Synthesis and Crystal Structures of 1-Alkoxy-3-alkylimidazolium Salts Including Ionic Liquids, 1-Alkylimidazole 3-oxides and 1-Alkylimidazole Perhydrates

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Functionalized quaternary imidazolium salts were prepared with the intention to obtain new ionic liquids (ILs). Thus, more than forty 3-alkoxy-1-alkylimidazolium salts, 3-alkoxy-1-alkyl-2-methylimidazolium salts, 1-methylimidazole 3-oxide and 1,2-dimethylimidazole 3-oxide as well as their salts, 1,3-dihydroxyimidazolium salts and 1,3-dihydroxy-2-methylimidazolium salts were synthesized and characterized by spectroscopy and, to a limited extent, by viscosity and conductivity measurements. Results of fourteen single crystal X-ray structure determinations are reported, among them also the parent compounds 1-hydroxyimidazole 3-oxide and 1-hydroxy-2-methylimidazole 3-oxide. Selective debenzylation of 1-benzyloxy-3-methyl imidazolium salts and mono-demethoxylation of 1,3-dimethoxyimidazolium salts were achieved by hydrogenolysis. In addition, a crystalline semiperhydrate of 1,2-dimethylimidazole was characterized. Furthermore, an addition compound of 1-methylimidazole 3-oxide with tris(2-thienyl)borane and a silver carbene complex derived from 1-benzyloxy-3-methylimidazolium hexafluorophosphate was crystallized and characterized.

Key words: Carbene, Degradability, Imidazolium, Ionic Liquid, *N*-Oxide, Perhydrate

Introduction

Room temperature ionic liquids (RTILs), formerly termed 'fused salts', represent the rare case of a family of compounds of different structural classes, which have been intentionally searched and found, namely for use as electrolytes [1]. Their further development was also primarily based on their applicability in electrochemistry [2, 3]. Meanwhile, they have found widespread applications (academic and commercial) in synthesis [4], catalysis [5, 6], analytical [7, 8] and material sciences [9, 10]. Due to their structural variability by simple chemical conversions, liquid or low-melting imidazolium salts have been published as a series as early as 1947 [11], and today they represent a predominant subclass of application-relevant ILs. The balance between chemical inertness and intended degradability requires detailed knowledge of the reactivity [12] of a certain IL. In particular, 'degradability by design' [13] may lead to even 'greener' solvents and technical working fluids [14, 15]. This concept was pursued by the incorporation of an N-O moiety into imidazolium-based ILs.

Two decades ago, some simple 1-alkoxy-3-alkylimidazolium salts were found to be liquid at r. t. [16]. This behavior was not well understood at that time, and only crystalline derivatives of this series were published [17]. In view of the growing number of applications of RTILs, this old class of compounds was revisited, and a combinatorial synthesis of a series of this type of ILs was developed. Thus, a two-step alkylation of 1-hydroxyimidazole [18] yielded 1-alkoxy-3-

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alkylimidazolium salts. Unsaturated substituents, such as propargyl (Prg) and allyl (All) groups, impose potential as selective metal extractants or as sacrificial substituents in electrochemistry [2, 5]. Moreover, they can be easily transformed into organometallic moieties bearing potential as precursors for catalysts which are compatible with ILs. In particular, the additional ether structure as a hydrogen bond acceptor may lead to interesting new properties such as altered solvation behavior. Evidently, modification can be achieved not only in cations but in anions as well, *e. g.* hydrophobic anions lead to ILs useful for tailored partitioning purposes.

The literature on imidazole *N*-oxides prior to 1970 has been reviewed [19], and 1-hydroxyimidazoles were also included. The known compounds usually have big substituents (phenyl, cyclohexyl) [20]. The focus of this work is on imidazolium salts and imidazole *N*-oxides, preferably with small or no substituents on ring carbon atoms.

This work is a continuation of our earlier studies on related 1,3-dialkoxyimidazolium salts [21].

Results and Discussion

The parent compound, 1-hydroxyimidazole 3-oxide (**1**), is readily accessible by cyclization of glyoxime and formaldehyde [22]. The employment of other aldehydes yields the corresponding 2-alkyl derivatives, such as 1-hydroxy-2-methylimidazole 3-oxide (**2**), and the use of glyoxal and hydroxylamine further simplifies the synthesis [18]. The use of diketones or their oximes gives 4,5-disubstituted products [23]. These compounds form association complexes by extremely strong hydrogen bonds [24]. Their ^{1}H NMR spectra are therefore dependent on the concentration [24], which was also observed for compounds **1** and **2**.

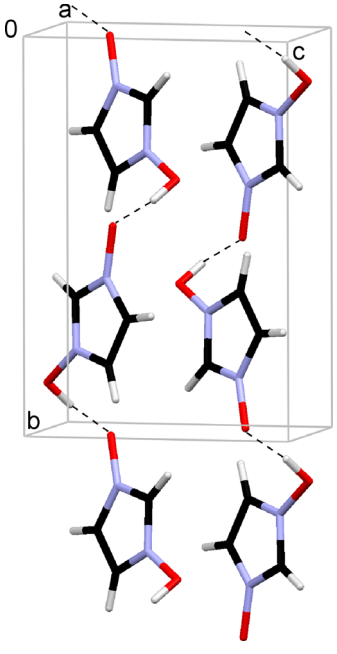


Fig. 1. Arrangement of the molecules of **1** in the crystal. Intermolecular hydrogen bonds are shown as dashed lines.

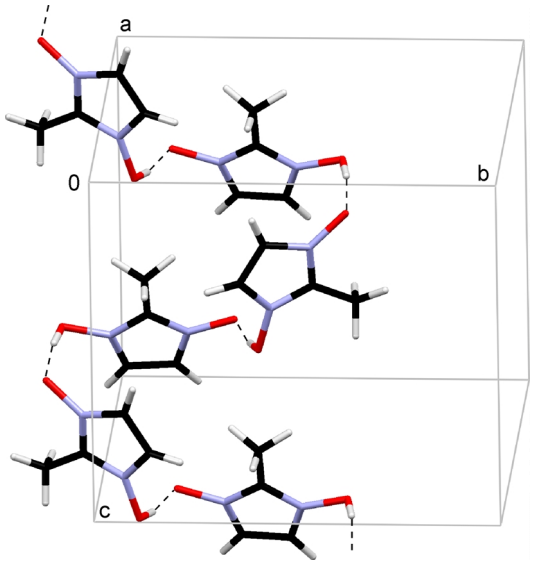
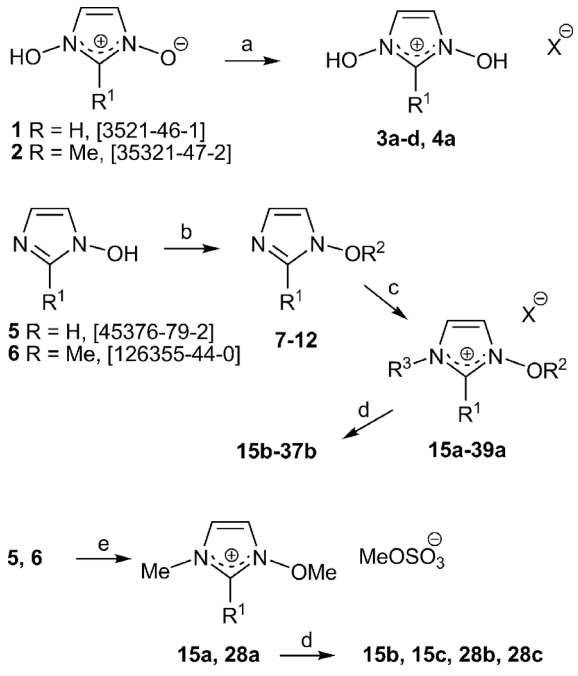


Fig. 2. Arrangement of the molecules of **2** in the crystal. Intermolecular hydrogen bonds are shown as dashed lines.

Single crystals of **1** and **2** were grown from methanol, and quite different structures were determined by X-ray diffraction. Thus, in 1-hydroxyimidazole 3-oxide (**1**), the heterocyclic rings are parallel, with very short O···O distances of 2.433 Å to the neighboring molecules at symmetry positions $(1-x, -1/2+y, 1/2-z)$ and $(1-x, 1/2+y, 1/2-z)$ forming linear chains in the direction of the crystallographic *b* axis (Fig. 1). In contrast, in 1-hydroxy-2-methylimidazole 3-oxide (**2**), the molecules form meandering chains in the direction of the crystallographic *c* axis (Fig. 2) with very short O···O distances of 2.441 Å to the neighboring molecule at $(x, 1/2-y, 1/2+z)$ and to the second independent molecule which in turn connects to the molecule at $(x, 1/2-y, -1/2+z)$. Notably, the O···O distance was previously deduced from IR spectra to be 2.4 Å [24]. It is also noteworthy that these compounds do not form hydrates, even when crystallized from water.



a) HX, H_2O; b) R^2X, Bu_4N^+ OH^-, CH_2Cl_2; c) R^3X, CH_3CN; d) ion metathesis; e) $(MeO)_2SO_2$, $NaHCO_3$.

	R^1	R^2	R^3	X
3a	H			Cl
3b	H			Br
3c	H			FAP
3d	H			Tf_2N
4a	Me			Cl
5	H			
6	Me			
7	H	Me		
8	H	All		
9	H	Bu		
10	H	Bn		
11	Me	All		
12	Me	Bu		
15b	H	Me	Me	PF_6
15c	H	Me	Me	Tf_2N
16a	H	Me	Et	I
16b	H	Me	Et	Tf_2N
17a	H	Me	Prg	Br
17b	H	Me	Prg	Tf_2N
18a	H	Me	All	I
18b	H	Me	All	Tf_2N
18c	H	Me	All	NO_2
18d	H	Me	All	NO_3
19a	H	All	Me	I
20a	H	All	Prg	Br
20b	H	All	Prg	Tf_2N
21a	H	All	All	I
22a	H	All	Bn	Br
23a	H	Bu	Me	I

	R^1	R^2	R^3	X
24a	H	Bu	Prg	Br
24b	H	Bu	Prg	ClO_4
25a	H	Bu	All	I
25b	H	Bu	All	Tf_2N
26a	H	Bu	Bn	Br
27a	H	Bn	Me	$MeOSO_3$
27b	H	Bn	Me	PF_6
27c	H	Bn	Me	Tf_2N
28a	Me	Me	Me	$MeOSO_3$
28b	Me	Me	Me	PF_6
28c	Me	Me	Me	Tf_2N
29a	Me	All	Me	I
29b	Me	All	Me	Tf_2N
30a	Me	All	Et	I
30b	Me	All	Et	Tf_2N
30c	Me	All	Et	FAP
31a	Me	All	Prg	Br
32a	Me	All	All	I
33a	Me	All	Bu	I
33b	Me	All	Bu	FAP
34a	Me	All	Bn	Br
35a	Me	Bu	Me	I
35b	Me	Bu	Me	Tf_2N
36a	Me	Bu	Et	I
36b	Me	Bu	Et	ClO_3
37a	Me	Bu	Prg	Br
37b	Me	Bu	Prg	Tf_2N
38a	Me	Bu	All	I
39a	Me	Bu	Bn	Br

Scheme 1.

Simple reactions should not be underestimated. They may lead from interesting structures to even more intriguing architectures. Thus, protonation of **1** and **2** gave both crystalline solids and protic ionic liquids, depending on the anion (Scheme 1). The chlorides **3a** and **4a** and the bromide **3b** form three totally different hydrogen bonding patterns, whereas the previously described bis(trifluoromethanesulfonyl)imide ('triflimide') **3c** [21] and the new tris(pentafluoroethyl)trifluorophosphate ('FAP') **3d** are highly interesting protic ionic liquids (PILs) [25] consisting of a very polar cation and a very hydrophobic anion. Unfortunately, their polarity on the Reichardt scale [26] could not be determined due to the insolubility of the dye. Although ^{19}F and ^{31}P NMR data are well documented [27, 28], to the best of our knowledge, we report here the first ^{13}C NMR data of the FAP anion, which are not amenable to direct measurement due to multiple couplings and sometimes are tacitly ignored [29]. The problem was convincingly solved by a two-dimensional ^{13}C-^{19}F correlation.

The crystal structures and hydrogen bonding patterns of **3a**, **3b**, and **4a** deserve some comments. In crystals of **3a**, the OH groups adopt an *anti* conformation and are rotated out of the ring plane by 60 and 80°, respectively (Fig. 3). H···Cl distances of 2.08 Å (O···Cl 2.937 Å, angle O–H···Cl 177°) and 2.15 Å (2.955 Å, 168°) were observed. The hydrogen-bonded rings in compound **3b** are in a common plane (Fig. 4). The OH groups adopt a *syn* conformation and are symmetrically rotated out of the ring plane by 87°.

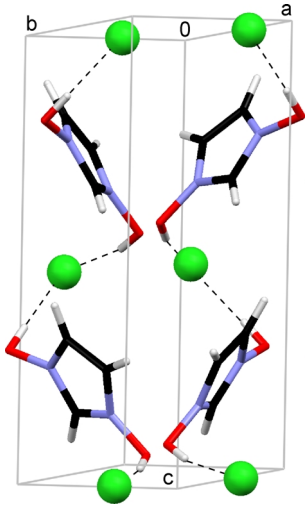


Fig. 3. Arrangement of the ions of **3a** in the crystal. Hydrogen bonds are shown as dashed lines.

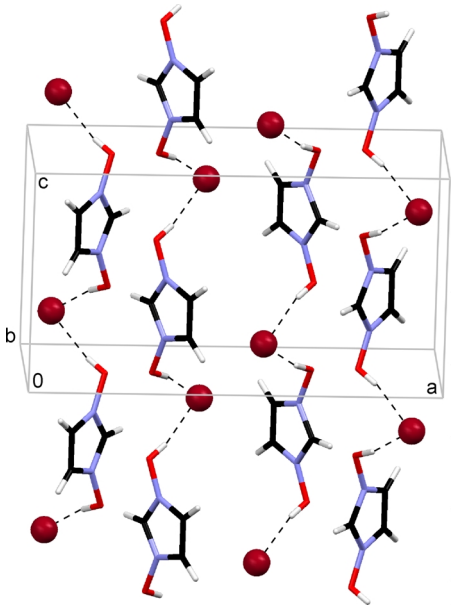


Fig. 4. Arrangement of the ions of **3b** in the crystal. Hydrogen bonds are shown as dashed lines.

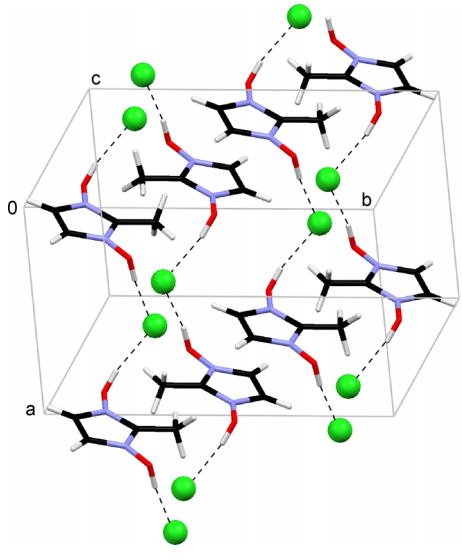


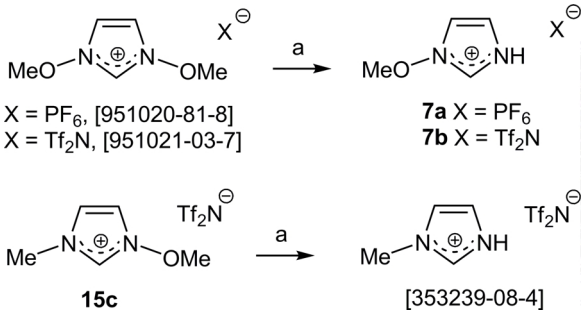
Fig. 5. Arrangement of the ions of **4a** in the crystal. Hydrogen bonds are shown as dashed lines.

The H···Br distance is 2.26 Å (O···Br 3.090 Å, angle O–H···Br 169°). In **4a**, the rings are parallel, the OH groups are *anti* and symmetrically rotated out of the ring plane by 72° (Fig. 5). H···Cl distances are 2.12 Å (O···Cl 2.959 Å, angle O–H···Cl 170°).

The major topic of this paper is, however, the synthesis of new ILs. Therefore, a series of 1-alkoxy-3-alkylimidazolium salts was prepared (Scheme 1), inluding unsaturated substituents, such as allyl and propargyl, as functionalized ILs [30]. Several methods were employed. A two-step alkylation of 1-hydroxyimidazoles **5** and **6** [18] yielded 1-alkoxy-3-alkylimidazolium salts with different alkyl groups. Exhaustive methylation of 1-hydroxyimidazole hydrochloride represents a simple and efficient procedure for the synthesis of the 1-methoxy-3-methylimidazolium salts (Scheme 1). Another possibility is the selective monodemethoxylation of 1,3-dimethoxyimidazolium salts by hydrogenolysis (Scheme 2), followed by quaternization. In cases when dimethyl sulfate was used as the alkylating reagent, the resulting methosulfates were not isolated. Instead the hexafluorophosphates were precipitated, which constitutes a superior method of purification. Ion metathesis of the bromides and iodides by the silver salt method gave the respective nitrate, nitrite, and the easily inflammable chlorate and perchlorate. The lipophilic ILs with triflimide and FAP anions were obtained by extraction from aqueous solution (Scheme 1). Selected conductivity and viscosity data are presented in Table 1. Some of these ILs are subcooled melts since they underwent slow crys-

Table 1. Density d (g cm^{-3}), viscosity η (mPa s) and conductivity σ (mS cm^{-1}) of selected ionic liquids.

	d (25 °C)	η (T, °C)	σ (25 °C)
23a	1.28	166 (60)	–
24a	1.25	226 (60)	
		87 (80)	–
26a	1.50	144 (60)	0.093
21a	1.45	90 (60)	0.540
22a	1.20	213 (60)	0.001
38a	1.30	187 (60)	0.118
39a	1.20	204 (70)	0.014
32a	1.10	240 (70)	–
31a	1.24	192 (80)	–



a) 4 bar H_2, Pd/C, MeOH, r. t.

Scheme 2.

tallization, sometimes after months, and it is possible that some others will do just that in the course of time.

The crystal structures of three typical examples were determined. The packing diagram of 1-benzyloxy-3-methylimidazolium hexafluorophosphate (**27b**) is shown in Fig. 6. In 1-allyloxy-2,3-dimethylimidazolium iodide (**29a**), weak C–H···I interactions were observed, with alternating H···I distances of 3.06 Å (C···I 3.975 Å, angle C–H···I 162°) and 3.11 Å (C···I 3.962 Å, angle C–H···I 150°), respectively. Another short contact between one of the CH_2 group hydrogens and O at $(x, -1/2-y, 1/2+z)$ with an H···O distance of 2.55 Å (C···O 3.037 Å, angle C–H···O 110°) was found (Fig. 7). Similarly, in 1-butyloxy-2,3-dimethylimidazolium iodide (**35a**), weak C–H···I interactions were found, with alternating H···I distances of 3.01 Å (C···I 3.919 Å, angle C–H···I 160°) and 3.12 Å (C···I 3.966 Å, angle C–H···I 149°), respectively. Again, a short contact between one of the CH_2 group hydrogens and O at $(1/2+x, -1/2-y, z)$ with an H···O distance of 2.58 Å (C···O 3.054 Å, angle C–H···O 110°) was observed (Fig. 8).

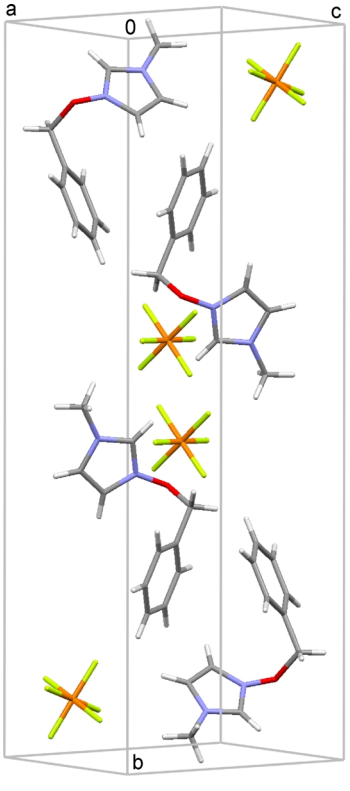


Fig. 6. Arrangement of the ions of **27b** in the crystal.

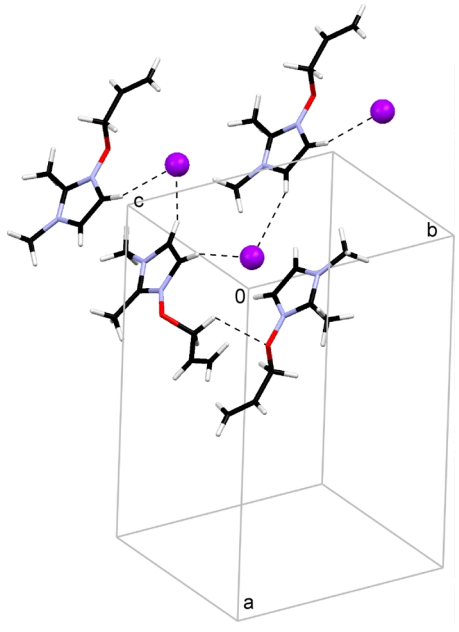


Fig. 7. Arrangement of the ions of **29a** in the crystal. Hydrogen bonds are shown as dashed lines.

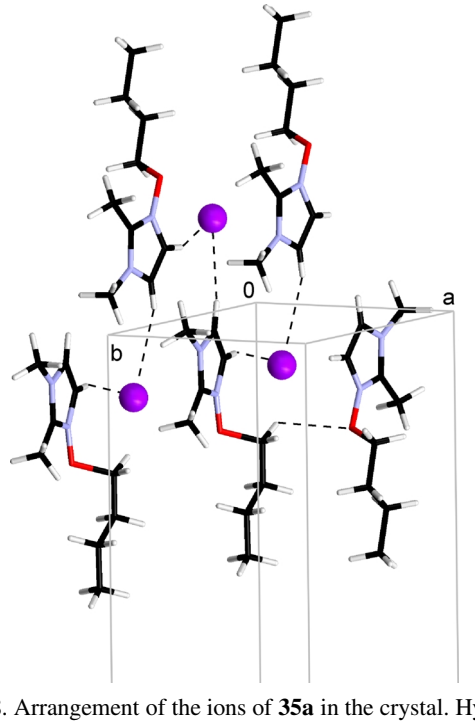
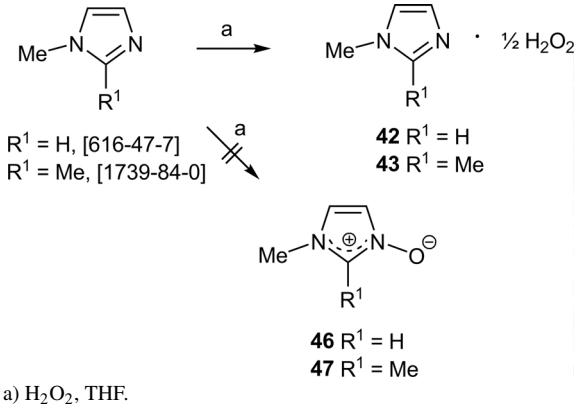


Fig. 8. Arrangement of the ions of **35a** in the crystal. Hydrogen bonds are shown as dashed lines.

We then turned our attention to imidazole *N*-oxides. Direct oxidation of imidazoles using peracids re-

portedly gave disappointing yields, due to re-deoxygenation by the oxidant [31]. So much the more interesting was a recent publication claiming an incredibly facile synthesis of 1-methylimidazole 3-oxide by oxidation of 1-methylimidazole with hydrogen peroxide [32]. In the light of the earlier results, that seemed to be almost too good to be true. Therefore, it prompted us to reinvestigate the chemistry of the imidazole *N*-oxides.

However, the ^{1}H NMR shift of 2-H in the product **42**, prepared as described [32], was not typical of a quaternary imidazolium compound. Furthermore, methylation of this compound, as described [32], gave a product with two identical methyl groups, indicative of a 1,3-dimethylimidazolium salt and not a 1-methoxy-3-methylimidazolium cation, which we were already familiar with. Moreover, applying the described procedure to 1-methylimidazole and 1-ethylimidazole, followed by ethylation and methylation, respectively, gave identical products instead of the expected isomeric 1-ethoxy-3-methylimidazolium and 1-ethyl-3-methoxyimidazolium salts. Thus, it became evident that the oxidation had not yielded the desired *N*-oxide. The final confirmation was received by crystal structures of the actual alkylation products, 1-ethyl-3-methylimidazolium isolated as the tetraphenylborate, and the primary oxidation product which turned out to be a hydrogen peroxide addition compound (Scheme 3). The crystal structure of the stable 1,2-dimethylimidazole semiperhydrate (**43**) showed a H_2O_2 molecule coordinated to two imidazole molecules (second molecule at $1-x$, y, $-z$), with an H···N distance of 1.73 Å (O···N 2.730 Å, angle O–H···N 171°) (Fig. 9). The O–O bond length is 1.431 Å, and the torsion angle of the H_2O_2 molecule was found to be 85°.



a) H_2O_2, THF.

Scheme 3.

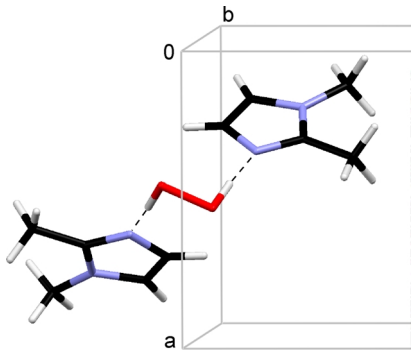
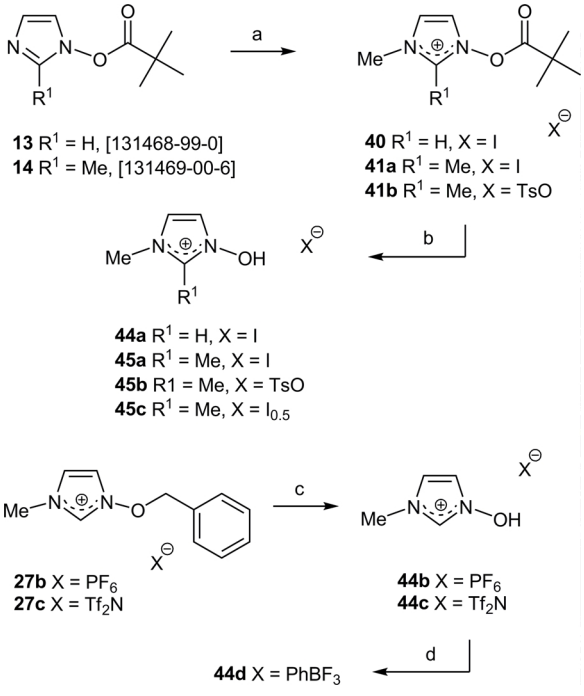


Fig. 9. Arrangement of the molecules of **43** in the crystal. Hydrogen bonds are shown as dashed lines.

This stable, water-free, liquid stoichiometric perhydrate may be considered as a substitute for the respective DABCO or urea perhydrates.

As an alternative pathway, preparation of imidazole *N*-oxides from 1-hydroxyimidazoles requires *O*-protection. A tried and confirmed procedure involves *O*-pivaloylation of 1-hydroxyimidazoles to form **13** and **14**, *N*-quaternation to form **40a**, **41a**, and **41b**, followed by deprotection to yield a salt of the *N*-oxide [17] (Scheme 4). This method was used for



a) alkylation; b) MeOH; c) 1 bar H_2, Pd/C, MeOH, 0 °C; d) ion metathesis.

Scheme 4.

the preparation of compounds **44a** – **45c**. The drawback of this approach is that the pivaloyl derivatives are rather unstable. A new and better approach is *via* quaternization of 1-benzyloxyimidazole (**10**), which can be conveniently prepared by a known method from **1** [33]. The selective hydrogenation of 1-benzyloxyimidazole to 1-hydroxyimidazole has been described [33]. Consequently, we investigated and found that the same method could be applied for the mild debenzylation of quaternary 3-methyl-1-benzyloxyimidazolium salts (Scheme 4) without disturbing the N–O bond, even after a prolonged reaction time. Now, this opens a new, straightforward access to 3-alkylimidazole 1-oxide salts. The iodide **44a**, hexafluorophosphate **44b**, and triflimide **44c** were prepared, but all remained liquid. At last, the phenyltrifluoroborate **44d** was obtained as a crystalline solid.

In the crystal of 1-hydroxy-2,3-dimethylimidazolium tosylate (**45b**), hydrogen bonds with an H···O distance of 1.72 Å (O···O 2.546 Å, angle O–H···O 162°) were observed (Fig. 10). Crystals of bis(1,2-dimethylimidazole 3-oxide) hydroiodide **45c** were fortuitously obtained from the mother liquor of the corresponding pivaloyl derivative **41a**, obviously because of hydrolysis. Hydrogen bonds between a protonated and an unprotonated *N*-oxide molecule were found (Fig. 11),

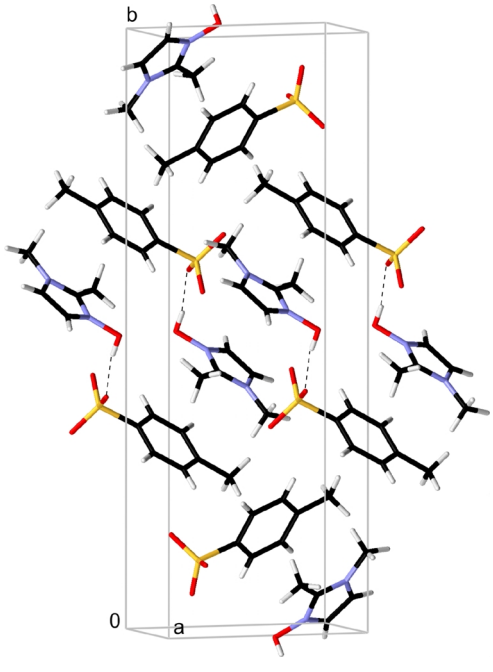


Fig. 10. Arrangement of the molecules of **45b** in the crystal. Intermolecular hydrogen bonds are shown as dashed lines.

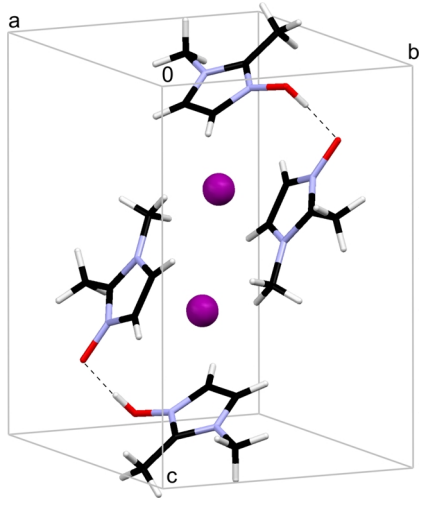
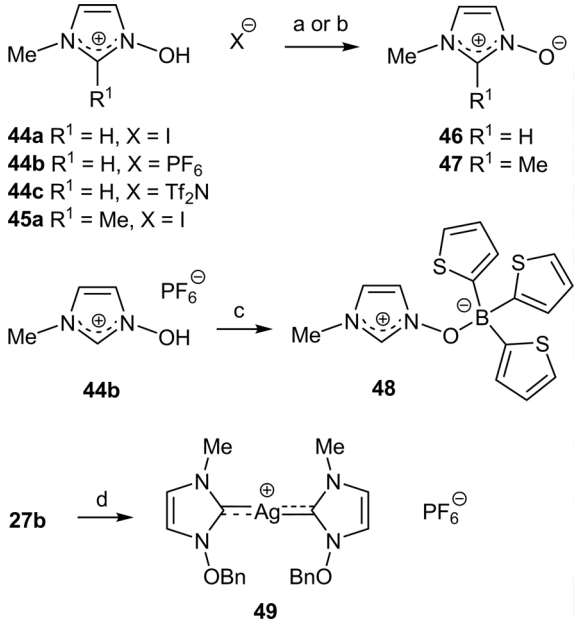


Fig. 11. Arrangement of the ions of **45c** in the crystal. Intermolecular hydrogen bonds are shown as dashed lines.

with an H···O distance of 1.59 Å (O···O 2.427 Å, angle O–H···O 174°).

First, the *N*-oxides **46** and **47** were obtained by treatment of the hydroiodides **44a** and **45a** with silver oxide in methanol (Scheme 5) as brown oils, probably due to the presence of iodine and colloidal silver and, in the case of **46**, possibly due to partial carbene forma-



a) Ag_2O, MeOH; b) IRA 400, H_2O/MeOH; c) $KB(C_4H_3S)_4$, H_2O; d) Ag_2O, MeOH.

Scheme 5.

tion. The 2-methyl compound **47** was subsequently purified by crystallization. However, a purer sample of **46** was only obtained by hydrogenolysis of 1-benzyloxy-3-methylimidazolium hexafluorophosphate (**27b**) and triflimide (**27c**), respectively, and neutralization of the resulting salts using an anion exchange resin in aqueous solution (Scheme 5). Nonetheless, it did not crystallize at r. t. It is noteworthy that the reported [34] rearrangement of 2-unsubstituted *N*-oxides to imidazol-2-ones was not observed at all.

In general, we observed that the 2-methyl compounds crystallized better than the unsubstituted ones. Hence, the crystal structure of 1,2-dimethylimidazole 3-oxide (**47**) was readily obtained (Fig. 12). So far, attempts to grow suitable crystals of 1-methylimidazole 3-oxide (**46**) or protonated derivatives thereof were unsuccessful. However, in analogy to the reported dethienylation of potassium tetrakis(2-thienyl)borate by pyridine hydrochloride [35], the respective reaction (Scheme 5) with 1-hydroxy-3-methylimidazolium hexafluorophosphate (**44b**) led to immediate precipitation of the crystalline 1-methylimidazole 3-oxide tris(2-thienyl)borane adduct (**48**). The molecular structure of this compound is shown in Fig. 13 as the ultimate proof of the N–O moiety. Finally, a crystalline silver carbene complex **49** was obtained from 1-benzyloxy-3-methylimidazolium hexafluorophosphate and silver oxide (Scheme 5), the first one with this type of ligand (Fig. 14).

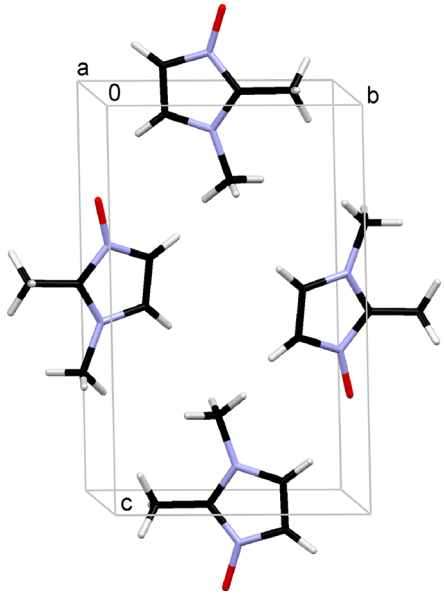


Fig. 12. Arrangement of the molecules of **47** in the crystal.

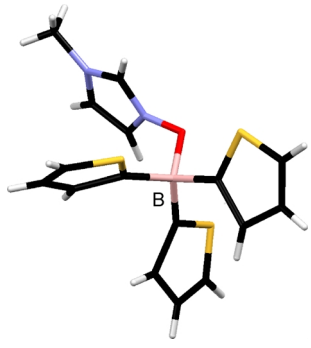


Fig. 13. Molecular structure of **48**.

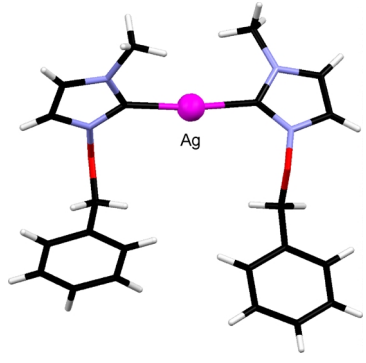


Fig. 14. Molecular structure of **49** (hexafluorophosphate ion omitted for clarity).

'Degradability by design' seems to be a promising concept which has been implemented by the incorporation of a N–O moiety into imidazolium-based ILs. For example, demethoxylation by hydrogenolysis of 1-methoxy-3-methylimidazolium salts leads to the destruction of the quaternary character of the salt (Scheme 2). It can be expected that this reaction may be generally applied to 1-alkyl-3-methoxyimidazolium salts. Thus, 1-alkyl-3-methoxyimidazolium salts may become new valuable and degradable work-horse ILs.

Conclusion

After all, some general conclusions can be drawn. The title compounds can be synthesized by more or less efficient methods to give new ILs or interesting crystalline solids. Most interesting appear to be the selective hydrogenations which will be the subject of further investigations. Obviously, these hydrogenations can be tailored to cleave the N–O or C–O bonds depending on the respective substituents and by selecting the appropriate conditions. This property makes 1-alk-

oxy-3-alkylimidazolium salts an interesting new class of patent-free ILs.

Experimental Section

NMR spectra were recorded using Varian Gemini 200, Bruker DPX 300, and Varian Unity 500 spectrometers. IR spectra were obtained with a Nicolet 5700 FT spectrometer, X-ray diffraction data were collected on Nonius Kappa CCD and Stoe IPDS 2 diffractometers. Viscosity measurements were performed with a rolling ball viscometer AMV200 (Anton Paar/Austria) connected to a thermostat; the capillary was charged and sealed under argon in a M. Braun Labstar glovebox. Conductivities were measured with a Metrohm 712 Conductometer. Due to the extreme hygroscopicity of most of the compounds, only a selected number was subjected to elemental analysis, performed at the Institute of Physical Chemistry, Microanalytical Laboratory, University of Vienna.

*1-Hydroxyimidazole 3-oxide (**1**)*

M. p., ^{1}H NMR, and ^{13}C NMR: see ref. [18]. – IR (neat): ν = 3165, 3137, 3106, 1531, 1375, 1272, 1196, 1064, 985, 782, 727, 598 cm^{-1}.

*1-Hydroxy-2-methylimidazole 3-oxide (**2**)*

M. p., ^{1}H NMR, and ^{13}C NMR: see ref. [18]. – IR (neat): ν = 3117, 1573, 1383, 1365, 1349, 1227, 1190, 1083, 977, 893, 753, 600 cm^{-1}.

*1,3-Dihydroxyimidazolium chloride (**3a**)*

A solution of 1-hydroxyimidazole 3-oxide (**1**) (5.0 g, 50 mmol) in H_2O (2 mL) and conc. HCl (5 mL) was evaporated under reduced pressure at 60 °C to yield colorless crystals (100 %). Single crystals were grown from MeOH. M. p. 114 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 3.6 (br s, 2H), 7.87 (d, J = 1.8 Hz, 2H), 9.75 (t, J = 1.8 Hz, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 118.1 (2C), 127.9. – IR (neat): ν = 3162, 3138, 3099, 2971, 2823, 2560, 1587, 1574, 1469, 1342, 1152, 1077, 1009, 802, 695, 588, 481 cm^{-1}.

*1,3-Dihydroxyimidazolium bromide (**3b**)*

Slow evaporation of a solution of **1** and HBr in MeOH/H_2O. M. p. 126 – 127 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 4.5 (br s, 2H), 7.93 (d, J = 1.9 Hz, 2H), 9.85 (t, J = 2.0 Hz, 1H). – IR (neat): ν = 3158, 3135, 3116, 3103, 2908, 2695, 1551, 1480, 1403, 1360, 1336, 1152, 1006, 804, 762, 743, 723, 662, 586 cm^{-1}.

*1,3-Dihydroxyimidazolium tris(pentafluoroethyl)trifluorophosphate (**3c**)*

1,3-dihydroxyimidazolium chloride (**3a**; 0.25 g, 1.8 mmol) and potassium tris(pentafluoroethyl)trifluorophosphate (0.88 g, 1.8 mmol) were stirred in H_2O (5 mL) for 10 min. Repeated extraction with CH_2Cl_2 (5 × 10 mL) and evaporation of the solvent yielded 0.62 g (63 %). n_D^{20} = 1.3666. – ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 6.2 (br s, 2H), 7.17 (d, J = 2.2 Hz, 2H), 8.62 (t, J = 2.2 Hz, 1H). – ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 117.5 (2C), 119.3 (CF_2), 121.2 (CF_2), 122.0 (CF_3), 122.8 (CF_3), 126.4. – ^{19}F NMR (188 MHz, CD_2Cl_2): δ = −44.6 (md, J_{F-P} = 887 Hz, 1F), −79.9 (m, 3F), −81.6 (m, 6F), −87.9 (md, J_{F-P} = 897 Hz, 2F), −115.4 (md, J_{F-P} = 81 Hz, 2F), −115.8 (md, J_{F-P} = 97 Hz, 4F). – IR (neat): ν = 3176, 2800, 1618, 1497, 1296, 1185, 1127, 1098, 969, 793, 706, 617 cm^{-1}.

*1,3-Dihydroxy-2-methylimidazolium chloride (**4a**)*

Same procedure as for **3a**. M. p. 141 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.58 (s, 3H), 3.9 (br s, 2H), 7.89 (s, 2H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 7.5, 116.6 (2C), 136.7. – IR (neat): ν = 3124, 3099, 2888, 2853, 2631, 1600, 1471, 1357, 1112, 952, 737, 709, 677, 622, 530 cm^{-1}.

*1-Hydroxyimidazole (**5**) and 1-hydroxy-2-methylimidazole (**6**)*

Prepared as described earlier [18].

*1-Methoxyimidazolium hexafluorophosphate (**7a**)*

A solution of 1,3-dimethoxyimidazolium hexafluorophosphate [21] (10.0 g, 36 mmol) in MeOH (180 mL) was hydrogenated at ambient temperature / 4 bar for 7 h using 5 % Pd/C (0.5 g) as catalyst. The mixture was filtered, and the solvent evaporated to give 8.8 g (90 %) of the product. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 4.22 (s, 3H), 7.67 (s, 1H), 8.16 (s, 1H), 9.52 (s, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 69.3, 118.2, 118.4, 131.5. – IR (neat): ν = 3348, 3190, 3160, 1572, 1454, 1442, 1011, 953, 810, 741, 613, 550 cm^{-1}.

*1-Methoxyimidazolium bis(trifluoromethanesulfonyl)imide (**7b**)*

Same procedure as for **7a**. IR (neat): ν = 3153, 1573, 1345, 1179, 1129, 1051, 1010, 952, 790, 740, 608, 570, 511 cm^{-1}.

*General procedure for the preparation of compounds **9**, **11** and **12***

These compounds were prepared by the previously published method in an analogous manner as the known compounds **7** and **8** [17]. 1-Benzyloxyimidazole (**10**) was pre-

pared by the action of PCl_3 upon 1-benzyloxyimidazole 3-oxide as described [33].

*1-Butyloxyimidazole (**9**)*

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.96 (t, J = 7.2 Hz, 3H), 1.46 (m, 2H), 1.68 (m, 2H), 4.17 (t, J = 6.5 Hz, 2H), 6.94 (t, J = 1.2, 1H), 7.07 (t, J = 1.2, 1H), 7.60 (t, J = 1.2, 1H).

*1-Allyloxy-2-methylimidazole (**11**)*

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.30 (s, 3H), 4.50 (d, J = 7.0 Hz, 2H), 5.24 – 5.34 (m, 2H), 5.85 – 6.05 (m, 1H), 6.73 (d, J = 1.5 Hz, 1H), 6.92 (d, J = 1.5 Hz, 1H).

*1-Butyloxy-2-methylimidazole (**12**)*

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.3 Hz, 3H), 1.42 (m, 2H), 1.66 (m, 2H), 4.03 (t, J = 6.6 Hz, 2H), 6.74 (d, J = 1.2 Hz, 1H), 6.92 (d, J = 1.2 Hz, 1H).

*1-Pivaloyloxyimidazole (**13**) and 2-methyl-1-pivaloyloxyimidazole (**14**)*

Prepared as described earlier [17].

*1-Methoxy-3-methylimidazolium hexafluorophosphate (**15b**)*

A mixture of dimethyl sulfate (4.62 g, 0.036 mol) and 1-hydroxyimidazole hydrochloride (2.2 g, 0.018 mol) was stirred at 50 °C overnight. $NaHCO_3$ (1.51 g, 0.018 mol) was added, and stirring was continued for 6 h at r. t., then another portion of $NaHCO_3$ (1.51 g, 0.018 mol) was added. The product, 1-methoxy-3-methylimidazolium methosulfate (**15a**), was not isolated, but converted to the hexafluorophosphate. Addition of H_2O (20 mL) yielded a clear solution to which NH_4PF_6 (2.94 g, 0.018 mol) was added. The precipitate was ultrasonicated for 1 h, filtered, and dried to give the product as a colorless powder. Single crystals were obtained by slow evaporation of a MeOH solution. M. p. 100 – 101 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 3.83 (s, 3H), 4.21 (s, 3H), 7.72 (t, J = 1.8 Hz, 1H), 8.19 (t, J = 1.8 Hz, 1H), 9.60 (t, J = 1.8 Hz, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 36.6, 69.6, 118.5, 121.8, 133.0. – IR (neat): ν = 3163, 1644, 1449, 1299, 1139, 1027, 952, 835, 730, 557 cm^{-1}.

*1-Methoxy-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (**15c**)*

From **15b** by the general procedure for **16b** – **37b**. n_D^{20} = 1.4235. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 3.82 (s, 3H), 4.21 (s, 3H), 7.72 (t, J = 1.9 Hz, 1H), 8.20 (t, J = 1.9 Hz, 1H), 9.60 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3148, 1347, 1328, 1176, 1132, 1051, 951, 740, 612, 569, 510 cm^{-1}.

*General procedure for the preparation of compounds **16a** – **39a** and **16b** – **37b***

The alkylating reagent (0.011 mol) was added to a solution of 1-alkoxyimidazole (0.010 mol) in anhydrous CH_3CN (5 mL). The reaction mixture was stirred for 3 d at r. t. The solvent was evaporated, and the residue was washed with Et_2O (3 × 20 mL). The products **16a** – **39a** were dried *in vacuo*. Ion metathesis was effected by addition of an aqueous solution of an equimolar amount of either the respective silver salt and centrifugation, or $LiTf_2N$ or KFAP, followed by extraction with CH_2Cl_2, and evaporation of the solvent to give **16b** – **37b**.

*3-Ethyl-1-methoxyimidazolium iodide (**16a**)*

Yield: 64 %. – M. p. 88 – 90 °C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.67 (t, J = 7.4 Hz, 3H), 4.45 (s, 3H), 4.55 (q, J = 7.4 Hz, 2H), 7.56 (t, J = 2.0 Hz, 1H), 7.66 (t, J = 2.0 Hz, 1H), 10.46 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3054, 3018, 2937, 1643, 1563, 1546, 1442, 1324, 1157, 1025, 944, 840, 767, 649, 621, 589 cm^{-1}.

*3-Ethyl-1-methoxyimidazolium bis(trifluoromethanesulfonyl)imide (**16b**)*

n_D^{20} = 1.4250. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.60 (t, J = 7.4 Hz, 3H), 4.31 (s, 3H), 4.33 (q, J = 7.4 Hz, 2H), 7.32 (t, J = 2.0 Hz, 1H), 7.52 (t, J = 2.0 Hz, 1H), 9.11 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3145, 1566, 1546, 1347, 1327, 1177, 1132, 1051, 950, 740, 611, 569, 508 cm^{-1}.

*1-Methoxy-3-propargylimidazolium bromide (**17a**)*

Yield: 88 %. – M. p. 85 – 86 °C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.79 (t, J = 2.6 Hz, 1H), 4.43 (s, 3H), 5.57 (d, J = 2.6 Hz, 2H), 7.71 (t, J = 2.0 Hz, 1H), 7.74 (t, J = 2.0 Hz, 1H), 10.81 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3053, 3019, 2937, 2124, 1564, 1442, 1324, 1157, 1024, 944, 840, 767, 621, 590 cm^{-1}. – $C_7H_9BrN_2O$ (217.06): calcd. C 38.73, H 4.18, N 12.91; found C 37.48, H 4.43, N 12.38.

*1-Methoxy-3-propargylimidazolium bis(trifluoromethanesulfonyl)imide (**17b**)*

Yield: 66 %. – n_D^{20} = 1.4366. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.78 (t, J = 2.6 Hz, 1H), 4.34 (s, 3H), 5.12 (d, J = 2.6 Hz, 2H), 7.51 (t, J = 2.0 Hz, 1H), 7.57 (t, J = 2.0 Hz, 1H), 9.17 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3145, 1564, 1447, 1346, 1327, 1178, 1131, 1050, 949, 740, 598, 569, 509 cm^{-1}.

*3-Allyl-1-methoxyimidazolium iodide (**18a**)*

Yield: 92 %. – M. p. 74 – 77 °C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.45 (s, 3H), 5.14 (d, J = 6.6 Hz, 2H), 5.52 –

5.67 (m, 2H), 6.03 – 6.23 (m, 1H), 7.53 (t, J = 2.0 Hz, 1H), 7.75 (t, J = 2.0 Hz, 1H), 10.31 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3065, 3008, 2937, 1560, 1443, 1309, 1157, 1055, 1022, 936, 850, 752, 680, 625, 611, 572 cm^{-1}. – $C_7H_{11}IN_2O$ (266.08): calcd. C 31.60, H 4.17, N 10.53; found C 31.64, H 4.17, N 10.46.

*3-Allyl-1-methoxyimidazolium bis(trifluoromethanesulfonyl)imide (**18b**)*

Yield: 57 %. – n_D^{20} = 1.4349. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.32 (s, 3H), 4.85 (d, J = 6.6 Hz, 2H), 5.51 – 5.59 (m, 2H), 5.91 – 6.11 (m, 1H), 7.30 (t, J = 2.0 Hz, 1H), 7.55 (t, J = 2.0 Hz, 1H), 9.06 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3145, 1347, 1328, 1178, 1132, 1052, 949, 740, 611, 569, 509 cm^{-1}.

*3-Allyl-1-methoxyimidazolium nitrite (**18c**)*

Yield: 68 %. – n_D^{20} = 1.4884. – ^{1}H NMR (200 MHz, [D_6]DMSO): δ = 4.25 (s, 3H), 4.82 (d, J = 6.0 Hz, 2H), 5.31 – 5.41 (m, 2H), 6.05 (m, 1H), 7.79 (t, J = 2.0 Hz, 1H), 8.28 (t, J = 2.0 Hz, 1H), 9.77 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3080, 1646, 1562, 1448, 1328, 1212, 1022, 946, 749, 610 cm^{-1}.

*3-Allyl-1-methoxyimidazolium nitrate (**18d**)*

Yield: 89 %. – n_D^{20} = 1.5159. – ^{1}H NMR (200 MHz, [D_6]DMSO): δ = 4.25 (s, 3H), 4.82 (d, J = 6.0 Hz, 2H), 5.30 – 5.41 (m, 2H), 6.05 (m, 1H), 7.78 (t, J = 2.0 Hz, 1H), 8.28 (t, J = 2.0 Hz, 1H), 9.74 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3085, 1562, 1448, 1320, 1158, 1022, 946, 829, 746, 679, 625, 610 cm^{-1}.

*1-Allyloxy-3-methylimidazolium iodide (**19a**)*

Yield: 61 %. – n_D^{20} = 1.5920. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.20 (s, 3H), 5.05 (d, J = 6.9 Hz, 2H), 5.52 – 5.65 (m, 2H), 6.01 – 6.22 (m, 1H), 7.53 (m, 2H), 10.26 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3066, 1570, 1540, 1421, 1323, 1153, 1020, 937, 885, 731, 617, 585 cm^{-1}.

*1-Allyloxy-3-propargylimidazolium bromide (**20a**)*

Yield: 83 %. – M. p. 59 – 61 °C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.79 (t, J = 2.6 Hz, 1H), 5.04 (d, J = 6.9 Hz, 2H), 5.52 – 5.62 (m, 2H), 5.58 (d, J = 2.6 Hz, 2H), 6.00 – 6.20 (m, 1H), 7.71 (t, J = 2.0 Hz, 1H), 7.74 (t, J = 2.0 Hz, 1H), 10.71 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3165, 3109, 3046, 2937, 2119, 1558, 1434, 1422, 1304, 1151, 1016, 940, 917, 729, 719, 605 cm^{-1}.

*1-Allyloxy-3-propargylimidazolium bis(trifluoromethanesulfonyl)imide (**20b**)*

Yield: 57 %. – n_D^{20} = 1.4414. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.77 (t, J = 2.6 Hz, 1H), 4.91 (d, J = 7.0 Hz, 2H), 5.12 (d, J = 2.6 Hz, 2H), 5.47 – 5.59 (m, 2H), 5.96 – 6.17 (m, 1H), 7.48 (t, J = 2.0 Hz, 1H), 7.50 (t, J = 2.0 Hz, 1H), 9.12 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3146, 1346, 1327, 1181, 1132, 1052, 951, 739, 612, 599, 569, 509 cm^{-1}.

*3-Allyl-1-allyloxyimidazolium iodide (**21a**)*

Yield: 68 %. – n_D^{20} = 1.5960. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.08 (d, J = 6.8 Hz, 2H), 5.15 (d, J = 6.5 Hz, 2H), 5.50 – 5.66 (m, 4H), 6.00 – 6.22 (m, 2H), 7.45 (t, J = 2.0 Hz, 1H), 7.57 (t, J = 2.0 Hz, 1H), 10.31 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3061, 2973, 1559, 1539, 1444, 1422, 1318, 1147, 1020, 992, 936, 885, 730, 622, 603 cm^{-1}.

*1-Allyloxy-3-benzylimidazolium bromide (**22a**)*

Yield: 93 %. – n_D^{20} = 1.5875. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.97 (d, J = 6.9 Hz, 2H), 5.43 – 5.55 (m, 2H), 5.72 (s, 2H), 5.95 – 6.16 (m, 1H), 7.35 – 7.60 (m, 6H), 7.66 (t, J = 2.0 Hz, 1H), 10.86 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3031, 2967, 1558, 1540, 1497, 1456, 1312, 1146, 1020, 935, 885, 711, 697, 600 cm^{-1}.

*1-Butyloxy-3-methylimidazolium iodide (**23a**)*

Yield: 67 %. – n_D^{20} = 1.5680. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.3 Hz, 3H), 1.52 (m, 2H), 1.88 (m, 2H), 4.22 (s, 3H), 4.59 (t, J = 6.6 Hz, 2H), 7.57 (d, J = 2.0 Hz, 1H), 7.63 (d, J = 2.0 Hz, 1H), 10.26 (t, J = 2.0 Hz, 1H). – IR (neat): ν = 3063, 2958, 2872, 1569, 1465, 1329, 1156, 1054, 1020, 933, 834, 735, 618, 594 cm^{-1}. – $C_8H_{15}IN_2O$ (282.12): calcd. C 34.06, H 5.36, N 9.93; found C 33.92, H 5.56, N 10.17.

*1-Butyloxy-3-propargylimidazolium bromide (**24a**)*

Yield: 92 %. – n_D^{20} = 1.5401. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.3 Hz, 3H), 1.52 (m, 2H), 1.79 (m, 2H), 2.83 (t, J = 2.6 Hz, 1H), 4.58 (t, J = 6.6 Hz, 2H), 5.60 (d, J = 2.6 Hz, 2H), 7.79 (t, J = 2.0 Hz, 1H), 7.82 (t, J = 2.0 Hz, 1H), 10.96 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3041, 2958, 2933, 2873, 2122, 1558, 1465, 1319, 1149, 1012, 934, 835, 734, 704, 601 cm^{-1}.

*1-Butyloxy-3-propargylimidazolium perchlorate (**24b**)*

Yield: 82 %. – n_D^{20} = 1.4875. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.3 Hz, 3H), 1.33 – 1.51 (m, 2H), 1.65 – 1.80 (m, 2H), 2.71 (t, J = 2.4 Hz, 1H), 4.44 (t, J = 6.5 Hz, 2H), 5.12 (d, J = 2.4 Hz, 2H), 7.50 (m, 2H), 9.12 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3137, 2962, 1562, 1331, 1072, 932, 835, 733, 619 cm^{-1}.

*3-Allyl-1-butyloxyimidazolium iodide (**25a**)*

Yield: 71 %. – M. p. 55 – 56 °C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.3 Hz, 3H), 1.52 (m, 2H), 1.77 (m, 2H), 4.62 (t, J = 6.6 Hz, 2H), 5.17 (d, J = 6.6 Hz, 2H),

5.51 – 5.66 (m, 2H), 6.12 (m, 1H), 7.50 (t, J = 2.0 Hz, 1H), 7.58 (t, J = 2.0 Hz, 1H), 10.34 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3068, 2957, 2931, 2872, 1558, 1314, 1154, 1023, 992, 930, 834, 748, 715, 630, 604, 573 cm^{-1}. – $C_{10}H_{17}IN_2O$ (308.16): calcd. C 38.98, H 5.56, N 9.09; found C 39.10, H 5.55, N 9.08.

*3-Allyl-1-butyloxyimidazolium bis(trifluoromethanesulfonyl)imide (**25b**)*

Yield: 93 %. – n_D^{20} = 1.4434. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.3 Hz, 3H), 1.39 – 1.58 (m, 2H), 1.72 – 1.86 (m, 2H), 4.47 (t, J = 6.6 Hz, 2H), 4.87 (d, J = 6.6 Hz, 2H), 5.49 – 5.58 (m, 2H), 5.92 – 6.12 (m, 1H), 7.32 (t, J = 2.0 Hz, 1H), 7.50 (t, J = 2.0 Hz, 1H), 9.10 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3142, 2966, 1347, 1328, 1180, 1133, 1052, 738, 611, 569, 510 cm^{-1}.

*3-Benzyl-1-butyloxyimidazolium bromide (**26a**)*

Yield: 95 %. – n_D^{20} = 1.5699. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.96 (t, J = 7.3 Hz, 3H), 1.47 (m, 2H), 1.76 (m, 2H), 4.54 (t, J = 6.6 Hz, 2H), 5.76 (s, 2H), 7.37 – 7.41 (m, 3H), 7.46 (t, J = 2.0 Hz, 1H), 7.50 (t, J = 2.0 Hz, 1H), 7.57 – 7.62 (m, 2H), 10.96 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3031, 2958, 2873, 1558, 1541, 1497, 1456, 1316, 1148, 1012, 934, 705, 602 cm^{-1}.

*1-Benzyloxy-3-methylimidazolium methosulfate (**27a**)*

A solution of 1-benzyloxyimidazole **10** (2.16 g, 12.4 mmol) and dimethyl sulfate (3.13 g, 2.48 mmol) was stirred at ambient temperature for 6 d. Not isolated, but converted to **27b**.

*1-Benzyloxy-3-methylimidazolium hexafluorophosphate (**27b**)*

From **27a**, by the same procedure as for **15b** (70 % yield from **10**). Crystals from MeOH. M. p. 83 – 84 °C. – ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 3.80 (s, 3H), 5.45 (s, 2H), 7.46 (s, 5H), 7.69 (t, J = 1.9 Hz, 1H), 8.06 (t, J = 1.9 Hz, 1H), 9.49 (t, J = 1.8 Hz, 1H). – ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 36.5, 83.2, 119.2, 121.6, 128.9 (2C), 130.0, 130.1 (2C), 132.1, 133.4. – IR (neat): ν = 3170, 1453, 1323, 1215, 1155, 1025, 837, 757, 733, 701, 645, 626, 588, 553 cm^{-1}.

*1-Benzyloxy-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (**27c**)*

n_D^{20} = 1.4718. – ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 3.81 (s, 3H), 5.45 (s, 2H), 7.46 (s, 5H), 7.70 (t, J = 1.7 Hz, 1H), 8.07 (t, J = 1.7 Hz, 1H), 9.50 (t, J = 1.7 Hz, 1H). – ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 36.5, 83.3, 119.3, 119.6 (q, J = 322 Hz, 2C), 121.6, 128.9 (2C), 130.0, 130.1 (2C), 132.2, 133.4. – IR (neat): ν = 3147, 1575, 1458, 1347, 1327, 1176, 1132, 1051, 947, 909, 845, 789, 760, 732, 699, 653, 599, 569, 510 cm^{-1}.

*1-Methoxy-2,3-dimethylimidazolium hexafluorophosphate (**28b**)*

Same procedure as for compound **15b** (methosulfate **28a** not isolated). Yield: 48 %. – M. p. 153 – 154 °C. – ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 2.57 (s, 3H), 3.73 (s, 3H), 4.15 (s, 3H), 7.62 (s, 1H), 8.10 (s, 1H). – ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 8.1, 35.1, 68.4, 116.6, 120.2, 141.6. – IR (neat): ν = 3154, 1597, 1460, 1448, 1339, 1244, 967, 952, 823, 728, 655, 555 cm^{-1}.

*1-Methoxy-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide (**28c**)*

Yield: 48 %. – n_D^{20} = 1.4330. – ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 2.57 (s, 3H), 3.73 (s, 3H), 4.15 (s, 3H), 7.64 (d, J = 2.2 Hz, 1H), 8.11 (d, J = 2.2 Hz, 1H). – ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 8.2, 35.1, 68.4, 116.6, 119.5 (q, J = 321 Hz, 2C), 120.2, 141.6. – IR (neat): ν = 3149, 2956, 1594, 1447, 1348, 1331, 1177, 1133, 1052, 1011, 951, 789, 739, 653, 612, 569, 511 cm^{-1}.

*1-Allyloxy-2,3-dimethylimidazolium iodide (**29a**)*

Yield: 68 %. – M. p. 126 – 127 °C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.86 (s, 3H), 4.03 (s, 3H), 5.04 (d, J = 6.9 Hz, 2H), 5.51 – 5.71 (m, 2H), 5.99 – 6.19 (m, 1H), 7.63 (d, J = 2.4 Hz, 1H), 7.65 (d, J = 2.4 Hz, 1H). – IR (neat): ν = 3067, 1610, 1597, 1427, 1335, 1244, 1198, 946, 926, 772, 748, 634, 516 cm^{-1}.

*1-Allyloxy-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide (**29b**)*

Yield: 53 %. – n_D^{20} = 1.4370. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.66 (s, 3H), 3.84 (s, 3H), 4.83 (d, J = 6.9 Hz, 2H), 5.49 – 5.57 (m, 2H), 6.04 (m, 1H), 7.21 (d, J = 2.3 Hz, 1H), 7.38 (d, J = 2.3 Hz, 1H). – IR (neat): ν = 3148, 1593, 1347, 1328, 1177, 1133, 1052, 942, 893, 739, 612, 569, 509 cm^{-1}.

*1-Allyloxy-3-ethyl-2-methylimidazolium iodide (**30a**)*

Yield: 88 %. – M. p. 78 – 79 °C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.57 (t, J = 7.4 Hz, 3H), 2.88 (s, 3H), 4.37 (q, J = 7.4 Hz, 2H), 5.06 (d, J = 6.9 Hz, 2H), 5.51 – 5.70 (m, 2H), 5.99 – 6.20 (m, 1H), 7.65 (d, J = 2.4 Hz, 1H), 7.77 (d, J = 2.4 Hz, 1H). – IR (neat): ν = 3134, 3049, 2968, 1578, 1442, 1419, 1316, 1216, 1094, 1004, 968, 885, 864, 737, 676, 580 cm^{-1}.

*1-Allyloxy-3-ethyl-2-methylimidazolium bis(trifluoromethanesulfonyl)imide (**30b**)*

Yield: 57 %. – n_D^{20} = 1.4405. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.52 (t, J = 7.4 Hz, 3H), 2.68 (s, 3H), 4.19 (q, J = 7.4 Hz, 2H), 4.85 (d, J = 6.2 Hz, 2H), 5.49 – 5.57 (m, 2H), 5.94 – 6.15 (m, 1H), 7.27 (d, J = 2.4 Hz, 1H), 7.44 (d, J = 2.4 Hz, 1H). – IR (neat): ν = 3146, 1587, 1347, 1327, 1177, 1133, 1051, 739, 612, 569, 509 cm^{-1}.

*1-Allyloxy-3-ethyl-2-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (**30c**)*

Yield: 65 %. – n_D^{20} = 1.3869. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.46 (t, J = 7.4 Hz, 3H), 2.59 (s, 3H), 4.06 (q, J = 7.4 Hz, 2H), 4.73 (d, J = 6.7 Hz, 2H), 5.40 – 5.53 (m, 2H), 5.95 (m, 1H), 7.10 (d, J = 2.4 Hz, 1H), 7.30 (d, J = 2.4 Hz, 1H). – IR (neat): ν = 3163, 2997, 1712, 1587, 1428, 1315, 1297, 1219, 1190, 1138, 1100, 974, 814, 723, 620, 534 cm^{-1}.

*1-Allyloxy-2-methyl-3-propargylimidazolium bromide (**31a**)*

Yield: 95 %. – M. p. 91 – 92 °C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.67 (t, J = 2.6 Hz, 1H), 2.93 (s, 3H), 5.03 (d, J = 6.6 Hz, 2H), 5.40 (d, J = 2.6 Hz, 2H), 5.52 – 5.70 (m, 2H), 5.97 – 6.18 (m, 1H), 7.69 (d, J = 2.4 Hz, 1H), 7.81 (d, J = 2.4 Hz, 1H). – IR (neat): ν = 3055, 2916, 2120, 1584, 1423, 1321, 1201, 944, 887, 763, 669 cm^{-1}.

*3-Allyl-1-allyloxy-2-methylimidazolium iodide (**32a**)*

Yield: 98 %. – M. p. 61 – 62 °C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.86 (s, 3H), 4.99 (d, J = 6.0 Hz, 2H), 5.07 (d, J = 6.7 Hz, 2H), 5.34 – 5.71 (m, 4H), 5.97 – 6.20 (m, 2H), 7.54 (d, J = 2.4 Hz, 1H), 7.74 (d, J = 2.4 Hz, 1H). – IR (neat): ν = 3063, 1645, 1583, 1521, 1446, 1420, 1322, 1201, 993, 938, 887, 739, 678, 643 cm^{-1}.

*1-Allyloxy-3-butyl-2-methylimidazolium iodide (**33a**)*

Yield: 63 %. – M. p. 78 – 79 °C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.3 Hz, 3H), 1.33 – 1.51 (m, 2H), 1.79 – 1.94 (m, 2H), 2.86 (s, 3H), 4.28 (t, J = 7.5 Hz, 2H), 5.08 (d, J = 6.8 Hz, 2H), 5.51 – 5.71 (m, 2H), 5.96 – 6.19 (m, 1H), 7.54 (d, J = 2.4 Hz, 1H), 7.71 (d, J = 2.4 Hz, 1H). – IR (neat): ν = 3055, 2963, 2932, 2877, 1587, 1523, 1474, 1427, 1326, 1206, 1098, 996, 946, 925, 762, 670, 653, 520 cm^{-1}.

*1-Allyloxy-3-butyl-2-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (**33b**)*

Yield: 61 %. – n_D^{20} = 1.3921. – ^{1}H NMR (200 MHz, [D_6]DMSO): δ = 0.91 (t, J = 7.2 Hz, 3H), 1.27 (m, 2H), 1.71 (m, 2H), 2.62 (s, 3H), 4.10 (t, J = 7.3 Hz, 2H), 4.90 (d, J = 6.9 Hz, 2H), 5.40 – 5.49 (m, 2H), 6.10 (m, 1H), 7.74 (d, J = 2.4 Hz, 1H), 8.12 (d, J = 2.4 Hz, 1H). – IR (neat): ν = 3163, 2969, 1587, 1295, 1210, 1181, 1125, 1097, 960, 809, 717, 616, 532 cm^{-1}.

*1-Allyloxy-3-benzyl-2-methylimidazolium bromide (**34a**)*

Yield: 75 %. – n_D^{20} = 1.5970. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.81 (s, 3H), 5.02 (d, J = 6.9 Hz, 2H), 5.45 – 5.65 (m, 2H), 5.63 (s, 2H), 5.93 – 6.14 (m, 1H), 7.39 (s, 5H), 7.64 (d, J = 2.4 Hz, 1H), 7.75 (d, J = 2.4 Hz, 1H). – IR (neat): ν = 3040, 1584, 1497, 1455, 1321, 1196, 942, 886, 728, 699 cm^{-1}.

*1-Butyloxy-2,3-dimethylimidazolium iodide (**35a**)*

Yield: 90 %. – M. p. 117 – 119 °C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.3 Hz, 3H), 1.52 (m, 2H), 1.81 (m, 2H), 2.85 (s, 3H), 4.04 (s, 3H), 4.55 (t, J = 6.4 Hz, 2H), 7.63 (d, J = 2.4 Hz, 1H), 7.69 (d, J = 2.4 Hz, 1H). – IR (neat): ν = 3064, 2952, 2932, 2871, 1613, 1598, 1339, 1248, 1199, 1120, 1053, 1015, 933, 843, 771, 749, 647, 624, 595 cm^{-1}.

*1-Butyloxy-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide (**35b**)*

Yield: 74 %. – n_D^{20} = 1.4299. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.3 Hz, 3H), 1.41 – 1.59 (m, 2H), 1.72 – 1.86 (m, 2H), 2.66 (s, 3H), 3.84 (s, 3H), 4.37 (t, J = 6.5 Hz, 2H), 7.22 (d, J = 2.4 Hz, 1H), 7.38 (d, J = 2.4 Hz, 2H). – IR (neat): ν = 3147, 2967, 1594, 1347, 1329, 1178, 1133, 1052, 738, 612, 569, 509 cm^{-1}.

*1-Butyloxy-3-ethyl-2-methylimidazolium iodide (**36a**)*

Yield: 96 %. – n_D^{20} = 1.5580. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.00 (t, 3H), 1.43 – 1.62 (m, 2H), 1.57 (t, J = 7.4 Hz, 3H), 1.70 – 1.88 (m, 2H), 2.87 (s, 3H), 4.36 (q, J = 7.4 Hz, 2H), 4.58 (t, J = 6.4 Hz, 2H), 7.57 (d, J = 2.4 Hz, 1H), 7.60 (d, J = 2.4 Hz, 1H). – IR (neat): ν = 3059, 2958, 2934, 2872, 1584, 1465, 1326, 1214, 1058, 935, 741, 661 cm^{-1}.

*1-Butyloxy-3-ethyl-2-methylimidazolium chlorate (**36b**)*

Yield: 82 %. – n_D^{20} = 1.4875. – ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 0.93 (t, J = 7.4 Hz, 3H), 1.35 (t, J = 7.3 Hz, 3H), 1.43 (m, 2H), 1.71 (m, 2H), 2.60 (s, 3H), 4.11 (q, J = 7.3 Hz, 2H), 4.36 (t, J = 6.6 Hz, 2H), 7.74 (d, J = 2.4 Hz, 1H), 8.13 (d, J = 2.4 Hz, 1H). – IR (neat): ν = 3120, 2961, 2875, 1587, 1468, 1328, 1057, 959, 928, 743, 663, 603 cm^{-1}.

*1-Butyloxy-2-methyl-3-propargylimidazolium bromide (**37a**)*

Yield: 88 %. – M. p. 118 – 119 °C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.00 (t, J = 7.3 Hz, 3H), 1.43 – 1.61 (m, 2H), 1.74 – 1.88 (m, 2H), 2.67 (t, J = 2.6 Hz, 1H), 2.93 (s, 3H), 4.54 (t, J = 6.4 Hz, 2H), 5.43 (d, J = 2.6 Hz, 2H), 7.65

(d, J = 2.4 Hz, 1H), 7.86 (d, J = 2.4 Hz, 1H). – IR (neat): ν = 3187, 3064, 2957, 2931, 2897, 2119, 1583, 1477, 1371, 1354, 1326, 1199, 1070, 946, 747, 730, 681, 627, 512 cm^{-1}.

*1-Butyloxy-2-methyl-3-propargylimidazolium bis(trifluoromethanesulfonyl)imide (**37b**)*

Yield: 89 %. – n_D^{20} = 1.4440. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.00 (t, J = 7.3 Hz, 3H), 1.51 (m, 2H), 1.82 (m, 2H), 2.67 (t, J = 2.6 Hz, 1H), 2.75 (s, 3H), 4.41 (t, J = 6.5 Hz, 2H), 4.99 (d, J = 2.6 Hz, 2H), 7.38 (d, J = 2.4 Hz, 1H), 7.42 (d, J = 2.4 Hz, 1H). – IR (neat): ν = 3146, 2966, 1586, 1347, 1327, 1179, 1133, 1052, 737, 612, 569, 510 cm^{-1}.

*3-Allyl-1-butyloxy-2-methylimidazolium iodide (**38a**)*

Yield: 91 %. – n_D^{20} = 1.5710. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.00 (t, 3H), 1.43 – 1.61 (m, 2H), 1.74 – 1.88 (m, 2H), 2.86 (s, 3H), 4.58 (t, J = 6.4 Hz, 2H), 4.99 (d, J = 6.1 Hz, 2H), 5.34 – 5.50 (m, 2H), 5.97 – 6.17 (m, 1H), 7.54 (d, J = 2.4 Hz, 1H), 7.64 (d, J = 2.4 Hz, 1H). – IR (neat): ν = 3057, 2957, 2934, 2872, 1583, 1448, 1420, 1323, 1202, 991, 933, 838, 740, 639 cm^{-1}.

*3-Benzyl-1-butyloxy-2-methylimidazolium bromide (**39a**)*

Yield: 89 %. – M. p. 75 – 77 °C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.3 Hz, 3H), 1.40 – 1.58 (m, 2H), 1.71 – 1.85 (m, 2H), 2.83 (s, 3H), 4.52 (t, J = 6.4 Hz, 2H), 5.64 (s, 2H), 7.37 – 7.45 (m, 5H), 7.62 (s, 2H). – IR (neat): ν = 3035, 2959, 2873, 1584, 1455, 1326, 1198, 934, 727, 700 cm^{-1}.

*General procedure for the preparation of compounds **40**, **41a** and **41b***

In analogy to the previously published method [17].

*3-Methyl-1-pivaloyloxyimidazolium iodide (**40a**)*

From **13** and CH_3I (yield: 58 %). – ^{1}H NMR (200 MHz, [D_6]DMSO): δ = 1.10 (s, 9H), 3.74 (s, 3H), 7.44 (t, J = 1.8 Hz, 1H), 7.50 (t, J = 1.8 Hz, 1H), 8.83 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3055, 2976, 1803, 1051, 1003, 841, 732 cm^{-1}.

*2,3-Dimethyl-1-pivaloyloxyimidazolium iodide (**41a**)*

From **14** and CH_3I (yield: 88 %). – ^{1}H NMR (200 MHz, [D_6]DMSO): δ = 1.10 (s, 9H), 2.40 (s, 3H), 3.69 (s, 3H), 7.40 (d, J = 2.0 Hz, 1H), 7.46 (d, J = 2.0 Hz, 1H). – IR (neat): ν = 3062, 2976, 1801, 1049, 1007, 841, 726 cm^{-1}.

*2,3-Dimethyl-1-pivaloyloxyimidazolium tosylate (**41b**)*

From **14** and methyl tosylate (yield: 80 %). – ^{1}H NMR (200 MHz, [D_6]DMSO): δ = 1.21 (s, 9H), 2.30 (s, 3H), 2.51 (s, 3H), 3.74 (s, 3H), 7.12 (d, J = 7.9 Hz, 2H), 7.48 (d, J = 7.9 Hz, 2H), 7.58 (d, J = 2.0 Hz, 1H), 7.80 (d, J = 2.0 Hz, 1H). – IR (neat): ν = 3084, 2976, 1802, 1189, 1118, 1032, 1009, 678, 561 cm^{-1}.

*1-Methylimidazole semiperhydrate (**42**)*

To a stirred solution of 1-methylimidazole (8.50 g, 0.1 mol) in THF (200 mL) 30 % H_2O_2 (13.6 mL, 0.12 mol) was added. The reaction mixture was stirred at r. t. for 3 h. Then, water (200 mL) was added, and the mixture was extracted with dichloromethane (3 × 100 mL). The organic layers were combined, dried over anhydrous $MgSO_4$ and concentrated. The product was obtained as a yellow oil (90 %). n_D^{20} = 1.4805. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.68 (s, 3H), 6.86 (s, 1H), 7.03 (s, 1H), 7.42 (s, 1H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 33.6, 120.8, 129.8, 138.1. – IR (neat): ν = 3112, 2810, 1597, 1521, 1420, 1285, 1231, 1107, 1081, 1028, 922, 820, 740, 660, 616 cm^{-1}.

*1,2-Dimethylimidazole semiperhydrate (**43**)*

Same procedure as for **42**. Yield: 80 %. – M. p. 19 – 23 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.30 (s, 3H), 3.48 (s, 3H), 6.70 (s, 1H), 6.80 (s, 1H), 10.8 (br s, 1H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.7, 32.9, 120.5, 126.6, 145.1. – IR (neat): ν = 3114, 2794, 1505, 1438, 1411, 1280, 1145, 989, 742, 725, 674, 643 cm^{-1}.

*1-Hydroxy-3-methylimidazolium iodide (**44a**)*

In analogy to the published procedure [17] by methanolysis of **40a** (yield: 99 %). – ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 3.82 (s, 3H), 7.65 (t, J =1.8 Hz, 1H), 7.83 (t, J = 1.8 Hz, 1H), 9.27 (t, J = 1.8 Hz, 1H). – IR (neat): ν = 3069, 2945, 2824, 2687, 1566, 1330, 1160, 1022, 793, 719, 591 cm^{-1}.

*1-Hydroxy-3-methylimidazolium hexafluorophosphate (**44b**)*

A solution of **27b** (0.5 g, 1.5 mmol) in MeOH (50 mL) was hydrogenated using 10 % Pd/C (100 mg) at atmospheric pressure / 0 °C for 2 h. The mixture was filtered, and the solvent was evaporated to yield 170 mg (46 %). – ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 3.79 (s, 3H), 7.62 (t, J = 1.8 Hz, 1H), 7.85 (t, J = 1.8 Hz, 1H), 9.27 (t, J = 1.8 Hz, 1H). – ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 36.3, 120.1, 121.3, 132.0. – IR (neat): ν = 3166, 2716, 2651, 1574, 1340, 1165, 1030, 813, 731, 623, 600, 554 cm^{-1}.

*1-Hydroxy-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (**44c**)*

From **27c** by the same procedure as for **44b**. Yield: 99 %. – n_D^{20} = 1.4241. – ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 3.80 (s, 3H), 7.64 (t, J = 1.9 Hz, 1H), 7.88 (t, J = 1.9 Hz, 1H), 9.31 (t, J = 1.9 Hz, 1H). – IR (neat): ν = 3157, 2719, 2648, 1574, 1343, 1179, 1130, 1051, 791, 741, 598, 570, 511 cm^{-1}.

*1-Hydroxy-3-methylimidazolium phenyltrifluoroborate (**44d**)*

A solution of **44b** (0.21 g, 0.86 mmol) and potassium phenyltrifluoroborate (0.16 g, 0.87 mmol) in H_2O (5 mL) was extracted with CH_2Cl_2 (3 × 5 mL). The organic extracts were dried and evaporated to yield 0.1 g of **44d** (yield 48 %). M. p. 88 – 90 °C, converts rapidly to 1-methylimidazole 3-oxide phenyldifluoroborane adduct, m. p. 117 – 119 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 3.78 (s, 3H), 7.13 – 7.19 (m, 3H), 7.39 – 7.42 (m, 2H), 7.50 (s, 1H), 7.58 (s, 1H), 9.05 (s, 1H) ppm. – IR (neat): ν = 3156, 3130, 3102, 3013, 1598, 1566, 1552, 1435, 1339, 1271, 1243, 1220, 1164, 1074, 1036, 1001, 980, 921, 836, 759, 727, 709, 702, 658, 625, 608, 557, 510, 461 cm^{-1}.

*1-Hydroxy-2,3-dimethylimidazolium iodide (**45a**)*

In analogy to the published procedure [17] by methanolysis of **41a** (yield: 83 %). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.39 (s, 3H), 3.68 (s, 3H), 5.6 (br s, 1H), 7.42 (d, J = 2.1 Hz, 1H), 7.48 (d, J = 2.1 Hz, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 7.6, 34.8, 118.6 (2C), 138.1. – IR (neat): ν = 3081, 2948, 2817, 2714, 1584, 1434, 1333, 1182, 782, 744, 727, 643, 580, 503 cm^{-1}.

*1-Hydroxy-2,3-dimethylimidazolium tosylate (**45b**)*

In analogy to the published procedure [17] by methanolysis of **41b** (yield: 71 %). M. p. 143 – 146 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.28 (s, 3H), 2.48 (s, 3H), 3.71 (s, 3H), 7.11 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 2.2 Hz, 1H), 7.79 (d, J = 2.2 Hz, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 8.0, 20.9, 35.1, 118.6, 119.6, 125.5 (2C), 128.2 (2C), 138.1, 140.5, 145.2. – IR (neat): ν = 3132, 2436, 1343, 1229, 1153, 1112, 1103, 1024, 1001, 818, 748, 678, 643, 555 cm^{-1}.

*Bis(1,2-dimethylimidazole 3-oxide) hydroiodide (**45c**)*

Obtained from the mother liquor of the corresponding pivaloyl derivative **41a** upon standing for several days. M. p. 155 °C. – IR (neat): ν = 3101, 3076, 2978, 1575, 1442, 1335, 1250, 1135, 1047, 963, 764, 722, 643, 505 cm^{-1}.

*1-Methylimidazole 3-oxide (**46**)*

A solution of **44b** (5 g, 20 mmol) or **44c** in H_2O/MeOH (1 : 5, 120 mL) was stirred with IRA 400 (Fluka, OH form, 100 g) for 1 h, filtered and the solvent evaporated. The residue was dried over P_2O_5 to give 1.4 g of **46** (yield 71 %). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 3.59 (s, 3H), 7.08 (t, J = 1.8 Hz, 1H), 7.14 (t, J = 1.8 Hz, 1H), 8.22 (t, J = 1.8 Hz, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 35.0, 118.6, 120.9, 126.9. – IR (neat): ν = 3103, 3028, 1544, 1350, 1305, 1169, 1076, 1023, 733, 608, 479 cm^{-1}.

*1,2-Dimethylimidazole 3-oxide (**47**)*

Hydroiodide **45a** (7.0 g, 29.2 mmol) was dissolved in MeOH (150 mL), Ag_2O (3.45 g, 14.9 mmol) was added, and the mixture was ultrasonicated for 15 min. After filtration (0.22 μm), the solvent was evaporated. The residue was crystallized from CH_3CN and was dried over P_2O_5 to give 3.0 g (92 %) of the extremely hygroscopic product as deliquescent crystals. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.26 (s, 3H), 3.56 (s, 3H), 7.06 (d, J = 1.9 Hz, 1H), 7.10 (d, J = 1.9 Hz, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 7.2, 34.2, 116.4, 119.2, 133.9. – IR (neat): ν = 3084, 3040, 2925, 1563, 1454, 1367, 1306, 1248, 1124, 1102, 1041, 799, 757, 734, 654, 617, 588, 522 cm^{-1}.

Hydrogenation of 1-methoxy-3-methylimidazolium bis(trifluoromethanesulfonyl)imide

A solution of **15c** (325 mg, 0.8 mmol) in MeOH (10 mL) was hydrogenated at 4 bar / r. t. for 6 h using 5 % Pd/C (30 mg) as a catalyst. After filtration and evaporation of the solvent, the product obtained was spectroscopically identical with authentic 1-methylimidazolium bis(trifluoromethanesulfonyl)imide (CAS RN [353239-08-4]).

*1-Methylimidazole 3-oxide tris(2-thienyl)borane adduct (**48**)*

1-Hydroxy-3-methylimidazolium hexafluorophosphate (**44b**) (0.18 g, 0.73 mmol) dissolved in 1 mL of water was added to a solution of potassium tetrakis(2-thienyl)borate (0.28 g, 0.73 mmol) in 8 mL of methanol, whereupon a light yellowish precipitate separated immediately. The reaction mixture was ultrasonicated for 5 min and filtered. The product was washed with small portions of water and dried over P_2O_5 to yield 0.19 g of **48** (yield 72 %). Single crystals were grown from CH_2Cl_2. M. p. 139 – 141 °C. – ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 3.74 (s, 3H), 6.91 – 6.97 (m, 7H), 7.14 (t, J = 2.0 Hz, 1H), 7.30 (dd, J = 4.3 Hz, J = 1.5 Hz, 3H), 7.97 (t, J = 1.6 Hz, 1H). – ^{13}C NMR (75 MHz, [D$_6$]acetone): δ = 36.9, 120.4, 122.8, 126.9, 128.0, 131.3, 133.3, 157.1 (br, C on B). – IR (neat): ν = 3149, 3095, 1556, 1323, 1209, 1104, 1026, 997, 854, 811, 791, 721, 705, 691, 607 cm^{-1}.

*Bis(1-benzyloxy-3-methylimidazolin-2-ylidene)silver(I) hexafluorophosphate (**49**)*

A mixture of 1-benzyloxy-3-methylimidazolium hexafluorophosphate (**27b**) (0.25 g, 0.75 mmol) and Ag_2O (0.17 g, 0.75 mmol) was stirred in MeOH (12 mL) at r. t. for 6 d, protected from light, then filtered and allowed to evaporate to obtain colorless single crystals of the product.

X-Ray Structure Determination

Crystal data and structure refinement details are summarized in Table 2. CCDC 673922 – 673935 contain

Table 2. Crystal data and structure refinement details.

Compound	**1**	**2**	**3a**	**3b**	**4a**	**27b**	**29a**
CCDC no.	673922	673923	673924	673925	673926	673927	673928
Chemical formula	$C_3H_4N_2O_2$	$C_4H_6N_2O_2{\cdot}C_4H_6N_2O_2$	$C_3H_5ClN_2O_2$	$C_3H_5N_2O_2Br$	$C_4H_7ClN_2O_2$	$C_{11}H_{13}F_6N_2OP$	$C_8H_{13}N_2OI$
M_r	100.08	228.22	136.54	180.99	150.56	334.20	280.11
Crystal form, color	fragment, colorless	fragment, colorless	prism, colorless	fragment, colorless	fragment, colorless	fragment, colorless	plate, colorless
Crystal size, mm^3	$0.4\times0.2\times0.12$	$0.40\times0.20\times0.10$	$0.45\times0.3\times0.12$	$0.36\times0.28\times0.16$	$0.4\times0.28\times0.28$	$0.4\times0.15\times0.08$	$0.3\times0.24\times0.09$
Crystal system, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$	orthorhombic, $Pca2_1$	orthorhombic, *Pnam*	monoclinic, $C2/c$	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$
a, Å	5.7570(3)	9.5820(4)	12.2704(7)	13.963(3)	7.4624(12)	6.2917(2)	13.9340(9)
b, Å	10.1203(5)	11.1913(5)	4.0626(2)	5.4446(11)	13.362(2)	27.0293(8)	10.9684(7)
c, Å	7.0844(2)	9.7178(3)	11.2072(4)	7.7297(16)	6.9424(10)	8.7562(3)	7.3899(5)
α, deg	90	90	90	90	90	90	90
β, deg	98.396(3)	98.650(2)	90	90	112.189(11)	109.980(2)	102.131(5)
γ, deg	90	90	90	90	90	90	90
V, $Å^3$	408.33(3)	1030.24(7)	558.68(5)	587.6(2)	640.99(16)	1399.46(8)	1104.21(12)
Z	4	4	4	4	4	4	4
D_x, $g\,cm^{-3}$	1.628	1.471	1.623	2.046	1.56	1.586	1.685
μ (MoK_α), mm^{-1}	0.14	0.12	0.59	6.90	0.52	0.264	2.86
$F(000)$, e	208	480	280	352	312	680	544
Diffractometer	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Stoe IPDS 2	Stoe IPDS 2	Nonius KappaCCD	Stoe IPDS 2
Radiation type	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α
Data collection method	ϕ and ω scans	ϕ and ω scans	ϕ and ω scans	rotation method	rotation method	ϕ and ω scans	rotation method
Temperature, K	233(2)	233(2)	233(2)	173(2)	173(2)	233(2)	173(2)
θ_{max}, deg	27.0	24.0	26.4	24.6	24.6	25.0	25.1
h,k,l range	$0\rightarrow7$, ±12, $-9\rightarrow8$	$0\rightarrow10$, ±12, $-11\rightarrow10$	$-15\rightarrow12$, $-4\rightarrow5$, $-14\rightarrow12$	±16, ±6, $-8\rightarrow9$	±8, ±15, ±8	$-7\rightarrow6$, $-29\rightarrow32$, ±10	±16, ±13, ±8
Absorption correction	none	none	none	multi-scan	multi-scan	none	analytical
Measured reflections	2518	5186	2879	3226	1880	7590	6910
Independent reflections	882 (R_{int} = 0.020)	1592 (R_{int} = 0.037)	1089 (R_{int} = 0.020)	534 (R_{int} = 0.026)	1641 (R_{int} = 0.037)	2450 (R_{int} = 0.0223)	1954 (R_{int} = 0.031)
Observed reflections $[I\geq2\sigma(I)]$	833	1439	1076	490	532	2059	1711
Refinement on	F^2	F^2	F^2	F^2	F^2	F^2	F^2
Data/restraints/parameters	882/2/73	1592/0/149	1089/1/82	534/0/41	532/0/47	2450/0/192	1954/0/111
R_1/wR_2 $[F^2\geq2\sigma(F^2)]$	0.031/0.079	0.066/0.169	0.020/0.051	0.034/0.096	0.023/0.062	0.0411/0.1083	0.021/0.049
R_1/wR_2 (all data)	0.032/0.080	0.071/0.171	0.020/0.051	0.039/0.100	0.025/0.063	0.0493/0.1134	0.026/0.051
Goodness of fit	1.10	1.07	1.08	0.95	1.08	1.06	1.02
$\Delta\rho_{max/min}$, $e\,Å^{-3}$	0.18/−0.18	0.53/−0.22	0.14/−0.20	1.50/−0.39	0.18/−0.19	0.33/−0.256	0.35/−0.45

Table 2 (continued).

Compound	**35a**	**43**	**45b**	**45c**	**47**	**48**	**49**
CCDC no.	673929	673930	673931	673932	673933	673934	673935
Chemical formula	$C_9H_{17}N_2OI$	$C_5H_8N_2 \cdot 0 \cdot 5(H_2O_2)$	$C_7H_7O_3S \cdot C_5H_9N_2O$	$C_5H_9N_2O \cdot C_5H_8N_2OI$	$C_5H_8N_2O$	$C_{16}H_{15}BN_2OS_3$	$C_{22}H_{24}AgF_6N_4O_2P$
M_r	296.15	113.14	284.33	352.18	112.13	358.29	629.29
Crystal form, color	thin plate, colorless	fragment, colorless	prism, colorless	plate, colorless	fragment, colorless	prism, colorless	prism, colorless
Crystal size, mm^3	$0.43 \times 0.24 \times 0.03$	$0.48 \times 0.35 \times 0.20$	$0.3 \times 0.2 \times 0.15$	$0.30 \times 0.17 \times 0.04$	$0.32 \times 0.25 \times 0.16$	$0.28 \times 0.21 \times 0.12$	$0.22 \times 0.12 \times 0.04$
Crystal system, space group	orthorhombic, *Pcab*	orthorhombic, *Fd2d*	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$	monoclinic, $C2/c$
a, Å	7.4633(3)	7.5993(16)	6.9572(2)	7.8411(10)	7.243(2)	8.9375(2)	26.7720(3)
b, Å	10.8704(5)	13.862(3)	22.9214(7)	7.8590(11)	6.9901(14)	17.3444(6)	18.0140(3)
c, Å	30.8624(15)	24.101(7)	8.6175(3)	12.1615(16)	11.268(3)	11.0989(3)	22.6988(5)
α, deg	90	90	90	93.254(11)	90	90	90
β, deg	90	90	104.582(2)	98.431(10)	104.23(2)	96.203(2)	108.028(2)
γ, deg	90	90	90	110.224(10)	90	90	90
V, $Å^3$	2503.83(19)	2538.8(11)	1329.96(7)	690.95(16)	553.0(2)	1710.43(8)	10409.5(3)
Z	8	16	4	2	4	4	16
D_x, $g\,cm^{-3}$	1.571	1.184	1.420	1.693	1.346	1.391	1.606
μ (MoK_α), mm^{-1}	2.53	0.09	0.26	2.31	0.13	0.437	0.905
$F(000)$, e	1168	976	600	348	232	744	5056
Diffractometer	Stoe IPDS 2	Stoe IPDS 2	Nonius KappaCCD	Stoe IPDS 2	Stoe IPDS 2	Nonius KappaCCD	Nonius KappaCCD
Radiation type	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α
Data collection method	rotation method	rotation method	ϕ and ω scans	rotation method	rotation method	ϕ and ω scans	ϕ and ω scans
Temperature, K	173(2)	173(2)	233(2)	173(2)	173(2)	233(2)	233(2)
θ_{max}, deg	25.1	25.0	25.0	26.8	26.9	25.0	25.0
h,k,l range	$\pm 8, \pm 12, -36 \rightarrow 32$	$-8 \rightarrow 9, -16 \rightarrow 14, \pm 28$	$-8 \rightarrow 6, -25 \rightarrow 27, \pm 10$	$\pm 9, \pm 9, \pm 15$	$\pm 9, -8 \rightarrow 7, \pm 13$	$\pm 10, -20 \rightarrow 19, -13 \rightarrow 12$	$\pm 31, \pm 21, -26 \rightarrow 24$
Absorption correction	analytical	none	none	integration	none	none	none
Measured reflections	13146	3802	7306	10451	4016	8757	31102
Independent reflections	1930 ($R_{int} = 0.035$)	1048 ($R_{int} = 0.049$)	2333 ($R_{int} = 0.032$)	2913 ($R_{int} = 0.053$)	1095 ($R_{int} = 0.048$)	2985 ($R_{int} = 0.0253$)	9149 ($R_{int} = 0.0541$)
Observed reflections $[I \geq 2\sigma(I)]$	1638	856	1996	2683	821	2579	6538
Refinement on	F^2	F^2	F^2	F^2	F^2	F^2	F^2
Data/restraints/parameters	1930/0/121	1048/1/79	2333/1/180	2913/0/159	1095/0/76	2985/0/213	9149/0/744
R_1/wR_2 $[F^2 \geq 2\sigma(F^2)]$	0.031/0.063	0.052/0.112	0.037/0.098	0.022/0.050	0.044/0.098	0.0439/0.1135	0.0431/0.0844
R_1/wR_2 (all data)	0.045/0.066	0.070/0.119	0.046/0.103	0.025/0.051	0.067/0.106	0.0512/0.1179	0.0734/0.0936
Goodness of fit	1.09	1.12	1.06	1.07	1.02	1.05	1.02
$\Delta\rho_{max/min}$, $e\,Å^{-3}$	0.52/−0.63	0.16/−0.12	0.23/−0.27	0.70/−0.53	0.21/−0.17	0.426/−0.397	0.404/−0.524

the supplementary crystallographic data for this paper. Crystal data of 1-ethyl-3-methylimidazolium tetraphenylborate (CAS RN [65065-20-5]) and its acetone solvate have been deposited as numbers 673937 and 673936. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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