Pinacol Cross Coupling of 2-[*N*-(Alkoxycarbonyl)amino] Aldehydes and Aliphatic Aldehydes by $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$. Synthesis of *syn,syn*-3-[*N*-(Alkoxycarbonyl)amino] 1,2-Diols

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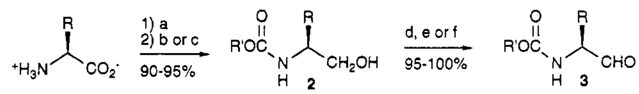
Abstract: Slow addition of 2-[*N*-(alkoxycarbonyl)amino] aldehydes to mixtures of $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ and aliphatic aldehydes gave *syn,syn*-3-[*N*-(alkoxycarbonyl)amino] 1,2-diols in good yield and high enantiomeric purity (>99:1). The alkyl group of the *N*-alkoxycarbonyl was shown to influence the yield: Me > allyl > Bn > *t*-Bu. Only the *syn,syn* diastereomer was observed (>20:1), except with *N*-Cbz-alaninal (10:1:1), *O*-benzyl-*N*-Cbz-serinal (7:1), and *N*-Cbz-prolinal (5:1 to 12:1). A new serinal derivative, *N*-Cbz-*O*-TBS-serinal, was cross coupled with *n*-pentadecanal to give a derivative of *xylo*-D-C_{18}-phytosphingosine.

Introduction

Interest in the biological activity of compounds containing the 3-amino 1,2-diol subunit has stimulated the development of several synthetic approaches to this important functional group.[1–5] For example, nucleophilic substitution of a 1,2,3-triol has been used[2] as well as disubstitution of the C=C bond of an allylic alcohol or allylic amine.[3] The reaction of a carbanion and a 2,3-dialkoxy aldimine (or equivalents thereof)[4] and the reaction of an α-amino carbanion and a 2-alkoxy aldehyde (or equivalents thereof)[5] have proven to be viable approaches as well. We have been investigating the stereoselective preparation of 1,2-diols via homocoupling and cross coupling of aldehydes by $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ (**1**).[6] In most instances, we have achieved efficient cross coupling by slow addition of a chelating aldehyde to a mixture of **1** and a nonchelating aldehyde. We anticipated that 2-[*N*-(alkoxycarbonyl)amino] aldehydes should be good candidates for chelating aldehydes and have the advantage of being available in enantiomerically pure form.[7] Herein we report that 2-[*N*-(alkoxycarbonyl)amino] aldehydes are cross coupled with aliphatic aldehydes by **1** to give 3-[*N*-(alkoxycarbonyl)amino] 1,2-diols.[8] In most instances, the reaction gives a good yield of one cross coupling product, the *syn,syn* diastereomer. Branching of the aliphatic aldehydes and several functional groups in the side chains of the 2-[*N*-(alkoxycarbonyl)amino] aldehydes was found not to impair cross coupling.

Scheme 1



[a] (a) $LiBH_4$, TMSCl, THF; (b) R'OCOCl, K_2CO_3, H_2O/THF; (c) di-*tert*-butyl dicarbonate, $CHCl_3$; (d) DMSO, $(COCl)_2$, Et_3N, –63 °C; (e) Py·SO_3, DMSO; (f) TEMPO (<1 mol %), NaOCl.

Results and Discussion

Synthesis of 2-[*N*-(Alkoxycarbonyl)amino] Aldehydes. The use of enantiomerically pure 2-[*N*-(alkoxycarbonyl)amino] aldehydes (**3**) in organic chemistry has instigated numerous studies directed at developing reasonable methods of their synthesis.[7] The major difficulty with these aldehydes (**3**) is their high susceptibility to racemization.[9] The most reliable and general methods yet developed utilize the Swern, Parikh-Doering, or TEMPO oxidation of the corresponding (*S*)-2-[*N*-(alkoxycarbonyl)amino] alcohols (**2**) to give the aldehydes **3** in high yields and high purity. The alcohols **2** in general are most easily made from the commercially available amino acid in two simple steps: reduction of the acid to the free amino alcohol[10] using $LiBH_4$/TMSCl[11] followed by immediate *N*-protection (Scheme 1). This method

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(1) For leading references on biologically active 3-amino 1,2-diol compounds, see: (a) Buchanan, J. G.; Lumbard, K. W.; Sturgeon, R. J.; Thompson, D. K.; Wightman, R. H. *J. Chem. Soc., Perkin Trans. 1* **1990**, 699. (b) Fleet, G. W.; Witty, D. R. *Tetrahedron: Asymmetry* **1990**, *1* (2), 119. (c) Ikemoto, N.; Schreiber, S. L. *J. Am. Chem. Soc.* **1990**, *112* (26), 9657. (d) Ballini, R.; Marcantoni, E.; Petrini, M. *J. Org. Chem.* **1992**, *57* (4), 1316. (e) Kleemann, H.; et al. *J. Med. Chem.* **1992**, *35* (3), 559. (f) Repine, J. T.; et al. *J. Med. Chem.* **1992**, *35* (6), 1032. (g) Dai, L.; Lou, B.; Zhang, Y. *J. Am. Chem. Soc.* **1988**, *110*, 5195. (h) Wehner, V.; Jager, V. *Angew. Chem., Int. Ed. Engl.* **1990**, *29* (10), 1171.

(2) For examples of this type of reaction, see: (a) Richardson, A. C. *Carbohydr. Res.* **1967**, *4*, 442. (b) Brimacombe, J. S.; Hanna, R.; Tucker, L. C. N. *Carbohydr. Res.* **1985**, *136*, 419.

(3) For examples of these types of reactions, see: (a) Hauser, F. M.; Rhee, R. P.; Ellenberger, S. R. *J. Org. Chem.* **1984**, *49*, 2236. (b) Roush, W. R.; Straub, J. A.; Brown, R. J. *J. Org. Chem.* **1987**, *52*, 5127. (c) Dai, L.; Lou, B.; Zhang, Y. *J. Am. Chem. Soc.* **1988**, *110*, 5195. (d) Caron, M.; Sharpless, K. B. *J. Org. Chem.* **1985**, *50*, 1560. (e) Jager, V.; Hummer, W.; Stahl, U.; Gracza, T. *Synthesis* **1991**, 769. (f) Jager, V.; Stahl, U.; Hummer, W. *Synthesis* **1991**, 776.

(4) For examples of this type of reaction, see: (a) Fuganti, C.; Grasselli, P.; Pedrocchi-Fantoni, G. *J. Org. Chem.* **1983**, *48*, 909. (b) Mukaiyama, T.; Goto, Y.; Shoda, S. *Chem. Lett.* **1983**, 671. (c) Kita, Y.; Itoh, F.; Tamura, O.; Ke, Y. Y. *Tetrahedron Lett.* **1987**, *28*, 1431.

(5) For examples of this type of reaction, see: (a) Hanessian, S.; Kloss, J. *Tetrahedron Lett.* **1985**, *26*, 1261. (b) Banfi, L.; Cardani, S.; Potenza, D.; Scolastico, C. *Tetrahedron Lett.* **1987**, *43*, 2317. (c) Wehner, V.; Jager, V. *Angew. Chem., Int. Ed. Engl.* **1990**, *29* (10), 1169.

(6) (a) Freudenberger, J. H.; Konradi, A. W.; Pedersen, S. F. *J. Am. Chem. Soc.* **1989**, *111*, 8014. (b) Takahara, P. M.; Freudenberger, J. H.; Konradi, A. W.; Pedersen, S. F. *Tetrahedron Lett.* **1989**, *30*, 7177. (c) Park, J.; Pedersen, S. F. *J. Org. Chem.* **1990**, *55*, 5924. (d) Konradi, A. W.; Pedersen, S. F. *J. Org. Chem.* **1990**, *55*, 4506. (e) Raw, A. S.; Pedersen, S. F. *J. Org. Chem.* **1991**, *56*, 830. (f) Konradi, A. W.; Pedersen, S. F. *J. Org. Chem.* **1992**, *57*, 28.

(7) For a review of α-amino aldehydes, see: Jurczak, J.; Golebiowski, A. *Chem. Rev.* **1989**, *89*, 149.

(8) Some of the results presented here were the subject of a preliminary communication: see ref 6d.

(9) Ito, A.; Takahashi, R.; Baba, Y. *Chem. Pharm. Bull.* **1975**, *23* (12), 3081.

(10) 2-Amino alcohols derived from the common amino acids are commercially available and were used in some cases; however, they are rather expensive when compared to their parent amino acids.

(11) Giannis, A.; Sandhoff, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28* (2), 218. Although $LiAlH_4$ is the traditional reagent, this new reduction method gave higher yields and purity and in general was more convenient.

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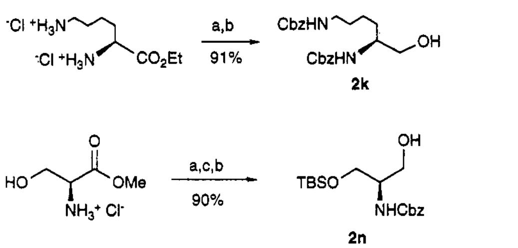
Scheme 2



[a] (a) $PhCH_2O_2CCl$, K_2CO_3, H_2O/THF; (b) $Ca(BH_4)_2$, EtOH/THF, 0 °C; (c) t-$BuMe_2SiCl$, imidazole, DMF.

consistently gave the alcohols **2** in >90% yield and >95% purity.

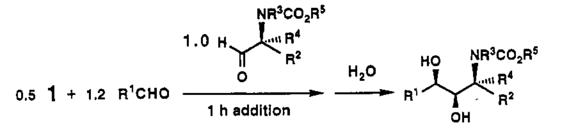
The general procedure (Scheme 1) could not be used in all cases. Preparations of *N,N*-bis-Cbz-L-lysinol (**2k**) and *N*-Cbz-*O*-TBS-L-serinol (**2n**) are illustrated in Scheme 2. L-Lysine ethyl ester dihydrochloride was bis-*N*-protected with benzyl chloroformate followed by reduction of the ethyl ester with $Ca(BH_4)_2$ in EtOH/THF to give **2k**. The synthesis of **2n** began from L-serine methyl ester hydrochloride, which was sequentially treated with benzyl chloroformate and *tert*-butyldimethylchlorosilane to give a fully protected methyl ester, in 96% mass recovery. Reduction of the methyl ester with $Ca(BH_4)_2$ in EtOH/THF gave **2n**, in 90% mass recovery from L-serine methyl ester hydrochloride. The crude alcohol **2n** was contaminated with a small amount (<5%) of benzyl alcohol but was judged to be pure enough for use in the next step.[12]

The modified Swern oxidation method of Luly and co-workers[13] was adapted to oxidize alcohols **2** (except **2o**) to afford aldehydes **3** in 95–100% mass recovery (Scheme 1, reagent d). As evidenced by TLC, the aldehydes prepared by this procedure were free of starting alcohol. The enantiomeric purity of the isolated aldehydes **3** was reported to be maintained if the experimental procedure is strictly adhered to. We confirmed their claim when preparing the synthetically useful serinal derivative **3n**. Swern oxidation of the alcohol **2n** gave **3n** in 86% mass recovery *from* L-serine methyl ester hydrochloride. The enantiomeric purity of the aldehyde **3n** was established by reducing some of **3n** back to **2n** using $NaBH_4$, followed by Mosher esterification.[14] ^{1}H NMR spectroscopy and GC analysis demonstrated that this ester was a single diastereomer (>99%) when compared with the Mosher ester of racemic **2n**.[15] The aldehyde **3n** was contaminated by a small amount (<5%) of benzaldehyde[16] but was used immediately in the next step to minimize racemization.

The method of Hamada and co-workers[17] was used to oxidize *N*-Cbz-methioninol (**2o**), which contains a methylthio functional group that may not tolerate the other methods (Scheme 1, reagent e). The aldehyde **3o** was at first obtained in 40–50% mass recovery; however, modification of the Hamada procedure by substituting saturated aqueous sodium chloride for ice–water as the quenching solution improved mass recoveries to 90–100% and is highly recommended. As evidenced by TLC, the aldehydes obtained by the modified Hamada procedure were contaminated by small quantities of the starting alcohols, despite the use of excess oxidant. Longer reaction times did not improve conversion of the alcohols and were subsequently avoided to minimize racemization of the product aldehydes.

The two oxidation methods described thus far work well for small-scale reactions (<20 g). For large-scale preparations of **3** (except **3o**), a TEMPO oxidation was utilized (Scheme 1, reagent f). The procedure of Leanna, Sowin, and Morton[18] uses catalytic TEMPO (<1 mol %) and commercial bleach as the net oxidant, making this method inexpensive and practical for large-scale oxidations. Regardless of the oxidation procedure used, all the aldehydes **3** prepared were used immediately and without further purification to avoid racemization.

Table 1. Pinacol Cross Coupling of *N*-Alkoxycarbonyl-2-Amino Aldehydes with Aliphatic Aldehydes by $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ (**1**)



entry	R¹	R²	R³	R⁴	R⁵	yield[a]	ds ratio[b]
a	*i*-Pr	*i*-Pr	H	H	*t*-Bu	70	>20:1
b	*i*-Pr	*i*-Pr	H	H	$PhCH_2$	76	>20:1
c	*i*-Bu	$PhCH_2$	H	H	*t*-Bu	67	>20:1
d	*i*-Bu	$PhCH_2$	H	H	$PhCH_2$	74	>20:1
e	*i*-Bu	$PhCH_2$	H	H	allyl	80	>20:1
f	*i*-Bu	$PhCH_2$	H	H	Me	84	>20:1
g	$Ph(CH_2)_2$	$PhCH_2$	H	H	*t*-Bu	67	>20:1
h	$Ph(CH_2)_2$	$PhCH_2$	H	H	$PhCH_2$	78	>20:1
i	$Ph(CH_2)_2$	$PhCH_2$	H	H	allyl	77	>20:1
j	$Ph(CH_2)_2$	$PhCH_2$	H	H	Me	83	>20:1
k	cyclo-C_6H_{11}	$CbzNH(CH_2)_4$	H	H	$PhCH_2$	75	>20:1
l	$Ph(CH_2)_2$	$PhCH_2OCH_2$	H	H	$PhCH_2$	54	7:1
m	*n*-$C_{12}H_{25}$	$PhCH_2OCH_2$	H	H	$PhCH_2$	41	>20:1[c]
n	*n*-$C_{14}H_{29}$	*t*-$BuMe_2SiOCH_2$	H	H	$PhCH_2$	58[d]	>20:1
o	*n*-C_5H_{11}	$CH_3S(CH_2)_2$	H	H	$PhCH_2$	62	>20:1
p	*n*-C_7H_{15}	Me	H	Me	$PhCH_2$	88	>20:1[e]
q	$Ph(CH_2)_2$	Me	H	H	$PhCH_2$	83	10:1:1
r	$Ph(CH_2)_2$	$-(CH_2)_3-$		H	$PhCH_2$	84	10:1:1:1[c,f]
s	*i*-Bu	$-(CH_2)_3-$		H	$PhCH_2$	92	5:1[c,f]
t	*i*-Pr	$-(CH_2)_3-$		H	$PhCH_2$	85	12:1[c,f]

[a] Purified yield from *N*-alkoxycarbonyl-2-amino alcohols (**2**). [b] Diastereoselectivity was determined by $^{13}C\{^1H\}$ NMR (DMSO-d_6, 98 °C). [c] Determined after chromatography. [d] Yield from L-serine methyl ester hydrochloride. [e] Product is racemic. [f] Inseparable by chromatography.

Vanadium(II) Pinacol Cross Coupling Reactions. The vanadium(II) reagent $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ (**1**) was generated by the reaction of $VCl_3(THF)_3$ and Zn dust in CH_2Cl_2 and was used *in situ*. The generation of **1** is most rapid at high concentration and therefore was performed at *ca.* 0.2 M $VCl_3(THF)_3$. Upon addition of an aliphatic aldehyde to the solution of **1**, a color change from green to brown is observed.[19] Slow addition (1 h) of **3** to this solution is necessary in order to minimize homocoupling of this aldehyde.[20] Following a workup employing either 10% sodium tartrate (best for potentially acid-sensitive substrates) or 1 M HCl, the products **4** were purified by recrystallization or flash chromatography in good yields (Table 1).

The relative configurations of the three stereocenters in the 3-[*N*-(alkoxycarbonyl)amino] 1,2-diols (**4a–t**) were determined from studies of derivatives. The *syn,syn* stereochemistry of **4m** was shown by removal of the Cbz and benzyl protecting groups (by hydrogenation) and acetylation to give the known tetraacetate of *xylo*-D-C_{16}-phytosphingosine (**9**) (Scheme 3).[21] Treatment of the 3-[*N*-(alkoxycarbonyl)amino] 1,2-diols bearing an NH function (**4a–o,q**) with either NaOH in MeOH or NaH in THF gave the hydroxyoxazolidinones (**5a–o,q**) (Scheme 4). Mea-

(12) The benzyl alcohol arises from hydrolysis of benzyl chloroformate during protection of the amino group, and from degradation of the *N*-Cbz group during reduction of the methyl ester by $Ca(BH_4)_2$.

(13) Luly, J. R.; Dellaria, J. J.; Soderquist, J. L.; Yi, N. *J. Org. Chem.* **1987**, *52*, 1487.

(14) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

(15) The Mosher ester of racemic **2n** was prepared by partial protection of *N*-Cbz-2-amino-1,3-propanediol with *tert*-butyldimethylchlorosilane, followed by Mosher esterification, and consisted of 1:1 mixture of diasterомers, which were well resolved by both ^{1}H NMR and GC.

(16) The benzaldehyde arises from oxidation of the benzyl alcohol contaminant.

(17) Hamada, Y.; Shioiri, T. *Chem. Pharm. Bull.* **1982**, *30*, 1921.

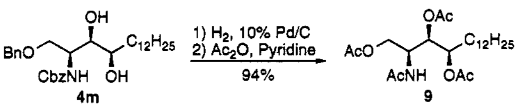
(18) Leanna, M. R.; Sowin, T. J.; Morton, H. E. *Tetrahedron Lett.* **1992**, *33* (35), 5029.

(19) Infrared spectra of mixtures of **1** and aliphatic aldehydes show varying degrees of coordination (20–60%) of the aldehyde carbonyl groups to vanadium (Takahara, P. M.; Pedersen, S. F. Unpublished results). However, several hours after preparation, aqueous workup of mixtures of **1** and aliphatic aldehydes gives back the aliphatic aldehydes and only traces (<5%) of homocoupling products (ref 6a).

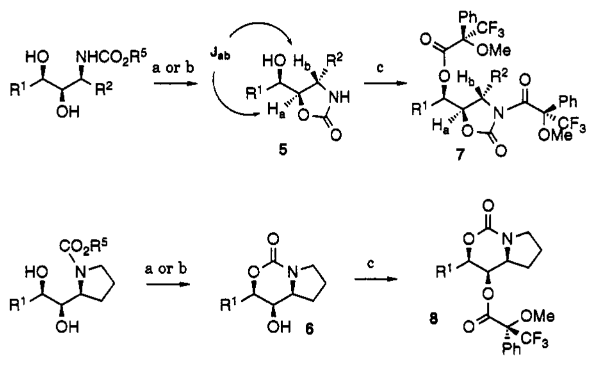
(20) (*S*)-*N*-Cbz-2-amino aldehydes are rapidly homocoupled by **1** to give C_2-symmetric (1*S*,2*R*,3*R*,4*S*)-1,4-bis[*N*-(benzyloxycarbonyl)amino] 2,3-diols in good yields (ref 6e). Infrared spectra of mixtures of **1** and *N*-Cbz-2-amino aldehydes show complete disappearance of the aldehyde carbonyl groups (free or coordinated), 10 min after preparation (Takahara, P. M.; Pedersen, S. F. Unpublished results).

(21) Sugiyama, S.; Honda, M.; Komori, T. *Liebigs Ann. Chem.* **1990**, 1069.

Scheme 3



Scheme 4



[a] (a) NaH, THF; (b) NaOH, MeOH; (c) Mosher chloride, DMAP, Et_3N.

surement of a ^{1}H NMR coupling constant (J_{ab} = 4–5 Hz) confirmed the *trans* substitution of the oxazolidinone rings in compounds **5a–o,q**.[22] X-ray crystallography of one hydroxy oxazolidinone (**5g**) established the configuration of the carbinol stereocenter and confirmed the presence of a five-membered ring.[23] The configurations of the carbinol stereocenter in the other hydroxy oxazolidinones **5** have been inferred. Two hydroxy oxazolidinones (**5a,g**) were purified in good yield. Treatment of the major *N*-Cbz-L-prolinal (**3r**) cross coupling products (**4r–t**) with either NaOH in MeOH or NaH in THF gave the cyclic six-membered hydroxy carbamates (**6r–t**) (Scheme 4). X-ray crystallography of **6r** established the configuration of its three stereocenters and confirmed the presence of a six-membered ring.[23] The configuration of the three stereocenters of the other six-membered hydroxy carbamates (**6s,t**) has been inferred, and two of these derivatives (**6r,s**) were purified, in fair yield.

The enantiomeric purities of seven 3-[*N*-(alkoxycarbonyl)-amino] 1,2-diols (**4a,b,g,h,k,o,s**) were determined by an application of Mosher's method. Mosher diesters of **4** were not prepared, because the room temperature NMR spectra of these compounds were complicated by hindered rotation. Instead, the crude hydroxy oxazolidinones **5** were acylated on both the OH and NH functions with Mosher chloride, and one of the crude six-membered hydroxy carbamates (**6s**) was acylated with Mosher chloride on the OH function (Scheme 4). The ^{19}F NMR spectra of the Mosher ester–imides (**7a,b,g,h,k,o**) show two peaks of equal integration, one sharp and one broad. Both diastereomers of the Mosher ester–imides (**7a,b,g,h,k,o**) and the Mosher ester (**8s**) were prepared using the two available enantiomers of Mosher chloride. Comparison of the ^{19}F and ^{1}H NMR spectra for each pair of diastereomeric Mosher derivatives showed no cross contamination, demonstrating the high enantiomeric purity of **4**.

The crude products of all the cross coupling reactions reported in Table 1 were analyzed by ^{1}H NMR, ^{13}C NMR, and TLC. In most cases, cross coupling reactions of 2-[*N*-(alkoxycarbonyl)-amino] aldehydes bearing an NH functional group gave one detectable (>20:1) 3-[*N*-(alkoxycarbonyl)amino] 1,2-diol (**4a–k,n–p**) and traces (<5%) of products arising from homocoupling of **3** and the aliphatic aldehyde. Even in the worst case scenario, *N*-Cbz-alaninal, where discrimination is required between Me and H, good diastereoselectivity (10:1:1) was still obtained. Neither α-branching of the aliphatic aldehyde (**4a,b,k,t**) nor several functional groups in the *N*-Cbz-2-amino aldehydes (**4k,n,o**) were observed to disrupt cross coupling. However, cross coupling reactions of *N*-Cbz-L-prolinal gave a major *N*-Cbz-3-amino 1,2-diol (**4r–t**) and also other detectable diastereomers. Representative α-, β- and γ-branched aldehydes were found to cross couple with *N*-Cbz-L-prolinal to give 12:1, 10:1:1:1, and 5:1 mixtures of diastereomers, respectively. To address whether the *N*-alkyl substituent in *N*-Cbz-L-prolinal is responsible for its lowered coupling diastereoselectivity, cross coupling reactions of *N*-benzyl-*N*-Cbz-L-phenylalaninal and *N*-methyl-*N*-Cbz-L-phenylalaninal with 3-phenylpropanal were performed. Each of these reactions gave a mixture of diastereomers (ca. 5:1), a decrease in selectivity when compared with entry h in Table 1.

On the basis of the results presented in Table 1, the effect of the *N*-alkoxycarbonyl group on the yield of the cross coupling reaction can be generalized: MeO_2C > Alloc > Cbz > Boc. The steric bulk of the alkyl group may be effecting the rate and stability of chelation and therefore is influencing the yield. Crude mass recoveries from the cross coupling reactions of *N*-Boc-2-amino aldehydes were *ca.* 90%, whereas other *N*-(alkoxycarbonyl)-2-amino aldehydes gave *ca.* 105%. The yields of the *N*-Boc-3-amino 1,2-diols (**4a,g**) are lower than the yields of the analogous *N*-Cbz-3-amino 1,2-diols (**4b,h**), reflecting the low mass recoveries obtained from *N*-Boc-2-amino aldehydes. We hypothesize that the low mass recoveries and yields obtained from the reactions of *N*-Boc-2-amino aldehydes reflect degradation of the acid-sensitive Boc group by V(III) Lewis acids present in the reaction and/or quench mixture. The decision of which chelating/protecting group to use in a synthesis depends greatly on subsequent use of the product. The Boc group is the only protecting group (of the four presented) that can be removed under mildly acidic conditions and therefore may be desirable even with the slightly lower yields observed. Although the Cbz group has the advantage of being easily removed by hydrogenation, it has two drawbacks. In the formation of *N*-Cbz-2-amino alcohols (Scheme 1), benzyl chloroformate is used; this invariably gives a small amount of benzyl alcohol byproduct, which is difficult to remove. Additionally benzyl chloroformate is slightly more expensive than allyl chloroformate and significantly more expensive than methyl chloroformate. The potential advantages of the Alloc group include its easy removal by catalytic palladium[24] and the fact that any allyl alcohol formed in the *N*-protection step (Scheme 1) is easily removed during solvent evaporation (or extraction). If basic hydrolysis of the alkoxycarbonyl group in **4** is acceptable in a given synthetic scheme, then the methoxycarbonyl group is clearly the most desirable functionality due to the convenience of using methyl chloroformate in the *N*-protection step and the high yields in the cross coupling reactions.

The 2-amino-3-hydroxy aldehyde serinal is a particularly useful synthetic intermediate, and we have therefore investigated its performance in pinacol coupling reactions. It is possible that the two commonly used protected forms of serinal, *N*-Boc-*N*,*O*-isopropylidene-L-serinal[25] and *N*-Boc-*O*-benzyl-L-serinal,[26] would undergo cross coupling with aliphatic aldehydes. However, each of these aldehydes presents some potential problems. *N*-Cbz-L-prolinal forms mixtures of diastereomers upon either homocoupling[27] or cross coupling by **1**. In both *N*-Cbz-L-prolinal and *N*-Boc-*N*,*O*-isopropylidene-L-serinal, the amino substituent and side chain are connected in a five-membered ring. On the basis of this structural analogy, we expect a mixture of diastereomers from pinacol coupling of *N*-Boc-*N*,*O*-isopropylidene-L-serinal by **1**. Relative to unfunctionalized aldehydes, β-benzyloxy aldehydes are homocoupled by **1** at a signficant rate.[28] We attribute this

(22) Rich, D. H.; Sun, E. T. O. *J. Med. Chem.* **1980**, *23*, 27.

(23) X-ray crystal structures were carried out by Dr. F. J. Hollander at the College of Chemistry X-ray facility (CHEXRAY), University of California, Berkeley, CA.

(24) Boullanger, P.; Descotes, G. *Tetrahedron Lett.* **1986**, *27* (23), 2599 and references therein.

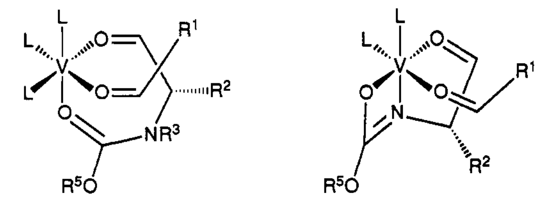
(25) Garner, G.; Park, J. M. *J. Org. Chem.* **1987**, *52*, 2361.

(26) Sugano, H.; Miyoshi, M. *J. Org. Chem.* **1976**, *41*, 2352.

(27) *N*-Cbz-L-prolinal also gives lower diastereoselectivity than other *N*-Cbz-2-amino aldehydes upon homocoupling by **1** (Konradi, A. W.; Pedersen, S. F. Unpublished results).

(28) Konradi, A. W.; Pedersen, S. F. Unpublished results.

Chart 1



Bidentate complex   Tridentate complex

result to chelation of β-benzyloxy aldehydes[29,30] to vanadium through the aldehyde and ether functions. *N*-Cbz-*O*-benzyl-L-serinal (**3l**) is a β-benzyloxy aldehyde and can chelate in two reactive modes: through the aldehyde and *N*-Cbz functions, and through the aldehyde and ether functions. To address this issue *N*-Cbz-*O*-benzyl-L-serinal (**3l**) was cross coupled with 3-phenylpropanal to give **4l** as a 7:1 mixture of diastereomers. The lowered diastereoselectivity and yield in this case, when compared with the cases of the majority of substrates presented in Table 1, suggest that the β-OBn group is having a negative effect on this reaction.

We suspected that changing the benzyloxy group to the "noncoordinating" (*tert*-butyldimethylsilyl)oxy group[30] would provide an ideally protected form of serinal. The cross coupling of *N*-Cbz-*O*-TBS-L-serinal (**3n**) and *n*-pentadecanal gave **4n**, a derivative of *xylo*-D-C_{18}-phytosphingosine, as one diastereomer (>20:1). A deprotected epimer of **4n**, *ribo*-D-C_{18}-phytosphingosine, is found in plants as the amides of α-hydroxy long-chain acids[31] and in human brain and kidney tissues as a component of the sphingolipids.[32] Several syntheses of optically active *ribo*-D-C_{18}-phytosphingosine have been described, starting from *erythro*-D-C_{18}-sphingosine,[33] sugars,[34] and small chiral aldehydes.[35] In addition to its novelty, several practical aspects of the synthesis of **4n** by cross coupling are noteworthy. Via cross coupling, several grams of **4n** were prepared in five steps and 58% yield from L-serine methyl ester hydrochloride. The only purification step in this sequence was chromatography of the final product.

Diastereoselective cross coupling of aldehydes requires discrimination of the faces of both reacting aldehydes. Differentiation of the faces of **3** and the aliphatic aldehyde during cross coupling may be controlled by how the aldehydes coordinate to vanadium. Assuming that **3** forms a chelate with vanadium, the reacting face of this aldehyde is determined by coordination of the aliphatic aldehyde on the less-hindered side of the chelate. The reacting face of the aliphatic aldehyde is determined by orientation of its alkyl substituent away from the chelate. A bidentate mode of chelation through both carbonyl oxygens of **3** is commonly assumed (Chart 1). However, one can also write a tridentate chelate (Chart 1) for 2-[*N*-(alkoxycarbonyl)amino] aldehydes bearing an NH group, if one assumes that deprotonation of the N–H is possible (*e.g.* by V(III) alkoxides generated during the course of these reactions). Vanadium complexes containing the four membered heterocyclic core in such a tridentate chelate have been structurally characterized.[36]

In summary, we have described a method that allows one to generate *syn,syn*-3-[*N*-(alkoxycarbonyl)amino] 1,2-diols from enantiomerically pure 2-amino aldehydes via a pinacol cross-coupling reaction. The practical experimental conditions along with the high selectivities of these reactions should find utility in many areas of organic synthesis. In the future, we will report on further applications of this coupling chemistry along with a method for selectively inverting either hydroxyl group in these products.

Experimental Section

General Methods. Melting points are uncorrected. Solvents used in moisture-sensitive reactions were dried using standard methods. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium–benzophenone ketyl. Dichloromethane (CH_2Cl_2) was distilled from CaH_2. Triethylamine (Et_3N) was distilled and stored over molecular sieves prior to use. Dimethyl sulfoxide (DMSO) was used directly from Aldrich Sure Seal bottles. Air-sensitive reactions were kept under N_2. The term "concentrated" refers to the removal of solvent using a rotary evaporator (15 Torr at 25 °C) and then using a high vacumm line (<0.5 Torr at 25 °C) until a constant weight was obtained. Thin-layer chromotography (TLC) was preformed using precoated Kieselgel 60 F-254 plates. Flash chromatography was performed using EM Science Silica Gel 60 (230–400 mesh). NMR spectra were obtained using a Bruker AM-400 or AM-500 spectrometry. ^1H NMR chemical shifts are reported in ppm relative to solvent resonance: $CDCl_3$, δ 7.24; $(CD_3)_2SO$, δ 2.49. Coupling constants (*J*) are reported in Hz. $^{13}C\{^1H\}$ NMR chemical shifts are reported in ppm relative to solvent resonance: $CDCl_3$, δ 77.0; $(CD_3)_2SO$, δ 39.5. Fast-atom bombardment mass spectra (FABMS) were performed using 3-nitrobenzyl alcohol (NBA) or thioglycerol/glycerol (TG/G) as the matrix. Optical rotation concentrations (*c*) are reported in g/100 mL. Elemental analyses were performed by the Microanalytical Laboratory at University of California, Berkeley, CA.

2-Amino Alcohols. Amino alcohols were either purchased or made from the corresponding amino acid by adapting the procedure of Giannis and Sandhoff.[11] The crude amino alcohols were *N*-protected without any further purification.

[*N*-(*tert*-Butoxycarbonyl)-2-amino]Alcohols (2a,c) (adapted from the procedure of Luly et al.[13]). To a stirring solution of 2-amino alcohol (10 mmol) in $HCCl_3$ (15 mL) was added di-*tert*-butyl dicarbonate (2.2 g, 10 mmol) in $HCCl_3$ (5 mL) over 5 min. After 4 h the reaction mixture was concentrated. The residue was dissolved in Et_2O (40 mL), which was washed with 0.5 M H_3PO_4 (10 mL), saturated NaCl (10 mL), saturated $NaHCO_3$ (10 mL), and saturated NaCl (10 mL), dried ($MgSO_4$), filtered, and concentrated to give *N*-Boc-2-amino alcohols in 90–100% mass recovery.

[*N*-(Benzyloxycarbonyl)-, [*N*-(Allyloxycarbonyl)-, and [*N*-(Methoxycarbonyl)-2-amino] Alcohols (2b,d–f,l,o–r). To a stirring solution of 2-amino alcohol (10 mmol) and K_2CO_3 (3.3 g, 20 mmol) in THF (10 mL) and H_2O (10 mL) at 0 °C was added alkyl chloroformate (11 mmol) dropwise over 5 min. After the mixture was stirred for 10 min, the ice bath was removed and stirring was continued for 2 h. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organics were washed with 1 M HCl (10 mL), saturated $NaHCO_3$ (10 mL), and saturated NaCl (10 mL), dried ($MgSO_4$), filtered, and concentrated to give [*N*-(alkoxycarbonyl)-2-amino] alcohols in 90–100% mass recovery.

Although [*N*-(alkoxycarbonyl)-2-amino] alcohols were typically obtained in high purity, recrystallization or chromatography was performed if ^1H or ^{13}C NMR spectra showed any impurities. ^1H and ^{13}C NMR spectra were consistent with formulated structures and/or the literature (see literature for more complete physical data of alcohols: **2a**,[37] **b**,[38,39] **c**,[13,37,39,40] **d**,[39–41] **l**,[42] **o**,[41] **p**,[43] **q**,[40,44] **r**[45]).

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NMR Data for [N-(Alkoxycarbonyl)amino] Alcohols in Cases Where ^{1}H and/or ^{13}C NMR Data Were Not Previously Reported. (2a): $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 18.4, 19.5, 28.3, 29.3, 58.0, 64.1, 79.5, 156.8. **(2c)**: $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 28.3, 37.4, 53.6, 64.0, 79.6, 126.4, 128.4, 129.3, 137.8, 156.1. **(2e)**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.70 (s, 1H), 2.84 (d, J = 7.1, 2H), 3.53 (dd, J = 5.0, 11.0, 1H), 3.63 (dd, J = 3.9, 11.1, 1H), 3.91 (br, 1H), 4.50 (d, J = 5.6, 2H), 5.14 (br, 1H), 5.17 (dd, J = 1.3, 10.4, 1H), 5.24 (dd, J = 1.5, 17.2, 1H), 5.85 (octet, J = 5.5, 1H), 7.18–7.30 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 37.3, 54.0, 63.7, 65.6, 117.7, 126.5, 128.5, 129.2, 132.6, 137.6, 156.3. **(2f)**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.83 (m, 1H), 2.83 (d, J = 7.2, 2H), 3.52 (dd, J = 5.1, 11.1, 1H), 3.60 (s, 3H), 3.62 (dd, J = 3.9, 11.2, 1H), 3.89 (br, 1H), 5.15 (br, 1H), 7.17–7.32 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 37.3, 52.1, 54.1, 63.7, 126.5, 128.5, 129.2, 137.6, 157.2. **(2l)**: $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 51.9, 62.4, 66.5, 69.5, 73.0, 127.4, 127.7, 127.8, 128.1, 128.2, 128.4, 136.1, 137.5, 156.3. **(2r)**: ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C) δ 1.66 (br, 1H), 1.79 (m, J = 6.3, 1H), 1.82 (m, J = 6.8, 1H), 1.99 (dq, J_d = 12.4, J_q = 7.3, 1H), 3.03 (br, 1H), 3.35–3.41 (m, 1H), 3.50–3.60 (m, 1H), 3.62 (m, 2H), 3.97 (m, 1H), 5.127 (s, 1H), 5.132 (s, 1H), 7.26–7.35 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 50 °C) δ 23.9, 28.6, 47.3, 60.6 (br), 66.5 (br), 67.2, 127.9, 128.0, 128.5, 136.7.

N,N-Bis-Cbz-L-lysinol (2k). To a stirring solution of L-lysine ethyl ester dihydrochloride (7.00 g, 28.3 mmol) and K_2CO_3 (28.08 g, 170 mmol) in H_2O (120 mL) at 0 °C was added benzyl chloroformate (10.11 mL, 12.08 g, 70.8 mmol) dropwise over 5 min. After the mixture was stirred for 10 min, the ice bath was removed and stirring was continued for 20 h. The layers were separated, and the aqueous layer was extracted with Et_2O (2 × 75 mL). The combined organics were washed with 10% tartaric acid (40 mL), H_2O (40 mL), saturated $NaHCO_3$ (40 mL), and saturated NaCl (40 mL), dried ($MgSO_4$), filtered, and concentrated to give 14.00 g of a clear oil. The clear oil and $CaCl_2$ (6.28 g, 56.6 mmol) were dissolved in THF (40 mL) and EtOH (60 mL), and the solution was cooled to 0 °C. While stirring, $NaBH_4$ (4.28 g, 113.2 mmol) was carefully added. The reaction was stirred for 20 h while slowly warming to room temperature. The excess $NaBH_4$ was quenched by slow addition (foaming!) of 10% tartaric acid (140 mL), and the mixture was extracted with Et_2O (200 mL, then 100 mL). The combined organics were washed with saturated $NaHCO_3$ (70 mL) and saturated NaCl (70 mL), dried (MgSO4), filtered, and concentrated to give 12.05 g of a clear oil (with some solid). The oil was purified by chromatography on silica gel using an eluant gradient (50%, 67%, 84%, 100% EtOAc in hexanes) to give 10.04 g (89%) of **2k** as an amorphous solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (m, 2H), 1.45 (m, 4H), 2.77 (br, 1H), 3.13 (br, 2H), 3.50 (dd, J = 4.2, 10.4, 1H), 3.59 (dd, J = 3.0, 13.9, 1H), 3.64 (br, 1H), 5.00 (br, 1H), 5.05 (s, 4H), 5.23 (br, 1H), 7.29 (s, 10H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 22.6, 29.6, 30.5, 40.2, 52.8, 64.9, 66.6, 66.7, 127.99, 128.01, 128.05, 128.4, 136.4, 136.5, 156.7.

N-Cbz-L-serine Methyl Ester. To a 0 °C solution of L-serine methyl ester hydrochloride (5.00 g, 32.1 mmol) and K_2CO_3·1.5 H_2O (15.9 g, 96.4 mmol) in H_2O (25 mL) was added a solution of benzyl chloroformate (5.05 mL, 6.03 g, 35.4 mmol) in THF (25 mL). The two phases were stirred vigorously together for 4 h while warming to room temperature, and then hexanes (25 mL) was added. The two phases were separated, and the aqueous layer was extracted with Et_2O (2 × 25 mL). The combined organic layers were washed with 5% citric acid (25 mL) and saturated NaCl (25 mL), dried ($MgSO_4$), filtered, and concentrated, to give 8.17 g (mass recovery 100%) of a clear oil. On the basis of TLC and ^{1}H NMR spectroscopy, the crude product was judged pure enough for use in the next step without purification. An analytical sample was purified by flash chromatography on silica gel using EtOAc/hexanes: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.03 (br, 1H), 3.75 (s, 3H), 3.89 (dd, J = 2.5, 11.0, 1H), 3.97 (dd, J = 2.7, 10.9, 1H), 4.43 (t, J = 3.7, 1H), 5.10 (s, 2H), 5.79 (d, J = 6.7, 1H), 7.34–7.29 (m, 5H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 52.7, 56.0, 63.2, 67.2, 128.1, 128.2, 128.5, 136.0, 156.2, 171.0; EIMS m/z 253 (M^+, 4), 194 (11), 162 (28), 150 (24), 132 (8), 108 (83), 91 (100); $[\alpha]^{20}_D$ +7.4° (c 1.99, $CHCl_3$). Anal. Calcd for $C_{12}H_{15}NO_5$: C, 56.91; H, 5.97; N, 5.53. Found: C, 57.23; H, 5.92; N, 5.28.

N-Cbz-O-TBS-L-serine Methyl Ester. To a solution of crude N-Cbz-L-serine methyl ester (7.97 g, 31.3 mmol) and imidazole (2.62 g, 38.5 mmol) in DMF (30 mL) was added *tert*-butyldimethylchlorosilane (5.32 g, 35.3 mmol). The mixture was stirred under an atmosphere of N_2 for 8 h, during which time a solid precipitate formed. The reaction mixture was poured into ice/water (150 mL), and the resulting suspension was sequentially extracted with Et_2O (150 mL) and hexanes (150 mL). The combined organic layers were washed with H_2O (3 × 100 mL) and saturated NaCl (100 mL), dried ($MgSO_4$), filtered, and concentrated, to give 11.00 g (96% from L-serine methyl ester hydrochloride) of a clear oil. On the basis of TLC and ^{1}H NMR spectroscopy, the crude product was judged pure enough for use in the next step without purification. An analytical sample was purified by flash chromatography on silica gel using EtOAc/hexanes: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.00 (s, 3H), 0.01 (s, 3H), 0.84 (s, 9H), 3.73 (s, 3H), 3.83 (dd, J = 2.9, 10.0, 1H), 4.06 (dd, J = 2.4, 10.0, 1H), 4.42 (m, 1H), 5.10 (d, J = 12.2, 1H), 5.14 (d, J = 12.2, 1H), 5.60 (d, J = 8.1, 1H), 7.37–7.31 (m, 5H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ −5.7, −5.6, 18.1, 25.6, 52.3, 55.9, 63.6, 67.0, 128.11, 128.15, 128.5, 136.2, 155.9, 170.9; EIMS m/z 367 (M^+, 3), 352 (5), 337 (13), 310 (55), 266 (30), 234 (34), 202 (36), 174 (67), 91 (100); $[\alpha]^{20}_D$ +18.6° (c 2.27, $CHCl_3$). Anal. Calcd for $C_{18}H_{29}NO_5Si$: C, 58.83; H, 7.95; N, 3.81. Found: C, 58.50; H, 7.90; N, 4.03.

N-Cbz-O-TBS-L-serinol (2n). To a 0 °C solution of crude N-Cbz-O-TBS-L-serine methyl ester (10.80 g, 30.3 mmol) and $CaCl_2$ (7.13 g, 64.2 mmol) in THF (40 mL) and absolute ethanol (60 mL) was added $NaBH_4$ (4.86 g, 128.4 mmol). The mixture was stirred under an atmosphere of N_2 for 3 h while warming to room temperature and then slowly poured into 5% citric acid (200 mL) at 0 °C, causing the evolution of much gas. The resulting suspension was extracted with Et_2O (2 × 150 mL), and the combined organic layers were washed with saturated $NaHCO_3$ (2 × 75 mL), H_2O (2 × 75 mL), and saturated NaCl (75 mL), dried ($MgSO_4$), filtered, and concentrated to give 9.43 g (mass recovery 94% from N-Cbz-O-TBS-L-serinol, 90% from L-serine methyl ester hydrochloride) of **2n** as a clear oil. On the basis of TLC and ^{1}H NMR spectroscopy, the crude product was judged pure enough for use in the next step without purification. An analytical sample was purified by flash chromatography on silica gel using EtOAc/hexanes: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.04 (s, 3H), 0.05 (s, 3H), 0.87 (s, 9H), 2.27 (br, 1H), 3.69 (dd, J = 10.8, 4.3, 1H), 3.72 (m, 1H), 3.77 (dd, J = 10.8, 3.0, 1H), 3.81 (dd, J = 10.2, 2.7, 1H), 3.84 (dd, J = 10.6, 2.7, 1H), 5.10 (s, 2H), 5.39 (d, J = 6.0, 1H), 7.35–7.31 (m, 5H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ −5.63, −5.61, 18.1, 25.8, 52.9, 63.8, 63.9, 66.8, 128.10, 128.14, 128.5, 136.3, 156.4; EIMS m/z 339 (M^+, 4), 308 (47), 282 (45), 264 (22), 238 (35), 174 (53), 131 (62), 120 (31), 108 (50), 101 (62), 91 (100); $[\alpha]^{20}_D$ +14.9° (c 2.15, $CHCl_3$). Anal. Calcd for $C_{17}H_{29}NO_4Si$: C, 60.14; H, 8.61; N, 4.13. Found: C, 59.92; H, 8.59; N, 4.11.

(S)-2-[N-(Alkoxycarbonyl)amino] Aldehydes (3, except 3o) (adapted from the procedure of Luly et al.[13]). To a stirred solution of oxalyl chloride (1.31 mL, 15.0 mmol) in dry CH_2Cl_2 (30 mL) at −63 °C (dry ice/$CHCl_3$) was added a solution of dry DMSO (1.42 mL, 20.0 mmol) in CH_2Cl_2 (30 mL) over 10 min. Immediately following, a solution of 10.0 mmol of (S)-2-[N-(alkoxycarbonyl)amino] alcohol (**2**) in CH_2Cl_2 (40 mL) was added over 10 min, resulting in a cloudy solution which was stirred for 20 min. Triethylamine (5.58 mL, 40.0 mmol) was then added over 5 min, generating first a clear solution and then a precipitate after stirring for 20 min at −63 °C. At this point TLC of the reaction showed no starting material. After the cooling bath was removed, 20% saturated $KHSO_4$ (40 mL) and hexanes (115 mL) were added, and the resulting mixture was stirred vigorously while warming, generating two phases. The layers were separated, and the aqueous phase was extracted with Et_2O (115 mL). The combined organic layers were washed with saturated $NaHCO_3$ (2 × 40 mL), H_2O (3 × 40 mL), and saturated NaCl (2 × 40 mL) and then dried ($MgSO_4$), filtered, and concentrated at or below room temperature, giving a white solid or a clear oil. The desired aldehydes were obtained in 95–105% mass recovery and were used immediately without further purification. ^{1}H NMR and ^{13}C NMR spectra of the crude aldehydes were consistent with the formulated structures and/or the literature (see literature for more complete physical data of aldehydes: **3a**,[46] **b**,[47] **c**,[46b] **d**,[39] **k**,[9] **l**,[40] **p**,[48] **q**,[9,49] **r**[9,17,50]).

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NMR Data for [*N*-(Alkoxycarbonyl)amino] Aldehydes in Cases Where ^{1}H and/or ^{13}C NMR Data Were Not Previously Reported. (3a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (d, *J* = 7.0, 3H), 1.03 (d, *J* = 6.9, 3H), 1.45 (s, 9H), 2.29 (sept, *J* = 6.5, 1H), 4.25 (m, 1H), 5.11 (br, 1H), 9.65 (s, 1H). (**3c**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (s, 9H), 3.11 (m, 2H), 4.41 (q, *J* = 6.6, 1H), 5.14 (br, 1H), 7.16–7.33 (m, 5H), 9.62 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 28.2, 35.3, 60.7, 80.0, 126.9, 128.4, 128.6, 129.2, 135.8, 155.3, 199.3. (**3e**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.09 (d, *J* = 6.7, 2H), 4.45 (q, *J* = 6.7, 1H), 4.52 (d, *J* = 5.6, 2H), 5.17 (dd, *J* = 1.3, 10.5, 1H), 5.25 (d, *J* = 17.1, 1H), 5.35 (br d, *J* = 5.4, 1H), 5.85 (octet, *J* = 5.5, 1H), 7.11–7.30 (m, 5H), 9.59 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 35.3, 60.9, 65.8, 117.8, 127.1, 128.7, 129.2, 132.4, 135.5, 155.7, 198.9. (**3f**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.11 (d, *J* = 6.5, 2H), 3.66 (s, 3H), 4.48 (q, 1H), 5.32 (br, 1H), 7.14–7.35 (m, 5H), 9.61 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 35.3, 52.4, 61.0, 127.1, 128.7, 129.2, 156.5, 198.9. (**3l**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (dd, *J* = 4.1, 9.3, 1H), 4.02 (dd, *J* = 3.2, 9.4, 1H), 4.36–4.39 (m, 1H), 4.48 (d, *J* = 6.0, 2H), 5.14 (s, 2H), 5.75 (d, *J* = 6.6, 1H), 7.25–7.36 (m, 10H), 9.62 (s, 1H). (**3n**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.02 (s, 6H), 0.84 (s, 9H), 3.87 (dd, *J* = 4.2, 10.5, 1H), 4.21 (dd, *J* = 3.0, 16.5, 1H), 4.31 (m, 1H), 5.12 (s, 2H), 5.62 (d, *J* = 6.6, 1H), 7.30–7.38 (m, 5H), 9.64 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ −5.71, −5.69, 18.1, 25.6, 61.2, 61.8, 67.0, 128.1, 128.2, 128.5, 136.1, 156.0, 198.8. (**3r**): (1:1 mixture of rotamers) ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.83–2.15 (m, 4H), 3.51–3.61 (m, 2H), 4.20 (m, 0.5H), 4.29 (m, 0.5H), 5.13 (s, 1H), 5.17 (d, *J* = 4.5, 1H), 7.28–7.40 (m, 5H), 9.49 (d, *J* = 1.6, 0.5H), 9.59 (d, *J* = 1.6, 0.5H).

***N*-Cbz-L-Methioninal (3o)**[9] (adapted from the procedure of Hamada et al.[17]). To a stirred solution of 10.0 mmol of *N*-Cbz-L-methioninol (**2o**) and triethylamine (4.18 mL, 30.0 mmol) in dry DMSO (30 mL) was added a solution of sulfur trioxide pyridine complex (4.77 g, 30 mmol) in DMSO (30 mL) over 7 min. The reaction vessel was maintained at 20 °C by immersion in a water bath. Following stirring for 1 h, the reaction solution was poured into saturated NaCl (325 mL) precooled to 0 °C, and the mixture was extracted with Et_2O (3 × 160 mL). The combined organic layers were washed with 5% citric acid (110 mL), H_2O (2 × 110 mL), saturated $NaHCO_3$ (110 mL), and saturated NaCl (110 mL) and then dried ($MgSO_4$), filtered, and concentrated at or below room temperature, giving a clear oil. The desired aldehyde (**3o**) was obtained in 90–100% mass recovery and was used immediately without further purification. ^{1}H NMR spectrum of the crude aldehyde was consistent with the formulated structure. TLC of the products obtained by this procedure typically showed some of the starting *N*-benzyloxycarbonyl-L-methioninol (**2o**).

***syn,syn*-3-[*N*-(Alkoxycarbonyl)amino] 1,2-Diols (4a–t).** Under an atmosphere of N_2, a mixture of $VCl_3(THF)_3$[51] (2.85 g, 7.63 mmol), zinc dust (300 mg, 4.59 mmol), and dry CH_2Cl_2 (40 mL) was stirred vigorously for 30 min to give a green solution. A solution of the aliphatic aldehyde (4.12 mmol) in dry CH_2Cl_2 (10 mL) was added over 1 min, generating a dark-brown solution. With stirring, a solution of 3.75 mmol of the [*N*-alkoxycarbonyl-2-amino] aldehyde **3** in dry CH_2Cl_2 (25 mL) was added dropwise over 45 min. After being stirred for an additional 30 min, the reaction mixture was opened to air and poured into 100 mL of 10% aqueous sodium tartrate (for *N*-Boc-2-amino aldehydes and *N*-Cbz-*O*-TBS-L-serinal) or 100 mL of 1 M HCl (for other [*N*-(alkoxycarbonyl)-2-amino] aldehydes). The two phases were stirred vigorously for 12 h, giving a blue-green aqueous layer and a pale-yellow CH_2Cl_2 layer. The aqueous phase was separated and extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were washed with saturated $NaHCO_3$ (50 mL), dried ($MgSO_4$), filtered, and concentrated, giving a yellow oil. The residue was purified by recrystallization or flash chromatography on silica gel using EtOAc/hexanes.

(3*R*,4*R*,5*S*)-5-[*N*-(*tert*-Butoxycarbonyl)amino]-2,6-dimethylheptane-3,4-diol (4a). Purified by flash chromatography to give 723 mg (70%) of a clear oil: ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 98 °C) δ 0.83 (d, *J* = 6.8, 3H), 0.86 (d, *J* = 6.8, 3H), 0.90 (d, *J* = 6.8, 3H), 0.91 (d, *J* = 6.7, 3H), 1.40 (s, 9H), 1.77–1.87 (m, 2H), 3.11 (dd, *J* = 3.9, 6.7, 1H), 3.24 (ddd, *J* = 2.8, 7.5, 9.7, 1H), 3.48 (dd, *J* = 2.8, 6.7, 1H), 5.49 (br, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2SO$, 98 °C) δ 15.2, 18.1, 19.2, 19.5, 27.7, 28.6, 29.5, 56.6, 70.4, 75.0, 77.1, 155.2; FABMS (TG/G) *m/z* 276 (MH^+, 77), 220 (84), 176 (100); $[\alpha]^{20}_D$ −34° (*c* 0.88, $CHCl_3$). Anal. Calcd for $C_{14}H_{29}NO_4$: C, 61.06; H, 10.61; N, 5.08. Found: C, 60.75; H, 10.43; N, 5.46.

(3*R*,4*R*,5*S*)-5-[*N*-(Benzyloxycarbonyl)amino]-2,6-dimethylheptane-3,4-diol (4b). Purified by flash chromatography to give 882 mg (76%) of a clear oil: ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 98 °C) δ 0.84 (d, *J* = 6.8, 3H), 0.862 (d, *J* = 6.8, 3H), 0.867 (d, *J* = 6.8, 3H), 0.92 (d, *J* = 6.7, 3H), 1.78 (d of sept, J_d = 4.4, J_{sept} = 6.8, 1H), 1.87 (octet, *J* = 6.8, 1H), 3.11 (dd, *J* = 4.4, 6.1, 1H), 3.34 (ddd, *J* = 3.3, 7.2, 9.7, 1H), 3.52 (dd, *J* = 3.3, 6.1, 1H), 5.03 (d, *J* = 12.7, 1H), 5.07 (d, *J* = 12.8, 1H), 6.02 (br, 1H), 7.27–7.34 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2SO$, 98 °C) δ 15.6, 17.9, 19.2, 19.4, 28.9, 29.3, 57.4, 64.8, 70.2, 74.9, 126.8, 126.9, 127.6, 137.0, 155.9; FABMS (NBA) *m/z* 310 (MH^+, 100), 266 (78), 176 (16); $[\alpha]^{20}_D$ −22.6° (*c* 1.25, $CHCl_3$). Anal. Calcd for $C_{17}H_{27}NO_4$: C, 65.99; H, 8.80; N, 4.53. Found: C, 65.64; H, 8.88; N, 4.49.

(2*S*,3*R*,4*R*)-2-[*N*-(*tert*-Butoxycarbonyl)amino]-6-methyl-1-phenylheptane-3,4-diol (4c). Purified by flash chromatography and lyophilized from benzene to give 541 mg (67%) of a white solid: mp 37–43 °C; R_f 0.30 (7:3 hexane/EtOAc); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 98 °C) δ 0.83 (d, *J* = 6.6, 3H), 0.86 (d, *J* = 6.7, 3H), 1.20 (m, 2H), 1.31 (s, 9H), 1.75 (sept of triplets, J_{sept} = 6.7, J_t = 1.6, 1H), 2.74 (dd, *J* = 13.6, 8.0, 1H), 2.83 (dd, *J* = 13.5, 6.5, 1H), 3.16 (dd, *J* = 2.8, 6.5, 1H), 3.4 (br, 2H), 3.45 (ddd, *J* = 3.6, 6.5, 9.0, 1H), 3.78 (m, 1H), 5.72 (br, 1H), 7.13–7.26 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2SO$, 98 °C) δ 21.1, 23.0, 23.5, 27.6, 38.1, 41.5, 52.6, 69.0, 74.1, 77.1, 125.2, 127.3, 128.6, 138.7; $^{13}C\{^1H\}$ NMR (100 MHz, $DCCl_3$) δ 21.2, 23.7, 24.2, 28.2, 39.1, 41.8, 52.9, 70.8, 74.8, 79.5, 126.3, 128.4, 129.3, 138.1, 155.9; FABMS (NBA) *m/z* 338.3 (MH^+, 32), 282.2 (44), 238.2 (100); $[\alpha]^{20}_D$ −22.3° (*c* 1.95, $CHCl_3$). Anal. Calcd for $C_{19}H_{31}NO_4$: C, 67.63; H, 9.26; N, 4.15. Found: C, 67.34; H, 9.23; N, 4.17.

(2*S*,3*R*,4*R*)-2-[*N*-(Benzyloxycarbonyl)amino]-6-methyl-1-phenylheptane-3,4-diol (4d). Purified by flash chromatography to give 2.29 g (74%) of a white solid: mp 113.5–114 °C; R_f 0.23 (7:3 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (d, *J* = 6.5, 3H), 0.87 (d, *J* = 6.6, 3H), 1.22 (m, 2H), 1.73 (sept, *J* = 6.7, 1H), 2.89 (d, *J* = 7.5, 2H), 3.1 (br, 1H), 3.25 (d, *J* = 6.9, 1H), 3.59 (m, 1H), 3.96 (m, 1H), 5.03 (s, 2H), 5.40 (d, *J* = 9.1, 1H), 7.16–7.34 (m, 10H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 21.2, 23.7, 24.2, 38.9, 41.8, 53.4, 66.7, 70.7, 74.5, 126.4, 127.9, 128.0, 128.4, 129.2, 136.4, 137.8, 156.3; IR (film) 3449, 3361, 3238, 2957, 1685, 1527, 1252, 1047 cm^{-1}; FABMS (NBA) *m/z* 372.2 (100, MH^+), 354.2 (8), 328.2 (72); $[\alpha]^{20}_D$ −19.3° (*c* 6.00, $CHCl_3$); FAB HRMS *m/z* calcd for $C_{22}H_{30}NO_4^+$ 372.2175, found 372.2174.

(2*S*,3*R*,4*R*)-2-[*N*-(Allyloxycarbonyl)amino]-6-methyl-1-phenylheptane-3,4-diol (4e). Purified by recrystallization from THF/hexanes to give 1.218 g (80%) of a white solid: mp 83–85 °C; R_f 0.31 (7:3 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (d, *J* = 6.4, 3H), 0.88 (d, *J* = 6.6, 3H), 1.22 (t, *J* = 6.4, 2H), 1.74 (sept, *J* = 6.6, 1H), 2.75 (br, 2H), 2.90 (d, *J* = 7.5, 2H), 3.26 (dd, *J* = 1.8, 7.0, 1H), 3.60 (q, *J* = 6.6, 1H), 3.92 (m, 1H), 4.49 (d, *J* = 6.4, 2H), 5.19 (m, 3H), 5.83 (m, 1H), 7.17–7.29 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 21.3, 23.7, 24.3, 39.0, 42.0, 53.5, 65.6, 70.8, 74.5, 117.6, 126.5, 128.5, 129.3, 132.7, 137.9, 156.3; $[\alpha]^{20}_D$ −13.6° (*c* 1.4, THF). Anal. Calcd for $C_{18}H_{27}NO_4$: C, 67.26; H, 8.47; N, 4.36. Found: C, 67.38; H, 8.41; N, 4.44.

(2*S*,3*R*,4*R*)-2-[*N*-(Methoxycarbonyl)amino]-6-methyl-1-phenylheptane-3,4-diol (4f). Purified by recrystallization from THF/hexanes to give 159 mg (84%) of a white solid: mp 89–90 °C; R_f 0.53 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (d, *J* = 6.4, 3H), 0.87 (d, *J* = 6.7, 3H), 1.22 (t, *J* = 6.6, 2H), 1.74 (sept, *J* = 6.5, 1H), 2.89 (d, *J* = 7.5, 2H), 3.01 (br, 2H), 3.25 (d, *J* = 6.9, 1H), 3.59 (s, 3H), 3.91 (m, 1H), 5.32 (br, 1H), 7.16–7.28 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 21.3, 23.7, 24.3, 38.9, 41.9, 52.2, 70.7, 74.4, 126.5, 128.5, 129.3, 137.9, 157.1; FABMS (TG/G) *m/z* 296.1 (100, MH^+), 278.1 (34), 238.1 (20), 178.1 (95); $[\alpha]^{20}_D$ −17.8° (*c* 2.30, $CHCl_3$). Anal. Calcd for $C_{22}H_{29}NO_4$: C, 65.06; H, 8.53; N, 4.74. Found: C, 65.25; H, 8.60; N, 4.63.

(2*R*,3*S*,4*S*)-2-[*N*-(*tert*-Butoxycarbonyl)amino]-1,6-diphenylhexane-3,4-diol (4g). Purified by flash chromatography to give 969 mg (67%) of a white solid: mp 127.5–128.5 °C; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 98 °C) δ 1.30 (s, 9H), 1.50–1.60 (m, 1H), 1.75–1.84 (m, 1H), 2.55 (ddd, *J* = 6.3, 9.9, 13.9, 1H), 2.68 (ddd, *J* = 5.4, 10.2, 14.5, 1H), 2.73 (dd, *J* = 7.9, 13.6, 1H), 2.83 (dd, *J* = 6.5, 13.6, 1H), 3.27 (dd, *J* = 3.0, 6.3, 1H), 3.44 (ddd, *J* = 3.6, 6.2, 8.4, 1H), 3.78–3.85 (m, 1H), 5.71 (br, 1H), 7.11–7.26 (m, 10H); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2SO$, 98 °C) δ 27.7, 31.0, 34.2, 38.2, 52.9, 70.5, 73.6, 77.4, 124.9, 125.3, 127.4, 127.5, 127.6, 128.7, 138.7, 142.0, 154.7; FABMS (TG/G) *m/z* 386 (MH^+, 15), 330 (13), 312 (6), 286 (95), 268 (8), 164 (15), 133 (100), 120 (43); $[\alpha]^{20}_D$ +11.0° (*c* 4.22, $CHCl_3$). Anal. Calcd for $C_{23}H_{31}NO_4$: C, 71.66; H, 8.10; N, 3.63. Found: C, 71.82; H, 8.06; N, 3.65.

(2*S*,3*R*,4*R*)-2-[*N*-(Benzyloxycarbonyl)amino]-1,6-diphenylhexane-3,4-diol (4h). Purified by recrystallization from THF/hexanes to give in two crops 1.23 g (78%) of a white solid: mp 148–150 °C; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 98 °C) δ 1.53–1.63 (m, 1H), 1.76–1.84 (m, 1H), 2.54

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(ddd, J = 6.5, 9.9, 13.8, 1H), 2.67 (ddd, J = 5.4, 10.1, 13.8, 1H), 2.76 (dd, J = 8.1, 13.6, 1H), 2.78 (dd, J = 6.3, 13.6, 1H), 3.31 (dd, J = 3.3, 5.8, 1H), 3.46 (ddd, J = 3.8, 5.9, J = 8.3, 1H), 3.86–3.92 (m, 1H), 4.95 (s, 2H), 6.29 (br, 1H), 7.11–7.33 (m, 15H); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2SO$, 98 °C) δ 30.8, 34.2, 37.6, 53.6, 64.7, 70.1, 73.3, 124.8, 125.2, 126.7, 126.9, 127.4, 127.48, 127.56, 127.6, 136.8, 138.6, 141.8, 155.2; FABMS (NBA) m/z 420 (MH$^+$, 83), 376 (42), 307 (22), 154 (100), 137 (60); $[\alpha]^{20}_D$ −7.83° (c 1.09, THF). Anal. Calcd for $C_{26}H_{29}NO_4$: C, 74.44; H, 6.97; N, 3.34. Found: C, 74.16; H, 6.93; N, 3.20.

(2*R*,3*S*,4*S*)-2-[*N*-(Allyloxycarbonyl)amino]-1,6-diphenylhexane-3,4-diol (4i). Purified by flash chromatography to give 710.6 mg (77%) of a white solid: mp 100.5–101 °C; R_f 0.13 (7:3 hexane/EtOAc); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 98 °C) δ 1.55–1.65 (m, 1H), 1.77–1.85 (m, 1H), 2.58 (ddd, J = 6.6, 9.8, 13.8, 1H), 2.69 (ddd, J = 5.4, 10.1, 13.7, 1H), 2.78 (dd, J = 8.0, 13.6, 1H), 2.89 (dd, J = 6.5, 13.6, 1H), 3.33 (dd, J = 3.2, 5.9, 1H), 3.48 (ddd, J = 2.9, 5.9, 8.3, 1H), 3.75 (br, 2H), 3.83–3.92 (m, 1H), 4.40 (d, J = 5.3, 2H), 5.11 (dd, J = 1.5, 10.5, 1H), 5.20 (dd, J = 1.6, 17.3, 1H), 5.82 (octet, J = 5.5, 1H), 6.21 (br, 1H), 7.10–7.28 (m, 10H); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2SO$, 98 °C) δ 30.8, 34.2, 37.7, 53.5, 63.7, 70.2, 73.3, 116.0, 124.8, 125.3, 127.4, 127.5, 127.6, 128.6, 133.2, 138.6, 141.9, 155.1; FABMS (NBA) m/z 370.2 (MH$^+$, 100), 352.2 (24), 308.2 (8), 204.1 (45); $[\alpha]^{20}_D$ −6.12 ° (c 1.65, THF). Anal. Calcd for $C_{22}HNO_4$: C, 71.52; H, 7.37; N, 3.79. Found: C, 71.83; H, 7.59; N, 3.85.

(2*R*,3*S*,4*S*)-2-[*N*-(Methoxycarbonyl)amino]-1,6-diphenylhexane-3,4-diol (4j). Purified by recrystallization (ether/hexanes) to give 604.8 mg (83%) of a white solid: mp 136.5–137 °C; R_f 0.15 (7:3 hexane/EtOAc); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 95 °C) δ 1.51–1.60 (m, 1H), 1.73–1.82 (m, 1H), 2.55 (ddd, J = 6.6, 9.6, 13.8, 1H), 2.65 (ddd, J = 5.4, 9.9, 13.8, 1H), 2.73 (dd, J = 8.0, 13.6, 1H), 2.85 (dd, J = 6.5, 13.6, 1H), 3.0 (br, 1H), 3.27 (dd, J = 3.3, 5.9, 1H), 3.40–3.45 (m, 1H), 3.45 (s, 3H), 3.80–3.86 (m, 1H), 6.15 (br, 1H), 7.11–7.27 (m, 10H); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2SO$, 95 °C) δ 30.8, 34.3, 37.7, 50.6, 53.6, 70.1, 73.3, 124.9, 125.3, 127.46, 127.57, 127.65, 128.6, 138.7, 141.9, 155.8; FABMS (TG/G) m/z 687.5 (2MH$^+$, 4), 417.3 (20), 366.2 (MNa$^+$, 8), 344.3 (MH$^+$, 88), 326.2 (MH$^+$ − H_2O, 25), 178.1 (100); $[\alpha]^{20}_D$ −3.43 ° (c 1.02, THF). Anal. Calcd for $C_{20}H_{25}NO_4$: C, 69.95; H, 7.34; N, 4.08. Found: C, 69.69; H, 7.46; N, 4.19.

(1*R*,2*R*,3*S*)-1-Cyclohexyl-3,7-bis[*N*-(benzyloxycarbonyl)amino]heptane-1,2-diol (4k). Purified by recrystallization from THF/hexanes to give in two crops 1.44 g (75%) of a white solid: mp 135–137 °C; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 98 °C) δ 1.04–1.73 (m, 17H), 3.03–2.97 (m, 2H), 3.14 (t, J = 5.0, 1H), 3.41 (t, J = 4.5, 1H), 3.52–3.59 (m, 1H), 5.01 (d, J = 12.7, 1H), 5.02 (s, 2H), 5.06 (d, J = 12.7, 1H), 6.17 (br, 1H), 6.67 (br, 1H), 7.25–7.39 (m, 10H); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2SO$, 98 °C) δ 22.4, 25.2, 25.4, 25.7, 26.8, 28.9, 29.0, 30.7, 40.0, 52.9, 64.7, 71.2, 73.7, 126.8, 126.90, 126.93, 126.96, 127.60, 127.64, 136.95, 136.98, 155.5, 155.6; FABMS (NBA) m/z 513 (MH$^+$, 100), 469 (74), 379 (23), 361 (22), 218 (33), 174 (40), 154 (50), 136 (41); $[\alpha]^{20}_D$ −2.93° (c 1.29, THF). Anal. Calcd for $C_{29}H_{40}N_2O_6$: C, 67.94; H, 7.86; N, 5.46. Found: C, 67.70; H, 7.77; N, 5.31.

(2*S*,3*R*,4*R*)-1-(Benzyloxy)-2-[*N*-(benzyloxycarbonyl)amino]-6-phenylhexane-3,4-diol (4l). Purified from a crude mixture that contained a 7:1 mixture of diastereomers by flash chromatography to give 498 mg (47%) of a white solid. An analytical sample was obtained by recrystallization from EtOAc/hexane: mp 97–99 °C; R_f 0.50 (8:2 CH_2Cl_2/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74–1.90 (m, 2H), 2.5 (br, 1H), 2.61–2.68 (m, 1H), 2.76–2.83 (m, 1H), 3.55–3.66 (m, 4H), 3.91 (d, J = 4.1, 1H), 4.48 (d, J = 7.6, 2H), 5.07 (d, J = 2.7, 2H), 5.36 (d, J = 8.8, 1H), 7.13–7.35 (m, 15H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 31.6, 34.6, 51.7, 66.9, 70.7, 70.8, 73.4, 74.0, 125.7, 127.6, 127.9, 128.0, 128.1, 128.3, 128.38, 128.43, 136.2, 137.3, 141.8, 156.5; FABMS (NBA) m/z 450.2 (MH$^+$, 100), 406.2 (56); $[\alpha]^{20}_D$ 24.4° (c 1.62, $CHCl_3$). Anal. Calcd for $C_{27}H_{31}NO_5$: C, 72.14; H, 6.95; N, 3.12. Found: C, 72.26; H, 7.12; N, 3.38. A minor diastereomer was isolated to give 69 mg (7%) of an oil: R_f 0.58 (8:2 CH_2Cl_2/EtOAc)

(2*S*,3*R*,4*R*)-1-(Benzyloxy)-2-[*N*-(benzyloxycarbonyl)amino]hexadecane-3,4-diol (4m). Purified by flash chromatography to give 280 mg (41%) of a white solid. An analytical sample was obtained by recrystallization from MeOH/H_2O: mp 76–78 °C; R_f 0.26 (7:3 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 6.8, 3H), 1.27 (s, 20H), 1.48 (m, 2H), 3.03 (br, 1H), 3.55–3.70 (m, 4H), 3.95 (br, 1H), 4.52 (dd, J = 8.2, 11.8, 2H), 5.11 (s, 2H), 5.50 (d, J = 8.9, 1H), 7.27–7.37 (m, 10H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 25.4, 29.3, 29.57, 29.59, 29.62, 29.64, 31.9, 33.2, 51.7, 66.9, 71.0, 71.5, 73.5, 74.1, 127.7, 127.90, 127.97, 128.09, 128.46, 128.47, 136.3, 137.4, 156.5; $[\alpha]^{20}_D$ +17.4° (c 3.12, $CHCl_3$). Anal. Calcd for $C_{31}H_{45}NO_5$: C, 72.48; H, 9.22; N, 2.73. Found: C, 72.17; H, 9.12; N, 2.78.

(2*S*,3*R*,4*R*)-2-[*N*-(Benzyloxycarbonyl)amino]-1-(*tert*-butyldimethylsiloxy)octadecane-3,4-diol (4n). Purified by flash chromatography to give 1.23 g (58% from L-serine methyl ester hydrochloride) of a pale-yellow oil: ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 0.01 (s, 6H), 0.82–0.85 (m, 12H), 1.12–1.41 (m, 26H), 3.30 (br, 2H), 3.39 (br, 1H), 3.48 (dd, J = 8.9, 12.9, 1H), 3.61 (d, J = 6, 2H), 4.30 (m, 1H), 4.97 (d, J = 12.7, 1H), 5.03 (d, J = 12.6, 1H), 6.59 (d, J = 7.8, 1H), 7.27–7.34 (m, 5H); $^{13}C\{^1H\}$ NMR (125 MHz, $(CD_3)_2SO$) δ −5.5, 13.8, 17.8, 22.1, 24.9, 25.6, 28.7, 29.1, 31.3, 32.7, 53.9, 62.4, 65.1, 70.5, 71.1, 127.4, 127.6, 128.2, 137.2, 155.9; FABMS (NBA) m/z 566 (MH$^+$, 93), 548 (15), 522 (100), 508 (45), 432 (34), 264 (22), 174 (39), 116 (41); $[\alpha]^{20}_D$ +20.7° (c 2.36, $CHCl_3$). Anal. Calcd for $C_{32}H_{59}NO_5Si$: C, 67.92; H, 10.51; N, 2.47. Found: C, 67.69 H, 10.11; N, 2.45.

(3*S*,4*R*,5*R*)-3-[*N*-(Benzyloxycarbonyl)amino]-1-(methylthio)decane-4,5-diol (4o). Purified by flash chromatography to give 859 mg (62%) of a white solid: mp 84–85 °C; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 98 °C) δ 0.87 (t, J = 6.9, 3H), 1.21–1.51 (m, 8H), 1.71–1.86 (m, 2H), 2.04 (s, 3H), 2.41–2.53 (m, 2H), 3.26 (dd, J = 3.7, 5.5, 1H), 3.38 (ddd, J = 3.8, 5.6, 7.7, 1H), 3.69–3.76 (m, 1H), 5.02 (d, J = 12.7, 1H), 5.07 (d, J = 12.7, 1H), 6.24 (br, 1H), 7.27–7.34 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2SO$, 98 °C) δ 13.0, 21.3, 24.2, 29.9, 30.7, 31.6, 32.5, 51.5, 64.8, 70.3, 74.0, 126.8, 126.9, 127.6, 136.9, 155.5; FABMS (NBA) m/z 370 (MH$^+$, 100), 232 (24), 154 (75), 136 (52); $[\alpha]^{20}_D$ +6.01° (c 1.48, $CHCl_3$). Anal. Calcd for $C_{19}H_{31}NO_4S$: C, 61.76; H, 8.46; N, 3.79. Found: C, 61.85; H, 8.55; N, 3.56.

(3,4-*syn*)-2-[*N*-(Benzyloxycarbonyl)amino]-2-methylundecane-3,4-diol (4p). Purified by flash chromatography to give 1.16 g (88%) of a white solid: mp 57–58 °C; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 98 °C) δ 0.88 (t, J = 6.9, 3H), 1.28–1.46 (m, 18H), 3.34 (s, 1H), 3.66 (t, J = 6.0, 1H), 4.96 (d, J = 12.7, 1H), 5.00 (d, J = 12.7, 1H), 6.45 (br, 1H), 7.27–7.36 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2SO$, 98 °C) δ 13.0, 21.4, 22.9, 23.4, 24.7, 28.0, 28.4, 30.6, 35.3, 55.6, 64.3, 68.2, 75.4, 126.9, 127.6, 137.0, 154.2; FABMS (TG/G) m/z 352 (MH$^+$, 63), 308 (24), 244 (10), 218 (100), 192 (18), 181 (17), 152 (90), 148 (30), 127 (22), 105 (31), 102 (36). Anal. Calcd for $C_{20}H_{33}NO_4$: C, 68.35; H, 9.46; N, 3.98. Found: C, 68.25; H, 9.42; N, 4.00.

(2*S*,3*R*,4*R*)-2-[*N*-(Benzyloxycarbonyl)amino]-6-phenylhexane-3,4-diol (4q). Purified from a crude mixture that contained a 10:1:1 mixture of diastereomers by flash chromatography to give 583.5 mg (68%) of a white solid. An analytical sample was obtained by recrystallization from THF/hexane: mp 93.5–94 °C; R_f 0.15 (7:3 hexane/EtOAc); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 80 °C) δ 1.09 (d, J = 6.7, 3H), 1.63–1.84 (m, 2H), 2.55–2.77 (m, 2H), 3.08 (br, 1H), 3.23 (q, J = 5.3, 1H), 3.44 (sextet, J = 5, 1H), 3.74 (m, 1H), 4.13 (dd, J = 6.3, 20.8, 1H), 5.03 (d, J = 2.9, 2H), 6.38 (br, 1H), 7.12–7.37 (m, 10H); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2SO$, 80 °C) δ 17.8, 31.2, 34.7, 48.2, 64.8, 69.9, 75.4, 125.0, 127.1, 127.2, 127.7, 127.77, 127.82, 137.0, 142.0, 155.3; FABMS (TG/G) m/z 344.3 (MH$^+$, 40), 300.3 (100), 210.2 (70); $[\alpha]^{20}_D$ +21.5° (c 1.00, $CHCl_3$). Anal. Calcd for $C_{20}H_{33}NO_4$: C, 69.95; H, 7.34; N, 4.08. Found: C, 69.91; H, 7.32; N, 4.05. Two minor diasteomers were isolated to give 69 mg (8%) and 60 mg (7%) as oils: R_f 0.20 and 0.17 (7:3 hexane/EtOAc).

(2*S*)-1-(Benzyloxycarbonyl)-2-[(1*R*,2*R*)-1,2-dihydroxy-4-phenylbutyl]pyrrolidine (4r). Purified by flash chromatography to give 1.18 g (85%) of a clear oil, consisting of a 10:1:1:1 mixture of diastereomers. A pure sample of the major diastereomer was obtained by recrystallization from EtOAc/hexanes: mp 81–82 °C; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 98 °C) δ 1.70–1.78 (m, 3H), 1.79–1.97 (m, 3H), 2.58 (ddd, J = 6.7, 9.5, 14.0, 1H), 2.70 (ddd, J = 6.0, 9.6, 14.0, 1H), 3.25–3.31 (m, 1H), 3.40 (dd, J = 3.3, 6.4, 1H), 3.44 (ddd, J = 3.3, 4.8, 7.8, 1H), 3.48–3.54 (m, 1H), 4.05 (dd, J = 6.4, 10.7, 1H), 5.06 (d, J = 12.8, 1H), 5.10 (d, J = 12.8, 1H), 7.12–7.36 (m, 10H); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2SO$, 98 °C) δ 22.7, 27.0, 31.1, 35.2, 46.2, 59.2, 65.5, 69.2, 74.2, 124.8, 126.8, 127.0, 127.4, 127.5, 127.6, 136.6, 141.9, 155.1; FABMS (NBA) m/z 370 (MH$^+$, 97), 326 (21), 307 (22), 204 (35), 160 (24), 154 (100), 137 (74), 107 (26); $[\alpha]^{20}_D$ −42.4° (c 1.04, CH_3OH). Anal. Calcd for $C_{22}H_{27}NO_4$: C, 71.52; H, 7.37; N, 3.79. Found: C, 71.35; H, 7.28; N, 3.67.

(2*S*)-1-(Benzyloxycarbonyl)-2-[(1*R*,2*R*)-1,2-dihydroxy-4-methylpentyl]pyrrolidine (4s). Purified by flash chromatography to give 1.11 g (92%) of a clear oil, consisting of a 5:1 mixture of diastereomers. A pure sample of the major diastereomer was prepared by hydrolysis and reprotection of **6s**, according to the following procedure. A solution of **6s** (106 mg, 0.338 mmol) and NaOH (135 mg, 3.38 mmol) in a mixture of EtOH (5.0 mL) and water (2.5 mL) was heated to reflux under nitrogen for 12 h. The solution was concentrated to one third the original volume and diluted water (2.0 mL). With stirring, $NaHCO_3$ (284 mg, 3.38 mmol) was added, followed by benzyl chloroformate (72 μL, 0.507 mmol) in Et_2O (2.0 mL). The two phases were stirred vigorously for 2 h and then separated. The aqueous layer was extracted with Et_2O (3 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash chromatography to give 95 mg (87%) of a clear oil: ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 98 °C) δ 0.86 (d, J = 6.5, 3H), 0.87 (d, J = 6.6, 3H), 1.27 (ddd, J = 4.7, 7.9, 13.6, 1H), 1.36 (ddd, J = 5.8, 8.5, 13.6, 1H), 1.68–1.77 (m, 2H), 1.89 (dd, J = 2.1, 4.6, 1H), 1.86–1.92 (m, 2H), 3.27–3.30 (m, 1H), 3.32 (dd, J = 3.0, 6.5, 1H), 3.47–3.55 (m, 2H), 4.04 (dd, J = 6.3, 11.2, 1H), 5.06 (d, J = 12.8, 1H), 5.11 (d, J = 12.8, 1H), 7.28–7.36 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2SO$, 98 °C) δ 21.6, 22.6, 22.8, 23.7, 27.1, 42.8, 46.3, 59.4, 65.6, 68.0, 74.6, 126.9, 127.1, 136.7, 155.1; FABMS (NBA) m/z 322 (MH^+, 100), 304 (8), 278 (46), 214 (9), 204 (29), 160 (29), 154 (13); $[\alpha]^{20}_D$ −46.7° (c 1.29, CH_3OH). Anal. Calcd for $C_{18}H_{27}NO_4$: C, 67.27; H, 8.47; N, 4.36; Found: C, 67.21; H, 8.33; N, 4.37.

(2*S*)-1-(Benzyloxycarbonyl)-2-[(1*R*,2*R*)-1,2-dihydroxy-3-methylbutyl]-pyrrolidine (4t). Purified by flash chromatography to give 968 mg (84%) of a clear oil, consisting of a 12:1 mixture of diastereomers. A pure sample of the major diastereomer was obtained from one of the chromatography fractions: ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 98 °C) δ 0.82 (d, J = 6.7, 3H), 0.88 (d, J = 6.7, 3H), 1.70–1.79 (m, 2H), 1.85–1.97 (m, 3H), 3.05 (dd, J = 2.4, 6.7, 1H), 3.31 (ddd, J = 5.2, 7.5, 10.6, 1H), 3.52 (dd, J = 6.6, 11.1, 1H), 3.54 (dd, J = 2.5, 6.7, 1H), 4.04 (dt, J_d = 3.7, J_t = 6.9, 1H), 5.06 (d, J = 12.8, 1H), 5.11 (d, J = 12.8, 1H), 7.28–7.36 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2SO$, 98 °C) δ 17.6, 18.6, 22.7, 26.8, 30.4, 46.3, 59.7, 65.5, 71.5, 74.1, 126.8, 127.0, 127.7, 136.7, 155.1; FABMS (G) m/z 308 (MH^+, 79), 264 (55), 204 (24), 174 (100), 160 (42); $[\alpha]^{20}_D$ −55.4° (c 1.71, CH_3OH). Anal. Calcd for $C_{17}H_{25}NO_4$: C, 66.43; H, 8.20; N, 4.56. Found: C, 66.45; H, 8.32; N, 4.45.

Hydroxy Oxazolidinones 5 and Cyclic Six-Membered Hydroxy Carbamates 6p–r: NaH in THF Procedure. To a stirred solution of 1.82 mmol of **4** in THF (10 mL) was added NaH (73 mg, 1.82 mmol, 60% suspension in mineral oil), causing the immediate evolution of gas. After stirring for 1 h, 50% saturated NH_4Cl (5 mL) was added to the reaction mixture, and the two phases were stirred vigorously together for 5 min. The THF layer was separated, and the aqueous layer was extracted with THF (10 mL) and CH_2Cl_2 (10 mL). The combined organic layers were washed with saturated NaCl (5 mL), dried ($MgSO_4$), filtered, and evaporated to give a mixture of **5** or **6r–t**, *tert*-butyl alcohol or benzyl alcohol, and mineral oil in 95–100% mass recovery. An aliquot of the crude product was saved for derivatization with Mosher chloride, and the remainder was purified by recrystallization or flash chromatography on silica gel using EtOAc/hexanes.

Hydroxy Oxazolidinones 5 and Cyclic Six-Membered Hydroxy Carbamates 6r–t: NaOH in Methanol Procedure. To a solution of 1.82 mmol of **4** in methanol (10 mL) was added solid NaOH (728 mg, 18.2 mmol). The mixture was stirred for 1 h, giving a clear solution, and then solid NH_4Cl (1.17 g, 21.8 mmol) was added, giving a suspension which was stirred for 10 h. The methanol was evaporated, giving a slurry, which was extracted with CH_2Cl_2 (2 × 10 mL). The CH_2Cl_2 extracts were dried ($MgSO_4$), filtered, and evaporated to give a mixture of **5** or **6r–t** and *tert*-butyl alcohol or benzyl alcohol in 95–100% mass recovery. An aliquot of the crude product was saved for derivatization with Mosher chloride, and the remainder was purified by recrystallization or flash chromatography on silica gel using EtOAc/hexanes.

(3*R*,4*R*,5*S*)-4-*O*,5-*N*-Carbonyl-5-amino-2,6-dimethylheptane-3,4-diol (5a). Purified by flash chromatography to give 293 mg (80%) of a white solid: mp 105 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.91 (d, J = 6.8, 3H), 0.95 (d, J = 6.7, 3H), 0.99 (d, J = 6.7, 3H), 1.05 (d, J = 6.7, 3H), 1.73 (octet, J = 6.7, 1H), 1.92 (octet, J = 6.7, 1H), 2.62 (br, 1H), 3.07 (dd, J = 2.2, 7.8, 1H), 3.59 (m, 1H), 4.36 (dd, J = 2.2, 5.5, 1H), 6.66 (br, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 17.8, 17.9, 18.8, 19.2, 30.9, 32.6, 60.1, 78.1, 80.2, 159.7; FABMS (TG/G) m/z 202 (MH^+, 100), 116 (19); $[\alpha]^{20}_D$ −107° (c 1.05, CH_3OH). Anal. Calcd for $C_{10}H_{19}NO_3$: C, 59.68; H, 9.51; N, 6.96. Found: C, 59.49; H, 9.45; N, 6.96.

(2*R*,3*S*,4*S*)-2-*N*,3-*O*-Carbonyl-2-amino-1,6-diphenylhexane-3,4-diol (5g). Purified by recrystallization from EtOAc/hexanes to give 487 mg (86%) of a white solid: mp 97–98 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.69 (m, 1H), 1.80 (m, 1H), 2.61 (m, 1H), 2.75 (m, 3H), 2.85 (dd, J = 7.5, 13.5, 1H), 3.30 (m, 1H), 3.96 (dd, J = 6.5, 12.7, 1H), 4.15 (dd, J = 3.4, 5.4, 1H), 7.20 (m, 10H), 5.91 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 31.5, 34.2, 41.6, 55.3, 70.8, 83.8, 125.9, 127.2, 128.37, 128.40, 128.9, 129.1, 135.7, 141.2, 158.7; FABMS (TG/G) m/z 623 (2M + H^+, 18), 334 (M + Na^+, 17), 312 (MH^+, 100), 268 (7), 176 (11), 164 (17); $[\alpha]^{20}_D$ +37.5° (c 5.65, $CHCl_3$). Anal. Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50. Found: C, 73.38; H, 6.88; N, 4.52. X-ray crystallography established the structure of this compound.[23]

(4*R*,5*R*,6*S*)-5-Hydroxy-4-(2-phenylethyl)-1-aza-2-oxo-3-oxabicyclo-[4.3.0]nonane (6r). Purified by recrystallization from CH_2Cl_2/EtOAc to give 304 mg (64%) of colorless prisms: mp 201–202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50–1.65 (m, 1H), 1.74–1.82 (m, 1H), 1.84–2.06 (m, 4H), 2.20–2.29 (m, 1H), 2.73–2.87 (m, 2H), 3.42–3.59 (m, 3H), 3.83 (br, 1H), 4.15 (dd, J = 5.3, 8.4, 1H), 7.18–7.29 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2SO$) δ 22.5, 26.7, 30.8, 32.7, 46.7, 60.6, 61.7, 79.0, 125.9, 128.3, 128.4, 141.5, 152.0; FABMS (NBA) m/z 262 (MH^+, 61), 154 (100), 137 (80), 107 (22); $[\alpha]^{20}_D$ +34.5° (c 1.06, CH_3OH). Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 69.12; H, 7.28; N, 5.31. X-ray crystallography established the structure of this compound.[23]

(4*R*,5*R*,6*S*)-5-Hydroxy-4-(2-methylpropyl)-1-aza-2-oxo-3-oxabicyclo-[4.3.0]nonane (6s). Purified by recrystallization from ethyl acetate to give 171 mg (44%) of colorless prisms: mp 152–153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (d, J = 6.4, 3H), 0.95 (d, J = 6.4, 3H), 1.59 (sept, J = 6.1, 1H), 1.95 (m, 6H), 3.43 (dt, J = 1.8, 10.7, 1H), 3.51 (dt, J = 7.2, 10.7, 1H), 3.63 (ddd, J = 2.6, 5.4, 10.4, 1H), 3.80 (d, J = 1.6, 1H), 4.28 (t, J = 6.7, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 22.3, 22.81, 22.85, 23.8, 26.9, 39.6, 46.8, 61.5, 63.8, 78.9, 153.3; FABMS (NBA) m/z 214 (MH^+, 100), 170 (23), 154 (32), 136 (39), 114 (75), 107 (20); $[\alpha]^{20}_D$ +3.0° (c 1.47, $CHCl_3$). Anal. Calcd for $C_{11}H_{19}NO_3$: C, 61.95; H, 8.98; N, 6.56. Found: C, 62.12; H, 8.91; N, 6.58.

***N*,*O*-bis[(*R*)-Methoxy(trifluoromethyl)phenylacetyl] Hydroxy Oxazolidinones 7 and *O*-[(*R*)-Methoxy(trifluoromethyl)phenylacetyl] Hydroxy Carbamate 8s.** To a mixture of 0.0808 mmol of crude **5** or **6s** and benzyl alcohol or *tert*-butyl alcohol (byproduct from the preparation of **5** and **6s**) were added dry CH_2Cl_2 (1.0 mL), 4-(dimethylamino)pyridine (35 mg, 0.29 mmol), triethylamine (79 μL, 57 mg, 0.57 mmol), and (*S*)-methoxy(trifluoromethyl)phenylacetyl chloride (53 μL, 72 mg, 0.29 mmol), giving a yellow solution after brief stirring. The reaction solution was allowed to stand for 16 h, at which point Et_2O (10 mL) was added, giving a suspension which was washed with 5% citric acid (4 mL), saturated $NaHCO_3$ (4 mL), and saturated NaCl (4 mL). The resulting homogeneous organic layer was dried by passing it through a plug of $MgSO_4$ in a pipet and concentrated, giving a residue consisting of **7** or **8s** and benzyl methoxy(trifluoromethyl)phenylacetate or *tert*-butyl methoxy-(trifluoromethyl)phenylacetate. The residue was analyzed by ^{1}H and ^{19}F NMR spectroscopy. The analogous *N*,*O*-bis[(*S*)-methoxy(trifluoromethyl)phenylacetyl] hydroxy oxazolidinones and *O*-[(*S*)-methoxy-(trifluoromethyl)phenylacetyl] hydroxy carbamates were prepared in the same manner using (*R*)-methoxy(trifluoromethyl)phenylacetyl chloride.

(2*S*,3*R*,4*R*)-2-Acetamido-1,3,4-triacetoxyhexadecane (9). The diol (**4m**) (26.1 mg, 0.0508 mmol), HCO_2H (75 μL, 2.0 mmol), 10% Pd/C (20 mg), and EtOH (1 mL) were stirred at room temperature for 40 h. The reaction mixture was filtered through Celite (prewetted with EtOH) and concentrated. ^{1}H NMR showed no signals in the aromatic region. The oil (2-amino-1,3,4-hexadecanetriol) was dissolved in pyridine (1.5 mL) and acetic anhydride (1.5 mL) and stirred for 2 h. The reaction mixture was concentrated to give **9** as a clear oil (21.8 mg, 0.0476 mmol, 94%). An analytical sample was prepared by chromatography (7:3 hexane/EtOAc): ^{1}H NMR (400 MHz, $CDCl_3$) δ .85 (t, J = 6.8, 3H), 1.18–1.27 (m, 20H), 1.55 (m, 2H), 1.99 (s, 3H), 2.03 (s, 3H), 2.04 (s, 3H), 2.06 (s, 3H), 3.99 (dd, J = 6.9, 6.9, 1H), 4.09 (dd, J = 14.3, 7.1, 1H), 4.49 (m, 1H), 5.02 (dd, J = 6.5, 12.8, 1H), 5.13 (dd, J = 6.5, 4.3, 1H), 5.74 (d, J = 9.4, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 14.1, 20.7, 20.9, 22.7, 23.2, 24.8, 29.24, 29.33, 29.38, 29.51, 29.61, 30.5, 31.9, 48.0, 62.9, 71.9, 72.2, 96.1, 169.8, 170.1, 170.5; structure confirmed by comparison of the ^{1}H and ^{13}C NMR spectra to the literature data.[21]

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