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Anti-Markovnikov Hydroamination of Aromatic Alkenes with Secondary Amines Catalyzed by Easily Accessible Yttrium Complexes

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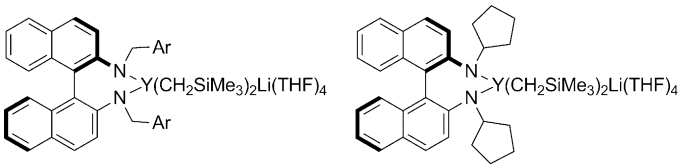
Binaphthylamido alkyl yttrium complexes have been proven to promote the anti-Markovnikov addition between various styrene derivatives and secondary amines efficiently. Although the reaction has to be performed at high temperature, it is realized advantageously with a 1:2 amine/alkene molar ratio to deliver the hydroamination product in a satisfactory isolated yield. Furthermore, the reaction with 2-vinylpyridine proceeds at room temperature within a few minutes with a low catalyst loading of 1 mol%. The procedure has been extended to a tandem intermolecular anti-Markovnikov–intramolecular Markovnikov hydroamination for which the chiral precatalyst delivered the targeted product in up to 85% yield and 48% enantiomeric excess.

Introduction

The direct addition reaction of the amine across a C=C bond, the so-called hydroamination reaction, is one of the more elegant and most atom economical methods for the formation of value-added N-containing compounds from relatively inexpensive and ubiquitous amines and alkenes.[1] Over the years, considerable effort has been devoted to the development of catalytic systems mainly for the selective intra-[2] or intermolecular[3] Markovnikov hydroamination reaction of alkenes and significant progress has been achieved in terms of activities, stereoselectivities, and scope of applications.[4] Conversely, and despite the industrial relevance of the products formed,[1] little work deals with catalytic systems that exhibit anti-Markovnikov regioselectivity.[5,6] Only a few metal systems based on either alkali,[6a,b] alkaline,[6c–f] rare-earth,[6g,h] or late transition metals[6i–m] or to a lower extent some metal-free systems[6n] have sporadically demonstrated such a regioselectivity with the scope of alkenes limited to vinylarene derivatives, such as styrene. To the best of our knowledge, there is no report of the direct anti-Markovnikov addition of amines on simple aliphatic alkenes.[7] This underlines the challenge related to the development of catalytic systems that display anti-Markovnikov reactivity.

Our group has recently reported the in situ preparation of chiral binaphthylamido alkyl yttrium complexes, such as **1** (Figure 1), and their successful use as highly active precatalysts for the intramolecular, enantioselective Markovnikov hydroamination of primary and secondary amines.[8] In this paper, we disclose our studies towards the applications of these systems in the more challenging intermolecular hydroamination reaction of alkenes. The reaction development and exploration of the substrate scope, described herein, demonstrate the efficiency of **1** as precatalysts for the highly selective, intermolecular anti-Markovnikov hydroamination of styrene derivatives and 2-vinylpyridine with secondary amines. Complex **1** has also the ability to catalytically promote a tandem[9] intermolecular anti-Markovnikov–intramolecular Markovnikov hydroamination reaction sequence. This work completes the rare contributions of rare-earth-based catalysts that display intermolecular anti-Markovnikov selectivity.[6g,h]



1a Ar = phenyl
1b Ar = 2-OMe-C_6H_4
1c Ar = 2,4,6-Me_3-C_6H_2
1d Ar = 9-anthryl

1e

Figure 1. Chiral binaphthylamido alkyl yttrium complexes.

Results and Discussion

Preliminary experiments were conducted to investigate the reaction between primary amines and simple aliphatic alkenes. Catalyst **1a** was thus engaged (10 mol%, 0.1 M) to test its ability to promote the intermolecular hydroamination of alkenes (pent-1-ene, hept-1-ene, and oct-1-ene) with benzylamine. The amine was first introduced in the catalyst solution followed by

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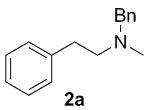
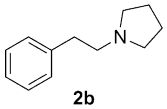
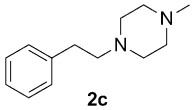
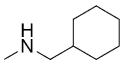
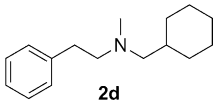
the alkene in a 15-fold excess, and the mixture was heated to 130 °C in deuterated toluene using ferrocene as an internal standard to follow the course of the reaction by NMR spectroscopy. In each case, precipitation occurred after 10 to 15 min of reaction time and no traces of any hydroamination product could be detected, even after prolonged reaction time (up to 120 h). Similar results were obtained if cyclopentylamine was used as the substrate under the same conditions. A control experiment was thus performed to evaluate the catalyst integrity under these reaction conditions. 2,2-Diphenylhex-4-enylamine was added in the same amount as benzylamine to 15 equivalents (equiv.) of pent-1-ene and allowed to react with **1a** (6 mol%) at 130 °C. Again, no hydroamination product that arises from an intermolecular process could be detected, but 2-ethyl-4,4-diphenylpyrrolidine was formed in only 49% yield (NMR). A complete conversion for the intramolecular hydroamination product should be expected under these conditions,[8] which indicates, therefore, that a partial catalyst deactivation occurred that led to its precipitation to a large extent. Other catalytic tests towards an intermolecular procedure were conducted in the presence of slightly activated alkenes such as norbornene or cyclohexa-1,3-diene. These alkenes were engaged in a 10-fold excess with benzylamine in the catalysis at 130 °C with **1a** for a prolonged reaction time without delivery of the expected products. Some hydroamination activity was, however, detected with the use of styrene as an activated alkene, for which the anti-Markovnikov product, benzylphenethylamine, could be detected as traces in the NMR spectrum. The major compound formed under these conditions issued from styrene polymerization. However, the reversal of the order of the introduction of the reagents on the catalyst influenced the course of the transformation greatly. If styrene was mixed firstly in the presence of the precatalyst before the introduction of the amine, the expected hydroamination product could be recovered in up to 50% yield (NMR). Unfortunately, these results remained not easily reproducible, and the formation of the product was always accompanied by a large amount of polymer formation and catalyst precipitation.

In an attempt to improve these results, more nucleophilic amines were then introduced and the use of secondary amines was privileged in this study. Accordingly, *N*-methylbenzylamine was reacted under the same conditions as those described for the use of primary amines with either pent-1-ene or norbornene in the presence of 10 mol% **1a** at 130 °C, but no hydroamination activity was observed. Nevertheless no precipitation occurred in these cases, which demonstrates that catalyst deactivation was negligible and could thus be ascribed conceivably to the presence of the primary amine. Delightfully, however, the reaction of *N*-methylbenzylamine with styrene (10 equiv.) delivered the expected benzylmethylphenethylamine (**2a**) with an almost complete conversion after 18 h. The only byproduct observed was polystyrene, the amount of which could be estimated by comparison with the ferrocene standard (Table 1, entry 1). The amine/alkene molar ratio could be decreased to 1:1 with these substrates (Table 1, entries 2 and 3), which allowed the preparation of the targeted product in a nearly quantitative yield free of any polystyrene after 88 h.

Table 1. Intermolecular anti-Markovnikov hydroamination reaction of styrene with secondary amines catalyzed by **1a**.

Entry[a]	Amine	Amine/alkene molar ratio	Product	*t* [h]	Conversion to hydroamination product [%][b,c]	Conversion to polymer [%][b]
1		1:10	 **2a**	5	80	10
				18	95	25
2		1:2		5	60	–
				24	80	5
				48	95 (91)	20
3		1:1		5	38	–
				24	56	–
				88	91	–
4		1:2	 **2b**	24	38	13
				48	49 (41)	18
5		1:2	 **2c**	2.5	63	–
				5	92 (67)	–
6		1:2	 **2d**	24	50	5
				48	63	9

[a] Reactions were performed in C_7D_8 at 130 °C under Ar with 10 mol% of catalyst unless otherwise stated. [b] Determined by in situ ^{1}H NMR spectroscopy using ferrocene (0.4 equiv.) as internal standard. [c] Isolated yield in brackets.

Such an equimolar ratio between both hydroamination partners is a noticeable result in the field of catalysis promoted by rare-earth elements, which demonstrates the high activity of **1a** under these conditions. It was further checked by control experiments that the presence of the catalyst did not impact the styrene polymerization rate, which only occurred because of the high reaction temperature. For the rest of the study an amine/alkene ratio of 1:2 was chosen as the best compromise for a high yield of the recovered product in a reasonable time (Table 1, entry 2).

Other secondary amines were tested in this intermolecular hydroamination reaction in an attempt to widen its scope. 1-Phenethylpyrrolidine (**2b**) could be prepared from styrene in a 1:2 ratio, but the conversion reached only 49% after two days. The amount of polystyrene also remained limited in this

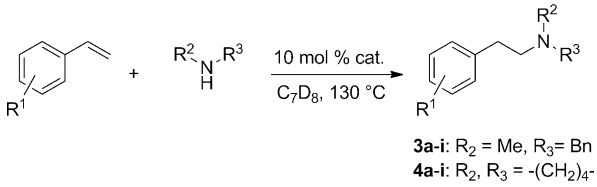
case (Table 1, entry 4). The reactivity of piperazine derivatives was also investigated as these substrates remained resistant to hydroamination with Rh-promoted catalysis by inhibition of the metal active sites.[10] The formation of 1-methyl-4-phenethylpiperazine (**2c**) was achieved readily in a short reaction time starting from 1-methylpiperazine (Table 1, entry 5), whereas the use of unprotected piperazine or morpholine led to the formation of a precipitate, and the expected products could not be quantified correctly. *N*-Methylcyclohexylmethylamine also reacted with styrene (Table 1, entry 6) to afford **2d**, but steric hindrance in close proximity to the N atom affected the course of the reaction dramatically. No hydroamination product could be detected on using either *N*-ethylbenzylamine or diethylamine even after a very long reaction time. Contrary to the observations made during the use of primary amines, the order of introduction of the reagents had no influence on the hydroamination yield.

N-Methylbenzylamine and pyrrolidine were further tested to examine the intermolecular hydroamination with various styrene derivatives that bear different substituents (i.e., –Cl, –OMe, –Me) in either the *ortho*, *meta*, or *para* position (Scheme 1 and Table 2). All expected hydroamination products were obtained in a moderate to high yield, except for pyrrolidine and 1-methoxy-4-vinylbenzene, which did not deliver any hydroamination product (Table 2, entry 15). Some

Table 2. Intermolecular anti-Markovnikov hydroamination reaction of styrene derivatives with *N*-methylbenzylamine or pyrrolidine catalyzed by **1a**.[a]

Entry	Amine: R^2, R^3	Styrene derivative: R^1	Product	*t* [h]	Conversion [%] Hydroamination product[b,c]	Polymer[b]
1	Bn, Me	*o*-Cl	**3a**	24	73 (67)	19
2		*m*-Cl	**3b**	24	28	34
3		*p*-Cl	**3c**	48	33	49
4		*o*-OMe	**3d**	3	85	–
				10	>98 (77)	10
5		*m*-OMe	**3e**	3	58	–
				48	93 (79)	16
6		*p*-OMe	**3f**	3	0	–
				48	15	17
7		*o*-Me	**3g**	5	62	–
				48	>98 (88)	12
8		*m*-Me	**3h**	5	70	–
				48	99 (63)	16
9		*p*-Me	**3i**	5	43	–
				48	93 (90)	23
10	$-(CH_2)_4-$	*o*-Cl	**4a**	24	98 (52)	11
11		*m*-Cl	**4b**	24	51 (47)	16
12		*p*-Cl	**4c**	48	75 (47)	23
13		*o*-OMe	**4d**	48	85 (41)	32
14		*m*-OMe	**4e**	48	76 (52)	12
15		*p*-OMe	**4f**	48	n.d.	n.d.
16		*o*-Me	**4g**	48	74 (57)	11
17		*m*-Me	**4h**	48	70 (32)	16
18		*p*-Me	**4i**	48	53 (32)	7

[a] Reactions were performed in C_7D_8 at 130 °C under Ar with 10 mol% of catalyst, amine (1 equiv.), and alkene (2 equiv.) unless otherwise stated. [b] Determined by in situ ^{1}H NMR spectroscopy using ferrocene (0.4 equiv.) as internal standard. [c] Isolated yield in brackets.



Scheme 1. Intramolecular anti-Markovnikov hydroamination reaction of styrene derivatives.

general trends may be deduced from the results given in Table 2, in which the presence of electron-donating groups seems to provide the targeted products with improved yields in comparison with unsubstituted styrene, which is even more significant if a substitution in the *ortho* position allows a supplementary coordination to the Y atom. Benzyl-[2-(2-methoxyphenyl)ethyl]methylamine (**3d**) was indeed obtained with a complete conversion in only 10 h (Table 2, entry 4), whereas the introduction of the *para*-OMe group on the styrene led to a drastic decrease of the reaction rate to yield **3f** (Table 2, entry 6), probably because of an important participation of the methoxy substituent to the coordination, which upset the necessary contribution of the double bond. Similarly high yields were obtained in the presence of the methyl-substituted styrene derivatives (Table 2, entries 7–9), but the introduction of a Cl atom on the styrene backbone reduces the reactivity with *N*-methylbenzylamine (Table 2, entries 1–3 versus Table 1, entry 2). Contrarily, the substitution on styrene led predominantly to better results in terms of conversion compared to the transformation with unmodified styrene for pyrrolidine (Table 2, entries 10–18 versus Table 1, entry 4). If we regard the chloride derivatives, the conversion could reach up to 98% for the reaction with 1-chloro-2-vinylbenzene to **4a** in only one day, accompanied with a low amount of residual styrene polymerization (Table 2, entry 10). Another noticeable result is the formation of 1-[2-(2-methoxyphenyl)ethyl]pyrrolidine (**4d**) in 85% yield (NMR; Table 2, entry 13).

The scope of the transformation was then studied in an attempt to react other derivatives based on the styrene core (Figure 2) with both amines. 2-Vinylnaphthalene (**5**) and 9-vi-

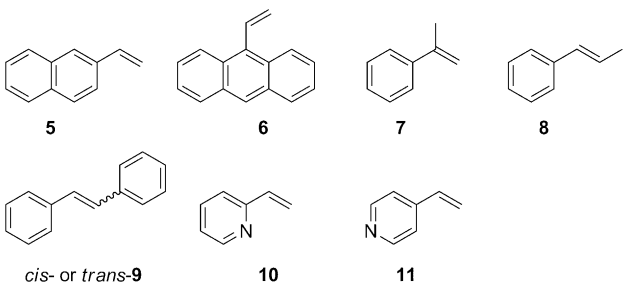


Figure 2. Styrene derivatives used in this study.

nylanthracene (**6**) were active substrates, although a poor reaction yield was recorded for **5** (Table 3, entries 1–2). If the amine/alkene ratio was maintained at 1:2, the polymerization of **5** could not be avoided, and the intermolecular hydroamination product reached only 16% in the case of benzylmethyl-(2-naphthalen-2-ylethyl)amine (**3j**; Table 3, entry 1), whereas pyrrolidine was slightly more active and delivered the hydroamination product **4j** in up to 33% yield (NMR; entry 10). No polymerization of **6** occurred under these reaction conditions, and the hydroamination products **3k** and **4k** were recovered in isolated yields of 83 and 45%, respectively (Table 3, entries 2 and 11). All hydroamination products produced by this new intermolecular procedure issued from an anti-Markovnikov regioselectivity. To gain a deeper insight into the selectivity of the transformation, isopropenylbenzene (**7**), propenylbenzene (**8**), and *cis*- and *trans*-stilbene (**9**) were investigated as alkene substrates. Unfortunately, none of them were reactive with either *N*-methylbenzylamine or pyrrolidine, even after 10 days of reaction at 130 °C (Table 3, entries 3–5 and 12–14).

As further coordination of the olefinic substrate was shown to accelerate the reaction rate, the reactivity of vinylpyridines **10** and **11** was investigated in this reaction. 4-Vinylpyridine (**11**) was proven to be unreactive to organolanthanide catalysis by Marks and co-workers and led to instantaneous catalyst precipitation,[2r] and, as far as we know, no report describes any intermolecular hydroamination with rare-earth elements for these substrates.[11] Beller and co-workers investigated the Rh-catalyzed hydroamination of vinylpyridines that occurred concurrently with oxidative amination in the presence of secondary amines.[12] Reactions were conducted in THF heated to reflux with an excess of the alkene (4:1), which led to different ratios of enamine to alkylamine depending on the substrate and the reaction conditions. Hartwig et al. studied the anti-Markovnikov Rh-catalyzed hydroamination on vinylarenes, and in this case, 2-vinylpyridine (**10**) reacted with dimethylamine to deliver the hydroamination product in a 9:1 ratio together with the enamine adduct.[6i] More recently, cation-exchange resins (Amberlyst-15) were demonstrated to catalyze the hydroamination of vinylpyridines with aliphatic or aromatic primary or secondary amines in ethanol heated to reflux.[13] These substrates were also considered by the group of Maurya and Pessoa, in the course of their studies towards the use of polymer-bound V^{IV} and V^{V} complexes.[14] In this case, however, a perfect regioselectivity towards the anti-Markovnikov products was not observed. Finally, these substrates were also treated with a combination of Cu and Ag salts but this catalysis was not successful (for **11**) or poorly effective (16% yield for **10**) in the presence of tosylamines.[15] Contrarily, catalyst **1a** is highly efficient to promote the reaction of *N*-methylbenzylamine with **10** at room temperature as benzylmethyl-(2-pyridin-2-ylethyl)-amine (**3o**) was produced in 58% yield (NMR) in only 5 min (Table 3, entry 6). If the catalyst quantity was diminished to only 1 mol%, the targeted product was delivered in a 91% yield (NMR; entry 7). Furthermore, the reaction could be conducted with an equimolar mixture of amine and alkene with the low amount of catalyst kept constant, and the hydroamination compound was produced again instantaneously in a 68% yield (NMR; entry 8).[16]

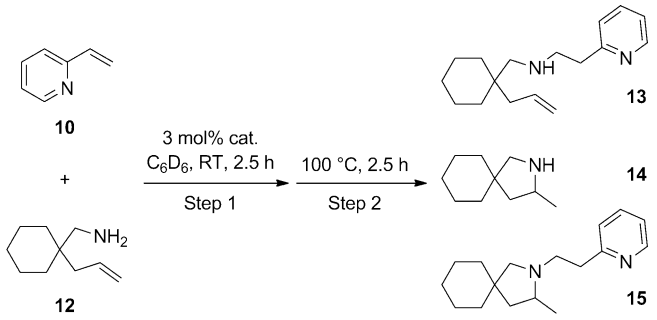
Table 3. Intermolecular anti-Markovnikov hydroamination reaction of aromatic alkenes **5**–**11** with *N*-methylbenzylamine or pyrrolidine catalyzed by **1a**.[a]

Entry	Amine: R^2, R^3	Alkene	Product	*t* [h]	Conversion [%] Hydroamination product[b,f]	Polymer[b]
1	Bn, Me	**5**	**3j**	24	10	69
				72	16	74
2		**6**	**3k**	24	52	–
				48	82	–
				120	91 (83)	
3		**7**	**3l**	240	–	–
4		**8**	**3m**	240	–	–
5		*cis*- or *trans*-**9**	**3n**	240	–	–
6[c]		**10**	**3o**	0.08	58	71
7[c,d]				0.08	91 (82)	55
8[c,d,e]				0.08	68	32
9[c,d]		**11**	**3p**	0.08	0	100
10	$-(CH_2)_4-$	**5**	**4j**	24	14	68
				72	33	72
11		**6**	**4k**	24	29	–
				48	41	–
				120	63 (45)	
12		**7**	**4l**	240	–	–
13		**8**	**4m**	240	–	–
14		*cis*- or *trans*-**9**	**4n**	240	–	–
15[c]		**10**	**4o**	0.08	82	59
16[c,d,e]				0.08	>98 (84)	0
17[c,d]		**11**	**4p**	0.08	0	100

[a] Reactions were performed in C_7D_8 at 130 °C under Ar with 10 mol% of catalyst, amine (1 equiv.), and alkene (2 equiv.) unless otherwise stated. [b] Determined by in situ ^{1}H NMR spectroscopy using ferrocene (0.4 equiv.) as internal standard. [c] C_6D_6, RT. [d] 1 mol% of catalyst. [e] amine/alkene = 1:1. [f] Isolated yield in brackets.

Under these conditions, the polymerization of **10** competes strongly for the hydroamination, and the yield of the resulting polymer was evaluated to be approximately 32% (entry 8).[17] Pyrrolidine could also be successfully added to **10** with this catalyst, and 2-(2-pyrrolidin-1-ylethyl)pyridine (**4o**) was produced quantitatively under very mild conditions (room temperature, 1 mol% of catalyst, amine/alkene = 1:1, 5 min) free of any traces of poly(vinylpyridine) (Table 3, entries 15–16). The location of the coordinating N atom in the *ortho* position of the reacting alkene is of utmost importance as **11** delivered only poly(vinylpyridine) and not a hydroamination product with any of the amines tested (Table 3, entries 9 and 17).

In a previous study, we demonstrated that chiral Y complexes **1a**–**e** were also efficient catalysts for the enantioselective cyclohydroamination of *C*-(1-allylcyclohexyl)methylamine (**12**) at room temperature, which led to the spiropyrrolidine **14** in high yields (>95%) and moderate enantiomeric excess (*ee*; 5–75%).[8b] To further extend the scope of the application of theses complexes, we next examined their ability to catalytically promote the tandem inter- and intramolecular reaction of **10** and **12** (Scheme 2).[18] In



Scheme 2. Tandem intermolecular anti-Markovnikov–intramolecular Markovnikov hydroamination reaction with **10** and **12**.

the presence of 3 mol% of **1a** at room temperature, the reaction of **10** (1.5 equiv.) and **12** (1 equiv.) provides a complete conversion (>95%) after 2.5 h and the formation of the intermolecular product **13**, the intramolecular product **14**, and the tandem product **15** in 26, 28, and 42% yields respectively (Scheme 2 and Table 4, entry 1). To our surprise, subsequent heating of the resulting reaction mixture at 100 °C for 2.5 h leads to the complete consumption of **13** and the recovery of **14** and **15** in 67 and 14% yields, respectively, with an *ee* of 10% for **15** (entry 2). The formation of **14** in 67% yield from a mixture of products **13**, **14**, and **15** in a ratio of 26:28:42 suggests that a retrohydroamination[19] reaction may occur at high temperature under these catalytic conditions. To gain more insight into this hypothetical pathway, the intermolecular product **13** and the tandem product **15** were isolated and treated independently with 3 mol% of **1a** firstly at room temperature for 2.5 h then at 100 °C for over 2.5 h (entries 3–6). At room temperature, the reaction of **13** only affords 25% of tandem product **15** after 2.5 h with no trace of the intramolecular product **14** (entry 3). However, further heating of the reaction mixture led to the appearance of **14**, the yield of which was determined to be 58% at the end of the reaction time (entry 4). The tandem product **15** was formed in 42% yield (entry 4). The same reactions conducted with the isolated tandem product **15** furnish 45% yield of **14** at 100 °C (entries 5–6). These experiments underline that, under this tandem process, **14** may arise from three distinct pathways. It can either emanate from **12** by classical intramolecular hydroamination, from **15** by direct retrohydroamination, or from **13** by a sequence of retrohydroamination and cyclohydroamination. The latter two routes, which are only promoted at higher temperatures, are the predominant pathways under these catalytic conditions (3 mol% of **1a**, 100 °C) and drive the formation of **14** as the main product (entry 2). The use of catalyst **1e** does not alter the outcome of the tandem process as the major product **14** is obtained in 65% yield and **15** in 14% yield, despite a better *ee* for the tandem product (entry 8). However, the use of catalysts **1b**–**d**, which bear bulkier substituents on the phenyl ring of the ligand, affords a better catalyst control over the selectivity of the tandem reaction as, in these cases, **15** is the sole product of the reaction with no substantial trace of **13** or **14** (<5%; entries 9–10, 12-15). Notably, in the case of **1b**, the selectivity in favor of the tandem product is temperature dependent as further heating the reaction mixture at 100 °C affords **15** in only 41% yield but with **14** in 55% (entry 11).[20] Nevertheless, despite these high selectivities, the enantioinduction was lower than that achieved with **1e** (entry 8 versus entries 11, 13, and 15).

Table 4. Tandem intermolecular anti-Markovnikov–intramolecular Markovnikov hydroamination reaction with **10** and **12** catalyzed by **1**.[a]

Entry	Catalyst	Step	Yield [%]			*ee* (**15**)[c]
			13[b,h]	**14**[b]	**15**[b,h]	[%]
1	**1a**	1	26	28	42	–
2		2	0	67	14	10
3[d]	**1a**	1	75	0	25	–
4[d]		2	0	58	42	–
5[e]	**1a**	1	0	0	100	–
6[e]		2	0	45	55	–
7	**1e**	1	66 (32)	10	19	–
8		2	0	65	14	48
9	**1b**	1	79	0	18	–
10		2[f]	0	0	88 (85)	29
11		2[g]	0	55	41	25
12	**1c**	1	50	0	59	–
13		2	0	0	82	31
14	**1d**	1	53	0	47	–
15		2	3	5	79	15

[a] Reactions were performed in C_6D_6 under Ar with 3 mol% of catalyst, **10** (1.5 equiv.), and **12** (1 equiv.) at RT (20–25 °C) for 2.5 h (step 1) then heated at 100 °C for 2.5 h (step 2), 100% conversion, unless otherwise stated. [b] Determined by in situ ^{1}H NMR spectroscopy using ferrocene (0.4 equiv.) as internal standard. [c] Determined by chiral SFC. [d] Reaction performed with isolated **13**. [e] Reaction performed with isolated **15**. [f] Reaction performed at 50 °C. [g] 20 h, 100 °C. [h] Isolated yield in brackets.

Conclusions

We have demonstrated that chiral binaphthylamido alkyl yttrium complex **1a** is an active precatalyst for the highly selective, intermolecular anti-Markovnikov hydroamination of secondary amines with styrene derivatives and 2-vinylpyridine at 130 °C and room temperature, respectively. The reaction development and exploration of the substrate scope highlight that the reactivity, reaction rate, and yield of anti-Markovnikov hydroamination products are highly substrate dependent. As a general trend, the introduction of a coordinating group at the *ortho* position of the vinyl group on styrene or the use of 2-vinylpyridine increase the addition rate and yield of the hydroamination product significantly. The use of bulky secondary amines or disubstituted alkenes lead to no catalytic activity as does the presence of a coordinating group at the *para* position of the styrene vinyl group. We have also established that chiral binaphthylamido alkyl yttrium complexes **1a**–**e** have the ability to catalytically promote the tandem intermolecular anti-Markovnikov hydroamination–intramolecular Markovnikov hydroamination reaction of 2-vinylpyridine and *C*-(1-allylcyclohexyl)-methylamine to give the tandem product in up to 85% yield and with an enantiomeric excess up to 48%. This work has brought to light that a retrohydroamination process might occur during this tandem reaction at high temperature, the

extent of which relies upon the nature of the substituents on the catalyst N atoms.

Experimental Section

General

All manipulations were performed under an Ar atmosphere by using standard Schlenk or glovebox techniques. [D_8]Toluene and [D_6]benzene were dried with sodium benzophenone ketyl, transferred under vacuum, and stored over activated 3 Å molecular sieves. Complexes **1a–e** were prepared from [$Li(THF)_4$][$Y(CH_2SiMe_3)_4$][21] and the appropriate ligand according to a reported procedure.[8] Compound **12** was prepared as reported.[22] All amines, styrene derivatives, and vinylpyridines were dried with calcium hydride and transferred under vacuum. 2-Vinylnaphthalene (**5**) and 9-vinylanthracene (**6**) were dried under vacuum. All amines and alkene derivatives were further dried for at least 2 h with 3 Å molecular sieves with a few drops of [D_8]toluene or [D_6]benzene prior to use. Bruker AM250, AV300, AV360, and DRX400 NMR spectrometers operating at 250, 300, 360, and 400 MHz, respectively, were used to record the ^{1}H NMR spectra. Chemical shifts were referenced internally according to the Me_4Si resonance. Mass spectra were recorded by using a Finnigan MAT 95 S spectrometer. Enantiomeric excesses of the product **15** were determined by supercritical fluid chromatography (SFC; Chiralpak AD-H (250×4.6 mm), P_{CO_2} = 100 bar, 4 mL min^{-1}, T = 30 °C, 3% MeOH as modifier).

Anti-Markovnikov hydroamination of styrene derivatives with *N*-methylbenzylamine or pyrrolidine

General procedure: In a glovebox, a solution of [$Li(THF)_4$][$Y(CH_2SiMe_3)_4$] (73 mg, 0.10 mmol) in C_7D_8 (500 μL) was added into a solution of (*R*)-2,2′-dibenzyl-1,1′-binaphthyldiamine ligand (46 mg, 0.10 mmol) in C_7D_8 (500 μL) at RT. The clear reaction mixture turned to a deep yellow colored solution. The homogeneous reaction solution was then allowed to stir 2 min at RT and an aliquot (450 μL) was transferred to a vial containing the appropriate secondary amine (0.45 mmol), the styrene derivative (0.90 mmol) and ferrocene (0.18 mmol). The reaction mixture was then introduced into a screw-tap or a J. Young-tap NMR tube and the progress of the reaction was monitored by ^{1}H NMR spectroscopy using ferrocene as internal standard. The reaction mixture was quenched with ethanol and dried under vacuum after addition of silica gel. The product was extracted from silica gel with ethanol and purified on a preparative TLC plate.

***N*-Benzyl-*N*-methyl-2-phenylethanamine (2a)**: (Table 1, entry 2) R_f = 0.48 (pentane/EtOAc 75:25); colorless oil (92 mg, 0.41 mmol, 91%); ^{1}H NMR (300 MHz, $CDCl_3$, 294 K): δ = 2.34 (s, 3H), 2.64–2.77 (m, 2H), 2.83–2.95 (m, 2H), 3.62 (s, 2H), 7.20–7.39 ppm (m, 10H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 294 K): δ = 34.1, 42.3, 59.4, 62.3, 126.1, 127.1, 128.4, 128.5, 128.9, 129.2, 139.1, 140.7 ppm; MS (EI): *m/z* (%): 134.0 (78), 90.9 (100); HRMS (ESI): *m/z*: calcd for $C_{16}H_{20}N$ (226.1590): $[M+H]^+$; found 226.1587. The spectra are in total accordance with the data described in the literature.[6a]

1-Phenethylpyrrolidine (2b): (Table 1, entry 4) R_f = 0.09 (pentane/EtOAc 75:25); yellow oil (29 mg, 0.17 mmol, 41%); ^{1}H NMR (300 MHz, $CDCl_3$, 294 K): δ = 1.75–1.94 (m, 4H), 2.55–2.68 (m, 4H), 2.68–2.78 (m, 2H), 2.83–2.91 (m, 2H), 7.16–7.37 ppm (m, 5H); $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$, 294 K): δ = 23.7, 35.9, 54.4, 58.5, 126.3, 128.6, 128.8, 140.5 ppm; MS (EI): *m/z* (%): 83.9 (100); HRMS (ESI): *m/z*: calcd for $C_{12}H_{18}N$ (176.1434): $[M+H]^+$; found 176.1433. The spectra are in total accordance with the data described in the literature.[6a]

1-Methyl-4-phenethylpiperazine (2c): (Table 1, entry 5) R_f = 0.09 (pentane/EtOAc 75:25); yellow oil (62 mg, 0.30 mmol, 67%); ^{1}H NMR (300 MHz, $CDCl_3$, 294 K): δ = 2.35 (s, 3H), 2.47–2.76 (m, 10H), 2.78–2.87 (m, 2H), 7.16–7.33 ppm (m, 5H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 294 K): δ = 33.7, 46.0, 53.0, 55.1, 60.5, 126.3, 128.6, 128.9, 140.3 ppm; MS (EI): *m/z* (%): 113.0 (100), 70.0 (88); HRMS (ESI): *m/z*: calcd for $C_{13}H_{21}N_2$ (205.1699): $[M+H]^+$; found 205.1705.

***N*-Benzyl-2-(2-chlorophenyl)-*N*-methylethanamine (3a)**: (Table 2, entry 1) R_f = 0.50 (pentane/EtOAc 75:25); yellow oil (69 mg, 0.27 mmol, 67%); ^{1}H NMR (360 MHz, $CDCl_3$, 294 K): δ = 2.35 (s, 3H), 2.67–2.74 (m, 2H), 2.96–3.04 (m, 2H), 3.63 (s, 2H), 7.11–7.37 ppm (m, 9H); $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$, 294 K): δ = 31.6, 42.3, 57.3, 62.2, 126.9, 127.2, 127.7, 128.4, 129.2, 129.6, 131.0, 134.3, 138.3, 139.1 ppm; MS (EI): *m/z* (%): 134.0 (79), 90.9 (100); HRMS (ESI): *m/z*: calcd for $C_{16}H_{19}ClN$ (260.1201): $[M+H]^+$; found 260.1202.

***N*-Benzyl-2-(2-methoxyphenyl)-*N*-methylethanamine (3d)**: (Table 2, entry 4) R_f = 0.52 (pentane/EtOAc 75:25); yellow oil (88 mg, 0.34 mmol, 77%); ^{1}H NMR (360 MHz, $CDCl_3$, 294 K): δ = 2.36 (s, 3H), 2.62–2.75 (m, 2H), 2.86–2.97 (m, 2H), 3.64 (s, 2H), 3.82 (s, 3H), 6.83–6.98 (m, 2H), 7.16–7.43 ppm (m, 7H); $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$, 294 K): δ = 28.3, 42.3, 55.4, 57.5, 62.1, 110.5, 120.6, 127.0, 127.4, 128.3, 129.1, 129.2, 130.5, 139.4, 157.8 ppm; MS (EI): *m/z* (%): 134.0 (89), 90.9 (100); HRMS (ESI): *m/z*: calcd for $C_{17}H_{22}NO$ (256.1696): $[M+H]^+$; found 256.1692. The spectra are in total accordance with the data described in the literature.[23]

***N*-Benzyl-2-(3-methoxyphenyl)-*N*-methylethanamine (3e)**: (Table 2, entry 5) R_f = 0.48 (pentane/EtOAc 75:25); yellow oil (91 mg, 0.36 mmol, 79%); ^{1}H NMR (300 MHz, $CDCl_3$, 294 K): δ = 2.33 (s, 3H), 2.64–2.74 (m, 2H), 2.82–2.91 (m, 2H), 3.62 (s, 2H), 3.82, (s, 3H), 6.73–6.86 (m, 3H), 7.17–7.40 ppm (m, 6H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 294 K): δ = 34.1, 42.3, 55.3, 59.2, 62.3, 111.4, 114.6, 121.3, 127.1, 128.4, 129.2, 129.4, 139.0, 142.3, 159.8 ppm; MS (EI): *m/z* (%): 134.0 (93), 90.9 (100); HRMS (ESI): *m/z*: calcd for $C_{17}H_{22}NO$ (256.1696) $[M+H]^+$; found 256.1694.

***N*-Benzyl-*N*-methyl-2-*o*-tolylethanamine (3g)**: (Table 2, entry 7) R_f = 0.56 (pentane/EtOAc 75:25); yellow oil (95 mg, 0.40 mmol, 88%); ^{1}H NMR (250 MHz, $CDCl_3$, 294 K): δ = 2.35 (s, 3H), 2.41 (s, 3H), 2.59–2.72 (m, 2H), 2.84–2.97 (m, 2H), 3.66 (s, 2H), 7.19 (s, 4H), 7.25–7.94 ppm (m, 5H); $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$, 294 K): δ = 19.4, 31.5, 42.4, 58.0, 62.5, 126.1, 126.3, 127.2, 128.4, 129.2, 129.5, 130.4, 136.2, 138.8, 139.2 ppm; MS (EI): *m/z* (%): 134.0 (82), 90.9 (100); HRMS (ESI): *m/z*: calcd for $C_{17}H_{22}N$ (240.1747): $[M+H]^+$; found 240.1747.

***N*-Benzyl-*N*-methyl-2-*m*-tolylethanamine (3h)**: (Table 2, entry 8) R_f = 0.61 (pentane/EtOAc 75:25); yellow oil (68 mg, 0.28 mmol, 63%); ^{1}H NMR (250 MHz, $CDCl_3$, 294 K): δ = 2.34 (s, 3H), 2.38 (s, 3H), 2.65–2.78 (m, 2H), 2.78–2.92 (m, 2H), 3.62 (s, 2H), 6.66–7.09 (m, 3H), 7.13–7.39 ppm (m, 6H); $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$, 294 K): δ = 21.6, 34.0, 42.3, 59.4, 62.4, 125.9, 126.9, 127.2, 128.4, 129.2, 129.7, 138.0, 139.1, 140.6 ppm; MS (EI): *m/z* (%): 134.0 (97), 90.9 (100); HRMS (ESI): *m/z*: calcd for $C_{17}H_{22}N$ (240.1747): $[M+H]^+$; found 240.1750.

***N*-Benzyl-*N*-methyl-2-*p*-tolylethanamine (3i)**: (Table 2, entry 9) R_f = 0.61 (pentane/EtOAc 75:25); yellow oil (100 mg, 0.42 mmol, 90%); ^{1}H NMR (250 MHz, $CDCl_3$, 294 K): δ = 2.33 (s, 3H), 2.37 (s, 3H), 2.60–2.78 (m, 2H), 2.78–2.91 (m, 2H), 3.62 (s, 2H), 7.14 (s, 4H), 7.22–7.41 ppm (m, 5H); $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$, 294 K): δ = 21.2, 33.6, 42.3, 59.5, 62.4, 127.1, 128.4, 128.8, 129.2, 135.5, 137.6,

139.1 ppm; MS (EI): *m/z* (%): 134.0 (88), 90.9 (100); HRMS (ESI): *m/z*: calcd for $C_{17}H_{22}N$ (240.1747): $[M+H]^+$; found 240.1745.

1-(2-Chlorophenethyl)pyrrolidine (4a): (Table 2, entry 10) $R_f = 0.09$ (pentane/EtOAc 75:25); yellow oil (49 mg, 0.23 mmol, 52%); ^{1}H NMR (360 MHz, $CDCl_3$, 294 K): $\delta = 1.76–1.87$ (m, 4H), 2.58–2.78 (m, 6H), 2.96–3.04 (m, 2H), 7.10–7.22 (m, 2H), 7.26 (dd, $J = 7.3$ Hz, 1.9 Hz, 1H), 7.33 ppm (dd, $J = 7.6$ Hz, 1.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$, 294 K): $\delta = 23.7$, 33.4, 54.3, 56.3, 127.0, 127.8, 129.6, 130.9, 134.2, 138.1 ppm; MS (EI): *m/z* (%): 84.0 (100); HRMS (ESI): *m/z*: calcd for $C_{12}H_{17}ClN$ (210.1044): $[M+H]^+$; found 210.1047.

1-(3-Chlorophenethyl)pyrrolidine (4b): (Table 2, entry 11) $R_f = 0.09$ (pentane/EtOAc 75:25); yellow oil (44 mg, 0.21 mmol, 47%); ^{1}H NMR (360 MHz, $CDCl_3$, 294 K): $\delta = 1.76–1.91$ (m, 4H), 2.58–2.70 (m, 4H), 2.70–2.78 (m, 2H), 2.81–2.90 (m, 2H), 7.06–7.14 (m, 1H), 7.14–7.25 ppm (m, 3H). $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$, 294 K): $\delta =$ 23.7, 35.2, 54.3, 57.9, 126.5, 127.0, 128.9, 129.8, 134.3, 142.3 ppm; MS (EI): *m/z* (%): 84.0 (100); HRMS (ESI): *m/z*: calcd for $C_{12}H_{17}ClN$ (210.1044): $[M+H]^+$; found 210.1044.

1-(4-Chlorophenethyl)pyrrolidine (4c): (Table 2, entry 12) $R_f = 0.09$ (pentane/EtOAc 75:25); yellow oil (44 mg, 0.21 mmol, 47%); ^{1}H NMR (360 MHz, $CDCl_3$, 294 K): $\delta = 1.82–1.97$ (m, 4H), 2.65–2.87 (m, 6H), 2.87–2.97 (m, 2H), 7.15 (d, $J = 8.3$ Hz, 2H), 7.26 ppm (m, $J = 8.5$ Hz, 2H); $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$, 294 K): $\delta = 23.7$, 34.5, 54.3, 57.9, 128.8, 130.2, 132.3, 138.2 ppm; MS (EI): *m/z* (%): 83.9 (100); HRMS (ESI): *m/z*: calcd for $C_{12}H_{17}ClN$ (210.1044): $[M+H]^+$; found 210.1042. The spectra are in total accordance with the data described in the literature.[6f]

1-(2-Methoxyphenethyl)pyrrolidine (4d): (Table 2, entry 13) $R_f =$ 0.08 (pentane/EtOAc 75:25); yellow oil (38 mg, 0.19 mmol, 41%); ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): $\delta = 1.76–1.88$ (m, 4H), 2.55–2.76 (m, 6H), 2.81–2.91 (m, 2H), 3.82 (s, 3H), 6.80–6.92 (m, 2H), 7.13–7.22 ppm (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 294 K): $\delta = 23.6$, 30.2, 54.3, 55.4, 56.7, 110.4, 120.6, 127.5, 128.9, 130.3, 157.6 ppm; MS (EI): *m/z* (%): 83.9 (100); HRMS (ESI): *m/z*: calcd for $C_{13}H_{20}NO$ (206.1539): $[M+H]^+$; found 206.1543.

1-(3-Methoxyphenethyl)pyrrolidine (4e): (Table 2, entry 14) $R_f =$ 0.14 (pentane/EtOAc 75:25); yellow oil (48 mg, 0.23 mmol, 52%); ^{1}H NMR (300 MHz, $CDCl_3$, 294 K): $\delta = 1.77–1.87$ (m, 4H), 2.56–2.65 (m, 4H), 2.67–2.77 (m, 2H), 2.78–2.88 (m, 2H), 3.79 (s, 3H), 6.68–6.85 (m, 3H), 7.2 ppm (dd, $J = 7.8$ Hz, 7.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 294 K): $\delta = 23.6$, 35.9, 54.3, 55.3, 58.3, 111.5, 114.6, 121.2, 129.5, 142.1, 159.8 ppm; MS (EI): *m/z* (%): 83.9 (100); HRMS (ESI): *m/z*: calcd for $C_{13}H_{20}NO$ (206.1539): $[M+H]^+$; found 206.1544.

1-(2-Methylphenethyl)pyrrolidine (4g): (Table 2, entry 16) $R_f = 0.19$ (pentane/EtOAc 75:25); yellow oil (48 mg, 0.25 mmol, 57%); ^{1}H NMR (360 MHz, $CDCl_3$, 294 K): $\delta = 1.81–2.01$ (m, 4H), 2.35 (s, 3H), 2.70–2.90 (m, 6H), 2.92–3.01 (m, 2H), 7.07–7.23 ppm (m, 4H); $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$, 294 K): $\delta = 19.5$, 23.7, 32.3, 54.2, 56.9, 126.3, 126.7,129.4, 130.5, 136.3, 137.6 ppm; MS (EI): *m/z* (%): 83.9 (100); HRMS (ESI): *m/z*: calcd for $C_{13}H_{20}N$ (190.1590): $[M+H]^+$; found 190.1594.

1-(3-Methylphenethyl)pyrrolidine (4h): (Table 2, entry 17) $R_f = 0.11$ (pentane/EtOAc 75:25); yellow oil (28 mg, 0.15 mmol, 32%); ^{1}H NMR (360 MHz, $CDCl_3$, 294 K): $\delta = 1.76–1.99$ (m, 4H), 2.34 (s, 3H), 2.54–2.65 (m, 4H), 2.66–2.77 (m, 2H), 2.78–2.87 (m, 2H), 6.99–7.06 (m, 3H), 7.18 ppm (dd, $J = 7.3$ Hz, 7.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 294 K): $\delta = 21.5$, 23.7, 35.9, 54.4, 58.6, 125.8, 126.9, 128.4, 129.6, 138.0, 140.6 ppm; MS (EI): *m/z* (%): 84.0 (100); HRMS (ESI): *m/z*: calcd for $C_{13}H_{20}N$ (190.1590): $[M+H]^+$: found 190.1589.

1-(4-Methylphenethyl)pyrrolidine (4i): (Table 2, entry 18) $R_f = 0.14$ (pentane/EtOAc 75:25); yellow oil (27 mg, 0.15 mmol, 32%); ^{1}H NMR (360 MHz, $CDCl_3$, 294 K): $\delta = 1.75–1.89$ (m, 4H), 2.33 (s, 3H), 2.53–2.63 (m, 4H), 2.64–2.74 (m, 2H), 2.78–2.88 (m, 2H), 7.07–7.15 ppm (m, 4H); $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$, 294 K): $\delta = 21.2$, 23.7, 35.5, 54.4, 58.7, 128.7, 129.2, 135.6, 137.6 ppm; MS (EI) *m/z* (%) 84.0 (100); HRMS (ESI): *m/z*: calcd for $C_{13}H_{20}N$ (190.1590): $[M+H]^+$; found 190.1587.

2-(Anthracen-9-yl)-*N*-benzyl-*N*-methylethanamine (3k): (Table 3, entry 2) $R_f = 0.60$ (pentane/EtOAc 75:25); yellow oil (122 mg, 0.37 mmol, 83%); ^{1}H NMR (360 MHz, $CDCl_3$, 294 K): $\delta = 2.58$ (s, 3H), 2.82–2.95 (m, 2H), 3.76 (s, 2H), 3.81–3.93 (m, 2H), 7.28–7.57 (m, 9H), 8.02 (dd, $J = 7.4$ Hz, 1.8 Hz, 2H), 8.24 (d, $J = 8.2$ Hz, 2H), 8.36 ppm (s, 1H); $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$, 294 K): $\delta = 26.3$, 42.7, 57.8, 62.5 124.4, 125.0, 125.8, 126.1, 127.3, 128.5, 129.3, 129.4, 130.0, 131.8, 132.5, 139.2 ppm; MS (EI): *m/z* (%): 191.1 (6), 134.0 (100), 90.9 (74); HRMS (ESI): *m/z*: calcd for $C_{24}H_{24}N$ (326.1903): $[M+H]^+$; found 326.1901.

1-[2-(Anthracen-9-yl)ethyl]pyrrolidine (4k): (Table 3, entry 11) $R_f =$ 0.16 (pentane/EtOAc 75:25); yellow oil (55 mg, 0.20 mmol, 45%); ^{1}H NMR (360 MHz, $CDCl_3$, 294 K): $\delta = 1.84–2.00$ (m, 4H), 2.71–2.93 (m, 6H), 3.82–3.95 (m, 2H), 7.42–7.58 (m, 4H), 8.02 (d, $J = 8.7$ Hz, 2H), 8.33 (d, $J = 9.9$ Hz, 2H), 8.35 ppm (s, 1H); $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$, 294 K): $\delta = 23.8$, 28.0, 54.5, 57.0, 124.4, 125.0, 125.9, 126.2, 129.4, 130.0, 131.8, 132.3 ppm; MS (EI): *m/z* (%): 204.1 (26), 191.1 (27), 98.0 (38), 84.0 (100), 71.0 (25); HRMS (ESI): *m/z*: calcd for $C_{20}H_{22}N$ (276.1747): $[M+H]^+$: found 276.1743.

Anti-Markovnikov hydroamination of 2-vinylpyridine (10) with *N*-methylbenzylamine or pyrrolidine

General procedure: In a glovebox, a solution of $[Li(THF)_4][Y(CH_2SiMe_3)_4]$ (12 mg, 0.025 mmol) in C_6D_6 (125 μL) was added to a solution of (*R*)-2,2′-dibenzyl-1,1′-binaphthyldiamine ligand (18 mg, 0.025 mmol) in C_6D_6 (125 μL) at RT. The clear reaction mixture turned to a deep yellow solution. The homogeneous reaction solution was then allowed to stir for 2 min at RT, and an aliquot (45 μL) was transferred to a vial under stirring that contained a C_6D_6 solution (450 μL) of the secondary amine (0.45 mmol), **10** (0.675 mmol), and ferrocene (0.18 mmol). The reaction mixture was then introduced into a screw-tap or a J. Young-tap NMR tube, and the progress of the reaction was monitored by ^{1}H NMR spectroscopy using ferrocene as an internal standard. The reaction mixture was quenched with ethanol and dried under vacuum after the addition of silica gel. The product was extracted from silica gel with ethanol and purified on a preparative TLC plate.

***N*-Benzyl-*N*-methyl-2-(pyridin-2-yl)ethanamine (3o)**: (Table 3, entry 7) $R_f = 0.48$ (CH_2Cl_2/MeOH 90:10); colorless oil (84 mg, 0.37 mmol, 82%; contaminated with 9% of the hydroaminoalkylation product; see Supporting Information); ^{1}H NMR (300 MHz, $CDCl_3$, 294 K): $\delta = 2.29$ (s, 3H), 2.78–2.88 (m, 2H), 2.97–3.07 (m, 2H), 3.57 (s, 2H), 7.02–7.36 (m, 7H), 7.58 (td, $J = 7.7$ Hz, 1.9 Hz, 1H), 8.52 ppm (d, $J = 4.9$ Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 294 K): $\delta = 36.4$, 42.2, 57.5, 62.4, 121.2, 123.4, 127.1, 128.3, 129.1, 136.3, 139.2, 149.4, 160.8 ppm; MS (EI): *m/z* (%): 134.0 (92), 90.9 (100); HRMS (ESI): *m/z*: calcd for $C_{15}H_{19}N_2$ (227.1543): $[M+H]^+$; found 227.1539.

2-[2-(Pyrrolidin-1-yl)ethyl]pyridine (4o): (Table 3, entry 16) $R_f =$ 0.51 (CH_2Cl_2/MeOH 90:10); colorless oil (67 mg, 0.38 mmol, 84%); ^{1}H NMR (360 MHz, $CDCl_3$, 294 K): $\delta = 1.72–1.83$ (m, 4H), 2.54–2.67 (m, 4H), 2.80–2.92 (m, 2H), 2.94–3.09 (m, 2H), 7.09 (dd, $J = 7.4$ Hz,

5.2 Hz, 1H), 7.18 (d, $J=7.7$ Hz, 1H), 7.57 (ddd, $J=7.7$ Hz, 7.7 Hz, 1.9 Hz, 1H), 8.51 ppm (d, $J=5.0$ Hz, 1H); $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$, 294 K): $\delta=23.7$, 38.2, 54.4, 56.4, 121.3, 123.3, 136.5, 149.4, 160.6 ppm; MS (EI): *m/z* (%): 105.0 (20), 83.9 (100), 79.0 (19); HRMS (ESI): *m/z*: calcd for $C_{11}H_{17}N_2$ (177.1386): $[M+H]^+$; found 177.1389.

Tandem reaction of 2-vinylpyridine (10) and *C*-(1-allylcyclohexyl)-methylamine (12)

In a glovebox, a solution of $[Li(THF)_4][Y(CH_2SiMe_3)_4]$ (12 mg, 0.024 mmol) in C_6D_6 (500 μL) was added to a solution of (*R*)-2,2′-disubstituted-1,1′-binaphthyldiamine ligand (0.024 mmol) in C_6D_6 (500 μL) at RT. The homogeneous reaction solution was then allowed to stir for 10 min at RT, and an aliquot (300 μL) was introduced quickly under stirring to a vial that contained a C_6D_6 solution (450 μL) of **12** (0.24 mmol), **10** (0.36 mmol), and ferrocene (0.096 mmol). The reaction mixture was then introduced into a screw-tap NMR tube, kept at RT for 2.5 h, then heated at 100 °C for 2.5 h. The progress of the reaction was monitored by ^1H NMR spectroscopy using ferrocene as an internal standard. The reaction mixture was quenched with ethanol and dried under vacuum after the addition of silica gel. The product was extracted from silica gel with ethanol and purified on a preparative TLC plate.

***N*-[(1-Allylcyclohexyl)methyl]-2-(pyridin-2-yl)ethanamine (13)**: (Table 4, entry 7) $R_f=0.54$ (CH_2Cl_2/MeOH/Et_3N 90:10:1); white powder (20 mg, 0.08 mmol, 32%); ^1H NMR (360 MHz, $CDCl_3$, 294 K): $\delta=1.35$–1.65 (m, 10H), 2.36 (d, $J=7.5$ Hz, 2H), 2.89 (bs, 2H), 3.37–3.55 (m, 4H), 5.10–5.22 (m, 2H), 5.83 (ddt, $J=17.0$ Hz, 10.1 Hz, 7.5 Hz, 1H), 7.18–7.26 (m, 2H), 7.69 (ddd, $J=7.7$ Hz, 7.7 Hz, 1.8 Hz, 1H), 8.39 ppm (d, $J=4.9$ Hz, 1H); $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$, 294 K): $\delta=21.4$, 25.9, 31.1, 33.5, 36.4, 39.5, 49.1, 54.9, 119.7, 122.7, 124.1, 132.9, 137.9, 148.2, 159.2 ppm; MS (EI): *m/z* (%): 134.9 (100), 106.0 (28); HRMS (ESI): *m/z*: calcd for $C_{17}H_{27}N_2$ (269.2169) $[M+H]^+$; found 269.2175.

3-Methyl-2-[2-(pyridin-2-yl)ethyl]-2-azaspiro[4.5]decane (15): (Table 4, entry 10) $R_f=0.44$ (CH_2Cl_2/MeOH/Et_3N 90:10:1); yellow oil (53 mg, 0.20 mmol, 85%); ^1H NMR (300 MHz, $CDCl_3$, 294 K): $\delta=1.08$ (d, $J=6.0$ Hz, 3H), 1.19–1.51 (m, 11H), 1.74 (dd, $J=12.4$ Hz, 6.5 Hz, 1H), 2.05 (d, $J=9.4$ Hz, 1H), 2.34–2.52 (m, 2H), 2.91–3.04 (m, 2H), 3.07–3.23 (m, 2H), 7.10 (ddd, $J=7.5$ Hz, 4.9 Hz, 1.0 Hz, 1H), 7.20 (d, $J=7.7$ Hz, 1H), 7.58 (ddd, $J=7.7$ Hz, 7.7 Hz, 1.9 Hz, 1H), 8.52 ppm (d, $J=4.9$ Hz, 1H); $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$, 294 K): $\delta=19.1$, 23.8, 23.9, 26.2, 37.4, 38.9, 39.6, 47.3, 54.2, 59.6, 66.8, 121.2, 123.4, 136.4, 149.4, 161.0 ppm; MS (EI): *m/z* (%): 166.1 (100), 106.0 (32); HRMS (ESI): *m/z*: calcd for $C_{17}H_{27}N_2$ (259.2169) $[M+H]^+$; found 259.2166.

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