Stereoselective Addition of 2-Furyllithium and 2-Thiazolyllithium to Sugar Nitrones. Synthesis of Carbon-Linked Glycoglycines

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Received February 14, 1997[⊗]

A route to epimeric carbon-linked glycoglycines that exploits the stereoselective addition of 2-lithiofuran and 2-lithiothiazole to sugar nitrones has been described. The reaction occurs with opposite diastereofacial selectivity depending on whether the free nitrone or the diethyl aluminum chloride precomplexed derivative is employed. The resulting furyl or thiazolyl hydroxylamines are dehydroxylated to amines by the action of titanium(III) chloride. From these compounds the amino acids are revealed by the oxidative cleavage of the furan ring or by the conversion of the thiazole into the formyl group and oxidation to carboxylic acid. Compounds have been prepared wherein the α-amino acid moiety is installed at C-4 and C-1 of furanoses (*ribo, manno, xylo, and lyxo*) and at C-5 and C-1 of a pyranose (*galacto*).

In respect to glycosyl amino acids of natural glycopeptides in which the carbohydrate and amino acid moieties are bound by the *O*- or *N*-glycosidic linkage,[1] synthetic *C*-glycosyl analogs feature a nonhydrolyzable carbon−carbon bond between the two moieties. Various types of *C*-glycosyl amino acids with carbon-carbon tethers of different length have been reported in recent years.[2,3] Moreover, α-aminouronic acids featuring the amino acid moiety at either C-4 of furanose or C-5 of pyranose ring constitute the central part of several nucleoside antibiotics.[4] These include amipurimycin,[5] miharamicyns,[6] polyoxins,[7] and nikkomycins.[8] Consequently, the ready availability of glycosyl α-amino acids has been often crucial to the successful syntheses of complex peptidyl nucleoside antibiotics.[9] Indeed, the syntheses of both α-aminofuranuronic[10] and α-aminopyranuronic acids[11] have been reported. However, most of those syntheses lack generality since they have been developed for the preparation of a single target compound.

On the other hand, in recent reports from these laboratories we have described a general method for converting aldehydes into α-amino aldehydes[12] and α-amino acids[13] with one more carbon atom. Key operations are the addition reactions of 2-lithiofuran (**1**) and 2-lithiothiazole (**2**) to the aldehyde-derived nitrones. The nitrone group serves as the precursor of the amino group whereas the heterocycle furnishes the formyl (from thiazole) or the carboxyl (from furan) group. It is noteworthy that

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⊗ Abstract published in *Advance ACS Abstracts,* July 1, 1997.

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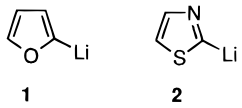
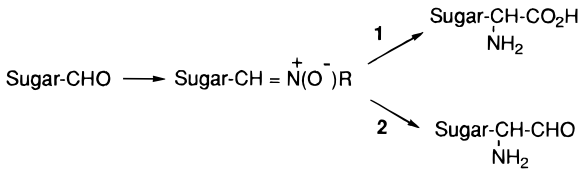
S0022-3263(97)00290-9 CCC: $14.00

in most of the cases examined the stereochemical outcome of the addition reaction can be controlled by the precomplexation of the nitrone with Lewis acids. Hence examples have been reported showing the conversion of chiral aldehydes into pairs of epimeric α-amino aldehydes[12] or α-amino acids.[13] Therefore we would like to report here the results of these approaches targeted to the synthesis of various carbon-linked glycoglycines including two cases wherein the amino acid moiety is installed at the anomeric carbon of the sugar (*C*-glycosyl glycines).[14]



1 **2**

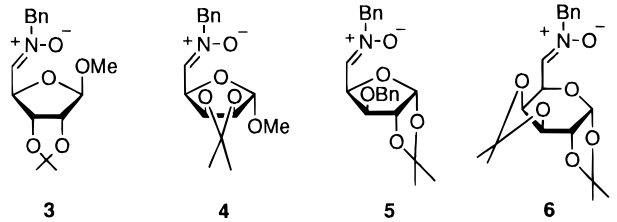


Results and Discussion

Although all the *C*-glycosyl α-amino aldehydes prepared by the nitrone−thiazole route[12] are precursors to amino acids through the oxidation of the formyl to the carboxylic group,[15] we thought that new oportunities for the synthesis of carbon-linked glycoglycines could develop from the nitrone−furan approach. First of all the furan ring can be directly converted into the carboxylate function through an oxidative cleavage;[16] second, the addition of **1** to nitrones derived from chiral alkoxy aldehydes[13] was in some cases more stereoselective than the addition of **2**.

First examined was the reaction of **1**, generated *in situ* from furan and butyllithium, with the readily available carbon-linked ribosyl **3**, lyxosyl **4**, xylosyl **5**, and galactosyl **6** nitrones[17] (Chart 1). In all cases the reaction in

Chart 1



3 **4** **5** **6**

THF or THF−Et_2O at −80 °C proceeded readily to give the hydroxylamines **7**−**10** (Scheme 1) as mixtures of diastereoisomers in good to excellent overall yield and stereoselectivity (Table 1). Reactions carried out in the absence of complexing agents gave compounds **7a**−**10a** as major products (Chart 2), whereas in the presence of 1.0 equiv of diethylaluminum chloride the epimers **7b**−**10b** were obtained in much larger amounts. The stereochemical assignment of these isomers is discussed below. While the overall yield of each isolated pair of epimeric hydroxylamines was comparable to that obtained[12] in the addition of 2-lithiothiazole (**2**) to the same nitrones **3**, **5**, and **6**, the diastereoselectivity was much higher. One can speculate that the addition of **1** occurs preferentially to the nitrone face opposite to that of the furanose or pyranose ring. Hence the formation of **7a**−**10a** indicates that the reactive conformation of nitrones **3**−**6** is that shown in Chart 1 whereas the Et_2AlCl-induced formation of the isomers **7b**−**10b** requires that the same nitrones adopt a different conformation because of the Lewis acid complexation.[18]

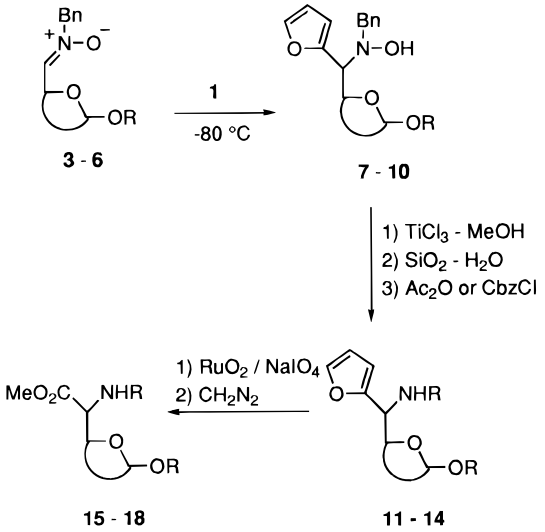
As the second step of the methodology we examined the reductive dehydroxylation of 2-furyl *N*-benzylhy-

Table 1. Addition of 2-Lithiofuran (1) to Carbon-Linked Glycosyl Nitrones 3-6[a]

nitrone	Lewis acid	hydroxylamines, ds (%)[b]	yield (%)[c]
3	none	**7a**, 95; **7b**, 5	88
	Et_2AlCl	**7a**, 18; **7b**, 82	85
4	none	**8a**, 78; **8b**, 22	82
	Et_2AlCl	**8a**, 12; **8b**, 88	81
5	none	**9a**, 93; **9b**, 7	90
	Et_2AlCl	**9a**, 7; **9b**, 93	84
6	none	**10a**, 82; **10b**, 18	80
	Et_2AlCl	**10a**, 6; **10b**, 94	96

[a] For the conditions employed, see the Experimental Section. [b] Determined by 1H NMR analysis of the crude mixture. [c] Overall yield of isolated mixture of diastereomers.

Scheme 1



(14) It is worth pointing out that the trivial name *C*-glycosyl α-amino acid appears appropriate only for compounds wherein the amino acid moiety is linked to the sugar anomeric carbon.

(15) In related research works we have experienced various oxidizing agents, all operating under mild and almost neutral reaction conditions. See: ref 12 and Dondoni, A.; Franco, S.; Merchan, F. L.; Merino, P.; Tejero, T. *Tetrahedron Lett.* **1993**, *34*, 5479. Dondoni, A.; Perrone, D.; Merino, P. *J. Chem. Soc., Chem. Commun.* **1991**, 1313.

(16) For the use of furan as precursor to the carboxylic group, see: (a) cleavage by O_3: Schmid, G.; Fukuyama, T.; Akasaka, K.; Kishi, Y. *J. Am. Chem. Soc.* **1979**, *101*, 259. Akita, H.; Koshiji, H.; Furuichi, A.; Horokoshi, K.; Oishi, T. *Chem. Pharm. Bull.* **1984**, *32*, 1242. Danishefsky, S. J.; Maring, C. J. *J. Am. Chem. Soc.* **1989**, *111*, 2193. Dondoni, A.; Marra, A.; Scherrmann, M.-C. *Tetrahedron Lett.* **1993**, *34*, 7323. (b) cleavage by RuO_2−$NaIO_4$: Mukaiyama, T. Tsuzuki, R.; Kato, *J. Chem. Lett.* **1985**, 837. Danishefsky, S. J.; Pearson, W. H.; Segmuller, B. E. *J. Am. Chem. Soc.* **1985**, 107, 1280. Danishefsky, S. J.; DeNinno, M. P.; Chen, S. *J. Am. Chem. Soc.* **1988**, *110*, 3929. Poss, H. A.; Reid, J. A. *Tetrahedron Lett.* **1992**, *33*, 1411. Marshall, J. A.; Luke, J. P. *J. Org. Chem.* **1993**, *58*, 6229.

(17) Dondoni, A.; Franco, S.; Junquera, F.; Merchan, F. L.; Merino, P.; Tejero, T. *Synth. Commun.* **1994**, *23*, 2537.

(18) The complexation as in the structure shown below exposes the opposite nitrone face to the attack of **1**.

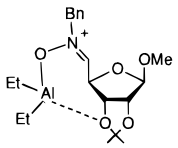
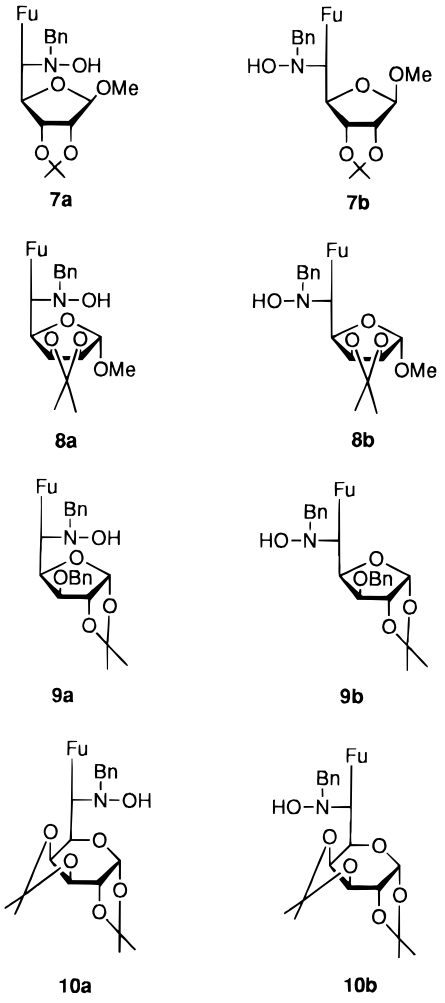
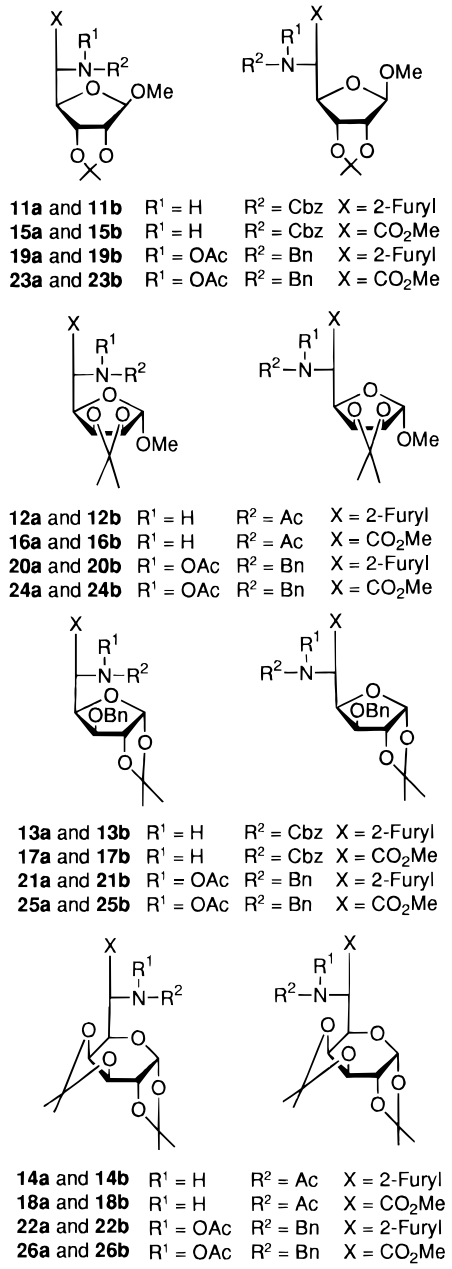


Chart 2[a]



[a] Fu = 2-furyl

Chart 3[a]



11a and **11b** R^1 = H R^2 = Cbz X = 2-Furyl
15a and **15b** R^1 = H R^2 = Cbz X = CO_2Me
19a and **19b** R^1 = OAc R^2 = Bn X = 2-Furyl
23a and **23b** R^1 = OAc R^2 = Bn X = CO_2Me

12a and **12b** R^1 = H R^2 = Ac X = 2-Furyl
16a and **16b** R^1 = H R^2 = Ac X = CO_2Me
20a and **20b** R^1 = OAc R^2 = Bn X = 2-Furyl
24a and **24b** R^1 = OAc R^2 = Bn X = CO_2Me

13a and **13b** R^1 = H R^2 = Cbz X = 2-Furyl
17a and **17b** R^1 = H R^2 = Cbz X = CO_2Me
21a and **21b** R^1 = OAc R^2 = Bn X = 2-Furyl
25a and **25b** R^1 = OAc R^2 = Bn X = CO_2Me

14a and **14b** R^1 = H R^2 = Ac X = 2-Furyl
18a and **18b** R^1 = H R^2 = Ac X = CO_2Me
22a and **22b** R^1 = OAc R^2 = Bn X = 2-Furyl
26a and **26b** R^1 = OAc R^2 = Bn X = CO_2Me

[a] Compounds on the left are isomers of the **a** series whereas those on the right belong to the **b** series.

droxylamines **7**−**10** into *N*-protected amines **11**−**14** (Scheme 1). Guided by previous work[13] showing that titanium(III) chloride[19] is a quite effective reagent for this transformation, we treated each isolated compound **7a-10a** and **7b-10b** with this titanium salt in 20% aqueous methanol. In most of the cases the reaction produced a mixture of benzaldimine and primary amine as shown by ^{1}H NMR analysis.[20] Treatment of the crude mixture with wet silica gel in dichloromethane completed the removal of the *N*-benzyl group. Hence the crude 2-furyl amines were protected by treatment with acetic anhydride or benzyl chloroformate and isolated as the corresponding *N*-acetyl (*N*-Ac) or benzyloxycarbonyl (*N*-Cbz) derivatives **11**−**14** (Chart 3). The overall yield of isolated products was 57−73%

The completion of the methodology required the conversion of the carbon-linked glycosyl furyl amines shown in Chart 3 into amino acids by revealing the carboxylate function from the furan ring (Scheme 1). The oxidative cleavage of this heterocycle by ozone or ruthenium tetraoxide has been reported in several instances[16] although it is known that these harsh conditions are not tolerated by a quite common hydroxyl protective group such as the benzyl group which is oxidized to benzoate.[21] Guided also in this circumstance by our previous work,[13] we oxidized furan derivatives **11a**−**14a** and the diastereomers **11b**−**14b** with ruthenium tetraoxide generated *in situ*, and the resulting crude product was treated with diazomethane. In all cases the reaction sequence produced the corresponding methyl esters **15a**−**18a** and **15b**−**18b** in 51−69% overall yield (Chart 3). Fortunately enough, also the esters **17a** and **17b** bearing a benzyl ether protective group were obtained in good yields.

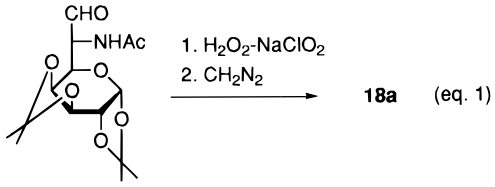
Having completed the whole sequence that had allowed conversion of each sugar nitrone **3**−**6** into a pair of L and D carbon-linked glycoglycinates **15**−**18**, we established

(19) Murahashi, S.-I. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2443.

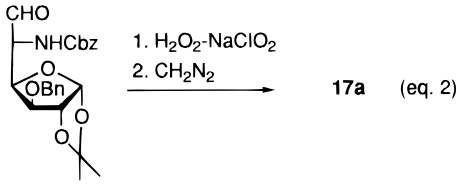
(20) The reaction with **7b** produced the benzaldimine as a major product. ^{1}H NMR ($CDCl_3$) δ: 1.32 (s, 3 H), 1.35 (s, 3 H), 3.14 (s, 3 H), 4.61 (m, 2 H), 4.84 (d, 1 H, J = 8.6 Hz), 4.96 (s, 1 H), 4.99 (d, 1 H, J = 6.1 Hz), 6.38 (m, 2 H), 7.30 (m, 5 H), 7.79 (m, 1 H), 8.20 (s, 1 H).

(21) For the removal of the benzyl ether protective group by O_3, see: Angibeaud, P.; Defaye, J.; Gadelle, A.; Utile, J. P. *Chem. Commun.* **1985**, 1123. For the oxidation of benzyl ethers to benzoates by RuO_2−$NaIO_4$, see: Schuda, P. F.; Cichowicz, M. B.; Heimann, M. R. *Tetrahedron Lett.* **1983**, *24*, 3829.

the configuration at the newly formed stereocenter bearing the amino group by using either the final amino ester or its hydroxylamine or amine precursor. The consistency of this method relied on the assumption that intermediates and products were configurationally stable under the various reaction conditions. Thus, in the *ribo* series, the configuration of the hydroxylamines **7a** and **7b** was established by comparative NOE experiments;[22] in the *xylo* and *lyxo* series the structures of compounds **9b** and **12b** were determined by X-ray crystallography;[23] finally, the configurations of **18a** and **17a** were established by converting the known[12] aldehydes **27** and **28** into **18a** and **17a**, respectively (eqs 1 and 2).



27



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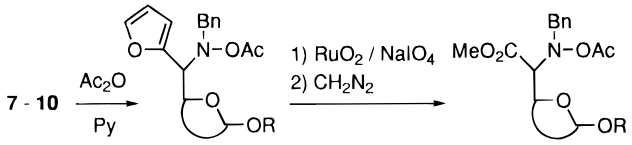
Given the ready access to furyl hydroxylamines **7**−**10** in both diastereomeric forms, we envisaged their conversion into amino acids without removing the *N*-hydroxy group (Scheme 2). Among the various classes of unusual amino acids, *N*-hydroxylamino derivatives are of special interest because of their wide occurrence in nature and participation in metabolic pathways.[24] Hence the carbon-linked glycosyl *N*-hydroxy glycines resulting from the elaboration of hydroxylamines **7**−**10** would constitute a new class of sugar amino acids of potential biological relevance. Thus, protection of the hydroxylamino group of compounds **7**−**10** by acetylation gave the *O*-acetyl derivatives **19**−**22** which in turn were converted into the carbon-linked glycosyl glycinates **23**−**26** by standard ruthenium-based furan-to-acid conversion and esterification (Chart 3). The yields in each step ranged between 51−68%.

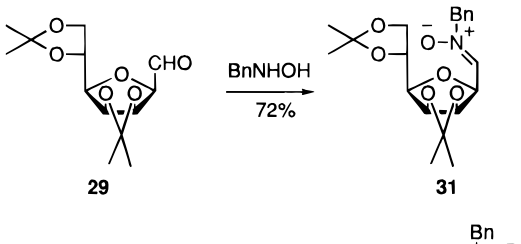
Scheme 2



19-22 23 - 26

The above nitrone−furan methodology appeared quite appealing for the installation of the amino acid function at the anomeric center of sugars and allow preparation of rather uncommon anomeric *C*-glycosyl glycines.[25] Our recent thiazole-based synthesis of anomeric *C*-formyl glycosides[26] provided the starting aldehydes for this approach. Thus the *C*-formyl mannofuranoside diacetonide **29** and tetrabenzyl galactopyranoside **30** were converted by reaction with benzylhydroxylamine into the corresponding *N*-benzyl nitrones **31** and **32** in very good yield (Scheme 3). Interestingly enough, while the aldehydes were sticky and hydratable oils, their nitrones appeared crystalline and stable compounds.

Scheme 3

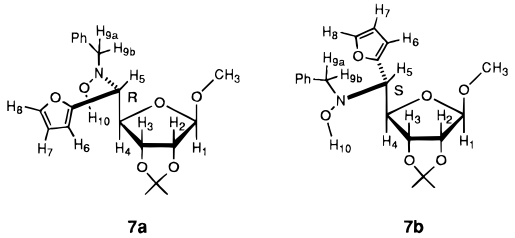


29 31

30 32

The reaction of 2-lithiofuran (**1**) with the nitrones **31** and **32** afforded the hydroxylamines **33** and **34**, respectively (Chart 4), as mixtures of diastereomers in good overall yields (Table 2). The reaction of the protected mannofuranoside nitrone **31** showed a reversal of diastereoselectivity in the presence of diethylaluminum chloride, while that of the galactoside nitrone **32** gave the same hydroxylamine **34b** as major product in both cases. These results suggest that the reactive conformation of **31** shown in Scheme 3 was changed by the presence of the Lewis acid whereas that of **32** remained the same. While the reasons for this behavior is open to conjectures, the observed stereochemical outcomes are consistent with the addition of the organometal **1** to the nitrone face opposite to that of the furanose or pyranose ring.

(22) Compound **7a** showed a significant NOE enhancement of the H_6 signal (furan ring) when H_3 was presaturated. For compound **7b** a NOE enhancement was observed for H_6 when the anomeric methoxy group was irradiated. Both diastereomers exhibited NOE between H_5 and H_3, as well as the anomeric methoxy group and H_5. Also the hydroxylamine proton (H_{10}) was affected when H_4 was irradiated in both **7a** and **7b**. These data indicated the spatial disposition shown below. The configurational assignment based on NOE was confirmed by the total synthesis of thymine polyoxin C starting from **7b**. See: Dondoni, A.; Junquera, F.; Merchan, F. L.; Merino, P.; Tejero, T. *Tetrahedron Lett.* **1994**, *35*, 9439 and the accompanying paper.



7a 7b

(23) The X-ray crystal analyses have been performed by one of us (P.M.) at the University of Zaragoza. Atomic coordinates, bond lengths and angles, thermal parameters, and structure factors for compounds **9b**, **12b**, and **35b** have been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2, 1EZ, UK. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Center. Some crystal data of these compounds and the relevant informations for their determinations are given in the Experimental Section.

(24) Ottenheim, H. C. J.; Herscheid, J. D. M. *Chem. Rev.* **1986**, *86*, 697.

(25) For some earlier examples, see ref 2a,b.

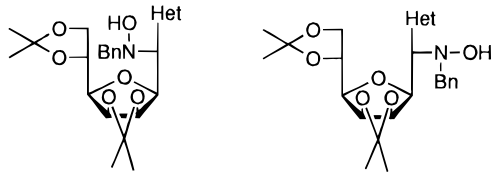
(26) Dondoni, A.; Scherrmann, M.-C. *J. Org. Chem.* **1994**, *59*, 6404.

Table 2. Addition of 2-Lithiofuran (1) and 2-Lithiothiazole (2) to *C*-Glycosyl Nitrones 31 and 32[a]

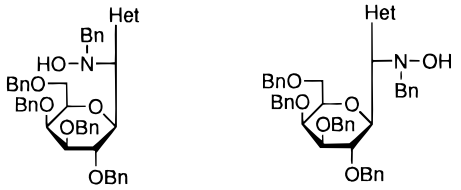
reaction	Lewis acid	hydroxylamines, ds (%)[b]	yield (%)[c]
31 + **1**	none	**33a**, 76; **33b**, 24	86
	Et_2AlCl	**33a**, 18; **33b**, 82	80
32 + **1**	none	**34a**, 30; **34b**, 70	78
	Et_2AlCl	**34a**, 12; **34b**, 88	81
31 + **2**	none	**35a**, 70; **35b**, 80	76
	Et_2AlCl	**35a**, 20; **35b**, 80	78
32 + **2**	none	**36a**, 34; **36b**, 66	75
	Et_2AlCl	**36a**, 29; **36b**, 71	76

[a] For the conditions employed, see the Experimental Section. [b] Determined by ^1H NMR analysis of the crude mixture. [c] Overall yield of isolated mixture of diastereomers.

Chart 4[a]



33a and **33b** Het = 2-Furyl
35a and **35b** Het = 2-Thiazolyl

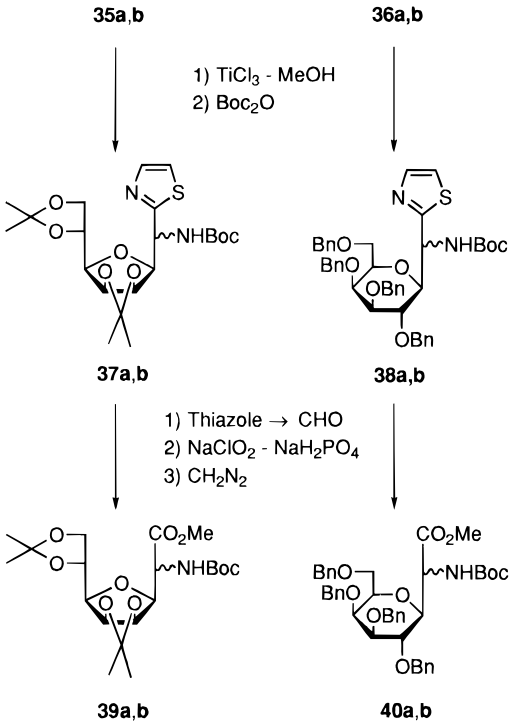


34a and **34b** Het = 2-Furyl
36a and **36b** Het = 2-Thiazolyl

[a] Compounds on the left are isomers of the **a** series whereas those on the right belong to the **b** series.

The reduction of hydroxylamines **33a,b** and **34a,b** to the corresponding amines upon treatment with titanium(III) chloride turned out to be unsuccessful. For instance, both **33a** and **33b** essentially decomposed to give complex mixtures of products as judged by ^1H NMR analysis. Hence the synthesis of anomeric *C*-glycosyl α-amino acids from the *C*-glycosyl nitrones **31** and **32** was approached via the thiazole-based aminohomologation route.[12] Unfortunately this route required an extra step consisting on the oxidation of the formyl group to carboxylic acid.[27] The addition of 2-lithiothiazole (**2**) to the nitrones **31** and **32** in Et_2O or THF−Et_2O at −80 °C either in the absence or in the presence of diethylaluminum chloride afforded the corresponding hydroxylamines **35** and **36** as mixtures of diastereomers (Chart 4). In each case the diastereomeric ratios and chemical yields were comparable to those of the reactions of the same nitrones with 2-lithiofuran (**1**) (Table 2). Moreover, compounds **35a,b** and **36a,b** afforded the corresponding *N*-Boc *C*-glycosyl amine **37a,b** and **38a,b** by the titanium(III) chloride method in good yield (62−66%) (Scheme 4). Then, these compounds were converted into the anomeric methyl *C*-glycosyl glycinates **39a,b** and **40a,b** by a reaction sequence involving the copper(II) chloride based cleavage of the thiazole ring into the formyl group,[28] the oxidation of the latter to carboxylic acid by sodium chlorite,[29] and finally the esterification with diazomethane. The successful synthesis of these amino acids demonstrates the complementary role of thiazole and furan heterocycles in this methodology.

Scheme 4



The structural assignment of the two sets of compounds derived from the anomeric sugar nitrones **31** and **32** was based on different techniques. In the thiazole series, the simplest and straightforward case was that of **35b** whose structure was established by X-ray crystallographic analysis.[23] For **36a** and **36b** the assignment was based on a CD study of the corresponding *N*-*tert*-butoxycarbonyl amines **38a** and **38b**. Recent work with several *N*-*tert*-butoxycarbonyl aminomethyl thiazoles[30] showed a positive Cotton effect in the range 217−230 nm for compounds with *R*-configuration at the α-center of the thiazole ring, whereas a negative Cotton effect was featured by compounds with *S*-configuration. Thus, the CD spectrum of **38a** showing a negative Cotton effect is consistent with the *S*-configuration whereas the positive value shown by **38b** indicates the *R*-configuration. The same relationship was observed with the *N*-*tert*-butoxycarbonyl amines **37a** and **37b**. The stereochemistry of the latter is consistent with that of its precursor **35b** determined by X-ray crystallography. Finally, also the

(27) We have previously commented on the various inconveniences that are encountered with the direct conversion of the thiazole ring into carboxylic group by oxidative cleavage with different reagents (Dondoni, A.; Marra, A.; Merino, P. *J. Am. Chem. Soc.* **1994**, *116*, 3324). On the other hand the synthesis of carboxylic acids via thiazole-to-formyl deblocking and subsequent oxidation under mild and neutral conditions is rewarded by high yields and compatibility of the method with different protective groups and various structural arrays. See also: Dondoni, A.; Perrone, D. *Synthesis* **1993**, 1162. Dondoni, A.; Scherrmann, M.-C. Marra, A.; Delépine, J.-L. *J. Org. Chem.* **1994**, *59*, 7517. Dondoni, A.; Boscarato, A.; Marra, A. *Tetrahedron Asymmetry* **1994**, *5*, 2209. Dondoni, A.; Perrone, D.; Semola, T. *Synthesis* **1995**, 181. Dondoni, A.; Marra, A.; Rojo, I.; Scherrmann, M.-C. *Tetrahedron* **1996**, *52*, 3057. Marra, A.; Dondoni, A.; Sansone, F. *J. Org. Chem.* **1996**, *61*, 5155.

(28) Dondoni, A.; Marra, A.; Perrone, D. *J. Org. Chem.* **1993**, *58*, 275.

(29) Dalcanale, E.; Montanari, F. *J. Org. Chem.* **1986**, *51*, 567.

(30) Merchan, F. L.; Merino, P.; Rojo, I.; Tejero, T., Dondoni, A. *Tetrahedron: Asymmetry* **1995**, *6*, 2145.

configuration of the furyl hydroxylamines **33** and **34** was assigned on the basis of a recent extensive work on the chiroptical properties of this class of compounds.[31] Hence, the negative Cotton effect shown by **33a** indicates the *S*-configuration and by contrast the positive effect shown by **33b** and **34b** reveals the *R*-configuration.

In conclusion, a new and quite general route to sugar glycines in both epimeric forms has been disclosed. While the present study has been mainly focussed on the installation of the amino acid side chain at C-4 of furanoses in view of the application of the method to the synthesis of peptidyl nucleoside antibiotics of the polyoxin family (see the accompanying paper), its scope appears extendable to C-5 of pyranoses and even more important to C-1 of both furanoses and pyranoses.

Experimental Section

General Methods. The reaction flasks and other equipment were stored in an oven at 130 °C overnight and assembled in a stream of argon. Syringes were assembled and fitted with needles while hot and cooled in a stream of argon. Special techniques were used in handling moisture- and air-sensitive materials,[32] and solvents were purified and dried by standard methods.[33] Preparative chromatography was performed on columns of silica gel (60−240 mesh), and solvents were distilled prior to use. Reactions were monitored by TLC on silica gel 60 F254; the positions of the spots were detected with 254 nm UV light and by charring with 50% methanolic sulfuric acid as staining system.

Melting points were determined on a Büchi 510 melting point apparatus and are uncorrected. Optical rotations were measured on a Perkin Elmer 241 polarimeter at 20 °C in the stated solvent. Elemental analyses were performed on a Perkin Elmer 240B microanalyzer. ^{1}H and ^{13}C NMR spectra were recorded either on a Varian 300 Unity or a Bruker 300 spectrometers operating at 300 MHz for ^{1}H and 75.5 MHz for ^{13}C at 20 °C in $CDCl_3$ unless otherwise specified. Chemical shifts are expressed in parts per million positive values downfield from internal TMS. Nitrones **3**−**6** were prepared as described.[17] Aldehydes **29** and **30** were prepared as described[26] and converted into the corresponding nitrones **31** and **32** as described below.

(*Z*)-2,5-Anhydro-1-(benzylimino)-1-deoxy-3,4:6,7-di-*O*-isopropylidene-D-*glycero*-D-*galacto*-heptitol)benzylamine *N*-Oxide (31). To a well-stirred solution of the aldehyde **29** (2.7 g, 10 mmol) in dichloromethane (75 mL) at room temperature were added *N*-benzylhydroxylamine (1.23 g, 10 mmol) and anhydrous magnesium sulfate (1.21 g, 10 mmol), and stirring was continued for 4 h. The mixture was filtered, and the solution was dried over $MgSO_4$. The evaporation of the solvent under reduced pressure and chromatography (20:80 hexane−diethyl ether) of the crude residue afforded 2.72 g (72%) of the nitrone **30** as a white solid: mp 87−89 °C; $[\alpha]_D = +74.6$ (*c* 1.20, $CHCl_3$); ^{1}H NMR δ 1.27 (s, 3 H), 1.33 (s, 3 H), 1.36 (s, 3 H), 1.40 (s, 3 H), 3.53 (dd, 1 H, J = 6.9, 3.2 Hz), 3.98 (dd, 1 H, J = 8.6, 4.9 Hz), 4.30 (dd, 1 H, J = 8.6, 6.0 Hz), 4.35 (ddd, 1 H, J = 6.9, 6.0, 4.9 Hz), 4.65 (t, 1 H, J = 3.7 Hz), 4.74 (dd, 1 H, J = 6.1, 3.9 Hz), 4.90 (ABq, 2 H, J = 11.6 Hz, $\Delta\delta$ = 0.047), 5.11 (dd, 1 H, J = 6.1, 4.2 Hz), 6.77 (d, 1 H, J = 4.2 Hz), 7.32−7.40 (m, 5 H); ^{13}C NMR δ 24.5, 25.10, 25.7, 26.9, 66.7, 69.0, 72.9, 78.2, 80.2, 80.6, 81.8, 109.1, 112.7, 128.9, 129.0, 129.3, 132.3, 135.7. Anal. Calcd for $C_{20}H_{27}NO_6$: C, 63.64; H, 7.21; N, 3.71. Found: C, 63.69; H, 7.46; N, 3.76.

(Z)-2,6-Anhydro-1-(benzylimino)-1-deoxy-3,4,5,7-tetra-*O*-benzyl-D-*glycero*-L-*manno*-heptitol)benzylamine *N*-Oxide (32). The aldehyde **30** (5.52 g, 10 mmol) was treated as described for compound **29**. Column chromatography (20:80 hexane−diethyl ether) of the residue gave 5.26 g (80%) of **32** as a white solid: mp 144−146 °C; $[\alpha]_D = +15.4$ (*c* 1.53, $CHCl_3$); ^{1}H NMR δ 3.46 (dd, 1 H, J = 9.3, 7.3 Hz), 3.51 (dd, 1 H, J = 9.5, 5.9 Hz), 3.63 (m, 1 H), 3.68 (dd, 1 H, J = 9.5, 2.7 Hz), 3.80 (t, 1 H, J = 9.5 Hz), 3.97 (d, 1 H, J = 2.7 Hz), 4.37 (d, 1 H, J = 11.7 Hz), 4.42 (d, 1 H, J = 11.7 Hz), 4.44 (d, 1 H, J = 11.2 Hz), 4.58 (d, 1 H, J = 11.2 Hz), 4.69 (ABq, 2 H, J = 12.0 Hz, $\Delta\delta$ = 0.018), 4.73 (m, 3 H), 4.82 (d, 1 H, J = 13.7 Hz), 4.89 (d, 1 H, J = 11.5 Hz), 6.46 (d, 1 H, J = 7.3 Hz), 7.19−7.38 (m, 25 H); ^{13}C NMR δ 68.2, 70.3, 72.3, 72.6, 73.4, 74.0, 74.6, 74.8, 76.8, 77.1, 127.6, 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.3, 128.4, 128.9, 129.0, 129.5, 132.2, 135.0, 137.8, 138.2, 138.2, 138.5. Anal. Calcd for $C_{42}H_{43}NO_6$: C, 76.69; H, 6.59; N, 2.13. Found: C, 76.64; H, 6.97; N, 2.09.

2-Lithiofuran (1). To a well-stirred solution of furan (1.02 g, 1.09 mL, 15 mmol) in THF (50 mL), cooled to −80 °C, were added butyllithium (10 mL of a 1.6 M solution in hexanes, 16 mmol), and the resulting solution was stirred at 0 °C for 2 h. The resulting solution of 2-lithiofuran (**1**) in THF (ca. 0.2 M) was maintained at 0 °C and used within a few hour period.

General Procedure for the Addition of 2-Lithiofuran (1) to Nitrones 3−6, 31, and 32. Method A. Without Lewis Acid. A cooled (−90 °C) solution of **1** in THF (prepared from 15 mmol of furan) was treated with a solution of the nitrone (5 mmol) in THF (30 mL) added drop by drop. The rate of the addition was adjusted so as to keep the internal temperature below −80 °C. This operation required ca. 30 min. The reaction mixture was stirred for an additional 2 h at −80 °C and then quenched with saturated aqueous NH_4Cl (25 mL). The mixture was stirred at ambient temperature for 10 min and diluted with diethyl ether (25 mL). The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3 × 25 mL). The combined organic extracts were washed with brine and dried over magnesium sulfate, and the solvent was evaporated under reduced pressure to give the crude hydroxylamines **7**−**10**, **33**, and **34**. The diastereoselectivity was established by ^{1}H NMR analysis. The crude products were purified by column chromatography on silica gel.

Method B. With Diethyl Aluminum Chloride. A 1.0 M solution of Et_2AlCl in hexane (5 mL, 5 mmol) was added via syringe under stirring to a solution of the nitrone (5 mmol) in diethyl ether (50 mL) at ambient temperature. The mixture was stirred at this temperature for 5 min, transferred under argon atmosphere into a dropping funnel, and slowly added to a cooled (−90 °C) solution of 2-lithiofuran (**1**) in THF (prepared from 15 mmol of furan). The rate of the addition was adjusted so as to keep the internal temperature below −80 °C. This operation required ca 1 h. The reaction mixture was stirred for an additional 2 h at −80 °C and then treated with 1.0 M aqueous NaOH (25 mL). After stirring for 15 min at room temperature, the mixture was extracted with diethyl ether (3 × 25 mL). The combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated in vacuo. The diastereoselectivity was determined by ^{1}H NMR analysis. The crude hydroxylamines **7**−**10**, **33**, and **34** were purified by column chromatography on silica gel.

Methyl *N*-Benzyl-5-deoxy-5-(2-furyl)-5-(hydroxyamino)-2,3-*O*-isopropylidene-α-L-*talo*-1,4-pentofuranoside (7a). From the nitrone **3** (1.54 g, 5 mmol) by method A. Isolated by column chromatography (80:20 hexane−diethyl ether): 1.58 g, 84%; white solid; mp 117−119 °C; $[\alpha]_D = -3.3$ (*c* 1.25, $CHCl_3$); ^{1}H NMR δ 1.23 (s, 3 H), 1.46 (s, 3 H), 3.34 (s, 3 H), 3.67 (AB q, 2 H, J = 13.0 Hz, $\Delta\delta$ = 0.02), 4.02 (d, 1 H, J = 10.4 Hz), 4.41 (dd, 1 H, J = 5.9, 1.1 Hz), 4.54 (d, 1 H, J = 5.9 Hz), 4.72 (dd, 1 H, J = 10.4, 1.1 Hz), 5.01 (s, 1 H), 5.38 (s, 1 H, ex D_2O), 6.44 (dd, 1 H, J = 3.3, 1.7 Hz), 6.45 (dd, 1 H, J = 3.3, 1.0 Hz), 7.20−7.35 (m, 5 H), 7.47 (dd, 1 H, J = 1.7, 1.0 Hz); ^{13}C NMR δ 25.0, 26.5, 55.3, 61.7, 66.1, 82.6, 85.0, 86.3, 109.9, 110.4, 110.7, 112.3, 127.3, 128.2, 129.5, 137.6, 142.3, 150.0. Anal. Calcd for $C_{20}H_{25}NO_6$: C, 63.99; H, 6.71; N, 3.73. Found: C, 64.14; H, 6.93; N, 3.48.

Methyl *N*-Benzyl-5-deoxy-5-(2-furyl)-5-(hydroxyamino)-2,3-*O*-isopropylidene-β-D-*allo*-1,4-pentofuranoside (7b). From the nitrone **3** (1.54 g, 5 mmol) by method B. Isolated by

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column chromatography (80:20 hexane−diethyl ether): 1.31 g, 70%; oil; $[\alpha]_D = -12.2$ (*c* 2.30, $CHCl_3$); ^1H NMR δ 1.34 (s, 3 H), 1.46 (s, 3 H), 3.04 (s, 3 H), 3.64 (d, 1 H, $J = 13.0$ Hz), 3.72 (d, 1 H, $J = 13.0$ Hz), 3.93 (d, 1 H, $J = 11.0$ Hz), 4.58 (d, 1 H, $J = 6.1$ Hz), 4.75 (dd, 1 H, $J = 11.0$, 1.0 Hz), 4.88 (s, 1 H), 4.97 (s, 1 H, ex D_2O), 5.16 (dd, 1 H, J =6.1, 1.0 Hz), 6.39 (dd, 1 H, $J = 3.3$, 0.7 Hz), 6.43 (dd, 1 H, $J = 3.3$, 1.8 Hz), 7.22−7.34 (m, 5 H), 7.47 (dd, 1 H, $J = 1.8$, 0.7 Hz); ^{13}C NMR δ 25.2, 26.5, 55.1, 62.0, 65.4, 82.5, 85.1, 86.0, 109.5, 110.4, 110.4, 112.4, 127.4, 128.3, 129.3, 137.5, 142.2, 150.4. Anal. Calcd for $C_{20}H_{25}NO_6$: C, 63.99; H, 6.71; N, 3.73. Found: C, 63.84; H, 6.80; N, 3.79.

Methyl *N*-Benzyl-5-deoxy-5-(2-furyl)-5-(hydroxyamino)-2,3-*O*-isopropylidne-*β*-L-*gulo*-1,4-pentofuranoside (8a). From the nitrone **4** (1.54 g, 5 mmol) by method A. Isolated by column chromatography (80:20 hexane−diethyl ether): 1.20 g, 64%; oil; $[\alpha]_D = +31.4$ (*c* 1.20, $CHCl_3$); ^1H NMR δ 1.19 (s, 3 H), 1.39 (s, 3 H), 3.38 (s, 3 H), 3.75 (s, 2 H), 4.43 (dd, 1 H, J = 5.8, 3.2 Hz), 4.47 (d, 1 H, $J = 10.2$ Hz), 4.51 (d, 1 H, $J = 5.8$ Hz), 4.62 (dd, 1 H, $J = 10.2$, 3.2 Hz), 4.99 (s, 1 H), 5.12 (s, 1 H, ex D_2O), 6.37 (d, 1 H, $J = 3.4$ Hz), 6.41 (dd, 1 H, $J = 3.4$, 1.7 Hz), 7.20−7.40 (m, 5 H), 7.45 (d, 1 H, $J = 1.7$ Hz); ^{13}C NMR δ 25.0, 26.1, 54.8, 60.8, 62.3, 78.3, 80.1, 84.5, 107.5, 110.0, 110.3, 112.6, 127.1, 128.2, 129.5, 137.8, 142.2, 150.0. Anal. Calcd for $C_{20}H_{25}NO_6$: C, 63.99; H, 6.71; N, 3.73. Found: C, 64.16; H, 6.95; N, 3.95.

Methyl *N*-Benzyl-5-deoxy-5-(2-furyl)-5-(hydroxyamino)-2,3-*O*-isopropylidene-α-D-*manno*-1,4-pentofuranoside (8b). From the nitrone **4** (1.54 g, 5 mmol) by method B. Isolated by column chromatography (80:20 hexane−diethyl ether): 1.33 g, 71%; white solid; mp 67−69 °C; $[\alpha]_D = +24.7$ (*c* 1.60, $CHCl_3$); ^1H NMR δ 1.32 (s, 3 H), 1.33 (s, 3 H), 3.22 (s, 3 H), 3.71 (d, 1 H, $J = 13.1$ Hz), 3.82 (d, 1 H, $J = 13.1$ Hz), 4.38 (d, 1 H, J = 9.9 Hz), 4.53 (d, 1 H, $J = 5.8$ Hz), 4.56 (dd, 1 H, $J = 9.9$, 3.2 Hz), 4.77 (bs, 1 H, ex D_2O), 4.80 (s, 1 H), 4.88 (dd, 1 H, J = 5.8, 3.2 Hz), 6.40 (dd, 1 H, $J = 3.1$, 0.9 Hz), 6.43 (dd, 1 H, J = 3.1, 1.9 Hz), 7.24−7.37 (m, 5 H), 7.45 (dd, 1 H, $J = 1.9$, 0.9 Hz); ^{13}C NMR δ 25.2, 26.1, 54.3, 61.4, 62.2, 78.5, 79.8, 84.7, 106.9, 110.2, 110.3, 112.3, 127.3, 128.1, 129.5, 137.4, 142.4, 150.4. Anal. Calcd for $C_{20}H_{25}NO_6$: C, 63.99; H, 6.71; N, 3.73. Found: C, 64.08; H, 6.86; N, 3.50.

***N*-Benzyl-3-*O*-benzyl-5-deoxy-5-(2-furyl)-5-(hydroxyamino)-1,2-*O*-isopropylidene-*β*-L-*ido*-1,4-pentofuranoside (9a).** From the nitrone **5** (1.92 g, 5 mmol) by method A. Isolated by column chromatography (60:40 hexane−diethyl ether): 1.90 g, 84%; white solid; mp 58−60 °C; $[\alpha]_D = -35.6$ (*c* 1.30, $CHCl_3$); ^1H NMR δ 1.31 (s, 3 H), 1.52 (s, 3 H), 3.65 (d, 1 H, $J = 2.8$ Hz), 3.68 (d, 1 H, $J = 13.4$ Hz), 3.82 (d, 1 H, $J = 13.4$ Hz), 4.09 (d, 1 H, $J = 11.4$ Hz), 4.37 (d, 1 H, $J = 11.4$ Hz), 4.47 (d, 1 H, $J = 10.0$ Hz), 4.53 (d, 1 H, $J = 3.6$ Hz), 4.90 (dd, 1 H, J = 10.0, 2.8 Hz), 5.13 (bs, 1 H, ex D_2O), 6.02 (d, 1 H, $J = 3.6$ Hz), 6.34 (d, 1 H, $J = 3.2$ Hz), 6.40 (dd, 1 H, $J = 3.2$, 1.7 Hz), 7.15−7.40 (m, 10 H), 7.44 (d, 1 H, $J = 1.7$ Hz); ^{13}C NMR δ 26.3, 26.9, 61.4, 62.7, 72.2, 79.2, 81.7, 82.4, 105.4, 109.9, 110.3, 111.7, 127.1, 127.6, 127.8, 128.1, 128.3, 129.4, 137.3, 137.8, 142.0, 150.1. Anal. Calcd for $C_{26}H_{29}NO_6$: C, 69.16; H, 6.47; N, 3.10. Found: C, 68.94; H, 6.40; N, 3.08.

***N*-Benzyl-3-*O*-benzyl-5-deoxy-5-(2-furyl)-5-(hydroxyamino)-1,2-*O*-isopropylidene-*β*-D-*gluco*-1,4-pentofuranose (9b).** From the nitrone **5** (1.92 g, 5 mmol) by method B. Isolated by column chromatography (60:40 hexane−diethyl ether): 1.76 g, 78%; white solid; mp 95−97 °C; $[\alpha]_D = -22.9$ (*c* 1.52, $CHCl_3$); ^1H NMR δ 1.29 (s, 3 H), 1.50 (s, 3 H), 3.71 (s, 2 H), 4.19 (d, 1 H, $J = 2.9$ Hz), 4.42 (s, 1 H, ex D_2O), 4.50 (d, 1 H, $J = 10.0$ Hz), 4.57 (d, 1 H, $J = 3.7$ Hz), 4.65 (d, 1 H, $J = 11.7$ Hz), 4.71 (d, 1 H, $J = 11.7$ Hz), 4.83 (dd, 1 H, $J = 10.0$, 2.9 Hz), 5.87 (d, 1 H, $J = 3.7$ Hz), 6.43 (dd, 1 H, $J = 3.2$, 1.7 Hz), 6.45 (dd, 1 H, $J = 3.2$, 0.7 Hz), 7.21−7.23 (m, 5 H), 7.30−7.33 (m, 5 H), 7.49 (dd, 1 H, $J = 1.7$, 0.7 Hz); ^{13}C NMR δ 26.3, 26.9, 61.4, 62.3, 72.5, 79.3, 81.8, 82.0, 105.0, 110.3, 110.7, 111.6, 127.3, 127.4, 127.8, 128.2, 128.4, 129.3, 137.5, 137.9, 142.5, 150.1. Anal. Calcd for $C_{26}H_{29}NO_6$: C, 69.16; H, 6.47; N, 3.10. Found: C, 69.32; H, 6.49; N, 3.25.

***N*-Benzyl-6-deoxy-1,2:3,4-di-*O*-isopropylidene-6-(2-furyl)-6-(hydroxyamino)-*β*-L-*glycero*-D-*galacto*-1,5-hexopyranose (10a).** From the nitrone **6** (1.82 g, 5 mmol) by method A. Isolated by column chromatography (80:20 hexane−diethyl ether): 1.42 g, 66%; oil; $[\alpha]_D = -54.8$ (*c* 1.36, $CHCl_3$); ^1H NMR δ 1.24 (s, 3 H), 1.33 (s, 3 H), 1.47 (s, 3 H), 1.57 (s, 3 H), 3.60 (d, 1 H, $J = 13.4$ Hz), 3.66 (d, 1 H, $J = 13.4$ Hz), 3.84 (dd, 1 H, $J = 8.1$, 1.2 Hz), 4.32 (dd, 1 H, $J = 5.1$, 2.4 Hz), 4.42 (d, 1 H, $J = 10.5$ Hz), 4.46 (dd, 1 H, $J = 10.5$, 1.2 Hz), 4.56 (dd, 1 H, $J = 8.1$, 2.4 Hz), 5.08 (bs, 1 H, ex D_2O), 5.64 (d, 1 H, $J = 5.1$ Hz), 6.38−6.44 (m, 2 H), 7.26−7.38 (m, 5 H), 7.46−7.50 (m, 1 H); ^{13}C NMR δ 24.3, 25.0, 25.9, 25.9, 60.3, 62.9, 67.0, 70.7, 70.9, 71.1, 97.0, 108.8, 109.4, 110.2, 110.4, 127.0, 128.0, 129.5, 138.0, 142.4, 150.0. Anal. Calcd for $C_{23}H_{29}NO_7$: C, 64.02; H, 6.77; N, 3.25. Found: C, 63.88; H, 6.81; N, 3.18.

***N*-Benzyl-6-deoxy-1,2:3,4-di-*O*-isopropylidene-6-(2-furyl)-6-(hydroxyamino)-α-D-*glycero*-D-*galacto*-1,5-hexopyranose (10b).** From the nitrone **6** (1.82 g, 5 mmol) by method B. Isolated by column chromatography (80:20 hexane−diethyl ether): 1.94 g, 90%; white solid; mp 184−186 °C; $[\alpha]_D = -73.2$ (*c* 0.25, $CHCl_3$); ^1H NMR δ 1.29 (s, 3 H), 1.38 (s, 6 H), 1.58 (s, 3 H), 3.80 (ABq, 2 H, $J = 13.7$ Hz, $\Delta\delta = 0.02$), 4.26 (dd, 1 H, $J = 5.1$, 2.2 Hz), 4.29 (d, 1 H, $J = 10.2$ Hz), 4.32 (bs, 1 H, ex D_2O), 4.42 (dd, 1 H, $J = 10.2$, 1.5 Hz), 4.62 (dd, 1 H, $J = 8.1$, 2.2 Hz), 4.66 (dd, 1 H, $J = 8.1$, 1.5 Hz), 5.44 (d, 1 H, $J = 5.1$ Hz), 6.40 (dd, 1 H, $J = 3.2$, 1.0 Hz), 6.42 (dd, 1 H, $J = 3.2$, 1.7 Hz), 7.26−7.39 (m, 5 H), 7.47 (dd, 1 H, $J = 1.7$, 1.0 Hz); ^{13}C NMR δ 24.5, 25.0, 26.0, 26.1, 62.2, 62.4, 66.7, 70.8, 71.0 (x2), 96.8, 108.6, 109.0, 110.3, 110.7, 127.20, 128.1, 129.3, 137.6, 142.3, 150.0. Anal. Calcd for $C_{23}H_{29}NO_7$: C, 64.02; H, 6.77; N, 3.25. Found: C, 63.82; H, 6.60; N, 3.34.

2,5-Anhydro-*N*-benzyl-1-deoxy-3,4:6,7-di-*O*-isopropylidene-1-(2-furyl)-1-(hydroxyamino)-D-*erythro*-L-*manno*-heptitol (33a). From the nitrone **31** (1.89 g, 5 mmol) by method A. Isolated by column chromatography (60:40 hexane−diethyl ether): 1.45 g, 65%; sticky oil; $[\alpha]_D = +2.1$ (*c* 3.2, $CHCl_3$); ^1H NMR δ 1.18 (s, 3 H), 1.34 (s, 3 H), 1.38 (s, 3 H), 1.45 (s, 3 H), 3.55 (dd, 1 H, $J = 7.7$, 3.7 Hz), 3.74 (ABq, 2 H, $J = 13.4$ Hz, $\Delta\delta = 0.05$), 4.11 (dd, 1 H, $J = 8.8$, 6.1 Hz), 4.16 (dd, 1 H, $J = 10.1$, 3.4 Hz), 4.20 (dd, 1 H, $J = 8.8$, 4.3 Hz), 4.32 (d, 1 H, $J = 10.1$ Hz), 4.41 (dd, 1 H, $J = 6.1$, 3.4 Hz), 4.42 (ddd, 1 H, $J = 7.7$, 6.1, 4.3 Hz), 4.67 (dd, 1 H, $J = 6.1$, 3.7 Hz), 6.18 (bs, 1 H, ex D_2O), 6.34 (dd, 1 H, J =3.2, 0.8 Hz), 6.40 (dd, 1 H, $J = 3.2$, 1.9 Hz), 7.21−7.34 (m, 5 H), 7.43 (dd, 1 H, J = 1.9, 0.8 Hz); ^{13}C NMR δ 24.7, 25.3, 25.7, 27.1, 61.0, 61.8, 66.9, 73.1, 80.2, 80.5, 81.2, 82.0, 109.1, 110.0, 110.2, 112.4, 127.1, 128.1, 129.5, 137.6, 142.1, 149.8. Anal. Calcd for $C_{24}H_{31}NO_7$: C, 64.70; H, 7.01; N, 3.14. Found: C, 64.94; H, 6.93; N, 3.09.

2,5-Anhydro-*N*-benzyl-1-deoxy-3,4:6,7-di-*O*-isopropylidene-1-(2-furyl)-1-(hydroxyamino)-D-*erythro*-L-*gluco*-heptitol (33b). From the nitrone **31** (1.89 g, 5 mmol) by method B. Isolated by column chromatography (60:40 hexane−diethyl ether): 1.47 g, 66%; oil; $[\alpha]_D = +5.1$ (*c* 1.04, $CHCl_3$); ^1H NMR δ 1.32 (s, 6 H), 1.33 (s, 3 H), 1.34 (s, 3 H), 3.45 (dd, 1 H, J = 7.5, 3.5 Hz), 3.65 (d, 1 H, J =13.1 Hz), 3.83 (d, 1 H, $J = 13.1$ Hz), 3.86 (dd, 1 H, $J = 8.7$, 6.4 Hz), 3.92 (dd, 1 H, $J = 8.7$, 4.5 Hz), 4.09 (dd, 1 H, $J = 9.3$, 3.3 Hz), 4.29 (ddd, 1 H, $J = 7.5$, 6.4, 4.5 Hz), 4.34 (d, 1 H, $J = 9.3$ Hz), 4.70 (dd, 1 H, J =5.8, 3.5 Hz), 4.88 (dd, 1 H, $J = 5.8$, 3.3 Hz), 5.66 (bs (1 H, ex D_2O), 6.33 (dd, 1 H, J =3.2, 0.9 Hz), 6.38 (dd, 1 H, $J = 3.2$, 1.8 Hz), 7.22−7.35 (m, 5 H), 7.43 (dd, 1 H, $J = 1.8$, 0.9 Hz); ^{13}C NMR δ 24.7, 25.4, 25.6, 26.8, 61.2, 62.2, 66.7, 73.0, 80.2, 80.6, 81.0, 81.6, 109.0, 110.1, 110.5, 112.1, 127.3, 128.1, 129.5, 137.3, 142.1, 150.2. Anal. Calcd for $C_{24}H_{31}NO_7$: C, 64.70; H, 7.01; N, 3.14. Found: C, 64.84; H, 6.80; N, 3.41.

2,6-Anhydro-*N*-benzyl-1-deoxy-1-(2-furyl)-1-(hydroxyamino)-3,4,5,7-tetra-*O*-benzyl-D-*threo*-L-*talo*-heptitol (34b). From the nitrone **32** (3.29 g, 5 mmol) by method B. Isolated by column chromatography (60:40 hexane−diethyl ether): 2.58 g, 71%; oil; $[\alpha]_D = +11.8$ (*c* 1.40, $CHCl_3$); ^1H NMR δ 3.53−3.62 (m, 3 H), 3.64, (dd, 1 H, $J = 9.3$, 2.6 Hz), 3.70 (d, 1 H, $J = 12.9$ Hz), 3.76 (t, 1 H, $J = 9.4$ Hz), 3.89 (d, 1 H, $J = 12.9$ Hz), 3.96 (dd, 1 H, $J = 2.6$, 0.5 Hz), 4.0 (dd, 1 H, $J = 9.4$, 3.9 Hz), 4.35 (d, 1 H, $J = 11.8$ Hz), 4.39 (d, 1 H, $J = 11.9$ Hz), 4.41 (d, 1 H, $J = 3.9$ Hz), 4.42 (d, 1 H, $J = 11.9$ Hz), 4.57 (d, 1 H, $J = 11.8$ Hz), 4.66 (d, 1 H, $J = 11.7$ Hz), 4.73 (d, 1 H, $J = 11.7$ Hz), 4.75 (d, 1 H, $J = 11.8$ Hz), 4.91 (d, 1 H, $J = 11.8$ Hz), 5.70 (bs, 1 H,

ex D_2O), 6.40 (dd, 1 H, J = 3.2, 1.8 Hz), 6.65 (dd, 1 H, J = 3.2, 0.7 Hz), 7.21−7.41 (m, 25 H), 7.47 (dd, 1 H, J = 1.8, 0.7 Hz); ^{13}C NMR δ 53.5, 61.3, 63.2, 69.1, 72.2, 73.5 (×2), 74.2, 75.3, 76.5, 81.4, 84.8, 110.6, 111.7, 126.0, 127.0, 127.3, 127.4, 127.6, 127.7, 127.7, 127.8, 127.9, 128.2, 128.3, 128.4, 128.5, 128.6, 129.9, 137.7, 137.8, 138.0, 138.2, 138.9, 141.7, 149.6. Anal. Calcd for $C_{46}H_{47}NO_7$: C, 76.11; H, 6.53; N, 1.93. Found: C, 75.83; H, 6.42; N, 1.65.

Methyl 5-((Benzyloxycarbonyl)amino)-5-deoxy-5-(2-furyl)-2,3-*O*-isopropylidene-α-L-*talo*-1,4-pentofuranoside (11a). A freshly solution of titanium(III) chloride (1.02 g, 6.6 mmol) in H_2O (4.1 mL) was added dropwise to a solution of the hydroxylamine **7a** (1.12 g, 3 mmol) in methanol (35 mL). The resulting mixture was stirred at ambient temperature for 15 min and then treated with 20% aqueous NaOH (5 mL). After 5 min stirring, CH_2Cl_2 (25 mL) and H_2O (10 mL) were added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 25 mL). The organic extracts were combined, dried ($MgSO_4$), and then concentrated under reduced pressure to 30 mL volume. Silica gel (6.8 g) and water (2.2 mL) were added, and the mixture was stirred vigorously at ambient temperature for 12 h. The mixture was filtered, and the filter was washed with AcOEt containing 0.5% Et_3N, (3 × 80 mL). The combined filtrates were dried ($MgSO_4$) and concentrated in vacuo. The crude primary amine was taken up in dioxane (35 mL) and the solution treated with 7% aqueous $NaHCO_3$ (15 mL). The resulting solution was stirred at 0 °C for 10 min, and then benzyl chloroformate (0.48 mL, 3.3 mmol) was added. After stirring at 0 °C for 30 min, water (60 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo to give the crude product which was purified by column chromatography on silica gel (80:20 hexane−diethyl ether) to give **11a** (0.85 g, 70%) as an oil: $[\alpha]_D$ = +13.9 (*c* 1.92, $CHCl_3$); ^{1}H NMR δ 1.26 (s, 3 H), 1.45 (s, 3 H), 3.32 (s, 3 H), 4.53 (d, 1 H, J = 5.8 Hz), 4.64 (d, 1 H, J = 5.8 Hz), 4.66 (d, 1 H, J = 4.9 Hz), 4.91−4.99 (m, 2 H), 5.09 (d, 1 H, J = 12.4 Hz), 5.14 (d, 1 H, J = 12.4 Hz), 6.02 (bd, 1 H, J = 8.8 Hz), 6.22 (d, 1 H, J = 3.4 Hz), 6.29 (dd, 1 H, J = 3.4, 1.9 Hz), 7.26−7.37 (m, 6 H); ^{13}C NMR δ 24.9, 26.4, 51.5, 55.7, 65.4, 82.1, 85.5, 87.8, 107.0, 110.2, 110.5, 112.6, 127.0, 127.6, 128.6, 136.5, 142.3, 152.4, 156.1. Anal. Calcd for $C_{21}H_{25}NO_7$: C, 62.52; H, 6.25; N, 3.47. Found: C, 62.70; H, 5.98; N, 3.47.

Methyl 5-((Benzyloxycarbonyl)amino)-5-deoxy-2,3-O-isopropylidene-5-(2-furyl)-β-D-*allo*-1,4-pentofuranoside (11b). From the hydroxylamine **7b** (1.29 g, 3 mmol) as described for the preparation of **11a**. Isolated by column chromatography (80:20 hexane−diethyl ether): 0.79 g, 65%; white solid; mp 84−86 °C; $[\alpha]_D$ = −88.1 (*c* 0.35, $CHCl_3$); ^{1}H NMR δ 1.28 (s, 3 H), 1.46 (s, 3 H), 3.18 (s, 3 H), 4.36 (d, 1 H, J = 10.2 Hz), 4.61 (d, 1 H, J = 5.8 Hz), 4.84−4.96 (m, 3 H), 5.06 (d, 1 H, J = 12.5 Hz), 5.12 (d, 1 H, J = 12.5 Hz), 5.20 (bd, 1 H, J = 8.3 Hz), 6.27 (dd, 1 H, J = 2.7, 0.9 Hz), 6.30 (dd, 1 H, J = 2.7, 1.9 Hz), 7.30−7.35 (m, 5 H), 7.37 (dd, 1 H J = 1.9, 0.9 Hz); ^{13}C NMR δ 25.2, 26.6, 51.5, 55.5, 67.2, 81.9, 85.3, 87.7, 108.1, 110.1, 110.3, 112.6, 128.2, 128.2, 128.5, 135.6, 142.2, 152.4, 155.9. Anal. Calcd for $C_{21}H_{25}NO_7$: C, 62.52; H, 6.25; N, 3.47. Found: C, 62.40; H, 6.48; N, 3.26.

3-*O*-Benzyl-5-((benzyloxycarbonyl)amino)-5-deoxy-5-(2-furyl)-1,2-*O*-isopropylidene-β-L-*ido*-1,4-pentofuranose (13a). From the hydroxylamine **9a** (1.29 g, 3 mmol) as described for the preparation of **11a**. Isolated by column chromatography (70:30 hexane−diethyl ether): 0.82 g, 57%; oil; $[\alpha]_D$ = −18.6 (*c* 1.10, $CHCl_3$); ^{1}H NMR δ 1.28 (s, 3 H), 1.47 (s, 3 H), 3.74 (d, 1 H, J = 3.2 Hz), 4.34 (d, 1 H, J = 11.6 Hz), 4.49 (d, 1 H, J = 11.6 Hz), 4.50 (d, 1 H, J = 4.7 Hz), 4.54 (d, 1 H J = 3.7 Hz), 5.04 (ABq, 2 H, J = 12.4 Hz, $\Delta\delta$ = 0.03), 5.21−5.32 (m, 2 H), 5.93 (d, 1 H, J = 3.7 Hz), 6.18 (d, 1 H, J = 3.2 Hz), 6.27 (dd, 1 H, J = 3.2, 1.8 Hz), 7.25−7.35 (m, 11 H); ^{13}C NMR δ 26.2, 26.8, 48.6, 66.7, 72.2, 80.3, 82.1, 82.2, 105.1, 107.2, 110.3, 111.8, 127.6, 127.8, 127.8, 127.9, 128.3, 128.4, 136.6, 137.2, 141.8, 152.4, 155.7. Anal. Calcd for $C_{27}H_{29}NO_7$: C, 67.63; H, 6.10; N, 2.92. Found: C, 67.50; H, 6.18; N, 3.06.

3-*O*-Benzyl-5-((benzyloxycarbonyl)amino)-5-deoxy-5-(2-furyl)-1,2-*O*-isopropylidene-α-D-*gluco*-1,4-pentofuranose (13b). From the hydroxylamine **9b** (1.29 g, 3 mmol) as described for the preparation of **11a**. Isolated by column chromatography (70:30 hexane−diethyl ether): 1.0 g, 70%; oil; $[\alpha]_D$ = −36.0 (*c* 0.85, $CHCl_3$); ^{1}H NMR δ 1.30 (s, 3 H), 1.47 (s, 3 H), 4.10 (d, 1 H, J = 3.6 Hz), 4.44 (d, 1 H, J = 11.7 Hz), 4.48 (dd, 1 H, J = 6.0, 3.3 Hz), 4.54 (d, 1 H, J = 3.3 Hz), 4.57 (d, 1 H, J = 11.7 Hz), 5.06 (s, 2 H), 5.41 (dd, 1 H, J = 8.7, 6.0 Hz), 5.94 (d, 1 H, J = 3.6 Hz), 6.18−6.22 (m, 1 H), 6.24 (bs, 1 H), 6.28−6.32 (m, 1 H), 7.25−7.39 (m, 11 H); ^{13}C NMR δ 26.2, 26.8, 49.6, 65.8, 66.6, 72.4, 78.7, 81.6, 104.9, 107.2, 110.4, 111.8, 127.1, 127.8, 128.0, 128.1, 128.3, 128.6, 136.6, 136.7, 142.0, 152.2, 155.9. Anal. Calcd for $C_{27}H_{29}NO_7$: C, 67.63; H, 6.10; N, 2.92. Found: C, 67.72; H, 6.02; N, 3.14.

Methyl 5-Acetamido-5-deoxy-5-(2-furyl)-2,3-O-isopropylidene-β-L-*gulo*-1,4-pentofuranoside (12a). The hydroxylamine **8a** (1.05 g, 3 mmol) was treated with $TiCl_3$ as described for the preparation of **11a**. Then, the crude amine was taken up in pyridine (5 mL) and treated with acetic anhydride (5 mL) and DMAP (9.2 g, 0.075 mmol) at room temperature. The resulting solution was stirred for 8 h at room temperature. The solvent was partially distilled at reduced pressure and the residue was partitioned between saturated aqueous $NaHCO_3$ (30 mL) and CH_2Cl_2 (30 mL). The organic layer was washed sequentially with saturated aqueous $CuSO_4$ (3 × 20 mL) and brine (20 mL), dried ($MgSO_4$), and evaporated under reduced pressure to give the crude product which was purified by column chromatography on silica gel (5:95 hexane−diethyl ether) to give **12a** (0.68 g, 73%) as a sticky oil: $[\alpha]_D$ = +71.8 (*c* 0.55, $CHCl_3$); ^{1}H NMR δ 1.24 (s, 3 H), 1.44 (s, 3 H), 1.98 (s, 3 H), 3.30 (s, 3 H), 4.28 (dd, 1 H, J = 6.6, 3.4 Hz), 4.52 (d, 1 H, J = 5.8 Hz), 4.57 (dd, 1 H, J = 5.8, 3.4 Hz), 4.92 (s, 1 H), 5.52 (dd, 1 H, J = 8.1, 6.6 Hz), 6.08 (bd, 1 H, J = 8.1 Hz), 6.27 (dd, 1 H, J = 3.2, 1.0 Hz), 6.29 (dd, 1 H, J = 3.2, 1.7 Hz), 7.31 (dd, 1 H, J = 1.7, 1.0 Hz); ^{13}C NMR δ 23.4, 24.6, 26.0, 46.2, 54.8, 79.0, 79.8, 84.9, 107.1, 107.2, 110.4, 112.8, 141.7, 152.4, 169.2. Anal. Calcd for $C_{15}H_{21}NO_6$: C, 57.87; H, 6.80; N, 4.50. Found: C, 57.81; H, 6.78; N, 4.76.

Methyl 5-Acetamido-5-deoxy-5-(2-furyl)-2,3-*O*-isopropylidene-α-D-*manno*-1,4-pentofuranoside (12b). From the hydroxylamine **8b** (1.05 g, 3 mmol) as described for the preparation of **12a**. Isolated by column chromatography (5:95 hexane−diethyl ether): 0.59 g, 63%; colorless crystals; mp 132−134 °C; $[\alpha]_D$ = −18.7 (*c* 0.80, $CHCl_3$); ^{1}H NMR δ 1.29 (s, 3 H), 1.53 (s, 3 H), 1.98 (s, 3 H), 3.31 (s, 3 H), 4.22 (dd, 1 H, J = 4.9, 3.2 Hz), 4.52 (d, 1 H, J = 5.8 Hz), 4.75 (dd, 1 H, J = 5.8, 3.2 Hz), 4.92 (s, 1 H), 5.69 (dd, 1 H, J = 8.8, 4.9 Hz), 6.28 (dd, 1 H, J = 3.4, 1.0 Hz), 6.31 (dd, 1 H, J = 3.4, 1.9 Hz), 7.17 (bd, 1 H, J = 8.8 Hz), 7.33 (dd, 1 H, J = 1.9, 1.0 Hz); ^{13}C NMR δ 23.5, 24.3, 26.0, 47.3, 54.8, 77.2, 81.0, 85.1, 106.8, 107.2, 110.4, 112.7, 141.9, 152.1, 169.5. Anal. Calcd for $C_{15}H_{21}NO_6$: C, 57.87; H, 6.80; N, 4.50. Found: C, 57.64; H, 7.03; N, 4.31.

6-Acetamido-6-deoxy-1,2:3,4-di-*O*-isopropylidene-6-(2-furyl)-β-L-*glycero*-D-*galacto*-1,5-hexopyranoside (14a). From the hydroxylamine **10a** (1.29 g, 3 mmol) as described for the preparation of **12a**. Isolated by column chromatography (20:80 hexane−diethyl ether): 0.69 g, 63%; white solid; mp 139−141 °C; $[\alpha]_D$ = −23.2 (*c* 0.47, $CHCl_3$); ^{1}H NMR δ 1.28 (s, 3 H), 1.33 (s, 3 H), 1.45 (s, 3 H), 1.54 (s, 3 H), 1.99 (s, 3 H), 4.03 (dd, 1 H, J = 7.8, 1.2 Hz), 4.12 (dd, 1 H, J = 7.1, 1.2 Hz), 4.32 (dd, 1 H, J = 5.1, 2.2 Hz), 4.56 (dd, 1 H, J = 7.8, 2.2 Hz), 5.39 (t, 1 H, J = 7.2 Hz), 5.59 (d, 1 H, J = 5.1 Hz), 6.08 (bd, 1 H, J = 7.3 Hz), 6.31 (dd, 1 H, J = 3.2, 1.7 Hz), 6.36 (dd, 1 H, J = 3.2, 0.9 Hz), 7.33 (dd, 1 H, J = 1.7, 0.9 Hz); ^{13}C NMR δ 23.3, 24.2, 24.9, 26.0 (x2), 47.8, 67.4, 70.7, 70.9, 71.4, 96.7, 107.8, 108.8, 109.5, 110.4, 141.7, 152.0, 170.0. Anal. Calcd for $C_{18}H_{25}NO_7$: C, 58.85; H, 6.86; N, 3.81. Found: C, 59.11; H, 6.74; N, 3.80.

6-Acetamido-6-deoxy-1,2:3,4-di-*O*-isopropylidene-6-(2-furyl)-α-D-*glycero*-D-*galacto*-1,5-hexopyranose (14b). From the hydroxylamine **10b** (1.29 g, 3 mmol) as described for the preparation of **12a**. Isolated by column chromatography (20:80 hexane−diethyl ether): 0.75 g, 68%; white solid; mp 116−118 °C; $[\alpha]_D$ = −63.8 (*c* 0.47, $CHCl_3$); ^{1}H NMR δ 1.32 (s, 6 H), 1.50 (s, 3 H), 1.53 (s, 3 H), 1.99 (s, 3 H), 4.17 (d, 1 H, J = 5.6 Hz), 4.22 (d, 1 H, J = 8.1 Hz), 4.32 (dd, 1 H, J = 4.9, 2.2 Hz),

4.57 (dd, 1 H, J = 8.1, 2.2 Hz), 5.44 (dd, 1 H, J = 8.3, 5.6 Hz), 5.55 (d, 1 H, J = 4.9 Hz), 6.26 (bd, 1 H, J = 2.9 Hz), 6.32 (dd, 1 H, J = 2.9, 1.2 Hz), 7.11 (bd, 1 H, J = 8.3 Hz), 7.33 (bd, 1 H, J = 1.2 Hz); ^{13}C NMR δ 23.4, 24.2, 24.9, 25.8, 26.0, 49.9, 66.1, 70.5, 71.0, 72.0, 96.8, 107.1, 108.8, 109.4, 110.4, 141.9, 152.0, 170.5. Anal. Calcd for $C_{18}H_{25}NO_7$: C, 58.85; H, 6.86; N, 3.81. Found: C, 58.74; H, 6.65; N, 3.59.

Methyl 5-(Acetoxyamino)-*N*-benzyl-5-deoxy-2,3-*O*-isopropylidene-5-(2-furyl)-α-L-*talo*-1,4-pentofuranoside (19a). A solution of the hydroxylamine **7a** (1.12 g, 3 mmol) in pyridine (7 mL) were treated with acetic anhydride (7 mL) and DMAP (6.1 mg, 0.05 mmol). The resulting mixture was stirred at room temperature for 2 h, and then CH_2Cl_2 (30 mL) and H_2O (30 mL) were added. The organic layer was washed sequentially with saturated aqueous $CuSO_4$ (3 × 20 mL) and brine (20 mL), dried ($MgSO_4$), and evaporated under reduced pressure to give the crude product which was purified by column chromatography on silica gel (20:80 hexane−diethyl ether) to give **19a** (1.15 g, 92%) as an oil: $[\alpha]_D$ = −6.0 (*c* 0.52, $CHCl_3$); ^{1}H NMR δ 1.20 (s, 3 H), 1.42 (s, 3 H), 1.96 (s, 3 H), 3.30 (s, 3 H), 3.75 (d, 1 H, J = 12.4 Hz), 3.94 (d, 1 H, J = 12.4 Hz), 4.18 (d, 1 H, J = 10.7 Hz), 4.33 (d, 1 H, J = 6.2 Hz), 4.48 (d, 1 H, J = 6.2 Hz), 4.54 (d, 1 H, J = 10.7 Hz), 4.98 (s, 1 H), 6.40−6.46 (m, 2 H), 7.24−7.38 (m, 5 H), 7.55 (bs, 1 H); ^{13}C NMR δ 19.7, 25.0, 26.5, 55.6, 60.7, 65.5, 82.6, 84.8, 86.0, 109.9, 110.8, 111.0, 112.5, 127.9, 128.4, 130.3, 135.5, 142.8, 149.3, 170.9. Anal. Calcd for $C_{22}H_{27}NO_7$: C, 63.30; H, 6.52; N, 3.36. Found: C, 63.34; H, 6.74; N, 3.18.

Methyl 5-(Acetoxyamino)-*N*-benzyl-5-deoxy-2,3-*O*-isopropylidene-5-(2-furyl)-β-D-*allo*-1,4-pentofuranoside (19b). From the hydroxylamine **7b** (1.29 g, 3 mmol) as described for the preparation of **19a**. Isolated by column chromatography (20:80 hexane−diethyl ether): 1.01 g, 81%; oil; $[\alpha]_D$ = −94.4 (*c* 0.24, $CHCl_3$); ^{1}H NMR δ 1.34 (s, 3 H), 1.44 (s, 3 H), 1.87 (s, 3 H), 2.97 (s, 3 H), 3.69 (d, 1 H, J = 13.3 Hz), 3.97 (d, 1 H, J = 13.3 Hz), 4.15 (d, 1 H, J = 11.1 Hz), 4.50−4.55 (m, 2 H), 4.83 (s, 1 H), 5.40 (d, 1 H, J = 5.6 Hz), 6.36 (dd, 1 H, J = 3.2, 0.9 Hz), 6.44 (dd, 1 H, J = 3.2, 1.9 Hz), 7.20−7.38 (m, 5 H), 7.50 (dd, 1 H, J = 1.9, 0.9 Hz); ^{13}C NMR δ 19.2, 25.3, 26.6, 55.2, 59.4, 64.1, 82.6, 85.0, 85.3, 110.2, 110.3, 110.9, 112.2, 127.7, 128.3, 129.3, 135.9, 142.5, 150.0, 169.2. Anal. Calcd for $C_{22}H_{27}NO_7$: C, 63.30; H, 6.52; N, 3.36. Found: C, 63.17; H, 6.28; N, 3.51.

Methyl 5-(Acetoxyamino)-*N*-benzyl-5-deoxy-2,3-*O*-isopropylidene-5-(2-furyl)-β-L-*gulo*-1,4-pentofuranoside (20a). From the hydroxylamine **8a** (1.05 g, 3 mmol) as described for the preparation of **19a**. Isolated by column chromatography (60:40 hexane−diethyl ether): 1.05 g, 84%; oil; $[\alpha]_D$ = +11.5 (*c* 1.11, $CHCl_3$); ^{1}H NMR δ 1.16 (s, 3 H), 1.37 (s, 3 H), 1.82 (s, 3 H), 3.32 (s, 3 H), 3.93 (ABq, 2 H, J = 13.2 Hz, $\Delta\delta$ = 0.07), 4.37 (dd, 1 H, J = 5.6, 2.9 Hz), 4.20−4.28 (m, 2 H), 4.54 (d, 1 H, J = 10.0 Hz), 4.96 (s, 1 H), 6.36 (dd, 1 H, J = 3.2, 0.7 Hz), 6.40 (dd, 1 H, J = 3.2, 1.7 Hz), 7.24−7.40 (m, 5 H), 7.44 (dd, 1 H, J = 1.7, 0.7 Hz); ^{13}C NMR δ 19.3, 25.1, 26.1, 54.8, 60.6, 61.9, 78.2, 80.4, 84.4, 107.6, 110.2, 110.3, 112.6, 127.6, 128.2, 130.0 134.8, 142.3, 149.4, 170.7. Anal. Calcd for $C_{22}H_{27}NO_7$: C, 63.30; H, 6.52; N, 3.36. Found: C, 63.19; H, 6.31; N, 3.50.

Methyl 5-(Acetoxyamino)-*N*-benzyl-5-deoxy-2,3-*O*-isopropylidene-5-(2-furyl)-α-D-*manno*-1,4-pentofuranoside (20b). From the hydroxylamine **8b** (1.05 g, 3 mmol) as described for the preparation of **19a**. Isolated by column chromatography (80:20 hexane−diethyl ether): 1.0 g, 80%; white solid; mp 71−73 °C; $[\alpha]_D$ = +54.6 (*c* 1.60, $CHCl_3$); ^{1}H NMR δ 1.22 (s, 3 H), 1.29 (s, 3 H), 1.84 (s, 3 H), 3.22 (s, 3 H), 3.93 (d, 1 H, J = 12.9 Hz), 4.23 (d, 1 H, J = 12.9 Hz), 4.37 (dd, 1 H, J = 9.7, 3.2 Hz), 4.48 (d, 1 H, J = 9.7 Hz), 4.52 (d, 1 H, J = 5.8 Hz), 4.78 (s, 1 H), 5.03 (dd, 1 H, J = 5.8, 3.2 Hz), 6.38 (dd, 1 H, J = 3.2, 0.7 Hz), 6.42 (dd, 1 H, J = 3.2, 1.9 Hz), 7.23−7.31 (m, 3 H), 7.37−7.42 (m, 2 H), 7.47 (dd, 1 H, J = 1.9, 0.7 Hz); ^{13}C NMR δ 19.3, 25.1, 25.8, 54.4, 60.7, 60.9, 78.4, 80.1, 84.6, 107.4, 110.2, 110.4, 112.1, 127.5, 128.0, 129.7, 135.8, 142.3, 149.9, 169.5. Anal. Calcd for $C_{22}H_{27}NO_7$: C, 63.30; H, 6.52; N, 3.36. Found: C, 63.20; H, 6.86; N, 3.57.

5-(Acetoxyamino)-*N*-benzyl-3-*O*-benzyl-5-deoxy-1,2-*O*-isopropylidene-5-(2-furyl)-β-L-*ido*-1,4-pentofuranose (21a). From the hydroxylamine **9a** (1.28 g, 3 mmol) as described for the preparation of **19a**. Isolated by column chromatography (60:40 hexane−diethyl ether): 1.38 g, 93%; oil; $[\alpha]_D$ = −43.9 (*c* 1.40, $CHCl_3$); ^{1}H NMR δ 1.28 (s, 3 H), 1.48 (s, 3 H), 1.80 (s, 3 H), 3.61 (d, 1 H, J = 2.9 Hz), 3.90 (d, 1 H, J = 13.3 Hz), 3.98 (d, 1 H, J = 11.2 Hz), 4.00 (d, 1 H, J = 13.3 Hz), 4.27 (d, 1 H, J = 11.2 Hz), 4.45 (d, 1 H, J = 3.8 Hz), 4.51 (d, 1 H, J = 9.5 Hz), 4.73 (dd, 1 H, J = 9.5, 2.9 Hz), 5.95 (d, 1 H, J = 3.8 Hz), 6.33 (dd, 1 H, J = 3.3, 0.7 Hz), 6.36 (dd, 1 H, J = 3.3, 1.8 Hz), 7.11−7.17 (m, 2 H), 7.22−7.36 (m, 8H), 7.41 (dd, 1 H, J = 1.8, 0.7 Hz); ^{13}C NMR δ 19.3, 26.4, 26.8, 61.0, 63.5, 72.2, 79.1, 81.2, 82.8, 105.4, 110.1, 110.4, 111.9, 127.6, 127.6, 127.8, 128.3, 128.3, 129.9, 136.0, 137.1, 142.1, 149.5, 171.9. Anal. Calcd for $C_{28}H_{31}NO_7$: C, 68.14; H, 6.33; N, 2.84. Found: C, 67.93; H, 6.25; N, 2.66.

5-(Acetoxyamino)-*N*-benzyl-3-*O*-benzyl-5-deoxy-1,2-*O*-isopropylidene-5-(2-furyl)-β-D-*gluco*-1,4-pentofuranoside (21b). From the hydroxylamine **9b** (1.28 g, 3 mmol) as described for the preparation of **19a**. Isolated by column chromatography (60:40 hexane−diethyl ether): 1.38 g, 93%; white solid; mp 108−110 °C; $[\alpha]_D$ = −4.7 (*c* 0.19, $CHCl_3$); ^{1}H NMR δ 1.25 (s, 3 H), 1.46 (s, 3 H), 1.84 (s, 3 H), 3.84 (d, 1 H, J = 12.5 Hz), 3.92 (d, 1 H, J = 12.5 Hz), 4.36 (d, 1 H, J = 2.1 Hz), 4.44 (d, 1 H, J = 3.8 Hz), 4.52−4.58 (m, 2 H), 4.70 (ABq, 2 H, J = 10.6 Hz, $\Delta\delta$ = 0.02), 5.80 (d, 1 H, J = 3.8 Hz), 6.40−6.43 (m, 2 H), 7.14−7.32 (m, 10H), 7.47 (dd, 1 H, J = 1.6, 0.9 Hz); ^{13}C NMR δ 19.1, 26.4, 26.9, 60.6, 60.8, 72.6, 79.4, 81.9, 82.3, 105.0, 110.2, 110.8, 111.6, 127.4, 127.5, 127.6, 128.1, 128.3, 129.6, 135.6, 138.2, 142.5, 149.7, 169.2. Anal. Calcd for $C_{28}H_{31}NO_7$: C, 68.14; H, 6.33; N, 2.84. Found: C, 68.13; H, 6.60; N, 2.73.

6-(Acetoxyamino)-*N*-benzyl-6-deoxy-1,2:3,4-*O*-isopropylidene-6-(2-furyl)-β-L-*glycero*-D-*galacto*-1,5-hexopyranose (22a). From the hydroxylamine **10a** (1.29 g, 3 mmol) as described for the preparation of **19a**. Isolated by column chromatography (70:30 hexane−diethyl ether): 1.25 g, 88%; oil; $[\alpha]_D$ = −47.5 (*c* 2.75, $CHCl_3$); ^{1}H NMR δ 1.19 (s, 3 H), 1.29 (s, 3 H), 1.40 (s, 3 H), 1.53 (s, 3 H), 1.85 (s, 3 H), 3.74 (dd, 1 H, J = 7.9, 1.7 Hz), 3.86 (s, 2 H), 4.28 (dd, 1 H, J = 5.1, 2.4 Hz), 4.29 (dd, 1 H, J = 10.5, 1.7 Hz), 4.49 (dd, 1 H, J = 7.9, 2.4 Hz), 4.51 (d, 1 H, J = 10.5 Hz), 5.62 (d, 1 H, J = 5.1 Hz), 6.38 (dd, 1 H, J = 3.3, 1.0 Hz), 6.40 (dd, 1 H, J = 3.3, 1.6 Hz), 7.24−7.38 (m, 5 H), 7.45 (dd, 1 H, J = 1.6, 1.0 Hz); ^{13}C NMR δ 19.8, 24.4, 24.9, 25.9, 25.9, 60.5, 62.3, 66.7, 70.4, 70.9, 71.2, 96.9, 108.7, 109.3, 110.4, 111.0, 127.7, 128.3, 130.2, 135.8, 142.6, 149.2, 172.4. Anal. Calcd for $C_{25}H_{31}NO_8$: C, 63.41; H, 6.60; N, 2.96. Found: C, 63.54; H, 6.73; N, 2.83.

6-(Acetoxyamino)-*N*-benzyl-6-deoxy-1,2:3,4-*O*-isopropylidene-6-(2-furyl)-α-D-*glycero*-D-*galacto*-1,5-hexopyranoside (22b). From the hydroxylamine **10b** (1.29 g, 3 mmol) as described for the preparation of **19a**. Isolated by column chromatography (80:20 hexane−diethyl ether): 1.28 g, 90%; oil; $[\alpha]_D$ = −32.8 (*c* 0.53, $CHCl_3$); ^{1}H NMR δ 1.30 (s, 3 H), 1.32 (s, 3 H), 1.37 (s, 3 H), 1.58 (s, 3 H), 1.85 (s, 3 H), 4.00 (d, 1 H, J = 12.7 Hz), 4.10 (d, 1 H, J = 12.7 Hz), 4.25 (dd, 1 H, J = 10.3, 1.5 Hz), 4.28 (dd, 1 H, J = 4.9, 2.2 Hz), 4.40 (d, 1 H, J = 10.3 Hz), 4.64 (dd, 1 H, J = 8.1, 2.2 Hz), 4.92 (dd, 1 H, J = 8.1, 1.5 Hz), 5.42 (d, 1 H, J = 4.9 Hz), 6.38 (dd, 1 H, J = 3.2, 0.7 Hz), 6.43 (dd, 1 H, J = 3.2, 1.7 Hz), 7.26−7.31 (m, 3 H), 7.41−7.46 (m, 2 H), 7.48 (dd, 1 H, J = 1.7, 0.7 Hz); ^{13}C NMR δ 19.1, 24.5, 25.0, 25.8, 25.8, 60.9, 60.9, 66.5, 70.6, 70.8, 70.9, 96.7, 108.4, 108.8, 110.1, 110.6, 127.5, 127.9, 129.7, 135.8 142.1, 149.7, 169.1. Anal. Calcd for $C_{25}H_{31}NO_8$: C, 63.41; H, 6.60; N, 2.96. Found: C, 63.18; H, 6.31; N, 3.13.

Methyl 5-((Benzyloxycarbonyl)amino)-5-deoxy-2,3-*O*-isopropylidene-1-*O*-methyl-α-L-*talo*-hexofuranuronate (15a). To a well-stirred mixture of CH_3CN, (10.3 mL), CCl_4 (6.9 mL), and H_2O (10.3 mL) were added $NaIO_4$ (1.07 g, 5 mmol) and $RuO_2{\cdot}H_2O$ (13.3 mg, 0.1 mmol) sequentially. The mixture was stirred vigorously at room temperature. After 30 min, $NaHCO_3$ (2.1 g, 25 mmol) was added in one portion followed by 5 mL of H_2O. After 15 min the resulting mixture was treated with a solution of **11a** (0.4 g, 1 mmol) in CH_3CN (0.8 mL). The solution turned black, and after 5 min enough $NaIO_4$ (ca. 0.3 g) was added in small portions to turn the color light green. The mixture was diluted with water (10 mL) and extracted with AcOEt (3 × 15 mL). The aqueous layer was

acidified with 1 N HCl to pH = 2−3 and reextracted with AcOEt (3 × 20 mL). The combined organic extracts were washed sequentially with 20% aqueous $NaHSO_3$ until colorless and brine (20 mL) and dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. The crude acid was dissolved in diethyl ether (20 mL), and the solution was cooled to 0 °C and treated with an ethereal solution of diazomethane until a slight yellow color persisted. The excess of diazomethane was eliminated by quenching with acetic acid. The resulting solution was concentrated under reduced pressure, and the crude ester was purified by column chromatography on silica gel (80:20 hexane−diethyl ether) to give **15a** (0.257 g, 65%) as a white solid: mp 59−61 °C; $[\alpha]_D = -32.5$ (*c* 0.87, $CHCl_3$); IR ^{1}H NMR δ 1.26 (s, 3 H), 1.44 (s, 3 H), 3.36 (s, 3 H), 3.74 (s, 3 H), 4.48−4.58 (m, 2 H), 4.67 (dd, 1 H, *J* = 6.0, 0.9 Hz), 4.82 (d, 1 H, *J* = 3.1 Hz), 4.91 (s, 1 H), 5.12 (ABq, 2 H, *J* = 12.5 Hz, $\Delta\delta$ = 0.03), 6.23 (bd, 1 H, *J* = 9.7 Hz), 7.25−7.38 (m, 5 H); ^{13}C NMR δ 24.96, 26.50, 52.38, 55.8, 56.4, 67.1, 81.8, 85.8, 87.3, 110.6, 112.7, 127.9, 128.1, 128.5, 136.6, 156.7, 170.0. Anal. Calcd for $C_{19}H_{25}NO_8$: C, 57.71; H, 6.37; N, 3.54. Found: C, 57.98; H, 6.18; N, 3.66.

Methyl 5-((Benzyloxycarbonyl)amino)-5-deoxy-2,3-*O*-isopropylidene-1-*O*-methyl-*β*-D-*allo*-hexofuranuronate (15b). From compound **11b** (0.4 g, 1 mmol) as described for the preparation of **15a**. Isolated by column chromatography (80:20 hexane−diethyl ether): 0.261 g, 66%; white solid; mp 68−70 °C; $[\alpha]_D = -12.8$ (*c* 2.86, $CHCl_3$); ^{1}H NMR δ 1.27 (s, 3 H), 1.43 (s, 3 H), 3.30 (s, 3 H), 3.72 (s, 3 H), 4.31 (dd, 1 H, *J* = 7.6, 1.1 Hz), 4.45 (pst, 1 H, *J* = 7.9 Hz), 4.52 (d, 1 H, *J* = 6.0 Hz), 4.89 (dd, 1 H, *J* = 6.0, 1.1 Hz), 4.93 (s, 1 H), 5.10 (s, 2 H), 5.50 (bd, 1 H, *J* =7.9 Hz), 7.25−7.35 (m, 5 H); ^{13}C NMR δ 25.1, 26.6, 52.3, 55.7, 56.8, 67.3, 81.4, 85.3, 87.9, 110.4, 112.7, 128.1, 128.2, 128.5, 136.2, 155.7, 170.3. Anal. Calcd for $C_{19}H_{25}NO_8$: C, 57.71; H, 6.37; N, 3.54. Found: C, 57.64; H, 6.53; N, 3.79.

Methyl 5-Acetamido-5-deoxy-2,3-*O*-isopropylidene-1-*O*-methyl-*β*-L-*gulo*-hexofuranuronate (16a). From compound **12a** (0.35 g, 1 mmol) as described for the preparation of **15a**. Isolated by column chromatography (5:95 hexane−diethyl ether): 0.176 g, 58%; oil; $[\alpha]_D = +32.2$ (*c* 0.35, $CHCl_3$); ^{1}H NMR δ 1.26 (s, 3 H), 1.41 (s, 3 H), 2.01 (s, 3 H), 3.27 (s, 3 H), 3.75 (s, 3 H), 4.32 (t, 1 H, *J* = 3.9 Hz), 4.53 (d, 1 H *J* = 5.8 Hz), 4.77 (dd, 1 H, *J* = 5.8, 3.6 Hz), 4.84 (dd, 1 H, *J* = 7.0, 4.4 Hz), 4.90 (s, 1 H), 6.23 (bd, 1 H, *J* = 7.0 Hz); ^{13}C NMR δ 23.1, 24.2, 25.8, 51.4, 52.7, 54.8, 77.1, 80.0, 84.9, 106.7, 112.8, 169.7, 170.6. Anal. Calcd for $C_{13}H_{21}NO_7$: C, 51.48; H, 6.98; N, 4.62. Found: C, 51.52; H, 6.64; N, 4.82.

Methyl 5-Acetamido-5-deoxy-2,3-*O*-isopropylidene-1-*O*-methyl-α-D-*manno*-hexofuranuronate (16b). From compound **12b** (0.35 g, 1 mmol) as described for the preparation of **15a**. Isolated by column chromatography (30:70 hexane−diethyl ether): 0.158 g, 52%; oil; $[\alpha]_D = +24.5$ (*c* 0.75, $CHCl_3$); ^{1}H NMR δ 1.27 (s, 3 H), 1.50 (s, 3 H), 2.01 (s, 3 H), 3.30 (s, 3 H), 3.75 (s, 3 H), 4.34 (dd, 1 H, *J* = 5.6, 3.4 Hz), 4.53 (d, 1 H *J* = 5.8 Hz), 4.76 (dd, 1 H, *J* = 5.8, 3.4 Hz), 4.91 (s, 1 H), 5.24 (dd, 1 H, *J* = 9.0, 5.6 Hz), 6.82 (bd, 1 H, *J* = 9.0 Hz); ^{13}C NMR δ 23.3, 24.1, 25.8, 51.6, 52.6, 54.9, 75.9, 80.4, 84.9, 106.7, 112.9, 170.0, 170.2. Anal. Calcd for $C_{13}H_{21}NO_7$: C, 51.48; H, 6.98; N, 4.62. Found: C, 51.70; H, 7.15; N, 4.39.

Methyl 3-*O*-Benzyl-5-((benzyloxycarbonyl)amino)-5-deoxy-1,2-*O*-isopropylidene-*β*-L-*ido*-hexofuranuronate (17a). From compound **13a** (0.48 g, 1 mmol) as described for the preparation of **15a**. Isolated by column chromatography (80:20 hexane−diethyl ether): 0.25 g, 53%; white solid; mp 81−83 °C; $[\alpha]_D = -18.1$ (*c* 0.50, $CHCl_3$); ^{1}H NMR δ 1.29 (s, 3 H), 1.45 (s, 3 H), 3.66 (s, 3 H), 4.05 (d, 1 H, *J* = 3.6 Hz), 4.47 (d, 1 H, *J* = 11.4 Hz), 4.50−4.55 (m, 2 H), 4.57 (d, 1 H, *J* = 11.4 Hz), 4.65 (dd, 1 H, *J* = 7.6, 6.1 Hz), 5.01 (d, 1 H, *J* = 12.3 Hz), 5.08 (d, 1 H, *J* = 12.3 Hz), 5.40 (bd, 1 H, *J* = 5.3 Hz), 5.89 (d, 1 H, *J* = 3.6 Hz), 7.27−7.35 (m, 10 H); ^{13}C NMR δ 26.3, 26.8, 52.6, 53.2, 67.0, 72.3, 78.6, 82.2, 82.4, 104.9, 112.1, 127.7, 127.9, 128.0, 128.1, 128.4, 128.5, 136.2, 136.9, 156.0, 170.7. Anal. Calcd for $C_{25}H_{29}NO_8$: C, 63.68; H, 6.20; N, 2.97. Found: C, 63.88; H, 6.14; N, 2.81.

Compound **17a** was also prepared by oxidation of the known[12] α-amino aldehyde **28**. To a solution of **28** (0.5 mmol) in CH_3CN, (5 mL) were added sequentially 35% aqueous H_2O_2 (0.1 mL), 1.2 M aqueous NaH_2PO_4 (0.5 mL), and 0.17 M aqueous ClO_2Na (3.5 mL). After 2 h the reaction mixture was acidified with 1 N HCl to pH = 2, and the resulting mixture was extracted with AcOEt (3 × 10 mL). The organic extracts were dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. This crude material was dissolved in Et_2O (20 mL), and the solution was cooled to 0 °C and treated with an ethereal solution of diazomethane until a slight yellow colour persisted. The excess of diazomethane was eliminated by quenching with acetic acid. The resulting solution was concentrated under reduced pressure, and the crude ester was purified by column chromatography on silica gel (80:20 hexane−diethyl ether) to give **17a** (0.20 g, 85%) whose characteristics matched those given above.

Methyl 3-*O*-Benzyl-5-((benzyloxycarbonyl)amino)-5-deoxy-1,2-*O*-isopropylidene-α-D-*gluco*-hexofuranuronate (17b). From compound **13b** (0.48 g, 1 mmol) as described for the preparation of **15a**. Isolated by column chromatography (60:40 hexane−diethyl ether): 0.321 g, 68%; oil; $[\alpha]_D = -14.4$ (*c* 1.07, $CHCl_3$); ^{1}H NMR δ 1.30 (s, 3 H), 1.47 (s, 3 H), 3.64 (s, 3 H), 4.03 (d, 1 H, *J* = 3.6 Hz), 4.42 (d, 1 H, *J* = 11.5 Hz), 4.54 (d, 1 H, *J* = 4.0 Hz), 4.58 (d, 1 H, *J* = 11.5 Hz), 4.62 (dd, 1 H, *J* = 6.0, 4.0 Hz), 4.96 (dd, 1 H, *J* = 9.2, 6.4 Hz), 5.10 (s, 2 H), 5.88 (bs, 1 H), 5.91 (d, 1 H, *J* = 3.6 Hz), 7.28−7.33 (m, 10 H); ^{13}C NMR δ 26.3, 26.9, 52.4, 53.6, 66.9, 72.4, 77.9, 81.8, 82.8, 105.1, 112.1, 127.9, 128.0, 128.3, 128.3, 128.4, 128.6, 136.3, 138.1, 163.5, 170.5. Anal. Calcd for $C_{25}H_{29}NO_8$: C, 63.68; H, 6.20; N, 2.97. Found: C, 63.99; H, 5.97; N, 2.79.

Methyl 6-Acetamido-6-deoxy-1,2:3,4-di-*O*-isopropylidene-*β*-L-*glycero*-D-*galacto*-heptopyranuronate (18a). From compound **14a** (0.43 g, 1 mmol) as described for the preparation of **15a**. Isolated by column chromatography (5:95 hexane−diethyl ether): 0.183 g, 51%; sticky oil; $[\alpha]_D = -78.0$ (*c* 0.45, $CHCl_3$); ^{1}H NMR δ 1.29 (s, 3 H), 1.30 (s, 3 H), 1.41 (s, 3 H), 1.50 (s, 3 H), 1.99 (s, 3 H), 3.73 (s, 3 H), 4.25 (dd, 1 H, *J* = 4.9, 2.2 Hz), 4.30−4.33 (m, 2 H), 4.57 (dd, 1 H, *J* = 7.6, 2.2 Hz), 4.75 (dd, 1 H, *J* = 6.9, 3.4 Hz), 5.47 (d, 1 H, *J* = 4.9 Hz), 6.30 (bd, 1 H, *J* = 6.9 Hz); ^{13}C NMR δ 23.1, 23.9, 25.0, 25.9, 25.9, 52.6, 54.0, 66.4, 71.0, 71.1, 72.2, 96.4, 109.0, 109.5, 170.1, 170.3. Anal. Calcd for $C_{16}H_{25}NO_8$: C, 53.47; H, 7.01; N, 3.90. Found: C, 53.60; H, 7.25; N, 3.71.

Compound **18a** was prepared also by oxidation of the known[12] α-amino aldehyde **27** (0.5 mmol) as described for the preparation of **17a** from **28**. Column chromatography (5:95 hexane−diethyl ether) gave **18a** (0.15 g, 84%) whose characteristics matched those given above.

Methyl 6-Acetamido-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-heptopyranuronate (18b). From compound **14b** (0.43 g, 1 mmol) as described for the preparation of **15a**. Isolated by column chromatography (5:95 hexane−diethyl ether): 0.183 g, 51%; sticky oil; (0.208 g, 58%, 5:95 hexane−diethyl ether); white solid; mp 124 °C; $[\alpha]_D = -44.3$ (*c* 0.40, $CHCl_3$); ^{1}H NMR δ 1.31 (s, 3 H), 1.32 (s, 3 H), 1.48 (s, 3 H), 1.51 (s, 3 H), 2.00 (s, 3 H), 3.74 (s, 3 H), 4.19 (dd, 1 H, *J* = 5.6, 1.7 Hz), 4.26 (dd, 1 H, *J* = 7.9, 1.7 Hz), 4.29 (dd, 1 H, *J* = 4.9, 2.4 Hz), 4.58 (dd, 1 H, *J* = 7.9, 2.4 Hz), 4.97 (dd, 1 H, *J* = 8.5, 5.6 Hz), 5.52 (d, 1 H, *J* = 4.9 Hz), 6.84 (bd, 1 H, *J* = 8.5 Hz); ^{13}C NMR δ 23.3, 24.12, 24.9, 25.8, 26.0, 52.6, 54.2, 65.2, 70.5, 71.0, 71.9, 96.7, 109.0, 109.8, 170.0, 170.3. Anal. Calcd for $C_{16}H_{25}NO_8$: C, 53.47; H, 7.01; N, 3.90. Found: C, 53.51; H, 6.87; N, 4.01.

Methyl 5-(Acetoxyamino)-*N*-benzyl-5-deoxy-2,3-*O*-isopropylidene-1-*O*-methyl-α-L-*talo*-hexofuranuronate (23a). From compound **19a** (0.41 g, 1 mmol) as described for the preparation of **15a**. Isolated by column chromatography (70:30 hexane−diethyl ether): 0.25 g, 61%; oil; $[\alpha]_D = -9.9$ (*c* 0.95, $CHCl_3$); ^{1}H NMR δ 1.28 (s, 3 H), 1.45 (s, 3 H), 1.81 (s, 3 H), 3.32 (s, 3 H), 3.79 (s, 3 H), 3.91 (d, 1 H, *J* = 9.0 Hz), 4.18 (d, 1 H, *J* = 13.3 Hz), 4.25 (d, 1 H, *J* = 13.3 Hz), 4.52 (d, 1 H, *J* = 6.0 Hz), 4.55 (dd, 1 H, *J* = 9.0, 1.5 Hz), 4.76 (dd, 1 H, *J* = 6.0, 1.5 Hz), 4.95 (s, 1 H), 7.20−7.45 (m, 5 H); ^{13}C NMR δ 18.8, 25.0, 26.5, 51.7, 55.7, 60.2, 70.3, 82.0, 84.7, 84.9, 110.0, 112.7, 127.7, 128.2, 129.7, 135.7, 168.7, 168.9. Anal. Calcd for $C_{20}H_{27}NO_8$: C, 58.67; H, 6.65; N, 3.42. Found: C, 58.90; H, 6.91; N, 3.64.

Methyl 5-(Acetoxyamino)-*N*-benzyl-5-deoxy-2,3-*O*-isopropylidene-1-*O*-methyl-*β*-D-*allo*-hexofuranuronate (23b). From compound **19b** (0.41 g, 1 mmol) as described for the preparation of **15a**. Isolated by column chromatography (80:20 hexane−diethyl ether): 0.24 g, 59%; oil; $[\alpha]_D = -35.2$ (*c* 0.81, $CHCl_3$); ^{1}H NMR δ 1.31 (s, 3 H), 1.43 (s, 3 H), 1.84 (s, 3 H), 3.20 (s, 3 H), 3.82 (d, 1 H, J = 11.0 Hz), 3.83 (s, 3 H), 4.04 (d, 1 H, J = 13.3 Hz), 4.20 (d, 1 H, J = 13.3 Hz), 4.44 (d, 1 H, J = 6.5 Hz), 4.48 (d, 1 H, J = 11.0 Hz), 4.88 (s, 1 H), 5.18 (d, 1 H, J = 6.5 Hz), 7.24−7.43 (m, 5 H); ^{13}C NMR δ 19.0, 26.5, 26.5, 51.9, 55.3, 59.5, 68.7, 81.8, 84.7, 84.9, 110.1, 112.4, 127.8, 128.3, 129.3, 135.5, 168.7, 168.8. Anal. Calcd for $C_{20}H_{27}NO_8$: C, 58.67; H, 6.65; N, 3.42. Found: C, 58.48; H, 6.72; N, 3.78.

Methyl 5-(Acetoxyamino)-*N*-benzyl-5-deoxy-2,3-*O*-isopropylidene-1-*O*-methyl-*β*-L-*gulo*-hexofuranuronate (24a). From compound **20a** (0.41 g, 1 mmol) as described for the preparation of **15a**. Isolated by column chromatography (80:20 hexane−diethyl ether): 0.23 g, 56%; oil; $[\alpha]_D = +57.4$ (*c* 0.96, $CHCl_3$); ^{1}H NMR δ 1.23 (s, 3 H), 1.29 (s, 3 H), 1.83 (s, 3 H), 3.35 (s, 3 H), 3.75 (s, 3 H), 3.94 (d, 1 H, J = 9.4 Hz), 4.29 (d, 1 H, J = 13.2 Hz), 4.34 (d, 1 H, J = 13.2 Hz), 4.42 (dd, 1 H, J = 9.4, 3.8 Hz), 4.51 (d, 1 H, J = 5.7 Hz), 4.75 (dd, 1 H, J = 5.7, 3.8 Hz), 4.92 (s, 1 H), 7.24−7.50 (m, 5 H); ^{13}C NMR δ 18.7, 25.0, 25.9, 51.7, 54.4, 61.5, 67.2, 77.1, 80.8, 84.5, 107.1, 112.6, 127.5, 128.1, 129.6, 136.0, 168.5, 169.3. Anal. Calcd for $C_{20}H_{27}NO_8$: C, 58.67; H, 6.65; N, 3.42. Found: C, 58.83; H, 6.69; N, 3.60.

Methyl 5-(Acetoxyamino)-*N*-benzyl-5-deoxy-2,3-*O*-isopropylidene-1-*O*-methyl-α-D-*manno*-hexofuranuronate (24b). From compound **20b** (0.41 g, 1 mmol) as described for the preparation of **15a**. Isolated by column chromatography (60:40 hexane−diethyl ether): 0.25 g, 61%; oil; $[\alpha]_D = +19.7$ (*c* 0.55, $CHCl_3$); ^{1}H NMR δ 1.25 (s, 3 H), 1.27 (s, 3 H), 1.81 (s, 3 H), 3.27 (s, 3 H), 3.83 (s, 3 H), 4.03 (d, 1 H, J = 10.2 Hz), 4.17 (d, 1 H, J = 13.0 Hz), 4.24 (dd, 1 H, J = 10.2, 3.2 Hz), 4.26 (d, 1 H, J = 13.0 Hz), 4.49 (d, 1 H, J = 5.6 Hz), 4.81 (s, 1 H), 5.00 (dd, 1 H, J = 5.6, 3.2 Hz), 7.24−7.50 (m, 5 H); ^{13}C NMR δ 19.1, 25.0, 26.0, 51.8, 54.4, 62.0, 66.2, 77.4, 80.0, 84.5, 107.5, 112.1, 127.7, 128.0, 129.8, 135.7, 168.1, 169.1. Anal. Calcd for $C_{20}H_{27}NO_8$: C, 58.67; H, 6.65; N, 3.42. Found: C, 58.43; H, 6.23; N, 3.18.

Methyl 5-(Acetoxyamino)-*N*-benzyl-3-*O*-benzyl-5-deoxy-1,2-*O*-isopropylidene-*β*-L-*ido*-hexofuranuronate (25a). From compound **21a** (0.49 g, 1 mmol) as described for the preparation of **15a**. Isolated by column chromatography (60:40 hexane−diethyl ether): 0.28 g, 58%, oil; $[\alpha]_D = -16.2$ (*c* 0.80, $CHCl_3$); ^{1}H NMR δ 1.31 (s, 3 H), 1.50 (s, 3 H), 1.80 (s, 3 H), 3.57 (s, 3 H), 4.00 (d, 1 H, J = 8.8 Hz), 4.10 (d, 1 H, J = 3.6 Hz), 4.20 (d, 1 H, J = 13.6 Hz), 4.31 (d, 1 H, J = 13.6 Hz), 4.32 (d, 1 H, J = 11.3 Hz), 4.55 (d, 1 H, J = 11.3 Hz), 4.56 (d, 1 H, J = 3.9 Hz), 4.72 (dd, 1 H, J = 8.8, 3.6 Hz), 5.96 (d, 1 H, J = 3.9 Hz), 7.20−7.42 (m, 10 H); ^{13}C NMR δ 19.0, 26.4, 26.9, 51.9, 61.7, 68.2, 72.0, 77.7, 81.4, 83.4, 105.3, 111.9, 127.7, 127.7, 128.0, 128.2, 128.4, 129.6, 136.0, 136.9, 168.7, 170.4. Anal. Calcd for $C_{26}H_{31}NO_8$: C, 64.32; H, 6.44; N, 2.88. Found: C, 64.19; H, 6.21; N, 2.54.

Methyl 5-(Acetoxyamino)-*N*-benzyl-3-*O*-benzyl-5-deoxy-1,2-*O*-isopropylidene-α-D-*gluco*-hexofuranuronate (25b). From compound **20b** (0.49 g, 1 mmol) as described for the preparation of **15a**. Isolated by column chromatography (60:40 hexane−diethyl ether): 0.33 g, 69%; oil; $[\alpha]_D = -26.2$ (*c* 0.81, $CHCl_3$); ^{1}H NMR δ 1.26 (s, 3 H), 1.46 (s, 3 H), 1.80 (s, 3 H), 3.83 (s, 3 H), 4.05 (d, 1 H, J = 13.1 Hz), 4.12 (d, 1 H, J = 10.0 Hz), 4.22 (d, 1 H, J = 13.1 Hz), 4.32 (d, 1 H, J = 3.3 Hz), 4.45 (d, 1 H, J = 3.7 Hz), 4.50 (dd, 1 H, J = 10.0, 3.3 Hz), 4.67 (s, 2 H), 5.85 (d, 1 H, J = 3.7 Hz), 7.18−7.36 (m, 10 H); ^{13}C NMR δ 18.9, 26.4, 27.0, 51.9, 61.6, 66.0, 72.6, 78.3, 81.8, 82.3, 105.2, 112.0, 127.5, 127.7, 127.8, 128.2, 128.4, 129.3, 135.4, 137.9, 168.3, 168.8. Anal. Calcd for $C_{26}H_{31}NO_8$: C, 64.32; H, 6.44; N, 2.88. Found: C, 64.55; H, 6.67; N, 3.00.

Methyl 6-(Acetoxyamino)-*N*-benzyl-6-deoxy-1,2:3,4-di-*O*-isopropylidene-*β*-L-*glycero*-D-*galacto*-heptopyranuronate (26a). From compound **22a** (0.47 g, 1 mmol) as described for the preparation of **15a**. Isolated by column chromatography (80:20 hexane−diethyl ether): 0.28 g, 59%; oil; $[\alpha]_D = -21.0$ (*c* 0.60, $CHCl_3$); ^{1}H NMR δ 1.26 (s, 3 H), 1.33 (s, 3 H), 1.35 (s, 3 H), 1.57 (s, 3 H), 1.83 (s, 3 H), 3.74 (s, 3 H), 3.98 (d, 1 H, J = 9.4 Hz), 4.24 (dd, 1 H, J = 7.8, 1.8 Hz), 4.26 (d, 1 H, J = 13.3 Hz), 4.32 (dd, 1 H, J = 5.1, 2.6 Hz), 4.34 (d, 1 H, J = 13.3 Hz), 4.40 (dd, 1 H, J = 9.4, 1.8 Hz), 4.58 (dd, 1 H, J = 7.8, 2.6 Hz), 5.58 (d, 1 H, J = 5.1 Hz), 7.22−7.25 (m, 5 H); ^{13}C NMR δ 19.1, 24.7, 25.0, 25.9, 26.0, 51.9, 61.2, 66.0, 67.0, 70.4 71.2, 71.8, 96.7, 109.0, 109.9, 127.6, 128.19, 129.92, 136.4, 168.8, 170.1. Anal. Calcd for $C_{23}H_{31}NO_9$: C, 59.35; H, 6.71; N, 3.01. Found: C, 59.60; H, 6.47; N, 3.25.

Methyl 6-(Acetoxyamino)-*N*-benzyl-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-heptopyranuronate (26b). From compound **20b** (0.47 g, 1 mmol) as described for the preparation of **15a**. Isolated by column chromatography (60:40 hexane−diethyl ether): 0.27 g, 58%; oil; $[\alpha]_D = -51.9$ (*c* 0.50, $CHCl_3$); ^{1}H NMR δ 1.26 (s, 3 H), 1.28 (s, 3 H), 1.30 (s, 3 H), 1.52 (s, 3 H), 1.82 (s, 3 H), 3.81 (s, 3 H), 3.87 (d, 1 H, J = 10.5 Hz), 4.15 (d, 1 H, J = 12.9 Hz), 4.19 (dd, 1 H, J = 10.5, 1.7 Hz), 4.22 (d, 1 H, J = 12.9 Hz), 4.24 (dd, 1 H, J = 4.7, 2.4 Hz), 4.58 (dd, 1 H, J = 8.1, 2.4 Hz), 4.78 (dd, 1 H, J = 8.1, 1.7 Hz), 5.39 (d, 1 H, J = 4.7 Hz), 7.25−7.41 (m, 5 H); ^{13}C NMR δ 18.7, 24.4, 25.1, 25.7, 25.8, 51.4, 60.6, 61.9, 66.2, 66.9, 70.6, 71.3, 96.3, 108.8, 108.9, 127.5, 127.9, 129.6, 135.7, 167.8, 168.6. Anal. Calcd for $C_{23}H_{31}NO_9$: C, 59.35; H, 6.71; N, 3.01. Found: C, 59.18; H, 6.90; N, 2.87.

2-Lithiothiazole (2). A solution of freshly distilled 2-bromothiazole (2.46 g, 1.35 mL, 15 mmol) in diethyl ether (30 mL) was added slowly to a stirred solution of butyllithum (10 mL of a 1.6 M solution in hexanes, 16 mmol) in 30 mL of diethyl ether, cooled to −90 °C. During this operation, the temperature of the solution was not allowed to rise above −70 °C. The mixture was stirred for 15 min at −80 °C, and the resulting pale yellow solution of 2-lithiothiazole (**2**) (ca. 0.2 M) was immediately used.

General Procedure for the Addition of 2-Lithiothiazole (2) to the Nitrones 31 and 32. Method A. Without Lewis Acid. A cooled (−90 °C) and stirred solution of 2-lithiothiazole (**2**) in diethyl ether (from 15 mmol of 2-bromothiazole) was treated with a solution of the nitrone (5 mmol) in THF (60 mL) added drop by drop. The rate of addition was controlled so that temperature of the reaction mixture did not exceed −80 °C. The mixture was stirred for 15 min at −80 °C and then quenched with saturated aqueous NH_4Cl (15 mL). The mixture was stirred at room temperature for 10 min and diluted with diethyl ether (25 mL). The organic layer was separated and the aqueous layer extracted with diethyl ether (3 × 50 mL). The combined organic extracts were washed with brine, and dried ($MgSO_4$), and the solvent was evaporated in vacuo. The diastereoselectivity (% ds) was determined by ^{1}H NMR analysis. The product was isolated by column chromatography on silica gel.

Method B. With Diethyl Aluminum Chloride. A 1.0 M solution of Et_2AlCl in hexane (5 mL, 5 mmol) was added via syringe under stirring to a solution of the nitrone (5 mmol) in diethyl ether (50 mL) at ambient temperature. Stirring was continued for 15 min. Then, the mixture was transferred under argon atmosphere into a dropping funnel and added drop by drop to a cooled (−90 °C) and stirred solution of 2-lithiothiazole (**2**) in diethyl ether (from 15 mmol of 2-bromothiazole). The rate of addition was controlled so that the temperature of the reaction mixture did not exceed −80 °C. The mixture was stirred for 30 min at −80 °C and then treated with 1 N aqueous NaOH (100 mL). After stirring for 15 min at room temperature, the mixture was extracted with diethyl ether (3 × 50 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The diastereoselectivity (% ds) was determined by ^{1}H NMR analysis. The product was isolated by column chromatography on silica gel.

2,5-Anhydro-*N*-benzyl-1-deoxy-3,4:6,7-di-*O*-isopropylidene-1-(hydroxyamino)-1-(2-thiazolyl)-D-*erythro*-L-*manno*-heptitol (35a). From the nitrone **31** (1.89 g, 5 mmol) by method A. Isolated by column chromatography (60:40 hexane−diethyl ether): 1.23 g, 53%; oil; $[\alpha]_D = +3.0$ (*c* 0.80, $CHCl_3$); ^{1}H NMR δ 1.23 (s, 3 H), 1.40 (s, 3 H), 1.41 (s, 3 H), 1.48 (s, 3 H), 3.62 (dd, 1 H, J = 6.8, 1.7 Hz), 3.93 (ABq, 2 H, J = 13.2 Hz, $\Delta\delta$ = 0.13), 4.14 (dd, 1 H, J = 8.8, 6.6 Hz), 4.17

(dd, 1 H, J = 8.8, 3.2 Hz), 4.35 (dd, 1 H, J =9.8, 1.5 Hz), 4.47 (ddd, 1 H, J = 6.8, 6.6, 3.2 Hz), 4.72 (m, 2 H), 4.78 (d, 1 H, J = 9.8 Hz), 6.16 (bs, 1 H, ex D_2O), 7.24−7.35 (m, 5 H), 7.37 (d, 1 H, J = 3.2 Hz), 7.80 (d, 1 H, J = 3.2 Hz); ^{13}C NMR δ 24.5, 25.3, 25.7, 27.0, 60.6, 65.1, 66.8, 73.1, 80.2, 81.2, 81.3, 82.0, 109.1, 112.5, 120.0, 127.2, 128.2, 129.35, 137.6, 142.0, 165.8. Anal. Calcd for $C_{23}H_{30}N_2O_6S$: C, 59.74; H, 6.54; N, 6.06. Found: C, 59.99; H, 6.46; N, 6.26.

2,5-Anhydro-*N*-benzyl-1-deoxy-3,4:6,7-di-*O*-isopropylidene-1-(hydroxyamino)-1-(2-thiazolyl)-D-*erythro*-L-*gluco*-heptitol (35b). From the nitrone **31** (1.89 g, 5 mmol) by method B. Isolated by column chromatography (60:40 hexane−diethyl ether): 1.43 g, 62%; colorless crystalline solid; mp 188−190°C; $[\alpha]_D$ = +10.9 (*c* 0.59, $CHCl_3$); ^{1}H NMR δ 1.32 (s, 9 H), 1.35 (s, 3 H), 3.49 (dd, 1 H, J = 7.1, 3.9 Hz), 3.75 (d, 1 H, J = 12.9 Hz), 3.84 (dd, 1 H, J = 8.8, 6.3 Hz), 3.94 (dd, 1 H, J = 8.8, 4.9 Hz), 4.15 (d, 1 H, J = 12.9 Hz), 4.18 (dd, 1 H, J = 9.0, 3.7 Hz), 4.31 (ddd, 1 H, J = 7.1, 6.3, 4.9 Hz), 4.59 (d, 1 H, J = 9.0 Hz), 4.74 (dd, 1 H, J = 6.1, 3.7 Hz), 4.90 (dd, 1 H, J = 6.1, 3.9 Hz), 6.85 (bs, 1 H, ex D_2O), 7.26−7.33 (m, 5 H), 7.36 (d, 1 H, J = 3.2 Hz), 7.82 (d, 1 H, J = 3.2 Hz); ^{13}C NMR δ 24.6, 25.4, 25.6, 26.7, 62.2, 63.3, 66.6, 73.0, 80.2, 80.8, 81.6, 81.8, 108.9, 112.2, 119.5, 127.4, 128.1, 129.3, 136.7, 141.5, 166.4. Anal. Calcd for $C_{23}H_{30}N_2O_6S$: C, 59.74; H, 6.54; N, 6.06. Found: C, 60.04; H, 6.62; N, 6.16.

2,6-Anhydro-*N*-benzyl-3,4,5,7-tetra-*O*-benzyl-1-deoxy-1-(2-thiazolyl)-1-(hydroxyamino)-D-*threo*-L-*galacto*-heptitol (36a). From the nitrone **32** (3.29 g, 5 mmol) by method A. Isolated by column chromatography (70:30 hexane−diethyl ether): 1.23 g, 33%; oil; $[\alpha]_D$ = +7.1 (*c* 1.23, $CHCl_3$); ^{1}H NMR δ 3.54−3.72 (m, 6 H), 3.87 (d, 1 H, J = 13.4 Hz), 4.02 (bd, 1 H, J = 2.7 Hz), 4.41 (d, 1 H, J = 11.7 Hz), 4.45 (d, 1 H, J = 11.7 Hz), 4.49 (d, 1 H, J = 10.6 Hz), 4.59 (t, 1 H, J = 9.4 Hz), 4.60 (d, 1 H, J = 11.7 Hz), 4.67 (d, 1 H, J = 11.5 Hz), 4.75 (d, 1 H, J = 11.5 Hz), 4.89 (d, 1 H, J = 10.6 Hz), 4.90 (d, 1 H, J = 2.7 Hz), 5.10 (d, 1 H, J = 11.7 Hz), 5.59 (s, 1 H, ex D_2O), 7.18−7.40 (m, 26 H), 7.82 (d, 1 H, J = 3.2 Hz); ^{13}C NMR δ 61.0, 65.0, 68.8, 72.3, 73.5, 73.6, 74.4, 74.9, 75.12, 77.5, 81.8, 85.0, 120.8, 127.1, 127.5, 127.5, 127.6, 127.6, 127.7, 127.8, 127.8, 127.9, 128.1, 128.2, 128.3, 128.4, 128.4, 129.5, 137.7, 137.8, 138.1, 138.4, 138.7, 140.9, 164.0. Anal. Calcd for $C_{45}H_{46}N_2O_6S$: C, 72.75; H, 6.24; N, 3.77. Found: C, 72.54; H, 6.55; N, 3.90.

2,6-Anhydro-*N*-benzyl-3,4,5,7-tetra-*O*-benzyl-1-deoxy-1-(2-thiazolyl)-1-(hydroxyamino)-D-*threo*-L-*talo*-heptitol (36b). From the nitrone **32** (3.29 g, 5 mmol) by method B. Isolated by column chromatography (70:30 hexane−diethyl ether): 2.00 g, 54%; oil; $[\alpha]_D$ = +18.5 (*c* 1.51, $CHCl_3$); ^{1}H NMR δ 3.55−3.67 (m, 5 H), 3.76 (ABq, 2 H, J = 12.4 Hz, $\Delta\delta$ = 0.01), 3.92 (m, 1 H), 4.04 (pseudo q, 1 H, J = 4.3 Hz), 4.42 (ABq, 2 H, J = 12.4 Hz, $\Delta\delta$ = 0.02), 4.53 (d, 1 H, J = 12.0 Hz), 4.66 (d, 1 H, J = 10.0 Hz), 4.68 (d, 1 H, J = 11.9 Hz), 4.75 (d, 1 H, J = 11.9 Hz), 4.78 (d, 1 H, J = 10.0 Hz), 4.89 (d, 1 H, J = 3.7 Hz), 4.92 (d, 1 H, J = 12.0 Hz), 5.69 (s, 1 H, ex D_2O), 7.12−7.41 (m, 26 H), 7.84 (d, 1 H, J = 3.2 Hz); ^{13}C NMR δ 61.2, 68.2, 69.1, 72.2, 73.5, 73.5, 74.0, 75.2, 75.9, 77.1, 81.1, 84.7, 121.1, 127.2, 127.3, 127.5, 127.6, 127.7, 127.7, 127.8, 128.1, 128.2, 128.3, 128.4, 128.4, 129.8, 137.4, 137.9, 138.1, 138.9, 141.1, 163.3. Anal. Calcd for $C_{45}H_{46}N_2O_6S$: C, 72.75; H, 6.24; N, 3.77. Found: C, 72.72; H, 6.04; N, 3.41.

2,5-Anhydro-1-((*tert*-butoxycarbonyl)amino)-1-deoxy-3,4:6,7-di-*O*-isopropylidene-1-(2-thiazolyl)-D-*erythro*-L-*manno*-heptitol (37a). A solution of the hydroxylamine **35a** (1.38 g, 3 mmol) in MeOH (35 mL) was treated with a 20% aqueous solution of $TiCl_3$ (1.16 g, 7.5 mmol of $TiCl_3$ in 4.7 mL of water) at room temperature for 15 min. Then, 5 M aqueous NaOH (10 mL) was added, and stirring was maintained for additional 5 min. After extraction with ethyl acetate (4 × 20 mL), the organic layer was washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The crude amine was taken up in dioxane (25 mL) and the solution treated with Boc_2O (1.44 g, 6.6 mmol). The reaction mixture was stirred at ambient temperature for 12 h and then partitioned between saturated aqueous $NaHCO_3$ (60 mL) and CH_2Cl_2 (40 mL), and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic extracts were dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. Column chromatography on silica gel (40:60 hexane−diethyl ether) gave **37a** (0.82 g, 60%) as an oil: $[\alpha]_D$ = −2.4 (*c* 1.02, $CHCl_3$); ^{1}H NMR δ 1.27 (s, 3 H), 1.35 (s, 3 H), 1.40 (s, 3 H), 1.43 (s, 9H), 1.44 (s, 3 H), 3.55 (bd, 1 H, J = 6.5 Hz), 4.01 (dd, 1 H, J = 8.8, 4.8 Hz), 4.04−4.10 (m, 2 H), 4.40 (ddd, 1 H, J = 6.5, 5.8, 4.8 Hz), 4.72 (dd, 1 H, J = 5.2, 1.5 Hz), 4.74 (dd, 1 H, J 5.2, 1.6 Hz), 5.38 (bt, 1 H, J = 5.4 Hz), 5.50 (bd (1 H, J = 5.6 Hz), 7.24 (d, 1 H, J = 3.2 Hz), 7.69 (d, 1 H, J = 3.2 Hz); ^{13}C NMR δ 24.2, 25.3, 25.6, 26.9, 28.3, 51.5, 66.8, 73.0, 79.9, 80.5, 80.9, 81.4, 81.9, 109.1, 112.7, 119.3, 142.4, 155.4, 171.1. Anal. Calcd for $C_{21}H_{32}N_2O_7S$: C, 55.25; H, 7.06; N, 6.14. Found: C, 55.56; H, 7.20; N, 6.32.

2,5-Anhydro-1-((*tert*-butoxycarbonyl)amino)-1-deoxy-3,4:6,7-di-*O*-isopropylidene-1-(2-thiazolyl)-D-*erythro*-L-*gluco*-heptitol (37b). From the hydroxylamine **35b** (1.38 g, 3 mmol) as described for the preparation of **37a**. Isolated by column chromatography (40:60 hexane−diethyl ether): 0.87 g, 63%; oil; $[\alpha]_D$ = +6.24 (*c* 0.5, $CHCl_3$); ^{1}H NMR δ 1.21 (s, 3 H), 1.36 (s, 3 H), 1.41 (s, 3 H), 1.44 (s, 9H), 1.52 (s, 3 H), 3.68 (dd, 1 H, J = 6.8, 3.7 Hz), 4.05−4.09 (m, 2 H), 4.28 (m, 1 H), 4.39 (q, 1 H, J = 5.7 Hz), 4.71 (dd, 1 H, J = 6.1, 3.7 Hz), 4.79 (dd, 1 H, J = 6.1, 3.3 Hz), 5.59 (dd, 1 H, J = 9.0, 4.2 Hz), 6.35 (bd, 1 H, J = 9.0 Hz), 7.23 (d, 1 H, J = 3.2 Hz), 7.70 (d, 1 H, J = 3.2 Hz); ^{13}C NMR δ 24.2, 25.0, 25.3, 26.6, 28.1, 53.0, 66.5, 73.0, 79.5, 79.7, 80.2, 81.1, 81.2, 108.8, 112.5, 118.9, 142.6, 155.8, 170.9. Anal. Calcd for $C_{21}H_{32}N_2O_7S$: C, 55.25; H, 7.06; N, 6.14. Found: C, 55.48; H, 7.17; N, 6.55.

2,6-Anhydro-3,4,5,7-tetra-*O*-benzyl-1-((*tert*-butoxycarbonyl)amino)-1-deoxy-1-(2-thiazolyl)-D-*threo*-L-*galacto*-heptitol (38a). From the hydroxylamine **36a** (2.22 g, 3 mmol) as described for the preparation of **37a**. Isolated by column chromatography (30:70 hexane−diethyl ether): 1.44 g, 65%; oil; $[\alpha]_D$ = +4.9 (*c* 0.58, $CHCl_3$); ^{1}H NMR δ 1.46 (s, 9 H), 3.40−3.45 (m, 1 H), 3.52−3.59 (m, 2 H), 3.70 (dd, 1 H, J = 9.0, 2.7 Hz), 3.91−4.04 (m, 2 H), 4.32 (ABq, 2 H, J = 11.8 Hz, $\Delta\delta$ = 0.010), 4.58 (d, 1 H, J = 11.6 Hz), 4.64−4.71 (m, 1 H), 4.74 (d, 1 H, J = 11.6 Hz), 4.78 (d, 1 H, J = 11.6 Hz), 4.92 (d, 1 H, J = 9.9 Hz), 5.00 (d, 1 H, J = 11.6 Hz), 5.57 (d, 1 H, J = 9.5 Hz), 5.80 (d, 1 H, J = 9.5 Hz), 5.82 (bs, 1 H), 7.14−7.42 (m, 21 H), 7.70 (d, 1 H, J = 3.2 Hz); ^{13}C NMR δ 28.4, 52.8, 68.7, 72.4, 73.4, 74.0, 74.5, 75.2, 75.7, 77.3, 80.1, 80.3, 84.2, 118.7, 127.1, 127.5, 127.6, 127.7, 127.8, 127.8, 129.9, 128.0, 128.3, 128.4, 128.5, 128.7, 138.0, 138.2, 138.3, 138.9, 142.89, 155.6, 172.7. Anal. Calcd for $C_{43}H_{48}N_2O_7S$: C, 70.08; H, 6.57; N, 3.80. Found: C, 69.99; H, 6.91; N, 3.58.

2,6-Anhydro-3,4,5,7-tetra-*O*-benzyl-1-((*tert*-butoxycarbonyl)amino)-1-deoxy-1-(2-thiazolyl)-D-*threo*-L-*talo*-heptitol (38b). From the hydroxylamine **36b** (2.22 g, 3 mmol) as described for the preparation of **37a**. Isolated by column chromatography (30:70 hexane−diethyl ether): 1.41 g, 64%; oil; $[\alpha]_D$ = +14.6 (*c* 0.90, $CHCl_3$); ^{1}H NMR δ 1.42 (s, 9 H), 3.53−3.71 (m, 4 H), 3.82−3.94 (m, 2 H), 4.44−4.51 (m, 2 H), 4.54 (d, 1 H, J = 11.9 Hz), 4.73 (d, 1 H, J = 11.7 Hz), 4.80 (d, 1 H, J = 11.7 Hz), 4.92 (d, 1 H, J = 10.3 Hz), 4.94 (d, 1 H, J = 11.9 Hz), 5.20 (d, 1 H, J = 10.3 Hz), 5.66 (bs, 1 H), 5.74 (d, 1 H, J = 9.0 Hz), 5.91 (d, 1 H, J = 9.0 Hz), 7.14−7.52 (m, 21 H), 7.78 (d, 1 H, J = 3.2 Hz); ^{13}C NMR δ 28.2, 53.2, 68.7, 71.9, 73.3 (x2), 73.6, 74.7, 74.9, 76.8, 79.8, 80.0, 84.3, 119.4, 126.7 126.9, 127.0, 127.1, 127.4, 127.5, 127.7, 127.9, 128.22, 128.3, 128.3, 137.6, 138.0, 138.4, 138.8, 141.8, 154.7, 168.7. Anal. Calcd for $C_{43}H_{48}N_2O_7S$: C, 70.08; H, 6.57; N, 3.80. Found: C, 70.30; H, 6.44; N, 3.70.

Methyl 2,5-Anhydro-2-((*tert*-butoxycarbonyl)amino)-2-deoxy-3,4:6,7-di-*O*-isopropylidene-D-*erythro*-L-*manno*-octonate (39a). A mixture of the thiazole derivative **37a** (0.44 g, 1 mmol), activated 4 Å molecular sieves (2.0 g), and CH_3CN (20 mL) was stirred at room temperature for 10 min while methyl trifluoromethanesulfonate (0.12 mL, 1.1 mmol) was added, and the suspension was stirred for 20 min. The solvent was removed under reduced pressure. The residue was taken up in MeOH (20 mL), cooled to 0 °C, and treated with $NaBH_4$ (0.0.84 g, 2.2 mmol). The mixture was stirred at room temperature for 15 min, diluted with acetone (2 mL), filtered through Celite, and concentrated in vacuo. The residue was taken up in 10:1 CH_3CN-H_2O (20 mL) and then treated with

CuO (0.24 g, 3 mmol) and $CuCl_2 \cdot 2H_2O$ (0.19 g, 1.1 mmol). The resulting suspension was stirred at room temperature for 10 min and then filtered through Celite and concentrated in vacuo at temperature below 30 °C. The residue was partitioned between brine (25 mL) and diethyl ether (25 mL). The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic extracts were washed with saturated aqueous EDTA (disodium salt) and brine, dried ($MgSO_4$), and passed through a plug of Florisil eluting with diethyl ether. The solvent was then evaporated under reduced pressure to give the essentially pure α-amino aldehyde which was taken up in CH_3CN (10 mL). The solution was treated with 35% aqueous H_2O_2 (0.2 mL), 1.2 M aqueous NaH_2PO_4 (1.0 mL), and 0.17 M aqueous $NaClO_2$ (7 mL). After 2 h the reaction mixture was acidified with 1 N aqueous HCl to pH = 2, and the resulting mixture was extracted with AcOEt (3 × 15 mL). The organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The crude acid was dissolved in Et_2O (50 mL), cooled to 0 °C, and treated with an ethereal solution of diazomethane until a slight yellow color persisted. The excess of diazomethane was eliminated by quenching with acetic acid. The resulting solution was concentrated under reduced pressure. Column chromatography on silica gel (20:80 hexane−diethyl ether) gave pure **39a** (0.24 g, 56%) as an oil: $[\alpha]_D = -25.7$ (*c* 0.25, $CHCl_3$); ^{1}H NMR δ 1.23 (s, 3 H), 1.29 (s, 3 H), 1.35 (s, 3 H), 1.41 (s, 9 H), 1.44 (s, 3 H), 3.51 (dd, 1 H, J = 7.4, 3.6 Hz), 3.74 (s, 3 H), 3.80 (t, 1 H, J = 4.0 Hz), 4.01 (dd, 1 H, J = 8.9, 4.9 Hz), 4.06 (dd, 1 H, J = 8.9, 5.9 Hz), 4.37 (ddd, 1 H, J = 7.4, 5.9, 4.9 Hz), 4.55 (dd, 1 H, J = 7.0, 4.8 Hz), 4.74 (dd, 1 H, J = 6.0, 3.6 Hz), 4.79 (dd, 1 H, J = 6.0, 3.8 Hz), 5.20 (bd, 1 H, J = 7.0 Hz); ^{13}C NMR δ 25.1, 25.4, 26.8, 28.2, 29.1, 52.4, 53.6, 66.7, 72.8, 79.4, 79.8, 80.3, 80.9, 81.1, 109.1, 112.7, 155.2, 170.9. Anal. Calcd for $C_{20}H_{33}NO_9$: C, 55.67; H, 7.71; N, 3.25. Found: C, 55.74; H, 7.59; N, 3.16.

Methyl 2,5-Anhydro-2-((*tert*-butoxycarbonyl)amino)-2-deoxy-3,4:6,7-di-*O*-isopropylidene-D-*erythro*-L-*gluco*-octonate (39b). From compound **37b** (0.44 g, 1 mmol) as described for the preparation of **39a**. Isolated by column chromatography (20:80 hexane−diethyl ether): 0.25 g, 58%; oil; $[\alpha]_D = -5.4$ (*c* 1.10, $CHCl_3$); ^{1}H NMR δ 1.23 (s, 3 H), 1.29 (s, 3 H), 1.42 (s, 12 H), 1.51 (s, 3 H), 3.59 (dd, 1 H, J = 7.8, 3.6 Hz), 3.72 (dd, 1 H, J = 11.5, 4.7 Hz), 3.75 (s, 3 H), 3.80 (dd, 1 H, J = 11.5, 3.4 Hz), 3.90 (d, 1 H, J = 5.5, 3.2 Hz), 3.96 (ddd, 1 H, J =7.8, 4.7, 3.4 Hz), 4.76 (dd, 1 H, J = 6.2, 3.2 Hz), 4.80 (dd, 1 H, J = 6.2, 3.6 Hz), 4.86 (dd, 1 H, J =9.0, 5.5 Hz), 5.65 (d, 1 H, J = 9.0 Hz); ^{13}C NMR δ 24.2, 25.4, 28.2, 28.3, 29.7, 52.5, 53.1, 64.3, 69.7, 78.9, 80.9, 81.0, 81.1, 81.3, 113.0, 113.1, 155.8, 170.7. Anal. Calcd for $C_{20}H_{33}NO_9$: C, 55.67; H, 7.71; N, 3.25. Found: C, 55.73; H, 7.78; N, 3.48.

Methyl 2,6-Anhydro-3,4,5,7-tetra-*O*-benzyl-2-((*tert*-butoxycarbonyl)amino)-2-deoxy-D-*threo*-L-*galacto*-octonate (40a). From compound **38a** (0.73 g, 1 mmol) as described for the preparation of **39a**. Isolated by column chromatography (60:40 hexane−diethyl ether): 0.38 g, 54%; oil; $[\alpha]_D = +9.4$ (*c* 0.69, $CHCl_3$); ^{1}H NMR δ 1.44 (s, 9 H), 3.45−3.58 (m, 4 H), 3.64 (dd, 1 H, J = 9.0, 2.4 Hz), 3.67 (s, 3 H), 3.82 (dd, 1 H, J = 9.7, 2.0 Hz), 3.90 (t, 1 H, J = 9.4 Hz), 3.96 (d, 1 H, J = 2.8 Hz), 4.40 (ABq, 2 H, J = 11.6, $\Delta\delta$ = 0.033), 4.56 (d, 1 H, J = 11.6 Hz), 4.58 (d, 1 H, J = 10.8 Hz), 4.71 (d, 1 H, J = 11.9 Hz), 4.76 (d, 1 H, J = 11.9 Hz), 4.84 (d, 1 H, J = 10.8 Hz), 4.96 (d, 1 H, J = 11.6 Hz), 5.38 (d, 1 H, J = 9.1 Hz), 7.22−7.39 (m, 20 H); ^{13}C NMR δ 28.3, 52.4, 53.6, 68.6, 72.3, 73.5, 73.8, 74.4, 74.73, 75.6, 77.3, 78.9, 79.9, 84.3, 127.5, 127.5, 127.6, 127.7, 127.8, 127.8, 128.4, 128.5, 128.7, 137.9, 138.1, 138.2, 138.8, 156.1, 171.6. Anal. Calcd for $C_{42}H_{49}NO_9$: C, 70.87; H, 6.94; N, 1.97. Found: C, 71.00; H, 7.31; N, 1.84.

Methyl 2,6-Anhydro-3,4,5,7-tetra-*O*-benzyl-2-((*tert*-butoxycarbonyl)amino)-2-deoxy-D-*threo*-L-*talo*-octonate (40b). From compound **38b** (0.73 g, 1 mmol) as described for the preparation of **39a**. Isolated by column chromatography (60:40 hexane−diethyl ether): 0.43 g, 60%; oil; $[\alpha]_D = -2.6$ (*c* 1.21, $CHCl_3$); ^{1}H NMR δ 1.42 (s, 9 H), 3.50−3.56 (m, 5 H), 3.58 (s, 3 H), 3.60 (dd, 1 H, J = 9.3, 2.8 Hz), 3.96 (d, 1 H, J = 2.7 Hz), 4.18 (t, 1 H, J = 9.6 Hz), 4.42 (ABq, 2 H, J = 11.9 Hz, $\Delta\delta$ = 0.026), 4.52 (d, 1 H, J = 11.7 Hz), 4.65 (d, 1 H, J = 11.6 Hz), 4.76 (d, 1 H, J = 1.7 Hz), 4.80 (d, 1 H, J = 10.6 Hz), 4.93 (d, 1 H, J = 11.6 Hz), 4.95 (d, 1 H, J = 10.6 Hz), 5.40 (d, 1 H, J = 9.4 Hz), 7.15−7.39 (m, 20 H); ^{13}C NMR δ 28.3, 52.1, 54.0, 68.4, 72.0, 73.4, 73.5, 74.2, 74.6, 74.9, 78.0, 79.1, 80.5, 84.8, 126.9, 127.1, 127.3, 127.5, 127.6, 127.7, 127.9, 128.0, 128.0, 128.1, 128.29, 128.4, 137.8, 138.18, 138.3, 139.0, 155.3, 170.0. Anal. Calcd for $C_{42}H_{49}NO_9$: C, 70.87; H, 6.94; N, 1.97. Found: C, 71.24; H, 6.83; N, 1.62.

Crystal Structure Analysis. Crystal data for **12b**: $C_{15}H_{21}NO_6$, tetragonal, space group $P4_3$, a = 9.899(2) Å, c = 16.384(3) Å, V = 1605.3(5) Å^3, Z = 4, D_c = 1.288 g cm^{-3}, μ = 0.10 cm^{-1}, $F(000)$ = 664, crystal dimensions 0.40 × 0.29 × 0.28 mm. Of the 1176 unique measured reflections, 1065 with $I \geq 2\sigma(I)$ were used in the refinement. The structure was solved by direct methods using SHELXS-86 (Sheldrick, G. M. *Program for Crystal Structure Solution*; University of Göttingen, Germany, 1986) and refined by full-matrix least squares with SHELXL-93 (Sheldrick, G. M. *Program for Crystal Structure Refinement*; University of Cambridge, England, 1993). Non-hydrogen atoms were refined with anisotropic temperature factors. The amide hydrogen bonded to N(1) was located by difference-Fourier map and refined, while the others were included at the calculated positions and refined in the riding mode with group temperature factors, respectively, for aromatic and aliphatic hydrogens. Final R_1 = 0.0381, final wR_2 = 0.1025, final S = 1.054. The data were collected on a Siemens *P*4 diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073), $\omega-2\theta$ scan technique ($2.06 \leq \theta \leq 22.49°$).

Crystal data for **9b**: $C_{26}H_{29}NO_6$, orthorhombic, space group $P2_12_12_1$, a = 8.253(5) Å, b = 12.340(5) Å, c = 23.770(5) V = 2420.7(18) Å^3, Z = 4, D_c = 1.239 g cm^{-3}, μ = 0.088 cm^{-1}, $F(000)$ = 960, crystal dimensions 0.68 × 0.22 × 0.04 mm. Of the 1909 unique measured reflections, 1305 with $I \geq 2\sigma(I)$ were used in the refinement. The structure was solved by direct methods using SIR-92 (A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, 1992) and refined by full-matrix least squares with SHELXL-93 (Sheldrick, G. M. *Program for Crystal Structure Refinement*; University of Cambridge, England, 1993). Non-hydrogen atoms were refined with anisotropic temperature factors, included at the calculated positions and refined in the riding mode with group temperature factors respectively for aromatic and aliphatic hydrogens. Final R_1 = 0.0704, final wR_2 = 0.3248, final S = 1.053. The data were collected on a Siemens P4 diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073), $\theta-2\theta$ scan technique ($1.86 \leq \theta \leq 24.91°$).

Crystal data for **35b**: $C_{23}H_{30}N_2O_6$, orthorhombic, space group $P2_12_12_1$, a = 9.294(2) Å, b = 11.809(2), c = 21.410(4) Å, V = 2349.8(8) Å^3, Z = 4, D_c = 1.307 g cm^{-3}, μ = 0.179 cm^{-1}, $F(000)$ = 984, crystal dimensions 0.30 × 0.30 × 0.10 mm. Of the 2169 unique measured reflections, 1230 with $I \geq 2\sigma(I)$ were used in the refinement. The structure was solved by direct methods using SHELXS-86 (Sheldrick, G. M. *Program for Crystal Structure Solution*; University of Göttingen, Germany, 1986) and refined by full-matrix least squares with SHELXL-93 (Sheldrick, G. M. *Program for Crystal Structure Refinement*; University of Cambridge, England, 1993). Non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were included at the calculated positions and refined in the riding mode. Final R_1 = 0.0676, final wR_2 = 0.1367, final S = 1.147. The data were collected on a Siemens P4 diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073), $\omega-2\theta$ scan technique ($1.90 \leq \theta \leq 22.50°$).

Acknowledgment. We wish to thank the Ministerio de Educacion y Ciencia (DGICYT, Madrid, Project PB94-0598) and the CNR, Roma, for financial support. We are also grateful to the Ministero degli Affari Esteri (Italy), and Ministère des Affaires Etrangères-Programme Lavoisier (France) for a postdoctoral fellowship to M.-C.S.

JO970290A