Organic & Biomolecular Chemistry

RSC Publishing

PAPER

View Article Online
View Journal

The Ti-BINOLate-catalyzed, enantioselective ring-opening of *meso*-aziridines with amines†

Cite this: DOI: 10.1039/c3ob40222c

Saravanan Peruncheralathan, Sandra Aurich, Henrik Teller and Christoph Schneider*

Received 31st January 2013,
Accepted 1st March 2013

DOI: 10.1039/c3ob40222c

www.rsc.org/obc

The titanium-BINOLate-catalyzed, highly enantioselective ring-opening reaction of *meso*-aziridines has been developed which furnishes *trans*-1,2-diamines in typically good yields and excellent enantioselectivities. *N*-Aryl aziridines attached to a 5- or 6-membered carbocyclic ring are among the best substrates for this process providing the products in up to >99% ee. The chiral catalyst is easily prepared *in situ* from commercially available components and does not require any laborious ligand synthesis. Structural investigations into the catalyst composition reveal an oligomeric structure of the active Ti-complex.

Introduction

Nucleophilic ring-opening reactions of small-ring heterocycles such as epoxides[1] and aziridines[2] continue to enjoy a prominent position in synthetic organic chemistry as they furnish valuable 1,2-difunctionalized fine chemicals in just one step. Whereas synthetic efforts were largely devoted to epoxide opening reactions initially, the attention within the synthetic community has shifted to aziridine ring-opening reactions in recent years. Highly valuable compounds such as 1,2-diamines,[3] 1,2-amino alcohols,[4] 1,2-cyano amines[5] and 1,2-amino sulfides[6] are easily accessible upon treatment with suitable nucleophiles according to this strategy. By using *meso*-aziridines as starting materials an enantioselective process can be envisioned in the presence of a chiral catalyst which is capable of differentiating the enantiotopic carbon atoms within the aziridine in a symmetry-breaking operation.

In the last decade or so quite a number of exceptional contributions in this area have been made which largely rest on silylated nucleophiles.[7] Jacobsen *et al.* reported the chromium-catalyzed, enantioselective addition of trimethylsilyl azide to *N*-benzyl aziridines proceeding with up to 94% ee.[8] A whole series of highly enantioselective processes both for the azide and cyanide addition to *N*-benzoyl aziridines was developed by Shibasaki *et al*.[9] As chiral catalysts they employed dinuclear gadolinium- and yttrium-carbohydrate-phosphinoxide complexes, respectively, which were assembled *in situ*, and provided the products with up to 98% ee. In addition, a heterodinuclear chiral lanthanumyttrium bissalicylimine complex was developed for the ring-opening with malonates.[9e] RajanBabu and co-workers successfully designed a dinuclear, structurally fully characterized, chiral yttrium-bissalicylimine complex for the addition of trimethylsilyl cyanide and trimethylsilyl azide to *N*-benzoyl aziridines giving rise to 1,2-cyano amides and 1,2-azido amides, respectively, with exceptional enantioselectivities of up to 99% ee.[10] Antilla *et al.* revealed the capacity of chiral phosphoric acids to catalyze the enantioselective ring-opening of *N*-benzoyl aziridines with trimethylsilyl azide which proceeded with up to 95% ee.[11]

Non-silylated heteronucleophiles have only recently been shown to add to *meso*-aziridines using a variety of chiral catalysts. Thus, Kobayashi *et al.* developed niobium-, zirconium-, and titanium-catalyzed protocols for the enantioselective addition of anilines to *N*-aryl-aziridines furnishing 1,2-diamines with typically moderate, in select cases however excellent enantioselectivities of up to 95% ee.[12] In each of these protocols specifically designed and individually prepared tri- and tetradentate BINOL-ligands were employed as chiral ligands. The enantioselective ring-opening of aziridines with thiols to give rise to 1,2-mercapto amines as reported recently by the groups of Antilla, Della Salla, and Tan could be accomplished through either Brønsted acid- or Brønsted base-catalysis, respectively, with excellent selectivity.[13] Enantioselective halogen additions to *meso*-aziridines have very recently been made possible through the work of Jacobsen and Ooi who employed phosphinothioureas and triazolium chlorides, respectively, as chiral catalysts.[14]

We have recently discovered the titanium-BINOLate-catalyzed, highly enantioselective ring-opening of *meso*-aziridines with anilines furnishing 1,2-diamines in typically good yields and with up to >99% ee.[15] In particular, aziridines with a 5- and 6-membered ring attached gave rise to exceptional enantioselectivities and delivered cyclic 1,2-*trans*-diamines

Institut für Organische Chemie, Universität Leipzig, Johannisallee 29, 04103 Leipzig, Germany. E-mail: schneider@chemie.uni-leipzig.de

†Electronic supplementary information (ESI) available: ^{1}H- and ^{13}C-NMR spectra of new subtances. See DOI: 10.1039/c3ob40222c

which were almost enantiomerically pure. In addition, the direct and user-friendly *in situ* preparation of the chiral catalyst from commercially available components made this protocol extremely simple as no laborious ligand synthesis was required. We now provide a full account of our work and report an extended product spectrum, a modified catalyst design, and detailed spectroscopic investigations into the catalyst structure.

Results and discussion

Based upon the well established capacity of early transition metal alkoxides to be highly reactive catalysts for transamidation reactions of amides[16] and ring-opening reactions of epoxides with amines[17] we expected them to be reactive in aziridine ring-opening as well. They are known to display strong Lewis acidity even in the presence of amines, have relatively short metal–ligand bond lengths, and their complexes with the chiral diol BINOL have been used in enantioselective catalysis many times.[18]

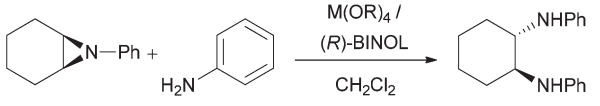
The ring-opening of 7-phenyl-7-azabicyclo[4.1.0]heptane (**1a**) with aniline (**2a**) (2 equiv.) was employed as a model reaction (Table 1). Complexes prepared *in situ* from $Zr(OiPr)_4$ and $Zr(OtBu)_4$ with (*R*)-BINOL catalyzed the reaction, but both the reaction rate and the enantioselectivity were less than satisfactory (entries 1 and 2). Interestingly, the enantioselectivity was significantly enhanced by adding *N*-methyl imidazole as a co-ligand for zirconium albeit at the expense of yield (entry 3).[19] Complexes of $Ti(OiPr)_4$ and (*R*)-BINOL proved to be both more reactive as well as more selective. Whereas the background reaction with $Ti(OiPr)_4$ alone furnished only trace amounts of product after 12 h, a 1 : 1-mixture of $Ti(OiPr)_4$ and (*R*)-BINOL catalyzed the reaction within 30 min at rt and yielded 83% of the product with an appreciable selectivity of 48% ee (entry 4). Lowering the reaction temperature to −40 °C further improved the enantioselectvity to 79% ee (entry 5).

Eventually, the key to success was a change in the metal–ligand ratio. Mixing 2.2 equiv. of (*R*)-BINOL relative to $Ti(OiPr)_4$ (10 mol%) in CH_2Cl_2 for 1 h at rt furnished a highly reactive as well as enantioselective chiral catalyst. At rt the catalyzed reaction was very rapid, but only marginally more selective than with the previous Ti-BINOLate-catalyst (entry 6). At −40 °C, however, this *in situ* prepared catalyst gave rise to *trans*-1,2-diamino cyclohexane (**3a**) in 81% yield and 97% ee within 5 h (entry 7).[20] Reaction temperatures above −40 °C led to significantly decreased selectivity whereas below −40 °C reaction times increased and yields eroded. When we employed only 1.1 equiv. of aniline a significant enhancement in yield to 94% was observed while the high enantioselectivity was almost maintained (entry 8). Hence, these conditions were used for the remaining optimization studies. $Ti(OtBu)_4$ in combination with (*R*)-BINOL slightly increased the selectivity to 98% ee whereas $Ti(OEt)_4$/(*R*)-BINOL gave rise to only 87% ee (entries 9 and 10). The enantioselectivity remained constant at 97–98% ee throughout the entire reaction ruling out that the gradually formed 1,2-diamine may act as a competitive chiral ligand for titanium.

Additives which had been found beneficial in many other Ti-BINOLate-catalyzed reactions were investigated next. With molecular sieves (4 Å) no change in yield or enantioselectivity was observed whereas the addition of water (10–20 equiv.) led to a dramatic drop in enantioselectivity indicating that anhydrous conditions were important for the success of the reaction. Optimal reaction conditions thus found called for mixing the Lewis acid $Ti(OtBu)_4$ (10 mol%) and (*R*)-BINOL (22 mol%) in CH_2Cl_2 (0.25 M towards aziridine) for 1 h at room temperature before the amine (1.1 equiv.) was added with subsequent stirring at rt for 30 min. The reaction mixture was then cooled down to −40 °C before aziridine **1a** was added and stirring was continued at −40 °C for the indicated period of time.

Having optimal reaction conditions for the ring-opening of *meso*-aziridines with amines in our hands we evaluated the substrate scope of this process (Table 2). A broad range of substituted anilines **2** were reacted with various 7-aryl-7 azabicyclo-[4.1.0]heptanes **1**. In general, best results were obtained with *para*-substituted anilines giving rise to both good to excellent yields and high enantioselectivities of up to 99% ee (entries 1–10). Anilines carrying electron-withdrawing substituent groups furnished products with lower enantiomeric excess (entries 7–9). The reaction with 4-aminobenzenethiol displayed an interesting chemoselectivity aspect: only the aminolysis of the aziridine occurred and no thiol addition was observed (entry 10). *meta*-Substituted anilines performed almost equally well with enantioselectivities ranging between 82 and 91% ee

Table 1 Optimization studies, effect of metal alkoxide, metal–ligand ratio, and temperature

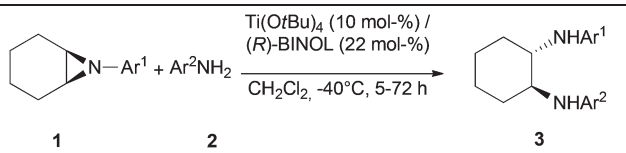


1a **2a** **3a**

Entry[a]	$M(OR)_4$	$M(OR)_4$/BINOL	T [°C]	t [h]	Yield[b] [%]	ee[c] [%]
1	$Zr(OiPr)_4$	1 : 1	rt	12	76	12
2	$Zr(OtBu)_4$	1 : 1	rt	12	95	28
3[d]	$Zr(OtBu)_4$	1 : 1	rt	12	35	70
4	$Ti(OiPr)_4$	1 : 1	rt	0.5	83	48
5	$Ti(OiPr)_4$	1 : 1	−40	14	51	79
6	$Ti(OiPr)_4$	1 : 2	rt	0.25	81	50
7	$Ti(OiPr)_4$	1 : 2	−40	5	81	97
8[e]	$Ti(OiPr)_4$	1 : 2	−40	5	94	96
9[e]	$Ti(OtBu)_4$	1 : 2	−40	5	92	98
10[e]	$Ti(OEt)_4$	1 : 2	−40	5	91	87

[a] Reaction conditions: *meso*-aziridine **1a** (1.0 equiv.), aniline **2a** (2.0 equiv.), $M(OR)_4$ (10 mol%), (*R*)-BINOL (11 or 22 mol%, respectively), 0.25 M in CH_2Cl_2. [b] Yield of isolated product. [c] Determined by HPLC using chiral stationary phases (see Experimental). [d] 22 mol% of *N*-methyl imidazole were used as an additive. [e] Reaction was carried out with 1.1 equiv. aniline **2a**.

Table 2 Titanium-BINOLate-catalyzed ring-opening of 7-azabicyclo[4.1.0]heptanes **1**



1 2 3

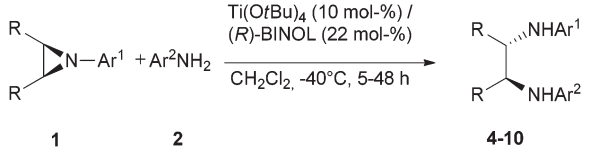
Entry[a]	*meso*-Aziridine **1** Ar^1 =	Aniline **2** Ar^2 =	Product **3**	Yield[b] [%]	ee[c] [%]
1	Ph (**1a**)	Ph	**3a**	92	98
2	**1a**	(4-Me-)Ph	**3b**	85	99
3	**1a**	(4-MeO-)Ph	**3c**	86	98
4	**1a**	(4-F-)Ph	**3d**	92	95
5	**1a**	(4-Cl-)Ph	**3e**	69	88
6	**1a**	(4-Br-)Ph	**3f**	91	91
7	**1a**	(4-CF_3)-Ph	**3g**	93	83
8[d]	**1a**	(4-CN)-Ph	**3h**	65	60
9	**1a**	(4-COOMe-)Ph	**3i**	90	77
10	**1a**	(4-SH-)Ph	**3k**	80	93
11	**1a**	(3-Me-)Ph	**3l**	89	86
12	**1a**	(3-MeO-)Ph	**3m**	88	91
13	**1a**	(3-Br-)Ph	**3n**	93	83
14	**1a**	(3-CF_3-)Ph	**3o**	90	82
15	**1a**	(2-Me-)Ph	**3p**	90	47
16	**1a**	(2-MeO-)Ph	**3q**	79	56
17	**1a**	(2-F-)Ph	**3r**	90	76
18	**1a**	(2-COOMe-)Ph	**3s**	75	22
19[d]	**1a**	1-Naphthyl	**3t**	86	77
20	**1a**	(2,4-F_2-)Ph	**3u**	88	65
21	**1a**	(3,4-$(MeO)_2$-)Ph	**3v**	81	98
22	**1a**	(3,4,5-$(MeO)_3$-)-Ph	**3w**	84	98
23[e]	**1a**	(1,4-$(NH_2)_2$)-Ph	**3x**	70	98
24	(4-MeO-)-Ph (**1b**)	Ph	**3c**	89	98
25	**1b**	(4-MeO-)Ph	**3y**	86	98
26[d]	(2-MeO-)-Ph (**1c**)	Ph	**3q**	79	88

[a] Reaction conditions: *meso*-aziridine **1** (1.0 equiv.), aniline **2** (1.1 equiv.), Ti(O*t*Bu)$_4$ (10 mol%), (*R*)-BINOL (22 mol%), 0.25 M in CH_2Cl_2, −40 °C. [b] Yield of isolated product. [c] Determined by HPLC using chiral stationary phases (see Experimental). [d] Reaction was carried out with 2.0 equiv. aniline. [e] Reaction was carried out with 0.5 equiv. aniline.

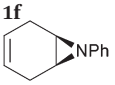
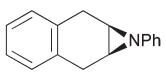
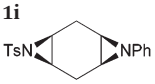
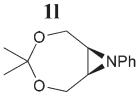
(entries 11–14). *ortho*-Substituted anilines, however, generally furnished 1,2-diamines with only moderate enantioselectivity probably for steric reasons (entries 15–18). More highly substituted anilines provided 1,2-diamines in high yields and excellent selectivities of up to 98% ee as long as the *ortho*-position was unsubstituted (entries 19–22). With bifunctional benzene-1,4-diamine (0.5 equiv.) as the nucleophile a double ring-opening occurred with **1a** to furnish tetramine **3w** in 70% yield and 98% ee and only small amounts of the corresponding *meso*-compound were formed (entry 23). Other *N*-aryl groups may be employed as well. *N*-2-Methoxyphenyl aziridine **1c** as well as *N*-4-methoxyphenyl aziridine **1b** were readily ring-opened with both aniline and *para*-anisidine to deliver products with up to 98% ee (entries 24 and 25).

Whereas the substrate scope was quite broad for anilines other amines such as for example aliphatic amines failed to participate in this reaction which we attribute to their higher basicity and hence stronger coordination to the Lewis acid preventing fast turnover. The same holds true for *N*-alkyl aziridines which reacted only very sluggishly under these conditions.

Table 3 Titanium-BINOLate-catalyzed ring-opening of *meso*-aziridines **1**



1 2 4-10

Entry[a]	*meso*-Aziridine **1**	Aniline **2** Ar =	Product	Yield[b] [%]	ee[c] [%]
1	 **1d**	Ph	**4a**	90	99
2	**1d**	(4-Me-)Ph	**4b**	83	99
3	**1d**	(4-MeO-)Ph	**4c**	77	97
4	**1d**	(4-CF_3-)Ph	**4d**	71	94
5	**1d**	(4-SH-)Ph	**4e**	76	99
6	 **1e**	Ph	**4f**	80	57
7	 **1f**	Ph	**4c**	96	99
8	**1f**	(4-MeO-)Ph	**4g**	75	99
9	 **1g**	Ph	**5a**	78	89
10	**1g**	(4-Me-)Ph	**5b**	89	90
11	**1g**	(4-MeO-)Ph	**5c**	78	87
12	 **1h**	Ph	**6a**	76	85[d]
13	 **1i**	Ph	**7a**	87	90
14	**1i**	(4-SH-)Ph	**7b**	74	53
15	 **1k**	Ph	**8a**	80	48
16	 **1l**	Ph	**9a**	85	17
17	 **1m**	Ph	**10a**	20	90

[a] Reaction conditions: *meso*-aziridine **1** (1.0 equiv.), aniline **2** (1.1 equiv.), Ti(O*t*Bu)$_4$ (10 mol%), (*R*)-BINOL (22 mol%), 0.25 M in CH_2Cl_2, −40 °C. [b] Yield of isolated product. [c] Determined by HPLC using chiral stationary phases (see Experimental). [d] After crystallization.

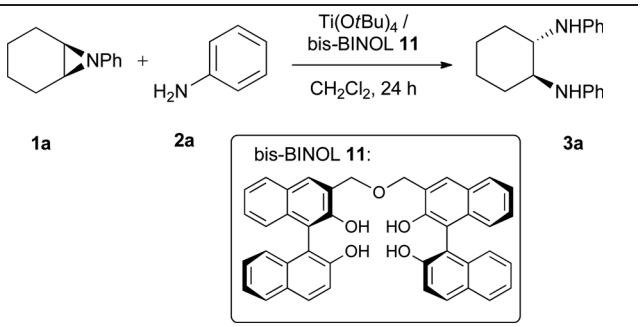
Subsequently we extended the substrate range to other cyclic as well as acyclic aziridines (Table 3). In particular, 6-aryl-6-azabicyclo[3.1.0]hexanes proved to be excellent substrates for this process. Thus, various anilines reacted with

1d–1f, respectively, to deliver *trans*-1,2-diamino cyclopentanes **4** in good yields and almost perfect enantioselectivity (entries 1–5 and 7–8). Aziridines with *N*-*ortho*-arylsubstituent retarded the reaction and significantly diminished the selectivity (entry 6). 7-Phenyl-7-azabicyclo[4.1.0]hept-3-ene **1g** behaved similarly as its saturated analogue and furnished products with around 90% ee (entries 9–11). The acyclic aziridine **1i** was ring-opened with aniline in good yield with 90% ee whereas the analogous reaction with 4-aminobenzenethiol delivered the 1,2-diamine **7b** with high chemoselectivity but only 53% ee (entries 13 and 14, respectively). Bisaziridine **1k** carrying both an *N*-aryl and an *N*-tosyl group was ring-opened exclusively on the aryl-substituted aziridine ring with only moderate enantioselectivity which may be caused by the Lewis basic heteroatoms of the sulfonyl group coordinating additionally to the chiral Lewis acid (entry 15). This effect may also be the origin for the low selectivity observed in the ring-opening of aziridine **1l** with a furyl backbone (entry 16). On the other hand, aziridine **1m** attached to a seven-membered ring with an acetal moiety was ring-opened in poor yield, but excellent enantioselectivity (entry 17).

At this point of the investigation we began to speculate about the exact structure of the chiral catalyst and wondered whether we could enhance its performance by further structural modifications. In particular, we became attracted to the observations reported by Shibasaki *et al.* who had reported the preparation and application of a linked bis-BINOL-ligand **11** coordinated to gallium(III) in epoxide opening[21] and to zinc(II) in aldol reactions,[22] respectively, which often provided better yields and enantioselectivities in the indicated reactions compared to the parent BINOL. In addition, Kobayashi *et al.* had shown that Mannich reactions were efficiently catalyzed with $Zr(OtBu)_4$ and a similar linked BINOL-ligand.[23] The underlying reason for this idea rested mainly on the 1 : 2-stoichiometry of Ti/BINOL which we had found important both for high rates and excellent enantioselectivities in the ring-opening reaction. In this respect the linked bis-BINOL-ligand **11** would ideally resemble two BINOL-ligands and possibly form a more stable and discrete Ti-complex for which additional structural information might be obtained. Accordingly, the Shibasaki-ligand **11** was prepared in a six-step sequence from (*R*)-BINOL based upon literature reports.[21]

In the model reaction of 7-phenyl-7-azabicyclo[4.1.0]-heptane (**1a**) with aniline (**2a**) the new chiral ligand was tested in combination with $Ti(OtBu)_4$ (Table 4). Using various Ti/ligand-ratios it became obvious that only the reaction rate was affected with a 1 : 1-ratio providing the most reactive catalyst and the optimal yield of 95%. The enantioselectivity, however, remained constant at 79% ee throughout these reactions indicating the rapid formation of a very stable, likely tetracoordinate chiral catalyst irrespective of the amount of ligand used (entries 1–3). More importantly, this selectivity only slightly eroded at higher temperature furnishing 1,2-diamine **3a** still with 72% ee at −20 °C providing the opportunity to employ this chiral catalyst in reactions with less reactive aziridines which required higher reaction temperatures (entry 4).

Table 4 Optimization of the reaction conditions with linked bis-BINOL **11**



Entry[a]	$Ti(OtBu)_4$/bis-BINOL **11**	T [°C]	Yield[b] [%]	ee[c] [%]
1	2 : 1	−40	60	79
2	1 : 1	−40	95	79
3	2 : 3	−40	55	79
4	1 : 1	−20	99	72
5	1 : 1	rt	n.d.	54

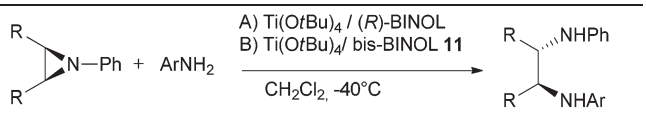
[a] Reaction conditions: *meso*-aziridine **1a** (1.0 equiv.), aniline **2a** (1.1 equiv.), $Ti(OtBu)_4$ (10 mol%), linked bis-BINOL **11** (11 mol%), 0.25 M in CH_2Cl_2. [b] Yield of isolated product. [c] Determined by HPLC using chiral stationary phases (see Experimental). n.d.: not determined.

We then repeated some of the ring-opening reactions with this new catalyst system which we had performed earlier with the $Ti(OtBu)_4$/(*R*)-BINOL-combination – in particular those with previously less satisfactory results (Table 5). In general, reactions which were efficiently catalyzed with the $Ti(OtBu)_4$/(*R*)-BINOL-combination at −40 °C did not give rise to improved results with the new catalyst (entries 1–8). As an exception electron-poor anilines which had earlier provided products with significantly diminished selectivity gave rise to similar or slightly improved enantioselectivity (entries 3, 4, 10, 11). A dramatic improvement of enantioselectivity was observed solely for 4,4-dimethyl-8-phenyl-3,5-dioxa-8-azabicyclo[5.1.0]octane (**1m**) at −20 °C which now provided 1,2-diamines **10a–10c** with good yields and 68–88% ee (entries 9–11). It appears that in this case the titanium catalyst benefits from additional coordination to the Lewis basic acetal oxygens.

For the sake of comparison we finally investigated a structurally well defined and characterized dinuclear titanium-BINOLate-complex in our aziridine ring-opening reactions which Maruoka had developed earlier for the enantioselective allylation of aldehydes.[24] This chiral catalyst was prepared *in situ* from $Ti(OiPr)_3Cl$, Ag_2O and (*R*)-BINOL and its structure was unambiguously proven to be the μ-oxo-bridged dinuclear complex **12** through positive ESI-mass spectrometry by the group of Maruoka.[24]

In our ring-opening reaction of *meso*-aziridine **1a**, this catalyst displayed good reactivity and furnished the 1,2-diamine product **3a** with excellent yields, but with only 65% ee at −40 °C. Lower as well as higher reaction temperatures did not improve the selectivity. This observation suggests that our chiral titanium-BINOLate catalyst made *in situ* from 2 equiv. of BINOL differs in constitution from the Maruoka catalyst significantly (Scheme 1).

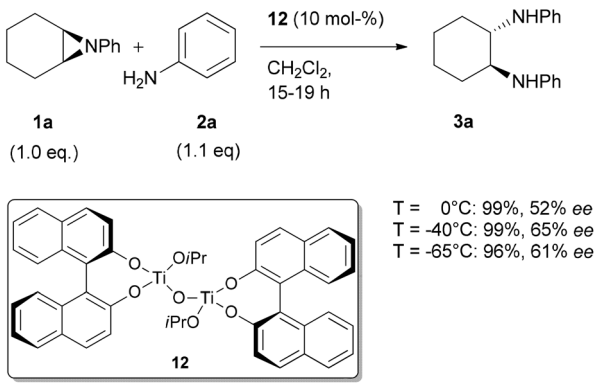
Table 5 Comparison of aminolyses of *meso*-aziridines with Ti(O*t*Bu)$_4$–BINOL and Ti(O*t*Bu)$_4$–bis-BINOL **11** complexes



1 2 3-5, 10

Entry[a]	Aziridine **1**	Aniline **2** (Ar)	Product	*t* [d]	Yield[b] [%]	ee[c] [%]
1	**1a**	Ph	**3a**	(A) 0.2	92	98
				(B) 1	95	79
2	**1a**	(4-MeO-)Ph	**3c**	(A) 1	86	98
				(B) 4	35	79
3	**1a**	(4-CN-)Ph	**3h**	(A) 1	65	60
				(B) 4	84	69
4	**1a**	(4-COOMe-)-Ph	**3i**	(A) 1	90	77
				(B) 4	72	78
5	**1a**	(3-OMe-)Ph	**3m**	(A) 1	88	91
				(B) 2	92	84
6	**1a**	(2-OMe-)Ph	**3p**	(A) 1	79	56
				(B) 2	90	55
7	**1d**	Ph	**4a**	(A) 1	90	>99
				(B) 4	18	35
8	**1f**	Ph	**5a**	(A) 5	78	89
				(B) 8	35	62
9	**1l**	Ph	**10a**	(A) 4	20	90
				(B) 8	17	87
				(A) 2[d]	88	40
				(B) 3[d]	85	88
10	**1l**	(4-COOMe-)-Ph	**10b**	(A) 5	87	31
				(B) 2[d]	66	78
11	**1l**	(4-CN-)Ph	**10c**	(A) 6	62	16
				(B) 3[d]	69	68

[a] Reaction conditions: *meso*-aziridine **1** (1.0 equiv.), aniline **2** (1.1 equiv.), Ti(O*t*Bu)$_4$ (10 mol%), (*R*)-BINOL (22 mol%) or bis-BINOL **11** (11 mol%), 0.25 M in CH_2Cl_2. [b] Yield of isolated product. [c] Determined by HPLC methods using chiral stationary phases (see Experimental). [d] Reaction was carried out at −20 °C.



Scheme 1 Aminolysis of 7-azabicyclo[4.1.0]heptane **1a** catalyzed through the dinuclear Maruoka-catalyst (**12**).

In an attempt to shed some light on the catalyst composition we finally performed some spectroscopic studies on the complex formed *in situ* in the reaction of Ti(O*t*Bu)$_4$ and (*R*)-BINOL or the linked bis-BINOL **11**, respectively, and aniline in CH_2Cl_2.[25]

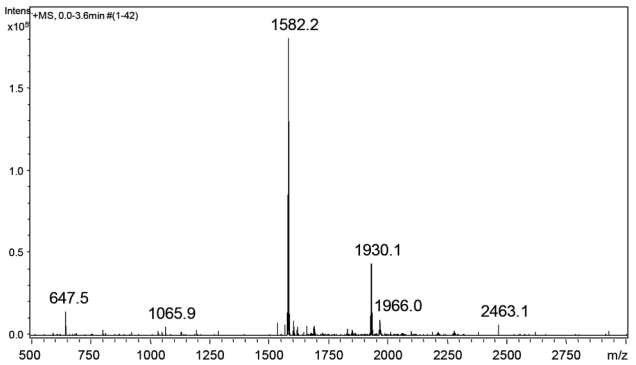


Fig. 1 Positive ESI-MS of a mixture of Ti(O*t*Bu)$_4$, (*R*)-BINOL, and aniline (1 : 2.2 : 10) in CH_2Cl_2–MeCN.

ESI-MS-experiments were carried out with a mixture of Ti(O*t*Bu)$_4$, (*R*)-BINOL and aniline (1 : 2.2 : 10) in CH_2Cl_2, which had been prepared according to the general synthetic protocol (Fig. 1). In the positive ESI-MS mode prominent signals at *m*/*z* 1582 and *m*/*z* 1930 were observed representing trinuclear and tetranuclear titanium complexes with the formal structures $[5BINOL + 3Ti + O + H]^+$ and $[6BINOL + 4Ti + 2O + H]^+$, respectively. The additional small peak at *m*/*z* 1966 has been established before and proven to be a μ-oxo-complex with the composition $[6BINOL + 4Ti + 2O + 2H_2O + H]^+$ by X-ray- and MS-studies.[25e] Upon addition of acetonitrile which facilitated ionization of the reaction sample in the mass spectrometer an additional peak at *m*/*z* 1850 with the formal structure of $[6BINOL + 3Ti + H]^+$ was observed in low intensity.

When the sample preparation included the addition of *meso*-aziridine **1a** as a potential ligand to titanium a signal at *m*/*z* 2764 was detected in the positive ESI-MS-mode indicating the formation of a complex with the formal composition $[6BINOL + 4Ti + 2O + 2H_2O + 3aziridine + 3aniline + H]^+$. A split-off of Δm 266 representing the combined mass of one aziridine and one aniline molecule was observed three successive times in LR-ESI-MS/MS further supporting the proposed composition. This analysis supports the assumption that a chiral oligomeric titanium complex binds to and activates both components and delivers the amine onto the aziridine in an intramolecular, highly enantioselective fashion.[26] All proposed structures were unambiguously proven by ESI-MS/MS (see the ESI†).

In agreement with the formation of oligomeric Ti-BINOL complexes observed in the ESI-MS experiments we found a positive nonlinear effect (NLE) in the reaction using BINOL-ligands with varying enantiomeric excess (Fig. 2). The weak, but still significant positive nonlinear effect is an indication that more than one chiral ligand is involved within the active chiral metal catalyst.

When we studied the complex prepared *in situ* from Ti(O*t*Bu)$_4$, the linked bis-BINOL ligand **11** and aniline (1 : 1.1 : 10) prepared and measured in CH_2Cl_2 according to the general synthetic protocol, we observed a very prominent single signal at *m*/*z* 1333 in the negative ESI-mode for which the formal composition $[2\ \mathbf{11} + 2Ti + H_2O - H]^-$ is assigned

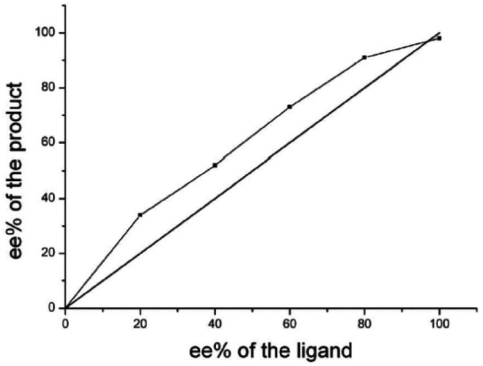


Fig. 2 Positive nonlinear effect of the Ti(O*t*Bu)$_4$–BINOL catalyzed aminolysis of *meso*-aziridine **1a** with aniline **2a**.

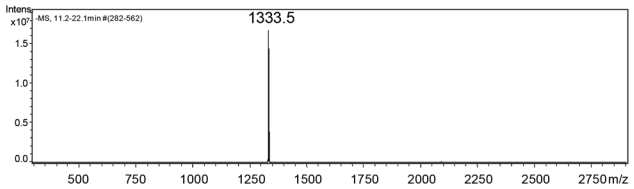


Fig. 3 Negative ESI-MS of a mixture of Ti(O*t*Bu)$_4$, bis-BINOL **11**, and aniline (1 : 1.1 : 10) in CH_2Cl_2.

(Fig. 3). After addition of acetonitrile for a more effective ionization additional signals at *m*/*z* 1317 and at *m*/*z* 659 were detected representing the formal structures [2 **11** + 2Ti + H]$^+$ and [**11** + Ti + H]$^+$, respectively. Upon addition of aziridine **1a** to the solution in CH_2Cl_2 an additional signal was cleanly detected in the positive ESI-mode at *m*/*z* 1583 for the structure [2 **11** + 2Ti + aziridine + aniline + H]$^+$. In LR-ESI(+)-MS/MS this signal underwent a split-off of Δ*m* 266 comprising one aziridine and one aniline molecule. Thus, the complex of two Ti^{IV} and two linked bis-BINOL ligands appears to be the reactive catalyst in the ring-opening reaction.

Conclusions

We have developed a highly enantioselective ring-opening reaction of *meso*-aziridines with anilines to furnish a broad range of *trans*-1,2-diamines in good to excellent yields and up to 99% ee. The chiral catalyst was easily prepared *in situ* from the commercially available components Ti(OiPr)$_4$ or Ti(O*t*Bu)$_4$ and (*R*)-BINOL in a 1 : 2-ratio. We also employed a chiral Ti-catalyst composed of a linked bis-BINOL ligand **11** as originally reported by Shibasaki which afforded higher yields and/or enantioselectivities in select cases. Investigations concerning the structure of the metal catalyst based upon HR-ESI-MS-experiments point to an oligomeric complex with dual activation of both components which is further supported through the observation of a positive nonlinear effect.

Experimental

General methods

All experiments were carried out in oven-dried glassware under an argon atmosphere. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution using a Varian Gemini 2000 spectrometer (200 or 300 MHz) and a Brucker Avance DRX 400 (400 MHz). The signals were referenced to residual chloroform (7.26 ppm, ^{1}H, 77.00 ppm, ^{13}C). Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet) and brs (broad singlet). Melting points were determined uncorrected on a Boetius heating table. IR spectra were obtained with an FTIR spectrometer (Genesis ATI Mattson/Unicam). UV spectra were recorded on a UV spectrometer (DU-650 Beckmann). Optical rotations were measured using a Polarotronic polarimeter (Schmidt & Haensch). High resolution ESI mass spectra were recorded on a Brucker APEX II FT-ICR, low resolution ESI-MS and ESI-MS/MS spectra were recorded on an ESQUIRE 3000 Plus (Bruker Daltonics). All EI mass spectra were recorded on a Finnigan MAT 8230. HPLC analyses were carried out on a Jasco MD-2010 plus instrument with a chiral stationary phase column (Daicel Chiralcel OD-H column or Daicel Chiralcel AD-H column). The solvents were distilled from the indicated drying reagents: dichloromethane (CaH_2). Diethyl ether, ethyl acetate, petroleum ether and *n*-hexane were technical grade and distilled from KOH, excepting ethyl acetate (distilled from $CaCl_2$). All reactions were monitored by TLC. Flash column chromatography was performed by using Merck silica gel 60 230-400 mesh (0.040–0.063 mm). Spots were monitored by thin-layer chromatography on precoated silica gel SILG/UV254 plates (Machery-Nagel & Co.), were visualized by UV and were treated with a solution of phosphomolybdic acid hydrate (5 g in 250 mL methanol) in methanol or vanilline (3.75 g, 75 mL glacial acetic acid, 36 mL sulfuric acid in 750 mL methanol) in methanol. The corresponding racemic products were prepared using racemic BINOL (Aldrich) as a catalyst. All *meso*-*N*-aryl-aziridines were prepared according to literature procedures.[3j]

General procedure for ring-opening of *meso*-*N*-aryl-aziridines

To a stirred solution of (*R*)-BINOL (31.5 mg, 0.11 mmol) in dry CH_2Cl_2 (0.8 mL) in a flame-dried round-bottom flask under an argon atmosphere was added Ti(O*t*Bu)$_4$ (19 μL, 0.05 mmol) as a solution in CH_2Cl_2 (0.4 mL) at rt. The color of the reaction mixture immediately became intensely red-brown and the solution was stirred for 1 h at the same temperature. Subsequently the aniline **2** (0.55 mmol) in CH_2Cl_2 (0.4 mL) was added and the mixture was stirred for an additional 30 min at rt. Then the reaction was cooled to −40 °C and *meso*-aziridine **1** (0.50 mmol) in CH_2Cl_2 (0.4 mL) was added. After the starting material had been completely consumed as judged by TLC-analysis the reaction was quenched through the addition of 0.5 mL Et_3N at −40 °C, then warmed to room temperature and the resulting yellow solution was purified by flash chromatography using *n*-hexane–ethyl acetate with 1% Et_3N as the eluent to afford the *trans*-1,2-diamine product.

(1*S*,2*S*)-*N*,*N*′-Diphenylcyclohexane-1,2-diamine (3a).[3j] Yield: 122 mg (92%), 98% ee as a colourless oil, reaction time 5 h.

$[\alpha]_D^{20}$ = −64.3 (*c* = 0.61, C_6H_6) [lit.[12a] $[\alpha]_{20}^{D}$ = −61.9 (*c* = 0.92, >99.9% ee, C_6H_6)].

R_f (EtOAc–petroleum ether, 1/10): 0.48.

UV (CH_3CN): λ_{max} (lg ε) = 296 (4.392), 250 (3.697) nm.

IR (film): ν (cm^{-1}) = 3386, 3084, 3050, 3019, 2930, 2855, 1600, 1497, 1448, 1318, 1255.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.19 (t, *J* = 8.0 Hz, 4H, 3,5-Ar**H**), 6.74 (t, *J* = 7.6 Hz, 2H, 4-Ar**H**), 6.64 (d, *J* = 8.0 Hz, 4H, 2,6-Ar**H**), 3.82 (brs, 2H, N**H**), 3.19–3.23 (m, 2H, C**H**-N), 2.36–2.39 (m, 2H, C$\mathbf{H}_2$), 1.77–1.87 (m, 2H, C$\mathbf{H}_2$), 1.41–1.46 (m, 2H, C$\mathbf{H}_2$), 1.21–1.29 (m, 2H, C$\mathbf{H}_2$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.8, 129.4, 117.6, 113.6, 57.3, 32.6, 24.7.

MS (ESI, MeOH): *m*/*z* = 267 $[M + H]^+$, 289 $[M + Na]^+$.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 6.09 min; major enantiomer (1*S*,2*S*) t_R = 7.40 min.

(1*S*,2*S*)-*N*-Phenyl-*N*′-*p*-tolylcyclohexane-1,2-diamine (3b).[3j] Yield: 119 mg (85%), 99% ee as a pale yellow oil.

$[\alpha]_D^{20}$ = −40.5 (*c* = 0.89, $CHCl_3$) [lit.[12a] $[\alpha]_D^{20}$ = −13.8 (*c* = 0.72, 48% ee, $CHCl_3$)].

R_f (EtOAc–petroleum ether, 1/10): 0.46.

UV (CH_3CN): λ_{max} (lg ε) = 298 (3.961), 251 (4.467), 231 (3.747) nm.

IR (as film in CCl_4): ν (cm^{-1}) = 3385, 3051, 3020, 2931, 2856, 1601, 1502, 1462, 1449, 1316, 1291, 1253.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.20 (t, *J* = 7.6 Hz, 2H, 3,5-Ar**H**), 7.02 (d, *J* = 8.4 Hz, 2H, 3′,5′-Ar**H**), 6.74 (t, *J* = 7.6 Hz, 1H, 4-Ar**H**), 6.65 (d, *J* = 7.6 Hz, 2H, 2,6-Ar**H**), 6.58 (d, *J* = 8.4 Hz, 2H, 2′,6′-Ar**H**), 3.80 (brs, 2H, N**H**), 3.22 (dt, *J* = 3.6, 9.0 Hz, 1H, C**H**-N), 3.19 (dt, *J* = 3.6, 9.0 Hz, 1H, C**H**-N), 2.36–2.39 (m, 2H, C$\mathbf{H}_2$), 2.28 (s, 3H, C$\mathbf{H}_3$), 1.79–1.82 (m, 2H, C$\mathbf{H}_2$), 1.42–1.47 (m, 2H, C$\mathbf{H}_2$), 1.21–1.29 (m, 2H, C$\mathbf{H}_2$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.9, 145.5, 129.9, 129.4, 127.0, 117.6, 113.9, 113.6, 57.7, 57.4, 32.71, 32.67, 24.77, 24.73, 20.5.

MS (ESI, MeOH): *m*/*z* = 281 $[M + H]^+$, 303 $[M + Na]^+$, 319 $[M + K]^+$.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 6.14 min; major enantiomer (1*S*,2*S*) t_R = 7.53 min.

(1*S*,2*S*)-*N*-(4-Methoxyphenyl)-*N*′-phenylcyclohexane-1,2-diamine (3c).[3j] Yield: 127 mg (86%), 98% ee as a yellow oil.

$[\alpha]_D^{20}$ = −40.6 (*c* = 0.69, $CHCl_3$) [lit.[12a] $[\alpha]_D^{20}$ = −26.4 (*c* = 1.33, 70% ee, $CHCl_3$)].

R_f (EtOAc–petroleum ether, 1/10): 0.22.

UV (CH_3CN): λ_{max} (lg ε) = 298 (4.357), 250 (3.658) nm.

IR (as film in CCl_4): ν (cm^{-1}) = 3371, 3051, 2932, 2855, 2831, 1601, 1511, 1463, 1450, 1357, 1290, 1241, 1179.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.19 (t, *J* = 7.6 Hz, 2H, 3,5-Ar**H**), 6.79 (dd, *J* = 2.4, 7.6 Hz, 2H, 3′,5′-Ar**H**), 6.73 (t, *J* = 7.2 Hz, 1H, 4-Ar**H**), 6.64 (d, *J* = 7.6 Hz, 2H, 2,6-Ar**H**), 6.62 (dd, *J* = 2.4, 7.6 Hz, 2H, 2′,6′-Ar**H**), 3.76 (s, 3H, OCH_3), 3.75 (brs, 2H, N**H**), 3.19 (dt, *J* = 3.6, 9.6 Hz, 1H, C**H**-N), 3.11 (dt, *J* = 3.6, 9.6 Hz, 1H, C**H**-N), 2.31–2.36 (m, 2H, C$\mathbf{H}_2$), 1.77–1.80 (m, 2H, C$\mathbf{H}_2$), 1.39–1.44 (m, 2H, C$\mathbf{H}_2$), 1.18–1.27 (m, 2H, C$\mathbf{H}_2$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 152.5, 147.9, 141.8, 129.4, 117.7, 115.4, 115.0, 113.7, 58.5, 57.5, 55.9, 32.75, 32.70, 24.7 (2C).

MS (ESI, MeOH): *m*/*z* = 297 $[M + H]^+$, 319.0 $[M + Na]^+$.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 11.59 min; major enantiomer (1*S*,2*S*) t_R = 13.33 min.

(1*S*,2*S*)-*N*-(4-Fluorophenyl)-*N*′-phenylcyclohexane-1,2-diamine (3d).[12a] Yield: 129 mg (92%), 95% ee as a colorless solid; m.p.: 63–65 °C.

$[\alpha]_D^{20}$ = −7.8 (*c* = 1.28, $CHCl_3$) [lit.[12a] $[\alpha]_D^{23}$ = −6.8 (*c* = 0.80, 59% ee, $CHCl_3$)].

R_f (EtOAc–petroleum ether, 1/10): 0.40.

UV (CH_3CN): λ_{max} (lg ε) = 301 (3.826), 250 (4.548), 233 (3.867) nm.

IR (KBr): ν (cm^{-1}) = 3397, 3054, 2935, 2851, 1600, 1502, 1431, 1320, 1291, 1199.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.19 (t, *J* = 7.6 Hz, 2H, 3,5-Ar**H**), 6.89 (t, *J* = 8.8 Hz, 2H, 3′,5′-Ar**H**), 6.73 (t, *J* = 7.2 Hz, 1H, 4-Ar**H**), 6.64 (d, *J* = 7.6 Hz, 2H, 2,6-Ar**H**), 6.55 (dd, *J* = 4.4, 8.8 Hz, 2H, 2′,6′-Ar**H**), 3.75 (brs, 2H, N**H**), 3.21 (dt, *J* = 3.6, 10.0 Hz, 1H, C**H**-N), 3.11 (dt, *J* = 3.6, 10.0 Hz, 1H, C**H**-N), 2.30–2.36 (m, 2H, C$\mathbf{H}_2$), 1.77–1.80 (m, 2H, C$\mathbf{H}_2$), 1.39–1.44 (m, 2H, C$\mathbf{H}_2$), 1.18–1.27 (m, 2H, C$\mathbf{H}_2$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 156.0 (d, $^1J_{CF}$ = 233.9 Hz), 147.8, 144.2, 129.4, 117.8, 115.8 (d, $^2J_{CF}$ = 22.3 Hz), 114.7 (d, $^3J_{CF}$ = 7.3 Hz), 113.7, 58.3, 57.4, 32.72, 32.64, 24.9, 24.7.

MS (ESI, MeOH): *m*/*z* (%) = 285 $[M + H]^+$, 307 $[M + Na]^+$.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 6.94 min; major enantiomer (1*S*,2*S*) t_R = 8.77 min.

(1*S*,2*S*)-*N*-(4-Chlorophenyl)-*N*′-phenylcyclohexane-1,2-diamine (3e).[3j] Yield: 104 mg (69%), 81% ee as a pale yellow oil; reaction time: 48 h.

$[\alpha]_D^{20}$ = −57.7 (*c* = 0.78, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/10) = 0.40.

UV (CH_3CN): λ_{max} (lg ε) = 287 (3.686), 257 (4.419) nm.

IR (as film): ν (cm^{-1}) = 3850, 3741, 3685, 3645, 3394, 3050, 3022, 2922, 2855, 2661, 2577, 1921, 1865, 1605, 1431, 1402, 1384, 1327, 1255, 1204, 1177, 1154, 1137, 1089, 1028, 1002, 993, 954, 875, 853, 824, 753, 694, 672, 631, 565, 505.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.21 (t, *J* = 7.2 Hz, 2H, 3,5-Ar**H**), 7.14 (d, *J* = 7.6 Hz, 2H, 3′,5′-Ar**H**), 6.76 (t, *J* = 7.2 Hz, 1H, 4-Ar**H**), 6.65 (d, *J* = 8.0 Hz, 2H, 2,6-Ar**H**), 6.55 (d, *J* = 7.6 Hz, 2H, 2′,6′-Ar**H**), 3.81 (brs, 2H, N**H**), 3.24 (dt, *J* = 3.2, 9.6 Hz, 1H, C**H**-N), 3.15 (dt, *J* = 3.2, 9.6 Hz, 1H, C**H**-N), 2.32–2.38 (m, 2H, C$\mathbf{H}_2$), 1.80–1.82 (m, 2H, C$\mathbf{H}_2$), 1.41–1.46 (m, 2H, C$\mathbf{H}_2$), 1.23–1.41 (m, 2H, C$\mathbf{H}_2$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.6, 146.4, 129.4, 129.1, 122.0, 117.8, 114.6, 113.6, 57.6, 57.2, 32.60, 32.45, 24.70, 24.67.

MS (EI, MeOH): *m*/*z* = 301 $[M + H]^+$, 323 $[M + Na]^+$, 339 $[M + K]^+$.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 7.33 min; major enantiomer (1*S*,2*S*) t_R = 9.87 min.

(1*S*,2*S*)-*N*-(4-Bromophenyl)-*N*′-phenylcyclohexane-1,2-diamine (3f).[15a] Yield: 157 mg (91%), 91% ee as a pale yellow oil.

$[\alpha]_D^{20} = -64.3$ (c = 0.93, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/10): 0.44.

UV (CH_3CN): λ_{max} (lg ε) = 298 (4.015), 256 (4.539), 238 (3.779) nm.

IR (as film): ν (cm^{-1}) = 3394, 3052, 2934, 2857, 1604, 1495, 1431, 1384, 1295, 1178.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, J = 8.8 Hz, 2H, 3′,5′-Ar**H**), 7.19 (t, J = 7.6 Hz, 2H, 3,5-Ar**H**), 6.74 (t, J = 7.2 Hz, 1H, 4-Ar**H**), 6.63 (d, J = 7.6 Hz, 2H, 2,6-Ar**H**), 6.49 (d, J = 8.8 Hz, 2H, 2′,6′-Ar**H**), 3.79 (brs, 2H, N**H**), 3.22 (dt, J = 3.6, 9.8 Hz, 1H, C**H**-N), 3.14 (dt, J = 3.6, 9.8 Hz, 1H, C**H**-N), 2.30–2.36 (m, 2H, C$\mathbf{H}_2$), 1.78–1.81 (m, 2H, C$\mathbf{H}_2$), 1.40–1.45 (m, 2H, C$\mathbf{H}_2$), 1.19–1.27 (m, 2H, C$\mathbf{H}_2$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.6, 146.8, 132.0, 129.4, 117.8, 115.1, 113.6, 109.1, 57.5, 57.2, 32.63, 32.44, 24.72, 24.63.

MS (ESI, MeOH): m/z = 345 $[M + H]^+$, 367 $[M + Na]^+$, 382 $[M + K]^+$.

HR-MS (ESI, MeOH): calcd for $C_{18}H_{22}N_2Br$ ($[M + H]^+$): 345.09611, found: 345.09611.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 7.74 min; major enantiomer (1*S*,2*S*) t_R = 10.75 min.

(1*S*,2*S*)-*N*-(Phenyl)-*N*′-(4-trifluoromethylphenyl)-cyclohexane-1,2-diamine (3g).[15e] Yield: 155 mg (93%), 86% ee as a colorless solid; reaction time: 36 h.

$[\alpha]_D^{20} = -35.8$ (c = 1.23, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/10) = 0.38.

UV (CH_3CN): λ_{max} (lg ε) = 261 (4.310) nm.

IR (KBr): ν (cm^{-1}) = 3346, 3052, 2934, 2850, 1619, 1602, 1536, 1503, 1462, 1452, 1432, 1339, 1257, 1192, 1154, 1138, 1093, 1066, 1003, 991, 953, 870, 820, 746, 693, 637, 589, 500.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, 2H, J = 8.5 Hz, 3′,5′-Ar**H**), 7.19 (dd, 2H, J = 7.5, 8.5 Hz, 3,5-Ar**H**), 6.74 (t, 1H, J = 7.5 Hz, 4-ArH), 6.63–6.65 (m, 4H, 2,6-Ar**H**, 2′,6′-Ar**H**), 4.11 (d, 1H, J = 4.0 Hz, N**H**), 3.64 (s, 2H, **H**C-N), 3.73 (s, 1H, N**H**), 2.27 (dt, 2H, J = 8.0, 13.5 Hz, C**H**H), 1.84 (quin, 2H, J = 8.0 Hz, C$\mathbf{H}_2$), 1.53–1.61 (m, 2H, CH**H**).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 150.3, 147.5, 129.5, 126.9 (q, $^3J_{CF}$ = 4.4 Hz), 125.1 (q, $^1J_{CF}$ = 270.5 Hz), 119.1 (q, $^2J_{CF}$ = 33.2 Hz), 117.9, 113.5, 112.4, 57.21, 57.15, 32.64, 32.39, 24.71, 24.57.

HR-MS (ESI, MeOH): calcd for $C_{18}H_{21}F_3N_2$ ($[M + H]^+$): 335.17351; found: 335.17313, calcd for $C_{18}H_{21}F_3N_2Na$ ($[M + Na]^+$): 357.15545; found: 357.15495.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 6.64 min; major enantiomer (1*S*,2*S*) t_R = 9.02 min.

(1*S*,2*S*)-*N*-(4-Cyanophenyl)-*N*′-phenylcyclohexane-1,2-diamine (3h). With bis-BINOL **11**: 61 mg (84%), 69% ee, reaction time 93 h.

$[\alpha]_D^{20} = -95.0°$ (c = 1.01, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/3) = 0.32.

UV (CH_3CN): λ_{max} (lg ε) = 288 (4.598), 248 (4.216), 247 (4.215) nm.

IR (as film): ν (cm^{-1}) = 3349, 3050, 2935, 2856, 2206, 1601, 1517, 1498, 1477, 1450, 1421, 1384, 1352, 1337, 1312, 1260, 1170, 1153, 1139, 1111, 1093, 992, 951, 874, 823, 746, 693, 542, 504.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, J = 8.4 Hz, 2H, 3′,5′-Ar**H**), 7.17 (t, J = 8.4 Hz, 2H, 2,4-Ar**H**), 6.72 (t, J = 7.2 Hz, 1H, 4-Ar**H**), 6.61 (d, J = 8.8 Hz, 2H, 2,6-Ar**H**), 6.53 (d, J = 8.8 Hz, 2H, 2′,6′-Ar**H**), 4.39 (brd, 1H, N**H**), 3.58 (brs, 1H, N**H**), 3.28 (dt, J = 3.6, 9.8 Hz, 1H, C**H**-N), 3.19–3.24 (m, 1H, C**H**-N), 2.28–2.34 (m, 2H, C$\mathbf{H}_2$), 1.79–1.82 (m, 2H, C$\mathbf{H}_2$), 1.28–1.45 (m, 2H, C$\mathbf{H}_2$), 1.22–1.28 (m, 2H, C$\mathbf{H}_2$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 151.0, 147.3, 133.8, 129.5, 120.5, 117.9, 113.5, 1112.7, 98.8, 57.1, 57.0, 32.6, 32.2, 24.7, 24.5.

HR-MS (ESI, MeOH): calcd for $C_{19}H_{22}N_3$ ($[M + H]^+$): 292.39808; found: 292.18107. calcd for $C_{19}H_{21}N_3Na$ ($[2M + Na]^+$): 605.33687; found: 605.33556.

HPLC: Chiralcel OD-H column, hexane–i-PrOH = 70/30, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 7.31 min; major enantiomer (1*S*,2*S*) t_R = 12.05 min.

(1*S*,2*S*)-*N*-(4-Carbomethoxyphenyl)-*N*′-phenylcyclohexane-1,2-diamine (3i). Yield: 146 mg (90%), 77% ee as a colourless viscous oil; reaction time: 48 h.

$[\alpha]_D^{20} = -102.9$ (c = 0.58, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/3) = 0.30.

UV (CH_3CN): λ_{max} (lg ε) = 245 (4.110) nm.

IR (as film): ν (cm^{-1}) = 3366, 3054, 3023, 2936, 2857, 1697, 1601, 1523, 1502, 1434, 1384, 1337, 1310, 1282, 1258, 1176, 1140, 1107, 1028, 993, 969, 955, 875, 837, 787, 694, 639, 506.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 8.4 Hz, 2H, 3′,5′-Ar**H**), 7.20 (t, J = 7.6 Hz, 2H, 2,4-Ar**H**), 6.73 (t, J = 7.2 Hz, 1H, 4-Ar**H**), 6.62 (d, J = 8.8 Hz, 2H, 2,6-Ar**H**), 6.54 (d, J = 7.6 Hz, 2H, 2′,6′-Ar**H**), 4.36 (brs, 1H, N**H**), 3.85 (s, 3H, OC$\mathbf{H}_3$), 3.71 (brs, 1H, N**H**), 3.23–3.28 (m, 2H, C**H**-N), 2.32–2.36 (m, 2H, C$\mathbf{H}_2$), 1.80–1.81 (m, 2H, C$\mathbf{H}_2$), 1.41–1.46 (m, 2H, C$\mathbf{H}_2$), 1.23–1.41 (m, 2H, C$\mathbf{H}_2$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.2, 151.6, 147.4, 131.6, 129.4, 118.2, 117.6, 113.4, 111.9, 57.0, 56.8, 51.5, 32.4, 32.3, 24.6, 24.5.

HR-MS (ESI, MeOH): calcd for $C_{20}H_{24}N_2NaO_2$ ($[M + Na]^+$): 347.17355; found: 347.17294.

HPLC: Chiralcel OD-H column, hexane–i-PrOH = 70/30, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 12.91 min; major enantiomer (1*S*,2*S*) t_R = 16.88 min.

4-((1*S*,2*S*)-2-(Phenylamino)cyclohexylamino)benzenethiol (3k). Yield: 127 mg (80%), 93% ee as a pale yellow oil.

$[\alpha]_D^{20} = -83.3$ (c = 1.74, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/10): 0.32.

UV (CH_3CN): λ_{max} (lg ε) = 260 (4.321) nm.

IR (as film in CCl_4): ν (cm^{-1}) = 3391, 3053, 3022, 2934, 2857, 1598, 1498, 1449, 1431, 1384, 1317, 1295, 1254, 1181, 1155, 1138, 1103, 1028, 873, 786, 693, 505.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.17–7.22 (m, 4H, 3,5-Ar**H**, 3′,5′-Ar**H**), 6.73 (t, J = 7.2 Hz, 1H, 4-Ar**H**), 6.63 (d, J = 8.7 Hz, 2H, 2,6-Ar**H**), 6.52 (d, J = 8.7 Hz, 2H, 2′,6′-Ar**H**), 3.74 (brs, 2H,

NH), 3.31 (s, 1H, SH), 3.23 (dt, J = 3.6, 9.3 Hz, 1H, CH-N), 3.14 (dt, J = 3.6, 9.3 Hz, 1H, CH-N), 2.30–2.37 (m, 2H, CH_2), 1.77–1.80 (m, 2H, CH_2), 1.39–1.46 (m, 2H, CH_2), 1.18–1.29 (m, 2H, CH_2).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.5, 146.7, 133.2, 129.3, 117.6, 114.7, 114.0, 113.4, 57.3, 57.1, 32.4, 32.3, 24.55, 24.50.

HR-MS (ESI, MeOH): calcd for $C_{18}H_{23}N_2S$ ($[M + H]^+$): 299.15819; found: 299.15765, calcd for $C_{18}H_{22}N_2NaS$ ($[M + Na]^+$): 321.14014; found: 321.13958, calcd for $C_{36}H_{44}N_4NaS_2$ ($[2M + Na]^+$): 619.29051; found: 619.28996.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 10.71 min; major enantiomer (1*S*,2*S*) t_R = 14.57 min.

(1*S*,2*S*)-*N*-Phenyl-*N*′-*m*-tolylcyclohexane-1,2-diamine (3l). Yield: 126 mg (89%), 86% ee as a pale yellow oil.

$[\alpha]_D^{20}$ = −25.5 (c = 0.549, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/10): 0.45.

UV (CH_3CN): λ_{max} (lg ε) = 253 (4.146) nm.

IR (film): ν (cm^{-1}) = 3386, 3049, 2932, 2856, 1601, 1502, 1431, 1383, 1321, 1256, 1204, 1179, 1136, 1105, 1071, 1028, 993, 866, 692.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.18 (dd, J = 7.6, 8.2 Hz, 2H, 3,5-ArH), 7.07 (dd, J = 7.6, 8.4 Hz, 1H, 5′-ArH), 6.72 (t, J = 7.6 Hz, 1H, 4-ArH), 6.62 (d, J = 7.6 Hz, 2H, 2,6-ArH), 6.54 (d, J = 7.2 Hz, 1H, 6′-ArH), 6.43–6.45 (m, 2H, 3′,4′-ArH), 3.79 (brs, 2H, NH), 3.16–3.24 (m, 2H, CH-N), 2.33–2.37 (m, 2H, CH_2), 2.28 (s, 3H, CH_3), 1.76–1.80 (m, 2H, CH_2), 1.40–1.46 (m, 2H, CH_2), 1.20–1.27 (m, 2H, CH_2).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.6 (2C), 138.9, 129.2, 129.1, 118.4, 117.4, 114.2, 113.4, 110.4, 57.1, 57.0, 32.5, 32.4, 24.54, 24.50, 21.5.

HR-MS (ESI, $CHCl_3$, MeOH): calcd for $C_{19}H_{25}N_2$ ($[M + H]^+$): 281.20177; found: 281.20123, calcd for $C_{19}H_{24}N_2Na$ ($[M + Na]^+$): 303.18372; found: 303.18317, calcd for $C_{38}H_{48}N_4Na$ ($[2M + Na]^+$): 584.37767; found: 583.37712.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 6.05 min; major enantiomer (1*S*,2*S*) t_R = 6.87 min.

(1*S*,2*S*)-*N*-(3-Methoxyphenyl)-*N*′-phenylcyclohexane-1,2-diamine (3m).[12a] Yield: 117 mg (88%), 91% ee as a pale yellow oil.

$[\alpha]_D^{20}$ = −28.0 (c = 3.24, $CHCl_3$). [lit.[12a] $[\alpha]_D^{25}$ = −14.1 (c = 1.19, 56% ee, $CHCl_3$)].

R_f (EtOAc–petroleum ether, 1/10): 0.23.

UV (CH_3CN): λ_{max} (lg ε) = 294 (3.734), 250 (4.344) nm.

IR (as film in CCl_4): ν (cm^{-1}) = 3384, 3050, 2930, 2855, 1914, 1614, 1487, 1450, 1358, 1258, 1212, 1161, 1137, 1106, 1049, 992, 953.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.21 (t, J = 7.5 Hz, 2H, 3,5-ArH), 7.11 (t, J = 7.8 Hz, 1H, 5′-ArH), 6.75 (dt, J = 0.9, 7.2 Hz, 1H, 4-ArH), 6.65 (d, J = 8.4 Hz, 2H, 2,6-ArH), 6.32 (dd, J = 2.4, 8.1 Hz, 1H, 6′-ArH), 6.26 (dd, J = 2.4, 8.1 Hz, 1H, 4′-ArH), 6.21 (t, J = 2.1 Hz, 1H, 2′-ArH), 3.87 (brs, 2H, NH), 3.79 (s, 3H, OCH_3), 3.21–3.23 (m, 2H, CH-N), 2.36–2.41 (m, 2H, CH_2), 1.79–1.82 (m, 2H, CH_2), 1.41–1.48 (m, 2H, CH_2), 1.23–1.27 (m, 2H, CH_2).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 160.8, 149.6, 149.0, 129.9, 129.2, 117.4, 113.4, 106.4, 102.5, 99.4, 57.2, 57.1, 55.0, 32.5, 34.4, 24.5 (2C).

HR-MS (ESI, $CHCl_3$–MeOH): calcd for $C_{19}H_{25}N_2O$ ($[M + H]^+$): 297.19669; found: 297.19614, calcd for $C_{19}H_{24}N_2NaO$ ($[M + Na]^+$): 319.17863; found: 319.17808, calcd for $C_{38}H_{48}F_2N_4NaO$ ($[2M + Na]^+$): 615.36750; found: 615.36695.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 90/10, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 8.34 min; major enantiomer (1*S*,2*S*) t_R = 9.64 min.

(1*S*,2*S*)-*N*-(3-Bromophenyl)-*N*′-phenylcyclohexane-1,2-diamine (3n).[3j] Yield: 160 mg (93%), 83% ee as a pale yellow oil.

$[\alpha]_D^{20}$ = −34.2 (c = 0.729, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/10): 0.42.

IR (film): ν (cm^{-1}) = 3392, 3053, 3021, 2933, 2857, 1595, 1498, 1480, 1448, 1384, 1317, 1254, 1204, 1179, 1155, 1137, 1106, 1028, 986, 889, 842, 825, 787, 761, 693.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.20 (dd, J = 7.5, 8.4 Hz, 2H, 3,5-ArH), 7.02 (t, J = 8.1 Hz, 1H, 5′-ArH), 6.83 (ddd, J = 0.9, 1.6, 7.8 Hz, 1H, 4′-ArH), 6.72–6.77 (m, 2H, 2′-ArH, 4-ArH), 6.63 (d, J = 8.0 Hz, 2H, 2,6-ArH), 6.51 (ddd, J = 0.9, 1.8, 7.3 Hz, 1H, 6′-ArH), 3.80 (brs, 2H, NH), 3.23 (dt, J = 3.6, 9.3 Hz, 1H, CH-N), 3.16 (dt, J = 3.6, 9.3 Hz, 1H, CH-N), 2.31–2.37 (m, 2H, CH_2), 1.78–1.82 (m, 2H, CH_2), 1.39–1.47 (m, 2H, CH_2), 1.21–1.25 (m, 2H, CH_2).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 149.8, 147.5, 130.5 129.3, 123.3, 120.1, 117.7, 115.7, 113.5, 112.2, 57.2, 57.0, 32.4, 32.3, 24.5, 24.4.

HR-MS (ESI, $CHCl_3$–MeOH): calcd for $C_{18}H_{22}Br\ N_2$ ($[M + H]^+$): 345.09664, found: 345.09609, calcd for $C_{18}H_{22}BrN_2Na$ ($[M + Na]^+$): 367.07858; found: 367.07803, calcd for $C_{38}H_{42}Br_2N_4Na$ ($[2M + Na]^+$): 711.16739; found: 711.16684.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 6.98 min; major enantiomer (1*S*,2*S*) t_R = 8.17 min.

(1*S*,2*S*)-*N*-Phenyl-*N*′-(3-trifluoromethylphenyl)cyclohexane-1,2-diamine (3o). Yield: 150 mg (90%), 82% ee as a colourless viscous liquid.

$[\alpha]_D^{20}$ = −15.9 (c = 2.819, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/10): 0.33.

UV (CH_3CN): λ_{max} (lg ε) = 253 (4.146) nm.

IR (film): ν (cm^{-1}) = 3393, 3053, 2936, 2858, 1601, 1502, 1433, 1383, 1341, 1317, 1255, 1165, 1125, 1069, 1028, 994, 899, 865, 824, 787, 696, 662, 500, 451.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.26 (t, J = 8.0 Hz, 1H, 5′-ArH), 7.21 (dd, J = 7.6, 8.4 Hz, 2H, 3,5-ArH), 6.95 (d, J = 7.6 Hz, 1H, 4′-ArH), 6.81 (s, 1H, 2′-ArH), 6.73–6.77 (m, 2H, 4-ArH, 6′-ArH), 6.65 (d, J = 8.0 Hz, 2H, 2,6-ArH), 4.06 (brs, 1H, NH), 3.67 (brs, 1H, NH), 3.22–3.28 (m, 2H, CH-N), 2.33–2.37 (m, 2H, CH_2), 1.81–1.84 (m, 2H, CH_2), 1.43–1.48 (m, 2H, CH_2), 1.25–1.31 (m, 2H, CH_2).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.9, 147.4, 131.5 (q, $^2J_{CF}$ = 31.6 Hz), 129.6, 129.3, 124.2 (q, $^1J_{CF}$ = 271 Hz), 117.7, 116.3, 113.7 (q, $^3J_{CF}$ = 3.8 Hz), 113.4, 109.3 (q, $^3J_{CF}$ = 3.8 Hz), 57.2, 57.0, 32.4, 32.2, 24.5, 24.4.

HR-MS (ESI, $CHCl_3$–MeOH): calcd for $C_{19}H_{22}F_3N_2$ ($[M + H]^+$): 335.17351; found: 335.17296, calcd for $C_{19}H_{21}F_3N_2Na$ ($[M + Na]^+$): 357.15545; found: 357.15490, calcd for $C_{38}H_{42}F_6N_4Na$ ($[2M + Na]^+$): 691.32114; found: 691.32059.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 5.33 min; major enantiomer (1*S*,2*S*) t_R = 6.04 min.

(1*S*,2*S*)-*N*-Phenyl-*N*′-*o*-tolylcyclohexane-1,2-diamine (3p).[3j] Yield: 126 mg (90%), 47% ee as a pale yellow oil.

$[\alpha]_D^{20}$ = +5.8° (*c* = 0.69, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/10): 0.46.

UV (CH_3CN): λ_{max} (lg ε) = 292 (3.827), 252 (4.453) nm.

IR (film): ν (cm^{-1}) = 3382, 2931, 2856, 1762, 1602, 1502, 1383, 1318, 1256, 1139, 1052, 875, 824, 786, 747, 692.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.16–7.26 (m, 3H, 3,5-Ar**H**, 5′-Ar**H**), 7.09 (dd, *J* = 0.6, 6.9 Hz, 1H, 3′-Ar**H**), 6.66–6.79 (m, 5H, 4-Ar**H**, 4′-Ar**H**, 2,6-Ar**H**, 6′-Ar**H**), 3.79 (brs, 2H, N**H**), 3.37 (dt, *J* = 3.6, 9.0 Hz, 1H, C**H**-N), 3.28 (dt, *J* = 3.6, 9.0 Hz, 1H, C**H**-N), 2.37–2.46 (m, 2H, C$\mathbf{H}_2$), 2.04 (s, 3H, C$\mathbf{H}_3$), 1.82–1.86 (m, 2H, C$\mathbf{H}_2$), 1.46–1.52 (m, 2H, C$\mathbf{H}_2$), 1.28–1.37 (m, 2H, C$\mathbf{H}_2$).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 147.9, 145.7, 130.3, 129.3, 126.9, 122.8, 117.5, 116.9, 113.4, 110.1, 57.7, 57.1, 32.70, 24.7, 24.6, 17.5.

HR-MS (ESI, $CHCl_3$–MeOH): calcd for $C_{19}H_{25}N_2$ ($[M + H]^+$): 281.20177; found: 281.20123, calcd for $C_{19}H_{24}N_2Na$ ($[M + Na]^+$): 303.18372; found: 303.18317, calcd for $C_{38}H_{48}N_4Na$ ($[2M + Na]^+$): 584.37767; found: 583.37712.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 5.01 min; major enantiomer (1*S*,2*S*) t_R = 6.50 min.

(1*S*,2*S*)-*N*-(2-Methoxyphenyl)-*N*′-phenylcyclohexane-1,2-diamine (3q).[12a] Yield: 117 mg (79%), 56% ee as a colourless solid; m.p.: 94–95 °C.

$[\alpha]_D^{20}$ = not measurable (*c* = 0.90, $CHCl_3$) [lit.[2] $[\alpha]_D^{25}$ = −4.1 (*c* = 1.25, 99% ee, $CHCl_3$)].

R_f (EtOAc–petroleum ether, 1/10): 0.24.

UV (CH_3CN): λ_{max} = 294, 252, 234 nm.

IR (as film in CCl_4): ν (cm^{-1}) = 3374, 3337, 3015, 2922, 1599, 1504, 1452, 1255, 1222, 1116.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.16–7.20 (m, 2H, 3,5-Ar**H**), 6.87–6.91 (m, 1H, 4-Ar**H**), 6.61–6.78 (m, 6H, 2,6-Ar**H**, 3′,4′,5′,6′-Ar**H**), 4.33 (brs, 1H, N**H**), 3.94 (brs, 1H, N**H**), 3.77 (s, 3H, OC$\mathbf{H}_3$), 3.26–3.28 (m, 2H, C**H**-N), 2.31–2.41 (m, 2H, C$\mathbf{H}_2$), 1.78–1.80 (m, 2H, C$\mathbf{H}_2$), 1.42–1.47 (m, 2H, C$\mathbf{H}_2$), 1.26–1.28 (m, 2H, C$\mathbf{H}_2$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 148.0, 147.4, 137.6, 129.3, 121.2, 117.4, 116.6, 113.7, 110.3, 109.8, 57.2, 56.8, 55.4, 32.5, 32.4, 24.8, 24.5.

MS (ESI, acetone): *m*/*z* = 297 $[M + H]^+$, 319 $[M + Na]^+$, 335 $[M + K]^+$.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 6.08 min; major enantiomer (1*S*,2*S*) t_R = 9.60 min.

(1*S*,2*S*)-*N*-(2-Fluorophenyl)-*N*′-phenylcyclohexane-1,2-diamine (3r). Yield: 126 mg (89%), 76% ee as a colourless oil.

$[\alpha]_D^{20}$ = −31.3 (*c* = 0.606, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/10): 0.40.

UV (CH_3CN): λ_{max} (lg ε) = 290 (3.691), 248 (4.297) nm.

IR (film): ν (cm^{-1}) = 3396, 3049, 3021, 2929, 2856, 2631, 1918, 1826, 1746, 1619, 1495, 1449, 1384, 1358, 1334, 1254, 1206, 1186, 1156, 1136, 1106, 1080, 1033, 993, 954, 939, 914, 976, 839, 784, 745, 693, 620, 550, 504, 445.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.23 (t, *J* = 7.6 Hz, 2H, 3,5-Ar**H**), 6.98–7.07 (m, 2H, 3′,5′-Ar**H**), 6.76–6.84 (m, 2H, 4′,6′-Ar**H**), 6.67–6.71 (m, 3H, 2,4,6-Ar**H**), 4.05 (brs, 1H, N**H**), 3.87 (brs, 1H, N**H**), 3.29 (brs, 2H, C**H**-N), 2.33–2.43 (m, 2H, C$\mathbf{H}_2$), 1.81–1.84 (m, 2H, C$\mathbf{H}_2$), 1.45–1.50 (m, 2H, C$\mathbf{H}_2$), 1.29–1.36 (m, 2H, C$\mathbf{H}_2$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 151.9 (d, $^1J_{CF}$ = 237 Hz), 147.6, 136.9 (d, $^2J_{CF}$ = 11.5 Hz), 129.2, 124.4 (d, $^4J_{CF}$ = 3.3 Hz), 117.5, 116.8 (d, $^3J_{CF}$ = 7.0 Hz), 114.7 (d, $^2J_{CF}$ = 18.7 Hz), 113.5, 112.6 (d, $^3J_{CF}$ = 3.2 Hz), 57.0, 56.8, 32.3, 32.2, 24.5, 24.3.

HR-MS (ESI, $CHCl_3$–MeOH): calcd for $C_{18}H_{22}FN_2$ ($[M + H]^+$): 285.17670; found: 285.17616, calcd for $C_{18}H_{21}FN_2Na$ ($[M + Na]^+$): 307.15865; found: 307.15810, calcd for $C_{36}H_{42}F_2N_4Na$ ($[2M + Na]^+$): 591.32752; found: 591.32697.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 5.48 min; major enantiomer (1*S*,2*S*) t_R = 6.91 min.

(1*S*,2*S*)-*N*-(2-Carbomethoxyphenyl)-*N*′-phenylcyclohexane-1,2-diamine (3s). Yield: 240 mg (75%), 22% ee as a colourless solid; m.p.: 105–106 °C.

$[\alpha]_D^{24}$ = −15.2 (*c* = 0.987, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/5): 0.28.

UV (CH_3CN): λ_{max} (lg ε) = 432 (2.951), 350 (3.701), 250 (4.135), 231 (3.937) nm.

IR (KBr): ν (cm^{-1}) = 3385, 3344, 3085, 3028, 2943, 2925, 2853, 1680, 1598, 1579, 1518, 1495, 1438, 1308, 1253, 1236, 1200, 1180, 1165, 1135, 1102, 1077, 1048, 990, 875, 846, 797, 743, 702, 690, 629, 558, 526, 478.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.87–7.90 (m, 2H, 3′-Ar**H**, N**H**), 7.33 (dt, *J* = 2.4, 7.8 Hz, 1H, 5′-Ar**H**), 7.14 (dd, *J* = 7.2, 7.2 Hz, 2H, 3,5-Ar**H**), 6.77 (d, *J* = 8.7 Hz, 1H, 6′-Ar**H**), 6.67 (t, *J* = 7.2 Hz, 1H, 4′-Ar**H**), 6.54–6.61 (m, 3H, 2,6-Ar**H**, 4-Ar**H**), 3.79 (brs, 2H, N**H**), 3.37 (dt, *J* = 3.6, 9.0 Hz, 1H, C**H**-N), 3.28 (dt, *J* = 3.6, 9.0 Hz, 1H, C**H**-N), 2.37–2.46 (m, 2H, C$\mathbf{H}_2$), 1.82–1.86 (m, 2H, C$\mathbf{H}_2$), 1.46–1.52 (m, 2H, C$\mathbf{H}_2$), 1.28–1.37 (m, 2H, C$\mathbf{H}_2$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.9, 150.6, 147.0, 134.4, 131.9, 129.1, 117.7, 114.5, 113.9, 111.5, 110.4, 56.4, 54.5, 51.4, 30.9, 26.8, 23.8, 23.5.

HR-MS (ESI, MeOH): calcd for $C_{20}H_{25}N_2O_2$ ($[M + H]^+$): 325.19105; found: 325.19089, calcd for $C_{20}H_{24}N_2O_2$ ($[M + Na]^+$): 347.17300; found: 347.17273, calcd for $C_{20}H_{42}F_2N_4Na$ ($[2M + Na]^+$): 671.35678; found: 671.35636.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 98/2, flow rate = 1.0 mL min^{-1}; major enantiomer (1*S*,2*S*) t_R = 8.72; minor enantiomer (1*R*,2*R*) t_R = 9.78 min.

(1*S*,2*S*)-*N*-(1-Naphthyl)-*N*′-phenylcyclohexane-1,2-diamine (3t).[3j] Yield: 142 mg (86%), 77% ee as a colorless solid; reaction time: 48 h.

R_f (EtOAc–petroleum ether, 1/10) = 0.40.

UV (CH_3CN): λ_{max} (lg ε) = 332 (4.037), 251 (4.546) nm.

IR (KBr): ν (cm^{-1}) = 3374, 3055, 2917, 2849, 1913, 1600, 1581, 1527, 1508, 1480, 1436, 1407, 1373, 1357, 1337, 1316, 1305, 1295, 1255, 1178, 1169, 1153, 1135, 1114, 1085, 1070, 1037, 1026, 1017, 991, 949, 863, 848, 787, 771, 746, 692, 642, 601, 573, 502, 466, 420.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 8.0 Hz, 1H, Ar**H**), 7.70 (d, J = 8.0 Hz, 1H, Ar**H**), 7.42–7.45 (m, 1H, Ar**H**), 7.37–7.39 (m, 2H, Ar**H**), 7.20–7.28 (m, 3H, Ar**H**), 6.77 (t, J = 7.2 Hz, 1H, Ar**H**), 6.69–6.71 (m, 3H, Ar**H**), 4.71 (brs, 1H, N**H**), 3.87 (brs, 1H, N**H**), 3.50 (dt, J = 3.2, 9.8 Hz, 1H, C**H**-N), 3.37 (dt, J = 3.2, 9.8 Hz, 1H, C**H**-N), 2.55 (d, J = 14 Hz, 1H, C$\mathbf{H}_2$), 2.41 (d, J = 14 Hz, 1H, C$\mathbf{H}_2$), 1.84–1.86 (m, 2H, C$\mathbf{H}_2$), 1.47–1.53 (m, 2H, C$\mathbf{H}_2$), 1.29–1.35 (m, 2H, C$\mathbf{H}_2$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.6, 142.9, 134.5, 129.5, 125.8, 124.8, 124.1, 120.3, 118.0, 117.6, 114.0, 105.0, 57.9, 57.3, 32.70, 32.12, 25.03, 24.66.

MS (EI, 70 eV): m/z (%) = 317 (100) $[M + H]^+$, 224, 174.

HPLC: Chiralcel OD-H column, hexane–i-PrOH = 85/15, flow rate = 1.0 mL min^{-1}; minor enantiomer (1R,2R) t_R = 8.63 min; major enantiomer (1S,2S) t_R = 19.51 min.

(1*S*,2*S*)-*N*-(2,4-Difluorophenyl)-*N*′-phenylcyclohexane-1,2-diamine (3u). Yield: 126 mg (83%) as a pale yellow oil; ee: 65%.

$[\alpha]_D^{20}$ = −24.1 (c = 0.706, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/10): 0.25.

UV (CH_3CN): λ_{max} (lg ε) = 297 (3.716), 249 (4.297) nm.

IR (film): ν (cm^{-1}) = 3395, 3052, 3021, 2933, 2857, 2661, 1826, 1602, 1503, 1431, 1383, 1304, 1265, 1213, 1196, 1179, 1141, 1098, 1083, 1028, 993, 960, 910, 872, 848, 825, 798, 749, 722, 693, 586, 539, 500, 450.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.18 (dd, J = 7.6, 8.6 Hz, 2H, 3,5-Ar**H**), 6.62–6.79 (m, 7H, 4′,6′,3′,5′,2,4,6-Ar**H**), 3.80 (brs, 2H, N**H**), 3.25 (dt, J = 3.6, 9.8 Hz, 1H, C**H**-N), 3.14–3.18 (m, 1H, C**H**-N), 2.33–2.36 (m, 2H, C$\mathbf{H}_2$), 1.77–1.79 (m, 2H, C$\mathbf{H}_2$), 1.40–1.45 (m, 2H, C$\mathbf{H}_2$), 1.23–1.39 (m, 2H, C$\mathbf{H}_2$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 154.3 (dd, $^{1,3}J_{CF}$ = 11, 237 Hz), 151.4 (dd, $^{1,3}J_{CF}$ = 11.5, 240 Hz), 147.5, 132.5 (dd, $^{2,4}J_{CF}$ = 2.8, 11.5 Hz), 129.2, 117.6, 113.6, 113.0 (dd, $^{3,3}J_{CF}$ = 4.4, 8.9 Hz), 110.5 (dd, $^{2,4}J_{CF}$ = 3.7, 21.6 Hz), 103.6 (dd, $^{2,2}J_{CF}$ = 23, 26.3 Hz), 57.5, 57.1, 32.3, 32.2, 24.4, 24.3.

HR-MS (ESI, $CHCl_3$–MeOH): calcd for $C_{18}H_{21}F_2N_2$ ($[M + H]^+$): 303.16728; found: 303.16673, calcd for $C_{18}H_{20}F_2N_2Na$ ($[M + Na]^+$): 325.14922; found: 325.14868, calcd for $C_{36}H_{40}F_4N_4Na$ ($[2M + Na]^+$): 627.30868; found: 627.30813.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1R,2R) t_R = 5.88 min; major enantiomer (1S,2S) t_R = 7.29 min.

(1*S*,2*S*)-*N*-(3,4-Dimethoxyphenyl)-*N*′-phenylcyclohexane-1,2-diamine (3v). Yield: 126 mg (81%), 98% ee as a pale yellow oil.

$[\alpha]_D^{20}$ = −111.6 (c = 0.197, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/3): 0.25.

UV (CH_3CN): λ_{max} (lg ε) = 297 (3.716), 249 (4.297) nm.

IR (film): ν (cm^{-1}) = 3370, 3051, 2997, 2932, 2855, 2831, 1601, 1513, 1463, 1383, 1295, 1258, 1235, 1210, 1168, 1139, 1104, 1127, 993, 954, 867, 825, 752, 694, 568, 504, 462.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.20 (m, 2H, 3,5-Ar**H**), 6.72–6.79 (m, 2H, 4-Ar**H**, 6′-Ar**H**), 6.66 (d, J = 8.4 Hz, 2H, 2,6-Ar**H**), 6.26 (d, J = 2.7 Hz, 1H, 2′-Ar**H**), 6.21 (dd, J = 2.7, 8.4 Hz, 1H, 5′-Ar**H**), 3.88 (brs, 1H, N**H**), 3.83 (s, 6H, OC$\mathbf{H}_3$), 3.68 (brs, 1H, N**H**), 3.18–3.25 (m, 1H, C**H**-N), 3.13 (dt, J = 3.3, 9.5 Hz, 1H, C**H**-N), 2.28–2.34 (m, 2H, C$\mathbf{H}_2$), 1.78–1.82 (m, 2H, C$\mathbf{H}_2$), 1.40–1.43 (m, 2H, C$\mathbf{H}_2$), 1.22–1.26 (m, 2H, C$\mathbf{H}_2$).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 149.9, 147.6, 142.3, 141.6, 129.1, 117.4, 113.4, 113.0, 104.1, 100.1, 58.0, 57.1, 56.5, 55.5, 32.4, 32.3, 24.4 (2C).

HR-MS (ESI, $CHCl_3$–MeOH): calcd for $C_{20}H_{27}N_2O_2$ ($[M + H]^+$): 327.20725; found: 327.20670, calcd for $C_{20}H_{26}N_2NaO_2$ ($[M + Na]^+$): 349.18920; found: 349.18865, calcd for $C_{40}H_{52}N_4NaO_4$ ($[2M + Na]^+$): 675.38863; found: 675.38808.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 85/15, flow rate = 1.0 mL min^{-1}; minor enantiomer (1R,2R) t_R = 11.15 min; major enantiomer (1S,2S) t_R = 12.57 min.

(1*S*,2*S*)-*N*-Phenyl-*N*′-(3,4,5-trimethoxyphenyl)cyclohexane-1,2-diamine (3w).[15d] Yield: 126 mg (84%), 98% ee as a pale yellow oil.

$[\alpha]_D^{20}$ = −25.2 (c = 2.857, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/3): 0.22.

UV (CH_3CN): λ_{max} (lg ε) = 248 (4.556) nm.

IR (film): ν (cm^{-1}) = 3369, 3052, 2933, 2856, 1601, 1506, 1463, 1451, 1430, 1412, 1384, 1315, 1278, 1236, 1204, 1184, 1127, 1011, 868, 787, 694, 633, 525.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.18 (d, J = 7.2, 8.8 Hz, 2H, 3,5-Ar**H**), 6.72 (t, J = 7.2 Hz, 1H, 4-Ar**H**), 6.64 (d, J = 8.8 Hz, 2H, 2,6-Ar**H**), 5.86 (s, 2H, 2′,6′-Ar**H**), 3.84 (brs, 2H, N**H**), 3.80 (s, 6H, OC$\mathbf{H}_3$), 3.77 (s, 3H, OC$\mathbf{H}_3$), 3.21 (dt, J = 3.2, 9.8 Hz, 1H, C**H**-N), 3.15 (dt, J = 3.2, 9.8 Hz, 1H, C**H**-N), 2.33–2.36 (m, 2H, C$\mathbf{H}_2$), 1.78–1.81 (m, 2H, C$\mathbf{H}_2$), 1.41–1.46 (m, 2H, C$\mathbf{H}_2$), 1.22–1.28 (m, 2H, C$\mathbf{H}_2$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.9, 147.6, 144.3, 130.2, 129.2, 117.5, 113.4, 91.2, 60.9, 57.6, 57.1, 55.9 (2C), 32.6, 32.3, 24.48, 24.46.

HR-MS (ESI, $CHCl_3$–MeOH): calcd for $C_{21}H_{29}N_2O_3$ ($[M + H]^+$): 357.21782; found: 357.21727, calcd for $C_{21}H_{28}N_2NaO_3$ ($[M + Na]^+$): 379.19976; found: 379.19921, calcd for $C_{42}H_{56}N_4NaO_6$ ($[2M + Na]^+$): 735.40976; found: 735.40976.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 85/15, flow rate = 1.0 mL min^{-1}; minor enantiomer (1R,2R) t_R = 14.98 min; major enantiomer (1S,2S) t_R = 16.50 min.

(1*S*,1′*S*,2*S*,2′*S*)-N^1,$N^{1'}$-(1,4-Phenylene)bis(N^2-phenylcyclohexane-1,2-diamine) (3x). Yield: 136 mg (70%), 98% ee as a colourless solid; m.p.: 120–121 °C.

$[\alpha]_D^{20}$ = −131.4 (c = 0.837, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/5): 0.34.

UV (CH_3CN): λ_{max} (lg ε) = 256 (4.507) nm.

IR (film): ν (cm^{-1}) = 3387, 3347, 3014, 2925, 2851, 1600, 1502, 1447, 1429, 1357, 1312, 1293, 1245, 1204, 1176, 1152, 1132, 1102, 991, 872, 825, 748, 692, 641, 566, 507, 477.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.19 (dd, J = 7.2, 8.4 Hz, 4H, 3,5-Ar**H**), 6.72 (t, J = 7.2 Hz, 2H, 4-Ar**H**), 6.65 (d, J = 8.4 Hz, 4H, 2,6-Ar**H**), 6.58 (s, 4H, 2′,3′,5′,6′-Ar**H**), 3.69 (brs, 4H, N**H**), 3.18 (dt, J = 3.6, 9.8 Hz, 2H, C**H**-N), 3.07 (dt, J = 3.6, 9.8 Hz, 2H,

CH-N), 2.26–2.31 (m, 4H, CH_2), 1.76–1.79 (m, 4H, CH_2), 1.38–1.44 (m, 4H, CH_2), 1.17–1.26 (m, 4H, CH_2).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.9, 140.9, 129.2, 117.5, 116.0, 113.6, 58.5, 57.3, 32.6, 32.5, 24.68, 24.64.

HR-MS (ESI, $CHCl_3$, MeOH): calcd for $C_{30}H_{38}N_4$ ($[M]^+$): 454.30965; found: 454.30915, calcd for $C_{30}H_{38}N_4Na$ ($[M + Na]^+$): 477.29942; found: 477.29911, calcd for $C_{60}H_{77}N_8$ ($[2M + H]^+$): 909.62712; found: 909.62624, calcd for $C_{60}H_{76}N_8Na$ ($[2M + Na]^+$): 931.60906; found: 931.60871.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 80/20, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,1′*R*,2*R*,2′*R*) t_R = 18.94 min; *meso* isomer t_R = 25.6 min; major enantiomer (1*S*,1′*S*,2*S*,2′*S*) t_R = 35.91 min.

(1*S*,2*S*)-*N*,*N*′-Di(4-methoxyphenyl)cyclohexane-1,2-diamine (3y). Yield: 140 mg (86%), 98% ee as a colorless solid; m.p.: 67–68 °C.

$[\alpha]_D^{20}$ = −35.0 (*c* = 0.97, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/3) = 0.37.

UV (CH_3CN): λ_{max} (lg ε) = 244 (4.234), 247 (4.231), 312 (3.608) nm.

IR (KBr): ν (cm^{-1}) = 3347, 3025, 2950, 1508, 1465, 1352, 1242, 1180.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.79 (dd, *J* = 2.4, 6.8 Hz, 4H, 3,5-Ar**H**), 6.63 (dd, *J* = 2.4, 6.8 Hz, 4H, 2,6-Ar**H**), 3.76 (s, 6H, OCH_3), 3.66 (brs, 2H, N**H**), 3.07–3.09 (m, 2H, C**H**-N), 2.30–2.33 (m, 2H, CH_2), 1.70–1.76 (m, 2H, CH_2), 1.37–1.41 (m, 2H, CH_2), 1.19–1.21 (m, 2H, CH_2).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 152.5, 141.9, 115.6, 115.0, 58.7, 55.9, 32.8, 24.8.

HR-MS (ESI, MeOH): calcd for $C_{20}H_{27}N_2O_2$ ($[M + H]^+$): 327.20670; found: 327.20660.

HPLC: Chiralcel OD-H column, hexane–i-PrOH = 70/30, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 81.12 min; major enantiomer (1*S*,2*S*) t_R = 109.05 min.

(1*S*,2*S*)-*N*,*N*′-Diphenylcyclopentane-1,2-diamine (4a).[3j] Yield: 130 mg (90%), >99% ee as a yellow oil.

$[\alpha]_D^{22}$ = +45.5 (*c* = 0.99, $CHCl_3$).

R_f (ether–petroleum ether, 1/4): 0.26.

UV (CH_3CN): λ_{max} (lg ε) = 201 (4.325), 206 (4.304), 251 (4.402) nm.

IR (film): ν (cm^{-1}) = 3393, 3050, 2958, 2871, 1601, 1431, 1384, 1321, 1179.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.16 (dd, *J* = 7.5, 8.5 Hz, 4H, 3,5-Ar**H**), 6.71 (t, *J* = 8.5 Hz, 2H, 4-Ar**H**), 6.63 (d, *J* = 8.5 Hz, 4H, 2,6-Ar**H**), 3.77 (brs, 2H, N**H**), 3.57–3.63 (m, 2H, **H**C-N), 2.25 (dq, *J* = 7.5, 13.5 Hz, 2H, C**H**H), 1.81 (quin, *J* = 7.5 Hz, 2H, CH_2), 1.53 (dq, *J* = 7.5 Hz, 13.5 Hz, 2H, CH**H**).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.7, 129.3, 117.5, 113.4, 60.6, 31.2, 21.4.

MS (EI, 70 eV): *m*/*z* (%) = 252 (11), 160 (100), 149 (10), 132 (85), 118 (48), 106 (65), 93 (85).

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 11.62 min; major enantiomer (1*S*,2*S*) t_R = 13.52 min.

(1*S*,2*S*)-*N*-Phenyl-*N*′-*p*-tolylcyclopentane-1,2-diamine (4b).[15a] Yield: 110 mg (83%), >99% ee as a yellow oil.

$[\alpha]_D^{22}$ = +28.1 (*c* = 1.02, $CHCl_3$).

R_f (ether–petroleum ether, 1/4) = 0.30.

UV ($CHCl_3$): λ_{max} (lg ε) = 250 (4.424), 295 (3.778) nm.

IR (film): ν (cm^{-1}) = 3391, 3018, 2957, 1601, 1504, 1430, 1316, 1242, 1180.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.19 (dd, *J* = 7.5, 8.5 Hz, 2H, 3,5-Ar**H**), 7.00 (d, *J* = 8.0 Hz, 2H, 3′,5′-Ar**H**), 6.73 (t, *J* = 7.5 Hz, 1H, 4-Ar**H**), 6.65 (d, *J* = 7.5 Hz, 2H, 2,6-Ar**H**), 6.58 (d, *J* = 8.5 Hz, 2H, 2′,6′-Ar**H**), 3.72 (brs, 2H, N**H**), 3.57–3.63 (m, 2H, **H**C-N), 2.21–2.30 (m, 5H, C**H**H,CH_3), 1.82 (quin, *J* = 7.5 Hz, 2H, CH_2), 1.54 (dt, *J* = 7.5, 13.5 Hz, 2H, CH**H**).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.8, 145.4, 129.8, 129.3, 126.8, 117.5, 113.6, 113.4, 60.99, 60.66, 31.19 (2C), 21.4, 20.3.

MS (EI, 70 eV): *m*/*z* (%) = 266 (73), 189 (72), 174 (100), 160 (79), 132 (16), 91 (9), 77 (12).

HR-MS (ESI, MeOH): calcd for $C_{18}H_{23}N_2$ ($[M + H]^+$): 267.18049; found: 267.18548.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 11.28 min; major enantiomer (1*S*,2*S*) t_R = 12.93 min.

(1*S*,2*S*)-*N*-(4-Methoxyphenyl)-*N*′-phenylcyclopentane-1,2-diamine (4c).[15a] Yield: 136 mg (96%), >99% ee as a yellow oil.

$[\alpha]_D^{22}$ = +24.4 (*c* = 1.02, $CHCl_3$).

R_f (ether–petroleum ether, 1/4): 0.14.

UV ($CHCl_3$): λ_{max} (lg ε) = 248 (4.350), 300 (3.653) nm.

IR (film): ν (cm^{-1}) = 3386, 3050, 2954, 1602, 1512, 1440, 1316, 1234, 1179.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.19 (t, 2H, 3,5-Ar**H**), 6.61–6.82 (m, 7H, Ar**H**), 3.76 (s, 3H, OCH_3), 3.75 (brs, 2H, N**H**), 3.57 (m, 2H, **H**C-N), 2.24 (dt, *J* = 7.0, 13.5 Hz, 2H, C**H**H), 1.81 (quin, *J* = 7.5 Hz, 2H, C**H**2), 1.53 (dt, *J* = 7.5, 13.5 Hz, 2H, CH**H**).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 152.3, 147.8, 141.9, 129.3, 117.5, 114.9, 114.8, 113.4, 61.6, 60.6, 55.8, 31.25, 31.19, 21.4.

MS (EI, 70 eV): *m*/*z* (%) = 282 (32), 190 (100), 160 (91), 132 (13), 123 (7), 93 (6); 77 (8).

HR-MS (ESI, MeOH): calcd for $C_{18}H_{23}N_2O$: 283.18104 ($[M + H]^+$); found: 283.18028.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 21.01 min; major enantiomer (1*S*,2*S*) t_R = 26.05 min.

(1*S*,2*S*)-*N*-Phenyl-*N*′-(4-trifluoromethylphenyl)-cyclopentane-1,2-diamine (4d).[15a] Yield: 114 mg (71%), 95% ee as a yellow oil.

$[\alpha]_D^{22}$ = +23.6 (*c* = 1.02, $CHCl_3$).

R_f (ether–petroleum ether, 1/4): 0.10.

UV ($CHCl_3$): λ_{max} (lg ε) = 259 (4.259), 287 (3.610), 341 (2.591) nm.

IR (film): ν (cm^{-1}) = 3396, 2960, 1615, 1503, 1432, 1326, 1158, 1108.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 8.5 Hz, 2H, 3′,5′-Ar**H**), 7.19 (dd, *J* = 7.5, 8.5 Hz, 2H, 3,5-Ar**H**), 6.74 (t, *J* = 7.5 Hz, 1H, 4-Ar**H**), 6.63–6.65 (m, 4H, 2,6-Ar**H**, 2′,6′-Ar**H**), 4.11 (d, *J* = 4.0 Hz, 1H, N**H**), 3.73 (brs, 1H, N**H**), 3.64 (s, 2H, **H**CN), 2.27 (dt, *J* = 8.0, 13.5 Hz, 2H, CH**H**), 1.84 (quin, *J* = 8.0 Hz, 2H, C**H**2), 1.53–1.61 (m, 2H, CH**H**).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 150.2, 147.4, 129.4, 126.6 (q, $^3J_{CF}$ = 3.7 Hz), 124.9 (q, $^1J_{CF}$ = 268.8 Hz), 118.9 (q, $^2J_{CF}$ = 33.0 Hz), 117.8, 113.4, 112.4, 60.71, 60.32, 31.23, 31.08, 21.5.

MS (EI, 70 eV): *m*/*z* (%) = 320 (17), 228 (100), 200 (9), 160 (68), 132 (17), 106 (11), 77 (7).

HR-MS (ESI, MeOH): calcd for $C_{18}H_{20}F_3N_2$ ($[M + H]^+$): 321.15786; found: 321.15712.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 14.87 min; major enantiomer (1*S*,2*S*) t_R = 18.31 min.

4-((1*S*,2*S*)-2-(Phenylamino)cyclopentylamino)benzenethiol (4e). Yield: 97 mg (68%), 99% ee as a pale yellow oil.

$[\alpha]_D^{20}$ = −3.2 (*c* = 0.936, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/10): 0.29.

UV (CH_3CN): λ_{max} (lg ε) = 256 (4.368) nm.

IR (as film in CCl_4): ν (cm^{-1}) = 3394, 3052, 3021, 2961, 2872, 1599, 1500, 1431, 1384, 1316, 1293, 1181, 1154, 1126, 871, 786, 693, 506.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.19 (dd, *J* = 7.2, 8.6 Hz, 4H, 3,5-Ar**H**, 3′,5′-Ar**H**), 6.73 (t, *J* = 7.2 Hz, 1H, 4-Ar**H**), 6.64 (d, *J* = 8.8 Hz, 2H, 2,6-Ar**H**), 6.54 (d, *J* = 8.8 Hz, 2H, 2′,6′-Ar**H**), 3.76 (brs, 2H, N**H**), 3.55–3.63 (m, 2H, C**H**-N), 3.30 (s, 1H, S**H**), 2.19–2.29 (m, 2H, C**H**$_2$), 1.78–1.86 (m, 2H, C**H**$_2$), 1.49–1.59 (m, 2H, C**H**$_2$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.5, 146.7, 133.2, 129.2, 117.6, 114.8, 114.0, 113.3, 60.65, 60.63, 31.1, 31.0, 21.4.

HR-MS (ESI, MeOH): calcd for $C_{17}H_{20}N_2NaS$ ($[M + Na]^+$): 307.12449; found: 307.12394, calcd for $C_{34}H_{40}N_4NaS_2$ ($[2M + Na]^+$): 591.25921; found: 591.25866.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 24.10 min; major enantiomer (1*S*,2*S*) t_R = 30.11 min.

(1*S*,2*S*)-*N*-(2-Methoxyphenyl)-*N*′-phenylcyclopentan-1,2-diamine (4f).[12a] Yield: 112 mg (80%), 57% ee as a yellow oil; m.p.: 127–128 °C, reaction time 24 h.

$[\alpha]_D^{22}$ = 21.7° (*c* = 1.00, $CHCl_3$).

R_f (ether–petroleum ether 1/4) = 0.33.

UV ($CHCl_3$): λ_{max} (lg ε) = 251 (4.399), 292 (3.892) nm.

IR (film): ν (cm^{-1}) = 3396, 3049, 2957, 2869, 2833, 1601, 1506, 1455, 1430, 1309, 1243, 1222, 1179, 1127, 1075, 1049, 1028, 993, 872, 810, 747, 693, 508.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.18 (dd, 2H, *J* = 7.5, 8.5 Hz, 2′-C**H**), 6.64–6.88 (m, 7H, Ar**H**), 4.33 (s, 1H, N**H**), 3.84 (s, 3H, OC**H**$_3$), 3.61–3.70 (m, 2H, **H**C-N), 2.21–2.33 (m, 2H, C**H**$_2$), 1.79 (m, 2H, C**H**$_2$), 1.53–1.63 (m, 2H, C**H**$_2$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.8 (**C**-4′), 146.9 (**C**-10′), 137.6 (**C**-5′), 129.2 (**C**-2′), 121.2 (**C**-7′), 117.4 (**C**-8′), 116.6 (**C**-1′), 113.4 (**C**-3′), 110.6 (**C**-6′), 109.4 (**C**-9′), 60.65 (**HC**-N), 60.38, 55.31 (O**C**H$_3$), 31.35 (**C**H$_2$), 31.27, 21.59.

MS (70 eV, EI): *m*/*z* (%) = 282 (12), 190 (55), 174 (38), 160 (100), 132 (18), 93 (12), 77 (16), 41 (7).

HPLC: Chiralcel OD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 16.6 min; major enantiomer (1*S*,2*S*) t_R = 22.2 min.

(1*S*,2*S*)-*N*,*N*′-Bis(4-methoxyphenyl)cyclopentane-1,2-diamine (4g).[15a] Yield: 117 mg (75%), >99% ee as a brown solid; m.p.: 127–128 °C.

$[\alpha]_D^{22}$ = + 10.0 (*c* = 1.02, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/3): 0.33.

UV ($CHCl_3$): λ_{max} (lg ε) = 203 (4.339), 248 (4.370), 314 (3.677) nm.

IR (film): ν (cm^{-1}) = 3373, 2965, 1615, 1509, 1464, 1312, 1258, 1229, 1174, 1029.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.77 (d, *J* = 9.0 Hz, 4H, 3,5-Ar**H**), 6.61 (d, *J* = 9.0 Hz, 4H, 2,6-Ar**H**), 3.75 (s, 6H, OC**H**$_3$), 3.48–3.54 (m, 4H, **H**C-N), 2.21 (dt, *J* = 7.0, 13.5 Hz, 2H, C**H**H), 1.79 (quin, *J* = 7.5 Hz, 2H, C**H**$_2$), 1.51 (dt, *J* = 7.5, 13.5 Hz, 2H, CH**H**).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 152.3, 141.9, 114.9, 114.8, 61.6, 55.8, 31.2, 21.4.

MS (EI, 70 eV): *m*/*z* (%) = 312 (40), 190 (100), 162 (11), 123 (7), 108 (8).

HR-MS (ESI, MeOH): calcd for $C_{19}H_{25}N_2O_2$ ($[M + H]^+$): 313.19160; found: 313.19080.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 31.39 min; major enantiomer (1*S*,2*S*) t_R = 37.69 min.

(1*S*,2*S*)-*N*,*N*′-Diphenylcyclohex-4-ene-1,2-diamine (5a).[15a] Yield: 103 mg (78%), 89% ee as a colorless solid; m.p.: 89–91 °C.

$[\alpha]_D^{20}$ = +122.0 (*c* = 1.18, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/10): 0.42.

UV ($CHCl_3$): λ_{max} (lg ε) = 295 (4.46), 252 (3.808) nm.

IR (KBr): ν (cm^{-1}) = 3372, 3049, 3014, 2925, 2846, 1696, 1498, 1427, 1317, 1289, 1107.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.21 (dd, *J* = 7.2, 8.6 Hz, 4H, 3,5-Ar**H**), 6.75 (t, *J* = 7.2 Hz, 2H, 4-Ar**H**), 6.64 (d, *J* = 7.6 Hz, 4H, 2,6-Ar**H**), 5.72 (s, 2H, C**H**═C**H**), 3.85 (brs, 2H, N**H**), 3.76 (brs, 2H, C**H**-N), 2.71 (d, *J* = 46.0 Hz, 2H, C**H**$_2$), 2.07 (d, *J* = 46.0 Hz, 2H, C**H**$_2$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.5, 129.6, 124.8, 117.8, 113.6, 50.9, 30.4.

MS (ESI, acetone): *m*/*z* = 265 $[M + H]^+$, 287 $[M + Na]^+$, 303 $[M + K]^+$.

HR-MS (ESI, MeOH): calcd for $C_{18}H_{21}N_2$ ($[M + H]^+$): 265.16993; found: 265.17001, calcd for $C_{18}H_{20}N_2Na$ ($[M + Na]^+$): 287.15187; found: 287.15208.

HPLC: Chiralcel OD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 17.61 min; major enantiomer (1*S*,2*S*) t_R = 22.25 min.

(1*S*,2*S*)-*N*-Phenyl-*N*′-*p*-tolylcyclohex-4-ene-1,2-diamine (5b).[15a] Yield: 124 mg (89%), 90% ee as a pale yellow oil.

$[\alpha]_D^{18}$ = +83.6 (*c* = 1.1, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/10) = 0.29.

UV ($CHCl_3$): λ_{max} (lg ε) = 296 (3.957), 250 (4.351), 234 (3.808) nm.

IR (film): ν (cm^{-1}) = 3383, 3023, 2918, 1601, 1431, 1384, 1181.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.22 (dd, *J* = 7.2, 8.4 Hz, 2H, 3,5-Ar**H**), 7.04 (d, *J* = 8.4 Hz, 2H, 3′,5′-Ar**H**), 6.76 (t, *J* = 7.2 Hz,

1H, 4-Ar**H**), 6.69 (d, *J* = 7.6 Hz, 2H, 2,6-Ar**H**), 6.63 (d, *J* = 8.4 Hz, 2H, 2′,6′-Ar**H**), 5.73 (s, 2H, C**H**=C**H**), 3.90 (brs, 1H, N**H**), 3.74 (brs, 3H, N**H**, C**H**-N), 2.71 (brd, 2H, C$\mathbf{H}_2$), 2.29 (s, 3H, C$\mathbf{H}_3$), 2.07 (brd, 2H, C$\mathbf{H}_2$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.5, 145.1, 130.0, 129.5, 127.1, 124.86, 124.75, 117.7, 113.83, 113.54, 51.1, 50.8, 30.3 (2C), 20.5.

HR-MS (ESI, MeOH): calcd for $C_{19}H_{23}N_2$ ($[M + H]^+$): 279.17830; found: 279.18568, calcd for $C_{19}H_{22}N_2Na$ ($[M + Na]^+$): 301.16807; found: 301.16746.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 7.84 min; major enantiomer (1*S*,2*S*) t_R = 9.13 min.

(1*S*,2*S*)-*N*-(4-Methoxyphenyl)-*N*′-phenylcyclohex-4-ene-1,2-diamine (5c).[15a] Yield: 115 mg (78%), 87% ee as a pale yellow oil.

$[\alpha]_D^{18}$ = +108.8 (*c* = 0.68, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/5): 0.32.

UV (CH_3CN): λ_{max} (lg ε) = 302 (3.813), 249 (4.362), 227 (3.669) nm.

IR (film): ν (cm^{-1}) = 3373, 3024, 2915, 2831, 1601, 1502, 1432, 1384, 1233, 1179.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.21 (dd, *J* = 7.6, 8.6 Hz, 2H, 3,5-Ar**H**), 6.81 (dd, *J* = 2.4, 6.8 Hz, 2H, 3′,5′-Ar**H**), 6.74 (t, *J* = 7.2 Hz, 1H, 4-Ar**H**), 6.64–6.68 (m, 4H, 2,6-Ar**H**, 2′,6′-Ar**H**), 5.71 (s, 2H, C**H**=C**H**), 3.90 (brs, 1H, N**H**), 3.77 (s, 3H, OC$\mathbf{H}_3$), 3.59–3.73 (m, 3H, N**H**, C**H**-N), 2.63–2.72 (m, 2H, C$\mathbf{H}_2$), 2.07 (dd, *J* = 4.0, 16.0 Hz, 2H, C$\mathbf{H}_2$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 152.5, 147.5, 141.5, 129.5, 124.89, 124.74, 117.7, 115.29, 115.11, 113.6, 55.9, 51.97, 51.05, 30.37, 30.36.

HR-MS (ESI, MeOH): calcd for $C_{19}H_{23}N_2O$ ($[M + H]^+$): 295.17321; found: 295.18061, calcd for $C_{19}H_{22}N_2ONa$ ($[M + Na]^+$): 317.16298; found: 317.16247.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 13.62 min; major enantiomer (1*S*,2*S*) t_R = 15.94 min.

(2*S*,3*S*)-N^2,N^3-Diphenyl-1,2,3,4-tetrahydronaphthalen-2,3-diamine (6a).[15e] Yield: 119 mg (76%), 76% ee as a colorless solid; m.p.: 129 °C.

$[\alpha]_D^{22}$ = +100.1° (*c* = 0.86, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/5): 0.53.

UV ($CHCl_3$): λ_{max} (lg ε) = 207 (4.430), 250 (4.472), 295 (3.625) nm.

IR (KBr): ν (cm^{-1}) = 3391, 3050, 2904, 1924, 1822, 1723, 1602, 1509, 1494, 1453, 1430, 1336, 1317, 1264, 1238, 1222, 1177, 1110, 1099, 1071, 1035, 992, 955, 870, 822, 767, 753, 736, 692, 584, 503, 435.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.11–7.24 (m, 8H, ArC**H**), 6.75 (t, 2H, *J* = 7.5 Hz, ArC**H**), 6.69 (d, 4H, *J* = 8.5 Hz, ArC**H**), 3.89 (br s, 4H, **H**C-N, N**H**), 3.44 (d, 2H, *J* = 17.5 Hz, C**H**H), 2.80 (dd, 2H, *J* = 5.0, 17.5 Hz, CH**H**).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 147.2 ($\mathbf{C}_q$), 133.6 ($\mathbf{C}_q$), 129.5 (Ar**C**H), 129.3 (Ar**C**H), 126.5 (Ar**C**H), 117.9 (Ar**C**H), 113.6 (Ar**C**H), 51.95 (H**C**-N), 34.28 ($\mathbf{C}H_2$) ppm.

MS (ESI, 70 eV): *m*/*z* (%) = 314 (19), 222 (100), 157 (15), 129 (9), 106 (70), 77 (21), 57 (7).

HR-MS (ESI, MeOH): calcd for $C_{22}H_{23}N_2$ ($[M + H]^+$): 315.18612; found: 315.18558.

HPLC: Chiralcel OD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 29.3 min; major enantiomer (1*S*,2*S*) t_R = 34.3 min.

(2*S*,3*S*)-*N*,*N*′-Diphenylbutane-2,3-diamine (7a).[15a] Yield: 104 mg (87%), 90% ee as a colorless oil.

$[\alpha]_D^{20}$ = +24.5 (*c* = 1.27, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/10): 0.29.

UV ($CHCl_3$): λ_{max} (lg ε) = 294 (3.949), 251 (4.363), 238 (3.671) nm.

IR (film): ν (cm^{-1}) = 3394, 3050, 2969, 1600, 1428, 1384, 1253, 1179.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.21 (dd, *J* = 7.6, 8.4 Hz, 4H, 3,5-Ar**H**), 6.74 (t, *J* = 7.2 Hz, 2H, 4-Ar**H**), 6.67 (d, *J* = 8.0 Hz, 4H, 2,6-Ar**H**), 3.64 (brs, 2H, N**H**), 3.58–3.63 (m, 2H, C**H**N), 1.25 (d, *J* = 6.0 Hz, 6H, C$\mathbf{H}_3$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.7, 129.5, 117.7, 113.7, 52.7, 17.1.

MS (ESI, MeOH): *m*/*z* (%) = 241 $[M + H]^+$, 263 $[M + Na]^+$.

HR-MS (ESI, MeOH): calcd for $C_{16}H_{21}N_2$ ($[M + H]^+$): 241.16993; found: 241.16998, calcd for $C_{16}H_{20}N_2Na$ ($[M + Na]^+$): 263.15187; found: 263.15198.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (2*R*,3*R*) t_R = 10.37 min; major enantiomer (2*S*,3*S*) t_R = 11.69 min.

4-[(2*S*,3*S*)-3-(Phenylamino)butan-2-ylamino]benzenethiol (7b). Yield: 83 mg (61%), 53% ee as a pale yellow colorless oil.

$[\alpha]_D^{20}$ = −4.1 (*c* = 3.42, $CHCl_3$).

R_f (EtOAc–petroleum ether, 1/10): 0.26.

UV ($CHCl_3$): λ_{max} (lg ε) = 260 (4.294) nm.

IR (film): ν (cm^{-1}) = 3390, 3051, 3019, 2970, 2928, 2554, 1598, 1497, 1383, 1318, 1252, 1181, 1145, 1076, 1019, 993, 873, 813, 788, 751, 693, 632, 507.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.21 (t, *J* = 8.0 Hz, 4H, 3,5-Ar**H**, 3′,5′-Ar**H**), 6.70 (t, *J* = 7.6 Hz, 1H, 4-Ar**H**), 6.66 (dd, *J* = 1.2, 8.6 Hz, 2H, 2,6-Ar**H**), 6.56 (dd, *J* = 1.2, 8.6 Hz, 2H, 2′,6′-Ar**H**), 3.67 (brs, 2H, N**H**), 3.53–3.61 (m, 2H, C**H**-N), 3.32 (s, 1H, S**H**), 1.22 (d, *J* = 6.4 Hz, 6H, C$\mathbf{H}_3$).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.3, 146.5, 133.3, 129.3, 117.6, 114.7, 114.1, 113.5, 52.5, 52.4, 16.9, 16.8.

HR-MS (ESI, MeOH): calcd for $C_{16}H_{21}N_2S$ ($[M + H]^+$): 273.14253; found: 273.14200, calcd for $C_{16}H_{20}N_2NaS$ ($[M + Na]^+$): 295.12449; found: 295.12394, calcd for $C_{32}H_{40}N_4NaS_2$ ($[2M + Na]^+$): 567.25921; found: 567.25866.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 95/5, flow rate = 1.0 mL min^{-1}; minor enantiomer (2*R*,3*R*) t_R = 14.07 min; major enantiomer (2*S*,3*S*) t_R = 11.63 min.

(1*R*,3*S*,4*S*,6*S*)-*N*,*N*′-Diphenyl-7-tosyl-7-azabicyclo[4.1.0]-heptane-3,4-diamine (8a). Yield: 173 mg (80%), 48% ee as a colorless solid, m.p.: 84.8 °C.

$[\alpha]_D^{20}$ = +8.2 (*c* = 0.973, $CHCl_3$).

R_f (ether–petroleum ether, 1/1): 0.3.

UV ($CHCl_3$): λ_{max} (lg ε) = 248 (4.188), 293 (3.487) nm.

IR (KBr): ν (cm^{-1}) = 3383, 3050, 2923, 1731, 1600, 1498, 1434, 1320, 1304, 1249, 1182, 1159, 1091, 1019, 992, 971, 935, 875, 847, 815, 750, 715, 693, 667, 582, 549, 508 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, J = 8.0 Hz, 2H, 2′,6′-Ar**H**), 7.38 (d, J = 8.0 Hz, 2H, 3′,5′-Ar**H**), 7.17 (ddd, J = 7.5, 8.5 Hz, 4H, 3,5-Ar**H**), 6.74 (dt, J = 7.5 Hz, 2H, 4-Ar**H**), 6.59 (d, J = 8.5 Hz, 2H, 2,6-Ar**H**), 6.56 (d, J = 8.5 Hz, 2H, 2,6-Ar**H**), 4.09 (d, J = 8.5 Hz, 1H, N**H**), 3.71 (d, J = 7.5 Hz, 1H, N**H**), 3.61 (m, 1H, C**H**-NH), 3.48 (m, 1H, C**H**-NH), 3.14 (m, 1H, C**H**-N), 3.08 (t, J = 6.0 Hz, 1H, C**H**-N), 2.58 (t, J = 6.0 Hz, 1H, C**H**H), 2.52 (dd, J = 5.5, 12.0 Hz, 1H, C**H**H), 2.48 (s, 3H, C**H**$_3$), 1.81 (d, J = 6.0 Hz, 1H, C**H**H), 1.77 (d, J = 6.0 Hz, 1H, C**H**H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 146.9, 146.6, 144.6, 135.3, 129.8, 129.4, 127.6, 118.2, 118.0, 113.5, 113.4, 51.0, 48.9, 38.9, 38.7, 28.5, 27.6, 21.6.

MS (70 eV, EI): m/z (%) = 433 (10), 278 (100), 223 (22), 185 (13), 173 (70), 106 (38), 91 (26), 65 (7).

HR-MS (ESI, $CHCl_3$–MeOH): calcd for $C_{25}H_{27}N_3O_2NaS$ ([M + Na]$^+$): 456.17217; found: 456.17162.

HPLC: Chiralcel OD column, hexane–i-PrOH = 80/20, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 49.7 min; major enantiomer (1*S*,2*S*) t_R = 92.3 min.

(3*S*,4*S*)-*N*,*N*′-Diphenyltetrahydrofuran-3,4-diamine (9a).[15e] Yield: 108 mg (85%), 17% ee as a yellow oil, reaction time: 48 h.

$[\alpha]_D^{22}$ = +3.9° (c 1.03, $CHCl_3$).

R_f (EtOAc–petroleum ether = 3/7) = 0.08.

UV ($CHCl_3$): λ_{max} (lg ε) = 248 (4.386), 293 (3.750) nm.

IR (KBr): ν (cm^{-1}) = 3383, 3329, 3023, 2878, 1602, 1522, 1498, 1434, 1380, 1314, 1292, 1272, 1249, 1176, 1153, 1132, 1077, 1027, 1004, 913, 875, 751, 694, 514.

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.21 (dd, 2H, J = 7.5, 8.5 Hz, 3,5-Ar**H**), 6.79 (t, 2H, J = 7.5 Hz, 4-Ar**H**), 6.65 (d, 4H, J = 8.5 Hz, 2,6-Ar**H**), 4.21 (dd, 2H, J = 4.5, 10.0 Hz, C**H**H), 3.91 (m, 4H, **H**C-N, N**H**), 3.76 (dd, 2H, J = 1.5, 10.0 Hz, OCH**H**).

^{13}C-NMR (50 MHz, $CDCl_3$): δ = 146.5 (1-Ar**C**$_q$), 129.4 (3,5-Ar**C**H), 118.3 (4-Ar**C**H), 113.6 (2,6-Ar**C**H), 72.82 (O**C**H$_2$), 60.09 (H**C**-N).

MS (70 eV, EI): m/z (%) = 254 (18), 162 (32), 119 (100), 77 (16), 51 (6).

HR-MS (ESI, $CHCl_3$–MeOH): calcd for $C_{16}H_{18}N_2ONa$ ([M + Na]$^+$): 277.13168; found: 277.13113.

HPLC: Chiralcel AD-H column, hexane–i-PrOH = 98/2, flow rate = 1.0 mL min^{-1}; minor enantiomer (1*R*,2*R*) t_R = 71.2 min; major enantiomer (1*S*,2*S*) t_R = 74.4 min.

(5*S*,6*S*)-2,2-Dimethyl-*N*,*N*′-diphenyl-1,3-dioxepan-5,6-diamine (10a).[15e] With bis-BINOL **11**: 65 mg (85%), 88% ee, colorless oil, reaction time: 3 d, −20 °C.

$[\alpha]_D^{24}$ +118.8° (c = 0.96, $CHCl_3$).

R_f (n-hexane–EtOAc 1 : 1): 0.59.

UV (CH_3CN): λ_{max} (lg ε) = 203 nm (4.30), 247 nm (4.19), 301 (3.22).

IR (KBr): ν (cm^{-1}) = 3415, 3051, 3020, 2989, 2940, 1921, 1602, 1506, 1450, 1432, 1375, 1317, 1278, 1217, 1180, 1156, 1129, 1046, 994, 953, 878, 831, 787, 750, 692, 619, 567, 537, 509.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.17–7.24 (m, 4H, 3′-Ar**H**), 6.62–6.79 (m, 6H, 2′-Ar**H**, 4′-Ar**H**), 4.41 (bs, 2H, N**H**), 4.01 (d, J = 12.5 Hz, 2H, 4-C**H**H, 7-C**H**H), 3.54–3.60 (m, 2H, 4-CH**H**, 7-CH**H**), 3.51 (bs, 2H, 5-C**H**-NH, 6-C**H**-NH), 1.42 (s, 6H, C**H**$_3$), ppm.

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 146.5 (1′-Ar**C**), 129.7 (3′-Ar**C**), 117.8 (4′-Ar**C**), 113.6 (2′-Ar**C**), 60.55 (4-**C**H$_2$, 7-**C**H$_2$), 102.1 (2-**C**), 54.14 (5-**C**H-NH, 6-**C**H-NH), 24.92 (**C**H$_3$) ppm.

MS (ESI in MeOH–CH_2Cl_2): m/z = 311.0 $[M - H]^-$.

HPLC: Chiralcel OD-H column, hexane–i-PrOH (95/5), flow rate = 1.0 mL min^{-1}; minor enantiomer t_R = 7.01 min; major enantiomer t_R = 7.97 min.

(5*S*,6*S*)-Methyl-4-((-2,2-dimethyl-6-(phenylamino)-1,3-dioxepan-5-yl)amino)benzoate (10b). With bis-BINOL **11**: 51 mg (66%), 78% ee, colorless solid, m.p.: 55–58 °C, reaction time: 2 d, −20 °C.

$[\alpha]_D^{24}$: +173.4° (c = 0.87, $CHCl_3$).

R_f (n-hexane–EtOAc 2 : 1): 0.34.

IR (KBr): ν (cm^{-1}) = 3407, 2987, 2943, 2360, 1705, 1606, 1525, 1505, 1434, 1376, 1317, 1276, 1216, 1176, 1112, 1045, 953, 878, 83 7, 771, 749, 694, 667, 505.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, J = 9.0 Hz, 2H, 3″-Ar**H**), 7.46–7.08 (m, 2H, 3′-Ar**H**), 6.88–6.61 (m, 5H, ArC**H**), 4.91 (d, J = 8.5 Hz, 1H, N**H**), 4.43 (s, 1H, N**H**), 4.02 (dd, J = 15.5, 12.0 Hz, 2H, C**H**$_2$), 3.86 (s, 3H, COOC**H**$_3$), 3.64–3.52 (m, 3H, C**H**$_2$, C**H**N), 3.49 (s, 1H, C**H**N), 1.42 (s, 6H, C**H**$_3$) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.3 (**C**OOMe), 150.3 (1′-Ar**C**), 146.3 (1″-Ar**C**), 132.0 (3″-Ar**C**), 129.8 (3′-Ar**C**), 118.9 (4″-Ar**C**), 118.2 (4′-Ar**C**), 113.7 (Ar**C**H), 112.1 (Ar**C**H), 102.3 (2-**C**), 60.54 (**C**H$_2$), 60.27 (**C**H$_2$), 53.99 (**C**HN), 53.54 (**C**HN), 51.73 (COO**C**H$_3$), 24.92 (**C**H$_3$), 24.87 (**C**H$_3$) ppm.

HR-MS (ESI in MeOH–$CHCl_3$): calcd for $C_{21}H_{27}N_2O_4$ ([M + H]$^+$): 371.19653; found: 371.19644.

HPLC: Chiralcel OD-H column, hexane–i-PrOH (60/40), flow rate = 1.0 mL min^{-1}; minor enantiomer t_R = 5.95 min; major enantiomer t_R = 7.23 min.

(5*S*,6*S*)-4-(2,2-Dimethyl-6-(phenylamino)-1,3-dioxepan-5-ylamino)benzonitrile (10c). With bis-BINOL **11**: 58 mg (69%), 68% ee colorless solid, m.p.: 165–168 °C, reaction time: 3 d, −20 °C.

$[\alpha]_D^{24}$: +165.6° (c = 0.93, $CHCl_3$).

R_f (n-hexane–EtOAc 2 : 1): 0.39.

IR (KBr): ν (cm^{-1}) = 3381, 3338, 2993, 2942, 2360, 2209, 1604, 1519, 1497, 1377, 1335, 1309, 1277, 1255, 1220, 1175, 1126, 1057, 1048, 882, 844, 795, 760, 694, 589, 552, 500, 419.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.46 (d, J = 9.0 Hz, 2H, 3″-Ar**H**), 7.33–7.18 (m, 2H, 3′-Ar**H**), 6.77 (t, J = 7.5 Hz, 1H, 4′-Ar**H**), 6.69 (t, J = 9.0 Hz, 4H, Ar**H**), 4.97 (d, J = 8.5 Hz, 1H, N**H**), 4.42 (s, 1H, N**H**), 4.01 (dd, J = 16.0, 12.0, 2H, C**H**$_2$), 3.72–3.36 (m, 4H, C**H**N, C**H**$_2$), 1.42 (s, 1H, C**H**$_3$) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 149.8 (1″-Ar**C**), 146.1 (1′-Ar**C**), 134.0 (3″-Ar**C**), 129.7 (3′-Ar**C**), 120.3 (**C**N), 118.3 (Ar**C**H), 113.7 (Ar**C**H), 112.7 (Ar**C**H), 102.4 (2-**C**), 99.22 (4″-Ar**C**), 60.43 (**C**H$_2$), 60.02 (**C**H$_2$), 53.95 (**C**HN), 53.42 (**C**HN), 24.85 (**C**H$_3$), 24.78 (**C**H$_3$) ppm.

HR-MS (ESI in MeOH–$CHCl_3$: calcd for $C_{20}H_{24}N_3O_2$ ($[M + H]^+$): 338.18630; found: 338.18621, calcd for $C_{40}H_{47}N_6O_4$ ($[2M + H]^+$): 675.36533; found: 675.36549.

HPLC: Chiralcel OD-H column, hexane–i-PrOH (60/40), flow rate = 1.0 mL min^{-1}; minor enantiomer t_R = 5.55 min; major enantiomer t_R = 6.21 min.

Acknowledgements

This work was generously supported by the Deutsche Forschungsgemeinschaft (SCHN 441/9-1). We gratefully acknowledge the support of Dr C. Birkemeyer (University of Leipzig) for obtaining and interpreting the MS data and the Alexander von Humboldt Foundation for a postdoctoral fellowship awarded to S. P. We thank Evonik, Chemetall, and BASF for the generous donation of chemicals.

Notes and references

1 Select reviews: (*a*) C. Schneider, *Synthesis*, 2006, 3919; (*b*) I. M. Pastor and M. Yus, *Curr. Org. Chem.*, 2005, **9**, 1; (*c*) E. N. Jacobsen and M. H. Wu, in *Comprehensive Asymmetric Catalysis*, ed. E. N. Jacobsen, A. Pfaltz and H. Yamamoto, 1999, vol. 2, p. 649.

2 Select reviews: (*a*) C. Schneider, *Angew. Chem., Int. Ed.*, 2009, **48**, 2082; (*b*) A. K. Yudin, *Aziridines and Epoxides in Organic Synthesis*, Wiley-VCH, Weinheim, Germany, 2006; (*c*) M. Pineschi, *Eur. J. Org. Chem.*, 2006, 4979; (*d*) X. E. Hu, *Tetrahedron*, 2004, **60**, 2701; (*e*) W. McCoull and F. A. Davis, *Synthesis*, 2000, 1347.

3 For select catalytic processes see: (*a*) D. Hong, X. Lin, Y. Zhu, M. Lei and Y. Wang, *Org. Lett.*, 2009, **11**, 5678; (*b*) A. Bisai, B. A. Bhanu Prasad and V. K. Singh, *Tetrahedron Lett.*, 2005, **46**, 7935; (*c*) J. Wu, X. Sun and Y. Li, *Eur. J. Org. Chem.*, 2005, 4271; (*d*) I. D. G. Watson and A. K. Yudin, *J. Org. Chem.*, 2003, **68**, 5160; (*e*) N. R. Swamy and Y. Venkateswarlu, *Synth. Commun.*, 2003, **33**, 547; (*f*) J. S. Yadav, B. V. S. Reddy, K. V. Rao, K. S. Raj and A. R. Prasad, *Synthesis*, 2002, 1061; (*g*) J. Cossy, V. Bellosta, V. Alauze and J. R. Desmurs, *Synthesis*, 2002, 2211; (*h*) X.-L. Hou, R.-H. Fan and L.-X. Dai, *J. Org. Chem.*, 2002, **67**, 5295; (*i*) M. Chandrasekhar, G. Sekar and V. K. Singh, *Tetrahedron Lett.*, 2000, **41**, 10079; (*j*) G. Sekar and V. K. Singh, *J. Org. Chem.*, 1999, **64**, 2537; (*k*) M. Meguro, N. Asao and Y. Yamamoto, *Tetrahedron Lett.*, 1994, **35**, 7395.

4 For select catalytic processes see: (*a*) S. Bhadra, L. Adak, S. Samanta, A. K. M. Maidul Islam, M. Mukherjee and B. C. Ranu, *J. Org. Chem.*, 2010, **75**, 8533; (*b*) M. Bera and S. Roy, *J. Org. Chem.*, 2009, **74**, 8814; (*c*) B. A. Bhanu Prasad, R. Sanghi and V. K. Singh, *Tetrahedron*, 2002, **58**, 7355; (*d*) X.-L. Hou, R.-H. Fan and L.-X. Dai, *J. Org. Chem.*, 2002, **67**, 5295; (*e*) B. A. Bhanu Prasad, G. Sekar and V. K. Singh, *Tetrahedron Lett.*, 2000, **41**, 4677.

5 For select catalytic processes see: (*a*) S. Matsukawa, H. Takahashi and T. Harada, *Synth. Commun.*, 2013, **43**, 406; (*b*) S. Matsukawa, H. Takahashi and T. Harada, *Org. Biomol. Chem.*, 2012, **10**, 4886; (*c*) Y. Hayashi, T. Kumamoto, T. Ishikawa, M. Kawahata and K. Yamaguchi, *Tetrahedron*, 2010, **66**, 3836; (*d*) I. Fujimori, T. Mita, K. Maki, M. Shiro, A. Sato, S. Furusho, M. Kanai and M. Shibasaki, *Tetrahedron*, 2007, **63**, 5820; (*e*) S. Minakata, Y. Okada, Y. Oderaotoshi and M. Komatsu, *Org. Lett.*, 2005, **7**, 3509; (*f*) S. H. Kang, M. Kim and D. H. Ryu, *Synlett*, 2003, **8**, 1149.

6 For select catalytic processes see: (*a*) Y. Zhang, C. W. Kee, R. Lee, X. Fu, J. Y. T. Soh, E. M. F. Loh, K. W. Huang and C. H. Tan, *Chem. Commun.*, 2011, 3897; (*b*) F. Zeng and H. Alper, *Org. Lett.*, 2010, **12**, 5567; (*c*) J. S. Yadav, B. V. S. Reddy, G. Baishya, P. Venkatram Reddy and A. V. Narsaiah, *Catal. Commun.*, 2006, **7**, 807; (*d*) J. Wu, X. Sun and Y. Li, *Eur. J. Org. Chem.*, 2005, 4271; (*e*) J. S. Yadav, B. V. Subba Reddy, G. Baishya, P. V. Reddy and S. J. Harshavardhan, *Synthesis*, 2004, 1854; (*f*) X.-L. Hou, R.-H. Fan and L.-X. Dai, *J. Org. Chem.*, 2002, **67**, 5295; (*g*) J. Wu, X.-L. Hou and L.-X. Dai, *J. Chem. Soc., Perkin Trans. 1*, 2001, 1314.

7 Recent short review: C. Schneider, *Angew. Chem., Int. Ed.*, 2009, **48**, 2082.

8 Z. Li, M. Fernandez and E. N. Jacobsen, *Org. Lett.*, 1999, **1**, 1611.

9 (*a*) K. Yabu, S. Masumoto, S. Yamasaki, Y. Hamashima, M. Kanai, W. Du, D. P. Curran and M. Shibasaki, *J. Am. Chem. Soc.*, 2001, **123**, 9908; (*b*) T. Mita, I. Fujimori, R. Wada, J. Wen, M. Kanai and M. Shibasaki, *J. Am. Chem. Soc.*, 2005, **127**, 11252; (*c*) Y. Fukuta, T. Mita, N. Fukuda, M. Kanai and M. Shibasaki, *J. Am. Chem. Soc.*, 2006, **128**, 6312; (*d*) I. Fujimori, T. Mita, K. Maki, M. Shiro, A. Sato, S. Furusho, M. Kanai and M. Shibasaki, *J. Am. Chem. Soc.*, 2006, **128**, 16438; (*e*) Y. Xu, L. Lin, M. Kanai, S. Matsunaga and M. Shibasaki, *J. Am. Chem. Soc.*, 2011, **133**, 5791.

10 (*a*) B. Wu, J. C. Gallucci, J. R. Parquette and T. V. RajanBabu, *Angew. Chem., Int. Ed.*, 2009, **48**, 1126; (*b*) B. Wu, J. R. Parquette and T. V. RajanBabu, *Science*, 2009, **326**, 1662.

11 E. B. Rowland, G. B. Rowland, E. Rivera-Otero and J. C. Antilla, *J. Am. Chem. Soc.*, 2007, **129**, 12084.

12 (*a*) K. Arai, S. Lucarini, M. S. Salter, K. Ohta, Y. Yamashita and S. Kobayashi, *J. Am. Chem. Soc.*, 2007, **129**, 8103; (*b*) R. Yu, Y. Yamashita and S. Kobayashi, *Adv. Synth. Catal.*, 2009, **351**, 147; (*c*) K. Seki, R. Yu, Y. Yamazaki, Y. Yamashita and S. Kobayashi, *Chem. Commun.*, 2009, 5722.

13 (*a*) S. E. Larson, J. C. Baso, G. Li and J. C. Antilla, *Org. Lett.*, 2009, **11**, 5186; (*b*) G. Della Sala and A. Lattanzi, *Org. Lett.*, 2009, **11**, 3330; (*c*) Y. Zhang, C. W. Kee, R. Lee, X. Fu, J. Y.-T. Soh, E. M. F. Loh, K.-W. Huang and C.-H. Tan, *Chem. Commun.*, 2011, **47**, 3897; for previous work in this area see: (*d*) Z.-B. Luo, X.-L. Hou and L.-X. Dai, *Tetrahedron: Asymmetry*, 2007, **18**, 443; (*e*) Z. Wang, X. Sun, S. Ye, W. Wang, B. Wang and J. Wu, *Tetrahedron: Asymmetry.*, 2008, **19**, 964.

14 (*a*) T. Mita and E. N. Jacobsen, *Synlett*, 2009, 1680; (*b*) K. Ohmatsu, Y. Hamajima and T. Ooi, *J. Am. Chem. Soc.*, 2012, **134**, 8794.

15 (*a*) S. Peruncheralathan, H. Teller and C. Schneider, *Angew. Chem., Int. Ed.*, 2009, **48**, 4849; for additional work from our group in this area see: (*b*) S. Peruncheralathan, M. Henze and C. Schneider, *Synlett*, 2007, 2289; (*c*) S. Peruncheralathan, M. Henze and C. Schneider, *Tetrahedron Lett.*, 2007, **48**, 6743; (*d*) A. Marti and C. Schneider, *Synlett*, 2011, 2513; (*e*) A. Marti, S. Peruncheralathan and C. Schneider, *Synthesis*, 2012, **44**, 27.

16 (*a*) C. Han, J. P. Lee, E. Lobkovsky and J. A. Porco, *J. Am. Chem. Soc.*, 2005, **127**, 10039; (*b*) S. E. Eldred, D. A. Stone, S. H. Gellman and S. S. Stahl, *J. Am. Chem. Soc.*, 2003, **125**, 3422.

17 S. Sagawa, H. Abe, Y. Hase and T. Inaba, *J. Org. Chem.*, 1999, **64**, 4962.

18 Select recent reviews: (*a*) J. M. Brunel, *Chem. Rev.*, 2005, **105**, 857; (*b*) D. J. Ramon and M. Yus, *Chem. Rev.*, 2006, **106**, 2126; (*c*) L. Pu, *Chem. Rev.*, 1998, **98**, 2405.

19 H. Ishitani, M. Ueno and S. Kobayashi, *J. Am. Chem. Soc.*, 2000, **122**, 8180.

20 Diamine **3a** has been employed as a chiral ligand, see: B. M. Trost and T. M. Lam, *J. Am. Chem. Soc.*, 2012, **134**, 11319–11321.

21 S. Matsunaga, J. Das, J. Roels, E. M. Vogl, N. Yamamoto, T. Iida, K. Yamaguchi and M. Shibasaki, *J. Am. Chem. Soc.*, 2000, **122**, 2252–2260.

22 N. Kumagai, S. Matsunaga, T. Kinoshita, S. Harada, S. Okada, S. Sakamoto, K. Yamaguchi and M. Shibasaki, *J. Am. Chem. Soc.*, 2003, **125**, 2169.

23 Y. Ihori, Y. Yamashita, H. Ishitani and S. Kobayashi, *J. Am. Chem. Soc.*, 2005, **127**, 15528.

24 H. Hanawa, T. Hashimoto and K. Maruoka, *J. Am. Chem. Soc.*, 2003, **125**, 1708.

25 For previous structural investigations into Ti-BINOLate-complexes see *e.g.*: (*a*) T. J. Boyle, D. L. Barnes, J. A. Heppert, L. Morales, F. Takusagawa and J. W. Conolly, *Organometallics*, 1992, **11**, 1112; (*b*) T. J. Boyle, N. W. Eilerts, J. A. Heppert and F. Takusagawa, *Organometallics*, 1994, **13**, 2218; (*c*) K. Mikami, M. Ueki, Y. Matsumoto and M. Terada, *Chirality*, 2001, **13**, 541; (*d*) T. J. Davis, J. Balsells, P. J. Carroll and P. J. Walsh, *Org. Lett.*, 2001, **3**, 699; (*e*) G. Pescitelli, L. Di Bari and P. Salvadori, *J. Organomet. Chem.*, 2006, **691**, 2311.

26 For previous examples of cooperative bimetallic catalysis see the following reviews: (*a*) J.-A. Ma and D. Cahard, *Angew. Chem., Int. Ed.*, 2004, **43**, 4566–4583; (*b*) H. Steinhagen and G. Helmchen, *Angew. Chem., Int. Ed.*, 1996, **35**, 2339–2342; select articles in the field of epoxide and aziridine ring-opening: (*c*) B. W. McCleland, W. A. Nugent and M. G. Finn, *J. Org. Chem.*, 1998, **63**, 6656–6662; (*d*) K. B. Hansen, J. L. Leighton and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1996, **118**, 10924–10925; (*e*) See ref. 9*c*; (*f*) See ref. 9*d*; (*g*) See ref. 10*a*.