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Efficient Catalytic Enantioselective Synthesis of Unsaturated Amines: Preparation of Small- and Medium-Ring Cyclic Amines through Mo-Catalyzed Asymmetric Ring-Closing Metathesis in the Absence of Solvent

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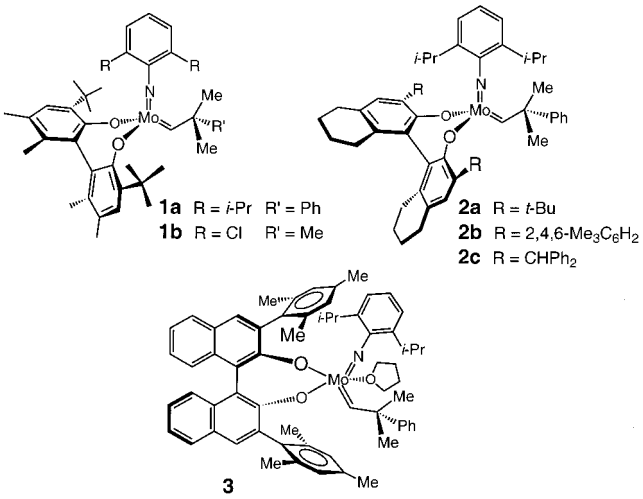
Abstract: The first catalytic asymmetric ring-closing metathesis method for the synthesis of N-containing heterocycles is reported; this is accomplished through Mo-catalyzed kinetic resolution or desymmetrization of unsaturated amines. Importantly, this catalytic asymmetric method delivers medium-ring unsaturated amines (including eight-membered rings) in high yield, with exceptional enantioselectivity and without the need for solvents. These enantioselective reactions can be effected by catalysts prepared in situ from commercially available reagents.

Introduction

An assortment of Mo-based catalysts (e.g., **1**−**3**, Chart 1) are now available that promote asymmetric ring-closing metathesis (ARCM),[1−3] allowing access to small-ring nonracemic carbocycles and oxygen-containing heterocycles. The first examples of catalytic asymmetric ring-opening metathesis (AROM), which may be followed by a tandem ring-closing[4] or cross metathesis,[5,6] have been outlined as well. Moreover, recent efforts have focused toward rendering the Mo-catalyzed asymmetric transformations practical: methods for in situ formation of chiral catalysts[7] and the development of the first polymer-supported chiral Mo-based metathesis catalyst[8] were recently disclosed.

Chart 1



Despite such advances, a number of critical issues remain to be addressed. One relates to the development of efficient catalytic asymmetric methods for enantioselective synthesis of N-containing compounds. The significance of such protocols would be because (i) amines are building blocks commonly found in medicinally important agents and (ii) there are relatively few efficient catalytic asymmetric methods for synthesis of chiral amines (particularly those not available by catalytic hydrogenation).[9] Herein, we disclose the first examples of catalytic ARCM

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(1) For recent reports on Mo-catalyzed ARCM, see: (a) Alexander, J. B.; La, D. S.; Cefalo, D. R.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 4041−4042. (b) La, D. S.; Alexander, J. B.; Cefalo, D. R.; Graf, D. D.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 9720−9721. (c) Zhu, S.; Cefalo, D. R.; La, D. S.; Jamieson, J. Y.; Davis, W. M.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 8251−8259. (d) Weatherhead, G. S.; Houser, J. H.; Ford, J. G.; Jamieson, J. Y.; Schrock, R. R.; Hoveyda, A. H. *Tetrahedron Lett.* **2000**, *41*, 9553−9559. (e) Schrock, R. R.; Jamieson, J. Y.; Dolman, S. J.; Miller, S. A.; Bonitatebus, P. J., Jr.; Hoveyda, A. H. *Organometallics* **2002**, *21*, 409−417.
(2) For an overview of catalytic enantioselective olefin metathesis, see: Hoveyda, A. H.; Schrock, R. R. *Chem. Eur. J.* **2001**, *7*, 945−950.
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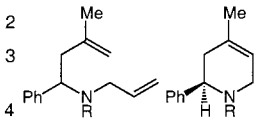
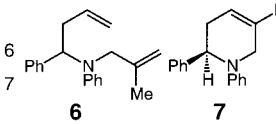
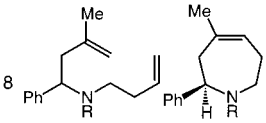
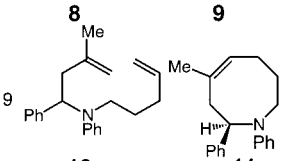
(5) (a) La, D. S.; Ford, J. G.; Sattely, E. S.; Bonitatebus, P. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 11603−11604. (b) La, D. S.; Sattely, E. S.; Ford, J. G.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2001**, *123*, 7767−7778.
(6) For a recent report on Ru-catalyzed AROM/CM, see: Van Veldhuizen, J. J.; Garber, S. B.; Kingsbury, J. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 4954−4955.
(7) Aeilts, S. L.; Cefalo, D. R.; Bonitatebus, P. J., Jr.; Houser, J. H.; Hoveyda, A. H.; Schrock, R. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1452−1456.
(8) Hultzsch, K. C.; Jernelius, J. A.; Hoveyda, A. H.; Schrock, R. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 589−593.

Table 1. Catalytic Kinetic Resolution of Acyclic Amines by ARCM[a]

entry	substrate	product		additive	time (h); conv (%)[b]	k_{rel}
1			**a** R = Ph	none	0.2; 21	3
2				diallyl ether	0.2; 18	8
3				ethylene (1 atm)	***0.1; 32***	***17***
4	**4**	**5**		none	12; 10	4
5			**b** R = *p*-OMeC$_6$H$_4$	ethylene (1 atm)	***12; 43***	***13***
6				none	0.2; 35	3
7				ethylene (1 atm)	0.1; 25	<2
	6	**7**				
8			R = *o*-OMeC$_6$H$_4$	none	***6; 30***	***13***
	8	**9**				
9				none	***6; 41***	***>50***
	10	**11**				

[a] Conditions: 5 mol % **1a**, C_6H_6, 22 °C. [b] Conversions to product determined by 400 MHz ^{1}H NMR analysis. Enantioselectivities determined by HPLC analysis (Chiralpak AD for entries 1−3, 6−7, Chiralcel OJ for entries 4, 5, and 8 and Chiralcel OD for entry 9).

reactions that provide unique, efficient, and highly enantioselective routes for preparation of functionalizable small- and medium-ring unsaturated amines that are not easily prepared in the optically enriched form by other methods.[10] Use of solvent is not required even when eight-membered ring products are prepared (<2% homocoupled products); this is particularly important since extensive efforts to synthesize cyclooctenes and oxacins by ARCM have only resulted in the formation of homodimeric adducts.[11] Indeed, on several additional fronts, the present studies demonstrate that catalytic ARCM of N-containing substrates should not be viewed as extensions of their hydrocarbon or oxygen-containing analogues. Reactivity and selectivity are dependent on the choice of the amine substituent (e.g., R in **4**, Table 1) which is not present with the previously reported non-amine systems. In addition, the results described below illustrate that the reactivity profiles of chiral Mo catalysts (e.g., **1**−**3**) may not be based on the parent achiral complex Mo(CHCMe$_2$Ph)(N(2,6-(*i*-Pr)$_2$C$_6$H$_3$))(OCMe(CF$_3$)$_2$)$_2$.[12] Amines that readily react with the achiral catalyst can be completely unreactive with chiral Mo catalysts.

Results and Discussion

1. Mo-Catalyzed Kinetic Resolution of Acyclic Amines. We began our studies by probing the Mo-catalyzed ARCM of tertiary amines by examination of catalytic kinetic resolutions of diene **4a** (Table 1, entries 1−3).[13] Initial studies, involving complexes that include those shown in Chart 1, clearly indicated that, whereas various derivatives of **4** such as the corresponding benzylamine and tosylamide react readily with the achiral Mo complex (see above),[14] none of the available chiral catalysts provide high reactivity and selectivity except with unsaturated arylamines (e.g., **4a**,**b**). Subsequent catalyst screening indicated that a number of chiral Mo complexes promote efficient ring closure of **4a** and that catalyst **1a** delivers a measurable amount of asymmetric induction (k_{rel} = 3). We judged that since the chiral complex likely first reacts with the less substituted terminal alkene in **4a** and may not differentiate between the matched and mismatched enantiomers, additives that facilitate the reversible Mo−alkylidene formation should prove beneficial (minimization of RCM of the mismatched isomer). Accordingly, on the basis of previous studies in these laboratories,[15] we examined the effect of diallyl ether (entry 2, Table 1) and ethylene (entry 3) on the rate and selectivity of the ARCM reactions. The presence of both additives leads to more facile ring closures and significant improvement in the efficiency of the kinetic resolution (k_{rel} = 17, entry 3). A similar trend is observed with diene **4b**, bearing the more electron-rich aryl unit. The importance of the nature of the amine substituent became further evident, as the reaction of **4b** proved to be noticeably less facile than that of **4a** (compare entry 1 vs 4, Table 1). Transposition of the terminal and 1,1-disubstituted olefin of the substrate gives rise to significant reduction in the efficiency of the resolution (**6**→**7**, entry 6−7). As illustrated in entries 8−9, **8** and **10** undergo kinetic resolution (k_{rel} = 13 and >50, respectively), giving rise to unsatuated azepine and azocine **9** and **11**.[16] Catalytic ARCM of **8** and **10** proceed with high selectivity without diallyl ether or ethylene; these two additives, in contrast to the previous cases, cause significant lowering of reaction efficiencies.[17]

2. Mo-Catalyzed Enantioselective Synthesis of Unsaturated Cyclic Amines. a. Enantioselective Synthesis of Six-Membered Ring Amines. At this point, we turned our attention to the enantioselective syntheses of cyclic unsaturated amines by desymmetrization processes. Triene **12** (Table 2) was prepared and the ability of chiral complexes (e.g., **1**−**3**) to promote its ARCM to afford **13** was examined. As the data in Table 2 indicate, these studies point to complexes **1a** and **2a**[1e] as the most effective catalysts. Since chiral biphenolate **1a** provides the highest levels of reactivity and enantioselectivity, it was selected for further examination.

(9) (a) Enders, D.; Reinhold: U. *Tetrahedron*: *Asymmetry* **1997**, *8*, 1895−1946. (b) Kobayashi, S.; Ishitani, H. *Chem. Rev.* **1999**, *99*, 1069−1094. (c) Porter, J. R.; Traverse, J. F.; Hoveyda, A. H.; Snapper, M. L. *J. Am. Chem. Soc.* **2001**, *123*, 10409−10410 and references therein.

(10) For a review on metal-catalyzed approaches to the synthesis of medium-ring structures, see: Yet, L. *Chem. Rev.* **2000**, *100*, 2963−3007.

(11) Unpublished results of A. F. Kiely. For enantioselective synthesis of seven-membered oxygen-containing heterocycles through Mo-catalyzed ARCM, see: Kiely, A. F.; Jernelius, J. A.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 2868−2869.

(12) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875−3886.

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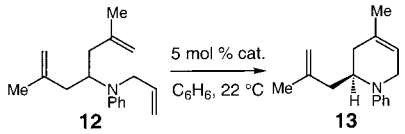
(14) For examples of RCM of amines catalyzed by **3**, see: (a) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 7324−7325. (b) Lee, K. L.; Goh, J. B.; Martin, S. F. *Tetrahedron Lett.* **2001**, *42*, 1635−1638. (c) Phillips, A. J.; Abell, A. D. *Aldrichimica Acta* **1999**, *32*, 75−89 and references therein.

(15) (a) Harrity, J. P. A.; Visser, M. S.; Gleason, J. D.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1997**, *119*, 1488−1489. (b) Harrity, J. P. A.; La, D. S.; Cefalo, D. R.; Visser, M. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1998**, *120*, 2343−2351. (c) Reference 4a.

(16) For entries 8−9, in addition to 30−45% cyclized product, ∼25% homocoupled products were also formed. Calculation of k_{rel} values (Kagan, H. B.; Fiaud, J. C. *Top. Stereochem.* **1988**, *18*, 249−330) is only an approximation of the relative rates of reactions of the two enantiomers, as it is based on a first-order equation, where a simultaneous process (homodimerization) does not occur.

(17) The adverse effect of diallyl ether and ethylene may be due to the slower rate of ring closure (intermediate alkylidene is capped before reacting with the neighboring 1,1-disubstituted alkene). This is not the case with **4**, due to faster rates of intramolecular reactions.

Table 2. Catalyst Screening for Desymmetrization of Unsaturated Amines by ARCM

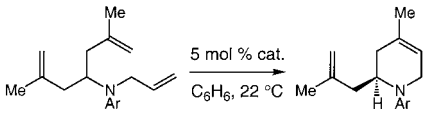


entry	catalyst	conv (%);[a] time (h)	ee (%)[b]
1	**1a**	95; 0.3	98
2	**1b**	95; 0.3	91
3	**2a**	95; 1	94
4	**2b**	95; 23	80
5	**2c**	95; 1	61
6	**3**	84; 23	51

[a] Conversions determined by 400 MHz ^{1}H NMR analysis. [b] Enantioselectivities determined by HPLC analysis (Chiralcel OJ column).

As shown in Table 3, in the presence of 5 mol % **1a**, **12** can be readily converted to **13** in 98% ee and 78% isolated yield (20 min, 22 °C; entry 1, Table 3). Amines bearing *p*-OMe (**14**→**15**) and *p*-Br (**16**→**17**) phenyl groups can be prepared efficiently and in ≥ 97% ee as well (Table 3, entries 2−3). When arylamines that bear an ortho substituent were examined (entries 4−5, Table 3), <5% conversion was observed (5 mol % **1a**). However, when catalyst screening was performed with this set of substrates, it was established that with 5 mol % chiral binaphtholate complex **2c**, ARCM of **18** and **20** proceeds to >98% conversion within 20 min to afford **19** and **21** in 84 and 82% ee, respectively. The data in Table 3 further underline the significant influence that the amine substituent can exert on the observed levels of enantioselectivity (e.g., entry 2 vs 4).[18]

Table 3. Asymmetric Synthesis of Unsaturated Six-Membered Ring Amines by Mo-Catalyzed ARCM[a]

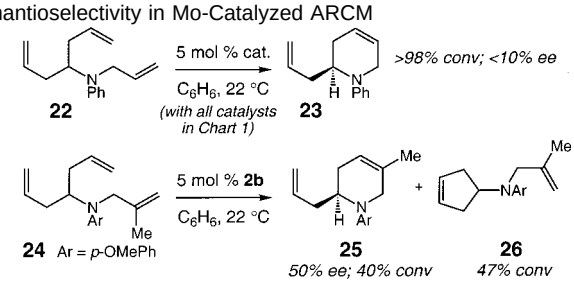


entry		substrate	product	catalyst	conv (%);[b] yield (%)[c]	ee (%)[d]
1	**12**	Ar = Ph	**13**	**1a**	95; 78	98
2	**14**	Ar = *p*-OMePh	**15**	**1a**	97; 81	97
3	**16**	Ar = *p*-BrPh	**17**	**1a**	>98; 81	98
4	**18**	Ar = *o*-OMePh	**19**	**2c**	>98; 77	84
5	**20**	Ar = *o*-BrPh	**21**	**2c**	>98; 90	82

[a] Conditions: 5 mol % catalyst, C_6H_6, 22 °C, 20−25 min. [b] Conversions to product determined by 500 MHz ^{1}H NMR analysis. [c] Isolated yields after purification. [d] Enantioselectivities determined by HPLC analysis (Chiralcel OJ for entries 1−2 and Chiralpak AD for entries 3−5).

b. Effect of Olefin Substitution on Catalytic ARCM Enantioselectivity. The reactivity and selectivity levels of catalytic desymmetrizations shown in Table 3 are sensitive to the substitution pattern of the olefins within a substrate. As illustrated in Scheme 1, similar to the more substituted triene **12** (entry 1, Table 2), the all-terminal **22** readily undergoes ring closure in the presence 5 mol % of the catalysts depicted in Chart 1; however, **23** is obtained in <10% ee in the presence of all catalysts in Chart 1.[19] In reactions involving triene **24**, ring closure is significantly slower than that of **12**, the product mixture is often contaminated with the cyclopentene **26**, and

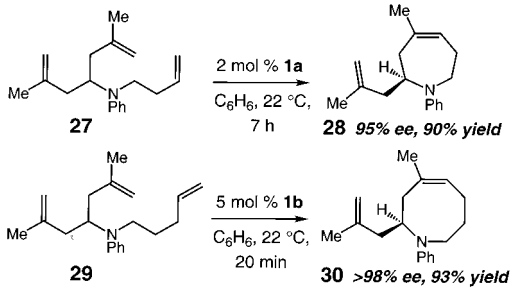
Scheme 1. Effect of Olefin Substitution on Levels of Enantioselectivity in Mo-Catalyzed ARCM



the most appreciable enantioselectivity observed for the formation of **25** is 50% ee with 5 mol % **2b**.

c. Enantioselective Synthesis of Seven- and Eight-Membered Ring Amines. Catalytic asymmetric synthesis of medium-ring unsaturated amines can be accomplished efficiently and with excellent enantioselectivity. As depicted in Scheme 2, chiral catalyst **1a** promotes the formation of the seven-membered ring amine **28** in 95% ee and 90% isolated yield. Perhaps more importantly, the Mo-catalyzed ARCM of **29**, effected in the presence of 5 mol % **1b**, delivers optically pure (>98% ee) eight-membered cyclic amine **30** in 93% yield after silica gel chromatography. *The facile asymmetric synthesis of **30** is particularly noteworthy, as it stands in contrast to our repeated attempts in accomplishing related enantioselective syntheses of eight-membered ring carbo- or oxygen-containing heterocycles, including substrates that benefit from reinforcing entropic factors.*[11] Catalytic ARCM of **27** and **29** (Scheme 2) are expectedly more facile with the more Lewis acidic complex **1b** (20 min vs 7−8 h for >95% conv at 22 °C with **1a**). However, whereas formation of **28** is more selective with **1a** (95% ee vs 87% ee with **1b**), **30** is formed as a single enantiomer when **1a** or **1b** is employed as the catalyst. Such observations, in addition to those depicted in Table 3 (above), point to the critical significance of the modularity of this class of chiral catalysts, allowing a range of chiral complexes to be available for screening.[1g,20]

Scheme 2. Enantioselective Synthesis of Medium-Ring Amines by Catalytic ARCM



d. Some Practical Aspects of Asymmetric Amine Synthesis. Several additional factors need to be mentioned that render the present catalytic enantioselective method of particular utility in asymmetric synthesis:

(1) On the basis of a recently reported procedure,[7] asymmetric amine syntheses can be carried out with catalysts prepared in situ, without prior isolation, from commercially available starting materials (not further purified). As an example, cyclic amine

(18) The stereochemical identity of cyclic amine **17** was established by X-ray crystallography; other stereochemical assignments in this study are by inference.

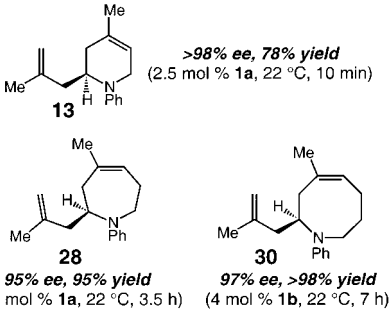
(19) Cyclopentene product from ring-closing metathesis was not observed in all instances (<2%).

(20) For a related discussion, see: Shimizu, K. D.; Snapper, M. L.; Hoveyda, A. H. *Chem. Eur. J.* **1998**, *4*, 1885−1889.

17 (Table 2) was synthesized by the in situ protocol in 90% ee and 94% isolated yield.

(2) Reactions can be carried out *in the absence of solvent* to afford products of high optical purity in an efficient and environmentally friendly manner. Particularly impressive are the Mo-catalyzed ARCM that deliver medium-ring amines (Scheme 3) in high optical purity and excellent yields without contamination by homodimeric or oligomeric products (<2%). It is noteworthy that monitoring of the reaction progress indicated that homodimeric products are formed initially during formation of **28** and **30**. Prolonged reaction times, however, allow for reversion[21] of such acyclic compounds to monomeric entities that eventually undergo ring closure to afford the cyclic trisubstituted alkenes.[22] The final products, due to the lack of reactivity of trisubstituted alkenes, are not prone to ring-opening metathesis.[21]

Scheme 3. Products from Catalytic ARCM Performed without Solvent



Conclusions

The present catalytic asymmetric metathesis protocol provides a unique and effective method for enantioselective synthesis of difficult-to-access cyclic amines. Catalytic kinetic resolution of trienes delivers optically enriched or pure acyclic and cyclic unsaturated amines. More importantly, a variety of small- and medium-ring unsaturated N-containing heterocycles can be synthesized through Mo-catalyzed asymmetric metathesis efficiently and with exceptional levels of enantioselectivity. That catalytic enantioselective syntheses of even medium-ring amines can be carried out in the absence of solvent renders this method particularly attractive from the environmental point of view. The availability of the in situ catalyst synthesis further enhances the practicality of the Mo-catalyzed protocol.

Development of additional methods for enantioselective synthesis of amines by catalytic olefin metathesis, applications to target-oriented synthesis and examination of related mechanistic issues are in progress and will be reported in due course.

Experimental Section

General. Infrared (IR) spectra were recorded on Perkin-Elmer 781 and ThermoNicolet Avatar 360 spectrophotometers, ν_{max} in cm^{-1}. Bands were characterized as broad (br), strong (s), medium (m), and weak (w). ^1H NMR spectra were recorded on Unity 300 (300 MHz), Varian VXR 500 (500 MHz), or Varian Gemini 2000 (400 MHz) spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (C_6D_6: δ 7.16, $CDCl_3$: δ 7.26). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), integration, and assignment. ^{13}C NMR spectra were recorded on Varian VXR 500 (125 MHz), Bruker 400 (100 MHz), and Varian Gemini 2000 (100 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal reference (C_6D_6: δ 128.4, $CDCl_3$: δ 77.7). Enantiomer ratios were determined by chiral HPLC (Chiral Technologies Chiralcel OJ (4.6 mm θ × 250 mm), Chiralcel OD (4.6 mm θ × 250 mm), Chiralpak AD (4.6 mm θ × 250 mm), or Chiralpak AS (4.6 mm θ × 250 mm)) in comparison with authentic racemic materials. Microanalyses were performed by Robertson Microlit Laboratories (Madison, NJ). High-resolution mass spectrometry was performed at the Massachusetts Institute of Technology, Department of Chemistry, Instrumentation Facility (Cambridge, MA) and at the University of Illinois Mass Spectrometry Laboratories (Urbana-Champaign, IL).

All reactions were conducted in oven- (135 °C) or flame-dried glassware under an inert atmosphere of dry N_2. All metathesis substrates were vigorously dried by repeated (three times) azeotropic distillation of water under high vacuum using benzene or stored over molecular sieves under a N_2 atmosphere. Handling of all Mo catalysts was performed in a drybox. Et_2O, toluene, and pentane were sparged with N_2 and then passed through an activated alumina column. Tetrahydrofuran, CH_2Cl_2, and benzene were sparged with N_2 and then passed through an activated alumina column or distilled from sodium/benzophenone ketal. Benzyl potassium was prepared by the literature method.[23] All reagents were used as received from Aldrich Chemical Co., Lancaster Synthesis, or Strem Chemicals, Inc. unless otherwise stated. Mo complexes **1a**,[1a] **2a**,[7] **1b**, **2b**, **2c**, and **3**[1e] were prepared according to published procedures.

Representative Procedure for Mo-Catalyzed Kinetic Resolution. The following procedure was performed entirely in a N_2 glovebox. A flask was charged with but-3-enyl(2-methoxyphenyl)-3-methyl-1-phenyl-but-3-enyl)amine (**8**) (250 μL of a 0.2 M solution in C_6H_6). A freshly prepared solution of **1a** (250 μL of a 0.01 M solution in C_6H_6) was then added through a syringe. A Teflon cap was used to securely seal the vial, and the reaction was stirred for 6 h. The reaction was subsequently removed from the glovebox and quenched by the addition of 0.5 mL of wet (nondistilled) Et_2O. The resulting solution was concentrated with N_2 purge to give a brown residue. Analysis of the mixture by ^1H NMR spectroscopy revealed 30% conversion to the desired product ((2-methoxyphenyl)-4-methyl-2-phenyl-2,3,6,7-tetrahydro-1*H*-azepine) (**9**) and 32% conversion to a mixture of cis and trans homodimers derived from the starting material (*N*,*N*′-bis(2-methoxyphenyl)-*N*,*N*′-bis(3-methyl-1-phenyl-but-3-enyl)hex-3-ene-1,6-diamine). The sample was purified by silica gel chromatography (40:1 pentane:Et_2O to 15:1 pentane:Et_2O). The ring-closed product and the starting material were analyzed by HPLC to establish enantiopurity.

Allyl(3-methyl-1-phenyl-but-3-enyl)phenylamine (4a): IR (Neat) 3057 (m), 2934 (m), 1658 (w), 1597 (s), 1510 (s), 1449 (m), 1393 (m), 1258 (m), 1171 (w); ^1H NMR (400 MHz, $CDCl_3$) δ 7.29−7.27 (m, 4H, Ar**H**), 7.24−7.17 (m, 3H, Ar**H**), 6.84−6.81 (m, 2H, Ar**H**), 6.71 (tt, J = 7.3, 0.9 Hz, 1H, Ar**H**), 5.69 (dddd, J = 17.2, 10.4, 5.1, 5.1 Hz, 1H, RC**H**=CH_2), 5.20 (dd, J = 7.3, 7.3 Hz, 1H, ArC**H**NAr), 5.09 (dddd, J = 17.4, 1.7, 1.7, 1.7 Hz, 1H, RHC=C**H**$_A$H$_B$), 5.02 (dddd, J = 10.3, 1.7, 1.7, 1.7 Hz, 1H, RHC=CH$_A$**H**$_B$), 4.79 (s(br), 1H, RC(CH$_3$)=C**H**$_A$H$_B$), 4.71 (s(br), 1H, RC(CH$_3$)=CH$_A$**H**$_B$), 3.78 (ABqddd, J = 17.0, 5.3, 1.8, 1.8 Hz, 2H, ArNC**H**$_A$**H**$_B$), 2.72 (ABqd, J = 15.6, 8.2 Hz, 2H, ArCHC**H**$_A$**H**$_B$), 1.75 (s(br), 3H, RC(C**H**$_3$)); ^{13}C NMR (100

(21) For previous reports involving the reversibility of olefin metathesis reactions, see: (a) Xu, Z.; Johannes, C. W.; Houri, A. F.; La, D. S.; Cogan, D. A.; Hofilena, G. E.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1997**, *119*, 10302−10316. (b) Marsella, N. J.; Maynard, H. D.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1101−1103. For a more recent application, see: (c) Smith, A. B.; Adams, C. M.; Kozmin, S. A. *J. Am. Chem. Soc.* **2001**, *123*, 990−991.

(22) As an example, in the catalytic ARCM of **27**, after 30 min and with 2.5 mol % **1a**, there is 12% unreacted substrate, 18% **27** and 60% of homodimeric adducts. After 3.5 h, 25% of the homodimer and 75% product is detected. Since no further conversion occurred after 5 h, another 1 mol % of **1a** was added which caused the reaction to proceed to >98% conversion to **28**.

(23) Lochmann, L.; Trekoval, J. *J. Organomet. Chem.* **1987**, *326*, 1−7.

MHz, $CDCl_3$) δ 149.5, 143.2, 141.7, 136.9, 129.5, 128.8, 128.3, 127.6, 117.6, 116.5, 114.8, 113.5, 60.6, 49.5, 40.6, 23.7. HRMS Calcd for $C_{20}H_{23}N$: 277.1830. Found: 277.1827. Anal. Calcd for $C_{20}H_{23}N$: C, 86.59; H, 8.36; N, 5.05. Found: C, 86.77; H, 8.40; N, 5.28.

Allyl(4-methoxyphenyl)(3-methyl-1-phenyl-but-3-enyl)amine (4b): IR (Neat) 3087 (w), 2949 (m), 2848 (w), 2383 (w), 1665 (w), 1527 (s), 1457 (m), 1250 (s), 1055 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16−7.13 (m, 2H, Ar**H**), 7.11−7.06 (m, 2H, Ar**H**), 7.04−6.99 (m, 1H, Ar**H**), 6.80 (**AA′XX′**, J = 9.3, 2.9 Hz, 2H, Ar**H**), 6.74 (AA′**XX′**, J = 9.3, 2.9 Hz, 2H, Ar**H**), 5.70 (dddd, J = 17.2, 10.3, 5.7, 5.7 Hz, 1H, RC**H**=CH_2), 4.98 (dddd, J = 17.4, 1.8, 1.8, 1.8 Hz, 1H, RCH=C**H**$_A$H$_B$), 4.89 (dddd, J = 10.3, 1.8, 1.8, 1.8 Hz, 1H, RCH=CH$_A$**H**$_B$) 4.80 (dd, J = 7.3, 7.3 Hz, 1H, ArNC**H**Ar), 4.74−4.80 (m, 1H, RC(CH$_3$)=C**H**$_A$H$_B$), 4.69 (s(br), 1H, RC(CH$_3$)=CH$_A$**H**$_B$), 3.59 (ABddd, J = 16.3, 5.1, 1.7, 1.7 Hz, 1H, ArNC**H**$_A$H$_B$R), 3.43 (ABdddd, J = 16.3, 5.7, 1.7, 1.7 Hz, 1H, ArNCH$_A$**H**$_B$R), 3.31 (s(br), 3H, OC**H**$_3$), 2.59 (ABd, J = 14.8, 7.1 Hz, 1H, ArCHC**H**$_A$H$_B$), 2.45 (ABd, J = 14.7, 7.7 Hz, 1H, ArCH-CH$_A$**H**$_B$), 1.55 (s(br), 3H, RC(C**H**$_3$)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 143.5, 143.2, 141.6, 137.2, 128.4, 128.3, 127.3, 120.2, 116.0, 114.7, 113.1, 63.4, 55.1, 50.7, 40.8, 22.9. HRMS Calcd for $C_{21}H_{25}NO$: 307.1936. Found: 307.1930. Anal. Calcd for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56. Found: C, 82.11; H, 8.24; N, 4.69.

(2-Methyl-allyl)phenyl(1-phenyl-but-3-enyl)amine (6): IR (Neat) 3069 (m), 3031 (m), 2980 (m), 2943 (m), 2861 (m), 1652 (w), 1615 (s), 1514 (s), 1457 (m), 1382 (m), 1243(m), 935 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.16 (m, 7H, Ar**H**), 6.80−6.77 (m, 2H, Ar**H**), 6.72 (tt, J = 7.3, 1.0 Hz, 1H, Ar**H**), 5.85 (dddd, J = 17.0, 10.1, 7.0, 7.0 Hz, 1H, RC**H**=CH_2), 5.11 (dddd, J = 17.2, 1.6, 1.6, 1.6 Hz, 1H, RCH=C**H**$_A$H$_B$), 5.05−5.00 (m, 2H, RCH=CH$_A$**H**$_B$, ArNC**H**Ar), 4.81−4.80 (m, 1H, RC(CH$_3$)=C**H**$_A$H$_B$), 4.76−4.75 (m, 1H, RC(CH$_3$)=CH$_A$**H**$_B$), 3.59 (ABq, J = 17.6 Hz, 2H, ArNC**H**$_A$**H**$_B$R), 2.84−2.72 (m, 2H, C**H**$_2$CH=CH_2), 1.57 (s(br), 3H, RC(C**H**$_3$)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 142.4, 141.4, 136.7, 129.5, 128.9, 128.6, 127.8, 118.1, 117.6, 115.6, 112.0, 63.3, 52.9, 36.8, 20.9. HRMS Calcd for $C_{20}H_{23}N$: 277.1830. Found: 277.1835. Anal. Calcd for $C_{20}H_{23}N$: C, 86.59; H, 8.36; N, 5.05. Found: C, 86.41; H, 8.31; N, 5.21.

But-3-enyl(2-methoxyphenyl)-3-methyl-1-phenyl-but-3-enyl)-amine (8): IR (Neat) 3081 (m), 2924 (s), 2846 (m), 1654 (m), 1604 (m), 1497 (s), 1462 (s), 1245 (s), 1033 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.18 (m, 5H, Ar**H**), 7.06−7.01 (m, 1H, Ar**H**), 6.90−6.82 (m, 3H, Ar**H**), 5.70−5.60 (m, 1H, RC**H**=CH_2), 4.87 (s(br), 1H, RCH=C**H**$_A$H$_B$), 4.85−4.82 (m, 1H, RCH=CH$_A$**H**$_B$), 4.65−4.61 (m, 2H, ArNC**H**Ar, RC(CH$_3$)=C**H**$_A$H$_B$), 4.52 (s(br), 1H, RC(CH$_3$)=CH$_A$**H**$_B$), 3.87 (s(br), 3H, OC**H**$_3$), 3.03−2.96 (m, 1H, ArNC**H**$_A$H$_B$R), 2.86−2.79 (m, 1H, ArNCH$_A$**H**$_B$R), 2.56−2.54 (m, 2H, ArCHC**H**$_2$), 1.99−1.84 (m, 2H, ArNCH$_2$C**H**$_2$R), 1.50 (s(br), 3H, RC(C**H**$_3$)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 143.5, 141.6, 138.1, 137.2, 128.8, 127.8, 126.9, 125.9, 124.1, 120.6, 115.2, 112.6, 112.1, 64.2, 55.7, 46.8, 41.0, 32.6, 22.8. HRMS Calcd for $C_{22}H_{27}NO$: 321.2093. Found: 321.2092. Anal. Calcd for $C_{22}H_{27}NO$: C, 82.20; H, 8.47; N, 4.36. Found: C, 81.91; H, 8.38; N, 4.12.

(3-Methyl-1-phenyl-but-3-enyl)pent-4-enyl-phenylamine (10): IR (Neat) 3074 (m), 2936 (s), 1659 (w), 1608 (s), 1501 (s), 1457 (m), 1375 (m), 1281 (m), 897 (m), 752 (s), 702 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.29 (m, 3H), 7.27−7.21 (m, 4H), 6.82 (d, J = 8.4 Hz, 2H), 6.7 (t, J = 7.3 Hz, 1H), 5.69 (dddd, J = 17.2, 10.3, 7.0, 7.0, 1H), 5.14 (dd, J = 7.3, 7.3 Hz, 1H), 4.95−4.90 (m, 2H), 4.78 (s(br), 1H), 4.72 (s(br), 1H), 3.15−3.00 (m, 2H), 2.76 (ABq, J = 15.4, 7.7 Hz, 1H), 2.67 (ABd, J = 15.0, 7.3 Hz, 1H), 1.91 (ABq, J = 7.3 Hz, 2H), 1.74 (s(br), 3H), 1.61−1.51 (m, 1H), 1.41−1.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 143.3, 141.7, 138.6, 129.7, 128.7, 128.5, 127.6, 117.5, 115.3, 115.1, 113.3, 61.3, 46.1, 40.2, 32.1, 27.7, 23.8. HRMS Calcd for $C_{22}H_{27}N$: 305.2143. Found: 305.2147.

Representative Procedure for a Kinetic Resolution using Diallyl Ether as an Additive. A procedure analagous to that for a typical kinetic resolution was followed with one exception. Before addition of the catalyst to begin the reaction, diallyl ether (6.11 mL, 0.0500 mmol, 1 equiv to starting material), distilled from CaH_2, was added via syringe to the starting material solution. In the above instance, analysis of the crude reaction ^{1}H NMR spectrum indicated only 20% conversion to a mixture of cis and trans dimer (*N*,*N*′-bis(2-methoxyphenyl)-*N*,*N*′-bis(3-methyl-1-phenyl-but-3-enyl)hex-3-ene-1,6-diamine).

Representative Procedure for Kinetic Resolution under an Ethylene Atmosphere. Solutions of starting material and catalyst were prepared in a glovebox as follows: A solution of allyl(3-methyl-1-phenyl-but-3-enyl)phenylamine (**4a**) (320 μL of a 0.2 M solution in C_6H_6) was placed in a flask and sealed securely with a septum. A separate vessel equipped with a stir bar was charged with a solution of **1a** (250 μL of a 0.01 M solution in C_6H_6). This flask was also sealed completely with a septum and Teflon tape. Both reaction vessels were removed from the glovebox. The flask containing the catalyst solution was connected to a full ethylene (99.99% anhydrous) balloon and purged for 5 s through an exit needle. (The balloon apparatus consisted of a triple-layered balloon connected to a short drying tube containing dryrite, which was fitted with an 18-gauge needle. The entire apparatus was assembled in the glovebox so as to exclude any air or moisture and then removed from the N_2 atmosphere and purged three times with anhydrous ethylene before filling.) The vessel containing the starting material solution was connected to a N_2 manifold. A portion of this solution (300 μL) was transferred to the catalyst solution by an airtight syringe that was first carefully purged with N_2. The mixture was stirred under an ethylene atmosphere for 10 min before 0.5 mL of wet Et_2O was added to deactivate the catalyst. The resulting solution was concentrated with a N_2 purge to give a brown residue. ^{1}H NMR analysis indicated 40% conversion to the desired product, 4-methyl-1,2-diphenyl-1,2,3,6-tetrahydropyridine (**5b**) and 60% unreacted starting material. The sample was concentrated in vacuo and then diluted with 0.5 mL of hexanes. The solution was then passed through a plug of Celite and charcoal to remove residual metal impurities. The resulting filtrate was analyzed by HPLC to establish product enantioselectivity. Isolation of the desired product from the reaction mixture was accomplished by silica gel chromatography (50:1 pentane:Et_2O).

4-Methyl-1,2-diphenyl-1,2,3,6-tetrahydropyridine (5a): IR (Neat) 2966 (m), 2930 (m), 2797 (m), 1600 (s), 1503 (s), 1449 (s), 1395 (s), 1310 (m), 1237 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.13 (m, 7H, Ar**H**), 6.86−6.83 (m, 2H, Ar**H**), 6.74 (tt, J = 7.2, 1.1 Hz, 1H, Ar**H**), 5.58−5.56 (m, 1H, C(CH$_3$)=C**H**R), 5.14 (dd, J = 6.2, 2.0 Hz, ArNC**H**Ar), 3.89 (ABm, J = 16.5 Hz, 1H, ArNC**H**$_A$H$_B$), 3.61 (ABm, J = 16.5 Hz, 1H, ArNCH$_A$**H**$_B$), 2.81 (ABm, J = 16.6 Hz, 1H, ArCHC**H**$_A$H$_B$), 2.41 (AB(br), J = 16.6 Hz, 1H, ArCHCH$_A$**H**$_B$), 1.75 (s(br), 3H, RC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 142.9, 131.9, 129.8, 128.8, 127.5, 127.3, 119.5, 118.5, 115.3, 56.5, 45.6, 36.2, 24.0. HRMS Calcd for $C_{18}H_{19}N$: 249.1517. Found: 249.1517.

1-(4-Methoxyphenyl)-4-methyl-2-phenyl-1,2,3,6-tetrahydropyridine (5b): IR (Neat) 3069 (w), 2930 (m), 2842 (m), 1514 (s), 1457 (m), 1250 (s), 1055 (m), 815 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21−7.11 (m, 5H, Ar**H**), 6.84 (**AA′XX′**, J = 9.3, 2.9 Hz, 2H, Ar**H**), 6.74 (AA′**XX′**, J = 9.3, 2.9 Hz, 2H, Ar**H**), 5.56 (s(br), 1H, C(CH$_3$)=C**H**R), 4.83 (dd, J = 5.9, 3.7 Hz, 1H, ArNC**H**Ar), 3.70 (s, 3H, OC**H**$_3$), 3.68−3.60 (m, 1H, ArNC**H**$_A$H$_B$), 3.56−3.48 (m, 1H, ArNCH$_A$**H**$_B$), 2.70 (ABm, J = 16.8 Hz, 1H, ArCHC**H**$_A$H$_B$), 2.37 (ABm, J = 16.8 Hz, 1H, ArCHCH$_A$**H**$_B$), 1.77 (s, 3H, RC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 145.1, 142.6, 132.4, 128.7, 127.9, 127.3, 120.0, 119.7, 115.0, 59.2, 56.2, 48.1, 37.1, 23.8. HRMS Calcd for $C_{19}H_{21}NO$: 279.1623. Found: 279.1625.

5-Methyl-1,2-diphenyl-1,2,3,6-tetrahydropyridine (7): IR (Neat) 3025 (m), 2911 (m), 2851 (m), 1598 (s), 1503 (s), 1449 (m), 1302 (m), 1253 (w), 1040 (w), 748 (m), 698 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.14 (m, 7H, Ar**H**), 6.87−6.84 (m, 2H, Ar**H**), 6.75 (t(br), J = 7.3 Hz, 1H, Ar**H**), 5.58−5.57 (m, 1H, C(CH$_3$)=C**H**R), 5.09 (dd, J = 6.4, 1.8 Hz, ArNC**H**Ar), 3.66 (ABq, J = 16.7 Hz, 1H, ArNC**H**$_A$H$_B$), 2.81 (ABm, J = 16.6 Hz, 1H, ArCHC**H**$_A$H$_B$), 2.53 (ABm, J = 16.7

Hz, 1H, ArCHCH$_A$**H**$_B$), 1.75 (s(br), 3H, RC**H**$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 143.1, 132.7, 129.8, 128.8, 127.5, 127.3, 118.53, 118.45, 115.2, 55.8, 49.6, 31.5, 21.6. HRMS Calcd for $C_{18}H_{19}N$: 249.1517. Found: 249.1518.

1-(2-Methoxyphenyl)-4-methyl-2-phenyl-2,3,6,7-tetrahydro-1*H*-azepine (9): IR (Neat) 3061 (w), 2955 (s), 2924 (s), 2837 (m), 1613 (m), 1495 (s), 1457 (m), 1252 (s), 1041 (s), 755 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.31 (m, 2H, Ar**H**), 7.18−7.13 (m, 2H, Ar**H**), 7.06 (tt, J = 7.2, 1.5 Hz, 1H, Ar**H**), 6.94 (dd, J = 8.1, 1.5 Hz, 1H, Ar**H**), 6.83−6.76 (m, 2H, Ar**H**), 6.70−6.66 (m, 1H, Ar**H**), 5.50−5.48 (m, 1H, C(CH$_3$)=C**H**R), 4.9 (dd, J = 9.2, 2.6 Hz, 1H, ArNC**H**Ar), 3.83 (s(br), 3H, OC**H**$_3$), 3.71 (ABdd, J = 14.5, 9.2, 2.6 Hz, 1H, ArNC**H**$_A$H$_B$), 3.56 (ABdd, J = 14.5, 7.0, 2.6 Hz, 1H, ArNCH$_A$**H**$_B$), 2.85 (ABd, J = 15.4, 9.0 Hz, 1H, ArCHC**H**$_A$H$_B$), 2.42 (ABm, J = 15.4 Hz, 1H, ArCHCH$_A$**H**$_B$), 2.47−2.38 (m, 1H, ArNCH$_2$C**H**$_A$H$_B$R), 2.16 (m, 1H, ArNCH$_2$CH$_A$**H**$_B$R), 1.69 (s(br), 3H, RC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 146.2, 141.7, 136.1, 128.6, 127.5, 126.9, 125.6, 123.0, 122.8, 121.0, 112.5, 64.3, 56.2, 51.3, 42.0, 29.2, 27.2. HRMS Calcd for $C_{20}H_{23}NO$: 293.1780. Found: 293.1780.

6-Methyl-1,8-diphenyl-1,2,3,4,7,8-hexahydroazocine (11): IR (Neat) 2932 (s), 2858 (m), 1605 (m), 1524 (s), 1401 (w), 1271 (w), 1160 (w), 752 (m), 703 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.28 (m, 2H), 7.23−7.19 (m, 3H), 7.12−7.14 (m, 2H), 6.71−6.69 (m, 2H), 6.62 (tt, J = 7.3, 0.9 Hz, 1H), 5.57 (t(br), J = 7.3 Hz, 1H), 5.14 (dd, J = 12.3, 3.8 Hz, 1H), 3.67 (ABm, J = 15.0 Hz, 1H), 3.42 (ABdd, J = 15.6, 11.9, 1.3, 1H), 2.97 (t, J = 13.0 Hz, 1H), 2.51 (dd, J = 13.6, 4.0 Hz, 1H), 2.22−2.06 (m, 2H), 1.99−1.89 (m, 1H), 1.82 (s(br), 3H), 1.3−1.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 143.07, 135.5, 129.9, 129.3, 128.0, 127.4, 127.3, 116.1, 112.0, 58.8, 48.7, 39.0, 29.4, 28.1, 24.2. HRMS Calcd for $C_{20}H_{23}N$: 278.1909. Found: 278.1912.

Representative Procedure for the Desymmetrization of Tertiary Amines through Ring-Closing Metathesis. Reaction was set up and run in a N_2 glovebox. Chiral complex **1a** (38 mg, 36 mmol) was added in one portion to a solution of allyl[3-methyl-1-(2-methyl-allyl)but-3-enyl]-4-methoxyphenylamine (**14**) (285 mg, 1.00 mmol) in C_6D_6 (1.00 mL) in a loosely capped flask equipped with a stir bar. After 20 min, ^{1}H NMR spectroscopy of an aliquot indicated the reaction was complete. The reaction was then removed from the glovebox and concentrated under reduced pressure to a brown residue. The product was purified by silica gel chromatography (pentane:Et_2O, 9:1) to give 4-methyl-2-(2-methyl-allyl)-1,4-methoxyphenyl-1,2,3,6-tetrahydropyridine (**15**) as an off-white solid, 208 mg (81% yield).

Representative Procedure for the Desymmetrization of Tertiary Amines through Ring-Closing Metathesis in the Absence of Solvent. Reaction was set up and run in a N_2 glovebox. Catalyst **1a** (19.0 mg, 25.0 mmol) was added in one portion to allyl[3-methyl-1-(2-methyl-allyl)but-3-enyl]phenylamine (**12**) (255 mg, 1.00 mmol) in a loosely capped vessel equipped with a stirbar. After 10 min, the mixture solidified. ^{1}H NMR of an aliquot (quenched by the addition of pyridine to ensure no more active catalyst remained) indicated the reaction had proceeded to >98% conversion. The desired product was obtained by silica gel chromatography (pentane:Et_2O, 97:3) to give 4-methyl-2-(2-methyl-allyl)-1-phenyl-1,2,3,6-tetrahydropyridine (**13**) as an off-white solid, 177 mg (78% yield).

4-Methyl-2-(2-methyl-allyl)-1-phenyl-1,2,3,6-tetrahydropyridine (13): IR (KBr) 3071 (m), 2835 (s), 1597 (s), 1499 (s), 1440 (m), 1385 (m), 1339 (m), 1234 (s), 1008 (m); ^{1}H NMR (500 MHz, C_6D_6) δ 7.27 (m, 2H, Ar**H**), 6.84 (m, 3H, Ar**H**), 5.27 (s(br), 1H, C**H**=CCH$_3$), 4.75 (s(br), 1H, CCH$_3$=C**H**$_a$H$_b$), 4.69 (s(br), 1H, CCH$_3$=CH$_a$**H**$_b$), 4.15 (pentet, J = 5.8 Hz, 1H, NC**H**CH$_2$), 3.59 (d(br), J = 16.8 Hz, 1H, NC**H**$_a$H$_b$CH), 3.31 (d(br), J = 16.8 Hz, 1H, NCH$_a$**H**$_b$CH), 2.28 (d(br), J = 16.0 Hz, 1H, CC**H**$_a$H$_b$C), 2.15 (dd, J = 13.3, 10.7 Hz, 1H, CCH$_a$**H**$_b$C), 2.07 (dd, J = 13.4, 4.3 Hz, 1H, CC**H**$_a$H$_b$C), 1.90 (d, J = 16.8 Hz, 1H, CCH$_a$**H**$_b$C), 1.62 (s, 3H, C**H**$_3$C), 1.55 (s, 3H, C**H**$_3$C); ^{13}C NMR (75 MHz, C_6D_6) δ 150.2, 144.2, 130.5, 129.9, 118.8, 118.4, 115.1, 113.1, 50.8, 44.1, 37.3, 32.6, 23.8, 22.7. HRMS (EI$^+$) Calcd for $C_{16}H_{21}N$: 227.1669. Found: 227.1682. Anal. Calcd. for $C_{16}H_{21}N$: C, 84.53; H, 9.31; N, 6.16. Found: sent. HPLC (Chiralcel OJ, 0.2% ^{i}-PrOH in hexane, 0 °C, 1.0 mL/min, 254 nm) 98% ee $[\alpha]^D$ = + 18.1 ± 0.1° (c = 0.95, $CHCl_3$).

4-Methyl-2-(2-methyl-allyl)-1-*p*-methoxyphenyl-1,2,3,6-tetrahydropyridine (15): IR (KBr) 3078.3 (m), 2912 (m), 1644 (m), 1512 (s), 1384 (s), 1230 (s), 1175 (s), 1039 (s); ^{1}H NMR (500 MHz, C_6D_6) δ 6.89 (m, 2H, Ar**H**), 6.81 (m, 2H, Ar**H**), 5.33 (s(br), 1H, C**H**=CCH$_3$), 4.77 (s(br), 1H, CCH$_3$=C**H**$_a$H$_b$), 4.72 (s(br), 1H, CCH$_3$=CH$_a$**H**$_b$), 4.02 (m, 1H, NC**H**CH$_2$), 3.53 (d(br), J = 16.5 Hz, 1H, NC**H**$_a$H$_b$CH), 3.40 (s, 3H, C**H**$_3$O), 3.37 (d(br), J = 16.8 Hz, 1H, NCH$_a$**H**$_b$CH), 2.36 (d(br), J = 16.5 Hz, 1H, CC**H**$_a$H$_b$C), 2.17 (dd, J = 10.1, 0.6 Hz, 1H, CCH$_a$**H**$_b$C), 2.12 (dd, J = 13.4, 4.3 Hz, 1H, CC**H**$_a$H$_b$C), 1.92 (d(br), J = 16.8 Hz, 1H, CCH$_a$**H**$_b$C), 1.65 (s, 3H, C**H**$_3$C), 1.57 (s, 3H, C**H**$_3$C); ^{13}C NMR (125 MHz, C_6D_6) δ 153.6, 144.7, 144.4, 130.7, 119.1, 117.6, 115.4, 113.0, 55.5, 52.6, 44.9, 37.0, 32.9, 23.9, 22.8. HRMS (EI$^+$) Calcd for $C_{17}H_{23}NO$: 257.1774. Found: 257.1777. Anal. Calcd. for $C_{17}H_{23}NO$: C, 79.33; H, 9.01; N, 5.44. Found: C, 79.86; H, 9.54; N, 5.18. HPLC (Chiralcel OJ, 10% ^{i}PrOH in hexane, 1.0 mL/min, 235 nm) 94% ee $[\alpha]^D$ = + 15.2 ± 0.1° (c = 1.15, $CHCl_3$).

4-Methyl-2-(2-methyl-allyl)-1-*p*-bromophenyl-1,2,3,6-tetrahydropyridine (17): IR (Neat) 3069 (m), 2926 (m), 1592 (m), 1497 (s), 1457 (m), 1388 (m), 1283 (m), 1238 (m), 1176 (m); ^{1}H NMR (500 MHz, C_6D_6) δ 7.30 (dd, J = 7.0, 2.1 Hz, 2H, Ar**H**), 6.43 (dd, J = 7.0, 2.1 Hz, 2H, Ar**H**), 5.21 (s(br), 1H, C**H**=CCH$_3$), 4.73 (s(br), 2H, CCH$_3$=C**H**$_a$H$_b$), 4.64 (s(br), 2H, CCH$_3$=CH$_a$**H**$_b$), 3.92 (pentet, J = 4.5 Hz, 1H, NC**H**CH$_2$), 3.35 (d(br), J = 16.8 Hz, 1H, NC**H**$_a$H$_b$CH), 3.11 (d(br), J = 16.8 Hz, 1H, NCH$_a$**H**$_b$CH), 2.20 (d(br), J = 16.8 Hz, 1H, CC**H**$_a$H$_b$C), 2.05 (dd, J = 13.4, 10.1 Hz, 1H, CC**H**$_a$H$_b$C), 1.93 (dd, J = 13.4, 4.6 Hz, 1H, CCH$_a$**H**$_b$C), 1.82 (d(br), J = 16.8 Hz, 1H, CCH$_a$**H**$_b$C), 1.60 (s, 3H, C**H**$_3$C), 1.50 (s, 3H, C**H**$_3$C); ^{13}C NMR (125 MHz, C_6D_6) δ 150.0, 143.8, 132.6, 130.5, 118.3, 116.5, 113.4, 110.2, 50.7, 44.0, 37.4, 32.5, 23.8, 22.7. HRMS (EI$^+$) Calcd for $C_{16}H_{20}NBr$: 305.0074. Found: 305,0673. HPLC (Chiralpak AD, 0.1% ^{i}PrOH in hexane, 1.0 mL/min, 254 nm) 97% ee $[\alpha]^D$ = + 15.4 ± 0.1° (c = 1.0, $CHCl_3$).

4-Methyl-2-(2-methyl-allyl)-1-*o*-methoxyphenyl-1,2,3,6-tetrahydropyridine (19): IR (Neat) 3068 (s), 2910 (s), 1644 (s), 1594 (m), 1500 (s), 1454 (s), 1389 (m), 1294 (m), 1233 (s), 1180 (m), 1030; ^{1}H NMR (500 MHz, C_6D_6) δ 6.94 (m, 3H, Ar**H**), 6.67 (m, 1H, Ar**H**), 5.38 (s(br), 1H, C**H**=CCH$_3$), 4.38 (s(br), 2H, CCH$_3$=C**H**$_2$), 4.25 (m, 1H, NC**H**CH$_2$), 3.75 (d(br), J = 16.8 Hz, 1H, NC**H**$_a$H$_b$CH), 3.41 (s, 3H, C**H**$_3$O), 3.38 (d(br), J = 16.8 Hz, 1H, NCH$_a$**H**$_b$CH), 2.54 (m, 1H, CC**H**$_a$H$_b$C), 2.27 (m, 2H, CC**H**$_2$C), 1.88 (d(br), J = 16.8 Hz, 1H, CC**H**$_a$H$_b$C), 1.65 (s, 3H, C**H**$_3$C), 1.58 (s, 3H, C**H**$_3$C); ^{13}C NMR (125 MHz, C_6D_6) δ 153.8, 144.7, 141.6, 131.4, 122.7, 121.9, 121.3, 119.8, 113.1, 112.8, 55.7, 52.6, 45.8, 38.7, 33.4, 24.1, 22.7. (EI$^+$) Calcd for $C_{17}H_{23}NO$: 257.1774. Found:257.1784. HPLC (Chiralpak AD, 0.1% ^{i}PrOH in hexane, 1.0 mL/min, 254 nm) 85% ee $[\alpha]^D$ = + 6.6 ± 0.1° (c = 1.0, $CHCl_3$).

4-Methyl-2-(2-methyl-allyl)-1-*o*-bromophenyl-1,2,3,6-tetrahydropyridine (21): IR (Neat) 3069 (m), 2910 (m), 1634 (w), 1584 (m), 1473 (s), 1387 (m), 1283 (m), 1174 (m), 1025 (m); ^{1}H NMR (500 MHz, C_6D_6) δ 7.51 (dd, J = 7.9, 1.5 Hz, 2H, Ar**H**), 6.95 (dt, J = 7.6, 1.5 Hz, 1H, Ar**H**), 6.87 (dd, J = 7.9, 1.5 Hz, 1H, Ar**H**), 6.57 (dt, J = 7.9, 1.5 Hz, 1H, Ar**H**), 5.28 (s(br), 1H, C**H**=CCH$_3$), 4.73 (m, 2H, CCH$_3$=C**H**$_2$), 3.99 (m, 1H, NC**H**CH$_2$), 3.69 (d(br), J = 16.8 Hz, 1H, NC**H**$_a$H$_b$CH), 3.14 (d(br), J = 16.8 Hz, 1H, NCH$_a$**H**$_b$CH), 2.46 (d(br), J = 16.8 Hz, 1H, CC**H**$_a$H$_b$C), 2.26 (m, 2H, CC**H**$_2$C), 1.83 (d(br), J = 16.8 Hz, 1H, CCH$_a$**H**$_b$C), 1.62 (s, 3H, C**H**$_3$C), 1.50 (s, 3H, C**H**$_3$C); ^{13}C NMR (125 MHz, C_6D_6) δ 150.8, 144.1, 134.6, 131.8, 124.4, 123.7, 121.0, 119.3, 113.3, 107.1, 54.0, 46.3, 38.3, 32.0, 24.0, 22.6. Anal. Calcd. for $C_{16}H_{20}NBr$: C, 62.75; H, 6.58; N, 4.57. Found: C, 63.02; H, 6.55; N, 4.36. HPLC (Chiralpak AD, 0.1% ^{i}PrOH in hexane, 1.0 mL/min, 265 nm) 82% ee $[\alpha]^D$ = + 3.3 ± 0.1° (c = 1.0, $CHCl_3$).

2-Allyl-1-phenyl-1,2,3,6-tetrahydropyridine (23): IR (Neat) 3036

(m), 2922 (m), 1639 (m), 1598 (s), 1502 (s), 1390 (m), 1237 (m), 1036 (m); ^{1}H NMR (500 MHz, C_6D_6) δ 7.25 (m, 2H, Ar**H**), 6.83 (t, J = 7.5 Hz, 1H, Ar**H**), 6.76 (d, J = 7.5 Hz, 2H, Ar**H**), 5.62−5.49 (m, 3H, C**H**═CH_2), 4.91 (m, 2H, CH═C**H**$_2$), 3.92 (m, 1H, NC**H**CH), 3.52 (dd-(br), J = 17.5, 2.5 Hz, 1H, NC**H**$_a$H$_b$CH), 3.25 (dd(br), J = 17.5, 2.5 Hz, 1H, NCH$_a$**H**$_b$CH), 2.30 (d(br), J = 17.0 Hz, 1H, CC**H**$_a$H$_b$C), 2.20−2.07 (m, 2H, CC**H**$_2$C), 1.91 (d(br), J = 17.0 Hz, 1H, CCH$_a$**H**$_b$C,); ^{13}C NMR (125 MHz, C_6D_6) δ 137.0, 129.9, 128.7, 125.1, 123.2, 118.5, 116.9, 115.2, 52.4, 44.0, 33.9, 28.4. HRMS (EI$^+$) Calcd for $C_{14}H_{17}N$: 199.1356. Found: 199.1360.

2-Allyl-1-(4-methoxyphenyl)-5-methyl-1,2,3,6-tetrahydropyridine (25): IR (Neat) 3074 (m), 2927 (s), 1639 (m), 1511 (s), 1394 (m), 1245 (s), 1181 (m), 1041 (s); ^{1}H NMR (500 MHz, C_6D_6) δ 6.89 (m, 2H, Ar**H**), 6.79 (m, 2H, Ar**H**), 5.66 (m, 1H, C**H**═CH_2), 5.37 (m, 1H, CH_2C**H**═C(CH_3)), 4.98−4.93 (m, 2H, CH═C**H**$_2$), 3.79 (m, 1H, NC**H**CH_2), 3.43 (s, 3H, C**H**$_3$O), 3.37 (d(br), J = 16.8 Hz, 1H, NC**H**$_a$H$_b$-CH), 3.26 (d(br), J = 16.8 Hz, 1H, NCH$_a$**H**$_b$CH), 2.38 (m(br), 1H, CC**H**$_a$H$_b$C), 2.20 (dt, J = 13.7, 3.1 Hz, 1H, CCH$_a$**H**$_b$C), 2.11 (dt, J = 13.7, 8.9 Hz, 1H, CC**H**$_a$H$_b$C), 1.98 (dd(br), J = 16.8, 3.1 Hz, 1H, CCH$_a$**H**$_b$C), 1.54 (s, 3H, C**H**$_3$C); ^{13}C NMR (125 MHz, C_6D_6) δ 153.8, 144.8, 137.3, 131.8, 118.4, 118.0, 116.8, 115.3, 55.5, 54.1, 49.1, 33.7, 28.5, 21.1. HRMS (EI$^+$) Calcd for $C_{16}H_{21}NO$: 243.1618. Found: 243.1614.

4-Methyl-2-(2-methyl-allyl)-1-phenyl-2,3,6,7-tetrahydro-1*H*-azepine (28): IR (Neat) 3511 (m), 3071 (s), 2964 (s), 1910 (w), 1646 (s), 1380 (s), 1236 (s), 1034 (s); ^{1}H NMR (500 MHz, C_6D_6) δ 7.26 (m, 2H, Ar**H**), 6.76 (m, 3H, Ar**H**), 5.21 (s(br), 1H, NCH_2C**H**═CCH_3), 4.80 (m, 2H, CCH_3═C**H**$_2$), 4.01 (septet, J = 4.6 Hz, 1H, NC**H**CH_2), 3.40 (dt, J = 11.9, 3.4 Hz, 1H, NC**H**$_a$H$_b$$CH_2$), 3.27 (td, J = 15.3, 4.3 Hz, 1H, NCH$_a$**H**$_b$$CH_2$), 2.44 (dd, J = 13.7, 5.0 Hz, 2H, CC**H**$_2$C), 2.21−2.06 (m, 6H, CC**H**$_2$C), 1.87 (d(br), J = 15.3 Hz, 1H, CC**H**$_a$H$_b$C), 1.61 (m, 6H, C**H**$_3$C); ^{13}C NMR (125 MHz, C_6D_6) δ 149.4, 143.6, 133.6, 130.4, 123.8, 116.6, 113.2, 112.7, 55.9, 41.4, 41.3, 36.8, 28.9, 27.5, 23.0. Anal. Calcd. for $C_{19}H_{27}N$: C, 84.70; H, 10.1; N, 5.20. Found: C, 84.97; H, 10.4; N, 5.08. HPLC (Chiralcel OD, 2.0% ^{i}PrOH in hexane, 1.0 mL/min, 254 nm) 95% ee $[\alpha]^D = -20.9 \pm 0.1°$ (c = 1.0, $CHCl_3$).

6-Methyl-8-(2-methyl-allyl)-1-phenyl-1,2,3,4,7,8-hexahydroazocine (30): IR (Neat) 3509 (m), 3070 (m), 2963 (s), 1646 (m), 1596 (s), 1503 (s), 1440 (m), 1397 (m), 1346 (s), 1232 (s), 1187 (s), 1151 (s), 1047 (s); ^{1}H NMR (500 MHz, C_6D_6) δ 7.25 (m, 2H, Ar**H**), 6.72 (m, 3H, Ar**H**), 5.38 (dt, J = 7.3, 1.5 Hz, 1H, N$(CH_2)_3$C**H**═CCH_3), 4.75 (m, 2H, CCH_3═C**H**$_2$), 4.13 (m, 1H, NC**H**CH_2), 3.27 (dt, J = 15.6, 3.1 Hz, 1H, NC**H**$_a$H$_b$$(CH_2)_2$), 2.94 (dt, J = 11.9, 3.1 Hz, 1H, NCH$_a$**H**$_b$-$(CH_2)_2$), 2.29−1.77 (m, 7H, CC**H**$_2$C), 1.67 (s, 3H, C**H**$_3$C), 1.56 (s, 3H, C**H**$_3$C), 1.12 (m, 1H, CC**H**$_2$C); ^{13}C NMR (125 MHz, C_6D_6) δ 149.3, 143.6, 135.4, 130.1, 127.0, 116.2, 113.1, 112.2, 54.2, 41.2, 36.6, 30.2, 28.0, 22.7. HRMS (EI$^+$) Calcd for $C_{18}H_{25}N$: 255.1982. Found: 255.1992. HPLC (Chiralcel OD, 0.1% ^{i}PrOH in hexane, 1.0 mL/min, 254 nm) > 98% ee $[\alpha]^D = +9.0 \pm 0.1°$ (c = 1.15, $CHCl_3$).

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Supporting Information Available: Experimental procedures and spectral and analytical data for all substrates and crystallographic data (PDF). This material is available free of charge via the Internet at http//:www.acs.pubs.org.

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