously added with vigorous stirring. The reaction flask was equipped with reflux condenser, and the reaction mixture was refluxed with stirring for 5 h until full conversion. It was cooled, the solvent was removed in vacuum and the residue was diluted with dry hexane (250 mL) followed by stirring for 1 h. The insoluble inorganic residue was allowed to settle overnight. The yields and titres of products **10** were estimated by drawing aliquots of clear hexane solutions, evaporation, drying in high vacuum at room temperature and weighing the residues. The resulting clear homogeneous stock solutions of products **10** (> 90% yields for all) can be stored for several weeks at ambient temperature under inert atmosphere.

2-Chloro-*N,N′*-dialkyl-4,5-dimethylimidazolium tetrafluoroborates (11^{+}BF$_4^{-}$). General procedure (GP3.1): A stock solution of compound **10** (15.0 mmol) in hexane was added to the reaction flask. The hexane was removed in vacuum, THF (60 mL) was added to the solid residue, and the resulting solution was cooled to –40 °C. Hexachloroethane (3.80 g, 16.0 mmol) was added in one portion with vigorous stirring, the reaction mixture was allowed to gradually warm to ambient temperature and stirred for 24 h. It was poured into a separation funnel containing a two-phase mixture of $CHCl_3$ (100 mL) / 10% aq. $NaBF_4$ (100 mL)

followed by vigorous shaking. The organic layer was separated, and the aqueous was extracted once with $CHCl_3$ (20 mL). The combined organic layers were dried ($MgSO_4$) and filtered. The volatiles were removed in vacuum, and the solid residue was dried in high vacuum at 50 °C overnight to remove residual traces of C_2Cl_6 yielding pure product **11**$^+BF_4^-$ after recrystallization. For preparation of ONf^- salts, KONf (6.76 g. 20 mmol) / H_2O (100 mL) was used instead of aq. $NaBF_4$.

Synthesis of 2-chloro-*N*,*N*′-dialkyl-4,5-dimethylimidazolium tetrafluoroborates (11$^+BF_4^-$) from imidazole-2-thiones 9. *One-pot potassium free protocol* (GP 3.2): Freshly distilled diglyme (150 mL) was added to a flask with Na (5.8 g, 250 mmol) under an inert atmosphere. The flask was heated with a heat-gun until the sodium melted, and stirring was continued at this temperature for 10 min. After cooling to room temperature, imidazole-2-thione **9** (50 mmol) was added and the reaction mixture was stirred at 110 °C for 24 h (^{1}H NMR control). After cooling to room temperature stirring was stopped, and the inorganic residue was allowed to precipitate during 12 h. The supernatant was carefully transferred via cannula into a second flask (Traces of fine white particles do not harm) and cooled to –40 °C. Hexachloroethane (13.0 g, 55 mmol) was added with vigorous stirring and the reaction mixture was warmed to room temperature during 2 h. After stirring overnight, toluene (150 mL) was added, and the precipitate was collected on a glass filter over Celite and washed twice with toluene (50 mL). The product/celite mixture was taken up in $CHCl_3$. The resulting suspension was filtered from celite and the organic layer was transferred with chloroform (200 mL) directly to a separation funnel. A diluted aq. solution of $NaBF_4$ (27.5 g, 250 mmol) was added, the two-phase mixture was shaken vigorously and the layers were separated. The aqueous was extracted once with a small portion of chloroform. The combined chloroform fractions were dried ($MgSO_4$), filtered and evaporated under reduced pressure yielding pure product **11** after recrystallization.

2-Amino-*N*,*N*′-dialkyl-4,5-dimethylimidazolium tetrafluoroborates (22H$^+BF_4^-$). General procedure (GP4): Hexane was removed from a stock solution of compound **10** (15.0 mmol) in vacuum, and the resulting solid residue was dissolved in THF (15 mL). A solution of *tert*-butyl azide (1.64 g, 16.5 mmol) in toluene (16.5 mL) was slowly added with vigorous stirring. After 5 min, the reaction mixture was warmed to 60 °C and stirred for 30 min yielding triazene **23** (NMR monitoring). The volatiles were removed in vacuum, and the residue was

dissolved in MeOH (15 mL). Solid NH_4BF_4 (2.36 g, 22.5 mmol) was slowly added (Caution: effervescence due to evolution of N_2 and isobutylene!) and the reaction mixture was stirred for 15 min. After aqueous work up as described in **GP3.1**, pure products **22**$H^+BF_4^-$ were isolated as colorless crystalline solids.

(1,3-Dialkyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylideneamino)-1,3-dialkyl-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate and nonaflate salts (1$^+BF_4^-$, 1$^+ONf^-$) and 2-[tris(dimethylamino)phosphoranylidenamino]-1,3-dialkyl-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate and nonaflate salts (2$^+BF_4^-$, 2$^+ONf^-$). General procedure (GP5.1): Pre-dried KF (232 mg, 4.0 mmol) was strongly heated with a heat-gun in high vacuum in a flask for a few minutes to remove traces of moisture. It was cooled under argon, and the flask was equipped with a magnetic stirring bar. Dry dibenzo-18-crown-6 (72 mg, 0.2 mmol) was added. Salts **11**$^+BF_4^-$ or **11**$^+ONf^-$ (2.0 mmol) and **14** (535 mg, 2.0 mmol) or **16** (500 mg, 2.0 mmol) were added followed by MeCN (2 mL), and the reaction mixture was stirred for 48 h at room temperature. After completion of the reaction indicated by ^{1}H NMR, the suspension was poured into a separation funnel containing a two-phase mixture of $CHCl_3$ (50 mL) / diluted aq. $NaBF_4$ (1.1 g, 10.0 mmol) or KONf (676 mg, 2.0 mmol) followed by vigorous shaking. The organic layer was separated, and the aqueous was extracted once with $CHCl_3$ (20 mL). The combined chloroform fractions were dried ($MgSO_4$), filtered and evaporated under reduced pressure. To the residue MeOH (2 mL) was added and crystalline crown was removed by filtration. Evaporation of the mother liquid and drying in high vacuum gave title products of >95% purity containing traces of the crown.

(1,3-Dialkyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylideneamino)-1,3-dialkyl-4,5-dimethyl-1*H*-imidazolium tetrafluoroborates (1$^+BF_4^-$) and 2-[tris(dimethylamino)phosphoranylidenamino]-1,3-dialkyl-4,5-dimethyl-1*H*-imidazolium tetrafluoroborates (2$^+BF_4^-$). General procedure (GP5.2): Pre-dried KF (1.40 g, 24.0 mmol) was strongly heated with a heat-gun in high vacuum in a flask for a few minutes to remove traces of moisture. It was cooled under argon, and the flask was equipped with a magnetic stirring bar. Salts **11**$^+BF_4^-$ (3.0 mmol) and **22**$H^+BF_4^-$ (3.0 mmol) or **25**$H^+BF_4^-$ (3.0 mmol) were added followed by MeCN (6 mL), and the reaction mixture was stirred for 48 h at ambient temperature (for **1a**,**c** and **2a**) or at 60 °C (for **1b** and **2b**), after which the ^{1}H NMR spectrum of the reaction mixtures indicated full conversion of the starting materials. The

suspension was then poured into a separation funnel containing a two-phase mixture of $CHCl_3$ (50 mL) / 12% aq. $NaBF_4$ (110 mL) followed by vigorous shaking. The organic layer was separated, and the aqueous was extracted once with $CHCl_3$ (20 mL). The combined organic layers were dried ($MgSO_4$) and filtered. The volatiles were removed in vacuum, and the solid residue was dried in high vacuum to afford pure products $\mathbf{1}^+BF_4^-$ or $\mathbf{2}^+BF_4^-$ as a beige crystalline solids.

Synthesis of *N*-alkyl 1,3-dialkyl-4,5-dimethylimidazol-2-ylidene amine salts $4H^+BF_4^-$ from 2-chloroimidazolium salts $11^+BF_4^-$. General procedure (GP6.1): Pre-dried KF (3.49 g, 60 mmol) was heated in a reaction flask with a heat-gun in vacuum for a few minutes to remove traces of moisture. After cooling, a magnetic stirring bar, 2-chloroimidazolium salt $\mathbf{11}^+BF_4^-$ (10 mmol), MeCN (30 mL) and corresponding amine RNH_2 or its salt RNH_3Cl (15-30 mmol) were added subsequently. The reaction mixture was stirred at the specified temperature for the given time (see at the individual compounds). After completion of the reaction indicated by ^1H NMR a small portion of chloroform was added. After stirring for 5 min the suspension was filtered through Schott glass filter (por. 4) or funnel with cotton directly to a separation funnel, and the solid residue was washed a few times with small portions of chloroform. A diluted aq. solution of $NaBF_4$ (5.5 g, 50 mmol) was added to the chloroform solution followed by vigorous shaking. The layers were separated. The aqueous was extracted once with a small portion of chloroform. The combined chloroform fractions were dried ($MgSO_4$), filtered and evaporated under reduced pressure. A few mL of EtOAc or Et_2O was added to residual oil often resulting in crystallization of the crude product. The mixture was evaporated in vacuum, yielding the target salt after recrystallization.

Synthesis of *N*-alkyl- or *N*-aryl-1,3-alkyl-4,5-dimethylimidazol-2-ylidene amine salts $4H^+BF_4^-$ from 2-fluoroimidazolium salt $26^+BF_4^-$. General procedure (GP6.2): To a solution of 2-fluoroimidazolium salt $\mathbf{26}^+BF_4^-$ (6 mmol) in MeCN (18 mL) the primary amine (13-18 mmol) was added, and the reaction mixture was stirred at the specified temperature for the given time until the ^1H NMR spectrum of the reaction mixture indicated full conversion of the starting materials. The reaction mixture was poured into a separation funnel containing a two-phase mixture of chloroform / aq. $NaBF_4$ / aq. ammonia followed by vigorous shaking. The organic layer was separated, and the aqueous was extracted once with a small portion of

chloroform. The combined chloroform fractions were dried ($MgSO_4$), filtered and evaporated under reduced pressure to give the target salts after recrystallization.

Liberation of *N,N'*-dialkyl-4,5-dimethylimidazol-2-ylidene amine bases 4 from corresponding salts. General procedure (GP7): Salts **4**$H^+BF_4^-$ (1 mmol) were dissolved in MeOH (1 mL). Hexane (5 mL) was added followed by 50% aq. KOH solution (1 mL) with vigorous stirring. The mixture was stirred at ambient temperature for several minutes. The hexane layer was carefully separated via cannula into a flask filled with argon. Extraction of the mixture with hexane (5 mL) was repeated twice. The combined hexane fractions were dried over BaO, filtered, evaporated and dried in high vacuum at 50 °C to give pure bases **4**.

Synthesis of BIG salts 6$H^+BF_4^-$ from 2-chloroimidazolium salts 11$^+BF_4^-$. General procedure (GP 8):

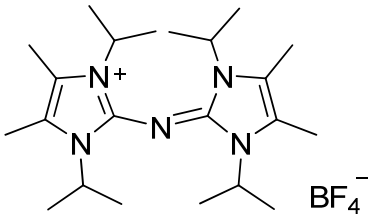
a) Synthesis of *N*-isopropylguanidinium iodide (41):[113,114] To a flask equipped with a reflux condenser and a magnetic stirring bar immersed in an ice bath salt **40**$^+I^-$ (4.36 g, 20.0 mmol) was added. Cold water (3 mL) was added followed by *i*$PrNH_2$ (3.54 g, 60 mmol) with stirring (Caution: MeSH evolution!). The reaction mixture was stirred overnight at room temperature followed by reflux for 4 h (NMR monitoring in D_2O or CD_3OD). The solution was evaporated in vacuum, MeCN (10 mL) and Et_3N (1 mL) was added and the mixture was stirred for 5 min. Evaporation of the solvent and drying of the residue in high vacuum at 50-60 °C for 2 h gave the desired *N*-isopropylguanidinium iodide (**41**) in form of a colorless syrup, which was stored under Ar and used in the next step without further purification. Yield > 95%.

b) Imidazolation: Pre-dried KF (1.86 g, 32.0 mmol) was heated in a reaction flask with a heat-gun in vacuum for a few minutes to remove traces of moisture. After cooling a magnetic stirring bar, 2-chloroimidazolium salt **11**$^+BF_4^-$ (4.0 mmol), MeCN (6 mL) and the corresponding guanidinium salt (2.0 mmol) were added subsequently. The reaction mixture was stirred at the specified temperature for the given time (see at the individual compounds). After completion of the reaction as indicated by ^1H NMR, a portion of chloroform (20 mL) was added. After stirring for 5 min the suspension was filtered through a Schott glass filter (por. 4) or funnel with cotton directly to a separation funnel, and the solid residue was washed a few times with small portions of chloroform. The organic solution in the separation funnel was vigorously shaken twice with a diluted aq. solution of $NaBF_4$ (2.2 g, 20.0 mmol). The aqueous layers were combined and extracted once with a small portion of chloroform. The

combined chloroform fractions were dried ($MgSO_4$), filtered and evaporated under reduced pressure. The residue was dissolved in EtOAc (4-12 mL) and the crystalline product was precipitated by addition of excess of Et_2O with stirring, filtered and dried in vacuum.

Liberation of BIG bases 6 from corresponding salts. General procedure (GP9): To a mixture of salt **6**$H^+BF_4^-$ (1 mmol) in THF (3 mL) was added 1 M solution of *t*BuOK in THF (1.2-1.25 mL) at –78 °C with stirring and the mixture was warmed to room temperature and additionally stirred for 30 min. Toluene (3 mL) was added and the mixture was evaporated under reduced pressure. Hexane (5 mL) was added.* After few minutes of vigorous stirring the solid residue was allowed to precipitate. The hexane layer was separated by cannula and filtered via micron filter into a flask filled with argon. The residue was extracted once with small portion of hexane. The combined hexane solution was evaporated and dried in high vacuum (0.1-0.3 Torr) for 1-2 h at 60-70 °C to give pure base **6**.

2-(1,3-Diisopropyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylideneamino)-1,3-diisopropyl-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate (1a$^+BF_4^-$):



Was prepared according to **GP5.1** starting from **11a**$^+BF_4^-$ (605 mg, 2.0 mmol) and **14** (535 mg, 2.0 mmol) in 96% yield (0.89 g). Was prepared according to **GP5.2** starting from 2-chloroimidazolium salt **11a**$^+BF_4^-$ (0.908 g, 3.0 mmol) and 2-aminoimidazolium salt **22a**$H^+BF_4^-$ (0.849 g, 3.0 mmol).

Yield: 1.08 g (78%) as a pale yellow solid, m.p. 151–153 °C (from hexane / EtOAc, 1:6);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (d, ^3J = 7.0 Hz, 24H, 4×CH*Me*$_2$), 2.19 (s, 12H, 4×Me), 4.21 (sept, ^3J = 7.0 Hz, 4H, 4×NCH);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.2 (Me), 21.2 (CH*Me*$_2$), 48.0 (NCH), 119.5 (C=C), 144.5 (CNC);

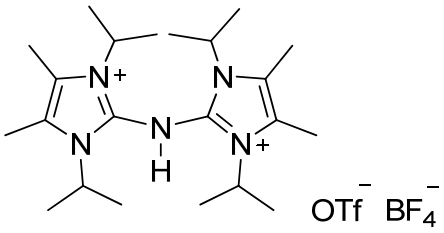
IR (neat): $\tilde{\nu}$ = 1051 (vs), 1096 (m), 1367 (m), 1425 (m), 1573 (s), 2995 cm^{-1} (w);

ESI (pos.), *m/z* (%): 374 (100) [M$^+$];

* Toluene (1 mL) was added to pure hexane to dissolve the product, if it crystallized while extraction.

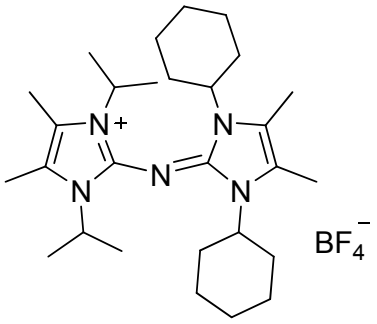
HRMS (ESI$^+$), *m/z*: calcd for $C_{22}H_{40}N_5^+$: 374.3278 [M^+]; found: 374.3279;
Elemental analysis calcd (%) for $C_{22}H_{40}BF_4N_5$ (461.39): C 57.27, H 8.74, N 15.18; found: C 57.06, H 8.56, N 14.78.

Reactions of the salt 1a$^+$ with TfOMe or TfOH. 2,2'-Azanediylbis(1,3-diisopropyl-4,5-dimethyl-1*H*-imidazolium) tetrafluoroborate triflate (1aH$^+$BF$_4^-$OTf$^-$):



A sample of **1a**$^+$$BF_4^-$ (46 mg, 0.10 mmol) in $CDCl_3$ was treated with TfOMe (18 mg, 0.11 mmol). No reaction occurred after 24 h at ambient temperature. Heating for one week at 80 °C resulted in disappearance of the signal of TfOMe and formation of **1a**$^+$$BF_4^-$·HOTf whose authenticity was verified by matching the NMR data with those of a reference sample obtained by protonation of **1a**$^+$$BF_4^-$ (46 mg, 0.10 mmol) with TfOH (15 mg, 0.10 mmol) in $CHCl_3$ (*ca*. –80 °C to r.t., then high vacuum) to give quantitative yield of **1a**$^+$$BF_4^-$·HOTf as a yellow oil. The salt had low solubility in $CHCl_3$ and made second layer.
^{1}H NMR (400 MHz, CD_3CN): δ = 1.49 (d, ^3J = 7.0 Hz, 24H, 4×CH*Me*$_2$), 2.35 (s, 12H, 4×Me), 4.50 (sept, ^3J = 7.0 Hz, 4H, 4×NCH), 8.69 (br s, NH, integral intensity reduced due to H–D exchange);
^{13}C NMR (101 MHz, CD_3CN): δ = 10.7 (Me), 21.1 (CH*Me*$_2$), 52.2 (NCH), 121.8 (q, ^1J(C,F) = 320.2 Hz, CF_3SO_3), 127.1 (C=C), 134.8 (CNC).

2-(1,3-Dicyclohexyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylideneamino)-1,3-diisopropyl-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate (1ac$^+$BF$_4^-$):



Was prepared according to **GP5.2** starting from 2-chloroimidazolium salt **11c**$^+$BF$_4^-$ (0.383 g, 1.0 mmol) and 2-aminoimidazolium salt **22a**H$^+$BF$_4^-$ (0.283 g, 1.0 mmol).

Yield: 0.38 g (71%) as a colorless solid, m.p. 160 °C (from EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98–1.25 (m, 6H, 3×CH_2), 1.38 (d, ^3J = 7.0 Hz, 12H, 2×CH*Me*$_2$), 1.56–1.99 (m, 14H, 7×CH_2), 2.14 (s, 12H, 4×Me), 3.55–3.73 (m, 2H, 2×CH), 4.12 (sept, ^3J = 6.9 Hz, 2H, 2×*CH*Me$_2$);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.2 (Me), 10.5 (Me), 21.2 (CH*Me*$_2$), 25.2 (CH_2), 26.3 (CH_2), 31.3 (CH_2), 48.1 (*C*HMe$_2$), 57.0 (CH), 119.3 (C=C), 119.8 (C=C), 144.6 (NCN);

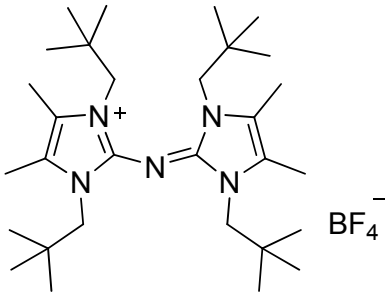
IR (neat): $\tilde{\nu}$ = 894 (w), 1033 (vs), 1047 (vs), 1092 (m), 1234 (w), 1261 (w), 1379 (m), 1426 (m), 1586 (s), 2858 (w), 2929 cm^{-1} (w);

ESI (pos.), *m/z* (%): 454 (100) [M$^+$];

HRMS (ESI$^+$), *m/z*: calcd for $C_{28}H_{48}N_5$: 454.3904 [M$^+$]; found: 454.3903;

Elemental analysis calcd (%) for $C_{28}H_{48}BF_4N_5$ (541.52): C 62.10, H 8.93, N 12.93; found: C 61.92, H 8.51, N 12.74.

2-(1,3-Dineopentyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylideneamino)-1,3-dineopentyl-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate (1b$^+$BF$_4^-$):



Was prepared according to **GP5.2** starting from 2-chloroimidazolium salt **11b**$^+$BF$_4^-$ (1.08 g, 3.0 mmol) and 2-aminoimidazolium salt **22b**H$^+$BF$_4^-$ (1.02 g, 3.0 mmol).

Yield: 1.67 g (84%) as a pale yellow solid; recrystallization from hexane / EtOAc (1:1) gave a colorless inclusion compound **1b**·1/2EtOAc, m.p. 145–148 °C, after further crystallization, the m.p. was increased to 202–204 °C;

^{1}H NMR (500 MHz, CD_3OD, 313 K): δ = 0.95 (br s, 36H, 4×CMe_3), 2.21 (s, 12H, 4×Me), 3.59 (br s, 8H, 4×NCH_2);

^{13}C NMR (126 MHz, CD_3OD, 313 K): δ = 10.0 (br, Me), 28.7 (br, C*Me*$_3$), 35.9 (br, *C*Me_3), 54.3 (br, NCH_2), 121.4 (br, C=C), 148.8 (CNC);

^{1}H NMR (500 MHz, DMSO-d6, 373 K): δ = 0.92 (s, 36H, 4×CMe_3), 2.18 (s, 12H, 4×Me), 2.89 (br s, 8H, 4×NCH_2);

^{1}H NMR (500 MHz, CD_3OD, 240 K): δ = 0.80 (s, 18H, 2×CMe_3), 1.09 (s, 18H, 2×CMe_3), 2.20 (s, 6H, 2×Me), 2.24 (s, 6H, 2×Me), 2.79 (d, ^2J = 15.3 Hz, 2H, NCH_2), 3.60 (d, ^2J = 14.1 Hz, 2H, NCH_2), 3.71 (d, ^2J = 15.3 Hz, 2H, NCH_2), 3.88 (d, ^2J = 14.1 Hz, 2H, NCH_2);

^{13}C NMR (126 MHz, CD_3OD, 240 K): δ = 9.9 (Me), 10.2 (Me), 28.4 (C*Me*$_3$), 28.9 (C*Me*$_3$), 35.8 (*C*Me_3), 36.2 (*C*Me_3), 53.6 (NCH_2), 54.4 (NCH_2), 121.0 (C=C), 121.6 (C=C), 148.3 (CNC);

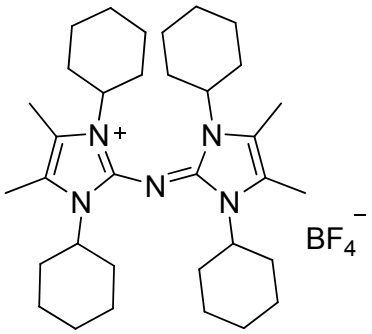
IR (neat): $\tilde{\nu}$ = 1030 (vs), 1048 (vs), 1397 (m), 1475 (m), 1580 (vs), 2874 (w), 2957 cm^{-1} (m);

ESI (pos.), *m/z* (%): 486 (100) [M$^+$];

HRMS (ESI$^+$), *m/z*: calcd for $C_{30}H_{56}N_5^+$: 486.4530 [M$^+$]; found: 486.4527;

Elemental analysis calcd (%) for $C_{30}H_{56}BF_4N_5$ 1/2$C_4H_8O_2$ (617.66): C 62.23, H 9.79, N 11.34; found: C 62.28, H 9.79, N 11.43.

2-(1,3-Dicyclohexyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylideneamino)-1,3-dicyclohexyl-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate (1c$^+$BF$_4^-$):



Was prepared according to **GP5.2** starting from 2-chloroimidazolium salt **11c**$^+$BF$_4^-$ (1.15 g, 3.0 mmol) and 2-aminoimidazolium salt **22c**H$^+$BF$_4^-$ (1.090 g, 3.0 mmol).

Yield: 1.62 g (87%) as a pale yellow solid, m.p. 76–78 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05–1.30 (m, 12H, 6×CH_2), 1.61–2.12 (m, 28H, 14×CH_2), 2.21 (s, 12H, 4×Me), 3.68 (br t, 4H, 4×NCH);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.5 (Me), 25.0 (CH_2), 26.2 (CH_2), 31.1 (CH_2), 57.0 (NCH), 119.4 (C=C), 144.6 (CNC);

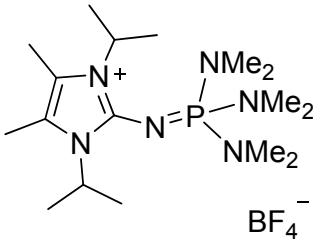
IR (neat): $\tilde{\nu}$ = 1048 (vs), 1378 (m), 1413 (m), 1585 (s), 2854 (w), 2928 cm^{-1} (m);

ESI (pos.), *m/z* (%): 534 (100) [M$^+$];

HRMS (ESI$^+$), *m/z*: calcd for $C_{34}H_{56}N_5^+$: 534.4530 [M$^+$]; found: 534.4528;

Elemental analysis calcd (%) for $C_{34}H_{56}BF_4N_5$ (621.65): C 65.69, H 9.08, N 11.27; found: C 65.39, H 8.97, N 10.99.

2-[Tris(dimethylamino)phosphoranylidenamino]-1,3-diisopropyl-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate (2a$^+$BF$_4^-$):



Was prepared according to **GP5.1** starting from **11a**$^+$BF$_4^-$ (605 mg, 2.0 mmol) and **16** (500 mg, 2.0 mmol) in 92% yield (0.95 g). Was prepared according to **GP5.2** starting from 2-chloroimidazolium salt **11a**$^+$BF$_4^-$ (0.908 g, 3.0 mmol) and salt **25**H$^+$BF$_4^-$ (0.798 g, 3.0 mmol).

Yield: 1.27 g (95%) as a pale yellow solid, m.p. 99–101 °C (from hexane / EtOAc, 1:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.47 (d, ^{3}J = 7.1 Hz, 12H, 2×CH*Me*$_2$), 2.21 (s, 6H, 2×Me), 2.72 (d, ^{3}J(H,P) = 10.0 Hz, 18H, 3×NMe_2), 4.68 (sept, ^{3}J = 7.1 Hz, 2H, 2×NCH);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.1 (Me), 21.3 (CH*Me*$_2$), 37.1 (d, ^{2}J(C,P) = 4.2 Hz, NMe_2), 47.5 (NCH), 119.2 (C=C), 142.3 (d, ^{2}J(C,P) = 14.8 Hz, CNP);

^{31}P NMR (162 MHz, $CDCl_3$): δ = 17.88;

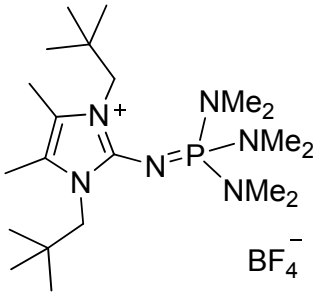
IR (neat): $\tilde{\nu}$ = 737 (m), 756 (m), 974 (vs), 1035 (vs), 1048 (vs), 1408 (m), 1568 (m), 2930 cm^{-1} (w);

ESI (pos.), *m/z* (%): 357 (100) [M^+];

HRMS (ESI^+), *m/z*: calcd for $C_{17}H_{38}N_6P^+$: 357.2890 [M^+]; found: 357.2889;

Elemental analysis calcd (%) for $C_{17}H_{38}BF_4N_6P$ (444.30): C 45.96, H 8.62, N 18.92; found: C 45.80, H 8.43, N 18.90.

2-[Tris(dimethylamino)phosphoranylidenamino]-1,3-dineopentyl-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate (2b$^+$BF$_4^-$):



Was prepared according to **GP5.1** starting from **11b**$^+$$BF_4^-$ (717 mg, 2.0 mmol) and **16** (500 mg, 2.0 mmol) in 96% yield (0.96 g). Was prepared according to **GP5.2** starting from 2-chloroimidazolium salt **11b**$^+$$BF_4^-$ (1.076 g, 3.0 mmol) and salt **25**$H^+$$BF_4^-$ (0.798 g, 3.0 mmol). Yield: 1.37 g (91%) as a colorless solid, m.p. 52–55 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (s, 18H, 2×CMe_3), 2.17 (s, 6H, 2×Me), 2.65 (d, ^{3}J(H,P) = 9.9 Hz, 18H, 3×NMe_2), NCH_2 peaks not observed due to very strong broadening;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.4 (Me), 28.3 (C*Me*$_3$), 34.8 (*C*Me_3), 37.2 (d, ^{2}J(C,P) = 3.9 Hz, NMe_2), 52.8 (NCH_2), 120.3 (C=C), 148.2 (d, ^{2}J(C,P) = 10.15 Hz, CNP);

^{31}P NMR (162 MHz, $CDCl_3$): δ = 22.73;

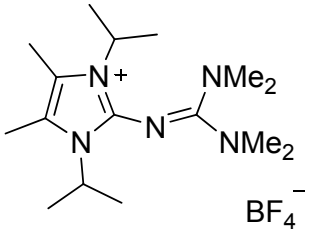
IR (neat): $\tilde{\nu}$ = 680 (s), 744 (vs), 977 (s), 1119 (m), 1182 (s), 1549 (m), 2957 cm^{-1} (w);

ESI (pos.), *m/z* (%): 413 (100) [M^+];

HRMS (ESI^+), *m/z*: calcd for $C_{21}H_{46}N_6P^+$: 413.3516 [M^+]; found: 413.3510;

Elemental analysis calcd (%) for $C_{28}H_{53}N_6O_3PS$ (500.41): C 57.51, H 9.13, N 14.37; found: C 57.36, H 9.00, N 14.11.

2-[Bis(dimethylamino)methyleneamino]-1,3-diisopropyl-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate ($3a^+BF_4^-$):



Pre-dried KF (0.23 g, 4.0 mmol) was strongly heated in a reaction flask with a heat-gun in high vacuum for a few minutes to remove traces of moisture and cooled to room temperature under argon. The flask was equipped with a magnetic stirring bar and MeCN (2 mL). $(Me_2N)_2C{=}NH$ (0.13 mL, 1.0 mmol), and 2-chloroimidazolium salt $\mathbf{11a}^+BF_4^-$ (0.30 g, 1.0 mmol) were successively added. The reaction mixture was stirred for 24 h at ambient temperature. Aqueous work up as described in the **GP5.2** furnished the pure product.

Yield: 0.35 g (91%) as a pale yellow solid, m.p. 169–171 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.46 (d, ^3J = 7.1 Hz, 12H, 2×CH*Me*$_2$), 2.24 (s, 6H, 2×Me), 2.88 (s, 12H, 2×NMe_2), 4.28 (sept, ^3J = 7.1 Hz, 2H, 2×NCH);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.1 (Me), 21.0 (CH*Me*$_2$), 39.7 (NMe_2), 48.5 (NCH), 120.6 (C=C), 145.7 (CN), 161.4 (N=*C*$(NMe_2)_2$);

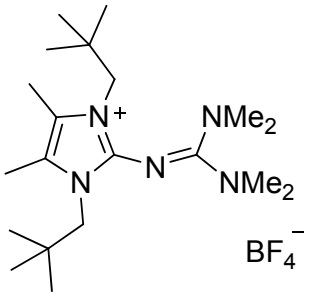
IR (neat): $\tilde{\nu}$ = 1034 (vs), 1045 (vs), 1399 (m), 1430 (m), 1533 (s), 2933 (w), 2971 cm^{-1} (w);

ESI (pos.), *m/z* (%): 294 (100) [M^+];

HRMS (ESI^+), *m/z*: calcd for $C_{16}H_{32}N_5^+$: 294.2652 [M^+]; found: 294.2653;

Elemental analysis calcd (%) for $C_{16}H_{32}BF_4N_5$ (381.26): C 50.40, H 8.46, N 18.37; found: C 50.15, H 8.43, N 18.08.

2-[Bis(dimethylamino)methyleneamino]-4,5-dimethyl-1,3-dineopentyl-1*H*-imidazolium ($3b^+BF_4^-$):



Was prepared as described above for compound $\mathbf{3a}^+BF_4^-$ starting from salt $\mathbf{11b}^+BF_4^-$ (0.364 g, 1.0 mmol).

Yield: 0.39 g (89%) as brownish solid, recrystallization from EtOAc gave a colorless inclusion compound $\mathbf{3b}^+BF_4^- \cdot 1/4EtOAc$, m.p. 128–130 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99 (s, 18H, 2×CMe_3), 2.20 (s, 6H, 2×Me), 2.81 (s, 12H, 2×NMe_2), 3.60 (s, 4H, 2×CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.0 (Me), 28.5 (C*Me*$_3$), 34.4 (*C*Me_3), 39.5 (NMe_2), 53.5 (NCH_2), 121.5 (C=C), 149.1 (CN), 161.0 (N=*C*$(NMe_2)_2$);

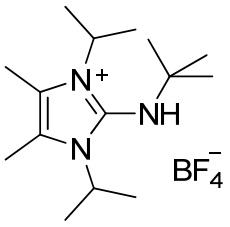
IR (neat): $\tilde{\nu}$ = 1030 (vs), 1047 (vs), 1068 (s), 1162 (w), 1369 (m), 1394 (s), 1427 (m), 1441 (m), 1474 (m), 1531 (s), 1568 (m), 2875 (w), 2958 cm^{-1} (w);

ESI (pos.), *m/z* (%): 350 (100) [M^+];

HRMS (ESI^+), *m/z*: calcd for $C_{20}H_{40}N_5^+$: 350.3278 [M^+]; found: 350.3276;

Elemental analysis calcd (%) for $C_{20}H_{40}BF_4N_5 \bullet 1/4C_4H_8O_2$ (459.40): C 54.90, H 9.22, N 15.24; found: C 54.94, H 9.27, N 15.09.

2-(*tert*-Butylamino)-1,3-diisopropyl-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate ($4aH^+BF_4^-$):



Was synthesized according to **GP6.1** starting from $\mathbf{11a}^+BF_4^-$ (3.03 g, 10.0 mmol) and *t*$BuNH_2$ (3.15 mL, 30.0 mmol); Reaction time: 3 d at room temperature.

Yield: 3.05 g (90%) as colorless crystals, m.p. 149–150 °C (from EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 9H, CMe_3), 1.54 (d, ^{3}J = 7.1 Hz, 12H, 2×CH*Me*$_2$), 2.34 (s, 6H, 2×Me), 4.51 (s, 1H, NH), 5.01 (sept, ^{3}J = 7.1 Hz, 2H, 2×CH);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.2 (Me), 21.3 (CH*Me*$_2$), 30.7 (C*Me*$_3$), 50.3 (*C*HMe$_2$), 55.6 (*C*Me$_3$), 124.3 (C=C), 141.6 (CNH);

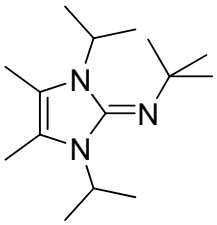
IR (neat): $\tilde{\nu}$ = 1013 (vs), 1053 (vs), 1085 (vs), 1192 (m), 1212 (m), 1373 (m), 1391 (m), 1409 (m), 1472 (w), 1519 (m), 1629 (w), 2982 (w), 3342 cm^{-1} (w);

ESI (pos.), *m/z* (%): 252 (100) [M^+];

HRMS (ESI$^+$), *m/z*: calcd for $C_{15}H_{30}N_3^+$: 252.2434 [M^+]; found: 252.2434;

Elemental analysis calcd (%) for $C_{15}H_{30}BF_4N_3$ (339.22): C 53.11, H 8.91, N 12.39; found: C 53.19, H 9.00, N 12.20.

***N-tert*-Butyl-(1,3-diisopropyl-4,5-dimethyl-1*H*-imidazol-2-ylidene) amine (4a):**



Was synthesized according to **GP7** starting from **4a**H$^+$BF$_4^-$ (14.46 g, 42.6 mmol).

Yield: 7.64 g (76%) as colorless oil; Compound is sensitive to CO_2 of air;

^{1}H NMR (400 MHz, C_6D_6): δ = 1.23 (d, ^{3}J = 7.1 Hz, 12H, 2×CH*Me*$_2$), 1.57 (s, 9H, CMe_3), 1.72 (s, 6H, 2×Me), 4.54 (sept, ^{3}J = 7.1 Hz, 2H, 2×CH);

^{13}C NMR (101 MHz, C_6D_6): δ = 11.1 (Me), 21.0 (CH*Me*$_2$), 33.7 (C*Me*$_3$), 47.1 (*C*HMe$_2$), 51.7 (*C*Me$_3$), 116.1 (C=C), 146.2 (NCN);

^{1}H NMR (400 MHz, CD_3CN): δ = 1.25 (d, ^{3}J = 7.1 Hz, 12H, 2×CH*Me*$_2$), 1.25 (s, 9H, CMe_3), 1.97 (s, 6H, 2×Me), 4.42 (sept, ^{3}J = 7.1 Hz, 2H, 2×CH);

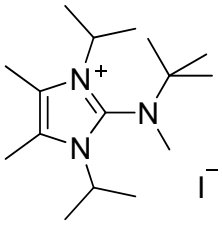
^{13}C NMR (101 MHz, CD_3CN): δ = 11.3 (Me), 21.2 (CH*Me*$_2$), 33.6 (C*Me*$_3$), 47.8 (*C*HMe$_2$), 52.2 (*C*Me$_3$), 117.2 (C=C), 147.4 (NCN);

IR (hexane): $\tilde{\nu}$ = 1632 (vs), 1679 (m), 1685 cm^{-1} (m);

CI (pos.), *m/z* (%): 154 (15) [M+H–C_3H_6–C_4H_8]$^+$, 196 (10) [M+H–C_4H_8]$^+$, 208 (24) [M–C_3H_7]$^+$, 209 (52) [M–C_3H_6]$^{+\cdot}$, 210 (75) [M+H–C_3H_6]$^+$, 236 (40) [M–CH_3]$^+$, 250 (20) [M–H]$^+$, 251 (48) [$M^{+\cdot}$], 252 (100) [M+H]$^+$;

HRMS (CI$^+$), *m/z*: calcd for $C_{15}H_{30}N_3^+$: 252.2440 [M+H]$^+$; found: 252.2445.

2-[*tert*-Butyl(methyl)amino]-1,3-diisopropyl-4,5-dimethyl-1*H*-imidazolium iodide (4aMe$^+$I$^-$):



To a solution of base **4a** (0.50 g, 2.0 mmol) in dry hexane (25 mL) MeI (0.5 mL, 8.0 mmol) was added dropwise at room temperature. After 24 h of stirring at room temperature the resulting suspension was filtered, washed with hexane and dried in vacuum to give the title compound after recrystallization.

Yield: 0.50 g (64%) as a colorless solid, m. p. 204–205 °C (from EtOAc / MeOH, 100:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 9H, CMe_3), 1.64 (d, ^3J = 7.1 Hz, 6H, 2×Me), 1.65 (d, ^3J = 7.1 Hz, 6H, 2×Me), 2.42 (s, 6H, 2×Me), 2.90 (s, 3H, NMe), 4.74 (sept, ^3J = 7.1 Hz, 2H, 2×CH);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.7 (Me), 21.0 (CH*Me*Me), 22.2 (CHMe*Me*), 28.4 (C*Me*$_3$), 35.0 (NMe), 50.1 (*C*HMe$_2$), 56.9 (*C*Me$_3$), 125.0 (C=C), 142.5 (NCN);

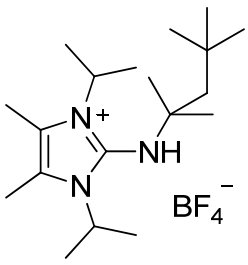
IR (neat): $\tilde{\nu}$ = 911 (m), 1027 (m), 1109 (s), 1199 (s), 1215 (s), 1370 (vs), 1397 (vs), 1424 (s), 1522 (m), 1627 (m), 2813 (w), 2877 (w), 2934 (m), 2972 cm^{-1} (m);

ESI (pos.), *m/z* (%): 266 (100) [M$^+$];

HRMS (ESI$^+$), *m/z*: calcd for $C_{16}H_{32}N_3^+$: 266.2591 [M$^+$]; found: 266.2591;

Elemental analysis calcd (%) for $C_{16}H_{32}IN_3$ (393.35): C 48.86, H 8.20, N 10.68; found: C 49.05, H 8.26, N 10.63.

1,3-Diisopropyl-4,5-dimethyl-2-[(2,4,4-trimethylpentan-2-yl)amino]-1*H*-imidazolium tetrafluoroborate (4bH$^+$BF$_4^-$):



Was synthesized according to **GP6.1** starting from **11a**$^+$BF$_4^-$ (3.03 g, 10.0 mmol) and *t*OctNH$_2$ (5.0 mL, 30.0 mmol); Reaction time: 3 d at room temperature. To remove residual

*t*OctNH$_2$ from the product after filtration of KF the solvent was evaporated in vacuo, the resulting oil was mixed with a small amount of diglyme and the mixture was evaporated in high vacuum. The procedure was repeated once. The residue was diluted with chloroform followed by an aq. NaBF$_4$ work up. After evaporation of the solvent, the resulting oil was dried for a few hours in high vacuum at 70 °C with stirring.

Yield: 3.64 g (92%) as colorless viscous oil slowly crystallizing on storage, m.p. 88–89 °C;

^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.07 (s, 9H, CMe$_3$), 1.28 (s, 6H, CMe$_2$), 1.54 (d, ^3J = 7.1 Hz, 12H, 2×CH*Me*$_2$), 1.63 (s, 2H, CH$_2$), 2.33 (s, 6H, 2×Me), 4.40 (s, 1H, NH), 5.01 (sept, ^3J = 6.9 Hz, 2H, 2×CH);

^{13}C NMR (101 MHz, CDCl$_3$): δ = 10.3 (Me), 21.2 (CH*Me*$_2$), 29.9 (C*Me*$_2$), 31.70 (*C*Me$_3$), 31.73 (C*Me*$_3$), 50.2 (*C*HMe$_2$), 56.5 (CH$_2$), 59.7 (*C*Me$_2$), 124.3 (C=C), 141.5 (CNH);

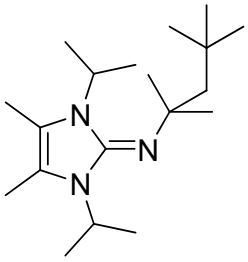
IR (neat): $\tilde{\nu}$ = 997 (vs), 1036 (s), 1072 (vs), 1111 (m), 1209 (m), 1377 (m), 1389 (m), 1462 (w), 1517 (m), 1633 (w), 1704 (w), 2942 (w), 2974 (w), 3346 cm^{-1} (w);

ESI (pos.), *m/z* (%): 308 (100) [M$^+$];

HRMS (ESI$^+$), *m/z*: calcd for C$_{19}$H$_{38}$N$_3^+$: 308.3060 [M$^+$]; found: 308.3060;

Elemental analysis calcd (%) for C$_{19}$H$_{38}$BF$_4$N$_3$ (395.33): C 57.72, H 9.69, N 10.63; found: C 57.82, H 9.77, N 10.37.

_N_-(1,3-Diisopropyl-4,5-dimethyl-1_H_-imidazol-2-ylidene)-2,4,4-trimethylpent-2-yl amine (4b):



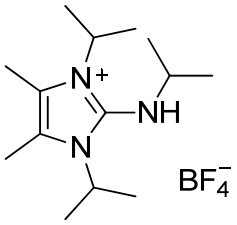
Was synthesized according to **GP7** starting from salt **4b**H$^+$BF$_4^-$ (3.39 g, 8.6 mmol).

Yield: 1.84 g (70%) as a pale yellow oil; Compound is sensitive to CO$_2$ of air;

^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 1.24 (d, ^3J = 7.2 Hz, 12H, 2×CH*Me*$_2$), 1.25 (s, 9H, CMe$_3$), 1.58 (s, 6H, CMe$_2$), 1.72 (s, 6H, 2×Me), 1.80 (s, 2H, CH$_2$), 4.45 (br s, 2H, 2×CH);

^{13}C NMR (101 MHz, C$_6$D$_6$): δ = 11.1 (Me), 21.4 (CH*Me*$_2$), 32.4, 32.5, 34.5 (C*Me*$_2$ and CMe$_3$), 47.2 (CH*Me*$_2$), 55.9, 57.5 (CH$_2$ and *C*Me$_2$), 116.2 (C=C), 145.7 (NCN).

1,3-Diisopropyl-2-(isopropylamino)-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate (4cH$^+$BF$_4^-$):



Was synthesized according to **GP6.1** starting from **11a**$^+$BF$_4^-$ (0.91 g, 3.0 mmol), KF (1.05 g, 18.0 mmol), *i*PrNH$_2$ (0.36 g, 6.0 mmol) in MeCN (9 mL); Reaction time: 2 d at room temperature. The crude solid was recrystallized from EtOAc.

Yield: 0.81 g (83%) as a colorless solid, m.p. 96–97.5 °C (from MeO*t*Bu / EtOAc, 1:2);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (d, ^3J = 6.4 Hz, 6H, CH*Me$_2$*), 1.54 (d, ^3J = 7.1 Hz, 12H, 2×CH*Me$_2$*), 2.31 (s, 6H, 2×Me), 3.35 (oct, ^3J = 6.7 Hz, 1H, CH), 4.86 (sept, ^3J = 7.0 Hz, 3H, 2×CH and NH);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.1 (Me), 21.3 (CH*Me$_2$*), 23.1 (CH*Me$_2$*), 50.0 (*C*HMe$_2$), 51.5 (*C*HMe$_2$), 123.4 (C=C), 143.0 (CNH);

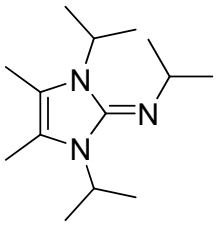
IR (neat): $\tilde{\nu}$ = 1006 (vs), 1057 (vs), 1110 (m), 1126 (m), 1212 (w), 1322 (w), 1379 (w), 1413 (w), 1463 (w), 1523 (m), 1544 (m), 1634 (w), 2884 (w), 2940 (w), 2977 (w), 3327 cm^{-1} (m);

ESI (pos.), *m/z* (%): 238 (100) [M$^+$];

HRMS (ESI$^+$), *m/z*: calcd for $C_{14}H_{28}N_3^+$: 238.2278 [M$^+$]; found: 238.2274;

Elemental analysis calcd (%) for $C_{14}H_{28}BF_4N_3$ (325.20): C 51.71, H 8.68, N 12.92; found: C 51.69, H 8.72, N 12.79.

***N*-(1,3-Diisopropyl-4,5-dimethyl-1*H*-imidazol-2-ylidene)prop-2-yl amine (4c):**



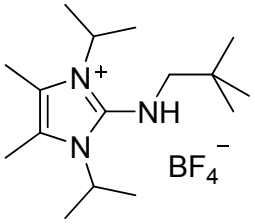
Was synthesized according to **GP7** starting from **4c**H$^+$BF$_4^-$ (0.85 g, 2.6 mmol).

Yield: 0.56 g (91%) as a pale yellow oil; Compound is sensitive to CO_2 of air;

^{1}H NMR (400 MHz, C_6D_6): δ = 1.25 (d, ^3J = 7.1 Hz, 12H, 2×CH*Me$_2$*), 1.45 (d, ^3J = 5.9 Hz, 6H, CH*Me$_2$*), 1.69 (s, 6H, 2×Me), 4.07 (sept, ^3J = 6.0 Hz, 1H, CH), 4.38–4.57 (m, 2H, 2×CH);

^{13}C NMR (101 MHz, C_6D_6): δ = 10.9 (Me), 21.3 (CH*Me*$_2$), 27.3 (CH*Me*$_2$), 47.0 (*C*HMe$_2$), 48.1 (*C*HMe$_2$), 116.2 (C=C), 148.8 (CN).

1,3-Diisopropyl-4,5-dimethyl-2-(neopentylamino)-1*H*-imidazolium tetrafluoroborate (4dH$^+$BF$_4^-$):



Was synthesized according to **GP6.1** starting from **11a**$^+$BF$_4^-$ (3.63 g, 12.0 mmol), KF (4.18 g, 72.0 mmol), NpNH$_2$ (1.26 g, 18.0 mmol) in MeCN (36 mL); Reaction time: 2 d at room temperature. Separation funnel solvent mixture: chloroform / aq. solution NaBF$_4$ (13.2 g, 120.0 mmol).

Yield: 3.40 g (80%) as a colorless solid, m.p. 146–147 °C (from EtOAc / hexane, 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (s, 9H, CMe$_3$), 1.55 (d, ^3J = 7.1 Hz, 12H, 2×CH*Me*$_2$), 2.29 (s, 6H, 2×Me), 2.78 (d, ^3J = 6.7 Hz, 2H, CH$_2$), 4.52 (t, ^3J = 6.6 Hz, 1H, NH), 4.88 (sept, ^3J = 7.0 Hz, 2H, 2×CH);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.0 (Me), 21.3 (CH*Me*$_2$), 27.2 (C*Me*$_3$), 32.4 (*C*Me$_3$), 49.8 (*C*HMe$_2$), 61.3 (CH$_2$), 123.4 (C=C), 143.7 (CNH);

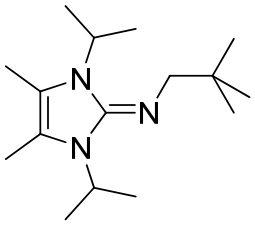
IR (neat): $\tilde{\nu}$ = 912 (w), 1012 (vs), 1058 (vs), 1219 (m), 1460 (m), 1533 (w), 1632 (w), 2948 (w), 3337 cm^{-1} (w);

ESI (pos.), *m/z* (%): 266 (100) [M$^+$];

HRMS (ESI$^+$), *m/z*: calcd for $C_{16}H_{32}N_3^+$: 266.2591 [M$^+$]; found: 266.2590;

Elemental analysis calcd (%) for $C_{16}H_{32}BF_4N_3$ (353.25): C 54.40, H 9.13, N 11.90; found: C 54.60, H 9.22, N 11.90.

_N_-(1,3-Diisopropyl-4,5-dimethyl-1_H_-imidazol-2-ylidene)-2,2-dimethylprop-1-yl amine (4d):



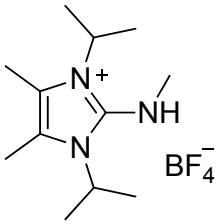
Was synthesized according to **GP7** starting from **4d**$H^+BF_4^-$ (1.41 g, 4.0 mmol).

Yield: 0.77 g (86%) as a pale yellow oil; Compound is sensitive to CO_2 of air;

^{1}H NMR (400 MHz, C_6D_6): δ = 1.22 (s, 9H, CMe_3), 1.24 (d, ^3J = 7.0 Hz, 12H, 2×CHMe_2), 1.69 (s, 6H, 2×Me), 3.41 (s, 2H, CH_2), 4.48–4.62 (m, 2H, 2×CH);

^{13}C NMR (101 MHz, C_6D_6): δ = 10.9 (Me), 21.5 (CHMe_2), 28.4 (CMe_3), 34.0 (*C*Me_3), 46.2 (*C*HMe_2), 62.3 (CH_2), 115.9 (C=C), 150.6 (CN).

1,3-Diisopropyl-4,5-dimethyl-2-(methylamino)-1_H_-imidazolium tetrafluoroborate (4e$H^+BF_4^-$):



Was synthesized according to **GP6.1** starting from **11a**$^+BF_4^-$ (3.03 g, 10.0 mmol), KF (5.23 g, 90.0 mmol), $MeNH_3Cl$ (1.35 g, 20.0 mmol); Reaction time: 2 d at room temperature.

Yield: 2.65 g (89%) as a colorless solid, m.p. 81–82 °C (from EtOAc / Et_2O);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.56 (d, ^3J = 7.1 Hz, 12H, 2×CHMe_2), 2.28 (s, 6H, 2×Me), 2.91 (d, ^3J = 5.3 Hz, 3H, NMe), 4.69–4.87 (m, 3H, 2×CH, NH);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 9.9 (Me), 21.3 (CHMe_2), 35.5 (CH_3), 49.8 (*C*HMe_2), 123.0 (C=C), 144.6 (CNH);

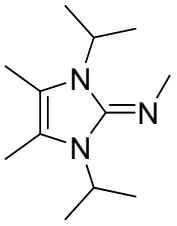
IR (neat): $\tilde{\nu}$ = 914 (w), 1003 (vs), 1061 (vs), 1110 (m), 1219 (w), 1379 (w), 1400 (w), 1525 (w), 1559 (m), 1637 (w), 2944 (w), 2987 (w), 3357 cm^{-1} (w);

ESI (pos.), *m/z* (%): 210 (100) [M^+], 168 (14) [M–C_3H_6]$^+$;

HRMS (ESI$^+$), *m/z*: calcd for $C_{12}H_{24}N_3^+$: 210.1965 [M^+]; found: 210.1966;

Elemental analysis calcd (%) for $C_{12}H_{24}BF_4N_3$ (297.14): C 48.50, H 8.14, N 14.14; found: C 48.65, H 8.23, N 14.09.

***N*-(1,3-Diisopropyl-4,5-dimethyl-1*H*-imidazol-2-ylidene)methyl amine (4e):**



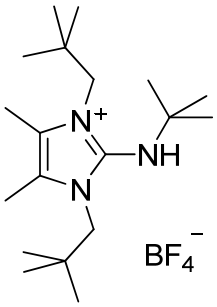
Was synthesized according to **GP7** starting from **4e**$H^+BF_4^-$ (1.19 g, 4.0 mmol).

Yield: 0.75 g (90%) as a pale yellow oil; Compound is sensitive to CO_2 of air;

^{1}H NMR (400 MHz, C_6D_6): δ = 1.23 (d, ^3J = 7.1 Hz, 12H, 2×CH*Me*$_2$), 1.72 (s, 6H, 2×Me), 3.48 (s, 3H, NMe), 4.56 (sept, ^3J = 7.0 Hz, 2H, 2×CH);

^{13}C NMR (101 MHz, C_6D_6): δ = 10.9 (Me), 21.4 (CH*Me*$_2$), 37.1 (NMe), 46.0 (*C*HMe$_2$), 116.1 (C=C), 152.0 (CN).

2-(*tert*-Butylamino)-4,5-dimethyl-1,3-dineopentyl-1*H*-imidazolium tetrafluoroborate (4f$H^+BF_4^-$):



Was synthesized according to **GP6.1** starting from **11b**$^+BF_4^-$ (2.10 g, 5.85 mmol), KF (1.80 g, 31.0 mmol), *t*BuNH$_2$ (2.0 mL, 18.5 mmol) in MeCN (22.5 mL); Reaction time: 1 d at room temperature and 1 d at 60 °C. Separation funnel solvent mixture: chloroform / aq. solution $NaBF_4$ (6.6 g, 60.0 mmol).

Yield: 1.78 g (77%) as off-white solid, m.p. 176–177 °C (from EtOAc / MeOH, 15:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.01 (s, 18H, 2×CMe_3), 1.30 (s, 9H, CMe_3), 2.31 (s, 6H, 2×Me), 3.53 (s, 1H, NH), 3.90 (br s, 2H, CH_2), 4.13 (br s, 2H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.3 (Me), 28.2 (C*Me*$_3$), 31.0 (NC*Me*$_3$), 35.1 (2×*C*Me$_3$), 55.4 (CH_2), 58.6 (N*C*Me$_3$), 125.4 (C=C), 143.7 (CNH);

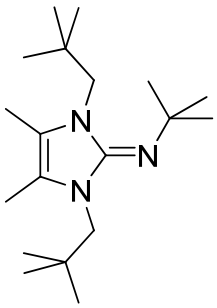
IR (neat): $\tilde{\nu}$ = 851 (w), 1022 (vs), 1043 (vs), 1058 (vs), 1101 (m), 1205 (w), 1367 (m), 1399 (m), 1459 (m), 1478 (m), 1530 (w), 1627 (w), 2877 (w), 2969 (w), 3378 cm^{-1} (w);

ESI (pos.), *m/z* (%): 308 (100) [M$^+$];

HRMS (ESI$^+$), *m/z*: calcd for $C_{19}H_{38}N_3^+$: 308.3060 [M^+]; found: 308.3059;

Elemental analysis calcd (%) for $C_{19}H_{38}BF_4N_3$ (395.33): C 57.72, H 9.69, N 10.63; found: C 57.87, H 9.78, N 10.46.

***N-tert*-Butyl-(4,5-dimethyl-1,3-dineopentyl-1*H*-imidazol-2-ylidene) amine (4f):**



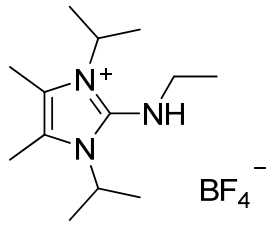
Was synthesized according to **GP7** starting from **4f**$H^+BF_4^-$ (0.67 g, 1.68 mmol).

Yield: 0.45 g (88%) as a pale yellow oil; Compound is sensitive to CO_2 of air;

^{1}H NMR (400 MHz, C_6D_6): δ = 1.00 (s, 18H, 2×CMe_3), 1.55 (s, 9H, CMe_3), 1.65 (s, 6H, 2×Me), 3.43 (br s, 4H, 2×CH_2);

^{13}C NMR (101 MHz, C_6D_6): δ = 10.3 (Me), 29.1 (C*Me*$_3$), 33.2 (NC*Me*$_3$), 35.5 (2×*C*Me_3), 51.9 (N*C*Me_3), 54.2 (CH_2), 116.7 (C=C), 149.8 (CN).

2-(Ethylamino)-1,3-diisopropyl-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate (4g$H^+BF_4^-$):



Was synthesized according to **GP6.1** starting from **11a**$^+BF_4^-$ (2.82 g, 9.3 mmol), $EtNH_2$ (1.26 g, 28.0 mmol), KF (5.23 g, 90.0 mmol) in MeCN (30 mL); Reaction time: 2 d at room temperature.

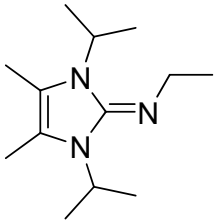
Yield: 2.46 g (85%) as a colorless solid, m.p. 66–68 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (t, ^3J = 7.2 Hz, 3H, Me), 1.55 (d, ^3J = 7.1 Hz, 12H, 2×CH*Me*$_2$), 2.29 (s, 6H, 2×Me), 3.06–3.23 (m, 2H, CH_2), 4.73–4.93 (m, 3H, 2×CH, NH);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.0 (Me), 15.6 (Me), 21.3 (CH*Me*$_2$), 44.4 (CH_2N), 49.9 (*C*HMe_2), 123.2 (C=C), 143.7 (CNH);

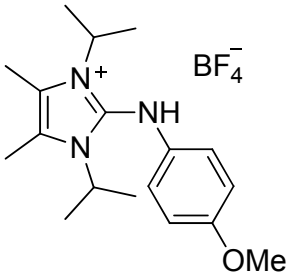
IR (neat): $\tilde{\nu}$ = 1008 (vs), 1054 (vs), 1111 (m), 1215 (w), 1378 (w), 1410 (w), 1462 (w), 1515 (w), 1635 (w), 2882 (w), 2940 (w), 2981 (w), 3344 cm^{-1} (w);
ESI (pos.), *m/z* (%): 224 (100) $[M^+]$, 182 (12) $[M–C_3H_6]^+$;
HRMS (ESI^+), *m/z*: calcd for $C_{13}H_{26}N_3^+$: 224.2121 $[M^+]$; found: 224.2121.

_N_-(1,3-Diisopropyl-4,5-dimethyl-1_H_-imidazol-2-ylidene)ethyl amine (4g):



Was synthesized according to **GP7** starting from **4g**$H^+BF_4^-$ (1.00 g, 3.2 mmol).
Yield: 0.58 g (81%) as a pale yellow oil; Compound is sensitive to CO_2 of air;
^{1}H NMR (400 MHz, C_6D_6): δ = 1.24 (d, ^3J = 7.1 Hz, 12H, 2×Me), 1.46 (t, ^3J = 7.0 Hz, 3H, Me), 1.72 (s, 6H, 2×Me), 3.66 (q, ^3J = 7.0 Hz, 2H, CH_2), 4.41–4.59 (m, 2H, 2×CH);
^{13}C NMR (101 MHz, C_6D_6): δ = 10.9 (Me), 20.5 (Me), 21.3 (CH*Me*$_2$), 44.0 (CH_2N), 46.3 (*C*HMe_2), 115.9 (C=C), 150.2 (CNH).

1,3-Diisopropyl-2-[(4-methoxyphenyl)amino]-4,5-dimethyl-1_H_-imidazolium tetrafluoroborate (4h$H^+BF_4^-$):



Was synthesized according to **GP6.2** starting from **26a**$^+BF_4^-$ (1.72 g, 6.0 mmol) and *p*-anisidine (1.63 g, 13.2 mmol). Reaction time: 3 days at 60 °C; Separation funnel solvent mixture: chloroform / aq. $NaBF_4$ (1.32 g, 12.0 mmol) / 1 M aq. NH_3 (30 mL). After work up, drying and evaporation, a stirring bar and Et_2O (20 ml) were added to the resulting dark oil. After 10 min of stirring the flask was transferred to fridge for crystallization. The crystalline materia was filtered off, dried in high vacuum providing a grey solid product (> 95% by ^{1}H NMR), which may be additionally recrystallized to colorless crystalline product from EtOAc.
Yield: 1.93 (82%) as a grey solid, m.p. 122–123 °C (from EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.48 (d, ^3J = 7.1 Hz, 12H, 2×CH*Me*$_2$), 2.35 (s, 6H, 2×Me), 3.75 (s, 3H, OMe), 4.73 (sept, ^3J = 7.0 Hz, 2H, 2×*CH*Me$_2$), 6.60 (d, ^3J = 9.0 Hz, 2H, 2×CH), 6.80 (d, ^3J = 9.0 Hz, 2H, 2×CH), 7.04 (s, 1H, NH);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.0 (Me), 21.1 (CH*Me*$_2$), 50.8 (*C*HMe$_2$), 55.7 (OMe), 115.3 (CH), 116.0 (CH), 124.8 (C=C), 136.5 (C), 138.1 (C), 154.8 (C);

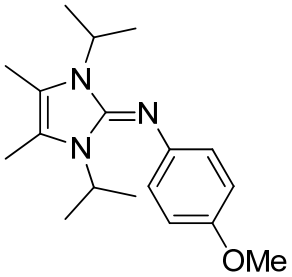
IR (neat): $\tilde{\nu}$ = 727 (m), 819 (s), 1028 (vs), 1058 (vs), 1242 (s), 1373 (m), 1454 (m), 1470 (m), 1511 (vs), 1547 (w), 1631 (w), 2945 (w), 2978 (w), 3330 cm^{-1} (w);

ESI (pos.), *m/z* (%): 302 (100) [M$^+$];

HRMS (ESI$^+$), *m/z*: calcd for $C_{18}H_{28}ON_3^+$: 302.2227 [M$^+$]; found: 302.2225;

Elemental analysis calcd (%) for $C_{18}H_{28}BF_4N_3O$ (389.24): C 55.54, H 7.25, N 10.80; found: C 55.38, H 7.35, N 10.69.

_N_-(1,3-Diisopropyl-4,5-dimethyl-1_H_-imidazol-2-ylidene)-4-methoxyaniline (4h):



Was synthesized according to **GP7** starting from **4h**H$^+$BF$_4^-$ (0.83 g, 2.24 mmol).

Yield: 0.61 g (90%) as a colorless crystalline compound;

^{1}H NMR (400 MHz, C_6D_6): δ = 1.14 (d, ^3J = 7.1 Hz, 12H, 2×CH*Me*$_2$), 1.65 (s, 6H, 2×Me), 3.46 (s, 3H, OMe), 4.55–4.76 (m, 2H, 2×*CH*Me$_2$), 6.89–6.97 (m, 2H, 2×CH), 7.06–7.13 (m, 2H, 2×CH);

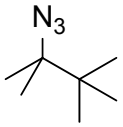
^{13}C NMR (101 MHz, C_6D_6): δ = 10.3 (Me), 20.9 (CH*Me*$_2$), 46.5 (*C*HMe$_2$), 55.4 (OMe), 115.3 (CH), 116.6 (C=C), 120.7 (CH), 147.6 (C), 148.6 (C), 152.6 (C);

IR (hexane): $\tilde{\nu}$ = 1502 (vs), 1570 (m), 1598 (vs), 1612 (s), 1671 cm^{-1} (w);

CI (pos.), *m/z* (%): 259 (15) [M–C_3H_6]$^{+\cdot}$, 260 (20) [M+H–C_3H_6]$^+$, 286 (100) [M–CH_3]$^+$, 301 (47) [M]$^{+\cdot}$, 302 (70) [M+H]$^+$;

HRMS (CI$^+$), *m/z*: calcd for $C_{18}H_{28}N_3O^+$: 302.2232 [M+H]$^+$; found: 302.2233.

2-Azido-2,3,3-trimethylbutane:[127]

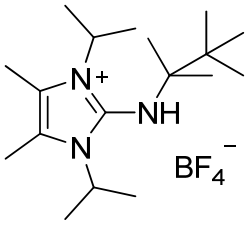


Was prepared starting from 2,3,3-trimethylbutan-2-ol analogously to *tert*-butyl azide preparation,[83] reaction time 3 days with continuous stirring, yield 93%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (s, 9H), 1.28 (s, 6H);

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 22.0 (Me), 25.7 (Me), 37.9 (C), 67.4 (C);

1,3-Diisopropyl-4,5-dimethyl-2-[(2,3,3-trimethylbut-2-yl)amino]-1*H*-imidazolium tetrafluoroborate (4iH$^+$BF$_4^-$):



Was synthesized according to **GP6.2** starting from 2-fluoroimidazolium salt **26a**$^+$$BF_4^-$ (1.72 g, 6.0 mmol), *t*HeptNH_2 (2.07 g, 18.0 mmol) in MeCN (6 mL); The reaction mixture was stirred at 45 °C for 7 d and at 65 °C for 2 d. Washing with a mixture of a 3 M aq. solution of $NaBF_4$ (20 mL) and 13 M aq. NH_3 (5 mL) was used for work up.

Yield: 1.60 g (70%) as a colorless solid, m.p. 222–223 °C (from EtOAc / MeOH, 9:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 (s, 6H, CMe_2), 1.13 (s, 9H, CMe_3), 1.54 (d, ^3J = 7.1 Hz, 12H, 2×CH*Me*$_2$), 2.33 (s, 6H, 2×Me), 4.29 (s, 1H, NH), 5.00 (sept, ^3J = 7.0 Hz, 2H, 2×CH);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.4 (Me), 21.2 (CH*Me*$_2$), 24.0, 25.7, 38.3, 50.0, 63.6 (*t*Heptyl and *C*HMe_2), 124.6 (C=C), 141.7 (CNH);

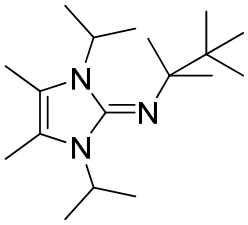
IR (neat): $\tilde{\nu}$ = 1034 (vs), 1053 (vs), 1145 (m), 1209 (w), 1375 (m), 1472 (m), 1504 (m), 1630 (w), 2956 (w), 2982 (w), 3387 cm^{-1} (w);

ESI (pos.), *m/z* (%): 294 (100) [M$^+$], 196 (12) [M–C_7H_{14}]$^+$;

HRMS (ESI$^+$), *m/z*: calcd for $C_{18}H_{36}N_3^+$: 294.2904 [M$^+$]; found: 294.2904;

Elemental analysis calcd (%) for $C_{18}H_{36}BF_4N_3$ (381.30): C 56.70, H 9.52, N 11.02; found: C 56.73, H 10.02, N 10.90.

***N*-(1,3-Diisopropyl-4,5-dimethyl-1*H*-imidazol-2-ylidene)-2,3,3-trimethylbut-2-yl amine (4i):**



Was synthesized according to **GP7** starting from **4i**$H^+BF_4^-$ (0.71 g, 1.87 mmol).

Yield: 0.49 g (89%) as a colorless solid; Compound is sensitive to CO_2 of air;

^{1}H NMR (400 MHz, C_6D_6): δ = 1.16 (d, ^3J = 7.1 Hz, 12H, 2×CH*Me*$_2$), 1.30 (s, 9H, CMe_3), 1.45 (s, 6H, CMe_2), 1.75 (s, 6H, 2×Me), 4.84 (sept, ^3J = 7.1 Hz, 2H, 2×CH);

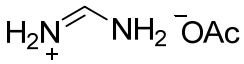
^{13}C NMR (101 MHz, C_6D_6): δ = 11.3 (Me), 21.4 (CH*Me*$_2$), 24.3, 26.7, 41.5, 46.7, 58.5 (*t*Heptyl and *C*HMe_2), 116.4 (C=C), 146.5 (CN);

IR (hexane): $\tilde{\nu}$ = 1634 (vs), 1680 (m), 1696 cm^{-1} (w);

CI (pos.), *m/z* (%): 194 (15) $[M–C_7H_{15}]^+$, 196 (22) $[M+H–C_7H_{14}]^+$, 236 (100) $[M–C_4H_9]^+$, 278 (53) $[M–CH_3]^+$, 292 (20) $[M–H]^+$, 294 (80) $[M+H]^+$;

HRMS (CI^+), *m/z*: calcd for $C_{18}H_{36}N_3^+$: 294.2909; found: 294.2906.

Aminomethaniminium acetate:

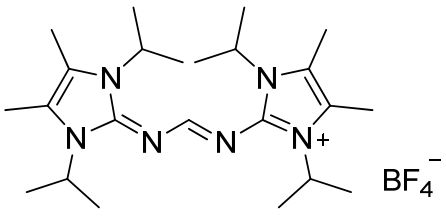


Was prepared in 52% yield (3.5 g) according to literature procedure.[108]

^{1}H NMR (400 MHz, CD_3OD): δ = 3.46 (s, 3H, Me), 6.97 (s, 4H, 2×NH_2), 9.38 (s, 1H, CH);

^{13}C NMR (101 MHz, CD_3OD): δ = 24.3 (Me), 158.9 (CH), 180.7 (C=O).

2-[(1,3-Diisopropyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylideneamino)methyleneamino]-1,3-diisopropyl-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate (5a$^+$BF$_4^-$):



To cold MeOH (20 mL) was added AcCl (1.57 g, 20.0 mmol) dropwise at 5 ºC. After 10 min of stirring at 5 ºC, formamidinium acetate (0.42 g, 4.0 mmol) was added and the reaction

mixture was warmed to room temperature. The solvent was evaporated, the residue was diluted with EtOAc (2 mL), evaporated and dried in high vacuum. In the second flask KF (3.70 g, 64.0 mmol) was prepared as described in **GP6.1**, and after cooling it was added to the first flask containing formamidinium chloride and **11a**$^{+}BF_4^{-}$ (2.42 g, 8.0 mmol) in MeCN (12 mL). After 2 d of stirring at room temperature the reaction mixture was worked up according to **GP6.1**. After drying, the residue was dissolved in EtOAc (20 mL), the solid product was precipitated by addition of Et_2O (10 mL) with stirring, filtered and dried in vacuum.

Yield: 1.54 g (79%) as cream-colored crystalline compound, m.p. 113–114 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.50 (d, ^3J = 7.1 Hz, 24H, 4×CH*Me*$_2$), 2.27 (s, 12H, 4×Me), 4.52 (sept, ^3J = 7.1 Hz, 4H, 4×*CH*Me$_2$), 7.64 (s, 1H, CH);

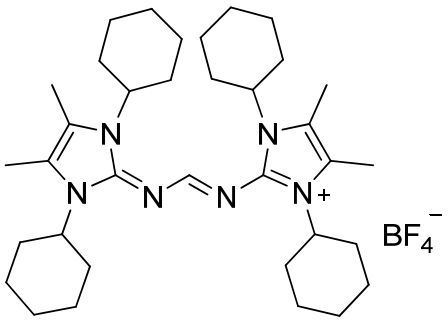
^{13}C NMR (101 MHz, $CDCl_3$): δ = 9.7 (Me), 21.1 (CH*Me*$_2$), 48.6 (*C*HMe$_2$), 121.1 (C=C), 147.9 (CN), 160.2 (CH);

IR (neat): $\tilde{\nu}$ = 910 (w), 993 (m), 1033 (vs), 1048 (vs), 1092 (m), 1209 (w), 1286 (w), 1374 (m), 1436 (s), 1469 (s), 1491 (s), 1537 (m), 1587 (m), 2881 (w), 2942 (w), 2978 cm^{-1} (w);

ESI (pos.), *m/z* (%): 401 (100) [M$^+$];

HRMS (ESI$^+$), *m/z*: calcd for $C_{23}H_{41}N_6^+$: 401.3387 [M$^+$]; found: 401.3388.

1,3-Dicyclohexyl-2-[(1,3-dicyclohexyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylideneamino)methyleneamino]-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate (5b$^{+}BF_4^{-}$):



The compound was prepared according to the procedure described above for **5a**$^{+}BF_4^{-}$ starting from formamidinium acetate (0.21 g, 2.0 mmol), KF (1.90 g, 32.0 mmol) and **11c**$^{+}BF_4^{-}$ (1.53 g, 4.0 mmol) in MeCN (6 mL). Complete conversion of starting material was observed after stirring at room temperature for 24 h.

Yield 1.08 g (83%) as a pale yellow solid, m.p. 110 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09–1.42 (m, 12H, 6×CH_2), 1.61–2.12 (m, 28H, 14×CH_2), 2.28 (s, 12H, 4×Me), 3.96–4.15 (m, 4H, 4×CH), 7.72 (s, 1H, CH);

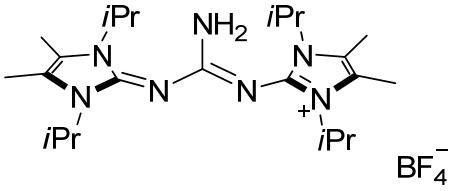
^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.4 (Me), 25.1 (CH_2), 26.2 (CH_2), 31.4 (CH_2), 57.4 (CH), 121.4 (C=C), 148.5 (CN), 160.4 (CH);

IR (neat): $\tilde{\nu}$ = 895 (m), 1033 (vs), 1051 (vs), 1345 (m), 1380 (s), 1438 (s), 1492 (vs), 1540 (m), 1569 (m), 2856 (w), 2930 cm^{-1} (m);

ESI (pos.), *m/z* (%): 561 (100) [M^+];

HRMS (ESI$^+$), *m/z*: calcd for $C_{35}H_{57}N_6^+$: 561.4639 [M^+]; found: 561.4638.

2-[Amino(1,3-diisopropyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylideneamino)methyleneamino]-1,3-diisopropyl-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate (6aH$^+$BF$_4^-$):



Was prepared according to **GP8** using KF (2.80 g, 48.0 mmol), 2-chloroimidazolium salt **11a**$^+$$BF_4^-$ (1.82 g, 6.0 mmol) and guanidinium chloride (0.29 g, 3.0 mmol) in MeCN (9 mL), $NaBF_4$ (3.30 g, 30.0 mmol); Reaction time: 2 d at room temperature.

Yield: 1.33 g (88%) as cream-colored crystalline compound, m.p. 192–193 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.48 (d, ^3J = 7.1 Hz, 24H, 4×CH*Me*$_2$), 2.23 (s, 12H, 4×Me), 4.56 (sept, ^3J = 7.1 Hz, 4H, 4×CH), 4.83 (s, 2H, NH_2);

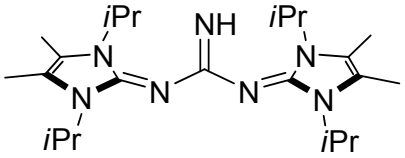
^{13}C NMR (101 MHz, $CDCl_3$): δ = 9.8 (Me), 21.1 (CH*Me*$_2$), 48.1 (*C*HMe$_2$), 120.6 (C=C), 146.8 (CN), 158.4 (C–NH_2);

IR (neat): $\tilde{\nu}$ = 721 (w), 771 (w), 912 (w), 1024 (vs), 1053 (vs), 1101 (m), 1199 (w), 1220 (w), 1368 (s), 1386 (m), 1422 (vs), 1499 (vs), 1557 (m), 1644 (w), 2938 (w), 2977 (w), 3154 (w), 3311 (w), 3420 cm^{-1} (w);

ESI (pos.), *m/z* (%): 416 (100) [M^+];

HRMS (ESI$^+$), *m/z*: calcd for $C_{23}H_{42}N_7^+$: 416.3496 [M^+]; found: 416.3494.

1,3-Bis(1,3-diisopropyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylidene)guanidine (6a):



Was prepared according to **GP9** starting from **6a**$H^+BF_4^-$ (0.50 g, 1.0 mmol).

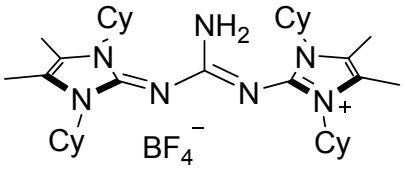
Yield: 0.39 g (94%) as colorless crystals; Compound is sensitive to CO_2 of air;

^{1}H NMR (400 MHz, DMSO-d6): δ = 1.31 (d, ^3J = 7.1 Hz, 24H, 4×CH*Me*$_2$), 2.08 (s, 12H, 4×Me), 4.64 (sept, ^3J = 7.1 Hz, 4H, 4×CH);

^{1}H NMR (400 MHz, C_6D_6): δ = 1.36 (d, ^3J = 7.1 Hz, 24H, 4×CH*Me*$_2$), 1.76 (s, 12H, 4×Me), 5.10 (sept, ^3J = 7.0 Hz, 4H, 2×CH), 5.65 (s, 1H, NH);

^{13}C NMR (101 MHz, C_6D_6): δ = 10.1 (Me), 21.5 (CH*Me*$_2$), 46.8 (*C*HMe$_2$), 116.6 (C=C), 149.7 (CN), 166.9 (CN).

2-[Amino(1,3-dicyclohexyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylideneamino)methyleneamino]-1,3-dicyclohexyl-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate (6b$H^+BF_4^-$):



Was prepared according to **GP8** starting from 2-chloroimidazolium salt **11c**$^+BF_4^-$ (1.53 g, 4.0 mmol) and guanidinium chloride (0.19 g, 2.0 mmol); Reaction time: 2 d at room temperature.

Yield: 0.98 g (74%) as cream-colored crystalline compound, m.p. 170–172 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07–1.41 (m, 14H, 7×CH_2), 1.63–1.72 (m, 4H, 2×CH_2), 1.81–1.98 (m, 22H, 11×CH_2), 2.21 (s, 12H, 4×Me), 4.07 (br s, 4H, 4×NCH), 5.00 (br s, 2H, NH_2);

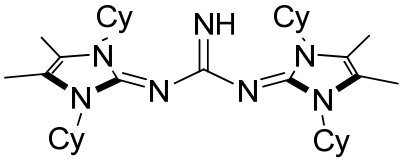
^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.3 (Me), 25.0 (CH_2), 26.1 (CH_2), 30.8 (CH_2), 57.3 (CH), 121.5 (C=C), 126.2 (CN), 157.3 (CN);

IR (neat): $\tilde{\nu}$ = 894 (m), 1020 (vs), 1057 (vs), 1347 (m), 1419 (vs), 1437 (vs), 1488 (vs), 1558 (m), 1638 (w), 2857 (w), 2930 (m), 3184 (w), 3415 cm^{-1} (w);

ESI (pos.), *m/z* (%): 576.5 (100) [M$^+$];

HRMS (ESI$^+$), *m/z*: calcd for $C_{35}H_{58}N_7^+$: 576.4748 [M$^+$]; found: 576.4747.

1,3-Bis(1,3-dicyclohexyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylidene)guanidine (6b):



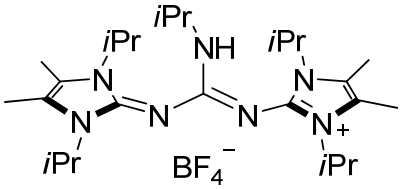
Was prepared according to **GP9** starting from **6b**$H^+BF_4^-$ (0.33 g, 0.5 mmol).

Yield: 0.21 g (75%) as pale yellow viscous oil; Compound is sensitive to CO_2 of air;

^{1}H NMR (400 MHz, C_6D_6): δ = 1.03–1.25 (m, 4H, 4×C*H*H), 1.33–1.53 (m, 8H, 4×CH_2), 1.54–1.67 (m, 4H, 4×CH*H*), 1.69-2.27 (m, 24H, 12×CH_2), 1.81 (s, 12H, 4×Me), 4.53 (br s, 4H, 4×NCH), 5.10 (br s, 1H, NH);

^{13}C NMR (101 MHz, C_6D_6): δ = 10.4 (Me), 26.2 (CH_2), 27.2 (CH_2), 31.6 (CH_2), 55.7 (CH), 116.8 (C=C), 150.4 (CN), 168.5 (CN).

2-[(1,3-Diisopropyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylideneamino)(isopropylamino)methyleneamino]-1,3-diisopropyl-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate (6c$H^+BF_4^-$):



Was prepared according to **GP8** starting from **11a**$^+BF_4^-$ (1.21 g, 4.0 mmol) and guanidinium iodide **41** (0.46 g, 2.0 mmol); Reaction time: 2 d at 40 °C and 1 d at 60 °C.

Yield: 0.74 g (68%) as cream-colored crystalline compound, m.p. 191–192 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21 (d, ^3J = 6.1 Hz, 6H, CH*Me*$_2$), 1.48 (d, ^3J = 7.1 Hz, 24H, 4×CH*Me*$_2$), 2.23 (s, 12H, 4×Me), 4.01–4.19 (m, 2H, CH and NH), 4.52 (sept, ^3J = 7.1 Hz, 4H, 4×CH);

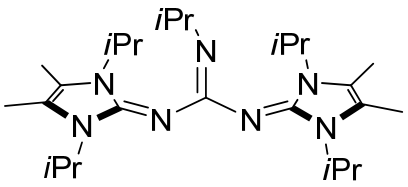
^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.0 (Me), 21.3 (CH*Me*$_2$), 23.1 (CH*Me*$_2$), 44.2 (*C*HMe$_2$), 48.0 (*C*HMe$_2$), 120.4 (C=C), 147.8 (CN), 156.7 (CN);

IR (neat): $\tilde{\nu}$ = 713 (m), 770 (w), 954 (w), 1021 (vs), 1056 (vs), 1105 (m), 1175 (w), 1206 (w), 1220 (w), 1373 (s) (w), 1397 (s), 1426 (vs), 1474 (vs), 1509 (s), 1542 (s), 1569 (m), 2939 (w), 2978 (w), 3375 cm^{-1} (w).

ESI (pos.), *m/z* (%): 458 (100) [M^+];

HRMS (ESI$^+$), *m/z*: calcd for $C_{26}H_{48}N_7^+$: 458.3966 [M^+]; found: 458.3965.

1,3-Bis(1,3-diisopropyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylidene)-2-isopropylguanidine (6c):



Was prepared according to **GP9** starting from **6c**$H^+BF_4^-$ (0.125 g, 0.23 mmol).

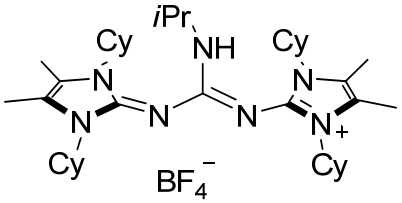
Yield: 87 mg (83%) as pale yellow viscous oil; Compound is sensitive to CO_2 of air;

^{1}H NMR (400 MHz, C_6D_6): δ = 1.34 (d, ^3J = 6.0 Hz, 12H, 2×CH*Me*$_2$), 1.36 (d, ^3J = 6.0 Hz, 12H, 2×CH*Me*$_2$), 1.65 (d, ^3J = 6.3 Hz, 6H, CH*Me*$_2$), 1.72 (s, 6H, 2×Me), 1.74 (s, 6H, 2×Me), 4.61 (sept, ^3J = 6.3 Hz, 1H, CH), 4.80–5.00 (m, 2H, 2×CH), 5.00–5.20 (m, 2H, 2×CH);

^{1}H NMR (400 MHz, DMSO-d6): δ = 0.94 (d, ^3J = 6.2 Hz, 6H, CH*Me*$_2$), 1.25 (d, ^3J = 7.0 Hz, 12H, 2×CH*Me*$_2$), 1.29 (d, ^3J = 6.8 Hz, 12H, 2×CH*Me*$_2$), 2.04 (s, 12H, 4×Me), 3.73 (sept, ^3J = 6.3 Hz, 1H, CH), 4.57 (sept, ^3J = 7.0 Hz, 2H, 2×CH), 4.73 (sept, ^3J = 6.8 Hz, 2H, 2×CH);

^{13}C NMR (101 MHz, DMSO-d6): δ = 9.8 (Me), 20.9/21.0 (CH*Me*$_2$), 25.1 (CH*Me*$_2$), 45.3/45.4 (*C*HMe$_2$), 47.1 (*C*HMe$_2$), 115.7/115.8 (C=C), 147.4/148.0 (CN), 157.4 (CN).

1,3-Dicyclohexyl-2-[(1,3-dicyclohexyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylideneamino)(isopropylamino)methyleneamino]-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate (6d$H^+BF_4^-$):



Was prepared according to **GP8** starting from **11c**$^+BF_4^-$ (1.53 g, 4.0 mmol) and guanidinium iodide **41** (0.46 g, 2.0 mmol); Reaction time: 2 d at 40 °C and 1 d at 60 °C.

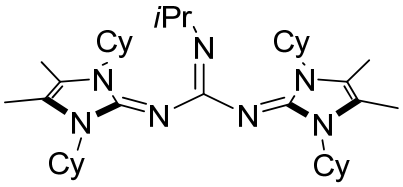
Yield: 0.86 g (61%) as cream-colored crystalline compound, m.p. 217–218 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (d, ^3J = 6.2 Hz, 6H, CH*Me*$_2$), 1.04–1.42 (m, 12H, 6×CH_2), 1.65–2.00 (m, 28H, 14×CH_2), 2.26 (s, 12H, 4×Me), 4.01–4.29 (m, 6H, 4×CH, C*H*Me$_2$ and NH);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.8 (Me), 23.3 (CH*Me*$_2$), 25.3 (CH_2), 26.3 (CH_2), 31.1 (CH_2), 44.4 (*C*HMe$_2$), 56.8 (CH), 120.8 (C=C), 148.0 (CN), 155.9 (CN);

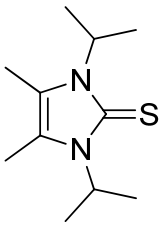
IR (neat): $\tilde{\nu}$ = 894 (w), 992 (m), 1022 (vs), 1056 (vs), 1193 (w), 1357 (m), 1385 (m), 1398 (s), 1416 (vs), 1474 (vs), 1502 (m), 1540 (s), 1576 (m), 2856 (w), 2932 (m), 3371 cm^{-1} (w);
ESI (pos.), *m/z* (%): 618 (100) [M^+];
HRMS (ESI$^+$), *m/z*: calcd for $C_{38}H_{64}N_7^+$: 618.5218 [M^+]; found: 618.5214.

1,3-Bis(1,3-dicyclohexyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylidene)-2-isopropylguanidine (6d):



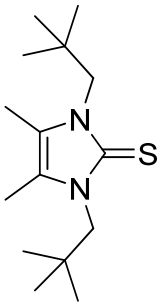
Was prepared according to **GP9** starting from **6d**$H^+BF_4^-$ (0.706 g, 1.0 mmol).
Yield: 0.587 g (95%) as colorless crystals (74% after recrystallization from hexane); Compound is sensitive to CO_2 of air;
^{1}H NMR (400 MHz, C_6D_6): δ = 0.93–1.18 (m, 4H, 2×CH_2), 1.39–1.56 (m, 8H, 4×CH_2), 1.56–1.94 (m, 20H, 10×CH_2), 1.66 (d, ^3J = 6.3 Hz, 6H, CH*Me*$_2$), 1.76 (s, 6H, 2×Me), 1.85 (s, 6H, 2×Me), 1.94–2.17 (m, 8H, 4×CH_2), 4.31–4.55 (m, 2H, CH and C*H*Me$_2$), 4.55–4.92 (m, 3H, 3×CH);
^{13}C NMR (101 MHz, C_6D_6): δ = 10.7/11.2 (Me), 25.8 (CH*Me*$_2$), 26.2 (CH_2), 27.0 (CH_2), 31.8 (CH_2), 48.6 (*C*HMe$_2$), 54.6/55.3 (CH), 116.9 (C=C), 149.0 (CN), 159.4 (CN).

1,3-Diisopropyl-4,5-dimethyl-1*H*-imidazole-2(3*H*)-thione (9a):



Was prepared according to **GP1** starting from **8a** (16.03 g, 100.0 mmol), work up: The reaction mixture was slowly cooled with stirring while in the oil bath overnight to give white crystals. After further cooling to –20 °C the precipitate was filtered off, washed a few times with cold methanol (–20 °C), collected and dried in high vacuum furnishing pure product **9a** (18.05 g, 85%) as colorless crystals. ^{1}H and ^{13}C NMR data of **9a** were in good agreement with those reported in the literature.[66]

1,3-Dineopentyl-4,5-dimethyl-1*H*-imidazole-2(3*H*)-thione (9b):[128]



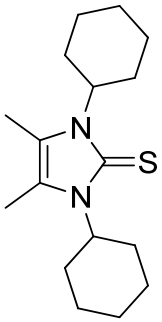
Was prepared according to **GP1** starting from **8b** (21.64 g, 100.0 mmol), work up: The reaction mixture was cooled to ambient temperature, the solvent was evaporated in vacuum, and the residual oil was distilled in high vacuum (165 °C / 0.3 mbar) to give the title product.

Yield: 21.48 g (80%) as a pale yellow solid;

^{1}H NMR (400 MHz, C_6D_6): δ = 1.01 (s, 18H, 2×CMe_3), 1.60 (s, 6H, 2×Me), 4.75 (br s, 2×NCH_2, reduced intensity due to very strong broadening);

^{13}C NMR (101 MHz, C_6D_6): δ = 10.4 (Me), 29.3 (C*Me*$_3$), 35.2 (*C*Me_3), 54.9 (NCH_2), 121.1 (C=C), 167.6 (C=S);

1,3-Dicyclohexyl-4,5-dimethyl-1*H*-imidazole-2(3*H*)-thione (9c):



Was prepared according to **GP1** starting from **8c** (24.04 g, 100.0 mmol), work up: The reaction mixture was cooled to ambient temperature, the solvent was evaporated in vacuum, and the residual oil was dried in high vacuum (150 °C / 0.05 mbar) for 2 h to give the product **9c**.

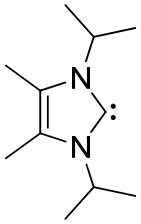
Yield: 28.08 g (96%) as a tawny glass;

^{1}H NMR (400 MHz, C_6D_6): δ = 0.76–1.09 (m, 2H, CH_2), 1.16–1.68 (m, 14H, 7×CH_2), 1.68–2.00 (m, 4H, 2×CH_2), 1.78 (s, 6H, 2×Me), 5.86 (br s, 2H, 2×NCH);

^{13}C NMR (101 MHz, C_6D_6): δ = 10.6 (Me), 25.9 (CH_2), 26.6 (CH_2), 31.4 (CH_2), 58.0 (NCH), 120.8 (C=C), 164.1 (C=S);

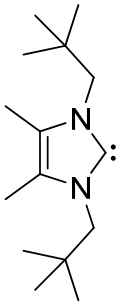
IR (neat): $\tilde{\nu}$ = 894 (m), 990 (m), 1004 (m), 1078 (m), 1141 (w), 1240 (s), 1261 (m), 1318 (s), 1363 (vs), 1413 (m), 1447 (m), 1531 (w), 1639 (w), 2852 (s), 2924 (s), 3285 cm^{-1} (w);
EI (70 eV), *m/z* (%): 292 (100) [$M^{+\bullet}$], 210 (57) [$M–C_6H_{10}]^+$, 128 (24) [$M–2C_6H_{10}]^+$;
HRMS (EI), *m/z*: calcd for $C_{17}H_{28}N_2S^+$: 292.1973 [$M^{+\bullet}$]; found: 292.1966;

1,3-Diisopropyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylidene (10a):



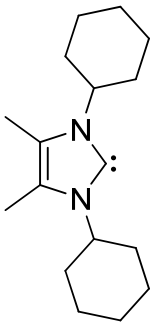
Was prepared according to **GP2**; ^{1}H and ^{13}C NMR data of **10a** were in good agreement with those reported in the literature.[66]

1,3-Dineopentyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylidene (10b):



Was prepared according to **GP2**.
^{1}H NMR (400 MHz, C_6D_6): δ = 1.00 (s, 18H, 2×CMe_3), 1.76 (s, 6H, 2×Me), 3.69 (s, 4H, 2×NCH_2);
^{13}C NMR (101 MHz, C_6D_6): δ = 10.1 (Me), 28.5 (C*Me*$_3$), 33.5 (*C*Me_3), 58.3 (NCH_2), 122.7 (C=C), 216.8 (C).

1,3-Dicyclohexyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylidene (10c):

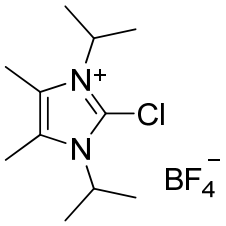


Was prepared according to **GP2**.

^{1}H NMR (400 MHz, C_6D_6): δ = 1.11–1.33 (m, 6H, 3×CH_2), 1.44–1.61 (m, 2H, CH_2), 1.66–1.86 (m, 10H, 2×CH_2 and 2×Me), 1.94–2.10 (m, 4H, 2×CH_2), 2.24–2.47 (m, 4H, 2×CH_2), 3.66 (tt, *J* = 11.6 Hz, *J* = 3.8 Hz, 2H, 2×NCH);

^{13}C NMR (101 MHz, C_6D_6): δ = 8.8 (Me), 26.0 (CH_2), 26.5 (CH_2), 35.5 (CH_2), 58.7 (NCH), 121.5 (C=C), 203.4 (C).

2-Chloro-1,3-diisopropyl-4,5-dimethylimidazolium tetrafluoroborate ($11a^+BF_4^-$):



Was prepared according to **GP3.1** starting from **10a** (15 mmol) in 69% (3.13 g) yield and according to one-pot procedure **GP3.2** starting from **9a** (50 mmol) in 64% (9.68 g) overall yield as colorless crystals, m.p. 156–158 °C (from EtOAc / MeOH, 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.64 (d, ^{3}J = 7.0 Hz, 12H, 2×CH*Me*$_2$), 2.35 (s, 6H, 2×Me), 4.85 (sept, ^{3}J = 7.0 Hz, 2H, 2×NCH);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 9.9 (Me), 20.4 (CH*Me*$_2$), 52.8 (NCH), 126.4 (C–Cl), 128.2 (C=C);

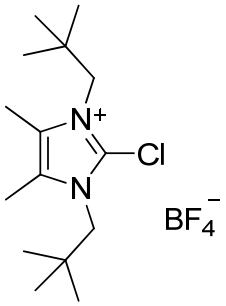
IR (neat): $\tilde{\nu}$ = 899 (w), 1032 (vs), 1044 (vs), 1093 (m), 1377 (w), 1454 (m), 1506 (m), 2953 (w), 2993 cm^{-1} (w);

ESI (pos.), *m/z* (%): 215 (100) [M^+], 173 (13) [$M–C_3H_6$]$^+$;

HRMS (ESI$^+$), *m/z*: calcd for $C_{11}H_{20}{}^{35}ClN_2^+$: 215.1310 [$M^+$]; found: 215.1311;

Elemental analysis calcd (%) for $C_{11}H_{20}BClF_4N_2$ (302.55): C 43.67, H 6.66, N 9.26; found: C 43.77, H 6.69, N 9.12.

2-Chloro-1,3-dineopentyl-4,5-dimethylimidazolium tetrafluoroborate ($11b^+BF_4^-$):



Was prepared according to **GP3.1** starting from **10b** (15 mmol) in 95% yield (5.11 g) as a brownish solid (>95% of purity by ^{1}H NMR) and according to one-pot procedure **GP3.2** starting from **9b** (8.2 g, 30.5 mmol) in 35% overall yield (3.83 g) as colorless crystals, m.p. 130–132 °C (from EtOAc).

^{1}H NMR (400 MHz, CD_3CN): δ = 1.04 (s, 18H, 2×CMe_3), 2.30 (s, 6H, 2×Me), 4.00 (s, 4H, 2×NCH_2);

^{13}C NMR (101 MHz, CD_3CN): δ = 10.8 (Me), 28.1 (C*Me*$_3$), 35.5 (*C*Me_3), 57.6 (CH_2), 130.3 (C=C), 131.6 (C–Cl);

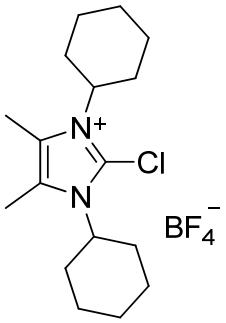
IR (neat): $\tilde{\nu}$ = 1034 (vs), 1048 (vs), 1101 (m), 1372 (w), 1484 (w), 1506 (w), 2876 (w), 2953 cm^{-1} (w);

ESI (pos.), *m/z* (%): 271 (100) [M^+];

HRMS (ESI^+), *m/z*: calcd for $C_{15}H_{28}{}^{35}ClN_2^+$: 271.1936 [$M^+$]; found: 271.1936;

Elemental analysis calcd (%) for $C_{15}H_{28}BClF_4N_2$ (358.65): C 50.23, H 7.87, N 7.81; found: C 50.50, H 7.95, N 7.67.

2-Chloro-1,3-dicyclohexyl-4,5-dimethylimidazolium tetrafluoroborate ($11c^+BF_4^-$):



Was prepared according to **GP3.1** starting from **10c**.

Yield: 3.73 g (65%) as colorless crystals, m.p. 102–104 °C (from EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14–1.33 (m, 2H, CH_2), 1.35–1.54 (m, 4H, 2×CH_2), 1.69–1.82 (m, 2H, CH_2), 1.86–2.16 (m, 12H, 6×CH_2), 2.36 (s, 6H, 2×Me), 4.25–4.46 (m, 2H, 2×NCH);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.3 (Me), 24.8 (CH_2), 25.8 (CH_2), 30.2 (CH_2), 61.0 (NCH), 126.6 (C–Cl), 128.4 (C=C);

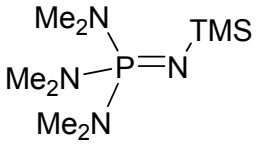
IR (neat): $\tilde{\nu}$ = 1026 (vs), 1070 (vs), 1094 (s), 1443 (m), 1496 (w), 2860 (w), 2938 cm^{-1} (w);

ESI (pos.), *m/z* (%): 295 (100) [M^+];

HRMS (ESI^+), *m/z*: calcd for $C_{17}H_{28}{}^{35}ClN_2^+$: 295.1936 [$M^+$]; found: 295.1936;

Elemental analysis calcd (%) for $C_{17}H_{28}BClF_4N_2$ (382.68): C 53.36, H 7.38, N 7.32; found: C 53.49, H 7.39, N 7.20.

Trimethylsilylimino tris(dimethylamino)phosphorane (16):[77,78]



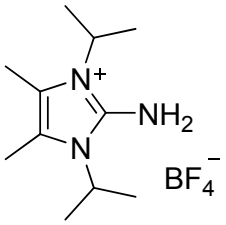
$TMSN_3$ (3.80 g, 33.0 mmol) was added dropwise to $P(NMe_2)_3$ (3.54 g, 21.0 mmol), after 4 days of stirring at room temperature, additional amount of $TMSN_3$ (1 mL) was added. After 3 days of stirring the reaction mixture was evaporated at room temperature in vacuum (> 0.1 torr), the residue was distilled, fraction with b.p. 61–61 °C (0.15 torr) was collected.

Yield: 4.50 g (86%) as colorless liquid; Compound is very sensitive to hydrolysis;

^{1}H NMR (400 MHz, C_6D_6): δ = 0.37 (s, 9H, $SiMe_3$), 2.41 (d, ^{3}J(H,P) = 10.2 Hz, 18H, 6×Me);

^{13}C NMR (101 MHz, C_6D_6): δ = 4.7 (d, ^{3}J(C,P) = 3.0 Hz, SiMe), 37.3 (d, ^{2}J(C,P) = 3.6 Hz, Me).

2-Amino-1,3-diisopropyl-4,5-dimethylimidazolium tetrafluoroborate (22a$H^+BF_4^-$):



Was prepared according to **GP4** starting from **10a**.

Yield: 3.40 g (80%) as colorless crystals, m.p. 119–122 °C (from Et_2O / EtOAc, 1:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.52 (d, ^3J = 7.0 Hz, 12H, 2×CH*Me*$_2$), 2.18 (s, 6H, 2×Me), 4.52 (sept, ^3J = 7.0 Hz, 2H, 2×NCH), 5.82 (s, 2H, NH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 9.7 (Me), 20.6 (CH*Me*$_2$), 48.5 (NCH), 119.9 (C=C), 143.3 (C-NH_2);

IR (neat): $\tilde{\nu}$ = 1020 (vs), 1514 (s), 1647 (s), 2941 (w), 2987 (w), 3283 (w), 3364 (m), 3445 cm^{-1} (w);

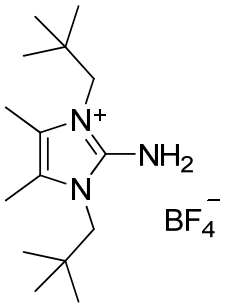
ESI (pos.), *m/z* (%): 196 (100) [M^+];

HRMS (ESI$^+$) *m/z*: calcd for $C_{11}H_{22}N_3^+$: 196.1808 [M^+], found: 196.1808;

Elemental analysis calcd (%) for $C_{11}H_{22}BF_4N_3$ (283.12): C 46.67, H 7.83, N 14.84; found: C 46.81, H 7.88, N 14.69.

Treatment of the sample of **22a**H$^+$ with MeONa in MeOH at room temperature gave quantitatively the conjugated base **22a**, whose NMR data matched those described in the literature.[48]

2-Amino-1,3-dineopentyl-4,5-dimethylimidazolium tetrafluoroborate (22bH$^+$BF$_4^-$):



Was prepared according to **GP4** starting from **10b**.

Yield: 4.07 g (80%) as colorless crystals, m.p. 198–200 °C (from EtOAc / MeOH, 50:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (s, 18H, 2×CMe_3), 2.11 (s, 6H, 2×Me), 3.70 (s, 4H, 2×NCH_2), 6.09 (s, 2H, NH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 9.7 (Me), 28.1 (C*Me*$_3$), 34.9 (*C*Me$_3$), 53.6 (CH_2), 120.3 (C=C), 147.1 (C-NH_2);

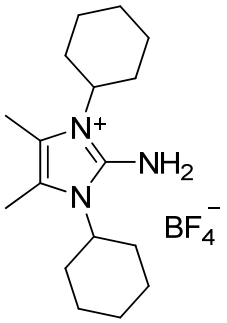
IR (neat): $\tilde{\nu}$ = 1017 (vs), 1036 (vs), 1368 (m), 1482 (m), 1531 (m), 1656 (s), 2959 (w), 3361 (w), 3424 cm^{-1} (w);

ESI (pos.), *m/z* (%): 252 (100) [M^+];

HRMS (ESI$^+$), *m/z*: calcd for $C_{15}H_{30}N_3^+$: 252.2434 [M^+]; found: 252.2434;

Elemental analysis calcd (%) for $C_{15}H_{30}BF_4N_3$ (339.22): C 53.11, H 8.91, N 12.39; found: C 53.25, H 8.97, N 12.27.

2-Amino-1,3-dicyclohexyl-4,5-dimethylimidazolium tetrafluoroborate (22cH$^+$BF$_4^-$):



Was prepared according to **GP4** starting from **10c**.

Yield: 3.54 g (65%) as colorless crystals, m.p. 178–180 °C (from EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14–1.36 (m, 2H, CH_2), 1.41–1.64 (m, 4H, 2×CH_2), 1.65–1.79 (m, 2H, CH_2), 1.79–2.11 (m, 12H, 6×CH_2), 2.20 (s, 6H, 2×Me), 3.94–4.12 (m, 2H, 2×NCH), 5.89 (s, 2H, NH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.1 (Me), 24.8 (CH_2), 25.6 (CH_2), 30.6 (CH_2), 56.8 (NCH), 119.9 (C=C), 143.5 (C-NH_2);

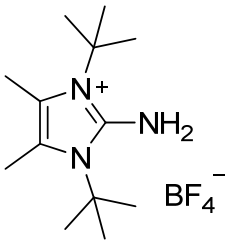
IR (neat): $\tilde{\nu}$ = 1018 (vs), 1451 (w), 1515 (m), 1656 (m), 2862 (w), 2936 (w), 3275 (w), 3352 (w), 3414 cm^{-1} (w);

ESI (pos.), *m/z* (%): 276 (100) [M$^+$];

HRMS (ESI$^+$), *m/z*: calcd for $C_{17}H_{30}N_3^+$: 276.2434 [M$^+$]; found: 276.2434;

Elemental analysis calcd (%) for $C_{17}H_{30}BF_4N_3$ (363.24): C 56.21, H 8.32, N 11.57; found: C 56.18, H 8.41, N 11.33.

2-Amino-1,3-di-*tert*-butyl-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate (22iH$^+$BF$_4^-$):



Was obtained by slightly modified **GP4**: To a solution of **10i** (0.42 g, 2.0 mmol) in benzene (2.5 mL) *tert*-butyl azide (0.40 g, 4.0 mmol) was added at room temperature, and the mixture was stirred at 50 °C for 16 h (NMR monitoring). After evaporation of hexane triazene **23i** was quenched with MeOH (10 mL) (Caution: effervescence due to evolution of N_2 and isobutylene!) followed by addition of NH_4BF_4 (1.06 g, 10.0 mmol). The reaction mixture was

diluted with $CHCl_3$ (15 mL), washed with water (2×5 mL), dried and evaporated under reduced pressure to give after recrystallization the title compound.

Yield: 0.38 g (61%) as a colorless solid, m.p. 144–145 °C (from EtOAc / MeOH, 30:1); An additional amount of **22i**$H^+BF_4^-$ can be obtained by evaporation of the filtrate;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.77 (s, 18H, 2×CMe_3), 2.28 (s, 6H, 2×Me), 5.80 (s, 2H, NH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 13.7 (Me), 30.6 (C*Me*$_3$), 62.1 (*C*Me_3), 122.0 (C=C), 145.7 (NCN);

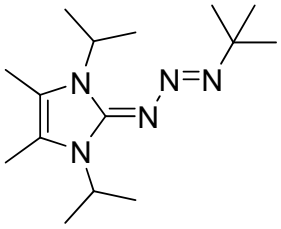
IR (neat): $\tilde{\nu}$ = 1004 (s), 1046 (vs), 1188 (m), 1385 (w), 1458 (w), 1495 (w), 1624 (m), 1642 (m), 2998 (w), 3423 (w), 3512 cm^{-1} (w);

ESI (pos.), *m/z* (%): 224 (100) [M^+];

HRMS (ESI$^+$), *m/z*: calcd for $C_{13}H_{26}N_3$: 224.2121 [M^+]; found: 224.2120;

Elemental analysis calcd (%) for $C_{13}H_{26}BF_4N_3$ (311.17): C 50.18, H 8.42, N 13.50; found: C 50.10, H 8.38, N 13.36.

2-(3-*tert*-Butyltriaz-2-enylidene)-1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazole (23a):

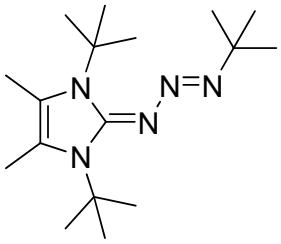


A sample of the intermediate **23a** was obtained from **10a** and *tert*-butyl azide as described in **GP4**, > 99% yield, beige crystalline solid gradually turning dark on exposure to air.

^{1}H NMR (400 MHz, C_6D_6): δ = 1.21 (d, ^3J = 7.2 Hz, 12H, 2×CH*Me*$_2$), 1.49 (s, 9H, CMe_3), 1.63 (s, 6H, 2×Me), 5.13 (br s, 2H, 2×NCH);

^{13}C NMR (101 MHz, C_6D_6): δ = 10.1 (Me), 21.4 (CH*Me*$_2$), 29.4 (C*Me*$_3$), 47.9 (*C*HMe_2), 60.0 (*C*Me_3), 117.8 (C=C), 153.2 (C=N).

1,3-Di-*tert*-butyl-2-(3-*tert*-butyltriaz-2-enylidene)-4,5-dimethyl-2,3-dihydro-1*H*-imidazole (23i):

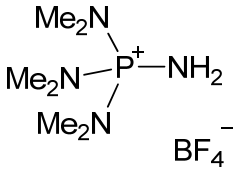


A sample of the intermediate **23i** was obtained in > 99% yield from **10i** and *tert*-butyl azide as described in synthesis of **22i**$H^+BF_4^-$. The title compound was recrystallized from hexane with few drops of triethylamine at –25 °C (colorless solid). Compound is sensitive to CO_2/H_2O of air;

^{1}H NMR (400 MHz, C_6D_6): δ = 1.53 (s, 9H, CMe_3), 1.53 (s, 18H, 2×CMe_3), 1.72 (s, 6H, 2×Me);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 13.9 (Me), 29.8 (C*Me*$_3$), 31.4 (C*Me*$_3$), 60.0 (*C*Me_3), 60.3 (*C*Me_3), 120.4 (C=C), 160.5 (NCN).

Aminotris(dimethylamino)phosphonium tetrafluoroborate (25$H^+BF_4^-$):[8]



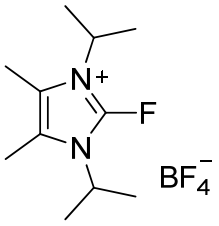
$P(NMe_2)_3$ (7.67 g, 47.0 mmol) was carefully dropwise added to a solution of *tert*-butyl azide (5.52 g, 55.7 mmol) in toluene (5 mL) with vigorous stirring at –20 °C. The reaction mixture was gradually warmed to ambient temperature overnight yielding triazene **24**.[81] The reaction mixture was then cooled to –20 °C, and CF_3CO_2H (8.04 g, 70.5 mmol) was added dropwise over a period of 10 min. The cooling bath was removed, and the reaction mixture was stirred for additional 15 min. After aqueous work up as described in **GP3.1**, pure product was isolated as a colorless crystalline solid (11.4 g, 91% yield). The spectral data of **25**$H^+BF_4^-$ were in good agreement with those reported in the literature.[8]

IR (neat): $\tilde{\nu}$ = 740 (m), 760 (m), 950 (s), 991 (vs), 1048 (s), 1175 (m), 1313 (m), 1460 (w), 1567 (w), 2917 (w), 3320 (w), 3405 cm^{-1} (w);

ESI (pos.), *m/z* (%): 179 (100) [M^+];

HRMS (ESI^+), *m/z*: calcd for $C_6H_{20}N_4P^+$: 179.1420 [M^+]; found: 179.1420.

2-Fluoro-1,3-diisopropyl-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate (26a$^+$BF$_4^-$):[73]



Synthesis from **11a**$^+$BF$_4^-$ (9.08 g, 30 mmol) according to **GP4** in the absence of amines. Reaction time: 3 d at room temperature. The crude solid should be crystallized from EtOAc as soon as possible, because of slow decomposition. Recrystallized **26a**$^+$BF$_4^-$ can be stored at ambient temperature in a closed vessel.

Yield: 6.79 g (79%) as cream-colored solid, m.p. 129–130 °C (from EtOAc);

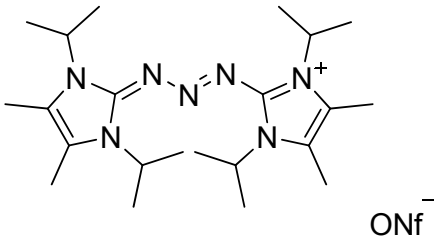
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.60 (dd, ^3J = 6.9 Hz, ^5J(H,F) = 1.8 Hz, 12H, 2×CH*Me*$_2$), 2.24 (d, ^5J(H,F) = 0.5 Hz, 6H, 2×Me), 4.54 (sept, ^3J = 6.9 Hz, 2H, 2×NCH);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 8.8 (Me), 21.0 (d, ^4J(C,F) = 2.4 Hz, CH*Me*$_2$), 51.4 (*C*HMe$_2$), 121.4 (d, ^3J(C,F) = 4.1 Hz, C=C), 143.1 (d, ^1J(C,F) = 284.2 Hz, C-F);

ESI (pos.), *m/z* (%): 199 (100) [M$^+$], 157 (64) [M–C_3H_6]$^+$;

HRMS (ESI$^+$), *m/z*: calcd for $C_{11}H_{20}N_2F^+$: 199.1605 [M$^+$]; found: 199.1605.

2-[(1,3-Diisopropyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylidene)triaz-1-enyl]-1,3-diisopropyl-4,5-dimethyl-1*H*-imidazolium nonaflate (29a$^+$ONf$^-$):



Solid carbene **10a** (1.46 g, 8.13 mmol) prepared in a Schlenk tube by evaporation of a stock hexane solution was dissolved in THF (18 mL), and the solution was cooled to –78 °C. NfN_3 (1.32 g, 4.07 mmol) was added dropwise and the reaction mixture was warmed slowly to room temperature overnight with stirring. The solvent was evaporated in vacuum and the residue was dried in high vacuum to give **29a**$^+$Nf$^-$. MeOH (4.5 mL) and 30% aq. H_2O_2 (2 mL) were added. After 5 d of stirring at room temperature, completion of Nf$^-$ oxidation to ONf$^-$ was checked by ^{19}F NMR. The solvent was carefully evaporated in vacuum (protective

shield!), diglyme (5 mL) was added and evaporated with stirring in high vacuum at 40 °C overnight resulting in **29a**$^{+}$ONf^{-}.

Yield: 2.71 g (95%) as orange oil;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (d, ^{3}J = 7.1 Hz, 24H, 4×CH*Me*$_2$), 2.28 (s, 12H, 4×Me), 4.69 (sept, ^{3}J = 7.0 Hz, 4H, 4×NCH);

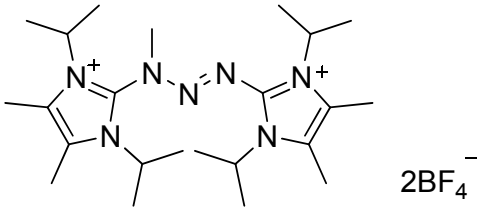
^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.0 (Me), 21.5 (CH*Me*$_2$), 21.6 (CH*Me*$_2$), 49.6 (*C*HMe$_2$), 123.0 (C=), 148.3 (CN), signals of ONf^{-} were not observed;

IR (neat): $\tilde{\nu}$ = 1049 (s), 1130 (s), 1207 (vs), 1232 (vs), 1254 (vs), 1318 (m), 1449 (w), 1501 (w), 1639 (w), 1706 (w), 2940 (w), 2981 cm^{-1} (w);

ESI (pos.), *m/z* (%): 402 (100) [M^{+}];

HRMS (ESI^{+}), *m/z*: calcd for $C_{22}H_{40}N_7^{+}$: 402.3340 [M^{+}]; found: 402.3340.

2,2'-(3-Methyltriaz-1-ene-1,3-diyl)bis(1,3-diisopropyl-4,5-dimethyl-1*H*-imidazolium) ditetrafluoroborate (30^{2+}(BF$_4^{-}$)$_2$):



Compound **29a**$^{+}$Nf^{-} (2.35 g, 3.4 mmol) and MeI (1.42 g, 10.0 mmol) were heated in MeCN (3.5 mL) at 70 °C for 3 days. The solvent was evaporated, NMP (3 mL) was added and the mixture was evaporated and dried in high vacuum (10^{-2} torr) at 60 °C overnight. Dichloromethane (35 mL) was added to the residue, and the two-phase mixture was shaken vigorously with diluted aq. $NaBF_4$ (2×35 mmol). The combined aqueous layers were washed with CH_2Cl_2 (10 mL). The combined organic layers were dried, concentrated to 5 mL, and the title compound was precipitated by addition of an excess of EtOAc.

Yield: 1.32 g (65%) as a colorless solid; m.p. 217–219 °C;

^{1}H NMR (400 MHz, CD_3CN): δ = 1.36–1.61 (m, 24H, 2×CH*Me*$_2$), 2.35 (s, 6H, 2×Me), 2.40 (s, 6H, 2×Me), 3.71 (s, 3H, NMe), 4.46–4.67 (m, 2H, 2×CH), 4.74–4.97 (m, 2H, 2×CH);

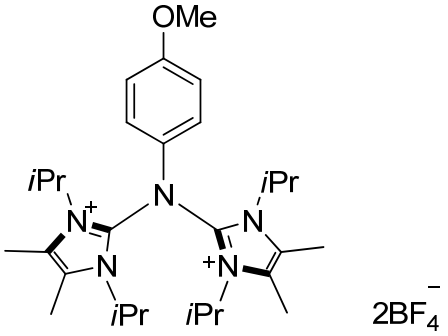
^{13}C NMR (101 MHz, CD_3CN): δ = 10.1 (Me), 10.3 (Me), 21.3 (CH*Me*$_2$), 40.3 (NMe), 52.2 (CH), 52.9 (CH), 128.1 (C=C), 128.6 (C=C), 135.5 (C), 141.2 (C).

IR (neat): $\tilde{\nu}$ = 716 (w), 743 (w), 764 (w), 913 (w), 1022 (vs), 1046 (vs), 1224 (m), 1380 (w), 1407 (w), 1437 (m), 1466 (m), 1514 (m), 1624 (w), 2992 cm^{-1} (w);

ESI (pos.), *m/z* (%): 416 (100) $[M–H]^+$, 208 (15) $[M]^{2+}$;

HRMS (ESI^+), *m/z*: calcd for $C_{23}H_{42}N_7^+$: 416.3496 $[M–H]^+$; found: 416.3493.

2,2'-(4-Methoxyphenylazanediyl)bis(1,3-diisopropyl-4,5-dimethyl-1*H*-imidazol-3-ium) ditetrafluoroborate ($32^{2+}(BF_4^-)_2$):



Was synthesized according to **GP6.1** starting from **11a**$^+BF_4^-$ (1.82 g, 6.0 mmol), *p*-anisidine (0.37 g, 3.0 mmol) and KF (2.09 g, 36.0 mmol). Reaction time: 3 d at 60 °C. The product was precipitated from EtOAc / MeCN (1:1) by addition of Et_2O.

Yield: 1.61 g (82%) as a colorless solid, m.p. 294–295 °C;

^1H NMR (400 MHz, CD_3CN): δ = 0.86 (d, ^3J = 6.7 Hz, 6H, 2×Me), 1.15 (d, ^3J = 7.2 Hz, 6H, 2×Me), 1.53 (d, ^3J = 6.9 Hz, 6H, 2×Me), 1.72 (d, ^3J = 7.1 Hz, 6H, 2×Me), 2.29 (s, 6H, 2×Me), 2.37 (s, 6H, 2×Me), 3.83 (s, 3H, MeO), 4.21 (sept, ^3J = 7.1 Hz, 2H, 2×C*H*Me_2), 4.61 (sept, ^3J = 6.9 Hz, 2H, 2×C*H*Me_2), 7.02–7.10 (m, 2H, 2×CH), 7.13–7.20 (m, 2H, 2×CH);

^{13}C NMR (101 MHz, CD_3CN): δ = 11.0 (Me), 11.2 (Me), 19.4 (CH*Me*), 20.7 (CH*Me*), 21.2 (CH*Me*), 21.7 (CH*Me*), 52.5 (*C*HMe_2), 53.7 (*C*HMe_2), 56.9 (OMe), 117.2 (CH), 126.3 (CH), 128.8 (C), 129.5 (C), 134.3 (C), 135.0 (C), 160.9 (C);

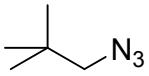
IR (neat): $\tilde{\nu}$ = 831 (m), 1033 (vs), 1093 (m), 1180 (w), 1211 (m), 1233 (m), 1250 (w), 1471 (m), 1506 (m), 1625 (w), 2944 cm^{-1} (w);

ESI (pos.), *m/z* (%): 568 (75) $[M•BF_4]^+$, 438 (12) $[M–C_3H_7]^+$, 240 (100) $[M^{2+}]$, 220 (28) $[M–C_3H_6]^{2+}$;

HRMS (ESI^+), *m/z*: calcd for $C_{29}H_{47}ON_5BF_4^+$ and $C_{29}H_{47}ON_5^{2+}$: 568.3804 $[M•BF_4]^+$ and 240.6885 $[M^{2+}]$; found: 568.3814 and 240.6884;

Elemental analysis calcd (%) for $C_{29}H_{47}B_2F_8N_5O_2$ (655.32): C 53.15, H 7.23, N 10.69; found: C 53.43, H 7.20, N 10.73.

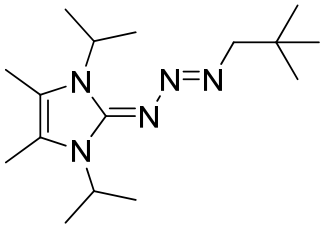
1-Azido-2,2-dimethylpropane: [95,96,129]



A mixture of NpOTs (20.1 g, 83 mmol) and NaN_3 (8.2 g, 125 mmol) was stirred in NMP (80 mL) at 105 °C with a reflux condenser for 3 days. Careful distillation of the target product from the reaction mixture under reduced pressure into a flask with cooling gave 8.68 g (93%) of colorless oil. ^{1}H NMR was in good agreement with that reported in the literature.[129]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (s, 9H, CMe_3), 3.06 (s, 2H, CH_2).

1,3-Diisopropyl-4,5-dimethyl-2-(3-neopentyltriaz-2-enylidene)-2,3-dihydro-1*H*-imidazole (33):



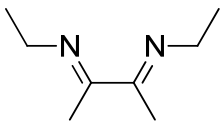
To a solution of **10b** (1.64 g, 9.1 mmol) in THF (10 mL) was added NpN_3 (1.30 g, 11.0 mmol) at –20 °C, the mixture was warmed to room temperature and stirred overnight. Evaporation of the solvent and excess azide gave the pure title compound. Compound is sensitive to CO_2/H_2O of air.

Yield: 2.56 g (96%) as a colorless solid, m.p. 78–81 °C;

^{1}H NMR (400 MHz, C_6D_6): δ = 1.22 (d, ^3J = 7.1 Hz, 12H, CH*Me*$_2$),1.23 (s, 9H, CMe_3), 1.59 (s, 6H, 2×Me), 3.79 (s, 2H, CH_2), 4.94 (br s, 2H, 2×CH).

^{13}C NMR (101 MHz, C_6D_6): δ = 9.9 (Me), 21.4 (CH*Me*$_2$), 28.9 (CMe_3), 32.9 (C), 48.1 (*C*HMe_2), 74.1 (CH_2), 117.8 (C=C), 153.6 (CN).

***N,N′*-(Butane-2,3-diylidene)diethanamine (34):**



Was prepared according to literature procedure.[99,100]

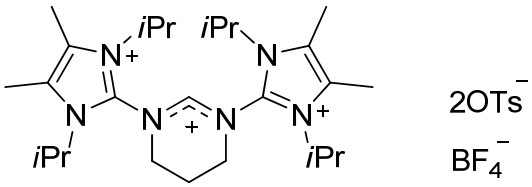
Butan-2,3-dione (17.2 g, 200 mmol) was added dropwise to a cooled to –10 °C $EtNH_2$ (130 mL of 70% aq. solution). The mixture was warmed to room temperature and stirred for 36 h. The reaction mixture was poured into ice-water (100 mL) and extracted with pentane

(3×50mL). The combined pentane layers were dried and evaporated, and the residue was fractionally distilled to give 11.6 g (39%) of the target product, b.p. 76–78 °C / 30–32 mbar.

^{1}H NMR (400 MHz, CD_3CN): δ = 1.27 (t, ^{3}J = 7.0 Hz, 6H, 2×Me), 2.05 (s, 6H, 2×Me), 3.46 (q, ^{3}J = 7.0 Hz, 4H, 2×CH_2);

^{13}C NMR (101 MHz, CD_3CN): δ = 12.5 (Me), 15.7 (Me), 46.7 (CH_2), 167.8 (CN).

2,2'-(5,6-Dihydropyrimidin-1-ium-1,3(4*H*)-diyl)bis(1,3-diisopropyl-4,5-dimethyl-1*H*-imidazolium) ditosylate tetrafluoroborate (36^{3+}BF_4^-(OTs^-)$_2$):



Compound **5a**$^{+}BF_4^-$ (0.410 g, 0.82 mmol) and 1,3-propylene ditosylate (0.315 g, 0.82 mmol) were mixed in DMF (1 mL) at room temperature, and the mixture was stirred at 80 °C for 3 d. The solid precipitate was filtered under argon, washed with dry CH_2Cl_2 (compound is slightly soluble) and dried in high vacuum to give trication **36**$^{3+}BF_4^-$(OTs^-)$_2$. Compound is very sensitive to hydrolysis.

Yield: 0.358 g (50%) as a white powder;

^{1}H NMR (400 MHz, DMSO-d6): δ = 1.46 (d, ^{3}J = 6.9 Hz, 12H, 4×Me), 1.56 (d, ^{3}J = 6.8 Hz, 12H, 4×Me), 2.29 (s, 6H, 2×Me), 2.39 (s, 12H, 4×Me), 2.74–2.85 (m, 2H, CH_2), 4.08–4.44 (m, 4H, 2×CH_2), 4.80 (sept, ^{3}J = 6.9 Hz, 4H, 4×CH), 7.13 (d, ^{3}J = 7.9 Hz, 4H, 4×CH), 7.37 (d, ^{3}J = 8.0 Hz, 4H, 4×CH), 10.40 (s, 1H, CH);

^{13}C NMR (101 MHz, DMSO-d6): δ = 9.6 (Me), 17.3 (CH_2), 20.0 (Me), 20.3 (Me), 20.7 (Me), 49.5 (NCH_2), 52.0 (NCH), 125.2 (CH), 127.9 (C), 128.1 (CH), 130.0 (C), 138.0 (C), 144.8 (C), 163.1 (CH).

4. PTC Activity Experiments

To a solution of KCN (130 mg, 2.00 mmol) in water (1 mL) was added tetrafluoroborate salt **1a-c** (0.04 mmol) followed by benzylbromide (171 mg, 1.00 mmol). The two-phase mixture was intensively stirred at room temperature for 3 h. The mixture was extracted with *tert*-butyl methyl ether (3×10 mL), the combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was filtered through SiO_2 eluating with *t*BuOMe to give pure phenylacetonitrile. For yields see Table 2.1.

5. Stability Experiments

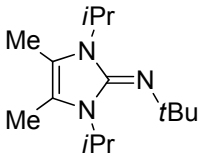
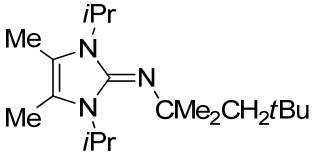
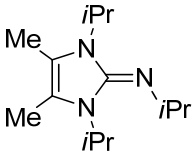
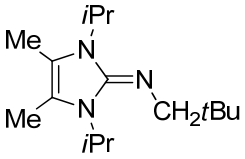
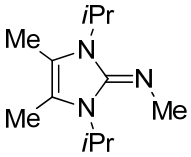
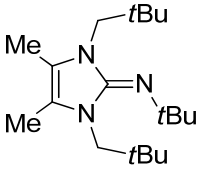
Stability test of cations 1^+–3^+ and P_5^+ under phase-transfer conditions. Method A: Aqueous KOH (50%, 1.5 mL) was added to a Schlenk tube containing a solution of the corresponding tetrafluoroborate salt (0.50 mmol) in chlorobenzene (1.5 mL) and a quantitative NMR standard, dibenzo-18-crown-6 or 18-crown-6 (chosen to avoid overlaps of the NMR signals with those of the cations tested). The resulting two-phase mixture was refluxed with stirring for 16–48 h under argon atmosphere (see Table 2.2). The progress of the reaction was monitored by ^1H and ^{31}P NMR (if applicable) of aliquots taken from the chlorobenzene phase in $(CD_3)_2SO$.

Stability test of cations $1b^+$, $2b^+$ and P_5^+ under homogeneous conditions. Method B: The corresponding tetrafluoroborate salts (0.20 mmol) was added to a solution of KOH (1 mmol) in ethylene glycol (1 mL) in a Schlenk tube. The resulting solution was reflux for 24 h under argon atmosphere (see Table 2.2). The progress of the reaction was monitored by ^1H and ^{31}P (for P_5^+) NMR spectra.

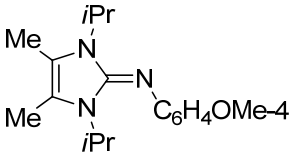
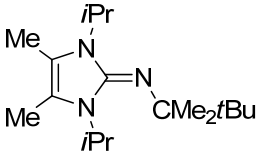
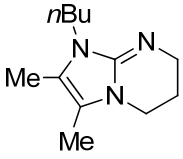
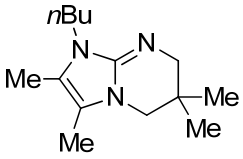
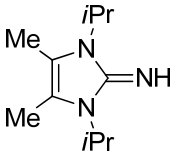
Stability test of cations $1a^+$ and $1b^+$ under phase-transfer conditions. Method C: Aqueous NaOH (50%, 7 g) was added to a flask containing a solution of the corresponding chloride salt (0.50 mmol) in chlorobenzene (7 mL). The mixture was stirred at 100 ºC under argon atmosphere. The progress of the reaction was monitored by ^1H NMR of aliquots taken from the chlorobenzene phase in $CDCl_3$.

6. Basicity of IMAM bases

Table 1. Summary of basicity measurements and calculations of the title compounds.*

Base	Structure	Basicity		ΔNICS(1), ppm	Change of dihedral angle on protonation
		pK_{BH+} MeCN	GB_{calc}, kcal mol^{-1}		
4a		30.21	257.8	-4.23	24.6 → 84.5
4b		29.97	259.2	-3.89	30.6 → 89.4
4c		27.86	254.7	-3.88	13.1 → 80.5
4d		26.29	253.1	-3.44	15.8 → 30.1
4e		27.2	253.4	-2.90	11.5 → 72.0
4f		29.90	256.2	-4.01	22.6 → 73.9

* Measurements of basicities of the title compounds as well as calculations were performed in Leito's group (University of Tartu, Estonia).

4h		23.26	249.4	-2.98	28.3 → 57.5
4i		29.47	257.6	-4.38	25.7 → 89.9
4k		25.54	250.2	-2.18	4.2 → 3.4
4l		25.33	251.0	-2.31	2.8 → 10.5
22a		24.46	248.0	-2.52	0.8 → 20.1

7. Estimation of the nucleophilicity of IMAM bases 4a,b

Base **4a** (148.1 mg, 0.589 mmol), *t*BuP$_1$(pyrr) (192.1 mg, 0.615 mmol) and toluene (55.3 mg, 0.6 mmol) were added to a mixture of MeCN-d3 (0.8 mL) and PhCl (0.4 mL). Methyl iodide (42.6 mg, 0.3 mmol) was added while stirring, and the mixture was stirred for 15 min at ambient temperature. The relative concentrations of methylated products **4a**Me$^+$/toluene and *t*BuP$_1$(pyrr)Me$^+$/toluene were obtained from ^{1}H NMR spectra. Excess of methyl iodide (170.3 mg, 1.2 mmol) was added to the reaction mixture with stirring. The mixture was stirred at ambient temperature for 15 min. The second pair of relative concentrations of fully methylated products **4a**Me$^+$/toluene and *t*BuP$_1$(pyrr)Me$^+$/toluene were obtained from ^{1}H NMR spectra. The conversion of methylation for both **4a** ($C_{\mathbf{4aMe}}$ = 0.594) and *t*BuP$_1$(pyrr) ($C_{\mathbf{P1Me}}$ = 0.015) after the first addition of methyl iodide was calculated by dividing the first relative concentration by the second one for each base. From Eq. 1 the ratio between rate constants of methylation for **4a** and *t*BuP$_1$(pyrr) was obtained, $k_{\mathbf{4a}}/k_{\mathbf{P1}} \sim 60$.

$$k_{\mathbf{4}}/k_{\mathbf{P1}} = \ln(1 - C_{\mathbf{4Me}}) / \ln(1 - C_{\mathbf{P1Me}}) \qquad \textbf{(Eq. 1)}$$

Base **4b** (80.3 mg, 0.261 mmol), *t*BuP$_1$(pyrr) (79.0 mg, 0.253 mmol) were added to a mixture of MeCN-d3 (1 mL) and PhCl (0.5 mL). Methyl iodide (34.9 mg, 0.246 mmol) was added with stirring. The mixture was stirred at ambient temperature for 15 min. The ratio between relative concentrations of methylated products **4b**Me$^+$ and *t*BuP$_1$(pyrr)Me$^+$ was obtained from ^{1}H NMR spectra. The conversions of methylation for both **4b** ($C_{\mathbf{4bMe}}$ = 0.728) and *t*BuP$_1$(pyrr) ($C_{\mathbf{P1Me}}$ = 0.224) were calculated. By insertion into Eq. 1, the ratio between rate constants of methylation for **4b** and *t*BuP$_1$(pyrr) was obtained, $k_{\mathbf{4b}}/k_{\mathbf{P1}} \sim 5.1$.

8. Estimation of the basicity of bases by NMR

DMSO-d6 was distilled and dried over 3 Å molecular sieves; MeCN-d3 was dried over 4 Å molecular sieves. All manipulations (sample preparation, basicity experiments) were carried out under an argon atmosphere using a NMR tube filling manifold (Aldrich) at ambient temperature. ^{1}H NMR spectra of reaction mixtures were measured twice (in 15 min and 1-24 h after mixing) to demonstrate constancy of spectra during time.

IMAM base 4a in MeCN

IMAM salt **4a**H^+ (100 μmol) and *t*BuP_1(pyrr) base (100 μmol) were mixed in MeCN-d3 (0.5 mL) in a 5 mm NMR tube with stirring at room temperature and ^{1}H NMR spectra were recorded.

The chemical shift difference Δ = δ(C2) – δ(C4,5) for the signals of **4a**/**4a**H^+ mixture was measured (17.33 ppm). Using the Eq. 3.2 the relative concentrations of **4a** and **4a**H^+ in the reaction mixture were calculated. After insertion in Eq. 3.1, the value of estimated basicity for IMAM base pK_{BH+} in MeCN was found to be ~ 30.5.

BIG bases 6a,c in MeCN and DMSO

BIG salts **6a**,**c**H^+ (200 μmol) and *t*BuP_2(dma) base (200 μmol) were mixed in MeCN-d3 (0.5 mL) in a 5 mm NMR tube upon stirring at room temperature and ^{1}H NMR spectra were recorded.

Relative concentrations of both the protonated form *t*BuP_2(dma)H^+ and its base were calculated from phosphorous coupling constants $^2J_{P\text{-}P}$ for the mixture *t*BuP_2(dma) / *t*BuP_2(dma)H^+ in ^{31}P NMR spectra according to Eq. 4.2. Insertion of the equilibrium concentrations into Eq. 4.1 gave the value of pK_{BH+}^{MeCN} for **6a** ~ 34.5 and pK_{BH+}^{MeCN} for **6c** ~ 35.0.

In a reversed experiment BIG base **6a** (200 μmol) and *t*BuP_2(dma)H^+OMs^- salt (200 μmol) were mixed in DMSO-d6 (0.5 mL) in a 5 mm NMR tube with stirring at room temperature and ^{1}H NMR spectra were recorded, the difference between pK_{BH+}^{DMSO}(**6a**) and pK_{BH+}^{DMSO}(*t*BuP_2(dma)) was estimated to be ~ 1.0.

Imimidazol-2-ylidene in DMSO

Indicator anions were obtained by deprotonation of indicators with *t*BuOK in THF.

Imidazol-2-ylidene **10i** (100 μmol) and indicator (Ind-H) (100 μmol) were mixed in DMSO-d6 (0.5 mL) in a 5 mm NMR tube with stirring at room temperature.

Calculations of basicity of imidazol-2-ylidene **10i** was performed by comparison of Ind-H, Ind^- relative concentrations in ^{1}H NMR spectra, using Eq. 5.1.

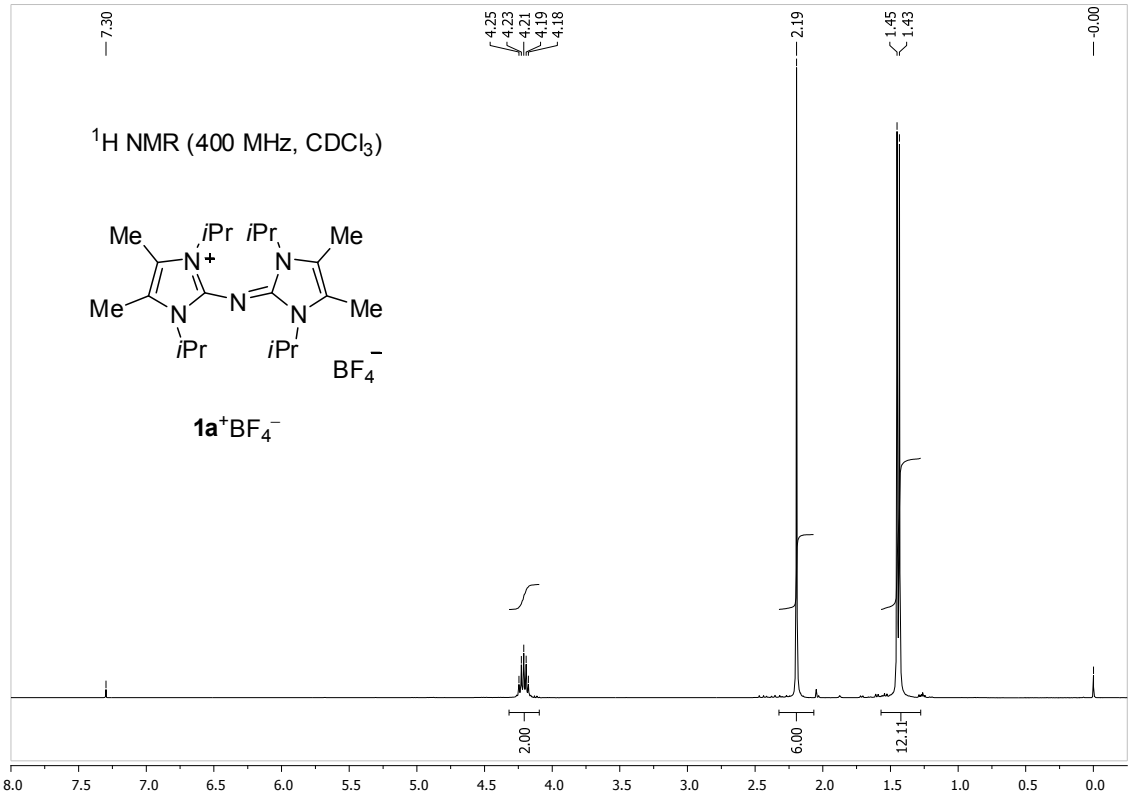
Ind-H – 1,2,3,4,5-pentamethylcyclopentadiene, pK_{BH+} (**10i**) ≈ 24.6(0)

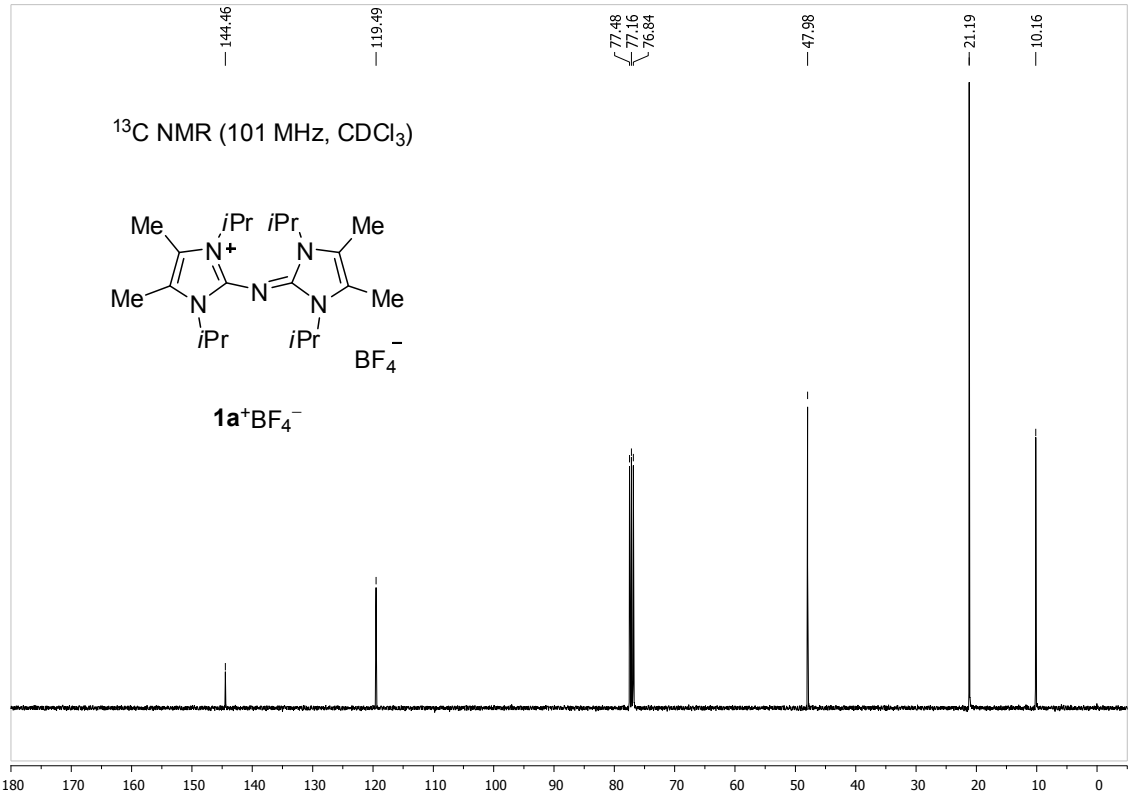
Ind-H – 2-(dimethylamino)fluorene, pK_{BH+} (**10i**) ≈ 24.8(8)

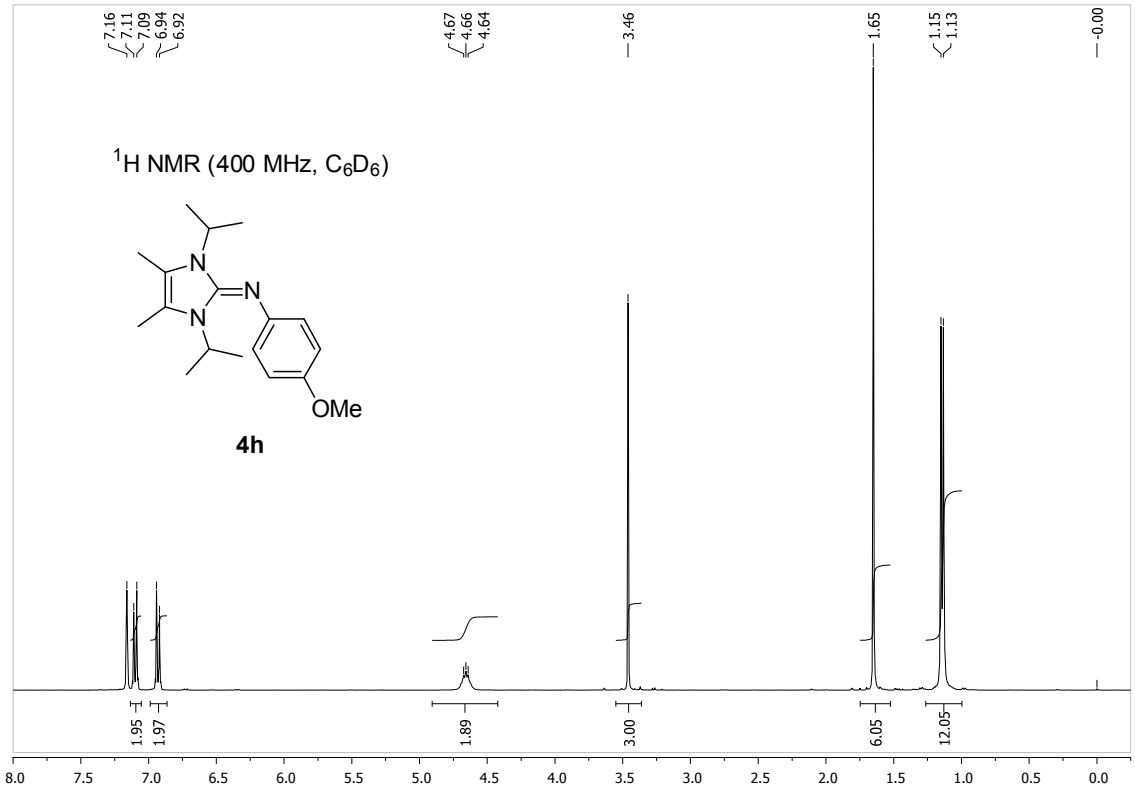
Ind-H – 9-*tert*-butylfluorene, pK_{BH+} (**10i**) ≈ 24.9(2)

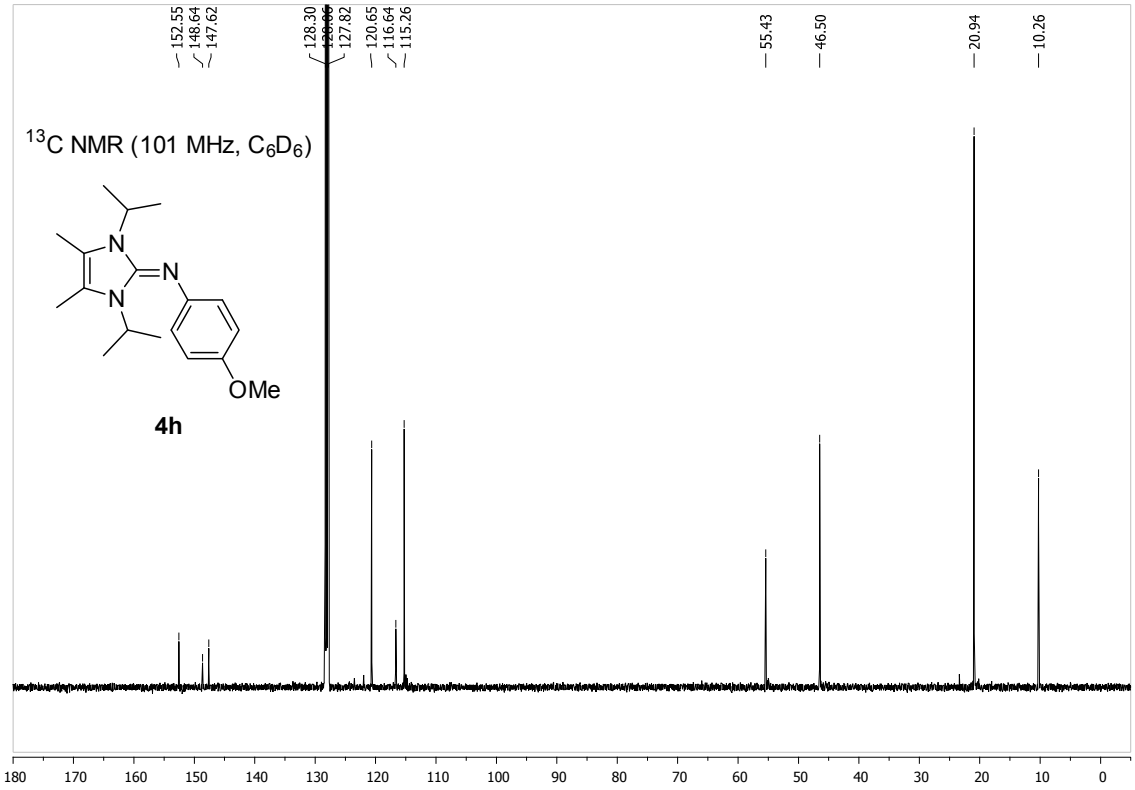
Average pK_{BH+} (**10i**|DMSO-d6) = 24.8±0.17[117]

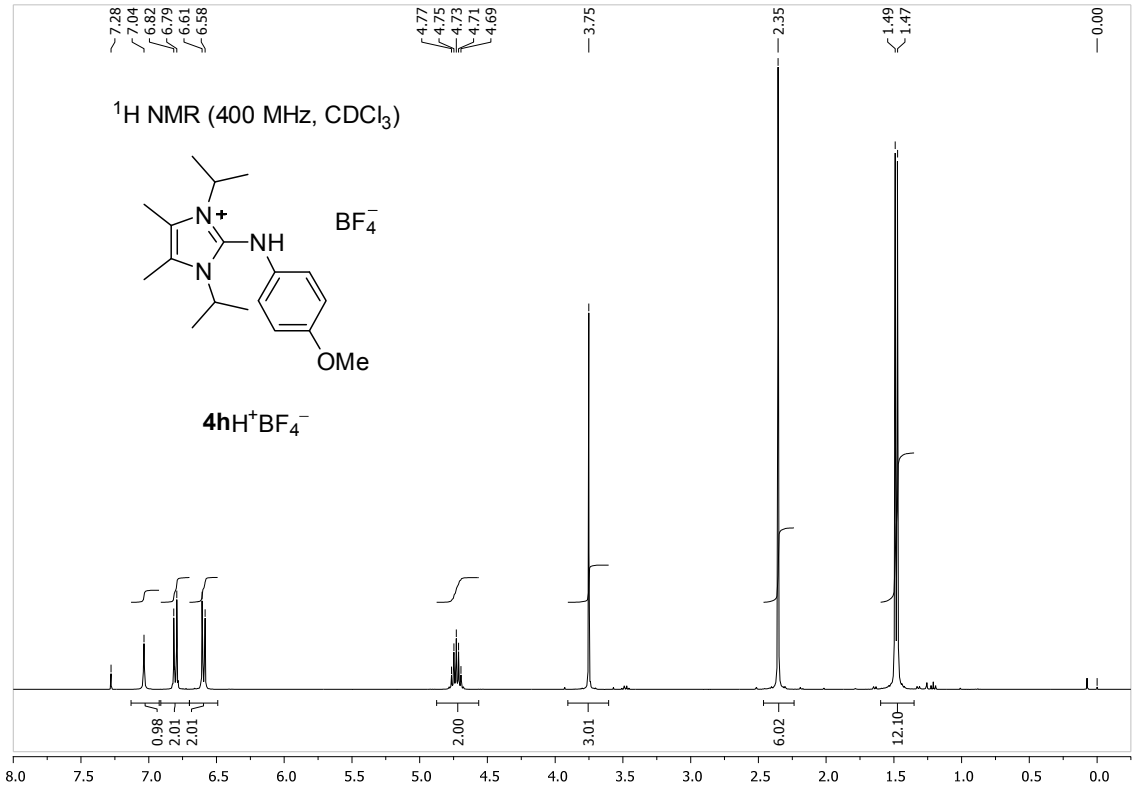
Selected NMR Spectra

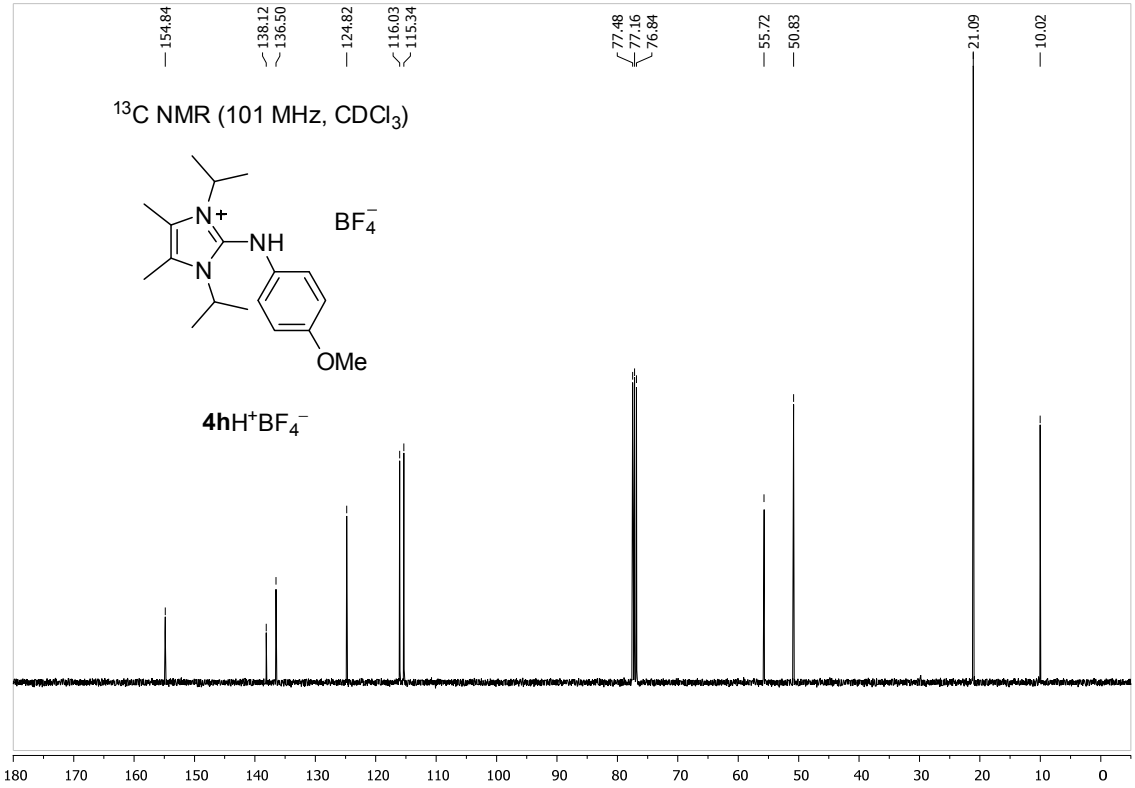


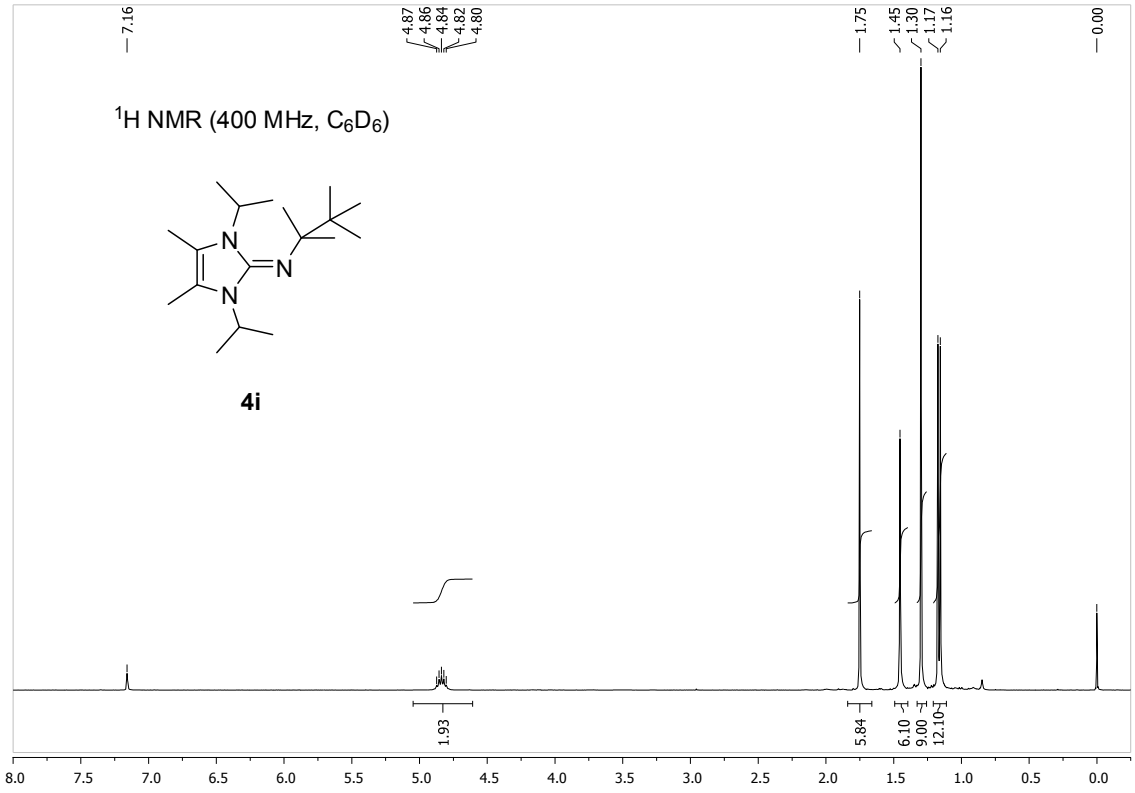



7.16
7.11
7.09
6.94
6.92
4.67
4.66
4.64
3.46
1.65
1.15
1.13
-0.00
^{1}H NMR (400 MHz, C_6D_6)
N
N
N
OMe
4h
1.95
1.97
1.89
3.00
6.05
12.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

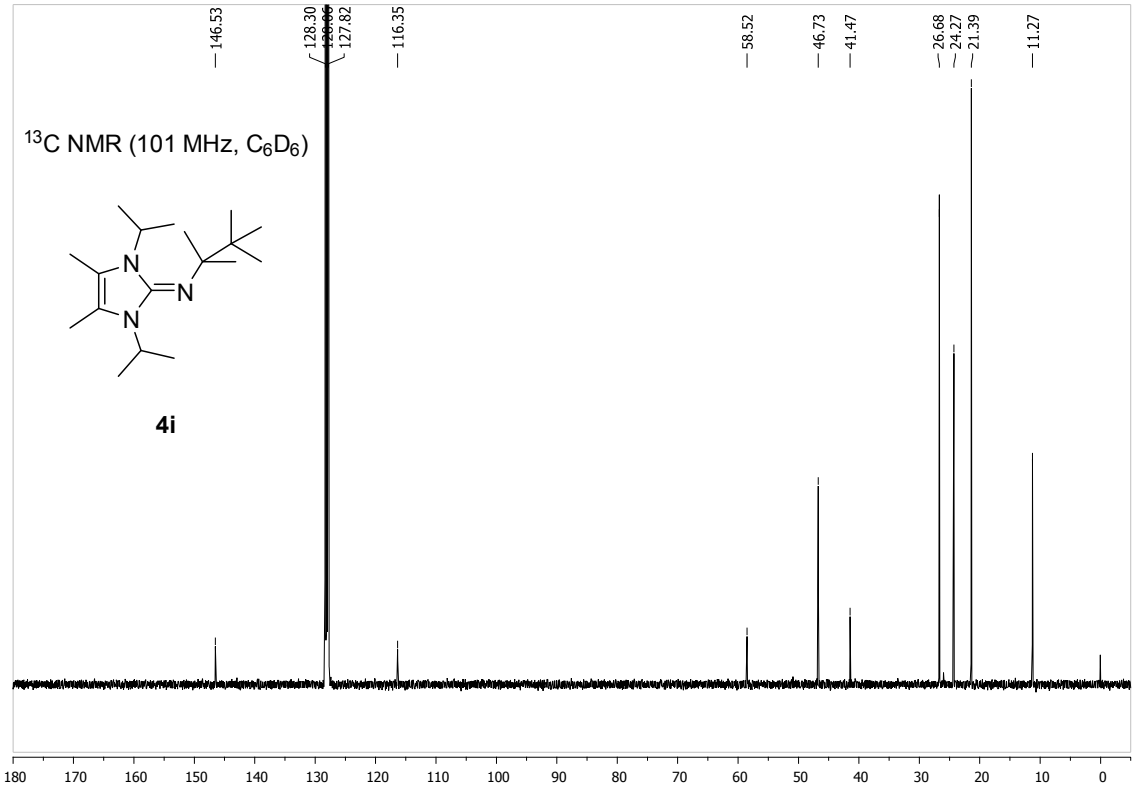

152.55
148.64
147.62
128.30
128.06
127.82
120.65
116.64
115.26
55.43
46.50
20.94
10.26
^{13}C NMR (101 MHz, C_6D_6)
N
N
N
OMe
4h
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.28
7.04
6.82
6.79
6.61
6.58
4.77
4.75
4.73
4.71
4.69
3.75
2.35
1.49
1.47
0.00
^{1}H NMR (400 MHz, $CDCl_3$)
BF_4^-
NH
N+
N
OMe
4h$H^+BF_4^-$
0.98
2.01
2.01
2.00
3.01
6.02
12.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

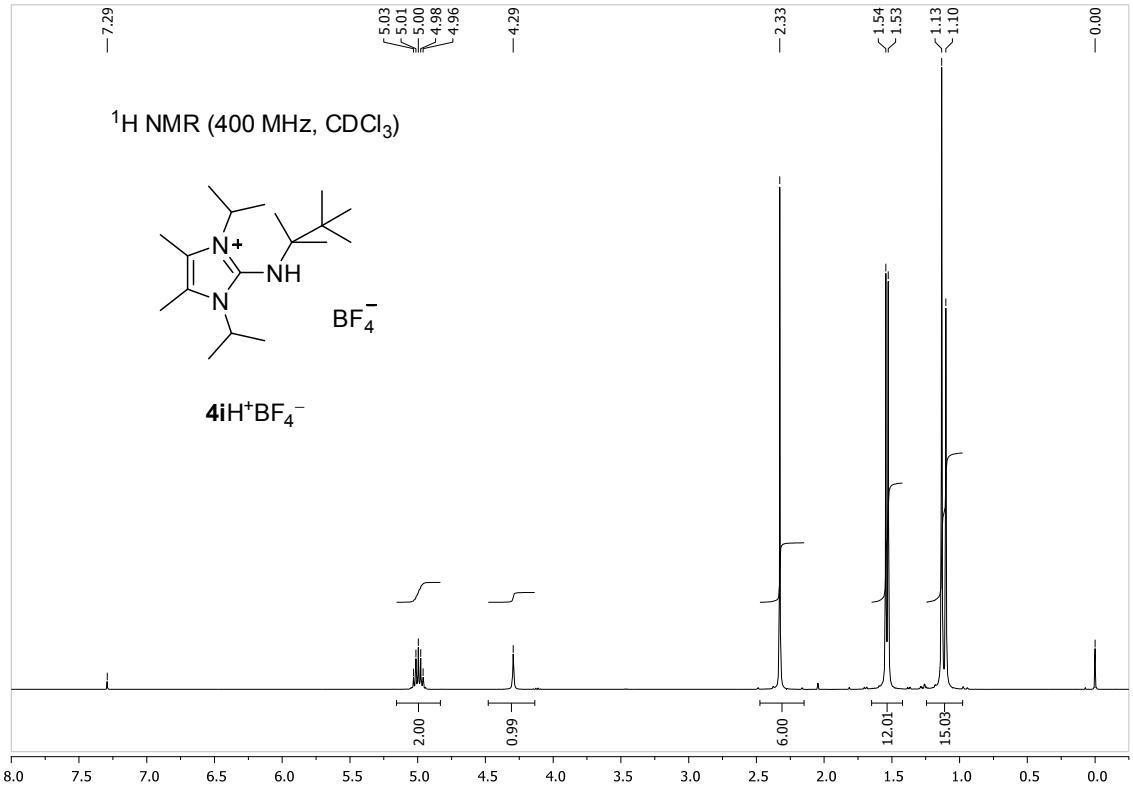

154.84
138.12
136.50
124.82
116.03
115.34
77.48
77.16
76.84
55.72
50.83
21.09
10.02
^{13}C NMR (101 MHz, $CDCl_3$)
BF_4^-
NH
N+
N
OMe
4h$H^+BF_4^-$
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

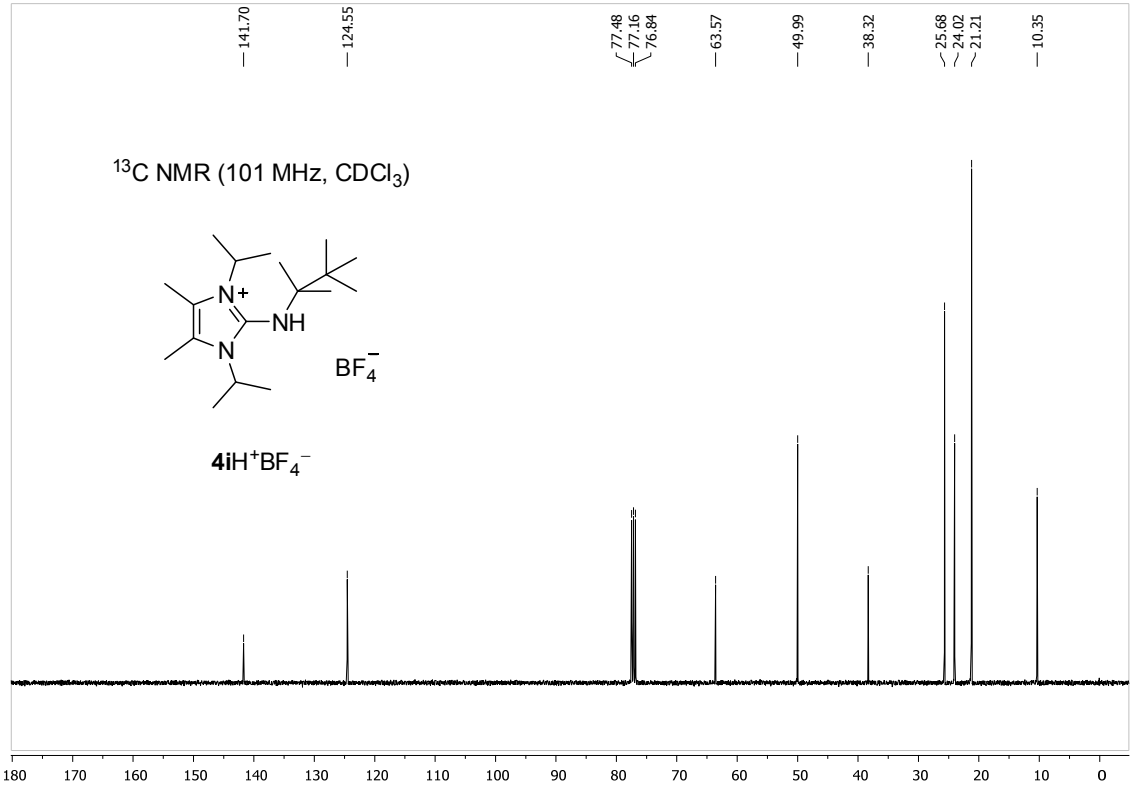

7.16
4.87
4.86
4.84
4.82
4.80
1.75
1.45
1.30
1.17
1.16
0.00
^{1}H NMR (400 MHz, C_6D_6)
N
N
N
1.93
5.84
6.10
9.00
12.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

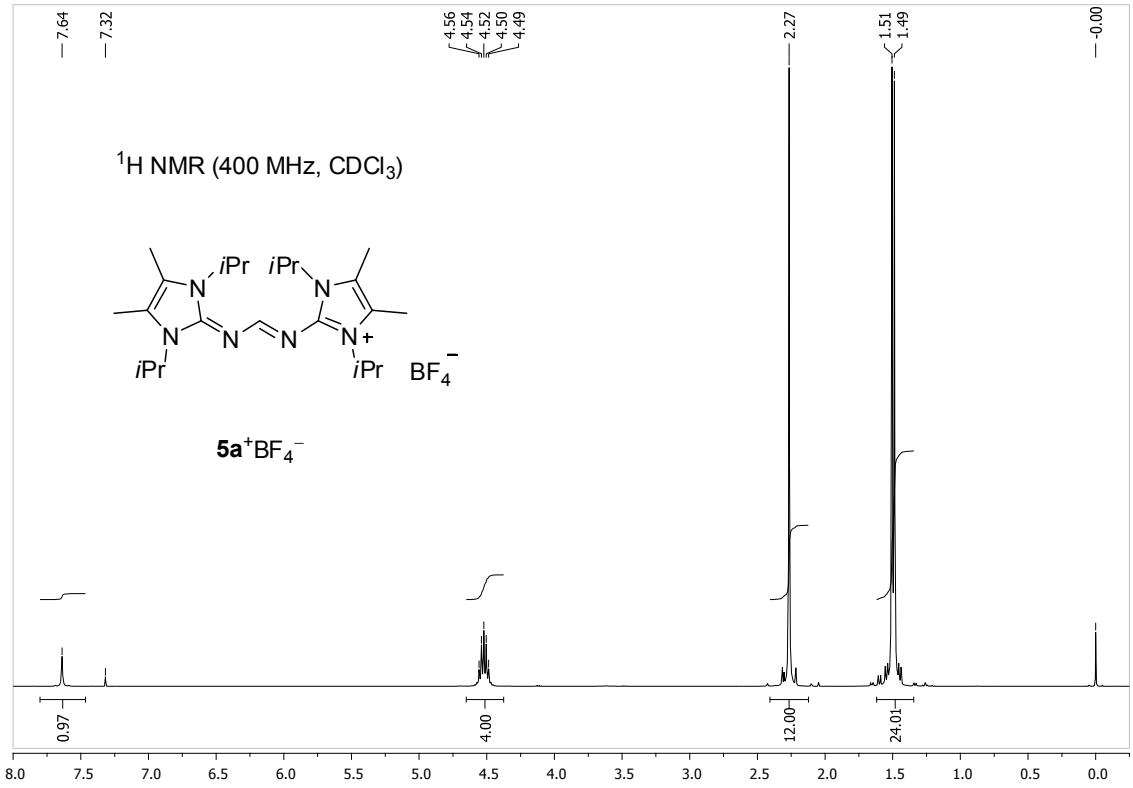
4i

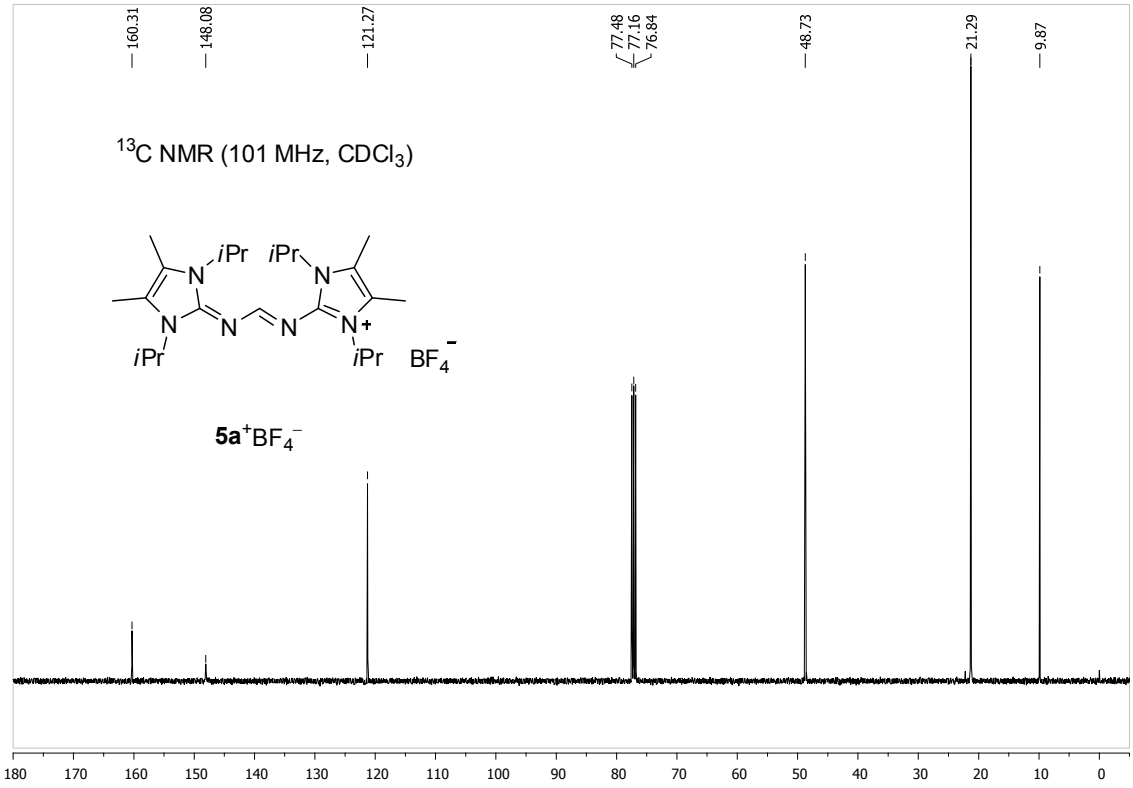

146.53
128.30
128.06
127.82
116.35
58.52
46.73
41.47
26.68
24.27
21.39
11.27
^{13}C NMR (101 MHz, C_6D_6)
N
N
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

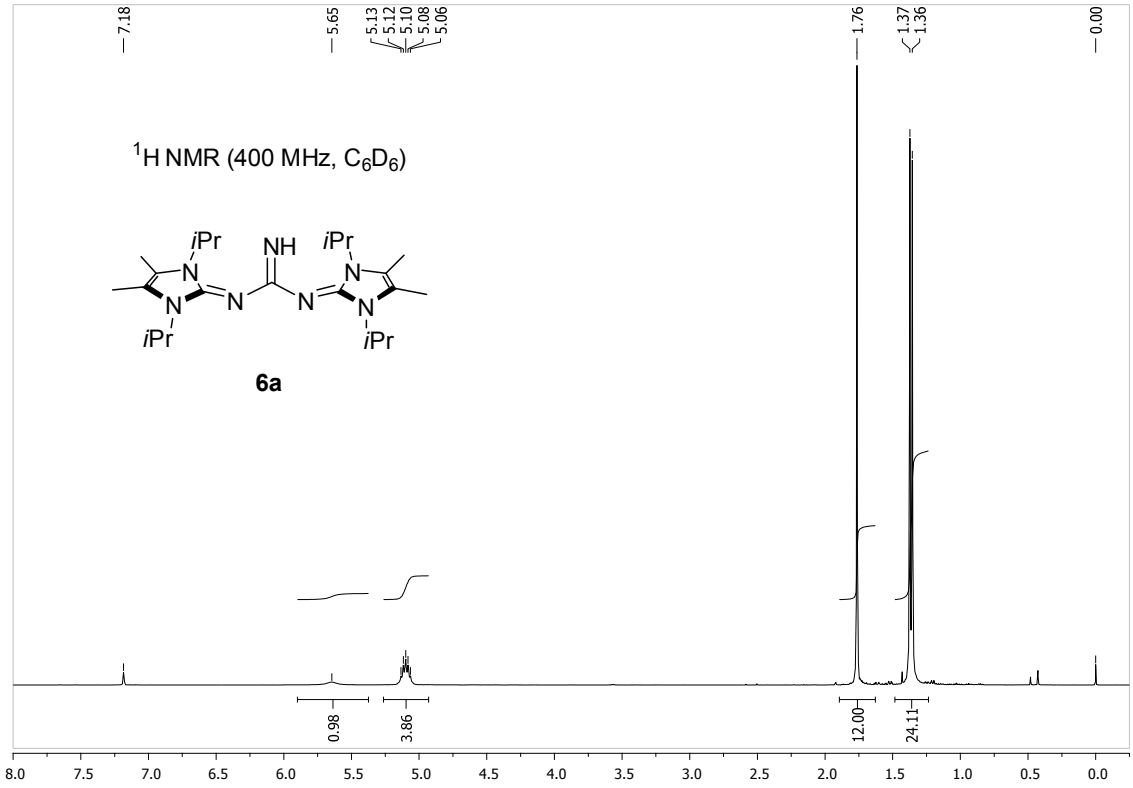
4i


7.29
5.03
5.01
5.00
4.98
4.96
4.29
2.33
1.54
1.53
1.13
1.10
0.00
^{1}H NMR (400 MHz, $CDCl_3$)
N+
NH
N
BF_4^-
4i$H^+BF_4^-$
2.00
0.99
6.00
12.01
15.03
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

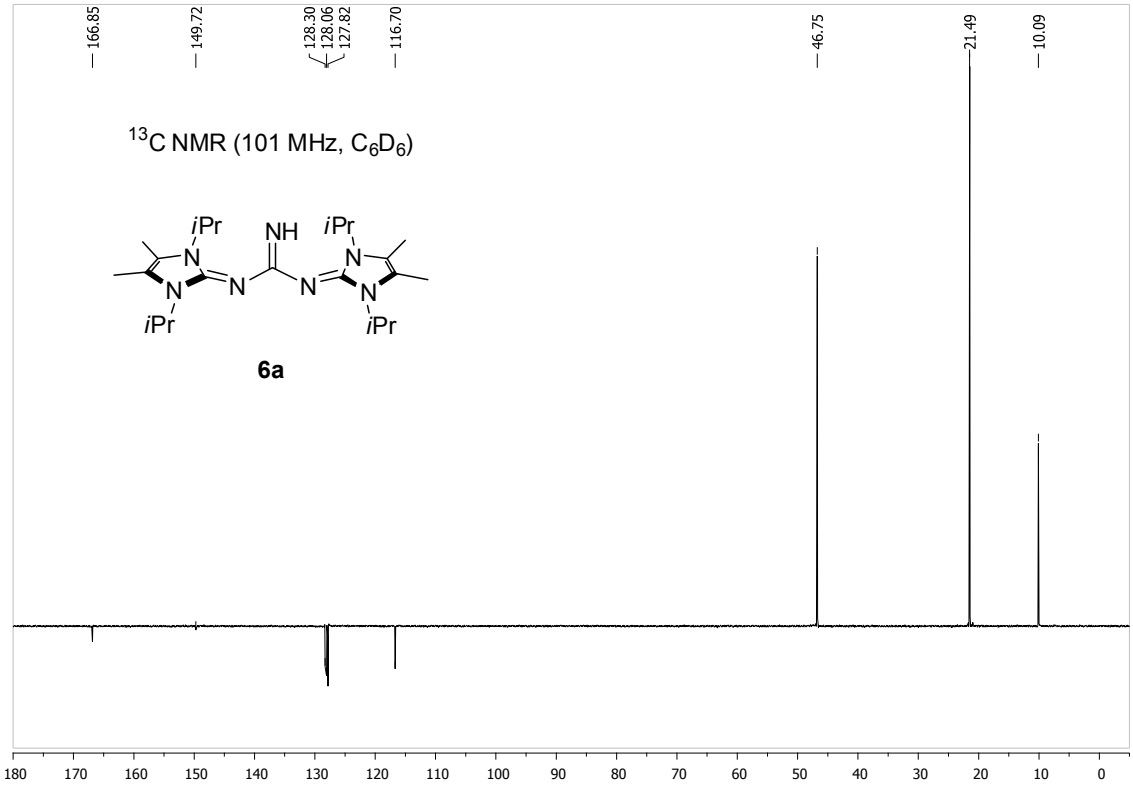

141.70
124.55
77.48
77.16
76.84
63.57
49.99
38.32
25.68
24.02
21.21
10.35
^{13}C NMR (101 MHz, $CDCl_3$)
N+
NH
N
BF_4^-
4i$H^+BF_4^-$
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.64
7.32
4.56
4.54
4.52
4.50
4.49
2.27
1.51
1.49
-0.00
^{1}H NMR (400 MHz, $CDCl_3$)
*i*Pr
*i*Pr
*i*Pr
*i*Pr
BF_4^-
5a$^+BF_4^-$
0.97
4.00
12.00
24.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

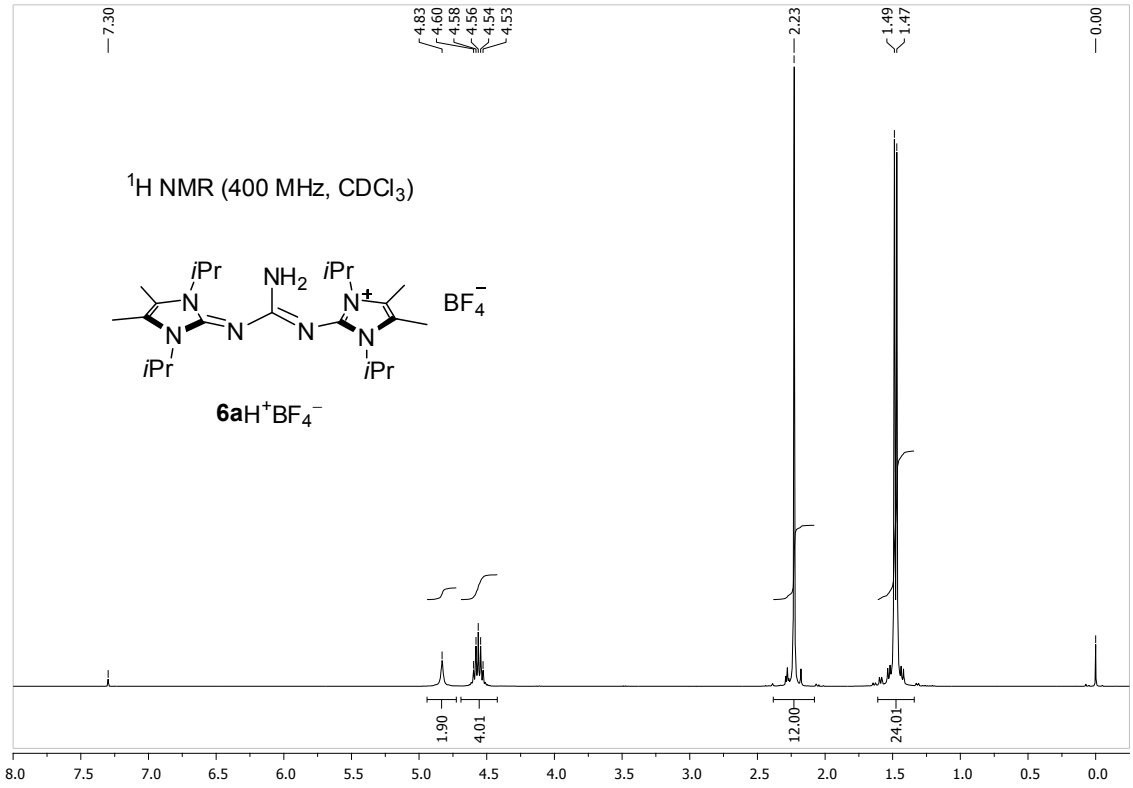

160.31
148.08
121.27
77.48
77.16
76.84
48.73
21.29
9.87
^{13}C NMR (101 MHz, $CDCl_3$)
*i*Pr
*i*Pr
*i*Pr
*i*Pr
BF_4^-
5a$^+BF_4^-$
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

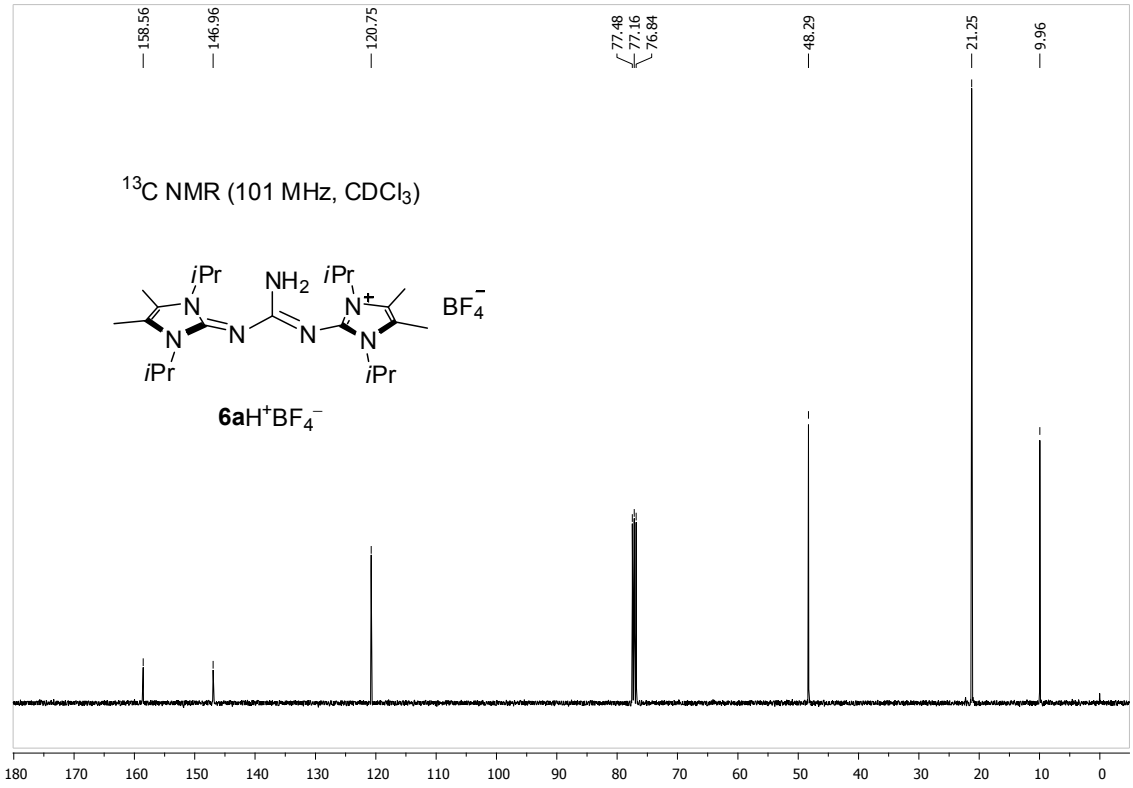

7.18
5.65
5.13
5.12
5.10
5.08
5.06
1.76
1.37
1.36
0.00
^{1}H NMR (400 MHz, C_6D_6)
*i*Pr
NH
*i*Pr
*i*Pr
*i*Pr
0.98
3.86
12.00
24.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

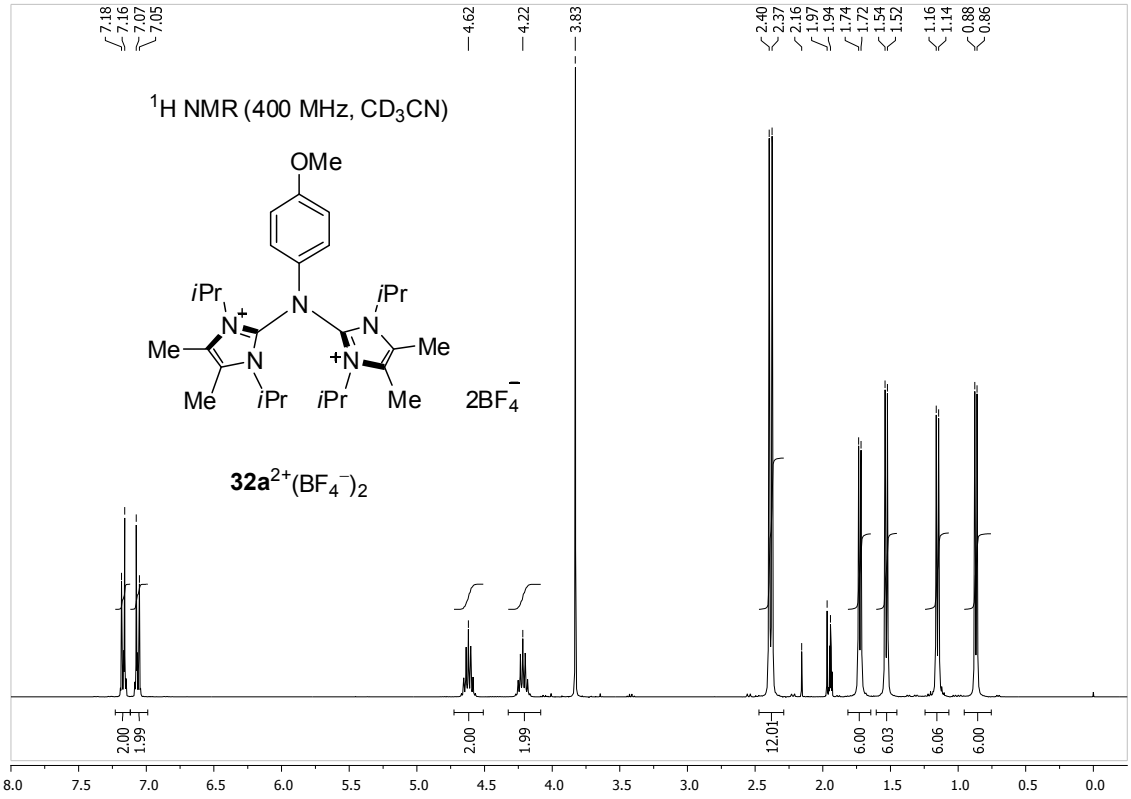
6a

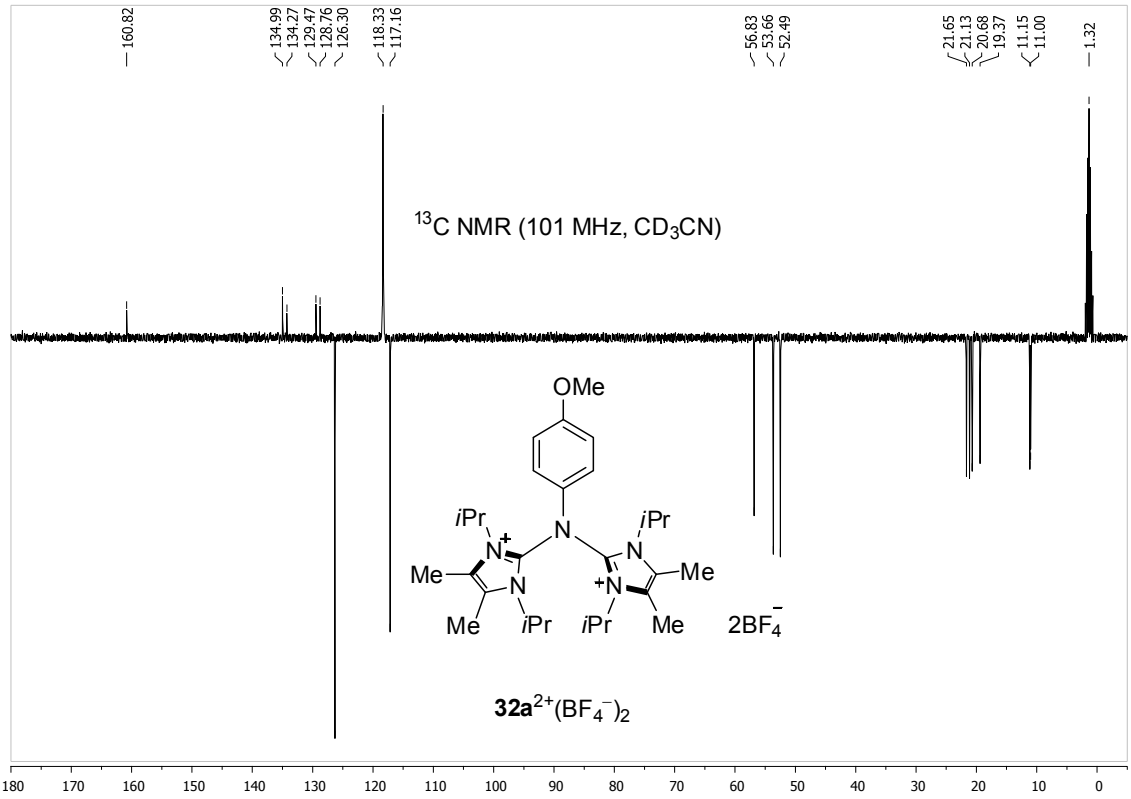

166.85
149.72
128.30
128.06
127.82
116.70
46.75
21.49
10.09
^{13}C NMR (101 MHz, C_6D_6)
*i*Pr
NH
*i*Pr
*i*Pr
*i*Pr
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

6a


7.30
4.83
4.60
4.58
4.56
4.54
4.53
2.23
1.49
1.47
0.00
^{1}H NMR (400 MHz, $CDCl_3$)
*i*Pr
NH$_2$
*i*Pr
BF$_4^-$
*i*Pr
*i*Pr
6aH$^+$BF$_4^-$
1.90
4.01
12.00
24.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


158.56
146.96
120.75
77.48
77.16
76.84
48.29
21.25
9.96
^{13}C NMR (101 MHz, $CDCl_3$)
*i*Pr
NH$_2$
*i*Pr
BF$_4^-$
*i*Pr
*i*Pr
6aH$^+$BF$_4^-$
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.18
7.16
7.07
7.05
4.62
4.22
3.83
2.40
2.37
2.16
1.97
1.94
1.74
1.72
1.54
1.52
1.16
1.14
0.88
0.86
^{1}H NMR (400 MHz, CD_3CN)
OMe
*i*Pr
*i*Pr
Me
Me
Me
*i*Pr
*i*Pr
Me
$2BF_4^-$
32a$^{2+}(BF_4^-)_2$
2.00
1.99
2.00
1.99
12.01
6.00
6.03
6.06
6.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


160.82
134.99
134.27
129.47
128.76
126.30
118.33
117.16
56.83
53.66
52.49
21.65
21.13
20.68
19.37
11.15
11.00
1.32
^{13}C NMR (101 MHz, CD_3CN)
OMe
*i*Pr
*i*Pr
Me
Me
Me
*i*Pr
*i*Pr
Me
$2BF_4^-$
32a$^{2+}(BF_4^-)_2$
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Crystallographic Data

Data were collected on Bruker APEX-II CCD (**4h**$H^+BF_4^-$, **4h**) and Nonius Kappa CCD (all other crystals) diffractometers at a temperature of 150 K. Structures were solved by direct methods (SIR92)[130] and refined by full-matrix least squares based on F^2 (SHELXL97).[131] The hydrogen atoms in all structures were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2-1.5\ U_{eq}$ (pivot atom). The hydrogen atom of >N-H moieties was found on difference Fourier maps and refined isotropically.

Salts **1a**$^+OTs^-$ or **1b**$^+I^-$ were prepared from corresponding tetrafluoroborates using excess of KOTs or KI in MeOH followed by filtration of KBF_4, evaporation of solvent under reduced pressure, extraction of target salts with $CHCl_3$ and evaporation. Slow cooling of saturated solution of **1a**$^+OTs^-$ or **1b**$^+I^-$ in EtOAc or EtOAc / hexane (1:1) respectively afforded crystals suitable for X-ray analysis. Suitable crystals of **23a** were obtained by crystallization from PhMe. X-Ray quality crystals of salts **4a**$H^+BF_4^-$ and **4i**$H^+BF_4^-$ were grown from EtOAc / MeOH, of **4h**$H^+BF_4^-$ from EtOAc, and of base **4h** from hexane by slow cooling of saturated solutions. X-Ray quality crystals of **5a**$^+$**5a**$H^{2+}(BF_4^-)_3$ and **30a**$^+(BF_4^-)_2$ were obtained by crystallization from EtOAc.

X-ray crystallographic data are given in Tables 2, 3 and 4.

CCDC 729001–729003 for **23a**, **1a**$^+OTs^-$ and **1b**$^+I^-$ respectively, 769494 for **4a**$H^+BF_4^-$, 830319–830321 for **4i**$H^+BF_4^-$, **4h**, **4h**$H^+BF_4^-$ respectively contain the supplementary crystallographic data. These data can be obtained from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. X-Ray crystallographic data of **1a**$^{+}$OTs^{-}, **1b**$^{+}$I^{-} and **4a**H^{+}BF$_4^{-}$.

Compound	**1a**$^{+}$OTs^{-}	**1b**$^{+}$I^{-}	**4a**H^{+}BF$_4^{-}$
Formula	$C_{22}H_{40}N_5 \cdot C_7H_7O_3S$	$3(C_{30}H_{56}N_5)\ C_4H_8O_2 \cdot 3(I)$	$C_{15}H_{30}N_3BF_4$
M_r	545.78	1929.20	339.23
Crystal habit	colourless plate	colourless plate	colorless plate
Crystal size (mm)	0.5 × 0.4 × 0.1	0.3 × 0.2 × 0.1	0.4 × 0.12 × 0.1
Crystal system	orthorhombic	triclinic	orthorhombic
Space group	*Pna2*$_1$	$P\bar{1}$	$P2_12_12_1$
a (Å)	21.7539 (4)	10.76990 (10)	9.9090 (4)
b (Å)	8.77290 (10)	16.8764 (2)	10.6410 (2)
c (Å)	15.6722 (3)	30.3494 (4)	17.1690 (7)
α (°)	90	74.8719 (7)	90
β (°)	90	89.6370 (9)	90
γ (°)	90	83.1406 (7)	90
V (Å^3)	2990.96 (9)	5285.16 (11)	1810.33 (11)
Z	4	2	4
D_x (Mg m^{-3})	1.212	1.212	1.245
μ (mm^{-1})	0.15	0.94	0.10
F(000)	1184	2040	728
T (K)	150 (2)	150 (2)	150 (2)
θ_{max} (°)	26.0	26.0	27.5
No. of reflections:			
Measured	41476	80527	16309
Unique	5606	20711	4143
R_{int}[a]	0.040	0.045	0.052
Refined parameters	356	1021	221
$wR(F^2$, all refl.)[b]	0.091	0.079	0.097
$R(F, >4\sigma(F))$[c]	0.036	0.035	0.042
GOF[d]	1.04	0.89	1.05
max./min Δρ (e Å^{-3})	0.12/−0.28	0.74/−0.76	0.15/-0.27

[a] $R_{int} = \Sigma \left| F_o^2 - F_{o,mean}^2 \right| / \Sigma F_o^2$. [b] Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$. [c] $R(F) = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{½}$. [d] $GOF = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$.

Table 3. X-Ray crystallographic data of **4h**$H^+BF_4^-$, **4h** and **4i**$H^+BF_4^-$.

Compound	**4h**$H^+BF_4^-$	**4h**	**4i**$H^+BF_4^-$
Formula	$C_{18}H_{28}N_3OBF_4$	$C_{18}H_{27}N_3O$	$C_{18}H_{36}N_3 \cdot BF_4$
M_r	389.24	301.43	381.31
Crystal habit	colorless plate	colorless prism	colorless plate
Crystal size (mm)	0.56 × 0.28 × 0.27	0.78 × 0.43 × 0.32	0.4 × 0.3 × 0.12
Crystal system	monoclinic	monoclinic	triclinic
Space group	*C*2/*c*	$P2_1/c$	$P\bar{1}$
a (Å)	33.575 (3)	12.4823 (4)	9.9413 (5)
b (Å)	8.6587 (8)	10.8254 (4)	10.4839 (4)
c (Å)	15.1732 (12)	12.9650 (5)	10.5226 (5)
α (°)	90	90	77.687 (3)
β (°)	111.928	98.714 (2)	79.700 (3)
γ (°)	90	90	83.885 (3)
V (Å^3)	4092.0 (6)	1731.68 (11)	1051.54 (8)
Z	8	4	2
D_x (Mg m^{-3})	1.264	1.156	1.204
μ (mm^{-1})	0.10	0.07	0.10
F(000)	1648	656	412
T (K)	150 (2)	150 (2)	150 (2)
θ_{max} (°)	27.5	27.5	27.1
No. of reflections:			
Measured	17321	21299	19984
Unique	4702	3981	4605
R_{int}[a]	0.033	0.027	0.030
Refined parameters	268	206	250
$wR(F^2$, all refl.)[b]	0.152	0.117	0.128
$R(F, >4\sigma(F))$[c]	0.055	0.044	0.048
GOF[d]	1.03	1.03	0.99
max./min Δρ (e Å^{-3})	0.43/-0.39	0.47/-0.25	0.24/-0.26

[a] $R_{int} = \Sigma \left| F_o^2 - F_{o,mean}^2 \right| / \Sigma F_o^2$. [b] Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$. [c] $R(F) = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{1/2}$. [d] $GOF = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$.

Table 4. X-Ray crystallographic data for $\mathbf{5a}^{+}\mathbf{5a}H^{2+}(BF_4^-)_3$, **23a** and $\mathbf{30a}^{2+}(BF_4^-)_2$.

Compound	$\mathbf{5a}^{+}\mathbf{5a}H^{2+}(BF_4^-)_3$	**23a**	$\mathbf{30a}^{2+}(BF_4^-)_2$
Formula	$C_{23}H_{42}N_6 \cdot C_{23}H_{41}N_6 \cdot C_4H_8O_2 \cdot 3(BF_4)$	$C_{15}H_{29}N_5$	$C_{23}H_{43}N_7 \cdot 2(BF_4)$
M_r	1152.78	279.43	591.26
Crystal habit	colourless bar	colourless plate	colorless plate
Crystal size (mm)	0.5 × 0.15 × 0.1	0.4 × 0.4 × 0.3	0.4 × 0.24 × 0.08
Crystal system	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$Pna2_1$	Cm
a (Å)	11.9970 (2)	12.6964 (2)	11.6768 (2)
b (Å)	12.5393 (2)	14.7323 (3)	10.5789 (3)
c (Å)	23.0570 (5)	9.1166 (2)	12.6160 (3)
α (°)	99.2608 (11)	90	90
β (°)	100.3798 (11)	90	101.8328 (15)
γ (°)	109.5772 (10)	90	90
V (Å^3)	3121.57 (10)	1705.23 (6)	1525.31 (6)
Z	2	4	2
D_x (Mg m^{-3})	1.226	1.088	1.287
μ (mm^{-1})	0.10	0.07	0.11
F(000)	1228	616	624
T (K)	150 (2)	150 (2)	150 (2)
θ_{max} (°)	26.0	27.5	27.5
No. of reflections:			
measured	51312	25895	18616
unique	12296	3753	3498
R_{int} [a]	0.033	0.032	0.031
Refined parameters	750	190	211
$wR(F^2$, all refl.) [b]	0.145	0.097	0.164
$R(F, >4\sigma(F))$ [c]	0.05	0.036	0.057
GOF [d]	1.05	1.05	0.96
max./min Δρ (e Å^{-3})	0.56/−0.38	0.19/−0.15	0.50/−0.43

[a] $R_{int} = \Sigma \left| F_o^2 - F_{o,mean}^2 \right| / \Sigma F_o^2$. [b] Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$. [c] $R(F) = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{½}$. [d] $GOF = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$.

Abbreviations

B(s)	base(s)
BH^+	protonated form of a base, conjugated acid
BIG	*N*,*N*′-bis(1,3-dialkylimidazol-2-ylidene)guanidine
BIF	*N*,*N*′-bis(1,3-dialkylimidazol-2-ylidene)formamidine
BIMA	bis(*N,N*′-dialkylimidazolium)amide [cation]
CI	chemical ionization
Cp*	1,2,3,4,5-pentamethylcyclopentadienyl
Cy	cyclohexyl
DCM	dichloromethane
DBU	1,8-diazadicyclo[5.4.0]undec-7-ene
DLC(s)	delocalized lipophilic cation(s)
(dma)	dimetylamino substituted
DME	1,2-dimethoxyethane
DMF	*N*,*N*-dimethylformamide
DMSO	dimethyl sulfoxide
ESI	electro-spray ionization
GB	gas phase basicity
GC MS	gas chromatograph with mass analyzer
HMPA	hexamethylphosphoric triamide
HR MS	high resolution mass spectroscopy
Im	imidazolium
IMAM	1,3-dialkyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylidene amino group
MS	mass spectroscopy
Nf	nonaflyl (nonafluorobutanesulfonyl)
NICS	nucleus-independent chemical shift
NMP	*N*-methyl-2-pyrrolidone
NMR	nuclear magnetic resonance
Np	neopentyl
P_n	Schwesinger's phosphazene base of *n* generation (*n* - amount of P atoms)
P_n^+	Schwesinger's phosphazene cation of *n* generation (*n* - amount of P atoms)
PA	proton affinity

PIMA	tris(dimethylamino)phosphonium-*N,N′*-dialkylimidazolium-amide [cation]
pK_a	–log(K_a), where K_a is acid dissociation constant
pK_{BH+}	–log(K_a), where K_a is conjugated acid BH^+ dissociation constant
pK_{ip}	$\Delta pK_{ip} + pK_{[IndH+A-]ip}$, where $\Delta pK_{ip} = -\log(K)$, $K = [B:][IndH^+A^-]_{ip} / [BH^+A^-]_{ip}[Ind]$
PMG	pentamethylguanidine
PTC	phase-transfer catalysis/catalyst
Py	pyridine
(pyrr)	pyrrolidino substituted
r.t.	room temperature
SB(s)	superbase(s)
SBH^+	protonated form of a superbase, conjugated acid
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TIMA	tetramethylamidinium-*N,N′*-dialkylimidazolium-amide [cation]
(tmg)	*N*,*N*,*N′*,*N′*-tetramethylguanidine substituted
TMG	*N*,*N*,*N′*,*N′*-tetramethylguanidine
TMS	trimethylsilyl
*t*Hept	1,1,2,2-tetramethylpropyl
Ts	tosyl (*p*-toluenesulfonyl)
OTf	triflate (trifluoromethanesulfonate)
*t*Oct	1,1,3,3-tetramethylbutyl

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Curriculum Vitae

Roman A. Kunetskiy

Date of birth:	18 January 1984, Moscow, Russia
Marital status:	Married
Citizenship:	Russian Federation
Present address:	Zengrova 17/2557, 16000 Prague 6, Czech Republic
E-mail:	roman.kunetskiy@gmail.com

Education:

2007 – present	Ph. D., Department of Nature Science, Charles University, Prague, Czech Republic Supervisor: Dr. Ullrich Jahn
2000 –2006	M. Sc., Department of Chemistry of Russ. Acad. Sci., D. I. Mendeleev University of Chemistry and Chemical Technology, Moscow, Russia Supervisor: Dr. Alexander D. Dilman Diploma thesis title: "A New Approach for the Synthesis of Five Membered Cyclic Alkyl Nitronates (Isoxazoline-*N*-oxides)"
1999 – 2000	Moscow Chemical Lyceum (High School № 1303), Moscow, Russia

Work experience:

2007 – present	Ph. D., Department of Organic Synthesis, Institute of Organic Chemistry and Biochemistry of Cz. Acad. Sci., Prague, Czech Republic Group of Dr. Ullrich Jahn (Since 10 Sep 2010) Group of Dr. Ilya M. Lyapkalo
2006 (4 months)	Research Assistant, Department of NanoBiophotonics, Max Planck Institute for Biophysical Chemistry, Göttingen, Germany Group of Prof. Dr. Stefan W. Hell
2000 – 2006	Research Assistant, N. D. Zelinsky Institute of Organic Chemistry of Russ. Acad. Sci., Moscow, Russia Group of Prof. Dr. Sema L. Ioffe

Publications:	9 Publications in peer-reviewed journals, 1 Patent Application
Professional skills:	Organic synthesis, methodology, modern methods of analysis, isolation and purification, basicity and nucleophilicity estimation
Language skills:	Fluent English, pre-intermediate Czech, native Russian
Fields of interest:	Methodology, Organic Synthesis and Mechanisms, Superbases, NHCs, Fluorescence probes, Fluorescence Microscopy and Photomicrography

Awards and Activities:

2011	2nd prize winner, poster, XXIII Conference on Advances in Organic Synthesis (CAOS 2011). Hradec Králové, Czech Republic.

List of Publications

10) **Roman A. Kunetskiy**, Svetlana M. Polyakova, Jiří Vavřík, Ivana Císařová, Jaan Saame, Eva Roos Nerut, Ivar Koppel, Ilmar A. Koppel, Agnes Kütt, Ivo Leito, and Ilya M. Lyapkalo. A New Class of Organosuperbases *N*-Alkyl- and *N*-Aryl-1,3-dialkyl-4,5-dimethylimidazol-2-ylidene Imines: Synthesis, Structure, pK_{BH}+ Measurements, and Properties. *Chem. Eur. J.*, submitted.

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