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Enantioselective synthesis of heterocyclic β-aminoalcohols catalysed by a samarium iodo binaphtholate

Myriam Martin, Sophie Bezzenine-Lafollée,* Richard Gil and Jacqueline Collin*

Laboratoire de Catalyse Moléculaire, UMR 8182, ICMMO, Université Paris-Sud, 91405 Orsay, France

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Abstract—Enantioselective aminolysis of *meso*-epoxides including a heterocycle catalysed by a samarium iodo binaphtholate has been studied. New β-amino alcohols have been isolated with enantiomeric excesses up to 70%.

1. Introduction

The synthesis of enantioenriched aminoalcohols is a highly important topic for chemists since these molecules are widely employed as chiral auxiliaries, ligands or building blocks in the design of sophisticated molecules.[1,2] Numerous synthetic routes have been reported for their preparation,[3] yet new methods following green chemistry criteria such as atom economy and/or catalytic reactions are still being developed.[4] Epoxides, which are easily available, can be readily transformed by reactions with various nucleophiles into 1,2-substituted derivatives and especially into β-aminoalcohols. For the enantioselective catalysed ring-opening of epoxides, either the desymmetrisation of *meso*-epoxides or the kinetic resolution of unsymmetrical epoxides can be envisaged.[5] The first route leading to enantioenriched β-aminoalcohols from *meso*-epoxides using chiral catalysts involved trimethylsilyl azide as the nucleophile and afforded β-azidotrimethylsilyl ethers, which were further reduced. Initial examples based on titanium and ligands such as tartrates and Schiff bases, catalysed the formation of β-azidotrimethylsilyl ethers with low enantiomeric excesses.[6] An efficient catalyst was prepared in situ from $Zr(O\textit{t}\text{-}Bu)_4$ and (*S*,*S*,*S*)-triisopropanolamine by Nugent et al. furnished azido silyl ethers with up to 93% ee, while a similar zirconium-based catalyst with a bispicolinic amide ligand was less enantioselective.[7] The chiral chromium(III) salen complexes developed by Jacobsen et al. catalysed the azidolysis of *meso*-epoxides with enantiomeric excesses up of to 98%.[8] This very efficient procedure avoided the use of solvent and allowed the reuse of the catalyst.

However, the enantioselective ring-opening of epoxides by amines which is more attractive for the preparation of β-aminoalcohols in terms of atom economy and efficiency has attracted increased interest only recently. Most of the chiral catalysts reported up to date are based on lanthanides. The first enantioselective aminolyses of *meso*-epoxides were described by Wu using in situ prepared catalysts from (*R*)-binaphthol and lanthanide chlorides and by Hou with ytterbium triflate in the presence of (*R*)-binaphthol and diphenyl benzyl amine.[9] The latter system initially developed by Kobayashi et al. for the catalysis of Diels–Alder reactions,[10] allowed the preparation of β-aminoalcohols from *meso*-epoxides and aromatic amines with enantiomeric excesses of up to 80%. Shibasaki and co-workers studied an in situ prepared catalyst based on $Pr(O\text{-}\textit{i}Pr)_3$, (*R*)-BINOL and $Ph_3P{=}O$, which performed the ring-opening of cyclic epoxides by *p*-anisidine with up to 65% ee, and was applied to the formal synthesis of 4-demethoxydaunomycin.[11] Schneider et al. examined various rare earth triflates and different chiral ligands and found that the system generated in situ from $Sc(OTf)_3$ and a chiral bipyridine ligand, catalysed the desymmetrisation of aliphatic and aromatic *meso*-epoxides by aromatic amines.[12] This catalyst provided high asymmetric inductions (up to 97% ee) for aromatic *meso*-epoxides. Kobayashi et al. developed one of the rare enantioselective Lewis acid catalysed reactions in water with $Sc(DS)_3$ coordinated by the same chiral bipyridine ligand as the previous group. This system was also highly enantioselective for the

* Corresponding authors. Fax: +33 (0) 1 69154680 (J.C.); e-mail: jacollin@icmo.u-psud.fr

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aminolysis of aromatic substituted *meso*-epoxides (up to 96%).[13]

Enantioselective catalysts for the aminolysis of *meso*-epoxides based on transition metals were also considered. Through the use of titanium coordinated with binaphthol up to 93% ee were obtained for the ring-opening of epoxides by aliphatic amines, although this catalyst was only efficient for seven-membered ring cyclic epoxides including ketal groups.[14] Kureshy et al. have extended the use of this catalyst to reactions involving stilbene oxide and cyclohexene oxide with various aromatic amines.[15] The β-aminoalcohols could be isolated with enantiomeric excesses of up to 78% and the catalyst could be reused. The reactions were greatly accelerated under microwave irradiation with marginal effect on enantioselectivity. The most active and enantioselective catalysts for the aminolysis of *meso*-epoxides have been recently described by two groups. Schneider et al. who reported the use of $In(OTf)_3$ coordinated by a chiral bipyridine ligand, synthesised aminoalcohols from aromatic epoxides and aromatic amines with enantiomeric excesses up to 98%.[12c] The niobium catalyst prepared from $Nb(OMe)_5$ and a tetradentate binol ligand reported by Kobayashi et al. afforded high enantiomeric excesses for the reactions of *meso*-epoxides with aromatic amines (up to 96%) and the catalytic ratio was decreased to 0.25% without lowering the enantioselectivity.[16]

The kinetic resolution of unsymmetrical epoxides was first investigated by Jacobsen et al. who studied the resolution of terminal epoxides with trimethylsilyl azide catalysed by a Cr(III)(salen) azide complex and prepared 1-azido-2-silyl ethers with 88–98% ee.[17] Bartoli et al. reported the kinetic resolution of aromatic epoxides with aromatic amines with a similar Cr(III)(salen) chloride catalyst, which led regioselectively to 1,2-*anti*-aminoalcohols in 82–90% ee.[18] Carbamates were employed as nucleophiles for the kinetic resolution of terminal epoxides catalysed by a Co(III)(salen) complex and provided *N*-Boc or *N*-Cbz protected β-aminoalcohols with 99% ee.[18b] The niobium complex prepared from $Nb(OMe)_5$ and tetradentate binol ligand catalysed the ring-opening of unsymmetrical disubstituted epoxides at the less hindered position with 85–99% ee for the major product.[16b]

Our previous studies investigated the activity of samarium diiodide as an efficient Lewis acid catalyst for a wide range of carbon–carbon bond forming reactions, such as Mukaiyama aldol reactions, Diels–Alder reactions, or tandem Mukaiyama Michael-aldol reactions,[19] and carbon–nitrogen forming reactions, such as aza-Michael reactions.[20] We also found that samarium diiodide catalyses the ring-opening of epoxides with various nucleophiles such as trimethylsilyl azide, trimethylsilyl cyanide and amines leading to the corresponding opening products in mild conditions.[21] Next, we developed the enantioselective version of some of these reactions with lanthanide iodo binaphtholates as catalysts and isolated the products of iminoaldol and aza-Michael reactions in high enantiomeric excesses.[22] In a previous report, we described the desymmetrisation of cyclic *meso*-epoxides by aromatic amines catalysed by samarium iodo binaphtholate.[23] These reactions allowed us to prepare the corresponding β-amino alcohols with enantiomeric excesses of up to 93%, which are the highest values reported for these transformations. Herein we report the enantioselective ring-opening of cyclic *meso*-epoxides by amines catalysed by a samarium iodo binaphtholate to substrates containing an heteroatom in the cycle for the synthesis of more functionalised enantiomerically enriched β-amino alcohols. No results concerning the desymmetrisation of such epoxides by amines had been described when this study was initiated, the first examples being reported during the preparation of this manuscript.[16b]

2. Results and discussion

Over the course of our previous work concerning the enantioselective catalysed aminolysis of cyclic *meso*-epoxides by aromatic amines, we had compared the activity and selectivity of lanthanum and samarium iodo binaphtholates and found higher asymmetric inductions with a samarium complex.[23] The preparation of the catalyst was realised by the reaction of potassium bis binaphtholate with samarium triiodide in THF and improved by the use of potassium diphenyl methide as a potassium source. The enantioselectivities provided by lanthanide iodo binaphtholates are dramatically influenced by temperature, since enantioselectivity increased with temperature for iminoaldol reactions,[22b] and isoinversion effects were observed for aza-Michael reactions,[22c] as well as for the aminolysis of cyclic *meso*-epoxides.[23] To initiate our study we selected 2,5-dihydrofuran oxide and the electron enriched aromatic amines, *o*- and *p*-anisidine, since these amines afforded β-aminoalcohols with high enantiomeric excesses in the case of the ring-opening of cyclohexene, cyclopentene oxide and cyclohexadiene monoxide. The influences of several parameters on the enantioselectivity of these two reactions, such as the temperature of the reaction and the solvent, were examined and the results are shown in Table 1.

We first examined the reaction of 2,5-dihydrofuran oxide **2a** with *o*-anisidine **3a** under the conditions we have formerly described.[23] The amine was added to 10 mol % samarium iodo binaphtholate **1** in methylene chloride in the presence of molecular sieves, followed by the addition of epoxide **2a** at room temperature (Scheme 1). The β-aminoalcohol **4aa** was obtained with total conversion and 30% ee after three days (Table 1, entry 1). An increase in the reaction temperature (entry 2) resulted in a higher value for the ee (48% at 40 °C) while an increase in the ratio **3a**/**2a** was detrimental to the enantioselectivity (entry 3). In order to perform the reactions at higher temperature we investigated the use of dichloroethane as a solvent and found at 40 °C an enantiomeric excess close to that obtained in dichloromethane (entry 4). The reactions were further performed at higher temperature but it led to a decrease in the enantiomeric excesses (entries 5 and 6). The aminolysis of **2a** with *p*-anisidine **3b** was first performed in dichloromethane at 25 °C, which provided the β-aminoalcohol **4ab** with a good enantiomeric excess (70%) (entry 8). An increase in the temperature and in

Table 1. Enantioselective aminolysis of epoxide **2a** catalysed by samarium complex **1**

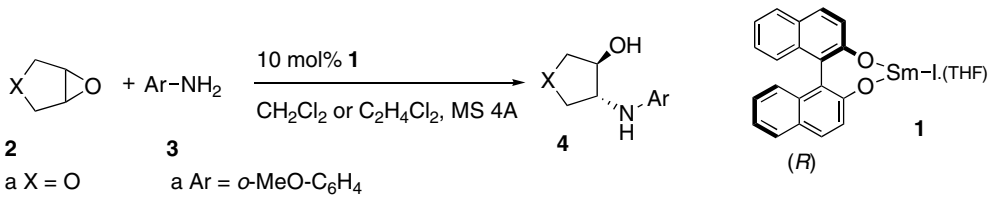
Entry	RNH_2	Solvent	Product	T (°C)	t (h)	Yield[a] (%)	ee (%)
1	**3a** *o*-MeO–C_6H_4–NH_2	CH_2Cl_2	**4aa**	25	80	77	30
2	**3a** *o*-MeO–C_6H_4–NH_2	CH_2Cl_2	**4aa**	40	48	55	48
3	**3a** *o*-MeO–C_6H_4–NH_2[b]	CH_2Cl_2	**4aa**	40	80	47	31
4	**3a** *o*-MeO–C_6H_4–NH_2	$C_2H_4Cl_2$	**4aa**	40	48	54	41
5	**3a** *o*-MeO–C_6H_4–NH_2	$C_2H_4Cl_2$	**4aa**	60	40	55	34
6	**3a** *o*-MeO–C_6H_4–NH_2	$C_2H_4Cl_2$	**4aa**	80	40	63	30
7	**3a** *o*-MeO–C_6H_4–NH_2[c]	$C_2H_4Cl_2$	**4aa**	40	48	35	52
8	**3b** *p*-MeO–C_6H_4–NH_2	CH_2Cl_2	**4ab**	25	24	32	70
9	**3b** *p*-MeO–C_6H_4–NH_2[b]	CH_2Cl_2	**4ab**	25	24	10[d]	63
10	**3b** *p*-MeO–C_6H_4–NH_2	CH_2Cl_2	**4ab**	40	48	64	64
11	**3b** *p*-MeO–C_6H_4–NH_2[b]	CH_2Cl_2	**4ab**	40	24	22[e]	69
12	**3b** *p*-MeO–C_6H_4–NH_2	CH_2Cl_2	**4ab**	0	72	15	48
13	**3b** *p*-MeO–C_6H_4–NH_2	$C_2H_4Cl_2$	**4ab**	40	48	70	68
14	**3b** *p*-MeO–C_6H_4–NH_2[c]	$C_2H_4Cl_2$	**4ab**	40	48	42	66

[a] Isolated yield, 100% conversion, reaction performed with 10% catalyst **1** and ratio **3/2**: 1.2.
[b] Ratio **3/2**: 2.
[c] 5% Catalyst **1**.
[d] 15% Conversion.
[e] 25% Conversion.

the ratio **3b/2a** for reactions realised in dichloromethane (entries 9–11) led to small variations in the enantiomeric excesses of **4ab**. A decrease in reaction temperature to 0 °C did not allow us to improve the asymmetric induction (entry 12). The reaction was next carried out in dichloroethane at 40 °C which proved to be the best conditions for the aminolysis by *o*-anisidine. Product **4ab** was obtained in good yield and with 68% ee (entry 13). For the ring-opening of 2,5-dihydrofuran oxide **2a,** the highest asymmetric inductions were obtained with dichloroethane as solvent and at 40 °C with a ratio **3/2**: 1.2. A lower amount of catalyst of 5% did not decrease the enantioselectivity since in dichloroethane at 40 °C, β-aminoalcohols **4aa** and **4ab** were isolated with 52% ee and 66% ee, respectively (entries 7 and 14).

The presence of heteroatoms in the epoxide results in a stronger coordination to the Lewis acid catalyst and reactivity of the nucleophiles is decreased. The aminolyses of 2,5-dihydrofuran oxide **2a** described above are thus performed at higher temperatures than the similar ring-opening of cyclopentene oxide.[23] We next examined the possibility of including other functions in the cycle of the epoxide such as carbamates or ketals. Desymmetrisations of various epoxides by *o*- and *p*-anisidine and by aniline have been studied and the results collected in Table 2. All reactions were performed in dichloroethane using 10 mol % of catalyst **1**. The ring-opening of 2,5-dihydrofuran oxide **2a** was realised with aniline **3c** under the same conditions as aromatic amines substituted by electrodonating groups (40 °C, 48 h) with total conversion and 42% ee (Table 2, entries 1–3). In reactions involving epoxide **2a**, the highest ee (70%) was obtained with *p*-anisidine **3b** while *o*-anisidine **3a** and aniline **3c** afforded identical values. Aminolysis with amine **3a** of epoxide **2b** with a *N*-Cbz group included in the five-membered ring was first conducted under the conditions optimised for the desymmetrisation of **2a**. The β-aminoalcohol **4ba** was obtained with 40% ee but conversion was not complete (entry 4). At a higher temperature, a total conversion was observed with unchanged enantioselectivity (entry 5). The reaction of epoxide **2b** with *p*-anisidine **3b** afforded lower enantiomeric excesses than with *o*-anisidine **3a** at different temperatures (entries 6–8), in contrast to that observed with epoxide **2a**, including an oxygen atom in the cycle. Similarly the ring-opening of **2b** with aniline was achieved with very low enantioselectivity (entry 9).

In order to improve the asymmetric induction of the desymmetrisation of epoxides containing nitrogen func-



Scheme 1.

Table 2. Enantioselective aminolysis of epoxides **2** by aromatic amines catalysed by samarium complex **1**

Entry	Epoxide	RNH_2	Product	T (°C)	t (h)	Conversion (yield)[a]	ee[c] (%)
1	**2a**	**3a** *o*-MeO–C_6H_4–NH_2	**4aa**	40	40	100 (54)	41
2	**2a**	**3b** *p*-MeO–C_6H_4–NH_2	**4ab**	40	48	100 (70)	68
3	**2a**	**3c** $PhNH_2$	**4ac**	40	48	100 (71)	42
4	**2b**	**3a** *o*-MeO–C_6H_4–NH_2	**4ba**	40	48	72 (65)	40
5	**2b**	**3a** *o*-MeO–C_6H_4–NH_2	**4ba**	80	48	100 (80)	43
6	**2b**	**3b** *p*-MeO–C_6H_4–NH_2	**4bb**	40	48	100 (52)	17
7	**2b**	**3b** *p*-MeO–C_6H_4–NH_2	**4bb**	60	20	59 (33)	12
8	**2b**	**3b** *p*-MeO–C_6H_4–NH_2	**4bb**	80	48	100 (80)	10
9	**2b**	**3c** $PhNH_2$	**4bc**	80	48	90 (88)	16
10	**2c**	**3a** *o*-MeO–C_6H_4–NH_2	**4ca**	80	20	100 (55)	54
11	**2c**	**3a** *o*-MeO–C_6H_4–NH_2	**4ca**	60	65	100 (95)	58
12	**2c**	**3b** *p*-MeO–C_6H_4–NH_2	**4cb**	80	20	100	37
13	**2c**	**3b** *p*-MeO–C_6H_4–NH_2	**4cb**	60	40	100 (74)	47
14	**2c**	**3c** $PhNH_2$	**4cc**	60	48	100 (93)	42
15	**2d**	**3a** *o*-MeO–C_6H_4–NH_2	**4da**	60	72	(43)[b]	29
16	**2d**	**3b** *p*-MeO–C_6H_4–NH_2	**4db**	60	72	(47)[b]	0
17	**2e**	**3a** *o*-MeO–C_6H_4–NH_2	**4ea**	25	72	100 (54)	15
18	**2e**	**3a** *o*-MeO–C_6H_4–NH_2	**4ea**	40	40	100 (70)	26
19	**2e**	**3a** *o*-MeO–C_6H_4–NH_2	**4ea**	60	18	100 (76)	21
20	**2e**	**3a** *o*-MeO–C_6H_4–NH_2	**4ea**	80	18	100 (82)	18
21	**2e**	**3b** *p*-MeO–C_6H_4–NH_2	**4eb**	40	40	100 (65)	13

[a] Conversion % (isolated yield %), reaction performed with 10% catalyst **1** and ratio **3**/**2**: 1.2.
[b] Conversion could not be measured by ^1H NMR of crude product.
[c] Configuration of the products, indicated in Section 4, have been determined by the comparison of the sign of the specific rotation with the literature or by analogy.[16b]

tionalities, we tested substrate **2c** with a different nitrogen protecting group, such as Boc. With *o*- and *p*-anisidine, the ring-opening reactions were performed at 60 °C and 80 °C and slightly higher excesses were found at 60 °C (entries 10–13). The best values of the enantiomeric excesses found for **4ca** and **4cb** were 58% and 47%, respectively. As observed with the *N*-Cbz substituted epoxide, the enantioselectivity is higher with *o*-anisidine than with *p*-anisidine. Using aniline, aminolysis of **2c** furnished product **4ca** with a total conversion and 42% ee at 60 °C (entry 14). Substrate **2c** with a more bulky N-protecting group than **2b** afforded higher enantiomeric excesses. Epoxide **2d** N-substituted with Fmoc as a bulkier protecting group was therefore examined for the ring-opening reactions with **3a** and **3b**. These reactions were achieved, with low conversions, after three days at 60 °C, and a small enantiomeric excess was observed for **4da**, while **4db** was isolated in racemic form (entries 15 and 16). Comparison of the aminolysis at 60 °C of epoxides containing *N*-Boc and *N*-Fmoc groups (entries 11 and 15, 13 and 16) indicated a diminution of the rates and the enantioselectivities of the reactions with the latter. Since epoxide **2d** is more difficult to prepare and to purify than **2b** and **2c** we did not conduct further investigations with this substrate. Better asymmetric inductions have been found for the aminolyses of *N*-Boc substituted epoxide **4c** compared to other carbamate derivatives and the highest enantiomeric excess (58%) was obtained for the ring-opening with *o*-anisidine. The only results reported so far for the enantioselective aminolysis of epoxides with heterocycles using a chiral niobium catalyst have provided higher levels of enantioselectivity than catalyst **1** for epoxides **2a**, **2b** and **2c** (78–81%). However, reactions were realised with aniline as the sole amine and no reaction using aromatic amine with easily deprotecting N-substituent was described.[16b]

We have also carried out the aminolysis of epoxide **2e** including a ketal function, which afforded the products with good yields but low enantioselectivities at all temperatures (entries 17–21). The best result was obtained using *o*-anisidine at 40 °C.

The epoxides examined herein are far less active than cyclic epoxides without a heteroatom in the ring since the latter reactions have been achieved overnight at −40 °C with total conversion. This is not surprising as the presence of the heteroatom probably enhances the coordination to samarium and lowers the reaction rate. More unexpected is the behaviour with temperature of the desymmetrisation of O and N-substituted cyclic epoxides by aromatic amines. For simple cyclic epoxides, a dramatic influence of temperature on the enantioselectivity has been observed with an isoinversion effect.[24] The temperature of inversion of −40 °C which has been determined carefully for one reaction, allowed us to obtain very high enantiomeric excesses for various reactions involving similar epoxides and aromatic amines.[23] In the present case, a small range of temperatures is available and in general, no significant effect of temperature on asymmetric induction has been noticed. For the reaction leading to β-aminoalcohol **4aa**, only the variation of the enantiomeric excess with temperature seems not monotonous with an isoinversion effect and ee maximal at 40 °C. Optimal temperatures were further determined for other reactions.

Herein we have succeeded in isolating several new enantiomerically enriched β-aminoalcohols. Since these molecules contain both heterocycles and easily removable N-protecting groups,[25] the reactions are a useful tool for the direct preparation of various chiral synthons.

3. Conclusion

We have found that a samarium iodo binaphtholate catalyses the desymmetrisation by aromatic amines of cyclic *meso*-epoxides containing O and N functionalities leading to new enantiomerically enriched heterocyclic β-amino-alcohols with up to 70% ee. *p*-Anisidine afforded the highest enantioselectivity for an epoxide, containing an oxygen as heteroatom while the reaction of *N*-Boc substituted epoxide with *o*-anisidine gave the highest ee for the ring-opening of epoxides including a nitrogen heterocycle. We are currently working to improve the activity and enantioselectivity of the catalysts for the preparation of β-amino-alcohols by aminolytic desymmetrisation of epoxides and studying the synthetic applications of these reactions.

4. Experimental

4.1. General

All manipulations were carried out under an argon atmosphere using standard Schlenk or glove box techniques. Dichloromethane and dichloroethane were distilled from CaH_2 and degassed immediately prior to use. The method for preparing samarium iodobinaphtholate had been previously described.[23] All catalysts have been prepared from enantiopure (*R*)-1,1-binaphthol. Epoxides **2a** and **2b** were synthesised according to the literature procedures.[26–28] The *tert*-butyl 6-oxa-3-aza-bicyclo[3.1.0]hexane-3-carboxylate **2c** was obtained by the reaction of commercially available 3-pyrroline with *t*-butyl dicarbonate followed by epoxidation. Epoxides and amines were distilled and degassed or recrystallised prior to use.

^1H and ^{13}C NMR spectra were recorded on Bruker AM 360, AM 300 and AM 250 spectrometers, operating at 360, 300 and 250 MHz for ^1H and at 90.6, 75 and 62.5 MHz for ^{13}C in $CDCl_3$. Chemical shifts for ^1H and ^{13}C spectra were referenced internally according to the residual solvent resonances and reported in ppm relative to $CDCl_3$ (7.27 ppm for ^1H and 77 ppm for ^{13}C). Infrared spectra were recorded on a Perkin Elmer 1000 FT-IR spectrometer as KBr disks or in $CHCl_3$ solution using CaF_2 cells and reported in cm^{-1}. High resolution mass spectra were measured on a Finnigan MAT 95 S spectrometer or at 70 eV (EI) with a Trace DSQ Thermo Electron spectrometer. Optical rotations were measured by using a Perkin Elmer 241 polarimeter at room temperature in a cell of 1 dm length at the sodium D line ($\lambda = 589$ nm) and were reported as follows: $[\alpha]_D^{20}$ (*c* in g per 100 mL, $CHCl_3$). HPLC analyses were performed on a Thermo Separation Product Pompe P100 with an UV detector and chiral stationary-phase columns (Whelk O1, Chiralcel OD-H or Chiralcel OJ, Chiralpak AD or Chiralpak IA). All the crude products were purified by preparative thin layer chromatography on silica gel 60 PF_{254} (heptane/ethyl acetate 50:50).

4.2. Typical procedure for the aminolysis of epoxides

In the glove box, samarium iodo binaphtholate **1** (32.5 mg, 0.05 mmol) and molecular sieves 4 Å (100 mg) were weighed in a Schlenk tube and dichloroethane (5 mL) was added. *ortho*-Anisidine **3b** (74 mg, 0.6 mmol) was added to the solution, which was stirred at room temperature for 15 min. Outside the glove box, the reaction was heated at 40 °C and a solution of 2,5-dihydrofuran oxide **2a** (43 mg, 0.5 mmol) in dichloroethane (1 mL) was then added by syringe. After stirring at 40 °C for 48 h, the reaction mixture was hydrolysed with 0.1 M HCl, diluted with CH_2Cl_2 and neutralised with 0.1 M NaOH. The aqueous layer was extracted with EtOAc. The crude product was purified by preparative thin layer chromatography on silica gel (heptane/EtOAc 50:50). The enantiomeric excess of **4aa** was determined by HPLC analysis as described below.

4.3. (1*R*,2*R*)-4-Oxa-2-(2-methoxyphenylamino)cyclopentanol 4aa

Oil. $[\alpha]_D^{20} = +7.9$ (*c* 1.0, $CHCl_3$) for 48% ee; IR (CaF_2, $CHCl_3$) (cm^{-1}): *v* 3618, 3021, 2977, 1515, 1215, 1047; ^1H NMR (360 MHz, $CDCl_3$): δ 3.74 (1H, dd, $J = 9.5$ Hz, $J = 2.5$ Hz), 3.77–3.80 (1H, m), 3.84 (3H, s, CH_3), 3.81–3.89 (1H, m, CH_2), 4.04 (1H, dd, $J = 10.1$ Hz, $J = 4.4$ Hz), 4.32 (2H, m), 6.72–6.81 (3H, m), 6.89–6.93 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.3, 61.5, 72.5, 74.3, 75.9, 109.5, 110.4, 117.3, 121.2, 136.4, 146.8; HRMS calcd for $C_{11}H_{15}O_3NNa$ (MNa^+): 232.0944, found: 232.0949; HPLC (Welk O1 column, flow rate: 0.8 mL min^{-1}, hexane/ethanol 95:5, column temperature: 15 °C, λ: 254 nm, $t_{R(minor)} = 24.9$ min, $t_{R(major)} = 26.4$ min).

4.4. (1*R*,2*R*)-4-Oxa-2-(4-methoxyphenylamino)cyclopentanol 4ab

Mp: 130–132 °C. $[\alpha]_D^{20} = +8.1$ (*c* 1.0, $CHCl_3$) for 66% ee; IR (CaF_2, $CHCl_3$) (cm^{-1}): *v* 3684, 3622, 3021, 2977, 2930, 1364, 1216, 1046; ^1H NMR (360 MHz, $CDCl_3$): δ 3.67 (1H, dd, $J = 9.6$ Hz, $J = 2.5$ Hz), 3.76 (3H, s), 3.73–3.79 (1H, m), 3.82–3.86 (1H, m), 4.04 (1H, dd, $J = 11.3$ Hz, $J = 4.3$ Hz), 4.24–4.29 (2H, m), 6.64 (2H, d, $J = 9.0$ Hz), 6.81 (2H, d, $J = 8.8$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.7, 62.6, 72.5, 74.5, 76.0, 114.6, 115.0, 140.5, 152.6; HRMS (EI) calcd for $C_{11}H_{15}O_3N$ (M): 209.1046, found: 209.1054; HPLC (Chiralpak AD column, flow rate: 0.5 mL min^{-1}, hexane/isopropanol 90:10, λ: 254 nm, $t_{R(major)} = 37.4$ min, $t_{R(minor)} = 42.6$ min).

4.5. (1*R*,2*R*)-4-Oxa-2-phenylaminocyclopentanol 4ac

Mp: 102–104 °C. $[\alpha]_D^{20} = +11.0$ (*c* 0.7, $CHCl_3$) for 44% ee, lit.[16b] $[\alpha]_D^{20} = +27.4$ (*c* 0.54, $CHCl_3$) for 75% ee; HPLC (Chiralcel OJ column, flow rate: 0.7 mL min^{-1}, hexane/isopropanol 75:25, λ: 254 nm, $t_{R(major)} = 13.1$ min, $t_{R(minor)} = 15.3$ min).

4.6. (3*R*,4*R*)-Benzyl 3-hydroxy-4-(2-methoxyphenylamino)pyrrolidine-1-carboxylate 4ba

Oil. $[\alpha]_D^{20} = +12.1$ (*c* 1.0, $CHCl_3$) for 43% ee; IR (CaF_2, $CHCl_3$) (cm^{-1}): *v* 3616, 3425, 3021, 2976, 1693, 1603, 1515, 1456, 1428, 1358, 1207; ^1H NMR (250 MHz, $CDCl_3$): δ 3.37–3.55 (2H, m), 3.71 (1H, dd, $J = 12.0$ Hz, $J = 4.4$ Hz), 3.83 (3H, s), 3.89–3.97 (2H, m), 4.26–4.30

(2H, m), 5.16 (2H, s), 6.70–6.94 (4H, m), 7.28–7.44 (5H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$, rotamers): δ 50.4, 50.7, 51.9, 52.3, 55.7, 58.6, 59.1, 67.0, 73.0, 73.8, 109.5, 110.1, 117.4, 121.1, 127.8, 128.4, 136.1, 136.4, 146.7, 155.2; HRMS calcd for $C_{19}H_{22}O_4N_2Na$ (MNa^+): 365.1472, found: 365.1469; HPLC (Chiralpak AD column, flow rate: 0.8 mL min^{-1}, hexane/isopropanol 85:15, λ: 254 nm, $t_{R(minor)} = 16.4$ min, $t_{R(major)} = 20.6$ min).

4.7. (3*R*,4*R*)-Benzyl 3-hydroxy-4-(4-methoxyphenylamino)pyrrolidine-1-carboxylate 4bb

Mp: 129–132 °C. $[\alpha]_D^{20} = +3.0$ (c 1.0, $CHCl_3$) for 10 ee%; IR (CaF_2, $CHCl_3$) (cm^{-1}): ν 3684, 3622, 3019, 2977, 1699, 1514, 1424, 1211, 1046; ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.34–3.54 (2H, m), 3.75 (3H, s), 3.68–3.85 (2H, m), 3.86–3.98 (1H, m), 4.24–4.33 (1H, m), 5.15 (2H, s), 6.61 (2H, d, $J = 8.6$ Hz), 6.80 (2H, d, $J = 8.6$ Hz), 7.29–7.42 (5H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$, rotamers): δ 50.3, 50.7, 51.9, 52.3, 55.7, 59.6, 60.2, 67.0, 73.1, 73.9, 114.7, 115.0, 127.9, 128.0, 128.5, 136.5, 140.2, 152.8, 155.2; HRMS calcd for $C_{19}H_{22}O_4N_2Na$ (MNa^+): 365.1472, found: 365.1473; HPLC (Chiralcel OD-H column, flow rate: 0.8 mL min^{-1}, hexane/ethanol 85:15, λ: 254 nm, $t_{R(major)} =$ 24.1 min, $t_{R(minor)} = 28.1$ min).

4.8. (3*R*,4*R*)-Benzyl 3-hydroxy-4-(phenylamino)pyrrolidine-1-carboxylate 4bc

Mp: 109–112 °C. $[\alpha]_D^{20} = +5.1$ (c 1.0, $CHCl_3$) for 16% ee, lit.[16b] $[\alpha]_D^{20} = +16.9$ (c 1.67, $CHCl_3$) for 87% ee; HPLC (Chiralcel OD-H column, flow rate: 0.8 mL min^{-1}, hexane/ethanol 75:25, λ: 254 nm, $t_{R(minor)} = 9.4$ min, $t_{R(major)} = 10.8$ min).

4.9. (3*R*,4*R*)-*tert*-Butyl 3-hydroxy-4-(2-methoxyphenylamino)pyrrolidine-1-carboxylate 4ca

Mp: 123–126 °C. $[\alpha]_D^{20} = +11.4$ (c 1.0, $CHCl_3$) for 58% ee; IR (KBr) (cm^{-1}): ν 3478, 2945, 1682, 1601, 1513, 1413, 1233, 1161, 1120, 1024, 742; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.48 (9H, s), 3.26–3.50 (2H, m), 3.58–3.71 (1H, m), 3.73–3.98 (2H, m), 3.84 (3H, s), 4.21–4.33 (1H, m), 6.68–6.88 (4H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$, rotamers): δ 28.5, 50.1, 50.5, 51.7, 52.3, 55.3, 58.7, 59.0, 73.0, 73.8, 79.8, 109.5, 110.1, 117.2, 121.2, 136.3, 146.7, 154.9; HRMS calcd for $C_{16}H_{24}O_4N_2$ (M): 308.1731, found: 308.1725; HPLC (Chiralpak IA column, flow rate: 0.5 mL min^{-1}, hexane/isopropanol 85:15, λ: 254 nm, $t_{R(minor)} = 13.1$ min, $t_{R(major)} = 14.2$ min).

4.10. (3*R*,4*R*)-*tert*-Butyl 3-hydroxy-4-(4-methoxyphenylamino)pyrrolidine-1-carboxylate 4cb

Mp: 103–106 °C. $[\alpha]_D^{20} = +7.5$ (c 0.94, $CHCl_3$) for 47% ee; IR (KBr) (cm^{-1}): ν 3385, 3338, 2975, 2923, 1685, 1662, 1515, 1424, 1246, 1122; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.47 (9H, s), 3.21–3.42 (2H, m), 3.62–3.65 (1H, m), 3.75 (3H, s), 3.74–3.97 (2H, m), 4.24 (1H, br s), 6.61 (2H, d, $J = 8.7$ Hz), 6.79 (2H, d, $J = 8.7$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$, rotamers): δ 28.4, 50.1, 50.5, 51.7, 52.0, 55.7, 59.7, 60.2, 73.2, 73.9, 79.8, 114.6, 114.9, 140.5, 152.6, 154.8; MS (ESI) m/z: 331.1 (MNa^+, 100%); HPLC (Chiralpak IA column, flow rate: 0.5 mL min^{-1}, hexane/isopropanol 95:5, λ: 254 nm, $t_{R(minor)} = 44.7$ min, $t_{R(major)} = 47.6$ min).

4.11. (3*R*,4*R*)-*tert*-Butyl 3-hydroxy-4-(phenylamino)pyrrolidine-1-carboxylate 4cc

Mp: 144–147 °C. $[\alpha]_D^{20} = +12.5$ (c 0.82, $CHCl_3$) for 42% ee, lit.[16b] $[\alpha]_D^{20} = +19.3$ (c 1.72, $CHCl_3$) for 89% ee; HPLC (Chiralcel OD-H column, flow rate: 0.7 mL min^{-1}, hexane/isopropanol 75:25, λ: 254 nm, $t_{R(minor)} = 8.4$ min, $t_{R(major)} = 10.7$ min).

4.12. 9*H*-Fluoren-9-ylmethyl 3-hydroxy-4-(2-methoxyphenyl-amino)pyrrolidine-1-carboxylate 4da

Mp: 129–132 °C. IR (KBr) (cm^{-1}): ν 3422, 2926, 1674, 1603, 1513, 1448, 1425, 1349, 1223, 1116, 737; ^{1}H NMR (360 MHz, $CDCl_3$): δ 3.35–3.59 (2H, m), 3.68–3.79 (1H, m), 3.85 (3H, s), 3.80–4.05 (2H, m), 4.19–4.30 (1H, m), 4.31–4.57 (3H, m), 6.64–6.97 (4H, m), 7.25–7.50 (4H, m), 7.53–7.69 (2H, m), 7.72–7.88 (2H, m); ^{13}C NMR (90.6 MHz, $CDCl_3$, rotamers): δ 47.3, 50.3, 50.7, 52.0, 52.4, 55.4, 58.7, 59.2, 67.4, 73.3, 74.1, 109.7, 110.2, 117.6, 119.9, 121.2, 125.1, 127.0, 127.7, 136.1, 141.3, 143.9, 146.8, 155.2; HRMS calcd for $C_{26}H_{26}O_4N_2Na$ (MNa^+): 453.1785, found: 453.1803; HPLC (Chiralpak IA column, flow rate: 0.8 mL min^{-1}, hexane/isopropanol 75:25, λ: 254 nm, $t_{R(minor)} = 12.0$ min, $t_{R(major)} = 20.1$ min).

4.13. 9*H*-Fluoren-9-ylmethyl 3-hydroxy-4-(4-methoxyphenyl-amino)pyrrolidine-1-carboxylate 4db

Mp: 106–110 °C. IR (KBr) (cm^{-1}): ν 3355, 2946, 1671, 1513, 1452, 1350, 1243, 1124, 758, 740; ^{1}H NMR (360 MHz, $CDCl_3$): δ 3.26–3.56 (2H, m), 3.63–3.98 (3H, m), 3.76 (3H, s), 4.18–4.34 (2H, m), 4.36–4.51 (2H, m), 6.56–6.69 (2H, d, $J = 8.8$ Hz), 6.72–6.88 (2H, m), 7.23–7.48 (4H, m), 7.52–7.67 (2H, m), 7.69–7.85 (2H, m); ^{13}C NMR (90.6 MHz, $CDCl_3$, rotamers): δ 47.3, 50.3, 50.6, 51.9, 52.3, 55.8, 59.6, 60.2, 67.3, 73.1, 74.0, 114.7, 115.0, 119.9, 125.0, 127.0, 127.7, 140.2, 141.3, 143.9, 152.8, 155.1; HRMS calcd for $C_{26}H_{26}O_4N_2Na$ (MNa^+): 453.1785, found: 453.1798; HPLC (Chiralpak IA column, flow rate: 0.8 mL min^{-1}, hexane/isopropanol 75:25, λ: 254 nm, $t_{R(minor)} = 14.5$ min, $t_{R(major)} = 18.8$ min).

4.14. 2,2-Dimethyl-6-(2-methoxyphenylamino)-1,3-dioxepan-5-ol 4ea

Oil. $[\alpha]_D^{20} = +4.7$ (c 1, $CHCl_3$) for 26% ee; IR (CaF_2, $CHCl_3$) (cm^{-1}): ν 3620, 3568, 3434, 2976, 2944, 1602, 1515, 1457, 1430; ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.41 (6H, s), 3.45–3.72 (4H, m), 3.86 (3H, s), 3.92–4.07 (2H, m), 6.60–6.96 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.5, 55.4, 56.4, 59.9, 61.2, 69.4, 101.8, 109.7, 110.1, 116.7, 121.2, 136.1, 146.7; HRMS (EI) calcd for $C_{14}H_{21}O_4N$ (M): 267.1465, found: 267.1460; HPLC (Chiralpak IA column, flow rate: 0.6 mL min^{-1}, hexane/isopropanol 90:10, λ: 254 nm, $t_{R(minor)} =$ 12.9 min, $t_{R(major)} = 13.8$ min).

4.15. 2,2-Dimethyl-6-(4-methoxyphenylamino)-1,3-dioxepan-5-ol 4eb

Oil. $[\alpha]_D^{20} = +6.8$ (c 0.68, $CHCl_3$) for 13% ee; IR (CaF_2, $CHCl_3$) (cm^{-1}): ν 3650, 3616, 3564, 3430, 2945, 2902, 1618, 1513, 1465, 1386, 1286; ^1H NMR (300 MHz, $CDCl_3$): δ 1.38 (6H, s), 3.30–3.40 (1H, m), 3.48–3.62 (2H, m), 3.66–3.76 (1H, m), 3.74 (3H, s), 3.95 (2H, dd, $J = 30.1$ Hz, $J = 12.4$ Hz), 6.62 (2H, d, $J = 8.6$ Hz), 6.78 (2H, d, $J = 8.6$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.6, 55.8, 57.7, 59.8, 61.2, 69.6, 101.8, 114.3, 115.1, 140.4, 152.1; HRMS (EI) calcd for $C_{14}H_{21}O_4N$ (M): 267.1465, found: 267.1459; HPLC (Chiralcel OD-H column, flow rate: 0.5 mL min^{-1}, hexane/isopropanol 98/2, λ: 254 nm, $t_{R(major)} =$ 46.4 min, $t_{R(minor)} = 55.7$ min).

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