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C_1-Symmetric Rare-Earth-Metal Aminodiolate Complexes for Intra- and Intermolecular Asymmetric Hydroamination of Alkenes

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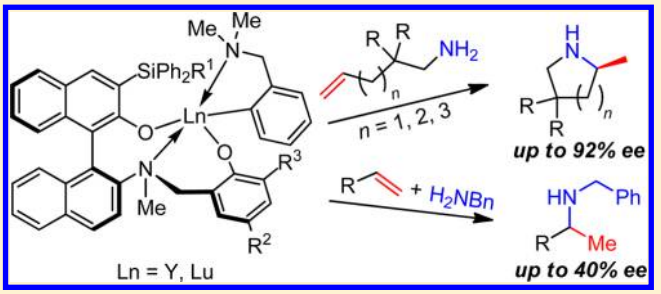
Supporting Information

ABSTRACT: A series of novel C_1-symmetric aminodiolate rare-earth-metal complexes have been prepared via arene elimination from $[Ln(o\text{-}C_6H_4CH_2NMe_2)_3]$ (Ln = Y, Lu) and the corresponding aminodiol proligand. The NOBIN-derived aminodiolate ligands feature sterically demanding triphenylsilyl and methyldiphenylsilyl ortho substituents on the naphtholate moiety and substituents of varying steric demand ranging from *tert*-butyl to tris(3,5-xylyl)silyl on the phenolate moiety. Complexes with a triphenylsilyl substituent on the naphtholate moiety displayed good catalytic activity in the hydroamination/cyclization of aminoalkenes, while complexes with a methyldiphenylsilyl substituent exhibited somewhat lower reactivity. The highest enantioselectivities for five- and six-membered-ring formation were observed utilizing complex **9c-Lu** (R^1 = Ph, R^2 = Me, R^3 = $SiPh_3$) in the cyclization of (2,2-diphenylpent-4-enyl)amine (92% ee, N_t = 200 h^{-1} at 25 °C) and (2,2-diphenylhex-5-enyl)amine (73% ee, N_t = 20 h^{-1} at 25 °C). The complexes can be applied in asymmetric intermolecular hydroaminations of 1-heptene and 4-phenyl-1-butene with benzylamine with enantioselectivities of up to 40% ee using complex **9b-Y** (R^1 = Ph, R^2 = Me, R^3 = $SiPh_2Me$). Here the higher catalytic activities are achieved with catalysts having a methyldiphenylsilyl substituent on the naphtholate moiety. Lanthanum aminodiolate catalysts generated in situ from $[La\{CH(C_6H_5)NMe_2\}_3]$ did not exhibit improved catalytic activity in the intermolecular hydroamination in comparison to the corresponding yttrium and lutetium catalysts. The overall catalytic activities of the aminodiolate complexes are somewhat diminished in comparison to previously studied binaphtholate complexes due to the presence of the additional amine donor site in the ligand framework.



INTRODUCTION

The development of efficient synthetic protocols for the synthesis of nitrogen-containing molecules is an area of intense research, thanks to their importance as bulk chemicals, specialty chemicals, and pharmaceuticals.[1] The hydroamination reaction offers a waste-free, highly atom efficient, and green pathway to produce amines, enamines, and imines via the catalyzed addition of amines to unsaturated carbon−carbon bonds.[2−6] Most alkene hydroamination studies have focused on the intramolecular reaction, while studies of the intermolecular process are relatively scarce. The intermolecular hydroamination of activated alkenes, such as vinyl arenes, norbornene derivatives, conjugated dienes, and allenes, is significantly more facile[7,8] than the addition of amines to simple, unactivated alkenes.[9,10]

The generation of new stereogenic centers during the C−N bond forming process has been an area of particular interest, but the development of chiral catalysts for the asymmetric hydroamination of alkenes (AHA) has remained quite challenging,[8,10−14] especially for intermolecular reactions.[8,10]

Rare-earth-metal complexes are among the most active hydroamination catalysts for a broad spectrum of hydroamination substrates, including alkenes, alkynes, conjugated dienes, and allenes.[2,3a,b] A variety of chiral rare-earth-metal catalysts for asymmetric intramolecular hydroamination reactions have been developed,[12,13] but only a few of these catalysts achieve enantioselectivities exceeding 90% ee.[12r,u,13d] Our group has previously studied rare-earth-metal binaphtholate complexes **I-Ln** (Chart 1), which are among the most active and most stereoselective catalysts for hydroamination/cyclization of aminoalkenes.[13b,d] These catalysts have also been successfully applied in the kinetic resolution of racemic aminoalkenes,[13b,d,e] and they have remained so far the only catalysts to achieve stereocontrolled intermolecular hydroaminations of unactivated alkenes with simple amines.[10b] Although the latter transformation catalyzed by **I-Ln** shows the general feasibility of the approach itself, it still requires rather forcing reaction conditions and suffers from moderate selectivity and a need to employ a large (10−15-fold) excess of alkene. It may be envisioned that at least some of these drawbacks result from the high Lewis acidity of the electron-deficient binaphtholate complex **I-Ln** that leads to a stronger binding of exogenous amine molecules to the metal center and coincidental diminished catalytic activity.

The diamino bis(thiophenolate) complexes **II** reported by Livinghouse and co-workers achieved high enantioselectivities

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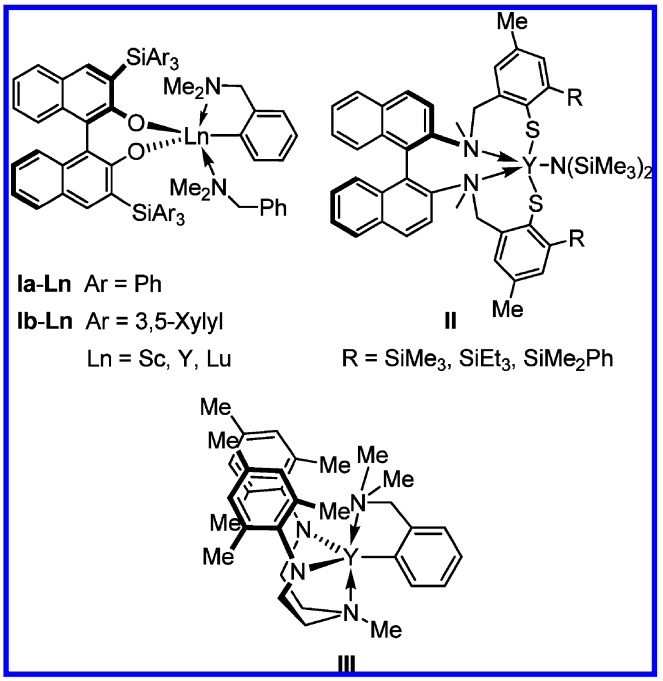
Chart 1. Rare-Earth-Metal Hydroamination Catalysts with X_2 (I), L_2X_2 (II), and LX_2 Type Ligands (III)



(up to 89% ee) for a broad range of aminoalkene substrates.[12g] Unfortunately, these catalysts exhibit diminished catalytic activity in comparison to complexes **I** and require prolonged reaction times at ambient temperatures. Thus, it appears that the reduced reactivity of complexes **II** results from an electronic oversaturation of the metal center by the L_2X_2-type diamino bis(thiophenolate) ligands in comparison to the X_2-type binaphtholate ligands in **I**. Previous studies in our group have shown that complexes containing (achiral) tridentate diamido-amine ligands exhibit excellent catalytic activity at ambient temperature,[15] which suggests that spectator ligands of the general LX_2 type provide an electronic environment favorable for catalytic hydroamination. We therefore envisioned that a catalyst system incorporating a chiral LX_2 type ligand should possess good catalytic activity, while the larger bite angle of the ligand should provide an opportunity for improved control of stereoselectivity.

Herein we present our studies on the synthesis of novel chiral C_1-symmetric rare-earth-metal aminodiolate complexes and their application in asymmetric intra- and intermolecular hydroaminations of unactivated alkenes with simple amines.

RESULTS AND DISCUSSION

Ligand Design and Preparation. As the potential model system, we chose the chiral C_1-symmetric NOBIN-derived aminodiolate complexes **IV** (Figure 1).[16,17] On the basis of previous experience, we decided to incorporate sterically demanding substituents in the ortho position of the aryloxide groups in order to prevent catalyst aggregation,[13a,c,17] increase catalytic activity,[13d] and improve stereoselectivity.[13d] Thus, the ability to easily tune the ortho substituents R^1 and R^3 is important to adapt the catalyst design successfully.

The silylated NOBIN derivatives **4a,b** were chosen as key precursors for the diol proligand preparation. **4a,b** were synthesized from the *O,N*-bis-protected NOBIN derivative **1** according to Scheme 1 in six steps, several of which can be

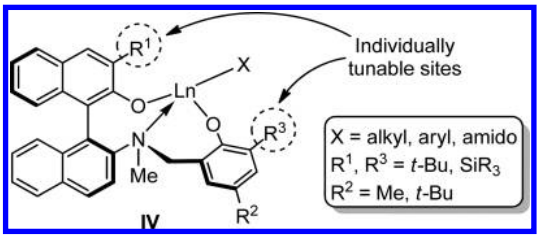


Figure 1. Generic design for NOBIN-derived rare-earth-metal aminodiolate complexes.

performed in a single pot and do not require product isolation. The well-documented literature procedure for the multigram-scale preparation of compound **1**[18] starting from BINOL in 88% yield over four steps represents one of the most concise routes to chiral NOBIN ligands.[19] Removal of the MOM group from **3a,b** required protection of the amino group, which was otherwise hampering the acid-catalyzed hydrolysis of the acetal under conditions compatible with acid-sensitive silyl groups. Subsequently, the trifluoroacetyl group was easily removed with $NaBH_4$ to give the silylated NOBIN derivatives **4a,b**.

The amino alcohols **4** can be condensed with variously substituted salicylaldehydes **5**[20] utilizing typical salen coupling methodology. The resulting Schiff bases were subsequently reduced to the salan-type aminodiols **6** with lithium aluminum hydride. The attempted reductive amination of amines **6** with formaldehyde led to an unexpected result, as a redox-neutral cyclization to the cyclic aminals **7** proceeded cleanly instead of formation of the anticipated *N*-methyl derivative **8**. However, the latter were obtained via reduction of the somewhat air-sensitive aminals **7** with lithium aluminum hydride. Attempts to introduce larger alkyl substituents on nitrogen via reductive amination of other aldehydes, e.g. benzaldehyde, have been plagued by low yields and were not explored further.

A number of NOBIN-based aminodiol proligands **8**, such as the 3-triphenylsilyl-substituted **8a–f** and the 3-methyldiphenylsilyl-substituted **8g–h**, were obtained using this methodology.

Complex Synthesis. With the aminodiol proligands **8a–h** in hand, we proceeded with the synthesis of the corresponding yttrium and lutetium aminodiolate complexes using the well-known tris(aryl) rare-earth-metal precursors $[Ln(o\text{-}C_6H_4CH_2NMe_2)_3]$ (Ln = Y, Lu)[21] (Scheme 2).

The arene elimination proceeded smoothly at room temperature or slightly elevated temperature. The yttrium complexes **9-Y** were obtained for the whole family of proligands **8a–h**, while lutetium complexes were only prepared from **8a,c–f**. Although the reactions proceeded cleanly by NMR spectroscopy (see the Supporting Information), removal of traces of free *N,N*-dimethylbenzylamine proved to be difficult in preparative-scale reactions.[22] Therefore, the catalysts were generally prepared *in situ* or stored as a frozen stock solution in C_6D_6 at −30 °C and were then used directly in catalytic reactions without isolation. Complexes **9-Ln** did not show any noticeable decomposition after heating to 150 °C for 1 h in solution, but the isolated solid catalysts were found to decompose above 60 °C.

The ^1H and ^{13}C NMR spectra of complexes **9a–h** reflect their highly unsymmetric structure, giving rise to the maximum number of possible signals. Both methylene protons of the ortho-metalated *N,N*-dimethylbenzylamine ligand as well as both *N*-methyl groups are diastereotopic, indicating tight binding of the amino group on the NMR time scale. The ^1H NMR spectra of the complexes display broad features at room temperature, which may be caused by hindered rotation of the sterically demanding

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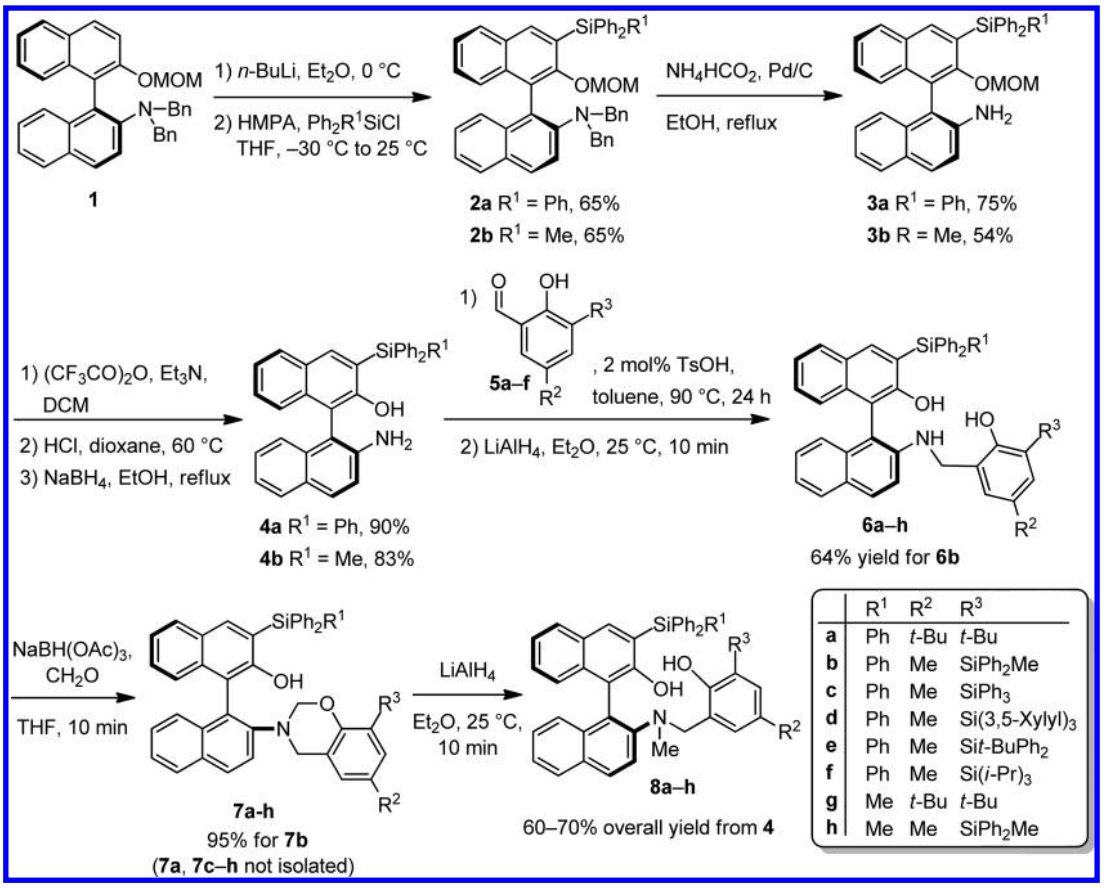
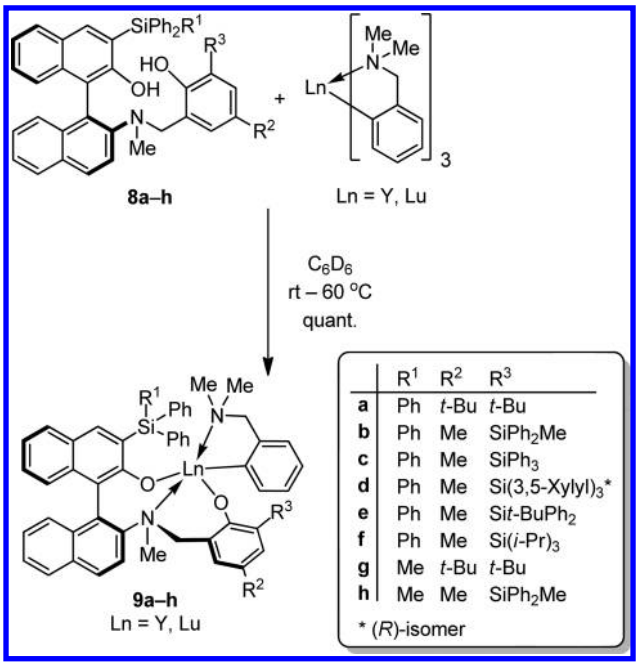
Scheme 1. Synthesis of NOBIN-Derived Aminodiol Proligands 8a–h



Scheme 2. Preparation of Rare-Earth-Metal Aminodiolates 9



ortho substituents on the phenolate and naphtholate moieties. The aminodiolate complexes **9a–h** do not retain a coordinated molecule of *N*,*N*-dimethylbenzylamine—in contrast to binaphtholate complexes **Ia,b**—according to their ^{1}H and ^{13}C NMR spectra. This observation is indicative of the reduced Lewis acidity of **9a–h** in comparison to **Ia,b** as well as increased steric protection from the tridentate ligand framework. Another important observation was the steric versatility of the diolate complexes accessible via the arene elimination route depicted in Scheme 2. The steric demand ranges from the highly hindered complexes **9c–e** to the sterically significantly less hindered complex **9g-Y**, which features a methyldiphenylsilyl and a *tert*-butyl substituent. This should be compared to *tert*-butyl-substituted biphenolate complexes that form dimeric species[13a,c] and thermally unstable methyldiphenylsilyl-substituted binaphtholate arene complexes.[23] This broader scope in tolerated ortho substituents can presumably be attributed to the increased ligand denticity and bite angle of the NOBIN-derived aminodiolate ligands **8** in comparison to the binaphtholate ligands in complexes **I**.

While a monomeric structure of the aminodiolate complexes **9** could not be proven unambiguously in the absence of crystallographic structure analysis, there is ample evidence to suggest that the complexes are indeed monomeric, as shown in Scheme 2. The complexes exhibit good solubility in aromatic solvents, whereas dimeric binaphtholate complexes tend to have low solubility.[13a,c] The yttrium complexes exhibit a clean doublet signal in the ^{13}C{^{1}H} NMR spectrum for the ipso carbon of the ortho-metalated *N*,*N*-dimethylbenzylamine ligand, and no evidence of a coupling to a second yttrium is discernible. There is also no NMR spectroscopic evidence to support the presence of a second species (e.g., from a monomer/dimer equilibrium) similar to previously studied biphenolate complexes.[13a,c] The lack of binding of free *N*,*N*-dimethylbenzylamine underlines the increased steric hindrance and electronic donation from the aminodiolate ligands to the metal, in comparison to

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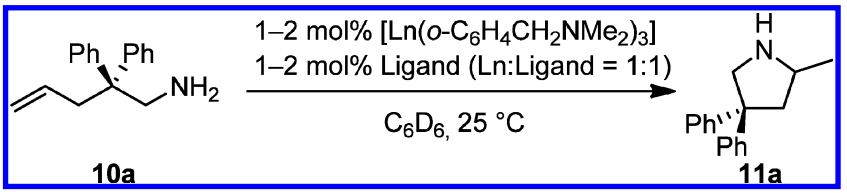
Table 1. Catalyst Evaluation of Aminodiolate Complexes in the Hydroamination/Cyclization of 10a



entry	Ln[a]	ligand[a]	cat./sub, mol %	t, min[b]	N_t, h^{-1} [c]	% ee[d] (confign)
1	Y	(*S*)-**8a**	1	30	200	17 (*S*)
2	Lu	(*S*)-**8a**	2	30	100	48 (*S*)
3	Y	(*S*)-**8b**	2	15	230	6 (*S*)
4	Y	(*S*)-**8c**	2.2	6	400	27 (*S*)
5	Lu	(*S*)-**8c**	1.4	15	200	92 (*S*)[e]
6	Sc	(*S*)-**8c**	2	60	50	5 (*S*)
7	Y	(*R*)-**8d**	2	20	150	8 (*R*)
8	Lu	(*R*)-**8d**	1	40	150	4 (*R*)
9	Y	(*S*)-**8e**	2	15	200	48 (*S*)
10	Lu	(*S*)-**8e**	2	30	100	77 (*S*)
11	Y	(*S*)-**8f**	1	15	400	51 (*S*)
12	Lu	(*S*)-**8f**	1	45	130	68 (*S*)
13	Y	(*S*)-**8g**	2	60	50	48 (*R*)
14	Y	(*S*)-**8h**	2	75	40	13 (*S*)

[a]The precatalysts were prepared in situ via reaction of a 1:1 mixture of [Ln(*o*-$C_6H_4CH_2NMe_2)_3$] (Ln = Sc, Y, Lu)[21] and ligand **8a–h** in C_6D_6. The complete conversion to the desired complex was confirmed by NMR spectroscopy. [b]Time for >95% conversion. [c]Overall turnover frequency. [d]Determined by ^{19}F NMR spectroscopy of the corresponding Mosher amide. [e]Determined by chiral HPLC of the corresponding *N*-benzamide.

complexes containing 3,3′-silyl-substituted binaphtholate ligands, which are known to form monomeric species.[13d]

Catalytic Intramolecular Hydroamination. For the initial evaluation of the catalytic activity of complexes **9a–h**, formed in situ from [Ln(*o*-$C_6H_4CH_2NMe_2)_3$] (Ln = Sc, Y, Lu)[21] and the corresponding aminodiol proligand **8a–h**, we chose the aminopentene substrate **10a**. Catalysts derived from the triphenylsilyl-substituted ligands **8a–f** showed high turnover frequencies for the cyclization of aminopentene **10a** (Table 1, entries 1–12). The activity is on the same order of magnitude as observed for **I-Ln**.[13d] The silyl substituent on the phenolate moiety does not significantly influence the catalytic efficiency, and the yttrium and lutetium catalysts reached turnover frequencies in the range of 100–400 h^{-1} at room temperature. We were also able to investigate a scandium catalyst derived from ligand **8c** which exhibited a somewhat lower turnover frequency of 50 h^{-1} (Table 1, entry 6). However, the sterically less encumbered yttrium catalysts derived from the methyldiphenylsilyl-substituted ligands **8g,h** displayed a somewhat lower reactivity (Table 1, entries 13 and 14).

The stereoselectivity of the hydroamination/cyclization has a nonlinear dependence of the steric bulk of the substituent on the phenolate moiety of the complex. A moderate stereoselectivity is observed for the yttrium catalyst containing the *tert*-butyl-substituted ligand **8a** (Table 1, entry 1); however, the slightly bulkier methyldiphenylsilyl-substituted ligand **8b** was less selective, while the more encumbered yttrium complexes derived from **8c,e** resulted in slightly higher selectivities. The lutetium complexes exhibited in general a higher selectivity than the corresponding yttrium congeners, which is in agreement with previous findings for binaphtholate complexes **Ia,b** that generally showed lower selectivities for larger rare-earth metals.[13d] However, this trend does not hold true for the smaller scandium catalyst, which provided almost racemic products (Table 1, entry 6). It seems very likely that the larger bite angle of the aminodiolate ligand in comparison to the binaphtholate ligands used in complexes **Ia,b** results in a steric overcrowding around the smallest rare-earth metal, thus significantly diminishing the possibility of the scandium catalyst to discriminate the two diastereomeric cyclization transition states. The highest enantioselectivity of 92% ee was observed for the lutetium complex with two triphenylsilyl substituents (Table 1, entry 5). Interestingly, most *S*-configured catalysts formed the *S* enantiomer of the hydroamination product preferentially, which is in contrast to the selectivity observed with the binaphtholate complexes **Ia,b**.[13d] However, the yttrium catalyst based on the sterically least demanding ligand, (*S*)-**8g**, produced **11a** with the opposite *R* configuration. Such a reversal of enantioselectivity within a family of catalysts is not uncommon.[12a,b,d,13f]

In order to get a deeper insight into the catalytic properties of the novel catalysts, we investigated the catalytic hydroamination/cyclization of a broader range of aminoalkenes (Table 2). The lutetium catalyst **9c-Lu** derived from the bis(triphenylsilyl)-substituted ligand **8c**, which had provided the highest selectivity in the cyclization of **10a**, achieved the hydroamination/cyclization of aminopentenes **10b–d** and aminohexene **12** with moderate enantioselectivities (52–73% ee), but the cyclization of aminoheptene **14** to form the azepane **15** proceeded in only 27% ee. Interestingly, piperidine **13** was formed in 73% ee, which is among the highest selectivities reached to date in the hydroamination of aminohexene substrates (Table 2, entry 20).[24] While hydroamination/cyclization of the activated substrates **10a–c** catalyzed by **9c-Lu** was only slightly less efficient than that catalyzed by **I-Ln**, the unbiased aminopentene **10d** required heating to 80 °C to achieve appreciable turnover, whereas this substrate is cyclized by binaphtholate lutetium catalysts **Ib-Lu** at room temperature.[13d]

As expected, scandium was significantly less active than either lutetium or yttrium (Table 2, entry 6 vs entries 4 and 5 and entry 13 vs entry 12), and in agreement with the results for aminopentene **10a**, it was also shown to be less selective.

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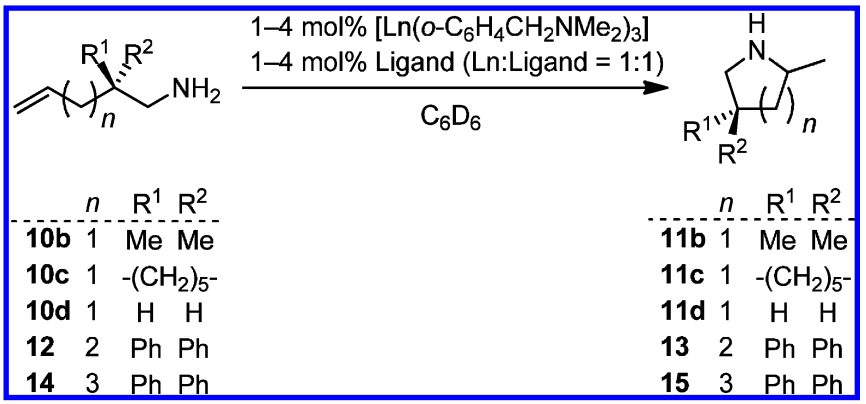
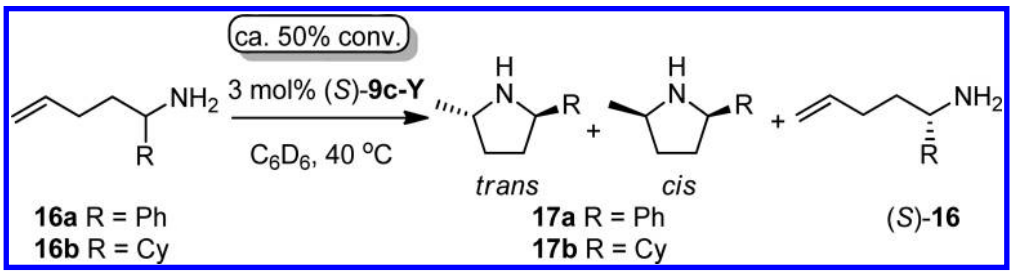
Table 2. Hydroamination/Cyclization of Various Aminoalkenes Catalyzed by Aminodiolate Yttrium, Lutetium, and Scandium Complexes



entry	substrate	Ln[a]	ligand[a]	cat./sub, mol %	T, °C	t, h[b]	N_p, h^{-1} [c]	% ee[d] (confign)
1	**10b**	Y	(*S*)-**8a**	2	40	4	12	18 (*S*)
2	**10b**	Lu	(*S*)-**8a**	2	40	4	12	52 (*S*)
3	**10b**	Y	(*S*)-**8b**	2	40	5	6	5 (*S*)
4	**10b**	Y	(*S*)-**8c**	2	40	3	15	35 (*S*)
5	**10b**	Lu	(*S*)-**8c**	1.4	40	7	12	62 (*S*)
6	**10b**	Sc	(*S*)-**8c**	4	40	96	0.4	18 (*S*)
7	**10b**	Y	(*R*)-**8d**	2	40	12	6	6 (*R*)
8	**10b**	Lu	(*R*)-**8d**	2	40	12	6	10 (*R*)
9	**10b**	Y	(*S*)-**8e**	2	40	7	7	47 (*S*)
10	**10b**	Lu	(*S*)-**8e**	2	40	3	17	63 (*S*)
11	**10c**	Y	(*S*)-**8a**	1	25	0.9	110	30 (*S*)
12	**10c**	Lu	(*S*)-**8c**	1.4	25	0.6	200	52 (*S*)
13	**10c**	Sc	(*S*)-**8c**	2	25	72	0.7	7 (*S*)
14	**10c**	Lu	(*R*)-**8d**	2	25	1.6	30	4 (*R*)
15	**10c**	Y	(*S*)-**8e**	2	25	1.5	30	10 (*S*)
16	**10c**	Lu	(*S*)-**8e**	2	25	4	25	46 (*S*)
17	**10d**	Lu	(*S*)-**8a**	2	80	10	5	66 (*S*)
18	**10d**	Lu	(*S*)-**8c**	4	80	1.6	15	59 (*S*)
19	**10d**	Lu	(*S*)-**8f**	2	80	50	1	47 (*S*)
20	**12**	Lu	(*S*)-**8c**	2	25	2.7	20	73
21	**12**	Y	(*R*)-**8d**	2	60	0.33	150	37
22	**14**	Lu	(*S*)-**8c**	4	90	51	0.5	27

[a]The precatalysts were prepared in situ via reaction of a 1:1 mixture of $[Ln(o\text{-}C_6H_4CH_2NMe_2)_3]$ (Ln = Sc, Y, Lu)[21] and ligand **8a**–**h** in C_6D_6. The complete conversion to the desired complex was confirmed by NMR spectroscopy. [b]Time to >95% conversion. [c]Overall turnover frequency. [d]Determined by ^{19}F NMR spectroscopy of the corresponding Mosher amide.

Table 3. Catalytic Kinetic Resolution of Chiral Aminopentenes with (*S*)-9c-Y Prepared in Situ from $[Y(o\text{-}C_6H_4CH_2NMe_2)_3]$ and (*S*)-8c



entry	substrate	t, h	conversn, %	trans:cis	ee of recov **16**, %	f
1	**16a**	19	55	≥50:1	62	5.9
2	**16b**	20	54	9:1	46	3.4

[a]For a definition of the resolution factor f see ref 25.

These results suggest that scandium will require a ligand where the steric demand of the substituents has been adapted more specifically to the small ionic radius of that element.

The yttrium catalyst containing the bis(triphenylsilyl)-substituted ligand **8c** was also evaluated in the kinetic resolution of chiral racemic aminoalkenes (Table 3).[13b,d,e] These substrates

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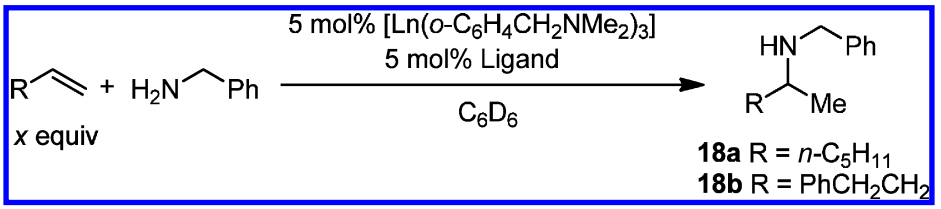
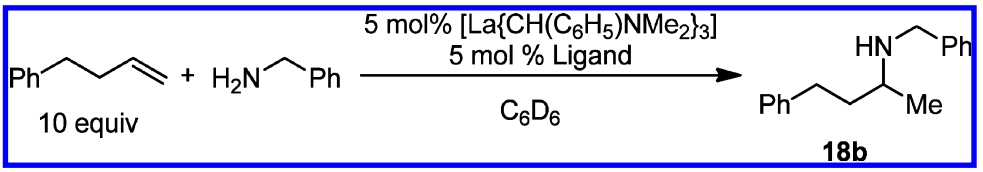
Table 4. Intermolecular Hydroamination of Terminal Alkenes Catalyzed by Aminodiolate Complexes



entry	R	Ln[a]	ligand[a]	*x*	*T*, °C	*t*, h	conversn, %[b] (yield, %)[c]	ee, %[d] (confign)
1	n-C_5H_{11}	Y	(*S*)-**8a**	15	150	96	85 (62)	36 (*R*)
2	n-C_5H_{11}	Lu	(*S*)-**8a**	15	150	96	75 (62)	7 (*R*)
3	n-C_5H_{11}	Y	(*S*)-**8c**	15	170	120	trace	
4	n-C_5H_{11}	Y	(*R*)-**8d**	15	170	120	trace	
5	n-C_5H_{11}	Y	(*S*)-**8h**	15	170	90	70 (53)	4 (*S*)
6	$PhCH_2CH_2$	Y	(*S*)-**8a**	10	150	76	80 (67)	17 (*R*)
7	$PhCH_2CH_2$	Lu	(*S*)-**8a**	10	150	96	75 (61)	9 (*R*)
8	$PhCH_2CH_2$	Y	(*S*)-**8b**	10	150	96	70 (52)	40 (*R*)
9	$PhCH_2CH_2$	Y	(*S*)-**8g**	10	150	50	80 (63)	20 (*R*)
10	$PhCH_2CH_2$	Y	(*S*)-**8h**	10	150	48	85 (66)	5 (*R*)

[a]The precatalysts were prepared in situ via reaction of a 1:1 mixture of $[Ln(o\text{-}C_6H_4CH_2NMe_2)_3]$ (Ln = Y, Lu)[21] and ligand **8a**–**d**,**g**,**h** in C_6D_6. The complete conversion to the desired complex was confirmed by NMR spectroscopy. [b]By ^1H NMR spectroscopic analysis. [c]Isolated yield after column chromatography. [d]Determined by chiral HPLC of the corresponding *N*-benzamide.

Table 5. Lanthanum-Catalyzed Intermolecular Hydroamination of Terminal Alkenes



entry	ligand[a]	*T*, °C	*t*, h	conversn, %[b] (yield, %)[c]	ee, %[d] (confign)
1	(*S*)-**8a**	170	48	trace	
2	(*S*)-**8c**	150	96	85 (61)	38 (*R*)
3	(*R*)-**8d**	150	120	90 (66)	28 (*S*)
4	(*S*)-**8h**	170	48	trace	

[a]The precatalysts were prepared in situ via reaction of a 1:1 mixture of $[La\{CH(C_6H_5)NMe_2\}_3]$[26] and ligand **8a**,**c**,**d**,**h** in C_6D_6. [b]By ^1H NMR spectroscopic analysis. [c]Isolated yield after column chromatography. [d]Determined by chiral HPLC of the corresponding *N*-benzamide.

were previously cyclized by the binaphtholate catalysts **I-Ln** with resolution factors[25] of up to 19 for **16a** and 6 for **16b**.[13b,d,e] In line with the observed reversal of enantioselectivity in the hydroamination/cyclization of achiral aminoalkenes in comparison to the selectivity observed for **I-Ln**, the reisolated, slower reacting enantiomer of aminoalkenes **16a**,**b** obtained in the resolution with (*S*)-**9c-Y** had an *S* configuration, which is the opposite selectivity observed for **I-Ln**.

Intermolecular Asymmetric Hydroamination. On the basis of the catalytic results obtained in the intramolecular hydroaminations, we were optimistic that intermolecular asymmetric hydroamination may be attainable with these novel aminodiolate complexes as well. Indeed, we found that the aminodiolate complexes **9** catalyze the addition of benzylamine to 1-heptene and 4-phenyl-1-butene, leading exclusively to the Markovnikov products (Table 4) under conditions comparable to those used for complexes **I**. The *S*-configured catalysts generally produce the *R* product enantiomers, which is again opposite to the selectivity pattern observed for the binaphtholate complexes **I**.

The aminodiolate complexes were less reactive than complex **Ia-Y**,[10b] and the reactivity drops significantly with increasing steric bulk of the ligand. Thus, no reactivity was observed for the sterically encumbered bis(trisaryl)silyl-substituted yttrium complexes **9c-Y** and **9d-Y**, which have silyl substitution patterns similar to those of binaphtholate complexes **Ia-Y** and **Ib-Y**, respectively. For the complexes with a triphenylsilyl substituent on the naphtholate moiety, only the least encumbered complexes with *tert*-butyl (derived from ligand **8a**) and methyldiphenylsilyl-substituents (derived from ligand **8b**) on the phenolate moiety were catalytically active. However, yttrium complexes prepared from the sterically less demanding ligands **8g**,**h** with methyldiphenylsilyl substituents on the naphtholate moiety displayed higher reactivity (Table 4, entries 9 and 10) comparable in magnitude to that of **I-Ln**. Unfortunately, the selectivity drops significantly when the steric bulk is decreased, and only 40% ee was achieved for the secondary amine **18b** using **9b-Y** (Table 4, entry 8). Similar to the reactivity of complexes **9** in the intramolecular hydroamination, the increased denticity and larger bite angle of the aminodiolate ligand is favorable for utilizing midsized *tert*-butyl and methyldiphenylsilyl substituents in the intermolecular hydroamination; neither of these substituents were suitable to form viable monomeric diolate hydroamination catalysts.[13a,c,23]

Lanthanum Catalysts for Intermolecular Hydroamination. The catalytic activity of rare-earth-metal-based hydroamination catalysts generally increases with increasing size of the metal ionic radius. Therefore, we were anticipating that

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lanthanum aminodiolate complexes should also perform better than their smaller yttrium and lutetium congeners. Unfortunately, attempts to prepare aminodiolate lanthanum amido complexes via amine elimination from the lanthanum tris(amide) $[La\{N(SiMe_3)_2\}_3]$ and the proligand **8** did not produce a well-defined species and the crude reaction mixtures were catalytically inactive in the intermolecular hydroamination. While the lanthanum tris(aryl) complex $[La(o\text{-}C_6H_4CH_2NMe_2)_3]$ is unavailable, we decided to utilize its constitutional isomer $[La\{CH(C_6H_5)NMe_2\}_3]$, which has been recently introduced by Behrle and Schmidt.[26] Indeed, treatment of $[La\{CH(C_6H_5)NMe_2\}_3]$ with the appropriate proligand **8** generated a species that was catalytically active in the intermolecular hydroamination (Table 5). The ^{1}H NMR spectra of the crude reaction mixtures in toluene-d_8 showed broad signals even at −80 °C, presumably due to the fluxional character of the (dimethylamino)benzyl lanthanum moiety.[26]

It appears that the larger lanthanum indeed demands a different level of steric protection for catalytic activity in intermolecular hydroamination. While the triphenylsilyl-substituted yttrium complexes derived from **8c,d** were catalytically inactive, the corresponding lanthanum aminodiolate complexes were catalytically active. Lanthanum complexes prepared from the sterically less demanding ligands **8a,h** produced only traces of hydroamination product. The lanthanum catalyst based on ligand **8c** produced the hydroamination product **18b** in 38% ee (Table 5, entry 2). The activity and selectivity of this complex is quite comparable to those of the yttrium catalysts utilizing ligands **8a,b** (Table 4, entries 1 and 8). Hence, it appears that contrary to general wisdom in hydroamination catalysis,[2,3a,b] the larger lanthanum metal did not significantly improve catalytic activity for intermolecular hydroamination.

SUMMARY

A new family of C_1-symmetric NOBIN-derived aminodiolate diolate complexes **9-Ln** featuring various degrees of steric protection were synthesized. The complexes were shown to be catalytically active in intra- and intermolecular asymmetric hydroaminations of unactivated alkenes. The most active systems can reach catalytic activity comparable in magnitude to—or only slightly lower than—the binaphtholate complexes **I** in the case of intramolecular hydroamination of the Thorpe−Ingold-activated aminoalkenes **10a−c** and **12** with complexes **9a−f** and in intermolecular hydroaminations with catalysts **9g-Y** and **9h-Y**. The slightly diminished catalytic activity of catalysts **9-Ln** in comparison to **I-Ln** can be attributed to the additional amine donor site in the aminodiolate ligand framework. The broad spectrum of substituents tolerated in the precatalysts allowed us to observe the highest and lowest acceptable level of steric bulk required for catalytic activity with midsized (Lu, Y) and large (La) rare-earth metals. The hydroamination of aminopentenes and aminohexenes proceeded with enantioselectivities of up to 92 and 73% ee, respectively. Scandium was significantly less active and less enantioselective in intramolecular hydroamination reactions utilizing the bis(triphenylsilyl)-substituted ligand **8c**, suggesting that this ligand is too crowded for the smallest rare-earth metal. The intermolecular hydroamination of simple terminal alkenes with benzylamine was achieved with enantioselectivities of up to 40% ee, which is slightly lower than the selectivities observed previously for binaphtholate catalysts **I**. In addition, several lanthanum-based hydroamination catalysts were applied in the intermolecular hydroamination as well and enantioselectivities of up to 38% ee were achieved. The enantioselectivity of the intramolecular hydroamination as well as the reactivity in the intermolecular hydroamination are critically dependent on the steric features of the ligand framework. The steric requirements for the ligand set seem to be different in intramolecular and intermolecular hydroamination reactions. In order to achieve more efficient intermolecular hydroaminations and allow a more rational catalyst design, it will be important to better understand these steric and electronic factors that influence catalytic performance.

EXPERIMENTAL SECTION

General Considerations. All reactions with air- or moisture sensitive materials were performed in oven (120 °C) and flame-dried glassware under an inert atmosphere of argon, employing standard Schlenk and glovebox techniques. Alkenes and C_6D_6 were distilled from sodium/benzophenone ketyl. Amines and aminoalkenes were distilled twice from finely powdered CaH_2. DMF was distilled from CaH_2. All other commercially available starting materials were used as received. ^{1}H, ^{13}C{^{1}H}, and ^{19}F NMR spectra were recorded on Varian (400 and 500 MHz) spectrometers at 25 °C unless stated otherwise. Chemical shifts are reported in ppm downfield from tetramethylsilane with the nondeuterated portion of the solvent as internal standard. Mass spectra were recorded on a Finnigan LCQ-DUO mass spectrometer. Silica gel (230−400 mesh, Sorbent Technologies) and alumina (80−200 mesh, EMD) were used for column chromatography. Elemental analyses were performed by Robertson Microlit Laboratories, Inc., Ledgewood, NJ.

(*S*)-Mosher acid was transformed into the corresponding (*R*)-Mosher acid chloride according to a literature protocol.[27] *N*,*N*-Dibenzyl-*N*-[2′-(methoxymethoxy)-1,1′-binaphthalen-2-yl]amine (**1**),[18] 3,5-di-*tert*-butylsalicylaldehyde (**5a**),[28] and silyl-substituted salicylaldehydes **5b,c,e,f**,[29] as well as the rare-earth-metal precursors $[Ln(o\text{-}C_6H_4CH_2NMe_2)_3]$ (Ln = Sc, Y, Lu),[21] and $[La\{CH(C_6H_5)NMe_2\}_3]$,[26] were prepared according to literature protocols. The aminoalkene substrates (2,2-diphenylpent-4-enyl)amine (**10a**),[12d] (2,2-dimethylpent-4-enyl)amine (**10b**),[30a] (1-allylcyclohexyl)methylamine (**10c**),[30b] pent-4-en-1-ylamine (**10d**),[30c] (2,2-diphenylhex-5-enyl)amine (**12**),[30d] (2,2-diphenylhept-6-enyl)amine (**14**),[30e] (1-phenylpent-4-en-1-yl)-amine (**16a**),[13d] and (1-cyclohexylpent-4-en-1-yl)amine (**16b**)[13e] were synthesized according to literature protocols. The hydroamination products 2-methyl-4,4-diphenylpyrrolidine (**11a**),[12d] 2,4,4-trimethylpyrrolidine (**11b**),[30c] 3-methyl-2-azaspiro[4.5]decane (**11c**),[12h] 2-methylpyrrolidine (**11d**),[30c] 2-methyl-5,5-diphenylpiperidine (**13**),[12d] 2-methyl-6,6-diphenylazepane (**15**),[14l,30f] 2-methyl-5-phenylpyrrolidine (**17a**),[13d] 2-cyclohexyl-5-methylpyrrolidine (**17b**),[13e] *N*-benzylheptan-2-amine (**18a**),[10b,31] and *N*-benzyl-4-phenylbutan-2-amine (**18b**)[10b,31] are known compounds and were identified by comparison to the literature NMR spectroscopic data. Catalytic intramolecular hydroamination reactions of aminoalkenes and kinetic resolution experiments were performed as previously reported.[13d,e] The absolute configuration of the hydroamination/cyclization products was determined by comparison of the ^{19}F NMR spectroscopic data of the Mosher amides with the assignments reported previously.[13d]

Chlorotris(3,5-xylyl)silane.[32] To a solution of 5-bromo-*m*-xylene (11.1 g, 60.0 mmol) in Et_2O (75 mL) was added dropwise *n*-BuLi (1.6 M in hexanes, 37.5 mL, 60.0 mmol) at 10 °C. After 4 h at this temperature, $SiCl_4$ (2.3 mL, 3.40 g, 20.0 mmol) was added dropwise at −10 °C. The resulting mixture was warmed to room temperature and stirred overnight. The solvent was removed in vacuo, and the residue was extracted with warm toluene (2 × 20 mL). The combined extracts were concentrated in vacuo, and the residue was recrystallized from hexanes. After filtration, 3.48 g (47% yield) of the target product was obtained in the form of white crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (s, 6H), 7.10 (s, 3H, aryl-H), 2.31 (s, 18H, 6 CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 137.4, 132.9, 132.8, 132.4 (aryl), 21.4 (CH_3).

General Procedure for the Synthesis of 2 via Silylation of Protected NOBIN Derivative 1. To a stirred solution of **1** (4.58 g, 9.0 mmol) in Et_2O (80 mL) was added dropwise *n*-BuLi (2.5 M in hexanes, 4.7 mL, 11.7 mmol) at 0 °C. The mixture was stirred at this temperature

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for 5 h and then for 2 h at room temperature and was then cooled to −30 °C. THF (50 mL), a solution of the chlorosilane (11.7 mmol) in THF (10 mL), and HMPA (3.0 mL, 12 mmol) were added to the solution in that order. The dark brown solution was warmed to room temperature slowly and was stirred overnight. The mixture was quenched with a saturated ammonium chloride solution (100 mL), and the product was extracted with dichloromethane (2 × 50 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography.

*N,N-Dibenzyl-N-[2′-(methoxymethoxy)-3′-(triphenylsilyl)-1,1′-binaphthalen-2-yl]amine (**2a**).* Purified by column chromatography on silica (hexanes/toluene 1/1) to give 4.50 g (65%) of **2a** as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.71 (d, ^3J(H,H) = 8.8 Hz, 1H), 7.68 (d, ^3J(H,H) = 7.8 Hz, 1H), 7.63 (d, ^3J(H,H) = 8.3 Hz, 1H), 7.57 (d, ^3J(H,H) = 7.8 Hz, 6H, $SiPh_3$), 7.30−7.10 (m, 14H), 7.05 (vt, ^3J(H,H) = 8.1, 7.1 Hz, 1H), 7.00−6.89 (m, 7H), 6.85−6.80 (m, 4H, aryl-H), 3.94 (m, 5H, 2CH_2Ph, CH_2O), 3.65 (d, 1H, ^2J(H,H) = 5.1 Hz, CH_2O), 2.04 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 157.4, 148.7, 141.2, 138.4, 136.5, 135.9, 135.09, 135.06, 130.3, 130.1, 129.3, 126.0, 125.1, 124.5, 124.1, 122.8, 97.4 (CH_2O), 56.6 (CH_3), 55.8 (CH_2Ph).

*N,N-Dibenzyl-N-[2′-(methoxymethoxy)-3′-(methyldiphenylsilyl)-1,1′-binaphthalen-2-yl]amine (**2b**).* Purified by column chromatography on silica (hexanes/DCM 5/3) to give 4.13 g (65%) of **2b** as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.83 (d, ^3J(H,H) = 8.8 Hz, 1H), 7.79 (d, ^3J(H,H) = 8.1 Hz, 1H), 7.73 (d, ^3J(H,H) = 8.3 Hz, 1H), 7.61 (d, ^3J(H,H) = 7.3 Hz, 2H), 7.55 (d, ^3J(H,H) = 7.3 Hz, 2H), 7.44−7.29 (m, 9H), 7.21−7.10 (m, 9H), 7.00 (d, ^3J(H,H) = 8.6 Hz, 1H), 6.92 (dd, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 2.0 Hz, 4H, aryl-H), 4.05 (d, ^2J(H,H) = 14.4 Hz, 2H, PhCH_2N), 3.99 (d, ^2J(H,H) = 4.7 Hz, 1H, CH_2O), 3.95 (d, ^2J(H,H) = 4.7 Hz, 1H, CH_2O), 3.89 (d, ^2J(H,H) = 14.4 Hz, 2H, PhCH_2N), 2.33 (s, 3H, CH_3O), 0.96 (s, 3H, $SiCH_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 157.2 (CO), 148.9, 139.9, 138.5, 137.3, 136.7, 145.6, 135.5, 135.1, 135.0, 130.9, 130.4, 130.2, 129.3, 129.2, 128.9, 128.5, 128.3, 127.9, 127.82, 127.78, 127.7, 127.6, 127.1, 126.6, 126.3, 126.2, 126.1, 125.5, 124.5, 124.2, 122.7 (aryl), 97.8 (CH_2O), 56.6 (CH_3O), 56.0 (CH_2Ph), −3.0 ($SiCH_3$).

General Procedure for the Synthesis of 3 via Debenzylation of Amine 2. To a stirred suspension of **2** (4.60 mmol) in absolute ethanol (150 mL) was added ammonium formate (5.00 g, 80 mmol) and 10% Pd on charcoal (1.20 g, 0.23 mmol), and the mixture was refluxed for 2 days. *Caution!* Condensation of ammonium salts in a reflux condenser may result in an isolated overpressured system. The mixture was cooled and filtered through Celite, and the filtrate was concentrated in vacuo and treated with 2% KOH solution (100 mL). The product was extracted with dichloromethane (2 × 100 mL). The combined organic extracts were dried (Na_2SO_4), and the solvent was evaporated. The residue was purified by flash chromatography.

*2′-(Methoxymethoxy)-3′-(triphenylsilyl)-1,1′-binaphthalen-2-amine (**3a**).* Purified on a short silica column (hexanes/DCM 1/1) to give 2.01 g (75%) of **3a** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.77 (d, ^3J(H,H) = 8.6 Hz, 1H), 7.78−7.73 (m, 2H), 7.67 (d, ^3J(H,H) = 7.8 Hz, 6H), 7.43−7.30 (m, 12H), 7.26−7.16 (m, 3H), 7.07 (d, ^3J(H,H) = 8.6 Hz, 1H, aryl-H), 3.91 (d, 1H, ^2J(H,H) = 5.1 Hz, CH_2O), 3.87 (d, 1H, ^2J(H,H) = 5.1 Hz, CH_2O), 3.7 (br s, 2H, NH_2), 2.20 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.0, 142.6, 141.1, 136.5, 135.0, 134.9, 134.3, 130.6, 129.49, 129.45, 124.4, 122.2, 121.7, 118.0, 114.0 (aryl), 97.4 (CH_2), 55.6 (CH_3). MS (ESI): m/z 587.9 $[M + H]^+$.

*2′-(Methoxymethoxy)-3′-(methyldiphenylsilyl)-1,1′-binaphthalen-2-amine (**3b**).* Purified on a short silica column (hexanes/DCM 1/1) to give 1.32 g (54%) of **3b** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.78−7.73 (m, 3H), 7.64−7.62 (m, 4H), 7.41−7.31 (m, 7H), 7.29−7.27 (m, 2H), 7.23−7.20 (m, 2H), 7.11 (m, 1H), 7.07 (d, ^3J(H,H) = 9.0 Hz, 1H, aryl-H), 4.21 (d, 1H, ^2J(H,H) = 4.6 Hz, CH_2O), 4.14 (d, 1H, ^2J(H,H) = 4.6 Hz, CH_2O), 3.70 (br s, 2H, NH_2), 2.46 (s, 3H, CH_3O), 1.03 (s, 3H, CH_3Si). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 158.0 (CO), 142.5, 140.0, 136.8, 136.8, 135.2, 134.8, 134.2, 133.9, 130.9, 130.7, 129.5, 129.22, 129.20, 128.5, 128.0, 127.9, 127.79, 127.77, 127.4, 126.6, 125.2, 124.8, 124.5, 122.2, 121.8, 118.0, 114.0 (aryl), 97.8 (CH_2), 56.1 (CH_3O), −2.9 ($SiCH_3$). MS (ESI): m/z 526.2 $[M + H]^+$.

General Procedure for the Deprotection of Acetal 3. To a stirred solution of **3** (3.4 mmol) and Et_3N (0.71 mL, 5.0 mmol) in dichloromethane (20 mL) was added dropwise trifluoroacetic anhydride (0.53 mL, 4.0 mmol) at 0 °C. The mixture was stirred at room temperature for 2 min, washed with 1 M HCl (5 mL), and concentrated in vacuo. The residue was dissolved in dioxane (10 mL), and 12 M HCl (1 mL) was added. The mixture was stirred overnight at 65 °C. The mixture was neutralized with a saturated $NaHCO_3$ solution, and the product was extracted with ethyl acetate (2 × 75 mL). The combined organic extracts were dried (Na_2SO_4), and the solvent was evaporated. The residue was dissolved in ethanol (10 mL) and treated with $NaBH_4$ (0.34 g, 10 mmol). The mixture was stirred at room temperature overnight and was quenched by addition of 2% KOH solution (50 mL). The product was extracted with dichloromethane (2 × 50 mL). The combined organic extracts were dried (Na_2SO_4) and passed through a short silica plug, and the solvent was evaporated to give **4**.

*2′-Amino-3-(triphenylsilyl)-1,1′-binaphthalen-2-ol (**4a**).* White solid, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.79 (d, ^3J(H,H) = 9.0 Hz, 1H), 7.78−7.72 (m, 2H), 7.67 (d, ^3J(H,H) = 8.2 Hz, 6H), 7.43−7.34 (m, 8H), 7.30−7.19 (m, 6H), 7.14−7.11 (m, 1H), 7.09 (d, ^3J(H,H) = 9.0 Hz, 1H, aryl-H), 5.29 (s, 1H, OH), 3.76 (br s, 2H, NH_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.6 (CO), 143.7, 141.2, 136.3, 134.6, 134.0, 130.5, 129.4, 129.2, 123.5, 123.4, 122.7, 118.1, 113.7, 108.6 (aryl).

*2′-Amino-3-(methyldiphenylsilyl)-1,1′-binaphthalen-2-ol (**4b**).* Off-white solid, 83% yield. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.19 (s, 1H), 7.75−7.69 (m, 4H), 7.56 (d, ^3J(H,H) = 6.7 Hz, 4H), 7.41−7.33 (m, 6H), 7.22−7.20 (m, 2H), 7.16 (d, ^3J(H,H) = 8.8 Hz, 1H), 7.12−7.06 (m, 2H), 6.93 (m, 1H), 6.79 (d, ^3J(H,H) = 7.3 Hz, 1H, aryl-H), 4.69 (br s, 2H, NH_2), 0.92 (s, 3H, $SiCH_3$). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ 157.1 (CO), 144.9, 138.4, 136.8, 136.7, 134.9, 134.8, 134.7, 134.4, 133.9, 129.08, 129.05, 129.0, 128.3, 127.9, 127.72, 127.68, 127.4, 126.9, 125.84, 125.81, 124.0, 123.0, 120.7, 118.7, 113.8, 108.5 (aryl), −2.9 ($SiCH_3$).

General Procedure for the Synthesis of Salicylaldehydes 5d,e. In a procedure that was adopted from ref 29, KH (400 mg, 10.0 mmol) was added slowly to a solution of 2,6-dibromo-4-methylphenol (5.00 mmol) in THF (25 mL) at 0 °C. After the mixture was stirred for 30 min, the appropriate chlorosilane (5.00 mmol) was added in one portion. The reaction mixture was heated to reflux for 16−48 h (monitored by TLC). The solvent was then removed in vacuo and the residue diluted with hexanes (100 mL) and water (50 mL). The layers were separated, and the organic layer was washed with aqueous HCl (0.2 N, 30 mL), water (30 mL), and brine (30 mL). The solution was then dried (Na_2SO_4) and concentrated in vacuo. The crude silyl ethers were used directly in the next step without further purification.

A solution of silyl ether (1.50 mmol) in Et_2O (3.0 mL) was cooled to −78 °C, and then *t*-BuLi (1.7 M in pentane, 3.53 mL, 6.00 mmol) was added dropwise. The dark red reaction mixture was stirred for 1.5 h with warming to 0 °C. The mixture was then cooled to −78 °C and DMF (0.465 mL, 6.00 mmol) was added in one portion. The reaction mixture was warmed to 0 °C and was then quenched with saturated aqueous NH_4Cl (5.0 mL) and diluted with EtOAc (75 mL). The layers were separated, and the organic layer was washed with H_2O (2 × 15 mL) and brine (25 mL), dried (Na_2SO_4), and concentrated in vacuo to afford the crude salicylaldehyde **5**. Flash chromatography (silica gel, EtOAc/hexanes, DCM/hexanes, or benzene/hexanes) afforded the pure salicyladehyde **5**.

*2-Hydroxy-5-methyl-3-[tris(3,5-dimethylphenyl)silyl]-benzaldehyde (**5d**).* White solid, purified by flash chromatography on silica (hexanes/DCM 3/1), 48% yield. ^{1}H NMR (500 MHz, C_6D_6): δ 11.81 (s, 1H, CHO), 9.21 (s, 1H, OH), 7.70−7.68 (m, 7H), 6.91 (s, 3H), 6.62 (s, 1H, aryl-H), 2.10 (s, 18 H, 6 CH_3), 1.86 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 196.5 (CHO), 165.3 (CO), 147.1, 137.2, 135.9, 134.9, 134.7, 131.7, 128.6, 124.8, 120.1 (aryl), 21.4 (CH_3), 20.1 (CH_3).

*3-(tert-Butyldiphenylsilyl)-2-hydroxy-5-methylbenzaldehyde (**5e**).* White solid, purified by flash chromatography on silica (hexanes/

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toluene =2:1−1:1), 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.43 (s, 1H, CHO), 9.89 (s, 1H, OH), 7.56−7.54 (m, 4H), 7.44−7.34 (m, 7H), 7.20 (s, 1H, aryl-H), 2.21 (s, 3H, CH_3), 1.21 (s, 9H, *t*-Bu). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 196.7 (CHO), 164.4 (CO), 147.7, 136.1, 135.5, 134.8, 129.1, 128.6, 127.6, 124.0, 119.5 (aryl), 29.6 ($C(CH_3)_3$), 20.4 ($ArCH_3$), 18.5 ($C(CH_3)_3$).

General Procedure for the Preparation of Aminodiol Proligands 8. To a suspension of aminophenol **4** (0.55 mmol) and aldehyde **5** (0.60 mmol) in toluene (10 mL) was added TsOH·H_2O (3.1 mg, 2 mol %), and the mixture was stirred at 100 °C for 2 days. The solvent was evaporated, and the residue was purified by flash chromatography on a short silica pad (hexanes/EtOAc 10/1). The eluate was evaporated, and the residue was immediately subjected to the reduction as follows. The yellow Schiff base was dissolved in Et_2O (15 mL), and $LiAlH_4$ (100 mg, 3.1 mmol) was added in one portion. The originally yellow solution turned green immediately upon addition of the hydride. The mixture was stirred at room temperature for an additional 10 min (TLC), quenched with 2% KOH (10 mL), and extracted with ethyl acetate (2 × 20 mL). The combined organic extracts were dried (Na_2SO_4), and the solvent was evaporated to yield crude secondary amine **6**. Compound **6b** was characterized by NMR spectroscopy; other secondary amines were used further without characterization. The salane compound **6** was dissolved in THF (10 mL), and formalin (30% solution, 0.36 mL, 4 mmol) and $NaBH(OAc)_3$ (420 mg, 2.0 mmol) were added in one portion at room temperature. The mixture was stirred for 20 min (monitored by TLC) and then quenched with 2% KOH (20 mL) and extracted with Et_2O (2 × 50 mL). The combined organic layers were dried (Na_2SO_4) and passed through a short alumina plug. Compound **7b** was characterized by NMR spectroscopy, and all other aminals were used further without characterization. To a stirred eluate containing cyclic aminal intermediate **7** was added $LiAlH_4$ (40 mg, 1.0 mmol) in one portion at room temperature. The mixture was stirred for 10 min and then quenched with 2% KOH (50 mL) and extracted with Et_2O (3 × 40 mL). The combined organic layers were passed through a short alumina plug and concentrated. The residue was dissolved in benzene (5 mL) and freeze-dried to yield the proligand **8**.

*2′-{[2-Hydroxy-5-methyl-3-(methyldiphenylsilyl)benzyl]amino}-3-(triphenylsilyl)-1,1′-binaphthalen-2-ol (**6b**).* Obtained via the general procedure from **4a** and **5b**. White solid, 64% yield. ^{1}H NMR (500 MHz, C_6D_6): δ 8.23 (s, 1H), 7.86−7.84 (m, 6H), 7.65 (m, 2H), 7.61−7.57 (m, 3H), 7.49 (d, ^3J(H,H) = 9.1 Hz, 1H), 7.39 (d, ^3J(H,H) = 7.6 Hz, 1H), 7.27−7.20 (m, 11H), 7.14−7.06 (m, 11H), 7.02−6.98 (m, 2H), 6.75 (s, 1H), 3.82 (vt, ^3J(H,H) = 4.7, 3.7 Hz, 1H, NH), 3.64 (dd, ^2J(H,H) = 15.7 Hz, ^3J(H,H) = 3.7 Hz, 1H, CH_2), 3.59 (dd, ^2J(H,H) = 15.7 Hz, ^3J(H,H) = 4.7 Hz, 1H, CH_2), 2.03 (s, 3H, $ArCH_3$), 0.93 (s, 3H, $SiCH_3$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 159.9, 156.4 (CO), 145.2, 142.0, 137.18, 137.17, 137.1, 136.9, 135.62, 135.60, 135.31, 135.1, 134.0, 131.0, 130.9, 129.9, 129.7, 129.46, 129.44, 129.1, 128.6, 128.5, 128.08, 128.06, 124.5, 124.3, 124.2, 124.1, 123.8, 122.8, 122.7, 116.2, 113.5, 112.9 (aryl), 48.1 (CH_2), 20.6 ($ArCH_3$), −2.6 ($SiCH_3$).

*2′-[6-Methyl-8-(methyldiphenylsilyl)-2H-1,3-benzoxazin-3(4H)-yl]-3-(triphenylsilyl)-1,1′-binaphthalen-2-ol (**7b**).* To a stirred solution of **6b** (340 mg, 0.4 mmol) and formalin (0.36 mL, 4 mmol) in THF (10 mL) was added $NaBH(OAc)_3$ (420 mg, 2 mmol) in one portion at room temperature. The mixture was stirred for 10 min and then quenched with 2% KOH (10 mL) and extracted with Et_2O (2 × 50 mL). The combined organic layers were passed through a short alumina plug and evaporated to give 300 mg (96%) of the cyclic aminal **7b** as an off-white solid which quickly oxidizes in air. ^{1}H NMR (400 MHz, C_6D_6): δ 8.15 (s, 1H), 7.82 (d, ^3J(H,H) = 7.0 Hz, 6H), 7.63−7.59 (m, 6H), 7.39−7.35 (m, 2H), 7.30 (d, ^3J(H,H) = 8.6 Hz, 1H), 7.22−7.05 (m, 13H), 7.11−7.05 (m, 4H), 6.98−6.92 (m, 4H), 6.23 (s, 1H, aryl-H), 5.07 (s, 1H, OH), 4.60 (d, ^2J(H,H) = 10.6 Hz, 1H, OCH_2), 4.35 (d, ^2J(H,H) = 10.6 Hz, 1H, OCH_2), 3.82 (d, ^2J(H,H) = 16.8 Hz, 1H, CH_2), 3.82 (d, ^2J(H,H) = 16.8 Hz, 1H, CH_2), 3.76 (d, ^2J(H,H) = 16.8 Hz, 1H, CH_2), 1.89 (s, 3H, $ArCH_3$), 0.91 (s, 3H, $SiCH_3$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 157.2, 155.2 (CO), 147.8, 141.3, 137.32, 137.28, 136.9, 136.4, 135.68, 135.67, 135.5, 135.4, 134.1, 131.6, 130.6, 129.9, 129.8, 129.64, 129.58, 129.35, 129.32, 129.29, 128.5, 128.1, 128.0, 127.9, 127.2, 125.7, 125.2, 125.0, 124.8, 123.7, 123.66, 123.62, 122.92, 121.78, 120.2, 117.2 (aryl), 79.8 (OCH_2), 51.6 (NCH_2), 20.5 ($ArCH_3$), −2.6 ($SiCH_3$).

*2′-[(3,5-Di-tert-butyl-2-hydroxybenzyl)methylamino]-3-(triphenylsilyl)-1,1′-binaphthalen-2-ol (**8a**).* Prepared from **4a** and **5a**. White solid, 79% yield. ^{1}H NMR (500 MHz, C_6D_6): δ 8.74 (s, 1H), 8.21 (s, 1H), 7.82 (d, ^3J(H,H) = 7.6 Hz, 6H), 7.78 (d, ^3J(H,H) = 8.8 Hz, 1H), 7.72 (d, ^3J(H,H) = 8.3 Hz, 1H), 7.54 (d, ^3J(H,H) = 7.8 Hz, 1H), 7.49 (d, ^3J(H,H) = 8.6 Hz, 1H), 7.40 (m, 1H), 7.35 (d, ^3J(H,H) = 8.8 Hz, 1H), 7.25 (vt, ^3J(H,H) = 7.6, 7.3 Hz, 1H), 7.20 (t, ^3J(H,H) = 7.8 Hz, 3H), 7.14 (m, 1H), 7.12−7.08 (t, ^3J(H,H) = 7.6 Hz, 6H), 7.05−7.00 (m, 3H), 6.93 (s, 1H, aryl-H), 4.29 (s, 1H, OH), 3.92 (d, ^2J(H,H) = 13.2 Hz, 1H, CH_2), 3.58 (d, ^2J(H,H) = 13.2 Hz, 1H, CH_2), 2.31 (s, 3H, CH_3), 1.40 (s, 9 H, $C(CH_3)_3$), 1.33 (s, 9H, $C(CH_3)_3$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 155.4, 154.5, 151.0, 142.1, 140.4, 136.9, 135.9, 135.6, 135.1, 133.9, 132.8, 130.7, 130.6, 129.6, 129.3, 128.5, 128.3, 128.1, 127.9, 127.5, 126.5, 126.4, 123.9, 123.8, 123.7, 123.3, 121.3, 120.3, 115.9 (aryl), 63.6 (CH_2), 40.4 (NCH_3), 35.0 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 32.0 ($C(CH_3)_3$), 29.7 ($C(CH_3)_3$). Anal. Calcd for $C_{54}H_{53}NO_2Si$: C, 83.57; H, 6.88; N, 1.80. Found: C, 82.31; H, 7.06; N, 1.68.

*2′-{[2-Hydroxy-5-methyl-3-(methyldiphenylsilyl)benzyl]-methylamino}-3-(triphenylsilyl)-1,1′-binaphthalen-2-ol (**8b**).* Prepared from **7b**. White solid, 97% yield. ^{1}H NMR (500 MHz, C_6D_6): δ 8.24 (s, 1H), 8.14 (s, 1H), 7.84 (d, ^3J(H,H) = 6.8 Hz, 6H), 7.75 (d, ^3J(H,H) = 9.1 Hz, 1H), 7.70 (d, ^3J(H,H) = 7.8 Hz, 1H), 7.61−7.56 (m, 2H), 7.48 (d, ^3J(H,H) = 6.4 Hz, 2H), 7.44 (m, ^3J(H,H) = 8.7 Hz, 1H), 7.31−7.28 (m, 2H), 7.24 (t, ^3J(H,H) = 7.6 Hz, 6H), 7.18−7.08 (m, 11H), 7.03−6.93 (m, 3H), 6.73 (s, 1H, aryl-H), 4.26 (s, 1H, OH), 3.87 (d, ^2J(H,H) = 13.2 Hz, 1H, CH_2), 3.61 (d, ^2J(H,H) = 13.2 Hz, 1H, CH_2), 2.24 (s, 3H, NCH_3), 2.06 (s, 3H, $ArCH_3$), 0.78 (s, 3H, $SiCH_3$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 160.8, 155.2 (CO), 150.9, 142.1, 137.73, 137.65, 137.63, 136.9, 135.7, 135.5, 135.2, 135.1, 133.8, 132.6, 132.1, 130.7, 130.2, 129.6, 129.4, 129.1, 128.9, 128.5, 128.1, 127.93, 127.89, 127.77, 127.6, 127.5, 127.3, 126.3, 126.1, 123.8, 123.6, 123.4, 122.2, 120.1, 115.8 (aryl), 62.0 (CH_2), 40.7 (NCH_3), 20.6 ($ArCH_3$), −2.3 ($SiCH_3$). Anal. Calcd for $C_{60}H_{51}NO_2Si_2$: C, 82.43; H, 5.88; N, 1.60. Found: C, 82.06; H, 6.52; N, 1.54.

*2′-{[2-Hydroxy-5-methyl-3-(triphenylsilyl)benzyl]methylamino}-3-(triphenylsilyl)-1,1′-binaphthalen-2-ol (**8c**).* Prepared from **4a** and **5c**. White solid, 72% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 8.06 (s, 1H), 7.82 (s, 1H), 7.77 (d, ^3J(H,H) = 7.0 Hz, 6H), 7.67 (d, ^3J(H,H) = 9.0 Hz, 1H), 7.63 (d, ^3J(H,H) = 8.2 Hz, 1H), 7.57 (d, ^3J(H,H) = 7.4 Hz, 6H), 7.36 (d, ^3J(H,H) = 8.6 Hz, 1H), 7.22−6.93 (m, 23H), 6.74−6.70 (m, 2H, aryl-H), 4.25 (s, 1H, OH), 3.84 (d, ^2J(H,H) = 12.9 Hz, 1H, CH_2), 3.58 (d, ^2J(H,H) = 12.9 Hz, 1H, CH_2), 2.15 (s, 3H, NCH_3), 1.99 (s, 3 H, $ArCH_3$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 160.4, 155.0 (CO), 150.8, 142.1, 138.8, 136.9, 136.8, 135.7, 135.3, 134.6, 133.7, 132.8, 132.2, 130.5, 130.0, 129.6, 129.3, 129.2, 128.1, 127.8, 127.5, 126.1, 126.0, 125.7, 124.0, 123.3, 122.8, 121.1, 120.9, 120.8, 115.9 (aryl), 60.9 (CH_2), 40.5 (NCH_3), 20.6 ($ArCH_3$). Anal. Calcd for $C_{65}H_{53}NO_2Si_2$: C, 83.38; H, 5.71; N, 1.50. Found: C, 83.68; H, 5.72; N, 1.54.

*2′-{[2-Hydroxy-5-methyl-3-[tris(3,5-dimethylphenyl)silyl]benzyl]-methyl)amino}-3-(triphenylsilyl)-1,1′-binaphthalen-2-ol (**8d**).* Prepared from **4a** and **5d**. White solid, 82% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 8.12 (s, 1H), 7.80 (d, ^3J(H,H) = 7.8 Hz, 6H), 7.64 (d, ^3J(H,H) = 8.2 Hz, 1H), 7.63 (d, ^3J(H,H) = 9.0 Hz, 1H), 7.59 (m, 1H), 7.57 (s, 6H), 7.39−7.36 (m, 3 H), 7.26 (d, ^3J(H,H) = 9.3 Hz, 1H), 7.22−7.16 (m, 9 H), 7.09 (d, ^3J(H,H) = 8.6 Hz, 1H), 7.02 (t, ^3J(H,H) = 7.7 Hz, 1H), 6.97 (vt, ^3J(H,H) = 8.1, 6.9 Hz, 1H), 6.90 (d, ^3J(H,H) = 7.7 Hz, 1H), 6.87 (s, 3H), 6.63 (s, 1H, aryl-H), 4.79 (s, 1H, OH), 3.93 (d, ^2J(H,H) = 13.7 Hz, 1H, CH_2), 3.90 (d, ^2J(H,H) = 13.7 Hz, 1H, CH_2), 2.43 (s, 3H, NCH_3), 2.09 (s, 18H, 6 $ArCH_3$), 1.95 (s, 3H, $ArCH_3$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 160.0, 155.4, 150.6, 141.5, 138.7, 137.0, 136.9, 135.5, 135.4, 135.3, 134.6, 134.1, 133.3, 131.7, 131.5, 130.4, 129.7, 129.6, 129.2, 128.8, 128.5, 128.0, 127.3, 125.58, 125.55, 124.4, 124.2, 123.8, 123.7, 122.7, 122.1, 121.4, 116.9 (aryl), 58.5 (CH_2), 40.4 (NCH_3), 21.5 ($ArCH_3$), 20.6 ($ArCH_3$).

*2′-{[3-(tert-Butyldiphenylsilyl)-2-hydroxy-5-methylbenzyl]-methylamino}-3-(triphenylsilyl)-1,1′-binaphthalen-2-ol (**8e**).* Prepared from **4a** and **5e**. White solid, 85% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 8.13 (br s, 1H), 8.02 (s, 1H), 7.76 (d, ^3J(H,H) = 7.1 Hz, 6H),

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7.71 (d, ^3J(H,H) = 9.0 Hz, 1H), 7.65 (d, ^3J(H,H) = 8.2 Hz, 1H), 7.61 (d, ^3J(H,H) = 6.7 Hz, 2H), 7.52 (d, ^3J(H,H) = 7.1 Hz, 2H), 7.33 (d, ^3J(H,H) = 8.6 Hz, 1H), 7.29 (d, ^3J(H,H) = 9.0 Hz, 1H), 7.21−6.95 (m, 21H), 6.83 (vt, ^3J(H,H) = 6.7, 7.8 Hz, 1 H), 6.70 (s, 1H, aryl-H), 4.19 (s, 1H, OH), 3.98 (d, ^2J(H,H) = 13.3 Hz, 1H, CH_2), 3.56 (d, ^2J(H,H) = 13.3 Hz, 1H, CH_2), 2.29 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 1.10 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 160.1, 155.1, 150.9, 142.3, 139.9, 136.9, 136.75, 136.72, 136.3, 135.2, 134.8, 133.7, 132.6, 132.3, 130.7, 129.6, 128.9, 128.8, 128.5, 128.1, 127.9, 127.7, 127.5, 127.0, 126.3, 126.0, 124.0, 123.4, 123.2, 121.6, 121.0, 120.5, 115.8 (aryl), 62.1 (CH_2), 40.6 (NCH_3), 30.3, 20.6, 18.8. Anal. Calcd for $C_{63}H_{57}NO_2Si_2$: C, 82.58; H, 6.27; N, 1.53. Found: C, 81.72; H, 6.33; N, 1.43.

*2′-{[2-Hydroxy-5-methyl-3-(triisopropylsilyl)benzyl]-methylamino}-3-(triphenylsilyl)-1,1′-binaphthalen-2-ol (**8f**).* Prepared from **4a** and **5f**. White solid, 60% yield. ^1H NMR (300 MHz, C_6D_6): δ 8.14 (s, 1H), 8.05 (s, 1H), 7.78 (d, ^3J(H,H) = 8.6 Hz, 6H), 7.74 (m, 1H), 7.69 (d, ^3J(H,H) = 7.9 Hz, 1H), 7.48 (d, ^3J(H,H) = 7.9 Hz, 1H), 7.40 (d, ^3J(H,H) = 8.5 Hz, 1H), 7.30 (d, ^3J(H,H) = 9.1 Hz, 1H), 7.25−7.04 (m, 14H), 6.74 (br s, 1H, aryl-H), 4.18 (s, 1H, OH), 3.90 (d, ^2J(H,H) = 13.2 Hz, 1H, CH_2), 3.57 (d, ^2J(H,H) = 13.2 Hz, 1H, CH_2), 2.27 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 1.30 (sept, ^3J(H,H) = 6.5 Hz, 3H, 3 $CH(CH_3)_2$), 1.09−1.04 (m, 18H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 160.6, 155.2 (CO), 151.0, 142.1, 137.1, 136.9, 135.4, 135.2, 133.8, 132.7, 131.2, 130.7, 130.3, 129.6, 129.4, 128.5, 127.9, 127.5, 127.3, 127.2, 126.4, 126.0, 123.8, 123.7, 123.6, 121.5, 121.0, 120.2, 115.7 (aryl), 62.2 (CH_2), 40.7 (NCH_3), 20.9 ($ArCH_3$), 19.5 ($CH(CH_3)_2$), 19.4 ($CH(CH_3)_2$), 12.0 ($CH(CH_3)_2$).

*2′-[(3,5-Di-tert-Butyl-2-hydroxybenzyl)methylamino]-3-(methyldiphenylsilyl)-1,1′-binaphthalen-2-ol (**8g**).* Prepared from **4b** and **5a**. White solid, 71% yield. ^1H NMR (500 MHz, C_6D_6): δ 8.61 (s, 1H), 8.13 (s, 1H), 7.74 (d, ^3J(H,H) = 8.6 Hz, 6H), 7.71−7.66 (m, 4H), 7.55 (d, ^3J(H,H) = 8.2 Hz, 1H), 7.41 (d, ^3J(H,H) = 8.2 Hz, 1H), 7.36 (d, ^4J(H,H) = 2.4 Hz, 1H), 7.31 (d, ^3J(H,H) = 8.4 Hz, 1H), 7.20−7.11 (m, 6H, aryl-H overlapping with C_6D_5H), 7.05−7.01 (m, 1H), 6.99−6.93 (m, 5H), 6.87 (d, ^4J(H,H) = 2.4 Hz, 1H, aryl-H), 4.27 (s, 1H, OH), 3.82 (d, ^2J(H,H) = 13.3 Hz, 1H, CH_2), 3.63 (d, ^2J(H,H) = 13.3 Hz, 1H, CH_2), 2.24 (s, 3H, CH_3), 1.35 (s, 9 H, $C(CH_3)_3$), 1.34 (s, 9H, $C(CH_3)_3$), 1.02 (s, 3H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 155.5, 154.4 (CO), 151.0, 140.8, 140.7, 140.4, 137.1, 136.8, 135.9, 135.8, 135.7, 135.5, 135.4, 134.0, 132.7, 130.9, 130.7, 130.4, 129.4, 129.3, 126.5, 125.3, 123.9, 123.7, 123.4, 123.2, 121.4, 121.3, 120.3, 115.3 (aryl), 63.3 (CH_2), 40.4 (NCH_3), 35.0 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 32.1 ($C(CH_3)_3$), 29.8 ($C(CH_3)_3$), −2.9 ($SiCH_3$).

*2′-{[2-Hydroxy-5-methyl-3-(methyldiphenylsilyl)benzyl]-methylamino}-3-(methyldiphenylsilyl)-1,1′-binaphthalen-2-ol (**8h**).* Prepared from **4b** and **5b**. White solid, 93% yield. ^1H NMR (500 MHz, C_6D_6): δ 8.17 (s, 1H), 8.03 (s, 1H), 7.75 (d, ^3J(H,H) = 8.6 Hz, 1H), 7.68 (m, 5H), 7.60 (m, 1H), 7.49 (d, ^3J(H,H) = 7.1 Hz, 1H), 7.39 (d, ^3J(H,H) = 7.8 Hz, 1H), 7.31 (d, ^3J(H,H) = 8.6 Hz, 1H), 7.24−7.08 (m, 15H), 6.98 (m, 4H), 6.70 (s, 1H, aryl-H), 4.31 (s, 1H, OH), 3.82 (d, ^2J(H,H) = 13.2 Hz, 1H, CH_2), 3.67 (d, ^2J(H,H) = 13.2 Hz, 1H, CH_2), 2.23 (s, 3H, NCH_3), 2.04 (s, 3H, $ArCH_3$), 1.00 (s, 3H, $SiCH_3$), 0.85 (s, 3H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 160.8, 155.4 (CO), 150.9, 140.7, 137.74, 137.66, 137.2, 136.8, 135.8, 135.7, 135.6, 135.0, 133.9, 132.5, 132.2, 130.8, 130.0, 129.44, 129.38, 128.9, 128.5, 127.1, 126.3, 126.2, 124.9, 123.7, 122.1, 121.2, 120.1, 115.2 (aryl), 61.8 (CH_2), 40.8 (NCH_3), 20.5 ($ArCH_3$), −2.3 ($SiCH_3$), −2.7 ($SiCH_3$).

General Procedure for the NMR-Scale Preparation of 9-Ln. To a mixture of diol proligand **8** (0.05 mmol) and the rare-earth-metal precursor (0.05 mmol) was added C_6D_6 (490 mg, 500 μL). The mixture was shaken vigorously and then left for 5 min at room temperature or slightly elevated temperature. Clean quantitative conversion to the diolate complex **9-Ln** was confirmed by NMR spectroscopy. Aliquots of the resulting complex solution were used directly for the catalytic experiments.

*(S)-[Y{NOBIN-TPS/t-Bu}(o-$C_6H_4CH_2NMe_2$)] ((S)-**9a-Y**).* To a mixture of (*S*)-**8a** (28.4 mg, 0.036 mmol) and [Y(*o*-$C_6H_4CH_2NMe_2)_3$] (18.0 mg, 0.036 mmol) was added C_6D_6 (0.55 mL). The mixture was kept at room temperature for 2 h. ^1H and ^{13}C NMR spectra showed clean formation of (*S*)-**9a-Y**, which was used directly for catalytic experiments. ^1H NMR (500 MHz, C_6D_6): δ 7.99 (d, ^3J(H,H) = 9.0 Hz, 1H), 7.88 (s, 1H), 7.74 (d, ^3J(H,H) = 7.8 Hz, 6H), 7.68 (d, ^3J(H,H) = 8.2 Hz, 1H), 7.65 (d, ^3J(H,H) = 9.3 Hz, 1H), 7.62 (d, ^3J(H,H) = 8.1 Hz, 1H), 7.51 (s, 1H), 7.32−7.26 (m, 7H), 7.13−6.79 (m, 20H, aryl-H), 4.48 (d, ^2J(H,H) = 12.2 Hz, 1H, CH_2N), 3.60 (d, ^2J(H,H) = 12.2 Hz, 1H, CH_2N), 3.53 (d, ^2J(H,H) = 13.7 Hz, 1H, *o*-$C_6H_4CH_2NMe_2$), 3.25 (s, 4H, free $C_6H_5NCH_2NMe_2$), 2.98 (d, ^2J(H,H) = 13.7 Hz, 1H, *o*-$C_6H_4CH_2NMe_2$), 2.47 (s, 3H, NCH_3), 2.06 (s, 12 H, free $C_6H_5CH_2NMe_2$), 1.75 (br s, 3H, *o*-$C_6H_4CH_2NMe_2$), 1.44 (s, 9 H, $C(CH_3)_3$), 1.41 (s, 9H, $C(CH_3)_3$), 1.01 (s, 3H, *o*-$C_6H_4CH_2NMe_2$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 179.7 (d, ^1J(C,Y) = 62 Hz, C−Y), 164.4 (CO), 161.1 (CO), 146.1, 142.9, 142.3, 140.0, 138.3, 138.2, 137.8, 136.8, 136.6, 136.1, 135.7, 132.1, 131.3, 130.9, 129.6, 129.1, 128.9, 128.5, 128.3, 127.6, 127.5, 127.4, 127.2, 127.0, 126.4, 126.3, 126.2, 125.4, 125.0, 124.9, 124.4, 123.,7 121.8, 120.0, 118.2 (aryl), 67.0 (CH_2N), 64.5 (free $C_6H_5CH_2NMe_2$), 59.1 (CH_2N), 45.4 (free $C_6H_5CH_2NMe_2$), 44.5 ($N(CH_3)_2$), 43.2 ($N(CH_3)_2$), 38.5 (CH_3N), 35.4 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$), 30.1 ($C(CH_3)_3$).

*(S)-[Lu{NOBIN-TPS/t-Bu}(o-$C_6H_4CH_2NMe_2$)] ((S)-**9a-Lu**).* To a mixture of (*S*)-**8a** (23.6 mg, 0.038 mmol) and [Lu(*o*-$C_6H_4CH_2NMe_2)_3$] (22.0 mg, 0.038 mmol) was added C_6D_6 (0.55 mL). The mixture was kept at room temperature for 30 min. ^1H and ^{13}C NMR spectra showed clean formation of (*S*)-**9a-Lu**, which was used directly for catalytic experiments. ^1H NMR (500 MHz, C_6D_6, 60 °C): δ 7.98 (d, ^3J(H,H) = 9.0 Hz, 1H), 7.92 (s, 1H), 7.76 (d, ^3J(H,H) = 7.8 Hz, 6H), 7.66 (d, ^3J(H,H) = 9.0 Hz, 1H), 7.62 (d, ^3J(H,H) = 8.8 Hz, 1H), 7.55 (d, ^4J(H,H) = 2.2 Hz, 1H), 7.32−7.26 (m, 6H), 7.19−6.90 (m, 20H, aryl-H), 6.86−6.78 (m, 3H), 6.64 (d, ^3J(H,H) = 7.3 Hz, 1H), 6.48 (d, ^3J(H,H) = 7.3 Hz, 1H), 4.57 (d, ^2J(H,H) = 12.2 Hz, 1H, CH_2N), 3.69 (d, ^2J(H,H) = 12.2 Hz, 1H, CH_2N), 3.62 (d, ^2J(H,H) = 13.7 Hz, 1H, *o*-$C_6H_4CH_2NMe_2$), 3.24 (s, 4H, free $C_6H_5NCH_2NMe_2$), 2.88 (d, ^2J(H,H) = 13.7 Hz, 1H, *o*-$C_6H_4CH_2NMe_2$), 2.44 (s, 3H, NCH_3), 2.06 (s, 12 H, free $C_6H_5CH_2NMe_2$), 1.75 (s, 3H, *o*-$C_6H_4CH_2NMe_2$), 1.46 (s, 9 H, $C(CH_3)_3$), 1.42 (s, 9H, $C(CH_3)_3$), 1.31 (s, 3H, *o*-$C_6H_4CH_2NMe_2$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 187.5 (C−Lu), 165.0 (CO), 161.5 (CO), 146.2, 143.0, 140.0, 139.7, 138.3, 137.8, 136.8, 136.7, 136.2, 132.1, 130.6, 129.6, 129.1, 128.93, 128.87, 128.5, 128.4, 128.3, 127.9, 127.7, 127.4, 120.1, 118.3 (aryl), 66.2 (CH_2N), 64.5 (free $C_6H_5CH_2NMe_2$), 59.2 (CH_2N), 45.4 (free $C_6H_5CH_2NMe_2$), 44.8 ($N(CH_3)_2$), 43.6 ($N(CH_3)_2$), 38.6 (CH_3N), 35.3 ($C(CH_3)_3$), 34.2 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$), 30.7 ($C(CH_3)_3$).

*(S)-[Y{NOBIN-TPS/$SiPh_2$Me}(o-$C_6H_4CH_2NMe_2$)] ((S)-**9b-Y**).* To a mixture of (*S*)-**8b** (29.0 mg, 0.033 mmol) and [Y(*o*-$C_6H_4CH_2NMe_2)_3$] (16.3 mg, 0.033 mmol) was added C_6D_6 (0.55 mL). The mixture was kept at room temperature for 30 min. ^1H and ^{13}C NMR spectra showed clean formation of (*S*)-**9b-Y**, which was used directly for catalytic experiments. ^1H NMR (500 MHz, C_6D_6, 60 °C): δ 7.94 (d, ^3J(H,H) = 9.0 Hz, 1H), 7.76 (d, ^3J(H,H) = 7.8 Hz, 6H), 7.53−6.57 (m, 40H), 6.54 (m, 2H, aryl-H), 4.47 (d, ^2J(H,H) = 12.2 Hz, 1H, CH_2N), 3.78 (d, ^2J(H,H) = 12.2 Hz, 1H, CH_2N), 3.21 (s, 4H, free $C_6H_5NCH_2NMe_2$), 2.70 (d, ^2J(H,H) = 13.7 Hz, 1H, *o*-$C_6H_4CH_2NMe_2$), 2.47 (s, 3H, NCH_3), 2.32 (d, ^2J(H,H) = 13.7 Hz, 1H, *o*-$C_6H_4CH_2NMe_2$), 2.03 (s, 12 H, free $C_6H_5CH_2NMe_2$), 1.22 (s, 3H, *o*-$C_6H_4CH_2NMe_2$), 1.04 (s, 3H, *o*-$C_6H_4CH_2NMe_2$), 0.78 (s, 3H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 179.4 (d, ^1J(C,Y) = 61 Hz, C−Y), 168.4 (CO), 164.6 (CO), 146.5, 143.0, 140.4, 140.0, 139.0, 138.1, 137.72, 137.67, 137.03, 136.98, 136.9, 136.8, 136.7, 136.1, 136.0, 135.6, 135.4, 135.3, 132.0, 131.0, 129.81, 129.76, 129.3, 129.1, 129.04, 129.01, 128.54, 128.50, 128.45, 128.4, 128.1, 127.6, 127.4, 127.2, 126.5, 126.4, 126.0, 125.3, 125.2, 124.8, 124.6, 122.7, 121.8, 121.31, 120.0, 118.2 (aryl), 65.9 (CH_2N), 64.5 (free $C_6H_5CH_2NMe_2$), 58.7 (CH_2N), 45.4 (free $C_6H_5CH_2NMe_2$), 44.0 ($N(CH_3)_2$), 42.6 ($N(CH_3)_2$), 38.7 (NCH_3), 20.5 ($ArCH_3$), −1.0 ($SiCH_3$).

*(S)-[Y{NOBIN-TPS/TPS}(o-$C_6H_4CH_2NMe_2$)] ((S)-**9c-Y**).* To a mixture of (*S*)-**8c** (23.4 mg, 0.025 mmol) and [Y(*o*-$C_6H_4CH_2NMe_2)_3$] (12.3 mg, 0.025 mmol) was added C_6D_6 (0.55 mL). The mixture was kept at room temperature for 30 min. ^1H and ^{13}C NMR spectra showed clean formation of (*S*)-**9c-Y**, which was used directly for catalytic experiments. ^1H NMR (500 MHz, C_6D_6, 65 °C): δ 7.98 (s, 1H), 7.86 (d, ^3J(H,H) =

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9.3 Hz, 1H), 7.72 (d, ^3J(H,H) = 7.8 Hz, 6H), 7.69 (m, 2H), 7.60 (d ^3J(H,H) = 7.8 Hz, 6H), 7.58 (m, 2H), 7.37 (d, ^3J(H,H) = 8.8 Hz, 2H), 7.27 (d, ^3J(H,H) = 7.1 Hz, 12H), 7.20 (m, 1H), 7.18−6.85 (m, 27H, including 10 H from free $C_6H_5CH_2NMe_2$ and 10H from C_6D_5H), 6.77 (m, 2H), 6.71 (m, 1H), 6.86−6.78 (m, 3H), 6.57 (d, ^3J(H,H) = 8.3 Hz, 1H), 6.47 (d, ^3J(H,H) = 7.3 Hz, 1H, aryl), 4.42 (d, ^2J(H,H) = 12.7 Hz, 1H, CH_2N), 4.26 (d, ^2J(H,H) = 12.7 Hz, 1H, CH_2N), 3.24 (s, 4H, free $C_6H_5NCH_2NMe_2$), 2.75 (d, ^2J(H,H) = 13.9 Hz, 1H, o-$C_6H_4CH_2NMe_2$), 2.66 (s, 3H, NCH_3), 2.49 (d, ^2J(H,H) = 13.7 Hz, 1H, o-$C_6H_4CH_2NMe_2$), 2.07 (3H, CH_3C), 2.06 (s, 12 H, free $C_6H_5CH_2NMe_2$), 0.86 (br s, 6H, o-$C_6H_4CH_2NMe_2$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 179.9 (d, ^1J(C,Y) = 60 Hz, C−Y), 168.3 (CO), 164.9 (CO), 146.6, 143.0, 141.0, 140.0, 138.4, 137.6, 136.93, 136.87, 136.81, 136.75, 135.6, 135.4, 131.8, 130.8, 130.7, 129.7, 129.3, 129.1, 128.5, 128.3, 128.1, 127.9, 127.5, 127.4, 127.2, 126.7, 126.5, 125.9, 125.5, 125.2, 125.7, 124.6, 123.7, 121.9, 120.4, 120.3, 118.1 (aryl), 66.5 (CH_2N), 64.5 (free $C_6H_5CH_2NMe_2$), 58.9 (CH_2N), 45.4 (free $C_6H_5CH_2NMe_2$), 43.0 ($N(CH_3)_2$), 42.9 ($N(CH_3)_2$), 39.4 (CH_3N), 20.6 (CH_3C).

*(S)-[Lu{NOBIN-TPS/TPS}(o-$C_6H_4CH_2NMe_2$)] ((S)-**9c-Lu**).* To a mixture of (*S*)-**8c** (23.4 mg, 0.025 mmol) and [Lu(o-$C_6H_4CH_2NMe_2)_3$] (14.3 mg, 0.025 mmol) was added C_6D_6 (0.55 mL). The mixture was kept at room temperature for 30 min. ^1H and ^{13}C NMR spectra showed clean formation of (*S*)-**9c-Lu**, which was used directly for catalytic experiments. ^1H NMR (300 MHz, C_6D_6,): δ 8.04 (s, 1H), 7.92−7.82 (br m, 2H), 7.74 (d, ^3J(H,H) = 8.0 Hz, 6H), 7.67 (br s, 1H) 7.64−7.58 (m, 7H), 7.41 (d, ^3J(H,H) = 6.8 Hz, 1H), 7.32−7.25 (m, 5H), 7.18−7.03 (m, 15H), 6.96−6.91 (m, 12H), 6.88−6.82 (m, 2H), 6.80−6.76 (m, 2H), 6.61 (d, ^3J(H,H) =7.9 Hz, 2H), 6.48−6.46 (m, 2H, aryl-H), 4.48 (br s, 1H, CH_2), 4.22 (br s, 1H, CH_2), 3.23 (s, 4H, free $C_6H_5CH_2NMe_2$), 2.95 (br s, 1H, o-$C_6H_4CH_2NMe_2$), 2.72 (s, 3H, NCH_3), 2.38 (d, ^2J(H,H) = 13.2 Hz, 1H, o-$C_6H_4CH_2NMe_2$), 2.07 (s, 3H, $ArCH_3$), 2.02 (s, 12H, free $C_6H_5CH_2NMe_2$), 1.00 (s, 3H, o-$C_6H_4CH_2NMe_2$), 0.55 (s, 3H, o-$C_6H_4CH_2NMe_2$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 187.5 (C−Lu), 167.4, 165.2, 147.2, 147.0, 143.2, 142.5, 141.0, 139.9, 139.8, 139.3, 137.81, 136.76, 136.5, 132.0, 129.5, 129.2, 129.0, 128.9, 128.3, 127.3, 127.0, 127.3, 126.8, 126.1, 125.6, 125.3, 125.1, 124.9, 124.7, 122.8, 120.9, 120.2, 118.0 (aryl), 65.4 (CH_2N), 64.5 (free $C_6H_5CH_2NMe_2$), 46.1 ($N(CH_3)_2$), 45.3 (free $C_6H_5CH_2NMe_2$), 43.0 ($N(CH_3)_2$), 20.4 ($ArCH_3$).

*(R)-[Y{NOBIN-TPS/Si(Xylyl)$_3$}(o-$C_6H_4CH_2NMe_2$)] ((R)-**9d-Y**).* To a mixture of (*R*)-**8d** (30.8 mg, 0.030 mmol) and [Y(o-$C_6H_4CH_2NMe_2)_3$] (14.8 mg, 0.030 mmol) was added C_6D_6 (0.55 mL). The mixture was kept at 60 °C for 3 h. ^1H and ^{13}C NMR spectra showed clean formation of (*R*)-**9d-Y**, which was used directly for catalytic experiments. ^1H NMR (400 MHz, C_6D_6): δ 8.03 (s, 1H), 8.01 (d, ^3J(H,H) = 9.0 Hz, 1H), 7.77 (d, ^3J(H,H) = 9.3 Hz, 1H), 7.69 (d, ^3J(H,H) = 8.0 Hz, 6H), 7.65 (d, ^3J(H,H) = 8.3 Hz, 1H), 7.55 (s, 6H), 7.53 (m, 1H), 7.39 (br s, 1H), 7.35 (d ^3J(H,H) = 7.8 Hz, 1H), 7.31 (d ^3J(H,H) = 7.8 Hz, 3H), 7.19−7.01 (m, 14H, including 10H from $C_6H_5CHNMe_2$ and 1H from C_6D_5H), 6.90−6.75 (m, 13H), 6.72 (d, ^3J(H,H) = 7.6 Hz, 1H), 6.67 (d, ^3J(H,H) = 8.3 Hz, 1H, aryl-H), 5.16 (d, ^2J(H,H) = 13.0 Hz, 1H, CH_2N), 4.08 (d, ^2J(H,H) = 13.0 Hz, 1H, CH_2N), 3.37 (d, ^2J(H,H) = 13.7 Hz, 1H, o-$C_6H_4CH_2NMe_2$), 3.23 (s, 4H, free $C_6H_5NCH_2NMe_2$), 2.84 (s, 3H, NCH_3), 2.29 (d, ^2J(H,H) = 13.7 Hz, 1H, o-$C_6H_4CH_2NMe_2$), 2.08 (3H, $ArCH_3$), 2.06 (s, 12 H, free $C_6H_5CH_2NMe_2$), 1.97 (s, 18H, 6 $ArCH_3$), 1.15 (s, 3H, o-$C_6H_4CH_2NMe_2$), 0.45 (s, 3H, o-$C_6H_4CH_2NMe_2$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 179.5 (d, ^1J(C,Y) = 61 Hz, C−Y), 168.1 (CO), 164.0 (CO), 146.9, 143.3, 143.0, 141.4, 140.0, 139.0, 138.0, 137.3, 137.2, 136.7, 136.6, 135.7, 135.6, 134.8, 132.4, 131.4, 130.4, 129.4, 129.1, 128.9, 128.53, 128.46, 128.3, 128.2, 127.9, 127.2, 126.7, 126.4, 126.3, 125.7, 125.4, 125.3, 124.8, 123.6, 122.0, 121.4, 120.0, 117.1 (aryl), 66.8 (CH_2N), 64.5 (free $C_6H_5CH_2NMe_2$), 58.4 (CH_2N), 45.4 (free $C_6H_5CH_2NMe_2$), 42.7 ($N(CH_3)_2$), 42.5 ($N(CH_3)_2$), 40.2 (NCH_3), 21.4 (6 $ArCH_3$), 20.6 ($ArCH_3$).

*(R)-[Lu{NOBIN-TPS/Si(Xylyl)$_3$}(o-$C_6H_4CH_2NMe_2$)] ((R)-**9d-Lu**).* To a mixture of (*R*)-**8d** (30.8 mg, 0.030 mmol) and [Lu(o-$C_6H_4CH_2NMe_2)_3$] (16.0 mg, 0.030 mmol) was added C_6D_6 (0.55 mL). The mixture was kept at room temperature for 1 h. ^1H and ^{13}C NMR spectra showed clean formation of (*R*)-**9d-Lu**, which was used directly for catalytic experiments. ^1H NMR (500 MHz, C_6D_6): δ 8.07 (s, 1H), 8.06 (m, 1H), 7.76 (d, ^3J(H,H) = 9.1 Hz, 1H), 7.71 (d, ^3J(H,H) = 7.3 Hz, 6H), 7.62 (d, ^3J(H,H) = 8.3 Hz, 1H), 7.57 (s, 6H), 7.44 (m, 1H), 7.32 (d ^3J(H,H) = 8.1 Hz, 6H), 7.21−7.01 (m, 15H including 10H from $C_6H_5CHNMe_2$ and 2H from C_6D_5H), 6.90−6.75 (m, 14H), 6.64 (d, ^3J(H,H) = 8.3 Hz, 1H, aryl-H), 5.20 (br s, 1H, CH_2N), 3.93 (br s, 1H, CH_2N), 3.55 (br s, 1H, o-$C_6H_4CH_2NMe_2$), 3.22 (s, 4H, free $C_6H_5NCH_2NMe_2$), 2.88 (s, 3H, NCH_3), 2.19 (d, ^2J(H,H) = 14.7 Hz, 1H, o-$C_6H_4CH_2NMe_2$), 2.08 (3H, $ArCH_3$), 2.04 (s, 12 H, free $C_6H_5CH_2NMe_2$), 1.97 (s, 18H, 6 $ArCH_3$), 1.23 (s, 3H, o-$C_6H_4CH_2NMe_2$), 0.35 (s, 3H, o-$C_6H_4CH_2NMe_2$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 187.2 (C−Lu), 168.5 (CO), 164.5 (CO), 147.1, 143.1, 142.9, 141.5, 140.3, 140.0, 137.9, 137.2, 136.8, 136.5, 135.9, 135.6, 134.8, 132.4, 131.5, 130.2, 129.4, 129.1, 128.8, 128.54, 128.47, 128.3, 127.7, 127.6, 127.2, 126.9, 125.7, 124.9, 122.0, 120.0 (aryl), 65.8 (CH_2N), 64.5 (free $C_6H_5CH_2NMe_2$), 58.1 (CH_2N), 45.4 (free $C_6H_5CH_2NMe_2$), 42.8 ($N(CH_3)_2$), 42.5 ($N(CH_3)_2$), 40.3 (NCH_3), 21.4 (6 $ArCH_3$), 20.6 ($ArCH_3$).

*(S)-[Y{NOBIN-TPS/TBDPS}(o-$C_6H_4CH_2NMe_2$)] ((S)-**9e-Y**).* To a mixture of (*S*)-**8e** (27.5 mg, 0.030 mmol) and [Y(o-$C_6H_4CH_2NMe_2)_3$] (14.8 mg, 0.030 mmol) was added C_6D_6 (0.55 mL). The mixture was kept at 60 °C for 1 h. The ^1H and ^{13}C NMR spectra showed clean formation of (*S*)-**9e-Y**, which was used directly for catalytic experiments. ^1H NMR (400 MHz, C_6D_6, 70 °C): δ 7.95 (s, 1H), 7.76−7.71 (m, 7H), 7.61 (d, ^3J(H,H) = 7.0 Hz, 2H), 7.58 (d, ^4J(H,H) = 2.4 Hz, 1H), 7.52 (m, 3H), 7.47 (d, ^3J(H,H) = 9.4 Hz, 1H), 7.40 (d, ^3J(H,H) = 8.6 Hz, 1H), 7.36 (d, ^3J(H,H) = 7.4 Hz, 1H), 7.27 (d, ^3J(H,H) = 7.4 Hz, 4H), 7.15−6.83 (m, 34H, including 10H from free $PhCH_2NMe_2$), 6.82 (d, ^4J(H,H) = 2.1 Hz, 1H), 6.57 (d, ^3J(H,H) = 8.2 Hz, 1H), 6.43 (d, ^3J(H,H) = 7.4 Hz, 1H, aryl-H), 4.34 (d, ^2J(H,H) = 13.3 Hz, 1H, $ArCH_2N$), 4.19 (d, ^2J(H,H) = 13.3 Hz, 1H, $ArCH_2N$), 3.24 (s, 4H, free $C_6H_5NCH_2NMe_2$), 2.56 (s, 3H, $ArCH_2NMe$), 2.55 (d, ^2J(H,H) = 14.1 Hz, 1H, o-$C_6H_4CH_2NMe_2$), 2.48 (d, ^2J(H,H) = 14.1 Hz, 1H, o-$C_6H_4CH_2NMe_2$), 2.20 (s, 3H, $ArCH_3$), 2.06 (s, 12 H, free $C_6H_5CH_2NMe_2$), 1.10 (s, 9H, $C(CH_3)_3$), 0.94 (br s, 6H, o-$C_6H_4CH_2NMe_2$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 180.3 (d, ^1J(C,Y) = 59 Hz, C−Y), 168.0, 166.1, 146.3, 143.0, 140.2, 140.0, 138.9, 137.3, 137.2, 136.85, 136.81, 136.79, 136.3, 134.9, 131.2, 131.1, 129.7, 129.1, 129.0, 128.6, 128.53, 128.45, 128.4, 128.29, 128.26, 127.9, 127.4, 127.2, 126.9, 126.3, 125.7, 124.8, 124.7, 124.4, 124.3, 121.8, 120.7, 120.5, 118.6 (aryl), 66.5 (o-$C_6H_4CH_2NMe_2$), 64.5 (free $C_6H_5CH_2NMe_2$), 58.6 (NCH_3), 45.4 (free $C_6H_5CH_2NMe_2$), 43.5 (o-$C_6H_4CH_2NMe_2$), 43.1 (o-$C_6H_4CH_2NMe_2$), 38.9 (NCH_3), 29.8 ($C(CH_3)_3$), 20.7 ($ArCH_3$), 19.3 ($C(CH_3)_3$).

*(S)-[Lu{NOBIN-TPS/TBDPS}(o-$C_6H_4CH_2NMe_2$)] ((S)-**9e-Lu**).* To a mixture of (*S*)-**8e** (27.5 mg, 0.030 mmol) and [Lu(o-$C_6H_4CH_2NMe_2)_3$] (17.8 mg, 0.030 mmol) was added C_6D_6 (0.55 mL). The mixture was kept at 60 °C for 30 min. ^1H NMR (500 MHz, C_6D_6): δ 8.00 (s, 1H), 7.75 (d, ^3J(H,H) = 9.3 Hz, 6H), 7.67−7.64 (m, 3H), 7.60 (d, ^3J(H,H) = 9.0 Hz, 1H), 7.53−7.40 (m, 4H), 7.31−7.25 (m, 5H), 7.17−6.99 (m, 24H, including 10H from free $PhCH_2NMe_2$), 6.83−6.76 (m, 5H), 6.56 (d, ^3J(H,H) = 7.3 Hz, 1H), 6.43 (br s, 1H), 4.3 (br s 2H, $ArCH_2N$), 3.22 (s, 4H, free $C_6H_5NCH_2NMe_2$), 2.64−2.56 (m, 4H, $ArCH_2NMe$ and o-$C_6H_4CH_2NMe_2$), 2.50 (d, ^2J(H,H) = 13.5 Hz, 1H, o-$C_6H_4CH_2NMe_2$), 2.22 (s, 3H, $ArCH_3$), 2.05 (s, 12 H, free $C_6H_5CH_2NMe_2$), 1.09 (s, 9H, $C(CH_3)_3$), 1.05 (s, 3H, o-$C_6H_4CH_2NMe_2$), 0.78 (s, 3H, o-$C_6H_4CH_2NMe_2$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 187.6 (C−Lu), 168.2, 165.4, 146.8, 143.3, 140.3, 140.0, 139.7, 137.9, 137.2, 137.0, 136.8, 136.3, 131.9, 129.7, 129.1, 129.0, 128.9, 128.7, 128.53, 128.46, 128.3, 127.6, 127.39, 127.36, 127.2, 126.6, 126.0, 125.7, 125.1, 125.0, 124.8, 121.9, 121.0, 120.4, 118.3 (aryl), 68.2 (CH_2N), 65.5 (o-$C_6H_4CH_2NMe_2$), 64.5 (free $C_6H_5CH_2NMe_2$), 45.4 (free $C_6H_5CH_2NMe_2$), 43.9 (o-$C_6H_4CH_2NMe_2$), 43.3 (o-$C_6H_4CH_2NMe_2$), 29.8($C(CH_3)_3$), 20.7 ($ArCH_3$), 19.3 ($C(CH_3)_3$).

*(S)-[Y{NOBIN-TPS/TIPS}(o-$C_6H_4CH_2NMe_2$)] ((S)-**9f-Y**).* To a mixture of (*S*)-**8f** (19.3 mg, 0.023 mmol) and [Y(o-$C_6H_4CH_2NMe_2)_3$] (11.3 mg, 0.023 mmol) was added C_6D_6 (0.52 mL). The mixture was kept at room temperature for 10 min. The ^1H and ^{13}C NMR spectra showed clean formation of (*S*)-**9f-Y**, which was used directly for catalytic experiments. ^1H NMR (500 MHz, C_6D_6, 70 °C): δ 7.95 (s, 1H), 7.91 (d, ^3J(H,H) =

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9.1 Hz, 2H), 7.75 (d, ^3J(H,H) = 7.0 Hz, 6H), 7.56 (d, ^3J(H,H) = 7.8 Hz, 1H), 7.53 (d, ^3J(H,H) = 8.6 Hz, 1H), 7.38 (d, ^3J(H,H) = 7.8 Hz, 1H), 7.32−7.25 (m, 5H), 7.17−6.86 (m, 23H, including 10H from free $PhCH_2NMe_2$), 6.67 (m, 2H), 6.57 (d, ^3J(H,H) = 7.3 Hz, 1H, aryl-H), 4.35 (d, ^2J(H,H) = 12.7 Hz, 1H, $ArCH_2N$), 3.99 (d, ^2J(H,H) = 12.7 Hz, 1H, $ArCH_2N$), 3.51 (d, ^2J(H,H) = 13.9 Hz, 1H, *o*-$C_6H_4CH_2NMe_2$), 3.25 (s, 4H, free $C_6H_5NCH_2NMe_2$), 2.87 (d, ^2J(H,H) = 13.9 Hz, 1H, *o*-$C_6H_4CH_2NMe_2$), 2.50 (s, 3H, $ArCH_2NMe$), 2.23 (s, 3H, $ArCH_3$), 2.06 (s, 12 H, free $C_6H_5CH_2NMe_2$), 1.53 (br s, 3H, *o*-$C_6H_4CH_2NMe_2$), 1.53 (br s, 3H, *o*-$C_6H_4CH_2NMe_2$), 6.57 (sept, ^3J(H,H) = 7.6 Hz, 3H, 3 $CH(CH_3)_2$), 1.10 (d, ^3J(H,H) = 7.6 Hz, 9H, 3 $CH(CH_3)_2$), 1.05 (d, ^3J(H,H) = 7.6 Hz, 9H, 3 $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 180.0 (d, ^1J(C,Y) = 58 Hz, C−Y), 167.7, 166.4, 146.0, 143.0, 140.0, 139.1, 138.2, 136.8, 136.7, 134.1, 131.9, 129.6, 129.14, 129.10, 128.54, 128.45, 127.4, 127.2, 126.9, 126.4, 126.3, 126.0, 124.9, 124.6, 124.4, 124.2, 123.8, 122.0, 121.8, 120.6, 118.4 (aryl), 67.4 (*o*-$C_6H_4CH_2NMe_2$), 64.5 (free $C_6H_5CH_2NMe_2$), 58.0 (CH_2N), 45.4 (free $C_6H_5CH_2NMe_2$), 44.0 (*o*-$C_6H_4CH_2NMe_2$), 42.9 (*o*-$C_6H_4CH_2NMe_2$), 38.2 (NCH_3), 20.8 ($ArCH_3$), 19.7 ($CH(CH_3)_2$), 13.1 ($CH(CH_3)_2$).

*(S)-[Lu{NOBIN-TPS/TIPS}(o-$C_6H_4CH_2NMe_2$)] ((S)-**9f-Lu**).* To a mixture of (*S*)-**8f** (19.4 mg, 0.023 mmol) and [Lu(*o*-$C_6H_4CH_2NMe_2)_3$] (13.6 mg, 0.023 mmol) was added C_6D_6 (0.52 mL). The mixture was kept at room temperature for 30 min. The ^1H and ^{13}C NMR spectra showed clean formation of (*S*)-**9f-Lu**, which was used directly for catalytic experiments. ^1H NMR (400 MHz, C_6D_6, 70 °C): δ 7.95 (s, 1H), 7.91 (d, ^3J(H,H) = 9.1 Hz, 2H), 7.75 (d, ^3J(H,H) = 7.0 Hz, 6H), 7.56 (d, ^3J(H,H) = 7.8 Hz, 1H), 7.53 (d, ^3J(H,H) = 8.6 Hz, 1H), 7.38 (d, ^3J(H,H) = 7.8 Hz, 1H), 7.32−7.25 (m, 5H), 7.17−6.86 (m, 23H, including 10H from free $PhCH_2NMe_2$), 6.67 (m, 2H), 6.57 (d, ^3J(H,H) = 7.3 Hz, 1H, aryl-H), 4.35 (d, ^2J(H,H) = 12.7 Hz, 1H, $ArCH_2N$), 3.99 (d, ^2J(H,H) = 12.7 Hz, 1H, $ArCH_2N$), 3.51 (d, ^2J(H,H) = 13.9 Hz, 1H, *o*-$C_6H_4CH_2NMe_2$), 3.24 (s, 4H, free $C_6H_5NCH_2NMe_2$), 2.87 (d, ^2J(H,H) = 13.9 Hz, 1H, *o*-$C_6H_4CH_2NMe_2$), 2.50 (s, 3H, $ArCH_2NMe$), 2.23 (s, 3H, $ArCH_3$), 2.05 (s, 12 H, free $C_6H_5CH_2NMe_2$), 1.53 (br s, 3H, *o*-$C_6H_4CH_2NMe_2$), 1.53 (br s, 3H, *o*-$C_6H_4CH_2NMe_2$), 6.57 (sept, ^3J(H,H) = 7.6 Hz, 3H, 3 $CH(CH_3)_2$), 1.10 (d, ^3J(H,H) = 7.6 Hz, 9H, 3 $CH(CH_3)_2$), 1.05 (d, ^3J(H,H) = 7.6 Hz, 9H, 3 $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 187.5 (C−Lu), 168.4, 165.7, 146.3, 143.1, 140.0, 139.8, 138.6, 137.7, 136.83, 136.77, 136.0, 133.9, 131.8, 130.7, 129.6, 129.1, 128.9, 128.5, 127.94, 127.88, 127.6, 127.41, 127.4, 127.2, 126.3, 126.2, 126.1, 125.28, 125.25, 124.93, 124.86, 122.3, 121.9, 120.1 (aryl), 66.1 (*o*-$C_6H_4CH_2NMe_2$), 64.5 (free $C_6H_5CH_2NMe_2$), 58.5 (CH_2N), 45.4 (free $C_6H_5CH_2NMe_2$), 43.8 (*o*-$C_6H_4CH_2NMe_2$), 43.4 (*o*-$C_6H_4CH_2NMe_2$), 38.6 (NCH_3), 20.8 ($ArCH_3$), 19.6 ($CH(CH_3)_2$), 19.5 ($CH(CH_3)_2$), 13.1 ($CH(CH_3)_2$).

*(S)-[Y{NOBIN-SiPh$_2$Me/t-Bu}(o-$C_6H_4CH_2NMe_2$)] ((S)-**9g-Y**).* To a mixture of (*S*)-**8g** (26.5 mg, 0.037 mmol) and [Y(*o*-$C_6H_4CH_2NMe_2)_3$] (18.2 mg, 0.037 mmol) was added C_6D_6 (0.55 mL). The mixture was kept at room temperature for 3 h. ^1H and ^{13}C NMR spectra showed clean formation of (*S*)-**9g-Y**, which was used directly for catalytic experiments. ^1H NMR (500 MHz, C_6D_6, 65 °C): δ 8.03 (d, ^3J(H,H) = 9.1 Hz, 1H), 7.87 (s, 1H), 7.69−7.60 (m, 6H), 7.53 (d, ^4J(H,H) = 2.4 Hz, 1H), 7.43 (d, ^3J(H,H) = 8.6 Hz, 1H), 7.34−6.98 (m, 26H, including 10H from free $PhCH_2NMe_2$), 6.91 (d, ^4J(H,H) = 2.4 Hz, 1H), 6.84 (m, 2H), 6.66 (d, ^3J(H,H) = 7.3 Hz, 1H), 6.44 (m, 1H aryl-H), 4.46 (d, ^2J(H,H) = 12.5 Hz, 1H, CH_2N), 3.83 (d, ^2J(H,H) = 13.9 Hz, 1H, *o*-$C_6H_4CH_2NMe_2$), 3.69 (d, ^2J(H,H) = 12.5 Hz, 1H, CH_2N), 3.25 (s, 4H, free $C_6H_5NCH_2NMe_2$), 2.92 (d, ^2J(H,H) = 13.9 Hz, 1H, *o*-$C_6H_4CH_2NMe_2$), 2.23 (br s, 3H, *o*-$C_6H_4CH_2NMe_2$), 2.16 (br s, 3H, NCH_3), 2.05 (s, 12 H, free $C_6H_5CH_2NMe_2$), 1.58 (s, 9H, $C(CH_3)_3$), 1.40 (s, 9H, $C(CH_3)_3$), 0.98 (s, 3H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 179.9 (d, ^1J(C,Y) = 57 Hz, C−Y), 164.5 (CO), 161.0 (CO), 146.2, 141.7, 141.6, 140.0, 138.9, 138.4, 138.2, 137.6, 136.0, 135.7, 132.1, 131.9, 131.0, 129.6, 129.2, 129.1, 128.9, 127.2, 127.0, 126.6, 126.2, 125.6, 124.9, 124.7, 124.4, 123.7, 121.7, 120.3, 117.1 (aryl), 67.3 (CH_2N), 64.5 (free $C_6H_5CH_2NMe_2$), 58.3 (CH_2N), 45.4 (free $C_6H_5CH_2NMe_2$), 42.9 ($N(CH_3)_2$), 38.8 (NCH_3), 35.4($C(CH_3)_3$), 34.2 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$), 30.3 ($C(CH_3)_3$), −1.7 ($SiCH_3$).

*(S)-[Y{NOBIN-SiPh$_2$Me/SiPh$_2$Me}(o-$C_6H_4CH_2NMe_2$)] ((S)-**9h-Y**).* To a mixture of (*S*)-**8h** (38.9 mg, 0.048 mmol) and [Y(*o*-$C_6H_4CH_2NMe_2)_3$] (23.7 mg, 0.048 mmol) was added C_6D_6 (0.55 mL). The mixture was kept at 50 °C for 40 min. ^1H and ^{13}C NMR spectra showed clean formation of (*S*)-**9h-Y**, which was used directly for catalytic experiments. ^1H NMR (500 MHz, C_6D_6, 65 °C): δ 8.03 (d, ^3J(H,H) = 9.0 Hz, 1H), 7.93 (s, 1H), 7.14−7.70 (m, 6H), 7.65 (m, 4H), 7.58 (d, ^3J(H,H) = 6.6 Hz, 1H), 7.51 (m, 1H), 7.42−7.38 (m, 3H), 7.31−6.99 (m, 30H, including 10H from free $PhCH_2NMe_2$), 6.88 (m, 2H), 6.83 (d, ^4J(H,H) = 2.2 Hz, 1H), 6.62 (d, ^3J(H,H) = 7.3 Hz, 1H), 6.47 (m, 1H, aryl-H), 4.62 (d, ^2J(H,H) = 12.7 Hz, 1H, CH_2N), 3.87 (d, ^2J(H,H) = 12.7 Hz, 1H, CH_2N), 3.29 (s, 4H, free $C_6H_5NCH_2NMe_2$), 3.11 (d, ^2J(H,H) = 13.9 Hz, 1H, *o*-$C_6H_4CH_2NMe_2$), 2.52 (d, ^2J(H,H) = 13.9 Hz, 1H, *o*-$C_6H_4CH_2NMe_2$), 2.35 (s, 3H, NCH_3), 2.10 (s, 12 H, free $C_6H_5CH_2NMe_2$), 2.08 (s, 3H, *o*-$C_6H_4CH_2NMe_2$), 1.55 (s, 3H, *o*-$C_6H_4CH_2NMe_2$), 1.09 (s, 3H, $SiCH_3$), 1.07 (s, 3H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 179.4 (d, ^1J(C,Y) = 61 Hz, C−Y), 168.2 (CO), 164.4 (CO), 146.5, 141.7, 141.6, 140.2, 140.0, 138.8, 138.6, 138.2, 137.8, 137.4, 137.3, 136.1, 136.0, 135.9, 135.7, 135.6, 135.3, 135.2, 132.1, 131.0, 129.8, 129.6, 129.3, 129.2, 129.1, 128.9, 128.5, 128.3, 127.7, 127.3, 127.2, 125.5, 125.4, 124.8, 124.7, 122.6, 121.9, 121.7, 120.1, 117.1 (aryl), 66.3 (CH_2N), 64.5 (free $C_6H_5CH_2NMe_2$), 57.9 (CH_2N), 45.4 (free $C_6H_5CH_2NMe_2$), 42.4 ($N(CH_3)_2$), 39.0 (NCH_3), 20.5 ($ArCH_3$), −0.8 ($SiCH_3$), −2.1 ($SiCH_3$).

Typical Procedure for Intermolecular Hydroamination Reactions.[10b] In the glovebox, a screw-cap NMR tube was charged with an appropriate amine (0.2 mmol), alkene (3 mmol), and a solution of the catalyst (0.1 M in C_6D_6, 0.1 mL, 10.0 μmol, 5 mol %). The tube was then sealed, removed from the glovebox, and placed into the thermostated oil bath. The progress of the reaction was monitored by ^1H NMR spectroscopy. After completion of the reaction, the mixture was concentrated in vacuo and purified by column chromatography on a 3 cm height pad of silica or alumina.

*(R)-N-Benzylheptan-2-amine (**17a**).*[31] Prepared from 1-heptene and benzylamine according to Table 4, entry 1. Purified by column chromatography on alumina (hexanes/EtOAc 100/0.6). Yield 62%; colorless oil, 36% ee. ^1H NMR (400 MHz, $CDCl_3$): δ 7.33−7.30 (m, 4H, aryl-H), 7.25−7.21 (m, 1H, aryl-H), 3.82 (d, ^2J(H,H) = 13.0 Hz, 1H, $PhCH_2NH$), 3.73 (d, ^2J(H,H) = 13.0 Hz, 1H, $PhCH_2NH$), 2.68 (sext, ^3J(H,H) = 6.2 Hz, 1H, CHNH), 1.50−1.41 (m, 1H, CH_2) 1.34−1.23 (m, 8H, CH_2 and NH), 1.07 (d, ^3J(H,H) = 6.2 Hz, 3H, CH_3CHNH), 0.89 (t, ^3J(H,H) = 6.9 Hz, 3H; CH_3CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 140.9 (C_{ipso}), 128.4, 128.1, 126.8 (aryl), 52.5 ($CH(CH_3)$-NH), 51.4 (CH_2NH), 37.1 (CH_2), 32.1 (CH_2), 25.7 (CH_2), 22.7 (CH_2), 20.3 (CH_3CHNH), 14.1 (CH_3CH_2).

*(R)-N-Benzyl-4-phenylbutan-2-amine (**17b**).*[31] Prepared from 4-phenyl-1-butene and benzylamine according to Table 4, entry 8. Purified by column chromatography on silica (CH_2Cl_2/7 M NH_3 in MeOH 100/1). Yield 52%; colorless oil, 40% ee. ^1H NMR (500 MHz, $CDCl_3$,): δ 7.34−7.22 (m, 7H), 7.19−7.16 (m, 3H, aryl-H), 3.82 (d, ^2J(H,H) = 13.0 Hz, 1H, $PhCH_2NH$), 3.73 (d, ^2J(H,H) = 12.9 Hz, 1H, $PhCH_2NH$), 2.69 (sext, ^3J(H,H) = 6.3 Hz, 1H, CHNH), 2.70−2.61 (m, 2H), 1.85−1.78 (m, 1H), 1.71−1.64 (m, 1H), 1.49 (br s, 1H, NH), 1.14 (d, ^3J(H,H) = 6.4 Hz, 3H, CH_3CHNH). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 142.5 (C_{quart}), 140.8 (C_{quart}), 128.35, 128.32, 128.30. 128.1, 126.8, 125.7 (aryl), 52.0 ($CH(CH_3)NH$), 51.3 (CH_2NH), 38.7 (CH_2), 32.3 (CH_2), 20.4 (CH_3).

Determination of Enantiomeric Excess via Chiral HPLC. *N-benzoylation of Isolated Hydroamination Product.* The hydroamination product (0.1 mmol) was dissolved in CH_2Cl_2 (1 mL), and then DIPEA (26 mg, 0.2 mmol) and benzoyl chloride (21 mg, 0.15 mmol) were added. The mixture was stirred at room temperature for 3 h. Volatiles were removed in vacuo, and the residue was partitioned between Et_2O (2 mL) and 2 M NaOH (2 mL). The resulting emulsion was stirred for 2 h, and then the organic layer was separated, washed with brine (1 mL), dried (Na_2SO_4), and concentrated. The residue was purified by flash chromatography on silica (CH_2Cl_2), if necessary, or was directly subjected to a chiral HPLC analysis. Absolute configurations of intra-[13d] and intermolecular[10b] hydroamination products were assigned

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according to ^{19}F NMR spectroscopic analysis of the corresponding Mosher amides as described previously.

N-(1-Methylhexyl)benzamide. Prepared from **17a**. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 65 °C): δ 7.52−7.16 (m, 10H, aryl-H), 4.87 (d, ^{2}J(H,H) = 15.2 Hz, 1H, CHN), 4.45 (d, ^{2}J(H,H) = 15.2 Hz, 1H, CHN), 3.94 (br s, 1H, CHN), 1.56 (br s, 1H), 1.31−1.05 (br s, 10H), 0.82 (m, 4H). A ^{13}C NMR spectrum could not be acquired, as signals are very broad and obscure due to rotamer interconversion. HPLC (AS-H, hexane/2-propanol 90/10, 1 mL/min): t_R 13.3 min (*R* isomer), 22.3 min (*S* isomer).

N-(1-Methyl-3-phenylpropyl)benzamide. Prepared from **17b**. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 65 °C): δ 8.10 (d, ^{3}J(H,H) = 7.8 Hz, 1H), 7.60−6.96 (m, 14H, aryl-H), 4.71 (br s, 1H, CHN), 4.58 (d, ^{2}J(H,H) = 14.5 Hz, 1H, CHN), 2.49 (br s, 2H), 1.99 (br s, 1H), 1.17 (br s, 1H), 1.19 (d, ^{3}J(H,H) = 12.3 Hz, 3H, CH_3). A ^{13}C NMR spectrum could not be acquired, as signals are very broad and obscure due to rotamer interconversion. HPLC (AS-H, hexane/2-propanol 90/10, 1 mL/min): t_R 25.5 min (*R* isomer), 45.5 min (*S* isomer).

N-Benzoyl-2-methyl-4,4-diphenylpyrrolidine.[33] Prepared from **11a**. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, 65 °C): δ 7.45−7.04 (m, 15H, aryl-H), 4.26−4.15 (m, 2H), 3.86 (br s, 1H), 2.93 (br s, 1H), 2.34 (m, 1H), 1.44 (br m, 3H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 65 °C): δ 170.0 (CO), 145.6, 137.5, 128.6, 128.5, 128.4, 126.8, 126.63, 126.56 (aryl), 59.6, 52.7, 45.8, 30.7, 20.0 (CH_3). HPLC (OD-H, hexane/2-propanol 90/10, 1 mL/min): t_R 13.0 min (*S* isomer), 21.9 min (*R* isomer).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra of ligand precursors, ligands, and complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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