Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

A General Method for the Vinylation of Nitrones. Synthesis of Allyl Hydroxylamines and Allyl Amines

Pedro Merino [a], Sonia Anoro [a], Santiago Franco [a], Jose M. Gascon [a], Victor Martin [a], Francisco L. Merchan [a], Julia Revuelta [a], Tomas Tejero [a] & Victoria Tuñon [a]

[a] Departamento de Química Orgánica, ICMA, Facultad de Ciencias , Universidad de Zaragoza , E-50009, Aragon, Spain Fax: E-mail:
Published online: 04 Dec 2007.

SYNTHETIC COMMUNICATIONS, 30(16), 2989–3021 (2000)

A GENERAL METHOD FOR THE VINYLATION OF NITRONES. SYNTHESIS OF ALLYL HYDROXYLAMINES AND ALLYL AMINES

Pedro Merino,* Sonia Anoro, Santiago Franco, Jose M. Gascon, Victor Martin, Francisco L. Merchan, Julia Revuelta, Tomas Tejero and Victoria Tuñon

Departamento de Química Orgánica, ICMA, Facultad de Ciencias, Universidad de Zaragoza, E-50009 Aragon, Spain. Fax: +34 976 762075.
E-mail: pmerino@posta.unizar.es

ABSTRACT

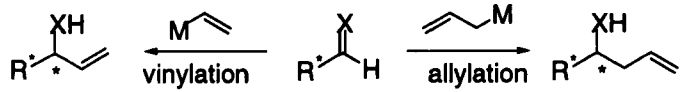
An examination of the vinylation of several nitrones is presented. Whereas a complete diastereofacial discrimination was observed upon the addition of vinyl organometallic reagents to α-alkoxy nitrones, the same reaction with α-amino nitrones gave *syn* adducts in all cases, with the only exception of a L-serine-derived α-amino monoprotected nitrone. The obtained allyl hydroxylamines were easily transformed into synthetically valuable allyl amines.

INTRODUCTION

The diastereo and enantioselective allylation of aldehydes and ketones has been extensively investigated in the past years as an alternative to conventional aldol methodology.[1] This kind of reaction has also been performed on imino derivatives such as imines,[2] oximes,[3] hydrazones[4] and nitrones.[5] The nucleophilic addition of organometallic reagents to the carbon-nitrogen double bonds constitutes an extremely useful method for preparing a variety of amines.[6] The usefulness of this

* To whom correspondence should be addressed

reaction can be extended by the addition of not only allyl derivatives (allylation) but also vinyl reagents (vinylation).



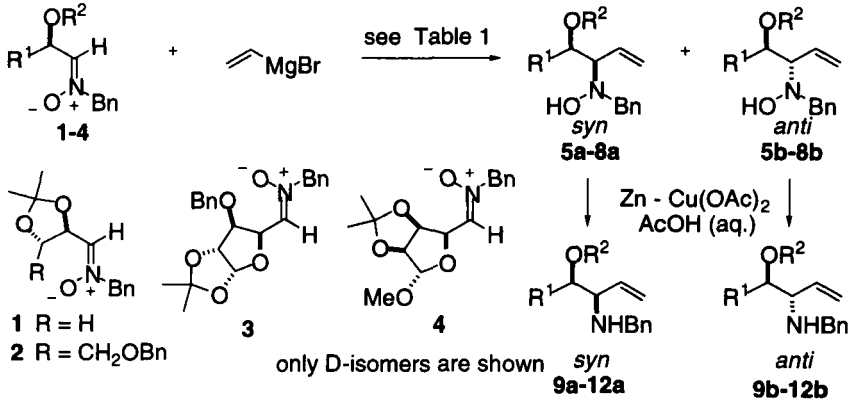
M = Metal X = O, NR, N(OR), NNR^1R^2, $N^+(O^-)R$

To our knowledge, very few investigations on the diastereoselective vinylation of imino substrates have been reported and only particular reactions have been studied.[7] In our continuing studies on nucleophilic additions to nitrones[8] we now wish to present in detail the first example of a general procedure for the vinylation of nitrones, its application to chiral substrates and the efficient transformation of the resulting hydroxylamines into synthetically interesting allyl amines.[9] The allyl amino functionality is a characteristic structural feature of many natural products and drugs, and play an important role as building blocks in the preparation of nitrogenated compounds. Because of their importance, numerous methods for the synthesis of variously substituted allyl amines have been reported so far.[10] Among the different types of electrophiles containing a C=N bond, nitrones are excellent substrates because of the presence of the nitrone oxygen atom. As we have recently reported,[11] the presence of such an oxygen is fundamental for the use of precomplexing agents to control the selectivity of the process. In addition, the use of nitrones as starting materials allow to obtain hydroxylamines which, in turn, can be further converted into amines.

RESULTS AND DISCUSSION

The results concerning vinylation of chiral α-alkoxy nitrones **1-4** are summarized in Table 1 and illustrated in Scheme 1. The addition of an excess of 1.5 equivalents of vinylmagnesium bromide in THF at –30 °C proceeded in good yields and gave the corresponding *syn* adducts preferentially (Table 1, entries 1, 5,

8, and 11). With respect to our previous communication[9a] we observed that carrying out the reaction at –30°C and using 1.5 equivalents of organometallic reagent better results on both selectivity and chemical yield were obtained. At lower temperature the reaction did not go to completion (10% of conversion at –60°C after 72 h). An additional modification which we sought to employ was the use of vinyllithium in place of vinylmagnesium bromide in order to investigate the influence of the metal atom in the selectivity of the reaction. However, in our initial experiments no stereocontrol was observed. Similarly, the use of other organometallic vinyl reagents, including cerium, copper and aluminium reagents, did not improve the obtained results with the magnesium derivative.[9a]



Scheme 1

According to our previous experience with other nucleophiles,[8,11] precomplexing of nitrones **34-37** with 1.0 equivalent of diethylaluminium chloride followed by addition of 1.5 equivalents of vinyl magnesium bromide afforded the *anti* hydroxylamines predominantly (Table 1, entries 4, 7, 10 and 13).

The addition of other Lewis acids such as zinc dibromide and magnesium dibromide resulted in a low degree of selectivity with a slight preference for the *syn* isomer (Table 1, entries 2, 3, 6, 9 and 12).

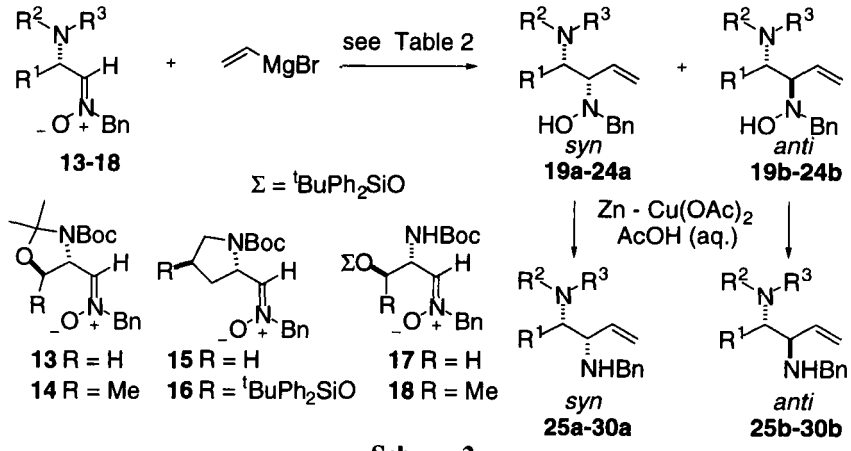
Table 1. Vinylation of chiral α-alkoxy nitrones **1-4** (Scheme 1)

entry	nitrone	additive[a]	syn : anti[b]	hydroxyl amine[c]	yield (%)[d]	allyl amine[e]	yield (%)[f]
1	**1**	none	78 : 22	**5a**	90	**9a**	80
2		$ZnBr_2$	55 : 45	**5a**	88		
3		$MgBr_2$	56 : 44	**5a**	92		
4		Et_2AlCl	8 : 92	**5b**	96	**9b**	76
5	**2**	none	70 : 30	**6a**	92	**10a**	78
6		$ZnBr_2$	60 : 40	**6a**	91		
7		Et_2AlCl	13 : 87	**6b**	90	**10b**	70
8	**3**	none	60 : 40	**7a**	91	**11a**	72
9		$ZnBr_2$	55 : 45	**7a**	91		
10		Et_2AlCl	33 : 77	**7b**	90	**11b**	80
11	**4**	none	70 : 30	**8a**	93	**12a**	78
12		$ZnBr_2$	61 : 39	**8a**	76		
13		Et_2AlCl	6 : 94	**8b**	81	**12b**	80

[a] 1.0 equiv was used. [b] measured on the corresponding signals of the NMR spectra. [c] obtained as major adduct.[d] isolated yield of mixture of diastereomers. [e] obtained from major hydroxylamine. [f] isolated yield.

The obtained hydroxylamines **5-8** were then deoxygenated to allyl amines **9-12** by using the system Zn (0) / Cu (II). The progress of the reaction was monitored by TLC analysis. Once the reduction was complete (*ca.* 1h) the reaction mixture was treated with the disodium salt of EDTA and made alkaline NaOH 3N. Extractive work-up provided the allylamine; rigorous purification of the products was necessary to remove small amounts of Zn salts which remain complexed to the double bond. Thus, additional whasings of the organic layer with a saturated aqueous solution of the disodium salt of EDTA provided the allylamines with no further purification required.

We also examined the addition of vinylmagnesium bromide to α-amino nitrones **46-51** (Scheme 2). The results are summarized in Table 2. The vinylation of α-amino diprotected nitrones **46-49** smoothly proceeded to give *syn* hydroxylamines in good stereoselectivity (Table 2, entries 1, 5, 8 and 11). In particular, nitrones **46** and **47** afforded the *syn* adduct as the only detectable product. On the other hand, whereas vinylation of **50** afforded the *anti* hydroxylamine preferentially (Table 2, entry 13), the threonine-derived nitrone **51** turned to give *syn* selectivity (Table 2, entry 16). This result was in good agreement with prior reports from this laboratory in which the tunable selectivity induced by different protection of the hydroxy and amino groups in the L-serine-derived nitrones **46** and **50** was discussed.[13]



Scheme 2

In the case of α-amino nitrones **13-18** the use of several Lewis acids such as zinc dibromide (Table 2, entry 2), magnesium dibromide (Table 2, entries 3, 6, 9, 14 and 17) and diethyl aluminium chloride (Table 2, entries 4, 7, 10, 12, 15 and 18) virtually gave the same selectivity that in the absence of any additive.

Table 2. Vinylation of chiral α-amino nitrones **13-18**

entry	nitrone	additive[a]	syn : anti[b]	hydroxy lamine[c]	yield (%)[d]	allyl amine[e]	yield (%)[f]
1	**13**	none	>95 : 5	**19a**	90	**25a**	76
2		$ZnBr_2$	>95 : 5	**19a**	87		
3		$MgBr_2$	>95 : 5	**19a**	84		
4		Et_2AlCl	>95 : 5	**19a**	76		
5	**14**	none	>95 : 5	**20a**	92	**26a**	78
6		$MgBr_2$	>95 : 5	**20a**	91		
7		Et_2AlCl	>95 : 5	**20a**	90		
8	**15**	none	80 : 20	**21a**	88	**27a**	74
9		$MgBr_2$	78 : 22	**21a**	89		
10		Et_2AlCl	81 : 19	**21a**	86		
11	**16**	none	92 : 8	**22a**	90	**28a**	89
12		Et_2AlCl	90 : 10	**22a**	92		
13	**17**	none	10 : 90	**23b**	86	**29b**	72
14		$MgBr_2$	18 : 82	**23b**	88		
15		Et_2AlCl	20 : 80	**23b**	83		
16	**18**	none	92 : 8	**24a**	86	**30a**	74
17		$MgBr_2$	90 : 10	**24a**	79		
18		Et_2AlCl	90 : 10	**24a**	80		

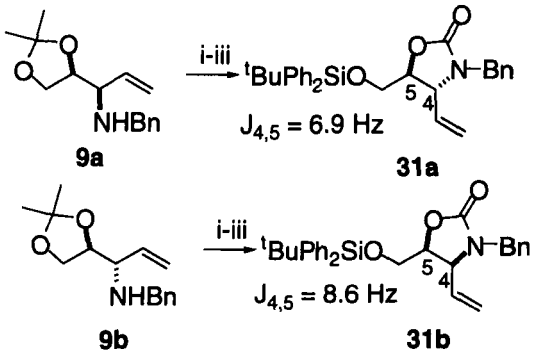
[a] 1.0 equiv was used. [b] measured on the corresponding signals of the NMR spectra. [c] obtained as major compound. [d] isolated yield of mixture of diastereomers. [e] obtained from major hydroxylamine. [f] isolated yield.

That the Lewis acid-promoted reaction of vinyl magnesium bromide with compounds **13-18** did not exhibit a different behaviour is consistent with our earlier reports concerning the asymmetric additions of several nucleophiles to α-amino nitrones.[14] The reduction of the major adducts with the usual Zn(0) / Cu(II) couple gave the corresponding allylamines **25-30** in good yields as expected (Scheme 2, Table 2).

Structure elucidation of the allyl hydroxylamines. The stereochemistry of the products were assigned by NMR methods and correlation with known compounds synthesized previously. Epimeric allyl amines **9a** and **9b** were easily converted into isoxazolidin-2-ones **31a** and **31b**, respectively (Scheme 3).

Then the relative stereochemistries of **31a** and **31b** were assigned according to an empirical rule, *i.e.* coupling constants of *trans* isomers are smaller than those of *cis* isomers.[15] As expected, the signal due to H-4 in *trans* isomer **31a** appears with smaller coupling constant $J_{4,5}$ that of the corresponding *cis* isomer **31b**.

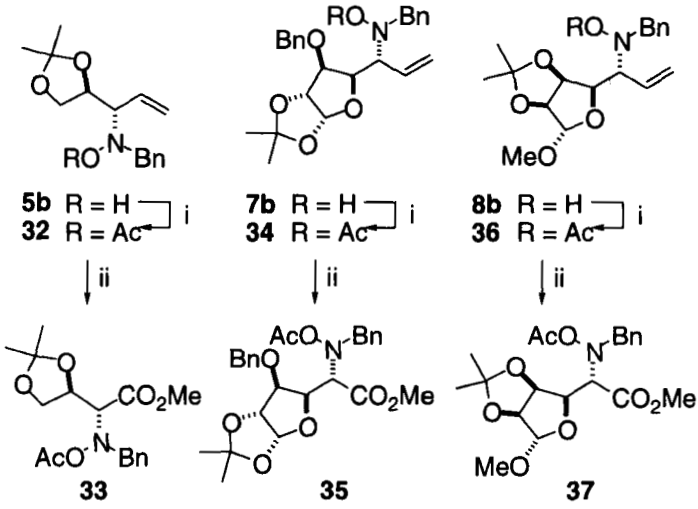
In addition, hydroxylamine **5b** was converted into N-acetoxy α-amino acid **33** of known configuration (Scheme 4).[16] Similarly, compounds **7b** and **8b** were



Reagents and conditions. i, p-TosOH, MeOH, reflux, 1 h. ii, ^{t}BuMeSiCl, CH_2Cl_2, DMAP, 16 h, r.t. iii, Im_2CO, THF, 24 h, r.t.

Scheme 3

transformed into the corresponding glycosyl N-hydroxy α-amino acid derivatives **35** and **37**, respectively, as shown in Scheme 4. These transformations involved O-acetylation and oxidative cleavage of the vinyl group, followed by *in situ* esterification of the resulting carboxylic acid. In all cases the physical and spectroscopic properties of the obtained compounds were identical to those previously reported by us.[17]



Reagents and conditions. i, Ac_2O, Py, 2 h, r.t. ii, CH_3CN-CCl_4-H_2O, $RuCl_3$, $NaIO_4$, 30 min, r.t.; then CH_2N_2, Et_2O.

Scheme 4

Assuming that the probability of a total reversal of the stereochemical progress of the reaction in both senses (*syn* and *anti*) is small, the stereochemistry of hydroxylamines **6a** and **6b** was assigned by analogy to the above cases.

For α-amino hydroxylamines **19a**-**22a**, the vicinal proton coupling constants ($J_{a,b}$) for the two protons of the two carbon atoms bearing nitrogen substituents are normally expected to be within the 9-10 Hz range for *syn* compounds. This

empirical rule, recently reported from this laboratory,[18] is a consequence of a strong intramolecular hydrogen bond between the carbamate group and the hydroxyamino group present in this class of compounds (Figure 1).[19] In all cases the $J_{a,b}$ coupling constants of *syn* hydroxylamines **19a**-**22a** fell within the expected range (see Table 3). Thus ^1H NMR alone could be relied on as a definitive analytical tool in establishing relative stereochemistry in this conformationally fixed system.

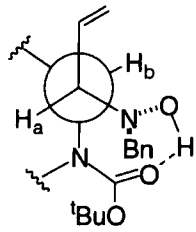


Figure 1. Preferred conformation of α-amino nitrones

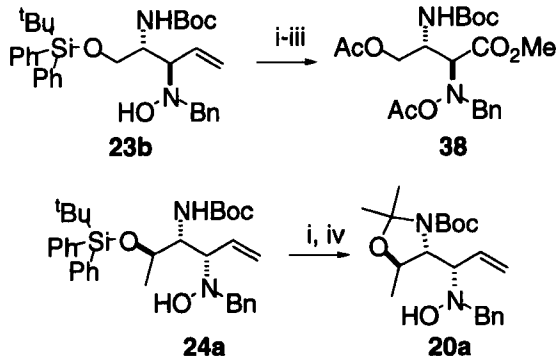
Table 3. Selected ^1H NMR data for *syn* hydroxylamines **19a**-**22a**.[a]

hydroxyl amine	δ H_a (ppm)	δ H_b (ppm)	$J_{a,b}$ (Hz)	δ NO*H* (ppm)
19a	2.98	4.11	10.2	7.40
20a	2.95	3.95	10.0	7.40
21a	2.72	4.10	9.9	7.78
22a	2.40	4.20	10.0	7.55

[a] ^1H NMR spectra were recorded in $CDCl_3$ at –40°C using a Bruker 300 ARX NMR instrument.

The configurational assignment of hydroxylamines **23b** and **24a**, derived from α-amino monoprotected nitrones, was made on the basis of chemical proofs. α-Amino hydroxylamine **23b** was converted into diaminoacid derivative **38** upon desilylation, acetylation and oxidative cleavage of the vinyl group followed by

esterification with diazomethane (Scheme 5). The structure of **38** was given by comparison with the previously reported data.[13a] Configurational assignment for **24a** rests on its conversion to hydroxylamine **20a** (Scheme 5). The spectroscopic data of this compound were superimposable with those of the same product obtained by direct vinylation of nitrone **14** as indicated above.



Reagents and conditions. i, Bu_4NF, THF, r.t, 1h. ii, Ac_2O, Py, 2 h, r.t. iii, CH_3CN-CCl_4-H_2O, $RuCl_3$, $NaIO_4$, 30 min, r.t.; then CH_2N_2, Et_2O. iv, 2,2-DMP, BF_3Et_2O, acetone, r.t., 6 h.

Scheme 5

CONCLUSIONS

In conclusion, we have screened a variety of chiral and achiral nitrones for the nucleophilic addition of vinylmagnesium bromide (vinylation). The present methodology offers a facile method for the stereoselective preparation of both allyl hydroxylamines and amines. The stereoselectivity of the addition process, in the case of chiral substrates, was found to depend on several parameters. For α-alkoxy nitrones the choice of the appropriate Lewis acid offers both of the possible diastereomers proceeding of the precursor nitrone, *syn* and *anti* selectively. On the other hand, α-amino nitrones showed to have no dependence

of the presence of Lewis acids giving rise *syn* adducts preferentially with the only exception of a L-serine derived α-amino monoprotected nitrone. An important facet of this study is the observation that clean transformation of hydroxyamino into amino groups may be carried out over a variety of substrates under mild conditions. The reported transformations promises to elevate the synthetic utility of other readily available hydroxylamines for the preparation of optically active nitrogenated compounds. Further studies for applying the above exposed methodology to the synthesis of nitrogenated natural products and derivatives are ongoing in our laboratory.

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[20] and solvents were purified and dried by standard methods.[21] 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. N-

Benzyl nitrones were prepared according to our previously reported procedure.[22] Vinylmagnesium bromide was commercially available (Aldrich) and was used as received.

Nucleophilic Addition of Vinyl Magnesium Bromide to nitrones. General Procedure. Method A (without Lewis acids). To a stirred solution of nitrone (1 mmol) in anhydrous THF (30 mL) at –30 °C, was added vinyl magnesium bromide (1.5 mL of a 1.0 M solution in THF, 1.5 mmol) dropwise. The resulting suspension was stirred at –30 °C for 2 hours. The reaction mixture was diluted with saturated aqueous NH_4Cl (25 mL) and Et_2O (25 mL). The phases were separated and the aqueous layer was extracted into Et_2O (2 x 25 mL). The combined organic extracts were washed with brine (25 mL), dried ($MgSO_4$) and evaporated under reduced pressure to yield the crude mixture of hydroxylamines. A sample of the crude product was used to measure the isomers ratio by NMR spectroscopy. The product was further purified by column chromatography on silica gel (eluent is indicated in brackets).

Method B (with Lewis acids). To a stirred solution of nitrone (1 mmol) in anhydrous Et_2O (30 mL) at room temperature, was added the corresponding Lewis acid (1 mmol) and the resulting mixture was stirred at room temperature for 15 min. The reaction mixture was then cooled to –30 °C and treated with vinyl magnesium bromide (0.5 mL of a 3.0 M solution in Et_2O, 1.5 mmol) dropwise. The resulting suspension was stirred at –30 °C for 2 hours. The reaction mixture was diluted with 1N NaOH (20 mL) and Et_2O (20 mL). The phases were separated and the aqueous layer was extracted into diethyl ether (2 x 25 mL). The combined organic extracts were washed with brine (25 mL), dried ($MgSO_4$) and evaporated under reduced pressure to yield the crude mixture of hydroxylamines. A sample of the crude product was used to measure the isomers ratio by NMR

spectroscopy. The product was further purified by column chromatography on silica gel (eluent is indicated in brackets).

(3R,4S)-3-(N-Benzylhydroxyamino)-4,5-dihydroxy-4,5-O-isopropylidene-1-pentene (5a). Method A. (hexane-diethyl ether, 60:40); (0.184 g, 70%); oil; $[\alpha]_D$ +28.2 (c 0.43, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.33 (s, 6H), 3.16 (dd, 1H, J = 7.9, 9.3 Hz), 3.70 (dd, 1H, J = 6.4, 8.5 Hz), 3.76 (d, 1H, J = 13.0 Hz), 3.91 (dd, 1H, J = 6.4, 8.5 Hz), 3.98 (d, 1H, J = 13.0 Hz), 4.38 (pseudo td, 1H, J = 6.4, 7.9 Hz), 5.21 (dd, 1H, J = 1.8, 17.4 Hz), 5.39 (dd, 1H, J = 1.8, 10.4 Hz), 5.92 (ddd, 1H, J = 9.3, 10.4, 17.4 Hz), 6.50 (bs, 1H, ex. D_2O), 7.20-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 25.4, 26.5, 61.4, 66.7, 70.6, 75.3, 109.1, 121.5, 127.0, 128.0, 129.2, 131.3, 137.0. Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.42; H, 8.04; N, 5.32. Found: C, 68.38; H, 8.23; N, 5.56.

(3S,4S)-3-(N-Benzylhydroxyamino)-4,5-dihydroxy-4,5-O-isopropylidene-1-pentene (5b). Method B (Et_2AlCl). (hexane-diethyl ether, 60:40); (0.232 g, 88%); oil; $[\alpha]_D$ -44.8 (c 1.10, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.37 (s, 3H), 1.43 (s, 3H), 3.07 (dd, 1H, J =6.8, 9.2 Hz), 3.64 (d, 1H, J =13.2 Hz), 3.80 (dd, 1H, J = 6.8, 8.4 Hz), 3.95 (d, 1H, J = 13.2 Hz), 4.08 (dd, 1H, J = 6.4, 8.4 Hz), 4.41 (pseudo q, 1H, J = 6.5 Hz), 5.25 (dd, 1H, J = 1.8, 17.4 Hz), 5.47 (dd, 1H, J = 1.8, 10.4 Hz), 5.93 (bs, 1H, ex. D_2O), 6.05 (ddd, 1H, J = 9.2, 10.4, 17.4 Hz), 7.22-7.45 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 25.4, 26.5, 61.7, 67.8, 72.0, 76.6, 109.3, 121.5, 127.3, 128.3, 129.5, 132.1, 137.6. Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.42; H, 8.04; N, 5.32. Found: C, 68.59; H, 7.82; N, 5.61.

(3R,4S,5S)-3-(N-Benzylhydroxyamino)-6-O-benzyl-4,5-O-isopropylidene-4,5,6-trihydroxy-1-pentene (6a). Method A. (hexane-diethyl ether, 80:20); (0.245 g, 64%); oil; $[\alpha]_D$ +27.5 (c 0.11, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.38 (s, 3H), 1.40 (s, 3H), 3.11 (dd, 1H, J = 6.9, 9.1 Hz), 3.66 (dd, 1H, J = 5.7, 9.9 Hz), 3.69 (d, 1H, J = 13.3 Hz), 3.77 (dd, 1H, J = 4.5 , 9.9 Hz), 3.95 (d, 1H, J = 13.3 Hz), 4.26

(m, 2H), 4.57 (s, 2H), 5.24 (dd, 1H, J = 1.8, 17.4 Hz), 5.38 (bs, 1H, ex. D2O), 5.48 (dd, 1H, J =1.8, 10.3 Hz), 6.13 (ddd, 1H, J =9.1, 10.3, 17.4 Hz), 7.21-7.38 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 27.0, 27.1, 61.2, 71.6, 72.0, 73.6, 78.0, 79.3, 109.3, 121.3, 127.1, 127.7, 128.2, 128.3(2C), 129.1, 132.2, 137.4, 137.8. Anal. Calcd for $C_{23}H_{29}NO_4$: C, 72.04; H, 7.62; N, 3.65. Found: C, 72.31; H, 7.86; N, 3.71.

(3S,4S,5S)-3-(N-Benzylhydroxyamino)-6-O-benzyl-4,5-O-isopropylidene-4,5,6-trihydroxy-1-pentene (6b). Method B (Et_2AlCl). (hexane-diethyl ether, 80:20); (0.300 g, 78%); oil; $[\alpha]_D$ –4.6 (c 0.51, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.37 (s, 3H), 1.39 (s, 3H), 3.27 (dd, 1H, J = 7.0, 8.9 Hz), 3.52 (m, 2H), 3.74 (d, 1H, J = 13.0 Hz), 4.03 (d, 1H, J = 13.0 Hz), 4.14 (m, 1H), 4.25 (pseudo t, 1H, J = 6.6 Hz), 4.52 (s, 2H), 4.57 (bs, 1H, ex. D2O), 5.20 (dd, 1H, J = 1.7, 17.5 Hz), 5.37 (dd, 1H, J = 1.7, 10.5 Hz), 5.91 (ddd, 1H, J = 8.9, 10.5, 17.5 Hz), 7.19-7.36 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 27.1, 27.2, 61.4, 70.7, 71.0, 73.4, 77.4, 78.4, 109.4, 121.7, 127.2, 127.7, 127.8, 127.9, 128.2, 129.3, 131.5, 137.5, 137.8. Anal. Calcd for $C_{23}H_{29}NO_4$: C, 72.04; H, 7.62; N, 3.65. Found: C, 72.26; H, 7.58; N, 3.88.

N-Benzyl-3-O-benzyl-5-deoxy-5-(hydroxyamino)-5-vinyl-1,2-O-isopropylidene-β-L-ido-1,4-pentofuranoside (7a). Method A. (hexane-ethyl acetate, 80:20); (0.226 g, 55%); oil; $[\alpha]_D$ -55.5 (c 0.55; $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.32 (s, 3H), 1.49 (s, 3H), 3.75 (t, 1H, J = 4.7 Hz), 3.77 (d, 1H, J = 13.6 Hz), 3.82 (d, 1H, J = 2.9 Hz), 3.95 (d, 1H, J = 13.5 Hz), 4.41 (d, 1H, J = 11.5 Hz), 4.52 (dd, 1H, J = 2.8, 9.8 Hz), 4.58 (d, 1H, J = 2.2 Hz), 4.60 (d, 1H, J = 12.8 Hz), 5.06 (bs, 1H, ex. D_2O), 5.24 (dd, 1H, J = 1.2, 17.4 Hz), 5,.6 (dd, 1H, J=1.9, 10.4), 6.01 (d, 1H, J=3.8), 5.92 (m, 1H), 7.18-7.43 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 26.3, 26.7, 61.3, 67.8, 71.9, 79.5, 81.3, 82.4, 105.3, 11.6, 121.2, 127.0, 127.5, 127.8, 128.1, 128.4, 129.4, 131.6, 137.5, 138.1. Anal. Calcd for $C_{24}H_{29}NO_5$: C, 70.05; H, 7.10; N, 3.40. Found: C, 69.86; H, 7.37; N, 3.51.

N-Benzyl-3-O-benzyl-5-deoxy-5-(hydroxyamino)-5-vinyl-1,2-O-isopropylidene-α-D-gluco-1,4-pentofuranoside (7b). Method B (Et_2AlCl). (hexane-ethyl acetate, 80:20); (0.284 g, 69%); oil; $[\alpha]_D$ +20.5 (c 1.15; $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.30 (s, 3H), 1.50 (s, 3H), 3.70 (d, 1H, J = 13.3 Hz), 3.74 (t, 1H, J = 9.3 Hz), 3.93 (d, 1H, J = 13.3 Hz), 4.12 (d, 1H, J = 3.2 Hz), 4.50 (dd, 1H, J = 2.8, 9.4 Hz), 4.55 (d, 1H, J = 3.8 Hz), 4.62 (d, 1H, J = 11.7 Hz), 4.69 (d, 1H, J = 11.7 Hz), 4.80 (bs, 1H, ex. D_2O), 5.35 (dd, 1H, J = 1.7, 17.3 Hz), 5.50 (dd, 1H, J = 1.8, 10.3 Hz), 5.91 (d, 1H, J = 3.8 Hz), 6.18 (ddd, 1H, J = 7.5, 9.9, 17.4 Hz), 7.30 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 26.3, 26.8, 61.9, 67.1, 72.5, 80.2, 82.0, 82.1, 104.8, 111.5, 121.2, 127.3, 127.5, 127.8, 128.3, 128.5, 129.4, 132.5, 137.9 (2C). Anal. Calcd for $C_{24}H_{29}NO_5$: C, 70.05; H, 7.10; N, 3.40. Found: C, 69.93; H, 7.02; N, 3.63.

N-Benzyl-5-deoxy-5-(hydroxyamino)-5-vinyl-2,3-O-isopropylidene-1-O-methyl-β-L-gulo-1,4-pentofuranoside (8a). Method A. (hexane-ethyl acetate, 80:20); (0.218 g, 65%); oil; $[\alpha]_D$ +9.0 (c 0.38, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.24 (s, 3H), 1.33 (s, 3H), 3.35(s, 3H), 3.72 (t, 1H, J = 9.1 Hz), 3.84 (d, 1H, J = 13.4 Hz), 4.03 (d, 1H, J = 13.4 Hz), 4.21 (dd, 1H, J = 3.2, 9.8 Hz), 4.48 (d, 1H, J = 5.9 Hz), 4.56 (dd, 1H, J = 3.2, 5.9 Hz), 4.92 (s, 1H), 5.34 (dd, 1H, J = 2.0, 17.6 Hz), 5.4 (dd, 1H, J = 2.0, 10.7 Hz), 5.64 (bs, 1H, ex. D_2O), 5.98 (ddd, 1H, J = 8.5, 10.5, 17.3 Hz), 7.25 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 25.3, 26.2, 54.9, 61.0, 66.8, 79.2, 80.3, 84.7, 107.6, 112.4, 121.6, 127.1, 128.3, 129.4, 131.40, 138.0. Anal. Calcd for $C_{18}H_{25}NO_5$: C, 64.46; H, 7.51; N, 4.18. Found: C, 64.69; H, 7.82; N, 4.27.

N-Benzyl-5-deoxy-5-(hydroxyamino)-5-vinyl-2,3-O-isopropylidene-1-O-methyl-α-D-manno-1,4-pentofuranoside (8b). Method B (Et_2AlCl). (hexane-diethyl ether, 80:20); (0.255 g, 76%); white solid; mp 84-86 °C; $[\alpha]_D$ +64.0 (c 0.29, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.29 (s, 3H), 1.32 (s, 3H), 3.27 (s, 3H), 3.65 (t, 1H, J = 8.9 Hz), 3.76 (d, 1H, J = 13.2 Hz), 3.95 (d, 1H, J = 13.2 Hz), 4.18 (dd, 1H,

J = 3.4, 9.0 Hz), 4.50 (d, 1H, J = 5.9 Hz), 4.78 (dd, 1H, J = 3.4, 5.9 Hz), 4.84 (s, 1H), 5.30 (bs, 1H, ex. D_2O), 5.32 (dd, 1H, J = 1.5, 16.1 Hz), 5.44 (dd, 1H, J = 1.7, 10.2 Hz), 6.06 (ddd, 1H, J = 9.0, 10.3, 19.0 Hz), 7.30 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 25.2, 26.1, 54.5, 61.7, 66.8, 79.4, 80.0, 84.7, 106.9, 112.2, 120.9, 127.3, 128.2, 129.6, 132.6, 137.7. Anal. Calcd for $C_{18}H_{25}NO_5$: C, 64.46; H, 7.51; N, 4.18. Found: C, 64.23; H, 7.40; N, 4.35.

(3S,4R)-3-(N-Benzylhydroxyamino)-4-(tert-butoxycarbonylamino)-5-hydroxy-4,5-O-isopropylidene-1-pentene (19a). Method A. (hexane-diethyl ether, 80:20); (0.312 g, 86 %); oil; $[\alpha]_D$ –49.9 (c 0.86, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.41 (s, 3H), 1.49 (s, 3H), 1.54 (s, 9H), 2.97 (t, 1H, J = 9.8 Hz), 3.73 (d, 1H, J = 13.5 Hz), 3.82 (m, 2H), 3.96 (d, 1H, J = 13.5 Hz), 4.13 (dd, 1H, J = 3.8, 9.9 Hz), 5.25 (dd, 1H, J = 2.0, 17.5 Hz), 5.49 (dd, 1H, J = 2.0, 10.5 Hz), 6.05 (ddd, 1H, J = 1.0, 10.5, 17.5 Hz), 7.10-7.40 (m, 5H), 7.44 (bs, 1H, ex. D_2O); ^{13}C NMR ($CDCl_3$) δ 24.6, 27.6, 28.4, 57.9, 60.3, 65.2, 70.2, 80.8, 93.8, 121.9, 126.7, 127.9, 128.7, 133.2, 138.5, 154.5. Anal. Calcd for $C_{20}H_{30}N_2O_4$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.40; H, 8.18; N, 7.90.

(3S,4R,5R)-3-(N-Benzylhydroxyamino)-4-(tert-butoxycarbonylamino)-5-hydroxy-4,5-O-isopropylidene-1-hexene (20a). Method A. (hexane-diethyl ether, 80:20); (0.328 g, 87%); oil; $[\alpha]_D$ –49.5 (c 1.10, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.26 (d, 3H, J = 6.4 Hz), 1.29 (s, 3H), 1.53 (s, 9H), 1.61 (s, 3H), 2.95 (t, 1H, J = 9.9 Hz), 3.68 (d, 1H, J = 13.6 Hz), 3.93 (d, 1H, J = 9.9 Hz), 3.96 (d, 1H, J = 13.6 Hz), 4.08 (q, 1H, J = 6.4 Hz), 5.24 (dd, 1H, J = 1.8, 17.7 Hz), 5.48 (dd, 1H, J = 1.8, 10.3 Hz), 6.05 (dt, 1H, J = 10.3, 17.7 Hz), 7.25-7.46 (m, 5H), 7.39 (bs, 1H, ex. D_2O); ^{13}C NMR ($CDCl_3$) δ 22.0, 28.3, 28.5, 29.8, 60.4, 63.9, 70.8, 74.3, 81.0, 94.1, 122.0, 126.9, 128.0, 128.9, 133.3, 138.4, 154.7. Anal. Calcd for $C_{21}H_{32}N_2O_4$: C, 66.99; H, 8.57; N, 7.44. Found: C,66.78 ; H, 8.90; N, 7.26.

(3S)-3-(N-Benzylhydroxyamino)-3-[(2S)-1-(tert-butoxycarbonylamino)-pyrrolidin-2-yl]-1-propene (21a). Method A. (hexane-ethyl acetate, 96:4); (0.233 g, 70%); $[\alpha]_D$ –39.0 (c 1.64, $CHCl_3$); oil; ^1H NMR ($CDCl_3$) δ 1.51 (s, 9H), 1.62-1.95 (m, 4H), 2.69 (t, 1H, J = 9.9 Hz), 3.27-3.43 (m, 2H), 3.61 (d, 1H, J = 14.7 Hz), 3.90 (d, 1H, J = 14.7 Hz), 4.08 (d, 1H, J = 9.9 Hz), 5.13 (dd, 1H, J = 1.1, 17.1 Hz), 5.40 (dd, 1H, J = 1.1, 10.2 Hz), 6.01 (dt, 1H, J = 9.9, 17.1 Hz), 7.20-7.35 (m, 5H), 7.74 (bs, 1H ex. D_2O); ^{13}C NMR ($CDCl_3$) δ 23.0, 27.6, 28.6, 46.0, 57.6, 60.3, 71.1, 79.6, 120.1, 126.4, 127.8, 128.3, 134.1, 139.1, 156.4. Anal. Calcd for $C_{19}H_{28}N_2O_3$: C, 68.65; H, 8.49; N, 8.43. Found: C, 68.84; H, 8.15; N, 8.24.

(3S)-3-(N-Benzylhydroxyamino)-3-[(2S,4R)-1-(tert-butoxycarbonylamino)-4-(tert-butyldi-phenylsiloxy)pyrrolidin-2-yl]-1-propene (22a). Method A. (hexane-diethyl ether, 90:10); (0.487 g, 83%); $[\alpha]_D$ –18.8 (c 1.30, $CHCl_3$); oil; ^1H NMR ($CDCl_3$) δ 1.08 (s, 9H), 1.54 (s, 9H), 1.75 (m, 1H), 1.96 (ddd, 1H, J = 6.1, 8.1, 13.7 Hz), 2.50 (t, 1H, J = 9.5 Hz), 3.22 (dd, 1H, J 0 5.6, 11.5 Hz), 3.51 (dd, 1H, J = 3.7, 11.5 Hz), 3.59 (d, 1H, J = 14.2 Hz), 3.91 (d, 1H, J = 14.2 Hz), 4.19 (dd, 1H, J = 3.4, 9.5 Hz), 4.30 (m, 1H), 4.86 (dd, 1H, J = 1.7, 17.1 Hz), 5.29 (dd, 1H, J = 1.7, 10.3 Hz), 5.95 (ddd, 1H, J = 3.4, 10.3, 17.1 Hz), 7.06-7.48 (m, 11H), 7.56 (bs, 1H ex. D_2O), 7.68-7.77 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 19.1, 26.9, 28.6, 37.7, 54.1, 56.4, 60.1, 71.5, 72.5, 79.7, 120.4, 126.5, 127.7, 127.8 (2C), 127.9, 128.3, 129.8 (2C), 133.4, 133.9, 135.7 (2C), 139.4, 154.5. Anal. Calcd for $C_{35}H_{46}N_2O_4Si$: C, 71.63; H, 7.90; N, 4.77. Found: C, 71.48; H, 7.77; N, 4.98.

(3S,4R)-3-(N-Benzylhydroxyamino)-4-(tert-butoxycarbonylamino)-5-(tert-butyldiphenylsiloxy)-1-pentene (23a). Method A. (hexane-diethyl ether, 95:5); (0.090 g, 16%); oil; ^1H NMR ($CDCl_3$) δ (selected signals) 0.98 (s, 9H), 1.45 (s, 9H), 3.30 (t, 1H, J = 9.5 Hz), 3.70 (d, 1H, J = 13.9 Hz), 3.76 (m, 2H), 4.00 (d, 1H, J = 13.9 Hz), 4.29 (d, 1H, J = 8.5 Hz), 4.93 (d, 1H, J = 9.3 Hz), 5.10 (dd, 1H, J =

2.0, 17.3 Hz), 5.38 (dd, 1H, J = 2.0, 10.5 Hz), 5.90 (dt, 1H, J = 10.5, 17.3 Hz), 7.11 (bs, 1H, ex. D_2O), 7.30-7-43 (m, 11H), 7.62-7.81 (m, 4H).

(3R,4R)-3-(N-Benzylhydroxyamino)-4-(tert-butoxycarbonylamino)-5-(tert-butyldiphenyl-siloxy)-1-pentene (23b). Method A. (hexane-diethyl ether, 95:5); (0.432 g, 77%); oil; $[\alpha]_D$ –4.94 (c 1.10, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.04 (s, 9H), 1.44 (s, 9H), 3.30 (dd, 1H, J = 4.6, 9.0 Hz), 3.58 (d, 1H, J = 14.0 Hz), 3.70 (m, 2H), 4.02 (d, 1H, J = 14.0 Hz), 4.31 (m, 1H), 4.60 (d, 1H, J = 9.8 Hz), 5.30 (m, 2H), 5.80 (m, 1H), 6.36 (bs, 1H, ex. D_2O), 7.28-7-41 (m, 11H), 7.60-7.80 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 19.2, 26.8, 28.4, 52.5, 61.7, 63.4, 72.1, 79.9, 120.8, 127.0, 127.7, 127.8, 128.0, 129.8 (2C), 129.9, 133.1, 133.3, 133.5, 135.6 (2C), 138.6, 156.2. Anal. Calcd for $C_{33}H_{44}N_2O_4Si$: C, 70.68; H, 7.91; N, 5.00. Found: C, 70.26; H, 8.03; N, 5.26.

(3S,4R,5R)-3-(N-Benzylhydroxyamino)-4-(tert-butoxycarbonylamino)-5-(tert-butyldi-phenylsiloxy)-1-hexene (24a). Method A. (hexane-diethyl ether, 90:10); (0.454 g, 79%); oil; $[\alpha]_D$ –75.2 (c 1.90, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.92 (s, 9H), 1.08 (d, 3H, J = 6.3 Hz), 1.56 (s, 9H), 3.10 (t, 1H, J = 9.9 Hz), 3.56 (t, 1H, J = 10.3 Hz), 3.76 (d, 1H, J = 13.6 Hz), 3.99 (m, 1H), 4.03 (d, 1H, J = 13.6 Hz), 4.81 (dd, 1H, J = 2.2, 17.6 Hz), 5.08 (d, 1H, J = 10.1 Hz), 5.26 (dd, 1H, J = 2.2, 10.3 Hz), 5.80 (dt, 1H, J = 10.3, 17.6 Hz), 6.90 (bs, 1H, ex. D_2O), 7.30-7.44 (m, 11H), 7.53-7.80 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 19.2, 22.0, 27.1, 28.6, 57.5, 60.2, 68.3, 69.5, 80.0, 121.6, 126.9, 127.5, 127.6, 128.2, 128.6, 129.7, 129.9, 132.7, 133.0, 134.1, 135.9 (2C), 138.6, 158.9. Anal. Calcd for $C_{33}H_{46}N_2O_4Si$: C, 71.04; H, 8.07; N, 4.87. Found: C, 71.22; H, 7.83; N, 5.07.

Reduction of Allyl Hydroxylamines to Allyl Amines. General Procedure. To a well-stirred solution of copper (II) acetate (15 mg, 0.1 mmol) in acetic acid (1.5 ml) at room temperature, was added zinc dust (0.34 g, 5.1 mmol). The resulting suspension was stirred at room temperature for 15 min; then a solution of

hydroxylamine (1 mmol) was added and the mixture was heated at 70 °C for 1 hour. The grey suspension was allowed to cool to room temperature and disodium salt of EDTA was added (2.0 g). The resulting mixture was made alkaline (pH=10) by addition of 3 N NaOH and then diluted with saturated aqueous ammonium chloride (20 mL) and dichloromethane (20 mL). The phases were separated and the aqueous layer extracted into dichloromethane (3 x 25 mL). The combined organic extracts were washed with a saturated aqueous solution of the disodium salt of EDTA (3 x 25 mL) and brine (25 mL), dried over magnesium sulfate, filtered and concentrated under reduced pressure to give the allylamine essentially pure.

(3R,4S)-3-Benzylamino-4,5-dihydroxy-4,5-O-isopropylidene-1-pentene (9a). (0.198 g, 80%); oil; $[\alpha]_D$ –27.4 (c 1.21, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.30 (s, 3H), 1.31 (s, 3H), 2.00 (bs, 1H, ex. D_2O), 3.05 (t, 1H, J = 8.3 Hz), 3.60 (d, 1H, J = 13.6 Hz), 3.71 (dd, J = 5.9, 8.2 Hz), 3.90 (d, 1H, J = 13.6 Hz), 3.88 (m, 1H), 4.02 (m, 1H), 5.25 (m, 2H), 5.58 (ddd, 1H, J = 8.4, 9.7, 17.6 Hz), 7.20-7.32 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 25.4, 26.8, 50.6, 64.3, 66.6, 77.7, 109.6, 119.6, 126.9, 128.2, 128.5, 136.5, 139.8. Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.97; H, 8.47; N, 5.31.

(3S,4S)-3-Benzylamino-4,5-dihydroxy-4,5-O-isopropylidene-1-pentene (9b). (0.188 g, 76%); oil; $[\alpha]_D$ +10.0 (c 0.47, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.32 (s, 3H), 1.39 (s, 3H), 1.70 (bs, 1H, ex. D_2O), 3.18 (dd, 1H, J = 4.9, 8.3 Hz), 3.60 (d, 1H, J = 13.4 Hz), 3.86 (d, 1H, J = 13.4 Hz), 3.90 (dd, 1H, J = 7.5, 8.1 Hz), 3.97 (dd, J = 6.4, 8.1 Hz), 4.14 (ddd, 1H, J = 4.9, 6.4, 7.5 Hz), 5.22 (dd, 1H, J = 1.1, 17.1 Hz), 5.30 (dd, 1H, J = 1.1, 9.8 Hz), 5.68 (ddd, 1H, J = 8.3, 9.8, 17.1 Hz), ; ^{13}C NMR ($CDCl_3$) δ 25.1, 26.4, 50.9, 62.1, 66.1, 78.3, 109.1, 118.3, 126.8, 128.1, 128.3, 136.6, 140.4. Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.63; H, 8.39; N, 5.77.

(3R,4S,5S)-3-Benzylamino-6-O-benzyl-4,5-O-isopropylidene-4,5,6-trihydroxy-1-pentene (10a). (0.287 g, 78%); oil; $[\alpha]_D$ –43.4 (c 0.23, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.33 (s, 3H), 1.37 (s, 3H), 1.63 (bs, 1H, ex. D_2O), 3.08 (dd, 1H, J = 7.3, 8.3 Hz), 3.45 (dd, 1H, J = 6.4, 10.5 Hz), 3.54 (dd, 1H, J = 3.3, 10.5 Hz), 3.59 (d, 1H, J = 13.5 Hz), 3.76 (pseudo t, 1H, J = 7.3 Hz), 3.85 (d, 1H, J = 13.5 Hz), 4.11 (ddd, 1H, J = 3.3, 6.4, 7.3 Hz), 4.52 (bs, 2H), 5.15 (m, 2H), 5.54 (ddd, 1H, J = 8.3, 10.1, 17.3 Hz), 7.29-7.39 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 26.9, 27.0, 50.5, 63.9, 70.8, 73.3, 78.0, 79.7, 109.5, 119.2, 126.9, 127.7, 128.2, 128.4 (2C), 129.0, 130.2, 136.8 (2C). Anal. Calcd for $C_{23}H_{29}NO_3$: C, 75.17; H, 7.95; N, 3.81. Found: C, 75.05; H, 8.08; N, 3.92.

(3S,4S,5S)-3-Benzylamino-6-O-benzyl-4,5-O-isopropylidene-4,5,6-trihydroxy-1-pentene (10b). (0.257 g, 70%); oil; $[\alpha]_D$ –22.8 (c 0.25, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.36 (s, 3H), 1.37 (s, 3H), 1.70 (bs, 1H, ex. D_2O), 3.15 (dd, 1H, J = 4.7, 8.4 Hz), 3.56 (dd, 1H, J = 5.5, 10.3 Hz), 3.59 (dd, 1H, J = 13.2 Hz), 3.62 (dd, 1H, J = 4.1, 10.3 Hz), 3.83 (d, 1H, J = 13.2 Hz), 3.88 (dd, 1H, J = 4.7, 8.1 Hz), 4.10 (ddd, 1H, J = 4.1, 5.5, 8.1 Hz), 4.60 (bs, 2H), 5.13 (dd, 1H, J = 1.8, 7.6 Hz), 5.24 (dd, 1H, J = 1.8, 10.2 Hz), 5.70 (ddd, 1H, J = 8.4, 10.2, 17.6 Hz), 7.28-7.40 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 27.0 (2C), 50.9, 62.1, 71.2, 73.4, 77.6, 80.5, 109.1, 118.7, 126.8, 127.6, 127.7, 128.2, 128.3 (2C), 129.0, 136.4, 138.1. Anal. Calcd for $C_{23}H_{29}NO_3$: C, 75.17; H, 7.95; N, 3.81. Found: C, 75.24; H, 8.17; N, 3.60.

3-O-Benzyl-5-deoxy-5-benzylamino-5-vinyl-1,2-O-isopropylidene-β-L-ido-1,4-pentofuranoside (11a). (0.285 g, 72%); oil; $[\alpha]_D$ –15.2 (c 0.60, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.28 (s, 3H), 1.46 (s, 3H), 3.00 (bs, 1H, ex. D_2O), 3.63 (d, 1H, J = 12.8 Hz), 3.65 (t, 1H, J = 8.9 Hz), 3.83 (d, 1H, J = 3.0 Hz), 3.84 (d, 1H, J = 12.8 Hz), 4.15 (dd, 1H, J = 3.0, 9.3 Hz), 4.41 (d, 1H, J = 11.6 Hz), 4.56 (d, 1H, J = 3.7 Hz), 4.58 (d, 1H, J = 11.6 Hz), 5.27 (m, 2H), 5.69 (ddd, 1H, J = 8.2, 10.0, 17.7 Hz), 5.91 (d, 1H, J = 3.7 Hz), 7.2-7.4 (m, 10H).; ^{13}C NMR ($CDCl_3$) δ 26.3, 26.7,

51.3, 60.1, 72.0, 81.8, 82.0, 82.3, 105.0, 111.8, 119.6, 126.9, 127.7, 127.8, 127.90, 128.4, 128.4, 129.4, 135.9, 137.3. Anal. Calcd for $C_{24}H_{29}NO_4$: C, 72.89; H, 7.39; N, 3.54. Found: C, 72.74; H, 7.52; N, 3.26.

3-O-Benzyl-5-deoxy-5-benzylamino-5-vinyl-1,2-O-isopropylidene-α-D-gluco-1,4-pentofuranoside (11b). (0.316 g, 80%); oil; $[\alpha]_D$ −11.3 (c 0.50, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.28 (s, 3H), 1.45 (s, 3H), 2.03 (bs, 1H, ex. D_2O), 3.53 (t, 1H, J = 8.5 Hz), 3.57 (d, 1H, J = 13.0 Hz), 3.82 (d, 1H, J = 13.0 Hz), 4.02 (dd, 1H, J = 3.0, 8.8 Hz), 4.06 (d, 1H, J = 2.9 Hz), 4.50 (d, 1H, J = 11.7 Hz), 4.59 (d, 1H, J = 4.6 Hz), 4.68 (d, 1H, J = 11.7 Hz), 5.23 (d, 1H, J = 7.9 Hz), 5.28 (s, 1H), 5.75 (ddd, 1H, J = 8.2, 10.6, 16.6 Hz), 5.92 (d, 1H, J = 3.7 Hz), 7.17-7.30 (m, 10H).; ^{13}C NMR ($CDCl_3$) δ 26.3, 26.7, 51.0, 59.2, 72.0, 81.5, 81.8, 82.6, 104.9, 111.5, 118.0, 126.9, 127.8, 127.9, 128.1, 128.3, 128.5, 129.3, 137.4, 137.6. Anal. Calcd for $C_{24}H_{29}NO_4$: C, 72.89; H, 7.39; N, 3.54. Found: C, 72.74; H, 7.52; N, 3.26.

5-Benzylamino-5-deoxy-5-vinyl-2,3-O-isopropylidene-1-O-methyl-β-L-gulo-1,4-pentofuranoside (12a). (0.249 g, 78%); oil; $[\alpha]_D$ 8.9 (c 0.35, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.22 (s, 3H), 1.33 (s, 3H), 2.04 (bs, 1H, ex. D_2O), 3.29 (s, 3H), 3.62 (t, 1H, J = 8.4 Hz), 3.72 (d, 1H, J = 13.3 Hz), 3.91 (dd, 1H, J = 3.2, 9.3 Hz), 3.97 (d, 1H, J = 13.3 Hz), 4.49 (d, 1H, J = 5.9 Hz), 4.57 (dd, 1H, J = 3.2, 5.9 Hz), 4.86 (s, 1H), 5.33 (dd, 1H, J = 1.5, 10.3 Hz), 5.44 (dd, 1H, J = 1.5, 17.2 Hz), 5.84 (ddd, 1H, J = 7.6, 10.3, 17.2 Hz), 7.32 (m, 5H).; ^{13}C NMR ($CDCl_3$) δ 25.0, 26.0, 50.6, 54.7, 59.2, 79.9, 81.2, 85.0, 107.0, 112.4, 120.2, 127.2, 128.4, 128.5, 134.7, 138.2. Anal. Calcd for $C_{18}H_{25}NO_4$: C, 67.69; H, 7.89; N, 4.39. Found: C, 67.94; H, 7.92; N, 4.57.

5-Benzylamino-5-deoxy-5-vinyl-2,3-O-isopropylidene-1-O-methyl-α-D-manno-1,4-pentofuranoside (12b). (0.256 g, 80%); oil; $[\alpha]_D$ −5.8 (c 0.63, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.28 (s, 3H), 1.35 (s, 3H), 2.62 (bs, 1H, ex. D_2O), 3.26 (s, 3H), 3.48 (t, 1H, J = 8.5 Hz), 3.71 (d, 1H, J = 13.2 Hz), 3.86 (dd, 1H, J =

3.7, 8.8 Hz), 3.92 (d, 1H, J = 13.2 Hz), 4.51 (d, 1H, J = 5.8 Hz), 4.78 (dd, 1H, J = 3.3, 5.9 Hz), 4.86 (s, 1H), 5.28 (m, 2H), 5.81 (ddd, 1H, J = 8.1, 10.3, 17.8 Hz), 7.18-7.36 (m, 5H).; ^{13}C NMR ($CDCl_3$) δ 24.9, 25.9, 50.4, 54.4, 59.5, 79.3, 81.6, 84.8, 106.7, 112.5, 118.5, 126.9, 128.2, 128.3, 132.7, 137.1. Anal. Calcd for $C_{18}H_{25}NO_4$: C, 67.69; H, 7.89; N, 4.39. Found: C, 67.94; H, 7.92; N, 4.57.

(3S,4R)-3-Benzylamino-4-(tert-butoxycarbonylamino)-5-hydroxy-4,5-O-isopropylidene-1-pentene (25a). (0.263 g, 76%); oil; $[\alpha]_D$ –23.2 (c 0.47, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.23 (s, 3H), 1.29 (s, 3H), 1.43 (s, 9H), 1.73 (bs, 1H, ex. D_2O), 3.40 (m, 1H), 3.62 (d, 1H, J = 13.4 Hz), 3.81 (d, 1H, J = 13.4 Hz), 3.85 (m, 1H), 4.00 (m, 2H), 5.20 (m, 2H), 5.68 (dt, 1H, J = 10.1, 17.7 Hz), 7.28-7.36 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 26.3, 28.5, 29.7, 53.6, 60.2, 60.3, 64.2, 80.1, 95.0, 118.7, 126.8, 128.1, 128.3, 134.6, 137.6, 156.2. Anal. Calcd for $C_{20}H_{30}N_2O_3$: C, 69.33; H, 8.73; N, 8.09. Found: C, 69.12; H, 8.84; N, 7.79.

(3S,4R,5R)-3-Benzylamino-4-(tert-butoxycarbonylamino)-5-hydroxy-4,5-O-isopropylidene-1-hexene (26a). (0.281 g, 78%); oil; $[\alpha]_D$ –14.5 (c 0.68, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.25 (d, 3H, J = 6.3 Hz), 1.27 (s, 3H), 1.48 (s, 3H), 1.50 (s, 9H), 1.80 (bs, 1H, ex. D_2O), 3.50 (m, 1H), 3.62 (d, 1H, J = 13.4 Hz), 3.85 (d, 1H, J = 13.6 Hz), 3.96 (m, 2H), 5.36 (m, 2H), 5.86 (dt, 1H, J = 10.2, 17.4 Hz), 7.29-7.43 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 20.1, 26.7, 27.4, 28.9, 56.7, 61.8, 72.5, 72.8, 80.3, 95.0, 123.1, 127.2, 128.5, 128.8, 134.1, 137.9, 155.6. Anal. Calcd for $C_{21}H_{32}N_2O_3$: C, 69.97; H, 8.95; N, 7.77. Found: C, 69.64; H, 8.84; N, 7.59.

(3S)-3-Benzylamino-3-[(2S)-1-(tert-butoxycarbonylamino)pyrrolidin-2-yl]-1-propene (27a). (0.234g, 74%); oil; $[\alpha]_D$ –45.9 (c 0.36, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.40 (s, 9H), 1.68 (bs, 1H, ex. D_2O), 1.72-189 (m, 4H), 3.15 (m, 1H), 3.35 (dd, 1H, J = 6.3, 7.9 Hz), 3.45 (m, 1H), 3.64 (d, 1H, J = 13.4 Hz), 3.85 (d, 1H, J = 13.4 Hz), 3.94 (m, 1H), 5.11 (dd, 1H, J = 1.7, 17.8 Hz), 5.20 (dd, 1H, J = 1.7, 10.5 Hz), 5.65 (ddd, 1H, J = 7.9, 10.5, 17.8 Hz), 7.24-7.29 (m, 5H); ^{13}C NMR

($CDCl_3$) δ 23.9, 27.1, 28.5, 46.7, 51.2, 60.4, 64.7, 79.5, 118.1, 126.9, 128.2, 128.4, 137.3, 140.0, 154.9. Anal. Calcd for $C_{19}H_{28}N_2O_2$: C, 72.12; H, 8.92; N, 8.85. Found: C, 72.48; H, 8.65; N, 8.73.

(3S)-3-Benzylamino-3-[(2S,4R)-1-(tert-butoxycarbonylamino)-4-(tert-butyldiphenylsiloxy)pyrrolidin-2-yl]-1-propene (28a). (0.508 g, 89%); oil; $[\alpha]_D$ –7.8 (c 0.34, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.04 (s, 9H), 1.43 (s, 9H), 1.78 (m, 1H), 1.96 (ddd, 1H, J = 4.1, 7.9, 13.1 Hz), 2.00 (bs, 1H, ex. D_2O), 3.05 (dd, 1H, J = 4.6, 11.2 Hz), 3.35 (pseudo t, 1H, J = 7.3 Hz), 3.49 (m, 1H), 3.69 (d, 1H, J = 13.9 Hz), 3.9 (m, 1H), 4.21 (d, 1H, J = 13.9 Hz), 4.55 (m, 1H), 5.05 (bd, 1H, J = 17.4 Hz), 5.19 (bd, 1H, J = 10.5 Hz), 5.80 (m, 1H), 7.25-7.30 (m, 5H), 7.32-7.41 (m, 6H), 7.59-7.64 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 19.1, 26.9, 28.4, 37.2, 50.5, 55.2, 59.1, 71.0 (2C), 78.8, 120.1, 127.7 (2C), 127.9, 128.5, 128.6, 129.7, 129.8 (2C), 133.8 (2C), 135.7 (2C), 138.9, 154.0. Anal. Calcd for $C_{35}H_{46}N_2O_3Si$: C, 73.64; H, 8.12; N, 4.91. Found: C, 73.81; H, 8.45; N, 4.73.

(3R,4R)-3-Benzylamino-4-(tert-butoxycarbonylamino)-5-(tert-butyldiphenylsiloxy)-1-pentene (29b). (0.392 g, 72%); oil; $[\alpha]_D$ –7.1 (c 0.25, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.99 (s, 9H), 1.49 (s, 9H), 1.78 (bs, 1H, ex. D_2O), 3.33 (dd, 1H, J = 5.5, 8.2 Hz), 3.55 (d, 1H, J = 13.4 Hz), 3.70 (m, 3H), 3.82 (d, 1H, J = 13.4 Hz), 5.00 (bd, 1H, J = 8.4 Hz), 5.16 (m, 2H), 5.68 (ddd, 1H, J = 8.4, 10.8, 17.3 Hz), 7.30-7.62 (m, 11H), 7.63-7.72 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 19.2, 27.3, 28.4, 51.4, 55.6, 62.5, 64.0, 79.1, 117.8, 126.8, 127.8 (2C), 128.3, 129.7 (2C), 130.0, 133.1, 133.2, 133.6, 135.6, 135.7, 138.0, 155.9. Anal. Calcd for $C_{33}H_{44}N_2O_3Si$: C, 72.75; H, 8.14; N, 5.14. Found: C, 72.90; H, 7.95; N, 5.38.

(3S,4R,5R)-3-Benzylamino-4-(tert-butoxycarbonylamino)-5-(tert-butyldiphenylsiloxy)-1-hexene (30a). (0.391 g, 74%); oil; $[\alpha]_D$ –18.5 (c 0.12, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.96 (s, 9H), 1.16 (d, 3H, J = 6.7 Hz), 1.49 (s, 9H), 1.99 (bs, 1H, ex. D_2O), 3.24 (pseudo t, 1H, J = 8.8 Hz), 3.48 (pseudo t, 1H, J = 9.0 Hz),

3.60 (d, 1H, J = 13.6 Hz), 3.91 (d, 1H, J = 13.6 Hz), 4.11 (dq, 1H, J = 6.7, 9.0 Hz), 4.90 (d, 1H, J = 8.1 Hz), 5.02 (dd, 1H, J = 1.6, 17.4 Hz), 5.13 (dd, 1H, J = 1.6, 10.0 Hz), 5.80 (ddd, 1H, J = 8.8, 10.0, 17.4 Hz), 7.29-7.46 (m, 11H), 7.60-7.81 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 19.6, 23.1, 27.5, 29.4, 58.1, 63.7, 64.9, 70.6, 79.9, 120.5, 126.8, 127.6 (2C), 128.4, 128.9, 129.6 (2C), 132.6, 133.4, 133.8, 136.2, 136.4, 139.3, 156.7. Anal. Calcd for $C_{34}H_{46}N_2O_3Si$: C, 73.08; H, 8.30; N, 5.01. Found: C, 73.27; H, 8.55; N, 5.23.

(4R,5S)-3-Benzyl-5-(*tert*-butyldiphenylsiloxymethyl)-4-vinyl-1,3-oxazolidin-2-one (31a) and (4S,5S)-3-Benzyl-5-(*tert*-butyldiphenylsiloxymethyl)-4-vinyl-1,3-oxazolidin-2-one (31b). A solution of the corresponding diastereomeric allylamine **9** (50 mg, 0.2 mmol) in MeOH (20 mL) was treated with p-TosOH (14.2 mg, 0.1 mmol) and the resulting solution was refluxing until no starting material was observed (TLC, ca. 1 h). The reaction mixture was concentrated and the residue was partitioned between saturated aqueous $NaHCO_3$ (20 mL) and EtOAc (20 mL). The organic layer was separated and the aqueous layer was reextracted with EtOAc (2 x 10 mL). The combined organic extracts were dried ($MgSO_4$), concentrated under reduced pressure and the residue was dissolved in CH_2Cl_2 (15 mL). To the resulting solution $^tBuPh_2SiCl$ (57.6 mg, 0.21 mmol) and DMAP (5 mg, 0.04 mmol) were added and stirring was maintained for 16 h. The reaction mixture was diluted with H_2O (10 mL) and the organic layer separated, dried ($MgSO_4$) and concentrated under reduced pressure. To the residue dissolved in anhydrous THF (10 mL) was added N,N'-carbonyldiimidazole (60 mg, 0.42 mmol) at room temperature. The resulting mixture was stirred for 24 h and concentrated under reduced pressure. Chromatography on silica gel (hexane / EtOAc, 20:80) of the crude product afforded the corresponding oxazolidin-2-one.

(31a): (40 mg, 42%); syrup; $[\alpha]_D$ +43.5 (c 0.14, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.02 (s, 9H), 3.75 (dd, 1H, J = 4.6, 11.5 Hz), 3.80 (dd, 1H, J = 3.6, 11.5 Hz), 3.93

(d, 1H, J = 14.9 Hz), 4.10 (dd, 1H, J = 8.6, 9.1 Hz), 4.52 (ddd, 1H, J = 3.6, 4.6, 8.6 Hz), 4.83 (d, 1H, J = 14.9 Hz), 5.20 (d, 1H, J = 17.1 Hz), 5.35 (d, 1H, J = 10.1 Hz), 5.87 (ddd, 1H, J = 9.1, 10.1, 17.1 Hz), 7.30-7.70 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 19.0, 26.6, 45.8, 59.4, 62.1, 78.9, 121.4. 127.7-127.9 (4C), 128.4, 128.6, 129.8, 131.7, 132.4, 132.8, 134.7, 135.4, 135.6, 157.5. Anal. Calcd for $C_{29}H_{33}NO_3Si$: C, 73.85; H, 7.05; N, 2.97. Found: C, 74.00; H, 7.29; N, 2.72.

(31b): (45 mg, 48%); sticky oil; $[\alpha]_D$ +21.9 (c 0.18, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.95 (s, 9H), 3.62 (dd, 1H, J = 3.4, 11.6 Hz), 3.83 (dd, 1H, J = 3.7, 11.6 Hz), 3.98 (d, 1H, J = 15.0 Hz), 4.03 (dd, 1H, J = 6.9, 8.7 Hz), 4.15 (ddd, 1H, J = 3.4, 3.7, 6.9 Hz), 4.81 (d, 1H, J = 15.0 Hz), 5.14 (d, 1H, J = 17.0 Hz), 5.30 (d, 1H, J = 9.9 Hz), 5.67 (ddd, 1H, J = 8.7, 9.9, 17.0 Hz), 7.28-7.64 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 19.1, 26.7, 45.8, 60.2, 62.1, 77.4, 122.3, 127.7-127.8 (4C), 128.4, 128.6, 129.8, 132.3, 132.5, 132.8, 135.4, 135.6, 135.9, 157.6. Anal. Calcd for $C_{29}H_{33}NO_3Si$: C, 73.85; H, 7.05; N, 2.97. Found: C, 74.11; H, 6.81; N, 3.19.

Acetylation of hydroxylamines. General Procedure. To a stirred solution of the corresponding hydroxylamine (0.5 mmol) in pyridine (1 mL) was added acetic anhydride (0.53 mL, 5.62 mmol). After being stirred for 2 h at room temperature the mixture was diluted with Et_2O (15 mL) and washed with saturated aqueous $CuSO_4$ (3 x 10 mL) and brine (1 x 10 mL). The aqueous layer was reextracted with Et_2O (10 mL) and the combined organic extracts were washed with saturated aqueous $NaHCO_3$ (3 x 10 mL) and brine (1 x 10 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography.

(3S,4S)-3-(N-Benzylacetoxyamino)-4,5-dihydroxy-4,5-O-isopropylidene-1-pentene (32). (hexane-diethyl ether, 60:40); (0.153 g, 100%); sticky oil; $[\alpha]_D$ -22.2 (c 0.21, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.27 (s, 3H), 1.31 (s, 3H), 2.18 (s, 3H), 3.19 (dd, 1H, J = 8.0, 9.2 Hz), 3.86 (d, 1H, J = 13.4 Hz), 3.94 (dd, 1H, J = 5.6, 8.0

Hz), 4.06 (d, 1H, J = 13.4 Hz), 4.09 (dt, 1H, J = 5.6, 8.0 Hz), 4.11 (m, 1H), 5.24 (dd, 1H, J = 1.7, 17.3 Hz), 5.51 (dd, 1H, J = 1.7, 10.3 Hz), 6.00 (ddd, 1H, J = 9.2, 10.3, 17.3 Hz), 7.20-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 19.2, 25.1, 26.6, 60.1, 68.0, 70.9, 75.8, 109.4, 122.4, 127.5, 128.3, 129.3, 131.2, 135.8, 169.4. Anal. Calcd for $C_{17}H_{23}NO_4$: C, 66.86; H, 7.59; N, 4.59. Found: C, 66.63; H, 7.38; N, 4.40.

5-(N-Benzylacetoxyamino)-3-O-benzyl-5-deoxy-5-vinyl-1,2-O-isopropyliden-α-D-gluco-1,4-pentafuranoside (34). (hexane-ethyl acetate, 70:30); (0.227g, 100%); oil; $[\alpha]_D$ +48.1 (c 0.35, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.24 (s, 3H), 1.42 (s, 3H), 1.82 (s, 3H), 3.82 (t, 1H, J=9.3), 3.84 (d, 1H, J=13.0), 4.07 (d, 1H, J=12.9), 4.16 (dd, 1H, J=2.9, 9.3), 4.27 (d, 1H, J=2.9), 4.44 (d, 1H, J=3.8), 4.65 (s, 2H), 5.35 (dd, 1H, J=1.6, 17.3), 5.52 (dd, 1H, J=1.5, 10.3), 5.84 (d, 1H, J=3.7), 6.06 (ddd, 1H, J=7.7, 9.6, 17.4), 7.15-7.37 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 19.1, 26.2, 26.8, 60.5, 66.1, 72.6, 80.0, 82.1, 82.6, 104.9, 111.4, 122.2, 127.5, 127.6, 128.2, 128.3, 129.7, 131.8, 135.7, 138.7, 138.2, 169.1. Anal. Calcd for $C_{26}H_{31}NO_6$: C, 68.48; H, 6.44; N, 3.19. Found: C, 68.27; H, 6.11; N, 3.76.

5-(Acetoxyamino)-N-benzyl-5-deoxy-5-vinyl-2,3-O-isopropyliden-1-O-methyl-α-D-manno-1,4-pentofuranoside (36). (hexane-ethyl acetate, 70:30); (0.189 g, 100%); oil; $[\alpha]_D$ +77.6 (c 0.60, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.28 (s, 3H), 1.29 (s, 3H), 1.87 (s, 3H), 3.27 (s, 3H), 3.79 (t, 1H, J = 8.9 Hz), 3.93-4.01 (m, 2H), 4.12 (d, 1H, J = 12.8 Hz), 4.49 (d, 1H, J = 5.8 Hz), 4.84 (s, 1H), 4.94 (dd, 1H, J = 3.4, 5.6 Hz), 5.32 (m, 2H), 5.99 (ddd, 1H, J = 7.7, 9.8, 17.5 Hz), 7.23-7.42 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 19.3, 25.1, 26.0, 54.6, 60.3, 66.0, 79.4, 80.1, 84.5, 107.4, 112.1, 121.6, 127.5, 128.0, 129.8, 131.8, 135.9, 169.5. Anal. Calcd for $C_{20}H_{27}NO_6$: C, 63.64; H, 7.21; N, 3.71. Found: C, 63.39; H, 6.94; N, 3.87.

Oxidative cleavage of vinyl group. To a vigorously stirred solution of vinyl derivative (0.2 mmol) and $NaIO_4$ (257 mg, 1.20 mmol) in a mixed solvent of CCl_4

(0.7 mL), CH_3CN (0.7 mL) and H_2O (1.2 mmol) at 0°C was added $RuCl_3$ x H_2O (0.8 mg, 4.65μmol) and the resulting mixture was stirred at room temperature for 30 min. After dilution with H_2O (8 mL) the mixture was extracted with EtOAc (3 x 10 mL). The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was taken up in Et_2O (10 mL), cooled to 0°C and treated with an ethereal solution of diazomethane until the yellow colour persisted. Ten drops of AcOH were added and the mixture was washed with aqueous sodium bicarbonate (10 mL) and brine (10 mL). The organic extract was dried ($MgSO_4$) and evaporated under reduced pressure. The crude product was purified by column chromatography.

Methyl (2R,3S)-2-(N-benzylacetoxyamino)-3,4-dihydroxy-3,4-O-isopropylidenebutanoate (33). (hexane-ethyl acetate, 85:15); (49 mg, 73%); oil; $[\alpha]_D$ +4.1 (c 0.18, $CHCl_3$) [Lit.[16] $[\alpha]_D$ +3.9 (c 0.30, $CHCl_3$)]; Anal. Calcd for $C_{17}H_{23}NO_6$: C, 60.52; H, 6.87; N, 4.15. Found: C, 60.77; H, 6.61; N, 4.33. The ^1H and ^{13}C NMR spectra showed to be identical to those described previously in ref. 16.

Methyl 5-(N-benzylacetoxyamino)-3-O-benzyl-5-deoxy-1,2-O-isopropyliden-α-L-ido-hexafuranuronate (35). (hexane-ethyl acetate, 80:20); (79 mg, 81%); oil; $[\alpha]_D$ –26.8 (c 0.19, $CHCl_3$) [Lit.[17] $[\alpha]_D$ –26.2 (c 0.81, $CHCl_3$)]; Anal. Calcd for $C_{26}H_{31}NO_8$: C, 64.32; H, 6.44; N, 2.88. Found: C, 64.57; H, 6.20; N, 2.57. The ^1H and ^{13}C NMR spectra showed to be identical to those described previously in ref. 17.

Methyl 5-(N-benzylacetoxyamino)-5-deoxy-2,3-O-isopropyliden-1-O-methyl-α-L-gulo-hexafuranuronate (37). (hexane-ethyl acetate, 80:20); (64 mg, 78%); oil; $[\alpha]_D$ +18.8 (c 0.20, $CHCl_3$) [Lit.[17] $[\alpha]_D$ +19.7 (c 0.55, $CHCl_3$)]; Anal. Calcd for $C_{20}H_{27}NO_8$: C, 58.67; H, 6.65; N, 3.42. Found: C, 58.41; H, 6.38; N, 3.68. The ^1H and ^{13}C NMR spectra showed to be identical to those described previously in ref. 17.

Methyl (2S,3R)-4-acetoxy-2-(N-benzylacetoxyamino)-3-[(*tert*-butoxycarbonyl)amino]butanoate (38). A solution of **23b** (0.110 g, 0.2 mmol), in anhydrous THF (10 mL) at ambient temperature was treated with 0.22 mL (0.22 mmol) of a 1.0 M solution of Bu_4NF in anhydrous THF. After 1 h the reaction was quenched by the addition of saturated aqueous $NaHCO_3$ and the resulting mixture partitioned between EtOAc (15 mL) and H_2O (10 mL). The layers were separated and the aqueous layer was reextracted with EtOAc (2 x 10 ml). The organic extracts were combined, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was dissolved in pyridine (0.8 mL) and acetic anhydride (0.4 mL, 4.24 mmol) was added. After being stirred for 2 h at room temperature the mixture was diluted with EtOAc (10 mL) and washed with saturated aqueous $CuSO_4$ (3 x 10 mL) and brine (1 x 10 mL). The aqueous layer was reextracted with EtOAc (10 mL) and the combined organic extracts were washed with saturated aqueous $NaHCO_3$ (3 x 10 mL) and brine (1 x 10 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The resulting crude product was oxidized with $RuCl_3$ as described above to afford after purification by column chromatography (hexane-ethyl acetate, 70:30) compound **38** as an oil; (49 mg, 56%); oil; $[\alpha]_D$ –3.0 (c 0.15, $CHCl_3$) [Lit.[13a] $[\alpha]_D$ –3.6 (c 1.00, $CHCl_3$)]; Anal. Calcd for $C_{21}H_{30}N_2O_8$: C, 57.52; H, 6.90; N, 6.39. Found: C, 57.33; H, 7.14; N, 6.02. The ^1H and ^{13}C NMR spectra showed to be identical to those described previously in ref. 13a

(3S,4R,5R)-3-(N-Benzylhydroxyamino)-4-(tert-butoxycarbonylamino)-5-hydroxy-4,5-O-isopropylidene-1-hexene (20a). From 24a. Allyl hydroxylamine **24a** (62 mg, 0.1 mmol) was desilylated as described above to afford a crude product which was dissolved in acetone (10 mL) and treated with 2,2-dimethoxypropane (3 mL) and BF_3 Et_2O (0.1 mL). The resulting mixture was stirred for 2 h and the reaction was quenched by adding Et_3N (0.1 mL). The

solvent was evaporated under reduced pressure and the residue purified by column chromatography (hexane-diethyl ether, 80:20) to afford 28 mg (75%) of **20a**. Their physical and spectroscopic (^{1}H and ^{13}C NMR spectra) properties showed to be identical to those described above for the same compound obtained by direct vinylation of nitrone **18**.

ACKNOWLEDGEMENTS

This work was supported by the Ministerio de Educacion y Ciencia (Project PB97-1014, DGES, Madrid, Spain). V.T. thanks the Direccion General de Enseñanza Superior for a predoctoral fellowship.

REFERENCES AND NOTES

1. For leading references see *inter alia*: (a) Katritzky, A.R.; Piffl, M.; Lang, H. and Anders, E. *Chem. Rev.* **1999**, *99*, 665. (b) Vincent, M.A.; Hillier, I.H.; Hall, R.J. and Thomas, E.J. *J. Org. Chem.* **1999**, *64*, 4680. (c) Hanessian, S.; Margarita, R.; Hall, A. and Luo, X. *Tetrahedron Lett.* **1998**, *39*, 5883. (d) Iseki, K.; Kuroki, Y.; Takahashi, M.; Kishimoto, S. and Kobayashi, Y. *Tetrahedron* , **1997**, *53*, 3513. (e) Almendros, P. and Thomas, E.J. *J. Chem. Soc. Perkin Trans 1* **1997**, 2561. (f) Hanessian, S.; Park, H. and Yang, R.-Y. *Synlett* **1997**, 353. (g) Thomas, E.J. *Chem. Commun.* **1997**, 411. (h) McNeill, A.H. and Thomas, E.J. *Synthesis* **1994**, 322. (i) Yamamoto, Y. and Asao, N. *Chem. Rev.* **1993**, *93*, 2207. (j) Hafner, A.; Duthaler, R.O.; Marti, R.; Rihs, G.; Rothe-Streit, P. and Schwarzenbach, F. *J. Am. Chem. Soc.* **1992**, *114*, 2321. (k) Hoffmann, R.W. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 556.

2. (a) Masuyama Y.; Tosa, J. and Kurusu, Y. *Chem. Commun.* **1999**, 1075. (b) Fang, X.; Johannsen, M.; Yao, S.; Gathergood, N.; Hazell, R.N. and Jorgensen, K.A. *J. Org. Chem.* **1999**, *64*, 4844. (c) Wang, D.-K.; Zhou, Y.-G.; Tang, Y.; Hou, X.-L. and Dai, L.-X. *J. Org. Chem.* **1999**, *64*, 4233. (d) Nakamura, K.; Nakamura, H. and Yamamoto, Y. *J. Org. Chem.* **1999**, *64*,

2614. (e) Chen, G.-M.; Ramachandran, P.V. and Brown, H.C. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 825. (f) Negoro, N.; Yanada, R.; Okaniwa, M.; Yamada, K. and Fujita, T. *Synlett* **1998**, 835. (g) Basile, T.; Bocoum, A.; Savoia, D. and Umani-Ronchi, A. *J. Org. Chem.* **1994**, *59*, 7766. (h) Hallett, D. and Thomas, E.J. *Chem. Commun.* **1995**, 657. (i) Yamamoto, Y.; Nishii, S.; Maruyama, K.; Komatsu, T. and Ito, W. *J. Am. Chem. Soc.* **1986**, *108*, 7778. (j) Yamamoto, Y.; Komatsu, T. and Maruyama, K. *J. Org. Chem.* **1985**, *50*, 3115. (k) Yamamoto, Y.; Ito, W. and Maruyama, K. *Chem. Commun.* **1985**, 1131. (l) Wuts, P.G.M. and Jung, Y.-W. *J. Org. Chem.* **1991**, *56*, 365. (m) Yanagisawa, A.; Ogasawara, K.; Yasue, K. and Yamamoto, H. *Chem. Commun.* **1996**, 367. (n) Wang, D.-K.; Dai, L.-X. and Hou, X.-L. *Tetrahedron Lett.* **1995**, *36*, 8649. (o) Masse, C.E. and Panek, J.S. *Chem. Rev.* **1995**, *95*, 1293. (p) Alvaro, G.; Martelli, G.; Savoia, D. and Zoffoli, A. *Synthesis* **1998**, 1773. (q) Bandini, M.; Cozzi, P.G.; Umani-Ronchi, A. and Villa, M. *Tetrahedron* **1999**, *55*, 8103. See also refs. 1g and 1i.

3. (a) Marco, J.A.; Carda, M.; Murga, J.; Rodriguez, S.; Falomir, E. and Oliva, M. *Tetrahedron: Asymmetry* **1998**, *9*, 1679. (b) Marco, J.A.; Carda, M.; Murga, J.; Gonzalez, F. and Falomir, E. *Tetrahedron Lett.* **1997**, *38*, 1841. (c) Brown, D.S.; Gallagher, P.T.; Lightfoot, A.P.; Moody, C.J.; Slawin, A.M.Z. and Swann, E. *Tetrahedron* **1995**, *51*, 11473.

4. Denmark, S.E.; Weber, T. and Piotrowski, D.W. *J. Am. Chem. Soc.* **1987**, *109*, 2224.

5. (a) Lombardo, M.; Spada, S. and Trombini, C. *Eur. J. Org. Chem.* **1998**, 2361. (b) Gianotti, M.; Lombardo, M. and Trombini, C. *Tetrahedron Lett.* **1998**, *39*, 1643. (c) Fiumana, A.; Lombardo, M. and Trombini, C. *J. Org. Chem.* **1997**, *62*, 5623. (d) Wuts, P.G.M. and Jung, Y.-W. *J. Org. Chem.* **1988**, *53*, 1957. (e) Mancini, F.; Piazza, M.G. and Trombini, C. *J. Org. Chem.*

1991, *56*, 4246. (f) Marco, J.A.; Carda, M.; Murga, J.; Portoles, R.; Falomir, E. and Lex, J. *Tetrahedron Lett.* **1998**, *39*, 3237. (g) Dhavale, D.D.; Gentilucci, L.; Piazza, M.G. and Trombini, C. *Liebigs Ann. Chem.* **1992**, 1289. (h) Merino, P.; Franco, S.; Gascon, J.M.; Merchan, F.L. and Tejero, T. *Tetrahedron: Asymmetry* **1999**, *10*, 1867.

6. "Formation of C-C bonds by Addition to Imino Groups", (several authors) In "Stereoselective Synthesis, Houben-Weyl, Helmchen, G.; Hoffmann, R.W.; Mulzer, J. and Schaumann, E., Eds., Thieme, Stuttgart, 1996; Vol. 3, p 1833 and references cited therein.

7. Imines: (a) Schwardt, O.; Veith, U.; Gaspard, C. and Jager, V. *Synthesis* **1999**, 1473. (b) Cogan, D.A.; Liu, G. and Ellman, J. *Tetrahedron* **1999**, *55*, 8883. (c) Hamon, D.P.G.; Massy-Westropp, R.A. and Razzino, P. *Tetrahedron* **1992**, *48*, 5163. (d) Tomioka, K.; Inoue, I.; Shindo, M. and Koga, K. *Tetrahedron Lett.* **1990**, *31*, 6681. (e) Betz, J. and Heuschmann, M. *Tetrahedron Lett.* **1995**, *36*, 4043. (f) Scialdone, M.A. and Meyers, A.I. *Tetrahedron Lett.* **1994**, *35*, 7533. Hydrazones: (g) Claremon, D.A.; Lumma, P.K. and Phillips, B.T. *J. Am. Chem. Soc.* **1986**, *108*, 8265. Nitrones: (h) Ammenn, J.; Altman, K.-H. and Bellus, D. *Helv. Chim. Acta* **1997**, *80*, 1589. (i) Chang, Z.-Y. and Coates, R.M. *J. Org. Chem.* **1990**, *55*, 3475. See also ref. 5f.

8. For reviews see: (a) Merino, P.; Franco, S.; Merchan, F.L. and Tejero, T. *Synlett* in press. (b) Merino, P. and Tejero, T. *Molecules* **1999**, *4*, 165. (c) Merino, P.; Franco, S.; Merchan, F.L. and Tejero, T. In *Recent Res. Devel. in Synth. Organic Chem.* Pandalai, S.G. (Ed.); Transworld Research Network, Trivandrum, India. **1998**, Vol. 1, pp. 109.

9. For preliminary communications see: (a) Merino, P.; Anoro, S.; Castillo, E.; Merchan, F.L. and Tejero, T. *Tetrahedron: Asymmetry* **1996**, *7*, 1887. (b)

Dondoni, A.; Merchan, F.L.; Merino, P. and Tejero, T. *Synth. Commun.* **1994**, *24*, 2551.

10. For some recent references see: (a) Xu, Q. and Dittmer, D.C. *Tetrahedron Lett.* **1999**, *40*, 2255. (b) Kumar, H.M.S.; Anjaneyulu, S.; Reddy, B.V.S. and Yadav, J.S. *Synlett* **1999**, 551. (c) Chandrasekhar, S. and Mohapatra, S. *Tetrahedron Lett.* **1998**, *39*, 6415. (d) Katritzky, A.R.; Cheng, D. and Li, J. *J. Org. Chem.* **1998**, *63*, 3438. (e) Alcon, M.; Poch, M.; Moyano, A.; Pericas, M.A. and Riera, A. *Tetrahedron: Asymmetry* **1997**, *8*, 2967. (f) Veenstra, S.J. and Schmid, P. *Tetrahedron Lett.* **1997**, *38*, 997. (g) Reginato, G.; Mordini, A:; Messina, F.; Degl'Innocenti, A. and Poli, G. *Tetrahedron* **1996**, *52*, 10985. (h) Enders, D. and Schankat, J. *Helv. Chim. Acta* **1995**, *78*, 970. (i) Palacios, F.; Aparicio, D. and Garcia, J. *Synlett* **1994**, 260. (j) Larock, R.C.; Wang, Y.; Lu, Y. and Russell, C.E. *J. Org. Chem.* **1994**, *59*, 8107. (k) Alcon, M.; Canas, M.; Poch, M.; Moyano, A.; Pericas, M. and Riera, A. *Tetrahedron Lett.* **1994**, *35*, 1589. For a review see: (l) Cheik, R.B.; Chaabouni, R.; Laurent, A.; Mison, P. and Nafti, A. *Synthesis* **1983**, 685.
11. Merino, P.; Castillo, E.; Franco, S.; Merchan, F.L.and Tejero, T. *Tetrahedron* **1998**, *54*, 12301.
12. Wakefield, B.J. "Organolithium Methods", London, Academic Press, 1988, p. 46.
13. Merino, P.; Franco, S.; Merchan, F.L. and Tejero, T. *J. Org. Chem.* **1998**, *63*, 5627.
14. Merino, P.; Lanaspa, A.; Merchan, F.L. and Tejero, T. *J. Org. Chem.* **1996**, *61*, 9028.
15. Murakami, M.; Ito, H. and Ito, Y. *J. Org. Chem.* **1993**, *58*, 6766.
16. Merino, P.; Franco, S.; Merchan, F.L. and Tejero, T. *Tetrahedron: Asymmetry* **1997**, *8*, 3489.

17. Dondoni, A.; Junquera, F.; Merchan, F.L.; Merino, P.; Scherrmann, M.-C. and Tejero, T. *J. Org. Chem.* **1997**, *62*, 5484.

18. Merino, P.; Franco, S.; Gascon, J.M.; Merchan, F.L. and Tejero, T. *Tetrahedron: Asymmetry* **1999**, *10*, 1861.

19. Merino, P.; Merchan, F.L.; Tejero, T. and Lanaspa, A. *Acta Cryst. Sect. C.* **1996**, *52*, 2536.

20. Shriver, D.F.. and Dredzon, M.A. "The Manipulation of Air-Sensitive Compounds", 2nd edition, Wiley-Interscience, New York, 1986.

21. Perrin, D.D. and Armarego, W.L.F. "Purification of Laboratory Chemicals", 3rd edition, Pergamon, Oxford, 1988.

22. Dondoni, A.; Franco, S.; Junquera, F.; Merchan, F.L.; Merino, P.; Tejero, T. *Synth. Commun.* **1994**, *24*, 2537-2550.

Received in the UK 9/30/99