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Highly Efficient Recyclable Co^{III}–salen Complexes in the Catalyzed Asymmetric Aminolytic Kinetic Resolution of Aryloxy/Terminal Epoxides for the Simultaneous Production of *N*-Protected 1,2-Amino Alcohols and the Corresponding Epoxides in High Optical Purity

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Chiral Co^{III}–salen complexes **1**–**6** bearing different substituents at the 3,3′- and 5,5′-positions of the salen unit, namely H, *t*Bu, morpholinomethyl, and piperidinomethyl, have been synthesized. These complexes were used as catalysts in an environmentally benign protocol for the highly enantioselective aminolytic kinetic resolution (AKR) of racemic aryloxy/terminal epoxides with various carbamates as the nucleophile in the presence of different ionic liquids at room temperature. Excellent yields (>99 % with respect to the nucleophile) of *N*-protected 1,2-amino alcohols with high regio- and enantioselectivities (*ee* >99 %) were achieved with the simultaneous formation of the corresponding epoxides with high chiral purity (*ee* up to >99 %) and in quantitative yields with catalyst **1** in the ionic liquid [bmim]PF_6 as the reaction medium in around 5 h. The catalyst is recyclable in this ionic-liquid-mediated AKR process (up to six cycles with no loss of performance), and the process is five times faster than the homogeneous process performed with conventional organic solvents.

Introduction

Chiral β-amino alcohols are valuable intermediates in the synthesis of a variety of biologically active compounds and play a very significant role in asymmetric catalysis.[1] Various efficient methods have been reported for the synthesis of chiral *syn*-β-amino alcohols, noteworthy among them are the amino hydroxylation of olefins,[2] the addition of α-hydroxy ketones to imines,[3] and the asymmetric ring-opening (ARO)/aminolytic kinetic resolution (AKR) of *meso*/racemic terminal *trans*-epoxides with alkyl/arylamines by using different chiral catalysts.[4–8] Bartoli and co-workers[9] demonstrated for the first time a very simple experimental procedure for the synthesis of chiral *syn*/*anti*-β-amino alcohols by AKR of terminal/*trans*-aromatic epoxides with aniline/carbamates using Cr^{III}– and Co^{III}–salen complexes as catalysts. Excellent results in terms of the yields and enantioselectivities of β-amino alcohols were achieved with these complexes. Incidentally, the same chiral Co^{III}–salen complexes were successfully used by Jacobsen and co-workers for the hydrolytic kinetic resolution (HKR) of terminal epoxides with water as a nucleophile.[10] These monomeric chiral salen complexes are often highly soluble in the reaction media making them difficult to recover and recycle. In our quest to develop recyclable catalysts,[6f–6h] we have reported the ARO/AKR of *meso*/*trans*-epoxides using recyclable catalysts derived from Ti^{IV}/Cr^{III} with chiral BINOL[6f]/Schiff bases[6h] as ligands under ambient,[6f] thermal,[6f] and microwave-irradiation[11] reaction conditions. These systems worked well when organic solvents were used as the reaction medium, which is not desirable from an environmental point of view. Ionic liquids are currently viewed as future reaction media in the chemical industry as an eco-friendly alternative to conventionally used hazardous organic solvents.[12] It has also been observed that switching over to an ionic liquid from a traditional organic solvent often results in a significant improvement in the reactivity and selectivity of a catalytic system.[13] Song and co-workers previously reported that the use of ionic liquids enabled Cr^{III}– and Co^{III}–salen catalysts to be recycled in the HKR of racemic epoxides and in the enantioselective ring-opening of *meso*-epoxides.[14] In this work we have synthesized chiral Co^{III}–salen complexes **1**–**6** with different substituents at the 3,3′- and 5,5′-positions of the salen unit, namely H, *t*Bu, morpholinomethyl, and piperidinomethyl (Figure 1), and used them as catalysts for the AKR of racemic aryloxy/terminal epoxides with various carbamates as the nucleo-

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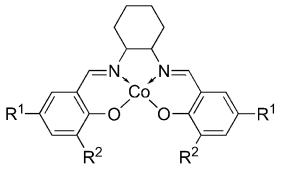
phile in ionic liquids at room temperature. This protocol provided *N*-protected 1,2-amino alcohols in excellent yields (>99% with respect to the nucleophile) with high regio- and enantioselectivities (*ee* up to >99%) with the simultaneous production of the corresponding chirally enriched epoxides with high optical purity (*ee* >99%) and in quantitative yields. These systems are recyclable as well as allowing reactions to be several times faster than the corresponding systems in organic solvents.[9b]



1 R^1= *t*Bu, R^2 = *t*Bu
2 R^1= H, R^2 = H
3 R^1= H, R_2 = *t*Bu
4 R^1 = *t*Bu, R^2 = H
5 R^1= *t*Bu, R^2 = morpholinomethylene
6 R^1= *t*Bu, R^2 = piperidinomethylene

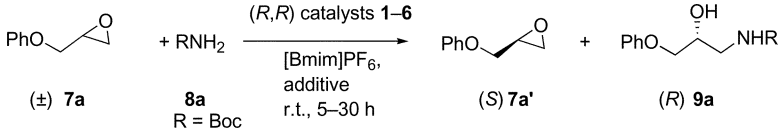
Figure 1. Structures of the catalysts **1**–**6**.

Results and Discussion

Chiral salen complexes **1**–**6** were obtained by the reaction of the corresponding chiral salen ligands, namely, (1*R*,2*R*)-*N*,*N*′-bis[3,5-di(*tert*-butyl)salicylidene]cyclohexane-1,2-diamine,[15a] (1*R*,2*R*)-*N*,*N*′-disalicylidenecyclohexane-1,2-diamine, (1*R*,2*R*)-*N*,*N*′-bis[3-(*tert*-butyl)salicylidene]cyclohexane-1,2-diamine, (1*R*,2*R*)-*N*,*N*′-bis[5-(*tert*-butyl)salicylidene]cyclohexane-1,2-diamine,[15b] (1*R*,2*R*)-*N*,*N*′-bis[3-(morpholinomethyl)-5-(*tert*-butyl)salicylidene]cyclohexane-1,2-diamine, and (1*R*,2*R*)-*N*,*N*′-bis[3-(piperidinomethyl)-5-(*tert*-butyl)salicylidene]cyclohexane-1,2-diamine[15c] with Co^{II} acetate under an inert gas (Figure 1). All the chiral metal complexes were characterized by microanalysis, IR and UV/Vis spectroscopy, and optical rotation (data are given in the Exp. Sect.).

In our first round of catalytic studies, complex **1** (1 mol-%) was explored for its catalytic activity in the AKR of 1,2-epoxy-3-phenoxypropane (**7a**; 2.2 mmol) as a representative substrate with *tert*-butyl carbamate ($BocNH_2$, **8a**; 1.0 mmol) as the nucleophile in 1-butyl-3-methylimidazolium ([bmim]PF_6, as a representative ionic liquid) as the reaction medium at room temperature under nitrogen. Under the given reaction conditions no products were formed even after 48 h (Table 1, Entry 1). However, when the same reaction was conducted in the presence of acetic acid as an additive under atmospheric conditions, the reaction proceeded well to give the *N*-protected amino alcohol **9a** in good yield (76%) and high chiral purity (*ee* 93%; Table 1, Entry 2) at room temp. in 12 h with excellent recovery of the chirally enriched epoxide (*ee* 91%). It has been reported that the oxidation of Co^{II} to Co^{III} with the use of an acidic additive in air is responsible for the change in the activity of the complex.[9b] When *p*-nitrobenzoic acid (PNBA) was used in place of acetic acid at room temp. over 5 h, the activity and enantioselectivity of the product **9a** was improved further[10] (Table 1, Entry 3). In this reaction, although the *N*-protected amino alcohol was obtained in

Table 1. Optimization of the reaction conditions for the enantioselective AKR of **7a** with **8a** in [Bmim]PF_6.



(±) **7a** **8a** R = Boc (*S*) **7a'** (*R*) **9a**

Entry	Catalyst	Additive	Time [h]	Chirally enriched unreacted epoxide[a] **7a**′ *ee* [%][b]	*N*-protected 1,2-amino alcohol **9a** Conversion [%][c]	*ee* [%][c]
1[d]	**1**	–	48	–	–	–
2[e]	**1**	acetic acid	12	91	76	93
3[e]	**1**	PNBA	5	90	88	>99
4[f]	**1**	PNBA	5	99	>99	>99
5[f]	**2**	PNBA	10	43	>99	48
6[f]	**3**	PNBA	18	68	>99	72
7[f]	**4**	PNBA	19	65	>99	69
8[f]	**5**	PNBA	30	71	>99	75
9[f]	**6**	PNBA	30	77	>99	80
10[g]	**1**	PNBA	15	>99	>99	>99
11[h]	**1**	PNBA	26	>99	>99	>99
12[i]	**1**	PNBA	24	>99	>99	>99
13[j]	**1**	PNBA	7	>99	>99	>99

[a] Unreacted epoxide after AKR reaction recovered in quantitative yield. [b] Based on HPLC (Chiral pack OD Column) by using the calibration curve of the racemic epoxide. [c] Based on HPLC (Chiral pack AD-H Column) by using the calibration curve of the racemic *N*-protected amino alcohol. [d] The reaction was conducted with an epoxide/RNH_2/catalyst ratio of 2.2:1.0:0.02 mmol in 300 mg of the ionic liquid. [e] The reaction was conducted with an epoxide/RNH_2/catalyst/acetic acid/PNBA ratio of 2.2:1.0:0.02:0.02 mmol in 300 mg of the ionic liquid. [f] The reaction was conducted with an epoxide/RNH_2/catalyst/PNBA ratio of 2.0:1.0:0.02:0.02 mmol in 300 mg of the ionic liquid. [g] Catalyst loading of 0.5 mol-%. [h] Catalyst loading of 0.25 mol-%. [i] The reaction was conducted at 10 °C. [j] The reaction was conducted with 10 mmol of **7a** and 5 mmol of **8a** in 1500 mg of the ionic liquid with the other conditions as for Entry 4.

>99% *ee*, the *ee* of the unreacted epoxide was only 90% as we used **7a** in slightly more than stoichiometric amounts (2.2 mmol) with respect to **8a** [1.0 mmol; Figure 2 (**Y**)]. However, on conducting this reaction in an exact stoichiometric ratio of **7a** (2.0 mmol) and **8a** (1.0 mmol), there was no reduction in the *ee* of the *N*-protected amino alcohol **9a** (>99%; Entry 4), but there was a significant improvement in the *ee* (>99%) of the recovered **7′a** [Figure 2 (**X**)]. This behavior has been reported earlier by Melchiorre and coworkers in the epoxide ring-opening reaction.[16] Hence, in our subsequent catalytic reactions to evaluate the efficacies of complexes **2**–**6** in the AKR reaction we maintained this same stoichiometry of **7a** and **8a** (Entries 5–9). The complexes **2**–**6**, which bear different groups, namely H, *t*Bu, morpholinomethyl, and piperidinomethyl, at the 3,3′- and 5,5′-positions of the salen ligand, are known to influence the catalytic activities and enantioselectivities of various reactions.[15b] For our reaction, the salen complex with no substituents (catalyst **2**) showed high activity (conversion >99% with respect to **8a**) in terms of the formation of *N*-protected amino alcohol **9a**, but only moderate enantioselectivity (*ee* 48%). Also, the *ee* of the remaining epoxide was only moderate (43%; Entry 5). The presence of a *t*Bu group at either the 3,3′- or 5,5′-positions (catalysts **3** and **4**, respectively) of the salen unit enhanced the enantioselectivity significantly (Entries 6 and 7), but the reaction took longer to reach completion (18–19 h). The presence of an aminoalkyl group at the 3,3′-positions with a *t*Bu group at the 5,5′-positions showed further improvements in enantioselectivity, but the reaction took even longer (30 h) to reach completion (Entries 8 and 9). Therefore, it is evident from the results in Table 1 that the 3,3′- and the 5,5′-positions of the salen moiety should preferably bear a *t*Bu group (catalyst **1**) for high activity and enantioselectivity in the AKR reaction (Entry 4; Figure 3).

Complex **1** was found to be the most active and enantioselective catalyst at a loading of 1 mol-%, as shown in our above trial run, hence it was pertinent to examine the effect of catalyst loading on the AKR reaction. Accordingly, we reduced the catalyst loading to 0.5 and 0.25 mol-% and found that under these conditions there was no fall in the enantioselectivity of the product, but the reaction took

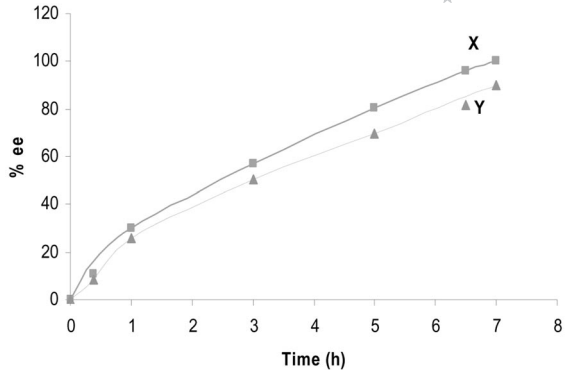


Figure 2. *ee* versus time for glycidyl 2-methylphenyl ether (**7b**) in the AKR by using $BocNH_2$ (**8a**) as the nucleophile. (**X**) 2.0 mmol **7b** and 1.0 mmol **8a**; (**Y**) 2.2 mmol **7b** and 1.0 mmol **8a**.

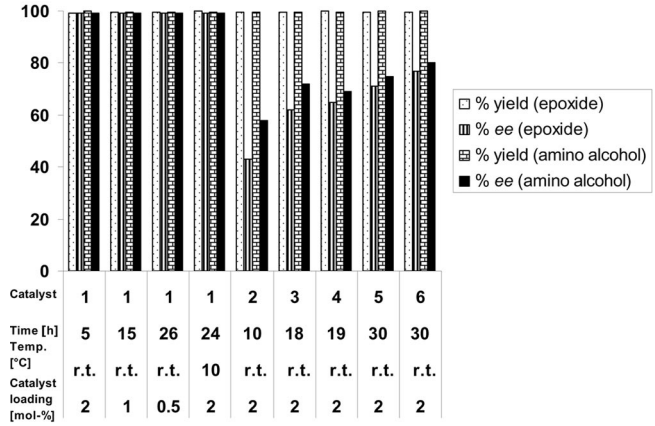
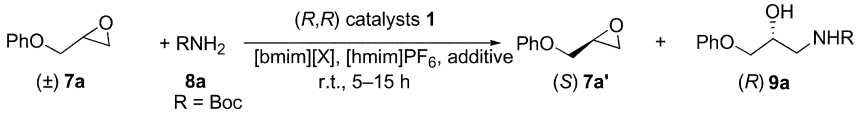


Figure 3. Optimization of the reaction conditions for the enantioselective AKR of **7a** with **8a** in $[bmim]PF_6$.

Table 2. Enantioselective AKR of **7a** with **8a** in different ionic liquids [bmim][X].[a]

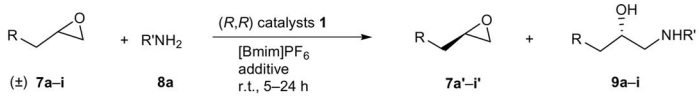


X = PF_6^- (**A**), NO_3^- (**B**), BF_4^- (**C**), SbF_6^- (**D**), Cl^- (**E**), $AlCl_4^-$ (**F**)

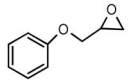
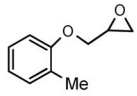
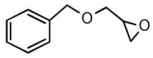
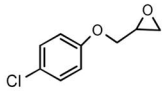
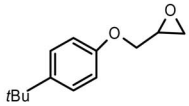
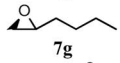
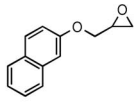
Entry	X	Time [h]	Unreacted epoxide **7a′** *ee* [%]	*N*-protected 1,2-amino alcohol **9a** Conversion [%][c]	*ee* [%][d]
1	A	5	>99	>99	99
2	B	12	81	78	95
3	C	12	34	44	34
4	D	12	14	56	18
5	E	12	–	–	–
6	F	12	racemic	>99	racemic
7[b]	A	15	8	>99	10

[a] Conditions: 2.0 mmol **7a**–**e**, 1.0 mmol **8a**–**c**, 0.02 mmol catalyst **1**, and 0.02 mmol PNBA in 300 mg of different ionic liquids at room temp. [b] $[hmim]PF_6$ as the ionic liquid. [c] Based on HPLC (Chiral pack OD Column) by using the calibration curve of the racemic epoxide. [d] Based on HPLC (Chiral pack AD-H Column) by using the calibration curve of the racemic *N*-protected amino alcohol.

Table 3. Enantioselective AKR of **7a**–**i** with **8a** in [bmim]PF_6.[a]



R = OPh, Ph, Cl, *n*-hexyl, *O*-naphthyl
R' = Boc

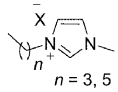
Entry	Epoxide	RNH_2	Time [h]	*ee* of unreacted epoxide [%]	*N*-protected 1,2-amino alcohol [%] Conversion[b]	*ee*[c]	TOF[d]
1	 **7a**	**8a**	5	>99	>99 (**9a**)	>99	9.9
2	 **7b**	**8a**	7	>99	>99 (**9b**)	>99	7.1
3	 **7c**	**8a**	7	>99	>99 (**9c**)	>99	7.1
4	 **7d**	**8a**	7.5	>99	>99 (**9d**)	>99	6.6
5	 **7e**	**8a**	7.5	>99	>99 (**9e**)	>99	6.6
6	 **7f**	**8a**	8	99[e]	98 (**9h**)	>99	6.1
7	 **7g**	**8a**	10	>99[e]	99 (**9i**)	>99	5.0
8	 **7h**	**8a**	24	61[e]	90(**9f**)	49	1.9
9	 **7i**	**8a**	10	89[e]	88 (**9g**)	40	4.4

[a] Conditions: 2.0 mmol **7a**–**i**, 1.0 mmol **8a**, 0.02 mmol catalyst **1**, and 0.02 mmol PNBA in [bmim]PF_6 at room temp. [b] Based on HPLC (Chiral pack OD column) by using the calibration curve of the racemic epoxide. [c] Based on HPLC (Chiral pack AD-H column) by using the calibration curve of the racemic *N*-protected amino alcohol. [d] TOF = [product]/[catalyst] × time [h^{-1}]. [e] Based on GC (Chiraldex GTA column).

longer to reach completion (15 and 26 h, respectively; Entries 10 and 11). Therefore, a catalyst loading of 1 mol-% was taken as optimum for this AKR protocol (Entry 4). We also established that room temp. is the preferred temperature for the AKR reaction, because by lowering the temperature to 10 °C it took 24 h to obtain a similar conversion and enantioselectivity (Entry 12). This protocol worked well even on a relatively large scale (10 mM) in 7 h (Table 1, Entry 13).

It has been reported in the literature that the anion [X^-] in the ionic liquids [bmim][X] greatly influences the catalytic activity and enantioselectivity of a variety of reactions.[12] Therefore, we carried out the above optimized AKR reaction (Table 2, Entry 1) in the presence of ionic liquids with different anions, namely NO_3^- (**B**), BF_4^- (**C**), SbF_6^- (**D**), Cl^- (**E**), and $AlCl_4^-$ (**F**; Figure 4). However, with the exception of the ionic liquid [bmim][NO_3] (**B**; Entry 2), for which the yield and *ee* of the *N*-protected 1,2-amino alcohol **9a** were found to be 78 and 95%, respectively, other ionic liquids fared very badly in terms of enantioselectivity (Entries 3–6). Furthermore, the use of 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim]PF_6) as the ionic liquid yielded the desired product in high yield in 15 h (Entry 7), but with poor *ee*. This behavior of long-chain ionic liquids has been reported previously, but for a different reaction.[17] Therefore, [bmim]PF_6 (**A**) was the best ionic liquid to use for the AKR of **7a** with **8a** as the nucleophile. Bartoli et al.[9b] has reported similar reactions with catalyst **1** (1.5 mol-%) in the presence of PNBA using dichloromethane, tetrahydrofuran, and *tert*-butyl methyl ether (TBME)

as the solvent, giving the *N*-protected amino alcohols in excellent yields and enantioselectivities in 24 h. On the other hand the use of the ionic liquid with the anion **A** with complex **1** not only improved the reactivity (5 h for complete consumption of **8a**), but both the *N*-protected amino alcohol **9a** and the unreacted epoxide **7a′** were obtained with excellent chiral purity (*ee* >99%; Entry 1).



n = 3, 5

X = PF_6 (**A**), NO_3^- (**B**), BF_4^- (**C**), SbF_6^- (**D**), Cl^- (**E**) and $AlCl_4^-$ (**F**)

Figure 4. Structures of the ionic liquids.

The above-optimized reaction protocol for the AKR was further extended to the epoxide ring-opening of different aryloxy/terminal epoxides, namely 1,2-epoxy-3-phenoxypropane (**7a**), glycidyl 2-methylphenyl ether (**7b**), benzyl glycidyl ether (**7c**), 4-chlorophenyl glycidyl ether (**7d**), 4-*tert*-butylphenyl glycidyl ether (**7e**), epichlorohydrin (**7f**), 1,2-epoxyhexane (**7g**), styrene oxide (**7h**), and glycidyl 1-naphthyl ether (**7i**) with *tert*-butyl carbamate ($BocNH_2$; **8a**) as the nucleophile by using catalyst **1** in the presence of PNBA as an additive with [bmim]PF_6 as the ionic liquid. Excellent yields (>99%) and absolute regioselectivities for the terminal *N*-protected 1,2-amino alcohols **9a**–**g** with >99% *ee* were achieved in 5–10 h (Table 3, Entries 1–7). Agreeably, the corresponding epoxides **7a′**–**g′** were also recovered in quantitative yields (>99%) and with excellent optical purity (>99%; Table 3, Entries 1–7). Ironically, styrene oxide and glycidyl 1-naphthyl ether gave epoxide ring-opened products in moderate *ee*s (Entries 8 and 9). Nevertheless, comparison of the results of our ionic liquid protocol (TOF = 9.97; Table 3, Entry 1) with those of a conventional solvent protocol (TOF = 2.06)[9b] shows the former has a distinct advantage in terms of high reactivity, as reflected in their TOF values for the same reaction. We further extended this protocol to the ring-opening reaction of aryloxy epoxides **7b**–**e** with urethane (**8b**) or benzyl carbamate (**8c**) as the nucleophile using the catalyst **1** in the presence of PNBA and [bmim]PF_6 (Table 4). All the data showed excellent conversions and regio- and enantioselectivities in the ring-opened products with quantitative recovery of the epoxides with excellent chiral purity (Table 4, Entries 1–10).

Notwithstanding their high activity, the catalyst and additive used in this ionic liquid protocol are recyclable, as evidenced by recycling experiments (Table 5). The recyclability experiments were carried out with 1,2-epoxy-3-phenoxypropane (**7a**; 2.0 mmol) as a representative substrate with *tert*-butyl carbamate ($BocNH_2$, **8a**; 1.0 mmol) as the nucleophile in [bmim]PF_6 (as a representative ionic liquid) as the reaction medium at room temperature by using the complex **1** (1 mol-%) in the presence of PNBA as additive. After completion of the catalytic reaction, the products were extracted with *n*-hexane/diethyl ether (75:25). The *N*-protected amino alcohol **9a** and chirally enriched epoxide **7′a** were recovered from the organic layer by column chromatography. The recovered ionic liquid was dried in vacuo and contained the catalyst and additive, as evidenced by IR spectroscopy (Figure 5, Z). The recovered ionic liquid was used in subsequent reactions without any further processing, which worked well for up to six catalytic cycles, with retention of reactivity and enantioselectivity. However, in the seventh cycle there was a drop in enantioselectivity (Table 5). From the recycling experiments it is evident that Co^{III}–salen is stable during the course of the AKR reaction (Figure 5) and does not require additional quantities of additive to reoxidize the cobalt.

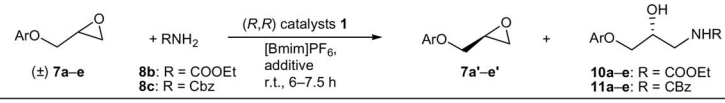
Conclusions

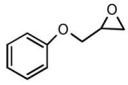
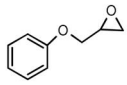
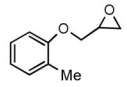
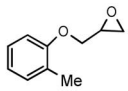
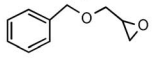
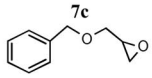
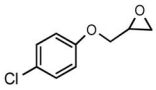
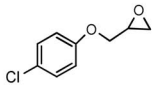
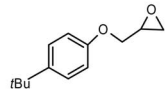
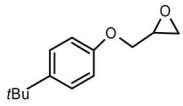
A series of chiral salen complexes bearing different substituents at the 3,3′- and 5,5′-positions of the salicylaldehyde moiety have been synthesized and used as efficient catalysts in the AKRs of different racemic aryloxy/terminal epoxides **7a**–**i** with **8a**–**c** as nucleophiles in the presence of different ionic liquids as the reaction medium at room temp. *N*-Protected 1,2-amino alcohols **9a**–**g** with high chiral purity (*ee* >99%) were obtained when [bmim]PF_6 was used as the reaction medium with catalyst **1** along with the corresponding epoxides **7a′**–**g′** with high optical purity (*ee* >99%) in 5–10 h. The ring-opened products formed from styrene oxide and glycidyl 1-naphthyl ether, however, were obtained with moderate chiral purity. This AKR system proceeds five times faster in the presence of the ionic liquid than in the presence of conventional organic solvents, and the system worked well for up to six cycles with retention of enantioselectivity.

Experimental Section

Experimental Methods: Cobalt acetate and acetic acid were purchased from s.d. Fine Chemicals and were used as received. *p*-Nitrobenzoic acid, racemic aryloxy/terminal epoxides, namely 1,2-epoxy-3-phenoxypropane (**7a**), glycidyl 2-methylphenyl ether (**7b**), benzyl glycidyl ether (**7c**), 4-chlorophenyl glycidyl ether (**7d**), 3-*tert*-butylphenyl glycidyl ether (**7e**), epichlorohydrin (**7f**), 1,2-epoxyhexane (**7g**), styrene oxide (**7h**), glycidyl 1-naphthyl ether (**7i**), *tert*-butyl carbamate ($BocNH_2$; **8a**), urethane (NH_2COOEt; **8b**), benzyl carbamate ($CbzNH_2$; **8c**), 2-*tert*-butylphenol, 4-*tert*-butylphenol, and 2,4-di-*tert*-butylphenol were purchased from Aldrich. 3-*tert*-Butylsalicylaldehyde, 5-*tert*-butylsalicylaldehyde, and 3,5-di-*tert*-butylsalicylaldehyde were synthesized according to the reported method.[15a] The (–)-(1*R*,2*R*)-diaminocyclohexane was resolved from the technical grade racemic *trans*-1,2-diaminocyclohexane according to the reported method.[15a] The solvents were dried according to standard procedures, distilled, and stored under nitrogen. NMR spectra were obtained with a Bruker F113V spectrometer (500 and 125 MHz for ^1H and ^{13}C NMR, respectively) and are referenced internally with TMS. FTIR spectra were recorded with a Perkin–Elmer Spectrum GX spectrometer in KBr window. High-resolution mass spectra were obtained with LC-MS (Q-TOFF), LC (Waters), and MS (Micromass) instruments. For product purification, flash chromatography was performed by using silica gel (60–200 mesh) purchased from s.d. Fine Chemcals Limited, Mumbai (India). The

Table 4. Enantioselective AKR of **7a**–**e** with **8b**–**c** in [bmim]PF_6.[a]



Entry	Epoxide	RNH_2	Time [h]	*ee* of unreacted epoxide [%]	*N*-protected 1,2-amino alcohol [%] Conversion[b]	*ee*[c]	TOF[d]
1	 **7a**	**8b**	6	>99	>99 (**10a**)	>99	8.3
2	 **7a**	**8c**	6	>99	>99 (**11a**)	>99	8.3
3	 **7b**	**8b**	7	>99	>99 (**10b**)	>99	7.1
4	 **7b**	**8c**	7	>99	>99 (**11b**)	>99	7.1
5	 **7c**	**8b**	7	>99	>99 (**10c**)	>99	7.1
6	 **7c**	**8c**	7	99	>99 (**11c**)	>99	7.1
7	 **7d**	**8b**	6	>99	>99 (**10d**)	>99	8.3
8	 **7d**	**8c**	7.5	>99	>99 (**11d**)	>99	6.6
9	 **7e**	**8b**	7.5	>99	>99 (**10e**)	>99	6.6
10	 **7e**	**8c**	7.5	>99	>99 (**11e**)	>99	6.6

[a] Conditions: 2.0 mmol **7a**–**e**, 1.0 mmol **8a**–**c**, 0.02 mmol catalyst **1**, and 0.02 mmol PNBA in [bmim]PF_6 at room temp. [b] Based on HPLC (Chiral pack OD column) by using the calibration curve of the racemic epoxide. [c] Based on HPLC (Chiral pack AD-H column) by using the calibration curve of the racemic *N*-protected amino alcohol. [d] TOF = [product]/[catalyst] × time [h^{-1}].

Table 5. Enantioselective AKR of **7a** with **8a** in [bmim]PF_6 using recovered complex **1**.

Run	1	2	3	4	5	6	7
Time [h]	5	5.5	6	6	6	6	6
Conversion [%][a]	99	99	99	99	99	99	99
ee [%][b]	>99	>99	>99	>99	>99	>99	88

[a] Based on HPLC (Chiral pack OD column) by using the calibration curve of the racemic epoxide **7a**. [b] Based on HPLC (Chiral pack AD-H column) by using the calibration curve of the racemic *N*-protected amino alcohol.

enantiomeric excesses (*ee*s) of the products were determined by HPLC (Shimadzu SCL-10AVP) by using Daicel Chiralpak AD-H, OD, and OJ chiral columns (wavelength 243 nm) with 2-propanol/hexane as the eluent. Optical rotations were measured with a Digipol 781 Automatic Polarimeter from Rudolph Instruments.

Preparation of the Catalysts: Chiral salen complexes **1**–**4**, namely {(1*R*,2*R*)-*N*,*N*′-bis[3,5-di(*tert*-butyl)salicylidene]cyclohexane-1,2-diaminato}cobalt(II) (**1**),[15a] [(1*R*,2*R*)-*N*,*N*′-disalicylidenecyclohexane-1,2-diaminato]cobalt(II) (**2**), {(1*R*,2*R*)-*N*,*N*′-bis[3-(*tert*-butyl)-salicylidene]cyclohexane-1,2-diaminato}cobalt(II) (**3**), {(1*R*,2*R*)-*N*,*N*′-bis[5-(*tert*-butyl)salicylidene]cyclohexane-1,2-diaminato}-cobalt(II) (**4**), were synthesized according to the reported procedure under an inert gas.[15b] {(1*R*,2*R*)-*N*,*N*′-Bis[5-*tert*-butyl-3-(morpholinomethyl)salicylidene]cyclohexane-1,2-diaminato}cobalt(II) (**5**) and {(1*R*,2*R*)-*N*,*N*′-bis[5-*tert*-butyl-3-(piperidinomethyl)salicylid-

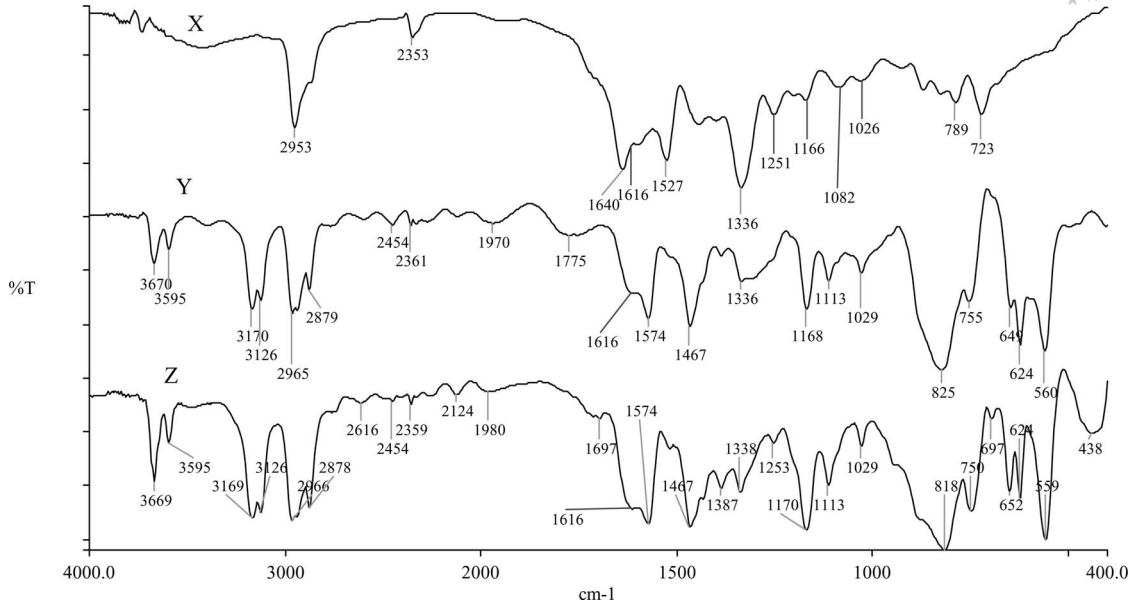


Figure 5. IR spectra of the Co^{III}–salen complex before addition of the ionic liquid (X), after addition of the ionic liquid (Y), and the Co^{III}–salen complex in the ionic liquid (Z) recovered after the catalytic reaction.

ene]cyclohexane-1,2-diaminato}cobalt(II) (**6**) were synthesized and characterized as described below. A solution of cobalt acetate (1 equiv.) in water (2 mL) was added to a solution of (1*R*,2*R*)-*N*,*N*′-bis[5-*tert*-butyl-3-(morpholinomethyl)salicylidene]cyclohexane-1,2-diamine/(1*R*,2*R*)-*N*,*N*′-bis[5-*tert*-butyl-3-(piperidinomethyl)salicylidene]cyclohexane-1,2-diamine[15c] (1 equiv.) in ethanol (10 mL) at reflux under an inert gas. A brick-red precipitate appeared immediately; however, the mixture was heated at reflux for an additional 2 h. The desired Co^{II} complex was filtered off, washed with absolute ethanol, and dried in vacuo.

Characterization Data for Complex 5: M.p. >360 °C. Yield: 0.59 g (85%). $[a]_D^{27}$ = +15.65 (*c* = 0.260, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 2951, 2864, 1636, 1596, 1538, 1454, 1393, 1254, 1201, 1121, 1041, 936, 870, 752, 652 cm^{-1}. UV/Vis: λ_{max} (ε, $M^{-1}cm^{-1}$) = 268 (8458), 396 (8305), 447 (5430), 531 (789) nm. $C_{38}H_{54}CoN_4O_4$ (689.35): calcd. C 66.17, H 7.89, N 8.12; found C 66.09, H 7.81, N 8.0 9.

Characterization Data for Complex 6: M.p. >360 °C. Yield: 0.56 g (83%). $[a]_D^{27}$ = +223 (*c* = 0.009, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 2950, 2863, 1637, 1554, 1453, 1394, 1269, 1040, 953, 869, 734, 553 cm^{-1}. UV/Vis: λ_{max} (ε, $M^{-1}cm^{-1}$) = 268 (9227), 413 (8366), 488 (3121), 537 (1479) nm. $C_{40}H_{58}CoN_4O_2$ (685.39): calcd. C 70.05, H 8.52, N 8.17; found C 69.97, H 8.46, N 8.13.

Typical Procedure for the AKR of Racemic Terminal Epoxides: In a small vial equipped with a magnetic stirring bar, the (salen)Co^{II} complexes **1**–**6** (0.02 mmol) were dissolved in TBME as the solvent and treated with acetic acid/PNBA (0.02 mmol). The resulting dark-brown solution was stirred exposed to air at room temp. for 1 h. The solvent was completely removed, and an appropriate ionic liquid (300 mg) was added to the resulting solid followed by the appropriate carbamate **8a**–**c** (0.1 mmol). The resulting mixture was stirred for 5 min, and then the desired epoxide **7a**–**i** (0.2 mmol) was added. The reaction mixture was stirred until the HPLC analysis showed disappearance of the peak of the (*R*) enantiomer of the epoxide (for HPLC profiles of the products please see the Supporting Information). At the end of the reaction, the crude mixture was repeatedly extracted with *n*-hexane/diethyl ether (75:25). The product, *N*-protected 1,2-amino alcohols **9a**–**i**, **10a**–**e**, and **11a**–**e**, and the unreacted enantio-enriched epoxide **7a**′–**i**′ were recovered by flash chromatography. The remaining ionic liquid layer was dried under vacuum and stored in a desiccator for use in subsequent catalytic runs. The enantiomeric excesses (*ee*s) of the products **9a**–**i**, **10a**–**e**, and **11a**–**e** were determined by HPLC analysis using Daicel Chiralpak AD-H columns with *i*PrOH/hexane (90:10) as eluent (see the Supporting Information). HPLC traces of the products were compared with the corresponding racemic samples prepared with racemic (salen)Co^{III} complexes as the catalyst.

***tert*-Butyl [(*R*)-2-Hydroxy-3-phenoxypropyl]carbamate (9a):**[9b] White solid; m.p. 82–85 °C. $[a]_D^{27}$ = +10.4 (*c* = 2, $CHCl_3$) for >99% *ee*. MS (ESI): *m*/*z* = 268 $[M + H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.42 (s, 9 H), 3.19 (br. s, 1 H, OH), 3.25–3.33 (m, 1 H), 3.45–3.54 (m, 1 H), 3.91–4.03 (m, 2 H), 4.06–4.17 (m, 1 H), 4.97 (br. s, 1 H, NH), 6.92–7.01 (m, 3 H), 7.25–7.31 (m, 2 H) ppm. HPLC [Daicel Chiralpack AD-H, hexane/2-propanol (90:10), flow rate = 0.75 mL min^{-1}; t_R = 12.1 min (*R*, major) and 15.9 min (*S*, minor)].

Ethyl [(*R*)-2-Hydroxy-3-phenoxypropyl]carbamate (10a):[9b] Colorless oil. $[a]_D^{27}$ = +8.6 (*c* = 1.04, $CHCl_3$) for >99% *ee*. MS (ESI): *m*/*z* = 238 $[M + H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.27 (t, *J* = 7.2 Hz, 3 H), 3.15 (br. s, 1 H), 3.33–3.41 (m, 1 H), 3.47–3.57 (m, 1 H), 3.94 (dd, *J* = 6.4, 9.6 Hz, 1 H), 3.97 (dd, *J* = 4.8, 9.6 Hz, 1 H), 4.06–4.16 (m, 1 H), 4.12 (q, *J* = 7.2 Hz, 2 H), 5.15 (br. s, 1 H), 6.87–7.01 (m, 3 H), 7.28–7.33 (m, 2 H) ppm. HPLC [Daicel Chiralpack AD-H, hexane/2-propanol (90:10), flow rate = 0.75 mL min^{-1}; t_R = 12.7 min (*R*, major) and 15.5 min (*S*, minor)].

Benzyl [(*R*)-2-Hydroxy-3-phenoxypropyl]carbamate (11a):[9b] White solid; m.p. 79–82 °C. $[a]_D^{27}$ = +6.8 (*c* = 1.04, $CHCl_3$) for >99% *ee*. MS (ESI): *m*/*z* = 302 $[M + H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.94 (d, *J* = 4.0 Hz, 1 H), 3.33–3.41 (m, 1 H), 3.51–3.57 (m, 1 H), 3.91–4.00 (m, 2 H), 4.05–4.14 (m, 1 H), 5.14 (s, 2 H), 5.22 (br. s, 1 H), 6.82–7.00 (m, 3 H), 7.26–7.44 (m, 7 H) ppm. HPLC [Daicel Chiralpack AD-H, hexane/2-propanol (90:10), flow rate = 0.75 mL min^{-1}; t_R = 23.6 min (*R*, major) and 28.6 min (*S*, minor)].

***tert*-Butyl [(*R*)-2-Hydroxy-3-(*o*-tolyloxy)propyl]carbamate (9b):** White solid; m.p. 98–102 °C. $[a]_D^{27}$ = +17.0 (*c* = 2, $CHCl_3$) for

>99% *ee*. MS (ESI): *m*/*z* = 282 [M + H]$^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.45 (s, 9 H), 2.27 (s, 3 H), 2.12 (br. s, 1 H), 3.78 (br. s, 1 H), 3.85 (br. s, 1 H), 4.03–4.04 (m, 2 H), 4.13 (m, 1 H), 6.81–6.82 (d, *J* = 8 Hz, 1 H), 6.87–6.89 (t, *J* = 7 Hz, 1 H), 7.13–7.14 (m, 2 H) ppm. $C_{15}H_{23}NO_4$ (281.16): calcd. C 64.03, H 8.24, N 4.98; found C 64.06, H 8.20, N 4.96. HPLC [Daicel Chiralpack AD-H, hexane/2-propanol (90:10), flow rate = 0.75 mL min^{-1}; t_R = 34.52 min (*R*, major) and 41.62 min (*S*, minor)].

Ethyl [(*R*)-2-Hydroxy-3-(*o*-tolyloxy)propyl]carbamate (10b): Oil. $[\alpha]_D^{27}$ = +19.24 (*c* = 0.15, $CHCl_3$) for >99% *ee*. MS (ESI): *m*/*z* = 240 [M + H]$^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.24–1.27 (t, *J* = 7 Hz, 3 H), 1.64 (s, 1 H), 2.24 (s, 3 H), 2.70 (br. s, 1 H), 3.80 (br. s, 1 H), 3.87–4.07 (t, *J* = 5 Hz, 1 H), 4.10–4.14 (q, *J* = 7 Hz, 2 H), 4.61–4.63 (m, 2 H), 6.82–6.84 (d, *J* = 8 Hz, 1 H), 6.88–6.91 (t, *J* = 7.5 Hz, 1 H), 7.14–7.26 (m, 2 H) ppm. $C_{13}H_{19}NO_4$ (253.13): calcd. C 61.64, H 7.56, N 5.53; found C 61.20, H 7.53, N 5.42. HPLC [Daicel Chiralpack AD-H, hexane/2-propanol (90:10), flow rate = 0.75 mL min^{-1}; t_R = 35.31 min (*R*, major) and 42.61 min (*S*, minor)].

Benzyl [(*R*)-2-Hydroxy-3-(*o*-tolyloxy)propyl]carbamate (11b): White solid; m.p. 98–105 °C. $[\alpha]_D^{27}$ = +12.8 (*c* = 0.25, $CHCl_3$) for >99% *ee*. MS (ESI): *m*/*z* = 361 [M + H]$^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.23 (s, 3 H), 2.58 (s, 1 H), 2.94 (br. s, 1 H), 3.75–3.79 (dd, *J* = 6.5, 5 Hz, 1 H), 3.84–3.86 (d, *J* = 10.5 Hz, 1 H), 4.04 (s, 1 H), 4.86 (br. s, 2 H), 5.09 (s, 2 H), 6.81–6.83 (d, *J* = 8 Hz, 1 H), 6.88 (br. s, 1 H), 7.13–7.15 (m, 2 H), 7.35 (br. s, 5 H) ppm. $C_{18}H_{21}NO_4$ (315.15): calcd. C 68.55, H 6.71, N 4.44; found C 68.51, H 6.69, N 4.47. HPLC [Daicel Chiralpack AD-H, hexane/2-propanol (90:10), flow rate = 0.75 mL min^{-1}; t_R = 36.65 min (*R*, major) and 44.20 min (*S*, minor)].

***tert*-Butyl [(*R*)-3-(Benzyloxy)-2-hydroxypropyl]carbamate (9c):** White solid; m.p. 102–105 °C. $[\alpha]_D^{27}$ = +116.6 (*c* = 0.02, $CHCl_3$) for >99% *ee*. MS (ESI): *m*/*z* = 282 [M + H]$^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.45 (s, 9 H), 2.64 (br. s, 1 H), 2.98 (br. s, 1 H), 3.54–3.57 (br. s, 2 H), 3.56 (br. s, 1 H), 3.64 (br. s, 1 H), 3.90 (br. s, 1 H), 4.55, (s, 2 H), 7.27–7.35 (br. s, 5 H) ppm. $C_{15}H_{23}NO_4$ (281.16): calcd. C 64.03, H 8.24, N 4.98; found C 64.01, H 8.20, N 4.95. HPLC [Daicel Chiralpack AD-H, hexane/2-propanol (90:10), flow rate = 0.75 mL min^{-1}; t_R = 44.43 min (*R*, major) and 46.24 min (*S*, minor)].

Ethyl [(*R*)-3-(Benzyloxy)-2-hydroxypropyl]carbamate (10c): Yellow oil. $[\alpha]_D^{27}$ = +129.0 (*c* = 0.031, $CHCl_3$) for >99% *ee*. MS (ESI): *m*/*z* = 282 [M + H]$^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.23–1.26 (t, *J* = 7 Hz, 3 H), 2.95 (br. s, 1 H), 3.31 (br. s, 1 H), 3.51–3.55 (dd, *J* = 9.5, 7 Hz, 2 H), 3.60–3.62 (m, 1 H), 3.67 (br. s, 1 H), 3.90 (br. s, 1 H), 4.08–4.12 (q, *J* = 7 Hz, 2 H), 4.45 (s, 2 H), 7.29–7.35 (br. m, 5 H) ppm. $C_{13}H_{19}NO_4$ (253.13): calcd. C 61.64, H 7.56, N 5.53; found C 61.61, H 7.58, N 5.50. HPLC [Daicel Chiralpack AD-H, hexane/2-propanol (90:10), flow rate = 0.75 mL min^{-1}; t_R = 43.68 min (*R*, major) and 45.41 min (*S*, minor)].

Benzyl [(*R*)-3-(Benzyloxy)-2-hydroxypropyl]carbamate (11c): White solid; m.p. 108–110 °C. $[\alpha]_D^{27}$ = +125.2 (*c* = 0.023, $CHCl_3$) for >99% *ee*. MS (ESI): *m*/*z* = 282 [M + H]$^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.85 (br. s, 1 H), 2.89 (br. s, 1 H), 3.52–3.57 (m, 2 H), 3.63 (br. s, 1 H), 3.90 (br. s, 1 H), 4.85 (br. s, 2 H), 5.10 (s, 2 H), 7.26–7.36 (m, 10 H) ppm. $C_{18}H_{21}NO_4$ (315.15): calcd. C 68.55, H 6.71, N 4.44; found C 68.52, H 6.69, N 4.42. HPLC [Daicel Chiralpack AD-H, hexane/2-propanol (90:10), flow rate = 0.75 mL min^{-1}; t_R = 45.35 min (*R*, major) and 47.22 min (*S*, minor)].

***tert*-Butyl [(*R*)-3-(4-Chlorophenoxy)-2-hydroxypropyl]carbamate (9d):** White solid; m.p. 92–95 °C. $[\alpha]_D^{27}$ = +25.0 (*c* = 0.16, $CHCl_3$) for >99% *ee*. MS (ESI): *m*/*z* = 302 [M + H]$^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (s, 9 H), 3.70 (br. s, 1 H), 3.77 (br. s, 1 H), 3.85–3.96 (m, 2 H), 4.07–4.08 (m, 2 H), 5.07 (br. s, 1 H), 6.81–6.83 (d, *J* = 6 Hz, 2 H), 7.26–7.27 (d, *J* = 6 Hz, 2 H) ppm. $C_{14}H_{20}ClNO_4$ (301.11): calcd. C 55.72, H 6.68, N 4.64; found C 55.70, H 6.69, N 4.60. HPLC [Daicel Chiralpack AD-H, hexane/2-propanol (90:10), flow rate = 0.75 mL min^{-1}; t_R = 24.09 min (*R*, major) and 33.41 min (*S*, minor)].

Ethyl [(*R*)-3-(4-Chlorophenoxy)-2-hydroxypropyl]carbamate (10d): Oil. $[\alpha]_D^{27}$ = +11.9 (*c* = 0.24, $CHCl_3$) for >99% *ee*. MS (ESI): *m*/*z* = 274 [M + H]$^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.24–1.27 (t, *J* = 7 Hz, 3 H), 1.80 (br. s, 1 H), 3.77–3.99 (m, 3 H), 4.09, (br. s, 1 H), 4.09–4.14 (q, *J* = 7 Hz, 2 H), 4.68–4.69 (m, 2 H), 6.82–6.88 (m, 4 H) ppm. $C_{12}H_{16}ClNO_4$ (273.08): calcd. C 52.66, H 5.89, N 5.12; found C 52.68, H 5.90, N 5.14. HPLC [Daicel Chiralpack AD-H, hexane/2-propanol (90:10), flow rate = 0.75 mL min^{-1}; t_R = 21.86 min (*R*, major) and 30.32 min (*S*, minor)].

Benzyl [(*R*)-3-(4-Chlorophenoxy)-2-hydroxypropyl]carbamate (11d): White solid; m.p. 86–90 °C. $[\alpha]_D^{27}$ = +17.1 (*c* = 0.2, $CHCl_3$) for >99% *ee*. MS (ESI): *m*/*z* = 336 [M + H]$^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 4 Hz, 2 H), 7.34–7.30 (m, 5 H), 6.80–6.84 (d, *J* = 8.5 Hz, 2 H), 5.10 (s, 2 H), 4.70 (s, 1 H), 4.13–4.17 (m, 1 H), 4.06–4.03 (m, 2 H), 3.85–3.82 (m, 1 H), 3.76–3.73 (m, 1 H), 3.49 (s, 1 H) ppm. $C_{17}H_{18}ClNO_4$ (335.09): calcd. C 60.81, H 5.40, N 4.17; found C 60.79, H 5.41, N 4.19. HPLC [Daicel Chiralpack AD-H, hexane/2-propanol (90:10), flow rate = 0.75 mL min^{-1}; t_R = 23.46 min (*R*, major) and 32.55 min (*S*, minor)].

***tert*-Butyl [(*R*)-3-(4-*tert*-Butylphenoxy)-2-hydroxypropyl]carbamate (9e):** White solid; m.p. 115–120 °C. $[\alpha]_D^{27}$ = +588.17 (*c* = 0.012, $CHCl_3$) for >99% *ee*. MS (ESI): *m*/*z* = 323 [M + H]$^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.30 (s, 9 H), 1.45 (s, 9 H), 2.80 (br. s, 1 H), 3.75–3.84 (br. s, 2 H), 3.84 (br. s, 1 H), 4.03–4.09 (m, 1 H), 4.49–4.57 (br. s, 2 H), 6.83–6.86 (dd, *J* = 4, 4.5 Hz, 2 H), 7.30–7.31 (t, *J* = 7.5 Hz, 2 H) ppm. $C_{18}H_{29}NO_4$ (323.21): calcd. C 66.84, H 9.04, N 4.33; found C 66.82, H 9.01, N 4.35. HPLC [Daicel Chiralpack AD-H, hexane/2-propanol (90:10), flow rate = 0.75 mL min^{-1}; t_R = 26.31 min (*R*, major) and 36.88 min (*S*, minor)].

Ethyl [(*R*)-3-(4-*tert*-Butylphenoxy)-2-hydroxypropyl]carbamate (10e): Oil. $[\alpha]_D^{27}$ = +24.96 (*c* = 0.16, $CHCl_3$) for >99% *ee*. MS (ESI): *m*/*z* = 295 [M + H]$^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 10 Hz, 2 H), 6.89 (d, *J* = 5.5 Hz, 2 H), 5.11 (s, 1 H), 4.60 (d, *J* = 12.5 Hz, 2 H), 4.44–4.33 (m, 3 H), 4.1–4.0 (m. 2 H), 3.41 (s, 1 H), 1.30 (br., 3 H), 1.60 (s, 9 H) ppm. $C_{16}H_{25}NO_4$ (295.18): calcd. C 65.06, H 8.53, N 4.74; found C 65.02, H 8.50, N 4.77. HPLC [Daicel Chiralpack AD-H, hexane/2-propanol (90:10), flow rate = 0.75 mL min^{-1}; t_R = 26.29 min (*R*, major) and 36.84 min (*S*, minor)].

Benzyl [(*R*)-3-(4-*tert*-Butylphenoxy)-2-hydroxypropyl]carbamate (11e): White solid; m.p. 110–115 °C. $[\alpha]_D^{27}$ = +245.91 (*c* = 0.02, $CHCl_3$) for >99% *ee*. MS (ESI): *m*/*z* = 357 [M + H]$^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.19 (s, 9 H), 3.02 (br. s, 1 H), 3.21 (br. s, 1 H), 3.42–3.45 (m, 2 H), 3.62–3.63 (d, *J* = 5 Hz, 1 H), 3.68–3.69 (d, *J* = 3.5 Hz, 1 H), 3.78–3.80 (t, *J* = 4.5 Hz, 1 H), 5.08 (s, 2 H), 7.6–7.35 (m, 9 H) ppm. $C_{21}H_{27}NO_4$ (257.19): calcd. C 70.56, H 7.61, N 3.92; found C 70.57, H 7.63, N 3.90. HPLC [Daicel Chiralpack AD-H, hexane/2-propanol (90:10), flow rate = 0.75 mL min^{-1}; t_R = 26.70 min (*R*, major) and 37.94 min (*S*, minor)].

***tert*-Butyl [(*R*)-3-Chloro-2-hydroxypropyl]carbamate (9f):**[9b] Colorless oil. MS (ESI): *m*/*z* = 210 [M + H]$^+$. ^{1}H NMR ($CDCl_3$): δ =

1.45 (s, 9 H), 3.25 (br. s, 1 H, OH), 3.43–3.59 (m, 2 H), 3.58–3.76 (m, 2 H), 4.26 (m, 1 H), 4.95 (br. s, 1 H, NH) ppm. HPLC [Daicel Chiralpack AD-H, hexane/2-propanol (85:15), flow rate = 0.75 mL min^{-1}; t_S = 36.88 min (*S*, minor) and 58.91 min (*R*, major)].

***tert*-Butyl [(*R*)-2-Hydroxyhexyl]carbamate (9g):**[9b] Colorless oil. MS (ESI): *m*/*z* = 218 [M + H]$^-$. ^{1}H NMR ($CDCl_3$): δ = 0.87 (t, *J* = 7.2 Hz, 3 H), 1.26–1.41 (m, 4 H), 1.43–1.52 (m, 2 H), 1.44 (s, 9 H), 2.63 (br. s, 1 H, OH), 2.95–3.04 (m, 1 H), 3.25–3.35 (m, 1 H), 3.63–3.73 (m, 1 H), 5.03 (br. s, 1 H, NH) ppm. HPLC [Daicel Chiralpack AS-H, hexane/2-propanol (98:2), flow rate = 0.75 mL min^{-1}; t_S = 7.1 min (*S*, minor) and 9.2 min (*R*, major)].

***tert*-Butyl [(*R*)-2-Hydroxy-2-phenylethyl]carbamate (9h):**[9b] White solid; m.p. 120–123 °C. MS (ESI): *m*/*z* = 238 [M + H]$^+$. ^{1}H NMR ($CDCl_3$): δ = 1.43 (s, 9 H), 2.98 (br. s, 1 H, OH), 3.21–3.30 (m, 1 H), 3.42–3.52 (m, 1 H), 4.77–4.85 (m, 1 H), 4.90 (br. s, 1 H, NH), 7.26–7.41 (m, 5 H) ppm. HPLC [Daicel Chiralpack AS-H, hexane/2-propanol (98:2), flow rate = 0.75 mL min^{-1}; t_R = 35.5 min (*R*, major) and 37.3 min (*S*, minor)].

***tert*-Butyl [(*R*)-2-Hydroxy-3-(naphthalen-1-yloxy)propyl]carbamate (9i):**[9b] White solid; m.p. 102–107 °C. MS (ESI): *m*/*z* = 318 [M + H]$^+$. ^{1}H NMR ($CDCl_3$): δ = 1.46 (s, 9 H), 3.35 (br. s, 1 H, OH), 3.36–3.47 (m, 1 H), 3.55–3.65 (m, 1 H), 4.17 (d, *J* = 5.6 Hz, 2 H), 4.23–4.31 (m, 1 H), 5.04 (br. s, 1 H, NH), 6.81–6.86 (m, 1 H), 7.37–7.54 (m, 4 H), 7.79–7.84 (m, 1 H), 8.18–8.23 (m, 1 H) ppm. HPLC [Daicel Chiralpack AD-H, hexane/2-propanol (95:5), flow rate = 0.75 mL min^{-1}; t_R = 28.4 min (*R*, major) and 30.6 min (*S*, minor)].

Recycling of the Catalyst 1: At the end of the catalytic run (checked by TLC) the products were isolated by stirring the reaction mixture in *n*-hexane/diethyl ether (75:25) for 10 min. The upper phase was then decanted to separate it from the ionic liquid. The *N*-protected amino alcohol **9a** and the chirally enriched epoxide **7a′** were recovered from the organic layer by column chromatography. The ionic liquid phase containing catalyst **1** was dried in vacuo and used without any further processing in the subsequent AKR of 1,2-epoxy-3-phenoxypropane (**7a**) as a representative substrate with *tert*-butyl carbamate ($BocNH_2$, **8a**) as the nucleophile.

Supporting Information (see footnote on the first page of this article): Experiential procedures, full characterization and HPLC analysis of the products.

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