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# Synthesis of 2-Amino glycal Derivatives and their Conversion into Highly Functionalised β-Enamino Ketones

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A general method for the synthesis of 2-amino glycals employing 2-amino sugar derivatives as precursors is described. A new 2-(amino-disubstituted) glycal backbone is obtained independently of the aglycon and nitrogen substituents, the configuration of the C-1, C-2 and C-3 atoms of the starting amino sugar and the oxidative system employed. The reactivity of these new 2-amino glycals with amines has been studied. The reactions were performed with two differently *N*-substituted amino glycals and a variety of alkyl- and arylamines. Highly functionalised β-enamino ketones were obtained by this method.

## Introduction

In the overwhelming majority of cases, carbohydrates found in nature do not occur in a free form but are linked to each other or to other types of compound (aglycones) through glycosidic bonds. Compounds possessing O-, S- or N-glycosidic linkages occur in nature.[1] Glycosidation reactions play a central role in carbohydrate chemistry for several reasons. The rapidly growing interest in the biological roles of glycoconjugates (glycoproteins, glycolipids and proteoglycans)[2] requires homogeneous materials to study. On other hand, carbohydrates, which contain several functional groups and stereogenic centres in one molecular unit, are important as tools in stereochemical differentiation, as starting materials in the synthesis of interesting enantiopure compounds,[3] as chiral templates in asymmetric transformations[4] and as chiral auxiliaries in stereoselective synthesis.[5] In this sense we have used amino sugars as chiral templates in the stereoselective synthesis of diamino sugars,[6] chiral oxazolidines,[7] chiral oxiranes,[8] chiral cyclopropanes[9] and compounds with potential anticancer activity.[10]

Glycal derivatives play an important role in carbohydrate chemistry as precursor compounds in the stereoselective synthesis of O-glycosides,[11] oligosaccharides,[12] *S*-glycosides,[13] 2-deoxynucleosides,[14] C-glycosides,[15] C-nucleosides,[16] glycopeptides[17] and α,β-unsaturated lactones.[18] Different researchers have studied the preparation of glycal and 2-hydroxy glycal derivatives[19] as well as their reactivity in cyclopropanation, epoxidation, hydroboration and halofluorination reactions.[20] 3-Amino glycal derivatives have been used as precursors of glycosidic moieties of antitumour compounds.[21]

However, antecedents for the synthesis of 2-amino glycal derivatives are scarce and tend to be non-general procedures.[22] With regard to the development of suitable methods for the synthesis of a variety of 2-amino glycals, we reported for the first time a good general procedure for the synthesis of 2-[(acyl)(alkyl)amino]-1,5-anhydro-4,6-*O*-(*R*)-benzylidene-2-deoxy-*erythro*-hex-1-en-3-uloses of type **1**[23] by an oxidative reaction of a variety of 2-[(acyl)(alkyl)-amino] and 2-(dialkylamino) sugars. The initial work was aimed at demonstrating the simplicity and effectiveness of the method, which produced good chemical yields without the formation of by-products. Two general procedures for the preparation of 2-amino glycals have since been described: one uses glycosyl sulfoxides (obtained from the corresponding thioglycosides) as substrates for a β-elimination reaction in which 2-substituted glycals (2-hydroxy and 2-amino derivatives) are synthesised[24] and the other employs selenoglycosides as precursors for an oxidation that produces anomeric selenoxides, which, by a spontaneous in situ *syn* elimination, yield the desired 2-substituted (protected 2-hydroxy and 2-amino) glycals.[25] In both cases, these compounds have the general structure **2**, compounds different to ours in which the presence of the carbonyl group at C-3 powers their chemical reactivity and versatility.

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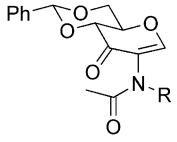

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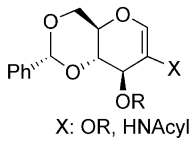
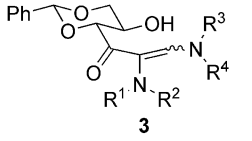



2

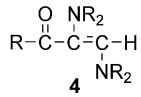
In this article we present our efforts to improve our method, applying it to a variety of 2-[(acyl)(alkyl)amino] and 2-(dialkylamino) sugar precursors to demonstrate its versatility. The 2-amino glycals obtained do not depend on the nature of the aglycon, the substituents on the nitrogen or the configuration of the C-1, C-2 and C-3 atoms of the sugar residue. The 2-[(*N*,*N*-disubstituted)amino]-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-*erythro*-hex-1-en-3-uloses obtained were subjected to a simple reaction with different primary and secondary amines to obtain, in good chemical yields, β-enamino ketones **3** with an additional nitrogenated function at the 2-position [dialkylamino or (acyl)(alkyl)-amino].



3

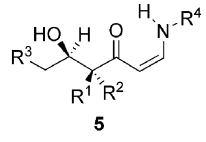
$R^1$: alkyl
$R^2$: acetyl, alkyl
$R^3$: alkyl
$R^4$: H, alkyl

Compounds of this kind, with the general structure of enediamino ketones **4** (R = alkyl, aryl), have been prepared previously by reactions between α-halogenated β-keto acetals and secondary amines.[26] However, we synthesised the enediamino ketones from 2-amino glycals as precursors so that the stereochemistry of the sugar moiety as well as its functionality are present in these compounds.



4

During the preparation of this manuscript, a paper was published describing the Michael addition of amines to hex-1-en-3-uloses (**5**) to give β-enamino ketones diastereoselectively[27]. The subsequent hydrodeamination reaction performed by hydrogenation on a palladium catalyst generated the corresponding 1,2-dideoxy-D-*threo*-3-hexulose derivatives, which can be used as precursors for the synthesis of a β-mannosidase inhibitor.

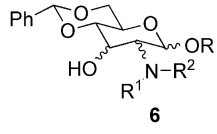


5

$R^1$: H, OBn
$R^2$: OBn, H
$R^3$: OBn
$R^4$: alkyl

## Results and Discussion

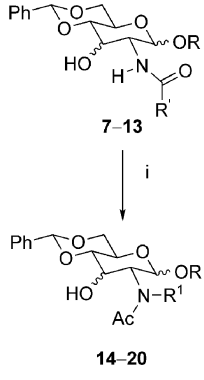
As the general method for obtaining the new 2-amino glycals involves the oxidation of *N*,*N*-disubstituted 2-amino sugar derivatives **6**, first we describe the preparation of the precursors that will be subjected to this oxidation reaction. We distinguish two different simple synthetic routes that are widely used in monosaccharide chemistry and furnish good chemical yields. The aim was to prepare a range of structurally related 2-amino sugar precursors that differ in the nature of both the aglycon and the substituents on the nitrogen at C-2 and in the configuration of C-1, C-2 and C-3 (α or β anomers, *gluco*, *allo* or *altro* configurations) for subjection to two different oxidative reactions.



6

$R^1$: alkyl
$R^2$: acetyl, alkyl

The *gluco* and *allo* compounds **14**–**20** (Scheme 1) were obtained from the corresponding alkyl 2-(acylamino)-4,6-*O*-(*R*)-benzylidene-2-deoxy-D-hexopyranosides **7**–**13** by reaction with $LiAlH_4$, yielding substrates with different substituents on the nitrogen at the 2-position of the sugar. Subsequent acetylation followed by treatment with sodium methoxide in methanol yielded the first group of compounds [an (acyl)(alkyl)amino group at the 2-position of the sugar and OH at the 3-position], which were used to obtain the new 2-amino glycals.



7–13

i



14–20

**7** R = Bn, R′ =Ph, α-*gluco*
**8** R = Bn, R′ =Ph, β-*gluco*
**9** R = Bn, R′ = Me, α-*gluco*
**10** R = Bn, R′ = Me, β-*gluco*
**11** R = Bn, R′ = Me, β-*allo*
**12** R = Bn, R′ = H, α-*gluco*
**13** R = *n*$C_{12}H_{25}$, R′ = Me, β-*gluco*

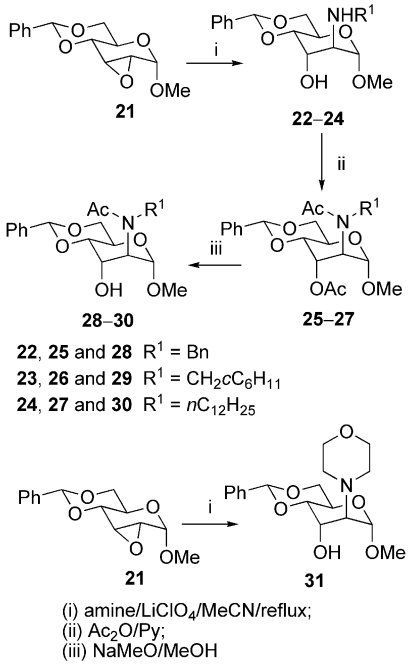
**14** R = Bn, $R^1$ = Bn, α-*gluco*
**15** R = Bn, $R^1$ = Bn, β-*gluco*
**16** R = Bn, $R^1$ = Et, α-*gluco*
**17** R = Bn, $R^1$ = Et, β-*gluco*
**18** R = Bn, $R^1$ = Et, β-*allo*
**19** R = Bn, $R^1$ = Me, α-*gluco*
**20** R = *n*$C_{12}H_{25}$, $R^1$ = Et, β-*gluco*

Scheme 1. Reagents and conditions: (i) 1. $LiAlH_4$, THF, reflux; 2. $Ac_2O$, Py; 3. MeONa, MeOH, 63–76%.

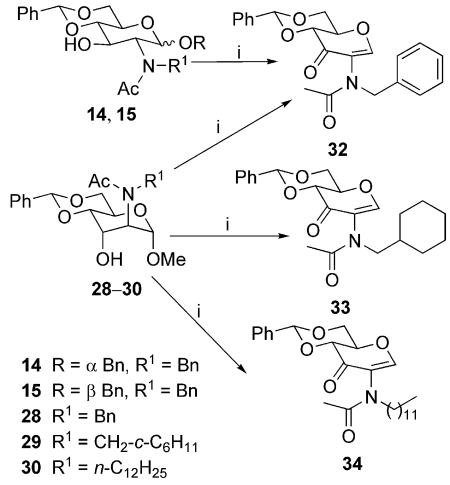
Compounds with the general structure **6** with an *altro* configuration were obtained regio- and stereoselectively (NMR spectroscopic data) from the corresponding methyl 2,3-anhydro-4,6-*O*-(*R*)-benzylidene-α-D-allopyranoside (**21**) by an oxirane ring-opening reaction with various primary and secondary amines.[28] By using a primary amine, the products **22**–**24** were obtained. These were acetylated to give **25**–**27** and subsequent treatment with sodium methoxide yielded the products **28**–**30**. Ring-opening of the oxirane **21** with a secondary amine gave compound **31** directly, which was subsequently subjected to oxidation (Scheme 2).

The *N*,*N*-disubstituted amino sugars synthesised were subjected to two different oxidative reactions. Compounds **14**, **15** and **28**–**30** were oxidised with PCC to give the products **32**–**34** in good yields and without the formation of by-products (Scheme 3).




Scheme 2. Reagents and conditions: (i) amine, $LiClO_4$, MeCN, reflux, 89–96%; (ii) $Ac_2O$, Py, 79–86%; (iii) MeONa, MeOH, 72–90%.

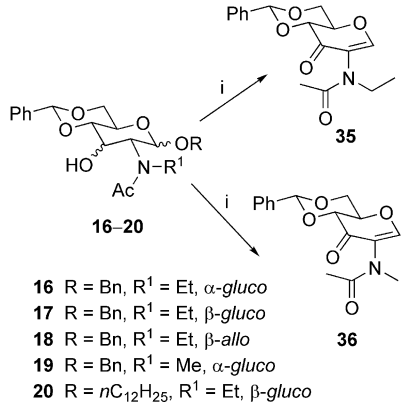



Scheme 3. Reagents and conditions: (i) PCC, molecular sieves (3 Å), $CH_2Cl_2$, 67–87%.

Compounds **14**, **15** (benzyl α- and β-D-glucopyranoside derivatives) and **28** (methyl α-D-altropyranoside derivative), with the same substituents on the nitrogen atom, were oxidised by using the PCC/DCM system (Scheme 3) to give the product **32** in similar yields of 80, 84 and 84%, respectively.

The substrates **29** and **30** (methyl α-D-altropyranoside derivatives) were oxidised efficiently to give the products **33** and **34**, which have a similar general structure to **32** but with different alkyl groups on the nitrogen atom (cyclohexylmethyl and dodecyl, respectively), in yields of 67 and 87%, respectively (Scheme 3).

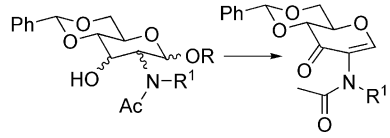
Oxidation of compounds **16**–**20** by this method gave low yields because of the usual work-up conditions (low solubility of the reaction product in diethyl ether), therefore we subjected these compounds to oxidation by the second oxidative system. Thus, compounds **16**–**20** were oxidised efficiently with the DMSO/DCC system to give compounds **35** and **36** (Scheme 4).




Scheme 4. Reagents and conditions: (i) DMSO, molecular sieves (3 Å), DCC, 75–86%.

The oxidation of **16** and **17** (benzyl α- and β-D-glucopyranoside derivatives), **18** (benzyl β-D-allopyranoside derivative) and **20** (dodecyl β-D-glucopyranoside derivative), all with the same substitution on the nitrogen atom, by this procedure yielded compound **35** in yields of 75, 77, 77 and 80%, respectively. Finally, compound **19**, which possesses a different alkyl group on the nitrogen atom, was oxidised by this method and compound **36** was obtained in a yield of 86% (Scheme 4).

The two oxidation reactions yielded the same type of product, 2-[(acyl)(alkyl)amino]-1,5-anhydro-4,6-*O*-(*R*)-benzylidene-2-deoxy-*erythro*-hex-1-en-3-ulose with a different *N*-alkyl group in 2-position of the sugar precursor. Both reactions took place by oxidation at the 3-position to give a keto function and elimination of the alkoxide at the anomeric position.



To verify the generality of this method for the synthesis of 2-amino glycals and the independence of the oxidative system used, we also oxidised compounds **14**, **15** and **28** by using the second oxidative procedure (DMSO/DCC) and compound **32** was again obtained in good yields of 88, 91 and 90%, respectively.

The results of these oxidation reactions for the different compounds studied (Table 1) indicate that the preparation of the 2-amino glycal derivatives is independent of the nature of the aglycon and nitrogen substituents and the configuration at C-1, C-2 and C-3 of the starting material and reveal the general character of the procedure.

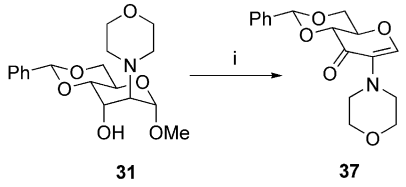
  

Table 1. Yields of the products from the oxidation of the (acyl)-(alkyl)amino sugar derivatives.

| Entry | SM[a] | Configuration[b] | Oxidative system[c] | Product | Yield [%] |
|---|---|---|---|---|---|
| 1 | **14** | benzyl α-*gluco* | A | **32** | 80 |
| 2 | **15** | benzyl β-*gluco* | A | **32** | 84 |
| 3 | **28** | methyl α-*altro* | A | **32** | 84 |
| 4 | **14** | benzyl α-*gluco* | B | **32** | 88 |
| 5 | **15** | benzyl β-*gluco* | B | **32** | 91 |
| 6 | **28** | methyl α-*altro* | B | **32** | 90 |
| 7 | **29** | methyl α-*altro* | A | **33** | 67 |
| 8 | **30** | methyl α-*altro* | A | **34** | 87 |
| 9 | **16** | benzyl α-*gluco* | B | **35** | 75 |
| 10 | **17** | benzyl β-*gluco* | B | **35** | 77 |
| 11 | **18** | benzyl β-*allo* | B | **35** | 77 |
| 12 | **20** | dodecyl β-*gluco* | B | **35** | 80 |
| 13 | **19** | benzyl α-*gluco* | B | **36** | 86 |

[a] Starting material. [b] Configuration of the sugar moiety. [c] Oxidative system employed: (A) $PCC/CH_2Cl_2$; (B) DMSO/DCC.

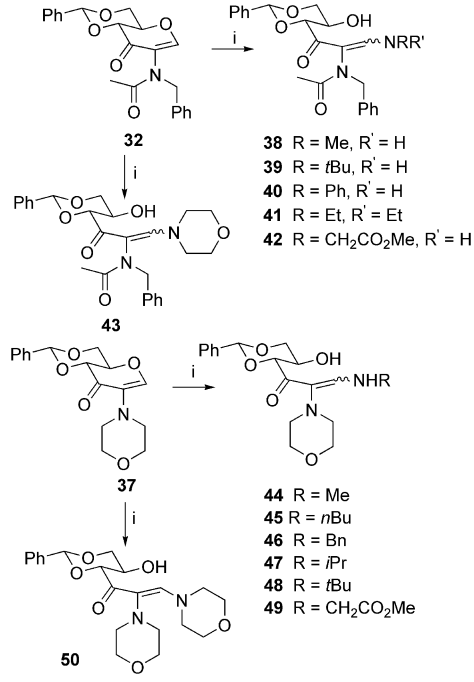
Oxidation of compound **31** with the second oxidising system (DMSO/DCC) gave 2-(dialkylamino)-1,5-anhydro-4,6-*O*-(*R*)-benzylidene-2-deoxy-*erythro*-hex-1-en-3-ulose (**37**) in good yield (Scheme 5).




Scheme 5. Reagents and conditions: (i) DMSO, molecular sieves (3 Å), DCC, 72%.

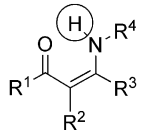
The $^1H$ NMR spectra of the *N*,*N*-disubstituted 2-amino-1,5-anhydro-4,6-*O*-(*R*)-benzylidene-2-deoxy-*erythro*-hex-1-en-3-uloses **32**–**37** exhibit the signal from the proton at the 1-position of the sugar at around 7.0–8.0 ppm. The $^{13}C$ NMR spectra exhibit the signal due to C-2 at around 120 ppm and the signal arising from C-1 at around 160 ppm.

Having obtained the new 2-amino glycals, the next step was to study their reactivity towards amines. As substrates for the reactions with amines, two types of precursor were chosen: 2-(acetyl-benzylamino)-1,5-anhydro-4,6-*O*-(*R*)-benzylidene-2-deoxy-D-*erythro*-hex-1-en-3-ulose (**32**) and 1,5-anhydro-4,6-*O*-(*R*)-benzylidene-2-deoxy-2-morpholino-D-*erythro*-hex-1-en-3-ulose (**37**). Both compounds reacted with several primary and secondary amines to give the β-enamino ketones **38**–**43** and **44**–**50**, respectively (Scheme 6). The reactions were clean, smooth and fast (20 min from **32** and 2 h from **37**) and they appeared to occur by nucleophilic addition at C-1 concomitant with pyranose ring-opening with no intermediary products being detected.[27]




Scheme 6. Reagents and conditions: (i) amine, EtOH, r.t., 61–80%.

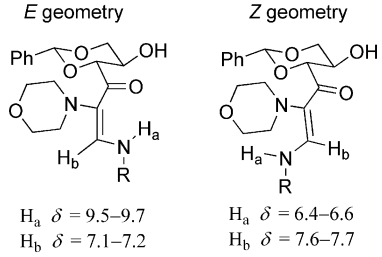
To determine the configurations of compounds **38**–**50** we analysed their NMR spectra. It has previously been reported that the NMR spectra of β-enamino ketones exhibit NH signals in the low-field region, which suggests strong hydrogen-bonding between the amino group and the carbonyl oxygen atom and that they have a *cis* structure.[29] In relation to the configurations of the compounds obtained from the reactions between glycals and amines, another group recently postulated the formation of an intramolecular hydrogen bond between the hydrogen atom of the added amine and the carbonyl at the 3-position of the β-enamino ketone finally obtained to explain the postulated geometry.[27] The signal arising from the amino proton at C-1 appears at higher chemical shifts ($\delta \approx 10$ ppm).




In our case, compounds **44**–**49** (with a morpholino group at the 2-position) were obtained as a mixture of diastereoisomers with the diastereoselectivity favouring the *Z* configuration (*Z*/*E* ratio between 2.1–3.5). All the minor stereoisomers exhibit the signal arising from the NH at the 1-position at around $\delta$ = 9.5–9.7 ppm (COSY experiments), which has been attributed to an intramolecular hydrogen bond as previously mentioned, and a doublet resonance for the alkene proton at C-1 at $\delta$ = 7.1–7.2 ppm. Thus, we tentatively assigned the *E* configuration to these minor stereoisomers. However, for the major stereoisomers, the signal from NH at the 1-position appears at lower chemical shifts ($\delta$ = 6.4–6.6 ppm, COSY experiments) and the signal from

the alkene proton at the 1-position is at $\delta$ = 7.6–7.7 ppm. For these stereoisomers, therefore, the *Z* configuration was tentatively assigned.




To prove this assignment we performed two-dimensional NMR experiments. The NOESY spectrum of compound **44** shows, for the minor stereoisomer, a correlation between the alkene proton at the 1-position and the protons of both $CH_2$ groups next to the nitrogen in the morpholine ring. This allowed us to confirm its *E* configuration. However, this correlation is not present in the major stereoisomer, in accord with a *Z* configuration (Figure 1). These data are in agreement with the results of the NMR studies described above.

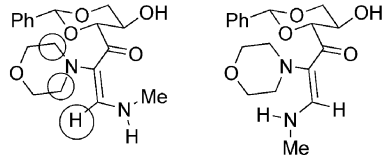



Figure 1. *E*/*Z* configurations for compound **44** showing the correlations observed by NOESY experiments for the *E* configuration.

For compound **50** only one stereoisomer was obtained. The chemical shifts and profiles of the signals of the protons and carbon atoms of this compound are analogous to those of the major isomers of compounds **44**–**49**. Thus, in the same way, the *Z* configuration was tentatively assigned. See Tables 2 and 3 for the $^1H$ and $^{13}C$ NMR chemical shifts of compounds **44**–**50**.

Table 2. $^1H$ NMR spectroscopic data for the characteristic protons in compounds **44**–**50**.[a]

| Entry | Cp | $\delta$ [ppm] | | | |
|---|---|---|---|---|---|
| | | N–H (M)/(m) | 1-H (M)/(m) | 4-H (M)/(m) | PhCH (M)/(m) |
| 1 | **44** | 6.58/9.56 | 7.55/7.11 | 4.38/4.87 | 5.60/5.53 |
| 2 | **45** | 6.67/9.78 | 7.58/7.16 | 4.36/4.87 | 5.61/5.53 |
| 3 | **46** | 6.87/9.99 | 7.62/7.06 | 4.30/4.82 | 5.51/5.45 |
| 4 | **47** | 6.41/9.73 | 7.56/7.14 | 4.30/4.80 | 5.55/5.45 |
| 5 | **48** | 6.38/10.0 | 7.73/7.31 | 4.41/4.91 | 5.67/5.56 |
| 6 | **49** | 6.67/9.58 | 7.55/7.09 | 4.36/4.89 | 5.58/5.54 |
| 7 | **50**[b] | – | 7.24 | 4.41 | 5.62 |

[a] (M) for the major and (m) for the minor stereoisomer. [b] One stereoisomer observed.

Based on these results we believe that for these substrates there is a preference for the *Z* geometry. The proportion of the *E* geometry is increased when the amine added can form an intramolecular hydrogen bridge with the carbonyl oxygen at the 3-position (primary amines; **44**–**49**) and even more so when the amine added has a bulky group (*i*Pr and *t*Bu; compounds **47** and **48**, Table 4, entries 7 and 8, respectively).

Table 3. $^{13}C$ NMR spectroscopic data for the characteristic carbons in compounds **44**–**50**.[a]

| Entry | Cp | $\delta$ [ppm] | | | | |
|---|---|---|---|---|---|---|
| | | C-3 (M)/(m) | C-4 (M)/(m) | C-5 (M)/(m) | C-6 (M)/(m) | PhCH (M)/(m) |
| 1 | **44** | 186.4/ 191.1 | 79.9/ 78.5 | 61.2/ 60.2 | 70.5/ 70.6 | 99.7/ 99.9 |
| 2 | **45** | 186.7/ 191.4 | 80.2/ 78.5 | 61.2/ 60.2 | 70.5/ 70.7 | 99.7/ 100.0 |
| 3 | **46** | 187.8/ 192.8 | 81.0/ 79.5 | 61.9/ 61.2 | 71.4/ 71.6 | 100.6/ 100.9 |
| 4 | **47** | 189.7/ 192.3 | 81.3/ 79.4 | 62.3/ 61.2 | 71.4/ 71.6 | 100.6/ 100.9 |
| 5 | **48** | 187.9/ 192.2 | 81.9/ 79.5 | 62.5/ 61.2 | 71.6/ 71.4 | 100.6/ 100.9 |
| 6 | **49** | 187.4/ 192.4 | 79.9/ 78.5 | 61.0/ 60.2 | 70.5/ 70.6 | 99.7/ 100.0 |
| 7 | **50**[b] | 189.9 | 80.2 | 61.2 | 70.4 | 99.7 |

[a] (M) for the major and (m) for the minor stereoisomer. [b] One stereoisomer observed.

Table 4. *Z*/*E* ratio for compounds **38**–**42** and **44**–**50**.[a]

| Entry | Compound | *Z*/*E* ratio |
|---|---|---|
| 1 | **38** | 13.3/1 |
| 2 | **39** | 9.5/1 |
| 3 | **42** | 11.5/1 |
| 4 | **44** | 3.1:1 |
| 5 | **45** | 2.7:1 |
| 6 | **46** | 3.0:1 |
| 7 | **47** | 2.2:1 |
| 8 | **48** | 2.1:1 |
| 9 | **49** | 3.5:1 |
| 10 | **50**[b] | 1.0:0 |

[a] The ratio was determined by direct $^1H$ NMR examination of the diastereoisomeric mixture. [b] Tentative assignment.

A similar $^1H$ NMR analysis was performed on compounds **38**–**43**, obtained from the reactions between compound **32** and different amines. In all cases we observed double signals despite recording the spectra at 110 °C. We think that this is because we have not reached a high enough temperature for the signals to collapse to single ones and so the spectra still show a mixture of conformers. Indeed, both signals have very similar chemical shifts (see Table 5); in fact, the differences in the chemical shifts are smaller than the differences observed for the diastereoisomeric mixtures obtained from product **37** with different amines.

Because the $^1H$ NMR spectra recorded at 110 °C present unresolved signals due to being close to the coalescence temperature, the NMR spectroscopic data presented are those recorded at 90 °C in [$D_6$]DMSO with a similar signal pattern.

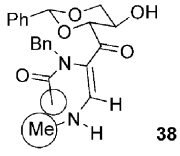
A further two-dimensional NMR analysis was performed on compound **38**, by way of ROESY experiments. A correlation between the methyl group of the amine at

Table 5. $^1$H NMR spectroscopic data for the characteristic protons in compounds **38**–**43**.

| Entry | Cp | δ [ppm] | | | |
|---|---|---|---|---|---|
| | | N–H | 1-H | 4-H | PhCH |
| 1 | **38** | 6.51 | 7.61/7.64 | 4.42 | 5.58/5.59 |
| 2 | **39** | 6.01 | 7.71/7.74 | 4.42/4.46 | 5.64/5.65 |
| 3 | **40** | 8.66 | 8.14/8.19 | 4.61/4.66 | 5.69/5.71 |
| 4 | **41** | – | 7.53/7.57 | 4.51/4.52 | 5.63/5.65 |
| 5 | **42** | 6.86 | 7.69/7.72 | 4.41 | 5.55/5.56 |
| 6 | **43** | – | 7.55/7.57 | 4.85/4.88 | 5.64/5.65 |

C-1 and the methyl of the acetamide function at C-2 was observed. The *Z* configuration was assigned to this compound (Figure 2).




**38**

Figure 2. Correlation detected for compound **38** by ROESY experiments.

Also, for compounds **38**, **39** and **42**, the small signal observed at 9–10 ppm was attributed to NH, which forms an intramolecular hydrogen bond with the carbonyl group at the 3-position[27,29] and, as we previously explained, this is in accord with the presence of the *E* stereoisomer. The diastereoisomeric excesses (determined by direct $^1$H NMR examination of the two NH signals at 6–7 and 10 ppm) are 86, 81 and 84%, respectively.

According to these results and based on the fact that the chemical shifts and profiles of the signals of the protons and carbon atoms of these compounds are analogous to those of the major isomer in compounds **44**–**49**, the *Z* configuration was also tentatively assigned to the major stereoisomer of compounds **38**–**43**.

## Conclusions

In this work we have presented an effective, simple and general method for obtaining 2-amino glycals from *N*,*N*-disubstituted 2-amino sugars. We have demonstrated that obtaining these new 2-amino glycal derivatives does not depend on the nature of the aglycon or the substituents on the nitrogen atom, the configuration of C-1, C-2 and C-3 of the carbohydrate precursors, or the oxidative procedure employed. Thus, a range of differently substituted glycals has been obtained.

Given the importance of glycals as synthetic intermediaries of diverse biologically active compounds, in this work we have begun the study of the reactivity of new glycals obtained with different amines. The reactions took place cleanly to give new β-enamino ketones (with an additional amine function). We carried out these reactions with two different glycal precursors (with an amide or amine function at the 2-position of the glycal) and with different primary and secondary alkyl- or arylamines. In all cases, the reactions gave high yields. This methodology is an effective way of obtaining new β-enamino ketones that have a potentially modifiable chemical structure.

Based on the NMR studies of these compounds with an amide function at the 2-position, the β-enamino ketones were obtained in high diastereoisomeric excesses with the major stereoisomer assigned the *Z* configuration.

The products in which the nitrogen at the 2-position of the glycal (the nitrogenated function borne on the amino sugar precursor) forms part of a morpholine ring were obtained as a mixture of *Z*/*E* diastereoisomers. The proportion of the *Z* stereoisomer is slightly higher and was the only product obtained in the reaction of this glycal with morpholine as the nucleophilic amine.

Given that we have just described the synthesis of glycals and their reactions with different amines using methods that are simple and, above all, general, our next aim is to determine the relationship between the substituents on both the nitrogen atom at the 2-position of the glycal precursor and the amine added and the diastereoselectivity of the addition reaction. Further studies on this topic are in progress.

## Experimental Section

**General Methods:** All chemicals were purchased and used without further purification. Evaporations were conducted under reduced pressure. Preparative chromatography was performed on silica gel 60 (E. Merck). Kieselgel 60 $F_{254}$ (E. Merck) was used for TLC. Optical rotations were determined with a Bellingham + Stanley P-20 polarimeter at 25 °C. Mass spectra were recorded with a Micromass AUTOSPECQ mass spectrometer at 70 eV for EI and at 150 eV for CI; HRMS measurements were made with resolutions of 10000. FAB mass spectra were recorded by using a thioglycerol matrix. NMR spectra were recorded with a Bruker AC-200 spectrometer at 200 MHz for $^1$H NMR and 50 MHz for $^{13}$C NMR and with a Bruker AV500 spectrometer at 500 MHz for $^1$H NMR and 125 MHz for $^{13}$C NMR. The chemical shifts are reported in ppm on the δ scale relative to TMS. DEPT, COSY, HSQC, NOESY and ROESY experiments were performed to assign the NMR signals and the configurations of the products from the reactions of the glycals with amines.

**Synthesis of Alkyl 2-(Acetyl-alkylamino)-4,6-*O*-(*R*)-benzylidene-2-deoxy-D-hexopyranosides 14–20:** A solution of alkyl 2-acylamino-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (**7**–**13**; 10.0 mmol) in distilled and dry THF (200 mL) was stirred under argon at reflux. A 1 M solution of $LiAlH_4$ in THF (15 mmol) was added and the reaction mixture was stirred at reflux overnight and then left to cool to room temperature. A saturated aqueous sodium sulfate solution (4.5 mL) was added dropwise. The solid was removed by filtration and washed with anhydrous THF. The filtrate was concentrated to dryness to give a solid, which was recrystallised from 96% ethanol. These compounds were characterised by mass and NMR analyses and used in the following reactions.

A solution of alkyl 2-(alkylamino)-4,6-*O*-(*R*)-benzylidene-2-deoxy-D-hexopyranoside (10.0 mmol) was acetylated in the usual way with acetic anhydride in pyridine (1:1; 20 mL). The reaction mixture was kept for 2 d at room temperature and then poured into ice/water and the precipitate obtained was isolated by filtration. The solid was dissolved in methanol (50 mL) and a solution of sodium methoxide (1.0 mmol) in methanol (10 mL) was added. After 30 min at

room temperature, the mixture was neutralised by the addition of Dowex 50 resin ($H^+$ form), filtered and the solvents evaporated to dryness. The compound obtained was purified by recrystallisation from 96% ethanol or by column chromatography.

**Benzyl 2-(Acetyl-benzylamino)-4,6-*O*-(*R*)-benzylidene-2-deoxy-α-D-glucopyranoside (14):** Yield 3.6 g (75%); m.p. 70–71 °C. $[\alpha]_D$ = +103.0 (*c* = 1.2, $CH_2Cl_2$). $^1H$ NMR (200 MHz, [D$_6$]DMSO, 100 °C): $\delta$ = 1.98 (s, 3 H, $CH_3$), 5.07 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1-H), 5.60 (s, 1 H, PhC*H*), 7.0–7.5 (m, 15 H, 3 Ph) ppm. $^{13}C$ NMR (50 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 22.3, 22.4 ($CH_3$), 45.9, 48.1 (N*C*H$_2$Ph), 57.4 (C-2), 62.2, 62.9 (C-5), 65.4, 65.6 (C-3), 67.9 (C-6), 68.8, 69.2 (O*C*H$_2$Ph), 82.3, 82.6 (C-4), 97.9, 98.6 (C-1), 100.7, 100.8 (Ph*C*H), 125.7–139.9 (3 Ph), 171.7, 172.5 (C=O) ppm. MS (CI): *m*/*z* (%) = 490 (100) $[M]^{+\cdot}$. HRMS (CI): calcd. For $C_{29}H_{32}NO_6$ [M + H]$^+$ 490.222963; found 490.222753. $C_{29}H_{31}NO_6$ (489.56): calcd. C 71.15, H 6.38, N 2.86; found C 70.98, H 6.12, N 2.81.

**Benzyl 2-(Acetyl-benzylamino)-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (15):** Yield 3.5 g (72%); m.p. 64–65 °C. $[\alpha]_D$ = –68.6 (*c* = 1.8, $CH_2Cl_2$). $^1H$ NMR (200 MHz, [D$_6$]DMSO, 110 °C): $\delta$ = 2.05 (s, 3 H, $CH_3$), 4.63 (d, $J_{1,2}$ = 8.3 Hz, 1 H, 1-H), 5.59 (s, 1 H, PhC*H*), 7.1–7.5 (m, 15 H, 3 Ph) ppm. $^{13}C$ NMR (50 MHz, [D$_6$]-DMSO, 25 °C): $\delta$ = 22.3 ($CH_3$), 44.3 (N*C*H$_2$Ph), 65.1, 65.2 (C-2, C-5), 67.7 (C-3), 67.9 (C-6), 70.0 (O*C*H$_2$Ph), 81.4 (C-4), 99.3 (C-1), 100.7 (Ph*C*H), 126.2–139.5 (3 Ph), 171.7 (C=O) ppm. MS (CI): *m*/*z* (%) = 490 (100) $[M]^{+\cdot}$. HRMS (CI): calcd. for $C_{29}H_{32}NO_6$ [M + H]$^+$ 490.222963; found 490.222427. $C_{29}H_{31}NO_6$ (489.56): calcd. C 71.15, H 6.38, N 2.86; found C 71.37, H 6.35, N 3.00.

**Benzyl 2-(Acetyl-ethylamino)-4,6-*O*-(*R*)-benzylidene-2-deoxy-α-D-glucopyranoside (16):** Yield 3.2 g (76%); m.p. 67–68 °C. $[\alpha]_D$ = +124.3 (*c* = 1.6, $CH_2Cl_2$). $^1H$ NMR (200 MHz, [D$_6$]DMSO, 100 °C): $\delta$ = 0.98, 1.12 (2 t, *J* = 7.0, 6.8 Hz, 3 H, NCH$_2$C*H*$_3$), 2.02, 2.04 (2 s, 3 H, $CH_3$CON), 4.4–4.7 (m, 3 H, OC*H*$_2$Ph, 6$_e$-H), 4.78, 5.09 (2 d, $J_{1,2}$ = 3.3, 3.6 Hz, 1-H), 5.41, 5.51 (2 d, $J_{3,OH}$ = 6.1, 5.9 Hz, OH), 5.63 (s, 1 H, PhC*H*), 7.5–7.2 (m, 10 H, 2 Ph) ppm. $^{13}C$ NMR (50 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 13.7, 15.1 (NCH$_2$*C*H$_3$), 21.5, 22.3 (*C*H$_3$CON), 37.7, 39.5 (N*C*H$_2$CH$_3$), 57.4, 62.1 (C-2), 62.7 (C-5), 65.4, 65.8 (C-3), 67.9 (C-6), 68.9, 69.1 (O*C*H$_2$Ph), 82.4, 82.8 (C-4), 97.4, 98.8 (C-1), 100.9 (Ph*C*H), 126.4–137.7 (2 Ph), 170.6, 171.2 (C=O) ppm. MS (CI): *m*/*z* (%) = 428 (100) [M + H]$^+$. $C_{24}H_{29}NO_6$ (427.49): calcd. C 67.43, H 6.84, N 3.28; found C 67.66, H 6.85, N 3.17.

**Benzyl 2-(Acetyl-ethylamino)-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (17):** Yield 2.9 g (70%); m.p. 60–61 °C. $[\alpha]_D$ = –74.3 (*c* = 1.2, $CH_2Cl_2$). $^1H$ NMR (200 MHz, [D$_6$]DMSO, 100 °C): $\delta$ = 1.09 (t, *J* = 7.0 Hz, 3 H, NCH$_2$C*H*$_3$), 1.99 (s, 3 H, $CH_3$CON), 3.2–3.6 (m, 6 H, 2-H, 3-H, 4-H, 5-H, NC*H*$_2$CH$_3$), 3.75 (t, $J_{5,6a}$ = $J_{6e,6a}$ = 10.0 Hz, 1 H, 6$_a$-H), 4.2–4.3 (m, 2 H, 1-H, 6$_e$-H), 4.55 (d, $J_{gem}$ = 12.1 Hz, OC$H_A$H$_B$Ph), 4.78 (d, $J_{gem}$ = 12.1 Hz, OCH$_A$$H_B$Ph), 5.59 (s, 1 H, PhC*H*), 7.2–7.5 (m, 10 H, 2 Ph) ppm. $^{13}C$ NMR (50 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 13.9 (NCH$_2$*C*H$_3$), 22.2 (*C*H$_3$CON), 36.2 (N*C*H$_2$CH$_3$), 64.9, 65.2 (C-2, C-5), 67.8 (C-3), 67.9 (C-6), 70.3 (O*C*H$_2$Ph), 81.6, 81.9 (C-4), 99.2 (C-1), 100.7 (Ph*C*H), 126.3–137.8 (2 Ph), 170.6 (C=O) ppm. MS (CI): *m*/*z* (%) = 428 (100) [M + H]$^+$. $C_{24}H_{29}NO_6$ (427.49): calcd. C 67.43, H 6.84, N 3.28; found C 67.68, H 6.84, N 3.14.

**Benzyl 2-(Acetyl-ethylamino)-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-allopyranoside (18):** Yield 2.8 g (67%); m.p. 59–60 °C. $[\alpha]_D$ = –44.1 (*c* = 1.0, $CH_2Cl_2$). MS (CI): *m*/*z* (%) = 428 (100) [M + H]$^+$. $^1H$ NMR (200 MHz, [D$_6$]DMSO, 100 °C): $\delta$ = 1.12 (t, *J* = 7.0 Hz, 3 H, NCH$_2$C*H*$_3$), 2.03 (s, 3 H, $CH_3$CON), 3.45 (m, 2 H, NC*H*$_2$CH$_3$), 3.7–3.8 (m, 2 H, 4-H, 6$_a$-H), 4.03 (dt, $J_{4,5}$ = $J_{5,6a}$ = 9.8, $J_{5,6e}$ = 5.0 Hz, 5-H), 4.2–4.3 (m, 3 H, 2-H, 3-H, 6$_e$-H), 4.59 (d, $J_{gem}$ = 12.0 Hz, OC$H_A$H$_B$Ph), 4.80 (d, $J_{gem}$ = 12.0 Hz, OCH$_A$$H_B$Ph), 5.27 (d, $J_{3,OH}$ = 8.0 Hz, OH), 4.75 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1-H), 5.64 (s, 1 H, PhC*H*), 7.2–7.5 (m, 10 H, 2 Ph) ppm. $^{13}C$ NMR (50 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 13.9, 15.2 (NCH$_2$*C*H$_3$), 21.3, 22.4 (*C*H$_3$CON), 38.4 (N*C*H$_2$CH$_3$), 60.5 (C-2), 63.0, 63.1 (C-5), 68.3 (C-6), 68.9, 69.8 (C-3), 70.0 (O*C*H$_2$Ph), 78.8, 78.9 (C-4), 97.3, 97.4 (C-1), 100.5, 100.6 (Ph*C*H), 126.0–137.7 (2 Ph), 170.2, 171.0 (C=O) ppm. $C_{24}H_{29}NO_6$ (427.49): calcd. C 67.43, H 6.84, N 3.28; found C 67.32, H 6.90, N 3.25.

**Benzyl 2-(Acetyl-methylamino)-4,6-*O*-(*R*)-benzylidene-2-deoxy-α-D-glucopyranoside (19):** Yield 3.1 g (76%); m.p. 89–91 °C. $[\alpha]_D$ = +111.8 (*c* = 1.2, $CH_2Cl_2$). $^1H$ NMR (200 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 1.99, 2.04 (2 s, 3 H, $CH_3$CON), 2.83, 2.97 (2 s, 3 H, NCH$_3$), 4.3–4.7 (m, 3 H, OC*H*$_2$Ph, 6$_e$-H), 4.80, 5.11 (2 d, $J_{1,2}$ = 3.3, 3.5 Hz, 1-H), 5.42, 5.52 (2 d, $J_{3,OH}$ = 6.3, 5.9 Hz, OH), 5.63 (s, 1 H, PhC*H*), 7.3–7.5 (m, 10 H, 2 Ph) ppm. $^{13}C$ NMR (50 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 21.8, 22.2 (*C*H$_3$CON), 28.8, 32.0 (NCH$_3$), 56.9, 61.5 (C-2), 62.9, 63.1 (C-5), 65.0, 65.5 (C-3), 67.9 (C-6), 68.7, 69.0 (O*C*H$_2$Ph), 81.9, 82.3 (C-4), 97.7, 98.9 (C-1), 100.8 (Ph*C*H), 126.4–137.7 (2 Ph), 170.5, 171.0 (C=O) ppm. MS (CI): *m*/*z* (%) = 414 (50) [M + H]$^+$. HRMS (CI): calcd. for $C_{23}H_{28}NO_6$ [M + H]$^+$ 414.191663; found 414.189950. $C_{23}H_{27}NO_6$ (413.46): calcd. C 66.81, H 6.58, N 3.39; found C 66.66, H 6.85, N 3.17.

**1-Dodecyl 2-(Acetyl-ethylamino)-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (20):** Yield 3.1 g (63%). $^1H$ NMR (200 MHz, [D$_6$]DMSO, 90 °C): $\delta$ = 0.88 (t, *J* = 6.7 Hz, 3 H, $CH_3$), 1.12 (m, 3 H, NCH$_2$C*H*$_3$), 1.3–1.6 [m, 20 H, (CH$_2$)$_{10}$], 2.01 (s, 3 H, $CH_3$CON), 4.69 (d, $J_{1,2}$ = 8.2 Hz, 1 H, 1-H), 5.58 (s, 1 H, PhC*H*), 7.3–7.5 (m, 5 H, Ph) ppm. $^{13}C$ NMR (50 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 13.8, 14.0 (2 $CH_3$), 22.1 (*C*H$_3$CON), 22.2–29.0 [(CH$_2$)$_{10}$], 36.2 (N*C*H$_2$CH$_3$), 64.9, 65.1 (C-2, C-5), 67.8 (C-3), 67.9 (C-6), 68.9 (O*C*H$_2$Ph), 81.7, 82.0 (C-4), 99.7 (C-1), 100.7 (Ph*C*H), 126.3–137.7 (Ph), 170.6 (C=O) ppm. MS (CI): *m*/*z* (%) = 506 (100) [M + H]$^+$. HRMS (CI): calcd. for $C_{29}H_{48}NO_6$ [M + H]$^+$ 506.348164; found 506.347411.

**Synthesis of Methyl 2-(Alkylamino)-4,6-*O*-(*R*)-benzylidene-2-deoxy-α-D-altropyranosides 22–24, 31:** A solution of the oxirane (10 mmol) and $LiClO_4$ (20 mmol) in MeCN (40 mL) was heated whilst stirring at 90 °C and the corresponding amine (40 mmol) was added. The mixture was stirred until completion of the reaction (TLC). It was then left to cool to room temperature and poured into ice/water with stirring. In most cases, the precipitate obtained was filtered off and crystallised from EtOH or EtOH/water. In some cases, when the reaction mixture was soluble in ice/water, the aqueous solution was extracted with $CH_2C1_2$ and the combined extracts were washed with water. The organic phase was dried ($Na_2SO_4$) and evaporated in vacuo to dryness. The solid obtained was crystallised or fractionated by chromatography on a silica gel column.

**Methyl 2-(Benzylamino)-4,6-*O*-(*R*)-benzylidene-2-deoxy-α-D-altropyranoside (22):** Yield 3.5 g (95%); m.p. 164–165 °C. $[\alpha]_D$ = +43.0 (*c* = 0.7, $CH_2Cl_2$). $^1H$ NMR (200 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 2.75 (d, $J_{2,3}$ = 2.0 Hz, 1 H, 2-H), 3.36 (s, 3 H, $OCH_3$), 3.65–3.75 (m, 3 H, NC*H*$_2$Ph, 6$_a$-H), 3.9–4.1 (m, 3 H, 3-H, 4-H, 5-H), 4.20 (dd, $J_{5,6e}$ = 4.8, $J_{6a,6e}$ = 9.7 Hz, 1 H, 6$_e$-H), 4.50 (d, $J_{3,OH}$ = 5.0 Hz, OH), 4.59 (s, 1 H, 1-H), 5.64 (s, 1 H, PhC*H*), 7.2–7.5 (m, 10 H, 2 Ph) ppm. $^{13}C$ NMR (50 MHz, [D$_6$]DMSO, 25 °C) $\delta$ = 51.3 (N*C*H$_2$Ph), 51.3 ($OCH_3$), 57.7 (C-5), 60.7 (C-2), 66.9 (C-3), 68.5 (C-6), 76.4 (C-4), 100.5 (C-1), 101.1 (Ph*C*H), 126.4–140.6 (2 Ph) ppm. MS (CI): *m*/*z* (%) = 372 (100) [M + H]$^+$. $C_{21}H_{25}NO_5$

(371.43): calcd. C 67.91, H 6.78, N 3.77; found C 67.66, H 6.93, N 3.53.

**Methyl 4,6-*O*-(*R*)-Benzylidene-2-[(cyclohexylmethyl)amino]-2-deoxy-α-D-altropyranoside (23):** Yield 3.5 g (96%); m.p. 123–125 °C. $[a]_D$ = +36.9 (*c* = 1.7, $CH_2Cl_2$). $^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.8–1.8 (m, 11 H, *c*-$C_6H_{11}$), 2.49 (m, 2 H, NC$H_2$R), 2.97 (d, $J_{2,3}$ = 2.4 Hz, 1 H, 2-H), 3.41 (s, 3 H, $OCH_3$), 3.7–3.9 (m, 2 H, 4-H, $6_a$-H), 4.1–4.4 (m, 3 H, 3-H, 5-H, $6_e$-H), 4.61 (s, 1 H, 1-H), 5.61 (s, 1 H, PhC*H*), 7.5–7.3 (m, 5 H, Ph) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$, 25 °C) δ = 25.9–31.3 [$(CH_2)_5$], 38.0 (CH), 55.3 (N$CH_2$R), 55.5 ($OCH_3$), 58.4 (C-5), 60.9 (C-2), 68.5 (C-3), 69.2 (C-6), 76.9 (C-4), 101.5 (C-1), 102.2 (Ph*C*H), 126.2–137.3 (Ph) ppm. MS (CI): *m*/*z* (%) = 378 (85) $[M + H]^+$. HRMS (EI): calcd. for $C_{21}H_{31}NO_5$ $[M]^{+\cdot}$ 377.220223; found 377.219005. $C_{21}H_{31}NO_5$ (377.47): calcd. C 66.82, H 8.28, N 3.71; found C 66.84, H 8.23, N 3.75.

**Methyl 4,6-*O*-(*R*)-Benzylidene-2-deoxy-2-(1-dodecylamino)-α-D-altropyranoside (24):** Yield 4.2 g (95%); m.p. 136–138 °C. $[a]_D$ = +42.3 (*c* = 2.1, $CH_2Cl_2$). $^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.86 (t, *J* = 6.9 Hz, 3 H, $CH_3$), 1.2–1.6 [m, 20 H $(CH_2)_{10}$], 2.65 (t, 2 H, NC$H_2$R), 3.00 (d, $J_{2,3}$ = 2.8 Hz, 1 H, 2-H), 3.41 (s, 3 H, $OCH_3$), 3.7–3.9 (m, 2 H, 4-H, $6_a$-H), 4.07 (t, $J_{2,3}$ = $J_{3,4}$ = 2.8 Hz, 1 H, 3-H), 4.15 (m, 1 H, 5-H), 4.30 (m, 1 H, $6_e$-H), 4.61 (s, 1 H, 1-H), 5.60 (s, 1 H, PhC*H*), 7.3–7.5 (m, 5 H, Ph) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$, 25 °C): δ = 14.1 ($CH_3$), 22.7–31.9 [$(CH_2)_{10}$], 48.6 (N$CH_2$R), 55.6 ($OCH_3$), 58.5 (C-2), 60.7 (C-5), 68.5 (C-3), 69.2 (C-6), 76.8 (C-4), 101.4 (C-1), 102.3 (Ph*C*H), 126.2–137.3 (Ph) ppm. MS (CI): *m*/*z* (%) = 450 (100) $[M + H]^+$. HRMS (EI): calcd. for $C_{26}H_{43}NO_5$ $[M]^{+\cdot}$ 449.314124; found 449.312115. $C_{26}H_{43}NO_5$ (449.62): calcd. C 69.45, H 9.64, N 3.12; found C 69.44, H 9.37, N 2.93.

**Methyl 4,6-*O*-(*R*)-Benzylidene-2-deoxy-2-morpholino-α-D-altropyranoside (31):** Yield 3.1 g (89%); m.p. 118–119 °C. $[a]_D$ = +71.7 (*c* = 1.3, $CH_2Cl_2$). $^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 2.65 (m, 4 H, $CH_2NCH_2$), 2.78 (d, $J_{2,3}$ = 2.3 Hz, 1 H, 2-H), 3.14 (d, $J_{3,OH}$ = 6.7 Hz, 1 H, OH), 3.40 (s, 3 H, $OCH_3$), 3.68 (t, *J* = 4.6 Hz, 4 H, $CH_2OCH_2$), 3.78 (t, $J_{5,6a}$ = $J_{6a,6e}$ = 10.0 Hz, 1 H, $6_a$-H), 3.91 (dd, $J_{3,4}$ = 3.1, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H), 4.1–4.2 (m, 2 H, 3-H, 5-H), 4.31 (dd, $J_{5,6e}$ = 5.0, $J_{6a,6e}$ = 10.0 Hz, 1 H, $6_e$-H), 4.82 (s, 1 H, 1-H), 5.63 (s, 1 H, PhC*H*), 7.3–7.5 (m, 5 H, Ph) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$, 25 °C): δ = 51.2 ($CH_2NCH_2$), 55.5 ($OCH_3$), 57.9 (C-2), 66.0 (C-5), 67.0 (C-3), 67.3 ($CH_2OCH_2$), 69.3 (C-6), 77.4 (C-4), 100.0 (C-1), 102.2 (Ph*C*H), 126.2–137.2 (Ph) ppm. MS (CI): *m*/*z* (%) = 352 (100) $[M + H]^+$. $C_{18}H_{25}NO_6$ (351.39): calcd. C 61.52, H 7.17, N 3.99; found C 61.73, H 7.05, N 3.86.

**Synthesis of Methyl 3-*O*-Acetyl-2-(acetyl-alkylamino)-4,6-*O*-(*R*)-benzylidene-2-deoxy-α-D-altropyranoside (25–27):** A solution of methyl 2-alkylamino-4,6-*O*-(*R*)-benzylidene-2-deoxy-α-D-altropyranoside (**22**–**24**; 10.0 mmol) was acetylated in the usual way with acetic anhydride/pyridine (1:1; 40 mL). The reaction mixture was kept for 2 d at room temperature and then poured into ice/water. The precipitate obtained was isolated by filtration. The solid obtained was purified by chromatography on a silica gel column.

**Methyl 3-*O*-Acetyl-2-(acetyl-benzylamino)-4,6-*O*-(*R*)-benzylidene-2-deoxy-α-D-altropyranoside (25):** Yield 3.9 g (86%); m.p. 183–185 °C. $[a]_D$ = +33.4 (*c* = 1.6, $CH_2Cl_2$). $^1H$ NMR (200 MHz, [$D_6$]-DMSO, 80 °C): δ = 1.95, 2.12 (2 s, 6 H, 2 $CH_3CO$), 3.29 (m, 3 H, $OCH_3$), 3.69 (t, $J_{5,6a}$ = $J_{6a,6e}$ = 9.9 Hz, 1 H, $6_a$-H), 3.95–4.05 (m, 2 H, 4-H, 5-H), 4.2–4.3 (m, 2 H, 2-H, $6_e$-H), 4.75 (s, 2 H, NC$H_2$Ph), 4.81 (d, $J_{1,2}$ = 2.7 Hz, 1 H, 1-H), 5.30 (t, $J_{2,3}$ = $J_{3,4}$ = 2.8 Hz, 1 H, 3-H), 5.48 (s, 1 H, PhC*H*), 7.2–7.4 (m, 10 H, 2 Ph) ppm. $^{13}C$ NMR (50 MHz, [$D_6$]DMSO, 25 °C): δ = 20.7, 21.8, 22.0 (2 *C*$H_3$CO), 45.8, 50.0 (N*C*$H_2$Ph), 55.0 ($OCH_3$), 57.9, 58.4, 60.0 (C-2, C-5), 68.3 (C-6), 67.7, 69.1 (C-3), 73.0, 73.8 (C-4), 98.4 (C-1), 100.8 (Ph*C*H), 125.8–138.5 (2 Ph), 169.0, 169.9, 171.3 (2C=O) ppm. MS (CI): *m*/*z* (%) = 456 (100) $[M + H]^+$. $C_{25}H_{29}NO_7$ (455.50): calcd. C 65.92, H 6.42, N 3.08; found C 66.18, H 6.68, N 2.90.

**Methyl 3-*O*-Acetyl-2-[acetyl(methylcyclohexyl)amino]-4,6-*O*-(*R*)-benzylidene--2-deoxy-α-D-altropyranoside (26):** Yield 3.6 g (79%); m.p. 152–154 °C. $[a]_D$ = +28.2 (*c* = 1.7, $CH_2Cl_2$). $^1H$ NMR (200 MHz, [$D_6$]DMSO, 80 °C): δ = 0.9–1.8 (m, 11 H, *c*-$C_6H_{11}$), 2.03, 2.05 (2 s, 6 H, 2 $CH_3CO$), 3.15 (m, 2 H, NC$H_2$R), 3.33 (s, 3 H, $OCH_3$), 3.54 (dd, $J_{1,2}$ = 4.5, $J_{2,3}$ = 3.5 Hz, 1 H, 2-H), 3.73 (t, $J_{5,6a}$ = $J_{6a,6e}$ = 10.0 Hz, 1 H, $6_a$-H), 3.98 (dt, $J_{4,5}$ = $J_{5,6a}$ = 10.0, $J_{5,6e}$ = 5.0 Hz, 1 H, 5-H), 4.7–4.9 (m, 2 H, 4-H, $6_e$-H), 4.92 (d, $J_{1,2}$ = 4.7 Hz, 1 H, 1-H), 5.47 (dd, $J_{2,3}$ = 3.6, $J_{3,4}$ = 4.5 Hz, 1 H, 3-H), 5.65 (s, 1 H, PhC*H*), 7.3–7.4 (m, 5 H, Ph) ppm. $^{13}C$ NMR (50 MHz, [$D_6$]DMSO, 25 °C): δ = 20.7, 22.3 (2 *C*$H_3$CO), 25.7–30.2 [$(CH_2)_5$], 37.0 (CH), 55.4 ($OCH_3$), 56.7 (N*C*$H_2$R), 60.0 (C-5), 63.5 (C-2), 68.8 (C-6), 69.0 (C-3), 73.5 (C-4), 98.3 (C-1), 100.1 (Ph*C*H), 126.0–137.7 (Ph) ppm. MS (CI): *m*/*z* (%) = 462 (100) $[M + H]^+$. HRMS (EI): calcd. for $C_{25}H_{35}NO_7$ $[M]^{+\cdot}$ 461.241353; found 461.239426. $C_{25}H_{35}NO_7$ (461.55): calcd. C 65.06, H 7.64, N 3.03; found C 65.30, H 7.41, N 3.07.

**Methyl 3-*O*-Acetyl-2-[acetyl(1-dodecyl)amino]-4,6-*O*-(*R*)-benzylidene-2-deoxy-α-D-altropyranoside (27):** Yield 4.5 g (84%); m.p. 103–105 °C. $[a]_D$ = +48.0 (*c* = 0.5, $CH_2Cl_2$). $^1H$ NMR (200 MHz, [$D_6$]DMSO, 100 °C): δ = 0.86 (t, *J* = 7.0 Hz, 3 H, $CH_3$), 1.2–1.7 [m, 20 H $(CH_2)_{10}$], 2.03, 2.08 (2 s, 6 H, 2 $CH_3CO$), 3.2–3.5 (m, 5 H, NC$H_2$R, $OCH_3$), 3.74 (t, $J_{5,6a}$ = $J_{6a,6e}$ = 9.9 Hz, 1 H, $6_a$-H, 3.93 (t, $J_{1,2}$ = $J_{2,3}$ = 3.3 Hz, 1 H, 2-H), 4.04 (dt, $J_{4,5}$ = $J_{5,6a}$ = 9.7, $J_{5,6e}$ = 4.8 Hz, 1 H, 5-H), 4.17 (dd, $J_{3,4}$ = 4.4, $J_{4,5}$ = 9.8 Hz, 1 H, 4-H), 4.29 (dd, $J_{5,6e}$ = 4.8, $J_{6a,6e}$ = 9.9 Hz, 1 H, $6_e$-H), 4.83 (d, $J_{1,2}$ = 3.3 Hz, 1 H, 1-H), 5.32 (dd, $J_{2,3}$ = 3.4, $J_{3,4}$ = 4.3 Hz, 1 H, 3-H), 5.66 (s, 1 H, PhC*H*), 7.3–7.4 (m, 5 H, Ph) ppm. $^{13}C$ NMR (50 MHz, [$D_6$]DMSO, 25 °C): δ = 13.9 ($CH_3$), 20.7, 21.6 (2 *C*$H_3$CO), 22.1–31.2 [$(CH_2)_{10}$], 43.0, 47.8 (N*C*$H_2$R), 54.9 ($OCH_3$), 58.5, 58.7 (C-5), 59.3, 59.9 (C-2), 68.5 (C-6), 68.3, 69.4 (C-3), 73.1, 73.8 (C-4), 98.8 (C-1), 100.9 (Ph*C*H), 126.0–137.6 (Ph), 169.2, 170.4 (2 C=O) ppm. MS (CI): *m*/*z* (%) = 534 (100) $[M + H]^+$. $C_{30}H_{47}NO_7$ (533.70): calcd. C 67.51, H 8.88, N 2.62; found C 67.60, H 9.00, N 2.34.

**Synthesis of Methyl 2-(Acetyl-alkylamino)-4,6-*O*-(*R*)-benzylidene-2-deoxy-α-D-altropyranosides 28–30:** A solution of sodium methoxide (1.0 mmol) in methanol (10 mL) was added to a solution of methyl 3-*O*-acetyl-2-(acetyl-alkylamino)-4,6-*O*-(*R*)-benzylidene-2-deoxy-α-D-altropyranoside (**25**–**27**; 10.0 mmol) in methanol (50 mL). After 50 min at room temperature the mixture was neutralised by addition of Dowex 50 resin ($H^+$ form), filtered and the solvents evaporated to dryness. The compound obtained was purified by chromatography on a silica gel column.

**Methyl 2-(Acetyl-benzylamino)-4,6-*O*-(*R*)-benzylidene-2-deoxy-α-D-altropyranoside (28):** Yield 3.4 g (83%); m.p. 188–190 °C. $[a]_D$ = +48.3 (*c* = 1.2, $CH_2Cl_2$). $^1H$ NMR (200 MHz, [$D_6$]DMSO, 110 °C): δ = 2.09 (s, 3 H, $CH_3CON$), 3.22 (m, 3 H, $OCH_3$), 3.66 (t, $J_{5,6a}$ = $J_{6a,6e}$ = 9.9 Hz, 1 H, $6_a$-H), 3.75 (dd, $J_{3,4}$ = 3.7, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H), 3.98 (t, $J_{2,3}$ = $J_{3,4}$ = 3.6 Hz, 1 H, 3-H), 4.07 (m, 1 H, 5-H), 4.23 (m, 1 H, $6_e$-H), 4.35 (t, $J_{1,2}$ = $J_{2,3}$ = 3.5 Hz, 1 H, 2-H), 4.71 (d, $J_{1,2}$ = 3.3 Hz, 1 H, 1-H), 4.80 (m, 2 H, NC$H_2$Ph), 5.47 (s, 1 H, PhC*H*), 7.2–7.5 (m, 10 H, 2 Ph) ppm. $^{13}C$ NMR (50 MHz, [$D_6$]-DMSO, 25 °C): δ = 22.0 (*C*$H_3$CON), 45.9, 49.0 (N*C*$H_2$Ph), 54.6 ($OCH_3$), 57.4 (C-5), 59.1, 63.0 (C-2), 66.8, 68.1 (C-3), 68.4 (C-6), 75.7, 76.5 (C-4), 98.6, 98.8 (C-1), 100.9 (Ph*C*H), 125.3–139.4 (2 Ph), 170.9, 171.1 (C=O) ppm. MS (CI): *m*/*z* (%) = 414 (100) [M +

H]$^+$. $C_{23}H_{27}NO_6$ (413.46): calcd. C 66.81, H 6.58, N 3.39; found C 66.61, H 6.53, N 3.47.

**Methyl 2-[Acetyl(cyclohexylmethyl)amino]-4,6-*O*-(*R*)-benzylidene-2-deoxy-α-D-altropyranoside (29):** Yield 3.8 g (90%); m.p. 54–56 °C. $[\alpha]_D$ = +57.2 ($c$ = 0.7, $CH_2Cl_2$). $^1$H NMR (200 MHz, [D$_6$]DMSO, 80 °C): $\delta$ = 0.8–1.9 (m, 11 H, $c$-$C_6H_{11}$), 2.08 (s, 3 H, $CH_3CON$), 3.2–3.5 (m, 5 H, NC$H_2$R, $OCH_3$), 3.5–3.8 (m, 2 H, 3-H, 6$_a$-H), 4.0–4.2 (m, 2 H, 4-H, 5-H), 4.30 (m, 1 H, 6$_e$-H), 4.50 (br. s, 1 H, 2-H), 4.86 (d, $J_{1,2}$ = 3.3 Hz, 1 H, 1-H), 5.67 (s, 1 H, PhC$H$), 7.3–7.6 (m, 5 H, Ph) ppm. $^{13}$C NMR (50 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 22.4 ($CH_3$CON), 25.7–30.7 [$(CH_2)_5$], 36.7, 37.0 (CH), 54.8, 55.3 ($OCH_3$), 49.1, 56.4 (N$CH_2$R), 57.6, 59.1 (C-5), 63.4, 66.3 (C-2), 67.8, 68.3 (C-3), 68.6, 69.0 (C-6), 76.1 (C-4), 98.6, 99.4 (C-1), 100.6, 100.9 (Ph$CH$), 126.5–137.9 (Ph), 170.5, 171.2 (C=O) ppm. MS (CI): $m/z$ (%) = 420 (100) [M + H]$^+$. HRMS (EI): calcd. for $C_{23}H_{33}NO_6$ [M]$^{+\cdot}$ 419.230788; found 419.229786. $C_{23}H_{33}NO_6$ (419.51): calcd. C 65.85, H 7.93, N 3.34; found C 65.54, H 7.77, N 3.29.

**Methyl 2-[Acetyl(1-dodecyl)amino]-4,6-*O*-(*R*)-benzylidene-2-deoxy-2-*N*-α-D-altropyranoside (30):** Yield 3.5 g (72%); m.p. 77–79 °C. $[\alpha]_D$ = +232.9 ($c$ = 2.2, $CH_2Cl_2$). $^1$H NMR (200 MHz, [D$_6$]DMSO, 100 °C): $\delta$ = 0.86 (t, $J$ = 7.0 Hz, 3 H, $CH_3$), 1.2–1.7 [m, 20 H, $(CH_2)_{10}$], 2.07 (s, 3 H, $CH_3CON$), 3.2–3.5 (m, 5 H, NC$H_2$R, $OCH_3$), 3.71 (t, $J_{5,6a}$ = $J_{6a,6e}$ = 9.9 Hz, 1 H, 6$_a$-H), 4.27 (dd, $J_{5,6e}$ = 4.9, $J_{6a,6e}$ = 10.0 Hz, 1 H, 6$_e$-H), 4.78 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1-H), 5.68 (s, 1 H, PhC$H$), 7.3–7.5 (m, 5 H, Ph) ppm. $^{13}$C NMR (50 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 13.9 ($CH_3$), 21.6, 22.0 ($CH_3$CON), 22.2–31.2 [$(CH_2)_{10}$], 43.3, 47.0 (N$CH_2$R), 54.7 ($OCH_3$), 57.3, 57.6 (C-5), 60.9, 63.2 (C-2), 67.3, 68.4 (C-3), 68.7 (C-6), 76.1, 76.6 (C-4), 99.2 (C-1), 100.9 (Ph$CH$), 126.4–137.7 (Ph), 170.0 (C=O) ppm. MS (CI): $m/z$ (%) = 492 (100) [M + H]$^+$. HRMS (CI): calcd. for $C_{28}H_{46}NO_6$ [M + H]$^+$ 492.332514; found 492.333125. $C_{28}H_{45}NO_6$ (491.66): calcd. C 68.40, H 9.23, N 2.85; found C 68.39, H 9.10, N 2.64.

### Oxidation Reactions

**Procedure A:** Pyridinium chlorochromate (4 mmol) and molecular sieves (3 Å, 10 g) were added to a solution of 2-[(acyl)(alkyl)amino] sugar derivatives **14**, **15** and **28**–**30** (2.0 mmol) in dry dichloromethane (40 mL). The reaction mixture was stirred vigorously overnight at room temperature. After completion of the reaction (TLC), diethyl ether was added and the mixture was filtered through a glass filter filled with silica gel containing $CaSO_4$ (10%). Removal of the solvent by evaporation in vacuo gave a pure compound.

**2-*N*-Acetyl-2-amino-1,5-anhydro-2-*N*-benzyl-4,6-*O*-(*R*)-benzylidene-2-deoxy-D-*erythro*-hex-1-en-3-ulose (32):** Yield 0.61 g (80%) from compound **14**, 0.64 g (84%) from compound **15** and 0.64 g (84%) from compound **28**; m.p. 78–80 °C. $[\alpha]_D$ = +109.0 ($c$ = 0.6, $CH_2Cl_2$). $^1$H NMR (500 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 1.85, 1.98 (2 s, 3 H, $CH_3CON$), 3.90, 4.00 (2 d, $J_{gem}$ = 14.6, 14.5 Hz, 1 H, NC$H_A$H$_B$Ph), 4.06 (m, 1 H, 6$_a$-H), 4.41 (m, 1 H, 6$_e$-H), 4.68 (m, 1 H, 5-H), 4.77, 4.94 (2 d, $J_{4,5}$ = 13.1, 12.7 Hz, 1 H, 4-H), 5.06, 5.11 (2 d, $J_{gem}$ = 14.7, 14.4 Hz, 1 H, NCH$_A$$H_B$Ph), 5.69, 5.71 (2 s, 1 H, PhC$H$), 7.3–7.5 (m, 10 H, 2 Ph), 7.59, 7.62 (2 s, 1 H, 1-H) ppm. When the spectrum was recorded at 110 °C, all the double signals collapsed to single signals. $^{13}$C NMR (50 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 20.7, 20.9 ($CH_3$CON), 48.6, 50.4, (N$CH_2$Ph), 65.9 (C-6), 71.9 (C-5), 75.1 (C-4), 99.8, 100.0 (Ph$CH$), 120.1, 120.5 (C-2), 126.6–136.9 (2 Ph), 161.9, 162.3 (C-1), 169.9, 170.4 ($CH_3$CON), 184.8, 185.1 (C-3) ppm. MS (CI): $m/z$ (%) = 380 (100) [M + H]$^+$. $C_{22}H_{21}NO_5$ (379.41): calcd. C 69.65, H 5.58, N 3.69; found C 69.43, H 5.76, N 3.74.

**2-[Acetyl(cyclohexylmethyl)amino]-1,5-anhydro-4,6-*O*-(*R*)-benzylidene-2-deoxy-D-*erythro*-hex-1-en-3-ulose (33):** Yield 0.51 g (67%); m.p. 72–74 °C. $[\alpha]_D$ = +125.1 ($c$ = 0.3, $CH_2Cl_2$). $^1$H NMR (200 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 0.8–1.7 (m, 11 H, $c$-$C_6H_{11}$), 1.76, 1.88 (2 s, 3 H, $CH_3CON$), 2.7–3.6 (4 m, 2 H, NC$H_2$R), 4.10, 4.11 (2 t, $J_{5,6a}$ = $J_{6a,6e}$ = 10.1 Hz, 1 H, 6$_a$-H), 4.46 (dd, $J_{5,6e}$ = 5.1, $J_{6a,6e}$ = 10.2 Hz, 1 H, 6$_e$-H), 4.69 (m, 1 H, 5-H), 4.94, 4.97 (2 d, $J_{4,5}$ = 13.0 Hz, 1 H, 4-H), 5.72, 5.73 (2 s, 1 H, PhC$H$), 7.3–7.5 (m, 5 H, Ph), 7.96, 8.00 (2 s, 1 H, 1-H) ppm. When the spectrum was recorded at 90 °C all the double signals collapsed to single signals. $^{13}$C NMR (50 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 21.6, 21.8 ($CH_3$CON), 25.3–30.2 [$(CH_2)_5$], 35.7 (CH), 51.8, 53.5 (N$CH_2$R), 66.7 (C-6), 72.5, 72.6 (C-5), 75.8 (C-4), 100.6, 100.7 (Ph$CH$), 121.6, 122.1 (C-2), 126.3–136.8 (Ph), 162.6, 163.2 (C-1), 170.6, 171.1 ($CH_3$CON), 185.8, 186.0 (C-3) ppm. MS (CI): $m/z$ (%) = 386 (100) [M + H]$^+$. HRMS (EI): calcd. for $C_{22}H_{27}NO_5$ [M]$^{+\cdot}$ 385.188923; found 385.188494. $C_{22}H_{27}NO_5$ (385.45): calcd. C 68.55, H 7.06, N 3.63; found C 68.51, H 7.23, N 3.50.

**2-[Acetyl(1-dodecyl)amino]-1,5-anhydro-4,6-*O*-(*R*)-benzylidene-2-deoxy-D-*erythro*-hex-1-en-3-ulose (34):** Syrup, yield 0.80 g (87%). $^1$H NMR (500 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 0.84 (t, $J$ = 6.9 Hz, 3 H, $CH_3$), 1.1–1.4 [m, 20 H, $(CH_2)_{10}$], 1.74, 1.86 (2 s, 3 H, $CH_3CON$), 2.9–3.6 (4 m, 2 H, NC$H_2$R), 4.11 (t, $J_{5,6a}$ = $J_{6a,6e}$ = 10.1 Hz, 1 H, 6$_a$-H), 4.46 (dd, $J_{5,6e}$ = 5.2, $J_{6a,6e}$ = 10.2 Hz, 1 H, 6$_e$-H), 4.68 (m, 1 H, 5-H), 4.95 (d, $J_{4,5}$ = 13.1 Hz, 1 H, 4-H), 5.72, 5.73 (2 s, 1 H, PhC$H$), 7.3–7.5 (m, 5 H, Ph), 7.95, 7.99 (2 s, 1 H, 1-H) ppm. When the spectrum was recorded at 110 °C all the double signals collapsed to single signals. $^{13}$C NMR (50 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 13.9 ($CH_3$), 21.5, 21.7 ($CH_3$CON), 22.1–31.3 [$(CH_2)_{10}$], 46.2, 47.8 (N$CH_2$R), 66.7 (C-6), 72.5, 72.6 (C-5), 75.8, 75.9 (C-4), 100.6, 100.7 (Ph$CH$), 121.3, 121.7 (C-2), 126.3–136.7 (Ph), 162.5, 163.0 (C-1), 170.1, 170.6 ($CH_3$CON), 185.8, 186.0 (C-3) ppm. MS (CI): $m/z$ (%) = 458 (100) [M + H]$^+$. HRMS (EI): calcd. for $C_{22}H_{39}NO_5$ [M]$^{+\cdot}$ 457.282824; found 457.278976.

**Procedure B:** Dicyclohexylcarbodiimide (8.0 mmol) was added to a stirred mixture of 2-[(acyl)(alkyl)amino] or 2-(dialkylamino) sugars **16**–**20** (2.0 mmol), molecular sieves (3 Å, 1 g) and anhydrous dimethyl sulfoxide (30–40 mL) cooled to 0 °C. After 10 min, anhydrous orthophosphoric acid (8.4 mmol) was added portionwise with cooling (ice bath) so that the temperature was kept at 25–30 °C. The reaction mixture was stirred for 24 h at room temperature. The solids were removed by filtration and washed with dimethyl sulfoxide and acetone. The solution was diluted with four volumes of dichloromethane, water was added and then a potassium carbonate solution (2.4 M) was added to bring the aqueous phase to about pH 8. The aqueous layer was extracted with dichloromethane and the combined extracts were washed with water until neutral. The organic phase was dried ($Na_2SO_4$) and evaporated in vacuo to dryness. The solid obtained was crystallised or fractionated by chromatography on a silica gel column.

**2-(Acetyl-ethylamino)-1,5-anhydro-4,6-*O*-(*R*)-benzylidene-2-deoxy-D-*erythro*-hex-1-en-3-ulose (35):** Yield 0.48 g (75%) from compound **16**, 0.59 g (77%) from compound **17**, 0.48 g (77%) from compound **18** and 0.51 g (80%) from compound **20**; m.p. 118–119 °C. $[\alpha]_D$ = –95.0 ($c$ = 0.5, $CH_2Cl_2$). $^1$H NMR (500 MHz, [D$_6$]-DMSO, 25 °C): $\delta$ = 1.98 (s, 3 H, $CH_3CON$), 3.23 (t, 3 H, $NCH_2CH_3$), 3.52, 3.58 (2 m, 2 H, NC$H_2CH_3$), 4.25 (m, 1 H, 6$_a$-H), 4.48 (dd, $J_{5,6e}$ = 5.1, $J_{6a,6e}$ = 10.3 Hz, 1 H, 6$_e$-H), 4.54 (m, 1 H, 5-H), 4.75, 4.80 (2 d, $J_{4,5}$ = 12.1, 12.1 Hz, 1 H, 4-H), 5.51, 5.52 (2 s, 1 H, PhC$H$), 7.2–7.5 (m, 5 H, Ph), 8.03, 8.06 (2 s, 1 H, 1-H) ppm. When the spectrum was recorded at 110 °C all the double signals collapsed to single signals. $^{13}$C NMR (50 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 18.3, 18.5 ($NCH_2CH_3$), 21.1, 21.3 ($CH_3$CON), 49.5, 50.8 (N$CH_2CH_3$), 66.8 (C-6), 72.3, 72.7 (C-5), 75.6 (C-4), 100.0,

100.6 (PhCH), 122.8, 123.0 (C-2), 126.2–142.5 (Ph), 162.1, 162.6 (C-1), 170.0, 170.9 ($CH_3CON$), 185.4, 185.5 (C-3) ppm. MS (CI): *m*/*z* (%) = 318 (50) $[M + H]^+$. HRMS (CI): calcd. for $C_{17}H_{20}NO_5$ $[M + H]^+$ 318.1341; found 318.1336.

**2-(Acetyl-methylamino)-1,5-anhydro-4,6-*O*-(*R*)-benzylidene-2-deoxy-D-*erythro*-hex-1-en-3-ulose (36):** Yield 0.52 g (86%); m.p. 140–142 °C. $[\alpha]_D$ = +195.8 (*c* = 0.5, $CH_2Cl_2$). $^1$H NMR (500 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 1.77, 1.88 (2 s, 3 H, $CH_3CON$), 2.84, 2.94 (2 s, 3 H, $NCH_3$), 4.10 (t, $J_{5,6a} = J_{6a,6e}$ = 10.2 Hz, 1 H, $6_a$-H), 4.45 (dd, $J_{5,6e}$ = 5.1, $J_{6a,6e}$ = 10.3 Hz, 1 H, $6_e$-H), 4.65 (m, 1 H, 5-H), 4.89, 4.96 (2 d, $J_{4,5}$ = 13.0, 13.0 Hz, 1 H, 4-H), 5.72, 5.73 (2 s, 1 H, PhC*H*), 7.3–7.5 (m, 5 H, Ph), 8.03, 8.06 (2 s, 1 H, 1-H) ppm. When the spectrum was recorded at 110 °C all the double signals collapsed to single signals. $^{13}$C NMR (50 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 21.2, 21.4 ($CH_3CON$), 34.9, 36.8 ($NCH_3$), 66.6 (C-6), 72.4, 72.8 (C-5), 75.8 (C-4), 100.6 (PhCH), 123.0, 123.5 (C-2), 126.2–142.5 (Ph), 162.2, 162.9 (C-1), 170.0, 170.9 ($CH_3CON$), 185.4, 185.7 (C-3) ppm. MS (CI): *m*/*z* (%) = 304 (100) $[M + H]^+$. $C_{16}H_{17}NO_5$ (303.31): calcd. C 63.36, H 5.65, N 4.62; found C 63.51, H 5.23, N 4.50.

**1,5-Anhydro-4,6-*O*-(*R*)-benzylidene-2-deoxy-2-morpholino-D-*erythro*-hex-1-en-3-ulose (37):** Yield 0.45 g (72%); m.p. 196–198 °C. $[\alpha]_D$ = +149.1 (*c* = 0.5, $CH_2Cl_2$). $^1$H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta$ = 2.85 (m, 4 H, $CH_2NCH_2$), 3.78 (m, 4 H, $CH_2OCH_2$), 4.00 (t, $J_{5,6a} = J_{6a,6e}$ = 10.2 Hz, 1 H, $6_a$-H), 4.31 (m, 1 H, 5-H), 4.4–4.5 (m, 2 H, 4-H, $6_e$-H), 5.56 (s, 1 H, PhC*H*), 7.00 (s, 1 H, 1-H), 7.35–7.55 (m, 5 H, Ph) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$, 25 °C): $\delta$ = 51.1 ($CH_2NCH_2$), 66.9 ($CH_2OCH_2$), 68.0 (C-6), 72.4 (C-5), 77.6 (C-4), 102.0 (PhCH), 126.4–136.3 (Ph), 130.8 (C-2), 150.7 (C-1), 185.7 (C-3) ppm. MS (CI): *m*/*z* (%) = 318 (100) $[M + H]^+$. HRMS (CI): calcd. for $C_{21}H_{29}N_2O_6$ $[M + H]^+$ 318.1328; found 318.1336. $C_{17}H_{19}NO_5$ (317.34): calcd. C 64.34, H 6.03, N 4.41; found C 64.57, H 6.23, N 4.46.

**Reaction of the Amino Glycals with Amines:** The corresponding amine (2.0 mmol) dissolved in ethanol was added to a solution of compound **32** or **37** (0.38 g, 1.0 mmol) in ethanol (10 mL), and the solution was kept at room temperature until TLC showed that all the starting material had reacted (20 min from **32**, 2 h from **37**). The solvent was removed by evaporation to dryness and the solid obtained was purified by flash chromatography.

**(4*R*,5*R*)-2-(Acetyl-benzylamino)-4,6-*O*-(*R*)-benzylidene-1-(methylamino)-4,5,6-trihydroxyhex-1-en-3-one (38):** Yield 0.33 g (80%); m.p. 86–87 °C. $[\alpha]_D$ = –48.7 (*c* = 0.5, $CH_2Cl_2$). $^1$H NMR (500 MHz, [D$_6$]DMSO, 90 °C): $\delta$ = 1.74, 1.76 (2 s, 3 H, $CH_3CON$), 2.72 (d, *J* = 4.9 Hz, 1 H, $NCH_3$), 3.59 (m, 1 H, $6_a$-H), 3.92 (m, 1 H, 5-H), 4.09, 4.11 (2 d, $J_{gem}$ = 13.8 Hz, $NCH_AH_BPh$), 4.16 (m, 1 H, $6_e$-H), 4.42 (m, 1 H, 4-H), 4.80, 4.84 (2 m, 1 H, OH), 4.80, 4.84 (2 d, $J_{gem}$ = 13.8 Hz, 1 H, $NCH_AH_BPh$), 5.58, 5.59 (2 s, 1 H, PhC*H*), 6.51 (m, 1 H, NH), 7.13–7.42 (m, 10 H, 2 Ph), 7.61, 7.64 (2 d, $J_{1,NH}$ = 11.6 Hz, 1 H, 1-H) ppm. $^{13}$C NMR (125 MHz, [D$_6$]DMSO, 80 °C): $\delta$ = 20.9, 21.1 ($CH_3CON$), 34.4 ($NCH_3$) 48.9, 49.0 ($NCH_2Ph$), 61.1, 61.4 (C-5), 70.7, 70.8 (C-6), 78.6, 79.1 (C-4), 99.7, 99.8 (PhCH), 114.2 (C-2), 126.1–138.0 (Ph), 151.9 (C-1), 171.4, 171.6 ($CH_3CON$), 184.9 (C-3) ppm. MS (CI): *m*/*z* (%) = 411 (100) $[M + H]^+$. $C_{23}H_{26}N_2O_5$ (410.46): calcd. C 67.30, H 6.38, N 6.82; found C 67.52, H 6.45, N 7.12.

**(4*R*,5*R*)-2-(Acetyl-benzylamino)-4,6-*O*-(*R*)-benzylidene-1-[(*tert*-butyl)amino]-4,5,6-trihydroxyhex-1-en-3-one (39):** Yield 0.33 g (73%); m.p. 80–82 °C. $[\alpha]_D$ = –59.5 (*c* = 0.5, $CH_2Cl_2$). $^1$H NMR (500 MHz, [D$_6$]DMSO, 90 °C): $\delta$ = 0.97, 0.98 [2 s, 9 H, $C(CH_3)_3$], 1.75, 1.76 (2 s, 3 H, $CH_3CON$), 3.63 (m, 1 H, $6_a$-H), 3.79, 3.84 (2 d, $J_{gem}$ = 13.7 Hz, 1 H, $NCH_AH_BPh$), 3.95 (m, 1 H, 5-H), 4.20 (m, 2 H, $6_e$-H), 4.42, 4.46 (2 d, $J_{4,5}$ = 9.1 Hz, 1 H, 4-H), 4.79 (m, 1 H, OH), 5.10 (d, $J_{gem}$ = 13.7 Hz, 1 H, $NCH_AH_BPh$), 5.64, 5.65 (2 s, 1 H, PhC*H*), 6.01 (m, 1 H, NH), 7.13–7.43 (m, 10 H, 2 Ph), 7.71, 7.74 (2 d, $J_{1,NH}$ = 9.0 Hz, 1 H, 1-H) ppm. $^{13}$C NMR (125 MHz, [D$_6$]DMSO, 80 °C): $\delta$ = 21.0, 21.3 [$NC(CH_3)_3$], 29.0, 29.1 ($CH_3CON$), 48.4, 48.9 ($NCH_2Ph$), 51.8, 52.4 [$NC(CH_3)_3$], 61.7, 62.0 (C-5), 70.8, 70.9 (C-6), 80.0, 80.7 (C-4), 99.7, 100.2 (PhCH), 112.8, 113.1 (C-2), 125.9–138.0 (Ph), 148.6, 148.7 (C-1), 171.7, 171.9 ($CH_3CON$), 185.6 (C-3) ppm. MS (FAB): *m*/*z* (%) = 475 (100) $[M + Na]^+$. $C_{26}H_{32}N_2O_5$ (452.54): calcd. C 68.97, H 7.12, N 6.19; found C 68.65, H 7.17, N 5.91.

**(4*R*,5*R*)-2-(Acetyl-benzylamino)-4,6-*O*-(*R*)-benzylidene-1-(phenylamino)-4,5,6-trihydroxyhex-1-en-3-one (40):** Yield 0.32 g (68%); m.p. 93–94 °C. $[\alpha]_D$ = –73.4 (*c* = 1.0, $CH_2Cl_2$). $^1$H NMR (500 MHz, [D$_6$]DMSO, 90 °C): $\delta$ = 1.80, 181 (2 s, 3 H, $CH_3CON$), 3.65 (t, $J_{5,6a} = J_{6a,6e}$ = 10.4 Hz, 1 H, $6_a$-H), 3.87, 3.94 (2 m, 1 H, 5-H), 4.15–4.20 (m, 2 H, $6_e$-H, $NCH_AH_BPh$), 4.61, 4.66 (2 d, $J_{4,5}$ = 9.1, 9.0 Hz, 1 H, 4-H), 4.82, 4.86 (2 m, 1 H, OH), 4.89, 4.90 (2 d, *J* = 13.8 Hz, 1 H, $NCH_AH_BPh$), 5.69, 5.71 (2 s, 1 H, PhC*H*), 6.9–7.4 (m, 15 H, 3 Ph), 8.14, 8.19 (2 s, 1 H, 1-H), 8.66 (m, 1 H, NH) ppm. MS (EI): *m*/*z* (%) = 472 (50) $[M]^{+\cdot}$. $^1$HRMS (EI): calcd. for $C_{28}H_{28}N_2O_5$ $[M]^{+\cdot}$ 472.1998; found 472.2003. $C_{28}H_{28}N_2O_5$ (472.53): calcd. C 71.17, H 5.97, N 5.93; found C 70.87, H 6.01, N 5.77.

**(4*R*,5*R*)-2-(Acetyl-2-benzylamino)-4,6-*O*-(*R*)-benzylidene-1-(diethylamino)-4,5,6-trihydroxyhex-1-en-3-one (41):** Obtained as a syrup; yield 0.31 g (68%). $[\alpha]_D$ = +39.5 (*c* = 1.0, $CH_2Cl_2$). $^1$H NMR (500 MHz, [D$_6$]DMSO, 90 °C): $\delta$ = 0.88 [t, *J* = 7.0 Hz, 6 H, $N(CH_2CH_3)_2$], 1.81, 183 (2 s, 3 H, $CH_3CON$), 3.00, 3.25 [2 m, 4 H, $N(CH_2CH_3)_2$], 3.62 (m, 1 H, $6_a$-H), 3.90 (m, 1 H, 5-H), 4.03, 4.04 (2 d, $J_{gem}$ = 13.7 Hz, 1 H, $NCH_AH_BPh$), 4.19 (dd, $J_{5,6e}$ = 5.4, $J_{6a,6e}$ = 10.7 Hz, 1 H, $6_e$-H), 4.51, 4.52 (2 d, $J_{4,5}$ = 9.0, 8.9 Hz, 1 H, 4-H), 4.81 (m, 1 H, OH), 4.86, 4.92 (2 d, $J_{gem}$ = 13.7 Hz, 1 H, $NCH_AH_BPh$), 5.63, 5.65 (2 s, 1 H, PhC*H*), 7.3–7.5 (m, 5 H, Ph), 7.53, 7.57 (2 s, 1 H, 1-H) ppm. $^{13}$C NMR (125 MHz, [D$_6$]DMSO, 80 °C): $\delta$ = 13.5 [$N(CH_2CH_3)_2$], 21.3, 21.4 ($CH_3CON$), 49.6, 49.8 [$N(CH_2CH_3)_2$], 51.1, 51.4 ($NCH_2Ph$), 61.7, 62.0 (C-5), 70.8, 70.9 (C-6), 80.0, 80.5 (C-4), 100.0, 100.1 (PhCH), 112.8, 113.1 (C-2), 125.9–138.0 (Ph), 148.6, 148.7 (C-1), 172.0, 172.1 ($CH_3CON$), 187.8 (C-3) ppm. MS (CI): *m*/*z* (%) = 453 (100) $[M + H]^+$. HRMS (CI): calcd. for $C_{26}H_{33}N_2O_5$ $[M + H]^+$ 453.2389; found 453.2379. $C_{26}H_{32}N_2O_5$ (452.54): calcd. C 68.97, H 7.12, N 6.19; found C 68.85, H 7.17, N 5.98.

**(4*R*,5*R*)-2-(Acetyl-benzylamino)-4,6-*O*-(*R*)-benzylidene-1-[(methoxycarbonylmethyl)amino]-4,5,6-trihydroxyhex-1-en-3-one (42):** Yield 0.29 g (62%). $[\alpha]_D$ = –54.4 (*c* = 0.5, $CH_2Cl_2$). $^1$H NMR (500 MHz, [D$_6$]DMSO, 90 °C): $\delta$ = 1.81, 182 (2 s, 3 H, $CH_3CON$), 3.56 (m, 1 H, $6_a$-H), 3.63, 3.64 (2 s, 3 H, $NCH_2CO_2CH_3$), 3.80–4.00 (m, 3 H, $NCH_2Ph$, 5-H), 4.16 (m, 1 H, $6_e$-H), 4.28 (m, 1 H, $NCH_AH_BCO_2CH_3$), 4.41 (m, 1 H, 4-H), 4.6–4.8 (m, 2 H, $NCH_AH_BCO_2CH_3$, OH), 5.55, 5.56 (2 s, 1 H, PhC*H*), 6.86 (m, 1 H, NH), 7.1–7.4 (m, 10 H, 2 Ph), 7.69, 7.72 (2 d, $J_{1,NH}$ = 8.6 Hz, 1 H, 1-H) ppm. $^{13}$C NMR (125 MHz, [D$_6$]DMSO, 90 °C): $\delta$ = 20.3, 20.5 ($CH_3CON$), 47.9 ($NCH_2Ph$), 49.1, 49.5 ($NCH_2CO_2CH_3$), 51.3 ($NCH_2CO_2CH_3$), 61.0 (C-5), 70.5 (C-6), 79.1, 79.5 (C-4), 99.5, 99.6 (PhCH), 115.2 (C-2), 125.7–137.6 (2 Ph), 150.3, 150.5 (C-1), 169.6 ($NCH_2CO_2CH_3$), 171.1, 171.2 ($CH_3CON$), 186.1 (C-3) ppm. MS (EI): *m*/*z* (%) = 468 (20) $[M]^{+\cdot}$. HRMS (EI): calcd. for $C_{25}H_{28}N_2O_7$ $[M]^{+\cdot}$ 468.1897; found 468.1883. $C_{25}H_{28}N_2O_7$ (468.50): calcd. C 64.09, H 6.02, N 5.98; found C 64.32, H 6.15, N 6.12.

**(4*R*,5*R*)-2-(Acetyl-benzylamino)-4,6-*O*-(*R*)-benzylidene-1-morpholino-4,5,6-trihydroxyhex-1-en-3-one (43):** Obtained as a syrup; yield 0.30 g (64%). $[\alpha]_D$ = –74.4 (*c* = 0.5, $CH_2Cl_2$). $^1$H NMR (500 MHz,

[D$_6$]DMSO, 90 °C): $\delta$ = 1.79, 1.81 (2 s, 3 H, $CH_3CON$), 3.10–3.40 (m, 8 H, 4 $CH_2$), 3.62 (m, 1 H, $6_a$-H), 4.87, 4.89 (2 d, $J$ = 13.7, 13.6 Hz, 1 H, NC$H_AH_B$Ph), 3.98 (m, 1 H, 5-H), 4.20 (dd, $J_{5,6e}$ = 5.4, $J_{6a,6e}$ = 10.7 Hz, 1 H, $6_e$-H), 4.57 (m, 1 H, OH), 4.85, 4.88 (2 d, $J_{4,5}$ = 5.5, 5.7 Hz, 1 H, 4-H), 4.99, 5.07 (2 d, $J_{gem}$ = 13.7 Hz, 1 H, $NCH_AH_B$Ph), 5.64, 5.65 (2 s, 1 H, PhC*H*), 7.2–7.5 (m, 10 H, Ph), 7.55, 7.57 (2 s, 1 H, 1-H) ppm. $^{13}$C NMR (125 MHz, [D$_6$]-DMSO, 90 °C): $\delta$ = 20.9, 21.0 ($CH_3$CON), 49.6 ($CH_2NCH_2$), 50.1, 50.4 (N$CH_2$Ph), 61.1, 61.4 (C-5), 65.4 ($CH_2OCH_2$), 70.4, 70.5 (C-6), 79.0, 79.2 (C-4), 99.5, 99.6 (PhCH), 112.3, 112.7 (C-2), 125.6–137.6 (2 Ph), 147.9 (C-1), 171.4, 171.5 ($CH_3CO$N), 187.7 (C-3) ppm. MS (EI): $m/z$ (%) = 466 (70) [M]$^{+\cdot}$. HRMS (EI): calcd. for $C_{26}H_{30}N_2O_6$ [M]$^{+\cdot}$ 466.2104; found 466.2121.

**(4*R*,5*R*)-4,6-*O*-(*R*)-Benzylidene-1-(methylamino)-2-morpholino-4,5,6-trihydroxyhex-1-en-3-one (44):** The solid compound was obtained as a *Z*/*E* mixture in a 3:1 ratio; yield 0.27 g (77%). $[\alpha]_D$ = +131.7 ($c$ = 1.0, $CH_2Cl_2$). $^1$H NMR (500 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 2.68, 2.86 (2 m, 4 H, $CH_2NCH_2$), 2.97 (d, $J$ = 4.9 Hz, 3 H, $NCH_3$), 3.56–3.62 (m, 5 H, $6_a$-H, $CH_2OCH_2$), 3.90, 3.98 (2 m, 1 H, 5-H), 4.15 (dd, $J_{5,6e}$ = 5.5, $J_{6a,6e}$ = 10.7 Hz, 1 H, $6_e$-H), 4.38 (d, $J_{4,5}$ = 9.0 Hz, 0.75 H, 4-H major), 4.64 (m, 1 H, OH), 4.87 (d, $J_{4,5}$ = 9.4 Hz, 0.25 H, 4-H minor), 5.53 (s, 0.25 H, PhC*H* minor), 5.60 (s, 0.75 H, PhC*H* major), 6.58 (m, 0.75 H, NH major), 7.11 (s, 0.25 H, 1-H minor), 7.3–7.4 (m, 5 H, Ph), 7.55 (s, 0.75 H, 1-H major), 9.56 (m, 0.25 H, NH minor) ppm. $^{13}$C NMR (125 MHz, [D$_6$]-DMSO, 25 °C): $\delta$ = 33.4 ($NCH_3$ major), 33.8 ($NCH_3$ minor), 49.2 ($CH_2NCH_2$), 61.2 (C-5 major), 60.2 (C-5 minor), 66.7 ($CH_2OCH_2$), 70.5 (C-6 major), 70.6 (C-6 minor), 78.5 (C-4 minor), 79.9 (C-4 major), 99.7 (PhCH major), 99.9 (PhCH minor), 121.6 (C-2 minor), 121.8 (C-2 major), 125.6–137.8 (Ph), 151.4 (C-1 major), 151.5 (C-1 minor), 186.4 (C-3 major), 191.1 (C-3 minor) ppm. MS (EI): $m/z$ (%) = 348 (60) [M]$^+$. HRMS (EI): calcd. for $C_{18}H_{24}N_2O_6$ [M]$^+$ 348.1685; found 348.1695. $C_{18}H_{24}N_2O_5$ (348.39): calcd. C 62.05, H 6.94, N 8.04; found C 61.89, H 7.10, N 7.88.

**(4*R*,5*R*)-1-Amino-4,6-*O*-(*R*)-benzylidene-1-*N*-butyl-2-morpholino-4,5,6-trihydroxyhex-1-en-3-one (45):** The solid compound was obtained as a *Z*/*E* mixture in a 2.7:1 ratio; yield 0.27 g (69%). $[\alpha]_D$ = –125.0 ($c$ = 0.9, $CH_2Cl_2$). $^1$H NMR (500 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 0.88 (m, 3 H, $CH_3$), 1.31, 1.50 [2 m, 4 H, $(CH_2)_2$], 2.68, 2.86 (2 m, 4 H, $CH_2NCH_2$), 3.24 (m, 2 H, $NCH_2$), 3.55–3.64 (m, 5 H, $6_a$-H, $CH_2OCH_2$), 3.90, 3.98 (2 m, 1 H, 5-H), 4.15 (m, 1 H, $6_e$-H), 4.36 (d, $J_{4,5}$ = 9.1 Hz, 0.73 H, 4-H major), 4.64, 4.69 (2 m, 1 H, OH), 4.87 (d, $J_{4,5}$ = 9.4 Hz, 0.27 H, 4-H minor), 5.53 (s, 0.27 H, PhC*H* minor), 5.61 (s, 0.73 H, PhC*H* major), 6.67 (m, 0.73 H, NH major), 7.16 (d, $J_{1,NH}$ = 12.8 Hz, 0.27 H, 1-H minor), 7.3–7.4 (m, 5 H, Ph), 7.58 (s, $J_{1,NH}$ = 13.4 Hz, 0.73 H, 1-H major), 9.78 (m, 0.27 H, NH minor) ppm. $^{13}$C NMR (125 MHz, [D$_6$]DMSO, 25 °C) $\delta$ = 12.8, 12.9 ($CH_3$), 18.6, 32.1, 32.4 [$(CH_2)_2$], 46.1 ($NCH_2$ major), 47.2 ($NCH_2$ minor), 49.2, 54.0 ($CH_2NCH_2$), 60.2 (C-5 minor), 61.2 (C-5 major), 66.7, 66.8 ($CH_2OCH_2$), 70.5 (C-6 major), 70.7 (C-6 minor), 78.5 (C-4 minor), 80.2 (C-4 major), 99.7 (PhCH major), 100.0 (PhCH minor), 121.5 (C-2), 125.6–137.8 (Ph), 150.4 (C-1), 186.7 (C-3 major), 191.4 (C-3 minor) ppm. MS (EI): $m/z$ (%) = 390 (100) [M]$^+$. HRMS (EI): calcd. for $C_{21}H_{30}N_2O_5$ [M]$^+$ 390.2155; found 390.2145. $C_{21}H_{30}N_2O_5$ (390.47): calcd. C 64.59, H 7.74, N 7.17; found C 64.65, H 7.57, N 6.91.

**(4*R*,5*R*)-1-(Benzylamino)-4,6-*O*-(*R*)-benzylidene-2-morpholino-4,5,6-trihydroxyhex-1-en-3-one (46):** The syrupy compound was obtained as a *Z*/*E* mixture in a 3:1 ratio; yield 0.30 g (71%). $[\alpha]_D$ = –83.5 ($c$ = 1.5, $CH_2Cl_2$). $^1$H NMR (500 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 2.63, 2.83 (2 m, 4 H, $CH_2NCH_2$), 3.50 (t, $J_{5,6a}$ = $J_{6a,6e}$ = 10.6 Hz, 1 H, $6_a$-H), 3.55 (m, 4 H, $CH_2OCH_2$), 3.84 (m, 0.75 H, 5-H major), 3.91 (m, 0.25 H, 5-H minor), 4.08 (dd, $J_{5,6e}$ = 5.4, $J_{6a,6e}$ = 10.6 Hz, 1 H, $6_e$-H), 4.30 (d, $J_{4,5}$ = 9.4 Hz, 0.75 H, 4-H major), 4.40 (d, 2 H, NC$H_2$Ph), 4.61, 4.68 (2 m, 1 H, OH), 4.82 (d, $J_{4,5}$ = 9.4 Hz, 0.25 H, 4-H minor), 5.45 (s, 0.33 H, PhC*H* minor), 5.51 (s, 0.75 H, PhC*H* major), 6.87 (m, 0.75 H, NH major), 7.06 (d, $J_{1,NH}$ = 12.7 Hz, 0.25 H, 1-H minor), 7.2–7.3 (m, 5 H, Ph), 7.62 (d, $J_{1,NH}$ = 13.1 Hz, 0.75 H, 1-H major), 9.99 (m, 0.25 H, NH minor) ppm. $^{13}$C NMR (125 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 50.2, 55.0 ($CH_2NCH_2$), 54.1 (N$CH_2$Ph) 61.2 (C-5 minor), 61.9 (C-5 major), 67.6, 67.7 ($CH_2OCH_2$), 71.4 (C-6 major), 71.6 (C-6 minor), 79.5 (C-4 minor), 81.0 (C-4 major), 100.6 (PhCH major), 100.9 (PhCH minor), 122.9 (C-2 minor), 123.1 (C-2 major), 126.5–139.3 (Ph), 150.1 (C-1 minor), 150.5 (C-1 major), 187.8 (C-3 major), 192.8 (C-3 minor) ppm. MS (EI): $m/z$ (%) = 424 (100) [M]$^+$. HRMS (EI): calcd. for $C_{24}H_{28}N_2O_5$ [M]$^+$ 424.1998; found 424.1991.

**(4*R*,5*R*)-4,6-*O*-(*R*)-Benzylidene-1-(isopropylamino)-2-morpholino-4,5,6-trihydroxyhex-1-en-3-one (47):** The syrupy compound was obtained as a *Z*/*E* mixture in a 2.2:1 ratio; yield 0.30 g (80%). $[\alpha]_D$ = –30.4 ($c$ = 0.7, $CH_2Cl_2$). $^1$H NMR (500 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 1.10, 1.12 (2 d, $J$ = 3.7 Hz, 6 H, 2 $CH_3$), 2.63, 2.83 (2 m, 4 H, $CH_2NCH_2$), 3.52 [m, 6 H, $CH_2OCH_2$, $6_a$-H, NC*H*$(CH_3)_2$], 3.81 (m, 0.69 H, 5-H major), 3.90 (m, 0.31 H, 5-H minor), 4.08 (dd, $J_{5,6a}$ = 5.7, $J_{6a,6e}$ = 10.7 Hz, 1 H, $6_e$-H), 4.30 (d, $J_{4,5}$ = 9.4 Hz, 0.69 H, 4-H major), 4.62, 4.69 (2 m, 1 H, OH), 4.80 (d, $J_{4,5}$ = 9.3 Hz, 0.31 H, 4-H minor), 5.45 (s, 0.31 H, PhC*H* minor), 5.55 (s, 0.69 H, PhC*H* major), 6.41 (m, 0.69 H, NH major), 7.14 (d, $J_{1,NH}$ = 13.0 Hz, 0.31 H, 1-H minor), 7.2–7.3 (m, 5 H, Ph), 7.56 (s, $J_{1,NH}$ = 13.0 Hz, 0.69 H, 1-H major), 9.73 (m, 0.31 H, NH minor) ppm. $^{13}$C NMR (125 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 23.7, 23.8 (2 $CH_3$), 48.4, 54.9 ($CH_2NCH_2$), 50.5 [N$CH(CH_3)$], 61.2 (C-5 minor), 62.3 (C-5 major), 67.6, 67.8 ($CH_2OCH_2$), 71.4 (C-6 major), 71.6 (C-6 minor), 79.4 (C-4 minor), 81.3 (C-4 major), 100.6 (PhCH major), 100.9 (PhCH minor), 122.4 (C-2 minor), 122.7 (C-2 major), 126.5–139.3 (Ph), 149.0 (C-1), 189.7 (C-3 major), 192.3 (C-3 minor) ppm. MS (EI): $m/z$ (%) = 376 (100) [M]$^+$. HRMS (EI): calcd. for $C_{20}H_{28}N_2O_5$ [M]$^+$ 376.1998; found 376.1982.

**(4*R*,5*R*)-4,6-*O*-(*R*)-Benzylidene-1-[(*tert*-butyl)amino]-2-morpholino-4,5,6-trihydroxyhex-1-en-3-one (48):** The syrupy compound was obtained as a *Z*/*E* mixture in a 2.1:1 ratio; yield 0.24 g (61%). $[\alpha]_D$ = +124.2 ($c$ = 0.8, $CH_2Cl_2$). $^1$H NMR (500 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 1.25, 1.29, 1.31 (3 s, 3 $CH_3$), 2.73, 2.89 (2 m, 4 H, $CH_2NCH_2$), 3.63 (m, 5 H, $CH_2OCH_2$, $6_a$-H), 3.91 (m, 0.68 H, 5-H major), 4.01 (m, 0.32 H, 5-H minor), 4.19 (dd, $J_{5,6a}$ = 5.5, $J_{6a,6e}$ = 10.6 Hz, 1 H, $6_e$-H), 4.41 (d, $J_{4,5}$ = 9.4 Hz, 0.68 H, 4-H major), 4.72, 4.75 (2 m, 1 H, OH), 4.91 (d, $J_{4,5}$ = 9.3 Hz, 0.32 H, 4-H minor), 5.56 (s, 0.32 H, PhC*H* minor), 5.67 (s, 0.68 H, PhC*H* major), 6.38 (m, 0.68 H, NH major), 7.31 (d, $J_{1,NH}$ = 13.0 Hz, 0.32 H, 1-H minor), 7.3–7.4 (m, 5 H, Ph), 7.73 (s, $J_{1,NH}$ = 13.0 Hz, 0.68 H, 1-H major), 10.02 (m, 0.32 H, NH minor) ppm. $^{13}$C NMR (125 MHz, [D$_6$]-DMSO, 25 °C) $\delta$ = 29.2, 30.1, 30.3 (3 $CH_3$), 50.0, 54.9 ($CH_2NCH_2$), 57.9 [N$C(CH_3)_3$], 61.2 (C-5 minor), 62.5 (C-5 major), 67.7, 67.9 ($CH_2OCH_2$), 71.4 (C-6 major), 71.6 (C-6 minor), 79.5 (C-4 minor), 81.9 (C-4 major), 100.6 (PhCH major), 100.9 (PhCH minor), 122.6 (C-2 minor), 122.7 (C-2 major), 126.6–138.8 (Ph), 146.9 (C-1), 187.9 (C-3 major), 192.2 (C-3 minor) ppm. MS (CI): $m/z$ (%) = 391 (100) [M + H]$^+$. HRMS (CI): calcd. for $C_{21}H_{31}N_2O_5$ [M + H]$^+$ 391.2233; found 391.2238. $C_{21}H_{30}N_2O_5$ (390.47): calcd. C 64.59, H 7.74, N 7.17; found C 64.65, H 7.17, N 6.91.

**(4*R*,5*R*)-4,6-*O*-(*R*)-Benzylidene-1-[(methoxycarbonylmethyl)amino]-2-morpholino-4,5,6-trihydroxyhex-1-en-3-one (49):** The syrupy compound was obtained as a *Z*/*E* mixture in a 3.5:1 ratio; yield 0.26 g (64%). $[\alpha]_D$ = –174.0 ($c$ = 0.5, $CH_2Cl_2$). $^1$H NMR (500 MHz, [D$_6$]-

DMSO, 25 °C): $\delta$ = 2.68, 2.89 (2 m, 4 H, $CH_2NCH_2$), 3.24 (m, 2 H, $NCH_2$), 3.56 (t, $J_{5,6a} = J_{6a,6e}$ = 10.5 Hz, 1 H, $6_a$-H), 3.64 (m, 4 H, $CH_2OCH_2$), 3.69, 3.70 (2 s, 3 H, $NCH_2CO_2CH_3$), 3.91, 3.99 (2 m, 1 H, 5-H), 4.08 (m, 2 H, $NCH_2CO_2CH_3$), 4.15 (m, 1 H, $6_e$-H), 4.36 (d, $J_{4,5}$ = 9.1 Hz, 0.78 H, 4-H major), 4.68, 4.75 (2 m, 1 H, OH), 4.89 (d, $J_{4,5}$ = 9.4 Hz, 0.22 H, 4-H minor), 5.54 (s, 0.22 H, PhC*H* minor), 5.58 (s, 0.78 H, PhC*H* major), 6.77 (m, 0.78 H, NH major), 7.09 (d, $J_{1,NH}$ = 12.7 Hz, 0.22 H, 1-H minor), 7.3–7.4 (m, 5 H, Ph), 7.55 (s, $J_{1,NH}$ = 12.9 Hz, 0.78 H, 1-H major), 9.58 (m, 0.22 H, NH minor) ppm. $^{13}$C NMR (125 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 47.4 ($NCH_2CO_2CH_3$), 49.1, 54.0 ($CH_2NCH_2$), 51.2 ($NCH_2CO_2CH_3$ major), 51.3 ($NCH_2CO_2CH_3$ minor), 60.2 (C-5 minor), 61.0 (C-5 major), 66.7, 66.8 ($CH_2OCH_2$), 70.5 (C-6 major), 70.6 (C-6 minor), 78.5 (C-4 minor), 79.9 (C-4 major), 99.7 (PhCH major), 100.0 (PhCH minor), 122.7 (C-2 minor), 122.9 (C-2 major), 125.6–137.7 (Ph), 150.1 (C-1 minor), 150.2 (C-1 major), 169.9 ($NCH_2CO_2CH_3$ minor), 170.1 ($NCH_2CO_2CH_3$ major), 187.4 (C-3 major), 192.4 (C-3 minor) ppm. MS (EI): *m*/*z* (%) = 406 (85) [M]$^+$. HRMS (EI): calcd. for $C_{20}H_{26}N_2O_7$ [M]$^+$ 406.1740; found 406.1752.

**(*Z*)-(4*R*,5*R*)-4,6-*O*-(*R*)-Benzylidene-1,2-dimorpholino-4,5,6-trihydroxyhex-1-en-3-one (50):** Yield 0.32 g (79%). $[\alpha]_D$ = –79.2 (*c* = 1.0, $CH_2Cl_2$). $^1$H NMR (500 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 2.95 (m, 4 H, $CH_2NCH_2$), 3.56–3.62 (m, 5 H, $6_a$-H, $CH_2OCH_2$), 3.65 (m, 4 H, $CH_2OCH_2$), 3.85 (m, 4 H, $CH_2NCH_2$), 3.91 (m, 1 H, 5-H), 4.16 (dd, $J_{5,6e}$ = 5.4, $J_{6a,6e}$ = 10.7 Hz, 1 H, $6_e$-H), 4.41 (d, $J_{4,5}$ = 9.0 Hz, 1 H, 4-H), 4.67 (m, 1 H, OH), 5.62 (s, 1 H, PhC*H*), 7.24 (s, 1 H, 1-H), 7.30–7.45 (m, 5 H, Ph) ppm. $^{13}$C NMR (125 MHz, [D$_6$]DMSO, 25 °C) $\delta$ = 49.2, 54.1 (2 $CH_2NCH_2$), 61.2 (C-5), 65.9, 66.0 (2 $CH_2OCH_2$), 70.4 (C-6), 80.2 (C-4), 99.7 (PhCH), 121.6 (C-2), 125.6–137.8 (Ph), 147.6 (C-1), 189.9 (C-3) ppm. MS (CI): *m*/*z* (%) = 405 (85) [M + H]$^+$. HRMS (CI): calcd. for $C_{21}H_{29}N_2O_6$ [M + H]$^+$ 405.2026; found 405.2013. $C_{21}H_{28}N_2O_6$ (404.46): calcd. C 62.36, H 6.98, N 6.93; found C 62.12, H 7.17, N 5.91.

**Supporting Information** (see also the footnote on the first page of this article): The synthesis and characterization of *N*,*N*-substituted 2-amino sugar derivatives **14**–**31** employed as precursors, the new 2-amino glycals **32**–**37** obtained by two oxidative procedures and the products **38**–**50** of their reactions with different amines. $^1$H NMR spectra of glycals **32**, **35**, **37** and β-enamino ketones **38**–**50**, NOESY spectrum of compound **44** and ROESY spectrum of compound **38**.

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