Synthesis of Enantiopure *syn*-β-Amino Alcohols. A Simple Case of Chelation-Controlled Additions of Diethylzinc to α-(Dibenzylamino) Aldehydes†

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Enantiomerically pure *syn*-2-amino alcohols **6** are prepared by addition of diethylzinc to chiral α-(dibenzylamino) aldehydes **4**. The addition is highly stereoselective, leading to *syn*-2-(dibenzylamino) alcohols **5** with excellent diastereomeric excesses (76−98%). Debenzylation of **5** by hydrogenolysis on Pearlman's catalyst yields quantitatively the amino alcohols **6**.

Introduction

N-Protected amino aldehydes have been widely used as chiral building blocks for a wide variety of compounds.[1] Most of the reactions on this class of compounds are directed to the synthesis of biologically important β-amino alcohols, and it is well known that, contrary to α-alkoxy derivatives, additions of organometallics to *N*,*N*-dibenzylamino aldehydes lead to *anti* adducts.[2]

This behavior is explained on the basis of a nonchelated transition state and has been confirmed thoroughly,[3] but "inducing the opposite diastereoselectivity in favour of chelation control remains a challenge".[5] Only partial success has been achieved by using a combination of less sterically demanding protective groups on the nitrogen or monoprotected aminoaldehydes[4] and cuprates,[2] manganese reagents[5] or chromium derivatives[6] as nucleophiles; allyltin[7] and allylsilanes[8] in the presence of different Lewis acids have also been used. On the other hand, phenyl or vinyl additions on aluminoxy acetals derived from α-amino esters lead to the chelation control products.[9]

Organozinc reagents have also been used as nucleophiles in diastereoselective additions to chiral amino aldehydes, but always associated to Lewis acids[2] or to amino alcohols acting as a catalyst;[10] in both cases, the reactions proceed with modest diastereoselectivity. Quite surprisingly, there are few precedents in the literature on the reactivity of dialkylzincs toward α-(*N*,*N*-dibenzylamino) aldehydes,[11] probably as a consequence of the very low reactivity of these organometallics.[12] It is well known that the nucleophilicity of diethylzinc is increased by coordination to donor ligands, and this is the basis of the catalyzed enantioselective additions to carbonyl compounds.[13]

On the basis of a previous work on the enantioselective ethylation of aldehydes,[14] we decided to explore the unreported reactivity of chiral α-(*N*,*N*-dibenzylamino) aldehydes with diethylzinc without any additional reagent, in the hope that (a) the donor properties of the dibenzylamino group present at the substrates might be sufficient to enhance the reactivity of diethylzinc[15] and (b) the diastereoselection might be dictated by the stereochemistry at the starting amino aldehyde.[16]

Results and Discussion

Starting α-amino aldehydes **4a**−**f** were prepared by Swern oxidation[17] of 2-(dibenzylamino) alcohols **3a**−**f** obtained by a modified reported procedure[2] as summarized in Scheme 1. To this end, natural α-amino acids were reduced by sodium borohydride−boron trifluoride in THF at reflux[18] to 2-amino alcohols **1b**−**e**, which after treatment with benzyl bromide and potassium carbonate in acetonitrile at reflux were transformed into 2-(dibenzylamino) alcohols **3b**−**e** in excellent yields.

An alternative route was used to prepare **3a** and **3f**; *N*,*N*-dibenzylalaninol was obtained from alanine methyl

†Dedicated to Prof. William S. Johnson. In Memoriam.

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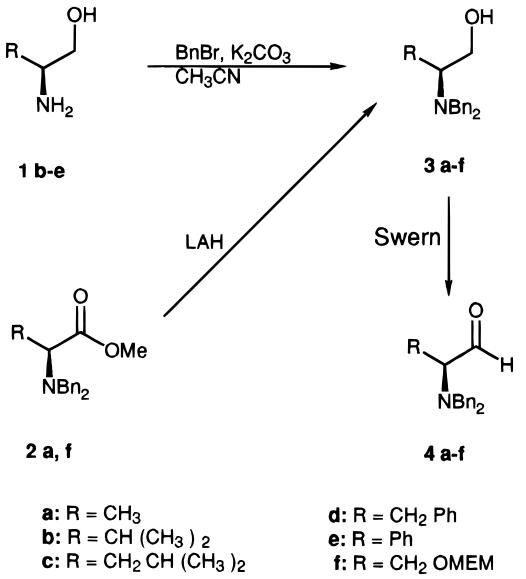
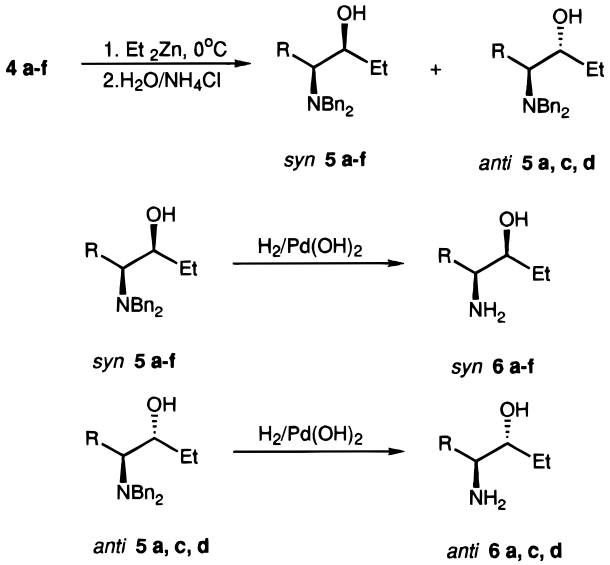
Scheme 1



Scheme 2



ester by sequential dibenzylation with benzyl bromide in the presence of potassium carbonate and lithium aluminum hydride reduction in boiling THF, whereas **3f** was prepared in the same way by LAH reduction of methyl *N*,*N*-dibenzylserinate where the hydroxyl group was previously protected as its MEM derivative by reaction with MEMCl in the presence of *N*,*N*-diisopropylethylamine.[19]

Treatment of the *N*,*N*-dibenzylamino aldehydes **4a**−**f** with 2 equiv of Et_2Zn in toluene at 0 °C gave, after hydrolysis, the corresponding *syn* amino alcohols **5a**−**f** in good chemical yields and excellent stereoselectivity (Scheme 2 and Table 1). The degree of stereoselection was moderately affected by the size of the substituent at the stereogenic center in the α-amino aldehyde. The molar ratio of reagents does not modify the stereoselectivity but decreases the chemical yield as shown in the reaction of **4c** with 1.1 equiv of Et_2Zn (entry 4 in Table 1). The sense and degree of stereoselection are not affected by the presence of an additional donor heteroatom in the dibenzylamino aldehyde **4f** (entry 8 in Table 1).

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Table 1. Stereoselective Addition of Et_2Zn to *N*,*N*-Dibenzylamino Aldehydes 4a−f

entry	aldehyde	time (h)	yield[a] (%)	5	syn/anti[b]
1	**4a**	16	95	**5a**	88:12
2	**4b**	36	64	**5b**	>99:<1
3	**4c**	24	62	**5c**	92:8
4	**4c**	24	48[c]	**5c**	92:8
5	**4d**	17	70	**5d**	90:10
6	**4e**	19	65	**5e**	>99:<1
7	*ent*-**4e**	15	68	*ent*-**5e**	>99:<1
8	**4f**	24	70	**5f**	95:5

[a] Numbers reflect the combined yield of diastereomers after purification by flash chromatography. [b] Determined by ^{1}H-NMR analysis of the crude of reactions. [c] This reaction was carried out with 1 equiv of Et_2Zn, and in the final mixture 25% of **4c** was recovered unchanged.

Scheme 3

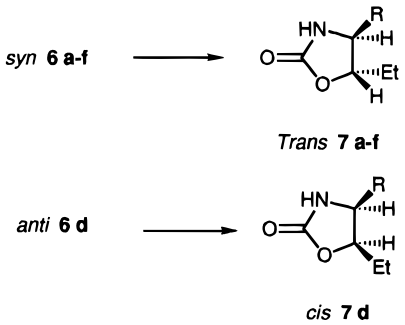

Table 2. Chemical Shifts and Coupling Constants for 4-H and 5-H in Oxazolidinones 7

oxazolidinone	δ_{4-H} (ppm)	δ_{5-H} (ppm)	$J_{4,5}$ (Hz)
trans-**7a**	3.59	4.04	6.3
trans-**7b**	3.19	4.21	5.0
trans-**7d**	3.67	4.24	5.3
cis-**7d**	3.97	4.58	7.3
trans-**7e**	4.51	4.27	6.9
ent-trans-**7e**	4.51	4.27	6.9
trans-**7f**	3.39	4.18	5.1

After separation by flash chromatography[20] *syn*-**5a**−**f** and *anti*-**5a,c,d** were debenzylated to the final β-amino alcohols *syn*-**6a**−**f** and *anti*-**6a,c,d** by hydrogenolysis[21] on Pearlman's catalyst in excellent chemical yields.

Assignment of the absolute stereochemistry of amino alcohols **6** was made by ^{1}H NMR spectroscopy and by comparison of the specific rotations of their derivatives. Thus, the amino alcohols *syn*-**6a**−**f** and *ent-syn*-**6e** were transformed into the oxazolidinones *trans*-**7a**−**f** and *ent-trans*-**7e** and *anti*-**6d** into *cis*-**7d**, respectively, by treatment with a solution of phosgene in toluene.[22] The signs and values of the specific rotation for compounds *trans*-**7a**−**d** are coincident with those previously described,[23] whereas the vicinal coupling constants between the ring protons in *trans* oxazolidinones (5.0−6.3 Hz) are smaller[24] than in *cis*-**7d** (7.3 Hz) (Scheme 3 and Table 2).

The stereochemistry of oxazolidinone **7e** ($J_{4,5}$ = 6.9 Hz) was deduced through NOE experiments; an Overhauser effect of 17% was measured for the 4-H proton upon irradiation of the CH_2 of the ethyl group at C-5, confirm-

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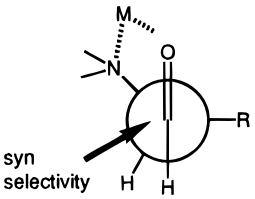

Figure 1.

ing the *cis* relationship of these substituents and thus the *trans* relative stereochemistry for 4-H and 5-H.

Finally, the identity of the minor diastereomers *anti*-**5a** and *anti*-**5c** obtained by us was established by comparison of their physical and spectroscopic properties with those obtained as major components in the reactions of **4a** and **4c** with ethylmagnesium bromide as described by Reetz.[2]

This unprecedent *syn* selectivity for the addition to dibenzylamino aldehydes can be explained by ethylation from the less hindered *si* face of the carbonyl group in a Cram chelate complex (Figure 1). Moreover, the efficient alkylation observed for the compounds described here is in contrast with the low reactivity of diethylzinc with aldehydes and can be attributed to the well-known "ligand acceleration" promoted by the amino group[13] present in α-(dibenzylamino) aldehydes. Nevertheless, the nature of the reaction intermediate probably was rather complex, and the ethylzinc alkoxide formed in the reaction is likely to be involved in the reactive species.

In summary, diethylzinc shows a very high *syn* selectivity in reactions with chiral α-(dibenzylamino) aldehydes, and the reactions described here are complementary and constitute an alternative to the use of other organometallics described in the literature.

Experimental Section

General Procedures. Optical rotations were measured on a digital polarimeter in a 1-dm cell. ^{1}H-NMR and ^{13}C-NMR were taken at 300 and 75 MHz, respectively, in $CDCl_3$, and chemical shifts are given in ppm relative to TMS as internal standard. Only the most significant IR signals are given, and microanalyses have been done at the Department of Inorganic Chemistry. Chromatographic separations was done by flash chromatography using 240−400 mesh silica gel.

The starting α-(dibenzylamino) aldehydes were prepared by a modified described method.[2] Diethylzinc (1 M solution in hexanes) is commercially available. All the reactions were carried out in oven-dried glassware under argon atmosphere. Solvents were distilled prior to use: toluene and THF from benzophenone ketyl, CH_2Cl_2 from CaH_2, and methanol from magnesium turnings.

Alkylation of Amino Aldehydes 4 with Et_2Zn. General Method. A 50 mL oven-dried flask equipped with a septum and a magnetic stirrer and purged with argon was charged with the corresponding *N*,*N*-dibenzylamino aldehyde (2 mmol) in 8 mL of anhydrous toluene. The solution was cooled to 0 °C (ice bath), and 4 mL of a 1 M solution of diethylzinc in hexane (4 mmol, 2 equiv) was injected through the septum. The mixture was stirred at that temperature until the reaction was finished (TLC) and then quenched with 40 mL of an aqueous saturated solution of ammonium chloride. The organic layer was separated, and the aqueous phase was extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The solvents were eliminated on a Rotavapor, and the residue was purified by flash chromatography (silica gel, hexane/ethyl acetate).

(2*S*,3*S*)-2-(*N*,*N*-Dibenzylamino)-3-pentanol (*syn*-5a): hexane/EtOAc 10/1; 84% yield; colorless oil; $[\alpha]^{23}_D = +70.5$ (*c* 1, $CHCl_3$); IR (film) 3420 cm^{-1}; ^{1}H NMR δ 0.93 (t, 3H, *J* = 7.3 Hz), 1.00 (d, 3H, *J* = 6.7 Hz), 1.14 (m, 1H), 1.54 (m, 1H), 2.55 (dq, 1H, J_1 = 6.7 Hz, J_2 = 2.7 Hz), 3.30 (d, 2H, *J* = 13.6 Hz), 3.41 (m, 1H); 3.82 (d, 2H, *J* = 13.6 Hz), 7.20−7.40 (m, 10H); ^{13}C NMR δ 7.9, 9.9, 26.4, 53.1, 57.9, 71.8, 127.1,128.4, 128.9, 138.8.

(2*S*,3*R*)-2-(*N*,*N*-Dibenzylamino)-3-pentanol (*anti*-5a): hexane/EtOAc 10/1; 11% yield; colorless oil; $[\alpha]^{23}_D = +48.2$ (*c* 1, $CHCl_3$); IR (film) 3320 cm^{-1}; ^{1}H NMR δ 0.87 (t, 3H, *J* = 7.4 Hz), 1.11 (d, 3H, *J* = 6.8 Hz), 1.30 (m, 1H); 1.77 (m, 2H), 2.71 (m, 1H), 3.47 (d, 2H, *J* = 13.8 Hz), 3.52 (m, 1H), 3.76 (d, 2H, *J* = 13.8 Hz), 7.15−7.40 (m, 10H); ^{13}C NMR δ 8.5, 10.2, 27.1, 54.6, 56.9, 75.0, 126.8, 128.1, 128.6, 140.0.

(3*S*,4*S*)-4-(*N*,*N*-Dibenzylamino)-5-methyl-3-hexanol (*syn*-5b): hexane/EtOAc 15/1; 64% yield; colorless oil; $[\alpha]^{23}_D = +12.5$ (*c* 1, $CHCl_3$); IR (film) 3380 cm^{-1}; ^{1}H NMR δ 0.93 (t, 3H, *J* = 7.3 Hz), 1.03 (d, 3H, *J* = 7.0 Hz), 1.06 (d, 3H, *J* = 7.0 Hz), 1.11 (m, 1H), 1.58 (m, 1H), 2.25 (m, 1H), 2.33 (dd, 1H, J_1 = 9.3 Hz, J_2 = 2.1 Hz), 3.43 (d, 2H, *J* = 13.0 Hz), 3.67 (m, 1H), 3.92 (d, 2H, *J* = 13.0 Hz), 4.50 (br s, 1H), 7.20−7.40 (m, 10H); ^{13}C NMR δ 10.1, 19.1, 23.9, 24.6, 27.9, 53.8, 65.3, 68.2, 127.1, 128.3, 129.1, 138.9 .

(3*S*,4*S*)-4-(*N*,*N*-Dibenzylamino)-6-methyl-3-heptanol (*syn*-5c): hexane/EtOAc 15/1; 57% yield; colorless oil; $[\alpha]^{23}_D = +34.3$ (*c* 1, $CHCl_3$); IR (film) 3440 cm^{-1}; ^{1}H NMR δ 0.92 (t, 3H, *J* = 7.3 Hz), 0.94 (d, 6H, *J* = 6.4 Hz), 1.18 (m, 2H), 1.57 (m, 2H), 1.70 (m, 1H), 2.48 (m, 1H), 3.38 (m, 1H), 3.41 (d, 2H, *J* = 13.4 Hz), 3.85 (d, 2H, *J* = 13.4 Hz), 4.55 (br s, 1H), 7.20−7.40 (m, 10H); ^{13}C NMR δ 10.2, 22.9, 23.4, 26.6, 35.6, 53.7, 60.4, 72.3, 127.1, 128.4, 128.9, 139.1.

(3*R*,4*S*)-4-(*N*,*N*-Dibenzylamino)-6-methyl-3-heptanol (*anti*-5c): hexane/EtOAc 15/1; 5% yield; colorless oil; $[\alpha]^{23}_D = +15.7$ (*c* 1, $CHCl_3$); IR (film) 3420 cm^{-1}; ^{1}H NMR δ: 0.72 (d, 3H, *J* = 6.5 Hz), 0.91 (d, 3H, *J* = 6.6 Hz), 0.94 (t, 3H, *J* = 7.3 Hz), 1.15−1.65 (m, 4H), 1.76 (m, 1H), 2.10 (br s, 1H), 2.72 (dt, 1H, J_1 = 7.0 Hz, J_2 = 3.6 Hz), 3.63 (d, 2H, *J* = 13.6 Hz), 3.65 (m, 1H), 3.68 (d, 2H, *J* = 13.6 Hz), 7.20−7.40 (m, 10H); ^{13}C NMR δ 11.1, 22.7, 23.1, 24.7, 27.6, 34.4, 55.0, 58.1, 72.2, 126.9, 128.2, 129.0, 140.2.

(2*S*,3*S*)-2-(*N*,*N*-Dibenzylamino)-1-phenyl-3-pentanol (*syn*-5d): hexane/EtOAc 8/1; 63%; colorless oil; $[\alpha]^{23}_D = +25.0$ (*c* 1, $CHCl_3$); IR (film) 3400 cm^{-1}; ^{1}H NMR δ 0.81 (t, 3H, *J* = 7.3 Hz), 1.06 (m, 1H), 1.46 (m, 1H), 2.65 (dd, 1H, J_1 = 14.3 Hz, J_2 = 6.0 Hz), 2.88 (m, 1H), 3.07 (dd, 1H, J_1 = 14.3 Hz, J_2 = 6.5 Hz), 3.35 (d, 2H, *J* = 13.2 Hz), 3.52 (m, 1H), 3.89 (d, 2H, *J* = 13.2 Hz), 4.47 (s, 1H), 7.10−7.40 (m, 15H); ^{13}C NMR δ 9.7, 26.8, 32.2, 53.7, 63.3, 71.3, 126.1, 127.1, 128.3, 128.4, 128.9, 129.0, 138.7, 140.4.

(2*S*,3*R*)-2-(*N*,*N*-Dibenzylamino)-1-phenyl-3-pentanol (*anti*-5d): hexane/EtOAc 8/1; 7% yield; colorless oil; $[\alpha]^{23}_D = +20.1$ (*c* 1, $CHCl_3$); IR (film) 3420 cm^{-1}; ^{1}H NMR δ 0.88 (t, 3H, *J* = 7.3 Hz), 1.37 (m, 1H), 1.68 (m, 1H), 1.90 (br s, 1H), 2.80 (dd, 1H, J_1 = 12.7 Hz, J_2 = 5.8 Hz), 3.05 (m, 2H), 3.60 (m, 1H), 3.65 (d, 2H, *J* = 13.8 Hz), 3.77 (d, 2H, *J* = 13.8 Hz), 7.10−7.40 (m, 15H); ^{13}C NMR δ 10.9, 27.6, 31.9, 55.0, 63.0, 73.2, 125.9, 126.9, 128.2, 128.3, 128.7, 129.3, 139.7, 140.6.

(1*S*,2*S*)-1-(*N*,*N*-Dibenzylamino)-1-phenyl-2-butanol (*syn*-5e): hexane/EtOAc 15/1; 65% yield; colorless solid; mp 85−86 °C (from hexane); $[\alpha]^{23}_D = +151.5$ (*c* 1, $CHCl_3$); IR (KBr) 3420 cm^{-1}; ^{1}H NMR δ 0.86 (t, 3H, *J* =7.3 Hz), 1.04 (m, 1H), 1.26 (m, 1H), 3.02 (d, 2H, *J* = 13.3 Hz), 3.49 (d, *J* = 10.3 Hz), 3.96 (d, 2H, *J* = 13.3 Hz), 4.15 (m, 1H), 4.50 (br s, 1H), 7.15 (m 15H); ^{13}C NMR δ 10.0, 26.7, 53.5, 67.1, 69.0, 127.2, 127.8, 128.2, 128.5, 129.0, 129.9, 134.1, 138.6. Anal. Calcd for $C_{24}H_{27}NO$: C, 83.44; H, 7.88; N, 4.05. Found: C, 83.20; H, 7.74; N, 4.21.

(1*R*,2*R*)-1-(*N*,*N*-Dibenzylamino)-1-phenyl-2-butanol (*syn-ent*-5e): 68% yield; white solid; mp 85−86 °C (from hexane); $[\alpha]^{23}_D = -151.3$ (*c* 1, $CHCl_3$).

(2*S*,3*S*)-2-(*N*,*N*-Dibenzylamino)-1-[(2-methoxyethoxy)-methoxy]-3-pentanol (*syn*-5f): hexane/EtOAc 5/1; 67% yield; colorless oil; $[\alpha]^{23}_D = +58.3$ (*c* 1, $CHCl_3$); IR (film) 3420 cm^{-1}; ^{1}H NMR δ 0.90 (t, 3H, *J* = 7.4 Hz), 1.20 (m, 1H), 1.57 (m, 1H), 2.69 (m, 1H), 3.43 (s, 3H), 3.56 (d, 2H, *J* = 13.2 Hz), 3.60 (m, 3H), 3.77 (m, 4H), 3.96 (d, 2H, *J* = 13.2 Hz), 4.25 (br s, 1H),

4.75 (s, 2H), 7.20−7.40 (m, 10H); ^{13}C NMR δ 9.8, 26.5, 54.2, 58.9, 61.2, 64.2, 67.0, 68.3, 71.6, 95.4, 127.0, 128.2, 129.0, 138.8.

(2*S*,3*R*)-2-(*N*,*N*-Dibenzylamino)-1-((2-methoxyethoxy) methoxy)-3-pentanol (*anti*-5f): hexane/EtOAc 5/1; 3% yield; colorless oil; IR (film) 3400 cm^{-1}; ^{1}H NMR δ 0.86 (t, 3H, J = 7.4 Hz), 1.32 (m, 1H), 1.85 (m, 1H), 2.65 (br s, 1H), 2.74 (dt, J_1 = 7.4 Hz, J_2 = 4.9 Hz), 3.41 (s, 3H), 3.58 (m, 4H), 3.75 (m, 3H), 3.86 (d, 2H, J = 13.8 Hz), 3.96 (m, 2H), 4.75 (s, 2H), 7.10−7.35 (m, 10H); ^{13}C NMR δ 10.0, 27.4, 55.2, 59.0, 60.1, 65.3, 67.2, 71.7, 72.7, 95.7, 126.9, 128.2, 128.8, 139.8.

General Method for the Hydrogenolysis of *N*,*N*-Dibenzylamino Alcohols 5.[21] To a solution of the appropriate *N*,*N*-dibenzylamino alcohol **5** (1.0 mmol) in 10 mL of dry methanol was added 50 mg of 20% $Pd(OH)_2$−C in one portion. The mixture was stirred under 1 atm of hydrogen, and the reaction was monitored by TLC analysis. After completion of the reaction, the catalyst was removed by filtration through Celite and washed with 20 mL of methanol. The solvent was evaporated under reduced pressure to afford the pure product.

(2*S*,3*S*)-2-Amino-3-pentanol (*syn*-6a): 92% yield; colorless solid; mp 67−68 °C (from hexane); $[\alpha]^{23}_D$ = −15.9 (*c* 0.34, CH_3OH); IR (film) 3380 cm^{-1}; ^{1}H NMR δ 0.98 (t, 3H, J = 7.4 Hz), 1.10 (d, 3H, J = 6.4 Hz) ; 1.37 (m, 1H), 1.57 (m, 1H), 2.56 (br s, 3H), 2.77 (m, 1H), 3.13 (ddd, 1H, J_1 = 8.1 Hz, J_2 = 6.6 Hz, J_3 = 3.5 Hz); ^{13}C NMR δ 9.9, 20.0, 26.5, 50.7, 76.6. Anal. Calcd for $C_5H_{13}NO$: C, 58.21; H, 12.70; N, 13.58. Found: C, 58.06; H, 12.89; N, 13.42.

(2*S*,3*R*)-2-Amino-3-pentanol (*anti*-6a): 91% yield; colorless oil; $[\alpha]^{23}_D$ = +14.0 (*c* 1, $CHCl_3$); IR (film) 3380 cm^{-1}; ^{1}H NMR δ 0.98 (t, 3H, J = 7.4 Hz), 1.04 (d, 3H, J = 6.6 Hz), 1.42 (m, 2H), 2.91 (br s, 3H), 3.01 (dq, 1H, J_1 = 6.6 Hz, J_2 = 3.2 Hz), 3.44 (m, 1H); ^{13}C NMR δ 10.5, 16.1, 25.4, 50.2, 75.4. Anal. Calcd for $C_5H_{13}NO$: C, 58.21; H, 12.70; N, 13.58. Found: C, 58.09; H, 12.83; N, 13.44.

(3*S*,4*S*)-3-Amino-2-methyl-4-hexanol (*syn*-6b): 70% yield; colorless oil; $[\alpha]^{23}_D$ = −8.4 (*c* 0.7, $CHCl_3$); IR (film) 3300 cm^{-1}; ^{1}H NMR δ 0.87 (d, 3H, J = 6.8 Hz), 0.98 (m, 6H), 1.40 (m, 1H), 1.55 (m, 1H), 1.83 (m, 1H), 2.46 (dd, 1H, J_1 = 6.5 Hz, J_2 = 4.5 Hz), 2.73 (br s, 3H), 3.38 (ddd, 1H, J_1 = 8.1 Hz, J_2 = 6.5 Hz, J_3 = 3.8 Hz); ^{13}C NMR δ 10.0, 16.2, 20.4, 26.9, 29.0, 60.2, 72.4. Anal. Calcd for $C_7H_{17}NO$: C, 64.07; H, 13.06; N, 10.67. Found: C, 63.92; H, 13.18; N, 10.49.

(3*S*,4*S*)-4-Amino-6-methyl-3-heptanol (*syn*-6c): 92% yield; colorless oil; $[\alpha]^{23}_D$ = −31.0 (*c* 1, $CHCl_3$); IR (film) 3320 cm^{-1}; ^{1}H NMR δ 0.90 (d, 3H, J = 6.6 Hz), 0.94 (d, 3H, J = 6.6 Hz), 0.98 (t, 3H, J = 7.4 Hz), 1.25 (m, 2H), 1.42 (m, 1H), 1.56 (m, 1H), 1.73 (m, 1H), 2.36 (br s, 3H), 2.66 (m, 1H), 3.17 (ddd, 1H, J_1 = 8.2 Hz, J_2 = 5.8 Hz, J_3 = 3.9 Hz); ^{13}C NMR δ 10.0, 21.5, 23.5, 24.5, 26.7, 43.2, 52.6, 75.1. Anal. Calcd for $C_8H_{19}NO$: C, 66.16; H, 13.19; N, 9.64. Found: C, 66.28; H, 13.22; N, 9.51.

(3*S*,4*R*)-4-Amino-6-methyl-3-heptanol (*anti*-6c): 60% yield; colorless oil; $[\alpha]^{23}_D$ = −4.8 (*c* 0.8, $CHCl_3$); IR (film) 3300 cm^{-1}; ^{1}H NMR δ 0.89 (d, 3H, J = 6.6 Hz), 0.95 (d, 3H, J = 6.6 Hz), 0.99 (t, 3H, J = 7.3 Hz), 1.23 (m, 2H), 1.41 (m, 2H), 1.68 (m, 1H), 2.22 (br s, 3H), 2.88 (m, 1H), 3.41 (m, 1H); ^{13}C NMR δ 10.6, 21.5, 23.8, 24.4, 24.6, 40.8, 52.7, 75.8. Anal. Calcd for $C_8H_{19}NO$: C, 66.16; H, 13.19; N, 9.64. Found: C, 66.35; H, 13.28; N, 9.47.

(2*S*,3*S*)-2-Amino-1-phenyl-3-pentanol (*syn*-6d): 86% yield; colorless oil; $[\alpha]^{23}_D$ = −72.5 (*c* 2, $CHCl_3$); IR (film) 3340 cm^{-1}; ^{1}H NMR δ 1.01 (t, 3H, J = 7.3 Hz), 1.55 (m, 2H), 2.31 (br s, 3H), 2.51 (m, 1H), 2.92 (m, 2H), 3.32 (m, 1H), 7.15−7.35 (m, 5H); ^{13}C NMR δ 10.1, 27.0, 40.4, 56.2, 74.4, 126.2, 128.4, 129.1, 138.8. Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.54; H, 9.66; N, 7.68.

(2*S*,3*R*)-2-Amino-1-phenyl-3-pentanol (*anti*-6d): 80% yield; colorless solid; mp 103−104 °C (from hexane); $[\alpha]^{23}_D$ = −39.0 (*c* 1, $CHCl_3$); IR (KBr) 3420 cm^{-1}; ^{1}H NMR δ 1.05 (t, 3H, J = 7.4 Hz), 1.56 (m, 2H), 1.85 (br s, 3H), 2.45 (dd, 1H, J_1 = 13.5 Hz, J_2 = 10.5 Hz), 2.89 (dd, 1H, J_1 = 13.5 Hz, J_2 = 3.4 Hz), 3.07 (m, 1H), 3.51 (m, 1H), 7.20−7.40 (m, 5H); ^{13}C NMR δ 10.6, 25.3, 37.6, 56.4, 75.3, 126.2, 128.5, 129.1, 139.3. Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.59; H, 9.72; N, 7.60.

(1*S*,2*S*)-1-Amino-1-phenyl-2-butanol (*syn*-6e): 85% yield; colorless solid; mp 80−81 °C (from hexane); $[\alpha]^{23}_D$ = +31.2 (*c* 1, $CHCl_3$); IR (KBr) 3320, 3260 cm^{-1}; ^{1}H NMR δ 0.93 (t, 3H, J = 7.3 Hz), 1.33 (m, 2H), 2.87 (br s, 3H), 3.55 (m, 1H), 3.68 (d, 1H, J = 7.9 Hz), 7.20−7.40 (m, 5H); ^{13}C NMR δ: 10.1, 26.3, 61.0, 76.5, 127.1, 127.3, 128.4, 142.8. Anal. Calcd for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 71.72; H: 9.48; N, 8.18.

(1*R*,2*R*)-1-Amino-1-phenyl-2-butanol (*syn*-ent-6e): 94% yield; white solid; mp 80−81 °C (from hexane); $[\alpha]^{23}_D$ = −32.9 (*c* 1.1, $CHCl_3$). Anal. Calcd for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.49; H, 8.95; N, 8.41.

(2*S*,3*S*)-2-Amino-1-((2-methoxyethoxy)methoxy)-3-pentanol (*syn*-6f): 98% yield; colorless oil; $[\alpha]^{23}_D$ = −3.2 (*c* 1, $CHCl_3$); IR (film) 3360 cm^{-1}; ^{1}H NMR δ 0.99 (t, 3H, J = 7.4 Hz), 1.54 (m, 2H), 2.56 (br s, 3H), 2.93 (m, 1H), 3.40 (s, 3H), 3.47 (m, 1H), 3.57 (m, 3H), 3.70 (m, 3H), 4.74 (s, 2H); ^{13}C NMR δ 10.0, 26.8, 54.3, 58.9, 66.9, 70.1, 71.6, 72.2, 95.5. Anal. Calcd for $C_9H_{21}NO_4$: C, 52.15; H, 10.21; N, 6.76. Found: C, 52.36; H, 10.38; N, 6.52.

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Supporting Information Available: Copies of ^{13}C NMR spectra for compounds **5a**−**f** and **6a**−**f**, general experimental procedures for the preparation of dibenzylamino alcohols **3a**−**f**, dibenzylamino aldehydes **4a**−**f**, and oxazolidinones **7a**−**f**, as well as physical and spectroscopic data for these compounds (25 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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