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New axially chiral *atropos* and *tropos* secondary diamines as ligands for enantioselective intramolecular hydroamination

Isabelle Aillaud,[a] Karen Wright,[b] Jacqueline Collin,[a] Emmanuelle Schulz[a,*] and Jean-Paul Mazaleyrat[b,*]

[a]*Equipe de Catalyse Moléculaire, ICMMO, UMR 8182, Université Paris-Sud 11, Bât 420, 91405 Orsay Cedex, France*
[b]*ILV, UMR CNRS 8180, Université de Versailles, 78035 Versailles Cedex, France*

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Abstract—The highly constrained, axially chiral *atropos* diamines (R^i,*S*,*S*)-**1**, (R^i,*R*,*R*)-**1** and (R^i,*S*,*R*)-**1** and their *tropos* analogue (R^i)-**2** have been prepared via bis-N,N-dialkylation of (*R*)-2,2′-diamino-1,1′-binaphthyl, using either (*R*)- or (*S*)-2,2′-bis(bromomethyl)-1,1′-binaphthyl and 2,2′-bis(bromomethyl)-1,1′-biphenyl as alkylating agents, followed by selective nickel chloride-catalysed bis(monohydrogenolysis) of the tertiary amino groups of the so-obtained (R^i,*R*,*R*)-**4**, (R^i,*S*,*S*)-**4**, (R^i,*R*,*S*)-**4** and (R^i)-**6**, respectively, by lithium aluminium hydride in refluxing THF or THF/diglyme. The diamines (R^i,*S*,*S*)-**1**, (R^i,*R*,*R*)-**1**, (R^i,*S*,*R*)-**1** and (R^i)-**2** have been evaluated as ligands for ytterbium-catalysed intramolecular hydroamination and compared to the ligand 1,1′-binaphthyl-2,2′-bis(benzylamine) (R^i)-**3**. They afforded highly active catalysts for the cyclisation of aminopentenes and aminohexenes with up to 58% ee.

1. Introduction

Enantioselective hydroamination reactions have been the focus of increased interest in recent years as atom economic ways for the formation of carbon–nitrogen bonds, and especially for intramolecular reactions, which allow the synthesis of scalemic nitrogen heterocycles.[1] Since the pioneering work of Marks et al. showing the activity and enantioselectivity of lanthanocenes for the catalysis of intramolecular hydroamination,[2] a large variety of ligands and different metals have been evaluated. Up until now, rare earths afforded the most active catalysts. As for numerous other catalytic reactions, ligands with chiral binaphthyl or biphenyl moieties have allowed the preparation of efficient enantioselective rare earth-catalysts for the cyclisation of aminoalkenes. Bisphenolate and bisnaphtholates have been studied by Hultzsch et al. and furnished the highest enantiomeric excess to date (95%) for an intramolecular hydroamination reaction.[3] Phosphine oxide-substituted bisnaphtholate and bisphenolate or bis thiolate ligands with chirality arising from a biphenylamine or binaphthylamine moiety were also successfully used for enantioselective rare-earth-catalysed hydroaminations.[4] The use of biaryl amines with axial chirality for the preparation of rare earth amides was first described by Scott et al., although low enantioselectivities were obtained for the cyclisation of an aminopentene.[5]

In previous studies, we synthesised a new family of lanthanide amide ate complexes from 1,1′-binaphthyl-2,2′-bis(alkylamines), by metathetic reactions of the dilithium salts of the ligands with anhydrous $LnCl_3$. These ate complexes were efficiently used as enantioselective catalysts for the intramolecular hydroamination of *gem*-substituted aminopentene or aminohexene derivatives to the corresponding chiral pyrrolidines or piperidines. Ytterbium catalysts in particular combined a high reactivity (>90–100% conversion within a few hours at 25 °C with a catalyst ratio of 6 mol %) and moderate to high enantioselectivities (up to 87% ee).[6] In the search for even more potent catalysts, we considered the introduction of binaphthyl or biphenyl units linked via a methylene spacer to the NH groups instead of alkyl substituents, to enhance both steric and chiral barriers. Herein we report the synthesis of highly constrained polybinaphthyl diastereoisomeric diamines

* Corresponding authors. Fax: +33 0 1 69 15 46 80 (E.S.); fax: +33 0 1 39 25 44 52 (J.-P.M.); e-mail addresses: emmaschulz@icmo.u-psud.fr; jean-paul.mazaleyrat@chimie.uvsq.fr

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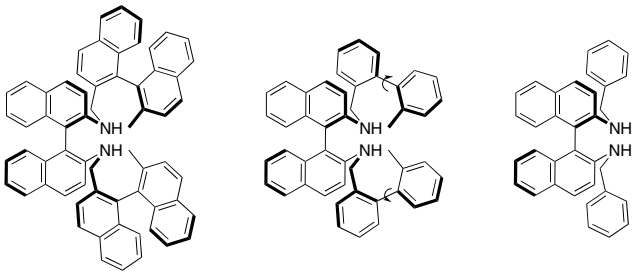

Figure 1. Chemical structures of the polybinaphthyl/biphenyl *atropos* and *tropos* diamines (R^i,*S*,*S*)-**1** [or (R^i,*R*,*R*)-**1** or (R^i,*S*,*R*)-**1** (not shown)] and (R^i)-**2** compared to the 1,1′-binaphthyl-2,2′-bis(benzylamine) model (R^i)-**3**.

(R^i,*S*,*S*)-**1**, (R^i,*R*,*R*)-**1**, (R^i,*S*,*R*)-**1** and their conformationally labile analogue (R^i)-**2**, (Fig. 1).[†] Their use as ytterbium ligands for the enantioselective catalysis of intramolecular hydroamination is reported and compared to the results obtained with 1,1′-binaphthyl-2,2′-bis(benzylamine) (R^i)-**3** as a ligand.[6b]

The chiral rigid *atropos*[7] ligands (R^i,*S*,*S*)-**1**, (R^i,*R*,*R*)-**1** and (R^i,*S*,*R*)-**1** belong to the class of 2,2′-substituted-1,1′-binaphthyl derivatives, a very important family of compounds, showing outstanding chiral discrimination properties in a variety of reactions.[8] Multibinaphthyl oxygen-, nitrogen- or phosphorous-based dimers, oligomers and polymers have also been widely used as chiral auxiliaries to provide high levels of stereochemical control.[9] On the other hand the use of chiral flexible *tropos*[7] ligands, such as (R^i)-**2** in which asymmetric activation by the internal (R^i)-binaphthyl moiety through *tropo*-inversion of the chiral axis of the biphenyl units may occur, has been shown to allow remarkable amplification of both catalytic activity and enantioselectivity.[10] Herein we report an efficient method for the synthesis of these chiral diamines as single enantiomers.

2. Results and discussion

2.1. Synthesis

The bis-secondary diamines (R^i,*S*,*S*)-**1**, (R^i,*R*,*R*)-**1**, (R^i,*S*,*R*)-**1** and (R^i)-**2** were readily prepared in two steps from (*R*)-2,2′-diamino-1,1′-binaphthyl. The *gem*-dialkylation with exclusive formation of a seven-membered ring system in the reaction of primary or secondary amines with either 2,2′-bis(bromomethyl)-1,1′-binaphthyl or 2,2′-bis(bromomethyl)-1,1′-biphenyl was established in the 1950's,[11] and has very often been exploited in the synthesis of a variety of catalysts.[10c–e,12–17] The treatment of enantiomerically pure (*R*)-2,2′-diamino-1,1′-binaphthyl with resolved, enantiomerically pure (*R*)-2,2′-bis(bromomethyl)-1,1′-binaphthyl,[15–19] and an excess of diisopropylethylamine (DIEA) in toluene–acetonitrile 1:1 at 85 °C for 6 days, gave the bis-tertiary diamine (R^i,*R*,*R*)-**4** in 66% yield, accompanied by the corresponding primary–tertiary diamine (R^i,*R*)-**5** in 29% yield.[‡] In the same manner, the treatment of enantiomerically pure (*R*)-2,2′-diamino-1,1′-binaphthyl with enantiomerically pure (*S*)-2,2′-bis(bromomethyl)-1,1′-binaphthyl[15–19] and DIEA in toluene–acetonitrile 1:1 at 85 °C for 7 days afforded (R^i,*S*,*S*)-**4** in 87% yield and (R^i,*S*)-**5** in 12% yield. The reaction of the side products (R^i,*R*)-**5** and (R^i,*S*)-**5** with enantiomerically pure (*S*)- and (*R*)-2,2′-bis(bromomethyl)-1,1′-binaphthyl, respectively, under similar experimental conditions, gave (R^i,*R*,*S*)-**4** in 49% and 47% yields. Finally, the reaction of enantiomerically pure (*R*)-2,2′-diamino-1,1′-binaphthyl with 2,2′-bis(bromomethyl)-1,1′-biphenyl under the same conditions afforded (R^i)-**6** in 87% yield after 6 days at 85 °C (Fig. 2).

The formation of the target bis-secondary diamines (R^i,*S*,*S*)-**1**, (R^i,*R*,*R*)-**1** and (R^i,*S*,*R*)-**1** from (R^i,*R*,*R*)-**4**, (R^i,*S*,*S*)-**4** and (R^i,*R*,*S*)-**4**, respectively, was expected to occur following our previously reported results: the hydrogenolysis of related N-substituted 4,5-dihydro-3*H*-dinaphtho[2,1-c:1′,2′-e]azepines and the corresponding quaternary ammonium salts by lithium aluminium hydride, provided easy access to the unsymmetrical binaphthyl secondary or tertiary amines in high yields.[13] However, when (R^i,*R*,*R*)-**4** was treated with a large excess of $LiAlH_4$ in refluxing THF, no reaction occurred after 24 h. The important steric constraint associated with the chemical structure of (R^i,*R*,*R*)-**4** could explain its lack of reactivity. The reaction was then attempted in the presence of nickel(II) chloride, previously shown to be a highly efficient catalyst for the total hydrogenolysis of quaternary ammonium salts of N-substituted 4,5-dihydro-3*H*-dinaphtho[2,1-c:1′,2′-e]azepines derived from *l*-ephedrine, to form 2,2′-dimethyl-1,1′-binaphthyl[15] (Fig. 3).

When (R^i,*R*,*R*)-**4** was treated with a large excess of $LiAlH_4$ and $NiCl_2$ in refluxing THF for only 7 h, the desired diamine (R^i,*S*,*S*)-**1** was indeed obtained as a single product, in 83–88% yield after chromatography. Several duplicate experiments at various scales (up to 0.43 mmol) and with various reaction times (7 h and 16 h) gave a similar yield (see Section 4).

Similar treatment of (R^i,*S*,*S*)-**4** and (R^i,*R*,*S*)-**4** with $LiAlH_4$ and $NiCl_2$ in refluxing THF for 7–16 h afforded the target bis-secondary diamines (R^i,*R*,*R*)-**1** in 73–80% yield and (R^i,*S*,*R*)-**1** in 62% yield, respectively. Remarkably, the expected formation of 2,2′-dimethyl-1,1′-binaphthyl as a side product did not occur.[13,15] Nickel chloride had been previously shown to catalyse the hydrogenolysis of both aryl allyl ethers and aryl benzyl ethers by lithium aluminium hydride,[20] as well as the hydrogenolysis of *N*-alkyl-*N*-allyl-arylamines, but surprisingly not of *N*-alkyl-*N*-benzyl-arylamines.[21] In this case, and for the

[†] For clarity, we have denoted (R^i) as the absolute configuration of the internal 2,2′-diamino-1,1′-binaphthyl moiety of the different compounds.

[‡] Prolonged reaction time (12 days) resulted in a decreased yield in both (R^i,*R*,*R*)-**4** (51%) and (R^i,*R*)-**5** (6%), possibly because of product decomposition.

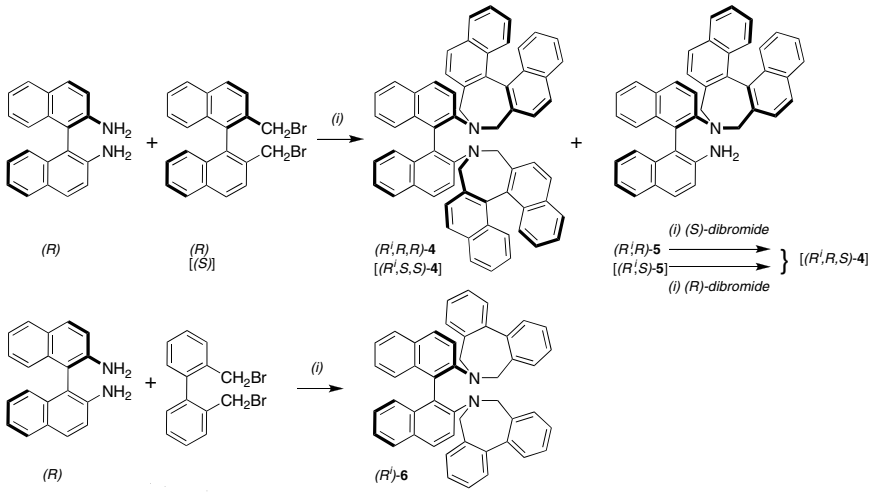

Figure 2. Synthesis of the diamines (R^i,*R*,*R*)-**4**, (R^i,*S*,*S*)-**4**, (R^i,*R*,*S*)-**4** [and the side-products (R^i,*R*)-**5**, (R^i,*S*)-**5**] and (R^i)-**6** by the reaction of (*R*)-2,2′-diamino-1,1′-binaphthyl with (*R*)- and/or (*S*)-2,2′-bis(bromomethyl)-1,1′-binaphthyl and 2,2′-bis(bromomethyl)-1,1′-biphenyl, respectively. Reagents and conditions: (i) DIEA; toluene–acetonitrile 1:1; 85 °C.

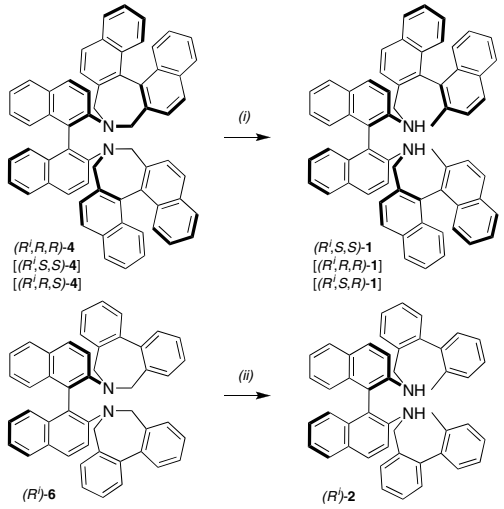

Figure 3. Synthesis of the target secondary diamines (R^i,*S*,*S*)-**1**, (R^i,*R*,*R*)-**1**, (R^i,*S*,*R*)-**1** and (R^i)-**2** resulting from selective bis(mono-hydrogenolysis) of (R^i,*R*,*R*)-**4**, (R^i,*S*,*S*)-**4**, (R^i,*R*,*S*)-**4** and (R^i)-**6**, respectively. Reagents and conditions: (i) $LiAlH_4$; $NiCl_2$; THF; 85 °C; (ii) $LiAlH_4$; $NiCl_2$; THF/diglyme; 155 °C.

sterically constrained bis-tertiary diamines **4** with two 4,5-dihydro-3*H*-dinaphtho[2,1-c:1′,2′-e]azepines linked to a 1,1′-binaphthyl unit at its 2,2′ positions, catalysis by $NiCl_2$ is required. This allowed a very clean reaction selectively providing two secondary amino groups by bis(mono-hydrogenolysis). The expected[22] absence of racemisation of the binaphthyl units in both steps 1 and 2, is inferred from the formation of a single stereoisomer for each reaction product, as shown by the ^{1}H NMR spectra of all the polybinaphthyl diamines (Table 1): as in previously reported examples,[13] a single pattern was always observed in $CDCl_3$ at 300 MHz for the benzylic-like $ArCH_2$–NR_2 protons of (R^i,*R*,*R*)-**4**, (R^i,*S*,*S*)-**4**, (R^i,*R*,*S*)-**4** and (R^i,*R*)-**5**, (R^i,*S*)-**5** (AB quartet), as well as for either the benzylic-like $ArCH_2$–NHR protons (singlet) or the $ArCH_3$ protons (singlet) of (R^i,*S*,*S*)-**1**, (R^i,*R*,*R*)-**1** and (R^i,*S*,*R*)-**1**, with no extra signals arising from other stereoisomers.

Table 1. Chemical shifts δ (ppm) of the $ArCH_2N$ and $ArCH_3$ signals in the ^{1}H NMR spectra of the various diamines in $CDCl_3$ solution

Diamine	$ArCH_2N$	$ArCH_3$
(R^i,*R*,*R*)-**4**	3.88 (d) and 3.58 (d)	
(R^i,*S*,*S*)-**4**	3.99 (d) and 3.57 (d)	
(R^i,*R*,*S*)-**4**	3.93 (d) and 3.73 (d)	
	3.87 (d) and 3.55 (d)	
(R^i,*R*)-**5**	4.10 (d) and 3.55 (d)	
(R^i,*S*)-**5**	4.10 (d) and 3.64 (d)	
(R^i,*S*,*S*)-**1**	4.01 (s)	2.00 (s)
(R^i,*R*,*R*)-**1**	4.03 (s)	1.99 (s)
(R^i,*S*,*R*)-**1**	4.02 (s) and 4.00 (s)	2.03 (s) and 1.97 (s)

For the *tropos* bis-tertiary diamine (R^i)-**6**, hydrogenolysis did not occur under the same experimental conditions as for (R^i,*R*,*R*)-**4** ($LiAlH_4$ and $NiCl_2$ in refluxing THF at 85 °C) even after prolonged reaction time (72 h). However, when the reaction was performed in a mixture of diglyme and THF (5:6) (but not in diglyme alone, in which only decomposition occurred) at 155 °C for 1.5 h, the selective bis(mono-hydrogenolysis) furnished the desired secondary diamine (R^i)-**2** in 56% yield.

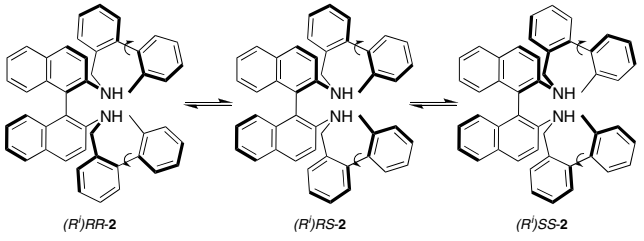

Figure 4. Conformational equilibrium between the three diastereoisomeric conformers (R^i)*RR*-**2**, (R^i)*RS*-**2** and (R^i)*SS*-**2** of the diamine (R^i)-**2**.

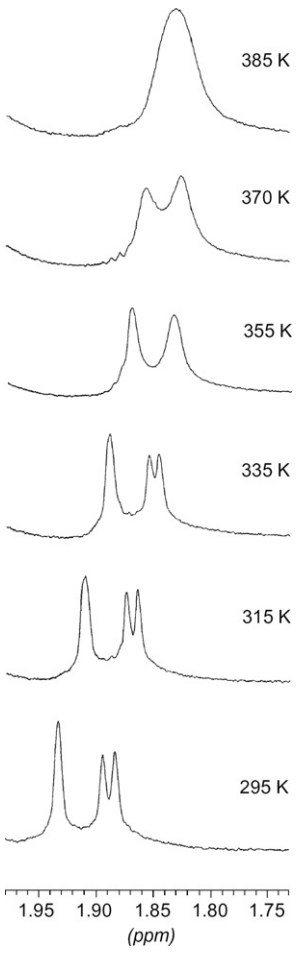

Figure 5. Temperature-dependent ^{1}H NMR (300 MHz) pattern of the $ArCH_3$ protons of the three diastereoisomeric conformers (R^i)*RS*-**2** (δ 1.93 ppm at 295 K), (R^i)*RR*-**2** and (R^i)*SS*-**2** (δ 1.89 ppm and/or 1.88 ppm at 295 K) in toluene-d_8. Observed coalescence temperatures for the couple (R^i)*RR*-**2** and (R^i)*SS*-**2**: $T_{C_1} \sim 355$ K ($\Delta\nu_1 = 3.3$ Hz at 295 K), and for the couple (R^i)*RS*-**2** and (R^i)*RR* or (R^i)*SS*-**2**: $T_{C_2} \sim 385$ K (average $\Delta\nu_2 \sim 13.2$ Hz at 295 K).

Interestingly, the ^{1}H NMR spectrum of (R^i)-**2** at room temperature in either $CDCl_3$ or in benzene-d_6 or toluene-d_8 shows the presence of the three expected conformers (R^i)*RR*-**2**, (R^i)*RS*-**2** and (R^i)*SS*-**2** (Fig. 4) exchanging slowly on the NMR timescale, in a ca. 1:2:1 ratio as determined by the integration of their respective $ArCH_3$ singlets. The $ArCH_3$ singlet at lower field is assigned to (R^i)*RS*-**2** (the same compound as (R^i)*SR*-**2**) on the basis of its double intensity. The two $ArCH_3$ singlets of equal half intensity at higher field are ambiguously assigned to either one of the (R^i)*RR*-**2** and (R^i)*SS*-**2** conformers.

Evolution of the ^{1}H NMR spectrum (300 MHz) of (R^i)-**2** in toluene-d_8 with temperature (Fig. 5) shows that coalescence of the $ArCH_3$ singlets assigned to the (R^i)*RR*-**2** and (R^i)*SS*-**2** pair of conformers ($\Delta\nu_1 = 3.3$ Hz) occurs at $T_{C_1} \sim 355$ K, while coalescence of the $ArCH_3$ singlets assigned to the (R^i)*RS*-**2** and (R^i)*RR* or (R^i)*SS*-**2** pair of conformers (average $\Delta\nu_2 \sim 13.2$ Hz) occurs at $T_{C_2} \sim 385$ K, in agreement with a calculated[23] rotational energy barrier of ca. 20 kcal mol^{-1}.

Altogether, the straightforward synthesis of four new enantiopure ligands based on the binaphthyl diamine backbone was achieved in two steps, while fine tuning of the experimental parameters provided the desired compounds in high yield with the retention of their enantiomeric purity.

2.2. Evaluation of ligands (R^i)-1 to (R^i)-3 in the ytterbium-catalysed intramolecular hydroamination of various aminoalkenes

In our previous studies on hydroamination reactions catalysed by lanthanide ate complexes coordinated by N-substituted binaphthylamine ligands, we found that ytterbium-based catalysts afforded the highest enantiomeric excesses.[6] We thus focused on the evaluation of our new ligands with this metal. The ate complexes were

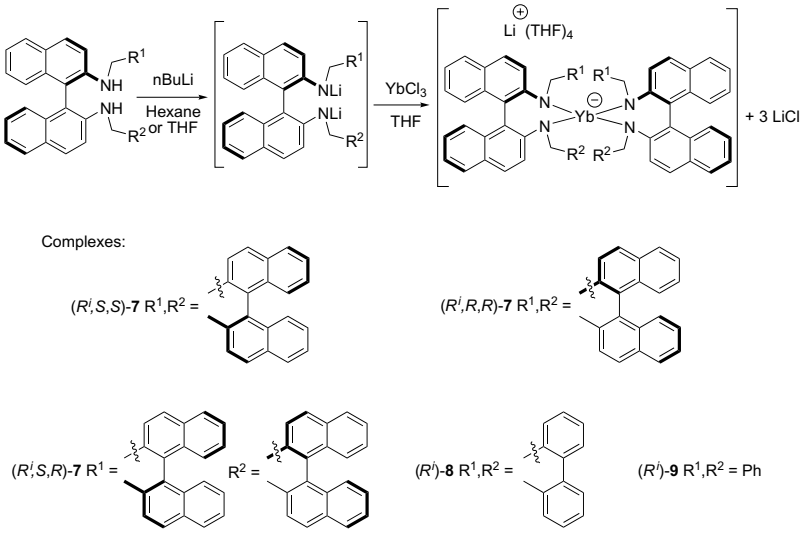

Figure 6. Synthesis of new chiral amido ate complexes of ytterbium.

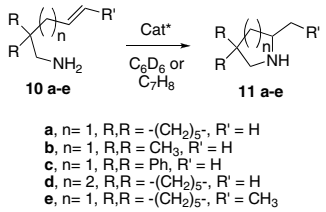

Figure 7. Intramolecular hydroamination reactions for the synthesis of scalemic N-heterocycles.

synthesised as previously reported in two steps, by the metathesis reaction of 2 equiv of the bis lithium salt of the ligand with anhydrous $YbCl_3$. Indeed, Li_2-{(R^i)-$C_{20}H_{12}(NCH_2Ph)_2$} was prepared by the reaction of ligand (R^i)-**3** with *n*-BuLi in hexane and the subsequent metathesis reaction was performed in THF at room temperature. This complex was previously isolated and characterised.[6b] As ligands (R^i,*S*,*S*)-**1**, (R^i,*R*,*R*)-**1**, (R^i,*S*,*R*)-**1** and (R^i)-**2** were not soluble in hexane, the corresponding complexes, [(R^i,*S*,*S*)-**7**, (R^i,*R*,*R*)-**7**, (R^i,*S*,*R*)-**7** and (R^i)-**8**] were prepared in THF at room temperature (Fig. 6). Complexes (R^i,*S*,*S*)-**7**, (R^i,*S*,*R*)-**7** and (R^i)-**8** were obtained as green powders and complex (R^i,*R*,*R*)-**7** as a brown powder, after evaporation of solvent. These complexes were not isolated but used in situ immediately after their preparation for catalytic intramolecular hydroamination tests (see Fig. 7).

All ytterbium catalysts were active for the hydroamination/cyclisation of aminopentene derivatives and of *C*-(1-but-3-enyl-cyclohexyl)-methylamine. Various results were obtained according to the targeted substrates but as a general trend, complexes **7** proved to be the most active species of the series. For example, whereas *C*-(1-allyl-cyclohexyl)-methylamine **10a** was completely transformed in almost one day with catalysts (R^i)-**8** and (R^i)-**9**, only about 3.5 h were necessary in the presence of catalysts **7** (Table 2, entries 1–5). This was also observed with other substrates. The three complexes **7** gave similar results in terms of activity with all the substrates tested. As already observed from our previous results,[6b] these benzyl-type substituted catalysts were less enantioselective but more active compared to those bearing more sterically hindered substituents directly bonded to the nitrogen atoms. 3-Methyl-2-aza-spiro[4.5]decane **11a** was obtained with up to 38% ee, this highest value arising from the use of catalyst (R^i)-**9** (Table 2, entry 5). The cyclisation in the presence of a more sterically demanding catalyst ((R^i)-**8**) or with complexes containing additional chirality elements [(R^i,*S*,*S*)-**7**, (R^i,*R*,*R*)-**7** or (R^i,*S*,*R*)-**7**] did not provide the expected product with improved enantioselectivity (Table 2, entries 1–4). 1,1-Dimethyl-but-3-enylamine **10b**, known as the test substrate for intramolecular asymmetric hydroamination, was smoothly transformed at room temperature to provide 2,4,4-trimethyl-pyrrolidine **11b** with up to 32% ee (Table 2, entries 6–10). As already noted,[6c–e] and due to an important Thorpe–Ingold effect, the *gem*-substituted aminopentene **10c** was rapidly cyclised in a few hours with up to 58% ee, the highest value obtained with this series of catalysts. Interestingly, complex (R^i)-**9** afforded the expected product rapidly, with the major enantiomer bearing the opposite configuration to that obtained with the other catalysts (Table 2, entries 11–15). Piperidine **11d** was obtained at room temperature with all catalysts, indicating a higher activity than those furnished by other lanthanide ate complexes.[6c–e] Complete conversion in 18 h was observed by using catalyst (R^i,*S*,*S*)-**7** and the product was isolated with 43% ee (Table 2, entries 16–20). *C*-(1-But-2-enyl-cyclohexyl)-methylamine **10e**, a more demanding substrate possessing an internal double bond, was next engaged in the reaction, albeit at high temperature to promote cyclisation. Complete conversion was obtained with catalysts (R^i,*R*,*R*)-**7**, (R^i,*S*,*R*)-**7** and (R^i)-**8**; unfortunately product **11e** was isolated in only 13% ee. Complex (R^i)-**9** led to a slower reaction but interestingly with a higher value of 38% for the enantiomeric excess. Increasing the temperature to 120 °C allowed a better conversion for this cyclisation but with a decrease in the enantioselectivity (23% ee, Table 2, entries 21–26). The synthesis of this type of product has rarely been described by intramolecular asymmetric hydroamination, and lower enantiomeric excesses were reported for pyrrolidines resulting from aminoalkenes with internal double bonds.[6e,24] Also worth mentioning are the similar enantiomeric values obtained in almost all cases with the

Table 2. Comparison of ligands for the ytterbium-catalysed enantioselective cyclisation of aminoalkenes

Entry	Product	Catalyst[a,b]	Time (h)	Conversion (%)	ee (%)
1		(R^i,*S*,*S*)-**7**	3.5	93	21
2		(R^i,*R*,*R*)-**7**	4.5	100	16
3	**11a**	(R^i,*S*,*R*)-**7**	3	69	28
4		(R^i)-**8**	21	96	28
5		(R^i)-**9**	23	92	38
6		(R^i,*S*,*S*)-**7**	24	97	32
7		(R^i,*R*,*R*)-**7**	8.5	100	17
8	**11b**	(R^i,*S*,*R*)-**7**	27	99	22
9		(R^i)-**8**	45	>90	28
10		(R^i)-**9**	96	94	22
11		(R^i,*S*,*S*)-**7**	1.5	100	56
12		(R^i,*R*,*R*)-**7**	1.5	100	50
13	**11c**	(R^i,*S*,*R*)-**7**	3	100	58
14		(R^i)-**8**	1.5	100	52
15		(R^i)-**9**	0.5	100	−23[c]
16		(R^i,*S*,*S*)-**7**	18	100	43[d]
17		(R^i,*R*,*R*)-**7**	8.5	89	38
18	**11d**	(R^i,*S*,*R*)-**7**	27	100	44[e]
19		(R^i)-**8**	45	100	44
20		(R^i)-**9**	130	100	39
21		(R^i,*S*,*S*)-**7**[f]	72	31	23
22		(R^i,*R*,*R*)-**7**[f]	120	100	11
23	**11e**	(R^i,*S*,*R*)-**7**[f]	96	100	13
24		(R^i)-**8**[f]	144	100	11
25		(R^i)-**9**[f]	288	57	38
26		(R^i)-**9**[g]	168	82	23

[a] 6 mol % catalyst.
[b] C_6D_6 at 25 °C.
[c] The absolute configuration of product **11c** was opposite to that obtained with catalysts **7** and (R^i)-**8**.
[d] 75% conv. after 4.5 h.
[e] Reaction time not optimised.
[f] C_7H_8 at 110 °C.
[g] C_7H_8 at 120 °C.

diastereoisomeric complexes **7** although (R^i,*R*,*R*)-**7** furnished slightly lower values. From these results it can be concluded that the chirality arising from the binaphthyldiamine unit is of major importance for the enantiofacial discrimination of the transformation. Additional stereogenic centres do not alter the enantioselectivity in a significant manner.

3. Conclusion

The straightforward synthesis of highly constrained, enantiomerically pure, *atropos* polybinaphthyl diamines (R^i,*R*,*R*)-**4**, (R^i,*S*,*S*)-**4**, (R^i,*R*,*S*)-**4** and (R^i,*S*,*S*)-**1**, (R^i,*R*,*R*)-**1**, (R^i,*S*,*R*)-**1**, as well as the corresponding *tropos* diamines (R^i)-**6** and (R^i)-**2** opens the route to libraries of new chiral binaphthyl-based derivatives. Both reaction steps can be applied to a variety of linear or cyclic diamines or polyamines, either achiral or chiral, to obtain the corresponding series of binaphthyl tertiary and/or secondary diamine catalysts with potentially interesting chiral recognition properties. The first step, *gem*-dialkylation of amines using as alkylating agent either 2,2′-bis(bromomethyl)-1,1′-biphenyl or the (*R*)- as well as the (*S*)-enantiomer of 2,2′-bis(bromomethyl)-1,1′-binaphthyl both easily accessible by several procedures,[15–19] has been widely used. It always occurs with the exclusive formation of seven-membered ring alkyl tertiary amines or diamines. We have now demonstrated that the second step involving a selective bis(mono-hydrogenolysis) of the biphenylic or binaphthylic tertiary amino groups by lithium aluminium hydride in the presence of nickel chloride, proceeds in high yield to afford binaphthylic bis(biphenyl) and bis(binaphthyl)-substituted secondary diamines with steric and chiral constraints.

The new *atropos* diamines (R^i,*S*,*S*)-**1**, (R^i,*R*,*R*)-**1** and (R^i,*S*,*R*)-**1** or the *tropos* one (R^i)-**2** have been used to prepare ytterbium ate complexes, which catalyse the formation of scalemic pyrrolidines and a piperidine. Although the introduction of additional chiral moieties on the ligand did not increase the enantioselectivity of the transformation, the replacement of the phenyl substituent by a binaphthyl backbone unexpectedly increased the rates of the cyclisation reactions. Albeit the enantiomeric excesses remain modest, these catalysts exhibited higher activities than the other lanthanide ate complexes we have previously studied. The formation of a six-membered nitrogen heterocycle at room temperature is particularly interesting.[6d,e] Based on these results, we are currently studying more active and enantioselective catalysts aimed at promoting the intramolecular hydroamination of more demanding substrates.

4. Experimental

4.1. General experimental

For the preparation of catalysts and the realisation of the catalytic tests, manipulations were carried out under an argon atmosphere using standard Schlenk or glove box techniques. THF and diethyl ether were distilled from sodium benzophenone ketyl and degassed immediately prior to use. Hexane and toluene were distilled from CaH_2 and degassed immediately prior to use. Deuterated benzene was dried with sodium benzophenone ketyl and vacuum-transferred. Bruker AV 300 and AC 300 NMR spectrometers (operating at 300 MHz) were used for recording NMR spectra. Chemical shifts for ^1H and ^{13}C spectra were referenced internally according to the residual solvent resonances and reported relative to tetramethylsilane. Splitting patterns are abbreviated as follows: (s) singlet, (d) doublet, (t) triplet, (q) quartet, (m) multiplet. Mass spectra (electrospray mode) were recorded on a Hewlett–Packard HP5989MS spectrometer. High resolution mass spectra were performed on a Q-TOF Ultima Bruker mass spectrometer (Université d'Amiens, France). Elemental analyses were performed by the C.N.R.S. Service of Microanalyses in Gif-sur-Yvette (France). Melting points were determined with a temperature increase of 3 °C/min and are uncorrected. The optical rotations were measured by using a Perkin Elmer 241 polarimeter at room temperature in a 1 dm thermostated cell (with an accuracy of 0.3%), and were reported as follows: $[\alpha]_\lambda^{rt}$ (*c* in g per 100 mL, solvent). Analytical thin-layer chromatography (TLC), preparative TLC and column chromatography were performed on Silica Gel F 254 (Merck), Silica Gel G-25 (1 mm) (Macherey-Nagel) and kieselgel gel 60 (0.040–0.063 mm) (Merck), respectively. UV light (254 nm) allowed the visualisation of the spots after TLC runs for all compounds, even at low concentration. Enantiomeric excesses of the products have been determined by GC or HPLC analyses after derivatisation, and compared to racemic products prepared with $Y[N(TMS)_2]_3$, using the methods previously described.[6c,e] GC analyses were performed on Fisons 800 apparatus with a DB1 column (30 m × 0.32 mm × 0.5 μm) and HPLC analyses on Thermo Separation Product Spectra Series tsp 100 P100/UV100 or Perkin Elmer Pump Series 200/ DAD 20. Enantiomerically pure (+)-(*R*)-2,2′-bis-(bromomethyl)-1,1′-binaphthyl,[15] and the substrates **4a**–**e** for the hydroamination/cyclisation reactions[6c–e] were prepared as previously described. Enantiomerically pure (+)-(*R*)-2,2′-diamino-1,1′-binaphthyl and anhydrous $YbCl_3$ were purchased. All other commercially available chemicals were used after the appropriate purification.

4.2. Alkylation of (+)-(*R*)-2,2′-diamino-1,1′-binaphthyl by (+)-(*R*)- and (−)-(*S*)-2,2′-bis-(bromomethyl)-1,1′-binaphthyl, and by 2,2′-bis-(bromomethyl)-1,1′-biphenyl

(a) To a solution of (+)-(*R*)-2,2′-diamino-1,1′-binaphthyl (0.355 g; 1.25 mmol) and (+)-(*R*)-2,2′-bis-(bromomethyl)-1,1′-binaphthyl (1.100 g; 2.50 mmol) in toluene (15 mL) and acetonitrile (15 mL) was added DIEA (1.09 mL; 6.25 mmol). The solution was stirred under argon at 85 °C for 6 days, and then evaporated in vacuo. The residue was dissolved in CH_2Cl_2 (150 mL); kieselgel Si 60 (15 g) was added and the mixture was evaporated in vacuo at 50 °C. The resulting product-impregnated silica gel was poured onto the top of a 3 × 57 cm column of kieselgel Si 60 made up with cyclohexane–CH_2Cl_2 7:3. Elution with cyclohexane–CH_2Cl_2 7:3–3:7 followed by preparative TLC of the impure fractions on silica gel with eluent cyclo-

hexane–CH_2Cl_2 7:3, afforded 0.696 g (66%) of pure diamine (R^i,*R*,*R*)-**4** (see Section 4.3), 0.206 g (29%) of pure diamine (R^i,*R*)-**5** (see Section 4.4) and 0.071 g (6%) of recovered (*R*)-dibromide. In a second run, a solution of (+)-(*R*)-2,2′-diamino-1,1′-binaphthyl (0.284 g; 1.00 mmol), (+)-(*R*)-2,2′-bis-(bromomethyl)-1,1′-binaphthyl (0.968 g; 2.20 mmol) and DIEA (0.87 mL; 5.00 mmol) in toluene (10 mL) and acetonitrile (10 mL), was stirred under argon at 85 °C for 12 days. Column chromatography of the crude product followed by preparative TLC of the impure fractions in the same conditions as above afforded 0.431 g (51%) of pure (R^i,*R*,*R*)-**4**, 0.035 g (6%) of pure (R^i,*R*)-**5** and 0.085 g (9%) of recovered (*R*)-dibromide.

(b) A solution of (+)-(*R*)-2,2′-diamino-1,1′-binaphthyl (0.355 g; 1.25 mmol), (−)-(*S*)-2,2′-bis-(bromomethyl)-1,1′-binaphthyl (1.100 g; 2.50 mmol) and DIEA (1.09 mL; 6.25 mmol) in toluene (15 mL) and acetonitrile (15 mL), was stirred under argon at 85 °C for 7 days, and then evaporated in vacuo. Column chromatography of the crude product followed by preparative TLC of the impure fractions under the same conditions as above afforded 0.912 g (87%) of pure (R^i,*S*,*S*)-**4** (see Section 4.5), 0.087 g (12%) of pure (R^i,*S*)-**5** (see Section 4.6) and 0.014 g (1%) of recovered (*S*)-dibromide.

(c) A solution of diamine (R^i,*R*)-**5** (0.226 g; 0.40 mmol), (−)-(*S*)-2,2′-bis-(bromomethyl)-1,1′-binaphthyl (0.193 g; 0.43 mmol) and DIEA (0.2 mL; 1.15 mmol) in toluene (10 mL) and acetonitrile (10 mL), was stirred under argon at 85 °C for 8 days, and then evaporated in vacuo. Preparative TLC of the crude product on silica gel with eluent cyclohexane–CH_2Cl_2 7:3 afforded 0.166 g (49%) of pure (R^i,*R*,*S*)-**4** (see Section 4.7). The remaining starting materials, (R^i,*R*)-**5** and (*S*)-dibromide, were not isolated.

(d) A solution of diamine (R^i,*S*)-**5** (0.075 g; 0.13 mmol), (+)-(*R*)-2,2′-bis-(bromomethyl)-1,1′-binaphthyl (0.071 g; 0.16 mmol) and DIEA (0.06 mL; 0.03 mmol) in toluene (10 mL) and acetonitrile (10 mL), was stirred under argon at 85 °C for 7 days, and then evaporated in vacuo. Preparative TLC of the crude product on silica gel with eluent cyclohexane–CH_2Cl_2 7:3 afforded 0.053 g (47%) of pure (R^i,*R*,*S*)-**4** (see Section 4.7). The remaining starting materials, (R^i,*S*)-**5** and (*R*)-dibromide, were not isolated.

(e) A solution of (+)-(*R*)-2,2′-diamino-1,1′-binaphthyl (0.703 g; 2.47 mmol), 2,2′-bis-(bromomethyl)-1,1′-biphenyl (1.851 g; 5.44 mmol) and DIEA (2.15 mL; 12.35 mmol) in toluene (25 mL) and acetonitrile (25 mL), was stirred under argon at 85 °C for 6 days, and then evaporated in vacuo. The residue was chromatographed on a 4 × 85 cm column of silica gel eluted with cyclohexane–CH_2Cl_2 7:3–3:7 to afford 1.384 g (87%) of pure (R^i)-**6** (see Section 4.8).

4.3. Diamine (R^i,*R*,*R*)-4

Pale yellow solid. Mp = 204–207 °C. R_f = 0.54 (cyclohexane–CH_2Cl_2 7:3); 0.73 (cyclohexane–CH_2Cl_2 1:1). ^{1}H NMR ($CDCl_3$): δ 8.02 [m (t-like), $J \sim 8.7$ Hz, 4H, ArH], 7.91 [d, $J = 8.1$ Hz, 4H, ArH], 7.85 [d, $J = 8.3$ Hz, 4H, ArH], 7.68 [d, $J = 8.8$ Hz, 2H, ArH], 7.48–7.39 [m, 6H, ArH], 7.34 [d, $J = 8.3$ Hz, 4H, ArH], 7.26 [m, 4H, ArH], 7.19 [m (t-like), 4H, ArH], 6.84 [d, $J = 8.3$ Hz, 4H, ArH], 3.88 and 3.58 [d, $J = 12.5$ Hz, 4H and d, $J = 12.5$ Hz, 4H, Ar–CH_2N]. ^{13}C NMR ($CDCl_3$): δ 149.6 (C_{Ar}–NR_2), 134.8, 134.2, 134.1, 132.8, 131.4, 131.2, 131.0, 128.7, 128.5, 128.1, 128.0, 127.43, 127.41, 126.3, 126.0, 125.5, 125.2, 124.9, 124.3 (C_{Ar}), 54.9 (Ar–CH_2N). $[\alpha]^{25}_{589} = -78$; $[\alpha]^{25}_{578} = -83$; $[\alpha]^{25}_{546} = -92$; $[\alpha]^{25}_{436} = -238$ (*c* 0.2, $CHCl_3$). MS (ES^+) *m*/*z* (relative intensity): 841.8 (100) $[M+H]^+$, 864.1 (12) $[M+Na]^+$. TOF-MS (ES^+) *m*/*z* (relative intensity): 841.4 (100) $[M+H]^+$, 863.3 (10) $[M+Na]^+$, 879.4 (3) $[M+K]^+$. TOF-HRMS (ES^+), calcd for $[M+H]^+$ ($C_{64}H_{45}N_2$): 841.3583. Found: 841.3638. Anal. Calcd for $C_{64}H_{44}N_2{\cdot}2H_2O$ (877.040): C, 87.64; H, 5.52; N, 3.19. Found: C, 87.71; H, 5.53; N, 3.14.

4.4. Diamine (R^i,*R*)-5

Yellow solid. Mp = 195–198 °C. R_f = 0.15 (cyclohexane–CH_2Cl_2 7:3); 0.34 (cyclohexane–CH_2Cl_2 1:1); 0.65 (CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 7.91–7.87 [m, 4H, ArH], 7.83 [d, $J = 8.3$ Hz, 2H, ArH], 7.71 [m (t-like), 2H, ArH], 7.47–7.28 [m, 8H, ArH], 7.26–7.18 [m, 6H, ArH], 7.09 [m (t-like), 2H, ArH], 3.84 [m (br), 2H, NH_2], 4.10 and 3.55 [d, $J = 12.2$ Hz, 2H and d, $J = 12.0$ Hz, 2H, Ar–CH_2N]. ^{13}C NMR ($CDCl_3$): δ 149.0 (C_{Ar}–NR_2), 141.8 (C_{Ar}–NH_2), 134.5, 133.8, 133.2, 132.95, 132.89, 131.1, 130.1, 129.0, 128.9, 128.6, 128.3, 128.2, 128.1, 127.9, 127.6, 127.4, 126.7, 126.1, 125.6, 125.3, 124.9, 124.4, 123.9, 123.2, 122.1, 121.1, 118.0, 116.5 (C_{Ar}), 53.9 (Ar–CH_2N). $[\alpha]^{25}_{589} = +535$; $[\alpha]^{25}_{578} = +572$; $[\alpha]^{25}_{546} = +701$; $[\alpha]^{25}_{436} = +1970$ (*c* 0.2, $CHCl_3$). MS (ES^+) *m*/*z* (relative intensity): 563.4 (100) $[M+H]^+$, 585.4 (46) $[M+Na]^+$, 601.3 (18) $[M+K]^+$. TOF-MS (ES^+) *m*/*z* (relative intensity): 563.3 (100) $[M+H]^+$, 585.2 (22) $[M+Na]^+$, 601.2 (5) $[M+K]^+$. TOF-HRMS (ES^+), calcd for $[M+H]^+$ ($C_{42}H_{31}N_2$): 563.2487. Found: 563.2509. Anal. Calcd for $C_{42}H_{30}N_2{\cdot}1.7H_2O$ (593.303): C, 85.01; H, 5.67; N, 4.72. Found: C, 84.97; H, 5.61; N, 4.11.

4.5. Diamine (R^i,*S*,*S*)-4

Pale yellow solid. Mp = 222–228 °C. R_f = 0.47 (cyclohexane–CH_2Cl_2 7:3); 0.69 (cyclohexane–CH_2Cl_2 1:1). ^{1}H NMR ($CDCl_3$): δ 7.99 [d, $J \sim 8.3$ Hz, 4H, ArH], 7.97 [d (br), $J \sim 7.9$ Hz, 4H, ArH], 7.82 [d, $J = 7.7$ Hz, 2H, ArH], 7.73 [d, $J = 8.8$ Hz, 2H, ArH], 7.57–7.23 [m, 22H, ArH], 3.99 and 3.57 [d, $J = 12.1$ Hz, 4H and d, $J = 12.1$ Hz, 4H, Ar–CH_2N]. ^{13}C NMR ($CDCl_3$): δ 147.3 (C_{Ar}–NR_2), 135.0, 134.7, 134.0, 133.0, 131.2, 129.6, 128.5, 128.2, 128.1, 127.8, 127.4, 126.5, 126.1, 125.7, 125.4, 125.1, 123.4, 120.2 (C_{Ar}), 53.7 (Ar–CH_2N). $[\alpha]^{25}_{589} = -1164$; $[\alpha]^{25}_{578} = -1235$; $[\alpha]^{25}_{546} = -1505$; $[\alpha]^{25}_{436} = -4526$ (*c* 0.23, $CHCl_3$). MS (ES^+) *m*/*z* (relative intensity): 841.8 (100) $[M+H]^+$. TOF-MS (ES^+) *m*/*z* (relative intensity): 841.4 (100) $[M+H]^+$. TOF-HRMS (ES^+), calcd for $[M+H]^+$ ($C_{64}H_{45}N_2$): 841.3583. Found: 841.3550. Anal. Calcd for $C_{64}H_{44}N_2{\cdot}0.5H_2O$ (850.016): C, 90.43; H, 5.34; N, 3.29. Found: C, 90.61; H, 5.55; N, 3.14.

4.6. Diamine (R^i,*S*)-5

Yellow solid. Mp = 175–185 °C. R_f = 0.09 (cyclohexane–CH_2Cl_2 7:3); 0.25 (cyclohexane–CH_2Cl_2 1:1). ^{1}H NMR ($CDCl_3$): δ 7.96–7.86 [m, 6H, ArH], 7.77 [d, J = 7.9 Hz, 1H, ArH], 7.71 [d, J = 8.7 Hz, 1H, ArH], 7.58–7.18 [m, 15H, ArH], 7.04 [d, J = 8.7 Hz, 1H, ArH], 3.80 [m (br), 2H, NH_2], 4.10 and 3.64 [d, J = 12.1 Hz, 2H and d, J = 12.1 Hz, 2H, Ar–CH_2N]. ^{13}C NMR ($CDCl_3$): δ 148.0 (C_{Ar}–NR_2), 141.7 (C_{Ar}–NH_2), 134.7, 134.6, 134.0, 133.7, 133.0, 131.1, 129.9, 129.0, 128.75, 128.69, 128.2, 127.8, 127.4, 127.3, 126.7, 126.4, 125.9, 125.7, 125.6, 125.4, 124.7, 123.8, 122.9, 122.0, 120.0, 118.9, 116.3 (C_{Ar}), 54.1 (Ar–CH_2N). $[\alpha]_{589}^{25} = -507$; $[\alpha]_{578}^{25} = -544$; $[\alpha]_{546}^{25} = -656$; $[\alpha]_{436}^{25} = -1779$ (*c* 0.2, $CHCl_3$). MS (ES^+) *m*/*z* (relative intensity): 563.4 (100) $[M+H]^+$. TOF-MS (ES^+) *m*/*z* (relative intensity): 563.3 (100) $[M+H]^+$. TOF-HRMS (ES^+), calcd for $[M+H]^+$ ($C_{42}H_{31}N_2$): 563.2487. Found: 563.2479. Anal. Calcd for $C_{42}H_{30}N_2{\cdot}0.5H_2O$ (571.684): C, 88.23; H, 5.47; N, 4.63. Found: C, 88.69; H, 5.55; N, 4.63.

4.7. Diamine (R^i,*R*,*S*)-4

Pale yellow solid. Mp = 196–206 °C. R_f = 0.45 (cyclohexane–CH_2Cl_2 7:3). ^{1}H NMR ($CDCl_3$): δ 7.97–7.75 [m, 10H, ArH], 7.72 [d, J = 8.3 Hz, 2H, ArH], 7.62–7.39 [m, 14H, ArH], 7.32–7.17 [m, 6H, ArH], 7.06 [d, J = 8.3 Hz, 2H, ArH], 6.89 [d, J = 8.3 Hz, 2H, ArH], 3.93 and 3.73 [d, J = 12.5 Hz, 2H and d, J = 12.5 Hz, 2H, Ar–CH_2N], 3.87 and 3.55 [d, J = 11.9 Hz, 2H and d, J = 11.9 Hz, 2H, Ar–CH_2N]. ^{13}C NMR ($CDCl_3$): δ 149.6, 147.7 (C_{Ar}–NR_2), 134.8, 134.7, 134.53, 134.47, 134.2, 133.7, 132.9, 131.34, 131.32, 131.1, 130.9, 129.6, 128.9, 128.6, 128.4, 128.2, 127.9, 127.6, 127.5, 127.3, 126.5, 126.4, 126.1, 125.7, 125.6, 125.5, 125.4, 125.3, 125.2, 124.9, 124.3, 123.4, 120.2 (C_{Ar}), 54.9, 53.8 (Ar–CH_2N). $[\alpha]_{589}^{25} = -533$; $[\alpha]_{578}^{25} = -566$; $[\alpha]_{546}^{25} = -685$; $[\alpha]_{436}^{25} = -2070$ (*c* 0.2, $CHCl_3$). MS (ES^+) *m*/*z* (relative intensity): 841.7 (100) $[M+H]^+$. TOF-MS (ES^+) *m*/*z* (relative intensity): 841.4 (100) $[M+H]^+$. TOF-HRMS (ES^+), calcd for $[M+H]^+$ ($C_{64}H_{45}N_2$): 841.3583. Found: 841.3559. Anal. Calcd for $C_{64}H_{44}N_2{\cdot}0.5H_2O$ (850.016): C, 90.42; H, 5.34; N, 3.30. Found: C, 90.21; H, 5.95; N, 3.07.

4.8. Diamine (R^i)-6

Pale yellow foam. R_f = 0.53 (cyclohexane–CH_2Cl_2 7:3). ^{1}H NMR ($CDCl_3$): δ 7.90 [d, J = 8.6 Hz, 4H, ArH], 7.57 [d, J = 8.8 Hz, 2H, ArH], 7.45–7.22 [m, 18H, ArH], 6.84 [d, J = 7.3 Hz, 4H, ArH], 3.73 and 3.66 [d, J = 12.5 Hz, 4H and d, J = 12.5 Hz, 4H, Ar–CH_2N]. ^{13}C NMR ($CDCl_3$): δ 140.9 (C_{Ar}–NR_2), 135.6, 134.6, 130.4, 129.5, 128.5, 128.0, 127.8, 127.7, 127.4, 126.3, 126.1, 123.9, 122.5 (C_{Ar}), 54.5 (Ar–CH_2N). $[\alpha]_{589}^{25} = -279$; $[\alpha]_{578}^{25} = -293$; $[\alpha]_{546}^{25} = -357$; $[\alpha]_{436}^{25} = -1096$ (*c* 0.5, CH_2Cl_2). CI-MS (NH_3) *m*/*z* (relative intensity): 641 (100) $[M+H]^+$. Anal. Calcd for $C_{48}H_{36}N_2{\cdot}0.5H_2O$ (649.792): C, 88.72; H, 5.74; N, 4.31. Found: C, 88.69; H, 5.91; N, 4.07.

4.9. Hydrogenolysis of (R^i,*R*,*R*)-4, (R^i,*S*,*S*)-4, (R^i,*R*,*S*)-4 and (R^i)-6

(a) To a solution of (R^i,*R*,*R*)-**4** (0.118 g; 0.14 mmol) in THF (15 mL) was added $LiAlH_4$ (0.25 g; 6.5 mmol) by portions, under an argon stream. The reaction mixture was stirred under argon at 80 °C for 24 h, cooled to room temperature, hydrolysed by the cautious addition of H_2O (ca. 0.5 mL), then 15% aq NaOH (ca. 0.5 mL), then H_2O (ca. 1 mL), and then filtered on sintered glass through Celite. The filtrate was diluted with CH_2Cl_2 (ca. 150 mL), and the solution was washed with H_2O (3 × 100 mL), dried ($MgSO_4$), filtered and evaporated in vacuo. The crude product (0.120 g) consisted of unreacted (R^i,*R*,*R*)-**4** with no trace of (R^i,*S*,*S*)-**1** by TLC, ^{1}H/^{13}C NMR and MS (ES^+).

(b) To a solution of (R^i,*R*,*R*)-**4** (0.360 g; 0.43 mmol) in THF (100 mL) was added anhydrous $NiCl_2$ (0.150 g; 1.1 mmol). The suspension was magnetically stirred at room temperature and $LiAlH_4$ (1.500 g; 39 mmol) was added by portions, under argon stream. The resulting black-greenish solution was stirred under argon at 85 °C for 7.5 h, cooled to room temperature, hydrolysed by the cautious addition of H_2O (ca. 2 mL), then 15% aq NaOH (ca. 3 mL), then H_2O (ca. 8 mL). The mixture was filtered on sintered glass through Celite and the solid washed with CH_2Cl_2 (ca. 400 mL). The whole filtrate was repeatedly washed with H_2O (3 × 400 mL), dried over $MgSO_4$, filtered and evaporated in vacuo. The crude product, which presented a single spot on analytical TLC (with no trace of the starting diamine), was chromatographed on two preparative TLC plates of silica gel (1 mm) eluted with cyclohexane–CH_2Cl_2 7:3 to afford 0.319 g (88%) of pure diamine (R^i,*S*,*S*)-**1** (see Section 4.10). Four other runs under similar experimental conditions always gave (R^i,*S*,*S*)-**1** as single product in high yield: (1) Treatment of (R^i,*R*,*R*)-**4** (0.331 g; 0.39 mmol) in THF (100 mL) with $NiCl_2$ (0.150 g) and $LiAlH_4$ (1.500 g) at 85 °C for 7 h, afforded 0.279 g (84%) of pure (R^i,*S*,*S*)-**1** after chromatography. (2) Treatment of (R^i,*R*,*R*)-**4** (0.0507 g; 0.060 mmol) in THF (15 mL) with $NiCl_2$ (0.025 g) and $LiAlH_4$ (0.25 g) at 85 °C for 16 h, afforded 0.0425 g (84%) of pure (R^i,*S*,*S*)-**1**. (3) Treatment of (R^i,*R*,*R*)-**4** (0.0509 g; 0.060 mmol) in THF (15 mL) with $NiCl_2$ (0.025 g) and $LiAlH_4$ (0.25 g) at 85 °C for 6.5 h, afforded 0.042 g (82%) of pure (R^i,*S*,*S*)-**1**. (4) Treatment of (R^i,*R*,*R*)-**4** (0.0664 g; 0.079 mmol) in THF (15 mL) with $NiCl_2$ (0.025 g) and $LiAlH_4$ (0.25 g) at 85 °C for 7 h, afforded 0.0554 g (83%) of pure (R^i,*S*,*S*)-**1**.

(c) A solution of (R^i,*S*,*S*)-**4** (0.460 g; 0.55 mmol), anhydrous $NiCl_2$ (0.150 g; 1.1 mmol) and $LiAlH_4$ (1.500 g; 39 mmol) in THF (100 mL) was stirred under argon at 85 °C for 16 h, cooled to room temperature, hydrolysed by the cautious addition of H_2O and 15% aq NaOH as above in (b). The mixture was filtered on sintered glass over Celite, the solid was washed with CH_2Cl_2 (ca. 400 mL) and the whole filtrate was repeatedly washed with H_2O

(3 × 400 mL), dried over $MgSO_4$, filtered and evaporated in vacuo. The crude product was chromatographed on two preparative TLC plates of silica gel (1 mm) eluted with cyclohexane–CH_2Cl_2 7:3 to afford 0.368 g (80%) of pure diamine (R^i,*R*,*R*)-**1** (see Section 4.11). In a second run under similar experimental conditions, treatment of (R^i,*S*,*S*)-**4** (0.447 g; 0.53 mmol) in THF (100 mL) with $NiCl_2$ (0.150 g) and $LiAlH_4$ (1.500 g) at 85 °C for 7 h, afforded 0.327 g (73%) of pure (R^i,*R*,*R*)-**1** after chromatography.

(d) A solution of (R^i,*R*,*S*)-**4** (0.191 g; 0.23 mmol), anhydrous $NiCl_2$ (0.075 g; 0.55 mmol) and $LiAlH_4$ (0.750 g; 19.5 mmol) in THF (50 mL) was stirred under argon at 85 °C for 7.5 h, cooled to room temperature, hydrolysed by cautious addition of H_2O and 15% aq NaOH as above in paragraph (b). The mixture was filtered on a sintered glass over Celite, the solid was washed with CH_2Cl_2 (ca. 400 mL) and the whole filtrate was repeatedly washed with H_2O (3 × 400 mL), dried over $MgSO_4$, filtered and evaporated in vacuo. The crude product was chromatographed on two preparative TLC plates of silica gel (1 mm) eluted with cyclohexane–CH_2Cl_2 7:3 to afford 0.119 g (62%) of pure diamine (R^i,*S*,*R*)-**1** (see Section 4.12).

(e) To a solution of (R^i)-**6** (0.490 g; 0.76 mmol) in THF (12 mL) and diglyme (10 mL) was added anhydrous $NiCl_2$ (0.2 g; 1.5 mmol). The suspension was magnetically stirred at room temperature and $LiAlH_4$ (0.87 g; 22 mmol) was added by portions, under argon stream. The resulting black-greenish solution was stirred under argon at 155 °C for 1.5 h, cooled to room temperature, hydrolysed by the cautious addition of H_2O (ca. 5 mL), then 15% aq NaOH (ca. 5 mL), and then H_2O (ca. 10 mL), and then filtered on a sintered glass through Celite. The filtrate was diluted with CH_2Cl_2 (ca. 300 mL), and the solution was washed with H_2O (3 × 100 mL), dried over $MgSO_4$, filtered and evaporated in vacuo. The crude product was dissolved in a minimum of hot CH_2Cl_2 and the same volume of cyclohexane was added. The solution was kept at 4 °C, resulting in the crystallisation of (R^i)-**2** (0.276 g; 56%) (see Section 4.13).

4.10. Diamine (R^i,*S*,*S*)-1

Pale yellow solid. Mp = 123–127 °C. R_f = 0.50 (cyclohexane–CH_2Cl_2 7:3). ^{1}H NMR ($CDCl_3$): δ 7.93–7.86 [m, 6H, ArH], 7.76–7.68 [m, 6H, ArH], 7.54 [d, J = 8.7 Hz, 2H, ArH], 7.48–7.40 [m, 6H, ArH], 7.28–7.17 [m, 8H, ArH], 7.13–7.05 [m, 6H, ArH], 6.91 [d, J = 8.8 Hz, 2H, ArH], 4.22 [s (br), 2H, NH], 4.01 [s, 4H, Ar–CH_2N], 2.00 [s, 6H, Ar–CH_3]. ^{13}C NMR ($CDCl_3$): δ 144.0 (C_{Ar}–NHR), 135.6, 134.5, 134.3, 133.8, 133.6, 132.8, 132.5, 132.2, 129.4, 128.7, 128.1, 128.04, 127.98, 127.88, 127.82, 127.6, 126.7, 126.3, 126.2, 125.6, 125.5, 125.4, 125.2, 124.4, 123.8, 121.9, 114.0, 111.6 (C_{Ar}), 45.3 (Ar–CH_2NHR), 20.1 (Ar–CH_3). $[\alpha]^{25}_{589} = -41$; $[\alpha]^{25}_{578} = -42$; $[\alpha]^{25}_{546} = -50$; $[\alpha]^{25}_{436} = -177$ (*c* 0.2, $CHCl_3$). MS (ES^+) *m*/*z* (relative intensity): 845.7 (18) $[M+H]^+$, 867.8 (100) $[M+Na]^+$. TOF-MS (ES^+) *m*/*z* (relative intensity): 845.4 (14) $[M+H]^+$, 867.4 (100) $[M+Na]^+$, 883.4 (3) $[M+K]^+$. HRMS (ES^+), calcd for $[M+Na]^+$ ($C_{64}H_{48}N_2Na$): 867.3715. Found: 867.3757. Anal. Calcd for $C_{64}H_{48}N_2{\cdot}4H_2O$ (917.104): C, 83.81; H, 6.15; N, 3.05. Found: C, 83.78; H, 5.63; N, 2.87.

4.11. Diamine (R^i,*R*,*R*)-1

Pale yellow solid. Mp = 152–160 °C. R_f = 0.41 (cyclohexane–CH_2Cl_2 7:3). ^{1}H NMR ($CDCl_3$): δ 7.94–7.82 [m, 6H, ArH], 7.76–7.57 [m, 8H, ArH], 7.47–7.42 [m, 6H, ArH], 7.28–7.00 [m, 14H, ArH], 6.90 [d, J = 8.8 Hz, 2H, ArH], 4.24 [s (br), 2H, NH], 4.03 [s, 4H, Ar–CH_2N], 1.99 [s, 6H, Ar–CH_3]. ^{13}C NMR ($CDCl_3$): δ 144.0 (C_{Ar}–NHR), 135.6, 134.5, 134.4, 133.8, 133.5, 132.8, 132.5, 132.2, 129.4, 128.8, 128.4, 128.1, 128.03, 127.99, 127.9, 127.8, 127.6, 127.0, 126.7, 126.3, 126.2, 125.9, 125.6, 125.5, 125.4, 125.1, 124.5, 123.8, 121.9, 113.9, 111.6 (C_{Ar}), 45.4 (Ar–CH_2NHR), 20.0 (Ar–CH_3). $[\alpha]^{25}_{589} = -23$; $[\alpha]^{25}_{578} = -24$; $[\alpha]^{25}_{546} = -26$; $[\alpha]^{25}_{436} = -124$ (*c* 0.2, $CHCl_3$). MS (ES^+) *m*/*z* (relative intensity): 845.5 (100) $[M+H]^+$. TOF-MS (ES^+) *m*/*z* (relative intensity): 867.0 (100) $[M+Na]^+$. TOF-HRMS (ES^+), calcd for $[M+Na]^+$ ($C_{64}H_{48}N_2Na$): 867.3715. Found: 867.3741. Anal. Calcd for $C_{64}H_{48}N_2$ (845.040): C, 90.96; H, 5.73; N, 3.31. Found: C, 90.81; H, 5.93; N, 3.11.

4.12. Diamine (R^i,*S*,*R*)-1

Pale yellow solid. Mp = 120–128 °C. R_f = 0.37 (cyclohexane–CH_2Cl_2 7:3). ^{1}H NMR ($CDCl_3$): δ 7.92–7.82 [m, 6H, ArH], 7.75–7.51 [m, 8H, ArH], 7.48–7.39 [m, 6H, ArH], 7.27–7.00 [m, 14H, ArH], 6.92 [d, J = 8.8 Hz, 1H, ArH], 6.88 [d, J = 8.8 Hz, 1H, ArH], 4.22 [s (br), 2H, NH], 4.02 [s, 2H, Ar–CH_2N], 4.00 [s, 2H, Ar–CH_2N], 2.03 [s, 3H, Ar–CH_3], 1.97 [s, 3H, Ar–CH_3]. ^{13}C NMR ($CDCl_3$): δ 144.02, 143.95 (C_{Ar}–NHR), 135.6, 135.5, 134.45, 134.42, 134.39, 133.2, 133.8, 133.7, 133.6, 133.5, 132.8, 132.7, 132.6, 132.5, 132.2, 129.44, 129.40, 128.7, 128.1, 128.04, 127.98, 127.92, 127.89, 127.83, 127.79, 127.59, 127.57, 12 6.7, 126.32, 126.26, 125.62, 125.56, 125.5,125.44, 125.39, 125.3, 125.1, 124.6, 124.3, 123.8, 121.9, 113.94, 113.87, 111.62, 111.56 (C_{Ar}), 45.5, 45.3 (Ar–CH_2NHR), 20.1, 20.0 (Ar–CH_3). $[\alpha]^{25}_{589} = -27$; $[\alpha]^{25}_{578} = -28$; $[\alpha]^{25}_{546} = -31$; $[\alpha]^{25}_{436} = -128$ (*c* 0.18, $CHCl_3$). MS (ES^+) *m*/*z* (relative intensity): 845.5 (100) $[M+H]^+$. TOF-MS (ES^+) *m*/*z* (relative intensity): 867.4 (100) $[M+Na]^+$. TOF-HRMS (ES^+), calcd for $[M+Na]^+$ ($C_{64}H_{48}N_2Na$): 867.3715. Found: 867.3709. Anal. Calcd for $C_{64}H_{48}N_2$ (845.040): C, 90.96; H, 5.73; N, 3.31. Found: C, 90.43; H, 6.05; N, 3.05.

4.13. Diamine (R^i)-2

White solid. Mp = 133–135 °C. R_f = 0.38 (EtOAc–CH_2Cl_2 3:97). ^{1}H NMR (C_6D_6): δ 7.67–7.63 [m, 4H, ArH], 7.39–7.36 [m, 2H, ArH], 7.29–7.21 [m, 2H, ArH], 7.15–6.96 [m, 20H, ArH], 4.20–4.14 [m, 2H, NH], 3.87–3.78 and 3.73–3.62 [2m, 4H, Ar–CH_2N], 1.93 [s, 3H, Ar–CH_3], 1.88, 1.87 [2s, 3H, Ar–CH_3]. ^{1}H NMR (toluene-d_8): δ 7.64–7.61 [m, 4H, ArH], 7.31 [m, 2H, ArH], 7.21–6.98 [m, 22H, ArH], 4.10 [m, 2H, NH], 3.73–3.64 [m, 4H, Ar–CH_2N], 1.93 [s, 3H, Ar–CH_3], 1.89, 1.88 [2s, 3H, Ar–CH_3]. ^{13}C NMR (C_6D_6): δ 144.5 (C_{Ar}–NHR), 140.8, 140.7, 137.6, 135.9, 134.7, 134.6, 130.4, 130.0 129.9,

129.7, 129.5, 129.4, 128.6, 128.5, 128.3, 128.0, 127.7, 127.5, 127.2, 127.1, 127.0, 126.9, 126.8, 126.0, 124.5, 124.4, 122.4, 122.3, 114.3, 112.4 (C_{Ar}), 45.5, 45.4 (Ar–CH_2N), 20.0, 19.9 (Ar–CH_3). $[\alpha]_{589}^{25} = +13$; $[\alpha]_{578}^{25} = +15$; $[\alpha]_{546}^{25} = +21$; $[\alpha]_{436}^{25} = +81$ (*c* 0.5, CH_2Cl_2). ES-MS *m*/*z* (relative intensity): 667.3 (100) $[M+Na]^+$, 645 (7) $[M+H]^+$. Anal. Calcd for $C_{48}H_{40}N_2{\cdot}1.5H_2O$ (671.84): C, 85.81; H, 6.45; N, 4.17. Found: C, 86.07; H, 6.71; N, 3.66.

4.14. Preparation of (+)-(*R*)-2,2′-bis(benzylamino)-1,1′-binaphthyl (*R*^{i})-3

To a solution of (+)-(*R*)-2,2′-diamino-1,1′-binaphthyl (1.22 g, 4.30 mmol) in THF (30 mL) was added triethylamine (2.20 mL, 15.50 mmol) by syringe. Benzoyl chloride (1.00 mL, 8.50 mmol) was then added dropwise under argon. A suspension appeared immediately and the reaction mixture was heated at 60 °C for 2 h and stirred at room temperature overnight. The solid was separated from the mixture by filtration. The solvent was concentrated in vacuo and the crude product was used in the following step without purification. THF (30 mL) was added, and the solution was added dropwise under argon to a suspension of $LiAlH_4$ (1.63 g, 43.00 mmol) in THF (50 mL) at 0 °C. The reaction mixture was allowed to warm up to room temperature overnight, and then heated at 60 °C for 4 h. The mixture was hydrolysed with water until the formation of white hydroxide aluminium salts. The solid was separated from the mixture by filtration. The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (heptanes–ethyl acetate = 99.5:0.5) to give a pale yellow solid (1.32 g, 65% yield). Mp = 134 °C. $R_f = 0.3$ (heptanes–ethyl acetate 99.5:0.5). ^{1}H NMR ($CDCl_3$): δ 7.89–7.81 [m, 4H, ArH], 7.27–7.11 [m, 18H, ArH], 4.47–4.45 [m, 4H, CH_2–Ph] and 4.39 [br s, 2H, NH]. ^{13}C NMR ($CDCl_3$): δ 144.2, 139.8, 133.8 (C_{Ar}), 129.6, 128.4, 128.1 (CH_{Ar}), 127.7 (C_{Ar}), 126.8, 126.7 (CH_{Ar}), 123.9, 122.0, 114.1 (CH_{Ar}), 111.9 (C_{Ar}), 47.5 (CH_2–Ph). $[\alpha]_{589}^{25} = +84$; $[\alpha]_{578}^{25} = +91$; $[\alpha]_{546}^{25} = +114$; $[\alpha]_{436}^{25} = +353$ (*c* 1.4, $CHCl_3$). Anal. Calcd for $C_{34}H_{28}N_2$ (464.60): C, 87.90; H, 6.07; N, 6.03. Found: C, 87.46; H, 6.12; N, 5.92.

4.15. Intramolecular hydroamination reactions

4.15.1. In situ preparation of ytterbium ate complexes (*R*^{i},*S*,*S*)-7, (*R*^{i},*R*,*R*)-7, (*R*^{i},*S*,*R*)-7 and (*R*^{i})-8. In an argon-filled glove box, the ligand (0.12 mmol) was solubilised in THF (2 mL) in a Schlenk flask equipped with a magnetic stirring bar. *n*-BuLi (1.6 M in hexanes, 0.15 mL, 0.24 mmol) was added dropwise and the reaction mixture was stirred for 10 min. $YbCl_3$ (16.5 mg, 0.06 mmol) was then added to the solution of the bis lithium salt of the ligand in THF. The reaction mixture was stirred at room temperature for 45 min and THF was evaporated in vacuo. The crude product was dissolved in C_6D_6 or toluene and the solution was immediately used for the catalytic tests.

4.15.2. In situ preparation of ytterbium ate complex (*R*^{i})-9. In an argon-filled glove box, ligand (*R*^{i})-**3** (54.8 mg, 0.12 mmol) was dissolved in hexanes (2 mL) in a Schlenk flask equipped with a magnetic stirring bar. *n*-BuLi (1.6 M in hexanes, 0.15 mL, 0.24 mmol) was added dropwise and the reaction mixture was stirred for 10 min to give a yellowish suspension. The solvent was evaporated in vacuo. $YbCl_3$ (16.5 mg, 0.06 mmol) was added to the solution of the bis lithium salt of the ligand in THF (2 mL). The reaction mixture was stirred at room temperature for 45 min and THF was evaporated in vacuo. The crude product was dissolved in C_6D_6 or toluene and the solution was immediately used for the catalytic tests.

4.15.3. General procedures for NMR-scale asymmetric hydroamination–cyclisation of aminoalkenes. For the cyclisation of aminoalkenes performed at room temperature the appropriate aminoalkene (0.20 mmol) was dissolved in C_6D_6 (0.1 mL) in the glove box and dried on 4 Å molecular sieves for 2 h at room temperature. A solution of the ytterbium catalyst in C_6D_6 (0.7 mL) was introduced into a J. Young NMR tube equipped with a teflon valve, and the aminoalkene solution was then added. The hydroamination reaction was monitored by ^{1}H NMR by the observation of the decrease of the olefinic protons signals. After the appropriate time, the reaction was quenched with CH_2Cl_2.

For the cyclisation of aminoalkenes performed at 110 °C and 120 °C, the appropriate aminoalkene (0.20 mmol) was dissolved in toluene (0.1 mL) in the glove box and dried on 4 Å molecular sieves for 2 h at room temperature. A solution of the ytterbium catalyst in toluene (0.7 mL) was introduced into a sealed tube and the aminoalkene solution was then added. The sealed tube was heated out of the glove box during the appropriate time. The reaction was quenched with CH_2Cl_2. The reaction products were derivatised and the enantiomeric excesses were measured as previously described.[6c,e]

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