3 H), 0.96 (d, J = 6.7 Hz, 3 H), 1.12 (t, J = 7.2 Hz, 3 H), 1.22 (t, J = 7.2 Hz, 3 H), 1.26 (d, J = 7.1 Hz, 3 H), 1.70 (d, of septet, J = 6.8, 6.7 Hz, 1 H), 2.80 (dq, J = 4.2, 7.1 Hz, 1 H), 3.28 (ddd, J = 4.2, 6.8, 8.3 Hz, 1 H), 3.36 (q, J = 7.2 Hz, 2 H), 3.37 (q, J = 7.1 Hz, 2 H), 4.38 (d, J = 8.3 Hz, 1 H).

***N*-(3-Hydroxy-2,4,4-trimethylpentanoyl)pyrrolidine (21i and 22i).** TASF (1 M THF solution, 0.05 mL, 0.05 mmol) was added to a DMPU (1 mL) solution of **20i** (106 mg, 0.51 mmol) and diphenylsilane (0.110 mL, 0.60 mmol) at 0 °C, and the mixture was stirred for 14 h at 0 °C. Diphenylsilane (0.050 mL, 0.27 mmol) was added, and stirring was continued for 24 h at room temperature. Acid treatment and workup followed by purification by preparative TLC (CH_2Cl_2–ethyl ether, 9:1) gave *N*-(3-hydroxy-2,4,4-trimethylpentanoyl)pyrrolidine, 96 mg (90% yield), as a colorless oil. The threo:erythro ratio was 91:9 (90-MHz ^1H NMR analysis). Repeated recrystallization from diethyl ether–hexane afforded pure threo isomer **21i** as colorless crystals: mp 60 °C; ^1H NMR ($CDCl_3$) δ 0.89 (s, 9 H), 1.34 (d, J = 7 Hz, 3 H), 1.8–2.1 (m, 4 H), 2.69 (dq, J = 2, 6 Hz, 1 H), 3.17 (br s, 1 H), 3.3–3.6 (m, 4 H), 5.73 (br s, 1 H); IR (KBr) 3360, 2990, 2890, 1069, 1473, 1431, 1254, 1131, 985, 610 cm^{-1}; MS (70 eV), m/z (relative intensity) 198 (M^+ – Me, 5), 156 (80), 127 (13), 99 (12), 98 (100), 72 (16), 71 (10), 70 (22), 56 (10), 55 (31), 43 (16), 41 (16), 29 (14). Anal. Calcd for $C_{12}H_{23}NO_2$: C, 67.56; H, 10.87; N, 6.57. Found: C, 67.45; H, 10.67; N, 6.48.

Chemical shifts of α-methyl groups of **21** and **22** in ^{13}C NMR are as follows: **21b**, 17.4; **22b**, 10.4; **21g**, 16.0; **22g**, 10.3; **21h**, 16.0; **22h**, 10.1; **21i**, 18.0; **22i**, 11.8.

***threo*-*N*-[2-Methyl-3-(dimethylphenylsiloxy)-3-phenylpropanoyl]piperidine**: ^1H NMR ($CDCl_3$) δ 0.13 (s, 3 H), 0.22 (d, J = 6.4 Hz, 3 H), 1.3–1.8 (m, 6 H), 3.07 (dq, J = 9.6, 6.4 Hz, 1 H), 3.3–3.7 (m, 4 H), 4.81 (d, J = 9.6 Hz, 1 H), 7.1–7.5 (m, 10 H).

Registry No. **3a**, 112-44-7; **3b**, 100-52-7; **3c**, 104-55-2; **3d**, 66-25-1; **3e**, 111-13-7; **3f**, 98-86-2; **3g**, 13891-87-7; **3h**, 583-60-8; **4a**, 91110-95-1; **4b**, 17908-86-0; **4b′**, 13959-92-7; **4c**, 91110-96-2; **4d″**, 18754-85-3; **4e**, 91110-97-3; **4f**, 34074-18-5; **4f***, 98-85-1; **4g**, 91110-98-4; *cis*-**4h***, 7443-70-1; *trans*-**4h***, 7443-52-9; *cis*-**4h**, 116596-11-3; *trans*-**4h**, 116596-12-4; **8**, 116596-13-5; *syn*-**9**, 5381-86-2; *anti*-**9**, 59825-14-8; **11**, 114660-36-5; **12**, 98264-23-4; **13a**, 91111-01-2; **13a′**, 1030-23-5; **13a″** (isomer 1), 116595-99-4; **13a″** (isomer 2), 116596-18-0; **13b**, 116696-50-5; **13b′**, 91111-02-3; **13b″** (isomer 1), 116696-51-6; **13b″** (isomer 2), 116696-52-7; **13c**, 116596-00-0; **13d**, 7472-23-3; **13e**, 15351-09-4; **14a**, 88196-06-9; **14b**, 91177-70-7; **14b′**, 91111-06-7; **14c**, 38217-37-7; **14d**, 1460-57-7; **14e**, 62560-55-8; **15a**, 40421-52-1; **15b**, 67470-74-0; **15b′**, 91111-07-8; **15c**, 38196-27-9; **15d**, 1792-81-0; **15e**, 39263-91-7; **16a**, 4478-63-1; **16b**, 4587-00-2; **17a**, 6464-55-7; **17b**, 22520-27-0; **18a**, 6464-37-5; **18b**, 22520-26-9; **19** (isomer 1), 80952-63-2; **19** (isomer 2), 80928-01-4; **20a**, 29540-54-3; **20b**, 51975-15-6; **20c**, 106181-33-3; **20d**, 24956-53-4; **20e**, 106181-34-4; **20f**, 106181-35-5; **20g**, 116596-01-1; **20h**, 116596-02-2; **20i**, 116596-03-3; **21b**, 106181-39-9; **21c**, 76943-97-0; **21d**, 116596-04-4; **21e**, 106181-40-2; **21f**, 106181-41-3; **21g**, 116596-05-5; **21h**, 116596-06-6; **21i**, 116596-07-7; **22g**, 116596-08-8; **22h**, 116596-09-9; **22i**, 116596-10-2; **23**, 32213-47-1; **24a**, 2042-85-5; **24b**, 16819-77-5; **25a**, 7693-84-7; **25b**, 1502-78-9; **26b**, 1502-77-8; TASF, 59201-86-4; TBAF, 429-41-4; $RhCl(PPh_3)_3$, 14694-95-2; CsF, 13400-13-0; KF, 7789-23-3; $PhMe_2SiH$, 766-77-8; (p-$F_3CC_6H_4$)Me_2SiH, 19254-78-5; (p-$MeOC_6H_4$)Me_2SiH, 1432-38-8; (p-MeC_6H_4)Me_2SiH, 1432-39-9; Ph_2MeSiH, 776-76-1; (i-PrO)Ph_2SiH, 40391-86-4; (i-PrO)$_3SiH$, 6675-79-2; Ph_2SiH_2, 775-12-2; $HSiMe_2Tol$, 1432-39-9; $FSiMe_2Ph$, 454-57-9; Et_3SiH, 617-86-7; Ph_3SiH, 789-25-3; deuteriodimethylphenylsilane, 22034-19-1; 1-phenylethanol, 98-85-1; 1-deuterio-1-phenylethanol, 3101-96-0; bis(dimethylsilyl)amine, 15933-59-2; 1,3-diphenyl-3-hydroxypropan-1-one, 42052-51-7; cyclohexanecarboxaldehyde, 2043-61-0; cyclohexylmethanol, 100-49-2; chlorodimethylphenylsilane, 768-33-2; 4-bromoanisole, 104-92-7; chlorodimethylsilane, 1066-35-9; (*p*-chlorophenyl)dimethylsilane, 1432-31-1; (*S*)-2-acetoxypropionyl chloride, 36394-75-9; 2-bromo-1-phenyl-1-propanone, 2114-00-3; *cis*-2-(benzoyloxy)cyclohexanol, 37854-36-7; *trans*-2-(benzoyloxy)-cyclohexanol, 59694-07-4; (*S*)-*N*,*N*-dimethyl-2-(1-ethoxyethoxy)propanamide, 116596-14-6; (*S*)-*N*,*N*-dimethyl-2-hydroxypropanamide, 53636-17-2; ethyl vinyl ether, 109-92-2; (*S*)-*N*,*N*-dimethyl-2-*tert*-butoxypropanamide, 116596-15-7; (*S*)-*N*,*N*-dimethyl-2-(2-tetrahydropyranyloxy)propanamide (isomer 1), 116596-16-8; (*S*)-*N*,*N*-dimethyl-2-(2-tetrahydropyranyloxy)-propanamide (isomer 2), 116596-17-9; (*E*)-(2-phenylethenyl)-magnesium bromide, 35672-47-0; 2-(benzyloxy)propanoic acid, 6625-78-1; 1,1-dimethoxycyclohexane, 933-40-4; (3*S*,4*S*,1*E*)-3,4-(cyclohexylidenedioxy)-1-phenyl-1-pentene, 116696-53-8; (3*R*,4*S*,1*E*)-3,4-(cyclohexylidenedioxy)-1-phenyl-1-pentene, 116696-54-9; bis(trimethylsilyl)sulfate, 18306-29-1; (2*S*,3*S*)-2,3-(cyclohexylidenedioxy)butanenitrile, 90458-03-0; (2*R*,3*S*)-2,3-(cyclohexylidenedioxy)butanenitrile, 90458-04-1; (2*S*,3*S*)-2,3-(cyclohexylidenedioxy)butanenitrile oxime, 91517-10-1; (2*R*,3*S*)-2,3-(cyclohexylidenedioxy)butanenitrile oxime, 116696-55-0; *N*,*N*-diethylpropanamide, 1114-51-8; propanoyl chloride, 79-03-8; *threo*-*N*-[2-methyl-3-(dimethylphenylsiloxy)-3-phenylpropanoyl]piperidine, 116596-19-1.

Erythro-Directive Reduction of α-Substituted Alkanones by Means of Hydrosilanes in Acidic Media

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Hydrosilane reduced α-oxy and α-amino ketones and β-keto acid derivatives in trifluoroacetic acid to afford the corresponding erythro alcohols with high diastereoselectivity. The reaction proceeded without racemization at the carbon α to the carbonyl group. The erythro-directive reduction was explained in terms of the proton-bridged Cram cyclic model and successfully applied to the synthesis of physiologically important amino alcohols such as *l*-ephedrine, *l*-methoxamine, and *erythro*-2-methyl-3-piperidino-1-phenylpropanol.

Reduction of carbonyl compounds with chemoselective reagents is a prevailing synthetic strategy for alcohols but still remains problematic with respect to the selectivity.[1] For this purpose, hydrosilane-based reduction is of considerable interest, since the organosilanes are fairly stable under ordinary conditions and become reactive only in the presence of such a promoter as a transition-metal complex,[2]

(1) (a) Hudlicky, M. *Reduction in Organic Chemistry*; Ellis Horwood: Chichester, England, 1984. (b) Brown, H. C.; Krishnamurthy, S. *Tetrahedron* **1979**, *35*, 567.

(2) Ojima, I.; Kogure, T. *Organometallics* **1982**, *1*, 1390.

0022-3263/88/1953-5415$01.50/0

Table I. Hydrosilane/H$^+$ Reduction of α-Oxy and α-Amino Ketones and β-Keto Acid Derivatives

run	ketone[a]	hydrosilane[b]	acid	condtns: temp, (°C), time (h)	prod[c]	% yield[d]	erythro:threo[e] (2:3)
1	**1a**	$PhMe_2SiH$	CF_3COOH[f]	0, 2.5	**2a**	87	>99:1
2	**1a**	$PhMe_2SiH$	$AlCl_3$[g]	0, 2.5	**2a**	64 (74)[h]	70:30
3	**1a**	Et_3SiH	$TfOSiMe_3$[i]	0, 24	**2a**	65 (77)[h]	71:29
4	**1b**	$PhMe_2SiH$	CF_3COOH	0, 4	**2b**	87	>99:1
5	**1c**	$PhMe_2SiH$	CF_3COOH	0, 20	**2c**	66	98:2
6	**1d**	$PhMe_2SiH$	CF_3COOH	0, 0.25	**2d**	84	>99:1
7	**1e**	$PhMe_2SiH$	CF_3COOH	rt,[j] 12	nr[p]	–	–
8	**1f**	$PhMe_2SiH$	CF_3COOH	0, 6	**2f**[k]	72	93:7
9	**1f**	Et_3SiH	CF_3COOH	0, 0.5	**2f**	61	84:16
10	**1g**	$PhMe_2SiH$	CF_3COOH	0, 12	**2g + 3g**	82	47:53
11	**1h**	$PhMe_2SiH$	CF_3COOH	0, 4	**2h**	98	>99:1
12	**1i**	$PhMe_2SiH$	CF_3COOH	0, 3	**2i**	99	99:1
13	**1j**	$PhMe_2SiH$	CF_3COOH	0, 5	**2j**	93	>99:1
14	**1k**	$PhMe_2SiH$	CF_3COOH	0, 6	**2k**	98	>99:1
15	**1l**	$PhMe_2SiH$	CF_3COOH	0, 3	**2l**	94	98:2
16	**1m**	$PhMe_2SiH$	CF_3COOH	0, 6	**2m**	91	98:2[l]
17	**1n**	$PhMe_2SiH$	CF_3COOH	0, 20	**2n**	89	99:1
18	**1o**	$PhMe_2SiH$	CF_3COOH	0, 16	**2o**	65[m,n]	>99:1
19	**1p**	$PhMe_2SiH$	CF_3COOH	0, 5	**2p**	98	>99:1
20	**1q**[o]	$PhMe_2SiH$	CF_3COOH	0, 4	**2q**	98	>99:1
21	**1r**	$PhMe_2SiH$	CF_3COOH	0, 3	**2r**	87	>99:1
22	**1r**	$PhMe_2SiH$	$TfOSiMe_3$[i]	rt, 15	**2r**	83	79:21
23	**1r**	$PhMe_2SiH$	$AlCl_3$[g]	rt, 12	**2r**	66	78:22
24	**1s**	$PhMe_2SiH$	CF_3COOH	0, 4	**2s + 3s**	90	1:1

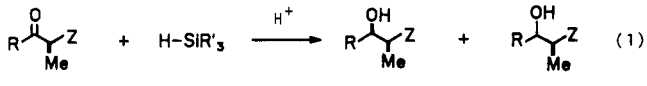
[a] Although racemic ketones were employed unless otherwise noted, one enantiomer is shown in each case for the sake of simplicity. [b] Typically, 1.1–1.2 mol of hydrosilane was employed. [c] The isolated major isomer is shown. [d] The total yield is given. [e] Determined by ^1H NMR analysis by 90- or 400-MHz ^1H NMR analysis unless otherwise noted. [f] Typically, 1–2 mL/mmol of CF_3COOH was employed. [g] One mole of $AlCl_3$ was employed. [h] Yield based on the consumed 1. [i] Tf = CF_3SO_2; 1 mol of $TfOSiMe_3$ was employed. [j] Room temperature. [k] The benzoyl group was removed under basic conditions (1 M KOH–MeOH, room temperature). [l] GLC analysis. [m] An NMR yield. [n] The alcohol **2n** (24%) was also formed. [o] Optically pure **1q** was employed. [p] No reaction.

fluoride ion,[3] or a Lewis acid.[4] In particular, the stereochemical course of the hydrosilane-based reduction has recently been shown to be controlled by the choice of catalyst.[5] Experimental details of the reduction of α-amino and α-oxy ketones and β-keto acid derivatives by means of hydrosilane in acidic media are reported herein. With the hydrosilane/H$^+$ reagent, the corresponding erythro alcohols in synthetically useful levels of diastereomeric purity are now readily accessible, and thus, β- and γ-amino alcohols are prepared successfully.

Results and Discussion

Reduction with hydrosilanes under acidic conditions has long been known as an ionic hydrogenation.[4] Ketone carbonyls are usually reduced to methylene moieties and/or dimeric ethers. Particularly, aromatic ketones are converted thoroughly into hydrocarbons, since the rate of reduction of the benzylic alcohol intermediates is higher than that of the starting ketones. In addition, there have been no reports on the chemo- and stereocontrolled reduction of ketones with the hydrosilane/H$^+$ reagents.[4]

The reduction of α-amino and α-oxy ketones and β-keto acid derivatives with the hydrosilane/H$^+$ reagent was found to proceed at 0 °C in trifluoroacetic acid (TFA) to afford the corresponding alcohols (eq 1). In contrast to the commonly observed overreduction, an α-amino ketone **1a** was reduced to give the alcohol in excellent yield. Formation of the hydrocarbon was not detected by common analytical methods. In addition, *the alcohol consisted of only its erythro isomer* ***2a*** *(>99% selectivity)* (run 1 of Table I).[6,7]



(1)

a: R = Ph, Z = NHCOOEt
b: R = Ph, Z = NHCOOMe
c: R = Ph, Z = $NHSO_2Ph$
d: R = 2,5-$(MeO)_2C_6H_3$, Z = NHCOOMe
e: R = Ph, Z = NMe_2
f: R = Ph, Z = OCOPh
g: R = *n*-Bu, Z = OCH_2Ph
h: R = Ph, Z = $CONEt_2$
i: R = Ph, Z = 
j: R = Ph, Z = 
k: R = 4-ClC_6H_4, Z = 
l: R = Me, Z = $CONEt_2$
m: R = Et, Z = $CONEt_2$
n: R = *i*-Pr, Z = $CONEt_2$
o: R = $CH_2{=}C(CH_3)$, Z = $CONEt_2$
p: R = Ph, Z = 
q: R = Ph, Z = 
r: R = Ph, Z = COOMe
s: R = Me, Z = COOEt

Highly erythro selective reduction was recognized for other substrates except **1g** and **1s**. Such Lewis acids as aluminum chloride and trimethylsilyl trifluoromethanesulfonate also promote the reduction but with inferior selectivity (runs 2, 3, 22, and 23). In the case of 2-(dimethylamino)-1-phenyl-1-propanone (**1e**), the ammonium salt formation (run 7) preceded to inhibit the carbonyl reduction. Whereas methyl 2-benzoylpropanoate (**1r**) gave an erythro alcohol **2r** predominantly, ethyl 2-acetylpropanoate (**1s**) exhibited no stereoselection. However, various β-keto amide derivatives underwent the erythro-selective reduction (runs 11–20) (selectivity >98%).

It is worthy of note that no epimerization at the chiral center took place during the reaction under these acidic

(3) Fujita, M.; Hiyama, T. *J. Org. Chem.*, preceding article in this issue and references cited therein.

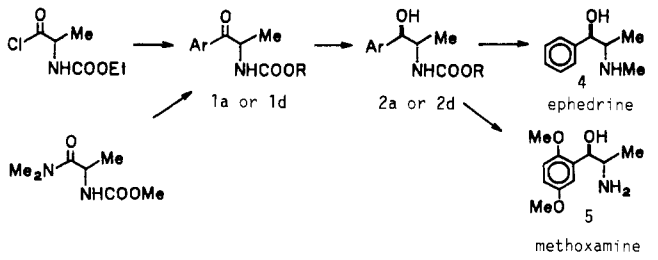
(4) Kursanov, D. N.; Parnes, Z. N.; Loim, N. M. *Synthesis* **1974**, 633. Mechanistic aspects of hydrosilane/H$^+$ reduction: Doyle, M. P.; West, C. T. *J. Org. Chem.* **1975**, *40*, 3835.

(5) Preliminary communications dealing with certain aspects of this work: (a) Fujita, M.; Hiyama, T. *J. Am. Chem. Soc.* **1984**, *106*, 4629; **1985**, *107*, 8294. (b) Fujita, M.; Oishi, T.; Hiyama, T. *Chem. Lett.* **1986**, 837.

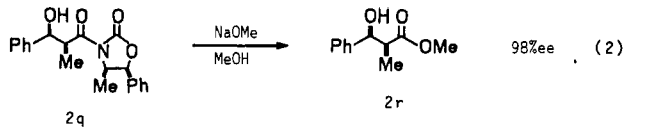
(6) The relative stereochemical nomenclature proposed by Noyori (Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1983**, *105*, 1598, footnote 32) is pertinent throughout this work.

(7) Reported stereoselectivities[10] with other reagents are generally low (erythro:threo = 1:1 to 4:1).

Scheme I

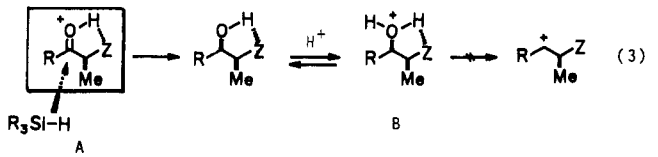


conditions (runs 4, 6, and 20). Particularly, optically active *N*-acyloxazolidin-2-one **1q** was transformed, after the carbonyl reduction, to methyl (2*S*,3*S*)-2-methyl-3-phenyl-3-hydroxypropanoate (**2r**), which was shown to have >98% enantiomeric purity by 400-MHz ^{1}H NMR analysis using Eu(tfc)$_3$ as a chiral shift reagent (eq 2).



The erythro-selective reduction may be explained in terms of the proton-bridged Cram cyclic model (A).[8] Particularly, the high chemo- and stereoselectivity observed for **1h–r** is attributable to the cationic transition state well stabilized by aryl and carbamoyl groups. Substrates that lack such electronic stabilization may be reduced in a nonselective manner as observed for **1g** and **1s**.

Although highly erythro selective reduction of these substrates can be also achieved with Zn(BH$_4$)$_2$ as reported by Nakata, Oishi, and their co-workers,[9] this reagent generally requires a low reaction temperature (usually −78 °C) and careful experimentation due to its pyrophoric and hygroscopic properties.



In addition to the stereochemical control element, the group Z plays a role of stabilization of the resultant alcohol to prevent overreduction. The chelation by the coordinative Z group like B in eq 3 is possibly responsible for suppressing the elimination of the hydroxyl group.

Stereoselective Synthesis of Amino Alcohols of Biological Interest. The erythro-selective reduction was soon applied to the chiral synthesis of biologically active compounds. Starting with (*S*)-alanine, we prepared (*S*)-**1a** and (*S*)-**1d** in optically pure form through Rapoport's procedure.[10] The reduction of (*S*)-**1a** or (*S*)-**1d** with dimethylphenylsilane in TFA gave (1*S*,2*R*)-**2a** or (1*S*,2*R*)-**2d** in good yields, respectively (Table I, runs 5 and 10). Lithium aluminum hydride reduction of (1*S*,2*R*)-**2a** gave *l*-ephedrine (**4**) in 80% yield, while alkaline hydrolysis of (1*S*,2*R*)-**2d** afforded *l*-methoxamine (**5**) in 83% yield (Scheme I). Spectral data as well as optical rotations of these were fully identical with the reported values.

Furthermore, the reduction of **1j** followed by LiAlH$_4$ reduction gave pharmacologically useful *erythro*-γ-amino alcohol **6**[11] (eq 4).

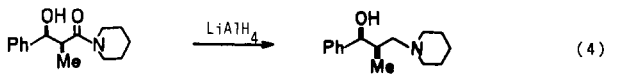
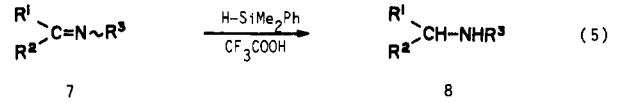


Table II. Reduction of Imines and Oximes with PhMe$_2$SiH/H$^+$ Reagent[a]

substrate	condtns	% yield of 8
7a	rt, overnight	75
7b	rt, overnight	67
7c	rt, overnight	78
7d	rt, 24 h[b]	65
7e	50 °C, 5 days[c]	23
7f	rt, overnight	77

[a] Carried out with HSiMe$_2$Ph (1.2 mol) in TFA or TFA–CH$_2$Cl$_2$ (1:1) (1–2 mL/mmol). [b] KF (1 mol) was added. [c] HSiMe$_2$Ph (2 mol) was employed.

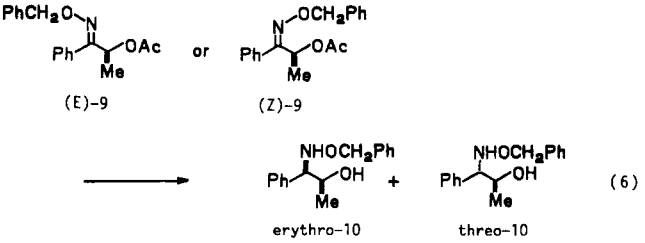
Reduction of C=N Bonds by Means of Hydrosilane. Although transition metal catalyzed hydrosilylation of imines is well-established,[12] very little attention has been paid to the acid-catalyzed reduction of C=N bonds by means of hydrosilane. Loim succeeded in reducing imines ArCH=NAr′ only with Et$_3$SiH–CF$_3$COOH.[13] We found that the hydrosilane/H$^+$ reagent reduces various imines and oximes in good yields (eq 5), in some cases stereospecifically.



a: R^1 = Ph, R^2 = H, R^3 = OCH$_2$Ph
b: R^1 = Ph, R^2 = Me, R^3 = OCOMe
c: R^1 = Ph, R^2 = Me, R^3 = OCOPh
d: R^1,R^2 = (CH$_2$)$_5$, R^3 = OCH$_2$Ph
e: R^1 = C$_7$H$_{15}$, R^2 = Me, R^3 = OCH$_2$Ph
f: R^1 = Ph, R^2 = H, R^3 = Ph

When benzylidene(benzyloxy)amine (**7a**) was allowed to react with 1.2 molar equiv of dimethylphenylsilane in TFA at room temperature, the reduction proceeded smoothly, and *N*-(benzyloxy)benzylamine (**8a**) was isolated in 75% yield. O-Protected oximes of benzaldehyde, acetophenone, and cyclohexanone (**7a–d**) were easily reduced, whereas an acyclic aliphatic derivative **7e** was reduced only in 23% yield even under forcing conditions (50 °C, 5 days, with 2 mol of HSiMe$_2$Ph). Results are summarized in Table II.

It is noteworthy that stereospecificity was observed in the hydrosilane/H$^+$ reduction of (2-acetoxy-1-phenylpropylidene)(benzyloxy)amine (**9**) (eq 6). When (*E*)-**9**[14]



was allowed to react with PhMe$_2$SiH in CF$_3$COOH (room

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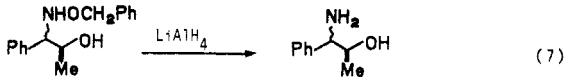
Table III. $PhMe_2SiH/H^+$ and $LiAlH_4$ Reduction of 9

starting material	reducing agent	solvent	% yield	*erythro*-10: *threo*-10
(*E*)-9	$HSiMe_2Ph$	TFA	73	99:1
(*E*)-9	$LiAlH_4$	Et_2O	46	82:18
(*Z*)-9	$HSiMe_2Ph$	TFA	77	24:76
(*Z*)-9	$LiAlH_4$	Et_2O	39	58:42

temperature, overnight), *erythro*-1-phenyl-1-[(benzyloxy)amino]-2-propanol (**10**) was obtained in 99% selectivity (77% yield) after alkaline hydrolysis. In contrast, (*Z*)-**9** gave *threo*-**10** preferentially (erythro:threo = 24:76). These results contrast to lithium aluminum hydride reduction,[15] wherein no stereospecificity was observed. Results are summarized in Table III. Since (*Z*)–(*E*) isomerization[16] of oximes is facile, both isomers of **10** can be obtained by repeating separation and isomerization of **9** followed by the stereospecific reduction.

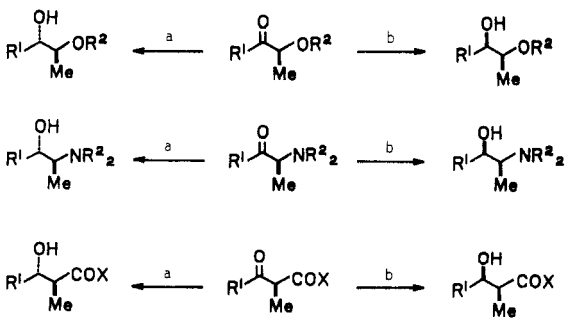
The high erythro selectivity observed in the reduction of (*E*)-**9** should be ascribed again to the proton-bridged Cram cyclic model like the reduction of **1**. On the other hand, the same transition-state model is not applicable to (*Z*)-**9**. The threo selectivity for (*Z*)-**9** may be attributed to nucleophilic attack of the hydrosilane molecule on the $C{=}NH^+OCH_2Ph$ moiety through the Felkin transition-state model.[17]

Lithium aluminum hydride reduction of **10** (erythro:threo = 24:76) afforded a mixture of *erythro*- and *threo*-1-phenyl-1-amino-2-propanol (**11**) in a ratio of 2:8 (eq 7). This transformation confirmed the stereochemistry of **10**.[18] The erythro isomer of the amino alcohol **11** is naturally occurring norisoephedrine.[19]



10 11 (7)

Conclusion. The reduction with hydrosilane/H^+ reagent is shown to be a powerful and reliable method for the synthesis of erythro isomers of 2-amino alcohols, 1,2-diols, and 3-hydroxyalkanoic acid derivatives and compensates the threo-directing reduction with the hydrosilane/F^- reagent.[3] Thus, both threo- and erythro-selective reductions of various α-substituted alkanones using the same hydrosilanes are achieved simply by a proper selection of the catalyst as summarized below.



(a) (i) $HSiR_3/F^-$, (ii) H_3O^+; (b) $HSiR_3/H^+$

Experimental Section

Instrumentation and methods are the same as those described in the preceding paper. Trifluoroacetic acid and dimethylphenylsilane were purchased from Tokyo Kasei Co. Ltd and Shin-etsu Kagaku Co. Ltd, respectively, and used directly. Other reagents were purchased from Tokyo Kasei Co. Ltd or Aldrich Co. Ltd and used directly or after distillation.

Preparation of α-Substituted Alkanones (1). Ketones **1a** and **1c** were prepared according to the procedure described in ref 10 and gave the following spectral data.

(*S*)-2-[(Ethoxycarbonyl)amino]-1-phenyl-1-propanone (1a): bp 130 °C (bath temp) (3 Torr); mp 64 °C (lit.[10] mp 62–63 °C); $[\alpha]^{20}_D$ −5.12° (*c* 5.0, CH_2Cl_2) [lit.[10] $[\alpha]^{23}_D$ −5.9° (*c* 5, CH_2Cl_2)].

(*S*)-2-[(Phenylsulfonyl)amino]-1-phenyl-1-propanone (1c): mp 95–97 °C (lit.[10] mp 97–98 °C); $[\alpha]^{23}_D$ 54.8° (*c* 1.08, CH_2Cl_2) (corresponding to 89% optical purity) [lit.[10] $[\alpha]^{23}_D$ 61.4° (*c* 2, CH_2Cl_2)].

(*S*)-2-[(Methoxycarbonyl)amino]-1-phenyl-1-propanone (1b). Phenylmagnesium bromide (0.92 M THF solution, 20 mL, 18.4 mmol) was added to a THF (10 mL) solution of (*S*)-*N*,*N*-dimethyl-2-[(methoxycarbonyl)amino]propanamide[20] (1.21 g, 7.0 mmol), and the mixture was stirred for 3 h. Workup and distillation gave (*S*)-**1b**, 1.43 g (99%), as a colorless oil: bp 170 °C (bath temp) (4 Torr); $[\alpha]^{23}_D$ −15.2° (*c* 1.68, CH_2Cl_2) [lit.[10] $[\alpha]^{23}_D$ −15.2° (*c* 2, CH_2Cl_2)].

(*S*)-2-[(Methoxycarbonyl)amino]-1-(2,5-dimethoxyphenyl)-1-propanone (1d). To a THF (10 mL) solution of 2-bromo-1,4-dimethoxybenzene (1.33 g, 6.1 mmol) was added butyllithium (2.3 M hexane solution, 2.65 mL, 6.1 mmol) over 5 min at −20 °C. After the mixture was stirred for 0.5 h at −20 °C, a THF (5 mL) solution of *N*,*N*-dimethyl-2-[(methoxycarbonyl)amino]propanamide (0.35 g, 2.0 mmol) was added over a period of 5 min, and the solution was stirred for an additional 40 min at −20 °C. The solution was quenched with saturated NH_4Cl aqueous solution (10 mL) and extracted with diethyl ether (10 mL × 3). The extract was dried over anhydrous $MgSO_4$, filtrated, and concentrated in vacuo. The residue was purified by column chromatography (silica gel, CH_2Cl_2–AcOEt) to give (*S*)-**1d**, 0.53 g (99.6%), as colorless crystals: mp 88 °C; $[\alpha]^{20}_D$ −33.1 (*c* 1.07, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.34 (d, *J* = 7.2 Hz, 3 H), 3.68 (s, 3 H), 3.79 (s, 3 H), 3.89 (s, 3 H), 5.40 (q, *J* = 7.2 Hz, 1 H), 5.77 (br, 1 H); IR (KBr) 3380, 1709, 1680, 1539, 1500, 1256, 1230, 1052, 1040, 814 cm^{-1}; MS (70 eV), *m*/*z* (relative intensity) 267 (M^+, 9), 166 (11), 165 (100), 122 (5), 107 (9), 102 (38), 77 (8), 59 (5), 58 (16), 30 (7), 15 (6). Anal. Calcd for $C_{13}H_{17}NO_5$: C, 58.42; H, 6.41; N, 5.24. Found: C, 58.30; H, 6.51; N, 5.08.

***N*,*N*-Diethyl-3-oxo-2,4-dimethyl-4-pentenamide (1o):** prepared according to the procedure for **1d**; ^1H NMR ($CDCl_3$) δ 1.11 (t, *J* = 7 Hz, 3 H), 1.18 (t, *J* = 7 Hz, 3 H), 1.37 (d, *J* = 7 Hz, 3 H), 1.92 (dd, *J* = 1.0, 1.3 Hz, 3 H), 3.2–3.55 (m, 4 H), 4.14 (q, *J* = 7 Hz, 1 H), 5.77 (dd, *J* = 1.3, 2.8 Hz, 1 H), 5.92 (m, 1 H); IR (neat) 2980, 2945, 1696, 1632, 1452, 1430, 1378, 1042, 793 cm^{-1}; MS (70 eV), *m*/*z* (relative intensity) 198 (M^+ + 1, 54), 197 (M^+, 36), 170 (33), 157 (20), 154 (16), 142 (17), 141 (21), 140 (20), 129 (23), 128 (20), 114 (17), 100 (61), 98 (15), 72 (100), 69 (96), 58 (88), 44 (23), 43 (22), 41 (60), 39 (15), 29 (35), 27 (18); exact mass calcd for $C_{11}H_{19}NO_2$, M^+, 197.1414, found *m*/*z* 197.1439.

3-Propanoyl-2-oxazolidinone. To a THF (10 mL) solution of 2-oxazolidinone (1.74 g, 20.0 mmol) was added butyllithium (1.79 M hexane solution, 12.3 mL, 22.0 mmol) at −78 °C. After the mixture was stirred at room temperature for 0.5 h, propanoyl chloride (2.1 mL, 24 mmol) was added to the solution, and the whole was stirred for an additional 0.5 h. Workup and recrystallization from diethyl ether–hexane gave the desired compound, 2.57 g (90%), as colorless crystals: mp 82–83 °C; ^1H NMR ($CDCl_3$) δ 1.17 (t, *J* = 7.2 Hz, 3 H), 2.91 (q, *J* = 7.2 Hz, 2 H), 3.9–4.1 (m, 2 H), 4.3–4.5 (m, 2 H); IR (KBr) 1772, 1704, 1389, 1367, 1266, 1216, 944 cm^{-1}.

3-(2-Benzoylpropanoyl)-2-oxazolidinone (1p). To a THF (20 mL) solution of 3-propanoyl-2-oxazolidinone (0.64 g, 4.5 mmol) was added LDA (0.5 M THF solution, 9.0 mL, 4.5 mmol) at −78 °C, and the solution was stirred for 0.5 h at −78 °C. The cold lithium enolate solution thus prepared was then added to a THF

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solution of benzoyl chloride (1.0 mL, 8.6 mmol) through a syringe, and the mixture was stirred for 0.5 min. Workup and purification by column chromatography (silica gel, CH_2Cl_2–hexane) gave **1p**, 1.02 g (92%), as colorless crystals: mp 136 °C; ^1H NMR ($CDCl_3$) δ 1.45 (d, J = 7.2 Hz, 3 H), 3.9–4.2 (m, 2 H), 4.2–4.5 (m, 2 H), 5.37 (q, J = 7.2 Hz, 1 H), 7.3–7.6 (m, 3 H), 7.8–8.0 (m, 2 H); IR (KBr) 1764, 1710, 1683, 1393, 1362, 1294, 1233, 1206, 1134, 1033, 971, 712 cm^{-1}; MS (70 eV), m/z (relative intensity) 247 (M^+, trace), 106 (8), 105 (100), 77 (21), 51 (7). Anal. Calcd for $C_{13}H_{13}NO_4 \cdot {}^1/_8H_2O$: C, 62.58; H, 5.35; N, 5.61. Found: C, 62.56; H, 5.39; N, 5.58.

(4*R*,5*S*)-4-Methyl-5-phenyl-2-oxazolidinone.[21] Reported methods were modified by using ethyl chloroformate. To a sodium hydroxide (1 M aqueous solution) (50 mL) solution of (1*S*,2*R*)-norephedrine hydrochloride (5.6 g, 30 mmol) was added ethyl chloroformate (3.0 mL, 31 mmol), and the whole was stirred for 40 min at room temperature. Workup gave crude (1*S*,2*R*)-1-phenyl-2-[(ethoxycarbonyl)amino]propanol, 5.5 g, as an oil, which was employed for the next step without purification: ^1H NMR ($CDCl_3$) δ 0.99 (d, J = 7 Hz, 3 H), 1.24 (t, J = 7 Hz, 3 H), 2.83 (br s, 1 H), 3.8–4.2 (m, 1 H), 4.10 (q, J = 7 Hz, 2 H), 4.84 (d, J = 3 Hz, 1 H), 4.9 (br s, 1 H), 7.34 (s, 5 H).

The crude alcohol (5.5 g) was treated with a methanol solution of potassium hydroxide (1 M, 50 mL). The mixture was stirred for 3 h at 50 °C and heated to reflux for an additional 3 h before quenching with acetic acid. Workup followed by purification by column chromatography (silica gel, diethyl ether) afforded the title compound, 3.80 g (86%), as colorless crystals: mp 121 °C (lit.[21] mp 120–121 °C); $[\alpha]^{20}_D$ +136.1° (c 0.97, $CHCl_3$) [lit.[21] $[\alpha]^{20}_D$ +163.7° (c 1, $CHCl_3$)]; ^1H NMR ($CDCl_3$) δ 0.81 (d, J = 7 Hz, 3 H), 4.18 (dq, J = 8, 7 Hz, 1 H), 5.68 (d, J = 8 Hz, 1 H), 6.27 (br s, 1 H), 7.2–7.5 (m, 5 H); IR (KBr) 3280, 1730, 1452, 1427, 1387, 1353, 1237, 1124, 1111, 993, 960 cm^{-1}.

(4*R*,5*S*)-3-Propanoyl-4-methyl-5-phenyl-2-oxazolidinone.[21] This compound was prepared in a similar manner to that for 3-propanoyl-2-oxazolidinone in 86% yield as a colorless oil: $[\alpha]^{20}_D$ +38.73° (c 1.89, CH_2Cl_2) [lit.[21] $[\alpha]^{20}_D$ +43.8° (c 2, CH_2Cl_2)].

(4*R*,5*S*,2′*S*)-3-(2′-Benzoylpropanoyl)-4-methyl-5-phenyl-2-oxazolidinone (1g). This compound was prepared according to the procedure described in ref 21: 88% yield; colorless crystals; mp 162 °C (lit.[9e] mp 164.5–165 °C); $[\alpha]^{20}_D$ +153° (c 0.47, CH_2Cl_2) [lit.[9e] $[\alpha]^{20}_D$ +154.5° (c 0.52, CH_2Cl_2)].

Hydrosilane/H$^+$ Reduction of 1. A procedure for the reduction of **1a** with $PhMe_2SiH$ in TFA is representative.

Dimethylphenylsilane (0.184 mL, 1.20 mmol) was added slowly to a trifluoroacetic acid (1 mL) solution of (*S*)-**1a** (221 mg, 1.00 mmol) at 0 °C, and the solution was stirred for 2.5 h at 0 °C. Saturated $NaHCO_3$ aqueous solution (20 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (10 mL). The extract was dried over anhydrous $MgSO_4$, filtrated, and concentrated under reduced pressure to give the crude product, whose ^1H NMR spectra showed exclusive formation (>99% selectivity) of (1*R*,2*S*)-2-[(ethoxycarbonyl)amino]-1-phenyl-1-propanol (**2a**). Purification by preparative TLC (silica gel, AcOEt–hexane, 1:1) afforded (1*R*,2*S*)-**2a** (194 mg, 87%) as colorless crystals: mp 71 °C; $[\alpha]^{20}_D$ −41° (c 0.245, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 0.99 (d, J = 7 Hz, 3 H), 1.24 (t, J = 7 Hz, 3 H), 2.83 (br s, 1 H), 3.8–4.2 (m, 1 H), 4.10 (q, J = 7.2 Hz, 2 H), 4.84 (d, J = 3 Hz, 1 H), 4.9 (br s, 1 H), 7.34 (s, 5 H); IR (KBr) 3350, 1694, 1552, 1273, 1043, 1028, 708 cm^{-1}; MS (70 eV), m/z (relative intensity) 223 (M^+, trace), 117 (18), 116 (66), 107 (11), 88 (21), 79 (15), 77 (14), 72 (11), 51 (5), 44 (100), 29 (23), 27 (7), 18 (5). Anal. Calcd for $C_{12}H_{17}NO_3$: C, 64.55; H, 7.67; N, 6.27. Found: C, 64.35; H, 7.53; N, 6.25.

(1*R*,2*S*)-2-[(Methoxycarbonyl)amino]-1-phenyl-1-propanol (2b): bp 130 °C (bath temp) (1 Torr); $[\alpha]^{20}_D$ −29.2° ($CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.99 (d, J = 7 Hz, 3 H), 2.6 (br, 1 H), 3.67 (s, 3 H), 4.00 (m, 1 H), 4.85 (d, J = 3 Hz, 1 H), 4.9 (br s, 1 H), 7.34 (s, 5 H); IR (neat) 3430, 1702, 1527, 1451, 1250, 1066, 701 cm^{-1}; MS (70 eV), m/z (relative intensity) 209 (M^+, trace), 107 (14), 103 (23), 102 (100), 88 (23), 79 (17), 77 (17), 59 (11), 58 (36), 44 (11), 30 (16), 15 (12). Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 62.93; H, 7.26; N, 6.64.

(1*R*,2*S*)-2-[(Phenylsulfonyl)amino]-1-phenyl-1-propanol (2c): $[\alpha]^{23}_D$ −7.93° (c 0.71, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 0.84 (d, J = 8 Hz, 3 H), 2.87 (d, J = 5 Hz, 1 H), 3.53 (dq, J = 3, 8 Hz, 1 H), 4.78 (dd, J = 5, 3 Hz, 1 H), 5.20 (d, J = 9 Hz, 1 H), 7.28 (s, 5 H), 7.4–7.7 (m, 3 H), 7.7–8.1 (m, 2 H); IR (neat) 3520, 3280, 1443, 1322, 1158, 1090, 970, 898, 751, 720, 701, 688, 580 cm^{-1}; MS (70 eV), m/z (relative intensity) 186 (5), 185 (11), 184 (100), 141 (60), 1207 (54), 79 (23), 78 (15), 77 (93), 51 (17), 44 (35).

(1*R*,2*S*)-2-[(Methoxycarbonyl)amino]-1-(2,5-dimethoxyphenyl)-1-propanol (2d): mp 95–96 °C; $[\alpha]^{20}_D$ −31.7° (c 1.05, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.03 (d, J = 7 Hz, 3 H), 3.13 (br d, J = 5 Hz, 1 H), 3.63 (s, 3 H), 3.77 (s, 3 H), 3.80 (s, 3 H), 4.1 (m, 1 H), 5.03 (dd, J = 4, 5 Hz, 1 H), 5.1 (br s, 1 H), 6.77 (m, 2 H), 6.97 (m, 1 H); IR (KBr) 3455, 3370, 1700, 1674, 1558, 1507, 1256, 1249, 1069 cm^{-1}; MS (70 eV), m/z (relative intensity) 269 (M^+, 8), 168 (15), 167 (100), 152 (10), 139 (35), 137 (18), 124 (14), 102 (50), 88 (18), 58 (21), 15 (10). Anal. Calcd for $C_{13}H_{19}NO_5$: C, 57.98; H, 7.11; N, 5.20. Found: C, 58.18; H, 7.25; N, 5.08.

***erythro*-2-(Benzyloxy)-3-heptanol (2g):** ^1H NMR ($CDCl_3$) δ 0.7–1.1 (m, 3 H), 1.17 (d, J = 6 Hz, 3 H), 1.2–1.6 (m, 6 H), 2.4 (br s, 1 H), 3.2–3.5 (m, 2 H), 4.46 (d, J = 12 Hz, 1 H), 4.54 (d, J = 12 Hz, 1 H), 7.28 (s, 5 H). The spectral data of the threo isomer **3g** are as follows: ^1H NMR ($CDCl_3$) δ 0.7–1.1 (m, 3 H), 1.12 (d, J = 6 Hz, 3 H), 1.2–1.6 (m, 6 H), 2.15 (br s, 1 H), 3.1–3.4 (m, 2 H), 4.35 (d, J = 12 Hz, 1 H), 4.57 (d, J = 12 Hz, 1 H), 7.12 (s, 5 H); IR (neat) 3470, 2980, 2955, 2885, 1456, 1380, 1113, 1090, 1078, 1031, 736, 702 cm^{-1}.

***erythro*-*N*,*N*-Diethyl-3-hydroxy-2-methyl-3-phenylpropanamide (2h):** colorless crystals; mp 72–73 °C; exclusive formation of **2h** was observed by 400-MHz ^1H NMR analysis of the crude reaction mixture; ^1H NMR ($CDCl_3$) δ 1.05 (d, J = 7.1 Hz, 3 H), 1.19 (t, J = 7.1 Hz, 3 H), 1.20 (t, J = 7.2 Hz, 3 H), 2.78 (dq, J = 2.7, 7.1 Hz, 1 H), 3.2–3.5 (m, 4 H), 5.05 (d, J = 2.7 Hz, 1 H), 5.13 (s, 1 H), 7.2–7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.4, 13.0, 14.9, 40.4, 41.6, 42.2, 77.3, 126.1 (2 C), 127.2, 128.2 (2 C), 142.0, 176.8; IR (KBr) 3420, 1612, 1471, 1449, 1033, 770, 708, 534 cm^{-1}; MS (70 eV), m/z (relative intensity) 235 (M^+, 9), 220 (19), 129 (100), 114 (28), 107 (24), 105 (10), 101 (15), 100 (52), 79 (28), 77 (27), 74 (15), 72 (29), 58 (76), 57 (19), 56 (10), 44 (45), 42 (12), 30 (10), 29 (41), 28 (10), 27 (15). Anal. Calcd for $C_{14}H_{21}NO_2$: C, 71.46; H, 8.99; N, 5.95. Found: C, 71.48; H, 8.89; N, 5.84.

***erythro*-*N*-(3-Hydroxy-2-methyl-3-phenylpropanoyl)-pyrrolidine (2i):** colorless crystals. The ratio erythro:threo was 99:1 by HPLC analysis [column, Waters μBondapak C18; solvent, CH_3CN–H_2O (1:3); flow rate, 2 mL/min]: t_R **2i**, 3.5 min; the threo isomer **3i**, 5 min. Recrystallization gave pure **2i**: mp 119 °C; ^1H NMR ($CDCl_3$) δ 1.04 (d, J = 7 Hz, 3 H), 1.7–2.1 (m, 4 H), 2.70 (dq, J = 3, 7 Hz, 1 H), 3.3–3.6 (m, 4 H), 4.90 (s, 1 H), 5.07 (d, J = 3 Hz, 1 H), 7.30 (br s, 5 H); IR (KBr) 3380, 1612, 1608, 1446, 1046, 769, 708 cm^{-1}; MS (70 eV), m/z (relative intensity) 234 (M^+, 3), 218 (21), 127 (100), 126 (13), 107 (10), 99 (22), 98 (27), 79 (12), 77 (13), 72 (14), 71 (18), 70 (25), 55 (14), 43 (20). Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 71.95; H, 8.23; N, 5.87.

***erythro*-*N*-(3-Hydroxy-2-methyl-3-phenylpropanoyl)-piperidine (2j):** colorless crystals; mp 100–101 °C; exclusive formation of **2j** was observed by 400-MHz ^1H NMR analysis; ^1H NMR ($CDCl_3$) δ 1.03 (d, J = 7.2 Hz, 3 H), 1.5–1.7 (m, 7 H), 2.84 (dq, J = 2.4, 7.2 Hz, 1 H), 3.35–3.70 (m, 4 H), 5.01 (br s, 1 H), 5.12 (d, J = 2.3 Hz, 1 H), 7.2–7.4 (m, 5 H); IR (KBr) 3350, 1606 cm^{-1}; MS (70 eV), m/z (relative intensity) 247 (M^+, 7), 232 (20), 141 (100), 112 (26), 84 (43), 79 (20). Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.74; H, 8.56; N, 5.66. Found: C, 72.74; H, 8.69; N, 5.52.

***erythro*-*N*-[3-(4-Chlorophenyl)-3-hydroxy-2-methylpropanoyl]pyrrolidine (2k):** colorless crystals; mp 76–78 °C; ^1H NMR ($CDCl_3$) δ 1.00 (d, J = 7 Hz, 3 H), 1.7–2.0 (m, 4 H), 2.64 (dq, J = 3, 7 Hz, 1 H), 3.2–3.6 (m, 4 H), 4.24 (s, 1 H), 5.04 (d, J = 3 Hz, 1 H), 7.28 (s, 5 H); IR (KBr) 3440, 1607, 1494, 1465, 1436, 1408, 986, 804 cm^{-1}; MS (70 eV), m/z (relative intensity) 269 (M^+ + 2, 3), 267 (M^+, 9), 252 (26), 141 (12), 128 (10), 127 (100), 126 (17), 99 (24), 98 (31), 77 (18), 72 (14), 71 (15), 70 (20), 55 (11), 43 (15). Anal. Calcd for $C_{14}H_{18}ClNO_2$: C, 62.82; H, 6.78; N, 5.23. Found: C, 62.64; H, 6.71; N, 5.23.

***N*,*N*-Diethyl-3-hydroxy-2-methylbutanamide (2l + 3l).** Dimethylphenylsilane (0.041 mL, 0.27 mmol) was added to a trifluoroacetic acid (0.4 mL) solution of **1l** (38 mg, 0.22 mmol) at 0 °C, and the solution was stirred for 3 h at 0 °C. Saturated

(21) Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2127.

$NaHCO_3$ aqueous solution was added to the reaction mixture, and the resulting mixture was extracted with diethyl ether (5 mL × 3). The ethereal extract was dried over anhydrous $MgSO_4$, filtrated, and concentrated in vacuo to give a crude product. Analysis with 400-MHz ^1H NMR revealed the erythro:threo ratio (**2l**:**3l**) of the product to be 98:2. Purification by preparative TLC (silica gel, AcOEt–hexane, 1:1) gave *N,N*-diethyl-3-hydroxy-2-methylbutanamide, 36 mg (94%), as a colorless oil. The erythro isomer **2l**: ^1H NMR ($CDCl_3$) δ 1.13 (t, J = 7.2 Hz, 3 H), 1.16 (d, J = 6.4 Hz, 3 H), 1.17 (d, J = 7.1 Hz, 3 H), 1.20 (t, J = 7.2 Hz, 3 H), 2.51 (dq, J = 2.4, 7.1 Hz, 1 H), 3.21–3.53 (m, 4 H), 4.06 (dd, J = 2.4, 6.4 Hz, 1 H), 4.62 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.3, 13.0, 14.8, 19.9, 40.1, 40.2, 42.1, 67.4, 177.1; IR (neat) 3430, 2990, 1618, 1467, 1385, 1100 cm^{-1}; MS (70 eV), m/z (relative intensity) 173 (M^+, trace), 158 (11), 140 (10), 129 (23), 101 (13), 100 (44), 73 (18), 72 (34), 58 (100), 57 (29), 56 (14), 55 (14), 45 (31), 44 (36), 43 (13), 42 (18), 30 (14), 29 (48), 28 (17), 27 (27); exact mass calcd for $C_9H_{19}NO_2$, M^+, 173.1414, found m/z 173.1417.

Sodium borohydride reduction of **1l** (2 molar equiv, 0 °C, 0.5 h, MeOH) afforded a mixture of **2l** and **3l** (94%) in a ratio of 37:63. The NMR spectra corresponding to **3l** are as follows: ^1H NMR ($CDCl_3$) δ 1.13 (t, J = 7.1 Hz, 3 H), 1.21 (t, J = 7.1 Hz, 3 H), 1.22 (d, J = 6.4 Hz, 3 H), 1.23 (d, J = 7.1 Hz, 3 H), 2.58 (dq, J = 5.0, 7.1 Hz, 1 H), 4.18 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.1, 14.8, 15.7, 21.6, 41.2, 41.8, 42.1, 70.3, 175.9.

***erythro*-*N,N*-Diethyl-3-hydroxy-2-methylpentanamide (2m).** The ratio erythro:threo was estimated to be 98:2 by GLC analysis of the crude product: t_R **2m**, 14.9 min; the threo isomer **3m**, 16.7 min (column: 10% PEG-20M on Gasport H; 180 °C; N_2, 0.75 kg/m^2). **2m**: ^1H NMR ($CDCl_3$) δ 0.96 (t, J = 7.0 Hz, 3 H), 1.04 (t, J = 7.0 Hz, 3 H), 1.16 (d, J = 6.9 Hz, 3 H), 1.18 (t, J = 7.0 Hz, 3 H), 1.3–1.8 (m, 2 H), 2.62 (dq, J = 2.2, 6.9 Hz, 1 H), 3.2–3.6 (m, 4 H), 3.77 (ddd, J = 2.23, 5.5, 7.5 Hz, 1 H), 4.58 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.3, 10.5, 13.0, 14.9, 26.8, 38.2, 40.3, 42.2, 73.1, 177.3; IR (neat) 3440, 2985, 2950, 1620, 1466, 1097, 977 cm^{-1}; MS (70 eV), m/z (relative intensity) 187 (M^+, 1), 129 (54), 100 (61), 72 (46), 59 (22), 58 (100), 57 (33), 44 (33), 29 (47), 28 (41); exact mass calcd for $C_{10}H_{21}NO_2$, M^+, 187.1571, found m/z 187.1546.

***erythro*-*N,N*-Diethyl-3-hydroxy-2,4-dimethylpentanamide (2n).** Exclusive formation of **2n** (>99%) was observed by 400-MHz ^1H NMR analysis of the crude reaction mixture: a colorless oil; 89% yield; ^1H NMR ($CDCl_3$) δ 0.86 (d, J = 6.7 Hz, 3 H), 1.05 (d, J = 6.6 Hz, 3 H), 1.13 (t, J = 7.0 Hz, 3 H), 1.14 (d, J = 7 Hz, 3 H), 1.21 (t, J = 7.2 Hz, 3 H), 1.71 (septet, J = 6.6 Hz, 1 H), 2.81 (dq, J = 1.9, 7.1 Hz, 1 H), 3.21–3.32 (m, 2 H), 3.34–3.53 (m, 3 H), 4.92 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.0, 13.0, 14.8, 18.9, 19.7, 30.4, 35.6, 40.4, 42.3, 77.3, 177.4; IR (neat) 3440, 2980, 2950, 1618, 1252 cm^{-1}; MS (70 eV), m/z (relative intensity) 201 (M^+, 2), 186 (21), 158 (34), 129 (53), 114 (19), 101 (16), 100 (100), 74 (25), 73 (25), 42 (41), 58 (70), 57 (21), 55 (11), 44 (28), 43 (13), 41 (11), 28 (33), 27 (14). Anal. Calcd for $C_{11}H_{23}NO_2$: C, 65.63; H, 11.52; N, 6.96. Found: C, 65.37; H, 11.62; N, 6.72.

Reduction of 1o. To a trifluoroacetic acid (0.1 mL) solution of **1o** (19 mg, 0.095 mmol) was added dimethylphenylsilane (0.017 mL, 0.11 mmol) at 0 °C, and the solution was stirred for 16 h at 0 °C before neutralization with saturated $NaHCO_3$ aqueous solution. Workup and purification by preparative TLC (silica gel, CH_2Cl_2–ethyl ether, 9:1) gave a mixture of *erythro-N,N*-diethyl-3-hydroxy-2,4-dimethyl-4-pentenamide (**2o**) and **2n** (total 17 mg, 89% yield) in a ratio of 73:27. No detectable amount of the threo isomers was observed in 400-MHz ^1H NMR analysis of the crude reaction mixture. The following ^1H NMR absorptions are ascribed to **2o**: δ 1.11 (t, J = 6.9 Hz, 3 H), 1.14 (t, J = 7.0 Hz, 3 H), 1.22 (d, J = 7.8 Hz, 3 H), 1.71 (dd, J = 1.4, 0.8 Hz, 3 H), 2.75 (m, 1 H), 3.2–3.6 (m, 4 H), 4.35 (m, 1 H), 5.00, (m, 1 H), 5.20 (m, 1 H).

Reduction of **1o** with sodium borohydride (1.2 molar equiv, 0 °C, 1.5 h, MeOH) gave a mixture of **2o**, **3o**, **2n**, and **3n** in a ratio of 28:39:10:23. From this mixture, the following ^1H NMR spectral data ($CDCl_3$) were assigned to **3o**: δ 1.21 (d, J = 7.1 Hz, 3 H), 1.75 (m, 3 H), 4.14 (d, J = 5.4 Hz, 1 H), 4.90 (m, 1 H), 4.98 (m, 1 H).

***erythro*-3-(3-Hydroxy-2-methyl-3-phenylpropanoyl)-2-oxazolidinone (2p)**: colorless crystals; mp 95–98 °C; ^1H NMR ($CDCl_3$) δ 1.14 (d, J = 7.0 Hz, 3 H), 3.13 (s, 1 H), 3.91–4.14 (m, 2 H), 4.11 (dq, J = 3.8, 7.0 Hz, 1 H), 4.29–4.42 (m, 2 H), 5.12 (d, J = 3.8 Hz, 1 H), 7.2–7.4 (m, 5 H); IR (KBr) 3525, 1784, 1754, 1706, 1393, 1370, 1250, 1232 cm^{-1}; MS (70 eV), m/z (relative intensity) 249 (M^+, 3), 143 (77), 134 (13), 115 (33), 107 (28), 106 (30), 105 (41), 88 (100), 79 (33), 78 (11), 77 (58), 57 (37), 56 (21), 51 (20), 44 (14), 29 (21), 28 (15), 27 (15). Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62. Found: C, 62.68; H, 6.21; N, 5.59.

(4*R*,5*S*,2*S*′,3*S*′)-3-(3′-Hydroxy-2′-methyl-3′-phenylpropanoyl)-4-methyl-5-phenyl-2-oxazolidinone (2q): colorless crystals; mp 177 °C; $[\alpha]^{20}_D$ +48.5° (c 0.88, $CHCl_3$); ^1H NMR ($CHCl_3$) δ 0.75 (d, J = 6.6 Hz, 3 H), 1.18 (d, J = 7.0 Hz, 3 H), 3.02 (br d, J = 2.3 Hz, 1 H), 4.21 (dq, J = 4.2, 7.0 Hz, 1 H), 4.74 (dq, J = 6.6, 7.3 Hz, 1 H), 5.12 (br dd, J = 2.3, 4.2 Hz, 1 H), 5.63 (d, J = 7.3 Hz, 1 H), 7.3–7.5 (m, 5 H); IR (KBr) 3480, 1788, 1688, 1368, 1351, 1346, 1239, 1198, 701 cm^{-1}; MS (70 eV), m/z (relative intensity) 339 (M^+, 2), 233 (49), 134 (13), 118 (36), 117 (17), 116 (19), 107 (100), 106 (43), 105 (54), 91 (16), 79 (33), 78 (13), 77 (62), 70 (71), 57 (86), 56 (12), 51 (28), 50 (12), 42 (14), 29 (26), 27 (13). Anal. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13. Found: C, 70.59; H, 6.27; N, 3.91.

Reduction of Ethyl 2-Benzoylpropanoate (1r). Dimethylphenylsilane (160 mg, 1.17 mmol) was added to a trifluoroacetic acid (0.5 mL) solution of **1r** (192 mg, 1.00 mmol) at 0 °C, and the solution was stirred for 3 h at that temperature. Trifluoroacetylation of the product occurred to some extent as observed by ^1H NMR analysis of the reaction mixture. Methanol (2 mL) was added to the solution, and stirring was continued for an additional 0.5 h at room temperature. Workup and purification by preparative TLC gave methyl *erythro*-3-hydroxy-2-methyl-3-phenylpropanoate (**2r**), 169 mg (87%), as a colorless oil. The ratio of erythro:threo was estimated to be >99:1 by 90-MHz ^1H NMR analysis: ^1H NMR ($CDCl_3$) δ 1.12 (d, J = 7.0 Hz, 3 H), 2.77 (dq, J = 4.9, 7.0 Hz, 1 H), 3.23 (br s, 1 H), 3.58 (s, 3 H), 5.00 (d, J = 4.9 Hz, 1 H), 7.28 (s, 5 H).

Reduction of **1r** with $NaBH_4$ (1 molar equiv, 0 °C, 40 min, MeOH) afforded a mixture of **3r** and **2r** in a ratio of 78:22. From this mixture, ^1H NMR spectral data ($CDCl_3$) of **3r** were obtained: δ 0.95 (d, J = 7.0 Hz, 3 H), 2.75 (dq, J = 8.9, 7.0 Hz, 1 H), 3.17 (d, J = 4.8 Hz, 1 H), 3.67 (s, 3 H), 4.66 (dd, J = 4.8, 8.9 Hz, 1 H), 7.27 (s, 5 H).

(1*R*,2*S*)-2-(Methylamino)-1-phenyl-1-propanol (*l*-Ephedrine) (4). Lithium aluminum hydride (125 mg, 3.3 mmol) was added to a THF (3 mL) solution of (1*R*,2*S*)-**2a** (0.34 g, 1.51 mmol), and the solution was stirred for 1.5 h at 60 °C before addition of water (0.5 mL). The precipitates were filtered off through a Celite column, and the filtrate was concentrated. Preparative TLC gave **4**, 198 mg (80%), as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.84 (d, J = 6 Hz, 3 H), 2.45 (s, 3 H), 2.4–2.9 (m, 3 H), 4.74 (d, J = 3 Hz, 1 H), 7.32 (s, 5 H). *l*-Ephedrine hydrochloride: $[\alpha]^{20}_D$ −33.51° (c 1.15, H_2O) [lit.[22] $[\alpha]^{20}_D$ −34° (H_2O)].

(1*R*,2*S*)-2-Amino-1-(2,5-dimethoxyphenyl)-1-propanol (*l*-Methoxamine) (5). To a methanol (12 mL) solution of (1*S*,2*S*)-**3g** (0.27 g, 1.00 mmol) were added water (4 mL) and potassium hydroxide (0.29 g, 5.2 mmol), and the resulting solution was heated to reflux. After being refluxed for 24 h, the solution was acidified by the addition of 15% phosphoric acid, washed with CH_2Cl_2 (10 mL × 2), made alkaline with excess K_2CO_3, then saturated with NaCl, and extracted with diethyl ether (10 mL × 3). The ethereal extract was dried over anhydrous K_2CO_3, filtered, and concentrated. The resulting oil was distilled to afford **5**, 175 mg (83%), as a colorless oil: bp 120 °C (bath temp) (1 Torr); ^1H NMR ($CDCl_3$) δ 0.97 (d, J = 7 Hz, 3 H), 2.08 (br s, 3 H), 3.22 (dq, J = 7, 5 Hz, 1 H), 3.76 (s, 6 H), 4.74 (d, J = 5 Hz, 1 H), 6.76 (m, 2 H), 6.99 (m, 1 H); IR (neat) 3380, 3300, 3180, 2970, 2950, 1500, 1220, 1050 cm^{-1}. *l*-Methoxamine hydrochloride: mp 183–185 °C (lit.[23] mp 182–183 °C); $[\alpha]^{25}_D$ −27.9° (c 3.09, H_2O) [lit.[23] $[\alpha]^{25}_D$ −28.5° (c 4, H_2O)].

Methanolysis of (4*R*,5*S*,2*S*′,3*S*′)-2q. To a methanol (1 mL) and CH_2Cl_2 (0.5 mL) solution of (4*R*,5*S*,2*S*′,3*S*′)-**2q** was added

(22) *The Merck Index*, 10th ed.; Merck: Rahway, NJ, 1983; No. 3558, p 520.
(23) Baltzly, R.; Mehta, N. B. *J. Med. Chem.* **1968**, *11*, 833.
(24) For example: Bigelow, L. A.; Eatough, H. *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. I, p 80.

sodium methoxide (0.1 M methanol solution, 1.1 mL, 0.11 mmol) at 0 °C, and the solution was stirred for 15 min at 0 °C. Addition of saturated NH_4Cl aqueous solution (2 mL) and workup followed by purification by preparative TLC (silica gel, CH_2Cl_2–diethyl ether, 9:1) afforded (2*S*,3*R*)-**2r**, 18 mg (93%), as a colorless oil. No racemization at the chiral center was observed by ^1H NMR analysis. The enantiomeric excess value was estimated to be >98% by 400-MHz ^1H NMR analysis using $Eu(tfc)_3$ as a chiral shift reagent. (2*S*,3*S*)-**2r**: $[\alpha]^{25}_D$ −24.7° (*c* 1.1, $CHCl_3$) [lit.[21] $[\alpha]^{25}_D$ −23.1° (*c* 3.2, $CHCl_3$)]; ^1H NMR ($CDCl_3$) δ 1.13 (d, *J* = 7 Hz, 3 H), 2.80 (dq, *J* = 4, 7 Hz, 1 H), 3.68 (s, 3 H), 5.07 (d, *J* = 4 Hz, 1 H), 7.2–7.4 (m, 5 H).

***erythro*-*N*-(3-Hydroxy-2-methyl-3-phenylpropyl)-piperidine (6).**[11] To a THF (2 mL) solution of **2j** (50 mg, 0.20 mmol) was added $LiAlH_4$ (40 mg, 1.05 mmol), and the mixture was heated to reflux for 5 h. Workup and purification gave **6**, 41 mg (81%), as a colorless oil.

Preparation of Oximes. (2-Acetoxy-1-phenylpropylidene)(benzyloxy)amine (9). A tetrahydrofuran (THF) (5 mL) solution of 2-acetoxy-1-phenyl-1-propanone (0.25 g, 1.31 mmol) and pyridine (1 mL) was heated to reflux with stirring for 3 days. After THF was removed under reduced pressure, the resulting mixture was diluted with water (30 mL) and extracted with diethyl ether (30 mL). The ethereal extract was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure, and the residue was subjected to preparative TLC (silica gel, hexane–AcOEt, 10:1) to give (*E*)-**9**, 78 mg (20%), and (*Z*)-**9**, 80 mg (21%), along with recovered starting ketone, 113 mg (45%), as a colorless oil.

(*E*)-**9**: R_f 0.45 (hexane–AcOEt, 5:1); ^1H NMR ($CDCl_3$) δ 1.39 (d, *J* = 6.3 Hz, 3 H), 1.95 (s, 3 H), 5.10 (s, 2 H), 5.70 (q, *J* = 6.3 Hz, 1 H), 7.26 (s, 5 H), 7.38 (s, 5 H); IR (neat) 3050, 3025, 2775, 2925, 2870, 1740, 1495, 1450, 1440, 1365, 1230, 1140, 1100, 1060, 1025, 1005, 980, 940, 930, 910, 845, 775, 750, 730, 690 cm^{-1}; MS (70 eV), *m*/*z* (relative intensity) 297 (M^+, 3), 225 (18), 207 (11), 194 (10), 147 (21), 118 (10), 117 (93), 92 (31), 91 (100), 77 (27), 65 (17), 51 (14), 43 (81). Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.70; H, 6.44; N, 4.71. Found: C, 72.67; H, 6.57; N, 4.54.

(*Z*)-**9**: R_f 0.50 (hexane–AcOEt, 5:1); ^1H NMR ($CDCl_3$) δ 1.60 (d, *J* = 6.9 Hz, 3 H), 1.83 (s, 3 H), 5.24 (s, 2 H), 1.22 (q, *J* = 6.9 Hz, 1 H), 7.26–7.47 (m, 8 H), 7.5–7.63 (m, 2 H); IR (neat) 3050, 3025, 2975, 2925, 2870, 1740, 1495, 1450, 1440, 1365, 1230, 1140, 1100, 1060, 1025, 1005, 980, 940, 930, 910, 845, 775, 750, 730, 690 cm^{-1}; MS (70 eV), *m*/*z* (relative intensity) 297 (M^+, 3), 225 (18), 207 (11), 194 (10), 147 (21), 118 (10), 117 (93), 92 (31), 91 (100), 77 (27), 65 (17), 51 (14), 43 (81). Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.70; H, 6.44; N, 4.71. Found: C, 72.67; H, 6.57; N, 4.54.

Benzylidene(benzyloxy)amine (**7a**), cyclohexylidene(benzyloxy)amine (**7d**), 2-nonylidene(benzyloxy)amine (**7e**), and (1-phenylethylidene)hydroxyamine (**7g**) were prepared by standard methods.[24] Acetylation and benzoylation of **7g** were carried out according to ref 15 to give (1-phenylethylidene)acetoxyamine (**7b**) and (1-phenylethylidene)(benzoyloxy)amine (**7c**).

Reduction of Imines and Oximes with Hydrosilane/H^+. To a dichloromethane (0.5 mL) solution of **7a** (50 mg, 0.28 mmol) were added dimethylphenylsilane (46 mg, 0.34 mmol) and trifluoroacetic acid (0.0065 mL, 0.85 mmol) at 0 °C. The solution was warmed to room temperature and stirred overnight. To this solution was added saturated $NaHCO_3$ aqueous solution (5 mL), and the resulting mixture was extracted with dichloromethane (10 mL × 3). The extract was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give an oil. Purification of the oil by preparative TLC afforded benzylphenylamine, 39 mg (77% yield), as a colorless oil.

Hydrosilane/H^+ Reduction of 9. Dimethylphenylsilane (0.034 mL, 0.22 mmol) was added to a trifluoroacetic acid (0.5 mL) solution of (*E*)-**9** at 0 °C. The solution was warmed to room temperature and stirred overnight at 0 °C. To this solution was added saturated $NaHCO_3$ aqueous solution (10 mL), and the resulting mixture was extracted with diethyl ether (20 mL × 2). The extract was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give a crude oil. Purification by preparative TLC (silica gel, hexane–AcOEt, 5:1) afforded 1-[(benzyloxy)amino]-1-phenyl-2-propyl acetate, 34 mg (75%), as a colorless oil.

The *erythro*-acetate: ^1H NMR ($CDCl_3$) δ 1.14 (d, *J* = 6.3 Hz, 3 H), 2.07 (s, 3 H), 4.09 (d, *J* = 3.9 Hz, 1 H), 4.67 (s, 2 H), 5.13–5.63 (m, 2 H), 7.32 (s, 5 H), 7.36 (s, 5 H); IR (neat) 3470, 3270, 3075, 3050, 3000, 2940, 2875, 1735, 1495, 1450, 1370, 1240, 1205, 1140, 1125, 1055, 1030, 950, 910, 800, 750, 735, 700 cm^{-1}.

The *threo*-acetate: ^1H NMR ($CDCl_3$) δ 1.03 (d, *J* = 6.0 Hz, 3 H), 2.19 (s, 3 H), 4.06 (d, *J* = 8.5 Hz, 1 H), 4.47 (d, *J* = 2.4 Hz, 1 H), 4.72 (d, *J* = 8.5 Hz, 1 H), 5.10 (dq, *J* = 2.4, 6.0 Hz, 1 H), 5.9 (br s, 1 H), 7.2–7.4 (m, 10 H); IR (neat) 1738, 1453, 1372, 1242, 750, 700 cm^{-1}.

The acetate obtained as above was dissolved in a NaOH methanol solution (1 M, 1 mL), and the solution was stirred for 3 h. Workup followed by purification by preparative TLC (silica gel, hexane–AcOEt, 5:1) afforded 1-[(benzyloxy)amino]-1-phenyl-2-propanol (**10**), 28 mg (97%), as a colorless oil. The ratio erythro:threo was estimated to be 99:1 by 400-MHz ^1H NMR.

erythro-**10**: ^1H NMR ($CDCl_3$) δ 1.01 (d, *J* = 6.5 Hz, 3 H), 3.97 (d, *J* = 3.6 Hz, 1 H), 4.19 (dq, *J* = 3.6, 6.5 Hz, 1 H), 4.72 (d, *J* = 11.6 Hz, 1 H), 4.74 (d, *J* = 11.6 Hz, 1 H), 7.31 (br s, 5 H), 7.34 (br s, 5 H); IR (neat) 3400, 3075, 3040, 2975, 2930, 2870, 1760, 1750, 1495, 1450, 1385, 1365, 1305, 1240, 1210, 1110, 1080, 1020, 800, 750, 695 cm^{-1}; MS (70 eV), *m*/*z* (relative intensity) 212 (49), 104 (12), 91 (100), 77 (15).

Starting with (*Z*)-**9**, we obtained a mixture of *erythro*- and *threo*-**10** in a ratio of 24:76.

threo-**10**: ^1H NMR δ 0.97 (d, *J* = 6.3 Hz, 3 H), 2.87 (br s, 1 H), 3.77 (d, *J* = 8.8 Hz, 1 H), 3.95 (dq, *J* = 8.8, 6.3 Hz, 1 H), 4.59 (d, *J* = 11.5 Hz, 1 H), 4.64 (d, *J* = 11.5 Hz, 1 H), 6.05 (br s, 1 H), 7.2–7.4 (m, 10 H).

Lithium Aluminum Hydride Reduction of 9. To a diethyl ether (2.0 mL) solution of (*E*)-**9** (22 mg, 0.07 mmol) was added lithium aluminum hydride (8 mg, 0.21 mmol) at 0 °C. The solution was warmed to room temperature and stirred overnight. Workup and purification by preparative TLC (hexane–AcOEt, 2:1) gave **10**, 9 mg (46%, erythro:threo = 82:18).

Lithium Aluminum Hydride Reduction of 10. To a tetrahydrofuran (5 mL) solution of **10** (28 mg, 0.11 mmol; erythro:threo = 24:76) was added lithium aluminum hydride (10 mg, 0.26 mmol) at room temperature. The mixture was heated to reflux for 3 h. Workup and purification by preparative TLC (silica gel, AcOEt–methanol, 9:1) gave 1-amino-1-phenyl-2-propanol (**11**), 7.8 mg (47%), as a colorless oil. The ratio erythro:threo was estimated to be 18:82 by 400-MHz ^1H NMR analysis.

Registry No. **1a**, 79219-15-1; **1b**, 77447-97-3; **1c**, 79821-75-3; **1d**, 91111-05-6; **1e**, 35026-77-8; **1f**, 91111-00-1; **1g**, 116701-60-1; **1h**, 116782-17-3; **1i**, 116782-18-4; **1j**, 116782-19-5; **1k**, 116782-20-8; **1l**, 116782-21-9; **1m**, 116782-22-0; **1n**, 116782-23-1; **1o**, 116836-59-0; **1p**, 116782-24-2; **1q**, 88635-97-6; **1r**, 116782-25-3; **1s**, 66841-52-9; **2a**, 79297-23-7; **2b**, 113323-00-5; **2c**, 91111-08-9; **2d**, 91111-10-3; **2f**, 116701-61-2; **2f** (benzoyl deriv), 66841-45-0; **2g**, 116782-26-4; **2h**, 116782-28-6; **2i**, 116836-45-4; **2j**, 116836-46-5; **2k**, 116836-47-6; **2l**, 116782-29-7; **2m**, 116782-30-0; **2n**, 116782-31-1; **2o**, 116701-63-4; **2p**, 116836-48-7; **2q**, 99210-94-3; **2r**, 76549-03-6; **2s**, 86853-34-1; **3a**, 79297-22-6; **3f**, 116701-62-3; **3f** (benzoyl deriv), 116782-33-3; **3l**, 116836-49-8; **3n**, 116782-34-4; **3o**, 116782-35-5; **3r**, 94199-26-5; **3s**, 78088-28-5; **4**, 299-42-3; **4**·HCl, 50-98-6; **5**, 13699-29-1; **5**·HCl, 16122-04-6; **6**, 116782-36-6; **7a**, 17146-21-3; **7b**, 19433-17-1; **7c**, 26060-56-0; **7d**, 19731-71-6; **7e**, 107002-86-8; **7f**, 538-51-2; **7g**, 613-91-2; **8a**, 4383-24-8; **8b**, 116701-66-7; **8c**, 116782-38-8; **8d**, 107032-14-4; **8e**, 116701-67-8; **8f**, 103-32-2; (*E*)-**9**, 116701-65-6; (*Z*)-**9**, 116724-35-7; *erythro*-**10**, 116701-70-3; *threo*-**10**, 116701-71-4; *erythro*-**10** acetate, 116701-68-9; *threo*-**10** acetate, 116701-69-0; *erythro*-**11**, 63204-69-3; *threo*-**11**, 63204-70-6; $PhMe_2SiH$, 766-77-8; Et_3SiH, 617-86-7; $PhCH_2ONH_2$, 622-33-3; 2-bromo-1,4-dimethoxybenzene, 25245-34-5; *N*,*N*-dimethyl-2-[(methoxycarbonyl)amino]propanamide, 116701-64-5; 3-propanoyl-2-oxazolidinone, 60420-27-1; 2-oxazolidinone, 497-25-6; propanoyl chloride, 79-03-8; benzoyl chloride, 98-88-4; (4*R*,5*S*)-4-methyl-5-phenyl-2-oxazolidinone, 77943-39-6; (1*S*,2*R*)-norephedrine·HCl, 40626-29-7; ethyl chloroformate, 541-41-3; (1*S*,2*R*)-1-phenyl-2-[(ethoxycarbonyl)amino]propanol, 116782-32-2; (4*R*,5*S*)-3-propanoyl-4-methyl-5-phenyl-2-oxazolidinone, 77877-20-4; 2-acetoxy-1-phenyl-1-propanone, 116782-37-7; (*S*)-*N*,*N*-dimethyl-2-[(methoxycarbonyl)amino]propanamide, 91110-99-5.