Convenient Asymmetric Syntheses of *anti*-β-Amino Alcohols

Anthony G. M. Barrett,* Mark A. Seefeld, Andrew J. P. White, and David J. Williams

Imperial College of Science, Technology & Medicine, London SW7 2AY, England

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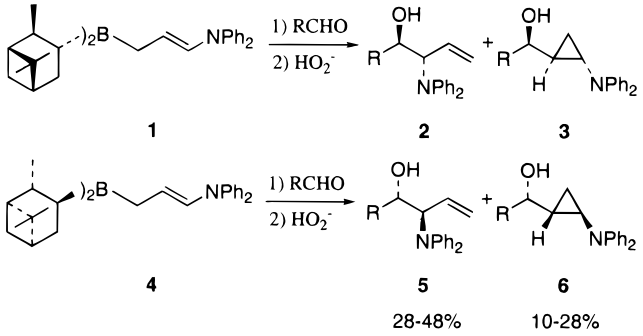
Condensation of allylborane reagents **9** and **12** with aldehydes gave *anti*-3-[(diphenylmethylene)-amino]-1-alken-4-ols **10** and **13** with high relative and absolute stereocontrol. Subsequent deprotection gave the corresponding free *anti*-3-amino-1-alken-4-ols **11** and **14**. Alternatively, reaction of imines **13a**, **13f**, and **13g** with trifluoromethanesulfonic anhydride and acidic methanol gave, *via* rearrangement, double inversion, and hydrolysis, the isomeric *anti*-4-amino-1-alken-3-ols **22**, **38a**, and **38b** in good yield. The stereochemistry of the rearrangement products has been established by a single crystal X-ray study of compound **37** and by chemical correlation.

Introduction

2-Amino alcohols are common structural subunits that occur in diverse biologically active natural products and related fine chemicals.[1] Many methods have been employed to construct compounds containing such functionality, yet relatively few concise strategies exist to generate vicinal aminols stereoselectively. Generally, two distinct methods are employed to introduce such units. Firstly, amino alcohol entities may be introduced without altering the carbon skeleton of a molecule. Such a process is exemplified by the ring opening of epoxides with a nitrogen centered nucleophile.[2] Alternatively, the vicinal amino alcohol array may be elaborated with the simultaneous construction of the interconnecting C−C bond.[3] This process can be much more valuable since it leads to an increase in the complexity of the carbon skeleton in addition to the introduction of heteroatoms. We have recently reported[4,5] an example of this second strategy. In an extension of allylborane chemistry,[6] we showed that the antipodal *B*-[(*E*)-3-(diphenylamino)allyl]-diisopinocampheylboranes **1** and **4** were useful reagents for masked aldol chemistry. Condensation of aldehydes with boranes **1** and **4** gave β-hydroxy-*N*,*N*-diphenylamines **2** and **5** with high *anti*-diastereoselectivity and high enantioselectivity. Unfortunately, there were serious limitations associated with this methodology. The product β-hydroxy *N*,*N*-diphenylamines **2** and **5** could not be easily deprotected to reveal the parent β-hydroxy primary amines. Additionally significant quantities of cyclopropane side products **3** and **6** were also formed (Scheme 1). Prior to this work, Hoffmann and Metternich reported the formation of related cyclopropane

Scheme 1



systems in allylboration reactions.[7] Subsequently we reported[8] the use of *B*-[(*E*)-3-[(diphenylmethylene)amino]-allyl]diisopinocampheylboranes **9** and **12** in asymmetric synthesis. Condensation of boranes **9** and **12** with aldehydes and deprotection gave the amino alcohols **11** and **14**. Herein we report full experimental details of this improved methodology and describe an unexpected rearrangement reaction that proceeds with double inversion and is also useful in asymmetric synthesis.

Results and Discussion

In principle, deprotonation of a suitably protected derivative of allylamine[9] and condensation with (−)- or (+)-(chloro)diisopinocampheylborane should provide the corresponding protected (amino-1-propen-3-yl)diisopinocampheylborane derivatives such as **9** and **12** respectively. Such reagents should react with aldehydes to provide protected 3-amino-1-alken-4-ol derivatives such as **10** and **13**. Clearly for this chemistry to be viable the choice of protecting group on nitrogen is crucial. The protecting group must be removable under mild conditions yet withstand strongly basic reagents. Secondly, the allyl amine system should stereoselectively produce *E*-allyl metal derivatives upon deprotonation and remain configurationally stable upon lithium to boron transmetalation. This is essential to ensure good *anti*-stereocontrol. Finally, the protecting group must mask the

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1996.

(1) *Dictionary of Antibiotics and Related Substances*, Bycroft, B. W., Ed.; Chapman and Hall: London, 1988.

(2) Mitsunobu, O. Synthesis of Amines and Ammonium Salts. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Winterfeldt, E., Eds.; Pergamon Press: Oxford, 1991; Vol. 6, pp 88−93.

(3) (a) Yamamoto, H.; Hattori, K. *Tetrahedron* **1994**, *50*, 2785. (b) Ito, Y.; Ito, H.; Murakami, M. *J. Org. Chem.* **1993**, *58*, 6766. (c) Taguchi, T.; Ito, H.; Hanzawa, Y. *Tetrahedron Lett.* **1992**, *33*, 4469.

(4) Barrett, A. G. M.; Seefeld, M. A. *J. Chem. Soc., Chem. Commun.* **1993**, 339.

(5) Barrett, A. G. M.; Seefeld, M. A. *Tetrahedron* **1993**, *49*, 7857.

(6) (a) Roush, W. R. Allyl Organometallics. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Heathcock, C. H., Eds.; Pergamon Press: Oxford, 1991; Vol. 2, pp 1−53. (b) Brown, H. C.; Jadhav, P. K., Bhat, K. S. *J. Am. Chem. Soc.* **1988**, *110*, 1535. (c) Jadhav, P. K.; Bhat, K. S.; Perumal, P. T., Brown, H. C. *J. Org. Chem.* **1986**, *51*, 432. (d) Brown, H. C., Bhat, K. S. *J. Am. Chem. Soc.* **1986**, *108*, 5919.

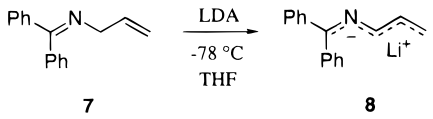
(7) Hoffmann, R. W.; Metternich, R. *Justus Liebigs Ann. Chem.* **1985**, 2390.

(8) Barrett, A. G. M.; Seefeld, M. A., Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1994,** 1053.

(9) (a) Barluenga, J.; González, R.; Fañanás, F. J.; Yus, M., Foubelo, F. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1069. (b) Beak, P., Resek, J. E. *Tetrahedron Lett.* **1993**, *34*, 3043. (c) Eisch, J. J., Shah, J. H. *J. Org. Chem.* **1991**, *56*, 2955. (d) Biellmann, J.-F.; Ducep, J.-B.; *Org. React.* **1982**, *27*, ch. 1.

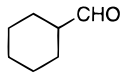
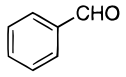
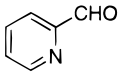
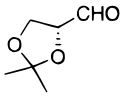
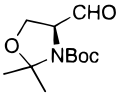
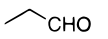
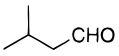
0022-3263/96/1961-2677$12.00/0

Scheme 2



7 **8**

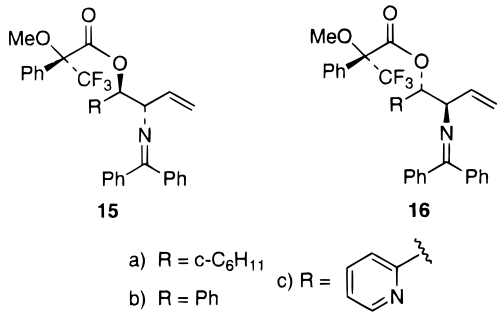
Table 1. Reaction of Aldehydes with Boranes 9 and 12

Entry	Aldehyde	Product (%)	Ds	%ee
1		**10a** (56)	≥95:5	91
2		**13a** (61)	≥95:5	93
3		**10b** (53)	≥95:5	93
4		**13b** (52)	≥95:5	90
5		**10c** (49)	≥95:5	91
6		**13c** (51)	≥95:5	90
7		**10d** (43)	≥95:5	----
8		**10d** (30), **13d** (11)	2.7:1	----
9		**10e** (17), **13e** (21)	1:1.2	----
10		**10e** (40)	≥95:5	----
11		**10f** (48)	≥95:5	----
12		**10g** (41)	≥95:5	----

amine in such a manner that enamine reactivity is reduced to suppress the formation of cyclopropane products such as **3** and **6**. The requirements of reduced nucleophilicity and ease of removal should be both fulfilled using an imine protection strategy. Würthwein and Wolf[10] have shown that 1,1-diphenyl-2-aza-1,4-pentadiene (**7**) upon deprotonation with LDA in THF at −78 °C gave an all *trans*-W-anionic species **8** (Scheme 2). The reaction of carbanion **8** with electrophiles resulted primarily in γ-substitution; however, this was dependent on several variables including solvent polarity and electrophile reactivity.[11] The ability of carbanion **8** to react regiospecifically at the distal carbon and maintain an all *trans*-W-configuration upon addition of a chiral borane had not been investigated prior to our preliminary communication.[8]

Following the Würthwein precedent,[10] 1,1-diphenyl-2-aza-1,4-pentadiene (**7**) was deprotonated with LDA in THF at −78 °C to give, upon reaction with (−)-*B*-chlorodiisopinocampheylborane [(−)-$(Ipc)_2BCl$], an adduct, presumably the *E*-allylborane **9**. *In situ* reaction with cyclohexanecarboxaldehyde gave, on basic hydrogen peroxide workup, the *anti*-β-hydroxy amine **10a** (R = c-C_6H_{11}) in 56% yield (Scheme 3). Deprotection of imine **10a** gave the corresponding amino alcohol **11a** in 98% yield. In the same manner, reaction of the imine **7** with LDA in THF at −78 °C, followed by metathetic exchange with (+)-*B*-chlorodiisopinocampheylborane [(+)-$(Ipc)_2BCl$] and reaction with cyclohexanecarboxaldehyde gave the antipodal imine **13a** (R = c-C_6H_{11}). Subsequent deprotection of **13a** furnished the free amine **14a** in 98% yield. Several other aldehydes were reacted under similar conditions to give the corresponding *anti*-β-hydroxyimines **10** and **13** (Table 1).

The relative and absolute stereochemistries of the product imines requires substantiation. Examination of ^1H NMR and ^{13}C NMR spectra showed the diastereoselectivity of the reaction to be at least 95% *anti* in all cases. The enantioselectivities were determined by converting each pair of vicinal imino alcohols **10** and **13** into their corresponding Mosher esters **15** and **16**.[12] The enantio-



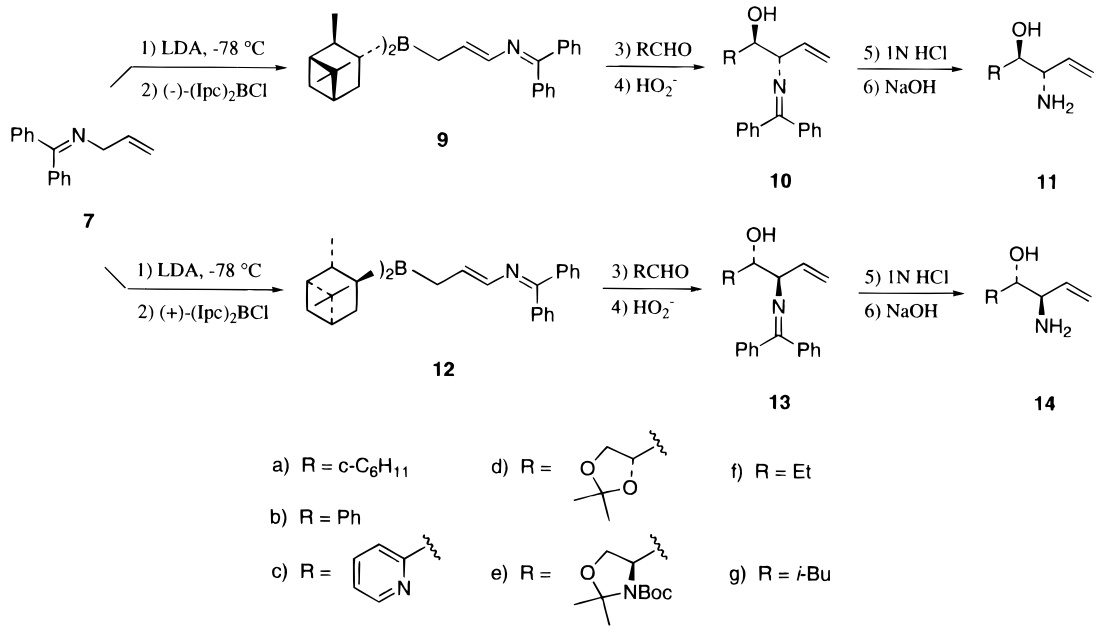
meric excesses were measured to be ≥90% by ^1H NMR in all cases except in those resulting from mismatched stereochemical biases between reagent and substrate (entries 8 and 9). The stereochemistry of one *anti*-β-imino alcohol has been formally established by carrying out an X-ray crystallographic study of **10d**.[7] This study unequivocally established the relative and hence the absolute stereochemistry of alcohol **10d** and, by implication, all the other imino alcohols in Table 1. These results are in full accord with the established stereoselectivities of other Brown allylborane and aldehyde condensation reactions.[5,6]

We sought to convert the product imino alcohols **13** stereospecifically into aziridines **19** *via* activation of the hydroxyl group as derivative **17**, cyclization via an S_N2 manifold, and nucleophilic addition to the resultant iminium species **18** (Scheme 4).[13] Unfortunately, all our attempts to convert imino alcohols **13** directly into aziridines **19** met with failure giving intractable polymerized material. However, these studies led to the discovery of an unexpected rearrangement reaction. The addition of 2,6-lutidine and trifluoromethanesulfonic anhydride to alcohol **13a** in CH_2Cl_2 at 0 °C resulted in the formation of a single low molecular weight substance (Scheme 5). The ^1H NMR spectrum of the new product **21** showed what appeared to be a 1:1 mixture of imino alcohols isomeric with the starting material **13a**. Initially, we suspected that the unknown product may have contained the *syn*-isomer **20** although this expectation was later proven unfounded. A sample of the *syn*-isomer **20** admixed with **13a** was prepared by carrying out the allylboration reaction at −50 °C rather than −78 °C (Scheme 6). This provided an inseparable mixture of the imino alcohol **13a** and the corresponding *syn*-diastereoisomer **20** (9:1). The decrease in diastereoselectivity at elevated temperatures, which presumably takes place *via* reversible allylboron migration and *E,Z* isomerization of

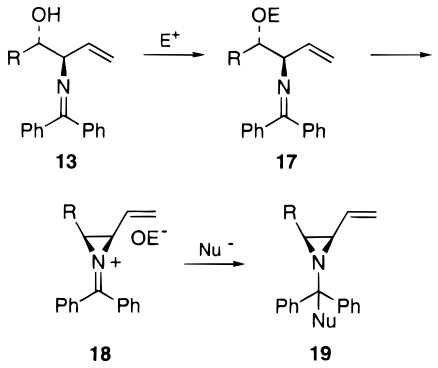
(10) Würthwein, E.-U.; Wolf, G. *Chem. Ber.* **1991**, *124*, 655.
(11) Würthwein, E.-U.; Wolf, G. *Tetrahedron Lett.* **1988**, *29*, 3647.

(12) (a) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512. (b) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.
(13) For similar examples, see: (a) De Kimpe, N.; De Smaele, D. *Tetrahedron Lett.* **1994**, *35*, 8023. (b) De Kimpe, N.; Boelens, M.; Piqueur, J.; Baele, J. *Tetrahedron Lett.* **1994**, *35*, 1925. (c) De Kimpe, N.; Boelens, M. *J. Chem. Soc., Chem. Commun.* **1993**, 916.

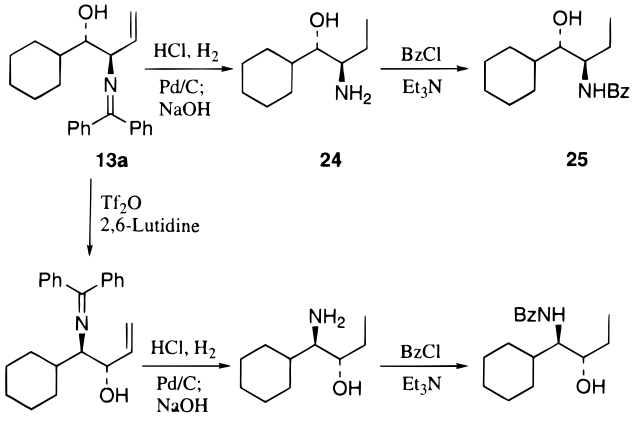
Scheme 3



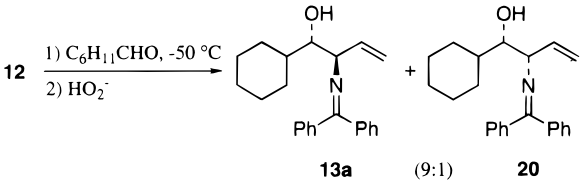
Scheme 4



Scheme 5



Scheme 6



the intermediate allylborane derivative, is well established with crotonylborane systems.[6] The ^{1}H NMR spectrum of the diastereoisomeric mixture {δ 3.45 [1H, m, C*H*(NR)], *syn* and 3.62 [1H, m, C*H*(OH)], *syn*} showed that the rearranged product **21** in Scheme 6 was neither alcohol **13a** nor **20**.

Hydrolysis of imino alcohol **21** with 1 M hydrogen chloride in methanol, hydrogenation over 5% palladium on carbon and benzoylation (BzCl, Et_3N) gave, surprisingly, a single diastereoisomeric benzamido alcohol **23**. The imino alcohol **13a** was also converted into the corresponding benzamide **25** by hydrogenation/hydrogenolysis and benzoylation. Samples of the racemic *syn* and *anti* benzamido alcohols **29**, **30**, **34**, and **35** were synthesized independently from nitropropane **26** and (nitromethyl)cyclohexane **31**[14] using the Seebach modification of the Henry reaction[15] (Scheme 7). The relative stereochemistries of the nitro alcohol products **27**, **28**, **32**, and **33** were assigned based on comparative ^{13}C NMR shift correlations for the (CNO_2) and (COH) peaks as described by Seebach.[15] The resultant nitroaldol isomers were chromatographically separated, hydrogenated over 10% palladium on carbon, and subsequently benzoylated to provide the racemic amides **29**, **30**, **34**, and **35**. Comparison of the ^{1}H and ^{13}C NMR spectra of each racemic compound with products **23** and **25** showed the constitution and relative stereochemistry of benzamide **23** to be the same as that of structure **34**.

The relative stereochemistry of compound **21** was also determined by converting the amino alcohol **22** into the oxazolidinone **36** using bis(trichloromethyl) carbonate and Hunig's base (Scheme 8). Irradiation of the H-5 proton resonance (δ 4.47) of oxazolidinone **36** produced a large NOE (8.6%) of the signal for H-4 (δ 3.56). In addition, the coupling constant between H-4 and H-5 protons (J 7.1 Hz) was consistent with the *cis* structure **36**.[16] These results are in agreement with the assignment of the stereochemistry of the amino alcohol precursor **22** as *anti*. The determination of enantiomeric purity of the amino alcohol **22** was confirmed by analysis of the

(14) Kornblum, N.; Larson, H. O.; Blackwood, R. K.; Mooberry, D. D.; Oliveto, E. P.; Graham, G. E. *J. Am. Chem. Soc.* **1956**, *78*, 1497.
(15) Seebach, D.; Beck, A. K.; Mukhopadhyay, T.; Thomas, E. *Helv. Chim. Acta* **1982**, *65*, 1101.
(16) For a similar analysis, see: Bergmeier, S. C.; Stanchina, D. M. *Tetrahedron Lett.* **1995**, *36*, 4533 and references therein.

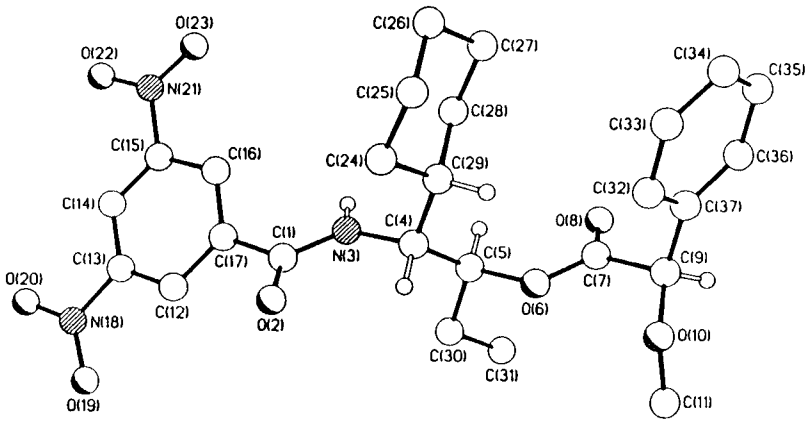
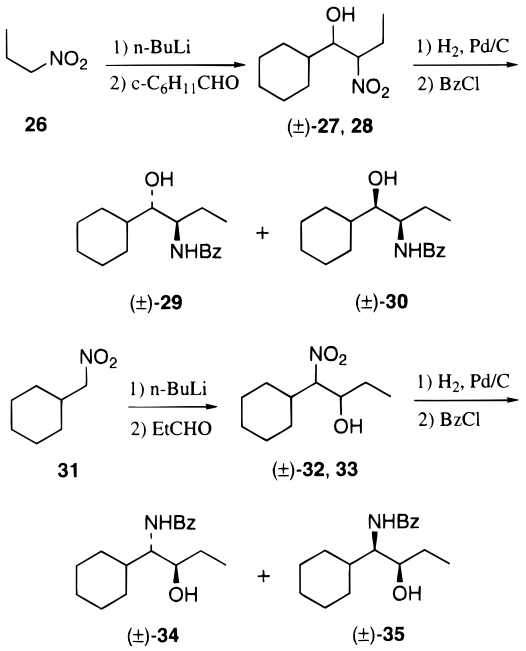
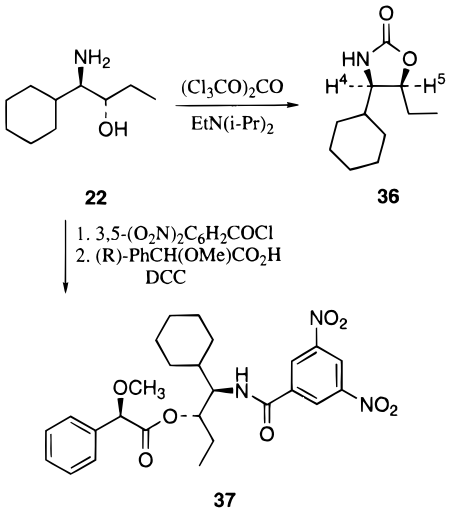


Figure 1.

Scheme 7

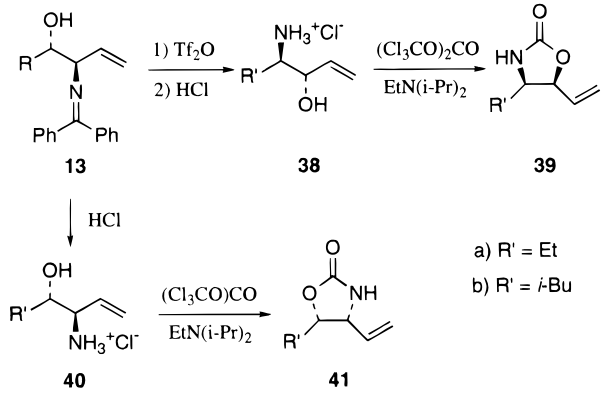


Scheme 8



^{1}H and ^{13}C NMR spectra of the dinitrobenzoyl (*R*)-*O*-methylmandelate derivative **37**. These analyses revealed the diastereomeric purity of **37** to be ~90%. This result is consistent with retention of the enantiomeric purity of the initial imino alcohol **13a**, but inconsistent with the

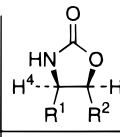
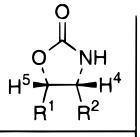
Scheme 9



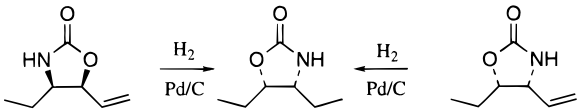
^{1}H NMR spectrum of **21** which indicated a 1:1 mixture of products. It is reasonable to postulate that the position now occupied by the diphenylmethylene group (C-1) in the rearranged product **21** is sterically encumbered by the cyclohexyl ring and that imine **21** thus exists as a mixture of rotamers. This hypothesis was consistent with the result of converting imino alcohol **21** into amino alcohol **22**. Free rotation about the C−N bond of deprotected amine **22** showed the product to be in fact a single diastereoisomer. An X-ray crystallographic study of ester[19] **37** confirmed its relative and absolute stereochemistry as a doubly inverted product (Figure 1). The results suggest that the stereospecific formation of product **21** may involve the intermediacy of an aziridinium species **18** and S_N2 ring opening without allylic rearrangement (Scheme 4).

Further examples of this novel rearrangement were sought by treating both compounds **10d** and **13b** with trifluoromethanesulfonic anhydride. Unfortunately, this gave only a complex intractable mixture of products. In contrast, reaction of the simple alkylimino alcohol derivative **13f** with trifluoromethanesulfonic anhydride and subsequent acidification (1 M HCl in methanol) gave the amino alcohol hydrochloride **38a** in 38% yield (Scheme 9). ^{1}H NMR analysis of the corresponding oxazolidinone **39a** showed the coupling constant of protons H-4 and H-5 (*J* 7.9 Hz) to be fully consistant with the *cis*-stereochemistry. The parent imino alcohol **13f** was also converted into the corresponding oxazolidinone **41a** by hydrolysis and condensation with bis(trichloromethyl) carbonate. Again analysis of the ^{1}H NMR spectrum (*J* 7.8 Hz) further confirmed the *cis* geometry of oxazolidinone **39a** (Table 2). Final confirmation was achieved by hydrogenating both oxazolidinones **39a** and **41a** to give the

Table 2. Vicinal Coupling Constants of *cis*-Oxazolidinones

J (Hz) H-4, H-5		
R^1= c-C_6H_{11}, R^2= Et	**36** (7.1)	----
R^1= Et, R^2= vinyl	**39a** (7.9)	**41a** (7.8)
R^1= *i*-Bu, R^2= vinyl	**39b** (7.6)	**41b** (7.6)
R^1= Et, R^2=Et	**42** (7.5)	----

Scheme 10



39a **42** **41a**

identical dihydro derivative **42** (Scheme 10). One other imino alcohol compound **10g** was investigated in this regard. Rearrangement of the imino alcohol **13g** with trifluoromethanesulfonic anhydride and Hunig's base followed by acid hydrolysis gave the amino alcohol **38b** in 31% yield.

The enantioselective production of vicinal amino alcohols *via* a one-pot procedure should be applicable to synthesis of natural products. In addition, the stereospecific rearrangement of the product imino alcohols should provide a complementary procedure for amino alcohol synthesis.

Experimental Section

All solvents were redistilled prior to use. (Nitromethyl)-cyclohexane (**31**),[14] 2,3-*O*-isopropylidene-D-glyceraldehyde,[17] and 1,1-dimethylethyl (*S*)-4-formyl-2,2-dimethyl-3-oxazolidinecarboxylate[18] were prepared according to reported procedures. All other reagents were purchased from commercial sources and used without further purification.

(−)-(1*R*,2*S*)-1-Cyclohexyl-2-[(diphenylmethylene)amino]-3-buten-1-ol (10a) (General Procedure). To a stirred solution of diisopropylamine (0.70 mL, 5.0 mmol) in THF (30 mL) under N_2 at −78 °C was added n-BuLi in hexane (2.5 M, 2.0 mL). The solution was kept at −78 °C for 25 min. 1,1-Diphenyl-2-aza-1,4-pentadiene (**7**) (1.11 g, 5.0 mmol) in THF (2 mL) was added with stirring at −78 °C. After 3 h, (−)-*B*-chlorodiisopinocampheylborane (1.60 g, 5.0 mmol) in THF (5 mL) was added to the dark red mixture which was maintained at −78 °C for 2 h. To this solution was added cyclohexanecarboxaldehyde (0.45 g, 4.0 mmol) in THF (1 mL). The reaction mixture was maintained at −78 °C for 3 h after which aqueous NaOH (2 mL, 2.5 M) and 30% H_2O_2 (2 mL) were added. The reaction mixture was stirred at room temperature for 12 h and diluted with ether (40 mL), and the organic phase was separated and dried ($MgSO_4$). Evaporation and chromatography (silica gel, hexane−EtOAc, 4:1) gave imine **10a** (0.75 g, 56%) as a white solid: mp 92−93 °C (hexane−EtOAc); TLC R_f 0.51 (hexane−EtOAc, 4:1); $[\alpha]^{24}_D$ −27.3° (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 3503 (OH), 3079, 3059, 2924, 2851, 1623 (C=N), 1446, 1106 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.61−7.12 (m, 10H), 6.05 (ddd, 1H, *J* 17.3, 9.4, 6.7 Hz), 5.15 (dd, 1H, *J* 9.4, 1.2 Hz), 4.92 (dd, 1H, *J* 17.3, 1.2 Hz), 3.95 (dd, 1H, *J* 6.7, 4.6 Hz), 3.34 (dd, 1H, *J* 6.6, 4.6 Hz), 1.84−0.84 (m, 11H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 168.3, 139.8, 136.9, 136.3, 130.5, 128.8, 128.6, 128.3, 128.0, 127.9, 117.3, 78.6, 67.6, 39.7, 29.1, 28.5, 26.8, 26.3, 26.1; MS (EI) *m*/*z* (rel intensity) 333 (M + , 2), 315 [(M − H_2O)$^+$, 1], 256 (20), 220 (100), 165 (40), 55 (41); HRMS (EI, 70 eV) *m*/*z* calcd for $C_{23}H_{27}NO$ (M +) 333.2093, found 333.2086. Anal. Calcd for $C_{23}H_{27}NO$: requires C, 82.84; H, 8.16; N 4.20. Found: C, 82.56; H, 8.13; N, 4.15. A sample of **10a** (15 mg, 0.04 mmol), (*R*)-Mosher acid (23 mg, 0.10 mmol) and 4-(dimethylamino)pyridine (5 mg) were dissolved in CH_2Cl_2 (10 mL). 1,3-Dicyclohexylcarbodiimide (21 mg, 0.10 mmol) in CH_2Cl_2 was added, and the course of the reaction was monitored by TLC (silica gel, CH_2Cl_2). After 2 h, the entire mixture was directly chromatographed on silica gel and eluted with CH_2Cl_2. Evaporation of the solvent gave the crude ester **15a** (37 mg, 96%) as a light yellow oil. This material was used directly without any further purification, for the determination of the enantioselectivity of the reaction. ^1H NMR (500 MHz, $CDCl_3$) δ 7.70−7.13 (m, 15H), 6.01 (m, 1H), 5.13 (m, 1H), 5.11 (m, 2H), 4.90 (d, 1H, *J* 17.3 Hz), 4.13 (m, 1H), 3.64 (s, 3H), 1.64−0.75 (m, 11H).

Preparation of Imines 10 and 13. Condensation of various aldehydes with boranes **9** and **12** following the general procedure above were used to prepare the following derivatives. In several cases esterification with (*R*)-Mosher acid was used to determine the enantioselectivity of reaction.

(+)-(1*S*,2*R*)-1-Cyclohexyl-2-diphenylmethyleneamino-3-buten-1-ol (13a). Imino alcohol **13a** (72 mg, 61%) was obtained as a white solid: mp 92−93 °C (hexane−EtOAc); TLC R_f 0.51 (hexane−EtOAc, 4:1); $[\alpha]^{24}_D$ +27.0° (*c* 0.7, $CHCl_3$); IR ($CHCl_3$) 3513 (OH), 3080, 3059, 2927, 2851, 1621 (C=N), 1446, 1103 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.66−7.14 (m, 10H), 6.06 (ddd, 1H, *J* 17.4, 9.4, 6.7 Hz), 5.16 (dd, 1H, *J* 9.4, 1.0 Hz), 4.95 (dd, 1H *J* 17.4, 1.0 Hz), 3.97 (dd, 1H, *J* 6.5, 4.7 Hz), 3.37 (dd, 1H, *J* 6.7, 4.7 Hz), 1.90−0.93 (m, 11H); ^{13}C NMR (67.5 MHz, $CDCl_3$) 168.3, 139.8, 136.8, 136.2, 130.4, 128.8, 128.5, 128.3, 128.0, 127.9, 117.4, 78.6, 67.5, 39.6, 29.0, 28.5, 26.7, 26.3, 26.1; MS (EI) *m*/*z* (rel intensity) 333 (M$^+$, 1), 315 [(M − H_2O)$^+$, 2], 256 (22), 220 (100), 165 (45), 54 (40); HRMS (EI, 70 eV) *m*/*z* calcd for $C_{23}H_{27}NO$ (M$^+$) 333.2093, found 333.2078. Anal. Calcd for $C_{23}H_{27}NO$: C, 82.84; H, 8.16; N, 4.20. Found: C, 82.60; H, 7.78; N, 4.25. Mosher ester **16a**: ^1H NMR (270 MHz, $CDCl_3$) δ 7.83−7.12 (m, 15H), 5.84 (m, 1H), 5.26 (dd, 1H, *J* 7.5, 4.9 Hz), 4.95 (d, 1H, *J* 10.5 Hz), 4.84 (d, 1H, *J* 17.3 Hz), 4.06 (app t, 1H, *J* 6.6 Hz), 3.51 (s, 3H), 1.67−0.89 (m, 11H).

(+)-(1*R*,2*S*)-2-[(Diphenylmethylene)amino]-1-phenyl-3-buten-1-ol (10b). Imino alcohol **10b** (96 mg, 53%) was obtained as a white solid: mp 97−98 °C (hexane−EtOAc); TLC R_f 0.33 (hexane−EtOAc, 4:1); $[\alpha]^{24}_D$ +34.3° (*c* 0.7, $CHCl_3$); IR ($CHCl_3$) 3441 (OH), 3080, 3059, 3027, 2888, 1623 (C=N), 1445, 1150 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, 2H, *J* 6.5 Hz), 7.42−7.17 (m, 11H), 6.85 (m, 2H), 6.01 (ddd, 1H, *J* 17.4, 10.4, 6.6 Hz), 5.15 (d, 1H, *J* 10.4 Hz), 4.99 (d, 1H, *J* 17.4 Hz), 4.81 (d, 1H, *J* 5.9 Hz), 4.00 (app t, 1H, *J* 6.4 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.0, 141.1, 139.8, 136.7, 136.6, 130.4, 128.8, 128.7, 128.4, 128.3, 128.2, 127.8, 127.6, 127.0, 117.8, 76.7, 72.2; MS (CI, NH_3) *m*/*z* 328 (M + H)$^+$, 310 (M + H-H_2O)$^+$, 220, 165, 146, 117; HRMS (CI, NH_3) *m*/*z* calcd for $C_{23}H_{22}NO$ (M + H)$^+$ 328.1701, found 328.1700; Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.28. Found: C, 84.77; H, 6.19; N, 4.18. Mosher ester **15b**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.50−7.10 (m, 18H), 6.78 (d, 2H, *J* 6.9 Hz), 6.16 (d, 1H, *J* 7.2 Hz), 6.08 (ddd, 1H, *J* 17.3, 10.4, 6.9 Hz), 5.19 (d, 1H, *J* 10.4 Hz), 5.07 (d, 1H, *J* 17.3 Hz), 4.25 (app t, 1H, *J* 7.0 Hz), 3.57 (s, 3H).

(−)-(1*S*,2*R*)-2-[(Diphenylmethylene)amino]-1-phenyl-3-buten-1-ol (13b). Imino alcohol **13b** (67 mg, 52%) was obtained as a white solid: mp 97−98 °C (hexane−EtOAc); TLC R_f 0.33 (hexane−EtOAc, 4:1); $[\alpha]^{24}_D$ −35.0° (*c* 0.8, $CHCl_3$); IR ($CHCl_3$) 3566 (OH), 3059, 3027, 2890, 1622 (C=N), 1598, 1491, 1151 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.55 (m, 2H), 7.41−7.21 (m, 11H), 6.84 (m, 2H), 6.01 (ddd, 1H, *J* 16.1, 10.0, 6.0 Hz), 5.17 (d, 1H, *J* 10.0 Hz), 5.00 (d, 1H, *J* 16.1 Hz), 4.83 (d, 1H, *J* 5.9 Hz), 4.01 (app t, 1H, *J* 6.1 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.0, 141.1, 139.8, 136.8, 136.7, 130.4, 128.8, 128.7,

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(18) Garner, P.; Park, J. M. *J. Org. Chem.* **1987**, *52*, 2361.
(19) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

128.4, 128.3, 128.2, 127.8, 127.6, 127.0, 117.8, 76.7, 72.2; MS (CI, NH_3) *m/z* 328 $(M + H)^+$, 220, 165, 146, 117; HRMS (CI, NH_3) *m/z* calcd for $C_{23}H_{22}NO$ $(M + H)^+$ 328.1701, found 328.1720. Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.28. Found: C, 84.67; H, 6.31; N, 4.10. Mosher ester **16b**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.47−7.26 (m, 18H), 6.72 (d, 2H, *J* 7.0 Hz), 6.24 (d, 1H, *J* 8.0 Hz), 5.91 (ddd, 1H, *J* 17.3, 10.3, 6.9 Hz), 5.02 (d, 1H, *J* 10.3 Hz), 4.93 (d, 1H, *J* 17.3 Hz), 4.22 (app t, 1H, *J* 6.9 Hz), 3.44 (s, 3H).

(+)-(1*S*,2*S*)-2-[(Diphenylmethylene)amino]-1-(2-pyridinyl)-3-buten-1-ol (10c). Imino alcohol **10c** (116 mg, 49%) was obtained as a yellow oil: TLC R_f 0.32 (hexane−EtOAc, 1:1); $[\alpha]^{24}_D$ +41.1° (*c* 0.7, $CHCl_3$); IR ($CHCl_3$) 3480 (OH), 3281, 3080, 3022, 2922, 1623 (C=N), 1592, 1472 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.49 (m, 1H), 7.77−7.23 (m, 10H), 6.70 (m, 2H), 6.13 (ddd, 1H, *J* 17.2, 10.4, 6.0 Hz), 5.18 (d, 1H, *J* 10.5 Hz), 4.97 (d, 1H, *J* 17.2 Hz), 4.90 (m, 1H), 4.03 (app t, 1H, *J* 6.3 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.8, 159.9, 148.3, 139.6, 137.2, 136.5, 134.2, 130.2, 128.6, 128.4, 128.1, 127.5, 126.4, 122.5, 116.6, 76.2, 71.4; MS (CI, NH_3) *m/z* 329 $(M + H)^+$, 311, 220, 183, 165, 145, 77; HRMS (CI, NH_3) *m/z* calcd for $C_{22}H_{21}N_2O$ $(M + H)^+$ 329.1654, found 329.1674. Mosher ester **15c**: ^1H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, 1H, *J* 4.9 Hz), 7.54−6.97 (m, 18H), 6.24 (d, 1H, *J* 5.6 Hz), 5.99 (m, 1H), 5.09 (d, 1H, *J* 10.5 Hz), 4.88 (d, 1H, *J* 17.2 Hz), 4.54 (m, 1H), 3.57 (s, 3H).

(−)-(1*R*,2*R*)-2-[(Diphenylmethylene)amino]-1-(2-pyridinyl)-3-buten-1-ol (13c). Imino alcohol **13c** (88 mg, 51%) was obtained as a yellow oil: TLC R_f 0.32 (hexane−EtOAc, 1:1); $[\alpha]^{24}_D$ −40.6° (*c* 0.9, $CHCl_3$); IR ($CHCl_3$) 3436 (OH), 3080, 3022, 2923, 1623 (C=N), 1592, 1474 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 8.51 (m, 1H), 7.79−7.13 (m, 11H), 6.70 (m, 2H), 6.13 (ddd, 1H, *J* 17.1, 10.5, 5.9 Hz), 5.19 (d, 1H, *J* 10.5 Hz), 4.98 (d, 1H, *J* 17.1 Hz), 4.91 (d, 1H, *J* 6.4 Hz), 4.04 (app t, 1H, *J* 6.2 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.8, 159.9, 148.3, 139.6, 137.2, 136.5, 134.2, 130.2, 128.6, 128.4, 128.3, 128.1, 127.5, 126.4, 122.5, 116.6, 76.2, 71.4; MS (CI, NH_3) *m/z* 329 $(M + H)^+$, 311, 220, 183, 165, 145; HRMS (CI, NH_3) *m/z* calcd for $C_{22}H_{21}N_2O$ $(M + H)^+$ 329.1654, found 329.1669. Mosher ester **16c**: ^1H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, 1H, *J* 4.9 Hz), 7.62−7.14 (m, 17H), 6.81 (d, 1H, *J* 7.1 Hz), 6.20 (d, 1H, *J* 7.2 Hz), 5.82 (m, 1H), 4.96 (d, 1H, *J* 10.4 Hz), 4.84 (d, 1H, *J* 17.4 Hz), 4.49 (app t, 1H, *J* 6.8 Hz), 3.44 (s, 3H).

(−)-(4*R*)-2,2-Dimethyl-4-[2(*S*)-[(diphenylmethylene)amino]-1(*S*)-hydroxy-3-buten-1-yl]-1,3-dioxolane (10d). Imino alcohol **10d** (67 mg, 43%) was obtained as a white solid: mp 136−137 °C (CH_3OH); TLC R_f 0.49 (hexane−EtOAc, 2:1); $[\alpha]^{24}_D$ −18.7° (*c* 1.7, $CHCl_3$); IR ($CHCl_3$) 3179 (OH), 3080, 2988, 2905, 1621 (C=N) 1122 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.62−7.12 (m, 10H), 6.01 (ddd, 1H, *J* 17.3, 10.5, 6.3 Hz), 5.15 (dd, 1H, *J* 10.5, 1.5 Hz), 5.01 (dd, 1H, *J* 17.3, 1.5 Hz), 4.17−3.93 (m, 4H), 3.80 (app t, 1H, *J* 5.0 Hz), 1.31 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.2, 139.6, 136.5, 136.0, 130.5, 128.8, 128.6, 128.5, 128.3, 127.8, 117.3, 108.7, 76.2, 74.2, 66.8, 66.1, 26.9, 25.5; MS (CI, NH_3) *m/z* 352 $(M + H)^+$, 220, 165, 117; HRMS (CI, NH_3) *m/z* calcd for $C_{22}H_{26}NO_3$ $(M + H)^+$ 352.1913, found 352.1923. Anal. Calcd for $C_{22}H_{25}NO_3$: C, 75.19; H, 7.17; N, 3.99. Found: C, 74.94; H, 6.94; N, 4.24.

(4*R*)-2,2-Dimethyl-4-[2(*R*)-[(diphenylmethylene)amino]-1(*R*)-hydroxy-3-buten-1-yl]-1,3-dioxolane (13d). Imino alcohol **13d** (59 mg, 41% as a 30:11 diastereoisomeric ratio of **10d** and **13d**) was obtained as a white solid: mp 96−98 °C (hexane−EtOAc); TLC R_f 0.48 (hexane−EtOAc, 2:1); IR ($CHCl_3$) 3176, 3080, 2988, 2904, 1621 (C=N), 1121 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.69−7.12 (m, 10H), 6.05 (m, 1H), 5.13 (d, 1H, *J* 10.4 Hz), 4.92 (d, 1H, *J* 17.3 Hz), 4.11−3.81 (m, 4H), 3.85 (app t, 1H, *J* 6.2 Hz), 1.37 (s, 3H), 1.32 (s, 3H); MS (CI, NH_3) *m/z* 352 $(M + H)^+$, 274, 250, 220, 182; HRMS (CI, NH_3) *m/z* calcd for $C_{22}H_{26}NO_3$ $(M + H)^+$ 352.1913, found 352.1933.

***tert*-Butyl4(*S*)-[2(*S*)-[(Diphenylmethylene)amino]-1(*R*)-hydroxy-3-buten-1-yl]-2,2-dimethyl-3-oxazolidinecarboxylate (10e).** Imino alcohol **10e** (50 mg, 38% as a 17:21 diastereoisomeric ratio of **10e** and **13e**) was obtained as a yellow oil: TLC R_f 0.68 (hexane−EtOAc, 2:1); IR ($CHCl_3$) 3452 (OH), 3060, 2978, 2879, 1692 (NCO_2), 1662 (C=N), 1447 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.74−7.09 (m, 10H), 6.07 (m, 1H), 5.13 (d, 1H, *J* 17.0 Hz), 4.91 (d, 1H, *J* 10.4 Hz), 4.17−3.48 (m, 5H), 1.42 (s, 6H), 1.38 (s, 9H); MS (CI, NH_3) *m/z* 451 $(M + H)^+$, 395, 250, 221, 167; HRMS (CI, NH_3) *m/z* calcd for $C_{27}H_{35}N_2O_4$ $(M + H)^+$ 451.2597, found 451.2628.

(−)-*tert*-Butyl 4(*S*)-[2(*R*)-[(Diphenylmethylene)amino]-1(*S*)-hydroxy-3-buten-1-yl]-2,2-dimethyl-3-oxazolidinecarboxylate (13e). Imino alcohol **13e** (89 mg, 40%) was obtained as a yellow solid: mp 90−92 °C (hexane−EtOAc); TLC R_f 0.68 (hexane−EtOAc, 2:1); $[\alpha]^{24}_D$ −25.2° (*c* 1.1, $CHCl_3$); IR ($CHCl_3$) 3452 (OH), 3041, 2977, 2876, 1693 (NCO_2), 1662 (C=N), 1447 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, 2H, *J* 7.2 Hz), 7.38−7.08 (m, 8H), 6.04 (m, 1H), 5.09 (d, 1H, *J* 9.8 Hz), 5.00 (d, 1H, *J* 17.4 Hz), 4.14−4.07 (m, 3H), 3.95 (m, 1H), 3.81 (m, 1H), 1.47 (s, 3H), 1.42 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.6, 152.1, 139.3, 136.9, 136.2, 130.2, 128.5, 128.4, 128.3, 128.0, 127.5, 116.4, 93.3, 79.9, 74.4, 67.6, 63.9, 58.1, 28.4, 28.3, 27.9, 26.3, 25.9; MS (CI, NH_3) *m/z* 451 $(M + H)^+$, 250, 221, 183, 167; HRMS (CI, NH_3) *m/z* calcd for $C_{27}H_{35}N_2O_4$ $(M + H)^+$ 451.2597, found 451.2610. Anal. Calcd for $C_{27}H_{34}N_2O_4$: C, 71.97; H, 7.61; N, 6.22. Found C, 71.96; H, 7.85; N, 6.01.

(+)-(3*R*,4*S*)-3-[(Diphenylmethylene)amino]-1-hexen-4-ol (13f). Imino alcohol **13f** (42 mg, 48%) was obtained as a colorless oil: TLC R_f 0.27 (hexane−EtOAc, 4:1); $[\alpha]^{24}_D$ +19.1° (*c* 0.8, $CHCl_3$); IR (neat) 3512 (OH), 3060, 2966, 2877, 1660 (C=N), 1128 (C−O) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.82−7.45 (m, 10H), 5.97 (ddd, 1H, *J* 17.5, 10.1, 8.2 Hz), 5.49 (d, 1H, *J* 17.5 Hz), 5.46 (d, 1H, *J* 10.1 Hz), 3.97−3.85 (m, 2H), 1.44 (m, 2H), 0.95 (t, 3H, *J* 7.3 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 168.4, 137.7, 136.4, 132.4, 130.3, 128.3, 128.1, 127.8, 126.5, 125.6, 117.4, 80.5, 70.2, 26.0, 10.8; MS (CI, NH_3) *m/z* 280 $(M + H)^+$, 221, 200, 183, 105; HRMS (CI, NH_3) *m/z* calcd for $C_{19}H_{22}NO$ $(M + H)^+$ 280.1701, found 280.1701.

(+)-(3*R*,4*S*)-3-[(Diphenylmethylene)amino]-6-methyl-1-hepten-4-ol (13g). Imino alcohol **13g** (47 mg, 41%) was obtained as a colorless oil: TLC R_f 0.32 (hexane−EtOAc, 4:1); $[\alpha]^{24}_D$ +23.4° (*c* 0.7, $CHCl_3$); IR (neat) 3524 (OH), 3060, 2965, 2876, 1660 (C=N), 1077 (C−O) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.79−7.45 (m, 10H), 5.95 (ddd, 1H, *J* 16.3, 10.0, 7.5 Hz), 5.47 (d, 1H, *J* 16.3 Hz), 5.45 (d, 1H, *J* 10.0 Hz), 4.18 (m, 1H), 3.78 (m, 1H), 1.74 (m, 1H), 1.40 (m, 1H), 1.11 (m, 1H), 0.91 (d, 3H, *J* 6.4 Hz), 0.88 (d, 3H, *J* 6.4 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 162.9, 137.5, 132.4, 130.0, 129.2, 128.2, 122.8, 68.4, 58.9, 42.0, 24.3, 23.2, 21.9, MS (CI, NH_3) *m/z* 308 $(M + H)^+$, 222, 200, 182, 105; HRMS (CI, NH_3) *m/z* calcd for $C_{21}H_{26}NO$ $(M + H)^+$ 308.2014, found 308.2003.

Preparation of (−)-(1*R*,2*S*)-2-Amino-1-cyclohexyl-3-buten-1-ol (11a). Imine **10a** (66 mg, 0.2 mmol) in MeOH (1 mL) was added to 10 mL of a 1 M HCl/CH_3OH solution (1:1 v/v) at 0 °C, and the mixture was stirred for 15 min. The reaction solution was concentrated under reduced pressure and washed with ether (2 × 10 mL) and the aqueous residue basified with NaOH (5 mL, 2.5 M in H_2O). Extraction with ethyl acetate (3 × 10 mL), drying (K_2CO_3), and concentration *in vacuo* gave **11a** (33mg, 98%) as a white solid: mp 65−66 °C ($CHCl_3$); $[\alpha]^{24}_D$ −19.2° (*c* 0.8, $CHCl_3$); IR ($CHCl_3$) 3374 (OH), 3298, 3073, 2922, 2851, 1574, 1449, 1105 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.87 (ddd, 1H, *J* 17.0, 9.1, 7.3 Hz), 5.20 (d, 1H, *J* 17.0 Hz), 5.18 (d, 1H, *J* 9.1 Hz), 3.51 (m, 1H), 3.20 (dd, 1H, *J* 8.1, 3.4 Hz), 1.91−1.00 (m, 11H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 137.8, 117.0, 78.3, 55.8, 40.4, 29.4, 29.0, 26.7, 26.2, 26.1; MS (CI, NH_3) *m/z* 170 $(M + H)^+$, 152, 57; HRMS (CI, NH_3) *m/z* calcd for $C_{10}H_{20}NO$ $(M + H)^+$ 170.1545, found 170.1538.

(+)-(1*S*,2*R*)-2-Amino-1-cyclohexyl-3-buten-1-ol (14a). Amino alcohol **14a** (33 mg, 97%), prepared from **13a** using the procedure for **11a**, was obtained as a white solid: mp 65−66 °C ($CHCl_3$); $[\alpha]^{24}_D$ +19.1° (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 3347, 3297, 3074, 3005, 2922, 2851, 1573, 1449, 1105 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.89 (ddd, 1H, *J* 17.0, 9.2, 7.4 Hz), 5.20 (d, 1H, *J* 17.0 Hz), 5.17 (d, 1H, *J* 9.2 Hz), 3.50 (m, 1H), 3.20 (dd, 1H, *J* 8.3, 3.6 Hz), 1.99−0.96 (m, 11H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 137.8, 116.9, 78.3, 55.8, 40.4, 29.4, 29.0, 26.7, 26.2, 26.0; MS (CI, NH_3) *m/z* 170 $(M + H)^+$, 152, 57; HRMS (CI, NH_3) *m/z* calcd for $C_{10}H_{20}NO$ $(M + H)^+$ 170.1545, found 170.1544.

Preparation of (−)-(1*R*,2*S*)-1-Cyclohexyl-1-[(diphenylmethylene)amino]-3-buten-2-ol (21). To a stirred solution of iminol **13a** (50 mg, 0.15 mmol) and 2,6-lutidine (35 μL, 0.30 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added trifluoromethanesulfonic anhydride (29 μL, 0.17 mmol) dropwise. After 12 h at 0 °C under N_2, H_2O (1 mL) was added and the organic phase separated, concentrated under reduced pressure, and chromatographed on silica (hexane-Et_2O, 4:1) to give **21** (22 mg, 44%) as a yellow oil. TLC R_f 0.41 (hexane−EtOAc, 4:1); $[\alpha]^{24}_D$ −35.8° (*c* 1.0, $CHCl_3$); IR (neat) 3451 (OH), 3060, 3020, 2926, 2851, 1621 (C═N), 1446, 1197 (C−O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.8−7.0 (m, 10H), 6.04 (m, 1H), 5.06 (app t, 1H, *J* 10.5Hz), 4.90 (2d, 1H, *J* 17.3 Hz), 4.37, 4.09, 3.96 (3m, 2H), 1.68−0.71 (m, 11H); ^{13}C NMR (75.1 MHz, $CDCl_3$) δ 168.8, 168.6, 140.1, 140.0, 138.0, 137.5, 137.1, 136.9, 132.8, 130.4, 129.1, 128.9, 128.7, 128.6, 128.4, 128.0, 117.6, 117.2, 83.1, 82.7, 66.8, 66.7, 39.6, 39.2, 30.8, 30.1, 28.0, 27.4, 26.7, 26.6, 26.5, 26.2; MS (CI, NH_3) *m*/*z* 334 $(M + H)^+$, 222, 200, 183, 168, 105, 83; HRMS (CI, NH_3) *m*/*z* calcd for $C_{23}H_{28}NO$ $(M + H)^+$ 334.2172, found 334.2172.

Preparation of (−)-(1*R*,2*S*)-1-Amino-1-cyclohexylbutan-2-ol (22). Imino alcohol **21** (60 mg, 0.18 mmol), MeOH (10 mL), and 3 M HCl (1 mL) were allowed to react for 10 min when 5% Pd/C (20 mg) was added, and the mixture was hydrogenated at 1 atm for 12 h. The reaction slurry was filtered through celite and concentrated under reduced pressure. The residual aqueous phase was washed with Et_2O (2 × 10 mL), basified with aqueous 10% NaOH (3 mL), and extracted with EtOAc (4 × 15 mL). The EtOAc fractions were combined, dried over K_2CO_3, and concentrated *in vacuo* to **21** (28 mg, 0.16 mmol, 90%) as a white solid: mp 75−77 °C ($CHCl_3$); $[\alpha]^{24}_D$ −12.2° (*c* 0.25, CH_3OH); IR ($CHCl_3$) 3424 (OH), 3294, 2925, 2874, 1571, 1449, 1105 (C−O) cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ 3.39 (m, 1H), 2.36 (m, 1H), 1.80−1.02 (m, 13H), 0.99 (t, 3H, *J* 7.4 Hz); ^{13}C NMR (75.1 MHz, CD_3OD) δ 74.1, 60.8, 41.6, 31.7, 29.1, 28.1, 27.8, 27.6, 27.5, 10.6; MS (CI, NH_3) *m*/*z* 172 $(M + H)^+$, 151, 137, 98, 58; HRMS (CI, NH_3) *m*/*z* calcd for $C_{10}H_{22}NO$ $(M + H)^+$ 172.1701, found 172.1701.

(−)-(1*R*,2*S*)-1-Benzamido-1-cyclohexylbutan-2-ol (23). To a stirred solution of amino alcohol **22** (20 mg, 0.12 mmol) and Et_3N (25 μL, 0.20 mmol) in CH_2Cl_2 at room temperature was added benzoyl chloride (18 μL, 0.15 mmol). After 12 h the reaction mixture was concentrated under reduced pressure and chromatographed on silica (hexane−EtOAc, 4:1) to afford **23** (27 mg, 0.10 mmol, 83%) as a white solid: mp 191−192 °C ($CHCl_3$); TLC R_f 0.47 (hexane−EtOAc, 1:1); $[\alpha]^{24}_D$ −34.3° (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 3326, 2928, 2853, 1637 (C═O), 1531, 1102 (C-O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (m, 2H), 7.46 (m, 3H), 6.18 (d, 1H, *J* 9.4 Hz), 4.10 (m, 1H), 3.74 (m, 1H), 1.94−1.09 (m, 13H), 1.04 (t, 3H, *J* 7.4 Hz); ^{13}C NMR (75.1 MHz, $CDCl_3$) δ 168.5, 134.5, 131.6, 128.7, 127.0, 74.3, 59.1, 38.7, 30.9, 29.0, 26.2, 26.1, 25.9, 25.7, 10.5; MS (CI, NH_3) *m*/*z* 276 $(M + H)^+$, 258, 216, 122; HRMS (CI, NH_3) *m*/*z* calcd for $C_{17}H_{26}NO_2$ $(M + H)^+$ 276.1963, found 276.1950. Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15; N, 5.09. Found: C, 74.28; H, 9.06; N, 4.99.

(+)-(1*S*,2*R*)-2-Amino-1-cyclohexylbutan-1-ol (24). Amino alcohol **24** (62 mg, 81%), prepared from **13a** according to the procedure described for **22**, was obtained as a white solid: mp 167−169 °C ($CHCl_3$); $[\alpha]^{24}_D$ +6.9° (*c* 0.5, CH_3OH); IR ($CHCl_3$) 3364 (OH), 3295, 2924, 2875, 1577 (C-N), 1462, 1103 (C−O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.13 (dd, 1H, *J* 8.0, 4.0 Hz), 2.76 (m, 1H), 1.96−0.81 (m, 16H); ^{13}C NMR (75.1 MHz, CD_3OD) δ 75.5, 53.6, 39.2, 28.2, 28.1, 25.4, 24.9, 24.8, 19.4, 8.6; MS (CI, NH_3) *m*/*z* 172 $(M + H)^+$, 154, 88, 58; HRMS (CI, NH_3) *m*/*z* calcd for $C_{10}H_{22}NO$ $(M + H)^+$ 172.1701, found 172.1699.

(+)-(1*S*,2*R*)-2-Benzamido-1-cyclohexylbutan-1-ol (25). Amide **25** (72 mg, 90%), prepared using the same method as for **23**, was obtained as a white solid: mp 185−187 °C ($CHCl_3$); TLC R_f 0.46 (hexane−EtOAc, 1:1); $[\alpha]^{24}_D$ +26.8° (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 3327, 2928, 2853, 1632 (C═O), 1532, 1105 (C−O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (m, 2H), 7.45 (m, 3H), 6.49 (d, 1H, *J* 8.9 Hz), 4.27 (m, 1H), 3.46 (m, 1H), 2.07−1.06 (m, 13H), 0.98 (t, 3H, *J* 7.4 Hz); ^{13}C NMR (75.1 MHz, $CDCl_3$) δ 167.4, 134.9, 131.4, 128.5, 126.9, 78.8, 52.7, 40.8, 29.6, 28.9, 26.3, 25.9, 25.8, 20.8, 10.8; MS (CI, NH_3) *m*/*z* 551 $(2M + H)^+$, 276 $(M + H)^+$, 258, 216, 139, 122; HRMS (CI, NH_3) *m*/*z* calcd for $C_{17}H_{26}NO_2$ $(M + H)^+$ 276.1963, found 276.1942; Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.14, H, 9.15; N, 5.09. Found: C, 73.84; H, 8.85; N, 4.94.

Preparation of (1*S,2*R**)-1-Cyclohexyl-2-nitrobutan-1-ol (27) and (1*R**,2*R**)-1-Cyclohexyl-2-nitrobutan-1-ol (28).** Nitro alcohols **27** and **28** were synthesized from cyclohexanecarboxaldehyde and nitropropane (**26**) using the procedure reported by Seebach[15] *et al.* giving *syn*-**28** (0.70 g, 39%) as a yellow oil and *anti*-**27** (0.34 g, 20%) as an orange solid. *anti*-Isomer **27**: mp 65−67 °C ($CHCl_3$); TLC R_f 0.20 (hexane−EtOAc, 4:1); IR (neat) 3536 (OH), 3455, 2973, 2928, 2882, 1552 (C-NO_2), 1450, 1101 (C−O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.47 (ddd, 1H, *J* 11.1, 4.8, 4.5 Hz), 3.72 (dd, 1H, *J* 7.4, 4.5 Hz), 2.12−0.98 (m, 13H), 0.92 (t, 3H, *J* 7.4 Hz); ^{13}C NMR (75.1 MHz, $CDCl_3$) δ 91.9, 76.8, 40.6, 29.7, 28.3, 26.5, 26.3, 26.0, 21.7, 10.9; MS (CI, NH_3) *m*/*z* 219 $(M + NH_4)^+$, 184, 172, 154, 137, 95, 81, 58; HRMS (CI, NH_3) *m*/*z* calcd for $C_{10}H_{23}N_2O_3$ $(M + NH_4)^+$ 219.1709, found 219.1713. Anal. Calcd for $C_{10}H_{19}NO_3$: C, 59.66; H, 9.52; N, 6.96. Found: C, 59.62; H, 9.33; N, 6.85. *syn*-Isomer **28**: TLC R_f 0.25 (hexane−EtOAc, 4:1); IR (neat) 3544, 3446, 2973, 2929, 2882, 1552 (C−NO_2), 1449, 1101 (C−O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.58 (ddd, 1H, *J* 5.8, 4.9, 4.5 Hz), 3.62 (dd, 1H, *J* 5.9, 5.8 Hz), 2.11−1.13 (m, 13H), 0.99 (t, 3H, *J* 7.4 Hz); ^{13}C NMR (75.1 MHz, $CDCl_3$) δ 92.2, 76.3, 40.7, 30.2, 27.2, 26.5, 26.4, 26.1, 24.4, 10.6; MS (CI, NH_3) *m*/*z* 219 $(M + NH_4)^+$, 184, 172, 154, 137, 95, 81, 58; HRMS (CI, NH_3) *m*/*z* calcd for $C_{10}H_{23}N_2O_3$ $(M + NH_4)^+$ 219.1709, found 219.1702.

Preparation of (1*S,2*R**)-2-Benzamido-1-cyclohexylbutan-1-ol (29).** (1*S**,2*R**)-1-Cyclohexyl-2-nitrobutan-1-ol (**27**)(0.70 g, 3.50 mmol) in MeOH (50 mL), 3 M HCl (1 mL), and 10% Pd/C (∼100 mg) were hydrogenated at 600 psi for 16 h at 70 °C. The reaction slurry was filtered through Celite and concentrated under reduced pressure. The remaining aqueous fraction was washed with Et_2O (2 × 10 mL) and basified with aqueous 10% NaOH. Extraction of the basic residue with EtOAc (4 × 25 mL), drying over K_2CO_3, and *in vacuo* concentration afforded a white solid. This solid was dissolved in CH_2Cl_2 (10 mL) and added to a stirred solution of Et_3N (0.46 mL, 3.50 mmol) in CH_2Cl_2 (15 mL). Benzoyl chloride (0.29 mL, 2.5 mmol) was added dropwise to the reaction solution at 0 °C. After 12 h the solution was concentrated *in vacuo* and chromatographed on silica (hexane−EtOAc, 1:1) to afford **29** (0.50 g, 57%) as white solid: mp 161−163 °C ($CHCl_3$); TLC R_f 0.46 (hexane−EtOAc, 1:1); IR ($CHCl_3$) 3327, 2928, 2853, 1632 (C═O), 1532, 1105 (C−O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (m, 2H), 7.46 (m, 3H), 6.49 (d, 1H, *J* 8.9 Hz), 4.26 (m, 1H), 3.44 (m, 1H), 1.99−1.11 (m, 13H), 1.04 (t, 3H, *J* 7.4 Hz); ^{13}C NMR (75.1 MHz, $CDCl_3$) δ 167.4, 134.9, 131,4, 128.6, 126.9, 78.8, 52.7, 40.8, 29.6, 28.9, 26.3, 25.9, 25.8, 20.8, 10.8; MS (CI, NH_3) *m*/*z* 276 $(M + H)^+$, 258, 216, 139, 122; HRMS (CI, NH_3) *m*/*z* calcd for $C_{17}H_{26}NO_2$ $(M + H)^+$ 276.1963, found 276.1957. Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.13; H, 9.16; N, 5.09. Found: C, 74.29; H, 8.78; N, 4.97.

(1*R,2*R**)-2-Benzamido-1-cyclohexylbutan-1-ol (30).** Amide **30** (0.24 g, 59%), prepared using the same procedure as for **29**, was obtained as a white solid: mp 137−139 °C ($CHCl_3$); TLC R_f 0.40 (hexane−EtOAc, 1:1); IR ($CHCl_3$) 3327, 2928, 2853, 1637 (C═O), 1531, 1101 (C−O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (m, 2H), 7.45 (m, 3H), 4.26 (m, 1H), 3.44 (m, 1H), 2.06−1.07 (m, 13H), 1.01 (t, 3H, *J* 7.4 Hz); ^{13}C NMR (75.1 MHz, $CDCl_3$) δ 167.3, 134.5, 131.4, 128.6, 126.9, 78.8, 52.7, 40.8, 29.6, 28.9, 26.3, 25.9, 25.8, 20.8, 10.8; MS (CI, NH_3) *m*/*z* 276 $(M + H)^+$, 258, 216, 174, 153; HRMS (CI, NH_3) *m*/*z* calcd for $C_{17}H_{26}NO_2$ $(M + H)^+$ 276.1963, found 276.1962. Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.13; H, 9.16; N, 5.09. Found: C, 74.24; H, 9.00; N, 5.09.

Preparation of (1*R,2*S**)-1-Cyclohexyl-1-nitrobutan-2-ol (32) and (1*R**,2*R**)-1-Cyclohexyl-1-nitrobutan-2-ol (33).** Nitro alcohols **32** and **33** were prepared from (nitromethyl)cyclohexane (**31**)[14] and propanal according to the procedure reported by Seebach[15] *et al.* giving *anti*-**32** (0.25 g, 12%) as a colorless oil and *syn*-**33** (0.65 g, 32%) as a colorless oil.

anti-Isomer **32**: TLC R_f 0.12 (hexane-Et_2O, 4:1); IR (neat) 3550 (OH), 3480, 2974, 2928, 2882, 1552 (C−NO_2), 1450, 1108 (C−O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.34 (dd, 1H, *J* 6.4, 5.7 Hz), 3.97 (m, 1H), 2.12−1.04 (m, 13H), 1.00 (t, 3H, *J* 7.4 Hz); ^{13}C NMR (75.1 MHz, $CDCl_3$) δ 97.2, 72.0, 38.0, 30.3, 29.1, 26.7, 26.4, 26.3, 26.1, 10.2; MS (CI, NH_3) *m*/*z* 219 $(M + NH_4)^+$, 172, 154, 137, 58; HRMS (CI, NH_3) *m*/*z* calcd for $C_{10}H_{23}N_2O_3$ $(M + NH_4)^+$ 219.1709, found 219.1727. *syn*-Isomer **33**: TLC R_f 0.15 (hexane-Et_2O, 4:1); IR (neat) 3550 (OH), 3479, 2974, 2929, 2882, 1552 (C−NO_2), 1450, 1103 (C−O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.18 (dd, 1H, *J* 7.2, 4.1 Hz), 3.77 (m, 1H), 2.16−0.98 (m, 13H), 0.95 (t, 3H, *J* 7.4 Hz); ^{13}C NMR (75.1 MHz, $CDCl_3$) δ 97.3, 70.6, 38.0, 29.5, 27.7, 26.4, 26.2, 26.0, 25.8, 10.5; MS (CI, NH_3) *m*/*z* 219 $(M + NH_4)^+$, 172, 154, 137, 58; HRMS (CI, NH_3) *m*/*z* calcd for $C_{10}H_{23}N_2O_3$ $(M + NH_4)^+$ 219.1709, found 219.1730.

(1*S,2*R**)-1-Benzamido-1-cyclohexylbutan-2-ol (34).** Amide **34** (0.17 g, 56%), prepared using the same procedure as for **29**, was obtained as a white solid: mp 168−169 °C ($CHCl_3$); TLC R_f 0.45 (hexane−EtOAc, 1:1); IR ($CHCl_3$) 3326, 2928, 2853, 1637 (C═O), 1531, 1102 (C−O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (m, 2H), 7.46 (m, 3H), 6.20 (d, 1H, *J* 9.4 Hz), 4.10 (m, 1H), 3.72 (m, 1H), 1.94−1.09 (m, 13H), 1.04 (t, 3H, *J* 7.4 Hz); ^{13}C NMR (75.1 MHz, $CDCl_3$) δ 168.5, 134.5, 131.6, 128.7, 127.0, 74.3, 59.0, 38.7, 30.9, 29.0, 26.2, 26.1, 25.9, 25.7, 10.5; MS (CI, NH_3) *m*/*z* 276 $(M + H)^+$, 258, 216, 163, 122; HRMS (CI, NH_3) *m*/*z* calcd for $C_{17}H_{26}NO_2$ $(M + H)^+$ 276.1963, found 276.1948. Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.13; H, 9.16; N, 5.09. Found: C, 74.37; H, 8.92; N, 4.98.

(1*R,2*R**)-1-Benzamido-1-cyclohexylbutan-2-ol (35).** Amide **35** (0.18 g, 51%), prepared using the same procedure as for **29**, was obtained as a white solid: mp 144−145 °C ($CHCl_3$); TLC R_f 0.49 (hexane−EtOAc, 1:1); IR ($CHCl_3$) 3326, 2928, 2853, 1637 (C═O), 1531, 1104 (C−O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.72 (m, 2H), 7.36 (m, 3H), 6.39 (d, 1H, *J* 9.0 Hz), 3.79 (m, 2H), 1.92−1.00 (m, 13H), 0.94 (t, 3H, *J* 7.4 Hz); ^{13}C NMR (75.1 MHz, $CDCl_3$) δ 168.0, 134.8, 131.4, 128.6, 126.9, 72.0, 57.3, 39.7, 30.2, 29.9, 28.0, 26.4, 26.3, 26.2, 10.2; MS (CI, NH_3) *m*/*z* 258 $(M + H - H_2O)^+$, 216, 174, 167, 122; HRMS (CI, NH_3) *m*/*z* calcd for $C_{17}H_{24}NO$ $(M + H\text{-}H_2O)^+$ 258.1858, found 258.1854. Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.13; H, 9.16; N, 5.09. Found: C, 74.31; H, 8.90; N, 4.85.

(−)-*cis*-(4*R*,5*S*)-4-Cyclohexyl-5-ethyl-1,3-oxazolidin-2-one (36). To a stirred solution of amino alcohol **22** (21 mg, 0.12 mmol) and diisopropylethylamine (47 μL, 0.27 mmol) in CH_2Cl_2 (5 mL) at 0 °C was added triphosgene (18 mg, 0.06 mmol). The reaction solution was allowed to warm to room temperature with stirring for 12 h. H_2O (1 mL) and EtOAc (15 mL) were added to the mixture, and the organic phase was separated, dried over Na_2SO_4, concentrated under reduced pressure, and chromatographed on silica (EtOAc) to afford **36** (21 mg, 85%) as colorless crystals: mp 143−144 °C ($CHCl_3$); TLC R_f 0.62 (EtOAc); $[\alpha]^{24}_D$ −17.8° (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 2928, 2854, 1750 (C═O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.57 (s, 1H), 4.47 (m, 1H), 3.56 (app t, 1H, *J* 7.1 Hz), 1.86−1.11 (m, 13H), 1.07 (t, 13H, *J* 7.4 Hz); ^{13}C NMR (75.1 MHz, $CDCl_3$) δ 160.3, 81.9, 61.1, 37.5, 30.4, 29.0, 26.0, 25.7, 25.5, 22.0, 10.5; MS (CI, NH_3) *m*/*z* 215 $(M + H)^+$, 198, 72; HRMS (CI, NH_3) *m*/*z* calcd for $C_{11}H_{23}N_2O_2$ $(M + NH_4)^+$ 215.1760, found 215.1757. Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.96; H, 9.71; N, 7.10. Found: C, 66.93; H, 9.45; N, 6.83.

(−)-(1*R*,2*S*)-1-Cyclohexyl-1-(3,5-dinitrobenzamido)-2-[2(*R*)-methoxyphenylacetoxy] butane (37). To a stirred solution of amino alcohol **22** (34 mg, 0.20 mmol) in CH_2Cl_2 (10 mL) was added 2,6-lutidine (31 μL, 0.27 mmol) and 3,5-dinitrobenzoyl chloride (46 mg, 0.21 mmol). After stirring for 12 h at room temperature the reaction was filtered through silica and concentrated *in vacuo*. The crude solid was redissolved in dry CH_2Cl_2 (10 mL) and placed under an atmosphere of nitrogen. To the reaction solution was added dicyclohexylcarbodiimide (82 mg, 0.40 mmol), (*R*)-*O*-methylmandelic acid (66 mg, 0.40 mmol), and 4-(dimethylamino)pyridine (5 mg). After 3 h the mixture was concentrated under reduced pressure and directly chromatographed on silica (hexane−EtOAc, 4:1) to give **37** (72 mg, 70% overall) as a white solid. Recrystallization (CH_3OH, −10 °C) gave **37** as colorless needles: mp 182−184 °C (CH_3OH); TLC R_f 0.46 (hexane−EtOAc, 4:1); $[\alpha]^{24}_D$ −10.2° (*c* 0.7, $CHCl_3$); IR ($CHCl_3$) 3096, 2929, 2852, 1737 (C═O), 1673 (C═O), 1543 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.91 (s, 2H), 7.45−7.31 (m, 5H), 6.49 (d, 1H, *J* 9.8 Hz), 5.00 (m, 1H), 4.81 (s, 1H), 4.31 (m, 1H), 3.49 (s, 3H), 1.77−0.90 (m, 13H), 0.71 (t, 3H, *J* 7.4 Hz); ^{13}C NMR (75.1 MHz, $CDCl_3$) δ 171.3, 162.6, 148.7, 138.1, 136.1, 128.8, 128.6, 127.1, 127.0, 121.0, 82.7, 57.6, 38.3, 30.8, 28.5, 26.0, 25.9, 25.8, 23.9, 9.7; MS (CI, NH_3) *m*/*z* 531 $(M + NH_4)^+$, 484, 454, 348, 318, 184, 121; HRMS (CI, NH_3) *m*/*z* calcd for $C_{26}H_{35}N_4O_8$ $(M + NH_4)^+$ 531.2455, found 531.2474. Anal. Calcd for $C_{26}H_{31}N_3O_8$: C, 59.99;H, 6.04; N, 8.40. Found: C, 60.26; H, 6.09; N, 8.41.

(−)-(3*S*,4*R*)-4-Amino-1-hexen-3-ol Hydrochloride (38a). To a stirred solution of imino alcohol **13f** (60 mg, 0.22 mmol) and 2,6-lutidine (52 μL, 0.45 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added trifluoromethanesulfonic anhydride (56 μL, 0.33 mmol) dropwise. The mixture was stirred for 8 h, filtered through silica, concentrated *in vacuo*, and acidified (1 M HCl in MeOH). The resulting aqueous residue was washed with EtOAc (3 × 10 mL) and concentrated under reduced pressure to afford amino alcohol **38a** (12 mg, 38%) as a colorless viscous oil: $[\alpha]^{24}_D$ −8.9° (*c* 0.35, H_2O); IR (neat) 3390, 2969, 2930, 1605 (C═C), 1505, 992 (C−O) cm^{-1}; ^1H NMR (500 MHz, D_2O) δ 5.84 (ddd, 1H, *J* 17.3, 10.6, 6.0 Hz), 5.40 (d, 1H, *J* 17.3 Hz), 5.37 (d, 1H, *J* 10.6 Hz), 4.38 (dd, 1H, *J* 5.2, 4.4 Hz), 3.25 (m, 1H), 1.67 (m, 1H), 1.55 (m, 1H), 0.96 (t, 3H, *J* 7.5 Hz); ^{13}C NMR (100 MHz, D_2O) δ 134.3, 119.9, 71.7, 57.6, 21.8, 10.0; FABMS (3-NBA) *m*/*z* 267 $[2(M + H) + H]^+$, 231 $[2(M - Cl)+H]^+$, 116 $(M + H - Cl)^+$, 57; HRFABMS (3-NBA) *m*/*z* calcd for $C_6H_{14}NO$ $(M + H - Cl)^+$ 116.1075, found 116.1081.

(−)-(3*S*,4*R*)-4-Amino-6-methyl-1-hepten-3-ol Hydrochloride (38b). Amine hydrochloride **38b** (14 mg, 31%), prepared from **13g** as for **38a**, was obtained as a colorless oil using the procedure described for **38b**: $[\alpha]^{24}_D$ −11.3° (*c* 0.20, H_2O); IR (neat) 3360, 2957, 2932, 1602, 1501, 1050 (C−O) cm^{-1}; ^1H NMR (500 MHz, D_2O) δ 5.85 (ddd, 1H, *J* 17.2, 10.7, 5.7 Hz), 5.42 (d, 1H, *J* 17.2 Hz), 5.37 (d, 1H, *J* 10.7 Hz), 4.40 (app t, 1H, *J* 5.4 Hz), 3.42 (m, 1H), 1.69−1.10 (m, 3H), 0.91 (d, 3H, *J* 6.5 Hz), 0.88 (d, 3H, *J* 6.5 Hz); ^{13}C NMR (100 MHz, D_2O) δ 134.2, 119.8, 72.0, 54.2, 37.3, 24.4, 22.8, 21.5; FABMS (3-NBA) *m*/*z* 323 $[2(M + H) - Cl]^+$, 287 $[2(M - Cl) + H]^+$, 144 $(M + H - Cl)^+$, 85; HRFABMS (3-NBA) *m*/*z* calcd for $C_8H_{18}NO$ $(M + H - Cl)^+$ 144.1388, found 144.1389.

(−)-*cis*-(4*R*,5*S*)-5-Ethenyl-4-ethyl-1,3-oxazolidin-2-one (39a). Oxazolidinone **39a** (12 mg, 77%), prepared from **38a** using the same procedure as for **36**, was obtained as a yellow oil: TLC R_f 0.55 (EtOAc); $[\alpha]^{24}_D$ −40.6° (*c* 0.7, $CHCl_3$); IR ($CHCl_3$) 2929, 2879, 1751 (C═O), 1127 (C−O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.32 (br s, 1H), 5.91 (ddd, 1H, *J* 17.1, 10.5, 7.9 Hz), 5.46 (d, 1H, *J* 17.1 Hz), 5.38 (d, 1H, *J* 10.5 Hz), 5.05 (app t, 1H, *J* 7.9 Hz), 3.81 (m, 1H), 1.52 (m, 2H), 0.96 (t, 3H, *J* 7.4 Hz); ^{13}C NMR (75.1 MHz, $CDCl_3$) δ 159.3, 131.0, 118.8, 80.6, 57.5, 24.1, 10.3; MS (CI, NH_3) *m*/*z* 159 (M + $NH_4)^+$, 142 $(M + H)^+$, 98; HRMS (CI, NH_3) *m*/*z* calcd for $C_7H_{15}N_2O_2$ $(M + NH_4)^+$ 159.1134, found 159.1136; Anal. Calcd for $C_7H_{11}NO_2$: C, 59.56; H, 7.85; N, 9.92. Found: C, 59.82; H, 7.96; N, 9.89.

(−)-*cis*-(4*R*,5*S*)-5-Ethenyl-4-(2-methylpropyl)-1,3-oxazolidin-2-one (39b). Oxazolidinone **39b** (16 mg, 80%), prepared from **38b** using the same procedure as for **36**, was obtained as a yellow oil: TLC R_f 0.58 (EtOAc); $[\alpha]^{24}_D$ −37.1° (*c* 0.3, $CHCl_3$); IR ($CHCl_3$) 2955, 2871, 1747 (C═O), 1120 (C−O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.89 (ddd, 1H, *J* 17.2, 10.5, 6.5 Hz), 5.45 (d, 1H, *J* 17.2 Hz), 5.38 (d, 1H, *J* 10.5 Hz), 5.34 (br s, 1H), 5.06 (app t, 1H, *J* 7.6 Hz), 3.97 (m, 1H), 1.80−1.15 (m, 3H), 0.98 (d, 3H, *J* 6.5 Hz), 0.92 (d, 3H, *J* 6.5 Hz); ^{13}C NMR (75.1 MHz, $CDCl_3$) δ 159.3, 131.0, 120.1, 80.6, 53.9, 39.7, 25.1, 23.4, 21.4; MS (CI, NH_3) *m*/*z* 187 $(M + NH_4)^+$, 170 $(M + H)^+$, 126; HRMS (CI, NH_3) *m*/*z* calcd for $C_9H_{19}N_2O_2$ $(M + NH_4)^+$ 187.1446, found 187.1446.

(+)-(3*R*,4*S*)-3-Amino-1-hexen-4-ol Hydrochloride (40a). Imino alcohol **13f** (76 mg, 0.27 mmol) was added with stirring to (6 mL) of 1 M HCl/CH_3OH solution (1:1, v/v). After 15 min, the solution was concentrated *in vacuo*, and the aqueous residue was washed with EtOAc (3 × 10 mL) and concentrated

under reduced pressure to give **40a** (38 mg, 93%) as a colorless viscous oil: $[\alpha]^{24}_D$ +14.0° (*c* 0.4, H_2O); IR (neat) 3376, 2968, 2937, 1602, 1503 cm^{-1}; ^1H NMR (300 MHz, D_2O) δ 5.82 (ddd, 1H, *J* 17.3, 10.3, 8.1 Hz), 5.48 (d, 1H, *J* 10.3 Hz), 5.40 (d, 1H, *J* 17.3 Hz), 3.83 (m, 1H), 3.73 (m, 1H), 1.46 (m, 2H), 0.89 (t, 3H, *J* 7.4 Hz); ^{13}C NMR (75.1 MHz, D_2O) δ 128.6, 122.7, 72.1, 57.5, 25.8, 9.4; FABMS (3-NBA) *m*/*z* 267 $[2(M + H) - Cl]^+$, 231 $[2(M - Cl) + H]^+$, 116 $(M + H - Cl)^+$, and 57; HRFABMS (CI, NH_3) *m*/*z* calcd for $C_6H_{14}NO$ $(M + H - Cl)^+$ 116.1075, found 116.1067.

(+)-(3*R*,4*S*)-3-Amino-6-methyl-1-hepten-4-ol Hydrochloride (40b). Amine hydrochloride **40b** (18 mg, 96%), prepared from **13g** as for **40a**, was obtained as a white solid: mp 115−117 °C (EtOAc); $[\alpha]^{24}_D$ +17.3° (*c* 0.45, H_2O); IR (KBr) 3330, 3052, 2952, 2897, 1603 (C=C), 1051 (C-O) cm^{-1}; ^1H NMR (300 MHz, D_2O) δ 5.76 (ddd, 1H, *J* 17.3, 10.5, 8.2 Hz), 5.39 (d, 1H, *J* 10.5 Hz), 5.33 (d, 1H, *J* 17.3 Hz), 3.87 (m, 1H), 3.70 (m, 1H), 1.61 (m, 1H), 1.26 (m, 1H), 1.13 (m, 1H), 0.80 (d, 3H, *J* 7.0 Hz), 0.77 (d, 3H, *J* 7.0 Hz); ^{13}C NMR (300 MHz, D_2O) δ 128.6, 122.6, 68.6, 58.0, 41.4, 23.7, 22.5, 20.9; FABMS (3-NBA) *m*/*z* 323 $[2(M + H)\text{-}Cl]^+$, 287 $[2(M - Cl) + H]^+$, 144 $(M + H - Cl)^+$, 85, 57; HRFABMS (3-NBA) *m*/*z* calcd for $C_8H_{18}NO$ $(M + H - Cl)^+$ 144.1388, found 144.1397. Anal. Calcd for $C_8H_{18}ClNO$: C, 53.46; H, 10.10; N, 7.79. Found: C, 53.19; H, 10.33; N, 7.62.

(+)-*cis*-(4*R*,5*S*)-4-Ethenyl-5-ethyl-1,3-oxazolidin-2-one (41a). Oxazolidinone **41a** (71 mg, 76%), prepared from **40a** using the same procedure as for **36**, was obtained as a white solid: mp 55−56 °C ($CHCl_3$); TLC R_f 0.48 (EtOAc); $[\alpha]^{24}_D$ +31.4° (*c* 0.7, $CHCl_3$); IR ($CHCl_3$) 2925, 2854, 1748 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.83 (ddd, 1H, *J* 16.2, 10.5, 7.8 Hz), 5.77 (br s, 1H), 5.34 (d, 1H, *J* 10.5 Hz), 5.30 (d, 1H, *J* 16.2 Hz), 4.56 (m, 1H), 4.30 (app t, 1H, *J* 7.8 Hz), 1.73 (m, 1H), 1.60 (m, 1H), 1.03 (t, 3H, *J* 7.4 Hz); ^{13}C NMR (75.1 MHz, $CDCl_3$) δ 159.3, 133.1, 119.3, 81.6, 58.3, 23.6, 10.1; MS (CI, NH_3) *m*/*z* 159 $(M + NH_4)^+$, 142 $(M + H)^+$, 74; HRMS (CI, NH_3) *m*/*z* calcd for $C_7H_{15}N_2O_2$ $(M + NH_4)^+$ 159.1134, found 159.1135. Anal. Calcd for $C_7H_{11}NO_2$: C, 59.56; H, 7.85; N, 9.92. Found: C, 59.74; H, 7.89; N, 9.95.

(+)-*cis*-(4*R*,5*S*)-4-Ethenyl-5-(2-methylpropyl)-1,3-oxazolidin-2-one (41b). Oxazolidinone **41b** (34 mg, 79%), prepared from **40b** using the same procedure as for **36**, was obtained as a yellow oil: TLC R_f 0.53 (EtOAc); $[\alpha]^{24}_D$ +25.5° (*c* 0.65, $CHCl_3$); IR ($CHCl_3$) 2958, 2873, 1751 (C=O), 1124 (C-O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.60 (br s, 1H), 5.78 (ddd, 1H, *J* 17.2, 10.0, 7.6 Hz), 5.25 (d, 1H, *J* 17.2 Hz), 5.24 (d, 1H, *J* 10.0 Hz), 4.70 (m, 1H), 4.25 (app t, 1H, *J* 7.6 Hz), 1.81 (m, 1H), 1.56 (m, 1H), 1.24 (m, 1H), 0.93 (d, 3H, *J* 7.0 Hz), 0.89 (d, 3H, *J* 7.0 Hz); ^{13}C NMR (75.1 MHz, $CDCl_3$) δ 159.9, 133.2, 119.0, 78.5, 58.4, 39.1, 24.8, 23.2, 21.7; MS (CI, NH_3) *m*/*z* 187 $(M + NH_4)^+$, 170 $(M + H)^+$, 126; HRMS (CI, NH_3) *m*/*z* calcd for $C_9H_{19}N_2O_2$ $(M + NH_4)^+$ 187.1446, found 187.1439.

(+)-*cis*-(4*R*,5*S*)-4,5-Diethyl-1,3-oxazolidin-2-one (42). Oxazolidinone **41a** (30 mg, 0.20 mmol), 5% Pd/C (20 mg), and MeOH (5 mL) were hydrogenated at 1 atm for 12 h and filtered through Celite. The filtrate was concentrated under reduced pressure to afford a colorless low melting solid (28 mg, 90%): mp 33−34 °C ($CHCl_3$); TLC R_f 0.43 (hexane−EtOAc, 1:1); $[\alpha]^{24}_D$ +11.6° (*c* 0.9, $CHCl_3$); IR ($CHCl_3$) 3258 (NH), 2972, 2881, 1748 (C=O), 1028 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.84 (br s, 1H), 4.52 (ddd, 1H, *J* 7.5, 4.3, 4.3 Hz), 3.67 (m, 1H), 1.84−1.41 (m, 4H), 1.08 (t, 3H, *J* 7.4, Hz), 0.98 (t, 3H, *J* 7.4 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 159.4, 82.2, 57.5, 23.2, 22.7, 10.82, 10.79; MS (CI, NH_3) *m*/*z* 304 $(2M + NH_4)^+$, 287 $(2M + H)^+$, 161 $(M + NH_4)^+$, 144 $(M + H)^+$; HRMS (CI, NH_3) *m*/*z* calcd for $C_7H_{17}N_2O_2$ $(M + NH_4)^+$ 161.1298, found 161.1294.

Compound **39a** was reduced using the above procedure to give **42** in 85% yield as a low melting colorless solid. Mp 32−33 °C (hexane−EtOAc); mixed mp 32−33 °C (hexane−EtOAc); $[\alpha]^{24}_D$ +11.1° (*c* 0.75, $CHCl_3$). All spectroscopic data were identical with the above data.

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Supporting Information Available: ^1H NMR and ^{13}C NMR spectra for **10c**, **11a**, **13c**, **13f**, **13g**, **14a**, **21**, **22**, **24**, **28**, **29**, **32**, **33**, **34**, **35**, **38a-b**, **39b**, **40a**, **41b**, **42**, and a 9:1 mixture of **13a** and **20** (43 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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