DOI: 10.1002/chem.200601307

Scandium–Bipyridine-Catalyzed Enantioselective Aminolysis of *meso*-Epoxides

Enzo Mai and Christoph Schneider*[a]

Abstract: The scandium–bipyridine-catalyzed enantioselective addition of anilines and *O*-alkyl hydroxylamines to *meso*-epoxides has been optimized and extended to a broad range of epoxides and amines. Whereas aromatic *meso*-epoxides generally furnished the corresponding 1,2-amino alcohols in excellent enantioselectivities, aliphatic *meso*-epoxides only gave rise to moderate enantioselectivities in the aminolysis. The catalyst loading may be lowered to just 5 mol% with only marginal effects on yield and enantioselectivity. A strong positive nonlinear effect has been observed, pointing to aggregation phenomena of the catalyst.

Keywords: amino alcohols · aminolysis · asymmetric catalysis · epoxides · scandium bipyridine

Introduction

The catalytic, enantioselective ring opening of *meso*-epoxides is a valuable tool for the synthesis of 1,2-difunctionalized fine chemicals in a highly enantiomerically enriched form.[1] The chiral catalyst, typically a chiral Lewis acid, has to differentiate between the two enantiotopic carbon atoms of the epoxide and direct the incoming nucleophile selectively to one of them in a clean S_N2-type pathway. In the past, this strategy has been widely employed for the synthesis of 1,2-azido alcohols,[2] 1,2-halohydrins,[3] 1,2-cyano alcohols,[4] 1,2-diol monoester and monoethers,[5] and 1,2-mercapto alcohols,[6] many of which have been obtained thus far in good to excellent enantioselectivities. Alternatively, chiral Ti^{III} complexes have been employed to reductively open *meso*-epoxides to furnish enantiomerically enriched radical anions, which were then trapped with either hydrogen donors or alkenes.[7]

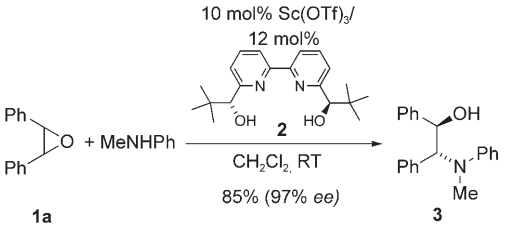
The nucleophilic addition of amines to epoxides catalyzed by Lewis acids typically suffers from compatibility problems between the Lewis basic amine and the Lewis acid catalyst which tend to coordinate to one another irreversibly. A solution to this problem was first shown in the work of Crotti who found that lanthanide triflates, such as $Yb(OTf)_3$, are effective catalysts for the aminolysis of 1,2-epoxides, presumably because they are able to exert their exceptional Lewis acidity even in the presence of the amine.[8,9]

Subsequently, Hou et al. developed a $Yb(OTf)_3$-(*R*)-BINOL-catalyst (BINOL = 2,2′-dihydroxy-1,1′-binaphthyl) which in combination with a tertiary amine catalyzed the addition of aniline to cyclohexene oxide in excellent yield and with 80% *ee* (*ee* = enantiomeric excess).[10] Whereas some other anilines could be readily employed in this reaction with comparable success, the substrate scope on the epoxide part proved to be very narrow. Thus, cyclopentene oxide, *cis*-2-butene oxide, and *cis*-stilbene oxide all gave rise to low enantioselectivity in the reaction with aniline. Inaba et al. utilized a chiral titanium catalyst made from equimolar amounts of $Ti(OiPr)_4$ and (*S*)-BINOL (1 mol%) for the addition of benzyl amine to a seven-membered cyclic epoxide containing a ketal moiety epoxide which proceeded in excellent yield and enantioselectivity.[11] Again, other epoxides failed to yield the products in good enantioselectivity. In a formal total synthesis of 4-demethoxy daunomycin, Shibasaki et al. employed a $Pr(OiPr)_3$-(*R*)-BINOL-complex (10 mol%) for the catalytic enantioselective addition of *p*-anisidine to a benzo-annelated cyclohexene oxide and obtained the ring-opened 1,2-amino alcohol in 75% yield and 50% *ee*.[12] Bartoli et al. showed that a Cr^{III} salen catalyst was effective in the aminolysis of *cis*-stilbene oxide furnishing the 1,2-amino alcohol in good yields and with 80–90% *ee*.[13] Very high enantioselectivities of greater than 90% *ee* were reported by Collin et al. for the aminolysis of cyclic *meso*-epoxides with 10 mol% of the Sm^{III} iodo-(*S*)-BINOL complex.[14] Kureshy et al.[15] reported the $Ti(OiPr)_4$-(*S*)-BINOL-catalyzed aminolysis of *cis*-stilbene oxide and

[a] Dipl.-Chem. E. Mai, Prof. Dr. C. Schneider
Institut für Organische Chemie, Universität Leipzig
Johannisallee 29, 04103 Leipzig (Germany)
Fax: (+49) 341-973-6599
E-mail: schneider@chemie.uni-leipzig.de

cyclohexene oxide with anilines furnishing the corresponding 1,2-amino alcohols in good yields and with moderate enantioselectivities ranging from 39–78% *ee*.

We have recently discovered the scandium–bipyridine-catalyzed aminolysis of *meso*-epoxides.[16] For example, *cis*-stilbene oxide (**1a**) was ring-opened with *N*-methylaniline to furnish 1,2-amino alcohol **3** in 85% yield and with 97% *ee* when catalyzed with a chiral catalyst composed of 10 mol% of $Sc(OTf)_3$ and 12 mol% of bipyridine **2** (Scheme 1). This



Scheme 1. Scandium–bipyridine-catalyzed aminolysis of *cis*-stilbene oxide (**1a**).

ligand was introduced into the field of asymmetric catalysis by Bolm et al. in 1990.[17] Subsequently, Kobayashi et al.[18a] established that just 1 mol% of this scandium–bipyridine complex with dodecyl sulfate counterions was sufficient for the aminolysis of epoxides in water and comparable levels of enantioselectivity were obtained as for the reaction run in dichloromethane.

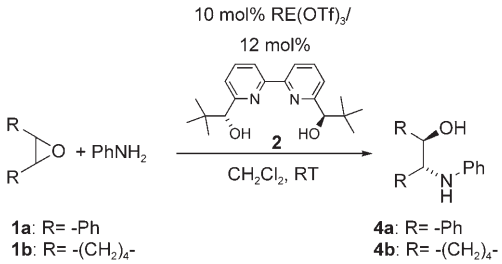
We have now investigated this process in more detail and report here a full account and experimental details of this work.

Results and Discussion

Our preliminary experiments had shown that 10 mol% of the scandium–bipyridine complex effectively catalyzed the aminolysis of various *meso*-epoxides with anilines in excellent yields and with up to 97% *ee*. To further optimize this process and investigate scope and limitations we decided to select the reactions of *cis*-stilbene oxide (**1a**) as an aromatic substrate and cyclohexene oxide (**1b**) as an aliphatic epoxide with aniline as model reactions which were carefully investigated with respect to metal triflate, solvent, temperature, ligand architecture, and catalyst loading.

Influence of the metal center: As $Sc(OTf)_3$ in combination with the bipyridine ligand performed very well in the aminolysis of epoxides, we screened selected other rare earth (RE) metal triflates in the two model reactions with respect to their activity and enantioselectivity. All reactions were conducted with 10 mol% of metal triflates and 12 mol% of bipyridine ligand **2** in CH_2Cl_2 as solvent at room temperature (Table 1). While all metal triflate-bipyridine complexes exhibited good to excellent catalytic activity in both reactions, the enantioselectivity proved to be very dependent on the metal triflate employed. Cyclohexene oxide (**1b**) was

Table 1. Influence of the metal triflate in the reactions of **1a** and **1b** with aniline.



Entry	Lewis acid	Yield **4a** [%][a]	*ee* **4a** [%][b]	Yield **4b** [%][a]	*ee* **4b** [%][b]
1	$Sc(OTf)_3$	95	93	71	40
2	$Y(OTf)_3$	82	86	99	29
3	$Ce(OTf)_3$	0	n.d.	94	10
4	$Sm(OTf)_3$	84	79	99	9
5	$Yb(OTf)_3$	80	90	97	6

[a] Isolated yield after chromatography. [b] Determined by HPLC on a chiral Chiralcel OD column.

ring-opened with only moderate enantioselectivity with the scandium–bipyridine catalyst at RT, which significantly decreased with $Y(OTf)_3$–bipyridine and was almost lost with the other lanthanide-bipyridine catalysts. On the other hand, in the reaction of *cis*-stilbene oxide (**1a**) with aniline, some more lanthanide-bipyridine complexes exhibited good to very good enantioselectivity, for example, the yttrium-, samarium-, and ytterbium-complexes whereas the cerium–bipyridine complex did not give rise to any product formation.

Optimization of solvent: In the related alcoholysis of epoxides which we developed in a parallel study,[16] we found that CH_2Cl_2 was optimal in terms of yield and enantioselectivity.

The use of highly dipolar and coordinating solvents (THF, DMF, CH_3CN) resulted in no or very little product formation, whereas nonpolar solvents, such as diethyl ether and toluene, led to good yields but very low enantioselectivities in the ring-opening event. Hence, we undertook a study of other chlorinated solvents in our model reactions which included $CHCl_3$ and 1,2-dichloroethane under otherwise identical reaction conditions. Inspection of Table 2 clearly reveals that CH_2Cl_2 remained the best solvent in terms of yield although comparable albeit slightly lower levels of

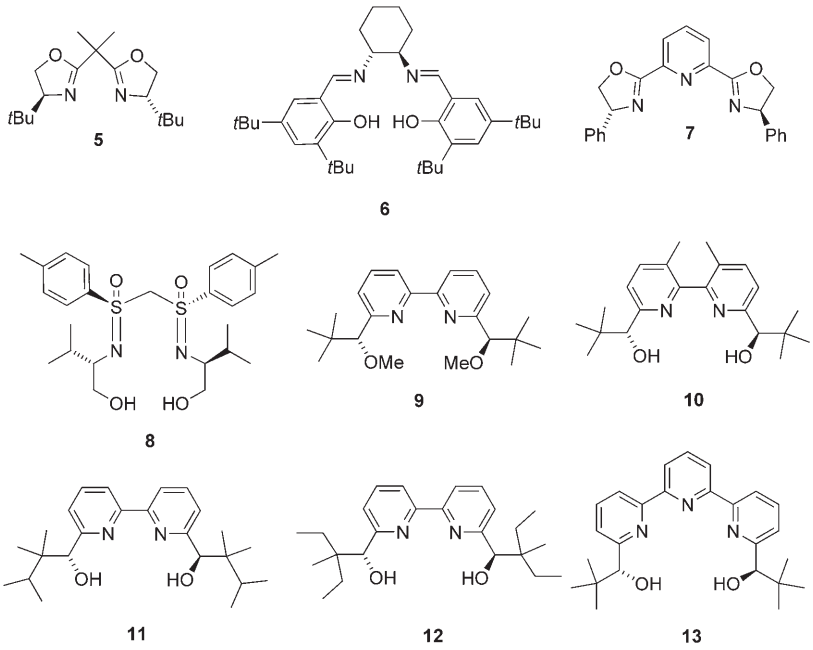
Table 2. Optimization of solvent in the reactions of **1a** and **1b** with aniline.[a]

Entry	Epoxide	Solvent	Yield [%][b]	*ee* [%][c]
1	**1a**	CH_2Cl_2	95	93
2	**1a**	1,2-dichloroethane	72	92
3	**1a**	$CHCl_3$	73	91
4	**1b**	CH_2Cl_2	96	54
5	**1b**	1,2-dichloroethane	89	48
6	**1b**	$CHCl_3$	79	40

[a] Reaction was performed with 10 mol% catalyst at RT (entries 1–3) or −20 °C (entries 4–6) for 24 h. The amount of aniline was 1 equiv (entries 1–3) or 2 equiv (entries 4–6). [b] Isolated yield after chromatography. [c] Determined by HPLC on a chiral Chiralcel OD column.

enantioselectivity were obtained with $CHCl_3$ and $C_2H_4Cl_2$ in both reactions.

Optimization of the ligand: In our preliminary experiments, we had investigated a number of so-called privileged chiral ligands for the scandium–catalyzed aminolysis of *cis*-stilbene oxide (**1a**) and cyclohexene oxide (**1b**), for example, bisoxazoline **5**, salen **6**, pyridine bisoxazoline **7**, and bissulfoximine **8**.[19]



Scandium complexes composed of $Sc(OTf)_3$ and bisoxazolines and pyridine bisoxazolines are known in the literature and have been employed in Diels–Alder reactions,[20a] syntheses of homopropargylic alcohols and dihydrofurans,[20b] Nazarov reactions,[20c] 1,3-dipolar cycloadditions,[20d] Friedel–Crafts alkylations of indoles,[20e] and aldol additions to glyoxylate esters.[20f] When the ligands **5**–**8** in combination with $Sc(OTf)_3$ were used in our two model reactions, very low enantioselectivities were obtained (Table 3, entries 1–4).

Table 3. Optimization of ligand architecture in the model reactions of *cis*-stilbene oxide (**1a**) and cyclohexene oxide (**1b**) with aniline (for ligands see structures **5**–**13**).[a]

Entry	Ligand	Yield **4a** [%][b]	*ee* **4a** [%][c]	Yield **4b** [%][b]	*ee* **4b** [%][c]
1	**5**	93	30[d]	86	1
2	**6**	62	0	96	14
3	**7**	91	22	98	18
4	**8**	–	–	71	6
5	**2**	95	93	71	40
6	**9**	63	0	80	0
7	**10**	89	86	93	0
8	**11**	81	89	91	36
9	**12**	87	92	91	29
10	**13**	60	51	93	6

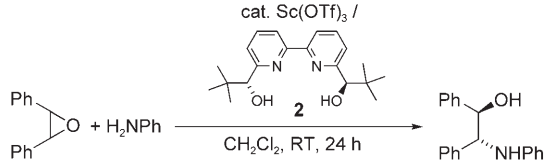
[a] Reactions conditions as given in Table 1. [b] Isolated yield after chromatography. [c] Determined by HPLC on a chiral Chiralcel OD column. [d] Compound *ent*-**4a**.

In the scandium–catalyzed aminolysis of epoxides, the bipyridine ligand **2** was obviously superior to the other chiral ligands so it was interesting to modify the ligand backbone at specific sites: first, we were interested to find out if an enantioselective catalyst required the free hydroxyl groups in the bipyridine ligand. It turned out that the bis-*O*-methyleted bipyridine **9** formed an active but completely unselective chiral catalyst, suggesting that additional hydrogen bonding might be involved in the transition state of the reaction (Table 3, entry 6). Secondly, we attempted to increase the steric bulk of the *t*Bu groups at the chiral centers even further on the assumption that this might also increase the enantioselectivity of the reaction. The new chiral ligands **11** and **12** were prepared along the same synthetic route which did not exhibit, however, any further improvement in yield or enantioselectivity (Table 3, entries 8 and 9). A further point of modification concerned the bipyridine backbone of the ligand. From crystal structure analyses of the $ScBr_3$–bipyridine[18c] and $Y(OTf)_3$–bipyridine complexes[38] it was known that there is a slight distortion between the two pyridine rings even in the metal complexes of **2**. Accordingly, it was interesting to investigate the influence of this torsion angle on the enantioselectivity of the reaction. Chiral bipyridine **10** carrying two additional *ortho* methyl groups in the pyridine rings was synthesized according to a procedure established by Denmark et al.[21] on the expectation that they would increase the torsion angle between the pyridine rings and possibly influence the enantioselectivity of the reaction. It turned out, however, that the $Sc(OTf)_3$-ligand **10** complex gave inferior results in both reactions: whereas the aminolysis of *cis*-stilbene oxide (**1a**) proceeded with a slightly decreased enantioselectivity of 86% *ee*, cyclohexene oxide (**1b**) was ring-opened with no enantioselectivity (Table 3, entry 7). The last modification of the ligand architecture which we undertook concerned the change from a bipyridine to a tripyridine backbone in ligand **13**. Under the assumption of a pentagonal-bipyramidal coordination geometry around the metal center,[18c] this five-coordinate ligand should be easily accommodated in the plane of a scandium complex. The enantioselectivity obtained with the $Sc(OTf)_3$-ligand **13** complex was, however, lower than with the parent bipyridine ligand **2** (Table 3, entry 10).

Catalyst loading and nonlinear effect: The practicality and efficiency of a given catalytic process is directly related to the catalyst loading, which should be as low as possible. To

explore the threshold of catalytic efficiency, different catalyst loadings between 1 and 10 mol% were investigated in the reaction of *cis*-stilbene oxide (**1a**) and aniline with the standard $Sc(OTf)_3$–bipyridine **2** complex (Table 4).

Table 4. Investigation of catalyst loading.



1a 4a

Entry	Catalyst loading [mol%]	Yield [%][a]	*ee* [%][b]
1	10	95	93
2	5	89	90
3	2	92	80
4	1	95	71

[a] Isolated yield after chromatography. [b] Determined by HPLC on a chiral Chiralcel OD column.

The reaction with a catalyst loading of 10 mol% provided the ring-opened 1,2-amino alcohol **4a** with 93% *ee* and in 95% yield (Table 4, entry 1). The catalyst loading may be lowered to 5 mol% and the enantioselectivity only dropped slightly to 90% *ee* (entry 2). A further decrease of catalyst loading to only 2 mol% led to a visibly lower enantioselectivity (entry 3). With 1 mol% of catalyst, the product was obtained in 95 and 71% *ee* (entry 4). Thus, by lowering the catalyst loading below 5 mol%, the enantioselectivity of the reaction eroded, although catalytic effiency was maintained.

Furthermore, we investigated the relationship between catalyst *ee* and product *ee* (Figure 1) as nonlinear effects have been observed in many catalytic enantioselective processes. Indeed, we found a strong positive nonlinear effect in the aminolysis of *cis*-stilbene oxide: with only 25% ligand *ee*, the product had 76% *ee* and with just 56% *ee* in the ligand, the product was formed in almost the same enantioselectivity as with enantiopure ligand (90 versus 93% *ee*). Apparently, aggregation of two or more monomeric catalyst species into catalytically inactive complexes enhance the proportion of the predominating and catalytically active catalyst enantiomer.[22]

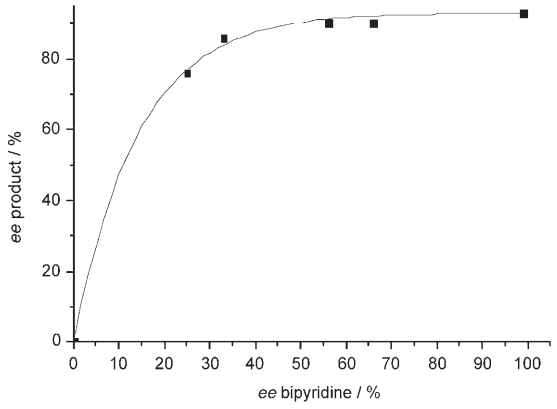


Figure 1. Relationship between catalyst *ee* and product *ee*.

Scope of the aminolysis: According to the optimized reaction conditions discussed above, *meso*-epoxides **1** were treated with aniline (2 equiv) and 10 mol% of the scandium–bipyridine catalyst in dichloromethane, giving rise to a broad range of 1,2-amino alcohols **4**. The results are summarized in Table 5. In general, aromatic *meso*-epoxides furnished the desired 1,2-amino alcohols **4** in good yields (76–95%) and the highest enantioselectivities (82–97% *ee*) currently possible for the aminolysis of *meso*-epoxides (Table 5, entries 1, 9–11).

Aliphatic epoxides reacted with aniline in good yields and only moderate enantioselectivities (entries 2–8). Epoxides with longer side chains gave better enantioselectivities (entry 6, 74% *ee*) compared to *cis*-butene oxide (**1e**) (entry 5, 60% *ee*), whereas epoxides with β-branched alkyl side chains gave diminished enantioselectivities (entry 7, 49% *ee*). Optimal temperatures were found individually for every substrate and represent a compromise between reactivity and selectivity.

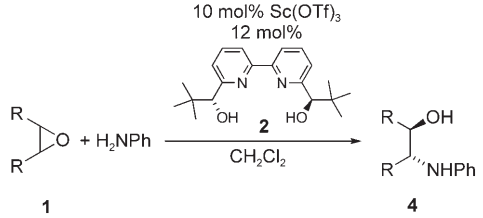
Further investigation was directed at improving the scope of the aminolysis of *cis*-stilbene oxide (**1a**) and cyclohexene oxide (**1b**) with respect to the amines (Table 6). Sterically hindered anilines led to a further increase in enantioselectivity. Thus, *N*-methyl-aniline gave the desired amino alcohol **3** in 97% *ee* and with 85% yield (entry 1). Also electron-deficient anilines, for example, *para*-chloro aniline yielded 1,2-amino alcohol **14** in 94% yield with 95% *ee* (entry 2). The ring opening of *cis*-stilbene oxide (**1a**) with electron-rich amines proceeded with slightly lower enantioselectivity at room temperature which may, however, be compensated by decreasing the reaction temperature. Thus, the enantioselectivity of the aminolysis with *para*-anisidine was improved from 82% *ee* at RT to 90% at 0°C (entry 4). The *para*-methoxy phenyl group had the additional advantage that it may be oxidatively cleaved off the product with cerium ammonium nitrate.[13]

The desymmetrization of cyclohexene oxide (**1b**) with electron-deficient or sterically hindered anilines was not more selective than with aniline. The amino alcohols **18**–**21** were obtained in high yield and with moderate enantioselectivities (entries 6–9) The reactions of cyclohexene oxide with *O*-benzyl hydroxylamine and benzyl amine proceeded in good yields but low enantioselectivities (entries 10–11).

Conclusion

The catalytic, enantioselective ring opening of *meso*-epoxides with amines is an excellent method to furnish valuable, enantiomerically enriched 1,2-amino alcohols. In this study, we have developed the scandium–bipyridine-catalyzed aminolysis of *meso*-epoxides and have optimized this process with respect to metal, ligand, solvent, catalyst loading, epox-

Table 5. Scope of the aminolysis with respect to the epoxide component.



1 4

1a: R= Ph **1e**: R= Me **1i**: R= naphthyl
1b: R= -$(CH_2)_4$- **1f**: R= *n*Pr **1k**: R= 3-Me-Ph
1c: R= -$(CH_2)_3$- **1g**: R= *i*Pr **1l**: R= 4-Cl-Ph
1d: R= -$(CH_2)_5$- **1h**: R= benzyl

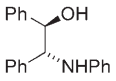
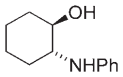
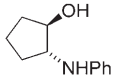
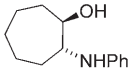
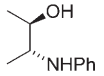
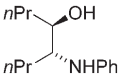
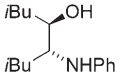
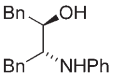
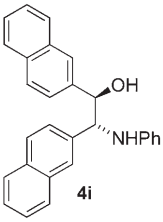
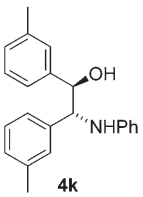
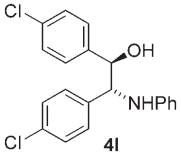
Entry	Epoxide	Product[a]	*T* [°C]	Yield [%][b]	*ee* [%][c]
1	**1a**	 **4a**	RT	95	93
2	**1b**	 **4b**	−20	96	54
3	**1c**	 **4c**	−20	89	41
4	**1d**	 **4d**	0	73	10
5	**1e**	 **4e**	0	92	60
6	**1f**	 **4f**	RT	74	74
7	**1g**	 **4g**	RT	61	49
8	**1h**	 **4h**	0	49[d]	44
9	**1i**	 **4i**	RT	76	82
10	**1k**	 **4k**	RT	91	93

Table 5. (Continued)

Entry	Epoxide	Product[a]	*T* [°C]	Yield [%][b]	*ee* [%][c]
11	**1l**	 **4l**	RT	93	92

[a] The absolute configuration of the products was determined by comparison of the rotation values with literature values or by analogy. [b] Isolated yield after chromatography. [c] Determined by HPLC. [d] 48% starting material recovered.

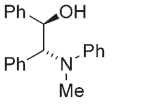
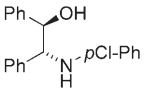
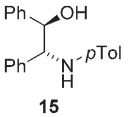
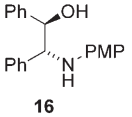
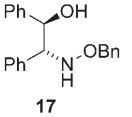
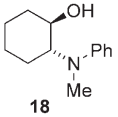
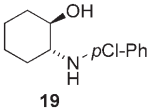
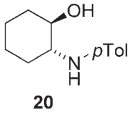
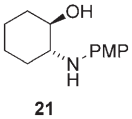
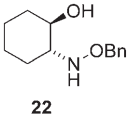
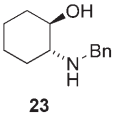
ide, and amine components. Aromatic *meso*-epoxides turned out to be excellent substrates which were ring-opened with typically >90% *ee*, whereas aliphatic *meso*-epoxides gave rise to only moderate enantioselectivity. While most reactions were conducted with 10 mol% catalyst, it was shown that the amount can be reduced to just 5 mol% without significant effects on yield and enantioselectivity. A significant positive nonlinear effect was observed, pointing to aggregation phenomena of the catalyst.

Experimental Section

General: All reactions were performed in flame-dried glassware under an atmosphere of dry nitrogen. The following reaction solvents were distilled from the indicated drying agents: dichloromethane (CaH_2), THF ($LiAlH_4$, triphenylmethane), diethyl ether (Na, benzophenone), toluene (Na, benzophenone), *N*,*N*-dimethylformamide (Acros ACS grade), acetonitrile (Acros ACS grade), chloroform (Acros ACS grade). Diethyl ether, petroleum ether (b.p. 30–75 °C), and ethyl acetate for chromatography were technical grade and distilled from KOH or $CaCl_2$. All reactions were monitored by TLC on precoated silica gel SIL G/UV254 plates (Machery, Nagel); spots were visualized by treatment with a solution of vanillin (0.5 g), concd acetic acid (10 mL), and concd H_2SO_4 (5 mL) in methanol (90 mL) or molybdophosphoric acid (5 g) in ethanol (250 mL). Flash column chromatography was performed by using Merck silica gel 60 230–400 mesh. Bipyridine **2** was best prepared according to a new protocol developed by Kobayashi.[18b] (*Z*)-1,2-Di(naphthalen-2-yl)ethene and (*Z*)-1,2-di-*m*-tolylethene were prepared according to literature procedures.[23] All other chemicals were used as received from commercial suppliers. ^1H and ^{13}C NMR spectra were recorded with VARIAN Gemini 200 (200 MHz), VARIAN Gemini 300 (300 MHz) spectrometers or an Bruker Avance DRX 400 (400 MHz) spectrometer in $CDCl_3$ at 25 °C with TMS as internal standard. IR spectra were obtained with a FTIR spectrometer (Genesis ATI, Mattson/Unicam). UV spectra were obtained with a Beckmann DU-650 spectrometer. Melting points are uncorrected. Optical rotations were measured by using a Polarotronic polarometer (Schmidt & Haensch). HPLC analyses were performed on a JASCO MD-2010 plus instrument with a chiral stationary-phase column (Chiralcel OD purchased from Daicel). Mass spectra were measured at 70 eV (EI) with a Finnigan MAT 95 A spectrometer. High-resolution mass spectra (HRMS; ESI/Na) were measured with a Bruker Daltonics APEX II FTICR spectrometer.

2-Phenylethyltriphenylphosphonium bromide:[24] 2-Phenylethyl bromide (4.63 g, 25.0 mmol) and triphenylphosphine (6.56 g, 25.0 mmol) were stirred neat at 130 °C for 19 h in a sealed flask. The product was obtained as white solid and used without further purification in the next step. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.98–3.13 (m, 2H; CH_2), 4.07–4.21 (m,

Table 6. Scope of the aminolysis with respect to the amine component.

Entry	Epoxide	Amine	Product[a]	T [°C]	Yield [%][b]	*ee* [%][c]
1	**1a**	$PhNHCH_3$	 **3**	RT	85	97
2	**1a**	4-Cl-$PhNH_2$	 **14**	RT	94	95
3	**1a**	4-Me-$PhNH_2$	 **15**	RT	93	87
4	**1a**	4-MeO-$PhNH_2$	 **16**	RT	93	82 (90)[d]
5	**1a**	$BnONH_2$	 **17**	RT	75	86
6	**1b**	$PhNHCH_3$	 **18**	RT	92	30
7	**1b**	4-Cl-$PhNH_2$	 **19**	−20	91	43
8	**1b**	4-Me-$PhNH_2$	 **20**	−10	89	52
9	**1b**	4-MeO-$PhNH_2$	 **21**	−20	83	48
10	**1b**	$BnONH_2$	 **22**	−20	85	26
11	**1b**	$BnNH_2$	 **23**	RT	92	10[e]

[a] The absolute configuration of the products was determined by comparison of the rotation values with literature values or by analogy. [b] Isolated yield after chromatography. [c] Determined by HPLC. [d] Values in brackets refer to reactions at 0 °C. [e] Determined after conversion into the Mosher ester.

2H; CH_2), 7.13–7.30 (m, 5H; ArH), 7.62–7.90 ppm (m, 15H; ArH); ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 25.30$ ppm.

***cis*-1,4-Diphenyl-2-butene**:[25,26] A solution of KHMDS in toluene (0.5 M, 20.0 mL) was added dropwise by syringe to a stirred suspension of 2-phenylethyltriphenylphosphonium bromide (4.47 g, 10.0 mmol) in diethyl ether (30 mL) and the resulting mixture was stirred for 1 h. After the addition of phenyl acetaldehyde (0.93 mL, 8.0 mmol), the mixture was stirred for 5 h and quenched with water. The mixture was dried over $MgSO_4$, filtered, and evaporated in vacuo. The residue was diluted with petroleum ether and filtered. The filtrate was concentrated under reduced pressure and the crude product was purified by Kugelrohr distillation (179 °C/0.5 Torr). The title compound was obtained as a colorless oil (0.92 g, 55%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.54$ (d, $J = 5.5$ Hz, 4H; CH_2), 5.72–5.75 (m, 2H; CH), 7.22–7.35 ppm (m, 10H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 33.69$, 126.1, 128.5, 128.6, 129.2, 140.9 ppm.

2-Methylbutyltriphenylphosphonium bromide:[24] 3-Methylbutyl bromide (3.77 g, 25.0 mmol) and triphenylphosphine (6.56 g, 25.0 mmol) were stirred at 100 °C for 24 h in a sealed flask. The product was obtained as a white solid and used without further purification in the next step. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.97$ (d, $J = 6.5$ Hz, 6H; CH_3), 1.44–1.55 (m, 2H; CH_2), 2.01 (sept, $J = 6.5$ Hz, 1H; CH), 3.69–3.79 (m, 2H; CH_2), 7.70–7.89 ppm (m, 15H; ArH); ^{31}P NMR (121 MHz, $CDCl_3$): $\delta =$ 26.18 ppm.

***cis*-2,7-Dimethyl-4-octene**:[27] A solution of NaHMDS in THF (2 M, 11.0 mL) was added dropwise by syringe to a stirred suspension of 2-methylbutyltriphenylphosphonium bromide (8.27 g, 20.0 mmol) in diethyl ether (30 mL), and the resulting mixture was stirred for 1.5 h. After the addition of 3-methylbutanal (2.2 mL, 20.0 mmol), the mixture was stirred for 2 h and quenched with water. The mixture was dried over $MgSO_4$, filtered, and concentred under reduced pressure. The residue was diluted with petroleum ether and filtered. The filtrate was concentrated under reduced pressure and the crude product was purified by Kugelrohr distillation (80 °C/30 mbar). The title compound was obtained as colorless oil (2.64 g, 94%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.89$ (d, $J = 6.5$ Hz, 12H; CH_3), 1.59 (sept, $J = 6.5$ Hz, 2H; CH), 1.89–1.93 (m, 4H; CH_2), 5.39–5.42 ppm (m, 2H; CH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 22.41$, 28.73, 36.46, 129.3 ppm.

Epoxidation of the olefins (general procedure I): Alkene (1 equiv) was added to a stirred solution of *m*CPBA (*m*CPBA = *meta*-chloroperbenzoic acid, 2.2 equiv) in dichloromethane at 0 °C. The reaction mixture was stirred overnight at RT. The white precipitate was sucked off and the organic layer was concentrated under reduced pressure. The concentrated reaction mixture was diluted with saturated $NaHCO_3$ solution (70 mL) and extracted with diethyl ether (4 × 30 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, and filtered. The solvents were evaporated under reduced pressure. The residue was purified by flash chromatography over silica gel or by distillation.

***cis*-Stilbene oxide**[28] **(1a)**: Following general procedure I, *cis*-stilbene (2.02 g, 11.2 mmol) was treated with *m*CPBA (4.25 g, 24.6 mmol). Flash chromatography (diethyl ether/petroleum ether 1:19) afforded **1a** as a colorless liquid (2.09 g, 95%) which solidified on standing. M.p. 37–38 °C; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 4.37$ (s, 2H; CH), 7.18 ppm (s, 10H; ArH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 59.88$, 127.0, 127.6, 127.9, 134.5 ppm.

***cis*-Cycloheptene oxide**[29] **(1d)**: Following general procedure I, cycloheptene (1.20 mL, 10.0 mmol) was treated with *m*CPBA (3.97 g, 22.0 mmol). Flash chromatography (diethyl ether/pentane 1:9) afforded **1d** as a colorless liquid (673 mg, 62%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.37$–1.65 (m, 6H; CH_2), 1.84–1.96 (m, 4H; CH_2), 3.05–3.10 ppm (m, 2H; CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 24.60$, 29.17, 31.18, 56.21 ppm.

***cis*-4-Octene oxide**[30] **(1f)**: *cis*-4-Octene (0.99 g, 8.80 mmol) was added to a stirred solution of *m*CPBA (3.97 g, 22.0 mmol) in dichloromethane (50 mL) at RT. The reaction mixture was stirred overnight at RT. The white precipitate was sucked off and the organic layer was concentrated under reduced pressure. The concentrated reaction mixture was diluted with saturated $NaHCO_3$ solution (70 mL) and extracted with diethyl ether (4 × 30 mL). The combined organic layers were dried over $MgSO_4$ and filtered. The solvents were evaporated under reduced pressure. Kugelrohr distillation (95 °C/60 mbar) afforded **1f** as a colorless liquid (471 mg, 46%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.98$ (t, $J = 7.0$ Hz, 6H; CH_3), 1.43–1.58 (m, 8H; CH_2), 2.88–2.94 ppm (m, 2H; CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 14.02$, 19.87, 29.82, 56.99 ppm.

***cis*-2,7-Dimethyl-4-octene oxide (1g)**: Following general procedure I, *cis*-2,7-dimethyl-4-octene (1.40 g, 10.0 mmol) was treated with *m*CPBA (3.80 g, 22.0 mmol). Flash chromatography over silica gel (diethyl ether/petroleum ether 1:19) afforded **1g** as a colorless liquid (813 mg, 52%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.97$ (d, $J = 6.5$ Hz, 6H; CH_3), 0.99 (d, $J = 6.5$ Hz, 6H; CH_3), 1.32–1.48 (m, 4H; CH_2), 1.81 (sept, $J = 6.5$ Hz, 2H; CH), 2.91–2.97 ppm (m, 2H; CH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 22.57$, 22.89, 26.72, 36.74, 55.72 ppm.

***cis*-2,3-Dibenzyloxirane[26] (1h)**: 1,4-Diphenyl-2-butene (842 mg, 4.00 mmol) was added to a stirred solution of *m*CPBA (1.52 g, 8.80 mmol) in dichloromethane (20 mL) at RT. The reaction mixture was stirred overnight at RT. The white precipitate was sucked off and the organic layer was concentrated under reduced pressure. The concentrated reaction mixture was diluted with saturated $NaHCO_3$ solution (50 mL) and extracted with diethyl ether (4×25 mL). The combined organic layers were dried over $MgSO_4$ and filtered. The solvents were evaporated under reduced pressure. The residue was purified by flash chromatography over silica gel (diethyl ether/petroleum ether 1:19). The title compound was obtained as a white solid (549 mg, 61%). M.p. 30–32 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.94$–3.09 (m, 4H; CH_2), 3.27–3.30 (m, 2H; CH), 7.27–7.38 ppm (m, 10H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 34.44$, 57.48, 126.6, 128.6, 128.8, 137.7 ppm.

***cis*-1,2-Bis-(2′-naphthyl)ethane oxide[31] (1i)**: (*Z*)-1,2-Di(naphthalen-2-yl)ethene (135 mg, 0.48 mmol) was added to a stirred solution of *m*CPBA (183 mg, 1.06 mmol) in dichloromethane at RT. The reaction mixture was stirred overnight at RT. The white precipitate was sucked off and the organic layer was concentrated under reduced pressure. The concentrated reaction mixture was diluted with saturated $NaHCO_3$ solution and extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$ and filtered. The solvents were evaporated under reduced pressure. The residue was purified by flash chromatography over silica gel (diethyl ether/petroleum ether 1:19). The title compound was obtained as a white solid (90 mg, 63%). M.p. 107–109 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.60$ (s, 2H; CH), 7.29 (dd, $J = 8.5$, 1.5 Hz, 2H; ArH), 7.34–7.42 (m, 4H; ArH), 7.60 (d, $J = 8.5$ Hz, 2H; ArH), 7.67–7.73 (m, 4H; ArH), 7.78 ppm (s, 2H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 60.24$, 124.4, 125.8, 126.0, 126.2, 127.5, 127.6, 127.8, 131.8, 132.8 ppm.

***cis*-1,2-Bis-(*m*-tolyl)ethane oxide (1k)**: (*Z*)-1,2-Di-*m*-tolylethene (275 mg, 1.32 mmol) was added to a stirred solution of *m*CPBA (501 mg, 2.90 mmol) in dichloromethane at RT. The reaction mixture was stirred overnight at RT. The white precipitate was sucked off and the organic layer was concentrated under reduced pressure. The concentrated reaction mixture was diluted with saturated $NaHCO_3$ solution and extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$ and filtered. The solvents were evaporated under reduced pressure. The residue was purified by flash chromatography over silica gel (diethyl ether/petroleum ether 1:19). The title compound was obtained as colorless oil (549 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.26$ (s, 6H; CH_3), 4.33 (s, 2H; CH), 6.97–7.11 ppm (m, 8H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.61$, 60.16, 124.2, 127.9, 128.0, 128.5, 134.6, 137.6 ppm.

***cis*-1,2-Bis-(*p*-chlorophenyl)ethane oxide[32] (1l)**: A solution of tris(diethylamino)phosphine (4.00 mL, 15.0 mmol) in benzene/hexane (5 mL) was added by a syringe pump to a cooled solution of *p*-chlorobenzaldehyde (5.12 g, 36.4 mmol) in benzene (2 mL) over 2 h. The reaction mixture was stirred for 24 h at RT. The reaction mixture was poured onto water (75 mL) and extracted with dichloromethane (3×75 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The *cis* and *trans* epoxide were separated by flash chromatography over silca gel (diethyl ether/petroleum ether 1:19). The title compound was obtained as white solid (0.61 g, 15%) after purification in vacuo (100 °C/10 Torr) and by a second flash chromatography (diethyl ether/petroleum ether 1:19). M.p. 90–93 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.32$ (s, 2H; CH), 7.08 (d, $J = 8.5$ Hz, 4H; ArH), 7.17 ppm (d, $J = 8.5$ Hz, 4H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 59.11$, 128.1, 128.2, 132.5, 133.6 ppm.

(*R*,*R*)-6,6′-Bis(1-methoxy-2,2-dimethylpropyl)-2,2′-bipyridine[17] (9): Bipyridine **2** (0.10 g, 0.30 mmol) was added to a suspension of sodium hydride (22 mg, 0.92 mmol) in THF (2 mL) and the solution was stirred at RT. Methyl iodide (0.18 g, 1.30 mmol) was added after 1 h and the reaction quenched with water (2 mL) after stirring overnight at RT. The layers were separated and the aqueous layer was extracted with diethyl ether (4×4 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The title compound was obtained by flash chromatography over silica gel (diethyl ether/petroleum ether 1:15) as white crystals (77 mg, 72%). M.p. 161–162 °C; $[\alpha]_D^{23} = +150.3°$ ($c = 1.1$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.97$ (s, 18H; $C(CH_3)_3$), 3.27 (s, 6H; CH_3), 4.07 (s, 2H; CH–OMe), 7.38 (dd, $J = 7.5$, 1.3 Hz, 2H; ArH), 7.79 (dd, $J = 7.8$, 7.5 Hz, 2H; ArH), 8.25 ppm (dd, $J = 7.8$, 1.3 Hz, 2H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 26.56$, 35.82, 58.09, 93.13, 119.8, 121.9, 136.9, 155.4, 160.1 ppm; IR (KBr): $\tilde{\nu} =$ 3448, 2969, 2863, 1571, 1436, 1392, 1101, 814, 777, 673, 631 cm^{-1}; MS (70 eV, EI): m/z (%) = 356 (10) $[M]^+$, 341 (5), 300 (43), 285 (47), 253 (100), 227 (15), 213 (8), 57 (8).

[2-(5-Methylpyridyl)]-2,2-dimethylpropanon:[21] A stirred solution of 2-bromo-5-methylpyridine (4.30 g, 25.0 mmol) in diethyl ether was cooled to −78 °C, then a solution of *n*BuLi in hexane (2.5 m, 11.0 mL) was added slowly over 15 min. The resulting solution was stirred for 30 min at −78 °C before pivalonitrile (3.30 mL, 30.0 mmol) was added. The mixture was stirred for 1 h at −78 °C and then warmed up to RT. Upon adding H_2SO_4 (2 N, 90 mL), the mixture was stirred at 60 °C for 2 h. The layers were separated and the aqueous layer was extracted with diethyl ether (3×25 mL). The combined organic layers were washed with saturated aqueous Na_2CO_3 solution, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the crude product by flash chromatography over silica gel (ethyl acetate/petroleum ether 1:10) afforded 3.97 g (89%) of the title compound as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.45$ (s, 9H; CH_3), 2.38 (s, 3H; CH_3), 7.55–7.60 (m, 1H; ArH), 7.83 (d, $J = 8.0$ Hz, 1H; ArH), 8.43–8.44 ppm (m, 1H; ArH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 18.54$, 27.49, 44.03, 123.3, 135.9, 136.9, 148.1, 152.2 ppm; IR (film): $\tilde{\nu} = 2955$, 2928, 2868, 1682, 1566, 1481, 1297, 1199, 964, 849 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε) = 205 (3.691), 238 (3.916), 269 nm (3.678); MS (70 eV, EI): m/z (%): 177 (7) $[M]^+$, 162 (8), 149 (6), 120 (7), 93 (100), 65 (15), 41 (15).

(*R*)-1-[2-(5-Methylpyridyl)]-2,2-dimethylpropanol:[21] A mixture of (−)-DipCl (DipCl = *B*-chlorodiisopinocampheylborane, 8.30 g, 26.0 mmol) and the pyridyl ketone prepared above (3.10 g, 17.0 mmol) was stirred at RT for 6 d. The mixture was dissolved in diethyl ether (80 mL), followed by the addition of diethanolamine (5.80 g 55.0 mmol), and the resulting mixture was stirred overnight at RT. The white precipitate was filtered through a pad of Celite and the filtrate was dried over $MgSO_4$. After filtration and concentration under reduced pressure, the crude product was purified by flash chromatography over silica gel (ethyl acetate/petroleum ether 1:5) affording 2.38 g (76%) of the title compound as a colorless oil. $[\alpha]_D^{24} = +32.4°$ ($c = 1.03$ in EtOH); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.91$ (s, 9H; $C(CH_3)_3$), 2.33 (s, 3H; CH_3), 4.24–4.31 (m, 2H; CH and OH), 7.08 (d, $J = 6.0$ Hz, 1H; ArH), 7.42–7.45 (m, 1H; ArH), 8.37 ppm (s, 1H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.05$, 25.84, 36.22, 80.07, 122.2, 131.6, 136.1, 148.1, 157.0 ppm; IR (film): $\tilde{\nu} = 3224$, 2953, 2868, 1605, 1572, 1486, 1463, 1421, 1385, 1364, 1346, 1306, 1239, 1210, 1182, 1132, 1075, 1036, 1017, 910, 835 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε) = 215 (3.744), 266 nm (3.690); MS (ESI): m/z: 179.9 $[M+H]^+$.

(*R*)-5-Methyl-2-(1-*tert*-butyldimethylsilyloxy-2,2-dimethylpropyl)pyridine: TBSOTf (TBSOTF = *tert*-butyldimethylsilyl trifluoromethanesulfonate, 4.60 mL, 20.0 mmol) and 2,6-lutidine (3.10 mL, 27.0 mmol) were added to a stirred solution of the pyridyl carbinol prepared above (2.38 g, 13.3 mmol) in dichloromethane (30 mL) at 0 °C. The resulting solution was stirred for 2.5 h at RT and was then quenched with saturated aqueous $NaHCO_3$ solution (40 mL). The layers were separated and the aqueous layer was extracted with dichloromethane (3×20 mL). The combined organic layers were dried over $MgSO_4$ and filtered. The residue obtained after removal of the solvent was purified by flash chromatography over silica gel (ethyl acetate/petroleum ether 1:9). The title compound was obtained as a colorless oil (3.82 g, 98%). $[\alpha]_D^{27} = +67.2°$ ($c = 1.07$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.34$ (s, 3H; $SiCH_3$), 0.02 (s, 3H; $SiCH_3$), 0.88 (s, 9H; $SiC(CH_3)_3$), 0.89 (s, 9H; $C(CH_3)_3$), 2.31 (s, 3H;

CH_3), 4.43 (s, 1H; CH), 7.31 (d, $J=6.0$ Hz, 1H; ArH), 7.43 (dd, $J=8.0$, 2.0 Hz, 1H; ArH), 8.29 ppm (m, 1H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=-5.32$, -4.74, 18.08, 18.13, 25.86, 26.03, 36.24, 83.43, 121.9, 131.0, 136.0, 147.7, 160.0 ppm; IR (film): $\tilde{\nu}=2955$, 2930, 2858, 1484, 1472, 1462, 1254, 1081, 875, 836, 778 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε) = 211 (3.923), 266 nm (3.594); MS (70 eV, EI): m/z (%): 293 (<1) $[M]^+$, 278 (9), 236 (100), 179 (62), 146 (10), 111 (20), 73 (71); elemental analysis calcd (%) for $C_{17}H_{31}NOSi$ (293.52): C 69.56, H 10.65; found: C 69.18, H 10.25.

(*R*)-5-Methyl-2-(1-*tert*-butyldimethylsilyloxy-2,2-dimethylpropyl)pyridine *N*-oxide: The silylated pyridyl carbinol prepared above (3.52 g, 12.0 mmol) was dissolved in dichloromethane (40 mL), treated with *m*CPBA (3.12 g, 18.0 mmol) at 0°C and stirred overnight at RT. The mixture was quenched with cold 40% aqueous KOH solution and stirred for 1 h. The layers were separated and the aqueous layer was extracted with dichloromethane (4×20 mL). The combined organic layers were dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. Purification of the crude product by flash chromatography over silica gel (CH_2Cl_2/MeOH 20:1) afforded the title compound as colorless oil (3.53 g, 95%). $[\alpha]_D^{27}=+17.0°$ ($c=1.14$ in CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=-0.29$ (s, 3H; $SiCH_3$), 0.07 (s, 3H; $SiCH_3$), 0.88 (s, 9H; $SiC(CH_3)_3$), 0.96 (s, 9H; $C(CH_3)_3$), 2.28 (s, 3H; CH_3), 5.41 (s, 1H; CH), 7.04 (d, $J=8.0$ Hz, 1H; ArH), 7.34 (d, $J=8.0$ Hz, 1H; ArH), 8.04 ppm (s, 1H; ArH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=-5.38$, -5.21, 17.91, 17.95, 25.46, 25.76, 37.72, 72.56, 125.6, 125.9, 134.1, 139.0, 151.0 ppm; IR (film): $\tilde{\nu}=$ 2954, 2929, 2858, 1472, 1462, 1385, 1259, 1075, 1029, 866, 841, 777 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε) = 224 (4.422), 271 nm (4.270); MS (70 eV, EI): m/z (%): 309 (<1) $[M]^+$, 293 (2), 278 (4), 252 (20), 236 (100), 179 (339), 73 (54); HRMS (ESI): calcd for $C_{17}H_{31}NNaO_2Si$: 332.20163; found: 332.20177 $[M+Na]^+$.

(*R*,*R*)-3,3′-Bismethyl-6,6′-bis(1-*tert*-butyldimethylsilyloxy-2,2-dimethylpropyl)-2,2′-bipyridine bis-*N*-oxide: A solution of *n*BuLi in hexane (2.5 m, 2.00 mL) was added to a solution of 2,2,6,6-tetramethylpiperidine (0.85 mL, 5.00 mmol) in THF (5 mL) and the resulting mixture was stirred for 3 h at 0°C. This freshly prepared LiTMP (TMP = 2,2,6,6-tetramethylpiperidene) solution was added to a solution of the N-oxide prepared above (1.55 g, 5.00 mmol) in diethyl ether (10 mL) at −78°C. After the reaction mixture had been stirred for 16 h at −78°C, a solution of iodine (0.63 g, 2.5 mmol) in THF was slowly added to the resulting deep-red mixture at −78°C. The mixture was further stirred at −78°C for 2 h, then the cooling bath was removed and the reaction mixture was brought up to RT and stirred for 2 h. The reaction was quenched with water (5 mL), followed by saturated aqueous $NaHSO_3$ solution (5 mL). The mixture was diluted with aqueous ammonia solution (25 mL) and the layers were separated. The aqueous layer was extracted with dichloromethane (3×30 mL). The combined organic layers were dried over $MgSO_4$, filtered, and the solvents were removed under reduced pressure. Purification of the crude product by flash chromatography over silica gel (diethyl ether/petroleum ether 1:6) afforded the title compound as a pale-yellow solid (996 mg, 65%). M.p. 67–69°C; $[\alpha]_D^{27}=-100.4°$ ($c=1.45$ in CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=-0.23$ (s, 6H; $SiCH_3$), 0.02 (s, 6H; $SiCH_3$), 0.87 (s, 18H; $SiC(CH_3)_3$), 0.94 (s, 18H; $C(CH_3)_3$), 2.05 (s, 6H; CH_3), 5.47 (s, 2H; CH), 7.07 (d, $J=8.0$ Hz, 2H; ArH), 7.38 ppm (d, $J=$ 8.0 Hz, 2H; ArH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=-5.50$, -5.10, 17.88, 25.75, 27.50, 37.88, 74.56, 118.5, 124.3, 124.4, 140.8, 151.3 ppm; IR (KBr): $\tilde{\nu}=2954$, 2858, 1474, 1393, 1365, 1329, 1244, 1080, 1029, 892, 858, 835, 816, 777 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε) = 232 (4.556), 270 nm (4.205); MS (ESI): m/z: 1255.8 $[2M+Na]^+$, 639.4 $[M+Na]^+$, 617.4 $[M+H]^+$; elemental analysis calcd (%) for $C_{34}H_{60}N_2O_4Si_2$ (617.02): C 66.18, H 9.80; found: C 65.82, H 9.46.

(*R*,*R*)-3,3′-Bismethyl-6,6′-bis(1-hydroxy-2,2-dimethylpropyl)-2,2′-bipyridine (10): A tetrabutylammonium fluoride solution (1M, 3.0 mL, 3.0 mmol) was added to a solution of the bipyridine bis-*N*-oxide prepared above (358 mg, 0.50 mmol) in THF (25 mL), and the resulting mixture was stirred overnight over molecular sieves. The reaction was quenched with water (10 mL), then the layers were separated and the aqueous layer was extracted with dichloromethane (3×20 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, and filtered. The solvents were evaporated in vacuo and the residue was dissolved in wet THF (10 mL). After addition of acetic acid (1 mL) and Zn powder (327 mg, 5.00 mmol), the mixture was refluxed for 8 h. Ammonia solution (25%, 30 mL) was added, the layers were separated, and the aqueous layer was extracted with dichloromethane (4×15 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography over silica gel (ethyl acetate/petroleum ether 1:2) and recrystallisation from hexane/toluene. The title compound was obtained as white crystals (90 mg, 51%). M.p. 107–110°C; $[\alpha]_D^{24}=+12.0°$ ($c=1.86$ in CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=0.93$ (s, 18H; CH_3), 2.16 (s, 6H; CH_3), 4.38 (s, 4H; CH and OH), 7.15 (d, $J=$ 8.0 Hz, 2H; ArH), 7.59 ppm (d, $J=8.0$ Hz, 2H; ArH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=18.51$, 25.93, 36.34, 79.92, 121.9, 130.5, 138.1, 155.2, 156.2 ppm; IR (KBr): $\tilde{\nu}=3456$, 2954, 2864, 1452, 1394, 1334, 1070, 1014, 835 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε) = 205 (4.072), 275 nm (3.913); MS (ESI): m/z: 767.5 $[2M+MeOH+Na]^+$, 735.5 $[2M+Na]^+$, 411.3 $[M+MeOH+Na]^+$, 379.2 $[M+Na]^+$, 357.3 $[M+H]^+$; HRMS (ESI): calcd for $C_{22}H_{32}NaN_2O_2$: 379.23560; found: 379.23586 $[M+Na]^+$.

(*R*)-1-(6-Bromopyridin-2-yl)-2,2,3-trimethylbutanol: A stirred solution of 2,6-dibromopyridine (6.72 g, 3.00 mmol) in diethyl ether (20 mL) was cooled to −78°C, then a solution of *n*BuLi in hexane (2.5M, 12.3 mL) was added dropwise over 15 min and stirred for 1.5 h at −78°C. A solution of CuI (2.67 g, 14.0 mmol) and dimethylsulfide (12 mL) in diethyl ether (20 mL) was added to the resulting mixture. After the reaction mixture had been stirred for 1 h at −78°C, 2,2,3-trimethylbutane acid chloride[33] was added. The mixture was stirred for 2 h at −78°C and then brought up to RT. The mixture was quenched with saturated aqueous NH_4Cl solution (40 mL), stirred for 15 min, then the layers were separated. The aqueous layer was extracted with diethyl ether (3×20 mL). The combined organic layers were washed with water, dried over $MgSO_4$, and filtered. After evaporation of the solvent, the residue was separated by flash chromatography (diethyl ether/petroleum ether 1:19). The semisolid was dissolved in hot hexane and filtered after cooling. The filtrate was concentrated under reduced pressure and yielded 1-(6-bromopyridin-2-yl)-2,2,3-trimethylbutanon as a colorless oil (2.62 g, 75%). The pyridyl ketone was then enantioselectively hydrogenated according to the protocol described by Kobayashi[18b] and yielded the title compound as a colorless oil (847 mg, 53%). $[\alpha]_D^{25}=-32.8°$ ($c=1.21$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.67$ (s, 3H; CH_3), 0.77 (s, 3H; CH_3), 0.92 (d, $J=$ 7.0 Hz, 3H; CH_3), 0.95 (d, $J=7.0$ Hz, 3H; CH_3), 1.89 (sept, $J=7.0$ Hz, 1H; CH), 3.52 (d, $J=7.5$ Hz, 1H; OH), 4.63 (d, $J=7.5$ Hz, 1H; CH), 7.17 (d, $J=7.5$ Hz, 1H; ArH), 7.37 (d, $J=7.5$ Hz, 1H; ArH), 7.49 ppm (dd, $J=7.5$, 7.5 Hz, 1H; ArH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=17.54$, 17.59, 18.57, 18.95, 32.70, 40.98, 77.07, 121.7, 126.8, 137.8, 140.6, 162.5 ppm; IR (film): $\tilde{\nu}=3439$, 2967, 2876, 1582, 1555, 1467, 1435, 1394, 1368, 1159, 1123, 1045, 792, 753, 695 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε) = 202 (3.762), 210 (3.727), 268 nm (3.539); MS (ESI): m/z (%): 294.0 $[M+Na]^+$, 272.0 $[M+H]^+$; HRMS (ESI): calcd for $C_{12}H_{18}BrNNaO$: 294.04640; found: 294.04656 $[M+Na]^+$.

(*R*,*R*)-6,6′-Bis(1-hydroxy-2,2,3-trimethylbutanyl)bipyridine (11): PPh_3 (2.02 g, 7.70 mmol) and zinc powder (137 mg, 2.10 mmol) were added to a stirred solution of $NiCl_2{\cdot}6H_20$ (451 mg, 1.90 mmol) in degassed DMF (10 mL) heated to 70°C. The brown reaction mixture was stirred at 70°C for 1 h followed by addition of pyridyl carbinol prepared above (434 mg, 1.60 mmol). After the reaction mixture had been stirred at 70°C for 2 h, the reaction mixture was cooled to RT. Addition of aqueous 5% NH_3 solution (10 mL) resulted in brown precipitation. The whole reaction mixture was extracted with a diethyl ether/dichloromethane 1:2 mixture (5×25 mL). The organic layers were concentrated under reduced pressure and diluted with dichloromethane. The organic layer was first washed with water (5×25 mL) and second with brine (25 mL). The organic layer was dried over $MgSO_4$ and filtered. The solvents were removed under reduced pressure. The yellow crude product was purified by flash chromatography over silica gel (ethyl acetate/petroleum ether 1:9→1:6). The title compound (105 mg, 34%) was obtained after recrystallisation from hexane/toluene. M.p. 170–173°C $[\alpha]_D^{23}=-49.4°$ ($c=1.03$ in $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=0.74$ (s, 6H; CH_3), 0.82 (s, 6H; CH_3), 0.96 (d, $J=7.0$ Hz, 6H; CH_3), 1.0 (d, $J=7.0$ Hz, 6H; CH_3), 1.96 (sept, $J=$ 7.0 Hz, 2H; CH), 4.32 (d, $J=7.0$ Hz, 2H; OH), 4.74 (d, $J=7.0$ Hz, 2H;

CH), 7.23 (d, $J=8.0$ Hz, 2H; ArH), 7.78 (dd, $J=8.0$, 8.0 Hz, 2H; ArH), 8.30 ppm (d, $J=8.0$ Hz, 2H; ArH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 17.70, 17.68, 18.75, 19.10, 32.80, 41.03, 77.00, 119.5, 123.2, 136.6, 153.9, 159.8 ppm; IR (KBr): $\tilde{\nu}=3406$, 2968, 1567, 1434, 1047, 808 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε) = 201 (4.211), 239 (3.783), 289 nm (4.034); MS (ESI): m/z (%): 407.3 $[M+Na]^+$, 385.3 $[M+H]^+$.

1-(6-Bromopyridin-2-yl)-2-ethyl-2-methylbutan-1-one: A stirred suspension of 2,6-dibromopyridine (5.00 g, 21.0 mmol) in 100 mL diethyl ether was cooled to −78 °C. Then a solution of *n*BuLi in hexane (2.5 M, 9.90 mL, 25.0 mmol) was added to this suspension. The clear pale-yellow solution was stirred at −78 °C for a further 30 min followed by the addition of 2-ethyl-2-methylbutyronitrile (3.00 g, 25.0 mmol, purity 92 %). The deep-red reaction mixture was stirred at −78 °C for 1 h, followed by warming up to RT. After addition of H_2SO_4 (2 N, 90 mL), the pale-yellow reaction mixture was refluxed at 60 °C for 2 h. The aqueous phase was extracted with diethyl ether (3 × 25 mL). The combined organic layers were rinsed with saturated Na_2CO_3 solution (25 mL), dried over $MgSO_4$ and filtered. The solvents were removed under reduced pressure. The title compound was obtained as a yellow oil (5.50 g, 97 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.76$ (t, $J=7.5$ Hz, 6H), 1.26 (s, 3H), 1.76 (dq, $J=$ 15.0, 7.5 Hz, 2H), 2.28 (dq, $J=15.0$, 7.5 Hz, 2H), 7.58 (dd, $J=8.0$, 1.0 Hz, 1H), 7.65 (dd, $J=8.0$, 7.5 Hz, 1 HH), 7.83 ppm (dd, $J=7.5$, 1.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=8.946$, 20.72, 31.14, 52.25, 122.0, 130.5, 139.0, 139.7, 155.4, 205.0 ppm; IR (film): $\tilde{\nu}=2968$, 2936, 2877, 1684, 1569, 1555, 1461, 1427, 1382, 1122 cm^{-1}; MS (ESI): m/z: 292.0 $[M+Na]^+$, 270.0 $[M+H]^+$; HRMS (ESI): calcd for $C_{12}H_{16}BrNNaO$: 292.03075; found: 292.03087 $[M+Na]^+$.

(*R*)-1-(6-Bromopyridin-2-yl)-2-ethyl-2-methylbutan-1-ol: The pyridyl ketone prepared above was enantioselectively hydrogenated according to the protocol described by Kobayashi[18b] and yielded the title compound after flash chromatography over silica gel (diethyl ether/petroleum ether 1:9) as a colorless oil (2.10 g, 52 %). $[\alpha]_D^{25}=-26.4°$ ($c=1.01$ in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.73$ (s, 3H), 0.84 (t, $J=7.5$ Hz, 3H), 0.84 (t, $J=7.5$ Hz, 3H), 1.18–1.34 (m, 3H), 1.55 (dq, $J=15.0$, 7.5 Hz, 1H), 3.56 (d, $J=7.5$ Hz, 1H), 4.53 (d, $J=7.5$ Hz, 1H), 7.16 (d, $J=7.5$ Hz, 1H), 7.36 (d, $J=8.0$, 1HH), 7.48 ppm (dd, $J=8.0$, 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=7.836$, 7.868, 19.31, 26.95, 27.37, 41.07, 76.95, 121.5, 126.5, 137.8, 140.6, 162.3 ppm; IR (film): $\tilde{\nu}=3438$, 2965, 2937, 2879, 1581, 1555, 1461, 1435, 1382, 1122 cm^{-1}; MS (ESI): m/z: 294.0 $[M+Na]^+$, 567.1 $[2M+Na]^+$; elemental analysis calcd (%) for $C_{12}H_{18}BrNO$: C 52.95, H 6.67; found: C 52.83, H 6.81.

(*R*,*R*)-6,6′-Bis(1-hydroxy-2-ethyl-2-methylbutyl)-2,2′-bipyridine (12): The pyridyl carbinol prepared above was reductively dimerized with $NiCl_2{\cdot}6H_2O$, PPh_3, and zinc powder in DMF at 70 °C as described for **11**. The crude product obtained was purified by flash chromatography over silica gel (diethyl ether/petroleum ether 1:4 for separation of PPh_3, then 1:1) and recrystallized two times from hexane. The title compound was obtained as a white solid (587 mg, 39 %). M.p. 85–87 °C; $[\alpha]_D^{25}=-40.2°$ ($c=1.12$ in $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=0.80$–0.92 (m, 18H), 1.20–1.40 (m, 6H), 1.64 (dq, $J=15.0$, 7.5 Hz, 2H), 4.34 (d, $J=7.0$ Hz, 2H), 4.65 (d, $J=7.0$ Hz, 2H), 7.22 (d, $J=8.0$ Hz, 2H), 7.77 (t, $J=8.0$ Hz, 2 HH), 8.29 ppm (d, $J=8.0$ Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=$ 7.968, 19.54, 27.13, 27.55, 41.04, 76.87, 119.4, 123.0, 136.6, 153.8, 159.6 ppm; IR (KBr): $\tilde{\nu}=3417$, 3097, 3055, 2964, 2877, 1570, 1434, 1390, 1108, 812, 767 cm^{-1}; MS (ESI): m/z: 791.5 $[2M+Na]^+$, 407.3 $[M+Na]^+$, 385.3 $[M+H]^+$; HRMS (ESI): calcd for $C_{24}H_{37}N_2O_2$: 385.28506; found: 385.28495 $[M+H]^+$.

(*R*)-6-Bromo-2-(1-*tert*-butyldimethylsilyloxy-2,2-dimethylpropyl)pyridine: TBSOTf (3.40 mL, 15.0 mmol) and 2,6-lutidine (2.40 mL, 20.0 mmol) were added to a stirred solution of (*R*)-6-bromopyridin-2-yl-2,2-dimethylpropan-1-ol (2.44 g, 10.0 mmol) in dichloromethane (45 mL) at 0 °C. The resulting solution was stirred overnight at RT and quenched with saturated aqueous $NaHCO_3$ solution (40 mL). The layers were separated, the aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$ and filtered. The residue obtained after removal of the solvent was purified by flash chromatography over silica gel (diethyl ether/petroleum ether 1:19). The title compound was obtained as colorless oil (3.44 g, 96 %). M.p. 73–75 °C; $[\alpha]_D^{30}=+49.2°$ ($c=1.00$ in CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=-0.31$ (s, 3H, $SiCH_3$), 0.04 (s, 3H, $SiCH_3$), 0.88 (s, 9H; $SiC(CH_3)_3$), 0.90 (s, 9H; $C(CH_3)_3$), 4.45 (s, 1H; CH), 7.31 (dd, $J=$ 8.0, 1.0 Hz, 1H; ArH), 7.39 (dd, $J=8.0$, 1.0 Hz, 1H; ArH), 7.5 ppm (t, $J=8.0$ Hz, 1H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=-5.29$, −4.65, 18.02, 25.82, 25.91, 36.37, 82.59, 121.2, 126.0, 137.7, 139.7, 164.9 ppm; IR (film): $\tilde{\nu}=3061$, 2957, 2930, 2884, 2858, 1583, 1555, 1471, 1392, 1359, 1259, 1249, 1117, 1073, 876, 777, 701 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε) = 217 (3.671), 267 nm (3.614); MS (70 eV, EI): m/z (%): 358 (7) $[M]^+$, 237 (16), 188 (100), 160 (18), 102 (62), 57 (32); HRMS (ESI): calcd for $C_{16}H_{29}{\cdot}BrNOSi$: 358.11963; found: 358.11976 $[M+H]^+$.

(*R*,*R*)-6,6′-Bis(1-hydroxy-2,2-dimethylpropyl)terpyridine (13): A stirred solution of the bromopyridine prepared above (1.08 g, 3.00 mmol) in THF (10 mL) was cooled to −78 °C, then a solution of *n*BuLi in hexane (2.5 m, 1.44 mL) was added dropwise. The resulting solution was stirred for 30 min at −78 °C before a solution of $ZnCl_2$ in THF (2 m, 7.20 mL) was added and the mixture warmed to RT over 1 h. $Pd(PPh_3)_4$ (348 mg, 10 mol %) and 2,6-dibromopyridine (720 mg, 3.00 mmol) were added and the mixture was heated under reflux for 4 h. EDTA/Na_2CO_3 solution (75 mL) was added, the layers were separated, and the aqueous layer was extracted with diethyl ether (3 × 30 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue which contained a mixture of the title compound and monocoupled product was dissolved in THF (10 mL) and treated with *n*BuLi (2.5 m, 1.44 mL), $ZnCl_2$ (2 M, 7.20 mL), and $Pd(PPh_3)_4$ (348 mg, 10 mol %) following the procedure above. This mixture was refluxed for 24 h and then worked up as described above. The crude product was filtered over silica gel (diethyl ether/petroleum ether 1: 99). After evaporation of the solvent, the residue was dissolved in THF (10 mL) and treated with tetrabutylammonium fluoride solution (1 M, 18 mL, 18 mmol) for 4 h. The reaction was quenched with water (20 mL), the layers were separated and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure and flash chromatography (ethyl acetate/petroleum ether 1:3) afforded the title compound as white crystals (360 mg, 30 %), which was purified by recrystallization (hexane/toluene) (297 mg, 24 %). M.p. 203–206 °C; $[\alpha]_D^{30}=-14.4°$ ($c=1.04$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.98$ (s, 18H; $C(CH_3)_3$), 4.45 (s, 4H; CH and OH), 7.23 (d, $J=7.5$ Hz, 2H; ArH), 7.81 (dd, $J=7.5$, 7.5 Hz, 2H; ArH), 7.95 (dd, $J=8.0$, 8.0 Hz, 1H; ArH), 8.42 (d, $J=8.0$ Hz, 2H; ArH), 8.52 (d, $J=7.5$ Hz, 2H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=25.91$, 36.27, 80.22, 119.7, 120.9, 122.9, 136.5, 137.8, 154.2, 154.9, 159.2 ppm; IR (film): $\tilde{\nu}=3375$, 3060, 2962, 2665, 1569, 1432, 1361, 1074, 1049, 1012, 805, 768, 632 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε) = 212 (4.442), 251 (4.458), 288 nm (4.551); MS (ESI): m/z (%): 460.2 $[M+MeOH+Na]^+$, 428.2 $[M+Na]^+$, 406.3 $[M+H]^+$; elemental analysis calcd (%) for $C_{25}H_{31}N_3O_2$ (405.24): C 74.04, H 7.70; found: C 73.72, H 7.77.

Scandium–bipyridine-catalyzed aminolysis of *meso*-epoxides (general procedure II): A solution of $Sc(OTf)_3$ (25.0 mg, 10 mol %) and chiral bipyridine **2** (17.0 mg, 10 mol %) in dichloromethane (2 mL) was stirred for 5 min, then the epoxide (0.5 mmol) was added. The reaction mixture was cooled to the temperature given and the amine (1 mmol) was added. After the reaction was completed, the solvent was evaporated and the product was purified by flash column chromatography over silica gel.

Scandium–bipyridine-catalyzed aminolysis of *meso*-epoxides (general procedure III): A solution of $Sc(OTf)_3$ (25.0 mg, 10 mol %) and chiral bipyridine **2** (17.0 mg, 10 mol %) in dichloromethane (2 mL) was stirred for 5 min, then the epoxide (0.5 mmol) was added. The reaction mixture was cooled to the temperature given and the amine (0.5 mmol) was added. After the reaction was completed, the solvent was evaporated and the product was purified by flash column chromatography over silica gel.

Scandium–bipyridine-catalyzed aminolysis of *meso*-epoxides (general procedure IV): A solution of $Sc(OTf)_3$ (25.0 mg, 10 mol %) and chiral bipyridine **2** (20.0 mg, 12 mol %) in dichloromethane (2 mL) was stirred for 5 min, then the epoxide (0.5 mmol) was added. The reaction mixture was cooled to the temperature given and the amine (1 mmol) was added.

After the reaction was completed, the solvent was evaporated and the product was purified by flash column chromatography over silica gel.

(1*R*,2*R*)-2-(*N*-Methyl-*N*-phenylamino)-1,2-diphenylethanol (3): Following general procedure IV, *cis*-stilbene oxide (**1a**) (98 mg, 0.50 mmol) was treated with *N*-methyl aniline (107 mg, 1.00 mmol) at RT. Flash chromatography (diethyl ether/petroleum ether 1:4) afforded **3** as a colorless solid (116 mg, 85%). R_f=0.37 (diethyl ether/petroleum ether 1:2); m.p. 56–60°C; $[\alpha]_D^{23}=-184.4°$; (c=1.00 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.71 (s, 3H; CH_3), 3.99 (s, 1H; OH), 4.88 (d, J=10 Hz, 1H; CH), 5.30 (d, J=10 Hz, 1H; CH), 6.91–7.04 (m, 5H; PhH), 7.15–7.32 (m, 8H; PhH), 7.41 ppm (dd, J=8.5, 2.0 Hz, 2H; PhH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=32.8, 71.6, 73.9, 117.9, 120.5, 127.5, 127.8, 127.9, 128.1, 128.4, 128.9, 129.3, 134.7, 140.8, 151.5 ppm; IR (KBr): $\tilde{\nu}$=3419, 3028, 2883, 1597, 1496, 1450, 1386, 1253, 1186, 1025, 754, 696 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε)=200 (4.187), 208 (5.251), 255 nm (4.080); MS (ESI): m/z: 629.3 [2M+Na]$^+$, 326.2 [M+Na]$^+$, 304.2 [M+H]$^+$; HRMS (ESI): calcd for $C_{21}H_{21}NaNO$: 326.15154; found: 326.15177 [M+Na]$^+$. The enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 90:10, flow 0.8 mL min^{-1}) λ=251 nm, (1*S*,2*S*): 20.3 min; (1*R*,2*R*): 21.8 min; 97% *ee*.

(1*R*,2*R*)-1,2-Diphenyl-2-(phenylamino)ethanol[10] (4a): Following general procedure III, *cis*-stilbene oxide (**1a**) (98 mg, 0.50 mmol) was treated with aniline (46 μL, 0.50 mmol) at RT. Flash chromatography (diethyl ether/petroleum ether 1:8) afforded **4a** as a colorless solid (138 mg, 95%). R_f=0.27 (diethyl ether/petroleum ether 1:2); m.p. 100–103°C; $[\alpha]_D^{23}=+48.6°$ (c=0.53 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.75 (brs, 1H; NH), 4.60 (d, J=6.9 Hz, 1H; CH), 4.76 (brs, 1H; OH), 4.91 (d, J=6.0 Hz, 1H; CH), 6.60–6.64 (m, 2H; PhH), 6.72–6.78 (m, 1H; PhH), 7.16–7.19 (m, 2H; PhH), 7.26–7.40 ppm (m, 10H; PhH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=64.8, 78.1, 114.2, 118.0, 126.7, 127.4, 127.6, 128.0, 128.3, 128.6, 129.1, 140.3, 140.6, 147.3 ppm; IR (KBr): $\tilde{\nu}$=3545, 3406, 3031, 2879, 2846, 1601, 1498, 1450, 1427, 1319, 1034, 758, 700 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε)=201 (4.167), 210 (4.196), 247 (4.102), 295 nm (3.292); MS (70 eV, EI): m/z (%): 289 (1) [M]$^+$, 182 (100), 104 (20), 86 (79), 84 (99), 77 (30), 51 (5); MS (ESI): m/z: 601.3 [2M+Na]$^+$, 312.1 [M+Na]$^+$, 290.2 [M+H]$^+$; the enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 85:15, flow 1 mL min^{-1}) λ=247 nm, (1*R*,2*R*): 13.6 min; (1*S*,2*S*): 17.5 min; 93% *ee*.

(1*R*,2*R*)-2-(Phenylamino)cyclohexanol[10] (4b): Following general procedure II, cyclohexene oxide (51 μL, 0.50 mmol) was treated with aniline (91 μL, 1.00 mmol) at −20°C. Flash chromatography (diethyl ether/petroleum ether 1:2) afforded **4b** as a pale-yellow solid (92 mg, 96%). R_f= 0.12 (diethyl ether/petroleum ether 1:2); m.p. 57–59°C; $[\alpha]_D^{23}=-37.7°$ (c=0.54 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.03–1.08 (m, 1H), 1.27–1.43 (m, 3H), 1.71–1.81 (m, 2H), 2.11–2.15 (m, 2H), 3.10–3.18 (m, 3H; CH, NH, OH), 3.35 (td, J=10.0, 4.5 Hz, 1H; CH), 6.71–6.79 (m, 3H; PhH), 7.17–7.22 ppm (m, 2H; PhH); ^{13}C NMR (50 MHz, $CDCl_3$): δ=24.6, 25.2, 31.8, 33.5, 60.3, 74.7, 114.6, 129.6, 148.2 ppm; IR (KBr): $\tilde{\nu}$= 3390, 3049, 2931, 2856, 1600, 1502, 1448, 1068, 748 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε)=201 (4.036), 205 (4.030), 248 (4.049), 296 nm (3.252); MS (70 eV, EI): m/z (%): 191 (39) [M]$^+$, 148 (14), 132 (100), 118 (25), 106 (40), 93 (15), 77 (23); the enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 85:15, flow 1 mL min^{-1}) λ=247 nm, (1*S*,2*S*): 10.3 min; (1*R*,2*R*): 11.9 min; 54% *ee*.

(1*R*,2*R*)-2-(Phenylamino)cyclopentanol[10] (4c): Following general procedure II, cyclopentene oxide (44 μL, 0.50 mmol) was treated with aniline (91 μL, 1.00 mmol) at −20°C. Flash chromatography (diethyl ether/petroleum ether 1:2) afforded **4c** as a pale-yellow solid (79 mg, 89%). R_f= 0.18 (diethyl ether/petroleum ether 1:2); m.p. 52–56°C; $[\alpha]_D^{23}=-12.8°$ (c=0.55 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.36–1.46 (m, 1H; CH_2), 1.59–1.72 (m, 1H; CH_2), 1.72–1.88 (m, 2H; CH_2), 1.90–2.04 (m, 1H; CH_2), 2.22–2.34 (m, 1H; CH_2), 2.71 (brs, 2H; OH and NH), 3.58–3.64 (m, 1H; CH), 4.06 (dt, J=4.5, 6.0 Hz, 1H; CH), 6.65–6.75 (m, 3H; PhH), 7.15–7.22 ppm (m, 2H; PhH); ^{13}C NMR (75 MHz, $CDCl_3$): δ= 21.14, 31.31, 32.99, 62.19, 78.36, 113.4, 117.6, 129.4, 147.9 ppm; IR (KBr): $\tilde{\nu}$=3527, 3373, 2958, 1601, 1502, 1315, 1105, 750 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε)=203 (3.962), 206 (3.961), 249 (4.089), 297 nm (3.355); MS (70 eV, EI): m/z (%): 177 (52) [M]$^+$, 132 (100), 118 (14), 106 (44), 93 (15), 77 (17); the enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 85:15, flow 1 mL min^{-1}) λ=247, (1*S*,2*S*): 15.5 min, (1*R*,2*R*): 17.7 min; 41% *ee*.

(1*R*,2*R*)-2-Phenylaminocycloheptanol[34] (4d): Following general procedure IV, cycloheptene oxide (**1d**) (58 μL, 0.50 mmol) was treated with aniline (91 μL, 1.00 mmol) at RT for 6.5 h. Flash chromatography (ethyl acetate/petroleum ether 1:4) afforded **4d** as a brown viscous oil (48 mg, 47%). R_f=0.19 (diethyl ether/petroleum ether 1:3); $[\alpha]_D^{28}=-7.3°$ (c=1.42 in CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.26–1.80 (m, 8H; CH_2), 1.87–2.08 (m, 2H; CH_2), 3.13 (brs, 2H; NH and OH), 3.24 (td, J=9.0, 3.5 Hz, 1H; CH), 3.46 (td, J=9.0, 3.5 Hz 1H; CH), 6.67–6.82 (m, 3H; PhH), 7.15–7.24 ppm (m, 2H; PhH); ^{13}C NMR (100 MHz,$CDCl_3$): δ= 22.14, 24.04, 27.19, 30.27, 32.83, 62.74, 76.55, 114.9, 118.7, 129.3, 147.5 ppm; IR (film): $\tilde{\nu}$=3394, 3051, 2929, 2859, 1602, 1501, 1459, 1321, 1246, 1178, 1080, 1059, 1026, 749, 993 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε)=203 (3.987), 245 (4.103), 291 nm (3.462); MS (ESI): m/z: 228.0 [M+Na]$^+$, 206.0 [M+H]$^+$; the enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 85:15, flow 1.0 mL min^{-1}) λ=243 nm, (1*S*,2*S*): 9.9 min; (1*R*,2*R*): 11.3 min; 10% *ee*.

(2*R*,3*R*)-3-(Phenylamino)butanol[10] (4e): Following general procedure III, *cis*-2,3-epoxy butane (44 μL, 0.50 mmol) was treated with aniline (46 μL, 0.50 mmol) at 0°C. Flash chromatography (diethyl ether/petroleum ether 1:2) afforded **4e** as a colorless liquid (76 mg, 92%). R_f=0.14 (diethyl ether/petroleum ether 1:2); $[\alpha]_D^{23}=-58.8°$ (c=0.93 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.16 (d, J=6.5 Hz, 3H; CH_3), 1.27 (d, J=6.5 Hz, 3H; CH_3), 2.70 (brs, 1H; NH), 3.34 (quint, J=6.5 Hz, 2H; CH and OH), 3.65 (quint, J=6.5 Hz, 1H; CH), 6.67–6.78 (m, 3H; PhH), 7.16–7.23 ppm (m, 2H; PhH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=17.4, 19.6, 56.1, 71.4, 114.4, 118.3, 129.4, 147.9 ppm; IR (film): $\tilde{\nu}$=3398, 3050, 2972, 2927, 2357, 1601, 1504, 1452, 1315, 1253, 1170, 1091, 748, 692 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε)=200 (3.989), 205 (4.044), 248 (4.112), 297 nm (3.317); MS (70 eV, EI): m/z (%): 165 (9) [M]$^+$, 120 (100), 93 (6), 77 (15), 51 (6); HRMS (ESI): calcd for $C_{22}H_{24}NO$: 318.18524; found: 318.18521 [M+H]$^+$; the enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 95:5, flow 1 mL min^{-1}) λ=247 nm, (2*S*,3*S*): 17.2 min; (2*R*,3*R*): 18.6 min; 60% *ee*.

(3*R*,4*R*)-4-*N*-Phenylamino-3-octanol (4f): Following general procedure IV, *cis*-4-octene oxide (**1f**) (64 mg, 0.50 mmol) was treated with aniline (91 μL, 1.00 mmol) at RT. Flash chromatography (diethyl ether/petroleum ether 1:3) afforded **4f** as a pale brown oil (82 mg, 74%). R_f=0.27 (diethyl ether/petroleum ether 1:3); $[\alpha]_D^{23}=-0.95°$ (c=1.05 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.89 (d, J=7.0 Hz, 3H; CH_3), 0.93 (d, J=7.0 Hz, 3H; CH_3), 1.29–1.67 (m, 8H; CH_2), 2.17 (brs, 1H, NH), 3.28 (dt, J=7.5, 5.0 Hz 1H; CH), 3.56–3.62 (m, 2H; CH, OH), 6.63–6.71 (m, 3H; PhH), 7.13–7.18 ppm (m, 2H; PhH); ^{13}C NMR (75 MHz,$CDCl_3$): δ= 14.11, 14.19, 19.12, 19.43, 34.85, 36.20, 58.03, 73.21, 113.4, 117.4, 129.3, 148.6 ppm; IR (film): $\tilde{\nu}$=3405, 3052, 3020, 2957, 2932, 2871, 1602, 1505, 1464, 1431, 1320, 1259, 747, 692 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε)=201 (4.148), 207 (4.150), 250 (4.284), 299 nm (3.489); MS (ESI): m/z: 244.1 [M+Na]$^+$, 222.1 [M+H]$^+$; HRMS (ESI): calcd for $C_{14}H_{24}NO$: 222.18524; found: 222.18532 [M+H]$^+$; the enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 95:5, flow 0.8 mL min^{-1}) λ=247 nm, (3*R*,4*R*): 10.8 min; (3*S*,4*S*): 12.3 min; 74% *ee*.

(4*R*,5*R*)-2,7-Dimethyl-4-*N*-phenylamino-5-octanol (4g): Following general procedure IV, *cis*-2,7-dimethyl-4-octene oxide (**1g**) (78 mg, 0.50 mmol) was treated with aniline (91 μL, 1.00 mmol) at RT. Flash chromatography (diethyl ether/petroleum ether 1:3) afforded **4g** as a colorless oil (76 mg, 61%). R_f=0.23 (diethyl ether/petroleum ether 1:3); $[\alpha]_D^{23}=+10.6°$ (c= 0.73 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.85 (d, J=6.5 Hz, 3H; CH_3), 0.91 (d, J=6.5 Hz, 3H; CH_3), 0.92 (d, J=6.5 Hz, 3H; CH_3), 0.94 (d, J=6.5 Hz, 3H; CH_3), 1.25–1.34 (m, 1H), 1.38–1.54 (m, 3H), 1.70 (sept, J=7.0 Hz, 1H), 1.76–1.89 (m, 1H), 2.10 (brs, 1H; NH), 3.27–3.33 (m, 1H; CH), 3.48 (brs, 1H; OH), 3.59–3.65 (m, 1H; CH), 6.63–6.71 (m, 3H; PhH), 7.15–7.18 ppm (m, 2H; PhH); ^{13}C NMR (75 MHz,$CDCl_3$): δ= 21.89, 22.45, 23.33, 23.70, 24.80, 24.88, 42.31, 43.37, 56.81, 71.89, 113.3, 117.4, 129.3, 148.7 ppm; IR (film): $\tilde{\nu}$=3404, 3053, 3020, 2956, 2869, 1602, 1504, 1467, 747, 692 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε)=204 (3.949), 251 (4.099), 299 nm (3.299); MS (ESI): m/z: 272.1 [M+Na]$^+$, 250.1 [M+H$^+$];

HRMS (ESI): calcd for $C_{16}H_{28}NO$: 250.21654; found: 250.21657 $[M+H]^+$. The enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 95:5, flow 0.8 mL min^{-1}) $\lambda = 247$ nm, (3*R*,4*R*): 8.3 min; (3*S*,4*S*): 10.5 min; 49% *ee*.

(2*R*,3*R*)-1,4-Diphenyl-3-*N*-phenylamino-2-butanol (4h): Following general procedure IV, *cis*-dibenzyloxirane (**1h**) (112 mg, 0.50 mmol) was treated with aniline (91 μL, 1.00 mmol) at 0°C. Flash chromatography (diethyl ether/petroleum ether 2:3) afforded **4h** as a pale-yellow viscous oil (78 mg, 49%). $R_f = 0.21$ (diethyl ether/petroleum ether 1:3); $[\alpha]_D^{25} = +11.4°$ ($c = 0.91$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.78$ (br s, 1H; NH), 2.81–3.02 (m, 4H; CH_2), 3.62–3.67 (m 1H; CH), 3.90–3.95 (m, 1H; CH), 4.14 (br s, 1H; OH), 6.66–6.76 (m, 3H; PhH), 7.13–7.32 ppm (m, 12H; PhH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 37.63$, 40.84, 57.18, 71.96, 113.4, 117.3, 126.3, 126.5, 128.5, 128.6, 129.2, 129.3, 129.4, 138.1, 138.6 ppm; IR (film): $\tilde{\nu} = 3564$, 3406, 3083, 3058, 3025, 2853, 1600, 1504, 1391, 746 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε) = 212 (4.223), 253 (4.244), 298 nm (3.419); MS (70 eV, EI): *m*/*z* (%): 317 (3) $[M]^+$, 299 (2), 252 (4), 226 (91), 196 (93), 104 (100), 91 (100), 77 (99); the enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 90:10, flow 0.8 mL min^{-1}) $\lambda =$ 247 nm, (1*R*,2*R*): 13.2 min; (1*S*,2*S*): 15.5 min; 44% *ee*.

(1*R*,2*R*)-1,2-Bis(2′-naphthyl)-2-(phenylamino)ethanol (4i): A solution of $Sc(OTf)_3$ (8 mg, 10 mol%) and chiral bipyridine **2** (7 mg, 12 mol%) in dichloromethane (1 mL) was stirred for 10 min at RT. Then *cis*-1,2-bis(2′-naphthyl)ethane oxide (**1i**) (50.0 mg, 0.17 mmol) was added. The resulting solution was stirred for 5 min, then aniline (31 μL, 0.34 mmol) was added. After 8 h of stirring the solvent was evaporated. The product was purified by flash column chromatography over silica gel (dichloromethane/petroleum ether 9:1), affording **4i** as a white solid (50 mg, 76%). $R_f = 0.37$ (CH_2Cl_2); m.p. 147–150°C; $[\alpha]_D^{23} = +109.4°$ ($c = 0.89$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.80$ (br s, 1H; NH), 4.84 (d, $J = 5.5$ Hz, 2H; CH, OH), 5.13 (d, $J = 5.5$ Hz, 1H; CH), 6.58–6.7 (m, 3H; ArH), 7.04–7.11 (m, 2H; ArH), 7.38 (ddd, $J = 8.5$, 6.5, 2.0 Hz, 2H; ArH), 7.44–7.53 (m, 4H; ArH), 7.74–7.85 ppm (m, 8H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 64.7$, 78.0, 114.3, 118.1, 124.5, 125.4, 125.7, 126.0, 126.1, 126.2, 126.3, 126.3, 127.8, 128.1, 128.2, 128.5, 129.2, 133.1, 133.2, 133.2, 133.5, 137.9, 138.1, 147.3 ppm; IR (KBr): $\tilde{\nu} = 3415$, 3053, 2924, 1600, 1502, 750 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε) = 203 (4.417), 230 (4.603), 350 nm (2.504); MS (70 eV, EI): *m*/*z* (%): 371 (2), 267 (1), 232 (100), 155 (5), 127 (6), 104 (23), 77 (22); MS (ESI): *m*/*z*: 801.3 $[2M+Na]^+$, 412.2 $[M+Na]^+$, 390.2 $[M+H]^+$; HRMS (ESI): calcd for $C_{28}H_{24}NO$: 412.16719; found: 412.16698 $[M+H]^+$; the enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 90:10, flow: 0.8 mL min^{-1}) $\lambda = 227$ nm, (1*S*,2*S*): 31.9 min; (1*R*,2*R*): 38.7 min; 82% *ee*.

(1*R*,2*R*)-2-(Phenylamino)-1,2-bis(*m*-tolyl)ethanol (4k): A solution of $Sc(OTf)_3$ (11 mg, 10 mol%) and chiral bipyridine **2** (9 mg, 12 mol%) in dichloromethane (1 mL) was stirred for 5 min at RT. Then *cis*-1,2-bis-(*m*-tolyl)ethane oxide (**1k**) (50 mg, 0.22 mmol) was added. The resulting solution was stirred for 5 min, then aniline (40 μL, 0.44 mmol) was added. After 7 h of stirring the solvent was evaporated. The product was purified by flash column chromatography over silica gel (diethyl ether/petroleum ether 1:4), affording **4k** as a pale-yellow viscous oil (65 mg, 93%). $R_f =$ 0.3 (diethyl ether/petroleum ether 1:2); $[\alpha]_D^{23} = +50.2°$ ($c = 0.89$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.33$ (s, 3H; CH_3), 2.36 (s, 3H; CH_3), 2.57 (br s, 1H; NH), 4.52 (d, $J = 5.0$ Hz, 1H; CH), 4.68 (br s, 1H; OH), 4.86 (d, $J = 5.0$ Hz, 1H; CH), 6.57 (dd, $J = 8.5$, 1.0 Hz, 2H; ArH), 6.69 (dd, $J = 7.5$, 7.5 Hz, 1H; ArH), 7.07–7.24 ppm (m, 10H; ArH); ^{13}C NMR (75 MHz,$CDCl_3$): $\delta = 21.5$, 21.6, 54.6, 78.0, 114.1, 117.8, 123.6, 128.0, 128.2, 128.4, 128.5, 128.6, 129.1, 137.9, 138.2, 140.4, 140.6, 147.5 ppm; IR (film): $\tilde{\nu} = 3398$, 3024, 2920, 1601, 1502, 1313, 1105, 794 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε) = 212 (4.262), 248 (4.144), 295 nm (3.292); MS (ESI): *m*/*z*: 657.3 $[2M+Na]^+$, 340.2 $[M+Na]^+$, 318.2 $[M+H]^+$; HRMS (ESI): calcd for $C_{22}H_{23}NaNO$: 340.16719; found: 340.16711 $[M+Na]^+$; the enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 90:10, flow: 0.8 mL min^{-1}) $\lambda = 199$ nm, (1*R*,2*R*): 15.9 min; (1*S*,2*S*): 21.1 min; 91% *ee*.

(1*R*,2*R*)-1,2-Di(*p*-chlorophenyl)-2-(phenylamino)ethanol (4l): A solution of $Sc(OTf)_3$ (12 mg, 10 mol%) and chiral bipyridine **2** (10 mg, 12 mol%) in dichloromethane (1 mL) was stirred for 5 min at RT. Then *cis*-1,2-bis-(*p*-chlorophenyl)ethane oxide (**1l**) (66 mg, 0.25 mmol) was added. The resulting solution was stirred for 5 min, then aniline (46 μL, 0.50 mmol) was added. After 1 d of stirring, the solvent was evaporated. The product was purified by flash column chromatography over silica gel (diethyl ether/petroleum ether 1:4) affording **4l** as a pale-yellow viscous oil (83 mg, 93%). $R_f = 0.31$ (diethyl ether/petroleum ether 1:2); $[\alpha]_D^{25} = +34.3°$ ($c =$ 1.26 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.62$ (br s, 1H; NH), 4.28 br s, 1H; OH), 4.44 (d, $J = 6.5$ Hz, 1H; CH), 4.78 (d, $J = 6.5$ Hz, 1H; CH), 6.50–6.52 (m, 2H; ArH), 6.67–6.71 (m, 1H; ArH), 7.06–7.17 (m, 6H; ArH), 7.22–7.27 ppm (m, 4H; ArH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 64.27$, 77.35, 114.2, 118.4, 128.0, 128.5, 128.6, 128.8, 129.1, 133.3, 133.8, 138.4, 138.8, 146.7 ppm; IR (film): $\tilde{\nu} = 3400$, 3052, 3026, 2923, 1601, 1489, 1431, 1316, 1091, 1013, 834, 752, 733, 692 cm; UV/Vis (CH_3CN): λ_{max} (lg ε) = 202 (4.339), 209 (4.303), 224 (4.372), 243 (4.220), 292 nm (3.490); MS (ESI): *m*/*z*: 380.0 $[M+Na]^+$, 358.0 $[M+H]^+$; HRMS (ESI): calcd for $C_{20}H_{18}Cl_2NO$: 358.07600; found: 358.07612 $[M+H]^+$; the enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 85:15, flow: 1.0 mL min^{-1}) $\lambda = 209$ nm, (1*R*,2*R*): 15.8 min; (1*S*,2*S*): 23.6 min; 92% ee.

(1*R*,2*R*)-2-(4-Chlorophenylamino)-1,2-diphenylethanol[35] (14): Following general procedure IV, *cis*-stilbene oxide (**1a**) (98 mg, 0.50 mmol) was treated with *p*-chloro aniline (128 mg, 1.00 mmol) at RT. Flash chromatography (diethyl ether/petroleum ether 1:2) afforded **14** as a pale-yellow viscous oil (153 mg, 95%). $R_f = 0.29$ (diethyl ether/petroleum ether 1:2); $[\alpha]_D^{23} = +34.2°$ ($c = 1.09$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.43$ (br s, 1H; NH), 4.48 (d, $J = 5.5$ Hz; CH), 4.75 (br s, 1H; OH); 4.87 (d, $J =$ 5.5 Hz; CH), 6.43 (d, $J = 9.0$ Hz; ArH), 7.00 (d, $J = 9.0$ Hz; ArH), 7.19–7.31 ppm (m, 10H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 64.62$, 77.92, 115.1, 122.4, 126.4, 127.2, 127.6, 128.0, 128.3, 128.6, 128.8, 139.7, 140.4, 146 ppm; IR (film in CCl_4): $\tilde{\nu} = 3405$, 3063, 3030, 2888, 1599, 1497, 1454, 1315, 816, 788, 766, 700 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε) = 202 (4.331), 210 (4.366), 255 (4.399), 306 nm (3.464); Ms (ESI): *m*/*z*: 346.0 $[M+Na]^+$, 324.1 $[M+H]^+$; the enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 85:15, flow 1.0 mL min^{-1}) $\lambda = 247$ nm, (1*S*,2*S*): 15.7 min; (1*R*,2*R*): 17.7 min. 95% *ee*.

(1*R*,2*R*)-2-(4-Methylphenylamino)-1,2-diphenylethanol[35] (15): Following general procedure IV, *cis*-stilbene oxide (**1a**) (98 mg, 0.50 mmol) was treated with *p*-toluidine (107 mg, 1.00 mmol) at RT. Flash chromatography (diethyl ether/petroleum ether 1:3) afforded **15** as a solid (153 mg, 95%). $R_f = 0.25$ (diethyl ether/petroleum ether 1:3); m.p. 83–86°C; $[\alpha]_D^{25} = +31.4°$ ($c = 1.54$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.20$ (s, 3H; CH_3), 2.61 (br s, 1H; NH), 4.48 (br d, $J = 6.0$ Hz, 2H; CH, OH), 4.84 (d, $J = 6.0$ Hz, 1H; CH), 6.46 (d, $J = 8.0$ Hz, 2H; ArH), 6.87 (d, $J =$ 8.0 Hz, 2H; ArH), 7.20–7.25 ppm (m, 10H; ArH); ^{13}C NMR (75 MHz,$CDCl_3$): $\delta = 20.32$, 65.18, 78.03, 114.3, 126.6, 127.2, 127.3, 127.4, 127.8, 128.2, 128.5, 129.5, 140.2, 140.5, 144.9 ppm; IR (KBr): $\tilde{\nu} = 3611$, 3390, 3061, 3026, 2871, 1815, 1519, 1454, 1317, 1260, 1038, 1022, 805, 766, 697 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε) = 205 (4.336), 215 (4.316), 251 (4.313), 281 nm (3.699); MS (ESI): *m*/*z*: 304.1 $[M+H]^+$; the enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 94:6, flow: 0.8 mL min^{-1}) $\lambda = 247$ nm, (1*S*,2*S*): 37.9 min; (1*R*,2*R*): 40.2 min; 87% *ee*.

(1*R*,2*R*)-2-(4-Methoxyphenylamino)-1,2-diphenylethanol[35] (16): Following general procedure IV, *cis*-stilbene oxide (**1a**) (98 mg, 0.50 mmol) was treated with *p*-anisidine (123 mg, 1.00 mmol) at 0°C. Flash chromatography (diethyl ether/petroleum ether 1:3) afforded **16** as a brown solid (139 mg, 87%). $R_f = 0.4$ (diethyl ether/petroleum ether 1:1); m.p. 91–95°C; $[\alpha]_D^{23} = +25.1°$ ($c = 0.61$ in CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 3.66$ (s, 3H; OCH_3), 4.40 (d, $J = 6.5$ Hz, 1H; CH), 4.81 (d, $J = 6.5$ Hz, 1H; CH), 6.51 (d, $J = 9.0$ Hz, 2H; ArH), 6.66 ppm (d, $J = 9.0$ Hz, 1H; ArH), 7.17–7.25 (m, 10H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.8$, 66.3, 78.2, 114.8, 115.9, 126.8, 127.5, 127.9, 128.2, 128.5, 140.3, 140.7, 141.4 ppm; IR (KBr): $\tilde{\nu} = 3479$, 3428, 3027, 2933, 2831, 1807, 1510, 1452, 1240, 1030, 820, 762, 698 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε) = 200 (4.139), 208 (4.250), 246 (4.072), 314 nm (3.403); MS (70 eV, EI): *m*/*z* (%): 319 (1) $[M]^+$, 301 (1), 212 (100), 168 (8), 134 (10), 91 (5), 77 (9); MS (ESI): *m*/*z*: 661.3 $[2M+Na]^+$, 342.1 $[M+Na]^+$, 320.2 $[M+H]^+$; the enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 90:10, flow: 0.8 mL min^{-1}) $\lambda = 243$ nm, (1*S*,2*S*): 31.9 min; (1*R*,2*R*): 38.7 min; 90% *ee*.

(1*R*,2*R*)-2-(Benzyloxyamino)-1,2-diphenylethanol (17): Following general procedure IV, *cis*-stilbene oxide (**1a**) (98 mg, 0.50 mmol) was treated with *O*-benzyl hydroxylamine (123 μL, 1.00 mmol) at RT. Flash chromatography (diethyl ether/petroleum ether 1:4) afforded **17** as a colorless solid (120 mg, 75%). R_f=0.25 (diethyl ether/petroleum ether 1:2); m.p. 44–47°C; $[\alpha]_D^{23}$=+42.6° (c=0.98 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.22 (br s, 1H; NH), 4.17 (d, J=9.0 Hz, 1H; CH), 4.62 (d, J=11.5 Hz, 1H; CH_2), 4.67 (d, J=11.5 Hz, 1H; CH_2), 4.83 (d, J=9.0 Hz, 1H; CH), 6.34 (br s, 1H; OH), 7.07–7.37 ppm (m, 15H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=71.9, 76.4, 76.7, 127.0, 127.7, 127.8, 128.1, 128.1, 128.2, 128.5, 128.6, 128.7, 137.4, 138.5, 140.9 ppm; IR (KBr): $\tilde{\nu}$=3421, 2358, 2330, 1630, 1450, 1028, 754, 698, 575 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε)=206 (4.096), 212 (4.133), 258 nm (3.137); MS (70 eV, EI): m/z (%): 320 (1) $[M+1]^+$, 302 (1), 274 (0,5), 212 (95), 107 (11), 91 (100), 77 (28); MS (ESI): m/z: 661.3 $[2M+Na]^+$, 342.1 $[M+Na]^+$, 320.2 $[M+H]^+$; HRMS (ESI): calcd for $C_{21}H_{22}NO$: 342.14645; found: 342.14598 $[M+H]^+$; the enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 90:10, flow: 0.8 mL min^{-1}) λ=203 nm, (1*R*,2*R*): 20.6 min; (1*S*,2*S*): 25.7 min; 86% *ee*.

(1*R*,2*R*)-2-(*N*-Methyl-*N*-phenylamino)-cyclohexanol[34] (18): Following general procedure IV, cyclohexene oxide (**1b**) (51 μL, 0.50 mmol) was treated with *N*-methyl aniline (0.11 mL, 1.00 mmol) at RT. Flash chromatography (diethyl ether/petroleum ether 1:4) afforded **18** as a colorless oil (95 mg, 93%). R_f=0.22 (diethyl ether/petroleum ether 1:2); $[\alpha]_D^{23}$=+24.8° (c=1.16 in CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.21–1.44 (m, 4H; CH_2), 1.68–1.77 (m, 3H; CH_2), 2.17 (m, 1H; CH_2), 2.76 (s, 3H; CH_3), 2.80 (br s, 1H; OH), 3.35–3.47 (m, 1H; CH), 3.65 (td, J=10.0, 4.5 Hz 1H; CH), 6.83 (dd, J=8.0, 8.0 Hz 1H; PhH), 6.94 (d, J=8.0 Hz, 2H; PhH), 7.25 ppm (dd, J=8.0, 8.0 Hz, 2H; PhH); ^{13}C NMR (50 MHz, $CDCl_3$): δ=24.45, 25.60, 26.15, 31.22, 33.47, 67.14, 70.13, 115.7, 118.7, 129.2, 151.5 ppm; IR (film): $\tilde{\nu}$=3433, 2929, 2858, 1597, 1500, 1450, 1296, 1072, 748 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε)=198 (3.998), 204 (4.018), 207 (4.023), 256 (4.116), 301 (3.238), 346 nm (0.499); MS (70 eV, EI): m/z (%): 205 (32) $[M]^+$, 146 (100), 132 (19), 120 (30), 106 (9), 91 (10), 77 (16), 51 (5); the enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 95:5, flow: 1.0 mL min^{-1}) λ=251 nm, (1*S*,2*S*): 11.2 min; (1*R*,2*R*): 12.4 min; 30% *ee*.

(1*R*,2*R*)-2-(4-Chlorophenylamino)cyclohexanol[10] (19): Following general procedure IV, cyclohexene oxide (**1b**) (51 μL, 0.50 mmol) was treated with *p*-chloro aniline (128 mg, 1.00 mmol) at −20°C. Flash chromatography (dichloromethane/ethyl acetate 25:1) afforded **19** as a pale-brown solid (103 mg, 91%). R_f=0.25 (dichloromethane/ethyl acetate 25:1); m.p. 93–94°C; $[\alpha]_D^{30}$=−28.5° (c=1.32 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.02–1.10 (m, 1H; CH_2), 1.23–1.40 (m, 3H; CH_2), 1.71–1.80 (m, 2H; CH_2), 2.07–2.13 (m, 2H; CH_2), 3.04–3.12 (m, 1H; CH), 3.35 (td, J=9.5, 4.0 Hz, 1H; CH), 6.64 (d, J=9.0 Hz, 2H; ArH), 7.12 ppm (d, J=9.0 Hz, 2H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=24.18, 24.87, 31.44, 33.19, 60.25, 74.43, 115.3, 122.7, 129.1, 146.4 ppm; IR (KBr): $\tilde{\nu}$=3389, 2922, 2856, 1597, 1507, 1490, 1323, 1058, 1038, 808 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε)=206 (3.954), 257 (4.061), 308 nm (3.169); MS (ESI): m/z: 248.0 $[M+Na]^+$ 226.0 $[M+H]^+$; the enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 90:10, flow: 1.0 mL min^{-1}) λ=243 nm, (1*S*,2*S*): 10.9 min; (1*R*,2*R*): 18.2 min; 43% *ee*.

(1*R*,2*R*)-2-(4-Methylphenylamino)cyclohexanol[36] (20): Following general procedure IV, cyclohexene oxide (**1b**) (51 μL, 0.50 mmol) was treated with *p*-toluidine (107 mg, 1.00 mmol) at −10°C. Flash chromatography (dichloromethane/ethyl acetate 25:1) afforded **20** as a pale-brown solid (91 mg, 89%). R_f=0.20 (dichloromethane/ethyl acetate 50:1); m.p. 50–53°C; $[\alpha]_D^{25}$=−42.8° (c=1.04 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.98–1.09 (m, 1H; CH_2), 1.27–1.42 (m, 3H; CH_2), 1.70–1.79 (m, 2H; CH_2), 2.09–2.14 (m, 2H; CH_2), 2.25 (s, 3H; CH_3), 3.04 (s, 2H; NH and OH), 3.05–3.13 (m, 1H; CH), 3.33 (td, J=9.5, 4.0 Hz, 1H; CH), 6.65 (d, J=9.0 Hz, 2H; ArH), 7.00 ppm (d, J=9.0 Hz, 2H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.35, 24.24, 25.04, 31.51, 33.04, 60.63, 74.43, 114.7, 127.7, 129.8, 145.3 ppm; IR (KBr): $\tilde{\nu}$=3518, 3357, 2919, 2854, 1618, 1523, 1066, 805 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε)=206 (4.093), 249 (4.118), 302 nm (3.324); MS (70 eV, EI): m/z (%): 205 (43) $[M]^+$, 183 (16), 158 (8), 146 (92), 120 (31), 106 (100), 91 (36), 77 (23), 67 (40); the enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 85:15, flow: 0.8 mL min^{-1}) λ=247 nm, (1*S*,2*S*): 9.2 min; (1*R*,2*R*): 15.1 min; 52% *ee*.

(1*R*,2*R*)-2-(4-Methoxyphenylamino)cyclohexanol[10] (21): Following general procedure IV, cyclohexene oxide (**1b**) (51 μL, 0.50 mmol) was treated with *p*-anisidine (123 mg, 1.00 mmol) at −20°C. Flash chromatography (diethyl ether/petroleum ether 1:2) afforded **21** as a pale-brown solid (92 mg, 83%). R_f=0.24 (diethyl ether/petroleum ether 1:1); m.p. 66–69°C; $[\alpha]_D^{23}$=−36.6° (c=0.72 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.94–1.07 (m, 1H; CH_2), 1.25–1.45 (m, 3H; CH_2), 1.67–1.79 (m, 2H; CH_2), 2.06–2.16 (m, 2H; CH_2), 2.92–3.04 (m, 3H; CH, OH and NH), 3.32 (td, J=10.0, 5.0 Hz, 1H; CH), 3.75 (s, 3H; CH_3), 6.66–6.72 (m, 2H; ArH), 6.76–6.81 ppm (m, 2H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=24.57, 25.38, 31.81, 33.37, 56.02, 61.97, 74.68, 115.1, 116.6, 141.9, 153.2 ppm; IR (KBr): $\tilde{\nu}$=3388, 2929, 2859, 1514, 1448, 1331, 1302, 1246, 1180, 1035, 812 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε)=202 (3.933), 205 (3.922), 246 (3.956), 314 nm (3.241); MS (70 eV, EI): m/z (%): 221 (86) $[M]^+$, 162 (100), 136 (43), 149 (21), 108 (18), 91 (43), 77 (7), 41 (12); the enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 85:15, flow 1.0 mL min^{-1}) λ=243 nm, (1*S*,2*S*): 10.2 min; (1*R*,2*R*): 13.9 min; 48% *ee*.

(1*R*,2*R*)-2-(Benzyloxyamino)cyclohexanol[37] (22): Following general procedure IV, cyclohexene oxide (**1b**) (51 μL, 0.50 mmol) was treated with *O*-benzyl hydroxylamine (123 mg, 1.00 mmol) at −20°C. Flash chromatography (diethyl ether/petroleum ether 1:1) afforded **22** as a colorless oil (94 mg, 85%). R_f=0.15 (diethyl ether/petroleum ether 1:1); $[\alpha]_D^{23}$=−6.6° (c=1.05 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.20–1.28 (m, 4H; CH_2), 1.70 (m, 2H; CH_2), 1.91–2.02 (m, 2H; CH_2), 2.63–2.71 (m, 1H, CH), 3.11 (br s, 1H; NH), 3.40–3.48 (m, 1H; CH), 4.71 (s, 2H; CH_2), 5.80 (br s, 1H; OH), 7.30–7.36 ppm (m, 5H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=24.30, 24.77, 28.96, 33.80, 65.64, 72.38, 77.80, 128.0, 128.3, 128.4, 128.5, 128.5, 137.6 ppm; IR (film): λ=3419, 3030, 2931, 2858, 1361, 1045, 991, 734, 696 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε)=205 nm (3.636); MS (70 eV, EI): m/z (%): 221 (36) $[M]^+$, 186 (7), 129 (11), 91 (100), 77 (32), 41(32); the enantiomeric assay: Chiralcel OD, isocratic (*n*-hexane/*i*PrOH 90:10, flow 0.8 mL min^{-1}) λ=209 nm, (1*R*,2*R*): 11.1 min; (1*S*,2*S*): 13.0 min; 26% *ee*.

(1*R*,2*R*)-2-(Benzylamino)cyclohexanol[36] (23): Following general procedure IV, cyclohexene oxide (**1b**) (58 μL, 0.50 mmol) was treated with benzylamine (110 μL, 1.00 mmol) at RT for 2 d. Flash chromatography (ethyl acetate/dichloromethane 1:1 5% NEt_3) afforded **23** as a pale-yellow solid (94 mg, 92%). R_f=0.35 (ethyl acetate/dichloromethane 1:1 10% NEt_3); m.p. 52–54°C; $[\alpha]_D^{27}$=−14.5° (c=1.15 in CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.88–1.07 (m, 1H; CH_2), 1.17–1.32 (m, 3H; CH_2), 1.68–1.76 (m, 2H; CH_2), 1.99–2.35 (m, 3H; CH_2 and CH), 3.20 (td, J=9.5, 5.0 Hz, 1H; CH), 3.69 (d, J=13.0 Hz; CH_2), 3.96 (d, J=13.0 Hz; CH_2), 7.23–7.38 ppm (m, 5H; ArH); ^{13}C NMR (75 MHz,$CDCl_3$): δ=24.29, 25.05, 30.44, 33.30, 50.72, 63.03, 73.70, 126.9, 128.0, 128.3, 140.5 ppm; IR (KBr): ν=3295, 3060, 3023, 2928, 2853, 1450, 1430, 1100, 1060, 1029, 748, 700 cm^{-1}; UV/Vis (CH_3CN): λ_{max} (lg ε)=208 (3.911), 270 nm (3.905); MS (ESI): m/z: 206.0 $[M+H]^+$; the enantiomeric assay: Mosher ester, 10% *ee*.

Acknowledgements

Support of this work through the Deutsche Forschungsgemeinschaft (Schn 441/3–2) is most gratefully acknowledged. We thank Wacker AG for the generous donation of TBSCl and Prof. Michael Reggelin (TU Darmstadt) for providing the bissulfoximine ligand **8**.

[1] Reviews: a) D. M. Hodgson, A. R. Gibbs, G. P. Lee, *Tetrahedron* **1996**, *52*, 14361; b) E. N. Jacobsen, M. H. Wu, *Comprehensive Asymmetric Catalysis, Vol. 3* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), **1999**, p. 1309; c) C. Schneider, *Synthesis* **2006**, 3919.

[2] For example: a) H. Yamashita, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1213; b) W. M. Nugent, *J. Am. Chem. Soc.* **1992**, *114*, 2768; c) L. E. Martinez, J. L. Leighton, D. H. Carsten, E. N. Jacobsen, *J. Am. Chem.*

Soc. **1995**, *117*, 5897; d) Review: E. N. Jacobsen, *Acc. Chem. Res.* **2000**, *33*, 421.
[3] a) S. E. Denmark, P. A. Barsanti, K. T. Wong, R. A. Stavenger, *J. Org. Chem.* **1998**, *63*, 2428; b) W. A. Nugent, *J. Am. Chem. Soc.* **1998**, *120*, 7139; c) B. Tao, M. M. C. Lo, G. C. Fu, *J. Am. Chem. Soc.* **2001**, *123*, 353; d) M. Nakajima, M. Saito, M. Uemura, S. Hashimoto, *Tetrahedron Lett.* **2002**, *43*, 8827.
[4] a) B. M. Cole, K. D. Shimizu, C. A. Krueger, J. P. A. Harrity, M. L. Snapper, A. H. Hoveyda, *Angew. Chem.* **1996**, *108*, 1776; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1668; b) K. D. Shimizu, B. M. Cole, C. A. Krueger, K. W. Kuntz, M. L. Snapper, A. H. Hoveyda, *Angew. Chem.* **1997**, *109*, 1782; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1703; c) S. E. Schaus, E. N. Jacobsen, *Org. Lett.* **2000**, *2*, 1001.
[5] a) E. N. Jacobsen, F. Kakiuchi, R. G. Konsler, J. F. Larrow, M. Tokunaga, *Tetrahedron Lett.* **1997**, *38*, 773; b) S. Matsunaga, J. Das, J. Roels, E. M. Vogl, N. Yamamoto, T. Iida, K. Yamaguchi, M. Shibasaki, *J. Am. Chem. Soc.* **2000**, *122*, 2252.
[6] a) T. Iida, N. Yamamoto, H. Sasai, M. Shibasaki, *J. Am. Chem. Soc.* **1997**, *119*, 4783; b) M. H. Wu, E. N. Jacobsen, *J. Org. Chem.* **1998**, *63*, 5252; c) J. Wu, X.-L. Hou, L.-X. Dai, L.-J. Xia, M.-H. Tang, *Tetrahedron: Asymmetry* **1998**, *9*, 3431.
[7] A. Gansäuer, T. Lauterbach, H. Bluhm, M. Noltemeyer, *Angew. Chem.* **1999**, *111*, 3112; *Angew. Chem. Int. Ed.* **1999**, *38*, 2909.
[8] M. Chini, P. Crotti, L. Favero, F. Macchia, M. Pineschi, *Tetrahedron Lett.* **1994**, *35*, 433.
[9] Reviews about rare earth metal triflates: S. Kobayashi, *Eur. J. Org. Chem.* **1999**, 15; S. Kobayashi, M. Sugiura, H. Kitagawa, W. W.-L. Lam, *Chem. Rev.* **2002**, *102*, 2227.
[10] X. L. Hou, J. Wu, L. X. Dai, L. J. Xia, M. H. Tang, *Tetrahedron: Asymmetry* **1998**, *9*, 1747.
[11] S. Sagawa, H. Abe, Y. Hase, T. Inaba, *J. Org. Chem.* **1999**, *64*, 4962.
[12] A. Sekine, T. Ohshima, M. Shibasaki, *Tetrahedron* **2002**, *58*, 75.
[13] G. Bartoli, M. Basco, A. Carlone, M. Locatelli, M. Massaccesi, P. Melchiorre, L. Sambri, *Org. Lett.* **2004**, *6*, 2173.
[14] F. Carree, R. Gil, J. Collin *Org. Lett.* **2005**, *7*, 1023; F. Carree, R. R. Gil, J. Collin, *Tetrahedron Lett.* **2004**, *45*, 7749.
[15] R. I. Kureshy, S. Singh, N. H. Khan, S. H. R. Abdi, E. Suresh, R. V. Jasra, *Eur. J. Org. Chem.* **2006**, 1303; R. I. Kureshy, S. Singh, N. Khan, S. H. R. Abdi, S. Agrawal, V. J. Mayani, R. V. Jasra, *Tetrahedron Lett.* **2006**, *47*, 5277.
[16] C. Schneider, A. R. Sreekanth, E. Mai, *Angew. Chem.* **2004**, *116*, 5809; *Angew. Chem. Int. Ed.* **2004**, *43*, 5691.
[17] C. Bolm, M. Zehnder, D. Bur, *Angew. Chem.* **1990**, *102*, 206; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 191; C. Bolm, M. Ewald, M. Zehnder, M. A. Neuburger, *Chem. Ber.* **1992**, *125*, 453.
[18] a) S. Azoulay, K. Manabe, S. Kobayashi, *Org. Lett.* **2005**, *7*, 4593; b) S. Ishikawa, T. Hamada, K. Manabe, S. Kobayashi, *Synthesis* **2005**, 2176; c) S. Ishikawa, T. Hamada, K. Manabe, S. Kobayashi, *J. Am. Chem. Soc.* **2004**, *126*, 12236; Kobayashi et al. have independently developed this chiral catalyst for Mukaiyama aldol reactions in aqueous solution.
[19] M. Reggelin, H. Weinberger, V. Spohr, *Adv. Synth. Catal.* **2004**, *346*, 1295.
[20] See for example: a) H. C. Aspinall, *Chem. Rev.* **2002**, *102*, 1807; b) D. A. Evans, Z. K. Sweeney, T. Rovis, J. S. Tedrow, *J. Am. Chem. Soc.* **2001**, *123*, 12095; c) G. Liang, D. Trauner, *J. Am. Chem. Soc.* **2004**, *126*, 9544; d) H. Suga, K. Inoue, S. Inoue, A. Kakehi, *J. Am. Chem. Soc.* **2002**, *124*, 14836; e) D. A. Evans, K. A. Scheidt, K. R. Fandrick, H. W. Lam, J. Wu, *J. Am. Chem. Soc.* **2003**, *125*, 10780; f) D. A. Evans, C. E. Masse, J. Wu, *Org. Lett.* **2002**, *4*, 3375.
[21] S. E. Denmark, Y. Fan, *J. Am. Chem. Soc.* **2002**, *124*, 4233.
[22] Excellent review about nonlinear effects: H. Kagan, C. Girard, *Angew. Chem.* **1998**, *110*, 3088; *Angew. Chem. Int. Ed.* **1998**, *37*, 2922.
[23] H. Shechter, B. K. Ravi Shankar, *Tetrahedron Lett.* **1982**, *23*, 2277.
[24] M. Werner, D. S. Stephenson, G. Szeimies, *Liebigs Ann.* **1996**, 1705.
[25] J. B. Lambert, H. W. Mark, E. S. Magyar, *J. Am. Chem. Soc.* **1977**, *99*, 3059.
[26] P. Crotti, M. Ferretti, F. Macchia, A. Stoppioni, *J. Org. Chem.* **1984**, *49*, 4706.
[27] J. Huang, V. Goedken, H. M. Walborsky, *J. Org. Chem.* **1988**, *53*, 4128.
[28] C. Carter, S. Fletcher, A. Nelson, *Tetrahedron: Asymmetry* **2003**, *14*, 1995.
[29] F. Fringuelli, R. Germani, F. Pizzo, G. Savelli, *Tetrahedron Lett.* **1989**, *30*, 1427.
[30] T. Iwahama, S. Sakaguchi, Y. Ishii, *Heterocycles* **2000**, *52*, 693.
[31] H. E. Zimmerman, C. E. Caufield, R. K. King, *J. Am. Chem. Soc.* **1985**, *107*, 7732.
[32] L. Zhao, B. Han, Z. Huang, M. Miller, H. Huang, D. Malashock, Z. Zhu, A. Milan, D. E. Robertson, D. P. Weiner, M. J. Burk, *J. Am. Chem. Soc.* **2004**, *126*, 11156.
[33] B. Fathi, E. Giovannini, *Helv. Chim. Acta* **2002**, *85*, 2083.
[34] G. Sekar, V. K. Singh, *J. Org. Chem.* **1999**, *64*, 287–289.
[35] B. Alcaide, C. López-Mardomingo, R. Pérez-Ossorio, J. Plumet, *J. Chem. Soc. Perkin Trans. 2* **1983**, 1649.
[36] A. K. Chakraborti, S. Rudrawar, A. Kondaskar, *Eur. J. Org. Chem.* **2004**, 3597.
[37] M. Beaton, D. Gani, *Tetrahedron Lett.* **1998**, *39*, 8549.
[38] A. Marx, C. Schneider, unpublished results.

Received: September 11, 2006
Published online: December 13, 2006

