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# New chiral ionic liquids based on imidazolinium salts

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ABSTRACT

The preparation and application of a new series of chiral ionic liquids are described. The salts are based on imidazolinium cations. Some of the cations also incorporated an axial chirality at the C(2) position next to the central chirality. These cations display a very high rotational barrier along the arene–imidazolinium axis. Furthermore, an analogue with a chiral anion was prepared. The salts have low melting points. Their potential as solvents and as chiral shift reagents was explored, resulting for the first time in an example of a chiral ionic liquid as a shift reagent for a neutral compound.



## 1. Introduction

Over the years, ionic liquids and salts with a melting point below 100 °C have proven to be a promising class of organic materials due to their potential as novel solvents for reactions and electrochemical processes.[1] Many of these liquids could be potential 'green solvents', due to their negligible vapor pressure or efficient recovery.[2] However, a few studies have been reported that show that ionic liquids are not inert but do react with some reagents,[3,4] which could be a disadvantage in some applications, for example, in recovery. Imidazolium cations are most frequently applied in many standard ionic liquids. These cations can be deprotonated with medium and strong bases.[5–9] Therefore, a number of alternative ionic liquids have recently been reported, which can be used in the presence of basic Grignard reagents.[10–15] The first example, reported by Clyburne et al.,[10] was a phosphonium ionic liquid. Thereafter, we reported the application of an imidazolinium salt.[11]

Handy reported that an *i*Pr group at the C-2 position of an imidazolium cation leads to a base-stable imidazolium RTIL for the Grignard addition to aldehydes.[13] In addition, Chan et al.[12] reported the application of *n*-butylpyridinium tetrafluoroborate in this reaction. It was also possible to prepare the Grignard reagent in this ionic liquid. In addition, Itho reported the use of salts based on phosphonium cations with alkyl ether side arms for the Grignard addition to aldehydes.[15]

If ionic liquids are chiral, they have an additional potential as chiral solvents, shift reagents, and catalysts.[16–31] Most of these chiral ionic liquids incorporate a central chirality and only a few are known based on planar[28] and axial chirality.[30] Chiral ionic liquids based on imidazolinium salts can have a stereogenic center at the C(4) or C(5) position, and it is known that no racemization occurs at these positions.[31] Due to our efforts on the chiral ionic liquids,[32–36] we were interested in preparing chiral analogues of imidazolinium salts incorporating ether functions with a different chiral environment and an aryl substituent at the C(2) position, which would also allow the introduction of an axial chirality. The salts were investigated as solvents in the Grignard addition to aldehydes and as chiral shift reagents.

## 2. Results and discussion

The synthesis of chiral ionic liquids is shown in Scheme 1. First L-valinol[37] **1a** was reacted with either benzoyl- or *o*-toluoyl chloride in the presence of potassium carbonate in methanol.[38] The corresponding amides could be obtained as white solids in 73% yield for **2a** and 95% yield for **2b**, respectively. Furthermore, the achiral *N*-benzoylethylamine **2c** and *N*-(2-hydroxyethyl)-2-methylbenzamide **2d** were obtained from ethanolamine **1b** and benzoyl chloride or toluoyl chloride in 93% and 71% yield, respectively.

These amides were then treated with neat thionyl chloride and subsequently with aqueous methylamine to give the desired 1-methylimidazolines. (*S*)-4-Isopropyl-1-methyl-2-phenyl-4,5-dihydro-1*H*-imidazole **3a** was isolated in 82% yield, whereas (*S*)-4-isopropyl-1-methyl-2-*o*-tolyl-4,5-dihydro-1*H*-imidazole **3b** was obtained only in 47% yield probably due to increased steric hindrance during the reaction with thionyl chloride. 1-Methyl-phenyl-4,5-dihydro-1*H*-imidazole **3c** was obtained as a colorless liquid in 77% yield, whereas 1-methyl-2-*o*-tolyl-4,5-dihydro-1*H*-imidazole **3d** was obtained in 67% yield.

The prepared 4,5-dihydro-1*H*-imidazoles **3a–d** were afterwards subjected to nucleophilic substitution reactions with electrophiles containing ether moieties, namely MOM-chloride, MEM-chloride, and (−)-menthyl chloride. (−)-Menthyl chloride was prepared via the standard procedure from menthol, paraformaldehyde, and hydrochloric acid.[39] The chlorides obtained were directly dissolved in water and the addition of $LiNTf_2$ led to the precipitation of the chiral ionic liquids. Depending on the synthetic route, the final

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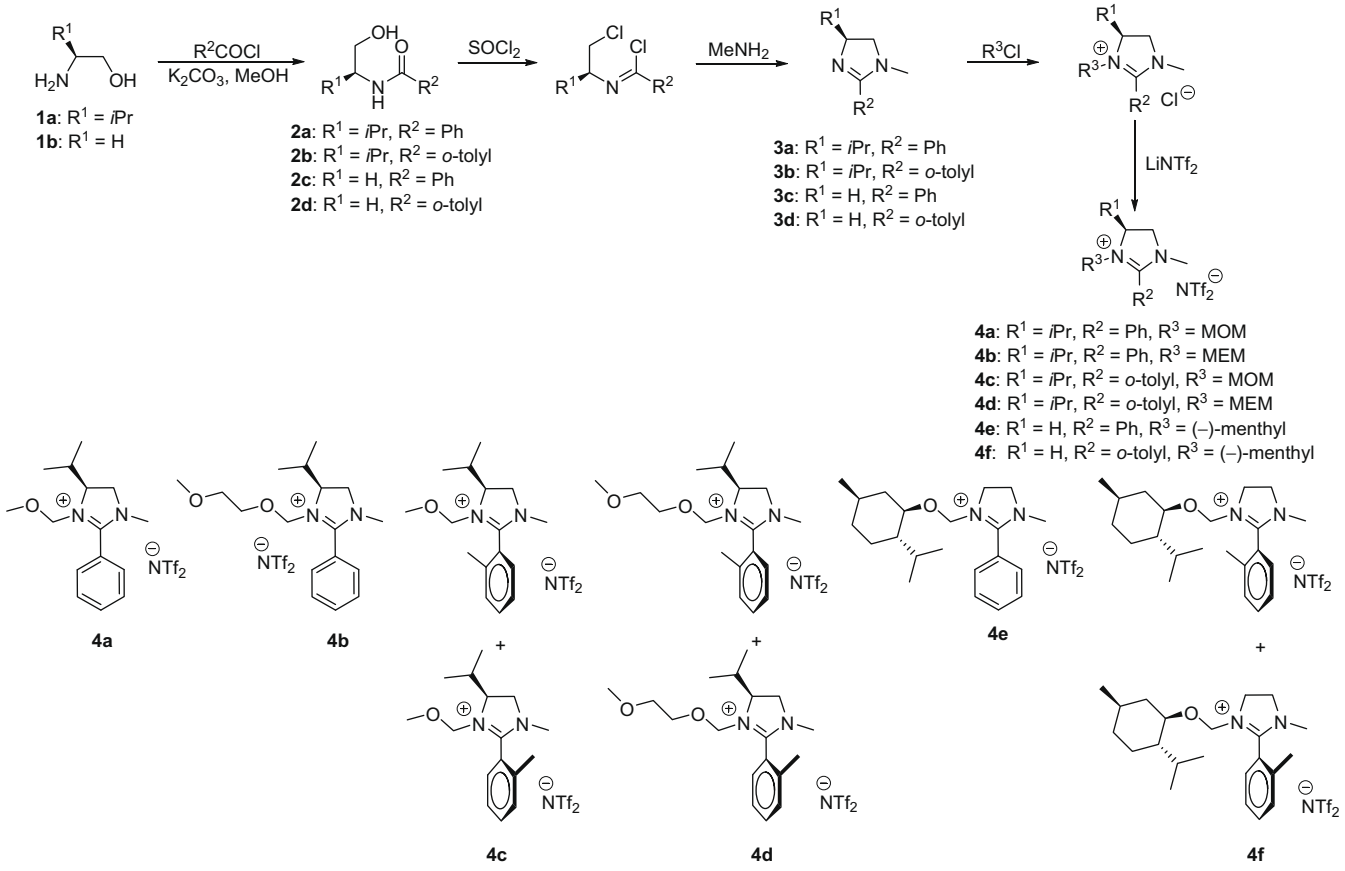



**Scheme 1.** Synthesis of chiral ionic liquids.

cation carried the chiral information directly at the imidazolium ring or at the imidazoline nitrogen atom.

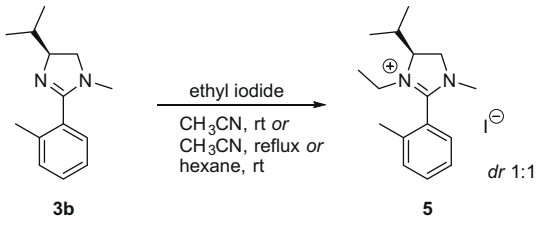
All the salts prepared are ionic liquids, respectively, with melting points at 39 °C, **4a**; 44 °C, **4c;** and 58 °C, **4e** or are room-temperature ionic liquids at 20 °C, **4b**, **4d**, and **4f**.

The ionic liquids, which have an *o*-tolyl group at the C2-position of the imidazolinium ring, also have next to an element of central chirality an element of axial chirality. The rotation around the axis is hindered, which makes it possible to observe in the NMR separate signals for each diastereomer. Scheme 1 shows the different diastereomers of the ionic liquids bearing additional axial chirality.

The diastereomeric ratios for the described ionic liquids were calculated from the $^1$H NMR data. The following ratios were observed: 3:2, **4c;** 4:3, **4d;** and 1:1, **4f**. It was not possible to separate the diastereomers with any of the several standard methods or with HPLC with normal or reversed phase. The assignment of the peaks to a specific diastereomer was not possible by NOE. However, it is reasonable to assume for **4c** and **4d** that the less sterically demanding diastereomer is formed in excess.

While free rotation in salts **4c**, **4d,** and **4f** is restricted, there is no rotational barrier in the corresponding imidazolines **3c**, **3d,** and **3f**. The tolyl group is locked in the quaternization process and an obviously high rotation barrier prevents free rotation around the C2–C(tolyl) axis because of steric hindrance between the newly introduced substituent at the C1-carbon and the methyl group of the tolyl ring. In order to determine the rotational barrier, IL **4c** was heated in DMSO-$d_6$ during the NMR measurement from rt to 50, 100, and 150 °C in order to evaluate any changes in the diastereomeric ratio. However, even at 150 °C, no change in the NMR was observed meaning that one can assume a high rotational barrier around the imidazolinium–tolyl C–C axis.

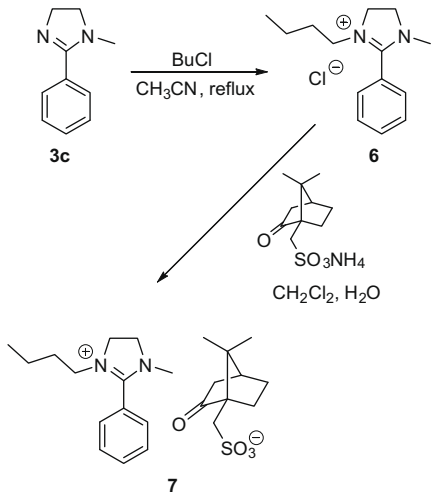
To explore whether the reaction temperature of the quaternization step would have an influence on the diastereomeric ratio of the product, imidazoline **3b** was reacted with ethyliodide in acetonitrile at rt and at reflux. In addition, acetonitrile was replaced with hexane and the reaction was carried out at rt to investigate the influence of the solvent (Scheme 2). From the obtained NMR data, in all cases, a diastereomeric ratio of ~1:1 was obtained.



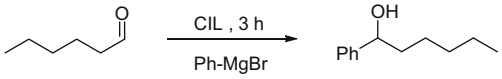

**Scheme 2.** Synthesis of salt **5**.

An imidazolinium salt was prepared with a chiral anion based on (−)-camphorsulfonic acid as shown in Scheme 3. The precursor **3c** was treated with butyl chloride in refluxing acetonitrile to give the desired product **6** in 65% yield. Subsequent anion metathesis with commercially available (−)-ammonium camphorsulfonate gave the new rt chiral ionic liquid **7** in 86% yield.

The ionic liquids **4a–f** were tested in the Grignard addition to aldehydes (Scheme 4). The THF solvent of the commercial Grignard solution was evaporated under high vacuum and the ionic liquid was added to the remaining solid Grignard. After heating to




**Scheme 3.** Synthesis of salt **7**.




**Scheme 4.** Grignard addition to aldehydes.

40 °C, the aldehyde was added and the reaction mixture was stirred for 3 h.

Ionic liquids **4e** and **4f** gave the desired product in yields comparable to an achiral analogue.[11] Since ionic liquid **4e** gave the highest yield, the addition of phenylmagnesiumbromide to 1-naphthaldehyde was also tested herein. The corresponding product was isolated in 52% yield. In all the reactions, no optical activity was found. Two reactions were carried out in the presence of a Lewis acid and **4a** as a solvent. Moreover, 10 mol % of the Lewis acids, zinc chloride or scandium triflate, was used. However, the yields decreased to 30% with zinc chloride and to 20% with scandium triflate.

Next, the behavior of the salts as chiral shift reagents was tested with enantiomerically and diastereomerically pure ionic liquids **4a**, **4b**, and **4e**, and with ionic liquid **7**. For the NMR measurements, racemic Mosher's acid potassium salt with 18-crown-6 or 1-phenyl-2,2,2-trifluoroethanol was used. In a typical NMR experiment, the CIL/substrate ratio was 2:1. With **4a** and **4b**, racemic potassium Mosher's carboxylate and 18-crown-6, a splitting of 15.14 Hz and 5.17 Hz in the $^{19}F$ NMR was observed when $CDCl_3$ was used as a solvent. In the $^{1}H$ NMR no splitting was found. With salt **4e** no splitting was observed in either the $^{1}H$ or $^{19}F$ NMR.

In order to evaluate salt **7**, Mosheŕs acid was added to the salt in toluene-$d_8$. However, no splitting was observed. Next (±)-1-phenyl-2,2,2-trifluoroethanol with **7** in $CDCl_3$ showed no splitting of the C1-proton of the alcohol, but a downfield shift of 0.2 ppm was observed. The results changed drastically when toluene-$d_8$ was used as the solvent. The alcohol's C1-proton signal was shifted from 4.38 ppm (without ionic liquid) to 5.62 ppm. Also a splitting of the quadruplet was observed. The chiral recognition by ionic liquid **7** caused a splitting of about 2.5 Hz in the $^{1}H$ NMR. However, in some cases, a splitting of the quadruplet signal was observed although no ionic liquid was applied. This was due to the fact that the decreased humidity of the reagents and solvents used in the experiments caused a further coupling of the CH-proton of the alcohol with the hydroxyl proton. To exclude this influence in determining the splitting, enantiomerically enriched 1-phenyl-2,2,2-trifluoroethanol [(*S*)-enriched, 50% ee and 33% ee] was applied. In the $^{19}F$ NMR, the splitting of the $CF_3$ doublet was 6.9 Hz as shown in Figure 1.

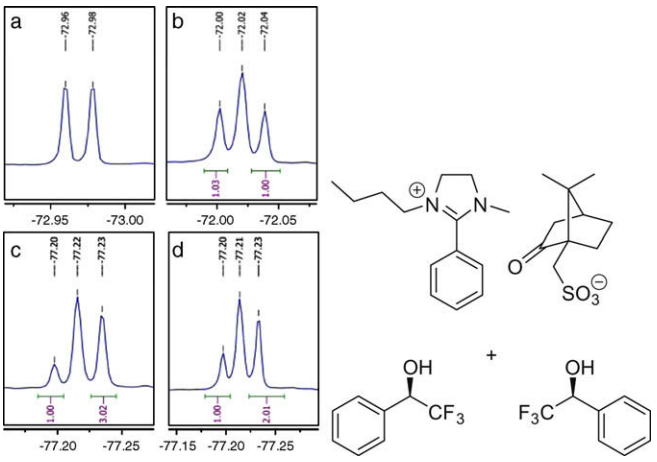



**Figure 1.** (a) (±)-1-Phenyl-2,2,2-trifluoroethanol in toluene-$d_8$, (b) (±)-1-phenyl-2,2,2-trifluoroethanol (1 equiv) + **7** (2 equiv) in toluene-$d_8$, 1-phenyl-2,2,2-trifluoroethanol [50% ee, (*S*)-enriched, 1 equiv] + **7** (2 equiv) in toluene-$d_8$, (c) 1-phenyl-2,2,2-trifluoroethanol [33% ee, (*S*)-enriched, 1 equiv] + **7** (2 equiv) in toluene-$d_8$.

## 3. Conclusion

In conclusion, it was possible to synthesize a series of chiral ionic liquids containing ether functions of which some incorporated axial chirality. In the future, analogues with larger groups in the backbone of the imidazolinium ring and at the *ortho* position of the aryl substituent will be prepared in order to increase the diastereoselectivity. While the ionic liquids did not induce any asymmetric excess in the addition of Grignard reagent to aldehydes, it was possible to show that they are able to form diastereomeric salt pairs with Mosher's carboxylates. More importantly, it was possible to show that a salt with a chiral camphor sulfonate anion can be used as a chiral shift reagent for a neutral alcohol.

## 4. Experimental

### 4.1. General experimental

Toluene was dried over sodium. L-Valinol **1a**[37] was prepared according to the literature. Flash column chromatography[40] was performed on silica gel. All reactions were monitored by TLC plates. $^{1}H$ NMR spectra were acquired with a Bruker AC 200F (200 MHz) at ambient temperature. Chemical $^{13}C$ NMR spectra were recorded at ambient temperature with AC 200F (50 MHz) instruments and chemical shifts were reported in parts per million (ppm) relative to tetramethylsilane as the internal standard. NMR samples were dissolved if not otherwise stated in $CDCl_3$. Mass spectra (ESI) were recorded with a Hewlett–Packard MS LC/MSD Series 1100 MSD instrument, while HRMS were recorded on a Bruker Daltonik Tesla-Fourier Transform-Ion Cyclotron Resonance Mass spectrometer mit Electrospray-Ionisierung by Dr. Dräger at the Institute of Organic Chemistry, University of Hannover. Infrared spectra were recorded with a Bruker Vektor 22 FTIR spectrometer, as KBr pellets in case of solid compounds and as thin films between NaCl plates in cases of oils and liquids. HPLC analysis was carried out using a Daicel CHIRALPACK OD-H column with a Waters 510 Pump system, an ISCO Model UA-5 UV–vis Detector (254 nm), and a Waters 410 differential refractometer. Melting points were taken with a Dr. Tottoli apparatus and are uncorrected.

### 4.2. Preparation of hydroxy-protected bis-hydroxy amines

#### 4.2.1. Preparation of benzamides 2a–2d: General procedure

Potassium carbonate (12.5 g) was suspended in methanol (400 mL). The aminoalcohol **1a** or **1b** (83.1 mmol) was added and the mixture was cooled down to 0 °C. Afterwards, the acid chloride (91.4 mmol) was added and the mixture was stirred for 15 h at rt. The remaining solid was decanted off and the solvent was distilled off. Water (100 mL) and chloroform (200 mL) were added and the mixture was stirred for 15 min. The organic phase was separated, and the aqueous phase was washed with chloroform (3 × 100 mL). The combined organic phases were dried over sodium sulfate. After distilling off the solvent, the remaining solid was washed with a small amount of cold toluene and afterwards dried in high vacuum.

**4.2.1.1. (*S*)-*N*-(1-Hydroxy-3-methylbutan-2-yl)-benzamide 2a.** As a white solid (73%). $^1$H NMR (200 MHz) $\delta$ 7.91–7.63 (m, 2H), 7.61–7.30 (m, 3H), 6.60 (d, $J$ = 8.3 Hz, 1H), 4.03–3.80 (m, 1H), 3.82–3.64 (m, 2H), 3.19 (s, 1H), 2.19–1.78 (m, 1H), 1.00 (d, $J$ = 3.2 Hz, 3H), 0.97 (d, $J$ = 3.3 Hz, 3H); $^{13}$C NMR (50 MHz) $\delta$ 168.5, 134.6, 131.6, 128.7, 127.1, 63.6, 57.5, 29.3, 19.7, 19.1. The spectral data were consistent with literature values.[41]

**4.2.1.2. (*S*)-*N*-(1-Hydroxy-3-methylbutan-2-yl)-2-methylbenzamid 2b.** As a white solid (95%). Mp 89.2 °C; $[\alpha]_D^{25} = -27.8$ ($c$ 0.42, $CHCl_3$); MS (EI), $m/e$ 222 ($M^+$+H, 3%), 136 (11), 119 (100), 91 (42); IR (KBr) 3293, 3069, 2964, 2880, 2360, 1638, 1538, 1463, 1338, 1314, 1068, 1017, 901, 878, 845, 778, 742, 724, 698 cm$^{-1}$; $^1$H NMR (200 MHz) $\delta$ 7.35–7.02 (m, 4H), 5.99 (d, $J$ = 7.7 Hz, 1H), 3.93–3.75 (m, 1H), 3.74–3.56 (m, 2H), 2.78 (s, 1H), 2.36 (s, 3H), 1.99–1.78 (m, 1H), 0.95 (d, $J$ = 3.3 Hz, 3H), 0.91 (d, $J$ = 3.4 Hz, 3H); $^{13}$C NMR (50 MHz) $\delta$ 171.2, 136.7, 136.0, 131.1, 130.0, 126.7, 125.9, 64.0, 57.4, 29.2, 19.9, 19.7, 19.0. HRMS (EI): calcd for $C_{13}H_{19}NO_2$ [M$^+$]: 221.1416, found 221.1418.

**4.2.1.3. *N*-(2-Hydroxyethyl)-benzamide 2c.** As a white solid (93%). $^1$H NMR (200 MHz) $\delta$ 7.85–7.66 (m, 2H), 7.52–7.14 (m, 4H), 4.05 (s, 1H), 3.74 (t, $J$ = 4.9 Hz, 2H), 3.62–3.45 (m, 2H), OH-proton not observed; $^{13}$C NMR (50 MHz) $\delta$ 168.9, 134.1, 131.7, 128.6, 127.1, 61.8, 42.9. The spectral data were consistent with literature values.[42]

**4.2.1.4. *N*-(2-Hydroxyethyl)-2-methylbenzamide 2d.** As a white solid (71%). Mp 65 °C; MS (EI), $m/e$ 179 ($M^+$, 7%), 136 (11), 119 (100), 91 (57), 77 (3); IR (KBr) 3279, 3070, 3025, 2971, 2932, 2884, 1966, 1933, 1816, 1637, 1420, 1315, 1164, 1119, 1095, 1047, 883, 868, 779, 755, 729, 702, 659, 521, 461, 416 cm$^{-1}$; $^1$H NMR (200 MHz) $\delta$ 7.42–7.06 (m, 4H), 6.48 (s, 1H), 3.83–3.63 (m, 2H), 3.61–3.42 (m, 2H), 3.23 (s, 1H), 2.40 (s, 3H); $^{13}$C NMR (50 MHz) $\delta$ 171.4, 136.1, 136.0, 131.1, 130.1, 126.9, 125.8, 62.2, 42.7, 19.8. Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.97; H, 7.38; N, 7.82.

#### 4.2.2. Preparation of imidazolines 3a–3d: General procedure

Hydroxybenzamides **2a**–**2d** (197 mmol) were carefully treated with neat thionyl chloride (0.79 mol). The resulting solution was refluxed for 4 h. The excess of thionyl chloride was distilled off. Dry diethyl ether (200 mL) was added to the remaining oil. The small amount of insoluble solid was filtered off and the filtrate was cooled down to 0 °C. Aqueous methyl amine solution (200 mL, 11.85 M) was added and the resulting mixture was stirred for 1 h at rt. The organic phase was separated, and the aqueous phase was washed with chloroform (3 × 300 mL). The combined organic phases were dried over sodium sulfate. After distilling off the solvent, the remaining oil was purified via bulb-to-bulb distillation.

**4.2.2.1. (*S*)-4-Isopropyl-1-methyl-2-phenyl-4,5-dihydro-1*H*-imidazole 3a.** As a colorless liquid (82%). $[\alpha]_D^{25} = -84.0$ ($c$ 1.07, $CHCl_3$); MS (EI), $m/e$ 202 ($M^+$, 3%), 185 (3), 174 (5), 159 (100), 132 (3), 118 (7), 104 (20), 91 (10), 77 (27); IR (NaCl) 3060, 3022, 2955, 2870, 1957, 1895, 1653, 1614, 1597, 1573, 1448, 1383, 1364, 1310, 1264, 1217, 1064, 1026, 971, 945, 923, 778, 702, 588, 544, 433 cm$^{-1}$; $^1$H NMR (200 MHz) $\delta$ 7.52–7.34 (m, 2H), 7.34–7.18 (m, 3H), 3.77 (ddd, $J$ = 10.4, 9.2, 6.0 Hz, 1H), 3.40 (dd, $J$ = 10.3, 9.2 Hz, 1H), 2.94 (t, $J$ = 9.2 Hz, 1H), 2.63 (s, 3H), 1.89–1.63 (m, 1H), 0.92 (d, $J$ = 6.8 Hz, 3H), 0.83 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (50 MHz) $\delta$ 166.3, 131.1, 129.2, 127.9 (2C), 70.0, 55.9, 35.8, 32.9, 18.8, 17.8. HRMS (EI): calcd for $C_{13}H_{18}N_2$ [M$^+$]: 202.1470, found 202.1472.

**4.2.2.2. (*S*)-4-Isopropyl-1-methyl-2-*o*-tolyl-4,5-dihydro-1*H*-imidazole 3b.** As a yellow liquid (47%). $[\alpha]_D^{25} = +58.3$ ($c$ 1.43, $CHCl_3$); MS (EI), $m/e$ 216 ($M^+$, 18%), 201 (5), 173 (100), 117 (22), 103 (8), 91 (21), 85 (7), 77 (11); IR (NaCl) 3061, 3022, 2955, 2870, 1619, 1597, 1497, 1458, 1382, 1364, 1309, 1262, 1232, 1061, 1040, 944, 771, 732, 588, 532, 446, 436, 428 cm$^{-1}$; $^1$H NMR (200 MHz) $\delta$ 7.34–7.13 (m, 5H), 3.92 (ddd, $J$ = 10.3, 9.2, 6.0 Hz, 1H), 3.47 (dd, $J$ = 18.3, 9.2 Hz, 1H), 3.08 (t, $J$ = 9.2 Hz, 1H), 2.57 (s, 3H), 2.32 (s, 3H), 1.98–1.74 (m, 1H), 1.03 (d, $J$ = 6.8 Hz, 3H), 0.96 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (50 MHz) $\delta$ 166.2, 136.3, 131.5, 130.2, 129.1, 128.7, 125.7, 70.7, 55.3, 34.5, 33.2, 19.5, 19.1, 18.4. HRMS (EI): calcd for $C_{14}H_{20}N_2$ [M$^+$]: 216.1626, found 216.1625.

**4.2.2.3. 1-Methyl-phenyl-4,5-dihydro-1*H*-imidazole 3c.** As a colorless liquid (77%). $^1$H NMR (200 MHz) $\delta$ 7.60–7.45 (m, 2H), 7.46–7.30 (m, 3H), 3.95–3.76 (m, 2H), 3.52–3.33 (m, 2H), 2.78 (s, 3H); $^{13}$C NMR (50 MHz) $\delta$ 168.1, 131.3, 129.6, 128.2, 128.1, 54.1, 53.2, 36.4. The spectral data were consistent with literature values.[43]

**4.2.2.4. 1-Methyl-2-*o*-tolyl-4,5-dihydro-1*H*-imidazole 3d.** As a colorless liquid (67%). MS (EI), $m/e$ 173 (88%, [M$^+$]), 159 (67%), 91 (23%), 84 (100%), 77 (28%); IR (NaCl) 3061, 3022, 2926, 2861, 1922, 1720, 1618, 1595, 1496, 1451, 1381, 1327, 1272, 1227, 1182, 1119, 1085, 1057, 1039, 989, 942, 770, 731, 589, 533 cm$^{-1}$; $^1$H NMR (200 MHz) $\delta$ 7.36–7.13 (m, 4H), 3.98–3.78 (m, 2H), 3.49–3.30 (m, 2H), 2.57 (s, 3H), 2.32 (s, 3H); $^{13}$C NMR (50 MHz) $\delta$ 167.4, 136.2, 131.4, 130.0, 128.9, 128.3, 125.5, 53.4, 53.0, 34.6, 19.2. HRMS (EI): calcd for $C_{11}H_{14}N_2$ [M$^+$]: 174.1157, found 174.1158.

#### 4.2.3. Synthesis of ionic liquids 4a–4f: General procedure

The particular 4,5-dihydro-1*H*-imidazole (5.2 mmol) was dissolved in dry acetonitrile (3 mL), and the electrophilic chloride [MOM-, MEM-, or (−)-menthyl chloride] was added (10.4 mmol). The solution was refluxed for 15 h. After cooling the solvent the remaining electrophile was distilled off. The remainder was dissolved in water (10 mL), and $LiNTf_2$ (7.8 mmol) in water (5 mL) was added. An organic phase separated immediately. The mixture was stirred for an additional 30 min. The water was decanted off and the ionic liquid was washed three times with water. Dichloromethane was added and the organic phase was dried over sodium sulfate. After distilling off the solvent, the ionic liquids were dried under high vacuum for at least 15 h at 50 °C.

**4.2.3.1. (*S*)-4-Isopropyl-3-(methoxymethyl)-1-methyl-2-phenyl-4,5-dihydro-1*H*-imidazol-3-ium bis(trifluoromethylsulfonyl) amide 4a.** As an orange solid (77%). Mp 39 °C; $[\alpha]_D^{25} = +20.1$ ($c$ 1.33, $CHCl_3$); MS (EI), $m/e$ 247 ([M$_{cation}$]$^+$, 100%), 203 (29), 159 (21), 118 (8), 77 (6); MS (ESI, 0 V) $m/e$ 247.3 ([M$_{cation}$]$^+$, 100%); IR (KBr) 3320, 2968, 1624, 1604, 1549, 1491, 1467, 1449, 1395, 1353, 1288, 1195, 1137, 1098, 1057, 944, 917, 788, 740, 700, 654, 617 cm$^{-1}$; $^1$H NMR (400 MHz) $\delta$ 7.81–7.49 (m, 5H), 4.60–

4.17 (m, 4H), 3.72 (dd, $J$ = 10.8, 7.2 Hz, 1H), 3.18 (s, 3H), 3.06 (s, 3H), 2.47–2.20 (m, 1H), 1.02 (d, $J$ = 0.9 Hz, 3H), 0.98 (d, $J$ = 1.3 Hz, 3H); $^{13}$C NMR (100 MHz) $\delta$ 167.7, 133.8, 130.0, 128.8, 121.1, 120.1 (q, $J_{CF}$ = 321 Hz), 78.1, 64.6, 56.4, 51.8, 34.8, 28.9, 17.7, 14.5. Anal. Calcd for $C_{17}H_{23}F_6N_3O_5S_2$: C, 38.71; H, 4.39; N, 7.97. Found: C, 38.58; H, 4.28; N, 8.04.

**4.2.3.2. (*S*)-4-Isopropyl-3-((2-methoxyethoxy)methyl)-1-methyl-2-phenyl-4,5-dihydro-1*H*-imidazol-3-ium bis(trifluoromethylsulfonyl)amide 4b.** As a yellow liquid (77%). $[\alpha]_D^{25} = +18.0$ ($c$ 1.29, $CHCl_3$); MS (EI), $m/e$ 291 ([M$_{cation}$]$^+$, 100%), 247 (11), 203 (13), 159 (23); MS (ESI, 0 V) $m/e$ 290.9 ([M$_{cation}$]$^+$, 100%); IR (KBr) 3308, 3067, 2968, 2883, 2360 1929, 1623, 1604, 1549, 1491, 1466, 1449, 1352, 1352, 1192, 1136, 1093, 1058, 787, 740, 700, 654, 616, 571, 513, 462, 444, 436 cm$^{-1}$; $^1$H NMR (400 MHz) $\delta$ 7.78–7.54 (m, 5H), 4.70 (d, $J$ = 10.9 Hz, 1H), 4.59 (d, $J$ = 10.9 Hz, 1H), 4.49 (ddd, $J$ = 12.0, 8.1, 3.6 Hz, 1H), 4.24 (t, $J$ = 12.0 Hz, 1H), 3.80 (dd, $J$ = 12.0, 8.1 Hz, 1H), 3.56–3.37 (m, 4H), 3.29 (s, 3H), 3.07 (s, 3H), 2.47–2.27 (m, 1H), 1.03 (d, $J$ = 1.8, 3H), 1.01 (d, $J$ = 2.0 Hz, 3H); $^{13}$C NMR (100 MHz) $\delta$ 167.3, 133.6, 129.9, 128.7, 120.9, 120.0 (q, $J_{CF}$ = 321 Hz,), 76.3, 71.5, 68.3, 63.6, 58.8, 51.5, 34.6, 28.1, 17.6, 14.2. Anal. Calcd for $C_{19}H_{27}F_6N_3O_6S_2$: C, 39.93; H, 4.76; N, 7.35. Found: C, 40.07; H, 4.76; N, 7.45.

**4.2.3.3. (*S*)-4-Isopropyl-3-(methoxymethyl)-1-methyl-2-*o*-tolyl-4,5-dihydro-1*H*-imidazol-3-ium bis(trifluoromethylsul-fonyl)amide (mixture of diastereomers, dr ~ 2:3) 4c.** As a yellow solid (73%). MS (EI), $m/e$ 261 ([M$_{cation}$]$^+$, 100%), 246 (2), 218 (13); MS (ESI, 0 V) $m/e$ 261.8 ([M$_{cation}$]$^+$, 100%); IR (KBr) 3306, 2963, 2771, 2683, 2593, 2366, 2194, 2017, 1930, 1847, 1770, 1625, 1550, 1467, 1350, 1284, 1052, 942, 916, 789, 772, 739, 699, 613, 569, 514 cm$^{-1}$; $^1$H NMR (400 MHz) (diastereomer 1, 40%) $\delta$ 7.66–7.25 (m, 4H), 4.65–4.18 (m, 4H), 3.86 (ddd, $J$ = 14.9, 12.1, 8.9 Hz, 1H), 3.18 (s, 3H), 2.98 (s, 3H), 2.43–2.34 (m, 1H), 2.33 (s, 3H), 1.09–0.97 (m, 6H); $^{13}$C NMR (100 MHz) (diastereomer 1, 40%) $\delta$ 167.8, 137.0, 133.4, 131.7, 128.2, 127.3, 120.5, 119.9 (q, $J_{CF}$ = 321 Hz), 76.9, 64.1, 56.7, 51.3, 34.08, 28.3, 18.8, 17.6, 14.3; $^1$H NMR (400 MHz) (diastereomer 2, 60%) $\delta$ 7.66–7.25 (m, 4H), 4.65–4.18 (m, 4H), 3.86 (ddd, $J$ = 14.9, 12.1, 8.9 Hz, 1H), 3.17 (s, 3H), 2.97 (s, 3H), 2.43–2.34 (m, 1H), 2.29 (s, 3H), 1.09–0.97 (m, 6H); $^{13}$C NMR (100 MHz) (diastereomer 2, 60%) $\delta$ 167.4, 136.3, 133.1, 131.5, 128.3, 127.4, 121.0, 119.9 (q, $J_{CF}$ = 321 Hz), 77.2, 63.8, 56.6, 51.1, 34.13, 27.7, 19.1, 17.8, 14.7. Anal. Calcd for $C_{18}H_{25}F_6N_3O_5S_2$: C, 39.92; H, 4.65; N, 7.76. Found: C, 40.17; H, 4.76; N, 7.73.

**4.2.3.4. (*S*)-4-Isopropyl-3-((2-methoxyethoxy)methyl)-1-methyl-2-*o*-tolyl-4,5-dihydro-1*H*-imidazol-3-ium bis(trifluoromethylsulfonyl)amide (mixture of diastereomers, dr ~ 1:1.1) 4d.** As a yellow liquid (62%). MS (EI), $m/e$ 261 305 ([M$_{cation}$]$^+$, 100%), 261 (9), 217 (11), 173 (11), 132 (2); MS (ESI, 0 V) $m/e$ 305.1 ([M$_{cation}$]$^+$, 100%); IR (NaCl) 3312, 3067, 2968, 2937, 2883, 2591, 2366, 1931, 1847, 1799, 1623, 1604, 1550, 1465, 1352, 1287, 1190, 1135, 1057, 985, 942, 890, 850, 788, 769, 7,39, 655, 617, 571, 513 cm$^{-1}$; $^1$H NMR (400 MHz) (diastereomer 1, 48%) $\delta$ 7.65–7.22 (m, 4H), 4.75–4.38 (m, 3H), 4.36–4.14 (m, 1H), 3.83 (dd, $J$ = 20.6, 10.6 Hz, 1H), 3.57–3.28 (m, 4H), 3.24 (s, 3H), 2.97 (s, 3H), 2.45–2.34 (m, 1H), 2.33 (s, 3H), 1.11–0.92 (m, 6H); $^{13}$C NMR (100 MHz) (diastereomer 1, 48%) $\delta$ 167.9, 137.3, 133.4, 131.85, 128.2, 127.4, 120.7, 119.9 (q, $J_{CF}$ = 321 Hz), 76.1, 71.8, 68.7, 63.8, 58.9, 51.4, 34.2, 28.2, 18.9, 17.7, 14.4; $^1$H NMR (400 MHz) (diastereomer 2, 52%) $\delta$ 7.65–7.22 (m, 4H), 4.75–4.38 (m, 3H), 4.36–4.14 (m, 1H), 3.83 (dd, $J$ = 20.6, 10.6 Hz, 1H), 3.57–3.28 (m, 4H), 3.25 (s, 3H), 2.96 (s, 3H), 2.45–2.34 (m, 1H), 2.26 (s, 3H), 1.11–0.92 (m, 6H); $^{13}$C NMR (100 MHz) (diastereomer 2, 52%) $\delta$ 167.4, 136.2, 133.2, 131.5, 128.5, 127.6, 121.0, 119.9 (q, $J_{CF}$ = 321 Hz), 75.8, 71.6, 68.6, 63.6, 59.0, 51.2, 34.2, 27.6, 19.3, 17.9, 14.8. Anal. Calcd for $C_{20}H_{29}F_6N_3O_6S_2$: C, 41.02; H, 4.99; N, 7.18. Found: C, 40.93; H, 4.85; N, 7.16.

**4.2.3.5. 3-(((1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyloxy)-methyl)-1-methyl-2-phenyl-4,5-dihydro-1*H*-imidazol-3-ium bis(trifluoromethylsulfonyl)amide 4e.** As a white solid (75%). Mp 58.5 °C; $[\alpha]_D^{25} = -39.7$ ($c$ 1.02, $CHCl_3$); MS (EI), $m/e$ 328 ([M$_{cation}$]$^+$, 100%), 190 (27), 174 (11), 163 (33), 119 (20); MS (ESI, 0 V) $m/e$ 250.1 (58%), 330.0 ([M$_{cation}$]$^+$, 5), 488.7 (100); IR (KBr) 3328, 3094, 3068, 2965, 2877, 2361, 1932, 1847, 1621, 1569, 1493, 1459, 1412, 1352, 1191, 1139, 1057, 935, 923, 850, 790, 774, 740, 708, 657, 619, 601, 570, 507 cm$^{-1}$; $^1$H NMR (400 MHz) $\delta$ 7.74–7.49 (m, 5H), 4.60 (d, $J$ = 10.4 Hz, 1H), 4.55 (d, $J$ = 10.4 Hz, 1H), 4.16 (s, 4H), 3.01 (s, 3H), 3.01–2.92 (m, 1H), 2.08–1.92 (m, 1H), 1.67–1.49 (m, 3H), 1.26–1.08 (m, 2H), 0.94–0.86 (m, 1H), 0.84 (d, $J$ = 7.0 Hz, 3H), 0.79 (d, $J$ = 6.5 Hz, 3H), 0.77–0.64 (m, 2H), 0.63 (d, $J$ = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz) $\delta$ 166.9, 133.5, 129.8, 128.6, 120.9, 119.9 (q, $J_{CF}$ = 321 Hz), 77.5, 74.8, 50.8, 47.9, 46.9, 39.8, 34.7, 34.1, 31.2, 25.4, 22.9, 22.0, 20.9, 15.8. HRMS (ESI): calcd for $C_{21}H_{33}N_2O$ [M$^+_{cation}$]: 329.2593, found 329.2597.

**4.2.3.6. 3-(((1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyloxy)-methyl)-1-methyl-2-*o*-tolyl-4,5-dihydro-1*H*-imidazol-3-ium bis(trifluoromethylsulfonyl)amide (mixture of diastereomers, dr ~ 1:1.2) 4f.** As a colorless liquid (69%). MS (EI), $m/e$ 343 ([M$_{cation}$]$^+$, 100%), 329 (2), 203 (39), 175 (54); MS (ESI, 0 V) $m/e$ 343.0 ([M$_{cation}$]$^+$, 97%); IR (NaCl) 3324, 3066, 2957, 2929, 2873, 2725, 2597, 2378, 2191, 1929, 1846, 1798, 1620, 1604, 1558, 1490, 1457, 1354, 1294, 1183, 1138, 1058, 935, 844, 788, 766, 740, 655, 617, 571, 513 cm$^{-1}$; $^1$H NMR (400 MHz) (diastereomer 1, 45.5%) $\delta$ 7.60–7.44 (m, 1H), 7.46–7.31 (m, 3H), 4.60–4.36 (m, 2H), 4.31–4.07 (m, 4H), 3.03–2.84 (m, 4H), 2.26 (d, $J$ = 2.3, 3H), 2.04–1.78 (m, 1H), 1.64–1.44 (m, 3H), 1.27–1.03 (m, 2H), 0.94–0.82 (m, 1H), 0.81–0.72 (m, 7H), 0.71–0.62 (m, 1H), 0.53 (d, $J$ = 3.4 Hz, 3H); $^{13}$C NMR (100 MHz) (diastereomer 1, 45.5%) $\delta$ 167.0, 136.7, 133.0, 131.4, 128.4, 127.2, 120.5, 119.9 (q, $J_{CF}$ = 321 Hz), 77.3, 74.5, 50.4, 47.9, 31.3, 25.2, 22.8, 21.9, 20.8, 18.8, 15.6; $^1$H NMR (400 MHz) (diastereomer 2, 54.5%) $\delta$ 7.60–7.44 (m, 1H), 7.46–7.31 (m, 3H), 4.60–4.36 (m, 2H), 4.31–4.07 (m, 4H), 3.03–2.84 (m, 4H), 2.26 (d, $J$ = 2.3, 3H), 2.04–1.78 (m, 1H), 1.64–1.44 (m, 3H), 1.27–1.03 (m, 2H), 0.94–0.82 (m, 1H), 0.81–0.72 (m, 7H), 0.71–0.62 (m, 1H), 0.59 (d, $J$ = 3.6 Hz, 3H); $^{13}$C NMR (100 MHz) (diastereomer 2, 54.5%) $\delta$ 166.9, 136.9, 133.0, 131.4, 128.2, 127.1, 120.5, 119.9 (q, $J_{CF}$ = 321 Hz), 77.4, 74.5, 50.5, 47.9, 31.1, 25.3, 22.8, 21.9, 20.8, 18.7, 15.7. Anal. Calcd for $C_{24}H_{35}F_6N_3O_5S_2$: C, 46.22; H, 5.66; N, 6.74. Found: C, 45.89; H, 5.83; N, 6.89.

**4.2.3.7. (*S*)-3-Ethyl-4-isopropyl-1-methyl-2-*o*-tolyl-4,5-dihydro-1*H*-imidazol-3-ium iodide (mixture of diastereomers, dr ~ 1:1) 5.** As a yellow solid (46%). MS (EI), $m/e$ 245 ([M$_{cation}$]$^+$, 46%), 216 (8), 173 (52), 132 (5), 119 (67), 91 (26), 84 (100), 51 (51); MS (ESI, 0 V) $m/e$ 245.2 ([M$_{cation}$]$^+$, 100%), 617.2 (2[M$_{cation}$]$^+$ + [M$_{anion}$]$^-$, 40%); IR (KBr) 3427, 2959, 2872, 1601, 1561, 1487, 1457, 1416, 1397, 1380, 1345, 1274, 1209, 1163, 1112, 1096, 1075, 1042, 947, 811, 788, 732, 595 cm$^{-1}$; $^1$H NMR (400 MHz) (diastereomer 1) $\delta$ 8.19 (dd, $J$ = 7.6, 1.0, 1H), 7.62–7.37 (m, 3H), 4.94–4.77 (m, 1H), 4.67 (dd, $J$ = 12.8, 11.3, 1H), 3.75 (dd, $J$ = 11.1, 8.7, 1H), 3.36–3.22 (m, 2H), 3.04 (s, 3H), 2.48 (s, 3H), 2.43–2.31 (m, 1H), 1.27 (t, $J$ = 7.3, 3H), 1.10–1.02 (m, 6H); $^{13}$C NMR (100 MHz) (diastereomer 1) $\delta$ 166.1, 135.0, 133.0, 131.9, 129.8, 127.4, 121.5, 63.2, 51.0, 40.7, 34.7, 26.9, 20.5, 18.2, 15.2, 13.0; $^1$H NMR (400 MHz) (diastereomer 2) $\delta$ 7.62–7.37 (m, 3H), 7.23 (d, $J$ = 7.7, 1H), 4.94–4.77 (m, 2H), 3.89 (dd, $J$ = 10.0, 5.9, 1H), 3.36–3.22 (m, 1H), 3.16 (dq, $J$ = 14.6, 7.4, 1H), 2.97 (s, 3H), 2.43–2.31 (m, 1H), 2.29 (s, 3H), 1.23 (t, $J$ = 7.3, 3H), 1.10–1.02 (m, 6H); $^{13}$C NMR (100 MHz) (diastereomer 2) $\delta$ 165.9, 137.0, 132.5, 130.9, 127.7, 127.6, 122.0, 63.5, 51.4, 40.1, 34.6,

27.6, 19.3, 17.9, 14.8, 13.5. HRMS (ESI): calcd for $C_{16}H_{25}N_2$ [$M^+_{cation}$]: 245.2018, found 245.2023.

**4.2.3.8. 3-Butyl-1-methyl-2-phenyl-4,5-dihydro-1*H*-imidazol-3-ium chloride 6.** As an orange, highly hygroscopic solid (65%). MS (EI), *m/e* 217 ([$M_{cation}$]$^+$, 100%), 77 (54), 57 (24); MS (ESI, 0 V) *m/e* 217.3 ([$M_{cation}$]$^+$, 100%); IR (KBr) 3412, 2960, 2933, 2873, 2427, 1607, 1574, 1491, 1462, 1446, 1375, 1299, 1077, 1029, 932, 774, 707, 657, 637, 535 cm$^{-1}$; $^1$H NMR (200 MHz) $\delta$ 7.88–7.74 (m, 2H), 7.73–7.54 (m, 3H), 4.51–4.18 (m, 4H), 3.30 (t, $J$ = 7.4 Hz, 2H), 3.05 (s, 3H), 1.73–1.50 (m, 2H), 1.25 (dq, $J$ = 14.2, 7.2 Hz, 2H), 0.81 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (50 MHz) $\delta$ 165.6, 132.1, 129.1, 128.2, 121.4, 50.3, 47.7, 47.2, 34.5, 28.5, 19.0, 12.8. HRMS (ESI): calcd for $C_{14}H_{21}N_2$ [$M^+_{cation}$]: 217.1705, found 217.1700.

**4.2.3.9. 3-Butyl-1-methyl-2-phenyl-4,5-dihydro-1*H*-imidazol-3-ium ((1*S*,4*S*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonate 7.** Salt **6** (29.4 mmol) was dissolved in dichloromethane (50 mL). This solution was added to (−)-camphor-10-sulfonic acid ammonium salt (29.4 mmol) in water (15 mL). The mixture was stirred for 1 h at rt. The aqueous phase was discarded. The organic phase was washed three times with a minimum amount of water. The organic phase was dried over sodium sulfate. After evaporating the solvent, ionic liquid **7** was obtained as a yellow liquid (86%). $[\alpha]_D^{25} = -19.2$ ($c$ 1.43, $CHCl_3$); MS (EI), *m/e* 217 ([$M_{cation}$]$^+$, 100%), 77 (94); MS (ESI, 0 V) *m/e* 217.3 ([$M_{cation}$]$^+$, 100%), 665.2 (2[$M_{cation}$]$^+$ + [$M_{anion}$]$^-$, 30%); IR (KBr) 3465, 3056, 2959, 2876, 2478, 1741, 1607, 1575, 1468, 1417, 1300, 1174, 1038, 934, 855, 773, 708, 616, 582, 530 cm$^{-1}$; $^1$H NMR (400 MHz) $\delta$ 7.71–7.54 (m, 5H), 4.40–4.29 (m, 2H), 4.29–4.17 (m, 2H), 3.34 (d, $J$ = 14.7 Hz), 3.27 (t, $J$ = 7.6 Hz, 2H), 3.01 (s, 3H), 2.88–2.76 (m, 1H), 2.81 (d, $J$ = 14.7 Hz, 1H), 2.31 (dt, $J$ = 18.1, 3.9 Hz, 1H), 2.08–1.92 (m, 2H), 1.86 (d, $J$ = 18.1 Hz, 1H), 1.79–1.66 (m, 1H), 1.54 (quintuplett, $J$ = 7.6 Hz, 2H, C$H_2$)), 1.42–1.29 (m, 1H), 1.26–1.16 (sextett, $J$ = 7.6 Hz, 2H), 1.14 (s, 3H), 0.84 (s, 3H), 0.81 (t, $J$ = 7.3 Hz, 3H); $^{13}$C NMR (100 MHz) $\delta$ 217.0, 166.3, 132.4, 129.6, 128.4, 122.3, 58.5, 50.5, 48.0, 47.7, 47.5, 46.8, 42.9, 42.5, 34.6, 29.0, 27.0, 24.4, 20.1, 19.8, 19.4, 13.4. HRMS (ESI): calcd for $C_{14}H_{21}N_2$ [$M^+_{cation}$]: 217.1705, found 217.1705.

### 4.2.4. Grignard addition to aldehydes: General procedure

Phenylmagnesiumbromide solution (2.5 mL, 1 M in THF) was placed in a Schlenk tube. The solvent was distilled off, and the remaining solid was dried under high vacuum for at least 1 h. Ionic liquid was added and the mixture was heated to 40 °C. The aldehyde was added afterwards and the mixture was stirred for 3 h. Saturated ammonium chloride solution (2.5 mL) was added and the mixture was stirred for 15 min. The mixture was extracted several times with *n*-hexane. The combined organic phases were dried over sodium sulfate. After distilling off the solvent, the raw alcohols were purified by flash column chromatography (eluent PE/EE = 20:1). *The ionic liquids were recycled as follows*: After extraction of the raw product with *n*-hexane, dichloromethane was added to the remaining mixture. The two phases were separated and the organic phase was washed five times with water. The organic phase was afterwards dried over sodium sulfate and the solvent was distilled off. The recycled ionic liquids were dried under high vacuum.

### 4.3.3. Grignard addition to aldehydes in the presence of Lewis acid: General procedure

Phenylmagnesiumbromide solution (2.5 mL, 1 M in THF, 3 equiv) was placed in a Schlenk tube. The solvent was distilled off, and the remaining solid was dried under high vacuum for at least 1 h. Lewis acid (0.1 equiv) and ionic liquid **4a** (6 equiv) were added and the mixture was heated to 40 °C. Hexanal (1 equiv) was added afterwards and the mixture was stirred for 3 h. Work-up was as described above.

**4.3.3.1. 1-Phenylhexan-1-ol.** As a slightly yellow oil. $^1$H NMR (200 MHz) $\delta$ 7.34–7.10 (m, 5H), 4.53 (dd, $J$ = 7.2, 6.1 Hz, 1H), 2.27 (br s, 1H), 1.81–1.46 (m, 2H), 1.32–1.10 (m, 6H), 0.78 (t, $J$ = 6.4 Hz, 3H); $^{13}$C NMR (50 MHz) $\delta$ 145.0, 128.4, 127.4, 125.9, 74.6, 39.1, 31.8, 25.5, 22.6, 14.1. The spectral data were consistent with literature values.[44]

**4.3.3.2. Naphthalen-1-yl(phenyl)methanol.** As a white solid. $^1$H NMR (200 MHz) $\delta$ 8.10–7.91 (m, 1H), 7.92–7.69 (m, 2H), 7.60 (d, $J$ = 6.7, 1H), 7.53–7.14 (m, 8H), 6.48 (s, 1H), 2.43 (s, 1H); $^{13}$C NMR (50 MHz) $\delta$ 143.3, 138.9, 134.1, 130.8, 128.9, 128.7, 128.6, 127.8, 127.2, 126.3, 125.7, 125.5, 124.8, 124.1, 73.8. The spectral data were consistent with literature values.[45]

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