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Catalytic, Enantioselective Intramolecular Hydroamination of Primary Amines Tethered to Di- and Trisubstituted Alkenes

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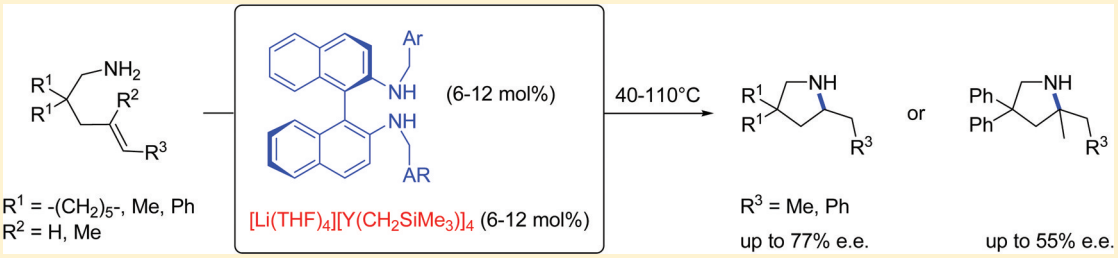
Supporting Information



ABSTRACT: The in situ preparation of chiral amido alkyl ate yttrium complexes from an array of chiral *N*-benzyl-like-substituted binaphthyldiamines is reported. These chiral heteroleptic complexes are shown to be efficient catalysts for the enantioselective intramolecular hydroamination of primary amines tethered to sterically demanding alkenes at high reaction temperatures. Fine tuning of their chiral environment allowed up to 77% ee to be reached for the cyclization of aminoalkenes bearing 1,2-dialkyl-substituted carbon−carbon double bonds. These chiral complexes also demonstrate the ability to promote the cyclization of amine-tethered trisubstituted alkenes in up to 55% ee, as the first report of the formation of enantioenriched quaternary centers by an hydroamination reaction.

INTRODUCTION

The hydroamination reaction and its asymmetric version developed dramatically in the last twenty years as can be attested by the exponentially increasing number of reports dealing with the progress of such methodologies in the literature.[1,2] These transformations indeed perfectly match the concept of sustainable chemistry since they allow the formation of new nitrogen−carbon bonds in an ideal atom efficiency and economy, starting from non activated substrates. Numerous proficient methodologies have thus been recently described that imply either the activation of the unsaturated carbon−carbon bond or the activation of the amine functionality through a catalyzed process. A rough description of these transformations involves a transition-metal catalysis in the former case,[3,4] whereas group IV metals[5] and rare-earth elements[6] are engaged in the later one. Marks and his group particularly pioneered this field, and demonstrated the ability of cyclopentadienyl-based lanthanide complexes to promote the intramolecular hydroamination of aminoolefins toward the formation of valuable nitrogen-containing heterocycles.[7] Nowadays, the scope of the transformation using rare-earth-based catalysts includes the facile formation of pyrrolidine and piperidine heterocycles in high yields and selectivities, starting from primary or secondary aminoolefins, possessing a terminal double bond.[8] Some examples related to the hydroamination/cyclization of aminoolefins possessing a styrenyl functionality (as more activated substrates) have been nevertheless successfully described in the presence of rare-earth-based catalysts and interestingly with high selectivities in the presence of asymmetric promoters.[9] However, very little success is described for the transformation of sterically encumbered double bonds and more specifically for the transformation of 1,2-dialkyl-disubstituted olefins. To the best of our knowledge, only the group of Marks described the efficiency of cyclopentadienyl-based lanthanide catalysts to achieve this transformation at high temperature for the synthesis of pyrrolidine and piperidine derivatives.[10] They also successfully reported the enantioselective version of this transformation by using C_1-symmetric organolanthanide catalysts leading to the targeted compounds with up to 68% ee.[11,12] Furthermore, the group of Molander was one of the first to achieve the intramolecular hydroamination of 1,1-disubstituted olefins with unhindered Sm- and Nd-based catalytic systems providing a variety of heterocycles containing quaternary centers.[13,14] Aminoolefins possessing this 1,1-methyl-substituted pattern have then been

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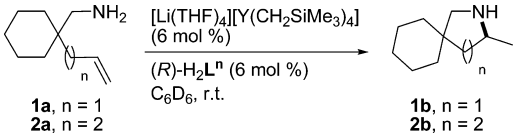
Table 1. AIH of Terminal Aminoalkenes 1a and 2a Promoted by Chiral Amido Alkyl Ate Yttrium catalysts[a]



entry	subst.	prod.	(*R*)-H_2L^n	*t* (h)	% conv.[b]	% ee[c]
1	**1a**	**1b**	(*R*)-H_2L^0	1	>99	75
2			(*R*)-H_2L^1	0.30	90	5
3			(*R*)-H_2L^2	0.30	97	12
4			(*R*)-H_2L^3	0.25	95	5
5			(*R*)-H_2L^4	0.16	>99	5
6			(*R*)-H_2L^5	0.25	>99	11
7			(*R*)-H_2L^6	0.25	95	9
8			(*R*)-H_2L^7	0.25	86	8
9			(*R*)-H_2L^9	0.25	95	16
10	**2a**	**2b**	(*R*)-H_2L^0	16[d]	95	40
11			(*R*)-H_2L^1	19	>99	30
12			(*R*)-H_2L^2	19	90	6
13			(*R*)-H_2L^3	19	87	15
14			(*R*)-H_2L^4	2	87	20
15			(*R*)-H_2L^5	2	88	20
16			(*R*)-H_2L^6	4	>99	26
17			(*R*)-H_2L^7	4	>99	23
18			(*R*)-H_2L^9	19	98	30

[a]Reactions performed in the presence of 6 mol % precatalyst, in C_6D_6, at rt. [b]Measured by ^{1}H NMR spectroscopy. [c]Determined by HPLC analysis of the product following derivatization (see Supporting Information). [d]The reaction was run at 50 °C.

used occasionally as test substrates to evaluate and classify the activity of new catalysts by several groups.[15] As far as we know, however, no report deals with the preparation of such quaternary centers by asymmetric intramolecular hydroamination (AIH) until now.

We previously reported a new and reliable route to chiral amido alkyl yttrium catalysts which proved to be highly efficient for the enantioselective cyclization of several 1,2-disubstituted aminoolefins.[16] We now describe in further details our simple methodology to prepare various chiral amido alkyl ate yttrium complexes, the chirality arising from a binaphthylamido backbone possessing different substituents on the nitrogen atoms. The in situ prepared precatalysts have been tested for their ability to promote the hydroamination/cyclization of demanding aminoolefins, and new scalemic heterocycles could be prepared through this procedure. Finally, these catalytic systems were efficient enough to promote the cyclization of not only 1,1-disubstituted- but also 1,1,2-trisubstituted olefins toward the formation of enantioenriched pyrrolidines possessing a new quaternary center.

RESULTS AND DISCUSSION

As we formerly described, the in situ preparation of the yttrium catalyst proceeded easily by reaction between the ate precursor complex $[Li(THF)_4][Y(CH_2TMS)_4]$[17] and one equivalent of ligand (*R*)-H_2L^n in C_6D_6 leading to the immediate formation of a yellow solution. The first NMR analyses performed with *N*-cyclopentyl-disubstituted ligand H_2L^0 indicated the expected set of signals confirming the formation of an amido alkyl ate complex, $[(R)\text{-}L^0][Y(CH_2TMS)_2Li(THF)_4]$. The ability of this new species to promote AIH was demonstrated with the direct use of the mixture for the cyclization of *C*-(1-allylcyclohexyl)-methyl amine **1a**, a test substrate bearing a terminal double bond (Table 1). The expected pyrrolidine **1b** was indeed obtained in 75% ee with a complete conversion after 1-h reaction time at room temperature (Table 1, entry 1). This result compared finely in terms both of activity and selectivity with those of our previously described alkyl binaphthylamido lanthanide-type catalysts.[18]

We report here in details our investigations on the efficiency of the catalysts prepared from ligands (*R*)-H_2L^n (n = 1−9) (Figure 1) for the intramolecular hydroamination of mono-

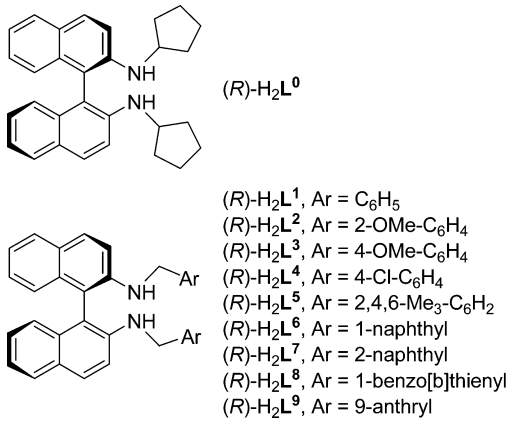


Figure 1. Chiral (*R*)-*N*-substituted binaphthyl diamine ligands.

substituted primary aminoolefins **1a** and **2a** (Table 1). The *N*-benzyl-substituted ligand (*R*)-H_2L^1 allowed a rapid cyclization of aminoolefin **1a**, albeit pyrrolidine **1b** was obtained in nearly racemic form (Table 1, entry 2). Further modification of the ligand with donating substituents at the ortho or para position of the phenyl group (entries 3−5) or steric modification (entries 6−9) did not enhance significantly the selectivity of the corresponding catalysts, albeit good activity was maintained.

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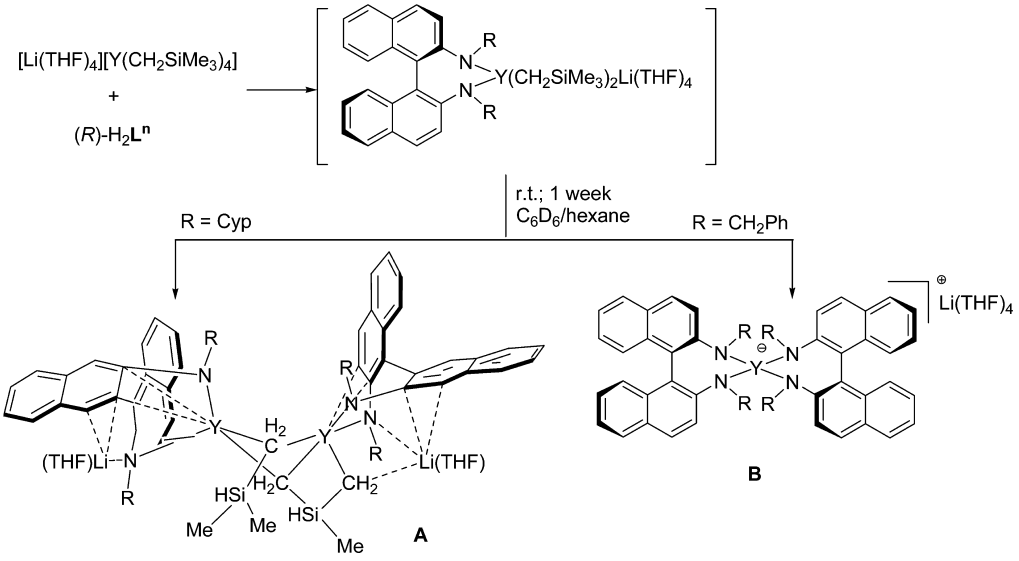
Scheme 1. Evolution in Solution of in Situ Prepared Complexes



High conversions were indeed observed in all cases within less than half an hour at room temperature. The cyclization of *gem*-dialkyl aminohexene **2a** which requires harsher conditions than those for **1a** was next examined. The catalyst prepared from ligand (*R*)-$H_2\mathbf{L}^0$ afforded the expected piperidine, but the reaction had to be conducted at 50 °C to achieve a high conversion (Table 1, entry 10). The use of the benzyl-like substituents led to more active catalysts since the transformation could be performed at room temperature and the *N*-benzyl-substituted ligand (*R*)-$H_2\mathbf{L}^1$ afforded total conversion in piperidine **2b** after one night at room temperature with 30% ee, a better value than that obtained for product **1b** (entry 11 versus entry 2 in Table 1). The use of different benzyl-like ligands allowed the activity of the corresponding catalysts (ligands (*R*)-$H_2\mathbf{L}^{4-7}$, entries 14−17) to be increased without enhancement of selectivity.

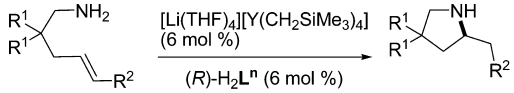
Comparison of the enantiomeric excesses reported in Table 1 with those given by catalysts prepared from *N*-cyclopentyl ligand (*R*)-$H_2\mathbf{L}^0$ either isolated[18b] or in situ prepared from yttrium chloride and BuLi[18a] indicates that *N*-cyclopentyl ligand (*R*)-$H_2\mathbf{L}^0$ affords more enantioselective catalysts than the benzyl-like ligands for the cyclization of monosubstituted aminoolefins leading to five- or six-membered nitrogen heterocycles.

Attempts were drawn toward the characterization of the new precatalytic species generated from in situ reaction between $[Li(THF)_4][Y(CH_2TMS)_4]$ and the *N*-modified binaphthyldiamine ligands (*R*)-$H_2\mathbf{L}^0$ and (*R*)-$H_2\mathbf{L}^1$. As we previously described,[16] crystallization of the mixture using (*R*)-$H_2\mathbf{L}^0$ in a hexane/benzene solution afforded crystals of a new dimeric heterobimetallic alkyl species $\{Li(THF)[\mu\text{-}(R)\text{-}\mathbf{L}^0]Y[\mu\text{-}CH_2SiMe_2CH_2\text{-}\mu]_2\}_2$, **A** (Scheme 1) which was isolated in 70% yield. This complex, resulting from C−H bond activation, was tested for its ability to promote the cyclization of substrate **1a** and led to catalytic results different from those reported for the in situ generated species. The dimeric complex proved indeed to be more enantioselective since pyrrolidine **1b** was isolated with a high ee value of 80%, but a 2-h reaction at room temperature was required to afford a complete conversion. A similar isolation attempt was performed starting from ligand (*R*)-$H_2\mathbf{L}^1$, and this procedure led again to the recovery of yellow crystals suitable to perform X-ray analysis. In this case, however, a different transformation occurred, and a new tetraamido ate yttrium complex **B** could be characterized. As we already described with similar ligands,[19] this complex was composed of a discrete lithium cation $Li(THF)_4^+$ and a discrete complex anion $\{Y[(R)\text{-}C_{20}H_{12}N_2(C_{14}H_{14})]_2\}^-$.[20] Involved in the catalytic transformation of substrate **1a**, this isolated species showed, once more, a different behavior as a more enantioselective catalyst (compared to that of its in situ prepared precursor [20% ee for **1b**]) but as a much less active promoter (17 h reaction time). The thus observed different catalytic efficiencies of the in situ generated complexes vs those of the isolated complexes demonstrate their structural dissimilarities.

As this first set of experiments demonstrated that the easily in situ generated catalytic precursors proved to be highly active species, the study was next extended to the cyclization of more challenging substrates. Ligands bearing benzyl-like substituents were considered as privileged structures for these transformations since corresponding catalysts showed enhanced activity compared to those prepared from the more sterically encumbered ligand (*R*)-$H_2\mathbf{L}^0$.

As demanding substrates, amines including 1,2-disubstituted double bonds were first examined (Scheme 2 and Table 2). A

Scheme 2. AIH of 1,2-Disubstituted Aminoalkenes



3a, R^1 = -$(CH_2)_5$-, R^2 = CH_3 — **3b**, R^1= -$(CH_2)_5$-, R^2 = CH_3
4a, R^1 = CH_3, R^2 = CH_3 — **4b**, R^1 = CH_3, R^2 = CH_3
5a, R^1 = C_6H_5, R^2 = CH_3 — **5b**, R^1 = C_6H_5, R^2 = CH_3
6a, R^1 = CH_3, R^2 = C_6H_5 — **6b**, R^1 = CH_3, R^2 = C_6H_5
7a, R^1 = C_6H_5, R^2 = C_6H_5 — **7b**, R^1 = C_6H_5, R^2 = C_6H_5

first test was realized to transform 2-cyclohexyl aminohex-4-ene **3a** in pyrrolidine **3b** in the presence of a catalyst prepared from (*R*)-$H_2\mathbf{L}^0$. A complete conversion could not be achieved even after three days reaction at 70 °C, and **3b** was formed in only 12% ee (Table 2, entry 1). Nevertheless, the use of the *N*-benzyl ligand (*R*)-$H_2\mathbf{L}^1$ promoted the transformation of **3a** into

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Table 2. AIH of 1,2-Disubstituted Aminoalkenes 3−5a Promoted by Chiral Amido Alkyl Ate Yttrium Catalysts[a]

entry	subst.	prod.	(*R*)-H_2L^n	*t* (h)	*T* (°C)	% conv.[b]	% ee[c,d]	(config.)
1	**3a**	**3b**	(*R*)-H_2L^0	74	70	58	12	
2			(*R*)-H_2L^1	19	70	83	49	
3			(*R*)-H_2L^2	70	110	50	35	
4			(*R*)-H_2L^3	19	70	87	53	
5			(*R*)-H_2L^4	19	70	93	55	
6			(*R*)-H_2L^5	50	70	79	47	
7			(*R*)-H_2L^6	19	70	87	47	
8			(*R*)-H_2L^7	19	70	97	47	
9			(*R*)-H_2L^8	36	110	5	nd	
10			(*R*)-H_2L^9	19	110	96 (50)[e]	68	
11	**4a**	**4b**	(*R*)-H_2L^1	110	110	77	20	
12			(*R*)-H_2L^4	120	110	88	20	
13			(*R*)-H_2L^6	120	110	89	13	
14			(*R*)-H_2L^9	110	110	91	52	
15	**5a**	**5b**	(*R*)-H_2L^1	15	50	>99	76	
16			(*R*)-H_2L^2	36	70	38	40	
17			(*R*)-H_2L^3	19	70	>99 (80)[e]	75	(*S*)
18				36	40	83	77	
19			(*R*)-H_2L^4	19	70	>99	73	
20			(*R*)-H_2L^5	36	70	40	<5	
21			(*R*)-H_2L^6	36	70	30	51	
22			(*R*)-H_2L^8	48	110	15	nd	
23			(*R*)-H_2L^9	70	70	33	−10	

[a]Reactions run in C_6D_6 (40 − 70 °C), in C_7D_8 (110 °C). [b]Measured by ^{1}H NMR spectroscopy. [c]Determined by HPLC analysis of the product following derivatization (see Supporting Information). [d]The negative sign indicates configuration opposite to that obtained in the other cases. [e]Isolated yield.

3b in a higher yield after one night at 70 °C with 49% ee (Table 2, entry 2). The use of ligands (*R*)-H_2L^3 and (*R*)-H_2L^4 with para substituents on the phenyl rings allowed the reaction to be performed in the same conditions with a slight increase in enantiomeric excess values (entries 4 and 5). With the bulkier ligands (*R*)-H_2L^2 and (*R*)-H_2L^5 with ortho substituents on the phenyl ring, higher reaction temperatures or longer reaction times were required for the formation of **3b** without increasing selectivity compared to those of the *N*-benzyl-substituted ligand (entries 3 and 6). The replacement of phenyl by 1- or 2-naphthyl groups (*R*)-H_2L^6 and (*R*)-H_2L^7 did not modify activity or enantioselectivity (entries 7 and 8 versus entry 2). The ligand (*R*)-H_2L^8 including a sulfur atom did not yield to an active catalytic species even at high temperature (entry 9). The best result in terms of enantioselectivity (68% ee) was reached by using binaphthyldiamine modified by an anthrylmethyl moiety (*R*)-H_2L^9, a high value taking into account that the transformation was run at 110 °C and turned to completion (entry 10). Some of these easily prepared catalyst solutions were examined for the cyclization of **4a**, a transformation previously only described by the group of Marks.[11] Delightfully, the catalysts were active at 110 °C (entries 11−14), and (*R*)-H_2L^9 led to the preparation of pyrrolidine **4b** in 52% ee, the highest value reported for this substrate to date (Table 2, entry 14). The more active *gem*-diphenyl-substituted substrate **5a** could be transformed at lower temperatures. *N*-benzyl-substituted ligand (*R*)-H_2L^1 and ligands (*R*)-H_2L^3 and (*R*)-H_2L^4 with para substituents on the phenyl ring led to high enantioselectivities for this reaction (entries 15, 17−19). With the bulkier ligands, lower selectivities and longer reaction times were observed (entries 16, 20−23). The highest activity and enantioselectivity (77% ee) were furnished by the ligand (*R*)-H_2L^3 with *p*-methoxy substituents on the phenyl rings (entry 18).

The cyclization of aminoolefins with a phenyl substituent on the double bond was studied as an efficient route toward nitrogen heterocycles including aromatic rings (Scheme 2, Table 3). Several ligands have been tested for the cyclization of

Table 3. AIH of 1,2-Disubstituted Aminoalkenes 6a and 7a Promoted by Chiral Amido Alkyl Ate Yttrium Catalysts[a]

entry	subst.	prod.	(*R*)-H_2L^n	*t*(h)	*T* (°C)	% conv.[b]	% ee[c,d]
1	**6a**	**6b**	(*R*)-H_2L^1	19	70	91	<5
2			(*R*)-H_2L^3	19	70	90	38
3			(*R*)-H_2L^6	19	70	93	<5
4			(*R*)-H_2L^9	36	70	70	20
5	**7a**	**7b**	(*R*)-H_2L^1	24	50	>99 (83)[e]	53
6			(*R*)-H_2L^2	19	70	>99	<5
7			(*R*)-H_2L^3	7	40	99	55
8			(*R*)-H_2L^4	2	70	>99	55
9			(*R*)-H_2L^5	19	70	>99	−11
10			(*R*)-H_2L^6	8	70	95	26
11			(*R*)-H_2L^8	19	70	92	27
12			(*R*)-H_2L^9	19	70	90	−19

[a]Reactions run in C_6D_6 (40−70 °C). [b]Measured by ^{1}H NMR spectroscopy. [c]Determined by HPLC analysis of the product following derivatization (see Supporting Information). [d]The negative sign indicates opposite configuration to that obtained in the other cases. [e]Isolated yield.

gem-dimethyl aminoolefin **6a**, and reactions could be performed at 70 °C with moderate enantioselectivities (entries 1−4). The highest enantiomeric excess value for **6b** (38%) was recorded with ligand (*R*)-H_2L^3 with *p*-methoxy substituent on the phenyl ring (entry 2). This cyclization has been performed by several

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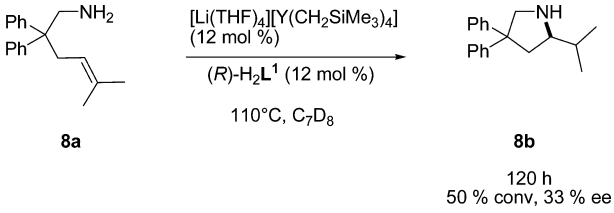
groups with chiral zirconium catalysts,[5d] yttrium bis thiolato catalysts,[9a] and scandium or lutetium binaphtholato complexes[8c] with better enantioselectivities. The cyclization of *gem*-diphenyl substrate **7a** has been examined with all ligands of the series. The best results in terms of enantioselectivity (53−55% ee) were furnished by ligands (*R*)-H_2**L**^{1} and (*R*)-H_2**L**$^{3-4}$ as observed for the formation of **5b** (Table 3, entries 5−12).

Since the cyclizations of aminoolefins including *gem*-diphenyl groups are in most cases faster than those of substrates with *gem*-dimethyl groups (compare the cyclizations of **5a** and **4a** and those of **7a** and **6a**), we focused on substrates with *gem*-diphenyl substituents in the *β*-position from the nitrogen for studying the hydroamination of highly hindered aminoolefins. The *N*-benzyl-substituted binaphthyl amine (*R*)-H_2**L**^{1} was selected as test ligand due to its efficiency and its easy availability. The synthesis of a pyrrolidine starting from the 1,2,2-trialkyl-substituted aminoalkene **8a** was first examined (Scheme 3). Satisfyingly, the targeted compound **8b** could be prepared, but an enhanced quantity of catalyst (12 mol %) was essential in this case, and the temperature of the reaction was raised up to 110 °C. Pyrrolidine **8b** bearing a isopropyl group was obtained with 50% conversion after 120 h and 33% ee. To the best of our knowledge, this result is the first report of a successful hydroamination reaction leading to this pyrrolidine bearing an isopropyl substituent in the *α*-position of the nitrogen atom[21] and thus the highest enantioselectivity so far.

Scheme 3. Formation of New Heterocycles by AIH of 1,2,2-Trisubstituted Aminoalkene 8a

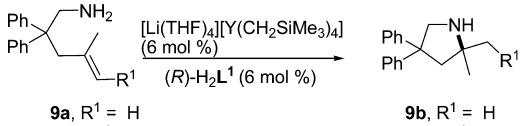


A last challenge was to perform the hydroamination of trisubstituted olefins with an internal substituent on the double bond for the enantioselective formation of quaternary centers (Table 4). To evaluate the feasibility of such transformations we first tested the cyclization of substrate **9a** with a methyl substituent on the internal carbon of the double bond into the achiral pyrrolidine **9b** using a catalyst prepared from racemic *N*-benzyl-substituted ligand H_2**L**^{1}.[15] We were pleased to find that the hydroamination reaction occurred in very mild conditions, at room temperature and within a short reaction time in spite of the encumbered double bond of **9a** (Table 4, entry 1). The hydroamination of the similar substrate **10a** with a phenyl substituent on the terminal carbon of the double bond could be performed with a variety of ligands at different temperatures (entries 2−8). Pyrrolidine **10b** was obtained at 70 °C with satisfying enantiomeric excesses with ligands (*R*)-H_2**L**^{1}, (*R*)-H_2**L**^{3} and (*R*)-H_2**L**^{6}. The best enantioselectivities were observed with ligands (*R*)-H_2**L**^{3} and (*R*)-H_2**L**^{6} (55% ee, entries 4 and 6) but the reaction was faster with *N*-benzyl-substituted ligands H_2**L**^{1} and H_2**L**^{3} (entries 2 and 4). Reaction could be performed at 110 °C with bulkier ligands (even anthrylmethyl-substituted (*R*)-H_2**L**^{9}) but with low values of enantiomeric excesses for pyrrolidine **10b** (entries 3, 5, 7, and 8). Ligand (*R*)-H_2**L**^{1} was thus selected for testing the hydroamination of substrate **11a** with a trialkyl-substituted inactivated double bond. To our delight the formation of pyrrolidine **11b** was observed at 110 °C within prolonged reaction time but with a good enantioselectivity (55% ee, entry 9). As far as we know, enantioselective hydroamination with the formation of a quaternary center was never reported, and the amido alkyl ate yttrium species described here were able to catalyze the formation of two such compounds.

CONCLUSION

We presented here a simple in situ synthesis of chiral amido alkyl ate yttrium complexes by stoichiometric combination of a well-known and room temperature stable yttrium precursor $[Li(THF)_4][Y(CH_2SiMe_3)_4]$ with a variety of chiral *N*-benzyl type-substituted binaphthylamine ligands. These complexes were active as catalysts for the room temperature cyclization of monosubstituted aminoalkenes leading to **1b** and **2b** as respectively a five- and a six-membered *N*-heterocycle, with low ee's (up to 30%). These new chiral amido alkyl ate complexes afforded a better efficiency for the asymmetric

Table 4. AIH of Trisubstituted Aminoalkenes 9−11a toward the Formation of Quaternary Centers[a]



entry	subst.	prod.	(*R*)-H_2**L**^{n}	*t* (h)	*T* (°C)	% conv.[b]	% ee[c]	(config.)
1	**9a**	**9b**	(±)-H_2**L**^{1}	1	25	90	–	
2	**10a**	**10b**	(*R*)-H_2**L**^{1}	19	70	97 (66)[d]	49	(*S*)
3			(*R*)-H_2**L**^{2}	48	110	98	11	
4			(*R*)-H_2**L**^{3}	19	70	99	55	
5			(*R*)-H_2**L**^{5}	19	110	96	8	
6			(*R*)-H_2**L**^{6}	36	70	98	55	
7			(*R*)-H_2**L**^{8}	48	110	50	15	
8			(*R*)-H_2**L**^{9}	36	110	98	5	
9	**11a**	**11b**[e]	(*R*)-H_2**L**^{1}	120	110	50	55	

[a]Reactions run in C_6D_6 (25−70 °C), in C_7D_8 (110 °C). [b]Measured by ^{1}H NMR spectroscopy. [c]Determined by HPLC analysis of the product following derivatization (see Supporting Information). [d]Isolated yield. [e]Reaction performed with 12 mol % cat.

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intramolecular hydroamination of more challenging substrates. Indeed, the demanding cyclization of primary amines tethered to 1,2-disubstituted alkenes was efficiently performed at high temperatures with yttrium complexes bearing binaphthylamine ligands substituted on nitrogen atoms by benzyl-like groups. Among the series of tested ligands, the *N*-anthrylmethyl-binaphthylamine ligand (*R*)-H_2**L**^{9} afforded the most enantioselective catalyst at 110 °C for the hydroamination/cyclization of *gem*-dialkyl aminoalkenes **3a** and **4a** including a 1,2-dialkyl-substituted double bond. For the reaction of other phenyl-containing substrates **5a**−**7a**, the best asymmetric inductions were reached by using complexes prepared from N-para-substituted benzyl ligands (*R*)-H_2**L**^{3} or (*R*)-H_2**L**^{4}. An enantiomeric excess value of 77% was indeed disclosed as the highest value reported so far for the asymmetric intramolecular hydroamination of amine-tethered 1,2-disubstituted alkenes. We also unveiled here the first examples of catalytic asymmetric hydroamination of aminoalkenes bearing trisubstituted double bonds. Quaternary centers were so generated from the cyclization of amines tethered to 1,1,2-trisubstituted alkenes under harsher reaction conditions than the cyclization of the corresponding disubstituted alkenes, and with enantioselectivities of up to 55%.

These results demonstrate that these easily accessible heteroleptic binaphthylamido alkyl ate yttrium complexes containing *N*-benzyl-like substituents have the ability to catalytically induce the enantioselective intramolecular hydroamination of very sterically demanding substrates in a stable and stereodefined environment even under harsh reaction conditions. Studies are currently ongoing to further improve the reactivity, enantioselectivity, and substrate scope of these new complexes in the catalytic hydroamination reaction of challenging substrates.

EXPERIMENTAL SECTION

All manipulations were carried out under an argon atmosphere by using standard Schlenk or glovebox techniques. THF was distilled from sodium benzophenone ketyl, degassed by freeze−pump−thaw method, and stored over activated 4 Å molecular sieves. Benzene-d_6, toluene-d_8, and diethyl ether were dried with sodium benzophenone ketyl, transferred under vacuum, and stored over activated 4 Å molecular sieves. Toluene was dried over CaH_2 powder and distilled prior to use. *n*-BuLi (1.6 M in hexanes) was purchased and used as received. $LiCH_2SiMe_3$ (1 M in pentane), (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine, and crotyl chloride and cinnamyl bromide were purchased and used without any further purification. Solid $LiCH_2SiMe_3$ was obtained by cold recrystallization of a 1 M pentane solution of $LiCH_2SiMe_3$. Ligands (*R*)-H_2**L**^{019} and (*R*)-H_2**L**^{122} were prepared according to reported procedures. Substrates **1a**,[19] **2a**,[23] **6a**,[8c] **8a**, and **9a**[15f] were prepared as reported. Substrates **3a**,[19] **4a**,[24] and **5a**[25] were prepared following a reported procedure using crotyl chloride (*trans*:*cis* = 85:15) instead of crotyl bromide. All substrates were dried overnight on 4 Å molecular sieves with a few drops of benzene-d_6 or toluene-d_8 prior to use. Chemical shifts for ^{1}H and ^{13}C spectra were referenced internally according to the residual solvent resonances and reported relative to tetramethylsilane. Infrared spectra were recorded on a FT-IR spectrometer as Nujol mulls or as KBr disks and are reported in cm^{-1}. Optical rotations are reported as follows: $[\alpha]_D$ (*c* in g per 100 mL in solvent).

Synthesis of 2,2,5-Triphenyl-pent-4-enylamine 7a. To a solution of diisopropylamine (6.2 mL, 44 mmol) in THF (30 mL) was added *n*-BuLi (1.6 M in hexanes, 30 mL, 48 mmol) dropwise at −20 °C, and the reaction mixture was stirred at −20 °C for 2 h. A solution of diphenylacetonitrile (7.2 g, 37 mmol) in THF (15 mL) was added dropwise at −20 °C, and the reaction mixture was stirred for 3 additional hours. A solution of (*E*)-cinnamylbromide (8.6 g, 44 mmol) in THF (15 mL) was added dropwise at −20 °C and the reaction mixture was allowed to warm up to room temperature overnight. It was hydrolyzed with water (30 mL), and the aqueous phase was extracted with ether (3 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The crude product was not isolated but used in the following step without any purification. It was solubilized in ether (15 mL) and added dropwise to a suspension of $LiAlH_4$ (2 g, 56 mmol) in ether (50 mL) at 0 °C. The reaction mixture was allowed to warm up to room temperature for 3 h and then hydrolyzed with water until the formation of white hydroxide aluminum salts. The solid was separated from the mixture by filtration. The organic layer was dried ($MgSO_4$), filtered, and concentrated. The residue was distilled (225 °C, 0.1 mbar) to afford a colorless liquid (5.0 g, 43%). IR ν_{max} (cm^{-1}) 3378, 3054, 3022, 2933, 2891, 1595, 1577, 1493, 1444, 1429, 1155, 1032, 969; ^{1}H NMR (250 MHz, $CDCl_3$) δ_H (ppm) 7.35−7.12 (m, 15H), 6.42 (d, *J* = 15.8 Hz, 1H), 5.82−5.77 (m, 1H), 3.36 (s, 2H), 3.10 (d, *J* = 17.6 Hz, 2H), 0.93 (br s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ_C (ppm) 146.4, 137.7, 132.9, 128.6, 128.4, 128.3, 127.2, 126.7, 126.3, 126.2, 52.1, 48.9, 40.5; HRMS (ESI) *m*/*z* calcd for $C_{23}H_{24}N$ [M + H]$^+$ 314.1903. Found 314.1902.

Synthesis of 4-Methyl-2,2,5-triphenyl-pent-4-en-1-amine 10a. *trans*-α-Methyl-cinnamaldehyde (10 g, 9.5 mL, 68 mmol) was solubilized in ether (15 mL) and added dropwise to a suspension of $LiAlH_4$ (5.2 g, 137 mmol) in ether (50 mL) at 0 °C. The reaction mixture was allowed to warm up to room temperature for 3 h and then hydrolyzed with water until the formation of white hydroxide aluminum salts. The solid was separated from the mixture by filtration. The organic layer was dried ($MgSO_4$), filtered, and concentrated to afford a colorless liquid (10 g, 67 mmol, 99%). (*E*)-2-Methyl-3-phenylprop-2-en-1-ol (10 g, 67 mmol) was solubilized in Et_2O (15 mL) and added dropwise to a suspension of PBr_3 (8.2 mL, 87 mmol) in ethanol (30 mL) at 0 °C. The reaction mixture was allowed to warm up to room temperature overnight and then hydrolyzed with water and NH_4Cl saturated. The aqueous phase was extracted with ether (3 × 30 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated to afford a colorless liquid (11.2 g, 53 mmol, 79%). To a solution of diisopropylamine (5.9 mL, 42 mmol) in THF (30 mL), *n*-BuLi (1.6 M in hexanes, 28 mL, 45 mmol) was added dropwise at −20 °C, and the reaction mixture was stirred at −20 °C for 2 h. A solution of diphenylacetonitrile (6.7 g, 35 mmol) in THF (15 mL) was added dropwise at −20 °C, and the reaction mixture was stirred for 3 additional hours. A solution of (*E*)-(3-bromo-2-methylprop-1-en-1-yl)benzene (11.2 g, 53 mmol) in THF (15 mL) was added dropwise at −20 °C, and the reaction mixture was allowed to warm up to room temperature overnight. It was hydrolyzed with water (30 mL), and the aqueous phase was extracted with ether (3 × 30 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 (cyclohexane/ethyl acetate 75/25) to give a white crystalline solid. It was solubilized in ether (15 mL) and added dropwise to a suspension of $LiAlH_4$ (2.0 g, 52 mmol) in ether (50 mL) at 0 °C. The reaction mixture was allowed to warm up to room temperature for 3 h and then hydrolyzed with water until the formation of white hydroxide aluminum salts. The solid was separated from the mixture by filtration. The organic layer was dried ($MgSO_4$), filtered, and concentrated. The residue was distillated (250 °C, 0.2 mbar) to afford a colorless liquid (6.6 g, 20 mmol, 57%). IR ν_{max} (cm^{-1}) 3083, 3054, 3022, 2922, 2857, 1948, 1806, 1598, 1493, 1443; ^{1}H NMR (250 MHz, $CDCl_3$) δ_H (ppm) 7.33−7.10 (m, 15H), 6.17 (s, 1H), 3.47 (s, 2H), 3.08 (s, 2H) 1.23 (s, 3H), 0.87 (br s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ_C (ppm) 147.1, 136.1, 129.9, 129.0, 128.6, 128.15, 128.1, 126.2, 126.1, 52.3, 47.95, 47.1, 20.2; HRMS (ESI) *m*/*z* calcd for $C_{24}H_{26}N$ [M + H]$^+$ 328.2060. Found 328.2043.

Synthesis of 4-Methyl-2,2-diphenyl-hex-4-en-1-amine 11a. Tiglic aldehyde (5 g, 59 mmol) was solubilized in ether (15 mL) and added dropwise to a suspension of $LiAlH_4$ (4.5 g, 118 mmol) in ether (50 mL) at 0 °C. The reaction mixture was allowed to warm up to room temperature for 3 h and then hydrolyzed with water until the formation of white hydroxide aluminum salts. The solid was separated from the mixture by filtration. The organic layer was dried ($MgSO_4$),

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filtered, and concentrated to afford a colorless liquid (4.5 g, 52 mmol). The (*E*)-2-methylbut-2-en-1-ol (4.5 g, 52 mmol) was solubilized in Et_2O (15 mL) and added dropwise to a suspension of PBr_3 (6.4 mL, 68 mmol) in ethanol (30 mL) at 0 °C. The reaction mixture was allowed to warm up to room temperature overnight and then was hydrolyzed with water and saturated NH_4Cl. The aqueous phase was extracted with ether (3 × 30 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated to afford a colorless liquid (5.9 g, 39 mmol). To a solution of diisopropylamine (4.3 mL, 31 mmol) in THF (30 mL) was added dropwise at −20 °C *n*-BuLi (1.6 M in hexanes, 21 mL, 34 mmol), and the reaction mixture was stirred at −20 °C for 2 h. A solution of diphenylacetonitrile (5.0 g, 26 mmol) in THF (15 mL) was added dropwise at −20 °C, and the reaction mixture was stirred for 3 additional hours. A solution of (*E*)-1-bromo-2-methylbut-2-ene (5.9 g, 39 mmol) in THF (15 mL) was added dropwise at −20 °C, and the reaction mixture was allowed to warm up to room temperature overnight. It was hydrolyzed with water (30 mL), and the aqueous phase was extracted with ether (3 × 30 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 (cyclohexane/ethyl acetate, 75/25) to give a white crystalline solid. It was solubilized in ether (15 mL) and added dropwise to a suspension of $LiAlH_4$ (1.5 g, 39 mmol) in ether (50 mL) at 0 °C. The reaction mixture was allowed to warm up to room temperature for 3 h and then hydrolyzed with water until the formation of white hydroxide aluminum salts. The solid was separated from the mixture by filtration. The organic layer was dried ($MgSO_4$), filtered, and concentrated. The residue was distillated (250 °C, 0.3 mbar) to afford a colorless liquid (4.1 g, 15 mmol, 59%). IR ν_{max} (cm^{-1}) 3086, 3022, 2919, 2858, 1947, 1804, 1598, 1495, 1444, 1380; ^1H NMR (250 MHz, $CDCl_3$) δ_H (ppm) 7.32−7.18 (m, 10H), 5.29−5.24 (m, 1H), 3.43 (s, 2H), 2.96 (s, 2H), 1.58 (d, *J* = 6.4 Hz, 3H), 1.01 (s, 3H), 0.83 (br s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ_C (ppm) 147.06, 132.5, 128.2, 127.7, 125.7, 123.5, 51.3, 47.5, 45.7, 17.25, 13.5; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{24}N$ $[M + H]^+$ 266.1903. Found 266.1893.

General Procedure for the Synthesis of Ligands (*R*)-H_2L^2 to (*R*)-H_2L^9. To a solution of (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine (0.500 g, 1.8 × 10^{-3} mol) in dry toluene (5 mL) at ambient temperature and under argon were successively added activated 4 Å molecular sieves and the corresponding aldehyde (3.9 × 10^{-3} mol). The reaction mixture was next heated at 110 °C for 2−5 days. After cooling down to room temperature, the reaction mixture was filtered, and the solid residue was washed several times with dry toluene. The colored filtrate was concentrated under reduced pressure to afford the crude bis-imine product as an oily residue. To a stirred suspension of lithium aluminum hydride (0.205 g, 5.4 × 10^{-3} mol) in diethyl ether (20 mL) at 0 °C and under argon was dropwise added a suspension of the crude bis-imine product in diethyl ether (20 mL). The reaction mixture was next allowed to warm up to ambient temperature and stirred overnight at the same temperature. Distilled water was added to the reaction mixture at 0 °C until the excess of hydride was neutralized. A gas evolution and the formation of a white precipitate were observed. The latter was filtered off through a paper filter and the filtrate was washed three times with a saturated aqueous solution of sodium chloride. The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo to give a slightly colored solid.

(*R*)-*N*²,*N*²′-Bis(2-methoxybenzyl)-1,1′-binaphthyl-2,2′-diamine H_2L^2. Purification by flash chromatography (pentanes/ethyl acetate, 95/5) to give a pale-white solid (0.750 g, 79%); mp 142 °C; $[\alpha]_D^{25}$ +65.7 (*c* = 1.1, $CHCl_3$); IR ν_{max} (cm^{-1}) 3405, 3047, 2932, 2897, 2834, 1616, 1596, 1509, 1488, 1459, 1424, 1302, 1243, 1125, 1197, 1028; ^1H NMR (250 MHz, $CDCl_3$) δ_H (ppm) 7.80 (d, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 2H,), 7.25−7.23 (m, 2H), 7.14−7.03 (m, 8H), 6.85 (d, *J* = 8.3 Hz, 2H), 6.73−6.63 (m, 4H), 4.34 (s, 6H), 3.41 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ_C (ppm) 157.3, 144.9, 134.2, 129.5, 128.4, 128.1, 127.8, 127.7, 126.6, 124.2, 121.9, 120.2, 114.7, 112.7, 110.0, 54.8, 43.5; Anal. Calcd for $C_{36}H_{32}N_2O_2$: C, 82.41; H, 6.15; N, 5.34; O, 6.10. Found: C, 82.31; H, 6.27; N, 5.16; O, 5.97.

(*R*)-*N*²,*N*²′-Bis(4-methoxybenzyl)-1,1′-binaphthyl-2,2′-diamine H_2L^3. Purification by flash chromatography (pentanes/ethyl acetate, 70/30) to give a pale-white solid (0.800 g, 88%); mp 125 °C; $[\alpha]^{25}_D$ +59.2 (*c* = 1.1, $CHCl_3$); IR ν_{max} (cm^{-1}) 3411, 3050, 2929, 2833, 2366, 1615, 1596, 1504, 1424, 1337, 1300, 1246, 1173, 1150, 1101, 1033; ^1H NMR (250 MHz, $CDCl_3$) δ_H (ppm) 7.91−7.83 (m, 4H), 7.28 (d, *J* = 7.7 Hz, 6H), 7.18 (d, *J* = 7.7 Hz, 6H), 6.83 (d, *J* = 8.3 Hz, 4H), 4.38 (s, 6H), 3.79 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ_C (ppm) 158.7, 144.4, 133.9, 131.8, 129.7, 128.3, 128.1, 127.8, 126.8, 124.0, 122.1, 114.4, 113.9, 112.1, 55.3, 47.2; Anal. Calcd for $C_{36}H_{32}N_2O_2$: C, 82.41; H, 6.15; N, 5.34; O, 6.10. Found: C, 82.32; H, 6.11; N, 5.37; O, 6.19.

(*R*)-*N*²,*N*²′-Bis(4-chlorobenzyl)-1,1′-binaphthyl-2,2′-diamine H_2L^4. Purification by flash chromatography (pentanes/ethyl acetate, 70/30) to give a pale-white solid (0.850 g, 93%). mp 118 °C; $[\alpha]^{25}_D$ +9.5 (*c* = 1.1, $CHCl_3$); IR ν_{max} (cm^{-1}) 3420, 3054, 2920, 1616, 1597, 1510, 1504, 1422, 1336, 1291, 1150, 1090, 810; ^1H NMR (250 MHz, $CDCl_3$) δ_H (ppm) 7.95−7.87 (m, 4H), 7.37−7.14 (m, 16H), 4.46 (br s, 4H), 4.37 (br s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ_C (ppm) 144.0, 138.5, 133.9, 132.8, 129.9, 128.8, 128.4, 128.3, 128.0, 127.0, 124.0, 122.4, 114.2, 112.3, 47.1; Anal. Calcd for $C_{34}H_{26}N_2Cl_2$: C, 76.55; H, 4.91; N, 5.25. Found: C, 76.08; H, 4.89; N, 5.23.

(*R*)-*N*²,*N*²′-Bis(2,4,6-trimethylbenzyl)-1,1′-binaphthyl-2,2′-diamine H_2L^5. Purification by flash chromatography (hexanes/ethyl acetate, 95/5) to give a slightly yellow solid (0.453 g, 46%); mp 110 °C; $[\alpha]^{25}_D$ +30.9 (*c* = 1.1, $CHCl_3$); IR ν_{max} (cm^{-1}) 3403, 2914, 1618, 1510, 1477, 1421, 1346, 1294, 1149, 1021, 850, 806; ^1H NMR (360 MHz, $CDCl_3$) δ_H (ppm) 7.73 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.05−6.97 (m, 4H), 6.87 (d, *J* = 8.3 Hz, 2H), 6.56 (s, 4H), 4.17 (d, *J* = 11.2 Hz, 2H), 4.05 (d, *J* = 11.2 Hz, 2H), 3.30 (br s, 2H), 2.03 (s, 6H), 1.95 (s, 12H); ^{13}C NMR (90 MHz, $CDCl_3$) δ_C (ppm) 145.4, 137.6, 137.0, 134.0, 131.9, 129.9, 129.0, 128.2, 128.1, 126.7, 124.0, 122.1, 114.7, 112.7, 43.6, 21.0, 19.3; HRMS (ESI) *m*/*z* Calcd for $C_{40}H_{41}N_2$ $[M + H]^+$ 549.3270. Found 549.3273.

(*R*)-*N*²,*N*²′-Bis(naphthalen-1-ylmethyl)-1,1′-binaphthyl-2,2′-diamine H_2L^6. Purification by flash chromatography (pentanes/ethyl acetate, 90/10) to give a pale-white solid (0.75 g, 73%); mp 134 °C; $[\alpha]^{25}_D$ 3.85 (*c* = 1.1, $CHCl_3$); IR ν_{max} (cm^{-1}) 1738, 1615, 1508, 1424, 1337, 1304, 1246, 1150, 1005, 855; ^1H NMR (250 MHz, DMSO) δ_H (ppm) 8.01 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.81−7.73 (m, 6H), 7.53−7.41 (s, 6H), 7.28−7.13 (m, 8H), 6.9 (d, *J* = 8.1 Hz, 2H), 4.90−4.86 (s, 6H). Due to poor solubility, further characterization data could not be obtained.

(*R*)-*N*²,*N*²′-Bis(naphthalen-2-ylmethyl)-1,1′-binaphthyl-2,2′-diamine H_2L^7. Purification by flash chromatography (pentanes/ethyl acetate, 70/30) to give a pale-white solid (0.600 g, 62%); mp 225 °C; $[\alpha]^{25}_D$ 6.6 (*c* = 1.1, $CHCl_3$); IR ν_{max} (cm^{-1}) 3413, 3050, 2346, 1616, 1508, 1423, 1337, 1323, 1301, 1239, 1213, 1149, 1125, 1021; ^1H NMR (250 MHz, $CDCl_3$) δ_H (ppm) 7.82−7.61 (m, 12H), 7.41−7.15 (m, 14H), 4.55 (s, 4H), 4.49 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ_C (ppm) 144.4, 137.5, 134.1, 133.5, 132.8, 129.9, 128.4, 128.0, 127.9, 127.8, 127.0, 126.2, 125.7, 125.4, 125.3, 124.1, 122.3, 114.5, 112.3, 47.9; Anal. Calcd for $C_{42}H_{32}N_2$: C, 89.33; H, 5.71; N, 4.96. Found: C, 89.21; H, 5.79; N, 4.93.

(*R*)-*N*²,*N*²′-Bis(benzothiophen-2-ylmethyl)-1,1′-binaphthyl-2,2′-diamine H_2L^8. Purification by flash chromatography (pentanes/ethyl acetate, 80/20) to give a pale-white solid (0.67 g, 64%); mp 101 °C; $[\alpha]^{25}_D$ 92.6 (*c* = 1.1, $CHCl_3$); IR ν_{max} (cm^{-1}) 1618, 1595, 1424, 1295, 1019, 1019, 742; ^1H NMR (250 MHz, $CDCl_3$) δ_H (ppm) 7.88 (d, *J* = 7.8 Hz, 2H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 7.7 Hz, 2H,), 7.33−7.17 (m, 10H), 7.09−7.07 (m, 4H), 4.61 (s, 4H), 4.41 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ_C (ppm) 145.2, 143.8, 139.9, 139.5, 134.0, 130.0, 128.3, 128.2, 127.1, 124.3, 124.2, 124.0, 123.3, 122.6, 122.5, 120.8, 114.3, 112.6, 43.8; HRMS (ESI) *m*/*z* Calcd for $C_{38}H_{29}N_2S_2$ $[M + H]^+$ 577.1767. Found 577.1754.

Synthesis of Ligand (*R*)-*N*²,*N*²′-Bis(anthracen-9-ylmethyl)-1,1′-binaphthyl-2,2′-diamine H_2L^9. To a solution of (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine (0.500 g, 1.8 × 10^{-3} mol) in xylene (5 mL) was added anthracene-9-carbaldehyde (1.0 g, 5.1 × 10^{-3} mol) at ambient temperature and under argon. The homogeneous reaction

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mixture was equipped with a Dean−Stark apparatus and next heated at 169 °C for 6 days. After cooling down to room temperature, the reaction mixture was filtered, and the red-orange solid residue was washed several times with dry xylene and dried under reduced pressure. The dried red/orange solid residue was portionwise added to a stirred suspension of lithium aluminum hydride (0.500 g, 13.2 × 10^{-3} mol) in THF (50 mL) at 0 °C under argon . The reaction mixture was next allowed to warm up to ambient temperature and stirred overnight at the same temperature. The solvent was concentrated in vacuo, and dried diethyl ether was added (50 mL). Distilled water was added to the reaction mixture at 0 °C until the excess of hydride was neutralized. The target product was obtained as a yellow suspension in ether. This phase was recovered, and DCM was added to give rise to a yellow solution. The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo to give a slightly colored solid. Purification by flash chromatography (chloroform) gave a pale-yellow solid (1 g, 55%). mp 263 °C; $[\alpha]^{25}_{D}$ +78.5 (c = 0.4, $CHCl_3$); IR ν_{max} (cm^{-1}) 3054, 2361, 2342, 1617, 1509, 1472, 1420, 1291, 810, 728; ^{1}H NMR (250 MHz, $CDCl_3$) δ_H (ppm) 8.29 (s, 2H), 7.88 (dd, J = 4.0 Hz, J = 9.2 Hz, 8H), 7.81 (d, J = 8.7 Hz, 2H), 7.69−7.66 (m, 2H), 7.51 (d, J = 9.2 Hz), 7.35−7.29 (m, 6H), 7.19−7.09 (m, 8H), 5.18 (dd, J = 8.2 Hz, J = 11.7 Hz, 2H), 4.99 (dd, J = 4.7 Hz, J = 10.5 Hz, 2H), 3.92−3.84 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ_C (ppm) 146.1, 134.1, 131.5, 130.6, 130.0, 129.4, 129.0, 128.5, 128.4, 128.3, 127.8, 127.0, 126.3, 125.1, 124.3, 124.1, 122.5, 115.6, 42.6; HRMS (ESI) m/z Calcd for $C_{50}H_{37}N_2$ $[M+H]^+$ 664.2904. Found 664.2823.

In Situ Preparation of Yttrium Complex by Reaction between $[Li(THF)_4][Y(CH_2SiMe_3)_4]$ and (*R*)-H_2L^0. In a glovebox, to a solution of $[Li(THF)_4][Y(CH_2SiMe_3)_4]$ (31 mg, 0.042 × 10^{-3} mol) in C_6D_6 (2 mL) was portionwise added (*R*)-H_2L^0 (18 mg, 0.042 × 10^{-3} mol). As the ligand was slowly added, the clear, slightly yellow reaction mixture turned to a deeper yellow/orange-colored solution. The homogeneous reaction solution was then allowed to stir 10 min at ambient temperature and transferred to a screw-tap NMR tube for analysis. ^{1}H NMR (250 MHz, C_6D_6) δ_H (ppm) 7.72 (br s, 2H), 7.51 (br s, 2H), 7.42−7.39 (m, 2H), 6.89 (br s, 6H), 4.29 (br s, 2H), 3.33 (s, 16H), 2.51 (br s, 2H), 2.28 (br s, 2H), 1.60 (br s, 12H), 1.31 (s, 16H), 0.27 (s, 18H), 0.00 (s, TMS), − 0.96 (br s, 4H); ^{13}C NMR (62.5 MHz, C_6D_6) δ_C (ppm) 133.1, 131.7, 129.1, 127.9, 122.2, 119.4, 119.3, 68.5, 59.3, 36.0, 35.9, 25.8, 25.0, 24.3, 4.8, 0.4.

General Procedure for NMR-Scale Asymmetric Intramolecular Hydroamination/Cyclization of 1a−7a and 9a−10a. In a glovebox, to a solution of $[Li(THF)_4][Y(CH_2SiMe_3)_4]$ (31 mg, 0.042 × 10^{-3} mol) in C_6D_6 or C_7D_8 (2 mL) was portionwise added the corresponding ligand (*R*)-H_2L^n (0.042 × 10^{-3} mol) as a solid. As the ligand was slowly added, the clear, slightly yellow reaction mixture turned to a deeper yellow/orange-colored solution. The homogeneous reaction solution was then allowed to stir 10 min at ambient temperature, and a 670 μL-aliquot of the mixture was taken off by a micropipet and transferred to a vial containing the substrate (0.23 × 10^{-3} mol). The reaction mixture was then introduced into a screw-tap NMR tube or a J. Young-tap NMR tube and placed in an oil bath heated at the required temperature. The conversion of the reaction was monitored by comparative integration of the signal relative to the olefinic protons of the substrate and the signal relative to the protons of the product. After the appropriate time, the reaction was quenched by addition of a small amount of CH_2Cl_2.

General Procedure for NMR-Scale Asymmetric Intramolecular Hydroamination/Cyclization of 8a and 11a. In a glovebox, to a solution of $[Li(THF)_4][Y(CH_2SiMe_3)_4]$ (31 mg, 0.042 × 10^{-3} mol) in C_7D_8 (2 mL) was portionwise added the corresponding ligand (*R*)-H_2L^1 (0.042 × 10^{-3} mol) as a solid. As the ligand was slowly added, the clear, slightly yellow reaction mixture turned to a deeper yellow/orange-colored solution. The homogeneous reaction solution was then allowed to stir 10 min at ambient temperature and 1340 μL-aliquot of the mixture was taken off by a micropipet and transferred to a vial containing the substrate (0.23 × 10^{-3} mol). The reaction mixture was then introduced into a J. Young tap NMR tube and placed in an oil bath heated at 110 °C. The conversion of the reaction was monitored by comparative integration of the signal relative to the olefinic protons of the substrate and the signal relative to the protons of the product. After the appropriate time, the reaction was quenched by addition of a small amount of CH_2Cl_2.

NMR-Scale Asymmetric Intramolecular Hydroamination/Cyclization of 1a Catalyzed by Isolated Complexes A and B. In a glovebox, crystals of complexes **A** or **B** (0.042 × 10^{-3} mol) were dissolved in C_6D_6 (2 mL), and a 670 μL-aliquot of the corresponding homogeneous solution was taken off by a micropipet and transferred to a vial containing **1a** (0.23 × 10^{-3} mol). The reaction mixture was then introduced into a screw-tap NMR tube. The conversion of the reaction was monitored by comparative integration of the signal relative to the olefinic protons of the substrate and the signal relative to the protons of the product. After the appropriate time, the reaction was quenched by addition of a small amount of CH_2Cl_2.

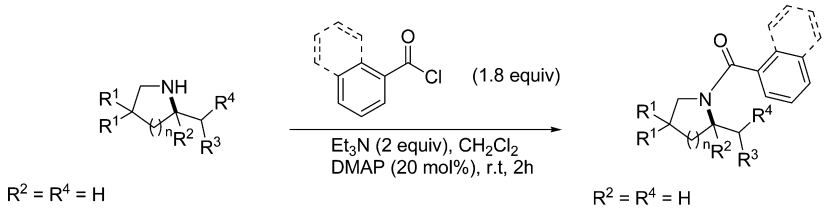
Procedures for Preparative-Scale Asymmetric Intramolecular Hydroamination/Cyclization: C-(1-But-2-enyl-cyclohexyl)-methylamine 3a to 3b. In the glovebox, (*R*)-H_2L^9 (28 mg, 0.042 × 10^{-3} mol) was added to a solution of $[Li(THF)_4][Y(CH_2SiMe_3)_4]$ (31 mg, 0.042 × 10^{-3} mol) in toluene (2 mL). The precatalyst (201 μmol) in toluene and **3a** (115.5 mg, 0.69 mmol) were loaded into a storage tube equipped with a magnetic stir bar and J. Young valve. The valve was then closed and the clear solution stirred for 36 h at 110 °C. The reaction was stopped with dichloromethane, and the residue was distilled (70 °C, 0.4 mbar) to afford a colorless liquid (50 mg, 50%). $[\alpha]^{25}_{D}$ +10.0 (c = 1.1, $CHCl_3$) for ee = 68%; IR ν_{max} (cm^{-1}) 2926, 2854, 1623, 1450; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm) 2.97−2.87 (m, 1H), 2.76 (d, J = 10.8 Hz, 1H), 2.61 (d, J = 10.8 Hz, 1H), 1.78−1.70 (m, 2H), 1.50−1.20 (m, 11H), 1.19−1.08 (m, 1H), 1.02−0.95 (m, 1H), 0.89 (t, J = 8.0 Hz, 3H); ^{13}C NMR (90 MHz, $CDCl_3$) δ_C (ppm) 60.8, 45.2, 38.7, 37.2, 29.9, 26.4, 24.1, 23.9, 11.9; HRMS (ESI) m/z Calcd for $C_{11}H_{21}N$ $[M^+]$ 167.1669. Found: 167.1671.

2,2-Diphenyl-hex-4-enylamine 5a to 5b. In the glovebox, (*R*)-H_2L^3 (22 mg, 0.042 × 10^{-3} mol) was added to a solution of $[Li(THF)_4][Y(CH_2SiMe_3)_4]$ (31 mg, 0.042 × 10^{-3} mol) in toluene (2 mL). The precatalyst (134 μmol in toluene) and **5a** (116.5 mg; 0.46 mmol) were loaded into a storage tube equipped with a magnetic stir bar and J. Young valve. The valve was then closed and the clear solution stirred for 19 h at 70 °C. The reaction mixture was stopped with dichloromethane and the residue was distilled (240 °C, 0.4 mbar) to afford a colorless liquid (94 mg, 80%). $[\alpha]^{25}_{D}$ +2.58 (c = 1.1, $CHCl_3$) for ee =75%; IR ν_{max} (cm^{-1}) 2918, 2877, 2710, 2553, 1601, 1493, 1456, 1380; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm) 7.34−7.09 (m, 10H), 3.67 (d, J = 11.1 Hz, 1H), 3.40 (d, J = 11.1 Hz, 1H), 3.17−3.08 (m, 1H), 2.73 (dd, J = 7.5 Hz, J = 14.2 Hz, 1H), 1.99 (dd, J = 9.1 Hz, J = 12.7 Hz, 1H), 1.73 (br s, 1H), 1.56−1.41 (m, 2H), 0.91 (t, J = 7.1 Hz, 3H); ^{13}C NMR (90 MHz, $CDCl_3$) δ_C (ppm) 148.0, 147.2, 128.6, 128.5, 127.3, 127.2, 126.2, 59.7, 57.9, 57.0, 45.2, 30.4; HRMS (ESI) m/z Calcd for $C_{18}H_{22}N$ $[M+H^+]$ 252.1747. Found: 252.1746.

2,2,5-Triphenyl-pent-4-enylamine 7a to 7b. In the glovebox, (*R*)-H_2L^1 (20 mg, 0.042 × 10^{-3} mol) was added to a solution of $[Li(THF)_4][Y(CH_2SiMe_3)_4]$ (31 mg, 0.042·10^{-3} mol) in toluene (2 mL). The precatalyst (134 μmol) in toluene and **7a** (151.5 mg; 0.46 mmol) were loaded into a storage tube equipped with a magnetic stir bar and J. Young valve. The valve was then closed and the clear solution stirred for 24 h at 50 °C. The reaction mixture was stopped with dichloromethane, and the residue was distilled (250 °C, 0.3 mbar) to afford a colorless liquid (120 mg, 83%). $[\alpha]^{25}_{D}$ +16.6 (c = 1.1, $CHCl_3$) for ee = 53%; IR ν_{max} (cm^{-1}) 3084, 3025, 2923, 2868, 1947, 1736, 1599, 1493, 1446, 1261, 1217, 1093, 1029, 753, 700; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm) δ 7.24−7.18 (m, 15H), 3.74 (d, J = 11.1 Hz, 1H), 3.61−3.48 (m, 1H), 3.52 (d, J = 11.1 Hz, 1H), 2.91 (dd, J = 6.9 Hz, J = 13.0 Hz, 1H), 2.78−2.70 (m, 2H), 2.21 (dd, J = 9.4 Hz, J = 12.8 Hz, 1H), 1.65 (br s, 1H); ^{13}C NMR (90 MHz, $CDCl_3$) δ_C (ppm) 147.9, 147.0, 140.1, 129.3, 128.6, 128.5, 128.2, 127.3, 127.1, 126.3, 126.2, 59.3, 57.9, 57.1, 45.1, 43.8; 11.8; HRMS (ESI) m/z Calcd for $C_{23}H_{23}N$ $[M^+]$: 313.1903. Found: 313.1896.

2-Benzyl-2-methyl-4,4-diphenylpyrrolidine 10a to 10b. In the glovebox, (*R*)-H_2L^1 (20 mg, 0.042 × 10^{-3} mol) was added to a solution of $[Li(THF)_4][Y(CH_2SiMe_3)_4]$ (31 mg, 0.042 × 10^{-3} mol) in

Scheme 4. Derivatization Procedure for the Determination of Enantiomeric Excess Values



$R^2 = R^4 = H$

1b, n = 1, R^1 = -$(CH_2)_5$-, R^3 = H
2b, n = 2, R^1 = -$(CH_2)_5$-, R^3 = H
3b, n = 1, R^1 =-$(CH_2)_5$-, R^3 = CH_3
4b, n = 1, R^1 = CH_3, R^3 = CH_3
5b, n = 1, R^1 = C_6H_5, R^3 = CH_3
6b, n = 1, R^1 = CH_3, R^3 = C_6H_5
7b, n = 1, R^1 = C_6H_5, R^3 = C_6H_5

$R^2 = H$

8b, n = 1, R^1 = C_6H_5, R^3 = R^4 = CH_3

$R^2 = CH_3$; $R^4 = H$

10b, n = 1, R^1 = C_6H_5, R^3 = C_6H_5
11b, n = 1, R^1 = C_6H_5, R^3 = CH_3

$R^2 = R^4 = H$

1c, n = 1, R^1 = -$(CH_2)_5$-, R^3 = H
2c, n = 2, R^1 = -$(CH_2)_5$-, R^3 = H
3c, n = 1, R^1 =-$(CH_2)_5$-, R^3 = CH_3
4c, n = 1, R^1 = CH_3, R^3 = CH_3
5c, n = 1, R^1 = C_6H_5, R^3 = CH_3
6c, n = 1, R^1 = CH_3, R^3 = C_6H_5
7c, n = 1, R^1 = C_6H_5, R^3 = C_6H_5

$R^2 = H$

8c, n = 1, R^1 = C_6H_5, R^3 = R^4 = CH_3

$R^2 = CH_3$; $R^4 = H$

10c, n = 1, R^1 = C_6H_5, R^3 = C_6H_5
11c, n = 1, R^1 = C_6H_5, R^3 = CH_3

toluene (2 mL). The precatalyst (67 μmol) in toluene and **10a** (75.3 mg; 0.23 mmol) were loaded into a storage tube equipped with a magnetic stir bar and J. Young valve. The valve was then closed and the clear solution stirred for 19 h at 70 °C. The reaction mixture was stopped with dichloromethane, and the residue was distilled (250 °C, 0.4 mbar) to afford a colorless liquid (50 mg, 66%). $[\alpha]^{25}_D$ +2.3 (c = 1.1, $CHCl_3$) for ee = 49%; IR ν_{max} (cm^{-1}) 3058, 3025, 2963, 2923, 1948, 1805, 1598, 1493, 1446; ^{1}H NMR (360 MHz, $CDCl_3$) δ_H (ppm) 7.47−7.12 (m, 15H), 3.75 (d, J = 11.7 Hz, 1H), 3.63 (d, J = 11.7 Hz, 1H), 2.77−2.63 (m, 3H), 2.50 (d, J = 12.3 Hz, 1H), 1.75 (br s, 1H), 1.08 (s, 3H); ^{13}C NMR (90 MHz, $CDCl_3$) δ_C (ppm) 148.0, 147.6, 138.7, 130.5, 128.4, 128.0, 127.0, 126.2, 125.9, 62.5, 57.5, 57.0, 50.6, 49.0; HRMS (ESI) m/z Calcd for $C_{24}H_{25}N$ [M + H^+]: 328.2060. Found: 328.2065.

Determination of the Enantiomeric Excess Values. The enantiomeric excess values were determined by HPLC analysis of the derivatized product using a (*S*,*S*)-Whelk-O1 column (EtOH/hexane 25/75; 0.9 mL·min^{-1}, λ 254 nm (**1c**, **2c**, **3c**−**5c**, **7c**) or iPrOH/hexane 25/75; 0.7 mL.min^{-1}, λ 254 nm (**6c**, **8c**, **10c**, **11c**): **Typical procedure of derivatization:** To a solution of the corresponding cyclized product (1 equiv.) in CH_2Cl_2 (4 mL) was added dimethylaminopyridine (0.2 equiv), triethylamine (2 equiv) and 1-naphtoyl chloride (1.8 equiv) (for **1b**, **2b**, **3b**, **4b**) or 2-benzoyl chloride (1.8 equiv) (for **5b**−**8b**, **10b**−**11b**) at ambient temperature. After stirring for 2 h, a saturated aqueous solution of ammonium chloride (4 mL) was poured into the reaction mixture, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were then washed with a saturated aqueous solution of ammonium chloride (5 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo. The crude product was purified by preparative TLC plate (silica gel) (EtOAc/pentane, 25/75) (Scheme 4).

1-Benzoyl-4,4-diphenyl-2(propan-2-yl)pyrrolidine 8c: IR ν_{max} (cm^{-1}) 665, 700, 754, 1074, 1301, 1402, 1487, 1519, 1645, 2922; ^{1}H NMR (250 MHz, $CDCl_3$) δ_H (ppm) 7.50−7.07 (m, 15H), 4.10 (d, J = 5.8 Hz, 1H), 3.88 (s, 1H), 2.85 (d, J = 7.3 Hz, 1H), 2.45−2.42 (m, 1H), 1.70−1.66 (m, 1H), 1.56 (s, 1H), 1.53 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ_C (ppm) 26.4, 31.4, 36.6, 37.6, 47.0, 53.5, 56.1, 126.4, 126.7, 126.8, 127.5, 128.4, 128.5, 128.7, 129.0, 131.5, 146.9; HRMS (ESI) m/z Calcd for $C_{26}H_{28}NO$ [M + H^+]: 370.2152. Found: 370.2135.

1-Benzoyl-2-ethyl-2-methyl-4,4-diphenylpyrrolidine 11c: IR ν_{max} (cm^{-1}) 550, 640, 765, 933, 1150, 1420, 2963, 3061; ^{1}H NMR (250 MHz, $CDCl_3$) δ_H (ppm) 7.08−7.48 (m, 15H), 4.31 (d, J = 12.4 Hz, 1H), 3.73 (d, J = 12.4 Hz, 1H), 2.93 (d, J = 12.4 Hz, 1H), 2.52 (d, J = 12.4 Hz, 1H), 1.93−2.05 (m, 2H), 1.19 (s, 3H), 1.00 (t, J = 7.6 Hz 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ_C (ppm) 146.3, 145.3, 139.3, 129.5, 128.7, 126.9, 126.7, 126.6, 126.2, 65.8, 60.4, 51.9, 49.4, 31.8, 29.9, 24.9; HRMS (ESI) m/z Calcd for $C_{26}H_{28}NO$ [M + H^+]: 370.2152. Found: 370.2165.

Retention Times of Derivatized Products. Retention times were compared to racemic standard samples prepared by hydroamination reaction with the racemic ligand H_2L^1 (prepared from a similar procedure as (*R*)-H_2L^1), followed by a derivatization reaction as mentioned above (Table 5).

Table 5. HPLC Retention Times

		retention time	
entry	cmpd	t_1 (major) min	t_2 (minor) min
1	**1c**	6.8	18.7
2	**2c**	6.4	16.9
3	**3c**	6.6	18.1
4	**4c**	6.5	15.5
5	**5c**	6.7	5.9
6	**6c**	17.6	46.4
7	**7c**	6.6	7.5
8	**8c**	16.3	32.2
9	**10c**	42.0	28.0
11	**11c**	52.7	23.7

Determination of the Absolute Configuration for 5b and 10b. The absolute (*S*) configuration of compound **5b** was attributed following a reported procedure.[26] **5b** was derivatized with (*R*)-Mosher chloride and corresponding diastereomers could be visualized by ^{1}H NMR spectroscopy. The ratio between both diastereomers corresponded to the HPLC-measured ee value (75%) and the major isomer was attributed the (*S*) configuration by comparison. **10b** was derivatized with (*R*)-Mosher chloride and the corresponding diastereomers (*R*,*S*)-**10b** and (*R*,*R*)-**10b** could be visualized by ^{1}H NMR spectroscopy. The ratio between both diastereomers corresponded to the HPLC-measured ee value (49%). The major isomer **I** (Figure S1, SI) was recrystallized in methanol at room temperature and characterized by X-ray structure and was attributed the (*S*) configuration.

■ ASSOCIATED CONTENT

Supporting Information

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HPLC chromatogram of **3c**−**8c** and **10c**−**11c**; ^{1}H NMR spectra of (*R*)-H_2**L**^{6}; ^{1}H and ^{13}C NMR spectra of (*R*)-H_2**L**$^{2-5}$, (*R*)-H_2**L**$^{7-9}$, and **10a**, **11a**, **10b**, and **11c**, **8c**; ORTEP diagram of I and B. This material is available free of charge via the Internet at http://pubs.acs.org.

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