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# Synthesis and Properties of Alkoxy- and Alkenyl-Substituted Peralkylated Imidazolium Ionic Liquids

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Novel peralkylated imidazolium ionic liquids bearing alkoxy and/or alkenyl side chains have been synthesized and studied. Different synthetic routes towards the imidazoles and the ionic liquids comprising bromide, iodide, methanesulfonate, bis(trifluoromethylsulfonyl)imide ($[NTf_2]^-$), and dicyanamide {$[N(CN)_2]^-$} as the anion were evaluated, and this led to a library of analogues, for which the melting points, viscosities, and electrochemical windows were determined. Incorporation of alkenyl moieties hindered solidification, except for cations with high symmetry. The alkoxy-derivatized ionic liquids are often crystalline; however, room-temperature ionic liquids (RTILs) were obtained with the weakly coordinating anions $[NTf_2]^-$ and $[N(CN)_2]^-$. For the viscosities of the peralkylated RTILs, an opposite trend was found, that is, the alkoxy derivatives are less viscous than their alkenyl-substituted analogues. Of the crystalline compounds, X-ray diffraction data were recorded and related to their molecular properties. Upon alkoxy substitution, the electrochemical cathodic limit potential was found to be more positive, whereas the complete electrochemical window of the alkenyl-substituted imidazolium salts was shifted to somewhat more positive potentials.

## 1. Introduction

Given that the stability of ionic liquids is crucial for several applications, research is being devoted to enhance it. Previous research has demonstrated that completely substituted imidazolium salts (in particular, 2-isopropyl-substituted imidazolium salts) possess improved thermal and (electro)chemical stability, whereas their melting points do not increase dramatically.[1] Due to the increased substitution of these peralkylated imidazolium ionic liquids, melting points ($T_m$) of *N*-ethyl-substituted analogues are above room temperature, whereas longer *N*-alkyl chains ($C_6$) decrease $T_m$ but increase viscosity.[1b] To decrease melting points and viscosities of short-chained, completely substituted imidazolium salts, the incorporation of different functional groups is evaluated.

Alkene functionalities were shown to reduce viscosity, and this was proposed to be due to increased planarity, which allows molecular "flow" with little resistance.[2] Schneider et al. found 1-allyl-3-methylimidazolium bromide ($[C_AC_1im][Br]$) to be crystalline, although it readily undercools.[3] Symmetrically allyl-functionalized 1,3-diallylimidazolium bromide and bis(trifluoromethylsulfonyl)imide ($[C_AC_Aim][Br]$ and $[C_AC_Aim][NTf_2]$) are not solid, and therefore, the allyl group seems to increase the undercooling properties, presumably by increasing the number of possible hydrogen-bond donor sites.[4]

The substitution of alkyl groups by isoelectronic alkyl ether chains leads to repulsion between neighboring oxygen atoms, which leads to significant ion pairing and to intermolecular hydrogen-bonding interactions between imidazolium hydrogen atoms and the lone pairs of electrons of the alkoxy oxygen atom. This combined effect leads, in general, to melting points ($T_m$) and glass transition temperatures ($T_g$) that are higher than those of the alkyl analogues.[5] However, the lone pairs of electrons of the oxygen atom are believed to reduce the electrostatic interaction between the anion and cation. Thus, a reduction in $T_m$ and in the viscosity is nonetheless observed upon substitution of alkyl chains by alkyl ether chains in imidazolium,[6] ammonium,[7] and phosphonium ionic liquids.[8] Moreover, as sometimes no difference is observed at all,[9] this trend is not unambiguously applicable to all ionic liquid analogues and should be investigated for every analogue separately.

Alkoxy moieties have already been introduced in ionic liquids to enhance metal complexation and transport properties, for example, for Li[10] and Mg.[11] The latter was introduced by means of commercial MeMgBr in THF solutions in, for instance, 1-allyl-3-(2-methoxyethyl)-2-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_{2O1}C_AC_1im][NTf_2]$) by Kakibe et al.[11b] This particular ionic liquid possesses improved conductivity and is sufficiently stable to withstand Grignard reagents.

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Given the omnipotence of organometallic compounds with regard to C–C bond formation, the application of Grignard reactions in ionic liquids has already attracted specific attention. Thus, phosphonium salts have so far been very successful: hydrophobic tetraoctylphosphonium bis(trifluoromethylsulfonyl)-imide allows addition reactions with commercial THF solutions of PhMgBr. The stability is attributed to the shielding of the most acidic protons by the long alkyl chains. Unfortunately, the lipophilic character of the cation hampers the extraction of the products.[12] In analogous salts substituted with an alkyl ether moiety, an accelerating effect of the addition reaction is observed. Although reaction with pure PhMgBr (i.e. after evaporation of THF) was successful, generation of the Grignard reagent in this ether-containing ionic liquid cannot be achieved.[13] Commercial solutions of Grignard reagents have also been applied in 2-substituted imidazolinium and imidazolium salts.[1a,14] The synthesis of the Grignard reagent was obtained by Chan et al. in *N*-butylpyridinium tetrafluoroborate ($[C_4py][BF_4]$).[15]

Imidazolium salts are cheap, have low viscosity, and are easily modified. This allows the design of a library of analogous, completely substituted imidazolium ionic liquids bearing different functionalities, the synthesis of which is described here. The rheological properties of a number of salts were examined along with their electrochemical stability, and the different properties were related to structural modifications. Crystallographic analysis was possible on some of the salts that are solid at room temperature, and the relationship between structure and melting point was examined.

## 2. Results and Discussion

### Synthesis of Imidazoles

During previous research in our group, a versatile one-pot Debus–Radziszewski method was developed to obtain 1-substituted imidazole derivatives with divergent substituents at the 1,2-positions by condensation of an alkyl amine, a dicarbonyl compound, an aldehyde, and an ammonia source.[1b] The same method was applied for the incorporation of alkoxy and alkenyl moieties (Scheme 1).

This method allowed the synthesis of 1*N*-allyl-2-isopropyl-4,5-dimethylimidazole (**4a**), 1*N*-(2-hydroxyethyl)-2-isopropyl-4,5-dimethylimidazole (**4b**), and 2-isopropyl-1*N*-(2-methoxyethyl)-4,5-dimethylimidazole (**4c**). The yield of the Radziszewski reaction was always of the same order of magnitude. However, the selectivity of the substituted imidazole over 1*N*-*H*-2-isopropyl-4,5-dimethylimidazole (**5**) differed.

The selectivity was related to the properties of the amine used (Table 1). Upon addition of $NH_4OAc$, competing transamination of intermediate imine **3** could occur. Imines with more electron-donating substituents led to higher selectivities. This is likely due to 1) higher stability of the intermediate imine towards transamination and 2) faster reaction to form the imidazole. Hence, the portionwise addition of $NH_4OAc$ and the diketone decreased the formation of the byproduct. Although a steric factor contributes, it is the electron-withdrawing nature of the hydroxy group that reduces the selectivity.

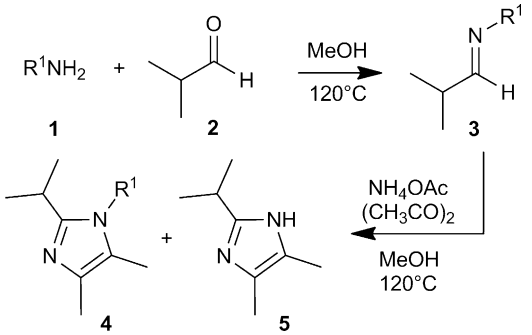
**Table 1.** Yield of **4** after distillation and selectivity in the modified Radziszewski reaction with different amines.

| 4 | Amine | Yield [%] | Selectivity [%] (**4**/**4** + **5**)[c] |
|---|---|---|---|
| **4a** | allylamine | 63 | 88 |
| **4b** | hydroxyethylamine | – | 75 |
| **4b** | hydroxyethylamine[a] | 38[b] | 95 |
| **4c** | methoxyethylamine | 53 | 86 |

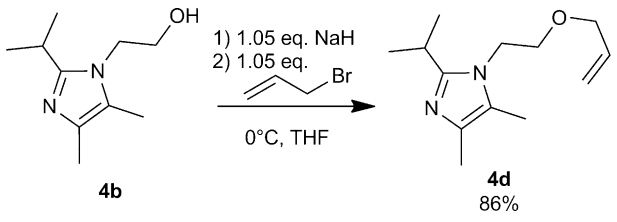
[a] Added in portions. [b] Yield of the crude product. [c] Measured by $^1$H NMR spectroscopy.

If present in large quantities, the formed 1*N*-*H* analogue could be precipitated from the crude reaction mixture in acetonitrile to yield the pure byproduct. During vacuum distillation, the remaining amount of the byproduct crystallized in the still, as it could not be distilled in the workable range due to its hydrogen-bonding properties. Analogously, hydroxyethyl derivative **4b** could not be distilled, and it was therefore applied as such for further functionalization with both dimethyl sulfate and iodomethane as methylating agents and allyl bromide. Although the methylating agents gave rise to the formation of *N*-alkylated products, the allyl bromide was found to be very selective towards *O*-alkylation (Scheme 2). The allyloxyethyl derivative was successfully distilled to obtain a clear yellow oil.

The distilled imidazole derivatives were obtained as clear liquids or as slightly yellowish liquids, the color of which some-




**Scheme 1.** Optimized Debus–Radziszewski reaction with the formation of product **4** and byproduct *NH*-imidazole **5**.




**Scheme 2.** Alkylation of crude *N*-(2-hydroxyethyl)imidazole (**4b**) with allyl bromide. The conversion was determined by analysis of the reaction mixture by $^1$H NMR spectroscopy and in reference to the amount of **4b** present in the crude starting material.

times spontaneously intensified over a few days; only **4c** was obtained as a solid.

**Table 2.** Overview of the synthesized ionic liquids, quaternization agent (RX), and physical state at room temperature.

| 6 | Ionic liquid[a] | $R^{1}$[b] | $R^{2}$[b] | RX | Physical state |
|---|---|---|---|---|---|
| **6a** | $[C_AC_1C_{i3}m_2im][OMs]$ | allyl | methyl | MeOMs | liquid |
| **6b** | $[C_AC_1C_{i3}m_2im][I]$ | allyl | methyl | MeI | liquid |
| **6c** | $[C_AC_1C_{i3}m_2im][NTf_2]$ | allyl | methyl | MeI | liquid |
| **6d** | $[C_AC_1C_{i3}m_2im][N(CN)_2]$ | allyl | methyl | MeI | liquid |
| **7a** | $[C_{2O1}C_1C_{i3}m_2im][OMs]$ | methoxyethyl | methyl | MeOMs | crystalline |
| **7b** | $[C_{2O1}C_1C_{i3}m_2im][I]$ | methoxyethyl | methyl | MeI | crystalline |
| **7c** | $[C_{2O1}C_1C_{i3}m_2im][NTf_2]$ | methoxyethyl | methyl | MeI | crystalline |
| **7d** | $[C_{2O1}C_1C_{i3}m_2im][N(CN)_2]$ | methoxyethyl | methyl | MeI | crystalline |
| **8a** | $[C_{2OA}C_1C_{i3}m_2im][OMs]$ | allyloxyethyl | methyl | MeOMs | liquid |
| **8b** | $[C_{2OA}C_1C_{i3}m_2im][I]$ | allyloxyethyl | methyl | MeI | liquid |
| **8c** | $[C_{2OA}C_1C_{i3}m_2im][NTf_2]$ | allyloxyethyl | methyl | MeI | liquid |
| **8d** | $[C_{2OA}C_1C_{i3}m_2im][N(CN)_2]$ | allyloxyethyl | methyl | MeI | liquid |
| **9a** | $[C_AC_2C_{i3}m_2im][OMs]$ | allyl | ethyl | AllOMs | liquid[c] |
| **9b** | $[C_AC_2C_{i3}m_2im][Br]$ | allyl | ethyl | AllBr | solid |
| **9c** | $[C_AC_2C_{i3}m_2im][NTf_2]$ | allyl | ethyl | AllBr | crystalline |
| **9d** | $[C_AC_2C_{i3}m_2im][N(CN)_2]$ | allyl | ethyl | AllBr | solid |
| **10a** | $[C_AC_AC_{i3}m_2im][OMs]$ | allyl | allyl | AllOMs | liquid[c] |
| **10b** | $[C_AC_AC_{i3}m_2im][Br]$ | allyl | allyl | AllBr | liquid[c] |
| **10c** | $[C_AC_AC_{i3}m_2im][NTf_2]$ | allyl | allyl | AllBr | crystalline |
| **10d** | $[C_AC_AC_{i3}m_2im][N(CN)_2]$ | allyl | allyl | AllBr | crystalline |
| **11a** | $[C_{2O1}C_AC_{i3}m_2im][OMs]$ | allyl | methoxyethyl | AllOMs | glass |
| **11b** | $[C_{2O1}C_AC_{i3}m_2im][Br]$ | allyl | methoxyethyl | AllBr | liquid |
| **11c** | $[C_{2O1}C_AC_{i3}m_2im][N(CN)_2]$ | allyl | methoxyethyl | AllBr | liquid |
| **11d** | $[C_{2O1}C_AC_{i3}m_2im][NTf_2]$ | allyl | methoxyethyl | AllBr | liquid |

[a] $C_{i3}$ = 2-isopropyl; for convenience, the *N*-methyl group is referred to as $C_1$. [b] $R^1$ and $R^2$ are the substituents as depicted in Scheme 5. [c] Very viscous liquid; very slow crystallization; not completely crystallized after several weeks.

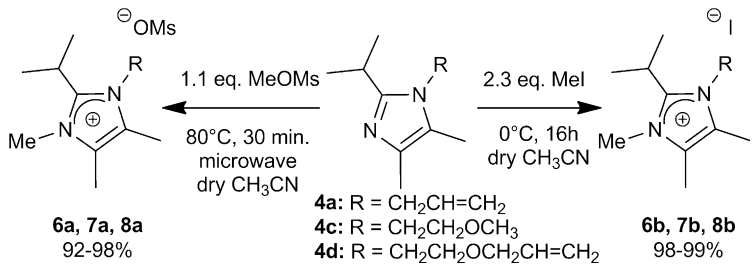
### Synthesis of Ionic Liquids

The least symmetric ionic liquids, which are those containing an *N*-methyl substituent (i.e. **6**–**8**), were synthesized by methylating the tetraalkyl imidazole (i.e. **4a**, **4c**, **4d**) with methyl iodide (MeI) or methyl methanesulfonate (MeOMs, Scheme 3). The methylation with MeI proceeded smoothly at 0 °C overnight, whereas the reaction with MeOMs needed to be heated at reflux for over 24 h. The latter reaction could be accelerated by microwave heating for 30 min at 80 °C. The low volatility of MeOMs allowed the use of a smaller excess amount of the methylating reagent. An overview of the nomenclature and alkylation agents used is given in Table 2.

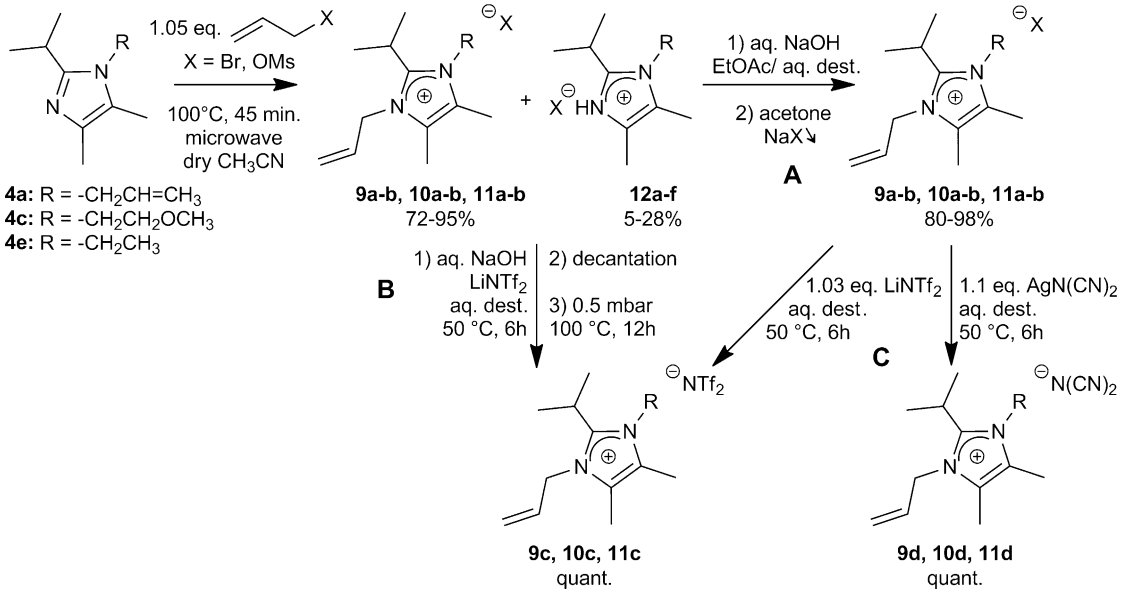
Quaternization with allyl bromide or allyl methanesulfonate always required high temperatures and/or long reaction times. As experiments in conventional flasks at 80 °C took 24 h to reach completion, microwave irradiation was also applied here to accelerate the synthesis (Scheme 4). In all allylation reactions, the formation of a byproduct was observed: small quadruplets of the $NCH_2$ group in the $^1$H NMR spectrum were visible upfield ($\delta$ = 4.2 ppm) relative to the resonance of the $NCH_2$ group of the desired end product ($\delta$ = 4.3 ppm), and this accounted for 11–28 mol% of the product mixture. Prolonged heating of the mixture under high vacuum and washing an aqueous solution with $Et_2O$ or EtOAc removed the starting materials; however, the byproduct was still present, and it was therefore concluded that it was most likely a salt.

The formation of HOMs or HBr by the action of water was proposed, and this would lead to inert protonated imidazoles (i.e. **12**, Scheme 4), although the presence of AllOH (All = allyl) could not be proven by LC–MS or GC. The use of intensively dried $CH_3CN$ did not decrease the formation of byproducts, whereas the use of dichloromethane led to the formation of multiple byproducts. Hence, the reaction mixture was neutralized with a stoichiometric amount of NaOH in demineralized water, and the formed neutral imidazole was extracted from the aqueous mixture with EtOAc. Upon removing the water by rotary evaporation or lyophilization, crystals of NaOMs or NaBr were formed in the ionic liquid. Dissolution of the mixture in hot acetone gave a fine suspension, which could be filtered after cooling (pathway A, Scheme 4); complete removal of NaOMs was confirmed by $^1$H NMR spectroscopy, although residual trace amounts of NaOH could not be excluded. NaBr was removed by precipitation from an aliquot of $CH_2Cl_2$ and consecutive filtration. Direct metathesis into the hydrophobic $[NTf_2]^-$ salt allowed the use of a small excess amount of NaOH solution (pathway B, Scheme 4). In this case, residual sodium salts were discarded with the aqueous phase, and the residual neutral imidazole was removed by distillation. The pentaalkylimidazolium derivatives were obtained quantitatively after metathesis.

To obtain the $[NTf_2]^-$ and $[N(CN)_2]^-$ analogues of both *N*-methylated and *N*-allylated analogues, standard metathesis reactions were applied (Scheme 4, pathway C), which involved the use of a small excess amount of $LiNTf_2$ or $AgN(CN)_2$ in an aqueous



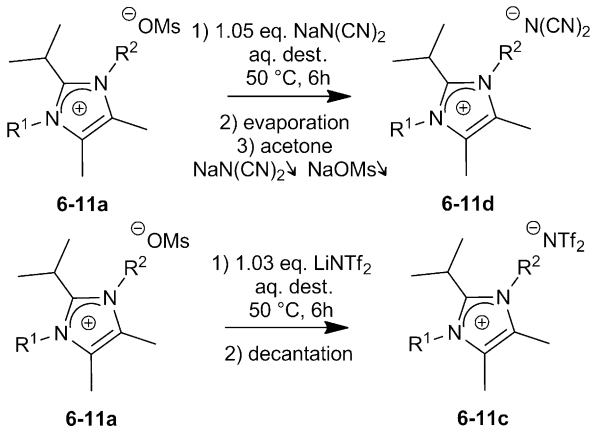

**Scheme 3.** Methylation of tetraalkyl imidazoles. Identification of the compounds is given in Table 2.




**Scheme 4.** Synthesis of allyl-functionalized imidazolium salts by quaternization and metathesis. X = OMs (**9a**–**11a**), X = Br (**9b**–**11b**). Identification of the compounds is given in Table 2. 1.0 mbar = 0.10 kPa; aq. dest = distilled water.

medium. In the synthesis of **9**–**11**, pathway B was followed. Given the precipitation of NaOMs in the ionic liquids and acetone and the ability to monitor residual NaOMs or HOMs species by $^1$H NMR spectroscopy, all $[NTf_2]^-$ and $[N(CN)_2]^-$ salts could be obtained by halide and silver-free ionic liquid synthesis by adding $LiNTf_2$ or $NaN(CN)_2$, respectively, to an aqueous solution of the methanesulfonate salts (Scheme 5). The $[NTf_2]^-$ salt was obtained by decanting and washing the organic layer, whereas the $[N(CN)_2]^-$ salt was obtained by evaporation of the aqueous solution and precipitation of the sodium salts in an acetone or $CH_2Cl_2$ solution.

The solid salts were recrystallized from acetone, which resulted in purification in addition to perfect decoloration. Coloration of the ionic liquids occurred upon methylation at both low and high temperatures. Unfortunately, efforts to perform postreaction decoloration, which included reverse-phase column chromatography and treatment with alumina and activated charcoal, were fruitless. A reduction in the level of coloration could, however, be obtained by heating the distilled scaffold imidazole derivatives at reflux with $NaBH_4$ (20 wt.%), which presumably resulted in reduction of the carbonyl compounds that were present. After secondary distillation, colorless liquid imidazole derivatives were obtained, which led to only slightly colored ionic liquids. Apart from four different *N*-allylimidazolium salts, three ether-containing imidazolium ionic liquids comprising different anions were synthesized (Figure 1).




**Scheme 5.** Metathesis of methanesulfonate $[OMs]^-$ salts. Identification of the compounds is given in Table 2.

### Melting Points and Viscosities

As can be seen in Table 2 the more symmetric compounds with noncoordinating anions (i.e. **9**, **10**) are (crystalline) solids. If the cations were combined with more basic anions ($[Br]^-$, $[OMs]^-$), very viscous liquids were obtained. Although some of them formed crystals at room temperature, isolation from the mother liquor could not be achieved. Readily crystallizable $[NTf_2]^-$ and $[N(CN)_2]^-$ salts indicate that, first, high symmetry in-

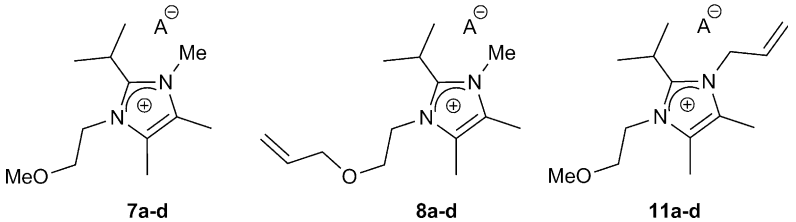



**Figure 1.** Ether-containing imidazolium ionic liquids. Anions ($A^-$): **a**: $[OMs]^-$; **7b**, **8b**: $[I]^-$; **11b**: $[Br]^-$; **c**: $[N(CN)_2]^-$; **d**: $[NTf_2]^-$.

duces rapid crystallization and that, second, the hydrogen-bonding capacities of $[Br]^-$ and $[OMs]^-$ hinder crystallization. This suggests a possible extra hydrogen-bonding site provided by the allyl group (apart from the isopropyl and $NCH_3$ protons). This extra hydrogen-bonding site increases entropy,[16] and the interaction with the coordinating anions is also visible by chemical shifts in the $^1H$ NMR spectra. In our studies, we never observed solidification of the $[C_AC_1C_{i3}im]^+$ analogues. The incorporation of methoxyethyl side chains ($C_{2O1}$) in the cation led to salts that crystallized more readily, although room-temperature ionic liquids (RTILs) were obtained if the cations were combined with $[NTf_2]^-$ or $[N(CN)_2]^-$ (see Table 3). Upon combination with an allyl substituent, solidification was again hindered. Only the $[C_{2O1}C_AC_{i3}m_2im][OMs]$ salt was found to solidify (as a glass). Hence, the main factor in the solidification of the salts is the methoxy group.

**Table 3.** Melting points [°C] of alkoxy- and alkenyl-derivatized imidazolium ionic liquids, $[R^1R^2C_{i3}m_2im][A]$.

| Ionic liquid | $R^1$ | $R^2$ | [OMs] (**a**) | [X][a] (**b**) | $[NTf_2]$ (**c**) | $[N(CN)_2]$ (**d**) |
|---|---|---|---|---|---|---|
| **7** | $C_{2O1}$ | $C_1$ | 132 | 123 | 22 | 20 |
| **9** | $C_A$ | $C_2$ | –[c] | 109 | 58 | 28 |
| **10** | $C_A$ | $C_A$ | 41 | –[c] | 63 | 60 |
| **11** | $C_{2O1}$ | $C_A$ | 70[b] | –[c] | –[c] | –[c] |

[a] For **7**, the [I] salt was used; otherwise, the [Br] salt was used. [b] Glass transition temperature. [c] Compound is liquid.

Solidification of **9b** and **10d** could be forced by rapidly undercooling the samples with liquid nitrogen and recrystallizing the thus-formed white flakes in acetone. In the single case of **10a**, the salt could be precipitated by adding ether dropwise to an acetone solution of the crude mixture. For other derivatives, rapid cooling did not lead to crystallized products. Holding the samples at different elevated temperatures for prolonged times to reduce viscosities and hence to promote crystal formation did not produce crystals in any case.

The viscosities of the liquid salts are given in Table 4. Halide and methanesulfonate salts are omitted because of their very high viscosities. The salts of analogues **7** and **9** (except **9c**) were found to be liquid at the analysis temperature and were therefore also analyzed. The viscosity of derivatives containing an alkoxy side chain was reduced relative to that of derivatives containing alkenyl side chains, which were very viscous. Of the derivatives with both functionalities (i.e. **8**, **11**), salts with the $[C_{20A}C_1C_1im]^+$ cation (i.e. **8**) bearing both functionalities in one substituent and substituted with an *N*-methyl group had the lowest viscosity.

**Table 4.** Viscosity and water content of $[R^1R^2C_{i3}m_2im][A]$ at 23 °C.

| Ionic liquid | $R^1$ | $R^2$ | Viscosity [mPa] (water content [ppm]) $[NTf_2]$ | $[N(CN)_2]$ |
|---|---|---|---|---|
| **6** | $C_A$ | $C_1$ | 721 (320) | 2520 (4860) |
| **7** | $C_{2O1}$ | $C_1$ | 131 (250) | 380 (330) |
| **8** | $C_{2OA}$ | $C_1$ | 286 (140) | 306 (310) |
| **9** | $C_A$ | $C_2$ | –[a] | 2350 (1370) |
| **11** | $C_{2O1}$ | $C_A$ | 860 (290) | 1075 (560) |

[a] Compound **9c** is solid.

## Crystallographic Analysis

The high melting points induced by the alkylation pattern of some of the ionic liquids described imply that it is possible to study them in the solid state. One of the most powerful techniques is single-crystal X-ray diffraction, which gives absolute atomic positions and arrangements of molecules as well as accurate intermolecular distances. From a comparison of the intermolecular distances in the different compounds, the relation between intermolecular interactions and melting point can be probed. We were able to grow single crystals and analyze them with X-ray diffraction in the cases of the following six compounds: **7a**, **7b**, **7c**, **9c**, **10c**, and **10d**. Within this set, **7a**, **7b**, and **7c** have the same cation; **7c**, **9c**, and **10c** have the same anion; and **10c** and **10d** also have the same cation, so influences of cation and anion can start to be studied.

For the crystal structures of **7a**, **7b**, and **10d**, which do not contain the $[NTf_2]^-$ anion, the crystallographic asymmetric units consist of one cation and one anion (Figures S1, S3, and S11 in the Supporting Information). For the crystal structures of **7c**, **9c**, and **10c**, which do contain $[NTf_2]^-$, the anion is disordered, and in each case, this disorder is over a crystallographic inversion center. In these structures, the crystallographic asymmetric units consist of one cation and two half anions (Figures S5, S7, and S9). Although the $[NTf_2]^-$ anion cannot possess inversion symmetry, this type of disorder has been seen a few times before.[17] Pertinent crystallographic data can be found in Table 5 and packing diagrams can be found in Figures S2, S4, S6, S8, S10, and S12.

The structures of **7a**, **7b**, and **7c** all contain a $[C_{201}C_1C_{i3}m_2im]^+$ cation, and in each structure, the $C_{2O1}$ group lies perpendicular to the imidazolium ring, as earlier observed in $[C_{201}C_1C_1im][Br]$, $[C_{201}C_1C_1im][PF_6]$,[9b] and $[C_{201}C_1im][I]$.[5a] Moreover, this was calculated by Fei et al.[5a] to be the most stable conformation of the $C_{2O1}$ group with respect to the imidazolium ring. In the cases of **7a** and **7b** (Figure 2), there is an intramolecular C–H···O hydrogen bond between one of the hydrogen atoms of the methyl on the isopropyl group; the H···O distance is 2.580 and 2.696 Å in **7a** and **7b**, respectively. In the case of **7c**, the closest H···O distance is 2.923 Å, which is too far to be considered an interaction.

The number and variety of intermolecular interactions vary between **7a**, **7b**, and **7c**. In **7a**, there is a total of eight cation–anion interactions through C–H···O from the cation to the methanesulfonate anion; each anion makes contact to five separate cations, and the H···O distances range from 2.352 to 2.651 Å (Figure 2). In **7b**, there are six cation–anion interactions through C–H···I interactions; each anion makes contact to five separate cations, and the H···I distances range from 3.089 to 3.279 Å (Figure 3). In strong contrast to **7a** and **7b**, **7c** con-

**Table 5.** X-ray crystallographic data of $[C_{2O1}C_1C_{i3}m_2im][OMs]$ (**7a**), $[C_{2O1}C_1C_{i3}m_2im][I]$ (**7b**), $[C_{2O1}C_1C_{i3}m_2im][NTf_2]$ (**7c**), $[C_AC_2C_{i3}m_2im][NTf_2]$ (**9c**), $[C_AC_AC_{i3}m_2im][NTf_2]$ (**10c**), and $[C_AC_AC_{i3}m_2im][NTf_2]$ (**10d**).

| Compound | 7a | 7b | 7c | 9c | 10c | 10d |
|---|---|---|---|---|---|---|
| chemical formula | $C_{13}H_{26}N_2O_4S$ | $C_{12}H_{23}IN_2O$ | $C_{14}H_{23}F_6N_3O_5S_2$ | $C_{15}H_{20}F_6N_3O_4S_2$ | $C_{16}H_{23}F_6N_3O_4S_2$ | $C_{16}H_{23}N_5$ |
| formula mass | 306.42 | 338.22 | 491.47 | 484.46 | 499.49 | 285.39 |
| crystal system | monoclinic | monoclinic | monoclinic | triclinic | triclinic | monoclinic |
| $a$ [Å] | 9.3642(4) | 9.31105(15) | 12.4660(6) | 7.8108(9) | 7.3943(4) | 9.2836(4) |
| $b$ [Å] | 12.7680(8) | 10.29884(17) | 9.3427(3) | 8.8216(9) | 8.6764(5) | 14.3471(6) |
| $c$ [Å] | 13.4253(5) | 15.0676(2) | 18.5598(8) | 16.6067(16) | 17.7367(13) | 12.2147(4) |
| $\alpha$ [°] | 90 | 90 | 90 | 77.281(8) | 81.037(5) | 90 |
| $\beta$ [°] | 93.630(4) | 94.426(2) | 102.795(5) | 77.206(9) | 82.003(6) | 92.855(4) |
| $\gamma$ [°] | 90 | 90 | 90 | 79.564(9) | 78.376(5) | 90 |
| unit cell volume [Å$^3$] | 1601.94(14) | 1440.57(4) | 2107.92(15) | 1077.89(19) | 1094.12(12) | 1624.89(11) |
| temperature [K] | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) |
| space group | $P2_1/n$ | $P2_1/n$ | $P2_1/c$ | $P$-1 | $P$-1 | $P2_1/n$ |
| formula units per unit cell, $Z$ | 4 | 4 | 4 | 2 | 2 | 4 |
| reflections measured | 6975 | 6273 | 9157 | 8256 | 8127 | 12906 |
| unique reflections | 3679 | 3304 | 4802 | 4879 | 4916 | 3871 |
| $R_{int}$ | 0.0224 | 0.0245 | 0.0204 | 0.0295 | 0.0259 | 0.0134 |
| final $R_1$ values[b] | 0.0372 | 0.0220 | 0.0687 | 0.0439 | 0.0406 | 0.0483 |
| final $wR(F^2)$ values[b] | 0.0909 | 0.0513 | 0.1216 | 0.0510 | 0.0951 | 0.1192 |
| Final $R_1$ values (all data) | 0.0433 | 0.0249 | 0.0818 | 0.1087 | 0.0503 | 0.0544 |
| final $wR(F^2)$ values (all data) | 0.0967 | 0.0532 | 0.1260 | 0.1152 | 0.1037 | 0.1237 |

[a] More detailed data can be found in the Supporting Information. [b] $I > 2\sigma(I)$.

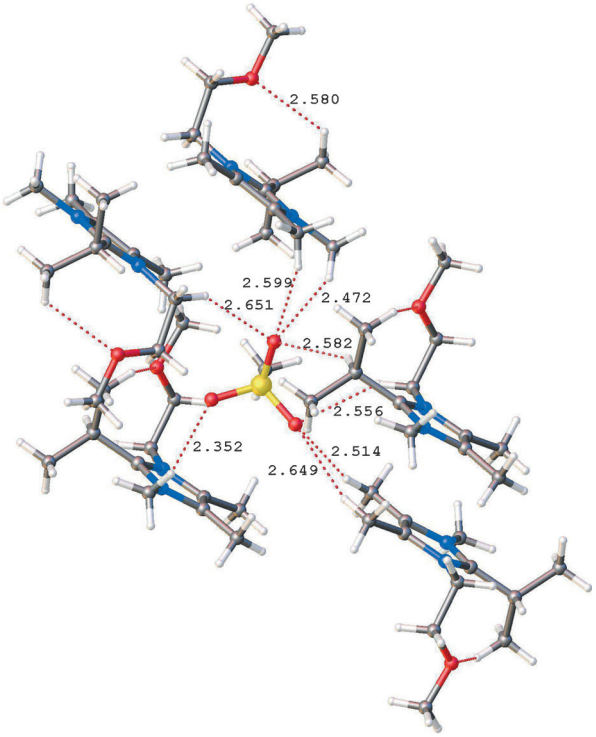



**Figure 2.** View of the crystal structure of **7a** showing the weak C–H···O hydrogen bonds formed.

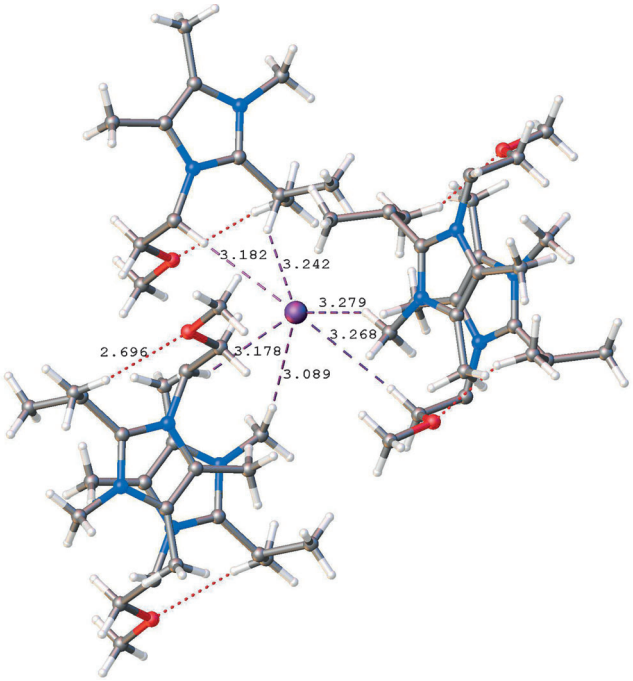



**Figure 3.** View of the crystal structure of **7b** showing the weak C–H···O and C–H···I hydrogen bonds formed

tains very few cation–anion interactions. In this structure, one of the crystallographically independent anions is not involved in any C–H···N/O/F interactions and the other anion is involved in one C–H···O interaction, but only in one of its disordered components, which is half of the total (Figure 4).

Comparing the melting points of **7a**, **7b**, and **7c** with the number of intra- and intermolecular interactions present in the crystal structures, a clear relationship can be found: **7a** has nine interactions and a melting point of 132 °C, **7b** has seven interactions and a melting point of 123 °C, and **7c** has 0.5 interactions and a melting point of 22 °C.

The structures of **7c**, **9c**, and **10c** all contain $[NTf_2]^-$ as the anion. Due to the disorder of the $[NTf_2]^-$ anion, it can be surmised that any intermolecular interactions are weak, because a strong interaction would force the anion into one of the dis-

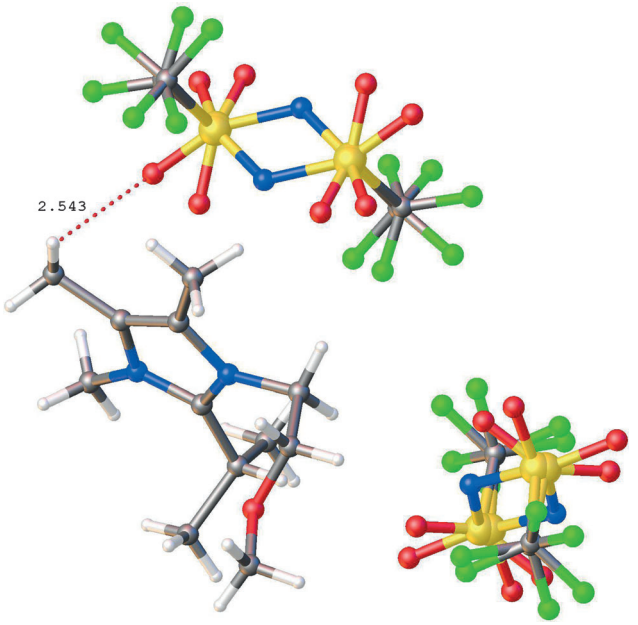



**Figure 4.** View of the crystal structure of **7c** showing the weak C–H···O hydrogen bond formed and the disorder of the two crystallographically distinct $[NTf_2]^-$ anions.

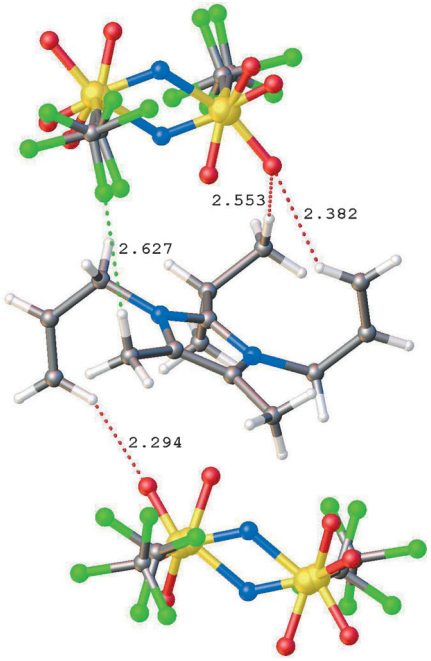



**Figure 6.** View of the crystal structure of **10c** showing the weak C–H···O and C–H···F hydrogen bonds formed and the disorder of the two crystallographically distinct $[NTf_2]^-$ anions.

ordered positions. Indeed, looking at the interactions in **7c** (Figure 4) and **9c** (Figure 5), there is only one C–H···O interaction (H···O 2.543 Å in **7c** and 2.552 Å in **9c**), which only exists to one of the crystallographically unique $[NTf_2]^-$ anions in one

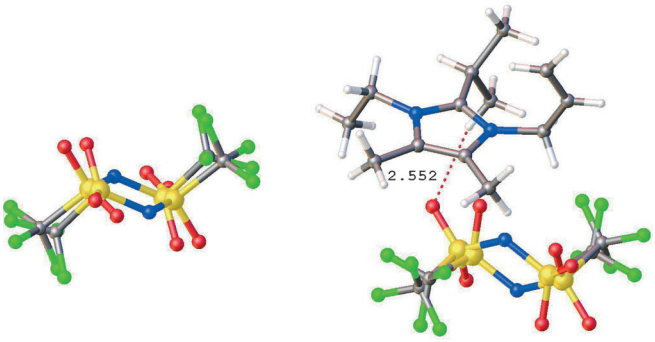



**Figure 5.** View of the crystal structure of **9c** showing the weak C–H···O hydrogen bond formed and the disorder of the two crystallographically distinct $[NTf_2]^-$ anions.

of its two possible disordered positions. In both **7c** and **9c**, the other crystallographically independent $[NTf_2]^-$ anion is not involved in any C–H···N/O/F interactions. In **10c**, there are four interactions in which both crystallographically independent $[NTf_2]^-$ anions are involved (Figure 6); there are three C–H···O interactions (H···O 2.294, 2.382, 2.553 Å) and one C–H···F interaction (H···F 2.627 Å), but these are only present in half of the disordered configurations.

Compounds **7c**, **9c**, and **10c** all contain a low number of intermolecular interactions in the crystal structure, and in each case, the melting point is low; in the case of **7c**, it is around room temperature (22 °C). Compound **10c** has the highest number of interactions and the highest melting point (63 °C), but **9c** has a much lower number of intermolecular interactions and only a slightly lower melting point (58 °C). There are only a few reports of the crystal structures of ionic liquids with an imidazolium core and a $[NTf_2]^-$ anion.[18] The most closely related to these compounds are 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_n mim][NTf_2]$, $n = 2$, 4, 6)[19] and pentamethylimidazolium bis(trifluoromethylsulfonyl)imide ($[m_5 im][NTf_2]$).[20] Although the $[C_n mim][NTf_2]$ compounds have melting points that are lower than that of **7c**, their crystal structures contain many C–H···N/O/F interactions.[19] $[m_5 im][NTf_2]$ also contains many C–H···N/O/F interactions, but this compound has a melting point of 118 °C.[20] Therefore, although a small number of C–H···N/O/F intermolecular interactions is a good indicator of the melting point, there are also other factors that affect it.

The structures of **10c** and **10d** both contain the $[C_A C_A C_{i3} m_2 im]^+$ cation motif, but it has a different conformation in the two structures. In **10c**, the two allyl groups are located on opposite sides of the imidazolium ring (Figure 6), whereas in **10d**, they are on the same side of the ring (Figure 7). The structure of **10d** contains three intermolecular C–H···N interactions between the cation and the $[N(CN)_2]^-$ anions (C–H···N 2.538, 2.539, 2.621 Å; Figure 7), which are comparable to those in **10c**, but **10d** has a lower melting point (47 vs 63 °C). Crystal structures of organic compounds containing the $[N(CN)_2]^-$ anion are rare,[18] presumably due to the propensity of $[N(CN)_2]^-$-containing compounds to form RTILs. Of the crystal structures determined, three contain an imidazo-

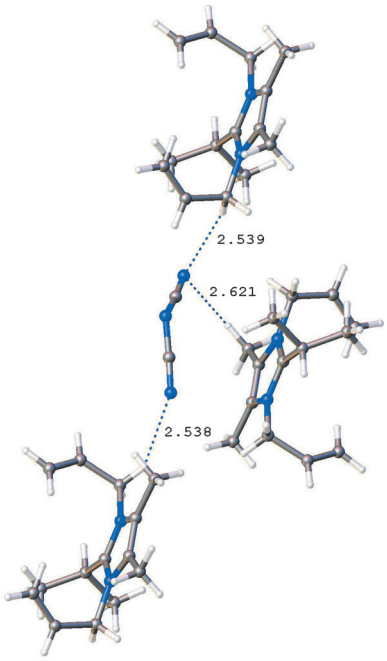



**Figure 7.** View of the crystal structure of **10 d** showing the weak C–H···N hydrogen bonds formed.

lium cation: 1-cyanomethyl-3-methylimidazolium dicyanamide {[$C_{1C\equiv N}C_1$im][$N(CN)_2$]},[21] 1,3-bis(dodecyl)imidazolium dicyanamide {[$C_{12}C_{12}$im][$N(CN)_2$]},[22] and 1-pent-2-ynyl-3-methylimidazolium dicyanamide {[($C_1C\equiv CC_2$)$C_1$im][$N(CN)_2$]}.[23] The structures of these compounds all contain a small number of intermolecular C–H···N interactions and have low melting points of 67, 44.1, and 59 °C, respectively.

### Electrochemical Analysis

In previous research in our group, it was shown that completely substituted imidazole derivatives possess wider electrochemical windows (ECWs) than their unsubstituted analogues.[1b] Hence, the effect of the functionalities on the ECW can be investigated without interference of the imidazolium ring hydrogen atoms, which are all substituted. In general, alkenes induce a minute increase in cathodic stability and a substantial increase in anodic stability,[2,24] whereas the effect of alkoxy groups on the ECW was earlier found to be very small or absent.[9a,11b] The anodic ($V_{an}$) and cathodic ($V_{cat}$) limit potentials and the ECWs ($\Delta V$) of **6**–**11 c** are given in Table 6 with a cutoff current density value of 0.25 A dm$^{-2}$, which is the value at which all noise can be ignored.

In the compounds analyzed, the introduction of the ether function decreased both the anodic and cathodic stability, but the decrease in the latter was more pronounced. This decrease in the cathodic stability of ether-functionalized cations was earlier attributed to a certain complexation of the lone pairs of electrons of the oxygen atom to the positive charge; this results in distribution of the charge and hence renders the parent cation more stable. At the same time, this also renders the ether function more prone to reduction, which decreases the overall cathodic stability.[25]

**Table 6.** Cathodic limit ($V_{cat}$), anodic limit ($V_{an}$) potential, and ECWs $\Delta V$ (vs $Fc^+$/Fc). Cutoff current density $j = 0.25$ A dm$^{-2}$, measured at 90 °C by cyclic voltammetry with a Pt working electrode.

| Ionic liquid | | $V_{cat}$ [V] | $V_{an}$ [V] | $\Delta V$ [V] |
|---|---|---|---|---|
| **6 c** | [$C_AC_1C_{i3}m_2$im][$NTf_2$] | −2.58 | 1.61 | 4.19 |
| **7 c** | [$C_{2O1}C_1C_{i3}m_2$im][$NTf_2$] | −2.24 | 1.47 | 3.71 |
| **8 c** | [$C_{2OA}C_1C_{i3}m_2$im][$NTf_2$] | −2.26 | 1.21 | 3.47 |
| **9 c** | [$C_AC_2C_{i3}m_2$im][$NTf_2$] | −2.44 | 1.68 | 4.12 |
| **10 c** | [$C_AC_AC_{i3}m_2$im][$NTf_2$] | −2.30 | 1.82 | 4.12 |
| **11 c** | [$C_{2O1}C_AC_{i3}m_2$im][$NTf_2$] | −2.33 | 1.49 | 3.82 |

On the anodic side, it appears that allyl groups can increase the oxidative stability [$V_{an}$(**6 c**) < $V_{an}$(**10 c**) and $V_{an}$(**7 c**) < $V_{an}$(**11 c**); Table 6]. Hence, there is a clear influence of the unsaturated side chains on the oxidative stability. Given the high vulnerability of unsaturated bonds towards oxidation compared to saturated side chains, this observation was attributed by Min et al. to the formation of a passivation layer on the electrode formed by oxidation of the unsaturated bonds.[2] However, introduction of allyl groups shifts the overall ECW to the anodic side (Figure 8), which can be attributed to electron withdrawal from the ring.

## 3. Conclusions

The previously reported modified Radziszewski reaction was successfully applied to the synthesis of alkenyl- and alkoxy-substituted imidazole derivatives, although byproducts formation was found to be dependent on the nature of the amine. The imidazole derivatives could be transformed into their corresponding ionic liquids through a straightforward method aided by microwave irradiation. In quaternization reactions with the use of allyl bromide and allyl methanesulfonate, extraction of a byproduct from the resulting ionic liquids was required. The obtained (metathesized) salts showed high crystallinity upon incorporating an alkoxy moiety due to the constrained conformation, but the salts showed improved undercooling properties if an allyl substituent was introduced, unless the salt possessed high symmetry. Crystallographic analysis showed that there is a broad correlation between the nature and number of intermolecular interactions in the crystal structure and the melting points of the compounds. The ECW of the alkenyl-substituted imidazolium salts was shifted towards more positive potentials, whereas derivatives with alkoxy substitution showed decreased ECWs, and in particular, the cathodic limit potential was more positive.

## Experimental Section

### Reactants

Allyl bromide (≥97%), allyl alcohol (≥98.5%), methyl methanesulfonate (≥99%), methanesulfonyl chloride (≥98%), allylamine (≥98%), 2-aminoethanol (≥98%), 2-methoxyethanamine (≥98%),

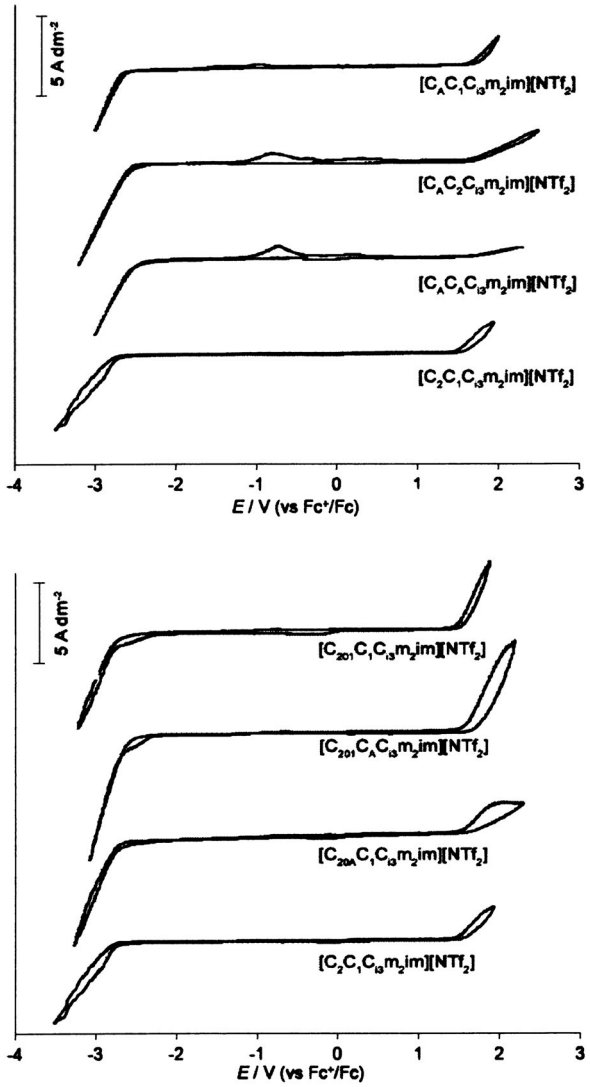



**Figure 8.** ECWs of alkenyl- (top) and alkoxy-functionalized (bottom) peralkylated ionic liquids. X axis: Potential *E* versus $Fc^+$/Fc. Y axis: current density, *j*, measured at 90 °C by cyclic voltammetry with a Pt working electrode.

ethylamine (≥99.5%), 2,3-butanedione (≥97%), isobutyraldehyde (≥98%), ammonium acetate (≥98%), silver nitrate (≥99.0%), sodium dicyanamide (96%), lithium bis(trifluoromethylsulfonyl)-imide (≥99.0%), iodomethane (≥99.0%), bromoethane (≥98%), acetophenone (≥99%), methanol, acetonitrile, dichloromethane, tetrahydrofuran, and ethyl acetate were purchased from Sigma–Aldrich; paraformaldehyde and acetaldehyde were purchased from ACROS Organics; and acetone was purchased from Fisher Chemicals. Allyl bromide was distilled prior to use. Acetone was dried over 3 Å molecular sieves. Acetonitrile was dried over anhydrous alumina and stored over 3 Å molecular sieves. $CH_2Cl_2$ was heated at reflux with CaH and distilled prior to use. THF was heated at reflux with sodium wire, containing benzophenone ketyl radical as an indicator, and distilled before use.

### Apparatus

Batch pressurized reactions were performed in 15 and 150 mL glass pressure vials with a polybutylene terephthalate (PBT) cap (Schott) and polytetrafluoroethylene (PTFE) seal for reactions up to 20 and 200 mmol, respectively. Microwave reactions were performed with a CEM Focused Microwave Synthesis System, Model Discover, with adaptable power from 0–300 W, equipped with an infrared thermosensor and monitored with the Synergy-software v. 1.32. Reagents were held in an 8 mL vial, sealed with a snap-on PTFE septum. The isothermal experiments were performed with the maximal power set to 50 W. $^1$H NMR, $^{13}$C NMR, $^{19}$F NMR, and HSQC spectroscopy experiments were performed with a JEOL ECP+ 300 spectrometer in $CDCl_3$ with tetramethylsilane (TMS) or $CFCl_3$ for $^{19}$F NMR experiments as the internal reference. IR spectra were recorded with a PerkinElmer Spectrum FTIR apparatus (ZnSe crystal; ATR mode). HPLC–MS spectra were recorded with an Agilent 1100 Series (ES, 4000 V) preceded by a reverse-phase LC column. GC analysis was performed with an Agilent 6890 GC Plus Series, with an EC5 capillary column (30 m×0.25 mm; coating thickness: 0.25 μm; injector temp.: 250 °C; carrier gas: He; flow rate: 1.0 mL min$^{-1}$; temp. profile: 80–200 °C at 10 °C min$^{-1}$, 200–280 °C at 30 °C min$^{-1}$, 5 min hold at 280 °C; detector: FID). High-resolution electrospray atmospheric-pressure chemical ionization (ESI/APCI) mass spectra were obtained with an Agilent Technologies 6210 Series Time-of-Flight. Elemental Analysis was performed with a PerkinElmer Elemental Analyzer 2400 Series II connected to an AD6 Autobalance and controller. All recorded analyses are reported. Water contents were measured in Hydranal 34812 (Fluka) with a 719S Titrino coulometric Karl Fischer titrator (Metrohm). Differential scanning calorimetry (DSC) measurements were done with a Mettler–Toledo 822 DSC apparatus (heating rate: 10 °C min$^{-1}$), and all samples were analyzed under a dry helium flow. Viscosities were analyzed with a Brookfield Viscometer DV-II Pro at 23 °C. Crystals of **7a**, **7b**, **7c**, **9c**, **10c**, and **10d** suitable for single-crystal X-ray diffraction were mounted on a nylon loop attached to a copper pin and placed into the cold stream of an Oxford Cryostream 700 at 100(2) K with an Agilent SuperNova diffractometer by using MoKα radiation ($\lambda = 0.71073$ Å). The absorption corrections were applied by using CrysAlisPro.[26] All structures were solved by using direct methods and refined by the full-matrix least-squares procedure in SHELXL.[27] All hydrogen atoms were placed in calculated positions and refined by using a riding model. A summary of the crystallographic data can be found in Table 5 and pictures of the asymmetric units and packing plots can be found in Figure S1–S12. CCDC 941088 (for **7a**), 941089 (for **7b**), 941090 (for **7c**), 941091 (for **9c**), 941093 (for **10c**), and 941093 (for **10d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. The program OLEX2 was also used in refinement and making pictures.[28] The crystal structures of **7c**, **9c**, and **10c** contained disorder of the $[NTf_2]^-$ anions. In each case, there are two crystallographically independent $[NTf_2]^-$ anions, which are both disordered over two positions over a crystallographic inversion center. In the case of **9c**, restraints were required for the thermal parameters of some C and F atoms to keep them reasonable, and in **10c**, one of the disordered carbon atoms required restraints to the thermal parameters to keep it more isotropic. Cyclic voltammograms were recorded with a Solartron SI 1287 Electrochemical Interface [scanning rate: 50 mV s$^{-1}$; platinum working and counter electrodes; reference electrode was platinum wire submerged in 1-butyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide separated from the testing solution by a fritted disk and calibrated with the ferrocenium/ferrocene ($Fc^+$/Fc) couple]. All cyclic voltammograms were recorded at 90 °C under an argon atmosphere and samples were dried prior to recording.

### Characterization of Imidazoles 4a and 4c

1-Allyl-2-isopropyl-4,5-dimethylimidazole (**4a**): B.p. 52 °C (0.10 kPa); $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.29$ [d, $^3J_{H,H} = 6.9$ Hz, 6H; $CH(CH_3)_2$], 2.05 (s, 3H; $CH_3C^{4/5}$), 2.16 (s, 3H; $CH_3C^{4/5}$), 2.81–2.95 [m, 1H; $CH(CH_3)_2$], 4.38 (dt, $^3J_{H,H} = 4.2$ Hz, $^4J_{H,H} = 2.0$ Hz, 2H; $CH_2$), 4.79 (dtd, $^3J_{H,H} = 17.2$ Hz, $^4J_{H,H} = 2.0$ Hz, $^2J_{H,H} = 1.1$ Hz, 1H; $CH{=}CH_EH_Z$), 5.15 (dtd, $^3J_{H,H} = 10.3$ Hz, $^4J_{H,H} = 2.0$ Hz, $^2J_{H,H} = 1.1$ Hz, 1H; $CH{=}CH_EH_Z$), 5.87 ppm (ddt, $^3J_{H,H} = 17.2$, 10.3, 4.2 Hz, 1H; $CH{=}CH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.58$ ($CH_3C^{4/5}$), 12.70 ($CH_3C^{4/5}$), 22.11 [$CH(CH_3)_2$], 26.03 [$CH(CH_3)_2$], 45.13 ($NCH_2$), 116.07 ($CH{=}CH_2$), 121.27 ($C^{4/5}$), 131.26 ($C^{4/5}$), 133.44 ($CH{=}CH_2$), 150.99 ppm ($C^2$); IR (ATR): $\tilde{\nu} = 917$, 1087, 1304, 1434, 2965 cm$^{-1}$; HRMS (ESI/APCI): *m/z*: calcd for $[C_{11}H_{19}N_2^+]$: 179.1543; found: 179.1540; yield: 63%; colorless liquid.

2-Isopropyl-1-(2-methoxyethyl)-4,5-dimethylimidazole (**4c**): B.p. 82 °C (0.10 kPa); $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.30$ [d, $^3J_{H,H} = 7.2$ Hz, 6H; $CH(CH_3)_2$], 2.10 (s, 3H; $CH_3C^{4/5}$), 2.14 (s, 3H; $CH_3C^{4/5}$), 2.93–3.06 (m, 1H; CH), 3.31 (t, $^3J_{H,H} = 6.1$ Hz, 2H; $CH_2O$), 3.50 (s, 3H, $OCH_3$), 3.93 ppm (t, $^3J_{H,H} = 4.8$ Hz, 2H; $NCH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.92$ ($CH_3C^4$), 12.63 ($CH_3C^{4/5}$), 22.18 [$CH(CH_3)_2$], 25.88 (CH), 43.07 ($NCH_2$), 59.09 ($OCH_3$), 71.94 ($CH_2O$), 121.06 ($C^{4/5}$), 131.35 ($C^{4/5}$), 151.44 ppm ($C^2$); IR (ATR): $\tilde{\nu} = 1086$, 1119, 1438, 2925 cm$^{-1}$; HRMS (ESI/APCI): *m/z*: calcd for $[C_{11}H_{21}N_2O^+]$: 197.1648; found: 197.1649; yield: 53%; white waxy solid.

### Procedure for the Synthesis of 1-(2-Hydroxyethyl)-2-Isopropyl-4,5-Dimethylimidazole (4b)

A glass, 150 mL pressure vial was charged with MeOH (50 mL) and a PTFE stirring bar. The solvent was allowed to cool to 0 °C and isobutyraldehyde (100 mmol, 7.21 g) and 2-aminoethanol (100 mmol, 6.11 g) were added. The vial was closed and submerged in a preheated oil bath at 120 °C with a temperature controller. After heating for 2 h with vigorous stirring, the reaction mixture was carefully cooled to 0 °C, the vial was opened, and 2,3-butanedione (25 mmol, 2.15 g) and $NH_4OAc$ (25 mmol, 1.93 g) were consecutively added. The vessel was closed immediately and heated in a preheated oil bath at 120 °C for 30 min under vigorous stirring. Then, three-times more, the reaction mixture was carefully cooled and 2,3-butanedione (25 mmol) and $NH_4OAc$ (25 mmol) were added, after which the reaction mixture was heated for 30 min more. After the final cooling, MeOH and the reaction water were removed in vacuo. The reaction mixture was dissolved in EtOAc and extracted with 0.5 M HCl (2×100 mL). The aqueous phase was neutralized with 3.0 M NaOH (50 mL) and extracted with EtOAc (3×40 mL). The combined organic phase was dried with $MgSO_4$. The solvent was removed in vacuo and a black oil (7.31 g) was obtained. The resulting oil was dissolved in an equal volume of boiling $CH_3CN$ and stored at −18 °C until all 1*H*-2-isopropyl-3,4-dimethylimidazole precipitated. If the oil was not sufficiently pure as determined by GC, an additional precipitation was applied. The solvent was removed from the resulting mother liquid by rotary evaporation, and the resulting product was further used for the synthesis of **4d**.

### Characterization of Imidazole 4b

1-(2-Hydroxyethyl)-2-isopropyl-4,5-dimethylimidazole (**4b**): $R_f = 0.07$ (hexanes/EtOAc = 4:6); $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta =$ 1.28 [d, $^3J_{H,H} = 7.2$ Hz, 6H; $CH(CH_3)_2$], 2.11 (s, 6H; $CH_3C^{4/5}$), 2.94–3.09 (m, 1H; CH), 3.79 (t, $^3J_{H,H} = 6.1$ Hz, 2H; $CH_2O$), 3.94 ppm (t, $^3J_{H,H} =$ 6.1 Hz, 2H; $NCH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.84$ ($CH_3C^{4/5}$), 12.09 ($CH_3C^{4/5}$), 22.02 [$CH(CH_3)_2$], 25.77 [$CH(CH_3)_2$], 45.42 ($NCH_2$), 60.71 ($CH_2O$), 121.34 ($C^{4/5}$), 130.71 ($C^{4/5}$), 151.41 ppm ($C^2$); IR (ATR): $\tilde{\nu} = 729$, 1086, 1738, 2966, 3112 cm$^{-1}$; HRMS (ESI/APCI): *m/z*: calcd for $[C_{10}H_{19}N_2O^+]$: 183.1492; found: 183.1495; yield (crude): 38%; black oil.

### Procedure for the Synthesis of 1-(2-Allyloxyethyl)-2-Isopropyl-4,5-Dimethylimidazole (4d)

Dry THF (80 mL) was added under a nitrogen atmosphere to a flame-dried, 250 mL flask containing crude 1-(2-hydroxyethyl)-2-isopropyl-4,5-dimethylimidazole (70 mmol, 12.81 g). The mixture was cooled to 0 °C and then pure NaH (77 mmol, 1.85 g) was slowly added. After stirring for 15 min, allyl bromide (73,5 mmol, 8.90 g) was added dropwise. The mixture was allowed to warm to room temperature overnight. Upon completion of the reaction, a fraction of the solvent was evaporated, and the resulting slurry was diluted in EtOAc and washed with a saturated aqueous solution of $NaHCO_3$ (2×80 mL) and water (1×40 mL). The organic layer was dried with $MgSO_4$ after which the solvent was removed by rotary evaporation. The resulting oil was distilled by short-path vacuum distillation (108 °C, 0.10 kPa) to obtain a yellow oil.

### Characterization of Imidazole 4d

1-(2-Allyloxyethyl)-2-isopropyl-4,5-dimethylimidazole (**4d**): B.p. 108 °C (0.10 kPa); $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.30$ [d, $^3J_{H,H} = 6.8$ Hz, 6H; $CH(CH_3)_2$], 2.11 (s, 3H; $CH_3C^{4/5}$), 2.14 (s, 3H; $CH_3C^{4/5}$), 2.95–3.09 [m, 1H; $CH(CH_3)_2$], 3.56 (t, $^3J_{H,H} = 6.3$ Hz, 2H; $CH_2O$), 3.93 (dt, $^3J_{H,H} = 5.4$ Hz, $^4J_{H,H} = 1.4$ Hz, 2H; $CH_2CH{=}CH_2$), 3.96 (t, $^3J_{H,H} = 6.3$ Hz, 2H; $NCH_2$), 5.17 (ddt, $^3J_{H,H} = 10.1$ Hz, $^2J_{H,H} = 3.3$ Hz, $^4J_{H,H} = 1.6$ Hz, 1H; $CH{=}CH_EH_Z$), 5.22 (ddt, $^3J_{H,H} = 17.3$ Hz, $^2J_{H,H} =$ 3.3 Hz, $^4J_{H,H} = 1.6$ Hz, 1H; $CH{=}CH_EH_Z$), 5.83 ppm (ddt, $^3J_{H,H} = 17.3$, 10.1, 5.4 Hz, 1H; $CH{=}CH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.95$ ($CH_3C^{4/5}$), 12.69 ($CH_3C^{4/5}$), 22.18 [$CH(CH_3)_2$], 25.82 (CH), 43.13 ($NCH_2$), 69.33 ($CH_2CH_2O$), 77.20 ($CH_2CH{=}CH_2$), 117.04 ($CH_2CH{=}CH_2$), 121.02 ($C^{4/5}$), 131.32 ($C^{4/5}$), 134.22 ($CH{=}CH_2$), 151.37 ppm ($C^2$); IR (ATR): $\tilde{\nu} = 1052$, 1134, 1175, 1378 cm$^{-1}$; HRMS (ESI/APCI): *m/z*: calcd for $[C_{13}H_{23}N_2O^+]$: 223.1805; found: 223.1807; yield: 86%; light yellow oil.

### Procedure for the Synthesis of 1-Allyl-2-Isopropyl-3,4,5-Trimethylimidazolium Methanesulfonate [$C_AC_1C_{i3}m_2im$][OMs] (6a)

1-Allyl-2-isopropyl-4,5-dimethylimidazole (10.4 mmol, 1.86 g) was added by syringe under a nitrogen atmosphere to a flame-dried, 8 mL vial containing dry acetonitrile (4 mL). Methyl methanesulfonate (11.4 mmol, 1.26 g, 1.1 equiv.) was then added. The headspace was filled with nitrogen and the vial was sealed with a PTFE cap. The mixture was irradiated for 30 min in a microwave reactor to a temperature of 80 °C. Upon completion of the reaction, the solvent was removed in vacuo, and the mixture was diluted with distilled water (25 mL) and washed with EtOAc (2×20 mL). The aqueous layer was evaporated and dried for 6 h at 100 °C and 0.10 kPa.

### Characterization of Methanesulfonate Ionic Liquids 6a and 7a

1-Allyl-2-isopropyl-3,4,5-trimethylimidazolium methanesulfonate [$C_AC_1C_i^3m_2im$][OMs] (**6a**): $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta =$ 1.50 [d, $^3J_{H,H} = 7.2$ Hz, 6H; $CH(CH_3)_2$], 2.23 (s, 3H; $CH_3C^{4/5}$), 2.29 (s, 3H; $CH_3C^{4/5}$), 2.70 (s, 3H; $CH_3SO_3$), 3.53–3.67 [m, 1H; $CH(CH_3)_2$], 3.84 (s, 3H; $CH_3SO_3$), 4.84–4.89 (m, 2H; $NCH_2$), 4.89 (d, $^3J_{H,H} =$ 17.1 Hz, 1H; $CH{=}CH_EH_Z$), 5.32 (d, $^3J_{H,H} = 10.5$ Hz, 1H; $CH{=}CH_EH_Z$), 5.90–6.04 ppm (ddt, $^3J_{H,H} = 17.1$, 10.5, 4.4 Hz, 1H; $CH{=}CH_2$); $^{13}$C NMR

(75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.66$ ($CH_3C^{4/5}$), 8.98 ($CH_3C^{4/5}$), 19.27 [$CH(CH_3)_2$], 25.31 [$CH(CH_3)_2$], 33.09 ($NCH_3$), 39.39 ($CH_3SO_3$), 47.65 ($NCH_2$), 117.76 ($CH{=}CH_2$), 125.90 ($C^{4/5}$), 126.97 ($C^{4/5}$), 131.02 ($CH{=}CH_2$), 148.39 ppm ($C^2$); IR (ATR): $\tilde{\nu} = 726$, 1036, 1192, 1452, 1523, 1651 $cm^{-1}$; MS (ES): *m/z* (%): 193.3 (100) [$M+H^+$]; yield: 98%; light yellow oil.

2-Isopropyl-1-(2-methoxyethyl)-3,4,5-trimethylimidazolium methanesulfonate [$C_{2O1}C_1C_{i3}m_2$im][OMs] (**7a**): $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.48$ [d, $^3J_{H,H} = 7.7$ Hz, 6H; $CH(CH_3)_2$], 2.28 (s, 3H; $CH_3C^{4/5}$), 2.30 (s, 3H; $CH_3C^{4/5}$), 2.71 (s, 3H; $CH_3SO_3$), 3.31 (s, 3H; $OCH_3$), 3.65 (t, $^3J_{H,H} = 5.0$ Hz, 2H; $CH_2O$), 3.67–3.81 (m, 1H; CH), 3.83 (s, 3H, $NCH_3$), 4.47 ppm (t, $^3J_{H,H} = 5.0$ Hz, 2H; $NCH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.89$ ($CH_3C^{4/5}$), 9.21 ($CH_3C^{4/5}$), 18.93 [$CH(CH_3)_2$], 25.18 (CH), 33.19 ($NCH_3$), 39.42 ($CH_3SO_3$), 46.00 ($NCH_2$), 59.09 ($OCH_3$), 70.36 ($CH_2O$), 125.76 ($C^{4/5}$), 126.76 ($C^{4/5}$), 148.96 ppm ($C^2$); IR (ATR): $\tilde{\nu} = 1039$, 1119, 1184, 1458, 1523 $cm^{-1}$; HRMS (ESI/APCI): *m/z*: calcd for [$C_{12}H_{23}N_2O^+$]: 211.1805; found: 211.1803; elemental analysis calcd (%) for $C_{13}H_{26}N_2O_4S$ (306.42): C 50.96, H 8.55, N 9.14; found C 50.51, H 9.11, N 9.00; yield: 96%; white crystals.

### Procedure for the Synthesis of 1-(2-Allyloxyethyl)-2-Isopropyl-3,4,5-Trimethylimidazolium Methanesulfonate [$C_{2OA}C_1C_{i3}m_2$im][OMs] (8a)

The synthesis procedure was analogous to the procedure applied for **6a**, although longer irradiation times were used for better conversion. The mixture was irradiated for 40 min in a microwave reactor to a temperature of 80 °C, and the longer reaction times led to significant coloration. Upon completion of the reaction, the solvent was removed in vacuo, and the mixture was diluted with distilled water (25 mL) and washed with $Et_2O$ (2×20 mL) because **8a** is more soluble in EtOAc than **6a**. The aqueous layer was evaporated and dried for 6 h at 100 °C and 0.10 kPa.

### Characterization of Methanesulfonate Ionic Liquid 8a

1-(2-Allyloxyethyl)-2-isopropyl-3,4,5-trimethylimidazolium methanesulfonate [$C_{2OA}C_1C_{i3}m_2$im][OMs] (**8a**): $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.48$ [d, $^3J_{H,H} = 7.7$ Hz, 6H; $CH(CH_3)_2$], 2.28 (s, 3H; $CH_3C^{4/5}$), 2.31 (s, 3H; $CH_3C^{4/5}$), 2.71 (s, 3H; $CH_3SO_3$), 3.65–3.85 [m, 1H; $CH(CH_3)_2$], 3.71 (t, $^3J_{H,H} = 5.0$ Hz, 6H; $CH_2O$), 3.82 (m, 3H; $NCH_3$), 3.95 (d, $^3J_{H,H} = 5.5$ Hz; $OCH_2CH$), 4.49 (t, $^3J_{H,H} = 5.0$ Hz, 2H; $NCH_2$), 5.18 (d, $^3J_{H,H} = 10.8$ Hz, 1H; $CH{=}CH_ZH_E$), 5.19 (d, $^3J_{H,H} = 16.8$ Hz, 1H; $CH{=}CH_ZH_E$), 5.79 ppm (ddt, $^3J_{H,H} = 16.8$, 10.8, 5.5 Hz, 1H; $CH{=}CH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.89$ ($CH_3C^{4/5}$), 9.24 ($CH_3C^{4/5}$), 18.99 [$CH(CH_3)_2$], 25.13 [$CH(CH_3)_2$], 32.21 ($NCH_3$), 39.45 ($CH_3SO_3$), 46.06 ($NCH_2$), 68.05 ($OCH_2CH$), 72.36 ($CH_2O$), 118.05 ($CH{=}CH_2$), 125.84 ($C^{4/5}$), 126.80 ($C^{4/5}$), 133.69 ($CH{=}CH_2$), 148.96 ppm ($C^2$); IR (ATR): $\tilde{\nu} = 763$, 1036, 1107, 1190 $cm^{-1}$; MS (ES): *m/z* (%): 237.3 (100) [$M+H^+$]; yield: 92%; yellow liquid.

### Procedure for the Synthesis of Allyloxy Methanesulfonate Ester

Allyl alcohol (189 mmol, 11.05 g,) and triethylamine (207 mmol, 29.2 mL, 1.1 equiv.) were added to a flame-dried, 250 mL flask equipped with a $CaCl_2$ tube and containing dry $CH_2Cl_2$ (80 mL). The mixture was vigorously stirred and allowed to cool in an ice bath, after which methanesulfonate chloride (207 mmol, 12.89 mL, 1.1 equiv.) was added dropwise by syringe. The reaction mixture was then allowed to warm to room temperature and stirred for 1 h. Upon completion of the reaction, the mixture was washed once with a saturated aqueous solution of $NaHCO_3$ and once with water. The organic layer was dried with $MgSO_4$ and filtered. The filtrate was evaporated in vacuo, and the product was distilled by short-path vacuum distillation (53 °C, 0.10 kPa).

### Procedure for the Synthesis of 1-Allyl-3-Ethyl-2-Isopropyl-4,5-Dimethylimidazolium Methanesulfonate [$C_AC_2C_{i3}m_2$im][OMs] (9a)

1-Ethyl-2-isopropyl-4,5-dimethylimidazole (10 mmol, 1.66 g) was added by syringe under a nitrogen atmosphere to a flame-dried, 8 mL vial containing dry acetonitrile (4 mL). Freshly distilled allyl methanesulfonate (10.5 mmol, 1.43 g, 1.05 equiv.) was then added. The headspace was filled with nitrogen, and the vial was sealed with a PTFE cap. The mixture was irradiated for 45 min in a microwave reactor to a temperature of 100 °C. Upon completion of the reaction, the solvent was removed in vacuo, and the mixture was diluted with distilled water (25 mL) containing NaOH (0.05 mol equiv. dependent on the fraction of **12** observed by $^1$H NMR spectroscopy). The aqueous layer was washed with EtOAc (2×20 mL). The water was removed by evaporation or lyophilization, and the product was diluted in an excess amount of boiling acetone and stored at −18 °C for several hours. The formed crystals were filtered off. The filtrate was evaporated and again diluted in boiling acetone, until no more crystals could be filtered off after storage at −18 °C. The resulting clear solution was evaporated, and the obtained oil was dried for 6 h at 100 °C and 0.10 kPa.

### Characterization of Methanesulfonate Ionic Liquids 9–11a

1-Allyl-3-ethyl-2-isopropyl-4,5-dimethylimidazolium methanesulfonate [$C_AC_2C_{i3}m_2$im][OMs] (**9a**): $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.44$ (d, $^3J_{H,H} = 7.3$ Hz, 3H; $CH_2CH_3$), 1.51 [d, $^3J_{H,H} = 7.7$ Hz, 6H; $CH(CH_3)_2$], 2.23 (s, 3H; $CH_3C^{4/5}$), 2.31 (s, 3H; $CH_3C^{4/5}$), 2.71 (s, 3H; $CH_3SO_3$), 3.59–3.68 [m, 1H; $CH(CH_3)_2$], 4.29 (t, $^3J_{H,H} = 7.3$ Hz, 3H; $CH_2CH_3$), 4.89 (d, $^3J_{H,H} = 18.7$ Hz, 1H; $CH{=}CH_EH_Z$), 4.89–4.97 (m, 2H; $CH_2CH{=}CH_2$), 5.33 (d, $^3J_{H,H} = 11.0$ Hz, 1H; $CH{=}CH_EH_Z$), 5.94–6.03 ppm (m, 1H; $CH{=}CH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.49$ ($CH_3C^{4/5}$), 8.64 ($CH_3C^{4/5}$), 15.60 ($CH_2CH_3$), 19.91 [$CH(CH_3)_2$], 25.18 [$CH(CH_3)_2$], 39.35 ($CH_3SO_3$), 41.15 ($CH_2CH_3$), 47.71 ($CH_2CH{=}CH_2$), 117.53 ($CH{=}CH_2$), 125.86 ($C^{4/5}$), 126.77 ($C^{4/5}$), 131.17 ($CH{=}CH_2$), 148.09 ppm ($C^2$); IR (ATR): $\tilde{\nu} = 1039$, 1181, 1513, 1648, 3432 $cm^{-1}$; MS (ES): *m/z* (%): 207.3 (100) [$M+H^+$]; yield: 78%; yellow oil.

1,3-Diallyl-2-isopropyl-4,5-dimethylimidazolium methanesulfonate [$C_AC_AC_{i3}m_2$im][OMs] (**10a**): $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.45$ [d, $^3J_{H,H} = 7.2$ Hz, 6H; $CH(CH_3)_2$], 2.28 (s, 6H; $CH_3C^{4/5}$), 2.83 (s, 3H; $CH_3SO_3$), 3.57–3.71 [m, 1H; $CH(CH_3)_2$], 4.86 (dt, $^3J_{H,H} = 17.5$ Hz, $^4J_{H,H} = 2.0$ Hz, 2H; $CH{=}CH_EH_Z$), 5.02 (dt, $^3J_{H,H} = 4.2$ Hz, $^4J_{H,H} = 2.0$ Hz, 4H; $NCH_2$), 5.35 (dt, $^3J_{H,H} = 10.6$ Hz, $^4J_{H,H} = 1.9$ Hz, 2H; $CH{=}CH_EH_Z$), 5.95 ppm (ddt, $^3J_{H,H} = 17.5$, 10.6, 4.2 Hz, 2H, $CH{=}CH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.58$ ($CH_3C^{4/5}$), 19.88 [$CH(CH_3)_2$], 25.30 [$CH(CH_3)_2$], 39.45 ($CH_3SO_3$), 47.82 ($CH_2CH{=}CH_2$), 117.48 ($CH{=}CH_2$), 126.58 ($C^4$, $C^5$), 131.08 (CH), 148.86 ppm ($C^2$); IR (ATR): $\tilde{\nu} = 920$, 1511, 1646; 2358, 3424 $cm^{-1}$; MS (ES): *m/z* (%): 219.3 (100) [$M+H^+$]; yield: 76%; colorless oil.

1-Allyl-2-isopropyl-3-(2-methoxyethyl)-4,5-dimethylimidazolium methanesulfonate [$C_{2O1}C_AC_{i3}m_2$im][OMs] (**11a**): $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.46$ [d, $^3J_{H,H} = 7.2$ Hz, 6H; $CH(CH_3)_2$], 2.20 (s, 3H; $CH_3C^{4/5}$), 2.33 (s, 3H; $CH_3C^{4/5}$), 2.72 (s, 3H; $CH_3SO_3$), 3.32 (s, 3H; $OCH_3$), 3.69 (t, $^3J_{H,H} = 5.0$ Hz, 2H; $CH_2O$), 3.69–3.85 [m, 1H; $CH(CH_3)_2$], 4.58 (t, $^3J_{H,H} = 5.0$ Hz, 2H; $CH_2CH_2O$), 4.82–4.83 (m, 2H; $CH_2CH{=}CH_2$), 4.95 (d, $^3J_{H,H} = 17.1$ Hz, 1H; $CH{=}CH_ZH_E$), 5.38 (d, $^3J_{H,H} = 10.5$ Hz, 1H; $CH{=}CH_ZH_E$), 5.90–6.02 ppm (m, 1H; $CH{=}CH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.52$ ($CH_3C^{4/5}$), 9.25 ($CH_3C^{4/5}$), 19.86

[$CH(CH_3)_2$], 25.39 [$CH(CH_3)_2$], 39.45 ($CH_3SO_3$), 46.23 ($CH_2CH_2O$), 47.94 ($CH_2CH{=}CH_2$), 59.12 ($OCH_3$), 70.32 ($CH_2O$), 118.07 ($CH{=}CH_2$), 126.49 ($C^{4/5}$), 126.57 ($C^{4/5}$), 130.82 ($CH{=}CH_2$), 149.51 ppm ($C^2$); IR (ATR): $\tilde{\nu}$ = 1038, 1117, 1181, 1513 $cm^{-1}$; MS (ES): *m/z* (%): 237.3 (100) [$M+H^+$]; yield: 75%; white glass.

### Characterization of Iodide Ionic Liquids 6–8 b

1-Allyl-2-isopropyl-3,4,5-trimethylimidazolium iodide [$C_AC_1C_{i3}m_2im$][I] (**6 b**): $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 1.52 [d, $^3J_{H,H}$ = 7.2 Hz, 6H; $CH(CH_3)_2$], 2.25 (s, 3H; $CH_3C^{4/5}$), 2.33 (s, 3H; $CH_3C^{4/5}$), 3.56–3.68 [m, 1H; $CH(CH_3)_2$] 3.88 (s, 3H; $NCH_3$), 4.87–4.91 (m, 2H; $NCH_2$), 4.98 (d, $^3J_{H,H}$ = 17.1 Hz, 1H; $CH{=}CH_EH_Z$), 5.35 (d, $^3J_{H,H}$ = 10.5 Hz, 1H; $CH{=}CH_EH_Z$), 5.93–6.02 ppm (m, 1H; $CH{=}CH_2$); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 9.24 ($CH_3C^{4/5}$), 9.82 ($CH_3C^{4/5}$), 19.73 [$CH(CH_3)_2$], 25.24 [$CH(CH_3)_2$], 34.43 ($NCH_3$), 48.32 ($NCH_2$), 118.07 ($CH{=}CH_2$), 125.78 ($C^{4/5}$), 127.02 ($C^{4/5}$), 130.63 ($CH{=}CH_2$), 148.25 ppm ($C^2$); IR (ATR): $\tilde{\nu}$ = 1222, 1362, 1444, 1521, 1707 $cm^{-1}$; MS (ES): *m/z* (%): 193.3 (100) [$M+H^+$]; yield: 98%; light yellow oil.

2-Isopropyl-1-(2-methoxyethyl)-3,4,5-trimethylimidazolium iodide [$C_{2O1}C_1C_{i3}m_2im$][I] (**7 b**): $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 1.50 [d, $^3J_{H,H}$ = 7.2 Hz, 6H; $CH(CH_3)_2$], 2.30 (s, 6H; $CH_3C^{4/5}$), 3.32 (s, 3H; $OCH_3$), 3.67 (t, $^3J_{H,H}$ = 4.8 Hz, 2H; $CH_2O$), 3.70–3.84 (m, 1H; CH), 3.84 (s, 3H, $NCH_3$), 4.46 ppm (t, $^3J_{H,H}$ = 4.8 Hz, 2H; $NCH_2$);$^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 9.65 ($CH_3C^{4/5}$), 9.88 ($CH_3C^{4/5}$), 19.36 [$CH(CH_3)_2$], 25.25 (CH), 34.31 ($NCH_3$), 46.71 ($NCH_2$), 59.26 ($OCH_3$), 70.39 ($CH_2O$), 125.73 ($C^{4/5}$), 126.89 ($C^{4/5}$), 148.86 ppm ($C^2$); IR (ATR): $\tilde{\nu}$ = 1108, 1446, 1523, 2971 $cm^{-1}$; HRMS (ESI/APCI): *m/z*: calcd for [$C_{12}H_{23}N_2O^+$]: 211.1805; found: 211.1810; elemental analysis calcd (%) for $C_{12}H_{23}IN_2O$ (338.23): C 42.61, H 6.85, N 8.28; found: C 42.09, H 6.77, N 8.09; yield: 99%; white crystals.

1-(2-Allyloxyethyl)-2-isopropyl-3,4,5-trimethylimidazolium iodide [$C_{2OA}C_1C_{i3}m_2im$][I] (**8 b**): $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 1.51 [d, $^3J_{H,H}$ = 7.2 Hz, 6H; $CH(CH_3)_2$], 2.29 (s, 3H; $CH_3C^{4/5}$), 2.32 (s, 3H; $CH_3C^{4/5}$), 3.72–3.90 [m, 1H; $CH(CH_3)_2$], 3.73 (t, $^3J_{H,H}$ = 5.1 Hz, 2H; $CH_2O$), 3.83 (s, 3H; $NCH_3$), 3.96 (dt, $^3J_{H,H}$ = 6.1 Hz, $^4J_{H,H}$ = 1.5 Hz; $OCH_2CH$), 4.49 (t, $^3J_{H,H}$ = 5.1 Hz, 2H; $NCH_2$), 5.19 (dt, $^3J_{H,H}$ = 10.6 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H; $CH{=}CH_ZH_E$), 5.20 (dt, $^3J_{H,H}$ = 16.7 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H; $CH{=}CH_ZH_E$), 5.80 ppm (ddt, $^3J_{H,H}$ = 16.7, 10.6, 6.1 Hz, 1H; $CH{=}CH_2$); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 9.63 ($CH_3C^{4/5}$), 9.86 ($CH_3C^{4/5}$), 19.39 [$CH(CH_3)_2$], 25.18 [$CH(CH_3)_2$], 34.28 ($NCH_2$), 46.75 ($NCH_3$), 68.02 ($OCH_2CH$), 72.36 ($CH_2O$), 118.08 ($CH{=}CH_2$), 125.76 ($C^{4/5}$), 126.89 ($C^{4/5}$), 133.63 ($CH{=}CH_2$), 148.82 ppm ($C^2$); IR (ATR): $\tilde{\nu}$ = 746, 920, 1110, 1447, 1522 $cm^{-1}$; HRMS (ESI/APCI): *m/z*: calcd for [$C_{14}H_{25}N_2O^+$]: 237.1961; found: 237.1963; yield: 99%; yellow liquid.

### Procedure for the Synthesis of 1-Allyl-3-Ethyl-2-Isopropyl-4,5-Dimethylimidazolium Bromide [$C_AC_2C_{i3}m_2im$][Br] (9 b)

1-Ethyl-2-isopropyl-4,5-dimethylimidazole (10 mmol, 1.66 g) was added by syringe under a nitrogen atmosphere to a flame-dried, 8 mL vial containing dry acetonitrile (4 mL). Distilled allyl bromide (10.5 mmol, 1.27 g, 1.05 equiv.) was then added. The headspace was filled with nitrogen, and the vial was sealed with a PTFE cap. The mixture was irradiated for 45 min in a microwave reactor to a temperature of 100 °C. Upon completion of the reaction, the solvent was removed in vacuo, and the mixture was diluted with distilled water (25 mL) containing NaOH (0.09 mol equiv. dependent on the fraction of **12** observed by $^1H$ NMR spectroscopy). The aqueous layer was washed with EtOAc (2×20 mL). The water was removed by evaporation or lyophilization, and the product was diluted in an excess amount of boiling dichloromethane and stored at −18 °C for several hours. The formed suspension was filtered off over filter paper. The filtrate was evaporated and again diluted in boiling dichloromethane, until no more suspension was visible after storage at −18 °C. The resulting clear solution was evaporated, and the obtained oil was dried for 6 h at 80 °C and 0.10 kPa.

### Characterization of Bromide Ionic Liquids 9–11 b

1-Allyl-3-ethyl-2-isopropyl-4,5-dimethylimidazolium bromide [$C_AC_2C_i^3m_2im$][Br] (**9 b**): $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 1.45 (d, $^3J_{H,H}$ = 7.3 Hz, 3H; $CH_2CH_3$), 1.52 [d, $^3J_{H,H}$ = 7.2 Hz, 6H; $CH(CH_3)_2$], 2.26 (s, 3H; $CH_3C^{4/5}$), 2.34 (s, 3H; $CH_3C^{4/5}$), 3.67–3.82 [m, 1H; $CH(CH_3)_2$], 4.36 (t, $^3J_{H,H}$ = 7.3 Hz, 3H; $CH_2CH_3$), 4.91 (d, $^3J_{H,H}$ = 17.2 Hz, 1H; $CH{=}CH_EH_Z$), 4.98–5.04 (m, 2H; $CH_2CH{=}CH_2$), 5.35 (d, $^3J_{H,H}$ = 10.5 Hz, 1H; $CH{=}CH_EH_Z$), 6.00 ppm (ddt, $^3J_{H,H}$ = 17.2, 10.5, 4.8 Hz, 1H; $CH{=}CH_2$); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 8.99 ($CH_3C^{4/5}$), 9.13 ($CH_3C^{4/5}$), 15.80 ($CH_2CH_3$), 20.35 [$CH(CH_3)_2$], 25.42 [$CH(CH_3)_2$], 41.77 ($CH_2CH_3$), 48.43 ($CH_2CH{=}CH_2$), 118.04 ($CH{=}CH_2$), 125.95 ($C^{4/5}$), 126.94 ($C^{4/5}$), 130.85 ($CH{=}CH_2$), 148.30 ppm ($C^2$); IR (ATR): $\tilde{\nu}$ = 1091, 1331, 1451, 1511, 1646, 2973, 3455 $cm^{-1}$; MS (ES): *m/z* (%): 207.3 (100) [$M+H^+$]; elemental analysis calcd (%) for $C_{13}H_{23}BrN_2$ (287.24): C 54.36, H 8.07, N 9.75; found: C 54.11, H 8.67, N 9.61; yield: 81%; white flakes.

1,3-Diallyl-2-isopropyl-4,5-dimethylimidazolium bromide [$C_AC_AC_i^3m_2im$][Br] (**10 b**): $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 1.46 [d, $^3J_{H,H}$ = 7.2 Hz, 6H; $CH(CH_3)_2$], 2.30 (s, 6H; $CH_3C^{4/5}$), 3.60–3.75 [m, 1H; $CH(CH_3)_2$], 4.87 (dt, $^3J_{H,H}$ = 17.1 Hz, $^4J_{H,H}$ = 1.8 Hz, 2H; $CH{=}CH_EH_Z$), 5.05–5.08 (m, 4H; $NCH_2$), 5.35 (dt, $^3J_{H,H}$ = 10.5 Hz, $^4J_{H,H}$ = 1.8 Hz, 2H; $CH{=}CH_EH_Z$), 6.06 ppm (ddt, $^3J_{H,H}$ = 17.1, 10.5, 4.3 Hz, 2H; $CH{=}CH_2$); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 8.81 ($CH_3C^{4/5}$), 20.05 [$CH(CH_3)_2$], 25.36 [$CH(CH_3)_2$], 48.09 ($CH_2CH{=}CH_2$), 117.55 ($CH{=}CH_2$), 126.69 ($C^4$, $C^5$), 131.00 ($CH{=}CH_2$), 148.88 ppm ($C^2$); IR (ATR): $\tilde{\nu}$ = 724, 921, 1510, 2175, 2977, 3416 $cm^{-1}$; HRMS (ESI/APCI): *m/z*: calcd for [$C_{14}H_{23}N_2^+$]: 219.1856; found: 219.1856; yield: 79%; reddish oil.

1-Allyl-2-isopropyl-3-(2-methoxyethyl)-4,5-dimethylimidazolium bromide [$C_{2O1}C_AC_{i3}m_2im$][Br] (**11 b**): $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 1.46 [d, $^3J_{H,H}$ = 7.2 Hz, 6H; $CH(CH_3)_2$], 2.23 (s, 3H; $CH_3C^{4/5}$), 2.35 (s, 3H; $CH_3C^{4/5}$), 3.32 (s, 3H; $OCH_3$), 3.70 (t, $^3J_{H,H}$ = 5.1 Hz, 2H; $CH_2O$), 3.78–3.91 [m, 1H; $CH(CH_3)_2$], 4.65 (t, $^3J_{H,H}$ = 5.1 Hz, 2H; $CH_2CH_2O$), 4.86–4.91 (m, 2H; $CH_2CH{=}CH_2$), 4.97 (dt, $^3J_{H,H}$ = 17.3 Hz, $^4J_{H,H}$ = 1.9 Hz, 1H; $CH{=}CH_ZH_E$), 5.39 (dt, $^3J_{H,H}$ = 11.0 Hz, $^4J_{H,H}$ = 1.9 Hz, 1H; $CH{=}CH_ZH_E$), 5.96 ppm (ddt, $^3J_{H,H}$ = 17.3, 11.0, 4.4 Hz, 1H; $CH{=}CH_2$); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 8.87 ($CH_3C^{4/5}$), 9.65 ($CH_3C^{4/5}$), 19.97 [$CH(CH_3)_2$], 25.30 [$CH(CH_3)_2$], 46.60 ($CH_2CH_2O$), 48.32 ($CH_2CH{=}CH_2$), 59.10 ($OCH_3$), 70.31 ($CH_2O$), 117.75 ($CH{=}CH_2$), 126.33 ($C^{4/5}$), 126.69 ($C^{4/5}$), 130.91 ($CH{=}CH_2$), 149.32 ppm ($C^2$); IR (ATR): $\tilde{\nu}$ = 1116, 1451, 1509, 1648, 2978, 3430 $cm^{-1}$; MS (ES): *m/z* (%): 237.3 (100) [$M+H^+$]; yield: 74%; yellow oil.

### Characterization of Bis(trifluoromethylsulfonyl)imide Ionic Liquids 6–11 c

1-Allyl-2-isopropyl-3,4,5-trimethylimidazolium bis(trifluoromethylsulfonyl)imide [$C_AC_1C_{i3}m_2im$][$NTf_2$] (**6 c**): $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 1.45 [d, $^3J_{H,H}$ = 7.2 Hz, 6H; $CH(CH_3)_2$], 2.19 (s, 3H; $CH_3C^{4/5}$), 2.25 (s, 3H; $CH_3C^{4/5}$), 3.38–3.50 [m, 1H; $CH(CH_3)_2$], 3.74 (s, 3H; $NCH_3$), 4.69–4.72 (m, 2H; $NCH_2$), 4.90 (d, $^3J_{H,H}$ = 17.1 Hz, 1H; $CH{=}CH_EH_Z$), 5.34 (d, $^3J_{H,H}$ = 10.5 Hz, 1H; $CH{=}CH_EH_Z$), 5.86–5.98 ppm (ddt, $^3J_{H,H}$ = 17.1, 10.5, 4.4 Hz, 1H; $CH{=}CH_2$); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 8.34 ($CH_3C^{4/5}$), 8.57 ($CH_3C^{4/5}$), 18.89 [$CH(CH_3)_2$], 25.36 [$CH(CH_3)_2$], 32.66 ($NCH_3$), 47.39 ($NCH_2$), 118.02 ($CH{=}CH_2$), 119.94 (q, $^1J_{C,F}$ = 321.1 Hz; $CF_3$), 125.92 ($C^{4/5}$), 127.17 ($C^{4/5}$),

130.56 (*C*H=$CH_2$), 148.21 ppm ($C^2$); $^{19}$F NMR (282 MHz, $CDCl_3$, 25 °C, $CFCl_3$): −79.32 ppm; IR (ATR): $\tilde{\nu}$ = 1053, 1134, 1176, 1348 $cm^{-1}$; HRMS (ESI/APCI): *m/z*: calcd for [$C_{12}H_{21}N_2^+$]: 193.1699; found: 193.1697; yield: 95%; light yellow oil.

2-Isopropyl-1-(2-methoxyethyl)-3,4,5-trimethylimidazolium bis(trifluoromethylsulfonyl)imide [$C_{2O1}C_1C_{i3}m_2$im][$NTf_2$] (**7c**): $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 1.45 [d, $^3J_{H,H}$ = 7.7 Hz, 6H; $CH(CH_3)_2$], 2.23 (s, 3H; $CH_3C^{4/5}$), 2.24 (s, 3H; $CH_3C^{4/5}$), 3.31 (s, 3H; $OCH_3$), 3.53–3.66 (m, 1H; CH), 3.59 (t, $^3J_{H,H}$ = 5.1 Hz, 2H; $CH_2O$), 3.73 (s, 3H, $NCH_3$), 4.25 ppm (t, $^3J_{H,H}$ = 5.1 Hz, 2H; $NCH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 8.50 ($CH_3C^{4/5}$), 8.86 ($CH_3C^{4/5}$), 18.60 [$CH(CH_3)_2$], 25.31 (CH), 32.81 ($NCH_3$), 45.70 ($NCH_2$), 59.04 ($OCH_3$), 70.13 ($CH_2O$), 119.98 (q, $^1J_{C,F}$ = 321.5 Hz; $CF_3$), 125.70 ($C^{4/5}$), 127.02 ($C^{4/5}$), 148.88 ppm ($C^2$); $^{19}$F NMR (282 MHz, $CDCl_3$, 25 °C, $CFCl_3$): −79.37 ppm; IR (ATR): $\tilde{\nu}$ = 1052, 1134, 1175, 1348 $cm^{-1}$; HRMS (ESI/APCI): *m/z*: calcd for [$C_{12}H_{23}N_2O^+$]: 211.1805; found: 211.1806; yield: 99%; white crystals.

1-(2-Allyloxyethyl)-2-isopropyl-3,4,5-trimethylimidazolium bis(trifluoromethylsulfonyl)imide [$C_{2OA}C_1C_{i3}m_2$im][$NTf_2$] (**8c**): $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 1.43 [d, $^3J_{H,H}$ = 7.2 Hz, 6H; $CH(CH_3)_2$], 2.22 ($CH_3C^{4/5}$), 2.23 ($CH_3C^{4/5}$), 3.58–3.70 [m, 1H; $CH(CH_3)_2$] 3.65 (t, $^3J_{H,H}$ = 5.0 Hz, 6H; $CH_2O$), 3.73 (m, 3H; $NCH_3$), 3.93 (d, $^3J_{H,H}$ = 5.4 Hz; $OCH_2CH$), 4.25 (t, $^3J_{H,H}$ = 5.0 Hz, 2H; $NCH_2$), 5.18 (d, $^3J_{H,H}$ = 10.6 Hz, 1H; CH=$CH_ZH_E$), 5.19 (d, $^3J_{H,H}$ = 17.3 Hz, 1H; CH=$CH_ZH_E$), 5.79 ppm (ddt, $^3J_{H,H}$ = 17.3, 10.6, 5.4 Hz, 1H; *C*H=$CH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 8.47 ($CH_3C^{4/5}$), 8.87 ($CH_3C^{4/5}$), 18.64 [$CH(CH_3)_2$], 25.24 [$CH(CH_3)_2$], 32.81 ($NCH_2$), 45.73 ($NCH_3$), 67.81 ($OCH_2CH$), 72.40 ($CH_2O$), 118.02 (CH=$CH_2$), 120.00 (q, $^1J_{C,F}$ = 321.5 Hz; $CF_3$), 125.75 ($C^{4/5}$), 127.02 ($C^{4/5}$), 133.79 (*C*H=$CH_2$), 148.83 ppm ($C^2$); $^{19}$F NMR (282 MHz, $CDCl_3$, 25 °C, $CFCl_3$): −79.35 ppm; IR (ATR): $\tilde{\nu}$ = 1054, 1135, 1179, 1348 $cm^{-1}$; MS (ES): *m/z* (%): 237.3 (100) [*M*+$H^+$]; yield: 99%; yellow liquid.

1-Allyl-3-ethyl-2-isopropyl-4,5-dimethylimidazolium bis(trifluoromethylsulfonyl)imide [$C_AC_2C_{i3}m_2$im][$NTf_2$] (**9c**): $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 1.42 (d, $^3J_{H,H}$ = 7.3 Hz, 3H; $CH_2CH_3$), 1.45 [d, $^3J_{H,H}$ = 7.2 Hz, 6H; $CH(CH_3)_2$], 2.19 (s, 3H; $CH_3C^{4/5}$), 2.27 (s, 3H; $CH_3C^{4/5}$), 3.41–3.55 [m, 1H; $CH(CH_3)_2$], 4.16 (t, $^3J_{H,H}$ = 7.3 Hz, 3H; $CH_2CH_3$), 4.73–4.74 (m, 2H; $CH_2CH$=$CH_2$), 4.89 (d, $^3J_{H,H}$ = 17.1 Hz, 1H; CH=$CH_EH_Z$), 5.35 (d, $^3J_{H,H}$ = 10.5 Hz, 1H; CH=$CH_EH_Z$), 5.99 ppm (ddt, $^3J_{H,H}$ = 17.1, 10.5, 4.4 Hz, 1H; *C*H=$CH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 8.29 ($CH_3C^{4/5}$), 8.43 ($CH_3C^{4/5}$), 15.33 ($CH_2CH_3$), 19.70 [$CH(CH_3)_2$], 25.38 [$CH(CH_3)_2$], 41.06 ($CH_2CH_3$), 47.62 ($CH_2CH$=$CH_2$), 118.14 (CH=$CH_2$), 119.96 (q, $^1J_{C,F}$ = 321.5 Hz; $CF_3$), 126.04 ($C^{4/5}$), 126.88 ($C^{4/5}$), 130.53 (*C*H=$CH_2$), 147.95 ppm ($C^2$); $^{19}$F NMR (282 MHz, $CDCl_3$, 25 °C, $CFCl_3$): −79.36 ppm; IR (ATR): $\tilde{\nu}$ = 1054, 1137, 1180, 1334, 1349 $cm^{-1}$; HRMS (ESI/APCI): *m/z*: calcd for [$C_{13}H_{23}N_2^+$]: 207.1856; found: 207.1850; yield: 98%; white crystals.

1,3-Diallyl-2-isopropyl-4,5-dimethylimidazolium bis(trifluoromethylsulfonyl)imide [$C_AC_AC_{i3}m_2$im][$NTf_2$] (**10c**): $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 1.40 [d, $^3J_{H,H}$ = 7.2 Hz, 6H; $CH(CH_3)_2$], 2.20 (s, 6H; $CH_3C^{4/5}$), 3.36–3.51 [m, 1H; $CH(CH_3)_2$], 4.75–4.77 (m, 4H; $NCH_2$), 4.86 (dt, $^3J_{H,H}$ = 17.1 Hz, $^4J_{H,H}$ = 1.9 Hz, 2H; CH=$CH_EH_Z$), 5.35 (dt, $^3J_{H,H}$ = 10.8 Hz, $^4J_{H,H}$ = 1.9 Hz, 2H; CH=$CH_EH_Z$), 5.95 ppm (ddt, $^3J_{H,H}$ = 17.1, 10.8, 4.1 Hz, 2H; *C*H=$CH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 8.37 ($CH_3C^{4/5}$), 19.65 [$CH(CH_3)_2$], 25.47 [$CH(CH_3)_2$], 47.64 ($CH_2CH$=$CH_2$), 118.07 (CH=$CH_2$), 119.83 (q, $^1J_{C,F}$ = 321.9 Hz; $CF_3$), 126.74 ($C^4$, $C^5$), 130.45 (CH), 148.60 ppm ($C^2$); $^{19}$F NMR (282 MHz, $CDCl_3$, 25 °C, $CFCl_3$): −79.31 ppm; IR (ATR): $\tilde{\nu}$ = 1053, 1138, 1177, 1347 $cm^{-1}$; HRMS (ESI/APCI): *m/z*: calcd for [$C_{14}H_{23}N_2^+$]: 219.1856; found: 219.1848; elemental analysis calcd (%) for $C_{16}H_{23}F_6N_3O_4S_2$ (499.49): C 38.47, H 4.64, N 8.41; found: C 38.29, H 4.26, N 8.28; yield: 98%; white crystals.

1-Allyl-2-isopropyl-3-(2-methoxyethyl)-4,5-dimethylimidazolium bis(trifluoromethylsulfonyl)imide [$C_{2O1}C_AC_i^3m_2$im][$NTf_2$] (**11c**): $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 1.43 [d, $^3J_{H,H}$ = 7.2 Hz, 6H; $CH(CH_3)_2$], 2.19 (s, 3H; $CH_3C^{4/5}$), 2.27 (s, 3H; $CH_3C^{4/5}$), 3.33 (s, 3H; $OCH_3$), 3.55–3.66 [m, 1H; $CH(CH_3)_2$], 3.63 (t, $^3J_{H,H}$ = 5.0 Hz, 2H; $CH_2O$), 4.32 (t, $^3J_{H,H}$ = 5.0 Hz, 2H; $CH_2CH_2O$), 4.74–4.78 (m, 2H; $CH_2CH$=$CH_2$), 4.95 (dd, $^3J_{H,H}$ = 18.2 Hz, $^2J_{H,H}$ = 1.1 Hz, 1H; CH=$CH_EH_Z$), 5.39 (dd, $^3J_{H,H}$ = 10.5 Hz, $^2J_{H,H}$ = 1.1 Hz, 1H; CH=$CH_EH_Z$), 5.87–5.98 ppm (m, 1H; *C*H=$CH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 8.28 ($CH_3C^{4/5}$), 8.93 ($CH_3C^{4/5}$), 19.56 [$CH(CH_3)_2$], 25.48 [$CH(CH_3)_2$], 45.88 ($CH_2CH_2O$), 47.79 ($CH_2CH$=$CH_2$), 59.07 ($OCH_3$), 69.97 ($CH_2O$), 118.31 (CH=$CH_2$), 119.91 (q, $^1J_{C,F}$ = 321.5 Hz; $CF_3$), 126.41 ($C^{4/5}$), 126.77 ($C^{4/5}$), 130.39 (*C*H=$CH_2$), 149.34 ppm ($C^2$); $^{19}$F NMR (282 MHz, $CDCl_3$, 25 °C, $CFCl_3$): −79.36 ppm; IR (ATR): $\tilde{\nu}$ = 1054, 1135, 1178, 1348 $cm^{-1}$; HRMS (ESI/APCI): *m/z*: calcd for [$C_{14}H_{25}N_2O^+$]: 237.1961; found: 237.1960; yield: 99%; yellow oil.

## Characterization of Dicyanamide Ionic Liquids 6–11 d

1-Allyl-2-isopropyl-3,4,5-trimethylimidazolium dicyanamide [$C_AC_1C_{i3}m_2$im][$N(CN)_2$] (**6d**): $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 1.52 [d, $^3J_{H,H}$ = 7.2 Hz, 6H; $CH(CH_3)_2$], 2.27 (s, 3H; $CH_3C^{4/5}$), 2.33 (s, 3H; $CH_3C^{4/5}$), 3.45–3.58 [m, 1H; $CH(CH_3)_2$], 3.83 (s, 3H; $NCH_3$), 4.79–4.83 (m, 2H; $NCH_2$), 4.94 (d, $^3J_{H,H}$ = 17.1 Hz, 1H; CH=$CH_EH_Z$), 5.38 (d, $^3J_{H,H}$ = 10.5 Hz, 1H; CH=$CH_EH_Z$), 5.89–6.02 ppm (m, 1H; *C*H=$CH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 8.69 ($CH_3C^{4/5}$), 8.96 ($CH_3C^{4/5}$), 19.18 [$CH(CH_3)_2$], 25.42 [$CH(CH_3)_2$], 32.93 ($NCH_3$), 47.58 ($NCH_2$), 118.36 (CH=$CH_2$), 119.69 [$N(CN)_2$], 126.02 ($C^{4/5}$), 127.15 ($C^{4/5}$), 130.42 (*C*H=$CH_2$), 148.24 ppm ($C^2$); IR (ATR): $\tilde{\nu}$ = 749, 1301, 1522, 2124, 2222 $cm^{-1}$; MS (ES): *m/z* (%): 193.3 (100) [*M*+$H^+$]; yield: 97%; light yellow oil.

2-Isopropyl-1-(2-methoxyethyl)-3,4,5-trimethylimidazolium dicyanamide [$C_{2O1}C_1C_{i3}m_2$im][$N(CN)_2$] (**7d**): $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 1.51 [d, $^3J_{H,H}$ = 7.7 Hz, 6H; $CH(CH_3)_2$], 2.30 (s, 3H; $CH_3C^{4/5}$), 2.32 (s, 3H; $CH_3C^{4/5}$), 3.34 (s, 3H; $OCH_3$), 3.57–3.66 (m, 1H; CH), 3.64 (t, $^3J_{H,H}$ = 5.0 Hz, 2H; $CH_2O$), 3.81 (s, 3H, $NCH_3$), 4.35 ppm (t, $^3J_{H,H}$ = 5.0 Hz, 2H; $NCH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 8.84 ($CH_3C^{4/5}$), 9.16 ($CH_3C^{4/5}$), 18.87 [$CH(CH_3)_2$], 25.36 (CH), 32.99 ($NCH_3$), 45.85 ($NCH_2$), 59.19 ($OCH_3$), 70.02 ($CH_2O$), 119.78 [$N(CN)_2$], 125.69 ($C^{4/5}$), 126.98 ($C^{4/5}$), 148.94 ppm ($C^2$); IR (ATR): $\tilde{\nu}$ = 1052, 1134, 1175, 1348 $cm^{-1}$; HRMS (ESI/APCI): *m/z*: calcd for [$C_{12}H_{23}N_2O^+$]: 211.1805; found: 211.1806; yield: 99%; white crystals.

1-(2-Allyloxyethyl)-2-isopropyl-3,4,5-trimethylimidazolium dicyanamide [$C_{2OA}C_1C_{i3}m_2$im][$N(CN)_2$] (**8d**): $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 1.50 [d, $^3J_{H,H}$ = 7.2 Hz, 6H; $CH(CH_3)_2$], 2.30 ($CH_3C^{4/5}$), 2.31 ($CH_3C^{4/5}$), 3.62–3.77 [m, 1H; $CH(CH_3)_2$], 3.70 (t, $^3J_{H,H}$ = 5.0 Hz, 6H; $CH_2O$), 3.81 (m, 3H; $NCH_3$), 3.97 (d, $^3J_{H,H}$ = 5.5 Hz; $OCH_2CH$), 4.35 (t, $^3J_{H,H}$ = 5.0 Hz, 2H; $NCH_2$), 5.20 (d, $^3J_{H,H}$ = 10.8 Hz, 1H; CH=$CH_ZH_E$), 5.21 (d, $^3J_{H,H}$ = 16.9 Hz, 1H; CH=$CH_ZH_E$), 5.81 ppm (ddt, $^3J_{H,H}$ = 16.9, 10.8, 5.5 Hz, 1H; *C*H=$CH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 8.78 ($CH_3C^{4/5}$), 9.11 ($CH_3C^{4/5}$), 18.86 [$CH(CH_3)_2$], 25.21 [$CH(CH_3)_2$], 32.98 ($NCH_3$), 45.82 ($NCH_2$), 67.67 ($OCH_2CH$), 72.36 ($CH_2O$), 118.14 (CH=$CH_2$), 119.69 [$N(CN)_2$], 125.69 ($C^{4/5}$), 126.95 ($C^{4/5}$), 133.60 (*C*H=$CH_2$), 148.82 ppm ($C^2$); IR (ATR): $\tilde{\nu}$ = 1111, 1311, 1523, 2130, 2232 $cm^{-1}$; HRMS (ESI/APCI): *m/z*: calcd for [$C_{14}H_{25}N_2O^+$]: 237.1961; found: 237.1965; yield: 96%; yellow liquid.

1-Allyl-3-ethyl-2-isopropyl-4,5-dimethylimidazolium dicyanamide [$C_AC_2C_{i3}m_2$im][$N(CN)_2$] (**9d**): $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 1.47 (d, $^3J_{H,H}$ = 7.2 Hz, 3H; $CH_2CH_3$), 1.53 [d, $^3J_{H,H}$ = 7.7 Hz, 6H; $CH(CH_3)_2$], 2.27 (s, 3H; $CH_3C^{4/5}$), 2.35 (s, 3H; $CH_3C^{4/5}$), 3.49–3.56 [m,

1H; C*H*($CH_3$)$_2$], 4.25 (t, $^3J_{H,H}$ = 7.2 Hz, 3H; C$H_2$CH$_3$), 4.81–4.85 (m, 2H; C$H_2$CH=CH$_2$), 4.95 (d, $^3J_{H,H}$ = 17.1 Hz, 1H; CH=CH$_E$H$_Z$), 5.39 (d, $^3J_{H,H}$ = 10.5 Hz, 1H; CH=C*H*$_E$H$_Z$), 5.96 ppm (ddt, $^3J_{H,H}$ = 17.1, 10.5, 4.6 Hz, 1H; C*H*=CH$_2$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 8.66 ($CH_3C^{4/5}$), 8.79 ($CH_3C^{4/5}$), 15.57 ($CH_2CH_3$), 20.00 [CH($CH_3$)$_2$], 25.53 [CH($CH_3$)$_2$], 41.25 ($CH_2CH_3$), 47.82 ($CH_2CH$=CH$_2$), 118.53 (CH=$CH_2$), 119.78 [N(CN)$_2$], 126.11 ($C^{4/5}$), 126.97 ($C^{4/5}$), 130.37 (*C*H=CH$_2$), 147.95 ppm ($C^2$); IR (ATR): $\tilde{\nu}$ = 1054, 1137, 1180, 1334, 1349 cm$^{-1}$; MS (ES): *m/z* (%): 207.3 (100) [*M*+H$^+$]; yield: 97%; yellow oil.

1,3-Diallyl-2-isopropyl-4,5-dimethylimidazolium dicyanamide [$C_AC_AC_{i3}m_2$im][N(CN)$_2$] (**10 d**): $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 1.48 [d, $^3J_{H,H}$ = 7.2 Hz, 6H; CH($CH_3$)$_2$], 2.28 (s, 6H; $CH_3C^{4/5}$), 3.47–3.52 [m, 1H; C*H*($CH_3$)$_2$], 4.85–4.87 (m, 4H; NCH$_2$), 4.92 (dt, $^3J_{H,H}$ = 17.4 Hz, $^4J_{H,H}$ = 1.9 Hz, 2H; CH=CH$_E$H$_Z$), 5.40 (dt, $^3J_{H,H}$ = 10.6 Hz, $^4J_{H,H}$ = 1.9 Hz, 2H; CH=C*H*$_E$H$_Z$), 5.99 ppm (ddt, $^3J_{H,H}$ = 17.4, 10.6, 4.4 Hz, 2H, C*H*=CH$_2$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 8.72 ($CH_3C^{4/5}$), 19.91 [CH($CH_3$)$_2$], 25.65 [CH($CH_3$)$_2$], 47.90 ($CH_2$CH=CH$_2$), 118.30 (CH=$CH_2$), 119.73 [N(CN)$_2$], 126.91 ($C^4$, $C^5$), 130.47 (CH), 148.60 ppm ($C^2$); IR (ATR): $\tilde{\nu}$ = 1302, 1514, 1648, 2131, 2224, 3463 cm$^{-1}$; MS (ES): *m/z* (%): 219.3 (100) [*M*+H$^+$]; yield: 98%; white crystals.

1-Allyl-2-isopropyl-3-(2-methoxyethyl)-4,5-dimethylimidazolium dicyanamide [$C_{2O1}C_AC_{i3}m_2$im][N(CN)$_2$] (**11 d**): $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 1.47 [d, $^3J_{H,H}$ = 7.2 Hz, 6H; CH($CH_3$)$_2$], 2.25 (s, 3H; $CH_3C^{4/5}$), 2.34 (s, 3H; $CH_3C^{4/5}$), 3.35 (s, 3H; $OCH_3$), 3.59–3.73 [m, 1H; C*H*($CH_3$)$_2$], 3.67 (t, $^3J_{H,H}$ = 5.0 Hz, 2H; $CH_2O$), 4.40 (t, $^3J_{H,H}$ = 5.0 Hz, 2H; $CH_2CH_2O$), 4.81–4.86 (m, 2H;$CH_2$CH=CH$_2$), 4.97 (d, $^3J_{H,H}$ = 17.1 Hz, 1H; CH=CH$_E$H$_Z$), 5.41 (d, $^3J_{H,H}$ = 10.5 Hz, 1H; CH=C*H*$_E$H$_Z$), 5.90–6.00 ppm (m, 1H; C*H*=CH$_2$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 8.47 ($CH_3C^{4/5}$), 8.86 ($CH_3C^{4/5}$), 19.70 [CH($CH_3$)$_2$], 25.48 [CH($CH_3$)$_2$], 45.94 ($CH_2CH_2O$), 47.85 ($CH_2$CH=CH$_2$), 59.15 ($OCH_3$), 69.93 ($CH_2O$), 118.42 (CH=$CH_2$), 119.73 [N(CN)$_2$], 126.34 ($C^{4/5}$), 126.79 ($C^{4/5}$), 130.36 (*C*H=CH$_2$), 149.35 ppm ($C^2$); IR (ATR): $\tilde{\nu}$ = 1304, 1513, 2126, 2224 cm$^{-1}$; MS (ES): *m/z* (%): 237.3 (100) [*M*+H$^+$]; yield: 86%; yellow oil.

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