



Optically active imidazole N-oxides derived from L-prolinamine¹

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ARTICLE INFO

Article history:

Received 5 June 2013

Accepted 12 July 2013

Dedicated to Professor Ernst Schaumann on the occasion of his 70th birthday

ABSTRACT

Starting with (S)-1-benzylprolinamine and α -hydroxyimino ketones, enantiomerically pure bisheterocyclic imidazole N-oxides bearing the (S)-configured N-benzyl(pyrrolidin-2-yl)methyl residue were prepared. These N-oxides reacted with 2,2,4,4-tetramethylcyclobutane-1,3-dithione to give the corresponding optically active imidazole-2-thione derivatives via a sulfur transfer reaction. Reduction of the N-oxides with Raney-nickel led to deoxygenation, whereas catalytic hydrogenation (Pd/C) in ethanol occurred with simultaneous deoxygenation and debenzilation, leading to optically active 1-(pyrrolidin-2-yl)methyl-1H-imidazoles. Alkylation of the prepared imidazole N-oxides and their respective imidazoles with butyl and hexyl bromide and subsequent anion exchange gave optically active N-alkoxy- and N-alkylimidazolium tetrafluoroborates, respectively, with the properties of 'room temperature ionic liquids'.

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1. Introduction

The importance of imidazole derivatives in organic, bioorganic, and medicinal chemistry as well as in material science is well documented.^{2–4} In recent years, numerous reports on the synthesis and diverse applications of imidazole N-oxides have been published.⁵ In contrast to six-membered N-heterocycles, imidazoles cannot be converted into their corresponding N-oxides by treatment with typical oxidizing reagents.⁶ Therefore, condensations of α -hydroxyimino ketones with methyldene amines (formaldehyde imines) were used as a convenient access to 2-unsubstituted imidazole N-oxides.^{5a,7} Starting with optically active primary amines, such as 1-phenylethylamine, *trans*-cyclohexane-1,2-diamine, as well as α -amino acid esters, the desired enantiomerically pure imidazole N-oxides were obtained as the sole products.⁸ Some of them were tested as ligands for the asymmetric allylations of aldehydes⁹ and in cyclopropanation reactions.¹⁰

L-Prolinamine ((2S)-pyrrolidin-2-yl)methylamine) is a useful and widely applied building block for the synthesis of optically ac-

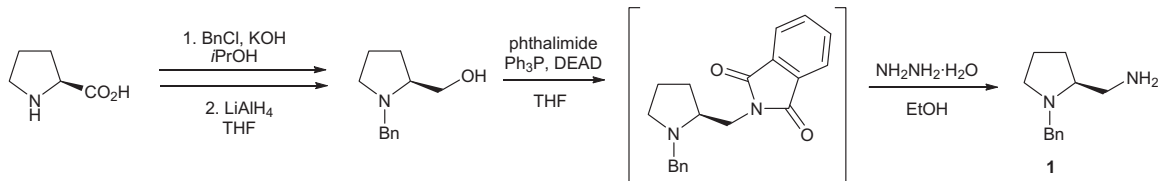
tive ligands of potential importance for asymmetric synthesis.¹¹ The non-protected prolinamine easily reacts with electron-deficient dicyanofumarates, and enantiomerically pure bicyclic pyrazinones are obtained chemoselectively.¹²

Our aim herein was the synthesis of a new series of optically active imidazole derivatives containing the chiral pyrrolidine fragment originating from L-prolinamine. Some of the products were used for the preparation of new imidazole-based optically active ionic liquids.

2. Results and discussion

The preparation of the starting N-benzylated L-prolinamine **1** can be achieved from methyl L-prolinate via aminolysis and reduction of the amide¹³ or from L-prolinol via the intermediate azide.^{11a} In addition, we developed a new approach to **1b** based on a Mitsunobu reaction via the intermediate phthalimide derivative (Scheme 1).

The condensation of **1** with paraformaldehyde led to methyldene prolinamine **2**, which spontaneously underwent trimeriza-

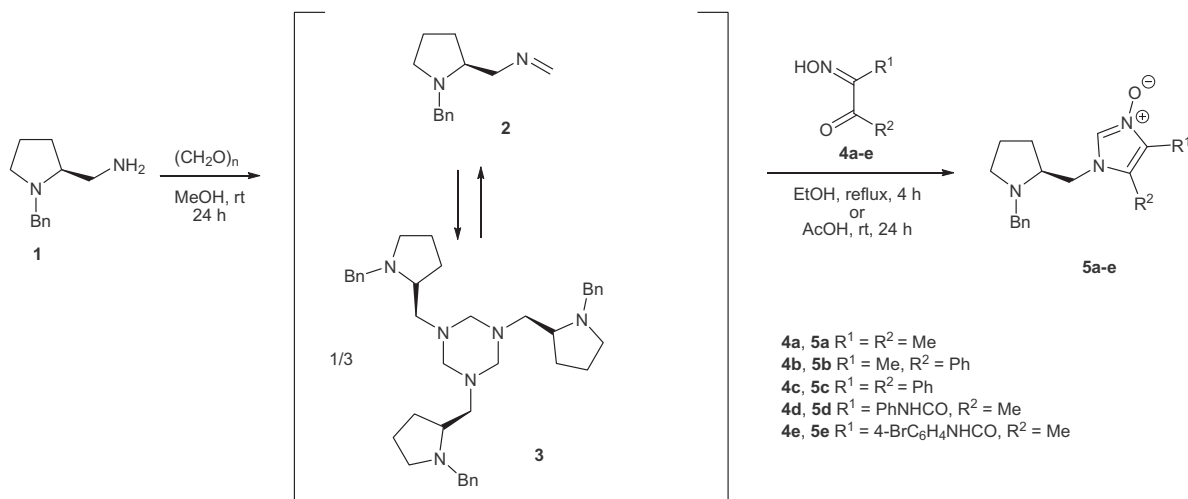


Scheme 1.

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tion to give the corresponding hexahydrotriazine **3** (Scheme 2). The structure of **3** was confirmed by the ^{13}C NMR spectrum, in which no signal for the imino group ($\text{N}=\text{CH}_2$) appeared. The trimerization of methyldene amines is a typical reaction,¹⁴ and only in the case of bulky substituents, for example, adamantan-1-yl, is the monomeric form stable under standard conditions.¹⁵ Herein, trimer **3** is believed to exist in solution in equilibrium with the monomeric form **2**.



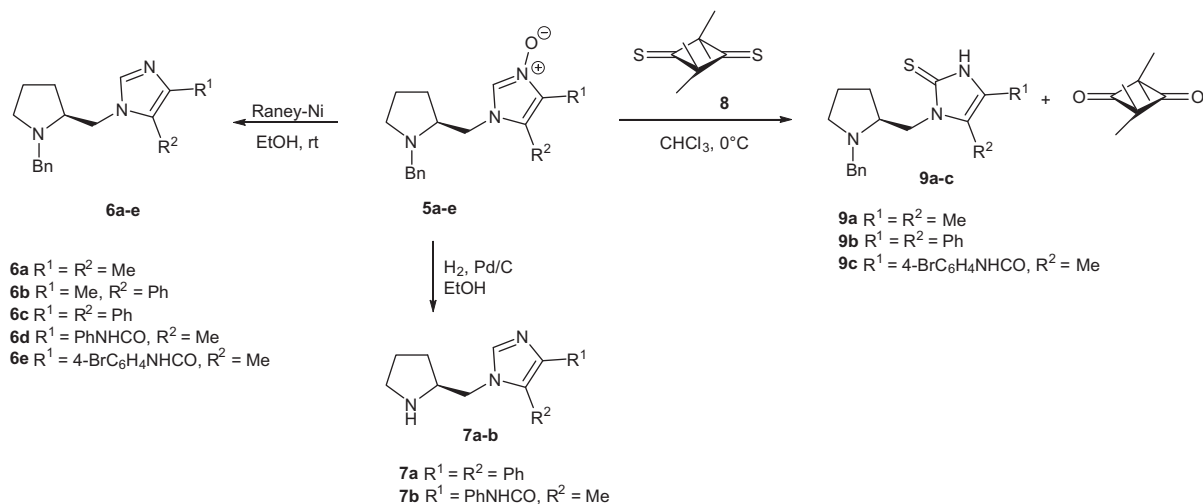
Scheme 2.

The latter reacts with α -hydroxyimino ketones **4a–e** in boiling ethanol (method A) or in glacial acetic acid at room temperature (method B) to yield the desired optically active imidazole N-oxides **5a–e** in good yields (Scheme 2). In order to examine the enantiopurity of these products, a sample of **5a** was dissolved in CDCl_3 with an equimolar amount of (*tert*-butyl)(phenyl)thiophosphinic acid (MOD reagent).¹⁶ The ^1H NMR spectrum showed only one set of signals, whereas in the case of racemic **5a** (*rac*-**5a**), the addition of MOD led to the appearance of two sets of signals. Thus, in the racemic product, the diagnostic H–C(2) signal of imidazole N-oxides appeared as two singlets located at 8.87 and 8.86 ppm. Similarly, one Me group gave two singlets at 1.95 and 1.94 ppm, whereas the second Me group of both enantiomers absorbed as a singlet at 2.08 ppm. Moreover, for all other signals observed, duplication was observed in the spectrum of *rac*-**5a**.

corresponding parent compounds have been alkylated to give imidazolium salts, which display the properties of ionic liquids.^{8d,19}

Treatment of imidazole N-oxides **5** with Raney-Ni in ethanol at room temperature led smoothly to selective deoxygenation to yield the corresponding imidazoles **6** (Scheme 3). Under these conditions, no debenzoylation of the pyrrolidine ring was observed. In a control experiment, the reaction mixture was heated at reflux, and in this case, a complex mixture of products was formed. Conversely, hydrogenolysis (H_2 , Pd/C) of **5c** and **5d** in ethanol led to deoxygenation and debenzoylation to yield **7a** and **7b**, respectively.

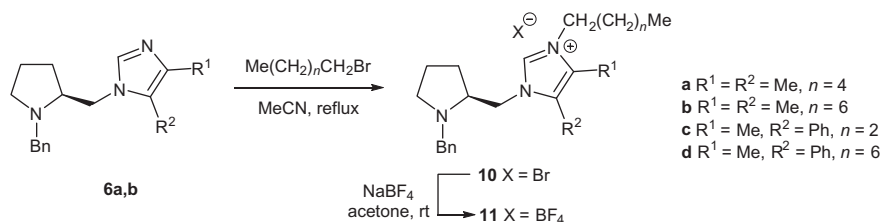
The 2-unsubstituted imidazole N-oxides **5a,c** and **e** reacted with 2,2,4,4-tetramethylcyclobutane-1,3-dithione **8** via the so-called ‘sulfur-transfer reaction’ to give optically active imidazole-2-thiones **9a–c** (Scheme 3).²⁰ In these reactions, imidazole N-oxides **5** react as ‘nitron-like’ 1,3-dipoles, and after the 1,3-dipolar



Scheme 3.

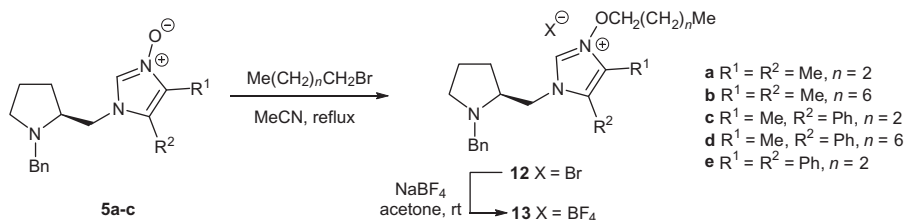
cycloaddition, the intermediate 1,4,2-oxathiazolidine undergoes a fragmentation to yield **9** and 2,2,4,4-tetramethyl-3-thioxocyclobutanone. The latter can undergo a 'sulfur-transfer reaction' with molecule **5** once more, leading to **9** and 2,2,4,4-tetramethylcyclobutane-1,3-dione. The obtained imidazole-2-thiones **9** are characterized by the thiourea moiety, which is of great importance in asymmetric synthesis and organocatalysis.²¹

The alkylation of imidazoles with long-chain alkyl bromides and subsequent anion exchange is a typical procedure for the preparation of imidazolium salts with the characteristic behavior of ionic liquids (ILs).²² Optically active ionic liquids are of special interest, but to date, proline-derived examples are rare.²³ Thus, imidazoles **6** were alkylated with butyl, hexyl, and octyl bromide in boiling acetonitrile. The imidazolium bromides **10** thus obtained were dissolved in acetone and treated with an equimolar amount of NaBF₄ at room temperature to give the corresponding tetrafluoroborates **11** (Scheme 4). All of them are liquids at room temperature and, therefore, belong to the class of optically active 'room temperature ionic liquids' (RTILs).



Scheme 4.

In a recent paper, we described the synthesis of a new type of ionic liquid containing a 3-alkoxyimidazolium cation.^{8d} Similarly, the alkylation of imidazole N-oxides **5** was carried out with equimolar amounts of the respective alkyl bromides in CHCl₃ solution at room temperature to give imidazolium bromides **12** (Scheme 5). The latter were transformed into the corresponding tetrafluoroborates **13** in the usual way. It is worth mentioning that under the applied reaction conditions, the alkylation of compounds **5** and **6** occurred selectively at the imidazole fragment.



Scheme 5.

3. Conclusion

The results described herein show that *N*-benzyl L-prolinamine is a useful starting material for the preparation of a new type of optically active 2-unsubstituted imidazole N-oxides. Based on the known reactivity of these N-oxides, they can be converted into a variety of other optically active imidazole derivatives such as the parent imidazoles and imidazole-2-thiones. The debenzilation with simultaneous deoxygenation of imidazole N-oxides **5** leading to imidazoles of type **7** can be achieved conveniently by hydrogenolysis under standard conditions. Alkylation of the prepared imidazole N-oxides as well as the corresponding imidazoles leads to *N*-alkoxyimidazolium and *N*-alkylimidazolium salts, respectively,

with the properties of optically active 'room temperature ionic liquids' (RTILs).

The optically active products described herein are of interest as potential ligands for asymmetric synthesis and for organocatalysis. The readily available ionic liquids can be used as reaction media for small-scale organic synthesis.

4. Experimental

4.1. General

Melting points were determined in a capillary using a Melt-Temp. II apparatus (Aldrich) or STUART SMP30 and are uncorrected. The IR Spectra were recorded on a NEXUS FT-IR spectrophotometer in KBr; absorptions (ν) in cm⁻¹. The ¹H and ¹³C{¹H} NMR spectra were measured on a Bruker Avance III instrument (600 and 150 MHz, resp.) using solvent signal as reference. Multiplicity of signals in the ¹³C NMR spectra was established using the HMQC technique. Chemical shifts (δ) are given in ppm and coupling con-

stants *J* in Hz. Assignments of signals in ¹³C NMR spectra were made on the basis of HMQC experiments. HR-MS: Bruker maXis spectrometer; ESI-MS: Varian 500. Optical rotations were determined on a PERKIN-ELMER 241 MC polarimeter for λ = 589 nm.

4.2. Starting materials

All solvents and reagents are commercially available and used as received. (2*S*)-Benzylproline²⁴ and α -hydroxyimino ketones **4**^{20a} were prepared according to known procedures.

4.2.1. [(2*S*)-*N*-Benzylpyrrolidin-2-yl]methanol (*N*-benzylprolinol)

A solution of (2*S*)-benzylproline (3 g, 14.6 mmol) in THF (30 ml) was cooled to 0 °C and a suspension of LiAlH₄ in THF (2 M, 21.9 mmol, 12.4 ml) was added dropwise. The mixture was stirred overnight at rt. Next, an aqueous solution of KOH (10%, 15 ml) was added and the organic product was extracted with Et₂O (3 × 15 ml). The organic layers were combined and dried (Na₂SO₄). After filtration, the solvent was evaporated and the crude, oily product was distilled in a Kugel-Rohr (75–78 °C, 0.1 hPa). Yield: 2.0 g (71%). Colorless oil. IR (film): ν 3405br, 2961m, 2872m, 2799m, 1879w, 1810w, 1721w, 1496m, 1453m, 1211m, 1049w, 1029w, 849m, 839s, 699s. ¹H NMR (CDCl₃): δ 7.32–7.25 (m, 5H, HC(arom.)); 3.92, 3.32 (AB, *J*_{AB} = 12.9, 2H, H₂C–Ph); 3.61 (dd,

$^2J_{\text{H,H}} = 10.8$, $^3J_{\text{H,H}} = 3.6$, 1H, H₂C–OH); 3.38 (dd, $^2J_{\text{H,H}} = 10.8$, $^3J_{\text{H,H}} = 1.8$, 1H, H₂C–OH); 2.96–2.90 (m, 1H, H₂C(5)); 2.72–2.65 (m, 1H, HC(2)); 2.29–2.22 (m, 1H, H₂C(5)); 1.93–1.85 (m, 1H, H₂C(3)); 1.82–1.75 (m, 1H, H₂C(3)); 1.71–1.59 (m, 2H, H₂C(4)). ^{13}C NMR (CDCl₃): δ 139.4 (1 C(arom.)); 128.7, 128.3, 127.1 (5 CH(arom.)); 64.3 (C(2)); 61.8 (CH₂–OH); 58.6 (CH₂–Ph); 54.5 (C(5)); 27.8 (C(3)); 23.5 (C(4)). $[\alpha]_{\text{D}}^{25} = -58$ (c 1.0, CHCl₃); lit.²⁵ $[\alpha]_{\text{D}}^{25} = -59.9$ (c 1.0, CHCl₃).

4.2.2. 1-[(2S)-N-Benzylpyrrolidin-2-yl]methanamine **1**

To the solution of triphenylphosphine (0.86 g, 3.3 mmol) and phthalimide (0.48 g, 3.3 mmol) in THF (10 ml), *N*-benzylprolinol (0.57 g, 3.0 mmol) dissolved in THF (2 ml) was added, and the solution was stirred magnetically for 10 min. After this time, diethyl azodicarboxylate (DEAD) (0.62 g, 3.6 mmol) was added dropwise, and the mixture obtained was heated at reflux for 8 h. Next, the solvent was removed under reduced pressure, the obtained residue was suspended in Et₂O (50 ml) and stirred for 1 h. Then, the precipitate was separated by filtration and the filtrate was removed under reduced pressure. The residue was dissolved in EtOH (20 ml), after which hydrazine monohydrate (0.4 g, 8.0 mmol) was added, the mixture was heated at reflux for 2 h, and after the addition of HCl (1 M, 3 ml), heating was continued for 30 min. The precipitate was filtered off and the solvents were removed under reduced pressure. The residue obtained was treated with aqueous NaOH (1 M, 5 ml), the organic product was extracted with Et₂O (3 × 25 ml), and the combined organic layers were dried (Na₂SO₄). After filtration, the Et₂O solution was concentrated under reduced pressure to give **1** as a pale yellow oil. The crude product was distilled in a Kugel-Rohr (50–52 °C, 0.1 hPa). Yield: 0.4 g (70%). Colorless oil. IR (film): ν 3365m, 3289br, 3027m, 2961m, 2871m, 2791m, 1950m, 1877m, 1810m, 1495s, 1453s, 1372m, 1121m, 1072m, 1028s, 910m, 738s, 699s. ^1H NMR (CDCl₃): δ 7.38–7.19 (m, 5H, HC(arom.)); 3.96, 3.30 (AB, $J_{\text{AB}} = 12.9$, 2H, H₂C–Ph); 2.97–2.90 (m, 1H, H₂C(5)); 2.75 (dd, $^2J_{\text{H,H}} = 12.9$, $^3J_{\text{H,H}} = 5.4$, 1H, H₂C–NH₂); 2.70 (dd, $^2J_{\text{H,H}} = 12.9$, $^3J_{\text{H,H}} = 3.6$, 1H, H₂C–NH₂); 2.58–2.53 (m, 1H, HC(2)); 2.25–2.17 (m, 1H, H₂C(5)); 1.95–1.87 (m, 1H, H₂C(3)); 1.77–1.63 (m, 2H, H₂C(4)); 1H, H₂C(3)). ^{13}C NMR (CDCl₃): δ 139.9 (1 C(arom.)); 128.7, 128.7, 126.8 (5 CH(arom.)); 65.5 (C(2)); 59.1 (CH₂–Ph); 54.6 (C(5)); 44.1 (CH₂–NH₂); 28.0 (C(3)); 23.0 (C(4)) ppm. $[\alpha]_{\text{D}}^{25} = -54$ (c 1.0, CH₂Cl₂); lit.²⁶ $[\alpha]_{\text{D}}^{25} = -55$ (c 9.97, CHCl₃).

4.2.3. 1-[(2S)-N-Benzylpyrrolidin-2-yl]-*N*-methylidenemethanamine **2** (resp. the trimer **3**)

To a magnetically stirred solution of **1** (1.81 g, 9.53 mmol) in MeOH (10 ml), paraformaldehyde (0.30 g, 10 mmol) was added, and the mixture was stirred overnight at rt. The solvent was then removed under reduced pressure. The oil obtained was used in the next step without purification. Yield: 1.92 g (98%). Pale yellow oil. IR (film): ν 3361br, 3085m, 3061m, 3026m, 2960m, 2872m, 2788m, 1946m, 1875m, 1808m, 1604m, 1495s, 1453s, 1604m, 1155w, 1028m, 916m, 735s, 698s. ^1H NMR (CDCl₃): δ 7.35–7.16 (m, 5H, HC(arom.)); 4.16, 3.23 (AB, $J_{\text{AB}} = 13.2$, 2H, H₂C–Ph); 3.47–3.32 (br, 2H, N–CH₂–N); 2.93–2.87 (m, 1H, HC(5)); 2.68 (dd, $^2J_{\text{H,H}} = 12.9$, $^3J_{\text{H,H}} = 4.8$, 1H, H₂C–N); 2.57–2.52 (m, 1H, HC(2)); 2.42 (dd, $^2J_{\text{H,H}} = 12.9$, $^3J_{\text{H,H}} = 6.6$, 1H, H₂C–N); 2.15–2.09 (m, 1H, HC(5)); 1.98–1.88 (m, 1H, HC(3)); 1.75–1.60 (m, 2H, H₂C(4)); 1H, H₂C(3)). ^{13}C NMR (CDCl₃): δ 139.9 (C(arom.)); 128.9, 128.2, 126.7 (5, CH(arom.)); 75.8 (N–CH₂–N); 62.4 (C(2)); 59.6 (CH₂–Ph); 57.6 (CH₂–N); 54.2 (C(5)); 30.2 (C(3)); 22.6 (C(4)). ESI–MS: m/z 203 (100, $[\text{M}+1]^+$). $[\alpha]_{\text{D}}^{25} = -14$ (c 1.0, CH₂Cl₂).

4.2.4. Synthesis of imidazole N-oxides **5**

Procedure A: A solution of **2** (10 mmol) and the corresponding α -hydroxyimino ketone **4** (10 mmol) in EtOH (5 ml) was heated at reflux for 3 h. Next, the solvent was removed under reduced pres-

sure, and the resulting residue was purified by column chromatography or by crystallization.

Procedure B: A mixture of **2** (10 mmol) and the corresponding **4** (10 mmol) in glacial acetic acid (15 ml) was magnetically stirred overnight at rt. Next, HCl gas was bubbled through the mixture for 1 h, after which Et₂O (ca. 100 ml) was added and the colorless precipitated hydrochloride was filtered, washed with cold Et₂O (3 × 20 ml), and dried under reduced pressure. The crude hydrochloride was dissolved in CH₂Cl₂ (25 ml), after which solid NaHCO₃ (1.5 g) was added, and stirring was continued for 1 h until the evolution of CO₂ ceased. The inorganic salts were filtered off and the solvent was removed. The crude products **5a–e** were purified by column chromatography or by crystallization.

4.2.4.1. 1-[(2S)-N-Benzylpyrrolidin-2-yl]methyl-4,5-dimethyl-1H-imidazole 3-oxide 5a. Yield: 2.5 g (88%). Colorless oil (SiO₂, MeOH/AcOEt, 1:1). IR (film): ν 3584–3028br, 2954m, 2926m, 2807m, 1627m, 1495m, 1453s, 1381m, 1338m, 1148m, 1041s, 843w, 733w, 702s. ^1H NMR (CDCl₃): δ 7.94 (s, 1H, HC(2)); 7.35–7.21 (m, 5H, HC(arom.)); 3.75, 3.54 (AB, $J_{\text{AB}} = 12.6$, 2H, H₂C–Ph); 3.68 (dd, $^2J_{\text{H,H}} = 14.4$, $^3J_{\text{H,H}} = 4.8$, 1H, H₂C–N); 3.60 (dd, $^2J_{\text{H,H}} = 14.4$, $^3J_{\text{H,H}} = 6.0$, 1H, H₂C–N); 3.04–2.99 (m, 1H, H₂C(5')); 2.92–2.86 (m, 1H, HC(2')); 2.39–2.32 (m, 1H, H₂C(5')); 2.15 (s, 3H, H₃C–C(4)); 2.05 (s, 3H, H₃C–C(5)); 1.93–1.85 (m, 1H, H₂C(3')); 1.75–1.69 (m, 1H, H₂C(4')); 1.68–1.59 (m, 1H, H₂C(4')); 1.49–1.43 (m, 1H, H₂C(3')). ^{13}C NMR (CDCl₃): δ 138.9 (C(arom.)); 128.8, 128.5, 127.3 (5 CH(arom.)); 126.3 (1 C(imid.)); 124.9 (HC(2)); 121.0 (1 C(imid.)); 63.2 (HC(2')); 60.1 (CH₂–Ph); 54.8 (C(5')); 49.1 (CH₂–N); 28.5 (C(3')); 23.3 (C(4')); 8.9 (CH₃–C(4)); 7.3 (CH₃–C(5)). HR-ESI-MS (MeOH + HCOOH): 286.1909 (calcd 286.1914 for C₁₇H₂₄N₃O, $[\text{M}+1]^+$). $[\alpha]_{\text{D}}^{25} = -18$ (c 1.0, CH₂Cl₂).

4.2.4.2. 1-[(2S)-N-Benzylpyrrolidin-2-yl]methyl-4-methyl-5-phenyl-1H-imidazole 3-oxide 5b. Yield: 1.3 g, 40% (method A), 2.7 g, 80% (method B). Colorless oil (SiO₂, MeOH/AcOEt, 1:1). IR (film): ν 3647–3028br, 2962m, 2876m, 2803m, 1683s, 1551m, 1496s, 1452m, 1381m, 1028m, 922w, 847w, 764m, 734m, 702m, 642s. ^1H NMR (CDCl₃): δ 8.29 (s, 1H, HC(2)); 7.49–7.45 (m, 3H, HC(arom.)); 7.32–7.29 (m, 2H, HC(arom.)); 7.26–7.24 (m, 3H, HC(arom.)); 7.23–7.20 (m, 2H, HC(arom.)); 3.77 (dd, $J_{\text{H,H}} = 14.4$, $J_{\text{H,H}} = 4.8$, 1H, H₂C–N); 3.64–3.58 (m, 1H, H₂C–Ph, 1H, H₂C–N); 3.38 (AB, $J_{\text{AB}} = 12.9$, 2H, H₂C–Ph); 2.96–2.91 (m, 1H, H₂C(5')); 2.71–2.68 (m, 1H, H₂C(2')); 2.28–2.22 (m, 1H, H₂C(5')); 2.19 (s, 3H, H₃C–C(4)); 1.75–1.73 (m, 1H, H₂C(3')); 1.63–1.60 (m, 1H, H₂C(4')); 1.53–1.48 (m, 1H, H₂C(4')); 1.33–1.29 (m, 1H, H₂C(3')). ^{13}C NMR (CDCl₃): δ 138.3 (1 C(arom.)); 130.7, 129.8, 129.4, 129.1, 129.1, 128.6, 127.5, 127.2 (9 signals for 10 CH(arom.), 2 C(arom.), 1 HC(2), 2 C(imid.)); 63.4 (HC(2')); 59.7 (CH₂–Ph); 54.5 (C(5')); 49.5 (CH₂–N); 28.5 (C(3')); 23.3 (C(4')); 7.9 (H₃C–C(4)). HR-ESI-MS (MeOH + HCOOH): 348.2068 (calcd 348.2070 for C₂₂H₂₆N₃O, $[\text{M}+1]^+$). $[\alpha]_{\text{D}}^{25} = -24$ (c 1.0, CH₂Cl₂).

4.2.4.3. 1-[(2S)-N-Benzylpyrrolidin-2-yl]methyl-4,5-diphenyl-1H-imidazole 3-oxide 5c. Yield: 2.6 g, 65% (method A), 3.1 g, 75% (method B). Colorless crystals. Mp 160–161 °C (CHCl₃/Et₂O). IR (KBr): ν 3646–3027br, 2961m, 2876w, 2810m, 1736m, 1604m, 1495m, 1445m, 1346m, 1193m, 1076m, 1039s, 918m, 864s, 762s, 700s, 656 m. ^1H NMR (CDCl₃): δ 8.35 (s, 1H, HC(2)); 7.55–7.52 (m, 2H, HC(arom.)); 7.43–7.36 (m, 3H, HC(arom.)); 7.32–7.28 (m, 2H, HC(arom.)); 7.27–7.19 (m, 8H, HC(arom.)); 3.75 (dd, $^2J_{\text{H,H}} = 14.0$, $^3J_{\text{H,H}} = 4.2$, 1H, H₂C–N); 3.62 (dd, $^2J_{\text{H,H}} = 14.0$, $^3J_{\text{H,H}} = 6.0$, 1H, H₂C–N); 3.63, 3.39 (AB, $J_{\text{AB}} = 13.2$, 2H, H₂C–Ph); 2.98–2.93 (m, 1H, H₂C(5')); 2.79–2.72 (m, 1H, HC(2')); 2.31–2.24 (m, 1H, H₂C(5')); 1.84–1.76 (m, 1H, H₂C(3')); 1.69–1.62 (m, 1H, H₂C(4')); 1.60–1.51 (m, 1H, H₂C(4')); 1.43–1.37 (m, 1H, H₂C(3')). ^{13}C NMR (CDCl₃): δ 138.7 (1 C(arom.)); 131.0, 130.2, 129.6, 129.5,

129.1, 128.8, 128.5, 128.1, 128.0, 127.7, 127.3, 127.3, 126.7 (2 C(arom.), 15 HC(arom.), 2 C(imid.)); 126.9 (HC(2)); 63.1 (HC(2')); 59.6 (CH₂-Ph); 54.4 (C(5')); 49.1 (CH₂-N); 28.4 (C(4')); 23.2 (C(3')). HR-ESI-MS (MeOH + HCOOH): 410.2228 (calcd 410.2227 for C₂₇H₂₈N₃O, [M+1]⁺). [α]_D²⁵ = −5 (c 1.0, CH₂Cl₂).

4.2.4.4. N-Phenyl-1-[(2S)-N-benzylpyrrolidin-2-yl]methyl]-5-methyl-1H-imidazole-4-carboxamide 3-oxide 5d. Yield: 3.0 g (78%). Colorless crystals. Mp 120–122 °C (Et₂O). IR (KBr): ν 3427br, 3171m, 3062m, 2978w, 2921w, 2798m, 1672s, 1619m, 1598m, 1560s, 1310s, 1273s, 759m, 750m, 701m, 630 m. ¹H NMR (CDCl₃): δ 12.98 (s, 1H, NH); 7.95 (s, 1H, HC(2)); 7.74–7.69 (m, 2H, HC(arom.)); 7.36–7.31 (m, 4H, HC(arom.)); 7.34–7.24 (m, 4H, HC(arom.)); 3.76, 3.63 (AB, J_{AB} = 13.6, 2H, H₂C-Ph); 3.76 (dd, ²J_{H,H} = 14.4, ³J_{H,H} = 4.8, 1H, H₂C-N); 3.66 (dd, ²J_{H,H} = 14.4, ³J_{H,H} = 5.40 Hz, 1H, H₂C-N); 3.10–3.04 (m, 1H, H₂C(5)); 3.02–2.96 (m, 1H, H₂C(2)); 2.58 (s, 3H, H₃C-C(5)); 2.47–2.40 (m, 1H, H₂C(5')); 2.00–1.91 (m, 1H, H₂C(3')); 1.80–1.73 (m, 1H, H₂C(4')); 1.65–1.56 (m, 1H, H₂C(4')); 1.48–1.41 (m, 1H, H₂C(3')). ¹³C NMR (CDCl₃): δ 157.9 (C=O); 138.7, 138.4 (2 C(arom.)); 131.5, 129.1, 129.0, 128.8, 127.7, 124.2, 121.7, 120.1 (10 CH(arom.), 2 C(imid.)); 126.0 (HC(2)); 62.8 (HC(2')); 60.3 (CH₂-Ph); 55.0 (C(5')); 48.7 (CH₂-N); 28.4 (C(3')); 23.7 (C(4')); 10.0 (H₃C-C(5)). HR-ESI-MS (MeOH + HCOOH): 391.2124 (calcd 391.2129 for C₂₃H₂₇N₄O₂, [M+1]⁺). [α]_D²⁵ = −27 (c 1.0, CH₂Cl₂).

4.2.4.5. N-(4-Bromophenyl)-1-[(2S)-N-benzylpyrrolidin-2-yl]methyl]-5-methyl-1H-imidazole-4-carboxamide 3-oxide 5e. Yield: 3.8 g (81%). Colorless crystals. Mp 168–170 °C (Acetone). IR (KBr): ν 3432br, 3077m, 2975w, 2939w, 2919w, 2802m, 1675s, 1612s, 1556s, 1488s, 1309m, 1069m, 817m, 757m, 702s, 636m, 503m. ¹H NMR (CDCl₃): δ 13.00 (s, 1H, NH); 7.91 (s, 1H, HC(2)); 7.63–7.59 (m, 2H, HC(arom.)); 7.45–7.41 (m, 2H, HC(arom.)); 7.35–7.31 (m, 2H, HC(arom.)); 7.29–7.25 (m, 3H, HC(arom.)); 3.65, 3.54 (AB, J_{AB} = 12.6, 2H, H₂C-Ph); 3.67 (dd, ²J_{H,H} = 14.4, ³J_{H,H} = 4.8, 1H, H₂C-N); 3.57 (dd, ²J_{H,H} = 14.4, ³J_{H,H} = 5.4, 1H, H₂C-N); 3.09–3.03 (m, 1H, H₂C(5')); 3.02–2.95 (m, 1H, H₂C(2')); 2.55 (s, 3H, H₃C-C(5)); 2.47–2.40 (m, 1H, H₂C(5')); 2.00–1.91 (m, 1H, H₂C(3')); 1.80–1.72 (m, 1H, H₂C(4')); 1.64–1.54 (m, 1H, H₂C(4')); 1.49–1.39 (m, 1H, H₂C(3')). ¹³C NMR (CDCl₃): δ 157.9 (C=O); 138.7, 137.5 (2 C(arom.)); 132.0, 131.7, 129.0, 128.8, 127.8, 122.2, 121.5, 116.7 (1 C(arom.), 9 CH(arom.), 2 C(imid.)); 126.1 (HC(2)); 62.8 (HC(2')); 60.3 (CH₂-Ph); 55.1 (C(5')); 48.8 (CH₂-N); 28.4 (C(3')); 23.7 (C(4')); 10.0 (H₃C-C(5)). HR-ESI-MS (MeOH + HCOOH): 469.1230 (calcd 469.1234 for C₂₃H₂₆BrN₄O₂, [M(⁷⁹Br)+1]⁺). [α]_D²⁵ = −22 (c 1.0, CH₂Cl₂).

4.2.5. Synthesis of imidazoles 6

To a magnetically stirred solution of imidazole N-oxide 5 (5 mmol) in EtOH (15 ml), a suspension of freshly prepared Raney-Nickel in EtOH was added in small portions at rt. The progress of the reaction was followed by TLC (SiO₂, MeOH/AcOEt 1:1). Next, the mixture was filtered and the filtrate was concentrated under reduced pressure. The crude products **6a–e** were purified by chromatography or by crystallization.

4.2.5.1. 1-[(2S)-N-Benzylpyrrolidin-2-yl]methyl]-4,5-dimethyl-1H-imidazole 6a. Yield: 1.0 g (75%). Pale yellow oil (SiO₂, MeOH/AcOEt, 1:1). IR (film): ν 3428br, 2926m, 2854w, 2360w, 2342w, 1637w, 1560m, 1416m, 1245m, 1216m, 1045w, 1021w, 801m, 748m, 700m. ¹H NMR (CDCl₃): δ 7.40 (s, 1H, HC(2)); 7.33–7.29 (m, 4H, HC(arom.)); 7.26–7.21 (m, 1H, HC(arom.)); 3.76 (dd, ²J_{H,H} = 14.4, ³J_{H,H} = 4.8, 1H, H₂C-N); 3.76, 3.44 (AB, J_{AB} = 13.2, 2H, H₂C-Ph); 3.66 (dd, ²J_{H,H} = 14.4, ³J_{H,H} = 7.2, 1H, H₂C-N); 3.31–2.96 (m, 1H, H₂C(5')); 2.87–2.82 (m, 1H, H₂C(2')); 2.33–2.27 (m, 1H, H₂C(5')); 2.13 (s, 3H, H₃C-C(4)); 2.06 (s, 3H, H₃C-C(5)); 1.89–

1.81 (m, 1H, H₂C(3')); 1.73–1.65 (m, 2H, H₂C(4')); 1.57–1.49 (m, 1H, H₂C(3')). ¹³C NMR (CDCl₃): δ 139.2 (1 C(arom.)); 132.0 (HC(2)); 129.8, 129.0, 126.7, 121.1, 120.2 (5 CH(arom.)); 2 C(imid.)); 63.5 (HC(2')); 59.1 (CH₂-Ph); 54.7 (C(5')); 49.6 (CH₂-N); 29.0 (C(3')); 23.3 (C(4')); 8.8 (H₃C-C(4)); 7.2 (H₃C-C(5)) ppm. HR-ESI-MS (MeOH + HCOOH): 270.1961 (calcd 270.1965 for C₁₇H₂₄N₃, [M+1]⁺). [α]_D²⁵ = −25 (c 1.0, CH₂Cl₂).

4.2.5.2. 1-[(2S)-N-Benzylpyrrolidin-2-yl]methyl]-4-methyl-5-phenyl-1H-imidazole 6b. Yield: 1.2 g (70%). Pale yellow oil (SiO₂, MeOH/AcOEt, 1:1). IR (film): ν 3583–3369br, 3059m, 3029m, 2948m, 2873m, 2796m, 1955m, 1888m, 1815m, 1688m, 1605w, 1493s, 1452m, 1207m, 1124m, 1029m, 966m, 701m. ¹H NMR (CDCl₃): δ 7.58 (s, 1H, HC(2)); 7.46–7.41 (m, 2H, HC(arom.)); 7.39–7.35 (m, 1H, HC(arom.)); 7.30–7.26 (m, 4H, HC(arom.)); 7.24–7.20 (m, 1H, HC(arom.)); 7.19–7.17 (m, 2H, HC(arom.)); 3.92 (dd, ²J_{H,H} = 14.4, ³J_{H,H} = 4.8, 1H, H₂C-N); 3.76 (dd, ²J_{H,H} = 14.4, ³J_{H,H} = 7.2, 1H, H₂C-N); 3.55, 3.19 (AB, J_{AB} = 13.2, 2H, H₂C-Ph); 2.89–2.85 (m, 1H, H₂C(5')); 2.63–2.57 (m, 1H, HC(2')); 2.18 (s, 3H, H₃C-C(4)); 2.18–2.13 (m, 1H, H₂C(5')); 1.73–1.65 (m, 1H, H₂C(3')); 1.62–1.50 (m, 2H, H₂C(4')); 1.40–1.34 (m, 1H, H₂C(3')). ¹³C NMR (CDCl₃): δ 139.4, 135.6 (2 C(arom.)); 136.9 (HC(2)); 130.9, 130.5, 129.0, 128.9, 128.5, 128.1, 127.2 (7 signals for 10 HC(arom.) + 2 C(imid.)); 63.7 (C(2')); 59.5 (CH₂-Ph); 54.6 (C(5')); 49.8 (CH₂-N); 29.1 (C(3')); 23.1 (C(4')); 13.4 (H₃C-C(4)). HR-ESI-MS (MeOH + HCOOH): 332.2121 (calcd 332.2121 for C₂₂H₂₆N₃, [M+1]⁺). [α]_D²⁵ = −25 (c 1.0, CH₂Cl₂).

4.2.5.3. 4,5-Diphenyl-1-[(2S)-N-benzylpyrrolidin-2-yl]methyl]-1H-imidazole 6c. Yield: 1.3 g (68%). Colorless crystals. Mp 118–119 °C (CH₂Cl₂/hexane). IR (KBr): ν 3432br, 3085m, 2971m, 2927m, 2905m, 2786m, 2723w, 1603m, 1505m, 1452m, 1369m, 1256m, 774m, 698s, 653m. ¹H NMR (CDCl₃): δ 7.76 (s, 1H, HC(2)); 7.54–7.45 (m, 5H, HC(arom.)); 7.39–7.36 (m, 2H, HC(arom.)); 7.33–7.28 (m, 2H, HC(arom.)); 7.27–7.21 (m, 5H, HC(arom.)); 7.17–7.14 (m, 1H, HC(arom.)); 3.88 (dd, ²J_{H,H} = 14.4, ³J_{H,H} = 5.4, 1H, H₂C-N); 3.74 (dd, ²J_{H,H} = 14.4, ³J_{H,H} = 7.2, 1H, H₂C-N); 3.58, 3.25 (AB, J_{AB} = 12.6, 2H, H₂C-Ph); 2.96–2.91 (m, 1H, H₂C(5')); 2.72–2.66 (m, 1H, HC(2')); 2.26–2.19 (m, 1H, H₂C(5')); 1.83–1.76 (m, 1H, H₂C(4')); 1.70–1.58 (m, 2H, H₂C(3')); 1.52–1.45 (m, 1H, H₂C(4')). ¹³C NMR (CDCl₃): δ 139.2, 138.2, 134.9 (3 C(arom.)); 137.7 (HC(2)); 131.4, 131.3, 129.3, 129.0, 128.9, 128.7, 128.5, 128.3, 127.2, 126.8, 126.4 (15 CH(arom.), 2 C(imid.)); 63.7 (HC(2')); 59.6 (CH₂-Ph); 54.6 (H₂C(5')); 49.4 (CH₂-N); 29.1 (C(4')); 23.2 (C(3')). HR-ESI-MS (MeOH + HCOOH): 394.2278 (calcd 394.2278 for C₂₇H₂₈N₃, [M+1]⁺). [α]_D²⁵ = −31 (c 1.0, CH₂Cl₂).

4.2.5.4. N-Phenyl-1-[(2S)-N-benzylpyrrolidin-2-yl]methyl]-5-methyl-1H-imidazole-4-carboxamide 6d. Yield: 1.3 g (72%). Colorless crystals. Mp 82–84 °C (Et₂O). IR (KBr): ν 3432br, 3270m, 3243m, 3121m, 3033m, 2969m, 2946m, 2779m, 1943w, 1968w, 1752w, 1660s, 1596s, 1537m, 1503s, 1440s, 1246s, 878m, 759s, 697s. ¹H NMR (CDCl₃): δ 9.03 (s, 1H, NH); 7.70–7.67 (m, 2H, HC(arom.)); 7.48 (s, 1H, HC(2)); 7.35–7.28 (m, 6H, HC(arom.)); 7.27–7.24 (m, 1H, HC(arom.)); 7.09–7.07 (m, 1H, HC(arom.)); 3.81 (dd, ²J_{H,H} = 14.4, ³J_{H,H} = 4.8, 1H, H₂C-N); 3.76 (dd, ²J_{H,H} = 14.4, ³J_{H,H} = 6.0, 1H, H₂C-N); 3.75, 3.49 (AB, J_{AB} = 13.2, 2H, H₂C-Ph); 3.04–2.98 (m, 1H, H₂C(5')); 2.96–2.90 (m, 1H, HC(2')); 2.57 (s, 3H, H₃C-C(5)); 2.39–2.31 (m, 1H, H₂C(5')); 1.93–1.85 (m, 1H, H₂C(3')); 1.75–1.69 (m, 1H, H₂C(4')); 1.67–1.58 (m, 1H, H₂C(4')); 1.54–1.46 (m, 1H, H₂C(3')). ¹³C NMR (CDCl₃): δ 162.1 (C=O); 139.3, 138.7 (2 C(arom.)); 136.1 (HC(2)); 133.2, 131.5, 129.1, 128.9, 128.7, 127.5, 123.7, 119.7 (10 HC(arom.), 2 C(imid.)); 63.4 (HC(2')); 60.2 (CH₂-Ph); 55.0 (H₂C(5')); 49.0 (CH₂-N); 29.0 (C(3')); 23.4 (C(4')); 9.9 (H₃C-C(5)). HR-ESI-MS (MeOH + HCOOH):

375.2178 (calcd 375.2179 for $C_{23}H_{27}N_4O$, $[M+1]^+$). $[\alpha]_D^{25} = -11$ (c 1.0, CH_2Cl_2).

4.2.5.5. N-(4-Bromophenyl)-1-[(2S)-N-benzylpyrrolidin-2-yl]-methyl-5-methyl-1H-imidazole-4-carboxamide 6e. Yield: 2.3 g (63%). Colorless oil (SiO_2 , MeOH/AcOEt, 1:3). IR (film): ν 3362br, 3180s, 3061m, 3028m, 2970m, 2872m, 2799m, 1951m, 1888m, 1671m, 1588m, 1506m, 1397m, 1241m, 1116m, 1060m, 1007s, 829s, 700m, 659m. 1H NMR ($CDCl_3$): δ 9.03 (s, 1H, NH); 7.69–7.57 (m, 2H, HC(arom.)); 7.48 (s, 1H, HC(2)); 7.44–7.41 (m, 1H, HC(arom.)); 7.34–7.24 (m, 6H, HC(arom.)); 3.80–3.74 (m, 2H, H_2C-N); 3.73, 3.50 (AB, $J_{AB} = 13.2$, 2H, H_2C-Ph); 3.04–2.98 (m, 1H, $H_2C(5')$); 2.96–2.91 (m, 1H, HC(2')); 2.55 (s, 3H, $H_3C-C(5)$); 2.38–2.31 (m, 1H, $H_2C(5')$); 1.94–1.86 (m, 1H, $H_2C(4')$); 1.76–1.69 (m, 1H, $H_2C(3')$); 1.66–1.58 (m, 1H, $H_2C(3')$); 1.53–1.46 (m, 1H, $H_2C(4')$). ^{13}C NMR ($CDCl_3$): δ 162.0 (C=O); 139.3, 137.8 (2 C(arom.)); 136.3 (HC(2)); 132.1, 129.1, 129.0, 128.7, 127.5, 121.2, 119.7, 116.1 (1 C(arom.)), 9 CH(arom.), 2 C(imid.); 63.4 (HC(2')); 60.2 (CH_2-Ph); 55.0 ($H_2C(5')$); 49.0 (CH_2-N); 29.0 (C(3')); 23.4 (C(4')); 9.9 ($H_3C-C(5)$). HR-ESI-MS (MeOH + HCOOH): 453.1279 (calcd 453.1285 for $C_{23}H_{26}BrN_4O$, $[M(^{79}Br)+1]^+$). $[\alpha]_D^{25} = -10$ (c 1.0, CH_2Cl_2).

4.2.6. General procedure for synthesis of imidazoles 7a and 7b

To a magnetically stirred solution of an imidazole N-oxide 5 (1 mmol) in MeOH (4 ml), 10% Pd/C (0.05 g) was added and the mixture stirred under H_2 atm until the reaction was complete (monitored by TLC). Then, the solid was filtered through Celite and the solvent was evaporated under reduced pressure. The product obtained was purified by column chromatography or by crystallization.

4.2.6.1. 4,5-Diphenyl-1-[(2S)-pyrrolidin-2-yl]methyl-1H-imidazole 7a. Yield: 0.277 mg (87%). Colorless crystals. Mp 123–125 °C (CH_2Cl_2 /hexane). IR (KBr): ν 3357br, 3049m, 2989m, 2834m, 2223w, 1509m, 1439m, 1357m, 1220m, 1033m, 907m, 895m, 802m, 731m. 1H NMR ($CDCl_3$): δ 7.74 (s, 1H, NH); 7.48–7.43 (m, 5H, HC(arom.)); 7.35–7.32 (m, 2H, HC(arom.)); 7.21–7.16 (m, 2H, HC(arom.)); 7.16–7.10 (m, 1H, HC(arom.)); 3.77 (dd, $^2J_{H,H} = 12.0$, $^3J_{H,H} = 6.0$, 1H, H_2C-N); 3.74 (dd, $^2J_{H,H} = 12.0$, $^3J_{H,H} = 3.6$, 1H, H_2C-N); 3.24–3.17 (m, 1H, HC(2')); 2.92–2.84 (m, 2H, $H_2C(5')$); 1.78–1.61 (m, 1H, $H_2C(3')$), 2H, $H_2C(4')$); 1.32–1.24 (m, 1H, $H_2C(3')$). ^{13}C NMR ($CDCl_3$): δ 138.4, 137.4, 134.9, 131.3, 131.2, 129.3, 128.9, 128.6, 128.3, 126.8, 126.4 (10 HC(arom.), 2 C(arom.), 3 C(imid.)); 58.6 (HC(2')); 50.5 (CH_2-N); 46.4 ($H_2C(5')$); 29.4 (C(4')); 25.3 (C(3')). HR-ESI-MS (MeOH + HCOOH): 302.1687 (calcd 302.1685 for $C_{17}H_{24}N_3S$, $[M+1]^+$). $[\alpha]_D^{25} = -18$ (c 1.0, CH_2Cl_2).

4.2.6.2. 5-Methyl-N-phenyl-1-[(2S)-pyrrolidin-2-yl]methyl-1H-imidazole-4-carboxamide 7b. Yield: 0.235 mg (83%). Colorless oil (SiO_2 , MeOH/AcOEt, 6:4). IR (film): ν 3366br, 3058m, 2961m, 2873m, 2246w, 1663m, 1597m, 1575m, 1442m, 1330m, 1243m, 1064m, 906m, 877m, 829m, 756m. 1H NMR ($CDCl_3$): δ 9.05 (s, 1H, NH); 7.68–7.64 (m, 2H, HC(arom.)); 7.47 (s, 1H, HC(2)); 7.33–7.28 (m, 2H, HC(arom.)); 7.08–7.03 (m, 1H, HC(arom.)); 3.86 (dd, $^2J_{H,H} = 14.1$, $^3J_{H,H} = 5.4$, 1H, H_2C-N); 3.78 (dd, $^2J_{H,H} = 14.1$, $^3J_{H,H} = 7.8$, 1H, H_2C-N); 3.41–3.35 (m, 1H, HC(2')); 2.94–2.89 (m, 2H, $H_2C(5')$); 2.60 (s, 3H, H_3C-N); 1.93–1.86 (m, 1H, $H_2C(3')$); 1.84–1.68 (m, 2H, $H_2C(4')$); 1.44–1.37 (m, 1H, $H_2C(3')$). ^{13}C NMR ($CDCl_3$): δ 162.1 (C=O); 138.6 (1 C(arom.)); 135.9, 133.1, 131.5, 129.0, 123.7, 119.7 (5 HC(arom.), 3 C(imid.)); 58.2 (CH_2-N); 50.1 (HC(2')); 46.5 ($H_2C(5')$); 29.4 (C(3')); 25.4 (C(4')); 9.8 (CH_3-N). HR-ESI-MS (MeOH + HCOOH): 302.1687 (calcd 302.1685 for $C_{17}H_{24}N_3S$, $[M+1]^+$). $[\alpha]_D^{25} = -24$ (c 1.0, CH_2Cl_2).

4.2.7. Synthesis of imidazole-2-thiones 9

To a magnetically stirred solution of an imidazole N-oxide 5 (4 mmol) in $CHCl_3$ (4 ml), 2,2,4,4-tetramethylcyclobutane-1,3-

dithione **8** (2 mmol) in $CHCl_3$ (2 ml) was added dropwise at 0 °C, and stirring was continued overnight at rt. Next, the solvent was evaporated under reduced pressure and the residue was washed with hexane. The resulting material was purified by crystallization.

4.2.7.1. 1-[(2S)-N-Benzylpyrrolidin-2-yl]methyl-4,5-dimethyl-1,3-dihydro-2H-imidazole-2-thione 9a. Yield: 0.8 g (68%). Colorless crystals. Mp 108–110 °C (CH_2Cl_2 /hexane). IR (KBr): ν 3432br, 3085m, 2943m, 2792m, 2522w, 1659s, 1499s, 1452m, 1393m, 1306m, 1127m, 1029m, 782m, 739s, 697s, 472s. 1H NMR ($CDCl_3$): δ 11.45 (s, 1H, NH); 7.27–7.23 (m, 4H, HC(arom.)); 7.21–7.17 (m, 1H, HC(arom.)); 4.02 (dd, $^2J_{H,H} = 13.3$, $^3J_{H,H} = 7.8$, 1H, H_2C-N); 3.78 (dd, $^2J_{H,H} = 13.3$, $^3J_{H,H} = 6.0$, 1H, H_2C-N); 3.87, 3.45 (AB, $J_{AB} = 13.2$, 2H, H_2C-Ph); 3.41–3.34 (m, 1H, HC(2')); 2.99–2.94 (m, 1H, $H_2C(5')$); 2.28 (m, 1H, $H_2C(5')$); 2.03 (s, 3H, $H_3C-C(4)$); 2.01 (s, 3H, $H_3C-C(5)$); 1.88–1.63 (m, 2H, $H_2C(4')$), 2H, $H_2C(3')$). ^{13}C NMR ($CDCl_3$): δ 158.5 (C=S); 139.2 (1 C(arom.)); 129.0, 128.3, 127.0, 122.2, 119.9 (5 HC(arom.), 1 C(arom.), 2 C(imid.)); 61.9 (HC(2')); 60.5 (CH_2-Ph); 54.8 ($H_2C(5')$); 49.4 (CH_2-N); 29.2 (C(4')); 23.6 (C(3')); 9.3 ($H_3C-C(5)$); 9.2 ($H_3C-C(4)$). HR-ESI-MS (MeOH + HCOOH): 302.1687 (calcd 302.1685 for $C_{17}H_{24}N_3S$, $[M+1]^+$). $[\alpha]_D^{25} = -19$ (c 1.0, CH_2Cl_2).

4.2.7.2. 1-[(2S)-N-Benzylpyrrolidin-2-yl]methyl-4,5-diphenyl-1,3-dihydro-2H-imidazole-2-thione 9b. Yield: 0.5 g (31%). Colorless crystals. Mp 197–199 °C (EtOH). IR (KBr): ν 3432br, 3058m, 2937m, 2807m, 1602m, 1492s, 1397s, 1202m, 1160m, 1119m, 1073m, 1027m, 700s, 682m, 556s. 1H NMR ($CDCl_3$): δ 11.30 (s, 1H, NH); 7.46–7.40 (m, 3H, HC(arom.)); 7.36–7.33 (m, 2H, HC(arom.)); 7.25–7.16 (m, 10H, HC(arom.)); 4.12 (dd, $^2J_{H,H} = 12.9$, $^3J_{H,H} = 9.0$, 1H, H_2C-N); 3.94 (dd, $^2J_{H,H} = 12.9$, $^3J_{H,H} = 4.2$, 1H, H_2C-N); 3.76, 3.22 (AB, $J_{AB} = 12.9$, 2H, H_2C-Ph); 3.21–3.25 (m, 1H, HC(2')); 2.81–2.76 (m, 1H, $H_2C(5')$); 2.20–2.15 (m, 1H, $H_2C(5')$); 1.73–1.66 (m, 1H, $H_2C(4')$). ^{13}C NMR ($CDCl_3$): δ 161.4 (C=S); 140.1 (1 C(arom.)); 131.7, 129.6, 129.3, 129.1, 129.0, 128.9, 128.3, 128.1, 127.9, 126.9, 126.8, 125.5 (12 signals for 15 HC(arom.), 3 C(arom.), 2 C(imid.)); 61.7 (HC(2')); 59.9 (CH_2-Ph); 54.3 (C(5')); 49.3 (CH_2-N); 29.1 (C(3')); 23.5 (C(4')). HR-ESI-MS (MeOH + HCOOH): 426.1998 (calcd 426.1999 for $C_{27}H_{28}N_3S$, $[M+1]^+$). $[\alpha]_D^{25} = -14$ (c 1.0, CH_2Cl_2).

4.2.7.3. N-(4-Bromophenyl)-1-[(2S)-N-benzylpyrrolidin-2-yl]methyl-5-methyl-2-thioxo-2,3-dihydro-1H-imidazole-4-carboxamide 9c. Yield: 0.8 g (41%). Colorless crystals. Mp 215 °C (EtOH) (decomposition). IR (KBr): ν 3432br, 3275m, 3125m, 3065m, 2952m, 2902w, 2787m, 1663s, 1625s, 1542s, 1489s, 1380m, 828m, 811m, 698m, 504m. 1H NMR ($CDCl_3$): δ 8.85 (s, 1H, HN); 7.73–7.66 (m, 2H, HC(arom.)); 7.45–7.41 (m, 2H, HC(arom.)); 7.24–7.20 (m, 4H, HC(arom.)); 7.15–7.10 (m, 1H, HC(arom.)); 4.11 (dd, $J_{H,H} = 13.3$, $J_{H,H} = 5.8$, 1H, H_2C-N); 3.85 (dd, $J_{H,H} = 13.3$, $J_{H,H} = 6.0$, 1H, H_2C-N); 3.74, 3.19 (AB, $J_{AB} = 12.9$, 2H, H_2C-Ph); 3.42–3.33 (m, 1H, $H_2C(5')$); 3.08–3.02 (m, 1H, HC(2')); 2.57 (s, 3H, $H_3C-C(5)$); 2.46–2.35 (m, 1H, $H_2C(5')$); 1.92–1.85 (m, 1H, $H_2C(4')$); 1.83–1.68 (m, 2H, $H_2C(3')$), 1H $H_2C(4')$). ^{13}C NMR ($CDCl_3$): δ 162.1 (C=S); 161.6 (C=O); 138.7, 138.0 (2 C(arom.)); 136.6 (HC(2)); 132.7, 129.6, 129.1, 128.9, 121.7, 119.7, 116.1 (9 HC(arom.), 1 C(arom.), 2 C(imid.)); 63.8 (C(2')); 60.9 (CH_2-Ph); 55.3 (C(5')); 49.2 (CH_2-N); 29.7 (C(3')); 23.1 (C(4')); 10.0 ($H_3C-C(5)$). HR-ESI-MS (MeOH + HCOOH): 485.1002 (calcd 485.1005 for $C_{23}H_{26}BrN_4OS$, $[M+1]^+$). $[\alpha]_D^{25} = -10$ (c 1.0, CH_2Cl_2).

4.2.8. Synthesis of 3-alkylimidazolium tetrafluoroborates 11

A solution of imidazole **6** (5 mmol) and alkyl bromide (5 mmol) in acetonitrile (5 ml) was heated at reflux for 16 h. The solvent was removed under reduced pressure, and the resulting product was washed with Et_2O (3 × 5 ml), and dried under high vacuum for

4 h. The imidazolium bromide obtained was stirred magnetically with an equimolar amount of solid NaBF₄ in acetone (5 ml) overnight at rt. The resulting suspension was filtered through neutral alumina (CHCl₃) and the solvent evaporated under reduced pressure.

4.2.8.1. 1-[(2S)-N-Benzylpyrrolidin-2-yl]methyl-3-hexyl-4,5-dimethyl-1H-imidazolium tetrafluoroborate 11a. Yield: 1.6 g (75%). Pale yellow oil (Al₂O₃, CHCl₃). IR (film): ν 3648w, 3628w, 3566m, 3154m, 3087m, 2956m, 2931m, 2805m, 1818m, 1564m, 1455m, 1058br, 742m, 703m, 626m. ¹H NMR (CDCl₃): δ 8.72 (HC(2)); 7.29–7.26 (m, 2H, HC(arom.)); 7.23–7.19 (m, 3H, HC(arom.)); 4.01–3.95 (m, 1H, H₂C–N, 2H, H₂C(alk.)); 3.89 (dd, ²J_{H,H} = 13.8, ³J_{H,H} = 6.6, 1H, H₂C–N); 3.59, 3.56 (AB, J_{AB} = 13.2, 2H, H₂C–Ph); 3.16–3.11 (m, 1H, HC(2')); 3.10–3.06 (m, 1H, H₂C(5')); 2.50–2.45 (m, 1H, H₂C(5')); 2.16 (s, 3H, H₃C–C(4)); 2.12 (s, 3H, H₃C–C(5)); 2.05–1.98 (m, 1H, H₂C(3')); 1.83–1.77 (m, 1H, H₂C(4')); 1.74–1.67 (m, 1H, H₂C(4')); 2H, H₂C(alk.); 1.55–1.50 (m, 1H, H₂C(3')); 1.32–1.24 (m, 6H, H₂C(alk.)); 0.85 (t, J_{H,H} = 7.2, 3H, H₃C–C(alk.)). ¹³C NMR (CDCl₃): δ 139.4 (1 C(arom.)); 135.4 (HC(2)); 128.9, 128.5, 127.3, 127.2, 126.0 (5 CH(arom.), 2 C(imid.)); 62.7 (HC(2')); 60.5 (CH₂–Ph); 54.9 (H₂C(5')); 50.8 (CH₂–N); 47.4, 31.3, 29.9 (3 C(alk.)); 28.5 (C(4')); 26.1 (C(alk.)); 23.9 (C(3')); 22.6 (C(alk.)); 14.1 (H₃C(alk.)); 8.7 (H₃C–C(5)); 8.5 (H₃C–C(4)). [α]_D²⁵ = –35 (c 1.0, CH₂Cl₂).

4.2.8.2. 1-[(2S)-N-Benzylpyrrolidin-2-yl]methyl-4,5-dimethyl-3-octyl-1H-imidazolium tetrafluoroborate 11b. Yield: 1.6 g (70%). Pale yellow oil (Al₂O₃, CHCl₃). IR (film): ν 3584w, 3154m, 3087m, 2928m, 2857m, 2806m, 1733w, 1699w, 1565s, 1454m, 1202m, 1058br, 828w, 742m, 703m. ¹H NMR (CDCl₃): δ 8.73 (s, 1H, HC(2)); 7.28–7.25 (m, 2H, HC(arom.)); 7.23–7.18 (m, 3H, HC(arom.)); 3.98 (dd, ²J_{H,H} = 14.4, ³J_{H,H} = 5.4, 1H, H₂C–N); 3.97–3.94 (m, 2H, H₂C(alk.)); 3.88 (dd, ²J_{H,H} = 14.4, ³J_{H,H} = 7.2, 1H, H₂C–N); 3.57, 3.55 (AB, J_{AB} = 13.6, 2H, H₂C–Ph); 3.16–3.11 (m, 1H, H₂C(2')); 3.10–3.05 (m, 1H, H₂C(5')); 2.50–2.44 (m, 1H, H₂C(5')); 2.15 (s, 3H, H₃C–C(4)); 2.10 (s, 3H, H₃C–C(5)); 1.97–1.82 (m, 1H, H₂C(3')); 1.82–1.77 (m, 1H, H₂C(3')); 1.74–1.67 (m, 1H, H₂C(4')), 2H, H₂C(alk.); 1.55–1.49 (m, 1H, H₂C(4')); 1.31–1.21 (m, 10H, H₂C(alk.)); 8.62 (t, J_{H,H} = 6.9, H₃C(alk.)). ¹³C NMR (CDCl₃): δ 139.3 (1 C(arom.)); 135.4 (HC(2)); 128.9, 128.5, 127.2, 127.2, 126.0 (5 HC(arom.), 2 C(imid.)); 62.6 (HC(2')); 60.4 (CH₂–Ph); 54.9 (C(5')); 50.8 (CH₂–N); 47.4, 31.8, 29.9, 29.2, 29.1 (5 C(alk.)); 28.4 (C(3')); 26.5 (C(alk.)); 23.9 (C(4')); 22.7 (C(alk.)); 14.2 (H₃C(alk.)); 8.7 (H₃C–C(4)); 8.5 (H₃C–C(5)). [α]_D²⁵ = –22 (c 1.0, CH₂Cl₂).

4.2.8.3. 1-[(2S)-N-Benzylpyrrolidin-2-yl]methyl-3-butyl-4-methyl-5-phenyl-1H-imidazolium tetrafluoroborate 11c. Yield: 1.6 g (68%). Pale yellow oil (Al₂O₃, CHCl₃). IR (film): ν 3151m, 3084m, 2961m, 2874m, 2807m, 1559m, 1497m, 1453m, 1203m, 1058m, 846w, 765m, 703s. ¹H NMR (CDCl₃): δ 8.91 (s, 1H, HC(2)); 7.55–7.50 (m, 3H, HC(arom.)); 7.29–7.26 (m, 4H, HC(arom.)); 7.24–7.21 (m, 1H, HC(arom.)); 7.17–7.15 (m, 2H, HC(arom.)); 4.09–4.07 (m, 2H, H₂C(alk.)); 3.97 (dd, ²J_{H,H} = 14.0, ³J_{H,H} = 5.4, 1H, H₂C–N); 3.93 (dd, ²J_{H,H} = 14.0, ³J_{H,H} = 6.6, 1H, H₂C–N); 3.52, 3.43 (AB, J_{AB} = 13.2, 2H, H₂C–Ph); 3.00–2.96 (m, 1H, H₂C(5')); 2.93–2.88 (m, 1H, H₂C(2')); 2.43–2.37 (m, 1H, H₂C(5')); 2.16 (s, 3H, H₃C–C(4)); 1.86–1.76 (m, 1H, H₂C(3')), 2H, H₂C(alk.); 1.74–1.66 (m, 1H, H₂C(4')); 1.60–1.53 (m, 1H, H₂C(4')); 1.44–1.38 (m, 2H, H₂C(alk.)); 1.36–1.31 (m, 1H, H₂C(3')); 0.97 (t, J_{H,H} = 7.50 Hz, H₃C(alk.)). ¹³C NMR (CDCl₃): δ 139.3 (1 C(arom.)); 136.2 (HC(2)); 131.7, 130.9, 130.7, 129.7, 128.9, 128.5, 127.5, 127.3, 125.6 (10 HC(arom.), 1 C(arom.)); 62.6 (HC(2')); 59.9 (CH₂–Ph); 54.4 (H₂C(5')); 50.9 (CH₂–N); 47.6, 31.8 (2 C(alk.)); 28.4 (C(3')); 23.7 (C(4')); 19.8 (C(alk.)); 13.6 (H₃C(alk.)); 8.9 (H₃C–C(4)). [α]_D²⁵ = –10 (c 1.0, CH₂Cl₂).

4.2.8.4. 1-[(2S)-N-Benzylpyrrolidin-2-yl]methyl-4-methyl-3-octyl-5-phenyl-1H-imidazolium tetrafluoroborate 11d. Yield: 1.9 g (72%). Pale yellow oil (Al₂O₃, CHCl₃). IR (film): ν 3627w, 3557w, 3151m, 3062m, 2927m, 2857m, 2804m, 1966m, 1900m, 1822m, 1559m, 1496m, 1459m, 1208m, 1058m, 926m, 843m, 763s, 703m. ¹H NMR (CDCl₃): δ 9.00 (s, 1H, HC(2)); 7.55–7.50 (m, 3H, HC(arom.)); 7.29–7.26 (m, 4H, HC(arom.)); 7.24–7.21 (m, 1H, HC(arom.)); 7.18–7.16 (m, 2H, HC(arom.)); 3.99 (dd, ²J_{H,H} = 14.0, ³J_{H,H} = 5.4, 1H, H₂C–N); 3.94 (dd, ²J_{H,H} = 14.0, ³J_{H,H} = 6.6, 1H, H₂C–N); 3.54, 3.43 (AB, J_{AB} = 13.2, 2H, H₂C–Ph); 3.00–2.96 (m, 1H, H₂C(5')); 2.94–2.90 (m, 1H, HC(2')); 2.42–2.37 (m, 1H, H₂C(5')); 2.16 (s, 3H, H₃C–C(5)); 1.87–1.77 (m, 2H, H₂C(alk.)), 1H, H₂C(4')); 1.73–1.67 (m, 1H, H₂C(3')); 1.60–1.52 (m, 1H, H₂C(3')); 1.39–1.21 (m, 10H, H₂C(alk.)), 1H, H₂C(4')); 0.87 (t, J_{H,H} = 7.2, H₃C(alk.)). ¹³C NMR (CDCl₃): δ 139.3 (1 C(arom.)); 136.2 (HC(2)); 131.7, 130.8, 130.7, 129.6, 128.9, 128.5, 127.5, 127.2, 125.5 (10 HC(arom.), 2 C(arom.)); 62.6 (C(imid.)); 59.9 (CH₂–Ph); 54.4 (H₂C(5')); 50.8 (CH₂–N); 47.8, 31.9, 29.9, 29.2 (4 C(alk.)); 29.2 (C(3')); 28.3, 26.6 (2 C(alk.)); 23.7 (C(4')); 22.8 (C(alk.)); 14.2 (H₃C(alk.)); 8.9 (H₃C–C(5)). [α]_D²⁵ = –27 (c 1.0, CH₂Cl₂).

4.2.9. Synthesis of 3-alkoxyimidazolium tetrafluoroborates 13

A solution of imidazole N-oxide **5** (5 mmol) and the corresponding alkyl bromide (5 mmol) in CHCl₃ (10 ml) was stirred magnetically at rt for 72 h. The solvent was then removed under reduced pressure and the crude product was washed with Et₂O (3 × 5 ml), and dried under high vacuum for 4 h. The imidazolium bromide obtained was stirred magnetically with an equimolar amount of solid NaBF₄ in acetone (5 ml) at rt overnight. The resulting suspension was filtered through neutral alumina (Et₂O) and the solvent evaporated under reduced pressure.

4.2.9.1. 1-[(2S)-N-Benzylpyrrolidin-2-yl]methyl-3-butoxy-4,5-dimethyl-1H-imidazolium tetrafluoroborate 13a. Yield: 1.8 g (78%). Pale yellow oil (Al₂O₃, CHCl₃). IR (film): ν 3585w, 3380m, 3140m, 2961m, 2874m, 2807m, 1684m, 1545m, 1496m, 1454m, 1259w, 1187w, 1058m, 936m, 848m, 820m, 735s, 703s, 613w. ¹H NMR (CDCl₃): δ 9.28 (s, 1H, HC(2)); 7.31–7.14 (m, 5H, HC(arom.)); 4.38–4.29 (m, 2H, H₂C(alk.)); 4.09 (dd, ²J_{H,H} = 14.4, ³J_{H,H} = 4.8, 1H, H₂C–N); 3.96 (dd, ²J_{H,H} = 14.4, ³J_{H,H} = 7.8, 1H, H₂C–N); 3.59, 3.56 (AB, J_{AB} = 13.2, 1H, H₂C–Ph); 3.19–3.11 (m, 1H, H₂C(5')), 1H, HC(2')); 2.57–2.52 (m, 1H, H₂C(5')); 2.15 (s, 3H, H₃C–C(4)); 2.08 (s, 3H, H₃C–C(5)); 2.06–2.00 (m, 1H, H₂C(3')); 1.86–1.79 (m, 1H, H₂C(4')); 1.79–1.71 (m, 2H, H₂C(alk.)), 1H, H₂C(4')); 1.56–1.44 (m, 2H, H₂C(alk.)), 1H, H₂C(3')); 0.97 (t, J_{H,H} = 7.2, H₃C(alk.)). ¹³C NMR (CDCl₃): δ 139.2 (1 C(arom.)); 131.7 (HC(2)); 129.0, 128.5, 127.3, 124.8, 123.5 (5 CH(arom.), 2 C(imid.)); 82.9 (C(alk.)); 62.5 (C(2')); 60.6 (CH₂–Ph); 55.0 (C(5')); 50.9 (CH₂–N); 29.9 (C(alk.)); 28.3 (C(3')); 24.0 (C(4')); 19.0 (C(alk.)); 13.9 (H₃C(alk.)); 8.7 (H₃C–C(5)); 7.2 (H₃C–C(4)). [α]_D²⁵ = –33 (c 1.0, CH₂Cl₂).

4.2.9.2. 1-[(2S)-N-Benzylpyrrolidin-2-yl]methyl-4,5-dimethyl-3-octyloxy-1H-imidazolium tetrafluoroborate 13b. Yield: 1.7 g (69%). Pale yellow oil (Al₂O₃, CHCl₃). IR (film): ν 3584w, 3566w, 3384m, 3139m, 3061m, 2928m, 2857m, 2807m, 1634m, 1546m, 1496w, 1454w, 1260w, 1059m, 945m, 807w, 736m, 703s, 648w. ¹H NMR (CDCl₃): δ 8.91 (s, 1H, HC(2)); 7.27–7.19 (m, 3H, HC(arom.)); 7.17–7.13 (m, 2H, HC(arom.)); 4.36–4.27 (m, 2H, H₂C(alk.)); 4.05 (dd, ²J_{H,H} = 14.4, ³J_{H,H} = 4.8, 1H, H₂C–N); 3.93 (dd, ²J_{H,H} = 14.4, ³J_{H,H} = 7.8, 1H, H₂C–N); 3.57, 3.55 (AB, J_{AB} = 13.2, 2H, H₂C–Ph); 3.16–3.10 (m, 1H, H₂C(5')), 1H, HC(2')); 2.57–2.52 (m, 1H, H₂C(5')); 2.15 (s, 3H, H₃C–C(4)); 2.08 (s, 3H, H₃C–C(5)); 2.07–2.01 (m, 1H, H₂C(3')); 1.86–1.80 (m, 1H, H₂C(4')); 1.78–1.71 (m, 2H, H₂C(alk.)), 1H, H₂C(4')); 1.54–1.49 (m, 1H, H₂C(3')); 1.56–1.40 (m, 2H, H₂C(alk.)); 1.35–1.24 (m, 8H, H₂C(alk.)); 0.89 (t, J_{H,H} = 7.2, 3H, H₃C(alk.)). ¹³C NMR (CDCl₃): δ 139.4 (1 C(arom.)); 131.3

(HC(2)); 129.0, 128.5, 127.3, 124.8, 123.5 (5 C(arom.), 2 C(imid.)); 62.4 (HC(2')); 60.6 (CH₂-Ph); 54.9 (C(5')); 50.9 (CH₂-N); 29.4, 28.3 (2 C(alk.)); 28.0 (C(3')); 25.7 (C(alk.)); 24.0 (C(4')); 22.8 (C(alk.)); 14.3 (H₃C(alk.)); 8.7 (H₃C-C(5)), 7.3 (H₃C-C(4)). $[\alpha]_D^{25} = -26$ (c 1.0, CH₂Cl₂).

4.2.9.3. 1-[[[(2S)-N-Benzylpyrrolidin-2-yl]methyl]-3-butoxy-4-methyl-5-phenyl-1H-imidazolium tetrafluoroborate 13c. Yield: 1.6 g (70%). Pale yellow oil (Al₂O₃, CHCl₃). IR (film): ν 3584w, 3366m, 3135m, 3061m, 2961m, 2874m, 2806m, 1679m, 1543m, 1496m, 1452m, 1380m, 1283w, 1058m, 934m, 822w, 756m, 736m, 702s. ¹H NMR (CDCl₃): δ 9.08 (s, 1H, HC(2)); 7.53–7.48 (m, 3H, HC(arom.)); 7.28–7.13 (m, 7H, HC(arom.)); 4.52–4.43 (m, 2H, H₂C(alk.)); 4.04 (dd, ²J_{H,H} = 14.4, ³J_{H,H} = 4.8, 1H, H₂C-N); 3.95 (dd, ²J_{H,H} = 14.4, ³J_{H,H} = 7.8, 1H, H₂C-N); 3.57, 3.45 (AB, J_{AB} = 12.6, 2H, H₂C-Ph); 3.06–3.02 (m, 1H, H₂C(5')); 2.91–2.86 (m, 1H, HC(2')); 2.52–2.47 (m, 1H, H₂C(5')); 2.16 (s, 3H, H₃C-C(4)); 1.86–1.79 (m, 2H, H₂C(alk.)), 1H, H₂C(3')); 1.78–1.71 (m, 1H, H₂C(4')); 1.63–1.50 (m, 2H, H₂C(alk.)); 1H, H₂C(4')); 1.43–1.28 (m, 1H, H₂C(3')); 1.00 (t, J_{H,H} = 7.2, 3H, H₃C(alk.)). ¹³C NMR (CDCl₃): δ 139.3 (1 C(arom.)); 132.1 (HC(2)); 130.9, 130.8, 129.7, 129.1, 129.0, 128.5, 127.3, 124.9, 124.8 (10 HC(arom.)); 1 C(arom.), 2 C(imid.)); 83.2 (C(alk.)); 62.3 (HC(2')); 60.1 (CH₂-Ph); 54.4 (C(5')); 50.6 (CH₂-N); 30.1 (C(alk.)); 27.9 (C(4')); 23.8 (C(3')); 19.1, 13.9 (2 C(alk.)); 7.5 (H₃C-C(4)). $[\alpha]_D^{25} = -25$ (c 1.0, CH₂Cl₂).

4.2.9.4. 1-[[[(2S)-N-Benzylpyrrolidin-2-yl]methyl]-3-hexyloxy-4-methyl-5-phenyl-1H-imidazolium tetrafluoroborate 13d. Yield: 1.9 g (76%). Pale yellow oil (Al₂O₃, CHCl₃). IR (film): ν 3584w, 3369m, 3135m, 3061m, 2930m, 2872m, 2807m, 1683m, 1542m, 1496m, 1453m, 1379m, 1283w, 1058m, 933m, 913m, 765m, 735m, 702s. ¹H NMR (CDCl₃): δ 9.10 (s, 1H, HC(2)); 7.55–7.48 (m, 3H, HC(arom.)); 7.29–7.14 (m, 7H, HC(arom.)); 4.51–4.42 (m, 2H, H₂C(alk.)); 4.04 (dd, ²J_{H,H} = 14.0, ³J_{H,H} = 4.8, 1H, H₂C-N); 3.95 (dd, ²J_{H,H} = 14.0, ³J_{H,H} = 7.8, 1H, H₂C-N); 3.57, 3.45 (AB, J_{AB} = 13.2, 2H, H₂C-Ph); 3.06–3.02 (m, 1H, H₂C(5')); 2.92–2.87 (m, 1H, HC(2')); 2.53–2.47 (m, 1H, H₂C(5')); 2.16 (s, 3H, H₃C-C(4)); 1.87–1.80 (m, 2H, H₂C(alk.)); 1H, H₂C(3')); 1.78–1.71 (m, 1H, H₂C(4')); 1.64–1.57 (m, 1H, H₂C(4')); 1.51–1.46 (m, 2H, H₂C(alk.)); 1.37–1.28 (m, 4H, H₂C(alk.)), 1H, H₂C(3')); 0.92 (t, J_{H,H} = 6.9, 3H, H₃C(alk.)). ¹³C NMR (CDCl₃): δ 139.3 (1 C(arom.)); 132.1 (HC(2)); 131.0, 130.9, 129.6, 129.1, 129.0, 128.5, 127.3, 124.9, 124.8 (10 HC(arom.)); 1 C(arom.), 2 C(imid.)); 83.5 (C(alk.)); 62.3 (HC(2')); 60.1 (CH₂-Ph); 54.4 (C(5')); 50.6 (CH₂-N); 31.6, 28.1 (2 C(alk.)); 27.9 (C(3')); 25.4 (C(alk.)); 23.8 (C(4')); 22.7 (C(alk.)); 14.2 (H₃C(alk.)); 7.6 (H₃C-C(4)). $[\alpha]_D^{25} = -17$ (c 1.0, CH₂Cl₂).

4.2.9.5. 1-[[[(2S)-N-Benzylpyrrolidin-2-yl]methyl]-3-butoxy-4,5-diphenyl-1H-imidazolium tetrafluoroborate 13e. Yield: 1.5 g (53%). Pale yellow oil (Al₂O₃, CHCl₃). IR (film): ν 3648w, 3584w, 3369w, 3135m, 3061m, 2961m, 2874m, 2808m, 1683m, 1494m, 1447m, 1271m, 1179m, 1058m, 934m, 819m, 763m, 735m, 700m, 607w. ¹H NMR (CDCl₃): δ 9.24 (s, 1H, HC(2)); 7.50–7.20 (m, 15H, HC(arom.)); 4.26–4.19 (m, 1H, H₂C-N, 2H, H₂C(alk.)); 4.10 (dd, ²J_{H,H} = 13.8, ³J_{H,H} = 7.2, 1H, H₂C-N); 3.65, 3.49 (AB, J_{AB} = 13.2, 2H, H₂C-Ph); 3.06–3.01 (m, 1H, H₂C(5')); 2.98–2.92 (m, 1H, HC(2')); 2.53–2.47 (m, 1H, H₂C(5')); 1.89–1.82 (m, 1H, H₂C(3')); 1.79–1.73 (m, 1H, H₂C(4')); 1.64–1.56 (m, 2H, H₂C(alk.)); 1H, H₂C(4')); 1.36–1.32 (m, 1H, H₂C(3')); 1.31–1.24 (m, 2H, H₂C(alk.)); 0.79 (t, J_{H,H} = 7.5, 3H, H₃C(alk.)). ¹³C NMR (CDCl₃): δ 139.3 (1 C(arom.)); 133.1 (HC(2)); 131.3, 130.9, 130.4, 129.8, 129.73, 129.68, 129.2, 129.1, 128.7, 127.6, 126.8, 124.6, 123.4 (15 HC(arom.)), 2 C(arom.), 2 C(imid.)); 83.4 (C(alk.)); 62.3 (C(2'));

59.8 (CH₂-Ph); 54.1 (C(5')); 50.4 (CH₂-N); 29.8 (C(alk.)); 23.6 (C(3')); 18.8 (C(4')); 13.7 (H₃C(alk.)). $[\alpha]_D^{25} = -16$ (c.0, CH₂Cl₂).

5. Uncited reference

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Acknowledgments

A.W. thanks the National Science Center (Cracow) for financial support (Grant Preludium # UMO-2012/07/N/ST5). The authors thank PD Dr. L. Bigler, University of Zürich, for ESI-HRMS.

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