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Easily Accessible Chiral Imidazolinium Salts Bearing Two Hydroxy-Containing Substituents as Shift Reagents and Carbene Precursors

Václav Jurčík,[a] Mazhar Gilani,[a] and René Wilhelm*[a]

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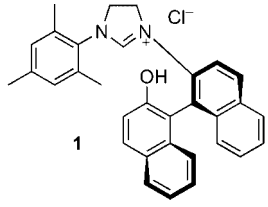
The behavior of new enantiopure imidazolinium salts bearing two hydroxy-containing substituents as chiral shift reagents and as carbene precursors for diethylzinc addition to aldehydes is presented. The new hydroxy-containing imidazolinium salts can be prepared in a few steps from amino alcohols and qualify as new tridentate ligands and ionic liquids.

Introduction

N-Heterocyclic carbenes (NHCs) have found an important role as ligands in various applications in organometallic chemistry in recent years.[1–3] In addition, various carbenes themselves can be used as organocatalysts.[4–6] The precursors of the corresponding carbenes are salts, some of which have been found to be ionic liquids, and recently a few examples of chiral ionic liquids based on chiral imidazolinium cations have been reported.[7,8] The examples of this class of chiral ionic liquids remain few in number in relation to other types of chiral ionic liquids.[9–11]

Examples of chiral imidazolinium and imidazolium salts incorporating substituents bearing hydroxy groups are rather rare. These salts act as precursors for bidentate ligands and can also be used as ionic liquids.[7] An interesting bidentate hydroxy-carbene ligand based on salt **1** was recently described by Hoveyda et al.[12] and applied with ruthenium in an asymmetric olefin metathesis, giving *ee*s of up to 96%. In addition, the carbene ligand was also investigated in a copper-catalyzed allylic alkylation, which gave the desired product in up to 98% *ee*. Furthermore, Arnold's group has synthesized salt **2**, a Cu^{I} complex with this carbene ligand having been isolated[13,14] and used as a catalyst in a diethylzinc conjugated addition to cyclohexenone, resulting in *ee*s of up to 51%. Very recently, Mauduit's group has reported the synthesis of salt **3** and has shown it to be possible to use this as a shift reagent for potassium Mosher's salt, with splittings of 60 Hz in ^{1}H NMR and 63 Hz in ^{19}F NMR spectroscopy.[7] Furthermore, the same group has also prepared salt **4** and various analogues based on different amino alcohols.[15,16] These salts were used as carbene precursors in the Cu^{II}-catalyzed addition of diethylzinc to cyclohexenone, with *ee*s of up to 93% being achieved. Moreover, the groups of Mauduit and Alexakis have used salts of type **4** together with other chiral imidazolinium salts in copper-catalyzed conjugated Grignard additions to 3-substituted cyclohexenones in order to create quaternary chiral centers, and have achieved *ee*s of up to 96%.[17]



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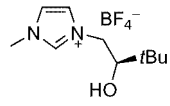

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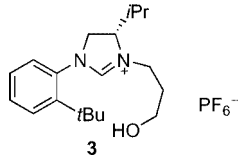

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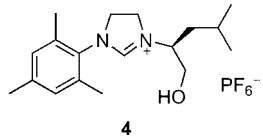

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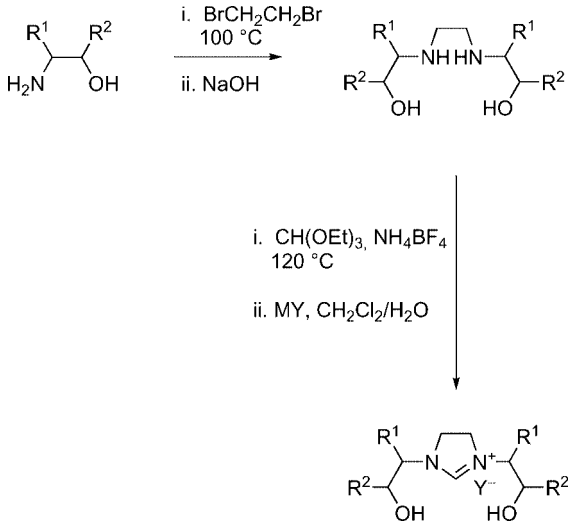
Because of our interest in imidazolinium salts as ionic liquids[18] and catalysts[19–21] we were keen to synthesize and investigate chiral imidazolinium salts incorporating two hydroxy groups on their substituents. These salts can be prepared by the route shown in Scheme 1, and their behavior as shift reagents and carbene ligands is presented here.

Results and Discussion

The appropriate bis(amino alcohol)s were first prepared from amino alcohols and 1,2-dibromoethane by a literature procedure,[22] as shown in Scheme 1. Bis(amino alcohol) **5**, derived from (–)-norephedrine, was isolated in 79% yield, while *ent*-**5** was prepared from (+)-norephedrine in the same

[a] Institute of Organic Chemistry, Clausthal University of Technology,
Leibnizstrasse 6, 38678 Clausthal-Zellerfeld, Germany
Fax: +49-5323-722834
E-mail: rene.wilhelm@tu-clausthal.de



Scheme 1.

yield. The bis(amino alcohol) **6** was obtained in 77% yield from L-valinol in 77% yield, while **7** was isolated in 91% yield after treatment of L-*tert*-leucinol with dibromoethane. Finally, bis(amino alcohol) **8** was isolated in 75% yield by starting from (–)-(1*R*,2*R*)-2-amino-1-phenylpropane-1,3-diol. The bis(amino alcohol) **9** was prepared from (1*R*,2*R*)-*trans*-diaminocyclohexane and cyclohexene oxide as described in the literature.[23]

The imidazolinium salts were prepared by direct treatment of the bis(amino alcohol)s with triethyl orthoformate in the presence of NH_4BF_4 as shown in Scheme 1. Optionally, more lipophilic anions could be introduced by counteranion exchange in a mixture of chloroform and water. The reaction proceeded in high yields, as shown in Table 1. In some cases anion exchange with $LiNTf_2$ was performed, although only moderate yields were achieved here (Table 1, Entries 5 and 7). Salts **12B**, **13A**, **13C**, and **14A** could qualify as ionic liquids, since their melting points are below 100 °C,[24] while salts **10B**, **10C**, **11A**, **11B**, and **12A** could qualify as room-temperature ionic liquids.

In view of previous reports of the use of thiazolinium-,[25] imidazolinium-,[7] or ammonium-based[26] chiral ionic liquids as chiral shift reagents, and also of our investigations with chiral bis(imidazolinium)-based salts,[19] several of the prepared salts were tested for their ability to interact with Mosher's carboxylate, by examination of differences in the chemical shifts of the OMe group and the CF_3 group in the two enantiomers of Mosher's carboxylate. For these experiments, enantioenriched (12% *ee*, in order to permit the assignment of signals to the corresponding enantiomers) potassium Mosher's carboxylate **15** was mixed with the chiral imidazolinium salts in different ratios (the mixtures were dissolved in [D_6]acetone) and ^{1}H NMR and ^{19}F NMR spectra were recorded. The results are summarized in Table 2.

When enantiopure salt **10A** with a BF_4^- counteranion was used in combination with Mosher's carboxylate (Table 2, Entry 2), no signal splitting was seen either in the ^{1}H NMR or in the ^{19}F NMR spectra. On changing the counteranion to NTf_2^-, a significant increase in the splitting, to 12 Hz in the ^{1}H NMR and 118 Hz in the ^{19}F NMR, was observed (Table 2, Entry 3). A picture of these spectra is shown in Figure 1. This splitting could not be improved by use of an excess of the imidazolinium salt (Table 2, Entry 4), but the splitting was increased further, to 24 in the ^{1}H NMR and 151 Hz in the ^{19}F NMR spectra, with a change in the counteranion to $B[C_6H_3(CF_3)_2]_4^-$ (Table 2, Entry 5). To the best of our knowledge this is the largest

Table 1. Preparation of imidazolinium salts containing hydroxylated substituents.

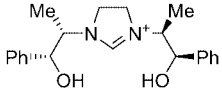
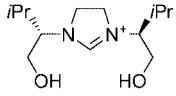
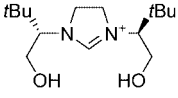
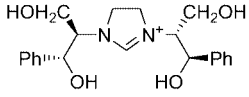
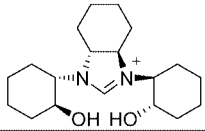
Entry	Diamine	Cation	Anion	Salt	Yield (%)
1	**5**		BF_4^-	**10A**	87
2	**5**		NTf_2^-	**10B**	93
3	**5**		$B[C_6H_3(CF_3)_2]_4^-$	**10C**	85
4	**6**		BF_4^-	**11A**	94
5	**6**		NTf_2^-	**11B**	52
6	**7**		BF_4^-	**12A**	88
7	**7**		NTf_2^-	**12B**	59
8	**8**		BF_4^-	**13A**	98
9	**8**		$B[C_6H_3(CF_3)_2]_4^-$	**13C**	80
10	**9**		BF_4^-	**14A**	93

Table 2. Chemical shifts δ of Mosher's carboxylate in ppm and $\Delta\delta$ values in Hz (400 MHz NMR spectroscopy).

Entry	Salt	Ratio	$\delta(^1H)$		$\delta(^{19}F)$		$\Delta\delta(^1H)$	$\Delta\delta(^{19}F)$
			(*S*)	(*R*)	(*S*)	(*R*)		
1	–	N/A	3.54	3.54	–71.59	–71.59	0	0
2	**10A**	1:1	3.54	3.54	–71.59	–71.59	0	0
3	**10B**	1:1	3.55	3.52	–70.90	–71.22	12	118
4	**10B**	3:1	3.55	3.52	–70.90	–71.22	12	118
5	**10C**	1:1	3.50	3.56	–71.39	–70.99	24	151
6	**11A**	1:1	3.590	3.587	–71.65	–71.70	1.2	18
7	**11B**	1:1	3.58	3.58	–71.63	–71.60	0	15
8	**13C**	1:1	3.55	3.55	–71.52	–71.50	0	7
9	**14A**	1:1	3.60	3.60	–71.32	–71.41	0	32

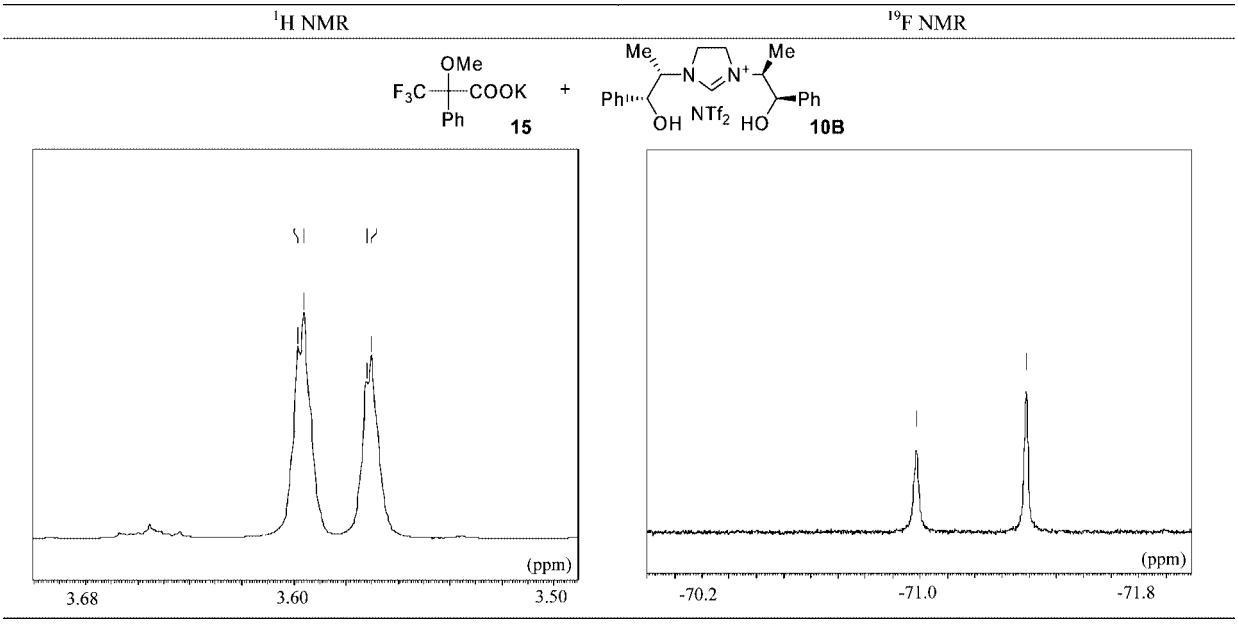
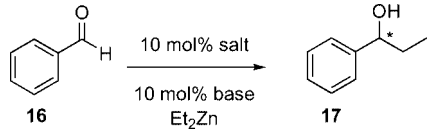


Figure 1. NMR spectra of salt **10B** with potassium Mosher's carboxylate (**15**).

reported ^{19}F NMR signal splitting obtained with an imidazolinium salt.

Salt **11A** showed a poor splitting, 1.2 Hz in the ^{1}H NMR and 18 Hz in the ^{19}F NMR (Table 2, Entry 6), while a change in the counteranion to NTf_2^- did not in this case result in any improved splitting (Table 2, Entry 7). Salt **13C**, with a $B[C_6H_3(CF_3)_2]_4^-$ moiety, showed no splitting in its ^{1}H NMR spectrum and a poor splitting of 7 Hz in its ^{19}F NMR spectrum (Table 2, Entry 9), while the BF_4^- salt **14A** displayed a splitting of 32 Hz in its ^{19}F NMR signal. An upfield shift of the signal in the ^{1}H NMR indicated interactions between the imidazolinium cation and the Mosher's salt, but no stereodiscrimination was observed (Table 2, Entry 9).

In order to demonstrate that the new imidazolinium salts bearing two hydroxy-containing substituents are potential new carbene ligands, they were tested in diethylzinc addition to aldehydes. This enantioselective C–C bond formation for the preparation of optically active secondary alcohols has been intensely studied with various catalytic systems.[27–29] The salts were first tested in the addition of diethylzinc to benzaldehyde (**16**), as shown in Scheme 2, the reactions being performed at room temperature and different solvents being tested. The results are summarized in Table 3.



Scheme 2.

In order to generate the carbene, imidazolinium salt **14A** was deprotonated with *t*BuOK in a PhMe solution. After 5 min of stirring, Et_2Zn (1.1 equiv.) was added, followed by benzaldehyde (1 equiv.). After 30 h of stirring at room temp. and quenching of the reaction mixture with HCl (1 M), the product was isolated in 67% yield and showing 66% *ee* (Table 3, Entry 2). When no base was present, no reaction occurred, indicating that the carbene generation is essential for the reaction to proceed (Table 3, Entry 1). The mechanism of the reaction has been thoroughly examined in the case of β-amino alcohol ligands.[30,31] In the present case, the carbene unit is probably taking over the role of the amine substituent of a β-amino alcohol.

Table 3. Addition of Et_2Zn to benzaldehyde (**16**).

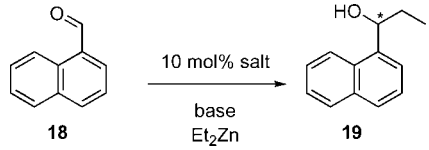
Entry	Catalyst	Solvent	Base	Yield [%]	*ee* [%]	Configuration
1	**14A**	PhMe	–	0	–	–
2	**14A**	PhMe	*t*BuOK	67	66	(*R*)
3	**10A**	THF	*t*BuOK	traces	–	–
4	**10A**	DME	*t*BuOK	0	–	–
5	**10A**	dioxane	*t*BuOK	0	–	–
6	***ent*-10A**	PhMe	*t*BuOK	57	40	(*S*)
7	**11A**	PhMe	*t*BuOK	38	35	(*R*)
8	**12A**	PhMe	*t*BuOK	70	8	(*R*)

Table 4. Addition of Et_2Zn to 1-naphthaldehyde (**18**).

Entry	Catalyst	Base	*T* [°C]	Yield [%]	*ee* [%]	Configuration
1	**10A**	*t*BuOK (0.1 equiv.)	room temp.	61	60	(*R*)
2	**10A**	KHMDS (0.1 equiv.)	room temp.	92	45	(*R*)
3	**10A**	KHMDS (0.2 equiv.)	room temp.	84	45	(*R*)
4	**10A**	KHMDS (0.3 equiv.)	room temp.	78	31	(*R*)
5	**10A**	KHMDS (0.1 equiv.)	–5	85	55	(*R*)
6	**10A**	KHMDS (0.1 equiv.)	–78	traces	–	–
7	**10A**	NaHMDS (0.1 equiv.)	room temp.	80	47	(*R*)
8	**10A**	LiHMDS (0.1 equiv.)	room temp.	76	36	(*R*)
9	**13A**	KHMDS (0.1 equiv.)	room temp.	60	33	(*R*)
10	**14A**	KHMDS (0.1 equiv.)	–25	58	25	(*R*)

Next, salt **13A** was tested in various solvents. In DME and dioxane the reaction did not give any product, while a reaction in THF gave only traces (Table 3, Entries 3–5). Finally, the reaction in PhMe gave the corresponding product in 57% yield and with 40% *ee* (Table 3, Entry 6). The L-valinol-based compound **11A** gave the alcohol **17** in 38% yield and with 35% *ee* (Table 3, Entry 7). Changing the *i*Pr groups to *t*Bu groups in catalyst **12A** resulted in an increase of the yield to 70% but an *ee* of only 8% was detected (Table 3, Entry 8).

1-Naphthaldehyde (**18**) was also used, as shown in Scheme 3, and the influence of different bases was investigated. The results are presented in Table 4.



Scheme 3.

When the reaction was conducted with catalyst **10A** in the presence of *t*BuOK as a base, the corresponding alcohol **19** was isolated in 61% yield and with 60% *ee* (Table 4, Entry 1). Changing the base to KHMDS resulted in a dramatic increase in the yield to 92%, but the *ee* decreased to 45% (Table 4, Entry 2). Use of 2 and 3 equiv. of the base resulted in decreases in the yield to 84 and 78%, respectively, while in the case of 3 equiv. the *ee* dropped to 31% (Table 4, Entries 3 and 4). If the reaction temperature was decreased to –5 °C, the yield decreased slightly to 85%, but the *ee* increased to 55% (Table 4, Entry 5). After a further reduction in temperature to –78 °C, only traces of compound **19** were isolated (Table 4, Entry 6). Performing the reaction with use of different hexamethyldisilazane salts resulted in yields of 80 and 76% and *ee*s of 47 and 33% (Table 4, Entries 7 and 8), showing that potassium is the best countercation for this type of reaction.

In order to show that the formed carbenes were stable under the optimized conditions, salt **10A** was dissolved in toluene. After the addition of *t*BuOK, diethylzinc was added and the solution was stirred overnight. After aqueous workup and extraction, salt **10A** was recovered and identified by ^{1}H NMR spectroscopy.

Conclusion

We have presented the preparation of a series of new, enantiopure imidazolinium salts bearing two hydroxylated substituents, which were shown to be efficient and reusable shift reagents for Mosher's carboxylate. In addition, they can be used as carbene ligands for the enantioselective addition of Et_2Zn to aldehydes and also qualify as new chiral ionic ligands. Further applications of this new class of potential tridentate ligands are currently being investigated in our group, and these will be reported soon.

Experimental Section

General Experimental: Flash column chromatography[32] was performed on Sorbisil C-60. Reactions were monitored by TLC on Merck silica gel 60 F254 plates. Elemental analysis were carried out by the Microanalytical Laboratory of the Institut für Pharmazeutische Chemie der Technische Universität Braunschweig with an Elemental Analyzer Model 1106 from Carlo Erba Instrumentazione. Infrared spectra were recorded with a Bruker Vektor 22 FTIR spectrometer, as KBr pellets in cases of solid compounds and as thin films between NaCl plates in cases of oils and liquids. ^{1}H NMR spectra were recorded at ambient temperature

with Bruker AMX 400 (400 MHz) and AC 200F (200 MHz) instruments with tetramethylsilane as internal standard. ^{13}C NMR spectra were recorded at ambient temperature with Bruker AMX 400 (100 MHz) and AC 200F (50 MHz) instruments and ^{19}F NMR spectra were recorded at ambient temperature with a Bruker AMX 400 (378 MHz) instrument. Mass spectra (ESI) were recorded with a Hewlett–Packard MS LC/MSD Series 1100 MSD instrument, while high-resolution mass spectra were measured with a Bruker Daltonik Tesla–Fourier Transform-Ion Cyclotron Resonance Mass Spectrometer. Melting points were taken with a Dr. Tottoli apparatus and are uncorrected. Reactions were performed under nitrogen. All solvents were dried by standard procedures before used in the reactions. L-Valinol,[33] L-*tert*-leucinol,[34] sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate,[35] (1*R*,2*S*)-2-({2-[(1*S*,2*R*)-2-hydroxy-1-methyl-2-phenylethylamino]ethyl}-amino)-1-phenylpropan-1-ol (**5**)[22] and compound **9**[23] were prepared according to literature procedures. (–)-Norephedrine, (+)-norephedrine, (–)-(1*R*,2*R*)-amino-1-phenylpropane-1,3-diol, aldehydes, potassium *tert*-butoxide, lithium bis(trifluoromethylsulfonyl)imide, and diethylzinc were purchased from Aldrich. Mosher's reagent was purchased from Lancaster.

Preparation of Diamines

General Procedure for the Preparation of Diamines by Alkylation with $BrCH_2CH_2Br$:[22] An amino alcohol (1.00 mmol) and dibromoethane (87 μL, 0.50 mmol) were placed in a pressure vessel, which was flushed with nitrogen and sealed. The reaction mixture was heated at 100 °C for 10 h, during which the reaction mixture solidified. After the system had cooled to room temp., the solid was dissolved in water (10 mL) and the aqueous phase was washed with $CHCl_3$ (3 × 3 mL). The aqueous phase was basified with NaOH (40 mg, 1 equiv.) and the precipitated free base was extracted with $CHCl_3$ (3 × 5 mL). The combined organic fractions were dried (Na_2SO_4) and the solvent was removed under reduced pressure to give the pure bis(amino alcohol).

(1*S*,2*R*)-2-[(2-{[(1*R*,2*S*)-2-Hydroxy-1-methyl-2-phenylethyl]amino}-ethyl)amino]-1-phenylpropan-1-ol (*ent*-5): This compound was prepared from (+)-norephedrine (5.01 g, 33.00 mmol) and dibromoethane (1.42 mL, 16.50 mmol), after basification with NaOH (2 M, 14.00 mL, 28.00 mmol), as a yellow oil (4.15 g, 79%). Spectral data are consistent with literature values.[36]

(*S*)-2-[(2-{[(*S*)-1-(Hydroxymethyl)-2-methylpropyl]amino}ethyl)-amino]-3-methylbutan-1-ol (6): This compound was prepared from L-valinol (1.23 g, 11.90 mmol) and dibromoethane (513 μL, 5.95 mmol), after basification with NaOH (2 M, 5.10 mL, 10.20 mmol), as a yellow oil (1.06 g, 77%). $[\alpha]_D^{22}$ = +14.3 (*c* = 0.65, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 3.67–3.59 (m, 2 H), 3.42–3.33 (m, 2 H), 2.90–2.50 (m, 4 H), 2.40–2.25 (m, 2 H), 1.90–1.70 (m, 2 H), 1.01–0.85 (m, 12 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 65.2, 62.0, 47.4, 29.4, 20.1, 18.7 ppm. IR (neat): $\tilde{\nu}$ = 3314 s, 2958 s, 2873 s, 1467 s, 1052 s, 452 s cm^{-1}. MS (ESI = 0 V): *m/z* (%) = 233.3 (100) $[M + H]^+$. The preparation of this compound by the reduction of a bis(amide) had previously been reported,[37] but no spectroscopic data were provided.

(*S*)-2-[(2-{[(*S*)-1-(Hydroxymethyl)-2-methylpropyl]amino}ethyl)-amino]-3-methylbutan-1-ol (7): This compound was prepared from L-*tert*-leucinol (2.00 g, 17.10 mmol) and dibromoethane (740 μL, 8.55 mmol), after basification with NaOH (2 M, 8.55 mL, 17.10 mmol), as a white solid (2.01 g, 91%). For elemental analysis the diamine was crystallized from EtOH; m.p. 53 °C. $[\alpha]_D^{22}$ = +53.8 (*c* = 0.34, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.71 (dd, *J* = 3.52, 10.6 Hz, 2 H), 3.55–3.42 (m, 2 H), 3.08 (d, *J* = 8.6 Hz), 2.73 (d, *J* = 8.6 Hz), 2.34 (dd, *J* = 3.52, 10.6 Hz, 2 H), 0.97 (s, 18 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 67.9, 62.9, 49.7, 34.4, 27.2 ppm. IR (KBr): $\tilde{\nu}$ = 3314 s, 2958 s, 2873 s, 1467 s, 1052 s, 452 s cm^{-1}. MS (EI): *m/z* (%) = 261 (10) $[M + H]^+$, 229 (15), 203 (25), 144 (25), 130 (100), 100 (50), 86 (50), 74 (40), 57 (45). HRMS (ESI): calcd. for $C_{14}H_{33}N_2O_2$ 261.2542; found 261.2546. $C_{14}H_{32}N_2O_2$ (260.4): C 64.57, H 12.39, N 10.76; found C 64.44, H 12.54, N 10.88.

(1*R*,1′*R*,2*R*,2′*R*)-2,2′-[Ethane-1,2-diylbis(azanediyl)]bis(1-phenylpropane-1,3-diol) (8): This compound was prepared from (–)-(1*R*,2*R*)-2-amino-1-phenylpropane-1,3-diol (1.15 g, 6.89 mmol) and dibromoethane (296 μL, 3.45 mmol) as a yellow oil (930 mg, 75%). $[\alpha]_D^{22}$ = –78.2 (*c* = 0.28, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.30 (m, 10 H), 4.60 (d, *J* = 7.6 Hz, 2 H), 3.65–3.55 (m, 2 H), 3.35–3.25 (m, 2 H), 2.80–2.60 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.0, 128.5, 127.8, 126.7, 73.8, 64.8, 60.2, 46.8 ppm. IR (neat): $\tilde{\nu}$ = 3356 vs, 2882 s, 1454 s, 1027 s, 759 vs, 702 vs cm^{-1}. MS (ESI = 0 V): *m/z* (%) = 361.0 (70) $[M + H]^+$. HRMS (ESI): calcd. for $C_{20}H_{29}N_2O_4$ 361.2127; found 361.2122.

General Procedure for Preparation of Imidazolium Tetrafluroborate Salts: A bis(amino alcohol) (1.00 mmol) was placed in a flask, and the counteranion source (typically NH_4BF_4, 1.00 mmol) and either triethyl orthoformate (148 mg, 165 μL, 1.00 mmol) or triethyl orthoacetate (127 μL 97%, 0.66 mmol) was added. The reaction vessel was flushed with nitrogen and sealed, and the mixture was heated to 120 °C for 2 h. After cooling, the mixture was dried under vacuum, in order to remove ethanol, formed during the reaction, to give the crude salt in high purity. Optionally, the product was crystallized from absolute ethanol.

General Procedure for the Counteranion Exchange with Lithium Bis-(trifluoromethylsulfonyl)imide: An imidazolinium tetrafluoroborate salt (1.00 mmol) was dissolved in CH_2Cl_2 (3 mL) and the mixture was vigorously stirred with a solution of $LiNTf_2$ (1.00 mmol) in water (3 mL) for 3 h. The organic phase was separated, washed with water (3 × 3 mL), and dried with molecular sieves (3 Å). The solvent was evaporated and the product was further dried under vacuum to give the corresponding imidazolinium bis(trifluoromethylsulfonyl)imide salt.

General Procedure for the Counteranion Exchange with Sodium Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate: An imidazolinium tetrafluroborate (1.00 mmol) was dissolved in CH_2Cl_2 (3 mL), and $NaB[C_6H_3(CF_3)_2]_4$ (1.00 mmol, 1 equiv.) and water (3 mL) were added sequentially. The reaction mixture was then vigorously stirred for 3 h. The organic phase was separated (centrifugation was used to improve separation if separation did not occur), washed with water (3 × 3 mL), and dried with molecular sieves (3 Å). The solvent was evaporated and the product was further dried in vacuo to give the corresponding imidazolinium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate salt.

1,3-Bis[(1*R*,2*S*)-2-hydroxy-1-methyl-2-phenylethyl]imidazolinium Tetrafluoroborate (10A): This compound was prepared from **5** (657 mg, 2.00 mmol), NH_4BF_4 (216 mg, 2.00 mmol), and $CH(OEt)_3$ (326 μL, 2.00 mmol) as described in the General Procedure. The reaction mixture was heated to 120 °C in a sealed vessel for 8 h, giving the title compound as a yellow solid (743 mg, 87%); m.p. 162 °C. $[\alpha]_D^{22}$ = +17.9 (*c* = 1.2, MeOH). ^1H NMR (200 MHz, [D$_6$]DMSO): δ = 8.32 (s, 1 H), 7.50–7.20 (m, 10 H), 5.95 (br. s, 2 H), 4.81 (d, *J* = 4.0 Hz, 2 H), 4.00–3.70 (m, 6 H), 1.08 (d, *J* = 6.9 Hz) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 156.2, 141.4, 128.1, 127.4, 126.1, 72.7, 58.6, 47.0, 12.1 ppm. IR (KBr): $\tilde{\nu}$ = 3273 s, 1652 vs, 1265 s, 1139 s, 1070 vs, 1015 s, 988 s, 704 s cm^{-1}. MS (ESI = 0 V): *m/z* (%) = 339 (100) $[M]^+$. HRMS (ESI): calcd for $C_{21}H_{27}N_2O_2^+$ 339.2073; found 339.2074.

1,3-Bis[(1*S*,2*R*)-2-hydroxy-1-methyl-2-phenylethyl]imidazolinium Tetrafluoroborate (*ent*-10A): This compound was prepared in the same manner, from ***ent*-5**.

1,3-Bis[(1*R*,2S)-2-hydroxy-1-methyl-2-phenylethyl]imidazolinium Bis(trifluoro-methylsulfonyl)imide (10B): This compound was prepared from **10A** (300 mg, 0.70 mmol) and $LiNTf_2$ (208 mg, 97%, 0.70 mmol) in a mixture of dichloromethane (DCM) (5 mL) and water (5 mL), as a yellow oil (404 mg, 93%). $[\alpha]_D^{22}$ = +20.8 (*c* = 0.9, MeOH). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.78 (s, 1 H), 7.37–7.20 (m, 10 H), 4.96 (d, *J* = 3.2 Hz, 2 H), 4.00–3.70 (m, 4 H), 3.16 (br. s, 2 H), 1.17 (d, *J* = 7.0 Hz, 6 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 155.6, 139.2, 128.7, 128.3, 125.9, 73.6, 59.5, 47.6, 12.2 ppm. IR (neat): $\tilde{\nu}$ = 3523 s, 1642 vs, 1352 vs, 1197 vs, 1137 vs, 1057 vs, 706 s, 617 s, 442 vs cm^{-1}. MS (ESI = 0 V): *m*/*z* (%) = 339.2 (100) $[M]^+$. HRMS (ESI): calcd. for $C_{21}H_{27}N_2O_2^+$ 339.2073; found 339.2073.

1,3-Bis[(1*S*,2*R*)-2-hydroxy-1-methyl-2-phenylethyl]imidazolinium Bis(trifluoro-methylsulfonyl)imide (*ent*-10B): This compound was prepared in the same manner, from ***ent*-10A**.

1,3-Bis[(1*R*,2*S*)-1-hydroxy-1-phenylpropan-2-yl]imidazolinium Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (10C): This compound was prepared from **10A** (200 mg, 0.47 mmol) and $NaB[C_6H_3(CF_3)_2]_4$ (416 mg, 0.47 mmol) in a mixture of DCM (5 mL) and water (5 mL), as a brown oil (477 mg, 84%). $[\alpha]_D^{22}$ = –53.2 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 8.33 (s, 1 H), 7.08 (br. s, 8 H), 7.69 (br. s, 4 H), 7.50–7.30 (m, 10 H), 5.20–5.05 (m, 2 H), 4.25–4.05 (m, 6 H), 2.88 (br. s, 2 H), 1.29 (d, *J* = 8.1 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 161.7 (q, *J* = 49.5 Hz), 156.4, 140.9, 134.6, 129.3 (q, *J* = 28.4 Hz), 128.4, 127.9, 126.2 124.5 (q, *J* = 269.8 Hz), 117.6, 73.8, 59.6, 52.5, 47.8, 47.6, 12.1 ppm. IR (KBr): $\tilde{\nu}$ = 1641 m, 1356 s, 1279 vs, 1124 vs, 682 m cm^{-1}. MS (ESI = 0 V): *m*/*z* (%) = 339.2 (100) $[M]^+$. HRMS (ESI): calcd. for $C_{21}H_{27}N_2O_2^+$ 339.2073; found 339.2079.

1,3-Bis[(*S*)-1-(hydroxymethyl)-2-methylpropyl]-4,5-imidazolinium Tetrafluoroborate (11A): This compound was prepared from **6** (12 mg, 1.34 mmol), NH_4BF_4 (141 mg, 1.34 mmol), and $CH(OEt)_3$ (220 μL, 1.34 mmol) as described in the General Procedure, as a yellow oil (418 mg, 94%). $[\alpha]_D^{22}$ = –10.6 (*c* = 0.68, acetone). ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 8.20 (s, 1 H), 4.07 (br. s, 2 H), 4.00–3.85 (m, 4 H), 3.75–3.25 (m, 6 H), 2.00–1.70 (m, 2 H), 0.91 (d, *J* = 6.5 Hz, 12 H) ppm. ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 160.1, 67.5, 59.8, 46.2, 27.9, 20.1, 19.4 ppm. IR (neat): $\tilde{\nu}$ = 3548 s, 2968 s, 2881 s, 1644 vs, 1472 s, 1394 s, 1254 s, 1074 vs, 446 s cm^{-1}. MS (ESI = 0 V): *m*/*z* = 243.2 [cation]. HRMS (ESI): calcd. for $C_{13}H_{27}N_2O_2^+$ 243.2073; found 243.2073.

1,3-Bis[(*S*)-1-(hydroxymethyl)-2-methylpropyl]-4,5-imidazolinium Bis(trifluoromethylsulfonyl)imide (11B): This compound was prepared from **11A** (235 mg, 0.71 mmol) and $LiNTf_2$ (204 mg, 0.71 mmol, 1 equiv.) in a mixture of DCM (5 mL) and water (5 mL), as a yellow oil (197 mg, 52%). $[\alpha]_D^{22}$ = –18.9 (*c* = 0.28, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.16 (s, 1 H), 4.00–3.80 (m, 4 H), 3.70–3.30 (m, 4 H), 3.09 (br. s, 2 H), 2.00–1.75 (m, 2 H), 0.99 (d, *J* = 6.7 Hz, 12 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 159.2, 66.9, 59.4, 45.3, 27.6, 19.7, 18.9 ppm. IR (neat): $\tilde{\nu}$ = 3537 m, 2971 s, 1644 vs, 1352 vs, 120 vs, 1137 vs, 1058 vs, 617 vs cm^{-1}. MS (ESI = 0 V): *m*/*z* = 243.3 $[M]^+$. HRMS (ESI): calcd. for $C_{13}H_{27}N_2O_2^+$ 243.2073; found 243.2077.

1,3-Bis[(*S*)-1-hydroxy-3,3-dimethylbut-2-yl]imidazolinium Tetrafluoroborate (12A): This compound was prepared from **7** (1.00 g, 3.85 mmol), NH_4BF_4 (615 mg, 3.85 mmol), and $CH(OEt)_3$ (633 μL, 3.85 mmol). The reaction mixture was heated at 120 °C for 8 h and standard workup gave the title compound as a colorless oil (1.30 g, 88%). $[\alpha]_D^{22}$ = +24.4 (*c* = 0.46, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (s, 1 H), 4.20–4.10 (m, 2 H), 4.10–4.00 (m, 2 H), 3.95 (dd, *J* = 3.7, 12.3 Hz, 2 H), 3.82 (t, *J* = 10.8 Hz, 2 H), 3.60 (dd, *J* = 3.7, 12.3 Hz), 1.04 (s, 18 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.2, 69.9, 57.8, 49.7, 33.8, 27.3 ppm. IR (neat): $\tilde{\nu}$ = 3541 s, 2967 vs, 1699 m, 1639 vs, 1479 s, 1409 m, 1373 s, 1283 s, 1237 m, 1058 vs, 451 s, 415 m, 406 m cm^{-1}. MS (ESI = 0 V): *m*/*z* = 271.3 [M(cation)]$^+$. HRMS (ESI): calcd. for $C_{15}H_{31}N_2O_2^+$ 271.2386; found 271.2396.

1,3-Bis[(*S*)-1-hydroxy-3,3-dimethylbut-2-yl]imidazolinium Bis(trifluoromethylsulfonyl)imide (12B): This compound was prepared from **12A** (294 mg, 0.86 mmol) and $LiNTf_2$ (246 mg, 0.86 mmol, 1 equiv.) in a mixture of DCM (5 mL) and water (5 mL), as a white solid (277 mg, 59%); m.p. 98 °C. $[\alpha]_D^{22}$ = +19.7 (*c* = 0.36, $CHCl_3$). ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 8.36 (s, 1 H), 4.25–4.05 (m, 4 H), 4.00–3.80 (m, 4 H), 3.60–3.45 (m, *J* = 10.8 Hz, 2 H), 0.93 (s, 18 H) ppm. ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 161.7, 121.0 (q, *J* = 319.5 Hz), 70.9, 57.9, 48.8, 34.4, 27.5 ppm. IR (KBr): $\tilde{\nu}$ = 3423 s, 1637 s, 1194 s, 1057 s cm^{-1}. MS (ESI = 0 V): *m*/*z* = 271.3 $[M]^+$. HRMS (ESI): calcd for $C_{15}H_{31}N_2O_2$ 271.2386; found 271.2381.

1,3-Bis[(1*R*,2*R*)-1,3-dihydroxy-1-phenylprop-2-yl]imidazolinium Tetrafluoroborate (13A): This compound was prepared from **8** (320 mg, 0.89 mmol), NH_4BF_4 (93 mg, 0.89 mmol), and $CH(OEt)_3$ (146 μL, 0.89 mmol) as described in the General Procedure. The mixture was heated at 120 °C for 16 h to give the title compound as a yellow solid (400 mg, 99%); m.p. 80–85 °C. $[\alpha]_D^{22}$ = –116.2 (*c* = 0.37, acetone). ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 8.27 (s, 1 H), 7.40–7.05 (m, 10 H), 4.92 (d, *J* = 6.3 Hz, 2 H), 4.10–3.40 (m, 10 H) ppm. ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 160.1, 142.4, 129.4, 128.8, 127.3, 71.4, 67.2, 60.3, 48.4 ppm. IR (KBr): $\tilde{\nu}$ = 3386 m, 1641 vs, 1063 vs, 704 s cm^{-1}. MS (ESI = 0 V): *m*/*z* (%) = 371 (100) $[M]^+$. HRMS (ESI): calcd. for $C_{21}H_{27}N_2O_4^+$ 371.1971; found 371.1980.

1,3-Bis[(1*R*,2*R*)-1,3-dihydroxy-1-phenylprop-2-yl]imidazolinium Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (13C): This compound was prepared from **13A** (100 mg, 0.22 mmol) and $NaB[C_6H_3(CF_3)_2]_4$ (193 mg, 0.22 mmol) in a mixture of DCM (3 mL) and water (3 mL), as a yellow solid (215 mg, 80%); m.p. 50 °C. $[\alpha]_D^{22}$ = –42.5 (*c* = 4.7, acetone). ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 8.32 (s, 1 H), 7.70 (br. s, 8 H), 7.55 (br. s, 4 H), 7.40–7.00 (m, 10 H), 5.10–4.90 (m, 2 H), 4.30–3.60 (m, 10 H) ppm. ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 161.6 (q, *J* = 49.5 Hz), 160.1, 142.4, 135.5, 120.0 (q, *J* = 28.4 Hz), 129.4, 128.9, 127.2, 125.3 (q, *J* = 269.8 Hz), 118.4, 71.6, 67.2, 60.4, 48.5 ppm. IR (KBr): $\tilde{\nu}$ = 1640 w, 1357 s, 1279 vs, 1124 s cm^{-1}. MS (ESI = 0 V): *m*/*z* (%) = 371 (100) $[M]^+$. HRMS (ESI): calcd. for $C_{21}H_{27}N_2O_4^+$ 371.1971; found 371.1974.

(3a*S*,7a*S*)-1,3-Bis[(1*R*,2*R*)-2-hydroxycyclohexyl]-3a,4,5,6,7,7a-hexahydro-3*H*-benzo[*d*]imidazol-1-ium Tetrafluoroborate (14A): This compound was prepared from **9** (310 mg, 1.00 mmol), NH_4BF_4 (113 mg, 1.00 mmol), and $CH(OEt)_3$ (163 μL, 1.00 mmol) as described in the General Procedure, as a yellow solid (380 mg, 93%); m.p. 56 °C. $[\alpha]_D^{22}$ = +7.1 (*c* = 0.1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.33 (s, 1 H), 4.23 (br. s, 2 H), 3.90–3.30 (m, 6 H), 2.50–0.80 (m, 24 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 158.8, 72.0, 68.9, 63.7, 34.6, 30.3, 28.5, 24.6, 24.0, 23.9 ppm. IR (KBr): $\tilde{\nu}$ = 3528 s, 2940 vs, 2865 s, 1607 vs, 1453 s, 1226 s, 1074 vs, 530 m cm^{-1}. MS (ESI = 0 V): *m*/*z* (%) = 321 (100) $[M]^+$. HRMS (ESI): calcd. for $C_{19}H_{33}N_2O_2^+$ 321.2542; found 321.2540.**Experiment for the Stereodiscrimination of Potassium Mosher's Carboxylate (15):** Mosher's salt (12% *ee*, 0.50 mmol) and the corresponding imidazolinium salt (0.50 mmol, 1 equiv.) were dissolved in [D$_6$]acetone

and the ^{1}H NMR and ^{19}F NMR spectra were recorded at room temp. For chemical shifts and stereodiscrimination see Table 2.

Regeneration of the Salt: Regeneration of imidazolinium salt **10A**. [D_6]Acetone was removed under reduced pressure and the remaining residue was dissolved in $CHCl_3$ (2 mL). The organic phase was washed with water (4 × 3 mL), dried with molecular sieves (3 Å), and concentrated, giving the pure imidazolinium salt **10A**.

General Procedure for Carbene-Catalyzed Et_2Zn Addition to Aldehydes: An imidazolinium salt (0.04 mmol) and *t*BuOK (4.5 mg, 0.04 mmol) were placed in a dry Schlenk flask and dissolved in dry toluene (1 mL). After the mixture had been stirred for 5 min, Et_2Zn (0.5 mL of a 1 M solution in hexane) was added, and after another 5 min, an aldehyde (0.40 mmol) was added. The mixture was stirred at room temp. for 30 h (for differences in reaction times and temperatures see Tables 3 and 4), quenched by the addition of HCl (1 M, 0.5 mL), and extracted with Et_2O (3 × 5 mL). The combined organic phases were dried (Na_2SO_4) and the solvent was removed under reduced pressure to give the crude product, which was purified by flash column chromatography (petroleum ether/ethyl acetate, 9:1) to give the corresponding alcohol.

1-Phenylpropan-1-ol (17): This compound was prepared as a colorless oil from benzaldehyde (**16**, 40 μL, 0.40 mmol) and Et_2Zn (0.50 mL, 1 M solution in hexane) in PhMe (1 mL) and the carbene generated from an imidazolinium salt (0.04 mmol) and *t*BuOK (4.5 mg, 0.04 mmol). For catalysts and yields, see Table 3. Spectral data are consistent with literature values.[38] The enantiomeric ratio was determined by HPLC [OD-H; *i*PrOH/hexane, 10:90; 0.2 mL min^{-1}; $t_1(R)$ = 32.6 min, $t_2(S)$ = 38.8 min].

1-(Naphth-1-yl)propan-1-ol (19): This compound was prepared as a colorless oil from 1-naphthaldehyde (**18**) (56 μL, 0.40 mmol) and Et_2Zn (0.5 mL 1 M solution in hexane) in PhMe (1 mL) and the carbene generated from an imidazolinium carbene precursor (0.04 mmol) and a base. For catalysts, bases, and yields, see Table 4. Spectral data are consistent with literature values.[39] The enantiomeric ratio was determined by HPLC [OD-H; *i*PrOH/hexane, 5:95; 0.4 mL min^{-1}; $t_1(S)$ = 28.4 min, $t_2(R)$ = 55.4 min].

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