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New Chiral Lanthanide Amide Ate Complexes for the Catalysed Synthesis of Scalemic Nitrogen-Containing Heterocycles

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Abstract: New chiral binaphthylamido yttrium and ytterbium ate complexes with lithium and potassium counterions have been synthesised and characterised. X-ray structures have been obtained for $[Li(thf)_4][Ln\{(R)\text{-}C_{20}H_{12}(NC_5H_9)_2\}_2]$ (Ln = Yb, Y) and $[K(thf)_5][Yb\{(R)\text{-}C_{20}H_{12}(NCH_2CMe_3)_2\}_2]$ as isostructural complexes. The efficiency of these complexes for the enantioselective intramolecular hydroamination was examined. $[Li(thf)_4][Yb\{(R)\text{-}C_{20}H_{12}(NC_5H_9)_2\}_2]$ afforded the highest enantiomeric excess (up to 87%) for the synthesis of a spiropyrrolidine, while $[Li(thf)_4][Y\{(R)\text{-}C_{20}H_{12}(NC_5H_9)_2\}_2]$ proved to be slightly more active. The role of the counter cation in the active catalytic species was evidenced by the comparison between lithium and potassium ate complexes. The most active catalyst of this series, $[Li(thf)_4][Yb\{(R)\text{-}C_{20}H_{12}(NCH_2CMe_3)_2\}_2]$, was successfully used for the cyclisation of aminopentenes with internal double bonds.

Keywords: asymmetric catalysis · heterocycles · hydroamination · lanthanides

Introduction

The development of efficient methodologies for the synthesis of scalemic nitrogen-containing heterocycles is of high importance in the context of the economical and environmental preparation of sophisticated substrates with biological activities. Intramolecular asymmetric catalytic hydroamination can readily answer this challenge by the efficient cyclisation of functionalised substrates. Until now, various amino–alkene, amino–diene and amino–allene derivatives were successfully enantioselectively transformed into the corresponding heterocycles by using lanthanide complexes.[1] This research field was initiated by the group of Marks at the beginning of the nineties, who proved that scalemic pyrrolidines (up to 74% *ee*)[2] and a piperidine (up to 67% *ee*)[3] could be obtained in the presence of chiral metallocenes. Almost ten years later, the first use of chiral non-metallocene lanthanide complexes was reported by Scott et al. for promoting the cyclisation of 2,2-dimethylpent-4-enylamine as a test substrate. They synthesised chiral bisarylamines[4] and bisaryloxides[5] as ligands for the preparation of yttrium and lanthanum complexes, respectively. The latter promoted the formation of the corresponding pyrrolidine albeit with low activity (reaction performed at 70 °C) and 61% enantiomeric excess. At the same time, the group of Hultzsch prepared various rare-earth bisphenolate and bisnaphtholate derivatives.[6] The corresponding yttrium complex afforded moderate activities in this transformation with enantiomeric excesses up to 57% for the intramolecular hydroamination of pent-4-enylamine. Hultzsch also described the kinetic resolution of 2-aminohex-5-ene with this catalyst. Simultaneously, we published the preparation of lanthanide amide ate complexes and obtained up to 53% *ee* for the cyclisation of a new substrate (*C*-(1-allylcyclohexyl)methylamine) at low temperature by using an ytterbium catalyst.[7] In 2003,

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. NMR spectra for ligand (*R*)-(+)-2,2′-bis(cyclopentylamino)-1,1′-binaphthyl and complexes Li-**5b** and K-**5b**.

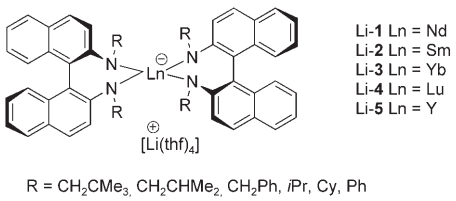
Marks reported the easy synthesis of enantioselective catalysts by the reaction of lanthanide amides with commercially available C_2-symmetric bisoxazolines.[8] These complexes proved to be active at room temperature (up to 67% *ee* for the test substrate) and promoted the hydroamination/cyclisation of several aminopentenes, aminohexenes and aminodienes.

Based on these preliminary results, these authors and other groups attempted both to find new active and enantioselective complexes to promote the asymmetric intramolecular hydroamination reaction, but also to extend their application to the transformation of other substrates. We have synthesised ytterbium and lutetium ionic complexes derived from enantiopure, substituted (*R*)-binaphthylamine ligands with isopropyl or cyclohexyl substituents; these complexes proved to be efficient catalysts for the cyclisation of various aminopentene derivatives (with up to 78% *ee*) and also to promote the formation of a piperidine (45% *ee* at 60°C).[9] Kim and Livinghouse[10] have synthesised amido yttrium complexes from $[Y\{N(tms)_2\}_3]$ and chiral bis(thiolate) ligands that catalysed the cyclisation of various aminopentenes and an aminohexene at 60°C, but with enantiomeric excesses above 80% for several substrates. Interestingly the cyclisation of 2,2-dimethyl-5-phenylpent-4-enylamine was considered and performed with success together with the transformation of a secondary amine, which occurred albeit with a longer reaction time. For the hydroamination/cyclisation of such methylaminoalkenes, much more efficient catalysts were prepared by Scott et al. as chiral zirconium–alkyl cations.[11] Chiral thiophosphinic amides were also proven by Livinghouse and co-workers to promote the cyclisation of the test substrate (up to 61% *ee* at room temperature) in the presence of a yttrium–trisamide precatalyst.[12] A chiral-bridged alkylaminotroponiminate complex of lutetium was reported by Roesky et al. as active catalyst for the preparation of the usual pyrrolidines and a piperidine.[13] However, the reactions had to be performed at high temperature to afford complete conversion in reasonable time and the enantiomeric excesses remained moderate (up to 44% *ee* for the piperidine). The best results in terms of enantioselectivity were very recently described by Hultzsch and co-workers.[14] The preparation of type 3,3′-bis(trisarylsilyl)-substituted binaphthol ligands led to corresponding rare-earth-metal complexes (Sc, Lu and Y) as active and enantioselective catalysts for the cyclisation of amino-olefins towards several pyrrolidines and piperidines; 2-methyl-4,4-diphenylpyrrolidine was prepared with up to 95% *ee*. The more demanding methylpent-4-enyl-amine, as a secondary amine, was cyclised with up to 53% *ee* with a scandium catalyst. Zirconium catalysts were further prepared aimed at promoting the intramolecular hydroamination reaction. The group of Bergman synthesised zirconium–bis(amido) catalysts from an in situ combination of diphosphinic amides and $Zr(NMe_2)_4$.[15] Those catalysts were active (at high temperature) for the transformation of the usual substrates with up to 80% *ee*. A methyl-2,3-dihydro-1*H*-indole derivative was also isolated with high enantioselectivity (70% *ee*) under those conditions. The group of Schafer[16] reported the synthesis of neutral, chiral, zirconium amidate complexes and their efficient use for the preparation of various pyrrolidines (up to 93% *ee*). Simultaneously, Scott et al. published very similar zirconium complexes and reported up to 91% *ee*.[17] Finally, Hultzsch et al. reported the first example of a chiral main-group metal as an efficient catalyst for the preparation of pyrrolidines.[18] A dimeric, proline-derived, diamidobinaphthyl dilithium salt was synthesised and promoted the cyclisation of various primary aminopentenes at room temperature with up to 75% *ee*. The development of new lanthanide catalysts in the last four years has thus allowed important improvement in terms of activity and enantioselectivity for obtaining some pyrrolidines with up to 95% *ee*. There is nevertheless always the need for the preparation of catalysts able to promote the cyclisation of more demanding substrates. The hydroamination procedure is indeed known to be considerably slowed down, if di- (or more-) substituted double bonds are involved, relative to the corresponding unsubstituted substrates. Hence, the higher temperature required to achieve a convenient conversion is sometimes detrimental to the enantioselectivity of the reaction if asymmetric processes are considered. To the best of our knowledge, only the group of Marks has studied the asymmetric cyclisation of 2,2-dimethylhex-4-enylamine in the presence of chiral metallocenes and afforded the corresponding pyrrolidine in up to 28% *ee* by performing the reaction at 80°C.[19] An analogous piperidine was interestingly isolated with 68% *ee*.

In such a context, we report here the preparation, characterisation of new lanthanide amide ate complexes and their use for promoting various hydroaminations/cyclisations with different aminopentene and aminohexene derivatives.

Results and Discussion

We have previously reported the preparation and the characterisation of a new family of lanthanide ate complexes $[Li(thf)_4][Ln\{(R)\text{-}C_{20}H_{12}(NR)_2\}_2]$ (Ln = Nd (Li-**1**), Sm (Li-**2**), Yb (Li-**3**), Lu (Li-**4**), Y (Li-**5**) R = CH_2CMe_3, CH_2CHMe_2, CH_2Ph, *i*Pr, Cy, Ph) derived from chiral disubstituted (*R*)-binaphthylamido ligands.[7,9,20,21] These compounds consist of a complex anion resulting from coordination of two (*R*)-binaphthylamine ligands to the lanthanide atom and a discrete counterion $[Li(thf)_4]^+$ and they are efficient catalysts for intramolecular hydroamination.



R = CH_2CMe_3, CH_2CHMe_2, CH_2Ph, *i*Pr, Cy, Ph

Both the influence of the nature of the lanthanide and of the alkyl substituent on the nitrogen atoms were evaluated on the cyclisation of various aminopentene derivatives.[9,20] The ytterbium and lutetium complexes with bulky substituents on the nitrogen atom (isopropyl, cyclohexyl) led to the highest enantioselectivities (up to 78% *ee* for a spiropyrrolidine), while ytterbium showed higher activities than lutetium complexes. We further prepared a similar yttrium ate complex Li-**5** (R = *i*Pr) and the corresponding neutral complex coordinated with the same chiral ligand, which led to different results in terms of activity and/or enantioselectivity for several hydroamination reactions, indicating that different active species were involved. With the neutral, chiral complex, higher rates of reaction and/or higher asymmetric inductions were generally observed for the formation of several pyrrolidines.[21] Yet, the synthesis of ate complexes is much more straightforward and we maintained our efforts towards more enantioselective and more active catalysts for widening the scope of substrates suitable for hydroamination reactions.

New lanthanide amide ate complexes are presented here with a special emphasis on the influence of the structure of the ligand, and the nature of the lanthanide and the alkaline cation on the rates and asymmetric inductions of hydroamination reactions. Particularly, optimised complexes have been tested for the intramolecular hydroamination of more demanding aminoalkenes.

Preparation and characterisation of lanthanide lithium ate complexes: The ate complexes $[Li(thf)_4][Ln\{(R)\text{-}C_{20}H_{12}(NR)_2\}_2]$ (R = C_6H_{11}, Ln = Yb (Li-**3a**); R = C_5H_9, Ln = Yb (Li-**3b**), Y (Li-**5b**)) were synthesised by metathesis reactions of anhydrous $LnCl_3$ with two equivalents of $Li_2\{(R)\text{-}C_{20}H_{12}(NR)_2\}$ in THF at ambient temperature (Scheme 1).

The preparation of complex Li-**3a** was previously reported.[9] Complexes Li-**3b** and Li-**5b** were purified by extraction of the solid residue after evaporation of THF with toluene and subsequent recrystallisation from THF/hexane mixtures. Complexes Li-**3b** and Li-**5b** were isolated in 52 and 53% yields, respectively. Both complexes were obtained as highly air- and moisture-sensitive crystalline solids that are soluble in THF and toluene and insoluble in hexane.

Clear single-crystal samples of complexes Li-**3b** (green) and Li-**5b** (orange) suitable for X-ray investigation were obtained by slow condensation of hexane into the concentrated solutions of the complexes in THF at room temperature. Both complexes crystallise in the monoclinic space group $P2_1$ ($Z = 2$). Complex Li-**5b** crystallises as a THF solvate with half a molecule of THF per molecule of complex $[Li(thf)_4][Y\{(R)\text{-}C_{20}H_{12}(NC_5H_9)_2\}_2]\cdot 0.5\,(C_4H_8O)$. Complex Li-**5b** crystallises with two crystallographically independent molecules in the asymmetric unit.

The molecular structures of complexes Li-**3b** and Li-**5b** are depicted in Figure 1; the crystal and structural refine-

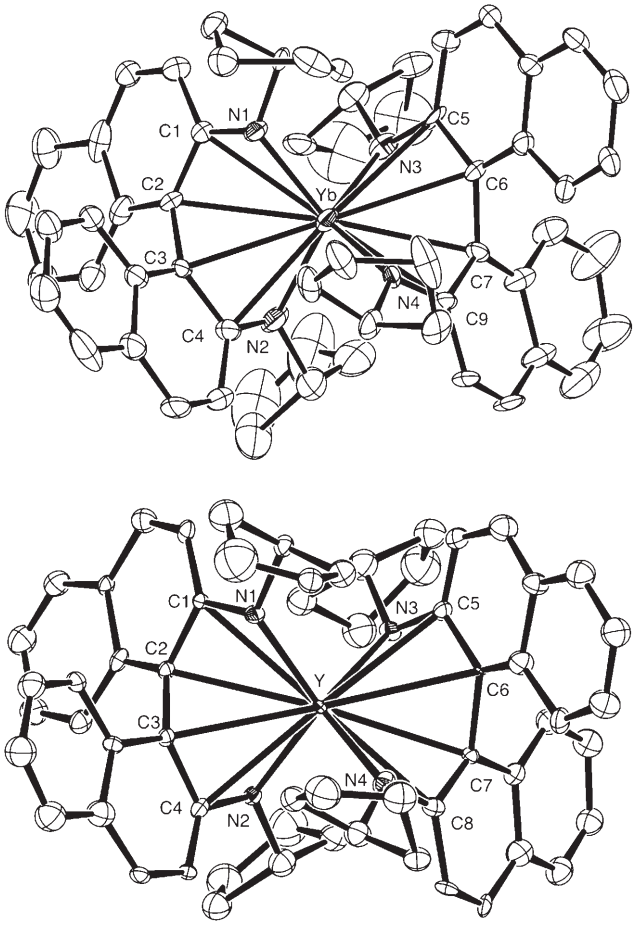
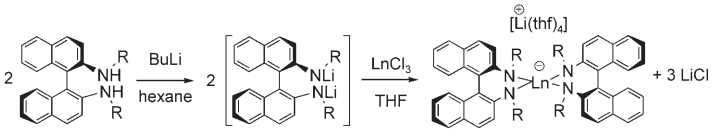


Figure 1. Top: ORTEP drawing of complex $[Li(thf)_4][Yb\{(R)\text{-}C_{20}H_{12}(NC_5H_9)_2\}_2]$ (Li-**3b**) with the atom-labelling scheme. Ellipsoids are drawn at the 30% probability level. The $[Li(thf)_4]^+$ ion and the hydrogen atoms are omitted for the sake of clarity. Selected bond lengths [Å] and angles [°]: Yb–N1 2.258(7), Yb–N2 2.268(9), Yb–N3 2.245(8), Yb–N4 2.252(7), Yb–C1 2.692(9), Yb–C2 2.775(10), Yb–C3 2.820(9), Yb–C4 2.755(8), Yb–C5 2.669(10), Yb–C6 2.808(9), N1-Yb-N2 121.8(3), N3-Yb-N4 120.1 (3). Bottom: ORTEP drawing of complex $[Li(thf)_4][Y\{(R)\text{-}C_{20}H_{12}(NC_5H_9)_2\}_2]$ (Li-**5b**) with the atom-labelling scheme. Ellipsoids are drawn at the 30% probability level. The $[Li(thf)_4]^+$ ion and the hydrogen atoms are omitted for the sake of clarity. Selected bond lengths [Å] and angles [°]: Y1–N1 2.28(2), Y1–N2 2.35(3), Y1–N3 2.30(2), Y1–N4 2.26(2), Y1–C1 2.77(2), Y1–C2 2.88(2), Y1–C3 2.83(3), Y1–C4 2.56(3), Y1–C5 2.65(2), Y1–C6 2.79(2), Y1–C7 2.84(3), Y1–C8 2.74(3), Y2–N5 2.27(2), Y2–N6 2.28(2), Y2–N7 2.269(19), Y2–N8 2.290(19), Y2–C9 2.78(2), Y2–C10 2.93(2), Y2–C11 2.82(2), Y2–C12 2.73(3), Y2–C13 2.83(2), Y2–C14 2.82(2), Y2–C15 2.80(2), Y2–C16 2.79(3), N1-Y1-N2 119.8(8), N3-Y2-N4 119.1(8), N7-Y2-N8 117.6(7), N5-Y2-N6 116.8(8).

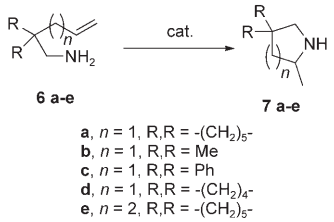


Ln = Yb, R = cyclohexyl, Li-**3a**
R = cyclopentyl, Li-**3b**
R = *i*Pr, Li-**3c**
R = CH_2CMe_3, Li-**3d**
Ln = Y, R = cyclopentyl, Li-**5b**
R = *i*Pr, Li-**5c**

Scheme 1. Synthesis of ytterbium and yttrium *N*-substituted-(*R*)-binaphthylamine lithium ate complexes.

ment data are listed in Table 1. X-ray single crystal structure analysis has revealed that the compounds are isostructural ionic complexes, containing a discrete cation $[Li(thf)_4]^+$ and a discrete complex anion $[Ln\{(R)\text{-}C_{20}H_{12}(NC_5H_9)_2\}_2]^-$, resulting from coordination of two diamido ligands to the trivalent lanthanide atom. The main geometric parameters of complexes Li-**3b** and Li-**5b** are very similar to those previously reported for related complexes.[7,20,21] The average Yb–N bond length (2.255(8) Å) and N-Yb-N bond angle (121.0(3)°) in complex Li-**3b** fall into the region observed for ytterbium ate complexes $[Li(thf)_4][Yb\{(R)\text{-}C_{20}H_{12}(NR)_2\}_2]$: R = CH_2CMe_3, 2.261(2) Å;[7] R = CH_2CHMe_2, 2.252(4) Å, 121.87(17)°;[20] R = *i*Pr, 2.246(4) Å, 119.87(17)°.[21] For complex Li-**5b** the average Y–N bond length (2.29(2) Å) and N-Y-N bond angle (118.3 (8)°) are close to the values found for yttrium ate complexes $[Li(thf)_4][Y\{(R)\text{-}C_{20}H_{12}(NR)_2\}_2]$: R = *i*Pr, 2.284(5) Å, 118.5(2)°;[21] R = Ph, 2.275(2) Å, 118.31(8)°.[21]

Catalytic hydroamination tests with lanthanide lithium ate complexes: In our initial studies on the synthesis of lanthanide ate complexes for the catalysis of hydroamination reactions we used a two-step procedure. The lithium binaphthylamine salts were first isolated and in a second step they afforded the lanthanide ate complexes by reaction with lanthanide chlorides. The complexes were separated from lithium chloride by extraction in toluene and recrystallised from THF/hexane mixtures before their use in catalytic hydroamination reactions. We observed then that higher activities were obtained for the cyclisation of *C*-(1-allyl-cyclohexyl)-methylamine if the catalysts were used without purification.[9] For the following results the catalysts were prepared from binaphthylamine in an improved procedure with shorter reaction times for the formation of both the dilithium salt (in hexanes) and the lanthanide ate complex (in THF). The hydroamination reactions were initiated immediately after the evaporation of the solvent from the lanthanide ate complex containing an admixture of LiCl. Such a procedure was applied to the synthesis of catalyst Li-**3a**, bearing (*R*)-*N*-cyclohexyl binaphthyl amine substituents. Tested for the cyclisation of *C*-(1-allylcyclohexyl)methylamine, it afforded the pyrrolidine **7a** (Scheme 2) in 24 h at room temperature with



Scheme 2. Synthesis of nitrogen heterocycles by catalysis with lanthanide lithium ate complexes.

Table 1. Crystallographic data and structure refinement details for Li-**3b**, Li-**5b**, and K-**3d**.

	Li-**3b**	Li-**5b**	K-**3d**
formula	$C_{76}H_{92}LiN_4O_4Yb$	$C_{156}H_{192}Li_2N_8O_9Y_2$	C_{80} H_{108} K N_4 O_5 Yb
M_r	1305.52	2514.88	1417.84
T [K]	180(1)	180(1)	180(1)
crystal system	monoclinic	monoclinic	orthorhombic
space group	$P2_1$	$P2_1$	$P2_12_12_1$
a [Å]	10.6012(9)	17.360(3)	11.059(5)
b [Å]	17.6720(15)	10.6930(18)	17.209(5)
c [Å]	18.9000(13)	37.347(4)	39.121(5)
β [°]	99.830(2)	91.330(3)	90
V [Å^3]	3488.8(5)	6930.8(18)	7445(4)
Z	2	2	4
ρ_{calcd} [mg m^{-3}]	1.243	1.205	1.265
μ [mm^{-1}]	1.390	0.894	1.363
F(000)	1362	2680	2980
crystal size [mm]	0.22×0.16×0.07	0.11×0.07×0.03	0.25×0.10×0.10
θ range [°]	1.59–26.45	1.58–20.17	1.91–24.21
index ranges	$-13 \le h \le 13$	$-9 \le h \le 14$	$-12 \le h \le 12$
	$-22 \le k \le 22$	$-4 \le k \le 9$	$-19 \le k \le 19$
	$-16 \le l \le 23$	$-22 \le l \le 23$	$-44 \le l \le 45$
reflns collected	35486	7946	48104
independent reflns	13975 [R_{int} = 0.0469]	5960 [R_{int} = 0.0280]	11546 [R_{int} = 0.1730]
completeness [%] (to θ [°])	98.6 (26.45)	65.1 (20.17)	98.5 (24.2)
absorption correction	Sadabs	Sadabs	multiscan
max/min transmission	0.751/0.911	0.928/0.974	0.8508/0.8391
flack parameter	0.070(15)	0.18(2)	0.01(2)
data/restraints/parameters	13975/0/775	5960/1580/1559	11546/1015/760
goodness-of-fit on F^2	1.084	1.019	0.898
final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0671	$R1$ = 0.0969	$R1$ = 0.0626
	$wR2$ = 0.0868	$wR2$ = 0.0978	$wR2$ = 0.1113
R indices (all data)	$R1$ = 0.1653	$R1$ = 0.2480	$R1$ = 0.1566
	$wR2$ = 0.1752	$wR2$ = 0.2486	$wR2$ = 0.1456
largest diff. peak/hole [e Å^{-3}]	0.809/−0.436	0.664/−0.742	1.361/−3.056

78% *ee*, an increase in enantioselectivity with respect to our previous results (65% *ee*). With the aim to increase the enantiomeric excess we decided to examine another ligand, (*R*)-*N*-cyclopentylbinaphthylamine, as a possible sterically more-demanding chelating group on the lanthanide. We synthesised this ligand according to the method described in our previous reports and the corresponding ytterbium ate complex Li-**3b** was prepared by the above-mentioned procedure.[9] Gratifyingly this catalyst promoted the cyclisation of *C*-(1-allylcyclohexyl)methylamine into the corresponding pyrrolidine **7a** within 20 h at room temperature with 87% *ee*. The study of hydroamination reactions catalysed by Li-**3b** was thus widened to several amino-olefins and the results are given in Table 2.

The influence of the temperature on the cyclisation of

Table 2. Enantioselective hydroamination reactions catalysed by ytterbium and yttrium *N*-substituted-(*R*)-binaphthylamine lithium ate complexes.

	Catalyst	Substrate	*T* [°C][a,b]	Cat. ratio [mol %]	*t* [h]	Conversion [%][c]	*ee* [%]
1	Li-**3b**	**6a**	0	6	168	92	85
2	Li-**3b**	**6a**	25	6	20	90	87
3	Li-**3b**	**6a**	60	6	15	92	78
4	Li-**3b**	**6b**	25	8	144	14	72
5	Li-**3b**	**6b**	60	6	17	94	69
6	Li-**3b**	**6c**	0	6	168	100	78
7	Li-**3b**	**6c**	25	6	18	100	76
8	Li-**3b**	**6d**	25	4	84	30	76
9	Li-**3b**	**6d**	60	4	15	100	73
10	Li-**3b**	**6e**	40	8	144	100	50
11	Li-**3b**	**6e**	60	4	40	100	51
12	Li-**3b**	**6e**	80	6	15	100	50
13	Li-**5b**	**6a**	0	6	144	54	75
14	Li-**5b**	**6a**	25	8	15	93	81
15	Li-**5b**	**6b**	25	6	180	49	64
16	Li-**5b**	**6b**	60	6	22	96	68
17	Li-**5b**	**6c**	0	6	96	94	75
18	Li-**5b**	**6c**	25	6	5	100	75
19	Li-**5b**	**6e**	60	6	24	100	41
20	Li-**3d**	**6a**	0	6	17	81	47
21	Li-**3d**	**6a**	25	7	1	91	41
22	Li-**3d**	**6a**	60	6	0.3	90	40
23	Li-**3d**	**6b**	25	8	17	84	10
24	Li-**3d**	**6c**	25	6	1.3	100	−17[d]
25	Li-**3d**	**6d**	25	6	17	95	10
26	Li-**3d**	**6e**	25	6	72	100	27
27	Li-**3d**	**6e**	60	4	16	100	30

[a] Reactions performed at 0 °C in C_7H_8. [b] Reactions performed at 25 °C, 60 °C and 80 °C in C_6D_6. [c] Conversion was measured by ^{1}H NMR spectroscopy. [d] The absolute configuration of product **7c** was opposite to that obtained with catalysts Li-**3b** and Li-**5b**.

C-(1-allylcyclohexyl)methylamine (**6a**) by catalyst Li-**3b** was first examined (Table 2, entries 1–3). At 0 °C hydroamination was performed with 85 % *ee*, a value close to that obtained at room temperature, but needed a long reaction time to be completed, while at 60 °C a small decrease in the enantiomeric excess was observed. The cyclisation of 2,2-dimethylpent-4-enylamine (**6b**) was interestingly realised with high conversion after one night at 60 °C and only a very slight decrease in enantioselectivity compared to the reaction at room temperature (entries 4, 5). With the *gem*-diphenylaminopentene (**6c**) a total conversion was observed after one night with a high value for the enantiomeric excess (76 %), which is not modified when the reaction is run at lower temperature (entries 6,7). The best conditions for the preparation of the spiropyrrolidine **7d** are to perform the reaction at 60 °C for a total conversion and 73 % *ee* (entries 8, 9). The variation of the temperature did not either modify the asymmetric induction for the transformation of the aminohexene **6e** and the piperidine is formed with complete conversion and 50 % *ee* after one night at 80 °C (entries 10–12). These results are significantly improved relative to those previously reported for the ytterbium ate complex Li-**3a**.[9] With catalyst Li-**3b** the pyrrolidines and piperidine are indeed cyclised with higher asymmetric inductions. Furthermore, the temperature marginally influences the enantiomeric excess of hydroamination reactions. All pyrrolidines could be synthesised with enantiomeric excesses over 70 %.

Till now, there are very few examples of enantioselective reactions involving sterically hindered substrates such as amines with disubstituted double bonds. For performing the cyclisation of such amino-olefins, very active catalysts are needed and we aimed at testing the performance of the lanthanide amide ate complexes for such reactions. In the course of our previous studies concerning the comparison of neutral and ate complexes, we prepared the yttrium ate complex coordinated by (*R*)-*N*-isopropylbinaphthylamine ligand $[Li(thf)_4][Y\{(R)\text{-}C_{20}H_{12}(NiPr)_2\}_2]$ (Li-**5c**).[21] This complex catalysed the hydroamination of **6a** within 20 h with 67 % *ee*. When the ytterbium ate complex prepared with the same ligand $[Li(thf)_4][Yb\{(R)\text{-}C_{20}H_{12}(NiPr)_2\}_2]$ (Li-**3c**) was used in this reaction, an identical enantiomeric excess was obtained but six days were necessary for a complete conversion, indicating the higher activity of the yttrium ate complex relative to the corresponding ytterbium one. This result prompted us to compare the activity and enantioselectivity of the ytterbium complex Li-**3b** with that of the yttrium complex Li-**5b**, coordinated by (*R*)-*N*-cyclopentylbinaphthylamine. The yttrium catalyst Li-**5b** afforded the three pyrrolidines **7a**, **7b** and **7c** with good enantioselectivities (Table 2, entries 13–18). The comparison with the corresponding ytterbium catalyst Li-**3b** showed that at the same temperature the activity is higher with yttrium. At room temperature the cyclisation of **6b** is promoted with yttrium (entry 15), while a lower conversion is only observed with ytterbium (entry 4). Similarly, reaction times are shorter with substrate **6c** using catalyst Li-**5b** (entries 17, 18) rather than Li-**3b** (entries 6, 7). A slight decrease of the enantiomeric excess with the temperature was observed for pyrrolidine **7a** using yttrium catalyst Li-**5b**, while no significant variation was observed for pyrrolidines **7b** and **7c**. The hydroamination of aminohexene **6e** was achieved in a shorter time with yttrium catalyst Li-**5b**, but with a decrease in the enantiomeric excess relative to Li-**3b** (entries 19 and 11).

We previously described the cyclisation of **6a** in 1 h, catalysed by an ytterbium ate complex Li-**3d** coordinated with (*R*)-*N*-neopentylbinaphthylamine.[7] Thus complex Li-**3d** proved to be more active for the cyclisation of **6a** than the other lanthanide ate complexes studied so far and the evaluation of this catalyst was extended to the preparation of other pyrrolidines and piperidines. To check its stability, complex Li-**3d** was tested in the hydroamination reaction of **6a** at 60 °C, which afforded the expected product with 40 % *ee*, as at room temperature (Table 2, entries 21 and 22). A total conversion of aminopentenes **6b** and **6d** in the corresponding pyrrolidines was observed at room temperature with catalyst Li-**3d** (entries 23 and 25), while with catalysts Li-**3b** or Li-**5b**, coordinated with a more bulky ligand, a temperature of 60 °C was necessary. The piperidine **7e** was prepared at 60 °C with the three ytterbium and yttrium cata-

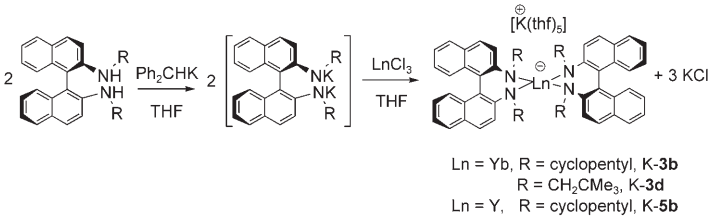
lysts, but the reaction was faster with Li-**3d** (entries 11, 19 and 27). Interestingly, catalyst Li-**3d** proved to be active enough for promoting this transformation at 25 °C (entry 26) and the spiropiperidine was prepared with 27 % *ee* and a complete conversion within three days. However, all hydroamination reactions performed with Li-**3d** exhibited only poor enantioselectivity. From the results gathered in Table 2 it appears that the ytterbium ate complex coordinated by (*R*)-*N*-neopentylbinaphthylamine (Li-**3d**) showed the highest activity, while ytterbium ate complex Li-**3b** with the bulkier (*R*)-*N*-cyclopentyl binaphthyl amine ligand afforded the highest enantiomeric excesses. However, the (*R*)-*N* cyclopentylbinaphthylamine yttrium ate complex Li-**5b** allowed us to prepare the pyrrolidines and piperidine with good enantiomeric excesses within short times.

Preparation and characterisation of lanthanide potassium ate complexes: So far, our efforts towards the improvement of the activity and enantioselectivity of lanthanide ate complexes for hydroamination reactions have been directed towards the choice of the lanthanide and the optimisation of the size of the nitrogen substituent. The differences in activity and enantioselectivity of hydroamination reactions catalysed by an yttrium ate complex and a neutral yttrium complex coordinated by (*R*)-*N*-isopropylbinaphthylamine ligand have indicated that probably both catalysts are not transformed in the same active species.[21] This suggested a possible participation of the alkaline cation in the catalytic cycle. Lanthanide potassium ate complexes have thus been synthesised and studied as intramolecular hydroamination catalysts.

The ate complexes containing the potassium counterion $[K(thf)_5][Ln\{(R)\text{-}C_{20}H_{12}(NR)_2\}_2]$ ($R = C_5H_9$, Ln = Yb (K-**3b**); Y (K-**5b**); $R = CH_2CMe_3$, Ln = Yb (K-**3d**)) have been synthesised by the reaction of anhydrous $LnCl_3$ with two equivalents of $K_2\{(R)\text{-}C_{20}H_{12}(NR)_2\}$ in THF at ambient temperature. The potassium derivatives $K_2\{(R)\text{-}C_{20}H_{12}(NR)_2\}$ were prepared by treatment of binaphthylamine ligands with two equivalents of Ph_2CHK in THF (20 °C) (Scheme 3).

Complexes K-**3b**, K-**5b** and K-**3d** were purified following the standard procedure described above for compounds Li-**3b** and Li-**5b**. They were isolated in 43, 57 and 64 % yields, respectively, as highly air- and moisture-sensitive crystalline solids. They are soluble in THF and toluene and insoluble in hexane.

Clear deep-red single-crystalline samples of the complex K-**3d** suitable for X-ray investigation were obtained by slow condensation of hexane into a concentrated solution of K-**3d** in THF at room temperature. It crystallises in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell. The molecular structure of complex K-**3d** is depicted in Figure 2; the crystal and structural refinement data are listed in Table 1. X-ray single crystal structure analysis reveals that compound K-**3d** is an ionic complex, containing discrete $[K(thf)_5]^+$ ions and discrete complex $[Yb\{(R)\text{-}C_{20}H_{12}(NCH_2CMe_3)_2\}_2]^-$ ions, resulting from coordination of two diamido ligands to the trivalent lanthanide atom. Surprisingly despite their identical nature and composition and similar geometry of the anionic fragment $[Yb\{(R)\text{-}C_{20}H_{12}(NCH_2CMe_3)_2\}_2]^-$ in complexes K-**3d** and Li-**3d**[7] the Yb–N bonds in complex K-**3d** are noticeably shorter (the average Yb–N bond length: 2.178(13) Å) compared to those in Li-**3d** (the average Yb–N bond length: 2.261(2) Å).[7] The N–Yb–N bond angles in complex K-**3d** (120.9(4), 116.8(4)°) are also smaller than the related angles in complex Li-**3d** (120.92(10), 122.13(11)°).[7] The potassium cation in K-**3d** is coordinated by five THF molecules, which is consistent with the bigger ionic radius of potassium relative to that of lithium.[22] Continuous drying of complex K-**3d** in vacuo at ambient temperature resulted in the loss of one THF molecule that was proved by the results of microanalysis.



Scheme 3. Synthesis of ytterbium and yttrium *N*-substituted-(*R*)-binaphthylamine potassium ate complexes.

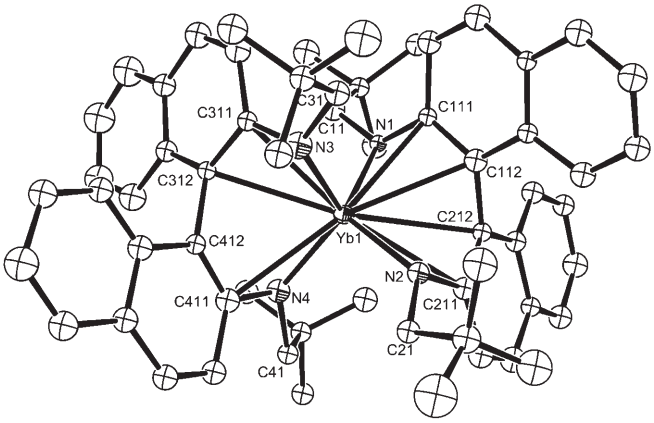


Figure 2. ORTEP drawing of complex $[K(thf)_5][Yb\{(R)\text{-}C_{20}H_{12}(NCH_2CMe_3)_2\}_2]$ (K-**3d**) with the atom-labelling scheme. Ellipsoids are drawn at the 30 % probability level. The $[K(thf)_5]^+$ ion and the hydrogen atoms are omitted for the sake of clarity. Selected bond lengths [Å] and angles [°]: Yb1–N1 2.234(10) , Yb1–N2 2.148(13), Yb1–N3 2.175(13), Yb1–N4 2.158(12), Yb1–C111 2.671(17), Yb1–C112 2.798(14), Yb1–C211 2.749(13), Yb1–C212 2.834(14), Yb1–C311 2.689(15), Yb1–C312 2.794(11), Yb1–C411 2.806(14), Yb1–C412 2.980(15), N1-Yb1-N2 120.9(4), N3-Yb1-N4 116.8(4).

Catalytic hydroamination tests with lanthanide potassium ate complexes: The activity and enantioselectivity of the three potassium ate complexes K-**3b**, K-**5b** and K-**3d** were further examined for the hydroamination reactions leading to the pyrrolidines and the piperidine described above and the results are gathered in Table 3. With the ytterbium potassium ate complex K-**3b**, coordinated by (*R*)-*N*-cyclopentylbinaphthylamine, the formation of pyrrolidines **7a** and **7c**

Table 3. Enantioselective hydroamination reactions catalysed by ytterbium and yttrium *N*-substituted-(*R*)-binaphthylamine potassium ate complexes.

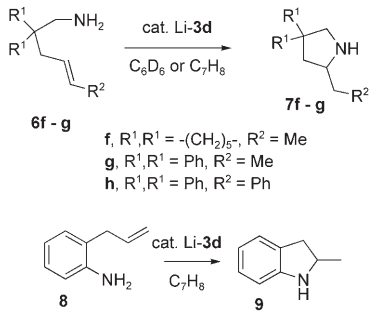
	Catalyst	Substrate	*T* [°C][a]	Cat. ratio [mol %]	*t* [h]	Conversion [%]	*ee* [%][b]
1	K-**3b**	**6a**	25	4	63	92	75
2	K-**3b**	**6b**	40	7	108	80	76
3	K-**3b**	**6c**	25	6	63	100	55
4	K-**3b**	**6e**	40	7	336	87	9
5	K-**5b**	**6a**	25	7	40	95	63
6	K-**5b**	**6b**	40	6	40	96	59
7	K-**5b**	**6c**	25	6	16	100	56
8	K-**5b**	**6e**	40	6	64	92	7
9	K-**3d**	**6a**	25	2	3	92	−45
10	K-**3d**	**6b**	25	6	144	71	−9
11	K-**3d**	**6c**	25	6	17	100	−31
12	K-**3d**	**6d**	25	6	68	96	−32
13	K-**3d**	**6e**	25	7	288	100	0

[a] Reactions performed in C_6D_6. [b] In entries 9–12, the negative sign indicates opposite configurations to those obtained with K-**3b** and K-**5b**.

could be realised at room temperature with 75% and 55% *ee*, respectively (entries 1 and 3). However, both activity and enantioselectivity were lower than those furnished by the corresponding lithium ate complex Li-**3b**. Substrates **6b** and **6e** could not be cyclised at room temperature with catalyst K-**3b** and the hydroamination reactions had to be performed at 40°C (entries 2 and 4). At higher temperature the potassium ate complexes are not stable and very low conversions are obtained. The potassium ate complex catalyst K-**3b** afforded the *gem*-dimethylpyrrolidine **7b** with higher enantiomeric excess (76%) than that obtained with the similar lithium ate complex. In contrast, the formation of the piperidine was slow and the asymmetric induction very low; these results might be explained by a lack of stability of the catalyst at this temperature. The comparison of the ytterbium and yttrium ate potassium complexes coordinated with the same ligand, (*R*)-*N*-cyclopentylbinaphthylamine, gave the same trend as that observed with the analogous lithium ate complexes. For the cyclisation of substrates **6a** (entries 1 and 5), **6b** (entries 2 and 6), **6c** (entries 3 and 7) and **6e** (entries 4 and 8) the reaction times were shorter for the yttrium complex K-**5b** and the enantiomeric excesses lower for pyrrolidines **7a** and **7b**, while no variation was noticed for pyrrolidine **7c** and piperidine **7e**. The comparison of the yttrium based catalyst Li-**5b** and K-**5b** (Table 2, entry 14 and Table 3 entry 5; Table 2, entry 18 and Table 3 entry 7) indicated an increase in the reaction time and a decrease in enantiomeric excesses from lithium to potassium. For yttrium and ytterbium ate complexes coordinated by (*R*)-*N*-cyclopentylbinaphthylamine, a similar variation of the catalytic properties for hydroamination reactions were observed when lithium is replaced by potassium (comparison of Li-**5b** with K-**5b** and Li-**3b** with K-**3b**). Next the ytterbium potassium ate complex K-**3d** coordinated by (*R*)-*N*-neopentylbinaphthylamine was tested in various hydroamination reactions (entries 9–13). As indicated above for lithium ate complexes, cyclisations in pyrrolidines and piperidines with catalyst K-**3d** were more rapid than with ytterbium and yttrium potassium K-**3b** and K-**5b** coordinated by a bulkier ligand : reaction time was shorter for spiropyrrolidine **7a** (see entries 1, 5, 9), while the formation of pyrrolidine **7b** and piperidine **7e** were realised at room temperature with K-**3d**. Surprisingly with this potassium ate complex for almost all pyrrolidines (except **7c**) the major enantiomer is different from that obtained using the similar ate complex Li-**3d**. Only moderate enantiomeric excesses are found, as for the corresponding lithium ate complex.

This inversion of the sense of asymmetric induction in the case of (*R*)-*N*-neopentylbinaphthylamine ligand clearly indicates that the active species in hydroamination reactions catalysed by ate complex is not a neutral species and the alkaline metal atom is somehow involved in the catalytic cycle. We have previously proposed structures for the intermediate catalytic species involved in the asymmetric hydroamination promoted by lanthanide ate complexes.[21] Our new results are in accordance with those hypotheses, but further studies are still needed for more precise explanations of the role of the second chiral ligand and of the associated alkaline cation.

Catalytic hydroamination tests with more demanding substrates: To widen the scope of the utilisation of our new chiral ate amide complexes, we have chosen to test the hydroamination/cyclisation of disubstituted amino-olefins (Scheme 4). We were furthermore interested in the preparation of 2,3-dihydro-1*H*-indole as an important substrate structure variation. To perform these challenging reactions, the more active catalyst of our series, the ytterbium ate complex Li-**3d**, was selected to expect convenient conversion. The results obtained are summarised in Table 4.



Scheme 4. Asymmetric intramolecular hydroamination of more demanding substrates.

The intramolecular hydroamination of 2-(1-but-2-enylcyclohexyl)ethylamine (**6f**) was first examined at different temperatures, and the use of toluene at 110°C yielded the expected ethyl-substituted pyrrolidine with 90% conversion (58% isolated yield) albeit with a four-day reaction time (Table 4, entry 1). Product **7f** was obtained with 27% *ee*, which is one of the best values reported to date for such a cyclisation. Analogously, and under the same conditions, the

Table 4. Hydroamination/cyclisation of more demanding substrates with catalyst Li-**3d**.

	Substrate	T [°C][a,b]	Cat. ratio [mol %]	t [h]	Conversion [%]	*ee* [%]
1	**6f**	110	4	96	90	27
2	**6g**	110	6	96	40	5
3	**6h**	25	6	0.7	100	0
4	**8**	110	4	96	68	0

[a] Reactions performed at 110 °C in C_7H_8. [b] Reactions performed at 25 °C in C_6D_6.

gem-diphenyl substituted derivative led to 2-ethyl-4,4-diphenylpyrrolidine (**7g**) with only a 40% conversion within four days. This result is in contrast with those previously described (Table 2) in which the cyclisation of the *gem*-diphenyl substrate always occurred faster than that of the corresponding cyclohexyl derivative. Moreover, in this case the ate ytterbium catalyst furnished a nearly racemic compound (Table 4, entry 2). The transformation of 2,2,5-triphenylpent-4-enylamine (**6h**) was also considered. In this case, however, the presence of the phenyl substituent on the double bond promoted the reaction, which could thus be smoothly performed at room temperature. A complete conversion was observed within 40 min (Table 4, entry 3) but 2-benzyl-4,4-diphenylpyrrolidine was unfortunately obtained as a racemic mixture. Finally, 2-allyl-phenylamine was submitted to the hydroamination procedure as a good model for bicyclic nitrogen heterocycles. The cyclisation occurred slowly at 110 °C, and a conversion of 68% was achieved after four days (Table 4, entry 4). The neopentyl ytterbium ate catalyst nevertheless did not induce any selectivity for this transformation.

Even if evident improvements are needed in terms of enantioselectivity for achieving these delicate transformations, their feasibility was here unambiguously demonstrated with lanthanide amide ate complexes.

Conclusion

We have presented the in-situ preparation of new lanthanide amide ate complexes bearing chiral *N*-cyclopentyl-substituted binaphthylamine ligands. The ytterbium complex Li-**3b** proved to be the most enantioselective catalyst we have published so far and the spiropyrrolidine **7a** was isolated with 87% *ee* after 20 h reaction at room temperature. As already noted in the isopropyl-substituted series,[21] the yttrium catalyst proved to be more active than its ytterbium counterpart for all the substrates tested. This enhanced activity is unfortunately accompanied with a slight decrease in the enantioselectivity. Both catalysts allowed the cyclisation for the synthesis of a piperidine, albeit by heating the reaction mixture, and 3-methyl-2-azaspiro[5.5]undecane (**7e**) was isolated with up to 51% *ee*.

Complex Li-**3d**, an amide ate complex bearing the less hindered neopentyl substituent at the nitrogen atom, was by far the more active complex of this series, since 2,2-dimethylpent-4-enylamine (**6b**) and the aminohexene derivative **6e** were efficiently transformed at room temperature. The enantiofacial discrimination with this catalyst was unfortunately diminished for all the substrates.

The role of the countercation was examined by the synthesis of analogous complexes K-**3b**, K-**5b** and K-**3d**. These complexes proved to be less stable than their lithium counterparts and crystals suitable for X-ray analysis were only obtained for K-**3d**. All these complexes promoted hydroamination cyclisations, albeit in a less efficient way than the analogous lithium ate complexes. Longer reaction times were required for achieving satisfying conversions and the enantiomeric excesses were generally lower. Moreover for several substrates, hydroamination transformations catalysed by K-**3d** afforded the products with a change of configuration in contrast to Li-**3d**. A similar observation was made for the hydroamination/cyclisation catalysed by organophosphine oxide substituted lanthanides that a small structural variation in the catalytic precursor, such as a slight decrease in the ionic radius, could promote an inversion in the sense of enantioselectivity.[23] In a previous report, we initiated a study of the mechanism of hydroamination reactions catalysed by lanthanide ate complexes.[21] The decoordination of one binaphthylamine ligand leading to a neutral trisamide species was envisaged. The comparison of the efficiency of an yttrium lithium ate and a neutral trisamide yttrium complex coordinated by the same *N*-isopropylbinaphthylamine ligand in various hydroamination reactions led to the conclusion that different active species were involved. This implies that the total decoordination of one binaphthylamine ligand in ate-catalysed reactions cannot be considered. The different results provided herein by lithium and potassium ate complexes similarly indicate that the active catalytic species is not the same in both cases. We thus assume that both ligands in ate complexes are in some way involved in the stereodifferentiating course of the transformation. The exact role of the counter cation is still unclear, but is certainly of major importance since it interestingly allows in some cases (compare in particular the catalytic results obtained by Li-**3d** and K-**3d**) to obtain the cyclised products with the opposite configurations. In this context, Shibasaki demonstrated that for enantioselective carbon–carbon bond formation promoted by heterobimetallic catalysts both lanthanide and alkali metals were involved in the reaction mechanism.[24]

The most active catalyst of our series, complex Li-**3d**, which posseses less bulky substituents on the nitrogen atoms, was involved in the transformation of more demanding substrates such as internal alkenes. Unhindered catalysts are more effective for the cyclisation of such alkenes as was already demonstrated with non-chiral lanthanide hydroamination catalysts by Molander et al.[25] and chiral catalysts by Marks et al.[19] To our delight the ate complex Li-**3d** indeed allowed the synthesis of 3-ethyl-2-azaspiro[4,5]decane with 27% *ee*. The synthesis of this type of product has been seldom described by intramolecular asymmetric hydroamination and similar enantiomeric excesses were reported

for pyrrolidines resulting from aminoalkenes with internal double bonds.[19]

Research is presently ongoing for the preparation of more active catalysts for widening the scope of substrates and synthesising structurally different nitrogen heterocycles by the atom-efficient hydroamination transformation.

Experimental Section

General considerations: All manipulations were carried out under an argon atmosphere by 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 was transferred under vacuum. Anhydrous $YbCl_3$ and YCl_3 and (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine were purchased. Compounds $Y[N(tms)_2]_3$,[26] (*R*)-(+)-2,2′-Bis(cyclopentylamino)-1,1′-binaphthyl,[27] and Ph_2CHK[28] were prepared according to reported procedures. The bis(*N*-neopentyl)binaphthylamine ligand and the complex Li-**3d** $[Li(thf)_4][Yb\{(R)\text{-}_{20}H_{12}N_2(C_5H_{11})\}_2]$ were prepared according to the procedure we previously described.[20] The substrates **6a**–**h** for the hydroamination/cyclisation reactions were prepared as previously reported.[9] Substrate **8** was synthesised according to the procedure described by Marks.[29] All other commercially available chemicals were used after the appropriate purification. Bruker AM250, Bruker AV300 and AV360 NMR spectrometers, (operating at 250, 300 and 360 MHz, respectively) were used for recording the NMR spectra. Chemical shifts for ^1H and ^{13}C spectra were referenced internally according to the residual solvent resonances and reported relative to tetramethylsilane. Infrared spectra were recorded on a Perkin–Elmer FT-IR spectrometer as Nujol mulls and are reported in cm^{-1}. Optical rotations are reported as follows: $[\alpha]_D^{RT}$ (*c* in g per 100 mL in solvent). Elemental analyses were performed by the Microanalytical Laboratory of the Institute of Organometallic Chemistry of RAS. Enantiomeric excesses of the products have been determined by GC (GC Fisons 800, column DB1 30 m × 0.32 mm × 0.5 μm) or HPLC (Thermo Separation Product Spectra Series tsp 100P100/UV100 or Perkin–Elmer Pump Series 200/DAD200) analyses after derivatisation, and compared to racemic products prepared with $Y[N(TMS)_2]_3$. The methods are detailed for each compound below.

Preparation of (*R*)-(+)-2,2′-bis(cyclopentylamino)-1,1′-binaphthyl: An aqueous solution of H_2SO_4 (20%, 8 mL) was added to a solution of cyclopentanone (4.1 g, 49.24 mmol) in THF (15 mL). A solution of (*R*)-binaphthylamine (1.0 g, 3.52 mmol) in THF (30 mL) was then slowly added by syringe. After one hour at room temperature, $NaBH_4$ (1.9 g, 49.24 mmol) was added in portions at 0°C. The reaction mixture was allowed to warm up to room temperature overnight. It was then poured into an aqueous solution of KOH (2%, 320 mL) and the aqueous phase was extracted with diethyl ether (3 × 300 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (heptanes/ethyl acetate = 9/1) to give a white powder (1.5 g, 3.46 mmol, 98% yield). $[\alpha]_D^{20} = +96.9$ (*c* = 0.84 in chloroform); ^1H NMR (250 MHz, C_6D_6, 25°C, TMS): $\delta = 7.84$ (d, $^3J(H,H) = 9.5$ Hz, 2H; CH Ar), 7.75 (d, $J = 7.6$ Hz, 2H; CH Ar), 7.28 (d, $^3J(H,H) = 8.2$ Hz, 2H; CH Ar), 7.24 (d, $^3J(H,H) = 8.8$ Hz, 2H; CH Ar), 7.02–7.12 (m, 4H; CH Ar), 3.81 (d, $^3J(H,H) = 8.2$ Hz, 2H; NH), 3.65–3.75 (m, 2H; CH), 1.49–1.71 (m, 4H; CH_2), 1.15–1.25 (m, 8H; CH_2), 0.92–1.12 ppm (m, 4H; CH_2); ^{13}C NMR (62.5 MHz, C_6D_6, 25°C, TMS): $\delta = 144.93$ (2C Ar), 134.68 (2C Ar), 129.96 (2CH Ar), 128.62 (2CH Ar), 128.26 (2C Ar), 127.21 (2CH Ar), 124.46 (2CH Ar), 122.36 (2CH Ar), 115.26 (2CH Ar), 112.82 (2C Ar), 55.02 (2CH), 33.71 ($2CH_2$), 33.63 ($2CH_2$), 23.88 ppm ($4CH_2$); IR (KBr): $\tilde{\nu} = 3400$, 3049, 2954, 2867, 1616, 1595, 1510, 1492, 1422, 818, 807, 746 cm^{-1}; HRMS (ESI): calcd for $C_{30}H_{32}N_2Na$: 443.2463; found: 443.2458.

Preparation of the bislithium salt of (*R*)-(+)-2,2′-bis(cyclopentylamino)-1,1′-binaphthyl: In an argon-filled glove box, (*R*)-(+)-2,2′-bis(cyclopentylamino)-1,1′-binaphthyl (50.0 mg, 0.12 mmol) was solubilised 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 introduced by a micro syringe and the reaction mixture was stirred for 10 min to give a yellow suspension. The solvent was evaporated in vacuo to afford the corresponding lithium amide salt as a yellow powder (40.0 mg, 0.09 mmol, 79% yield). ^1H NMR (360 MHz, $[D_8]$THF, 25°C, TMS): $\delta = 7.47$ (d, $^3J(H,H) = 9.1$ Hz, 2H; 2CH Ar), 7.35 (d, $^3J(H,H) = 7.9$ Hz, 2H; 2CH Ar), 7.14 (d, $^3J(H,H) = 9.0$ Hz, 2H; 2CH Ar), 6.65 (dd, $^3J(H,H) = 6.6$ Hz, $^3J(H,H) = 6.7$ Hz, 2H; 2CH Ar), 6.56 (dd, $^3J(H,H) = 6.7$ Hz, $^3J(H,H) = 6.6$ Hz, 2H; 2CH Ar), 6.41 (d, $^3J(H,H) = 8.5$ Hz, 2H; 2CH Ar), 3.84–3.90 (m, 2H; 2CH), 2.09–2.14 (m, 2H; $2CH_2$), 1.99–2.03 (m, 2H; $2CH_2$), 1.61–1.63 (m, 8H; $4CH_2$), 1.22–1.30 ppm (m, 4H; $2CH_2$); ^{13}C NMR (90 MHz, $[D_8]$THF, 25°C, TMS): $\delta = 156.89$ (2C Ar), 137.36 (2C Ar), 128.07 (2CH Ar), 126.73 (2CH Ar), 124.47 (2CH Ar), 124.01 (2C Ar), 123.83 (2CH Ar), 116.32 (2CH Ar), 115.81 (2CH Ar), 112.13 (2C Ar), 59.41 (2CH), 35.93 ($2CH_2$), 34.29 ($2CH_2$), 24.10 ppm ($4CH_2$); IR (KBr, Nujol): $\tilde{\nu} =$ 1611, 1592, 1497, 1421, 1337, 1287, 1242, 812, 748 cm^{-1}.

Preparation of complex $[Li(thf)_4][Yb\{(R)\text{-}C_{20}H_{12}N_2(C_{10}H_{18})\}_2]$ (Li-3b): In an argon-filled glove box, $YbCl_3$ (50.3 mg, 0.18 mmol) was added to a solution of the bislithium salt of (*R*)-(+)-2,2′-bis(cyclopentylamino)-1,1′-binaphthyl (155.6 mg, 0.36 mmol) in THF (2 mL). The reaction mixture was stirred at room temperature for 45 min and THF was evaporated in vacuo. The resulting solid was extracted with toluene (5 mL), the solution was centrifuged and the filtrate was concentrated in vacuo. The product was obtained as a green powder (117.5 mg, 0.09 mmol, 52% yield). The powder was dissolved in THF (1 mL) and a slow condensation of hexanes in the THF solution resulted in green crystals, suitable for X-ray analysis. IR (KBr, Nujol): $\tilde{\nu} = 1609$, 1591, 1539, 1495, 1420, 1333, 1247, 1209, 1043, 885, 809, 743 cm^{-1}; elemental analysis calcd (%) for $C_{76}H_{92}LiN_4O_4Yb$: C 69.92, H 7.10; found: C 69.74, H 7.10.

Preparation of $[Li(thf)_4][Y\{(R)\text{-}C_{20}H_{12}N_2(C_{10}H_{18})\}_2]$ (Li-5b): In an argon-filled glove box, YCl_3 (58.1 mg, 0.30 mmol) was added to a solution of the bislithium salt of (*R*)-(+)-2,2′-bis(cyclopentylamino)-1,1′-binaphthyl (259.2 mg, 0.60 mmol) in THF (5 mL). The reaction mixture was stirred at room temperature for 45 min and THF was evaporated in vacuo. The resulting solid was extracted with toluene (5 mL), the solution was centrifuged and the filtrate was concentrated in vacuo. The product was obtained as an orange powder (195.4 mg, 0.16 mmol, 53% yield). The powder was dissolved in THF (1 mL) and a slow condensation of hexanes in the THF solution resulted in orange crystals, suitable for X-ray analysis. ^1H NMR (250 MHz, C_6D_6, 25°C, TMS): $\delta = 7.91$ (d, $^3J(H,H) = 8.8$ Hz, 2H; 2CH Ar), 7.70–7.73 (m, 4H; 4CH Ar), 7.54–7.56 (m, 2H; 2CH Ar), 7.37–7.41 (m, 4H; 4CH Ar), 6.82–7.03 (m, 12H; 12CH Ar), 3.75–3.82 (m, 4H; 4CH), 3.33 (brs, 16H; 8αCH$_2$-THF), 2.41–2.57 (m, 2H; CH_2), 2.04–2.14 (m, 2H; CH_2), 1.58–1.69 (m, 2H; CH_2), 1.39–1.46 (m, 8H; $4CH_2$), 1.28 (brs, 16H; 8βCH$_2$-THF), 1.12–1.21 (m, 8H; $4CH_2$), 0.87–0.92 (m, 2H; CH_2), 0.59–0.65 ppm (m, 8H, $4CH_2$); ^{13}C NMR (62.5 MHz, C_6D_6, 25°C, TMS): $\delta = 150.87$ (4C Ar), 135.60 (4C Ar), 131.74 (4CH Ar), 131.27 (4CH Ar), 127.31 (4C Ar), 126.97 (4CH Ar), 124.65 (4CH Ar), 120.44 (4CH Ar), 119.17 (4CH Ar), 116.51 (4C Ar), 68.03 (αCH$_2$-THF), 58.95 (2CH), 58.41 (2CH), 35.65 ($2CH_2$), 35.09 ($2CH_2$), 34.93 ($2CH_2$), 34.33 ($2CH_2$), 25.55 (βCH$_2$-THF), 24.86 ($2CH_2$), 24.40 ($2CH_2$), 23.86 ($2CH_2$), 23.60 ppm ($2CH_2$); IR (KBr, Nujol): $\tilde{\nu} = 1608$, 1590, 1537, 1488, 1419, 1340, 1284, 1245, 1207, 1170, 1041, 953, 913, 883, 850, 808, 739 cm^{-1}; elemental analysis calcd (%) for $C_{76}H_{92}LiN_4O_4Y$: C 74.73, H 7.59, Y 7.28; found: C 75.03, H 7.62, Y 7.57.

Preparation of $[K(thf)_5][Yb\{(R)\text{-}C_{20}H_{12}N_2(C_{10}H_{18})\}_2]$ (K-3b): In an argon-filled glove box, (*R*)-(+)-2,2′-bis(cyclopentylamino)-1,1′-binaphthyl (302.4 mg, 0.72 mmol) was solubilised in THF (5 mL) in a Schlenk flask equipped with a magnetic stirring bar. Ph_2CHK (296.6 mg, 1.44 mmol) in THF (1 mL) was added slowly and the reaction mixture was stirred for 10 min, forming the bispotassium salt. $YbCl_3$ (99.7 mg, 0.36 mmol) was then added to this solution. The reaction mixture was stirred at room temperature for 45 min and THF was evaporated in vacuo. The resulting solid was extracted with toluene (5 mL), the solution was centrifuged and

the filtrate was concentrated in vacuo. The product was obtained as a reddish brown powder (215.0 mg, 0.15 mmol, 43% yield). The powder was dissolved in THF (1 mL) and a slow condensation of hexanes in the solution resulted in reddish brown crystals, not suitable for X-ray analysis. IR (KBr, Nujol): $\tilde{\nu}$ = 1616, 1595, 1507, 1491, 1421, 1349, 1327, 1248, 1210, 1185, 1050, 1019, 857, 808, 745 cm^{-1}; elemental analysis calcd (%) for $C_{76}H_{92}KN_4O_4Yb$: C 68.24, H 6.93, Yb 12.94; found: C 68.48, H 6.94, Yb 13.00.

Preparation of complex [K(thf)$_5$][Y{(*R*)-C$_{20}$H$_{12}$N$_2$(C$_{10}$H$_{18}$)}$_2$] (K-5b): In an argon-filled glove box, YCl_3 (69.7 mg, 0.36 mmol) was added slowly to a solution of the bispotassium salt of (*R*)-(+)-2,2′-bis(cyclopentylamino)-1,1′-binaphthyl in THF, prepared as described above for K-**3b**. The reaction mixture was stirred at room temperature for 45 min and THF was evaporated in vacuo. The resulting solid was extracted with toluene (5 mL), the solution was centrifuged and the filtrate was concentrated in vacuo. The product was obtained as an orange powder (256.0 mg, 0.20 mmol, 57% yield). The powder was dissolved in THF (1 mL) and a slow condensation of hexanes into the solution resulted in orange crystals not suitable for X-ray analysis. ^{1}H NMR (250 MHz, C_6D_6): δ = 7.84 (d, ^3J(H,H) = 8.8 Hz, 2H; 2CH Ar), 7.76 (d, ^3J(H,H) = 7.0 Hz, 2H; 2CH Ar), 7.28 (d, ^3J(H,H) = 7.0 Hz, 2H; 2CH Ar), 7.23 (d, ^3J(H,H) = 8.8 Hz, 2H; 2CH Ar), 7.02–7.12 (m, 16H; 16CH Ar), 3.70–3.82 (m, 4H; 4CH), 3.55–3.60 (m, 16H; 8αCH$_2$-THF), 1.47–1.70 (m, 8H; 4CH$_2$), 1.39–1.44 (m, 16H; 8βCH$_2$-THF), 1.30–1.36 (m, 4H; 2CH$_2$), 1.17–1.23 (m, 8H; 4CH$_2$), 0.89–1.13 ppm (m, 12H, 6CH$_2$); ^{13}C NMR (90 MHz, C_6D_6, 25°C, TMS): δ = 138.43 (4C Ar), 134.69 (4C Ar), 129.95 (2CH Ar), 129.30 (2CH Ar), 128.73 (2CH Ar), 128.61 (2CH Ar), 128.35 (4CH Ar), 127.23 (2CH Ar), 127.08 (4C Ar), 126.33 (2CH Ar), 124.46 (2CH Ar), 122.35 (2CH Ar), 117.52 (4C Ar), 115.25 (4CH Ar), 67.82 (αCH$_2$-THF), 55.01 (4CH), 42.19 (4CH$_2$), 33.71 (4CH$_2$), 33.61 (4CH$_2$), 25.81 (βCH$_2$-THF), 23.87 ppm (4CH$_2$); IR (KBr, Nujol): $\tilde{\nu}$ = 1605, 1591, 1538, 1493, 1419, 1367, 1350, 1327, 1291, 1247, 1052, 812, 742 cm^{-1}; elemental analysis calcd (%) for $C_{76}H_{92}KN_4O_4Y$: C 72.82, H 7.40; found: C 72.26, H 7.00.

Preparation of [K(thf)$_5$][Yb{(*R*)-C$_{20}$H$_{12}$N$_2$(CH$_2$CMe$_3$)}$_2$] (K-3d): In an argon-filled glove box, (*R*)-(+)-2,2′-bis(neopentylamino)-1,1′-binaphthyl (200.0 mg, 0.47 mmol) was solubilised in THF (3 mL) in a Schlenk flask equipped with a magnetic stirring bar. Ph_2CHK (195.3 mg, 0.95 mmol) in THF (1 mL) was added slowly and the reaction mixture was stirred for 2h forming the bispotassium salt. $YbCl_3$ (66.2 mg, 0.24 mmol) was then slowly added to this solution, the reaction mixture was stirred at room temperature overnight and THF was evaporated in vacuo. The resulting solid was extracted with toluene (5 mL), the solution was centrifuged and the filtrate was concentrated in vacuo. The product was obtained as a reddish brown powder (206.2 mg, 0.15 mmol, 64% yield). The powder was dissolved in THF (1 mL) and a slow condensation of hexanes in the solution resulted in reddish brown crystals, suitable for X-ray analysis. IR (KBr, Nujol): $\tilde{\nu}$ = 1607, 1590, 1538, 1496, 1421, 1364, 1336, 1317, 1283, 1244, 1210, 1094, 1055, 896, 810, 775, 744; elemental analysis calcd (%) for $C_{76}H_{88}KN_4O_4Yb$: C 67.83, H 7.49, Yb 12.86; found: C 68.02, H 8.82, Yb 13.16.

Synthesis of *C*-(1-but-2-enylcyclohexyl)methylamine (6f): *n*-Buli 2.5 M (32.80 mL, 82.00 mmol) was added dropwise to a solution of diisopropylamine (12.00 mL, 85.38 mmol) in THF (70 mL) at 0°C and the reaction mixture was stirred for 2 h. A solution of cyclohexane carbonitrile (8.2 mL, 68.32 mmol) in THF (15 mL) was added dropwise at 0°C and the reaction mixture was stirred for three additional hours. A solution of but-2-enyl bromide (9.6 mL, 78.75 mmol) in THF (15 mL) was added dropwise at 0°C and the reaction mixture was allowed to warm up to room temperature overnight. It was hydrolysed with water (100 mL) and the aqueous phase extracted with diethyl ether (3×100 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated in vacuo. The crude product was not isolated but used in the following step without purification. It was solubilised in diethyl ether (30 mL) and added dropwise to a suspension of $LiAlH_4$ (2.60 g, 68.32 mmol) in diethyl ether (120 mL) at 0°C. The reaction mixture was allowed to warm up to room temperature overnight and then 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 ($MgSO_4$), filtered and concentrated. The residue was distilled (100°C, 0.4 mbar) to afford a colourless liquid (6.04 g, 36.17 mmol, 53% yield). The product is a mixture of the *cis*/*trans* isomers (10:90). ^{1}H NMR (250 MHz, $CDCl_3$, 25°C, TMS) *trans* isomer: δ = 5.30–5.36 (m, 2H; 2CH), 2.39 (s, 2H; CH$_2$), 1.87 (d, ^3J(H,H) = 6.1 Hz; CH$_2$), 1.56 (d, ^3J(H,H) = 4.3 Hz, 3H; CH$_3$), 1.31–1.34 (m, 6H; 3CH$_2$), 1.15–1.22 (m, 4H; 2CH$_2$), 0.77–0.82 ppm (br s, 2H; NH$_2$); ^{13}C NMR (62.5 MHz, C_6D_6, 25°C, TMS): δ = 127.25 (CH), 127.15 (CH), 48.89 (CH$_2$), 38.52 (CH$_2$), 37.10 (C), 33.31 (2CH$_2$), 26.50 (CH$_2$), 21.58 (2CH$_2$), 18.09 ppm (CH$_3$); IR (CaF_2): $\tilde{\nu}$ = 3391, 3308, 3019, 2923, 2853, 1615, 1454, 1377, 968 cm^{-1}; HRMS (ESI): calcd for $C_{11}H_{22}N$: 168.1752; found: 168.1747.

Catalytic tests

General procedure for NMR-scale racemic hydroamination–cyclisation: For the cyclisations of aminoalkenes performed from 25°C to 80°C, in the glove box, the appropriate aminoalkene (0.20 mmol) was dissolved in C_6D_6 (0.1 mL) and dried on 4 Å molecular sieves for 2h at room temperature. [Y{N(SiMe$_3$)$_2$}$_3$] (11.2 mg, 0.02 mmol) was dissolved in C_6D_6 (0.7 mL) and introduced into a J. Young NMR tube equipped with a teflon valve, and the aminoalkene solution was then introduced. The NMR tube was heated out of the glove box at the appropriate temperature. The hydroamination reaction was monitored by ^{1}H NMR spectroscopy by observation of the decrease of the olefinic protons signals. After the appropriate time, the reaction was quenched with CH_2Cl_2.

For the cyclisations of aminoalkenes performed at 110°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 2h at room temperature. This solution was added to [Y{N(SiMe$_3$)$_2$}$_3$] (11.2 mg, 0.02 mmol) in solution in toluene (0.7 mL) in a sealed tube which was sealed and heated at 110°C for the appropriate time. The reaction was quenched with CH_2Cl_2.

*Typical procedure for the in-situ preparation of the Li ate complexes Li-**3a**, Li-**3b**, Li-**3d** and Li-**5b***: In an argon-filled glove box, the ligand (0.12 mmol) was solubilised 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 introduced through a microsyringe and the reaction mixture was stirred for 10 min (30 min for Li-**3d**) to give a yellowish suspension. The solvent was evaporated in vacuo. $LnCl_3$ (0.06 mmol) was added to the solution of the bislithium salt of the ligand in THF (2 mL). The reaction mixture was stirred at room temperature for 45 min (3 h for Li-**3d**) and THF was evaporated in vacuo. The crude mixture was directly used for the catalytic tests.

*Typical procedure for the preparation of the K ate complexes K-**3b**, K-**3d** and K-**5b***: 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. Ph_2CHK (49.0 mg, 0.24 mmol) in THF (0.5 mL) was added slowly and the reaction mixture was stirred for 10 min (2 h for K-**3d**). $LnCl_3$ (0.06 mmol) was then slowly added to the solution of the bis potassium salt of the ligand in THF. The reaction mixture was stirred at room temperature for 45 min (overnight for K-**3d**) and THF was evaporated in vacuo. The crude mixture was directly used for the catalytic tests.

General procedure for NMR-scale asymmetric hydroamination–cyclisation of aminoalkenes: For the cyclisation of aminoalkenes performed from 25°C to 80°C 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. The lanthanide catalyst was dissolved in C_6D_6 (0.7 mL) and introduced into a J. Young NMR tube equipped with a teflon valve and the aminoalkene solution was then introduced. The NMR tube was heated out of the glove box at the appropriate temperature. The hydroamination reaction was monitored by ^{1}H NMR spectroscopy by 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 0°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 0°C. The lanthanide catalyst was dissolved in toluene (0.5 mL) and cooled at 0°C for 30 min. The aminoalkene solution was added at 0°C to the catalyst solution and maintained at 0°C during the appropriate time. The reaction mixture was quenched with CH_2Cl_2.

For the cyclisation of aminoalkenes performed at 110 °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. The lanthanide catalyst was dissolved in toluene (0.7 mL) and introduced into an ampoule which was sealed and heated at 110 °C during the appropriate time. The reaction was quenched with CH_2Cl_2.

*3-Ethyl-2-azaspiro[4,5]decane (**7f**)*: Colourless oil; b.p. 100 °C, 0.4 mbar; $[\alpha]_D^{20} = +3.6$ ($c = 0.12$ in chloroform) for 27 % *ee*, 58 % isolated yield; ^{1}H NMR (400 MHz, C_6D_6, 25 °C, TMS): $\delta = 3.17$–3.28 (m, 1H; CH), 3.07 (d, ^3J(H,H) = 11.3 Hz, 1H; CH_2), 2.94 (d, ^3J(H,H) = 11.3 Hz; 1H; CH_2), 1.89–2.04 (m, 1H; CH_2), 1.09–1.63 (m, 13H; 6CH_2 + NH), 0.98 (t, ^3J-(H,H) = 7.6 Hz, 3H; CH_3), 0.86–0.89 ppm (m, 1H, CH_2); ^{13}C NMR (100 MHz, C_6D_6, 25 °C, TMS): $\delta = 60.44$ (CH), 42.54 (C), 37.62 (2CH_2), 36.37 (CH_2), 27.18 (CH_2), 26.07 (CH_2), 24.06 (CH_2), 23.46 (2CH_2), 11.78 ppm (CH_3); IR (CaF_2): $\tilde{\nu} = 2926$, 2854, 1623, 1450 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{22}N$: 252.1747; found: 252.1749.

*2-Ethyl-4,4-diphenylpyrrolidine (**7g**)*: Colourless oil; ^{1}H NMR (250 MHz, C_6D_6, 25 °C, TMS): $\delta = 7.06$–7.28 (m, 10H; 10CH Ar), 3.56 (d, ^3J(H,H) = 10.7 Hz, 1H; CH_2), 3.33 (d, ^3J(H,H) = 10.7 Hz, 1H; CH_2), 2.94–3.00 (m, 1H; CH_2), 2.48–2.55 (m, 1H; CH_2), 1.82–1.91 (m, 1H; CH), 1.47–1.50 (m, 1H; NH), 1.31–1.44 (m, 2H; CH_2), 0.90 ppm (t, ^3J(H,H) = 7.6 Hz, 3H; CH_3); ^{13}C NMR (62.5 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 148.70$ (C Ar), 147.92 (C Ar), 128.53 (4CH Ar), 127.59 (4CH Ar), 126.12 (2CH Ar), 59.50 (CH), 58.26 (CH_2), 56.93 (C), 45.51 (CH_2), 30.62 (CH_2), 11.79 ppm (CH_3); IR ($CHCl_3$): $\tilde{\nu} = 2918$, 2877, 2710, 2553, 1601, 1493, 1456, 1380 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{11}H_{21}N$: 167.1669; found: 167.1671.

Determination of enantiomeric excesses for the amine 7f, 7g, 7h and 9

*3-Ethyl-2-azaspiro[4,5]decane (**7f**)*: Dimethylaminopyridine (6.0 mg, 0.04 mmol), triethylamine (27.5 μL, 0.20 mmol) and Mosher chloride (37.0 μL, 0.20 mmol) were added to a solution of pyrrolidine **7f** (0.20 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred at room temperature for 2 h and then hydrolysed with water (5 mL). The aqueous phase was extracted with CH_2Cl_2 (3×5 mL). After drying, the crude product was dissolved in diethyl ether and injected on a GC capillary column DB-1 (80 °C (5 min) then 10 °C min^{-1} until 200 °C (20 min), $t_{1(major)} = 28.86$ min, $t_{2(minor)} = 29.57$ min).

*2-Ethyl-4,4-diphenylpyrrolidine (**7g**)*: Dimethylaminopyridine (6.0 mg, 0.04 mmol), triethylamine (27.5 μL, 0.20 mmol) and naphthoyl chloride (29.5 μL, 0.20 mmol) were added to a solution of pyrrolidine **7g**, (49.2 mg, 0.20 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred at room temperature for 2 h and then hydrolysed with water (5 mL). The aqueous phase was extracted with CH_2Cl_2 (3×5 mL). The combined organic layers were washed with a saturated solution of NH_4Cl, dried ($MgSO_4$), filtered and concentrated in vacuo. The crude product was purified by preparative silica plate (cyclohexane/AcOEt 75/25). The *ee* was determined by HPLC analysis using a (*S*,*S*)-Whelk O1 column (hexane/EtOH 75/25; flow: 0.9 mL min^{-1}, $t_{1(minor)} = 8.10$ min, $t_{2(major)} = 15.01$ min).

*2-Benzyl-4,4-diphenylpyrrolidine (**7h**)*: The same procedure for the preparation of the amide was used as described for **7g**. The *ee* was determined by HPLC analysis using a (*S*,*S*)-Whelk O1 column (hexane/EtOH 75/25; flow: 0.9 mL min^{-1}, $t_1 = 9.90$ min, $t_2 = 20.83$ min).

*2-Methylindoline (**9**)*: The same procedure for the preparation of the amide was used as described for **7g**. The *ee* was determined by HPLC analysis using a (*S*,*S*)-Whelk O1 column (hexane/EtOH 75/25; flow: 0.7 mL min^{-1}, $t_1 = 24.67$ min, $t_2 = 26.70$ min).

X-ray crystallography: Low-temperature diffraction data of Li-**3b**, Li-**5b**[30] were collected on a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), by performing ϕ and ω scans. The temperature of the crystal was maintained at the selected value (180 K) by means of a 700 series Cryostream cooling device to within an accuracy of ±1 K. For complex K-**3d**[30] the data were collected on Stoe IPDS diffractometer operating with monochromatic $Mo_K\alpha$ radiation ($\lambda = 0.71073$). The data were corrected for Lorentz, polarisation, and absorption effects. The structures were solved by direct methods with SHELXS-97[31] and refined against F^2 by full-matrix least-squares techniques with SHELXL-97[32] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.[33] The absolute configuration was determined by refining the Flack's[34] parameter using a large number of Friedel's pairs.

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