Electroorganic Chemistry. 144. Electroreductive Coupling of Ketones with *O*-Methyl Oximes, *N,N*-Dimethylhydrazones, and Nitrones. A Convenient Route to Synthesis of β-Amino Alcohol[1]

Tatsuya Shono,* Naoki Kise, Taku Fujimoto, Ayuko Yamanami, and Ryoji Nomura

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo, Kyoto 606-01, Japan

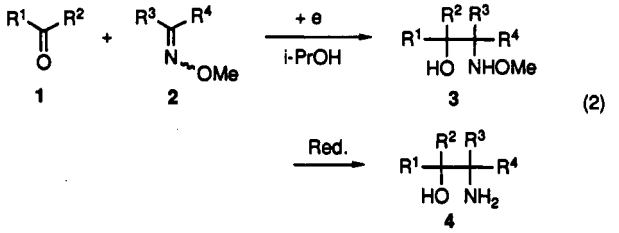
Received November 4, 1993

The intermolecular coupling of a variety of ketones with some types of *O*-methyl oximes took place when a mixture of both components was electrochemically reduced in i-PrOH with an Sn cathode. The product, β-methoxyamino alcohol was easily converted to β-amino alcohol by simple reduction. A chiral ligand effective for the enantioselective addition of diethylzinc to an aldehyde was easily obtained from the product formed by the electroreductive coupling of (−)-menthone with *O*-methylacetaldoxime. The intermolecular coupling of a ketone with a *N,N*-dimethylhydrazone or nitrone was also promoted by the electroreduction. Furthermore, the electroreductive coupling of a carbonyl group with an intramolecular *O*-methyl oxime moiety gave the corresponding cyclized product stereoselectively.

The electroreductive intra- and intermolecular couplings of ketones with a variety of unsaturated systems such as olefins,[2] acetylenes,[3] aromatic rings,[4] and nitriles[5] have been found and developed in our continuing studies of electroorganic chemistry. On the other hand, the reductive cross-coupling of a C=O group with a C=N group seems to provide a convenient route to the synthesis of β-amino alcohols (eq 1). Although it has already been reported

(1)

that the reductive coupling of aromatic imines with aldehydes or ketones is promoted by electroreduction[6] or metal reducing agents,[8] the reductive coupling of an aliphatic C=N group with a carbonyl group has rarely been reported.[10] However, it has been found in this study that the cross-coupling of ketone **1** with *O*-methyl oxime **2** is promoted effectively by electrochemical reduction,



(2)

and the product **3** is easily converted to the corresponding β-amino alcohol **4** (eq 2).

An effective chiral ligand for the enantioselective addition of diethylzinc to an aldehyde was obtained from (−)-menthone and *O*-methylacetaldoxime by using this electroreductive coupling as a key step. A similar reductive coupling of a ketone with a *N,N*-dimethylhydrazone or a nitrone was also found to be promoted by electroreduction. The coupling of a carbonyl group with an intramolecular *O*-methyloxime moiety was found to give the corresponding five- or six-membered product stereoselectively.

Results and Discussion

Electroreductive Intermolecular Coupling of Ketones with *O*-Methyl Oximes. The combination of cyclohexanone (**1a**) and 2.5 equiv of *O*-methylacetaldoxime (**2a**) was used as a typical example to scrutinize the reaction conditions of the coupling. When the electroreduction was carried out with an Sn cathode in a catholyte of i-PrOH containing Et_4NOTs under a constant current of 0.2 A, the coupled product **3a** was obtained in 95% yield. The reduction could also be carried out in an undivided cell, though the yield was lowered to some extent (85%). Electroreduction with a Pb (**3a**, 94%) or Cd (**3a**, 94%) cathode gave almost the same result as that with a Sn cathode, whereas a cathode made of Ag, Cu, Zn, or C-fiber gave a somewhat poorer result, and no reduced product was obtained with a Pt cathode. The yield decreased when the coupling was carried out in EtOH (**3a**, 62%), t-BuOH (**3a**, 68%), or DMF (**3a**, 52%). The effect of the cationic part of the supporting electrolyte was interesting. Namely, tetraalkylammonium salts such as Et_4NOTs and Bu_4-

* Abstract published in *Advance ACS Abstracts*, March 1, 1994.

(1) Preliminary report: Shono, T.; Kise, N.; Fujimoto, T. *Tetrahedron Lett.* **1991**, *32*, 525.

(2) (a) Shono, T.; Mitani, M. *J. Am. Chem. Soc.* **1971**, *93*, 5284. (b) Shono, T.; Nishiguchi, I.; Ohmizu, H.; Mitani, M. *J. Am. Chem. Soc.* **1978**, *100*, 545. (c) Shono, T.; Kashimura, S.; Mori, Y.; Hayashi, T.; Soejima, T.; Yamaguchi, Y. *J. Org. Chem.* **1989**, *54*, 6001.

(3) Shono, T.; Nishiguchi, I.; Ohmizu, H. *Chem. Lett.* **1976**, 1233.

(4) Shono, T.; Kise, N.; Suzumoto, T.; Morimoto, T. *J. Am. Chem. Soc.* **1986**, *108*, 4676.

(5) (a) Shono, T.; Kise, N. *Tetrahedron Lett.* **1990**, *31*, 1303. (b) Shono, T.; Kise, N.; Fujimoto, T.; Tominaga, N.; Morita, H. *J. Org. Chem.* **1992**, *57*, 7175.

(6) It has been reported that the electroreduction of a methanolic solution of *N*-methylbenzylideneamine and benzaldehyde gave a cross-coupled product though its yield was low (22%).[7a] On the other hand, we have recently reported that chlorotrimethylsilane effectively promotes the electroreductive intermolecular coupling of aromatic imine with some carbonyl compounds.[7b]

(7) (a) Horner, L.; Shaletz, D. H. *Justus Liebig Ann. Chem.* **1975**, 1210. (b) Shono, T.; Kise, N.; Kunimi, N.; Nomura, R. *Chem. Lett.* **1991**, 2191.

(8) The reductive coupling of aromatic imine with ketone or aldehyde promoted by $NbCl_3(DME)$[9a] or SmI_2[9b] has been reported.

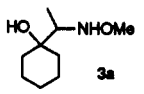
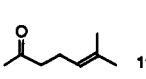
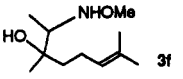
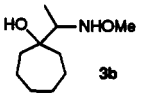
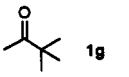
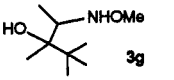
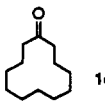
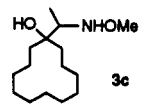
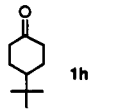
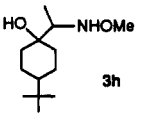
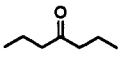
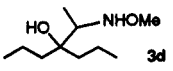
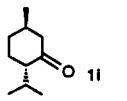
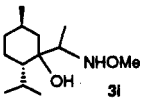
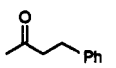
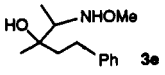
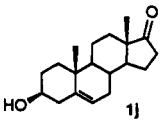
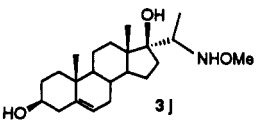
(9) (a) Roskamp, E. J.; Pedersen, S. F. *J. Am. Chem. Soc.* **1987**, *109*, 6551. (b) Imamoto, T.; Nishimura, S. *Chem. Lett.* **1990**, 1141.

(10) Only one example of reductive coupling of an aliphatic imine with 3-pentanone promoted by $NbCl_3(DME)$ has been reported, though the yield was low (34%).[9a] Recently, SmI_2–HMPA-promoted coupling of ketone or aldehyde with *O*-benzylformaldoxime has been reported.[11]

(11) Hamamoto, T.; Inanaga, J. *Tetrahedron Lett.* **1991**, *32*, 3555.

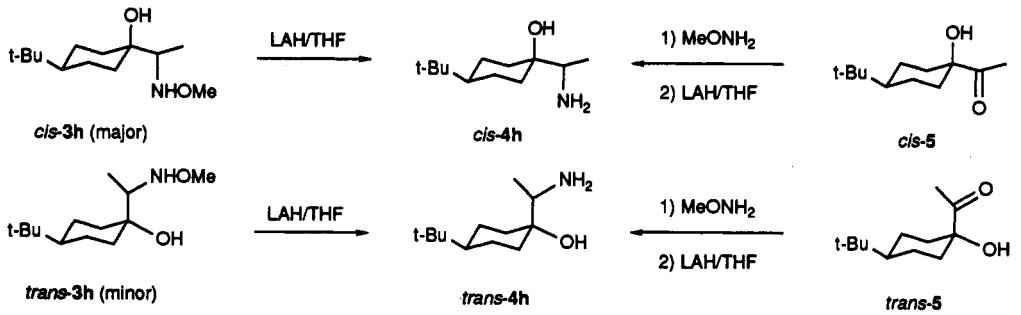
0022-3263/94/1959-1730$04.50/0

Table 1. Electroreductive Intermolecular Coupling of Ketones 1 with *O*-Methylacetaldoxime (2a)

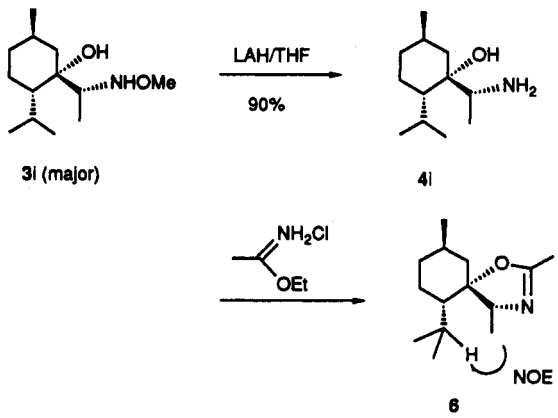
ketone 1	product 3	% yield of 3[a] (ds)[b]	ketone 1	product 3	% yield of 3[a] (ds)[b]
 1a	 3a	95	 1f	 3f	93 (50:50)[c]
 1b	 3b	94	 1g	 3g	53 (75:25)[c]
 1c	 3c	72	 1h	 3h	85 (70:30)[d]
 1d	 3d	94	 1i	 3i	55 (85:15)
 1e	 3e	96 (55:45)[c]	 1j	 3j	67[e] (50:50)

[a] Isolated yields. [b] Diastereomeric ratios determined by 200-MHz ^{1}H NMR ($CDCl_3$). [c] The stereoconfiguration of each isomer could not be assigned. [d] The ratio of *cis*:*trans*. [e] 10 equiv of **2a** was used.

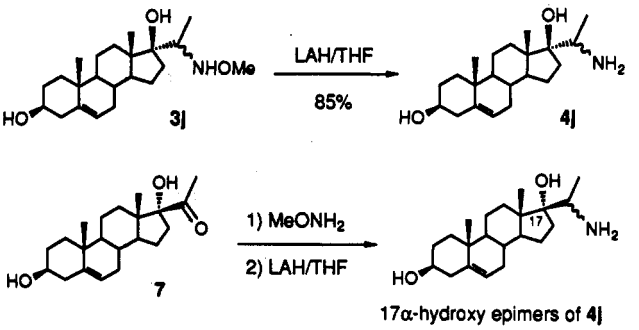
Scheme 1



Scheme 2



Scheme 3



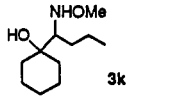
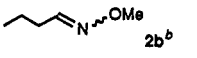
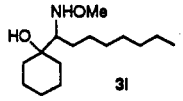
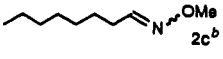
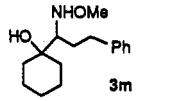
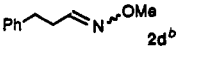
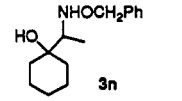
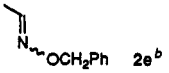
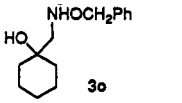
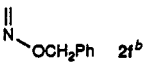
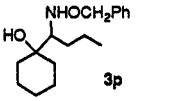
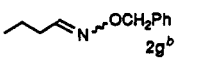
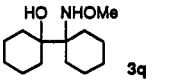
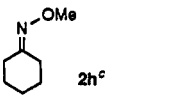
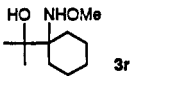
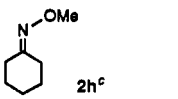
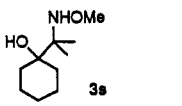
$NClO_4$ were essential for the electroreductive coupling, whereas no reaction other than simple reduction of the ketone took place when $LiClO_4$ was used as the electrolyte.

The coupling of other ketones (**1b–j**) with **2a** (2.5 equiv) carried out with an Sn cathode in i-PrOH are summarized in Table 1. Each of the products **3e–g** was obtained as a mixture of two diastereomers. 4-*tert*-Butylcyclohexanone (**1h**) also gave a mixture of *cis* and *trans* isomers (**3h**), and the stereoconfiguration of each isomer was determined by transformation of **3h** to β-amino alcohol **4h** followed by comparison of the ^{13}C NMR spectrum of **4h** with the spectrum of **4h** derived from the known compound **5**[5] (Scheme 1). Since *cis*-**3h** was the major isomer (70:30), this result suggested that the coupling of **1h** took place favorably at the less-hindered side, that is, the equatorial side.

Although four types of isomers might theoretically be formed, two stereoisomers (**3i**) were actually obtained with a 85:15 ratio in the coupling of (−)-menthone (**1i**). It was assumed that the major isomer of **3i** was also formed by the equatorial side (less-hindered side) attack on **1i**. Thus, the stereoconfiguration of the major isomer of **3i** could be assigned as shown in Scheme 2. This assignment was strongly supported by the NOE enhancement observed in the ^{1}H NMR spectrum of oxazoline **6**.

The coupling of dehydroepiandrosterone (**1j**) with **2a** afforded a 50:50 mixture of two isomers (**3j**) and both isomers had 17β-hydroxy configuration, since their reduced amines **4j** were spectroscopically inconsistent with the 17α-

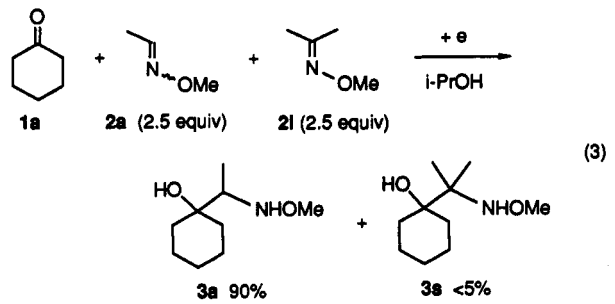
Table 2. Electroreductive Intermolecular Coupling of Ketones 1 with *O*-Alkyl Oximes 2

ketone 1	*O*-alkyl oxime 2	product 3	% yield of 3[a]
 1a	 3k	 2b[b]	88
 1a	 3l	 2c[b]	90
 1a	 3m	 2d[b]	94
 1a	 3n	 2e[b]	72
 1a	 3o	 2f[b]	39
 1a	 3p	 2g[b]	55
 1a	 3q	 2h[c]	65
 1k	 3r	 2h[c]	43
 1a	 3s	 2i[c]	30

[a] Isolated yields. [b] 2.5 equiv. [c] 10 equiv.

hydroxy epimers derived from 17α-hydroxypregnelone (7) (Scheme 3). This result showed the coupling of **1j** also occured predominantly at the less hindered side (α-side).

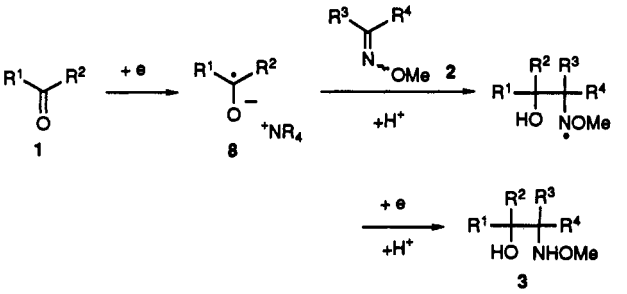
Some other *O*-methyl and *O*-benzyl oximes **2b–g** also coupled with either cyclohexanone or acetone by electroreduction under the same reaction conditions (Table 2). *O*-Methyl aldoximes **2b–d** yielded the coupled products with very high yields, whereas *O*-methyl ketoximes **2h,i** gave relatively low yields. The coupling of *O*-methylacetaldoxime (**2a**) with cyclohexanone (**1a**) was much faster than that of *O*-methylacetoxime (**2i**) with **1a** (eq 3).



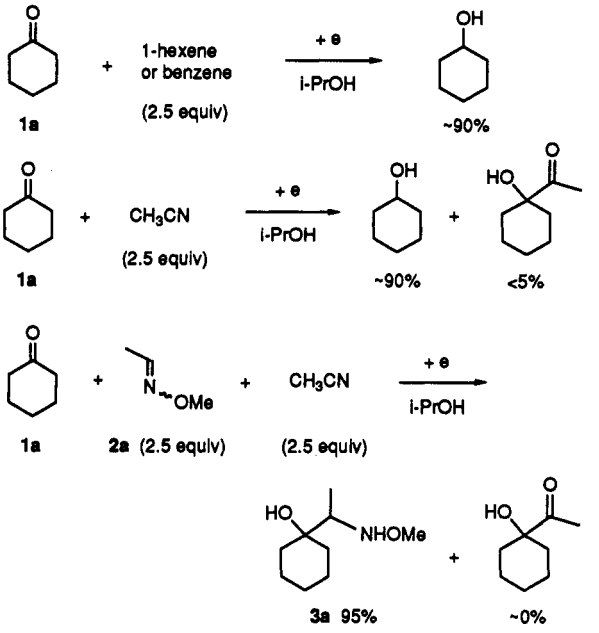
(3)

Reaction Mechanism. It is reasonable that the coupling is initiated by the electroreduction of ketone 1 but not *O*-methyl oxime 2 since it was confirmed that *O*-methyl oxime 2 was not electrochemically reducible under the same reaction conditions (constant current of 0.2 A) as the present coupling reaction. Furthermore, the key active intermediate of this coupling presumably is a radical not an anionic species, since the coupling was achievable in a protic solvent such as i-PrOH, and also the addition of 1 equiv of water to the reaction system did not adversely effect to the coupling.[5] A possible reaction mechanism for the coupling of 1 with 2 is depicted in Scheme 4.[12] Product 3 is formed by the addition of the anion radical 8 to the C=N bond of 2 followed by further one-electron transfer and protonation.

Scheme 4



Scheme 5



Comparison of the Reactivity of *O*-Methyl Oximes with Nitriles, Olefins, and Aromatic Rings. In the reaction with 8, the *O*-methyl oxime 2 was found to show the highest reactivity as the radical accepter when it was compared with nitrile, olefin, and aromatic ring, since the latter three types of compound gave very poor results in the electroreductive coupling with a ketone under the same reaction conditions (Scheme 5).[14]

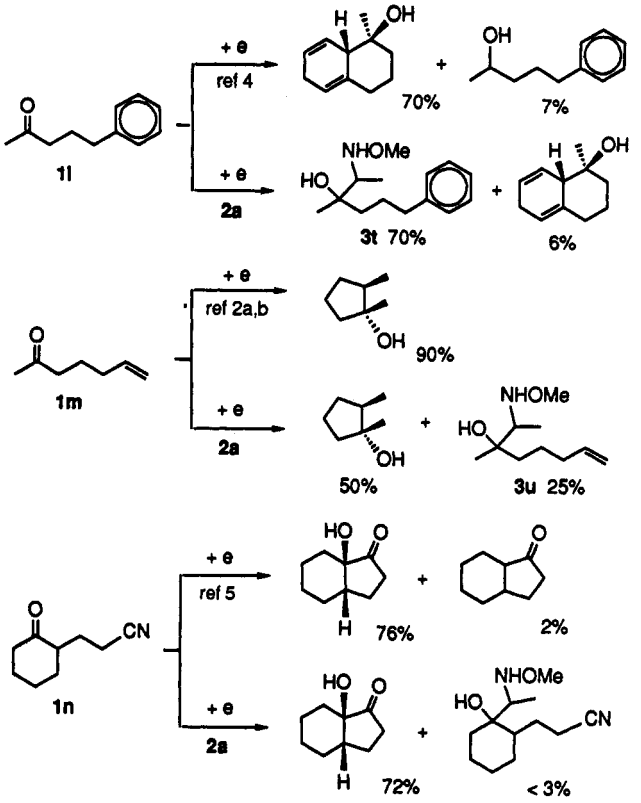
Since the reactivity of nitriles, olefins, and aromatic rings are too low in the intermolecular coupling with the carbonyl group, the intramolecular reactivity of those

(12) The inter-[13a] or intramolecular[13b-d] attack of a radical intermediate to *O*-alkyl oxime has been reported.

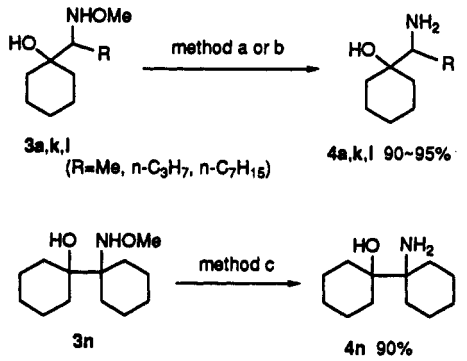
(13) (a) Hart, D. J.; Seely, F. L. *J. Am. Chem. Soc.* **1988**, *110*, 1631. (b) Corey, E. J.; Pyne, S. G. *Tetrahedron Lett.* **1983**, 2821. (c) Bartlett, P. A.; McLaren, K. L.; Ting, P. C. *J. Am. Chem. Soc.* **1988**, *110*, 1633. (d) Enholm, E. J.; Burroff, J. A.; Jaramillo, L. M. *Tetrahedron Lett.* **1990**, *31*, 3727.

(14) We have found that the electroreductive intermolecular coupling of a ketone with an olefin requires completely different reaction conditions from those of the intermolecular coupling of ketone with 2.[2c]

Scheme 6



Scheme 7



functional groups was compared with the intermolecular reactivity of **2a**. Thus, the electroreduction of **1l**, **1m**, or **1n** was carried out in the presence of **2a**, since the intramolecular coupling of **1l**, **1m**, or **1n** has already been found to be easily promoted by electroreduction [2,4,5] (Scheme 6). It was found that the intermolecular coupling of the carbonyl group of **1l** with **2a** took place in preference to the intramolecular coupling of **1l**. On the other hand, the electroreduction of **1m** gave intra- and intermolecularly coupled products in the ratio 2:1, and the intramolecular coupling was predominant in the electroreduction of **1n**. Hence, the order of the reactivity of those functional groups with the anion radical **8** seems to be *O*-methyl oximes >> nitrile > olefin > aromatic ring.

Reduction of 3 to 4. The coupled product **3** was easily reduced to the corresponding β-amino alcohol **4** in good yield by three different methods [a: H_2 (1 atm), cat. PtO_2/MeOH, rt, 8 h; b: LAH/THF, reflux, 6 h; c:[15] $NaBH_4$/$ZrCl_4$/CH_2Cl_2, rt, 2 h] (Scheme 7).

Synthesis of a Chiral Ligand for the Enantioselective Addition of Diethylzinc to an Aldehyde. The major isomer of **3i** was transformed to β-*N*,*N*-dimethylamino alcohol **9** by reduction with LAH followed by methylation with MeI (Scheme 8). The chiral β-amino alcohol **9** was an effective ligand for the enantioselective addition of diethylzinc to an aldehyde.[16] Several chiral secondary alcohols were obtained with high enantioselectivity when the addition of diethylzinc was carried out in the presence of a catalytic amount of **9** (eq 4), (Table 3).

Scheme 8

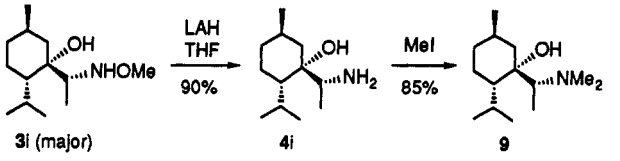
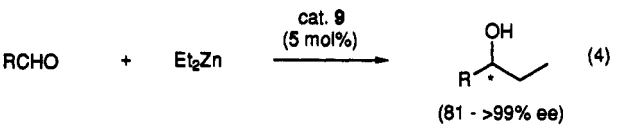


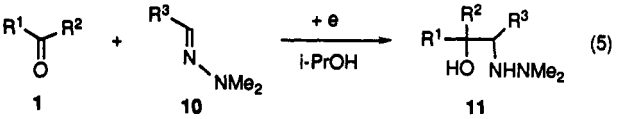
Table 3. Enantioselective Addition of Diethylzinc to Aldehydes

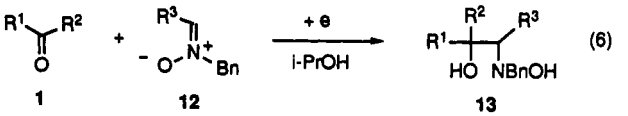
aldehyde	% yield[a]	% ee (config)[b]	$[\alpha]^{25}_D$, deg (*c*, solvent)
PhCHO	86	>99[c] (*S*)	−46.3 (3.2, $CHCl_3$)
p-$MeOC_6H_4CHO$	82	90[c](*S*)	−32.0 (4.9, benzene)
PhCH=CHCHO	96	87[c] (*S*)	−6.4 (3.6, $CHCl_3$)
n-$C_6H_{13}CHO$	80	81[d] (*S*)	+7.8 (2.9, $CHCl_3$)

[a] Isolated yields. [b] Determined by their optical rotations. Reported values are as follows: $[\alpha]_D$ −45.45° (*c* 5.15, $CHCl_3$) for (*S*)-1-phenylpropanol;[17] $[\alpha]_D$ −17.2° (*c* 5, benzene) for (*S*)-1-(4-methoxyphenyl)propanol in 51% ee;[18] $[\alpha]^{23}_D$ −6.6° (*c* 3.2, $CHCl_3$) for (*S*)-1-phenylpent-1-en-3-ol in 75% ee;[19] $[\alpha]^{24}_D$ +9.6° (*c* 8.3, $CHCl_3$) for (*S*)-3-nonanol.[20] [c] Determined by ^1H NMR of acetates of alcohols using $Eu(hfc)_3$. [d] Based on the optical rotation.



Electroreductive Intermolecular Coupling of Ketones with *N*,*N*-Dimethylhydrazones or Nitrones. Electroreduction of a mixture of ketone **1** and *N*,*N*-dimethylhydrazone **10** or α-alkyl-*N*-benzyl nitrone **12** with an Sn cathode in i-PrOH gave the intermolecularly coupled product **11** or **13** in moderate yield (eqs 5 or 6). The results





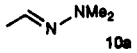
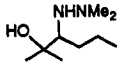
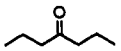
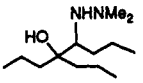
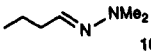
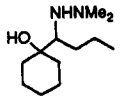
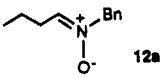
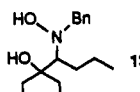
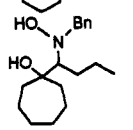
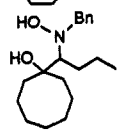
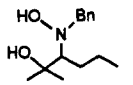
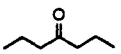
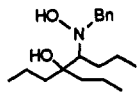
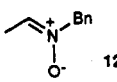
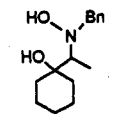
are summarized in Table 4. These reactions also seem to proceed via the addition of the anion radical **8** to **10** or **12** as the key reaction.

Electroreductive Intramolecular Coupling of Ketones with *O*-Methyl Oximes. The electroreduction of δ- or ε-keto *O*-methyl oxime **14**, carried out under conditions similar to those for the intermolecular coupling, gave the corresponding five- or six-membered product **15** as a

(15) Itsuno, S.; Sakurai, Y.; Ito, K. *Synthesis* **1988**, 995.

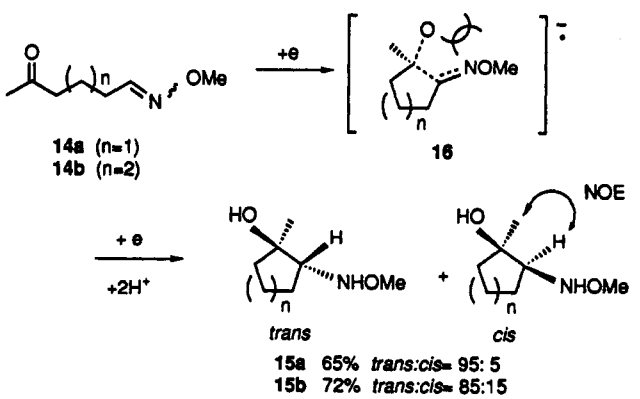
(16) Recent studies on the enantioselective addition of diethylzinc to an aldehyde in the presence of a chiral amino alcohol: (a) Oguni, N.; Matsuda, Y.; Kaneko, T. *J. Am. Chem. Soc.* **1988**, *110*, 7877. (b) Kitamura, M.; Okada, S.; Suga, S.: Noyori, R. *Ibid* **1989**, *111*, 4028. (c) Soai, K.; Niwa, S. *Chem. Lett.* **1989**, 481. (d) Shono, T.; Kise, N.; Shirakawa, E.; Matsumoto, H.; Okazaki, E. *J. Org. Chem.* **1991**, *56*, 3063.

Table 4. Electroreductive Coupling of Ketones with 10 or 12

ketone[a]	10 or 12	product	% yield[b]
	 10a	 11a	58
	10a		44
	10a	 11b	61
		 11c	41
	 10b	 11d	70
	 12a	 13a	
	12a		69
		 13b	
	12a		56
		 13c	
	12a	 13d	42
	12a	 13e	49
	 12b	 13f	56

[a] Ketone (10 mmol), 11 or 12 (2 mmol). [b] Isolated yields.

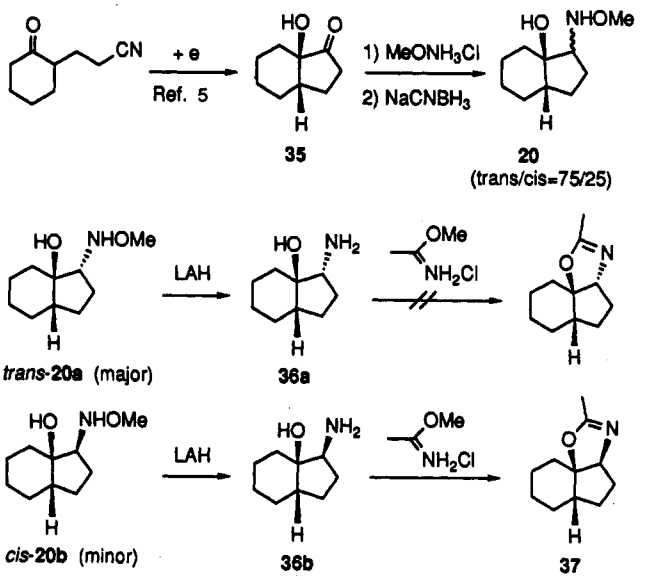
Scheme 9



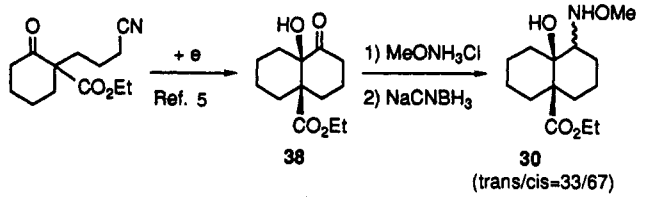
mixture of two diastereomers (Scheme 9). The stereoconfiguration of the major isomer of **15** was determined to be trans by NOE enhancement. This trans-selectivity is explained by the electronic repulsion between the negative charge located on the oxygen and nitrogen atoms in the intermediate **16**.

The other results of intramolecular coupling are summarized in Table 5. The electroreduction of **19** gave **20** as a 95:5 mixture of two diastereomers, and the stereo-

Scheme 10

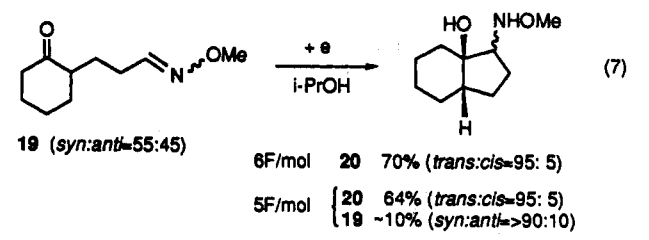


Scheme 11



configuration of each isomer was determined as shown in Scheme 10. Both isomers of **20** had a cis-fused ring structure, since they were consistent with the corresponding compounds prepared from a known compound **35**[5] having a cis-fused ring structure. The stereochemical arrangement of the methoxyamino group and hydroxyl group was trans in the major isomer of **20** (**20a**) since the amine **36a** did not form the corresponding oxazoline, whereas the amine **36b** derived from the minor isomer of **20** (**20b**) gave the oxazoline **37**. Similarly, **30** obtained from **29** was also found to have a cis-fused ring structure by comparison with the corresponding compounds derived from **38**[11] (Scheme 11). Although the stereochemical arrangement of the methoxyamino group and hydroxyl group could not be confirmed, the major isomer of **30** seems to be trans. It seems reasonable that the other products **18**, **22**, **26**, and **28** have also the cis-fused ring structure and the trans arrangement between the methoxyamino group and hydroxyl group. The three stereoconfigurations of **34** were determined by NOE.

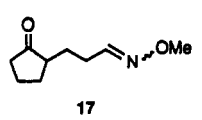
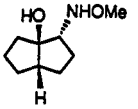
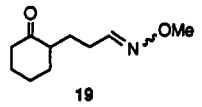
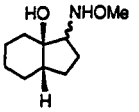
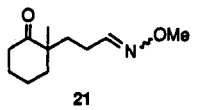
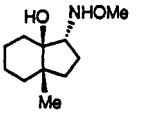
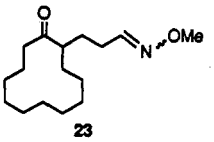
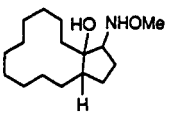
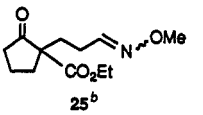
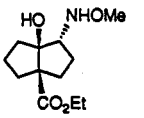
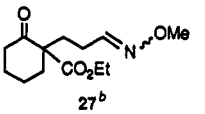
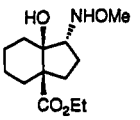
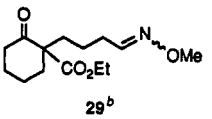
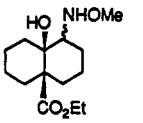
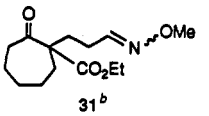
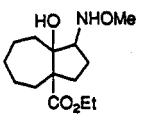
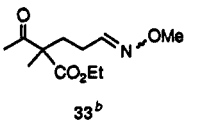
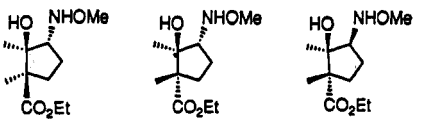
The following results may suggest that the reaction of the *anti*-form of the *O*-methyl oxime is faster than that of the *syn*-form (eq 7). Namely, when the electroreduction



(7)

of **19** (*syn:anti* = 55:45) was interrupted after 5 F/mol of electricity was passed, the recovered **19** was mainly the *syn*-form, though the stereostructure of the product **20** (*trans:cis* = 95:5) is the same as that obtained after the reaction was complete (6 F/mol).

Table 5. Electroreductive Intramolecular Coupling of δ- or ε-Keto *O*-Methyl Oximes

starting material	product and yield[a]
 **17**	 **18** 58% (single isomer)
 **19**	 **20** 70% (*trans:cis* = 95:5)
 **21**	 **22** 60% (single isomer)
 **23**	 **24** 63% (2 isomers, 70:30)
 **25**[b]	 **26** 60% (single isomer)
 **27**[b]	 **28** 64% (single isomer)
 **29**[b]	 **30** 73% (*trans:cis* = 80:20)
 **31**[b]	 **32** 81% (2 isomers, 80:20)
 **33**[b]	 **34a** **34b** **34c** 86% (3 isomers, **34a:34b:34c** = 45:40:15)

[a] Isolated yields. Diastereomeric ratio was determined by ^{1}H NMR. [b] Electroreduction was carried out without using diaphragm.

Experimental Section

^{1}H NMR spectra and ^{13}C NMR spectra were measured on a Varian Gemini-200 or a JEOL JNM-GX400 spectrometer.

Starting Materials. *O*-Methyl oximes **2a** and **2i** were prepared according to the reported method.[21] The other *O*-alkyl oximes **2b–e, g, i** were obtained by the usual *O*-alkylation of oximes with NaH (1.1 equiv) and MeI or BnBr (1.1 equiv) in THF (50–70% yields). *O*-Benzyl formaldoxime **2f** was prepared from *N*-(benzyloxy)amine and formalin. *N,N*-Dimethylhydrazones **10** were prepared from aldehydes and *N,N*-dimethylhydrazine by the usual method.[22] α-Alkyl-*N*-benzyl nitrones **12** were synthesized from aldehydes and *N*-hydroxybenzylamine[23] according to the known method.[24] (−)-Menthone (Aldrich Chemical Co.) and dehydroepiandrosterone (Tokyo Kasei Kogyo) were commercially available.

2a: bp 45–48 °C (760 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.82 (d, 1.35 H, *J* = 5.6 Hz), 1.84 (d, 1.65 H, *J* = 6.0 Hz), 3.81 (s, 1.65 H), 3.88 (s, 1.35 H), 6.74 (q, 0.45 H, *J* = 5.6 Hz), 7.40 (q, 0.55 H, *J* = 6.0 Hz).

2b: bp 65–70 °C (760 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.96 (t, 3 H, *J* = 6.0 Hz), 1.10–1.80 (m, 2 H), 2.00–2.50 (m, 2 H), 3.81 (s, 1.65 H), 3.87 (s, 1.35 H), 6.73 (q, 0.45 H, *J* = 5.6 Hz), 7.40 (q, 0.55 H, *J* = 6.0 Hz).

2c: bp 95–100 °C (760 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.96 (t, 3 H, *J* = 6.0 Hz), 1.10–1.80 (m, 10 H), 2.00–2.50 (m, 2 H), 3.81 (s, 1.65 H), 3.87 (s, 1.35 H), 6.73 (q, 0.45 H, *J* = 5.6 Hz), 7.40 (q, 0.55 H, *J* = 6.0 Hz).

2d: bp 67 °C (3 mmHg); ^{1}H NMR ($CDCl_3$) δ 2.45–2.60 (m, 2 H),2.75–2.87 (m, 2 H), 3.82 (s, 1.8 H), 3.86 (s, 1.2 H), 6.69 (t, 0.4 H, *J* = 5.6 Hz), 7.18–7.38 (m, 5 H), 7.41 (t, 0.6 H, *J* = 6.0 Hz).

2e: bp 62–64 °C (5 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.85 (d, 1.8 H, *J* = 5.9 Hz), 1.87 (d, 1.2 H, *J* = 5.0 Hz), 5.04 (s, 1.2 H), 5.12

(17) Pickard, R. H.; Kenyon, J. *J. Chem. Soc.* **1914**, 1115.
(18) Capillon, J.; Guette, J. *Tetrahedron* **1979**, *35*, 1817.
(19) Sato, T.; Gotoh, Y.; Wakabayashi, Y.; Fujisawa, T. *Tetrahedron Lett.* **1983**, *24*, 4123.
(20) Mukaiyama, T.; Hojo, K. *Chem. Lett.* **1976**, 893.
(21) Cresswell, V.; Leicester, J. *J. Chem. Soc.* **1952**, 514.
(22) Kelly, J. R.; Liu, H. *J. Am. Chem. Soc.* **1985**, *107*, 4998.
(23) Wheeler, O. H.; Gore, P. H. *J. Am. Chem. Soc.* **1956**, *78*, 3363.
(24) Kikugawa, Y.; Kawase, M. *Chem. Lett.* **1977**, 1279.

(s, 0.8 H), 6.80 (q, 0.4 H, J = 5.0 Hz), 7.18–7.40 (m, 5 H), 7.49 (q, 0.6 H, J = 5.9 Hz).

2f: bp 50 °C (5 mmHg); ^{1}H NMR ($CDCl_3$) δ 5.13 (s, 2 H), 6.48 (d, 1 H, J = 8.2 Hz), 7.09 (d, 1 H, J = 8.2 Hz), 7.37 (s, 5 H).

2g: bp 90–95 °C (6 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.94 (t, 1.8 H, J = 7.3 Hz), 0.95 (t, 1.2 H, J = 7.3 Hz), 1.40–1.62 (m, 2 H), 2.11–2.23 (m, 1.2 H), 2.30–2.41 (m, 0.8 H), 5.06 (s, 1.8 H), 5.11 (s, 1.2 H), 6.69 (t, 0.4 H, J = 5.4 Hz), 7.35 (br s, 5 H), 7.46 (t, 0.6 H, J = 6.3 Hz).

2h: bp 85–90 °C (100 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.53–1.76 (m, 6 H), 2.20 (t, 2 H, J = 6.4 Hz), 2.45 (t, 2 H, J = 6.5 Hz), 3.82 (s, 3 H).

2i: bp 60–65 °C (760 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.85 (s, 3 H), 1.88 (s, 3 H), 3.83 (s, 3 H).

10a: bp 85–90 °C (760 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.92 (d, 3 H, J = 5.1 Hz), 2.72 (s, 6 H), 6.72 (q, 1 H, J = 5.1 Hz).

10b: bp 121 °C (760 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 3 H, J = 7.4 Hz), 1.36 (m, 2 H), 2.21 (dt, 2 H, J = 7.7 and 5.7 Hz), 2.72 (s, 6 H), 6.67 (t, 1 H, J = 5.7 Hz).

12a: R_f 0.2 (silica gel, hexane–EtOAc, 1:2); ^{1}H NMR ($CDCl_3$) δ 0.94 (t, 3 H, J = 7.5 Hz), 1.52 (q, 2 H, J = 7.5 Hz), 2.48 (q, 2 H, J = 7.5 Hz), 4.89 (s, 2 H), 6.63 (t, 1 H, J = 5.6 Hz), 7.40 (s, 5 H).

12b: R_f 0.2 (silica gel, CH_2Cl_2–MeOH, 20:1); ^{1}H NMR ($CDCl_3$) δ 2.00 (d, 2 H, J = 5.9 Hz), 4.90 (s, 2 H), 6.72 (q, 1 H, J = 5.9 Hz), 7.40 (s, 5 H).

General Procedure for Electroreduction. A solution of Et_4NOTs (10 g) in i-PrOH (40 mL) was put into a divided cell (50-mL beaker) equipped with an Sn cathode (5 × 10 cm^2), a carbon rod anode, and a ceramic diaphragm. To the catholyte was added ketone 1 (3 mmol) and *O*-methyl oxime (7.5 mmol). Electricity was passed with constant current of 0.2 A until almost all of the ketone was consumed (2.5–6 F/mol). The catholyte was poured into water (200 mL) and extracted with Et_2O. The products were isolated by column chromatography on silica gel.

3a: R_f 0.2 (hexane–EtOAc, 5:1); IR (neat) 3450, 3260 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.08 (d, 3 H, J = 6.6 Hz), 1.20–1.80 (m, 10 H), 2.61 (br s, 1 H, OH), 2.86 (q, 1 H, J = 6.6 Hz), 3.46 (s, 3 H), 5.10 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 12.91 (q), 21.12 (t), 21.35 (t), 25.57 (t), 32.04 (t), 35.02 (t), 61.57 (q), 63.21 (d), 72.49 (s). Anal. Calcd for $C_9H_{19}NO_2$: C, 62.39; H, 11.05; N, 8.09. Found: C, 62.43; H, 11.09; N, 8.03.

3b: R_f 0.2 (hexane–EtOAc, 5:1); IR (neat) 3450, 3270 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.09 (d, 3 H, J = 6.6 Hz), 1.20–1.80 (m, 2 H) 2.76 (br s, 1 H, OH), 2.86 (q, 1 H, J = 6.6 Hz), 3.43 (s, 3 H), 5.29 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 13.23 (q), 21.91 (t), 22.15 (t), 29.32 (t), 29.43 (t), 35.36 (t), 38.97 (t), 61.49 (q), 64.26 (d), 76.27 (s). Anal. Calcd for $C_{10}H_{21}NO_2$: C, 64.52; H, 11.30; N, 7.48. Found: C, 64.67; H, 11.38; N, 7.40.

3c: R_f 0.2 (hexane–EtOAc, 5:1); IR (neat) 3460, 3270 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.18 (d, 3 H, J = 6.6 Hz), 1.20–1.80 (m, 22 H), 2.31 (br s, 1 H, OH), 2.80 (q, 1 H, J = 6.6 Hz), 3.44 (s, 3 H), 5.20 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 12.78 (q), 19.17 (t), 19.38 (t), 21.93 (t, 2 C), 22.37 (t), 22.44 (t), 25.86 (t), 26.45 (t, 2 C), 31.58 (t), 32.45 (t), 60.71 (d), 61.93 (q), 76.64 (s). Anal. Calcd for $C_{15}H_{31}NO_2$: C, 69.99; H, 12.14; N, 5.44. Found: C, 69.86; H, 12.25; N, 5.35.

3d: R_f 0.25 (hexane–EtOAc, 5:1); IR (neat) 3480, 3260 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.06 (d, 3 H, J = 7.0 Hz), 0.80–1.05 (m, 6 H), 1.15–1.55 (m, 8 H), 2.65 (br s, 1 H, OH), 2.98 (q, 1 H, J = 7.0 Hz), 3.45 (s, 3 H), 5.20 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 13.27 (q), 14.40 (q), 14.50 (q), 16.02 (t), 16.11 (t), 37.45 (t), 38.76 (t), 60.88 (q), 61.57 (d), 75.25 (s). Anal. Calcd for $C_{10}H_{23}NO_2$: C, 63.45; H, 12.25; N, 7.40. Found: C, 63.58; H, 12.36; N, 7.37.

3e (55:45 mixture of two diastereomers): R_f 0.1 (hexane–EtOAc, 5:1); IR (neat) 3440, 3270, 3090, 3070, 3040, 1610, 1500, 760, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10 (d, 3 H, J = 6.8 Hz), 1.15 (s, 1.35 H), 1.25 (s, 1.65 H), 1.60–1.85 (m, 2 H), 2.55–2.90 (m, 2 H), 3.04 (q, 0.55 H, J = 6.8 Hz), 3.09 (q, 0.45 H, J = 6.8 Hz), 3.12 (br s, 0.55 H, OH), 3.24 (brs, 0.45 H, OH), 3.53 (s, 1.65 H), 3.55 (s, 1.35 H), 5.30 (br s, 1 H, NH), 7.12–7.48 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 13.49 (q), 13.74 (q), 21.75 (q), 24.09 (q), 29.35 (t), 29.40 (t), 38.41 (t), 42.24 (t), 61.46 (q), 61.75 (q), 62.04 (d), 63.75 (d), 73.65 (s), 73.82 (s), 125.59 (d), 128.48 (d), 142.81 (s), 142.85 (s). Anal. Calcd for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48; N, 6.27. Found: C, 67.08; H, 9.57; N, 6.14.

3f (50:50 mixture of two diastereomers): R_f 0.2 (hexane–EtOAc, 5:1); IR (neat) 3470, 3260, 835 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.07 (d, 1.5 H, J = 6.9 Hz), 1.09 (s, 1.5 H), 1.10 (d, 1.5 H, J = 6.9 Hz), 1.18 (s, 1.5 H), 1.35–1.55 (m, 2 H), 1.62 (s, 3 H), 1.69 (s, 3 H), 1.90–2.25 (m, 2 H), 2.92 (br s, 0.5 H, OH), 2.99 (q, 0.5 H, J = 6.9 Hz), 3.02 (q, 0.5 H, J = 6.9 Hz), 3.03 (brs, 0.5 H, OH), 3.53 (s, 1.5 H), 3.54 (s, 1.5 H), 5.12 (t, 1 H, J = 7.0 Hz), 5.65 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 13.38 (q), 13.59 (q), 17.24 (q), 21.42 (t), 21.60 (t), 21.71 (q), 24.15 (q), 25.33 (q), 36.31 (t), 39.84 (t), 61.53 (q), 61.60 (q), 61.93 (d), 63.73 (d), 73.74 (s), 124.45 (d), 124.64 (d), 131.45 (s). Anal. Calcd for $C_{11}H_{23}NO_2$: C, 65.63; H, 11.52; N, 6.96. Found: C, 65.69; H, 11.68; N, 6.73.

3g (75:25 mixture of two diastereomers): R_f 0.25 (hexane–EtOAc, 5:1); IR (neat) 3470, 3260 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.99 (s, 2.25 H), 1.01 (6.75 H), 1.12 (s, 0.75 H), 1.15 (s, 2.25 H), 1.27 (d, 0.75 H, J = 6.7 Hz), 1.28 (d, 2.25 H, J = 6.7 Hz), 2.25 (br s, 1 H, OH), 3.24 (q, 0.75 H, J = 6.7 Hz), 3.31 (q, 0.25 H, J = 6.7 Hz), 3.54 (s, 2.25 H), 3.65 (s, 0.75 H), 5.30 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 15.32 (q), 16.25 (q), 17.78 (q), 19.46 (q), 25.75 (q), 26.37 (q), 37.40 (s), 38.20 (s), 60.04 (d), 61.35 (q), 62.73 (d), 76.45 (s). Anal. Calcd for $C_9H_{21}NO_2$: C, 61.67; H, 12.08; N, 7.99. Found: C, 61.73; H, 12.20; N, 8.03.

cis-**3h**: R_f 0.2 (hexane–EtOAc, 5:1); IR (neat) 3440, 3370 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (s, 9 H), 1.12 (d, 3 H, J = 6.0 Hz), 1.26–1.73 (m, 9 H), 2.71 (br s, 1 H, OH), 2.85 (q, 1 H, J = 6.0 Hz), 3.52 (s, 3 H), 5.20 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 13.23 (q), 21.87 (t), 22.07 (t), 27.35 (q, 3 C), 32.20 (t), 35.51 (t), 35.87 (s), 47.77 (d), 61.75 (q), 64.12 (d), 72.20 (s). Anal. Calcd for $C_{13}H_{27}NO_2$: C, 68.07; H, 11.87; N, 6.11. Found: C, 68.11; H, 11.94; N, 6.03.

trans-**3h**: R_f 0.15 (hexane–EtOAc, 5:1); IR (neat) 3430, 3360 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (s, 9 H), 1.17 (d, 3 H, J = 6.0 Hz), 1.27–2.23 (m, 9 H), 2.65 (br s, 1 H, OH), 3.24 (q, 1 H, J = 6.0 Hz), 3.53 (s, 3 H), 5.20 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 12.10 (q), 23.39 (t), 23.82 (t), 27.42 (q, 3 C), 32.09 (s), 35.91 (t), 36.78 (t), 47.19 (d), 55.56 (d), 61.96 (q), 73.09 (s). Anal. Calcd for $C_{13}H_{27}NO_2$: C, 68.07; H, 11.87; N, 6.11. Found: C, 68.08; H, 11.90; N, 6.06.

3i (major isomer): R_f 0.45 (hexane–EtOAc, 5:1); $[\alpha]^{20}_D$ −19.5° (*c* 4.3, $CHCl_3$); IR (neat) 3460, 3270 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (d, 6 H, J = 5.4 Hz), 0.91 (d, 3 H, J = 4.8 Hz), 0.97–1.10 (m, 1 H), 1.17 (d, 3 H, J = 6.8 Hz), 1.22–1.38 (m, 2 H), 1.40–1.55 (m, 3 H), 1.60–1.83 (m, 2 H), 1.90–2.13 (m, 1 H), 2.25 (s, 1H, OH), 3.16 (q, 1H, J = 6.8 Hz), 3.52 (s, 3 H), 5.52 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 13.74 (q), 17.68 (q), 20.22 (t), 22.26 (q), 23.10 (q), 26.27 (d), 27.83 (d), 34.67 (t), 44.57 (t), 45.67 (d), 61.72 (q), 63.61 (d), 75.95 (s). Anal. Calcd for $C_{13}H_{27}NO_2$: C, 68.07; H, 11.87; N, 6.11. Found: C, 68.16; H, 11.91; N, 5.95.

3j (50:50 mixture of two diastereomers): R_f 0.4 (hexane–EtOAc, 1:1); IR (KBr) 3430 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91 (s, 1.5 H), 0.93 (s, 1.5 H), 1.03 (s, 3 H), 1.32 (d, 1.5 H, J = 6.5 Hz), 1.34 (d, 1.5 H, J = 6.8 Hz), 0.90–2.40 (m, 20 H), 2.90 (br s, 1 H, OH), 3.07 (q, 0.5 H, J = 6.8 Hz), 3.22 (q, 0.5 H, J = 6.5 Hz), 3.41–3.71 (m, 1 H), 3.58 (s, 1.5 H), 3.63 (s, 1.5 H), 5.30–5.40 (m, 1 H), 5.70 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 14.78 (q,1C), 15.61 (q, 1C), 19.06 (q, 1C), 20.58 (t, 0.5C), 20.73 (t, 0.5C), 23.72 (t, 0.5C), 23.87 (t, 0.5C), 31.27 (t, 1C), 31.52 (t, 1C), 32.08 (t, 0.5C), 32.37 (d, 0.5C), 32.49 (d, 0.5C), 32.86 (t, 0.5C), 33.73 (t, 0.5C), 34.58 (t, 0.5C), 36.28 (s, 1C), 37.03 (t, 1C), 41.96 (t, 1C), 46.50 (s, 0.5C), 46.77 (s, 0.5C), 49.63 (d, 1C), 51.06 (d, 0.5C), 51.41 (d, 1C), 59.86 (d, 0.5C), 61.48 (q, 0.5C), 61.96 (q, 0.5C), 71.35 (d, 1C), 84.02 (s, 0.5C), 85.20 (s, 0.5C), 121.25 (d, 1C), 140.93 (s, 1C). Anal. Calcd for $C_{22}H_{37}NO_3$: C, 72.68; H, 10.26; N, 3.85. Found: C, 72.84; H, 10.39; N, 3.66.

3k: R_f 0.15 (hexane–EtOAc, 10:1); IR (neat) 3450, 3260 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.96 (t, 3 H, J = 6.0 Hz), 1.20–1.80 (m, 14 H), 2.52 (t, 1 H, J = 6.3 Hz), 2.93 (br s, 1 H, OH), 3.44 (s, 3 H), 5.73 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 13.85 (q), 20.33 (t), 21.31 (t), 21.55 (t), 25.65 (t), 29.10 (t), 32.85 (t), 35.29 (t), 61.40 (q), 67.96 (d), 73.07 (s). Anal. Calcd for $C_{11}H_{23}NO_2$: C, 65.63; H, 11.52; N, 6.96. Found: C, 65.70; H, 11.73; N, 6.74.

3l: R_f 0.4 (hexane–EtOAc, 5:1); IR (neat) 3460, 3260 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3 H, J = 6.0 Hz), 1.20–1.80 (m, 22 H), 2.33–2.70 (m, 1 H), 2.95 (br s, 1 H, OH), 3.43 (s, 3 H), 5.79 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.72 (q), 21.35 (t), 21.57 (t), 22.33 (t), 25.68 (t), 26.81 (t), 27.25 (t), 28.96 (t), 29.50 (t), 31.58 (t), 32.89 (t), 35.33 (t), 61.42 (q), 68.26 (d), 73.14 (s). Anal. Calcd

for $C_{15}H_{31}NO_2$: C, 69.99; H, 12.14; N, 5.44. Found: C, 69.84; H, 12.33; N, 5.25.

3m: R_f 0.3 (hexane–EtOAc, 5:1); IR (neat) 3460, 3260, 3080, 3060, 3030, 1605, 1500, 750, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00–2.00 (m, 12 H), 2.53–2.80 (m, 2 H), 2.83–3.20 (m, 1 H), 2.95 (br s, 1 H, OH), 3.54 (s, 3 H), 6.00 (br s, 1 H), 7.15–7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 21.26 (t), 21.53 (t), 25.58 (t), 28.59 (t), 32.96 (t), 33.32 (t), 35.14 (t), 61.68 (q), 67.39 (d), 73.19 (s), 125.82 (d), 128.36 (d, 4C), 142.26 (s). Anal. Calcd for $C_{16}H_{25}NO_2$: C, 72.96; H, 9.57; N, 5.32. Found: C, 73.05; H, 9.81; N, 5.22.

3n: R_f 0.25 (hexane–EtOAc, 5:1); IR (neat) 3450, 3270, 3090, 3070, 3040, 1500, 750, 740, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.14 (d, 3 H, J = 6.6 Hz), 1.28–1.65 (m, 10 H), 2.69 (b rs, 1H, OH), 2.92 (q, 1 H, J = 6.6 Hz), 4.69 (s, 2 H), 5.67 (br s, 1 H, NH), 7.34 (brs, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 13.05 (q), 21.17 (t), 21.42 (t), 25.59 (t), 32.14 (t), 35.10 (t), 63.33 (d), 72.63 (s), 76.16 (t), 127.89 (d), 128.46 (d, 4 C), 137.50 (s). Anal. Calcd for $C_{15}H_{23}NO_2$: C, 72.25; H, 9.30; N, 5.62. Found: C, 72.30; H, 9.43; N, 5.51.

3o: R_f 0.2 (hexane–EtOAc, 5:1); IR (neat) 3450, 3030, 735, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20–1.75 (m, 10 H), 2.64 (br s, 1 H, OH), 2.94 (s, 2 H), 4.71 (s, 2 H), 5.75 (brs, 1 H, NH), 7.35 (br s, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 21.80 (t, 2 C), 25.60 (t), 35.89 (t, 2 C), 60.43 (t), 70.97 (s), 75.85 (t), 128.10 (d), 128.55 (d, 2 C), 128.61 (d, 2 C), 137.38 (s). Anal. Calcd for $C_{14}H_{21}NO_2$: C, 71.46; H, 8.99; N, 5.95. Found: C, 71.58; H, 9.01; N, 5.88.

3p: R_f 0.5 (hexane–EtOAc, 5:1); IR (neat) 3450, 3050, 3025, 735, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 3 H, J = 7.0 Hz), 1.10–1.80 (m, 14 H), 2.61 (t, 1 H, J = 6.4 Hz), 3.04 (br s, 1 H, OH), 4.66 (d, 1 H, J = 11.6 Hz), 4.71 (d, 1 H, J = 11.6 Hz), 5.75 (br s, 1 H, NH), 7.34 (br s, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 13.91 (q), 20.32(t), 21.31 (t), 21.55 (t), 25.64 (t), 29.05 (t), 32.84 (t), 35.29 (t), 67.95 (d), 73.13 (s), 75.92 (t), 127.88 (d), 128.33 (d, 2 C), 128.40 (d, 2 C), 137.45 (s). Anal. Calcd for $C_{17}H_{27}NO_2$: C, 73.61; H, 9.81; N, 5.05. Found: C, 73.53; H, 9.86; N, 4.88.

3q: R_f 0.5 (hexane–EtOAc, 5:1); IR (neat) 3510, 3250 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87–1.70 (m, 20 H), 2.64 (br s, 1 H, OH), 3.44 (s, 3 H), 5.75 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 21.42 (t, 2 C), 21.50 (t, 2 C), 25.68 (t), 25.83 (t), 26.65 (t, 2 C), 31.47 (t, 2 C), 61.88 (q), 63.42 (s), 76.15 (s). Anal. Calcd for $C_{13}H_{25}NO_2$: C, 68.18; H, 11.08; N, 6.16. Found: C, 68.29; H, 11.20; N, 6.03.

3r: R_f 0.3 (hexane–EtOAc, 5:1); IR (neat) 3480, 3260 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 6 H), 1.25–1.80 (m, 11 H), 3.46 (s, 3 H), 5.78 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 21.33 (t, 2 C), 25.10 (q, 2 C), 25.57 (t), 26.99 (t, 2 C), 62.02 (q), 62.95 (s), 76.25 (s). Anal. Calcd for $C_{10}H_{21}NO_2$: C, 64.13; H, 9.57; N, 5.32. Found: C, 64.25; H, 9.71; N, 5.22.

3s: R_f 0.3 (hexane–EtOAc, 5:1); IR (neat) 3500, 3260 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.08 (s, 6 H), 1.25–1.80 (m, 10 H), 2.88 (br s, 1 H, OH), 3.43 (s, 3 H), 5.01 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 20.22 (q, 2 C), 21.39 (t, 2 C), 25.68 (t), 31.52 (t, 2 C), 62.64 (q), 62.84 (s), 75.33 (s). Anal. Calcd for $C_{10}H_{21}NO_2$: C, 64.13; H, 11.30; N, 7.48. Found: C, 64.23; H, 11.39; N, 7.34.

3t (50:50 mixture of two diastereomers): R_f 0.15 (hexane–EtOAc, 5:1); IR (neat) 3450, 3260, 3090, 3060, 3030, 1500, 750, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05 (d, 1.5 H, J = 6.6 Hz), 1.07 (s, 1.5 H), 1.08 (d, 1.5 H, J = 6.7 Hz), 1.16 (s, 1.5 H), 1.41–1.85 (m, 4 H), 2.62 (t, 2 H, J = 8.0 Hz), 2.95 (br s, 1 H, OH), 2.98 (q, 0.5 H, J = 6.7 Hz), 3.02 (q, 0.5 H, J = 6.6 Hz), 3.51 (s, 1.5 H), 3.52 (s, 1.5 H), 7.18–7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 13.54 (q), 13.74 (q), 21.97 (q), 24.48 (q), 24.77 (t), 25.17 (t), 36.24 (t), 36.38 (t), 39.66 (t), 61.74 (q), 61.89 (d), 63.78 (d), 73.87 (s), 73.97 (s), 125.85 (d), 128.43 (d), 128.54 (d), 142.62 (s). Anal. Calcd for $C_{11}H_{23}NO_2$: C, 65.63; H, 11.52; N, 6.96. Found: C, 65.75; H, 11.56; N, 6.98.

3u (50:50 mixture of two diastereomers): R_f 0.2 (hexane–EtOAc, 5:1); IR (neat) 3430, 3270, 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.07 (d, 1.5 H, J = 6.6 Hz), 1.08 (s, 1.5 H), 1.10 (d, 1.5 H, J = 6.6 Hz), 1.17 (s, 1.5 H), 1.42–1.66 (m, 4 H), 2.00–2.16 (m, 2 H), 2.93 (br s, 0.5 H, OH), 2.98 (q, 0.5 H, J = 6.6 Hz), 3.02 (q, 0.5 H, J = 6.6 Hz), 3.09 (br s, 0.5 H, OH), 3.53 (s, 3 H), 4.93–5.10 (m, 2 H), 5.63 (br s, 1 H, NH), 5.72–5.95 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.46 (q), 13.67 (q), 21.79 (q), 22.00 (t), 22.41 (t), 24.36 (q), 33.95 (t), 34.09 (t), 35.91 (t), 39.41 (t), 61.66 (q), 61.86 (d), 63.72 (d), 73.76 (s), 73.87 (s), 114.57 (t), 138.80 (d). Anal. Calcd for $C_{10}H_{21}NO_2$: C, 64.13; H, 11.30; N, 7.48. Found: C, 64.26; H, 11.42; N, 7.43.

11a: R_f 0.2 (hexane–EtOAc, 2:1); IR (neat) 3250 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.79–1.93 (m, 12 H) 0.91 (d, 3 H, J = 6.7 Hz), 2.44 (s, 6 H), 2.92 (q, 1 H, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 15.52 (q), 21.42 (t), 21.59 (t), 26.65 (t), 30.25 (t), 36.23 (t), 47.36 (q, 2 C), 58.79 (d), 74.66 (s). Anal. Calcd for $C_{10}H_{22}N_2O$: C, 64.47; H, 11.90; N, 15.04. Found: C, 64.55; H, 12.01; N, 14.98.

11b: R_f 0.05 (hexane–EtOAc, 2:1); IR (neat) 3500 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (d, 3 H, J = 6.7 Hz), 1.12 (s, 3 H), 1.17 (s, 3 H), 2.98 (q, 1 H, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 15.90 (q), 22.54 (q), 28.11 (q), 47.29 (q, 2 C), 58.50 (d), 74.65 (s). Anal. Calcd for $C_7H_{18}N_2O$: C, 57.49; H, 12.41; N, 19.16. Found: C, 57.57; H, 12.48; N, 19.04.

11c: R_f 0.3 (hexane–EtOAc, 2:1); IR (neat) 3250 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.80–1.00 (m, 9 H), 1.09–1.72 (m, 8 H), 2.44 (s, 6 H), 3.08 (q, 1 H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 13.71 (q), 14.51 (q), 14.78 (q), 15.67 (t), 16.11 (t), 36.70 (t), 39.69 (t), 46.84 (q, 2 C), 55.61 (d), 76.56 (s). Anal. Calcd for $C_{11}H_{26}N_2O$: C, 65.29; H, 12.95; N, 13.85. Found: C, 65.36; H, 12.92; N, 13.71.

11d: R_f 0.4 (hexane–EtOAc, 2:1); IR (neat) 3250 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 3 H, J = 7.0 Hz), 0.99–1.79 (m, 14 H), 2.44 (s, 6 H), 2.70 (dd, 1 H, J = 10.0 and 2.0 Hz); ^{13}C NMR ($CDCl_3$) δ 14.28 (q), 20.75 (t), 21.45 (t), 21.71 (t), 26.73 (t), 30.91 (t), 31.06 (t), 35.95 (t), 47.04 (q), 63.35 (d), 75.06 (s). Anal. Calcd for $C_{12}H_{28}N_2O$: C, 67.24; H, 12.23; N, 13.07. Found: C, 67.26; H, 12.20; N, 12.96.

13a: R_f 0.45 (hexane–EtOAc, 5:1); IR (neat) 3350, 975, 740, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 7.0 Hz), 1.12–1.78 (m, 14 H), 2.70 (t, 1 H, J = 8.0 Hz), 3.82 (d, 1 H, J = 13.2 Hz), 4.10 (d, 1 H, J = 13.2 Hz), 4.73 (br s, 1 H), 7.33 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.40 (q), 21.56 (t), 21.99 (t), 23.69 (t), 25.03 (t), 33.47 (t), 35.76 (t), 63.35 (t), 72.89 (d), 73.87 (s), 127.48 (d), 128.50 (d), 129.41 (d), 138.40 (s). Anal. Calcd for $C_{17}H_{27}NO_2$: C, 73.60; H, 9.81; N, 5.05. Found: C, 73.66; H, 9.87; N, 4.98.

13b: R_f 0.70 (hexane–EtOAc, 3:1); IR (neat) 3300, 725, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 6.0 Hz), 1.24–1.80 (m, 16 H), 2.55 (dd, 1H, J=7.5 and 3.5 Hz), 3.83 (d, 1 H, J = 13.0 Hz), 4.11 (d, 1 H, J = 13.0 Hz), 4.52 (br s, 1 H), 7.35 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.39 (q), 22.15 (t), 22.44 (t), 23.68 (t), 25.35(t), 29.47 (t), 29.54 (t), 36.67 (t), 39.55 (t), 63.46 (t), 73.55 (d), 77.69 (s), 127.34 (d), 128.39 (d), 129.38 (d), 138.45 (s). Anal. Calcd for $C_{18}H_{29}NO_2$: C, 74.18; H, 10.03; N, 4.81. Found: C, 74.25; H, 10.09; N, 4.75.

13c: R_f 0.35 (hexane–EtOAc, 2:1); IR (neat) 3300, 910, 730, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 7.0 Hz), 1.25–2.05 (m, 19 H), 2.54 (dd, 1 H, J = 5.0 and 3.0 Hz), 3.83 (d, 1 H, J = 12.0 Hz), 4.08 (d, 1 H, J = 12.0 Hz), 4.80 (br s, 1 H), 7.22–7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.93 (q), 22.01 (t), 22.50 (t), 24.43 (t), 25.17 (t), 25.27 (t), 28.26 (t), 28.80 (t), 33.27 (t), 34.97 (t), 53.53 (t), 72.00 (d), 78.19 (s), 127.91 (d), 128.94 (d), 129.81 (d), 138.83 (s). Anal. Calcd for $C_{19}H_{31}N_2O$: C, 74.71; H, 10.23; N, 4.59. Found: C, 74.76; H, 10.25; N, 4.58.

13d: R_f 0.55 (hexane–EtOAc, 2:1); IR (neat) 3250, 740, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.01 (t, 3 H, J = 7.2 Hz), 1.17 (s, 3 H), 1.25 (s, 3 H), 1.30–1.70 (m, 2 H), 1.90–2.10 (m 2 H), 2.55 (dd, 1 H, J = 7.5 and 4.0 Hz), 3.83 (d, 1 H, J = 13.1 Hz), 4.12 (d, 1 H, J = 13.1 Hz), 4.62 (br s, 1 H), 7.26–7.48 (m, 5 H); ^{13}C NMR-($CDCl_3$) δ 14.40 (q), 23.24 (t), 25.33 (q), 26.00 (t), 28.00 (q), 63.47 (t), 72.60 (s), 73.55 (d), 127.41 (d), 128.43 (d), 129.52 (d), 138.40 (s). Anal. Calcd for $C_{14}H_{23}N_2O$: C, 70.85; H, 9.77; N, 5.90. Found: C, 70.86; H, 9.87; N, 5.91.

13e: mp 98.5–99.5 °C (recrystallized from EtOH); R_f 0.4 (hexane–EtOAc, 5:1); IR (KBr) 3400, 750, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85–1.08 (m, 9 H), 1.15–1.60 (m, 12 H), 2.64 (dd, 1 H, J = 6.0 and 3.3 Hz), 3.80 (d, 1 H, J = 13.1 Hz), 4.10 (d, 1 H, J = 13.1 Hz), 4.65 (br s, 1 H), 7.30–7.49 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.94 (q), 15.04 (q), 16.74 (t), 17.26 (t), 24.20 (t), 25.49 (t), 38.63 (t), 39.00 (t), 63.81 (t), 70.36 (d), 77.60 (s), 127.95 (d), 128.94 (d), 129.84 (d), 138.72 (s). Anal. Calcd for $C_{18}H_{31}NO_2$: C, 73.67; H, 10.65; N, 4.77. Found: C, 73.52; H, 10.73; N, 4.79.

13f: R_f 0.55 (hexane–EtOAc, 2:1); IR (neat) 3350, 960, 740, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3 H, J = 7.0 Hz), 1.05–1.40 (m, 10 H), 2.70 (t, 1 H, J = 7.0 Hz), 3.75 (d, 1 H, J = 12.5 Hz), 4.04 (d, 1 H, J = 12.5 Hz), 4.52 (br s, 1 H), 7.28–7.55 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 5.46 (q), 21.55 (t), 22.33 (t), 33.86 (t), 36.12 (t), 62.98 (t), 67.33 (d), 73.86 (s), 127.83 (d), 128.82 (d), 129.88 (d), 138.65 (s). Anal. Calcd for $C_{15}H_{23}NO_2$: C, 72.25; H, 9.30; N, 5.62. Found: C, 72.33; H, 9.30; N, 5.64.

Reduction of 3 to 4. β-Methoxyamino alcohols **3a, h–l** were reduced to the corresponding β-amino alcohols **4** in 90–95% yields by treatment with LAH (1 mol equiv) in THF (reflux, 6 h). The reduction of **3a** and **3k** were also achieved quantitatively by hydrogenation in the presence of catalytic amounts of PtO_2 under H_2 (1 atm) at room temperature for 10 h. The reduction of **3o** was carried out according to the reported method[15] and **4o** was obtained in 90% yield. The products **4** were purified by Kugelrohr distillation or column chromatography on alumina.

4a: bp 100 °C (2 mmHg) (Kugelrohr); IR (neat) 3360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (d, 3 H, J = 6.6 Hz), 1.10–1.43 (m, 4 H), 1.43–1.75 (m, 9 H), 2.75 (q, 1 H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 17.36 (q), 21.28 (t), 21.56 (t), 25.57 (t), 31.32 (t), 34.67 (t), 54.01 (d), 71.65 (s). Anal. Calcd for $C_8H_{17}NO$: C, 67.09; H, 11.96; N, 9.78. Found: C, 67.18; H, 12.04; N, 9.66.

cis-**4h**: 130 °C (2 mmHg) (Kugelrohr); mp 62–63 °C; IR (KBr) 3350, 3290 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (s, 9 H), 1.05 (d, 3 H, J = 6.6 Hz), 1.18–1.67 (m, 12 H), 2.69 (q, 1 H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 17.61 (q), 22.08 (t), 22.28 (t), 27.32 (q, 3 C), 31.54 (t), 32.13 (s), 35.16 (t), 47.77 (d), 55.05 (d), 71.50 (s). Anal. Calcd for $C_{12}H_{25}NO$: C, 72.30; H, 12.64; N, 7.03. Found: C, 72.35; H, 12.67; N, 6.98.

trans-**4h**: 130 °C (2 mmHg) (Kugelrohr); mp 76–78 °C; IR (KBr) 3400 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (s, 9 H), 1.05 (d, 3 H, J = 6.6 Hz) 1.08–1.97 (m, 12 H), 3.27 (q, 1 H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 16.29 (q), 23.02 (t), 23.64 (t), 27.36 (q, 3 C), 32.01 (s), 35.10 (t), 36.20 (t), 45.94 (d), 47.15 (d), 71.69 (s). Anal. Calcd for $C_{12}H_{25}NO$: C, 72.30; H, 12.64; N, 7.03. Found: C, 72.37; H, 12.72; N, 7.01.

4i: 130 °C (2 mmHg) (Kugelrohr); $[\alpha]^{20}_D$ +11.3° (*c* 2.5, $CHCl_3$); IR (neat) 3300 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85–0.95 (m, 9 H), 0.97–1.12 (m, 1 H), 1.15 (d, 3 H, J = 6.7 Hz), 1.20–1.83 (m, 10 H), 1.92–2.12 (m, 1 H), 3.00 (q, 1 H, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 17.67 (q), 17.82 (q), 20.33 (t), 22.33 (q), 23.17 (q), 25.79 (d), 27.91 (d), 34.71 (t), 42.06 (t), 45.63 (d), 53.20 (d), 75.94 (s). Anal. Calcd for $C_{12}H_{25}NO$: C, 72.30; H, 12.64; N, 7.03. Found: C, 72.43; H, 12.69; N, 7.03.

4j (50:50 mixture of two diastereomers): IR (neat) 3360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (s, 1.5 H), 0.92 (s, 1.5 H), 1.02 (s, 3 H), 1.11 (d, 1.5 H, J = 6.5 Hz), 1.28 (d, 1.5 H, J = 6.7 Hz), 0.90–2.10 (m, 21 H), 2.15–2.40 (m, 2 H), 2.94 (q, 0.5 H, J = 6.7 Hz), 3.18 (q, 0.5 H, J = 6.5 Hz), 3.42–3.62 (m, 1 H), 5.33–5.42 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ .14.73 (q), 15.46 (q), 19.16 (q), 19.85 (q), 20.84 (t), 21.06 (q), 23.42 (t), 24.01 (t), 31.43 (t), 31.61 (t), 31.69 (t), 31.88 (t), 32.52 (d), 32.61 (d), 33.62 (t), 33.72 (t), 34.70 (t), 36.39 (t), 37.12 (t), 42.10 (t), 46.65 (s), 46.97 (s), 48.92 (d), 49.83 (d), 51.30 (d), 51.92 (d), 54.51 (d), 71.59 (d), 83.30 (s), 84.75 (s), 121.51 (d), 140.94 (s). Anal. Calcd for $C_{21}H_{35}NO_2$: C, 75.63; H, 10.58; N, 4.20. Found: C, 75.68; H, 10.60; N, 4.16.

4k: 130 °C (2 mmHg) (Kugelrohr); IR (neat) 3400 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (t, 3 H, J = 6.9 Hz), 1.08–1.80 (m, 13 H) 1.80–2.10 (m, 4 H) 2.45 (dd, 1 H, J = 10.5, 1.7 Hz); ^{13}C NMR ($CDCl_3$) δ 13.70 (q), 20.08 (t), 21.24 (t), 21.60 (t), 25.72 (t), 31.04 (t), 33.51 (t), 34.55 (t), 59.24 (d), 71.98 (s). Anal. Calcd for $C_{10}H_{21}NO$: C, 70.12; H, 12.36; N, 8.18. Found: C, 70.18; H, 12.44; N, 8.06.

4l: 150 °C (1 mmHg) (Kugelrohr); IR (neat) 3400 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, 3 H, J = 7.0 Hz), 1.10–2.10 (m, 25 H) 2.40–2.48 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.74 (q), 21.36 (t), 21.75 (t), 22.34 (t), 25.85 (t), 27.17 (t), 29.01 (t), 29.40 (t), 31.21 (t), 31.56 (t, 2 C), 34.73 (t), 59.50 (d), 71.87 (s). Anal. Calcd for $C_{14}H_{29}NO$: C, 73.95; H, 12.86; N, 6.16. Found: C, 74.05; H, 12.98; N, 6.01.

4o: 150 °C (1 mmHg) (Kugelrohr); mp 61–62 °C; IR (KBr) 3360, 3300, 3290 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.70–2.40 (m, 23 H); ^{13}C NMR ($CDCl_3$) δ 21.57 (t, 2 C), 21.75 (t, 2 C), 25.61 (t), 25.79 (t), 30.34 (t, 2 C), 30.67 (t, 2 C), 56.47 (s), 73.91 (s). Anal. Calcd for $C_{12}H_{23}NO$: C, 73.04; H, 11.75; N, 7.10. Found: C, 73.13; H, 11.78; N, 7.02.

Transformation of 5 to 4h. Each isomer of **5**[5] (1 mmol) was treated with *O*-methylhydroxylamine hydrochloride (1.1 mmol) in pyridine (5 mL) at room temperature for 12 h. The obtained oxime was reduced by LAH (1 mmol) in refluxing THF (5 mL) for 8 h. The products **4h** were consistent with the compounds prepared from **3h** by the method described above.

Transformation of 7 to epimer of 4j was achieved by the same method as above.

Epimer of 4j: mp 212–214 °C; IR (KBr) 3400, 1565 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.75 (s, 3 H), 1.02 (s, 3 H), 1.05 (d, 3 H, J = 6.6 Hz), 0.90–2.20 (m, 21 H), 2.20–2.40 (m, 2 H), 3.16 (q, 1 H, J = 6.6 Hz), 3.45–3.65 (m, 1 H), 5.33–5.42 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.56 (q), 18.00 (q), 19.19 (q), 20.41 (t), 23.42 (t), 31.27 (t), 31.44 (t), 31.65 (t), 31.79 (d), 36.31 (s), 37.07 (t), 37.87 (t), 42.12 (t), 45.69 (s), 49.45 (d), 51.46 (d), 51.94 (d), 71.60 (d), 84.28 (s), 121.76 (d), 140.84 (s). Anal. Calcd for $C_{21}H_{35}NO_2$: C, 75.63; H, 10.58; N, 4.20. Found: C, 75.70; H, 10.65; N, 4.02.

Synthesis of Oxazoline 6. A mixture of **4i** (1 mmol), ethyl acetimidate hydrochloride (1.2 mmol), and Et_3N (1.2 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 12 h. After the usual workup, the product **6** was isolated by column chromatography on silica gel. NOE enhancement was observed between a doublet at δ 1.30 and a multiplet at δ 1.90–2.12 in ^1H NMR.

6: R_f 0.25 (hexane–EtOAc); IR (neat) 1670, 930, 915 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.82 (d, 3 H, J = 6.8 Hz), 0.87 (d, 3 H, J = 7.0 Hz), 0.89 (d, 3 H, J = 6.3 Hz), 1.04–1.22 (m, 3 H), 1.30 (d, 3 H, J = 7.4 Hz), 1.35–1.84 (m, 5 H), 1.96 (d, 3 H, J = 1.8 Hz), 1.90–2.12 (m, 1 H), 3.62–3.79 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.25 (q), 14.45 (q), 18.11 (q), 21.89 (q and t, 2 C), 22.40 (q), 26.37 (d), 29.36 (d), 34.02 (t), 45.19 (d), 48.28 (t), 72.17 (d), 91.25 (s), 164.35 (s). Anal. Calcd for $C_{14}H_{25}NO$: C, 73.04; H, 11.75; N, 7.10. Found: C, 73.13; H, 11.78; N, 7.02.

Synthesis of 9. A mixture of **4i** (1 mmol), methyl iodide (2.2 mmol), and K_2CO_3 (2.2 mmol) in EtOH (5 mL) was stirred at room temperature for 2 days. After evaporation of EtOH, the product **9** was isolated by column chromatography on silica gel.

9: R_f 0.6 (EtOAc); $[\alpha]^{20}_D$ −15.9° (*c* 1.5, $CHCl_3$); IR (neat) 3500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (d, 6 H, J = 6.8 Hz), 0.91 (d, 3 H, J = 7.2 Hz), 0.99 (d, 3 H, J = 7.2 Hz), 1.40–1.80 (m, 9 H), 1.95–2.15 (m, 1 H), 2.28 (s, 6 H), 2.69 (q, 1 H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 6.35 (q), 18.07 (q), 20.91 (t), 22.55 (q), 23.17 (q), 25.64 (d), 28.26 (d), 34.85 (t), 43.69 (q, 2 C), 44.45 (t), 45.19 (d), 65.13 (d), 77.58 (s). Anal. Calcd for $C_{14}H_{29}NO$: C, 73.95; H, 12.86; N, 6.16. Found: C, 73.98; H, 12.90; N, 6.09.

General Procedure for Enantioselective Addition of Diethylzinc to Aldehyde. A mixture of diethylzinc (1 M hexane solution, 0.32 mL) and the chiral β-amino alcohol **9** (0.16 mmol) in toluene (5 mL) was refluxed for 30 min. Diethylzinc (1 M hexane solution, 4.8 mL) and aldehyde (3.2 mmol) were added to the mixture at 0 °C. The mixture was stirred for 6–12 h at this temperature. After 1 N HCl (20 mL) was added, the mixture was extracted with CH_2Cl_2. The product, secondary alcohol, was isolated by PTLC (silica gel, hexane–EtOAc).

Keto *O*-Methyl Oxime was obtained by treatment of the corresponding δ- or ε-keto aldehyde with *O*-methylhydroxylamine hydrochloride (1 equiv) in pyridine at room temperature for 12 h. Keto aldehyde was prepared by the reduction of ketal of δ- or ε-keto ester with DIBAL followed by acid hydrolysis of the ketal (for the synthesis of **14**, **17**, or **21**). The other δ-keto aldehyde was synthesized by 1,4-addition of enamine[25] (for the synthesis of **19** or **23**) or β-keto ester[26] (for the synthesis of **25**, **27**, or **31**) to acrolein. For the synthesis of **33**, δ-keto aldehyde was prepared by the alkylation of ethyl 2-methylacetoacetate with 2-(2-bromoethyl)-1,3-dioxolane and subsequent acid hydrolysis. ε-Keto *O*-methyl oxime **29** was obtained by the alkylation of ethyl 2-cyclohexanonecarboxylate with 4-bromobutyraldehyde *O*-methyl oxime. All of keto *O*-methyl oximes were isolated by column chromatography on silica gel.

14a: R_f 0.5 (hexane–EtOAc, 2:1); IR (neat) 1710, 870 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.67–1.86 (m, 2 H), 2.15 (s, 3 H), 2.17–2.38 (m, 2 H), 2.43–2.52 (m, 2 H), 3.82 (s, 1.65 H), 3.86 (s, 1.35 H), 6.62 (t, 0.45 H, J = 5.6 Hz), 7.34 (t, 0.55 H, J = 6.1 Hz). Anal. Calcd for $C_7H_{13}NO_2$: C, 58.72; H, 9.15; N, 9.78. Found: C, 58.86; H, 9.20; N, 9.75.

14b: R_f 0.6 (hexane–EtOAc, 2:1); IR (neat) 1710, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38–1.75 (m, 4 H), 2.14 (s, 3 H), 2.18–2.38 (m, 2 H), 2.46 (t, 2 H, J = 6.2 Hz), 3.81 (s, 1.65 H), 3.86 (s, 1.35 H), 6.62 (t, 0.45 H, J = 5.5 Hz), 7.36 (t, 0.55 H, J = 6.1 Hz). Anal. Calcd for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 8.91. Found: C, 61.18; H, 9.62; N, 8.85.

(25) Allan, R. D.; Cordiner, B. G.; Wells, R. J. *Tetrahedron Lett.* **1968**, 6055.

(26) Cope, A. C.; Synerholm, M. E. *J. Am. Chem. Soc.* **1950**, *72*, 5288.

17: R_f 0.4 (hexane–EtOAc, 2:1); IR (neat) 1730, 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.22–2.46 (m, 11 H), 3.81 (s, 1.65 H), 3.87 (s, 1.35 H), 6.63 (t, 0.45 H, J = 5.6 Hz), 7.36 (t, 0.55 H, J = 6.1 Hz). Anal. Calcd for $C_9H_{15}NO_2$: C, 63.88; H, 8.94; N, 8.28. Found: C, 63.94; H, 9.02; N, 8.22.

19: R_f 0.3 (hexane–EtOAc, 5:1); IR (neat) 1710, 1630, 870, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25–1.50 (m, 2 H), 1.50–2.50 (m, 11 H), 3.81 (s, 1.65 H), 3.85 (s, 1.35 H), 6.63 (t, 0.45 H, J = 5.5 Hz), 7.36 (t, 0.55 H, J = 6.1 Hz). Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.60; H, 9.38; N, 7.51.

21: R_f 0.5 (hexane–EtOAc, 2:1); IR (neat) 1710, 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 3 H), 1.52–2.60 (m, 12 H), 3.82 (s, 1.65 H), 3.86 (s, 1.35 H), 6.64 (t, 0.45 H, J = 5.6 Hz), 7.38 (t, 0.55 H, J = 6.1 Hz). Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N, 7.10. Found: C, 67.08; H, 9.79; N, 7.19.

23: R_f 0.6 (hexane–EtOAc, 5:1); IR (neat) 1705, 880 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10–2.00 (m, 19 H), 2.08–2.42 (m, 3 H), 2.50–2.77 (m, 3 H), 3.81 (s, 1.65 H), 3.85 (s, 1.35 H), 6.61 (t, 0.45 H, J = 5.5 Hz), 7.33 (t, 0.55 H, J = 6.0 Hz). Anal. Calcd for $C_{16}H_{29}NO_2$: C, 71.86; H, 10.93; N, 5.24. Found: C, 71.87; H, 10.90; N, 5.10.

25: R_f 0.25 (hexane–EtOAc, 5:1); IR (neat) 1740, 1720, 855 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (t, 3 H, J = 7.0 Hz), 1.42–2.61 (m, 10 H), 3.80 (s, 1.65 H), 3.86 (s, 1.35 H), 4.17 (q, 2 H, J = 7.1 Hz), 6.62 (t, 0.45 H, J = 5.6 Hz), 7.34 (t, 0.55 H, J = 6.1 Hz). Anal. Calcd for $C_{12}H_{19}NO_4$: C, 59.73; H, 7.94; N, 5.81. Found: C, 59.85; H, 8.00; N, 5.76.

27: R_f 0.35 (hexane–EtOAc, 5:1); IR (neat) 1710, 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.27 (t, 3 H, J = 7.0 Hz), 1.36–1.83 (m, 5 H), 1.92–2.35 (m, 4 H), 2.40–2.60 (m, 3 H), 3.80 (s, 1.65 H), 3.85 (s, 1.35 H), 4.22 (q, 2 H, J = 7.0 Hz), 6.62 (t, 0.45 H, J = 5.5 Hz), 7.36 (t, 0.55 H, J = 6.0 Hz). Anal. Calcd for $C_{13}H_{21}NO_4$: C, 61.15; H, 8.29; N, 5.49. Found: C, 61.18; H, 8.30; N, 5.41.

29: R_f 0.35 (hexane–EtOAc, 5:1); IR (neat) 1705, 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.27 (t, 3 H, J = 7.0 Hz), 1.33–2.10 (m, 9 H), 2.12–2.36 (m, 2 H), 2.40–2.60 (m, 3 H), 3.81 (s, 1.65 H), 3.86 (s, 1.35 H), 4.21 (q, 2 H, J = 7.0 Hz), 6.62 (t, 0.45 H, J = 5.4 Hz), 7.35 (t, 0.55 H, J = 6.2 Hz). Anal. Calcd for $C_{14}H_{23}NO_4$: C, 62.43; H, 8.61; N, 5.20. Found: C, 62.45; H, 8.62; N, 5.15.

31: R_f 0.3 (hexane–EtOAc, 2:1); IR (neat) 1710, 860 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.16–2.39 (m, 12 H), 1.27 (t, 3 H, J = 7.0 Hz), 2.40–2.76 (m, 2 H), 3.80 (s, 1.65 H), 3.85 (s, 1.35 H), 4.20 (q, 2 H, J = 7.0 Hz), 6.62 (t, 0.45 H, J = 5.3 Hz), 7.35 (t, 0.55 H, J = 5.7 Hz). Anal. Calcd for $C_{14}H_{23}NO_4$: C, 62.43; H, 8.61; N, 5.20. Found: C, 62.49; H, 8.63; N, 5.12.

33: R_f 0.3 (hexane–EtOAc, 5:1); IR (neat) 1710, 855 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.27 (t, 3 H, J = 7.0 Hz), 1.37 (s, 3 H), 1.80–2.30 (m, 4 H), 2.16 (s, 3 H), 3.81 (s, 1.65 H), 3.86 (s, 1.35 H), 4.21 (q, 2 H, J = 7.0 Hz), 6.63 (t, 0.45 H, J = 5.3 Hz), 7.35 (q, 0.55 H, J = 5.5 Hz). Anal. Calcd for $C_{11}H_{19}NO_4$: C, 57.62; H, 8.35; N, 6.11. Found: C, 57.68; H, 8.36; N, 6.03.

Electroreduction of keto *O*-methyl oxime was carried out under the same conditions as above, and the electricity was passed until almost all of the keto *O*-methyl oxime was consumed (5~6 F/mol). Electroreduction of β-keto ester **25**, **27**, **29**, **31**, or **33** was performed without using the diaphragm. The products were isolated by column chromatography on silica gel.

***trans*-15a**: R_f 0.3 (hexane–EtOAc, 1:1); IR (neat) 3360 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 3 H), 1.52–2.02 (m, 6 H), 2.40 (br s, 1 H, OH), 3.43 (t, 1 H, J = 9.0 Hz), 3.55 (s, 3 H), 5.50 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 19.28 (t), 21.82 (q), 26.64 (t), 38.78 (t), 61.42 (q), 69.03 (d), 80.06 (s). Anal. Calcd for $C_7H_{15}NO_2$: C, 57.90; H, 10.41; N, 9.65. Found: C, 57.95; H, 10.37; N, 9.54.

***trans*-15b**: R_f 0.2 (hexane–EtOAc, 2:1); IR (neat) 3400 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 3 H), 1.20–1.86 (8 H), 2.95 (dd, 1 H, J = 11.6 and 4.0 Hz), 3.24 (br s, 1 H, OH), 3.58 (s, 3 H), 5.50 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 20.15 (q), 22.88 (t), 24.41 (t), 27.21 (t), 39.73 (t), 61.71 (q), 66.45 (d), 72.78 (s). Anal. Calcd for $C_8H_{17}NO_2$: C, 60.34; H, 10.76; N, 8.80. Found: C, 60.35; H, 10.83; N, 8.67

***cis*-15b**: R_f 0.5 (hexane–EtOAc, 2:1); IR (neat) 3430 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (s, 3 H), 1.21–1.74 (m, 8 H), 2.60 (br s, 1 H, OH), 2.67 (dd, 1 H, J = 9.6 and 4.8 Hz), 3.46 (s, 3 H), 5.30 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 21.17 (t), 24.08 (t), 25.86 (t), 28.19 (q), 37.99 (t), 62.00 (q), 64.95 (d), 70.74 (s). Anal. Calcd for $C_8H_{17}NO_2$: C, 60.34; H,10.76; N, 8.80. Found: C, 60.41; H, 10.78; N, 8.65.

18: R_f 0.4 (hexane–EtOAc, 1:1); IR (neat) 3400 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.55–2.37 (m, 12 H), 3.54 (dd, 1 H, J = 11.7 and 6.1 Hz), 3.56 (s, 3 H), 5.60 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.43 (t), 27.31 (t), 27.76 (t), 34.59 (t), 36.24 (t), 49.85 (t), 61.53 (q), 70.02 (d), 91.78 (s). Anal. Calcd for $C_9H_{17}NO_2$: C, 63.13; H, 10.00; N, 8.18. Found: C, 63.17; H, 10.03; N, 8.08.

***trans*-20** (major): R_f 0.25 (hexane–EtOAc, 2:1); IR (neat) 3430 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.02–2.13 (m, 13 H), 2.48 (br s, 1 H, OH), 3.47–3.59 (m, 1 H), 3.54 (s, 3 H), 5.40 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 19.93 (t), 20.29 (t), 22.19 (t), 23.23 (t, 2 C), 27.35 (t), 41.80 (d), 61.24 (q), 69.21 (d), 78.12 (s). Anal. Calcd for $C_{10}H_{19}NO_2$: C, 64.83; H, 10.34; N, 7.56. Found: C, 64.85; H, 10.37; N, 7.47.

***cis*-20** (minor): R_f 0.3 (hexane–EtOAc, 2:1); IR (neat) 3430 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10–1.72 (m, 9 H), 1.80–2.10 (m, 4 H), 3.05 (br s, 1 H, OH), 3.48 (dd, 1 H, J = 9.2 and 7.1 Hz), 3.54 (s, 3 H), 5.60 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 22.73 (t), 23.90 (t), 25.46 (t), 26.92 (t), 28.88 (t), 34.57 (t), 45.92 (d), 61.82 (q), 63.13 (d), 78.64 (s). Anal. Calcd for $C_{10}H_{19}NO_2$: C, 64.83; H, 10.34; N, 7.56. Found: C, 64.88; H, 10.44; N, 7.51.

22: R_f 0.45 (hexane–EtOAc, 2:1); IR (neat) 3410 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.01 (s, 3 H), 1.03–2.33 (m, 13 H), 3.53 (s, 3 H), 3.82 (t, 1 H, J = 9.8 Hz), 5.50 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 20.52 (t), 21.36 (t), 21.86 (t), 24.73 (q), 29.06 (t), 29.79 (t), 32.78 (t), 42.75 (s), 61.42 (q), 66.99 (d), 79.40 (s). Anal. Calcd for $C_{11}H_{21}NO_2$: C, 66.29; H,10.62; N, 7.03. Found: C, 66.30; H, 10.68; N, 7.00.

24 (70:30 mixture of two diastereomers): R_f 0.25 (hexane–EtOAc, 2:1); IR (neat) 3430 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10–1.70 (m, 22 H), 1.80–2.10 (m, 4 H), 3.25–3.45 (m, 1 H), 3.51 (s, 0.9 H), 3.54 (s, 2.1 H), 5.53 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 20.54 (t), 20.85 (t), 22.83 (t), 23.15 (t), 23.27 (t), 23.71 (t), 23.87 (t), 24.66 (t), 25.09 (t), 25.24 (t), 25.43 (t), 26.20 (t), 26.43 (t), 26.66 (t), 27.12 (t), 27.21 (t), 27.80 (t), 28.09 (t), 28.71 (t), 34.83 (t), 41.40 (d), 46.94 (d), 61.35 (q), 70.77 (d), 72.87 (d), 82.68 (s), 85.05 (s). Anal. Calcd for $C_{16}H_{31}NO_2$: C, 71.32; H, 11.60; N, 5.20. Found: C, 71.44; H, 11.78; N, 5.03.

26: R_f 0.4 (hexane–EtOAc, 1:1); IR (neat) 3450, 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.28 (t, 3 H, J = 7.2 Hz), 1.32–2.55 (m, 11 H), 3.51–3.63 (m, 1 H), 3.55 (s, 3 H), 4.18 (q, 2 H, J = 7.2 Hz), 5.83 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 13.85 (q), 24.52 (t), 26.32 (t), 32.49 (t), 35.51 (t), 37.29 (t), 60.58 (t), 61.42 (s), 61.85 (q), 69.42 (d), 92.31 (s), 175.97 (s). Anal. Calcd for $C_{12}H_{21}NO_4$: C, 59.24; H, 8.70; N, 5.76. Found: C, 59.24; H, 8.73; N, 5.72.

28: R_f 0.35 (hexane–EtOAc, 2:1); IR (neat) 3450, 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.28 (t, 3 H, J = 7.2 Hz), 1.35–1.70 (m, 8 H), 1.80–2.18 (m, 4 H), 3.53 (s, 3 H), 3.54–3.65 (m, 1 H), 4.15 (br s, 1 H, OH), 4.18 (q, 2 H, J = 7.2 Hz), 5.77 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 13.67 (q), 19.89 (t), 20.48 (t), 23.78 (t), 25.71 (t), 28.01 (t), 28.67 (t), 53.52 (s), 60.69 (t), 61.57 (q), 67.76 (d), 78.73 (s), 178.43 (s). Anal. Calcd for $C_{13}H_{23}NO_4$: C, 60.68; H, 9.01; N, 5.44. Found: C, 60.75; H, 9.10; N, 5.29.

30 (major): R_f 0.35 (hexane–EtOAc, 5:1); IR (neat) 3450, 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (t, 3 H, J = 7.1 Hz), 1.30–2.10 (m, 13 H), 2.20–2.50 (m, 1 H), 3.08 (dd, 1 H, J = 11.4 and 4.5 Hz), 3.52 (s, 3 H), 4.10–4.28 (m, 2 H), 5.00 (br s, 1 H, OH), 6.33 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 13.78 (q), 19.86 (t), 20.19 (t), 21.39 (t), 26.12 (t), 27.50 (t), 29.36 (t), 31.80 (t), 50.69 (s), 60.80 (t), 62.59 (q), 65.69 (d), 73.76 (s), 179.42 (s). Anal. Calcd for $C_{14}H_{25}NO_4$: C, 61.96; H, 9.29; N, 5.16. Found: C, 62.04; H, 9.33; N, 5.10.

30 (minor): R_f 0.5 (hexane–EtOAc, 5:1); IR (neat) 3480, 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.28 (t, 3 H, J = 7.3 Hz), 1.36–2.10 (m, 13 H), 2.25–2.50 (m, 1 H), 3.22–3.38 (m, 1 H), 3.49 (s, 3 H), 4.18 (q, 2 H, J = 7.3 Hz), 4.60 (br s, 1 H, OH), 5.70 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 13.79 (q), 19.53 (t), 23.03 (t), 23.24 (t), 26.04 (t), 29.53 (t), 31.39 (t), 33.00 (t), 51.85 (s), 56.98 (d), 60.63 (t), 61.46 (q), 73.62 (s), 178.93 (s). Anal. Calcd for $C_{14}H_{25}NO_4$: C, 61.96; H, 9.29; N, 5.16. Found: C, 61.98; H, 9.36; N, 5.06.

32 (major): R_f 0.5 (hexane–EtOAc, 2:1); IR (neat) 3450, 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.29 (t, 3 H, J = 7.1 Hz), 1.36–2.35 (m, 15 H), 3.53 (s, 3 H), 3.65 (dd, 1 H, J = 9.9 and 7.4 Hz), 4.19 (q, 2 H, J = 7.1 Hz), 5.68 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 13.63 (q), 21.30 (t), 24.48 (t), 24.84 (t), 30.12 (t), 31.65 (t), 34.34 (t), 36.70 (t), 58.44 (s), 60.36 (t), 61.42 (q), 70.68 (d), 83.99 (s), 178.02 (s). Anal. Calcd for $C_{14}H_{25}NO_4$: C, 61.96; H, 9.29; N, 5.16. Found: C, 62.02; H, 9.35; N, 5.11.

32 (minor): R_f 0.4 (hexane–EtOAc, 2:1); IR (neat) 3450, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (t, 3 H, J = 7.1 Hz), 1.36–2.40 (m, 15 H), 3.42–3.55 (m, 1 H), 3.49 (s, 3 H), 4.08–4.25 (m, 2 H), 5.50 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 13.85 (q), 23.93 (t), 25.64 (t), 25.86 (t), 28.09 (t), 28.29 (t), 33.77 (t), 36.09 (t), 60.00 (s), 60.33 (t), 60.80 (q), 73.40 (d), 85.03 (s), 176.96 (s). Anal. Calcd for $C_{14}H_{25}NO_4$: C, 61.96; H, 9.29; N, 5.16. Found: C, 62.05; H, 9.28; N, 5.14.

34a: R_f 0.25 (hexane–EtOAc, 2:1); IR (neat) 3480, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12–1.40 (m, 1 H), 1.24 (s, 3 H), 1.27 (s, 3 H), 1.28 (t, 3 H, J = 7.3 Hz), 1.43–1.64 (m, 1 H), 2.00–2.18 (m, 1 H), 2.23–2.39 (m, 1 H), 3.42 (br s, 1 H, OH), 3.53 (s, 3 H), 3.48–3.60 (m, 1 H), 4.18 (q, 2 H, J = 7.3 Hz), 5.60 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 13.81 (q), 18.14 (q), 19.42 (q), 24.95 (t), 32.16 (t), 54.69 (s), 60.54 (t), 61.53 (q), 68.96 (d), 82.13 (s), 177.53 (s). Anal. Calcd for $C_{11}H_{21}NO_4$: C, 57.12; H, 9.15; N, 6.06. Found: C, 57.23; H, 9.12; N, 6.01.

34b: R_f 0.2 (hexane–EtOAc, 2:1); IR (neat) 3480, 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16 (s, 3 H), 1.18–1.38 (m, 1 H), 1.29 (t, 3 H, J = 7.1 Hz), 1.32 (s, 3 H), 1.50–1.65 (m, 1 H), 1.90–2.12 (m, 1 H), 2.20–2.40 (m, 1 H), 2.49 (br s, 1 H, OH), 3.55 (s, 3 H), 3.69 (t, 1 H, J = 9.2 Hz), 4.20 (q, 2 H, J = 7.1 Hz), 5.65 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 13.96 (q), 19.17 (q), 20.51 (q), 22.59 (t), 29.36 (t), 54.70 (s), 60.40 (t), 61.68 (q), 65.97 (d), 80.17 (s), 176.04 (s). Anal. Calcd for $C_{11}H_{21}NO_4$: C, 57.12; H, 9.15; N, 6.06. Found: C, 57.28; H, 9.20; N, 5.94.

34c: R_f 0.4 (hexane–EtOAc, 2:1); IR (neat) 3430, 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12–1.40 (m, 1 H), 1.23 (s, 3 H), 1.27 (s, 3 H), 1.27 (t, 3 H, J = 7.2 Hz), 1.60–1.82 (m, 1 H), 1.93–2.20 (m, 2 H), 3.38 (br s, 1 H, OH), 3.55 (s, 3 H), 3.64 (dd, 1 H, J = 9.4 and 8.0 Hz), 4.13 (q, 2 H, J = 7.2 Hz), 5.70 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 13.85 (q), 17.24 (q), 22.58 (q), 25.43 (t), 33.07 (t), 57.35 (s), 60.36 (t), 61.79 (q), 67.65 (d), 79.30 (s), 176.80 (s). Anal. Calcd for $C_{11}H_{21}NO_4$: C, 57.12; H, 9.15; N, 6.06. Found: C, 57.23; H, 9.21; N, 5.99.

Transformation of 35 to 20. A solution of **35**[5] (1 mmol) and *O*-methylhydroxylamine (1.2 mmol) in pyridine (5 mL) was stirred at room temperature for 12 h. After the usual workup, the crude oxime was treated with $NaCNBH_3$ (1.2 mmol) in methanol (5 mL) at pH 3–4 for 5 days.[27] Each isomer of **20** was isolated by column chromatography on silica gel. Transformation of **38**[11] to **30** was achieved by the same method.

Synthesis of Oxazoline 37. A suspension of *cis*-**20** (1 mmol) and LAH (1 mmol) in THF (5 mL) was refluxed for 8 h. After the usual workup, the crude **36b** was obtained. **36b**: IR (neat) 3450 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10–2.20 (m, 16 H), 3.27 (dd, 1H, J = 8.5 and 7.3 Hz).

A solution of **36b**, ethyl acetimidate hydrochloride (1.2 mmol), and Et_3N (1.2 mmol) in CH_2Cl_2 (5 mL) was refluxed for 5 h. The product **37** was isolated by column chromatography on silica gel. **37**: R_f 0.3 (hexane–EtOAc, 2:1); IR (neat) 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00–1.40 (m, 4 H), 1.55–2.15 (m, 9 H), 1.94 (d, 3 H, J = 1.0 Hz), 3.99 (d, 1 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 13.88 (q), 22.66 (t), 23.94 (t), 28.95 (t), 29.03 (t), 31.72 (t), 32.25 (t), 43.99 (d), 73.14 (d), 96.14 (s), 163.87 (s). Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.85; H, 9.61; N, 7.73.

(27) Borch, R. F.; Bernstein, M. D.; Durst, H. D. *J. Am Chem. Soc.* **1971**, *93*, 2897.