Catalytic Asymmetric Hydrogenation of Imines with a Chiral Titanocene Catalyst: Scope and Limitations

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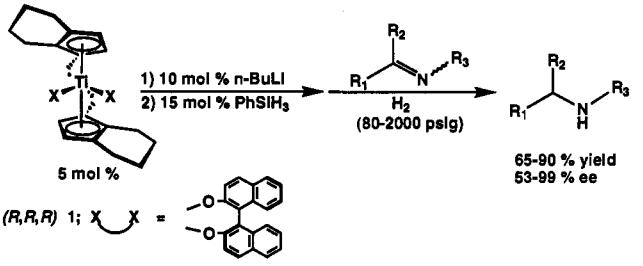
Abstract: The asymmetric hydrogenation of imines with a chiral titanocene catalyst derived from Brintzinger's *ansa*-titanocene complex **1** proceeds to afford amines with good to excellent enantioselectivity. The catalyst is particularly effective for the reduction of cyclic imines. For these substrates enantiomeric excesses from 95 to 99% were achieved. For acyclic imines lower enantiomeric excesses were observed. The reason for this is likely due to the fact that the acyclic imines are mixtures of *anti* and *syn* isomers which interconvert during the reaction. The catalyst was found to be tolerant of many functional groups found in organic synthesis. Thus the reaction represents an effective method for the synthesis of chiral cyclic amines.

The development of asymmetric catalysts for the hydrogenation of achiral substrates to form enantiomerically enriched products represents a major area of research.[1] Levels of selectivity that rival enzymatic systems have been achieved for the asymmetric hydrogenation of olefins[2] and ketones.[3] With the growing importance of enantiomerically pure nitrogen containing compounds in the pharmaceutical and agrochemical industries, the asymmetric hydrogenation of imines to enantiomerically enriched amines has received much attention recently.[4] Virtually all of the systems employed for this reaction have been derived from late transition metals and in general the substrates must possess a coordinating ligand such as a carbonyl group for high levels of reactivity and selectivity to be realized. As part of an ongoing study of the viability of titanium catalysts for the reduction of unsaturated organic compounds,[5] we have discovered a titanocene catalyst system for the asymmetric hydrogenation of imines.[6] A feature of this system is that no coordinating group is necessary for high levels of enantioselectivity to be achieved. The catalyst discriminates purely on the basis of the "shape" of the substrate. In this paper we present a full account of our studies of this system for the synthesis of enantiomerically enriched amines. A detailed account of the mechanistic investigations of this reaction will be presented in a forthcoming paper.

Scheme 1



Results and Discussion

The hydrogenation catalyst employed in our studies is generated *in situ* from the air stable chiral titanocene complex, *(R,R,R)*-**1**, first introduced by Brintzinger.[7] Treatment of a THF solution of *(R,R,R)*-**1** with 2 equiv of *n*-butyllithium followed by 3 equiv of phenylsilane[8] results in the formation of an active hydrogenation catalyst, presumed to be a titanium(III) hydride.[9] When solutions of this species are placed under a hydrogen atmosphere (80–2000 psig H_2), imines are catalytically reduced to the corresponding amines (Scheme 1). Although reduction of olefins with reduced titanocene complexes (usually generated from the titanocene dichloride derivative and 2 equiv of an alkyllithium or alkyl Grignard reagent under hydrogen atmosphere) has been investigated with achiral[10] and chiral[11] cyclopentadienyl ligands, this work represents the first example of reduction of imines with this type of catalyst.

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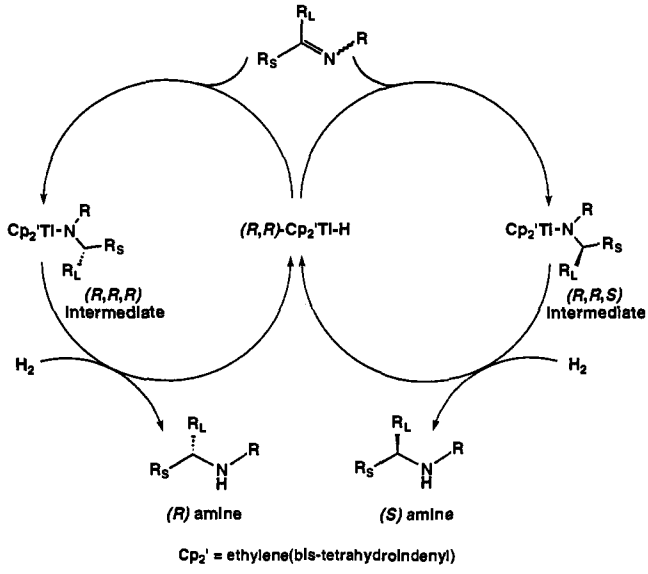
Scheme 2



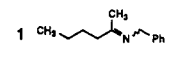
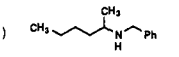
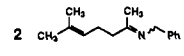
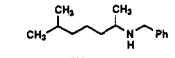
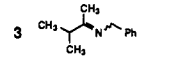
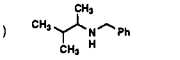
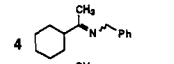
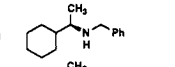
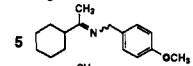
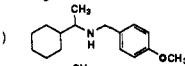
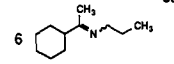
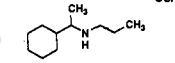
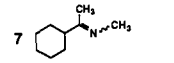
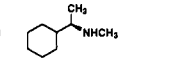
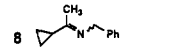
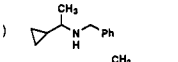
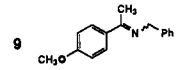
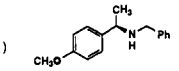
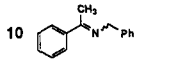
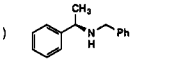
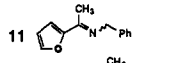
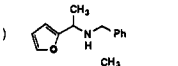
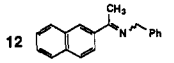
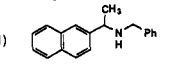
Our proposed catalytic cycle is presented in Scheme 2. The first step of the cycle is reaction of the titanium hydride with an imine, via a 1,2-insertion reaction, to form two diastereomeric titanium amide complexes. The second step is hydrogenolysis of the intermediate amide complexes, via a σ bond metathesis reaction,[12] to regenerate the titanium hydride and form the two amine enantiomers.

During the course of our investigations we found that acyclic imines showed different behavior with this system than cyclic imines. Therefore, these two classes of substrates will be discussed separately.

Hydrogenation of Acyclic Imines. Table 1 shows our results for the hydrogenation of several acyclic imines. An important characteristic of these substrates is that they exist as mixtures of *anti* and *syn* isomers.[13] This property becomes significant when considering the stereochemical outcome of the reaction. We chose to focus on the hydrogenation of *N*-benzyl imines since in most cases, the benzyl group could be subsequently removed to afford the primary amines.[14]

As can be seen in Table 1 the reaction proceeds to afford the amines with moderate to good enantiomeric excesses. When *(R,R,R)*-**1** is used as the catalyst precursor, imines are generally converted to the *(R)* enantiomers of the amines. For example, at 2000 psig of hydrogen pressure, *N*-(1-phenylethylidene)-benzylamine (entry 10) is converted to *N*-benzyl *(R)*-α-methylbenzylamine with an average ee of 77%. Likewise, *N*-(1-cyclohexylethylidene)benzylamine (entry 4) was hydrogenated at 2000 psig to the corresponding *(R)* amine with an ee of 76%. For entries 7 and 9 the isolated amines also had an *(R)* configuration. The absolute configurations were established by comparison of the optical rotation with known values. To account for these observations, we have proposed the model shown in Scheme 3. For proper overlap of the metal orbitals and the imine π orbitals[15] the plane defined by the nitrogen atom, the imine carbon and the imine substituents (R_S and R_L), must be orthogonal to the plane of the titanium, the nitrogen atom, and hydride ligand. An X-ray crystallographic study of a related niobocene olefin hydride complex supports this geometry for these types of

Table 1. Asymmetric Hydrogenation of Acyclic Imines[a]

Entry	Imine	(anti / syn)	Amine	Pressure (psig)	Yield (%)	ee (%)	(±)
1		(3.3:1)		2000	68	58 [b]	(-)
2		(3:1)		2000	64	62 [b]	(-)
3		(13:1)		2000	66	76 [b]	(-)
4		(11:1)		2000 500	93 85	76 43	(-) (-)
5		(14:1)		2000 500	92 81	78 62	(-) (-)
6		(9:1)		2000 80	70 65	79 [c] 4 [c]	(-) (+)
7		(11:1)		500 80	85 62	92 92	(-) (-)
8		(7.5:1)		2000	91	61	(-)
9		(17:1)		2000	86	86	(+)
10		(17:1)		2000 2000	81 93	77 [d] 85 [e]	(+) (+)
11		(10:1)		2000	70	53	(+)
12		(44:1)		2000	82	70	(+)

[a] Reactions were run using 5 mol % **1** as the *(R,R,R)* diastereomer unless otherwise noted. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. Elemental composition was determined by elemental analysis or high-resolution mass spectrometry. Enantiomeric excesses were determined by HPLC analysis using a Chiralcel OD HPLC column. Absolute configurations in entries 4, 7, 9, and 10 were determined by optical rotation. [b] With 10 mol % **1**. [c] The absolute configuration of the product is opposite to that observed at 2000 psig. [d] Enantiomeric excess of product ranged from 65–87% for several experiments. [e] With 2 mol % **1**.

complexes.[16] Interaction of an *anti* imine with the *(R,R)* titanium complex leads to two possible intermediates, **A** and **B**. In **A**, the nitrogen substituent is pointing down away from the cyclohexyl ring on the titanium complex while in **B** the nitrogen substituent is up and interacts unfavorably with the tetrahydroindenyl ligand. Thus **A** should be favored relative to **B** and for an *anti* imine the *(R)* amine is expected with the *(R,R)* catalyst. The effects of the substituents on the imine carbon (R_L and R_S) are small relative to the effects of the nitrogen substituent, R, because R is much closer to the ligand.

For a *syn* imine two intermediates **C** and **D** are also possible. In **C** an unfavorable interaction exists between the nitrogen substituent, R and the tetrahydroindenyl ligand. In **D** the nitrogen substituent points down, away from the ligand, minimizing any interaction. Therefore **D** is expected to be favored relative to **C**. Again the carbon substituents, R_S and R_L are more distant from the ligand so any effect of these groups are small. Thus with the *(R,R)* complex, the *syn* imine is expected to give the *(S)* amine. Importantly, this model predicts that *syn* and *anti* imines react to give the amine with opposite absolute configuration. Experimental evidence to support this prediction has been observed *(vide infra)*.

The enantiomeric excesses of the products correlate roughly with the *anti/syn* ratios of the imines. For example *N*-(1-methylpentylidene)benzylamine (entry 1, *anti/syn* = 3.3:1) and *N*-(1,5-dimethylhex-5-enylidene)benzylamine (entry 2, *anti/syn* = 3:1) are reduced, at 2000 psig and 65 °C, to the corresponding

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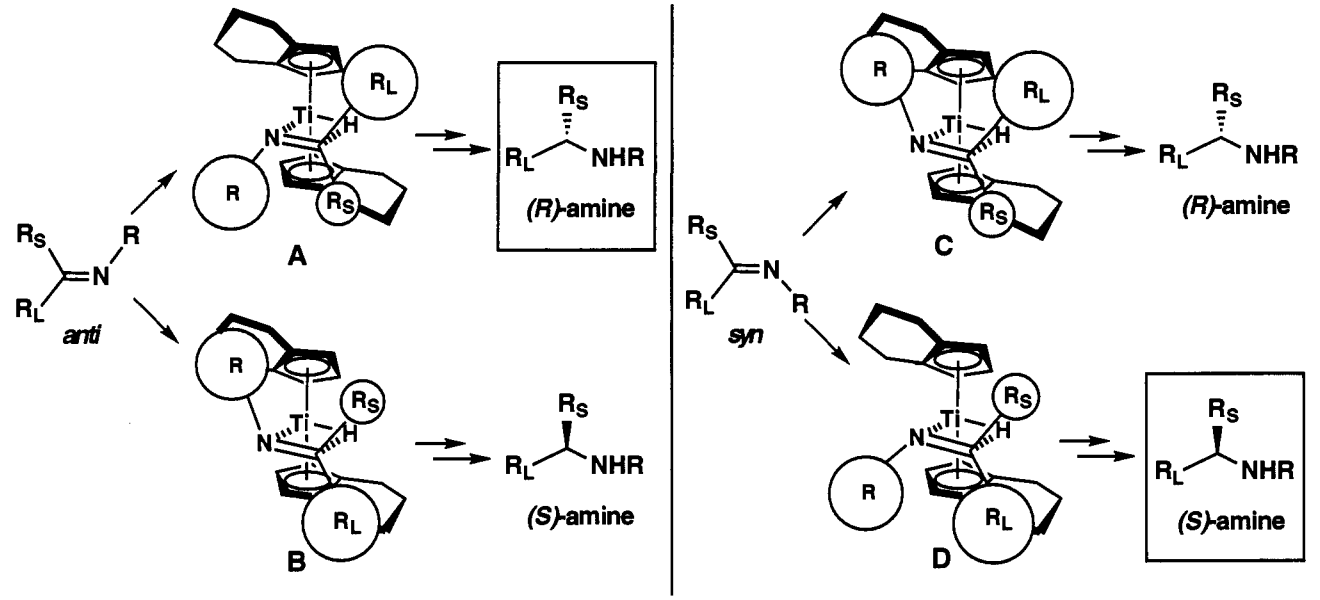
Scheme 3



amines with ee's of 58% and 62% respectively. *N*-(1,2-Dimethylpropylidene)benzylamine (entry 3, *anti/syn* = 13:1) and *N*-(1-cyclohexylethylidene)benzylamine (entry 4, *anti/syn* = 11:1) are both reduced to the corresponding amines, at 2000 psig, with 76% ee. As illustrated by entries 4 and 6 the ee changed very little when the nitrogen substituent was changed from a benzyl group to a propyl group. However, when the nitrogen substituent was a methyl group (entry 7, *anti/syn* = 11:1) the ee was significantly higher, 92% vs 76%, than when it was a benzyl group (entry 4). In addition, when the nitrogen substituent was a methyl group the reaction occurred at 80 psig of hydrogen with no effect on the enantiomeric excess (an explanation for this is offered below).

In order to increase the utility of this reaction for the synthesis of enantiomerically enriched amines, we examined the reaction at lower hydrogen pressures. We found, however, that for the hydrogenation of acyclic imines high hydrogen pressures are required to achieve the maximum ee's. For example, when *N*-(1-cyclohexylethylidene)benzylamine (entry 4) was hydrogenated at 2000 psig the ee of the isolated amine was 76%. However, when the hydrogen pressure was reduced to 500 psig the ee decreased to 43%. Similarly *N*-(1-cyclohexylethylidene)-4-methoxybenzylamine (entry 5) was hydrogenated at 2000 psig to the corresponding amine with an ee of 78%. When the reaction was run at 500 psig the ee of the amine was 62%. We also observed this behavior for nonbenzylic imines as demonstrated by the hydrogenation of *N*-(1-cyclohexylethylidene)propylamine (entry 6). At 2000 psig this imine was hydrogenated to the corresponding amine with an ee of 79%. When the reaction was conducted at 80 psig the amine was isolated with only a 4% ee. Interestingly the amine formed at 80 psig was of the opposite absolute configuration to that observed at 2000 psig. A pressure dependence was also observed for the imines in entries 2 and 10 and appears to be general for acyclic imines.

Experimental evidence suggests that this pressure dependence can be explained on the basis of the interconversion of the *anti* and *syn* isomers of the imine.[17] We observed that for the hydrogenation of *N*-(1-cyclohexylethylidene)benzylamine (entry 4) that the *syn* isomer reacts faster than the *anti* isomer. However the *syn* isomer does not completely disappear over the course of the reaction, suggesting that it is being replaced by isomerization of the *anti* isomer.[18] Since our transition state model for the reaction predicts that the *anti* and *syn* isomers react to form opposite enantiomers of the amine, as the pressure is lowered, more of the imine can react via the *syn* isomer and the observed ee of the product will be lower.

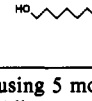
One exception to the pressure dependence for acyclic imines is the hydrogenation of *N*-(1-cyclohexylethylidene)methylamine (entry 7, *anti/syn* = 11:1). This imine was converted to the corresponding amine either at 500 psig or at 80 psig with 92% ee. The insensitivity of ee to changes in pressure for this imine is presumably due to the faster rate of hydrogenolysis relative to the rate of interconversion of *syn* and *anti* isomers. The *N*-methyl imine (entry 7) reacts *ca.* 16 times faster than the *N*-propyl imine (entry 6) which shows a dramatic pressure dependence, while the interconversion rate of *anti* and *syn* isomers should be similar for both substrates.[13,18] Furthermore, the ee for this substrate does not correlate very well to the *anti/syn* ratio. The reason for this is probably because the methyl group on the nitrogen is small. When this is the case R_S and R_L become more important in determining selectivity. Thus the energy difference between **C** and **D** (Scheme 3) and therefore the selectivity for hydrogenation of the *syn* isomer will be lower. This would result in a higher ee for the product since reaction through **C** gives the same enantiomer as reaction through **A**.

Hydrogenation of Cyclic Imines. Heterocyclic compounds, in which a nitrogen is bound to a stereogenic carbon, make up a large body of naturally occurring and medicinally important compounds. We therefore investigated the asymmetric hydrogenation of cyclic imines as a possible synthetic route to enantiomerically enriched cyclic amines. For many late transition metal catalysts asymmetric hydrogenation of cyclic imines has been less successful. Therefore, it was of particular interest to us to define the functional group compatibility of this catalyst system. Our results are presented in Table 2.

The hydrogenation of cyclic imines to cyclic amines was found to occur with excellent levels of enantiomeric excesses in all cases investigated. Furthermore, in almost all cases, the reactions could be conducted at much lower hydrogen pressure than for acyclic imines. A notable difference between the hydrogenation of cyclic imines and that of acyclic imines is that the enantiomeric excesses for cyclic imines are virtually insensitive to changes in hydrogen pressure. For example 2-phenyl-1-pyrroline (entry 1) was hydrogenated at 2000 psig, with *(R,R,R)*-**1**, to afford *(R)*-2-phenylpyrrolidine with an ee of >98%. That the product has an *(R)* absolute configuration is consistent with the model shown in

(17) Willoughby, C. A.; Buchwald, S. L. Submitted for publication.
(18) Smith, J. K.; Bergbreiter, D. E.; Newcomb, M. *J. Am. Chem. Soc.* **1983**, *105*, 4396.

Table 2. Asymmetric Hydrogenation of Cyclic Imines[a]

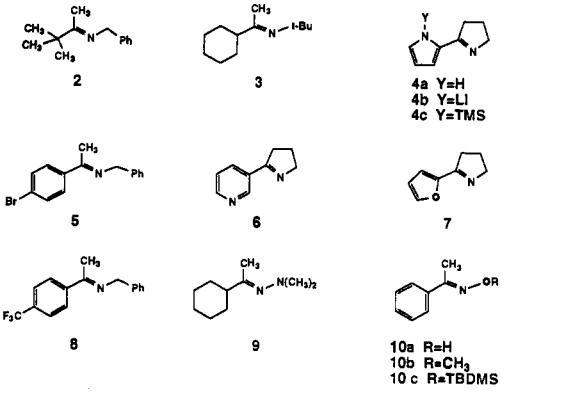
Entry	Imine	Amine	Pressure (psig)	T (° C)	Yield (%)	ee (%)	(±)
1			2000	65	77	98	(+)
			500	21	86	99	(+)
			80	65	84	99[b]	(+)
			80	65	83	99	(+)
2			2000	65	70	97	(+)
			500	65	78	98	(+)
3			500	45	71	98	(+)
			80	65	74	97	(+)
4			2000	65	82	98	(-)
			80	65	79	95	(-)
5			500	23	83	99	(+)
			80	65	72	99	(+)
6			80	50	79	99	(+)
7			80	50	73[c]	99	(+)
8			80	45	69[d]	99	(+)
9			80	45	72	99	(+)
10			2000	65	81	98	(+)
11			80	65	82	99	(+)
12			80	65	82	99	(+)
13			80[e]	65	84	99	(+)

[a] Reactions were run using 5 mol % **1**, as the *(R,R,R)* diastereomer unless otherwise noted. All new compounds were characterized by ^1H NMR, ^{13}C NMR, IR, and HRMS. Enantiomeric excesses were determined by HPLC analysis using a Chiralcel OD HPLC column. The absolute configurations in entries 1, 2, 4, and 5 were determined by optical rotation. Yields refer to isolated yields of products >95% purity unless otherwise noted. [b] With 1 mol % catalyst. [c] This yield includes 5–8% of the saturated compound and <1% of the *Z* isomer; the ee was determined on the product mixture. [d] This yield includes 14–18% of the *E* isomer and 13–19% of the saturated compound; the ee was determined by hydrogenating the mixture to the saturated compound (H_2, Pd/C) and measuring the ee of the product. [e] With 1.1 equiv phenylsilane/imine.

Scheme 3, since the imine has *anti* geometry. At 500 psig and at 80 psig the ee of the amine was 99%. Likewise, when the imine is part of a six or a seven membered ring as in entries 2 and 3, the ee was also found to be independent of hydrogen pressure. In both cases the amines were isolated with ee's ranging from 97–98%. Note that the *anti* imine (entry 2) also is converted to the *(R)* amine. For the hydrogenation of 6,7-dimethoxy-3,4-dihydro-1-methylisoquinoline (entry 4) a small effect of lowering the hydrogen pressure was observed. At 2000 psig the average ee of the amine was 98%, while at 80 psig the ee was 95%. Significantly this substrate, which has *syn* geometry, was hydrogenated by *(R,R,R)*-**1** to the *(S)* amine. This result supports the prediction that a *syn* imine reacts to give the *(S)* product (Scheme 3).

We next examined the functional group compatibility of our catalyst system by preparing and hydrogenating a number of 2-substituted pyrrolines with various organic groups. A substrate with a benzyl protected pyrrolyl substituent (entry 5) was of particular interest.[19] We found that this imine could be cleanly hydrogenated to the corresponding amine with excellent enantioselectivity. However the free pyrrole, **4a** (Table 3), caused destruction of the catalyst. The lithio derivative, **4b**, did not react at all, but the catalyst remained active.[20] This can be ascribed to chelation of the substrate to titanium through the

Table 3. Substrates Which Are Not Reduced to Amines



pyrrolyl nitrogen and the imine lone pair. When the substrate is coordinated in this manner, the proper orbital overlap necessary for 1,2-insertion cannot occur. The trimethylsilyl derivative, **4c**, also failed to react under standard conditions, presumably for steric reasons. An imine containing a pyridine substituent, 3-pyridyl-2-pyrroline (**6**), also failed to react under normal conditions. The reason for this is not clear at present. At 80 psig and 65 °C, 2-furyl-2-pyrroline (**7**) reacted to *ca.* 80% conversion after 60 h. Even at elevated hydrogen pressures (1000 psig, 65 C, 48 h) the reaction could not be forced to completion. This behavior may be due to product inhibition by binding of the amine to the metal in a bidentate fashion. Presumably as the concentration of amine increases the concentration of free catalyst decreases and the reaction slows down.[21]

Since early transition metal complexes are conventionally perceived to have limited functional group tolerance, we examined the selectivity of cyclic imines containing various organic functional groups (Table 2). As can be seen by entry 6 of Table 2, a trisubstituted olefin was completely tolerated under standard conditions. The amino olefin was isolated in good yield and with an excellent enantiomeric excess of 99%. No reduction of the olefin was observed. When the olefin was a bulky disubstituted one, as in an *(E)*-trimethylsilyl substituted olefin (entry 7), a small amount of reduction (*ca.* 5–8%) and isomerization to the *(Z)* isomer (*ca.* 1%) was observed. The product was isolated in good yield with an ee of 99%. Dialkyl substituted olefins (*i.e.* entry 8) were hydrogenated and isomerized concomitant with imine reduction. In this case *ca.* 13–18% reduction and *ca.* 14–18% isomerization to the *(E)* isomer was observed. However the ee of the products was 99%. This was determined by hydrogenating the product mixture (H_2, Pd/C) and measuring the ee of the saturated amine. The hydrogenation of a substrate containing a terminal olefin (entry 9) illustrates that terminal olefins are reduced faster than imines at 80 psig and 45 °C with this catalyst. The ee of the product was again excellent, 99%.

Substrates containing oxygenated functional groups were also found to be compatible with this methodology. For example, a substrate containing a *tert*-butyldimethylsilyl ether (entry 11) was hydrogenated to the corresponding amine with an ee of 99%. Interestingly a substrate containing an OH group (entry 13) was converted to the corresponding amino alcohol with an excellent ee, 99%. For this reaction it was necessary to add 1.1 equiv of phenylsilane. Presumably, silylation of the alcohol takes place prior to reduction of the imine.[22] A substrate containing an acetal (entry 12) was also hydrogenated to the corresponding amine in good yield with an ee of 99%. This result is interesting in view of the oxophilic nature of titanium. When a competition experiment between 2-phenylpyrroline and acetophenone was

(19) Hong, Y.-P.; Masamune, S. Unpublished results.
(20) The activity of the catalyst was checked by adding a small amount of 2-phenylpyrroline after several hours. The added 2-phenylpyrroline was hydrogenated to 2-phenylpyrrolidine.
(21) We have observed rate deceleration as product accumulates for other substrates containing coordinating groups such as an olefin or furan.
(22) (a) Bedard, T. C.; Corey, J. Y. *J. Organomet. Chem.* **1992**, *428*, 315. (b) Warner, B. P.; Buchwald S. L. Unpublished results.

conducted, no reaction of the imine was observed unless 1 equivalent of phenylsilane was added. Under these conditions the acetophenone was hydrosilylated before any imine was reduced. The 1-phenylethanol obtained from this reaction had an ee of 33%[5d] while the ee of the isolated *(R)*-2-phenylpyrrolidine was 98%. This result shows that while this catalyst is more reactive toward a carbonyl group than an imine, the presence of a ketone in the reaction mixture does not significantly affect the enantioselectivity of imine reduction.

Several other substrates were investigated with this system (Table 3). For example, imines containing a *tert*-butyl group, either on the nitrogen as in **3** or on the imine carbon as in **2** were found not to react, even under forcing conditions (2000 psig H_2, 65 °C). Presumably the bulkiness of the *tert*-butyl group makes the insertion step (see Scheme 2) unfavorable. An imine containing an aromatic bromide, **5**, was found to deactivate the catalyst. In this reaction *ca.* 5% of the debrominated imine was observed (GC/MS). Similar reactivity has been reported for reduced titanocene species[23] and is evidence that titanium is in the +3 oxidation state during the reaction. Imine **8** which contains a trifluoromethyl group, also destroyed the catalyst. In this case we were unable to determine the nature of the decomposition products. For substrates containing heteroatoms bound to nitrogen, deactivation of the catalyst was also observed. In the case of hydrazone **9**, the major species in the reaction was starting material. However, a trace of 1-cyclohexylethylamine was detected by GC/MS. For the reaction of oxime **10a** and its derivatives **10b** (R = CH_3) and **10c** (R = TBDMS), traces (*ca.* 2–4%) of 1-phenylethylamine were detected along with starting material. The presence of 1-phenylethylamine indicates that N–O bond cleavage occurred under the reaction conditions and that the C=N double bond was reduced prior to N–O bond cleavage. The N–O bond cleavage of hydroxyl amines has been previously observed with $TiCl_3$.[24]

Conclusions

The titanocene catalyzed asymmetric hydrogenation of imines has been shown to produce amines with good to excellent levels of enantioselectivity and in good isolated yield. While the enantiomeric excesses for acyclic imines (with the exception of *N*-methyl imines) are still below the level of practical utility, the catalyst system is particularly useful for the hydrogenation of cyclic imines, imines that have been hydrogenated less successfully with other metal catalysts.[4c-f] For these imines the titanocene catalyst system affords the amines with 95–99% enantiomeric excess. The system exhibits tolerance to several common organic functional groups, including trisubstituted olefins, acetals, and alcohols. An additional feature of our system is that a coordinating ligand in the substrate is not necessary for high selectivity. In fact, in some cases this appears have a negative effect on the reaction. This is in contrast to the late metal systems in which a coordinating group is often required for good enantioselectivity to be observed.[4]

Experimental Section

General Considerations. All reactions were conducted under an atmosphere of argon, nitrogen, or hydrogen using standard Schlenk and glove box techniques. Hydrogenation reactions were conducted in a Fisher-Porter bottle (purchased from Aerosol Lab Equipment, Walton, NY) or in a Parr model 4751 high pressure autoclave (Parr Instrument Co, Moline, IL). Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity-300, Varian XL-300, or Bruker AC-250 Fourier transform spectrometer. Infrared (IR) spectra were recorded on a Mattson Cygnus Starlab 100 or Perkin-Elmer 1600 series Fourier transform spectrometer. High-resolution mass spectra (HRMS) were recorded on a Finnigan system 8200 mass spectrometer. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Gas chromatographic (GC) analyses were performed on a Hewlett-Packard model 5890 gas chromatograph with a flame ionization detector and a model 3392A integrator using a 25 m capillary column with cross linked HP-1 or HP-17 as a stationary phase. High-performance liquid chromatography (HPLC) was conducted using a Hewlett-Packard model 1050 pumping system with a Hewlett-Packard model 1040A ultraviolet detector and a Chiralcel OD chiral stationary phase (Daicel Chemical Industries, Ltd.). Optical rotations were measured with a Perkin-Elmer model 241 polarimeter. Melting points were determined with a Haake Buchler melting point apparatus and are uncorrected.

Tetrahydrofuran (THF) and diethyl ether were dried and deoxygenated by refluxing and distilling from sodium/benzophenone ketyl under an argon atmosphere. For large scale preparations of complex **1**, THF was purchased from Aldrich Chemical Co. in Sure Seal bottles and used as recieved. Hexane and benzene were dried and deoxygenated by refluxing and distilling from sodium/benzophenone ketyl under a nitrogen atmosphere. Toluene was dried by refluxing and distilling from sodium metal under a nitrogen atmosphere. Diisopropylamine and methylene chloride were dried by refluxing and distilling from CaH_2 under a nitrogen atmosphere. Preparative flash chromatography was performed on silica (E. M. Science Kieselgel 60, 230–400 mesh) or neutral alumina (ICN Alumina N, Akt. I). Deactivated silica was prepared by washing silica with acetone and drying in the oven. All reagents, unless otherwise stated, are commercially available and were used as received.

Unless otherwise stated, yields refer to isolated yields of products of greater than 95% purity as estimated by capillary GC and/or ^{1}H NMR spectrometry. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, and IR spectrometry and by high-resolution mass spectrometry or elemental analysis.

Preparation of Materials. *rac*- and *meso*-Ethylene-1,2-bis(η^5-3-indenyl)titanium Dichloride. This complex was prepared by a modification of the original procedure.[7] In a 1 L Schlenk flask under an argon atmosphere 1,2-bis(3-indenyl)ethane[25] (12.92 g, 50 mmol) was dissolved in 500 mL of dry THF. The solution was cooled to 0 °C and a solution of *n*-butyllithium (2.5 M in hexanes, 40 mL, 100 mmol) was added. This mixture was allowed to warm to room temperature and stir for 30 min. It was then transferred dropwise, via cannula, under argon to a slurry of $TiCl_3$ (7.71 g, 50 mmol, purchased from Aldrich) in 500 mL of dry THF, over a period of 2 h. The resulting green-brown solution was allowed to stir for an additional 4 h. $CHCl_3$ (50 mL, 600 mmol) was then added to the mixture, and it was allowed to stir overnight. The resulting dark green solution was concentrated *in vacuo* to yield a brown air stable solid. The solid was washed with Et_2O (300 mL), water (50 mL), and aqueous HCl (4 M, 20 mL). The solid was again washed with water (20 mL) followed by ethanol (50 mL) and dried *in vacuo*. A brown solid (10.04 g, 53% yield) was recovered as a 1.1 to 1 mixture of *meso* to *rac* isomers (^{1}H NMR). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.6–7.1 (m, 16H), 6.9 (dd, 2H), 6.7 (dd, 2H), 6.5 (d, 2H), 6.0 (d, 2H), 4.8–3.7 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 128.6, 128.5, 128.4, 128.3, 126.1, 122.7, 122.2, 122.0, 119.7, 116.6, 115.5, 30.4, 29.6.

***rac*-Ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)titanium Dichloride.** This complex was prepared from *rac*- and *meso*-ethylene-1,2-bis(η^5-3-indenyl)titanium dichloride as described.[7] Yield: 75% (based on amount of *rac* isomer present in the initial mixture). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 6.6 (d, 2H), 5.56 (d, 2H), 3.3–3.0 (m, 6H), 2.7–2.5 (m, 4H), 2.5–2.3 (m, 2H), 2.3–1.8 (m, 4H), 1.45–1.6 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.79, 134.69, 128.94, 126.32, 111.55, 27.87, 24.50, 24.17, 21.77, 21.75.

(*R,R*)-Ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)titanium (*R*)-1,1′-Binaphth-2,2′-diolate. This complex was prepared as described[7,26] with a modification of the workup. A dry 1 L Schlenk flask under an argon atmosphere was charged with 5.0 g of sodium (50% dispersion in paraffin, 109 mmol). The solid sodium was washed, by cannula filtration, with dry hexanes (3 × 25 mL). Dry toluene (400 mL) was added and the mixture was stirred at 80 °C for 1 h. Solid *rac*-ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)titanium dichloride (5.0 g, 13 mmol) and solid *(R)*-1,1′-binaphth-2,2′-diol (1.87 g, 6.5 mmol, purchased from Aldrich) were then added to the solution. The mixture was stirred at 80 °C for 45 min (reaction times vary from 45 min to 4 h) at which point TLC analysis of an aliquot (1:1 methylene chloride/hexanes) showed no remaining *(R)*-1,1′-binaphth-2,2′-diol. The warm solution was filtered through celite and concentrated to give 7.06 g of a red air-stable solid. The desired *(R,R)*-ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)titanium *(R)*-1,1′-binaphth-2,2′-diolate was separated by flash chromatography under nitrogen on alumina using 1:1 methylene chloride/hexanes.

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(25) Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501.
(26) Collins, S.; Kuntz, B. A.; Hong, Y. *J. Org. Chem.* **1989**, *54*, 4154.

A red solid (3.5 g) was obtained which was recrystallized by dissolving it in methylene chloride and adding hexanes until crystals began to form. The mixture was allowed to stand until no further crystallization was apparent. Removal of the solvent yielded 2.83 g (73% yield based on one enantiomer) of product as dark red air-stable crystals. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.78 (d, 2H), 7.75 (d, 2H), 7.16 (t, 2H), 7.10 (d, 2H), 7.01 (t, 2H), 6.88 (d, 2H), 5.56 (m, 4H), 3.33 (m, 2H), 3.09 (m, 2H), 2.56 (m, 4H), 1.71 (m, 6H), 1.49 (m, 4H), 1.20 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.6, 137.13, 134,72, 132.88, 128.61, 128.30, 127.61, 126.94, 125.43, 125.09, 121.79, 121.42, 117.75, 116.20, 106.42, 27.44, 23.91, 23.17, 22.09, 21.81. $[\alpha]_{578} = -3690° \pm 44$ (c = 0.45 mg/mL in $CHCl_3$); lit.[7] $[\alpha]_{578} = +3100°$ (*(S,S,S)* diastereomer, c = 0.040 mg/mL in $CHCl_3$); lit.[26] $[\alpha]_{578} = +4085°$ (*(S,S,S)* diastereomer, c = 0.045 mg/mL in $CHCl_3$).

General Procedure for the Preparation of Acyclic Imines.[27] The ketone (1 equiv) and the appropriate amine (1 equiv) were dissolved in dry toluene (50–100 mL) in a round bottom flask under nitrogen. The flask was equipped with a reflux condenser and a Dean-Stark trap and the mixture was heated to reflux for 2–5 days after which the solvent was removed *in vacuo*. The imine products were purified by distillation or recrystallization. The ratio of geometric isomers was determined by ^{1}H NMR spectrometry.

***N*-(α-Methylbenzylidene)benzylamine.**[28] The general procedure was followed using benzylamine (10.9 mL, 100 mmol) and acetophenone (11.7 mL, 100 mmol). The compound was purified by distillation (132 °C, 0.08 mmHg) to afford 10.4 g (50% yield) of the desired product, which solidified on standing, as a 17:1 mixture of geometric isomers. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): major isomer δ 7.85 (m, 2H), 7.45–7.15 (m, 8H), 4.75 (s, 2H), 2.35 (s, 3H); minor isomer δ 4.42 (s, 2H), 2.39 (m 3H); aromatic resonances are obscured by those of the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): both isomers, δ 156.41, 141.62, 141.13, 130.13, 129.15, 128.92, 128.88, 128.81, 128.75, 128,24, 127.30, 127.25, 127.12, 127.08, 126.57, 57.79, 56.24, 18.33, some resonances of the minor isomer are obscured. IR (neat): 3083, 3023, 2857, 1631, 1602, 1576, 1493, 1447, 1376, 1349, 1301, 1283, 1268, 1044, 1025, 759, 730, 695, 689 cm^{-1}. Mp: 41.0–42.7 °C.

***N*-(1-Cyclopropylethylidene)benzylamine.** The general procedure was followed using benzylamine (2.73 mL, 25 mmol) and acetylcyclopropane (2.48 mL, 25 mmol). The compound was purified by distillation (73 °C, 0.1 mmHg) to afford 2.61 g (60% yield) of the desired product as a 7.5:1 mixture of geometric isomers. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): major isomer δ 7.34–7.19 (m, 5H), 4.47 (s, 2H), 1.79 (s, 3H), 1.8–1.65 (m, 1H), 0.88–0.71 (m, 4H); minor isomer δ 4.69 (s, 2H), 1.9–1.8 (m, 1H), all other resonances are obscured. ^{13}C NMR (75 MHz, $CDCl_3$): both isomers δ 170.9, 140.6, 128.2, 128.1, 127.6, 127.4, 126.3, 54.6, 54.3, 22.0, 20.5, 15.8, 12.7, 6.5, 5.7. IR (neat): 3085, 3062, 3025, 3003, 2863, 1494, 1451, 1385, 1369, 1345, 1300, 1264, 1210, 1176, 1116, 1026, 956, 892, 818, 731, 696 cm^{-1}. HRMS: calcd for $C_{12}H_{15}N$ 173.1204, found 173.1205.

***N*-(α-Methyl-4-methoxybenzylidene)benzylamine.**[29] The general procedure was followed using benzylamine (5.5 mL, 50 mmol) and 4-methoxyacetophenone (7.5 g, 50 mmol). The compound was purified by recrystallization from pentane to afford 2.51 g (18% yield) of the desired product as a 17:1 mixture of geometric isomers. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): major isomer δ 7.75 (d, 2H), 7.45 (d, 2H), 7.36–7.25 (m, 3H), 6.92 (d, 2H), 4.73 (s, 2H), 3.84 (s, 3H), 2.30 (s, 3H); minor isomer δ 7.15 (d, 2H), 4.50 (s, 2H), 2.39 (m 3H); some resonances are obscured by those of the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): major δ 164.8, 160.8, 140.7, 133.7, 128.2, 128.1, 127.6, 113.3, 55.4, 55.1, 15.3; minor δ 146.8, 131.8, 113.9, 29.5, 12.3; some resonances of the minor isomer are obscured. IR ($CDCl_3$): 3064, 3029, 2959, 2935, 2090, 2838, 2053, 1948, 1863, 1605, 1576, 1509, 1453, 1415, 1368, 1347, 1306, 1252, 1174, 1114, 1074, 1031, 928, 920, 910, 900, 893, 834, 804, 747, 734 cm^{-1}. Mp: 61.4–63.3 °C.

***N*-[1-(2-Furyl)ethylidene]benzylamine.** The general procedure was followed using benzylamine (5.5 mL, 50 mmol) and 2-acetylfuran (5.5 mL, 50 mmol). The compound was purified by distillation (106 °C, 0.22 mmHg) to afford 4.8 g (48% yield) of the desired product, which solidified on cooling (−10 °C), as a 10:1 mixture of geometric isomers. ^{1}H NMR (250 MHz, $CDCl_3$, TMS): major isomer δ 7.50 (d, 1H), 7.4–7.2 (m, 5H), 6.82 (d, 1H), 6.45 (dd, 1H), 4.75 (s, 2H), 2.25 (s, 3H); minor isomer δ 7.55 (d, 1H), 6.8 (d, 1H), 6.52 (dd, 1H), 4.85 (s, 2H), 2.48 (m, 3H); all aromatic resonances are obscured by those of the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): both isomers δ 157.76, 154.71, 144.49, 140.50, 128.94, 128.89, 128.23, 128.26, 127.10, 111.89, 111.83, 111.67, 55.82, 15.43; some resonances of the minor isomer are obscured. IR (neat): 3150, 3030, 2876, 2866, 1635, 1627, 1623, 1616, 1602, 1581, 1495, 1493, 1490, 1488, 1450, 1402, 1394, 1351, 1294, 1171, 1046, 1022, 765, 743, 734, 698 cm^{-1}. HRMS: calcd for $C_{13}H_{13}NO$ 199.0997, found 199.0995.

***N*-(1-Methylpentylidene)benzylamine.**[30] The general procedure was followed using benzylamine (3.25 mL, 30 mmol) and 2-hexanone (3.7 mL, 30 mmol). The product was purified by distillation (67 °C, 0.05 mmHg) to afford 3.64 g (64% yield) of a clear oil as a 3.3:1 mixture of geometric isomers. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): major isomer δ 7.31 (s, 2H), 7.30 (s, 2H), 7.25–7.21 (m, 1H), 4.47 (s, 2H), 2.32 (t, 2H), 1.89 (s, 3H), 1.60–1.54 (m, 2H), 1.39–1.31 (m, 2H), 0.92 (t, 3H); minor isomer δ 4.50 (s, 2H), 2.31 (t, 2H), 2.07 (m, 3H), 0.93 (t, 3H); all other resonances are obscured by those of the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): both isomers δ 171.33, 140.56, 128.34, 128.29, 127.74, 127.63, 126.46, 126.37, 55.06, 54.63, 42.61, 32.24, 28.74, 28.46, 22.92, 22.55, 17.48, 13.94, 13.83; some resonances of the minor isomer are obscured. IR (neat): 3063, 3027, 3000, 2956, 2930, 2871, 2861, 1660, 1495, 1466, 1452, 1434, 1420, 1376, 1367, 1347, 730, 696 cm^{-1}.

***N*-(1-Cyclohexylethylidene)benzylamine.** The general procedure was followed using benzylamine (2.18 mL, 20 mmol) and acetylcyclohexane (2.76 mL, 20 mmol). The reaction mixture was filtered through celite and concentrated to recover 3.7 g (85% yield) of a slightly yellow oil as a 11:1 mixture of geometric isomers. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): major isomer δ 7.33 (s, 2H), 7.31 (s, 2H), 7.26–7.20 (m, 1H), 4.50 (s, 2H), 2.35–2.0 (m, 1H), 1.86 (s, 3H), 1.86–1.77 (m, 5H), 1.44–1.22 (m, 5H); minor isomer δ 4.57 (s, 2H), 2.01 (m, 3H); all other resonances are obscured by those of the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): both isomers δ 174.65, 140.72, 128.32, 128.23, 127.69, 127.47, 126.40, 126.26, 54.64, 50.55, 30.20, 29.65, 26.16, 25.98, 15.70, 6.76; some resonances of the minor isomer are obscured. IR (neat): 3062, 3027, 2927–2851, 1657, 1494, 1450, 730, 696 cm^{-1}. HRMS: calcd for $C_{15}H_{21}N$ 215.1674, found 215.1675.

***N*-(1-Cyclohexylethylidene)-4-methoxybenzylamine.** The general procedure was followed using 4-methoxybenzylamine (2.61 mL, 20 mmol) and acetylcyclohexane (2.76 mL, 20 mmol). The reaction mixture concentrated to recover 5.64 g of a slightly yellow oil. The material was purified by vacuum distillation (142 °C, 0.011 mmHg) to afford 3.12 g (64% yield) of desired product as a 14:1 mixture of geometric isomers. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): major isomer δ 7.22 (d, 2H, J = 8.4 Hz), 6.86 (d, 2H, J = 8.4 Hz), 4.42 (s, 2H), 3.79 (s, 3H), 2.30–2.18 (m, 1H), 1.84 (s, 3H), 1.86–1.62 (m, 5H), 1.45–1.15 (m, 5H); minor isomer δ 4.5 (s, 2H), 2.75 (m, 1H), 1.99 (m, 3H); all other resonances are obscured by those of the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): both isomers δ 174.1, 158.0, 132.7, 128.3, 113.6, 113.5, 54.9, 53.9, 51.4, 50.3, 40.3, 30.0, 29.5, 26.0, 25.8, 21.7, 15.4; some resonances of the minor isomer are obscured. IR (neat): 2944, 2925, 2849, 2666, 2062, 1872, 1654, 1611, 1584, 1511, 1461, 1447, 1365, 1345, 1299, 1245, 1170, 1105, 1037, 910, 888, 815, 778, 752, 725, 702, 684, 668, 625 cm^{-1}. HRMS: calcd for $C_{16}H_{23}NO$ 245.17795, found 215.1780.

***N*-(1-Cyclohexylethylidene)propylamine.** A steel autoclave was charged with propylamine (12.5 mL, 150 mmol) and acetylcyclohexane (4.13 mL, 30 mmol). Ether (100 mL) was added along with 10 g of 3 Å molecular sieves. The vessel was sealed and heated to 100 °C for 48 h. The vessel was opened and the reaction mixture was filtered through celite and concentrated to recover 5.4 g of a slightly yellow oil. Fractional vacuum distillation (134 °C, 20 mmHg, using base washed glassware) afforded 2.61 g (52% yield) of desired product as a 9:1 mixture of geometric isomers. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): major isomer δ 3.2–3.15 (t, 2H), 2.21–2.10 (m, 1H), 1.78–1.54 (m, 7H), 1.74 (s, 3H), 1.48–1.17 (m, 5H), 0.94–0.89 (t, 3H); minor isomer δ 3.29–3.21 (t, 2H), 2.69–2.59 (m, 1H), 1.94 (s, 3H); all other resonances are obscured by those of the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): both isomers δ 172.9, 52.9, 51.7, 50.6, 40.2, 30.2, 29.8, 26.2, 24.2, 24.0, 23.6, 14.8, 12.0; some resonances of the minor isomer are obscured. IR (neat): 2927, 2852, 1659, 1449, 1374, 1306, 1243, 1198, 1065, 889 cm^{-1}. HRMS: calcd for $C_{11}H_{21}N$ 167.1674, found 167.1675.

***N*-(1-Cyclohexylethylidene)methylamine.** A steel autoclave was charged with methylamine (3.9 g, 127 mmol, condensed into a tared flask cooled with dry ice/acetone) and acetylcyclohexane (3.5 mL, 25 mmol). Ether (75 mL) was added along with 10 g of 3 A molecular sieves. The vessel was sealed and heated to 110 °C for 24 h. The vessel was opened, and the reaction mixture was filtered through celite and concentrated to recover

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a yellow oil. Fractional vacuum distillation (106 °C, 20 mmHg, using base washed glassware) afforded 2.01 g (59% yield) of desired product as a 11:1 mixture of geometric isomers. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): major isomer δ 3.07 (s, 3H), 2.12 (m, 1H), 1.85–1.6 (m, 8H), 1.40–1.10 (m, 5H); minor isomer 3.15 (s, 3H), 1.9 (s, 1H); all other resonances are obscured by those of the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): both isomers δ 175.3, 50.3, 38.4, 30.4, 29.3, 28.3, 26.2, 26.1, 25.9, 15.1; some resonances of the minor isomer are obscured. IR (neat): 2924, 2850, 2665, 1709, 1660, 1447, 1395, 1359, 1305, 1292, 1205, 1143, 1115, 1095, 955, 888, 855, 765, 745, 635, 619, 605 cm^{-1}. HRMS: calcd for $C_9H_{17}N$ 139.1361, found 139.1362.

N-(1,2-Dimethypropylidene)benzylamine.[31] Benzylamine (2.18 mL, 20 mmol) and 3-methyl-2-butanone (2.1 mL, 20 mmol) were dissolved in benzene under nitrogen containing 10 g of 3 A molecular sieves. The mixture was heated to reflux for 12 h. The solvent was removed *in vacuo*. The product was purified by distillation (73 °C, 0.26 mmHg) to afford 2.39 g (68% yield) of a clear oil as a 13:1 mixture of geometric isomers. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): major isomer δ 7.32 (s, 2H), 7.31 (s, 2H), 7.23–7.21 (m, 1H), 4.48 (s, 2H), 2.57 (m 1H), 1.84 (s, 3H), 1.12 (d, 6H); minor isomer δ 4.57 (s, 2H), 3.10 (m, 1H), 2.0 (m, 3H), 1.8 (d, 6H); all other resonances are obscured by those of the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): both isomers δ 175.25, 140.72, 128.39, 128.30, 127.73, 127.51, 126.35, 54.66, 40.21, 19.88, 14.98; some resonances of the minor isomer are obscured. IR (neat): 3027, 2965, 2870, 1661, 1495, 1464, 1452, 1365, 730, 696 cm^{-1}.

N-[1-(2-Naphthyl)ethylidene]benzylamine. The general procedure was followed using benzylamine (10.9 mL, 100 mmol) and 2-acetonaphthone (11.7 mL, 100 mmol). The compound was purified by recrystallization from toluene/hexanes to afford 3.74 g (71% yield) of the desired product as a 44:1 mixture of geometric isomers. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): major isomer δ 8.2 (s, 1H), 8.15 (dd, 1H), 7.89 (m, 1H), 7.82 (m, 2H), 7.5–7.4 (m, 4H), 4.8 (s, 2H), 2.4 (s 3H); minor isomer δ 4.49 (s, 2H), 2.73 (s, 3H); all other resonances are obscured by those of the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): (minor isomer not detected) δ 166.19, 141.08, 138.82, 134.56, 133.49, 129.24, 128.92, 128.30, 128.23, 128.09, 127.16, 127.09, 127.06, 126.63, 124.85, 56.33, 16.22. IR ($CHCl_3$): 3062, 3024, 3013, 2965, 1627, 1495, 1452, 1433, 1372, 1349, 1289, 1228, 1194, 1130, 1028, 892, 860, 824, 742, 732, 725, 698, 674, 665 cm^{-1}. HRMS: calcd for $C_{19}H_{17}N$ 259.1361, found 259.1360. Mp: 107.5–109.8 °C.

N-(1,5-Dimethylhex-5-enylidene)benzylamine. The general procedure was followed using benzylamine (2.18 mL, 20 mmol) and 6-methyl-5-hepten-2-one (2.95 mL, 20 mmol). The product was purified by distillation (107 °C, 0.25 mmHg) to afford 2.66 g (62% yield) of a yellow oil as a 3:1 mixture of geometric isomers. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): major isomer δ 7.31 (s, 2H), 7.30 (s, 2H), 7.25–7.21 (m, 1H), 5.14 (m, 1H), 4.48 (s, 2H), 2.40–2.25 (m, 4H), 1.89 (s, 3H), 1.68 (s, 3H), 1.61 (s, 3H); minor isomer δ 4.51 (s, 2H), 2.25–2.18 (m, 2H), 2.08 (m, 3H); all other resonances are obscured by those of the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): both isomers δ 170.80, 140.52, 131.01, 128.34, 128.27, 127.75, 127.82, 126.46, 126.35, 123.68, 55.05, 42.68, 25.87, 25.17, 17.64; some resonances of the minor isomer are obscured. IR (neat): 3085, 3062, 3027, 2966, 2856, 1659, 1495, 1452, 1437, 1419, 1375, 1368, 1347, 1028, 730, 696 cm^{-1}. HRMS: calcd for $C_{15}H_{21}N$ 215.1674, found 215.1672.

2-Phenyl-1-pyrroline. This compound was prepared by the method of Sorgi[32] from *N*-vinylpyrrolidinone (26.7 mL, 250 mmol) and methyl benzoate (31.1 mL, 250 mmol). Distillation (0.5 mmHg, 95 °C) afforded 12.51 g (34% yield) of the desired 2-phenyl-1-pyrroline which solidified on standing. ^{1}H NMR (300 MHz, $CDCl_3$, TMS), δ 7.85–7.81 (m, 2H), 7.42–7.37 (m, 3H), 4.09–4.03 (tt, 2H), 2.97–2.90 (tt, 2H), 2.07–1.97 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 173.16, 134.65, 130.32, 128.33, 127.53, 61.53, 34.88, 22.67. IR (neat): 3058, 3029, 2961–2859, 1615, 1574, 1495, 1446, 1340, 1046, 1026, 761, 693 cm^{-1}.

2-Phenyl-3,4,5,6-tetrahydropyridine. The procedure of Gallulo[33] was followed using 5-chlorovaleronitrile (3.38 mL, 30 mmol) and phenyllithium (18.3 mL, 33 mmol, 1.8 M in 7:3 cyclohexane/diethyl ether). The crude product was purified by distillation (109 °C, 0.8 mmHg) to afford 1.79 g (37% yield) of the desired material. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.76–7.70 (m, 2H), 7.36–7.31 (m, 3H), 3.84–3.77 (m, 2H), 2.62–2.54 (m, 2H), 1.83–1.74 (m, 2H), 1.74–1.60 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 165.26, 140.11, 129.25, 127.99, 125.69, 49.77, 26.81, 21.74, 19.62. IR (neat): 3082, 3056, 3034, 3024, 2933, 2844, 1635, 1577, 1446, 1358, 1352, 1330, 1237, 1062, 763, 743, 693 cm^{-1}.

2-Phenyl-4,5,6,7-tetrahydro-3*H*-azepine.[34] The method of Bielawski[35] was used to prepare 2-methyl-4,5,6,7-tetrahydro-3*H*-azepine from *N*-[(*E*)-2-phenylethenyl]hexahydroazepin-2-one[36] (10.3 g, 47 mmol) and phenyllithium (36 mL, 57 mmol, 1.0 M in 7:3 cyclohexane/ether). The crude product (7.75 g) was obtained as a mixture of the cyclic imine and the amino ketone as reported. The material was placed in a round bottom flask containing 10 mg of *p*-toluenesulfonic acid and 100 mL toluene. The flask was fitted with a reflux condenser and a Dean-Stark trap, and the system was purged with nitrogen. The mixture was refluxed for 15 h at which point an ^{1}H NMR spectrum showed that the product mixture contained mainly the desired imine. After removal of the solvent, fractional distillation (6 mmHg, 135 °C) afforded 2.90 g (37% yield) of the desired product. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.8–7.65 (m, 2H), 7.4–7.3 (m, 3H), 3.86–3.8 (m, 2H), 2.9–2.82 (m, 2H), 1.9–1.82 (m, 2H), 1.69–1.58 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.1, 141.3, 129.0, 128.0, 126.3, 52.3, 31.3, 30.7, 25.9, 23.5. IR (neat): 3080, 3054, 3030, 2921, 2848, 2682, 1953, 1890, 1809, 1631, 1576, 1492, 1469, 1445, 1362, 1343, 1334, 1281, 1257, 1218, 1195, 1177, 1146, 1097, 1078, 1053, 1026, 1000, 977, 917, 882, 855, 839, 766, 720, 694 cm^{-1}.

6,7-Dimethoxy-1-methyl-3,4-dihydroisoquinoline. This compound was prepared by the method of Brossi.[37] Yield: 72%. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 6.98 (s, 1H), 6.68 (s, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.65–3.60 (m, 2H), 2.65–2.60 (m, 2H), 2.36–2.35 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 163.49, 150.86, 147.48, 131,13, 122,53, 110.30, 109.19, 56.25, 55.93, 47.03, 25.75, 23.17. IR ($CHCl_3$): 3026, 3020, 3011, 2940, 2837, 1628, 1605, 1573, 1513, 1464, 1376, 1352, 1323, 1287, 1267, 1234, 1156, 1062, 861, 808, 779, 762, 742, 740, 737. Mp: 102.3–104.0 °C.

2-(*N*-Benzylpyrrol-2-yl)-1-pyrroline. This compound was provided by Professor Satoru Masamune and Dr. Yaping Hong.

5-Hexyl-1-pyrroline.[34] In a 250 mL Schlenk flask under argon magnesium turnings (2.4 g, 100 mmol) and I_2 (10 mg) were placed in 25 mL of diethyl ether. A solution of 1-iodohexane (7.4 mL, 50 mmol), in 25 mL of diethyl ether was added dropwise via cannula, and the mixture was allowed to stir at room temperature for 1 h. The resulting solution was the transferred via cannula (with filtering) to a two neck round bottom flask fitted with a reflux condenser. A solution of 4-chlorobutyronitrile (4.5 mL, 50 mmol) in 50 mL of ether was added dropwise via cannula and the reaction mixture was heated to reflux for 1.5 h. The flask was then fitted with a dropping funnel and distillation apparatus. While distilling off the ether, toluene was added through the dropping funnel to keep the volume in the reaction flask constant. When the temperature at the distillation head reached 110 °C the mixture was cooled to room temperature and washed with water (50 mL). The aqueous layer was extracted with ether, and the ether and toluene layers were combined and extracted with 1 M HCl (3 × 50 mL). The acid layers were neutralized with KOH and extracted with ether (4 × 75 mL). The ether layers were dried over magnesium sulfate and concentrated. The crude product was purified by Kugelrohr distillation to yield 2.3 g (30%) of the desired product. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 3.82–3.75 (tt, 2H), 2.47–2.41 (tt, 2H), 2.34–2.29 (t, 2H), 1.89–1.79 (m, 2H), 1.62–1.52 (m, 2H), 1.35–1.26 (m, 6H), 0.91–0.85 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 177.10, 59.68, 36.05, 32.72, 30.58, 28.15, 25.30, 21.51, 21.48, 12.94. IR (neat): 2955–2860, 1643, 1465, 1456, 1436, 1430, 1419, 1378, 1325, 1301, 1013, 957 cm^{-1}.

2-[1-(4-Methylpent-4-enyl)]-1-pyrroline. A dry flask under an argon atmosphere was charged with a magnetic stir bar, 100 mL of THF, and diisopropylamine (3.0 mL, 21 mmol). The solution was cooled to −5 °C and a solution of *n*-butyllithium (8.1 mL, 2.7 M in hexanes, 22 mmol) was added via syringe. The mixture was allowed to stir for 30 min and was cooled to −78 °C. 2-Methyl-1-pyrroline (1.89 mL, 20 mmol) was added, and the resulting yellow mixture was stirred for 30 min. 1-Bromo-3-methylbut-2-ene (2.76 mL, 24 mmol) was added dropwise via syringe. The solution was kept at −78 °C for 1 h and then warmed to room temperature and diluted with 100 mL of ether. The organic solution was extracted with three 25 mL portions of 1 M HCl. The combined aqueous layers were cooled to 0 °C, made basic with solid NaOH, and extracted

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with four 50 mL portions of methylene chloride. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Flash chromatography (silica, 95:5 hexane/triethylamine) afforded 2.13 g (71% yield) of the desired 2-[1-(4-methylpent-4-enyl)]-1-pyrroline as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 5.16–5.1 (m, 1H), 3.83–3.76 (m, 2H), 2.50–2.40 (m, 2H), 2.37–2.23 (m, 4H), 1.9–1.8 (m, 2H), 1.68 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.8, 131.9, 123.3, 60.6, 37.1, 33.7, 25.4, 24.8, 22.4, 17.4. IR (neat): 3268, 2918, 2864, 2729, 1644, 1449, 1431, 1326, 1339, 1303, 1223, 1130, 1104, 1056, 1014, 984, 949, 832 cm^{-1}. HRMS: calcd for $C_{10}H_{17}N$ 151.1361, found 151.1360.

(*E*)-2-[1-[6-(Trimethylsilyl)hex-5-enyl]]-1-pyrroline. A dry flask under an argon atmosphere was charged with a magnetic stir bar, 100 mL of THF, and diisopropylamine (2.2 mL 15.6 mmol). The solution was cooled to –5 °C, and a solution of *n*-butyllithium (10 mL, 1.56 M in hexanes, 15.6 mmol) was added via syringe. The mixture was allowed to stir for 30 min and was cooled to –78 °C. 2-Methyl-1-pyrroline (1.36 mL, 14.4 mmol) was added and the resulting yellow mixture was stirred for 30 min. *(E)*-5-Iodo-1-(trimethylsilyl)-1-pentene[38] (3.37 g, 90% pure, 12 mmol) was added dropwise via syringe. The solution was kept at –78 °C for 30 min and then warmed to room temperature and diluted with 50 mL of ether/20 mL of water. The layers were separated and the aqueous layer was extracted with two 50 mL portions of methylene chloride. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo* to provide 2.85 g of a yellow oil. Flash chromatography (silica, 97:3 hexane/triethylamine) afforded 2.22 g (83% yield) of the desired *(E)*-2-[1-[6-(trimethylsilyl)hex-5-enyl]]-1-pyrroline as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 6.1–5.95 (dt, J_1 = 18 Hz, J_2 = 12 Hz, 1H), 5.67–5.58 (d, J = 18 Hz, 1H), 3.83–3.76 (m, 2H), 2.47–2.41 (m, 2H), 2.35–2.3 (t, J = 6 Hz, 2H), 2.16–2.09 (m, 1H), 1.90–1.80 (m, 2H), 1.63–1.55 (m, 2H), 1.45–1.38 (m, 2H), 0.03 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.9, 146.5, 129.6, 60.7, 37.1, 36.4, 33.7, 28.6, 25.9, 22.6, –1.1. IR (neat): 2952, 2863, 1644, 1616, 1461, 1431, 1301, 1246, 987, 864, 837, 767, 730, 703, 613 cm^{-1}. HRMS: calcd for $C_{13}H_{25}NSi$ 223.1756, found 223.1757.

2-[1-(Hex-5-enyl)]-1-pyrroline. A dry flask under an argon atmosphere was charged with a magnetic stir bar, 100 mL of THF, and diisopropylamine (3.1 mL, 22 mmol). The solution was cooled to –5 °C, and a solution of *n*-butyllithium (13.3 mL, 1.7 M in hexanes, 22 mmol) was added via syringe. The mixture was allowed to stir for 30 min and then cooled to –78 °C. 2-Methyl-1-pyrroline (1.89 mL, 20 mmol) was added, and the resulting yellow mixture was stirred for 30 min. 1-Iodo-5-pentene[39] (4.31 g, 22 mmol) was added dropwise via syringe, and the mixture was stirred at –78 °C for 1 h. The solution was warmed to room temperature, quenched with 20 mL of saturated aqueous NH_4Cl and diluted with 100 mL of ether. The layers were separated and the aqueous layer was extracted with 100 mL of ether. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Flash chromatography (silica, 97:3 pentane/diethylamine) afforded 2.15 g (71% yield) of the desired 2-[1-(hex-5-enyl)]-1-pyrroline as a yellow oil. ^1H NMR (250 MHz, $CDCl_3$, TMS): δ 5.9–5.72 (m, 1H), 5.08–4.92 (m, 2H), 3.85–3.75 (m, 2H), 2.5–2.4 (t, J = 7.8 Hz, 2H), 2.39–2.3 (t, J = 7.2 Hz, 2H), 2.15–2.04 (m, 2H), 1.95–1.81 (m, 2H), 1.69–1.57 (m, 2H), 1.5–1.38 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.2, 137.9, 113.8, 60.3, 36.7, 33.1, 33.0, 28.3, 25.4, 22.1. IR (neat): 3075, 2928, 2862, 1821, 1641, 1461, 1449, 1430, 1301, 1213, 1147, 992, 968, 909 cm^{-1}. HRMS: calcd for $[M-H]^+$ $C_{10}H_{16}N$ 150.1283, found 150.1282.

2-[1-[4-(*tert*-Butyldimethylsiloxy)butyl]]-1-pyrroline. A dry flask under nitrogen was charged with 50 mL of DMF, *tert*-butyldimethylchlorosilane (6.0 g, 40 mmol), and imidazole (3.3 g, 48 mmol). 3-Bromopropanol (3.6 mL, 40 mmol) was added via syringe, and the mixture was allowed to stir overnight. The solution was diluted with 100 mL of ether, washed with three 50 mL portions of water, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was dissolved in 150 mL of acetone and NaI (30 g, 200 mmol) was added. The mixture was heated to reflux under a nitrogen atmosphere for 48 h. The acetone was removed by rotary evaporation; the residue was diluted with 100 mL of ether, washed with two 50 mL of portions water, and dried over $MgSO_4$. Removal of solvent afforded 10.2 g crude 1-(*tert*-butyldimethylsiloxy)-3-iodopropane[40] (86% pure, 70% crude yield). ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 3.66 (t, 2H), 3.27 (t, 2H), 1.99 (m, 2H), 0.89 (s, 9H), 0.07 (s, 6H).

A dry flask under an argon atmosphere was charged with a magnetic stir bar, 100 mL of THF, and diisopropylamine (2.9 mL, 21 mmol). The solution was cooled to –5 °C and a solution of *n*-butyllithium (7.4 mL, 2.7 M in hexanes, 20 mmol) was added via syringe. The mixture was allowed to stir for 30 min and was cooled to –78 °C. 2-Methyl-1-pyrroline (1.80 mL, 19 mmol) was added and the resulting yellow solution was stirred for 30 min. 1-(*tert*-Butyldimethylsiloxy)-3-iodopropane (6.9 g, 23 mmol) was added dropwise via syringe. After 1 h the mixture was quenched with 20 mL of saturated aqueous NH_4Cl and diluted with 100 mL of ether. The layers were separated and the aqueous layer was extracted with 50 mL of ether. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Flash chromatography (silica, 95:5 hexane/triethylamine) afforded 2.53 g (55% yield) of the desired 2-[1-[4-(*tert*-butyldimethylsiloxy)butyl]]-1-pyrroline as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 3.81–3.73 (m, 2H), 3.62–3.58 (t, J = 6.1 Hz, 2H), 2.48–2.39 (t, J = 7.8 Hz, 2H), 2.38–2.3 (t, J = 7.2 Hz, 2H), 1.89–1.78 (m, 2H), 1.68–1.49 (m, 4H), 0.86 (s, 9H), 0.02 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.1, 62.8, 60.7, 36.9, 33.5, 32.6, 25.9, 22.7, 22.5, 18.3, –5.3. IR (neat): 2954, 2857, 2737, 2709, 1643, 1471, 1462, 1431, 1387, 1360, 1343, 1301, 1255, 1188, 1102, 1040, 1006, 956, 939, 909, 894, 812, 775, 715, 662 cm^{-1}. HRMS: calcd for $C_{14}H_{29}NOSi$ 255.2018, found 255.2017.

2-[4-(1,3-Dioxolan-2-yl)butyl]-1-pyrroline. A dry round bottom flask under a nitrogen atmosphere was charged with a magnetic stir bar, 80 mL of acetone, NaI (24 g, 100 mmol), and $CaCO_3$ (20 g, 200 mmol). The mixture was stirred for 30 min and 2-(2-bromoethyl)-1,3-dioxolane (4.7 mL, 40 mmol) was added via syringe. The flask was fitted with a reflux condenser and the mixture was refluxed for 14 h. The acetone was removed by rotary evaporation, and the residue was diluted with 200 mL of ether/100 mL of water. The layers were separated, and the aqueous solution was extracted with 100 mL of ether. The combined organic portions were washed with 25 mL of saturated aqueous Na_2SO_3, and 25 mL of saturated brine, then dried over Na_2SO_4, and concentrated *in vacuo*. Flash chromatography (deactivated silica, see general considerations for preparation, 35:65 methylene chloride/pentane) afforded 6.52 g (71% yield) of the desired 2-(2-iodoethyl)-1,3-dioxolane[41] as a clear oil. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 4.75 (t, 1H), 4.0–3.82 (m, 4H), 3.21 (t, 2H), 2.25–2.19 (m, 2H).

A dry flask under an argon atmosphere was charged with a magnetic stir bar, 50 mL of THF, and diisopropylamine (3.1 mL, 22 mmol). The solution was cooled to –5 °C, and a solution of *n*-butyllithium (13.3 mL, 1.7 M in hexanes, 22 mmol) was added via syringe. The mixture was allowed to stir for 30 min and was cooled to -78 °C. 2-Methyl-1-pyrroline (1.89 mL, 20 mmol) was added and the resulting yellow mixture was stirred for 30 min. 2-(2-Iodoethyl)-1,3-dioxolane (4.31 g, 22 mmol) was added dropwise via syringe and the mixture was stirred at –78 °C for 1 h. The mixture was warmed to room temperature and washed with 50 mL of saturated brine. The aqueous layer was extracted with five 75 mL portions of ether (the product is somewhat soluble in aqueous media). The combined organic portions were dried over Na_2SO_4 and concentrated *in vacuo*. Flash chromatography (deactivated silica, see general considerations for preparation, first eluting with 1:1 methylene chloride/hexane then eluting with 5:47:48 triethylamine/methylene chloride/hexane) afforded 2.0 g (55% yield) of the desired 2-[4-(1,3-dioxolan-2-yl)butyl]-1-pyrroline as a clear oil. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 4.88–4.84 (t, J = 4.8 Hz, 1H), 3.99–3.89 (m, 2H), 3.86–3.74 (m, 4H), 2.48–2.42 (t, J = 7.8 Hz, 4H), 2.42–2.36 (t, J = 7.2 Hz, 2H), 1.90–1.8 (m, 2H), 1.8–1.65 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.6, 104.2, 64.9, 60.9, 37.2, 33.68, 33.5, 22.7, 20.9. IR (neat): 2952, 2868, 1642, 1459, 1431, 1410, 1301, 1213, 1139, 1028, 974, 942, 812 cm^{-1}. HRMS: calcd for $[M-H]^+$ $C_{10}H_{26}NO_2$ 182.1181, found 182.1178.

2-[1-(7-hydroxyheptyl)]-1-pyrroline. A dry flask under nitrogen was charged with 50 mL of DMF, *tert*-butyldimethylchlorosilane (6.0 g, 40 mmol), and imidazole (3.3 g, 48 mmol). 6-Chlorohexanol (3.75 mL, 40 mmol) was added via syringe, and the mixture was allowed to stir for 40 h. The solution was diluted with 200 mL of ether and washed with three 75 mL portions of water. The aqueous layer was extracted with 100 mL of ether, and the combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was dissolved in 150 mL of acetone and NaI (30 g, 200 mmol) was added. The mixture was heated to reflux under a nitrogen atmosphere for 15 h. The acetone was removed by rotary evaporation and the residue was diluted with 200 mL of ether/100 mL of water. The layers were separated and the organic layer was washed with 50 mL of saturated Na_2SO_3 and 50 mL of saturated brine. The organic portion was dried over $MgSO_4$ and concentrated *in vacuo* to

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(39) Cuny, G. C.; Buchwald, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 2066.
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afford 10.1 g of crude product. Kugelrohr distillation afforded 8.82 g (73% yield) of 1-(*tert*-butyldimethylsiloxy)-6-iodohexane.[42] ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 3.62–3.57 (t, 2H), 3.21–3.16 (t, 2H), 1.85–1.78 (m, 2H), 1.57–1.47 (m, 2H), 1.45–1.32 (m, 4H), 0.89 (s, 9H), 0.07 (s, 6H).

A dry flask under an argon atmosphere was charged with a magnetic stir bar, 50 mL of THF, and diisopropylamine (4.3 mL, 31 mmol). The solution was cooled to –5 °C, and a solution of *n*-butyllithium (12.3 mL, 2.7 M in hexanes, 31 mmol) was added via syringe. The mixture was allowed to stir for 30 min and was cooled to -78 °C. 2-Methyl-1-pyrroline (2.43 mL, 25.7 mmol) was added and the resulting yellow solution was stirred for 30 min. 1-(*tert*-Butyldimethylsiloxy)-6-iodohexane (8.82 g, 25.7 mmol) was added dropwise via syringe. After 30 min the mixture was warmed to room temperature and diluted with 100 mL of ether/50 mL of water. The layers were separated, and the aqueous layer was extracted with 50 mL of ether. The combined organic layers were washed with 30 mL of saturated brine, dried over Na_2SO_4, and concentrated to afford 8.23 g of crude 2-[1-(7-*tert*-butyldimethylsiloxyheptyl)]-1-pyrroline. The material was dissolved in 100 mL of methanol and 2 mL concentrated HCl was added. The mixture was stirred for 20 min and made basic (to pH 9) with 30% NaOH. The methanol was removed by rotary evaporation; the residue was diluted with 100 mL of ether and washed with 30 mL of 1 M NaOH/saturated NaCl. The aqueous layer was extracted with three 50 mL portions of ether and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Distillation (130 °C, 0.1 mmHg) afforded 2.40 g (51% yield) of the desired 2-[1-(7-hydroxyheptyl)]-1-pyrroline as a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 3.8–3.76 (m, 2H), 3.65–3.60 (t, J = 6.6 Hz, 2H), 2.48–2.40 (t, J = 7.5 Hz, 2H), 2.36–2.28 (t, J = 7.8 Hz, 2H), 1.91–1.8 (m, 2H), 1.8–1.65 (bs, 1H), 1.63–1.48 (m, 4H), 1.39–1.3 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.6, 62.1, 60.45, 37.0, 33.5, 32.6, 29.3, 29.0, 26.2, 22.6, 22.3. IR (neat): 3274, 2927, 2856, 1643, 1463, 1429, 1330, 1303, 1214, 1134, 1060, 1016, 960, 724 cm^{-1}. HRMS: calcd for $[M - H]^+$ $C_{11}H_{20}NO$ 182.1545, found 182.1549.

(*Z*)-2-[1-(Non-6-enyl)]-1-pyrroline. A dry round bottom flask was charged with 100 mL of THF, triethylamine (5 mL, 39 mmol) and *(Z)*-5-octen-1-ol (3.85 g, 30 mmol). The flask was purged with argon and cooled to 0 °C. Freshly distilled methanesulfonyl chloride (2.8 mL, 36 mmol) was added via syringe, and the mixture was stirred for 2 h. The mixture was diluted with 100 mL of ether and filtered through Celite. The solvent was removed *in vacuo* to afford 5.27 g of the crude mesylate. The compound was dissolved in 100 mL of acetone under a nitrogen atmosphere and NaI (20 g, 50 mmol) was added. Diisopropylethylamine (0.5 mL) was added and the mixture was stirred at room temperature for 36 h. The solvent was removed *in vacuo* and residue was diluted with 200 mL of ether/100 mL of water. The layers were separated and the organic layer was washed with saturated brine. The solvent was removed *in vacuo* and Kugelrohr distillation afforded 4.70 g (66% yield) of *(Z)*-1-iodooct-5-ene. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 5.41–5.22 (m, 2H), 3.21–3.16 (t, 2H), 2.1–1.93 (m, 4H), 1.86–1.78 (m, 2H), 1.51–1.4 (m, 2H), 0.98–0.93 (t, 3H).

A dry flask under an argon atmosphere was charged with a magnetic stir bar, 100 mL of THF, and diisopropylamine (3.2 mL, 23.7 mmol). The solution was cooled to –5 °C, and a solution of *n*-butyllithium (13.9 mL, 1.7 M in hexanes, 23.7 mmol) was added via syringe. The mixture was allowed to stir for 30 min and then cooled to –78 °C. 2-Methyl-1-pyrroline (1.87 mL, 19.7 mmol) was added, and the resulting yellow mixture was stirred for 40 min. *(Z)*-1-Iodooct-5-ene (4.7 g, 19.7 mmol) was added dropwise via syringe, and the mixture was stirred at –78 °C for 1 h. The solution was warmed to room temperature and diluted with 100 mL of ether. The mixture was washed with 50 mL of water and then 50 mL of saturated brine. The layers were separated, and the aqueous layer was extracted with 100 mL of ether. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Kugelrohr distillation afforded 3.34 g (88% yield) of the desired *(Z)*-2-[1-(non-6-enyl)]-1-pyrroline as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 5.9–5.72 (m, 1H), 5.35–5.22 (m, 2H), 3.8–3.72 (m, 2H), 2.46–2.39 (t, J = 7.8 Hz, 2H), 2.31–2.27 (t, J = 7.2 Hz, 2H), 2.08–1.95 (m, 4H), 1.88–1.76 (m, 2H), 1.38–1.28 (m, 4H), 0.95–0.89 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.0, 131.4, 128.8, 60.7, 37.1, 33.2, 29.5, 29.1, 26.9, 26.2, 22.5, 20.5, 14.3. IR (neat): 3003, 2930, 2858, 1643, 1461, 1301, 1011, 967 cm^{-1}. HRMS: calcd for $[M - H]^+$ $C_{13}H_{22}N$ 192.1752, found 192.1752.

(42) Booth, P. M.; Broughton, H. B.; Ford, M. J.; Fox, C. M. J.; Ley, S. V.; Slawin, A. M. Z.; Williams, D. J.; Woodward, P. R. *Tetrahedron* **1989**, *45*, 7565.

Asymmetric Hydrogenation Reactions. General Procedure A (for Reactions Run at 80 psig). A dry Fisher-Porter bottle properly fitted with a pressure coupling closure complete with a gas inlet, pressure gauge, inlet valve and a pressure release valve was charged with *(R,R)*-ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)titanium *(R)*-1,1′-binaphth-2,2′-diolate and a magnetic stir bar. The system was evacuated and filled with hydrogen (5–10 psig). THF (10 mL) was added via high-pressure syringe. After the complex had dissolved, a solution of *n*-butyllithium (1.6 M in hexanes, 2 equiv) was added and the mixture was stirred for 2–3 min at which point it was a green color. Phenylsilane (2.5–3 equiv) was added and no color change was observed. A solution of the imine (20 equiv, in 1–2 mL THF) was added via syringe and the vessel was placed in an oil bath at the indicated temperature. The pressure was then adjusted to the specified value (**Caution**: an appropriate safety shield should be used), and the mixture was allowed to stir for the indicated time. When the reaction had reached completion (GC[43]), the mixture was cooled and carefully vented. The amine was isolated as described below.

General Procedure B (for Reactions Run at >80 psig). In a dry Schlenk flask under an argon atmosphere, *(R,R)*-ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)titanium *(R)*-1,1′-binaphth-2,2′-diolate was dissolved in THF (10 mL). A solution of *n*-butyllithium (1.6 M in hexanes, 2 equiv) was added and the mixture was allowed to stir for 5 min at which point it was a brown-green color. Phenylsilane (2.5–3.0 equiv) was added, and mixture immediately turned dark brown. The resulting solution was moved into a dry box and transferred into a Parr high-pressure autoclave containing a magnetic stir bar. The imine (20 equiv based on Ti) was added. The vessel was sealed and moved to a fume hood where it was charged with hydrogen (specified below) and placed in an oil bath at the indicated temperature. The reaction mixture was allowed to stir for the specified time under hydrogen pressure. The vessel was cooled to room temperature, carefully vented, and opened to air. The solvent was removed *in vacuo*. The amine was isolated as described below.

Determination of Enantiomeric Excesses. The enantiomeric excesses of the amines were determined by HPLC analysis of the amines or the corresponding amide derivatives (see below) using a Chiralcel OD column. HPLC chromatograms were compared with those of the racemic compounds. In some cases ee's were determined by GC analysis of the α-methoxy-α-(trifluoromethyl)phenylacetamides amides using a Cyclodex B column (J & W Scientific).

General Procedure for the Preparation of Amides. The amine (10–20 mg) was dissolved in $CDCl_3$ and triethylamine (1.5 equiv) was added. The appropriate acid halide or acid anhydride (1 equiv) was added and the reaction was monitored by ^{1}H NMR. Upon completion the mixture was filtered through a plug of silica and the amide was recovered by removal of solvent.

General Procedure for the Preparation of (*S*)-α-Methoxy-α-(trifluoromethyl)phenylacetamides. The amine (0.08 mmol) was dissolved in $CDCl_3$ (700 μL) in an NMR tube. Triethylamine (15 μL, 0.12 mmol) was added followed by *(S)*-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride[44] (17.2 μL, 0.089 mmol). The mixture was shaken briefly and then allowed to stand for 30 min (or until the reaction was complete by ^{1}H NMR). Aqueous NaOH (5 M, 10 μL) was added, and the mixture was sonicated for 5 min. The mixture was then filtered through a plug of magnesium sulfate and concentrated to yield the *(S)*-α-methoxy-α-(trifluoromethyl)phenylacetamide.

Preparation of Racemic Amines. The racemic amines were prepared from the imines by sodium borohydride or lithium aluminum hydride reduction. Alternatively imines were reduced to racemic amines following general procedure A or B and using titanocene dichloride rather than [*(R,R)*-ethylene-1,2-bis(η^5-4,5,6,7 tetrahydroindenyl]titanium *(R)*-1,1′-binaphth-2,2′-diolate.

The following are representative experimental procedures for each example listed. Some reactions were initially carried out using 10 mol % catalyst and the products of these reactions were fully characterized. Subsequent experimentation showed that 5 mol % catalyst could be used in most cases. The products of these reactions were characterized by ^{1}H NMR and GC. Enantiomeric excesses were determined the same way and were comparable to those obtained using 10 mol % catalyst. In the following procedures "titanium complex" refers to [*(R,R)*-ethylene-1,2-bis(η^5-4,5,6,7 tetrahydroindenyl]titanium *(R)*-1,1′-binaphth-2,2′-diolate.

(43) By GC a trace of the imine is sometimes present. It may be formed from the amine on the GC injector (260 °C) as has been observed for similar compounds. See: Fales, H. M.; Comstock, W.; Jones, T. H. *Anal. Chem.* **1980**, *52*, 980.

(44) Prepared by treatment of the acid (Aldrich) with oxalyl chloride.

(*R*)-(+)-*N*-Benzyl-1-phenylethylamine[45] (at 2000 psig). *N*-(α-Methylbenzylidene)benzylamine (175 mg, 0.84 mmol) was reduced according to general procedure B with 10 mol % catalyst (titanium complex 50 mg, 0.084 mmol; *n*-butyllithium 130 μL, 1.29 M in hexanes, 0.168 mmol; phenylsilane 26 μL, 0.21 mmol). The vessel was charged to 2000 psig, and the mixture was stirred for 48 h in an oil bath at 65 °C. The THF was removed *in vacuo* and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (3 × 20 mL). The aqueous layers were combined and made basic with solid KOH and extracted with diethyl ether (4 × 30 mL). The ether layers were combined, dried over anhydrous sodium sulfate, and concentrated. The amine was purified by flash chromatography on silica (5:2:93 diethyl ether/triethylamine/hexanes) to afford 142 mg (80% yield) of product. HPLC analysis indicated 79% ee. ^{1}H NMR (300 MHz, C_6D_6, TMS): δ 7.3–7.08 (m, 10H), 3.59 (q, 1H, *J* = 6 .4Hz), 3.50 (dd, 2H, J_1 = 13.1, J_2 = 39 Hz), 1.18 (d, 3H, *J* = 6.8 Hz), 1.4–0.5 (bs, N–H). ^{13}C NMR (75 MHz, C_6D_6): δ 146.32, 141.43, 128.7, 128.49, 128.35 (obscured by solvent), 127.71, 127.13, 126.99, 57.88, 51.94, 24.90. IR (neat): 3370, 3250, 3083, 3062, 3026, 2962, 2924, 2902, 2862, 2833, 2812, 2805, 1492, 1452, 1125, 909, 761, 733, 699 cm^{-1}. $[\alpha]^{25°}$ = +44.3° ± 1.7° (*c* = 5.87 mg/mL in cyclopentane); lit.[47] (*(S)* enantiomer) $[\alpha]^{25°}$ = −49.2° (*c* = 6.04 mg/mL in cyclopentane).

(*R*)-(+)-*N*-Benzyl-1-phenylethylamine (at 2000 psig). *N*-(α-Methylbenzylidene)benzylamine (1.05 g, 5.0 mmol) was reduced following general procedure B with 2 mol % catalyst (titanium complex 59 mg, 0.10 mmol; *n*-butyllithium 117 μL, 1.71 M in hexanes, 0.20 mmol; phenylsilane 31 μL, 0.25 mmol). The vessel was charged to 2000 psig, and the mixture was stirred for 23 h in an oil bath at 65 °C. The THF was removed *in vacuo* and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (3 × 20 mL). The aqueous layers were combined and made basic with solid KOH and extracted with diethyl ether (4 × 50 mL). The ether layers were combined, dried over anhydrous sodium sulfate, and concentrated to afford the pure amine (982 mg, 93% yield). HPLC analysis indicated 85% ee.

(+)-*N*-Benzyl-1-(4-methoxyphenyl)ethylamine[46] (at 2000 psig). *N*-(α-Methyl-4-methoxybenzylidene)benzylamine (479 mg, 2.0 mmol) was reduced according to general procedure B with 5 mol % catalyst (titanium complex 59 mg, 0.1 mmol; *n*-butyllithium 129 μL, 1.55 M in hexanes, 0.2 mmol; phenylsilane 37 μL, 0.3 mmol). The vessel was charged to 2000 psig, and the mixture was stirred for 18 h in an oil bath at 65 °C. The THF was removed *in vacuo* and the residue was taken up in ethyl acetate. The ether layer was extracted with aqueous 1 M HCl (3 × 20 mL). The aqueous layers were combined and made basic with solid KOH and extracted with chloroform (4 × 30 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated to afford 416 mg (86% yield) of product. HPLC analysis indicated 86% ee. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.32–7.18 (m, 7H), 6.88 (d, 2H, *J* = 6 Hz), 3.81 (s, 3H), 3.76 (q, 1H, *J* = 6.6 Hz), 3.61 (dd, J_1 = 12.9 Hz, J_2 = 9.3 Hz), 1.52 (bs, 1H), 1.34 (d, 3H, *J* = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.6, 140.7, 137.7, 128.3, 128.1, 127.7, 126.7, 112.3, 56.8, 55.2, 51.6, 24.5. IR (neat): 3650, 3328, 3069, 3026, 2998, 2958, 2927, 2883, 2054, 1998, 1883, 1610, 1584, 1511, 1494, 1453, 1441, 1368, 1344, 1301, 1284, 1245, 1201, 1176, 1115, 1036, 909, 832, 808, 736, 694, 637 cm^{-1}. $[\alpha]^{22°}$ = +40.3° ± 1.3° (*c* = 7.7 mg/mL in methylene chloride).

(+)-*N*-Benzyl-1-(2-furyl)ethylamine (at 2000 psig). *N*-[1-(2-Furyl)-ethylidene]benzylamine (167 mg, 0.84 mmol) was reduced according to general procedure B with 10 mol % catalyst (titanium complex 50 mg, 0.084 mmol; *n*-butyllithium 130 μL, 1.29 M in hexanes, 0.168 mmol; phenylsilane 26 μL, 0.21 mmol). The vessel was charged to 2000 psig and the mixture was stirred for 48 h in an oil bath at 65 °C. The THF was removed *in vacuo* and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (3 × 20 mL). The aqueous layers were combined and made basic with solid KOH and extracted with diethyl ether (4 × 30 mL). The ether layers were combined, dried over anhydrous sodium sulfate, and concentrated. The amine was purified via flash chromatography on silica (1:2:97 diethyl ether/triethylamine/hexanes) to afford 101 mg (60% yield) product. HPLC analysis indicated 62% ee. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.76 (m, 1H), 7.35–7.2 (m, 5H), 6.3 (m, 1H), 6.15 (d, 1H, *J* = 2.7 Hz), 3.85 (q, 1H, *J* = 6.6 Hz), 3.7 (dd, 2H, J_1 = 13.8 Hz J_2 = 27 Hz), 1.65 (bs, N–H), 1.4 (d, 3H, *J* = 6.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.84, 141.36, 140.33, 128.35, 128.15, 126.89, 109.85, 105.39, 51.13, 50.52, 20.45. IR (neat): 3410, 3280, 3112, 3086, 3063, 3028, 2972, 2849, 1504, 1495, 1463, 1453, 1150, 1120, 1009, 910, 805, 735, 730, 698 cm^{-1}. $[\alpha]^{22°}$ = +50.0° ± 2.0° (*c* = 5.20 mg/mL in methylene chloride). Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51. Found: C, 77.86; H, 7.37.

(+)-*N*-Benzyl-1-(2-furyl)ethylamine (at 2000 psig). *N*-[1-(2-Furyl)-ethylidene]benzylamine (598 mg, 3.0 mmol) was reduced according to general procedure B with 5 mol % catalyst (titanium complex 89 mg, 0.15 mmol; *n*-butyllithium 175 μL, 1.71 M in hexanes, 0.30 mmol; phenylsilane 56 μL, 0.45 mmol). The vessel was charged to 2000 psig, and the mixture was stirred for 45 h in an oil bath at 65 °C. The THF was removed *in vacuo* and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (3 × 20 mL). The aqueous layers were combined and made basic with solid KOH and extracted with diethyl ether (4 × 40 mL). The ether layers were combined, dried over anhydrous sodium sulfate, and concentrated. The amine was purified by flash chromatography on silica (1:2:97 diethyl ether/triethylamine/hexanes) to afford 420 mg (70% yield) product. HPLC analysis indicated 53% ee.

(+)-*N*-Benzyl-1-(1-naphthyl)ethylamine (at 2000 psig). *N*-[1-(1-naphthyl)ethylidene]benzyl amine (519 mg, 2.0 mmol) was reduced by following general procedure B with 5 mol % catalyst (titanium complex 59 mg, 0.10 mmol; *n*-butyllithium 117 μL, 1.71 M in hexanes, 0.20 mmol; phenylsilane 37 μL, 0.30 mmol). The vessel was charged to 2000 psig and the mixture was stirred for 12 h in an oil bath at 65 °C. The THF was removed *in vacuo*, and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (3 × 20 mL). The aqueous layers were combined and made basic with NaOH and extracted with methylene chloride (4 × 30 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated. The amine was purified by flash chromatography on silica (1:2:97 diethyl ether/triethylamine/hexanes) to afford 492 mg (90% yield) of product. HPLC analysis indicated 69% ee. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.85–7.8 (m, 3H), 7.78 (d, 1H, *J* = 1 Hz), 7.54–7.43 (m, 5H), 3.98 (q, 1H, *J* = 6.6 Hz), 3.65 (dd, 2H, J_1 = 13.2 Hz, J_2 = 21 Hz), 1.64 (bs, N–H), 1.44 (d, 3H, *J* = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.97, 140.62, 133.46, 132.18, 128.31, 128.22, 128.07, 127.68, 127.6, 126.79, 125.87, 125.39, 125.32, 124.89, 57.57, 51.68, 24.44. IR (neat): 3322, 3083, 3055, 3025, 2962, 2923, 2868, 2822, 1679, 1632, 1600, 1584, 1506, 1494, 1452, 1369, 1314, 1175, 1130, 1118, 897, 856, 819, 746, 698 cm^{-1}. $[\alpha]^{22°}$ = +31.0° ± 1.7° (*c* = 2.9 mg/mL in methylene chloride). Anal. Calcd for $C_{19}H_{19}N$: C, 87.31; H, 7.33. Found: C, 87.17; H, 6.95.

(−)-*N*-Benzyl-2-aminohexane[47] (at 2000 psig). *N*-(1-Methylpentylidene)benzylamine (159 mg, 0.84 mmol) was reduced according to general procedure B with 10 mol % catalyst (titanium complex 50 mg, 0.084 mmol; *n*-butyllithium 130 μL, 1.29 M in hexanes, 0.168 mmol; phenylsilane 26 μL, 0.21 mmol). The vessel was charged to 2000 psig, and the mixture was stirred for 48 h in an oil bath at 65 °C. The THF was removed *in vacuo* and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (3 × 10 mL). The aqueous layers were combined and made basic with solid KOH and extracted with diethyl ether (4 × 20 mL). The amine was purified by flash chromatography on silica (1:2:97 diethyl ether/triethylamine/hexanes) to afford 105 mg (65% yield) product. HPLC analysis indicated 59% ee. ^{1}H NMR (300 MHz, C_6D_6, TMS): δ 7.40 (m, 2H), 7.33 (m, 2H), 7.11 (m, 1H), 3.65 (dd, 2H, J_1 = 13.2 Hz, J_2 = 30 Hz), 2.53 (m, 1H), 1.25–1.19 (m, 6H), 0.95 (d, 3H, *J* = 6.6 Hz), 0.87 (t, 3H, *J* = 5.5 Hz), 0.70 (bs, N–H). ^{13}C NMR (75 MHz, C_6D_6): δ 141.98, 128.45, 128.36, 126.90, 52.79, 51.68, 37.36, 28.44, 23.34, 20.63, 14.35. IR (neat): 3300, 3090, 3020, 2957, 2857, 1464, 1456, 1453, 731, 697 cm^{-1}. $[\alpha]^{22°}$ = −7.5° ± 0.9° (*c* = 5.32 mg/mL in methylene chloride).

(−)-*N*-Benzyl-1-cyclohexylethylamine[48] (at 2000 psig). *N*-(1-Cyclohexylethylidene)benzylamine (108 mg, 0.50 mmol) was reduced according to general procedure B with 10 mol % catalyst (titanium complex 30 mg, 0.050 mmol; *n*-butyllithium 78 μL, 1.29 M in hexanes, 0.10 mmol; phenylsilane 15 μL, 0.125 mmol). The vessel was charged to 2000 psig, and the mixture was stirred for 48 h in an oil bath at 65 °C. The THF was removed *in vacuo* and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (3 × 10 mL). The aqueous layers were combined and made basic with solid KOH and extracted with diethyl ether (4 × 20 mL) to afford the pure amine (88 mg, 81% yield). HPLC analysis indicated 84% ee. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.34–7.22 (m, 5H), 3.77 (dd, 2H, J_1 = 13.2 Hz, J_2 = 40.8 Hz), 2.49 (m, 1H), 1.76–1.64 (m, 5H), 1.36–0.97 (m, 7H), 1.02 (d, 3H, *J* = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 128.25, 128.075,

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128.036, 126.66, 57.05, 51.54, 42.97, 29.82, 28.07, 26.77, 26.64, 26.51, 16.73. IR (neat): 3320, 3062, 3026, 2923, 2851, 1495, 1471, 1464, 1450, 731, 697 cm^{-1}. $[\alpha]^{22°} = -22.4° \pm 1.6°$ (c = 3.12 mg/mL in methylene chloride).

(-)-*N*-Benzyl-1-cyclohexylethylamine (at 2000 psig). *N*-(1-Cyclohexylethylidene)benzylamine (430 mg, 2.0 mmol) was reduced according to general procedure B with 5 mol % catalyst (titanium complex 59 mg, 0.10 mmol; *n*-butyllithium 120 μL, 1.66 M in hexanes, 0.20 mmol; phenylsilane 37 μL, 0.30 mmol). The vessel was charged to 2000 psig and the mixture was stirred for 9 h in an oil bath at 65 °C. The THF was removed *in vacuo* and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (3 × 20 mL). The aqueous layers were combined and made basic with solid KOH and extracted with diethyl ether (4 × 30 mL) to afford the pure amine (400 mg, 93% yield). HPLC analysis indicated 76% ee.

(-)-*N*-Benzyl-1-cyclohexylethylamine (at 500 psig). *N*-(1-Cyclohexylethylidene)benzylamine (430 mg, 2.0 mmol) was reduced according to general procedure B with 5 mol % catalyst (titanium complex 59 mg, 0.10 mmol; *n*-butyllithium 120 μL, 1.66 M in hexanes, 0.20 mmol; phenylsilane 37 μL, 0.30 mmol). The vessel was charged to 500 psig, and the mixture was stirred for 72 h in an oil bath at 65 °C. The THF was removed *in vacuo* and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (3 × 20 mL). The aqueous layers were combined and made basic with solid KOH and extracted with diethyl ether (4 × 30 mL) to afford the pure amine (366 mg, 85% yield). HPLC analysis indicated 43% ee.

(-)-*N*-Benzyl-3-methyl-2-aminobutane[49] (at 2000 psig). *N*-(1,2 Dimethylpropylidene)benzylamine (147 mg, 0.84 mmol) was reduced according to general procedure B with 10 mol % catalyst (titanium complex 50 mg, 0.084 mmol; *n*-butyllithium 130 μL, 1.29 M in hexanes, 0.168 mmol; phenylsilane 26 μL, 0.21 mmol). The vessel was charged to 2000 psig, and the mixture was stirred for 48 h in an oil bath at 65 °C. The THF was removed *in vacuo* and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (3 × 10 mL). The aqueous layers were combined and made basic with solid KOH and extracted with diethyl ether (4 × 20 mL) to afford the pure amine (115 mg, 77% yield). HPLC analysis indicated 80% ee. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.35–7.30 (m, 4H), 7.2–7.3 (m, 1H), 3.77 (dd, 2H, J_1 = 17.4 Hz, J_2 = 34.8 Hz), 2.51 (m, 1H), 1.75 (m, 1H), 1.2 (bs, N–H), 0.99 (d, 3H, J = 6.6 Hz), 0.89 (d, 3H, J = 6.3 Hz), 0.87 (d, 3H, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$ 75 MHz TMS): δ 141.09, 128.34, 128.27, 128.05, 126.69, 57.53, 51.53, 32.21, 19.28, 17.25, 15.96. IR (neat): 3350, 3260, 3085, 3063, 3026, 2959, 2872, 2826, 2813, 2807, 1494, 1463, 1453, 1384, 1371, 1153, 1139, 1122, 1097, 1083, 1028, 733, 697 cm^{-1}. $[\alpha]^{22°} = -25.0° \pm 1.1°$ (c = 8.40 mg/mL in methylene chloride).

(-)-*N*-Benzyl-6-methyl-2-aminoheptane[50] (at 2000 psig). *N*-(1,5-Dimethylhex-5-enylidene)benzylamine (215 mg, 1.0 mmol) was reduced according to general procedure B with 10 mol % catalyst (titanium complex 59 mg, 0.10 mmol; *n*-butyllithium 155 μL, 1.29 M in hexanes, 0.20 mmol; phenylsilane 31 μL, 0.25 mmol). The vessel was charged to 2000 psig and the mixture was stirred for 48 h in an oil bath at 65 °C. The THF was removed *in vacuo*, and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (3 × 20 mL). The aqueous layers were combined and made basic with solid KOH and extracted with diethyl ether (4 × 30 mL). The amine was purified by flash chromatography on silica (1:2:97 diethyl ether/triethylamine/hexanes) to yield 145 mg (66% yield) of product. HPLC analysis indicated 60% ee. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.32–7.22 (m, 5H), 3.77 (dd, 2H, J_1 = 12.9 Hz, J_2 = 29.1 Hz), 2.88 (m, 1H), 1.54–1.31 (m, 2H), 1.31–1.26 (m, 4H), 1.26–1.13 (m, 2H), 1.07 (d, 3H, J = 6.0 Hz), 0.86 (d, 6H, J = 6.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.92, 128.27, 128.02, 126.68, 52.45, 51.39, 39.12, 37.32, 27.88, 23.65, 22.59, 222.53, 20.32. IR (neat): 3300, 3260, 3063, 3027, 2954, 2868, 1494, 1466, 1453, 1383, 1372, 1366, 1156, 1028, 731, 697 cm^{-1}. $[\alpha]^{22°} = -18.2° \pm 2.0°$ (c = 5.02 mg/mL in methylene chloride).

(-)-*N*-(4-Methoxybenzyl)-1-cyclohexylethylamine (at 500 psig). *N*-(1-Cyclohexylethylidene)-4-methoxybenzylamine (491 mg, 2.0 mmol) was reduced according to general procedure B with 5 mol % catalyst (titanium complex 59 mg, 0.1 mmol; *n*-butyllithium 113 μL, 1.76 M in hexanes, 0.20 mmol; phenylsilane 37 μL, 0.3 mmol). The vessel was charged to 500 psig, and the mixture was stirred for 68 h in an oil bath at 65 °C. The THF was removed *in vacuo*, and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (3 × 15 mL). The aqueous layers were combined and made basic with solid KOH and extracted with methylene chloride (4 × 20 mL) to afford the pure amine (400 mg, 81% yield). To determine the ee, the amine was debenzylated with 10% Pd/C and formic acid (30 min room temperature). HPLC analysis of the 1-naphthamide indicated 62% ee. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.26–7.21 (d, 2H, J = 8.6 Hz), 6.88–6.83 (d, 2H, J = 8.7 Hz), 3.79 (s, 3H), 3.8–3.6 (dd, 2H, J_1 = 12.9 Hz, J_2 = 28.8 Hz), 2.5–2.46 (m, 1H), 1.8–1.6 (m, 5H), 1.4–0.94 (m, 7H), 1.01 (d, 3H, J = 6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.4, 133.2, 129.2, 113.7, 56.9, 55.2, 50.9, 42.9, 29.8, 26.8, 26.6, 26.5, 16.7. IR (neat): 3300, 2923, 2849, 2350, 1898, 1810, 1584, 1511, 1448, 1371, 1321, 1299, 1248, 1172, 1105, 1030, 906, 891, 824, 734, 700 cm^{-1}. HRMS: calcd for $C_{16}H_{25}NO$ 247.1936, found 247.1934. $[\alpha]^{22°} = -16.4° \pm 1.6°$ (c = 3.12 mg/mL in methylene chloride).

(-)-*N*-(4-Methoxybenzyl)-1-cyclohexylethylamine (at 2000 psig). *N*-(1-Cyclohexylethylidene)-4-methoxybenzylamine (491 mg, 2.0 mmol) was reduced according to general procedure B with 5 mol % catalyst (titanium complex 59 mg, 0.1 mmol; *n*-butyllithium 115 μL, 1.74 M in hexanes, 0.20 mmol; phenylsilane 37 μL, 0.3 mmol). The vessel was charged to 2000 psig and the mixture was stirred for 15 h in an oil bath at 65 °C. The THF was removed *in vacuo* and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (4 × 10 mL). The aqueous layers were combined and made basic with solid KOH and extracted with methylene chloride (4 × 20 mL) to afford the pure amine (453 mg, 92% yield). To determine the ee, the amine was debenzylated with 10% Pd/C and formic acid (30 min rt). HPLC analysis of the 1-naphthamide indicated 78% ee.

(-)-*N*-Methyl-1-cyclohexylethylamine[51] (at 500 psig). *N*-(1-Cyclohexylethylidene)methylamine (279 mg, 2.0 mmol) was reduced according to general procedure B with 5 mol % catalyst (titanium complex 59 mg, 0.1 mmol; *n*-butyllithium 118 μL, 1.69 M in hexanes, 0.20 mmol; phenylsilane 37 μL, 0.3 mmol). The vessel was charged to 500 psig and the mixture was stirred for 45 h at room temperature. The THF was removed *in vacuo* and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (3 × 10 mL). The aqueous layers were combined and made basic with solid NaOH and extracted with methylene chloride (4 × 20 mL) to afford the pure amine (241 mg, 85% yield). HPLC analysis of the 1-naphthamide indicated 92% ee. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.4 (s, 3H), 2.5–2.32 (pentet, 1H, J = 6.3 Hz), 1.80–1.60 (m, 5H), 1.51 (bs, 1H), 1.4–0.95 (m, 6H), 0.99 (d, 3H, J = 6.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 59.6, 42.6, 34.2, 29.8, 27.9, 26.7, 26.6, 26.5, 16.0. IR (neat): 3676, 3300, 2920, 2850, 2784, 2700, 2662, 2602, 2361, 1593, 1476, 1448, 1371, 1337, 1294, 1263, 1239, 1191, 1155, 1134, 1093, 1052, 986, 927, 891, 837, 778, 735 cm^{-1}. $[\alpha]^{22°} = -13.7° \pm 1.6°$ (c = 2.19 mg/mL in methylene chloride).

(-)-*N*-Methyl-1-cyclohexylethylamine (at 80 psig). *N*-(1-Cyclohexylethylidene)methylamine (418 mg, 3.0 mmol) was reduced according to general procedure A with 5 mol % catalyst (titanium complex 89 mg, 0.15 mmol; *n*-butyllithium 176 μL, 1.70 M in hexanes, 0.3 mmol; phenylsilane 56 μL, 0.45 mmol). The vessel was charged to 80 psig and the mixture was stirred for 5 h in an oil bath at 65 °C. The THF was removed *in vacuo*, and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (3 × 15 mL). The aqueous layers were combined and made basic with solid KOH and extracted with methylene chloride (4 × 20 mL) to afford the pure amine (263 mg, 62% yield). HPLC analysis of the 1-naphthamide indicated 92% ee.

(-)-*N*-Propyl-1-cyclohexylethylamine (at 2000 psig). *N*-(1-Cyclohexylethylidene)propylamine (251 mg, 1.5 mmol) was reduced according to general procedure B with 5 mol % catalyst (titanium complex 45 mg, 0.075 mmol; *n*-butyllithium 80 μL, 1.87 M in hexanes, 0.15 mmol; phenylsilane 28 μL, 0.23 mmol). The vessel was charged to 2000 psig, and the mixture was stirred for 24 h in an oil bath at 65 °C. The THF was removed *in vacuo*, and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (3 × 10 mL). The aqueous layers were combined and made basic with solid NaOH and extracted with methylene chloride (4 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. Flash chromatography (silica, 1:99 triethylamine/hexanes) afforded the pure amine (175 mg, 70% yield). HPLC analysis of the 1-naphthamide indicated 79% ee. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.62–2.4 (m, 3H), 1.77–1,64 (m, 5H), 1.53–1.43 (sextet, 2H, J = 6.9 Hz), 1.35–1.13 (m, 3H), 0.96 (d, 3H, J = 6.6 Hz), 0.91 (t, 3H, J = 7.2 Hz), 1.04–0.8 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 57.8, 49.6, 30.0, 27.9, 26.8, 26.7, 26.6, 23.6, 16.9, 11.9. IR (neat): 3347, 2926, 2851, 1443, 1370, 1336, 1293, 1262, 1237,

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1190, 1154, 1124, 800, 711 cm^{-1}. HRMS: calcd for $C_{11}H_{23}N$ 169.1831, found 169.1830. $[\alpha]^{22°} = -17.3° \pm 1.6°$ (c = 29.5 mg/mL in methylene chloride).

N-Propyl-1-cyclohexylethylamine (at 80 psig). *N*-(1-Cyclohexylethylidene)propylamine (334 mg, 2.0 mmol) was reduced according to general procedure A with 5 mol % catalyst (titanium complex 59 mg, 0.1 mmol; *n*-butyllithium 121 μL, 1.65 M in hexanes, 0.2 mmol; phenylsilane 37 μL, 0.3 mmol). The vessel was charged to 80 psig, and the mixture was stirred for 81 h in an oil bath at 65 °C. The THF was removed *in vacuo*, and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (3 × 10 mL). The aqueous layers were combined and made basic with solid NaOH and extracted with methylene chloride (4 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated to afford the pure amine (220 mg, 65% yield). HPLC analysis of the 1-naphthamide indicated 4% ee; the opposite enantiomer as above was formed.

(–)-N-Benzyl-1-cyclopropylethylamine (at 2000 psig). *N*-(1-Cyclopropylethylidene)benzylamine (347 mg, 2.0 mmol) was reduced according to general procedure B with 5 mol % catalyst (titanium complex 59 mg, 0.1 mmol; *n*-butyllithium 120 μL, 1.66 M in hexanes, 0.2 mmol; phenylsilane 37 μL, 0.3 mmol). The vessel was charged to 2000 psig and the mixture was stirred for 14 h in an oil bath at 65 °C. The THF was removed *in vacuo*, and Kugelrohr distillation afforded the pure amine (321 mg, 91% yield). HPLC analysis indicated 61% ee. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.33–7.22 (m, 5H), 3.87–3.81 (dd, 2H, J_1 = 7.8 Hz, J_2 = 4 Hz), 1.91–1.88 (m, 1H), 1.5 (bs, 1H), 1.19–1.17 (d, 3H, J = 7 Hz), 0.79–0.75 (m, 1H), 0.51–0.41 (m, 2H), 0.17–0.13 (m, 1H), 0.09–0.03 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.8, 128.2, 127.9, 126.6, 58.2, 51.6, 20.4, 17.9, 4.3, 1.7. IR (neat): 3317, 3075, 3025, 2999, 2965, 2925, 2869, 2814, 1945, 1806, 1602, 1494, 1453, 1370, 1325, 1299, 1184, 1132, 1057, 1027, 1018, 979, 938, 914, 821, 734, 697 cm^{-1}. HRMS: calcd for $C_{12}H_{17}N$ 175.1365, found 175.1361. $[\alpha]^{22°} = -30.2° \pm 0.2°$ (c = 57.2 mg/mL in methylene chloride).

(*R*)-(+)-2-Phenylpyrrolidine[52] (at 2000 psig). 2-Phenylpyrroline (122 mg, 0.84 mmol) was reduced according to general procedure B with 10 mol % catalyst (titanium complex 50 mg, 0.084 mmol; *n*-butyllithium 130 μL, 1.29 M in hexanes, 0.168 mmol; phenylsilane 26 μL, 0.21 mmol). The vessel was charged to 2000 psig and the mixture was stirred for 48 h in an oil bath at 65 °C. The THF was removed *in vacuo*, and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (3 × 10 mL). The aqueous layers were combined and made basic with solid KOH and extracted with diethyl ether (4 × 20 mL) to afford the pure amine (92 mg, 74% yield). GC analysis of the *(S)*-α-methoxy-α-(trifluoromethyl)phenylacetamide indicated >98% ee. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): 7.38–7.31 (m, 4H), 7.29–7.20 (m, 1H), 4.11 (t, 1H, J = 7.5 Hz), 3.25–3.17 (m, 1H), 3.05–2.97 (m, 1H), 2.21–2.13 (m, 1H), 2.01–1.70 (m, 2H), 2.01 (bs, N–H), 1.73 –1.61 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.92, 128.28, 126.67, 126.44, 62.57, 47.01, 34.34, 25.60. IR (neat): 3338, 3318, 3276, 3081, 3026, 2961, 2870, 1602, 1490, 1453, 1419, 1101, 1068, 1027, 754, 699 cm^{-1}. $[\alpha]^{22°} = +64.0° \pm 2.7°$ (c = 3.75 mg/mL in methylene chloride); $[\alpha]^{22°} = +35.0° \pm 3.0°$ (c = 3.42 mg/mL in methanol) lit.[52] (*(S)* enantiomer); $[\alpha]^{22°} = -22.0°$ (c = 2.0 in methanol).

(*R*)-(+)-2-Phenylpyrrolidine (at 80 psig). General procedure A was used to reduce 2-phenyl-1-pyrroline (290 mg, 2.0 mmol) with 5 mol % catalyst (titanium complex 59 mg, 0.10 mmol; *n*-butyllithium 117 μL, 1.70 M in hexanes, 0.20 mmol; phenylsilane 37 μL, 0.30 mmol) at 80 psig of H_2 and 65 °C. The mixture was stirred for 7 h. The crude mixture was diluted with ether (10 mL) and extracted with 1 M HCl (3 × 10 mL). The aqueous portion was made basic with NaOH and extracted with methylene chloride (3 × 20 mL). The combined organic portions were dried over Na_2SO_4 and concentrated *in vacuo* to afford 247 mg (84% yield) of the desired *(R)*-(+)-2-phenylpyrrolidine. HPLC analysis of the 1-naphthamide (85:15 hexane/2-propanol) indicated 99% ee. $[\alpha]^{22°} = +65.3° \pm 1.1°$ (c = 11.3 mg/mL in methylene chloride).

(*R*)-(+)-2-Phenylpyrrolidine (at 500 psig). General procedure B was used to reduce 2-phenyl-1-pyrroline (218 mg, 1.5 mmol) with 5 mol % catalyst (titanium complex 45 mg, 0.075 mmol; *n*-butyllithium 85 μL, 1.76 M in hexanes, 0.15 mmol; phenylsilane 28 μL, 0.22 mmol) at 500 psig of H_2 and 21 °C. The mixture was stirred for 24 h. The crude mixture was diluted with ether (10 mL) and extracted with 1 M HCl (4 × 8 mL). The aqueous layers were made basic with NaOH and extracted with methylene chloride (3 × 15 mL). The combined organic portions were dried over Na_2SO_4 and concentrated to afford 190 mg (86% yield) of the desired *(R)*-(+)-2-phenylpyrrolidine with no further purification necessary. HPLC analysis of the 1-naphthamide (85:15 hexane/2-propanol) indicated 99% ee.

(*R*)-(+)-2-Phenylpyrrolidine (at 80 psig). General procedure A was used to reduce 2-phenyl-1-pyrroline (1.45 g, 10.0 mmol) with 1 mol % catalyst (titanium complex 59 mg, 0.10 mmol; *n*-butyllithium 122 μL, 1.64 M in hexanes, 0.20 mmol; phenylsilane 37 μL, 0.30 mmol) at 80 psig of H_2 and 65 °C. The mixture was stirred for 42 h. The solvent was removed *in vacuo*, and Kugelrohr distillation afforded 1.21 g (83% yield) of the desired *(R)*-(+)-2-phenylpyrrolidine. HPLC analysis of the 1-naphthamide (85:15 hexane/2-propanol) indicated 99% ee.

(*R*)-(+)-2-Phenylpyrrolidine (at 80 psig). General procedure A was used to reduce 2-phenyl-1-pyrroline (290 mg, 2.0 mmol) with 5 mol % catalyst (titanium complex 59 mg, 0.10 mmol; *n*-butyllithium 122 μL, 1.64 M in hexanes, 0.20 mmol; no phenylsilane used) at 80 psig of H_2 and 65 °C. The mixture was stirred for 8 h. The solvent was removed *in vacuo*, and Kugelrohr distillation afforded 235 mg (80% yield) of the desired *(R)*-(+)-2-phenylpyrrolidine. HPLC analysis of the 1-naphthamide (85:15 hexane/2-propanol) indicated >99% ee.

(*R*)-(+)-2-Phenylpiperidine[53] (at 2000 psig). 2-Pheny-3,4,5,6-tetrahydropyridine (80 mg, 0.5 mmol) was reduced according to general procedure B with 10 mol % catalyst (titanium complex 30 mg, 0.050 mmol; *n*-butyllithium 78 μL, 1.29 M in hexanes, 0.10 mmol; phenylsilane 16 μL, 0.125 mmol). The vessel was charged to 2000 psig, and the mixture was stirred for 48 h in an oil bath at 65 °C. The THF was removed *in vacuo*, and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (3 × 10 mL). The aqueous layers were combined and made basic with solid KOH and extracted with diethyl ether (4 × 20 mL) to afford the pure amine (65 mg, 81% yield). HPLC analysis indicated 95% ee. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): 7.37–7.21 (m, 5H), 3.59 (m, 1H), 3.18 (m, 1H), 2.79 (m, 1H), 1.90 (m, 1H), 1.81–1.77 (m, 1H), 1.69–1.64 (m, 2H including N–H), 1.58–1.47 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.58, 128.29, 126.92, 126.57, 62.33, 47.81, 34.99, 25.93, 25.43. IR (neat): 3322, 3270, 326, 3082, 3061, 3026, 2932, 2873, 2851, 2816, 2786, 2719, 2697, 1452, 1440, 1432, 1325, 1307, 1122, 1109, 1020, 753, 699 cm^{-1}. $[\alpha]^{22°} = +49.5° \pm 2.5°$ (c = 2.02 mg/mL in methylene chloride).

(*R*)-(+)-2-Phenylpiperidine (at 2000 psig). 2-Phenyl-3,4,5,6-tetrahydropyridine (318 mg, 2.0 mmol) was reduced according to general procedure B with 5 mol % catalyst (titanium complex 59 mg, 0.10 mmol; *n*-butyllithium 120 μL, 1.66 M in hexanes, 0.20 mmol; phenylsilane 37 μL, 0.30 mmol). The vessel was charged to 2000 psig, and the mixture was stirred for 11 h in a oil bath at 65 °C. The pure amine (225 mg, 70%) was obtained after chromatography (silica, 2:2:96 triethylamine/diethyl ether/hexanes). HPLC analysis indicated 97% ee.

(*R*)-(+)-2-Phenylpiperidine (at 500 psig). General procedure B was used to reduce 2-phenyl-3,4,5,6-tetrahydropyridine (318 mg, 2.0 mmol) with 5 mol % catalyst (titanium complex 59 mg, 0.10 mmol; *n*-butyllithium 122 μL, 1.63 M in hexanes, 0.20 mmol; phenylsilane 37 μL, 0.30 mmol) at 500 psig of H_2 and 65 °C. The mixture was stirred for 24 h. The crude mixture was diluted with ether (10 mL) and extracted with 1 M HCl (4 × 10 mL). The aqueous portions were made basic with NaOH and extracted with methylene chloride (3 × 20 mL). The combined organic portions were dried over Na_2SO_4 and concentrated. Flash chromatography (silica, 43:1:1 hexane/ether/diethylamine) afforded 248 mg (77% yield) of the desired *(R)*-(+)-2-phenylpiperidine. HPLC analysis of the trifluoroacetamide (98:2 hexane/2-propanol) indicated 98% ee. $[\alpha]^{22°} = +48.4° \pm 3.2°$ (c = 3.1 mg/mL in methylene chloride).

(+)-2-Phenylhexahydroazepine (at 80 psig). General procedure A was used to reduce 2-phenyl-4,5,6,7-tetrahydro-3*H*-azepine (347 mg, 2.0 mmol) with 5 mol % catalyst (titanium complex 59 mg, 0.10 mmol; *n*-butyllithium 122 μL, 1.63 M in hexanes, 0.20 mmol; phenylsilane 37 μL, 0.30 mmol) at 80 psig of H_2 and 65 °C. The mixture was stirred for 30 h. The crude mixture was diluted with ether (10 mL) and extracted with 1 M HCl (4 × 8 mL). The aqueous portion was made basic with NaOH and extracted with methylene chloride (3 × 20 mL). The combined organic portions were dried over Na_2SO_4 and concentrated. Flash chromatography (silica, 49:49:2 hexane/ether/diethylamine) afforded 278 mg (74% yield) of the desired (+)-2-phenylhexahydroazepine. HPLC analysis of the 1-naphthamide (93:7 hexane/2-propanol) indicated 97% ee. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.38–7.17 (m, 5H) 3.76–3.72 (dd, J_1 = 3.6 Hz, J_2 = 9.9 Hz, 1H), 3.17–3.10 (dt, J_1 = 13.5 Hz, J_2 = 4.2 Hz, 1H), 2.89–2.80 (m, 1H), 2.01–1.91 (m, 1H), 1.90–1.57 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.9, 128.1, 126.4, 126.1, 64.7, 48.0, 38.9, 30.8, 26.7, 25.9. IR (neat): 3650, 3335, 3082, 3060, 3025, 2924, 2851, 1940, 1874, 1806, 1757, 1633, 1601, 1584, 1492, 1449, 1355, 1337,

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1270, 1249, 1210, 1143, 1072, 1027, 999, 951, 915, 904, 840, 753, 699 cm^{-1}. HRMS: calcd for $C_{12}H_{17}N$ 175.1361, found 175.1360. $[\alpha]^{23°}$ = +62.0° ± 2° (c = 47.7 mg/mL in methylene chloride).

(+)-2-Phenylhexahydroazepine (at 80 psig). General procedure B was used to reduce 2-phenyl-4,5,6,7-tetrahydro-3*H*-azepine (347 mg, 2.0 mmol) with 5 mol % catalyst (titanium complex 59 mg, 0.10 mmol; *n*-butyllithium 122 μL, 1.63 M in hexanes, 0.20 mmol; phenylsilane 37 μL, 0.30 mmol) at 500 psig of H_2 and 45 °C. The mixture was stirred for 24 h. The crude mixture was diluted with ether (10 mL) and extracted with 1 M HCl (4 × 10 mL). The aqueous layers were made basic with NaOH and extracted with methylene chloride (3 × 20 mL). The combined organic portions were dried over Na_2SO_4 and concentrated. Flash chromatography (silica, 49:49:2 hexane/ether/diethylamine) afforded 249 mg (71% yield) of the desired (+)-2-phenylhexahydroazepine. HPLC analysis of the 1-naphthamide (93:7 hexane/2-propanol) indicated 98% ee.

(*S*)-(−)-6,7-Dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline[54] (at 2000 psig). 6,7-Dimethoxy-1-methyl-3,4-dihydroisoquinoline (172 mg, 0.84 mmol) was reduced according to general procedure B with 10 mol % catalyst (titanium complex 50 mg, 0.084 mmol; *n*-butyllithium 128 μL, 1.3 M in hexanes, 0.168 mmol; phenylsilane 26 μL, 0.21 mmol). The vessel was charged to 2000 psig, and the mixture was stirred for 48 h in an oil bath at 65 °C. The THF was removed *in vacuo* and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (3 × 20 mL). The aqueous layers were combined and made basic with solid KOH and extracted with diethyl ether (4 × 30 mL) to afford the pure amine (151 mg, 87% yield). HPLC analysis indicated 94% ee. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 6.63 (s, 1H), 6.57 (s, 1H), 4.04 (q, 1H, 6.6 Hz), 3.86 (s, 3H), 3.85 (s, 3H), 3.30–3.21 (dt, 1H, J_1 = 12.9 Hz, J_2 = 7.5 Hz), 3.05–2.95 (m, 1H), 2.83–2.74 (m, 1H), 2.65–2.60 (m, 1H), 1.65 (bs, N–H), 1.44 (d, 3H, J = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.30, 147.22, 132.55, 126.85, 111.84, 109.15, 55.98, 55.81, 51.21, 41.85, 29.58, 22.84. IR (KBr): 3327, 2956, 2972, 2849, 2831, 2793, 1609, 1513, 1463, 1452, 1371, 1353, 1324, 1307, 1292, 1266, 1256, 1222, 1126, 1117, 1098, 1029, 997, 857, 788 cm^{-1}. $[\alpha]^{21°}$ = −55.0° ± 2.0° (c = 4.90 mg/mL in ethanol); lit.[54a] $[\alpha]^{22°}$ = −41.5° (c = 1.71 in ethanol, 70% ee); lit.[54b] $[\alpha]^{22°}$ = −59.5° (c = 4.39 in ethanol).

(*S*)-(−)-6,7-Dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline (at 2000 psig). 6,7-Dimethoxy-1-methyl-3,4-dihydroisoquinoline (410 mg, 2.0 mmol) was reduced according to general procedure B with 5 mol % catalyst (titanium complex 59 mg, 0.10 mmol; *n*-butyllithium 120 μL, 1.66 M in hexanes, 0.20 mmol; phenylsilane 37 μL, 0.30 mmol). The vessel was charged to 2000 psig, and the mixture was stirred for 11 h in an oil bath at 65 °C. The amine was purified by flash chromatography on silica (3:5:92 triethylamine/methanol/ethyl acetate) to yield 370 mg (90% yield) product. HPLC analysis indicated 99% ee.

(*S*)-(−)-6,7-Dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline (at 80 psig). General procedure A was used to reduce 6,7-dimethoxy-1-methyl-3,4-dihydroisoquinoline (410 mg, 2.0 mmol) with 5 mol % catalyst (titanium complex 59 mg, 0.10 mmol; *n*-butyllithium 121 μL, 1.65 M in hexanes, 0.20 mmol; phenylsilane 37 μL, 0.30 mmol) at 80 psig of H_2 and 65 °C. The mixture was stirred for 50 h. The crude mixture was diluted with ether (10 mL) and extracted with 1 M HCl (3 × 10 mL). The aqueous layers were made basic with KOH and extracted with methylene chloride (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. Flash chromatography (silica, 92:5:3 ethyl acetate/methanol/triethylamine) afforded 339 mg (82% yield) of *(S)*-(−)-6,7-dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline. HPLC analysis of the amine (5:1 hexane/2-propanol) indicated 95% ee. $[\alpha]^{21°}$ = −54.3° ± 2.0° (c = 5.7 mg/mL in ethanol).

(*R*)-(−)-2-[2-(*N*-Benzylpyrrolyl)]pyrrolidine (at 80 psig). General procedure A was used to reduce 2-[2-(*N*-benzylpyrrolyl)]-1-pyrroline (449 mg, 2.0 mmol) with 5 mol % catalyst (titanium complex 59 mg, 0.10 mmol; *n*-butyllithium 122 μL, 1.63 M in hexanes, 0.20 mmol; phenylsilane 37 μL, 0.30 mmol) at 80 psig of H_2 and 65 °C. The mixture was stirred for 6 h. The crude mixture was washed with 1 M NaOH (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Flash chromatography (silica, 97:3 ethyl acetate/triethylamine) afforded 327 mg (72% yield) of *(R)*-(−)-2-[2-(*N*-benzylpyrrolyl)]pyrrolidine. HPLC analysis of the acetamide (5:1 hexane/2-propanol) indicated >99% ee. ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ 7.24–7.15 (m, 3H), 7.03–6.97 (m, 2H), 6.65–6.62 (m, 1H), 6.15–6.1 (m, 2H), 5.38–5.1 (dd, J = 17 Hz, 2H), 3.96–3.91 (t, J = 7 Hz, 1H), 3.14–3.07 (m, 1H), 2.89–2.79 (m, 1H), 2.03–1.72 (m, 4H), 1.52 (bs, N–H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.6, 134.8, 128.5, 127.1, 126.2, 121.9, 106.9, 105.0, 54.9, 50.2, 46.7, 31.6, 25.4. IR (neat): 3285, 3098, 3086, 3062, 3028, 2961, 2871, 1949, 1863, 1808, 1735, 1696, 1604, 1585, 1495, 1482, 1453, 1431, 1413, 1356, 1331, 1295, 1241, 1208, 1189, 1134, 1071, 1029, 1001, 951, 910, 844, 798, 776, 707, 622, 614 cm^{-1}. HRMS: calcd for $C_{15}H_{18}N_2$ 226.1470, found 226.1469. $[\alpha]^{22°}$ = −27.1° ± 1° (c = 7.5 mg/mL in methylene chloride). The absolute configuration was determined by optical rotation of the Cbz derivative[55] (prepared and measured by Dr. Yaping Hong).

(*R*)-(−)-2-[2-(*N*-Benzylpyrrolyl)]pyrrolidine (at 500 psig). General procedure B was used to reduce 2-[2-(*N*-benzylpyrrolyl)]-1-pyrroline (225 mg, 1.0 mmol) with 5 mol % catalyst (titanium complex 30 mg, 0.05 mmol; *n*-butyllithium 61 μL, 1.63 M in hexanes, 0.10 mmol; phenylsilane 19 μL, 0.15 mmol) at 500 psig of H_2 and 23 °C. The mixture was stirred for 24 h. The crude mixture was washed with 1 M NaOH (10 mL), dried over Na_2SO_4, and concentrated. Flash chromatography (silica, 97:3 ethyl acetate/triethylamine) afforded 189 mg (83% yield) of *(R)*-(−)-2-[2-(*N*-benzylpyrrolyl)]pyrrolidine. HPLC analysis of the acetamide (5:1 hexane/2-propanol) indicated >99% ee.

(+)-2-[1-(4-Methylpent-4-enyl)]pyrrolidine (at 80 psig). General procedure A was used to reduce 2-[1-(4-methylpent-4-enyl)]-1-pyrroline (454 mg, 3.0 mmol) with 5 mol % catalyst (titanium complex 90 mg, 0.15 mmol; *n*-butyllithium 184 μL, 1.65 M in hexanes, 0.30 mmol; phenylsilane 56 μL, 0.45 mmol) at 80 psig of H_2 and 50 °C. The mixture was stirred for 23 h. The solvent was removed *in vacuo* and the crude material was isolated by Kugelrohr distillation. Flash chromatography (silica, 97:3 methylene chloride/diethylamine) afforded 350 mg (76% yield) of (+)-2-[1-(4-methylpent-4-enyl)]pyrrolidine. HPLC analysis of the 1-naphthamide (91:9 hexane/2-propanol) indicated 99% ee. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 5.14–5.06 (m, 1H), 3.15–2.89 (m, 2H), 2.86–2.77 (m, 1H), 2.08–1.99 (m, 2H), 1.9–1.8 (m, 2H) 1.78–1.65 (m, 2H), 1.66 (s, 3H), 1.60 (s, 3H), 1.59–1.39 (m, 2H), 1.3–1.18 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.47, 124.3, 58.9, 46.5, 36.5, 31.8, 26.0, 25.7, 25.3, 17.6. IR (neat): 3350, 2961, 2921, 2856, 1616, 1539, 1400, 1107, 811, 614 cm^{-1}. HRMS: calcd for $C_{10}H_{19}N$ 153.1517, found 153.1516. $[\alpha]^{24°}$ = +17.0° ± 0.8° (c = 12.8 mg/mL in methylene chloride).

(+)-(*E*)-2-[1-[6-(Trimethylsilyl)hex-5-enyl]]pyrrolidine (at 80 psig). General procedure A was used to reduce *(E)*-2-[1-[6-(trimethylsilyl)-hex-5-enyl]]-1-pyrroline (223 mg, 1.0 mmol) with 5 mol % catalyst (titanium complex 30 mg, 0.05 mmol; *n*-butyllithium 60 μL, 1.66 M in hexanes, 0.10 mmol; phenylsilane 19 μL, 0.15 mmol) at 80 psig of H_2 and 50 °C. The mixture was stirred for 27 h at which time GC showed >94:<1:5 *E* isomer/*Z* isomer/saturated compound. Flash chromatography (silica, 96:4 methylene chloride/triethylamine) afforded 158 mg (70% yield) of a mixture of (+)-*(E)*-2-[1-[6-(trimethylsilyl)hex-5-enyl]]-pyrrolidine (>94%), *(Z)*-2-[1-[6-(trimethylsilyl)hex-5-enyl]]pyrrolidine (<1%), and 2-[1-[6-(trimethylsilyl)hexyl]]pyrrolidine (5%) as a yellow oil. HPLC analysis of the 1-naphthamide (91:9 hexane/2-propanol) indicated 99% ee for the mixture of compounds. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): (+)-*(E)*-2-[1-[6-(trimethylsilyl)hex-5-enyl]]pyrrolidine δ 6.05–5.95 (dt, J_1 = 18 Hz, J_2 = 6 Hz, 1H), 5.64–5.56 (d, J = 18 Hz, 1H), 3.03–2.75 (m, 3H), 2.12–2.06 (q, J = 6 Hz, 2H), 1.94 (bs, 1H), 1.94–1.65 (m, 3H), 1.5–1.13 (m, 7H), 0.25 (s, 9H); 2-[1-[6-(trimethylsilyl)hexyl]]pyrrolidine δ 0.5–0.4 (m, 2H), −0.49 (s, 9H), all other resonances are obscured. ^{13}C NMR (75 MHz, $CDCl_3$): (+)-*(E)*-2-[1-[6-(trimethylsilyl)hex-5-enyl]]pyrrolidine δ 146.7, 129.4, 59.2, 46.4, 36.6, 36.2, 31.8, 28.8, 27.0, 25.3, −1.1; 2-[1-[6-(trimethylsilyl)hexyl]]pyrrolidine δ 36.4, 33.5, 29.5, 27.5, 23.8, 16.7, −1.6, all other resonances are obscured. IR (neat, mixture): 3285, 2925, 2854, 1616, 1458, 1420, 1246, 1106, 987, 863, 837, 763, 730, 691 cm^{-1}. HRMS: (+)-*(E)*-2-[1-[6-(trimethylsilyl)hex-5-enyl]]pyrrolidine calcd for $C_{13}H_{27}NSi$ 225.1912, found 225.1911. $[\alpha]^{22°}$ (mixture) = +12.3° ± 0.5° (c = 19.5 mg/mL in methylene chloride).

(+)-2-Hexylpyrrolidine (at 2000 psig). 2-Hexylpyrroline (460 mg, 3.0 mmol) was reduced according to general procedure B with 5 mol % catalyst (titanium complex 89 mg, 0.15 mmol; *n*-butyllithium 175 μL, 1.71 M in hexanes, 0.30 mmol; phenylsilane 56 μL, 0.45 mmol). The vessel was charged to 2000 psig and the mixture was stirred for 8 h in an oil bath at 65 °C. The THF was removed *in vacuo*, and the residue was taken up in diethyl ether. The ether layer was extracted with aqueous 1 M HCl (3 × 20 mL). The aqueous layers were combined and made basic with solid KOH and extracted with diethyl ether (4 × 30 mL) to afford the pure amine (375 mg, 80% yield). GC analysis of the *(S)*-α-methoxy-α-(trifluoromethyl)phenylacetamide indicated >97% ee. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): 3.05–2.95 (m, 1H), 2.90 (t, 1H, J = 6.8 Hz), 2.85–2.75 (m, 1H), 1.93–1.80 (m, 1H), 1.78–1.65 (m, 2H), 1.57

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(bs, N–H), 1.5–1.18 (m, 11H), 0.80 (t, 3H, J = 6.6Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 59.23, 46.42, 36.42, 31.75, 31.69, 29.35, 27.35, 25.25, 22.46, 13.88. IR (neat): 3312, 3300, 3296, 2956, 2924, 2871, 2855, 1466, 1459, 1434, 1430, 1420, 1402, 1378, 1364, 1342, 1302, 1282, 1260, 1097, 811, 752 cm^{-1}. HRMS: calcd for $C_{10}H_{21}N$ 155.1674, found 155.1672. $[\alpha]^{24°}$ = +14.2° ± 0.8° (c = 12.0 mg/mL in methylene chloride).

(+)-2-Hexylpyrrolidine (at 80 psig). General procedure A was used to reduce 2-[1-(hex-5-enyl)]-1-pyrroline (302 mg, 2.0 mmol) with 5 mol % catalyst (titanium complex 59 mg, 0.10 mmol; n-butyllithium 121 μL, 1.65 M in hexanes, 0.20 mmol; phenylsilane 37 μL, 0.30 mmol) at 80 psig of H_2 and 45 °C. The mixture was stirred for 23 h (monitoring of the reaction by GC/MS showed that the olefin was reduced much faster than the imine). The solvent was removed *in vacuo*, and Kugelrohr distillation afforded 223 mg (72% yield) of (+)-2-hexylpyrrolidine. HPLC analysis of the 1-naphthamide (91:9 hexane/2-propanol) indicated 99% ee. $[\alpha]^{24°}$ = +15.1° ± 0.7° (c = 15.2 mg/mL in methylene chloride).

(+)-2-[1-[4-(*tert*-Butyldimethylsiloxy)butyl]]pyrrolidine (at 80 psig). General procedure A was used to reduce 2-[1-[4-(*tert*-butyldimethylsiloxy)butyl]]-1-pyrroline (510 mg, 2.0 mmol) with 5 mol % catalyst (titanium complex 59 mg, 0.10 mmol; n-butyllithium 121 μL, 1.65 M in hexanes, 0.20 mmol; phenylsilane 37 μL, 0.30 mmol) at 80 psig of H_2 and 65 °C. The mixture was stirred for 10 h. The solvent was removed *in vacuo*, and Kugelrohr distillation afforded 440 mg (85% yield) of (+)-2-[1-[4-(*tert*-butyldimethylsiloxy)butyl]]pyrrolidine. HPLC analysis of the 1-naphthamide (91:9 hexane/2-propanol) indicated 99% ee. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 3.6–3.58 (t, J = 6.6 Hz, 2H), 3.02–2.82 (m, 2H), 2.81–2.77 (m, 1H), 1.91–1.80 (m, 1H), 1.79–1.30 (m, 9H), 1.28–1.18 (m, 1H), 0.89 (s, 9H), 0.04 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 63.1, 59.3, 46.5, 36.8, 32.9, 31.8, 25.9, 25.4, 23.7, 18.3, –5.3. IR (neat): 3298, 2930, 2857, 2737, 1617, 1540, 1471, 1461, 1402, 1360, 1255, 1190, 1099, 1005, 938, 915, 836, 812, 774, 712, 66 cm^{-1}. HRMS: calcd for $C_{14}H_{31}NOSi$ 257.2175, found 257.2173. $[\alpha]^{24°}$ = +9.2° ± 0.7° (c = 14.1 mg/mL in methylene chloride).

(+)-2-[4-(1,3-Dioxolan-2-yl)butyl]pyrrolidine (at 80 psig). General procedure A was used to reduce 2-[4-(1,3-dioxolan-2-yl)butyl]-1-pyrroline (366 mg, 2 mmol) with 5 mol % catalyst (titanium complex 59 mg, 0.10 mmol; n-butyllithium 121 μL, 1.65 M in hexanes, 0.20 mmol; phenylsilane 37 μL, 0.30 mmol) at 80 psig of H_2 and 65 °C. The mixture was stirred for 16 h. The solvent was removed *in vacuo*, and Kugelrohr distillation afforded 314 mg (85% yield) (+)-2-[4-(1,3-dioxolan-2-yl)butyl]pyrrolidine. HPLC analysis of the 1-naphthamide (85:15 hexane/2-propanol) indicated 99% ee. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 4.86–4.82 (t, J = 4.8 Hz, 1H), 3.98–3.81 (m, 4H), 3.01–2.76 (m, 3H), 1.92–1.8 (m, 1H), 1.79–1.6 (m, 4H), 1.58–1.39 (m, 5H), 1.3–1.17 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 104.4, 64.8, 59.2, 46.6, 36.4, 34.0, 31.8, 25.4, 22.0. IR (neat): 3285, 2947, 2868, 1458, 1434, 1410, 1361, 1211, 1141, 1032, 942, 890, 708 cm^{-1}. HRMS: calcd for $[M-H]^+$, $C_{10}H_{18}NO_2$ 184.1338, found 184.1337. $[\alpha]^{24°}$ = +10.6° ± 0.4° (c = 25.5 mg/mL in methylene chloride).

(+)-2-[1-(7-Hydroxyheptyl)]pyrrolidine (at 80 psig). General procedure A was used to reduce 2-[1-(7-hydroxyheptyl)]-1-pyrroline (336 mg, 2.0 mmol) with 5 mol % catalyst (titanium complex 59 mg, 0.10 mmol; n-butyllithium 121 μL, 1.65 M in hexanes, 0.20 mmol; phenylsilane 271 μL, 2.2 mmol) at 80 psig of H_2 and 65 °C. The mixture was stirred for 8 h. The mixture was transferred to a round bottom flask, and 2 mL of 30% NaOH was added. After 4 h of stirring, the THF was removed in vacuo and the residue was diluted with 20 mL of chloroform/5 mL of saturated NaCl. The layers were separated and the aqueous layer was extracted with chloroform (2 × 20 mL). The chloroform layers were dried over Na_2SO_4 and concentrated. Flash chromatography (silica, 3:15:82 triethylamine/methanol/chloroform) afforded 319 mg (86% yield) (+)-2-[1-(7-hydroxyheptyl)]pyrrolidine as a white solid. HPLC analysis of the 1-naphthamide (80:20 hexane/2-propanol) indicated 99% ee. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 3.65–3.6 (t, J = 6.6 Hz, 2H), 3.02–2.7 (m, 3H), 1.9–1.6 (m, 5H) 1.6–1.14 (m, 13H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 62.4, 59.3, 46.4, 36.3, 32.9, 31.9, 29.8, 29.4, 27.4, 25.8, 25.4. IR (neat): 3230, 3100, 2920, 2850, 1460, 1373, 1344, 1138, 1082, 1051, 1013, 993, 947, 890, 772, 719 cm^{-1}. HRMS: calcd for $[M-H]^+$ $C_{11}H_{22}NO$ 184.1701, found 184.1703. $[\alpha]^{23°}$ = +12.2° ± 1.1° (c = 9.0 mg/mL in methylene chloride). Mp: 62–64.5 °C.

(+)-(*E*)-2-[1-(Non-6-enyl)]pyrrolidine (at 80 psig). General procedure A was used to reduce *(Z)*-2-[1-(non-6-enyl)]-1-pyrroline (290 mg, 1.5 mmol) with 5 mol % catalyst (titanium complex 45 mg, 0.075 mmol; n-butyllithium 90 μL, 1.66 M in hexanes, 0.15 mmol; phenylsilane 28 μL, 0.23 mmol) at 80 psig of H_2 and 50 °C. The mixture was stirred for 25 h. The mixture was concentrated and flash chromatography (silica, 97:3 methylene chloride/triethylamine) afforded 201 mg (69% yield) of a mixture of *(E)*-2-[1-(non-6-enyl)]pyrrolidine (68%), *(Z)*-2-[1-(non-6-enyl)]pyrrolidine (14%, prepared independently by sodium borohydride reduction of *(Z)*-2-[1-(non-6-enyl)]-1-pyrroline, spectral data below), and 2-(1-nonyl)pyrrolidine (18%, prepared independently by Pd/C hydrogenation of *(Z)*-2-[1-(non-6-enyl)]-1-pyrroline, spectral data below). These compounds were identified by GC/MS and ^{1}H NMR as the major components; in the ^{13}C NMR some extra peaks were present indicating the presence of small amounts of other olefin isomers. The position of the olefin in the major products was determined by selective homonuclear decoupling experiments; irradiation of the resonances at 1.98 ppm (allylic methylene) caused the two overlapping triplet resonances at 0.98–0.92 ppm (methyl groups for the E and Z isomers) to collapse to singlets; irradiation of the resonances at 1.33 (methylene) caused the triplet resonance at 0.91–0.83 (methyl group for the saturated compound) to collapse to a singlet. The ee was determined by reducing the product mixture with 10% Pd/C under 500 psig H_2 to 2-(1-nonyl)pyrrolidine. The crude 2-(1-nonyl)pyrrolidine was converted to the 1-naphthamide and HPLC analysis (91:9 2-propanol/hexane) indicated 99% ee.

Spectral data for product mixture are as follows. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): E and Z isomer δ 5.5–5.3 (m, 2H), 3.07–2.77 (m, 3H), 2.11–2.08 (bs, 1H), 2.08–1.61 (m, 7H), 1.57–1.18 (m, 10H), 0.98–0.92 (t, J = 7.5 Hz, 3H); the only resolved resonance for the saturated isomer was 0.9–0.83 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): E isomer only δ 131.7, 129.0, 59.3, 46.4, 36.3, 32.4, 31.8, 29.5, 29.3, 27.3, 25.5, 25.3, 14.0. IR (neat): 3283, 2959, 2924, 2853, 1459, 1374, 1298, 1080, 966, 724 cm^{-1}. HRMS: for major product (E isomer) calcd for $C_{13}H_{25}N$ 195.1987, found 195.1985. $[\alpha]^{23°}$ (mixture) = +12.4° ± 0.5° (c = 18.6 mg/mL in methylene chloride).

Spectral data for 2-(1-nonyl)pyrrolidine (independently prepared by Pd/C hydrogenation) are as follows. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 3.08–2.79 (m, 3H), 1.94–1.67 (m, 4H), 1.5–1.17 (m, 17H), 0.91–0.84 (t, 3H), J = 7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 59.4, 46.5, 36.5, 31.9, 29.8, 29.6, 29.5, 29.3, 27.5, 25.4, 22.6, 14.0. IR (neat): 3283, 2924, 2853, 1465, 1458, 753, 733 cm^{-1}. HRMS: calcd for $C_{13}H_{27}N$ 197.2143, found 197.2144.

Spectral data for *(Z)*-2-[1-(non-6-enyl)]pyrrolidine (independently prepared by sodium borohydride reduction) are as follows. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 5.45–5.25 (m, 2H), 3.08–2.77 (m, 3H), 2.12–1.55 (m, 8H), 1.55–1.15 (m, 10H), 0.99–0.9 (t, 3H, J = 7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.4, 129.1, 59.4, 46.6, 36.5, 31.9, 29.8, 29.5, 27.5, 27.1, 25.5, 20.6, 14.5.

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