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Exploration of 4,5-dimethyl-1*H*-imidazole N-oxide derivatives in the synthesis of new achiral and chiral ionic liquids

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ABSTRACT

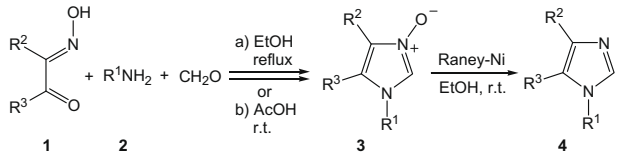
New 1-alkoxy-3-alkyl-4,5-dimethylimidazolium bromides were synthesized by alkylation of the corresponding 1-alkylimidazole 3-oxides, which were conveniently prepared via condensation of α-(hydroxyimino)ketones, primary aliphatic amines, and formaldehyde. By using enantiomerically pure chiral amines, optically active imidazolium salts were obtained. Treatment with sodium tetrafluoroborate in acetone yielded the corresponding imidazolium tetrafluoroborates. All these compounds, with only one exception, were obtained as oils, which are considered as potential ionic liquids and 'chiral ionic liquids'. The reduction of the chiral or non-chiral 1-alkylimidazole 3-oxides with Raney-Ni, followed by alkylation with alkyl bromides and subsequent ion exchange to tetrafluoroborates, gave the corresponding 1,3-dialkylimidazolium salts, most of them showing properties of ionic liquids. The alkylation of 1-butyl-4,5-dimethylimidazole 3-oxide and the corresponding imidazole, respectively, with 1,3-dibromopropane led to the first bis-imidazolium dibromides and bis-tetrafluoroborates.

1. Introduction

The rapidly increasing number of books,[1] review articles,[2] and original papers[3–5] dealing with the preparation, properties, and applications of ionic liquids (ILs) documents the growing importance of this class of compounds in almost all fields of chemistry and related disciplines. For the purpose of modern organic synthesis, chiral ionic liquids (CILs) and especially 'room temperature chiral ionic liquids' (RTCILs) are of interest. The 1,3-disubstituted imidazolium salts are by far the most frequently used group of substances displaying the required properties.

Chiral imidazolium ionic liquids (CIILs) can be prepared by alkylation of an achiral, 1-substituted imidazole with a chiral alkylating agent (e.g., 1-methylimidazole and (−)-myrtanol tosylate[6]). However, the alternative and most frequently used method is the preparation of an imidazole bearing a chiral residue, which is then alkylated with an achiral reagent. In this case, enantiomerically pure 1-phenylethylamine is often used as a starting material for the formation of a 1-substituted imidazole with the stereogenic center located at C(1) of the substituent (e.g., Refs. 7–9). Both approaches were applied to prepare imidazoles without substituents at C(4) and C(5).

In a series of recent papers, we reported the synthesis of 2-unsubstituted 1-alkyl-4,5-dialkyl/aryl-1*H*-imidazole 3-oxides **3**, which, after deoxygenation with Raney-Nickel, delivered the corresponding imidazoles **4**. Starting with easily available α-(hydroxyimino)ketones **1**, primary aliphatic amines **2**, and paraformaldehyde, achiral[10] and chiral imidazoles[11] were prepared in good yields (Scheme 1).



1 2 3 4

Scheme 1.

Using enantiomerically pure *trans*-cyclohexane-1,2-diamine, the corresponding optically active bis-imidazole derivatives were obtained.[11b]

In the published papers dealing with the preparation of ionic liquids, imidazole N-oxides have not been explored either directly or indirectly as imidazole building blocks. However, in a very recent paper, 1-hydroxyimidazole and the corresponding 2-methyl derivative were used for a stepwise preparation of a series of achiral 3-alkoxy-1-alkylimidazolium salts, which displayed properties of 'room temperature ionic liquids' (RTILs).[12] In this context, another paper deserves mentioning, in which 1-cyclohexyl-3-ethoxyimidazolium tetrafluoroborate was reported as the product of the ethylation of the corresponding N-oxide with triethyloxonium tetrafluoroborate.[13]

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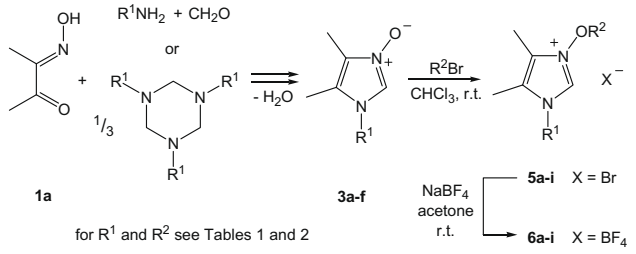
The goal of the study described in the present paper was the application of diverse 1,4,5-trisubstituted 1*H*-imidazole 3-oxides **3** and the corresponding imidazoles **4** in the synthesis of new achiral and chiral imidazolium salts with the properties of 'room temperature ionic liquids' (RTILs).

2. Results and discussion

For the present study, 4,5-dimethylimidazole 3-oxide was selected as the basic structure, because it is easily available and it was expected that the presence of two methyl groups does not influence significantly the physico-chemical properties of imidazolium salts expected as oily materials. For this reason, diacetylmonooxime **1a** was reacted with primary amines, aminoalcohols, and aminoesters in the presence of formaldehyde or with the corresponding hexahydro-1,3,5-triazines according to the reported protocols.[10a,e,11c] As a new example, 1-butyl-4,5-dimethyl-1*H*-imidazole 3-oxide **3a** was prepared by heating **1a** and 1,3,5-tributylhexahydro-1,3,5-triazine (a trimer of methylidene butylamine) in boiling ethanol (Scheme 2).



Scheme 2.

The imidazole N-oxides **3a–f** (Table 1) were used for O-alkylations using *n*-butyl and *n*-hexyl bromide, respectively. As already reported, 2-unsubstituted imidazole N-oxides **3** undergo a thermal isomerization to give imidazol-2-ones even at 80 °C (boiling benzene).[14] For this reason, the alkylation reactions were carried out in chloroform solution at room temperature. After three days, the 3-alkoxyimidazolium bromides **5a–i** were obtained in very good yields as pale yellow oils, with the exception of **5b**, which was a colorless solid (Table 2).

Table 1
1-Substituted 4,5-dimethylimidazole N-oxides **3** and the corresponding imidazoles **4**

No.	R^1	Yield	$[\alpha]_D^{20}$ (*c* 0.2, CH_2Cl_2)	Mp (°C)
3a	Bu	81	—	Oil
3b	*c*Hex	63	—	199–201
3c	CH_2CH_2OH	82	—	105–107[10e]
3d	$CH_2CH(OH)CH_3$ (*S*)	82	+42.0[a]	119–120[10e]
3e	$CH(CH_3)CO_2Me$ (*S*)	67	+47.1	144–146[11c]
3f	$CH(CH_3)CO_2Me$ (*R*)	72	−48.5	142–145[11c]
4a	Bu	91	—	Oil
4b	*c*Hex	86	—	Oil
4c	CH_2CH_2OH	74	—	94–98
4d	$CH_2CH(OH)CH_3$ (*S*)	75	+69.2	Oil
4e	$CH(CH_3)CO_2Me$ (*S*)	77	−9.9	Oil
4f	$CH(CH_3)CO_2Me$ (*R*)	65	+10.4	Oil

[a] $[\alpha]_D^{17}$ (*c* 1, MeOH).

The exchange of the bromide ion against the tetrafluoroborate ion was easily achieved by treatment of solutions of **5a–i** in acetone with a slight excess of solid $NaBF_4$ at room temperature. All of the prepared 3-alkoxyimidazolium tetrafluoroborates **6a–i** (Table 2) were well soluble not only in acetone but also in ethanol, chloroform, and water. On the other hand, they were insoluble in ether.

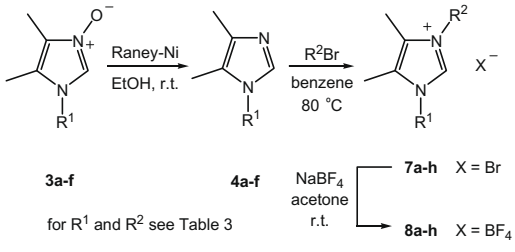
Table 2
1-Alkoxy-3-alkylimidazolium salts **5** and **6**

No.	R^1	R^2	X	Yield	$[\alpha]_D^{20}$ (*c* 0.2, CH_2Cl_2)	Mp (°C)
5a	Bu	Bu	Br	85	—	Oil
5b	*c*Hex	Bu	Br	81	—	58–62
5c	CH_2CH_2OH	Bu	Br	92	—	Oil
5d	CH_2CH_2OH	Hex	Br	85	—	Oil
5e	$CH_2CH(OH)CH_3$ (*S*)	Bu	Br	93	+13.7	Oil
5f	$CH(CH_3)CO_2Me$ (*S*)	Bu	Br	91	+14.2	Oil
5g	$CH(CH_3)CO_2Me$ (*R*)	Bu	Br	89	−15.8	Oil
5h	$CH(CH_3)CO_2Me$ (*S*)	Hex	Br	79	+11.1	Oil
5i	$CH(CH_3)CO_2Me$ (*R*)	Hex	Br	83	−12.0	Oil
6a	Bu	Bu	BF_4	97	—	Oil
6b	*c*Hex	Bu	BF_4	80	—	Oil
6c	CH_2CH_2OH	Bu	BF_4	89	—	Oil
6d	CH_2CH_2OH	Hex	BF_4	93	—	Oil
6e	$CH_2CH(OH)CH_3$ (*S*)	Bu	BF_4	91	+21.8	Oil
6f	$CH(CH_3)CO_2Me$ (*S*)	Bu	BF_4	92	+14.7	Oil
6g	$CH(CH_3)CO_2Me$ (*R*)	Bu	BF_4	88	−16.2	Oil
6h	$CH(CH_3)CO_2Me$ (*S*)	Hex	BF_4	92	+9.5	Oil
6i	$CH(CH_3)CO_2Me$ (*R*)	Hex	BF_4	93	−10.8	Oil

During the storage of **5** and **6** at room temperature, no decomposition was observed. Moreover, in the case of **5a**, the thermal stability was tested by heating of a sample at 100 °C, and after 45 min, the ^1H NMR spectrum showed that no changes took place. The compounds **5** and **6** were also stable when treated with diluted HCl solution at room temperature. In an additional experiment, a methanolic solution of **5a** was treated with $NaBH_4$ in order to test the stability of the N–O bond. After ca. 1 h under mild conditions (rt), 1-butyl-4,5-dimethylimidazole (**4a**) was isolated (33%, 50 min) accompanied by unchanged **5a**. Complete reduction was achieved after 16 h.

It is worth mentioning that in the case of enantiomerically pure amino components, that is, (*S*)-1-aminopropan-2-ol or methyl (*R*)- and (*S*)-alaninate, the known optically active imidazole N-oxides **3d**, **3e**, and **3f** were converted to the corresponding optically active 3-alkoxyimidazolium salts **5e–i** in good yields (Table 2). Their convenient preparation opens up access to a new type of optically active ionic liquids (RTCILs).

The deoxygenation of imidazole N-oxides **3a–f** to give **4a–f** was easily achieved by treatment with Raney-Ni in ethanol at room temperature (Scheme 3).[10e,11a,c] All of these compounds were used in alkylation reactions with *n*-butyl and *n*-hexyl bromide to give 1,3-dialkylimidazolium bromides **7** (Table 3). In this series, the reactions were carried out in boiling benzene, and after ca. 6 h, the conversions were complete. However, in the cases of **4e** and **4f**, partial decomposition was observed under the applied conditions and, for this reason, the alkylations with butyl bromide were performed at room temperature in CH_2Cl_2 solution using excess of the alkylating agent (3 equiv). The imidazolium bromides **7** were obtained as liquids in the case of **7c–f** and as solids in the case of **7a**,**b**,**g**,**h**.



Scheme 3.

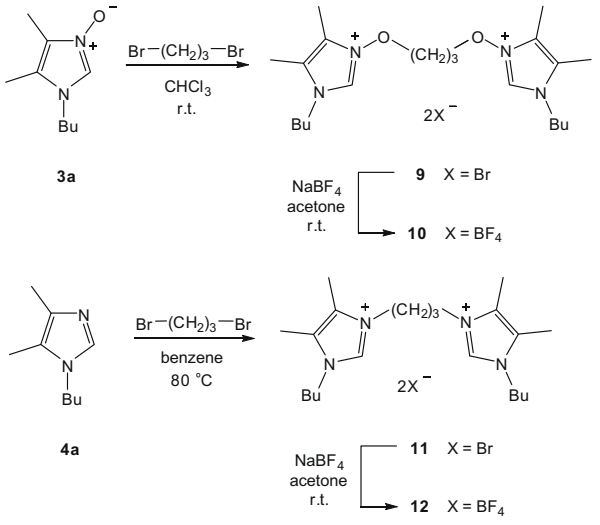
After the anion exchange $Br^- \rightarrow BF_4^-$, the salts **8a–f** were obtained as liquids, but **8g**,**h** were still solid materials with melting points below 100 °C (Table 3).

Table 3
1,3-Dialkylimidazolium salts **7** and **8**

No.	R^1	R^2	X	Yield	$[\alpha]_D^{20}$ (*c* 0.2, CH_2Cl_2)	Mp (°C)
7a	Bu	Bu	Br	94	—	83–86
7b	Bu	Hex	Br	89	—	118–120
7c	*c*Hex	Bu	Br	95	—	Oil
7d	*c*Hex	Hex	Br	91	—	Oil
7e	CH_2CH_2OH	Bu	Br	97	—	Oil
7f	$CH_2CH(OH)CH_3$ (*S*)	Bu	Br	84	+13.8	Oil
7g	$CH(CH_3)CO_2Me$ (*S*)	Bu	Br	53	+11.2	96–99
7h	$CH(CH_3)CO_2Me$ (*R*)	Bu	Br	44	−11.0	99–103
8a	Bu	Bu	BF_4	95	—	Oil
8b	Bu	Hex	BF_4	87	—	Oil
8c	*c*Hex	Bu	BF_4	97	—	Oil
8d	*c*Hex	Hex	BF_4	94	—	Oil
8e	CH_2CH_2OH	Bu	BF_4	98	—	Oil
8f	$CH_2CH(OH)CH_3$ (*S*)	Bu	BF_4	92	+21.2	Oil
8g	$CH(CH_3)CO_2Me$ (*S*)	Bu	BF_4	95	+10.3	64–66
8h	$CH(CH_3)CO_2Me$ (*R*)	Bu	BF_4	75	−8.2	67–68

Some spectroscopic properties of the imidazolium salts of type **5**/**6** and **7**/**8** deserve a short comment. In the ^{1}H NMR spectra of bromides **5**, the diagnostic signal of H–C(2) appeared always downfield-shifted in comparison with the corresponding tetrafluoroborates **6** ($\Delta\delta$ ca. 1–2 ppm). The same tendency was observed in the series of bromides **7** and tetrafluoroborates **8**. Whereas in the ^{13}C NMR spectra of **7** and **8** the signals of C(2) were registered at 135–132 ppm, the corresponding signals of the alkoxyimidazolium salts **5** and **6** were observed between 132 and 129 ppm. This trend of a high-field shift in the alkoxy-substituted imidazolium salts fits well with the data reported earlier.[13] In addition, the signals of the CH_2–O groups in **5** and **6** were located at 82–75 ppm.

In two recent papers, we presented the synthesis of a series of bis(imidazole N-oxides) based on the method depicted in Schemes 1 and 2. In this case, diamines were used for the reaction with formaldehyde and subsequent condensation with α-(hydroxyimino)ketones **1**.[10e,11b] In the present study, we decided to investigate whether bisimidazolium salts prepared via alkylation of imidazole N-oxides and the corresponding imidazoles, respectively, with 1,3-dibromopropane displayed properties of RTILs. As model compounds, 1-butyl-4,5-dimethyl-1*H*-imidazole 3-oxide **3a** and 1-butyl-4,5-dimethylimidazole **4a** were selected. The twofold alkylation with **3a** using 0.5 equiv of the dibromide occurred under typical conditions leading to the salt **9** as a pale yellow oil in 90% yield (Scheme 4). The subsequent conversion to the tetrafluoroborate **10** was easily achieved under standard conditions and afforded the oily product in high yield (91%).



Scheme 4.

Similarly, the alkylation of **4a** with 1,3-dibromopropane in boiling benzene gave the bis-imidazolium salt **11** as an oily material, and the tetrafluoroborate **12** prepared from this was obtained as a semi-solid substance.

3. Conclusions

The results presented here show that 1-substituted 4,5-dimethyl-1*H*-imidazole 3-oxides **3** can be used for the preparation of a new type of imidazole-based ionic liquids containing alkoxy residues at the N atom. All of the prepared bromides **5** and tetrafluoroborates **6** are oily materials at room temperature or solids with melting points below 100 °C. Similar properties were observed in the case of the bis-imidazolium salts **9** and **10**. Deoxygenation of the N-oxides **3** opens access to the corresponding 1,4,5-trisubstituted imidazoles **4**, which via alkylation were converted into the corresponding salts **7** and **8**. These materials displayed similar properties as **5** and **6** and, therefore, can be considered as potentially useful RTILs. It is worth pointing out that the described procedures open a relatively simple and efficient access to optically active RTCILs using enantiomerically pure 1-aminopropan-2-ol and methyl alaninate, respectively, as the amino component. Similar to the alkylimidazolium salts **7**/**8**, the 3-alkoxy analogues **5**/**6** proved to be stable at enhanced temperature. In addition, the presence of the oxygen atom enhances their ability to form liquid products. These properties are of crucial importance for potential applications of the new materials as a medium for organic reactions.

4. Experimental

4.1. General

Melting points were determined on a Melt-Temp. II apparatus (Aldrich) and are uncorrected. IR Spectra were recorded on a NEXUS FT-IR spectrophotometer in KBr, absorptions in cm^{-1}. ^{1}H and ^{13}C NMR Spectra were measured on a Tesla BS567A (80 and 20 MHz, resp.) or Bruker AC 300 instrument (300 and 75.5 MHz, resp.) in $CDCl_3$ or CD_3OD, chemical shifts (δ) in ppm (TMS = 0 ppm), coupling constants *J* in hertz. The multiplicity of the ^{13}C signals was deduced from DEPT spectra. Optical rotations were determined on an Automatic Digital Polarimeter Krüss P3002RS. HRMS Spectra were measured on a Finnigan MAT-95 instrument.

4.2. Starting materials: imidazole N-oxides

Synthesis, properties, and spectroscopic data of imidazole N-oxides **3b–f** have been described previously.[10a,b,e,11c]

4.2.1. Synthesis of 1-butyl-4,5-dimethyl-1*H*-imidazole 3-oxide 3a

A solution of diacetylmonooxime **1a** (10 mmol) and 1,3,5-tributylhexahydro-[1,3,5]triazine (3.4 mmol) in EtOH (40 mL) was heated at reflux for 3 h. Evaporation of the solvent under reduced pressure yielded a red oil, which was washed twice with Et_2O (2 × 15 mL). The crude product **3a** was purified by chromatography (SiO_2, AcOEt, then AcOEt:MeOH 1:1), and the viscous oily substance was used in the next step without further purification. Yield: 1.36 g (81%). Pale red oil. IR (film): *v* 3358vs, 3139s, 2958s, 2931s, 2873m, 1626m, 1456m (br), 1396m, 1381m, 1339s, 1255m, 1194m, 1150m, 1080m. ^{1}H NMR ($CDCl_3$): δ 7.78 (s, 1H, HC(2)); 3.77 (t, *J* = 7.6, 2H, CH_2N); 2.16, 2.13 (2s, 6H, 2Me); 2.05–1.11 (m, 4H, $2CH_2$); 0.95 (br t, 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): δ

125.2 (d, C(2)); 123.5, 120.1 (2s, C(4), C(5)); 44.6, 31.5, 18.6 (3t, $3CH_2$, Bu); 12.6 (q, CH_3, Bu); 7.7, 6.3 (2q, 2Me). HRMS (EI): Calcd for $C_9H_{16}N_2O$ (M^+): 168.1263, found 168.1259.

4.3. Synthesis of 1,4,5-trisubstituted imidazoles 4

To a magnetically stirred solution of the imidazole N-oxide **3** (10 mmol) in ethanol (20 mL), an ethanolic suspension of freshly prepared Raney-Nickel was added in small portions, and the progress of the reaction was followed by TLC (SiO_2, MeOH/AcOEt 1:3). After the starting N-oxide was completely reduced, the solution was filtered through a Celite® plug (ca. 10 cm, EtOH), the filtrate was concentrated, and dried under reduced pressure. The obtained highly pure product **4** was analyzed without further purification.

4.3.1. 1-Butyl-4,5-dimethyl-1*H*-imidazole 4a

Yield: 1.43 g (91%). Colorless oil. IR (film): *ν* 2959s, 2932s, 2873m, 1500s, 1451m, 1388m, 1380m, 1366m, 1233m, 1202m. ^{1}H NMR ($CDCl_3$): *δ* 7.31 (s, 1H, HC(2)); 3.76 (t, *J* = 6.8, 2H, CH_2N); 2.11, 2.10 (2s, 6H, 2Me); 1.82–1.05 (m, 4H, $2CH_2$); 1.93 (br t, 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): *δ* 133.5 (d, C(2)); 132.2, 120.6 (2s, C(4), C(5)); 43.2, 31.5, 18.3 (3t, $3CH_2$, Bu); 12.2 (q, Me, Bu); 11.3, 6.9 (2q, 2Me). HRMS (EI): Calcd for $C_9H_{16}N_2$ (M^+): 152.1313, found 152.1313.

4.3.2. 1-Cyclohexyl-4,5-dimethyl-1*H*-imidazole 4b

Yield: 1.53 g (86%). Pale yellow oil. IR (film): *ν* 2933vs, 2857s, 1592w, 1490s, 1451s, 1386m, 1314m, 1275m, 1242m, 1220s. ^{1}H NMR ($CDCl_3$): *δ* 7.39 (s, 1H, HC(2)); 3.88–3.43 (m, 1H, *c*Hex); 2.15, 2.12 (2s, 6H, 2Me); 2.11–1.12 (m, 10H, *c*Hex). ^{13}C NMR ($CDCl_3$): *δ* 132.0, 121.1 (2s, C(4), C(5)); 131.0 (d, C(2)); 53.8 (d, CH, *c*Hex); 33.4, 24.6, 23.9 (3t, $5CH_2$, *c*Hex); 11.6, 7.8 (2q, 2Me). HRMS (EI): Calcd for $C_{11}H_{18}N_2$ (M^+): 178.1470, found 178.1467.

4.3.3. 1-(2-Hydroxyethyl)-4,5-dimethyl-1*H*-imidazole 4c

Yield: 1.04 g (74%). Colorless solid. Mp 94–98 °C ([lit.[15]]: mp 103–106 °C). IR (KBr): *ν* 3096s (br), 2950–2700s, 1598m, 1509s, 1448m, 1249m, 1192m, 1073s, 849m. ^{1}H NMR ($CDCl_3$): *δ* 7.25 (s, 1H, HC(2)); 6.35 (br s, 1H, OH); 3.92–3.77 (m, 4H, $2CH_2$); 2.10, 2.01 (2s, 6H, 2Me). ^{13}C NMR ($CDCl_3$): *δ* 135.0 (d, C(2)); 132.1, 121.9 (2s, C(4); C(5)), 60.5, 47.7 (2t, $2CH_2$); 12.0, 8.2 (2q, 2Me). HRMS (EI): Calcd for $C_7H_{12}N_2O$ (M^+): 140.0950, found 140.0948.

4.3.4. (*S*)-1-(2-Hydroxypropyl)-4,5-dimethyl-1*H*-imidazole 4d

Yield: 1.23 g (75%). Pale yellow oil. $[\alpha]_D^{20} = +69.2$ (*c* 0.2, CH_2Cl_2). IR (film): *ν* 3400vs (br), 3150–2550s, 1597m, 1505s, 1448s, 1389m, 1371m, 1335m, 1305m, 1240m, 1201m, 1179m, 1139m, 1092m, 1077m, 944m, 783m. ^{1}H NMR ($CDCl_3$): *δ* 7.28 (s, 1H, HC(2)); 5.23 (br s, 1H, OH); 4.19–3.56 (m, 3H); 2.10, 2.00 (2s, 6H, 2Me); 1.25 (d, *J* = 6.4, 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): *δ* 135.4 (d, C(2)); 132.3, 121.7 (2s, C(4), C(5)); 65.8 (t, CH_2); 52.6 (d, CH); 20.5 (q, Me); 12.1, 8.4 (2q, 2Me). HRMS (EI): Calcd for $C_8H_{14}N_2O$ (M^+): 154.1100, found 154.1098.

4.3.5. Methyl (*S*)-2-(4,5-dimethyl-1*H*-imidazol-1-yl)propanoate 4e

Yield: 1.40 g (77%). Pale yellow oil. $[\alpha]_D^{20} = -9.9$ (*c* 0.2, CH_2Cl_2). IR (film): *ν* 2950–2850s, 1747vs (C=O), 1596m, 1493s, 1451s, 1388m, 1330m, 1305s, 1207vs, 1065m, 736m. ^{1}H NMR ($CDCl_3$): *δ* 7.47 (s, 1H, HC(2)); 4.69 (q, *J* = 7.4, 1H); 3.74 (s, 3H, MeO); 2.14, 2.09 (2s, 6H, 2Me); 1.74 (d, *J* = 7.4, 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): *δ* 170.8 (s, C=O); 133.6, 121.9 (C(4′), C(5′)); 133.0 (d, C(2)); 52.7 (q, MeO); 52.5 (d, CH); 17.6 (q, *Me*CH); 12.3, 8.2 (2q, 2Me). HRMS (EI): Calcd for $C_9H_{14}N_2O_2$ (M^+): 182.1055, found 182.1059.

4.3.6. Methyl (*R*)-2-(4,5-dimethyl-1*H*-imidazol-1-yl)propanoate 4f

Yield: 1.18 g (65%). $[\alpha]_D^{20} = +10.5$ (*c* 0.2, CH_2Cl_2).

4.4. Synthesis of 1-substituted 3-alkoxy-4,5-dimethylimidazolium bromides 5 and bis-imidazolium bromide 9

The solution of imidazole N-oxide **3** (1.0 mmol) and excess of the corresponding alkyl bromide (ca. 3–4 mmol) or 0.5 equiv of 1,3-dibromopropane (101 mg, 0.5 mmol) in $CHCl_3$ (3 mL) was magnetically stirred at rt for 72 h. After the solvent was removed in vacuo, the oily residue was washed with Et_2O (4 × 5 mL), dissolved in CH_2Cl_2, filtered, and dried. If necessary, crude products can be purified by chromatography on a short column with neutral alumina ($CHCl_3$, then acetone in the case of **5**, or acetone, then AcOEt:MeOH 1:1 in the case of **9**).

4.4.1. 1-Butoxy-3-butyl-4,5-dimethylimidazolium bromide 5a

Yield: 259 mg (85%). Pale orange oil. IR (film): *ν* 3089m, 2958s, 2934s, 2873s, 1631m, 1544m, 1466s (br), 1380m, 1340m, 1143m, 935m. ^{1}H NMR ($CDCl_3$): *δ* 10.85 (s, 1H, HC(2)); 4.54 (t, *J* = 6.6, 2H, CH_2O); 4.34 (t, *J* = 6.8, 2H, CH_2N); 2.27 (s, 6H, 2Me); 2.00–1.16 (m, 8H); 0.97 (t, *J* = 6.4, 6H, 2*Me*CH_2). ^{13}C NMR ($CDCl_3$): *δ* 132.3 (d, C(2)); 123.7, 123.6 (2s, C(4), C(5)); 82.9, 47.4, 31.9, 29.6, 19.4, 18.7 (6t, $6CH_2$, 2Bu); 13.6, 13.4 (2q, 2Me, 2Bu); 8.4, 7.0 (2q, 2Me).

4.4.2. 1-Butoxy-3-cyclohexyl-4,5-dimethylimidazolium bromide 5b

Yield: 268 mg (81%). Colorless crystals. Mp 58–62 °C (Et_2O). IR (KBr): *ν* 3440vs, 3374s, 3114m, 3039m, 2929vs (br), 2861s, 1633m, 1608m, 1542m, 1453m, 1394m, 1221m, 1190m, 1030m, 959s, 902m. ^{1}H NMR ($CDCl_3$): *δ* 10.91 (s, 1H, HC(2)); 4.63 (t, *J* = 6.1, 2H, CH_2O); 4.32–3.85 (m, 1H, *c*Hex); 2.31, 2.27 (2s, 6H, 2Me); 2.19–1.26 (m, 14H); 0.96 (t, *J* = 6.4, 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): *δ* 130.7 (d, C(2)); 123.7, 123.5 (2s, C(4), C(5)); 82.8, 33.0, 29.6, 25.3, 24.2, 18.7 (6t, $8CH_2$, Bu, *c*Hex); 58.4 (d, CH, *c*Hex); 13.7 (q, Me, Bu); 9.0, 7.1 (2q, 2Me).

4.4.3. 1-Butoxy-4,5-dimethyl-3-(2-hydroxyethyl)imidazolium bromide 5c

Yield: 270 mg (92%). Yellow oil. IR (film): *ν* 3304vs, 3000–2730s, 1632m, 1547m, 1456s, 1394m, 1343m, 1141m, 1073s. ^{1}H NMR ($CDCl_3$): *δ* 9.97 (s, 1H, HC(2)); 4.48 (t, *J* = 6.4, 2H, CH_2O); 4.41 (t, *J* = 4.8, 2H, CH_2O); 3.97 (t, *J* = 4.8, 2H, CH_2N); 2.28 (s, 6H, 2Me); 2.16–1.23 (m, 4H, Bu); 0.97 (t, *J* = 6.4, 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): *δ* 129.4 (d, C(2)); 123.2, 122.1 (2s, C(4), C(5)); 81.0, 57.5, 48.0, 27.9, 17.0 (5t, $5CH_2$); 11.9 (q, Me, Bu); 7.1, 5.4 (2q, 2Me).

4.4.4. 4,5-Dimethyl-1-hexyloxy-3-(2-hydroxyethyl)imidazolium bromide 5d

Yield: 273 mg (85%). Yellow oil. IR (film): *ν* 3319vs, 3000–2750s, 1699m, 1633m, 1546m, 1456s, 1395m, 1380m, 1343m, 1142m, 1073s. ^{1}H NMR ($CDCl_3$): *δ* 9.98 (s, 1H, HC(2)); 4.48 (t, *J* = 6.7, 2H, CH_2O); 4.44 (t, *J* = 5.4, 2H, CH_2O); 3.98 (t, *J* = 5.4, 2H, CH_2N); 2.28 (s, 6H, 2Me); 2.19–1.08 (m, 8H, Hex); 0.92 (t, *J* = 6.8, 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): *δ* 131.3 (d, C(2)); 124.9, 123.9 (2s, C(4), C(5)); 83.2, 59.3, 49.8, 31.4, 27.8, 25.2, 22.4 (7t, $7CH_2$); 13.9 (q, Me, Hex); 8.9, 7.2 (2q, 2Me).

4.4.5. (*S*)-1-Butoxy-4,5-dimethyl-3-(2-hydroxypropyl)imidazolium bromide 5e

Yield: 285 mg (93%). Pale yellow oil. $[\alpha]_D^{20} = +13.7$ (*c* 0.2, CH_2Cl_2). IR (film): *ν* 3324vs, 3000–2850s, 1633m, 1546m, 1457m, 1376m, 1346m, 1323m, 1255m, 1140m, 1075m, 937m, 747m. ^{1}H NMR ($CDCl_3$): *δ* 10.01 (s, 1H, HC(2)); 4.9 (s, 1H, OH); 4.49 (t, *J* = 6.8, 2H, CH_2O); 4.38–4.09 (m, 3H); 2.27 (s, 6H, 2Me); 2.04–

1.11 (m, 4H, Bu); 1.32 (d, J = 6.4, 3H, Me); 0.98 (t, J = 6.8, 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): δ 131.7 (d, C(2)); 124.7, 123.7 (2s, C(4), C(5)); 82.8, 64.8, 29.7, 18.7 (4t, 4CH_2); 53.6 (d, CH); 20.5 (q, Me); 10.2 (q, Me, Bu); 8.8, 7.1 (2q, 2Me).

4.4.6. (*S*)-1-Butoxy-4,5-dimethyl-3-[1-(methoxycarbonyl)ethyl]-imidazolium bromide 5f

Yield: 324 mg (91%). Pale yellow oil. $[\alpha]_D^{20} = +14.2$ (*c* 0.2, CH_2Cl_2). IR (film): *v* 3432vs, 3050–2800vs (br), 1747vs (C=O), 1636m, 1544m, 1455m, 1440m, 1317m, 1240m, 1213s, 1063m, 935m. ^{1}H NMR ($CDCl_3$): δ 10.86 (s, 1H, HC(2)); 5.72 (q, J = 7.7, 1H, MeC*H*); 4.62 (dt, J = 7.2, J = 0.9, 2H); 3.82 (s, 3H, MeO); 2.29, 2.24 (2s, 6H, 2Me); 2.03 (d, J = 7.7, 3H, *Me*CH); 1.95–1.37 (m, 4H); 0.97 (t, J = 6.0, 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): δ 167.9 (s, C=O); 130.8 (d, C(2)); 124.3, 123.4 (2s, C(4), C(5)); 82.0, 28.5, 16.4 (3t, 3CH_2); 55.3 (d, CH); 52.6 (q, MeO); 17.6 (q, *Me*CH); 12.6 (q, Me, Bu); 8.4, 6.2 (2q, 2Me).

4.4.7. (*R*)-1-Butoxy-4,5-dimethyl-3-[1-(methoxycarbonyl)ethyl]-imidazolium bromide 5g

Yield: 298 mg (89%). $[\alpha]_D^{20} = -15.8$ (*c* 0.2, CH_2Cl_2).

4.4.8. (*S*)-4,5-Dimethyl-1-hexyloxy-3-[1-(methoxycarbonyl)ethyl]-imidazolium bromide 5h

Yield: 287 mg (79%). Pale yellow oil. $[\alpha]_D^{20} = +11.1$ (*c* 0.2, CH_2Cl_2). IR (film): *v* 3424vs, 3050–2850vs (br), 1747vs (C=O), 1636m, 1544m, 1455m, 1440m, 1317m, 1298m, 1213s, 1107m, 1063m, 976m. ^{1}H NMR ($CDCl_3$): δ 10.82 (s, 1H, HC(2)); 5.72 (q, J = 7.5, 1H, MeC*H*); 4.61 (dt, J = 7.3, J = 0.8, 2H); 3.81 (s, 3H, MeO); 2.26, 2.22 (2s, 6H, 2Me); 2.04 (d, J = 7.5, 3H, *Me*CH); 2.05–1.11 (m, 8H); 0.91 (t, J = 6.0, 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): δ 168.0 (s, C=O); 130.9 (d, C(2)); 124.5, 123.6 (2s, C(4), C(5)); 82.4, 30.3, 26.6, 24.0, 16.5 (5t, 5CH_2, Hex); 55.4 (d, CH); 52.7 (q, MeO); 21.3 (q, *Me*CH); 12.9 (q, Me, Hex); 8.5, 6.3 (2q, 2Me).

4.4.9. (*R*)-4,5-Dimethyl-1-hexyloxy-3-[1-(methoxycarbonyl)-ethyl]imidazolium bromide 5i

Yield: 301 mg (83%). $[\alpha]_D^{20} = -12.0$ (*c* 0.2, CH_2Cl_2).

4.4.10. 1,1′-(Propane-1,3-diyloxy)bis(4,5-dimethyl-3-butylimidazolium) dibromide 9

Yield: 242 mg (90%). Pale yellow oil. IR (film): *v* 3100m, 2960s, 2934s, 2873s, 1632s, 1546m, 1467s, 1396m, 1379m, 1341m, 1144m, 1030m, 962m, 925m. ^{1}H NMR ($CDCl_3$): δ 10.96 (s, 2H, HC(2)); 4.88 (t, J = 6.8, 4H, 2CH_2O); 4.12 (t, J = 7.9, 4H, 2CH_2N); 2.68–1.19 (m, 14H); 2.38, 2.25 (2s, 12H, 4Me); 0.98 (br t, J = 5.9, 6H, 2*Me*CH_2). ^{13}C NMR ($CDCl_3$): δ 131.8 (d, C(2), C(2′)); 124.2, 124.0 (2s, C(4), C(5), C(4′), C(5′)); 78.6, 47.1, 31.2, 26.0, 19.0 (5t, 9CH_2); 13.0 (q, 2Me, Bu); 8.3, 7.1 (2q, 4Me).

4.5. Anion exchange reactions leading to compounds 6, 8, 10, and 12

To the magnetically stirred solution of imidazolium bromides of type **6** and **8** (1.0 mmol) or dibromides **9** and **11** (0.5 mmol) in acetone (2 mL), solid $NaBF_4$ (121 mg, 1.1 mmol) was added. After ca. 4 h, the resulting suspension was filtered through neutral alumina (acetone or AcOEt:MeOH 1:1) and the solvent removed under reduced pressure. The residue was dissolved in CH_2Cl_2, filtered, and dried (4 h/20 mm Hg). Some of the obtained products solidified after trituration with Et_2O.

4.5.1. 1-Butoxy-3-butyl-4,5-dimethylimidazolium tetrafluoroborate 6a

Yield: 303 mg (97%). Pale yellow oil. IR (film): *v* 3140s, 3065m, 2964s, 2937s, 2876s, 1701m, 1633m, 1549m, 1468s, 1396m, 1381m, 1341m, 1058vs (br, BF_4^-), 936m. ^{1}H NMR ($CDCl_3$): δ 9.05 (s, 1H, HC(2)); 4.41 (t, J = 6.4, 2H, CH_2O); 4.13 (t, J = 8.7, 2H, CH_2N); 2.29 (s, 6H, 2Me); 1.97–1.15 (m, 8H); 1.09–0.83 (m, 6H, 2*Me*CH_2). ^{13}C NMR ($CDCl_3$): δ 130.3 (d, C(2)); 124.6, 124.4 (2s, C(4), C(5)); 82.9, 47.6, 31.7, 29.7, 19.5, 18.8 (6t, 6CH_2); 13.7, 13.4 (2q, 2Me, Bu); 8.4, 7.1 (2q, 2Me).

4.5.2. 1-Butoxy-3-cyclohexyl-4,5-dimethylimidazolium tetrafluoroborate 6b

Yield: 270 mg (80%). Pale yellow oil. IR (film): *v* 3136s, 3053m, 2937vs, 2865s, 1632m, 1541m, 1456s, 1398m, 1370m, 1338m, 1281m, 1217m, 1185m, 1058vs (BF_4^-), 937m. ^{1}H NMR ($CDCl_3$): δ 9.17 (s, 1H, HC(2)); 4.43 (t, J = 6.2, 2H, CH_2O); 4.29–3.85 (m, 1H, *c*Hex); 2.26, 2.23 (2s, 6H, 2Me); 2.15–1.25 (m, 14H); 0.98 (t, J = 6.4, 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): δ 128.3 (d, C(2)); 124.42, 124.37 (2s, C(4), C(5)); 82.7, 32.7, 29.7, 25.3, 24.3, 18.7 (6t, 8CH_2, Bu, *c*Hex); 58.3 (d, CH, *c*Hex); 13.7 (q, Me, Bu); 8.5, 6.9 (2q, 2Me).

4.5.3. 1-Butoxy-4,5-dimethyl-3-(2-hydroxyethyl)imidazolium tetrafluoroborate 6c

Yield: 267 mg (89%). Pale yellow oil. IR (film): *v* 3307vs, 3142m, 3000–2850vs, 1699m, 1633m, 1548m, 1456m, 1395m, 1382m, 1360m, 1344m, 1240m, 1186m, 1142m, 1065vs (BF_4^-), 937m, 753m. ^{1}H NMR ($CDCl_3$): δ 9.43 (s, 1H, HC(2)); 4.45 (t, J = 6.0, 2H, CH_2O); 4.39–4.26 (m, 2H, CH_2O); 4.03–3.88 (m, 2H, CH_2N); 2.26 (s, 6H, 2Me); 2.06–1.19 (m, 4H, Bu); 0.98 (t, J = 6.8 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): δ 130.7 (d, C(2)); 125.0, 124.0 (2s, C(4), C(5)); 82.7, 59.3, 49.6, 29.6, 18.6 (5t, 5CH_2); 13.5 (q, Me, Bu); 8.5, 7.0 (2q, 2Me).

4.5.4. 4,5-Dimethyl-1-hexyloxy-3-(2-hydroxyethyl)imidazolium tetrafluoroborate 6d

Yield: 305 mg (93%). Pale yellow oil. IR (film): *v* 3316vs, 3144m, 3000–2850vs, 1634m, 1549m, 1456s, 1395m, 1343m, 1239m, 1186m, 1065vs (BF_4^-), 754vs, 666m. ^{1}H NMR ($CDCl_3$): δ 9.19 (s, 1H, HC(2)); 4.38 (t, J = 6.2, 2H, CH_2O); 4.27 (t, J = 4.8, 2H, CH_2O); 3.93 (t, J = 4.8, 2H, CH_2N); 2.28 (s, 6H, 2Me); 2.08–1.15 (m, 8H, Hex); 0.89 (t, J = 6.8, 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): δ 130.6 (d, C(2)); 125.2, 124.2 (2s, C(4), C(5)); 83.1, 59.6, 49.7, 31.4, 27.7, 25.1, 22.4 (7t, 7CH_2); 14.0 (q, Me, Hex); 8.6, 7.1 (2q, 2Me).

4.5.5. (*S*)-1-Butoxy-4,5-dimethyl-3-(2-hydroxypropyl)imidazolium tetrafluoroborate 6e

Yield: 286 mg (91%). Pale yellow oil. $[\alpha]_D^{20} = +21.8$ (*c* 0.2, CH_2Cl_2). IR (film): *v* 3532vs, 3146s, 3000–2850vs, 1633m, 1549m, 1459m, 1396m, 1382m, 1345m, 1320m, 1288m, 1255m, 1187m, 1065vs (br, BF_4^-), 938m, 763m. ^{1}H NMR ($CDCl_3$): δ 8.88 (s, 1H, HC(2)); 4.38 (t, J = 6.4, 2H, CH_2O); 4.17–3.88 (m, 3H); 3.52 (br s, 1H, OH); 2.25 (s, 6H, 2Me); 2.03–1.22 (m, 4H, *Me*CH_2); 1.28 (d, J = 6.4, 3H, *Me*CH); 0.97 (t, J = 6.6, 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): δ 130.6 (d, C(2)); 125.3, 124.2 (2s, C(4), C(5)); 82.7, 53.8, 29.7, 18.8 (4t, 4CH_2); 65.6 (d, CH); 20.3 (q, *Me*CH); 13.7 (q, Me, Bu); 8.6, 7.0 (2q, 2Me).

4.5.6. (*S*)-1-Butoxy-4,5-dimethyl-3-[1-(methoxycarbonyl)ethyl]-imidazolium tetrafluoroborate 6f

Yield: 317 mg (92%). Pale yellow oil. $[\alpha]_D^{20} = +14.7$ (*c* 0.2, CH_2Cl_2). IR (film): *v* 3140m, 3050–2850vs (br), 1750vs (C=O), 1636m, 1545m, 1456m, 1442m, 1389m, 1317m, 1241m, 1213s, 1062vs (br, BF_4^-). ^{1}H NMR ($CDCl_3$): δ 9.53 (s, 1H, HC(2)); 5.31 (q, J = 7.4, 1H, MeC*H*); 4.48 (dt, J = 6.2, J = 2.1, 2H); 3.82 (s, 3H, MeO); 2.30, 2.24 (2s, 6H, 2Me); 1.94 (d, J = 7.4, 3H, *Me*CH); 1.91–1.69 (m, 2H); 1.60–1.42 (m, 2H); 0.97 (t, J = 7.3, 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): δ 168.5 (s, C=O); 129.7 (d, C(2)); 125.2, 124.2 (2s, C(4), C(5)); 82.4, 29.0, 16.1 (3t, 3CH_2); 55.3 (d, CH); 53.0 (q, MeO); 18.0 (q, *Me*CH); 13.0 (q, Me, Bu); 8.1, 6.3 (2q, 2Me).

4.5.7. (*R*)-1-Butoxy-4,5-dimethyl-3-[1-(methoxycarbonyl)ethyl]-imidazolium tetrafluoroborate 6g

Yield: 301 mg (88%). $[\alpha]_D^{20} = -16.2$ (*c* 0.2, CH_2Cl_2).

4.5.8. (*S*)-4,5-Dimethyl-1-hexyloxy-3-[1-(methoxycarbonyl)ethyl]-imidazolium tetrafluoroborate 6h

Yield: 340 mg (92%). Pale yellow oil. $[\alpha]_D^{20} = +9.5$ (*c* 0.2, CH_2Cl_2). IR (film): *ν* 3140m, 3050–2850vs (br), 1751vs (C=O), 1636m, 1546m, 1455s, 1439s, 1389m, 1353m, 1316m, 1240s, 1213s, 1150m, 1062vs (BF_4^-), 977m. ^{1}H NMR ($CDCl_3$): *δ* 9.39 (s, 1H, HC(2)); 5.28 (q, *J* = 7.2, 1H, MeC*H*); 4.46 (dt, *J* = 6.4, *J* = 1.9, 2H); 3.82 (s, 3H, MeO); 2.30, 2.23 (2s, 6H, 2Me); 1.93 (d, *J* = 7.2, 3H, *Me*CH); 1.88–1.74 (m, 2H); 1.48–1.26 (m, 6H); 0.90 (t, *J* = 6.5, 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): *δ* 168.6 (s, C=O); 129.7 (d, C(2)); 125.4, 124.3 (2s, C(4), C(5)), 82.8, 30.8, 27.1, 24.5, 16.2 (5t, 5CH_2, Hex); 55.4 (d, CH); 53.2 (q, MeO); 21.8 (q, *Me*CH); 13.4 (q, Me, Hex); 8.2, 6.5 (2q, 2Me).

4.5.9. (*R*)-4,5-Dimethyl-1-hexyloxy-3-[1-(methoxycarbonyl)ethyl]-imidazolium tetrafluoroborate 6i

Yield: 344 mg (93%). $[\alpha]_D^{20} = -10.8$ (*c* 0.2, CH_2Cl_2).

4.5.10. 1,3-Dibutyl-4,5-dimethylimidazolium tetrafluoroborate 8a

Yield: 280 mg (95%). Pale yellow oil. IR (film): *ν* 3156m, 3091m, 2963s, 2936s, 2876m, 1632m, 1567m, 1467m (br), 1203m, 1054vs (br, BF_4^-). ^{1}H NMR ($CDCl_3$): *δ* 8.79 (s, 1H, HC(2)); 4.08 (t, *J* = 7.9, 4H, 2CH_2N); 2.24 (s, 6H, 2Me); 2.02–1.13 (m, 8H, 4CH_2); 0.95 (t, *J* = 7.2, 6H, 2*Me*CH_2). ^{13}C NMR ($CDCl_3$): *δ* 134.5 (d, C(2)); 126.7 (s, C(4), C(5)); 47.1, 31.7, 19.5 (3t, 6CH_2); 13.4 (q, 2Me, Bu); 8.4 (q, 2Me).

4.5.11. 1-Butyl-4,5-dimethyl-3-hexylimidazolium tetrafluoroborate 8b

Yield: 271 mg (87%). Pale yellow oil. IR (film): *ν* 3155m, 3090m, 2960s, 2934s, 2873s, 1632m, 1567m, 1467m, 1201m, 1058vs (br, BF_4^-). ^{1}H NMR ($CDCl_3$): *δ* 8.82 (s, 1H, HC(2)); 4.09 (t, *J* = 7.6, 4H, 2CH_2N); 2.25 (s, 6H, 2Me); 2.08–1.13 (m, 10H, 5CH_2); 1.10–0.73 (m, 6H, 2*Me*CH_2). ^{13}C NMR ($CDCl_3$): *δ* 134.0 (d, C(2)); 126.68, 126.62 (2s, C(4), C(5)); 47.0, 46.8, 31.4, 30.8, 29.5, 25.7, 22.2, 19.2 (8t, 8CH_2); 13.7, 13.2 (2q, 2Me, Hex, Bu); 8.1 (q, 2Me).

4.5.12. 3-Butyl-1-cyclohexyl-4,5-dimethylimidazolium tetrafluoroborate 8c

Yield: 312 mg (97%). Pale yellow oil. IR (film): *ν* 3153m, 3084m, 2937s, 2864m, 1630m, 1560m, 1456m, 1374m, 1235m, 1054vs (br, BF_4^-). ^{1}H NMR ($CDCl_3$): *δ* 8.81 (s, 1H, HC(2)); 4.12 (t, *J* = 7.5, 2H, CH_2N); 4.23–3.71 (m, 1H, *c*Hex); 2.24 (s, 6H, 2Me); 2.39–1.15 (m, 14H); 0.93 (t, *J* = 6.6, 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): *δ* 132.1 (d, C(2)); 126.3 (s, C(4), C(5)); 57.3 (d, CH, *c*Hex); 46.9, 32.7, 31.7, 25.4, 24.3, 19.2 (6t, 8CH_2); 13.2 (q, Me, Bu); 8.3, 8.0 (2q, 2Me).

4.5.13. 1-Cyclohexyl-4,5-dimethyl-3-hexylimidazolium tetrafluoroborate 8d

Yield: 329 mg (94%). Pale yellow oil. IR (film): *ν* 3153m, 3084m, 2934s, 2861s, 1630m, 1559m, 1456m, 1231m, 1197m, 1058vs (br, BF_4^-). ^{1}H NMR ($CDCl_3$): *δ* 8.83 (s, 1H, HC(2)); 4.12 (t, *J* = 7.4, 2H, CH_2N); 4.22–3.73 (m, 1H, *c*Hex); 2.21, 2.22 (2s, 6H, 2Me); 2.17–1.08 (m, 18H); 0.86 (br t, 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): *δ* 132.1 (d, C(2)); 126.34, 126.28 (2s, C(4), C(5)); 57.3 (d, CH, *c*Hex); 47.1, 32.7, 30.8, 29.7, 25.6, 25.1, 24.3, 22.1 (8t, 10CH_2); 13.7 (q, Me, Hex); 8.3, 8.0 (2q, 2Me).

4.5.14. 3-Butyl-4,5-dimethyl-1-(2-hydroxyethyl)imidazolium tetrafluoroborate 8e

Yield: 278 mg (98%). Pale yellow oil. IR (film): *ν* 3544vs, 3161m, 3095m, 3050–2850vs, 1633m, 1567s, 1458m, 1400m, 1358m, 1202m, 1062vs (br, BF_4^-). ^{1}H NMR ($CDCl_3$): *δ* 8.62 (s, 1H, HC(2)); 4.21 (t, *J* = 6.5, 2H, CH_2O); 4.08–3.81 (m, 4H); 2.24 (s, 6H, 2Me); 1.99–1.25 (m, 4H, Bu); 0.95 (t, *J* = 6.4, 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): *δ* 134.1 (d, C(2)); 127.2, 126.4 (2s, C(4), C(5)); 59.9, 49.0, 46.8, 31.3, 19.3 (5t, 5CH_2); 13.2 (q, Me, Bu); 8.1 (q, 2Me).

4.5.15. (*S*)-3-Butyl-4,5-dimethyl-1-(2-hydroxypropyl)imidazolium tetrafluoroborate 8f

Yield: 283 mg (92%). Pale yellow oil. $[\alpha]_D^{20} = +21.2$ (*c* 0.2, CH_2Cl_2). IR (film): *ν* 3533vs, 3160m, 3093m, 2966s, 2937s, 2877m, 1632m, 1567s, 1463s, 1400m, 1378m, 1285m, 1204s, 1062vs (br, BF_4^-). ^{1}H NMR ($CDCl_3$): *δ* 8.67 (s, 1H, HC(2)); 4.22–3.89 (m, 5H); 2.25 (s, 6H, 2Me); 2.03–1.19 (m, 4H, 2CH_2); 1.25 (d, *J* = 5.9, 3H, *Me*CH); 0.96 (t, *J* = 6.2, 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): *δ* 134.7 (d, C(2)); 127.3, 126.3 (2s, C(4), C(5)); 65.6 (d, CH); 53.4, 47.0, 31.4, 19.5 (4t, 4CH_2); 20.2 (q, *Me*CH); 13.4 (q, Me, Bu); 8.5, 8.3 (2q, 2Me).

4.5.16. (*S*)-1-Butyl-3-[1-(methoxycarbonyl)ethyl]-4,5-dimethylimidazolium tetrafluoroborate 8g

Yield: 310 mg (95%). Colorless solid. Mp 64–66 °C (Et_2O). $[\alpha]_D^{20} = +10.3$ (*c* 0.2, CH_2Cl_2). IR (KBr): *ν* 3158m, 3089m, 2963s, 2938m, 2877m, 1751vs (C=O), 1635m, 1565s, 1456s, 1401m, 1386m, 1308m, 1258m, 1212s, 1058vs (BF_4^-), 975m. ^{1}H NMR ($CDCl_3$): *δ* 8.91 (s, 1H, HC(2)); 5.13 (q, *J* = 7.7, 1H); 4.24 (t, *J* = 7.6, 2H); 3.79 (s, 3H, MeO); 2.28, 2.18 (2s, 6H, 2Me); 1.92 (d, *J* = 7.7, 3H, *Me*CH); 1.92–1.24 (m, 4H); 0.95 (t, *J* = 6.4, 3H, *Me*CH_2). ^{13}C NMR ($CDCl_3$): *δ* 169.1 (s, C=O); 134.0 (d, C(2)); 127.5, 126.8 (2s, C(4), C(5)); 55.2 (d, CH); 53.6 (q, MeO); 47.3, 31.6, 19.3 (3t, 3CH_2); 17.1 (q, *Me*CH); 13.4 (q, Me, Bu); 8.3, 8.1 (2q, 2Me).

4.5.17. (*R*)-1-Butyl-3-[1-(methoxycarbonyl)ethyl]-4,5-dimethylimidazolium tetrafluoroborate 8h

Yield: 244 mg (75%). Colorless solid. Mp 67–68 °C (Et_2O). $[\alpha]_D^{20} = -8.2$ (*c* 0.2, CH_2Cl_2).

4.5.18. 1,1′-(Propane-1,3-diyloxy)bis(4,5-dimethyl-3-butylimidazolium) tetrafluoroborate 10

Yield: 251 mg (91%). Colorless oil. IR (film): *ν* 3142m, 1964s, 1936s, 2876m, 1633m, 1549m, 1468 m (br), 1341m, 1187m, 1054vs (br, BF_4^-), 917m, 730s. ^{1}H NMR ($CDCl_3$): *δ* 9.23 (s, 2H, HC(2)); 4.61 (t, *J* = 6.0, 4H, 2CH_2O); 4.08 (t, *J* = 7.9, 4H, 2CH_2N); 2.46–1.14 (m, 14H); 2.31, 2.27 (2s, 12H, 4Me); 0.94 (t, *J* = 6.4, 6H, 2*Me*CH_2). ^{13}C NMR ($CDCl_3$): *δ* 130.2 (d, C(2), C(2′)); 124.76, 124.69 (2s, C(4), C(5), C(4′), C(5′)); 78.6, 47.4, 31.2, 26.0, 19.3 (5t, 9CH_2); 13.2 (q, 2Me, Bu); 8.2, 6.8 (2q, 4Me).

4.5.19. 1,1′-(Propane-1,3-diyl)bis(4,5-dimethyl-3-butylimidazolium) tetrafluoroborate 12

Yield: 213 mg (84%). Orange semi-solid. IR (film): *ν* 3156m, 3091m, 2963s, 2935s, 2875m, 1632m, 1567s, 1466s (br), 1201m, 1050vs (br, BF_4^-), 920m, 730s. ^{1}H NMR ($CDCl_3$): *δ* 9.35 (s, 2H, HC(2)); 4.42 (t, *J* = 7.3, 4H, 2CH_2N); 4.05 (t, *J* = 7.8, 4H, 2CH_2N); 2.70–1.14 (m, 14H); 2.37, 2.27 (2s, 12H, 4Me); 0.95 (t, *J* = 6.7, 6H, 2*Me*CH_2). ^{13}C NMR ($CDCl_3$): *δ* 134.0 (d, C(2), C(2′)); 127.3, 126.4 (2s, C(4), C(5), C(4′), C(5′)); 46.8, 43.5, 31.2, 29.7, 19.2 (5t, 9CH_2); 13.1 (q, 2Me, Bu); 8.2, 8.1 (2q, 4Me).

4.6. Synthesis of 1,3-disubstituted 4,5-dimethylimidazolium bromides 7 and bis-imidazolium bromide 11

The solution of imidazole **4** (1.0 mmol) and excess of the corresponding alkyl bromide (1.5 mmol) or 0.5 equiv of 1,3-diaminopropane (101 mg, 0.5 mmol) in benzene (5 mL) was heated at reflux for 6 h. Then, the solvent was removed (evaporated or decanted), the resulting product was washed with Et_2O (3 × 5 mL), and dried

under high vacuum for 4 h. The products **7a**, **7b**, **7g**, and **7h** solidified after trituration with Et_2O. If necessary, the crude products can be purified by chromatography on a short column of neutral alumina ($CHCl_3$, then acetone in the case of **7**; or acetone, then AcOEt:MeOH 1:1 in the case of **11**).

4.6.1. 1,3-Dibutyl-4,5-dimethylimidazolium bromide 7a

Yield: 272 mg (94%). Pale brown solid. Mp 83–86 °C (Et_2O). IR (KBr): *ν* 3010m, 2962vs, 2935s, 2876m, 1630m, 1567m, 1459m, 1245m, 1197m. ^{1}H NMR ($CDCl_3$): *δ* 10.39 (s, 1H, HC(2)); 4.22 (t, *J* = 8.4, 4H, $2CH_2N$); 2.25 (s, 6H, 2Me); 2.13–1.18 (m, 8H, $4CH_2$); 0.99 (br t, 6H, $2MeCH_2$). ^{13}C NMR ($CDCl_3$): *δ* 135.6 (d, C(2)); 126.1 (s, C(4), C(5)); 46.8, 31.7, 19.3 (3t, $6CH_2$); 13.3 (q, 2Me, Bu); 8.4 (q, 2Me).

4.6.2. 1-Butyl-4,5-dimethyl-3-hexylimidazolium bromide 7b

Yield: 282 mg (89%). Colorless solid. Mp 118–120 °C (Et_2O). IR (KBr): *ν* 2960s, 2931s, 2872m, 1630m, 1565m, 1468m, 1458m, 1199m. ^{1}H NMR ($CDCl_3$): *δ* 10.48 (s, 1H, HC(2)); 4.22, 4.21 (2t, *J* = 6.4, 4H, $2CH_2N$); 2.24 (s, 6H, 2Me); 2.12–1.12 (m, 12H, $6CH_2$); 1.07–0.69 (m, 6H, $2MeCH_2$). ^{13}C NMR ($CDCl_3$): *δ* 136.3 (d, C(2)); 126.0 (s, C(4), C(5)); 47.3, 47.1, 32.0, 31.1, 30.1, 26.0, 22.4, 19.6 (8t, $8CH_2$); 13.9, 13.5 (2q, 2Me, Hex, Bu); 8.5 (q, 2Me).

4.6.3. 3-Butyl-1-cyclohexyl-4,5-dimethylimidazolium bromide 7c

Yield: 301 mg (95%). Pale yellow oil. IR (film): *ν* 2933vs (br), 2860m, 1629m, 1557m, 1454m, 1233m, 1212m, 1196m. ^{1}H NMR ($CDCl_3$): *δ* 10.46 (s, 1H, HC(2)); 4.38 (t, *J* = 6.8, 2H, CH_2N); 4.27–3.60 (m, 1H, *c*Hex); 2.27 (s, 6H, 2Me); 2.39–1.13 (m, 14H, $7CH_2$); 0.95 (t, *J* = 6.4, 3H, $MeCH_2$). ^{13}C NMR ($CDCl_3$): *δ* 135.0 (d, C(2)); 125.9, 125.4 (2s, C(4), C(5)); 58.0 (d, CH, *c*Hex); 47.2, 33.3, 32.3, 25.5, 24.4, 19.6 (6t, $8CH_2$); 13.6 (q, Me, Bu); 8.8, 8.4 (2q, 2Me).

4.6.4. 1-Cyclohexyl-4,5-dimethyl-3-hexylimidazolium bromide 7d

Yield: 312 mg (91%). Pale yellow oil. IR (film): *ν* 2931vs, 2858m, 1629m, 1557m, 1467m, 1454m, 1232m, 1199m, 730m. ^{1}H NMR ($CDCl_3$): *δ* 10.44 (s, 1H, HC(2)); 4.32 (t, *J* = 7.2, 2H, CH_2N); 4.25–3.68 (m, 1H, *c*Hex); 2.28, 2.27 (2s, 6H, 2Me); 2.39–1.08 (m, 18H, $9CH_2$); 1.05–0.71 (m, 3H, $MeCH_2$). ^{13}C NMR ($CDCl_3$): *δ* 134.5 (d, C(2)); 125.8, 125.5 (2s, C(4), C(5)); 57.6 (d, CH, *c*Hex); 47.0, 33.0, 30.9, 30.0, 25.7, 25.2, 24.1, 22.1 (8t, $10CH_2$); 13.6 (q, Me, Hex); 8.6, 8.2 (2q, 2Me).

4.6.5. 3-Butyl-4,5-dimethyl-1-(2-hydroxyethyl)imidazolium bromide 7e

Yield: 269 mg (97%). Pale yellow oil. IR (film): *ν* 3288vs, 3050–2760s, 1632m, 1564s, 1459s, 1399m, 1375m, 1355m, 1200s, 1077s. ^{1}H NMR ($CDCl_3$): *δ* 9.65 (s, 1H, HC(2)); 4.38 (t, *J* = 5.2, 2H, CH_2O); 4.09 (t, *J* = 7.6, 2H, CH_2N); 3.98 (t, *J* = 5.2, 2H, CH_2N); 2.24, 2.22 (2s, 6H, 2Me); 2.07–1.18 (m, 4H, $2CH_2$); 0.96 (t, *J* = 6.4, 3H, $MeCH_2$). ^{13}C NMR ($CDCl_3$): *δ* 133.7 (d, C(2)); 125.1, 124.2 (2s, C(4), C(5)); 57.5, 47.5, 45.3, 29.9, 17.8 (5t, $5CH_2$); 11.7 (q, Me, Bu); 6.9, 6.3 (2q, 2Me).

4.6.6. (*S*)-3-Butyl-4,5-dimethyl-1-(2-hydroxypropyl)imidazolium bromide 7f

Yield: 253 mg (84%). Colorless oil. $[\alpha]_D^{20} = +13.8$ (*c* 0.2, CH_2Cl_2). IR (film): *ν* 3274vs, 2964s, 2933s, 2874m, 1632m, 1564m, 1463m, 1374m, 1200m, 1139m, 1084m, 730m. ^{1}H NMR ($CDCl_3$): *δ* 9.77 (s, 1H, HC(2)); 4.41–4.05 (m, 3H); 4.09 (t, *J* = 7.2, 2H, CH_2N); 2.24 (s, 6H, 2Me); 2.07–1.15 (m, 4H, $2CH_2$); 1.30 (d, *J* = 6.4, 3H, *Me*CH); 0.96 (t, *J* = 8.0, 3H, $MeCH_2$). ^{13}C NMR ($CDCl_3$): *δ* 136.0 (d, C(2)); 126.5, 125.6 (2s, C(4), C(5)); 64.7 (d, CH); 53.0, 46.9, 31.4, 19.3 (4t, $4CH_2$); 20.4 (q, *Me*CH); 13.2 (q, Me, Bu); 8.4, 8.3 (2q, 2Me).

4.6.7. (*S*)-1-Butyl-3-[1-(methoxycarbonyl)ethyl]-4,5-dimethylimidazolium bromide 7g

Yield: 169 mg (53%, modified procedure: 3 equiv of butyl bromide, CH_2Cl_2, rt, 48 h). Colorless solid. Mp 96–99 °C (Et_2O). $[\alpha]_D^{20} = +11.2$ (*c* 0.2, CH_2Cl_2). IR (film): *ν* 3050–2850vs (br), 1740vs (C=O), 1636m, 1565s, 1475m, 1464m, 1449m, 1419m, 1383m, 1293m, 1274s, 1246s, 1212s, 1095m, 1063m, 1022m, 954m. ^{1}H NMR ($CDCl_3$): *δ* 10.53 (s, 1H, HC(2)); 5.48 (q, *J* = 7.7, 1H, Me*CH*); 4.41 (dt, *J* = 7.6, *J* = 3.2, 2H); 3.79 (s, 3H, MeO); 2.26, 2.19 (2s, 6H, 2Me); 2.02 (d, *J* = 7.7, 3H, *Me*CH); 1.99–1.64 (m, 2H); 1.60–1.18 (m, 2H); 0.96 (t, *J* = 7.2, 3H, $MeCH_2$). ^{13}C NMR ($CDCl_3$): *δ* 168.9 (s, C=O); 135.6 (d, C(2)); 126.8, 126.4 (2s, C(4), C(5)); 55.5 (d, CH); 53.3 (q, MeO); 47.0, 31.5, 19.1 (3t, $3CH_2$, Bu); 17.1 (q, *Me*CH); 13.2 (q, Me, Bu); 8.8, 8.2 (2q, 2Me).

4.6.8. (*R*)-1-Butyl-3-[1-(methoxycarbonyl)ethyl]-4,5-dimethylimidazolium bromide 7h

Yield: 140 mg (44%, modified procedure: 3 equiv of butyl bromide, CH_2Cl_2, rt, 48 h). Mp 99–103 °C (Et_2O). $[\alpha]_D^{20} = -11.0$ (*c* 0.2, CH_2Cl_2).

4.6.9. 1,1′-(Propane-1,3-diyl)bis(4,5-dimethyl-3-butylimidazolium) dibromide 11

Yield: 227 mg (89%). Pale yellow oil. IR (film): *ν* 3136m, 2960s, 2933s, 2872m, 1698m, 1632s, 1564s, 1464s, 1399m, 1377m, 1246m, 1200s. ^{1}H NMR ($CDCl_3$): *δ* 10.29 (s, 2H, HC(2), 7HC(2′)); 4.66 (t, *J* = 6.7, 4H, $2CH_2N$); 4.07 (t, *J* = 6.8, 4H, HC(2), CH_2N); 2.91–1.14 (m, 14H); 2.50, 2.23 (2s, 12H, 4Me); 0.98 (br t, *J* = 5.6, 6H, $2MeCH_2$). ^{13}C NMR ($CDCl_3$): *δ* 134.4 (d, C(2), C(2′)); 127.0, 125.6 (2s, C(4), C(5), C(4′), C(5′)); 46.4, 43.2, 30.8, 29.5, 18.8 (5t, $9CH_2$); 12.7 (q, 2Me, Bu); 8.5, 7.9 (2q, 4Me).

4.7. Reaction of 5a with $NaBH_4$

To the solution of **5a** (3.01 g, 10.5 mmol) in MeOH (15 mL), solid $NaBH_4$ (1.03 g, 27 mmol) was added in small portions at 0 °C. After 30 min, the ice-bath was removed and stirring was continued for 20 min at rt, the solution was diluted with 10% HCl (15 mL) and stirred for another 20 min. Then, the organic solvents were removed under reduced pressure and the resulting aqueous solution extracted with Et_2O (3 × 20 mL). The organic layer was flash chromatographed (SiO_2, AcOEt:MeOH 2:1), the solvents removed, and the product dried in vacuum to give pure **4a** (0.51 g, 33%). Then, the water layer was treated with excess of solid $NaHCO_3$, extracted with CH_2Cl_2 (2 × 20 mL), dried with anhyd. Na_2SO_4, and filtered. The solvent was removed and pure **5a** (1.65 g) was isolated.

Note: Complete reduction of **5a** (0.83 g, 2.7 mmol) was achieved using 10 equiv of $NaBH_4$ in MeOH/H_2O mixture (rt, 16 h) to give **4a** in 75% yield.

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