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The preparation of new enantiopure imidazolinium salts and their evaluation as catalysts and shift reagents

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Abstract—A series of new chiral imidazolinium salts were prepared and tested as catalysts. It was possible to show that bis-imidazolinium salts had a higher reactivity than mono-imidazolinium salts. In addition a chiral discrimination of the bis-imidazolinium salts with the potassium salt of racemic Mosher's acid was proven by NMR studies.

1. Introduction

Recently, a few examples of chiral imidazolinium based ionic liquids have been reported.[1,2] However, the number of examples of this class of chiral ionic liquid remains small compared to other types of chiral ionic liquid.[3–5] Furthermore, we have shown that an achiral imidazolinium based ionic liquid is an inert medium for reactions involving medium and strong bases.[6] Chiral imidazolinium salts, which have a hydrogen atom on the C-2 position and a hydroxyl group incorporated were shown to be shift reagents for the racemic potassium salt of Mosher's acid.[2]

Due to the positive charge delocalized between the two nitrogen atoms and the C-2 carbon atom, the imidazolinium cation can act as a mild Lewis acid. It has been demonstrated that achiral imidazolinium salts are able to catalyze an aza Diels–Alder reaction or inverse electron demand aza Diels–Alder reaction,[7] which is one of the few examples of carbocation based Lewis acids in catalysis.[8–13] Due to the absence of a metal, these salts can contribute to the field of organocatalysis, which has attracted much interest in recent years.[14,15]

Herein, we report the preparation of a series of new chiral imidazolinium salts and their investigation as chiral metal-free Lewis acids and chiral shift reagents. In addition some of the salts presented also qualify as ionic liquids.[16]

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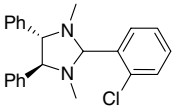
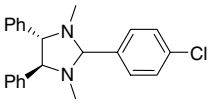
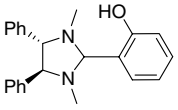
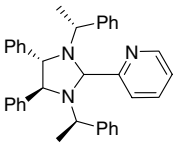
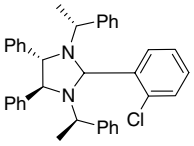
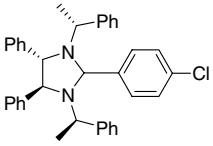
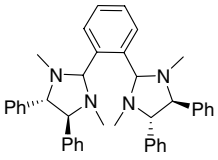
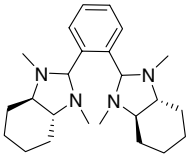
2. Results and discussion

2.1. Preparation

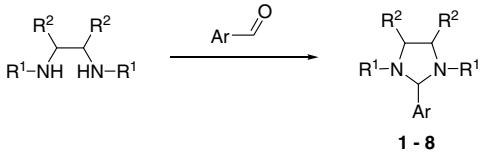
The first step was preparation of the appropriate enantiopure imidazolidines, which were used as the precursors of the desired chiral imidazolinium salts. The imidazolidines, bearing different substituents on the C-2 atom, were formed from chiral diamines and aldehydes (Table 1, Scheme 1). A convenient method to prepare aminals is the use of water as a solvent without the presence of a catalyst, which has recently been described by our group.[17] However, we found that some of the more complex chiral aminals were not formed by applying this procedure, probably due to a certain level of steric hindrance in the chiral diamines.

Therefore, we initially used a standard procedure, Dean–Stark/benzene/reflux,[18] in order to obtain the desired imidazolinium precursors (Table 1, entries 1, 2, 4 and 5). Over the course of our investigation we found that it was also possible to react the diamines with aldehydes under neat conditions in a sealed vessel at 120 °C, without the presence of a catalyst. The aminals were obtained in good to excellent yields (Table 1, entries 3 and 6). Moreover, it was possible to prepare bis-aminals from (−)-(1*S*,2*S*)-*N*,*N*′-dimethyl-1,2-diphenyl-1,2-ethylendiamine[19] or (+)-(1*R*,2*R*)-*N*,*N*′-dimethylcyclohexane-1,2-diamine[19] with phthaldialdehyde in excellent yields (Table 1, entries 7 and 8) under these conditions. However, when (1*S*,2*S*)-1,2-di-*tert*-butyl-*N*,*N*′-bis((*R*)-1-phenylethyl)ethane-1,2-diamine[20] was treated with phthaldialdehyde under neat conditions, no product

Table 1. Preparation of aminals

Entry	Diamine	Aldehyde	Method[a]	Aminal		Yield (%)
1	R^1 = Me, (*R*,*R*)-R^2 = Ph	2-Chlorobenzaldehyde	A		**1**	93
2	R^1 = Me, (*S*,*S*)-R^2 = Ph	4-Chlorobenzaldehyde	A		**2**	91
3		2-Hydroxybenzaldehyde	B		**3**	95
4	R^1 = (*R*)-MeBn, (*S*,*S*)-R^2 = Ph	Pyridine-2-carbaldehyde	A		**4**	95
5		2-Chlorobenzaldehyde	A		**5**	50
6		4-Chlorobenzaldehyde	B		**6**	77
7	R^1 = Me, (*S*,*S*)-R^2 = Ph	Phthaldialdehyde	B		**7**	87
8	R^1 = Me, (*R*,*R*)-R^2 = $(CH_2)_4$	Phthaldialdehyde	B		**8**	99
9	R^1 = (*R*)-MeBn, (*S*,*S*)-R^2 = ^{t}Bu	Phthaldialdehyde	B	—	**9**	0

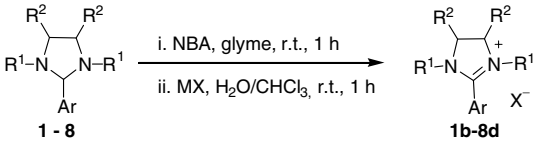
[a] Method A: Dean–Stark/benzene/reflux/24 h; method B: neat, 120 °C, 3 h.



Scheme 1. Preparation of aminals.

could be isolated (Table 1, entry 9). This may be due to the bulky *t*-butyl groups that are incorporated in the diamine.

The aminals were then transformed into the corresponding imidazolinium salts by applying a modified literature procedure.[21] The imidazolidines were oxidized with *N*-bromoacetamide (NBA) to the imidazolinium bromide salts (Scheme 2, Table 2), which were used directly in a counter anion exchange. In some cases, the bromide salts were isolated to confirm by NMR, that the bromide salt was



Scheme 2. Preparation of imidazolinium salts.

Table 2. Oxidation of aminals and counter anion exchange

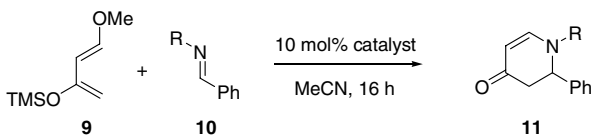
Entry	Aminal	Anion	Salt	Yield (%)
1	*ent*-**1**	PF_6^-	*ent*-**1b**	88
2	**1**	NTf_2^-	**1c**	58
3	**2**	Br^-	**2a**	99
4	**2**	NTf_2^-	**2c**	82
5	**2**	$B[3,5\text{-}(CF_3)_2\text{-}C_6H_3]_4^-$	**2d**	71
6	**4**	Br^-	**4a**	96
7	**4**	PF_6^-	**4b**	86
8	**4**	NTf_2^-	**4c**	57
9	**5**	Br^-	**5a**	89
10	**5**	PF_6^-	**5b**	94
11	**6**	PF_6^-	**6b**	72
12	**7**	NTf_2^-	**7c**	80
13	**7**	$B[3,5\text{-}(CF_3)_2\text{-}C_6H_3]_4^-$	**7d**	80
14	**8**	PF_6^-	**8b**	75
15	**8**	$B[3,5\text{-}(CF_3)_2\text{-}C_6H_3]_4^-$	**8d**	87

obtained in good purity and that all aminal was consumed (Table 2, entries 3, 6 and 9). The bromide salts were difficult to handle, due to their considerable hygroscopic behaviour. Bis-imidazolinium salts were prepared from the bis-aminals **7** and **8** in very good yields (Table 2, entries 12–15).

The counter anion exchange was performed by vigorous stirring of the imidazolinium bromide salt with the metal salt of the new desired anion in a $CHCl_3/H_2O$ mixture. The new imidazolinium salts remained in the organic phase, while the metal bromide salts were removed by washing the organic phase with water. Also, bis-imidazolinium salts **7c** and **8b** could be prepared in good yields following this procedure (Table 2, entries 12 and 15). Salts **6b** and **7d** could qualify as ionic liquids, since their melting points were below 100 °C.[16] Salts **1c**, **4a** and **4c** could qualify as room temperature ionic liquids.

2.2. Investigation of catalytic behaviour

2.2.1. Aza Diels–Alder reaction. Chiral salts *ent*-**1b**–**8d** were tested in the aza Diels–Alder reaction (Scheme 3). A few selected examples are presented in Table 3. In general, the salts showed good catalytic activity, however, no asymmetric induction was observed. When a tosyl substituent



Scheme 3. Aza Diels–Alder reaction.

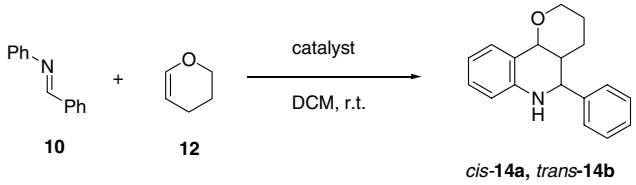
Table 3. Aza Diels–Alder reaction

Entry	Catalyst	R	T (°C)	Yield (%)
1	**5b**	Ph	0	76
2	**5b**	Ph	rt	82
3	**4b**	Ph	0	78
4[a]	**4b**	Ts	rt	35

[a] Reaction was performed in DCM.

was present on the imine nitrogen atom, a lower reactivity was observed, and no enantioselectivity was found (Table 3, entry 4).

2.2.2. Inverse electron demand aza Diels–Alder reaction. We then explored the enantiopure salts in the inverse electron demand aza Diels–Alder reaction of *N*-benzylideneaniline **10** and dihydropyran **12** (Scheme 4).



Scheme 4. Inverse electron demand aza Diels–Alder reaction.

The reaction with dihydropyran **12** and **10** was not sufficiently catalyzed by the mono-imidazolinium salts. For example, when 10 mol % of salt **6b** was used as the catalyst, only traces of the desired product were obtained after 72 h at rt. Bis-imidazolinium salt **7c** revealed a poor reactivity and **14a** and **14b** were isolated in 6% yield in a ratio of 58:42 after 112 h at rt. However, when salt **7d**, which incorporated the very lipophilic and large anion $B[3,5\text{-}(CF_3)_2\text{-}C_6H_3]_4^-$, was applied, the reactivity increased dramatically and **14a** and **14b** were obtained in 64% yield with a ratio of 54:46 after 16 h at rt. Both diastereomers were obtained as racemates. In addition, the bis-imidazolinium salt **8d** resulted in a yield of 67% after 96 h at 0 °C in a diastereomeric ratio of 60:40 for **14a** and **14b**. No enantiomeric excess was found.

2.3. Use as a shift reagent

Mono-imidazolinium salts bearing a hydrogen atom at the C-2 position and a hydroxy group on the side chain have been shown to be shift reagents for a racemate of potassium Mosher's carboxylate.[2] To the best of our knowledge, no imidazolinium salts with an aryl substituent at the C-2 position have been investigated as shift reagents. When

Table 4. Chemical shifts of Mosher's carboxylate in ppm and $\Delta\delta$ in Hz on a 400 MHz NMR

Entry	Salt	^1H $\delta(S)$	^1H $\delta(R)$	^{19}F $\delta(S)$	^{19}F $\delta(R)$	^1H $\Delta\delta$	^{19}F $\Delta\delta$
1	**8b**	3.59	3.57	−71.50	−71.64	6.3	53.0
2	**8d**	3.57	3.57	−71.67	−71.72	0	18.8
3	**7d**	3.58	3.60	−71.57	−71.49	4.3	27.1
4	**7c**	3.57	3.57	−71.84	−71.88	0	13.0

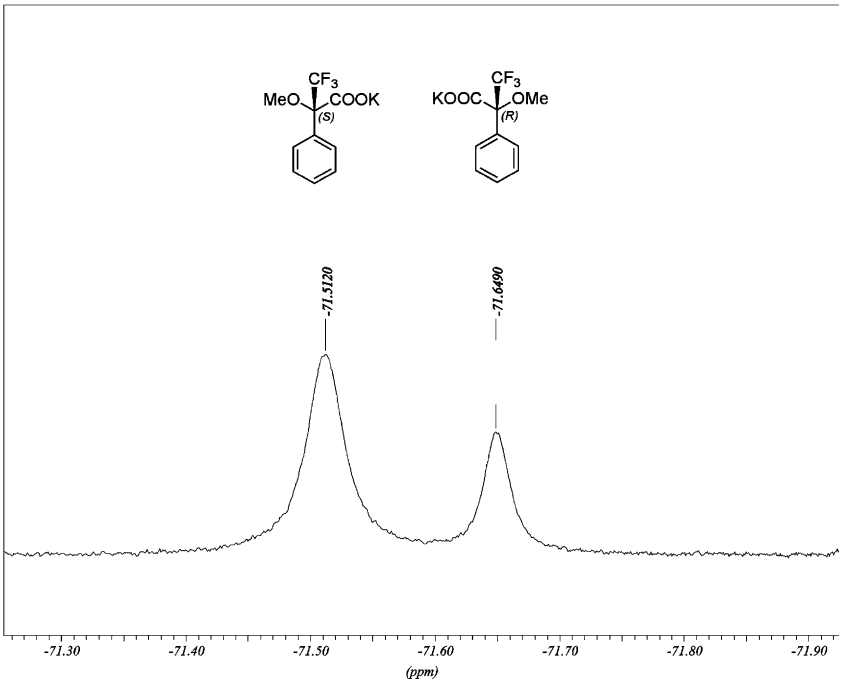


Figure 1. ^{19}F NMR spectra on a 400 MHz NMR measured at 375 MHz.

the mono-imidazolinium salts were applied, no splitting of either the ^{1}H or ^{19}F signal of Mosher's carboxylate was observed. However, the bis-imidazolinium salts **8b**, **8d**, **7d** and **7c** were able to divide the ^{19}F signal of the two enantiomers as shown in Table 4. Only **8b** and **7d** were also able to split the ^{1}H signal. The best result for an ^{19}F NMR with salt **8b** is depicted in Figure 1. In this example, an enantioenriched sample of 50% ee of Mosher's carboxylate was used, in order to assign the individual NMR signals to either the (*R*)- or (*S*)-enantiomer through integration.

3. Conclusion

In conclusion, we have prepared a range of new chiral mono- and bis-imidazolinium salts. It was shown that the bis-imidazolinium salts were far more active catalysts, however, no asymmetric induction was found in the test reactions. In addition, it was demonstrated that the bis-imidazolinium salts can be used as a shift reagent for the potassium salt of Mosher's acid.

4. Experimental

4.1. General experimental

Flash column chromatography[22] (FCC) was performed on Sorbisil C-60. The reactions were monitored by TLC with Merck Silica gel 60 F_{254} plates. Elemental analyses were carried out by the Microanalytical Laboratory of the Institut für Pharmazeutische Chemie der Technischen Universität Braunschweig. Infrared spectra were recorded on a Bruker Vector 22 FTIR instrument. NMR spectra were performed at ambient temperature on a Bruker AMX 400 and a Bruker AC 200F and, if not otherwise stated, measured in $CDCl_3$. Mass spectra were recorded on Hewlett–Packard 5898B (at 70 eV). Electron spray mass spectrometry was performed directly on a MS LC/MSD 1100 MSD from Hewlett–Packard. High resolution mass spectra were recorded at the Institute of Organic Chemistry, University of Hanover. Melting points are uncorrected. Reactions were performed under a nitrogen atmosphere. All solvents were dried using standard procedures, before using in the reactions. Sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,[23] (1*S*,2*S*)-1,2-diphenyl-*N*,*N*′-bis((*R*)-1-phenylethyl)ethane-1,2-diamine,[24] (+)-(1*R*,2*R*)-, (−)-(1*S*,2*S*)-*N*,*N*′-dimethyl-1,2-diphenyl-1,2-ethylendiamine[19] and (+)-(1*R*,2*R*)-*N*,*N*′-dimethylcyclohexane-1,2-diamine[19] were prepared according to the literature procedures. *N*-Bromoacetamide and racemic Mosher's acid were purchased from Lancaster. $LiNTf_2$ and KPF_6 were purchased from Aldrich.

4.2. Preparation of aminals

4.2.1. General procedure for the preparation of aminals (method A). A diamine (1 mmol), *p*-toluenesulfonic acid (5 mg) and an aldehyde (1 mmol) were dissolved in benzene (25 mL). The reaction mixture was refluxed on a Dean–Stark for 24 h. Benzene was removed under reduced pressure to give the crude product, which was purified by FCC (petroleum ether/ethyl acetate/Et_3N, 95/5/0.5) to give the desired aminal.

4.2.2. General procedure for the preparation of aminals under solvent free conditions (method B). A diamine (1 mmol) and an aldehyde (1 mmol) were placed in a pressure vessel equipped with a magnetic stirrer. The vessel was flushed with nitrogen, sealed and the reaction mixture

heated up to 120 °C for 16 h. After cooling to rt, the glassy solid formed was dissolved in DCM and dried over Na_2SO_4. The solvent was removed under reduced pressure and the remaining solid was dried under vacuum to give the corresponding aminal.

4.2.3. (+)-(4*R*,5*R*)-2-(2-Chlorophenyl)-1,3-dimethyl-4,5-diphenylimidazolidine 1. (+)-(4*R*,5*R*)-2-(2-Chlorophenyl)-1,3-dimethyl-4,5-diphenylimidazolidine **1** was prepared from (+)-(*R*,*R*)-*N*,*N*′-dimethyl-1,2-diphenylethylenediamine (500 mg, 2.08 mmol) and *o*-chlorobenzaldehyde (246 μL, 2.18 mmol) in benzene (50 mL) according to method A. FCC gave the *title compound* (+)-**1** as a white solid (700 mg, 93%). Mp 128 °C. $[\alpha]_D^{22} = 107.6$ (*c* 0.59, $CHCl_3$); MS (EI), *m*/*e* 361 (M^+-H, 30%), 244 (40), 243 (100), 208 (40), 152 (25); IR (KBr) 2792s, 1452s, 1263s, 1011s, 756vs, 699vs cm^{-1}; ^1H NMR (200 MHz): δ 8.02–7.98 (m, 1H), 7.43–7.16 (m, 13H), 5.38 (s, 1H, NC*H*N), 3.84 (d, $J = 8.5$ Hz, 2H, C*H*Ph), 3.63 (d, $J = 8.5$ Hz, 2H, C*H*Ph), 2.16 (s, 3H, NCH_3), 1.91 (s, 3H, NCH_3); ^{13}C NMR (50 MHz): δ 139.8, 139.3, 137.5, 130.9, 129.6, 129.1, 128.3, 128.2, 128.1, 128.0, 127.5, 127.4, 126.7, 83.2 (N*C*HN), 37.6 (*C*HPh), 35.6 (NCH_3). Anal. Calcd for $C_{23}H_{23}ClN_2$: C, 76.12; H, 6.39; N, 7.72. Found: C, 76.36; H, 6.26, N, 7.49.

4.2.4. (−)-(4*S*,5*S*)-2-(2-Chlorophenyl)-1,3-dimethyl-4,5-diphenylimidazolidine *ent*-1. (−)-(4*S*,5*S*)-2-(2-Chlorophenyl)-1,3-dimethyl-4,5-diphenylimidazolidine *ent*-**1** was prepared in the same way as the enantiomer above. The spectral data were consistent with the data of **1**.

4.2.5. (−)-(4*S*,5*S*)-2-(4-Chlorophenyl)-1,3-dimethyl-4,5-diphenylimidazolidine 2. (−)-(4*S*,5*S*)-2-(4-Chlorophenyl)-1,3-dimethyl-4,5-diphenylimidazolidine **2** was prepared from (+)-(*S*,*S*)-*N*,*N*′-dimethyl-1,2-diphenylethylenediamine (750 mg, 3.13 mmol) and 4-chlorobenzaldehyde (483 mg, 3.44 mmol) in benzene (50 mL) according to method A. FCC gave the *title compound* (−)-**2** as a white solid (1.029 g, 91%). Mp = 98 °C; $[\alpha]_D^{22} = -35.5$ (*c* 0.32, $CHCl_3$); MS (EI), *m*/*e* 360 (M^+, 40%), 244 (40), 243 (100), 165 (45), 152 (60), 139 (40), 118 (40), 91 (50), 77 (60), 69 (50), 51 (40); IR (KBr) 3425s, 2789s, 1599s, 1490s, 1451s, 1088s, 1009s, 841s, 759s, 698vs, 511s cm^{-1}; ^1H NMR (400 MHz): δ 7.61 (d, $J = 8.6$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 2H) 7.37–7.19 (m, 10H), 4.78 (s, 1H, NC*H*N), 3.91 (d, $J = 8.3$ Hz, 1H, C*H*Ph), 3.68 (d, $J = 8.3$ Hz, 1H, C*H*Ph), 2.20 (s, 3H, NCH_3), 1.88 (s, 3H, NCH_3); ^{13}C NMR (100 MHz): δ 140.1, 139.78, 139.73, 134.4, 131.1, 128.8, 128.7, 128.5, 128.3, 127.96, 127.92, 88.2 (N*C*HN), 77.9 (*C*HPh), 37.9 (NCH_3), 36.2 (NCH_3). Anal. Calcd for $C_{23}H_{23}ClN_2$: C, 76.12; H, 6.39; N, 7.72. Found: C, 76.26; H, 6.41; N, 7.73.

4.2.6. (−)-2-((4*S*,5*S*)-1,3-Dimethyl-4,5-diphenylimidazolidin-2-yl)phenol 3. (−)-2-((4*S*,5*S*)-1,3-Dimethyl-4,5-diphenylimidazolidin-2-yl)phenol **3** was prepared from (+)-(*S*,*S*)-*N*,*N*′-dimethyl-1,2-diphenylethylenediamine (608 mg, 2.53 mmol) and salicyl aldehyde (0.264 mL, 2.53 mmol) according to method B as a yellow oil which solidified (830 mg, 95%). Mp 40–42 °C; $[\alpha]_D^{22} = -38.9$ (*c* 0.18, $CHCl_3$); MS (EI), *m*/*e* 343 (M^+-H, 30%), 224 (100), 208 (30), 134 (30), 120 (25), 91 (30); IR (KBr) 2850w, 1619vs, 1480m, 1454m, 1261s, 1152m, 756s, 699s cm^{-1}; ^1H NMR (200 MHz): δ 7.40–7.13 (m, 12H), 6.94–6.84 (m, 2H), 4.84 (s, 1H, NC*H*N), 4.09 (d, $J = 8.7$ Hz, 2H, C*H*Ph), 3.61 (d, $J = 8.7$ Hz, 2H, C*H*Ph), 2.22 (s, 3H, NCH_3), 2.02 (s, 3H, NCH_3); ^{13}C NMR (50 MHz): δ 158.5 (*C*OH), 139.5, 137.2, 131.2, 130.2, 128.7, 128.3, 128.2, 128.1, 127.8, 127.7, 120.7, 119.1, 89.4 (N*C*HN), 36.9 (*C*HPh), 35.6 (NCH_3); HRMS (ESI) calculated for $C_{23}H_{24}N_2O^+$: 345.1967, found: 345.1981.

4.2.7. (+)-(4*S*,5*S*)-2-(2-Pyridinyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolidine 4. (+)-(4*S*,5*S*)-2-(2-Pyridinyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolidine **4** was prepared from (1*S*,2*S*)-1,2-diphenyl-*N*,*N*′-bis((*R*)-1-phenylethyl)ethane-1,2-diamine (1.50 g, 3.57 mmol), 2-pyridinecarbaldehyde (340 μL, 3.57 mmol) and *p*-toluenesulfonic acid (10 mg) in benzene (100 mL) according to method A. The reaction mixture was refluxed for 48 h. FCC gave the *title compound* (+)-**4** as a white solid (1.73 g, 95%). Mp 105–108 °C; $[\alpha]_D^{22} = +115.0$ (*c* 0.32, $CHCl_3$); MS (CI), *m*/*e* 432 (M^+−pyridinyl, 50%), 299 (60), 105 (100); IR (KBr) 3451vs, 1492s, 1453s, 1431s, 1104s, 760s, 699vs cm^{-1}; ^1H NMR (400 MHz): δ 8.57–8.54 (m, 1H), 7.40–7.00 (m, 20H), 6.80–6.70 (m, 3H), 5.34 (s, 1H, NC*H*N), 4.65 (d, $J = 7.9$ Hz, 1H, NC*H*Ph), 4.18 (d, $J = 7.9$ Hz, 1H, NC*H*Ph), 3.98 (q, $J = 7.0$ Hz, 1H, C*H*CH_3), 3.67 (q, $J = 7.0$ Hz, 1H, C*H*CH_3), 1.07 (d, $J = 7.1$ Hz, 3H, $CHCH_3$), 0.88 (d, $J = 7.1$ Hz, 3H, $CHCH_3$); ^{13}C NMR (100 MHz): δ 165.4, 148.5, 145.4, 143.2, 142.9, 142.5, 135.3, 128.9, 128.6, 128.34, 128.30, 128.28, 128.20, 128.0, 127.4, 127.3, 127.2, 127.1, 127.05, 124.6, 122.0, 83.2 (N*C*HN), 76.6 (*C*HPh), 73.6 (*C*HPh), 61.5 (CH*C*H_3), 57.3 (CH*C*H_3), 23.1 (CH*C*H_3), 22.5 (CH*C*H_3); HRMS (ESI) calculated for $C_{36}H_{35}N_3^+$: 510.2909, found: 510.2912.

4.2.8. (−)-(4*S*,5*S*)-2-(2-Chlorophenyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolidine 5. (−)-(4*S*,5*S*)-2-(2-Chlorophenyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)-imidazolidine **5** was prepared from (1*S*,2*S*)-1,2-diphenyl-*N*,*N*′-bis((*R*)-1-phenylethyl)ethane-1,2-diamine (1.00 g, 2.39 mmol), 2-chlorobenzaldehyde (336 mg, 2.39 mmol) and *p*-toluenesulfonic acid (50 mg) in benzene (75 mL) according to method A. The reaction mixture was refluxed for 48 h. FCC gave the *title compound* (−)-**5** as a white solid (640 mg, 50%). Mp 57–58 °C; $[\alpha]_D^{22} = -99.9$ (*c* 1.6, $CHCl_3$) MS (ESI, 0 V), *m*/*e* 541.2 (M^+-H, 100%); IR (KBr) 3027m, 1492s, 1453vs, 1222s, 1133s, 1027s, 756vs, 700vs cm^{-1}; ^1H NMR (400 MHz): δ 8.02 (d, $J = 7.7$ Hz, 1H), 7.40–6.70 (m, 23H), 6.00 (s, 1H, NC*H*N), 4.38 (d, $J = 8$ Hz, 1H, NC*H*Ph), 4.10 (d, $J = 8$ Hz, 1H, NC*H*Ph), 3.92–3.89 (m, 1H, C*H*CH_3), 3.70–3.67 (m, 1H, C*H*CH_3), 1.16 (d, $J = 8.1$ Hz, 3H, $CHCH_3$), 0.78 (d, $J = 7.0$ Hz, 3H, $CHCH_3$); ^{13}C NMR (100 MHz): δ 145.5, 142.7, 142.4, 140.6, 140.5, 134.8, 132.3, 129.2, 128.5, 128.4, 128.3, 128.1, 127.8, 127.75, 127.73, 127.67, 127.2, 127.0, 126.97, 126.93, 126.3, 126.0, 76.2 (N*C*HN), 74.7 (*C*HPh), 72.4 (*C*HPh), 58.6 (CH*C*H_3), 56.5 (CH*C*H_3), 21.7 (CH*C*H_3), 20.1 (CH*C*H_3). Anal. Calcd for $C_{37}H_{35}ClN_2$: C, 81.82; H, 6.50; 6.53; N, 5.16. Found: C, 81.78; H, 6.91; N, 5.05.

4.2.9. (−)-(4*S*,5*S*)-2-(4-Chlorophenyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolidine 6. (−)-(4*S*,5*S*)-2-(4-Chlorophenyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolidine **6** was prepared from (1*S*,2*S*)-1,2-diphenyl-*N*,*N*′-bis((*R*)-1-phenylethyl)ethane-1,2-diamine (821 mg, 2.00 mmol) and 4-chlorobenzaldehyde (290 mg, 2.00 mmol) according to method B. FCC gave the *title compound* (−)-**6** as a white solid (833 mg, 77%). Mp 53 °C; $[\alpha]_D^{22} = -12.8$ (*c* 0.2, $CHCl_3$); MS (ESI, 0 V), *m*/*e* 541.3 (M^+−H, 10%); IR (KBr) 3026m, 1490s, 1452s, 1225m, 1088m, 832m, 765s, 700vs cm^{-1}; ^1H NMR (200 MHz): δ 7.30–6.80 (m, 24H), 5.11 (s, 1H, NC*H*N), 4.31 (d, $J =$ 8.3 Hz, 1H, NC*H*Ph), 4.14 (d, $J = 8.3$ Hz, 1H, NC*H*Ph), 3.90 (q, $J = 7.0$ Hz, 1H, C*H*CH_3), 3.44 (q, $J = 7.0$ Hz, 1H, C*H*CH_3), 0.99 (d, $J = 7.0$ Hz, 3H, CHC*H*$_3$), 0.67 (d, $J = 7.0$ Hz, 3H, CHC*H*$_3$); ^{13}C NMR (50 MHz): δ 145.6, 143.4, 143.3, 141.5, 140.9, 132.5, 130.9, 128.3, 128.25, 128.1, 128.0, 127.9, 127.8, 127.6, 127.3, 127.13, 127.06, 126.9, 126.6, 126.2, 81.6 (N*C*HN), 75.8 (*C*HPh), 73.2 (*C*HPh), 60.4 (CH*C*H_3), 58.3 (CH*C*H_3), 24.7 (CH*C*H_3), 21.6 (CH*C*H_3). HRMS calculated for $C_{37}H_{36}ClN_2^+$: 543.2562; found: 543.2563.

4.2.10. (−)-(4*S*,5*S*)-1,3-Dimethyl-2-(2-((4*S*,5*S*)-1,3-dimethyl-4,5-diphenylimidazolidin-2-yl)phenyl)-4,5-diphenylimidazolidine 7. (−)-(4*S*,5*S*)-1,3-Dimethyl-2-(2-((4*S*,5*S*)-1,3-dimethyl-4,5-diphenylimidazolidin-2-yl)phenyl)-4,5-diphenylimidazolidine **7** was prepared from (1*S*,2*S*)-*N*,*N*′-dimethyl-1,2-diphenylethane-1,2-diamine (960 mg, 4 mmol) and phthaldialdehyde (269 mg, 2 mmol) according to method B as a yellow solid (1.01 g, 87%). Mp 83–85 °C; $[\alpha]_D^{22} = -89.8$ (*c* 0.44, $CHCl_3$); MS (EI), *m*/*e* 578 (M^+, 1%), 368 (100), 180 (20), 142 (10), 118 (20), 91 (10), 77 (10), 52 (10); IR (KBr) 3452vs, 1631m, 1451m, 1264m, 1161m, 1103m, 755s, 699s cm^{-1}; ^1H NMR (400 MHz): δ 8.13–8.11 (m, 2H), 7.57–7.50 (m, 2H), 7.48–7.27 (m, 20H), 5.52 (s, 2H, NC*H*N), 3.92 (d, $J = 8.4$ Hz, 2H, C*H*Ph), 3.59 (s, 2H, C*H*Ph), 2.18 (s, 6H, NCH_3), 2.07 (s, 6H, NCH_3); ^{13}C NMR (100 MHz): δ 141.8, 140.3, 138.9, 129.6, 128.9, 128.8, 128.5, 128.4, 128.3, 128.0, 127.6, 83.7 (N*C*HN), 78.8 (*C*HPh), 38.9 (N*C*H_3), 38.0 (N*C*H_3); HRMS calculated for $C_{40}H_{43}N_4^+$: 579.3488; found: 579.3466.

4.2.11. (+)-(3a*R*,7a*R*)-Octahydro-2-(2-((3a*R*,7a*R*)-octahydro-1,3-dimethyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazole 8. (+)-(3a*R*,7a*R*)-Octahydro-2-(2-((3a*R*,7a*R*)-octahydro-1,3-dimethyl-1*H*-benzo[*d*]-imidazol-2-yl)phenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazole **8** was prepared from (1*R*,2*R*)-*N*,*N*′-dimethylcyclohexane-1,2-diamine (119 mg, 0.84 mmol) and phthaldialdehyde (56 mg, 0.42 mmol) according to method B as a yellow solid (159 mg, 99%). Mp 98 °C; $[\alpha]_D^{22} = +103.6$ (*c* 1.48, $CHCl_3$); MS (ESI, 0 V), *m*/*e* 383.3 (M^++H, 100%); IR (KBr) 3441s, 2972s, 2931vs, 2455s, 2791s, 1452s, 1360s, 1190s, 1009s, 758s cm^{-1}; ^1H NMR (200 MHz): δ 7.80–7.60 (m, 2H), 7.32–7.27 (m, 2H), 4.85 (s, 2H, NC*H*N), 2.18 (s, 6H, NCH_3), 1.93 (s, 6H, NCH_3) 2.50–2.00 (m, 4H, NC*H*CH_2), 2.10–1.80 (m, 8H), 1.40–1.10 (m, 8H); ^{13}C NMR (50 MHz): δ 139.0,, 129.1, 127.4, 84.0 (N*C*HN), 69.8 (N*C*HCH_2), 68.98 (N*C*HCH_2), 37.3 (N*C*H_3), 37.0 (N*C*H_3), 29.4 (*C*H_2), 29.0 (*C*H_2), 24.7 (C*C*H_2), 24.4 (*C*H_2). HRMS calculated for $C_{24}H_{39}N_4^+$: 383.3169; found: 383.3171.

4.3. Preparation of salts

4.3.1. General procedure for the preparation of imidazolinium bromide salts. Imidazolidine (1 mmol) was dissolved in a minimal amount of 1,2-dimethoxyethane. *N*-Bromoacetamide (1 mmol) was added in two portions (0.5 mmol each) in an interval of 15 min. After the addition of the second portion, the reaction mixture was stirred for an additional hour. Diethyl ether (5 mL) was added and an oily solid formed. The solvent was decanted and the remaining solid was washed with diethyl ether (3 mL) and dried under high vacuum to give the corresponding bromide salt.

4.3.2. General procedure for the counter anion exchange with potassium hexafluorophosphate, lithium bis(trifluoromethylsulfonyl)imide or sodium tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate. Imidazolinium bromide salt (1 mmol) was dissolved in $CHCl_3$ (3 mL) and stirred vigorously with 1 equiv of KPF_6, $LiNTf_2$ or $NaB[3,5\text{-}(CF_3)_2\text{-}C_6H_3]_4$ in water (3 mL) for 30 min. The organic phase was separated, washed with water (3 × 3 mL) and dried over molecular sieves 3 Å. The solvent was evaporated and the product further dried overnight under high vacuum to give the corresponding imidazolinium hexafluorophosphate, bis-(trifluoromethylsulfonyl)imide or tetrakis(3,5-bis(trifluoromethyl)phenyl)borate salt.

4.3.3. (−)-(4*S*,5*S*)-2-(2-Chlorophenyl)-1,3-dimethyl-4,5-diphenylimidazolinium hexafluorophosphate *ent*-1b. (−)-(4*S*,5*S*)-2-(2-Chlorophenyl)-1,3-dimethyl-4,5-diphenylimidazolinium hexafluorophosphate *ent*-**1b** was prepared from (−)-(4*S*,5*S*)-2-(2-chlorophenyl)-1,3-dimethyl-4,5-diphenylimidazolidine *ent*-**1** (200 mg, 0.55 mmol) and NBA (80 mg, 0.55 mmol) in glyme (2 mL), followed by a counter anion exchange with KPF_6 (103 mg, 0.55 mmol) in a mixture of DCM (3 mL) and water (3 mL) as a white solid (245 mg, 88%). Mp 277 °C; $[\alpha]_D^{22} = -116.7$ (*c* 0.36, $CHCl_3$); MS (ESI, 0 V), *m*/*e* 361.1 (M^+, 100%); IR (KBr) 3453s, 1608vs, 837vs, 754s, 702s, 557s cm^{-1}; ^1H NMR (200 MHz): δ 8.20–8.10 (m, 1H), 7.56–7.32 (m, 13H), 5.42 (d, $J = 12.2$ Hz, 1H, C*H*), 5.00 (d, $J = 12.2$ Hz, 1H, C*H*Ph) 2.87 (s, 3H, NCH_3), 2.78 (s, 3H, NCH_3); ^{13}C NMR (50 MHz): δ 164.3 (N*C*$^+$N), 134.5, 134.3, 132.7, 131.6, 131.0, 130.4, 130.3, 130.2, 129.9, 129.8, 129.2, 128.5, 127.9, 121.5, 75.8 (*C*HPh), 74.4 (*C*HPh), 32.8 (N*C*H_3), 32.6 (N*C*H_3). HRMS (ESI) calculated for $C_{23}H_{22}N_2Cl^+$: 361.1472, found: 361.1458.

4.3.4. (+)-(4*R*,5*R*)-2-(2-Chlorophenyl)-1,3-dimethyl-4,5-diphenylimidazolinium bis(trifluoromethylsulfonyl)imide 1c. (+)-(4*R*,5*R*)-2-(2-Chlorophenyl)-1,3-dimethyl-4,5-diphenylimidazolinium bis(trifluoromethylsulfonyl)imide **1c** was prepared from aminal **1** (61 mg, 0.169 mmol) and NBA (24.5 mg, 0.17 mmol) in glyme (1 mL), followed by a counter anion exchange with $LiNTf_2$ (50 mg 97%, 0.17 mmol) in a mixture of $CHCl_3$ (3 mL) and water (3 mL) as a colourless oil (63 mg, 58%). $[\alpha]_D^{22} = +86.5$ (*c* 0.28, $CHCl_3$); MS (ESI, 0 V), *m*/*e* 361.0 (M^+, 100%); IR (KBr) 1607s, 1352s, 1195vs, 1135s, 1058s, 760m, 653m cm^{-1}; ^1H NMR

(400 MHz): δ 8.18–8.12 (m, 1H), 7.75–7.65 (m, 3H), 7.55–7.45 (m, 8H), 7.40–7.32 (m, 2H), 5.43 (d, $J = 12.1$ Hz, 1H, C*H*Ph), 4.99 (d, $J = 11.8$ Hz, 1H, C*H*Ph), 2.88 (s, 3H, NCH_3), 2.80 (s, 3H, NCH_3); ^{13}C NMR (100 MHz): δ 164.9 (NC$^+$N), 135.1, 134.7, 133.1, 131.9, 131.8, 131.0, 130.7, 130.65, 130.4, 130.3, 129.8, 128.8, 128.3, 121.9, 121.88, 76.5 (*C*HPh), 75.1 (*C*HPh), 33.6 (NH*C*H$_3$), 33.1 (NH*C*H$_3$). HRMS (ESI) calculated for $C_{23}H_{22}N_2Cl^+$: 361.1472, found: 361.1458.

4.3.5. (−)-(4*S*,5*S*)-2-(4-Chlorophenyl)-1,3-dimethyl-4,5-diphenylimidazolinium bromide 2a. (−)-(4*S*,5*S*)-2-(4-Chlorophenyl)-1,3-dimethyl-4,5-diphenylimidazolinium bromide **2a** was prepared from (4*S*,5*S*)-2-(4-chlorophenyl)-1,3-dimethyl-4,5-diphenylimidazolidine **2** (359 mg, 0.99 mmol) and NBA (144 mg, 0.99 mmol) in glyme (3 mL) as a white solid (446 mg, 99%). *Hygroscopic*. Mp 98 °C; $[\alpha]_D^{22} = -56.5$ (*c* 0.35, $CHCl_3$); MS (ESI, 0 V), *m*/*z* 361 (M^+, 100%); IR (KBr) 1605s, 1345s, 1327s, 1199vs, 1138s, 1058s, 616s cm^{-1}; ^{1}H NMR (200 MHz): δ 8.08 (d, $J = 8.34$ Hz, 2H), 7.58–7.55 (m, 6H), 7.38–7.35 9 (m, 6H), 5.33 (s, 2H, C*H*Ph), 2.87 (s, 6H, CH_3); ^{13}C NMR (50 MHz$_3$): δ 166.6 (NC$^+$N), 139.9, 133.4, 130.43, 130.38, 130.1, 129.7, 128.3, 120.3, 75.2 (*C*HPh), 33.6 (NCH_3); HRMS (ESI) calculated for $C_{23}H_{22}N_2Cl^+$: 361.1472, found: 361.1482.

4.3.6. (−)-(4*S*,5*S*)-2-(4-Chlorophenyl)-1,3-dimethyl-4,5-diphenylimidazolinium bis(trifluoromethylsulfonyl)imide 2c. (−)-(4*S*,5*S*)-2-(4-Chlorophenyl)-1,3-dimethyl-4,5-diphenylimidazolinium bis(trifluoromethylsulfonyl)imide **2c** was prepared from (4*S*,5*S*)-2-(4-chlorophenyl)-1,3-dimethyl-4,5-diphenylimidazoliniumbromide **2a** (330 mg, 0.75 mmol) and $LiNTf_2$ (236 mg, 0.82 mmol) in a mixture of $CHCl_3$ (2 mL) and water (2 mL) as a white solid (347 mg, 82%). Mp 102 °C; $[\alpha]_D^{22} = -62.4$ (*c* 0.34, $CHCl_3$); MS (EI), *m*/*e* 360 (M^+−H, 100%), 327 (5), 283 (5), 152 (10), 78 (5), 69 (30); IR (KBr) 1604vs, 1346vs, 1199vs, 1138s, 1158s, 616s, 512s cm^{-1}; ^{1}H NMR (200 MHz): δ 7.70–7.59 (m, 4H), 7.43–7.31 (m, 10H), 5.05 (s, 2H, C*H*Ph), 4.64 (s, 6H, NCH_3); ^{13}C NMR (50 MHz): δ 166.6 (NC$^+$N), 140.2, 133.3, 130.5, 130.3, 130.2, 129.8, 128.1, 120.0, 75.2 (*C*HPh), 33.6 (NCH_3). HRMS (ESI) calculated for $C_{23}H_{22}N_2Cl^+$: 361.1472, found: 361.1470.

4.3.7. (−)-(4*S*,5*S*)-2-(4-Chlorophenyl)-1,3-dimethyl-4,5-diphenylimidazolinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate 2d. (−)-(4*S*,5*S*)-2-(4-Chlorophenyl)-1,3-dimethyl-4,5-diphenylimidazolinium tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate **2d** was prepared from (4*S*,5*S*)-2-(4-chlorophenyl)-1,3-dimethyl-4,5-diphenylimidazolinium bromide **2a** (150 mg, 0.34 mmol) and NaB[3,5-(CF$_3$)$_2$-C$_6$H$_3$]$_4$ (300 mg, 0.34 mmol) in a mixture of $CHCl_3$ (3 mL) and water (3 mL) as a white solid (48 mg, 71%). mp 114 °C; $[\alpha]_D^{22} = -39.4$ (*c* 0.31, $CHCl_3$); MS (EI), *m*/*e* 361 (M^+, 20%), 243 (100), 228 (20), 165 (20), 152 (20), 118 (25); IR (KBr) 3426m, 1604s, 1356vs, 1278vs, 1127vs, 839s, 713s, 682s, 669m cm^{-1}; ^{1}H NMR (400 MHz): δ 7.80–7.69 (m, 10H), 7.59–7.46 (m, 12H), 7.26–7.25 (m, 4H), 4.98 (s, 2H, C*H*), 2.92 (s, 6H, CH_3); ^{13}C NMR (50 MHz) 166.4 (NC$^+$N), 162.1 (q, $J = 49.6$ Hz, B*C*), 142.3, 135.2 (BC*C*H), 133.8, 131.7, 131.5, 130.9, 129.5, 129.3 (q, $J = 28.4$ Hz, *C*CF$_3$), 126.9, 126.3, 125.0 (q, $J = 271$ Hz, C*C*F$_3$), 118.9, 117.95 (*C*HCCF$_3$), 75.5 (N*C*HPh), 34.2 (N*C*H$_3$). Anal. Calcd for $C_{55}H_{34}BClF_{24}$: C, 53.92; H, 2.80; N, 2.29. Found: C, 53.72; H, 2.84; N, 2.20; HRMS (ESI) calculated for $C_{23}H_{22}N_2Cl^+$: 361.1472, found: 361.1483.

4.3.8. (−)-(4*S*,5*S*)-2-(2-Pyridinyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolinium bromide 4a. (−)-(4*S*,5*S*)-2-(2-Pyridinyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolinium bromide **4a** was prepared from (4*S*,5*S*)-2-(pyridinyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolidine **4** (1.13 g, 2.23 mmol) and NBA (308 mg, 2.23 mmol) in Et_2O (5 mL) as a yellow oil (1.26 g, 96%). *Hygroscopic*. $[\alpha]_D^{22} = -85.9$ (*c* 0.67, $CHCl_3$); ^{1}H NMR (200 MHz): δ 9.57 (d, $J = 7.7$ Hz, 1H), 8.90 (d, $J = 3.8$ Hz, 1H), 8.32 (t, $J = 7.7$ Hz, 1H), 7.80–7.70 (8m, 1H), 7.30–6.90 (m, 20H), 5.20–4.90 (m, 4H, NC*H*Ph, PhC*H*CH$_3$), 1.65 (br s, 6H, CHCH_3); ^{13}C NMR (50 MHz): δ 164.2 (NC$^+$N), 150.3, 143.1, 139.4, 136.4, 135.1, 129.3, 129.2, 128.4, 128.3, 127.9, 127.6, 127.4, 72.1 (*C*HPh), 57.8 (NCHCH$_3$), 18.1 (CH*C*H$_3$); HRMS (ESI) calculated for $C_{36}H_{34}N_3^+$: 508.2753, found: 508.2758.

4.3.9. (−)-(4*S*,5*S*)-2-(2-Pyridinyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolinium hexafluorophosphate 4b. (−)-(4*S*,5*S*)-2-(2-Pyridinyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolinium hexafluorophosphate **4b** was prepared from (4*S*,5*S*)-2-(2-pyridyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolinium bromide **4a** (105 mg, 0.18 mmol) and KPF_6 (36 mg, 0.20 mmol) in a mixture of $CHCl_3$ (3 mL) and water (3 mL) as a white solid (100 mg, 86%). Mp 87 °C; $[\alpha]_D^{22} = -65.4$ (*c* 0.48, $CHCl_3$); MS (ESI, 0 V), *m*/*e* 508 (M^+); IR (KBr) 3423w, 1556s, 1456m, 1278m, 838vs, 757m, 696s, 557s cm^{-1}; ^{1}H NMR (200 MHz): δ 9.00 (d, $J = 4.2$ Hz, 1H) 8.58 (d, $J = 7.8$ Hz, 1H), 8.34–8.30 (m, 1H), 7.79–7.73 (m, 1H), 7.26–6.99 (m, 20H), 5.00–4.80 (m, 4H, C*H*Ph, C*H*CH$_3$), 1.56 (d, $J = 6.8$ Hz, 6H, NCH_3); ^{13}C NMR (50 MHz): δ 164.1 (NC$^+$N), 151.4, 142.7, 139.4, 136.0, 135.2, 129.5, 129.4, 128.7, 128.5, 127.9, 127.7, 126.6, 126.4, 71.4 (*C*HPh), 57.8 (NCHCH$_3$), 17.9 (CH*C*H$_3$); HRMS (ESI) calculated for $C_{36}H_{34}N_3^+$: 508.2753, found: 508.2752.

4.3.10. (−)-(4*S*,5*S*)-2-(2-Pyridinyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolinium bis(trifluoromethylsulfonyl)-imide 4c. (−)-(4*S*,5*S*)-2-(2-Pyridinyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolinium bis(trifluoromethylsulfonyl)imide **4c** was prepared from (4*S*,5*S*)-2-(2-pyridyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolinium bromide **4a** (300 mg, 0.51 mmol) and $LiNTf_2$ (176 mg, 0.61 mmol) in a mixture of DCM (3 mL) and water (3 mL) as a colourless liquid (230 mg, 57%). $[\alpha]_D^{22} = -50.0$ (*c* 0.46, $CHCl_3$); MS (ESI, 0 V), *m*/*e* 508.3 (M^+); IR (KBr) 1556m, 1353s, 1196vs, 1135m, 1058s, 696m cm^{-1}; ^{1}H NMR (200 MHz): δ 8.95–8.87 (m, 1H) 8.50 (d, $J = 6.8$ Hz, 1H), 8.27 (td, $J = 7.7$, 1.7 Hz, 1H), 7.75–7.60 (m, 1H), 7.25–6.70 (m, 20H), 4.90–4.70 (m, 4H, C*H*Ph, C*H*CH$_3$), 1.50 (d, $J = 7.0$ Hz, 6H, NCH_3); ^{13}C NMR (50 MHz): δ 163.1 (NC$^+$N), 150.1, 141.7, 138.5, 135.1, 134.2, 129.9, 128.4, 127.8, 127.5, 126.9, 126.7, 125.6, 125.4, 119.0 (q, $J = 64.9$ Hz, *C*F$_3$), 70.5 (*C*HPh), 56.8

(N*C*HCH$_3$), 12.0 (CH*C*H$_3$). HRMS (ESI) calculated for $C_{36}H_{34}N_3^+$: 508.2753, found: 508.2767.

4.3.11. (−)-(4*S*,5*S*)-2-(2-Chlorophenyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolinium bromide 5a. (−)-(4*S*,5*S*)-2-(2-Chlorophenyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolinium bromide **5a** was prepared from (4*S*,5*S*)-2-(2-chlorophenyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolidine **5** (100 mg, 0.18 mmol) and NBA (26.8 mg, 0.18 mmol) in glyme (1 mL) as a white solid (102 mg, 89%). *Hygroscopic*. $[\alpha]_D^{22} = -131.6$ (*c* 0.29, $CHCl_3$); ^{1}H NMR (400 MHz): δ 9.41 (d, $J = 7.2$, 1H), 7.90 (t, $J = 7.2$ Hz, 1H), 7.70 (t, $J = 7$ Hz, 1H), 7.55–6.90 (m, 18H), 6.65–6.58 (m, 2H), 6.63 (d, $J = 10.3$ Hz, 1H, C*H*Ph), 5.34 (q, $J = 7.2$ Hz, 1H, C*H*CH$_3$), 5.08 (d, $J = 10.3$ Hz, 1H, C*H*Ph), 4.83 (q, $J = 7.2$ Hz, 1H, C*H*CH$_3$), 1.75 (d, $J = 7.1$ Hz, 6H, CHC*H*$_3$); ^{13}C NMR (100 MHz): δ 165.3 (N*C*$^+$N), 138.03, 138.0, 136.0, 134.7, 134.2, 137.7, 132.8, 130.6, 129.95, 129.87, 129.7, 129.6, 129.5, 128.9, 128.7, 128.6, 128.5, 128.4, 128.2, 127.7, 123.5, 73.4 (*C*HPh), 72.9 (*C*HPh), 60.7 (N*C*HCH$_3$), 57.2 (N*C*HCH$_3$), 19.8 (CH*C*H$_3$), 17.0 (CH*C*H$_3$). This compound was used directly in the subsequent step.

4.3.12. (−)-(4*S*,5*S*)-2-(2-Chlorophenyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolinium hexafluorophosphate 5b. (−)-(4*S*,5*S*)-2-(2-Chlorophenyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolinium hexafluorophosphate **5b** was prepared from (4*R*,5*R*)-2-(2-chlorophenyl)-4,5-diphenyl-1,3-bis((*S*)-1-phenylethyl)imidazolinium bromide **5a** (88 mg, 0.14 mmol) and KPF_6 (29 mg, 0.16 mmol) in a mixture of $CHCl_3$ (3 mL) and water (3 mL) as a white solid (92 mg, 94%). Mp = 160 °C; $[\alpha]_D^{22} = -82.7$ (*c* 2.75, $CHCl_3$); MS (ESI, 0 V), *m*/*e* 541.3 (M^+, 100%); IR (Kbr) 2360m, 2341m, 1533s, 1456m, 840vs, 697s, 558s cm^{-1}; ^{1}H NMR (400 MHz): δ 8.49 (dd, $J = 7.7$, 1.4 Hz, 1H), 8.01–7.95 (m, 1H), 7.78 (td, $J = 5.6$, 1.5 Hz, 1H), 7.64 (d, $J = 8.0$ Hz, 1H), 7.40–6.95 (m, 16H), 6.85–6.80 (m, 2H), 6.65 (d, $J = 7.4$ Hz, 2H), 5.19 (d, $J = 8.4$ Hz, 1H, C*H*Ph), 5.00 (d, $J = 8.4$ Hz, 1H, C*H*Ph), 4.98 (q, $J = 7.1$ Hz, 1H, C*H*CH$_3$), 4.88 (q, $J = 7.1$ Hz, 1H, C*H*CH$_3$), 1.74 (d, $J = 7.1$ Hz, 3H, CHC*H*$_3$), 1.68 (d, $J = 7.1$ Hz, 3H, CHC*H*$_3$); ^{13}C NMR (100 MHz): δ 164.9 (N*C*$^+$N), 137.8, 136.6, 135.5, 135.2, 132.5, 132.4, 131.1, 130.5, 130.0, 129.9, 129.87, 129.8, 128.9, 128.7, 128.3, 127.8, 127.7, 127.65, 123.0, 72.6 (*C*HPh), 72.6 (*C*HPh), 59.8 (N*C*HCH$_3$), 57.7 (N*C*HCH$_3$), 18.4 (CH*C*H$_3$), 17.6 (CH*C*H$_3$); HRMS (ESI) calculated for $C_{37}H_{24}N_2Cl^+$: 541.2421, found: 541.2421.

4.3.13. (+)-(4*S*,5*S*)-2-(4-Chlorophenyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolinium hexafluorophosphate 6b. (+)-(4*S*,5*S*)-2-(4-Chlorophenyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolinium hexafluorophosphate **6b** was prepared when (4*S*,5*S*)-2-(4-chlorophenyl)-4,5-diphenyl-1,3-bis((*R*)-1-phenylethyl)imidazolidine **6** (200 mg, 0.368 mmol) was dissolved in glyme (1 mL) and NBA (27 mg, 0.18 mmol) added. The reaction mixture was stirred at rt for 15 min and a second portion of NBA (27 mg, 0.18 mmol) added. The reaction mixture was stirred for an additional 30 min, during which a yellow solid precipitated. Et_2O (3 mL) was added and the mixture stirred for 15 min in order to precipitate the rest of the imidazolinium bromide salt. The solvent was removed by filtration and the remaining solid washed with Et_2O (2 × 3 mL). The solid was dissolved in $CHCl_3$ (3 mL) and an aqueous solution of KPF_6 (68 mg, 0.368 mmol) was added. The mixture was stirred vigorously for 30 min and the aqueous phase removed. The organic phase was washed with water (3 × 3 mL), dried (3 Å MS) and the solvent was removed under reduced pressure to give the *title compound* **6b** as a yellow solid (183 mg, 72%). Mp 87 °C; $[\alpha]_D^{22} = +5.7$ (*c* 0.39, $CHCl_3$); MS (ESI, 0 V), *m*/*e* 541.0 (M^+, 100%); IR (KBr) 3441s, 1543m, 848vs, 696s, 557s cm^{-1}; ^{1}H NMR (200 MHz): δ 7.85 (dd, $J = 27.8$, 8.6 Hz, 4H), 7.40–6.75 (m, 20H), 4.97 (s, 2H, NC*H*Ph), 5.00–4.85 (m, 2H, NC*H*Me), 1.60 (d, $J = 7.2$ Hz, 6H, CHC*H*$_3$); ^{13}C NMR (50 MHz): δ 166.7 (N*C*$^+$N), 140.1, 136.1, 135.5, 131.0, 130.2, 129.6, 129.5, 128.7, 128.6, 126.6, 120.9, 71.7 (2C, N*C*HPh), 58.0 (2C, N*C*HCH$_3$), 17.9 (2C, CH*C*H$_3$); HRMS (ESI) calculated for $C_{37}H_{34}N_2Cl$: 541.2411, found: 541.2418.

4.3.14. (−)-(4*S*,5*S*)-1,3-Dimethyl-2-(2-((4*S*,5*S*)-1,3-dimethyl-4,5-diphenylimidazolidin-2-yl)phenyl)-4,5-diphenylimidazolinium bis-bis(trifluoromethylsulfonyl)imide 7c. (4*S*,5*S*)-1,3-Dimethyl-2-(2-((4*S*,5*S*)-1,3-dimethyl-4,5-diphenylimidazolidin-2-yl)phenyl)-4,5-diphenylimidazolidine **7** (500 mg, 0.864 mmol) was dissolved in glyme (3 mL) and NBA (128 mg, 0.864 mmol) was added. After 15 min, a second portion of NBA (128 mg, 0.864 mmol) was added. The reaction mixture was stirred overnight and Et_2O (5 mL) was added in order to precipitate the bromide salt formed. The precipitate was washed with Et_2O (2 × 5 mL) and dried in vacuo for 30 min. The bromide salt was dissolved in $CHCl_3$ (3 mL) and a solution of $LiNTf_2$ (574.16 mg, 2 mmol) in H_2O (2 mL) added. The mixture was stirred vigorously for 30 min, during which a white precipitate formed. The latter was filtered off, washed with $CHCl_3$ (3 mL), water (3 mL) and dried in vacuo to give the *title compound* **7c** as a white solid (622 mg, 80%). Mp 165 °C; $[\alpha]_D^{22} = -21$ (*c* 0.2, acetone); MS (ESI, 0 V), *m*/*e* 288 (M^{2+}, 100%), 856 (M^++NTf_2, 20); IR (KBr) 3425m, 1602s, 1350vs, 1197vs, 1058s, 616s cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.40–8.20 (m, 4H), 7.80–7.30 (m, 20H), 5.82 (d, $J = 14.0$ Hz, 2H, C*H*Ph), 5.39 (d, $J = 14.0$ Hz, 2H, C*H*Ph), 3.00–2.80 (m, 12H, NC*H*$_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.9 (N*C*$^+$N), 135.5, 134.6, 132.0, 133.2, 131.2, 130.8, 130.4, 130.2, 129.9, 129.85, 121.9, 120.4 (q, $J = 314.3$ Hz, CF_3), 76.4 (*C*HPh), 72.0 (*C*HPh), 35.4 (N*C*H$_3$), 34.9 (N*C*H$_3$). HRMS (ESI) calculated for $C_{40}H_{40}N_4^{2+}$: 288.1626, found: 288.1621.

4.3.15. (−)-(4*S*,5*S*)-1,3-Dimethyl-2-(2-((4*S*,5*S*)-1,3-dimethyl-4,5-diphenylimidazolidin-2-yl)phenyl)-4,5-diphenylimidazolinium bis-tetrakis(3,5-bis(trifluoromethyl)phenyl)borate 7d. (4*S*,5*S*)-1,3-Dimethyl-2-(2-((4*S*,5*S*)-1,3-dimethyl-4,5-diphenylimidazolidin-2-yl)phenyl)-4,5-diphenylimidazolidine **7** (250 mg, 0.43 mmol) was dissolved in a minimal amount of glyme (2 mL) and NBA (62 mg, 0.43 mmol) was added. After 15 min stirring at rt, a second portion of NBA (62 mg, 0.43 mmol) was added. The reaction mixture was stirred overnight and Et_2O (5 mL) was added in order to precipitate the formed bromide salt. The precipitate was washed with Et_2O (2 × 5 mL) and dried in vacuo for

30 min. The bromide salt was then dissolved in DCM (5 mL), followed by the addition of $NaB[3,5\text{-}(CF_3)_2\text{-}C_6H_3]_4$ (765.8 mg, 0.86 mmol) and water (3 mL). The mixture was stirred vigorously for 30 min. The organic phase was separated, washed with water (3 × 5 mL), dried (3 Å MS) and the solvent removed under reduced pressure. The remaining solid was further dried under high vacuum to give the *title compound* **7d** as a light brown solid (792 mg, 80%). Mp 66–68 °C; $[\alpha]_D^{22} = -25$ (*c* 0.45, acetone); MS (ESI, 0 V), *m*/*e* 288.2 (M^{2+}, 100%); IR (KBr) 1605m, 1356s, 1279vs, 1126s, 682m cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 8.30–8.20 (m, 4H), 7.60–7.40 (m, 44H), 5.91 (d, $J = 14.0$ Hz, 2H, C*H*Ph), 5.47 (d, $J = 14.0$ Hz, 2H, C*H*Ph), 2.99 (d, $J = 5.1$ Hz, 12H, NCH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.5 (NC^+N), 161.5 (q, $J = 49.6$ Hz, B*C*), 135.1, 134.2 (b, B*C*CH), 134.4, 133.6, 132.8, 130.7, 130.3, 130.0, 129.7, 129.5, 129.4, 128.9 (q, $J = 28.4$ Hz, CH*C*CF_3), 124.4 (q, $J = 271.2$ Hz, C*C*F_3), 121.6, 118.0 (*C*HCCF_3), 79.6 (N*C*HPh), 71.6 (N*C*HPh), 35.0 (N*C*H_3), 34.5 (N*C*H_3). HRMS (ESI) calculated for $C_{20}H_{20}N_2^{2+}$ 288.1626, found 288.1616.

4.3.16. (−)-(4*R*,5*R*)-1,3-Dimethyl-2-(2-((4*R*,5*R*)-1,3-dimethyl-4,5-diphenylimidazolidin-2-yl)phenyl)-4,5-diphenylimidazolinium bis-hexafluorophosphate 8b. (3a*R*,7a*R*)-Octahydro-2-(2-((3a*R*,7a*R*)-octahydro-1,3-dimethyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl)-1,3-dimethyl-1*H*- benzo[*d*]-imidazole **8** (140 mg, 0.37 mmol) was dissolved in a minimal amount of glyme (1.5 mL) and NBA (53 mg, 0.37 mmol) was added. After 15 min stirring at rt, a second portion (53 mg, 0.37 mmol) was added. The reaction mixture was stirred for 3 h during which a brown precipitate formed. The solvent was decanted and the precipitate washed with Et_2O and dissolved in $CHCl_3$ (2 mL). A solution of KPF_6 (135 mg, 0.732 mmol) in water (3 mL) was added and the mixture was vigorously stirred overnight during which a brown precipitate formed. The solvents were carefully removed and the rest was dried in vacuo to give the *title compound* **8b** as a brown solid (184 mg, 75%). Mp 145–150 °C; $[\alpha]_D^{22} = -7.7$ (*c* 0.3, acetone); MS (ESI, 50 V), *m*/*e* 190.1 (M^{2+}, 100%); IR (KBr) 2360m, 1589m, 839vs, 558s cm^{-1}; ^1H NMR (400 MHz, DMSO): δ 8.20–8.10 (m, 2H), 8.10–7.95 (m, 2H), 3.65–3.50 (m, 4H, C*H*), 3.05 (s, 6H, CH_3), 2.85 (s, 6H, CH_3), 2.40–2.25 (m, 4H, CH_2), 2.00–1.85 (m, 4H, CH_2), 1.60–1.25 (m, 8H, CH_2); ^{13}C NMR (100 MHz, DMSO): δ 165.3 (NC^+N), 134.5, 131.8, 121.8, 69.2 (N*C*HCH_2), 67.6 (N*C*HCH_2), 33.7 (*C*H_3), 32.8 (*C*H_3), 27.4 (*C*H_2), 27.3 (*C*H_2), 23.9 (*C*H_2), 23.7 (*C*H_2). HRMS (ESI) calculated for $C_{24}H_{36}N_4^{2+}$ 190.1471, found: 190.1470.

4.3.17. (−)-(4*R*,5*R*)-1,3-Dimethyl-2-(2-((4*R*,5*R*)-1,3-dimethyl-4,5-diphenylimidazolidin-2-yl)phenyl)-4,5-diphenylimidazolinium bis-tetrakis(3,5-bis(trifluoromethyl)phenyl)-borate 8d. (3a*R*,7a*R*)-Octahydro-2-(2-((3a*R*,7a*R*)-octahydro-1,3-dimethyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazole **8** (145 mg, 0.38 mmol) was dissolved in a minimal amount of glyme (3 mL) and NBA (55 mg, 0.19 mmol) was added. After 15 min stirring at rt a second portion (55 mg, 0.19 mmol) was added and the reaction mixture stirred for 3 h. Et_2O (5 mL) was added in order to precipitate the bromide salt formed. The precipitate was washed with Et_2O (2 × 5 mL) and dried in vacuo for 30 min. The bromide salt was dissolved in DCM (3 mL) and $NaB[3,5\text{-}(CF_3)_2\text{-}C_6H_3]_4$ (672.5 mg, 0.759 mmol) and water (3 mL) were added. The mixture was vigorously stirred for 30 min and the organic phase separated, washed with water (3 × 5 mL), dried (3 Å MS) and the solvent removed under reduced pressure. The remaining solid was further dried under high vacuum to give the *title compound* **8d** as a brown solid (677 mg, 87%). Mp 115 °C; $[\alpha]_D^{22} = -5.9$ (*c* 0.67, acetone); MS (ESI, 20 V), *m*/*e* 190.1 (M^{2+}, 100%); IR (KBr) 1612w, 1357s, 1280vs, 1125vs, 713m cm^{-1}; ^1H NMR (400 MHz, DMSO): δ 8.10–7.95 (m, 4H), 7.70–7.50 (m, 24H), 3.60–3.50 (m, 4H, N*C*HCH_2), 3.01 (s, 6H, NCH_3), 2.83 (s, 6H, CH_3), 2.40–2.20 (m, 4H, CH_2), 1.90–1.80 (m, 4H, CH_2), 1.60–1.40 (m, 4H, CH_2), 1.40–1.20 (m, 4H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9 (NC^+N), 160.0 (q, $J = 49.6$ Hz, B*C*), 134.0, 131.3, 128.4 (q, $J = 62.4$ Hz, *C*CF_3), 123.9 (q, $J = 271$ Hz, C*C*F_3), 121.2, 117.3, 68.7 (N*C*HCH_2), 67.1 (N*C*HCH_2), 33.1 (*C*H_3), 32.2 (*C*H_3), 26.7 (*C*H_2), 23.2 (*C*H_2), 23.0 (*C*H_2). HRMS (ESI) calculated for $C_{24}H_{36}N_4^{2+}$ 190.1470, found: 190.1469.

4.4. Imidazolinium salts as catalysts

4.4.1. General procedure for the imidazolinium salt catalyzed aza Diels–Alder reaction in acetonitrile. An imine (0.2 mmol) and catalyst (0.02 mmol, 10 mol %) were placed into a dry Schlenk flask under a nitrogen atmosphere. The reaction mixture was dissolved in dry acetonitrile (2 mL) and Danishefsky's diene (0.22 mmol, 43 μL) was added at once. After 16 h stirring at rt, the mixture was quenched with a saturated solution of potassium hydrogencarbonate (2 mL) and extracted with ethyl acetate (3 × 5 mL). The organic phases were combined, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. FCC (petroleum ether/ethyl acetate, 1/1) gave the desired product.

4.4.2. General procedure for the imidazolinium salt catalyzed inverse electron demand aza Diels–Alder reaction for mono-imidazolinium salts. Imine **10** (0.2 mmol) and the catalyst (0.02 mmol) were placed into a dry Schlenk flask under a nitrogen atmosphere. The reaction mixture was dissolved in dry acetonitrile (2 mL) and the dienophile 3,4-dihydro-2*H*-pyran **12** (0.4 mmol, 30.27 μL) or 3,4-dihydro-2*H*-pyran **13** (0.4 mmol, 36.18 μL) was added at once. The reaction mixture was stirred at rt between 16 and 112 h and the solvent was evaporated under reduced pressure. The products were isolated by FCC (petroleum ether/ethyl acetate, 95/5) to give the corresponding quinolines.

4.4.3. In DCM, catalyzed by bis-imidazolinium salts. *N*-Benzylidene aniline (54.3 mg, 0.3 mmol) and the catalyst (0.03 mmol) were placed into a dry Schlenk flask under a nitrogen atmosphere. The reaction mixture was dissolved in dry DCM (1 mL) and 3,4-dihydro-2*H*-pyran (56 μL, 0.6 mmol) added at once. The reaction mixture was stirred at rt (for different reaction times and temperatures see text in Section 2.2). The solvent was removed and the crude product purified by FCC (petroleum ether/ethyl acetate, 95/5) to give the corresponding quinolines.

4.4.4. 2,3-Dihydro-1,2-diphenylpyridin-4(1*H*)-one 11 (R = Ph). 2,3-Dihydro-1,2-diphenylpyridin-4(1*H*)-one **11** was prepared from **9** and **10** (R = Ph) as yellow solid. The spectral data were consistent with the literature values.[25]

4.4.5. 2-Phenyl-1-tosyl-2,3-dihydropyridin-4(1*H*)-one 11 (R = Ts). From (E)-N-(benzylidene) tosylamine (52 mg, 0.20 mmol) and Danishefsky's diene (43 μL, 0.22 mmol) in the presence of imidazolinium catalyst (0.02 mmol) as a white solid (23 mg, 35%). Spectral data were consistent with literature values.[26]

4.4.6. 3,4,4a,5,6,10b-Hexahydro-5-phenyl-2*H*-pyrano[3,2-*c*]-quinoline 14a and 14b. 3,4,4a,5,6,10b-Hexahydro-5-phenyl-2*H*-pyrano[3,2-*c*]quinoline **14a** and **14b** was prepared from benzylidene aniline (54 mg, 0.3 mmol) and dihydropyran (50 μL, 0.6 mmol) as a mixture of *cis*- and *trans*-diastereomers. The ratio of the diastereomers was determined after isolation by FCC.

Cis-isomer as a white solid: The spectral data were consistent with the literature values.[27] HPLC conditions: AD-H (2.5% *i*-PrOH/hexane, 0.3 mL/min) $t_1 = 71.2$ min, $t_2 = 83.8$ min.

Trans-isomer as a yellow oil: The spectral data were consistent with the literature values.[27] HPLC conditions: AD-H (2.5% *i*-PrOH/hexane, 0.4 mL/min) $t_1 = 38.5$ min, $t_2 = 59.1$ min.

4.5. NMR experiments with Mosher's acid salt

4.5.1. Preparation of racemic potassium Mosher's carboxylate. Racemic Mosher's acid (302 mg, 1.29 mmol) was dissolved in water (1 mL) and a solution of KOH (72 mg, 1.29 mmol) in water (3 mL) was added. The mixture was stirred at rt for 15 min and water was removed under reduced pressure. The remaining solid was further dried under high vacuum to give the potassium Mosher's carboxylate salt as a white solid (351 mg, quant.).

4.5.2. NMR experiment with the racemic Mosher's acid salt. Mosher's acid salt (1 mmol) and the corresponding imidazolinium salt (1 mmol) were dissolved in acetone-d_6 and the ^{1}H NMR and ^{19}F NMR spectra were recorded at rt. For results see Table 4.

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References

1. Génisson, Y.; Lauth-de Viguerie, N.; André, C.; Baltas, M.; Gorrichon, L. *Tetrahedron: Asymmetry* **2005**, *16*, 1017–1023.
2. Clavier, H.; Boulanger, L.; Audic, N.; Toupet, L.; Mauduit, M.; Guillemin, J. C. *Chem. Commun.* **2004**, 1224–1225.
3. Baudequin, C.; Baudoux, J.; Levillain, J.; Cahard, D.; Gaumont, A. C.; Plaquevent, J. C. *Tetrahedron: Asymmetry* **2003**, *14*, 3081–3093.
4. Ding, J.; Armstrong, D. W. *Chirality* **2005**, *17*, 281–292.
5. Baudequin, C.; Bregeon, D.; Levillain, J.; Guillen, F.; Plaquevent, J. C.; Gaumont, A. C. *Tetrahedron: Asymmetry* **2005**, *16*, 3921–3945.
6. Jurčík, V.; Wilhelm, R. *Green Chem.* **2005**, *7*, 844–848.
7. Jurčík, V.; Wilhelm, R. *Org. Biomol. Chem.* **2005**, *3*, 239–244.
8. Zhou, H.; Campbell, E. J.; Nguyen, S. T. *Org. Lett.* **2001**, *3*, 2229–2231.
9. Mukaiyama, T.; Yanagisawa, M.; Iida, D.; Hachiya, I. *Chem. Lett.* **2000**, 606–607.
10. Chen, C.-T.; Chao, S.-D.; Yen, K.-C.; Chen, C. H.; Chou, I.-C.; Hon, S.-W. *J. Am. Chem. Soc.* **1997**, *119*, 11341–11342.
11. Miura, K.; Ootsuka, K.; Suda, S.; Nishikori, H.; Hosomi, A. *Synlett* **2002**, 313–315.
12. Chen, C.-T.; Chao, S.-D.; Yen, K.-C. *Synlett* **1998**, 924–926.
13. Howarth, J.; Hanlon, K.; Fayne, D.; McCormac, P. *Tetrahedron Lett.* **1997**, *38*, 3097–3100.
14. Dalko, P. I.; Moisan, L. *Angew. Chem., Int. Ed.* **2004**, *43*, 5138–5175.
15. Berkessel, A.; Gröger, H. *Asymmetric Organocatalysis*; Wiley-VCH: Weinheim, 2004.
16. Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, 2003.
17. Jurčík, V.; Wilhelm, R. *Tetrahedron* **2004**, *60*, 3205–3210.
18. Stewart, A. T.; Hauser, C. R. *J. Am. Chem. Soc.* **1955**, *77*, 1098–1103.
19. Denmark, S. E.; Su, Y. P.; Nishigaichi, Y.; Coe, D. M.; Wong, K. T.; Winter, S. B. D.; Choi, J. Y. *J. Org. Chem.* **1999**, *64*, 1958–1967.
20. Roland, S.; Mangeney, P. *Eur. J. Org. Chem.* **2000**, *4*, 611–616.
21. Salerno, A.; Caterina, C.; Perillo, I. A. *Synth. Commun.* **2000**, *30*, 3369–3382.
22. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.
23. Yakelis, N. A.; Bergman, R. G. *Organometallics* **2005**, *24*, 3579–3581.
24. Bambridge, K.; Begley, M. J.; Simpkins, N. S. *Tetrahedron Lett.* **1994**, *35*, 3391–3394.
25. Yuan, Y.; Li, X.; Ding, K. L. *Org. Lett.* **2002**, *4*, 3309–3311.
26. Mancheno, O. G.; Arrayas, R. G.; Carretero, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 456–457.
27. Yadav, J. S.; Reddy, B. V. S.; Madhuri, C. R.; Sabitha, G. *Synthesis* **2001**, 1065–1068.