

CHAPTER 1

HYDROAMINATION OF ALKENES

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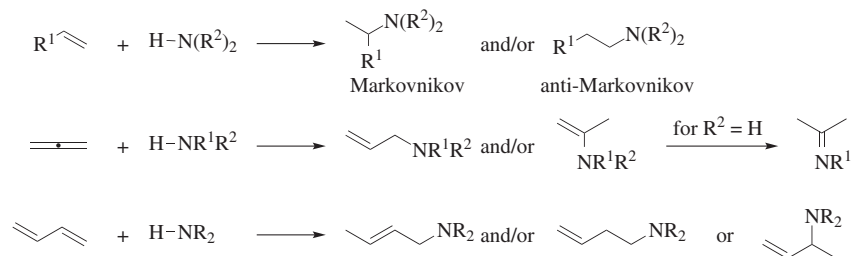
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INTRODUCTION*

The development of efficient synthetic procedures for establishing carbon–nitrogen bonds has received significant attention over the last one and a half centuries, due to the importance of nitrogen-containing compounds in biological systems and pharmaceutical applications.^{1,2} Although a large number of carbon–nitrogen bond-forming processes have been devised during this period, the hydroamination of alkenes represents, in principle, one of the most attractive and efficient routes. The catalytic hydroamination of alkenes, allenes, and dienes leads to amines, imines, and enamines. (Scheme 1).^{3–8} The reactions may also be performed in an intramolecular fashion.



Scheme 1

*Abbreviations used are defined on pp. 81–83.

The simplicity, high atom economy, and the use of readily available and inexpensive starting materials make the hydroamination reaction a highly desirable process for the synthesis of bulk and fine chemicals, as well as pharmaceuticals. Although only sporadic studies had emerged until 20 years ago, the field has drastically evolved over the last decade.⁷ The hydroamination reaction provides direct, potentially waste-free access to alkyl amines and nitrogen-containing heterocycles, in the simplest cases starting from alkenes and ammonia.

Hydroamination in the context of this review article is defined as the addition of HNR_2 across a non-activated, unsaturated carbon-carbon multiple bond. This review focuses on the hydroamination reaction of simple, non-activated alkenes. The addition of amines to slightly activated alkenes, such as vinyl arenes, 1,3-dienes, strained alkenes (norbornene derivatives, methylenecyclopropanes) and allenes is closely related and will be covered. Reactions of alkynes, however, are not covered due to volume size limitations.^{9–14} Aza-Michael reactions involving the addition of an N-H fragment across the conjugated or otherwise activated double bond of a Michael acceptor often proceed smoothly even in the absence of a catalyst and are therefore not covered herein.^{15,16} A number of reviews have appeared on various aspects of hydroamination of alkenes.^{3–8,16–41}

The scope of amine types includes ammonia, primary and secondary aliphatic and aromatic amines, azoles, and hydrazines. Although *N*-protected amines, such as ureas, carboxamides, and sulfonamides do not strictly belong to the amine compound class, the addition of these compounds to unsaturated compounds has seen significant progress, especially through the use of metal-free and late transition metal based catalysts. Thus, *N*-protected ammonia and primary amines are also included in this chapter.

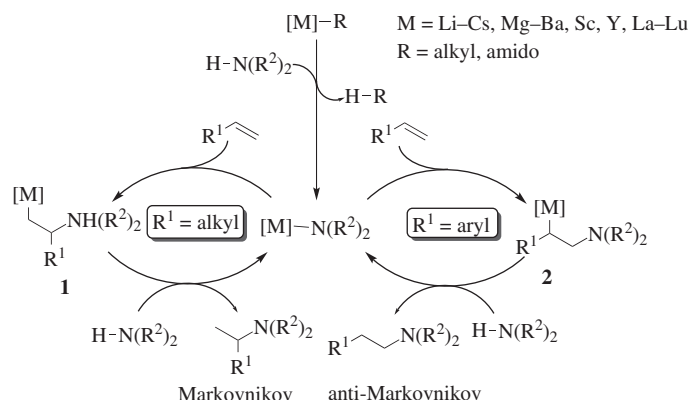
A large variety of catalyst systems are available, ranging from alkali,²⁰ alkaline earth,^{39,40} rare earth,^{25,36} Group 4 and Group 5 metals,⁴² to late transition-metal catalysts.^{16,21,24,29,31,35} Less prominent are Brønsted and Lewis acid-based catalyst systems.^{6,18,37} The mode of operation of the catalyst systems varies significantly and the different reaction mechanisms will be discussed briefly. Many of the catalyst systems are quite specific in their substrate scope, with only a limited number applicable to a broader range of substrates. Further challenges include control over Markovnikov/anti-Markovnikov regioselectivity²³ and 1,2 vs. 1,4 addition to dienes, processes that can be controlled to some extent by the proper choice of catalyst.

MECHANISM AND STEREOCHEMISTRY

Alkali, Alkaline Earth, and Rare Earth Metals

Generally, hydroamination reactions involving electropositive elements, such as alkali, alkaline earth, and rare earth (including Sc, Y, La to Lu) metal based catalyst systems proceed via a metal-amido species that undergoes nucleophilic addition to the alkene (Scheme 2). The regiochemistry of the addition is determined by the substituent attached to the alkene. Whereas aliphatic substituents predominantly lead

to the Markovnikov addition product with a terminal β -aminoalkyl metal intermediate **1**, aromatic substituents produce predominantly the anti-Markovnikov product due to the electronic stabilization of the benzylic metal intermediate **2** (via electron delocalization of the negative charge on the benzylic carbon as well as π -interaction of the aromatic ring with the metal center).^{43,44}



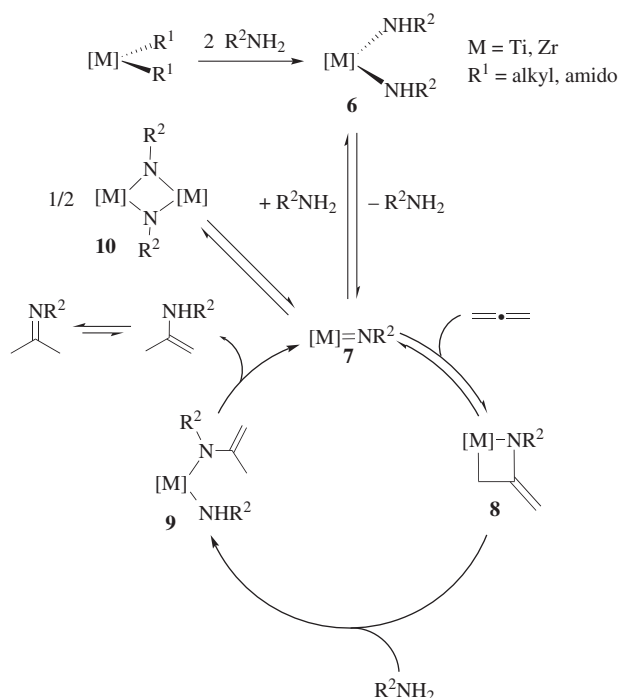
Scheme 2

The mechanism for the intramolecular hydroamination of aminoalkenes has been studied in more detail (Scheme 3), in particular for rare earth metal based catalyst systems,^{45,46} but alkali, alkaline earth, and actinide catalysts are presumed to operate in a similar fashion.^{47,48} The resting state of the catalyst is believed to be a metal-amido amine adduct **4** that is in equilibrium with the more electron-deficient, hence more reactive, metal-amido species **3**. The insertion of the alkene into the metal-amide bond is approximately thermoneutral and is considered to be the rate-determining step (RDS). This is followed by rapid, exothermic protonation of the resulting highly reactive metal-alkyl intermediate by excess amine substrate. The cyclization always generates the exocyclic hydroamination product because the *endo* cyclization has a high activation barrier,^{49–51} presumably as a result of steric strain. Observation of a significant primary kinetic isotope effect (KIE; k_H/k_D in the range of 2.3–5.2)^{45,52} is indicative of a partial N–H bond disruption in the transition state of the rate-determining alkene insertion step. A plausible explanation involves concerted proton transfer from a coordinated amine^{45,53,54} to the α carbon in the insertion step (Scheme 4). However, some experimental data, in particular the observation of sequential hydroamination/bicyclization sequences (Scheme 5),^{43,55–58} is in conflict with these findings, as the latter requires a finite lifetime for the rare earth metal alkyl intermediate. Therefore, the intermediacy of the metal-alkyl species **5** (Scheme 3) and its potential lifetime is unclear at present and is probably strongly dependent on catalyst and substrate structures.



The hydroamination of allenes catalyzed by Group 4 metals proceeds by a mechanism closely related to that of alkynes.^{10,11,14,59–63} The catalytically active metal-imido species **7** is generated via reversible α elimination of an amine from the bis-amido precursor **6**. A reversible, rate-determining [2 + 2]-cycloaddition of the imido species with the allene yields the azametallacyclobutane intermediate **8** (Scheme 6). Subsequent protonation of the azametallacyclobutane produces an

enamide amido complex **9** that undergoes α elimination of the enamine, regenerating the catalytically active imido species. Depending on the steric demand of the imido ligand and the ancillary ligands, the imido species is also in equilibrium with the bridged imido dimer **10**, favoring the dimeric species with decreasing steric demand of the ancillary and imido ligands. Hence, many sterically less-encumbered catalyst systems perform better with sterically demanding amines and the rate of the reaction generally does not correlate linearly with the concentration of the catalyst.

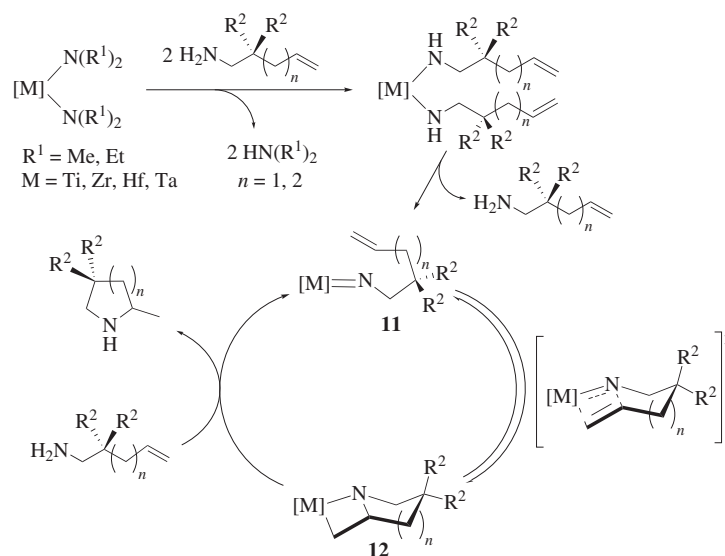


Scheme 6

The mode of operation of Group 5 metal catalysts in the hydroamination of allenes is unclear at present. The fact that only primary amines react with allenes (and alkenes) seems to support a metal-imido intermediate. However, mechanistic studies on the tantalum-catalyzed hydroamination of alkynes are unable to confirm this mechanistic scenario.^{64–66}

The mechanism of alkene hydroamination is much less well understood than the mechanism for alkyne and allene hydroamination and is still under significant debate.^{48,53,67–71} On the basis of the observation that most neutral Group 4 and Group 5 metal alkene hydroamination catalysts are unreactive towards secondary aminoalkene substrates, a mechanism analogous to that for alkyne and allene hydroamination involving metal-imido species as catalytically active species has

been proposed (Scheme 7).^{67,68,70} The reversible^{72,73} [2+2]-cycloaddition of the metal imido species **11** with the alkene moiety leads to an azametallacyclobutane **12** that is protolytically cleaved to regenerate the metal-imido species and release the hydroamination product. The significant activation barrier⁶¹ for this protonation step and the facile cycloreversion of the azametallacyclobutane **12** to the metal-imido species **11** is most likely responsible for the limited scope of neutral Group 4 and Group 5 metal based catalyst systems in the hydroamination of non-activated simple alkenes and the harsh reaction conditions required to achieve catalytic turnover.



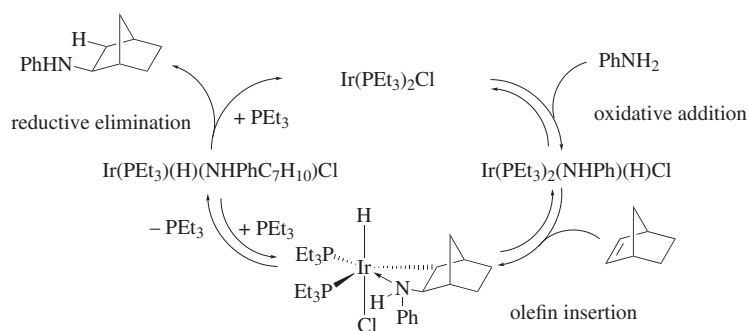
Scheme 7

However, a few (achiral) neutral, Group 4 metal catalyst systems are reported to catalyze the cyclization of secondary aminoalkenes and it is suggested that a lanthanide-like σ -bond metathesis mechanism (Scheme 3) is operating in these cases.^{48,69,74}

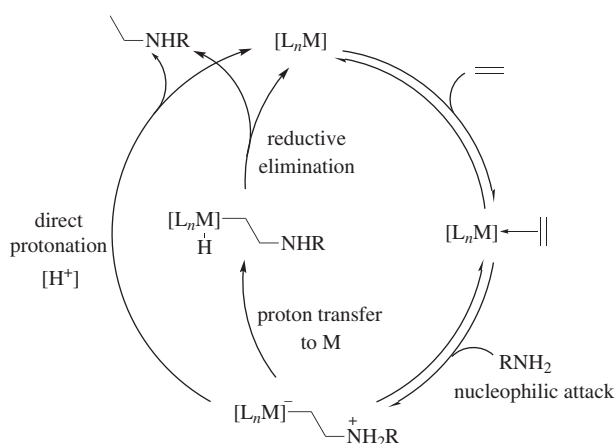
Late Transition Metals

The mechanism of late transition metal catalyzed hydroaminations is less intensively studied and they are much less well understood compared to early transition and rare earth metal catalyzed hydroaminations. However, it is established that late transition metal catalyzed hydroaminations may proceed via different mechanisms depending on the substrate and the catalyst employed. Generally, the reactions are thought to involve either amine activation (Scheme 8) or alkene activation (Scheme 9).^{21,75,76} Cleavage of the β -aminoalkyl metal species can occur either via direct

protonation from an external acid or via reductive elimination of a metal-hydrido alkyl intermediate (Scheme 9).



Scheme 8



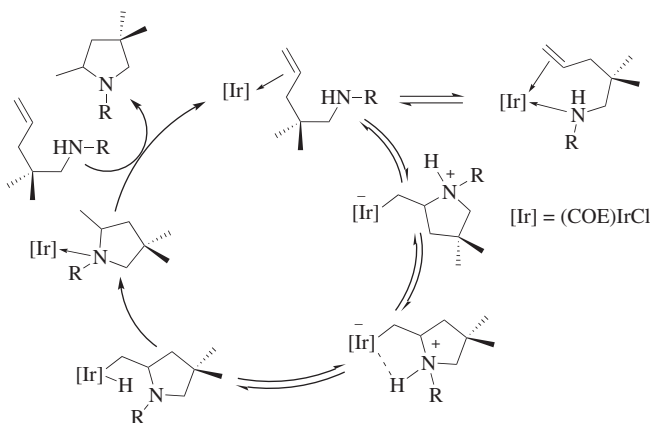
Scheme 9

The amine activation mechanism includes oxidative addition of an amino group, followed by insertion of the unsaturated carbon–carbon bond into the metal–amide bond and final reductive elimination. It is established that the iridium(I)-catalyzed hydroamination of strained alkenes, such as norbornene, with anilines proceeds via this mechanism (Scheme 8).^{77–79} Although amines other than anilines, such as ammonia, are also reported to undergo N–H oxidative addition to iridium^{80–82} and ruthenium⁸³ metal centers, no related catalytic systems are known. The *syn* insertion of an olefin into a palladium–amide bond has also been observed.^{84,85} However, these particular systems are not directly related to hydroamination processes. Nevertheless, the platinum-catalyzed intramolecular hydrohydrazination of *N*-protected alkenyl hydrazides proceeds via NH-activation/olefin insertion rather than through nucleophilic attack to a coordinated alkene.⁸⁶

Key steps of the alkene activation mechanism (Scheme 9) include nucleophilic attack of the amine on the metal-coordinated olefin, leading to a zwitterionic intermediate. Proton transfer from nitrogen to the metal produces a β -aminoalkyl metal species that then undergoes reductive elimination, cleaving the metal–carbon bond. The direct protonolysis of the metal–carbon bond in the zwitterionic ammonium intermediate is also possible in principle, but this step is less kinetically favorable than the stepwise process via reductive elimination.

DFT calculations suggest that the amine activation pathway is less favored than the alkene activation pathway for the intermolecular hydroamination of simple alkenes with aliphatic amines catalyzed by Group 9 and 10 metal complexes.⁸⁷ Similar studies of the platinum-catalyzed addition of aniline to ethylene show a high barrier for oxidative amine addition and reveal that nucleophilic attack on the coordinated ethylene is the rate-determining step.^{88,89}

The iridium-catalyzed intramolecular hydroamination of aliphatic aminoalkenes is also proposed to proceed via alkene activation (Scheme 10).⁹⁰ DFT calculations suggest that the irreversible metal–carbon bond cleavage is rate-limiting, which is in line with the observed large negative activation entropy. It should be noted that coordination of the alkenyl moiety of the substrate to the metal center may be disfavored by a competitive coordination of the amino group, which will not result in product formation. This explains why primary aminoalkenes are significantly less reactive than more sterically encumbered (and thus less prone to coordinate through nitrogen) secondary aminoalkenes for most late transition metal based systems. Another important observation is that not all late transition metal catalyzed systems are limited in turnover by the protonolysis step, given that some examples of “fast” protonolysis in a rhodium catalyst system with a κ^3 -P,O,P-xanthene-based ligand system are known.⁹¹

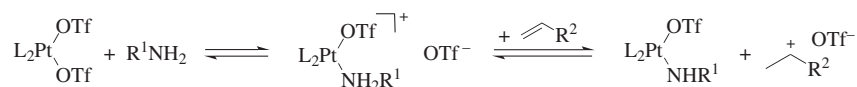


Scheme 10

Analogous alkene activation mechanisms are also proposed for a number of hydroaminations utilizing *N*-protected amines or less nucleophilic amines, such

as anilines. Mechanistic studies suggest that the protonolysis of the metal–carbon bond is the rate-determining step in the PNP-palladium-catalyzed [PNP = 2,6-bis((diphenylphosphanyl)methyl)pyridine] intramolecular hydroamination of alkenyl carbamates and carboxamides.⁹² A DFT study of the (phosphine)Au(I)-catalyzed addition of carbamates to 1,4-dienes leads to a similar conclusion.⁷⁵

It is important to note that in certain cases the role of the metal catalyst may be limited to the generation of an acid via ligand exchange with the *N*-protected amine followed by protonolysis of the alkene. This activates the alkene to nucleophilic transformations, since the addition of *N*-protected amines to alkenes is also efficiently catalyzed with Brønsted acids such as TfOH (Scheme 11).^{93,94}



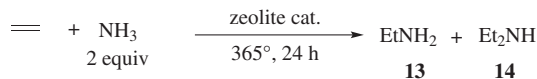
Scheme 11

SCOPE AND LIMITATIONS

Ethylene and Other Unactivated Alkenes

Simple alkenes are readily available feedstock in the chemical industry. Therefore, it is desirable to utilize them in highly atom-economical functionalization reactions, such as the hydroamination reaction. Although significant progress has been made in the area of intermolecular hydroamination of unactivated alkenes, overall, the process remains challenging and very few reactions have found synthetic or industrial application. The intermolecular hydroamination of unactivated alkenes is presented in Table 1A. Intramolecular hydroaminations of aminoalkenes are significantly more facile and will be covered in a later section.

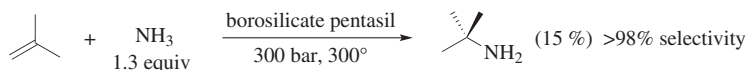
Intermolecular Hydroamination of C₂–C₄ Alkenes. Although the reaction of simple alkenes and amines is thermodynamically feasible ($\Delta G^0 \approx -14.7 \text{ kJ mol}^{-1}$ for the addition of ammonia to ethylene),¹⁷ the uncatalyzed process is kinetically disfavored.⁹⁵ Even if equilibrium can be reached it may favor the starting materials under the reaction conditions required to catalyze the process. Elevated temperatures and pressures are required in most cases, as well as the presence of a transition metal or main group metal catalyst. Robust, non-transition metal based heterogeneous catalysts can also facilitate the desired transformation. Various zeolites^{96–99} are active catalysts for the hydroamination of ethylene with ammonia. Harsh reaction conditions (up to 370°) are employed and typical conversions do not exceed 20%. An additional drawback is the uncontrolled polyalkylation of ammonia to give mixtures of mono-(13) and diethylamine (14) (Scheme 12).



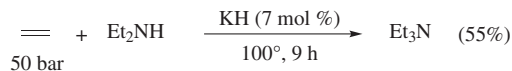
Catalyst	Yield (%) 13 + 14	13/14
H-Y Zeolite	12	81:19
H-Erionite	18	97:3

Scheme 12

A low selectivity to form the primary amine hydroamination product is also observed for the analogous reaction of propylene.^{97,100} The selectivity can be increased to >97% for propylene¹⁰¹ and >98% for isobutylene¹⁰² by use of a pentasil-type zeolite catalyst,^{101,103} with the latter process being commercialized by BASF (Scheme 13) as an industrial-scale approach to *tert*-butylamine. The catalytic activity is very sensitive to the amount and strength of Brønsted acid sites on these solid catalysts, and linear correlations between the SiO₂/Al₂O₃ ratio of H-MFI, H-Mordenite, and H-FAU solid catalysts are observed.¹⁰⁴ Overall, the harsh conditions restrict the use of heterogeneous zeolite-type catalysts to the reactions of C₂–C₄ alkenes with ammonia.^{104,105}

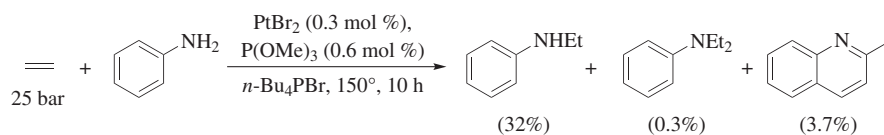
**Scheme 13**

Somewhat milder conditions for the hydroamination of “small” alkenes, which are not restricted to ammonia as a nitrogen source, are required for alkali metal catalysts. Whereas elemental lithium,¹⁰⁶ sodium,^{107,108} and potassium¹⁰⁷ require high reaction temperatures, more reactive alkali metal amides^{109–111} or hydrides¹¹² are more efficient catalysts. In general the process is not selective when ammonia is used; however, tertiary amines may be obtained selectively when secondary amines react with ethylene (Scheme 14).¹¹²

**Scheme 14**

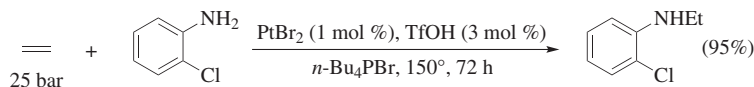
A variety of late transition metal complexes have been tested as homogeneous catalysts for the hydroamination of C₂–C₄ alkenes. In nearly all of these studies the addition of HNR₂ to both alkenes and alkynes proceeds with Markovnikov regioselectivity. Catalysts employing iron,¹¹³ ruthenium,^{113–116} rhodium,^{117–120} and platinum^{93,117,121–124} are reported for the hydroamination of C₂–C₄ alkenes. It is noteworthy that no transition metal based catalyst system for the addition of ammonia has been reported. So far, most catalyst systems are restricted to

weakly basic anilines or *N*-protected amines (amides, carbamates, sulfonamides). A typical hydroamination of aniline with ethylene is accompanied by a second hydroamination as well as oxidative arylation side reactions (Scheme 15).¹²¹ More basic alkylamines are unreactive under these conditions, presumably due to facile catalyst decomposition.¹²⁵



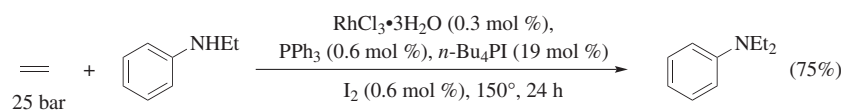
Scheme 15

When a sterically hindered and electronically deficient aniline is employed, a chemoselective transformation can be achieved (Scheme 16).¹²¹



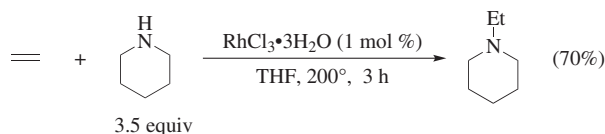
Scheme 16

A catalytic system based on rhodium trichloride shows high activity and excellent selectivity for the hydroamination of *N*-ethylaniline (Scheme 17).¹²⁰



Scheme 17

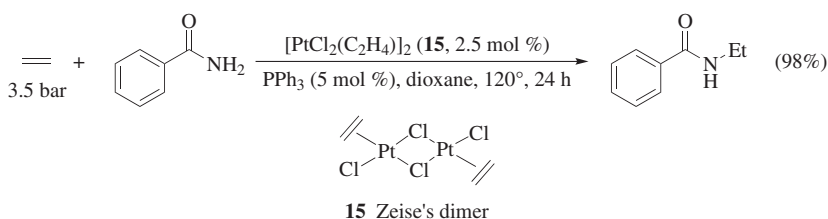
Most late transition metal based catalysts are applicable to less basic anilines. Reports on the reactivity of aliphatic amines are rare¹¹⁹ and typically involve cyclic secondary amines (Scheme 18).¹¹⁷



Scheme 18

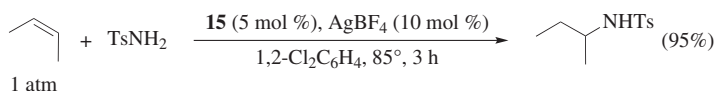
Whereas late transition metal catalyzed hydroaminations of alkenes with unprotected amines require high temperatures, even with anilines, reactions of *N*-protected

amines (e.g. amides, sulfonamides) are generally more feasible. Thus, the platinum-catalyzed reaction of benzamide with ethylene proceeds at 120° (Scheme 19).¹²²



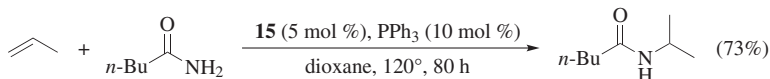
Scheme 19

The addition of tosylamide to the less reactive (*Z*)-2-butene is also catalyzed by the Zeise dimer **15** after activation with AgBF₄ (Scheme 20).⁹³



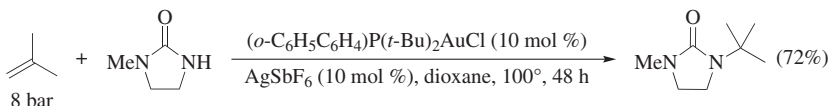
Scheme 20

An analogous reaction of a carboxamide with propylene gives exclusively the Markovnikov hydroamination product in good yield (Scheme 21).¹²²



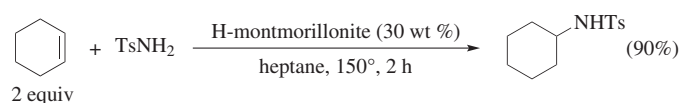
Scheme 21

The intermolecular Markovnikov addition of cyclic ureas to alkenes catalyzed by a cationic gold(I) phosphine complex is reported.¹²⁶ The reaction is not limited to C₂–C₄ and higher terminal alkenes but also succeeds with the sterically more challenging isobutylene (Scheme 22).



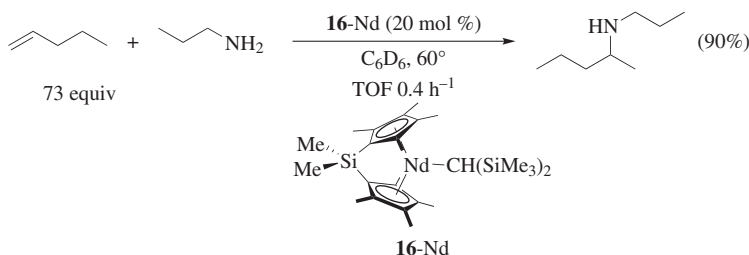
Scheme 22

Intermolecular Hydroamination of Unactivated Higher Alkenes. Inorganic zeolites and clays are significantly less efficient in the hydroamination of higher alkenes with unprotected amines and ammonia. However, heterogeneous catalysts can be successfully employed in the hydroamination of more reactive *N*-protected amines.¹²⁷ For example, H-montmorillonite clay can catalyze the addition of tosylamide to cyclohexene in good yield (Scheme 23). The analogous addition to acyclic terminal or internal alkenes proceeds with low regioselectivity and is accompanied by double bond migration.¹²⁷



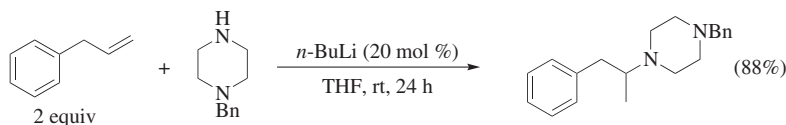
Scheme 23

The intermolecular lanthanide-catalyzed alkene hydroamination is feasible with the sterically open *ansa*-neodymocene **16**-Nd, but the number of examples remains small (Scheme 24).^{43,128} The reaction proceeds regioselectively in a Markovnikov fashion, but a large excess of alkene is required and the reaction is 2–3 orders of magnitude slower than the intramolecular process.



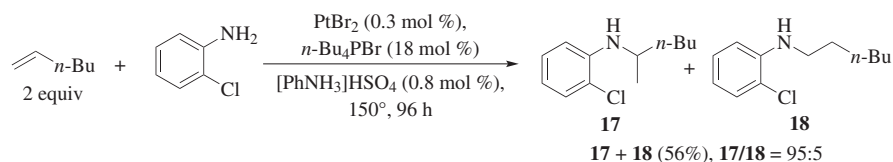
Scheme 24

Although the base-catalyzed hydroamination of higher alkenes is less developed than that of lower alkenes and vinyl arenes, activated allylarenes react smoothly under mild conditions in the presence of an alkyllithium or lithium amide.^{129,130} The enhanced reactivity presumably results from isomerization of allylbenzene to the more reactive β -methylstyrene derivative prior to the hydroamination step (Scheme 25).¹³⁰



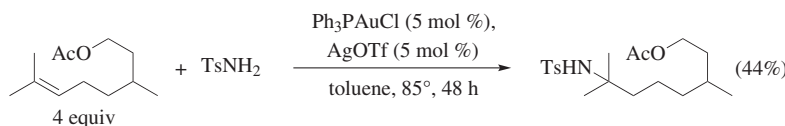
Scheme 25

A limited number of late transition metal catalyzed, intermolecular hydroaminations of higher alkenes with *N*-unprotected amines are known using catalysts based on platinum^{123,131} and rhodium.¹³² The reaction is limited to less nucleophilic anilines as the amine component (Scheme 26)¹²³ and the catalytic efficiency is predictably lower in comparison to reactions involving ethylene. The Markovnikov product **17** is formed preferentially to its isomer **18**.



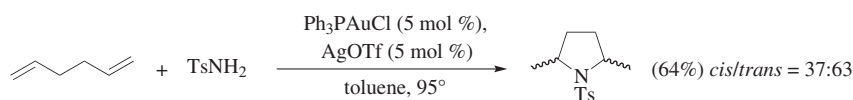
Scheme 26

The gold(I)-catalyzed hydroamination with sulfonamides can also be applied to more sterically encumbered trisubstituted alkenes. Exclusive Markovnikov addition is seen (Scheme 27).¹³³



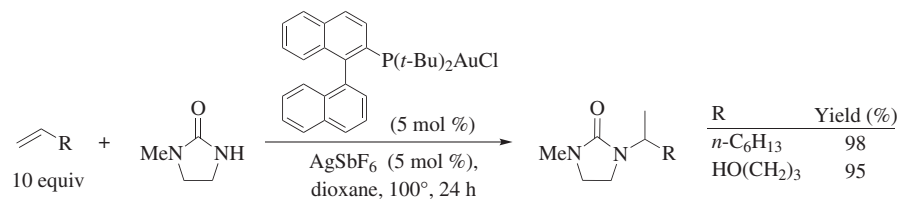
Scheme 27

An analogous reaction with a non-conjugated diene proceeds smoothly to a pyrrolidine product, as the intermediate secondary sulfonamide is also active in the gold-catalyzed hydroamination reaction (Scheme 28).¹³³



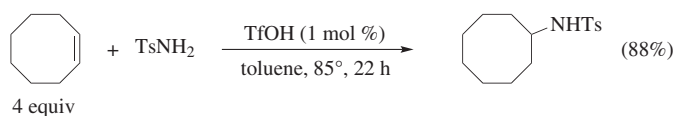
Scheme 28

A variety of functional groups, such as hydroxyl, ether, ester, and carboxylic acids are tolerated in the gold(I)-catalyzed Markovnikov addition of cyclic ureas to alkenes; however, a large excess of the alkene is required (Scheme 29).¹²⁶



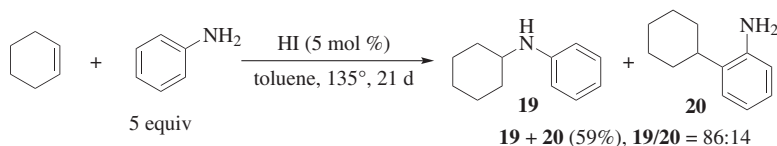
Scheme 29

Although homogeneous Brønsted acid catalyzed hydroaminations of C₂–C₄ alkenes are not known, higher alkenes are reported to undergo this reaction smoothly in the presence of triflic acid (Scheme 30).¹³⁴ However, reactions with analogous acyclic alkenes lack regioselectivity.¹³⁵ Several metal-mediated hydroamination reactions with protected amines are believed to proceed via an acid-catalyzed pathway.³⁷



Scheme 30

Although intermolecular Brønsted acid catalyzed hydroamination processes are most efficient for protected amines; however, some reactions with unprotected amines of low basicity such as hydrazines,^{136,137} azoles,^{138–141} and anilines^{142,143} are known. A significant drawback of Brønsted acid catalyzed hydroamination reactions involving aniline derivatives is the formation of hydroarylation byproducts as illustrated by constitutional isomers **19** and **20** resulting from the HI-catalyzed addition of aniline to cyclohexene (Scheme 31).¹⁴³

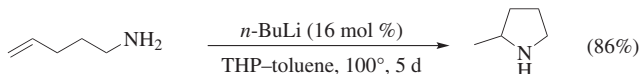


Scheme 31

Intramolecular Hydroamination of Aminoalkenes. In contrast to allenes, dienes, and strained alkenes, unactivated alkenes exhibit significantly different modes of reactivity in inter- vs. intramolecular hydroamination, with the latter process being much more facile. The vast majority of catalysts that operate in intramolecular aminoalkene hydroamination reactions cannot be applied to the more challenging intermolecular processes. Intramolecular aminoalkene hydroamination has captured the attention of many research groups, and the results are fully covered in Table 2A. A large number of catalyst systems based on alkali, alkaline earth, and early and late transition metals efficiently mediate the cyclization of aminoalkenes.

Relatively simple lithium-based precatalysts ranging from *n*-BuLi and LDA^{144–148} to more elaborate axially chiral lithium amides¹⁴⁹ (see “Enantioselective Intramolecular Hydroamination of Aminoalkenes” later in the text) can be employed for the intramolecular hydroamination of aminoalkenes. The cyclization of primary and secondary alkenyl amines affords pyrrolidine and piperidine derivatives. The formation of azepanes or larger azacycles has not yet been reported with these catalyst systems. The basicity of alkali metal based catalysts often results in

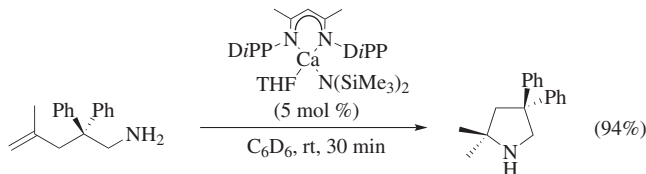
undesired side reactions, such as double bond migration. For the simple *n*-BuLi catalyst system this side reaction can be suppressed by using a THP–toluene solvent mixture (Scheme 32).¹⁴⁸



Scheme 32

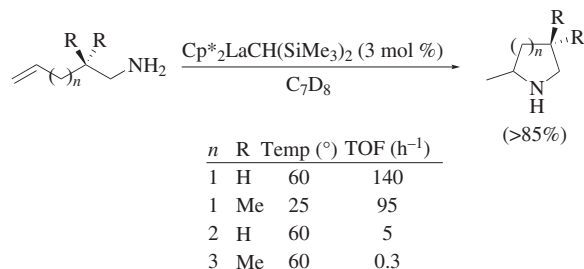
The reaction proceeds exclusively as an *exo* cyclization, similar to rare earth and early transition metal catalyzed cyclizations. The high nucleophilicity and basicity of organolithium reagents significantly limits the range of tolerated functional groups.

Alkaline earth metal-based systems featuring magnesium, calcium, strontium, and barium are in general more reactive and less basic than lithium-based catalysts, however, they display similar limitations with respect to their functional group tolerance.^{47,150–155} Azacycles with ring sizes ranging from 5- to 7-membered rings are accessible via exclusive *exo* cyclization of the corresponding aminopentenes, aminohexenes, and aminoheptenes. The rate of reaction significantly decreases with the increasing number of substituents on the double bond. Whereas *gem*-disubstituted alkenes still undergo the cyclization (Scheme 33),⁴⁷ 1,2-disubstituted alkenes and higher substituted alkenes are unreactive even at elevated temperatures.



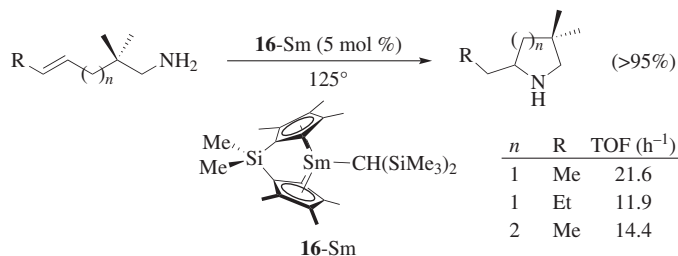
Scheme 33

With the exception of alkaline earth metal catalysts, rare earth metal based catalysts are by far the most active catalysts for the intramolecular hydroamination of *N*-unprotected primary and secondary amines.^{7,25,36} Similar to alkali and alkaline earth metal based catalyst systems, all cyclizations proceed with exclusive *exo* selectivity and allow the synthesis of 5- to 7-membered rings. The rate of cyclization decreases with increasing ring size ($5 > 6 \gg 7$), and the presence of increasingly sterically demanding *gem*-dialkyl substituents¹⁵⁶ results in significantly enhanced reactivity of the substrates (Scheme 34).⁴⁵ The rate of cyclization also increases with an increasing ionic radius of the rare earth metal and increasing openness of the coordination sphere.⁴⁵ Although metallocene catalysts are generally superior in reactivity, elaborate ligand frameworks are not necessarily required, as exemplified by the simple homoleptic tris(amides) Ln[N(SiMe₃)₂]₃ (Ln = Y, Nd, La).^{157,158}

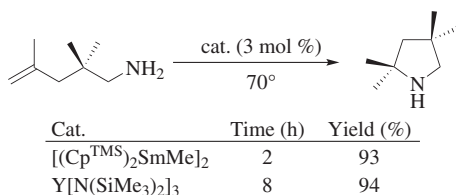


Scheme 34

The reactivity of 1,2- and *gem*-disubstituted alkenes is much lower than that of terminal alkenes (Schemes 35¹⁵⁹ and 36^{157,160}). Interestingly, the formation of pyrrolidines and piperidines proceeds with comparable rates, in contrast to the results obtained for terminal alkenes.



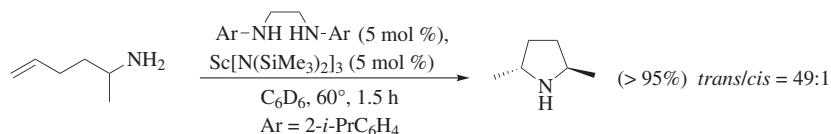
Scheme 35



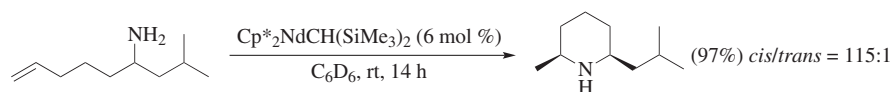
Scheme 36

The cyclization of chiral aminoalkenes can be performed with good to excellent diastereoselectivity.^{45,158,161–166} Whereas the cyclization of α -substituted aminopentene derivatives leads preferentially to *trans* 2,5-disubstituted pyrrolidines (Scheme 37),¹⁶⁵ the reaction of analogous aminohexene derivatives strongly favors the *cis* 2,6-disubstituted piperidines (Scheme 38).¹⁶¹ The preferred formation of *trans* disubstituted pyrrolidines can be explained by minimization of 1,3-diaxial interactions in the chair-like cyclization transition state that requires a coplanar alignment of the M–N and C=C bonds (Figure 1, left side). Analogous arguments for

aminohexene derivatives account for the preferred formation of *cis* 2,6-disubstituted piperidines (Figure 1, right side). The proximity of the stereocenter is crucial, as substituents placed in more remote positions relative to the amino group result in significantly diminished diastereoselectivities.



Scheme 37



Scheme 38

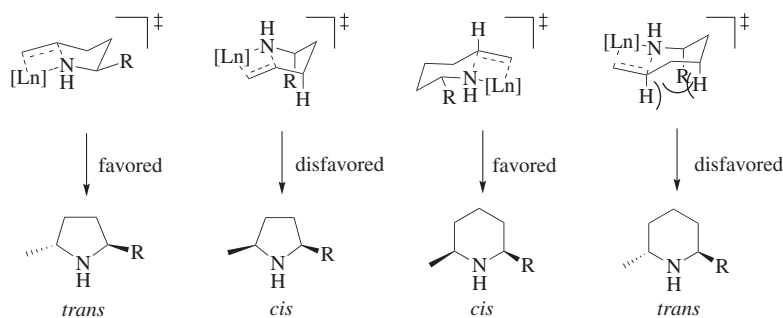
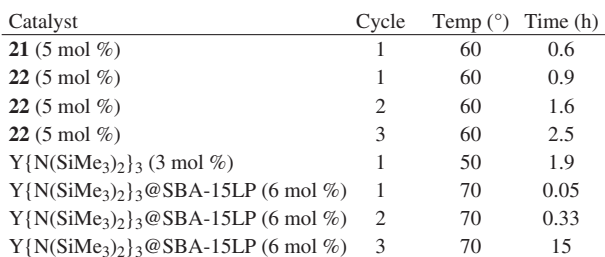
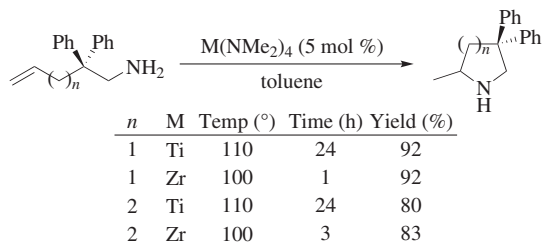


Figure 1. Stereomodels for observed diastereoselectivity in the cyclization of α -substituted aminopentene (left) and aminohexene (right) derivatives.

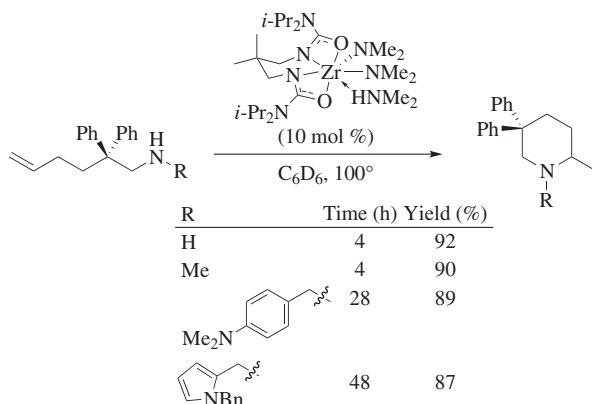
Compared to homogeneous catalysts, heterogeneous catalysts allow facile catalyst separation from the reaction mixture and have the potential for recycling. Several attempts to develop heterogeneous lanthanide-based catalysts have been reported. Resin-supported lanthanocene complexes attached to amine-functionalized cross-linked polystyrene supports, e.g. **22**, display activities similar to the homogeneous analog **21** and can be recycled at least two times (Scheme 39).¹⁶⁷ Grafting of homoleptic tris(amides) onto partially dehydroxylated mesoporous zeolites leads to activities higher than those of the tris(amides) in homogeneous solution.¹⁶⁸ The activity decreases in the order $\text{Y} > \text{La} > \text{Nd}$ and is also dependent on the pore size and particle morphology. However, the supported catalyst shows only limited recyclability.



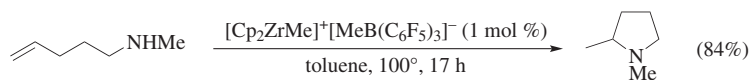
Group 4 metal complexes possess features that are potentially superior to those of rare earth metal complexes, as they are more tolerant of functional groups, easier to prepare, and easier to handle. Complexes based on titanium,^{67,69,169–179} zirconium,^{48,68–70,74,169–171,176,178,180–182} and hafnium¹⁷⁰ catalyze the hydroamination of aminoalkenes. In the simplest cases, commercially available homoleptic tetraamides such as $\text{Ti}(\text{NMe}_2)_4$ ⁶⁷ or $\text{Zr}(\text{NMe}_2)_4$ ⁶⁹ are catalysts for substrates activated by *gem*-dialkyl substitution (Scheme 40). Group 4 metal catalysts in general exhibit significantly lower catalytic activity when compared with rare earth metal based systems. Generally, the reactivity decreases in the order $\text{Zr} > \text{Hf} > \text{Ti}$, which is opposite to the trend observed in alkyne hydroaminations.^{10,11,14} The fact that neutral catalyst systems, with a few exceptions (Scheme 41),^{48,69,74,178} are confined to aminoalkenes with a primary amino group has been interpreted in support of a metal-imido based [2 + 2]-cycloaddition mechanism (Scheme 7). On the other hand, cationic catalyst systems,^{169,180} which are believed to operate via a lanthanide-like σ -bond metathesis mechanism, are limited to aminoalkenes with a secondary amino group. Primary aminoalkenes are thought to deactivate these cationic systems through a facile α -deprotonation of a cationic metal-amido species.¹⁸³ As an illustrative example, the cationic zirconocene $[\text{Cp}_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ cyclizes *N*-methyl aminoalkenes even in the absence of activating *gem*-dialkyl substituents (Scheme 42) and requires relatively low catalyst loadings in comparison to most other Group 4 metal catalysts.¹⁶⁹



Scheme 40

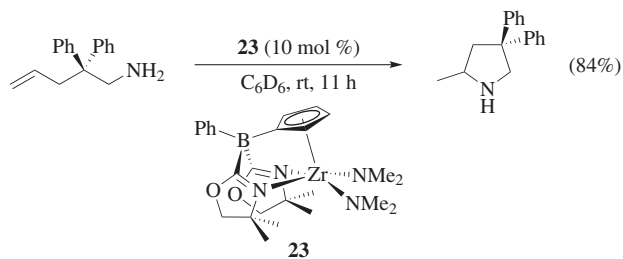


Scheme 41



Scheme 42

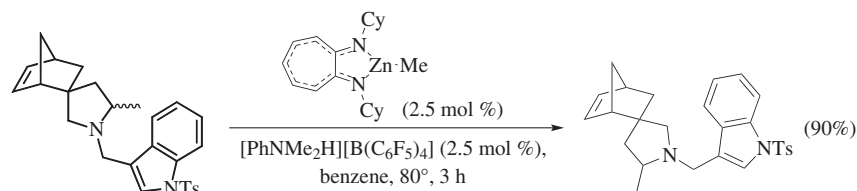
A significant increase in reactivity is achieved using the zwitterionic zirconium cyclopentadienyl-bis(oxazolidinyl)borate complex **23**, which permits the cyclization of Thorpe–Ingold activated substrates at room temperature (Scheme 43).¹⁸⁴ As will



Scheme 43

be discussed in the section on enantioselective reactions, a chiral variant of this complex is active even at -30° .⁵⁴

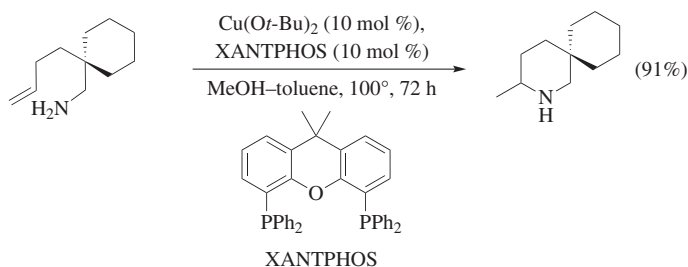
Aminotroponiminato zinc complexes catalyze the hydroamination of secondary aminoalkenes (Scheme 44),¹⁸⁵ and tolerate a variety of functional groups, including thioketals, silyl ethers, and sulfonimides.^{185–191} The catalytic activity is improved by using anilinium borate co-activators that generate cationic zinc species in situ. Anilinium borate itself is also a suitable catalyst¹⁷⁴ with comparable reactivity at elevated temperatures; however, in combination with Lewis acidic diethylzinc the reactions readily proceed at room temperature.¹⁹² The mechanisms involved in these catalysts are not known and may depend on whether the reactions proceed via neutral or cationic species.



Scheme 44

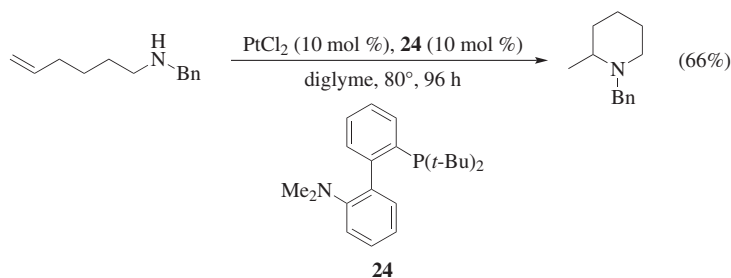
Catalysts based on late transition metals are typically less efficient than those based on rare earth metals. Their reactivity decreases from *N*-protected to secondary aminoalkenes, with few systems able to effect the cyclization of a primary aminoalkene. Nevertheless, enhanced functional group tolerance and simplicity of reaction setup is an advantage stimulating further development in this area.

The cyclization of primary aminoalkenes is catalyzed by complexes of platinum,^{193,194} gold,¹⁹⁵ rhodium,¹⁹⁶ and copper.¹⁹⁷ In most cases these catalysts either require the use of stoichiometric amounts of a Brønsted acid to complete the catalytic cycle, or are confined to Thorpe–Ingold activated aminoalkenes (Scheme 45).¹⁹⁷

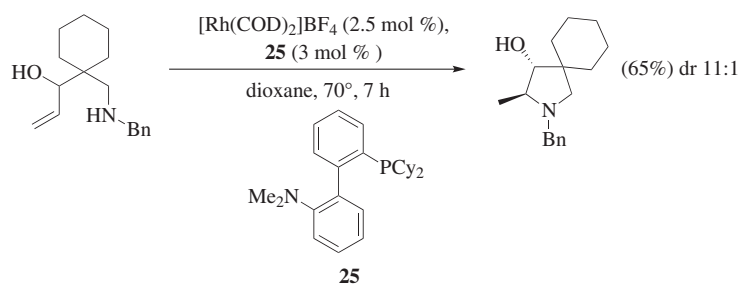


Scheme 45

A rhodium catalyst capable of cyclizing unbiased primary aminoalkenes is reported.⁹¹ However, cyclizations of secondary aminoalkenes with late transition metal catalysts are more facile.^{195–200} The steric and electronic features of the ligand employed exert considerable influence on the reactivity of the catalyst. Thus, the reactivity of PtCl_2 is significantly enhanced by the sterically demanding monophosphine ligand **24**, allowing the facile cyclization of an aminoalkene at 80° (Scheme 46).¹⁹⁹ In contrast, a less demanding triphenylphosphine-based system operates only at 120° ¹⁹⁸ and is similar in reactivity to “ligandless” PtCl_2 .²⁰¹ The range of tolerated functional groups is significantly broader than that for early transition metal catalysts, and even includes unprotected Hydroxy groups as shown in a cyclization facilitated by ligand **25** (Scheme 47).¹⁹⁶

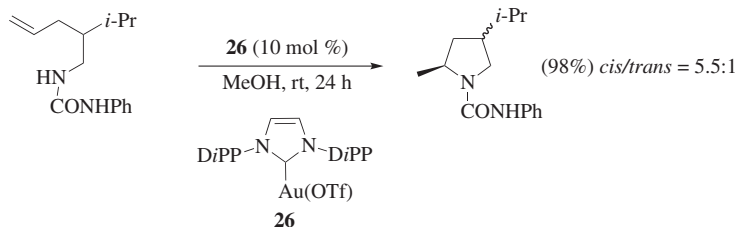


Scheme 46



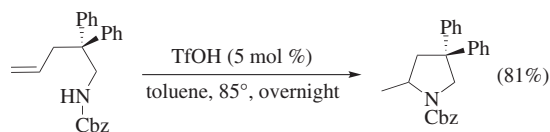
Scheme 47

Late transition metal catalyzed hydroaminations of *N*-protected alkenyl amines are successfully performed utilizing a variety of functionalized nitrogen moieties, including sulfonamides,²⁰² carbamates,^{92,133,203–206} amides,^{92,203,207} and ureas.²⁰⁸ Many reactions proceed at room temperature, which is not the case for *N*-unprotected primary or secondary aminoalkenes. A typical example is the gold-catalyzed cyclization of an *N*-alkenyl urea utilizing the *N*-heterocyclic carbene complex **26** (Scheme 48).²⁰⁸



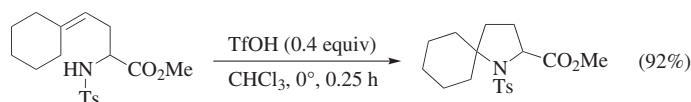
Scheme 48

It should be noted, however, that the reduced basicity of *N*-protected alkenyl amides allows their facile cyclization in the presence of Brønsted acid catalysts (Scheme 49), and some of the previously reported metal-catalyzed cyclizations are possibly catalyzed by the acid co-catalyst.^{134,209–212}



Scheme 49

5-*Endo* cyclizations of aminoalkenes are not observed in metal-catalyzed hydroaminations, but are observed in acid-catalyzed processes (Scheme 50).²¹⁰ Brønsted acids are also used in catalyzed cyclizations of *N*-unprotected aminoalkenes, but the reactivity is very low, presumably due to the strong basicity of the amine center.^{174,213}



Scheme 50

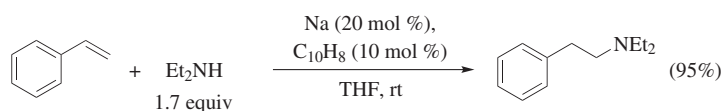
Hydroamination of Vinyl Arenes

Intermolecular Hydroamination of Vinyl Arenes. The reactivity of the double bond in vinyl arenes is significantly increased by conjugation to the aromatic ring system. Hence, vinyl arenes generally react more smoothly in hydroamination reactions in comparison to simple, unactivated alkenes, especially in intermolecular processes. Multiple catalytic systems featuring Brønsted acids and bases, and early and late transition metal based catalysts are successfully employed in inter- and intramolecular hydroaminations of vinyl arenes with both *N*-unprotected and *N*-protected amines of varying basicity. A particular challenge is the control of

Markovnikov and anti-Markovnikov regioselectivity. It should be noted that reactions of electron-deficient vinyl arenes (e.g. vinyl pyridines) are not covered, as they represent typical Michael acceptors with different reactivities. The intermolecular hydroamination of vinyl arenes is covered in Tables 1B.

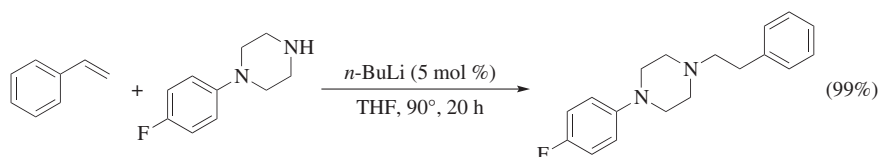
Vinyl arenes and stilbene derivatives react with ammonia and primary amines upon irradiation in the presence of the electron-transfer reagent dicyanobenzene.^{214–216}

Vinyl arenes readily react with amines under basic conditions. Sodium metal catalyzes the hydroamination of styrene with secondary^{217–221} or primary^{222,223} aliphatic amines at ambient or slightly elevated temperatures. The anti-Markovnikov addition of the amine moiety is favored (Scheme 51).²²¹



Scheme 51

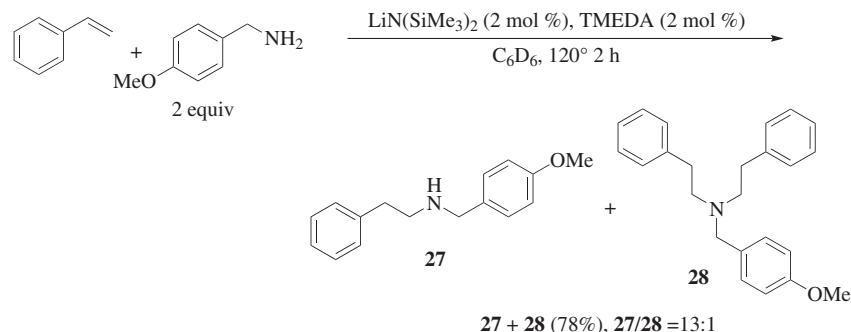
Readily available alkyllithium reagents can also be used as homogeneous base-type catalysts for anti-Markovnikov addition of primary^{224,225} and secondary^{130,224,226} amines to styrene derivatives. The reactions typically proceed in good to excellent yields to give β -phenylethylamine derivatives (Scheme 52).²²⁶ Unfortunately, ammonia does not exhibit the same reactivity as primary and secondary amines.



Scheme 52

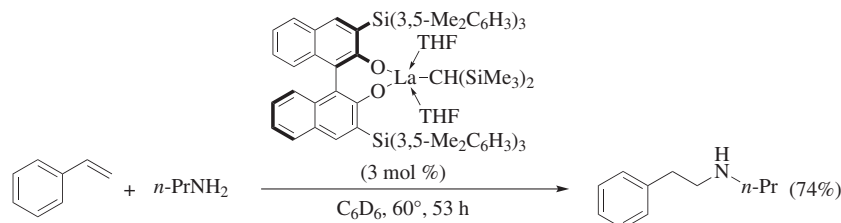
The simple lithium amide $\text{LiN}(\text{SiMe}_3)_2$ catalyzes the addition of aliphatic and (notably) aromatic amines to vinyl arenes.⁴⁴ The catalytic activity is increased by the addition of TMEDA and the reaction can be carried out in bulk without additional solvent. More reactive primary aliphatic amines also form bis-hydroamination products like **28** in addition to the target secondary amines like **27**, although the formation of the latter may be suppressed by using an excess of amine (Scheme 53). Less reactive aromatic amines and α -, and β -substituted vinyl arenes yield the corresponding mono-hydroamination adducts exclusively.⁴⁴ Other readily available alkali metal based catalysts include NaH ,¹³⁰ $t\text{-BuOK}$,^{225,227,228} and CsOH .²²⁹

Some of the most active rare earth metal based hydroamination catalysts (especially employing large rare earth metals like neodymium or lanthanum) also exhibit



Scheme 53

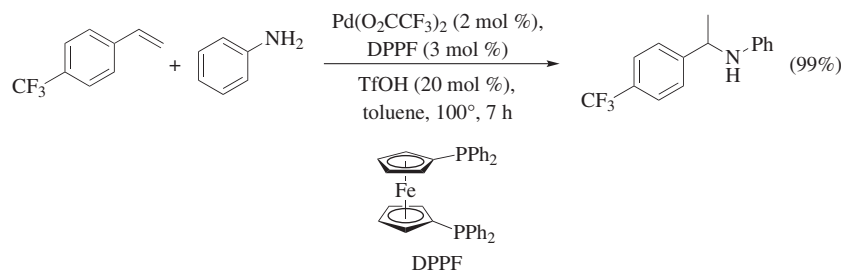
reactivity in vinyl arene hydroamination.^{43,52,230} The addition of an aliphatic amine proceeds in an anti-Markovnikov fashion similar to aminations using alkaline metal based catalysts (Scheme 54).⁵²



Scheme 54

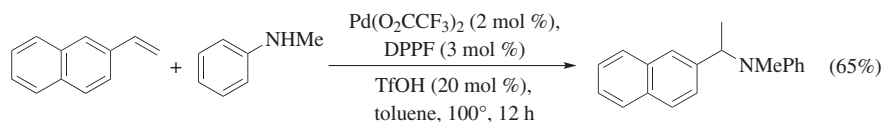
A range of late transition metal complexes catalyze the addition of *N*-unprotected amines to vinyl arenes. The most successful catalyst systems are based on palladium,^{231–239} ruthenium,^{240,241} and rhodium.^{132,242–244}

In sharp contrast to base-catalyzed hydroaminations, the palladium-catalyzed addition of amines to vinyl arenes proceeds regioselectively to afford the Markovnikov product. Typically, a simple palladium(II) precatalyst with a bulky chelating diphosphine ligand is employed (Scheme 55).²³¹ High yields and excellent regioselectivities are observed in the addition of aromatic amines.

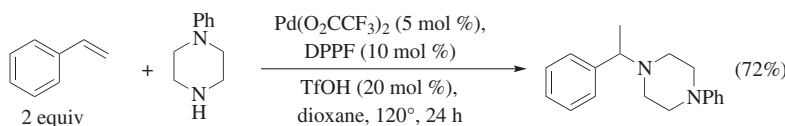


Scheme 55

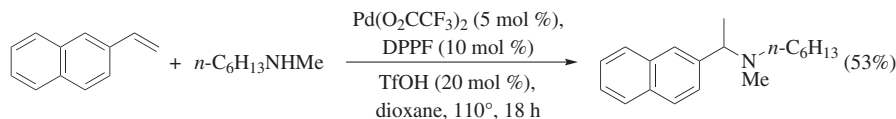
It should be noted that palladium-diphosphine catalyst systems are not applicable to primary aliphatic amines, although they can be applied to secondary alkylaryl-amines (Scheme 56).²³¹ Furthermore, the palladium-catalyzed hydroamination of vinyl arenes with cyclic secondary amines proceeds smoothly with excellent Markovnikov selectivity (Scheme 57).²³³ Reactions with acyclic dialkylamines are more sluggish (Scheme 58).



Scheme 56

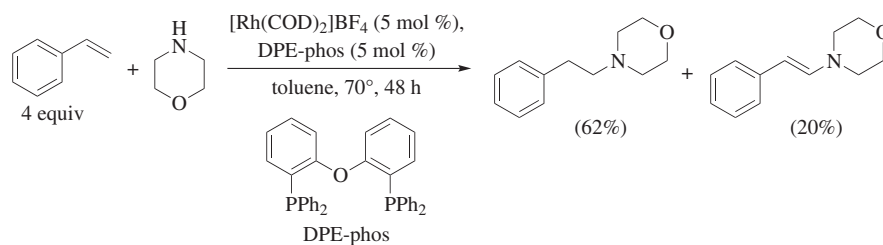


Scheme 57

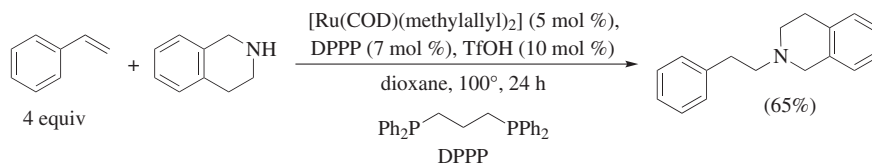


Scheme 58

Rhodium(I) complexes display anti-Markovnikov regioselectivity in the addition of aliphatic amines to vinyl arenes,^{243,244} in contrast to the Markovnikov regioselectivity observed with palladium-based catalyst systems. Unfortunately, the reaction is accompanied by a hydride-transfer oxidative hydroamination, producing a significant amount of the corresponding enamine (Scheme 59).²⁴⁴ However, ruthenium(II) diphosphine complexes perform the anti-Markovnikov addition to vinyl arenes with excellent regio- and chemoselectivity without formation of oxidative hydroamination byproducts.^{240,241} The catalyst is believed to operate through a η^6 -coordinated arene pathway, and the catalytic activity is enhanced by the presence of DPPP (Scheme 60).²⁴¹

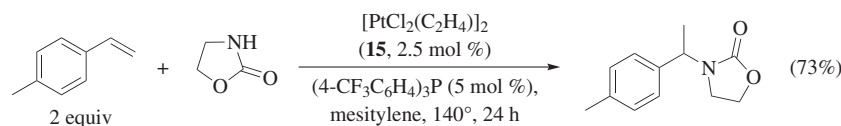


Scheme 59



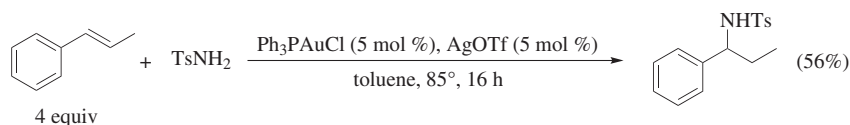
Scheme 60

Several other late transition metal based catalytic systems for intermolecular hydroamination of vinyl arenes are known. Zeise's dimer (**15**) shows activity in the Markovnikov addition of carboxamides, sulfonamides, and carbamates to styrene derivatives (Scheme 61).²⁴⁵



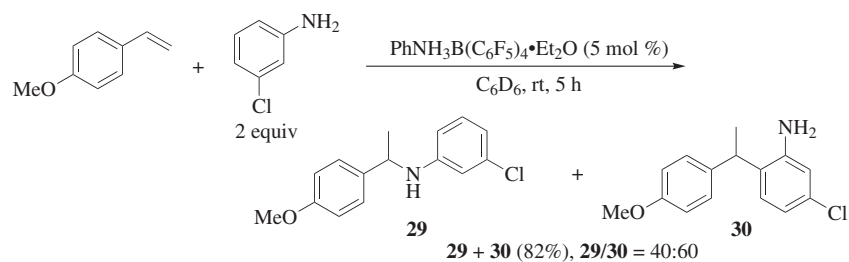
Scheme 61

The addition of sulfonamides^{133,202} and cyclic ureas¹²⁶ to vinyl arenes is catalyzed by cationic gold(I)-phosphine complexes (Scheme 62).¹³³ Additions of sulfonamides are also mediated by copper(II)-phosphine catalysts.²⁴⁶



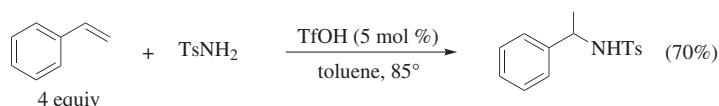
Scheme 62

Various Brønsted,^{142,143,242} Lewis,^{247,248} and heteropoly²⁴⁹ acids catalyze the addition of *N*-unprotected anilines to vinyl arenes. Unfortunately, these catalysts lack chemo- and regioselectivities and hydroarylation byproducts, such as substituted aniline **30**, are frequently formed in addition to the Markovnikov hydroamination product represented by **29** (Scheme 63).¹⁴²



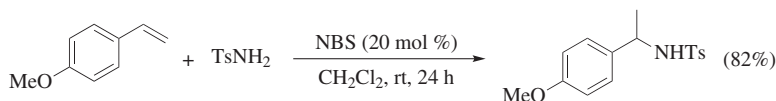
Scheme 63

Strong Brønsted acids, such as TfOH, catalyze the Markovnikov addition of amides¹³⁵ and sulfonamides^{134,246} to styrene at elevated temperatures (Scheme 64). Heteropoly acids²⁵⁰ and air- and moisture-stable Lewis acids, such as FeCl₃,²⁴⁸ Bi(OTf)₃, or Hf(OTf)₄,²⁵¹ also catalyze the Markovnikov addition of *N*-protected amines to vinyl arenes.



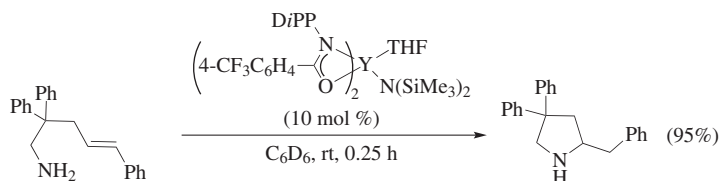
Scheme 64

Interestingly, NBS catalyzes the addition of carbamates and sulfonamides to electron-rich vinyl arenes smoothly at ambient temperature (Scheme 65).²⁵² This reaction is believed to proceed via the *N*-bromotosyl amide, which protonates the vinyl arene followed by nucleophilic attack of the amide. The iodine-catalyzed addition of sulfonamides to vinyl arenes requires higher temperatures.²⁵³

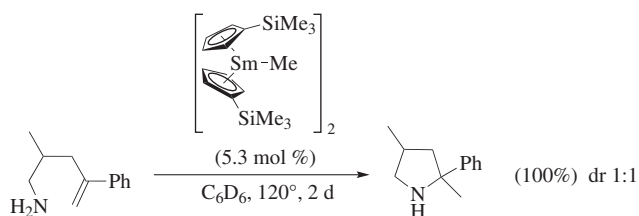


Scheme 65

Intramolecular Hydroamination of Vinyl Arenes. The intramolecular hydroamination of vinyl arenes is covered in Table 2B. The *exo* hydroamination of aryl-substituted aminoalkenes proceeds in a manner similar to the cyclization of normal aminoalkenes. Rare earth metal based complexes are among the most reactive catalysts (Scheme 66).^{52,254–259} Aryl-substituted aminoalkenes are typically less reactive than terminal aminoalkenes, therefore elevated temperatures are often required, especially when sterically more challenging 1,1-disubstituted aminoalkenes are cyclized (Scheme 67).¹⁶⁰

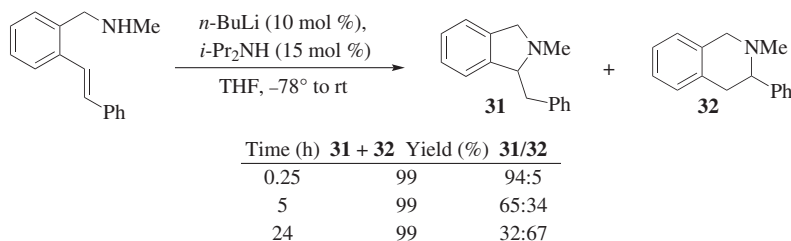


Scheme 66



Scheme 67

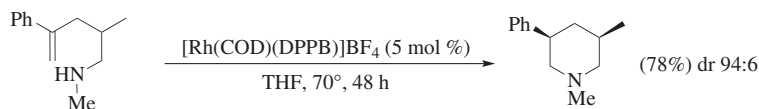
The cyclization of stilbene-derived aminoalkenes is achieved smoothly with lithium-based catalysts.²⁶⁰ However, the initially formed, 5-membered-ring product **31** (*exo* cyclization) slowly rearranges to the thermodynamically preferred 6-membered-ring product **32** (*endo* cyclization) (Scheme 68).



Scheme 68

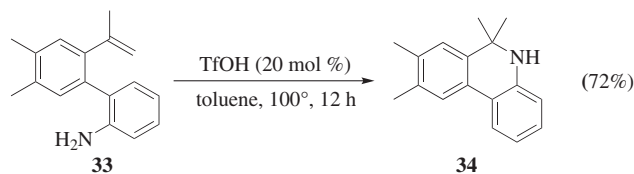
Intramolecular hydroaminations of vinyl arenes with titanium²⁴⁷ and zirconium^{68,170,261} catalysts are known, but elevated temperatures of up to 150° are required.

Only a few examples that employ late transition metal based catalysts are known. For example, a cationic rhodium(I) diphosphine complex is employed in the intramolecular hydroamination of secondary aminoalkenes (Scheme 69).²⁶²



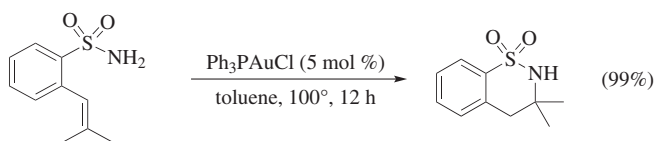
Scheme 69

The Brønsted acid catalyzed Markovnikov hydroamination of the biphenyl derivative **33** affords the phenanthridine derivative **34** in good yield (Scheme 70).²⁶³ This example represents the only metal-free, catalytic, intramolecular vinyl arene hydroamination of an *N*-unprotected amine.

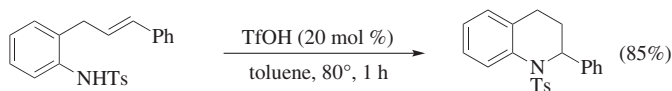


Scheme 70

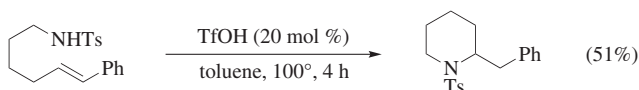
The hydroamination of *N*-protected vinyl aminoarenes generally proceeds via an *endo* cyclization, which is in contrast to that observed with *N*-unprotected amines. For example, the simple gold(I) monophosphine complex Ph_3PAuCl facilitates the intramolecular hydroamination of trisubstituted sulfonamidoalkenes (Scheme 71).²⁰² Electron-withdrawing protecting groups on the amine also activate substrates for Brønsted and Lewis acid catalyzed hydroaminations. Brønsted acid catalysts cyclize electron-deficient substrates, such as amides,²⁰⁹ sulfonamides,^{209–212} and carbamates²⁰⁹ with preferential 5- and 6-*endo* selectivity, presumably due to the stereoelectronic input from the aryl moiety (Scheme 72).²¹² However, in the case of aminohexenes, 6-*exo* cyclization takes place and no azepane formation is observed (Scheme 73).²⁰⁹ The FeCl_3 -catalyzed cyclization of sulfamidoalkenes also proceeds with *endo* selectivity in the presence of an aryl substituent in the vinylic position (Scheme 74), whereas in its absence the cyclization leads to the *exo* cyclization products.²⁰⁴



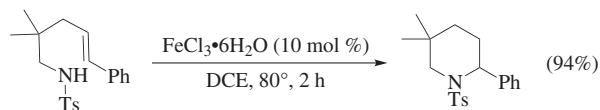
Scheme 71



Scheme 72



Scheme 73

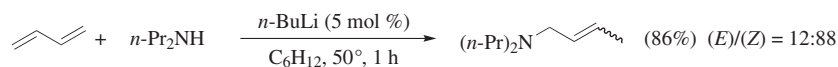


Scheme 74

Hydroamination of Conjugated Dienes

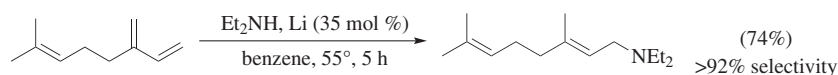
Intermolecular Hydroamination of 1,3-Dienes. Conjugated dienes can serve as reactive substrates in both inter- and intramolecular hydroamination processes since the reactivity of the conjugated system is significantly higher than that of an isolated double bond. In general, the reactivity of 1,3-dienes is similar to that of vinyl arenes with a notable difference resulting from more challenging regio- (1,2 vs. 1,4- addition) and chemoselectivity problems. Conjugated dienes are prone to undergo oligo- and polymerization in the presence of an amine when subjected to hydroamination conditions and this telomerization often accompanies the desired hydroamination reaction.³³ Intermolecular hydroaminations of conjugated dienes are covered in Table 1C.

The hydroamination of conjugated dienes with ammonia has been reported only for reactive aryl-substituted dienes under radical addition conditions in the presence of a photosensitizer.²⁶⁴ Hydroaminations with basic primary and secondary amines are promoted by a variety of catalysts including alkali metals and their readily available organometallic derivatives. Reactions of acyclic 1,3-dienes catalyzed by alkali metals,^{220,221,265–267} metal hydrides,²⁶⁸ and alkyl amides^{224,269,270} usually result in the regioselective formation of the sterically less hindered 1,4-addition product (Scheme 75).²⁷⁰ Primary aliphatic amines are capable of undergoing double hydroaminations under these conditions, typically leading to complex mixtures of mono- and bis-allyl amines.²²¹



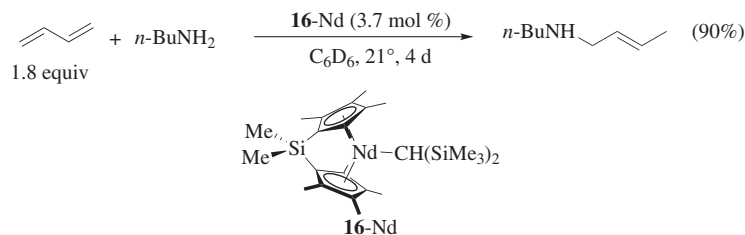
Scheme 75

Isolated double bonds are significantly less reactive than the conjugated diene moiety, as illustrated by the base-catalyzed, chemo- and regioselective hydroamination of myrcene (Scheme 76).²⁶⁷ This reaction is performed industrially on a multi-ton scale as part of the Takasago menthol synthesis.²⁷¹



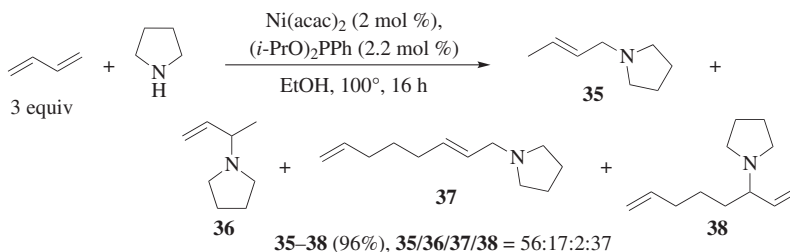
Scheme 76

A few examples of rare earth metal catalyzed diene hydroaminations are known. As in base-catalyzed intermolecular hydroaminations, the 1,4-addition product is formed (Scheme 77).^{43,128}

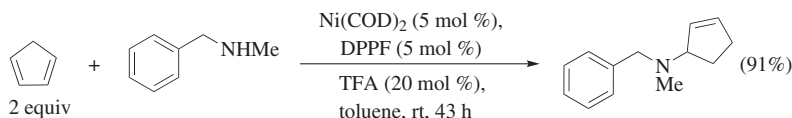


Scheme 77

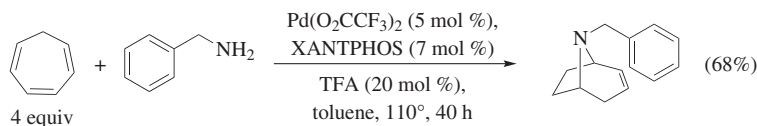
A variety of late transition metal based catalyst systems catalyze the addition of primary and secondary alkylamines to acyclic 1,3-dienes. The transition metals employed include cobalt, rhodium, iridium,²⁷² ruthenium,¹¹⁶ platinum,²⁷³ and many examples utilizing nickel^{272,274–277} and palladium.^{278–280} Unfortunately, none of these systems is able to either control regioselectivity of the addition or suppress diene oligomerization, and complex mixtures of unsaturated amines are obtained. In a typical example of a nickel-catalyzed addition of pyrrolidine to butadiene, a mixture of products **35–38** is formed (Scheme 78).²⁷⁴ Cyclic dienes, which lack the possibility of alternative addition pathways and do not undergo oligomerization, are less challenging substrates and the addition of alkylamines proceeds cleanly to afford cycloalkenyl derivatives (Scheme 79).²⁷⁷ This approach has also been successfully employed in the synthesis of bicyclic amines via palladium-catalyzed tandem inter/intramolecular hydroamination of cyclic 1,3,5-trienes (Scheme 80).²⁸¹



Scheme 78

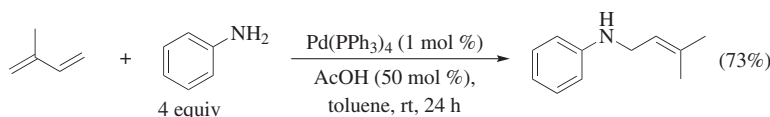


Scheme 79



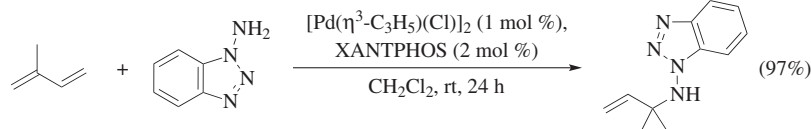
Scheme 80

Aniline derivatives are better-suited substrates for late transition metal based hydroamination catalysts because of their decreased basicity and nucleophilicity. The 1,4-addition of aromatic amines to acyclic and cyclic dienes can be performed in a regio- and chemoselective fashion in the presence of a relatively simple palladium(0) catalyst under mild conditions (Scheme 81).²⁸²



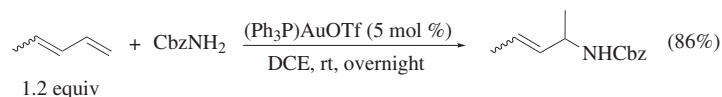
Scheme 81

The palladium-catalyzed addition of hydrazine and hydroxylamine derivatives to dienes proceeds with 1,2-regioselectivity to yield the sterically more encumbered *sec*- or *tert*-butylamines.²⁸³ The reaction is believed to proceed through the nucleophilic attack of the amine on a palladium-allyl species in agreement with the mechanism of allylic amination. In contrast to simple amines, hydrazines and hydroxylamines tend to irreversibly attack the more substituted site of the allylic intermediates to yield branched allyl amines as illustrated with isoprene as the substrate (Scheme 82).



Scheme 82

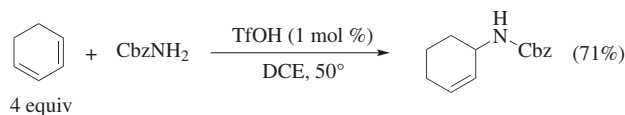
Late transition metal complexes can also catalyze the addition of *N*-protected amines to conjugated dienes. The gold(I)-catalyzed hydroamination of dienes with carbamates and sulfonamides^{75,284,285} proceeds regioselectively to yield *N*-protected allylic amines in high yields under significantly milder conditions than those required for *N*-unprotected primary and secondary amines (Scheme 83).²⁸⁴ Analogous reactions are also reported that utilize catalyst systems based on bismuth²⁸⁶ and copper.²⁴⁶



Scheme 83

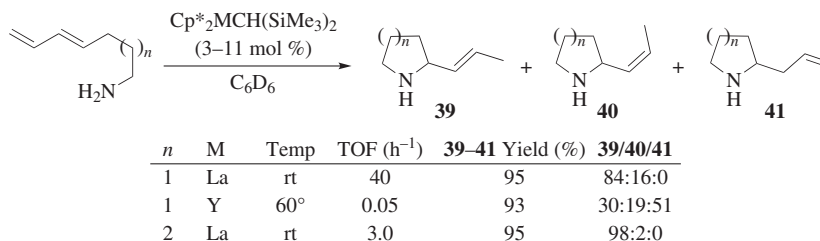
The reduced basicity and enhanced reactivity of *N*-protected amines, e.g. sulfonamides and carbamates, permit utilization of metal-free Brønsted acid catalysts, such as TfOH (Scheme 84)^{134,135} or heteropoly acids.²⁵⁰ However, the

application of these acid catalysts in hydroamination reactions with *N*-unprotected amines is less successful and, in these cases, the method is restricted to less basic anilines and suffers from poor chemoselectivity due to a competitive hydroarylation pathway.¹⁴²



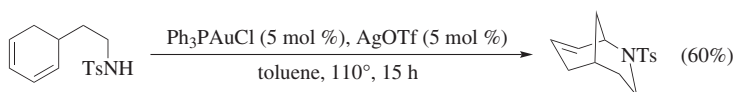
Scheme 84

Intramolecular Hydroamination of Aminodienes. The intramolecular hydroamination of conjugated dienes (covered in Table 2C) has drawn significantly less attention to date than the corresponding reaction of allenes. Most reported examples employ organo rare earth metal based catalyst systems for cyclizations of aminodienes. Hydroamination of terminal aminodienes is a facile process due to the transient formation of an η^3 -allyl intermediate, which forms (*E*) and (*Z*) alkenylpyrrolidines and alkenylpiperidines upon protonation.^{287,288} Under certain conditions, the allyl isomers are formed. Whereas the sterically more accessible lanthanocene $\text{Cp}^*_2\text{LaCH}(\text{SiMe}_3)_2$ provides predominantly (*E*) alkenylpyrrolidines and (*E*) alkenylpiperidines, the sterically more encumbered ytrocene $\text{Cp}^*_2\text{YCH}(\text{SiMe}_3)_2$ yields the alkenylpyrrolidine with eroded (*E*)/(*Z*) selectivity, as shown by the ratio of products **39** and **40**, and a significant amount of the allyl isomer **41** (Scheme 85).

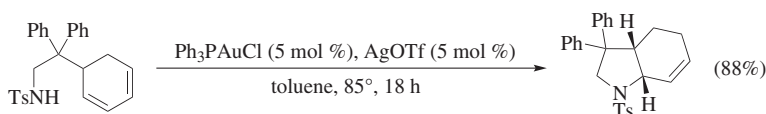


Scheme 85

Examples of late transition metal catalyzed aminodiene hydroaminations are scarce. For example, cationic phosphine-gold(I) complexes catalyze the cyclization of 1,3-cyclohexadienes bearing a tethered sulfonamide to form a morphan derivative via an apparent 1,2-addition (Scheme 86),²⁸⁹ which is in agreement with the preferred 1,2-addition observed in the corresponding intermolecular process.^{284,285} However, in the presence of sterically encumbering *gem*-diphenyl substituents, the reaction proceeds with exclusive 1,4-selectivity (Scheme 87).²⁸⁹



Scheme 86

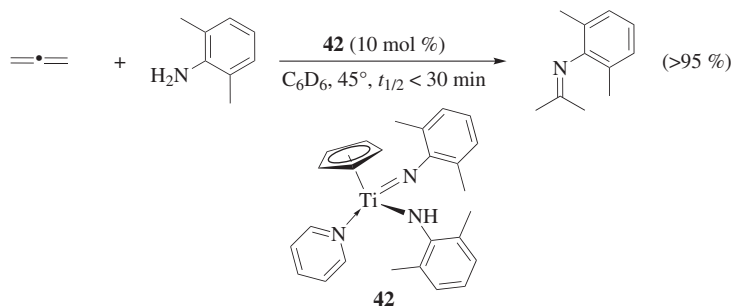


Scheme 87

Hydroamination of Allenes

Intermolecular Hydroamination of Allenes. The high reactivity of cumulated double bonds is key to a number of efficient hydroamination protocols that involve this class of compounds. The intermolecular hydroamination of allenes is presented in Table 1D.

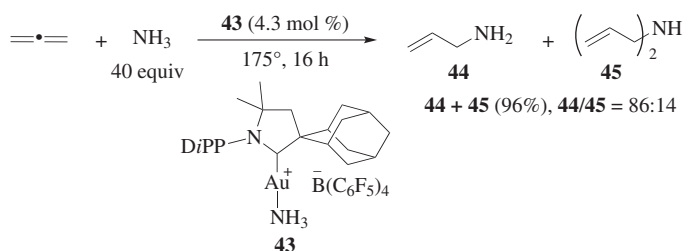
Early transition metal complexes catalyze the addition of amines to allenes to form the imine exclusively. Addition of 2,6-dimethylaniline to allene requires high reaction temperatures ($90\text{--}135^\circ$) and long reaction times (1–6 days) when mediated by zirconocene-⁵⁹ and tantalum-imido⁶⁴ catalysts. The titanium half-sandwich imido-amide complex **42** operates under significantly milder reaction conditions (Scheme 88).²⁹⁰ Because the metal-imido species are prone to dimerization, the reactions generally require sterically demanding aniline or amine substrates (e.g. *tert*-butylamine) to avoid catalyst deactivation.



Scheme 88

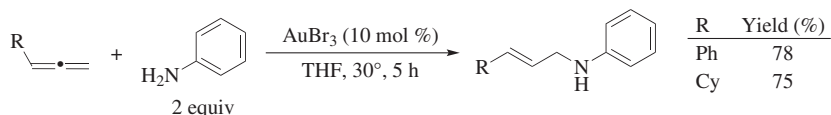
A few cases involving ammonia are known: for example, the cationic gold(I) NHC complex **43** mediates the intermolecular anti-Markovnikov hydroamination of allene at 175° , resulting in the primary and secondary amines **44** and **45** (Scheme 89).²⁹¹

Primary amines can be obtained selectively when a large excess of ammonia is employed, otherwise secondary and tertiary amines are formed predominantly.

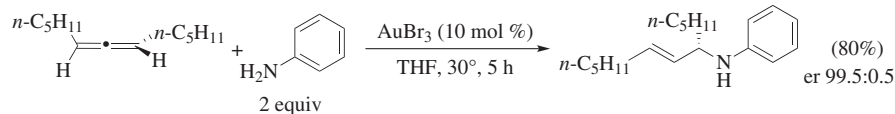


Scheme 89

In general, late transition metal catalyst systems are more versatile and exhibit superior catalytic activity in the formation of allyl amines. The addition of the more reactive aniline to monosubstituted allenes is catalyzed by a simple gold(III) salt at 30° (Scheme 90).²⁹² It is noteworthy that an analogous reaction of a chiral nonracemic allene proceeds with excellent stereoselectivity (Scheme 91).²⁹²

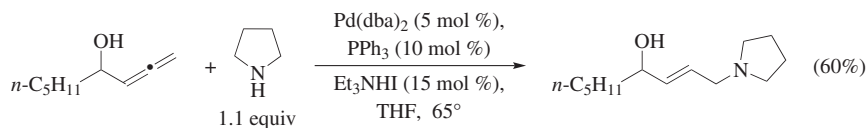


Scheme 90

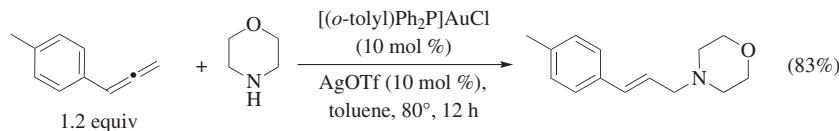


Scheme 91

The addition of a Secondary Amine to an allene moiety usually requires elevated temperatures and more sophisticated late transition metal catalyst systems, usually based on palladium^{293,294} or gold.²⁹⁵ The reactions generally favor the anti-Markovnikov addition to yield allylamines as the major products (Schemes 92²⁹³ and 93²⁹⁵).

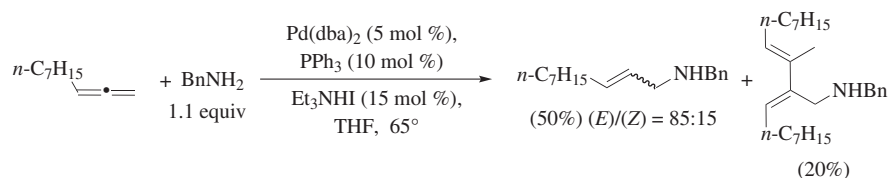


Scheme 92



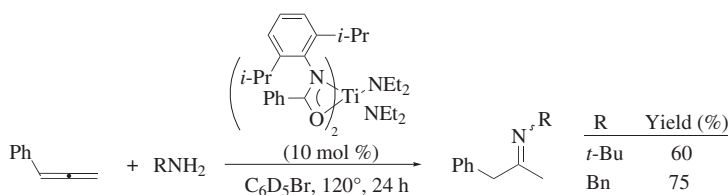
Scheme 93

A few reactions with primary amines are reported, and in contrast to secondary amines, the reaction is neither chemo- nor regioselective (Scheme 94).²⁹³



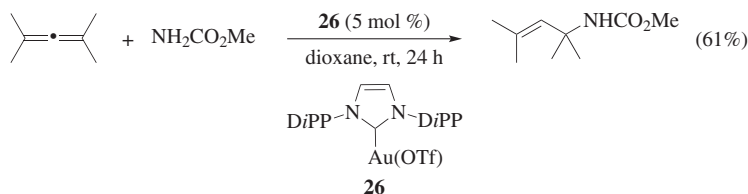
Scheme 94

Several examples of early transition metal catalyzed reactions involving primary amines are known. In contrast to late transition metal catalyzed reactions, the addition leads to the Schiff base and the reaction requires elevated temperatures (Scheme 95).²⁹⁶



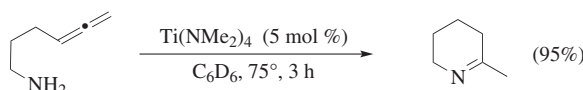
Scheme 95

The intermolecular hydroamination of allenes with *N*-protected amines is catalyzed by palladium²⁹⁴ and the cationic gold(I) *N*-heterocyclic carbene complex **26** (Scheme 96).²⁹⁷ The latter catalyst system is particularly efficient in the synthesis of *N*-protected allylic amines via addition of carbamates to allenes under mild conditions.



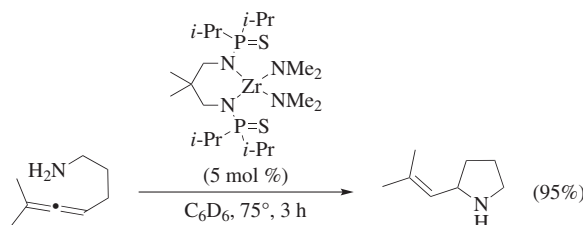
Scheme 96

Intramolecular Hydroamination of Aminoallenes. As evident from Table 2D, the cyclization of aminoallenes has been investigated more extensively than the intermolecular hydroamination process. Intramolecular hydroaminations of monosubstituted, terminal *N*-unprotected aminoallenes can be catalyzed by rare earth metal²⁹⁸ or Group 4 metal^{299,300} catalysts. The *endo* cyclization is most often accompanied by some *exo* cyclization, but in general the endocyclic product is formed preferentially and can be obtained exclusively with certain rare earth and Group 4 metal catalysts (Scheme 97).²⁹⁹

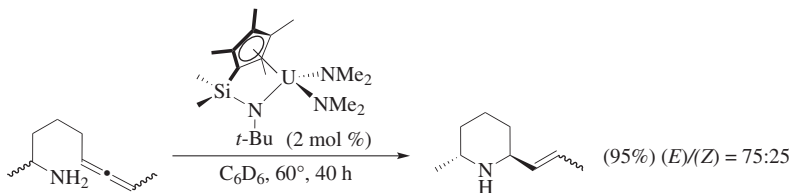


Scheme 97

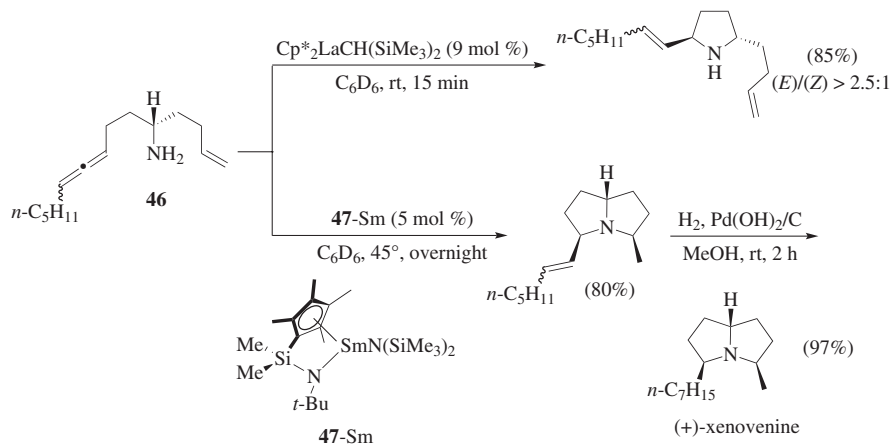
Cyclization of terminally substituted *N*-unprotected aminoallenes is a more facile process that can be catalyzed by rare earth,^{298,301–303} Group 4,^{300,304–307} and Group 5 metals,³⁰⁷ as well as actinides.²⁵⁶ The cyclization favors the *exo* product with internal allenes, and usually proceeds in a regioselective manner (Scheme 98).³⁰⁵ The formation of piperidine derivatives via *exo* cyclization of amino-5,6-dienes is in general more challenging (Scheme 99).^{256,298,301,302} When the reaction is performed in the presence of a terminal alkene moiety, for example with the aminoallene-alkene **46**,³⁰² the reaction preferentially occurs at the more reactive allene and leaves the alkene moiety untouched if a sterically more encumbered lanthanocene catalyst is employed (Scheme 100). However, facile bicyclization occurs when a sterically more open and geometrically constrained catalyst, such as **47-Sm**, is used. Subsequent hydrogenation provides ready access to the pyrrolizidine alkaloid (+)-xenovenine.



Scheme 98

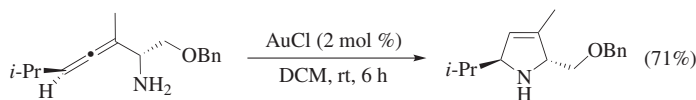


Scheme 99



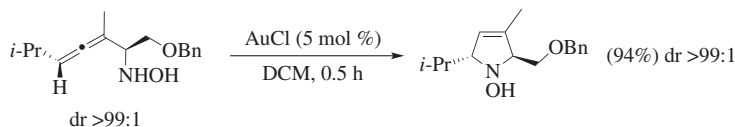
Scheme 100

N-Unprotected aminoallenes are also cyclized in the presence of late transition metal catalysts based on palladium,³⁰⁸ gold,^{309,310} and silver.^{311,312} The diastereo- and *endo*-selective ring closure of internal *N*-unprotected aminoallenes is also facilitated by gold(I) chloride at ambient temperature (Scheme 101).³⁰⁹ An analogous copper-catalyzed cyclization also proceeds without any noticeable epimerization.³¹³



Scheme 101

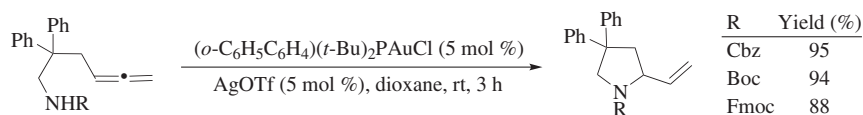
The gold(I) mediated 5-*endo* cyclization of allenic hydroxylamines allows the facile formation of cyclic *N*-hydroxylamines (Scheme 102).³¹⁴



Scheme 102

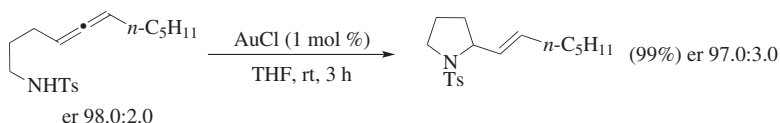
The intramolecular hydroamination of *N*-protected aminoallenes is extensively developed utilizing a variety of late transition metal based catalyst systems, with emphasis on asymmetric variants of the transformation. Several catalyst systems based on silver³¹⁵ and palladium³¹⁶ are known; however, most progress has been achieved with a variety of gold catalysts. For example, cationic gold(I) phosphine complexes efficiently facilitate the intramolecular hydroamination of various

N-protected terminal and internal aminoallenes to form 5- and 6-membered rings at room temperature (Scheme 103).³¹⁷



Scheme 103

Simple gold(I) and gold(III) salts also effectively catalyze the cyclization of *N*-protected aminoallenes.^{309,310,318} An important aspect is the stereospecificity observed for the hydroamination of a chiral *N*-protected aminoallene (Scheme 104).³¹⁸ Notably, the analogous palladium-catalyzed reaction proceeds with almost complete racemization, arguably indicating a different mechanism involving a π -allylpalladium intermediate.³¹⁹

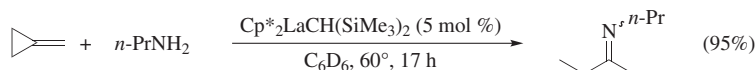


Scheme 104

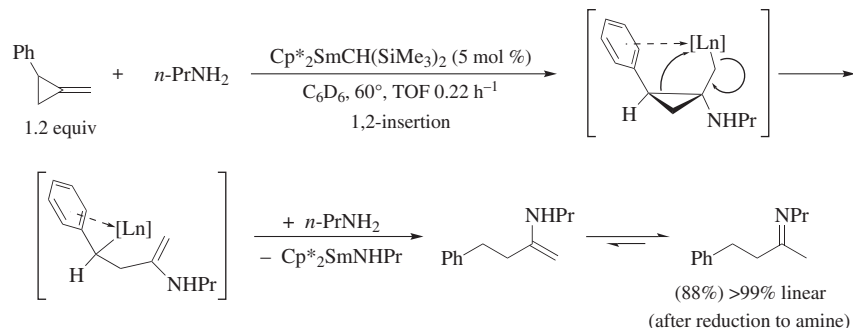
Hydroamination of Strained Alkenes

The enhanced reactivity of strained polycyclic alkenes, such as norbornene, has made them attractive model compounds for the hydroamination reaction. The intermolecular hydroamination of strained alkenes is presented in Table 1E.

Hydroamination of Methylenecyclopropanes. Methylenecyclopropanes are surprisingly stable, but exhibit unusual reactivity thanks to their ring strain.^{320,321} Similar to allenes they produce imines, enamines, or allylamines as hydroamination products. The rare earth metal catalyzed hydroamination of methylenecyclopropane proceeds smoothly with primary alkylamines to afford imines (Scheme 105).⁴³ When 2-phenyl-1-methylenecyclopropane is the substrate, the ring-opening forms the linear product predominantly (Scheme 106).⁴³ The primary 1,2-insertion product is stabilized by π -arene interaction, thus orienting the Ln–C bond *syn* to the appropriate cyclopropane C–C bond that leads upon ring cleavage to the favored linear product.

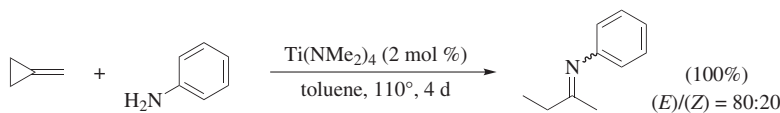


Scheme 105

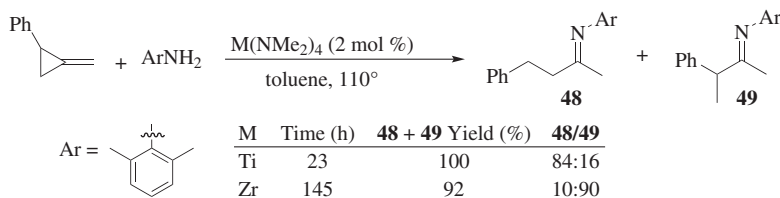


Scheme 106

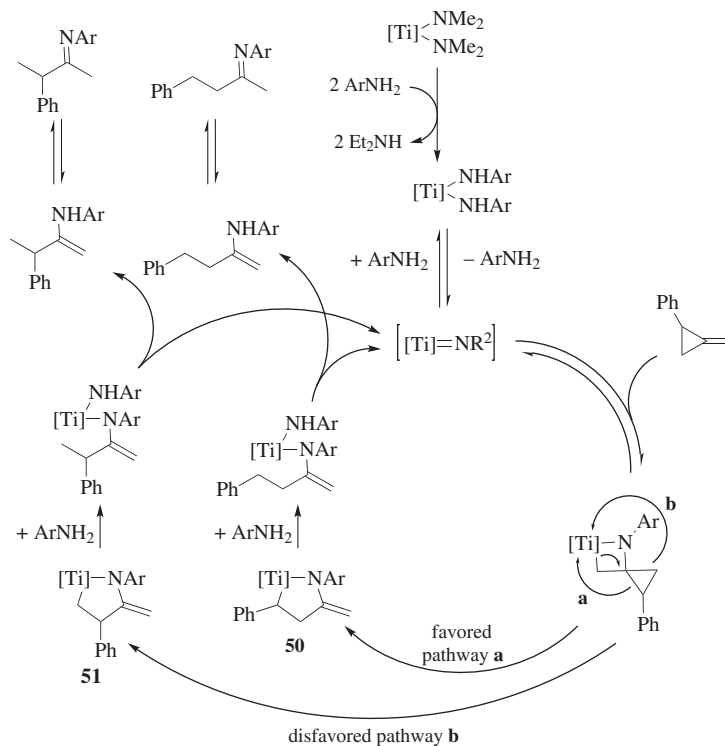
In one of the rare examples of an intermolecular Group 4 metal catalyzed alkene hydroamination, the analogous titanium-catalyzed addition of an aromatic amine to methylenecyclopropane affords the corresponding imine with predominant (*E*) selectivity (Scheme 107).³²² In the case of 2-phenyl-1-methylenecyclopropane, the ring-opening proceeds with moderate selectivity towards the linear product **48** using $\text{Ti}(\text{NMe}_2)_4$, whereas the corresponding zirconium complex $\text{Zr}(\text{NMe}_2)_4$ yields preferentially the branched product **49** with significantly lower reactivity (Scheme 108).³²² The titanium-catalyzed reaction is believed to proceed via a [2 + 2] cycloaddition between a metal imido species and the strained alkene (Scheme 109). The high regioselectivity results from a preference of the stabilized benzylic titanium intermediate **50** (pathway **a**) as opposed to a primary alkyl species **51** (pathway **b**). The switch in regioselectivity upon exchanging titanium for zirconium is proposed to result from an alternative protonation mechanism for the putative azametallacyclobutane intermediate, followed by subsequent ring opening of the cyclopropane via proton transfer from a metal-bound amido ligand to the sterically more accessible methylene ring carbon atom (Scheme 110).



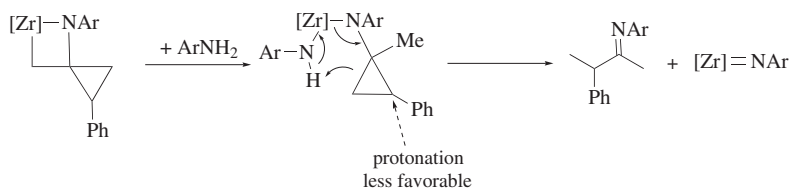
Scheme 107



Scheme 108

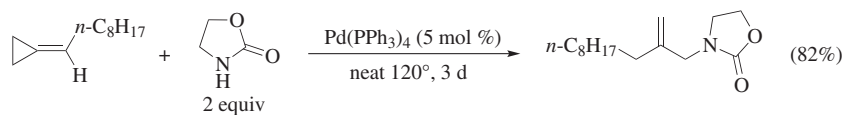


Scheme 109



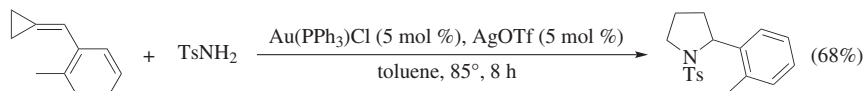
Scheme 110

A variety of late transition metal complexes are capable of catalyzing the addition of protected amines to methylenecyclopropanes. For example, $\text{Pd}(\text{PPh}_3)_4$ facilitates the addition of a cyclic carbamate (Scheme 111).³²³



Scheme 111

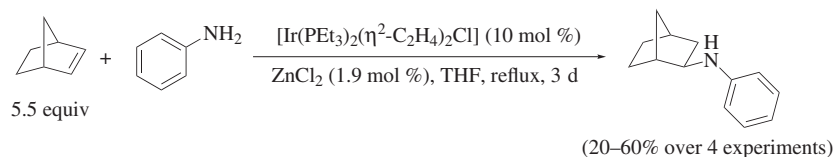
In certain cases, an unsaturated amine formed by a hydroamination/ring-opening step will undergo a second intramolecular hydroamination to afford an azacycle. Such gold-catalyzed tandem reactions are observed for (cyclopropylidenemethyl)benzene derivatives (Scheme 112).³²⁴



Scheme 112

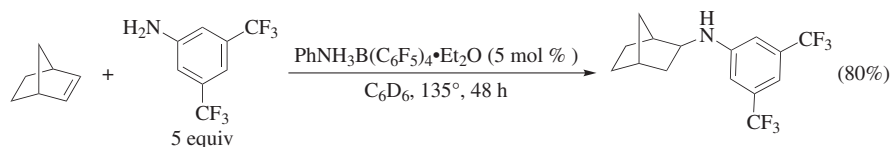
It should be noted that although most hydroamination reactions with methylenecyclopropanes demand elevated temperatures, their reactivity is superior to that of unstrained alkenes, which usually do not undergo analogous intermolecular amine additions.

Hydroamination of Norbornene. The enhanced reactivity of norbornene has enabled hydroamination with aromatic amines using iridium-based catalyst systems. The addition of aniline to norbornene proceeds with exclusive *exo* selectivity using an iridium(I) catalyst in the presence of ZnCl_2 as a cocatalyst (Scheme 113).⁷⁷ More recent studies have significantly expanded the utility of this reaction by applying chiral diphosphine iridium catalysts (see “Enantioselective Hydroamination of Norbornene”).^{78,79}



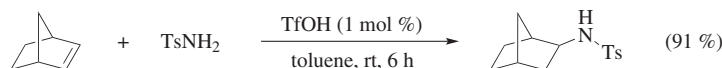
Scheme 113

As discussed further in the section “Enantioselective Hydroaminations of Norbornene”, iridium-based catalysts seem to provide the most efficient systems for the addition of aromatic amines to norbornene. However, other catalyst systems based on platinum,^{93,131,325} rhodium,^{325,326} or simple Lewis (e.g. AlCl_3 , FeCl_3 , BiCl_3 , ZrCl_4 ,³²⁷ TiCl_4 ³²⁸) and Brønsted^{142,143,329} acids are also employed. Often the Brønsted acid catalyzed hydroamination reaction competes with a hydroarylation side reaction. However, electron-deficient anilines react selectively through the hydroamination pathway (Scheme 114).¹⁴²



Scheme 114

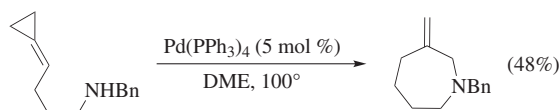
The electron-withdrawing nature of the sulfonyl group makes sulfonylamides suitable substrates for the hydroamination of norbornene. The reaction is susceptible to catalysis by, among others, triflic acid (Scheme 115),¹³⁵ $(\text{Ph}_3\text{P})\text{AuOTf}$,¹³³ $\text{Cu}(\text{OTf})_2$,²⁴⁶ InBr_3 ,³³⁰ heteropoly acids,²⁵⁰ and solid clays.¹²⁷



Scheme 115

Although the addition of anilines and sulfonylamides to norbornene proceeds relatively easily, neither alkali³³¹ nor late transition metal catalyzed^{332,333} reactions with aliphatic amines proceed with the required efficiency and selectivity.

Intramolecular Hydroamination of Strained Alkenes. Examples of intramolecular hydroamination utilizing a strained alkene are very rare (Table 2E). However, the reaction has some potential for the formation of azacycles with exocyclic double bonds. For example, 1-benzyl-3-methyleneazepane is accessible via the palladium-catalyzed cyclization of the corresponding cyclopropylidenealkylamine in moderate yield (Scheme 116) in one of the rare examples of 7-membered-ring formation via intramolecular hydroamination.³³⁴



Scheme 116

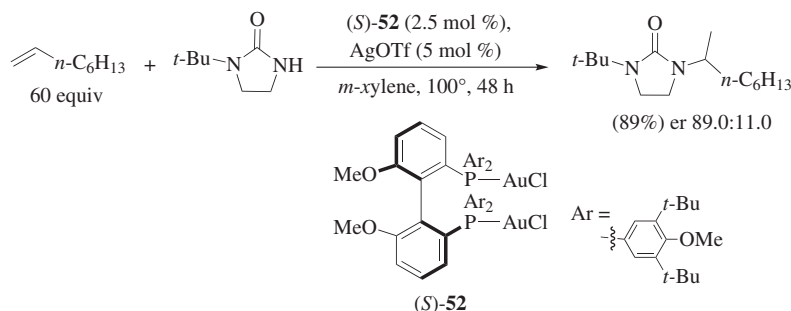
Enantioselective Hydroaminations

A large percentage of pharmacologically active molecules incorporate a nitrogen atom in one form or another. Many of these molecules are chiral, and the hydroamination reaction offers an outstanding opportunity to create chiral target molecules. This area of hydroamination catalysis has received increasing interest and a variety of highly selective catalyst systems have been developed. As with non-stereoselective hydroamination reactions, most of the studies involve intramolecular reactions, whereas, in general, intermolecular reactions remain significantly more challenging. A number of comprehensive reviews are available.^{7,22,26,27,30,32,34,38}

Enantioselective Intermolecular Hydroamination of Unactivated Alkenes.

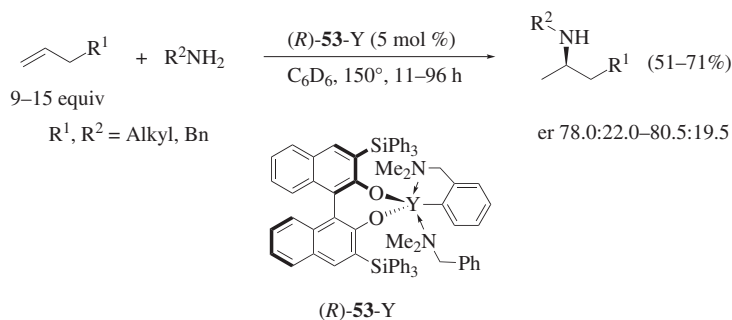
The enantioselective addition of amines to unactivated alkenes remains one of the great challenges in asymmetric catalysis and examples in the literature are rather limited in number and scope (covered in Table 3A).

The enantioselective Markovnikov-addition of cyclic ureas to alkenes is performed with the axially chiral MeOBIPHEP-ligated, bis-gold(I) catalyst (*S*)-**52** with enantiomeric ratios of up to 89.0:11.0 (Scheme 117).¹²⁶ Unfortunately, the reaction requires a large excess of the alkene substrate, since lower alkene loadings lead to diminished enantioselectivities.



Scheme 117

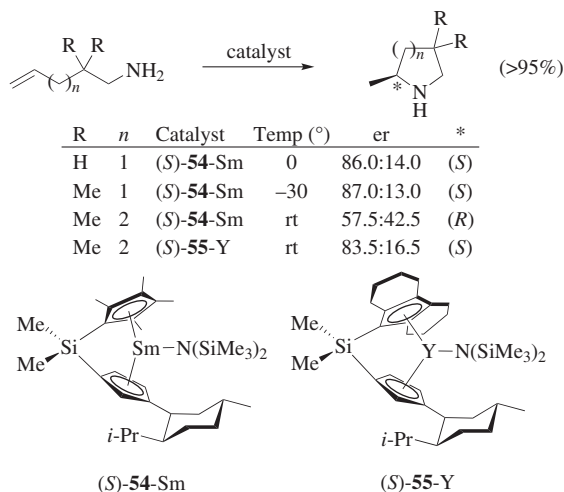
Efficient asymmetric hydroamination of non-activated alkenes with *N*-unprotected amines also remains elusive. Primary alkylamines react with terminal unactivated olefins with excellent Markovnikov selectivity in the presence of the yttrium binaphtholate catalyst (*R*)-**53**-Y (Scheme 118).³³⁵ The reactions require a 9- to 15-fold excess of the alkene and high reaction temperatures. Despite the harsh reaction conditions, moderate enantioselectivities of up to 80.5:19.5 er are observed.



Scheme 118

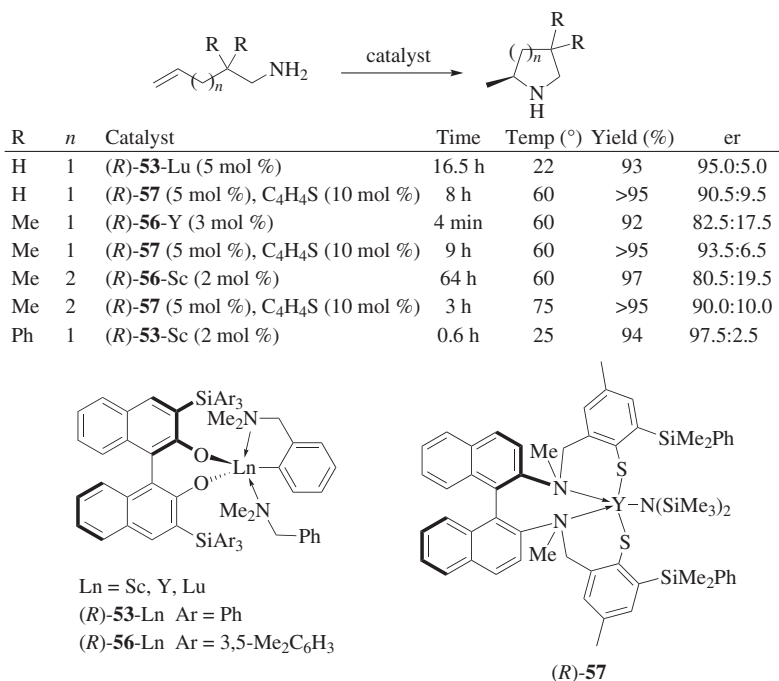
Enantioselective Intramolecular Hydroamination of Aminoalkenes. Among all enantioselective hydroamination reactions, the cyclization of aminoalkenes with chiral catalysts is the most extensively studied area (see Table 4A).

Chiral lanthanocene catalysts (*S*)-**54**-Sm and (*S*)-**55**-Y are employed for asymmetric, intramolecular hydroamination with enantiomeric ratios of up to 87.0:13.0 (Scheme 119).³³⁶⁻³³⁸ However, further improvement is thwarted by the poor configurational stability of the catalysts, which readily epimerize in solution.^{159,337-339}



Scheme 119

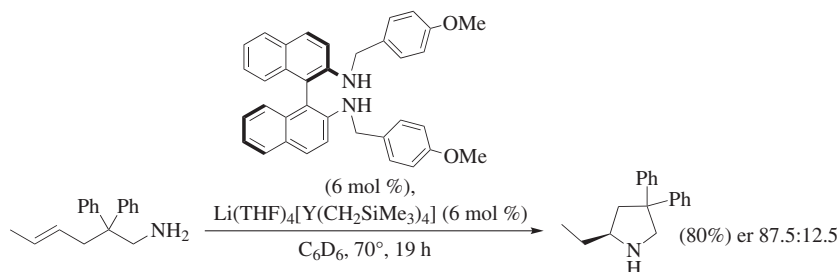
A number of chiral non-metallocene (e.g. cyclopentadienyl-free) rare earth metal complexes have been designed to overcome this limitation.^{7,26,27,30,32,34,38} Enantioselectivities of up to 97.5:2.5 er can be achieved using 3,3'-bis[tris(aryl)silyl]-substituted binaphtholate catalysts (*R*)-**53** and (*R*)-**56** with catalytic activities comparable to those of lanthanocenes (Scheme 120).^{52,340} The aminothiophenolate



Scheme 120

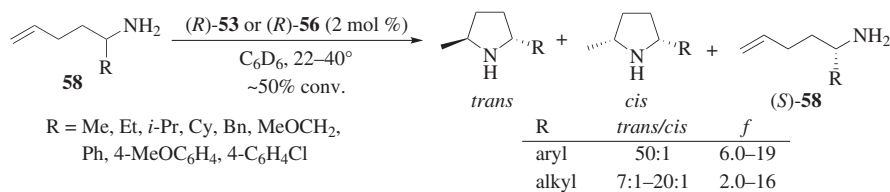
catalyst system (*R*)-**57** delivers enantioselectivities approaching 95.0:5.0 er for a broad range of aminoalkenes (Scheme 120).²⁵⁵ The larger bite angle of the amino(thio)phenolate ligand allows the chiral ligand to reach further around the metal, thus improving enantiofacial discrimination.³⁴¹ Unfortunately, the multidentate nature of the aminothiophenolate ligand in (*R*)-**57** electronically saturates the metal center more than the binaphtholate ligands in (*R*)-**53** and (*R*)-**56**, resulting in diminished catalytic performance, especially at ambient temperature.

As noted in the section on non-stereoselective hydroaminations, cyclizations of aminoalkenes with an internal double bond are significantly more difficult than cyclizations of aminoalkenes with a terminal double bond, and require elevated reaction temperatures (except for substrates with a phenyl substituent attached to the double bond). Therefore, only a few examples have been reported, and enantioselectivities are moderate (Scheme 121).²⁵⁸



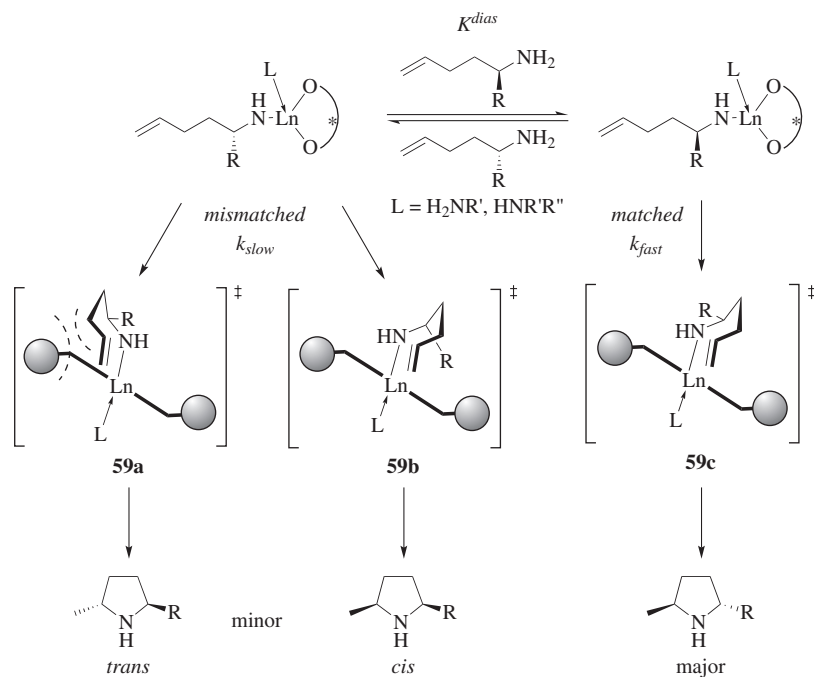
Scheme 121

The efficient kinetic resolution of chiral aminoalkenes can be accomplished using the binaphtholate complexes (*R*)-**53** and (*R*)-**56** (Scheme 122).^{52,340,342} In particular, chiral aminopentenes can be kinetically resolved with resolution factors *f* (defined as $f = K^{dias} \times k_{fast}/k_{slow}$; where K^{dias} is the Curtin–Hammett equilibrium constant between the two diastereomeric substrate/catalyst complexes and k_{fast}/k_{slow} is the ratio of the faster and the slower reaction rate constants) as high as 19 and the enantiomeric ratio for recovered starting material reaching $\geq 90:10$ at conversions close to 50%. 2,5-Disubstituted pyrrolidines are obtained with good to excellent *trans* diastereoselectivity, depending on the size of the α substituent. Kinetic resolution of the phenyl substituted **58** (R = Ph) using 1 mol % of (*R*)-**53**-Lu affords enantiopure (*S*)-**58** ($\geq 99.5:0.5$ er) in 33% re-isolated yield at 64% conversion.⁵²



Scheme 122

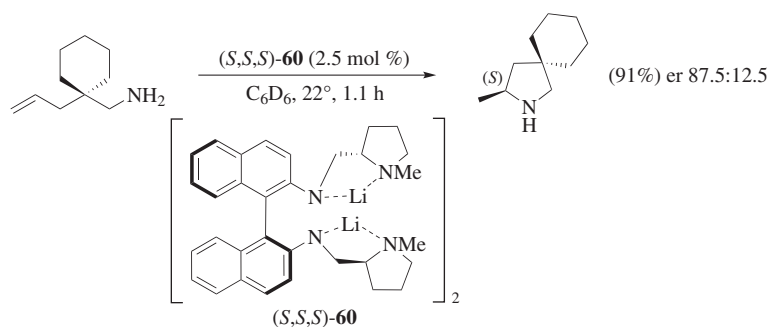
The cyclization of (*S*)-**58** ($R = \text{Ph}$) using (*R*)-binaphtholate complexes is impeded because of unfavorable steric interactions of the vinylic methylene protons with a tris-arylsilyl substituent in the chair-like transition state. (Stereomodels depicting these interactions for the kinetic resolution of α -substituted aminopentanes are shown in Scheme 123. For the matched substrate/catalyst pair only the pathway leading to the preferred *trans* isomer is shown.) Kinetic analysis of the kinetic resolution process indicates that the Curtin–Hammett equilibrium favors the matched substrate/catalyst combination in aminopentenes **58** containing α -aryl substituents,^{52,342} whereas aliphatic substituents shift this equilibrium in favor of the mismatched substrate/catalyst combination.³⁴² As noted above, the formation of the *trans* 2,5-disubstituted pyrrolidine is strongly favored in the case of the matched substrate/catalyst pair because of an equatorial placement of the α -substituent in the cyclization transition state (Scheme 123, **59c**, compare to Figure 1). The mismatched substrate/catalyst pair often shows diminished diastereoselectivity because the α -substituent must be placed in an axial orientation (Scheme 123, **59b**) to minimize steric interactions of the substrate with the large tris(aryl)silyl substituents on the binaphtholate ligand (Scheme 123, **59a**).



Scheme 123

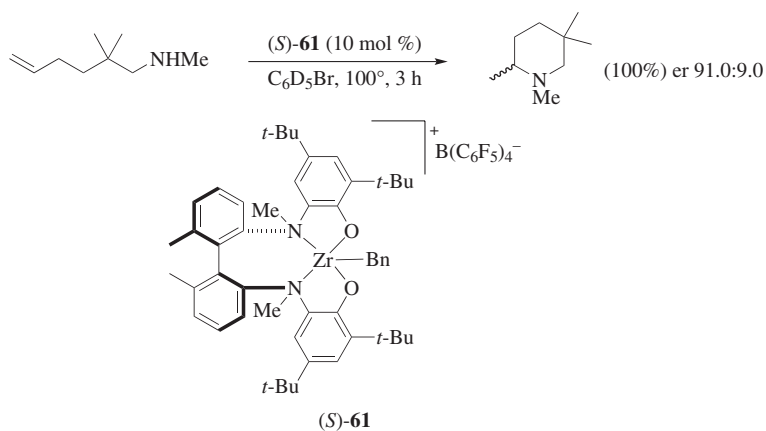
A few chiral, main group metal hydroamination catalysts have been developed. For example, the asymmetric cyclization of aminoalkenes is achieved with enantioselectivities of up to 87.5:12.5 or using the chiral diamidobinaphthyl lithium complex (*S,S,S*)-**60** (Scheme 124).¹⁴⁹ The unique reactivity of (*S,S,S*)-**60**, which allows

reactions at or below ambient temperature, is believed to stem from the close proximity of the two lithium centers coordinated by the proline-derived substituents. More simple lithium amides require significantly higher reaction temperatures and give inferior selectivities. Attempts to perform enantioselective hydroaminations with chiral, alkaline earth metal based catalysts are impeded by facile Schlenk equilibria of the catalyst species in solution.^{153,155} Similarly, attempts to perform enantioselective hydroaminations with chiral zinc catalysts have met limited success thus far.^{155,343}



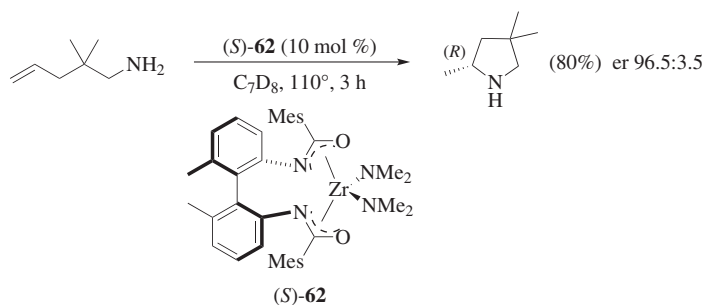
Scheme 124

The first chiral Group 4 metal catalyst system for asymmetric intramolecular hydroamination of aminoalkenes is based on the cationic aminophenolate complex **(S)-61**.¹⁸⁰ As noted in the section on achiral reactions, cationic Group 4 metal catalyst systems are limited to hydroaminations of aminoalkenes with a secondary amino group. Nevertheless, the reaction proceeds at 100° in bromobenzene to form hydroamination products with enantioselectivities of up to 91.0:9.0 er (Scheme 125).¹⁸⁰ One side reaction observed for this cationic catalyst system is double bond isomerization by C–H activation, and this can significantly reduce product enantioselectivity and yield.



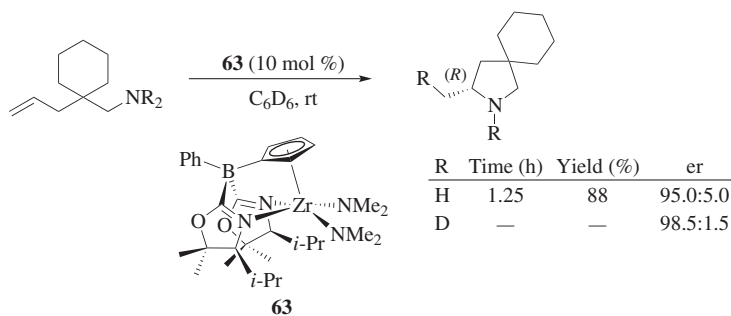
Scheme 125

A significantly larger variety of neutral, chiral Group 4 metal catalysts has been developed.^{170,344–348} These systems typically require reaction temperatures that range from 110–135° and employ 10–20 mol % catalyst loadings. Despite the high reaction temperatures, enantioselectivities exceeding 95.0:5.0 er have been achieved in the asymmetric, zirconium-catalyzed hydroamination of aminopentenes using the chiral bis-amidate catalyst (*S*)-**62** (Scheme 126).^{344–348}



Scheme 126

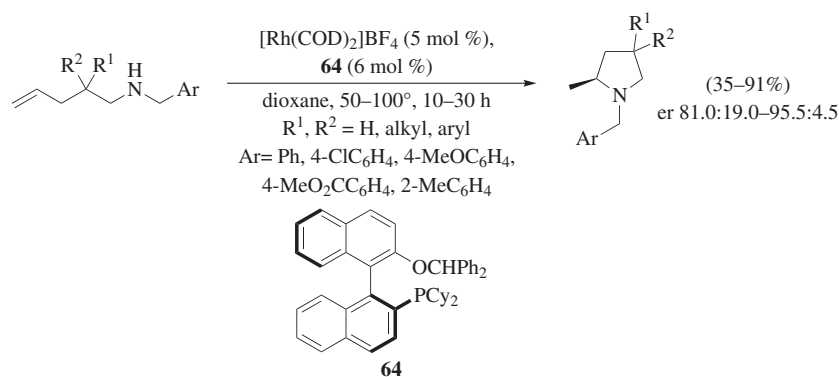
Similar to its achiral congener,¹⁸⁴ the chiral, zwitterionic zirconium cyclopentadienyl-bis(oxazolidinyl)borate complex **63**⁵⁴ possesses significantly improved reactivity compared to other Group 4 metal hydroamination catalysts. Thorpe–Ingold activated substrates are cyclized at temperatures as low as –30° with enantioselectivities of up to 99.0:1.0 er for *gem*-disubstituted aminopentenes, whereas amino-hexenes give inferior selectivities.⁵⁴ A pronounced primary kinetic isotope effect and isotopic perturbation of enantioselectivity resulting in higher selectivities for the *N*-deuterated substrates (Scheme 127) have been attributed to a concerted alkene insertion/protonolysis step.



Scheme 127

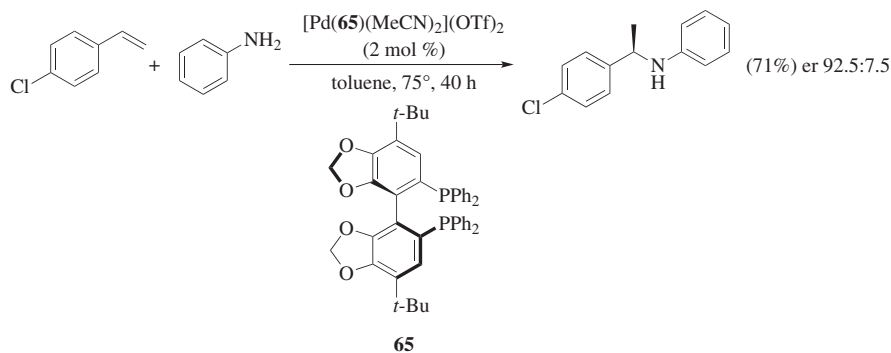
The limitations of late transition metal catalysts in the intramolecular hydroamination of aminoalkenes pose an even greater challenge with respect to enantioselective transformations, and examples are scarce. The asymmetric, rhodium-catalyzed

hydroamination of *N*-benzyl aminopentenes is achieved with the chiral biaryl phosphine **64** with enantioselectivities of up to 95.5:4.5 er (Scheme 128).³⁴⁹ Catalyst loadings are moderate (5 mol %) and reaction temperatures range from 50–100°. The method is significantly less efficient and less enantioselective for the synthesis of piperidines from *N*-benzyl aminohexenes.



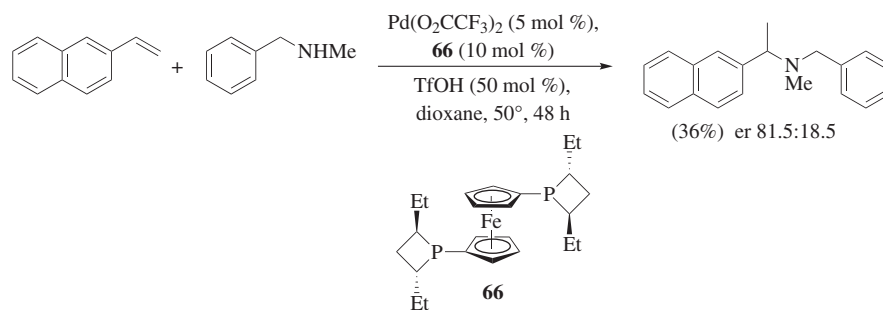
Scheme 128

Enantioselective Intermolecular Hydroamination of Vinyl Arenes. The hydroamination of vinyl arenes yields a new stereocenter only in the Markovnikov product, unless α - or β -substituted styrene derivatives are employed. Early transition metal catalysts generally produce the anti-Markovnikov product exclusively and therefore most examples (as tabulated in Table 3B) of stereoselective hydroaminations of vinyl arenes have been performed with late transition metal catalysts. For example, the palladium-catalyzed Markovnikov addition of aromatic amines to vinyl arenes is performed with moderate to high enantioselectivities with axially chiral diposphine ligands such as the 4,4'-disubstituted SEGPHOS **65** (Scheme 129).^{231,234,238}



Scheme 129

Although achiral palladium catalysts catalyze the addition of secondary alkylaryl amines and aliphatic cyclic secondary amines to vinyl arenes, the corresponding enantioselective examples with chiral catalysts are unknown.^{231,233} However, the enantioselective addition of *N*-methylbenzylamine to 2-vinylnaphthalene is achieved in moderate yield and enantioselectivity using the (*R,R*)-Et-FerroTANE ligand **66** (Scheme 130).²³³

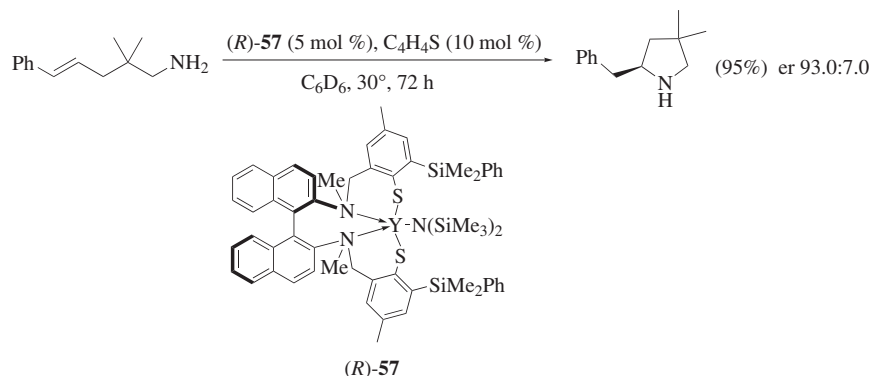


Scheme 130

Enantioselective Intramolecular Hydroamination Reactions of 1,3-Dienes.

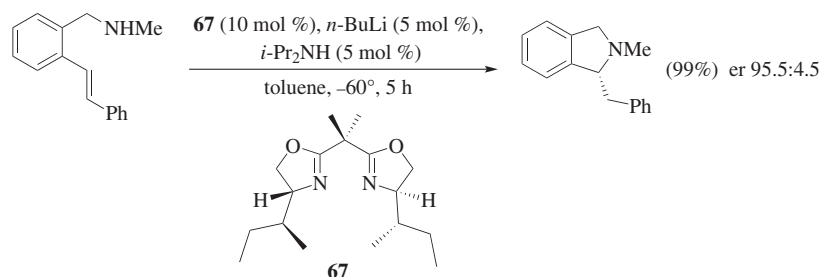
In contrast to intermolecular reactions, intramolecular asymmetric hydroaminations of vinyl arenes (covered in Table 4B) are performed exclusively with early transition metal and alkali metal catalysts, which reflects the superior reactivity of early transition metal catalysts in the cyclization of aminoalkenes in general.

The enantioselective cyclization of aryl-substituted aminoalkenes is achieved with a range of chiral, rare earth metal catalysts.^{52,255,258} The highest selectivity of 93.0:7.0 er is observed using the chiral aminothiophenolate yttrium complex (*R*)-**57** prepared in situ (Scheme 131).²⁵⁵



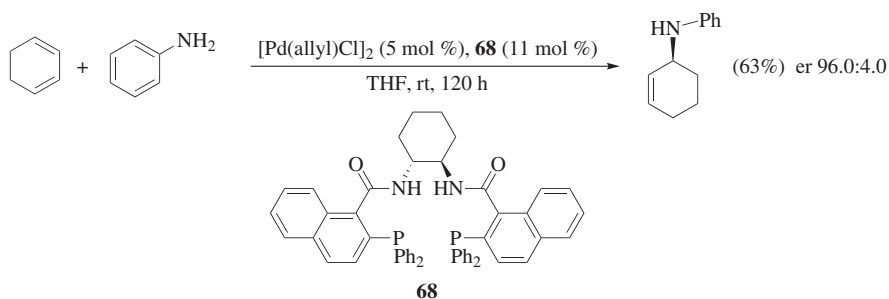
Scheme 131

A bis(oxazolinato)-lithium amide complex, prepared in situ from bis(oxazoline) **67** and *n*-BuLi, efficiently cyclizes stilbene-derived aminoalkenes at low temperature under kinetic control with high enantioselectivity (Scheme 132).²⁶⁰ This reaction is reversible in THF solution, producing the thermodynamically favored *endo* cyclization product at extended reaction times (see Scheme 68).



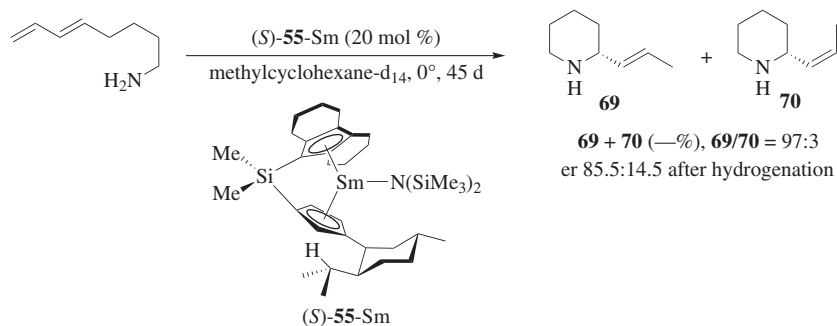
Scheme 132

Enantioselective Intermolecular Hydroamination of 1,3-Dienes. Asymmetric, intermolecular hydroamination reactions (covered in Table 3C) have been studied only with a limited number of nickel- and palladium-based catalyst systems. The most successful example is the highly enantioselective, palladium-catalyzed 1,4-addition of aromatic amines to cyclic dienes utilizing the diphosphine **68**, which is a naphthyl version of Trost's ligand (Scheme 133).²⁸²



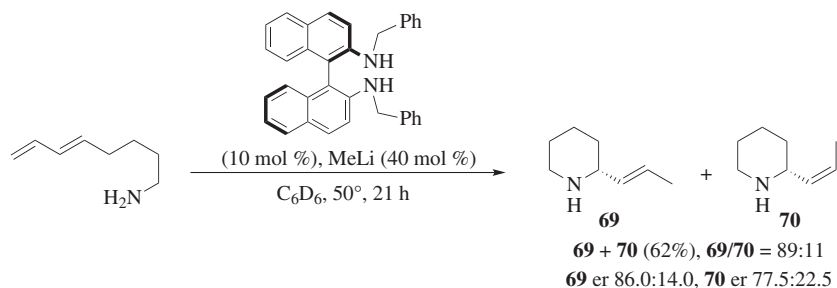
Scheme 133

Enantioselective Intramolecular Hydroamination of Aminodienes. Enantioselective, intramolecular hydroaminations of aminodienes (covered in Table 4C) are performed predominantly with early transition metal catalysts. Chiral organo rare earth metal catalysts, such as (*S*)-**55**-Sm, are used for asymmetric intramolecular hydroaminations to produce vinyl azacycles such as **69** and **70** exclusively with high (*E*) selectivity; however, enantioselectivities remain moderate (Scheme 134).²⁸⁸



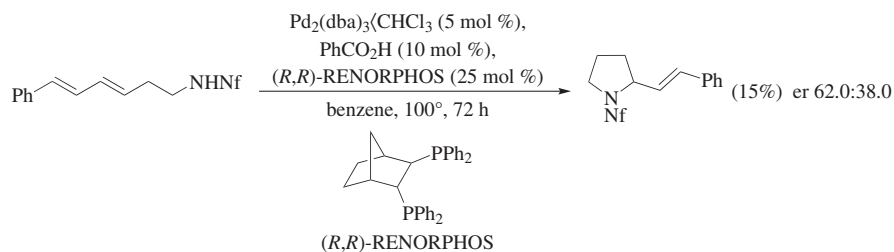
Scheme 134

The hydroamination/cyclization of terminal aminodienes is also catalyzed by chiral diamidobinaphthyl dilithium salts with up to 86.0:14.0 er (Scheme 135).³⁵⁰ Although the (*E*)/(*Z*) selectivity of the product is moderate in most cases, both diastereoisomers are obtained with comparable enantiomeric purity.



Scheme 135

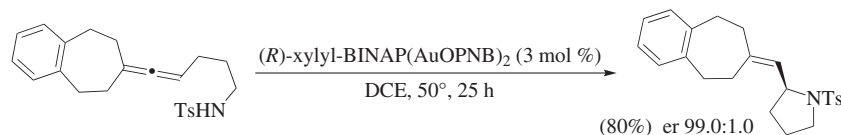
Although late transition metal complexes are also suitable for the cyclization of *N*-protected aminodienes, only a few enantioselective examples are reported, such as the cyclization of a dienyisulfonamide catalyzed by a chiral, palladium phosphine complex (Scheme 136).³¹⁶ Unfortunately, the enantioselectivity is low and a significant excess of the bidentate RENORPHOS ligand is required.



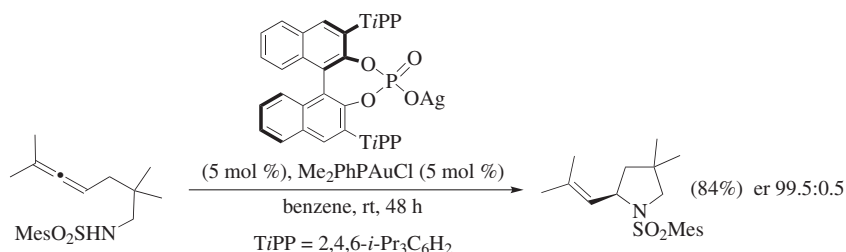
Scheme 136

Enantioselective Intramolecular Hydroamination of Aminoallenes.

Enantioselective, intermolecular hydroaminations of allenes have been reported only recently,^{351,352} except for the hydroamination of chiral allenes that proceed with high stereoselectivity using an achiral gold-catalyst (see Scheme 91 in the section “Intermolecular Hydroamination of Allenes”).²⁹² However, enantioselective intramolecular hydroaminations of allenes (covered in Table 4D) are well established using chiral gold catalysts. The highly stereoselective hydroamination of aminoallenes in the presence of an axially chiral diphosphine-gold(I) complex shows a pronounced counterion effect, with *p*-nitrobenzoate (OPNB) providing the most selective catalysts with up to 99.0:1.0 er (Scheme 137).³⁵³ The role of the counteranion is not limited to the enhancement of enantioselectivity, but can itself contribute to the stereinduction. Thus, a gold complex with a chiral phosphate counteranion displays excellent enantioselectivities in the cyclization of *N*-protected aminoallenes (Scheme 138).³⁵⁴ This approach is also successfully employed in the cyclization of allenic hydroxylamines and hydrazines.³⁵⁵



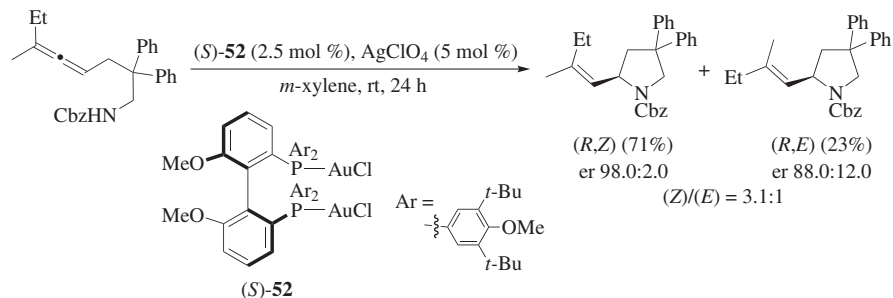
Scheme 137



Scheme 138

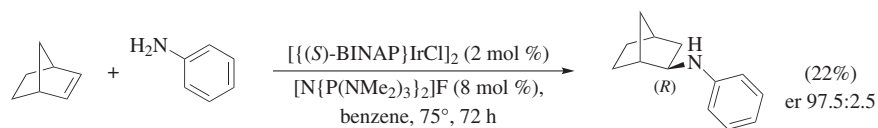
The ability of some gold(I) complexes to racemize allenes is exploited in the facile dynamic kinetic resolution of axially chiral *N*-(γ -allenyl) carbamates with trisubstituted allenyl groups.³⁵⁶ A mixture of the MeOBIPHEP-ligated bis-gold(I) complex (*S*)-**52** and AgClO₄ catalyzes the cyclization of Cbz-protected aminoallenes to yield predominantly the (*R*)-(*Z*)-vinylpyrrolidine with excellent enantioselectivity (Scheme 139).

Enantioselective Hydroamination of Norbornene. The higher reactivity of norbornene in intermolecular hydroamination has enabled the development of the first examples of enantioselective hydroamination reactions using chiral, iridium-based catalyst systems (see also Table 3E). The addition of aniline to norbornene



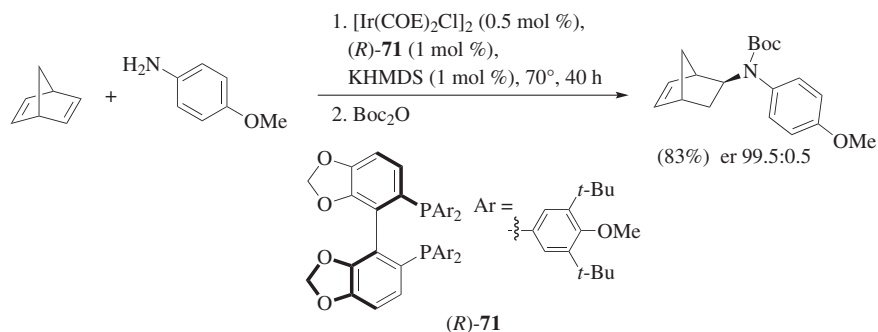
Scheme 139

is catalyzed by a BINAP-iridium(I) complex with enantioselectivities of up to 97.5:2.5 er in conjunction with Schwesinger's "naked" fluoride $[\text{N}\{\text{P}(\text{NMe}_2)_3\}_2]\text{F}$ as a co-catalyst (Scheme 140),⁷⁸ but unfortunately the yields are quite low. Higher yields are obtained using Josiphos-based ligands, but the increased reactivity is accompanied by a significant loss in enantioselectivity.⁷⁸

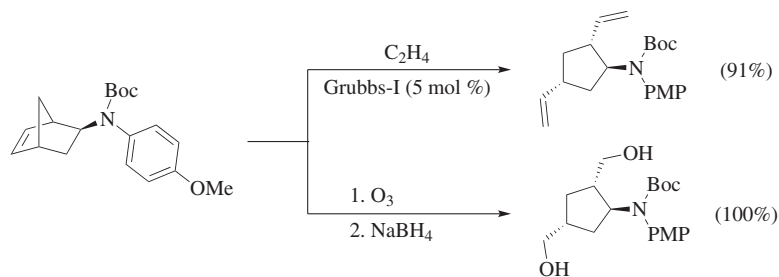


Scheme 140

This chemistry is extended to various bicyclic alkenes and dienes utilizing various chelating, axially chiral, bisphosphine iridium catalysts such as that formed from ligand **71** and $[\text{Ir}(\text{COE})_2\text{Cl}]_2$ (Scheme 141).⁷⁹ Further synthetic transformations of the chiral hydroamination product provide access to functionally substituted chiral cyclopentylamines with multiple stereocenters (Scheme 142). The scope of this reaction is somewhat limited with respect to the amine because alkylamines, such as octylamine or *N*-methylaniline, and sterically encumbered aniline derivatives, such as *o*-toluidine or *o*-anisidine, do not undergo hydroamination reactions under these conditions.



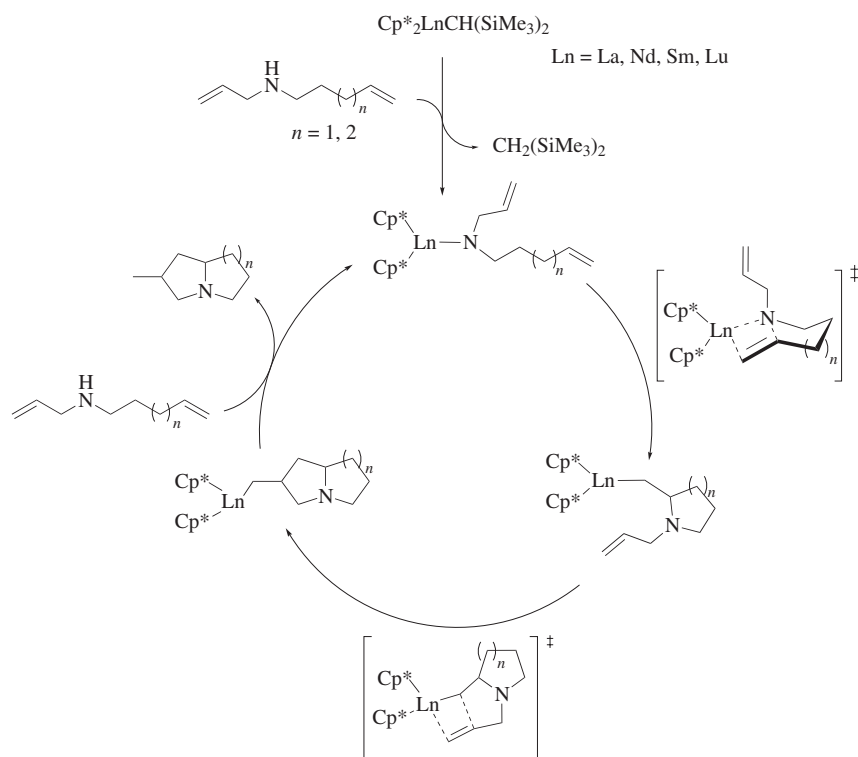
Scheme 141



Scheme 142

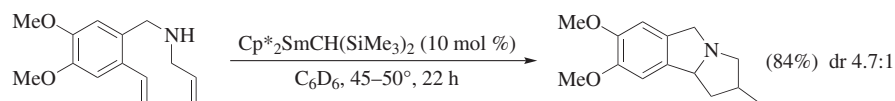
Hydroamination/Carbocyclization

Tandem hydroamination/carbocyclization of aminodialkenes, as summarized in Table 5, is a straightforward route to pyrrolizidines, indolizidines, and quinolizidines in a consecutive C–N and C–C bond forming process.^{43,55–58} For catalysts operating by a σ -bond metathesis mechanism (Scheme 143), the metal-alkyl intermediate



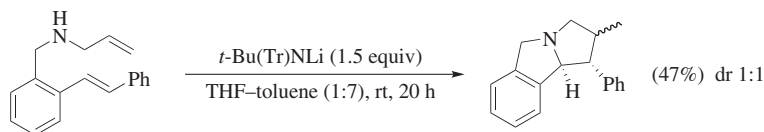
Scheme 143

formed after double bond insertion into the metal-amide bond may undergo a second insertion with an additional double bond present in the substrate to form a bicyclic product. The success of this tandem process depends on the relative rate of olefin insertion vs. protonolysis of the metal-alkyl intermediate, which seems to be controlled by the catalyst structure. In particular, lanthanocene complexes are efficient catalysts for this transformation, as shown in Scheme 144.⁵⁷



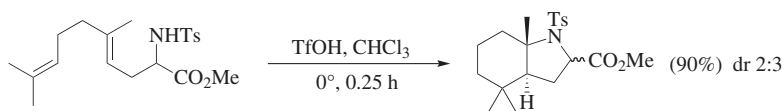
Scheme 144

Hindered lithium amides also induce the hydroamination/carbocyclization, although due to lower reactivity, one of the fragments involved has to be a stilbene moiety and more than stoichiometric amounts of the lithium reagent are required (Scheme 145).³⁵⁷



Scheme 145

The scope of hydroamination/carbocyclization also extends to Brønsted acid catalysts (Scheme 146).²¹⁰

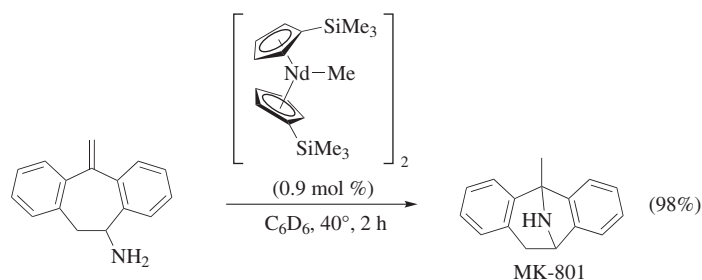


Scheme 146

APPLICATIONS TO SYNTHESIS

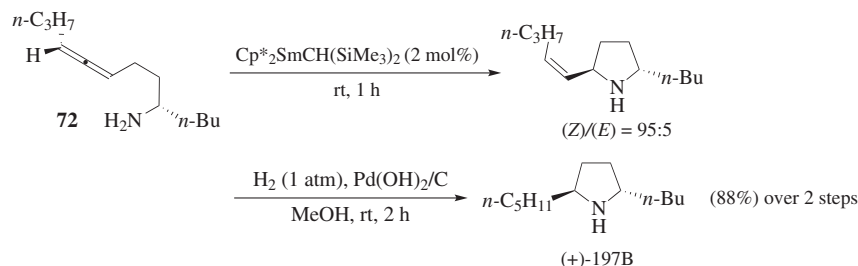
Intramolecular hydroamination reactions have been applied in the synthesis of various alkaloid skeletons and pharmacologically active molecules using rare earth metal complexes. Most of these examples use achiral catalysts that lead to racemic products, but some involve the reaction of an enantiomerically pure substrate leading to an enantiomerically pure product. Only a few examples are known in which enantiomerically pure products are obtained through the application of a chiral catalyst.

Rare earth metal catalysts are employed in the facile synthesis of the tetracyclic anticonvulsant drug dizocilpine (MK-801, Scheme 147).²⁵⁴ The cyclization, involving a sterically encumbered 1,1-disubstituted alkene, is facilitated by the proximity of the amino group in the substrate.



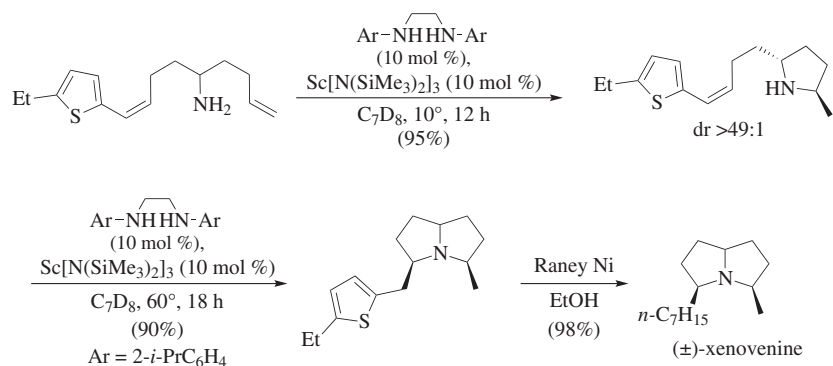
Scheme 147

Pyrrolidine- and pyrrolizidine-based alkaloids are also accessible by hydroamination/cyclization of aminoallenes. The pyrrolidine alkaloid (+)-197B (Scheme 148) is prepared using a hydroamination/cyclization reaction as the key step.³⁰² The cyclization of the α -substituted aminoallene **72** proceeds with good *trans* diastereoselectivity in a manner analogous to that advanced for the diastereoselective cyclization of α -substituted aminoalkenes (Figure 1, p. 20). In a similar manner, the pyrrolizidine alkaloid (+)-xenovenine is obtained via a highly stereoselective bicyclization of an aminoallene-alkene using a constrained-geometry catalyst (Scheme 100).



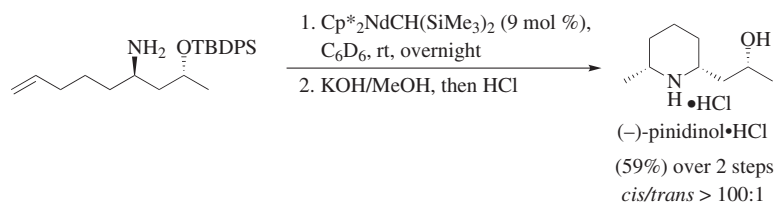
Scheme 148

The *trans* diastereoselective cyclization of α -substituted aminopentenes is applied to a racemic synthesis of xenovenine from a 2-(5-ethyl-2-thienyl)ethenyl-terminated aminobisalkene (Scheme 149).¹⁶⁶ The 2,5-disubstituted pyrrolidine intermediate is formed with high (49:1) *trans/cis* selectivity. The subsequent bicyclization proceeds only after increasing the reaction temperature to 60°, which furnishes the desired xenovenine after reductive desulfurization with Raney nickel.



Scheme 149

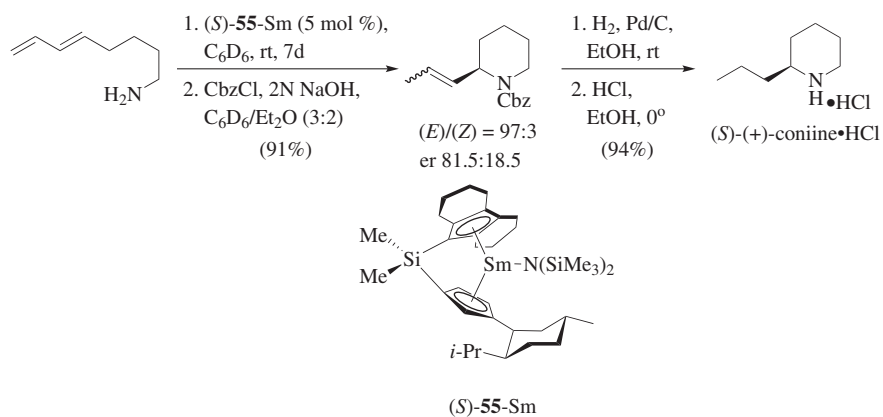
The *cis* diastereoselective cyclization of α -substituted aminohexenes is employed in the synthesis of 2,6-disubstituted piperidines, such as pinidinol (Scheme 150).¹⁶¹



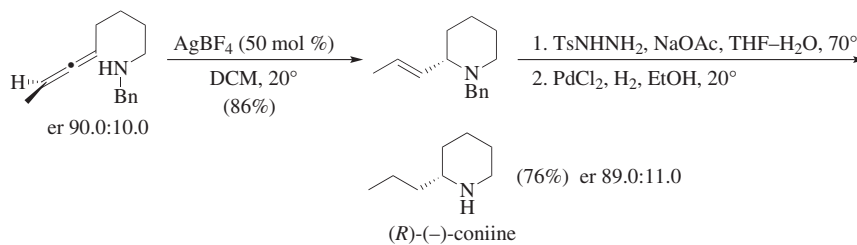
Scheme 150

The intramolecular hydroamination of aminodienes preferentially affords (*E*)/(*Z*)-alkenylpyrrolidines and alkenylpiperidines. The carbon–carbon double bond may be functionalized further or hydrogenated to yield the saturated product. This strategy provides facile access to azacycles with an exocyclic alkyl substituent other than methyl and avoids the use of aminoalkenes with an internal double bond, which generally require significantly harsher reaction conditions. For example, the chiral, organo rare earth metal catalyst (*S*)-**55**-Sm is used in the stereoselective synthesis of (*S*)-(+)-coniine by asymmetric cyclization of amino-octadiene followed by hydrogenolysis/reduction of the Cbz-protected vinylpiperidine (Scheme 151).²⁸⁸

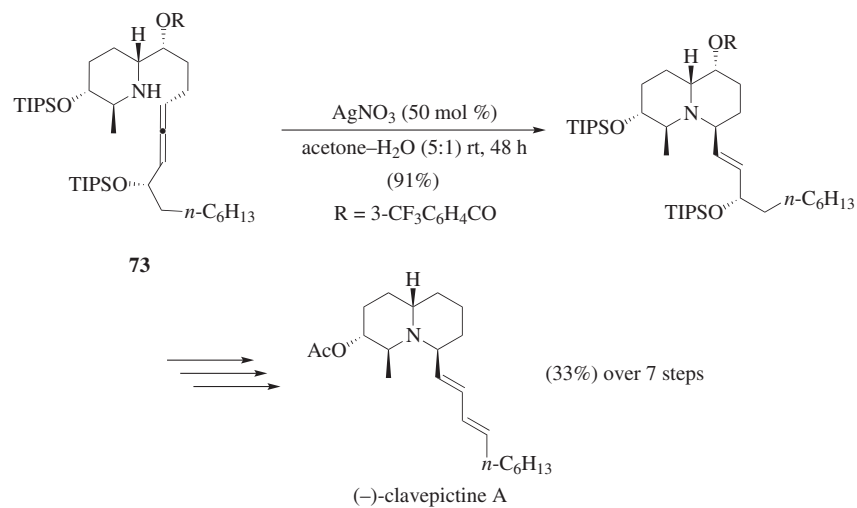
(*R*)-(-)-Coniine is synthesized by silver tetrafluoroborate catalyzed, stereoselective hydroamination of a 1,2-disubstituted chiral, nonracemic aminoallene (Scheme 152).³¹¹ Using the same method, the quinolizidine alkaloid (-)-clavicipitine A, which exhibits antimicrobial, antifungal, and antitumor activity, is prepared by silver nitrate-catalyzed, diastereoselective cyclization of the aminoallene **73** (Scheme 153).³¹² Subsequent deacylation provides access to (+)-clavicipitine B.



Scheme 151

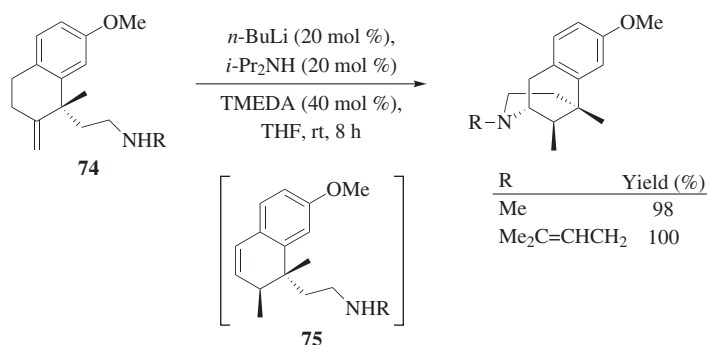


Scheme 152

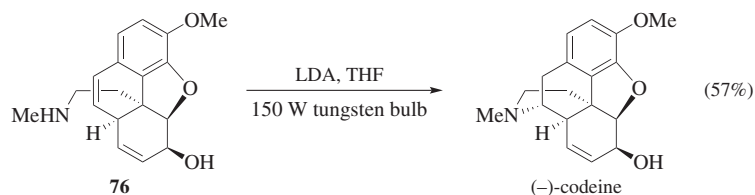


Scheme 153

Lithium-based hydroamination catalysts play not only a pivotal role in the industrial synthesis of menthol in the Takasago process (see Scheme 76), but are also applied in the synthesis of opium alkaloids and benzomorphans.^{145,358,359} The syntheses of *O*-methylmetazocine (R = Me) and *O*-methylpentazocine (R = Me₂C=CHCH₂) proceed by base-catalyzed isomerization followed by hydroamination (Scheme 154). The alkene **74** is initially isomerized to the vinyl arene **75**, which undergoes intramolecular hydroamination (Scheme 154).¹⁴⁵ The analogous synthesis of (–)-codeine by intramolecular hydroamination of the vinyl arene **76** requires irradiation with a 150 W tungsten bulb in the presence of LDA to induce the cyclization (Scheme 155).^{358,359} The addition is facilitated by single electron transfer,^{360–362} which is promoted by irradiation, and no hydroamination is observed in the absence of irradiation even under refluxing conditions. This lack of reactivity can be attributed to the extended conjugation in **76** as compared to the benzomorphan precursor **74**.



Scheme 154



Scheme 155

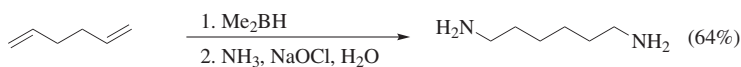
COMPARISON WITH OTHER METHODS

Hydroelementation/Amination

The hydroamination reaction represents the most straightforward approach to derive an alkylamine starting from an alkene. In certain cases, when the direct hydroamination reaction is not feasible, alternative methods can be employed. These

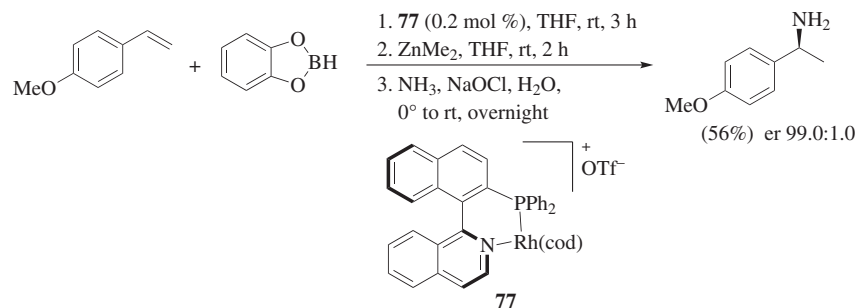
methods typically involve an addition of an H–Y moiety across the carbon–carbon double bond, which is typically less challenging than the hydroamination itself. Further Y/NR₂ transformation can be carried out in single or multiple steps to afford the target amine. This sequence is obviously less atom economical and includes more steps than the parent hydroamination; however, better control of regio- or stereoselectivity in the hydroelementation steps compared to the corresponding hydroamination may compensate for this disadvantage.

Catalytic Hydroboration/Amination. The reaction of alkylboranes, which are readily available via hydroboration, with compounds that contain electrophilic nitrogen such as chloramines, hydroxylamine-*O*-sulfonic acid, azides, and HN₃, is a well-documented route to primary and secondary amines.^{363–367} Notably, when enantiopure alkylboranes derived from camphenyl borane are employed, the corresponding chiral amines are obtained with complete retention of configuration. However, this approach requires multiple synthetic manipulations at the organoboron group.^{368–371} Simple dialkylborano groups, such as Me₂B, are readily cleaved by chloramine (Scheme 156).³⁷² Because the uncatalyzed addition of boranes to alkenes typically proceeds in an anti-Markovnikov fashion, this reaction constitutes an alternative approach to anti-Markovnikov hydroamination.



Scheme 156

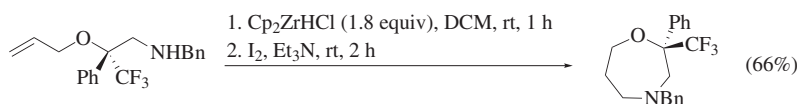
More recently, a catalytic one-pot approach to enantioselective, intermolecular hydroboration/amination of alkenes via a highly efficient, enantioselective rhodium-catalyzed (e.g., rhodium catalyst **77**) hydroboration with catecholborane^{373,374} has been developed. Subsequent alkylation of the alkylcatecholborane intermediate with an organozinc reagent gives the more reactive trialkylboranes that are treated with an appropriate chloramine to afford chiral primary or secondary amines (Scheme 157).^{375,376} This method represents an alternative to the Markovnikov intermolecular hydroamination of vinyl arenes.



Scheme 157

Although the treatment of alkylboranes with electrophilic nitrogen reagents is a facile approach to amines, the desired transformation can also be performed by oxidizing the borane followed by reductive amination of the resulting carbonyl compound.^{377–379}

Hydrozirconation/Iodination of Aminoalkenes. In general, RHet/RNH₂ transformations, where RHet is an alkene hydrometalation product, require electrophilic amine equivalents, which are often prepared in a separate step.³⁸⁰ However, if RHet can be transformed into the corresponding halide RX, the natural nucleophilicity of the amino group can be employed to afford the desired amine. This approach has been exploited in the synthesis of pyrrolidines³⁸¹ and oxazepanes³⁸² via stoichiometric hydrozirconation/iodination of an aminoalkene followed by nucleophilic ring closure. Thus, enantiomerically pure aminoalkenes are smoothly converted into the corresponding heterocycles (Scheme 158).³⁸²



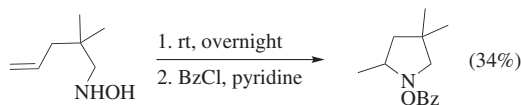
Scheme 158

As noted above, the intramolecular hydroamination of aminoalkenes generally proceeds via *exo* cyclization, whereas this method affords an alternative *endo* cyclization product. This sequence constitutes an interesting alternative to hydroamination, although the need to use stoichiometric amounts of Schwartz's reagent and iodine are significant disadvantages in comparison to the atom-economic hydroamination-based approach.

Cope-Type Hydroamination

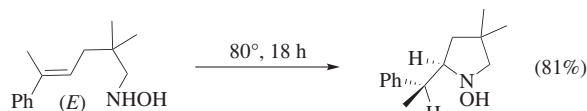
The so-called Cope-type hydroamination, which is also referred to as reverse Cope elimination, provides a conceptually different approach to the addition of a nitrogen-center to a carbon–carbon multiple bond. The hydroxylamine starting material and reaction product both contain nitrogen in a different oxidation level than the amines found in a conventional hydroamination processes. Another difference is that the reverse Cope elimination utilizes a proton from the hydroxylamine hydroxyl group in the addition process rather than a proton bound directly to nitrogen.

Early studies in the 1970's demonstrated that alkenyl hydroxylamines can spontaneously isomerize into *N*-hydroxypyrrolidines under mild conditions (Scheme 159).^{383,384}

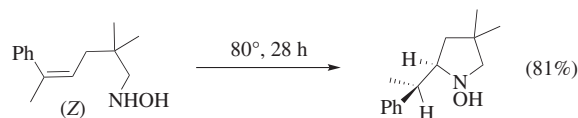


Scheme 159

It is noteworthy that the reaction does not require any catalyst. Moreover, the protocol can be applied to trisubstituted alkenes, which remain challenging substrates in the metal-catalyzed hydroamination of aminoalkenes. The reaction proceeds with high stereoselectivity (Schemes 160 and 161).³⁸⁵

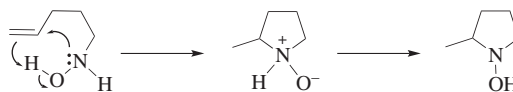


Scheme 160



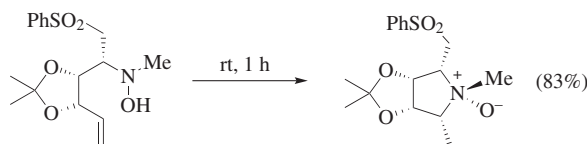
Scheme 161

The reaction mechanism is elucidated in several seminal contributions.^{385–388} It can be depicted as a thermal electrocyclic $[2\pi + 2\sigma + 2n]$ process with a five-centered transition state resembling that of the well-known Cope elimination reaction (Scheme 162).



Scheme 162

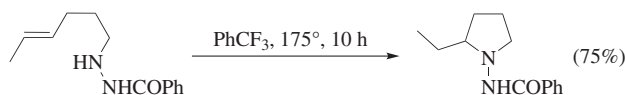
In the case of *N,N*-disubstituted hydroxylamines, proton transfer is not possible, and the corresponding *N*-oxides are the final reaction products (Scheme 163).³⁸⁹ This example illustrates that the reaction cannot be seen as a true hydroamination, since the presence of the N–H fragment is not required and the O–H bond is playing a key role in the addition sequence. It should also be pointed out that the cyclization of disubstituted hydroxylamines is reversible, which somewhat limits its synthetic usefulness.



Scheme 163

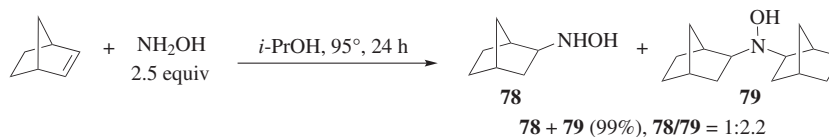
As noted earlier, the method is confined to hydroxylamine and hydrazine derivatives, many of which are not readily available and also are sensitive to oxidation. However, several protocols for the synthesis of heterocycles have been elaborated utilizing the intramolecular Cope hydroamination. An excellent overview covering the results in this field prior to 2004 is available.³⁹⁰

More recently, the utility of the alkenyl hydrazides in the Cope hydroamination has been demonstrated.^{391,392} Given the sensitivity of alkenyl hydroxylamines towards oxidation, more stable hydrazine derivatives are promising as practical reagents. The thermal cyclization of alkenyl hydrazides proceeds smoothly, although the required temperatures significantly exceed those needed for hydroxylamine cyclizations (Scheme 164). Six- and seven-membered-ring heterocycles are also accessible via this protocol, although temperatures up to 230° are required for the reaction to proceed.



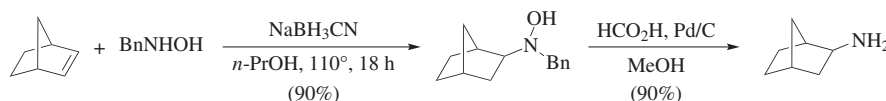
Scheme 164

The intermolecular Cope hydroamination of alkenes with hydroxylamines can be achieved with activated alkenes, such as vinyl arenes and norbornene.^{393,394} Reactions with the parent hydroxylamine are usually not selective and bis-hydroamination products such as **79** are formed in addition to the single adduct **78** (Scheme 165).



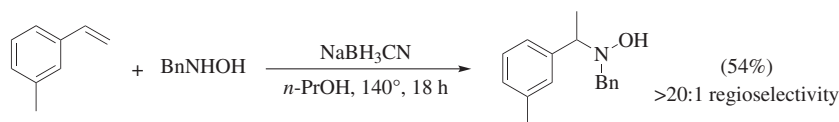
Scheme 165

Reactions of *N*-alkylhydroxylamines are restricted to a single hydroamination event, and the alkyl and hydroxy groups can be subsequently removed to yield a primary amine (Scheme 166).³⁹⁴ Although the reaction proceeds in the absence of a catalyst, addition of sodium cyanoborohydride improves the yields, most likely as an inhibitor for the decomposition of the reactants and products.



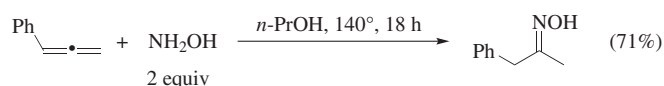
Scheme 166

Vinyl arenes yield Markovnikov hydroamination products with high regioselectivities (Scheme 167), although increasing amounts of the anti-Markovnikov products form from electron-poor or more sterically challenging aryl substituents.³⁹⁴

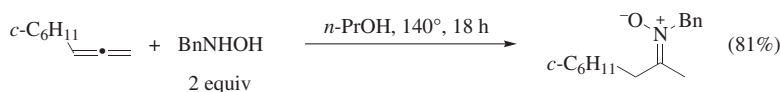


Scheme 167

Although the Cope hydroamination of dienes has not been reported, the hydroamination of allenes proceeds smoothly to give oximes or nitrones from hydroxylamine and alkylhydroxylamines respectively (Schemes 168 and 169).³⁹⁵



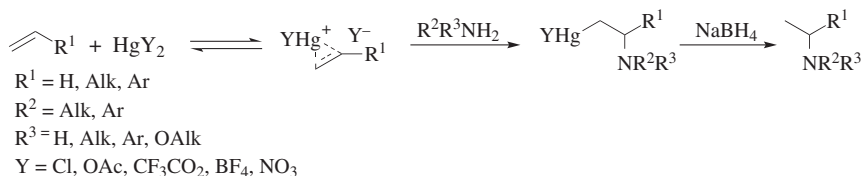
Scheme 168



Scheme 169

Aminomercuration/Demercuration

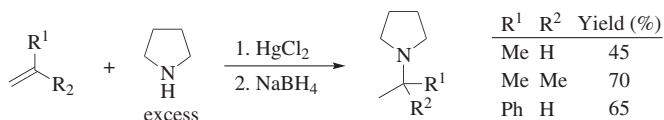
The mercury(II)-promoted addition of amines to alkenes followed by demercuration with a reducing agent is a well-established protocol for alkene-to-amine transformations. The reaction proceeds via formation of a mercurinium ion, which undergoes nucleophilic attack by an amine (Scheme 170). Sodium borohydride is generally used as a reducing agent. Extensive reviews on aminomercuration/demercuration are available.^{7,396}



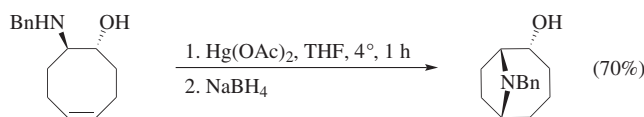
Scheme 170

The reaction using unactivated alkenes and a broad range of amines typically proceeds under ambient conditions or at slightly elevated temperatures,

and Markovnikov hydroamination products form exclusively in most cases (Scheme 171).³⁹⁷ Intramolecular aminomercuration is also feasible and a broad range of functional groups is tolerated (Scheme 172).³⁹⁸

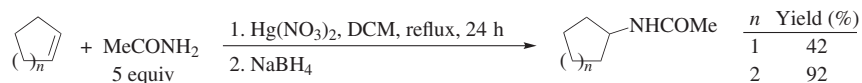


Scheme 171



Scheme 172

Notably, the aminomercuration protocol is also applicable to *N*-protected amines, such as carbamates, sulfonamides, and amides.⁷ In contrast to the hydroamination reaction, virtually identical reagents and reaction conditions are used for both free and protected amines (Scheme 173).³⁹⁹



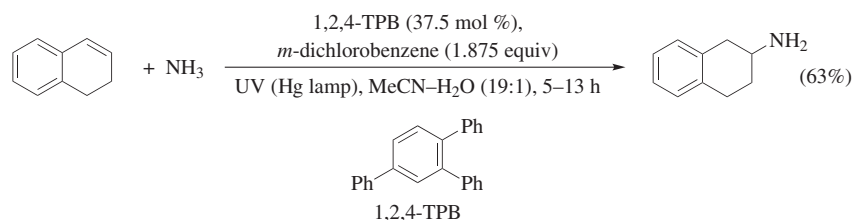
Scheme 173

Although the aminomercuration/demercuration protocol is relatively general, the requirement of stoichiometric amounts of highly toxic mercury salts precludes this process from large-scale application.

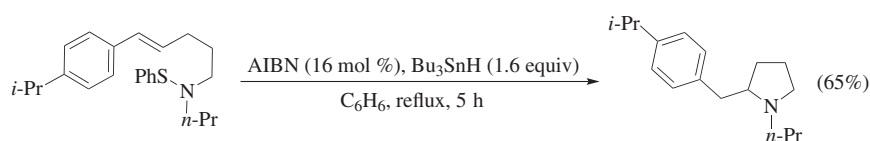
Radical-Transfer Hydroamination

Since most hydroamination protocols involve metal-based catalysts, the development of metal-free methods is an attractive goal. Radical chemistry is one possibility that might avoid the requirement for an elaborate and sometimes not readily available catalyst. Thus, nucleophilic radical photoamination of vinyl arenes and 1,3-butadiene derivatives with ammonia and amines proceeds smoothly in the presence of an appropriate sensitizer^{214–216,264,400} (e.g. Scheme 174)⁴⁰⁰ via the generation of a cation-radical from the activated olefin, which is then subjected to nucleophilic attack by an amine. Although this method requires substoichiometric amounts of photosensitizer, the reaction itself remains a simple addition of an amine to an olefin, i.e., hydroamination, and the reported examples are incorporated into the corresponding Tables of this chapter. Another possible approach to radical hydroamination involves the generation of aminyl radicals, since the ability of these species to add to a double bond,

especially in an intramolecular fashion, is well established.^{401–403} Unfortunately, no direct method to generate a neutral *N*-centered radical directly from a free amine is known to date. Typical nitrogen precursors include haloamines and phenylthio derivatives, which are either subjected to a reduction or irradiated to generate an aminyl radical. An obvious drawback is the required stoichiometric amount of a hydrogen donor, such as tributyltin hydride, to generate an alkyl amine (Scheme 175).⁴⁰⁴

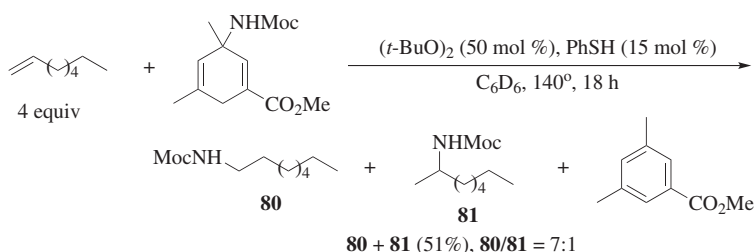


Scheme 174

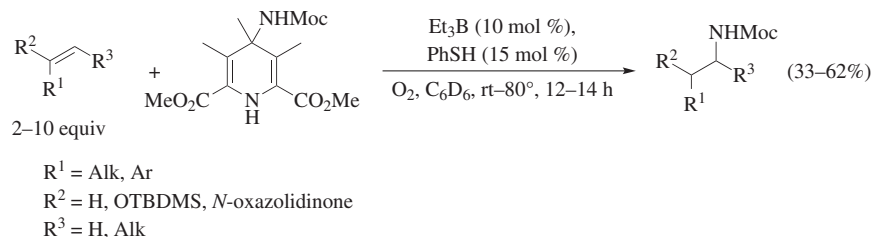


Scheme 175

Various substituted 1,4-cyclohexadiene precursors have been developed that generate aminyl radicals by an aromatization-driven process.^{405,406} Formal addition of the NH_2Moc fragment to alkenes proceeds in moderate to good yields and the anti-Markovnikov product **80** is formed preferentially to the Markovnikov addition product **81**. Addition of catalytic amounts of an alkyl- or arylthiol enhances the hydrogen transfer (Scheme 176).⁴⁰⁵ When an *N*-aminated Hantzsch dihydropyridine is employed as a nitrogen source, the radical transfer hydroamination takes place at lower temperatures (Scheme 177).⁴⁰⁷



Scheme 176

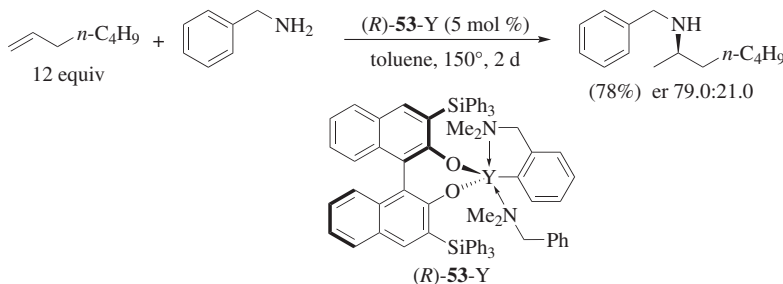


Scheme 177

EXPERIMENTAL CONDITIONS

All operations involving organometallic species must be performed under an inert atmosphere (nitrogen or argon) using dry solvents and utilizing standard glovebox or Schlenk line techniques unless stated otherwise. Etheral solvents (THF, Et_2O) are first dried over KOH and then distilled from sodium benzophenone ketyl. Non-polar aprotic solvents (hexanes, pentane, benzene, toluene) are purified by distillation from sodium/triglyme benzophenone ketyl. Halogenated solvents (DCM, $CHCl_3$) are distilled from calcium hydride.

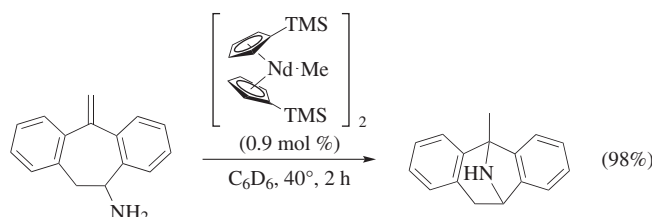
EXPERIMENTAL PROCEDURES



***(R)*-N-Benzylheptan-2-amine (Lanthanide-Catalyzed Asymmetric Intermolecular Hydroamination of an Aliphatic Terminal Alkene).**³³⁵

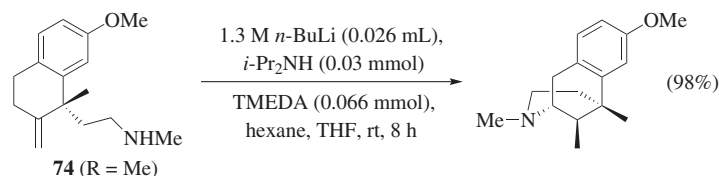
In a glovebox, a reaction tube equipped with a Teflon plug was charged with 1-heptene (1.70 mL, 1.18 g, 12.0 mmol), benzylamine (107 mg, 1.0 mmol), and a solution of (R) -**53-Y** (0.15 M in toluene, 330 μ L, 0.05 mmol). The tube was sealed, and kept for 2 d at 150° . The reaction mixture was cooled and transferred to a round-bottomed 50-mL flask containing alumina (1.0 g). The volatiles were removed at 100 mmHg, and the residue was loaded onto a 4-cm height alumina plug and eluted with pentane/ $EtOAc$ (100:0.6). The fraction containing the target compound (120 mL) was concentrated at 600 mmHg and the residue was dried at 50 mmHg for an additional 15 min to give the title compound as a colorless liquid (159 mg, 78%, er 79.0:21.0): 1H NMR ($CDCl_3$, 400 MHz) δ 0.89 (t, $J = 6.9$ Hz, 3H), 1.07 (d, $J = 6.2$ Hz, 3H), 1.23–1.34 (m, 8H), 1.41–1.50 (m, 1H), 2.68 (sext, $J = 6.2$ Hz, 1H), 3.73 (d, $J =$

13.0 Hz, 1H), 3.82 (d, $J = 13.0$ Hz, 1H), 7.21–7.25 (m, 1H), 7.30–7.32 (m, 4H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 14.1, 20.3, 22.7, 25.7, 32.1, 37.1, 51.4, 52.5, 126.8, 128.1, 128.4, 140.9. The enantiomeric excess was determined by ^{19}F NMR spectroscopy after debenzoylation of the hydroamination product with Pd on charcoal and ammonium formate followed by treatment with (*R*)-Mosher acid chloride and DIPEA. Mosher amide of hexan-2-amine: ^{19}F NMR (CDCl_3 , 470 MHz, 65°) δ –69.39 (*S*), –69.47 (*R*).



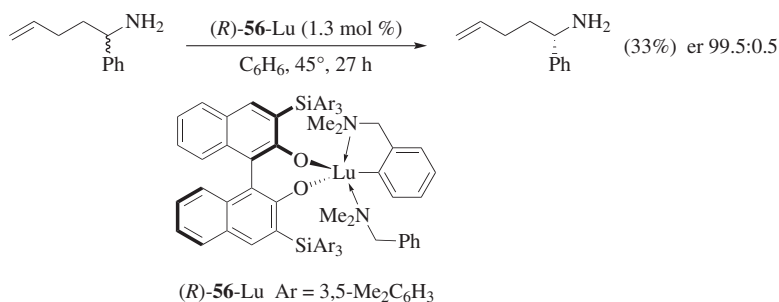
5-Methyl-10,11-dihydro-5H-dibenzo[*a,d*]cyclohepten-5,10-imine (MK-801) (Organolanthanide-Catalyzed Intramolecular Hydroamination of an Aminoalkene).²⁵⁴

In a nitrogen-filled glovebox, $[(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{NdMe}]_2$ (0.001 g, 0.9 mol %) was weighed into a vial and dissolved in C_6D_6 (0.5 mL). To this solution was added 5-methylene-10,11-dihydro-5H-dibenzo[*a,d*][7]annulen-10-amine (0.057 g, 0.258 mmol), and the light-blue solution was transferred into a tube equipped with a Teflon-valved top using additional C_6D_6 (0.5 mL) to rinse the vial. The mixture was then removed from the glovebox and heated to 40° , and the progress of the reaction was monitored by GC sampling of small aliquots. After 2 h the starting material was completely consumed. The solution was filtered through Florisil with Et_2O to remove the catalyst, and the filtrate was concentrated under vacuum. The residue was purified by Kugelrohr distillation to yield the title compound as a colorless oil (0.056 g, 98%): bp 100° (0.01 mm Hg); IR (neat) 3210.2, 3016.1, 1600.5 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 1.91 (s, 3H), 2.53 (br s, 1H), 2.72 (d, $J = 16.8$ Hz, 1H), 3.44 (dd, $J = 16.7, 5.8$ Hz, 1H), 4.69 (d, $J = 5.6$ Hz, 1H), 6.91–6.93 (m, 1H), 7.03–7.10 (m, 5H), 7.24–7.28 (m, 2H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 20.2, 34.4, 58.4, 64.1, 118.6, 121.4, 121.6, 125.7, 126.6, 126.9, 128.1, 130.2, 132.3, 144.4, 144.7, 152.1; LRMS–EI (m/z): 221 (100), 220 (93), 206 (33), 178 (74); HRMS (m/z): $[\text{M} - \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{15}\text{N}$, 220.1126; found, 220.1142.



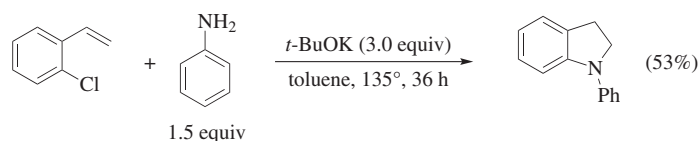
O-Methylmetazocine (Lithium Amide-Catalyzed Intramolecular Hydroamination of an Aminoalkene).¹⁴⁵ To a cooled solution (-78°) of aminoalkene **74** ($\text{R} = \text{Me}$, 40 mg, 0.16 mmol) in THF (1 mL) was added diisopropylamine (0.005 mL, 0.03 mmol), TMEDA (0.010 mL, 0.066 mmol) and *n*-BuLi (1.3 M

in hexane, 0.026 mL). The reaction mixture was warmed to rt and stirred for 8 h in an argon atmosphere. The solution was quenched with water, dried over Na_2SO_4 , and concentrated under vacuum. Flash column chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, 19:1 to 9:1) afforded the desired product (39 mg, 98%): $[\alpha]_{\text{D}} - 76.4$ (c 1.3, EtOH); IR (neat) 2960, 2905, 2836, 2797, 1608, 1496, 1463, 1281, 1238, 1046 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 0.85 (d, $J = 7.2$ Hz, 3H), 1.33 (m, 1H), 1.82 (td, $J = 12.7, 4.8$ Hz, 1H), 1.36 (s, 3H), 1.87 (m, 1H), 2.07 (td, $J = 12.3, 3.3$ Hz, 1H), 2.40 (s, 3H), 2.43 (ddd, $J = 11.9, 4.8, 1.6$ Hz, 1H), 2.60 (dd, $J = 18.2, 5.9$ Hz, 1H), 2.84 (dd, $J = 5.6, 3.2$ Hz, 1H), 2.97 (d, $J = 18.2$ Hz, 1H), 3.79 (s, 3H), 6.68 (dd, $J = 8.4, 2.7$ Hz, 1H), 6.78 (d, $J = 2.6$ Hz, 1H), 7.00 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 14.1, 22.4, 25.5, 36.0, 42.0, 42.3, 42.7, 47.4, 55.1, 59.2, 110.7, 111.2, 127.9, 128.8, 143.2, 157.9.



(S)-(+)-1-Phenylpent-4-en-1-amine (Kinetic Resolution of a Racemic Aminoalkene).⁵² In a glove box, a 25-mL flask was charged with *rac*-1-phenylpent-4-en-1-amine (1.600 g, 9.92 mmol), benzene (7 mL), and lutetium binaphtholate catalyst (R)-**56**-Lu (160 mg, 0.128 mmol, 1.3 mol %). The reaction mixture was kept at 45°. To monitor the conversion, small aliquots (50 μL) were taken, transferred into an NMR tube and diluted with CDCl_3 to 0.5 mL volume and a ^1H NMR spectrum was recorded. The conversion was 45% after 18.5 h and 64% after 27 h. The reaction flask was removed from the glovebox, and the mixture was treated with acetic acid (320 μL , 330 mg, 5.5 mmol) followed by benzaldehyde (640 mg, 6 mmol). The mixture was kept at rt for 2 h and was then transferred into a separatory funnel. Water (20 mL), benzene (10 mL), and hexanes (15 mL) were added. The funnel was shaken vigorously and the layers were separated. The organic layer was extracted with acetic acid (0.2 M, 10 mL). The hexanes/benzene layer containing the benzaldimine was evaporated, the residue was treated with HCl (2 M, 20 mL) and Et_2O (30 mL), and the mixture was stirred for 24 h at rt. The layers were separated and the organic layer was extracted with water (10 mL). The combined aqueous layers were evaporated. The residue was treated with sodium hydroxide solution and extracted with Et_2O . The ether solution was dried (Na_2SO_4) and evaporated. The residue was distilled under vacuum (120°, 1 mmHg) to give the enantioenriched starting material (530 mg, 33%, er 99.5:0.5) in analytically pure form: ^1H NMR (CDCl_3 , 400 MHz) δ 1.45 (br s, 2H), 1.75 (m, 2H), 2.04 (m, 2H),

3.89 (t, $J = 6.9$ Hz, 1H), 4.93–5.03 (m, 2H), 5.80 (m, 1H), 7.23 (m, 1H), 7.31 (m, 4H); ^{13}C NMR (CDCl_3 , 100.6 MHz) δ 30.7, 38.6, 55.6, 114.7, 126.3, 126.9, 128.4, 138.2, 146.4. Analytical data for the 1:1 hydrochloride salt: ^1H NMR (CDCl_3 , 300 MHz) δ 1.85–2.08 (m, 3H), 2.15 (m, 1H), 4.14 (m, 1H), 4.93–4.98 (m, 2H), 5.65 (m, 1H), 7.30–7.41 (m, 5H), 8.74 (br s, 3H); ^{13}C NMR (CDCl_3 , 100.6 MHz) δ 29.5, 33.5, 55.6, 116.3, 127.4, 129.0, 129.1, 136.0, 136.2. The enantiomeric ratio was determined via ^{19}F NMR of the Mosher amide: ^{19}F NMR (CDCl_3 , 282 MHz, 60°) δ -69.3 (*R*), -69.4 (*S*).

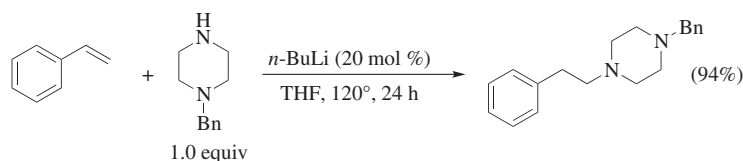


1-Phenyl-2,3-dihydroindole (Potassium-Catalyzed Addition of Aniline to 2-Chlorostyrene with Subsequent Cyclization).²²⁵ In an Ace pressure tube (38 mL) 2-chlorostyrene (0.28 g, 2.0 mmol) and aniline (0.28 g, 3.0 mmol) were dissolved in toluene (10 mL) under Ar. After addition of potassium *tert*-butoxide (0.67 g, 6.0 mmol), the sealed reaction vessel was placed in an oil bath preheated to 135° and the reaction mixture was stirred vigorously. After 36 h the mixture was allowed to cool to rt and water (20 mL) was added with stirring. The aqueous phase was extracted with CH_2Cl_2 (3×10 mL) and the combined organic phases were dried over MgSO_4 . The solvent was removed under vacuum and the resulting crude product was purified by column chromatography with hexane as eluent to afford the title product (0.21 g, 53%): ^1H NMR (CDCl_3 , 360 MHz) δ 3.10 (t, $J = 8.4$ Hz, 2H), 3.92 (t, $J = 8.4$ Hz, 2H), 6.73 (dd, $J = 7.5, 7.1$ Hz, 1H), 6.94 (t, $J = 7.1$ Hz, 1H), 7.05 (dd, $J = 8.0, 7.5$ Hz, 1H), 7.12 (d, $J = 8.0$ Hz, 1H), 7.14 (d, $J = 7.1$ Hz, 1H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.32 (dd, $J = 8.0, 7.1$ Hz, 2H); ^{13}C NMR (CDCl_3 , 90 MHz) δ 28.2, 52.1, 108.2, 117.7, 118.8, 120.9, 125.0, 127.1, 129.1, 131.2, 144.2, 147.1; MS (70 eV) m/z : M^+ 195 (5), 165 (70), 116, 91 (100), 77.

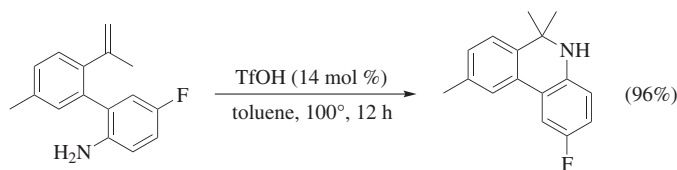


(*S*)-*N*-Phenyl-*N*-[1-{4-(trifluoromethyl)phenyl}ethyl]amine (Palladium-Catalyzed Asymmetric Intermolecular Hydroamination of a Vinyl Arene).²³¹ [(*R*)-BINAP]Pd(OTf)₂ (103 mg, 0.10 mmol) was suspended in toluene (0.5 mL) in a glovebox. The suspension was placed into a vial, which was sealed with a cap containing a PTFE septum, and the vial was removed from the glovebox. 4-(Trifluoromethyl)styrene (258 mg, 1.50 mmol) and aniline (93 mg, 1.00 mmol) were added to the reaction mixture by syringe which was then stirred at rt for 72 h, and adsorbed on silica gel, and the product was isolated by eluting with

EtOAc/hexanes (1:9) to give the title compound (212 mg, 80%, er 90.5:9.5 (*S*)): ^1H NMR (CDCl_3 , 400 MHz) δ 1.44 (d, $J = 6.8$ Hz, 3H), 3.90–4.05 (br s, 1H), 4.4 (q, $J = 6.8$ Hz, 1H), 6.39 (d, $J = 7.6$ Hz, 2H), 6.59 (t, $J = 7.6$ Hz, 1H), 6.99–7.05 (m, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.49 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 24.4, 52.6, 112.5, 116.9, 122.2, 124.8, 124.9 (q, $J = 4.2$ Hz), 125.4, 128.5, 146.1, 148.7. The enantiomeric purity was determined by capillary GLC analysis: t_R (*S*) 48.7 min, t_R (*R*) 49.4 min (permethylated β -Cyclodextrin chiral stationary phase column).

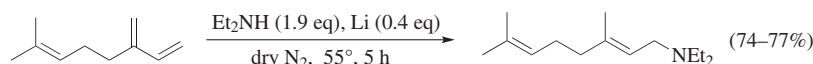


1-Phenylmethyl-4-(2-phenethyl)piperazine (Lithium-Catalyzed Intermolecular Hydroamination of Styrene).¹³⁰ *n*-Butyllithium (1.6 M in hexane, 0.29 mL 0.44 mmol) was added slowly at rt to a solution of *N*-benzylpiperazine (391 mg, 2.22 mmol) in THF (5 mL), and the mixture was stirred for 10 min. Styrene (231 mg, 2.22 mmol) was then added, and the mixture was stirred at 120° in a threaded tube. After 24 h the reaction mixture was allowed to cool to rt, and quenched with methanol (1 mL), and the solvent was removed under vacuum. Column chromatography (EtOAc/hexane, 4:1) afforded the title product (585 mg, 94%) as a colorless oil: IR (neat) 3026, 2938, 2808, 1602, 1495, 1156, 1133, 1009, 742, 698 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 2.35–2.55 (br, 8H), 2.52 (m, 2H), 2.71 (m, 2H), 3.45 (s, 2H), 7.12 (d, $J = 7.2$ Hz, 2H), 7.15–7.22 (m, 4H), 7.23–7.28 (m, 4H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 33.8, 53.3, 53.4, 60.7, 63.2, 126.2, 127.2, 128.4, 128.5, 128.9, 129.4, 138.3, 140.5; CIMS (70 eV) m/z : $[\text{M} + \text{H}]^+$ 281 (35), M^+ 280 (7), $[\text{M} - \text{Bn}]^+$ 189 (100), Bn^+ 91 (17).



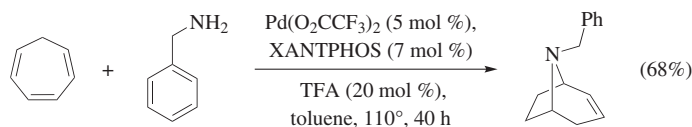
3-Fluoro-6,6,9-trimethyl-5,6-dihydrophenanthridine (Brønsted Acid-Catalyzed Intramolecular Hydroamination).²⁶³ 5-Fluoro-2'-isopropenyl-5'-methylbiphenyl-2-amine (78 mg, 0.32 mmol) and trifluoromethanesulfonic acid (4 μL , 45 μmol , 0.14 equiv) were stirred in a Pyrex tube in toluene (2.0 mL) at 100° for 12 h. After evaporation of the solvent under vacuum the crude product was purified by chromatography on silica (pentane/MTBE, 10:10, $R_f = 0.36$) to give the target compound (75 mg, 96%) as a white solid: IR (KBr) 3362, 2958, 1721, 1618, 1499, 1474, 1450, 1294, 1260, 1154, 1109, 1001, 840, 822, 576 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 1.60 (s, 6H), 2.49 (s, 3H), 3.83 (br s, 1H), 6.42–6.48

(m, 1H), 6.56–6.66 (m, 1H), 7.15–7.35 (m, 2H), 7.59 (m, 1H), 7.75 (m, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 21.2, 29.8, 53.7, 101.7 (d, $J = 24.3$ Hz), 105.5 (d, $J = 22.0$ Hz), 117.5 (d, $J = 2.3$ Hz), 122.9, 123.3, 124.7 (d, $J = 10.2$ Hz), 128.0, 129.7, 136.6, 137.3, 144.9 (d, $J = 10.7$ Hz), 163.4 (d, $J = 245.3$ Hz); EIMS (70 eV) m/z : M^+ 241 (5), $[\text{M} - \text{CH}_3]^+$ 226 (100), 211 (4), 183(6), 170 (3), 113 (5).



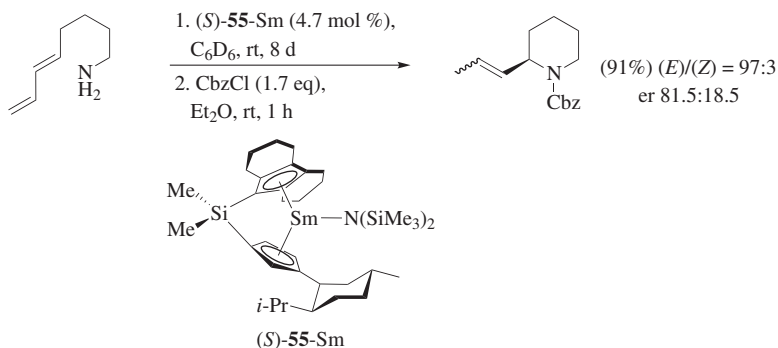
(*E*)-*N,N*-Diethyl-3,7-dimethyl-2,6-octadien-1-amine (*N,N*-Diethylgeranylamine) (Lithium-Catalyzed Addition of a Secondary Amine to a Diene).²⁶⁷

In a 50-mL, round-bottomed glass reactor equipped with a magnetic stirring bar were placed myrcene (13.60 g, 74 mmol), diethylamine (10.29 g, 141 mmol), and metallic lithium (0.185 g, 26.7 mmol) cut into small pieces. The vessel was flushed with dry nitrogen and sealed. The solution was stirred at 55° for 5 h. The vessel was cooled to rt and the contents were poured into ice water (30 mL). The upper organic layer was separated, and the aqueous layer was extracted with Et_2O (2 $\times$ 20 mL). The combined organic layers were washed with aqueous Na_2SO_4 solution, dried over anhydrous Na_2SO_4 , and evaporated under reduced pressure. Distillation of the residual liquid afforded unreacted myrcene (1.2–2.0 g) and the title product (12.66–13.28 g, 74–77%) as a colorless liquid, 92% pure according to GLC-analysis (Triton X-305, 0.28 mm $\times$ 30 m, 80–160°): bp 67–68° (0.5 mm Hg); IR (neat) 1660, 1200, 1165, 1050, 830 cm^{-1} ; ^1H NMR (CDCl_3 , 60 MHz) δ 0.96 (t, $J = 7$ Hz, 6H), 1.44–1.67 (m, 6H), 1.85–2.15 (m, 4H), 2.40 (q, $J = 7$ Hz, 4H), 2.92 (d, $J = 6.5$ Hz, 2H), 4.77–5.30 (m, 2H).



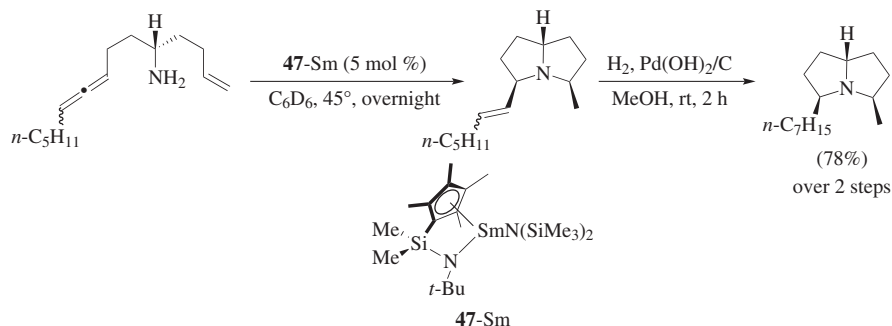
8-Phenylmethyl-8-azabicyclo[3.2.1]oct-2-ene (Palladium-Catalyzed Intermolecular Transannular Hydroamination of a Cyclic Triene).²⁸¹ In a glovebox, $\text{Pd}(\text{O}_2\text{CCF}_3)_2$ (8 mg, 0.025 mmol) and Xantphos (20 mg, 0.35 mmol) were weighed directly into a screw-capped vial. A stir bar, cycloheptatriene (2.00 mmol, 20 μL), dodecane (0.15 mmol) as an internal standard, and toluene (0.5 mL) were added successively and the reaction mixture was stirred for 2–3 min during which time the solution turned dark red. Benzylamine (53.5 mg, 0.50 mmol) was added and the vial was sealed with a cap containing a PTFE septum and removed from the glovebox. To the resulting solution was added trifluoroacetic acid (7.5 μL , 0.10 mmol) via syringe through the septum. The reaction mixture was heated to 110°. The reaction was monitored by GC until complete consumption of the amine. The resulting dark red suspension was adsorbed onto alumina or Chromatorex® NH and purified by flash chromatography (hexane/ EtOAc , 9:1 to 1:9) to give the target compound (68 mg,

68%) as a yellow oil: ^1H NMR (CDCl_3) δ 1.67 (dd, $J = 18.0, 2.4$ Hz, 1H), 1.88 (td, $J = 9.6, 2.8$ Hz, 1H), 2.00–2.05 (m, 1H), 2.20–2.25 (m, 1H), 2.54 (dd, $J = 18.0, 2.4$ Hz, 1H), 3.25 (t, $J = 4.8$ Hz, 1H), 3.31 (dd, $J = 4.8, 1.2$ Hz, 1H), 3.75 (dd, $J = 16.4, 13.4$ Hz, 2H), 5.67 (m, 1H), 5.80 (m, 1H), 7.25–7.29 (m, 1H), 7.32–7.36 (m, 2H), 7.40–7.43 (m, 2H); ^{13}C NMR (CDCl_3) δ 30.6, 32.4, 34.8, 53.7, 56.4, 57.1, 124.1, 127.3, 128.7, 129.3, 131.5, 140.5.

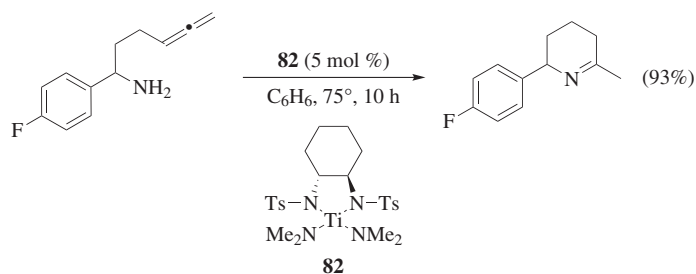


1-Benzyloxycarbonyl-2-[(*E*)-prop-1-enyl]piperidine (Organolanthanide-Catalyzed Intramolecular Hydroamination of an Aminodiene with Subsequent Protection).²⁸⁸

In a glovebox, (*S*)- $\text{Me}_2\text{Si}(\text{Cp})(-)\text{-menthyl}\text{SmN}(\text{SiMe}_3)_2$ ((*S*)-**55**-Sm) (34.1 mg, 45.8 μmol) was loaded into a storage tube equipped with a magnetic stirring bar and J. Young valve, and dissolved in C_6D_6 (3 mL). The initial color of the catalyst solution was orange. Next, a solution of (*E*)-octa-5,7-dien-1-amine in C_6D_6 (1.73 M, 0.5 mL, 0.87 mmol) was added to the catalyst solution via syringe. The color of the solution changed to light yellow upon the addition of the aminodiene. The tube was sealed and removed from the glovebox. The solution was stirred at room temperature for 8 d until the color turned back to orange. The reaction mixture was cooled to 0° , diluted with Et_2O (2 mL), and quenched with 2 N NaOH (1.5 mL). Then benzyl chloroformate (0.21 mL, 1.5 mmol) was added dropwise, and the mixture was allowed to warm to rt and stirred vigorously for 1 h. Next, the aqueous layer was separated and extracted with Et_2O (3×5 mL). The combined organic layers were washed with brine (5 mL), dried over MgSO_4 , and concentrated under vacuum. Flash column chromatography on silica (hexanes/ Et_2O , 6:1) afforded the title product (203.7 mg, 91%, 97:3 (*E*)/(*Z*) mixture, er 81.5:18.5) as a colorless oil: IR (neat) 3063, 3030, 2937, 2857, 1703, 1497, 1445, 1421, 1355, 1351, 1323, 1257 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 1.34–1.48 (m, 1H), 1.49–1.78 (m, 5H), 1.70 (d, $J = 4.5$ Hz, 3H), 2.92 (t, $J = 12.0$ Hz, 1H), 4.03 (d, $J = 13.0$, 1H), 4.84 (s, 1H), 4.73 (s, 1H), 5.13 and 5.17 (AB quartet, $J = 12.5$, 2H), 5.45–5.61 (m, 2H), 7.28–7.43 (m, 5H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 18.1, 19.6, 25.8, 29.6, 40.2, 52.4, 67.1, 127.1, 127.9, 128.0, 128.6, 129.2, 137.3, 155.9; MS (m/z): M^+ 259.2 (1), 168.1 (37), 124.1 (20), 92.1 (8), 91.1 (100), 82.1 (9), 65.1 (15), 55.1 (10). The enantiomeric ratio was determined from the optical rotation of the HCl salt of the hydrogenated product.

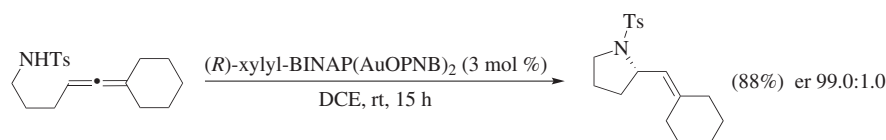


(3*S*,5*R*,8*S*)-3-(1-Heptyl)-5-methylpyrrolizidine ((+)-Xenovenine) (Organo-lanthanide-Catalyzed Stereoselective Intramolecular Hydroamination of an Aminoallene).³⁰² In a glovebox, **47-Sm** (4.7 mg, 8.8 μmol) and C_6D_6 (700 μL) were loaded into an NMR tube equipped with a Teflon valve. On the high vacuum line, the tube was evacuated after the precatalyst solution was frozen. Under a stream of Ar gas, (*S*)-5-aminopentadeca-1,8,9-triene (50 mg, 226 μmol) was then syringed in. The tube was sealed and the frozen reaction mixture was warmed to rt. After the mixture was shaken, the clear yellow solution was then warmed to 45°. When the reaction was complete (overnight), the contents were loaded onto a short column of silica gel and eluted with Et_2O yielding the bicyclic alkene as a 1:1 mixture of (*Z*) and (*E*) isomers. The crude product was dissolved in MeOH (2 mL) and hydrogenated over $\text{Pd}(\text{OH})_2/\text{C}$ (2 mg) for 2 h at 1 bar of H_2 pressure. The reaction mixture was filtered through a short plug of Celite which was then washed with Et_2O . The solvent was removed under vacuum to yield (+)-xenovenine (39.3 mg, 78%) as a pale-yellow liquid: $[\alpha]_{\text{D}}^{23} + 10.9$ (c 0.72, CHCl_3); IR (KBr, thin film) 2963, 2932, 2872, 1462, 1370 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 0.85 (t, $J = 7.0$ Hz, 3H), 1.10 (d, $J = 6.6$ Hz, 3H), 1.17–1.56 (m, 16H), 1.82–2.01 (m, 4H), 2.61 (m, 1H), 2.77 (m, 1H), 3.65 (m, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 14.1, 21.7, 22.7, 27.2, 29.3, 29.8, 31.7, 31.9, 32.0, 32.4, 34.4, 36.9, 61.8, 65.1, 66.7.



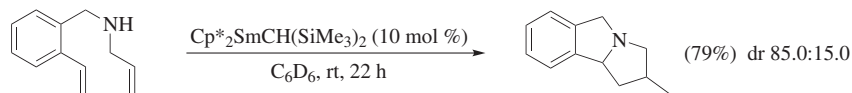
2-(4-Fluorophenyl)-6-methyl-2,3,4,5-tetrahydropyridine (Group 4 Metal-Catalyzed Intramolecular Hydroamination of an Aminoallene).³⁰⁰ A solution of 1-(4-fluorophenyl)hexa-4,5-dienyl-1-amine (121 mg, 0.63 mmol) and the titanium complex **82** (18 mg, 0.03 mmol) in benzene (3 mL) was heated for 10 h at 75°.

The solution was cooled and treated with 20 drops of methanolic NaOH (10%). The mixture was stirred for 0.5 h at room temperature and was concentrated under vacuum. The remaining residue was extracted with *n*-hexane (30 mL) and the extracts were filtered through K_2CO_3 to afford the title compound (112 mg, 93%) as a pale yellow oil with a purity of >95% by NMR: 1H NMR (CD_2Cl_2 , 300 MHz) δ 1.20–1.40 (m, 1H), 1.60–1.95 (m, 3H), 1.98 (d, $J = 2.0$ Hz, 3H), 2.10–2.30 (m, 2H), 4.43 (m, 1H), 7.01 (tm, $J = 8.9$ Hz, 2H), 7.23 (m, 2H); ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 19.0, 27.3, 30.6, 29.9, 60.8, 114.5, 114.8, 128.3, 128.4, 168.6; EIMS (m/z): M^+ 191 (81), 163 (14), 162 (14), 148 (11), 121 (100), 109 (10).



2-(Cyclohexylidenemethyl)-1-[(4-methylphenyl)sulfonyl]pyrrolidine (Gold-Catalyzed Asymmetric Intramolecular Hydroamination of a Protected Aminoallene).³⁵³

To a solution of *N*-(5-cyclohexylidenepent-4-enyl)-4-methylbenzenesulfonamide (50 mg, 0.157 mmol) in DCE (0.5 mL) was added (*R*)-xylyl-BINAP(AuOPNB)₂³⁵³ (6.9 mg, 4.7 μ mol). The resulting homogeneous mixture was protected from ambient light and stirred at rt. Upon completion, as judged by TLC analysis of the reaction mixture, the solution was purified by flash column chromatography on silica gel (hexanes/EtOAc, 12:1) to afford the title pyrrolidine as a colorless oil (44 mg, 88%, er 99.0:1.0): R_f 0.43 (hexanes/EtOAc, 3:1); t_R (minor) 10.8 min, t_R (major) 13.4 min (Chiralpak AD-H column, hexanes/*i*-PrOH, 95:5, 1 mL/min); $[\alpha]_D -54$ (c 1.0, $CHCl_3$); IR (thin film) 1342, 1156, 1092, 814 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 1.43–1.65 (m, 8H), 1.78–1.85 (m, 2H), 1.96–2.01 (m, 2H), 2.09–2.15 (m, 1H), 2.20–2.26 (m, 1H), 2.40 (s, 3H), 3.30–3.40 (m, 2H), 4.34–4.39 (m, 1H), 4.99 (d, $J = 9.2$ Hz, 1H), 7.26 (d, $J = 8.0$ Hz, 2H), 7.68 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 24.2, 26.7, 27.5, 28.2, 29.1, 34.0, 36.9, 48.6, 57.2, 122.7, 127.5, 129.4, 136.0, 140.7, 143.0; HRMS–EI (m/z): M^+ calcd for $C_{18}H_{25}NO_2S$, 319.1606; found 319.1601.



2-Methyl-2,3,5,9b-tetrahydro-1*H*-pyrrolo[2,1-*a*]isoindole (Lanthanide-Catalyzed Sequential Hydroamination/Carbocyclization).⁵⁷

A sealable NMR tube was charged with a solution of $(Cp^*)_2SmCH(SiMe_3)_2$ in C_6D_6 (1 wt % in 551 mg, 9.53 μ mol). The catalyst solution was then charged with an additional 400 mg of C_6D_6 and a solution of 2-ethenyl-*N*-2-propenylbenzenemethanamine in C_6D_6 (2.26 wt % in 730 mg, 95.2 μ mol). The NMR tube was sealed and allowed to sit at rt. Upon completion of the reaction, ~22 h, the green solution was charged with heptanes (3 mL) and allowed to oxidize in air for ~2 h. The yellow slurry was filtered

through Celite and the clear, pale-yellow solution was analyzed by GC (dr 85:15). The solvents were removed under vacuum and the resulting residue was purified by silica gel chromatography using EtOAc/hexanes and *i*-PrOH/EtOAc as eluent to yield the title compound (13.1 mg, 79%) as a 85:15 mixture of diastereomers: IR (CDCl₃) 2958.6, 2929.6, 2872.3, 2359.7, 2251.8, 2171.5, 1477.4, 1456.1, 1378.4, 1340.8, 1091.5, 1042.9 cm⁻¹; ¹³C NMR (CDCl₃, 125 MHz) δ 17.5, 18.3, 32.8, 35.6, 40.7, 41.0, 59.8, 61.8, 64.0, 64.4, 70.5, 70.8, 122.5, 122.6, 122.9, 123.2, 127.1, 127.2, 127.4, 127.5, 140.0, 140.9, 144.7, 145.3; MS–ESI (*m/z*): M⁺ 118 (25), 145 (18), 174 (100).

ABBREVIATIONS USED IN THE TABULAR SURVEY

The hydroamination of unactivated alkenes, vinyl arenes, dienes, allenes, and strained alkenes is presented in the appended tables. The tabular survey covers the literature reported through January 2011. Two references from 2012 comprising Table 3D were added during processing. A supplemental reference list is provided for reports appearing February 2011 through April 2015.

The tables are separated into five main sections: achiral intermolecular hydroamination (section 1), achiral intramolecular hydroamination (section 2), enantioselective intermolecular hydroamination (section 3), enantioselective intramolecular hydroamination (section 4), and tandem hydroamination/carbocyclization (section 5). Within the first four sections the tables are further divided into subsections based on the participating alkene as follows: alkenes (A), vinyl arenes (B), dienes (C), allenes (D), and strained alkenes (E). However, Table 4E was omitted due to lack of published examples of the corresponding enantioselective hydroaminations.

The entries within each table are arranged in order of increasing carbon number of the alkene (sections 1A–E and 3A–E) or aminoalkene (sections 2A–E, 4A–D, and 5) substrates. The carbon count is based on the total number of carbon atoms, not including protecting groups, simple alkyl and aryl groups on heteroatoms, and the ether portion of esters. Further arrangement is based on the amine carbon number for Tables 1A–E and 3A–E. The notation “(—)” is used for unreported yields, and “—” is used for unreported data or conditions.

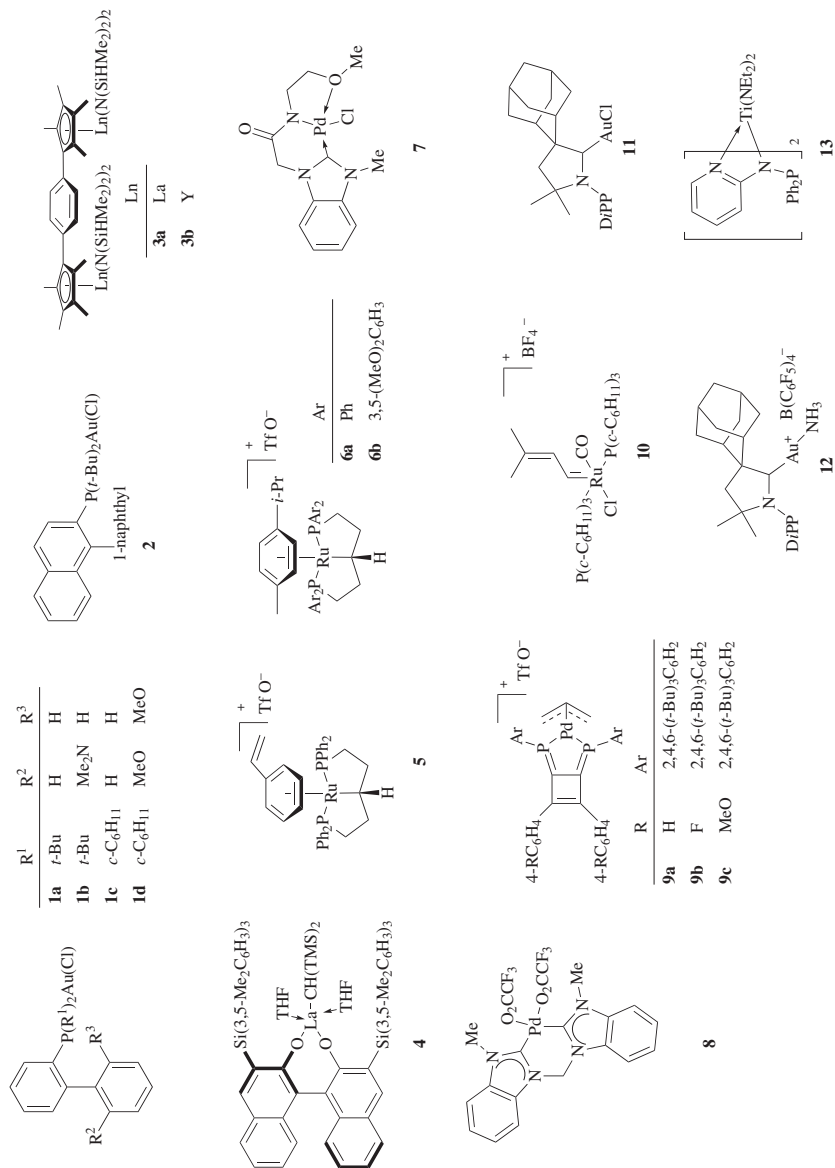
The following abbreviations, excluding those found in the “*The Journal of Organic Chemistry* Standard Abbreviations and Acronyms” list, are used in the Tabular Survey:

Au:PVP	gold nanoparticles stabilized with poly(<i>N</i> -vinylpyrrolidone)
BDPP	(2 <i>S</i> , 4 <i>S</i>)-(–)-2,4-bis(diphenylphosphino)pentane
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
BINOLP(O)OH	1,1′-binaphthyl-2,2-diylhydrogenphosphate
BIPHEMP	6,6-dimethyl-2,2-bis(diphenylphosphino)-1,1-biphenyl
BIPHE-phos	[3′-(diphenylphosphino)-1,1′-biphenyl-3-yl](diphenyl)phosphine
BMIm	1-butyl-3-methyl imidazolium
BN	2,2′-methylenedioxy-1,1′-binaphthalene
BSPy	<i>N</i> -(4-hydroxysulfonylbutyl)pyridinium
COD	1,5-cyclooctadiene

COE	cyclooctene
Cp*	pentamethylcyclopentadienyl
Cp''	tetramethylcyclopentadienyl
Cp ^{TMS}	trimethylsilylcyclopentadienyl
Cy	cyclohexyl
DavePHOS	2-dicyclohexylphosphino-2'-(<i>N,N</i> -dimethylamino)biphenyl
dba	dibenzylideneacetone
DBF-phos	[6-(diphenylphosphino)dibenzo[<i>b,d</i>]furan-4-yl](diphenyl)phosphine
DBMP	2,6-di- <i>tert</i> -butyl-4-methylpyridine
DCB	dicyanobenzene
DCB	1,3- or 1,4-dicyanobenzene
DCM	dichloromethane
DCPM	bis(dicyclohexylphosphino)methane
DIA	diisopropylamine
DIOP	diisopropylethylamine
DIPEA	<i>N,N</i> -diisopropylethylamine
DiPP	2,6-diisopropylphenyl
DIPPF	1,1'-bis(diisopropylphosphino)ferrocene
DMI	1,3-dimethylimidazolin-2-one
DNB	3,5-dinitrobenzoyl
DPE-phos	1,1'-[(oxydi-2,1-phenylene)]bis[1,1-diphenylphosphine]
DPPB	1,4-bis(diphenylphosphino)butane
DPPE	1,2-bis(diphenylphosphino)ethane
DPPEO	[2-(diphenylphosphino)ethyl](diphenyl)phosphine oxide
DPPF	1,1'-bis(diphenylphosphino)ferrocene
DPPH	2,2-diphenyl-1-picrylhydrazyl
DPPM	bis(diphenylphosphino)methane
DPPP	1,3-bis(diphenylphosphino)propane
DPPPent	1,5-bis(diphenylphosphino)pentane
DPPR	1,1'-bis(diphenylphosphino)rutenocene
EBI	ethylenebis(η^5 -indenyl)
EMIM	1-ethyl-3-methylimidazolium
GHSV	gas hourly space velocity
Grubbs-I	bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride
H-BEA	zeolite H-Beta
HMDS	hexamethyldisilazide
HMIIm	1-methylimidazolium
H-Mont	H-montmorillonite
IMes	1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
Ind	indenyl
IPr	1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene
KHMDS	potassium hexamethyldisilazide
KNHXyl	potassium (3,5-dimethylphenyl)amide
L	ligand
MEK	methyl ethyl ketone

MBsIm	1-butyl-3-(butyl-3-sulfonyl)imidazolium
MeO-BIPHEP	6,6-dimethoxy-2,2-bis(diphenylphosphino)-1,1-biphenyl
Moc	methoxycarbonyl
MOZ	p-methoxybenzyloxycarbonyl
MW	microwave radiation
NBD	norbornadiene
Nf	nonafluorobutanesulfonyl
NFA	nonafluorobutanesulfonic acid
NIXANTHPHOS	4,6-bis(diphenylphosphino)phenoxazine
Np	neopentyl
Ns	4-nitrobenzenesulfonyl
OHF	octahydrofluorenyl
OMIM	1-octyl-3-methylimidazolium
PC	propylene carbonate
Phen	phenanthroline
PhthalN	phthalimidoyl
PMA	phosphomolybdic acid
PMB	4-methoxybenzyl
PMP	4-methoxyphenyl
PNB	4-nitrobenzoyl
PNP	2,6-bis((diphenylphosphanyl)methyl)pyridine
PTFE	polytetrafluoroethylene
PVP	poly(N-vinylpyrrolidone)
RENORPHOS	[3-(diphenylphosphino)bicyclo[2.2.1]hept-2-yl](diphenyl)phosphine
SBA-15	ordered mesoporous silica
SEGPPOS	4,4'-bi-1,3-benzodioxole-5,5'-diylbis(diphenylphosphane)
SYNPHOS	[(5,6),(5',6')-bis(ethylenedioxy)biphenyl-2,2'-diyl]bis(diphenylphosphine)
TBDPS	<i>tert</i> -butyldiphenylsilyl
TBDMS	<i>tert</i> -butyldimethylsilyl
TCE	tetrachloroethane
<i>t</i> -BuXANTPHOS	9,9-dimethyl-4,5-bis(di- <i>tert</i> -butylphosphino)xanthene
TEA	triethylamine
TMDA	tetramethylenediamine
TMP	2,2,6,6-tetramethylpiperidine
TiPP	2,4,6-triisopropylphenyl
TOF	turnover frequency
TP	terphenyl
TPA	tungstophosphoric acid
TPB	triphenylbenzene
TPB	1,2,4- or 1,3,5-triphenylbenzene
TPPTS	3,3',3''-phosphanetriyltris(benzenesulfonic acid) trisodium salt
Troc	2,2,2-trichloroethoxycarbonyl
XANTPHOS	4,5-bis(diphenylphosphino)-9,9-dimethylxanthene
xylyl-BINAP	2,2'-bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl

CHART 1. CATALYSTS AND LIGANDS USED IN THE TABLES



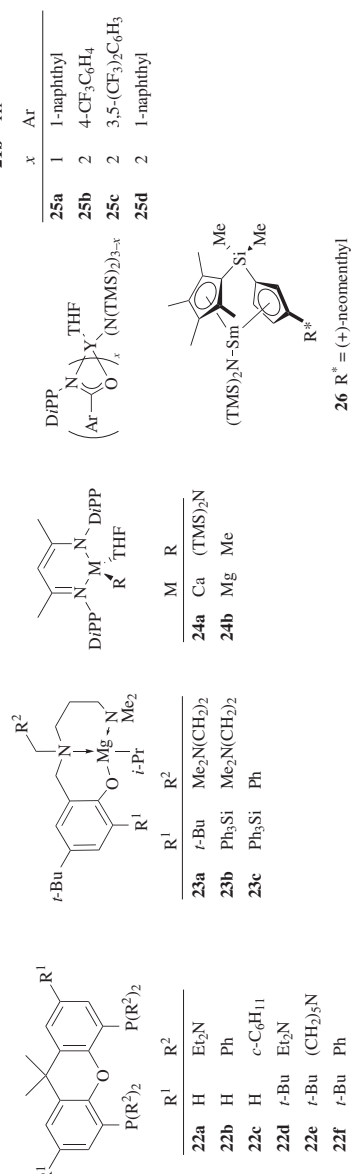
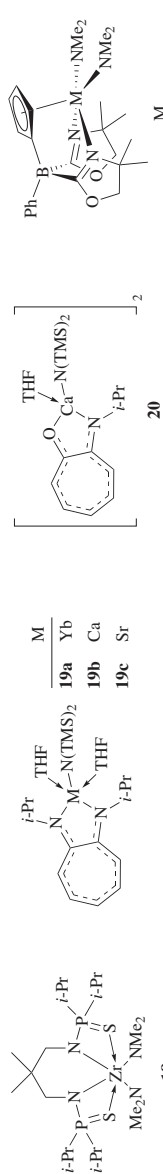
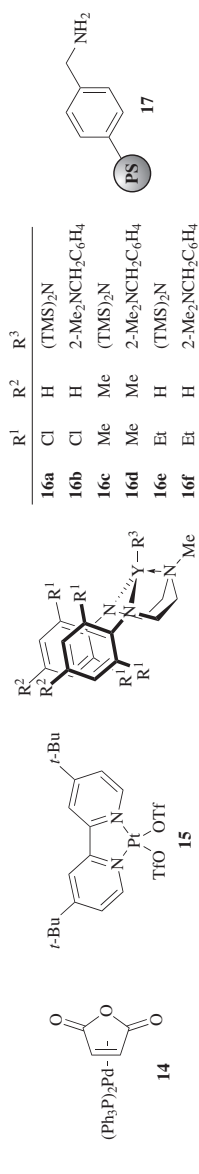
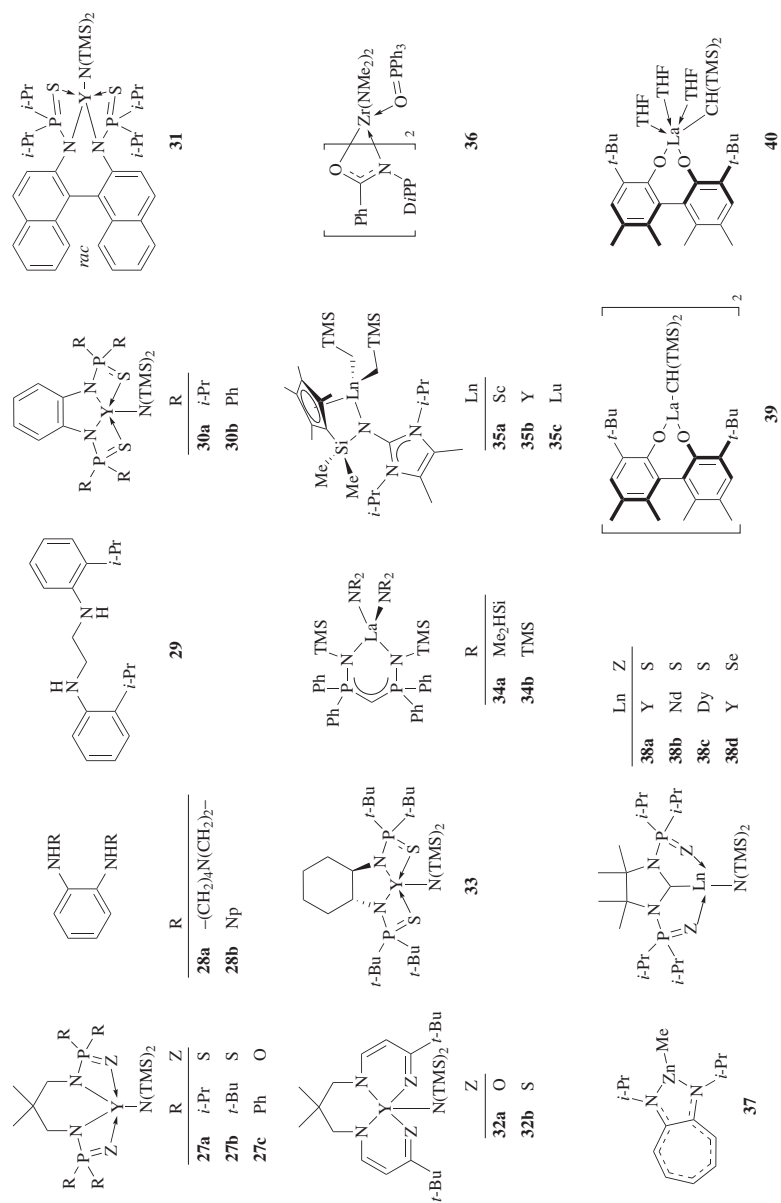
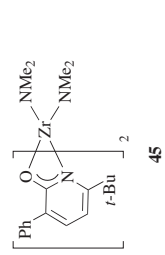
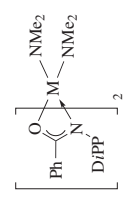


CHART 1. CATALYSTS AND LIGANDS USED IN THE TABLES (Continued)



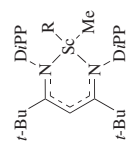


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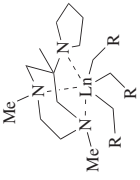
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44b



43a

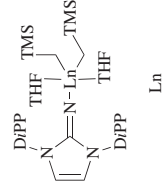
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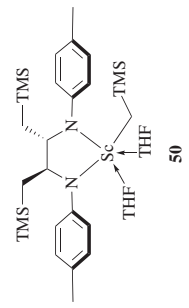
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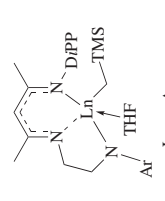


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41b



50



49a

49b

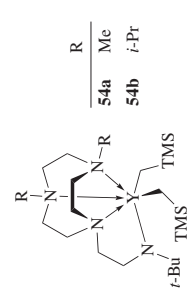
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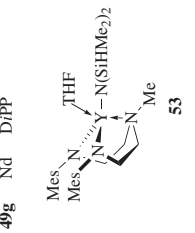
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49g

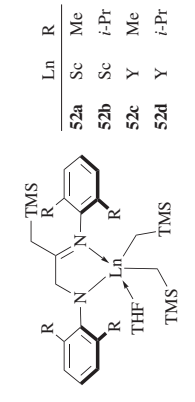


54a

54b



53

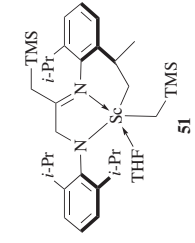


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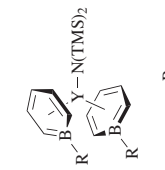
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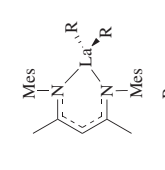
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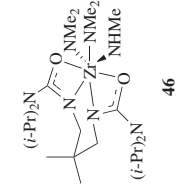
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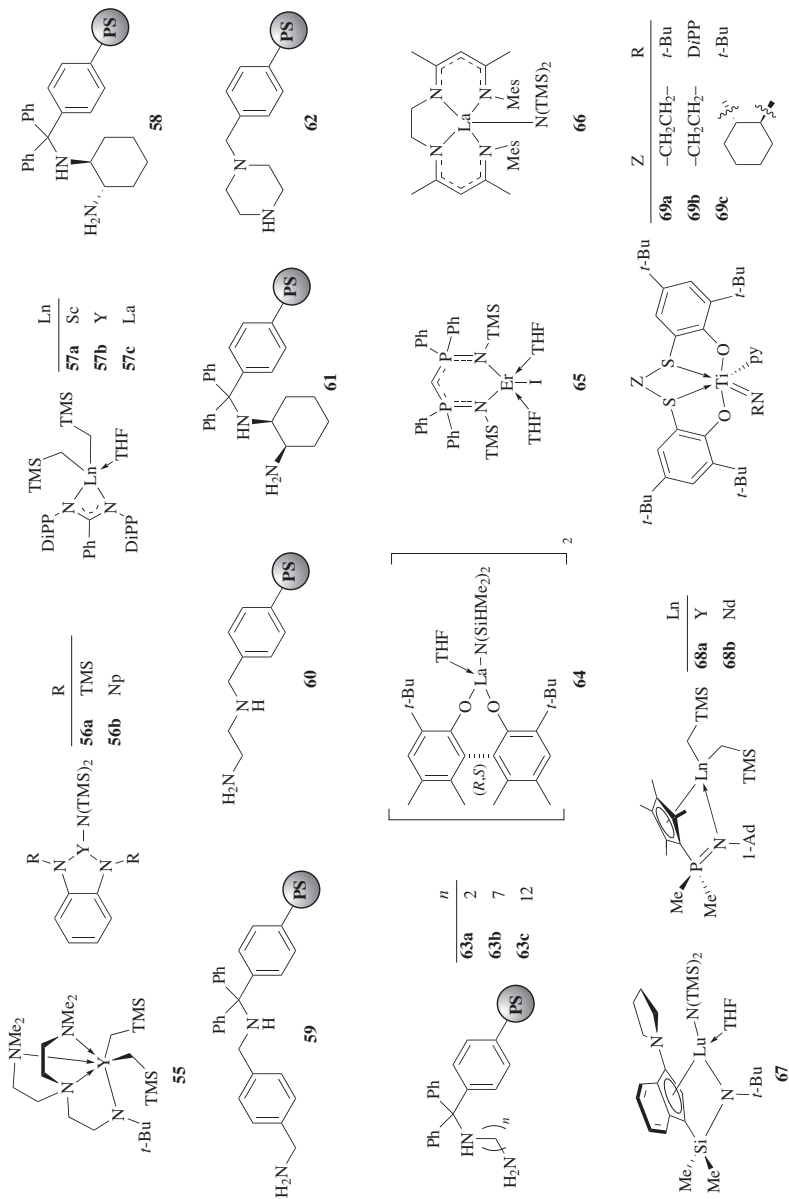
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47b



46

CHART 1. CATALYSTS AND LIGANDS USED IN THE TABLES (Continued)



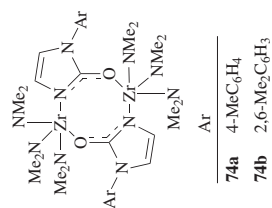
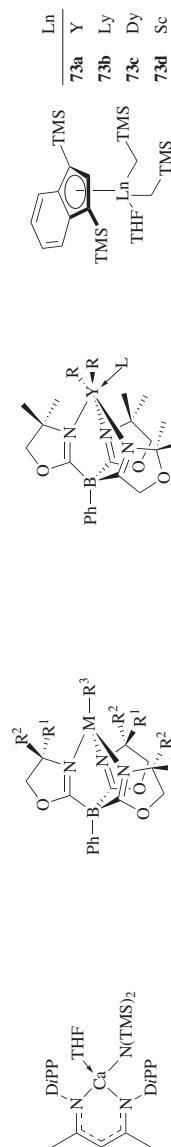
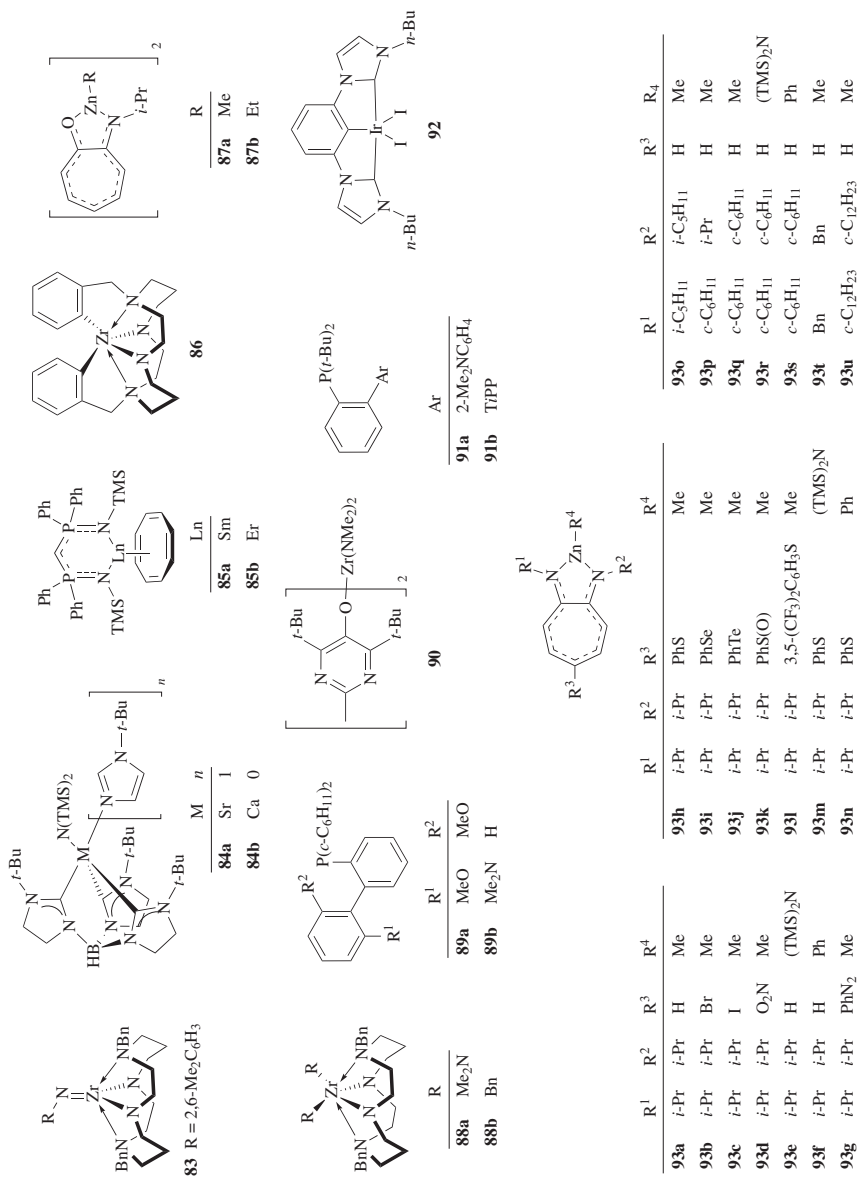


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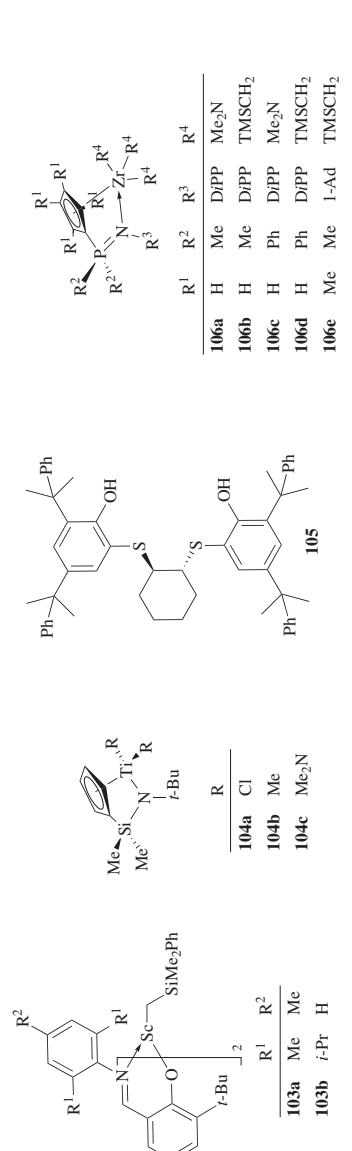
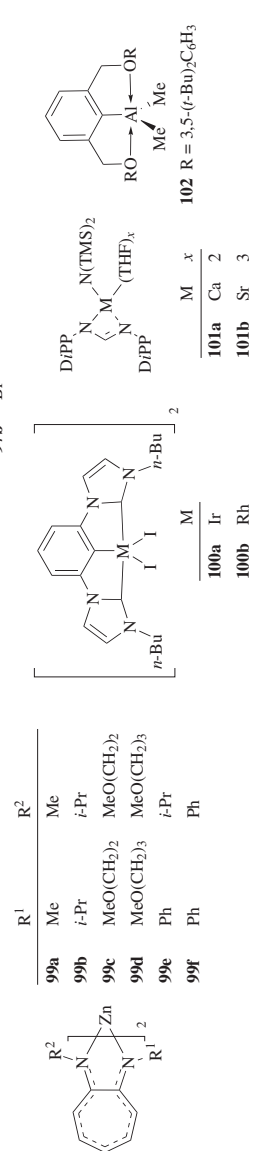
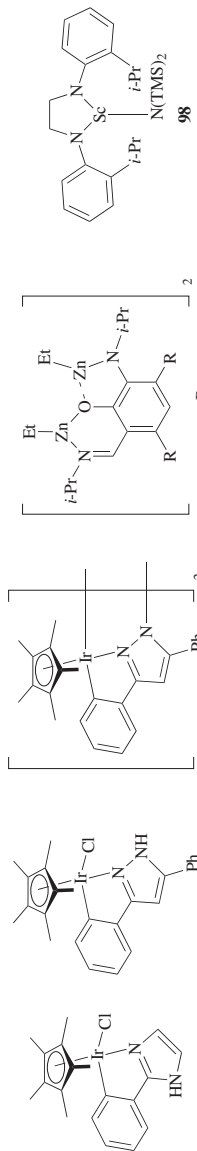
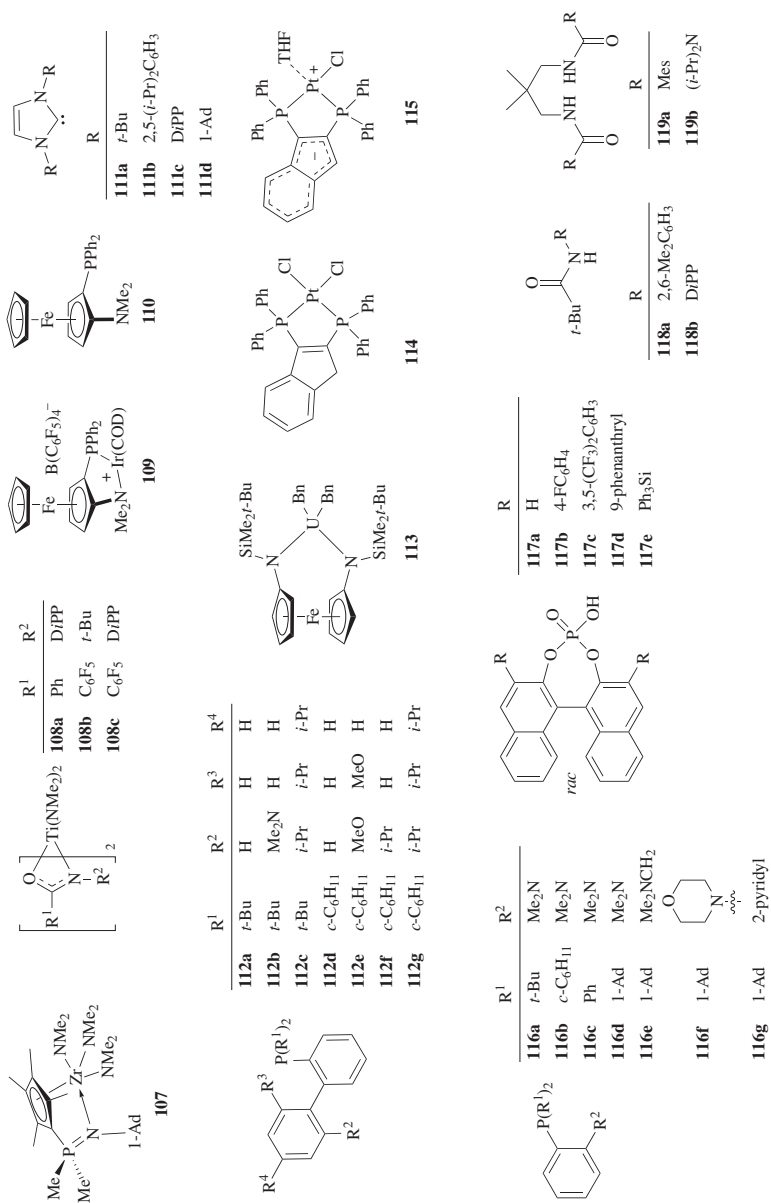


CHART 1. CATALYSTS AND LIGANDS USED IN THE TABLES (Continued)



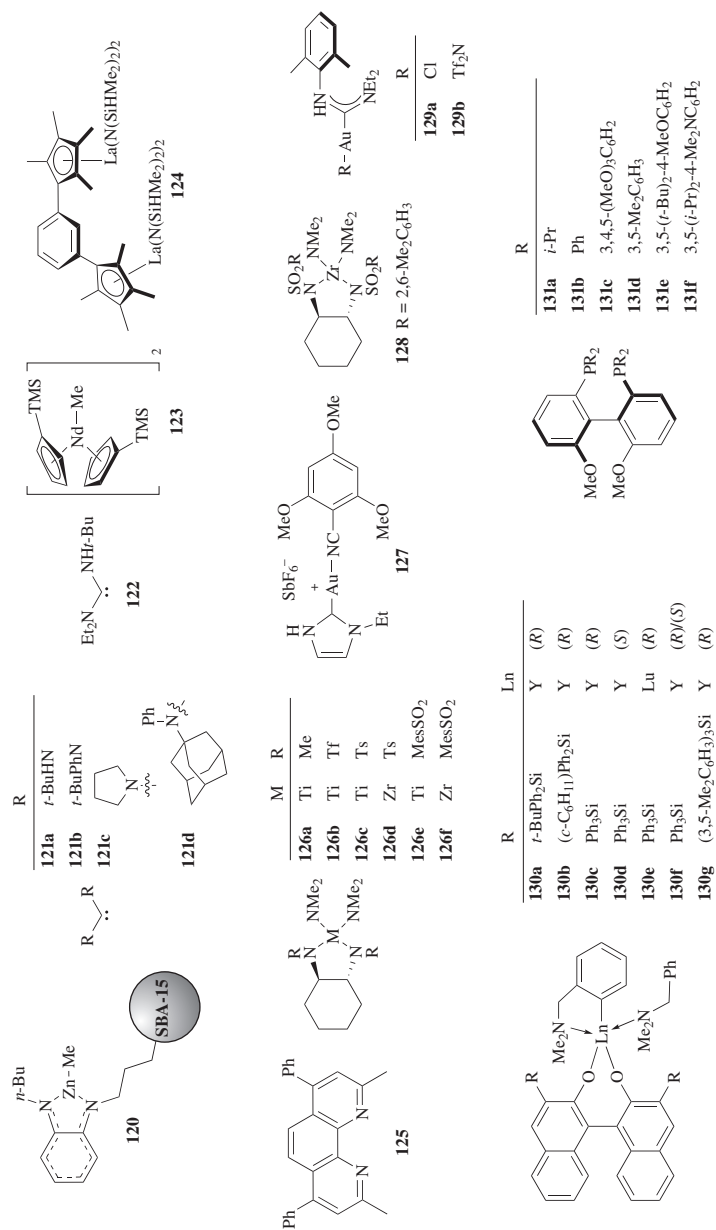
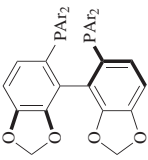
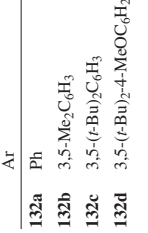
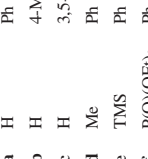
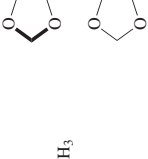
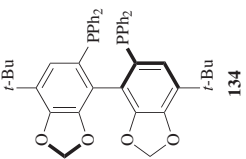
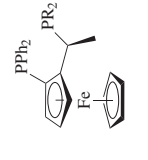
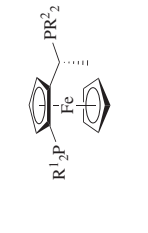
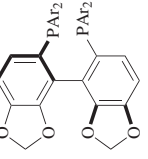
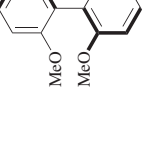
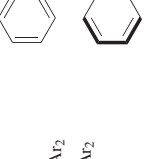
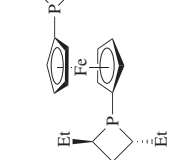
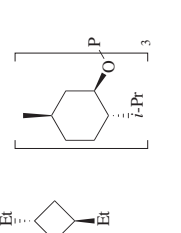
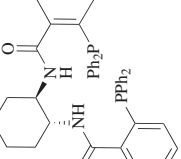
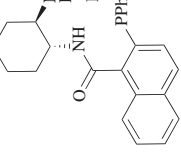
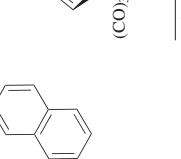


CHART 1. CATALYSTS AND LIGANDS USED IN THE TABLES (Continued)

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	132a	Ph
	132b	3,5-Me ₂ C ₆ H ₃
	132c	3,5-(<i>t</i> -Bu) ₂ C ₆ H ₃
	Ar	
	132d	3,5-(<i>t</i> -Bu) ₂ -4-MeOC ₆ H ₂
	R	
	133a	H
	133b	4-MeC ₆ H ₄
	133c	3,5-Me ₂ C ₆ H ₃
	Ar	
	133d	Ph
	133e	TMS
	133f	P(O)(OEt) ₂
	R	
	133g	Ph
	R	
	139a	HO
	139b	(<i>c</i> -C ₆ H ₁₁) ₂ P
	139c	Ph
	R	
	140a	<i>t</i> -Bu
	140b	<i>c</i> -C ₆ H ₁₁
	140c	Ph
	R ¹ R ²	
	140e	Ph Cy
	140f	Ph <i>t</i> -Bu
	140g	Cy Cy
	Ar	
	141a	Ph
	141b	3,5-Me ₂ C ₆ H ₃
	141c	3,5-(<i>t</i> -Bu) ₂ -4-MeOC ₆ H ₂
	Ar	
	142a	Ph
	142b	3,4,5-(MeO) ₃ C ₆ H ₂
	142c	3,5-Me ₂ C ₆ H ₃
	Ar	
	142d	3,5-(<i>t</i> -Bu) ₂ -4-MeOC ₆ H ₂
	R	
	135a	HO
	135b	(<i>c</i> -C ₆ H ₁₁) ₂ P
	135c	Ph
	Ar	
	136a	Ph
	136b	3,5-Me ₂ C ₆ H ₃
	136c	3,5-(<i>t</i> -Bu) ₂ -4-MeOC ₆ H ₂
	Ar	
	137a	Ph
	137b	3,5-Me ₂ C ₆ H ₃
	137c	3,5-(<i>t</i> -Bu) ₂ -4-MeOC ₆ H ₂
	Ar	
	138a	Ph
	138b	3,5-Me ₂ C ₆ H ₃
	138c	3,5-(<i>t</i> -Bu) ₂ -4-MeOC ₆ H ₂
	Ar	
	139a	Ph
	139b	3,5-Me ₂ C ₆ H ₃
	139c	3,5-(<i>t</i> -Bu) ₂ -4-MeOC ₆ H ₂

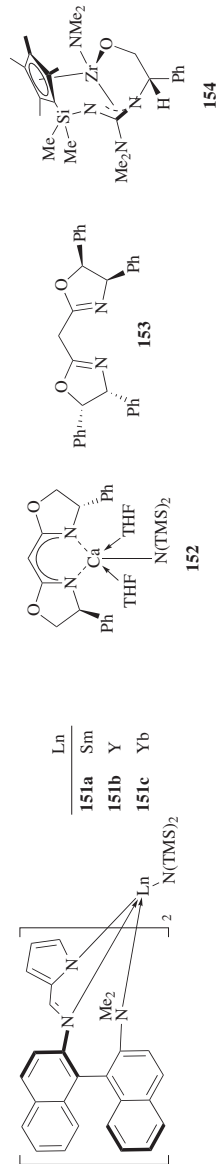
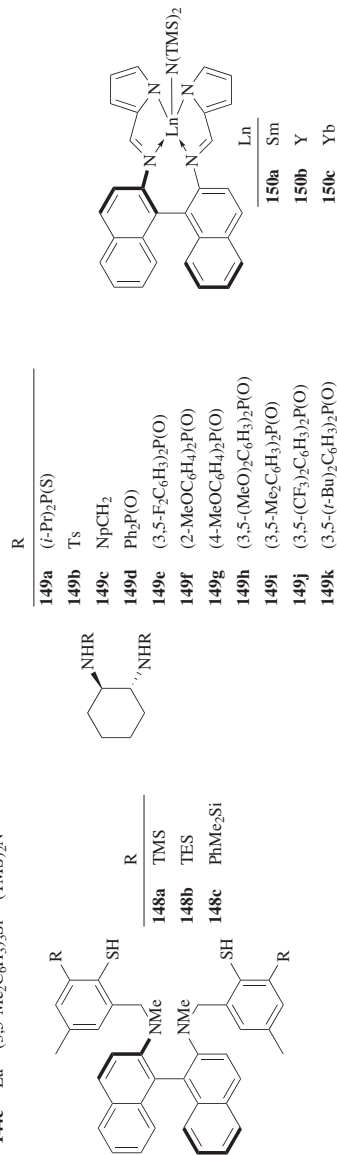
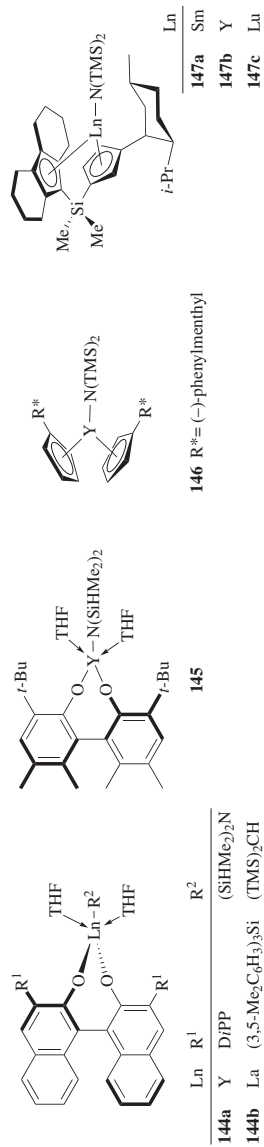
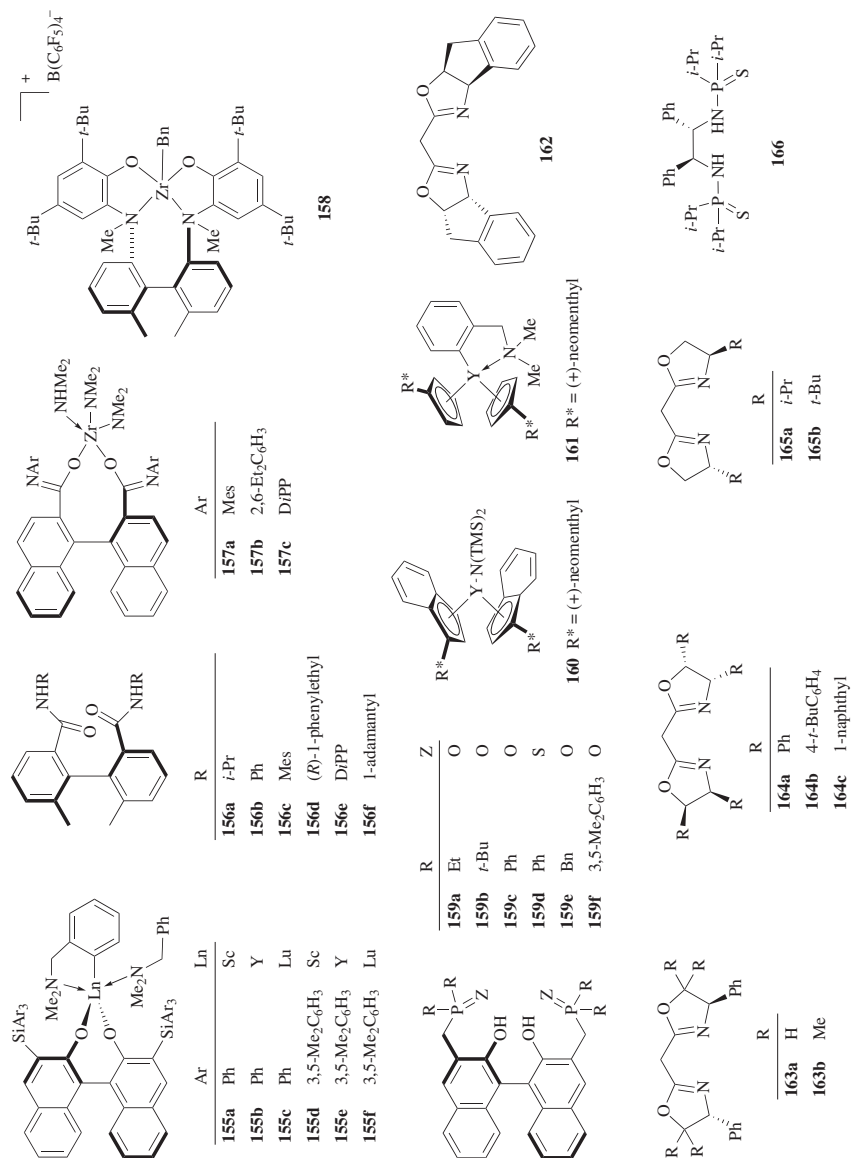


CHART 1. CATALYSTS AND LIGANDS USED IN THE TABLES (Continued)



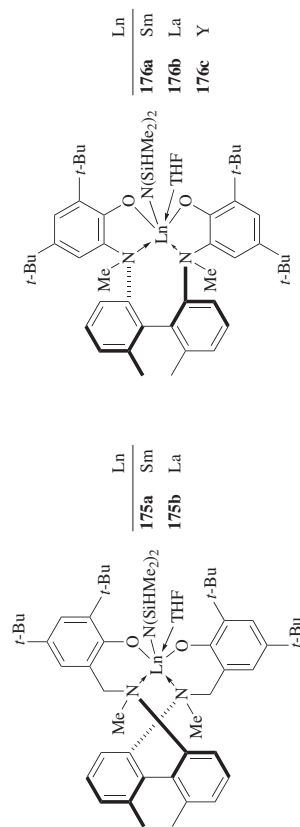
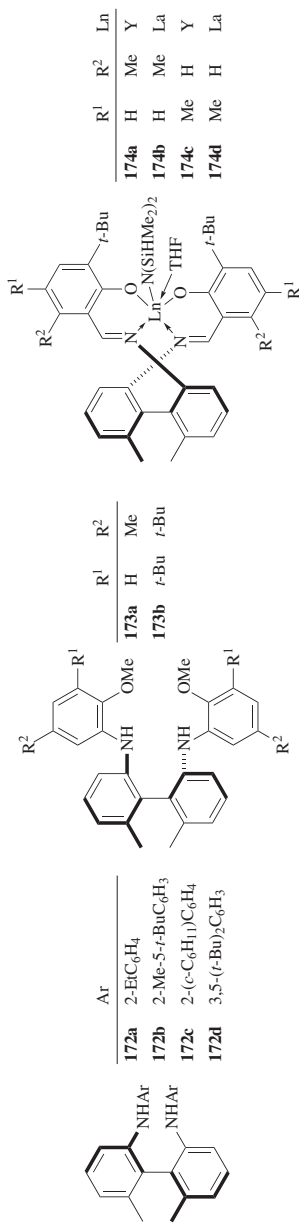
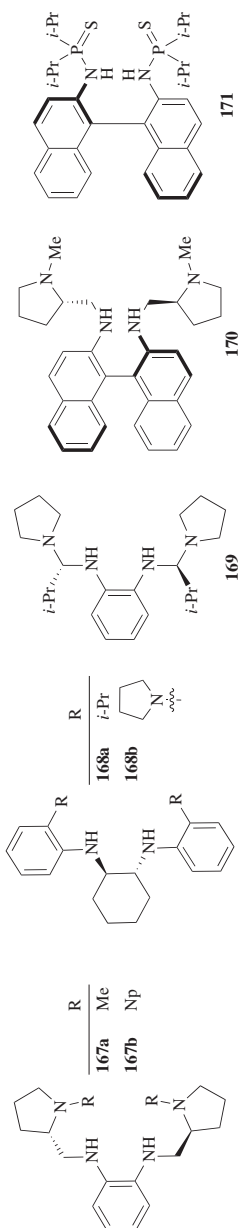
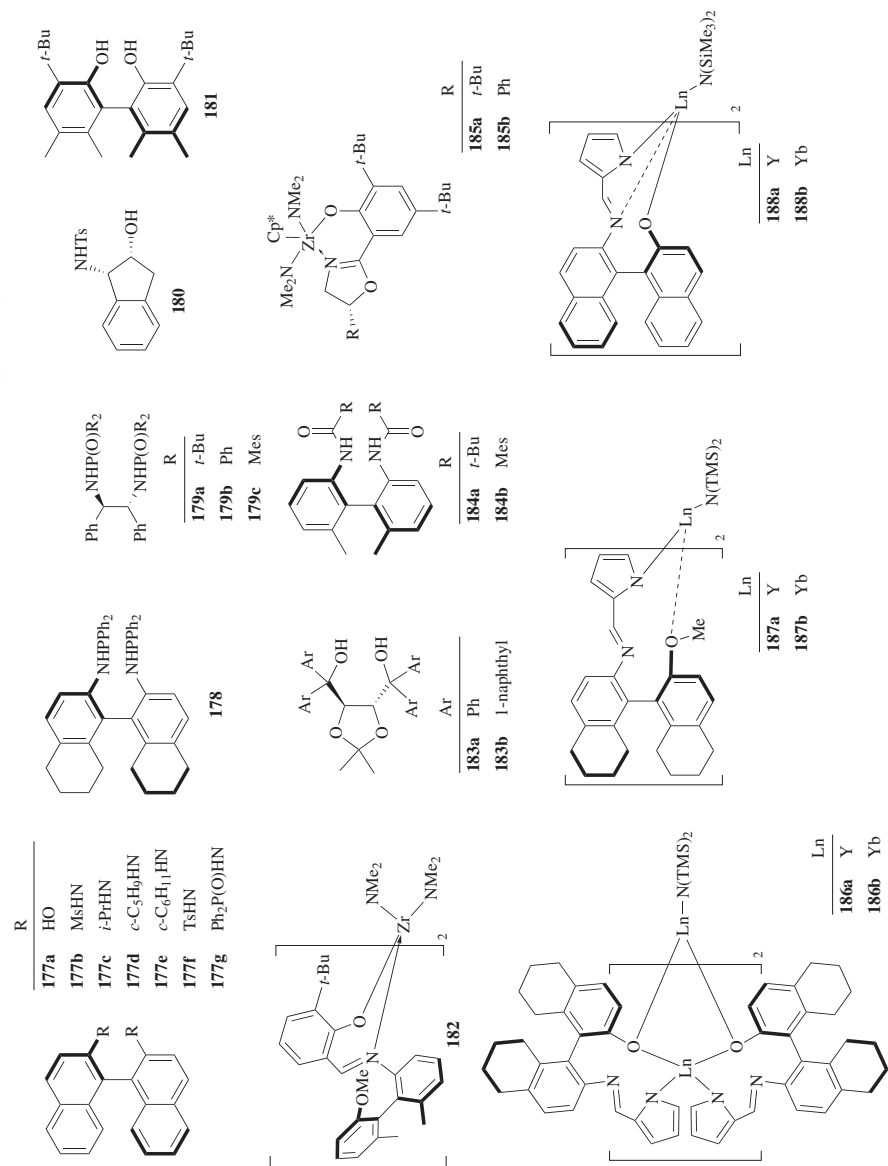


CHART 1. CATALYSTS AND LIGANDS USED IN THE TABLES (Continued)



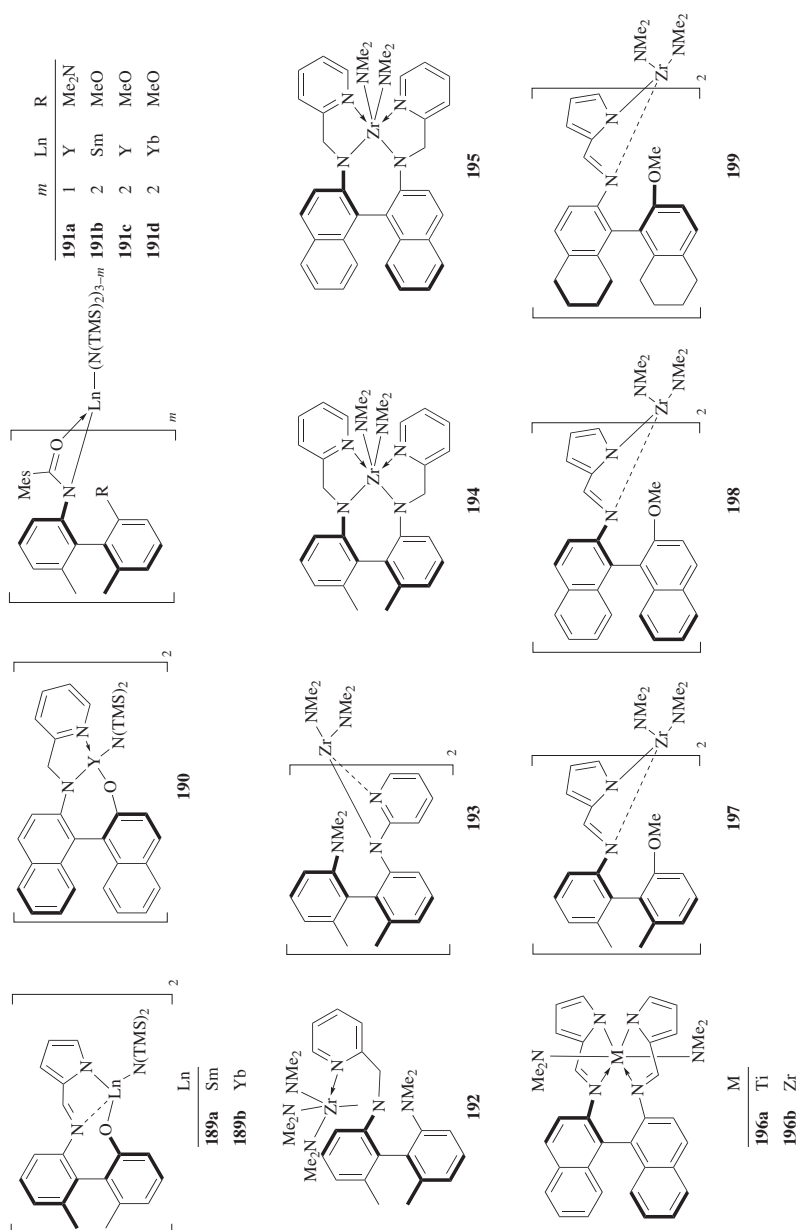
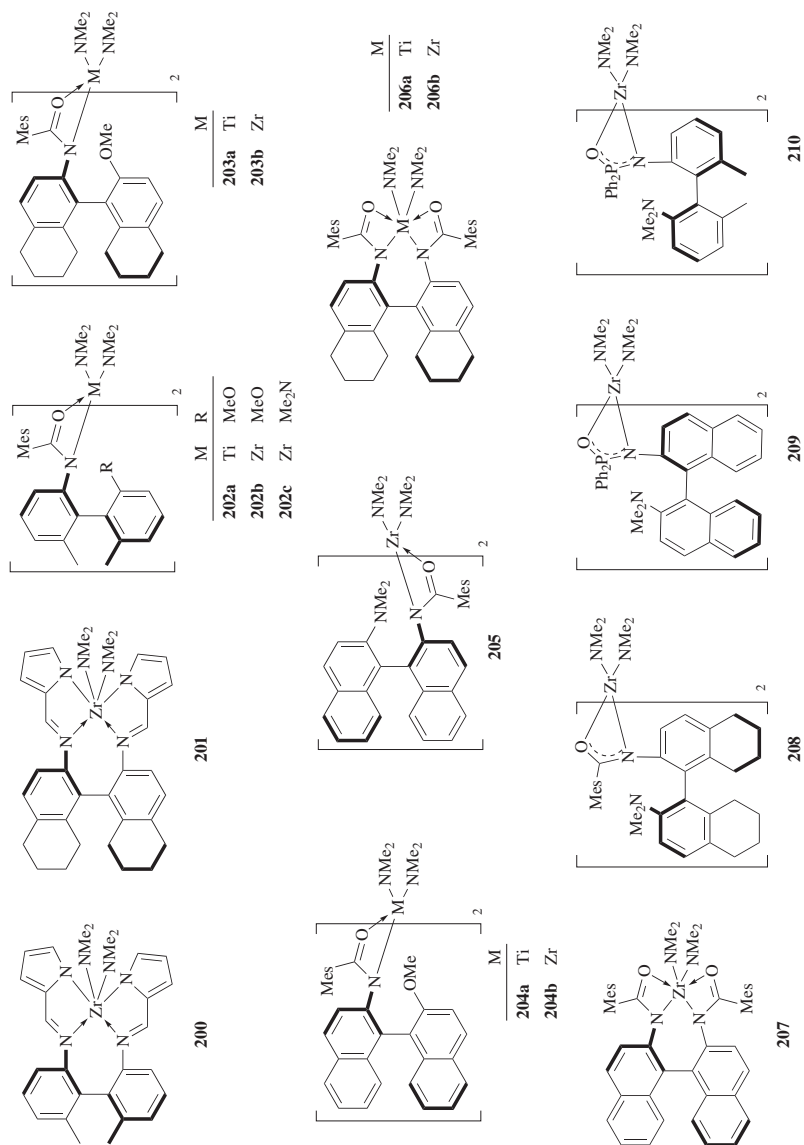


CHART 1. CATALYSTS AND LIGANDS USED IN THE TABLES (Continued)



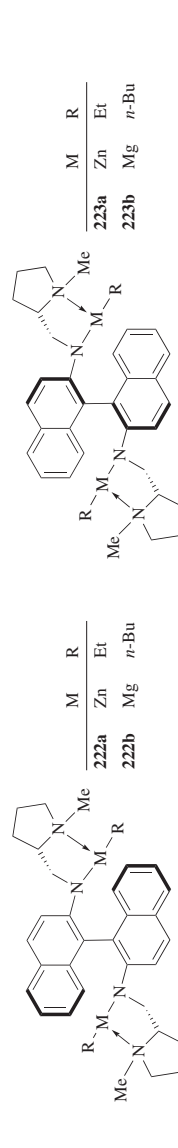
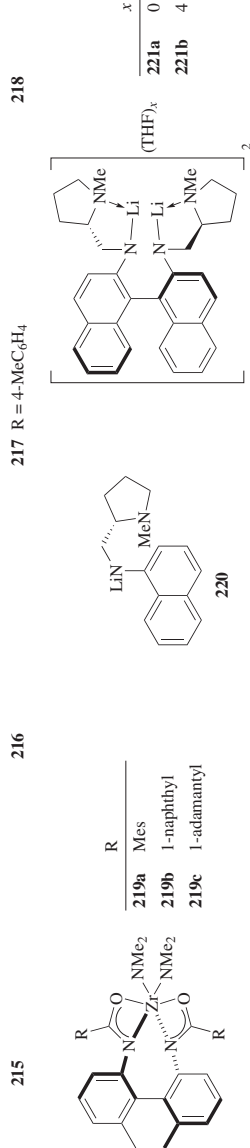
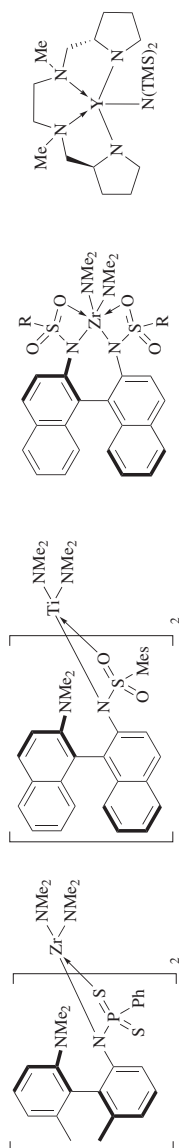
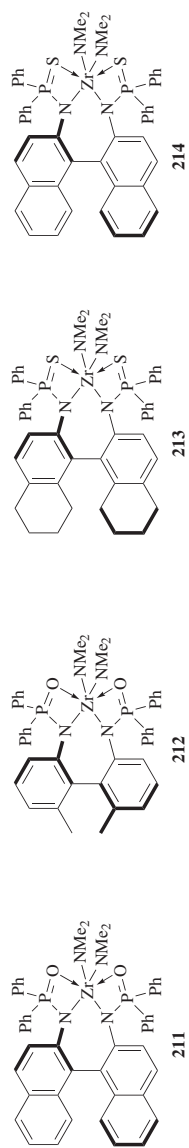
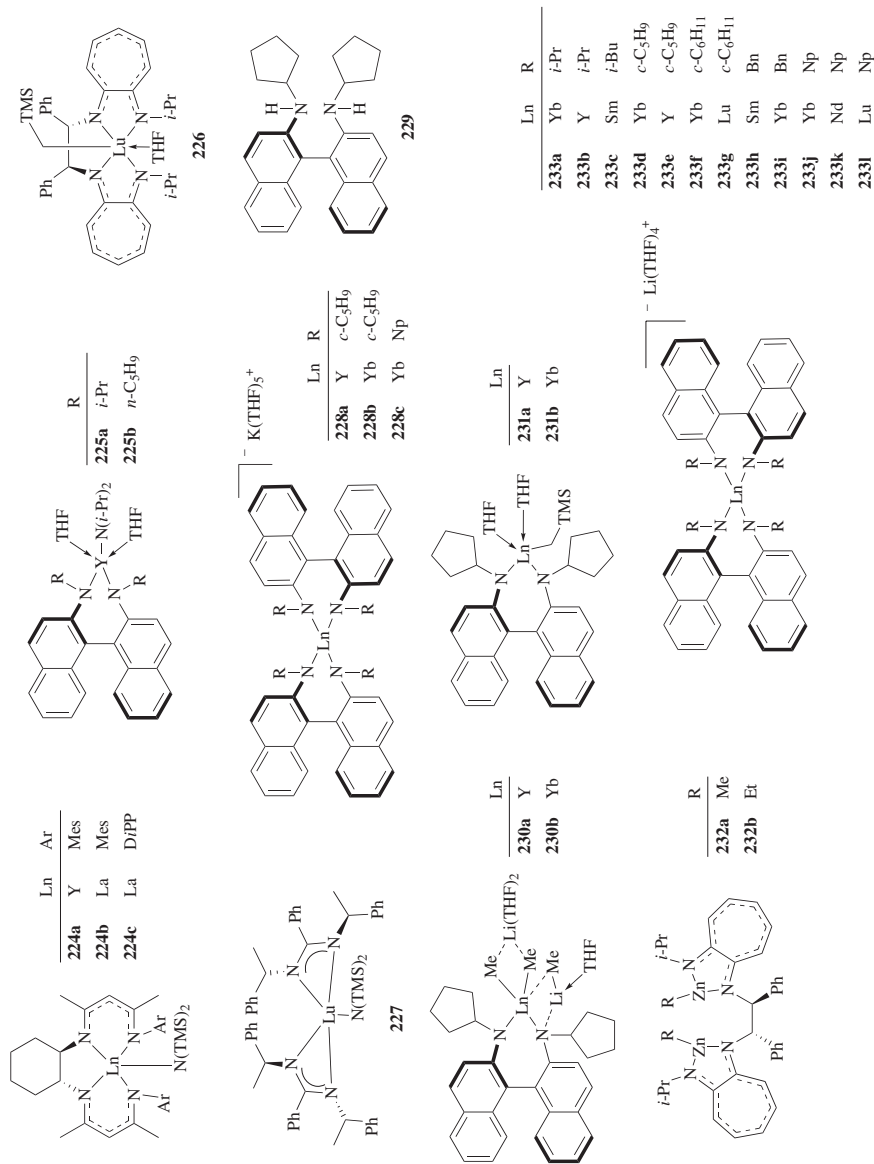


CHART 1. CATALYSTS AND LIGANDS USED IN THE TABLES (Continued)



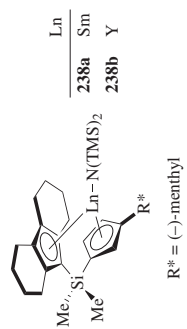
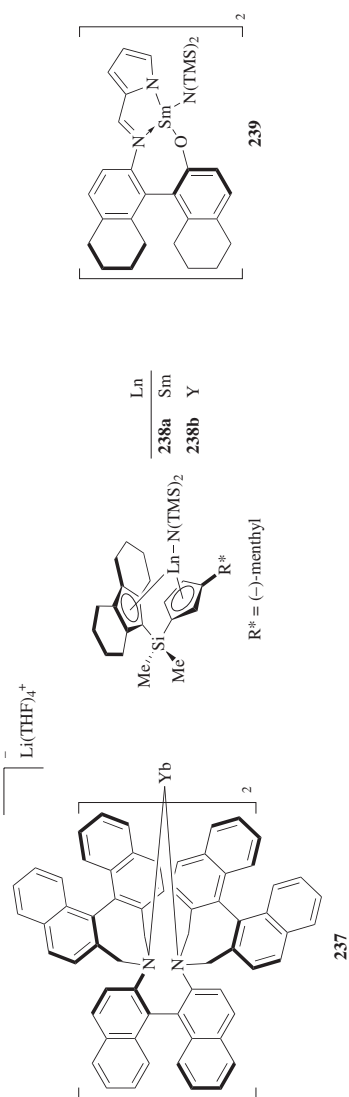
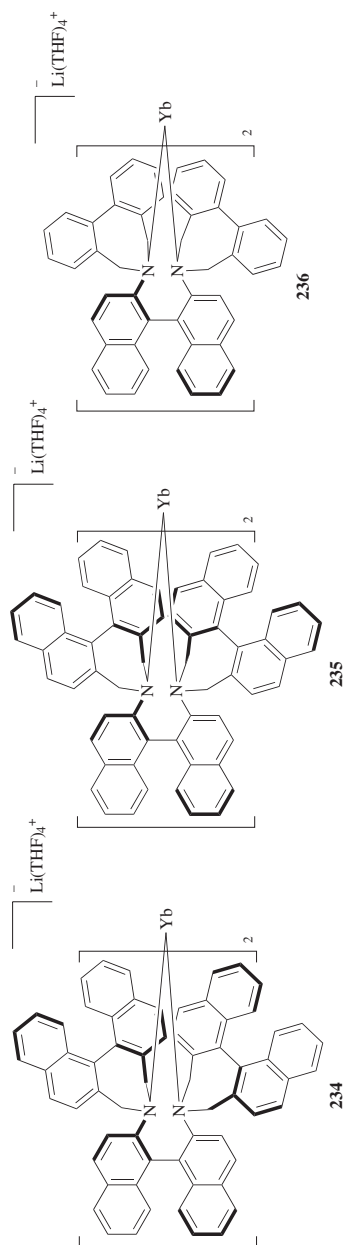


CHART 1. CATALYSTS AND LIGANDS USED IN THE TABLES (Continued)

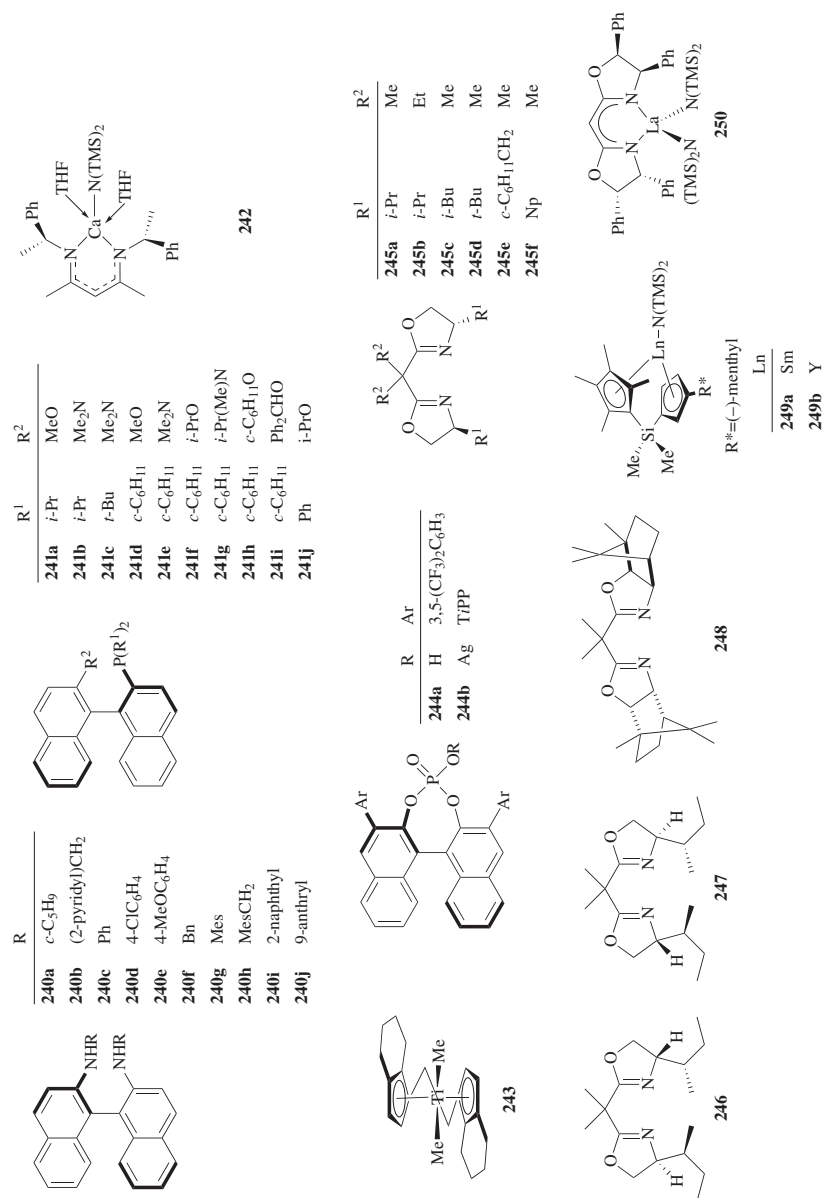


TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (Footnotes *a-h* may be found on p.163)

Alkene	Amine	Conditions		Product(s) and Yield(s) (%)				Refs.								
		Zeolite catalyst, 50 bar		EtNH ₂ I + Et ₂ NH II		x Catalyst Temp (°) I II										
C ₂ H ₂ C=CH ₂	NH ₃ (x eq)	x	Catalyst	Temp (°)	I	II	x	Catalyst	Temp (°)	I	II					
		3.6	H-chabazite/H-erionite	380	(11.2)	(1.1)	4.4	clinoptilolite	370	(12.8)	(0.9)	2.7	H-erionite	370	(8.9)	(1.3)
		3.7	H-chabazite/H-erionite	370	(9.9)	(0.6)	4.4	clinoptilolite	380	(13.6)	(1.2)	3.0	H-erionite	360	(7.8)	(0.9)
		4.0	H-chabazite/H-erionite	340	(4.1)	(—)	4.4	clinoptilolite	390	(14.3)	(1.4)	3.2	H-erionite	380	(11.8)	(1.6)
		4.0	H-chabazite/H-erionite	360	(7.9)	(—)	4.5	clinoptilolite	340	(4.4)	(—)	3.4	H-erionite	360	(8.3)	(1.0)
		4.0	H-chabazite/H-erionite	370	(10.4)	(0.7)	4.6	clinoptilolite	360	(11.4)	(—)	3.5	H-erionite	380	(10.6)	(1.7)
		4.1	H-chabazite/H-erionite	335	(1.9)	(—)	4.6	clinoptilolite	370	(13.6)	(1.3)	3.8	H-erionite	320	(1.5)	(0.06)
		4.1	H-chabazite/H-erionite	350	(4.7)	(—)	4.7	clinoptilolite	380	(13.2)	(1.2)	3.9	H-erionite	400	(14.3)	(2.2)
		4.1	H-chabazite/H-erionite	368	(7.0)	(—)	4.7	clinoptilolite	400	(16.3)	(1.7)	4.0	H-erionite	380	(13.3)	(1.9)
		4.1	H-chabazite/H-erionite	370	(7.1)	(0.07)	4.9	clinoptilolite	340	(6.6)	(—)	4.1	H-erionite	380	(11.8)	(1.7)
		4.1	H-chabazite/H-erionite	385	(6.9)	(1.14)	3.8	SK-500	335	(2.9)	(—)	4.3	H-erionite	320	(2.7)	(0.1)
		4.0	H-chabazite/H-erionite macroporous	350	(5.3)	(—)	3.8	SK-500	360	(8.5)	(—)	4.5	H-erionite	360	(6.9)	(0.5)
		4.2	H-chabazite/H-erionite macroporous	320	(1.9)	(—)	3.8	SK-500	400	(12.7)	(0.3)	4.7	H-erionite	340	(3.4)	(0.1)
		4.2	H-chabazite/H-erionite macroporous	370	(10.0)	(0.5)	4.0	SK-500	320	(—)	(—)	4.7	H-erionite	380	(11.6)	(1.3)
		4.3	H-chabazite/H-erionite macroporous	380	(10.7)	(0.6)	4.0	SK-500	335	(2.5)	(—)	5.2	H-erionite	380	(9.0)	(0.9)
		4.4	H-chabazite/H-erionite macroporous	390	(12.1)	(0.5)	4.0	SK-500	390	(12.2)	(0.6)	5.5	H-erionite	380	(11.9)	(1.1)
					4.1	SK-500	370	(11.1)	(7.3)	5.6	H-erionite	380	(13.2)	(1.2)		
					4.2	SK-500	380	(11.4)	(0.7)	5.7	H-erionite	400	(14.2)	(1.3)		
					4.3	SK-500	355	(3.4)	(—)	5.8	H-erionite	390	(13.8)	(1.3)		
					4.3	SK-500	360	(7.5)	(—)	5.8	H-erionite	390	(14.9)	(1.4)		
					4.3	SK-500	370	(9.0)	(0.4)	5.8	H-erionite	400	(16.5)	(1.4)		
					4.6	SK-500	350	(3.9)	(—)	8.0	H-erionite	375	(13.9)	(1.6)		

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

NH₃ (4 eq) Solid catalyst, 24 h EtNH₂ I + Et₂NH II 98

Catalyst	Temp (°)	I + II	I/II
—	370	(tr)	(—)
H-Y zeolite	370	(9)	87:13
H-mordenite	370	(6)	91:9
H-offretite	360	(12)	94:6
H-clinoptilolite	370	(14)	93:7
H-erionite	370	(11)	87:13
H-chabazite/H-erionite	370	(11)	94:6
Na-Y zeolite	370	(tr)	100:0
Na-offretite	370	(tr)	100:0
SiO ₂ /Al ₂ O ₃	370	(tr)	100:0

NH₃ (2 eq) Solid catalyst, 365°, 24 h EtNH₂ I + Et₂NH II 99

Catalyst	I + II	I/II
H-Y zeolite	(12)	81:19
H-erionite	(18)	97:3

NH₃ (2 eq) Solid zeolite catalyst, 290–305 bar EtNH₂ Catalyst Temp (°)

borosilicate pentasil	350	(4.6)
borosilicate pentasil	370	(6.9)
Na borosilicate pentasil	370	(6.6)
aluminosilicate pentasil	350	(3.0)
aluminosilicate pentasil	380	(6.1)
Zn-aluminosilicate pentasil	350	(4.6)

TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (Continued)

Alkene	Amine	Conditions		Product(s) and Yield(s) (%)			Refs.
		Solid catalyst, flow reactor		EtNH ₂	I + Et ₂ NH	II	
C ₂ H ₂ C=CH ₂	x	Catalyst	P (bar)	Temp (°)	I	II	
	2.3	SK-500	210	386	(10.4)	(—)	
	2.4	SK-500	210	403	(14.0)	(—)	
	3.9	H-mordenite	50	340	(3.5)	(0.07)	
	3.9	H-mordenite	50	350	(4.6)	(0.14)	
	3.9	H-mordenite	50	360	(7.3)	(0.23)	
	3.9	H-mordenite	50	370	(8.6)	(0.79)	
	3.9	H-mordenite	50	380	(11.2)	(1.3)	
	3.9	H-mordenite	50	390	(12.0)	(1.5)	
	3.9	H-mordenite	50	400	(12.3)	(—)	
	4	La zeolite Y	50	350	(3.9)	(—)	
	4	La zeolite Y	50	380	(8.6)	(0.55)	
	4	La zeolite Y	50	390	(9.7)	(0.79)	
	4	Na zeolite Y	50	350	(0.5)	(—)	
	4	Na zeolite Y	50	380	(1.3)	(—)	
	4	Na zeolite Y	50	400	(1.5)	(—)	
	4	NH ₄ zeolite Y	50	380	(7.8)	(0.62)	
	4	NH ₄ zeolite Y	50	385	(8.1)	(0.65)	
	4	NH ₄ zeolite Y	50	390	(8.3)	(—)	
	4	Zn zeolite Y	50	350	(0.2)	(—)	
	4	Cu zeolite Y	50	350	(2.1)	(—)	
	4	Cu zeolite Y	50	360	(2.7)	(—)	
	4	Cu zeolite Y	50	370	(3.6)	(—)	
	4	La zeolite Y	50	350	(1.0)	(—)	
	4	La zeolite Y	50	380	(3.0)	(—)	
	4	La zeolite Y	50	400	(5.3)	(0.14)	
	4	La zeolite Y	50	420	(7.4)	(0.37)	

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

H ₂ C=CH ₂ 1000 bar	NH ₃	Na (21 mol %), heptane, 200°, 9 h	EtNH ₂ I + Et ₂ NH II + Et ₃ N III I-III (42), I/II/III = 38:36:26	107																																																																																																			
	NH ₃	K (5 mol %), 200°, 9 h	Et ₂ NH I + Et ₃ N II I + II (13), I/II = 53:47	107																																																																																																			
H ₂ C=CH ₂ 980 bar	NH ₃	Li (24 mol %), 250°, 14.5 h	EtNH ₂ I + Et ₂ NH II + Et ₃ N III I-III (53), I/II/III = 9:30:61	106																																																																																																			
	NH ₃	MH (x mol %), 200°	EtNH ₂ I + Et ₂ NH II + Et ₃ N III <table><tr><th>M</th><th>x</th><th>Time (h)</th><th>I + II + III</th><th>I/II/III</th></tr><tr><td>Li</td><td>33</td><td>14</td><td>(21)</td><td>69:24:7</td></tr><tr><td>Na</td><td>5</td><td>15</td><td>(41)</td><td>71:22:7</td></tr></table>	M	x	Time (h)	I + II + III	I/II/III	Li	33	14	(21)	69:24:7	Na	5	15	(41)	71:22:7	106, 107																																																																																				
M	x	Time (h)	I + II + III	I/II/III																																																																																																			
Li	33	14	(21)	69:24:7																																																																																																			
Na	5	15	(41)	71:22:7																																																																																																			
H ₂ C=CH ₂ 1000 bar	NH ₃ (1.8 eq)	M ¹ NH ₂ (x mol %), M ² NH ₂ (y mol %)	EtNH ₂ I + Et ₂ NH II + Et ₃ N III <table><tr><th>M¹</th><th>x</th><th>M²</th><th>y</th><th>Temp (°)</th><th>Time (h)</th><th>I</th><th>II</th><th>III</th></tr><tr><td>Cs</td><td>8</td><td>—</td><td>—</td><td>101</td><td>1</td><td>(24)</td><td>(4.5)</td><td>(4.5)</td></tr><tr><td>Cs</td><td>5</td><td>—</td><td>—</td><td>101</td><td>1.5</td><td>(21)</td><td>(4.5)</td><td>(2.2)</td></tr><tr><td>Rb</td><td>7</td><td>—</td><td>—</td><td>101</td><td>3</td><td>(26)</td><td>(4.5)</td><td>(1.6)</td></tr><tr><td>Cs</td><td>4</td><td>K</td><td>3</td><td>101</td><td>1</td><td>(16)</td><td>(3.0)</td><td>(2.2)</td></tr><tr><td>Cs</td><td>4</td><td>K</td><td>3</td><td>101</td><td>3</td><td>(24)</td><td>(4.5)</td><td>(4.5)</td></tr><tr><td>Cs</td><td>4</td><td>K</td><td>3</td><td>101</td><td>6</td><td>(45)</td><td>(14)</td><td>(9.0)</td></tr><tr><td>Na</td><td>14</td><td>—</td><td>—</td><td>101</td><td>16.5</td><td>(1.5)</td><td>(—)</td><td>(—)</td></tr><tr><td>K</td><td>7</td><td>—</td><td>—</td><td>101</td><td>20.5</td><td>(1.2)</td><td>(0.2)</td><td>(—)</td></tr><tr><td>K</td><td>8</td><td>Na</td><td>17</td><td>101</td><td>19</td><td>(20)</td><td>(1.5)</td><td>(—)</td></tr><tr><td>Cs</td><td>2</td><td>—</td><td>—</td><td>111</td><td>1</td><td>(13)</td><td>(1.5)</td><td>(1.6)</td></tr></table>	M ¹	x	M ²	y	Temp (°)	Time (h)	I	II	III	Cs	8	—	—	101	1	(24)	(4.5)	(4.5)	Cs	5	—	—	101	1.5	(21)	(4.5)	(2.2)	Rb	7	—	—	101	3	(26)	(4.5)	(1.6)	Cs	4	K	3	101	1	(16)	(3.0)	(2.2)	Cs	4	K	3	101	3	(24)	(4.5)	(4.5)	Cs	4	K	3	101	6	(45)	(14)	(9.0)	Na	14	—	—	101	16.5	(1.5)	(—)	(—)	K	7	—	—	101	20.5	(1.2)	(0.2)	(—)	K	8	Na	17	101	19	(20)	(1.5)	(—)	Cs	2	—	—	111	1	(13)	(1.5)	(1.6)	109, 110
		M ¹	x	M ²	y	Temp (°)	Time (h)	I	II	III																																																																																													
Cs	8	—	—	101	1	(24)	(4.5)	(4.5)																																																																																															
Cs	5	—	—	101	1.5	(21)	(4.5)	(2.2)																																																																																															
Rb	7	—	—	101	3	(26)	(4.5)	(1.6)																																																																																															
Cs	4	K	3	101	1	(16)	(3.0)	(2.2)																																																																																															
Cs	4	K	3	101	3	(24)	(4.5)	(4.5)																																																																																															
Cs	4	K	3	101	6	(45)	(14)	(9.0)																																																																																															
Na	14	—	—	101	16.5	(1.5)	(—)	(—)																																																																																															
K	7	—	—	101	20.5	(1.2)	(0.2)	(—)																																																																																															
K	8	Na	17	101	19	(20)	(1.5)	(—)																																																																																															
Cs	2	—	—	111	1	(13)	(1.5)	(1.6)																																																																																															

TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (Continued)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																																																								
Please refer to the charts preceding the tables for structures indicated by the bold numbers.																																																												
C ₂ H ₂ C=CH ₂	NH ₃ (7 eq)	NH ₄ Cl/C, 350°, 7 h, flow reactor	EtNH ₂ (7.7)	408																																																								
	NH ₃ (12 eq)	NH ₄ Cl, 350°, 7 h, flow reactor	EtNH ₂ (40)	408																																																								
	NH ₃	NH ₄ Cl (1 mol %), UV (Hg), 8°, 4 h	EtNH ₂ (1)	409																																																								
	NH ₃	NH ₄ I (1 mol %), UV (Hg), 8°, 4 h	EtNH ₂ I + Et ₂ NH II I + II (9), <i>III</i> = 89:11	410																																																								
H ₂ C=CH ₂ 18 bar	NH ₃	NH ₄ Br (0.4 mol %), UV (Hg), 8°, 4 h	EtNH ₂ (9)	410																																																								
	NH ₃ (3 eq)	NH ₄ I (1.2 mol %), UV (Hg), 8°, 4 h	EtNH ₂ (6)	410																																																								
	NH ₃ (2 eq)	NH ₄ X (x mol %), solvent, 5 h	EtNH ₂ I + Et ₂ NH II + Et ₃ N III + EtOH IV	408																																																								
<table><tr><th>X</th><th>x</th><th>Solvent</th><th>Temp (°)</th><th>I</th><th>II</th><th>III</th><th>IV</th></tr><tr><td>I</td><td>24</td><td>neat</td><td>370</td><td>(9.3)</td><td>(0.2)</td><td>(tr)</td><td>(—)</td></tr><tr><td>I</td><td>37</td><td>neat</td><td>380</td><td>(4)</td><td>(tr)</td><td>(—)</td><td>(—)</td></tr><tr><td>I</td><td>106</td><td>H₂O</td><td>330</td><td>(2.9)</td><td>(5.7)</td><td>(0.1)</td><td>(4.5)</td></tr><tr><td>Cl</td><td>10</td><td>neat</td><td>350</td><td>(1.6)</td><td>(tr)</td><td>(—)</td><td>(—)</td></tr><tr><td>Br</td><td>13</td><td>neat</td><td>350</td><td>(0.46)</td><td>(—)</td><td>(—)</td><td>(—)</td></tr><tr><td>F</td><td>10</td><td>neat</td><td>350</td><td>(tr)</td><td>(—)</td><td>(—)</td><td>(—)</td></tr></table>					X	x	Solvent	Temp (°)	I	II	III	IV	I	24	neat	370	(9.3)	(0.2)	(tr)	(—)	I	37	neat	380	(4)	(tr)	(—)	(—)	I	106	H ₂ O	330	(2.9)	(5.7)	(0.1)	(4.5)	Cl	10	neat	350	(1.6)	(tr)	(—)	(—)	Br	13	neat	350	(0.46)	(—)	(—)	(—)	F	10	neat	350	(tr)	(—)	(—)	(—)
X	x	Solvent	Temp (°)	I	II	III	IV																																																					
I	24	neat	370	(9.3)	(0.2)	(tr)	(—)																																																					
I	37	neat	380	(4)	(tr)	(—)	(—)																																																					
I	106	H ₂ O	330	(2.9)	(5.7)	(0.1)	(4.5)																																																					
Cl	10	neat	350	(1.6)	(tr)	(—)	(—)																																																					
Br	13	neat	350	(0.46)	(—)	(—)	(—)																																																					
F	10	neat	350	(tr)	(—)	(—)	(—)																																																					



	Me_2NH	NH_4Cl (60 mol %), 325°, 5 h	Me_2NEt I + MeNEt_2 II	I + II (17), I/II = 53:47	408																				
$\text{H}_2\text{C}=\text{CH}_2$ 14 bar	Me_2NH	$\text{RuCl}_3\cdot 3\text{H}_2\text{O}$ (1 mol %), THF, 150–190°, 7 h	Me_2NEt I + MeNEt_2 II	I + II (34), I/II = 6:94	113, 114																				
	Me_2NH	Cp_2Ru (1 mol %), THF, 150–190°, 7 h	Me_2NEt (1)		113, 114																				
	Me_2NH	$[\text{Ru}(\text{NH}_3)_4(\text{OH})\text{Cl}]\cdot 2\text{H}_2\text{O}$ (1 mol %), THF, 150–190°, 7 h	Me_2NEt I + MeNEt_2 II	I + II (22), I/II = 5:95	113, 114																				
$\text{H}_2\text{C}=\text{CH}_2$ 10 bar	Me_2NH	NaNMe_2 (x mol %), dodecane, 50°	Me_2NEt	<table><tr><th>x</th><th>Time (min)</th></tr><tr><td>1</td><td>15 (26)</td></tr><tr><td>1</td><td>60 (68)</td></tr><tr><td>1</td><td>240 (99)</td></tr><tr><td>0.24</td><td>15 (9)</td></tr><tr><td>0.24</td><td>60 (36)</td></tr><tr><td>0.24</td><td>360 (97)</td></tr><tr><td>0.12</td><td>15 (8)</td></tr><tr><td>0.12</td><td>60 (29)</td></tr><tr><td>0.12</td><td>360 (90)</td></tr></table>	x	Time (min)	1	15 (26)	1	60 (68)	1	240 (99)	0.24	15 (9)	0.24	60 (36)	0.24	360 (97)	0.12	15 (8)	0.12	60 (29)	0.12	360 (90)	411
x	Time (min)																								
1	15 (26)																								
1	60 (68)																								
1	240 (99)																								
0.24	15 (9)																								
0.24	60 (36)																								
0.24	360 (97)																								
0.12	15 (8)																								
0.12	60 (29)																								
0.12	360 (90)																								
$\text{H}_2\text{C}=\text{CH}_2$ 1000 bar	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$	Na (27 mol %), 200°, 10 h	$\text{EtHN}-\text{CH}_2-\text{CH}_2-\text{NHEt}$ I + $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NEt}_2$ II	II	107, 106																				
			+ $\text{EtHN}-\text{CH}_2-\text{CH}_2-\text{NEt}_2$ III + $\text{Et}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NEt}_2$ IV	IV																					

I–IV (84), **I/II/III/IV** = 15:23:32:30

I–IV (84), **I/II/III/IV** = 15:23:32:30



TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (Continued)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>				
C ₂	H ₂ C=CH ₂	R ₂ NH (3.5 eq) RhCl ₃ •3H ₂ O (1 mol %), THF, 200°, 3 h	R ₂ NEt R Me (54) Et (4)	117
	H ₂ C=CH ₂ 3.5 bar	[PtCl ₂ (C ₂ H ₄) ₂] (2.5 mol %), PPh ₃ (5 mol %), dioxane, 120°, 36 h	 (90)	122
	H ₂ C=CH ₂ 1000 bar	RNH ₂	RNEt ₂ R n-Bu (43) s-Bu (18)	107
	H ₂ C=CH ₂	n-BuNH ₂ (6 eq) Acetone (0.6 eq), UV (Hg lamp), 8°, 4 h	n-BuNHEt (12)	409
	H ₂ C=CH ₂	n-BuNH ₂ Fe(CO) ₅ (5 mol %), P(OEt) ₃ (5 mol %), UV (Hg lamp), 35°, 4 h	n-BuNHEt (15.5)	409
C ₃	H ₂ C=CH ₂ 200 bar	n-BuNH ₂	n-BuNHEt I + II	331
		LiEt (4 mol %), TMEDA (17 mol %)	Time (h) I II 3.5 (28) (6) 37 (53) (44) 60 (52) (19)	



H ₂ C=CH ₂ 50 bar	Et ₂ NH	Catalyst (x mol %)	Et ₃ N	Catalyst	x	Temp (°)	Time (h)	112			
				NaH	12	120	3	(7)			
				NaH	12	120	6	(19)			
				NaH	12	120	9	(36)			
				NaH	12	120	13	(50)			
				KH	7	100	1	(1)			
				KH	7	100	3	(12)			
				KH	7	100	6	(38)			
				KH	7	100	9	(55)			
				H ₂ C=CH ₂ 40 bar	Et ₂ NH	NaNEt ₂ (x mol %), dodecane	Et ₃ N	x	Temp (°)	Time (min)	411
								1	70	15	(5)
1	70	60	(18)								
1	70	360	(54)								
				0.5	70	15	(3)				
				0.5	70	60	(13)				
				0.5	70	360	(42)				
				1	90	10	(8)				
				1	90	60	(28)				
				1	90	120	(31)				
				0.5	90	15	(8)				
				0.5	90	60	(18)				
				0.5	90	120	(22)				
				H ₂ C=CH ₂ 70 atm	Et ₂ NH	LiEt (6 mol %), TMEDA (27 mol %), 140°, 15 h	Et ₃ N	(83)			331
H ₂ C=CH ₂ 1000 bar	Et ₂ NH	Na (32 mol %), 225°, 16 h	Et ₃ N					(22)			107



TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (*Continued*)

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)						Refs.		
C ₂	H ₂ C=CH ₂ 21 bar	Et ₃ NH Fe(CO) ₅ (4 mol %), PPh ₃ (2 mol %), 130–150°, 7 h	Et ₃ N	I	+	EtNH ₂	II	I + II (47), I/II = 91:9	113, 114		
	H ₂ C=CH ₂ 14 bar	Et ₃ NH Fe(CO) ₅ (4 mol %), dioxane, 150–190°, 7 h	Et ₃ N	(13)						113, 114	
x atm	H ₂ C=CH ₂	Et ₃ NH MNEt ₂ (y mol %), TMEDA (z eq)	Et ₃ N	x M y z Temp (°) Time (h)							
				50	Li	1	0	120	—	(60)	412
				11	Li	4	0.5	80	18	(100)	413
x bar	H ₂ C=CH ₂	Et ₃ NH LiNEt ₂ (y mol %), TMEDA (z mol %), Solvent	Et ₃ N	x y z Solvent Temp (°) Time (h)							
				11	2.5	10	C ₇ H ₈	80	18	(33)	111
				20	2.5	5	C ₇ H ₈	110	12	(69)	
				20	2.5	10	C ₇ H ₈	80	10	(33)	
				20	2.5	10	C ₇ H ₈	80	18	(38)	
				20	3	0	C ₇ H ₈	80	18	(15)	
				20	3	10	C ₇ H ₈	80	18	(74)	
				20	5	10	C ₇ H ₈	80	18	(96)	
				20	8	28	neat	80	18	(84)	
				20	9	0	C ₇ H ₈	80	18	(22)	
				20	9	46	THF	80	18	(46)	
				20	9	46	C ₇ H ₈	80	18	(97)	
				20	9	46	cyclohexane	80	18	(95)	
				20	9	46	MTBE	80	18	(14)	
					40	2.5	5	C ₇ H ₈	rt	24	(3)
	40	2.5	5	C ₇ H ₈	40	12	(8)				
	40	2.5	5	C ₇ H ₈	80	12	(92)				
	40	2.5	5	C ₇ H ₈	80	18	(93)				
	60	2.5	5	C ₇ H ₈	80	12	(99)				

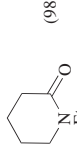
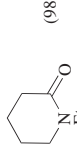
$\text{H}_2\text{C}=\text{CH}_2$ 40 bar	Et_3NH	LiNEt_2 (2.5 mol %), ligand (5 mol %), toluene, 80°, 12 h	Et_3N	111
Ligand	Ligand		Ligand	
—	(7)	—		(14)
DME	(—)	—		(90)
TMEDA	(92)	—		(tr)
$\text{Me}_2\text{NCH}_2\text{OH}$	(14)	—		(—)
$\text{Et}_2\text{N}(\text{CH}_2)_2\text{NEt}_2$	(19)	—		(9)
$\text{Me}_2\text{N}(\text{CH}_2)_3\text{NMe}_2$	(9)	—		(17)
$\text{Me}_2\text{N}(\text{CH}_2)_4\text{NMe}_2$	(7)	—		(—)
$(\text{Me}_2\text{N})_2\text{SiMe}_2$	(13)	—		(9)
sparteine	(36)	—		(17)
DABCO	(6)	—		(—)
diglyme	(—)	—		(9)
12-crown-4	(—)	—		(17)
18-crown-6	(—)	—		(—)
	(9)	—		(—)
	(11)	—		(—)

TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (*Continued*)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>				
C ₂ H ₂ C=CH ₂ 1 bar	Et ₃ NH	[Rh(CH ₃ COCH ₃)(C ₂ H ₄)(PPh ₃)]- PF ₆ , (1 mol %), rt, 2 h	Et ₃ N (99)	119
H ₂ C=CH ₂ 14 bar	Et ₃ NH	(η ⁴ -H ₂ C=CHCH=CH ₂)Fe(CO) ₃ (5 mol %), toluene, 150–190°, 7 h	Et ₃ N (13)	113, 114
H ₂ C=CH ₂ 21 bar	Et ₃ NH	Fe(CO) ₃ (5 mol %), 150–170°, 6 h	Et ₃ N I + EtNH ₂ II I + II (28), I/II = 93:7	113, 114
H ₂ C=CH ₂	 _n (x eq)	RhCl ₃ •3H ₂ O (1 mol %), THF, 3 h	 _n n Z x Temp (°) 1 CH ₂ 3.5 200 (36) 2 CH ₂ 0.67 180 (75) 2 CH ₂ 3.5 200 (70) 2 O 3.5 200 (tr)	117
H ₂ C=CH ₂ x bar	RNH ₂	Na (y mol %), 200°, 16 h	 _n RNEt ₂ x R y 500 s-C ₃ H ₁₁ 24 (12) 1000 n-C ₃ H ₁₁ 38 (33)	107
H ₂ C=CH ₂ 50 bar		LiNC ₅ H ₁₀ (1 mol %), 120°	(90)	412
H ₂ C=CH ₂ 1 bar		[Rh(CH ₃ COCH ₃)(C ₂ H ₄)(PPh ₃)]- PF ₆ , (1 mol %), rt, 2 h	(99)	119

$\text{H}_2\text{C}=\text{CH}_2$ 50 bar		Na (3 mol %), 100°, 3 h		414																																																				
$\text{H}_2\text{C}=\text{CH}_2$ 21 bar		Fe(CO) ₅ (4 mol %), PPh ₃ (2 mol %), HgCl ₂ (4 mol %), 130–150°, 7 h		113, 114																																																				
$\text{H}_2\text{C}=\text{CH}_2$ 40 bar		Catalyst (3.3 mol %), 100°	 I +  II	115																																																				
<table><tr><th>Catalyst</th><th>Time (h)</th><th>I + II</th><th>I/II</th></tr><tr><td>(PPh₃)₃RuCl₂</td><td>24</td><td>(1.3)</td><td>98:2</td></tr><tr><td>(PPh₃)₃RuCl₂</td><td>65</td><td>(3.3)</td><td>98:2</td></tr><tr><td>[(η⁶-C₆H₆)RuCl₂]₂</td><td>65</td><td>(3.3)</td><td>23:77</td></tr><tr><td>(PMe₃)₃RuCl₂</td><td>65</td><td>(—)</td><td>—</td></tr><tr><td>(P(OPh)₃)₃RuCl₂</td><td>65</td><td>(0.1)</td><td>98:2</td></tr><tr><td>(P(OMe)₃)₃RuCl₂</td><td>65</td><td>(0.7)</td><td>98:2</td></tr><tr><td>[CpRu(PPh₃)₂(C₂H₄)]BF₄</td><td>63</td><td>(3.3)</td><td>98:2</td></tr><tr><td>[CpRu(PMe₃)₂(C₂H₄)]BF₄</td><td>63</td><td>(—)</td><td>—</td></tr><tr><td>[CpRu(DPPE)(C₂H₄)]BF₄</td><td>63</td><td>(—)</td><td>—</td></tr><tr><td>[CpRu(P(4-FC₆H₄)₂(C₂H₄))]BF₄</td><td>63</td><td>(0.3)</td><td>98:2</td></tr><tr><td>[(η⁵-C₉H₇)Ru(PPh₃)₂(C₂H₄)]BF₄</td><td>63</td><td>(2.3)</td><td>98:2</td></tr><tr><td>[(η⁶-C₆H₆)Ru(C₃H₁₁N)]Cl₂</td><td>63</td><td>(0.3)</td><td>3:97</td></tr></table>					Catalyst	Time (h)	I + II	I/II	(PPh ₃) ₃ RuCl ₂	24	(1.3)	98:2	(PPh ₃) ₃ RuCl ₂	65	(3.3)	98:2	[(η ⁶ -C ₆ H ₆)RuCl ₂] ₂	65	(3.3)	23:77	(PMe ₃) ₃ RuCl ₂	65	(—)	—	(P(OPh) ₃) ₃ RuCl ₂	65	(0.1)	98:2	(P(OMe) ₃) ₃ RuCl ₂	65	(0.7)	98:2	[CpRu(PPh ₃) ₂ (C ₂ H ₄)]BF ₄	63	(3.3)	98:2	[CpRu(PMe ₃) ₂ (C ₂ H ₄)]BF ₄	63	(—)	—	[CpRu(DPPE)(C ₂ H ₄)]BF ₄	63	(—)	—	[CpRu(P(4-FC ₆ H ₄) ₂ (C ₂ H ₄))]BF ₄	63	(0.3)	98:2	[(η ⁵ -C ₉ H ₇)Ru(PPh ₃) ₂ (C ₂ H ₄)]BF ₄	63	(2.3)	98:2	[(η ⁶ -C ₆ H ₆)Ru(C ₃ H ₁₁ N)]Cl ₂	63	(0.3)	3:97
Catalyst	Time (h)	I + II	I/II																																																					
(PPh ₃) ₃ RuCl ₂	24	(1.3)	98:2																																																					
(PPh ₃) ₃ RuCl ₂	65	(3.3)	98:2																																																					
[(η ⁶ -C ₆ H ₆)RuCl ₂] ₂	65	(3.3)	23:77																																																					
(PMe ₃) ₃ RuCl ₂	65	(—)	—																																																					
(P(OPh) ₃) ₃ RuCl ₂	65	(0.1)	98:2																																																					
(P(OMe) ₃) ₃ RuCl ₂	65	(0.7)	98:2																																																					
[CpRu(PPh ₃) ₂ (C ₂ H ₄)]BF ₄	63	(3.3)	98:2																																																					
[CpRu(PMe ₃) ₂ (C ₂ H ₄)]BF ₄	63	(—)	—																																																					
[CpRu(DPPE)(C ₂ H ₄)]BF ₄	63	(—)	—																																																					
[CpRu(P(4-FC ₆ H ₄) ₂ (C ₂ H ₄))]BF ₄	63	(0.3)	98:2																																																					
[(η ⁵ -C ₉ H ₇)Ru(PPh ₃) ₂ (C ₂ H ₄)]BF ₄	63	(2.3)	98:2																																																					
[(η ⁶ -C ₆ H ₆)Ru(C ₃ H ₁₁ N)]Cl ₂	63	(0.3)	3:97																																																					
$\text{H}_2\text{C}=\text{CH}_2$ 30 bar		Na (4 mol %), pyridine (1 mol %), 100°, 10 h		415																																																				

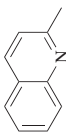
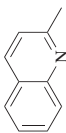
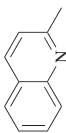
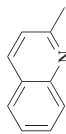
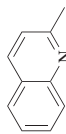
TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (Continued)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>				
C ₂			122	122
				
H ₂ C=CH ₂ 3.5 bar		[PtCl ₂ (C ₂ H ₄) ₂ (2.5 mol %), PPh ₃ (5 mol %), dioxane, 120°, 36 h		
		[PtCl ₂ (C ₂ H ₄) ₂ (2.5 mol %), PPh ₃ (5 mol %), dioxane, 120°		
			R	Time (h)
			<i>n</i> -Bu	20 (85)
			<i>t</i> -Bu	60 (82)
			<i>c</i> -C ₆ H ₁₁	40 (84)
			4-BrC ₆ H ₄	14 (85)
			4-O ₂ NC ₆ H ₄	80 (70)
			4-MeOC ₆ H ₄	36 (87)
			2-MeC ₆ H ₄	72 (75)
			4-MeC ₆ H ₄	12 (95)
			1-naphthyl	72 (91)
			2-naphthyl	36 (91)
H ₂ C=CH ₂	<i>n</i> -BuNH <i>Et</i> (3.5 eq)	RhCl ₃ •3H ₂ O (1 mol %), THF, 200°, 3 h	<i>n</i> -BuNEt ₂ (3)	117
H ₂ C=CH ₂ 10 eq		Na (2 eq), EtNH ₂ (3 eq), benzene, 225–245°, 3.5 h		108
H ₂ C=CH ₂ 40 bar	<i>n</i> -C ₆ H ₁₃ NH ₂	1. Na (10 mol %), butadiene (5 mol %), 10° 2. 160°, 1 h	<i>n</i> -C ₆ H ₁₃ NHEt I + <i>n</i> -C ₆ H ₁₃ NEt ₂ II + (<i>n</i> -C ₆ H ₁₃) ₂ NH III I + II + III (61), I/II/III = 73:16:21	414

[illegible]

TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (Continued)

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)							Refs.
C ₂	H ₂ C=CH ₂ 21 bar	PhNH ₂ Fe(CO) ₅ (4 mol %), PPh ₃ (2 mol %), 130–150°, 7 h	   							113, 114
			I-IV (16), I/III/IV = 61:16:17:6							
H ₂ C=CH ₂ 25 bar	PhNH ₂	RhCl ₃ •3H ₂ O (0.3 mol %), PPh ₃ (x mol %), <i>n</i> -Bu ₄ PX (y mol %), I ₂ (z mol %), 150°, 96 h	  							120
			<i>x</i>	<i>X</i>	<i>y</i>	<i>z</i>	I	II	III	
			0	—	0	0	(3.2)	(—)	(2.0)	
			0	Cl	19	0	(6.4)	(0.9)	(1.2)	
			0	Cl	43	0	(6.4)	(0.6)	(—)	
			0	Br	3	0	(9.8)	(—)	(1.7)	
			0	Br	19	0	(5.8)	(0.6)	(2.9)	
			0	Br	43	0	(5.2)	(—)	(2.0)	
			0	I	3	0	(2.0)	(—)	(0.6)	
			0	I	19	0	(4.9)	(0.6)	(2.6)	
			0	I	43	0	(3.7)	(0.9)	(2.9)	
			0.3	—	0	0	(3.5)	(0.3)	(1.2)	
			0.6	—	0	0	(5.8)	(0.6)	(0.6)	
			0.6	Cl	19	0	(2.6)	(—)	(—)	
			0.6	Cl	19	0	(9.8)	(0.9)	(1.7)	
			0.6	Br	19	0	(4.6)	(—)	(—)	
			0.6	Br	43	0	(3.2)	(—)	(—)	
			0.6	I	3	0	(14)	(0.9)	(—)	
			0.6	I	6	0	(21)	(1.7)	(—)	
			0.6	I	19	0	(37)	(27)	(1.2)	
			0.6	I	43	0	(29)	(35)	(1.4)	
			0.6	I	3	0.6	(44)	(7.2)	(—)	
			0.6	I	19	0.6	(8.1)	(65)	(0.9)	

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

$\text{H}_2\text{C}=\text{CH}_2$
 x bar
 PhNH_2
 RbCl_3 (y mol %), solvent
 PhNHt **I** +  **II**

x	y	Solvent	Temp (°)	Time (h)	I	II
10	0.05	neat	100	150	(1.8)	(0.12)
100	0.1	THF	150	15	(2.4)	(0.6)

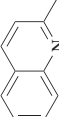
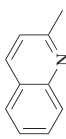
Catalyst (x mol %), (<i>n</i> -Bu) ₄ PX (y mol %), 150°, 10 h	PhNH ₂	PhNHcI	I	+	PhNEt ₂	II	+		III	123
		Catalyst	x	X	y	I + II + III	I/II/III			
		—	0	—	0	(—)	—			
		PtBr ₂	0.3	—	0	(5.8)	I only			
		PtBr ₂	0.3	Cl	2.9	(14)	91:9:0			
		PtBr ₂	0.3	Cl	18.2	(30)	92:2:6			
		PtBr ₂	0.3	Cl	42	(23)	95:1:4			
		PtBr ₂	0.3	Br	1.4	(40)	87:4:8			
		PtBr ₂	0.3	Br	2.9	(43)	89:3:8			
		PtBr ₂	0.3	Br	18.2	(37)	87:2:11			
		PtBr ₂	0.3	Br	42	(25)	86:1:12			
		PtBr ₂	0.3	I	1.4	(32)	93:2:5			
		PtBr ₂	0.3	I	2.9	(39)	91:2:7			
		PtBr ₂	0.3	I	18.2	(29)	80:1:17			
		PtBr ₂	0.3	I	42	(1.4)	I only			
		PtBr ₄	0.3	—	0	(14)	89:4:7			
		PtBr ₄	0.3	Cl	18	(22)	84:14:2			
		PtBr ₄	0.3	Br	18	(39)	85:6:7			
		PtBr ₄	0.3	I	18	(32)	84:2:13			
		PtCl ₄	0.3	—	0	(4.3)	I only			
		PtCl ₄	0.3	Cl	18	(13)	98:2:0			
		PtCl ₄	0.3	Br	18	(35)	90:3:7			
		PtCl ₄	0.3	I	18	(32)	86:2:11			

TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (Continued)														
Alkene	Amine	Conditions	Product(s) and Yield(s) (%)				Refs.							
$\text{H}_2\text{C}=\text{CH}_2$ x bar	PhNH_2	PtBr_2 (y mol %), ligand (0.5 mol %), solvent	PhNHet I + PhNEt_2 II + 	II	III									
						x	y	Ligand	Solvent	Temp (°)	Time (h)			
						10	0.3	—	$n\text{-Bu}_4\text{PBr}$	150	10	(21)	(0.3)	(2.3)
						25	0.14	—	$n\text{-Bu}_4\text{PBr}$	150	10	(14)	(0.1)	(2.2)
						25	0.3	—	$n\text{-Bu}_4\text{PBr}$	150	10	(23)	(0.3)	(3.1)
						25	0.3	—	aniline	150	10	(6.6)	(0.3)	(0.9)
						25	0.3	—	THF	150	10	(9.8)	(0.3)	(1.2)
						25	0.3	—	$n\text{-Bu}_4\text{PBr}$	120	10	(12)	(0.3)	(2.3)
						25	0.3	—	$n\text{-Bu}_4\text{PBr}$	180	10	(26)	(0.6)	(4.3)
						25	0.3	—	$n\text{-Bu}_4\text{PBr}$	150	5	(21)	(0.3)	(3.2)
						25	0.3	—	$n\text{-Bu}_4\text{PBr}$	150	2.5	(18)	(0.3)	(2.9)
						25	0.3	—	$n\text{-Bu}_4\text{Br}$	150	1	(11)	(0.3)	(1.4)
						25	0.3	—	$n\text{-Bu}_4\text{PBr/hexane}$	150	10	(33)	(0.6)	(4.9)
						25	0.3	—	$n\text{-Bu}_4\text{PBr/hexane}$	150	5	(29)	(0.3)	(3.7)
						25	0.3	—	$n\text{-Bu}_4\text{PBr/hexane}$	150	2.5	(22)	(0.3)	(2.9)
						25	0.3	—	$n\text{-Bu}_4\text{PBr/hexane}$	150	1	(13)	(0.3)	(2.3)
						25	0.3	—	hexane	150	10	(5.8)	(—)	(1.4)
						25	0.3	P(OMe)_3	$n\text{-Bu}_4\text{PBr}$	150	10	(0.6)	(0.3)	(0.6)
						25	0.3	PEt_3	$n\text{-Bu}_4\text{PBr}$	150	10	(17)	(0.3)	(3.7)
						25	0.3	PPh_3	$n\text{-Bu}_4\text{PBr}$	150	10	(32)	(0.3)	(3.7)
25	0.6	—	$n\text{-Bu}_4\text{PBr}$	150	10	(33)	(0.6)	(4.0)						
25	1.4	—	$n\text{-Bu}_4\text{PBr}$	150	10	(42)	(1.4)	(5.6)						
35	0.3	—	$n\text{-Bu}_4\text{PBr}$	150	10	(24)	(0.3)	(5.2)						
50	0.3	—	$n\text{-Bu}_4\text{PBr}$	150	10	(26)	(0.3)	(5.8)						

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₂

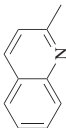
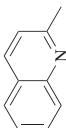
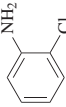
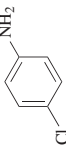
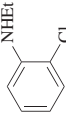
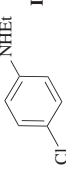
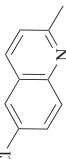
H ₂ C=CH ₂ 25 bar	PhNH ₂	Catalyst (0.3 mol %), NaX (x mol %), H ₂ O (y mL/mmol amine), 150°				PhNHet I + PhNEt ₂ II +	 III	418
		Catalyst	X	x	y	Time (h)	I + II + III	I/II/III
		PtBr ₂	—	—	0.33	10	(1.7)	5:0.1:1
		PtBr ₂	Br	43	0.33	10	(27)	85:1:8
		PtBr ₂	Br	43	0.33	24	(28)	90:1:8
		PtBr ₂	Br	43	0.33	48	(28)	90:1:8
		PtBr ₂	Br	3	0.33	10	(8)	24:0.3:3
		PtBr ₂	Br	29	0.33	10	(20)	64:1:6
		PtBr ₂	Br	57	0.33	10	(15)	45:1:5
		PtBr ₂	Br	144	0.33	10	(10)	27:6:3
		PtBr ₂	Br	3	0.11	10	(20)	62:2:7
		PtBr ₂	Br	29	0.11	10	(24)	74:3:8
		PtBr ₂	Br	57	0.11	10	(21)	61:3:8
		PtBr ₂	Br	144	0.11	10	(11)	31:2:7
		PtBr ₂	F	43	0.33	10	(1)	2:0:1
		PtBr ₂	Cl	43	0.33	10	(19)	60:1:5
		PtBr ₂	I	43	0.33	10	(2)	4:0.3:2
		K ₂ PtCl ₄	Br	43	0.33	10	(27)	86:1:8
		K ₂ PtBr ₄	Br	43	0.33	10	(25)	81:1:7
		PtCl ₂	Br	43	0.33	10	(23)	70:1:8
		PtI ₂	Br	43	0.33	10	(7)	19:1:2
		PtCl ₄	Br	43	0.33	10	(26)	80:2:8
		PtBr ₄	Br	43	0.33	10	(24)	76:3:6
		PdBr ₂	Br	43	0.33	10	(0.4)	1:0:0.3

TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (*Continued*)

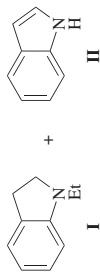
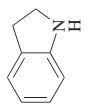
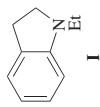
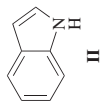
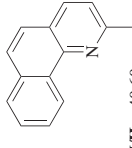
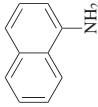
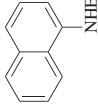
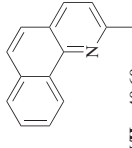
Alkene	Amine	Conditions	Product(s) and Yield(s) (%)			Refs.
C ₂ H ₂ C=CH ₂ 25 bar	PhNH ₂	PtBr ₂ (0.3 mol %), NaBr (43 mol %), additive (x mol %), H ₂ O (0.33 mL/mmol amine), 150°	PhNHet I + PhNEt ₂ II +  III			118
			Additive	x	Time (h)	I + II + III I/II/III
			—	—	10 ^a	(14) 43:2:5
			EtOH	76	10	(23) 72:2:8
			DMF	200	10	(1) 3:0:1
			DMSO	2.9	10	(9) 23:1:7
			DMSO	2.9	10 ^a	(6) 13:0.4:6
			DMSO	220	10	(0) —
			benzoquinone	2.9	10	(22) 69:1:7
			CuCl ₂	1.4	10	(5) 15:1:1
H ₂ C=CH ₂ 10 eq	 I +  II	PtBr ₂ (1 mol %), TfOH (3 mol %), <i>n</i> -Bu ₄ PBr, 150°, 72 h	 (95)			121
		[(P(<i>c</i> -C ₆ H ₁₁) ₃) ₂ (CO)(Cl)- Ru=CHCH=C(CH ₃) ₂)]BF ₄ (5 mol %), benzene, 80°, 48 h	 I +  II			116
			I + II (88), I/II = 46:54			

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.



$\text{H}_2\text{C}=\text{CH}_2$ 25 bar			PtBr_2 (0.3 mol %), <i>n</i> -Bu ₄ PBr, 150°, 10 h	 I	 II	 III	R^1 H Cl H H Me H	R^2 Cl H MeO Me H	I (27) (32) (6.3) (16) (24)	II (0.3) (—) (0.3) (0.3) (0.3)	III (8.9) (9.2) (2.6) (6.0) (7.8)	121
$\text{H}_2\text{C}=\text{CH}_2$ 60 bar			NaNH ₂ (8 mol %), 275°, 6 h	 (27)								414
$\text{H}_2\text{C}=\text{CH}_2$ 3.5 bar	PhNHMe		NaNH ₂ (9 mol %), neat 250°, 5 h	PhNMeEt (53)								414
			$[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$ (2.5 mol %), ligand (<i>x</i> mol %), dioxane									
			Ligand	<i>x</i>	Temp (°)	Time (h)						
			—	—	90	24	(44)					122
			P(2-MeC ₆ H ₄) ₃	5	120	24	(—)					122
			P(OMe) ₃	5	120	24	(95)					122
			P(OPh) ₃	5	120	24	(90)					122
			P(<i>t</i> -Bu) ₃	5	120	24	(—)					122
			PPh ₂ Et	5	120	24	(98)					122
			P(C ₆ F ₅) ₃	5	120	24	(75)					122
			P(<i>n</i> -Bu) ₃	5	120	17	(33)					122
			PPh ₃	5	120	24	(98)					122, 245
			PPh ₃	10	120	24	(—)					122

TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (Continued)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>				
C₂				
$\text{H}_2\text{C}=\text{CH}_2$ 200 atm	ArNH_2	Na (8 mol %), CuO (0.04 mol %), neat 290°	Ar	
			2-MeC ₆ H ₄ (68)	417
			3-MeC ₆ H ₄ (69)	
			4-MeC ₆ H ₄ (85)	
			2,4-Me ₂ C ₆ H ₃ (70)	
$\text{H}_2\text{C}=\text{CH}_2$ 60 bar	$n\text{-Bu}_2\text{NH}$	1. Na (13 mol %), butadiene (5 mol %), 10° 2. 135°, 5 h	ArNHet	
			$n\text{-Bu}_2\text{NEt}$ (63)	414
$\text{H}_2\text{C}=\text{CH}_2$ 25 bar	PhNHet	RhCl ₃ •3H ₂ O (0.3 mol %), PPh ₃ (0.6 mol %), $n\text{-Bu}_4\text{PI}$ (19 mol %), I ₂ (0.6 mol %), 150°, 24 h	PhNEt ₂ (75)	120
				
			I + II (81), I/II = 65:35	116
$\text{H}_2\text{C}=\text{CH}_2$ 10 eq		[(P(<i>c</i> -C ₆ H ₁₁) ₃) ₂ (CO)(Cl)- Ru=CHCH=C(CH ₃) ₂)BF ₄ (5 mol %), benzene, 80°, 36 h	 I	
			 II	
$\text{H}_2\text{C}=\text{CH}_2$ 500 bar		Na (62 mol %), 200°, 16 h		107
			 I + II (85), I/II = 40:60	
$\text{H}_2\text{C}=\text{CH}_2$ 10 eq		[(PCy ₃) ₂ (CO)(Cl)- Ru=CHCH=C(CH ₃) ₂)BF ₄ (5 mol %), benzene, 80°, 48 h	 I +  II	116

C₂₋₄

8 bar

1a (x mol %),
AgSbF₆ (x mol %),
dioxane, 100°

R Z x Time (h)

H	O	5	72	(75)
H	MeN	5	20	(99)
H	<i>i</i> -BuN	5	40	(80)
Me	MeN	5	62	(97)
Et	MeN	10	69	(99)

126

x bar

2 (x mol %),
AgSbF₆ (x mol %),
dioxane, 24 h

R	x	Temp (°)	
H	4	60	(99)
Me	8	100	(98)
Et	8	100	(96)

126

8 bar

1a (x mol %),
AgSbF₆ (x mol %),
dioxane, 100°

R	n	x	Time (h)	dr
H	1	5	20	(95) —
H	2	10	19	(98) —
Me	1	10	65	(85) —
Me	2	5	67	(86) —
Et	1	5	68	(86) 1:1

126

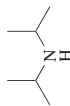
NH₃ (x eq)

Solid zeolite catalyst,
285–305 bar

x Catalyst Temp (°)

1.5	borosilicate pentasil	330	(8.6)	97
1.5	borosilicate pentasil	350	(11.0)	97
1.5	Na borosilicate pentasil	330	(9.7)	97
2	aluminosilicate pentasil	330	(7.1)	101
2	aluminosilicate pentasil	350	(10.0)	101
2	Zn-aluminosilicate pentasil	330	(8.5)	101
3	Na borosilicate pentasil	350	(11.1)	97

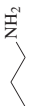
C₃

TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (<i>Continued</i>)																																																																																																														
Alkene	Amine	Conditions	Product(s) and Yield(s) (%)		Refs.																																																																																																									
 C ₃	NH ₃ (x eq)	Zeolite catalyst, 50 bar			100																																																																																																									
						<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>																																																																																																								
<table><tr><th>x</th><th>Catalyst</th><th>Temp (°)</th><th>I</th><th>II</th></tr><tr><td>2.0</td><td>H-offretite</td><td>300</td><td>(1.0)</td><td>(0.05)</td></tr><tr><td>2.0</td><td>H-offretite</td><td>320</td><td>(2.0)</td><td>(0.08)</td></tr><tr><td>2.0</td><td>H-offretite</td><td>340</td><td>(3.4)</td><td>(0.18)</td></tr><tr><td>2.0</td><td>H-offretite</td><td>350</td><td>(4.0)</td><td>(0.25)</td></tr><tr><td>2.0</td><td>H-offretite</td><td>350</td><td>(4.7)</td><td>(0.34)</td></tr><tr><td>2.0</td><td>H-offretite</td><td>350</td><td>(5.5)</td><td>(0.36)</td></tr><tr><td>4.0</td><td>H-offretite</td><td>300</td><td>(0.55)</td><td>(—)</td></tr><tr><td>4.0</td><td>H-offretite</td><td>320</td><td>(1.6)</td><td>(—)</td></tr><tr><td>4.0</td><td>H-offretite</td><td>340</td><td>(3.5)</td><td>(0.17)</td></tr><tr><td>4.0</td><td>H-offretite</td><td>350</td><td>(4.3)</td><td>(0.22)</td></tr><tr><td>4.0</td><td>H-offretite</td><td>350</td><td>(6.0)</td><td>(0.45)</td></tr><tr><td>4.0</td><td>H-offretite</td><td>350</td><td>(6.5)</td><td>(0.58)</td></tr><tr><td>4.1</td><td>H-erionite</td><td>320</td><td>(0.14)</td><td>(—)</td></tr><tr><td>4.5</td><td>H-erionite</td><td>340</td><td>(0.46)</td><td>(—)</td></tr><tr><td>4.6</td><td>H-erionite</td><td>380</td><td>(1.9)</td><td>(—)</td></tr><tr><td>4.7</td><td>H-erionite</td><td>400</td><td>(2.0)</td><td>(0.48)</td></tr><tr><td>5.0</td><td>H-erionite</td><td>360</td><td>(1.4)</td><td>(—)</td></tr><tr><td>3.9</td><td>H-clinoptilolite</td><td>340</td><td>(0.34)</td><td>(—)</td></tr><tr><td>4.0</td><td>H-clinoptilolite</td><td>320</td><td>(0.09)</td><td>(—)</td></tr><tr><td>4.1</td><td>H-clinoptilolite</td><td>360</td><td>(0.88)</td><td>(—)</td></tr></table>						x	Catalyst	Temp (°)	I	II	2.0	H-offretite	300	(1.0)	(0.05)	2.0	H-offretite	320	(2.0)	(0.08)	2.0	H-offretite	340	(3.4)	(0.18)	2.0	H-offretite	350	(4.0)	(0.25)	2.0	H-offretite	350	(4.7)	(0.34)	2.0	H-offretite	350	(5.5)	(0.36)	4.0	H-offretite	300	(0.55)	(—)	4.0	H-offretite	320	(1.6)	(—)	4.0	H-offretite	340	(3.5)	(0.17)	4.0	H-offretite	350	(4.3)	(0.22)	4.0	H-offretite	350	(6.0)	(0.45)	4.0	H-offretite	350	(6.5)	(0.58)	4.1	H-erionite	320	(0.14)	(—)	4.5	H-erionite	340	(0.46)	(—)	4.6	H-erionite	380	(1.9)	(—)	4.7	H-erionite	400	(2.0)	(0.48)	5.0	H-erionite	360	(1.4)	(—)	3.9	H-clinoptilolite	340	(0.34)	(—)	4.0	H-clinoptilolite	320	(0.09)	(—)	4.1	H-clinoptilolite	360	(0.88)	(—)
x	Catalyst	Temp (°)	I	II																																																																																																										
2.0	H-offretite	300	(1.0)	(0.05)																																																																																																										
2.0	H-offretite	320	(2.0)	(0.08)																																																																																																										
2.0	H-offretite	340	(3.4)	(0.18)																																																																																																										
2.0	H-offretite	350	(4.0)	(0.25)																																																																																																										
2.0	H-offretite	350	(4.7)	(0.34)																																																																																																										
2.0	H-offretite	350	(5.5)	(0.36)																																																																																																										
4.0	H-offretite	300	(0.55)	(—)																																																																																																										
4.0	H-offretite	320	(1.6)	(—)																																																																																																										
4.0	H-offretite	340	(3.5)	(0.17)																																																																																																										
4.0	H-offretite	350	(4.3)	(0.22)																																																																																																										
4.0	H-offretite	350	(6.0)	(0.45)																																																																																																										
4.0	H-offretite	350	(6.5)	(0.58)																																																																																																										
4.1	H-erionite	320	(0.14)	(—)																																																																																																										
4.5	H-erionite	340	(0.46)	(—)																																																																																																										
4.6	H-erionite	380	(1.9)	(—)																																																																																																										
4.7	H-erionite	400	(2.0)	(0.48)																																																																																																										
5.0	H-erionite	360	(1.4)	(—)																																																																																																										
3.9	H-clinoptilolite	340	(0.34)	(—)																																																																																																										
4.0	H-clinoptilolite	320	(0.09)	(—)																																																																																																										
4.1	H-clinoptilolite	360	(0.88)	(—)																																																																																																										

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

NH ₃ (x eq)		Solid catalyst, flow reactor				 I +  II		97				
x	Catalyst	Temp (°C)	P (bar)	GHSV ^b	I	II	Temp (°C)	P (bar)	GHSV ^b	I	II	
0.9	SK-500	360	290	—	(4.2)	(0.13)	330	80	1950	(7.7)	(0.27)	
0.9	SK-500	383	290	—	(7.1)	(0.55)	340	50	974	(13.3)	(0.2)	
0.9	SK-500	413	290	—	(6.5)	(0.27)	340	50	1950	(11.6)	(—)	
1	SK-500	400	290	—	(7.7)	(0.44)	350	50	974	(12.9)	(—)	
2	H-mordemite	330	50	2340	(6.4)	(0.2)	350	80	1950	(10.3)	(0.17)	
2	H-mordemite	340	50	2340	(7.8)	(0.4)	360	50	974	(13.5)	(—)	
2	H-mordemite	350	50	2340	(8.1)	(0.3)	370	50	1950	(14.0)	(0.15)	
4	H-mordemite	300	50	1960	(3)	(—)	340	50	1950	(9.5)	(0.11)	
4	H-mordemite	310	50	1960	(4.7)	(—)	350	50	1950	(10.5)	(0.09)	
4	H-mordemite	320	50	1960	(6.8)	(—)	325	50	1950	(0.2)	(—)	
4	H-mordemite	330	50	1960	(9.1)	(—)	380	50	1950	(1.6)	(—)	
4	H-mordemite	340	50	1960	(10.9)	(—)	400	50	1950	(2.8)	(—)	
4	H-mordemite	350	50	1960	(11.1)	(—)	430	50	1950	(3.4)	(0.19)	
4	La zeolite Y	290	80	1950	(1)	(—)	450	50	1950	(2.6)	(0.61)	
4	La zeolite Y	330	50	1950	(8)	(—)						
NH ₃ (3 eq)		Na (10 mol %), benzene, 950–1070 bar, 267–278°, 4 h				 I +  II	(23)		(tr)	108		
NH ₃		Na (7 mol %), solvent, 1000 bar, 250°, 18 h				 I +  II			Solvent neat	(23) (2.3)	(29) (2.5)	107,106

TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (Continued)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)		Refs.																											
 x eq	NH ₃	CsNH ₂ (y mol %), KNH ₂ (z mol %)	 I +  II		109, 110																											
			<table><tr><th>x</th><th>y</th><th>z</th><th>Temp (°)</th><th>Time (h)</th><th>I</th><th>II</th></tr><tr><td>0.7</td><td>6</td><td>0</td><td>116</td><td>19</td><td>(2.4)</td><td>(0.2)</td></tr><tr><td>1.2</td><td>11</td><td>8</td><td>139</td><td>17</td><td>(16)</td><td>(0.7)</td></tr><tr><td>1.2</td><td>15</td><td>4</td><td>139</td><td>18</td><td>(11)</td><td>(0.6)</td></tr></table>	x		y	z	Temp (°)	Time (h)	I	II	0.7	6	0	116	19	(2.4)	(0.2)	1.2	11	8	139	17	(16)	(0.7)	1.2	15	4	139	18	(11)	(0.6)
			x	y		z	Temp (°)	Time (h)	I	II																						
			0.7	6		0	116	19	(2.4)	(0.2)																						
1.2	11	8	139	17	(16)	(0.7)																										
1.2	15	4	139	18	(11)	(0.6)																										
	NH ₃ (5 eq)	NH ₄ I (3 mol %), n-Bu ₄ NI (0.5 mol %), UV (Hg), 8°, 4 h	 (3)		410																											
			 I +  II			408																										
	NH ₃ (2 eq)	NH ₄ I (60 mol %), H ₂ O, 335°, 5 h	 I +  II +  III +  IV		408																											
			I–IV (27), I/II/III/IV = 74:2:1:3																													
			 I +  II +  I + II (11), I/II = 81:19			408																										
 90 atm	Me ₂ NH	LiEt (4 mol %), 170°, 3 h	 (10)		331																											

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

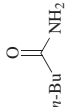
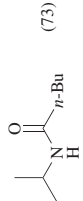
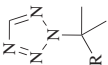
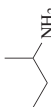
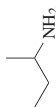
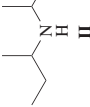
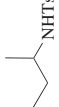
	$n\text{-BuNH}_2$	Na (32 mol %), 250°, 18 h		106
1000 bar			(36)	
		$[\text{PtCl}_2(\text{C}_2\text{H}_4)_2]$ (5 mol %), PPh ₃ (10 mol %), dioxane, 120°, 80 h		122
7 bar			(73)	
	PhNH ₂	Na (8 mol %), CuO (0.04 mol %), 300°		417
			(43)	
	PhNH ₂	NaNH ₂ (8 mol %), 330°, 0.5 h		414
50 bar			(6)	
	TsNH ₂	$[\text{PtCl}_2(\text{C}_2\text{H}_4)_2]$ (5 mol %), AgBF ₄ (10 mol %), 1, 2-dichlorobenzene, 85°, 3 h		93
1 atm			(95)	
C ₃₋₄		H ₂ SO ₄ , -20°		138
			R H (75) Me (80)	
C ₄		Zeolite catalyst, 40 bar		105
			Catalyst Temp (°)	
			HY2.5 330 (2.6)	
			HY15 340 (1.3)	
			BEA15 312 (2.2)	
			MOR6.9 347 (3.2)	
			MF115 322 (5.1)	

TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (*Continued*)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)				Refs.		
Please refer to the charts preceding the tables for structures indicated by the bold numbers.									
	NH ₃ (1.5 eq)	Zeolite catalyst		Catalyst	P (bar)	Temp (°)	97		
				borosilicate	300	330	(10.7)		
					aluminosilicate	290	300	(8.7)	
	EtNH ₂ (6 eq)	MEK (0.4 eq), UV (Hg), 8°, 4 h		(5.0)			409		
	NH ₃ (2 eq)	NH ₄ Cl (20 mol %), H ₂ O, 214 bar, 335°, 5 h	 I +  II +  III				408		
			+  IV +  V +  VI						
				I-VI (15), I/II/III/IV/V/VI = 61:0.18:24:1:7					
 1 atm	TsNH ₂	[PtCl ₂ (C ₂ H ₄) ₂] (5 mol %), AgBF ₄ (10 mol %), 1,2-dichlorobenzene, 85°, 3 h	 (95)				93		
	NH ₃ (x eq)	Solid catalyst, flow reactor		x	Catalyst	P (bar)	Temp (°)		
				1.3	SK-500	140	278	(6.1)	97
				2.7	SK-500	140	313	(6.5)	
				4	H-mordenite	50	300	(10.8)	
				4	H-mordenite	50	310	(8.8)	
				4	H-mordenite	50	320	(7.8)	
				4	H-mordenite	50	310	(6.2)	

NH ₃ (2 eq)	Solid catalyst, 52 bar, 24 h		Catalyst	Temp (°)		419
			SiO ₂ /Al ₂ O ₃	220	(tr)	
			SiO ₂ /Al ₂ O ₃	240	(0.5)	
			SiO ₂ /Al ₂ O ₃	260	(1.9)	
			SiO ₂ /Al ₂ O ₃	280	(5.0)	
			H-Y zeolite	220	(0.7)	
			H-Y zeolite	240	(3.3)	
			H-Y zeolite	260	(7.9)	
			H-Y zeolite	280	(8.6)	
			H-Y zeolite	300	(8.5)	
			SK-500 zeolite	220	(1.0)	
			SK-500 zeolite	240	(3.5)	
			SK-500 zeolite	260	(8.9)	
			SK-500 zeolite	280	(9.1)	
			SK-500 zeolite	300	(8.5)	
			H-mordenite	220	(0.9)	
			H-mordenite	240	(2.9)	
			H-mordenite	260	(5.9)	
			H-mordenite	280	(7.7)	
			H-mordenite	300	(8.3)	
			Na-Y zeolite	220	(tr)	
			Na-Y zeolite	240	(tr)	
			Na-Y zeolite	260	(tr)	
			Na-Y zeolite	280	(tr)	
			Na-Y zeolite	300	(tr)	

TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (*Continued*)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)		Refs.						
Please refer to the charts preceding the tables for structures indicated by the bold numbers.											
C₄ 	NH ₃ (x eq)	Zeolite catalyst									
				x	Catalyst	P (bar)	Temp (°)				
				1.3	borosilicate-boehmite	300	300	(12.7)	102		
				1.3	Cr-borosilicate-boehmite	300	300	(14.1)	102		
				1.3	Cr-borosilicate pentasil	300	300	(15.1)	102		
				1.5	borosilicate-SiO ₂	280	260	(20.3)	103		
				1.5	borosilicate-SiO ₂	280	270	(21.4)	103		
				1.5	borosilicate-SiO ₂	280	280	(18.8)	103		
				1.5	borosilicate-SiO ₂	280	300	(12.3)	103		
				1.5	borosilicate-boehmite	280	260	(23.0)	103		
				1.5	borosilicate-boehmite	280	270	(20.5)	103		
				1.5	borosilicate-boehmite	280	280	(18.1)	103		
				1.5	borosilicate-boehmite	280	300	(12.8)	103		
					NH ₃ (x eq)	Zeolite catalyst, 40 bar, 275°		x	Catalyst		
								1	HY2.5	(2.3)	105
								1	BEA15	(4.6)	
1	MFI14	(4.5)									
1	MOR6.9	(4.3)									
3	HY2.5	(3.2)									
3	BEA15	(8.2)									
3	MFI14	(8.9)									
3	MOR6.9	(5.6)									

NH₃ (x eq)

Solid zeolite catalyst

x	Zeolite	P (bar)	Temp (°)
1.5	borosilicate pentasil	280	300 (12.0)
1.5	borosilicate pentasil	570	330 (13.5)
1.5	borosilicate pentasil	295	350 (13.5)
1.5	boehmite-borosilicate pentasil	300	330 (13.5)
1.5	Na-borosilicate pentasil	275	330 (12.8)
1.3	boehmite-borosilicate-SiO ₂	300	300 (14.7)
1.3	boehmite-borosilicate-SiO ₂ -Al ₂ O ₃	300	300 (16.8)
1.3	H-borosilicate pentasil	300	300 (7.2)

NH₃ (x eq)

Solid zeolite catalyst

x	Zeolite	P (bar)	Temp (°)	GHSV ^c
1.3	aluminosilicate pentasil	300	300	10 (10.4)
1.3	Zn-aluminosilicate pentasil	300	300	5 (11.5)
1.3	iron silicate-boehmite	300	300	11 (10.6)
1.3	iron silicate-boehmite	300	300	9.5 (9.1)
1.3	Mn-aluminosilicate pentasil	295	300	10 (8.1)
1.5	aluminosilicate pentasil	295	320	— (10.7)
1.5	aluminosilicate pentasil	590	330	— (11.8)
1.5	Zn-aluminosilicate pentasil	285	330	— (10.6)
1.5	Zn-aluminosilicate pentasil	540	330	— (11.3)

TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (Continued)				
Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
	NH ₃ (x eq)	Montmorillonite clay, flow reactor		x Temp (°)
				2 250 (0.12)
				2 260 (0.81)
				2 262 (1.14)
				2 270 (1.58)
				2 280 (3.79)
				2 290 (8.53)
				2 300 (9.50)
				2 310 (8.58)
				2 320 (6.78)
				2 330 (7.27)
				2 340 (6.27)
				4 250 (0.16)
				4 260 (0.25)
				4 270 (1.88)
				4 280 (3.56)
				4 290 (12.49)
			Catalyst	
	NH ₃ (1.5–3 eq)	Solid catalyst, 200°		H-MFI-51 (12.9)
H-MFI-41 (10.2)				
H-MFI-25 (9.3)				
H-MOR-19 (8.0)				
H-MOR-16 (6.3)				
H-Y-40 (3.2)				
H-LTL-6 (1.7)				
H-OFF/ERI-8 (0.7)				
H-FER-16 (0.3)				
				C _{52.5} H _{0.3} PW ₁₂ O ₄₀ (2.4)
				420



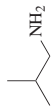
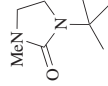
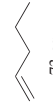
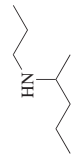
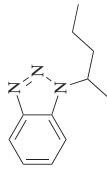
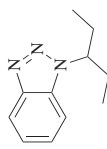
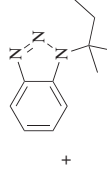
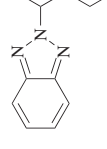
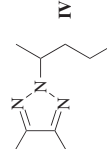
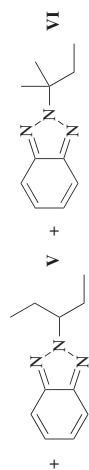
NH ₃ (3 eq)	Na (12.5 mol %), benzene, 650–700 bar, 250–265°, 1 h		(8)	C ₅₂ s ₈ H _{0.15} PW ₁₂ O ₄₀	(1.9)	108
				SiO ₂ –Al ₂ O ₃	(1.1)	
				SiO ₂ –TiO ₂	(0.5)	
				MgO	(—)	
NH ₃	Na (7 mol %), 740–960 bar, 200°, 15 h		(8.3)			107
NH ₃ (7 eq)	NH ₄ I (4 mol %), <i>n</i> -Bu ₄ NI (0.9 mol %), UV (Hg), 8°, 4 h		(1.3)			410
NH ₃ (1.5 eq)	NH ₄ Cl–CrCl ₃ /SiO ₂ , 275°, 4 h		(13.8)			408
NH ₃ (5 eq)	Catalyst (x mol %), H ₂ O		I + II	Time (h)	I II	421
NH ₃ (2 eq)	NH ₄ I (20 mol %), H ₂ O, 350°, 5 h		I + II	Time (h)	I II	408

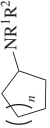
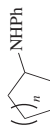
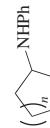
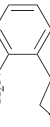
TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (*Continued*)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.															
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>																			
C ₄	NH ₃ (2 eq)	NH ₄ Cl (30 mol %), 315°, 2 h	 (0.94)	408															
	N ₂ H ₄ •HCl	1. HCl (1.2 eq), H ₂ O, 90°, 11 h 2. NaOH (aq)	 (79) ^d	136															
	N ₂ H ₄ •HCl	HCl (1.2 eq), H ₂ O, 100°, 5 h	 (28)	137															
C ₅	 8 bar	1a (10 mol %), AgSbF ₆ (10 mol %), dioxane, 100°, 48 h	 (72)	126															
	 73 eq	Me ₂ Si(C ₂ Me ₄) ₂ NdCH(SiMe ₃) ₂ (20 mol %), C ₆ D ₆ , 60°	 (90)	43															
	 1.5 eq	TsOH•H ₂ O (x mol %), 80°, 20 h	 I +  II	139															
<table border="1"> <thead> <tr> <th>x</th><th>I–III</th><th>I/II/III</th><th>IV–VI</th><th>IV/V/VI</th></tr> </thead> <tbody> <tr> <td>10</td><td>(18)</td><td>92:8:0</td><td>(9)</td><td>IV only</td></tr> <tr> <td>100</td><td>(23)</td><td>71:16:13</td><td>(15)</td><td>61:22:17</td></tr> </tbody> </table>					x	I–III	I/II/III	IV–VI	IV/V/VI	10	(18)	92:8:0	(9)	IV only	100	(23)	71:16:13	(15)	61:22:17
x	I–III	I/II/III	IV–VI	IV/V/VI															
10	(18)	92:8:0	(9)	IV only															
100	(23)	71:16:13	(15)	61:22:17															
			 +  III +  IV																



		$\text{Me}_2\text{Si}(\text{C}_3\text{Me}_4)_2\text{SnCH}(\text{SiMe}_3)_2$ (10 mol %), C_6D_6 , 60°		43																																																																																																									
	NH_3 (3 eq)	Borosilicate- SiO_2 , 425 bar, 300°		103																																																																																																									
TsNH_2	TsNH_2	$\text{Pt}(\text{COD})(\text{OTf})_2$ (10 mol %), 1,2-dichlorobenzene, 90° , 12 h		93																																																																																																									
C_{5-6} 	TsNH_2	H-mont (0.1 g/1 mmol amide), heptane, 150° , 5 h		127																																																																																																									
	TsNH_2	Catalyst (x mol %), solvent		422																																																																																																									
<table><tr><th>n</th><th>Catalyst</th><th>x</th><th>Solvent</th><th>Temp ($^\circ$)</th><th>Time (h)</th><th></th></tr><tr><td>1</td><td>$\text{Zr}(\text{OTf})_4$</td><td>5</td><td>$n\text{-C}_7\text{H}_{16}$</td><td>85</td><td>24</td><td>(80)</td></tr><tr><td>2</td><td>$\text{Cu}(\text{OTf})_2$</td><td>5</td><td>C_7H_8</td><td>85</td><td>22</td><td>(tr)</td></tr><tr><td>2</td><td>$\text{Sm}(\text{OTf})_3$</td><td>10</td><td>C_7H_8</td><td>85</td><td>22</td><td>(0)</td></tr><tr><td>2</td><td>$\text{Ni}(\text{OTf})_2$</td><td>10</td><td>C_7H_8</td><td>85</td><td>22</td><td>(0)</td></tr><tr><td>2</td><td>$\text{Zn}(\text{OTf})_2$</td><td>10</td><td>C_7H_8</td><td>85</td><td>22</td><td>(0)</td></tr><tr><td>2</td><td>$\text{Zr}(\text{OTf})_4$</td><td>5</td><td>C_7H_8</td><td>85</td><td>22</td><td>(94)</td></tr><tr><td>2</td><td>$\text{ZrOCl}_2 \cdot 2\text{H}_2\text{O}$</td><td>5</td><td>$\text{C}_7\text{H}_8$</td><td>85</td><td>22</td><td>(tr)</td></tr><tr><td>2</td><td>$\text{ZrSO}_4 \cdot \text{H}_2\text{O}$</td><td>5</td><td>$\text{C}_7\text{H}_8$</td><td>85</td><td>22</td><td>(tr)</td></tr><tr><td>2</td><td>ZrCl_4</td><td>5</td><td>C_7H_8</td><td>85</td><td>22</td><td>(<10)</td></tr><tr><td>2</td><td>$\text{Zr}(\text{OTf})_4$</td><td>2.5</td><td>$n\text{-C}_7\text{H}_{16}$</td><td>85</td><td>20</td><td>(93)</td></tr><tr><td>2</td><td>$\text{Zr}(\text{OTf})_4$</td><td>5</td><td>C_7H_8</td><td>rt</td><td>24</td><td>(<10)</td></tr><tr><td>2</td><td>$\text{Zr}(\text{OTf})_4$</td><td>5</td><td>DCE</td><td>85</td><td>20</td><td>(95)</td></tr><tr><td>2</td><td>$\text{Zr}(\text{OTf})_4$</td><td>5</td><td>dioxane</td><td>85</td><td>20</td><td>(38)</td></tr><tr><td>2</td><td>$\text{Zr}(\text{OTf})_4$</td><td>5</td><td>$n\text{-C}_7\text{H}_{16}$</td><td>85</td><td>20</td><td>(97)</td></tr></table>					n	Catalyst	x	Solvent	Temp ($^\circ$)	Time (h)		1	$\text{Zr}(\text{OTf})_4$	5	$n\text{-C}_7\text{H}_{16}$	85	24	(80)	2	$\text{Cu}(\text{OTf})_2$	5	C_7H_8	85	22	(tr)	2	$\text{Sm}(\text{OTf})_3$	10	C_7H_8	85	22	(0)	2	$\text{Ni}(\text{OTf})_2$	10	C_7H_8	85	22	(0)	2	$\text{Zn}(\text{OTf})_2$	10	C_7H_8	85	22	(0)	2	$\text{Zr}(\text{OTf})_4$	5	C_7H_8	85	22	(94)	2	$\text{ZrOCl}_2 \cdot 2\text{H}_2\text{O}$	5	C_7H_8	85	22	(tr)	2	$\text{ZrSO}_4 \cdot \text{H}_2\text{O}$	5	C_7H_8	85	22	(tr)	2	ZrCl_4	5	C_7H_8	85	22	(<10)	2	$\text{Zr}(\text{OTf})_4$	2.5	$n\text{-C}_7\text{H}_{16}$	85	20	(93)	2	$\text{Zr}(\text{OTf})_4$	5	C_7H_8	rt	24	(<10)	2	$\text{Zr}(\text{OTf})_4$	5	DCE	85	20	(95)	2	$\text{Zr}(\text{OTf})_4$	5	dioxane	85	20	(38)	2	$\text{Zr}(\text{OTf})_4$	5	$n\text{-C}_7\text{H}_{16}$	85	20	(97)
n	Catalyst	x	Solvent	Temp ($^\circ$)	Time (h)																																																																																																								
1	$\text{Zr}(\text{OTf})_4$	5	$n\text{-C}_7\text{H}_{16}$	85	24	(80)																																																																																																							
2	$\text{Cu}(\text{OTf})_2$	5	C_7H_8	85	22	(tr)																																																																																																							
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2	$\text{ZrOCl}_2 \cdot 2\text{H}_2\text{O}$	5	C_7H_8	85	22	(tr)																																																																																																							
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2	$\text{Zr}(\text{OTf})_4$	5	DCE	85	20	(95)																																																																																																							
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2	$\text{Zr}(\text{OTf})_4$	5	$n\text{-C}_7\text{H}_{16}$	85	20	(97)																																																																																																							

TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (Continued)

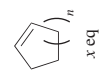
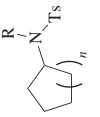
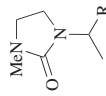
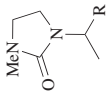
Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.									
Please refer to the charts preceding the tables for structures indicated by the bold numbers.													
C ₅₋₆  2 eq	R ¹ NHR ²	Catalyst (20 mol %), solvent, 85°		423									
					C ₅₋₇  2 eq	PhNH ₂	Pr(OTf) ₃ (2 mol %), I ₂ (6 mol %), <i>n</i> -Bu ₄ PI, 160°		424				
	<table><tr><th><i>n</i></th><th>Time (h)</th><th></th></tr><tr><td>1</td><td>48</td><td>(71)</td></tr><tr><td>2</td><td>36</td><td>(75)</td></tr><tr><td>3</td><td>36</td><td>(70)</td></tr></table>	<i>n</i>	Time (h)				1	48		(71)	2	36	(75)
<i>n</i>	Time (h)												
1	48	(71)											
2	36	(75)											
3	36	(70)											
C ₅₋₈  2 eq	PhNH ₂	PhNH ₃ B(C ₆ F ₅) ₄ •Et ₃ O (5 mol %), chlorobenzene, 135°, 7 d	 I +  II	142									
			<table><tr><th><i>n</i></th><th>I + II</th><th>I/II</th></tr><tr><td>1</td><td>(39)</td><td>II only</td></tr><tr><td>4</td><td>(45)</td><td>1:3</td></tr></table>		<i>n</i>	I + II	I/II	1	(39)	II only	4	(45)	1:3
<i>n</i>	I + II	I/II											
1	(39)	II only											
4	(45)	1:3											

 4 eq	RSO_2NH_2	PMA/SiO_2 (10 mol %), C_7H_8 , 120°	 NHSO_2R	n	R	Time (h)	
				1	4-MeC ₆ H ₄	1.2	(95)
				2	Me	1.5	(96)
				2	4-MeC ₆ H ₄	1.2	(98)
				4	Me	1.5	(94)
				4	4-MeC ₆ H ₄	1.3	(98)

TsNH_2	InBr_3 (20 mol %), C_7H_8 , 120°, 16 h	 NHTs	n	
			1	(86)
			3	(94)
			4	(44)

 x eq	RNHTs	Catalyst (y mol %), activator (z mol %), solvent	n	x	R	Catalyst	y	Activator	z	Solvent	Temp (°)	Time (h)	
			1	2	H	Ga	5	I ₂	7.5	neat	105	2	(88)
			2	1.2	H	GaCl ₃	24	—	—	C ₇ H ₈	105	24	(92)
			2	1.2	H	GaCl ₃	24	—	—	dioxane	105	24	(tr)
			2	1.2	H	GaCl ₃	24	—	—	THF	105	24	(tr)
			2	1.2	H	GaCl ₃	24	—	—	DCE	105	24	(65)
			2	1.2	H	GaCl ₃	12	—	—	C ₇ H ₈	105	24	(67)
			2	1.2	H	GaCl ₃	6	—	—	C ₇ H ₈	105	24	(55)
			2	2	H	GaCl ₃	5	—	—	neat	105	16	(94)
			2	2	H	GaCl ₃	5	—	—	neat	105	2	(86)
			2	2	H	GaBr ₃	5	—	—	neat	105	2	(84)
			2	2	H	Ga	5	I ₂	7.5	neat	105	2	(96)
			2	2	H	Ga	5	I ₂	7.5	neat	105	1	(83)
			2	2	H	Ga	1	I ₂	1.5	neat	105	21	(5)

TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (*Continued*)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
C₅₋₈  x eq	RNHTs	Catalyst (y mol %), activator (z mol %), solvent	 z	426
	n	Catalyst	Temp (°)	Time (h)
	2	Ga	90	2 (12)
	2	Ga	105	16 (tr)
	2	I ₂	105	16 (tr)
	2	Ga	105	24 (87)
	2	Ga	105	24 (30)
	2	Ga	105	24 (34)
	2	Ga	105	24 (27)
	3	Ga	105	2 (87)
	4	Ga	105	2 (tr)
			R	Time (h)
		1a (5 mol %), AgSbF ₆ (5 mol %), dioxane, 100°	HO ₂ C(CH ₂) ₂	40 (98)
			EtO ₂ C(CH ₂) ₄	40 (99)
			<i>n</i> -C ₆ H ₁₃	24 (38)
 10 eq		1a (5 mol %), AgSbF ₆ (5 mol %), dioxane, 100°	 R	126
		2 (5 mol %), AgZ (5 mol %), solvent, 100°	 R	
			HO(CH ₂) ₃	24 (98)
			BnO(CH ₂) ₃	40 (98)
			<i>n</i> -C ₆ H ₁₃	24 (96)
			<i>n</i> -C ₆ H ₁₃	24 (44)
			<i>n</i> -C ₆ H ₁₃	24 (26)
			<i>n</i> -C ₆ H ₁₃	24 (12)
			<i>n</i> -C ₆ H ₁₃	24 (6)
			<i>n</i> -C ₆ H ₁₃	24 (39)
			<i>n</i> -C ₆ H ₁₃	24 (80)
			<i>n</i> -C ₆ H ₁₃	24 (97)
			<i>n</i> -C ₆ H ₁₃	24 (40)
			<i>n</i> -C ₆ H ₁₃	24 (40)

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.



TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (*Continued*)

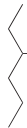
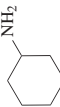
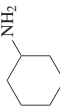
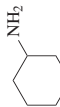
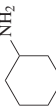
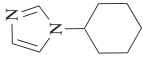
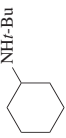
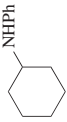
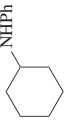
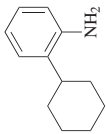
Alkene	Amine	Conditions	Product(s) and Yield(s) (%)		Refs.																			
Please refer to the charts preceding the tables for structures indicated by the bold numbers.																								
 4 eq	TsNH ₂	Catalyst (5 mol %), AgSbF ₆ (x mol %), DPPE (5 mol %), TCE, 20 h	 I +  NHTs II		427																			
		<table><tr><th>Catalyst</th><th>x</th><th>Temp (°)</th><th>I + II</th><th>I/II</th></tr><tr><td>CuBr</td><td>5</td><td>100</td><td>(tr)</td><td>—</td></tr><tr><td>CuBr</td><td>5</td><td>150</td><td>(tr)</td><td>—</td></tr><tr><td>CuBr₂</td><td>10</td><td>100</td><td>(90)</td><td>4:6</td></tr></table>	Catalyst	x	Temp (°)	I + II	I/II	CuBr	5	100	(tr)	—	CuBr	5	150	(tr)	—	CuBr ₂	10	100	(90)	4:6		
		Catalyst	x	Temp (°)	I + II	I/II																		
		CuBr	5	100	(tr)	—																		
CuBr	5	150	(tr)	—																				
CuBr ₂	10	100	(90)	4:6																				
 NHP I +  NHP II		I + II (2.7), I/II = 85:15	131																					
 2 eq	PhNH ₂	PtBr ₂ (0.3 mol %), <i>n</i> -Bu ₄ PBr (18 mol %), [PhNH ₃]HSO ₄ (0.8 mol %) 150°, 10 h	 NHNH ₂ (25) ^d		136																			
	NH ₃ •HCl	1. HCl (1.2 eq), H ₂ O, 71–82°, 10 h 2. NaOH (aq)	 NH ₂ (7.1)		103																			
 3.5 eq	NH ₃ (3 eq)	Borosilicate-SiO ₂ , 380 bar, 300°	 NH ₂ (3.4)		410																			
	NH ₃ (10 eq)	NH ₄ I (6 mol %), <i>n</i> -Bu ₄ NI (1 mol %), UV (Hg), 8°, 4 h	 NH ₂ (16)		106																			
	NH ₃	NaNH ₂ (9 mol %), 8500 bar, 200°, 20 h	 NH ₂ (10)		97																			
	NH ₃ (4.8 eq)	SK-500 zeolite, 210 bar, 335°																						

TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (*Continued*)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>				
C ₆	 (5 eq)	TfOH (20 mol %), PhCO ₂ Me (1.8 eq), EtOAc, UV, 24–48 h	 (40)	428
	<i>t</i> -BuNH ₂ (5 eq)	NH ₄ I (6 mol %), <i>n</i> -Bu ₄ NI (x mol %), UV (Hg), 8°, 4 h	 $\frac{x}{0 \quad (4)}$ 0.08 (9.5)	410
 2 eq	PhNH ₂	PtBr ₂ (0.3 mol %), <i>n</i> -Bu ₄ PBr (18 mol %), [PhNH ₃]HSO ₄ (0.8 mol %), 150°, 10 h	 (0.6)	131
	PhNH ₂ (5 eq)	HI (5 mol %), C ₇ H ₈	 I +  II	143
		Temp (°)	Time (h)	I + II
		135	168	(21)
		135	504	(59)
		150	70	(17)
				87:13 86:14 88:12

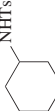
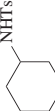
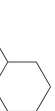
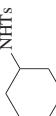
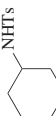
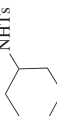
	TsNH ₂	Catalyst (0.1 g/1 mmol amide), heptane, 150°, 2 h		Catalyst — H-mont H-USY H-mordenite H-ZSM-5 mont K10 SO ₄ ²⁻ /ZrO ₂ Na ⁺ -mont TsOH•2H ₂ O H ₂ SO ₄	(—) (90) (63) (20) (tr) (tr) (tr) (—) (57) (44)	127		
	TsNH ₂	Solid catalyst (10 mol %), C ₇ H ₈ , 120°		Catalyst PMA/SiO ₂ HClO ₄ /SiO ₂ H ₂ SO ₄ /SiO ₂ NaHSO ₄ /SiO ₂ H-mont	Time (h) 1.2 2.5 3.5 4.0 5.0	425		
	TsNH ₂	Catalyst (x mol %), C ₇ H ₈		Catalyst — In(O ₂ CCF ₃) ₃ In(TfAcac) ₃ InF ₃ InF ₃ •H ₂ O InI ₃ InCl ₃ InBr ₃ InBr ₃ InBr ₃ InBr ₃ InBr ₃	x 20 20 20 20 20 20 20 20 10 20 20	Temp (°) 120 120 120 120 120 120 120 120 120 160 90	Time (h) 60 16 16 16 16 16 16 16 8 16 16 16	330

TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (Continued)																																																																											
Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																							
 2 eq C ₆	TsNH ₂	Ga (5 mol %, recycled), I ₂ (7.5 mol %), 105°, 2 h		Cycle 1 (96) 2 (96) 3 (93) 4 (81) 5 (75)	426																																																																						
 4 eq	TsNH ₂	Catalyst (5 mol %), AgSbF ₆ (x mol %), DPPE (5 mol %), additive (y mol %), TCE, 20 h			427																																																																						
<table><tr><th>Catalyst</th><th>x</th><th>Additive</th><th>y</th><th>Temp (°)</th></tr><tr><td>CuBr</td><td>5</td><td>—</td><td>—</td><td>100 (57)</td></tr><tr><td>CuBr</td><td>5</td><td>—</td><td>—</td><td>150 (82)</td></tr><tr><td>CuBr₂</td><td>10</td><td>—</td><td>—</td><td>100 (96)</td></tr><tr><td>CuBr₂</td><td>10</td><td>Cs₂CO₃</td><td>5</td><td>150 (0)</td></tr><tr><td>CuBr₂</td><td>10</td><td>2,6-(<i>t</i>-Bu)₂C₅H₃N</td><td>5.5</td><td>150 (0)</td></tr><tr><td>CuBr₂</td><td>10</td><td>phenothiazine</td><td>25</td><td>150 (0)</td></tr><tr><td>CuBr₂</td><td>10</td><td>TEMPO</td><td>5</td><td>150 (0)</td></tr><tr><td>CuBr₂</td><td>10</td><td>CaH₂</td><td>10</td><td>150 (32)</td></tr><tr><td>CuBr₂</td><td>10</td><td>hydroquinone</td><td>5</td><td>150 (23)</td></tr><tr><td>CuBr₂</td><td>10</td><td>benzoquinone</td><td>5</td><td>150 (0)</td></tr><tr><td>CuBr₂</td><td>10</td><td>PhSiMe₃</td><td>100</td><td>150 (0)</td></tr><tr><td>CuBr₂</td><td>10</td><td>Me₂O•HBF₄</td><td>5</td><td>150 (90)</td></tr><tr><td>Me₂O•HBF₄</td><td>0</td><td>—</td><td>—</td><td>150 (50)</td></tr></table>						Catalyst	x	Additive	y	Temp (°)	CuBr	5	—	—	100 (57)	CuBr	5	—	—	150 (82)	CuBr ₂	10	—	—	100 (96)	CuBr ₂	10	Cs ₂ CO ₃	5	150 (0)	CuBr ₂	10	2,6-(<i>t</i> -Bu) ₂ C ₅ H ₃ N	5.5	150 (0)	CuBr ₂	10	phenothiazine	25	150 (0)	CuBr ₂	10	TEMPO	5	150 (0)	CuBr ₂	10	CaH ₂	10	150 (32)	CuBr ₂	10	hydroquinone	5	150 (23)	CuBr ₂	10	benzoquinone	5	150 (0)	CuBr ₂	10	PhSiMe ₃	100	150 (0)	CuBr ₂	10	Me ₂ O•HBF ₄	5	150 (90)	Me ₂ O•HBF ₄	0	—	—	150 (50)
Catalyst	x	Additive	y	Temp (°)																																																																							
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 TsNH ₂		AgOTf (x mol %), solvent		x Solvent 2 C ₇ H ₈ 5 neat	429																																																																						
				Temp (°) 85 90 0.5'		Time (h) 14 (38) 0.5' (77)																																																																					

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

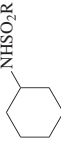
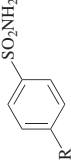
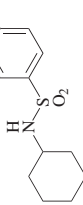
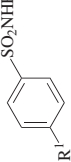
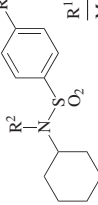
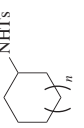
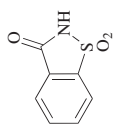
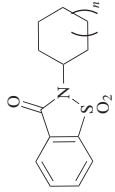
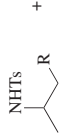
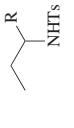
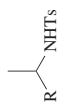
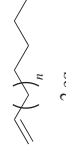
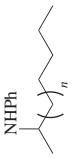
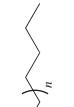
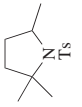
	RSO_2NH_2	$\text{Pt}(\text{COD})(\text{OTf})_2$ (10 mol %), 1,2-dichlorobenzene		R	Temp (°)	Time (h)	
				Me	110	30	(95) 93
				Ph	90	12	(95)
				4-ClC ₆ H ₄	90	12	(95)
				4-MeOC ₆ H ₄	90	12	(95)
				4-CF ₃ C ₆ H ₄	90	12	(95)
		TsOH (5 mol %), C ₇ H ₈ , 85°, overnight		R	Temp (°)	Time (h)	
				MeO	(95)		134
				Me	(85)		
		Ph_3PAuCl (5 mol %), AgOTf (5 mol %), C ₇ H ₈		R ¹ R ²	Temp (°)	Time (h)	
				MeO H	85	15	(89) 133
				Me H	85	15	(90)
				Me Me	95	44	(56)
	RNHTs	Ph_3PAuCl (5 mol %), AgOTf (5 mol %), DCE, MW, 140°		R	Time (min)		
				H	40	(86)	202
				Et	60	(50)	
	TsNH_2	TsOH (1 mol %), C ₇ H ₈ , 85°, 22 h		n			
				1	(58)		135
				3	(88)		

TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (*Continued*)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)				Refs.
C ₆₋₈  4 eq	TsNH ₂	((PhO) ₃ PAuCl/AgOTf (x mol %), C ₇ H ₈ , 85°, 24 h		$\begin{matrix} n & x \\ 1 & 2 & (64) \\ 3 & 1 & (75) \end{matrix}$			285
		PMA/SiO ₂ (10 mol %), C ₇ H ₈ , 120°		$\begin{matrix} n & \text{Time (h)} \\ 1 & 4 & (40) \\ 3 & 3.5 & (40) \end{matrix}$			425
C ₆₋₉  2 eq	RNHTs	Ga (5 mol %), I ₂ (7.5 mol %), 105°, 2 h	 + 	$\begin{matrix} R & I + II & I/II \\ n\text{-Pr} & (81) & 59:41 \\ Ph & (32) & I \text{ only} \end{matrix}$			426
C ₆₋₁₄  4 eq	TsNH ₂	PMA/SiO ₂ (10 mol %), C ₇ H ₈ , 120°		$\begin{matrix} R & \text{Time (h)} \\ n\text{-Bu} & 1.3 & (96) \\ n\text{-C}_6\text{H}_{13} & 1.2 & (95) \\ c\text{-C}_6\text{H}_{13} & 1.3 & (93) \\ n\text{-C}_{12}\text{H}_{25} & 1.3 & (92) \end{matrix}$			425
C ₇₋₈  2 eq	PhNH ₂	Pr(OTf) ₃ (2 mol %), I ₂ (6 mol %), n-Bu ₄ PI, 160°, 36 h	 + 	$\begin{matrix} n & I & II \\ 1 & (79) & (5) \\ 2 & (79) & (5) \end{matrix}$			424
C ₇ 	TsNH ₂	Ph ₃ PAuCl (5 mol %), AgOTf (5 mol %), C ₇ H ₈ , 95°	 (90)				133

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

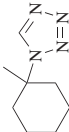
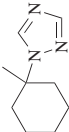
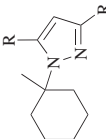
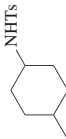
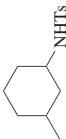
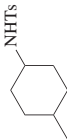
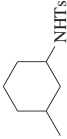
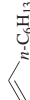
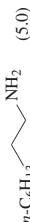
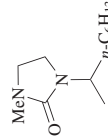
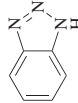
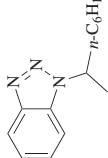
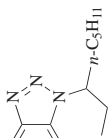
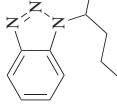
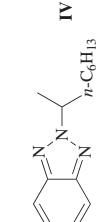
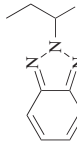
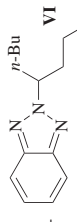
 5 eq ^g		TfOH (20 mol %), PhCO ₂ Me (1.8 eq), EtOAc, UV, 24–48 h	 (74)	428																																																																				
		TfOH (20 mol %), PhCO ₂ Me (1.8 eq), EtOAc, UV, 24–48 h	 (68)	428																																																																				
 5 eq ^g		TfOH (20 mol %), PhCO ₂ Me (1.8 eq), EtOAc, UV, 24–48 h		428																																																																				
<table> <tr> <th>x</th><th>Acid</th><th>Sensitizer</th><th>Solvent</th><th></th></tr> <tr> <td>0.2</td><td>TfOH</td><td>PhCO₂Me</td><td>EtOAc</td><td>(23)</td></tr> <tr> <td>0.2</td><td>TfOH</td><td>PhCO₂Me</td><td>EtOAc</td><td>(72)^g</td></tr> <tr> <td>1</td><td>AcOH</td><td>PhCO₂Me</td><td>EtOAc</td><td>(—)</td></tr> <tr> <td>1</td><td>TfOH</td><td>PhCO₂Me</td><td>EtOAc</td><td>(22)</td></tr> <tr> <td>1</td><td>TfOH</td><td>PhCO₂Me</td><td>dioxane</td><td>(26)</td></tr> <tr> <td>1</td><td>CF₃CO₂H</td><td>PhCO₂Me</td><td>EtOAc</td><td>(7)</td></tr> <tr> <td>2</td><td>TfOH</td><td>PhCO₂Me</td><td>EtOAc</td><td>(18)</td></tr> <tr> <td>7.6</td><td>—</td><td>4-xylene</td><td>dioxane</td><td>(—)</td></tr> <tr> <td>7.6</td><td>AcOH</td><td>4-xylene</td><td>dioxane</td><td>(4)</td></tr> <tr> <td>7.6</td><td>TfOH</td><td>4-xylene</td><td>dioxane</td><td>(13)</td></tr> <tr> <td>7.6</td><td>TfOH</td><td>4-xylene</td><td>EtOAc</td><td>(5)</td></tr> <tr> <td>7.6</td><td>TfOH</td><td>PhCO₂Me</td><td>dioxane</td><td>(14)</td></tr> </table>	x	Acid	Sensitizer	Solvent		0.2	TfOH	PhCO ₂ Me	EtOAc	(23)	0.2	TfOH	PhCO ₂ Me	EtOAc	(72) ^g	1	AcOH	PhCO ₂ Me	EtOAc	(—)	1	TfOH	PhCO ₂ Me	EtOAc	(22)	1	TfOH	PhCO ₂ Me	dioxane	(26)	1	CF ₃ CO ₂ H	PhCO ₂ Me	EtOAc	(7)	2	TfOH	PhCO ₂ Me	EtOAc	(18)	7.6	—	4-xylene	dioxane	(—)	7.6	AcOH	4-xylene	dioxane	(4)	7.6	TfOH	4-xylene	dioxane	(13)	7.6	TfOH	4-xylene	EtOAc	(5)	7.6	TfOH	PhCO ₂ Me	dioxane	(14)	<table> <tr> <td>R</td><td></td></tr> <tr> <td>H</td><td>(72)</td></tr> <tr> <td>Me</td><td>(47)</td></tr> </table>	R		H	(72)	Me	(47)
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TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (*Continued*)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.										
Please refer to the charts preceding the tables for structures indicated by the bold numbers.														
 4 eq		InBr ₃ (20 mol %), C ₇ H ₈ , 120°, 16 h	 I +  II I + II (65), I/II = 77:23	330										
		Zr(OTf) ₄ (5 mol %), C ₇ H ₈ , 85°, 24 h	 I +  II I + II (64), I/II = 1:1	422										
 2 eq	NH ₃ (10 eq)	Acetone (0.5 eq), UV (Hg), 8°, 5 h	 (5.0)	409										
		Catalyst (5 mol %), AgZ (5 mol %), dioxane, 100°, 24 h	 Catalyst Z 1a OTf (38) 1a SbF ₆ (96) 1b OTf (34) 1c OTf (16) 1d OTf (33)	126										
	 1.5 eq		TsOH•H ₂ O (x mol %), 80°, 20 h	 I +  II	139									
			x	<table><tr><th>I-III</th><th>I/II/III</th><th>IV-VI</th><th>IV/V/VI</th></tr><tr><td>10 (25)</td><td>I only</td><td>(20)</td><td>IV only</td></tr><tr><td>100 (30)</td><td>44:35:21</td><td>(28)</td><td>44:34:22</td></tr></table>  +  IV +  V +  VI	I-III	I/II/III	IV-VI	IV/V/VI	10 (25)	I only	(20)	IV only	100 (30)	44:35:21
I-III	I/II/III	IV-VI	IV/V/VI											
10 (25)	I only	(20)	IV only											
100 (30)	44:35:21	(28)	44:34:22											

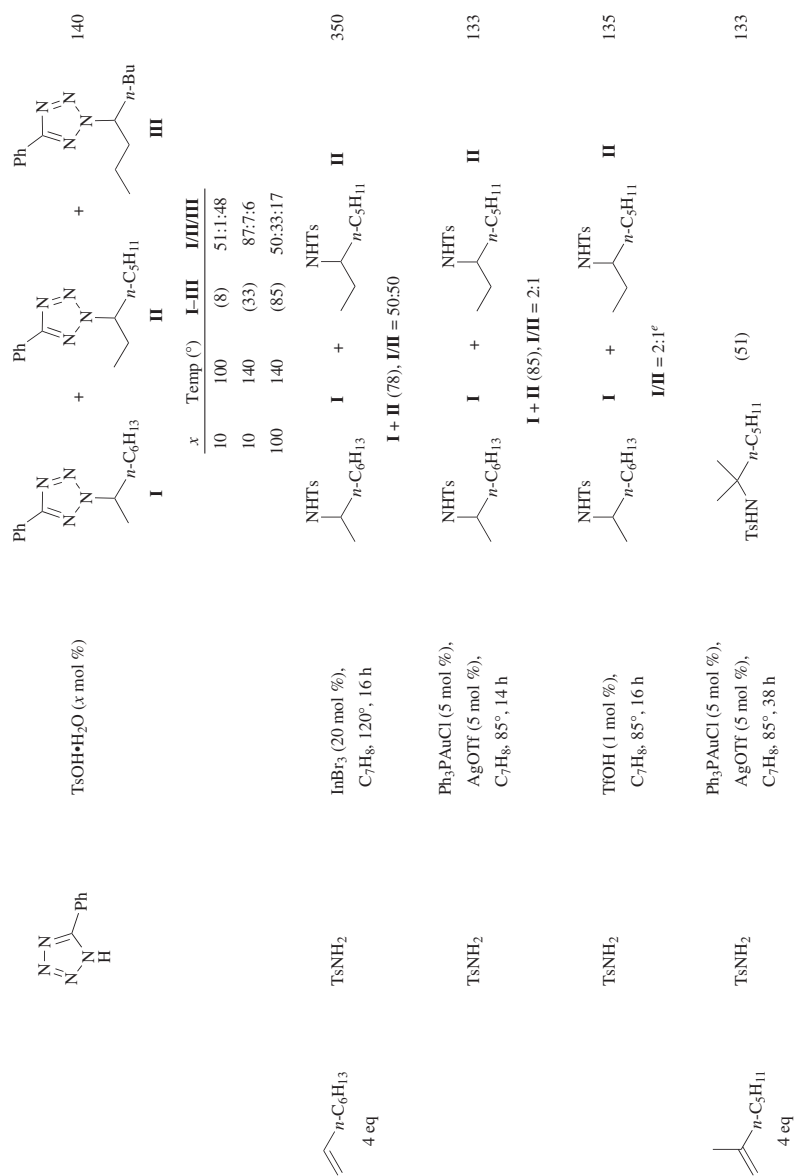
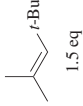
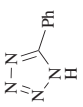
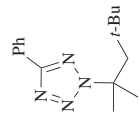
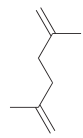
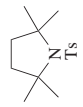
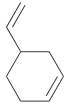
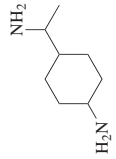
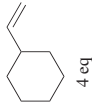
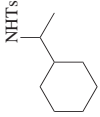
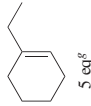
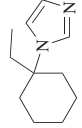
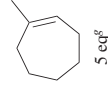
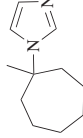


TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (*Continued*)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>				
 1.5 eq		TsOH•H ₂ O (10 mol %), 140°	 (90)	140
	TsNH ₂	Ph ₃ PAuCl (5 mol %), AgOTf (5 mol %), C ₇ H ₈ , 95°	 (80)	133
	NH ₃ (4 eq)	Zeolite catalyst		97
 4 eq	TsNH ₂	Catalyst (5 mol %), AgSbF ₆ (x mol %), DPPE (5 mol %), TCE	 NHT's	427
 5 eq ^g		TfOH (20 mol %), PhCO ₂ Me (1.8 eq), EtOAc, UV, 24–48 h	 (40)	428
 5 eq ^g		TfOH (20 mol %), PhCO ₂ Me (1.8 eq), EtOAc, UV, 24–48 h	 (45)	428

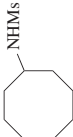
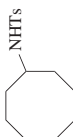
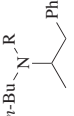
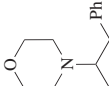
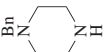
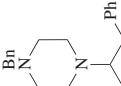
	MsNH ₂	PMA/SiO ₂ (10 mol %), C ₇ H ₈ , 120°		Time (h) 1.5 (94) 2.5 (92) 3.0 (90) 6.0 (80)	425																				
	TsNH ₂	Ph ₃ PAuCl (5 mol %), AgOTf (5 mol %), C ₇ H ₈ , 85°, 20 h		(83)	133																				
	<i>n</i> -BuNHR	<i>n</i> -BuLi (20 mol %), TMEDA (x mol %), solvent, 20 h		<table><tr><th>R</th><th>x</th><th>Solvent</th><th>Temp (°)</th></tr><tr><td>H</td><td>0</td><td>THF</td><td>50 (62)</td></tr><tr><td>H</td><td>20</td><td>C₇H₈</td><td>100 (41)</td></tr><tr><td>Me</td><td>0</td><td>THF</td><td>rt (66)</td></tr><tr><td>Me</td><td>20</td><td>C₇H₈</td><td>50 (36)</td></tr></table>	R	x	Solvent	Temp (°)	H	0	THF	50 (62)	H	20	C ₇ H ₈	100 (41)	Me	0	THF	rt (66)	Me	20	C ₇ H ₈	50 (36)	129
R	x	Solvent	Temp (°)																						
H	0	THF	50 (62)																						
H	20	C ₇ H ₈	100 (41)																						
Me	0	THF	rt (66)																						
Me	20	C ₇ H ₈	50 (36)																						
		<i>n</i> -BuLi (20 mol %), TMEDA (x mol %), solvent, 20 h		<table><tr><th>x</th><th>Solvent</th><th>Temp (°)</th></tr><tr><td>0</td><td>THF</td><td>rt (44)</td></tr><tr><td>0</td><td>THF</td><td>50 (88)</td></tr><tr><td>20</td><td>C₇H₈</td><td>100 (38)</td></tr></table>	x	Solvent	Temp (°)	0	THF	rt (44)	0	THF	50 (88)	20	C ₇ H ₈	100 (38)	129								
x	Solvent	Temp (°)																							
0	THF	rt (44)																							
0	THF	50 (88)																							
20	C ₇ H ₈	100 (38)																							
		<i>n</i> -BuLi (20 mol %), THF, rt, 24 h		(88)	130																				

TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (*Continued*)

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₉

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)				Refs.
 x eq		<i>n</i> -BuLi (20 mol %), TMEDA (<i>y</i> mol %), solvent, 20 h	<i>x</i>	<i>y</i>	Solvent	Temp	
			1	0	THF	rt	(68)
			2	0	THF	rt	(89)
			2	0	THF	−78° to rt	(91)
			2	0	THF	50°	(85)
			2	0	THF	100°	(60)
			2	20	THF	rt	(88)
			2	0	C ₇ H ₈	rt	(20)
			2	20	C ₇ H ₈	rt	(88)
			2	20	C ₇ H ₈	rt	(60)

 2 eq

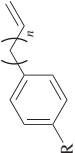


n-BuLi (30 mol %),
t-BuOK (30 mol %),
THF, 120°, 20 h

 (54)

129

C₉₋₁₀

 2 eq



Catalyst (2 mol %),
I₂ (*x* mol %), base (6 mol %),
solvent, 160°, 36 h

 **I** +  **II**

424

<i>n</i>	<i>R</i>	Catalyst	<i>x</i>	Base	Solvent	I + II	I/II
1	H	Pr(OTf) ₃	6	—	<i>n</i> -Bu ₄ PI	(56)	I only
2	H	—	6	—	<i>n</i> -Bu ₄ PI	(64)	91:9
2	H	Pr(OTf) ₃	0	—	[OMfm]Cl	(0)	—
2	H	Pr(OTf) ₃	0	—	[OMfm]BF ₄	(0)	—
2	H	Pr(OTf) ₃	0	—	<i>n</i> -Bu ₄ PBr	(22)	97:3
2	H	Pr(OTf) ₃	0	—	<i>n</i> -Bu ₄ PI	(71)	93:7
2	H	Pr(OTf) ₃	0	2,6-(<i>t</i> -Bu) ₂ C ₅ H ₃ N	<i>n</i> -Bu ₄ PI	(40)	96:4
2	H	Pr(OTf) ₃	0	Et ₃ N	<i>n</i> -Bu ₄ PI	(60)	95:5
2	H	Pr(OTf) ₃	6	—	DMF	(0)	—

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (*Continued*)

Refs.

Product(s) and Yield(s) (%)

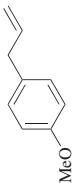
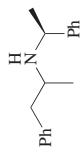
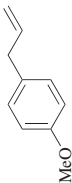
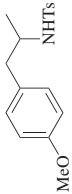
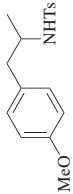
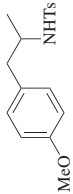
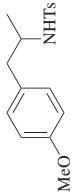
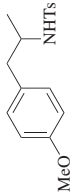
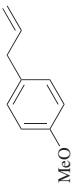
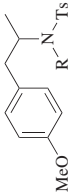
Alkene

Amine

Conditions

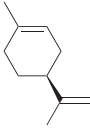
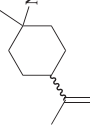
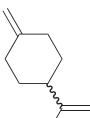
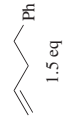
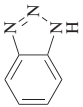
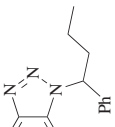
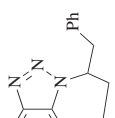
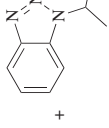
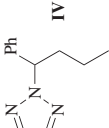
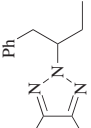
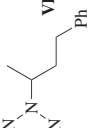
Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

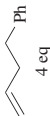
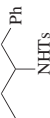
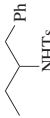
C₉

	TsNH ₂	<i>n</i> -BuLi (20 mol %), AgSbF ₆ (x mol %), DPPE (5 mol %), TCE		Catalyst	x	Temp (°)	Time (h)	427
				CuBr	5	100	20 (21)	
				CuBr	5	150	20 (25)	
				CuBr ₂	10	100	48 (88)	
		<i>n</i> -BuLi (20 mol %), TMEDA (x mol %), solvent, 50°, 20 h		x		Solvent		129
					0	THF	(65)	
					20	C ₇ H ₈	(22)	
		<i>n</i> -BuLi (20 mol %), TMEDA (20 mol %), solvent, 20 h		Solvent		Temp (°)	% de ^b	129
				THF		50	8 (32)	
				C ₇ H ₈		100	0 (36)	
	TsNH ₂	InBr ₃ (20 mol %), C ₇ H ₈ , 120°, 16 h		(78)				330
	TsNH ₂	Catalyst (5 mol %), C ₇ H ₈			+			285
	RNHTs	Ph ₃ PAuCl (5 mol %), AgOTf (5 mol %), C ₇ H ₈ , 85°		Catalyst		Temp (°)	I + II I/II	133
				((PhO) ₃ P)AuCl/AgOTf	85	24	(99) 10:1	
				((PhO) ₃ P)AuCl/AgOTf	90	0.5 ^f	(91) 10:1	
				TiOH	90	0.5 ^f	(75) 4:1	
				R		Time (h)		
				H		14	(95)	
				Me		48	(55)	

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

TABLE 1A. HYDROAMINATION OF SIMPLE ALKENES (*Continued*)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.								
Please refer to the charts preceding the tables for structures indicated by the bold numbers.												
 x eq		TfOH (20 mol %), PhCO ₂ Me (1.8 eq), EtOAc, UV	 I +  II	428								
			<table><tr><th>x</th><th>I + II</th><th>I/II</th><th>dr I^b</th></tr><tr><td>5^g</td><td>(81)</td><td>I only</td><td>—</td></tr><tr><td>1</td><td>(85)</td><td>35:65</td><td>1.3:1</td></tr></table>		x	I + II	I/II	dr I ^b	5 ^g	(81)	I only	—
x	I + II	I/II	dr I ^b									
5 ^g	(81)	I only	—									
1	(85)	35:65	1.3:1									
 1.5 eq		TsOH•H ₂ O (x mol %), 80°, 20 h	 I +  II	139								
			<table><tr><th>x</th><th>I–VI</th><th>I/II/III/IV/V/VI</th></tr><tr><td>10</td><td>(65)</td><td>0:0:66:0:0:34</td></tr><tr><td>100</td><td>(62)</td><td>17:9:16:7:10:41</td></tr></table>		x	I–VI	I/II/III/IV/V/VI	10	(65)	0:0:66:0:0:34	100	(62)
x	I–VI	I/II/III/IV/V/VI										
10	(65)	0:0:66:0:0:34										
100	(62)	17:9:16:7:10:41										
			 III +  IV +  V +  VI									

	TsNH ₂	InBr ₃ (20 mol %), toluene, 120°		 + 	330
4 eq					
			Time (h)	I + II	I/II
			16	(41)	70:30
			40	(60)	65:35
	TsNH ₂	H-mont (0.1 g/1 mmol amide), heptane, 150°, 12 h		 + 	127
				I + II (48), I/II = 3:1	
	PhNH ₂	PtBr ₂ (0.3 mol %), <i>n</i> -Bu ₄ PBr (18 mol %), [PhNH ₃]HSO ₄ (0.8 mol %), 150°, 96 h		 + 	131
				I + II (5.6), I/II = 95:5	

^a The reaction was carried out in an O₂ atmosphere.

^b GHSV is measured in (cm³ gas at standard temperature and pressure)/(cm³ catalyst h⁻¹).

^c GHSV is measured in (liter educt)/(g catalyst h).

^d The product was isolated as the *N,N*-dibenzoyl derivative.

^e The yield was not reported.

^f The reaction was carried out under microwave heating (70 W, 10 psi) with air stream cooling.

^g The alkene was added in portions.

^h The relative configuration was not reported.

TABLE 1B. HYDROAMINATION OF VINYL ARENES

Arene	Amine	Conditions	Product(s) and Yield(s) (%)		Refs.
C ₇₋₉ Ar-CH=CH ₂ 4 eq	Me ₂ NH	[Rh(COD)(DPE-phos)]BF ₄ (5 mol %), solvent, 70°	Ar-CH ₂ -CH ₂ -NMe ₂ I + Ar-CH=CH-NMe ₂ II	244	
			Ar		
			Solvent		
			Time (h)		
C ₇₋₁₂ Ar-CH=CH ₂ 2 eq	<i>n</i> -PrNH ₂	Cp* ₂ LaCH(TMS) ₂ (5 mol %), C ₆ D ₆	4-C ₃ H ₄ N	48	90:10
			3,4-(MeO) ₂ C ₆ H ₃	72	82:19
			4-MeC ₆ H ₄	72	54:46
			Ar	Temp (°)	
C ₈ Ph-CH=CH ₂ 1.5 eq	RNH ₂	Na (1 wt %), 150–200°	Ar-CH ₂ -CH ₂ -NHR	90	(—)
			Ph	90	(90)
			Me	120	(88)
			<i>n</i> -Pr	90	(82)
C ₈	RNH ₂	Na (1 wt %), 150–200°	4-MeOC ₆ H ₄	90	(30)
			4-Me ₂ NC ₆ H ₄	90	(85)
			4-MeSC ₆ H ₄	90	(93)
			4-MeC ₆ H ₄	90	(92)
			2-naphthyl	90	(92)
			R	Temp (°)	
			H	90	(8)
			Me	100	(10)
			<i>n</i> -Pr	180	(18)
			Me ₂ N(CH ₂) ₂	400	(40)
			Me ₂ N(CH ₂) ₃	250	(25)
			MeO(CH ₂) ₃	200	(20)
C ₈	RNH ₂	Na (1 wt %), 150–200°	<i>n</i> -BuO(CH ₂) ₃	250	(25)
			H ₂ N(CH ₂) ₆	400	(40)
			<i>c</i> -C ₆ H ₁₁	300	(30)
			Ph	700	(70)
C ₈	RNH ₂	Na (1 wt %), 150–200°	Bn	300	(30)
			BnCH ₂	300	(30)

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

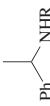
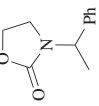
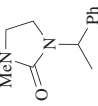
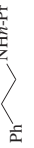
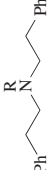
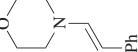
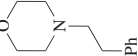
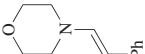
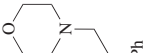
 2 eq	RNH ₂	<i>n</i> -BuLi (5 mol %), cyclohexane, 16 h		R		Temp (°)
				H	rt	(—)
				<i>n</i> -Pr	50	(33)
				<i>n</i> -Bu	50	(47)
				<i>n</i> -C ₅ H ₁₁	50	(32)
				R		Time (h)
				Ms	1.3	(95)
		PMA/SiO ₂ (10 mol %), C ₇ H ₈ , 120°		Ts	1.2	(96)
				R		Time (h)
				Ms	1.3	(95)
		[BSPy][OTf] (20 mol %), C ₇ H ₈ , 85°, 24 h		Ts	1.2	(96)
				R		Time (h)
				Ms	1.3	(95)
		2 (5 mol %), AgSbF ₆ (5 mol %), dioxane, 100°, 36 h		Ts	1.2	(96)
				R		Time (h)
				Ms	1.3	(95)
		3a (10 mol %), C ₆ D ₆		Ts	1.2	(96)
				R		Time (h)
				Ms	1.3	(95)
		4 (3 mol %) C ₆ D ₆ , 60°, 53 h		Ts	1.2	(96)
				R		Time (h)

TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Arene	Amine	Conditions	Product(s) and Yield(s) (%)			Refs.
C_8  1.5 eq	RNH ₂	Na (10 mol %), neat	 I +  II			223
			R	Temp (°)	Time (h)	
			<i>n</i> -Bu	46	3.0	
			<i>s</i> -Bu	60	4.3	
	 x eq	[Rh(diene) ₂]BF ₄ (y mol %), ligand (2y mol %), THF, reflux, 20 h	 I +  II +  III			243
			R	Temp (°)	Time (h)	
			<i>n</i> -Bu	46	3.0	
			<i>s</i> -Bu	60	4.3	
			<i>i</i> -Bu	65	4.1	30:70
			<i>t</i> -Bu	45	3.9	
					(24)	
					49:51	
x	Diene	Ligand	y	I + II	III	I/II
2	NBD	(4-FC ₆ H ₄) ₃ P	0.5	(13)	(15)	I only
2	NBD	(4-MeOC ₆ H ₄) ₃ P	0.5	(26)	(25)	5.5:1
2	NBD	(4-MeOC ₆ H ₄) ₃ P	1	(53)	(90)	6.5:1
2	COD	PPh ₃	1	(27)	(22)	8:1
2	COD	Ph ₂ P-pyridyl	1	(tr)	(tr)	—
4	COD	PPh ₃	2.5	(88)	(84)	5.3:1
4	COD	(4-FC ₆ H ₄) ₃ P	2.5	(29)	(29)	I only
4	COD	PPh ₃	2.5	(—)	(tr)	—
4	COD	2-MeOC ₆ H ₄ PPh ₂	2.5	(tr)	(tr)	—
4	COD	2-EtOC ₆ H ₄ PPh ₂	2.5	(2)	(2)	I only
4	COD	2-PhOC ₆ H ₄ PPh ₂	2.5	(58)	(49)	10.6:1
4	COD	2,6-(MeO) ₂ C ₆ H ₃ PPh ₂	2.5	(tr)	(tr)	—
4	COD	4-MeOC ₆ H ₄ PPh ₂	2.5	(52)	(54)	7.7:1
4	COD	(4-MeOC ₆ H ₄) ₂ PPh	2.5	(62)	(65)	9.3:1

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.



4	COD	P(<i>n</i> -Bu) ₃	2.5	(56)	(61)	I only
4	COD	P(<i>c</i> -C ₆ H ₁₁) ₃	2.5	(tr)	(tr)	—
4	COD	PMe ₃	2.5	(17)	(18)	I only
4	COD	DPPE	2.5	(tr)	(tr)	—
 [Rh(COD)₂]BF₄ (2.5 mol %), PPh₃ (5 mol %), additive (y mol %), solvent, 20 h  I + II + III  II + III  III 243						

x	Additive	y	Solvent	Temp (°)	I + II	III	I/II
0.25	—	—	THF	65	(53)	(35)	2.5:1
4	—	—	THF	65	(88)	(84)	5.3:1
4	HBE ₄	10	THF	65	(40)	(33)	4.7:1
4	HBE ₄	10	C ₇ H ₈	140	(11)	(82)	0.8:1
4	HBE ₄	20	C ₇ H ₈	140	(6)	(72)	0.2:1
4	<i>t</i> -BuOK	25	THF	65	(tr)	(tr)	0.1:1
4	DIPEA	5	THF	65	(86)	(78)	6.8:1
4	DIPEA	100	THF	65	(82)	(85)	15.4:
4	DIPEA	200	THF	65	(79)	(83)	12.1:1

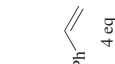
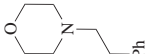
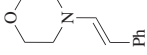
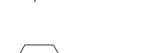
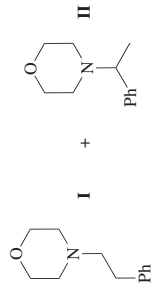
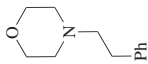
 4 eq	 I	+	 II	 I	x	I	II
[Rh(COD)₂]BF₄ (5 mol %), ligand (x mol %), C₇H₈, 70°, 48 h							
Ligand					5	(62)	(20)
DPE-phos					5	(—)	(1)
DPPE					5	(—)	(—)
DPPB					5	(1)	(1)
DPPP					5	(tr)	(9)
XANTPHOS					5	(3)	(40)
DBF-phos					5	(—)	(—)
BIPHEP					10	(17)	(78)
PPh ₃					5	(—)	(—)
					244		

TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Arene	Amine	Conditions	Product(s) and Yield(s) (%)						Refs.	
 2 eq		[Ru(COD)(methylallyl)₂] (x mol %), ligand (y mol %), acid (z mol %), dioxane, 100°, 24 h							240	
			x	Ligand	y	Acid	z	I	II	
			2	DPPP	3	TfOH	5	(90)	(tr)	
			5	—	—	TfOH	10	(—)	(tr)	
			5	DPPP	7	—	—	(—)	(—)	
			5	DPPP	7	TFA	10	(8)	(—)	
			5	DPPP	7	TfOH	10	(96)	(tr)	
			5	PPh ₃	14	TfOH	10	(36)	(9)	
			5	PEtPh ₂	14	TfOH	10	(61)	(3)	
			5	DPPB	7	TfOH	10	(54)	(12)	
			5	DPPH	7	TfOH	10	(33)	(2)	
			5	DPPF	7	TfOH	10	(55)	(44)	
			5	DPE-phos	7	TfOH	10	(19)	(2)	
		5 (5 mol %), dioxane, 100°							241	
			Time (h)							
			0.25							
			(22)							
			0.5							
			(40)							
			1							
			(64)							
			2							
			(80)							
			5							
			(96)							

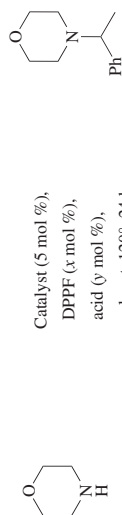
Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₈

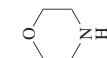
Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₈

	Catalyst	Time (min)	
	6a	15 (10)	
Catalyst (5 mol %), dioxane, 100°	6a	30 (32)	241
	6a	60 (56)	
	6a	120 (77)	
	6a	300 (94)	
	6a	350 ^b (50)	
	6b	103 ^b (50)	



Catalyst (5 mol %),
DPPF (x mol %),
acid (y mol %),
solvent, 120°, 24 h



Catalyst	x	Acid	y	Solvent	
—	0	TfOH	20	dioxane	(1)
Pd(DPPF)(OTf) ₂	0	—	—	dioxane	(1)
Pd(PPh ₃) ₄	0	TfOH	20	dioxane	(6)
Pd(O ₂ CCF ₃) ₂	0	TfOH	20	dioxane	(1)
Pd(DPPF)(OTf) ₂	5	TfOH	10	dioxane	(74)
Pd(O ₂ CCF ₃) ₂	5	TfOH	20	dioxane	(2)
Pd(O ₂ CCF ₃) ₂	10	—	—	dioxane	(2)
Pd(O ₂ CCF ₃) ₂	10	TfOH	20	dioxane	(79)
Pd(O ₂ CCF ₃) ₂	10	TfOH	20	toluene	(25)
Pd(O ₂ CCF ₃) ₂	10	TFA	20	dioxane	(19)
Pd(O ₂ CCF ₃) ₂	10	NFA	20	C ₇ H ₈	(72)
Pd(O ₂ CCF ₃) ₂	10	NFA	20	dioxane	(67)

TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Arene	Amine	Conditions	Product(s) and Yield(s) (%)					Refs.				
C ₈			<i>n</i>	Z	x	Temp	Time (h)	44				
			1	CH ₂	5	120°	1.5 (82)					
			1	CH ₂	5	rt	107 (79)					
			2	CH ₂	5	120°	1 (62)					
			2	CH ₂	5	rt	371 (68)					
			2	O	2	120°	3.2 (61)	44				
			2	O	5	rt	107 (96)					
			R									
			Et									
			MeOCH ₂ CH ₂									
			Bn					(39)	224			
			R	Solvent		Time (h)						
			Et	cyclohexane		23	(57)					
			Et	THF		4	(58)					
			<i>n</i> -Pr	cyclohexane		16	(47)					
			<i>n</i> -C ₉ H ₁₉					(41)	224			
			Ph-CH ₂ -CH ₂ -N(Me)- <i>n</i> -Bu (70)									
			<i>n</i> -BuLi (5 mol %), cyclohexane, 50°, 16 h									
			Na (1 wt %), 150–200°									
			(81)									
			Solvent					222				
			cyclohexane (81)									
			THF (82)									
			(81)									
			(82)									

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

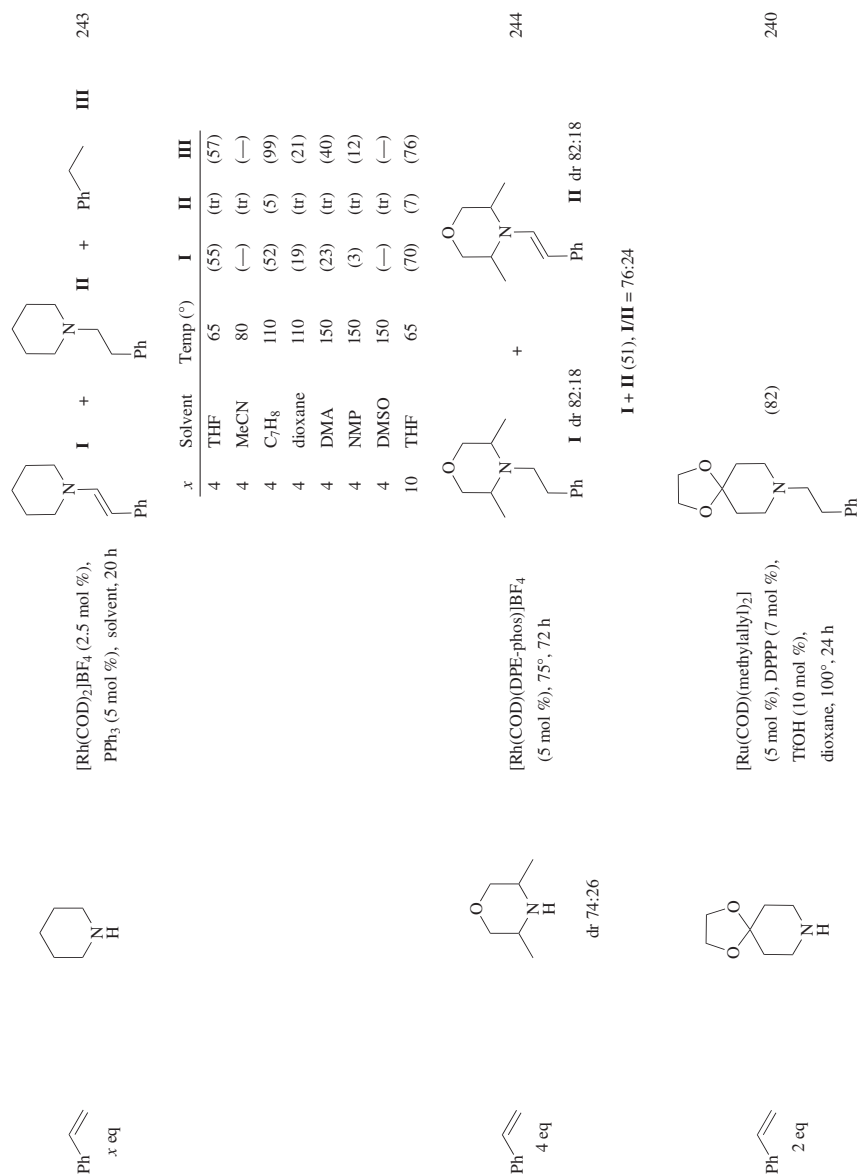
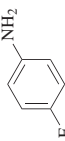
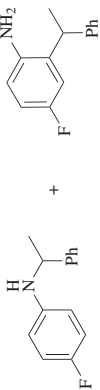
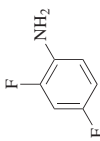
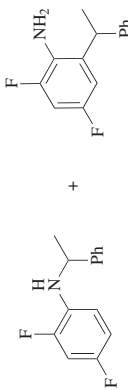


TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Arene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the bold numbers.				
 1.5 eq	PhNH ₂	8 (2 mol %), TFA (20 mol %), C ₇ H ₈ , 100°, 24 h	 (15)	430
	PhNH ₂	Catalyst (2 mol %), ligand (x mol %), acid (20 mol %), C ₇ H ₈ , 100°, 6 h		231
			(DPPF)Pd(OTf) ₂ — — — (96)	(—)
			Pd(PPh ₃) ₄ — — — (—)	(67)
			Pd(PPh ₃) ₄ — — — TFA	(83)
 1.5 eq	PhNH ₂	Pd(O ₂ CCF ₃) ₂ — — — (78)	3 — (99)	
		Pd(O ₂ CCF ₃) ₂ — — — (99)	3 TiOH — (28)	(68)
		Pd(O ₂ CCF ₃) ₂ — — — (28)	8 — TFA	(90)
		Pd(O ₂ CCF ₃) ₂ — — — (90)	8 TiOH — (28)	239
		Pd(DPPF)(CF ₃ CO ₂) ₂ /TFA/ [EMIM][OTf]/SiO ₂ (0.2 g/20 mmol aniline), octane, 125°		
	PhNH ₂ (2 eq)	9c (2 mol %), C ₇ H ₈ , 100°, 10 h	 (90)	232
	PhNH ₂ (x eq)	Catalyst (y mol %), THF, 20 h	 NHPh	227
		x Catalyst y Temp (°)		
		1 <i>n</i> -BuLi 10 100 (—)		227
		1 <i>n</i> -BuLi/K ₂ CO ₃ 10 120 (69)		
		1 <i>t</i> -BuOK 10 120 (85)		
		1 <i>t</i> -BuOLi 10 100 (—)		
		1 <i>t</i> -BuONa 10 100 (—)		
		1 K ₂ CO ₃ 10 100 (—)		
		2 <i>t</i> -BuOK 5 120 (96)		
		5 <i>t</i> -BuOK 10 120 (99)		

PhNH ₂ (3 eq)	[(PEt ₃) ₂ RhCl] (1 mol %), PhNH ₂ Li (10 mol %), 70°, 12 d		132
PhNH ₂ (x eq)	HI (5 mol %), C ₇ H ₈		143
PhNH ₂	Pd(OTf) ₂ , [EMIM][OTf], SiO ₂ , 240°		235

TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Arene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																																
 x eq	 (2 eq)	TiCl ₄ (20 mol %), C ₇ H ₈ , 170°, MW, 3 h	 I I + II (68), I/II = 32:68 II	247																																
	 (2 eq)	TPA (30 mg/1 mmol alkene), neat, 80°, 6 h	 I I + II (85), I/II = 52:48 II	249																																
 x eq	PhSO ₂ NH ₂	Bi(OTf) ₃ (y mol %), additive (10 mol %), dioxane	<table><tr><th>x</th><th>y</th><th>Additive</th><th>Temp</th></tr><tr><td>1.2</td><td>0</td><td>[Cu(CH₃CN)₄]PF₆</td><td>π (—)</td></tr><tr><td>1.2</td><td>10</td><td>—</td><td>π (21)</td></tr><tr><td>1.2</td><td>10</td><td>KPF₆</td><td>π (54)</td></tr><tr><td>1.2</td><td>10</td><td>[Cu(CH₃CN)₄]PF₆</td><td>π (62)</td></tr><tr><td>1.2</td><td>10</td><td>NH₄PF₆</td><td>π (44)</td></tr><tr><td>2</td><td>10</td><td>[Cu(CH₃CN)₄]PF₆</td><td>π (78)</td></tr><tr><td>2</td><td>10</td><td>[Cu(CH₃CN)₄]PF₆</td><td>40° (91)</td></tr></table>	x	y	Additive	Temp	1.2	0	[Cu(CH ₃ CN) ₄]PF ₆	π (—)	1.2	10	—	π (21)	1.2	10	KPF ₆	π (54)	1.2	10	[Cu(CH ₃ CN) ₄]PF ₆	π (62)	1.2	10	NH ₄ PF ₆	π (44)	2	10	[Cu(CH ₃ CN) ₄]PF ₆	π (78)	2	10	[Cu(CH ₃ CN) ₄]PF ₆	40° (91)	
x	y	Additive	Temp																																	
1.2	0	[Cu(CH ₃ CN) ₄]PF ₆	π (—)																																	
1.2	10	—	π (21)																																	
1.2	10	KPF ₆	π (54)																																	
1.2	10	[Cu(CH ₃ CN) ₄]PF ₆	π (62)																																	
1.2	10	NH ₄ PF ₆	π (44)																																	
2	10	[Cu(CH ₃ CN) ₄]PF ₆	π (78)																																	
2	10	[Cu(CH ₃ CN) ₄]PF ₆	40° (91)																																	

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C₈

C₈₋₉

R^1
 $\text{Ph}-\text{C}(\text{R}^2)=\text{CH}_2$
 3 eq

PhSO₂NH₂

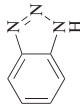
7 (4 mol %), AgBF₄ (4 mol %),
 toluene, 120°, 16 h

R^1 NHSO₂Ph
 $\text{Ph}-\text{C}(\text{R}^2)=\text{CH}_2$
 H H (65)
 H Me (50)
 Me H (90)

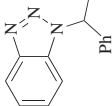
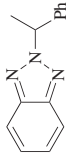
431

C₈

$\text{Ph}-\text{CH}=\text{CH}_2$
 1.5 eq



TsOH•H₂O (x mol %),
 80°, 12 h


I +  **II**

139

$\times$ **I + II** **I/II**
 10 (46) 87:13
 100 (50) 65:35

$\text{Ph}-\text{CH}=\text{CH}_2$

PhNHR

CsOH•H₂O (20 mol %),
 NMP, 120°, 12 h

R
 $\text{Ph}-\text{CH}(\text{R})-\text{CH}_2-\text{Ph}$
 H (69)
 Me (42)

229

NHR^2
 $\text{Ph}-\text{C}(\text{R}^1)=\text{CH}_2$
 (10 eq)

t-BuOK (1 eq), MW

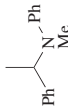
R^1 R^2 Time (min)
 H H 10 (81)
 H H₂N 1.5 (85)
 Me H 10 (56)

228

$\text{Ph}-\text{CH}=\text{CH}_2$
 10 eq

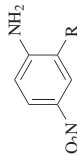
PhNHMe

(*t*-BuXANTPHOS)Pd(OTf)₂
 (5 mol %), C₇H₈, 80°

 (87)

236

$\text{Ph}-\text{CH}=\text{CH}_2$



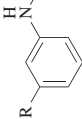
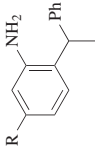
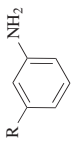
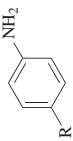
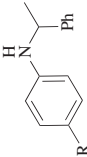
FeCl₃•6H₂O (10 mol %),
 DCE, 80°

R
 $\text{Ph}-\text{CH}(\text{R})-\text{CH}_2-\text{Ph}$
 H (70)
 Me (41)

248

TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

Arene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																																																							
C ₈		TPA (30 mg/1 mmol alkene), neat, 80°	 I +  II 249																																																								
		2 eq	<table> <tr> <th>R</th><th>Time (h)</th><th>I + II</th><th>I/II</th></tr> <tr> <td>O₂N</td><td>5</td><td>(93)</td><td>99:1</td></tr> <tr> <td>CF₃</td><td>3</td><td>(80)</td><td>69:31</td></tr> <tr> <td>CF₃</td><td>12</td><td>(85)</td><td>1:99</td></tr> </table>	R	Time (h)	I + II	I/II	O ₂ N	5	(93)	99:1	CF ₃	3	(80)	69:31	CF ₃	12	(85)	1:99																																								
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		[Pd(L)(MeCN)(H ₂ O)](OTf) ₂ (x mol %), neat		234																																																							
		1.5 eq	<table> <tr> <th>R</th><th>L</th><th>x</th><th>Temp (°)</th><th>Time (h)</th></tr> <tr> <td>H</td><td>DPPF</td><td>0.25</td><td>100</td><td>18 (100)</td></tr> <tr> <td>H</td><td>DPPF</td><td>0.5</td><td>100</td><td>18 (100)</td></tr> <tr> <td>H</td><td>DPPF</td><td>2</td><td>60</td><td>21 (25)</td></tr> <tr> <td>H</td><td>DPPF</td><td>2</td><td>80</td><td>20 (90)</td></tr> <tr> <td>H</td><td>DPPF</td><td>2</td><td>100</td><td>18 (92)</td></tr> <tr> <td>H</td><td>DPPR</td><td>2</td><td>100</td><td>18 (—)</td></tr> <tr> <td>H</td><td>DPPF</td><td>2</td><td>100</td><td>18 (59)</td></tr> <tr> <td>H</td><td>DPPE</td><td>2</td><td>100</td><td>18 (11)</td></tr> <tr> <td>MeO</td><td>DPPF</td><td>2</td><td>100</td><td>18 (85)</td></tr> <tr> <td>Cl</td><td>DPPF</td><td>2</td><td>100</td><td>18 (39)</td></tr> </table>	R	L	x	Temp (°)	Time (h)	H	DPPF	0.25	100	18 (100)	H	DPPF	0.5	100	18 (100)	H	DPPF	2	60	21 (25)	H	DPPF	2	80	20 (90)	H	DPPF	2	100	18 (92)	H	DPPR	2	100	18 (—)	H	DPPF	2	100	18 (59)	H	DPPE	2	100	18 (11)	MeO	DPPF	2	100	18 (85)	Cl	DPPF	2	100	18 (39)	
R	L	x	Temp (°)	Time (h)																																																							
H	DPPF	0.25	100	18 (100)																																																							
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		ArNH ₂	<table> <tr> <th>NHAr</th><th>x</th><th>Time (h)</th></tr> <tr> <td>Ph</td><td>0</td><td>12 (83)</td></tr> <tr> <td>Ph</td><td>3</td><td>7 (99)</td></tr> <tr> <td>4-MeOC₆H₄</td><td>0</td><td>12 (93)</td></tr> <tr> <td>4-MeOC₆H₄</td><td>3</td><td>7 (78)</td></tr> <tr> <td>2-MeC₆H₄</td><td>3</td><td>7 (68)</td></tr> <tr> <td>4-CF₃C₆H₄</td><td>0</td><td>12 (64)</td></tr> <tr> <td>1-naphthyl</td><td>3</td><td>7 (88)</td></tr> </table>	NHAr	x	Time (h)	Ph	0	12 (83)	Ph	3	7 (99)	4-MeOC ₆ H ₄	0	12 (93)	4-MeOC ₆ H ₄	3	7 (78)	2-MeC ₆ H ₄	3	7 (68)	4-CF ₃ C ₆ H ₄	0	12 (64)	1-naphthyl	3	7 (88)	231																															
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		Catalyst (2 mol %), DPPF (x mol %), acid (20 mol %), C ₇ H ₈ , 100°																																																									

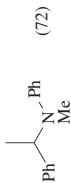
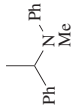
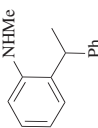
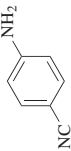
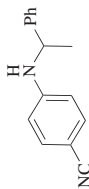
Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

$\text{Ph} \begin{array}{c} \diagup \\ \diagdown \end{array}$ 2 eq	ArNH_2	$[(\text{XANTPHOS})\text{Pd}(\eta^3\text{-allyl})]\text{OTf}$ (2 mol %), TfOH (x mol %), dioxane, 100°, 24 h	$\text{Ph} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{NHAr}$	Ar	x	x	237
				2-HOC ₆ H ₄	10	(80)	
				3-AcHNC ₆ H ₄	0	(91)	
				2-MeSC ₆ H ₄	10	(59)	
				4-MeSC ₆ H ₄	0	(88)	
				3-HO ₂ CC ₆ H ₄	10	(92)	
				2-EtO ₂ CC ₆ H ₄	10	(9)	
				3-EtO ₂ CC ₆ H ₄	10	(92)	
				4-EtO ₂ CC ₆ H ₄	10	(89)	
				2-NCC ₆ H ₄	10	(71)	
				3-NCC ₆ H ₄	10	(90)	
				4-NCC ₆ H ₄	10	(72)	
				4-H ₂ NCOC ₆ H ₄	0	(86)	
				4-HOCH ₂ CH ₂ C ₆ H ₄	10	(89)	
				3-AcC ₆ H ₄	10	(81) ^c	
				4-AcC ₆ H ₄	10	(71)	
$\text{Ph} \begin{array}{c} \diagup \\ \diagdown \end{array}$ x eq	BnNH_2	$\text{LiN}(\text{TMS})_2$ (y mol %), additive (y mol %), C ₆ D ₆ , 120°	$\text{Ph} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{NHBn}$	I + $\text{Ph} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{N} \begin{array}{c} \text{Bn} \\ \diagup \\ \diagdown \end{array} \text{Ph}$	I + II	I/II	II 44
			x y	Additive			
			0.5 2	TMEDA	(67)	20:1	
			0.5 2	(-)-sparteine	(74)	6:1	
			1 2	TMEDA	(62)	5:1	
			1.5 2	TMEDA	(73)	2.6:1	
			1.5 2	—	(44)	1.6:1	
			1.5 2.5	—	(67)	2:1	
			1.5 15	—	(51)	1.5:1	

TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₈

Arene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																						
 1.5 eq	PhNHMe	[(DPPF)Pd(MeCN)(H ₂ O)] (OTf) ₂ (2 mol %), neat, 100°, 18 h	 (72)	234																																																																						
	PhNHMe (2 eq)	TPA (30 mg/1 mmol alkene), neat	 I +  II	249																																																																						
 4 eq		Catalyst (2 mol %), ligand (x mol %), acid (y mol %), dioxane, 100°, 20 h		237																																																																						
<table> <tr> <th>Temp (°)</th><th>Time (h)</th><th>I + II</th><th>I/II</th></tr> <tr> <td>45</td><td>14</td><td>(82)</td><td>99:1</td></tr> <tr> <td>80</td><td>6</td><td>(89)</td><td>1:99</td></tr> </table>	Temp (°)	Time (h)	I + II	I/II	45	14	(82)	99:1	80	6	(89)	1:99	<table> <tr> <th>Catalyst</th><th>Ligand</th><th>x</th><th>Acid</th><th>y</th></tr> <tr> <td>—</td><td>—</td><td>—</td><td>TfOH</td><td>10 (—)</td></tr> <tr> <td>—</td><td>—</td><td>—</td><td>HBFe₄</td><td>10 (—)</td></tr> <tr> <td>(XANTPHOS)Pd(OTf)₂</td><td>—</td><td>—</td><td>—</td><td>(81)</td></tr> <tr> <td>(XANTPHOS)Pd(OTf)₂</td><td>—</td><td>—</td><td>TfOH</td><td>10 (93)</td></tr> <tr> <td>(XANTPHOS)PdCl₂</td><td>—</td><td>—</td><td>—</td><td>(—)</td></tr> <tr> <td>(DPPF)Pd(OTf)₂</td><td>—</td><td>—</td><td>—</td><td>(7)</td></tr> <tr> <td>[(XANTPHOS)Pd(MeCN)₂](OTf)₂</td><td>—</td><td>—</td><td>—</td><td>(76)</td></tr> <tr> <td>[(XANTPHOS)Pd(MeCN)₂](OTf)₂</td><td>—</td><td>—</td><td>TfOH</td><td>10 (91)</td></tr> <tr> <td>[(DPPF)Pd(MeCN)₂](OTf)₂</td><td>—</td><td>—</td><td>—</td><td>(9)</td></tr> <tr> <td>Pd(O₂-CCF₃)₂</td><td>XANTPHOS</td><td>3</td><td>TfOH</td><td>5 (66)</td></tr> <tr> <td>Pd(O₂-CCF₃)₂</td><td>DPPP</td><td>2</td><td>TfOH</td><td>20 (11)</td></tr> </table>	Catalyst	Ligand	x	Acid	y	—	—	—	TfOH	10 (—)	—	—	—	HBFe ₄	10 (—)	(XANTPHOS)Pd(OTf) ₂	—	—	—	(81)	(XANTPHOS)Pd(OTf) ₂	—	—	TfOH	10 (93)	(XANTPHOS)PdCl ₂	—	—	—	(—)	(DPPF)Pd(OTf) ₂	—	—	—	(7)	[(XANTPHOS)Pd(MeCN) ₂](OTf) ₂	—	—	—	(76)	[(XANTPHOS)Pd(MeCN) ₂](OTf) ₂	—	—	TfOH	10 (91)	[(DPPF)Pd(MeCN) ₂](OTf) ₂	—	—	—	(9)	Pd(O ₂ -CCF ₃) ₂	XANTPHOS	3	TfOH	5 (66)	Pd(O ₂ -CCF ₃) ₂	DPPP	2	TfOH	20 (11)	
Temp (°)	Time (h)	I + II	I/II																																																																							
45	14	(82)	99:1																																																																							
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Catalyst	Ligand	x	Acid	y																																																																						
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Pd(O ₂ -CCF ₃) ₂	XANTPHOS	3	TfOH	5 (66)																																																																						
Pd(O ₂ -CCF ₃) ₂	DPPP	2	TfOH	20 (11)																																																																						

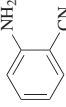
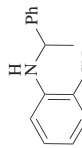
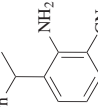
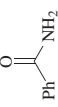
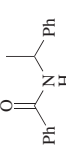
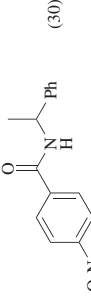
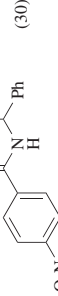
				247
4 eq	TiCl_4 (20 mol %), C_7H_8 , 130°, 22 h	I + II (62), I/II = 91:9		
				135
	TiOH (10 mol %), dioxane, 100°, 24 h			
	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (10 mol %), DCE, 80°			248

TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

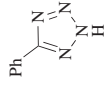
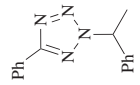
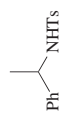
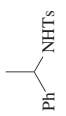
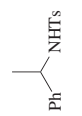
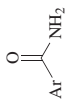
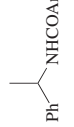
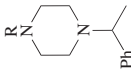
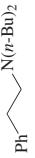
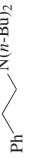
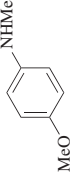
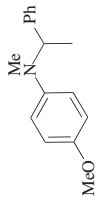
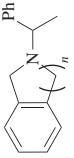
Arene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the bold numbers.				
C ₈			TsOH•H ₂ O (10 mol %), 140°, 24 h	 (68) 140
		TsNH ₂	TfOH (5 mol %), C ₇ H ₈ , 85°	 (70) 134
		TsNH ₂	AgOTf (5 mol %), C ₇ H ₈	Temp (°) Time (h) 85 14 (64) 90 0.5 ^d (58) 429
		TsNH ₂	Ph ₃ PAuCl (5 mol %), AgOTf (5 mol %), DCE, 140°, MW, 14 h	 (43) 202
		TsNH ₂	[(PhO) ₃ P]AuCl (5 mol %), AgOTf (5 mol %), C ₇ H ₈	Temp (°) Time (h) 85 14 (61) 90 0.5 ^d (66) 285
		TsNH ₂ (x eq)	Cu(OTf) ₂ (y mol %), (±)-BINAP (z mol %), dioxane, 75°, 18 h	 x y z 0.25 10 10 (75) 0.5 10 10 (72) 1 10 10 (70) 2 1 1 (93) 2 5 5 (97) 2 10 10 (98) 2 10 0 (42) 246

TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Arene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8  2 eq		$\text{Hf}(\text{OTf})_4$ (10 mol %), $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ (10 mol %), dioxane, 90°, 24 h	 Ar Ph 4- $\text{CF}_3\text{C}_6\text{H}_4$	251
		$\text{Pd}(\text{O}_2\text{CCF}_3)_2$ (5 mol %), DPPF (10 mol %), TiOH (20 mol %), dioxane, 24 h	 R Temp (°) EtO_2C 110 (63) Ph 120 (72)	233
	$n\text{-Bu}_2\text{NH}$	Na (20 mol %), 50°, 50 h	 (21)	t594
	$n\text{-Bu}_2\text{NH}$	Na (1 wt %), 150–200°	 (25)	t455
 Ph		$\text{Pd}(\text{O}_2\text{CCF}_3)_2$ (5 mol %), DPPF (3 mol %), TiOH (20 mol %), C_7H_8 , 100°, 12 h	 (54)	t169
		$\text{Pd}(\text{O}_2\text{CCF}_3)_2$ (5 mol %), DPPF (10 mol %), TiOH (20 mol %), dioxane, 120°, 24 h	 n x 1 4 (71) 2 2 (58)	t212

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

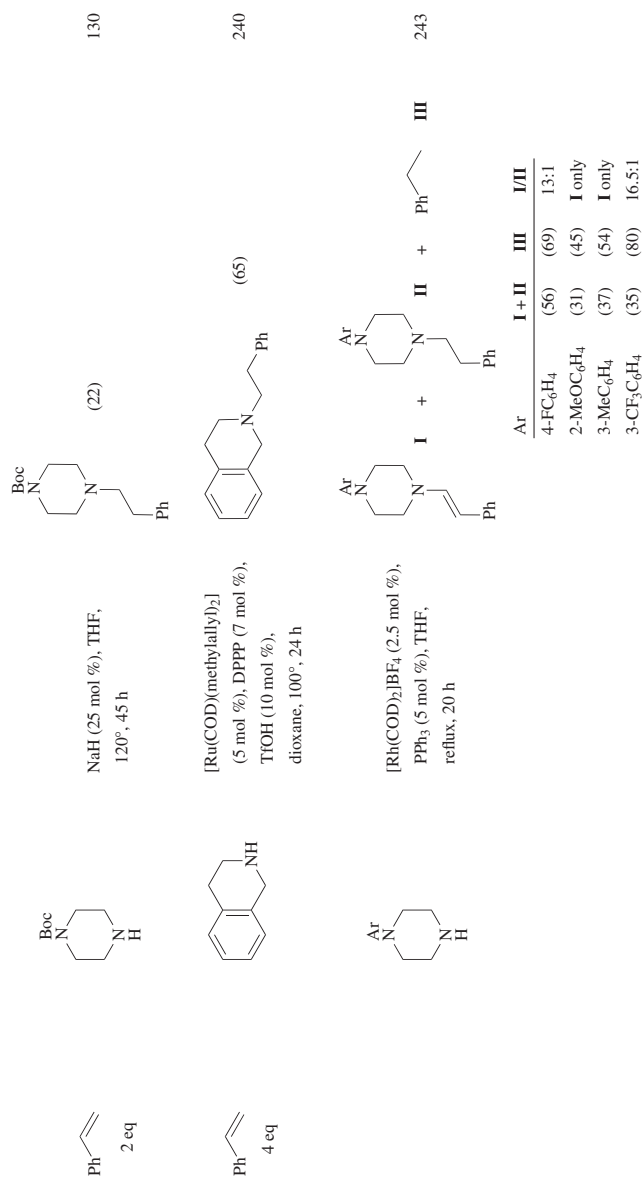


TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Refs.

Product(s) and Yield(s) (%)

Conditions

Amine

Arene

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₈

Catalyst	x	Solvent	Temp (°)	
<i>n</i> -BuLi	1	THF	90	(62)
<i>n</i> -BuLi	2.5	THF	90	(99)
<i>n</i> -BuLi	5	THF	90	(99)
<i>n</i> -BuLi	5	hexane	90	(66)
<i>n</i> -BuLi	5	toluene	120	(43)
<i>n</i> -BuLi	10	DME	85	(88)
<i>n</i> -BuLi	10	THF	90	(99)
<i>t</i> -BuOK	10	THF	90	(—)

Catalyst (x mol %), solvent, 20 h	

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TPA (30 mg/mmol alkene), neat	
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Temp (°)	Time (h)	I + II	I/II
45	14	(78)	99:1
80	6	(95)	1:99

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LiN(TMS) ₂ (2 mol %), TMEDA (2 mol %), C ₆ D ₆ , 120°, 19 h	
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Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₈

TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₈₋₉

R²NH₂
LiN(TMS)₂ (2 mol %),
additive (2 mol %), C₆D₆

44

R ¹	x	R ²	Additive	Temp (°)	Time (h)	I + II	I/II
H	0.5	PMB	TMEDA	120	1.9	(78)	13:1
H	1	<i>n</i> -Pr	TMEDA	120	5.5	(58)	4:1
H	1	Ph	TMEDA	120	113	(58)	I only
H	1.5	PMB	TMEDA	120	0.5	(50)	2.8:1
H	1.5	PMB	—	120	2.5	(52)	2.6:1
Cl	1	Bn	TMEDA	120	1	(33)	I only
Cl	1	Bn	TMEDA	rt	188	(50)	I only
MeO	1	Bn	TMEDA	120	19	(36)	3.5:1
MeO	1.5	PMB	—	120	22	(34)	I only
Me	1	Bn	TMEDA	120	19	(54)	7:1
Me	1.5	PMB	—	120	21	(44)	4:1

R²NH₂
Amberlyst-15
(0.75 g/mmol alkene),
[BMIM][BF₄], 80°, 5 h

432

R ¹	R ²	Time (h)	I	II
H	EtO ₂ C	3	(70)	(21)
H	CH ₂ =CHC(O)	3	(33)	(52)
H	PhSO ₂	5	(52)	(45)
H	Ts	5	(60)	(32)
H	Bz	5	(60)	(33)
Me	PhSO ₂	5	(28)	(7)
Me	Ts	5	(30)	(16)

Refs.

Product(s) and Yield(s) (%)

Conditions

Amine

Arene

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₈

M[N(TMS)₂]₂l₂ (5 mol %),
neat, 60°

433

C₈₋₁₂

2 eq

Pd(O₂CCF₃)₂ (5 mol %),
DPPF (10 mol %),
TfOH (20 mol %),
dioxane, 24 h

233

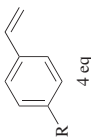
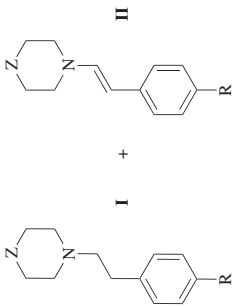
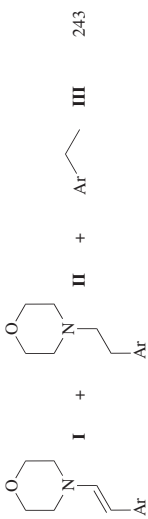
C₈₋₁₀

2 eq

[Ru(COD)(methylallyl)₂]
(5 mol %), ligand (7 mol %),
TfOH (10 mol %),
dioxane, 24 h

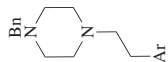
240

TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Arene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																																																
C ₈₋₉																																																				
		[Rh(COD)(DPE-phos)]BF ₄ (5 mol %), C ₇ H ₈ , 70°		244																																																
C ₈₋₁₂																																																				
		[Rh(COD) ₂]BF ₄ (2.5 mol %), PPh ₃ (5 mol %), THF, reflux, 20 h		243																																																
<table><tr><th>Ar</th><th>I + II</th><th>I/II</th><th>III</th></tr><tr><td>Ph</td><td>(88)</td><td>5.3:1</td><td>(84)</td></tr><tr><td>4-ClC₆H₄</td><td>(38)</td><td>5.7:1</td><td>(32)</td></tr><tr><td>4-FC₆H₄</td><td>(79)</td><td>3.3:1</td><td>(85)</td></tr><tr><td>4-MeOC₆H₄</td><td>(62)</td><td>4.2:1</td><td>(47)</td></tr><tr><td>3,4-(MeO)₂C₆H₃</td><td>(71)</td><td>2.1:1</td><td>(80)</td></tr><tr><td>2-MeC₆H₄</td><td>(33)</td><td>4.5:1</td><td>(20)</td></tr><tr><td>3-MeC₆H₄</td><td>(76)</td><td>4.4:1</td><td>(78)</td></tr><tr><td>4-MeC₆H₄</td><td>(91)</td><td>5.1:1</td><td>(99)</td></tr><tr><td>3-CF₃C₆H₄</td><td>(23)</td><td>10.5:1</td><td>(9)</td></tr><tr><td>2-naphthyl</td><td>(29)</td><td>8.6:1</td><td>(38)</td></tr><tr><td>4-PhC₆H₄</td><td>(14)</td><td>6.0:1</td><td>(21)</td></tr></table>					Ar	I + II	I/II	III	Ph	(88)	5.3:1	(84)	4-ClC ₆ H ₄	(38)	5.7:1	(32)	4-FC ₆ H ₄	(79)	3.3:1	(85)	4-MeOC ₆ H ₄	(62)	4.2:1	(47)	3,4-(MeO) ₂ C ₆ H ₃	(71)	2.1:1	(80)	2-MeC ₆ H ₄	(33)	4.5:1	(20)	3-MeC ₆ H ₄	(76)	4.4:1	(78)	4-MeC ₆ H ₄	(91)	5.1:1	(99)	3-CF ₃ C ₆ H ₄	(23)	10.5:1	(9)	2-naphthyl	(29)	8.6:1	(38)	4-PhC ₆ H ₄	(14)	6.0:1	(21)
Ar	I + II	I/II	III																																																	
Ph	(88)	5.3:1	(84)																																																	
4-ClC ₆ H ₄	(38)	5.7:1	(32)																																																	
4-FC ₆ H ₄	(79)	3.3:1	(85)																																																	
4-MeOC ₆ H ₄	(62)	4.2:1	(47)																																																	
3,4-(MeO) ₂ C ₆ H ₃	(71)	2.1:1	(80)																																																	
2-MeC ₆ H ₄	(33)	4.5:1	(20)																																																	
3-MeC ₆ H ₄	(76)	4.4:1	(78)																																																	
4-MeC ₆ H ₄	(91)	5.1:1	(99)																																																	
3-CF ₃ C ₆ H ₄	(23)	10.5:1	(9)																																																	
2-naphthyl	(29)	8.6:1	(38)																																																	
4-PhC ₆ H ₄	(14)	6.0:1	(21)																																																	

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

Ar	x	y	Temp	
Ph	1	10	120°	(94)
Ph	2	20	rt	(80)
3-ClC ₆ H ₄	1.5	10	120°	(88)
3-ClC ₆ H ₄	2	20	rt	(85)
4-ClC ₆ H ₄	1	10	65°	(38)
4-ClC ₆ H ₄	1	20	120°	(65)
4-ClC ₆ H ₄	2	20	rt	(60)
2-BrC ₆ H ₄	1	10	65°	(30)
2-BrC ₆ H ₄	1	20	rt	(59)
3-BrC ₆ H ₄	1	10	65°	(40)
3-BrC ₆ H ₄	2	20	rt	(41)
4-FC ₆ H ₄	0.33	20	120°	(57)
4-FC ₆ H ₄	1	10	65°	(15)
4-FC ₆ H ₄	1	20	70°	(11)
4-FC ₆ H ₄	2	20	rt	(87)
4-MeOC ₆ H ₄	1	10	65°	(71)
4-MeOC ₆ H ₄	1	20	120°	(92)
4-MeOC ₆ H ₄	2	20	rt	(99)
3-MeC ₆ H ₄	1	10	65°	(75)
3-MeC ₆ H ₄	2	20	rt	(47)
4-MeC ₆ H ₄	1	10	65°	(75)
4-MeC ₆ H ₄	1	20	120°	(95)
4-MeC ₆ H ₄	2	20	rt	(96)
3-CF ₃ C ₆ H ₄	1	10	120°	(60)
3-CF ₃ C ₆ H ₄	2	20	rt	(69)
2-naphthyl	2	20	rt	(94)
4-PhC ₆ H ₄	2	20	rt	(98)



n-BuLi (y mol %), THF, 24 h

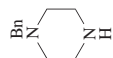
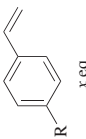
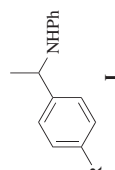
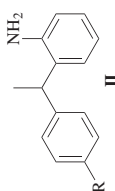
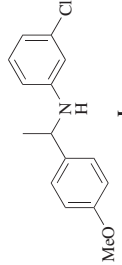
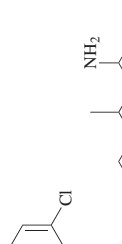
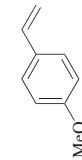
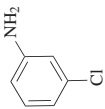
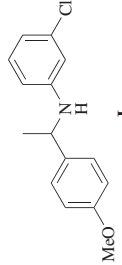
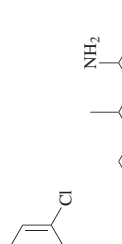
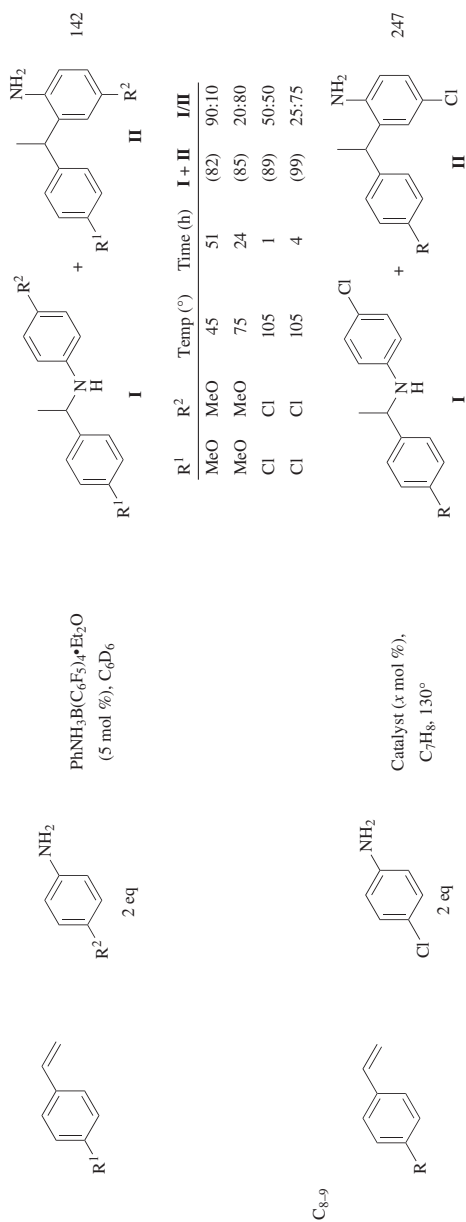


TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Arene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈ -12		<i>n</i> -BuLi (5 mol %), THF, 120°, 17 h	Ar ¹	Ar ²
			Ph	4-FC ₆ H ₄ (99)
			Ph	2-MeOC ₆ H ₄ (95)
			Ph	3-MeC ₆ H ₄ (99)
			Ph	3-CF ₃ -C ₆ H ₄ (89)
			4-ClC ₆ H ₄	4-FC ₆ H ₄ (98)
			4-MeOC ₆ H ₄	4-FC ₆ H ₄ (77)
			3-MeC ₆ H ₄	Ph (97)
			2-naphthyl	4-FC ₆ H ₄ (84)
				226
C ₈		LiN(TMS) ₂ (2 mol %), TMEDA (2 mol %), C ₆ D ₆ , 120°, 137 h		
			(36)	
		[Rh(COD)(DPE-phos)]BF ₄ (10 mol %), 70°, 48 h		
			I dr 17:83	
			II dr 17:83	
			I + II (62), I/II = 72:28	
			244	

TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

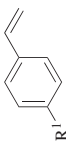
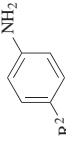
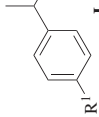
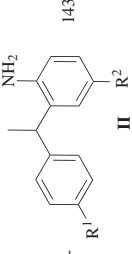
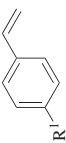
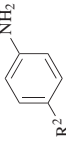
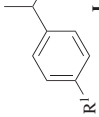
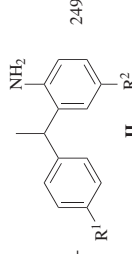
Arene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.				
Please refer to the charts preceding the tables for structures indicated by the bold numbers.								
 x eq	PhNH ₂	[Rh(COD) ₂][BF ₄] (2.5 mol %), PPh ₃ (10 mol %), acid (20 mol %), C ₇ H ₈	 I +  II 242					
	R	x	Acid	Temp (°)	I	II	III	
	H	1	HBFe ₄ •Et ₂ O	140	(6)	(13)	(tr)	
	H	5	HBFe ₄ •Et ₂ O	140	(24)	(57)	(tr)	
	H	5	HBFe ₄ •Et ₂ O	160	(3)	(51)	(2)	
	H	5	TfOH	140	(16)	(32)	(14)	
	H	10	HBFe ₄ •Et ₂ O	140	(24)	(64)	(tr)	
	F	5	HBFe ₄ •Et ₂ O	140	(23)	(31)	(tr)	
	MeO	2	HBFe ₄ •Et ₂ O	140	(2)	(61)	(tr)	
	MeO	5	HBFe ₄ •Et ₂ O	140	(5)	(46)	(tr)	
C ₈₋₁₂								
 x eq	PhNHMe	Catalyst (2 mol %), DPPF (x mol %), TfOH (20 mol %), C ₇ H ₈ , 100°, 12 h	 I +  II 142					
	Ar	Catalyst	x	Ar	Ph 2-naphthyl Pd(PPh ₃) ₄ Pd(CF ₃ CO ₂) ₂	x 0 3	(55) (65)	231
 2 eq		PhNH ₃ B(C ₆ F ₅) ₄ •Et ₂ O (5 mol %), C ₆ D ₆	 I +  II 142					
	Temp	Time (h)	I + II	I/II				
rt	5	(82)	40:60					
45°	14	(71)	II only					
C ₈								



R^1	R^2	Temp (°)	Time (h)	I + II	I/II
MeO	MeO	45	51	(82)	90:10
MeO	MeO	75	24	(85)	20:80
Cl	Cl	105	1	(89)	50:50
Cl	Cl	105	4	(99)	25:75

R	Catalyst	x	Time (h)	I + II	I/II
H	—	—	22	(—)	—
H	TiCl ₄	20	4f	(61)	13:87
H	TiCl ₄	20	22	(62)	61:39
H	TiCl ₄	100	22	(52)	16:84
H	H ₂ SO ₄	20	22	(—)	—
H	4-ClC ₆ H ₄ NH ₃ Cl	20	22	(—)	—
H	Cp ₂ TiCl ₂	20	22	(—)	—
F	TiCl ₄	20	6f	(66)	42:58
Me	TiCl ₄	20	2f	(68)	7:93
Me	TiCl ₄	20	22	(80)	41:59

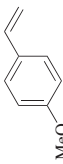
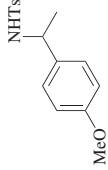
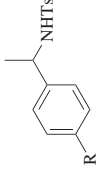
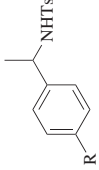
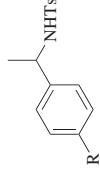
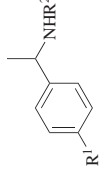
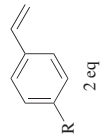
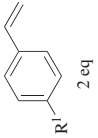
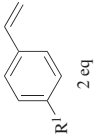
TABLE IB. HYDROAMINATION OF VINYL ARENES (Continued)

Arene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																																																
	 5 eq	HI (5 mol %), C ₇ H ₈ , 135°, 24 h	  143																																																	
			<table><tr><th>R¹</th><th>R²</th><th>I + II</th><th>I/II</th></tr><tr><td>H</td><td>H</td><td>(81)</td><td>65:35</td></tr><tr><td>H</td><td>Cl</td><td>(86)</td><td>40:60</td></tr><tr><td>F</td><td>H</td><td>(82)</td><td>70:30</td></tr><tr><td>F</td><td>Cl</td><td>(84)</td><td>56:44</td></tr><tr><td>F</td><td>MeO</td><td>(83)</td><td>45:55</td></tr><tr><td>MeO</td><td>H</td><td>(26)</td><td>II only</td></tr><tr><td>MeO</td><td>Cl</td><td>(83)</td><td>II only</td></tr><tr><td>Me</td><td>H</td><td>(80)</td><td>55:45</td></tr><tr><td>Me</td><td>Cl</td><td>(75)</td><td>12:88</td></tr><tr><td>CF₃</td><td>H</td><td>(10)</td><td>I only</td></tr><tr><td>CF₃</td><td>Cl</td><td>(32)</td><td>47:53</td></tr></table>	R ¹	R ²	I + II	I/II	H	H	(81)	65:35	H	Cl	(86)	40:60	F	H	(82)	70:30	F	Cl	(84)	56:44	F	MeO	(83)	45:55	MeO	H	(26)	II only	MeO	Cl	(83)	II only	Me	H	(80)	55:45	Me	Cl	(75)	12:88	CF ₃	H	(10)	I only	CF ₃	Cl	(32)	47:53	
R ¹	R ²	I + II	I/II																																																	
H	H	(81)	65:35																																																	
H	Cl	(86)	40:60																																																	
F	H	(82)	70:30																																																	
F	Cl	(84)	56:44																																																	
F	MeO	(83)	45:55																																																	
MeO	H	(26)	II only																																																	
MeO	Cl	(83)	II only																																																	
Me	H	(80)	55:45																																																	
Me	Cl	(75)	12:88																																																	
CF ₃	H	(10)	I only																																																	
CF ₃	Cl	(32)	47:53																																																	
	 2 eq	TPA (30 mg/mmol alkene), neat	  249																																																	
			<table><tr><th>R¹</th><th>R²</th><th>Temp (°)</th><th>Time (h)</th><th>I + II</th><th>I/II</th></tr><tr><td>H</td><td>Br</td><td>80</td><td>1</td><td>(75)</td><td>99:1</td></tr><tr><td>H</td><td>Br</td><td>80</td><td>6</td><td>(75)</td><td>25:70</td></tr><tr><td>H</td><td>Cl</td><td>80</td><td>3</td><td>(95)</td><td>65:35</td></tr><tr><td>H</td><td>F</td><td>80</td><td>4</td><td>(98)</td><td>50:50</td></tr><tr><td>H</td><td>O₂N</td><td>80</td><td>4</td><td>(96)</td><td>99:1</td></tr></table>	R ¹	R ²	Temp (°)	Time (h)	I + II	I/II	H	Br	80	1	(75)	99:1	H	Br	80	6	(75)	25:70	H	Cl	80	3	(95)	65:35	H	F	80	4	(98)	50:50	H	O ₂ N	80	4	(96)	99:1													
R ¹	R ²	Temp (°)	Time (h)	I + II	I/II																																															
H	Br	80	1	(75)	99:1																																															
H	Br	80	6	(75)	25:70																																															
H	Cl	80	3	(95)	65:35																																															
H	F	80	4	(98)	50:50																																															
H	O ₂ N	80	4	(96)	99:1																																															

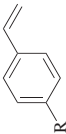
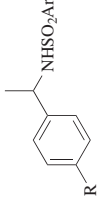
Please refer to the charts preceding the tables for structures indicated by the **bold numbers**.

C₈₋₉

TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Arene	Amine	Conditions	Product(s) and Yield(s) (%)		Refs.
	TsNH ₂	Catalyst (x mol %), solvent, rt, 24 h		Catalyst x Solvent NBS 10 DCM (60) NBS 20 DCM (82) NBS 20 MeCN (68) NBS 20 THF (18) AcNHBr 20 DCM (65)	252
				NCS 20 DCM (25) PyHBr ₃ 20 DCM (70) ZnBr ₂ 20 DCM (0)	
				R Temp (°) Time (h) H 45 22 (72) Cl 45 24 (91) Br 45 24 (89) Me rt 24 (70)	423
				R Temp (°) H 45 (78) Cl 45 (68) Me rt (64)	250
					422
 2 eq	TsNH ₂	[BSPy][OTf] (20 mol %), DCE			
 2 eq	R ² NH ₂	H ₃ SiW ₁₂ O ₄₀ nH ₂ O (100 mg/mmol TsNH ₂), DCE, 24 h			
 2 eq	R ² NH ₂	Zr(OTf) ₄ (5 mol %), solvent			

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

	ArSO_2NH_2	$\text{Bi}(\text{OTf})_3$ (10 mol %), [Cu(MeCN) $_4$](PF $_6$) (10 mol %), dioxane, 24 h		R	Ar	Temp (°)	
				H	Ph	40	(91) 251
				H	4-ClC $_6$ H $_4$	40	(88)
				H	2-O $_2$ NC $_6$ H $_4$	40	(54)
				H	4-MeOC $_6$ H $_4$	40	(97)
				H	2-MeC $_6$ H $_4$	40	(90)
				H	4-MeC $_6$ H $_4$	rt	(87)
				H	4-CF $_3$ -C $_6$ H $_4$	40	(80)
				Cl	4-MeC $_6$ H $_4$	40	(59)
				Me	4-MeC $_6$ H $_4$	rt	(tr)

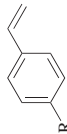
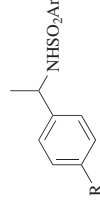
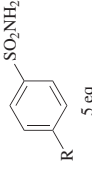
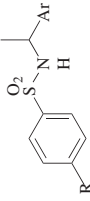
	ArSO_2NH_2	$\text{Hf}(\text{OTf})_4$ (γ mol %), [Cu(MeCN) $_4$](PF $_6$) (γ mol %), solvent		R	x	Ar	γ	Solvent	Temp	Time (h)	
				H	2	Ph	10	dioxane	40	24	(90)
				H	2	4-ClC $_6$ H $_4$	10	dioxane	40	24	(89)
				H	2	2-O $_2$ NC $_6$ H $_4$	10	dioxane	40	24	(67)
				H	2	4-MeOC $_6$ H $_4$	10	dioxane	40	24	(88)
				H	2	2-MeC $_6$ H $_4$	10	dioxane	40	24	(91)
				H	2	4-MeC $_6$ H $_4$	0.3	dioxane	rt	40	(76)
				H	2	4-MeC $_6$ H $_4$	1	dioxane	rt	24	(90)
				H	2	4-MeC $_6$ H $_4$	10	dioxane	rt	24	(90)
				H	2	4-CF $_3$ -C $_6$ H $_4$	10	dioxane	40	24	(82)
				Cl	2	4-MeC $_6$ H $_4$	10	dioxane	40	24	(99)
				Br	2	4-MeC $_6$ H $_4$	10	dioxane	40	24	(91)
				F	2	4-MeC $_6$ H $_4$	10	dioxane	40	24	(86)
				Me	2	4-MeC $_6$ H $_4$	10	dioxane	20	24	(20)
				Me	4	4-MeC $_6$ H $_4$	10	DME	8	72	(75)
				Me	4	4-MeC $_6$ H $_4$	10	dioxane	20	24	(44)

TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Arene	Amine	Conditions	Product(s) and Yield(s) (%)		Refs.
C ₈₋₉ 	 5 eq	FeCl ₃ •6H ₂ O (10 mol %), dioxane, 120°			
			Ar	R	248
			Ph	H	(59)
			4-BrC ₆ H ₄	Me	(69)
			4-FC ₆ H ₄	Me	(63)
C ₈₋₁₂ 	Ar ² SO ₂ NH ₂ (2 eq)	Cu(OTf) ₂ (5 mol %), (±)-BINAP (5 mol %), dioxane, 75°, 18 h			
			Ar ¹	I	
			Ar ²	II	
			I + II	III	
			Ph	4-O ₂ NC ₆ H ₄ (95)	I only
			4-FC ₆ H ₄	4-O ₂ NC ₆ H ₄ (83)	I only
			4-FC ₆ H ₄	4-MeC ₆ H ₄ (96)	I only
			4-ClC ₆ H ₄	4-O ₂ NC ₆ H ₄ (62)	I only
			4-ClC ₆ H ₄	4-MeC ₆ H ₄ (83)	I only
			4-MeOC ₆ H ₄	4-O ₂ NC ₆ H ₄ (58)	45:55
			4-MeOC ₆ H ₄	4-MeC ₆ H ₄ (61)	52:48
			4-MeC ₆ H ₄	4-O ₂ NC ₆ H ₄ (63)	I only
			4-MeC ₆ H ₄	4-MeC ₆ H ₄ (67)	I only
			2,4-Me ₂ -C ₆ H ₃	4-O ₂ NC ₆ H ₄ (43)	I only
			2,4-Me ₂ -C ₆ H ₃	4-MeC ₆ H ₄ (54)	I only
			2-naphthyl	4-O ₂ NC ₆ H ₄ (75)	II only
			2-naphthyl	4-MeC ₆ H ₄ (70)	I only
			Ar ¹	Ar ¹ -CH=CH-Ar ¹	II
			Ar ¹	Ar ¹ -CH=CH-Ar ¹	II
			Ar ¹	Ar ¹ -CH=CH-Ar ¹	II

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

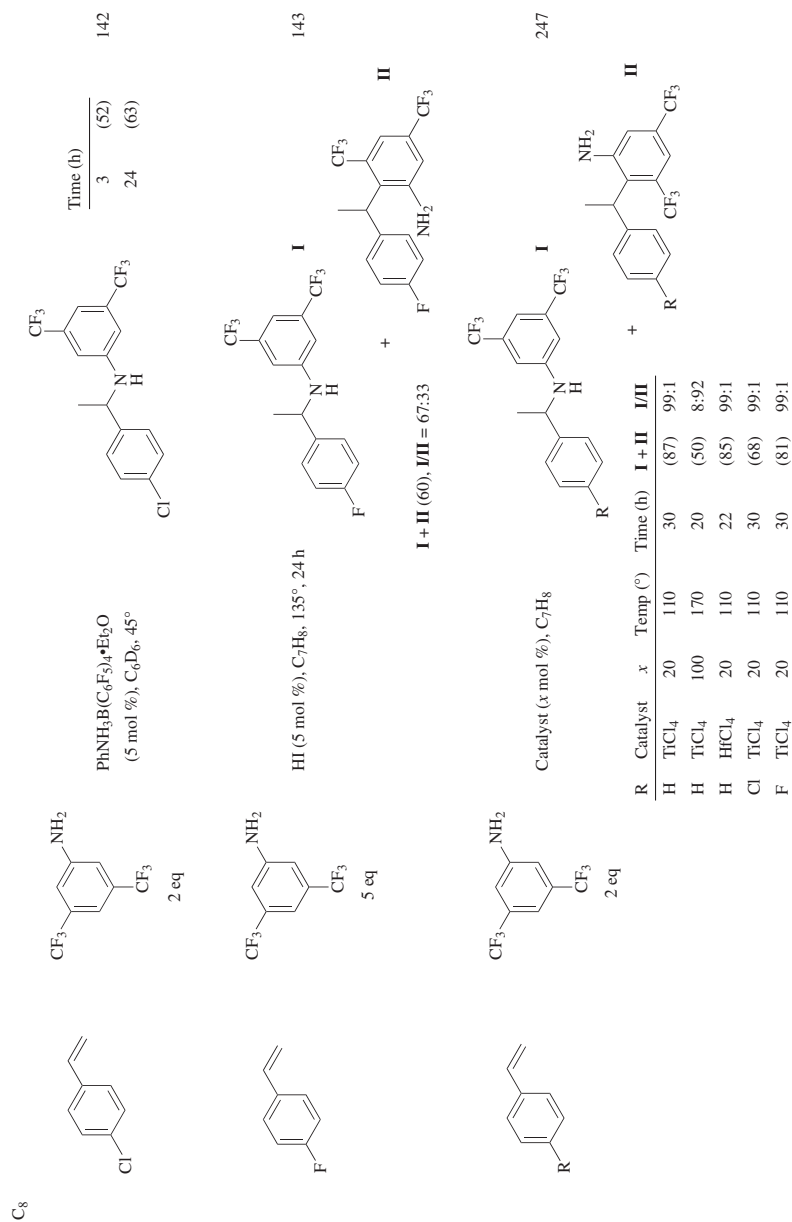
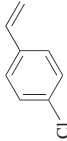
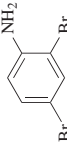
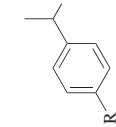
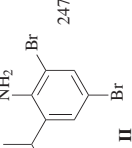
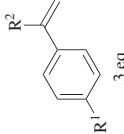
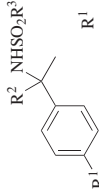
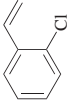
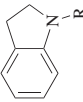
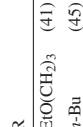
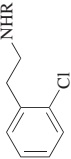
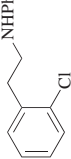
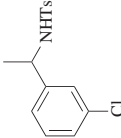


TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Arene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
	 2 eq	TiCl ₄ (20 mol %), C ₇ H ₈	  247	
 3 eq	R ³ SO ₂ NH ₂	I ₂ (10 mol %), C ₇ H ₈ , 110°	  253	
	RNH ₂ (1.5 eq)	1. <i>n</i> -BuLi (10 mol %), THF, -30° 2. <i>t</i> -BuOK (3 eq), C ₇ H ₈ , 135°	   225	

RNH ₂	<i>n</i> -BuLi (10 mol %), TMDA (25 mol %), C ₇ H ₈ , 120°		R EtO(CH ₂) ₃ (65) <i>n</i> -Bu (60) <i>t</i> -Bu (65) BnCH ₂ (69)	225
PhNH ₂ (10 eq)	<i>t</i> -BuOK (1 eq), MW, 3 min		(67)	228
PhNH ₂	<i>t</i> -BuOK (2 eq), MW, 5 min		(96)	228
ArNH ₂	<i>t</i> -BuOK (3 eq), C ₇ H ₈ , 135°		Ar Ph (53) 4-FC ₆ H ₄ (54) 2-MeOC ₆ H ₄ (58)	225
RNH ₂ (1.5 eq)	1. <i>n</i> -BuLi (10 mol %), THF, -30° 2. <i>t</i> -BuOK (3 eq), C ₇ H ₈ , 135°		R <i>n</i> -Bu (43) <i>t</i> -Bu (40) BnCH ₂ (43)	225
TsNH ₂	Hf(OTf) ₄ (10 mol %), [Cu(MeCN) ₄]PF ₆ (10 mol %), dioxane, 40°, 24 h		(61)	251

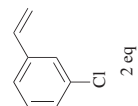
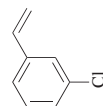
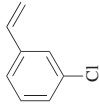
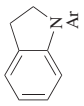
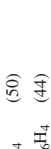
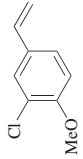
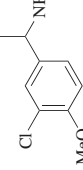
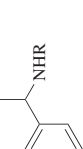
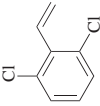
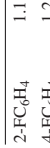
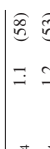
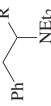
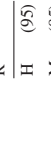
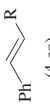
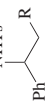
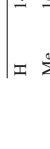
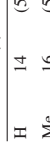


TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Arene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₈	ArNH ₂	<i>t</i> -BuOK (3 eq), C ₇ H ₈ , 135°	 Ar  (50)  (44)  (47)	225
	RNH ₂	NBS (20 mol %), DCM, rt, 24 h	 R  (80)  (78)	252
	ArNH ₂ (x eq)	<i>t</i> -BuOK (1.5 eq), C ₇ H ₈ , 135°	 Ar  (58)  (53)  (54)	225
 C ₈₋₉	Et ₂ NH (1.7 eq)	Na (20 mol %), naphthalene (10 mol %), THF, rt	 R  (95)  (85)	221 220
	TsNH ₂	Ph ₃ PAuCl (5 mol %), AgOTf (5 mol %), C ₇ H ₈ , 85°	 (4 eq) NHTs  R  (51)  (56)	133

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

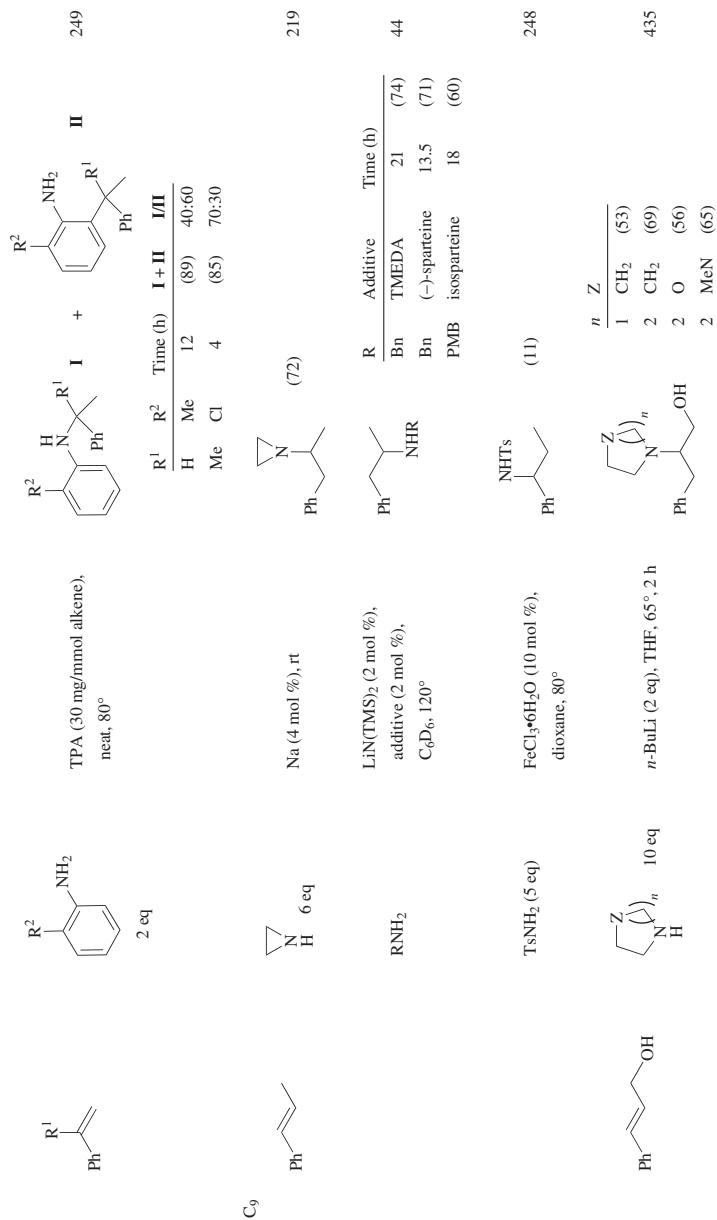


TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Arene

Amine

Conditions

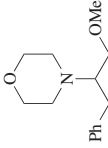
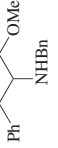
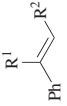
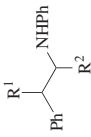
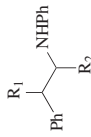
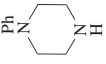
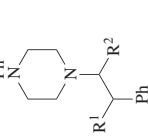
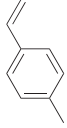
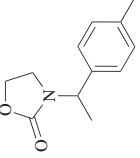
Product(s) and Yield(s) (%)

Refs.

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C ₉		R ⁴ NH ₂ (9 eq)	Sensitizer (1.9 eq), additive (0.4 eq), UV (Hg lamp), MeCN/H ₂ O (9:1), rt			215			
R ¹	R ²	R ³	R ⁴	Sensitizer	Additive	Time (h)	I	II ^f	dr II
H	H	MeO	H	1,4-DCB	—	9	(8)	(37)	1:0.7
H	H	MeO	H	1,3-DCB	—	4	(52)	(0)	—
H	H	MeO	H	1,3-DCB	1,3,5-Ph ₃ C ₆ H ₃	4	(91)	(0)	—
H	H	MeO	H	1,3-DCB	1,3-Ph ₂ C ₆ H ₄	5	(85)	(0)	—
H	H	MeO	H	1,3-DCB	1,2,4-Ph ₃ C ₆ H ₃	6	(67)	(0)	—
H	H	MeO	H	1,3-DCB	1,4-Ph ₂ C ₆ H ₄	4	(66)	(0)	—
H	H	MeO	H	1,3-DCB	biphenyl	6	(58)	(0)	—
H	H	MeO	<i>i</i> -Pr	1,4-DCB	—	3	(0)	(20)	1:0
H	H	MeO	<i>t</i> -Bu	1,4-DCB	—	3	(0)	(29)	1:0.2
H	MeO	H	H	1,4-DCB	—	18	(28)	(0)	—
H	MeO	H	H	1,4-DCB	1,3,5-Ph ₃ C ₆ H ₃	24	(46)	(0)	—
H	MeO	MeO	H	1,4-DCB	—	20	(29)	(2)	1:0
H	MeO	MeO	H	1,3-DCB	1,3,5-Ph ₃ C ₆ H ₃	18	(65)	(0)	—
MeO	H	H	H	1,4-DCB	—	4	(68)	(0)	—
MeO	H	H	H	1,4-DCB	1,3,5-Ph ₃ C ₆ H ₃	4	(75)	(0)	—
				LiN(TMS) ₂ (2 mol %), TMEDA (2 mol %), C ₆ D ₆ , 150°, 48 h			(53)		44

TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Arene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
	 10 eq	<i>n</i> -BuLi (1 eq), THF, −78° to reflux, 1–2 h	 (45)	435
	BnNH ₂	<i>n</i> -BuLi (1 eq), THF, −78° to reflux, 1–2 h	 (36)	435
	PhNH ₂	<i>t</i> -BuOK (10 mol %), THF, 160°, 20 h		227
	PhNH ₂ (10 eq)	<i>t</i> -BuOK (1 eq), MW, 10 min		228
		<i>n</i> -BuLi (5 mol %), THF, 90°, 17 h		226
 2 eq		[PtCl ₂ (H ₂ C=CH ₂) ₂] (2.5 mol %), (4-CF ₃ C ₆ H ₄) ₃ P (5 mol %), mesitylene, 140°, 24 h	 (73)	245

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₉

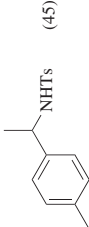
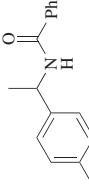
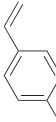
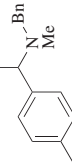
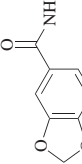
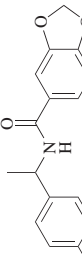
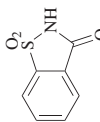
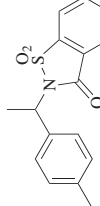
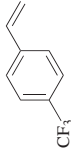
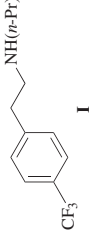
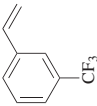
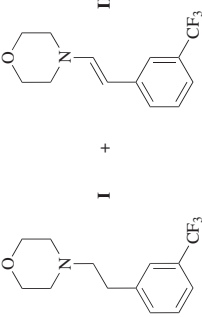
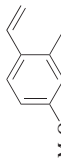
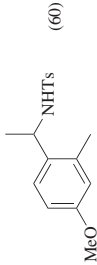
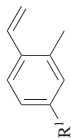
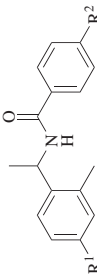
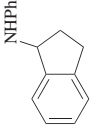
		[PtCl₂(H₂C=CH₂)₂] (2.5 mol %), (4-CF₃C₆H₄)₃P (5 mol %), mesitylene, 120°, 24 h	245																								
		[PtCl₂(H₂C=CH₂)₂] (2.5 mol %), ligand (5 mol %), solvent, 24 h	245																								
		<table><tr><th>Ligand</th><th>Solvent</th><th>Temp (°)</th></tr><tr><td>—</td><td>dioxane</td><td>120 (71)</td></tr><tr><td>PPh₃</td><td>dioxane</td><td>120 (24)</td></tr><tr><td>(4-CF₃C₆H₄)₃P</td><td>dioxane</td><td>120 (72)</td></tr><tr><td>(4-CF₃C₆H₄)₃P</td><td>dioxane</td><td>140 (77)</td></tr><tr><td>(4-CF₃C₆H₄)₃P</td><td>toluene</td><td>140 (81)</td></tr><tr><td>(4-CF₃C₆H₄)₃P</td><td>xylene</td><td>140 (79)</td></tr><tr><td>(4-CF₃C₆H₄)₃P</td><td>mesitylene</td><td>140 (85)</td></tr></table>	Ligand	Solvent	Temp (°)	—	dioxane	120 (71)	PPh ₃	dioxane	120 (24)	(4-CF ₃ C ₆ H ₄) ₃ P	dioxane	120 (72)	(4-CF ₃ C ₆ H ₄) ₃ P	dioxane	140 (77)	(4-CF ₃ C ₆ H ₄) ₃ P	toluene	140 (81)	(4-CF ₃ C ₆ H ₄) ₃ P	xylene	140 (79)	(4-CF ₃ C ₆ H ₄) ₃ P	mesitylene	140 (85)	
Ligand	Solvent	Temp (°)																									
—	dioxane	120 (71)																									
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(4-CF ₃ C ₆ H ₄) ₃ P	dioxane	120 (72)																									
(4-CF ₃ C ₆ H ₄) ₃ P	dioxane	140 (77)																									
(4-CF ₃ C ₆ H ₄) ₃ P	toluene	140 (81)																									
(4-CF ₃ C ₆ H ₄) ₃ P	xylene	140 (79)																									
(4-CF ₃ C ₆ H ₄) ₃ P	mesitylene	140 (85)																									
		Pd(O₂CCF₃)₂ (5 mol %), DPPF (10 mol %), TiOH (20 mol %), dioxane, 110°, 24 h	233																								
		[PtCl₂(H₂C=CH₂)₂] (2.5 mol %), (4-CF₃C₆H₄)₃P (5 mol %), mesitylene, 140°, 24 h	245																								
		I₂ (10 mol %), C₇H₈, 110°, 2 h	253																								

TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Arene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.												
Please refer to the charts preceding the tables for structures indicated by the bold numbers.																
C ₉	 2 eq	Cp* ₂ LaCH(SiMe ₃) ₂ (5 mol %), C ₆ D ₆ , 90°	 I + II (93), III = 96:4	43												
	 2 eq	[Rh(COD)(DPE-phos)]BF ₄ (10 mol %), 70°, 72 h	 I + II (41), III = 57:43	244												
C ₉₋₁₀		NBS (20 mol %), DCM, rt, 24 h	 (60)	252												
	 2 eq	[PtCl ₂ (H ₂ C=CH ₂) ₂] (2.5 mol %), (4-CF ₃ C ₆ H ₄) ₃ P (5 mol %), mesitylene, 140°, 24 h		<table><tr><th>R¹</th><th>R²</th><th></th></tr><tr><td>H</td><td>H</td><td>(68)</td></tr><tr><td>Me</td><td>H</td><td>(71)</td></tr><tr><td>Me</td><td>TBSO</td><td>(58)</td></tr></table>	R ¹	R ²		H	H	(68)	Me	H	(71)	Me	TBSO	(58)
R ¹	R ²															
H	H	(68)														
Me	H	(71)														
Me	TBSO	(58)														
C ₉	 4 eq	Pd(O ₂ CCF ₃) ₂ (10 mol %), DPPF (10 mol %), TfOH (10 mol %), neat, 110°	 (71)	236												

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

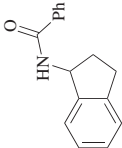
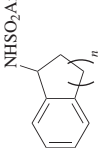
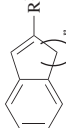
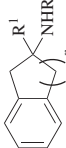
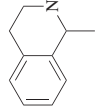
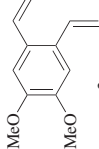
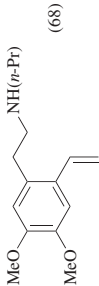
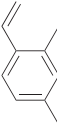
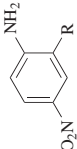
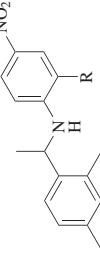
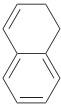
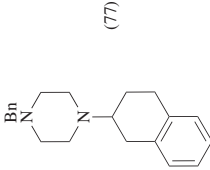
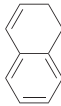
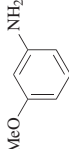
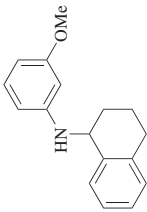
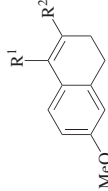
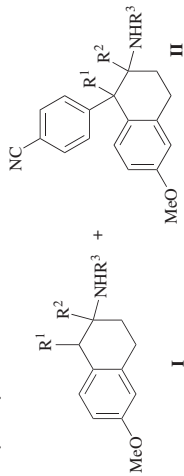
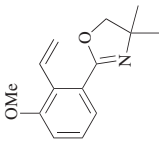
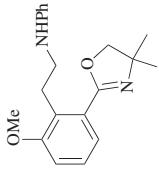
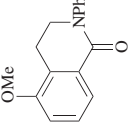
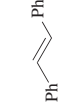
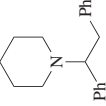
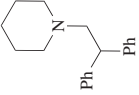
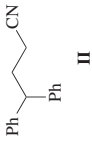
			[PtCl2(H2C=CH2)2 (5 mol %), (4-CF3C6H4)3P (10 mol %), mesitylene, 120°, 24 h	245																																																												
C9-10 2 eq	ArSO2NH2		I2 (10 mol %), C7H8, 110°	253																																																												
	R2NH2		1,3-dichlorobenzene (1.875 eq), additive (37.5 mol %), MeCN/H2O (19:1), UV (Hg lamp), 5–13 h	400																																																												
C9-11			<table> <tr> <th><i>n</i></th><th>R¹</th><th>R²</th><th>Additive</th></tr> <tr> <td>1</td><td>H</td><td>H</td><td>—</td></tr> <tr> <td>1</td><td>H</td><td>H</td><td>1,2,4-TPB (79)</td></tr> <tr> <td>1</td><td>H</td><td>H</td><td>1,3,5-TPB (12)</td></tr> <tr> <td>1</td><td>H</td><td>H</td><td>1,4-TP (76)</td></tr> <tr> <td>1</td><td>H</td><td>H</td><td>1,3-TP (34)</td></tr> <tr> <td>1</td><td>H</td><td><i>i</i>-Pr</td><td>1,2,4-TPB (52)</td></tr> <tr> <td>1</td><td>H</td><td><i>t</i>-Bu</td><td>1,2,4-TPB (49)</td></tr> <tr> <td>1</td><td>Me</td><td>H</td><td>— (31)</td></tr> <tr> <td>1</td><td>Me</td><td>H</td><td>BN (58)</td></tr> <tr> <td>1</td><td>Me</td><td>H</td><td>1,2,4-TPB (83)</td></tr> <tr> <td>2</td><td>H</td><td>H</td><td>— (16)</td></tr> <tr> <td>2</td><td>H</td><td>H</td><td>1,2,4-TPB (63)</td></tr> <tr> <td>3</td><td>H</td><td>H</td><td>— (31)</td></tr> <tr> <td>3</td><td>H</td><td>H</td><td>1,2,4-TPB (57)</td></tr> </table>	<i>n</i>	R ¹	R ²	Additive	1	H	H	—	1	H	H	1,2,4-TPB (79)	1	H	H	1,3,5-TPB (12)	1	H	H	1,4-TP (76)	1	H	H	1,3-TP (34)	1	H	<i>i</i> -Pr	1,2,4-TPB (52)	1	H	<i>t</i> -Bu	1,2,4-TPB (49)	1	Me	H	— (31)	1	Me	H	BN (58)	1	Me	H	1,2,4-TPB (83)	2	H	H	— (16)	2	H	H	1,2,4-TPB (63)	3	H	H	— (31)	3	H	H	1,2,4-TPB (57)	
<i>n</i>	R ¹	R ²	Additive																																																													
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1	H	H	1,2,4-TPB (79)																																																													
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	(<i>n</i> -Pr)3NH2		Cp ⁺ 2LaCH(TMS)2 (5 mol %), C7D8, 90°	43																																																												
C10 2 eq																																																																
	(<i>n</i> -Pr)3NH2		Cp ⁺ 2LaCH(TMS)2 (5 mol %), C7D8, 90°	43																																																												
C10 2 eq																																																																

TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Arene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																																																												
 C ₁₀		FeCl ₃ •6H ₂ O (10 mol %), dioxane, rt	 R H (43) Me (57)	248																																																												
	 2 eq		<i>n</i> -BuLi (20 mol %), THF, rt, 48 h	 (77)	130																																																											
 4 eq C ₁₀₋₁₁		Pd(O ₂ CCF ₃) ₂ (5 mol %), DPPF (5 mol %), TfOH (5 mol %), C ₇ H ₈ , 80°	 (8)	236																																																												
		R ³ NH ₂ (9 eq)	Sensitizer (1.9 eq), additive (0.4 eq), UV (Hg lamp), MeCN/H ₂ O (9:1), rt	 I R ¹ R ² NHR ³ MeO MeO MeO II R ¹ R ² NHR ³ MeO MeO MeO	215																																																											
<table><tr><th>R¹</th><th>R²</th><th>R³</th><th>Sensitizer</th><th>Additive</th><th>Time (h)</th><th>I^a</th><th>dr I</th><th>II^b</th><th>dr II</th></tr><tr><td>H</td><td>H</td><td>H</td><td>1,4-DCB</td><td>—</td><td>8</td><td>(6)</td><td>—</td><td>(37)</td><td>1:0</td></tr><tr><td>H</td><td>H</td><td>H</td><td>1,3-DCB</td><td>—</td><td>8</td><td>(23)</td><td>—</td><td>(0)</td><td>—</td></tr><tr><td>H</td><td>H</td><td>H</td><td>1,3-DCB</td><td>1,3,5-Ph₃C₆H₃</td><td>8</td><td>(29)</td><td>—</td><td>(0)</td><td>—</td></tr><tr><td>H</td><td>H</td><td><i>i</i>-Pr</td><td>1,4-DCB</td><td>—</td><td>8</td><td>(0)</td><td>—</td><td>(72)</td><td>1:1</td></tr><tr><td>H</td><td>H</td><td><i>t</i>-Bu</td><td>1,4-DCB</td><td>—</td><td>6</td><td>(0)</td><td>—</td><td>(49)</td><td>1:0</td></tr></table>					R ¹	R ²	R ³	Sensitizer	Additive	Time (h)	I ^a	dr I	II ^b	dr II	H	H	H	1,4-DCB	—	8	(6)	—	(37)	1:0	H	H	H	1,3-DCB	—	8	(23)	—	(0)	—	H	H	H	1,3-DCB	1,3,5-Ph ₃ C ₆ H ₃	8	(29)	—	(0)	—	H	H	<i>i</i> -Pr	1,4-DCB	—	8	(0)	—	(72)	1:1	H	H	<i>t</i> -Bu	1,4-DCB	—	6	(0)	—	(49)	1:0
R ¹	R ²	R ³	Sensitizer	Additive	Time (h)	I ^a	dr I	II ^b	dr II																																																							
H	H	H	1,4-DCB	—	8	(6)	—	(37)	1:0																																																							
H	H	H	1,3-DCB	—	8	(23)	—	(0)	—																																																							
H	H	H	1,3-DCB	1,3,5-Ph ₃ C ₆ H ₃	8	(29)	—	(0)	—																																																							
H	H	<i>i</i> -Pr	1,4-DCB	—	8	(0)	—	(72)	1:1																																																							
H	H	<i>t</i> -Bu	1,4-DCB	—	6	(0)	—	(49)	1:0																																																							

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Arene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₃	PhNH ₂ (10 eq)	<i>t</i> -BuOK (1 eq), MW, 5 min	 (100)	228
	PhNH ₂	1. <i>t</i> -BuOK (2 eq), MW, 5 min 2. (CO ₂ H) ₂ , MW, 0.5 min	 (90)	228
	 C ₁₄	<i>n</i> -BuLi (5 mol %), cyclohexane, 50 °, 48 h	 (10)	224
 C ₁₄	 (2 eq)	<i>n</i> -BuLi (5 mol %), cyclohexane, 50 °, 48 h	 (82)	224
	RNH ₂ (13 eq)	Sensitizer (2.9 eq), UV (Hg), 8–50 h	 I +  II +  III	437

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C14-15

DCB (1 eq), UV (Hg lamp),
MeCN/benzene/H₂O
(x:y:10 vol %), rt

214

R	Ar	x	y	Time (h)	I + II	I/II
H	Ph	90	0	20	(46)	—
H	Ph	70	20	31	(88)	—
H	4-ClC ₆ H ₄	70	20	8	(54)	1:0.9
H	2-MeOC ₆ H ₄	90	0	7	(59)	1:0.4
H	3-MeOC ₆ H ₄	90	0	10	(80)	1:0.7
H	3-MeOC ₆ H ₄	80	10	20	(91)	1:0.7
H	4-MeOC ₆ H ₄	90	0	21	(53)	I only
H	4-MeOC ₆ H ₄	80	10	15	(62)	I only
H	3,4-(MeO) ₂ C ₆ H ₃	90	0	20	(21)	I only
H	3,5-(MeO) ₂ C ₆ H ₃	90	0	20	(28)	1:0.7
H	3,5-(MeO) ₂ C ₆ H ₃	70	20	17	(60)	1:0.7
H	3,4,5-(MeO) ₃ C ₆ H ₂	90	0	20	(0)	—
H	3,4-(OCH ₂)OC ₆ H ₃	80	10	20	(21)	I only
H	4-MeC ₆ H ₄	70	20	20	(87)	1:0.6
MeO	4-MeOC ₆ H ₄	70	20	41	(44)	—
MeO	3,5-(MeO) ₂ C ₆ H ₃	70	20	20	(16)	I only

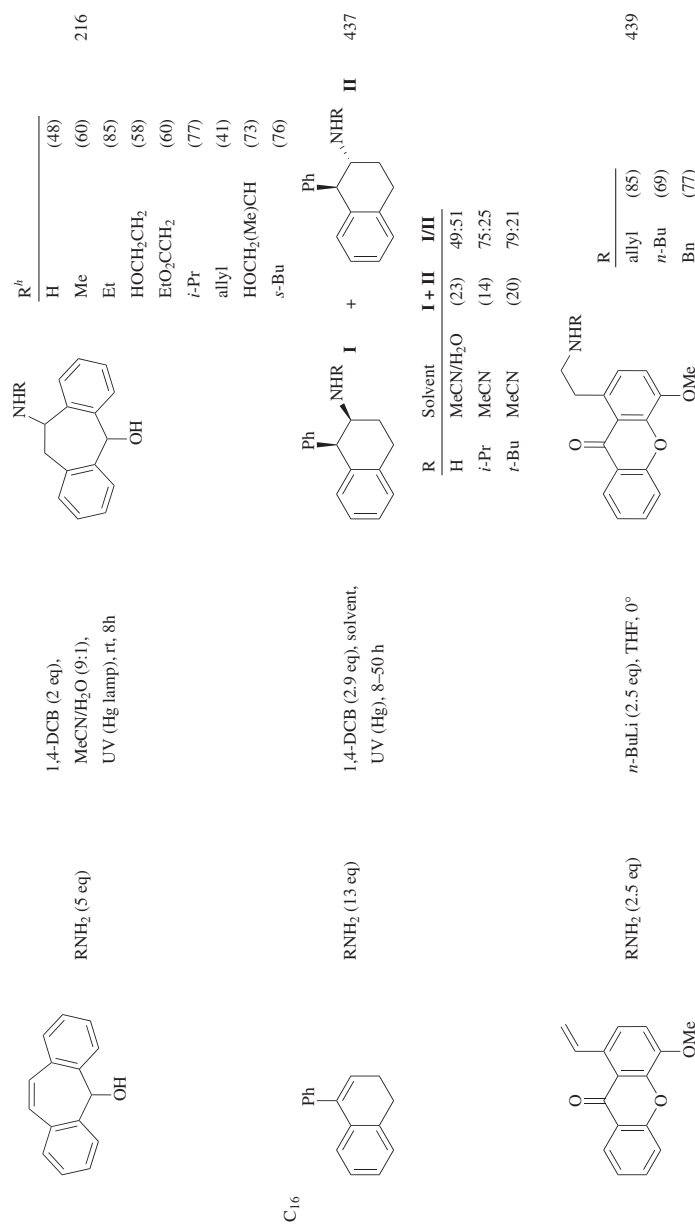
C₁₄₋₁₅

TABLE 1B. HYDROAMINATION OF VINYL ARENES (Continued)

Please refer to the charts preceding the tables for structures indicated by the **bold numbers**.

Arene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																																																	
C₁₄ 	$R^3-CH_2-NH_2$ (5 eq)	1,4-DCB (1 eq), MeCN/benzene/H ₂ O (x:2:y) UV (Hg), rt, 8–45 h	 I	 II																																																	
			<table> <tr> <th>R^1</th><th>R^2</th><th>R^3</th><th>x</th><th>y</th><th>I</th><th>II</th></tr> <tr> <td>H</td><td>H</td><td>Me(OH)CH</td><td>8</td><td>0</td><td>(93)</td><td>(0)</td></tr> <tr> <td>H</td><td>H</td><td>Ph(OH)CH</td><td>8</td><td>0</td><td>(82)</td><td>(0)</td></tr> <tr> <td>H</td><td>H</td><td>HOCH₂</td><td>7</td><td>1</td><td>(97)</td><td>(0)</td></tr> <tr> <td>H</td><td>H</td><td>(EtO)₂CH</td><td>7</td><td>1</td><td>(86)</td><td>(0)</td></tr> <tr> <td>MeO</td><td>H</td><td>(EtO)₂CH</td><td>7</td><td>1</td><td>(73)</td><td>(14)</td></tr> <tr> <td>MeO</td><td>MeO</td><td>(EtO)₂CH</td><td>7</td><td>1</td><td>(30)</td><td>(0)</td></tr> </table>	R^1	R^2	R^3	x	y	I	II	H	H	Me(OH)CH	8	0	(93)	(0)	H	H	Ph(OH)CH	8	0	(82)	(0)	H	H	HOCH ₂	7	1	(97)	(0)	H	H	(EtO) ₂ CH	7	1	(86)	(0)	MeO	H	(EtO) ₂ CH	7	1	(73)	(14)	MeO	MeO	(EtO) ₂ CH	7	1	(30)	(0)	438
R^1	R^2	R^3	x	y	I	II																																															
H	H	Me(OH)CH	8	0	(93)	(0)																																															
H	H	Ph(OH)CH	8	0	(82)	(0)																																															
H	H	HOCH ₂	7	1	(97)	(0)																																															
H	H	(EtO) ₂ CH	7	1	(86)	(0)																																															
MeO	H	(EtO) ₂ CH	7	1	(73)	(14)																																															
MeO	MeO	(EtO) ₂ CH	7	1	(30)	(0)																																															
 C₁₅	(<i>n</i> -Pr)NH ₂	Cp* ₂ LaCH(TMS) ₂ (5 mol %), C ₇ D ₈ , 90°	 (92)	43																																																	
 C₁₅	RNH ₂ (13 eq)	1,4-DCB (2.9 eq), solvent, UV (Hg), 8–50 h	 I	 II																																																	
			 III	437																																																	
			 IV	 V																																																	
			<table> <tr> <th>R</th><th>Solvent</th><th>I</th><th>II</th><th>III</th><th>IV</th><th>V</th></tr> <tr> <td>H</td><td>MeCN</td><td>(33)</td><td>(5)</td><td>(0)</td><td>(4)</td><td>(17)</td></tr> <tr> <td>HO(CH₂)₂</td><td>MeCN</td><td>(53)</td><td>(5)</td><td>(0.7)</td><td>(2)</td><td>(1)</td></tr> <tr> <td>MeO(CH₂)₂</td><td>MeCN</td><td>(40)</td><td>(tr)</td><td>(3)</td><td>(7)</td><td>(5)</td></tr> <tr> <td><i>i</i>-Pr</td><td>MeCN</td><td>(41)</td><td>(2)</td><td>(2)</td><td>(6)</td><td>(5)</td></tr> <tr> <td><i>t</i>-Bu</td><td>MeCN</td><td>(0)</td><td>(72)</td><td>(0)</td><td>(0)</td><td>(0)</td></tr> <tr> <td><i>t</i>-Bu</td><td>EtCN</td><td>(27)</td><td>(0)</td><td>(1)</td><td>(5)</td><td>(7)</td></tr> </table>	R	Solvent	I	II	III	IV	V	H	MeCN	(33)	(5)	(0)	(4)	(17)	HO(CH ₂) ₂	MeCN	(53)	(5)	(0.7)	(2)	(1)	MeO(CH ₂) ₂	MeCN	(40)	(tr)	(3)	(7)	(5)	<i>i</i> -Pr	MeCN	(41)	(2)	(2)	(6)	(5)	<i>t</i> -Bu	MeCN	(0)	(72)	(0)	(0)	(0)	<i>t</i> -Bu	EtCN	(27)	(0)	(1)	(5)	(7)	
R	Solvent	I	II	III	IV	V																																															
H	MeCN	(33)	(5)	(0)	(4)	(17)																																															
HO(CH ₂) ₂	MeCN	(53)	(5)	(0.7)	(2)	(1)																																															
MeO(CH ₂) ₂	MeCN	(40)	(tr)	(3)	(7)	(5)																																															
<i>i</i> -Pr	MeCN	(41)	(2)	(2)	(6)	(5)																																															
<i>t</i> -Bu	MeCN	(0)	(72)	(0)	(0)	(0)																																															
<i>t</i> -Bu	EtCN	(27)	(0)	(1)	(5)	(7)																																															

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.



^a Small quantities of polystyrene were also obtained.

^b The reaction stopped at 50% conversion.

^c XANTPHOS (2 mol %) and [Pd(CH₃CN)₄](BF₄)₂ (2 mol %) were used as a catalyst.

^d The reaction was carried out under microwave heating (70 W, 10 psi) with air stream cooling.

^e 97% FeCl₃ (Aldrich) was used.

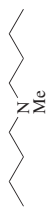
^f The reaction included microwave irradiation.

^g The relative stereochemistry was not reported.

^h The product was isolated as a *cis/trans* mixture of isomers with an unknown ratio.

TABLE 1C. HYDROAMINATION OF 1,3-DIENES

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

Diene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4  2 eq	MeNH ₂	1. NaH (26 mol %), 70–220°, 1 h 2. Pd/C, H ₂ (60 bar), cyclohexane, 150°, 4 h	 (18)	268
	EtNH ₂	Na (10 mol %), benzene, rt	 (65)	265
	R ₂ NH (x eq)	Catalyst (y mol %), solvent, rt	 R x Catalyst y Solvent Me 1.25 Na 2 Et₂O (82) 265 Et 1 Na 2 neat (76) 265 Et 1.6 Na/C₁₀H₈ 33 THF (85) 220	
 1.5 eq	Et ₂ NH (2 eq)	s-BuLi (5 mol %), solvent, 50°, 24 h	 Solvent (E)/(Z) cyclohexane (81)^a 20:79 THF (48) (E) only	224
	Et ₂ NH	PdBr ₂ (DPPE) ₂ (0.25 mol %), PhOH (2.5 mol %), 144–148°, 5 h	 (—)	278
	R ₂ NH	n-BuLi (5 mol %), cyclohexane, 50°	R (E)/(Z) Et (86) ^a 12:87 n-Pr (86) 12:87 i-Pr (9) 45:55 n-Bu (75) 14:86 i-Bu (84) 22:78	270

R_2NH (x eq)	R_2NLi (1 eq), cyclohexane, 50°, 1 h		R	x	(E)/(Z)	
Et			Et	0	(—)	—
Et			Et	3	(50)	2:98
n-Pr			n-Pr	0	(47)	7:93
i-Pr			i-Pr	3	(—)	—
n-Bu			n-Bu	3	(29)	5:95
i-Bu			i-Bu	0	(—)	—
i-Bu			i-Bu	3	(87)	20:80

R_2NH	Catalyst, PPh_3 (x mol %), $NaBH_4$ (y mol %), EtOH		I + 	II	272
			+ 	III + 	IV

217

R	Catalyst	x	y	Temp (°)	Time (h)	I-IV	III/IV
Et	$CoCl_2$ (2.5 mol %), $Al(Oi-Pr)_3$ (40 mol %)	7.5	10	100	16	(44)	14:42:41:3
n-Pr	$RhCl_3$ (0.8 mol %), Et_3N (0.8 mol %)	0	0	75	16	(68)	90:3:4:3
n-Pr	$RhCl_3$ (0.8 mol %), Ph_3As (2.4 mol %)	0	0	75	16	(66)	9:12:79:0
n-Pr	$RhCl_3$ (0.8 mol %)	0	0	75	15	(43)	70:18:12:0
n-Pr	$IrCl_3$ (1 mol %), HCl (1 mol %)	0	0	100	16	(100)	10:22:61:7
n-Pr	$RhCl_3$ (0.8 mol %)	0.8	0	75	15	(49)	10:23:67:0
n-Pr	$CoCl_2$ (2.5 mol %), $Al(Oi-Pr)_3$ (40 mol %)	7.5	10	100	16	(35)	22:20:54:4
n-Pr	$NiCl_2$ (8 mol %)	16	32	20	6	(46)	5:2:84:9
n-Pr	$CoCl_2$ (40 mol %),	40	60	20	11	(66)	29:55:8:8

(n-Bu) NH_2	$Me_2Si(C_5Me_4)_2NiCH(TMS)_2$ (3.7 mol %), C_6D_6 , 21°, 4 d		(90)	128
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1.8 eq

TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

Diene	Amine	Conditions	Product(s) and Yield(s) (%)			Refs.		
 1.5 eq	RNH ₂	PdBr ₂ (DPPE) ₂ (0.25 mol %), PhONa (2.5 mol %), PhOH (x mol %)	 I +  II			278		
		R	x	Temp (°)	Time (h)	I	II	
		<i>n</i> -Bu	2.5	130–139	5	(12)	(7)	
		<i>c</i> -C ₆ H ₁₁	2.5	141–146	20	(18)	(23)	
		Ph	0	155–158	20	(18)	(13)	
		Ph	2.5	155–162	0.5	(44)	(15)	
		Ph	5	85	3	(57)	(10)	
		4-MeC ₆ H ₄	2.5	85	3	(32)	(6)	
		Bn	2.5	145–153	3	(10)	(2)	
 3 eq	RNH ₂	Catalyst (2 mol %), NaBH ₄ (x mol %), (<i>i</i> -PrO) ₂ PPh (2.2 mol %), solvent, 100°	 I +  III +  IV			II	274	
		R	Catalyst	x	Solvent	Time (h)	I–IV	I/II/III/IV
		<i>n</i> -Bu	NiBr ₂	0	EtOH	1	(43)	32:47:21:0
		<i>n</i> -Bu	Ni(OAc) ₂	0	EtOH	1	(tr)	—
		<i>n</i> -Bu	Ni(OAc) ₂	0	EtOH	16	(43)	24:54:22:0
		<i>n</i> -Bu	Ni(acac) ₂	0.1	EtOH	1	(64)	42:58:0:0
		<i>n</i> -Bu	Ni(acac) ₂	0.1	EtOH	16	(31)	II only
		Ph	NiBr ₂	0	neat	16	(45)	62:38:0:0
		Ph	Ni(acac) ₂	0.1	EtOH	16	(37)	15:56:21:8
		4-MeOC ₆ H ₄	Ni(acac) ₂	0.1	EtOH	16	(58)	24:71:4:1

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₄

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₄

Diene	Amine	Conditions	Product(s) and Yield(s) (%)		Refs.																																																									
 3 eq		CoCl₂ (x mol %), PPh₃ (y mol %), NaBH₄ (z mol %), additive (40 mol %), EtOH	 I +  II	272																																																										
	 R =		 +  III + IV																																																											
<table> <tr> <th>x</th><th>y</th><th>z</th><th>Additive</th><th>Temp (°)</th><th>Time (h)</th><th>I-IV</th><th>III/III/IV</th></tr> <tr> <td>2.5</td><td>7.5</td><td>5</td><td>Al(Oi-Pr)₃</td><td>75</td><td>15.5</td><td>(37)</td><td>8:13:71:8</td></tr> <tr> <td>2.5</td><td>7.5</td><td>5</td><td>Al(Oi-Pr)₃</td><td>100</td><td>15.5</td><td>(60)</td><td>12:29:54:5</td></tr> <tr> <td>15</td><td>45</td><td>8</td><td>none</td><td>20</td><td>8</td><td>(98)</td><td>9:83:7:1</td></tr> <tr> <td>40</td><td>60</td><td>40</td><td>none</td><td>20</td><td>8</td><td>(98)</td><td>10:90:0:0</td></tr> </table>						x	y	z	Additive	Temp (°)	Time (h)	I-IV	III/III/IV	2.5	7.5	5	Al(Oi-Pr) ₃	75	15.5	(37)	8:13:71:8	2.5	7.5	5	Al(Oi-Pr) ₃	100	15.5	(60)	12:29:54:5	15	45	8	none	20	8	(98)	9:83:7:1	40	60	40	none	20	8	(98)	10:90:0:0																	
x	y	z	Additive	Temp (°)	Time (h)	I-IV	III/III/IV																																																							
2.5	7.5	5	Al(Oi-Pr) ₃	75	15.5	(37)	8:13:71:8																																																							
2.5	7.5	5	Al(Oi-Pr) ₃	100	15.5	(60)	12:29:54:5																																																							
15	45	8	none	20	8	(98)	9:83:7:1																																																							
40	60	40	none	20	8	(98)	10:90:0:0																																																							
	Catalyst (x mol %), additive (y mol %), EtOH, 75°, 16 h	 R =	 I +  II	272																																																										
			 +  III + IV																																																											
			<table> <tr> <th>Catalyst</th><th>x</th><th>Additive</th><th>y</th><th>I-IV</th><th>III/III/IV</th></tr> <tr> <td>RhCl₃</td><td>0.8</td><td>—</td><td>—</td><td>(77)</td><td>26:70:4:0</td></tr> <tr> <td>RhCl₃</td><td>0.8</td><td>PPh₃</td><td>0.8</td><td>(83)</td><td>12:26:57:5</td></tr> <tr> <td>RhCl₃</td><td>0.8</td><td>PPh₃</td><td>2.4</td><td>(33)</td><td>29:21:45:5</td></tr> <tr> <td>RhCl₃</td><td>0.8</td><td>AsPh₃</td><td>0.8</td><td>(91)</td><td>6:42:51:1</td></tr> <tr> <td>RhCl₃</td><td>0.8</td><td>Et₃N</td><td>2.4</td><td>(98)</td><td>25:73:2:0</td></tr> <tr> <td>RhCl₃</td><td>0.8</td><td>AsPh₃</td><td>2.4</td><td>(81)</td><td>2:30:66:2</td></tr> <tr> <td>RhCl₃</td><td>0.8</td><td>P(<i>c</i>-C₆H₁₁)₃</td><td>0.8</td><td>(74)</td><td>55:45:0:0</td></tr> <tr> <td>IrCl₃</td><td>1</td><td>—</td><td>—</td><td>(76)</td><td>5:14:60:21</td></tr> <tr> <td>IrCl₃</td><td>1</td><td>HCl</td><td>1</td><td>(100)</td><td>5:12:62:21</td></tr> </table>	Catalyst	x	Additive	y	I-IV	III/III/IV	RhCl ₃	0.8	—	—	(77)	26:70:4:0	RhCl ₃	0.8	PPh ₃	0.8	(83)	12:26:57:5	RhCl ₃	0.8	PPh ₃	2.4	(33)	29:21:45:5	RhCl ₃	0.8	AsPh ₃	0.8	(91)	6:42:51:1	RhCl ₃	0.8	Et ₃ N	2.4	(98)	25:73:2:0	RhCl ₃	0.8	AsPh ₃	2.4	(81)	2:30:66:2	RhCl ₃	0.8	P(<i>c</i> -C ₆ H ₁₁) ₃	0.8	(74)	55:45:0:0	IrCl ₃	1	—	—	(76)	5:14:60:21	IrCl ₃	1	HCl	1	(100)
Catalyst	x	Additive	y	I-IV	III/III/IV																																																									
RhCl ₃	0.8	—	—	(77)	26:70:4:0																																																									
RhCl ₃	0.8	PPh ₃	0.8	(83)	12:26:57:5																																																									
RhCl ₃	0.8	PPh ₃	2.4	(33)	29:21:45:5																																																									
RhCl ₃	0.8	AsPh ₃	0.8	(91)	6:42:51:1																																																									
RhCl ₃	0.8	Et ₃ N	2.4	(98)	25:73:2:0																																																									
RhCl ₃	0.8	AsPh ₃	2.4	(81)	2:30:66:2																																																									
RhCl ₃	0.8	P(<i>c</i> -C ₆ H ₁₁) ₃	0.8	(74)	55:45:0:0																																																									
IrCl ₃	1	—	—	(76)	5:14:60:21																																																									
IrCl ₃	1	HCl	1	(100)	5:12:62:21																																																									

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

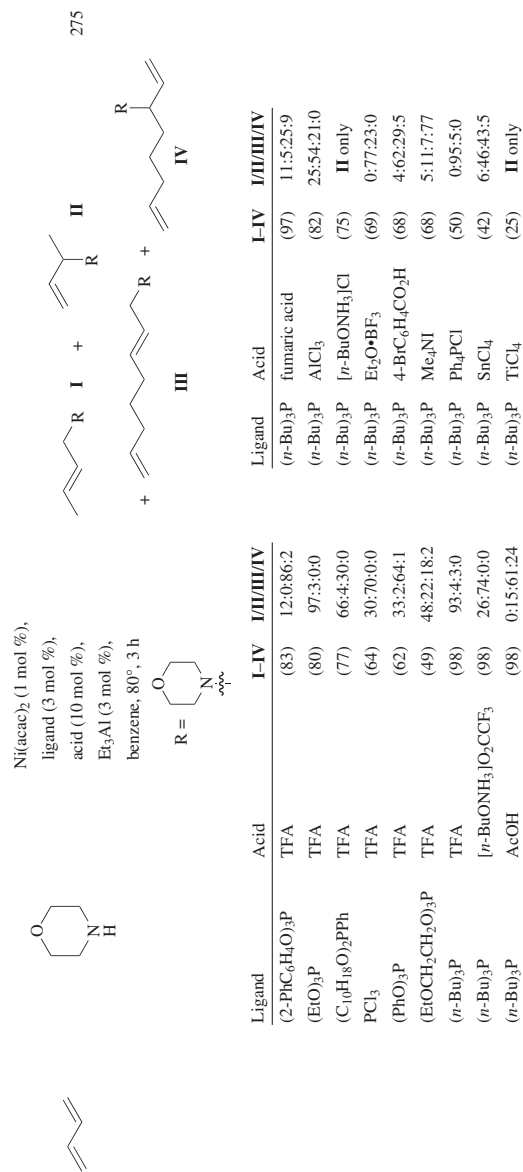
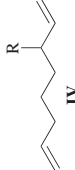


TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

Diene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																																				
 3 eq		NiBr₂ (2 mol %), phosphine (2.2 mol %), solvent	 I +  II	274																																																																																																				
		 R =	 III +  IV																																																																																																					
		<table> <tr> <th>Phosphine</th><th>Solvent</th><th>Temp (°)</th><th>Time (h)</th><th>I-IV</th><th>I/II/III/IV</th></tr> <tr> <td>(MeO)₃P</td><td>EtOH</td><td>100</td><td>1</td><td>(30)</td><td>32:46:20:2</td></tr> <tr> <td>(EtO)₃P</td><td>EtOH</td><td>100</td><td>1</td><td>(27)</td><td>38:49:12:1</td></tr> <tr> <td>(MeO)₂PPh</td><td>EtOH</td><td>100</td><td>1</td><td>(18)</td><td>64:36:0:0</td></tr> <tr> <td>(EtO)₂PPh</td><td>EtOH</td><td>100</td><td>1</td><td>(59)</td><td>39:44:15:2</td></tr> <tr> <td>(<i>i</i>-PrO)₂PPh</td><td>neat</td><td>50</td><td>1</td><td>(23)</td><td>24:42:33:1</td></tr> <tr> <td>(<i>i</i>-PrO)₂PPh</td><td>neat</td><td>75</td><td>1</td><td>(91)</td><td>23:42:33:2</td></tr> <tr> <td>(<i>i</i>-PrO)₂PPh</td><td>neat</td><td>100</td><td>1</td><td>(98)</td><td>36:29:33:2</td></tr> <tr> <td>(<i>i</i>-PrO)₂PPh</td><td>neat</td><td>100</td><td>0.5</td><td>(79)</td><td>32:33:33:2</td></tr> <tr> <td>(<i>i</i>-PrO)₂PPh</td><td>neat</td><td>100</td><td>5</td><td>(100)</td><td>35:22:41:2</td></tr> <tr> <td>(<i>i</i>-PrO)₂PPh</td><td>neat</td><td>100</td><td>16</td><td>(100)</td><td>44:19:36:1</td></tr> <tr> <td>(<i>i</i>-PrO)₂PPh</td><td>neat</td><td>100</td><td>24</td><td>(100)</td><td>47:18:34:1</td></tr> <tr> <td>(<i>i</i>-PrO)₂PPh</td><td><i>i</i>-PrOH</td><td>100</td><td>1</td><td>(93)</td><td>46:23:29:2</td></tr> <tr> <td>(<i>i</i>-PrO)₂PPh</td><td>benzene</td><td>100</td><td>1</td><td>(95)</td><td>28:33:37:2</td></tr> <tr> <td>(<i>i</i>-PrO)₂PPh</td><td>DMF</td><td>100</td><td>1</td><td>(100)</td><td>46:38:14:2</td></tr> <tr> <td>(<i>i</i>-PrO)₂PPh</td><td>Et₂O</td><td>100</td><td>1</td><td>(88)</td><td>31:32:35:2</td></tr> <tr> <td>(<i>i</i>-PrO)₂PPh</td><td>EtOH</td><td>100</td><td>1</td><td>(96)</td><td>59:31:9.5:0.5</td></tr> </table>	Phosphine	Solvent	Temp (°)	Time (h)	I-IV	I/II/III/IV	(MeO) ₃ P	EtOH	100	1	(30)	32:46:20:2	(EtO) ₃ P	EtOH	100	1	(27)	38:49:12:1	(MeO) ₂ PPh	EtOH	100	1	(18)	64:36:0:0	(EtO) ₂ PPh	EtOH	100	1	(59)	39:44:15:2	(<i>i</i> -PrO) ₂ PPh	neat	50	1	(23)	24:42:33:1	(<i>i</i> -PrO) ₂ PPh	neat	75	1	(91)	23:42:33:2	(<i>i</i> -PrO) ₂ PPh	neat	100	1	(98)	36:29:33:2	(<i>i</i> -PrO) ₂ PPh	neat	100	0.5	(79)	32:33:33:2	(<i>i</i> -PrO) ₂ PPh	neat	100	5	(100)	35:22:41:2	(<i>i</i> -PrO) ₂ PPh	neat	100	16	(100)	44:19:36:1	(<i>i</i> -PrO) ₂ PPh	neat	100	24	(100)	47:18:34:1	(<i>i</i> -PrO) ₂ PPh	<i>i</i> -PrOH	100	1	(93)	46:23:29:2	(<i>i</i> -PrO) ₂ PPh	benzene	100	1	(95)	28:33:37:2	(<i>i</i> -PrO) ₂ PPh	DMF	100	1	(100)	46:38:14:2	(<i>i</i> -PrO) ₂ PPh	Et ₂ O	100	1	(88)	31:32:35:2	(<i>i</i> -PrO) ₂ PPh	EtOH	100	1	(96)	59:31:9.5:0.5
Phosphine	Solvent	Temp (°)	Time (h)	I-IV	I/II/III/IV																																																																																																			
(MeO) ₃ P	EtOH	100	1	(30)	32:46:20:2																																																																																																			
(EtO) ₃ P	EtOH	100	1	(27)	38:49:12:1																																																																																																			
(MeO) ₂ PPh	EtOH	100	1	(18)	64:36:0:0																																																																																																			
(EtO) ₂ PPh	EtOH	100	1	(59)	39:44:15:2																																																																																																			
(<i>i</i> -PrO) ₂ PPh	neat	50	1	(23)	24:42:33:1																																																																																																			
(<i>i</i> -PrO) ₂ PPh	neat	75	1	(91)	23:42:33:2																																																																																																			
(<i>i</i> -PrO) ₂ PPh	neat	100	1	(98)	36:29:33:2																																																																																																			
(<i>i</i> -PrO) ₂ PPh	neat	100	0.5	(79)	32:33:33:2																																																																																																			
(<i>i</i> -PrO) ₂ PPh	neat	100	5	(100)	35:22:41:2																																																																																																			
(<i>i</i> -PrO) ₂ PPh	neat	100	16	(100)	44:19:36:1																																																																																																			
(<i>i</i> -PrO) ₂ PPh	neat	100	24	(100)	47:18:34:1																																																																																																			
(<i>i</i> -PrO) ₂ PPh	<i>i</i> -PrOH	100	1	(93)	46:23:29:2																																																																																																			
(<i>i</i> -PrO) ₂ PPh	benzene	100	1	(95)	28:33:37:2																																																																																																			
(<i>i</i> -PrO) ₂ PPh	DMF	100	1	(100)	46:38:14:2																																																																																																			
(<i>i</i> -PrO) ₂ PPh	Et ₂ O	100	1	(88)	31:32:35:2																																																																																																			
(<i>i</i> -PrO) ₂ PPh	EtOH	100	1	(96)	59:31:9.5:0.5																																																																																																			

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₄

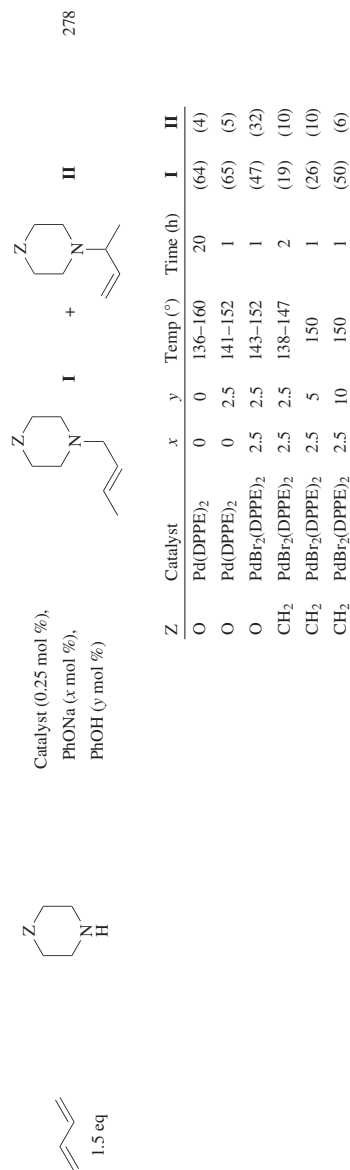
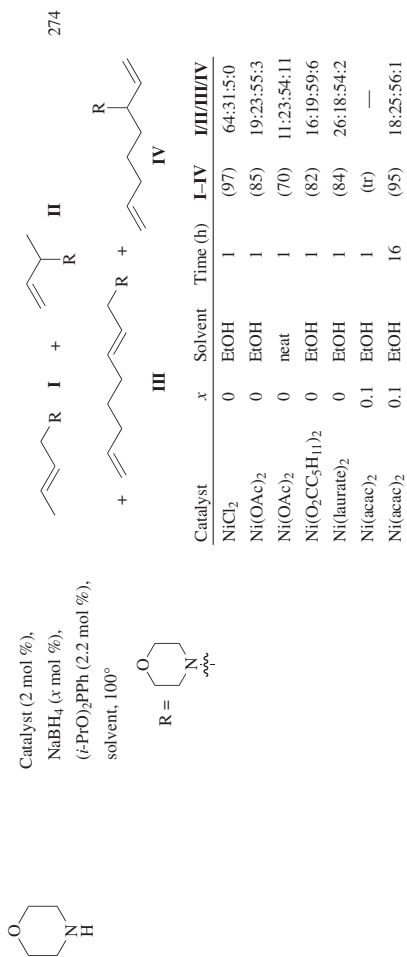
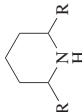
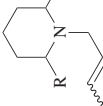
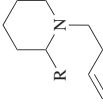


TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

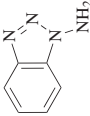
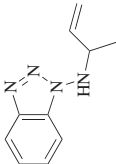
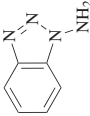
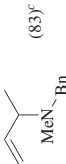
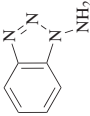
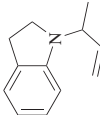
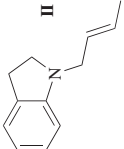
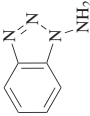
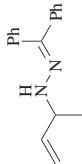
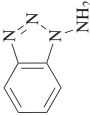
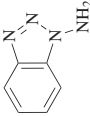
C₄

Diene	Amine	Conditions	Product(s) and Yield(s) (%)		Refs.			
	 (2 eq)	(<i>s</i> -Bu)Li (5 mol %), solvent, 50°		I + 	II 224			
			R	Solvent	Time (h)	I/II	(E)/(Z) I	
			H	cyclohexane	24	(83)	99:1	63:36
			H	THF	28	(58)	I only	(E) only
			Me	cyclohexane	17	(50)	I only	80:20
 3 eq		IrCl ₃ (0.8 mol %), EtOH, 75°, 16 h R = 		I + 	II			272
				III		IV		
			n	I-IV	I/II/III/IV			
			1	(82)	5:19:53:23			
			2	(100)	8:13:44:35			
 3 eq		Catalyst (2 mol %), (<i>i</i> -PrO) ₂ PPh (2.2 mol %), EtOH, 100° R = 		I + 	II			274
				III		IV		
			n	Catalyst	Time (h)	I-IV	I/II/III/IV	
			1	NiBr ₂	1	(86)	58:26:3:13	
			1	Ni(acac) ₂	16	(96)	56:17:2:37	
			2	Ni(acac) ₂	16	(92)	34:39:2:25	

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

		Na (2 mol %), benzene, rt		$\frac{n}{Z}$	265						
				1 CH ₂ (57)							
				2 MeN (85)							
				2 CH ₂ (74)							
	PhNH ₂	Catalyst (5 mol %), HBF ₄ •Et ₂ O (x mol %), benzene, 36 h		+		116					
Catalyst											
			x	Temp	I + II	I/II					
			0	45°	(92)	30:70					
			10	rt	(97)	30:70					
	PhNH ₂	CoCl ₂ (40 mol %), PPh ₃ (40 mol %), NaBH ₄ (60 mol %), rt, 11 h				272					
	PhNH ₂	Catalyst (x mol %), additive (y mol %), EtOH		+		272					
				+							
				+							
Catalyst											
			Catalyst	x	Additive	y	Temp (°)	Time (h)	I-IV	I/II/III/IV	
			RhCl ₃	0.8	none	—	75	15	(6)	19:81:0:0	
			IrCl ₃	1	HCl	1	100	16	(32)	24:40:23:5 ^b	
	PhNH ₂	Na (18 mol %), 120°, 18 h								(79)	440

TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

Diene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>				
C ₄		[Pd(allyl)Cl] ₂ (1 mol %), XANTPHOS (2 mol %), DCM, rt, 24 h	 (88)	283
		Ni(COD) ₂ (5 mol %), DPPF (5 mol %), TFA (20 mol %), C ₇ H ₈ , rt, 0.5 h	 (83) ^ʳ	277
		Catalyst (5 mol %), HBF ₄ •Et ₂ O (x mol %), benzene	 I +  II	116
C ₅		[Pd(allyl)Cl] ₂ (1 mol %), XANTPHOS (2 mol %), DCM, rt, 24 h	 (89)	283
		Na (2 mol %), solvent	 NR ₂	266
		R ₂ NH (1.25 eq)	 Et	(50) (75) (55)



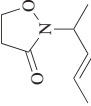
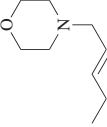
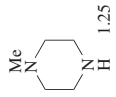
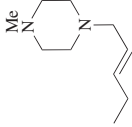
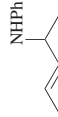
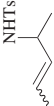
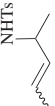
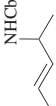
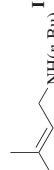
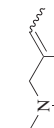
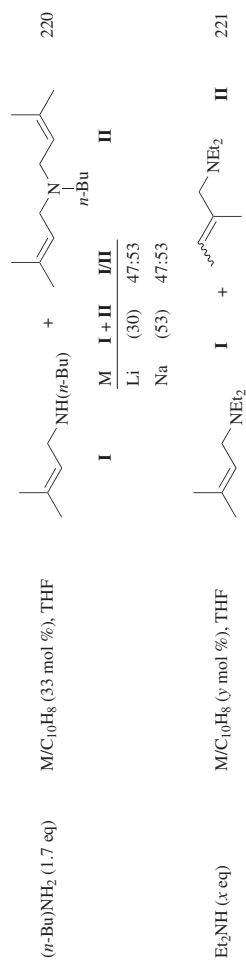
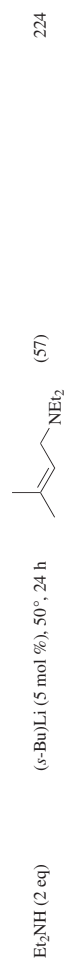
 2 eq		Bi(OTf)₃ (10 mol %), Cu(MeCN)₄PF₆ (10 mol %), DPPE (4 mol %), dioxane, 50°, 18 h	 (94)	286																
 1.25 eq	 1.25 eq	Na (2 mol %), neat, rt, 3 h	<table><tr><th colspan="2">n</th><th>Z</th><th></th></tr><tr><td>1</td><td>CH₂</td><td>(56)</td><td></td></tr><tr><td>2</td><td>MeN</td><td>(80)</td><td></td></tr><tr><td>2</td><td>CH₂</td><td>(70)</td><td></td></tr></table> 	n		Z		1	CH ₂	(56)		2	MeN	(80)		2	CH ₂	(70)		266
n		Z																		
1	CH ₂	(56)																		
2	MeN	(80)																		
2	CH ₂	(70)																		
 3 eq		Ni(acac)₂ (2 mol %), (<i>i</i>-PrO)₂PPh (2.2 mol %), NaBH₄ (1 mol %), 100°, 1 h	 I +  II I + II (80), I/II = 50:50	274																
 1.25 eq	 1.25 eq	Na (2 mol %), benzene, rt	 (92)	265																
 1.5 eq	 PhNH ₂	PdBr₂(DPPE)₂ (0.25 mol %), PhONa (2.5 mol %), PhOH (2.5 mol %), 130–140°, 24 h	 (52) +  NHPh (5)	278																

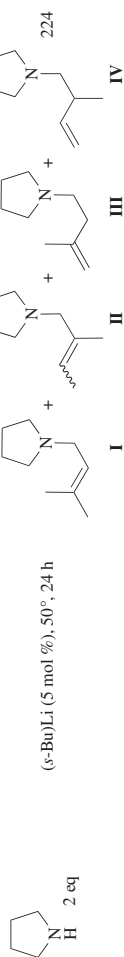
TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

Diene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the bold numbers.				
 4 eq (E)/(Z) = 1.8:1	TsNH ₂	[(PhO) ₃ P]AuCl (x mol %), AgOTf (x mol %), MW, solvent	 NHTs	285
 4 eq (E)/(Z) = 1.8:1	TsNH ₂	Catalyst (x mol %), solvent	 NHTs	429
 1.2 eq	CbzNH ₂	Ph ₃ PAuOTf (5 mol %), DCE, rt	 NHCbz (86)	284
	(n-Bu)NH ₂ (1.7 eq)	M/C ₁₀ H ₈ (33 mol %), THF	 I +  II	221
 +  III				
M I + II + III I/II/III Na (55) 30:35:35 Li (30) 25:30:45				

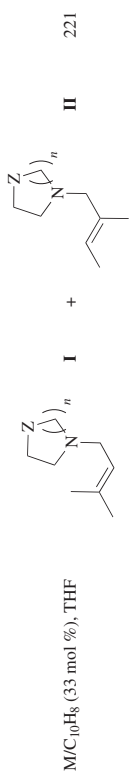


x	M	y	I + II	I/II
0.33	Na	17	(86)	34:63 ^b
0.5	Na	25	(94)	33:65 ^b
0.5	Na	33	(84)	37:61 ^b
0.67	Na	67	(74)	39:58 ^b
1	Na	33	(79)	59:41
1.2	Na	4	(91)	79:19 ^b
1.5	Na	50	(87)	85:15
1.5	Na	100	(84)	68:32
2.5	Na	50	(69)	79:21
3	Na	100	(68)	73:27
5	Na	100	(55)	77:23
1.2	Li	20	(57)	88:12
2.5	Li	50	(67)	86:14
2.5	K	50	(78)	68:29 ^b



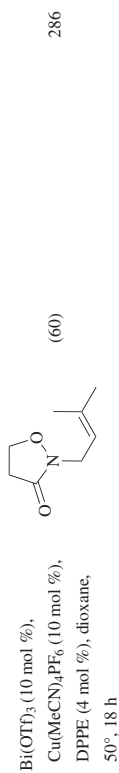


I-IV (95), I/II/III/IV = 76:15:7:2



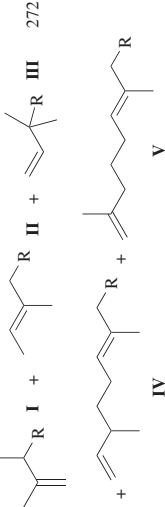
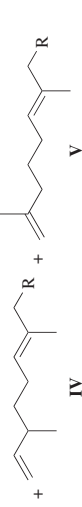
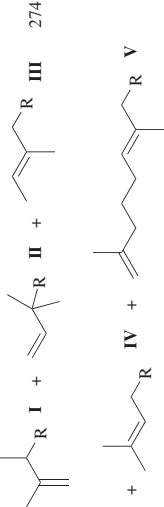
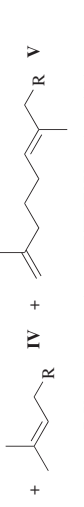
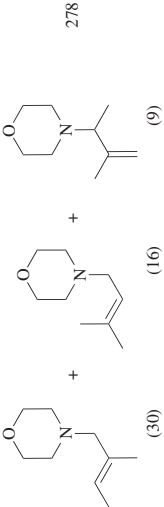
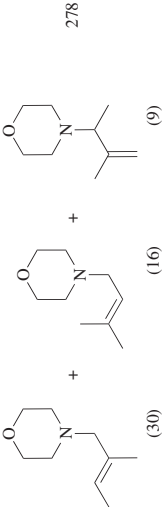
M/C₁₀H₈ (33 mol %), THF

<i>n</i>	Z	M	x	I + II	I/II
1	CH ₂	Na	2 (88)	76:19 ^b	
1	CH ₂	Li	2 (89)	74:26	
2	O	Na	2 (88)	76:20 ^b	
2	O	Li	2 (72)	69:31	
2	CH ₂	Na	0.5 (81)	59:38 ^b	
2	CH ₂	Na	2 (82)	72:24 ^b	
2	CH ₂	Li	2 (81)	76:24	



Bi(OTf)₃ (10 mol %),
Cu(MeCN)₄PF₆ (10 mol %),
DPPE (4 mol %), dioxane,
50°, 18 h

TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

Diene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 		NiCl_2 (8 mol %), PPh_3 (16 mol %), NaBH_4 (32 mol %), EtOH		272
		$\text{R} = $ 		272
		$\text{Ni}(\text{acac})_2$ (2 mol %), $(i\text{-PrO})_2\text{PPh}$ (2.2 mol %), NaBH_4 (1 mol %), 100° , 1 h		274
		$\text{R} = $ 		278
		$\text{PdBr}_2(\text{DPPE})_2$ (0.25 mol %), PhONa (2.5 mol %), PhOH (2.5 mol %), $140\text{--}146^\circ$, 2 h		278
		I-V (47% conversion), $\text{I/II/III/IV/V} = 10:14:54:5:17$		278

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

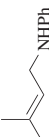
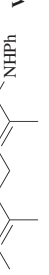
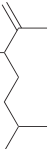
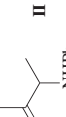
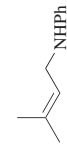
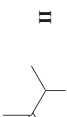
	PhNH ₂		Pd(acac) ₂ (1 mol %), P(OR) ₃ (x mol %), TFA (y mol %), MeCN				 I +  II		280
R	x	y	Temp (°)	Time (h)	I-IV	I/II/III/IV	V-VIII	V/VI/VII/VIII	
Me	1	1	100	34	(5)	23:28:6:43	(5)	—	 +  V
Me	1	4	100	37	(40)	37:26:2:35	(14)	8:27:42:2 ^b	 +  VI
Me	1	10	100	37	(4)	14:19:11:42	(0)	—	 +  VII
Me	2	4	20	168	(5)	40:12:6:42	(24)	9:20:42:0 ^b	 +  VIII
Me	4	4	100	32	(75)	84:9:1:5	(0)	—	
Me	4	10	100	32	(25)	86:4:0:10	(0)	—	
Me	4	20	100	32	(40)	61:17:5:17	(0)	—	
Et	0	10	100	32	(28)	50:20:10:21	(0)	—	
Et	1	1	100	31	(26)	34:31:9:26	(46)	7:26:49:5 ^b	
Et	1	1	100	82	(55)	22:31:10:37	(16)	8:22:48:3 ^b	
Et	1	4	100	85	(66)	18:15:10:57	(13)	11:26:45:3 ^b	
Et	1	10	100	32	(30)	56:18:1:25	(15)	13:25:43:8 ^b	
Et	2	4	20	168	(8)	55:22:4:19	(25)	10:23:40:8 ^b	
Et	2	4	100	32	(36)	53:20:5:22	(31)	7:25:47:4 ^b	
Et	2	10	100	32	(85)	51:14:9:26	(tr)	—	
Et	4	4	100	32	(62)	89:5:2:4	(0)	—	
Et	4	10	100	32	(59)	65:15:8:13	(0)	—	
Et	4	10	100	87	(34)	50:23:10:17	(0)	—	
Et	4	20	100	32	(33)	44:16:9:31	(0)	—	
Et	4	40	100	32	(30)	30:17:25:28	(0)	—	

TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

Diene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>				
 4.2 eq	PhNH ₂	Pd(acac) ₂ (0.5 mol %), P(OEt) ₃ (2 mol %), TFA (5 mol %), MeOH, 110°, 24 h	 I +  II	441
			+  +  III +  IV I-IV (60), I/II/III/IV = 27:37:11:25	
	PhNH ₂ (2 eq)	9c (2 mol %), C ₇ H ₈ , rt, 3 h	 I +  II I + II (92), I/II = 88:12	232
 10 eq	PhNH ₂ (4 eq)	Pd(PPh ₃) ₄ (1 mol %), AcOH (50 mol %), C ₇ H ₈ , rt	 (73)	282
 1.1 eq	PhNH ₂	10 (5 mol %), C ₇ H ₈ , 90°, 36 h	 I +  II I + II (68), I/II = 10:90	116
		Na (18 mol %), 120°, 18 h	 (29)	
				440

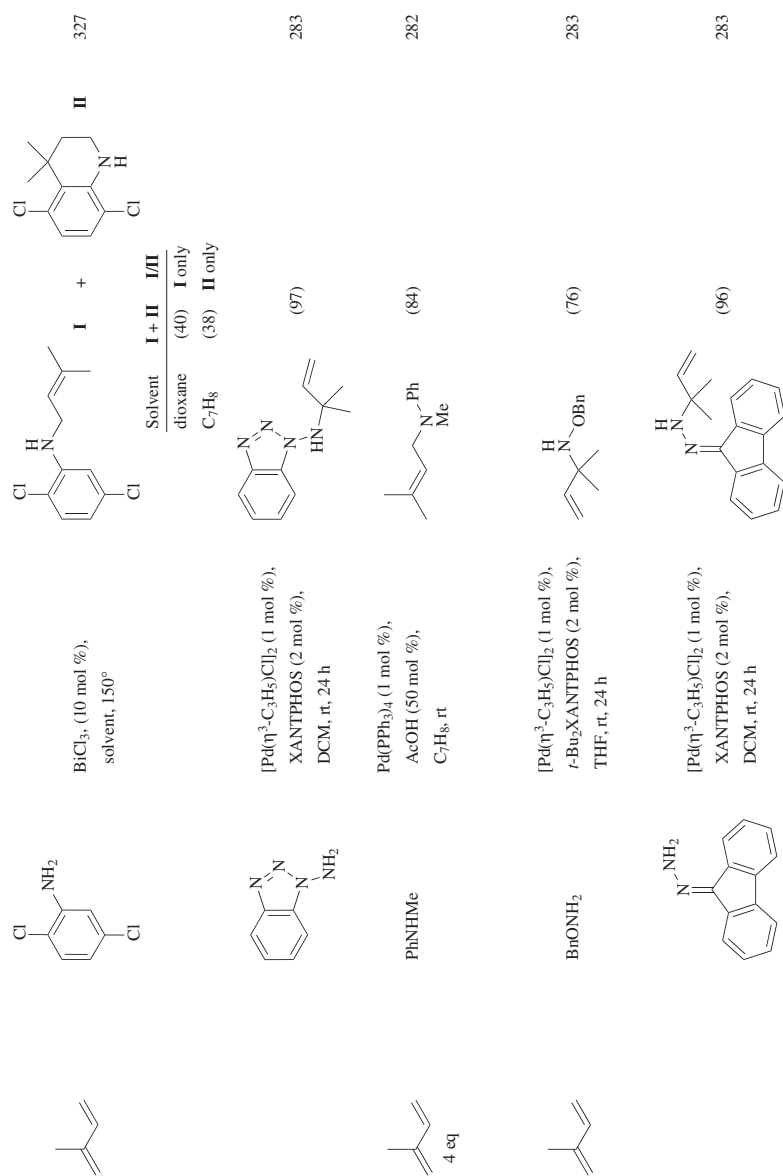
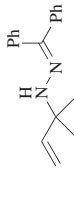
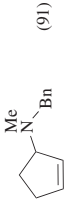
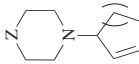
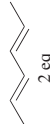
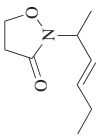


TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

Diene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.										
C ₅		Catalyst (x mol %), ligand (2 mol %), DCM, rt, 24 h		283										
														
C ₅₋₆	 2 eq	Ni(COD) ₂ (5 mol %), DPPF (5 mol %), TFA, (20 mol %), C ₇ H ₈ , rt, 43 h	 (91)	277										
	 n	Ni(acac) ₂ (1 mol %), (<i>n</i> -Bu) ₃ P (3 mol %), TFA (10 mol %), Et ₃ Al (2 mol %), benzene, 80°, 5 h	 <table data-bbox="1021 774 1159 911"> <tr> <th>n</th> <th>Z</th> </tr> <tr> <td>1</td> <td>O (60)</td> </tr> <tr> <td>1</td> <td>CH₂ (50)</td> </tr> <tr> <td>2</td> <td>O (80)</td> </tr> <tr> <td>2</td> <td>CH₂ (90)</td> </tr> </table>	n	Z	1	O (60)	1	CH ₂ (50)	2	O (80)	2	CH ₂ (90)	442
n	Z													
1	O (60)													
1	CH ₂ (50)													
2	O (80)													
2	CH ₂ (90)													
C ₆	 2 eq	Bi(OTf) ₃ (10 mol %), Cu(CH ₃ CN) ₄ PF ₆ (10 mol %), DPPE (4 mol %), dioxane, 50°, 18 h	 I +  II I + II (76), I/II = 1:2	286										

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

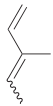
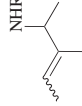
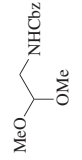
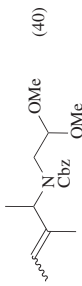
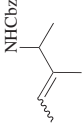
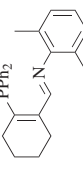
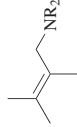
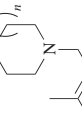
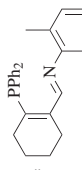
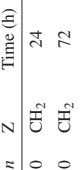
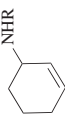
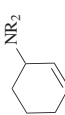
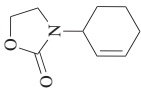
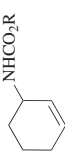
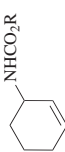
Diene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																												
Please refer to the charts preceding the tables for structures indicated by the bold numbers.																																
 C ₆ 1.2 eq	RNH ₂	Ph ₃ PAuOTf (5 mol %), DCE, rt, overnight	 R <table><tr><td>Moc</td><td>(77)</td></tr><tr><td>Ts</td><td>(81)</td></tr><tr><td>Cbz</td><td>(86)</td></tr><tr><td>Fmoc</td><td>(33)</td></tr></table>	Moc	(77)	Ts	(81)	Cbz	(86)	Fmoc	(33)	284																				
Moc	(77)																															
Ts	(81)																															
Cbz	(86)																															
Fmoc	(33)																															
	 MeO-CH ₂ -CH(NHCbz)-OMe	Ph ₃ PAuOTf (5 mol %), DCE, rt, 24 h	 (40)	284																												
	CbzNH ₂	TfOH (1 mol %), DCE, rt, overnight	 (83)	134																												
	R ₂ NH	[Pd(L)(C ₃ H ₅)]OTf (5 mol %), C ₆ D ₆ , 60° L = 	 R Time (h) <table><tr><td>Et</td><td>24</td><td>(38)</td></tr><tr><td>Et</td><td>72</td><td>(55)</td></tr><tr><td><i>i</i>-Pr</td><td>24</td><td>(0)</td></tr><tr><td><i>n</i>-Bu</td><td>24</td><td>(15)</td></tr><tr><td><i>n</i>-Bu</td><td>72</td><td>(36)</td></tr><tr><td>Bn</td><td>24</td><td>(tr)</td></tr></table>	Et	24	(38)	Et	72	(55)	<i>i</i> -Pr	24	(0)	<i>n</i> -Bu	24	(15)	<i>n</i> -Bu	72	(36)	Bn	24	(tr)	443										
Et	24	(38)																														
Et	72	(55)																														
<i>i</i> -Pr	24	(0)																														
<i>n</i> -Bu	24	(15)																														
<i>n</i> -Bu	72	(36)																														
Bn	24	(tr)																														
 C ₆ 1.2 eq	 Z	[Pd(L)(C ₃ H ₅)]OTf (5 mol %), C ₆ D ₆ , 60° L = 	 n Z Time (h) <table><tr><td>0</td><td>CH₂</td><td>24</td><td>(40)</td></tr><tr><td>0</td><td>CH₂</td><td>72</td><td>(56)</td></tr><tr><td>1</td><td>O</td><td>24</td><td>(89)</td></tr><tr><td>1</td><td>S</td><td>24</td><td>(49)</td></tr><tr><td>1</td><td>MeN</td><td>24</td><td>(38)</td></tr><tr><td>1</td><td>MeN</td><td>72</td><td>(49)</td></tr><tr><td>1</td><td>CH₂</td><td>24</td><td>(85)</td></tr></table>	0	CH ₂	24	(40)	0	CH ₂	72	(56)	1	O	24	(89)	1	S	24	(49)	1	MeN	24	(38)	1	MeN	72	(49)	1	CH ₂	24	(85)	443
0	CH ₂	24	(40)																													
0	CH ₂	72	(56)																													
1	O	24	(89)																													
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1	MeN	24	(38)																													
1	MeN	72	(49)																													
1	CH ₂	24	(85)																													

TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

Diene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.												
 2 eq C ₆	RNH ₂	Ni(COD) ₂ (5 mol %), DPPF (5 mol %), TFA (20 mol %), C ₇ H ₈ , rt	 <table><tr><th>R</th><th>Time (h)</th></tr><tr><td><i>n</i>-Bu</td><td>7 (89)</td></tr><tr><td><i>c</i>-C₆H₁₁</td><td>37 (82)</td></tr><tr><td>Bn</td><td>6 (93)</td></tr><tr><td>PMB</td><td>30 (87)</td></tr><tr><td>Ph₂CH</td><td>60 (85)</td></tr></table>	R	Time (h)	<i>n</i> -Bu	7 (89)	<i>c</i> -C ₆ H ₁₁	37 (82)	Bn	6 (93)	PMB	30 (87)	Ph ₂ CH	60 (85)	277
	R	Time (h)														
	<i>n</i> -Bu	7 (89)														
	<i>c</i> -C ₆ H ₁₁	37 (82)														
	Bn	6 (93)														
PMB	30 (87)															
Ph ₂ CH	60 (85)															
R ₂ NH	Ni(COD) ₂ (5 mol %), DPPF (5 mol %), TFA (20 mol %), C ₇ H ₈	 <table><tr><th>R</th><th>Temp</th><th>Time (h)</th></tr><tr><td>Et</td><td>rt</td><td>20 (78)</td></tr><tr><td>Bn</td><td>rt</td><td>113 (56)</td></tr><tr><td>Bn</td><td>60°</td><td>72 (71)</td></tr></table>	R	Temp	Time (h)	Et	rt	20 (78)	Bn	rt	113 (56)	Bn	60°	72 (71)	277	
R	Temp	Time (h)														
Et	rt	20 (78)														
Bn	rt	113 (56)														
Bn	60°	72 (71)														
	Bi(OTf) ₃ (10 mol %), additives, dioxane, 50°, 18 h	 Additives Cu(MeCN) ₄ PF ₆ (10 mol %), DPPE (4 mol %) KPF ₆ (10 mol %)	(92) (88)	286												
RO ₂ CNH ₂	Bi(OTf) ₃ (10 mol %), Cu(MeCN) ₄ PF ₆ (10 mol %), DPPE (4 mol %), dioxane, 50°, 18 h	 R <table><tr><th>R</th><th></th></tr><tr><td>Me</td><td>(96)</td></tr><tr><td><i>n</i>-Bu</td><td>(85)</td></tr><tr><td>Bn</td><td>(80)</td></tr></table>	R		Me	(96)	<i>n</i> -Bu	(85)	Bn	(80)		286				
R																
Me	(96)															
<i>n</i> -Bu	(85)															
Bn	(80)															
RO ₂ CNH ₂	Bi(OTf) ₃ (10 mol %), KPF ₆ (10 mol %), dioxane, 50°, 18 h	 R <table><tr><th>R</th><th></th></tr><tr><td>Me</td><td>(94)</td></tr><tr><td><i>n</i>-Bu</td><td>(72)</td></tr><tr><td>Bn</td><td>(72)</td></tr></table>	R		Me	(94)	<i>n</i> -Bu	(72)	Bn	(72)		286				
R																
Me	(94)															
<i>n</i> -Bu	(72)															
Bn	(72)															

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

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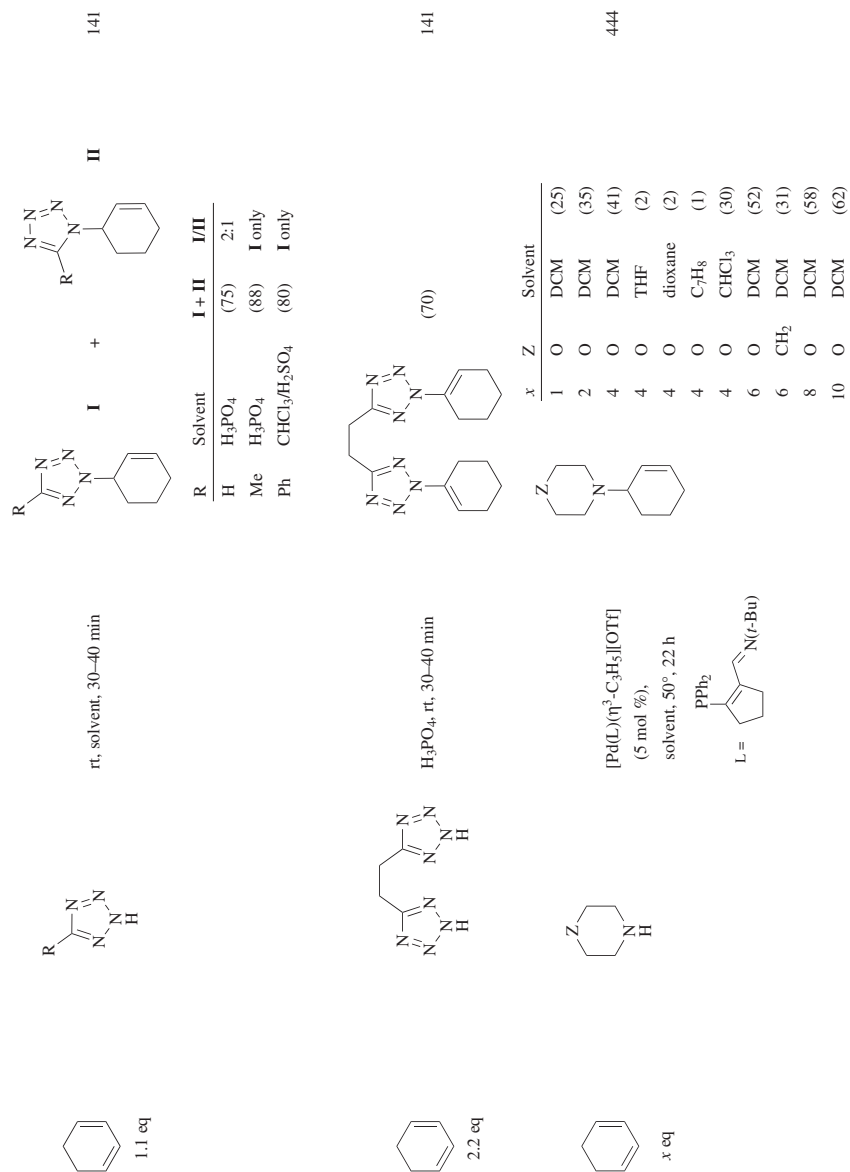
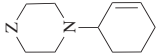
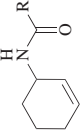
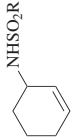


TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

Diene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																														
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>																																		
C ₆		2 eq	 Ni(COD) ₂ (5 mol %), DPPF (5 mol %), TFA (20 mol %), C ₇ H ₈ , rt, 20 h	277																														
		4 eq	 Bi(OTf) ₃ (10 mol %), Cu(MeCN) ₄ PF ₆ (10 mol %), DPPE (4 mol %), dioxane	286																														
			 Bi(OTf) ₃ (10 mol %), KPF ₆ (10 mol %), dioxane	286																														
			 PMA/SiO ₂ (10 mol %), C ₇ H ₈ , 120°	425																														
			 [(PhO) ₃ P]AuCl (x mol %), AgOTf (x mol %), solvent	285																														
<table border="1"> <thead> <tr> <th>R</th><th>x</th><th>Solvent</th><th>Temp (°)</th><th>Time (h)</th></tr> </thead> <tbody> <tr> <td>Me</td><td>5</td><td>dioxane</td><td>90</td><td>0.5 (85)</td></tr> <tr> <td>4-MeOC₆H₄</td><td>1</td><td>dioxane</td><td>90</td><td>0.5 (77)</td></tr> <tr> <td>4-MeC₆H₄</td><td>0.1</td><td>C₇H₈</td><td>85</td><td>14 (68)</td></tr> <tr> <td>4-MeC₆H₄</td><td>0.1</td><td>C₇H₈</td><td>90</td><td>0.25^d (66)</td></tr> <tr> <td>4-MeC₆H₄</td><td>1</td><td>DCM</td><td>rt</td><td>24 (99)</td></tr> </tbody> </table>					R	x	Solvent	Temp (°)	Time (h)	Me	5	dioxane	90	0.5 (85)	4-MeOC ₆ H ₄	1	dioxane	90	0.5 (77)	4-MeC ₆ H ₄	0.1	C ₇ H ₈	85	14 (68)	4-MeC ₆ H ₄	0.1	C ₇ H ₈	90	0.25 ^d (66)	4-MeC ₆ H ₄	1	DCM	rt	24 (99)
R	x	Solvent	Temp (°)	Time (h)																														
Me	5	dioxane	90	0.5 (85)																														
4-MeOC ₆ H ₄	1	dioxane	90	0.5 (77)																														
4-MeC ₆ H ₄	0.1	C ₇ H ₈	85	14 (68)																														
4-MeC ₆ H ₄	0.1	C ₇ H ₈	90	0.25 ^d (66)																														
4-MeC ₆ H ₄	1	DCM	rt	24 (99)																														

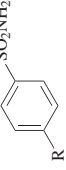
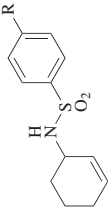
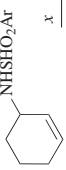
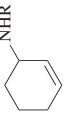
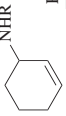
	$\text{H}_3\text{SiW}_{12}\text{O}_{40}\text{H}_2\text{O}$ (100 mg/mmol amide), DCE, 50°, 24 h		R H (48) Me (62)	250
ArSO_2NH_2	$\text{Bi}(\text{OTf})_3$ (10 mol %), $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (10 mol %), DPPF (4 mol %), dioxane		x Ar 2 Ph (80) 2 4-MeOC ₆ H ₄ (84) 2 4-MeC ₆ H ₄ (84) 2 4-CF ₃ C ₆ H ₄ (75) 4 2-O ₂ NC ₆ H ₄ (67)	286
RNH_2	$[\text{BSPy}][\text{OTf}]$ (20 mol %), DCE, 50°, 24 h		R Ts (54) Cbz (62)	423
RNH_2	$\text{Zr}(\text{OTf})_4$ (x mol %), solvent		R x Solvent Temp (°) Time (h) Ns 5 dioxane 90 21 (tr) Ts 5 DCE 50 10 (86) Ts 5 DCE rt 10 (48) Bz 10 DCE 100 24 (55) Cbz 5 DCE 50 22 (74)	422

TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

Diene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.							
 x eq	ArSO ₂ NH ₂	Bi(OTf) ₃ (x mol %), KPF ₆ (y mol %), dioxane	 NHSO ₂ Ar	286							
				x	Ar	y	Temp	Time (h)			
				1.2	Ph	5	rt	5	(73)		
				1.2	4-MeOC ₆ H ₄	5	rt	5	(84)		
				1.2	4-MeC ₆ H ₄	5	rt	3	(83)		
 2 eq	TsNH ₂	Bi(OTf) ₃ (x mol %), Cu(MeCN) ₄ PF ₆ (x mol %), DPPE (y mol %), dioxane, 50°	 NHTs	286							
				x	y	Time (h)					
				0.5	0.2	24	(80)				
				1	0.4	21	(83)				
				3	1.2	8	(87)				
	TsNH ₂	Cu(OTf) ₂ (5 mol %), DPPE (5 mol %), dioxane, 85°, 18 h	 NHTs	246							
				(92)							
				 1.2 eq	TsNH ₂	TfOH (1 mol %), DCE, 50°, 25 h	 NHTs	135			
								(63)			
								 2 eq	TsNH ₂	Ga (5 mol %), I ₂ (7.5 mol %), neat, 105°, 2 h	 NHTs
(20)											

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

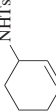
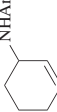
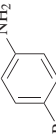
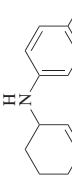
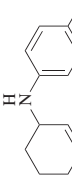
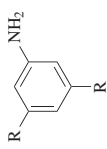
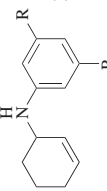
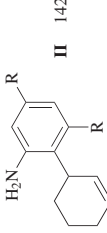
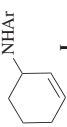
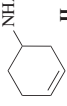
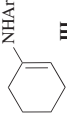
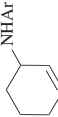
 4 eq	TsNH ₂	AgOTf (x mol %), solvent		x	Solvent	Temp	Time (h)	
				0.1	C ₇ H ₈	85°	14	(76)
				1	DCM	rt	24	(49)
 2 eq	ArNH ₂	Pd(PPh ₃) ₄ (2 mol %), TFA (10 mol %), C ₇ H ₈		Ar		Temp	Time (h)	
				Ph		rt	24	(99)
				2-BrC ₆ H ₄		rt	24	(95)
				2-MeOC ₆ H ₄		rt	24	(80)
				3-MeOC ₆ H ₄		rt	24	(95)
				4-MeOC ₆ H ₄		rt	24	(78)
				2-MeC ₆ H ₄		rt	24	(88)
				3-MeC ₆ H ₄		rt	24	(89)
				4-MeC ₆ H ₄		rt	24	(85)
				4-CF ₃ C ₆ H ₄		rt	48	(91)
				4-EtO ₂ CC ₆ H ₄		rt	48	(96)
				2-pyridyl		100°	24	(79) ^f
 2 eq		Catalyst (2 mol %), solvent, rt, 5 h						
				R	Catalyst	Solvent		
				H	9a	C ₇ H ₈	(89)	232
				H	9a	THF	(59)	
				H	9a	dioxane	(30)	
				H	9a	DCM	(2)	
				H	9a	DMF	(0)	
				H	9b	C ₇ H ₈	(58)	
				H	9c	C ₇ H ₈	(91)	
				F	9c	C ₇ H ₈	(90)	
				MeO	9c	C ₇ H ₈	(88)	

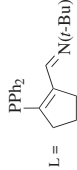
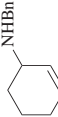
TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

Please refer to the charts preceding the tables for structures indicated by the **bold numbers**.

Diene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																						
C ₆	 2 eq	PhNH ₃ B(C ₆ F ₅) ₄ •Et ₂ O (5 mol %), chlorobenzene, 7 d	 I +  II 142																							
			<table> <tr> <th>R</th><th>Temp (°)</th><th>I + II</th><th>I/II</th></tr> <tr> <td>H</td><td>105</td><td>(56)</td><td>II only</td></tr> <tr> <td>CF₃</td><td>75</td><td>(20)</td><td>I only</td></tr> </table>	R	Temp (°)	I + II	I/II	H	105	(56)	II only	CF ₃	75	(20)	I only											
R	Temp (°)	I + II	I/II																							
H	105	(56)	II only																							
CF ₃	75	(20)	I only																							
 2 eq	ArNH ₂	H-BEA zeolite, C ₇ H ₈ , 111°	 I +  II +  III 445, 446																							
			<table> <tr> <th>Ar</th><th>I/II/III^g</th></tr> <tr> <td>Ph</td><td>90:3:7</td></tr> <tr> <td>4-ClC₆H₄</td><td>94:0:6</td></tr> <tr> <td>4-FC₆H₄</td><td>97:3:0</td></tr> <tr> <td>4-O₂NC₆H₄</td><td>I only</td></tr> <tr> <td>2-MeOC₆H₄</td><td>93:0:7</td></tr> <tr> <td>3-MeOC₆H₄</td><td>94:3:3</td></tr> <tr> <td>4-MeOC₆H₄</td><td>90:5:5</td></tr> <tr> <td>4-CF₃-C₆H₄</td><td>90:0:10</td></tr> <tr> <td>4-EtO₂CC₆H₄</td><td>I only</td></tr> <tr> <td>4-EtC₆H₄</td><td>94:6:0</td></tr> </table>	Ar	I/II/III ^g	Ph	90:3:7	4-ClC ₆ H ₄	94:0:6	4-FC ₆ H ₄	97:3:0	4-O ₂ NC ₆ H ₄	I only	2-MeOC ₆ H ₄	93:0:7	3-MeOC ₆ H ₄	94:3:3	4-MeOC ₆ H ₄	90:5:5	4-CF ₃ -C ₆ H ₄	90:0:10	4-EtO ₂ CC ₆ H ₄	I only	4-EtC ₆ H ₄	94:6:0	
Ar	I/II/III ^g																									
Ph	90:3:7																									
4-ClC ₆ H ₄	94:0:6																									
4-FC ₆ H ₄	97:3:0																									
4-O ₂ NC ₆ H ₄	I only																									
2-MeOC ₆ H ₄	93:0:7																									
3-MeOC ₆ H ₄	94:3:3																									
4-MeOC ₆ H ₄	90:5:5																									
4-CF ₃ -C ₆ H ₄	90:0:10																									
4-EtO ₂ CC ₆ H ₄	I only																									
4-EtC ₆ H ₄	94:6:0																									

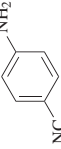
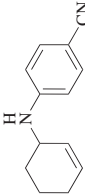
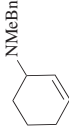
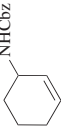
 x eq	ArNH ₂	[XANTPHOS]Pd(allyl)OTf (2 mol %), THF, 24 h		x	Ar	Temp	
				2	3-O ₂ NC ₆ H ₄	rt	(96)
				2	4-O ₂ NC ₆ H ₄	50°	(99)
				2	2-MeSC ₆ H ₄	rt	(99)
				2	4-MeSC ₆ H ₄	rt	(98)
				2	3-NCC ₆ H ₄	rt	(99)
				2	4-NCC ₆ H ₄	rt	(97)
				2	3-HO ₂ CC ₆ H ₄	rt	(81)
				2	4-AC ₆ H ₄	rt	(93)
				2	2-EtO ₂ CC ₆ H ₄	rt	(88)
				2	3-EtO ₂ CC ₆ H ₄	rt	(82)
				2	4-EtO ₂ CC ₆ H ₄	rt	(95)
				4	2-HOC ₆ H ₄	50°	(57)
				4	2-NCC ₆ H ₄	50°	(98)

237

 6 eq	BnNH ₂	[Pd(L)(allyl)][OTf] (5 mol %), 50°, 22 h 		(9)			
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444

TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

Diene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>				
 2 eq	 NC	Catalyst, (x mol %), ligand (2 mol %), additive (y mol %), solvent, rt, 20 h	 CN	237
 1.2 eq	BnNHMe	Ni(COD) ₂ (5 mol %), DPPF (5 mol %), TFA (20 mol %), C ₇ H ₈ , rt, 20 h	 NMeBn	277
 1.2 eq	CbzNH ₂	Ph ₃ PAuOTf (5 mol %), DCE, 50°, overnight	 NHCbz	284

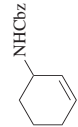
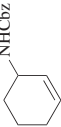
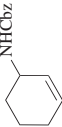
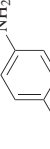
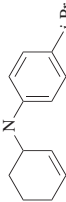
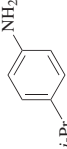
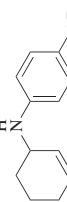
	2 eq		CbzNH_2	$\text{H}_3\text{SiW}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$ (100 mg/mmol amide), DCE, 50°, 25 h		(71)	250
	1.2 eq		CbzNH_2	TfOH (1 mol %), DCE, 50°		(71)	134
	4 eq		CbzNH_2	$\text{Bi}(\text{OTf})_3$ (10 mol %), additive (10 mol %), DPPF (x mol %), dioxane, 18 h		—	286
						KPF_6	0 rt (17)
						KPF_6	0 rt (79)
						KPF_6	0 50° (73)
						KPF_6	4 50° (42)
						NH_4PF_6	0 rt (74)
						$\text{Cu}(\text{MeCN})_4\text{PF}_6$	0 rt (79)
						$\text{Cu}(\text{MeCN})_4\text{PF}_6$	0 rt (71)
						$\text{Cu}(\text{MeCN})_4\text{PF}_6$	0 50° (66)
						$\text{Cu}(\text{MeCN})_4\text{PF}_6$	4 50° (80)
						$\text{Cu}(\text{OTf})(\text{C}_6\text{H}_5)_2$	0 rt (24)
				$\text{Zn}(\text{OTf})_2$ (1 mol %), hexanes, H_2O , 200°		(40)	447
				$\text{Zn}(\text{OTf})_2$ (1 mol %), hexanes, [EMIM][OTf], 200°		(75)	448

TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

Diene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>				
C ₆		[Pd(η^3 -C ₃ H ₅ Cl) ₂ (1 mol %), XANTPHOS (2 mol %), DCM, rt, 24 h	 (98)	283
C ₇		Pd(acac) ₂ (1 mol %), (<i>n</i> -Bu) ₃ P (3 mol %), TFA (10 mol %), Et ₃ Al (3 mol %), benzene, 100°, 8 h	 (60)	279
		Pd(acac) ₂ (1 mol %), (<i>n</i> -Bu) ₃ P (3 mol %), TFA (10 mol %), Et ₃ Al (3 mol %), benzene, 100°, 8 h	 (50)	279
		9c (2 mol %), C ₇ H ₈ , rt, 24 h	 (68)	232
		Ni(COD) ₂ (5 mol %), DPPF (5 mol %), TFA (20 mol %), C ₇ H ₈ , rt, 60 h	 (83)	277
		Pd(PPh ₃) ₄ (1 mol %), AcOH (50 mol %), C ₇ H ₈ , rt, 24 h	 (71)	282

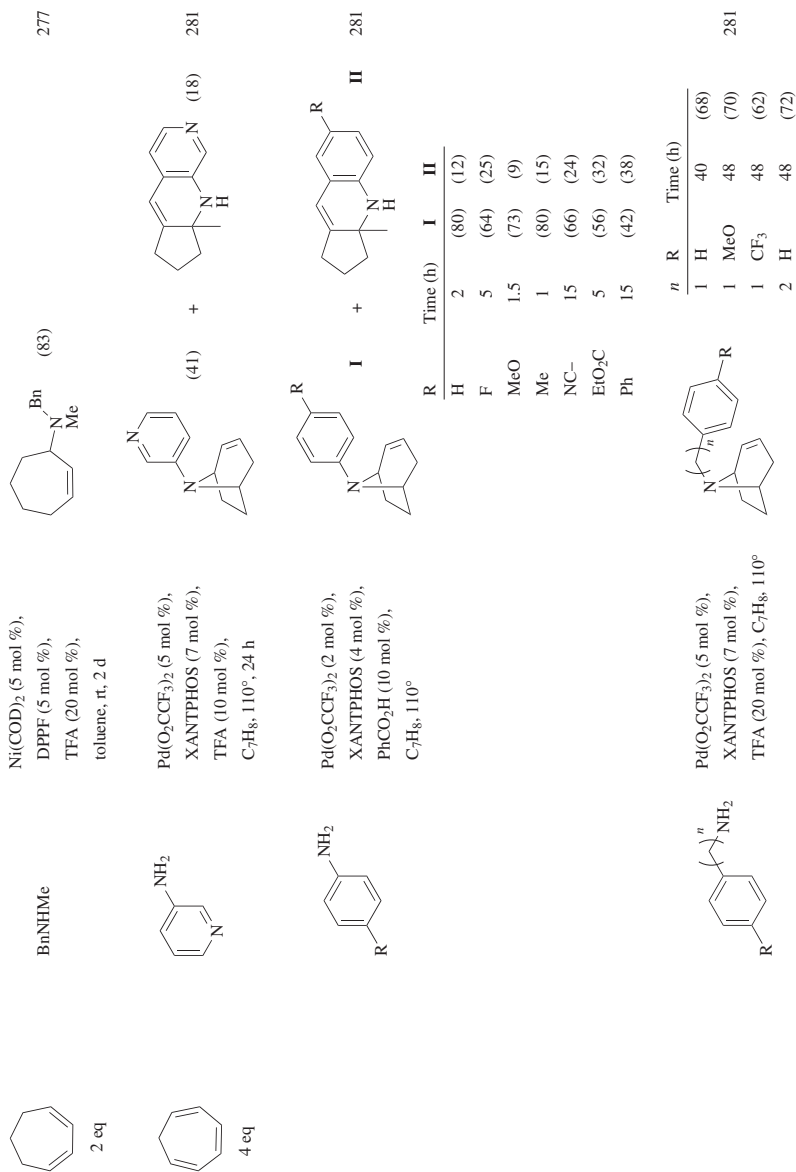
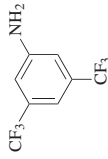
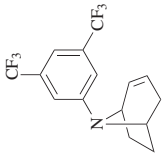
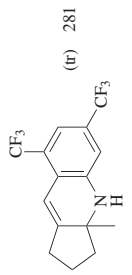
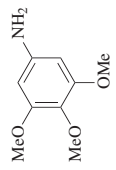
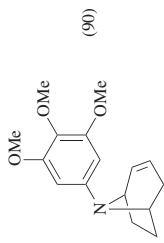
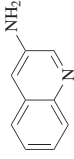
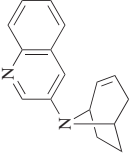
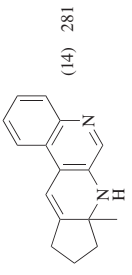
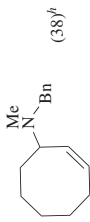
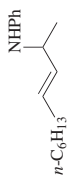
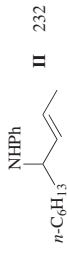


TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

Diene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7  4 eq		$Pd(O_2CCF_3)_2$ (2 mol %), XANTPHOS (4 mol %), $PhCO_2H$ (10 mol %), C_7H_8 , 110°, 72 h	 (61) +  (tr) 281	
		$Pd(O_2CCF_3)_2$ (2 mol %), XANTPHOS (4 mol %), $PhCO_2H$ (10 mol %), C_7H_8 , 110°, 1.5 h	 (90) 281	
		$Pd(O_2CCF_3)_2$ (2 mol %), XANTPHOS (4 mol %), $PhCO_2H$ (10 mol %), C_7H_8 , 110°, 1.5 h	 (58) +  (14) 281	
C_8  2 eq	BnNHMe	$Ni(COD)_2$ (5 mol %), DPPF (5 mol %), TFA (20 mol %), C_7H_8 , 60°, 84 h	 (38) [#] 277	
C_{10} 	$PhNH_2$ (2 eq)	$9c$ (2 mol %), C_7H_8 , rt, 6 h	 I +  II 232 I + II (80), I/II = 80:20	

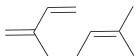
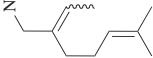
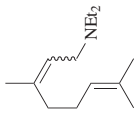
Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

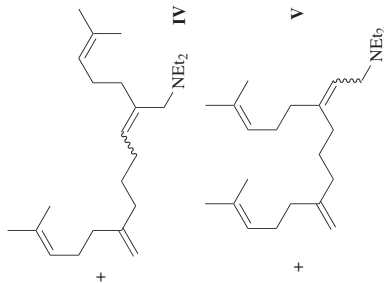
TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

Diene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
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Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

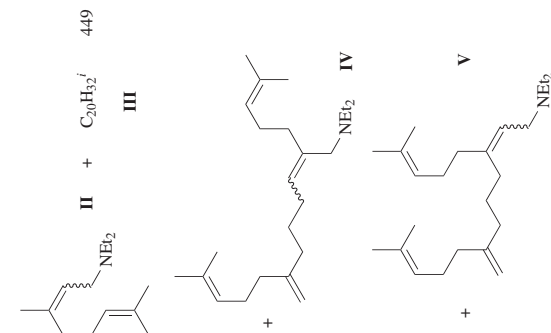
C₁₀

 2 eq	Et ₂ NH	[Pd(MeCN) ₄](BF ₄) ₂ (x mol %), PPh ₃ (y mol %), additive (z mol %), solvents (<i>al</i> b molar), 4 h	 I +	 II + C ₂₀ H ₃₂ ^{<i>i</i>} III	449							
x	y	Additive	z	Solvent <i>a</i>	Solvent <i>b</i>	<i>al</i> / <i>b</i>	Temp (°)	I + II	III	IV	V^b	
0.025	0.2	—	—	DMF	heptane	40:60	100	(0)	(4)	(37)	(1)	
0.05	0.2	—	—	MeCN	—	—	100	(0)	(7)	(3)	(2)	
0.05	0.2	—	—	DMF	—	—	100	(0)	(34)	(2)	(2)	
0.05	0.2	BF ₃ •Et ₂ O	0.25	DMF	—	—	100	(0)	(17)	(3)	(2)	
0.05	0.2	BF ₃ •Et ₂ O	2.5	DMF	—	—	100	(2)	(30)	(28)	(23)	
0.05	0.4	—	—	MeOH	—	—	100	(0)	(3)	(30)	(2)	
0.05	0.4	—	—	MeOH	octane	50:50	100	(2)	(6)	(42)	(3)	
0.05	0.4	—	—	MeOH	octane	40:60	100	(2)	(4)	(71)	(5)	
0.05	0.4	—	—	DMF	—	—	100	(0)	(1)	(69)	(3)	
0.05	0.4	—	—	DMF	heptane	60:40	100	(0)	(3)	(81)	(4)	
0.05	0.4	—	—	DMF	heptane	40:60	100	(0)	(3)	(85)	(2)	
0.05	0.4	—	—	DMF	heptane	30:70	100	(1)	(2)	(67)	(2)	
0.05	0.4	—	—	DMF	heptane	40:60	80	(0)	(1)	(38)	(2)	
0.05	0.4	—	—	DMF	heptane	40:60	100	(0)	(3)	(85)	(2)	
0.05	0.4	—	—	DMF	heptane	40:60	120	(1)	(3)	(65)	(2)	
0.1	0.8	—	—	DMF	heptane	40:60	100	(1)	(2)	(23)	(1)	



Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₁₀



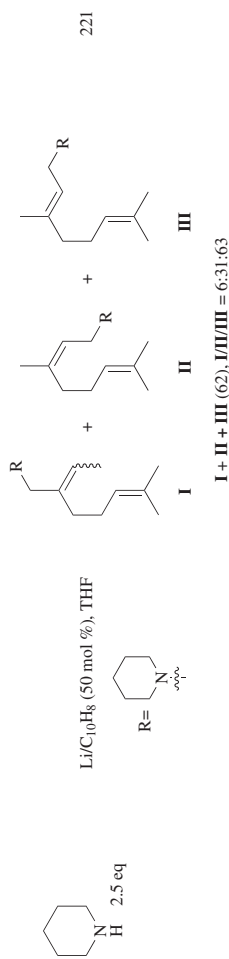
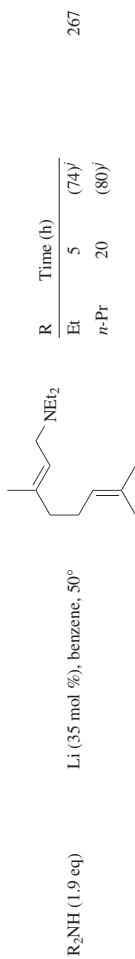
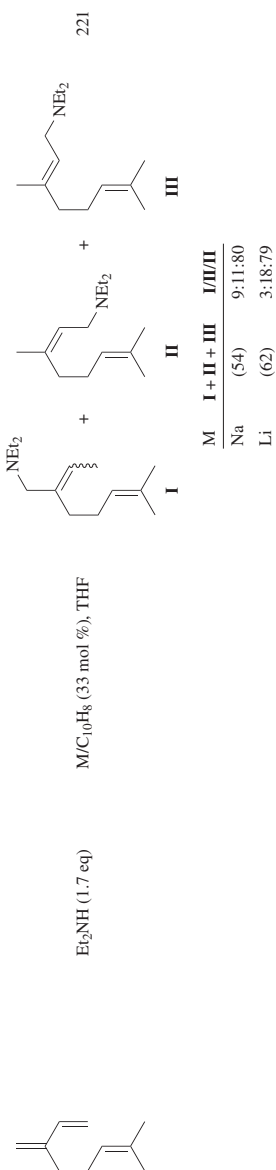
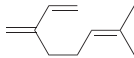
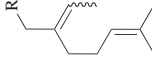
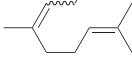
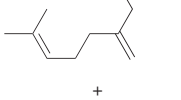
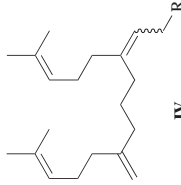


TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

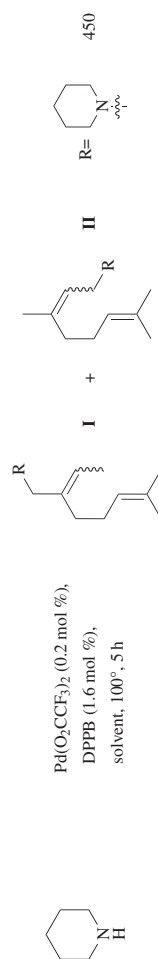
Diene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
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Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

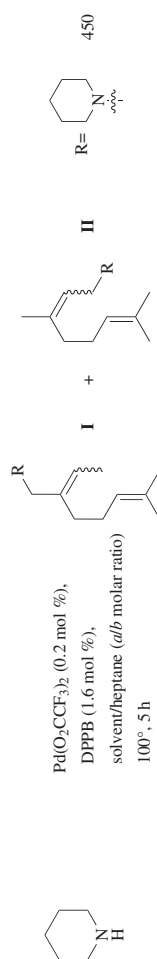
C₁₀

		Pd catalyst (0.2 mol %), ligand (x mol %), C ₇ H ₈ , 100°, 5 h	 I +  II  R =  450					
			 III +  IV					
Catalyst	Ligand	x	I	II	(E)/(Z)	III	IV	
Pd(O ₂ CCF ₃) ₂	DPE-phos	6.4	(5)	(12)	3.0:1	(0)	(0)	
Pd(O ₂ CCF ₃) ₂	DPE-phos	3.2	(28)	(50)	2.6:1	(0)	(0)	
Pd(O ₂ CCF ₃) ₂	DPE-phos	1.6	(4)	(8)	1.7:1	(0)	(0)	
Pd(O ₂ CCF ₃) ₂	XANTPHOS	6.4	(0)	(0)	—	(0)	(0)	
Pd(O ₂ CCF ₃) ₂	DPPE	6.4	(0)	(0)	—	(0)	(0)	
Pd(O ₂ CCF ₃) ₂	DPPP	6.4	(0)	(0)	—	(0)	(0)	
Pd(O ₂ CCF ₃) ₂	DPPB	6.4	(10)	(33)	3.1:1	(0)	(0)	
Pd(O ₂ CCF ₃) ₂	PPh ₃	6.4	(0)	(0)	—	(0)	(0)	
PdCl ₂	DPE-phos	6.4	(0)	(2)	E only	(0)	(0)	
PdCl ₂	DPPB	6.4	(0)	(3)	E only	(0)	(0)	
Pd(OAc) ₂	DPPB	6.5	(0)	(3)	E only	(0)	(0)	
Pd(OAc) ₂	DPE-phos	6.4	(0)	(2)	E only	(0)	(0)	
Pd(hfaoe) ₂	DPE-phos	6.4	(10)	(6)	2.0:1	(0)	(0)	
Pd(hfaoe) ₂	DPE-phos	3.2	(12)	(8)	1.7:1	(0)	(0)	
Pd(hfaoe) ₂	DPE-phos	1.6	(3)	(0)	—	(0)	(0)	
Pd(hfaoe) ₂	DPPB	6.4	(11)	(8)	1.7:1	(0)	(0)	
Pd(hfaoe) ₂	DPPB	3.2	(22)	(17)	2.4:1	(0)	(0)	
Pd(hfaoe) ₂	DPPB	1.6	(26)	(21)	3.2:1	(32)	(11)	
Pd(hfaoe) ₂	DPPB	0.8	(11)	(7)	2.5:1	(39)	(20)	
Pd(hfaoe) ₂	DPPB	0.4	(0)	(0)	—	(0)	(0)	

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.



Solvent	I	II	(<i>E</i>)/(<i>Z</i>) II	III	IV
C_7H_8	(26)	(66)	3.4:1	(2)	(1)
PC	(10)	(16)	1.7:1	(8)	(17)
DMF	(16)	(20)	1.9:1	(3)	(0)
NMP	(5)	(8)	1.7:1	(23)	(3)
DMSO	(11)	(13)	2.3:1	(0)	(0)
MeCN	(7)	(12)	2.0:1	(0)	(0)



Solvent	<i>a/b</i>	I + II	III + IV
DMF	40:60	(2)	(59)
DMF	50:50	(11)	(35)
DMF	60:40	(29)	(16)
MeCN	40:60	(71)	(4)
MeCN	50:50	(35)	(15)
MeCN	60:40	(42)	(8)

TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

C_{11–17}

Please refer to the charts preceding the tables for structures indicated by the **bold numbers**.

Refs.

Conditions

Amine

Diene

Product(s) and Yield(s) (%)

Refs.

Conditions

Amine

Diene

Product(s) and Yield(s) (%)

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Product(s) and Yield(s) (%)

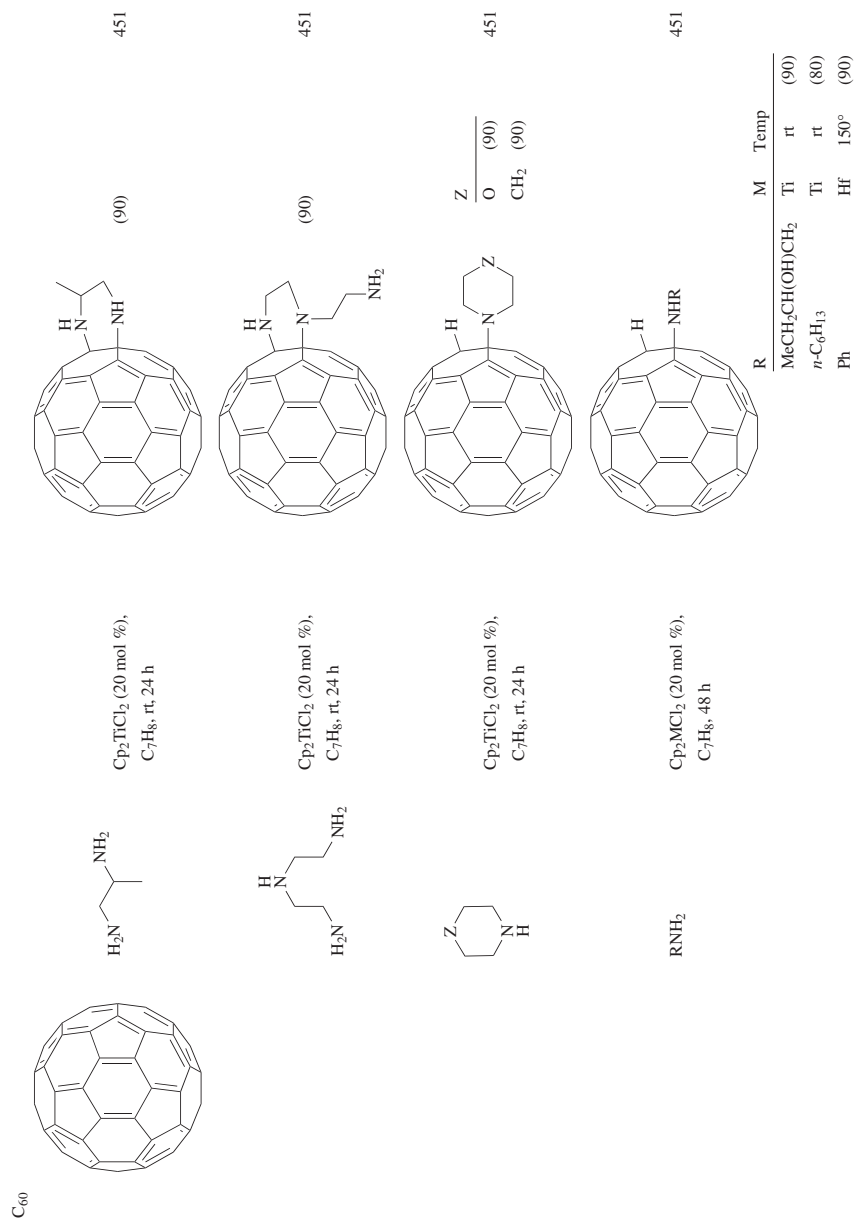
Refs.

Conditions

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

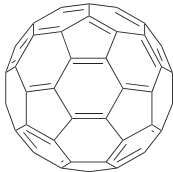
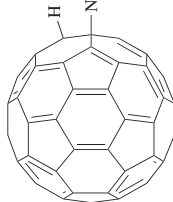
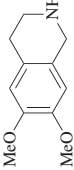
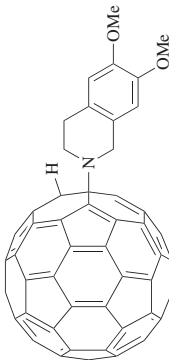
C_{11–17}

C₁₂



R	M	Temp
MeCH ₂ CH(OH)CH ₂	Ti	rt (90)
<i>n</i> -C ₆ H ₁₃	Ti	rt (80)
Ph	Hf	150° (90)

TABLE 1C. HYDROAMINATION OF 1,3-DIENES (Continued)

Diene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.															
	R ₂ NH	Cp ₂ MgCl ₂ (20 mol %), C ₇ H ₈ , 48 h		451															
			<table><tr><th>R</th><th>M</th><th>Temp (°)</th></tr><tr><td>Et</td><td>Ti</td><td>20 (90)</td></tr><tr><td>allyl</td><td>Ti</td><td>20 (90)</td></tr><tr><td>c-C₆H₁₁</td><td>Ti</td><td>20 (80)</td></tr><tr><td>Ph</td><td>Hf</td><td>150 (75)</td></tr></table>	R	M	Temp (°)	Et	Ti	20 (90)	allyl	Ti	20 (90)	c-C ₆ H ₁₁	Ti	20 (80)	Ph	Hf	150 (75)	
R	M	Temp (°)																	
Et	Ti	20 (90)																	
allyl	Ti	20 (90)																	
c-C ₆ H ₁₁	Ti	20 (80)																	
Ph	Hf	150 (75)																	
		Cp ₂ HfCl ₂ (20 mol %), C ₇ H ₈ , 150°, 9 h		451 (75)															

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₆₀

^a Trace amounts of 1,2-addition products are also found.

^b Other products were formed.

^c Three regioisomers are formed in a 27:2:2 ratio as determined by GC. The structure of the major isomer is shown.

^d The reaction is carried out under microwave heating (70 W, 10 psi) with air stream cooling.

^e Products include 8% of octadienyl amines.

^f The reaction conditions are [Pd(η³-C₃H₅)Cl₂] (2.5 mol %), PPh₃ (10 mol %), C₇H₈, 100°, 24 h.

^g The yield is not reported.

^h Three regioisomers are formed in a 14:4:7 ratio as determined by GC. The structure of the major isomer is shown.

ⁱ The products include myrcene dimers, for which the structures are not reported.

^j Isomer selectivity is 94%.

^k The products are isolated as *N*-acetylamides.

TABLE 1D. HYDROAMINATION OF ALLENES

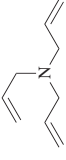
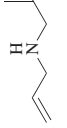
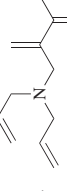
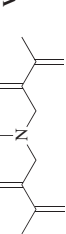
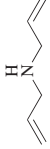
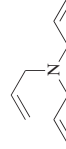
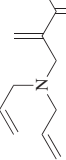
Allene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>				
C ₃ H ₂ C=•=CH ₂ 2 eq		PdCl ₂ (0.3 mol %), NaBH ₄ (0.3 mol %), PPh ₃ (0.3 mol %), neat	 I +  II 452	
			 III +  IV +  V	
			Temp (°) Time (h) I-V I/II/III/IV/V	
	60	1	(1.7)	—
	100	1	(56)	3:0:83:12:4
	100	3	(72)	1:0:80:9:10
	130	3	(93)	2:0:66:13:19
	150	1	(67)	11:1:69:9:8
H ₂ C=•=CH ₂	RNH ₂	Cp ₂ TiMe ₂ (10 mol %), C ₆ D ₆ , 90°	 NR	
			R Time (h) ^a	
			Me ₂ N 1.8 (90)	290
			<i>n</i> -Bu 0.5 (76)	
			4-MeOC ₆ H ₄ 18 (58)	
			4-MeC ₆ H ₄ 14 (78)	
			4-CF ₃ C ₆ H ₄ >48 (25)	
			2,6-Me ₂ C ₆ H ₃ 2 (87)	
			Ph(Me)CH 1.5 (90)	
			1-naphthyl 2 (95)	
H ₂ C=•=CH ₂ 2 eq		PdCl ₂ (0.3 mol %), NaBH ₄ (0.3 mol %), PPh ₃ (0.3 mol %), neat	 I +  II 452	
			Temp (°) Time (h) I + II I/II	
			100 1 (8) 55:45	
			130 6 (83) 11:89	

TABLE 1D. HYDROAMINATION OF ALLENES (Continued)

Allene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																																			
Please refer to the charts preceding the tables for structures indicated by the bold numbers.																																							
C ₃ H ₂ C=•=CH ₂ 2 eq		PdCl ₂ (0.3 mol %), NaBH ₄ (0.3 mol %), PPh ₃ (0.3 mol %), 130°, 6 h	 I + II (49), I/II = 30:70	452																																			
H ₂ C=•=CH ₂		Cp(ArNH)(py)Ti=NAr (10 mol %), C ₆ D ₆ , 45°, 0.5 h ^a Ar = 2,6-Me ₂ C ₆ H ₄	 (95)	290																																			
H ₂ C=•=CH ₂ 0.9 bar		Cp ₂ Zr(NH(2,6-Me ₂ C ₆ H ₄)) ₂ (2.7 mol %), benzene, 90°, 6 d	 (83)	59																																			
H ₂ C=•=CH ₂		[Bn ₂ Ti=N(CMe ₃)B(C ₆ F ₅) ₄] (5 mol %), chlorobenzene, 135°, 24 h	 (95)	64																																			
C ₃₋₅ R C=CH ₂ R	NH ₃ (x eq)	12 (y mol %), neat	 I + II	291																																			
<table><tr><th>R</th><th>x</th><th>y</th><th>Temp (°)</th><th>Time (h)</th><th>I + II + III</th><th>I/II/III</th></tr><tr><td>H</td><td>0.2</td><td>1.4</td><td>165</td><td>36</td><td>(91)</td><td>1.2:8:91</td></tr><tr><td>H</td><td>1.4</td><td>1.2</td><td>175</td><td>22</td><td>(98)</td><td>11:48:41</td></tr><tr><td>H</td><td>40</td><td>4.3</td><td>175</td><td>16</td><td>(96)</td><td>86:14</td></tr><tr><td>Me</td><td>0.8</td><td>1.3</td><td>155</td><td>22</td><td>(87)</td><td>1.5:27:72</td></tr></table>					R	x	y	Temp (°)	Time (h)	I + II + III	I/II/III	H	0.2	1.4	165	36	(91)	1.2:8:91	H	1.4	1.2	175	22	(98)	11:48:41	H	40	4.3	175	16	(96)	86:14	Me	0.8	1.3	155	22	(87)	1.5:27:72
R	x	y	Temp (°)	Time (h)	I + II + III	I/II/III																																	
H	0.2	1.4	165	36	(91)	1.2:8:91																																	
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H	40	4.3	175	16	(96)	86:14																																	
Me	0.8	1.3	155	22	(87)	1.5:27:72																																	
 III																																							

H

$$\begin{array}{c} \text{R}^2 \\ \diagup \\ \text{C}=\text{CH}_2 \\ \diagdown \\ \text{R}^1 \end{array}$$

$$(\text{R}^3)_2\text{NH}$$

11 (5 mol %),

$$\text{KB}(\text{C}_6\text{F}_5)_4 \text{ (5 mol \%),}$$

$$\text{C}_6\text{D}_6$$

$$\begin{array}{c} \text{R}^1 \\ \diagup \\ \text{C}=\text{CH}-\text{N}(\text{R}^3)_2 \\ \diagdown \\ \text{R}^2 \end{array}$$

R ¹	R ²	R ³	Temp (°)	Time (h)	(E)/(Z)
H	H	Et	150	24	(82)
H	H	Bn	70	12	(94)
Me	Me	Et	130	36	(98)
Me	Me	Bn	80	12	(99)
Ph	H	Et	165	24	(61)
					3.4:1

C₃₋₉

$$\begin{array}{c} \text{R}^1 \\ \diagup \\ \text{C}=\text{CH}_2 \\ \diagdown \\ \text{R}^2 \end{array}$$

11 (5 mol %),

$$\text{KB}(\text{C}_6\text{F}_5)_4 \text{ (5 mol \%),}$$

$$\text{C}_6\text{D}_6$$

453

C₃₋₅

$$\begin{array}{c} \text{R} \\ \diagup \\ \text{C}=\text{CH}_2 \\ \diagdown \\ \text{R} \end{array}$$

11 (5 mol %),

$$\text{KB}(\text{C}_6\text{F}_5)_4 \text{ (5 mol \%),}$$

$$\text{C}_6\text{D}_6, 70^\circ$$

R	n	Time (h)
H	1	3
Me	1	3
Me	2	9

453

11 (5 mol %),

$$\text{KB}(\text{C}_6\text{F}_5)_4 \text{ (5 mol \%),}$$

$$\text{C}_6\text{D}_6, 90^\circ$$

R	Time (h)
H	8
Me	12

453

TABLE 1D. HYDROAMINATION OF ALLENES (Continued)

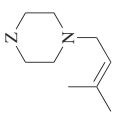
Allene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>				
C ₃	Bz-NMe 	Ph ₃ PAuCl (5 mol %), AgOTf (5 mol %), DCM, rt, 1 h	Ar 2-IC ₆ H ₄ (46) 3-MeOC ₆ H ₄ (47)	454
C ₄₊₁₂	R 	(IPr)AuCl (5 mol %), AgOTf (5 mol %), dioxane, rt, 24 h	 I + II	297
C ₅		R ¹ R ² NH	R 	I + II I/II
			MeO ₂ C (75)	II only
			MeO ₂ C(CH ₂) ₈ (88)	50:50
C ₅		(L)Pd(C ₃ H ₅)OTf (5 mol %), C ₆ D ₆ L =		R ¹ R ² Temp Time (h)
			Me	<i>n</i> -Bu rt 4 (98) 443
			Et	Et rt 3 (98)
			<i>i</i> -Pr	<i>i</i> -Pr rt 48 (0)
			<i>n</i> -Bu	<i>n</i> -Bu rt 3 (98)
C ₅		11 (5 mol %), KB(C ₆ F ₅) ₄ (5 mol %), C ₆ D ₆	Bn	Bn 50° 30 (98)
			R ¹ R ² Temp (°) Time (h)	
			Mes H 100 5 (74)	
			H <i>t</i> -Bu 150 30 (54)	
C ₅		R ¹ R ² NH	Ph H 70 12 (98)	
			4-ClC ₆ H ₄ H 70 12 (97)	
			4-MeOC ₆ H ₄ H 70 12 (97)	
C ₅		R ¹ R ² NH		453

RNH₂ (L)AuCl (5 mol %), AgOTf (5 mol %), dioxane, rt, 24 h



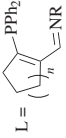
R	L	
MeO ₂ C	IPr	(57)
Cbz	(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	(58)
Cbz	(<i>c</i> -C ₆ H ₁₁) ₂ P(2-PhC ₆ H ₄)	(47)
Cbz	(<i>t</i> -Bu) ₂ P[2-(2,5-(MeO) ₂ C ₄ H ₃)C ₆ H ₄]	(25)
Cbz	(4-MeOC ₆ H ₄) ₃ P	(93)
Cbz	IPr	(94)
Finoc	IPr	(87)

297



443

Catalyst (5 mol %), C₆D₆, rt



Z	Catalyst	n	R	Time (h)	
—	(L)Pd(C ₃ H ₅)OTf	2	2,6-Me ₂ C ₆ H ₃	6	(98)
O	PdCl ₂	—	—	48	(0)
O	[Pd(C ₃ H ₅)Cl] ₂	—	—	48	(0)
O	[Pd(C ₃ H ₅)Cl] ₂ /2AgOTf	—	—	48	(0)
O	(L)PdCl ₂	1	<i>t</i> -Bu	48	(0)
O	(L)PdCl ₂	2	2,6-Me ₂ C ₆ H ₃	48	(0)
O	(L)PdCl ₂ /2AgOTf	1	<i>t</i> -Bu	48	(0)
O	(L)PdCl ₂ /2AgOTf	2	2,6-Me ₂ C ₆ H ₃	48	(0)
O	(L)Pd(C ₃ H ₅)Cl	1	<i>t</i> -Bu	48	(0)
O	(L)Pd(C ₃ H ₅)Cl	2	2,6-Me ₂ C ₆ H ₃	48	(0)

TABLE 1D. HYDROAMINATION OF ALLENES (Continued)

C₅

Allene

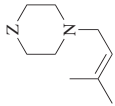
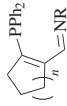
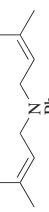
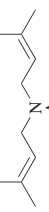
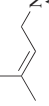
Amine

Conditions

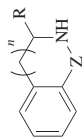
Product(s) and Yield(s) (%)

Refs.

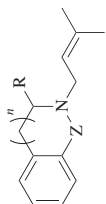
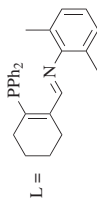
Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

			Catalyst (5 mol %), C ₆ D ₆ , rt			443	
			L = 				
Z	Catalyst	n	R	Time (h)			
O	(L)Pd(C ₃ H ₅)OTf	1	<i>t</i> -Bu	20	(98)		
O	(L)Pd(C ₃ H ₅)OTf	2	2,6-Me ₂ C ₆ H ₃	4	(98)		
O	(L)Pd(C ₃ H ₅)OTf/NEt ₃	2	2,6-Me ₂ C ₆ H ₃	24	(70)		
O	(L)Pd(C ₃ H ₅)OTf/HBF ₄	2	2,6-Me ₂ C ₆ H ₃	4	(97)		
S	(L)Pd(C ₃ H ₅)OTf	2	2,6-Me ₂ C ₆ H ₃	3	(98)		
MeN	(L)Pd(C ₃ H ₅)OTf	2	2,6-Me ₂ C ₆ H ₃	1	(98)		
CH ₂	(L)Pd(C ₃ H ₅)OTf	2	2,6-Me ₂ C ₆ H ₃	6	(98)		
PhNH ₂	11 (5 mol %), KB(C ₆ F ₅) ₄ (5 mol %), C ₆ D ₆ , 70°, 12 h		 I + II (95), III = 60:40			453	
ArNH ₂	(L)AuCl (5 mol %), AgOTf (5 mol %), solvent		 I +  II			455	
Ar	L	x	Solvent	Temp (°)	Time (h)	I + II	III
Ph	—	2	dioxane	45	12	(0)	—
Ph	IPr	2	C ₇ H ₈	rt	24	(10)	>25:1
Ph	IPr	2	dioxane	rt	24	(17)	>25:1
Ph	(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	2	dioxane	rt	24	(35)	>25:1
Ph	(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	2	dioxane	45	12	(100)	4.1:1

2-BrC ₆ H ₄	(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	2	dioxane	45	24	(87)	I only
3-BrC ₆ H ₄	(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	2	dioxane	45	12	(95)	3.1:1
4-BrC ₆ H ₄	(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	2	dioxane	45	12	(96)	1:1.4
4-BrC ₆ H ₄	(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	3	dioxane	45	12	(99)	II only
4-O ₂ NC ₆ H ₄	(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	2	dioxane	45	12	(99)	1:2
4-O ₂ NC ₆ H ₄	(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	3	dioxane	45	12	(99)	II only
2-Me-4-ClC ₆ H ₃	(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	2	dioxane	45	24	(86)	I only
1-naphthyl	(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	2	dioxane	45	24	(84)	I only



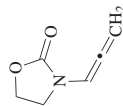
(L)Pd(C₃H₅)OTf (5 mol %),
C₆D₆



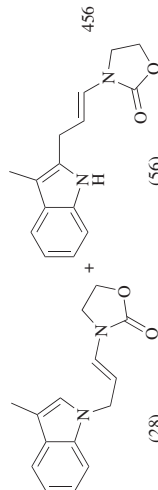
443

<i>n</i>	Z	R	Temp (°)	Time (h)
1	—	H	rt	24 (98)
1	—	Me	90	24 (28)
1	—	Me	90	96 (55)
1	CH ₂	H	rt	3 (98)
2	—	H	90	24 (11)
2	—	H	90	96 (25)

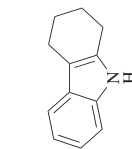
C₆



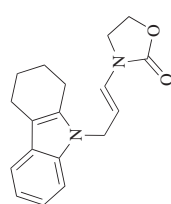
Ph₃PAuNTf₂ (5 mol %),
DCM, rt, 1 h



456



Ph₃PAuNTf₂ (5 mol %),
DCM, rt, 1 h



456

(78)

TABLE 1D. HYDROAMINATION OF ALLENES (Continued)

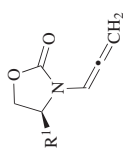
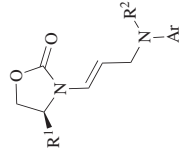
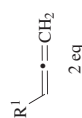
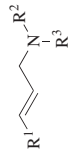
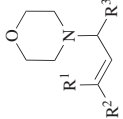
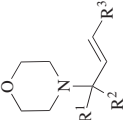
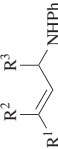
Allene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																																									
	ArNHR ²	Ph ₃ PAuCl (5 mol %), AgOTf (5 mol %), DCM, rt, 1 h		<table><tr><th>R¹</th><th>Ar</th><th>R²</th><th></th></tr><tr><td>H</td><td>Ph</td><td>H</td><td>(86)</td></tr><tr><td>H</td><td>4-BrC₆H₄</td><td>H</td><td>(79)</td></tr><tr><td>H</td><td>2-FC₆H₄</td><td>H</td><td>(90)</td></tr><tr><td>H</td><td>2-IC₆H₄</td><td>H</td><td>(98)</td></tr><tr><td>H</td><td>3-MeOC₆H₄</td><td>H</td><td>(61)</td></tr><tr><td>H</td><td>4-O₂NC₆H₄</td><td>Me</td><td>(98)</td></tr><tr><td>H</td><td>2-O₂N,4-MeOC₆H₃</td><td>H</td><td>(99)</td></tr><tr><td>H</td><td>4-EtO₂CC₆H₄</td><td>H</td><td>(91)</td></tr><tr><td>H</td><td>2,5-Me₂C₆H₃</td><td>H</td><td>(83)</td></tr><tr><td>Bn</td><td>Ph</td><td>H</td><td>(79)</td></tr><tr><td>Bn</td><td>2-IC₆H₄</td><td>H</td><td>(91)</td></tr></table>	R ¹	Ar	R ²		H	Ph	H	(86)	H	4-BrC ₆ H ₄	H	(79)	H	2-FC ₆ H ₄	H	(90)	H	2-IC ₆ H ₄	H	(98)	H	3-MeOC ₆ H ₄	H	(61)	H	4-O ₂ NC ₆ H ₄	Me	(98)	H	2-O ₂ N,4-MeOC ₆ H ₃	H	(99)	H	4-EtO ₂ CC ₆ H ₄	H	(91)	H	2,5-Me ₂ C ₆ H ₃	H	(83)	Bn	Ph	H	(79)	Bn	2-IC ₆ H ₄	H	(91)	454																																																								
R ¹	Ar	R ²																																																																																																											
H	Ph	H	(86)																																																																																																										
H	4-BrC ₆ H ₄	H	(79)																																																																																																										
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Bn	Ph	H	(79)																																																																																																										
Bn	2-IC ₆ H ₄	H	(91)																																																																																																										
	R ² R ³ NH	(L)PtCl ₂ (5 mol %), AgOTf (5 mol %), solvent, 80°		<table><tr><th>R¹</th><th>R²</th><th>R³</th><th>L</th><th>Solvent</th><th>Time (h)</th><th>(E)/(Z)</th><th></th></tr><tr><td>(MeO₂C)₂CHCH₂</td><td>Et</td><td>Et</td><td>DPPF</td><td>dioxane</td><td>24</td><td>(86)</td><td>9.6:1</td></tr><tr><td>(MeO₂C)₂CHCH₂</td><td></td><td>-(CH₂)₄-</td><td>DPPF</td><td>dioxane</td><td>24</td><td>(78)</td><td>8.4:1</td></tr><tr><td>(MeO₂C)₂CHCH₂</td><td></td><td>-(CH₂)₂O(CH₂)₂-</td><td>DPPF</td><td>dioxane</td><td>24</td><td>(89)</td><td>7.8:1</td></tr><tr><td>(MeO₂C)₂CHCH₂</td><td></td><td>-(CH₂)₅-</td><td>DPPF</td><td>dioxane</td><td>24</td><td>(78)</td><td>7.6:1</td></tr><tr><td>(MeO₂C)₂CHCH₂</td><td>n-Bu</td><td>n-Bu</td><td>DPPF</td><td>dioxane</td><td>24</td><td>(82)</td><td>17:1</td></tr><tr><td>(MeO₂C)₂CHCH₂</td><td>Bn</td><td>n-Bu</td><td>BIPHEP</td><td>dioxane</td><td>24</td><td>(22)</td><td>7.0:1</td></tr><tr><td>(MeO₂C)₂CHCH₂</td><td>Bn</td><td>n-Bu</td><td>BINAP</td><td>dioxane</td><td>24</td><td>(27)</td><td>4.1:1</td></tr><tr><td>(MeO₂C)₂CHCH₂</td><td>Bn</td><td>n-Bu</td><td>DPPF</td><td>dioxane</td><td>24</td><td>(70)</td><td>11:1</td></tr><tr><td>(MeO₂C)₂CHCH₂</td><td>Bn</td><td>n-Bu</td><td>DPE-phos</td><td>dioxane</td><td>24</td><td>(79)</td><td>5.6:1</td></tr><tr><td>(MeO₂C)₂CHCH₂</td><td>Bn</td><td>n-Bu</td><td>XANTPHOS</td><td>dioxane</td><td>24</td><td>(88)</td><td>5.0:1</td></tr><tr><td>(MeO₂C)₂CHCH₂</td><td>Bn</td><td>n-Bu</td><td>NIXANTPHOS</td><td>dioxane</td><td>24</td><td>(86)</td><td>6.5:1</td></tr><tr><td>(MeO₂C)₂CHCH₂</td><td>Bn</td><td>n-Bu</td><td>DPPF</td><td>MeOH</td><td>24</td><td>(20)</td><td>17:1</td></tr></table>	R ¹	R ²	R ³	L	Solvent	Time (h)	(E)/(Z)		(MeO ₂ C) ₂ CHCH ₂	Et	Et	DPPF	dioxane	24	(86)	9.6:1	(MeO ₂ C) ₂ CHCH ₂		-(CH ₂) ₄ -	DPPF	dioxane	24	(78)	8.4:1	(MeO ₂ C) ₂ CHCH ₂		-(CH ₂) ₂ O(CH ₂) ₂ -	DPPF	dioxane	24	(89)	7.8:1	(MeO ₂ C) ₂ CHCH ₂		-(CH ₂) ₅ -	DPPF	dioxane	24	(78)	7.6:1	(MeO ₂ C) ₂ CHCH ₂	n-Bu	n-Bu	DPPF	dioxane	24	(82)	17:1	(MeO ₂ C) ₂ CHCH ₂	Bn	n-Bu	BIPHEP	dioxane	24	(22)	7.0:1	(MeO ₂ C) ₂ CHCH ₂	Bn	n-Bu	BINAP	dioxane	24	(27)	4.1:1	(MeO ₂ C) ₂ CHCH ₂	Bn	n-Bu	DPPF	dioxane	24	(70)	11:1	(MeO ₂ C) ₂ CHCH ₂	Bn	n-Bu	DPE-phos	dioxane	24	(79)	5.6:1	(MeO ₂ C) ₂ CHCH ₂	Bn	n-Bu	XANTPHOS	dioxane	24	(88)	5.0:1	(MeO ₂ C) ₂ CHCH ₂	Bn	n-Bu	NIXANTPHOS	dioxane	24	(86)	6.5:1	(MeO ₂ C) ₂ CHCH ₂	Bn	n-Bu	DPPF	MeOH	24	(20)	17:1	457
R ¹	R ²	R ³	L	Solvent	Time (h)	(E)/(Z)																																																																																																							
(MeO ₂ C) ₂ CHCH ₂	Et	Et	DPPF	dioxane	24	(86)	9.6:1																																																																																																						
(MeO ₂ C) ₂ CHCH ₂		-(CH ₂) ₄ -	DPPF	dioxane	24	(78)	8.4:1																																																																																																						
(MeO ₂ C) ₂ CHCH ₂		-(CH ₂) ₂ O(CH ₂) ₂ -	DPPF	dioxane	24	(89)	7.8:1																																																																																																						
(MeO ₂ C) ₂ CHCH ₂		-(CH ₂) ₅ -	DPPF	dioxane	24	(78)	7.6:1																																																																																																						
(MeO ₂ C) ₂ CHCH ₂	n-Bu	n-Bu	DPPF	dioxane	24	(82)	17:1																																																																																																						
(MeO ₂ C) ₂ CHCH ₂	Bn	n-Bu	BIPHEP	dioxane	24	(22)	7.0:1																																																																																																						
(MeO ₂ C) ₂ CHCH ₂	Bn	n-Bu	BINAP	dioxane	24	(27)	4.1:1																																																																																																						
(MeO ₂ C) ₂ CHCH ₂	Bn	n-Bu	DPPF	dioxane	24	(70)	11:1																																																																																																						
(MeO ₂ C) ₂ CHCH ₂	Bn	n-Bu	DPE-phos	dioxane	24	(79)	5.6:1																																																																																																						
(MeO ₂ C) ₂ CHCH ₂	Bn	n-Bu	XANTPHOS	dioxane	24	(88)	5.0:1																																																																																																						
(MeO ₂ C) ₂ CHCH ₂	Bn	n-Bu	NIXANTPHOS	dioxane	24	(86)	6.5:1																																																																																																						
(MeO ₂ C) ₂ CHCH ₂	Bn	n-Bu	DPPF	MeOH	24	(20)	17:1																																																																																																						

TABLE 1D. HYDROAMINATION OF ALLENES (Continued)

Allene	Amine	Conditions	Product(s) and Yield(s) (%)		Refs.
$ \begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{R}^2 \end{array} \begin{array}{c} \text{R}^3 \\ \diagup \\ \text{C} \\ \diagdown \\ \text{R}^3 \end{array} $ 1.2 eq		$(i\text{-Bu})_2\text{P}(2\text{-PhC}_6\text{H}_4)\text{AuCl}$ (10 mol %), AgOTf (10 mol %), C_7H_8 , 80°	 I +	 II	458
			R ¹	R ²	R ³
			R ₁	R ₂	R ₃
			Time (h)		I/II
			24		I only
			12		I only
			24		I only
			24		I only
			6		I only
			36		84:16
			36		I only
			12		I only
			12		I only
			9		I only
			36		I only
			36		—
$ \begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{R}^2 \end{array} \begin{array}{c} \text{R}^3 \\ \diagup \\ \text{C} \\ \diagdown \\ \text{R}^3 \end{array} $ 1.2 eq	PhNH ₂ (2 eq)	AuBr ₃ (10 mol %), THF, 30°	 I +	 II	458
			R ¹	R ²	R ³
			Time (h)		I/II
			2		I only
			6		I only
			5		I only
			2		I only
			2		I only
			3		1:1
			2		I only
			3		I only
			3		I only

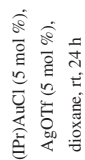
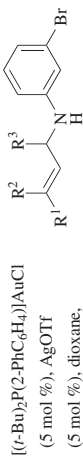
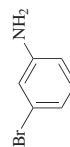
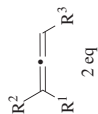
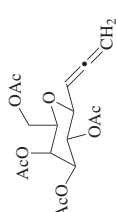
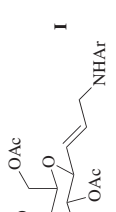
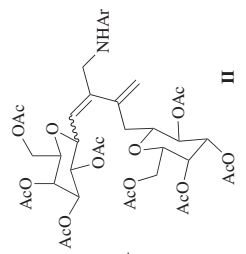
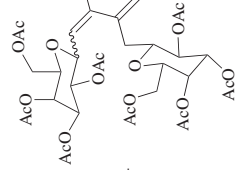
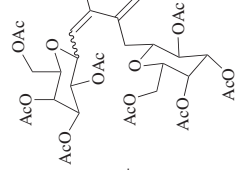
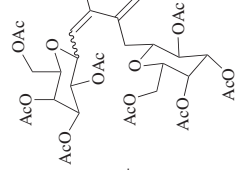
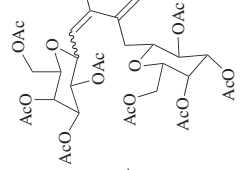
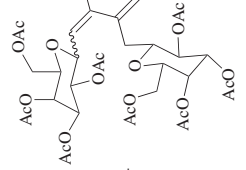
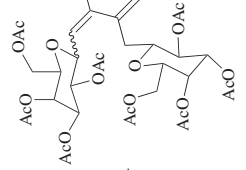
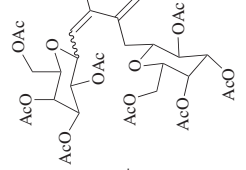
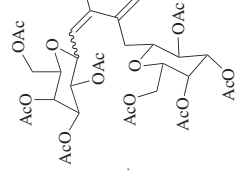
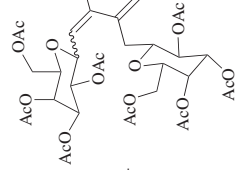
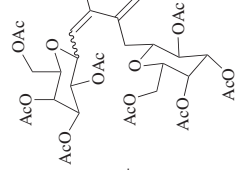
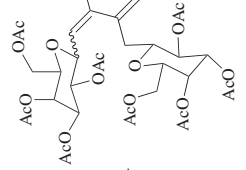
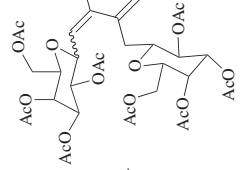
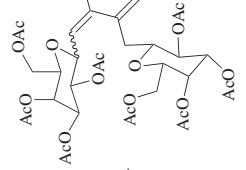
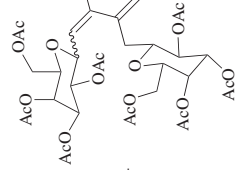
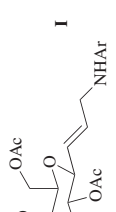
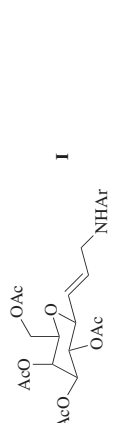
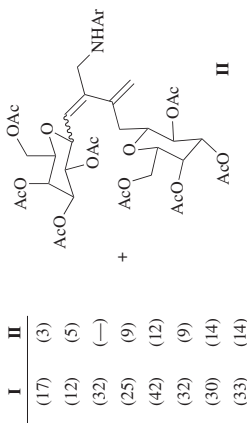


TABLE 1D. HYDROAMINATION OF ALLENES (Continued)

Allene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>				
 C₈	PhNH ₂ (3 eq)	Pd ₂ (dba) ₃ (x mol %), acid (y mol %), additive (10 mol %), solvent, 24 h	 I	459
			 II	
			 I	
			 II	
			 I	
			 II	
			 I	
			 II	
			 I	
			 II	
			 I	
			 II	
			 I	
			 II	
			 I	
			 II	
	PhNH ₂ (3 eq)	Pd(OAc) ₂ (x mol %), acid (y mol %), additive (z mol %), solvent, 24 h	 I	459

<i>x</i>	Acid	<i>y</i>	Additive	<i>z</i>	Solvent	Temp	I	II
5	—	—	—	—	THF	rt	(17)	(3)
5	—	—	—	—	THF	60°	(12)	(5)
5	—	—	LiCl	200	THF	rt	(32)	(—)
5	AcOH	20	—	—	THF	rt	(25)	(9)
5	TFA	20	—	—	THF	rt	(42)	(12)
5	TFA	20	—	—	THF	60°	(32)	(9)
5	TFA	20	—	—	DCM	rt	(30)	(14)
5	TFA	20	—	—	MeCN	rt	(33)	(14)
5	TFA	20	—	—	C ₇ H ₈	rt	(24)	(15)
5	TFA	20	—	—	dioxane	rt	(14)	(9)
5	TFA	20	Ph ₃ P	20	THF	rt	(6)	(48)
5	TFA	20	K ₂ S ₂ O ₈	100	THF	rt	(17)	(12)
5	TFA	20	K ₂ S ₂ O ₈	200	THF	rt	(31)	(—)
5	TFA	20	K ₂ S ₂ O ₈	250	THF	rt	(25)	(19)
5	TFA	50	LiCl	—	THF	rt	(31)	(16)
10	TFA	20	—	—	THF	rt	(21)	(13)

Ar	Catalyst	Additive	Temp	I	II
Ph	Pd ₂ (dba) ₃ •CHCl ₃	Ph ₃ P	60°	(29)	(18)
Ph	Pd ₂ (dba) ₃ •CHCl ₃	Ph ₃ P	rt	(10)	(46)
3-O ₂ NC ₆ H ₄	Pd(OAc) ₂	—	rt	(25)	(3)
4-O ₂ NC ₆ H ₄	Pd(OAc) ₂	—	rt	(22)	(—)
4-MeOC ₆ H ₄	Pd(OAc) ₂	—	rt	(16)	(—)
1-naphthyl	Pd(OAc) ₂	—	rt	(17)	(6)

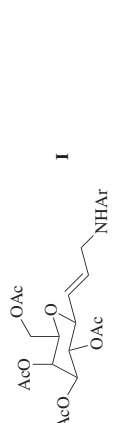
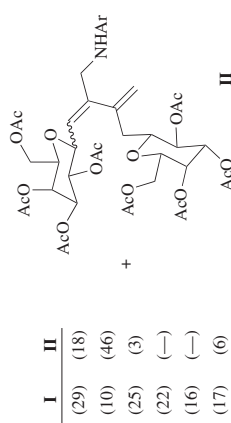



TABLE 1D. HYDROAMINATION OF ALLENES (Continued)

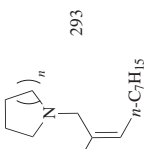
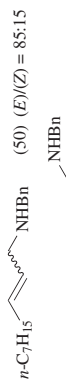
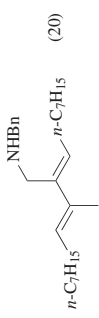
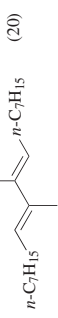
Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

Allene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																
C₉ 	 1.1 eq	Et ₃ NHI (15 mol %), Pd(dba) ₂ (5 mol %), PPh ₃ (10 mol %), THF, 65°	 (60)	293																
	RNH ₂	L ₂ Ti(NEt ₂) ₂ (10 mol %), C ₆ D ₅ Br, 120°, 24 h L =	 <table> <tr> <th>R</th> <th>(65)</th> <th>(60)</th> <th>(75)</th> </tr> <tr> <td><i>i</i>-Pr</td> <td></td> <td></td> <td></td> </tr> <tr> <td><i>i</i>-Bu</td> <td></td> <td></td> <td></td> </tr> <tr> <td>Bn</td> <td></td> <td></td> <td></td> </tr> </table>	R	(65)	(60)	(75)	<i>i</i> -Pr				<i>i</i> -Bu				Bn				296
R	(65)	(60)	(75)																	
<i>i</i> -Pr																				
<i>i</i> -Bu																				
Bn																				
	R ₂ NH (1.1 eq)	Et ₃ NHI (15 mol %), Pd(dba) ₂ (5 mol %), PPh ₃ (10 mol %), THF, 65°, 17–22 h	 I + <table> <tr> <th>R</th> <th>I</th> <th>II</th> <th>I (E)/(Z)</th> </tr> <tr> <td>Et</td> <td>(72)</td> <td>(19)</td> <td>98:2</td> </tr> <tr> <td>–(CH₂)₄–</td> <td>(89)</td> <td>(0)</td> <td>98:2</td> </tr> </table>	R	I	II	I (E)/(Z)	Et	(72)	(19)	98:2	–(CH ₂) ₄ –	(89)	(0)	98:2	293				
R	I	II	I (E)/(Z)																	
Et	(72)	(19)	98:2																	
–(CH ₂) ₄ –	(89)	(0)	98:2																	
	 1.1 eq	Pd ₂ (dba) ₃ •CHCl ₃ (5 mol %), DPPF (12 mol %), AcOH (x mol %), THF, 80°, 8 h	 <table> <tr> <th>x</th> <th>(10)</th> <th>(98)</th> <th>(100)</th> </tr> <tr> <td>0</td> <td></td> <td></td> <td></td> </tr> <tr> <td>20</td> <td></td> <td></td> <td></td> </tr> <tr> <td>100</td> <td></td> <td></td> <td></td> </tr> </table>	x	(10)	(98)	(100)	0				20				100				294
x	(10)	(98)	(100)																	
0																				
20																				
100																				
	ArNH ₂	1. L ₂ Ti(NEt ₂) ₂ (10 mol %), C ₇ H ₈ , 90°, 7 h 2. LiAlH ₄ , Et ₂ O	 <table> <tr> <th>Ar</th> <th>(64)</th> <th>(76)</th> </tr> <tr> <td>Ph</td> <td></td> <td></td> </tr> <tr> <td>2,6-Me₂C₆H₃</td> <td></td> <td></td> </tr> </table>	Ar	(64)	(76)	Ph			2,6-Me ₂ C ₆ H ₃			296							
Ar	(64)	(76)																		
Ph																				
2,6-Me ₂ C ₆ H ₃																				



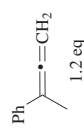
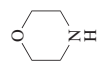
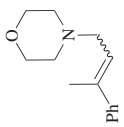
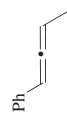
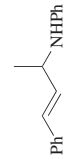
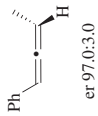
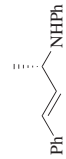
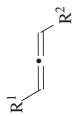
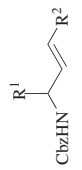
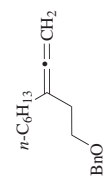
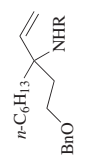
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	1.1 eq		294
	1.1 eq		294

TABLE 1D. HYDROAMINATION OF ALLENES (Continued)

Allene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																	
Please refer to the charts preceding the tables for structures indicated by the bold numbers.																					
$n\text{-C}_7\text{H}_{15}\text{CH}=\text{CH}_2$	 1.1 eq	Et_3NHI (15 mol %), $\text{Pd}(\text{dba})_2$ (5 mol %), PPh_3 (10 mol %), THF, 65°, 17–22 h	 293																		
		<table><tr><td>n</td><td>I</td><td>II</td><td>(E)/(Z) I</td></tr><tr><td>1</td><td>(53)</td><td>(0)</td><td>98:2</td></tr><tr><td>2</td><td>(64)</td><td>(14)</td><td>98:2</td></tr></table>	n	I	II	(E)/(Z) I	1	(53)	(0)	98:2	2	(64)	(14)	98:2							
n	I	II	(E)/(Z) I																		
1	(53)	(0)	98:2																		
2	(64)	(14)	98:2																		
C_{10-11}	BnNH_2 (1.1 eq)	Et_3NHI (15 mol %), $\text{Pd}(\text{dba})_2$ (5 mol %), PPh_3 (10 mol %), THF, 65°	 293																		
		 +  (20)																			
C_{10-11}	$(\text{R}^2)_2\text{NH}$ (1.1 eq)	$\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (5 mol %), DPPF (12 mol %), AcOH (20 mol %), THF, 80°	 294																		
		<table><tr><th>R^1</th><th>R^2</th><th>Time (h)</th></tr><tr><td>4-MeC₆H₄</td><td>EtO₂CCH₂</td><td>8 (73)</td></tr><tr><td>4-MeC₆H₄</td><td>Ph</td><td>8 (67)</td></tr><tr><td>4-MeC₆H₄</td><td>Bn</td><td>8 (99)</td></tr><tr><td>4-CF₃C₆H₄</td><td>EtO₂CCH₂</td><td>8 (67)</td></tr><tr><td>$n\text{-C}_8\text{H}_{17}$</td><td>EtO₂CCH₂</td><td>20–24 (32)</td></tr><tr><td>BnCH₂</td><td>EtO₂CCH₂</td><td>20–24 (83)</td></tr></table>	R^1	R^2	Time (h)	4-MeC ₆ H ₄	EtO ₂ CCH ₂	8 (73)	4-MeC ₆ H ₄	Ph	8 (67)	4-MeC ₆ H ₄	Bn	8 (99)	4-CF ₃ C ₆ H ₄	EtO ₂ CCH ₂	8 (67)	$n\text{-C}_8\text{H}_{17}$	EtO ₂ CCH ₂	20–24 (32)	BnCH ₂
R^1	R^2	Time (h)																			
4-MeC ₆ H ₄	EtO ₂ CCH ₂	8 (73)																			
4-MeC ₆ H ₄	Ph	8 (67)																			
4-MeC ₆ H ₄	Bn	8 (99)																			
4-CF ₃ C ₆ H ₄	EtO ₂ CCH ₂	8 (67)																			
$n\text{-C}_8\text{H}_{17}$	EtO ₂ CCH ₂	20–24 (32)																			
BnCH ₂	EtO ₂ CCH ₂	20–24 (83)																			

		(L) ₂ AuCl (10 mol %), AgOTf (10 mol %), C ₇ H ₈ , 80°, 12 h		L	(51) (30) (27) (63) (62) (83) (63) (79) (64) (32) (59)	295, 458
					(<i>i</i> -Bu) ₂ P(2-PhC ₆ H ₄) Ph ₃ P(2-C ₃ H ₄ N) Ph ₃ P(2-HOC ₆ H ₄) Ph ₃ P(2-MeOC ₆ H ₄) Ph ₃ P(4-MeOC ₆ H ₄) Ph ₃ P(2-MeC ₆ H ₄) Ph ₃ P(4-CF ₃ C ₆ H ₄) PhP(2-MeC ₆ H ₄) ₂ Ph ₃ P (2-MeC ₆ H ₄) ₃ P 	
				R	(97) (95) (98)	296

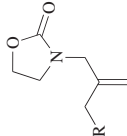
TABLE 1D. HYDROAMINATION OF ALLENES (Continued)

Allene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>				
C ₁₀ 		ClAu(PPh ₂ (4-MeC ₆ H ₄)) (10 mol %), AgOTf (10 mol %), toluene, 80°, 12 h	 (17), (<i>E</i>)/(<i>Z</i>) = 5:4	295
	PhNH ₂ (2 eq)	AuBr ₃ (10 mol %), THF, 30°, 1–5 h	 (9), (<i>E</i>)/(<i>Z</i>) = 3:7	292
	PhNH ₂ (2 eq)	AuBr ₃ (10 mol %), THF, 30°, 1–5 h	 (68)	292
C ₁₀₋₁₃ 	PhNH ₂ (2 eq)	AuBr ₃ (10 mol %), THF, 30°, 1–5 h	 (68) er 94.0:6.0	292
	ChzNH ₂	(IPr)AuCl (5 mol %), AgOTf (5 mol %), dioxane, rt, 24 h	 R ¹ R ² Me Ph (80) <i>c</i> -C ₆ H ₁₁ EtO ₂ CCH ₂ (81) Me BzOCH ₂ (84) <i>n</i> -C ₅ H ₁₁ <i>n</i> -C ₅ H ₁₁ (83)	297
C ₁₁ 	RNH ₂	(IPr)AuCl (5 mol %), AgOTf (5 mol %), dioxane, rt, 24 h	 R <i>n</i> -C ₆ H ₁₃ MeO ₂ C (58) BnO Chz (58)	297

C ₁₁₋₁₄		PhNH ₂ (2 eq)	AuBr ₃ (10 mol %), THF, 30°, 1–5 h			$\frac{n}{\text{I} + \text{II}}$ 1 (58) 1:1 2 (87) 1:1 3 (96) 1:1 4 (88) 1:1	292
C ₁₁		Bn ₂ NH (1.1 eq)	Pd ₂ (dba) ₃ •CHCl ₃ (5 mol %), DPPF (12 mol %), AcOH (20 mol %), THF, 80°				294
C ₁₃		PhNH ₂ (2 eq)	AuBr ₃ (10 mol %), THF, 30°, 1–5 h				292
C ₁₉		PhNH ₂ (2 eq)	AuBr ₃ (10 mol %), THF, 30°, 1–5 h				292
		H ₂ N ⁺ CO ₂ Me (x eq)	Ph ₃ PAuNTf ₂ (6 mol %), MeNO ₂ , 45°			$\frac{x}{\text{er}}$ 1 (81) 64.0:36.0 2 (75) 74.0:26.0 4 (81) 78.0:22.0 8 (79) 78.0:22.0	460

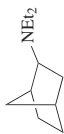
^a The half-life period was reported.

TABLE 1E. HYDROAMINATION OF STRAINED ALKENES

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)		Refs.
Please refer to the charts preceding the tables for structures indicated by the bold numbers.					
 C ₄ 1.2 eq	(<i>n</i> -Pr) ₃ NH ₂	Cp* ₂ LnCH(TMS) ₂ (5 mol %), C ₆ D ₆ , 60°	 Ln	Ln Time (h) La 17 (95) Sm 25 (95)	43
	RNH ₂	13 (2 mol %), C ₇ H ₈ , 110°	 R	R Time (h) Et 36 (90) <i>i</i> -Pr 36 (76) <i>n</i> -Bu 36 (56) Ph 45 (90)	(<i>E</i>)/(<i>Z</i>) 82:18 81:19 80:20 81:19
	ArNH ₂	M(NEt ₂) ₄ (2 mol %), C ₇ H ₈ , 110°	 N ⁺ Ar		
 C ₆₋₁₀					
 R	 H 2 eq	Pd(PPh ₃) ₄ (5 mol %), neat, 120°, 3 d	 R	R BnNHCH ₂ CH ₂ (72) <i>n</i> -C ₇ H ₁₅ (68) <i>n</i> -C ₈ H ₁₇ (82)	323

C₇Et₂NH (1.2 eq)

EtLi (6 mol %),
TMEDA (12 mol %),
150°, 4 h



(17)

331



4 eq



CuBr₂ (5 mol %),
AgSbF₆ (5 mol %),
DPPE (5 mol %),
TCE, 100°, 20 h

(95)

427



20 eq



2 (10 mol %),
AgSbF₆ (10 mol %),
dioxane, 100°, 70 h

(86)^a

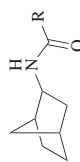
126



(4 eq)



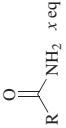
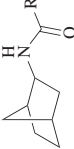
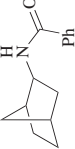
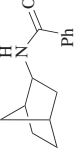
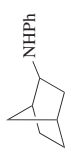
CuBr₂ (5 mol %),
AgZ (10 mol %),
DPPE (5 mol %), TCE



427

R	Z	Temp (°)	Time (h)	
MeO	BF ₄	100	30	(86)
BnO	BF ₄	100	30	(80)
Me	SbF ₆	100	70	(0)
ClCH ₂	BF ₄	100	48	(72)
CF ₃	BF ₄	100	20	(0)
Ph	SbF ₆	100	48	(35)
Ph	SbF ₆	150	20	(27)

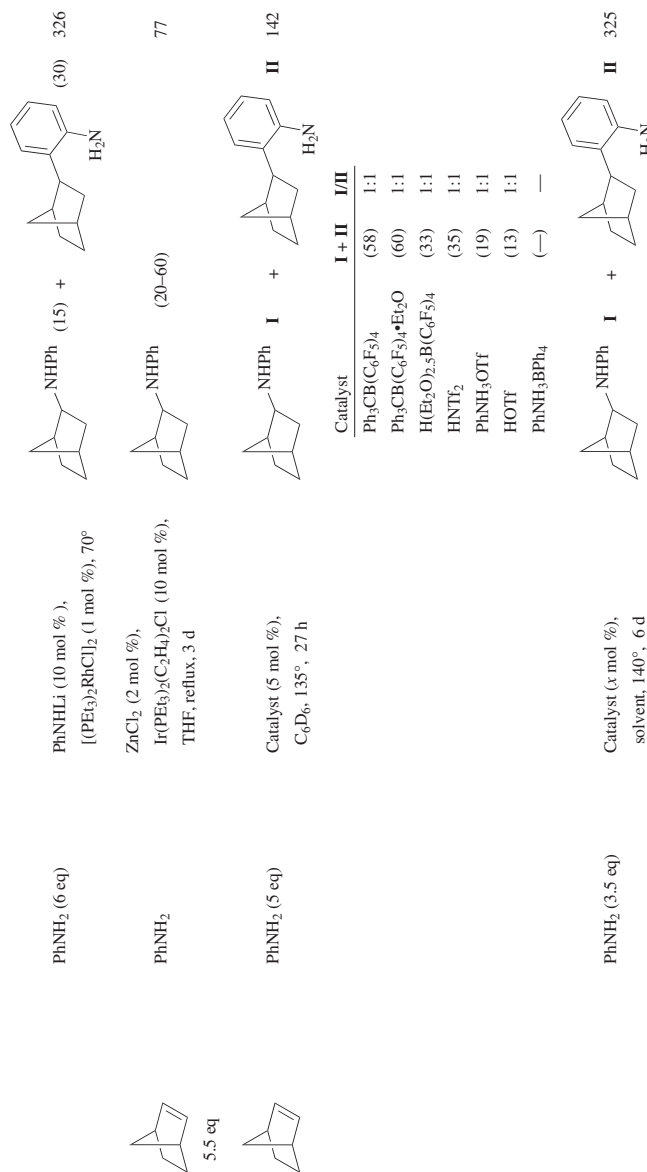
TABLE 1E. HYDROAMINATION OF STRAINED ALKENES (Continued)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>				
 C₇	 R	H-Mont (0.15 g/mmol alkene), dioxane		127
 2 eq	 Ph	15 (5 mol %), DCE, 100°, 3 d		94
 3 eq	 Ph	Amberlyst-15 (0.75 g/mmol alkene), [BMIm][BF₄] , 80°, 5 h		432
 2 eq	PhNH₂	PtBr₂ (0.3 mol %), (<i>n</i>-Bu)₄PBr (18 mol %), 150°, 96 h		131

I + II (22), I/II = 8:1

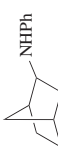
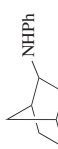
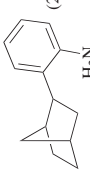
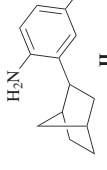
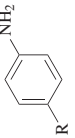
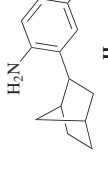
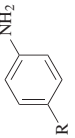
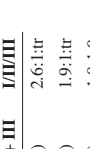
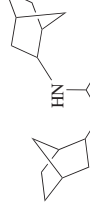
I

II



Catalyst	<i>x</i>	Solvent	I + II	I/II
$(\text{PPh}_3)_2\text{PtBr}_2$	0.4	<i>n</i> -Bu ₄ NBr	(14)	5.4:1
$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	1	[BMIm][PF ₆]	(8)	2:1
$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	1	[BMIm][Br]	(10)	5.5:1
$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	1	<i>n</i> -Bu ₄ NBr	(10)	3.1:1
$(\text{Ph}_3\text{P})_3\text{RhCl}$	1	<i>n</i> -Bu ₄ NBr	(4)	1.2:1
PtCl_2	1	<i>n</i> -Bu ₄ NBr	(10)	3.9:1
$(\text{Ph}_3\text{P})_2\text{Pt}(\text{OTf})_2$	1	<i>n</i> -Bu ₄ NBr	(4)	1.3:1
$[\text{P}(\text{OMe})_3]_2\text{PtBr}_2$	1	<i>n</i> -Bu ₄ NBr	(8)	2.5:1
$(\text{PPh}_3)_2\text{PtBr}_2$	1	<i>n</i> -Bu ₄ NBr	(18)	2.4:1
$(\text{PPh}_2\text{Me})_2\text{PtBr}_2$	1	THF	(3)	5.4:1

TABLE 1E. HYDROAMINATION OF STRAINED ALKENES (Continued)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																																								
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>																																												
 2 eq	PhNH ₂	Pr(OTf) ₃ (2 mol %), I ₂ (6 mol %), (<i>n</i> -Bu) ₄ PI, 160°, 36 h	 (61)	424																																								
	PhNH ₂ (2 eq)	[Bn ₂ Ta=N(<i>i</i> -Bu)]B(C ₆ F ₅) ₄ (5 mol %), C ₆ D ₅ Cl, 135°, 24 h	 (10) +  (22)	64																																								
	 4 eq	CuBr ₂ (5 mol %), AgZ (10 mol %), DPPE (5 mol %), TCE, 100°	 I +  II	427																																								
	 R	Acid (5 mol %), solvent, 135°, 24 h	 I +  II	329																																								
	 R		 I/II/III																																									
<table> <tr> <th>R</th><th>Acid</th><th>Solvent</th><th>I + II + III</th><th>I/II/III</th></tr> <tr> <td>H</td><td>—</td><td>[BMIm][InCl₄]</td><td>(37)</td><td>2.6:1:tr</td></tr> <tr> <td>H</td><td>TfOH</td><td>[BMIm][NTf₂]</td><td>(70)</td><td>1.9:1:tr</td></tr> <tr> <td>H</td><td>MsOH</td><td>[BMIm][NTf₂]</td><td>(48)</td><td>1.8:1:0</td></tr> <tr> <td>H</td><td>TFA</td><td>[BMIm][NTf₂]</td><td>(28)</td><td>1:1:tr</td></tr> <tr> <td>H</td><td>TsOH</td><td>[BMIm][NTf₂]</td><td>(22)</td><td>1.5:1:0</td></tr> <tr> <td>H</td><td>PhB(OH)₂</td><td>[BMIm][NTf₂]</td><td>(38)</td><td>1.6:1:0</td></tr> <tr> <td>H</td><td>HBF₄</td><td>[BMIm][NTf₂]</td><td>(80)</td><td>1.5:1:0</td></tr> </table>					R	Acid	Solvent	I + II + III	I/II/III	H	—	[BMIm][InCl ₄]	(37)	2.6:1:tr	H	TfOH	[BMIm][NTf ₂]	(70)	1.9:1:tr	H	MsOH	[BMIm][NTf ₂]	(48)	1.8:1:0	H	TFA	[BMIm][NTf ₂]	(28)	1:1:tr	H	TsOH	[BMIm][NTf ₂]	(22)	1.5:1:0	H	PhB(OH) ₂	[BMIm][NTf ₂]	(38)	1.6:1:0	H	HBF ₄	[BMIm][NTf ₂]	(80)	1.5:1:0
R	Acid	Solvent	I + II + III	I/II/III																																								
H	—	[BMIm][InCl ₄]	(37)	2.6:1:tr																																								
H	TfOH	[BMIm][NTf ₂]	(70)	1.9:1:tr																																								
H	MsOH	[BMIm][NTf ₂]	(48)	1.8:1:0																																								
H	TFA	[BMIm][NTf ₂]	(28)	1:1:tr																																								
H	TsOH	[BMIm][NTf ₂]	(22)	1.5:1:0																																								
H	PhB(OH) ₂	[BMIm][NTf ₂]	(38)	1.6:1:0																																								
H	HBF ₄	[BMIm][NTf ₂]	(80)	1.5:1:0																																								
 +  I																																												

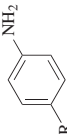
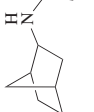
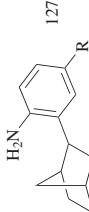
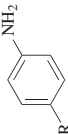
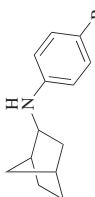
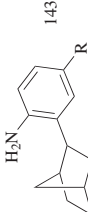
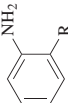
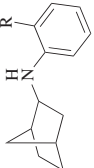
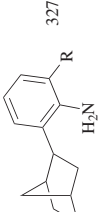
		 4 eq		 I		 II		 327	
		Catalyst (10 mol %), C ₇ H ₈ , 150°							
R	Catalyst	I + II	I/II	R	Catalyst	I + II	I/II	R	Catalyst
H	FeCl ₃	(0)	—	Br	FeCl ₃	(39)	I only		
H	ZrCl ₄	(43)	72:28	Br	ZrCl ₄	(63)	I only		
H	BiCl ₃	(61)	I only	Br	BiCl ₃	(70)	I only		
H	AlCl ₃	(52)	76:24	Br	AlCl ₃	(70)	92:8		
F	FeCl ₃	(tr)	I only	O ₂ N	FeCl ₃	(88)	I only		
F	ZrCl ₄	(59)	78:22	O ₂ N	ZrCl ₄	(61)	I only		
F	BiCl ₃	(64)	78:22	O ₂ N	BiCl ₃	(68)	I only		
F	AlCl ₃	(64)	87:13	O ₂ N	AlCl ₃	(tr)	I only		
Cl	FeCl ₃	(18)	I only	MeO	FeCl ₃	(0)	—		
Cl	ZrCl ₄	(55)	I only	MeO	ZrCl ₄	(0)	—		
Cl	BiCl ₃	(57)	I only	MeO	BiCl ₃	(0)	—		
Cl	AlCl ₃	(30)	I only	MeO	AlCl ₃	(0)	—		

Catalyst (10 mol %), C₇H₈, 150°

4 eq

327

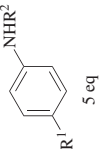
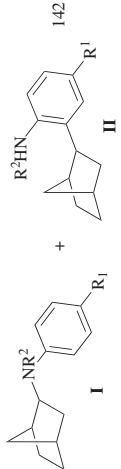
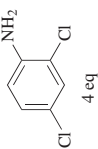
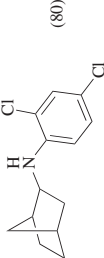
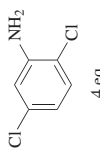
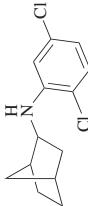
TABLE 1E. HYDROAMINATION OF STRAINED ALKENES (Continued)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																										
C₇	 2 eq	H-Mont (0.1 g/mmol alkene), heptane, 150°	 I  II 127																											
			<table> <tr> <th>R</th><th>I + II</th><th>I/II</th></tr> <tr> <td>H</td><td>(88)</td><td>1:1</td></tr> <tr> <td>Cl</td><td>(95)</td><td>8:1</td></tr> <tr> <td>O₂N</td><td>(97)</td><td>I only</td></tr> </table>		R	I + II	I/II	H	(88)	1:1	Cl	(95)	8:1	O ₂ N	(97)	I only														
R	I + II	I/II																												
H	(88)	1:1																												
Cl	(95)	8:1																												
O ₂ N	(97)	I only																												
C₇	 5 eq	HI (5 mol %), base (x mol %), C₇H₈, 135°, 24 h	 I  II 143																											
			<table> <tr> <th>R</th><th>Base</th><th>x</th><th>I + II</th><th>I/II</th></tr> <tr> <td>H</td><td>—</td><td>0</td><td>(73)</td><td>78:22</td></tr> <tr> <td>H</td><td>DBMP</td><td>25</td><td>(48)</td><td>82:18</td></tr> <tr> <td>H</td><td>Et₃N</td><td>5</td><td>(34)</td><td>77:23</td></tr> <tr> <td>Cl</td><td>—</td><td>0</td><td>(77)</td><td>87:23</td></tr> <tr> <td>MeO</td><td>—</td><td>0</td><td>(54)</td><td>70:30</td></tr> </table>		R	Base	x	I + II	I/II	H	—	0	(73)	78:22	H	DBMP	25	(48)	82:18	H	Et ₃ N	5	(34)	77:23	Cl	—	0	(77)	87:23	MeO
R	Base	x	I + II	I/II																										
H	—	0	(73)	78:22																										
H	DBMP	25	(48)	82:18																										
H	Et ₃ N	5	(34)	77:23																										
Cl	—	0	(77)	87:23																										
MeO	—	0	(54)	70:30																										
C₇	 4 eq	Catalyst (10 mol %), C₇H₈, 150°	 I  II 327																											
			<table> <tr> <th>R</th><th>Catalyst</th><th>I + II + III</th><th>I/II/III</th></tr> <tr> <td>F</td><td>FeCl₃</td><td>(30)</td><td>98:2:0</td></tr> <tr> <td>F</td><td>ZrCl₄</td><td>(74)</td><td>87:10:3</td></tr> <tr> <td>F</td><td>BiCl₃</td><td>(81)</td><td>87:10:3</td></tr> <tr> <td>F</td><td>AlCl₃</td><td>(44)</td><td>90:9:1</td></tr> <tr> <td>Cl</td><td>FeCl₃</td><td>(82)</td><td>97:3:0</td></tr> </table>		R	Catalyst	I + II + III	I/II/III	F	FeCl ₃	(30)	98:2:0	F	ZrCl ₄	(74)	87:10:3	F	BiCl ₃	(81)	87:10:3	F	AlCl ₃	(44)	90:9:1	Cl	FeCl ₃	(82)	97:3:0		
R	Catalyst	I + II + III	I/II/III																											
F	FeCl ₃	(30)	98:2:0																											
F	ZrCl ₄	(74)	87:10:3																											
F	BiCl ₃	(81)	87:10:3																											
F	AlCl ₃	(44)	90:9:1																											
Cl	FeCl ₃	(82)	97:3:0																											
C₇	 4 eq		 I  II																											
			 III																											

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

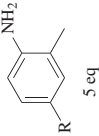
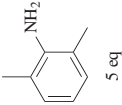
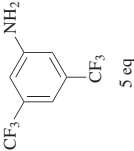
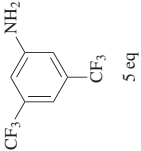
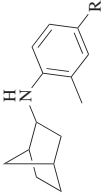
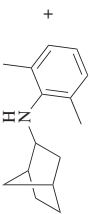
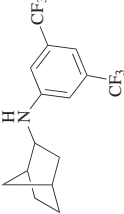
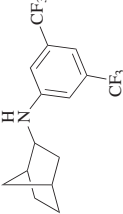
Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

TABLE 1E. HYDROAMINATION OF STRAINED ALKENES (Continued)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																																								
C₇ 	 5 eq	PhNH ₃ B(C ₆ F ₅) ₄ •Et ₂ O (5 mol %), C ₆ D ₆ , 135°, 48 h	 I II	142																																								
	 4 eq	BiCl ₃ (10 mol %), C ₇ H ₈ , 169°, 4 h	 (80)	463																																								
	 4 eq	Catalyst (x mol %), C ₇ H ₈		327, 463																																								
<table> <tr> <th>Catalyst</th><th>x</th><th>Temp (°)</th><th>Time (h)</th></tr> <tr> <td>FeCl₃</td><td>5</td><td>100</td><td>8 (38)</td></tr> <tr> <td>FeCl₃</td><td>5</td><td>135</td><td>8 (45)</td></tr> <tr> <td>FeCl₃</td><td>5</td><td>150</td><td>8 (49)</td></tr> <tr> <td>FeCl₃</td><td>5</td><td>169</td><td>8 (48)</td></tr> <tr> <td>FeCl₃</td><td>10</td><td>150</td><td>8 (54)</td></tr> <tr> <td>FeCl₃</td><td>15</td><td>150</td><td>8 (72)</td></tr> <tr> <td>FeCl₃</td><td>20</td><td>150</td><td>8 (71)</td></tr> <tr> <td>ZrCl₄</td><td>10</td><td>110</td><td>24 (tr)</td></tr> <tr> <td>ZrCl₄</td><td>10</td><td>169</td><td>24 (tr)</td></tr> </table>					Catalyst	x	Temp (°)	Time (h)	FeCl ₃	5	100	8 (38)	FeCl ₃	5	135	8 (45)	FeCl ₃	5	150	8 (49)	FeCl ₃	5	169	8 (48)	FeCl ₃	10	150	8 (54)	FeCl ₃	15	150	8 (72)	FeCl ₃	20	150	8 (71)	ZrCl ₄	10	110	24 (tr)	ZrCl ₄	10	169	24 (tr)
Catalyst	x	Temp (°)	Time (h)																																									
FeCl ₃	5	100	8 (38)																																									
FeCl ₃	5	135	8 (45)																																									
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FeCl ₃	5	169	8 (48)																																									
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FeCl ₃	15	150	8 (72)																																									
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ZrCl ₄	10	110	24 (tr)																																									
ZrCl ₄	10	169	24 (tr)																																									

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

Please refer to the charts preceding the tables for structures indicated by the **bold numbers**.

			
BiCl_3 (10 mol %), C_7H_8 , 150°	$\text{PhNH}_3\text{B}(\text{C}_6\text{F}_5)_4 \cdot \text{Et}_2\text{O}$ (5 mol %), C_6D_6 , 135° , 48 h	$\text{PhNH}_3\text{B}(\text{C}_6\text{F}_5)_4 \cdot \text{Et}_2\text{O}$ (5 mol %), C_6D_6 , 135° , 48 h	HI (5 mol %), C_7H_8 , 135° , 24 h
20	10	10	10
110	169	110	169
24	4	24	4
(61)	(60)	(61)	(60)
BiCl_3	BiCl_3	BiCl_3	BiCl_3
10	10	10	10
110	150	110	150
8	4	8	4
(50)	(71)	(50)	(71)
BiCl_3	BiCl_3	BiCl_3	BiCl_3
10	169	10	169
4	4	4	4
(61)	(61)	(61)	(61)
AlCl_3	AlCl_3	AlCl_3	AlCl_3
10	110	10	110
8	8	8	8
(42)	(67)	(42)	(67)
AlCl_3	AlCl_3	AlCl_3	AlCl_3
10	150	10	150
8	8	8	8
(28)	(65)	(28)	(65)
AlCl_3	AlCl_3	AlCl_3	AlCl_3
20	150	20	150
8	5	8	5
(tr)	(84)	(tr)	(84)
ZnCl_2	ZnCl_2	ZnCl_2	ZnCl_2
10	169	10	169
5	5	5	5
(84)	(6)	(84)	(6)
SnCl_4	SnCl_4	SnCl_4	SnCl_4
10	169	10	169
5	5	5	5
(6)	(6)	(6)	(6)
I_2	I_2	I_2	I_2
10	169	10	169
5	5	5	5
(6)	(6)	(6)	(6)
			
R	H	CF_3	CF_3
(15)	(73)	(80)	(64)
O_2N	O_2N	O_2N	O_2N
327	142	142	143

R

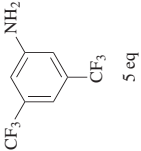
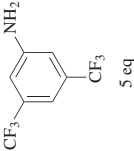
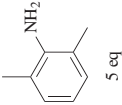
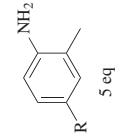
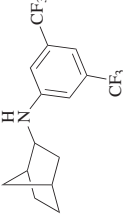
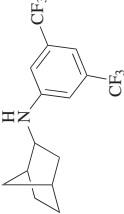
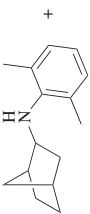
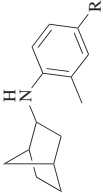
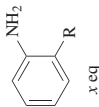
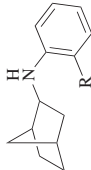
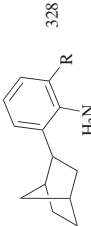
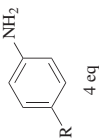
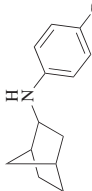
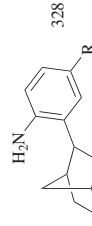


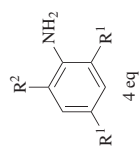
TABLE 1E. HYDROAMINATION OF STRAINED ALKENES (Continued)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)		Refs.																																																																				
C-7 	 <i>x</i> eq	TiCl ₄ (<i>y</i> mol %), toluene	 I	 II																																																																					
			<table> <tr> <th>R</th><th><i>x</i></th><th><i>y</i></th><th>Temp (°)</th><th>Time (h)</th><th>I</th><th>I/II</th></tr> <tr> <td>H</td><td>4</td><td>100</td><td>169</td><td>2</td><td>(48)</td><td>65:35</td></tr> <tr> <td>F</td><td>4</td><td>10</td><td>130</td><td>21</td><td>(70)</td><td>—</td></tr> <tr> <td>F</td><td>4</td><td>100</td><td>169</td><td>2</td><td>(80)</td><td>95:5</td></tr> <tr> <td>Cl</td><td>4</td><td>10</td><td>130</td><td>18</td><td>(89)</td><td>—</td></tr> <tr> <td>Cl</td><td>4</td><td>100</td><td>169</td><td>2</td><td>(78)</td><td>89:11</td></tr> <tr> <td>Br</td><td>4</td><td>10</td><td>110</td><td>18</td><td>(88)</td><td>—</td></tr> <tr> <td>Br</td><td>4</td><td>100</td><td>169</td><td>3</td><td>(81)</td><td>91:9</td></tr> <tr> <td>NC-</td><td>1</td><td>10</td><td>130</td><td>20</td><td>(45)</td><td>—</td></tr> <tr> <td>NC-</td><td>1</td><td>100</td><td>169</td><td>12</td><td>(47)</td><td>98:2</td></tr> </table>	R	<i>x</i>	<i>y</i>	Temp (°)	Time (h)	I	I/II	H	4	100	169	2	(48)	65:35	F	4	10	130	21	(70)	—	F	4	100	169	2	(80)	95:5	Cl	4	10	130	18	(89)	—	Cl	4	100	169	2	(78)	89:11	Br	4	10	110	18	(88)	—	Br	4	100	169	3	(81)	91:9	NC-	1	10	130	20	(45)	—	NC-	1	100	169	12	(47)	98:2
R	<i>x</i>	<i>y</i>	Temp (°)	Time (h)	I	I/II																																																																			
H	4	100	169	2	(48)	65:35																																																																			
F	4	10	130	21	(70)	—																																																																			
F	4	100	169	2	(80)	95:5																																																																			
Cl	4	10	130	18	(89)	—																																																																			
Cl	4	100	169	2	(78)	89:11																																																																			
Br	4	10	110	18	(88)	—																																																																			
Br	4	100	169	3	(81)	91:9																																																																			
NC-	1	10	130	20	(45)	—																																																																			
NC-	1	100	169	12	(47)	98:2																																																																			
	 4 eq	TiCl ₄ (100 mol %), toluene, 169°	 I	 II																																																																					
			<table> <tr> <th>R</th><th>Time (h)</th><th>I</th><th>I/II</th></tr> <tr> <td>F</td><td>4</td><td>(56)</td><td>76:24</td></tr> <tr> <td>Cl</td><td>4</td><td>(67)</td><td>83:17</td></tr> <tr> <td>Me</td><td>12</td><td>(24)</td><td>59:41</td></tr> </table>	R	Time (h)	I	I/II	F	4	(56)	76:24	Cl	4	(67)	83:17	Me	12	(24)	59:41																																																						
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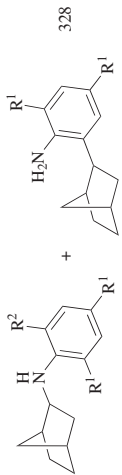
Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₇

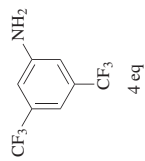


TiCl₄ (x mol %), toluene

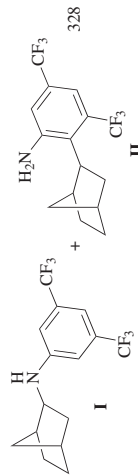


R ¹	R ²	x	Temp (°)	Time (h)	I	I/II
Br	H	10	110	20	(95)	—
Br	H	100	169	3	(83)	96:4
Me	Me	100	169	6	(60)	I only

291



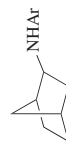
TiCl₄ (x mol %), toluene



x	Temp (°)	Time (h)	I	I/II
10	110	21	(83)	—
100	169	1	(54)	98:2

ArNH₂

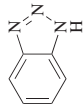
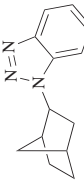
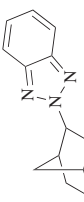
15 (5 mol %), DCE



94

Ar	Temp (°)	Time (h)
Ph	100	72 (0)
C ₆ F ₅	50	5 (95)
4-O ₂ NC ₆ H ₄	50	5 (95)
4-MeOC ₆ H ₄	100	72 (0)
3,5-(CF ₃) ₂ C ₆ H ₃	80	24 (95)

TABLE 1E. HYDROAMINATION OF STRAINED ALKENES (Continued)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)		Refs.
 C ₇	ArNH ₂	[(COD)Pt(OTf) ₂] (10 mol %), DCE		93	
			Ar	Temp (°)	Time (h)
			C ₆ F ₅	80	2 (100)
			4-O ₂ NC ₆ H ₄	90	16 (35)
			3,5-(CF ₃) ₂ C ₆ H ₃	90	16 (45)
 (4 eq)		CuBr ₂ (5 mol %), AgSbF ₆ (5 mol %), DPPE (5 mol %), TCE, 100°, 48 h	 +  (21)	427	
				Temp (°)	Time (h)
				80	24 (90)
 1.3 eq	MeSO ₂ NH ₂	H-Mont (0.1 g/mmol alkene), heptane		127	
	TsNH ₂	[(COD)Pt(OTf) ₂] (10 mol %), DCE, 75°, 2 h	 (92)	93	
				Temp (°)	Time (h)
				150	1 (96)
	TsNH ₂	TfOH (1 mol %), C ₇ H ₈ , rt, 6 h	 (91)	135	

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

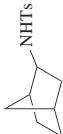
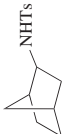
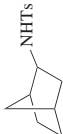
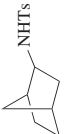
	TsNH ₂	[BSPy][OTf] (20 mol %), neat, 85°, 24 h		Run ^d 1 (97) 2 (95) 3 (94) 4 (90)	423																																																																																																									
	TsNH ₂	Catalyst (x mol %), C ₇ H ₈ , 120°		Catalyst PMA/SiO ₂ InBr ₃	Time (h) 10 (95) 20 (67) 16 (67) 330																																																																																																									
	TsNH ₂	Ga (5 mol %), I ₂ (7.5 mol %), Et ₂ O, 105°, 2 h		(96)	426																																																																																																									
	TsNH ₂	Catalyst (x mol %), ligand (x mol %), solvent			429																																																																																																									
<table><tr><th>Catalyst</th><th>x</th><th>Ligand</th><th>Solvent</th><th>Temp (°)</th><th>Time (h)</th><th></th></tr><tr><td>AgOTf</td><td>0.5</td><td>—</td><td>C₇H₈</td><td>85</td><td>4</td><td>(96)</td></tr><tr><td>AgOTf</td><td>0.5</td><td>—</td><td>C₇H₈</td><td>90^b</td><td>0.5</td><td>(82)</td></tr><tr><td>AgOTf</td><td>1</td><td>—</td><td>C₇H₈</td><td>90^b</td><td>0.5</td><td>(98)</td></tr><tr><td>AgOTf</td><td>1</td><td>Ph₃P</td><td>C₇H₈</td><td>90^b</td><td>0.5</td><td>(0)</td></tr><tr><td>AgOTf</td><td>1</td><td>(PhO)₃P</td><td>C₇H₈</td><td>90^b</td><td>0.5</td><td>(88)</td></tr><tr><td>AgOTf</td><td>5</td><td>—</td><td>DCM</td><td>rt</td><td>24</td><td>(97)</td></tr><tr><td>AgSbF₆</td><td>0.5</td><td>—</td><td>C₇H₈</td><td>90^b</td><td>0.5</td><td>(99)</td></tr><tr><td>AgSbF₆</td><td>1</td><td>—</td><td>C₇H₈</td><td>90^b</td><td>0.5</td><td>(99)</td></tr><tr><td>AgCl</td><td>1</td><td>—</td><td>C₇H₈</td><td>90^b</td><td>0.5</td><td>(0)</td></tr><tr><td>AgF</td><td>1</td><td>—</td><td>C₇H₈</td><td>90^b</td><td>0.5</td><td>(0)</td></tr><tr><td>AgNO₃</td><td>1</td><td>—</td><td>C₇H₈</td><td>90^b</td><td>0.5</td><td>(0)</td></tr><tr><td>AgBF₄</td><td>1</td><td>—</td><td>C₇H₈</td><td>90^b</td><td>0.5</td><td>(5)</td></tr><tr><td>AgClO₄</td><td>1</td><td>—</td><td>C₇H₈</td><td>90^b</td><td>0.5</td><td>(22)</td></tr><tr><td>AgOAc</td><td>1</td><td>—</td><td>C₇H₈</td><td>90^b</td><td>0.5</td><td>(0)</td></tr></table>						Catalyst	x	Ligand	Solvent	Temp (°)	Time (h)		AgOTf	0.5	—	C ₇ H ₈	85	4	(96)	AgOTf	0.5	—	C ₇ H ₈	90 ^b	0.5	(82)	AgOTf	1	—	C ₇ H ₈	90 ^b	0.5	(98)	AgOTf	1	Ph ₃ P	C ₇ H ₈	90 ^b	0.5	(0)	AgOTf	1	(PhO) ₃ P	C ₇ H ₈	90 ^b	0.5	(88)	AgOTf	5	—	DCM	rt	24	(97)	AgSbF ₆	0.5	—	C ₇ H ₈	90 ^b	0.5	(99)	AgSbF ₆	1	—	C ₇ H ₈	90 ^b	0.5	(99)	AgCl	1	—	C ₇ H ₈	90 ^b	0.5	(0)	AgF	1	—	C ₇ H ₈	90 ^b	0.5	(0)	AgNO ₃	1	—	C ₇ H ₈	90 ^b	0.5	(0)	AgBF ₄	1	—	C ₇ H ₈	90 ^b	0.5	(5)	AgClO ₄	1	—	C ₇ H ₈	90 ^b	0.5	(22)	AgOAc	1	—	C ₇ H ₈	90 ^b	0.5	(0)
Catalyst	x	Ligand	Solvent	Temp (°)	Time (h)																																																																																																									
AgOTf	0.5	—	C ₇ H ₈	85	4	(96)																																																																																																								
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TABLE 1E. HYDROAMINATION OF STRAINED ALKENES (*Continued*)

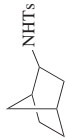
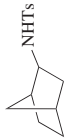
Alkene	Amine	Conditions	Product(s) and Yield(s) (%)		Refs.
 4 eq	TsNH ₂	CuBr ₂ (5 mol %), AgBF ₄ (10 mol %), DPPE (5 mol %), solvent	 NHTs	Solvent Temp Time (h)	427
				C ₇ H ₈ 60° 18	(90)
				C ₇ H ₈ rt 18	(70)
				DCE 60° 18	(95)
				DCE rt 18	(85)
				TCE rt 18	(95)
				TCE 60° 18	(95)
				TCE rt 3	(95)
				CHCl ₃ 25 18	(25)
				Et ₂ O rt 18	(0)
				THF 60° 18	(5)
				DME 60° 18	(30)
				MeCN 60° 18	(70)
 NHTs	TsNH ₂	CuBr ₂ (5 mol %), activator (10 mol %), ligand (x mol %), solvent	 NHTs	Solvent Temp Time (h)	427
				DCM rt 3	(0)
				DCM rt 3	(75)
				DCM rt 3	(95)
				DCM rt 3	(95)
				DCM rt 3	(45)
				DCM rt 3	(0)
				DCM rt 3	(68)
				DCM rt 3	(9)
				DCM rt 3	(5)
				DCM rt 3	(5)
				DCM rt 3	(5)
				DCM rt 3	(5)

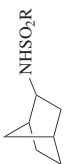
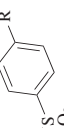


TABLE 1E. HYDROAMINATION OF STRAINED ALKENES (Continued)

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
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Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

 4 eq	RSO₂NH₂	Catalyst (x mol %), MW, solvent		285			
	R	Catalyst	x	Solvent	Temp (°)	Time (h)	
	Me	(PhO) ₃ P/AuCl/AgOTf	5	dioxane	90	0.5	(98)
	4-MeOC ₆ H ₄	(PhO) ₃ P/AuCl/AgOTf	5	C ₇ H ₈	90	0.5	(0)
	4-O ₂ NC ₆ H ₄	(PhO) ₃ P/AuCl/AgOTf	5	C ₇ H ₈	90	0.5	(96)
	4-MeC ₆ H ₄	TfOH	0.1	C ₇ H ₈	90	0.5	(99)
	4-MeC ₆ H ₄	(Me ₂ S)/AuCl/AgOTf	5	C ₇ H ₈	85	0.25	(99)
	4-MeC ₆ H ₄	(Ph ₃ P)/AuCl/AgOTf	0.1	C ₇ H ₈	90	0.5	(58)
	4-MeC ₆ H ₄	(Ph ₃ P)/AuCl/AgOTf	5	C ₇ H ₈	85	0.25	(99)
	4-MeC ₆ H ₄	(PhO) ₃ P/AuCl/AgOTf	0.01	C ₇ H ₈	90	0.5	(60)
	4-MeC ₆ H ₄	(PhO) ₃ P/AuCl/AgOTf	0.05	C ₇ H ₈	90	0.5	(94)
	4-MeC ₆ H ₄	(PhO) ₃ P/AuCl/AgOTf	0.1	C ₇ H ₈	90	0.5	(8)
	4-MeC ₆ H ₄	(PhO) ₃ P/AuCl/AgOTf	0.1	C ₇ H ₈	90	0.5	(99)
	4-MeC ₆ H ₄	(PhO) ₃ P/AuCl/AgOTf	1	C ₇ H ₈	90	0.5	(99)
	4-MeC ₆ H ₄	(3,5-(CF ₃) ₂ -C ₆ H ₃) ₃ P/AuCl/AgOTf	5	C ₇ H ₈	85	0.25	(99)
	 SO ₂ NH ₂	15 (5 mol %), DCE		 R	Temp (°)	Time (h)	94
				H	50	5	
				Cl	50	12	
				MeO	50	5	
				n-BuO	50	5	
				O ₂ N	80	12	
				Me	50	5	
				CF ₃	50	5	
				t-Bu	50	5	



		Ph₃PAuCl/AgOTf (5 mol %), MW, DCE, 140°, 40 min		<table><tr><th>R</th><th></th></tr><tr><td>H</td><td>(93)</td></tr><tr><td>Me</td><td>(97)</td></tr></table>	R		H	(93)	Me	(97)	202														
R																									
H	(93)																								
Me	(97)																								
		Ph₃PAuCl/AgOTf (5 mol %), C₇H₈, 85°, 15 h		<table><tr><th>R</th><th></th></tr><tr><td>MeO</td><td>(80)</td></tr><tr><td>Me</td><td>(89)</td></tr></table>	R		MeO	(80)	Me	(89)	133														
R																									
MeO	(80)																								
Me	(89)																								
		H₃SiW₁₂O₄₀•H₂O (100 mg/mmol amine), DCE, 85°		<table><tr><th>R¹</th><th>R²</th><th>Time (h)</th><th></th></tr><tr><td>H</td><td>H</td><td>28</td><td>(86)</td></tr><tr><td>O₂N</td><td>H</td><td>28</td><td>(85)</td></tr><tr><td>Me</td><td>H</td><td>24</td><td>(88)</td></tr><tr><td>Me</td><td>Me</td><td>24</td><td>(60)</td></tr></table>	R ¹	R ²	Time (h)		H	H	28	(86)	O ₂ N	H	28	(85)	Me	H	24	(88)	Me	Me	24	(60)	250
R ¹	R ²	Time (h)																							
H	H	28	(86)																						
O ₂ N	H	28	(85)																						
Me	H	24	(88)																						
Me	Me	24	(60)																						
		Cu(OTf)₂ (10 mol %), dioxane, 85°		<table><tr><th>R¹</th><th>R²</th><th></th></tr><tr><td>O₂N</td><td>H</td><td>(83)</td></tr><tr><td>Me</td><td>H</td><td>(95)</td></tr><tr><td>Me</td><td>Bn</td><td>(77)</td></tr></table>	R ¹	R ²		O ₂ N	H	(83)	Me	H	(95)	Me	Bn	(77)	246								
R ¹	R ²																								
O ₂ N	H	(83)																							
Me	H	(95)																							
Me	Bn	(77)																							
		H-Mont (0.15 g/mmol alkene), heptane			127																				

R ¹	R ²	x	Temp (°)	Time (h)	
Cl	H	0.67	150	1	(90)
MeO	H	1.5	150	1	(89)
O ₂ N	H	1.5	150	3	(85)
Me	H	0.67	80	16	(90)
Me	H	0.67	150	1	(95)
Me	Me	0.67	150	2	(76)



TABLE 1E. HYDROAMINATION OF STRAINED ALKENES (*Continued*)

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Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)		Refs.	
 2 eq	R¹R²NH	catalyst (x mol %), solvent	 NR ¹ R ²		423	
 4 eq	Et₂NH (1.2 eq)	EtLi (6 mol %), TMEDA (12 mol %), 150°, 13.5 h	 NEt ₂ (18) +  NEt ₂ (12)		331	
 4 eq	(<i>n</i>-Bu)NHMe	[Rh(COD) ₂](BF ₄) (5 mol %), PPh ₃ (10 mol %), THF, 100°, 20 h	 N(<i>n</i> -Bu)Me (51) +  N(<i>n</i> -Bu)Me (14)		333	
			 N(<i>n</i> -Bu)Me (35)			

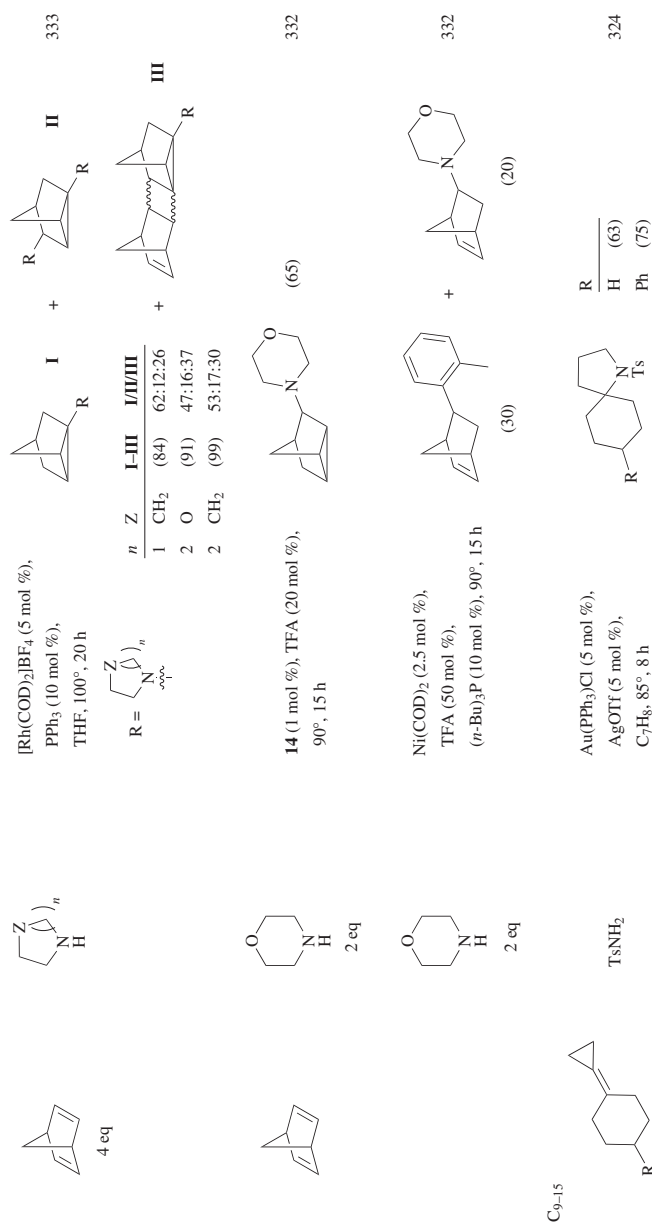
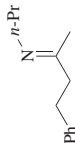
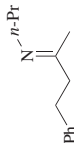
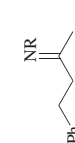
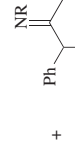
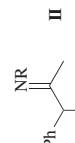
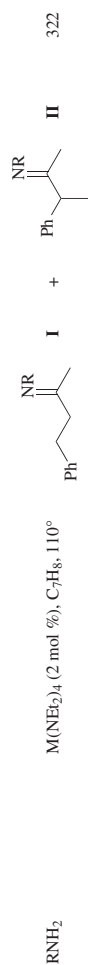


TABLE 1E. HYDROAMINATION OF STRAINED ALKENES (Continued)

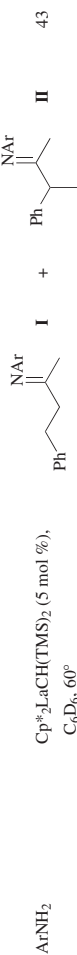
Alkene	Amine	Conditions	Product(s) and Yield(s) (%)			Refs.				
Please refer to the charts preceding the tables for structures indicated by the bold numbers.										
	<i>(n</i> -Pr) ₃ NH ₂	3a (5 mol %), C ₆ D ₆		Temp (°)		TOF (h ⁻¹)				
				60	—	(0)				
				90	0.009	(95)				
		120	0.05	(95)						
 1.2 eq	<i>(n</i> -Pr) ₃ NH ₂	Cp [*] ₂ LuCH(TMS) ₂ (5 mol %), C ₆ D ₆ , 60°		Ln		Time (h)				
				La	25	(95)				
				Sm	90	(95)				
	RNH ₂	13 (2 mol %), C ₇ H ₈ , 110°		I + 		II				
							Time (h)		I + II	I/II
							Et	4	(39)	I only
	Et	40	(100)	I only						
	<i>i</i> -Pr	96	(80)	84:16						
	<i>n</i> -Bu	20	(94)	I only						
	Ph	4	(73)	87:13						
	Ph	17	(100)	87:13						
	DIPP	120	(24)	I only						
	DIPP	1800	(100)	I only						
						322				

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.



$\text{M}(\text{NEt}_2)_4$ (2 mol %), C_7H_8 , 110°

R	M	Time (d)	I/II
<i>n</i> -Bu	Ti	1 (19)	90:10
<i>n</i> -Bu	Ti	11 (25)	90:10
<i>n</i> -Bu	Ti	46 (48)	90:10
Ph	Zr	— (—)	—
2,6-Me ₂ C ₆ H ₃	Zr	6 (92)	10:90
2,4,6-Me ₃ C ₆ H ₂	Zr	16 (89)	8:92
2,6- <i>i</i> -Pr ₂ C ₆ H ₃	Zr	9 (100)	29:71



$\text{Cp}^*\text{}_2\text{LaCH}(\text{TMS})_2$ (5 mol %),
 C_6D_6 , 60°

Ar	Time (h)	I + II ^c	I/II
Ph	80 (81)	(81)	88:12
4-Me ₂ NC ₆ H ₄	50 (56)	(56)	95:5
4-MeC ₆ H ₄	53 (92)	(92)	89:11



$[\text{Pd}(\text{allyl})\text{Cl}]_2$ (5 mol %),
 DPPE (12.5 mol %),
 DME, 100° , 3 d

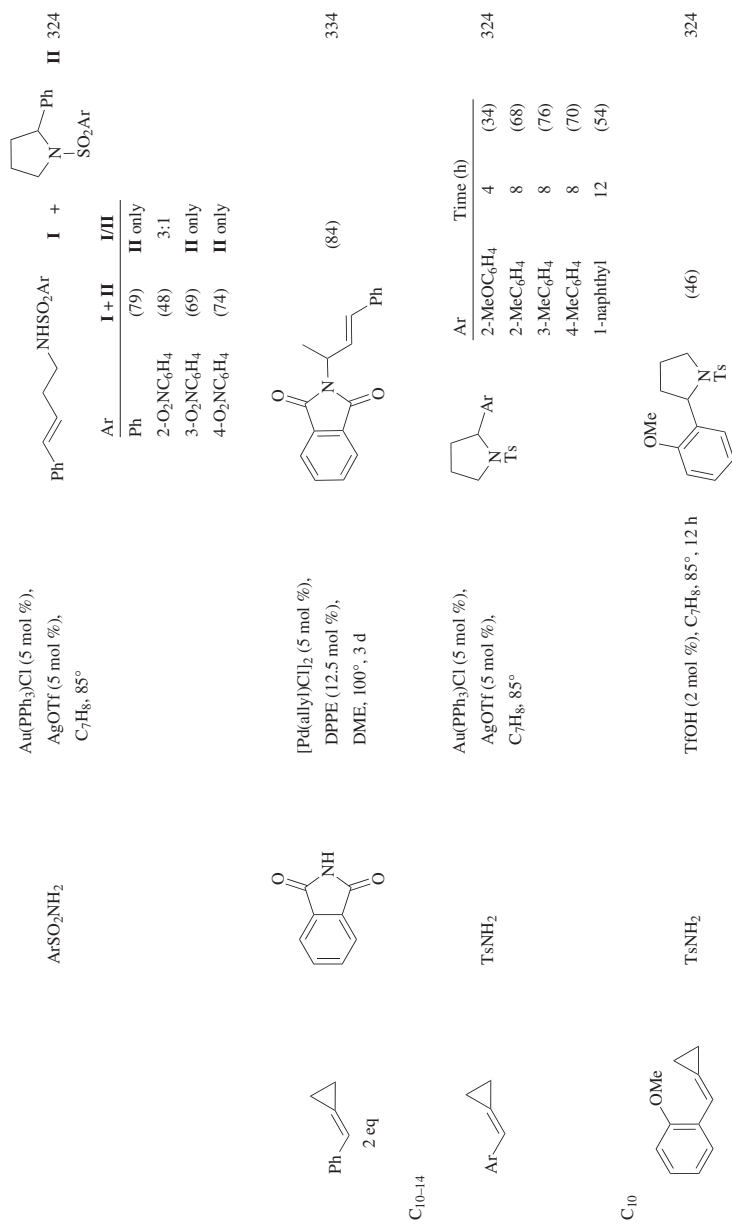
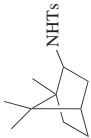
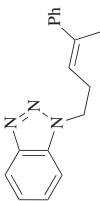


TABLE 1E. HYDROAMINATION OF STRAINED ALKENES (Continued)

Please refer to the charts preceding the tables for structures indicated by the **bold numbers**.

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀  4 eq	TsNH ₂	Catalyst (<i>x</i> mol %), neat, 85°, 14 h	 Catalyst <i>x</i> HOTf 1 (66) AgOTf 5 (79)	429
C ₁₁  3 eq		Au(PPh ₃)OTf (10 mol %), C ₇ H ₈ , 50°, 24 h	 (10)	464
 <i>x</i> eq	PhSO ₂ NH ₂	Catalyst (10 mol %), solvent, 24 h	 I + II	464

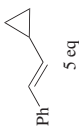
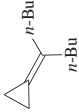
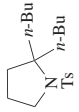
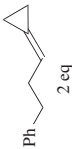
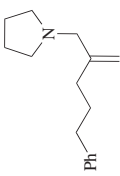
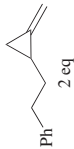
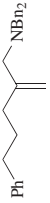
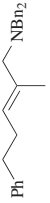
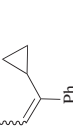
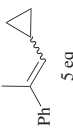
 3 eq C ₁₁₋₁₅	ArSO ₂ NH ₂	Au(PPh ₃)OTf (10 mol %), C ₇ H ₈ , 50°, 24 h		Ar	464	
 3 eq C ₁₁₋₁₅	TsNHMe	Au(PPh ₃)OTf (10 mol %), C ₇ H ₈ , 50°, 24 h		R c-C ₆ H ₁₁ Ph 4-ClC ₆ H ₄ 4-FC ₆ H ₄ 4-MeOC ₆ H ₄ 4-MeC ₆ H ₄ 4-CF ₃ C ₆ H ₄ BnCH ₂ 4- <i>t</i> -BuC ₆ H ₄ 2-naphthyl	dr 86:14 100:0 100:0 100:0 100:0 100:0 100:0 80:20 100:0 100:0	464
 5 eq C ₁₁	TsNHMe	Au(PPh ₃)OTf (10 mol %), C ₇ H ₈ , 80°, 63 h		(57)	464	
 3 eq C ₁₁₋₁₂	TsNH ₂	Au(PPh ₃)Cl (5 mol %), AgOTf (5 mol %), C ₇ H ₈ , 85°		R Ph 4-ClC ₆ H ₄ 3-BrC ₆ H ₄ 4-EtOC ₆ H ₄ 4-MeC ₆ H ₄ <i>n</i> -C ₇ H ₁₅	Time (h) 12 (68) 24 (43) 24 (47) 8 (71) 8 (72) 8 (64)	324

TABLE 1E. HYDROAMINATION OF STRAINED ALKENES (Continued)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
	TsNH ₂	Au(PPh ₃)Cl (5 mol %), AgOTf (5 mol %), C ₇ H ₈ , 85°, 8 h	 (70)	324
 2 eq		[Pd(allyl)Cl] ₂ (10 mol %), DPPE (25 mol %), DME, 100°, 3 d	 (64)	334
 2 eq	Bn ₂ NH	[Pd(allyl)Cl] ₂ (5 mol %), DPPE (12.5 mol %), DME, 100°, 3 d	 (82)	334
 3 eq	Bn ₂ NH	[Pd(allyl)Cl] ₂ (5 mol %), DPPE (12.5 mol %), DME, 100°, 3 d	 (30)	334
 3 eq	TsNHMe	Au(PPh ₃)OTf (10 mol %), C ₇ H ₈ , 50°, 24 h	 (76)	464
 5 eq	TsNHMe	Au(PPh ₃)OTf (10 mol %), C ₇ H ₈ , 80°, 63 h	 (54)	464

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₁₂

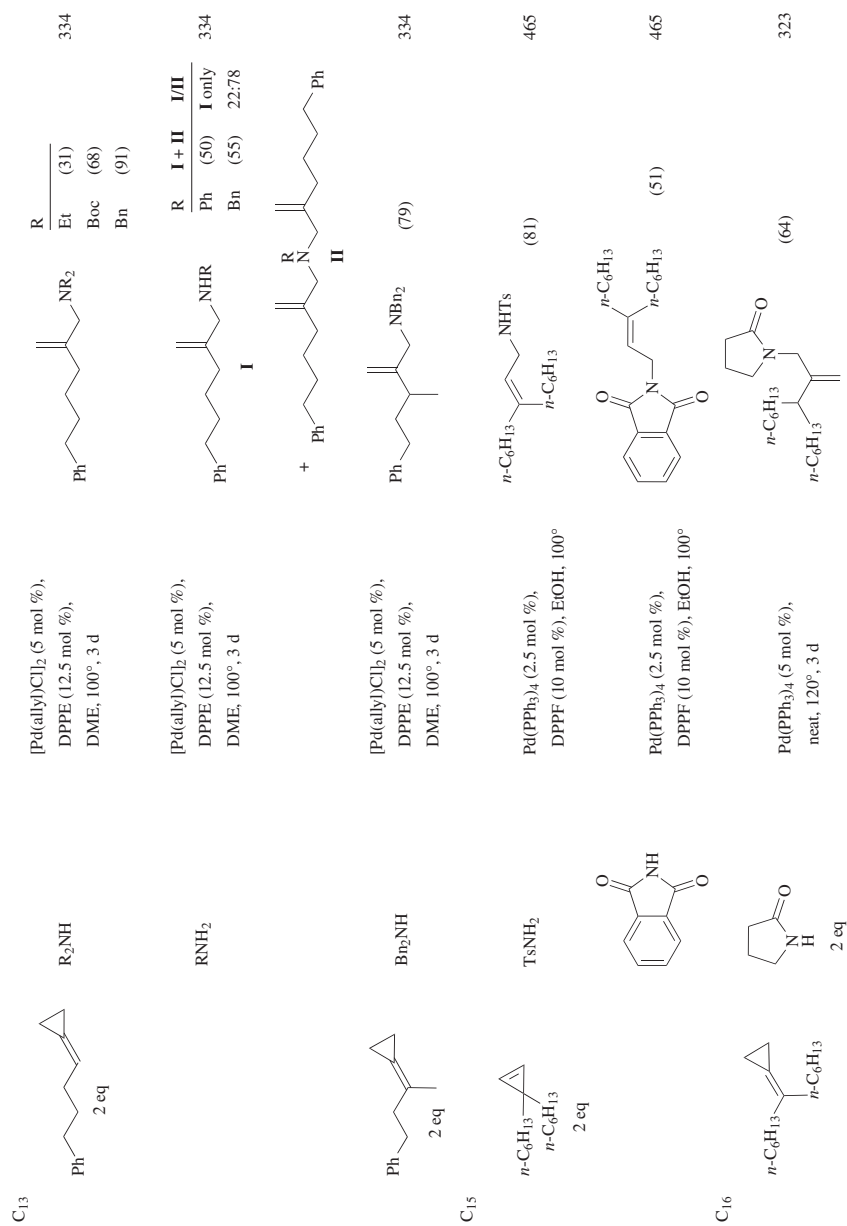
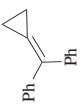
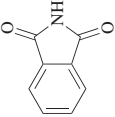


TABLE 1E. HYDROAMINATION OF STRAINED ALKENES (Continued)

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_{16}	 2 eq	$\text{Pd}(\text{PPh}_3)_4$ (5 mol %), ligand (10 mol %), neat, 120°, 2 d	Ligand — (95) DPPE (43) DPPP (45) DPPB (39) PPh ₃ (73) P(2-tolyl) ₃ (51) (<i>n</i> -Bu) ₃ PO (80)	323
	 2 eq	$\text{Pd}(\text{PPh}_3)_4$ (5 mol %), neat, 120°, 3 d	Z O (96) NH (84)	323
	 2 eq	$\text{Pd}(\text{PPh}_3)_4$ (5 mol %), neat, 120°, 3 d	(79)	323
	 2 eq	$\text{Pd}(\text{PPh}_3)_4$ (5 mol %), neat, 120°, 3 d	(95)	323

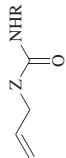
^a A single diastereomer was formed, for which the relative configuration was not determined.

^b The reaction conditions include microwave irradiation.

^c The product was isolated as the amine after reduction.

^d The catalyst from run 1 was reused in runs 2-4.

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES

Aminoalkene	Conditions	Product(s) and Yield(s) (%)				Refs.
	(PPh ₃)AuCl (x mol %), AgOTf (x mol %), C ₇ H ₈	Z	R	x	Temp (°)	Time (h)
		O	Ts	20	60	24
		CH ₂	Ph	20	100	30
		CH ₂	Ph	100	100	30
		CH ₂	4-ClC ₆ H ₄	100	100	30
	Catalyst (1–5 mol %), solvent	CH ₂	Bz	50	100	30
		CH ₂	Ts	50	60	24
						(—)
						(50)
						(89)
	Catalyst (1–5 mol %), solvent					
	Catalyst (3 mol %), C ₆ D ₆					

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
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Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C ₅		(<i>n</i> -Bu)Li (16 mol %), solvent, 2 h	 I +  II	148																								
			<table> <tr> <th>Solvent</th><th>Temp (°)</th><th>I + II</th><th>I/II</th></tr> <tr> <td>THF</td><td>20</td><td>(87)</td><td>7:93</td></tr> <tr> <td>THF</td><td>50</td><td>(95)</td><td>32:68</td></tr> <tr> <td>THP</td><td>90</td><td>(99)</td><td>71:29</td></tr> <tr> <td>C₇H₈</td><td>110</td><td>(99)</td><td>34:66</td></tr> <tr> <td>THP/C₇H₈ (1:1)</td><td>110</td><td>(99)</td><td>95:5</td></tr> </table>	Solvent	Temp (°)	I + II	I/II	THF	20	(87)	7:93	THF	50	(95)	32:68	THP	90	(99)	71:29	C ₇ H ₈	110	(99)	34:66	THP/C ₇ H ₈ (1:1)	110	(99)	95:5	
Solvent	Temp (°)	I + II	I/II																									
THF	20	(87)	7:93																									
THF	50	(95)	32:68																									
THP	90	(99)	71:29																									
C ₇ H ₈	110	(99)	34:66																									
THP/C ₇ H ₈ (1:1)	110	(99)	95:5																									
		(PPh ₃)AuCl (5 mol %), AgOTf (5 mol %), solvent	 I +  II	202																								
			<table> <tr> <th>Solvent</th><th>Temp (°)</th><th>Time (h)</th><th>I + II</th><th>I/II</th></tr> <tr> <td>C₇H₈</td><td>100</td><td>—</td><td>72</td><td>(95) I only</td></tr> <tr> <td>DCE</td><td>140</td><td>MW</td><td>0.67</td><td>(95) 10:7</td></tr> </table>	Solvent	Temp (°)	Time (h)	I + II	I/II	C ₇ H ₈	100	—	72	(95) I only	DCE	140	MW	0.67	(95) 10:7										
Solvent	Temp (°)	Time (h)	I + II	I/II																								
C ₇ H ₈	100	—	72	(95) I only																								
DCE	140	MW	0.67	(95) 10:7																								
		Me ₂ Si(C ₅ Me ₄) ₂ NdCH(TMS) ₂ (2.6 mol %), C ₇ D ₈ , rt, 3 h	 (95)	45																								
		[K ₂ PtCl ₄] (1 eq), HCl (10 eq), NaCl, H ₂ O, 60°	 R +  II	<table> <tr> <th>R</th><th>Time (h)</th><th>I + II</th><th>I/II</th></tr> <tr> <td>Me</td><td>7</td><td>(87)</td><td>88:12</td></tr> <tr> <td><i>n</i>-Pr</td><td>8</td><td>(83)</td><td>81:19</td></tr> <tr> <td><i>i</i>-Pr</td><td>19</td><td>(75)</td><td>69:31</td></tr> </table>	R	Time (h)	I + II	I/II	Me	7	(87)	88:12	<i>n</i> -Pr	8	(83)	81:19	<i>i</i> -Pr	19	(75)	69:31								
R	Time (h)	I + II	I/II																									
Me	7	(87)	88:12																									
<i>n</i> -Pr	8	(83)	81:19																									
<i>i</i> -Pr	19	(75)	69:31																									
		C ₈ F ₁₇ SO ₃ H (5 mol %), perfluorodecalin, C ₇ H ₈ , hexanes, reflux, 1 h	 (97)	211																								

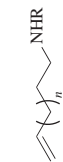
Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

Acid (20 mol %), Pd(PPh ₃) ₄ (x mol %), C ₇ H ₈			x	Temp (°)	Time (h)	209
—	—					
TrfOH	0	rt	0	100	24	(—)
TrfOH	0	100	0	100	48	(75)
TrfOH	0	100	0	100	2	(98)
TrfOH	5	100	5	100	2	(96)
TFA	0	100	0	100	24	(—)
AcOH	0	100	0	100	24	(—)
C ₆ F ₅ CO ₂ H	0	100	0	100	24	(—)
Tf ₂ O	0	100	0	100	2	(100)
H ₂ SO ₄	0	100	0	100	4	(90)

n	R	
1	Boc	(88)
1	Cbz	(82)
1	4-MeC ₆ H ₄ CO	(60)
2	Boc	(92)
2	Cbz	(76)

C₅₋₆

311

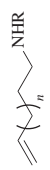
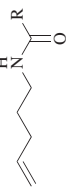
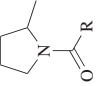


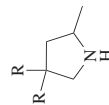
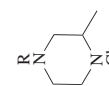
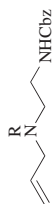
82 (5 mol %), AgOTf (10 mol %),
Cu(OTf)₂ (10 mol %),
MgSO₄, CH₂Cl₂, rt, 12 h



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TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>			
C₅₋₆ 	Catalyst (x mol %) 	169	
	1 Me [Cp ₂ ZrMe][MeB(C ₆ F ₅) ₃]	2 C ₆ D ₃ Br 80 7 (98)	
	1 Me [Cp ₂ ZrMe][MeB(C ₆ F ₅) ₃]	2 C ₆ D ₆ 80 10 (97)	
	1 Me [Cp ₂ ZrMe][MeB(C ₆ F ₅) ₃]	2 C ₆ D ₃ Br 100 1 (97)	
	1 Me [Cp ₂ ZrMe][MeB(C ₆ F ₅) ₃]	1 toluene 100 17 (99)	
	1 Me [Cp ₂ ZrMe][B(C ₆ F ₅) ₄]	2 C ₆ D ₃ Br 80 5 (91)	
	1 Me [Cp ⁸ ₂ ZrMe][MeB(C ₆ F ₅) ₃]	10 C ₆ D ₃ Br 100 74 (10)	
	1 Me [Cp ⁸ ₂ ZrMe][B(C ₆ F ₅) ₄]	10 C ₆ D ₃ Br 100 74 (11)	
	1 Me [Cp ₂ TiBn][B(C ₆ F ₅) ₄]	2 C ₆ D ₃ Br 100 218 (76)	
	1 Me [Cp ₂ ZrMe ₂]	10 C ₆ D ₃ Br 100 168 (—)	
	1 Me [Cp ₂ TiBn ₂]	10 C ₆ D ₃ Br 100 20 (—)	
	1 Me B(C ₆ F ₅) ₃	10 C ₆ D ₃ Br 100 24 (—)	
	1 Bn [Cp ₂ ZrMe][MeB(C ₆ F ₅) ₃]	2.5 C ₆ D ₃ Br 100 6 (94)	
	1 Bn [Cp ₂ ZrMe][B(C ₆ F ₅) ₄]	2 C ₆ D ₃ Br 100 4 (95)	
	1 Bn [Cp ₂ TiBn][B(C ₆ F ₅) ₄]	4 C ₆ D ₃ Br 100 132 (68)	
	2 Me [Cp ₂ ZrMe][MeB(C ₆ F ₅) ₃]	2 C ₆ D ₃ Br 100 87 (98)	
	2 Me [Cp ₂ ZrMe][B(C ₆ F ₅) ₄]	2 C ₆ D ₃ Br 100 12 (98)	
	2 Me [Cp ₂ TiBn][B(C ₆ F ₅) ₄]	4 C ₆ D ₃ Br 100 57 (42)	
C₅ 	Pt(bpy)Cl₂ (10 mol %), AgOTf (20 mol %), DMF-d₇, 120°, 24 h		86
	Au(IPr)Cl (10 mol %), AgOTf (10 mol %), MeOH, 45°, 24 h		208

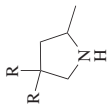
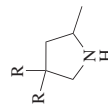


		R	Additive
82 (5 mol %),		CF ₃ CO	— (33)
AgBF ₄ (10 mol %),		CF ₃ CO	HBF ₄ •Et ₂ O (99)
additive (50 mol %),		Boc	— (—)
MgSO ₄ , CH ₂ Cl ₂ , rt, 20 h		Boc	HBF ₄ •Et ₂ O (20)
		2-Ns	— (97)
		Ts	— (89)

1. **17** (x mol %),
Ln precatalyst (5 mol %), C₆D₆, rt

R	Precatalyst	x	Cycle	Time (h) ^a
H	Cp ⁺ ₂ SmCH(TMS) ₂	0	1	2.2
H	Cp ⁺ ₂ SmCH(TMS) ₂	10	1	3.5
H	Cp ⁺ ₂ SmCH(TMS) ₂	10	2	4.7
H	Cp ⁺ ₂ SmCH(TMS) ₂	10	3	5.8
Me	Cp ⁺ ₂ SmCH(TMS) ₂	0	1	0.6
	Cp ⁺ ₂ SmCH(TMS) ₂	7.5	1	0.8
Me	Cp ⁺ ₂ SmCH(TMS) ₂	7.5	2	1.6
Me	Cp ⁺ ₂ SmCH(TMS) ₂	7.5	3	2.9
Me	Cp ⁺ ₂ SmCH(TMS) ₂	10	1	1.1
Me	Cp ⁺ ₂ SmCH(TMS) ₂	10	2	2.6
Me	Cp ⁺ ₂ SmCH(TMS) ₂	10	3	4.2
Me	Cp ⁺ ₂ SmCH(TMS) ₂	50	1	39
Me	Cp ⁺ ₂ SmCH(TMS) ₂	50	2	59
Me	[Me ₂ Si(C ₃ Me ₄)((<i>r</i> -Bu)N)]SmN(TMS) ₂	0	1	0.12
Me	[Me ₂ Si(C ₃ Me ₄)((<i>r</i> -Bu)N)]SmN(TMS) ₂	10	1	0.4
Me	[Me ₂ Si(C ₃ Me ₄)((<i>r</i> -Bu)N)]SmN(TMS) ₂	10	2	0.6
Me	[Me ₂ Si(C ₃ Me ₄)((<i>r</i> -Bu)N)]SmN(TMS) ₂	10	3	1.1
Me	Cp ⁺ ₂ LaCH(TMS) ₂	0	1	0.3
Me	Cp ⁺ ₂ LaCH(TMS) ₂	10	1	0.6
Me	Cp ⁺ ₂ LaCH(TMS) ₂	10	2	1.0
Me	Cp ⁺ ₂ LaCH(TMS) ₂	10	3	1.8

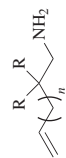
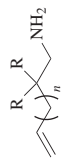
TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.				
	Catalyst (10 mol %), C ₆ D ₆		R	Catalyst	Temp	Time (h)	
			H	25a	110°	6.5	(95)
			H	25b	110°	6	(95)
			H	25c	110°	6	(88)
			H	25d	110°	24	(95)
			Me	25a	rt	2.5	(83)
			Me	25b	rt	2.5	(88)
			Me	25c	rt	2.5	(93)
			Me	25d	rt	4.5	(88)
			-(CH ₂) ₄ -	25a	rt	1.3	(92)
			-(CH ₂) ₄ -	25b	rt	1	(88)
			-(CH ₂) ₄ -	25c	rt	1	(95)
			-(CH ₂) ₄ -	25d	rt	1.8	(96)
	Ti catalyst (5 mol %), C ₇ H ₈ , 105°		R	Catalyst	Time (h)		
			H	Ti(NMe ₂) ₄	96	(—)	
			H	Ind ₂ Ti(NMe ₂) ₂	96	(—)	
			Me	Ti(NMe ₂) ₄	24	(48)	
			Me	Ti(NMe ₂) ₄	96	(87)	
			Me	Ind ₂ Ti(NMe ₂) ₂	24	(31)	
			Me	Ind ₂ Ti(NMe ₂) ₂	96	(74)	
			Me	Cp ₂ Ti(NMe ₂) ₂	24	(—)	

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₅₋₁₀ 172

C₅₋₇

C₅₋₁₇

Me	Cp ₂ Ti(NMe ₂) ₂	96	(tr)	
Me	[Me ₂ Si(C ₅ Me ₄)(<i>i</i> -BuN)]Ti(NMe ₂) ₂	24	(—)	
Me	[Me ₂ Si(C ₅ Me ₄)(<i>i</i> -BuN)]Ti(NMe ₂) ₂	96	(8)	
Me	Cp ² Ti(NMe ₂) ₂	24	(—)	
Me	Cp ² Ti(NMe ₂) ₂	96	(tr)	

<i>n</i>	R	Time (h)	
1	H	7	(67)
1	Me	24	(77)
2	H	45	(79)

[K₂PtCl₄] (1 eq), HCl (10 eq),
NaCl, H₂O, 60°

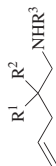
<i>n</i>	R	Catalyst	<i>x</i>	Temp	Time (h)	
1	H	19a	5	rt	170	(—)
1	H	19c	10	rt	72	(70)
1	Me	19a	2	rt	5.5	(40)
1	Me	19a	2	rt	22	(50)
1	Me	19a	2	rt	48	(70)
1	Me	19c	3	rt	72	(90)
1	—(CH ₂) ₈ —	19a	3	rt	1	(99)
1	—(CH ₂) ₅ —	19c	3	rt	9	(80)
1	Ph	19a	3	rt	0.25	(99)
1	Ph	19c	3	rt	1.5	(99)
2	Me	19c	2	60°	15	(>80)

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

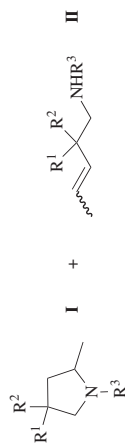
Please refer to the charts preceding the tables for structures indicated by the **bold numbers**.

n	R	Catalyst	x	Temp	Time (h)
1	H	19b	2	rt	40 (30)
1	H	19b	10	rt	40 (90)
1	H	20	7	110°	10 (80)
1	Me	19b	2	rt	3.5 (95)
1	Me	19b	10	rt	3 (99)
1	Me	20	4	rt	144 (80)
1	-(CH ₂) ₅ -	19b	2	rt	0.6 (99)
1	-(CH ₂) ₅ -	20	3	rt	8 (99)
1	Ph	19b	2	rt	1 (99)
1	Ph	19b	10	rt	0.25 (99)
1	Ph	20	5	rt	1 (99)
2	Me	19b	8	rt	47 (20)
2	Me	19b	8	60°	6 (70)
2	Me	19b	8	60°	15 (90)
2	Me	20	10	110°	48 (90)

C5-10



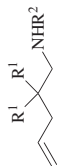
(*n*-Bu)Li (16 mol %), hexane/THF



144

317

C5-17



Catalyst (2 mol %),
[PhNHMe₂][B(C₆F₅)₄] (*x* mol %),
C₆D₆



471

R ¹	R ²	R ³	Temp	Time (h)	I + II	I/II
H	H	H	50°	2	(75)	32:68
H	H	Bn	50°	2	(79)	95:5
Me	H	H	50°	8	(81)	75:25
Me	Me	H	rt	2	(85)	I only
Me	Me	Et	rt	5	(84)	98:2
Me	Me	Bn	rt	5	(94)	98:2
-(CH ₂) ₅ -	H	H	rt	24	(91)	95:5
-(CH ₂) ₅ -	Et	Et	rt	5	(86)	98:2
-(CH ₂) ₅ -	Bn	Bn	rt	5	(99)	98:2

R ¹	R ²	Catalyst	<i>x</i>	Temp (°)	Time (h)
H	Me	Sc(CH ₂ Ph) ₃ (THF) ₃	0	60	0.5 (99)
H	Me	Sc(CH ₂ Ph) ₃ (THF) ₃	2	60	4 (72)
H	Me	Y(CH ₂ Ph) ₃ (THF) ₃	0	60	0.4 (99)
H	Me	Y(CH ₂ Ph) ₃ (THF) ₃	2	60	0.7 (99)
H	Me	La(CH ₂ Ph) ₃ (THF) ₃	0	60	0.25 (99)
H	Me	La(CH ₂ Ph) ₃ (THF) ₃	2	60	0.17 (99)
Ph	H	Sc(CH ₂ Ph) ₃ (THF) ₃	0	80	10 (40)
Ph	H	Sc(CH ₂ Ph) ₃ (THF) ₃	2	80	8 (99)
Ph	H	Y(CH ₂ Ph) ₃ (THF) ₃	0	80	10 (99)
Ph	H	Y(CH ₂ Ph) ₃ (THF) ₃	2	60	3 (88)
Ph	H	La(CH ₂ Ph) ₃ (THF) ₃	0	60	3 (99)
Ph	H	La(CH ₂ Ph) ₃ (THF) ₃	2	60	4 (51)

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₃-17

Catalyst (2 mol %),
[PhNHMe₂][B(C₆F₅)₄] (x mol %),
C₆D₆

R ¹	R ²	Catalyst	x	Temp (°)	Time (h)
H	Me	42a	0	60	0.5 (99)
H	Me	42a	2	60	4 (0)
H	Me	42b	0	60	0.4 (99)
H	Me	42b	2	60	5 (99)
H	Me	42c	0	60	0.25 (99)
H	Me	42c	2	60	0.17 (99)
Ph	H	42a	0	80	10 (54)
Ph	H	42a	2	80	4 (0)
Ph	H	42b	0	80	6.7 (99)
Ph	H	42b	2	60	0.1 (99)
Ph	H	42c	0	60	3.3 (99)
Ph	H	42c	2	60	1.2 (99)

22d (1.2x mol %),
[Rh(MeCN)₂COD][BF₄] (x mol %),
t-BuOH, 70°, 5 h

Catalyst (x mol %), dioxane, 24 h

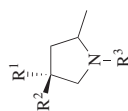
471

91

174



ZnEt₂ (2.5 mol %),
additive (2.5 mol %), C₆D₆

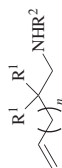
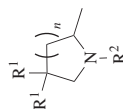


R ¹	R ²	Catalyst	x	Temp (°)
H	H	[PhNHMe ₂][B(C ₆ F ₅) ₄]	10	130 (74)
Me	H	[PhNHMe ₂][B(C ₆ F ₅) ₄]	10	120 (75)
-(CH ₂) ₅ -	H	[PhNHMe ₂][B(C ₆ F ₅) ₄]	10	120 (84)
Ph	MeO	NH ₄ (CF ₃ CO ₂)	20	130 (63)
Ph	Cl	NH ₄ (CF ₃ CO ₂)	20	130 (84)
Ph	MeO ₂ C	NH ₄ (CF ₃ CO ₂)	20	130 (93)
Ph	O ₂ N	NH ₄ (CF ₃ CO ₂)	20	130 (80)
Ph	NC-	NH ₄ (CF ₃ CO ₂)	20	130 (82)
Ph	HO	[PhNHMe ₂][B(C ₆ F ₅) ₄]	10	120 (84)

R ¹	R ²	R ³	Additive	Temp	Time (h)
H	H	CH ₂ =CH(CH ₂) ₃	[PhNHMe ₂][B(C ₆ F ₅) ₄]	180°	504 (90)
Me	Me	Bn	[PhNHMe ₂][B(C ₆ F ₅) ₄]	rt	5.5 (89)
allyl	Me	Bn	[PhNHMe ₂][B(C ₆ F ₅) ₄]	rt	2 (98)
-(CH ₂) ₅ -	Bn	Bn	NH ₄ BF ₄	80°	48 (0)
-(CH ₂) ₅ -	Bn	Bn	[PhNHMe ₂][BF ₄]	80°	48 (0)
-(CH ₂) ₅ -	Bn	Bn	[Et ₃ NH][BPh ₄]	80°	48 (0)
-(CH ₂) ₅ -	Bn	Bn	[PhNHMe ₂][BPh ₄]	80°	48 (0)
-(CH ₂) ₅ -	Bn	Bn	[PhNHMe ₂][OTf]	80°	504 (30)
-(CH ₂) ₅ -	Bn	Bn	HOTf	80°	504 (8)
-(CH ₂) ₅ -	Bn	Bn	[PhNHMe ₂][Al((CF ₃) ₂ CHO) ₄]	rt	120 (25)
-(CH ₂) ₅ -	Bn	Bn	[PhNHMe ₂][Al((CF ₃) ₃ CO) ₄]	rt	0.8 (99)
-(CH ₂) ₅ -	Bn	Bn	[PhNHMe ₂][B(C ₆ F ₅) ₄]	rt	0.6 (99)
Ph	Ph	Bn	[PhNHMe ₂][B(C ₆ F ₅) ₄]	rt	1.3 (94)
Ph	Ph	2-C ₄ H ₉ SCH ₂	[PhNHMe ₂][B(C ₆ F ₅) ₄]	rt	27 (98)
Ph	Ph	2-C ₄ H ₉ OCH ₂	[PhNHMe ₂][B(C ₆ F ₅) ₄]	rt	11 (93)
Ph	Ph	Me ₂ N	[PhNHMe ₂][B(C ₆ F ₅) ₄]	80°	3 (99)



TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)				Refs.																																																																														
Aminoalkene	Conditions	Product(s) and Yield(s) (%)																																																																																
Please refer to the charts preceding the tables for structures indicated by the bold numbers.																																																																																		
C ₅₋₈		$(n\text{-Bu})\text{Li}$ (16 mol %), THP/C ₇ H ₈ (1:1), 110°, 2 h		<table><tr><th><i>n</i></th><th>R¹</th><th>R²</th></tr><tr><td>1</td><td>H</td><td>H</td></tr><tr><td>1</td><td>H</td><td>Bn</td></tr><tr><td>2</td><td>H</td><td>Bn</td></tr><tr><td>2</td><td>Me</td><td>H</td></tr><tr><td>2</td><td>Me</td><td>Bn</td></tr></table>	<i>n</i>	R ¹	R ²	1	H	H	1	H	Bn	2	H	Bn	2	Me	H	2	Me	Bn																																																												
<i>n</i>	R ¹	R ²																																																																																
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2	Me	Bn																																																																																
				148																																																																														
C ₅₋₁₇		Catalyst (10 mol %), solvent, rt		<table><tr><th><i>n</i></th><th>R¹</th><th>R²</th><th>Catalyst</th><th>Solvent</th><th>Time (h)</th></tr><tr><td>1</td><td>H</td><td>H</td><td>21a</td><td>C₆D₆</td><td>17 (59)</td></tr><tr><td>1</td><td>H</td><td>H</td><td>21a</td><td>C₆D₆</td><td>33 (62)</td></tr><tr><td>1</td><td>H</td><td>H</td><td>21a</td><td>THF</td><td>11 (29)</td></tr><tr><td>1</td><td>Me</td><td>H</td><td>21a</td><td>C₆D₆</td><td>11 (85)</td></tr><tr><td>1</td><td>Me</td><td>H</td><td>21a</td><td>THF</td><td>11 (72)</td></tr><tr><td>1</td><td>-(CH₂)₅-</td><td>H</td><td>21a</td><td>C₆D₆</td><td>11 (92)</td></tr><tr><td>1</td><td>Ph</td><td>H</td><td>21a</td><td>C₆D₆</td><td>11 (90)</td></tr><tr><td>1</td><td>Ph</td><td>H</td><td>21a</td><td>THF</td><td>11 (68)</td></tr><tr><td>1</td><td>Ph</td><td>H</td><td>21a</td><td>THF</td><td>23 (87)</td></tr><tr><td>1</td><td>Ph</td><td>H</td><td>21b</td><td>C₆D₆</td><td>24 (29)</td></tr><tr><td>1</td><td>Ph</td><td>Me</td><td>21a</td><td>C₆D₆</td><td>48 (0)</td></tr><tr><td>2</td><td>-(CH₂)₅-</td><td>H</td><td>21a</td><td>C₆D₆</td><td>11 (87)</td></tr></table>	<i>n</i>	R ¹	R ²	Catalyst	Solvent	Time (h)	1	H	H	21a	C ₆ D ₆	17 (59)	1	H	H	21a	C ₆ D ₆	33 (62)	1	H	H	21a	THF	11 (29)	1	Me	H	21a	C ₆ D ₆	11 (85)	1	Me	H	21a	THF	11 (72)	1	-(CH ₂) ₅ -	H	21a	C ₆ D ₆	11 (92)	1	Ph	H	21a	C ₆ D ₆	11 (90)	1	Ph	H	21a	THF	11 (68)	1	Ph	H	21a	THF	23 (87)	1	Ph	H	21b	C ₆ D ₆	24 (29)	1	Ph	Me	21a	C ₆ D ₆	48 (0)	2	-(CH ₂) ₅ -	H	21a	C ₆ D ₆	11 (87)
<i>n</i>	R ¹	R ²	Catalyst	Solvent	Time (h)																																																																													
1	H	H	21a	C ₆ D ₆	17 (59)																																																																													
1	H	H	21a	C ₆ D ₆	33 (62)																																																																													
1	H	H	21a	THF	11 (29)																																																																													
1	Me	H	21a	C ₆ D ₆	11 (85)																																																																													
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1	-(CH ₂) ₅ -	H	21a	C ₆ D ₆	11 (92)																																																																													
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1	Ph	H	21b	C ₆ D ₆	24 (29)																																																																													
1	Ph	Me	21a	C ₆ D ₆	48 (0)																																																																													
2	-(CH ₂) ₅ -	H	21a	C ₆ D ₆	11 (87)																																																																													
				184																																																																														

C₅₋₁₁Ln catalyst (6 mol %), C₆D₆

<i>n</i>	R ¹	R ²	Catalyst	Temp	Time (h)	
1	H	Me	Li(THF) ₄ [Y(CH ₂ TMS) ₄]	50°	16	(95)
1	H	Me	Y(CH ₂ TMS) ₃ (THF) ₂	rt	16	(95)
1	Me	Me	Li(THF) ₄ [Y(CH ₂ TMS) ₄]	rt	16	(88)
1	Me	Me	Y(CH ₂ TMS) ₃ (THF) ₂	rt	0.25	(95)
1	Me	Me	Yb(CH ₂ TMS) ₃ (THF) ₂	rt	0.17	(95)
1	-(CH ₂) ₅ -	Me	Li(THF) ₄ [Y(CH ₂ TMS) ₄]	rt	0.25	(95)
1	-(CH ₂) ₅ -	Me	Y(CH ₂ TMS) ₃ (THF) ₂	rt	0.17	(95)
1	-(CH ₂) ₅ -	Me	Yb(CH ₂ TMS) ₃ (THF) ₂	rt	0.17	(95)
1	-(CH ₂) ₅ -	Bn	Li(THF) ₄ [Y(CH ₂ TMS) ₄]	50°	16	(95)
1	-(CH ₂) ₅ -	Bn	Y(CH ₂ TMS) ₃ (THF) ₂	rt	16	(95)
2	Me	Me	Li(THF) ₄ [Y(CH ₂ TMS) ₄]	rt	32	(95)
2	Me	Me	Y(CH ₂ TMS) ₃ (THF) ₂	rt	0.5	(95)
2	Me	Me	Yb(CH ₂ TMS) ₃ (THF) ₂	rt	0.17	(95)
2	-(CH ₂) ₅ -	Me	Li(THF) ₄ [Y(CH ₂ TMS) ₄]	rt	2.5	(95)
2	-(CH ₂) ₅ -	Me	Y(CH ₂ TMS) ₃ (THF) ₂	rt	0.17	(95)
2	-(CH ₂) ₅ -	Me	Yb(CH ₂ TMS) ₃ (THF) ₂	rt	0.17	(95)

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Refs.

Product(s) and Yield(s) (%)

Conditions

Aminoalkene

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₅-18

Ind₂M(NMe₂)₂ (5 mol %),
C₇D₈, 105°

<i>n</i>	R ¹	R ²	M	Time (h)	
1	H	H	Ti	96	(—)
1	H	H	Zr	96	(—)
1	H	H	Hf	96	(—)
1	Me	H	Ti	24	(31) ^b
1	Me	H	Ti	96	(74) ^b
1	Me	H	Zr	24	(30) ^b
1	Me	H	Zr	96	(58) ^b
1	Me	H	Hf	24	(tr) ^b
1	Me	H	Hf	96	(19) ^b
1	Ph	H	Ti	24	(96) ^b
1	Ph	H	Zr	24	(96) ^b
1	Ph	H	Hf	24	(98) ^b
1	Ph	Me	Ti	24	(—)
1	Ph	Me	Zr	24	(—)
1	Ph	Me	Hf	24	(—)
2	Ph	H	Ti	24	(89)
2	Ph	H	Zr	24	(95)
2	Ph	H	Hf	24	(98)

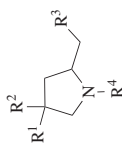
22d (1.2x mol %),
[Rh(MeCN)₂COD]BF₄ (x mol %),
(*t*-Bu)OH, 70°

<i>n</i>	R ¹	R ²	R ³	<i>x</i>	Time (h)	<i>I</i>	<i>I/II</i>	dr <i>I</i>
1	H	H	H	4	7	(76)	>95:5	—
1	H	TBSO	H	3	18	(71)	>95:5	1.6:1
1	H	Ph	H	3	15	(66)	9:5	1.3:1
1	H	4-MeO ₂ CC ₆ H ₄	H	3	21	(64)	10:1	1.6:1
1	H	4-HOCH ₂ C ₆ H ₄	H	5	18	(56)	7:1	1.1:1

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Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₅₋₁₈

Catalyst (x mol %), C₆D₆

R ¹	R ²	R ³	R ⁴	Catalyst	x	Temp	Time (h)	dr
H	H	H	H	23b	10	120°	50	(30) —
H	H	H	H	23b	20	120°	100	(87) —
Me	Me	H	H	23a	10	100°	40	(98) —
Me	Me	H	H	23b	10	100°	18	(98) —
Me	Me	H	H	23c	10	100°	40	(48) —
Me	allyl	H	H	23b	10	60°	18	(95) 1.3:1
Me	allyl	H	H	23c	10	100°	50	(79) 1.3:1
—(CH ₂) ₅ —	—	H	H	23a	10	rt	12	(98) —
—(CH ₂) ₅ —	—	H	H	23b	10	rt	6	(97) —
—(CH ₂) ₅ —	—	H	H	23b	5	rt	13	(96) —
—(CH ₂) ₅ —	—	H	H	23c	5	rt	22	(81) —
Ph	Ph	H	H	23a	10	rt	1.5	(99) —
Ph	Ph	H	H	23a	5	rt	4	(99) —
Ph	Ph	H	H	23b	3	rt	3	(99) —
Ph	Ph	H	H	23c	10	rt	1.5	(99) —
Ph	Ph	H	H	23c	5	rt	5	(98) —
Ph	Ph	Me	H	23a	20	150°	48	(47) —
Ph	Ph	Me	H	23b	20	150°	48	(69) —
Ph	Ph	H	Bn	23b	10	140°	96	(80) —

1	H	4-NCCH ₂ C ₆ H ₄	H	5	12	(79)	>95:5	1.5:1
1	H	4-AcC ₆ H ₄	H	5	16	(61)	10:1	1.5:1
1	Ph	Ph	Me	18	15	(40)	>95:5	—
2	H	H	H	4	8	(77)	>95:5	—

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Please refer to the charts preceding the tables for structures indicated by the **bold numbers**.

C₅-19

Aminoalkene

Conditions

Product(s) and Yield(s) (%)

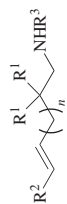
Refs.

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

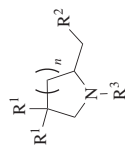
Catalyst (x mol %), C₆D₆

n	R ¹	R ²	R ³	Catalyst	x	Temp	Time (h)
1	H	H	H	24a	10	rt	21 (90)
1	H	H	allyl	24a	10	rt	48 (60)
1	Me	H	H	24a	2	rt	2 (95)
1	Me	H	H	24a	10	rt	0.25 (99)
1	-(CH ₂) ₅ -	H	H	24a	5	rt	0.25 (93)
1	-(CH ₂) ₅ -	H	H	24a	2	rt	1 (98)
1	-(CH ₂) ₅ -	H	H	24b	5	rt	2 (96)
1	Ph	H	H	24a	2	rt	0.25 (99)
1	Ph	H	H	24b	2	rt	2 (99)
1	Ph	Me	H	24a	5	rt	0.5 (94)
1	Ph	Me	H	24b	5	rt	0.5 (86)
2	Me	H	H	24a	10	60°	72 (85)
2	Me	H	H	24a	20	60°	6 (86)
2	Ph	H	H	24a	2	rt	24 (69)
2	Ph	H	H	24a	10	rt	4 (83)
2	Ph	H	H	24b	10	rt	4 (97)
3	Ph	H	H	24a	20	80°	24 (0)
3	Ph	H	H	24b	5	80°	132 (88)

47

C₅₋₁₈

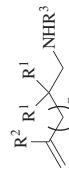
89b (x mol %),
[Rh(COD)₂]BF₄ (y mol %),
dioxane



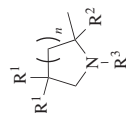
196

n	R ¹	R ²	R ³	x	y	Temp (°)	Time (h)
1	H	H	4-ClC ₆ H ₄ CH ₂	3	2.5	70	7 (69)
1	H	H	4-NCC ₆ H ₄ CH ₂	3	2.5	70	7 (62)
1	H	H	4-MeO ₂ CC ₆ H ₄ CH ₂	3	2.5	70	7 (72)
1	Me	H	Bn	3	2.5	70	7 (83)
1	-(CH ₂) ₅ -	H	H	6	5	100	10 (74)
1	-(CH ₂) ₅ -	H	Bn	3	2.5	70	7 (92)
1	Ph	H	H	6	5	100	10 (83)
1	Ph	H	c-C ₆ H ₁₁ CH ₂	3	2.5	70	7 (91)
1	Ph	H	Bn	3	2.5	70	7 (91)
1	Ph	Me	Me	6	5	100	7 (76)
2	H	H	Bn	3	2.5	70	7 (74)
2	Ph	H	H	6	5	100	10 (84)
2	Ph	H	Bn	3	2.5	70	7 (86)

325

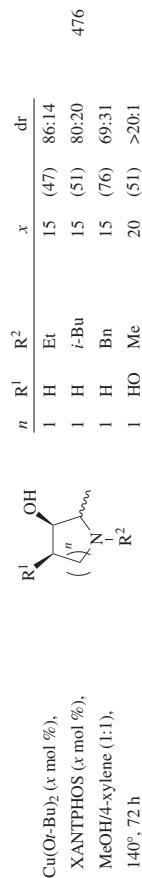
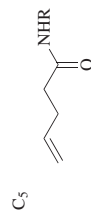
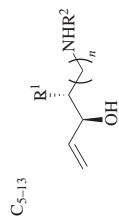
C₅₋₈

18 (x mol %), solvent

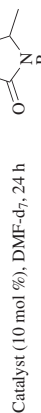


261, 68

n	R ¹	R ²	R ³	x	Solvent	Temp (°)	Time (h)
1	H	H	H	10	C ₆ D ₆	120	41 (89)
1	H	H	H	10	C ₇ D ₈	150	10 (91)
1	H	H	Me	5	C ₇ D ₈	150	18 (—)
1	Me	H	H	5	C ₆ D ₆	120	12 (94)
1	Me	H	H	5	C ₇ D ₈	150	2.5 (98)
1	Me	Me	H	5	C ₇ D ₈	150	104 (92)
1	Me	Me	H	10	C ₇ D ₈	150	45 (94)
2	Me	H	H	5	C ₆ D ₆	120	9 (99)
2	Me	H	H	5	C ₇ D ₈	150	1 (99)



86



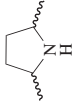
R	Catalyst	Temp (°)
AcHN	Pt(bpy)Me ₂	120 (66)
AcHN	[Pt(bpy)(MeCN) ₂](OTf) ₂	120 (94)
AcHN	Pt(bpy)Cl ₂	120 (0)
AcHN	Pt(2-pyridyl-C ₆ H ₄)Me(DMSO)	120 (80)
AcHN	[Pt(2-pyridyl-C ₆ H ₄)Cl ₂]	120 (64)
AcHN	Pt(2-pyridyl-C ₆ H ₄)Cl(DMSO)	120 (6)
AcHN	[Pt(2-pyridyl-C ₆ H ₄)(MeCN) ₂](OTf) ₂	120 (67)
AcHN	[Pt(2,2'-bipyridyl)(SeEt ₂) ₂]	120 (14)
AcHN	Pt(2,2'-bipyridyl)(MeCN) ₂	120 (4)
AcHN	[Pt(MeCN) ₄](OTf) ₂	120 (0)
AcHN	Pt(PPh ₃) ₂ Cl ₂	120 (0)
PhthalHN	Pt(bpy)Me ₂	80 (10)
PhthalHN	[Pt(bpy)(MeCN) ₂](OTf) ₂	80 (76)
PhthalHN	Pt(bpy)Cl ₂	80 (0)
PhthalHN	Pt(2-pyridyl-C ₆ H ₄)Me(DMSO)	80 (30)
PhthalHN	[Pt(2-pyridyl-C ₆ H ₄)Cl ₂]	80 (15)
PhthalHN	Pt(2-pyridyl-C ₆ H ₄)Cl(DMSO)	80 (35)
PhthalHN	[Pt(2-pyridyl-C ₆ H ₄)(MeCN) ₂](OTf) ₂	80 (65)
PhthalHN	[Pt(2,2'-bipyridyl)(SeEt ₂) ₂]	80 (0)
PhthalHN	Pt(2,2'-bipyridyl)(MeCN) ₂	80 (—)
PhthalHN	[Pt(MeCN) ₄](OTf) ₂	80 (0)
PhthalHN	Pt(PPh ₃) ₂ Cl ₂	80 (0)

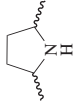


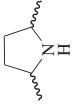
TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the bold numbers.			
C₅	P(<i>c</i> -C ₆ H ₁₁) ₃ AuCl (20 mol %), AgOTf (20 mol %), MW, DCE, 140°, 0.5 h	R Ph (57) 4-ClC₆H₄ (60) Bz (60)	202
C₅₋₇	TfOH (1 eq), C ₇ H ₈ , 100°	R Ar Time (h) H Ph 30 (99) H 4-O₂NC₆H₄ 1 (—) H 4-MeC₆H₄ 30 (99) Me Ph 5 (99) Me 4-MeC₆H₄ 5 (99)	209
C₅₋₈	Catalyst (10 mol %), DMF-d ₇	n R¹ R² R³ R⁴ Catalyst Temp (°) Time (h) dr 1 H H H Me₂N [Pt(bpy)(MeCN)₂](OTf)₂ 120 24 (16) — 1 H H H AcHN Pt(bpy)Cl₂/2AgOTf 120 24 (86) — 1 H H H CF₃COHN [Pt(bpy)(MeCN)₂](OTf)₂ 120 24 (100) — 1 H H H BocHN [Pt(bpy)(MeCN)₂](OTf)₂ 120 24 (0) — 1 H H H PhHN [Pt(bpy)(MeCN)₂](OTf)₂ 120 24 (16) — 1 H H H TsHN [Pt(bpy)(MeCN)₂](OTf)₂ 120 24 (7) — 1 H H H BzHN [Pt(bpy)(MeCN)₂](OTf)₂ 120 24 (77) — 1 H H H CbzHN [Pt(bpy)(MeCN)₂](OTf)₂ 120 24 (22) — 1 H H H PhthalN Pt(bpy)Cl₂/2AgOTf 80 24 (80) — 1 Me H H AcHN Pt(bpy)Cl₂/2AgOTf 120 24 (78) 3:1 1 Me H H PhthalN Pt(bpy)Cl₂/2AgOTf 80 24 (85) 1:1	86

1	Me	Me	H	AcHN	Pt(bpy)Cl ₂ /2AgOTf	120	48	(70)	—
1	Me	Me	H	PhthalN	Pt(bpy)Cl ₂ /2AgOTf	80	24	(82)	—
1	H	H	Me	AcHN	Pt(bpy)Cl ₂ /2AgOTf	120	24	(74)	2.5:1
1	H	H	Me	PhthalN	Pt(bpy)Cl ₂ /2AgOTf	80	24	(64)	6:1
2	H	H	H	AcHN	Pt(bpy)Cl ₂ /2AgOTf	120	24	(90)	—
2	Me	Me	H	AcHN	Pt(bpy)Cl ₂ /2AgOTf	120	24	(69)	—
2	Me	Me	H	PhthalN	Pt(bpy)Cl ₂ /2AgOTf	80	24	(82)	—

Catalyst (x mol %), C ₆ D ₆									
						Catalyst	x	Temp	Time (h)
						16a	1.6	rt	7.9
						16b	3	rt	6
						16c	3	rt	5.3
						16d	3	rt	5
						16d	3	60°	0.1
						16e	3	rt	4.4
						16f	3	rt	8
									<i>trans/cis</i>
									14:1
									158

Catalyst (x mol %), C ₇ D ₈									
						Catalyst	x	Temp	Time (h)
						19a	5	rt	21
						19a	5	rt	72
						19a	5	rt	120
						19b	2	rt	24
						19b	8	rt	9
						19c	8	rt	28
						20	2	rt	24
						20	8	rt	35
						36	10	110°	96
									<i>trans/cis</i>
									—
									469
									—
									469
									—
									469
									4:1
									151
									4:1
									151
									7:3
									469
									4:1
									151
									4:1
									151
									4:1
									151
									11.3:1
									181

Catalyst (5 mol %), C ₆ D ₆ , 60°									
						Catalyst		Time (h)	<i>trans/cis</i>
						27a	1	(95)	7:1
						27b	4.5	(95)	8:1
						27c	144	(tr)	—
						30a	3	(95)	9:1
						30b	22	(95)	7:1
						31	2	(95)	16:1
						33	15	(95)	8:1
									164

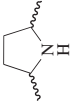
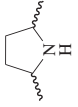
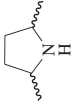
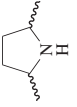
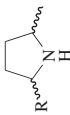
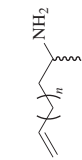
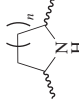
1. RNH(CH ₂) _n NHR (5 mol %), Y[N(TMS) ₂] ₃ (5 mol %) 2. Aminoalkene, C ₆ D ₆ , 60°		<i>n</i>	<i>R</i>	Time (h)	<i>trans/cis</i>	163
		2	2,6-Me ₂ C ₆ H ₃	1.2	(95)	19:1
		2	2-(<i>i</i> -Pr)C ₆ H ₄	0.25	(95)	19:1
		3	2-(<i>i</i> -Pr)C ₆ H ₄	42	(95)	11:1
1. RNHSiMe ₂ NHR (5 mol %), Y[N(TMS) ₂] ₃ (5 mol %) 2. Aminoalkene, C ₆ D ₆ , 60°		<i>R</i>		Time (h)	<i>trans/cis</i>	163
			4-MeC ₆ H ₄	11	(95)	19:1
			2-(<i>i</i> -Pr)C ₆ H ₄	2	(95)	16:1
1. 29 (5 mol %), Sc[N(TMS) ₂] ₃ C ₆ D ₆ , 120°, 2 h 2. Aminoalkene, C ₆ D ₆ , 60°, 1.5 h		(95)	<i>trans/cis</i> = 49:1			165
Ln catalyst (<i>x</i> mol %), solvent						
Catalyst	<i>x</i>	Solvent	Temp	Time (h)	<i>trans/cis</i>	
Cp* ₂ LaCH(TMS) ₂	2.7	C ₇ H ₈	0°	—	(95)	8:1
Cp* ₂ LaCH(TMS) ₂	2.7	C ₇ H ₈	rt	—	(95)	5:1
Cp* ₂ LaCH(TMS) ₂	2.7	C ₇ H ₈	50°	—	(95)	3:2
Cp* ₂ LaCH(TMS) ₂	2.7	C ₇ H ₈ ^d	rt	—	(95)	>50:1
Cp* ₂ LaCH(TMS) ₂	2.7	THF	rt	—	(95)	2:1
Cp* ₂ NdCH(TMS) ₂	2.7	C ₇ H ₈	rt	—	(95)	1:1.25
Cp* ₂ NdCH(TMS) ₂	2.7	C ₇ H ₈ ^d	rt	—	(95)	4:1
Me ₂ Si(C ₃ Me ₄) ₂ NdCH(TMS) ₂	2.7	C ₇ H ₈	rt	—	(95)	20:1
Cp* ₂ SmCH(TMS) ₂	2.7	C ₇ H ₈	rt	—	(95)	1:1.25
Me ₂ Si(C ₃ Me ₄) ₂ SmCH(TMS) ₂	2.7	C ₇ H ₈	rt	—	(95)	1:1
Cp* ₂ YCH(TMS) ₂	2.7	C ₇ H ₈	rt	—	(95)	8:1
Me ₂ Si(C ₃ Me ₄) ₂ YCH(TMS) ₂	2.7	C ₇ H ₈	rt	—	(95)	3:1
Me ₂ Si(C ₃ Me ₄)(C ₃ H ₇)YCH(TMS) ₂	2.7	C ₇ H ₈	rt	—	(95)	18:1
Me ₂ Si(C ₃ Me ₄)(C ₃ H ₇)LuCH(TMS) ₂	2.7	C ₇ H ₈	rt	—	(95)	4:1
La[N(TMS) ₂] ₃	3	C ₆ D ₆	90°	13	(90)	4:1
Y[N(TMS) ₂] ₃	3	C ₆ D ₆	90°	144	(94)	7:1
Nd[N(TMS) ₂] ₃	3	C ₆ D ₆	90°	24	(94)	4:1
Y(2-Me ₂ NCH ₂ C ₆ H ₄) ₃	6	C ₆ D ₆	90°	87	(88)	5.2:1

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.						
Please refer to the charts preceding the tables for structures indicated by the bold numbers.									
 C ₆	Catalyst (1–5 mol %), C ₇ H ₈	Catalyst	Temp	TOF (h ⁻¹)	trans/cis				
		[Cp* ₂ LaH] ₂	rt	84	(99)	5:1	466		
		Cp* ₂ Sm(THF) ₂	60°	40	(95)	5:1	467		
		MeO(CH ₂) ₅ SiMe(C ₃ Me ₄) ₂ YCH(TMS) ₂	60°	12	(95)	2:1	479		
		Me ₂ Si(C ₃ Me ₄) ₂ YCH(TMS) ₂	60°	6	(95)	7:1	479		
		[Me ₂ Si(C ₃ Me ₄)((<i>r</i> -Bu)N)]SmN(TMS) ₂	rt	24	(95)	10:1	480		
		[Me ₂ Si(C ₃ Me ₄)((<i>r</i> -Bu)N)]NdN(TMS) ₂	rt	24	(95)	10:1	480		
		[Me ₂ Si(C ₃ Me ₄)((<i>r</i> -Bu)N)]YbCH(TMS) ₂	rt	34	(95)	21:1	480		
		[Me ₂ Si(C ₃ Me ₄)((<i>r</i> -Bu)N)]LuCH(TMS) ₂	rt	38	(95)	17:1	480		
 C ₆₋₁₁	Catalyst (x mol %), C ₆ D ₆ , rt	R		Catalyst	x	Time (h)	trans/cis		
		Me	24a	20	48	89:11	(99)	47	
		Me	24b	20	48	92:8	(81)		
		Ph	24a	5	5	95:5	(87)		
		Ph	24a	10	2	95:5	(91)		
		Ph	24b	10	96	99:1	(72)		
 C ₆₋₇	Catalyst (x mol %), C ₆ D ₆	n		Catalyst	x	Temp (°)	Time (h)	trans/cis	
		1	38a	5	60	0.25	(95)	13:1	164
		1	38b	5	60	0.75	(95)	6:1	164
		1	38c	5	60	0.25	(41)	10:1	164
		1	38d	5	60	1	(95)	13:1	164
		1	39	2	rt	49	(93)	9:1	481
		1	40	2	60	5	(95)	5.3:1	481

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

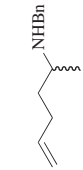
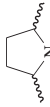
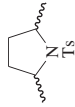
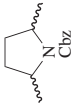
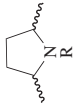
 C ₆	2	38a	5	120	1	(95)	1:4	164	
	2	38b	5	120	2	(95)	1:6	164	
	2	38c	5	120	1	(9)	1:5	164	
	2	39	2	80	38	(96)	1:3.7	481	
	2	40	2	80	42	(87)	1:4	481	
 NHTs	<i>n</i> -BuLi (16 mol %), hexane/THF, 50°, 2 h  +  (75), <i>cis/trans</i> = 78:22 (20)							144	
	FeCl ₃ ·6H ₂ O (10 mol %), DCE, 80°, 2 h  (97) dr 3.8:1							204	
 NHChz	Au[P(<i>n</i> -Bu) ₂ (2-PhC ₆ H ₄)]Cl (10 mol %), AgOTf (10 mol %), dioxane, 100°, 55 h  (91) dr 1.5:1							205	
	Catalyst (x mol %), solvent  R								
 NHR	R	Catalyst	x	Solvent	Temp (°)	Time (h)	<i>trans/cis</i>		
	H	(EBI)YbN(TMS) ₂	2.7	toluene	70	48	(86) ^e	10:1	482
	Me	[Cp ₂ ZrMe][MeB(C ₆ F ₅) ₃]	2	C ₆ D ₅ Br	80	15	(97)	1:3.3	169
	Me	[Cp ₂ ZrMe][MeB(C ₆ F ₅) ₃]	2	C ₆ D ₆	80	21	(99)	1:2.7	169
	Me	[Cp ₂ ZrMe][B(C ₆ F ₅) ₄]	2	C ₆ D ₅ Br	80	27	(92)	1:3	169
	Me	[Cp [*] ZrMe][B(C ₆ F ₅) ₄]	2	C ₆ D ₅ Br	100	107	(74)	2:1	169
	Me	[Cp ₂ TiBn][B(C ₆ F ₅) ₄]	5	C ₆ D ₅ Br	80	14.5	(99)	1:8.6	169
	Me	[Cp ₂ TiBn][B(C ₆ F ₅) ₄]	5	C ₆ D ₅ Br	100	13.5	(91)	1:4.9	169
<i>n</i> -Bu	(EBI)YbN(TMS) ₂	2.7	toluene	80	96	(0)		482	

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.																
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>																			
C ₆ 	[K ₂ PtCl ₄] (1 eq), HCl (10 eq), NaCl, H ₂ O, 60°, 21 d	(85), <i>trans/cis</i> = 88:12	194																
	1. 258 (5 mol %), Y[N(TMS) ₂] ₃ (5 mol %) 2. C ₆ D ₆ , 125°	(95), <i>trans/cis</i> = 9:1	163																
	<i>n</i> -BuLi (16 mol %), THP/C ₆ H ₈ (1:1), 110°, 2 h	(93), <i>trans/cis</i> = 1:1.4	148																
	[K ₂ PtCl ₄] (1 eq), HCl (10 eq), NaCl, H ₂ O, 60°, 8 d	(85), <i>trans/cis</i> = 38:62	194																
	Catalyst (1 mol %), toluene																		
<table> <tr> <th>Catalyst</th><th>Temp (°)</th><th>TOF (h⁻¹)</th><th><i>trans/cis</i></th></tr> <tr> <td>Cp*₂LaCH(TMS)₂</td><td>rt</td><td>36</td><td>(95) 1:1.5</td></tr> <tr> <td>MeO(CH₂)₅SiMe(CMe₄)₂YCH(TMS)₂</td><td>60</td><td>118</td><td>(95) 1:1</td></tr> <tr> <td>Me₂Si(C₃Me₄)₂YCH(TMS)₂</td><td>60</td><td>24</td><td>(95) 1:1</td></tr> </table>				Catalyst	Temp (°)	TOF (h ⁻¹)	<i>trans/cis</i>	Cp* ₂ LaCH(TMS) ₂	rt	36	(95) 1:1.5	MeO(CH ₂) ₅ SiMe(CMe ₄) ₂ YCH(TMS) ₂	60	118	(95) 1:1	Me ₂ Si(C ₃ Me ₄) ₂ YCH(TMS) ₂	60	24	(95) 1:1
Catalyst	Temp (°)	TOF (h ⁻¹)	<i>trans/cis</i>																
Cp* ₂ LaCH(TMS) ₂	rt	36	(95) 1:1.5																
MeO(CH ₂) ₅ SiMe(CMe ₄) ₂ YCH(TMS) ₂	60	118	(95) 1:1																
Me ₂ Si(C ₃ Me ₄) ₂ YCH(TMS) ₂	60	24	(95) 1:1																
			45																
			479																
			479																

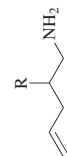
1. **258** (5 mol %),
 $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$ (5 mol %)
 2. C_6D_6 , 125°



(95), *trans/cis* = 1:1.5

163

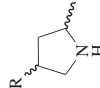
R	M	Temp (°)	Time (h)	<i>trans/cis</i>
Me	Ti	110	96	(62) —
Ph	Ti	110	168	(59) 1:1.4
Ph	Zr	150	120	(100) 1:1



$\text{M}(\text{NMe}_2)_4$ (5 mol %), C_7D_8



1. **29** (5 mol %),
 $\text{Sc}[\text{N}(\text{TMS})_2]_3$, C_6D_6 , 120°, 2 h
 2. Aminoalkene, C_6D_6 , 120°



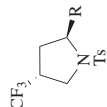
(95), *trans/cis* = 1:1.6

165

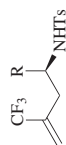
R	Time (h)	<i>trans/cis</i>
Me	84	(95) 1:1.6
Ph	72	(95) 1:2.1

R	Catalyst	Time (h)	<i>trans/cis</i>
Me	$\text{Y}[\text{N}(\text{TMS})_2]_3$	240	(95) 2:1
Me	$\text{Nd}[\text{N}(\text{TMS})_2]_3$	168	(95) 2:1
Ph	$\text{Y}[\text{N}(\text{TMS})_2]_3$	1.5	(95) 1.7:1
Ph	$\text{Nd}[\text{N}(\text{TMS})_2]_3$	1.5	(95) 2.2:1

Ln catalyst (2.7 mol %), C_6D_6 , 90°

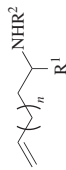
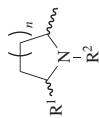
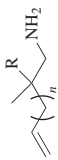
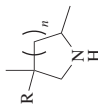
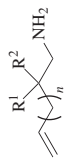
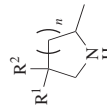
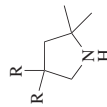


KOH (x eq), $(\text{CH}_2\text{OH})_2$, 130°, 20 h



R	x	<i>trans/cis</i>	<i>or trans</i>
PMBCH_2	5	(68) 70:30	99.5:0.5
Ph	5	(85) 92:8	—
$(2,4\text{-MeO})_2\text{C}_6\text{H}_3$	1.3	(74) 90:10	—

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.																																				
	<i>n</i> -BuLi (16 mol %), THP/C ₇ H ₈ (1:1), 110°	 <table><thead><tr><th><i>n</i></th><th>R¹</th><th>R²</th><th><i>trans/cis</i></th></tr></thead><tbody><tr><td>1</td><td>Me</td><td>Bn</td><td>(79) 15:85</td></tr><tr><td>1</td><td><i>n</i>-Pr</td><td>H</td><td>(73) 72:28</td></tr><tr><td>2</td><td><i>n</i>-Pr</td><td>H</td><td>(85) 25:75</td></tr></tbody></table>	<i>n</i>	R ¹	R ²	<i>trans/cis</i>	1	Me	Bn	(79) 15:85	1	<i>n</i> -Pr	H	(73) 72:28	2	<i>n</i> -Pr	H	(85) 25:75	148																				
<i>n</i>	R ¹	R ²	<i>trans/cis</i>																																				
1	Me	Bn	(79) 15:85																																				
1	<i>n</i> -Pr	H	(73) 72:28																																				
2	<i>n</i> -Pr	H	(85) 25:75																																				
	NaN(TMS) ₂ (20 mol %), SmI ₂ (10 mol %), THF, 60°	 <table><thead><tr><th><i>n</i></th><th>R</th><th>Time (h)</th></tr></thead><tbody><tr><td>1</td><td>H</td><td>100 (85)</td></tr><tr><td>1</td><td>Me</td><td>24 (87)</td></tr><tr><td>1</td><td>allyl</td><td>6 (93)</td></tr><tr><td>2</td><td>Me</td><td>24 (88)</td></tr></tbody></table>	<i>n</i>	R	Time (h)	1	H	100 (85)	1	Me	24 (87)	1	allyl	6 (93)	2	Me	24 (88)	484																					
<i>n</i>	R	Time (h)																																					
1	H	100 (85)																																					
1	Me	24 (87)																																					
1	allyl	6 (93)																																					
2	Me	24 (88)																																					
	Catalyst (<i>x</i> mol %), C ₆ D ₆	 <table><thead><tr><th><i>n</i></th><th>R¹</th><th>R²</th><th><i>x</i></th><th>Temp</th><th>Time (h)</th></tr></thead><tbody><tr><td>1</td><td>Me</td><td>H</td><td>43b</td><td>10 65°</td><td>96 (50)^c</td></tr><tr><td>1</td><td>Me</td><td>Me</td><td>43b</td><td>10 65°</td><td>24 (90)</td></tr><tr><td>1</td><td>Ph</td><td>Ph</td><td>43a</td><td>10 rt</td><td>135 (80)</td></tr><tr><td>1</td><td>Ph</td><td>Ph</td><td>43b</td><td>5 rt</td><td>2 (95)</td></tr><tr><td>2</td><td>Ph</td><td>Ph</td><td>43b</td><td>10 65°</td><td>24 (90)</td></tr></tbody></table>	<i>n</i>	R ¹	R ²	<i>x</i>	Temp	Time (h)	1	Me	H	43b	10 65°	96 (50) ^c	1	Me	Me	43b	10 65°	24 (90)	1	Ph	Ph	43a	10 rt	135 (80)	1	Ph	Ph	43b	5 rt	2 (95)	2	Ph	Ph	43b	10 65°	24 (90)	485
<i>n</i>	R ¹	R ²	<i>x</i>	Temp	Time (h)																																		
1	Me	H	43b	10 65°	96 (50) ^c																																		
1	Me	Me	43b	10 65°	24 (90)																																		
1	Ph	Ph	43a	10 rt	135 (80)																																		
1	Ph	Ph	43b	5 rt	2 (95)																																		
2	Ph	Ph	43b	10 65°	24 (90)																																		
	[Cp ^{TMS} ₂ LnMe] ₂ (4 mol %), solvent	 <table><thead><tr><th>R</th><th>Ln</th><th>Solvent</th><th>Temp</th><th>Time (h)</th></tr></thead><tbody><tr><td>H</td><td>Nd</td><td>C₆D₆</td><td>120°</td><td>12 (95)</td></tr><tr><td>Me</td><td>Sm</td><td>C₆D₆</td><td>70°</td><td>2 (93)</td></tr><tr><td>Me</td><td>Nd</td><td>neat</td><td>70°</td><td>1 (70)</td></tr><tr><td>-(CH₂)₅-</td><td>Sm</td><td>neat</td><td>rt</td><td>1 (92)</td></tr><tr><td>Ph</td><td>Sm</td><td>neat</td><td>rt</td><td>1 (98)</td></tr></tbody></table>	R	Ln	Solvent	Temp	Time (h)	H	Nd	C ₆ D ₆	120°	12 (95)	Me	Sm	C ₆ D ₆	70°	2 (93)	Me	Nd	neat	70°	1 (70)	-(CH ₂) ₅ -	Sm	neat	rt	1 (92)	Ph	Sm	neat	rt	1 (98)	160						
R	Ln	Solvent	Temp	Time (h)																																			
H	Nd	C ₆ D ₆	120°	12 (95)																																			
Me	Sm	C ₆ D ₆	70°	2 (93)																																			
Me	Nd	neat	70°	1 (70)																																			
-(CH ₂) ₅ -	Sm	neat	rt	1 (92)																																			
Ph	Sm	neat	rt	1 (98)																																			

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₆₋₉

C₆₋₁₈

C₆₋₁₇

Catalyst (5 mol %), C₆D₆

486

C₆₋₁₈

44a (5 mol %), C₇D₈, 110°

181

C₆₋₈

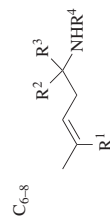
[K₂PtCl₄] (1 eq), HCl (10 eq),
NaCl, H₂O, 60°

194

R ¹	R ²	Catalyst	Temp	Time (min)	dr
Me	H	41a	120°	180	(100) 3:1
Me	H	41b	120°	60	(100) 3:1
H	Me	41a	60°	60	(92) —
H	Me	41b	60°	60	(90) —
H	-(CH ₂) ₅ -	41a	rt	5	(100) —
H	-(CH ₂) ₅ -	41b	rt	5	(100) —
H	Ph	41a	rt	5	(98) —
H	Ph	41b	rt	5	(98) —

<i>n</i>	R ¹	R ²	Time (h)
1	Me	H	144 (—)
1	H	Me	48 (12)
1	H	Me	120 (25)
1	H	Ph	10 (90)
2	H	Ph	48 (17)

R	Time (d)	I + II	I/II
H	67	(67)	9:91
Me	25	(58)	60:40



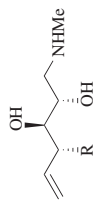
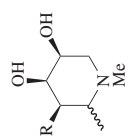
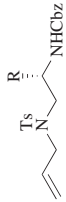
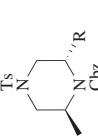
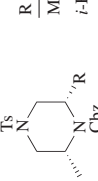
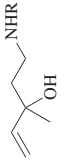
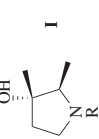
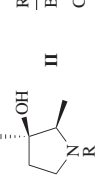
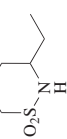
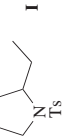
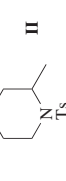
R ¹	R ²	R ³	R ⁴	x	Solvent	Temp (°)	Time (h)	dr
H	H	MeO ₂ C	Ts	0.6	CHCl ₃	62	4	(91) 2.5:1
H	Me	MeO ₂ C	Ts	0.6	CHCl ₃	62	4	(91) 2.5:1
H	Me	MeO ₂ C	2-Ns	1	CHCl ₃	62	4	(86) 3:1
H	Me	MeO ₂ C	4-Ns	1	CHCl ₃	62	4	(86) 3:1
H	Me	MeO ₂ C	2,4-(O ₂ N) ₂ C ₆ H ₃ SO ₂	1.4	CHCl ₃	62	4	(83) 3:1
Me	H	MeO ₂ C	Ac	0.2	C ₇ H ₈	100	4	(96) —
Me	H	MeO ₂ C	Ts	0.4	CHCl ₃	0	0.25	(95) —
Me	Me	MeO ₂ C	MeO ₂ C	2	CHCl ₃	rt	2	(69) —
Me	Me	MeO ₂ C	Ts	0.4	CHCl ₃	0	0.25	(97) —
Me	Me	MeO ₂ C	2-Ns	0.5	CHCl ₃	0	0.25	(89) —
Me	Me	MeO ₂ C	4-Ns	0.5	CHCl ₃	0	0.25	(87) —
Me	Me	MeO ₂ C	2,4-(O ₂ N) ₂ C ₆ H ₃ SO ₂	0.5	CHCl ₃	0	0.25	(87) —
Me	Me	CHO	Ts	0.4	CHCl ₃	0	0.25	(87) —

Ln catalyst (x mol %), C₆D₆

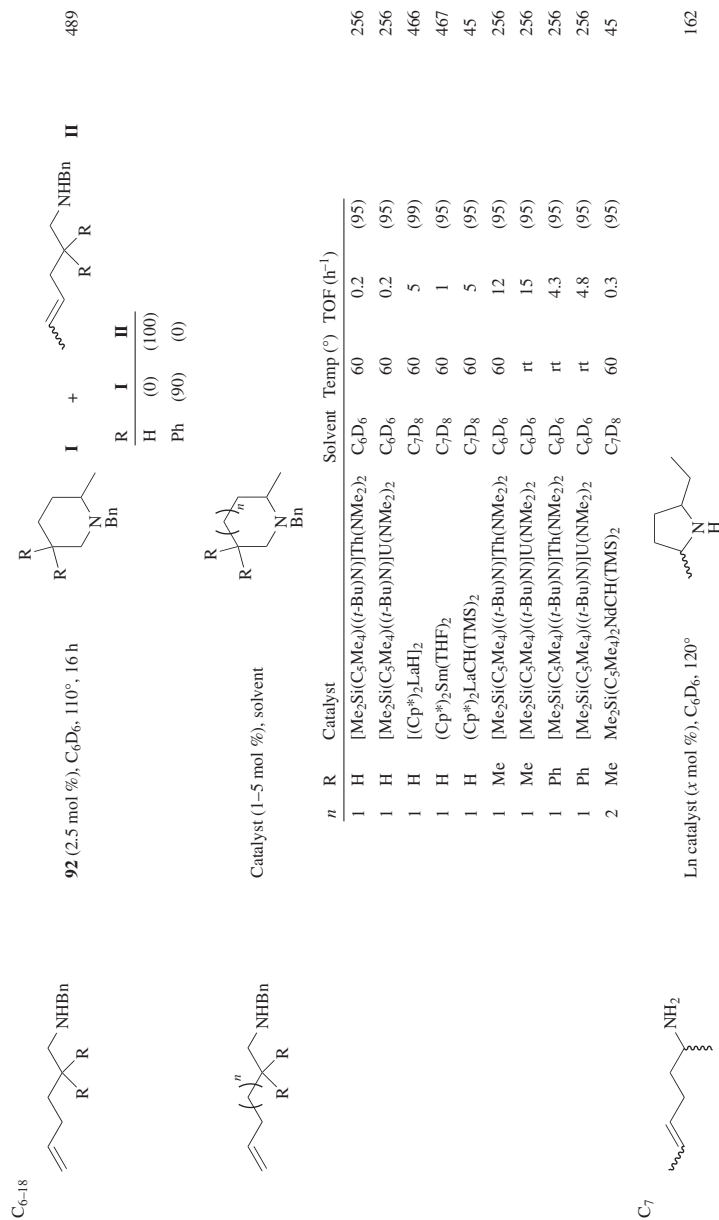


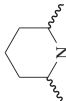
Catalyst	x	Temp (°)	Time (h)
[Me ₂ Si(C ₃ Me ₄)(<i>i</i> -BuN)]SmN(TMS) ₂	7.2	125	168 (42)
Et ₂ Si(C ₃ Me ₄)(C ₃ H ₄)NdCH(TMS) ₂	3.6	120	240 (56)
Me ₂ Si(C ₃ Me ₄) ₂ NdCH(TMS) ₂	3.3	125	165 (56)
Cp [*] ₂ LaCH(TMS) ₂	3.3	120	43 (95)
Cp [*] ₂ SmCH(TMS) ₂	3.3	125	100 (10)

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)				Refs.
Please refer to the charts preceding the tables for structures indicated by the bold numbers.						
C ₆	 Cu(O <i>t</i> -Bu) ₂ (x mol %), XANTPHOS (x mol %), MeOH/4-xylene (1:1), 140°, 72 h	 R H HO dr 20 30 62:38 (41) (53) 61:39				476
C ₆₋₁₂	 82 (5 mol %), AgBF ₄ (10 mol %), MgSO ₄ , CH ₂ Cl ₂ , rt, 20 h	 I	 II	R Me <i>i</i> -Bu <i>t</i> -Bu Bn (98) (94) (—) (93) >20:1 >20:1 19:1 — >20:1		206
C ₆	 82 (5 mol %), AgOTf (10 mol %), Cu(OTf) ₂ (10 mol %), MgSO ₄ , CH ₂ Cl ₂ , rt, 12 h	 I	 II	R Boc Cbz (88) (80) 80:20 80:20 80:20		203
C ₆	 (PPh ₃)AuCl (5 mol %), AgOTf (5 mol %), C ₇ H ₈ , 100°, 48 h	 (88)				202
C ₆	 C ₈ F ₁₇ SO ₃ H (5 mol %), perfluorodecalin, C ₇ H ₈ , hexanes, reflux, 1 h	 I	 II	I + II (96), I/II = 1:1		211

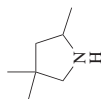
Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.



Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.																																				
Please refer to the charts preceding the tables for structures indicated by the bold numbers.																																							
C₇ 	1. RNH(CH ₂) _n NHR (5 mol %), Y[N(TMS) ₂] ₃ (5 mol %)		<i>n</i> R Time (min) <i>trans/cis</i>																																				
	2. Aminoalkene, C ₆ D ₆ , 120°		2 2,6-Me ₂ C ₆ H ₃ 45 (95) 1:4																																				
			2 2- <i>i</i> -PrC ₆ H ₄ 95 (95) 1:5																																				
			3 2,6-Me ₂ C ₆ H ₃ 15 (95) 1:4																																				
	Catalyst (x mol %), C ₆ D ₆																																						
<table><tr><th>Catalyst</th><th>x</th><th>Temp</th><th>Time (h)</th><th></th></tr><tr><td>Y[N(TMS)₂]₃</td><td>2.7</td><td>rt</td><td>6</td><td>(95)</td></tr><tr><td>Nd[N(TMS)₂]₃</td><td>2.7</td><td>rt</td><td>4</td><td>(95)</td></tr><tr><td>Y[N(SiHMe₂)₂]₃(THF)₂</td><td>3</td><td>50°</td><td>9</td><td>(34,5)</td></tr><tr><td>Y(2-Me₂NCH₂C₆H₄)₃</td><td>3</td><td>rt</td><td>13</td><td>(89)</td></tr><tr><td>LiN(TMS)₂</td><td>10</td><td>90°</td><td>38</td><td>(98)</td></tr></table>				Catalyst	x	Temp	Time (h)		Y[N(TMS) ₂] ₃	2.7	rt	6	(95)	Nd[N(TMS) ₂] ₃	2.7	rt	4	(95)	Y[N(SiHMe ₂) ₂] ₃ (THF) ₂	3	50°	9	(34,5)	Y(2-Me ₂ NCH ₂ C ₆ H ₄) ₃	3	rt	13	(89)	LiN(TMS) ₂	10	90°	38	(98)						
Catalyst	x	Temp	Time (h)																																				
Y[N(TMS) ₂] ₃	2.7	rt	6	(95)																																			
Nd[N(TMS) ₂] ₃	2.7	rt	4	(95)																																			
Y[N(SiHMe ₂) ₂] ₃ (THF) ₂	3	50°	9	(34,5)																																			
Y(2-Me ₂ NCH ₂ C ₆ H ₄) ₃	3	rt	13	(89)																																			
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				158																																			
				149																																			
<table><tr><th>Catalyst</th><th>x</th><th>Time (h)</th><th></th></tr><tr><td>49a</td><td>1</td><td>24</td><td>(tr)</td></tr><tr><td>49b</td><td>1</td><td>4</td><td>(98)</td></tr><tr><td>49c</td><td>1</td><td>12</td><td>(96)</td></tr><tr><td>49d</td><td>1</td><td>2</td><td>(97)</td></tr><tr><td>49e</td><td>1</td><td>1</td><td>(97)</td></tr><tr><td>49f</td><td>1</td><td>1</td><td>(98)</td></tr><tr><td>49g</td><td>0.5</td><td>1</td><td>(98)</td></tr><tr><td>49g</td><td>1</td><td>0.5</td><td>(98)</td></tr></table>				Catalyst	x	Time (h)		49a	1	24	(tr)	49b	1	4	(98)	49c	1	12	(96)	49d	1	2	(97)	49e	1	1	(97)	49f	1	1	(98)	49g	0.5	1	(98)	49g	1	0.5	(98)
Catalyst	x	Time (h)																																					
49a	1	24	(tr)																																				
49b	1	4	(98)																																				
49c	1	12	(96)																																				
49d	1	2	(97)																																				
49e	1	1	(97)																																				
49f	1	1	(98)																																				
49g	0.5	1	(98)																																				
49g	1	0.5	(98)																																				
	Catalyst (x mol %), C ₆ D ₆ , 60°		490																																				

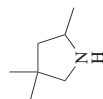


Catalyst (x mol %), C₆D₆



Catalyst	x	Temp	TOF (h ⁻¹)	
3a	3-5	rt	0.7	(95)
47a	4.7	60°	2.9 ^a	(—)
47b	4.3	rt	2.2 ^a	(—)

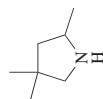
303
491
491



Catalyst (4 mol %), C₆D₆

Catalyst	Temp (°)	Time (h)	
53	40	13	(41)
53	60	2.5	(85)
64	70	11	(82)

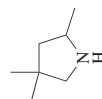
158
158
492



Catalyst (x mol %), THF (y mol %),
C₆D₆, rt

Catalyst	x	y	Time (h)	
16a	2	0	41	(92)
16b	3	0	25	(96)
16c	3	0	3.5	(96)
16c	3	3.6	3	(94)
16d	3	0	3.7	(95)
16d	5	5.5	2.6	(95)
16d	5	25	4	(96)
16e	3	0	4	(98)
16f	3	0	5	(97)

158

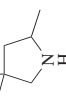
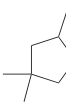
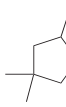
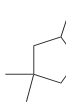


Catalyst (x mol %), C₆D₆

Catalyst	x	Temp (°)	Time (h)	
48a	3	90	4.7	(98)
48a	5	90	2.4	(98)
48b	3	90	1.5	(99)
48b	5	90	1.0	(98)
48c	3	90	4.7	(98)
48c	5	90	2.9	(98)
56a	2.7	45	54	(95)
56b	2.7	45	30	(95)

493
493
493
493
493
493
157
157

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)		Refs.
 C ₇	Catalyst (x mol %), rt	 I +  II		144
		Catalyst	x	Time (h)
		Na/K/Hg	—	hexanes 3 10:83
	Catalyst (1 mol %), [PhNHMe ₂][B(C ₆ F ₅) ₄] (x mol %), C ₆ D ₆ -Br, 50°		x	Time (h)
				(4-MeC ₆ H ₄ CH ₂) ₃ La(THF) ₃ 0 10 (45)
				(4-MeC ₆ H ₄ CH ₂) ₃ La(THF) ₃ 1 0.7 (99) 494
	Catalyst (1–5 mol %), C ₆ D ₆		x	Time (h)
				(4-MeC ₆ H ₄ CH ₂) ₃ La(THF) ₃ 2 1.4 (99)
				[(4-MeC ₆ H ₄ CH ₂) ₄ La][Li(THF) ₄] 0 12 (35)
			x	Time (h)
				[(4-MeC ₆ H ₄ CH ₂) ₄ La][Li(THF) ₄] 1 10 (31)
	Catalyst	Temp	TOF (h ⁻¹)	



Catalyst	Temp	TOF (h ⁻¹)	
[Cp* ₂ LaH] ₂	rt	125 (99)	466
[Me ₂ Si(C ₅ Me ₄) ₂ LuH] ₂	80°	75 (99)	466
[Cp* ₂ LuH] ₂	80°	1 (99)	466
Cp* ₂ Sm(THF) ₂	60°	50 (95)	467
Cp* ₂ LaCH(TMS) ₂	rt	95 (95)	45
Cp* ₂ SmCH(TMS) ₂	60°	48 (95)	45
Cp* ₂ LuCH(TMS) ₂	80°	1 (95)	45
Me ₂ Si(C ₅ Me ₄) ₂ LuCH(TMS) ₂	80°	75 (95)	45
[Me ₂ Si(C ₅ Me ₄)(C ₅ H ₄)]LuCH(TMS) ₂	80°	200 (95)	45
[Me ₂ Si(C ₅ Me ₄)(<i>i</i> -BuN)]SmN(TMS) ₂	rt	181 (95)	480
[Me ₂ Si(C ₅ Me ₄)(<i>i</i> -BuN)]NdN(TMS) ₂	rt	200 (95)	480
[Me ₂ Si(C ₅ Me ₄)(<i>i</i> -BuN)]YbCH(TMS) ₂	rt	10 (95)	480
[Me ₂ Si(C ₅ Me ₄)(<i>i</i> -BuN)]LuCH(TMS) ₂	rt	90 (95)	480
Cp* ₂ Th[N(TMS) ₂] ₂	60°	0.4 (95)	256

Catalyst (5 mol %),
[Ph₃C][B(C₆F₅)₄] (x mol %),
C₇D₈

Catalyst	x	Temp	Time (h)	
50	0	rt	5	(tr)
50	0	60°	5	(15)
50	5	rt	5	(9)
51	0	rt	5	(tr)
51	0	60°	2	(95)
51	5	rt	5	(20)
52a	0	rt	5	(tr)
52a	0	60°	5	(53)
52a	5	rt	5	(10)
52b	0	rt	5	(tr)
52b	0	60°	5	(95)
52b	5	rt	5	(48)
52c	0	rt	5	(64)
52d	0	rt	0.17	(95)

Y	5.7	SBA-15LP	1	70	<0.1	(100)	 (95)	165
Y	5.7	SBA-15LP	2	70	0.3	(90)		
Y	5.7	SBA-15LP	3	70	15.6	(90)		
Y	2.85	MCM-41	1	50	0.3	(90)		
Y	2.85	SiO ₂	1	50	10.0	(90)		
1. 29 (5 mol %) 2. Sc[N(TMS) ₂] ₃ , C ₆ D ₆ , 120°, 2 h 3. Aminoalkene, C ₆ D ₆ , 60°, 2.5 h								 167
1. Catalyst (10 mol %), Cp* ₂ SmCH(TMS) ₂ (5 mol %), C ₆ D ₆ , rt 2. Aminoalkene, C ₆ D ₆ , 60°								
</								

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene

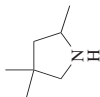
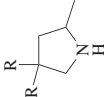
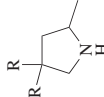
Conditions

Product(s) and Yield(s) (%)

Refs.

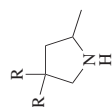
Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₇

	1. 62 (x mol %), Cp*₂SnCH(TMS)₂ (5 mol %), C₆D₆, rt 2. Aminoalkene, C₆D₆, 60°		<table> <tr> <th>x</th><th>Cycle</th><th>Time (h)^a</th></tr> <tr> <td>0</td><td>1</td><td>2.2</td></tr> <tr> <td>7.5</td><td>1</td><td>4.1</td></tr> <tr> <td>7.5</td><td>2</td><td>6.7</td></tr> <tr> <td>7.5</td><td>3</td><td>10.1</td></tr> <tr> <td>10</td><td>1</td><td>8.0</td></tr> <tr> <td>10</td><td>2</td><td>11.1</td></tr> <tr> <td>10</td><td>3</td><td>15.0</td></tr> </table>	x	Cycle	Time (h) ^a	0	1	2.2	7.5	1	4.1	7.5	2	6.7	7.5	3	10.1	10	1	8.0	10	2	11.1	10	3	15.0	167															
x	Cycle	Time (h) ^a																																									
0	1	2.2																																									
7.5	1	4.1																																									
7.5	2	6.7																																									
7.5	3	10.1																																									
10	1	8.0																																									
10	2	11.1																																									
10	3	15.0																																									
	Catalyst (5 mol %), C ₆ D ₆ , 105°, 24 h		<table> <tr> <th>R</th><th>Catalyst</th><th></th></tr> <tr> <td>Me</td><td>75</td><td>(0)</td></tr> <tr> <td>Me</td><td>76</td><td>(0)</td></tr> <tr> <td>Me</td><td>77</td><td>(18)^b</td></tr> <tr> <td>-(CH₂)₅-</td><td>75</td><td>(0)</td></tr> <tr> <td>-(CH₂)₅-</td><td>76</td><td>(0)</td></tr> <tr> <td>-(CH₂)₅-</td><td>77</td><td>(70)^b</td></tr> <tr> <td>Ph</td><td>75</td><td>(73)</td></tr> <tr> <td>Ph</td><td>76</td><td>(87)</td></tr> <tr> <td>Ph</td><td>77</td><td>(88)</td></tr> <tr> <td>Bn</td><td>75</td><td>(58)</td></tr> <tr> <td>Bn</td><td>76</td><td>(61)</td></tr> <tr> <td>Bn</td><td>77</td><td>(93)</td></tr> </table>	R	Catalyst		Me	75	(0)	Me	76	(0)	Me	77	(18) ^b	-(CH ₂) ₅ -	75	(0)	-(CH ₂) ₅ -	76	(0)	-(CH ₂) ₅ -	77	(70) ^b	Ph	75	(73)	Ph	76	(87)	Ph	77	(88)	Bn	75	(58)	Bn	76	(61)	Bn	77	(93)	498
R	Catalyst																																										
Me	75	(0)																																									
Me	76	(0)																																									
Me	77	(18) ^b																																									
-(CH ₂) ₅ -	75	(0)																																									
-(CH ₂) ₅ -	76	(0)																																									
-(CH ₂) ₅ -	77	(70) ^b																																									
Ph	75	(73)																																									
Ph	76	(87)																																									
Ph	77	(88)																																									
Bn	75	(58)																																									
Bn	76	(61)																																									
Bn	77	(93)																																									
	Catalyst (x mol %), C ₆ D ₆ , rt		<table> <tr> <th>R</th><th>Catalyst</th><th>TOF (h⁻¹)^a</th></tr> <tr> <td>Me</td><td>66</td><td>2.6</td></tr> <tr> <td>Me</td><td>67</td><td>19</td></tr> <tr> <td>-(CH₂)₅-</td><td>66</td><td>32</td></tr> <tr> <td>Ph</td><td>67</td><td>205</td></tr> </table>	R	Catalyst	TOF (h ⁻¹) ^a	Me	66	2.6	Me	67	19	-(CH ₂) ₅ -	66	32	Ph	67	205	491 499 491 499																								
R	Catalyst	TOF (h ⁻¹) ^a																																									
Me	66	2.6																																									
Me	67	19																																									
-(CH ₂) ₅ -	66	32																																									
Ph	67	205																																									

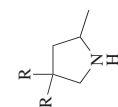
Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₇



Catalyst (x mol %), C₆D₆

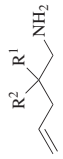
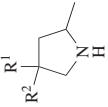
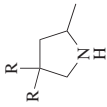
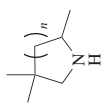
R	Catalyst	x	Temp	Time (min)	TOF (h ⁻¹)	
Me	65	5.0	120°	—	—	(—)
Me	68a	5.0	rt	15	15.2	(21)
Me	68b	4.9	rt	17	17.9	(24)
-(CH ₂) ₅ -	65	5.0	120°	—	0.19	(92)
Ph	68a	5.2	rt	15	70.5	(92)
Ph	68b	4.2	rt	6	78.0	(33)
						500
						501
						501
						500
						501
						501



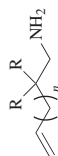
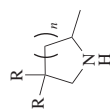
37 (x mol %),
[PhNHMe₂][B(C₆F₅)₄] (y mol %),
C₆D₆

R	x	y	Temp (°)	Time (h)	
Me	5	5	120	52	(46)
Me	13.3	0	120	72	(99)
-(CH ₂) ₅ -	5	0	120	28	(99)
-(CH ₂) ₅ -	5	5	120	8	(80)
-(CH ₂) ₅ -	10	0	100	30	(87)
Ph	5	5	120	5	(99)
Ph	10	0	100	24	(69)
Ph	10	0	120	12	(99)
					186

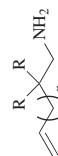
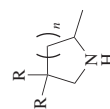
TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
	Catalyst (5 mol %), C ₇ D ₈ , 160°		dr
		Me 79a	38 (88) —
		Me 79b	48 (81) —
		-(CH ₂) ₄ - 79a	18 (92) —
		-(CH ₂) ₄ - 79b	28 (83) —
		-(CH ₂) ₅ - 79a	3 (98) —
		-(CH ₂) ₅ - 79b	14 (98) —
		H Ph 79a	11 (18) — ^c
		H Ph 79b	30 (19) — ^c
		allyl Ph 79a	1 (98) 1:1
	Catalyst (10 mol %), C ₇ D ₈ , 150°		dr
		Me 69a	1 (tr)
		-(CH ₂) ₅ - 69a	16 (92)
		-(CH ₂) ₅ - 69b	1 (tr)
		-(CH ₂) ₅ - 69c	22 (94)
		Ph 69a	29 (61)
		Ph 69b	23 (78)
		Ph 69c	14 (85)
	(EBI)YbN(TMS) ₂ (3 mol %), C ₇ H ₈		
		<i>n</i> Temp Time (h)	
		1 rt 70 (79) ^c	482
		2 80° 48 (92) ^c	

Please refer to the charts preceding the tables for structures indicated by the **bold numbers**.

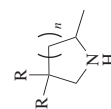
C₇₋₁₇Catalyst (x mol %), C₆D₆

<i>n</i>	R	Catalyst	<i>x</i>	Temp (°)	Time (h)	
1	Me	34b	1.3	60	6	(100)
1	Me	70	10	rt	0.25	(99)
1	-(CH ₂) ₅ -	34b	1.1	rt	150	(91)
1	-(CH ₂) ₅ -	34b	1.1	60	3	(100)
1	Ph	34b	2	60	1.5	(100)
1	Ph	70	10	rt	0.25	(99)
2	Me	34b	2.2	60	22	(100)
2	Me	70	10	60	72	(85)
2	Me	70	20	60	6	(86)

477
150
477
477
477
150
477
150
150C₇₋₁₈Catalyst (x mol %), C₆D₆, 60°

<i>n</i>	R	Catalyst	<i>x</i>	Time (h)	
1	Me	73a	1	0.5	(98)
1	Me	73b	1	0.8	(98)
1	Me	73c	1	0.3	(98)
1	Me	73d	1	24	(67)
2	Me	73a	2	4	(98)
2	Me	73c	1.5	5	(98)
2	Me	73c	2	3.5	(98)
2	Ph	73a	1	4.5	(98)
2	Ph	73c	1	4	(98)

259

36 (x mol %), C₇D₈, 110°

<i>n</i>	R	<i>x</i>	Time (h)	
1	Me	5	120	(73)
1	Me	10	96	(87)
1	Ph	5	4	(98)
2	Ph	5	24	(82)

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TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

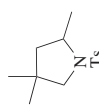
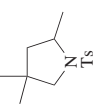
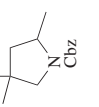
Refs.

Product(s) and Yield(s) (%)

Conditions

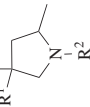
Aminoalkene

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C ₇		Ga (5 mol %), I ₂ (7.5 mol %), 105°, 2 h	 I +  II I + II (82), I/II = 88:12	427																
		FeCl ₃ •6H ₂ O (10 mol %), DCE, 80°	 I	204																
		82 (x mol %), AgOTf (2x mol %), Cu(OTf) ₂ (y mol %), CH ₂ Cl ₂ , rt, 12 h	 I	92 203 203 203 92 203 203																
			<table> <tr> <th>R</th><th>Time (h)</th><th>dr</th></tr> <tr> <td>I</td><td>9 (96)</td><td>1.1:1</td></tr> <tr> <td>MeO</td><td>21 (81)</td><td>1.3:1</td></tr> <tr> <td>TsO</td><td>4 (93)</td><td>2.1:1</td></tr> </table>	R	Time (h)	dr	I	9 (96)	1.1:1	MeO	21 (81)	1.3:1	TsO	4 (93)	2.1:1					
R	Time (h)	dr																		
I	9 (96)	1.1:1																		
MeO	21 (81)	1.3:1																		
TsO	4 (93)	2.1:1																		
			<table> <tr> <th>x</th><th>y</th></tr> <tr> <td>0</td><td>10 (—)</td></tr> <tr> <td>0.5</td><td>10 (84)</td></tr> <tr> <td>1</td><td>10 (91)</td></tr> <tr> <td>2.5</td><td>5 (93)</td></tr> <tr> <td>5</td><td>0 (94)</td></tr> <tr> <td>5</td><td>10 (97)</td></tr> <tr> <td>20</td><td>200 (98)</td></tr> </table>	x	y	0	10 (—)	0.5	10 (84)	1	10 (91)	2.5	5 (93)	5	0 (94)	5	10 (97)	20	200 (98)	
x	y																			
0	10 (—)																			
0.5	10 (84)																			
1	10 (91)																			
2.5	5 (93)																			
5	0 (94)																			
5	10 (97)																			
20	200 (98)																			

C₇₋₁₇

R ¹	R ²	Catalyst	Temp	TOF (h ⁻¹) ^a
Me	H	3a	rt	0.4
Me	H	3a	60°	2
Me	H	3b	rt	0.3
Me	Bn	3a	90°	0.03
Me	Bn	3a	120°	1
Me	Bn	3b	120°	0.04
Ph	Me	3a	60°	1



Catalyst (3–5 mol %), C₆D₆

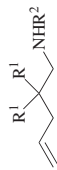




TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene

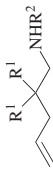
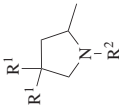
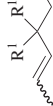
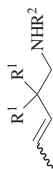
Conditions

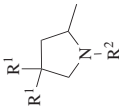
Product(s) and Yield(s) (%)

Refs.

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₇₋₁₇

	 Catalyst (2.5 mol %), C ₆ D ₆ , 110°	 I +  II	489																																																																																																						
		<table> <tr> <th>R¹</th><th>R²</th><th>Catalyst</th><th>Time (h)</th><th>I</th><th>II</th></tr> <tr> <td>Me</td><td><i>n</i>-Pr</td><td>100a</td><td>16</td><td>(80)</td><td>(10)</td></tr> <tr> <td>Me</td><td><i>i</i>-Pr</td><td>100a</td><td>16</td><td>(90)</td><td>(5)</td></tr> <tr> <td>Me</td><td>Ph</td><td>100a</td><td>16</td><td>(80)</td><td>(15)</td></tr> <tr> <td>Me</td><td>Bn</td><td>100a</td><td>16</td><td>(90)</td><td>(5)</td></tr> <tr> <td>-(CH₂)₄-</td><td>Bn</td><td>100b</td><td>16</td><td>(98)</td><td>(—)</td></tr> <tr> <td>-(CH₂)₅-</td><td>Bn</td><td>100b</td><td>22</td><td>(79)</td><td>(—)</td></tr> <tr> <td>Ph</td><td>H</td><td>100a</td><td>16</td><td>(—)</td><td>(50)</td></tr> <tr> <td>Ph</td><td>H</td><td>100b</td><td>16</td><td>(—)</td><td>(75)</td></tr> <tr> <td>Ph</td><td><i>n</i>-Pr</td><td>100a</td><td>16</td><td>(95)</td><td>(5)</td></tr> <tr> <td>Ph</td><td><i>n</i>-Pr</td><td>100b</td><td>16</td><td>(75)</td><td>(5)</td></tr> <tr> <td>Ph</td><td>Ph</td><td>100a</td><td>16</td><td>(98)</td><td>(2)</td></tr> <tr> <td>Ph</td><td>Ph</td><td>100b</td><td>16</td><td>(—)</td><td>(—)</td></tr> <tr> <td>Ph</td><td>Bn</td><td>100a</td><td>16</td><td>(98)</td><td>(—)</td></tr> <tr> <td>Ph</td><td>Bn</td><td>100b</td><td>16</td><td>(90)</td><td>(—)</td></tr> <tr> <td>Ph</td><td>4-BrC₆H₄CH₂</td><td>100a</td><td>16</td><td>(98)</td><td>(—)</td></tr> <tr> <td>Ph</td><td>4-BrC₆H₄CH₂</td><td>100b</td><td>16</td><td>(—)</td><td>(—)</td></tr> </table>	R ¹	R ²	Catalyst	Time (h)	I	II	Me	<i>n</i> -Pr	100a	16	(80)	(10)	Me	<i>i</i> -Pr	100a	16	(90)	(5)	Me	Ph	100a	16	(80)	(15)	Me	Bn	100a	16	(90)	(5)	-(CH ₂) ₄ -	Bn	100b	16	(98)	(—)	-(CH ₂) ₅ -	Bn	100b	22	(79)	(—)	Ph	H	100a	16	(—)	(50)	Ph	H	100b	16	(—)	(75)	Ph	<i>n</i> -Pr	100a	16	(95)	(5)	Ph	<i>n</i> -Pr	100b	16	(75)	(5)	Ph	Ph	100a	16	(98)	(2)	Ph	Ph	100b	16	(—)	(—)	Ph	Bn	100a	16	(98)	(—)	Ph	Bn	100b	16	(90)	(—)	Ph	4-BrC ₆ H ₄ CH ₂	100a	16	(98)	(—)	Ph	4-BrC ₆ H ₄ CH ₂	100b	16	(—)	(—)	
R ¹	R ²	Catalyst	Time (h)	I	II																																																																																																				
Me	<i>n</i> -Pr	100a	16	(80)	(10)																																																																																																				
Me	<i>i</i> -Pr	100a	16	(90)	(5)																																																																																																				
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Ph	H	100a	16	(—)	(50)																																																																																																				
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Ph	<i>n</i> -Pr	100b	16	(75)	(5)																																																																																																				
Ph	Ph	100a	16	(98)	(2)																																																																																																				
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Ph	4-BrC ₆ H ₄ CH ₂	100a	16	(98)	(—)																																																																																																				
Ph	4-BrC ₆ H ₄ CH ₂	100b	16	(—)	(—)																																																																																																				

 Ir catalyst (5 mol %), <i>t</i> -BuOK (<i>x</i> mol %), C ₇ H ₈ , 50°	<table> <tr> <th>R¹</th><th>R²</th><th>Catalyst</th><th><i>x</i></th><th>Time (h)</th><th></th></tr> <tr> <td>Me</td><td>Bn</td><td>96</td><td>0</td><td>15</td><td>(96)</td></tr> <tr> <td>Ph</td><td>H</td><td>95</td><td>0</td><td>6</td><td>(29)</td></tr> <tr> <td>Ph</td><td>H</td><td>96</td><td>0</td><td>15</td><td>(96)</td></tr> <tr> <td>Ph</td><td>H</td><td>94</td><td>5</td><td>6</td><td>(20)</td></tr> <tr> <td>Ph</td><td>H</td><td>95</td><td>5</td><td>6</td><td>(75)</td></tr> <tr> <td>Ph</td><td>H</td><td>95</td><td>5</td><td>15</td><td>(98)</td></tr> </table>	R ¹	R ²	Catalyst	<i>x</i>	Time (h)		Me	Bn	96	0	15	(96)	Ph	H	95	0	6	(29)	Ph	H	96	0	15	(96)	Ph	H	94	5	6	(20)	Ph	H	95	5	6	(75)	Ph	H	95	5	15	(98)	505
R ¹	R ²	Catalyst	<i>x</i>	Time (h)																																								
Me	Bn	96	0	15	(96)																																							
Ph	H	95	0	6	(29)																																							
Ph	H	96	0	15	(96)																																							
Ph	H	94	5	6	(20)																																							
Ph	H	95	5	6	(75)																																							
Ph	H	95	5	15	(98)																																							

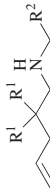
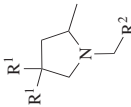
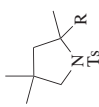
		R ¹	R ²	Time (h)
		Me	BnOCH ₂ CH ₂	22 (70)
		Me	<i>c</i> -C ₆ H ₁₁	17 (57)
		Me	Bn	9 (65)
		Ph	Bn	16 (75)
		Ph	4-BrC ₆ H ₄ CH ₂	18 (70)
		Ph	4-O ₂ NC ₆ H ₄ CH ₂	40 (72)
		Ph	3,4-(OCH ₂ O)C ₆ H ₃ CH ₂	20 (71)
		Ph	4-NCC ₆ H ₄ CH ₂	40 (64)
		Ph	4-MeO ₂ CC ₆ H ₄ CH ₂	36 (77)

[P(Cl₂CH₂=CH₂)₂] (2.5 mol %),
PPh₃ (5 mol %), dioxane, 120°

		R ¹	R ²	R ³	Catalyst	Temp	Time (h)
		Me	Me	Ph	97a	rt	38 (77)
		Me	Me	Ph	97a	80°	1 (83)
		Me	Me	Ph	97b	rt	30 (80)
		Me	Me	Ph	97b	80°	0.5 (88)
		Me	allyl	Ph	97a	rt	9 (93)
		Me	allyl	Ph	97b	rt	7 (92)
		-(CH ₂) ₅ -	2-furanyl	Ph	97a	rt	11 (82)
		-(CH ₂) ₅ -	2-furanyl	Ph	97b	rt	9 (88)
		-(CH ₂) ₅ -	Ph	Ph	97a	rt	11 (91)
		-(CH ₂) ₅ -	Ph	Ph	97b	rt	4.5 (93)
		Ph	2-furanyl	Ph	97a	rt	77 (93)
		Ph	2-furanyl	Ph	97a	80°	0.33 (98)
		Ph	2-furanyl	Ph	97b	rt	23 (94)
		Ph	2-furanyl	Ph	97b	80°	0.33 (97)
		Ph	2-thienyl	Ph	97a	rt	6 (93)
		Ph	2-thienyl	Ph	97b	rt	6 (96)
		Ph	Ph	Ph	97a	rt	8 (99)
		Ph	Ph	Ph	97b	rt	3 (99)

Catalyst (2.5 mol %),
[PhNHMe₂][B(C₆F₅)₄] (5 mol %),
C₆D₆

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

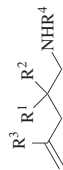
Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.																																	
	Catalyst (2.5 mol %), [PhNHMe ₂][B(C ₆ F ₅) ₄] (5 mol %), C ₆ D ₆ , 80°																																			
	<table><tr><th>R¹</th><th>R²</th><th>Catalyst</th><th>Time (h)</th></tr><tr><td>Me</td><td>Ph</td><td>93a</td><td>13 (60)</td></tr><tr><td>Me</td><td>Ph</td><td>93q</td><td>13 (83)</td></tr><tr><td>-S(CH₂)₃-</td><td>2-furanyl</td><td>93a</td><td>480 (88)</td></tr><tr><td>-S(CH₂)₃-</td><td>2-furanyl</td><td>93h</td><td>168 (96)</td></tr><tr><td>-S(CH₂)₃-</td><td>4-MeOC₆H₄</td><td>93a</td><td>648 (49)</td></tr><tr><td>-S(CH₂)₃-</td><td>4-MeOC₆H₄</td><td>93q</td><td>648 (97)</td></tr></table>	R ¹	R ²	Catalyst	Time (h)	Me	Ph	93a	13 (60)	Me	Ph	93q	13 (83)	-S(CH ₂) ₃ -	2-furanyl	93a	480 (88)	-S(CH ₂) ₃ -	2-furanyl	93h	168 (96)	-S(CH ₂) ₃ -	4-MeOC ₆ H ₄	93a	648 (49)	-S(CH ₂) ₃ -	4-MeOC ₆ H ₄	93q	648 (97)		185 185 189 189 185 185					
R ¹	R ²	Catalyst	Time (h)																																	
Me	Ph	93a	13 (60)																																	
Me	Ph	93q	13 (83)																																	
-S(CH ₂) ₃ -	2-furanyl	93a	480 (88)																																	
-S(CH ₂) ₃ -	2-furanyl	93h	168 (96)																																	
-S(CH ₂) ₃ -	4-MeOC ₆ H ₄	93a	648 (49)																																	
-S(CH ₂) ₃ -	4-MeOC ₆ H ₄	93q	648 (97)																																	
	FeCl ₃ ·6H ₂ O (10 mol %), solvent, 80°																																			
		<table><tr><th>R</th><th>Solvent</th><th>Time (h)</th></tr><tr><td>H</td><td>DCE</td><td>1 (56)</td></tr><tr><td>H</td><td>DCE</td><td>2 (97)</td></tr><tr><td>H</td><td>hexane</td><td>1 (52)</td></tr><tr><td>H</td><td>C₆H₆</td><td>1 (19)</td></tr><tr><td>H</td><td>dioxane</td><td>1 (9)</td></tr><tr><td>H</td><td>THF</td><td>1 (tr)</td></tr><tr><td>H</td><td><i>i</i>-PrOH</td><td>1 (tr)</td></tr><tr><td>H</td><td>DMSO</td><td>1 (—)</td></tr><tr><td>H</td><td>DMF</td><td>1 (—)</td></tr><tr><td>Me</td><td>DCE</td><td>2 (99)</td></tr></table>	R	Solvent	Time (h)	H	DCE	1 (56)	H	DCE	2 (97)	H	hexane	1 (52)	H	C ₆ H ₆	1 (19)	H	dioxane	1 (9)	H	THF	1 (tr)	H	<i>i</i> -PrOH	1 (tr)	H	DMSO	1 (—)	H	DMF	1 (—)	Me	DCE	2 (99)	204
R	Solvent	Time (h)																																		
H	DCE	1 (56)																																		
H	DCE	2 (97)																																		
H	hexane	1 (52)																																		
H	C ₆ H ₆	1 (19)																																		
H	dioxane	1 (9)																																		
H	THF	1 (tr)																																		
H	<i>i</i> -PrOH	1 (tr)																																		
H	DMSO	1 (—)																																		
H	DMF	1 (—)																																		
Me	DCE	2 (99)																																		

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₇₋₈

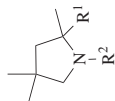


C₇₋₁₈



357

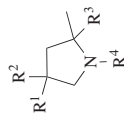
82 (10 mol %), AgOTf (10 mol %),
Cu(OTf)₂ (10 mol %), MgSO₄,
CH₂Cl₂, rt, 12 h



R ¹	R ²	
H	Ac	(68)
H	Boc	(75)
H	Ts	(—)
H	Cbz	(82)
H	4-MeC ₆ H ₄ CO ₂	(92)
Me	Cbz	(—)

203

Catalyst (x mol %), C₇D₈

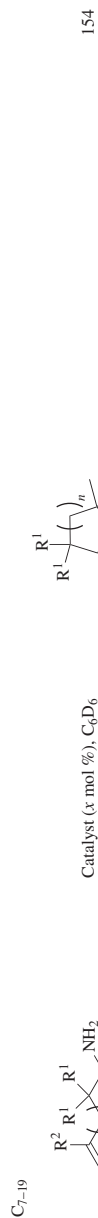


470

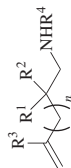
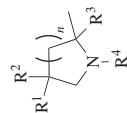
R ¹	R ²	R ³	R ⁴	Catalyst	x	Temp (°)	Time (h)	dr
Me	Me	H	H	74b	10	130	24	(79) —
Me	allyl	H	H	74b	5	130	0.75	(95) 3:2
—(CH ₂) ₅ —	H	H	H	74b	5	130	1.5	(95) —
—(CH ₂) ₅ —	H	Me	H	74b	10	130	24	(86) —
H	Ph	H	H	74b	10	130	4	(82) 7:3
Me	Ph	H	H	74b	5	130	1.5	(93) 4:1
Ph	Ph	H	H	74a	5	70	7.5	(95) —
Ph	Ph	H	H	74b	5	70	4.5	(95) —
Ph	Ph	H	H	74b	5	130	0.25	(95) —
Ph	Ph	H	Me	74b	10	130	19	(88) —
Ph	Ph	Me	H	74b	5	130	3	(87) —

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

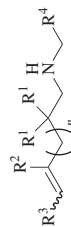
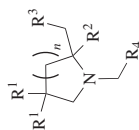
Please refer to the charts preceding the tables for structures indicated by the **bold numbers**.



$\text{N} \times \text{R}^2$ H	R^2	Catalyst	x	Temp	Time (h)
1	Me	78a	10	π	2
1	Me	78b	5	π	1
1	$-(\text{CH}_2)_5-$	78a	5	π	0.5
1	$-(\text{CH}_2)_5-$	78a	5	70°	0.15
1	$-(\text{CH}_2)_5-$	78b	5	π	0.15
1	Ph	78a	5	π	0.3
1	Ph	78b	5	π	0.15
1	Ph	78a	5	π	24
1	Ph	Me	5	70°	1
2	Ph	78a	5	π	24
2	Ph	78a	10	π	6
2	Ph	78b	5	π	5
3	Ph	78a	10	75°	72
3	Ph	78b	10	75°	48

[Ir(COD)Cl]₂ (x mol %), dioxane

<i>n</i>	R ¹	R ²	R ³	R ⁴	<i>x</i>	Temp (°)	Time (h)	dr
1	Me	Me	H	Bn	2.5	110	24	(84)
1	H	<i>i</i> -Pr	H	Bn	2.5	110	24	(81)
1	-(CH ₂) ₅ -	H	Bn	1.25	110	7	(86)	—
1	-(CH ₂) ₅ -	H	Ph	2.5	110	16	(95)	—
1	-(CH ₂) ₅ -	Me	Bn	2.5	110	48	(74)	—
1	Ph	allyl	H	Bn	1.25	110	16	(92)
1	Ph	Ph	Me	Ph	2.5	110	24	(0)
1	Ph	Ph	Me	Bn	1.25	110	16	(88)
2	Ph	Ph	H	Ph	2.5	110	16	(20)
2	Ph	Ph	H	Bn	2.5	80	24	(72)

[Ir(COD)Cl]₂ (x mol %), dioxane

<i>n</i>	R ¹	R ²	R ³	R ⁴	<i>x</i>	Temp (°)	Time (h)
1	Me	H	H	Ph	2.5	110	24
1	-(CH ₂) ₅ -	H	H	Ph	1.25	110	7
1	Ph	H	H	<i>c</i> -C ₆ H ₁₁	0.5	110	7
1	Ph	H	H	Ph	0.125	110	3
1	Ph	H	H	Ph	1.25	110	7
1	Ph	H	H	4-FC ₆ H ₄	1.25	110	7
1	Ph	H	H	4-ClC ₆ H ₄	0.5	110	3
1	Ph	H	H	4-MeOC ₆ H ₄	0.25	110	7
1	Ph	H	H	4-MeOC ₆ H ₄	1.25	110	3
1	Ph	H	H	4-MeC ₆ H ₄	0.5	110	7
1	Ph	H	H	4-MeO ₂ CC ₆ H ₄	0.5	110	3
1	Ph	Me	Me	Ph	5	110	48
1	Ph	H	H	Ph	1.25	110	16
2	Ph	H	H	Ph	2.5	80	24

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Refs.

Product(s) and Yield(s) (%)

Conditions

Aminoalkene

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₈

Catalyst (x mol %), C₆D₆

Catalyst	x	Temp (°)	Time (h)
[Me ₂ Si(C ₃ Me ₄)(<i>i</i> -BuN)]SmN(TMS) ₂	6.7	125	19 (95)
[Me ₂ Si(C ₃ Me ₄)(<i>i</i> -BuN)]YN(TMS) ₂	3.3	125	19 (95)
[Me ₂ Si(C ₃ Me ₄)(<i>i</i> -BuN)]YbCH(TMS) ₂	3.2	120	36 (70) ^g
Me ₂ Si(C ₃ Me ₄) ₂ NdCH(TMS) ₂	5.0	125	19 (95)
Cp* ₂ LaCH(TMS) ₂	4.8	125	12 (95)
Cp* ₂ SmCH(TMS) ₂	2.3	120	65 (20)
[Me ₂ Si(C ₃ Me ₄)(<i>i</i> -BuN)]Th(NMe ₂) ₂	2	100	— (90)
[Me ₂ Si(C ₃ Me ₄)(<i>i</i> -BuN)]U(NMe ₂) ₂	2	100	— (90)

162
162
162
162
162
162
256
256

Catalyst (5 mol %), C₆D₆, 125°

Catalyst	Time (h)
38a	14 (95)
38b	15 (95)
38c	14 (78)

164

1. RNH(CH₂)₂NHR (5 mol %),
Ln(N(TMS)₂)₃ (5 mol %)
2. Aminoalkene, C₆D₆, 125°

R	Ln	Time (h)
2,6-Me ₂ C ₆ H ₃	Nd	11 (95)
2- <i>i</i> -PrC ₆ H ₄	Nd	6.5 (95)
2- <i>i</i> -PrC ₆ H ₄	Y	12 (95)

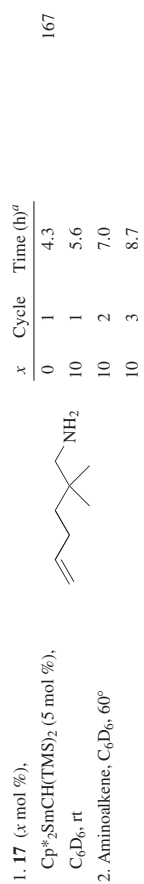
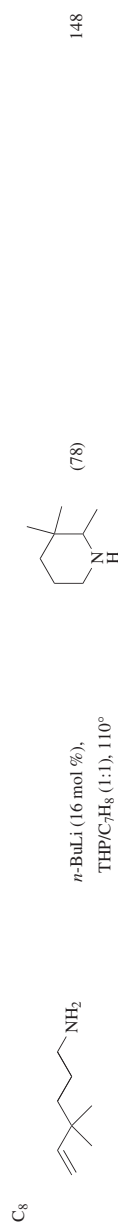
163

C₈₋₉

FeCl₃•6H₂O (10 mol %),
DCE, 80°, 3 h

R
Me (95)
Et (95)

204



<i>n</i>	R	Catalyst	<i>x</i>	Temp (°C)	Time (h)
1	Me	23b	10	120	40 (93)
1	Ph	23a	10	60	13 (99)
1	Ph	23b	10	60	2.5 (99)
1	Ph	23c	10	60	8 (99)
2	Ph	23a	20	120	20 (0)
2	Ph	23b	15	120	20 (0)

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Refs.

Product(s) and Yield(s) (%)

Conditions

Aminoalkene

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₈₋₁₉

Catalyst (5 mol %), C₇H₈

<i>n</i>	<i>R</i>	Catalyst	Temp (°)	Time (h)	<i>I</i> ^b	<i>II</i> ^b	<i>cis/trans II</i>
1	Me	Ti(NMe ₂) ₄	105	24	(72)	(26)	4:1
1	Me	Ind ₂ Ti(NMe ₂) ₂	105	24	(71)	(28)	4:1
1	Me	Ind ₂ Zr(NMe ₂) ₂	105	24	(95)	—	—
1	Me	Ind ₂ Hf(NMe ₂) ₂	105	24	(24)	—	—
2	Ph	Ti(NMe ₂) ₄	160	72	(9)	(66)	38:28
2	Ph	Ti(NMe ₂) ₄	145	96	(11)	(79)	55:24
2	Ph	TiBn ₄	160	72	(11)	(63)	46:17
2	Ph	TiBn ₄	145	196	(16)	(63)	35:28

C₈

n-BuLi (16 mol %),
hexane/THF, 50°, 20 h

FeCl₃•6H₂O (10 mol %),
DCE, 80°, 7 h

I + II (96), **I/II** = 3:1

Y[N(TMS)₂]₃ (x mol %), C₆D₆

<i>x</i>	Temp (°)	Time (h)
2,7	45	45
3	70	8

157

(93)

(94)

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Refs.

Product(s) and Yield(s) (%)

Conditions

Aminoalkene

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C ₈		Catalyst (1–5 mol %), C ₆ D ₆		+		256	
			Catalyst	Temp	TOF (h ⁻¹)	I + II	I/II
			[Me ₂ Si(C ₅ Me ₄)(<i>i</i> -BuN)]Th(NMe ₂) ₂	rt	12	(95)	I only
			[Me ₂ Si(C ₅ Me ₄)(<i>i</i> -BuN)]U(NMe ₂) ₂	rt	1.5	(95)	I only
			[Me ₂ Si(C ₅ Me ₄)(<i>i</i> -BuN)]Th(NMe ₂) ₂	100°	0.1	(95)	II only
			[Me ₂ Si(C ₅ Me ₄)(<i>i</i> -BuN)]U(NMe ₂) ₂	100°	0.1	(95)	II only
C ₈₋₁₁		[Ir(COD)Cl] ₂ (2.5 mol %), dioxane, 110°, 24 h		(81) dr 1.5:1			200
C ₈₋₁₁		82 (5 mol %), AgBF ₄ (10 mol %), MgSO ₄ , CH ₂ Cl ₂ , rt, 20 h		+		I + II	I/II
						<i>i</i> -Pr	(95) >20:1
						Ph	(88) 5:1
C ₈		Au[P(<i>i</i> -Bu) ₂ (2-PhC ₆ H ₄)]Cl (5 mol %), AgOTf (5 mol %), dioxane, 80°, 22 h		(96) dr 1.5:1			207
C ₈₋₁₁		Au(IPr)Cl (x mol %), AgOTf (x mol %), MeOH				<i>trans/cis</i>	208
						<i>i</i> -Pr	rt 1.5:5
						Ph	Et 5 45° 1:3.3
						Ph	Ph 10 45° 1:2.9

C₈

Catalyst (10 mol %),
additive (*x* mol %),
solvent, 60°, 48 h

484

C₈₋₉

n-BuLi (16 mol %),
THP/C₇H₈ (1:1), 110°

148

C₉

1. **29** (5 mol %), Sc[N(TMS)₂]₃,
C₆D₆, 120°, 2 h
2. Aminoalkene, C₆D₆

165

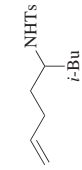
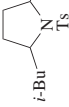
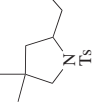
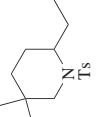
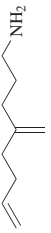
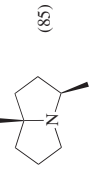
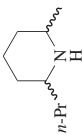
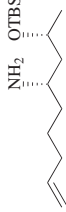
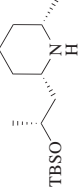
Temp	I + II	I/II	<i>trans/cis</i> I
rt	(95)	I only	49:1
60°	(95)	II only	—

Y[N(TMS)₂]₃ (2.7 mol %),
C₇H₈, 18 h

157

Temp (°)	I	II	III
10	(75) ^b	(6) ^b	(—)
70	(—)	(6)	(85)

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>			
	TiOH (20 mol %), C ₇ H ₈ , 100°, 2 h	 (58), <i>trans/cis</i> = 68:32	209
	FeCl ₃ ·6H ₂ O (10 mol %), DCE, 80°, 11 h	 I +  II I + II (95), I/II = 2:1	204
	[Cp ^{TMS} SmMe] ₂ (6.3 mol %), C ₆ D ₆ , 120°, 48 h	 (77)	160
	[Cp ^{TMS} NdMe] ₂ (5.5 mol %), C ₆ D ₆ , 120°, 20 h	 (85)	160
	Sm[N(TMS) ₂] ₂ (10 mol %), THP, 90°, 24 h	 (82), <i>trans/cis</i> = 1:5.7	484
	Cp ^{*2} NdCH(TMS) ₂ (5 mol %), C ₆ D ₆ , rt, 2 h	 (90)	161

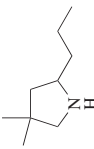
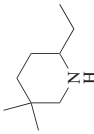
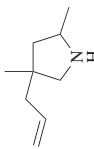
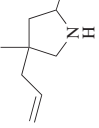
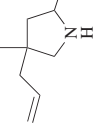
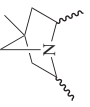
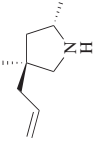
		$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)((i\text{-Bu})\text{N})]\text{LnR}(\text{TMS})_2$ (<i>x</i> mol %), C_6D_6 , 120°	Ln	R	<i>x</i>	Time (h)																																																				
			Sm	N	4.5	34	(93)																																																			
			Y	N	6.9	39	(98)																																																			
			Lu	CH	4.3	38	(95)																																																			
		Ln catalyst (<i>x</i> mol %), C_6D_6	<table><tr><th>Catalyst</th><th><i>x</i></th><th>Temp (°)</th><th>Time (h)</th><th></th></tr><tr><td>$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)((i\text{-Bu})\text{N})]\text{SmN}(\text{TMS})_2$</td><td>4.7</td><td>120</td><td>116</td><td>(95)</td></tr><tr><td>$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)((i\text{-Bu})\text{N})]\text{YN}(\text{TMS})_2$</td><td>4.0</td><td>120</td><td>107</td><td>(95)</td></tr><tr><td>$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)((i\text{-Bu})\text{N})]\text{YbCH}(\text{TMS})_2$</td><td>8.2</td><td>120</td><td>25</td><td>(95)</td></tr><tr><td>$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)((i\text{-Bu})\text{N})]\text{LuCH}(\text{TMS})_2$</td><td>5.9</td><td>120</td><td>46</td><td>(95)</td></tr><tr><td>$\text{Et}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{NdCH}(\text{TMS})_2$</td><td>5.0</td><td>125</td><td>137</td><td>(95)</td></tr><tr><td>$\text{Cp}^*_2\text{LaCH}(\text{TMS})_2$</td><td>6.1</td><td>120</td><td>4</td><td>(95)</td></tr><tr><td>$\text{Cp}^*_2\text{SmCH}(\text{TMS})_2$</td><td>4.5</td><td>120</td><td>26</td><td>(95)</td></tr><tr><td>$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)((i\text{-Bu})\text{N})]\text{Th}(\text{NMe}_2)_2$</td><td>2</td><td>100</td><td>—</td><td>(90)</td></tr><tr><td>$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)((i\text{-Bu})\text{N})]\text{U}(\text{NMe}_2)_2$</td><td>2</td><td>100</td><td>—</td><td>(90)</td></tr></table>					Catalyst	<i>x</i>	Temp (°)	Time (h)		$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)((i\text{-Bu})\text{N})]\text{SmN}(\text{TMS})_2$	4.7	120	116	(95)	$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)((i\text{-Bu})\text{N})]\text{YN}(\text{TMS})_2$	4.0	120	107	(95)	$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)((i\text{-Bu})\text{N})]\text{YbCH}(\text{TMS})_2$	8.2	120	25	(95)	$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)((i\text{-Bu})\text{N})]\text{LuCH}(\text{TMS})_2$	5.9	120	46	(95)	$\text{Et}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{NdCH}(\text{TMS})_2$	5.0	125	137	(95)	$\text{Cp}^*_2\text{LaCH}(\text{TMS})_2$	6.1	120	4	(95)	$\text{Cp}^*_2\text{SmCH}(\text{TMS})_2$	4.5	120	26	(95)	$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)((i\text{-Bu})\text{N})]\text{Th}(\text{NMe}_2)_2$	2	100	—	(90)	$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)((i\text{-Bu})\text{N})]\text{U}(\text{NMe}_2)_2$	2	100	—	(90)	
Catalyst	<i>x</i>	Temp (°)	Time (h)																																																							
$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)((i\text{-Bu})\text{N})]\text{SmN}(\text{TMS})_2$	4.7	120	116	(95)																																																						
$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)((i\text{-Bu})\text{N})]\text{YN}(\text{TMS})_2$	4.0	120	107	(95)																																																						
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$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)((i\text{-Bu})\text{N})]\text{LuCH}(\text{TMS})_2$	5.9	120	46	(95)																																																						
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$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)((i\text{-Bu})\text{N})]\text{Th}(\text{NMe}_2)_2$	2	100	—	(90)																																																						
$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)((i\text{-Bu})\text{N})]\text{U}(\text{NMe}_2)_2$	2	100	—	(90)																																																						
C_{9-15}		<i>n</i> -BuLi (16 mol %), THP/ <i>C</i> ₇ H ₈ (1:1), 110°	<table><tr><th>R</th><th></th></tr><tr><td>H</td><td>(85)</td></tr><tr><td>Ph</td><td>(84)</td></tr></table>					R		H	(85)	Ph	(84)	148																																												
R																																																										
H	(85)																																																									
Ph	(84)																																																									
C_9		<i>n</i> -BuLi (16 mol %), dioxane, rt, 3 h						148																																																		

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)		Refs.
	<i>n</i> -BuLi (16 mol %), THP/C ₇ H ₈ (1:1), 90°, 16 h	  I + II (80), I/II = 52:4	148	
	70 (x mol %), C ₆ D ₆ , rt	 x Time (h) dr 2 1 (95) 1:1 10 0.25 (99) — ^c	150 47	
	(EBI)YbN(TMS) ₂ (2 mol %), toluene, rt, 22 h	 (86) ^e dr 3:2	482	
	Catalyst (10 mol %), C ₆ D ₆ , 110°	 dr 1:1 Catalyst Time (h) 25a 3.5 (95) 25b 1 (85) 25c 1 (77) 25d 1 (95)	257	
	Ln[N(TMS) ₂] ₃ (3 mol %), C ₆ D ₆	  I II III IV Ln Temp Time (h) I + II + III + IV I/II/III/IV Y rt 0.5 (98) 1.3:1:0:0 Y 60° 4 (98) 0:0:1:1 La rt 1.7 (98) 1.4:1:0:0 La rt 45 (70) 0:0:1:1.5 La 60° 7.5 (92) 0:0:1:1:1	158	

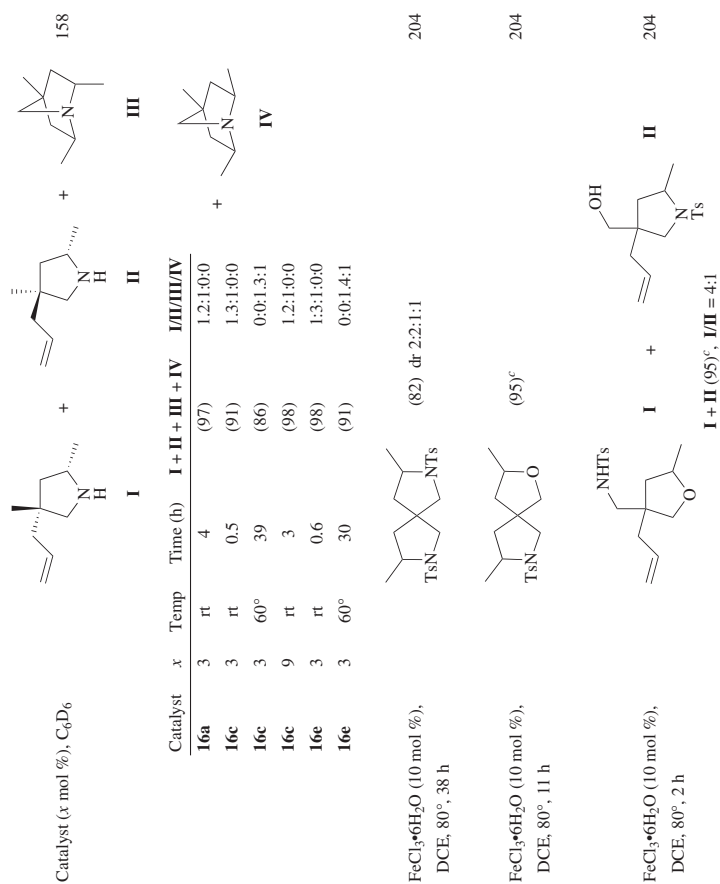
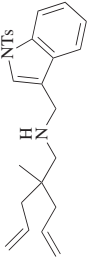
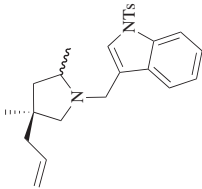
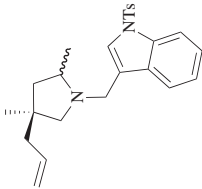
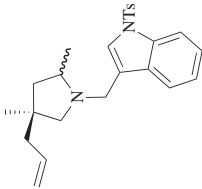
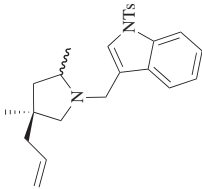
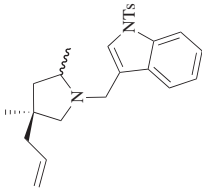
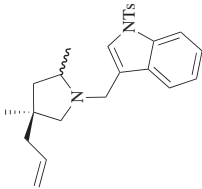
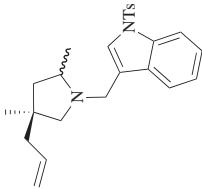
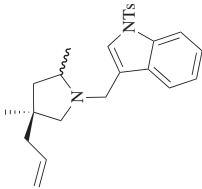
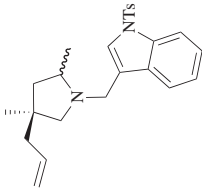
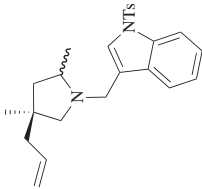
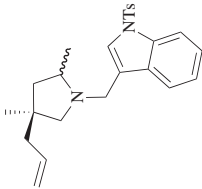
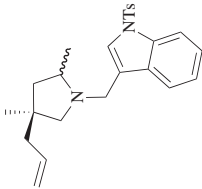
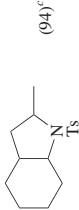
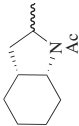
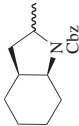


TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
	Catalyst (5 mol %), [PhNHMe ₂][B(C ₆ F ₅) ₄] (2.5 mol %), C ₆ D ₆ , 80°		93a 24 (99) 1.3:1
			93b 168 (55) 1.2:1
			93p 168 (59) 1.2:1
			93q 3 (99) 1.3:1
			93t 168 (47) 1.3:1
			93u 60 (99) 1.4:1
			99a 168 (62) 1:1
			99b 168 (56) 1.2:1
			99c 168 (3) —
			99d 168 (25) —
			99e 168 (70) 1.3:1
			99f 168 (71) 1.1:1
			(94) ^c 211
			(82) dr 2.5:1 207
			(95) dr 2.5:1 205

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₉

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Refs.

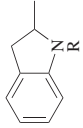
Product(s) and Yield(s) (%)

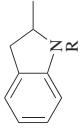
Conditions

Aminoalkene

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

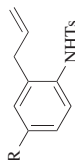
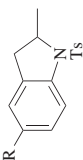
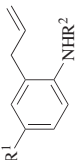
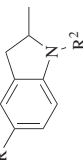
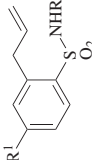
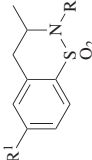
C ₉		82 (5 mol %), AgOTf (10 mol %), Cu(OTf) ₂ (10 mol %), MgSO ₄ , CH ₂ Cl ₂ , rt, 12 h	(32)	203																																																																																															
		Acid (20 mol %), solvent	<table> <tr> <th>Acid</th><th>Solvent</th><th>Temp (°)</th><th>Time (h)</th><th></th></tr> <tr> <td>—</td><td>C₇H₈</td><td>80</td><td>3</td><td>(—)</td></tr> <tr> <td>AcOH</td><td>C₇H₈</td><td>80</td><td>3</td><td>(—)</td></tr> <tr> <td>TsOH•H₂O</td><td>C₇H₈</td><td>80</td><td>3</td><td>(19)</td></tr> <tr> <td>TFA</td><td>C₇H₈</td><td>80</td><td>3</td><td>(—)</td></tr> <tr> <td>H₃PO₄</td><td>C₇H₈</td><td>80</td><td>3</td><td>(30)</td></tr> <tr> <td>H₂SO₄</td><td>C₇H₈</td><td>80</td><td>3</td><td>(87)</td></tr> <tr> <td>TfOH</td><td>C₇H₈</td><td>80</td><td>3</td><td>(98)</td></tr> <tr> <td>TfOH</td><td>C₇H₈</td><td>rt</td><td>24</td><td>(38)</td></tr> <tr> <td>TfOH</td><td>C₇H₈</td><td>110</td><td>3</td><td>(92)</td></tr> <tr> <td>TfOH</td><td>C₆H₆</td><td>80</td><td>3</td><td>(96)</td></tr> <tr> <td>TfOH</td><td>xylene</td><td>145</td><td>3</td><td>(69)</td></tr> <tr> <td>TfOH</td><td>DCM</td><td>40</td><td>3</td><td>(81)</td></tr> <tr> <td>TfOH</td><td>CHCl₃</td><td>62</td><td>3</td><td>(60)</td></tr> <tr> <td>TfOH</td><td>THF</td><td>67</td><td>3</td><td>(5)</td></tr> <tr> <td>TfOH</td><td>DME</td><td>86</td><td>3</td><td>(3)</td></tr> <tr> <td>TfOH</td><td>H₂O</td><td>100</td><td>3</td><td>(—)</td></tr> <tr> <td>TfOH</td><td>MeCN</td><td>83</td><td>3</td><td>(7)</td></tr> <tr> <td>TfOH</td><td>DMF</td><td>153</td><td>3</td><td>(—)</td></tr> </table>	Acid	Solvent	Temp (°)	Time (h)		—	C ₇ H ₈	80	3	(—)	AcOH	C ₇ H ₈	80	3	(—)	TsOH•H ₂ O	C ₇ H ₈	80	3	(19)	TFA	C ₇ H ₈	80	3	(—)	H ₃ PO ₄	C ₇ H ₈	80	3	(30)	H ₂ SO ₄	C ₇ H ₈	80	3	(87)	TfOH	C ₇ H ₈	80	3	(98)	TfOH	C ₇ H ₈	rt	24	(38)	TfOH	C ₇ H ₈	110	3	(92)	TfOH	C ₆ H ₆	80	3	(96)	TfOH	xylene	145	3	(69)	TfOH	DCM	40	3	(81)	TfOH	CHCl ₃	62	3	(60)	TfOH	THF	67	3	(5)	TfOH	DME	86	3	(3)	TfOH	H ₂ O	100	3	(—)	TfOH	MeCN	83	3	(7)	TfOH	DMF	153	3	(—)	212
Acid	Solvent	Temp (°)	Time (h)																																																																																																
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		Au[P(<i>n</i> -Bu) ₂ (2-PhC ₆ H ₄)]Cl (x mol %), AgOTf (x mol %), dioxane	<table> <tr> <th>R</th><th>x</th><th>Temp (°)</th><th>Time (h)</th><th></th></tr> <tr> <td>Ac</td><td>5</td><td>80</td><td>22</td><td>(99)</td></tr> <tr> <td>Chz</td><td>10</td><td>100</td><td>47</td><td>(59)</td></tr> </table>	R	x	Temp (°)	Time (h)		Ac	5	80	22	(99)	Chz	10	100	47	(59)	207 205																																																																																
R	x	Temp (°)	Time (h)																																																																																																
Ac	5	80	22	(99)																																																																																															
Chz	10	100	47	(59)																																																																																															

TiOH (x mol %), C ₇ H ₈				R		x		Temp (°)		Time (h)	
H				H		20		80		3	
										(—)	
Ms				Ms		20		80		3	
										(84)	
acryloyl				acryloyl		100		110		24	
										(tr)	
2-O ₂ NC ₆ H ₄ SO ₂				2-O ₂ NC ₆ H ₄ SO ₂		20		80		3	
										(88)	
3-O ₂ NC ₆ H ₄ SO ₂				3-O ₂ NC ₆ H ₄ SO ₂		20		80		3	
										(92)	
4-O ₂ NC ₆ H ₄ SO ₂				4-O ₂ NC ₆ H ₄ SO ₂		20		80		3	
										(85)	
Bz				Bz		110		110		72	
										(68)	
Chz				Chz		20		80		24	
										(—)	

Au catalyst (x mol %), AgOTf (y mol %), C ₇ H ₈				R		x		y		Temp (°)		Time (h)	
H				H		5		5		100		12	
												(—)	
Ac				Ac		5		5		100		12	
												(—)	
Ph				Ph		5		5		100		12	
												(—)	
Bz				Bz		5		5		100		12	
												(tr)	
Ts				Ts		0		5		80		12	
												(30)	
Ts				Ts		5		5		70		12	
												(tr)	
Ts				Ts		5		5		40		12	
												(—)	
Ts				Ts		5		5		80		12	
												(—)	
Ts				Ts		5		5		85		12	
												(99)	
Ts				Ts		5		5		85		10	
												(100)	
Ts				Ts		5		5		85		36	
												(100)	
Ts				Ts		5		5		85		10	
												(100)	
Ts				Ts		5		5		85		14	
												(100)	
Ts				Ts		5		5		85		36	
												(99)	
Ts				Ts		5		5		85		20	
												(81)	
Ts				Ts		5		5		85		20	
												(6)	
Ts				Ts		5		5		85		20	
												(5)	
Ts				Ts		2.5		2.5		85		20	
												(—)	

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TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.																																											
Please refer to the charts preceding the tables for structures indicated by the bold numbers.																																														
	TiOH (20 mol %), C ₇ H ₈ , 80°		<table><thead><tr><th>R</th><th>Time (h)</th></tr></thead><tbody><tr><td>H</td><td>3 (98)</td></tr><tr><td>Br</td><td>3.5 (94)</td></tr><tr><td>Cl</td><td>3.5 (81)</td></tr><tr><td>F</td><td>5 (90)</td></tr><tr><td>O₂N</td><td>8 (89)</td></tr><tr><td>MeO</td><td>0.5 (88)</td></tr><tr><td>Me</td><td>1 (92)</td></tr></tbody></table>	R	Time (h)	H	3 (98)	Br	3.5 (94)	Cl	3.5 (81)	F	5 (90)	O ₂ N	8 (89)	MeO	0.5 (88)	Me	1 (92)	212																										
R		Time (h)																																												
H		3 (98)																																												
Br		3.5 (94)																																												
Cl		3.5 (81)																																												
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	C ₈ F ₁₇ SO ₃ H (5 mol %), perfluorodecalin, C ₇ H ₈ , hexanes, reflux		<table><thead><tr><th>R¹</th><th>R²</th><th>Time (h)</th></tr></thead><tbody><tr><td>H</td><td>H</td><td>24 (—)</td></tr><tr><td>H</td><td>Ms</td><td>1 (88)</td></tr><tr><td>H</td><td>Ns</td><td>1 (93)</td></tr><tr><td>H</td><td>2-Ns</td><td>1 (92)</td></tr><tr><td>H</td><td>3-Ns</td><td>1 (91)</td></tr><tr><td>H</td><td>Bz</td><td>1 (tr)</td></tr><tr><td>H</td><td>Ts</td><td>1 (95)</td></tr><tr><td>Br</td><td>Ts</td><td>2 (91)</td></tr><tr><td>Cl</td><td>Ts</td><td>2 (91)</td></tr><tr><td>F</td><td>Ts</td><td>2.5 (90)</td></tr><tr><td>O₂N</td><td>Ts</td><td>5 (87)</td></tr><tr><td>MeO</td><td>Ts</td><td>0.5 (94)</td></tr><tr><td>Me</td><td>Ts</td><td>1 (95)</td></tr></tbody></table>	R ¹	R ²	Time (h)	H	H	24 (—)	H	Ms	1 (88)	H	Ns	1 (93)	H	2-Ns	1 (92)	H	3-Ns	1 (91)	H	Bz	1 (tr)	H	Ts	1 (95)	Br	Ts	2 (91)	Cl	Ts	2 (91)	F	Ts	2.5 (90)	O ₂ N	Ts	5 (87)	MeO	Ts	0.5 (94)	Me	Ts	1 (95)	211
R ¹		R ²	Time (h)																																											
H		H	24 (—)																																											
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Me		Ts	1 (95)																																											
		(PPh ₃)AuCl (5 mol %), AgOTf (5 mol %), C ₇ H ₈ , 100°		<table><thead><tr><th>R¹</th><th>R²</th><th>Time (h)</th></tr></thead><tbody><tr><td>H</td><td>H</td><td>48 (95)</td></tr><tr><td>MeO</td><td>H</td><td>48 (99)</td></tr><tr><td>Me</td><td>H</td><td>48 (99)</td></tr><tr><td>Me</td><td>Et</td><td>24 (95)</td></tr></tbody></table>	R ¹	R ²	Time (h)	H	H	48 (95)	MeO	H	48 (99)	Me	H	48 (99)	Me	Et	24 (95)	202																										
R ¹			R ²	Time (h)																																										
H	H		48 (95)																																											
MeO	H		48 (99)																																											
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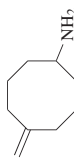
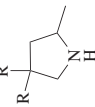
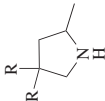
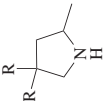
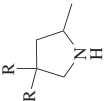
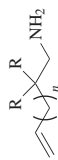
C ₉		[Cp ^{rw} ₂ NdMe ₂] ₂ (10.5 mol %), C ₆ D ₆ , 120°, 5 min	(94)	160															
C ₁₀		Catalyst (5 mol %), C ₆ D ₆	(99)	161															
<table><tr><th>Catalyst</th><th>Temp</th><th>trans/cis</th></tr><tr><td>Me₂Si(C₅Me₄)(C₃H₇)YCH(TMS)₂</td><td>rt</td><td>1:7</td></tr><tr><td>[Me₂Si(C₅Me₄)₂YMe]₂</td><td>rt</td><td>1:10</td></tr><tr><td>Cp*₂YMe(THF)</td><td>80°</td><td>1:17</td></tr><tr><td>Cp*₂NdCH(TMS)₂</td><td>rt</td><td>1:115</td></tr></table>					Catalyst	Temp	trans/cis	Me ₂ Si(C ₅ Me ₄)(C ₃ H ₇)YCH(TMS) ₂	rt	1:7	[Me ₂ Si(C ₅ Me ₄) ₂ YMe] ₂	rt	1:10	Cp* ₂ YMe(THF)	80°	1:17	Cp* ₂ NdCH(TMS) ₂	rt	1:115
Catalyst	Temp	trans/cis																	
Me ₂ Si(C ₅ Me ₄)(C ₃ H ₇)YCH(TMS) ₂	rt	1:7																	
[Me ₂ Si(C ₅ Me ₄) ₂ YMe] ₂	rt	1:10																	
Cp* ₂ YMe(THF)	80°	1:17																	
Cp* ₂ NdCH(TMS) ₂	rt	1:115																	
C ₁₀₋₁₇		86 (10 mol %), C ₇ D ₈ , 115°	<table><tr><th>R</th><th>Time (h)</th></tr><tr><td>-(CH₂)₅-</td><td>7 (98)</td></tr><tr><td>Ph</td><td>6 (90)</td></tr></table>	R	Time (h)	-(CH ₂) ₅ -	7 (98)	Ph	6 (90)	508									
R	Time (h)																		
-(CH ₂) ₅ -	7 (98)																		
Ph	6 (90)																		
		Catalyst (5 mol %), C ₆ D ₆ , 120°	<table><tr><th>R</th><th>Catalyst</th><th>TOF (h⁻¹)</th></tr><tr><td>-(CH₂)₅-</td><td>85a</td><td>0.13 (44)</td></tr><tr><td>-(CH₂)₅-</td><td>85b</td><td>0.20 (56)</td></tr><tr><td>Ph</td><td>85a</td><td>0.19 (75)</td></tr></table>	R	Catalyst	TOF (h ⁻¹)	-(CH ₂) ₅ -	85a	0.13 (44)	-(CH ₂) ₅ -	85b	0.20 (56)	Ph	85a	0.19 (75)	509			
R	Catalyst	TOF (h ⁻¹)																	
-(CH ₂) ₅ -	85a	0.13 (44)																	
-(CH ₂) ₅ -	85b	0.20 (56)																	
Ph	85a	0.19 (75)																	

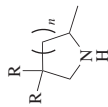
TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>			
 C ₁₀₋₁₇	Catalyst (x mol %), C ₆ D ₆ , 	478	
 Catalyst (x mol %), C ₆ D ₆ ,			

C₁₀₋₁₈



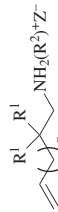
Catalyst (10 mol %), C₇D₈, 115°



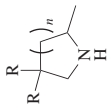
<i>n</i>	R ¹	Catalyst	Time (h)
1	-(CH ₂) ₅ -	88a	3 (98)
1	-(CH ₂) ₅ -	88b	3 (98)
1	Ph	88a	4.5 (98)
1	Ph	88b	4.5 (98)
2	Ph	88a	48 (98)
2	Ph	88b	48 (98)

508

C₁₀₋₁₁



1. **89a** (5 mol %), AuCl (5 mol %), AgOTf (5 mol %), C₇H₈, 80°, 24 h
2. NaOH, H₂O

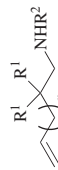


Catalyst (x mol %), C₇H₈, 110°

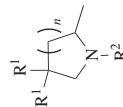
<i>n</i>	R	Catalyst	<i>x</i>	Time (h)
1	-(CH ₂) ₅ -	81b	2.5	3 (100)
1	Ph	81a	5	24 (40)
1	Ph	81b	2.5	1 (100)
2	Ph	81b	2.5	15 (100)

69

C₁₀₋₁₇



117e (x mol %), TCE, 130°, 20 h

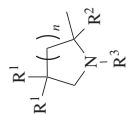
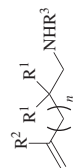


R ¹	R ²	<i>x</i>
-(CH ₂) ₅ -	Bn	20 (53)
Ph	Mes	10 (85)
Ph	4-ClC ₆ H ₄ CH ₂	10 (96)
Ph	4-O ₂ NC ₆ H ₄ CH ₂	10 (97)
Ph	4-MeOC ₆ H ₄ CH ₂	10 (96)
Ph	4-MeO ₂ CC ₆ H ₄ CH ₂	10 (95)
Ph	<i>n</i> -C ₈ H ₁₇	10 (93)

213

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

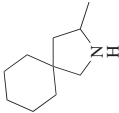
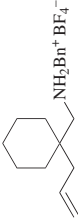
Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
C₁₀₋₁₇	Catalyst (2.5 mol %), [PhNHMe ₂][B(C ₆ F ₅) ₄] (2.5 mol %), C ₆ D ₆ , 80°	99a Ph 10 (91) 99b Ph 10 (91) 188 99c Ph 10 (23) 99d Ph 10 (94) 99e Ph 10 (88) 99f Ph 10 (84) 99a 2-furanyl 7 (91) 99b 2-furanyl 12 (91) 99c 2-furanyl 96 (99) 99d 2-furanyl 24 (78) 99e 2-furanyl 7 (99) 99f 2-furanyl 7 (99)	
C₁₀₋₁₈	[Ir(COD)Cl] ₂ (x mol %), NHEt ₃ Cl (y mol %), dioxane, 110°	90	

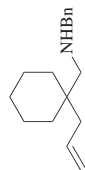


$\text{Cu}(\text{O}i\text{-Bu})_2$ (x mol %),
XANTPHOS (x mol %),
 $\text{MeOH}/\text{C}_7\text{H}_8$ (1:1)

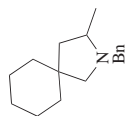
n	R^1	R^2	R^3	x	Temp ($^\circ$)	Time (h)
1	$-(\text{CH}_2)_5-$	H	H	15	100	72 (79)
1	$-(\text{CH}_2)_5-$	H	Me	10	100	4 (91)
1	Ph	H	H	15	100	72 (87)
1	Ph	H	Me	10	60	18 (80)
1	Ph	H	Et	10	100	48 (87)
1	Ph	H	Ac	10	100	48 (96)
1	Ph	H	n -Pr	10	100	48 (93)
1	Ph	H	i -Bu	10	100	48 (88)
1	Ph	H	$4\text{-FC}_6\text{H}_4\text{CH}_2$	10	100	48 (98)
1	Ph	H	$4\text{-MeOC}_6\text{H}_4\text{CH}_2$	15	100	48 (94)
1	Ph	H	Bn	15	100	48 (99)
1	Ph	H	Bz	10	140	48 (94)
1	Ph	H	BnCH ₂	10	100	48 (87)
1	Ph	H	$4\text{-MeO}_2\text{CC}_6\text{H}_4\text{CH}_2$	15	100	48 (86)
1	Ph	H	$4\text{-NCC}_6\text{H}_4\text{CH}_2$	15	100	48 (86)
1	Ph	Me	Me	15	140	48 (89)
2	$-(\text{CH}_2)_5-$	H	H	10	100	72 (91)
2	$-(\text{CH}_2)_5-$	H	Me	10	100	24 (94)
2	Ph	H	H	15	100	72 (87)
2	Ph	H	Me	10	100	24 (92)

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.																														
Please refer to the charts preceding the tables for structures indicated by the bold numbers.																																	
 C₁₀	 NaN(TMS) ₂ (20 mol %), SmI ₂ (10 mol %), THF, 60°, 24 h	(93)	484																														
	Catalyst (x mol %), C ₆ D ₆	<table><tr><th>Catalyst</th><th>x</th><th>Temp</th><th>Time (h)</th><th></th></tr><tr><td>Sm[N(TMS)₂]₃</td><td>5</td><td>rt</td><td>24</td><td>(100)</td></tr><tr><td>Et₂Zn</td><td>10</td><td>60°</td><td>100</td><td>(99)</td></tr></table>	Catalyst	x	Temp	Time (h)		Sm[N(TMS) ₂] ₃	5	rt	24	(100)	Et ₂ Zn	10	60°	100	(99)	511 155															
Catalyst	x	Temp	Time (h)																														
Sm[N(TMS) ₂] ₃	5	rt	24	(100)																													
Et ₂ Zn	10	60°	100	(99)																													
	83 (10 mol %), C ₇ D ₈ , 115° 7 h	(90)	508																														
 C₁₁	1. Catalyst (5 mol %), AuCl (5 mol %), AgOTf (5 mol %), solvent, 60° 2. NaOH, H ₂ O	<table><tr><th>Catalyst</th><th>Solvent</th><th></th></tr><tr><td>111b</td><td>—</td><td>(30)</td></tr><tr><td>112a</td><td>dioxane</td><td>(11)</td></tr><tr><td>112a</td><td>MeOH</td><td>(48)</td></tr><tr><td>112a</td><td>THF</td><td>(15)</td></tr><tr><td>112a</td><td>EtOAc</td><td>(37)</td></tr><tr><td>112a</td><td>C₇H₈</td><td>(61)</td></tr><tr><td>112b</td><td>C₇H₈</td><td>(77)</td></tr><tr><td>112d</td><td>C₇H₈</td><td>(27)</td></tr><tr><td>112e</td><td>C₇H₈</td><td>(99)</td></tr></table>	Catalyst	Solvent		111b	—	(30)	112a	dioxane	(11)	112a	MeOH	(48)	112a	THF	(15)	112a	EtOAc	(37)	112a	C ₇ H ₈	(61)	112b	C ₇ H ₈	(77)	112d	C ₇ H ₈	(27)	112e	C ₇ H ₈	(99)	195
	Catalyst	Solvent																															
111b	—	(30)																															
112a	dioxane	(11)																															
112a	MeOH	(48)																															
112a	THF	(15)																															
112a	EtOAc	(37)																															
112a	C ₇ H ₈	(61)																															
112b	C ₇ H ₈	(77)																															
112d	C ₇ H ₈	(27)																															
112e	C ₇ H ₈	(99)																															

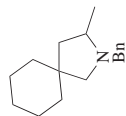


$[\text{PtCl}_2(\text{CH}_2=\text{CH}_2)]_2$ (2.5 mol %),
 PR_3 (5 mol %),
 diglyme, 80°, 6 h



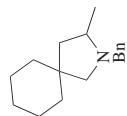
R
 2-MeC₆H₄ (55)
 4-MeC₆H₄ (22)

199



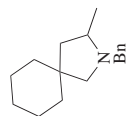
(64)

512



(27)

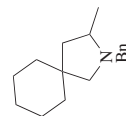
512



Catalyst

111b (20)
111d (45)

199

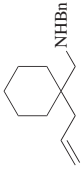
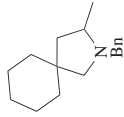


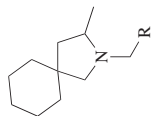
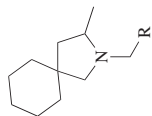
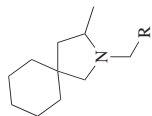
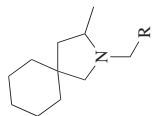
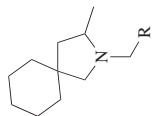
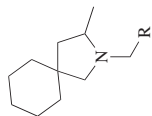
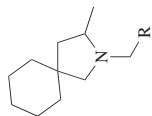
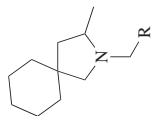
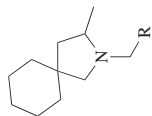
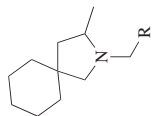
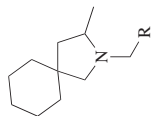
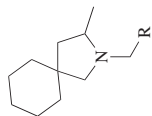
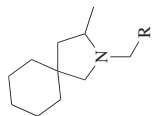
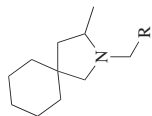
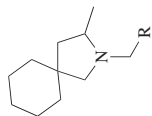
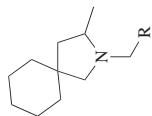
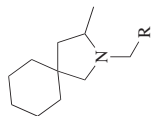
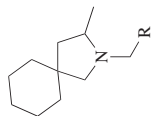
Catalyst

112a (98)
112b (100)
112c (100)
112e (72)
112f (82)
112g (79)

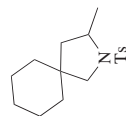
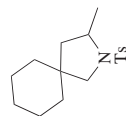
199

Catalyst (5 mol %), PtCl_2 (5 mol %),
 diglyme, 80°, 3 h

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the bold numbers.			
C₁₀ 	Pt catalyst (5 mol %), ligand (5 mol %), additive (5 mol %), dioxane, 5 h		201
Catalyst	Ligand	Additive	Temp (°)
(COD)PtCl ₂	—	—	65 (28)
(COD)PtCl ₂	—	—	80 (42)
(COD)PtCl ₂	—	—	110 (82)
PtCl ₂	—	—	110 (79)
PtCl ₂	PPh ₃	—	80 (13)
PtCl ₂	PPh ₃	—	110 (82)
PtCl ₂	116a	—	110 (8)
PtCl ₂	116b	—	110 (tr)
PtCl ₂	116c	—	110 (tr)
PtCl ₂	116d	—	110 (59)
PtCl ₂	116e	—	110 (8)
PtCl ₂	116f	—	110 (38)
PtCl ₂	116g	—	110 (11)
114	—	—	110 (76)
114	—	AgOTf	110 (81)
115	—	—	110 (86)
116d PtCl ₂	—	—	110 (83)

R	Catalyst	Time (h)	
	93a	4.5	(100)
	93h	2	(92)
	93q	1.3	(88)
	93a	0.5	(99)
	93b	0.75	(100)
	93c	10	(59)
	93d	10	(16)
	93g	10	(93)
	93h	2	(100)
	93i	10	(94)
	93j	10	(97)
	93k	10	(6)
	93l	10	(95)
	93o	10	(99)
	93p	10	(70)
	93q	0.3	(99)
	93t	10	(73)
	93u	1	(99)

Catalyst (2.5 mol %),
[PhNHMe₂][B(C₆F₅)₄] (2.5 mol %),
C₆D₆, 80°

	(99)	133
	(65), <i>trans/cis</i> = 11:1	196

(Ph₃P)AuCl (5 mol %),
AgOTf (5 mol %),
C₇H₈, 85°, 15 h

89b (2.5 mol %),
[Rh(COD)₂][BF₄] (3 mol %),
dioxane, 70°, 7 h

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
	Au[P(<i>n</i>-Bu)₂(2-PhC₆H₄)]Cl (5 mol %), AgOTf (5 mol %), dioxane, 60°		205
	Au[P(<i>n</i>-Bu)₂(2-PhC₆H₄)]Cl (5 mol %), AgOTf (5 mol %), dioxane		205
	[PtCl₂(CH₂=CH₂)₂] (2.5 mol %), PPh₃ (5 mol %), H₂O (x eq), dioxane, 120°		198
	Au(IPr)Cl (5 mol %), AgOTf (5 mol %), MeOH, rt, 24 h		208
	Au[P(<i>n</i>-Bu)₂(2-PhC₆H₄)]Cl (x mol %), AgOTf (x mol %), dioxane, 80°		207

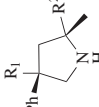
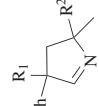
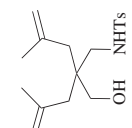
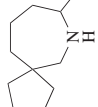
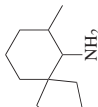
Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
C₁₀₋₁₁	<i>n</i>-BuLi (32 mol %), hexanes, rt to 60°, 6 h	R¹ R² <i>trans/cis</i> H <i>n</i>-Pr (65) — H Bn (87) — H (<i>R</i>)-CH₃(Ph)CH (75) —^c H (<i>S</i>)-CH₃(Ph)CH (79) —^c Me <i>n</i>-Pr (62) —^c Me Bn (63) 5.1	146
C₁₁	34b (1.7 mol %), C₆D₆, 60°, 36 h	(82) <i>trans/cis</i> = 79:21	477
	C₈F₁₇SO₃H (5 mol %), perfluorodecalin, C₇H₈, hexanes, reflux	(92) <i>trans/cis</i> = 91:9	211
	82 (5 mol %), AgOTf (10 mol %), Cu(OTf)₂ (10 mol %), MgSO₄, CH₂Cl₂, rt, 12 h	<i>trans/cis</i> = 30:70	203
	[PhNHMe₂][B(C₆F₅)₄] (10 mol %), dioxane, 120°, 24 h	(82) <i>dr</i> 2.6:1	174

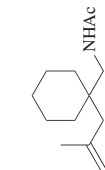
Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																										
Please refer to the charts preceding the tables for structures indicated by the bold numbers.																																																																																													
 C ₁₁ -18	Au:PVP (5 mol%), additive (x eq), solvent, 50°	 I +  II 514	514																																																																																										
	<table><tr><th>R¹</th><th>R²</th><th>Additive</th><th>x</th><th>Solvent</th><th>Time (h)</th><th>I</th><th>II</th><th>dr I</th></tr><tr><td>H</td><td>H</td><td>NH₄OAc</td><td>3</td><td>H₂O/EtOH</td><td>2</td><td>(99)</td><td>(0)</td><td>1.5:1</td></tr><tr><td>H</td><td>H</td><td>HCO₂H</td><td>4</td><td>pH 6.86 buffer/EtOH</td><td>10</td><td>(88)</td><td>(0)</td><td>1.2:1</td></tr><tr><td>H</td><td>H</td><td>HCO₂H/0.5 NH₃</td><td>10</td><td>pH 4.01 buffer/EtOH</td><td>4</td><td>(11)</td><td>(0)</td><td>1.1:1</td></tr><tr><td>Me</td><td>H</td><td>NH₄OAc</td><td>3</td><td>H₂O/EtOH</td><td>2</td><td>(84)</td><td>(0)</td><td>1.2:1</td></tr><tr><td>Me</td><td>H</td><td>HCO₂H</td><td>4</td><td>pH 6.86 buffer/EtOH</td><td>3</td><td>(99)</td><td>(0)</td><td>1.2:1</td></tr><tr><td>Me</td><td>H</td><td>HCO₂H/0.5 NH₃</td><td>10</td><td>pH 4.01 buffer/EtOH</td><td>2</td><td>(72)</td><td>(0)</td><td>1.2:1</td></tr><tr><td>Ph</td><td>Me</td><td>NH₄OAc</td><td>3</td><td>H₂O/EtOH</td><td>4</td><td>(83)</td><td>(0)</td><td>—</td></tr><tr><td>Ph</td><td>Me</td><td>HCO₂H</td><td>4</td><td>pH 6.86 buffer/EtOH</td><td>13</td><td>(77)</td><td>(4)</td><td>—</td></tr><tr><td>Ph</td><td>Me</td><td>HCO₂H/0.5 NH₃</td><td>10</td><td>pH 4.01 buffer/EtOH</td><td>4</td><td>(55)</td><td>(0)</td><td>—</td></tr></table>	R ¹	R ²	Additive	x	Solvent	Time (h)	I	II	dr I	H	H	NH ₄ OAc	3	H ₂ O/EtOH	2	(99)	(0)	1.5:1	H	H	HCO ₂ H	4	pH 6.86 buffer/EtOH	10	(88)	(0)	1.2:1	H	H	HCO ₂ H/0.5 NH ₃	10	pH 4.01 buffer/EtOH	4	(11)	(0)	1.1:1	Me	H	NH ₄ OAc	3	H ₂ O/EtOH	2	(84)	(0)	1.2:1	Me	H	HCO ₂ H	4	pH 6.86 buffer/EtOH	3	(99)	(0)	1.2:1	Me	H	HCO ₂ H/0.5 NH ₃	10	pH 4.01 buffer/EtOH	2	(72)	(0)	1.2:1	Ph	Me	NH ₄ OAc	3	H ₂ O/EtOH	4	(83)	(0)	—	Ph	Me	HCO ₂ H	4	pH 6.86 buffer/EtOH	13	(77)	(4)	—	Ph	Me	HCO ₂ H/0.5 NH ₃	10	pH 4.01 buffer/EtOH	4	(55)	(0)	—		
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 C ₁₁	(Ph ₃ P)AuCl (5 mol %), AgOTf (5 mol %), C ₇ H ₈ , 85°, 10 h	 (97) 133	133																																																																																										
	Catalyst (x mol %), C ₇ D ₈ , 145°	 I +  II 515	515																																																																																										
	<table><tr><th>Catalyst</th><th>x</th><th>Time (h)</th><th>I + II</th><th>I/II</th></tr><tr><td>44b</td><td>20</td><td>115</td><td>(55)</td><td>I only</td></tr><tr><td>45</td><td>5</td><td>148</td><td>(84)</td><td>1:2</td></tr><tr><td>45</td><td>10</td><td>48</td><td>(86)</td><td>1:3</td></tr><tr><td>45</td><td>20</td><td>22</td><td>(92)</td><td>1:5</td></tr></table>	Catalyst	x	Time (h)	I + II	I/II	44b	20	115	(55)	I only	45	5	148	(84)	1:2	45	10	48	(86)	1:3	45	20	22	(92)	1:5																																																																			
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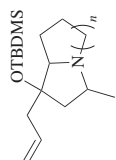
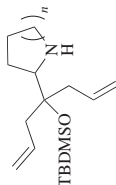


45	40	6	(96)	1:23
Zr(NMe ₂) ₄	20	21	(87)	1:10
Ti(NMe ₂) ₄	20	16	(95)	1:18



Au[P(*n*-Bu)₂(2-PhC₆H₄)Cl]₂ (5 mol %),
AgOTf (5 mol %), dioxane, 80°, 15 h

C₁₁-12



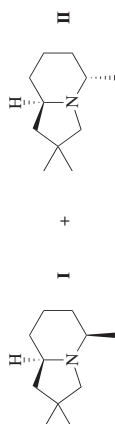
ZnEt₂ (2.5 mol %),
[PhNHMe₂][B(C₆F₅)₄] (2.5 mol %),
C₆D₆, rt

<i>n</i>	Time (h)	dr
1	0.67	(94) 2:1
2	0.5	(98) — ^c

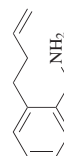
C₁₁



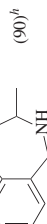
[Me₂Si(C₃Me₄)(*n*-BuN)]LnR(TMS)₂
(5 mol %), 2-xylene-*d*₁₀, 125°



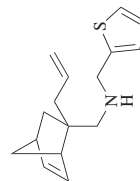
Ln	R	Time (d)	I + II	I/II
Sm	N	3	(85)	81:19
Yb	CH	2	(90)	—



46 (10 mol %), C₇D₈, 145°, 18 h



74

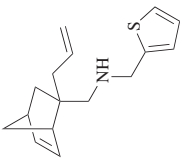
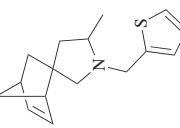
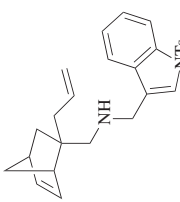
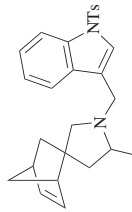


Catalyst (2.5 mol %),
[PhNHMe₂][B(C₆F₅)₄] (*x* mol %),
C₆D₆

Catalyst	<i>x</i>	Temp	Time (h)
97a	5	rt	68 (94)
97a	5	80°	1.5 (89)
97b	5	rt	38 (99)
97b	5	80°	1.5 (91)
ZnEt ₂	2.5	rt	27 (98)

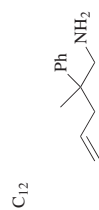
190
190
190
190
512

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

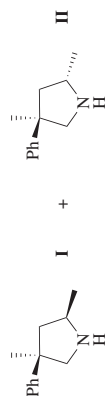
Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.					
	Catalyst (2.5 mol %), [PhNHMe ₂][B(C ₆ F ₅) ₄] (2.5 mol %), C ₆ D ₆ , 80°	 dr 1:1	Catalyst	Time (h)	Yield(s) (%)	Refs.		
			93a	30	(93)	185		
			93h	2	(96)	189		
			93o	7	(91)	188		
			93p	7	(83)	188		
			93q	2	(96)	185		
			93t	7	(80)	188		
			93u	4	(96)	188		
			99a	7	(82)	188		
			99b	7	(86)	188		
			99c	7	(60)	188		
			99d	7	(64)	188		
			99e	7	(77)	188		
99f	7	(87)	188					
	Catalyst (2.5 mol %), [PhNHMe ₂][B(C ₆ F ₅) ₄] (x mol %), C ₆ D ₆	 dr 1:1	Catalyst	x	Temp (°)	Time (h)	Yield(s) (%)	Refs.
			93a	2.5	80	20	(100)	185
			93h	2.5	80	12	(94)	189
			93q	2.5	80	3	(90)	185
			97a	5	rt	79	(94)	190
			97a	5	80	1	(96)	190
			97b	5	rt	69	(97)	190
			97b	5	80	0.83	(96)	190
ZnEt ₂	2.5	rt	18	(99)	512			

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₁₁

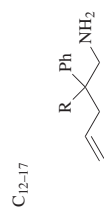


Catalyst (5 mol %), C₇D₈, 24 h

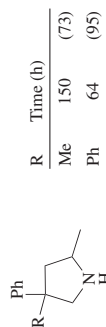


Catalyst	Temp (°)	I + II	I/II
Ti(NMe ₂) ₄	110	(52)	1.5:1
Ind ₂ TiMe ₂	105	(58) ^b	1.6:1
Ind ₂ ZrMe ₂	105	(58) ^b	1.7:1
Ind ₂ HfMe ₂	105	(70) ^b	2.4:1

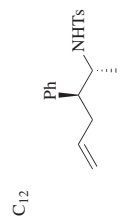
67
178
178
178



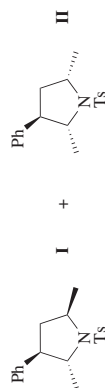
90 (5 mol %), C₇D₈, 110°



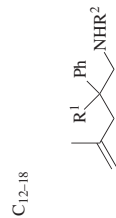
173



C₈F₁₇SO₃H (5 mol %),
perfluorodecalin,
C₇H₈, hexanes, reflux



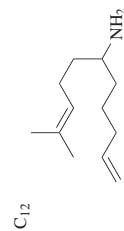
211



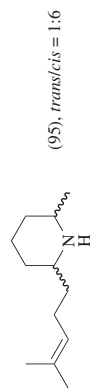
89b (x mol %),
[Rh(COD)₂][BF₄] (y mol %),
dioxane

R ¹	R ²	x	y	Temp (°)	Time (h)
H	Me	9	7.5	120	7 (80)
Ph	H	6	5	100	24 (96)
Ph	Me	3	2.5	70	7 (96)

I + II (96), I/II >99:1



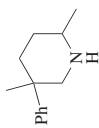
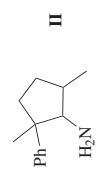
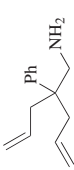
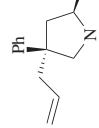
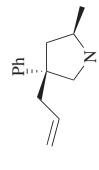
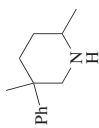
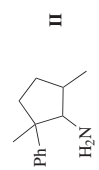
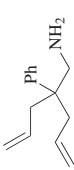
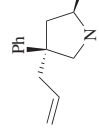
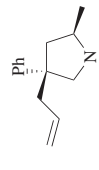
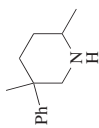
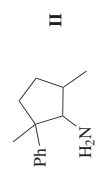
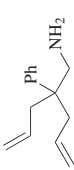
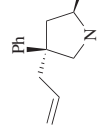
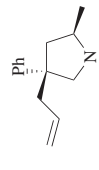
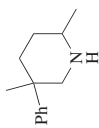
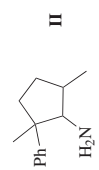
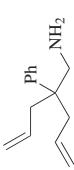
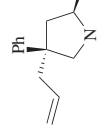
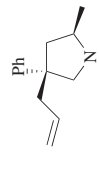
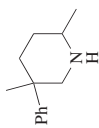
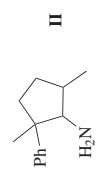
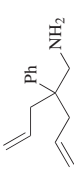
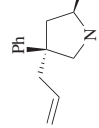
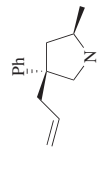
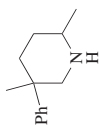
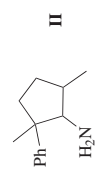
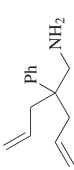
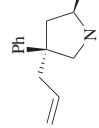
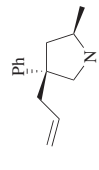
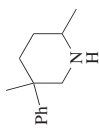
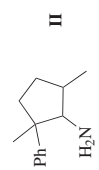
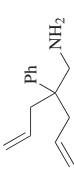
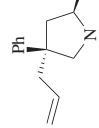
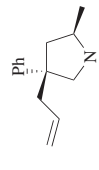
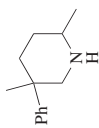
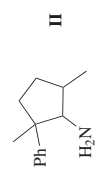
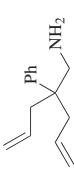
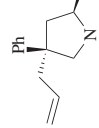
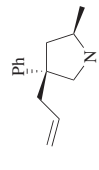
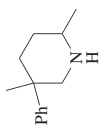
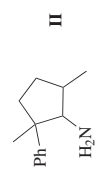
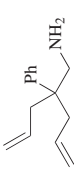
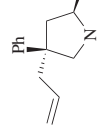
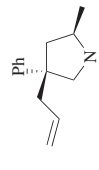
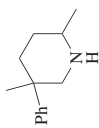
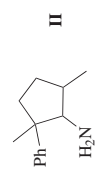
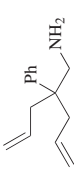
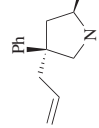
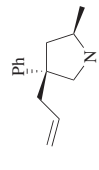
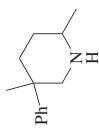
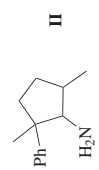
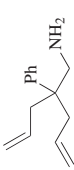
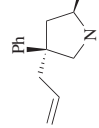
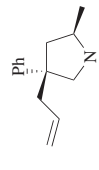
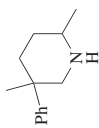
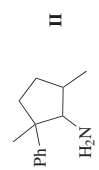
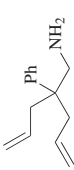
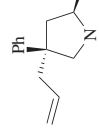
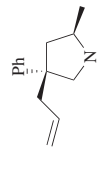
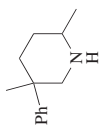
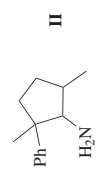
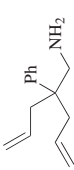
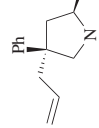
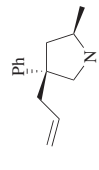
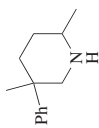
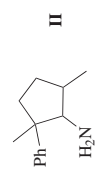
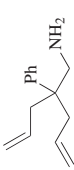
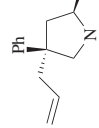
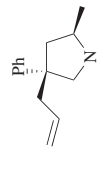
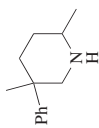
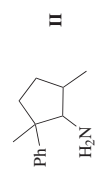
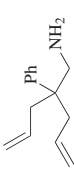
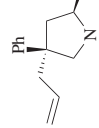
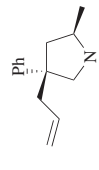
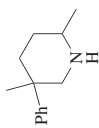
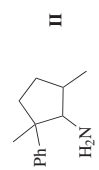
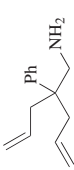
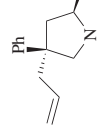
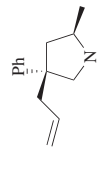
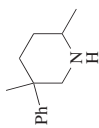
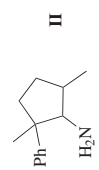
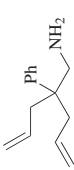
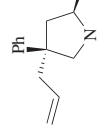
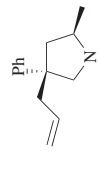
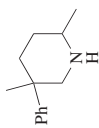
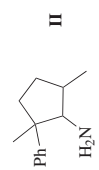
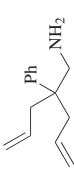
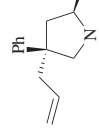
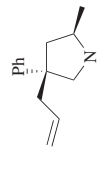
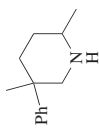
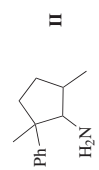
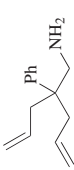
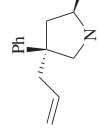
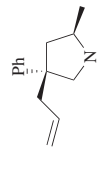
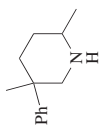
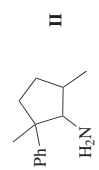
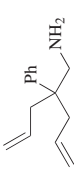
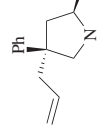
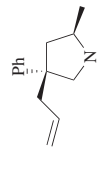
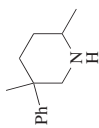
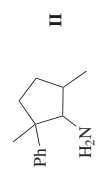
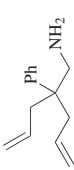
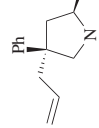
1. **29** (5 mol %),
Sc[N(TMS)₂]₃ C₆D₆, 120°, 2 h
2. Aminoalkene, C₆D₆, 60°, 18 h

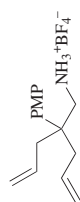


165

(95), *trans/cis* = 1:6

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

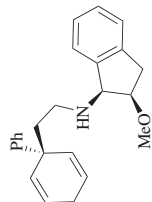
Aminoalkene	Conditions	Product(s) and Yield(s) (%)				Refs.
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+		69	474, 475
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>						
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+		69	474, 475
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>						
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+		69	474, 475
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>						
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+		69	474, 475
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>						
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+		69	474, 475
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>						
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+		69	474, 475
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>						
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+		69	474, 475
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>						
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+		69	474, 475
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>						
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+		69	474, 475
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>						
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+		69	474, 475
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>						
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+		69	474, 475
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>						
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+		69	474, 475
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>						
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+		69	474, 475
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>						
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+		69	474, 475
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>						
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+		69	474, 475
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>						
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+		69	474, 475
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>						
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+		69	474, 475
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>						
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+		69	474, 475
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>						
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+		69	474, 475
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>						
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+		69	474, 475
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>						
	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h		+		178	
	Zr(NMe ₂) ₄ (5 mol %), C ₇ D ₈ , 100°, 3 h		+			



1. **89a** (10 mol %), AuCl (10 mol %),
AgOTf (5 mol %), C₇H₈, 100°, 24 h
2. NaOH, H₂O

(93) dr 1.9:1

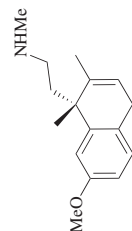
195



n-BuLi (20 mol %), THF, 20°, 4 h

(26) dr 90:10

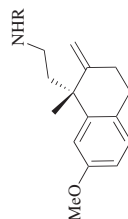
147



n-BuLi (20 mol %),
(*i*-Pr)₂NH (20 mol %), THF, rt, 0.5 h

(100)

145

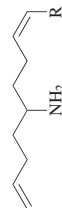


n-BuLi (20 mol %),
(*i*-Pr)₂NH (20 mol %),
TMEDA (40 mol %), THF, rt, 8 h

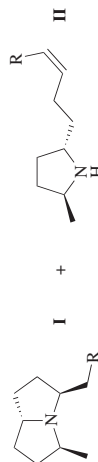
R	(98)	(100)
Me	(98)	(100)
Me ₂ C=CHCH ₂	(98)	(100)

145

C₁₅



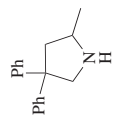
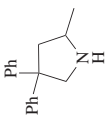
1. **98** (10 mol %), C₇D₈, 10°, 12 h
2. C₇D₈



R	Temp (°)	Time (h)	I	II
<i>n</i> -C ₆ H ₁₃	120	48	(32)	(68)
2-(5-EtC ₄ H ₂ S)	60	18	(90)	(0)

166

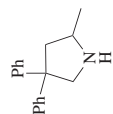
TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.											
 C ₁₇	[PhNHMe ₂][B(C ₆ F ₅) ₄] (20 mol %), dioxane, 120°, 18 h	(83) 	174											
	Catalyst (x mol %), C ₆ D ₆ , rt	<table> <tr> <th>Catalyst</th><th>x</th><th>TOF (h⁻¹)</th></tr> <tr> <td>101a</td><td>2</td><td>500 (99)</td></tr> <tr> <td>101b</td><td>3</td><td>75 (99)</td></tr> </table>	Catalyst	x	TOF (h ⁻¹)	101a	2	500 (99)	101b	3	75 (99)	152		
Catalyst	x	TOF (h ⁻¹)												
101a	2	500 (99)												
101b	3	75 (99)												
Catalyst (x mol %), C ₆ D ₆ , rt		516												
	<table> <tr> <th>Catalyst</th><th>x</th><th>Time (h)</th></tr> <tr> <td>Ca[N(TMS)₂]₂(THF)₂</td><td>5</td><td>1 (98)</td></tr> <tr> <td>(●≡SiOCa[N(TMS)₂]₂(THF)_{1.3}</td><td>10</td><td>16 (90)</td></tr> </table>	Catalyst	x	Time (h)	Ca[N(TMS) ₂] ₂ (THF) ₂	5	1 (98)	(●≡SiOCa[N(TMS) ₂] ₂ (THF) _{1.3}	10	16 (90)				
Catalyst	x	Time (h)												
Ca[N(TMS) ₂] ₂ (THF) ₂	5	1 (98)												
(●≡SiOCa[N(TMS) ₂] ₂ (THF) _{1.3}	10	16 (90)												
Catalyst (10 mol %), C ₆ D ₆	<table> <tr> <th>Catalyst</th><th>Temp (°)</th><th>Time (h)</th></tr> <tr> <td>102</td><td>150</td><td>100 (75)</td></tr> <tr> <td>103a</td><td>65</td><td>2 (95)</td></tr> <tr> <td>103b</td><td>65</td><td>18 (—)</td></tr> </table>	Catalyst	Temp (°)	Time (h)	102	150	100 (75)	103a	65	2 (95)	103b	65	18 (—)	517 485 485
Catalyst	Temp (°)	Time (h)												
102	150	100 (75)												
103a	65	2 (95)												
103b	65	18 (—)												
		<table> <tr> <th>Catalyst</th><th>Temp (°)</th></tr> <tr> <td>108a</td><td>(90)</td></tr> <tr> <td>108b</td><td>(4)</td></tr> <tr> <td>108c</td><td>(30)</td></tr> </table>	Catalyst	Temp (°)	108a	(90)	108b	(4)	108c	(30)	175			
Catalyst	Temp (°)													
108a	(90)													
108b	(4)													
108c	(30)													
Catalyst (5 mol %), C ₇ D ₈ , 110°, 24 h														

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

Please refer to the charts preceding the tables for structures indicated by the **bold numbers**.

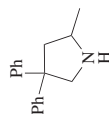
Catalyst	Additive	
104a	none	(0)
104b	none	(74)
104c	none	(26)
105	Ti(NMe ₂) ₄	(76)
105	Zr(NMe ₂) ₄	(82)



Catalyst (5 mol %), additive (5 mol %),
C₇H₈, 105°, 24 h

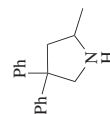
177
177
177
171
171

Catalyst	x	
106a	5.3	(100)
106b	5.3	(100)
106c	4.5	(67)
106d	4.7	(86)
106e	4.6	(100)
107	4.5	(100)



Catalyst (x mol %), C₆D₆, 100°, 16 h

501



Catalyst (1–5 mol %), C₆D₆

Catalyst	Temp	TOF (h ⁻¹)	
Y(2-C ₆ H ₄ CH ₂ NMe ₂) ₃	rt	27	(100)
Y(2-C ₆ H ₄ CH(CH ₃)NMe ₂) ₃	rt	57	(100)
Gd(2-C ₆ H ₄ C(CH ₃) ₂ NMe ₂) ₃	rt	80	(100)
[Me ₂ Si(C ₃ Me ₄)(<i>i</i> -Bu)N]Th(NMe ₂) ₂	rt	1460	(95)
[Me ₂ Si(C ₃ Me ₄)(<i>i</i> -Bu)N]U(NMe ₂) ₂	rt	430	(95)
[Me ₂ Si(C ₃ Me ₄) ₂]Th[N(TMS) ₂] ₂	rt	120	(95)
[Me ₂ Si(C ₃ Me ₄) ₂]UBr ₂	rt	29	(95)
Cp* ₂ Th[N(TMS) ₂] ₂	60°	2.8	(95)
Cp* ₂ U[N(TMS) ₂] ₂	60°	1.0	(95)

518
518
518
495
495
256
256
256
256

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

C₁₇

Aminoalkene

Conditions

Product(s) and Yield(s) (%)

Refs.

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

MCl₄ (20 mol %), additive (x eq),
C₇H₈, 120°, 18 h

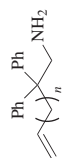
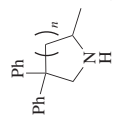
M	Additive	x
Ti	<i>i</i> -BuNH ₂	1.2 (11) ^j
Ti	2,6-(<i>i</i> -Bu) ₂ -C ₃ H ₃ N	1.2 (29) ^j
Ti	TMP	1.2 (26) ^j
Ti	LDA	0.8 (37) ^j
Hf	LDA	0.8 (59) ^j
Zr	LDA	0.8 (87) ^j
—	LDA	0.8 (6) ^j

174

Au:PVP (5 mol %), additive (x eq),
solvent

514

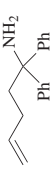
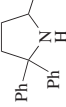
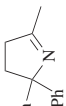
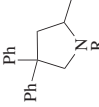
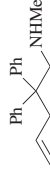
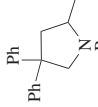
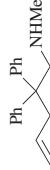
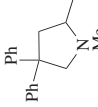
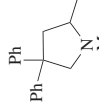
Additive	x	Solvent	Temp (°)	Time (h)	I	II	III
Cs ₂ CO ₃	3	H ₂ O/EtOH	50	4	(3)	(0)	(0)
Cs ₂ SO ₄	3	H ₂ O/EtOH	80	6	(25)	(2)	(28)
CsHCO ₂	3	H ₂ O/EtOH	50	4	(64)	(5)	(3)
NH ₄ HCO ₂	10	H ₂ O/EtOH	50	4	(83)	(4)	(7)
NH ₄ OAc	3	H ₂ O/EtOH	80	6	(18)	(tr)	(14)
HCO ₂ H	4	pH 6.86 buffer/EtOH	50	4	(80)	(3)	(3)
HCO ₂ H/0.5 NH ₃	10	pH 4.01 buffer/EtOH	50	4	(94)	(2)	(4)

C₁₇₋₁₉Catalyst (5 mol %), C₇H₈, 105°

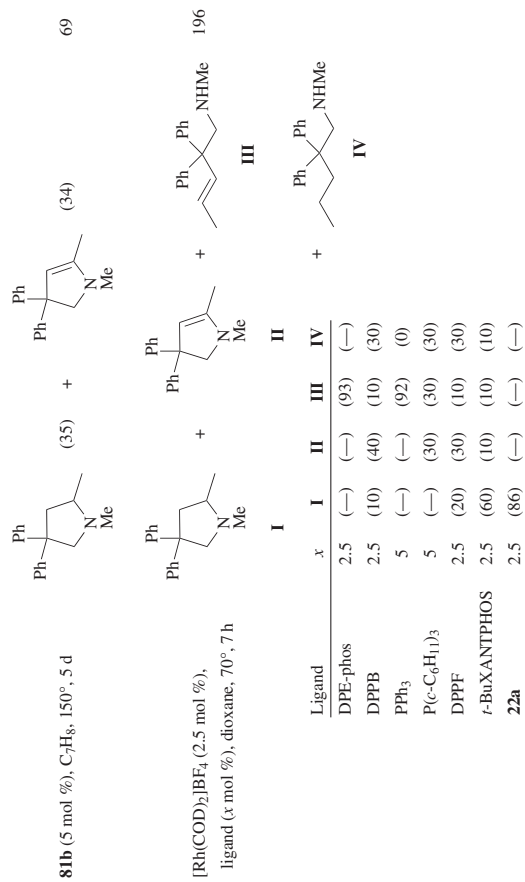
172

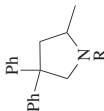
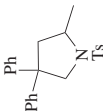
<i>n</i>	Catalyst	Time (h)
1	Ti(NMe ₂) ₄	0.5 (64)
1	Ti(NMe ₂) ₄	1 (91)
1	Ti(NMe ₂) ₄	24 (97)
1	Ind ₂ Ti(NMe ₂) ₂	2 (33)
1	Ind ₂ Ti(NMe ₂) ₂	4 (63)
1	Ind ₂ Ti(NMe ₂) ₂	6 (84)
1	Ind ₂ Ti(NMe ₂) ₂	8 (89)
1	Ind ₂ Ti(NMe ₂) ₂	15 (97)
1	Ind ₂ Ti(NMe ₂) ₂	24 (96)
1	Cp ₂ Ti(NMe ₂) ₂	4 (42)
1	Cp ₂ Ti(NMe ₂) ₂	6 (49)
1	Cp ₂ Ti(NMe ₂) ₂	25 (75)
1	Cp ₂ Ti(NMe ₂) ₂	34 (86)
1	Cp ₂ Ti(NMe ₂) ₂	72 (81)
1	[Me ₂ Si(C ₅ Me ₃)(<i>i</i> -BuN)]Ti(NMe ₂) ₂	24 (74)
1	Cp* ₂ Ti(NMe ₂) ₂	24 (10)
1	Ind ₂ TiCl ₂	24 (tr)
2	Ti(NMe ₂) ₄	24 (76)
2	Ind ₂ Ti(NMe ₂) ₂	24 (89)
2	Cp ₂ Ti(NMe ₂) ₂	24 (78)
2	[Me ₂ Si(C ₅ Me ₃)(<i>i</i> -BuN)]Ti(NMe ₂) ₂	24 (75)
3	Ti(NMe ₂) ₄	24 (—)
3	Ind ₂ Ti(NMe ₂) ₂	24 (—)

TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

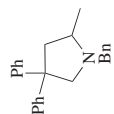
Aminoalkene	Conditions	Product(s) and Yield(s) (%)		Refs.
 C ₁₇	Au:PVP (5 mol %), additive (x eq), solvent, 27°	 I +	 II	514
 C ₁₈	(COD)PtCl ₂ (5 mol %), dioxane, 110°, 5 h	 R	 H	201
 C ₁₉	113 (2.5 mol %), C ₆ D ₆ , 70°	 R	 H	519
 C ₂₀	Catalyst (5 mol %), C ₇ D ₈ , 105°, 24 h	 R	 H	178
 C ₂₁	Catalyst (x mol %), 89b (2.5 mol %), dioxane, 70°, 7 h	 R	 H	196

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

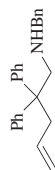


Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																																									
Please refer to the charts preceding the tables for structures indicated by the bold numbers.																																																																																																												
	Catalyst (x mol %), DPPE (x mol %), additive (2x mol %), TCE		427																																																																																																									
	<table><thead><tr><th>R</th><th>Catalyst</th><th>x</th><th>Additive</th><th>Temp (°)</th><th>Time (h)</th><th></th></tr></thead><tbody><tr><td>Me</td><td>CuBr₂</td><td>5</td><td>AgBF₄</td><td>100</td><td>20</td><td>(0)</td></tr><tr><td>Me</td><td>CuBr₂</td><td>5</td><td>AgBF₄</td><td>130</td><td>20</td><td>(40)</td></tr><tr><td>Me</td><td>CuBr₂</td><td>5</td><td>AgBF₄</td><td>150</td><td>20</td><td>(80)</td></tr><tr><td>Me</td><td>CuBr₂</td><td>5</td><td>AgBF₄</td><td>150</td><td>30</td><td>(89)</td></tr><tr><td><i>i</i>-Bu</td><td>—</td><td>2.5</td><td>Me₂O•HBF₄</td><td>130</td><td>20</td><td>(82)</td></tr><tr><td><i>i</i>-Bu</td><td>CuBr₂</td><td>5</td><td>AgBF₄</td><td>100</td><td>20</td><td>(10)</td></tr><tr><td><i>i</i>-Bu</td><td>CuBr₂</td><td>5</td><td>AgBF₄</td><td>130</td><td>20</td><td>(62)</td></tr><tr><td><i>i</i>-Bu</td><td>CuBr₂</td><td>5</td><td>AgBF₄</td><td>150</td><td>20</td><td>(93)</td></tr><tr><td>Bn</td><td>—</td><td>2.5</td><td>Me₂O•HBF₄</td><td>150</td><td>20</td><td>(91)</td></tr><tr><td>Bn</td><td>CuBr₂</td><td>5</td><td>AgBF₄</td><td>100</td><td>20</td><td>(0)</td></tr><tr><td>Bn</td><td>CuBr₂</td><td>5</td><td>AgBF₄</td><td>150</td><td>20</td><td>(79)</td></tr><tr><td>Bn</td><td>CuBr₂</td><td>5</td><td>AgBF₄</td><td>150</td><td>30</td><td>(85)</td></tr><tr><td><i>c</i>-C₆H₁₁CH₂</td><td>CuBr₂</td><td>5</td><td>AgBF₄</td><td>130</td><td>20</td><td>(41)</td></tr><tr><td><i>c</i>-C₆H₁₁CH₂</td><td>CuBr₂</td><td>5</td><td>AgBF₄</td><td>150</td><td>20</td><td>(94)</td></tr></tbody></table>	R	Catalyst	x	Additive	Temp (°)	Time (h)		Me	CuBr ₂	5	AgBF ₄	100	20	(0)	Me	CuBr ₂	5	AgBF ₄	130	20	(40)	Me	CuBr ₂	5	AgBF ₄	150	20	(80)	Me	CuBr ₂	5	AgBF ₄	150	30	(89)	<i>i</i> -Bu	—	2.5	Me ₂ O•HBF ₄	130	20	(82)	<i>i</i> -Bu	CuBr ₂	5	AgBF ₄	100	20	(10)	<i>i</i> -Bu	CuBr ₂	5	AgBF ₄	130	20	(62)	<i>i</i> -Bu	CuBr ₂	5	AgBF ₄	150	20	(93)	Bn	—	2.5	Me ₂ O•HBF ₄	150	20	(91)	Bn	CuBr ₂	5	AgBF ₄	100	20	(0)	Bn	CuBr ₂	5	AgBF ₄	150	20	(79)	Bn	CuBr ₂	5	AgBF ₄	150	30	(85)	<i>c</i> -C ₆ H ₁₁ CH ₂	CuBr ₂	5	AgBF ₄	130	20	(41)	<i>c</i> -C ₆ H ₁₁ CH ₂	CuBr ₂	5	AgBF ₄	150	20	(94)		
R	Catalyst	x	Additive	Temp (°)	Time (h)																																																																																																							
Me	CuBr ₂	5	AgBF ₄	100	20	(0)																																																																																																						
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Bn	CuBr ₂	5	AgBF ₄	150	20	(79)																																																																																																						
Bn	CuBr ₂	5	AgBF ₄	150	30	(85)																																																																																																						
<i>c</i> -C ₆ H ₁₁ CH ₂	CuBr ₂	5	AgBF ₄	130	20	(41)																																																																																																						
<i>c</i> -C ₆ H ₁₁ CH ₂	CuBr ₂	5	AgBF ₄	150	20	(94)																																																																																																						
	TfOH (5 mol %), C ₇ H ₈ , 85°, overnight		134																																																																																																									

Catalyst	<i>x</i>	Temp (°)	
—	0	130	(—)
(NH ₄) ₂ SO ₄	20	120	(—)
NH ₄ (CH ₃ CO ₂)	20	120	(7)
NH ₄ F	20	120	(tr)
NH ₄ Cl	20	120	(5)
NH ₄ Br	20	120	(5)
NH ₄ I	20	120	(10)
NH ₄ OTf	20	130	(20)
NH ₄ BF ₄	20	120	(25)
BINOL-P(O)OH	20	130	(33)
NH ₄ PF ₆	20	120	(39)
NH ₄ PF ₆	20	130	(44)
[PhNHMe ₂][B(C ₆ F ₅) ₄]	10	120	(83)
[PhNHMe ₂][B(C ₆ F ₅) ₄]	20	80	(76)
NH ₄ (CF ₃ CO ₂)	20	120	(56)
NH ₄ (CF ₃ CO ₂)	20	130	(74)



Catalyst (*x* mol %), dioxane, 24 h



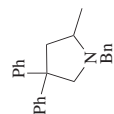
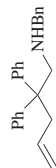
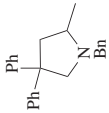
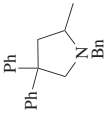
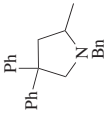


TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)					Refs.		
	Catalyst	x	Additive	y	Solvent	Temp (°)	Time (h)	200	
	—	—	—	—	dioxane	110	1		(tr)
	[Rh(COD)Cl] ₂	0.5	—	—	dioxane	110	1		(tr)
	[Rh(COD) ₂]BF ₄	2.5	Cy-DavePhos	3	dioxane	110	7		(tr)
	PCl ₂	2.5	<i>t</i> -Bu-DavePhos	2.5	dioxane	110	7		(95)
	(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)PAuCl	5	AgOTf	5	dioxane	110	7		(tr)
	[Ir(COE) ₂ Cl] ₂	0.5	—	—	dioxane	110	1		(10)
	[Ir(COD)OMe] ₂	0.5	—	—	dioxane	110	1		(7)
	[Cp*IrCl] ₂	0.5	—	—	dioxane	110	1		(tr)
	[Ir(MeCN) ₂ (COD)]BF ₄	1	—	—	dioxane	110	1		(28)
	[Ir(COD)(PCy ₃ (py))PF ₆]	1	—	—	dioxane	110	1		(10)
	[Ir(COD)Cl] ₂	0.05	—	—	dioxane	110	24		(≤50)
	[Ir(COD)Cl] ₂	0.125	—	—	dioxane	110	3		(95)
	[Ir(COD)Cl] ₂	0.5	—	—	dioxane	110	1		(95)
	[Ir(COD)Cl] ₂	0.5	AgBF ₄	1	dioxane	110	1		(95)
	[Ir(COD)Cl] ₂	1.25	—	—	dioxane	80	7	(95)	
	[Ir(COD)Cl] ₂	1.25	—	—	DCE	80	7	(61)	
	[Ir(COD)Cl] ₂	1.25	—	—	DME	80	7	(76)	
	[Ir(COD)Cl] ₂	1.25	—	—	C ₇ H ₈	80	7	(45)	
	[Ir(COD)Cl] ₂	2.5	—	—	dioxane	40	16	(15)	
	[Ir(COD)Cl] ₂	2.5	—	—	dioxane	40	16	(15)	

 $(\text{RO})_2\text{P}(\text{O})\text{OH}$ (x mol %), solvent, 130°, 20 h	R	x	Solvent	213
	<i>n</i> -Bu	0	dioxane	
	<i>n</i> -Bu	20	dioxane	
	Ph	10	TCE	
	Ph	20	dioxane	
	Ph	20	MeCN	
 Catalyst (x mol %), solvent, 20 h	Catalyst	x	Solvent	213
	117a	20	dioxane	
	117b	10	TCE	
	117c	20	dioxane	
	117c	20	TCE	
	117c	20	C ₇ H ₈	
 Catalyst (2.5 mol %), solvent, 110°, 16 h	Catalyst	x	Solvent	489
	117c	20	NMP	
	117d	10	TCE	
	117e	10	TCE	
	117e	10	TCE	
	117e	20	dioxane	

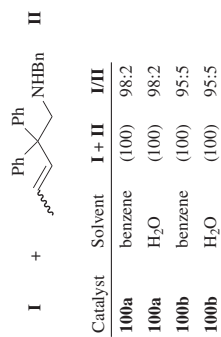
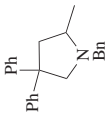
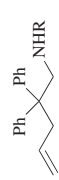
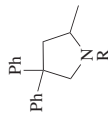
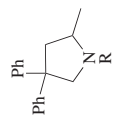


TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
	Catalyst (2.5 mol %), [PhNHMe ₂][B(C ₆ F ₅) ₄] (2.5 mol %), C ₆ D ₆ , 80°		189
		93a 1.6 (100)	189
		93b 17 (97)	513
		93e 1.6 (29)	191
		93f 1.6 (92)	191
		93h 0.7 (93)	189
		93i 8 (80)	513
		93j 26 (97)	513
		93l 27.5 (96)	513
		93m 1.2 (87)	191
		93n 0.7 (100)	191
		93q 0.3 (91)	185
		93r 12 (64)	191
		93s 1 (100)	191
	Au(IPr)Cl (5 mol %), AgOTf (5 mol %), dioxane		208
		R Ac rt 18 (83)	
		Ac 45° 15 (99)	
		PhHNCO rt 18 (96)	
		PhHNCO 45° 15 (93)	
		Chz rt 18 (20)	
		Chz 45° 15 (96)	

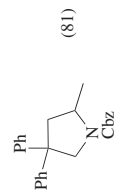
Please refer to the charts preceding the tables for structures indicated by the **bold numbers**.

C17



Au(L)Cl (5 mol %),
AgOTf (5 mol %), solvent

R	L	Solvent	Temp (°)	Time (h)
Boc	P(<i>t</i> -Bu) ₂ (2-PhC ₆ H ₄) ₃	dioxane	60	20 (96)
Cbz	PPh ₃	toluene	100	24 (59)
Cbz	PPh ₃	MeCN	100	24 (49)
Cbz	PPh ₃	DCE	100	24 (33)
Cbz	PPh ₃	dioxane	100	24 (75)
Cbz	P(4-MeOC ₆ H ₄) ₃	dioxane	100	24 (70)
Cbz	P(4-CF ₃ C ₆ H ₄) ₃	dioxane	100	24 (23)
Cbz	PMe ₂ Ph	dioxane	100	24 (7)
Cbz	P(<i>t</i> -Bu) ₂ (2-PhC ₆ H ₄) ₃	dioxane	60	18 (97)
Cbz	P(<i>t</i> -Bu) ₂ (2-PhC ₆ H ₄) ₃	dioxane	100	24 (98)
Moz	P(<i>t</i> -Bu) ₂ (2-PhC ₆ H ₄) ₃	dioxane	60	16 (95)
Fmoc	P(<i>t</i> -Bu) ₂ (2-PhC ₆ H ₄) ₃	dioxane	60	24 (93)



THOH (5 mol %), C₇H₈, 85°, overnight

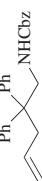


TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
C17	Catalyst (x mol %), dioxane		90
R	Catalyst	x	Time (h)
Ph	[Ir(COD)Cl] ₂	1.25	7 (95)
4-FC ₆ H ₄	[Ir(COD)Cl] ₂	1.25	7 (95)
4-MeOC ₆ H ₄	[Ir(COD)Cl] ₂	0.25	7 (94)
c-C ₆ H ₁₁ CH ₂	[Ir(COD)Cl] ₂	0.5	7 (88)
4-MeC ₆ H ₄	[Ir(COD)Cl] ₂	0.5	7 (96)
4-CF ₃ C ₆ H ₄	[Ir(COD)Cl] ₂	2.5	24 (67)
Bn	[Ir(COD)Cl] ₂	0.13	3 (88)
Bn	[Ir(COD)Cl] ₂	0.5	3 (95)
Bn	[Ir(COE) ₂ Cl] ₂	0.5	3 (10)
Bn	[Ir(COD)OMe] ₂	0.5	3 (7)
Bn	[Cp*IrCl] ₂	0.5	3 (tr)
Bn	[Rh(COD)Cl] ₂	0.5	3 (tr)
Bn	[Ir(COD) ₂ BF ₄]	1	3 (tr)
Bn	[Ir(COD)(MeCN) ₂][BF ₄]	1	3 (28)
Bn	[Ir(COD)PCy ₃ (py)]PF ₆	1	3 (10)
4-ClC ₆ H ₄ CH ₂	[Ir(COD)Cl] ₂	0.5	3 (85)
4-MeOC ₆ H ₄ CH ₂	[Ir(COD)Cl] ₂	1.25	3 (89)
4-MeO ₂ CC ₆ H ₄ CH ₂	[Ir(COD)Cl] ₂	0.5	3 (87)

	120 (150 mg/1 mmol amine), [PhNHMe ₂][B(C ₆ F ₅) ₄] (17 mol %), C ₇ H ₈ , 110°, 8 h	Run 1 (74) 2 (83) 3 (86) 4 (86) 5 (86) 6 (83) 1 ^k (70)
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520

	Catalyst (2.5 mol %), [PhNHMe ₂][B(C ₆ F ₅) ₄] (2.5 mol %), benzene, 80°	Catalyst 93a 93h	Time (h) 96 (95) 24 (96)
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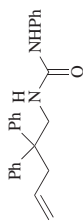
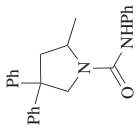
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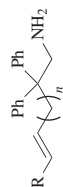
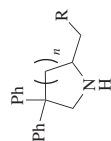
407

	Au(IPr)Cl (x mol %), AgOTf (x mol %), solvent, rt, 24 h	R Et Et Et 4-BrC ₆ H ₄ 4-MeOC ₆ H ₄ 4-AcC ₆ H ₄	x 1 5 5 5 5 5	Solvent MeOH dioxane MeOH/H ₂ O dioxane dioxane dioxane	(97) (91) (95) (99) (100) (100)
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208

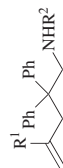
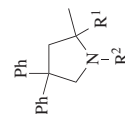
TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.																																																														
Please refer to the charts preceding the tables for structures indicated by the bold numbers.		Au(L)Cl (5 mol %), AgOTf (5 mol %), dioxane, rt	<table> <tr> <th>L</th><th>Time (h)</th></tr> <tr> <td>111a</td><td>24 (3)</td></tr> <tr> <td>111c</td><td>16 (98)</td></tr> <tr> <td>121a</td><td>24 (3)</td></tr> <tr> <td>121b</td><td>24 (87)</td></tr> <tr> <td>121c</td><td>24 (tr)</td></tr> <tr> <td>121d</td><td>24 (82)</td></tr> <tr> <td>122</td><td>24 (tr)</td></tr> </table>	L	Time (h)	111a	24 (3)	111c	16 (98)	121a	24 (3)	121b	24 (87)	121c	24 (tr)	121d	24 (82)	122	24 (tr)																																														
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		Catalyst (2.5 mol %), [PhNHMe ₂][B(C ₆ F ₅) ₄] (2.5 mol %), C ₆ D ₆ , 80°																																																															
		<table> <tr> <th>R</th><th>Catalyst</th><th>Time (h)</th></tr> <tr> <td>2-furanyl</td><td>93a</td><td>6 (99)</td></tr> <tr> <td>2-furanyl</td><td>93b</td><td>15 (97)</td></tr> <tr> <td>2-furanyl</td><td>93e</td><td>30 (70)</td></tr> <tr> <td>2-furanyl</td><td>93f</td><td>6 (100)</td></tr> <tr> <td>2-furanyl</td><td>93h</td><td>4 (96)</td></tr> <tr> <td>2-furanyl</td><td>93i</td><td>13 (94)</td></tr> <tr> <td>2-furanyl</td><td>93j</td><td>21 (100)</td></tr> <tr> <td>2-furanyl</td><td>93l</td><td>18 (99)</td></tr> <tr> <td>2-furanyl</td><td>93m</td><td>29 (100)</td></tr> <tr> <td>2-furanyl</td><td>93n</td><td>4 (100)</td></tr> <tr> <td>2-furanyl</td><td>93o</td><td>9 (99)</td></tr> <tr> <td>2-furanyl</td><td>93q</td><td>2.5 (95)</td></tr> <tr> <td>2-furanyl</td><td>93q</td><td>7 (99)</td></tr> <tr> <td>2-furanyl</td><td>93r</td><td>30 (100)</td></tr> <tr> <td>2-furanyl</td><td>93s</td><td>2.5 (100)</td></tr> <tr> <td>2-furanyl</td><td>93t</td><td>7 (99)</td></tr> <tr> <td>2-furanyl</td><td>93u</td><td>5 (99)</td></tr> <tr> <td>2-thienyl</td><td>93a</td><td>0.3 (100)</td></tr> <tr> <td>2-thienyl</td><td>93b</td><td>4.5 (100)</td></tr> <tr> <td>2-thienyl</td><td>93h</td><td>5 (100)</td></tr> </table>	R	Catalyst	Time (h)	2-furanyl	93a	6 (99)	2-furanyl	93b	15 (97)	2-furanyl	93e	30 (70)	2-furanyl	93f	6 (100)	2-furanyl	93h	4 (96)	2-furanyl	93i	13 (94)	2-furanyl	93j	21 (100)	2-furanyl	93l	18 (99)	2-furanyl	93m	29 (100)	2-furanyl	93n	4 (100)	2-furanyl	93o	9 (99)	2-furanyl	93q	2.5 (95)	2-furanyl	93q	7 (99)	2-furanyl	93r	30 (100)	2-furanyl	93s	2.5 (100)	2-furanyl	93t	7 (99)	2-furanyl	93u	5 (99)	2-thienyl	93a	0.3 (100)	2-thienyl	93b	4.5 (100)	2-thienyl	93h	5 (100)
R	Catalyst	Time (h)																																																															
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C₁₇₋₂₃Catalyst (10 mol %), C₆D₆

2-thienyl	93i	6.5	(97)	513
2-thienyl	93l	8.5	(100)	513
2-thienyl	93q	0.1	(97)	185
2-pyridyl	93a	504	(100)	185
2-pyridyl	93q	432	(96)	185

<i>n</i>	R	Catalyst	Temp (°)	Time (h)	
1	H	25a	rt	0.25	(94)
1	H	25b	rt	0.25	(94)
1	H	25c	rt	0.25	(93)
1	H	25d	rt	0.25	(95)
1	Me	25a	65	17	(86)
1	Me	25b	65	18	(95)
1	Me	25c	65	17	(95)
1	Me	25d	65	18	(95)
1	Ph	25a	rt	17	(89)
1	Ph	25b	rt	0.25	(95)
1	Ph	25c	rt	0.25	(95)
1	Ph	25d	rt	6	(99)
2	H	25a	65	0.8	(86)
2	H	25b	65	0.8	(95)
2	H	25c	65	0.8	(95)
2	H	25d	65	1.8	(95)
3	H	25a	110	16	(92)
3	H	25b	110	21	(85)
3	H	25c	110	19	(82)
3	H	25d	110	30	(81)

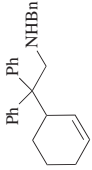
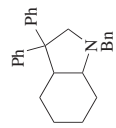
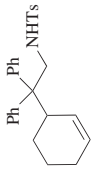
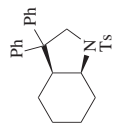
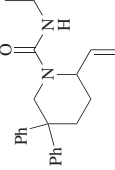
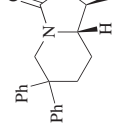
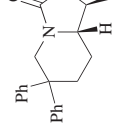
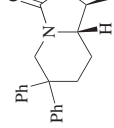
C₁₇₋₁₈(Ph₃P)AuCl (5 mol %),
AgOTf (5 mol %), C₇H₈, 85°

R ¹	R ²	Time (h)	
H	Ac	48	(—)
H	Ns	48	(99)
H	Ts	17	(96)
Me	Ts	15	(91)

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TABLE 2A. HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[\text{Ir}(\text{COD})\text{Cl}]_2$ (5 mol %), dioxane, 110°, 48 h	 (88) ^c	90
	$(\text{Ph}_3\text{P})\text{AuCl}$ (5 mol %), AgOTf (5 mol %), C_7H_8 , 85°, 15 h	 (95)	133
	$(\text{IPr})\text{AuCl}$ (5 mol %), additive (5 mol %), DCM, rt	 (52)	522
		 (66)	(48)
		 (98)	(98)

^a Conversion was >95% based on NMR spectroscopy.

^b The product was isolated as the *N*-benzoyl derivative.

^c The dr was not reported.

^d The reaction was carried out in the presence of 3 eq *n*-propylamine.

^e The product was isolated as the *N*-acetyl derivative.

^f Using racemic starting material, the relative product configuration is shown.

^g The hydrochloride salt was used.

^h The product was isolated as the *N*-tosyl derivative.

ⁱ The yield given is the isolated yield after deprotection of the MOM group.

^j The product was isolated as the *N*-trifluoroacetamide.

^k The catalyst was stored for 130 days before use.

TABLE 2B. HYDROAMINATION/CYCLIZATION OF VINYL ARENES

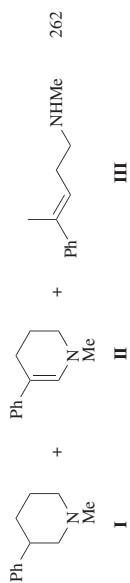
Arene	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																											
 C ₁₀	Acid (20 mol %), Pd(PPh ₃) ₄ (x mol %), C ₇ H ₈	<table><thead><tr><th>R</th><th>Acid</th><th>x</th><th>Temp (°)</th><th>Time (h)</th><th></th></tr></thead><tbody><tr><td>H</td><td>TfOH</td><td>5</td><td>100</td><td>26</td><td>(—)</td></tr><tr><td>H</td><td>H₂SO₄</td><td>0</td><td>100</td><td>24</td><td>(41)</td></tr><tr><td>Ac</td><td>TsOH</td><td>0</td><td>100</td><td>24</td><td>(—)</td></tr><tr><td>Ac</td><td>H₂SO₄</td><td>0</td><td>100</td><td>24</td><td>(32)</td></tr><tr><td>Ns</td><td>TfOH</td><td>0</td><td>100</td><td>4</td><td>(95)</td></tr><tr><td>Ns</td><td>H₂SO₄</td><td>0</td><td>100</td><td>100</td><td>(58)</td></tr><tr><td>Ts</td><td>—</td><td>0</td><td>100</td><td>24</td><td>(—)</td></tr><tr><td>Ts</td><td>TfOH</td><td>0</td><td>rt</td><td>72</td><td>(65)</td></tr><tr><td>Ts</td><td>TfOH</td><td>0</td><td>100</td><td>2</td><td>(98)</td></tr><tr><td>Ts</td><td>TfOH</td><td>5</td><td>100</td><td>2</td><td>(92)</td></tr><tr><td>Cbz</td><td>TfOH</td><td>0</td><td>100</td><td>24</td><td>(—)</td></tr><tr><td>Cbz</td><td>H₂SO₄</td><td>0</td><td>100</td><td>24</td><td>(49)</td></tr><tr><td>Fmoc</td><td>TfOH</td><td>0</td><td>100</td><td>26</td><td>(100)</td></tr><tr><td>Fmoc</td><td>H₂SO₄</td><td>0</td><td>100</td><td>24</td><td>(37)</td></tr></tbody></table>	R	Acid	x	Temp (°)	Time (h)		H	TfOH	5	100	26	(—)	H	H ₂ SO ₄	0	100	24	(41)	Ac	TsOH	0	100	24	(—)	Ac	H ₂ SO ₄	0	100	24	(32)	Ns	TfOH	0	100	4	(95)	Ns	H ₂ SO ₄	0	100	100	(58)	Ts	—	0	100	24	(—)	Ts	TfOH	0	rt	72	(65)	Ts	TfOH	0	100	2	(98)	Ts	TfOH	5	100	2	(92)	Cbz	TfOH	0	100	24	(—)	Cbz	H ₂ SO ₄	0	100	24	(49)	Fmoc	TfOH	0	100	26	(100)	Fmoc	H ₂ SO ₄	0	100	24	(37)		209
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 C ₁₀₋₁₁	C ₈ F ₁₇ SO ₃ H (5 mol %), perfluorodecalin, C ₇ H ₈ , hexanes, reflux, 1 h	<table><thead><tr><th colspan="2">n</th></tr></thead><tbody><tr><td>1</td><td>(91)</td></tr><tr><td>2</td><td>(88)</td></tr></tbody></table>	n		1	(91)	2	(88)		211																																																																																				
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TABLE 2B. HYDROAMINATION/CYCLIZATION OF VINYL ARENES (Continued)

Arene	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																					
C₁₀₋₁₁	Acid (20 mol %), C ₇ H ₈ , 100°	<table><thead><tr><th><i>n</i></th><th>Ar</th><th>Acid</th><th>Time (h)</th><th></th></tr></thead><tbody><tr><td>1</td><td>Ph</td><td>TfOH</td><td>2</td><td>(83)</td></tr><tr><td>1</td><td>Ph</td><td>H₂SO₄</td><td>4</td><td>(80)</td></tr><tr><td>1</td><td>4-ClC₆H₄</td><td>TfOH</td><td>2</td><td>(88)</td></tr><tr><td>1</td><td>4-ClC₆H₄</td><td>H₂SO₄</td><td>4</td><td>(93)</td></tr><tr><td>1</td><td>4-MeOC₆H₄</td><td>TfOH</td><td>2</td><td>(—)</td></tr><tr><td>1</td><td>4-MeOC₆H₄</td><td>H₂SO₄</td><td>4</td><td>(27)</td></tr><tr><td>1</td><td>4-O₂NC₆H₄</td><td>TfOH</td><td>24</td><td>(—)</td></tr><tr><td>1</td><td>4-O₂NC₆H₄</td><td>H₂SO₄</td><td>24</td><td>(—)</td></tr><tr><td>1</td><td>2-MeC₆H₄</td><td>TfOH</td><td>2</td><td>(81)</td></tr><tr><td>1</td><td>2-MeC₆H₄</td><td>H₂SO₄</td><td>10</td><td>(80)</td></tr><tr><td>1</td><td>3-MeC₆H₄</td><td>TfOH</td><td>2</td><td>(99)</td></tr><tr><td>1</td><td>3-MeC₆H₄</td><td>H₂SO₄</td><td>6</td><td>(90)</td></tr><tr><td>1</td><td>4-MeC₆H₄</td><td>TfOH</td><td>2</td><td>(77)</td></tr><tr><td>1</td><td>4-MeC₆H₄</td><td>H₂SO₄</td><td>4</td><td>(75)</td></tr><tr><td>2</td><td>Ph</td><td>TfOH</td><td>2</td><td>(83)</td></tr><tr><td>2</td><td>Ph</td><td>H₂SO₄</td><td>24</td><td>(80)</td></tr></tbody></table>	<i>n</i>	Ar	Acid	Time (h)		1	Ph	TfOH	2	(83)	1	Ph	H ₂ SO ₄	4	(80)	1	4-ClC ₆ H ₄	TfOH	2	(88)	1	4-ClC ₆ H ₄	H ₂ SO ₄	4	(93)	1	4-MeOC ₆ H ₄	TfOH	2	(—)	1	4-MeOC ₆ H ₄	H ₂ SO ₄	4	(27)	1	4-O ₂ NC ₆ H ₄	TfOH	24	(—)	1	4-O ₂ NC ₆ H ₄	H ₂ SO ₄	24	(—)	1	2-MeC ₆ H ₄	TfOH	2	(81)	1	2-MeC ₆ H ₄	H ₂ SO ₄	10	(80)	1	3-MeC ₆ H ₄	TfOH	2	(99)	1	3-MeC ₆ H ₄	H ₂ SO ₄	6	(90)	1	4-MeC ₆ H ₄	TfOH	2	(77)	1	4-MeC ₆ H ₄	H ₂ SO ₄	4	(75)	2	Ph	TfOH	2	(83)	2	Ph	H ₂ SO ₄	24	(80)	209
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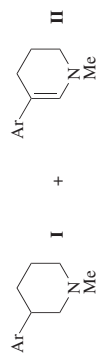
C₁₁

[Rh(COD)₂]BF₄ (5 mol %),
ligand (5 mol %), dioxane, 70°, 24 h



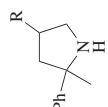
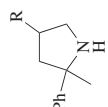
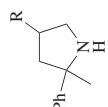
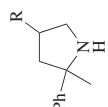
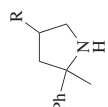
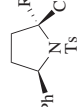
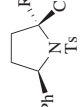
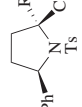
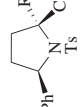
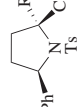
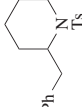
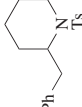
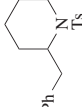
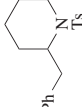
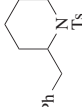
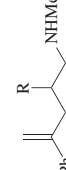
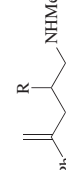
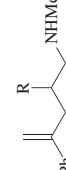
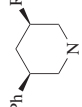
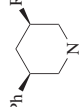
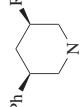
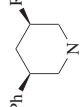
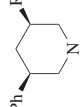
Ligand	I	II	III
DPE-phos	(10)	(12)	(10)
BINAP	(14)	(3)	(—)
DPPF	(44)	(16)	(tr)
XANTPHOS	(tr)	(5)	(41)
DPPP	(—)	(—)	(—)
DPPB	(84)	(7)	(tr)
PPh ₃	(—)	(23)	(58)
PEtPh ₂	(—)	(16)	(33)

[Rh(COD)(DPPB)]BF₄ (5 mol %),
THF



Ar	Temp (°)	Time (h)	I	II
Ph	80	24	(76)	(4)
4-FC ₆ H ₄	80	24	(87)	(3)
4-MeOC ₆ H ₄	80	24	(78)	(1)
4-MeOC ₆ H ₄	70	48	(83)	(1)
3,4-F ₂ C ₆ H ₃	80	72	(71)	(tr)
3,4-(MeO) ₂ C ₆ H ₃	80	24	(82)	(3)

TABLE 2B. HYDROAMINATION/CYCLIZATION OF VINYL ARENES (Continued)

Arene	Conditions	Product(s) and Yield(s) (%)					Refs.
						160	
							
						210, 488	
							
						209	
							
						262	
							

C₁₃

Catalyst (1–5 mol %), C₆D₆

(90)

256

Catalyst	Temp (°)	TOF (h ⁻¹)
[Me ₂ Si(C ₃ Me ₄)(<i>i</i> -BuN)]Th(NMe ₂) ₂	60	1.3
[Me ₂ Si(C ₃ Me ₄)(<i>i</i> -BuN)]U(NMe ₂) ₂	60	0.9
(Me ₂ Si(C ₃ Me ₄) ₂)Th(N(TMS) ₂) ₂	100	5.8
(Me ₂ Si(C ₃ Me ₄) ₂)U(N(TMS) ₂) ₂	100	7.0
Cp* ₂ Th(N(TMS) ₂) ₂	100	0.2
Cp* ₂ U(N(TMS) ₂) ₂	100	0.5

C₁₃–23

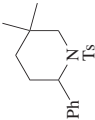
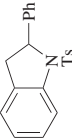
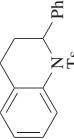
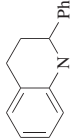
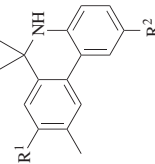
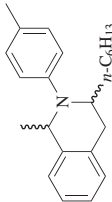
Catalyst (x mol %), C₆D₆

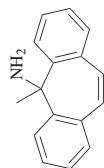
18 (x mol %), C₇D₈, 150°

261, 68

R	Catalyst	x	Temp	Time (h)	
Me	19b	10	rt	0.16	(80) 469
Me	19c	10	rt	0.16	(80) 469
Me	23a	10	100°	7	(99) 473
Me	23b	10	100°	12	(99) 473
Me	23c	10	100°	24	(98) 473
Me	73a	3	60°	9	(98) 259
Me	73c	3	60°	6.5	(98) 259
Ph	23a	10	rt	2	(99) 473
Ph	23b	10	rt	1.5	(99) 473
Ph	23c	10	rt	2	(99) 473
Ph	73a	1	60°	3	(98) 259
Ph	73c	1	60°	2.5	(98) 259

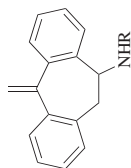
TABLE 2B. HYDROAMINATION/CYCLIZATION OF VINYL ARENES (Continued)

Arene	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the bold numbers .			
C ₁₃	FeCl ₃ •6H ₂ O (10 mol %), DCE, 80°, 2 h	 (94)	204
C ₁₄	TfOH (20 mol %), C ₇ H ₈ , 80°, 1 h	 (75)	212
C ₁₅	TfOH (20 mol %), C ₇ H ₈ , 80°, 1 h	 (85)	212
C ₁₆₋₁₇	C ₈ F ₁₇ SO ₃ H (5 mol %), perfluorodecalin, C ₇ H ₈ , hexanes, reflux, 1 h	 (83)	211
	TfOH (20 mol %), C ₇ H ₈ , 100°, 12 h	 R ¹ R ² H F (96) H Me (44) Me H (72)	263
C ₂₃	TiCl ₄ (20 mol %), C ₇ H ₈ , 150°	 (63) dr = 4:1	247



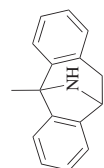
t-BuOK (1 eq), DMSO, 125°, 18 h

523



123 (x mol %), C₆D₆, 2 h

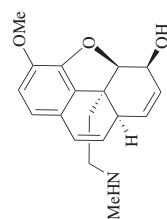
254



(80)

R	x	Temp (°)
H	1	40 (98)
Me	6	50 (94)

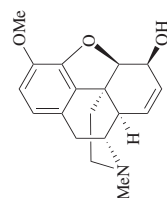
419



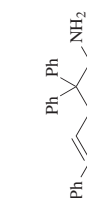
C₂₃

LDA (6 eq), 150W lamp,
THF, -78° to rt, 6 h

358



(57)



Catalyst (10 mol %), C₆D₆, rt

257

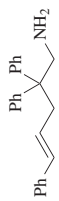
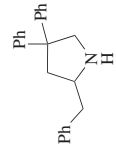
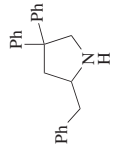
Catalyst	Time (h)	
25a	17	(89)
25b	0.25	(95)
25c	0.25	(95)
25d	6	(99)

Catalyst	Temp (°)	
Ti(NMe ₂) ₄	110	(77)
Zr(NMe ₂) ₄	110	(100)
Ind ₂ Ti(NMe ₂) ₂	105	(57) ^a
Ind ₂ Zr(NMe ₂) ₂	105	(45) ^a
Ind ₂ Hf(NMe ₂) ₂	105	(63) ^a

Catalyst (5 mol %), C₇D₈, 96 h

67
69
178
178
178

TABLE 2B. HYDROAMINATION/CYCLIZATION OF VINYL ARENES (Continued)

Arene	Conditions	Product(s) and Yield(s) (%)				Refs.
	Catalyst (x mol %), C ₇ D ₈ , 110°		Catalyst	x	Time (h)	
			36	5	96	(38)
			36	10	192	(48)
			45	10	96	(—)
	81b (2.5 mol %), C ₇ H ₈ , 110°, 96 h	 (55)				69

^a The product was isolated as the *N*-benzoyl derivative.

TABLE 2C. HYDROAMINATION/CYCLIZATION OF AMINODIENES

Aminodiene

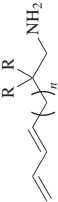
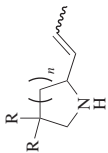
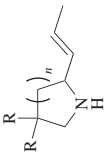
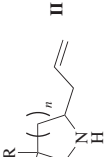
Conditions

Product(s) and Yield(s) (%)

Refs.

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

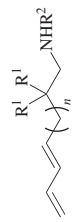
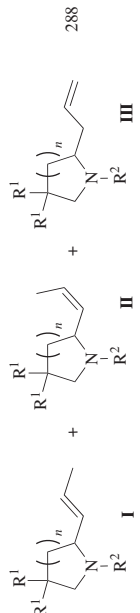
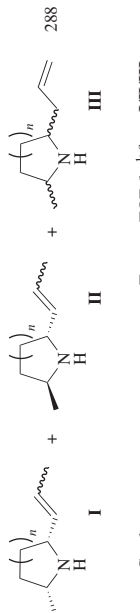
C₇₋₁₀

	Catalyst (3–5 mol %), C₆D₆		<i>n</i> R Catalyst Temp TOF (h⁻¹)^a (<i>E</i>)/(<i>Z</i>)	303 303 303 303 303 230 230 303 303 230
			1 H 3a rt 0.07 41:59	303
			1 H 3a 60° 10 43:57	303
			1 H 124 rt 0.02 38:62	303
			1 H 124 60° 0.9 27:73	303
			2 H 3a rt 0.008 94:6	230
			2 H 3a 60° 1 57:43	230
			2 Me 3a 60° 0.2 47:63	230
			2 Me 3a 60° 10 57:43	303
			2 Me 3b rt 0.03 60:40	303
			2 Me 124 60° 4 27:73	230
Catalyst (3–10 mol %), C₆D₆	<i>n</i> R Catalyst Temp (°) TOF (h⁻¹)^a I/II	 	256	
			1 H [Me₂Si(C₃Me₄)(<i>i</i>-Bu)N][Th(NMe₂)₂] 60 3.0 2:98	
			1 H [Me₂Si(C₃Me₄)(<i>i</i>-Bu)N][U(NMe₂)₂] 60 5.5 7:93	
			1 H [Me₂Si(C₃Me₄)₂][Th(N(TMS))₂] 60 1.9 29:71	
			1 H [Me₂Si(C₃Me₄)₂]UBn₂ 60 0.8 85:15	
			1 H Cp*₂Th(N(TMS))₂ 80 0.2 24:76	
			1 H Cp*₂U(N(TMS))₂ 80 0.2 65:35	
			2 Me [Me₂Si(C₃Me₄)(<i>i</i>-Bu)N][Th(NMe₂)₂] 60 6.1 7:93	
			2 Me [Me₂Si(C₃Me₄)(<i>i</i>-Bu)N][U(NMe₂)₂] 60 19.9 19:81	

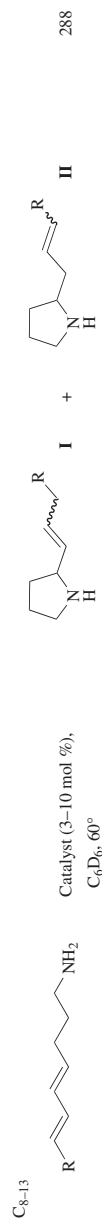
Please refer to the charts preceding the tables for structures indicated by the **bold numbers**.

C₇₋₁₀

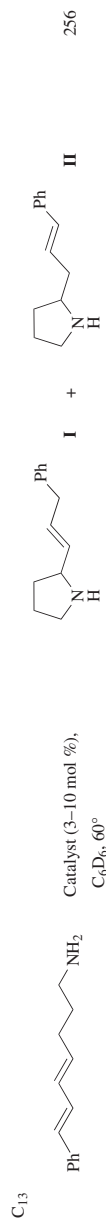
TABLE 2C. HYDROAMINATION/CYCLIZATION OF AMINODIENES (Continued)

Aminodiene	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₇₋₁₀	Catalyst (3–10 mol %), C ₆ D ₆	 288	
 C ₈₋₉	Catalyst (5 mol %), C ₆ D ₆	 288	

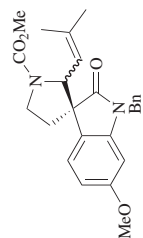
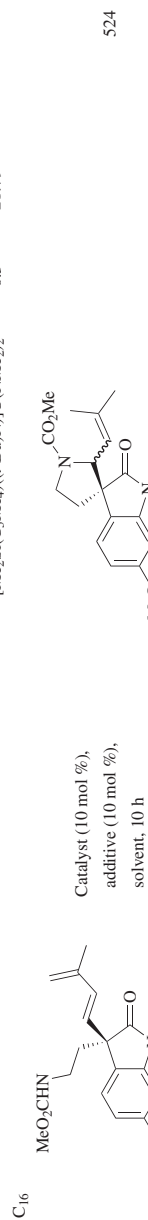
Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.



R	Catalyst	TOF (h ⁻¹)	I + II	(E)/(Z) I	(E)/(Z) II	I/II
Me	$Cp^*_2LaCH(TMS)_2$	1.8	(94)	(E) only	76:24	38:62
Me	$Cp^*_2SmCH(TMS)_2$	0.02	(93)	(E) only	93:7	23:77
Ph	$Cp^*_2LaCH(TMS)_2$	89	(92)	—	>94:6	II only
Ph	$Cp^*_2SmCH(TMS)_2$	2.3	(90)	—	>94:6	II only

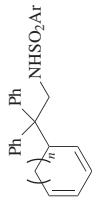
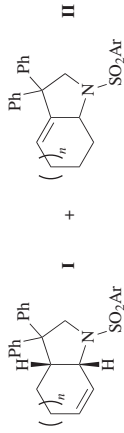


Catalyst	TOF (h ⁻¹) ^a	I/II
$[Me_2Si(C_5Me_4)((t-Bu)N)]Th(NMe_2)_2$	0.02	31:69
$[Me_2Si(C_5Me_4)((t-Bu)N)]U(NMe_2)_2$	0.3	21:79



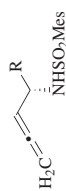
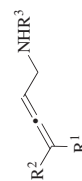
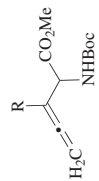
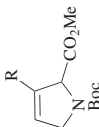
Catalyst	Additive	Solvent	Temp (°)	dr
$Bi(OTf)_3$	—	xylene	130	(49) 3:1
$Bi(OTf)_3$	$[Cu(MeCN)_4]PF_6$	dioxane	50	(66) 3:1
$Bi(OTf)_3$	KPF_6	dioxane	50	(83) 3:1
$Hf(OTf)_4$	—	xylene	130	(41) 2:1
$Hf(OTf)_4$	KPF_6	dioxane	50	(57) 3:1
$Sc(OTf)_2$	KPF_6	dioxane	50	(58) 3:1
$Zn(OTf)_2$	KPF_6	dioxane	50	(0) 3:1

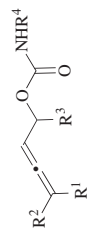
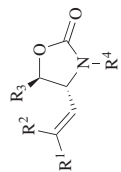
TABLE 2C. HYDROAMINATION/CYCLIZATION OF AMINODIENES (Continued)

Aminodiene	Conditions	Product(s) and Yield(s) (%)	Refs.																																																
	(Ph₃P)/AuCl (5 mol %), AgOTf (10 mol %), C₇H₈, 85°, 18 h	I + II 	289																																																
		<table> <tr> <th><i>n</i></th><th>Ar</th><th>I</th><th>II</th></tr> <tr> <td>1</td><td>Ph</td><td>(88)</td><td>(—)</td></tr> <tr> <td>1</td><td>4-FC₆H₄</td><td>(80)</td><td>(—)</td></tr> <tr> <td>1</td><td>3-O₂NC₆H₄</td><td>(84)</td><td>(—)</td></tr> <tr> <td>1</td><td>4-MeOC₆H₄</td><td>(85)</td><td>(—)</td></tr> <tr> <td>1</td><td>4-MeC₆H₄</td><td>(88)</td><td>(—)</td></tr> <tr> <td>1</td><td>Mes</td><td>(0)</td><td>(—)</td></tr> <tr> <td>2</td><td>Ph</td><td>(86)</td><td>(—)</td></tr> <tr> <td>2</td><td>4-FC₆H₄</td><td>(—)</td><td>(82)</td></tr> <tr> <td>2</td><td>4-O₂NC₆H₄</td><td>(78)</td><td>(—)</td></tr> <tr> <td>2</td><td>4-MeOC₆H₄</td><td>(84)</td><td>(—)</td></tr> <tr> <td>2</td><td>4-MeC₆H₄</td><td>(83)</td><td>(—)</td></tr> </table>	<i>n</i>	Ar	I	II	1	Ph	(88)	(—)	1	4-FC ₆ H ₄	(80)	(—)	1	3-O ₂ NC ₆ H ₄	(84)	(—)	1	4-MeOC ₆ H ₄	(85)	(—)	1	4-MeC ₆ H ₄	(88)	(—)	1	Mes	(0)	(—)	2	Ph	(86)	(—)	2	4-FC ₆ H ₄	(—)	(82)	2	4-O ₂ NC ₆ H ₄	(78)	(—)	2	4-MeOC ₆ H ₄	(84)	(—)	2	4-MeC ₆ H ₄	(83)	(—)	
<i>n</i>	Ar	I	II																																																
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1	4-FC ₆ H ₄	(80)	(—)																																																
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2	4-MeC ₆ H ₄	(83)	(—)																																																

^a Greater than 95% conversion was observed.

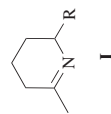
TABLE 2D. HYDROAMINATION/CYCLIZATION OF AMINOALLENES

Aminoallene	Conditions	Product(s) and Yield(s) (%)	Refs.																																																												
Please refer to the charts preceding the tables for structures indicated by the bold numbers.																																																															
C ₄₋₈ 	K ₂ CO ₃ (x eq), solvent	 525																																																													
	<table><tr><th>R</th><th>x</th><th>Solvent</th><th>Temp (°)</th><th>Time (h)</th><th></th></tr><tr><td>H</td><td>1</td><td>DMF</td><td>153</td><td>1</td><td>(77)</td></tr><tr><td><i>i</i>-Pr</td><td>0.1</td><td>DMF</td><td>153</td><td>120</td><td>(47)</td></tr><tr><td><i>i</i>-Pr</td><td>0.5</td><td>DMF</td><td>153</td><td>24</td><td>(71)</td></tr><tr><td><i>i</i>-Pr</td><td>1</td><td>NMP</td><td>180</td><td>3</td><td>(80)</td></tr><tr><td><i>i</i>-Pr</td><td>1</td><td>DMF</td><td>153</td><td>6</td><td>(84)</td></tr><tr><td><i>i</i>-Pr</td><td>1</td><td>DMSO</td><td>180</td><td>3</td><td>(61)</td></tr><tr><td><i>i</i>-Pr</td><td>1</td><td>DMI</td><td>180</td><td>1</td><td>(75)</td></tr><tr><td>(<i>S</i>)-<i>s</i>-Bu</td><td>1</td><td>DMF</td><td>153</td><td>72</td><td>(60)</td></tr><tr><td><i>t</i>-Bu</td><td>1</td><td>DMF</td><td>153</td><td>20</td><td>(78)</td></tr></table>	R	x	Solvent	Temp (°)	Time (h)		H	1	DMF	153	1	(77)	<i>i</i> -Pr	0.1	DMF	153	120	(47)	<i>i</i> -Pr	0.5	DMF	153	24	(71)	<i>i</i> -Pr	1	NMP	180	3	(80)	<i>i</i> -Pr	1	DMF	153	6	(84)	<i>i</i> -Pr	1	DMSO	180	3	(61)	<i>i</i> -Pr	1	DMI	180	1	(75)	(<i>S</i>)- <i>s</i> -Bu	1	DMF	153	72	(60)	<i>t</i> -Bu	1	DMF	153	20	(78)		
R	x	Solvent	Temp (°)	Time (h)																																																											
H	1	DMF	153	1	(77)																																																										
<i>i</i> -Pr	0.1	DMF	153	120	(47)																																																										
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(<i>S</i>)- <i>s</i> -Bu	1	DMF	153	72	(60)																																																										
<i>t</i> -Bu	1	DMF	153	20	(78)																																																										
C ₄₋₉ 	AgBF ₄ (5 mol %), CHCl ₃ , rt, 5 h	 526																																																													
C ₅₋₆ 	Catalyst (5 mol %), additive (5 mol %), solvent	 527																																																													
	<table><tr><th>R</th><th>Catalyst</th><th>Additive</th><th>Solvent</th><th>Temp</th><th></th></tr><tr><td>H</td><td>AuCl₃</td><td>—</td><td>MeCN</td><td>60°</td><td>(65)</td></tr><tr><td>AcOCH₂</td><td>Ph₃PAuCl</td><td>AgBF₄</td><td>DCM</td><td>rt</td><td>(86)</td></tr></table>	R	Catalyst	Additive	Solvent	Temp		H	AuCl ₃	—	MeCN	60°	(65)	AcOCH ₂	Ph ₃ PAuCl	AgBF ₄	DCM	rt	(86)																																												
R	Catalyst	Additive	Solvent	Temp																																																											
H	AuCl ₃	—	MeCN	60°	(65)																																																										
AcOCH ₂	Ph ₃ PAuCl	AgBF ₄	DCM	rt	(86)																																																										

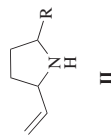
C₅₋₉Catalyst (10 mol %),
base (10 mol %), solvent

529

R ¹	R ²	R ³	R ⁴	Catalyst	Base	Solvent	Temp (°)	Time (h)	dr
H	H	H	Ts	AgNCO	Et ₃ N	benzene	50	6	(78) —
H	H	Et	Ts	AgOTf	Et ₃ N	benzene	50	6	(74) 1.5:1
H	H	Et	Ts	AgOTf	Et ₃ N	THF	67	23	(75) 1.5:1
H	H	Et	Ac	AgNCO	<i>t</i> -BuOK	benzene	80	49	(34) 3.8:1
Me	H	Me	Ts	AgNCO	Et ₃ N	benzene	50	5	(91) 1.8:1
H	H	<i>n</i> -Pr	Ts	CuCl	Et ₃ N	THF	67	19	(tr) —
H	H	<i>n</i> -Pr	Ts	AgNCO	Et ₃ N	benzene	50	25	(73) 1.8:1
H	H	<i>i</i> -Pr	Ts	AgOTf	Et ₃ N	benzene	50	43	(74) 7.1:1
H	H	<i>t</i> -Bu	Ts	AgOTf	Et ₃ N	benzene	80	20	(55) >30:1
Me	Me	Et	Ts	AgOTf	Et ₃ N	benzene	50	32	(57) 4.9:1

C₆₋₇Cp*₂LaCH(TMS)₂ (2 mol %),
C₆D₆

I

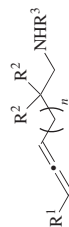


II

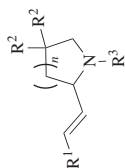
R	I + II	I/II
H	(91)	90:10
Me	(95)	87:13

298

C₆-18



Catalyst (5 mol %), DCM, rt

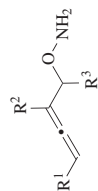
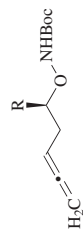


313

<i>n</i>	R ¹	R ²	R ³	Catalyst	Time (h)
1	H	H	Bn	CuCl	24 (90)
1	H	H	Bn	CuBr	24 (99)
1	H	H	Bn	CuI	24 (98)
1	H	H	Bn	CuF ₂	24 (tr)
1	H	H	Bn	CuCl ₂	24 (99)
1	H	H	Bn	Cu(OTf) ₂	24 (98)
1	H	H	Bn	Cu(OTf) ₂ , DPPE	24 (tr)
1	H	H	Bn	(IMes)CuCl	24 (tr)
1	H	H	Bn	AgOTf	3 (98)
1	H	H	Bn	AuCl ₃	72 (98)
1	H	H	Ts	Cu(OTf) ₂	24 (tr)
1	H	H	Bz	Cu(OTf) ₂	24 (tr)
1	<i>n</i> -Pr	H	Bn	Cu(OTf) ₂	24 (88)
1	H	Ph	CBz	Cu(OTf) ₂	24 (tr)
1	H	Ph	H	Cu(OTf) ₂	24 (88)
2	H	H	Bn	Cu(OTf) ₂	48 (17)

TABLE 2D. HYDROAMINATION/CYCLIZATION OF AMINOALLENES (Continued)

Aminoallene	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																																
C₆₋₁₂	PdCl₂ (5 mol %), 125 (x mol %), maleic anhydride (10 mol %), NaOAc (1 eq), O₂ (1 atm), <i>i</i>-PrOH	319																																																																																																	
	<table> <tr> <th><i>n</i></th><th>R¹</th><th>R²</th><th>R³</th><th>R⁴</th><th>R⁵</th><th><i>x</i></th><th>Temp (°)</th></tr> <tr> <td>1</td><td>H</td><td>H</td><td>H</td><td>H</td><td>Ts</td><td>20</td><td>60 (41)</td></tr> <tr> <td>1</td><td>H</td><td>H</td><td>H</td><td>Me</td><td>Ts</td><td>10</td><td>60 (69)</td></tr> <tr> <td>1</td><td>Me</td><td>H</td><td>H</td><td>H</td><td>Ts</td><td>20</td><td>60 (82)</td></tr> <tr> <td>1</td><td>Me</td><td>H</td><td>H</td><td>H</td><td>Ns</td><td>20</td><td>60 (20)</td></tr> <tr> <td>1</td><td>Me</td><td>Me</td><td>H</td><td>H</td><td>Ts</td><td>20</td><td>60 (85)</td></tr> <tr> <td>1</td><td>Me</td><td>H</td><td>Me</td><td>H</td><td>Ts</td><td>10</td><td>50 (67)</td></tr> <tr> <td>1</td><td><i>i</i>-Pr</td><td>H</td><td>H</td><td>H</td><td>Ts</td><td>10</td><td>60 (71)</td></tr> <tr> <td>1</td><td>Me</td><td>Me</td><td>Me</td><td>H</td><td>Ts</td><td>10</td><td>60 (78)</td></tr> <tr> <td>1</td><td>H</td><td>H</td><td>H</td><td><i>n</i>-C₃H₁₁</td><td>Ts</td><td>10</td><td>60 (52)</td></tr> <tr> <td>1</td><td><i>n</i>-C₃H₁₁</td><td>H</td><td>H</td><td>H</td><td>Ts</td><td>20</td><td>60 (72)</td></tr> <tr> <td>2</td><td><i>n</i>-C₃H₁₁</td><td>H</td><td>H</td><td>H</td><td>Ts</td><td>20</td><td>75 (61)</td></tr> </table>	<i>n</i>	R ¹	R ²	R ³	R ⁴	R ⁵	<i>x</i>	Temp (°)	1	H	H	H	H	Ts	20	60 (41)	1	H	H	H	Me	Ts	10	60 (69)	1	Me	H	H	H	Ts	20	60 (82)	1	Me	H	H	H	Ns	20	60 (20)	1	Me	Me	H	H	Ts	20	60 (85)	1	Me	H	Me	H	Ts	10	50 (67)	1	<i>i</i> -Pr	H	H	H	Ts	10	60 (71)	1	Me	Me	Me	H	Ts	10	60 (78)	1	H	H	H	<i>n</i> -C ₃ H ₁₁	Ts	10	60 (52)	1	<i>n</i> -C ₃ H ₁₁	H	H	H	Ts	20	60 (72)	2	<i>n</i> -C ₃ H ₁₁	H	H	H	Ts	20	75 (61)		
<i>n</i>	R ¹	R ²	R ³	R ⁴	R ⁵	<i>x</i>	Temp (°)																																																																																												
1	H	H	H	H	Ts	20	60 (41)																																																																																												
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1	<i>i</i> -Pr	H	H	H	Ts	10	60 (71)																																																																																												
1	Me	Me	Me	H	Ts	10	60 (78)																																																																																												
1	H	H	H	<i>n</i> -C ₃ H ₁₁	Ts	10	60 (52)																																																																																												
1	<i>n</i> -C ₃ H ₁₁	H	H	H	Ts	20	60 (72)																																																																																												
2	<i>n</i> -C ₃ H ₁₁	H	H	H	Ts	20	75 (61)																																																																																												
C₆	Catalyst (x mol %), solvent, rt	<table> <tr> <th>Catalyst</th><th><i>x</i></th><th>Solvent</th><th><i>trans/cis</i></th></tr> <tr> <td>AgNO₃</td><td>20</td><td>acetone/H₂O</td><td>(45) 1.7:1</td></tr> <tr> <td>AgBF₄</td><td>35</td><td>DCM</td><td>(46) 10:1</td></tr> <tr> <td>AgNO₃, SiO₂</td><td>20</td><td>DCM</td><td>(23) 7:1</td></tr> <tr> <td>AgOTf</td><td>20</td><td>acetone/H₂O</td><td>(96) 1:1</td></tr> <tr> <td>AgOTf</td><td>20</td><td>DCM</td><td>(91) 22:1</td></tr> <tr> <td>HBF₄</td><td>30</td><td>DCM</td><td>(0) —</td></tr> </table>	Catalyst	<i>x</i>	Solvent	<i>trans/cis</i>	AgNO ₃	20	acetone/H ₂ O	(45) 1.7:1	AgBF ₄	35	DCM	(46) 10:1	AgNO ₃ , SiO ₂	20	DCM	(23) 7:1	AgOTf	20	acetone/H ₂ O	(96) 1:1	AgOTf	20	DCM	(91) 22:1	HBF ₄	30	DCM	(0) —	531																																																																				
Catalyst	<i>x</i>	Solvent	<i>trans/cis</i>																																																																																																
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HBF ₄	30	DCM	(0) —																																																																																																

C₆₋₁₃C₆₋₈

	R ¹	R ²	R ³	dr
	H	Me	TBSOCH ₂	(78) 95:5
	H	Me	BnOCH ₂	(72) 95:5
	Me	H	Me	(86) 51:49
	<i>i</i> -Pr	H	EtO ₂ C(CH ₂) ₂	(86) —
	<i>n</i> -Bu	Me	BnOCH ₂	(77) —
	Me	H	BnCH ₂	(87) —

[(2,4-(*i*-Bu)₂C₆H₃O₃)₃PAu(PhCN)]⁺
SbF₆[−] (5 mol %), DCM, 2 h, rt

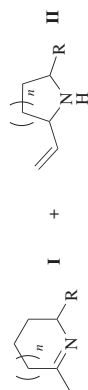
Catalyst (x mol %),
additive (y mol %),
solvent, rt, 8 h

R	Catalyst	x	Additive	y	Solvent	<i>cis</i> / <i>trans</i>	
Me	AgBF ₄	5	—	—	DCM	(40) 4.0:1	532
Me	AgBF ₄	8	—	—	DCM	(63) 8.0:1	532
Me	AgBF ₄	10	—	—	DCM	(90) 13:1	532
Me	AgBF ₄	20	—	—	DCM	(86) 10:1	532
Me	AgBF ₄	40	—	—	DCM	(95) 9.0:1	532
Me	AgBF ₄	50	—	—	DCM	(99) 6.0:1	532
Me	AgBF ₄	60	—	—	DCM	(97) 6.5:1	532
Me	AgBF ₄	80	—	—	DCM	(95) 5.5:1	532
Me	AgBF ₄	100	—	—	DCM	(96) 4.5:1	532
Me	AgNO ₃	20	(Me ₂ N) ₂ C=NH	10	acetone/H ₂ O	(83) 4:1	533
<i>n</i> -Pr	AuCl ₃	5	CaCO ₃	5	DCM/MeCN	(76) 4.0:1	534
<i>n</i> -Pr	Ph ₃ PAuCl	10	AgOTf	10	DCM/MeCN	(86) 2.6:1	534
<i>n</i> -Pr	AgOTf	10	—	—	DCM	(99) 4.6:1	534
<i>n</i> -Pr	AgOTf	20	—	—	DCM	(95) 4.0:1	534
<i>n</i> -Pr	AgNO ₃	5	(Me ₂ N) ₂ C=NH	2.5	acetone/H ₂ O	(30) —	534
<i>n</i> -Pr	AgNO ₃	10	(Me ₂ N) ₂ C=NH	5	acetone/H ₂ O	(93) 4.8:1	534
<i>n</i> -Pr	AgNO ₃	20	(Me ₂ N) ₂ C=NH	10	acetone/H ₂ O	(97) 5.1:1	534
<i>n</i> -Pr	AgNO ₃	40	(Me ₂ N) ₂ C=NH	20	acetone/H ₂ O	(99) 5.0:1	534
<i>n</i> -Pr	AgNO ₃	60	(Me ₂ N) ₂ C=NH	30	acetone/H ₂ O	(99) 5.4:1	534
<i>n</i> -Pr	AgBF ₄	10	—	—	DCM	(94) 11.5:1	534
<i>n</i> -Pr	AgBF ₄	20	—	—	DCM	(99) 9.0:1	534
<i>n</i> -Pr	AgBF ₄	40	—	—	DCM	(99) 4.0:1	534

TABLE 2D. HYDROAMINATION/CYCLIZATION OF AMINOALLENES (Continued)

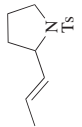
Aminoallene	Conditions	Product(s) and Yield(s) (%)	Refs.
C₆₋₁₂	AuCl ₃ (5 mol %), MeCN, reflux	I + II	535
C₆₋₁₃	Catalyst (x mol %), C ₆ D ₆	I + II + III	298 299 299 299 300 300 299 299 299 299 300 300 299 299 299 299

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₆-14Catalyst (5 mol %), C₆D₆

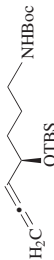
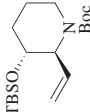
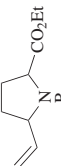
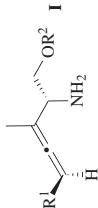
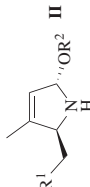
<i>n</i>	R	Catalyst	Temp (°)	Time (h)	I + II	I/II	
1	H	126c	75	5	(100)	I only	299
1	H	126a	rt	24	(18)	I only	300
1	H	126a	75	3	(72)	I only	300
1	H	126e	rt	3	(100)	I only	300
1	H	126b	rt	6.5	(92)	I only	300
1	H	126d	75	18	(10)	I only	300
1	H	126d	135	18	(96)	I only	300
1	H	126f	75	18	(100)	I only	300
1	Ph	126c	75	1	(84)	I only	299
1	4-FC ₆ H ₄	126c	75	10	(93)	I only	299
1	4-MeOC ₆ H ₄	126c	75	1.5	(95)	I only	299
1	2,4-Cl ₂ C ₆ H ₃	126c	75	2	(88)	I only	299
1	4-MeC ₆ H ₄	126c	75	5	(79)	I only	299
1	4-MeC ₆ H ₄	126e	75	0.5	(88)	I only	300
2	4-MeC ₆ H ₄	126c	135	36	(64)	I only	299

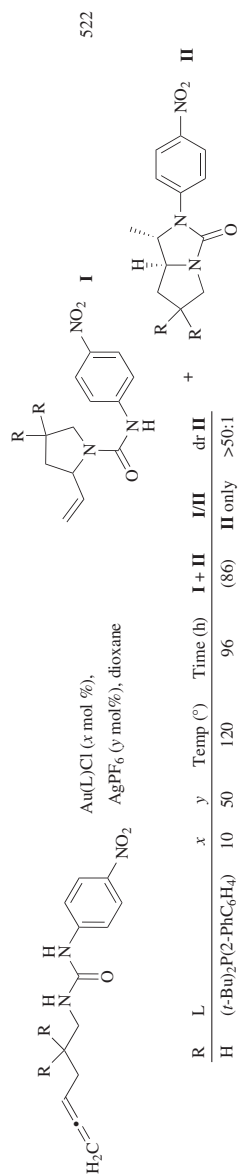
TABLE 2D. HYDROAMINATION/CYCLIZATION OF AMINOALLENES (Continued)

Aminoallene	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the bold numbers .			
 C ₇	Catalyst (5 mol %), ligand (10 mol %), additive (20 mol %), NaOAc (1 eq), solvent, 60°	 319	

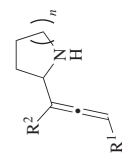
C_{7-8}		Catalyst (α mol %), C_6D_6	n	Catalyst	x	Temp	Time (h)	TOF (h^{-1}) ^d	(<i>E</i>)/(<i>Z</i>)	
			1	$Cp^*_2YCH(TMS)_2$	2	rt	—	31.4	(—)	14:86
			1	$Cp^*_2SmCH(TMS)_2$	2	rt	—	13.0	(—)	12:86
			1	$Cp^*_2LuCH(TMS)_2$	2	rt	—	7.3	(—)	19:81
			1	$Cp^*_2LaCH(TMS)_2$	2	rt	—	4.1	(—)	21:79
			1	18	5	75°	2	—	(96)	1:2
			2	$Cp^*_2YCH(TMS)_2$	2	—	—	—	(—)	20:80
			2	$Cp^*_2SmCH(TMS)_2$	2	—	—	—	(—)	5:95
			2	$Me_2Si(C_3Me_4)(t-BuN)Th(NMe_2)_2$	2	60°	—	0.01	(—)	—
			2	$Me_2Si(C_3Me_4)(t-BuN)U(NMe_2)_2$	2	60°	—	0.1	(—)	—
			2	18	5	75°	12	—	(93)	1:1
C_{7-9}							R		R	(<i>E</i>)/(<i>Z</i>)
				(2-PhC ₆ H ₄)(<i>t</i> -Bu) ₂ PAuCl (5 mol %), AgOTf (5 mol %), dioxane, rt, 3 h				Me	(92)	>50:1
C_7									<i>n</i> -Pr	(98)
				(2-PhC ₆ H ₄)(<i>t</i> -Bu) ₂ PAuCl (5 mol %), AgOTf (5 mol %), dioxane, rt, 3 h					dr 4:1	(90)
				(2-PhC ₆ H ₄)(<i>t</i> -Bu) ₂ PAuCl (5 mol %), AgOTf (5 mol %), dioxane, rt, 3 h						(97)

TABLE 2D. HYDROAMINATION/CYCLIZATION OF AMINOALLENES (Continued)

Aminoallene	Conditions	Product(s) and Yield(s) (%)	Refs.																																																	
C₇ 	AuCl ₃ (5 mol %), CaCO ₃ (1 eq), solvent, rt, 1h	 Solvent MeCN (13) DCM/MeCN (99)	536																																																	
C₇₋₁₂ 	AgBF ₄ (10–100 mol %), DCM, rt, 0.5–4 h	 R <i>cis/trans</i> H (30) 1:1 MeO₂C (83) >50:1 Boc (70) >50:1 Bn (93) >50:1 Ts (100) >50:1	537 538 537 538 538																																																	
C₇₋₁₂  I	Catalyst (2 mol %), DCM, rt	 II	309																																																	
<table><tr><th>R¹</th><th>R²</th><th>dr I</th><th>Catalyst</th><th>Time (h)</th><th>II</th><th>dr II</th></tr><tr><td>Me</td><td>Bn</td><td>90:10</td><td>AuCl₃</td><td>140</td><td>(71)</td><td>90:10</td></tr><tr><td>Me</td><td>Bn</td><td>90:10</td><td>AuCl</td><td>6</td><td>(60)</td><td>90:10</td></tr><tr><td><i>i</i>-Pr</td><td>Bn</td><td>99:1</td><td>AuCl₃</td><td>140</td><td>(74)</td><td>99:1</td></tr><tr><td><i>i</i>-Pr</td><td>Bn</td><td>99:1</td><td>AuCl</td><td>6</td><td>(71)</td><td>99:1</td></tr><tr><td>Ph</td><td>TBS</td><td>>99:1</td><td>AuCl₃</td><td>140</td><td>(79)</td><td>>99:1</td></tr><tr><td>Ph</td><td>TBS</td><td>>99:1</td><td>AuCl</td><td>5</td><td>(69)</td><td>>99:1</td></tr></table>				R ¹	R ²	dr I	Catalyst	Time (h)	II	dr II	Me	Bn	90:10	AuCl ₃	140	(71)	90:10	Me	Bn	90:10	AuCl	6	(60)	90:10	<i>i</i> -Pr	Bn	99:1	AuCl ₃	140	(74)	99:1	<i>i</i> -Pr	Bn	99:1	AuCl	6	(71)	99:1	Ph	TBS	>99:1	AuCl ₃	140	(79)	>99:1	Ph	TBS	>99:1	AuCl	5	(69)	>99:1
R ¹	R ²	dr I	Catalyst	Time (h)	II	dr II																																														
Me	Bn	90:10	AuCl ₃	140	(71)	90:10																																														
Me	Bn	90:10	AuCl	6	(60)	90:10																																														
<i>i</i> -Pr	Bn	99:1	AuCl ₃	140	(74)	99:1																																														
<i>i</i> -Pr	Bn	99:1	AuCl	6	(71)	99:1																																														
Ph	TBS	>99:1	AuCl ₃	140	(79)	>99:1																																														
Ph	TBS	>99:1	AuCl	5	(69)	>99:1																																														



R	L	x	y	Temp (°C)	Time (h)	I + II	I/II	dr II
H	(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	10	50	120	96	(86)	II only	>50:1
Ph	(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	5	5	rt	24	(100)	98:2	—
Ph	(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	10	10	100	16	(100)	1:1.25	—
Ph	(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	10	50	100	16	(100)	1:2.5	—
Ph	(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	10	50	120	96	(82)	2:98	25:1
Ph	IPr	5	5	rt	24	(100)	98:2	—
Ph	IPr	10	10	100	16	(100)	1:1	—



Catalyst (x mol %), solvent

n	R ¹	R ²	Catalyst	x	Solvent	Temp	dr
1	H	H	AgNO ₃	20	acetone	rt	(50)
1	Me	<i>n</i> -Bu	AgNO ₃	20	acetone	rt	(90)
1	Me	<i>n</i> -Bu	Ru ₃ (CO) ₁₂	1	dioxane	100°	(78)
1	<i>i</i> -Pr	PhCO ₂ (CH ₂) ₂	AgNO ₃	20	acetone	rt	(47)
1	Me	Ph	AgNO ₃	20	acetone	rt	(67)
1	Me	Ph	Ru ₃ (CO) ₁₂	1	dioxane	100°	(86)
1	<i>i</i> -Pr	<i>n</i> -Bu	AgNO ₃	20	acetone	rt	(64)
1	<i>i</i> -Pr	Ph	AgNO ₃	20	acetone	rt	(69)
1	Ph	<i>n</i> -Bu	AgNO ₃	20	acetone	rt	(69)
1	<i>i</i> -Pr	Ph(CH ₂) ₃	AgNO ₃	20	acetone	rt	(60)
2	Me	<i>n</i> -Bu	AgNO ₃	20	acetone	rt	(67)
2	Me	<i>n</i> -Bu	Ru ₃ (CO) ₁₂	1	dioxane	100°	(55)
2	Me	Ph	AgNO ₃	20	acetone	rt	(63)

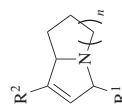


TABLE 2D. HYDROAMINATION/CYCLIZATION OF AMINOALLENES (Continued)

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C7-11

C7-11

Catalyst (x mol %),
additive (x mol %), solvent

<i>n</i>	<i>R</i> ¹	<i>R</i> ²	<i>R</i> ³	Catalyst	<i>x</i>	Additive	Solvent	Temp	Time (h)	
1	H	H	H	AuCl ₃	10	—	MeCN	82°	22	(75)
1	H	H	AcO	Ph ₃ PAuCl	5	AgBF ₄	DCM	rt	24	(0)
1	Me	H	H	Ph ₃ PAuCl	5	AgBF ₄	DCM	rt	4	(93)
1	AcOCH ₂	H	H	AuCl ₃	5	—	DCM	rt	0.5	(74)
1	AcOCH ₂	H	H	Ph ₃ PAuCl	5	AgBF ₄	DCM	rt	4	(92)
1	BnOCH ₂	H	H	Ph ₃ PAuCl	5	AgBF ₄	DCM	rt	4	(80)
1	BnOCH ₂	H	AcO	Ph ₃ PAuCl	5	AgBF ₄	DCM	rt	6	(85)
1	H	<i>n</i> -Pr	H	Ph ₃ PAuCl	5	AgBF ₄	DCM	rt	4	(90)
2	H	H	H	AuCl ₃	10	—	MeCN	82°	20	(65)
2	Me	H	H	Ph ₃ PAuCl	5	AgBF ₄	DCM	rt	6	(82)
2	AcOCH ₂	H	H	Ph ₃ PAuCl	5	AgBF ₄	DCM	rt	7	(75)
2	H	<i>n</i> -Pr	H	Ph ₃ PAuCl	5	AgBF ₄	DCM	rt	7	(71)
3	H	H	H	AuCl ₃	10	—	MeCN	82°	22	(52)
3	Me	H	H	Ph ₃ PAuCl	5	AgBF ₄	DCM	rt	24	(79)

527

C₇₋₂₀

(IPr)AuCl (5 mol %),
AgPF₆ (5 mol %), DCM, rt

522

dr > 98:2

Z	R ¹	R ²	Time (h)
O	H	4-O ₂ NC ₆ H ₄	16 (90)
TsN	H	4-O ₂ NC ₆ H ₄	24 (86)
CH ₂	H	4-O ₂ NC ₆ H ₄	16 (83)
CH ₂	Ph	Ph	16 (94)
CH ₂	Ph	4-MeOC ₆ H ₄	16 (96)
CH ₂	Ph	4-O ₂ NC ₆ H ₄	2 (93)
CH ₂	Ph	Bn	16 (96)

C₈

18, (5 mol %), C₆D₆, 75°, 3 h

(95)

305

(2-PhC₆H₄)(*i*-Bu)₂PAuCl (5 mol %),
AgOTf (5 mol %), dioxane, rt, 3 h

(96)

317

K₂CO₃ (1 eq), DMF, reflux

R ¹	R ²	Time (h)
H	Me	312 (75)
Me	H	24 (87)

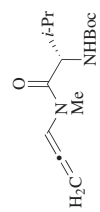
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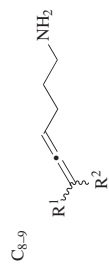
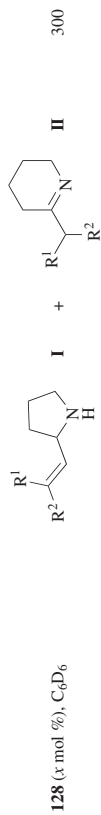
K₂CO₃ (1 eq), DMF, reflux

R ¹	R ²	Time (h)
H	Me	18 (80)
Me	H	102 (83)

525

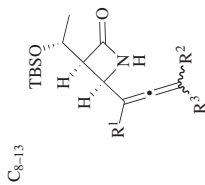
TABLE 2D. HYDROAMINATION/CYCLIZATION OF AMINOALLENES (Continued)

Aminoallene	Conditions				Product(s) and Yield(s) (%)	Refs.
	Catalyst	Solvent	I	II	III	IV
	H ₂ SO ₄	MeCN	(15)	(85)	(—)	(—)
	AuCl	C ₇ H ₈	(—)	(—)	(5)	(—)
	AuCl	MeCN	(—)	(—)	(7)	(—)
	(Ph ₃ P)/AuOTf	DCM	(—)	(—)	(10)	(—)
	(Ph ₃ P)/AuOTf, AcOH	DCM	(—)	(—)	(8)	(—)
	AuCl ₃	MeCN	(90)	(—)	(10)	(—)
	AuCl ₃	dioxane	(10)	(—)	(10)	(—)
	AuCl ₃	AcOH	(—)	(—)	(10)	(90)
	AuCl ₃	DCM	(—)	(—)	(5)	(—)
	AuCl ₃ , AgBF ₄	C ₇ H ₈	(—)	(—)	(5)	(—)
	NaAuCl ₄ •2H ₂ O	MeCN	(39)	(—)	(10)	(—)
	NaAuCl ₄ •2H ₂ O	DCM	(—)	(—)	(5)	(—)
	NaAuCl ₄ •2H ₂ O	dioxane	(—)	(—)	(5)	(—)
	AuCl, AgOTf	MeCN	(—)	(—)	(10)	(—)
	AuCl ₃ , AgOTf	AcOH	(—)	(—)	(10)	(90)
	(2-PhC ₆ H ₄)(<i>i</i> -Bu) ₂ PAuCl (5 mol %), AgOTf (5 mol %), dioxane, rt, 3 h				(96), (E)/(Z) > 50:1	317
	AgBF ₄ (50 mol %), DCM, rt				(86)	311

C₈-9

128 (*x* mol %), C₆D₆

300

C₈-13 AgBF_4 (*x* eq), DCM, rt

315

R ¹	R ²	R ³	x	Time (h)	dr
H	H	H	0.5	2	—
H	H	Me	1.0	15	(65) 2.0:1
Me	H	H	0.14	8	—
Me	H	Me	1.3	15	(62) 2.8:1
H	Me	<i>n</i> -Bu	0.5	18	(58) 2.2:1

C₈₋₁₅Catalyst (5 mol %), C₆D₆

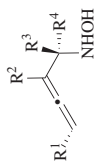
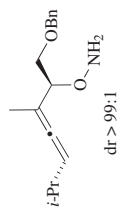
300

R ¹	R ²	Catalyst	Temp (°)	Time (h)
H	Et	126c	75	2 (70)
H	Et	126e	75	2 (96)
H	<i>n</i> -Pr	126e	75	7 (100)
4-MeC ₆ H ₄	Et	126e	105	2 (100)
4-MeC ₆ H ₄	Et	126b	75	20 (87)

TABLE 2D. HYDROAMINATION/CYCLIZATION OF AMINOALLENES (Continued)

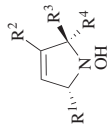
Aminoallene	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the bold numbers.			
C₉			
	(2-PhC ₆ H ₄) <i>i</i> -Bu ₂ PAuCl (5 mol %), AgOTf (5 mol %), dioxane, rt, 3 h		317
	PdCl ₂ (5 mol %), 131 (10 mol %), maleic anhydride (20 mol %), NaOAc (1 eq), O ₂ (1 atm), <i>i</i> -PrOH, 60°		319
	Catalyst (<i>x</i> mol %), solvent, rt		314
	AuCl ₃ (2 mol %), solvent		310

R	Solvent	Temp	Time (h)	dr
H	DCM	rt	140	(74) 99:1
Ms	DCM	rt	0.5	(77) 94:6
Ac	DCM	rt	0.5	(80) 70:30

C₉₋₁₃C₉

Boc	DCM	rt	0.5	(69)	46:54
Ts	DCM	rt	0.5	(93)	95:5
Ts	DCM	0°	1	(95)	96:4
Ts	THF	rt	1.5	(95)	93:7

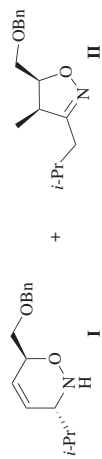
AuCl (5 mol %), DCM, rt, 2 h



314

R ¹	R ²	R ³	R ⁴	
<i>i</i> -Pr	Me	H	BnOCH ₂	(76)
<i>i</i> -Pr	H	H	EtO ₂ C(CH ₂) ₂	(80)
<i>n</i> -Bu	Me	HOCH ₂	H	(73)
<i>n</i> -Bu	Me	BnOCH ₂	H	(67)
Ph	Me	BnOCH ₂	H	(78)
Me	H	H	BnCH ₂	(77)

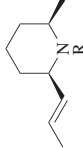
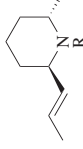
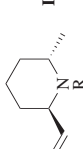
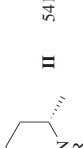
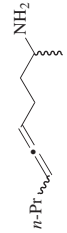
Catalyst (5 mol %), solvent, rt

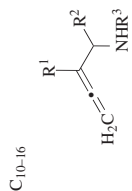


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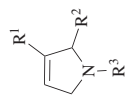
Catalyst	Solvent	Time (h)	I	dr I	II	dr II
AuCl	DCM	2.5	(47)	>99:1	(19)	87:13
AuCl ₃	DCM	2.5	(49)	>99:1	(15)	89:11
AuCl ₃	MeCN	3	(35)	>97:3	(16)	87:13
AuCl ₃	THF	62	(40)	>98:2	(26)	87:13
[(Ph ₃ P) ₄ Au]BF ₄	DCM	1.5	(3)	—	(69)	79:21
[(2,4-(<i>i</i> -Bu) ₂ C ₆ H ₃ O) ₃ PAu(PhCN)]SbF ₆	DCM	1.5	(3)	—	(81)	94:6

TABLE 2D. HYDROAMINATION/CYCLIZATION OF AMINOALLENES (Continued)

Aminoallene	Conditions	Product(s) and Yield(s) (%)				Refs.
 C ₉	Catalyst (2 mol %), C ₆ D ₆	Catalyst	Temp	TOF (h ⁻¹)	<i>trans/cis</i>	(<i>E</i>)/(<i>Z</i>)
		Cp [*] ₂ SnCH(TMS) ₂	rt	0.23	—	45:55
		Me ₂ Si(C ₃ Me ₄)/(<i>r</i> -BuN)Th(NMe ₂) ₂	60°	0.1	60:40	—
		Me ₂ Si(C ₃ Me ₄)/(<i>r</i> -BuN)U(NMe ₂) ₂	60°	1.3	75:25	—
 C ₁₀	AgNO ₃ (0.3 mol %), acetone/H ₂ O (1:1)	 I	 II	 I + II	 I + II + III	541
		R	Temp	Time (h)		
		H	rt	24	(100)	62:38
		H	60°	48	(100)	70:30
		Bn	rt	48	(100)	50:50
 C ₁₀	Catalyst (x mol %), C ₆ D ₆	x	Temp	TOF (h ⁻¹)	<i>trans/cis</i>	(<i>E</i>)/(<i>Z</i>)
		Cp [*] ₂ YCH(TMS) ₂	2	—	— ^e	33:67
		Cp [*] ₂ SnCH(TMS) ₂	2	rt	— ^e	42:58
		Cp [*] ₂ LaCH(TMS) ₂	2	—	620 ^f	45:55
		[Me ₂ Si(C ₃ Me ₄)/(<i>r</i> -BuN)Th(NMe ₂) ₂	2	rt	2.7 ^e	90:10
		[Me ₂ Si(C ₃ Me ₄)/(<i>r</i> -BuN)U(NMe ₂) ₂	2	rt	29 ^e	80:20
		Me ₂ Si(C ₃ Me ₄) ₂ Th[N(TMS) ₂] ₂	2	rt	0.03 ^e	60:40



Me ₂ Si(C ₅ Me ₄) ₂ UBn ₂	2	rt	0.3 ^c	(—)	60:40	—	256
Cp [®] ₂ Th[N(TMS) ₂] ₂	2	100°	0.3 ^c	(—)	70:30	—	256
Cp [®] ₂ U[N(TMS) ₂] ₂	2	100°	0.8 ^c	(—)	65:35	—	256
3a	3–5	rt	0.8	(95)	—	44:56	303
124	3–5	rt	0.3	(95)	—	42:58	303

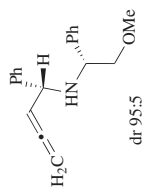


Catalyst (5 mol %), DCM, rt

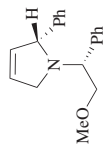
313

R ¹	R ²	R ³	Catalyst	Time (h)
H	Ph	Bn	Cu(OTf) ₂	24 (96)
H	Ph	Bn	CuCl	24 (55)
H	Ph	Bn	CuI	15 (98)
H	Ph	Bn	CuCl ₂	24 (96)
H	4-BrC ₆ H ₄	<i>i</i> -Pr	Cu(OTf) ₂	24 (89)
Ph	Ph	Bn	Cu(OTf) ₂	24 (95)
Ph	Ph	Bn	AuCl ₃	96 (51)

C₁₀



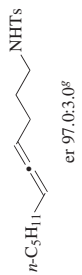
Catalyst (5 mol %), DCM, rt, 24 h



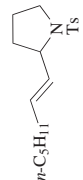
Catalyst	dr	(95)	(86)	(88)
CuI	95:5			
CuCl ₂				
Cu(OTf) ₂				

313

C₁₁



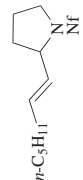
AuCl (2 mol %), THF, rt, 3 h



(99) er 97.0:3.0^g

318

Pd₂(dba)₃•CHCl₃ (5 mol %),
PhCO₂H (10 mol %),
(*R,R*)-RENORPHOS (25 mol %),
benzene, 100°, 72 h



(85) er 50.0:50.0

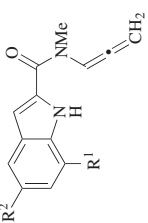
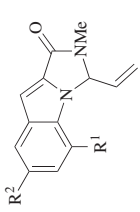
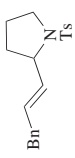
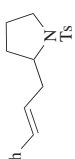
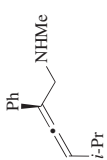
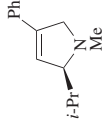
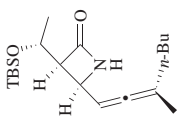
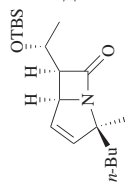
316

TABLE 2D. HYDROAMINATION/CYCLIZATION OF AMINOALLENES (Continued)

Aminoallene	Conditions	Product(s) and Yield(s) (%)	Refs.																																																							
Please refer to the charts preceding the tables for structures indicated by the bold numbers.																																																										
C ₁₁₋₁₂																																																										
	Catalyst (x mol %), THF, rt		318																																																							
		<table><tr><th>n</th><th>R</th><th>Catalyst</th><th>x</th><th>Time (h)</th></tr><tr><td>1</td><td>H₂N</td><td>AuCl</td><td>5</td><td>24</td></tr><tr><td>1</td><td>EtO₂C</td><td>AuCl</td><td>2</td><td>3</td></tr><tr><td>1</td><td>Nf</td><td>AuCl</td><td>5</td><td>24</td></tr><tr><td>1</td><td>Ts</td><td>AuCl</td><td>2</td><td>3</td></tr><tr><td>1</td><td>Ts</td><td>AuCl₃</td><td>2</td><td>3</td></tr><tr><td>1</td><td>Ts</td><td>AuBr₃</td><td>2</td><td>3</td></tr><tr><td>1</td><td>Bn</td><td>AuCl</td><td>5</td><td>24</td></tr><tr><td>1</td><td>Cbz</td><td>AuCl</td><td>2</td><td>3</td></tr><tr><td>2</td><td>Ts</td><td>AuCl</td><td>5</td><td>24</td></tr><tr><td>2</td><td>Cbz</td><td>AuCl</td><td>5</td><td>24</td></tr></table>	n	R	Catalyst	x	Time (h)	1	H ₂ N	AuCl	5	24	1	EtO ₂ C	AuCl	2	3	1	Nf	AuCl	5	24	1	Ts	AuCl	2	3	1	Ts	AuCl ₃	2	3	1	Ts	AuBr ₃	2	3	1	Bn	AuCl	5	24	1	Cbz	AuCl	2	3	2	Ts	AuCl	5	24	2	Cbz	AuCl	5	24	(—) (97) (—) (99) (98) (99) (76) (99) (53) (80)
n	R	Catalyst	x	Time (h)																																																						
1	H ₂ N	AuCl	5	24																																																						
1	EtO ₂ C	AuCl	2	3																																																						
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1	Cbz	AuCl	2	3																																																						
2	Ts	AuCl	5	24																																																						
2	Cbz	AuCl	5	24																																																						
C ₁₁	AgNO ₃ (20 mol %), (Me ₂ N) ₂ C=NH (10 mol %), acetone/H ₂ O (5:1), rt, 30 h		<table><tr><th>R</th><th>cis/trans</th></tr><tr><td>H</td><td>(0)</td></tr><tr><td>Boc</td><td>(98)</td></tr><tr><td>2-Ns</td><td>(0)</td></tr><tr><td>Cbz</td><td>(93)</td></tr></table>	R	cis/trans	H	(0)	Boc	(98)	2-Ns	(0)	Cbz	(93)	533																																												
R	cis/trans																																																									
H	(0)																																																									
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2-Ns	(0)																																																									
Cbz	(93)																																																									
C ₁₂	AgBF ₄ (10–100 mol %), DCM, rt, 12–24 h		(86) dr > 50:1	542																																																						
	AgBF ₄ (10–100 mol %), DCM, rt, 12–24 h		(87) dr 1:1	542																																																						

		AgBF ₄ (10–100 mol %), DCM, rt, 12–24 h	(92) dr >50:1	542
		(2-PhC ₆ H ₄)(<i>n</i> -Bu) ₂ PAuCl (5 mol %), AgOTf (5 mol %), dioxane, rt, 3 h	(80) dr 16:1	317
		[η ³ -C ₃ H ₅ PdCl] ₂ (5 mol %), DPPF (10 mol %), AcOH (1 eq), THF, reflux	<i>n</i> R Time (h) <i>trans/cis</i> 1 H 3 (41) ^b 50:50 1 Tf 2 (80) 6:94 2 H 4 (52) 5:95	308
		Cp ⁺ ₂ SnCH(TMS) ₂ (2 mol %), C ₆ D ₆ , rt, 1 h	(95) (<i>E</i>)/(<i>Z</i>) = 5:95	298
		Catalyst (<i>x</i> mol %), additive (<i>y</i> mol %), DCM	<i>n</i> -C ₆ H ₁₃ OTBS dr 85:15	309
		Catalyst <i>x</i> Additive <i>y</i> Temp Time (h)		
		AuI 2 — — rt 4 (76)		
		AuCl 2 — — rt 6 (61)		
		AuCl 5 — — rt 1 (70)		
		AuCl ₃ 2 — — rt 140 (82)		
		AuCl ₃ 2 — — reflux 8 (83)		
		AuCl ₃ 2 bpy 4 rt 72 (62)		
		AuCl ₃ 2 bpy 4 reflux 6 (67)		
		AuCl ₃ 2 HO(CH ₂) ₄ CN 4 rt 72 (64)		
		AuCl ₃ 2 HO(CH ₂) ₄ CN 4 reflux 6 (67)		
		AuCl ₃ 5 — — rt 48 (80)		
		AuBr ₃ 2 — — rt 140 (71)		
		AuBr ₃ 5 — — rt 48 (73)		
		Ph ₃ PAuCl 4 AgSbF ₆ 6 rt 72 (64)		
		Ph ₃ PAuCl 5 — — rt 168 (—)		
		(2-PhC ₆ H ₄)(<i>n</i> -Bu) ₂ PAuCl 2 — — rt 168 (—)		

TABLE 2D. HYDROAMINATION/CYCLIZATION OF AMINOALLENES (Continued)

Aminoallene	Conditions	Product(s) and Yield(s) (%)	Refs.																														
C₁₂₋₁₉ 	Pd(PPh₃)₄ (5 mol %), MW, C₇H₈, 150°, 1 h	 <table><tr><th>R¹</th><th>R²</th><th></th></tr><tr><td>H</td><td>Cl</td><td>(85)</td></tr><tr><td>H</td><td>MeO</td><td>(67)</td></tr><tr><td>O₂N</td><td>H</td><td>(58)</td></tr><tr><td>H</td><td>Me</td><td>(78)</td></tr><tr><td>H</td><td>2-C₄H₅S</td><td>(72)</td></tr><tr><td>H</td><td>Ph</td><td>(63)</td></tr><tr><td>H</td><td>4-ClC₆H₄</td><td>(85)</td></tr><tr><td>H</td><td>4-MeOC₆H₄</td><td>(89)</td></tr><tr><td>H</td><td>4-MeC₆H₄</td><td>(69)</td></tr></table>	R ¹	R ²		H	Cl	(85)	H	MeO	(67)	O ₂ N	H	(58)	H	Me	(78)	H	2-C ₄ H ₅ S	(72)	H	Ph	(63)	H	4-ClC ₆ H ₄	(85)	H	4-MeOC ₆ H ₄	(89)	H	4-MeC ₆ H ₄	(69)	543
R ¹	R ²																																
H	Cl	(85)																															
H	MeO	(67)																															
O ₂ N	H	(58)																															
H	Me	(78)																															
H	2-C ₄ H ₅ S	(72)																															
H	Ph	(63)																															
H	4-ClC ₆ H ₄	(85)																															
H	4-MeOC ₆ H ₄	(89)																															
H	4-MeC ₆ H ₄	(69)																															
C₁₃ 	PdCl₂ (5 mol %), 125 (10 mol %), maleic anhydride (10 mol %), NaOAc (1 eq), O₂ (1 atm), <i>i</i>-PrOH, 60°	 I + II (64), I/II = 1:1.2 	319																														
	AgNO₃ (20 mol %), acetone, rt	 (70) er 85.0:15.0	540																														
	AgBF₄ (x eq), DCM, rt, 18 h	 I + II <table><tr><th>x</th><th>I + II</th><th>I/II</th></tr><tr><td>0.5</td><td>(60)</td><td>II only</td></tr><tr><td>2</td><td>(48)</td><td>I only</td></tr></table>	x	I + II	I/II	0.5	(60)	II only	2	(48)	I only	315																					
x	I + II	I/II																															
0.5	(60)	II only																															
2	(48)	I only																															

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

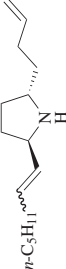
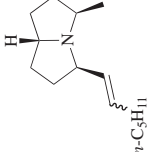
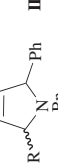
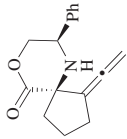
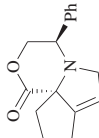
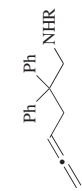
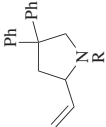
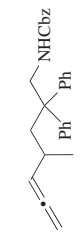
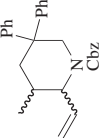
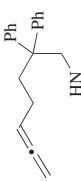
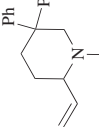
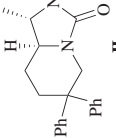
C ₁₄₋₁₅		$n\text{-C}_3\text{H}_{11}$	$\text{Cp}^*\text{LnCH}(\text{TMS})_2$ (2 mol %), C ₆ D ₆		298 302
C ₁₅		$n\text{-C}_3\text{H}_{11}$	Catalyst (1–5 mol %), C ₆ D ₆		302
C ₁₆		$n\text{-C}_3\text{H}_{11}$	$[\text{Me}_2\text{Si}(\text{C}_3\text{Me}_4)((\text{r-Bu})\text{N})]\text{SmN}(\text{TMS})_2$ (2 mol %), C ₆ D ₆ , 45°		302
C ₁₆		$n\text{-C}_3\text{H}_{11}$	Catalyst (5 mol %), DCM, rt		313

TABLE 2D. HYDROAMINATION/CYCLIZATION OF AMINOALLENES (Continued)

Aminoallene	Conditions	Product(s) and Yield(s) (%)	Refs.																															
C₁₆ 	AuCl ₃ (5 mol %), DCM, rt, 6 h	 (80)	544																															
C₁₈ 	Catalyst (5 mol %), AgOTf (x mol %), dioxane, rt	 R	<table><tr><th>R</th><th>Catalyst</th><th>x</th><th>Time (h)</th><th></th></tr><tr><td>Boc</td><td>(2-PhC₆H₄)(<i>t</i>-Bu)₂PtAuCl</td><td>5</td><td>3</td><td>(94)</td></tr><tr><td>Cbz</td><td>(2-PhC₆H₄)(<i>t</i>-Bu)₂PtAuCl</td><td>5</td><td>3</td><td>(95)</td></tr><tr><td>Cbz</td><td>129a</td><td>5</td><td>24</td><td>(92)</td></tr><tr><td>Cbz</td><td>129b</td><td>0</td><td>24</td><td>(78)</td></tr><tr><td>Fmoc</td><td>(2-PhC₆H₄)(<i>t</i>-Bu)₂PtAuCl</td><td>5</td><td>3</td><td>(88)</td></tr></table>	R	Catalyst	x	Time (h)		Boc	(2-PhC ₆ H ₄)(<i>t</i> -Bu) ₂ PtAuCl	5	3	(94)	Cbz	(2-PhC ₆ H ₄)(<i>t</i> -Bu) ₂ PtAuCl	5	3	(95)	Cbz	129a	5	24	(92)	Cbz	129b	0	24	(78)	Fmoc	(2-PhC ₆ H ₄)(<i>t</i> -Bu) ₂ PtAuCl	5	3	(88)	317 317 545 545 317
R	Catalyst	x	Time (h)																															
Boc	(2-PhC ₆ H ₄)(<i>t</i> -Bu) ₂ PtAuCl	5	3	(94)																														
Cbz	(2-PhC ₆ H ₄)(<i>t</i> -Bu) ₂ PtAuCl	5	3	(95)																														
Cbz	129a	5	24	(92)																														
Cbz	129b	0	24	(78)																														
Fmoc	(2-PhC ₆ H ₄)(<i>t</i> -Bu) ₂ PtAuCl	5	3	(88)																														
C₂₀ 	(2-PhC ₆ H ₄)(<i>t</i> -Bu) ₂ PtAuCl (5 mol %), AgOTf (5 mol %), dioxane, rt, 22 h	 (92), <i>trans/cis</i> = 1:7	317																															
	Au(L)Cl (5 mol %), additive (5 mol %), DCM, rt	 I +  II	522																															

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

L	Additive	Time (h)	I + II	III	dr II
(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	AgOTf	24	(100)	4:1	—
(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	AgSbF ₆	24	(100)	3.8:1	—
(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	AgClO ₄	24	(100)	4.2:1	—
(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	AgOAc	24	(100)	5:1	—
(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	AgBF ₄	24	(100)	4:1	—
(<i>t</i> -Bu) ₂ P(2-PhC ₆ H ₄)	AgPF ₆	2	(100)	1:16	11:1
IPr	AgOTf	24	(100)	2.5:1	—
IPr	AgSbF ₆	24	(100)	4:1	—
IPr	AgPF ₆	2	(100)	1:50	>50:1

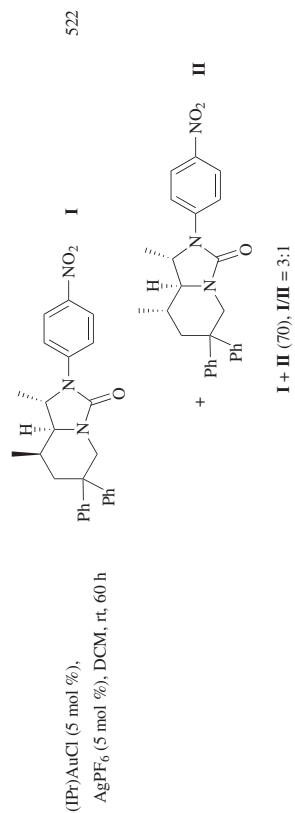
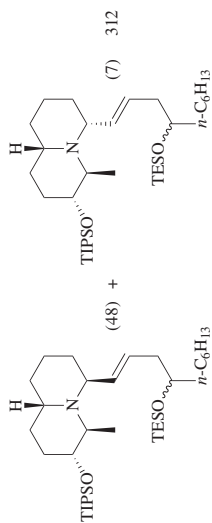
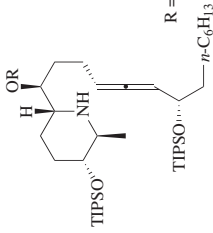
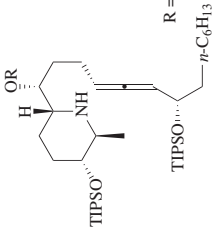


TABLE 2D. HYDROAMINATION/CYCLIZATION OF AMINOALLENES (Continued)

Aminoallene	Conditions	Product(s) and Yield(s) (%)	Refs.
 312	AgNO₃ (50 mol %), acetone/H₂O (5:1), rt, 48 h R = 3-CF₃-C₆H₄CO	(94) 312	312
 312	AgNO₃ (50 mol %), acetone/H₂O (5:1), rt, 48 h R = 3-CF₃-C₆H₄CO	(91) 312	312

^a Double dilution was used.

^b The reaction was conducted under an air atmosphere.

^c The reaction was conducted under an N₂ atmosphere.

^d The conversion was >95% (NMR).

^e *t*-BuNH₂ (10 mol %) was added to the reaction.

^f The product was isolated as the hydrogenated product.

^g The absolute configuration was not reported.

^h The product was isolated as the *N*-tosyl amide.

TABLE 2E. HYDROAMINATION/CYCLIZATION OF STRAINED AMINOALKENES

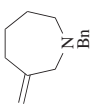
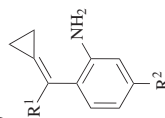
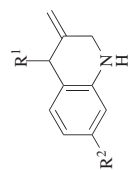
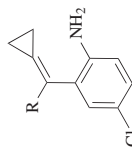
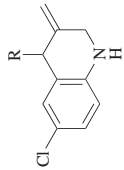
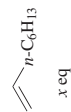
Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.												
C₇ 	Pd(PPh ₃) ₄ (5 mol %), DME, 100°	 (48)	334												
C₁₁₋₁₇ 	Pd(PPh ₃) ₄ (5 mol %), P(<i>Or</i> -Bu) ₃ (15 mol %), neat, 120°, 3 d	<table><tr><th>R¹</th><th>R²</th><th></th></tr><tr><td>Me</td><td>H</td><td>(74)</td></tr><tr><td>Ph</td><td>H</td><td>(86)</td></tr><tr><td>Ph</td><td>Me</td><td>(86)</td></tr></table> 	R ¹	R ²		Me	H	(74)	Ph	H	(86)	Ph	Me	(86)	323
R ¹	R ²														
Me	H	(74)													
Ph	H	(86)													
Ph	Me	(86)													
C₁₆ 	Pd(PPh ₃) ₄ (5 mol %), P(<i>Or</i> -Bu) ₃ (15 mol %), neat, 3 d	<table><tr><th>R</th><th>Temp (°)</th><th></th></tr><tr><td>Ph</td><td>100</td><td>(71)</td></tr><tr><td>2-ClC₆H₄</td><td>120</td><td>(70)</td></tr></table> 	R	Temp (°)		Ph	100	(71)	2-ClC ₆ H ₄	120	(70)	323			
R	Temp (°)														
Ph	100	(71)													
2-ClC ₆ H ₄	120	(70)													

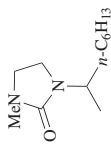
TABLE 3A. ENANTIOSELECTIVE HYDROAMINATION OF SIMPLE ALKENES

Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.

Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
R^1 x eq	R^2NH_2	$\text{Catalyst (y mol \%, C}_6\text{D}_6)$		
		R^1 x R^2 Catalyst γ Temp (°) Time (h) er		
		NHR^2 		
C_{5-10}				335

C₈

L(AuCl)₂ (2.5 mol %),
AgY (5 mol %),
solvent, 48 h

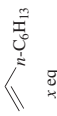
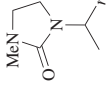


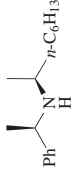
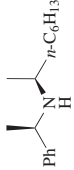
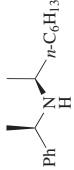
126

x	L	Y	Solvent	Temp (°)	er ^{a,b}
6	131e	SbF ₆	dioxane	60	69.0:31.0
6	131e	OTf	MeOH	60	69.0:31.0
6	131e	OTf	DMSO	60	—
6	131e	OTf	C ₇ H ₈	60	77.0:23.0
6	131e	OTf	dioxane	60	74.0:26.0
6	131e	OTf	MeNO ₂	60	—
6	131e	OTf	MeCN	60	67.0:33.0
6	131e	OTf	THF	60	73.0:27.0
15	131e	BF ₄	dioxane	80	73.0:27.0
15	131e	OTf	dioxane	80	—
15	131e	PF ₆	dioxane	80	73.5:26.5
15	131e	OTf	dioxane	80	81.0:19.0
15	131e	ClO ₄	dioxane	80	73.5:26.5
15	131e	AsF ₆	dioxane	80	72.5:27.5
15	131e	OTf	C ₇ H ₈	60	83.0:17.0
15	131e	OTf	dioxane	60	80.5:19.5
15	131f	OTf	C ₇ H ₈	60	—
15	131f	OTf	dioxane	60	—
30	131e	OTf	C ₇ H ₈	60	85.5:14.5
30	131e	OTf	<i>m</i> -xylene	60	87.0:13.0

TABLE 3A. ENANTIOSELECTIVE HYDROAMINATION OF SIMPLE ALKENES (Continued)

Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.

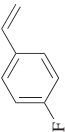
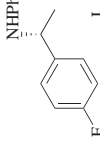
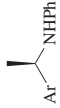
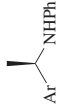
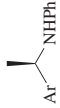
Alkene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 			126	
		$L(AuCl)_2$ (2.5 mol %), $AgOTf$ (5 mol %), solvent, 48 h		
x	L	Solvent	Temp (°)	er ^d
15	131a	C_7H_8	60	(—) ^b 84.0:16.0
15	131a	dioxane	60	(—) ^b 78.5:21.5
15	132c	C_7H_8	60	(—) ^b —
15	132c	dioxane	60	(—) ^b 53.5:46.5
15	132d	C_7H_8	60	(—) ^b 75.0:25.0
15	132d	dioxane	60	(—) ^b 78.0:22.0
30	131a	C_7H_8	60	(—) ^b 84.5:15.5
30	131a	m-xylene	60	(—) ^b 85.0:15.0
30	131e	m-xylene	60	(38) 87.0:13.0
30	131e	m-xylene	100	(100) 86.5:13.5
30	131e	m-xylene	120	(100) 86.5:13.5
60	131e	m-xylene	100	(100) 88:12
60	131e	m-xylene	120	(100) 87.5:12.5

		Catalyst (x mol %), C ₆ D ₆	x	Temp (°)	Time (h)	% r	335
			8	170	96	(tr)	
		130c 130d	5	150	48	(75) 73	126
			5	150	48	(75)	
		131e (AuCl) ₂ (2.5 mol %), AgOTf (5 mol %), 3-xylene, 100°, 48 h	R ¹ R R ² R ³				cr ^d
			n-C ₆ H ₁₃ Me (86) 88.0:12.0 n-C ₆ H ₁₃ <i>t</i> -Bu (89) 89.0:11.0 n-C ₆ H ₁₃ Ph (80) 85.5:14.5 n-C ₆ H ₁₃ 4-FC ₆ H ₄ (81) 87.0:13.0 n-C ₆ H ₁₇ Me (83) 86.5:13.5 n-C ₁₀ H ₂₁ Me (76) 87.5:12.5				

^a The absolute configuration was not reported.

^b The yield was not reported.

TABLE 3B. ENANTIOSELECTIVE HYDROAMINATION OF VINYL ARENES

Arene	Amine	Conditions	Product(s) and Yield(s) (%)				Refs.		
Please refer to the chart preceding the tables for structures indicated by the bold numbers.									
C ₈	 1.5 eq	PhNH ₂	[(<i>R</i>)-BINAP]Pd(MeCN)(H ₂ O)](OTf) ₂ (2 mol %), neat		Temp (°)	Time (h)	er	234	
					80	72	(93)		
					100	18	(75)		
		PhNH ₂	[Pd(L)(MeCN) ₂](OTf) ₂ (2 mol %), C ₇ H ₈ , 75°, 40 h					238	
					L		er		
					133a	(80)	84.5:15.5		
					133b	(45)	79.5:20.5		
					133c	(15)	73.0:27.0		
C ₈₋₁₂		PhNH ₂	[Pd(L)(MeCN) ₂](OTf) ₂ (2 mol %), C ₇ H ₈ , 75°, 40 h		133d	(20)	83.0:17.0	238	
					133e	(85)	89.5:10.5		
					133f	(50)	87.0:13.0		
					133g	(80)	86.5:13.5		
					(<i>S</i>)-SEGPHOS	(77)	88.0:12.0		
		PhNH ₂	[Pd(L)(MeCN) ₂](OTf) ₂ (2 mol %), C ₇ H ₈ , 75°, 40 h		(<i>S</i>)- <i>t</i> -Bu-SEGPHOS	(65)	92.0:8.0	238	
					L		er		
					Ph	133a	(75)		85.5:14.5
					Ph	133e	(51)		89.5:10.5
					Ph	134	(65)		90.5:9.5
	PhNH ₂	[Pd(L)(MeCN) ₂](OTf) ₂ (2 mol %), C ₇ H ₈ , 75°, 40 h		4-ClC ₆ H ₄	133a	(87)	86.5:13.5	238	
				4-ClC ₆ H ₄	133e	(70)	87.5:12.5		
				4-ClC ₆ H ₄	134	(71)	92.5:7.5		
				4-CF ₃ C ₆ H ₄	133a	(92)	82.0:18.0		
				4-CF ₃ C ₆ H ₄	133e	(92)	85.0:15.0		

C ₉₋₁₂		PhNH ₂	[((R)-BINAP)Pd(OTf) ₂] (10 mol %), C ₇ H ₈		231
C ₁₂		BnNHMe	Pd(O ₂ CCF ₃) ₂ (5 mol %), 135 (10 mol %), TfOH (50 mol %), dioxane, 50°, 48 h		233

^a The absolute configuration was not reported.

4-CF ₃ C ₆ H ₄	134	(72)	92.5:7.5
4-MeO ₂ CC ₆ H ₄	133a	(85)	85.0:15.0
4-MeO ₂ CC ₆ H ₄	133e	(85)	87.0:13.0
4-MeO ₂ CC ₆ H ₄	134	(70)	92.0:8.0
1-naphthyl	133a	(89)	63.5:36.5
1-naphthyl	133e	(85)	70.5:29.5
1-naphthyl	134	(89)	65.5:34.5
2-naphthyl	133a	(97)	66.0:34.0
2-naphthyl	133e	(82)	68.0:32.0
2-naphthyl	134	(81)	71.0:29.0
6-MeO-2-naphthyl	133a	(86)	71.5:28.5
6-MeO-2-naphthyl	133e	(79)	79.5:20.5
6-MeO-2-naphthyl	134	(72)	75.0:25.0

TABLE 3C. ENANTIOSELECTIVE HYDROAMINATION OF 1,3-DIENES

Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.

Diene

Amine

Conditions

Product(s) and Yield(s) (%)

Refs.

Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.

C₄



2 eq



Ni(acac)₂ (0.7 mol %),
136 (2 mol %),
TFA (3 mol %),
Et₃Al (3 mol %),
benzene, -8°, 30 d



I

+



II

+



III

R =  **276**



Ni(acac)₂ (0.7 mol %),
(*n*-Bu)₃P (2 mol %),
additive (3 mol %),
Et₃Al (3 mol %),
benzene, -8°, 30 d



I

+



II

+



III

R =  **276**

C₆



4 eq

PhNH₂

NHPh

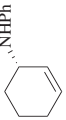
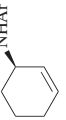
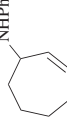
[Pd(allyl)Cl]₂ (2.5 mol %),
L (5 mol %), C₇H₈, rt, 72 h

L

(<i>R</i>)-BINAP	(99)	53.5:46.5
(<i>S,S</i>)-DIOP	(84)	52.0:48.0
(<i>S,S</i>)-BDPP	(31)	67.0:33.0

er

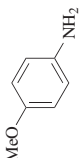
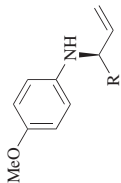
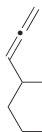
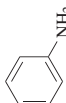
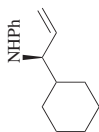
282

	PhNH ₂	[Pd(allyl)Cl] ₂ (2.5 mol %), 137 (5 mol %), C ₇ H ₈ , rt, 72 h		(6S) er 55.5:44.5	282																																																	
	ArNH ₂	[Pd(allyl)Cl] ₂ (x mol %), 138 (y mol %), C ₇ H ₈ , rt			282																																																	
<table border="1"> <thead> <tr> <th colspan="2">Ar</th><th>x</th><th>y</th><th>Time (h)</th><th>er</th></tr> </thead> <tbody> <tr> <td rowspan="4">Ph</td><td>2.5</td><td>5</td><td>72</td><td>(61)</td><td>95.5:4.5</td></tr> <tr> <td>2.5</td><td>5</td><td>72</td><td>(94)</td><td>75.0:25.0</td></tr> <tr> <td>5</td><td>11</td><td>120</td><td>(87)</td><td>94.5:5.5</td></tr> <tr> <td>5</td><td>11</td><td>120</td><td>(63)</td><td>96.0:4.0</td></tr> <tr> <td rowspan="2">2-MeC₆H₄</td><td>5</td><td>11</td><td>120</td><td>(59)</td><td>95.0:5.0</td></tr> <tr> <td>5</td><td>11</td><td>120</td><td>(78)</td><td>93.0:7.0</td></tr> <tr> <td rowspan="2">4-MeC₆H₄</td><td>5</td><td>11</td><td>120</td><td>(73)</td><td>97.5:2.5</td></tr> <tr> <td>5</td><td>11</td><td>120</td><td>(83)</td><td>97.5:2.5</td></tr> </tbody> </table>						Ar		x	y	Time (h)	er	Ph	2.5	5	72	(61)	95.5:4.5	2.5	5	72	(94)	75.0:25.0	5	11	120	(87)	94.5:5.5	5	11	120	(63)	96.0:4.0	2-MeC ₆ H ₄	5	11	120	(59)	95.0:5.0	5	11	120	(78)	93.0:7.0	4-MeC ₆ H ₄	5	11	120	(73)	97.5:2.5	5	11	120	(83)	97.5:2.5
Ar		x	y	Time (h)	er																																																	
Ph	2.5	5	72	(61)	95.5:4.5																																																	
	2.5	5	72	(94)	75.0:25.0																																																	
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2-MeC ₆ H ₄	5	11	120	(59)	95.0:5.0																																																	
	5	11	120	(78)	93.0:7.0																																																	
4-MeC ₆ H ₄	5	11	120	(73)	97.5:2.5																																																	
	5	11	120	(83)	97.5:2.5																																																	
	PhNH ₂	[Pd(allyl)Cl] ₂ (5 mol %), 138 (11 mol %), C ₇ H ₈ , rt		(2S) er 80.0:20.0 ^b	282																																																	

^a Other isomers were also formed.^b The absolute configuration was not reported.

TABLE 3D. ENANTIOSELECTIVE HYDROAMINATION OF ALLENES

Please refer to Chart 2 preceding the tables for the ligand structures corresponding to the **bold numbers**.

Allene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																											
 1.2 eq		[Rh(COD)Cl] ₂ (1 mol %), 140g (3 mol %), 0.4 M DCE/EtOH (9:1), 80°, 19 h		352																																																																											
			<table><tr><th>R</th><th>er</th></tr><tr><td>TBSOCH₂CH₂</td><td>(85) 90.0:10.0</td></tr><tr><td>TrOCH₂CH₂</td><td>(82) 92.5:7.5</td></tr><tr><td>N-phthaloyl-CH₂CH₂CH₂</td><td>(99) 92.0:8.0</td></tr><tr><td>n-C₆H₁₃</td><td>(78) 90.0:10.0</td></tr><tr><td>BnCH₂</td><td>(73) 92.0:8.0</td></tr></table>	R	er	TBSOCH ₂ CH ₂	(85) 90.0:10.0	TrOCH ₂ CH ₂	(82) 92.5:7.5	N-phthaloyl-CH ₂ CH ₂ CH ₂	(99) 92.0:8.0	n-C ₆ H ₁₃	(78) 90.0:10.0	BnCH ₂	(73) 92.0:8.0																																																																
R	er																																																																														
TBSOCH ₂ CH ₂	(85) 90.0:10.0																																																																														
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N-phthaloyl-CH ₂ CH ₂ CH ₂	(99) 92.0:8.0																																																																														
n-C ₆ H ₁₃	(78) 90.0:10.0																																																																														
BnCH ₂	(73) 92.0:8.0																																																																														
 x eq		[Rh(COD)Cl] ₂ (y mol %), L (z mol %), 0.4 M DCE/EtOH, 80°, 18 h		352																																																																											
			<table><tr><th>x</th><th>y</th><th>L</th><th>z</th><th>DCE/EtOH</th><th>er</th></tr><tr><td>1.5</td><td>1.25</td><td>259</td><td>5</td><td>1:2</td><td>(69) —</td></tr><tr><td>1.5</td><td>1.25</td><td>260</td><td>5</td><td>1:2</td><td>(26) 77.0:23.0</td></tr><tr><td>1.5</td><td>1.25</td><td>261</td><td>5</td><td>1:2</td><td>(11) 66.5:33.5</td></tr><tr><td>1.5</td><td>1.25</td><td>131b</td><td>5</td><td>1:2</td><td>(55) 66.0:34.0</td></tr><tr><td>1.5</td><td>1.25</td><td>140e</td><td>5</td><td>1:2</td><td>(33) 83.0:17.0</td></tr><tr><td>1.5</td><td>1.25</td><td>140f</td><td>5</td><td>1:2</td><td>(0) —</td></tr><tr><td>1.5</td><td>1.25</td><td>140g</td><td>5</td><td>1:2</td><td>(83) 89.0:11.0</td></tr><tr><td>1.5</td><td>1</td><td>140g</td><td>3</td><td>1:2</td><td>(85) 87.0:13.0</td></tr><tr><td>1.5</td><td>1</td><td>140g</td><td>3</td><td>9:1</td><td>(95) 94.5:5.5</td></tr><tr><td>1.5</td><td>1.25</td><td>140g</td><td>5</td><td>1:0</td><td>(63) 92.0:8.0</td></tr><tr><td>1.2</td><td>1</td><td>140g</td><td>3</td><td>9:1</td><td>(94) 94.5:5.5</td></tr><tr><td>1.5</td><td>0.1</td><td>140g</td><td>0.3</td><td>9:1</td><td>(50) 90.0:10.0</td></tr></table>	x	y	L	z	DCE/EtOH	er	1.5	1.25	259	5	1:2	(69) —	1.5	1.25	260	5	1:2	(26) 77.0:23.0	1.5	1.25	261	5	1:2	(11) 66.5:33.5	1.5	1.25	131b	5	1:2	(55) 66.0:34.0	1.5	1.25	140e	5	1:2	(33) 83.0:17.0	1.5	1.25	140f	5	1:2	(0) —	1.5	1.25	140g	5	1:2	(83) 89.0:11.0	1.5	1	140g	3	1:2	(85) 87.0:13.0	1.5	1	140g	3	9:1	(95) 94.5:5.5	1.5	1.25	140g	5	1:0	(63) 92.0:8.0	1.2	1	140g	3	9:1	(94) 94.5:5.5	1.5	0.1	140g	0.3
x	y	L	z	DCE/EtOH	er																																																																										
1.5	1.25	259	5	1:2	(69) —																																																																										
1.5	1.25	260	5	1:2	(26) 77.0:23.0																																																																										
1.5	1.25	261	5	1:2	(11) 66.5:33.5																																																																										
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1.5	1	140g	3	1:2	(85) 87.0:13.0																																																																										
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1.2	1	140g	3	9:1	(94) 94.5:5.5																																																																										
1.5	0.1	140g	0.3	9:1	(50) 90.0:10.0																																																																										

ArNH ₂	1.2 eq	[Rh(COD)Cl] ₂ (1 mol %), 140g (3 mol %), 0.4 M DCE/EtOH (9:1)	NHAr
Ar	Temp (°)	er	
Ph	80	(94)	94.5:5.5
2-MeC ₆ H ₄	80	(85)	94.5:5.5
3-MeC ₆ H ₄	80	(80)	94.5:5.5
4-MeC ₆ H ₄	80	(85)	93.5:6.5
4-FC ₆ H ₄	80	(78)	94.5:5.5
3-ClC ₆ H ₄	80	(64)	94.0:6.0
4-ClC ₆ H ₄	80	(76)	94.0:6.0
3-BrC ₆ H ₄	80	(72)	94.0:6.0
4-BrC ₆ H ₄	80	(76)	95.0:5.0
4-IC ₆ H ₄	70	(73)	92.0:8.0
4-MeOC ₆ H ₄	80	(88)	94.0:6.0
4-MeSC ₆ H ₄	80	(83)	95.0:5.0
4-HOC ₆ H ₄	80	(82)	89.0:11.0
4-EtO ₂ CC ₆ H ₄	100	(43)	91.0:9.0
4-AcC ₆ H ₄	100	(44)	89.0:11.0
4-CF ₃ C ₆ H ₄	100	(44)	91.5:8.5
4-HOCH ₂ CH ₂ C ₆ H ₄	80	(96)	93.5:6.5
5-indolyl	70	(80)	89.0:11.0
1-naphthyl	100	(84)	93.0:7.0

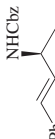
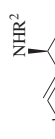
351

C_{10}	351

	$[L(AuCl)_2]$ (2.5 mol %), AgX (5 mol %), solvent, rt, 24 h				
x	L	AgX	Solvent		*
1.0	(R)- 142d	AgOTf	dioxane	(35)	75.0:25.0 (R)
1.0	(R)- 141c	AgOTf	dioxane	(15)	72.0:28.0 (R)
1.0	(S)- 142d	AgSbF ₆	dioxane	(20)	80.0:20.0 (S)
1.0	(S)- 142d	AgPF ₆	dioxane	(12)	83.0:17.0 (S)

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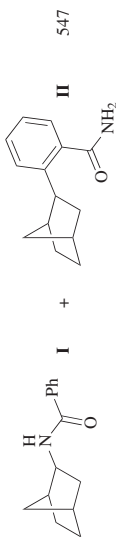
TABLE 3D. ENANTIOSELECTIVE HYDROAMINATION OF ALLENES (Continued)

Allene	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.																																																												
Please refer to Chart 2 preceding the tables for the ligand structures corresponding to the bold numbers.																																																																
 x eq	 NH_2Cbz	 [L(AuCl) ₂] (2.5 mol %), AgX (5 mol %), solvent, rt, 24 h		352																																																												
		x	L																																																													
		1.0	(S)- 142d																																																													
		1.0	(S)- 142d																																																													
		1.0	(S)- 142d																																																													
		1.0	(S)- 142d																																																													
		1.0	(S)- 142d																																																													
 1.5 eq	 R^2NH_2	 [L(AuCl) ₂](AuCl) ₂] (2.5 mol %), AgBF ₄ (5 mol %), dioxane, rt		352																																																												
		x	L																																																													
		1.0	(S)- 142d																																																													
		1.0	(S)- 142d																																																													
		1.0	(S)- 142d																																																													
		1.0	(S)- 142d																																																													
		1.0	(S)- 142d																																																													
<table><tr><th>R¹</th><th>R²</th><th>Time (h)</th><th>er</th></tr><tr><td>Cy</td><td>Cbz</td><td>24</td><td>(94)</td></tr><tr><td>Ph</td><td>MeO₂C</td><td>24</td><td>(81)</td></tr><tr><td>Ph</td><td>Fmoc</td><td>24</td><td>(79)</td></tr><tr><td>Ph</td><td>Troc</td><td>24</td><td>(43)</td></tr><tr><td>2-BrC₆H₄</td><td>Cbz</td><td>24</td><td>(69)</td></tr><tr><td>4-BrC₆H₄</td><td>Cbz</td><td>24</td><td>(99)</td></tr><tr><td>4-MeOC₆H₄</td><td>Cbz</td><td>24</td><td>(85)</td></tr><tr><td>2-MeC₆H₄</td><td>Cbz</td><td>24</td><td>(82)</td></tr><tr><td>4-MeC₆H₄</td><td>Cbz</td><td>24</td><td>(97)</td></tr><tr><td>4-CF₃C₆H₄</td><td>Cbz</td><td>24</td><td>(82)</td></tr><tr><td>2,6-Me₂C₆H₃</td><td>Cbz</td><td>48</td><td>(42)</td></tr><tr><td>3,5-Me₂C₆H₃</td><td>Cbz</td><td>48</td><td>(44)</td></tr><tr><td>2-<i>i</i>-PrC₆H₄</td><td>Cbz</td><td>48</td><td>(80)</td></tr><tr><td>2-PhC₆H₄</td><td>Cbz</td><td>24</td><td>(86)</td></tr></table>					R ¹	R ²	Time (h)	er	Cy	Cbz	24	(94)	Ph	MeO ₂ C	24	(81)	Ph	Fmoc	24	(79)	Ph	Troc	24	(43)	2-BrC ₆ H ₄	Cbz	24	(69)	4-BrC ₆ H ₄	Cbz	24	(99)	4-MeOC ₆ H ₄	Cbz	24	(85)	2-MeC ₆ H ₄	Cbz	24	(82)	4-MeC ₆ H ₄	Cbz	24	(97)	4-CF ₃ C ₆ H ₄	Cbz	24	(82)	2,6-Me ₂ C ₆ H ₃	Cbz	48	(42)	3,5-Me ₂ C ₆ H ₃	Cbz	48	(44)	2- <i>i</i> -PrC ₆ H ₄	Cbz	48	(80)	2-PhC ₆ H ₄	Cbz	24	(86)
R ¹	R ²	Time (h)	er																																																													
Cy	Cbz	24	(94)																																																													
Ph	MeO ₂ C	24	(81)																																																													
Ph	Fmoc	24	(79)																																																													
Ph	Troc	24	(43)																																																													
2-BrC ₆ H ₄	Cbz	24	(69)																																																													
4-BrC ₆ H ₄	Cbz	24	(99)																																																													
4-MeOC ₆ H ₄	Cbz	24	(85)																																																													
2-MeC ₆ H ₄	Cbz	24	(82)																																																													
4-MeC ₆ H ₄	Cbz	24	(97)																																																													
4-CF ₃ C ₆ H ₄	Cbz	24	(82)																																																													
2,6-Me ₂ C ₆ H ₃	Cbz	48	(42)																																																													
3,5-Me ₂ C ₆ H ₃	Cbz	48	(44)																																																													
2- <i>i</i> -PrC ₆ H ₄	Cbz	48	(80)																																																													
2-PhC ₆ H ₄	Cbz	24	(86)																																																													

^a The reaction time was 48 h. The yield was determined by GC analysis.



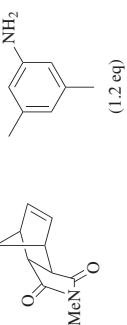
[Ir(CI)L₂ (0.5 mol %),
toluene, 100°, 72 h



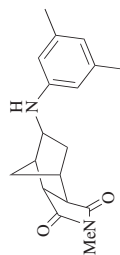
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L	I + II	I/II	er I	er II
(R)-BIPHEMP	(15)	1:2	82.5:17.5	92.5:7.5
(R)-MeO-BIPHEP	(50)	I only	89.5:10.5	—
(S)-BINAP	(34)	7:1	85.0:15.0	90.5:9.5

C₉



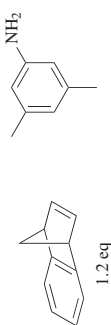
141c (2 mol %)
[Ir(COE)₂Cl]₂ (1 mol %),
KHMDS (2 mol %), 100°, 12 h



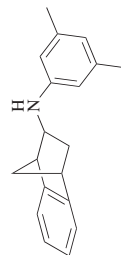
(84) er 99.0:1.0

79

C₁₁

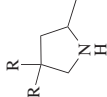
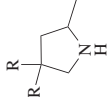
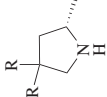
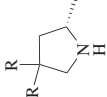


141c (2 mol %)
[Ir(COE)₂Cl]₂ (1 mol %),
KHMDS (2 mol %), 100°, 12 h

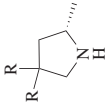
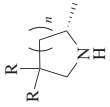
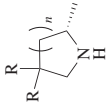


(90) er 99.5:0.5

79

Aminoalkene	Conditions	Product(s) and Yield(s) (%)				Refs.	
Please refer to the charts preceding the tables for structures indicated by the bold numbers.							
	Catalyst (2 mol %), C ₆ D ₆ , rt		Catalyst	Temp (°)	Time (h)	er ^d	
			155a	60	76	(94) 66.5:33.5	
			155b	60	2.3	(96) 51.0:49.0	
			155d	60	44	(93) 76.5:23.5	
			155f	rt	120	(96) 58.5:41.5	
	Catalyst (2 mol %), C ₆ D ₆		R	Catalyst	Temp (°)	Time (h)	er ^d
			H	39	60	25	(98) 50.0:50.0
			H	40	60	19	(99) 51.0:49.0
			Me	39	rt	1	(98) 54.0:46.0
			Me	40	rt	1.5	(95) 54.0:46.0
	Catalyst (4 mol %), C ₆ D ₆		R	Catalyst	Temp (°)	Time (h)	er ^d
			H	144a	70	43	(91) 78.5:21.5
			H	144a	100	16	(99) 76.0:24.0
			H	145	80	23	(13) —
			Me	144a	50	40	(75) 64.6:35.4
	146 (3 mol %), C ₆ D ₆		Me	144a	60	7	(92) 64.15:35.85
			Me	144a	100	0.75	(99) 64.0:36.0
			Me	145	70	22	(77) 68.0:32.0
			R	Temp	Time (h)	er	
			H	100°	65	67.5:32.5	339
	146 (3 mol %), C ₆ D ₆		Me	rt	115	64.0:36.0	
			Me	60°	1	63.0:37.0	

Please refer to the charts preceding the tables for structures indicated by the **bold numbers**.

	Catalyst (x mol %), C ₆ D ₆ , rt	R	Catalyst	x	Time (h)	er
		H	144b	3	1.4	(89) 86.0:14.0
		H	144c	1.7	5.5	(95) 85.5:14.5
		Me	144b	3.5	0.45	(95) 65.5:34.5
	Catalyst (0.6–3 mol %), C ₆ D ₆	n	Catalyst	Temp	TOF (h ⁻¹) ^a	er
		1	H	147a	rt	2.6 73.0:27.0
		1	H	147a	60°	28.4 68.5:31.5
		1	H	147b	60°	2.9 52.5:47.5
	C ₅₋₈	1	H	147c	rt	— 42.0:58.0
		1	Me	147a	rt	33.4 66.0:34.0
		1	Me	147b	rt	— 58.5:41.5
		1	Me	147c	60°	— 50.75:49.25
		2	H	147a	60°	6.6 55.0:45.0
		2	H	147b	60°	3.6 51.6:48.4
		2	Me	147a	rt	0.6 70.5:29.5
		2	Me	147a	40°	1.8 70.5:29.5
		2	Me	147a	60°	89.4 71.5:28.5
		2	Me	147b	rt	2.1 83.5:16.5
		2	Me	147b	60°	86 77.0:23.0
		2	Me	147c	60°	— 57.5:42.5

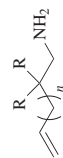
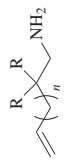
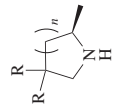


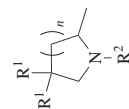
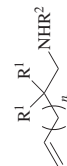
TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																																																																																		
Please refer to the charts preceding the tables for structures indicated by the bold numbers.																																																																																																																																																					
 $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_3\text{R}^*)\text{LnCH}(\text{TMS})_2$ (0.5–2 mol %), C ₇ D ₈	 337																																																																																																																																																				
<table><tr><th><i>n</i></th><th>R</th><th>R*</th><th>Ln</th><th>Temp</th><th>TOF (h⁻¹)</th><th>er</th></tr><tr><td>1</td><td>H</td><td>(+)-neomenthyl</td><td>La (R,S)</td><td>rt</td><td>—</td><td>68.0:32.0</td></tr><tr><td>1</td><td>H</td><td>(+)-neomenthyl</td><td>Nd (R,S)</td><td>rt</td><td>93</td><td>77.5:22.5</td></tr><tr><td>1</td><td>H</td><td>(+)-neomenthyl</td><td>Nd (R,S)</td><td>0°</td><td>11</td><td>82.0:18.0</td></tr><tr><td>1</td><td>H</td><td>(+)-neomenthyl</td><td>Sm (R,S)</td><td>rt</td><td>42</td><td>80.5:19.5</td></tr><tr><td>1</td><td>H</td><td>(+)-neomenthyl</td><td>Sm (R)</td><td>rt</td><td>62</td><td>76.0:24.0</td></tr><tr><td>1</td><td>H</td><td>(+)-neomenthyl</td><td>Sm (R)</td><td>0°</td><td>—</td><td>79.0:21.0</td></tr><tr><td>1</td><td>H</td><td>(+)-neomenthyl</td><td>Y (R,S)</td><td>rt</td><td>4</td><td>73.5:26.5</td></tr><tr><td>1</td><td>H</td><td>(+)-neomenthyl</td><td>Lu (R,S)</td><td>rt</td><td>—</td><td>35.5:64.5</td></tr><tr><td>1</td><td>H</td><td>(-)-menthyl</td><td>Y (R)</td><td>rt</td><td>—</td><td>15.5:84.5</td></tr><tr><td>1</td><td>H</td><td>(-)-phenylmenthyl</td><td>Y (R)</td><td>rt</td><td>—</td><td>18.0:82.0</td></tr><tr><td>1</td><td>Me</td><td>(+)-neomenthyl</td><td>Nd (R,S)</td><td>-20°</td><td>—</td><td>80.5:19.5</td></tr><tr><td>1</td><td>Me</td><td>(+)-neomenthyl</td><td>Sm (R)</td><td>rt</td><td>—</td><td>75.5:24.5</td></tr><tr><td>1</td><td>Me</td><td>(+)-neomenthyl</td><td>Sm (R)</td><td>0°</td><td>—</td><td>77.0:23.0</td></tr><tr><td>1</td><td>Me</td><td>(+)-neomenthyl</td><td>Sm (R)</td><td>-30°</td><td>—</td><td>82.0:18.0</td></tr><tr><td>1</td><td>Me</td><td>(+)-neomenthyl</td><td>Y (R,S)</td><td>rt</td><td>38</td><td>68.0:32.0</td></tr><tr><td>1</td><td>Me</td><td>(+)-neomenthyl</td><td>Lu (R,S)</td><td>rt</td><td>—</td><td>32.0:68.0</td></tr><tr><td>1</td><td>Me</td><td>(-)-menthyl</td><td>Y (R)</td><td>rt</td><td>9</td><td>28.5:71.5</td></tr><tr><td>1</td><td>Me</td><td>(-)-menthyl</td><td>Lu (R)</td><td>rt</td><td>—</td><td>64.5:35.5</td></tr><tr><td>1</td><td>Me</td><td>(-)-phenylmenthyl</td><td>Y (R)</td><td>rt</td><td>8</td><td>22.0:78.0</td></tr><tr><td>2</td><td>Me</td><td>(+)-neomenthyl</td><td>Sm (R)</td><td>rt</td><td>—</td><td>58.5:41.5</td></tr></table>	<i>n</i>	R	R*	Ln	Temp	TOF (h ⁻¹)	er	1	H	(+)-neomenthyl	La (R,S)	rt	—	68.0:32.0	1	H	(+)-neomenthyl	Nd (R,S)	rt	93	77.5:22.5	1	H	(+)-neomenthyl	Nd (R,S)	0°	11	82.0:18.0	1	H	(+)-neomenthyl	Sm (R,S)	rt	42	80.5:19.5	1	H	(+)-neomenthyl	Sm (R)	rt	62	76.0:24.0	1	H	(+)-neomenthyl	Sm (R)	0°	—	79.0:21.0	1	H	(+)-neomenthyl	Y (R,S)	rt	4	73.5:26.5	1	H	(+)-neomenthyl	Lu (R,S)	rt	—	35.5:64.5	1	H	(-)-menthyl	Y (R)	rt	—	15.5:84.5	1	H	(-)-phenylmenthyl	Y (R)	rt	—	18.0:82.0	1	Me	(+)-neomenthyl	Nd (R,S)	-20°	—	80.5:19.5	1	Me	(+)-neomenthyl	Sm (R)	rt	—	75.5:24.5	1	Me	(+)-neomenthyl	Sm (R)	0°	—	77.0:23.0	1	Me	(+)-neomenthyl	Sm (R)	-30°	—	82.0:18.0	1	Me	(+)-neomenthyl	Y (R,S)	rt	38	68.0:32.0	1	Me	(+)-neomenthyl	Lu (R,S)	rt	—	32.0:68.0	1	Me	(-)-menthyl	Y (R)	rt	9	28.5:71.5	1	Me	(-)-menthyl	Lu (R)	rt	—	64.5:35.5	1	Me	(-)-phenylmenthyl	Y (R)	rt	8	22.0:78.0	2	Me	(+)-neomenthyl	Sm (R)	rt	—	58.5:41.5		
<i>n</i>	R	R*	Ln	Temp	TOF (h ⁻¹)	er																																																																																																																																															
1	H	(+)-neomenthyl	La (R,S)	rt	—	68.0:32.0																																																																																																																																															
1	H	(+)-neomenthyl	Nd (R,S)	rt	93	77.5:22.5																																																																																																																																															
1	H	(+)-neomenthyl	Nd (R,S)	0°	11	82.0:18.0																																																																																																																																															
1	H	(+)-neomenthyl	Sm (R,S)	rt	42	80.5:19.5																																																																																																																																															
1	H	(+)-neomenthyl	Sm (R)	rt	62	76.0:24.0																																																																																																																																															
1	H	(+)-neomenthyl	Sm (R)	0°	—	79.0:21.0																																																																																																																																															
1	H	(+)-neomenthyl	Y (R,S)	rt	4	73.5:26.5																																																																																																																																															
1	H	(+)-neomenthyl	Lu (R,S)	rt	—	35.5:64.5																																																																																																																																															
1	H	(-)-menthyl	Y (R)	rt	—	15.5:84.5																																																																																																																																															
1	H	(-)-phenylmenthyl	Y (R)	rt	—	18.0:82.0																																																																																																																																															
1	Me	(+)-neomenthyl	Nd (R,S)	-20°	—	80.5:19.5																																																																																																																																															
1	Me	(+)-neomenthyl	Sm (R)	rt	—	75.5:24.5																																																																																																																																															
1	Me	(+)-neomenthyl	Sm (R)	0°	—	77.0:23.0																																																																																																																																															
1	Me	(+)-neomenthyl	Sm (R)	-30°	—	82.0:18.0																																																																																																																																															
1	Me	(+)-neomenthyl	Y (R,S)	rt	38	68.0:32.0																																																																																																																																															
1	Me	(+)-neomenthyl	Lu (R,S)	rt	—	32.0:68.0																																																																																																																																															
1	Me	(-)-menthyl	Y (R)	rt	9	28.5:71.5																																																																																																																																															
1	Me	(-)-menthyl	Lu (R)	rt	—	64.5:35.5																																																																																																																																															
1	Me	(-)-phenylmenthyl	Y (R)	rt	8	22.0:78.0																																																																																																																																															
2	Me	(+)-neomenthyl	Sm (R)	rt	—	58.5:41.5																																																																																																																																															



<i>n</i>	<i>R</i>	<i>R</i> [*]	<i>Ln</i>	Temp	TOF (h ⁻¹)	er
1	H	(+)-neomenthyl	La (<i>R</i>)	rt	—	65.5:34.5
1	H	(+)-neomenthyl	Sm (<i>S</i>)	rt	33	77.5:22.5
1	H	(+)-neomenthyl	Y (<i>R</i>)	rt	—	75.0:25.0
1	H	(-)-menthyl	Sm (<i>S</i>)	rt	33	19.0:81.0
1	H	(-)-menthyl	Sm (<i>S</i>)	0°	—	14.0:86.0
1	H	(-)-menthyl	Sm (<i>R</i>)	rt	—	20.0:80.0
1	Me	(+)-neomenthyl	La (<i>R</i>)	rt	—	57.0:43.0
1	Me	(+)-neomenthyl	Y (<i>R</i>)	rt	21	70.0:30.0
1	Me	(+)-neomenthyl	Lu (<i>R</i>)	rt	—	30.0:70.0
1	Me	(-)-menthyl	Sm (<i>S</i>)	rt	84	23.5:76.5
1	Me	(-)-menthyl	Sm (<i>S</i>)	0°	—	19.5:80.5
1	Me	(-)-menthyl	Sm (<i>S</i>)	-30°	—	13.0:87.0
1	Me	(-)-phenylmenthyl	Y (<i>R,S</i>)	rt	—	23.0:77.0
2	Me	(-)-menthyl	Sm (<i>S</i>)	rt	2	57.5:42.5

1. Catalyst (5 mol %),
Y[N(TMS)₂]₃ (5 mol %),
C₄H₉Si (10 mol %), C₆D₆
2. Aminoalkene, C₆D₆



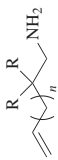
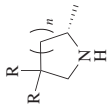
<i>n</i>	<i>R</i> ¹	<i>R</i> ²	Catalyst	Temp (°)	Time (h)	er ^{a,b}
1	H	H	148a	60	10	84.5:15.5
1	H	H	148b	60	5	86.5:13.5
1	H	H	148c	60	8	90.5:9.5
1	H	Me	148a	60	36	80.0:20.0
1	H	Me	148b	60	38	81.5:18.5
1	H	Me	148c	60	30	84.5:15.5
1	Me	H	148a	30	552	94.5:5.5
1	Me	H	148a	60	15	89.0:11.0
1	Me	H	148b	60	12	91.5:8.5
1	Me	H	148c	60	9	93.5:6.5
2	Me	H	148a	60	18	82.5:17.5
2	Me	H	148b	60	10	87.5:12.5
2	Me	H	148c	75	3	90.0:10.0

TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

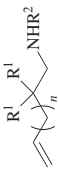
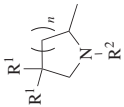
Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
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Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₅₋₈

	149i (1.1x mol %), Zr(NMe ₂) ₄ (x mol %), C ₇ H ₈		170
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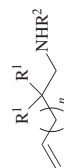
n	R	x	Temp (°)	Time (h)	er
1	H	20	135	72	(33) ^c 81.0:19.0 ^a
1	Me	10	115	48	(91) ^c 90.0:10.0
1	Me	10	115	48	(78) ^c 90.0:10.0
1	Me	20	115	24	(95) ^d 90.0:10.0
2	H	10	135	24	(79) ^c 66.5:33.5 ^a
2	Me	10	85	48	(91) ^c 75.5:24.5 ^a
2	Me	20	85	24	(99) ^c 75.5:24.5 ^a

	158 (x mol %), C ₆ D ₃ Br		180
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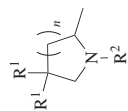
n	R ¹	R ²	x	Temp (°)	Time (h)	er ^d
1	H	Me	10	100	4	(100) 82.0:18.0
1	Me	Me	5	70	48	(70) 57.0:43.0
2	Me	Me	10	100	3	(100) 91.0:9.0
2	Me	PMB	10	100	192	(100) —

Please refer to the charts preceding the tables for structures indicated by the **bold numbers**.

C₅₋₁₀

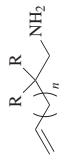
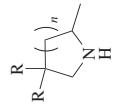
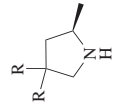


Catalyst (x mol %), C₆D₆



n	R ¹	R ²	Catalyst	x	Temp (°)	Time (h)	er ^a
1	H	H	150a	5	60	6	(46) 53.7:46.3
1	H	H	150b	5	60	6	(86) 56.0:44.0
1	H	H	150c	5	60	6	(35) 51.3:48.7
1	H	Me	150a	5	60	6	(25) 52.8:47.2
1	H	Me	150b	5	60	6	(68) 55.0:45.0
1	H	Me	150c	5	60	6	(30) 51.1:48.9
1	Me	H	150a	5	rt	20	(51) 60.5:39.5
1	Me	H	150a	5	60	6	(44) 62.0:38.0
1	Me	H	150b	1	rt	20	(59) 62.0:38.0
1	Me	H	150b	3	rt	20	(97) 60.5:39.5
1	Me	H	150b	5	rt	20	(98) 59.0:41.0
1	Me	H	150b	5	60	6	(93) 60.0:40.0
1	Me	H	150c	5	rt	20	(35) 53.6:46.4
1	Me	H	150c	5	60	6	(50) 52.7:47.3
1	-(CH ₂) ₅ -	H	150a	5	60	6	(50) 59.5:40.5
1	-(CH ₂) ₅ -	H	150b	5	60	6	(82) 61.0:39.0
1	-(CH ₂) ₅ -	H	150c	5	60	6	(43) 52.85:47.15
2	Me	H	150a	5	60	6	(40) 55.5:45.5
2	Me	H	150b	5	60	6	(75) 57.0:43.0
2	Me	H	150c	5	60	6	(28) 52.3:47.7

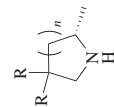
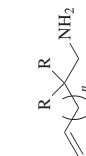
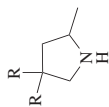
TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the bold numbers .			
C₅₋₁₀ 	Catalyst (x mol %), C₆D₆		549
	<i>n</i>	<i>x</i>	
	1	H	3
		151a	60
			36
	1	H	3
		151b	60
			36
	1	H	3
		151c	60
			36
	1	Me	5
		151a	rt
			24
	1	Me	5
		151b	rt
			24
	1	Me	5
		151c	rt
			24
	1	Me	5
		151c	60
			24
	1	-(CH ₂) ₅ -	3
		151a	60
			36
	1	-(CH ₂) ₅ -	3
		151b	60
			36
	1	-(CH ₂) ₅ -	3
		151c	60
			36
	2	Me	5
		151a	120
			60
	2	Me	5
		151b	120
			60
	2	Me	5
		151c	120
			160
			(—)
			er ^d
			69.0:31.0
			(80)
			74.0:26.0
			(95)
			78.0:22.0
			(32)
			77.5:22.5
			(77)
			80.0:20.0
			(92)
			85.5:14.5
			(70)
			82.5:17.5
			(56)
			66.5:33.5
			(88)
			71.0:29.0
			(100)
			75.5:24.5
			(31)
			58.0:42.0
			(46)
			62.5:37.5
			(92)
			(—)
			—
C₅₋₁₇ 	152 (10 mol %), C₆D₆, rt		153
		R	Time (h)
		H	84
		(4)	—
		Ph	1
		(98)	52.5:47.5



153 (x mol %),
Ln[N(TMS)₂]₃ (5 mol %), C₆D₆

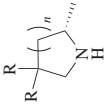
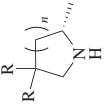
R	x	Ln	Temp	TOF (h ⁻¹) ^b	er
H	6	La	rt	0.9	70.0:30.0
Me	0	Sm	rt	5.2	50.0:50.0
Me	0	La	rt	7.7	50.0:50.0
Me	6	Sm	rt	13	77.5:22.5
Me	6	Nd	rt	10	80.5:19.5
Me	6	La	rt	25	83.5:16.5
Me	11.5	Sm	60°	—	80.0:20.0
Me	11.5	La	rt	10	81.5:18.5
Ph	6	La	rt	660	67.0:33.0



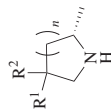
Catalyst (x mol %), C₆D₆

n	R	Catalyst	x	Temp	Time (h)	er
1	H	155a	2	60°	96	(96) 90.0:10.0
1	H	155d	2	60°	27	(95) 93.5:6.5
1	Me	155a	2	60°	5.5	(93) 86.5:13.5
1	Me	155d	2	rt	192	(91) 79.0:21.0
1	Me	155d	2.5	60°	10.5	(94) 78.0:22.0
1	-(CH ₂) ₅ -	155a	2	rt	6	(97) 92.5:7.5
1	-(CH ₂) ₅ -	155d	2	rt	13	(96) 80.5:19.5
1	Ph	155a	2	rt	0.6	(94) 97.5:2.5
1	Ph	155d	2	rt	3	(96) 87.0:13.0
2	H	155a	2	80°	84	(95) 58.0:42.0
2	H	155d	2	80°	23	(94) 71.5:28.5
2	Me	155a	2	60°	20	(97) 70.0:30.0
2	Me	155d	2	60°	64	(97) 80.5:19.5

TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the bold numbers.			
C₅₋₁₇ 	Catalyst (x mol %), THF (y mol %), C ₆ D ₆		52
	n R	Catalyst x y Temp Time (h) er	
	1 H	155b 1 3 rt 53.5 (96) 85.0:15.0	
	1 H	155b 2 0 rt 24 (95) 85.0:15.0	
	1 H	155b 2 0 60° 0.8 (95) 83.0:17.0	
	1 H	155b 4 0 rt 20 (94) 91.5:8.5	
	1 Me	155b 1.5 4.5 rt 2 (95) 69.0:31.0	
	1 Me	155b 2 450 rt 24 (94) 65.5:34.5	
	1 Me	155b 3 0 60° 0.07 (92) 82.5:17.5	
	1 Me	155b 4 0 rt 3 (95) 71.5:28.5	
	1 Me	155e 4 0 rt 2 (95) 76.5:23.5	
	1 -(CH ₂) ₅ -	155b 2 0 rt 0.1 (95) 91.5:8.5	
	1 -(CH ₂) ₅ -	155e 2 0 rt 0.5 (95) 89.0:11.0	
	1 Ph	155b 2 3 rt 0.06 (96) 92.0:8.0	
	1 Ph	155e 2 0 rt 0.06 (94) 88.5:11.5	
	2 H	155e 2 0 80° 40 (92) 73.0:27.0	
	2 Me	155e 2 0 60° 20 (97) 68.0:32.0	
Catalyst (x mol %), C₆D₆ 	n R	Catalyst x y Temp Time (h) er	52
	1 H	155c 2 60° 4 (96) 86.0:14.0	
	1 H	155f 4 0° 190 (92) ^f 96.0:4.0	
	1 H	155f 5 rt 16.5 (93) 95.0:5.0	

Catalyst (x mol %),
Zr(NMe₂)₄ (x mol %), C₆D₆



n	R ¹	R ²	Catalyst	x	Temp (°)	Time (h)	dr	er
1	H	H	155f	5	145	120	(27)	—
1	Me	Me	156f	5	110	7	(94)	—
1	Me	allyl	156f	5	110	3	(68)	83.5:16.5
1	—(CH ₂) ₄ —	156e	5	110	5	5	(87)	86.5:13.5/83.0:17.0
1	—(CH ₂) ₅ —	156a	10	110	3	3	(91)	78.5:21.5
1	—(CH ₂) ₅ —	156b	10	110	19	19	(89)	53.0:47.0
1	—(CH ₂) ₅ —	156c	10	110	2	2	(91)	53.5:46.5
1	—(CH ₂) ₅ —	156e	10	110	3	3	(92)	63.0:37.0
1	—(CH ₂) ₅ —	156f	10	110	3	3	(92)	58.5:41.5
1	H	Ph	156f	5	110	3	(92)	76.0:24.0
1	Me	Ph	156f	5	110	96	(24)	68.5:31.5/52.5:47.5
1	Ph	Ph	156f	5	110	3	(92)	72.5:27.5/87.0:13.0
1	Ph	Ph	156a	10	110	24	(90)	56.5:43.5
1	Ph	Ph	156b	10	110	24	(92)	61.0:39.0
1	Ph	Ph	156c	10	110	1	(90)	58.0:42.0
1	Ph	Ph	156d	10	110	1	(93)	53.5:46.5
1	Ph	Ph	156e	10	110	1.25	(92)	59.5:40.5
1	Ph	Ph	156f	5	110	1	(92)	63.5:36.5
1	Ph	Ph	156f	10	110	1	(92)	64.0:36.0
2	Me	Me	156f	5	110	48	(98)	61.5:38.5

TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene

Conditions

Product(s) and Yield(s) (%)

Refs.

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

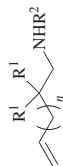
C ₅₋₁₈	C ₅₋₁₉																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
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Please refer to the charts preceding the tables for structures indicated by the **bold numbers**.

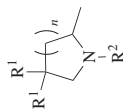


2	Ph	Ph	157a	4	100	3	(95)	—	66.5:33.5 ^a
2	Ph	Ph	157b	2	100	7	(95)	—	63.0:37.0 ^a
3	H	Ph	157b	10	120	72	(94)	—	76.5:22.5 ^a
3	Ph	Ph	157a	8	120	51	(95)	—	80.0:20.0 ^a

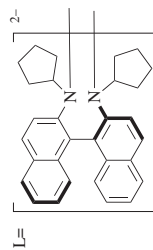
C₅₋₁₁



Catalyst (6 mol %), C₆D₆



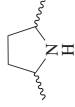
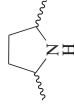
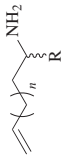
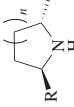
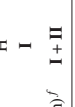
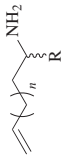
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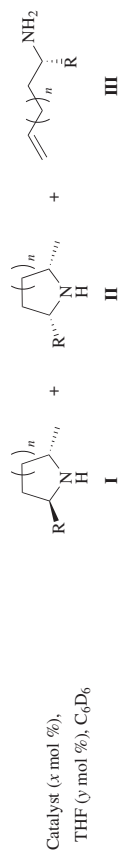
n	R ¹	R ²	Catalyst	Temp	Time (h)	er ^a
1	H	Me	Li(THF) ₄ [LY(CH ₂ TMS) ₂] ₂	70°	24	(95) 64.0:36.0
1	H	Me	LYCH ₂ TMS(THF) ₂	50°	5	(95) 76.5:23.5
1	Me	Me	Li(THF) ₄ [LY(CH ₂ TMS) ₂] ₂	50°	16	(85) 83.0:17.0
1	Me	Me	Li(THF) ₄ [LY(CH ₂ TMS) ₂] ₂	rt	84	(95) 80.0:20.0
1	Me	Me	LYCH ₂ TMS(THF) ₂	rt	0.17	(95) 90.0:10.0
1	-(CH ₂) ₅ -	Me	Li(THF) ₄ [LY(CH ₂ TMS) ₂] ₂	rt	0.17	(95) 86.0:14.0
1	-(CH ₂) ₅ -	Me	LYCH ₂ TMS(THF) ₂	rt	0.17	(95) 91.5:8.5
1	-(CH ₂) ₅ -	Me	LYbCH ₂ TMS(THF) ₂	rt	0.17	(95) 90.5:9.5
1	-(CH ₂) ₅ -	Bn	Li(THF) ₄ [LY(CH ₂ TMS) ₂] ₂	50°	16	(0) —
1	-(CH ₂) ₅ -	Bn	LYCH ₂ TMS(THF) ₂	50°	16	(95) 60.0:40.0
2	Me	Me	Li(THF) ₄ [LY(CH ₂ TMS) ₂] ₂	50°	16	(95) 61.5:38.5
2	Me	Me	LYCH ₂ TMS(THF) ₂	rt	0.5	(95) 63.5:36.5
2	Me	Me	LYbCH ₂ TMS(THF) ₂	rt	0.17	(95) 73.0:27.0
2	-(CH ₂) ₅ -	Me	Li(THF) ₄ [LY(CH ₂ TMS) ₂] ₂	rt	3	(95) 62.5:37.5
2	-(CH ₂) ₅ -	Me	LYCH ₂ TMS(THF) ₂	rt	0.17	(95) 63.5:36.5
2	-(CH ₂) ₅ -	Me	LYbCH ₂ TMS(THF) ₂	rt	0.17	(95) 69.0:31.0

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TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the bold numbers.			
 C ₅	Catalyst (1.2x mol %), [Rh(COD) ₂][BF ₄] (x mol %), dioxane		349
	Ar	Catalyst x Time (h) er	
	Ph	241i 10 20 (48) 95.0:5.0	
	4-ClC ₆ H ₄	241h 5 20 (63) 92.5:7.5	
	4-MeOC ₆ H ₄	241h 5 30 (35) 92.5:7.5	
 C ₆	2-MeC ₆ H ₄	241h 5 20 (50) 93.0:7.0	
	4-MeO ₂ CC ₆ H ₄	241h 5 20 (61) 91.5:8.5	
	144a (4 mol %), C ₆ D ₆ , 90°, 1.5 h ^f	 (61) +  (40)	492
	<i>trans/cis</i> = 6.4:1 er 67.5:32.5 (<i>trans</i>)		
	144b (1.5 mol %), C ₆ D ₆ , rt, 25 h ^f	 (42) +  (40)	52
 C ₆₋₁₂	<i>trans/cis</i> = 10:1 er 86.5:13.5 (<i>trans</i>)		
	Catalyst (2 mol %), C ₆ D ₆	 I +  II +  III	
	n R	Time (h) ^f I + II I/II er I er II er III	
	1 Me	155a 40 94 (45) 10:1 82.0:18.0 (39) 86.5:13.5	52
	1 Me	155d 40 94 (44) 7:1 85.5:14.5 (38) 86.5:13.5	52
 C ₆₋₁₂	<i>c</i> -C ₆ H ₁₁	155a 40 34 (75) — — (—) 83.5:16.5	342
	<i>c</i> -C ₆ H ₁₁	155d 40 49 (47) — — (—) 66.0:34.0	342

1	4-ClC ₆ H ₄	155a	50	22	(60)	—	—	(—)	90.5:9.5	342
1	4-ClC ₆ H ₄	155d	50	24	(49)	—	—	(—)	84.0:16.0	342
1	4-MeOC ₆ H ₄	155a	50	35	(55)	—	—	(—)	84.5:15.5	342
1	4-MeOC ₆ H ₄	155d	50	22	(51)	—	—	(—)	77.0:23.0	342
1	Bn	155a	40	40	(64)	—	—	(—)	80.0:20.0	342
1	Bn	155d	40	33	(55)	—	—	(—)	73.5:26.5	342
2	Ph	155a	80	—	(47)	1:7	—	(—)	59.0:41.0	342
2	Ph	155d	80	—	(60)	1:4	—	(—)	73.5:26.5	342



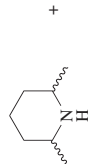
<i>n</i>	R	Catalyst	<i>x</i>	<i>y</i>	Temp	Time (h) ^f	I + II	I/II	er I	III	er III
1	Me	155b	2	0	rt	25.5	(49)	11:1	84.0:16.0	(39)	86.0:14.0
1	Me	155b	2	4	rt	15	(47)	8:1	79.0:21.0	(40)	84.0:16.0
1	Me	155e	2	0	rt	26	(46)	13:1	89.0:11.0	(39)	90.0:10.0
1	Et	155b	1	0	rt	4.5	(47)	16:1	—	(42)	75.5:24.5
1	Et	155e	1	0	rt	6	(46)	20:1	—	(39)	78.5:21.5
1	MOM	155b	2	0	40°	85	(50)	—	—	(—)	66.5:33.5
1	MOM	155e	2	0	40°	180	(45)	—	—	(—)	60.0:40.0
1	<i>i</i> -Pr	155b	1.5	0	rt	6	(49)	18:1	—	(40)	68.5:31.5
1	<i>i</i> -Pr	155e	1.5	0	rt	24	(47)	7:1	—	(46)	72.0:28.0
1	<i>c</i> -C ₆ H ₁₁	155b	2	0	rt	8	(56)	—	—	(—)	74.5:25.5
1	<i>c</i> -C ₆ H ₁₁	155e	2	0	rt	46	(59)	—	—	(—)	77.0:23.0
1	4-ClC ₆ H ₄	155b	2	0	40°	18	(48)	>50:1	—	(33)	85.5:14.5
1	4-ClC ₆ H ₄	155e	2	0	40°	10	(51)	—	—	(44)	90.0:10.0
1	4-MeOC ₆ H ₄	155b	2	0	40°	8	(47)	>50:1	—	(43)	89.0:11.0
1	4-MeOC ₆ H ₄	155e	2	0	40°	14	(34)	—	—	(—)	70.0:30.0
1	Ph	155b	2	0	rt	95	(41)	>50:1	81.5:18.5	(47)	87.0:13.0
1	Ph	155e	2	0	40°	18	(50)	>50:1	—	(41)	81.5:18.5
1	Bn	155b	1.5	0	rt	9	(39)	20:1	70.0:30.0	(45)	71.0:29.0
1	Bn	155e	2	0	rt	27	(46)	20:1	67.0:33.0	(44)	69.0:31.0
2	Ph	155b	2	0	80°	—	(45)	1:3	—	(—)	55.5:44.5
2	Ph	155e	2	0	80°	—	(72)	1:2.5	—	(—)	55.5:44.5

TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)						Refs.					
	Catalyst (x mol %), C ₆ D ₆	<i>n</i>	R	Catalyst	<i>x</i>	Temp (°C)	Time (h) ^f	I + II	I/II	er I	III	er III	
1	Me	155c	2	rt	42	(50)	10:1	79.0:21.0	(37)	86.5:13.5	52		
1	Me	155f	2	rt	24.5	(47)	9:1	86.5:13.5	(38)	87.5:12.5	52		
1	MOM	155c	2	40	120	(59)	—	—	—	—	54.5:45.5	342	
1	MOM	155f	2	40	94	(56)	—	—	—	—	54.5:45.5	342	
1	<i>c</i> -C ₆ H ₁₁	155c	2	rt	23	(47)	—	—	—	—	75.5:24.5	342	
1	<i>c</i> -C ₆ H ₁₁	155f	2	rt	47	(46)	—	—	—	—	72.0:28.0	342	
1	4-ClC ₆ H ₄	155c	2	40	17	(55)	—	—	—	—	88.5:11.5	342	
1	4-ClC ₆ H ₄	155f	2	40	21	(50)	—	—	—	—	84.0:16.0	342	
1	4-MeOC ₆ H ₄	155c	2	40	26	(47)	—	—	—	—	85.0:15.0	342	
1	4-MeOC ₆ H ₄	155f	2	40	24	(52)	—	—	—	—	85.0:15.0	342	
1	Ph	155c	2	40	15	(51)	>50:1	—	(42)	91.5:8.5	52		
1	Ph	155f	1	40	—	(—)	>50:1	—	(33)	99.5:0.5	52		
1	Ph	155f	1.5	rt	40	(51)	>50:1	—	(46)	79.5:20.5	52		
1	Bn	155c	2	rt	26	(50)	—	—	—	—	66.0:34.0	342	
1	Bn	155f	2	rt	13	(70)	—	—	—	—	71.0:29.0	342	
2	Ph	155c	2	80	—	(51)	1:2.5	—	—	—	63.0:37.0	342	
2	Ph	155f	2	80	—	(55)	1:6	—	—	—	65.5:34.5	342	

C₇

155e (1 mol %), C₆D₆, 80°, 25 h^f



+



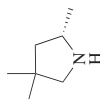
52

(62), *trans/cis* = 1:1.3

er 82.5:17.5^g



160 (3 mol %), C₆D₆, rt, 6.25 h



(80) er 55.5:44.5

339

161 (4 mol %), C₆D₆, 65°, 65 h



(96) er 61.0:39.0

339

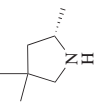
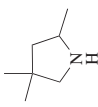
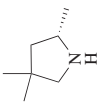
Catalyst (6 mol %),
La[N(TMS)₂]₃ (5 mol %), C₆D₆, rt



Catalyst	TOF (h ⁻¹)	er
162	(98)	—
165a	(—)	62.5:37.5
165b	(—)	53.0:47.0
		69.5:30.5

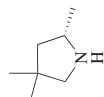
550

TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the bold numbers.			
C₇ 	Catalyst (6 mol %), La[N(TMS) ₂] ₃ (5 mol %), C ₆ D ₆ , rt		550
		Catalyst	er
		TOF (h ⁻¹) ^b	
		163a	7.1 78.0:22.0
		163b	21 80.5:19.5
	1. Ligand (5 mol %), Y[N(TMS) ₂] ₃ (5 mol %), C ₆ D ₆ , 120° 2. Aminoalkene, C ₆ D ₆		261
		166	rt 4 61.0:39.0
		167a	10° 168 83.0:17.0
		167a	rt 22 78.0:22.0
		167b	rt 288 52.5:47.5
	1. Catalyst (3.3 mol %), Ln precatalyst (3 mol %), C ₇ D ₈ , 50° 2. Aminoalkene, C ₇ D ₈		555
		168a	rt 15 50.0:50.0
		168b	rt 3 58.5:41.5
		169	rt 800 55.0:45.0
		170	60° 5.5 51.0:49.0
		Catalyst Precatalyst Temp (°) Time (d) er ^b	
			172a [Y(N(<i>i</i> -Pr) ₂) ₃ (THF) ₂] 35 5 60.0:40.0
			172b [Y(N(<i>i</i> -Pr) ₂) ₃ (THF) ₂] 35 5 60.5:39.5
			172c [Y(N(<i>i</i> -Pr) ₂) ₃ (THF) ₂] 35 5 61.5:38.5
			172d [Y(N(SiHMe ₂) ₂) ₃ (THF) ₂] 60 14 75.0:25.0
			172d [Sm{N(SiHMe ₂) ₂ } ₃ (THF) ₂] 60 7 66.5:33.5
			172d [La{N(SiHMe ₂) ₂ } ₃ (THF) ₂] 60 7 59.0:41.0
			172d [Y(N(<i>i</i> -Pr) ₂) ₃ (THF) ₂] 35 5 72.5:27.5

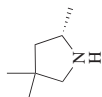


1. Catalyst (4.4 mol %),
Ln precatalyst (4 mol %),
C₆D₆, 50°
2. Aminoalkene, C₆D₆, 60°



556

Catalyst	Precatalyst	Time (d)	er ^{a,b}
173a	[La{N(SiHMe ₂) ₂] ₃ (THF) ₂]	5	67.0:33.0
173a	[Y{N(SiHMe ₂) ₂] ₃ (THF) ₂]	7	70.0:30.0
173b	[Y{N(SiHMe ₂) ₂] ₃ (THF) ₂]	8	60.5:39.5



1. **159a** (5 mol %),
Ln[N(TMS)₂]₃ (5 mol %),
C₆D₆, rt
2. Aminoalkene, C₆D₆

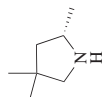
554

Ln	Temp (°)	TOF (h ⁻¹) ^b	er
La	rt	0.06	77.5:22.5
La	60	2.0	80.5:19.5
Nd	rt	0.05	82.5:17.5
Nd	60	1.4	80.5:19.5
Sm	rt	0.04	81.5:18.5
Sm	60	0.57	77.5:22.5
Y	60	0.25	54.8:45.2
Lu	60	0.07	53.75:46.25
Sc	120	0.01	26.5:73.5

485

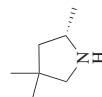


1. **159b** (5 mol %),
Ln[N(TMS)₂]₃ (5 mol %),
C₆D₆, rt
2. Aminoalkene, C₆D₆



554

Ln	Temp	TOF (h ⁻¹) ^b	er
La	rt	0.31	61.5:38.5
Nd	rt	3.0	68.5:31.5
Sm	rt	4.2	68.0:32.0
Y	rt	20	66.0:34.0
Lu	rt	1.2	68.5:31.5
Sc	120°	0.26	50.85:49.15



1. **159c** (5 mol %),
Ln[N(TMS)₂]₃ (5 mol %),
C₆D₆, rt
2. Aminoalkene, C₆D₆

554

Ln	Temp (°)	TOF (h ⁻¹) ^b	er
La	rt	0.006	60.0:40.0
La	60	0.38	63.0:37.0
La	90	1.3	64.5:35.5
Nd	60	0.69	63.5:36.5
Sm	60	0.26	70.0:30.0
Y	60	0.47	77.0:23.0
Lu	60	0.16	80.5:19.5
Sc	120	0.28	21.0:79.0



TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. 159d (5 mol %), Ln[N(TMS) ₂] ₃ (5 mol %), C ₆ D ₆ , rt	Ln TOF (h ⁻¹) ^b er Sm 0.26 49.6:50.4 Y 0.82 53.7:46.3	554
	2. Aminoalkene, C ₆ D ₆ , 60°		
	1. 159e (5 mol %), Ln[N(TMS) ₂] ₃ (5 mol %), C ₆ D ₆ , rt	Ln Temp TOF (h ⁻¹) ^b er La rt 0.16 70.0:30.0 Nd rt 0.23 66.0:34.0 Sm rt 0.14 56.5:43.5 Y 60° 0.24 69.5:30.5 Lu 60° 0.07 63.5:36.5 Sc 120° 0.02 53.95:46.05	554
	2. Aminoalkene, C ₆ D ₆		
	1. 159f (5 mol %), Ln[N(TMS) ₂] ₃ (5 mol %), C ₆ D ₆ , rt	Ln Temp (°) TOF (h ⁻¹) ^b er La 60 0.96 — ^h Nd 60 3.1 61.5:38.5 Sm 60 3.9 67.5:32.5 Y 60 2.8 71.0:29.0 Lu 60 0.49 63.0:37.0 Sc 120 — —	554
	2. Aminoalkene, C ₆ D ₆		
	Catalyst (1 mol %), C ₆ D ₆ , 70°	Catalyst Time (h) er ^d 174a 24 (45) — 174a 72 (100) 52.5:47.5 174b 24 (49) — 174c 24 (12) — 174d 24 (9) — 175a 30 (100) 63.5:36.5 175b 40 (100) 80.5:19.5	341

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

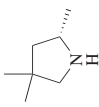
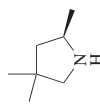
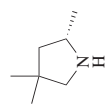
 Catalyst (1 mol %), C ₆ D ₆ , 70°	 Catalyst (22 mol %), M(NMe ₂) ₄ (20 mol %), toluene, 135°, 24 h	Catalyst	Time (h)	er	341
		176a	44	(100) 50.0:50.0	
		176b	40	(100) 50.0:50.0	
		176c	24	(100) 55.5:44.5	
		Catalyst	M	er	170
		177a	Ti	(tr) ^c —	
		177a	Zr	(97) ^c <52.5:47.5	
		177a	Hf	(63) ^c 40.5:59.5	
		177b	Ti	(97) ^c —	
		177b	Zr	(94) ^c 61.5:38.5	
		177b	Hf	(94) ^c 63.0:37.0	
		177c	Ti	(8) ^c <52.5:47.5	
		177c	Zr	(96) ^c <52.5:47.5	
		177c	Hf	(76) ^c <52.5:47.5	
		177f	Ti	(tr) ^c —	
		177f	Zr	(92) ^c 59.0:41.0	
		177f	Hf	(94) ^c 65.0:35.0	
		177g	Zr	(63) ^c 42.0:58.0	
		183a	Ti	(59) ^c 43.5:56.5	
		183a	Zr	(97) ^c 62.0:38.0	
		183a	Hf	(98) ^c 54.5:45.5	
		183b	Ti	(52) ^c 53.0:47.0	
		183b	Zr	(98) ^c 63.5:36.5	
		183b	Hf	(99) ^c 56.0:44.0	

TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

C₇



Catalyst (22 mol %),
M(NMe₂)₄ (20 mol %),
toluene, 135°, 24 h



Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst M er	
		149b Ti (tr) ^c —	170
		149b Zr (92) ^c 60.5:39.5	
		149b Hf (94) ^c 56.5:43.5	
		149c Ti (97) ^c 54.5:45.5	
		149c Zr (94) ^c 60.0:40.0	
		149c Hf (94) ^c 56.5:43.5	
		149d Ti (8) ^c 52.5:47.5	
		149d Zr (96) ^c 83.5:16.5	
		149d Hf (76) ^c 79.0:21.0	
		149e Zr (92) ^c 81.5:18.5	
		149f Zr (95) ^c 88.0:12.0	
		149g Zr (99) ^c 85.0:15.0	
		149h Zr (99) ^c 84.0:16.0	
		149i Zr (99) ^c 87.5:12.5	
		149j Zr (—) —	
		149k Zr (98) ^c 81.0:19.0	
		178 Ti (tr) ^c —	
		178 Zr (tr) ^c —	
		178 Hf (tr) ^c —	
		179a Zr (tr) ^c —	
		179b Zr (96) ^c 75.0:25.0	
		179c Zr (95) ^c 77.5:22.5	

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

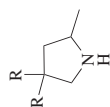
Please refer to the charts preceding the tables for structures indicated by the bold numbers.

C₇

Catalyst (22 mol %), M(NMe ₂) ₄ (20 mol %), C ₇ H ₈ , 135°, 24 h																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																						
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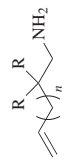
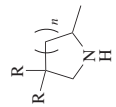
TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

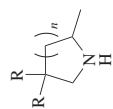
Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>			
 C_7	 Catalyst (10 mol %), C_7D_8, 110°	 n	 $e^{a,b}$
		1 185a	85.0:15.0
		1 185b	75.5:24.5
		2 185a	57.0:43.0
 C_{7-10}	 Catalyst (x mol %), C_6D_6	 n	 $e^{a,b}$
		1 185b	79.0:21.0
		2 185a	57.0:43.0
		2 185b	79.0:21.0
 C_{7-10}	 Catalyst (x mol %), C_6D_6	 n	
		 $e^{a,b}$	
		 n	
		 $e^{a,b}$	
		 n	
		 $e^{a,b}$	
		 n	
		 $e^{a,b}$	
 C_{7-10}	 Catalyst (5 mol %), C_6D_6	 n	
		 $e^{a,b}$	
		 n	
		 $e^{a,b}$	
		 n	
		 $e^{a,b}$	
		 n	
		 $e^{a,b}$	

C₇₋₉Catalyst (x mol %), C₆D₆

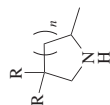
R	Catalyst	x	Temp	Time (h)	ea ^d	
Me	233a	10	rt	168	(49)	84.5:15.5
Me	233a	10	60°	46	(98)	71.0:29.0
Me	233b	10	rt	44	(73)	70.0:30.0
Me	233d	6	60°	17	(94)	84.5:15.5
Me	233d	8	rt	144	(14)	86.0:14.0
Me	233e	6	rt	180	(49)	82.0:18.0
Me	233e	6	60°	22	(46)	84.0:16.0
Me	233f	10	rt	48	(34)	87.5:12.5
Me	233f	10	rt	168	(77)	86.5:13.5
Me	233g	10	rt	120	(91)	83.0:17.0
Me	233i	6	rt	96	(94)	61.0:39.0
Me	233j	8	rt	17	(84)	55.0:45.0
-(CH ₂) ₄ -	233b	8	rt	44	(73)	70.0:30.0
-(CH ₂) ₄ -	233d	4	rt	84	(30)	88.0:12.0
-(CH ₂) ₄ -	233d	4	60°	15	(100)	86.5:13.5
-(CH ₂) ₄ -	233f	10	0°	144	(36)	89.0:11.0
-(CH ₂) ₄ -	233f	10	0°	384	(74)	88.5:11.5
-(CH ₂) ₄ -	233f	10	rt	96	(83)	84.5:15.5
-(CH ₂) ₄ -	233g	10	0°	96	(10)	87.5:12.5
-(CH ₂) ₄ -	233g	10	rt	48	(80)	84.0:16.0
-(CH ₂) ₄ -	233j	6	rt	17	(95)	55.0:45.0

TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)						Refs.
Please refer to the charts preceding the tables for structures indicated by the bold numbers .								
		Catalyst (x mol %), C ₆ D ₆						
n	R	Catalyst	x	Temp (°)	Time (h)	e ^d		
1	Me	187a	5	rt	48	(93)	69.5:30.5	557
1	Me	187b	5	60	48	(65)	72.0:28.0	557
1	Me	188a	5	rt	48	(81)	52.7:47.3	560
1	Me	188b	5	120	160	(0)	—	560
1	Me	189a	5	rt	48	(100)	68.5:31.5	560
1	Me	189b	5	rt	48	(55)	71.5:28.5	560
1	Me	190	2.5	rt	16	(95)	77.0:23.0	566
1	—(CH ₂) ₅ —	187a	5	rt	48	(100)	67.5:32.5	557
1	—(CH ₂) ₅ —	187b	5	60	48	(75)	69.0:31.0	557
1	—(CH ₂) ₅ —	188a	5	60	90	(92)	55.5:44.5	560
1	—(CH ₂) ₅ —	189a	5	60	48	(93)	58.0:42.0	560
1	—(CH ₂) ₅ —	189b	5	60	60	(96)	61.5:38.5	560
1	—(CH ₂) ₅ —	190	2.5	rt	16	(100)	74.0:26.0	566
2	Me	187a	5	120	48	(82)	58.0:42.0	557
2	Me	187b	5	120	48	(51)	61.0:39.0	557
2	Me	188a	5	120	90	(9.4)	62.0:38.0	560
2	Me	189a	5	120	48	(78)	62.5:37.5	560
2	Me	189b	5	120	48	(75)	67.0:33.0	560
2	Me	190	2.5	120	16	(92)	65.0:35.0	566

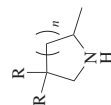
Catalyst (5 mol %), C₆D₆

<i>n</i>	R	Catalyst	Temp (°)	Time (h)	Yield (%)	er ^d
1	Me	191a	60	16	(100)	56.5:43.5
1	Me	191b	60	16	(95)	83.0:17.0
1	Me	191b	rt	48	(27)	87.0:13.0
1	Me	191c	60	16	(97)	77.0:23.0
1	Me	191d	60	16	(90)	75.0:25.0
1	-(CH ₂) ₅ -	191a	60	16	(100)	56.0:44.0
1	-(CH ₂) ₅ -	191b	60	16	(98)	80.0:20.0
1	-(CH ₂) ₅ -	191c	60	16	(95)	74.0:26.0
1	-(CH ₂) ₅ -	191d	60	16	(92)	72.5:27.5
2	Me	191a	120	24	(100)	62.0:38.0
2	Me	191b	120	24	(92)	69.0:31.0
2	Me	191c	120	24	(95)	67.0:33.0
2	Me	191d	120	24	(90)	64.0:36.0



Catalyst (10 mol %), C₆D₆, 120°, 60 h

<i>n</i>	R	Catalyst	er ^d	
1	Me	197	(95)	55.0:45.0
1	Me	198	(89)	67.5:32.5
1	Me	199	(85)	76.0:24.0
1	-(CH ₂) ₅ -	197	(100)	54.85:45.15
1	-(CH ₂) ₅ -	198	(100)	64.0:36.0
1	-(CH ₂) ₅ -	199	(91)	71.0:29.0
2	Me	197	(85)	52.8:47.2
2	Me	198	(86)	54.75:45.25
2	Me	199	(82)	62.5:37.5



Catalyst (10 mol %), C₆D₆, 120°

<i>n</i>	R	Catalyst	Time (h)	er ^d	
1	Me	202a	48	(96)	75.5:24.5
1	Me	202b	24	(100)	71.5:28.5
1	Me	203a	48	(86)	73.0:27.0
1	Me	203b	24	(100)	69.0:31.0
1	Me	204a	48	(93)	84.0:16.0
1	Me	204b	24	(100)	80.5:19.5
1	-(CH ₂) ₅ -	202a	36	(100)	73.0:27.0
1	-(CH ₂) ₅ -	202b	16	(100)	69.5:30.5
1	-(CH ₂) ₅ -	203a	36	(100)	71.0:29.0
1	-(CH ₂) ₅ -	203b	16	(100)	68.0:32.0
1	-(CH ₂) ₅ -	204a	36	(100)	76.0:24.0
1	-(CH ₂) ₅ -	204b	16	(100)	71.5:28.5
2	Me	202a	48	(100)	62.0:38.0
2	Me	202b	24	(100)	60.5:39.5
2	Me	203a	48	(90)	61.5:38.5
2	Me	203b	24	(100)	59.5:40.5
2	Me	204a	48	(98)	62.5:37.5
2	Me	204b	24	(100)	60.0:40.0



TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Refs.

Product(s) and Yield(s) (%)

Conditions

Aminoalkene

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₇₋₁₀

205 (10 mol %), C₆D₆

568

<i>n</i>	R	Temp (°)	Time (h)	er ^d
1	Me	120	60	(87) 86.0:14.0
1	Me	120	72	(100) 85.0:15.0
1	Me	90	60	(83) 83.5:16.5
1	-(CH ₂) ₅ -	120	48	(95) 77.0:23.0
2	Me	120	72	(85) 69.0:31.0

Catalyst (10 mol %), C₆D₆, 120°, 48 h

569

<i>n</i>	R	Catalyst	er ^d
1	Me	213	(90) 65.0:35.0
1	Me	214	(100) 68.5:31.5
1	Me	216	(45) 63.0:37.0
1	-(CH ₂) ₅ -	213	(100) 64.0:36.0
1	-(CH ₂) ₅ -	214	(100) 65.0:35.0
1	-(CH ₂) ₅ -	216	(87) 63.0:37.0
2	Me	213	(100) 58.0:42.0
2	Me	214	(100) 62.0:38.0
2	Me	216	(37) 60.5:39.5

C₇₋₁₇

Catalyst (x mol %), C₆D₆

570

<i>n</i>	R	Catalyst	x	Temp	Time (h)	er ^d
1	Me	218	7	rt	8	(95) 55.5:44.5
1	Me	220	10	120°	333	(56) 51.0:49.0
1	Me	226	1	100°	80	(99) 55.0:45.0
1	-(CH ₂) ₅ -	218	10	rt	0.5	(100) 55.5:44.5
1	-(CH ₂) ₅ -	226	1	60°	12	(99) 57.0:43.0
1	Ph	220	10	120°	140	(0) —

570

149

571

570

571

149

1	Ph	226	1	rt	2	(99)	54.5:45.5	571
2	Me	226	2	100°	20	(99)	72.0:28.0	571
2	-(CH ₂) ₅ -	218	8	rt	64	(100)	52.5:47.5	570



<i>n</i>	R	Catalyst	<i>x</i>	Temp	Time (h)		cr ^d
1	Me	225a	11	rt	23	(77)	84.0:16.0
1	-(CH ₂) ₄ -	225a	10	rt	72	(95)	75.0:25.0
1	-(CH ₂) ₅ -	225a	4	rt	4	(100)	84.0:16.0
1	-(CH ₂) ₅ -	225b	6	rt	1.2	(95)	90.5:9.5
1	Ph	225a	6	rt	12	(100)	82.5:17.5
1	Ph	225b	6	rt	1	(92)	86.0:14.0
2	-(CH ₂) ₅ -	225a	10	rt	288	(50)	59.5:40.5
2	-(CH ₂) ₅ -	225a	14	60°	8	(100)	59.0:41.0
2	-(CH ₂) ₅ -	225b	6	60°	19	(100)	67.0:33.0



<i>n</i>	R	Catalyst	<i>x</i>	Temp	Time (h)		cr ^d
1	Me	228a	6	40°	40	(96)	79.5:20.5
1	Me	228b	7	40°	108	(80)	88.0:12.0
1	Me	228c	6	rt	144	(71)	48.5:51.5
1	-(CH ₂) ₄ -	228c	6	rt	68	(96)	34.0:66.0
1	-(CH ₂) ₅ -	228a	7	rt	40	(95)	81.5:18.5
1	-(CH ₂) ₅ -	228b	4	rt	63	(92)	87.5:12.5
1	-(CH ₂) ₅ -	228c	2	rt	3	(92)	27.5:72.5
1	Ph	228a	6	rt	16	(100)	78.0:22.0
1	Ph	228b	6	rt	63	(100)	77.5:22.5
1	Ph	228c	6	rt	17	(100)	34.5:65.5
2	-(CH ₂) ₅ -	228a	6	40°	64	(92)	53.5:46.5
2	-(CH ₂) ₅ -	228b	7	40°	336	(87)	54.5:45.5
2	-(CH ₂) ₅ -	228c	7	rt	288	(100)	50.0:50.0

TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Refs.

Product(s) and Yield(s) (%)

Conditions

Aminoalkene

Please refer to the charts preceding the tables for structures indicated by the **bold numbers**.

C₇₋₁₇

1. **229** (6 mol %), YCl₃ (6 mol %), *n*-BuLi (24 mol %), THF, 10 min, vac
2. Aminoalkene, C₆D₆, rt

<i>n</i>	R	Time (h)	er ^d
1	Me	24	(83) 88.0:12.0
1	-(CH ₂) ₅ -	2	(94) 87.5:12.5
1	-(CH ₂) ₅ -	3	(92) 86.5:13.5
1	Ph	0.75	(95) 87.5:12.5
2	-(CH ₂) ₅ -	139	(84) 68.0:32.0

<i>n</i>	R	Time (h)	er ^d
1	Me	23	(85) 88.0:12.0
1	-(CH ₂) ₅ -	1	(90) 85.5:14.5
1	-(CH ₂) ₅ -	17	(95) 82.5:17.5
1	Ph	0.6	(90) 88.5:11.5
2	-(CH ₂) ₅ -	96	(95) 69.0:31.0

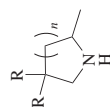
229 (6 mol %), YCl₃(THF)₃ (6 mol %), C₆D₆, rt

Catalyst (6 mol %), C₆D₆

<i>n</i>	R	Catalyst	Temp	Time (h)	er ^d
1	Me	230a	rt	48	(92) 87.5:12.5
1	Me	230b	rt	144	(21) 91.5:8.5
1	Me	230b	60°	22	(90) 87.0:13.0
1	-(CH ₂) ₅ -	230a	rt	2.3	(90) 87.5:12.5
1	-(CH ₂) ₅ -	230b	rt	24	(92) 89.5:10.5
1	Ph	230a	rt	1.9	(100) 86.0:14.0
1	Ph	230b	rt	7	(85) 87.0:13.0
2	-(CH ₂) ₅ -	230a	rt	120	(87) 66.5:33.5
2	-(CH ₂) ₅ -	230b	60°	29	(100) 69.5:30.5

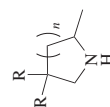
574

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.



Catalyst (6 mol %), C₆D₆

<i>n</i>	R	Catalyst	Temp	Time (h)	er ^d
1	Me	231a	rt	144	(94) 88.5:11.5
1	Me	231a	60°	3.3	(92) 82.0:18.0
1	Me	231b	60°	23	(95) 84.5:15.5
1	-(CH ₂) ₅ -	231a	rt	3.3	(89) 87.5:12.5
1	-(CH ₂) ₅ -	231b	rt	23	(92) 90.5:9.5
1	Ph	231a	rt	2.3	(100) 83.0:17.0
1	Ph	231b	rt	7	(100) 87.5:12.5
2	-(CH ₂) ₅ -	231a	60°	27	(100) 62.5:37.5
2	-(CH ₂) ₅ -	231b	60°	23	(100) 69.0:31.0

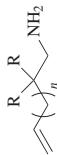
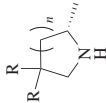


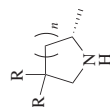
Catalyst (x mol %), C₆D₆, 120°

<i>n</i>	R	Catalyst	<i>x</i>	Time (h)	
1	Me	232a	10	80	(99)
1	Me	232b	8	60	(100)
1	-(CH ₂) ₅ -	232a	10	93	(99)
1	-(CH ₂) ₅ -	232b	5	46	(100)
1	Ph	232a	10	24	(99)
1	Ph	232b	5	43	(100)
2	Me	232b	5	86	(87)

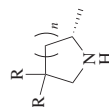
er <55.0:45.0

TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.		
Please refer to the charts preceding the tables for structures indicated by the bold numbers .					
	Catalyst (10 mol %), C ₆ D ₆ , 120°, 48 h		575		
<i>n</i>	<i>R</i>	Catalyst	Time (h)	er	
1	Me	193	24	(100)	66.0:34.0
1	Me	194	24	(96)	62.0:38.0
1	Me	200	24	(100)	60.5:39.5
1	Me	212	24	(86)	53.4:46.6
1	Me	215	24	(92)	69.5:31.5
1	-(CH ₂) ₅ -	193	16	(94)	62.0:38.0 ^a
1	-(CH ₂) ₅ -	194	16	(100)	59.5:40.5 ^a
1	-(CH ₂) ₅ -	200	16	(100)	58.5:41.5 ^a
1	-(CH ₂) ₅ -	212	16	(93)	54.45:45.55 ^a
1	-(CH ₂) ₅ -	215	16	(100)	64.0:36.0 ^a
2	Me	193	24	(100)	60.0:40.0 ^a
2	Me	194	24	(100)	59.0:41.0 ^a
2	Me	200	24	(100)	58.0:42.0 ^a
2	Me	212	24	(95)	55.5:44.5 ^a
2	Me	215	24	(100)	62.0:38.0 ^a

Catalyst (10 mol %), C₆D₆, 120°

<i>n</i>	R	Catalyst	Time (h)	er
1	Me	201	60 (87)	61.5:38.5
1	Me	211	36 (95)	56.5:43.5
1	-(CH ₂) ₅ -	201	24 (97)	54.3:45.7 ^u
1	-(CH ₂) ₅ -	211	24 (98)	57.0:43.0 ^u
2	Me	201	60 (100)	54.0:46.0 ^u
2	Me	211	84 (100)	60.5:39.5 ^u

Catalyst (x mol %), C₆D₆

<i>n</i>	R	Catalyst	<i>x</i>	Temp (°)	Time (h)	er
1	Me	206a	10	120	60 (20)	95.5:4.5
1	Me	206b	5	90	96 (94)	89.0:11.0
1	Me	206b	10	70	160 (58)	96.5:3.5
1	Me	206b	10	90	48 (100)	96.5:3.5
1	Me	206b	10	120	16 (100)	93.0:7.0
1	Me	207	5	90	96 (100)	86.0:14.0
1	Me	207	10	70	160 (50)	82.5:17.5
1	Me	207	10	90	48 (30)	93.0:7.0
1	Me	207	10	120	16 (100)	93.0:7.0
1	-(CH ₂) ₅ -	206b	10	120	24 (98)	87.0:13.0 ^u
1	-(CH ₂) ₅ -	207	10	120	24 (100)	81.5:18.5 ^u
2	Me	206b	10	120	60 (100)	68.0:32.0 ^u
2	Me	207	10	120	72 (100)	66.0:34.0 ^u

TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
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Please refer to the charts preceding the tables for structures indicated by the **bold numbers**.

C₇₋₁₇

Catalyst (x mol %), C₆D₆

149

R	Catalyst	x	Temp	Time (h)	er
Me	221a	5	rt	42	(96) 84.0:16.0
Me	221a	7.5	rt	9	(96) 82.0:18.0
Me	221a	25	rt	45	(93) 83.5:16.5
Me	221b	5	80°	407	(66) 76.5:23.5
-(CH ₂) ₅ -	221a	2.5	rt	1.1	(91) 87.5:12.5
-(CH ₂) ₅ -	221a	5	60°	91	(64) 84.5:15.5
-(CH ₂) ₅ -	221b	5	rt	2	(98) 82.0:18.0
Ph	221a	5	rt	0.8	(97) 65.5:34.5
Ph	221b	5	80°	27	(70) 62.0:38.0

Catalyst (x mol %), C₆D₆

155

R	Catalyst	x	Temp	Time (h)	er
Me	222a	5	90°	140	(94) 51.0:49.0
Me	222b	5	100°	22	(99) 52.0:48.0
-(CH ₂) ₅ -	222a	5	80°	50	(97) 52.5:47.5
-(CH ₂) ₅ -	222b	5	rt	22	(94) 50.0:50.0
Ph	222a	5	60°	140	(88) 56.5:43.5
Ph	222b	4	rt	0.33	(99) 47.0:53.0



155

R	Catalyst	Temp (°)	Time (h)	er
Me	223a	100	89	(99) 51.5:48.5
Me	223b	100	21	(99) 50.0:50.0
-(CH ₂) ₅ -	223a	100	20	(97) 50.0:50.0
-(CH ₂) ₅ -	223b	rt	3.5	(80) 53.0:47.0
Ph	223a	100	71	(99) 64.5:35.5
Ph	223b	rt	0.17	(99) 57.0:43.0



491

R	Catalyst	x	y	Temp	TOF (h ⁻¹) ^b	er
Me	224a	4.3	0	60°	0.2	37.5:62.5
Me	224b	3.2	0	rt	1.7	55.5:44.5
Me	224c	2.6	0	60°	2.1	82.0:18.0
Me	224c	9.6	0	rt	0.2	88.0:12.0
-(CH ₂) ₅ -	224a	3.0	0	60°	2.6	29.0:71.0
-(CH ₂) ₅ -	224b	2.6	0	rt	26	52.5:47.5
-(CH ₂) ₅ -	224c	3.0	0	rt	2.3	76.5:23.5
Ph	224a	3.5	0	60°	2.6	44.5:55.5
Ph	224b	1.5	0	rt	50	57.0:43.0
Ph	224b	3.0	0	rt	36	55.5:44.5
Ph	224c	2.7	89	rt	2.9	82.0:18.0
Ph	224c	3.5	0	rt	2.7	80.5:19.5

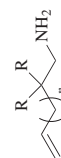
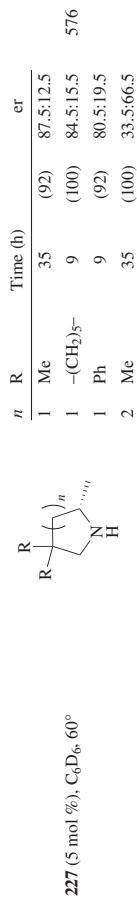


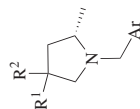
TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₇₋₁₁		219a (10 mol %), C ₇ D ₈ , 110°		217 (10 mol %), C ₆ D ₆ , 120°		218 (10 mol %), C ₆ D ₆ , 120°
C₇₋₁₀		219b (10 mol %), C ₇ D ₈ , 110°		217 (10 mol %), C ₆ D ₆ , 120°		218 (10 mol %), C ₆ D ₆ , 120°
C₇₋₁₇		219c (10 mol %), C ₇ D ₈ , 110°		217 (10 mol %), C ₆ D ₆ , 120°		218 (10 mol %), C ₆ D ₆ , 120°

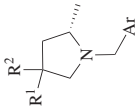
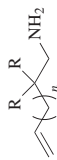
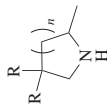
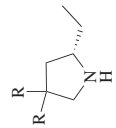


Catalyst (1.2x mol %),

[Rh(COD)₂]BF₄ (x mol %), dioxane

R ¹	R ²	Ar	Catalyst	x	Temp (°)	Time (h)	er	dr
Me	Me	2-MeC ₆ H ₄	241i	5	70	20	(75)	81.0:19.0
-(CH ₂) ₅ -	Me	2-MeC ₆ H ₄	241i	5	70	20	(80)	81.5:18.5
H	Ph	2-MeC ₆ H ₄	241i	5	70	20	(80)	93.5:6.5/95.5:4.5
Ph	Ph	Ph	241a	5	70	7-15	(94)	71.0:29.0
Ph	Ph	Ph	241b	5	70	7-15	(83)	60.0:40.0
Ph	Ph	Ph	241c	5	70	7-15	(8)	—
Ph	Ph	Ph	241d	5	70	7-15	(96)	76.5:23.5
Ph	Ph	Ph	241e	5	70	7-15	(95)	69.0:31.0
Ph	Ph	Ph	241f	5	70	7-15	(98)	85.0:15.0
Ph	Ph	Ph	241g	5	70	7-15	(95)	69.5:30.5
Ph	Ph	Ph	241h	5	70	7-15	(95)	87.5:12.5

TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.																																																	
Please refer to the charts preceding the tables for structures indicated by the bold numbers.																																																				
C ₇₋₁₇	  Catalyst (1.2x mol %), [Rh(COD)₂]BF₄ (x mol %), dioxane	<table><tr><th>Ar</th><th>Catalyst</th><th>x</th><th>Temp (°)</th><th>Time (h)</th><th>er</th><th>dr</th></tr><tr><td>R = Ph</td><td>241i</td><td>5</td><td>50</td><td>24</td><td>(90)</td><td>91.5:8.5</td></tr><tr><td>Ph</td><td>241i</td><td>5</td><td>70</td><td>15</td><td>(91)</td><td>90.0:10.0</td></tr><tr><td>Ph</td><td>241j</td><td>5</td><td>70</td><td>7-15</td><td>(9)</td><td>—</td></tr><tr><td>2-MeC₆H₄</td><td>241i</td><td>2.5</td><td>70</td><td>20</td><td>(88)</td><td>92.0:8.0</td></tr><tr><td>2-MeC₆H₄</td><td>241i</td><td>5</td><td>50</td><td>24</td><td>(91)</td><td>94.0:6.0</td></tr><tr><td>2-MeC₆H₄</td><td>241i</td><td>5</td><td>70</td><td>15</td><td>(92)</td><td>92.0:8.0</td></tr></table>	Ar	Catalyst	x	Temp (°)	Time (h)	er	dr	R = Ph	241i	5	50	24	(90)	91.5:8.5	Ph	241i	5	70	15	(91)	90.0:10.0	Ph	241j	5	70	7-15	(9)	—	2-MeC ₆ H ₄	241i	2.5	70	20	(88)	92.0:8.0	2-MeC ₆ H ₄	241i	5	50	24	(91)	94.0:6.0	2-MeC ₆ H ₄	241i	5	70	15	(92)	92.0:8.0	349
Ar	Catalyst	x	Temp (°)	Time (h)	er	dr																																														
R = Ph	241i	5	50	24	(90)	91.5:8.5																																														
Ph	241i	5	70	15	(91)	90.0:10.0																																														
Ph	241j	5	70	7-15	(9)	—																																														
2-MeC ₆ H ₄	241i	2.5	70	20	(88)	92.0:8.0																																														
2-MeC ₆ H ₄	241i	5	50	24	(91)	94.0:6.0																																														
2-MeC ₆ H ₄	241i	5	70	15	(92)	92.0:8.0																																														
C ₈₋₁₀	  239 (2.5 mol %), C₆D₆, 16 h	<table><tr><th>n</th><th>R</th><th>Temp</th><th>er^d</th></tr><tr><td>1</td><td>-(CH₂)₅-</td><td>rt</td><td>(98)</td></tr><tr><td>2</td><td>Me</td><td>rt</td><td>(100)</td></tr><tr><td>2</td><td>Me</td><td>120°</td><td>(95)</td></tr></table>	n	R	Temp	er ^d	1	-(CH ₂) ₅ -	rt	(98)	2	Me	rt	(100)	2	Me	120°	(95)	566																																	
n	R	Temp	er ^d																																																	
1	-(CH ₂) ₅ -	rt	(98)																																																	
2	Me	rt	(100)																																																	
2	Me	120°	(95)																																																	
C ₈₋₁₈	  Catalyst (6 mol %), Li(THF)₄[Y(CH₂TMS)₄] (6 mol %), C₆D₆	<table><tr><th>R</th><th>Catalyst</th><th>Temp (°)</th><th>Time (h)</th><th>er</th></tr><tr><td>Me</td><td>240d</td><td>110</td><td>120</td><td>(88)</td></tr><tr><td>Me</td><td>240j</td><td>110</td><td>110</td><td>(91)</td></tr><tr><td>-(CH₂)₅-</td><td>240a</td><td>70</td><td>74</td><td>(58)</td></tr><tr><td>-(CH₂)₅-</td><td>240c</td><td>70</td><td>19</td><td>(83)</td></tr><tr><td>-(CH₂)₅-</td><td>240d</td><td>70</td><td>19</td><td>(93)</td></tr><tr><td>-(CH₂)₅-</td><td>240e</td><td>70</td><td>19</td><td>(87)</td></tr><tr><td>-(CH₂)₅-</td><td>240g</td><td>70</td><td>50</td><td>(79)</td></tr><tr><td>-(CH₂)₅-</td><td>240i</td><td>70</td><td>19</td><td>(97)</td></tr></table>	R	Catalyst	Temp (°)	Time (h)	er	Me	240d	110	120	(88)	Me	240j	110	110	(91)	-(CH ₂) ₅ -	240a	70	74	(58)	-(CH ₂) ₅ -	240c	70	19	(83)	-(CH ₂) ₅ -	240d	70	19	(93)	-(CH ₂) ₅ -	240e	70	19	(87)	-(CH ₂) ₅ -	240g	70	50	(79)	-(CH ₂) ₅ -	240i	70	19	(97)	258				
R	Catalyst	Temp (°)	Time (h)	er																																																
Me	240d	110	120	(88)																																																
Me	240j	110	110	(91)																																																
-(CH ₂) ₅ -	240a	70	74	(58)																																																
-(CH ₂) ₅ -	240c	70	19	(83)																																																
-(CH ₂) ₅ -	240d	70	19	(93)																																																
-(CH ₂) ₅ -	240e	70	19	(87)																																																
-(CH ₂) ₅ -	240g	70	50	(79)																																																
-(CH ₂) ₅ -	240i	70	19	(97)																																																

-(CH ₂) ₅ -	240j	110	19	(96)	84.0:16.0
Ph	240a	70	36	(72)	67.5:32.5
Ph	240a	70	120	(48)	74.5:25.5
Ph	240c	50	15	(100)	88.0:12.0
Ph	240d	70	19	(100)	86.5:13.5
Ph	240e	40	36	(83)	88.5:11.5
Ph	240e	70	19	(100)	87.5:12.5

Catalyst (5 mol %), C₆D₆

159

n	R	Catalyst	Temp (°)	TOF (h ⁻¹) ^b	er ^d
1	Me	26	80	0.26	64.0:36.0
1	Me	238a	80	0.18	62.0:38.0
1	Me	238b	100	0.07	63.0:37.0
1	Et	26	80	0.15	66.0:34.0
1	Et	238a	80	0.06	61.0:39.0
1	Et	238b	10	0.06	64.0:36.0
2	Me	26	80	0.16	58.0:42.0
2	Me	238a	80	0.11	58.0:42.0
2	Me	238b	60	0.03	16.0:84.0
2	Me	238b	80	0.16	18.0:82.0
2	Me	238b	100	0.30	21.0:79.0

C₈C₉

164a (6 mol %),
La[N(TMS)₂]₃ (5 mol %), C₆D₆, 60°

(98) er 78.0:22.0

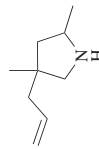
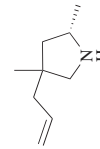
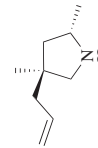
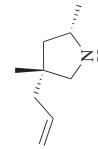
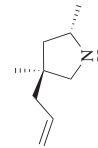
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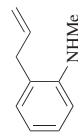
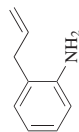
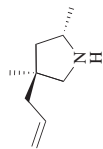
Catalyst (x mol %), C₆D₆, rt

Catalyst	x	Time (h)	dr	er ^d
146	3	68	(100)	1.18:1
160	0.5	2.3	(68)	1.34:1
160	1.5	0.5	(96)	1.55:1
161	3	2.6	(100)	1.36:1

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TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.																								
Please refer to the charts preceding the tables for structures indicated by the bold numbers.																											
	Catalyst (x mol %), C ₆ D ₆		481																								
	39 2 29 0.4 (99) 1.15:1 52.5:47.5/59.0:41.0		481																								
	40 2 rt 0.15 (99) 1.4:1 50.5:49.5/64.0:36.0		492																								
	144a 10 70 72 (49) 54:46 66.5:33.5/66.5:33.5		492																								
	144a 10 90 6.5 (99) 53:47 66.0:34.0/67.0:33.0		492																								
	Catalyst (2 mol %), C ₆ D ₆ , rt		52																								
	<table><tr><th>Catalyst</th><th>Time (h)</th><th>dr</th><th>er^d</th></tr><tr><td>155a</td><td>23 (93)</td><td>2.7:1</td><td>94.0:6.0/89.0:11.0</td></tr><tr><td>155b</td><td>1 (95)</td><td>1.8:1</td><td>81.5:18.5/82.5:17.5</td></tr><tr><td>155c</td><td>0.8 (94)</td><td>2.3:1</td><td>93.0:7.0/88.0:12.0</td></tr><tr><td>155e</td><td>1.2 (94)</td><td>1.4:1</td><td>82.5:17.5/82.5:17.5</td></tr><tr><td>155f</td><td>1.6 (95)</td><td>1.6:1</td><td>88.5:11.5/87.0:13.0</td></tr></table>		Catalyst	Time (h)	dr	er ^d	155a	23 (93)	2.7:1	94.0:6.0/89.0:11.0	155b	1 (95)	1.8:1	81.5:18.5/82.5:17.5	155c	0.8 (94)	2.3:1	93.0:7.0/88.0:12.0	155e	1.2 (94)	1.4:1	82.5:17.5/82.5:17.5	155f	1.6 (95)	1.6:1	88.5:11.5/87.0:13.0	
	Catalyst	Time (h)	dr	er ^d																							
	155a	23 (93)	2.7:1	94.0:6.0/89.0:11.0																							
	155b	1 (95)	1.8:1	81.5:18.5/82.5:17.5																							
	155c	0.8 (94)	2.3:1	93.0:7.0/88.0:12.0																							
	155e	1.2 (94)	1.4:1	82.5:17.5/82.5:17.5																							
	155f	1.6 (95)	1.6:1	88.5:11.5/87.0:13.0																							
221a (5 mol %), C ₆ D ₆ , rt, 2 h		149																									
		(54) er 82.0:18.0																									
		(44) er 86.0:14.0																									



219a (10 mol %), C₇D₈, 110°

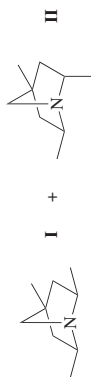
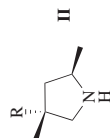
221a (5 mol %), C₇D₈, rt, 6 d

233j (4 mol %), C₇H₈, 110°, 96 h

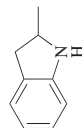
241i (6 mol %),
[Rh(COD)₂BF₄] (5 mol %),
dioxane, 100°, 10 h

158 (10 mol %), C₆D₅Br, 70°, 3 h

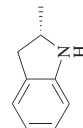
R	Time (h)	I + II	I/II	er I	er II
allyl	2	(82)	2.3:1	96.0:4.0	94.0:6.0
Ph	12	(94)	1.9:1	81.0:19.0	93.0:7.0



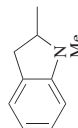
I + II (70), I/II = 8:1



(68) er 50.0:50.0

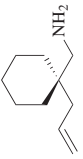
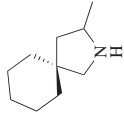


(85) er 82.0:18.0



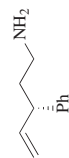
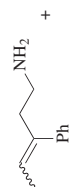
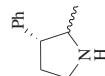
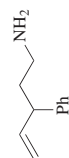
(100) er^d 60.0:40.0

TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)					Refs.
		Catalyst	x	y	z	Time (h)	ee ^d
 C10	1. Catalyst (x mol %), YCl ₃ (y mol %), <i>n</i> -BuLi (z mol %), THF, 10 min, vac 2. Aminoalkene, C ₆ D ₆ , rt	177c	6	6	24	3.5	(96) 83.5:16.5
		177d	0	0	24	24	(0) —
		177d	0	6	24	24	(57) —
		177d	6	0	24	24	(0) —
		177d	6	3	12	5	(94) 87.5:12.5
		177d	6	6	12	24	(99) 80.0:20.0
		177d	6	6	18	5	(91) 87.5:12.5
		177d	6	6	24	2	(94) 87.5:12.5
		177e	6	6	24	5	(92) 81.5:18.5
 Catalyst (x mol %), solvent		Catalyst	x	Solvent	Temp	Time (h)	ee ^d
		233a	3.6	C ₆ D ₆	rt	1.5	(87) 70.4:29.5
		233a	5	C ₆ D ₆	rt	48	(67) 85.0:15.0
		233a	5	C ₆ D ₆	rt	144	(100) 83.0:17.0
		233a	6	C ₇ D ₈	rt	0.5	(94) 70.0:30.0
		233a	6.6	C ₆ D ₆	rt	1	(91) 70.5:29.5
		233b	7	C ₆ D ₆	rt	20	(100) 83.5:16.5
		233c	12	C ₆ D ₆	rt	2	(84) 63.0:37.0
		233d	6	C ₆ D ₆	0	168	(92) 92.5:7.5
		233d	6	C ₆ D ₆	rt	20	(90) 93.5:6.5
		233d	6	C ₆ D ₆	60°	15	(92) 89.0:11.0
		233e	6	C ₆ D ₆	0	144	(54) 87.5:12.5
		233e	8	C ₆ D ₆	rt	15	(93) 90.5:9.5
		233f	6	C ₆ D ₆	rt	18	(94) 82.5:17.5

233f	10	C ₆ D ₆	0°	96	(88)	88.0:12.0	561
233f	10	C ₆ D ₆	rt	20	(58)	84.0:16.0	561
233g	8	C ₆ D ₆	rt	44	(100)	83.0:17.0	561
233g	10	C ₆ D ₆	0°	88	(75)	84.0:16.0	561
233h	5	C ₆ D ₆	rt	2	(78)	62.0:38.0	511
233i	6	C ₆ D ₆	rt	23	(92)	69.0:31.0	564
233j	3	C ₆ D ₆	rt	1.5	(98)	54.5:45.5	577
233j	5	C ₆ D ₆	rt	18	(14)	74.5:25.5	577
233j	5	C ₆ D ₆	rt	48	(67)	85.0:15.0	577
233j	5	C ₆ D ₆	rt	144	(100)	83.0:17.0	577
233j	6	C ₆ D ₆	0°	17	(81)	73.5:26.5	565
233j	6	C ₆ D ₆	60°	0.3	(90)	70.0:30.0	565
233j	6	C ₇ D ₈	-20°	24	(13)	76.5:23.5	511
233j	6	C ₇ D ₈	0°	17	(81)	73.5:26.5	511
233j	7	C ₆ D ₆	rt	0.5	(100)	56.0:44.0	577
233j	7	C ₆ D ₆	rt	1	(91)	70.5:29.5	565
233k	7	C ₆ D ₆	rt	3	(84)	50.5:49.5	577
233l	17	C ₆ D ₆	rt	3	(91)	58.0:42.0	577

C₁₁



III

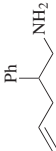
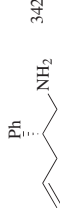
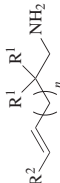
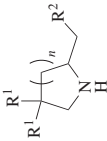
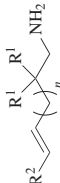
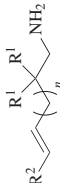
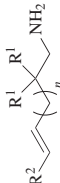
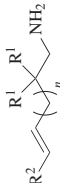
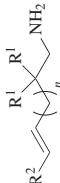
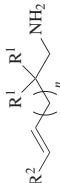
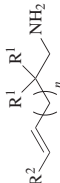
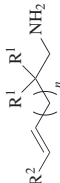
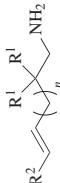
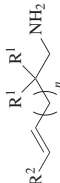
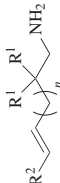
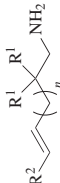
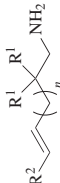
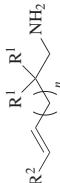
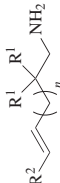
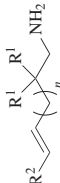
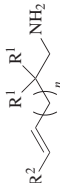
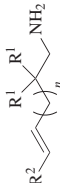
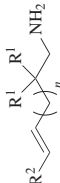
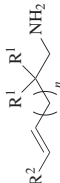
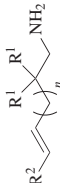
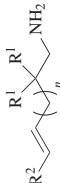
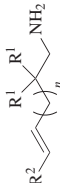
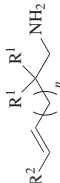
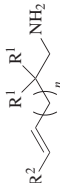
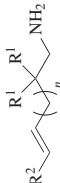
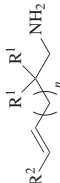
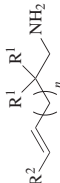
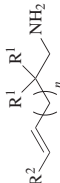
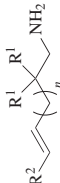
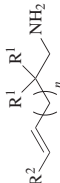
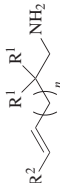
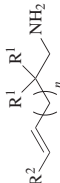
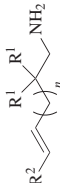
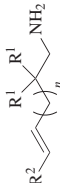
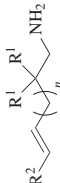
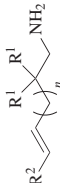
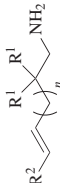
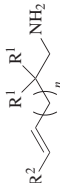
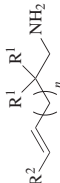
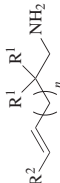
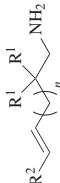
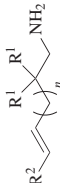
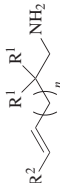
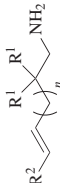
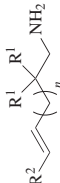
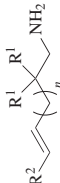
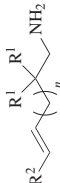
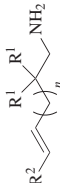
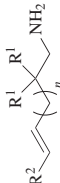
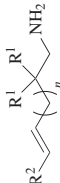
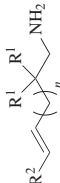
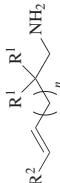
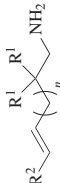
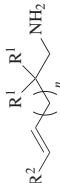
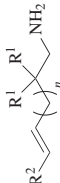
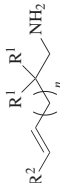
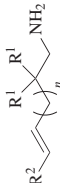
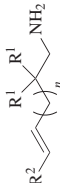
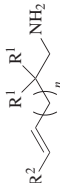
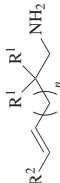
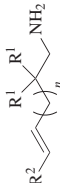
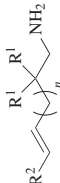
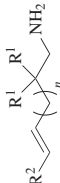
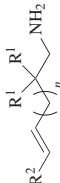
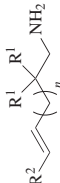
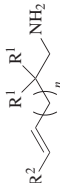
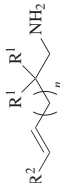
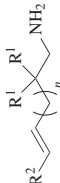
II

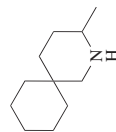
I

Catalyst	I + II	I/II	er III
155b	(45)/	7:1	69.5:30.5
155e	(44)/	6:1	82.5:17.5

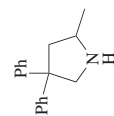
Catalyst (2 mol %), C₆D₆, 30°

TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.				
Please refer to the charts preceding the tables for structures indicated by the bold numbers .							
 C ₁₁	Catalyst (2 mol %), C ₆ D ₆ , rt	 I	+	 II	+	 III	342
		Catalyst					
		I + II					
		I/II					
		er III					
		155a (54) ^f 1:1.3 67.0:33.0					
		155b (53) ^f 1:1.3 58.5:41.5					
 C ₁₁₋₁₈	Catalyst (x mol %), C ₆ D ₆						
		155c (51) ^f 1:1.3 63.0:37.0					
		155d (50) ^f 1:1.2 55.5:44.5					
		155e (47) ^f 1:1.2 58.5:41.5					
155f (55) ^f 1:1.2 65.5:34.5							
 C ₁₁₋₁₈							
 C ₁₁₋₁₈							
 C ₁₁₋₁₈							
 C ₁₁₋₁₈							
 C ₁₁₋₁₈							
 C ₁₁₋₁₈							
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C₁₁Catalyst (x mol %), C₆D₆

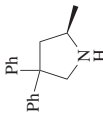
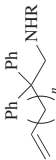
Catalyst	x	Temp (°)	Time (h)	e st	
233b	10	60	17	(90)	64.5:35.5
233d	4	60	40	(100)	75.5:24.5
233d	6	80	15	(100)	75.0:25.0
233d	8	40	144	(100)	75.0:25.0
233e	6	60	24	(100)	70.5:29.5
233f	6	60	66	(85)	72.5:27.5
233j	4	60	16	(100)	65.0:35.0
233j	6	rt	72	(100)	63.5:36.5

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565C₁₇Catalyst (x mol %), C₆D₆

Catalyst	x	Temp	Time (h)	e st	
233a	10	rt	24	(100)	75.0:25.0
233b	5	rt	43	(100)	75.0:25.0
233d	6	0°	168	(100)	89.0:11.0
233d	6	rt	18	(100)	88.0:12.0
233e	6	0°	96	(94)	87.5:12.5
233e	6	rt	5	(100)	87.5:12.5
233f	3	rt	21	(100)	81.0:19.0
233f	10	0°	144	(100)	83.0:17.0
233g	2	rt	21	(100)	80.0:20.0
233j	6	rt	1.3	(100)	41.5:58.5

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TABLE 4A. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.																																										
 C₁₇	243 (5 mol %), C ₇ H ₈ , 105°, 24 h	(74) <i>er</i> ^d 51.0:49.0	172																																										
 C₁₇₋₁₈	242 (10 mol %), C ₆ D ₆ , 20°, 1 h	(98) <i>er</i> 55.0:45.0	153																																										
 C₁₇₋₁₈	1. Catalyst (x mol %), C ₆ D ₆ 2. C ₇ D ₈ , 110°	<table><thead><tr><th>n</th><th>R</th><th>Catalyst</th><th>x</th><th>Time (h)</th><th><i>er</i></th></tr></thead><tbody><tr><td>1</td><td>H</td><td>219a</td><td>5</td><td>2.5</td><td>(98) 87.0:13.0</td></tr><tr><td>1</td><td>H</td><td>219a</td><td>10</td><td>1.25</td><td>(98) 87.0:13.0</td></tr><tr><td>1</td><td>H</td><td>219b</td><td>10</td><td>18</td><td>(98) 65.5:34.5</td></tr><tr><td>1</td><td>H</td><td>219c</td><td>10</td><td>3</td><td>(98) 69.5:30.5</td></tr><tr><td>1</td><td>Ph</td><td>219a</td><td>10</td><td>—</td><td>(0) —</td></tr><tr><td>2</td><td>H</td><td>219a</td><td>10</td><td>—</td><td>(91) 64.5:35.5</td></tr></tbody></table>	n	R	Catalyst	x	Time (h)	<i>er</i>	1	H	219a	5	2.5	(98) 87.0:13.0	1	H	219a	10	1.25	(98) 87.0:13.0	1	H	219b	10	18	(98) 65.5:34.5	1	H	219c	10	3	(98) 69.5:30.5	1	Ph	219a	10	—	(0) —	2	H	219a	10	—	(91) 64.5:35.5	345, 346
n	R	Catalyst	x	Time (h)	<i>er</i>																																								
1	H	219a	5	2.5	(98) 87.0:13.0																																								
1	H	219a	10	1.25	(98) 87.0:13.0																																								
1	H	219b	10	18	(98) 65.5:34.5																																								
1	H	219c	10	3	(98) 69.5:30.5																																								
1	Ph	219a	10	—	(0) —																																								
2	H	219a	10	—	(91) 64.5:35.5																																								
 C₁₇	244a (20 mol %), TCE, 130°, 20 h	(97) <i>er</i> 58.5:41.5	213																																										

^a The absolute configuration was not reported.

^b The conversion was >95% based on NMR analysis.

^c The product was isolated as the N-trifluoroacetamide.

^d The product was isolated as the 2-naphthoyl amide.

^e C_7D_8 was used as the solvent.

^f This was a kinetic resolution experiment, and the reaction was stopped at this point.

^g The yield was not reported.

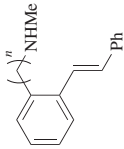
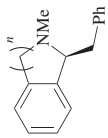
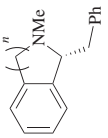
^h Double bond isomerization occurred.

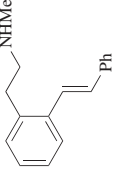
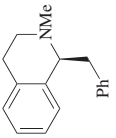
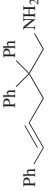
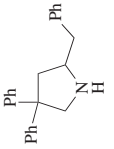
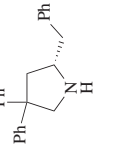
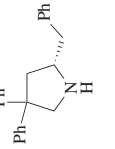
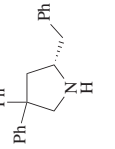
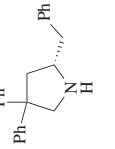
ⁱ The amino alkene reactant was the minor component in a 2:2:1 mixture of stereoisomers.

TABLE 4B. ENANTIOSELECTIVE INTRAMOLECULAR HYDROAMINATION OF VINYL ARENES

Vinyl Arene	Conditions	Product(s) and Yield(s) (%)	Refs.																				
Please refer to the charts preceding the tables for structures indicated by the bold numbers.																							
	221a (5 mol %), C ₆ D ₆ , rt, 5 min		149																				
	149i (22 mol %), Zr(NMe ₂) ₄ (20 mol %), C ₇ H ₈ , 135°, 24 h		170																				
	1. Catalyst (5 mol %), Y[N(TMS) ₂] ₃ (5 mol %), C ₄ H ₄ S (10 mol %), C ₆ D ₆ , 60–75° 2. Aminoalkene, C ₆ D ₆	<table><tr><th>Catalyst</th><th>Temp (°)</th><th>Time (h)</th><th><i>er</i>^{d,c}</th></tr><tr><td>148a</td><td>60</td><td>8</td><td>86.5:13.5</td></tr><tr><td>148b</td><td>60</td><td>9</td><td>90.0:10.0</td></tr><tr><td>148c</td><td>30</td><td>72</td><td>93.0:7.0</td></tr><tr><td>148c</td><td>60</td><td>3</td><td>91.0:9.0</td></tr></table>	Catalyst	Temp (°)	Time (h)	<i>er</i> ^{d,c}	148a	60	8	86.5:13.5	148b	60	9	90.0:10.0	148c	30	72	93.0:7.0	148c	60	3	91.0:9.0	255
	Catalyst	Temp (°)	Time (h)	<i>er</i> ^{d,c}																			
148a	60	8	86.5:13.5																				
148b	60	9	90.0:10.0																				
148c	30	72	93.0:7.0																				
148c	60	3	91.0:9.0																				
Catalyst (2 mol %), C ₆ D ₆	<table><tr><th>Catalyst</th><th>Temp (°)</th><th>Time (h)</th><th><i>er</i></th></tr><tr><td>155a</td><td>100</td><td>72</td><td>(91) 86.0:14.0</td></tr><tr><td>155c</td><td>60</td><td>10</td><td>(98) 83.5:16.5</td></tr><tr><td>155e</td><td>60</td><td>23</td><td>(96) 62.5:37.5</td></tr><tr><td>155f</td><td>60</td><td>28</td><td>(96) 61.5:38.5</td></tr></table>	Catalyst	Temp (°)	Time (h)	<i>er</i>	155a	100	72	(91) 86.0:14.0	155c	60	10	(98) 83.5:16.5	155e	60	23	(96) 62.5:37.5	155f	60	28	(96) 61.5:38.5	52	
Catalyst	Temp (°)	Time (h)	<i>er</i>																				
155a	100	72	(91) 86.0:14.0																				
155c	60	10	(98) 83.5:16.5																				
155e	60	23	(96) 62.5:37.5																				
155f	60	28	(96) 61.5:38.5																				

TABLE 4B. ENANTIOSELECTIVE INTRAMOLECULAR HYDROAMINATION OF VINYL ARENES (Continued)

Vinyl Arene	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the bold numbers .			
 C ₁₅₋₁₆	Catalyst (40 mol %), <i>n</i> -BuLi (20 mol %), (<i>i</i> -Pr) ₂ NH (20 mol %), C ₇ H ₈	 260	
	Catalyst (2x mol %), <i>n</i> -BuLi (x mol %), (<i>i</i> -Pr) ₂ NH (x mol %), C ₇ H ₈ , -60°	 260	

C ₁₆		245a (<i>x</i> mol %), <i>n</i> -BuLi (<i>y</i> mol %), (<i>i</i> -Pr) ₂ NH (<i>z</i> mol %), C ₇ H ₈ , 5 h		er			
				<i>x</i>	<i>y</i>	<i>z</i>	Temp (°)
C ₂₃		Catalyst (6 mol %) C ₆ D ₆		0	20	20	-60 (0)
				20	10	0	rt (99)
				40	20	0	-60 (22)
				40	20	20	-60 (99)
				150	120	0	-60 (6)
		Catalyst (6 mol %), Li(THF) ₄ [Y(CH ₂ TMS) ₄] (6 mol %), C ₆ D ₆		er			
				Catalyst	Temp	Time (h)	er
				157a	110°	16	(95) 54.0:46.0 ^a
				233j	rt	0.7	(100) 50.0:50.0
				240a	40	19	(95) 61.0:39.0
				240c	50	24	(100) 76.5:23.5
				240d	60	2	100 77.5:22.5
				240e	40	7	(99) 77.5:22.5

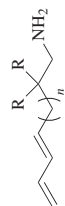
^a The absolute configuration was not reported.

^b The product was isolated as *N*-trifluoroacetamide.

^c The conversion was >95%.

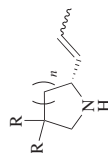
TABLE 4C. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINODIENES

Aminodiene	Conditions					Product(s) and Yield(s) (%)			Refs.
	<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>								
C ₇₋₈	1. Catalyst (x mol %), RLi (y mol %), solvent, rt, 10 min								
	2. C ₆ D ₆								
	<i>n</i>	Catalyst	<i>x</i>	<i>R</i>	<i>y</i>	Solvent	Temp	Time (h)	er [(<i>E</i>)/(<i>Z</i>)]
	1	240a	10	Me	40	Et ₂ O	rt	2	(95) 71.5:28.5/66.0:34.0
	1	240b	10	Me	40	Et ₂ O	rt	2	(89) 51.0:49.0 ^a /37.0:63.0
	1	240f	2	Me	8	Et ₂ O	rt	3.5	(95) 84:16 73.0:27.0/64.5:35.5
	1	240f	10	Me	20	THF	rt	0.33	(95) 84:16 75.5:24.5/51.5:48.5
	1	240f	10	Me	20	Et ₂ O	rt	0.25	(95) 92:8 74.5:25.5/73.5:26.5
	1	240f	10	Me	40	THF	rt	0.33	(95) 77:23 76.0:24.0/50.0:50.0
	1	240f	10	Me	40	Et ₂ O/(EtO) ₂ CH ₂	rt	0.17	(95) 92:8 73.5:26.5/26.5:73.5
	1	240f	10	Me	40	Et ₂ O	rt	0.17	(95) 92:8 75.5:24.5/75.0:25.0
	1	240f	10	Me	40	Et ₂ O	rt	0.17	(95) 92:8 75.5:24.5/79.0:21.0
	1	240f	10	Me	60	THF	rt	0.5	(95) 72:28 78.5:21.5/52.0:48.0
	1	240f	10	Me	60	Et ₂ O	rt	0.25	(95) 85:15 75.0:25.0/53.0:47.0
	1	240f	10	<i>n</i> -Bu	30	Et ₂ O	rt	0.25	(95) 85:15 79.0:21.0/53.0:47.0 ^a
	1	240f	10	TMSCH ₂	20	Et ₂ O	rt	0.5	(89) 93:7 74.5:25.5/30.0:70.0
	1	240h	10	Me	40	Et ₂ O	rt	3	(95) 25:75 54.5:45.5/51.0:49.0 ^a
	1	240i	10	Me	40	Et ₂ O	rt	2	(95) 55:45 65.0:35.0/55.0:45.0
	2	240a	10	Me	40	Et ₂ O	50°	27	(95) 66:34 78.0:22.0/54.5:45.5
	2	240f	10	Me	40	Et ₂ O	50°	46	(95) 89:11 86.0:14.0/77.5:22.5
	2	240h	10	Me	40	Et ₂ O	50°	21	(95) 80:20 54.5:45.5/38.5:61.5
	2	240i	10	Me	40	Et ₂ O	50°	27	(95) 86:14 75.5:24.5/52.5:47.5 ^a

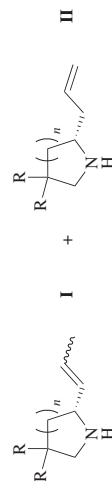
C₇₋₁₀

Catalyst (4–20 mol %), solvent

288



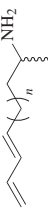
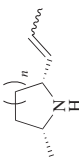
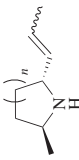
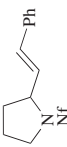
<i>n</i>	R	Catalyst	Solvent	Temp	TOF (h ⁻¹) ^b	(<i>E</i>)/(<i>Z</i>)	er ^c
1	H	238a	C ₆ D ₆	rt	12	93:7	61.5:38.5 ^a
1	H	249a	C ₆ D ₆	rt	74	98:2	62.5:37.5 ^a
1	H	249b	C ₆ D ₆	rt	0.09	98:2	70.5:29.5 ^a
2	H	238a	C ₆ D ₆	rt	0.11	97:3	81.5:18.5
2	H	238a	C ₇ D ₈	0°	—	96:4	82.0:18.0
2	H	238a	<i>c</i> -C ₆ D ₁₂	rt	0.04	96:4	82.0:18.0
2	H	238a	<i>c</i> -C ₆ D ₁₂	0°	—	95:5	84.5:15.5
2	H	238a	CD ₃ C ₆ D ₁₁	rt	0.09	97:3	82.0:18.0
2	H	238a	CD ₃ C ₆ D ₁₁	0°	—	97:3	85.5:14.5
2	H	238a	pentane	rt	0.08	97:3	82.5:17.5
2	H	249a	C ₆ D ₆	rt	0.1	98:2	68.5:31.5
2	Me	238a	C ₆ D ₆	rt	1.7	96:4	59.5:40.5 ^a
2	Me	238a	<i>c</i> -C ₆ D ₁₂	0°	—	97:3	62.0:38.0 ^a

250 (4–20 mol %), C₆D₆

288

<i>n</i>	R	Temp	TOF (h ⁻¹) ^b	I/II	(<i>E</i>)/(<i>Z</i>)	I	er ^c
1	H	rt	3.0	I only	63:37	I	58.5:41.5 ^a
2	H	60°	0.61	I only	41:59	I	77.0:23.0
2	Me	rt	1.4	96:4	40:60		72.5:27.5 ^a

TABLE 4C. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINODIENES (Continued)

Aminodiene	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the bold numbers.			
 C₈₋₉	238a (5 mol %), C ₆ D ₆ , rt	 I +  II	288
		<i>n</i> TOF (h ⁻¹) ^b I/II	
 C₁₂	Pd ₂ (dba) ₃ •CHCl ₃ (5 mol %), PhCO ₂ H (10 mol %), (<i>R,R</i>)-RENORPHOS (25 mol %), benzene, 100°, 72 h	 (15) er ^c 62.0:38.0	316
		<i>n</i> TOF (h ⁻¹) ^b I/II	

^aThe absolute configuration was not reported.

^bThe conversion was >95 %.

^cThe er value is after double bond hydrogenation. The absolute configuration of the major isomer is shown unless stated otherwise.

TABLE 4D. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALLENES

Aminoallene

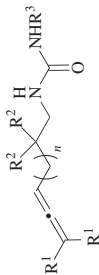
Conditions

Product(s) and Yield(s) (%)

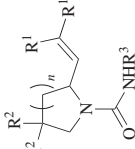
Refs.

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₆-20



255 (5 mol %),
 AgZ (10 mol %), solvent



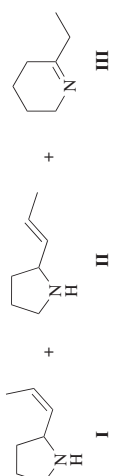
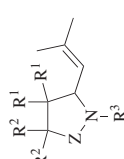
578

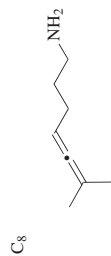
<i>n</i>	R ¹	R ²	R ³	Z	Solvent	Temp	Time (h)	er ^d
1	H	H	4-O ₂ NC ₆ H ₄	BF ₄	Et ₂ O	rt	48	(82) 53.5:46.5
1	H	-(CH ₂) ₅ -	4-O ₂ NC ₆ H ₄	BF ₄	Et ₂ O	rt	48	(76) 69.5:30.5
1	H	Ph	<i>n</i> -Bu	BF ₄	Et ₂ O	rt	20	(90) 75.0:25.0
1	H	Ph	Ph	SbF ₆	Et ₂ O	0°	10	(98) 91.0:9.0
1	H	Ph	4-IC ₆ H ₄	BF ₄	Et ₂ O	rt	24	(88) 90.5:9.5
1	H	Ph	4-O ₂ NC ₆ H ₄	BF ₄	Et ₂ O	rt	48	(90) 96.5:3.5
1	H	Ph	4-O ₂ NC ₆ H ₄	BF ₄	dioxane	rt	36	(30) 94.0:6.0
1	H	Ph	4-O ₂ NC ₆ H ₄	BF ₄	C ₇ H ₈	rt	48	(tr) —
1	H	Ph	4-O ₂ NC ₆ H ₄	BF ₄	THF	rt	36	(tr) 54.5:45.5
1	H	Ph	4-O ₂ NC ₆ H ₄	BF ₄	MeOH	rt	48	(30) 62.0:38.0
1	H	Ph	4-O ₂ NC ₆ H ₄	BF ₄	DCM	rt	36	(50) 75.5:24.5
1	H	Ph	4-O ₂ NC ₆ H ₄	BF ₄	CHCl ₃	rt	36	(85) 79.0:21.0
1	H	Ph	4-O ₂ NC ₆ H ₄	BF ₄	MeCN	rt	36	(90) 50.0:50.0
1	H	Ph	4-MeOC ₆ H ₄	BF ₄	Et ₂ O	rt	16	(90) 86.0:14.0
1	H	Ph	PMB	BF ₄	Et ₂ O	rt	2	(89) 86.0:14.0
1	H	Ph	3,5-(CF ₃) ₂ C ₆ H ₃	BF ₄	Et ₂ O	rt	20	(92) 91.5:8.5
1	Me	Ph	4-O ₂ NC ₆ H ₄	BF ₄	Et ₂ O	rt	48	(91) 78.0:22.0
2	H	Ph	4-O ₂ NC ₆ H ₄	BF ₄	Et ₂ O	rt	48	(89) 76.5:23.5

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₆₋₂₀

TABLE 4D. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALLENES (Continued)

Aminoallene	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Please refer to the charts preceding the tables for structures indicated by the bold numbers.</i>			
C ₆	255 (2.5 mol %), AgClO ₄ (5 mol %), 3-xylene, -20°, 24 h	 (99) <i>er</i> 67.0:33.0	579
C ₇	1. Catalyst (5.1 mol %), Ti(NMe ₂) ₄ (4.9 mol %), C ₆ D ₆ , rt 2. Aminoallene, C ₆ D ₆ , 110°	 I + II + III	304
C ₇₋₁₀	L(AuOPNB) ₂ (x mol %), solvent		355



R ¹	R ²	Z	R ³	L	x	Solvent	Temp (°)	Time (h)	er
H	H	O	BocN	143b	3	DCM	rt	24	(91) 99.0:1.0
H	H	BocN	MesSO ₂	141c	5	MeNO ₂	50	15	(98) 99.5:0.5
H	Me	O	Boc	142d	5	MeNO ₂	50	24	(94) 81.5:18.5
Me	H	O	Boc	142d	5	MeNO ₂	50	24	(73) 99.5:0.5
H	Me	CH ₂ O	Boc	142d	5	MeNO ₂	50	24	(79) 94.5:5.5

1. Catalyst (5.1 mol %), Ti(NMe ₂) ₄ (4.9 mol %), C ₆ D ₆ , rt		Catalyst	Time (h)	er ^{a,b}
2. Aminoallene, C ₆ D ₆ , 110°	253a		18	52.0:48.0
	253b		—	49.0:51.0
	253c		—	52.5:47.5
	253d		—	—
	253e		18	52.0:48.0
	253f		—	49.5:50.5
	253g		—	50.5:49.5
	253h		—	52.5:47.5
	253i		17	52.5:47.5
	253j		—	51.0:49.0
	253k		—	55.0:45.0
	253l		—	50.0:50.0
	253m		22	56.0:44.0
	253n		16	51.0:49.0
	253o		—	48.0:52.0
	253p		—	51.5:48.5
	253q		—	58.0:42.0
	253r		16	53.0:47.0
	253s		—	49.5:50.5
	253t		—	47.5:52.5
	253u		—	58.0:42.0
	253v		20	57.5:42.5
	253w		—	49.0:51.0
	253x		—	50.5:49.5
	253y		—	53.5:46.5

TABLE 4D. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALLENES (Continued)

Aminoallene	Conditions	Product(s) and Yield(s) (%)				Refs.
	Catalyst	Ligand	x	Temp (°)	Time (h)	er ^d
 C₈	1. Catalyst (x mol %), ligand (x mol %), C ₆ D ₆ , rt 2. Aminoallene, C ₆ D ₆					
	Ti(NMe ₂) ₄	254a	5	135	40	(65) 51.5:48.5
	Ti(NMe ₂) ₄	254a	10	125	51	(38) 55.5:44.5
	Ta(NMe ₂) ₅	254a	5	125	132	(20) 38.0:62.0
	Ta(NMe ₂) ₅	254a	5	135	124	(60) 39.5:60.5
	Ti(NMe ₂) ₄	254b	5	135	18	(73) 52.0:48.0
	Ti(NMe ₂) ₄	254b	10	125	51	(61) 54.5:45.5
	Ta(NMe ₂) ₅	254b	5	125	115	(85) 36.0:64.0
	Ta(NMe ₂) ₅	254b	5	135	69	(32) 47.5:52.5
	Ti(NMe ₂) ₄	254c	5	125	49	(29) 50.0:50.0
	Ti(NMe ₂) ₄	254c	5	135	15	(85) 53.5:46.5
	Ta(NMe ₂) ₅	254c	5	125	71	(100) 33.0:67.0
	Ta(NMe ₂) ₅	254c	5	135	69	(34) 41.5:58.5
	Ti(NMe ₂) ₄	254d	5	125	40	(33) 52.0:48.0
	Ti(NMe ₂) ₄	254d	5	135	18	(95) 53.0:47.0
	Ta(NMe ₂) ₅	254d	5	125	17	(88) 38.0:62.0
	Ta(NMe ₂) ₅	254d	5	135	18	(100) 42.5:57.5
	Ti(NMe ₂) ₄	254e	10	125	49	(55) 54.0:46.0
	Ti(NMe ₂) ₄	254e	10	135	40	(61) 53.5:46.5
	Ta(NMe ₂) ₅	254e	5	125	15	(100) 40.0:60.0
	Ta(NMe ₂) ₅	254e	5	135	18	(100) 37.0:63.0
	Ti(NMe ₂) ₄	254f	5	125	27	(45) 52.5:47.5
	Ti(NMe ₂) ₄	254f	5	135	37	(80) 51.0:49.0
	Ta(NMe ₂) ₅	254f	5	125	15	(100) 38.5:61.5
	Ta(NMe ₂) ₅	254f	5	135	19	(100) 46.5:53.5

Please refer to the charts preceding the tables for structures indicated by the **bold numbers**.

TABLE 4D. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALLENES (Continued)

Aminoallene

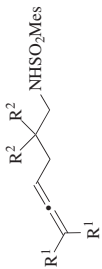
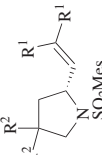
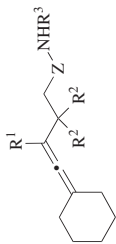
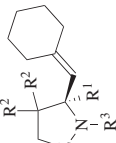
Conditions

Product(s) and Yield(s) (%)

Refs.

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

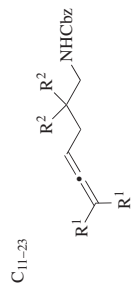
C₀₋₁₃

	244b (5 mol %), Me ₂ PhAuCl (5 mol %), benzene, rt, 48 h		<table> <tr> <th>R¹</th><th>R²</th><th>er</th></tr> <tr> <td>Me</td><td>Me</td><td>(84) 99.5:0.5</td></tr> <tr> <td>-(CH₂)₄-</td><td>H</td><td>(88) 99.0:1.0</td></tr> <tr> <td>-(CH₂)₅-</td><td>H</td><td>(97) 98.0:2.0</td></tr> <tr> <td>Me</td><td>-(CH₂)₅-</td><td>(73) 99.0:1.0</td></tr> </table>	R ¹	R ²	er	Me	Me	(84) 99.5:0.5	-(CH ₂) ₄ -	H	(88) 99.0:1.0	-(CH ₂) ₅ -	H	(97) 98.0:2.0	Me	-(CH ₂) ₅ -	(73) 99.0:1.0	354
R ¹	R ²	er																	
Me	Me	(84) 99.5:0.5																	
-(CH ₂) ₄ -	H	(88) 99.0:1.0																	
-(CH ₂) ₅ -	H	(97) 98.0:2.0																	
Me	-(CH ₂) ₅ -	(73) 99.0:1.0																	
	L(AuOPNB) ₂ (x mol %), solvent			355															

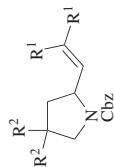
R ¹	R ²	Z	R ³	L	x	Solvent	Temp (°)	Time (h)	er
H	H	BocN	H	143b	5	MeNO ₂	50	15	(46) 52.5:47.5 ^a
H	H	BocN	Boc	143b	5	MeNO ₂	50	15	(98) 85.0:15.0 ^a
H	H	BocN	MesSO ₂	143b	5	MeNO ₂	50	15	(98) 90.0:10.0 ^a
H	H	BocN	MesSO ₂	141c	5	MeNO ₂	50	15	(78) 98.5:1.5
H	H	O	H	143b	3	DCM	rt	18	(92) 55.0:45.0 ^a
H	H	O	Cbz	143b	3	DCM	rt	24	(8) —
H	H	O	Boc	143b	3	DCM	rt	24	(93) 96.5:3.5
H	H	CH ₂ O	Boc	143b	5	MeNO ₂	65	36	(63) 94.5:5.5
Me	H	O	H	143b	5	DCM	rt	24	(98) 66.0:34.0 ^a
Me	H	O	H	142d	5	DCM	rt	24	(80) 74.5:25.5 ^a
Me	H	O	Boc	143b	5	DCM	rt	24	(50) 58.5:41.5 ^a
H	Me	CH ₂ O	Boc	143b	5	MeNO ₂	50	24	(85) 94.5:5.5

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.

C₁₀₋₁₃

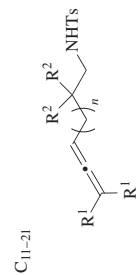


255 (2.5 mol %),
AgClO₄ (5 mol %),
m-xylene

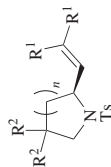


579

R ¹	R ²	Temp (°)	Time (h)	er ^d
H	-(CH ₂) ₅ -	-40	24	(98) 75.0:25.0
Me	Ph	-20	48	(80) 90.0:10.0
Et	Ph	0-rt	48	(83) 95.5:4.5
-(CH ₂) ₅ -	Ph	0	24	(91) 88.0:12.0



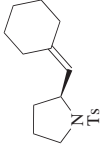
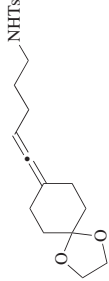
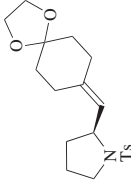
257 (x mol %), solvent, rt



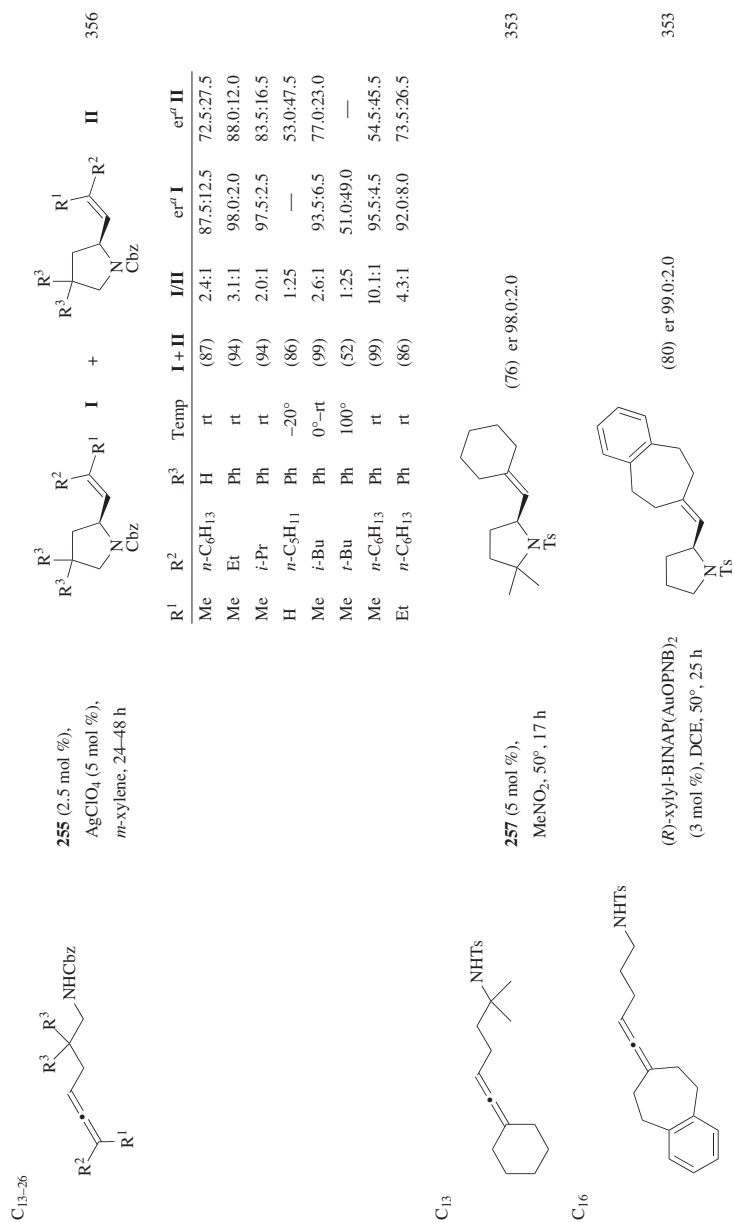
353

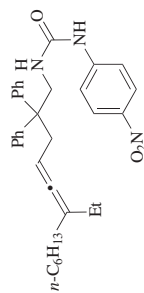
<i>n</i>	R ¹	R ²	<i>x</i>	Solvent	Time (h)	er
1	-(CH ₂) ₅ -	H	3	DCE	15	(85) 98.5:1.5
2	Me	H	5	MeNO ₂	15	(88) 90.5:9.5
2	Et	H	5	MeNO ₂	24	(41) 87.0:13.0
2	Me	Me	5	MeNO ₂	24	(70) 99.0:1.0
2	Me	-(CH ₂) ₅ -	5	MeNO ₂	17	(66) 98.5:1.5
2	Me	Ph	5	MeNO ₂	24	(70) 94.0:6.0

TABLE 4D. ENANTIOSELECTIVE HYDROAMINATION/CYCLIZATION OF AMINOALLENES (Continued)

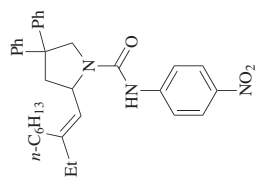
Aminoallene	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₁	Au catalyst (3 mol %), additive (x mol %), DCE, rt	 353	353
 C ₁₂	(R)-xylyl-BINAP(AuOPNB) ₂ (3 mol %), DCE, rt, 25 h	 (79) er 99.0:1.0	353

Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.



C₂₆

255 (5 mol %),
AgBF₄ (10 mol %),
Et₂O/CHCl₃ (x/y)

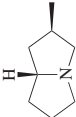
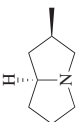
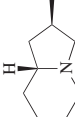
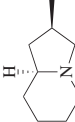
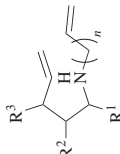
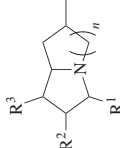


578

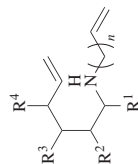
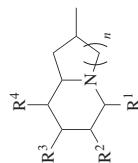
x	y	Temp	Time (h)	dr	er major/minor
0	100	rt	16	75:25 (100)	77.5:22.5/66.5:33.5
50	50	rt	16	80:20 (100)	92.0:8.0/82.0:18.0
75	25	rt	16	74:26 (100)	94.0:6.0/92.5:7.5
75	25	0°	36	57:43 (97)	95.5:4.5/95.0:5.0
80	20	rt	16	72:28 (100)	92.0:8.0/92.5:7.5
83	17	rt	16	83:17 (100)	87.5:12.5/85.0:15.0
100	0	rt	16	— (0)	—

^a The absolute configuration was not reported.^b The product was isolated as the hydrogenated compound.^c The conversion was >95% (NMR).

TABLE 5. HYDROAMINATION/CARBOCYCLIZATION OF AMINOALKENES

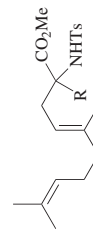
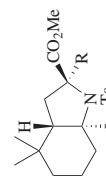
Aminoalkene	Conditions	Product(s) and Yield(s) (%)		Refs.			
C ₈	Catalyst (2 mol %), C ₆ D ₆		I + 	56			
	Catalyst	Temp (°)	TOF (h ⁻¹)	I + II III			
	Cp* ₂ SmCH(TMS) ₂	21	55	(93) 55:45			
	Me ₂ Si(C ₃ Me ₄) ₂ NdCH(TMS) ₂	60	1	(93) 55:45			
C ₉	Cp* ₂ SmCH(TMS) ₂ (2 mol %), C ₆ D ₆ , 21°						
					I + 	56	
C ₉₋₁₀		I + II (88), III 15:85, TOF 5 h ⁻¹					
	Cp* ₂ LnCH(TMS) ₂ (10 mol %), C ₆ D ₆				58		
	<i>n</i>	R ¹	R ²	R ³	Ln	Temp	dr
	1	H	H	Me	Sm	rt	(88) 1:5:1
	1	H	Me	H	Sm	rt	(83) 1.3:1
	1	Me	H	H	Sm	50°	(83) 2:1
	2	H	H	Me	Sm	rt	(91) 6:1
	2	H	H	Me	Nd	rt	(—) ^a 7:1
	2	H	Me	H	Sm	rt	(84) 1:1
	2	H	Me	H	Nd	rt	(—) ^a 1:1
	2	Me	H	H	Sm	50°	(91) 25:1
	2	Me	H	H	Nd	50°	(—) ^a 10:1

<i>n</i>	R ¹	R ²	R ³	Ln	Temp	dr
1	H	H	Me	Sm	rt	(88) 1:5:1
1	H	Me	H	Sm	rt	(83) 1:3:1
1	Me	H	H	Sm	50°	(83) 2:1
2	H	H	Me	Sm	rt	(91) 6:1
2	H	H	Me	Nd	rt	(—) ^a 7:1
2	H	Me	H	Sm	rt	(84) 1:1
2	H	Me	H	Nd	rt	(—) ^a 1:1
2	Me	H	H	Sm	50°	(91) 25:1
2	Me	H	H	Nd	50°	(—) ^a 10:1

C₁₀₋₁₁Catalyst (10 mol %), C₆D₆

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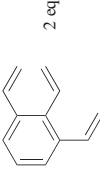
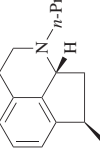
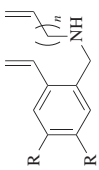
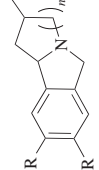
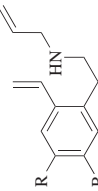
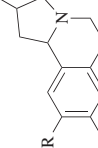
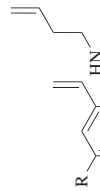
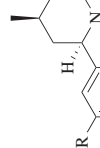
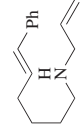
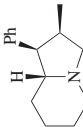
<i>n</i>	R ¹	R ²	R ³	R ⁴	Catalyst	Temp	dr
1	H	H	H	Me	Cp* ₂ NdCH(TMS) ₂	rt	(81) 5.2:3.1:1:1
1	H	H	H	Me	Cp* ₂ SmCH(TMS) ₂	rt	(—) ^a 4:3:1.4:1
1	H	H	Me	H	Cp* ₂ NdCH(TMS) ₂	rt	(86) 8.5:6.5:1
1	H	H	Me	H	Cp* ₂ SmCH(TMS) ₂	rt	(—) ^a 2.8:2.3:1
1	H	Me	H	H	Cp* ₂ NdCH(TMS) ₂	40°	(86) 27:1
1	H	Me	H	H	Cp* ₂ SmCH(TMS) ₂	40°	(—) ^a 23:1
1	Me	H	H	H	Cp* ₂ SmCH(TMS) ₂	50°	(87) 8.3:1.3:1
2	H	H	H	H	Cp* ₂ NdCH(TMS) ₂	rt	(85) >50:1
2	H	H	H	Me	Cp* ₂ NdCH(TMS) ₂	rt	(89) 1:1.9
2	H	H	Me	H	Cp* ₂ NdCH(TMS) ₂	rt	(86) 1:1.3
2	H	Me	H	H	Cp* ₂ NdCH(TMS) ₂	50°	(90) >20:1
2	H	Me	H	H	[(Me ₃ SiC ₃ H ₄) ₂ NdMe] ₂	90°	(—) —
2	Me	H	H	H	Cp* ₂ NdCH(TMS) ₂	70°	(—) —
2	Me	H	H	H	[(Me ₃ SiC ₃ H ₄) ₂ NdMe] ₂	70°	(—) ^a >50:1
2	Me	H	H	H	Me ₂ Si(C ₃ Me ₄) ₂ NdCH(TMS) ₂	40°	(91) >2.5:1

C₁₂₋₁₃TiOH, CHCl₃, 0°, 0.25 h

210, 488

	R	dr
	H (88)	3:1
	Me (91)	3:2

TABLE 5. HYDROAMINATION/CARBOCYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.
C₁₂  2 eq	(<i>n</i>-Pr)₃NH₂, Cp*₂SmCH(TMS)₂ (5 mol %), C₇D₈, 90°	 (88)	43
C₁₂₋₁₃ 	Cp*₂SmCH(TMS)₂ (10 mol %), C₆D₆, 22 h	 (89)	57
C₁₃ 	Cp*₂NdCH(TMS)₂ (10 mol %), C₆D₆, rt, 22 h	 (82)	57
C₁₄ 	Cp*₂NdCH(TMS)₂ (10 mol %), C₆D₆, 22 h	 (73)	57
C₁₅ 	<i>t</i>-Bu(Tf)₂NLi (1.5 eq), THF/C₇H₈ (1:7), rt, 20 h	 (96)	357

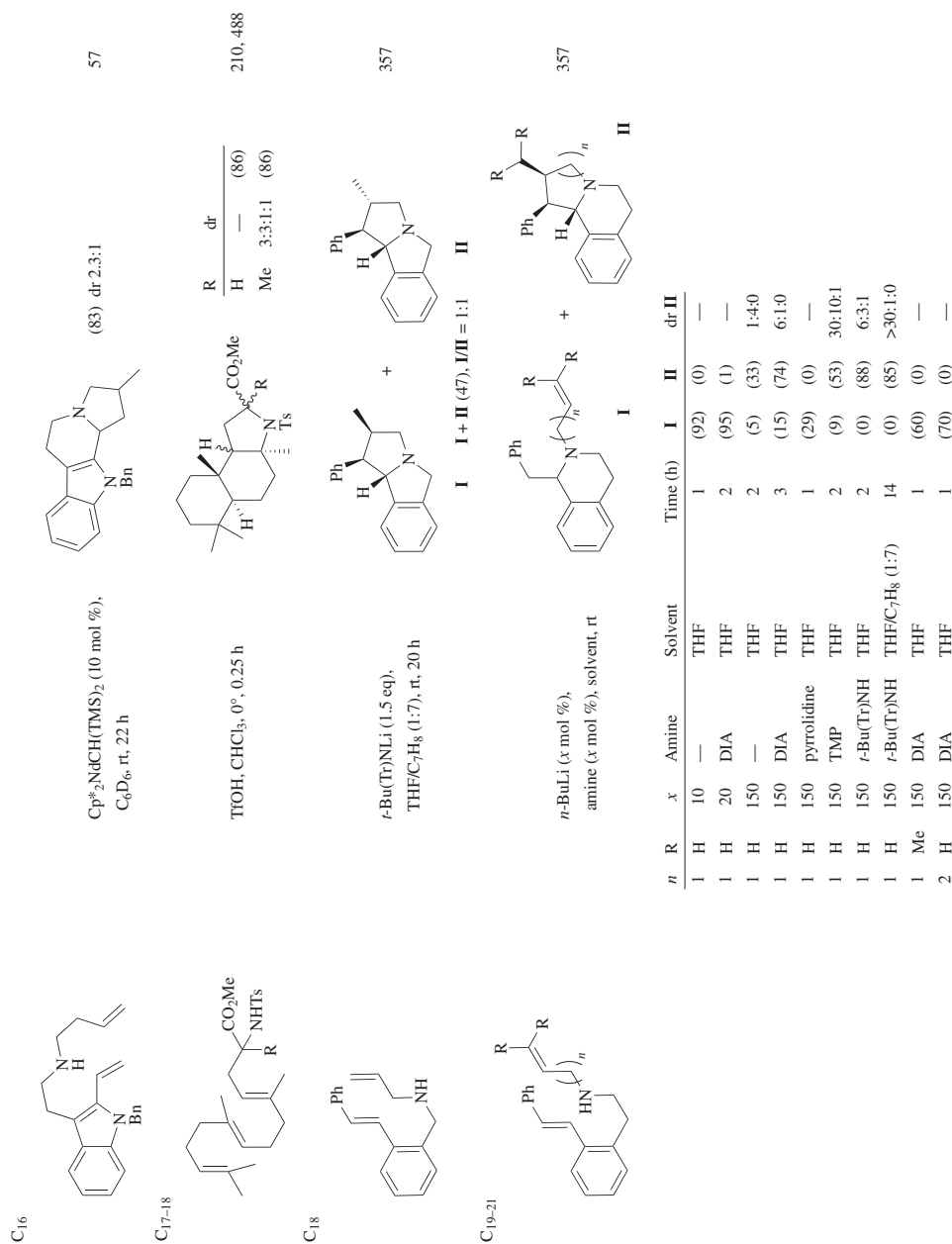
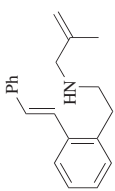
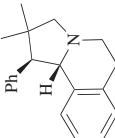
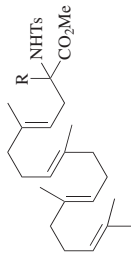
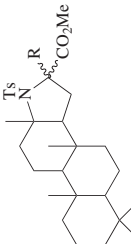


TABLE 5. HYDROAMINATION/CARBOCYCLIZATION OF AMINOALKENES (Continued)

Aminoalkene	Conditions	Product(s) and Yield(s) (%)	Refs.									
C₂₀ 	<i>t</i> -Bu(Trt)NLi (1.5 eq), THF, rt, 4 h	 (75)	357									
C₂₂₋₂₃ 	TfOH, CHCl ₃ , 0°, 0.25 h	 <table><tr><th>R</th><th>(80)^c</th><th>(83)^c</th></tr><tr><td>H</td><td></td><td></td></tr><tr><td>Me</td><td></td><td></td></tr></table>	R	(80) ^c	(83) ^c	H			Me			210, 488
R	(80) ^c	(83) ^c										
H												
Me												

^a The products were not isolated.

^b The products were not isolated due to low stability.

^c The reaction gave a mixture of diastereomers for which the dr was not reported.

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