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1,3-Dipolar cycloaddition between *N*-benzyl-*C*-glycosyl nitrones and methyl acrylate en route to glycosyl pyrrolidines

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Abstract—1,3-Dipolar cycloaddition reactions between three *N*-benzyl-*C*-glycosyl nitrones and methyl acrylate afforded key intermediates for the synthesis of glycosyl pyrrolidines. The best result was obtained with a D-galactose derived nitrone which afforded only one isomer in quantitative yield. Absolute configurations were assigned by applying the Kakisawa's rule and X-ray diffraction methods.

1. Introduction

The chemistry of imino disaccharides[1] has become of great interest in recent years because they can be powerful glycosidase inhibitors, thus having an enormous potential as bactericidal or as antidiabetes agents.[2] A number of synthetic routes have been developed to various imino disaccharides, including MDL25,637,[2b] in which one of the sugar moieties has been replaced by a piperidine ring.[3]

The glycosidic linkage can also be replaced by different sequences of atoms and the imino sugar can be either a piperidine or a pyrrolidine ring (Fig. 1, $o=1$, 2). For instance, imino disaccharides linked by glycosidic bonds extended with additional carbon atoms have been prepared.[4] The synthesis of nitrogen[5] and sulfur[6] containing links between the sugar and imino sugar moieties have also been reported. Among the non-hydrolyzable linkages, the all-carbon link leading to imino-*C*-disaccharides[7] (Fig. 1, X = $-(CH_2)_n-$, $n=0$, 1, 2) is considered the closest in structure to natural sequences.[8] The first example of imino-*C*-disaccharides was reported by Johnson et al.[9] In this regard, the Vogel group pioneered the elaboration of flexible methodologies for the preparation of imino-*C*-disaccharides from the so-called 'naked sugars'.[10] Recently, other research groups have reported some approaches starting from natural sugars.[11]

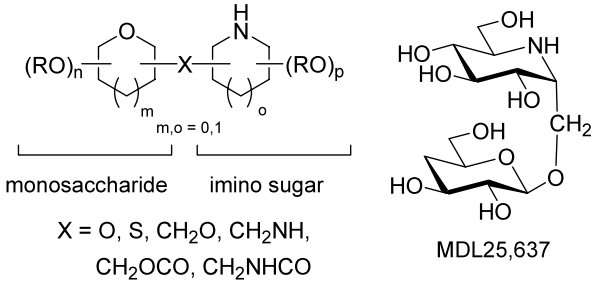

Figure 1. Imino disaccharides.

In particular, Brandi and Goti et al. applied an elegant strategy, based on cycloaddition chemistry, to the synthesis of imino-*C*-disaccharides in which a pyranose ring is directly linked (X = 0) to a hydroxylated pyrrolidine.[12] The key step of this approach consisted of the 1,3-dipolar cycloaddition between a cyclic nitrone and a glycal.

In this context and based on our previous experience,[13] we envisioned that a pyrrolidinyl sugar system **A** might be a valuable key intermediate for the preparation of several carbohydrate mimics. Compound **A** would be derived from isoxazolidine **B** which could be prepared

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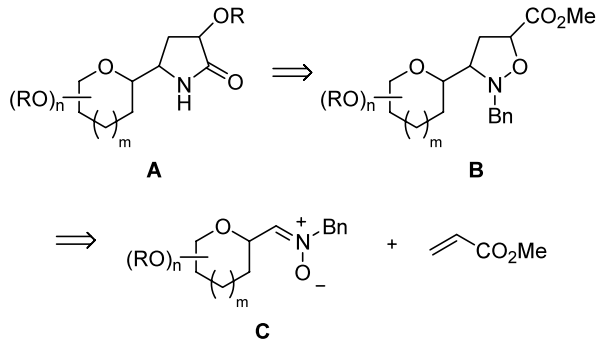


Scheme 1.

through the cycloaddition between an *N*-benzyl-*C*-glycosyl nitrone[14] **C** and methyl acrylate (Scheme 1).[15] Herein we report our results on the cycloaddition reaction between *C*-furanosyl/*C*-pyranosyl nitrones **C** and methyl acrylate, and the further elaboration of the obtained glycosyl isoxazolidines into glycosyl pyrrolidines **A**.

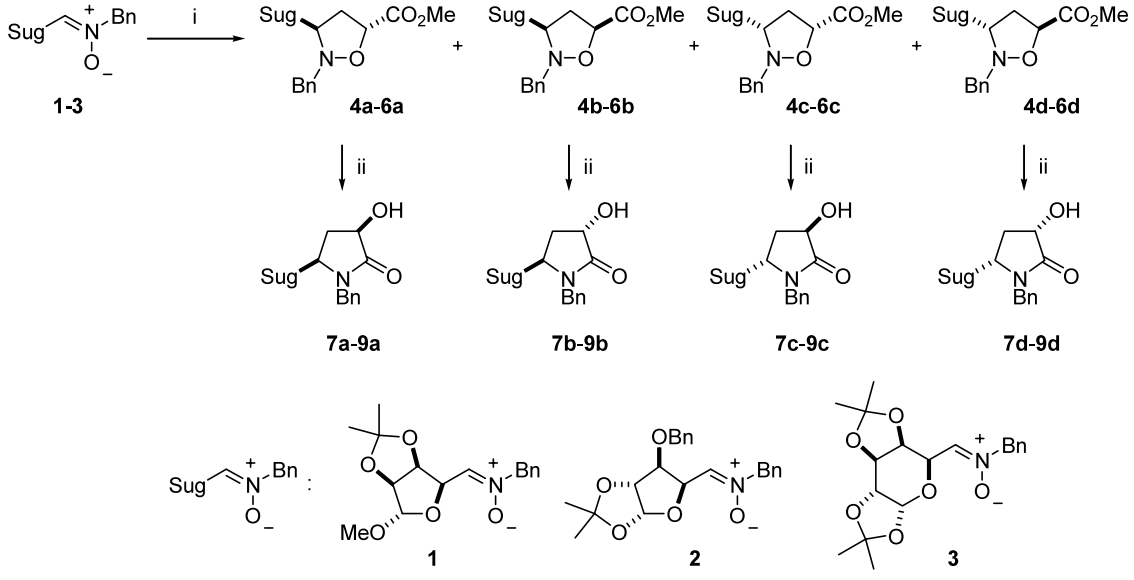
2. Results and discussion

2.1. Cycloaddition reactions and synthesis of imino-*C*-disaccharides

The nitrones **1**–**3** used in this study were easily prepared from the corresponding aldehyde following our previously described procedure.[16] Condensation of nitrones **1**–**3** with an excess of methyl acrylate under several conditions afforded the corresponding mixtures of isoxazolidines. In all cases the chemical yield of the reaction was quantitative. The results of the reactions illustrated in Scheme 2 are collected in Table 1.

It was found that furanosyl nitrones **1** and **2** reacted with methyl acrylate to give mixtures of all possible 3,5-disubstituted isoxazolidines **4** and **5**. In all cases purification by radial chromatography allowed the isolation of pure compounds. Whereas the regioselectivity of the reaction was very high (the corresponding 3,4-regioisomers were not detected), both the *endo*/*exo* selectivity and the diastereofacial induction (*Re*/*Si*) were rather low (Table 1, entries 1–9). The cycloaddition proved to be not dependent of the reaction conditions (solvent and temperature). Even the use of microwaves (Table 1, entry 4) did not substantially change the ratio of the products, although it did accelerate the reaction rate considerably. In general, a slight trend towards *endo* adducts (as expected for cycloadditions with electron-poor alkenes) and *Re* attacks was observed. On the other hand, pyranosyl nitrone **3** was much more selective. Indeed, cycloaddition at ambient temperatures afforded only one detectable (NMR) adduct (Table 1, entry 11) which was identified as *Re-endo* **6a**. The obtained isoxazolidines were transformed into the corresponding *N*-benzyl-3-hydroxy-2-pyrrolidinones by treatment with Zn in acetic acid (Scheme 2).[13]

Spectroscopic data and chemical behavior supported the structural assignments made to adducts **4**–**6** given in Table 1. The relative *cis*/*trans* configuration was assigned by NOE experiments (Fig. 2). Thus, for *trans*-compounds **4a**–**6a** and **4d**–**6d**, irradiation of H-3 only produced a strong enhancement of H-4a (15–17%) and irradiation of H-5 only produced enhancement of H-4b (11–17%). In addition, irradiation of H-4a and H-4b in the same experiment produced enhancements of H-3 (9–11%) and H-5 (8–12%). For *cis*-compounds **4b**–**6b** and **4c**–**6c**, irradiation of H-4a produced enhancements of both H-3 (5–17%) and H-5 (14–17%). Irradiation of H-5 produced enhancement of H-4a (10–15%) and a smaller enhancement of H-3 (5–6%). Irradiation of H-3 produced enhancement of H-4a (8–12%) and H-5 (5–6%). The relative configuration between the isoxazolidine ring and the sugar moiety could not be



Scheme 2. *Reagents and conditions*: (i) Methyl acrylate. See Table 1; (ii) Zn/AcOH–H_2O, 60°C, 5 h.

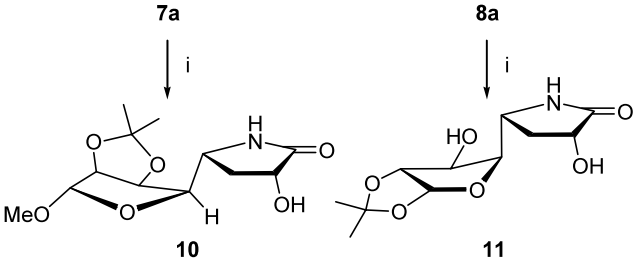
Table 1. Cycloaddition reactions between nitrones **1**–**3** and methyl acrylate[a] and further conversion to pyrroldinones **7**–**9**

Entry	Nitrone	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]	Isoxazolidine **a**:**b**:**c**:**d**[c]	*endo*/*exo*[d]	*Re*/*Si*[e]	Pyrrolidinone
1	**1**	Neat	80	0.5	100	**4** 34:25:22:19	53:47	59:41	**7**
2	**1**	Neat	25	2	100	**4** 32:27:22:19	51:49	59:41	**7**
3	**1**	Neat	−18	6	100	**4** 33:28:21:18	51:49	61:39	**7**
4	**1**	Neat	MW[f]	0.1	100	**4** 35:24:22:19	54:46	59:41	**7**
5	**1**	$CHCl_3$	25	72	100	**4** 41:25:18:16	57:43	66:34	**7**
6	**1**	Toluene	25	72	100	**4** 34:27:24:15	49:51	61:39	**7**
7	**2**	Neat	80	0.5	100	**5** 36:19:21:24	60:40	55:45	**8**
8	**2**	Neat	25	2	100	**5** 34:26:20:20	54:46	60:40	**8**
9	**2**	$CHCl_3$	25	90	100	**5** 39:22:20:19	58:42	61:39	**8**
10	**3**	Neat	80	0.5	100	**6** 74:5:11:10	84:16	79:21	**9**
11	**3**	Neat	25	4	100	**6** 100:0:0:0[g]	100:0	100:0	**9**
12	**3**	$CHCl_3$	25	72	100	**6** 78:7:7:8	86:14	85:15	**9**

[a] The reaction was stopped when no more starting material was observed (TLC).
[b] All reactions showed quantitative yields calculated with respect to the isolated mixture of isoxazolidines.
[c] Measured by NMR in the crude mixture of the reaction.
[d] Referred to the **a**+**d**:**b**+**c** ratio.
[e] Referred to the **a**+**b**:**c**+**d** ratio.
[f] Carried out in a conventional oven at 700 W.
[g] Only one isomer could be detected by NMR noise-to-signal ratio.

determined by spectroscopic means and it was assigned from further derivatives as discussed below.

N-Debenzylation was quantitatively achieved for compounds **7a** and **8a** by reaction with lithium in liquid ammonia (Scheme 3).



Scheme 3. *Reagents and conditions*: (i) Li/liquid NH_3.

In the case of compound **8a** the *O*-benzyl group was also eliminated and **11** was obtained. Compounds **10** and **11** can be considered immediate precursors of glycosyl pyrrolidines. The pyranosyl pyrrolidinone **9a** was further converted, after *N*-debenzylation with lithium in liquid ammonia into protected galactosyl pyrrolidine **15** by sequential *O*- and *N*-protection and reduction of the lactam moiety with $LiEt_3BH$ (Scheme 4). Compound **15** was obtained as a 3:1 mixture of isomers which were identified by NMR (see Section 4).

2.2. Determination of the absolute configuration

In order to determine the absolute configuration of the new stereogenic centers we applied Kakisawa's rule[17] for inferring the orientation of the hydroxyl group at C-3 in the pyrrolidinone rings. Since the relative *cis*/*trans*-configuration had been previously assigned, it was only necessary to prepare the corresponding Mosher esters of compounds **7a**, **7c**, **8a**, **8c**, **9a** and **9c**. For a

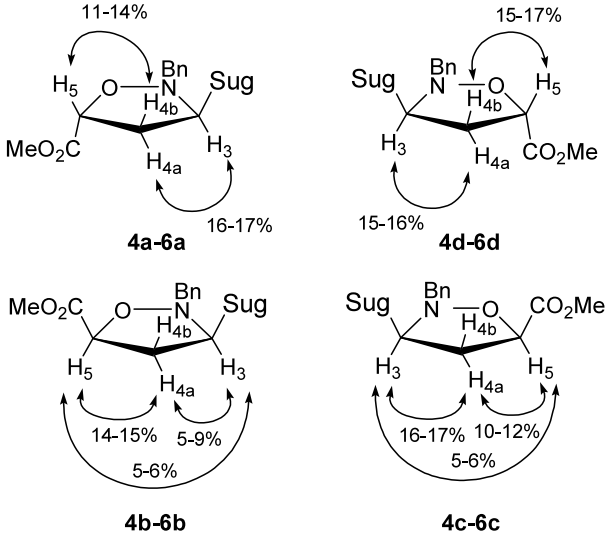
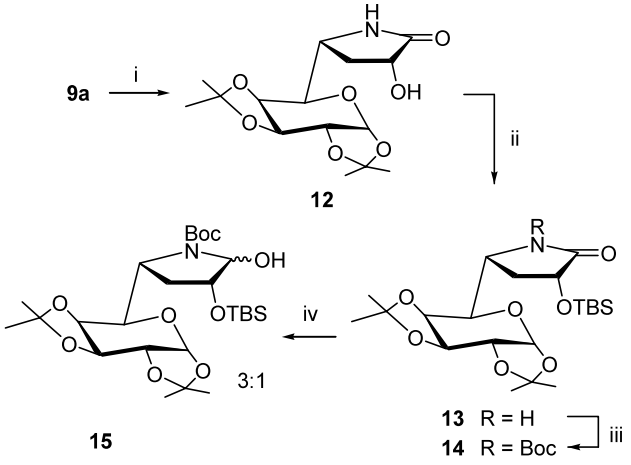


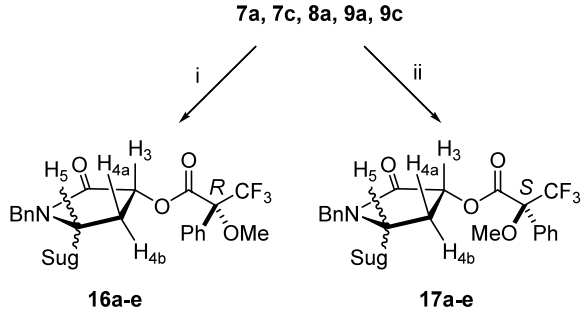
Figure 2. Selected NOE observed for **4**–**6** (η_{obs} given as percent of η_{max}).

successful application of Kakisawa's rule, we need a comparison between values corresponding to a pair of isomers having an opposite configuration. As a result we synthesized the corresponding Mosher esters derived from (*R*)- and (*S*)-Mosher acids (Scheme 5). This methodology is equivalent to that of preparing the esters of racemic mixtures using an only enantiomerically pure Mosher acid. Condensation of the corresponding alcohols with the acid chloride afforded pairs of diastereomeric esters which were purified by radial chromatography.

Only in the case of compound **8c** did we find that the reaction did not work and the corresponding esters could not be obtained. The ^1H NMR spectra of the esters were recorded and the differences in the chemical



Scheme 4. *Reagents and conditions*: (i) Li/liquid NH_3; (ii) TBSCl, DMF, imidazole; (iii) Boc_2O, DMPA, NEt_3, CH_2Cl_2; (iv) $LiEt_3BH$, THF.



Scheme 5. *Reagents and conditions*: (i) (+)-(*R*)-MTPA-Cl, DCC, DMAP, CH_2Cl_2; (ii) (−)-(*S*)-MTPA-Cl, DCC, DMAP, CH_2Cl_2.

shift calculated. The data are collected in Table 2. According to Kakisawa's rule, the methylene group (H_{4a} and H_{4b}) is selectively shielded by the phenyl group when the two groups are located on the same side of the plane containing H_3 and the carbonyl group (compounds **16a**–**e** in Scheme 4). In this way the absolute configuration (*R* or *S*) at the C-3 of the pyrrolidine ring could be determined independently of the other asymmetric centers of the molecule. By defining $\Delta\delta_a$ and $\Delta\delta_b$ as indicated in Eqs. (1) and (2) ($\delta_S H_{4a}$ and $\delta_S H_{4b}$ refers to the chemical shifts of (*S*)-MTPA esters, and $\delta_R H_{4a}$ and $\delta_R H_{4b}$ refers to the chemical shifts of (*R*)-MTPA esters), positive and negative values would indicate (*R*) and (*S*)-configurations, respectively, at C-3 in the pyrrolidine ring.

$$\Delta\delta_a = \delta_S H_{4a} - \delta_R H_{4a} \quad (1)$$

$$\Delta\delta_b = \delta_S H_{4b} - \delta_R H_{4b} \quad (2)$$

As indicated in Table 2 it was confirmed as an (*R*)-configuration for compounds **7a**, **7c**, **8a**, **9a** and **9c** thus unequivocally ascertaining the absolute configuration for the rest of isomers, too.

In addition, we were able to obtain a single crystal of compound **9a** suitable for carrying out an X-ray analysis. This analysis[18] (Fig. 3) further confirmed the assigned configuration for that compound.

3. Conclusions

In conclusion, we have studied the 1,3-dipolar cycloaddition between *N*-benzyl-*C*-glycosyl nitrones and methyl acrylate as a novel route for the preparation of glycosyl pyrrolidines. Of the three chiral non-racemic nitrones used in this work, the furanosyl nitrones **1** and **2** showed little *endo*/*exo* and diastereofacial selectivities, whereas the pyranosyl nitrone **3** was much more selective and only one isomer was obtained. The synthetic utility of the methodology was addressed by preparing the protected glycosyl pyrrolidine **15**, consisting of a D-galactosyl unit directly linked to a 2,3-dihydroxypyrrolidine. The complete protection of all functional groups in **15** but leaving the free hydroxyl group at C-2 in the pyrrolidine ring, made this compound to be considered as a useful building block for the construction of more complex structures by means of glycosilation reactions. Further studies in connection to the enhancement of the selectivities for furanosyl nitrones and application to the synthesis of carbohydrate mimics are the subject of ongoing investigations.

Table 2. Selected chemical shifts and differences for **16a**–**e** and **17a**–**e**[a]

	MTPA-Cl	Ester	δH_{4a}	$\Delta\delta_a$	δH_{4b}	$\Delta\delta_b$	Conf.
7a	*R*	**16a**	2.63	+0.01	2.22	+0.14	*R*
	S	**17a**	2.64		2.36		
7c	*R*	**16b**	2.37	+0.03	2.08	+0.18	*R*
	S	**17b**	2.40		2.26		
8a	*R*	**16c**	2.58	+0.02	2.22	+0.18	*R*
	S	**17c**	2.60		2.40		
9a	*R*	**16d**	2.60	+0.03	2.26	+0.15	*R*
	S	**17d**	2.63		2.41		
9c	*R*	**16e**	2.52	+0.02	1.92	+0.19	*R*
	S	**17e**	2.54		2.11		

[a] All reactions were carried out neat except for entry 6 which was carried out in toluene as a solvent.

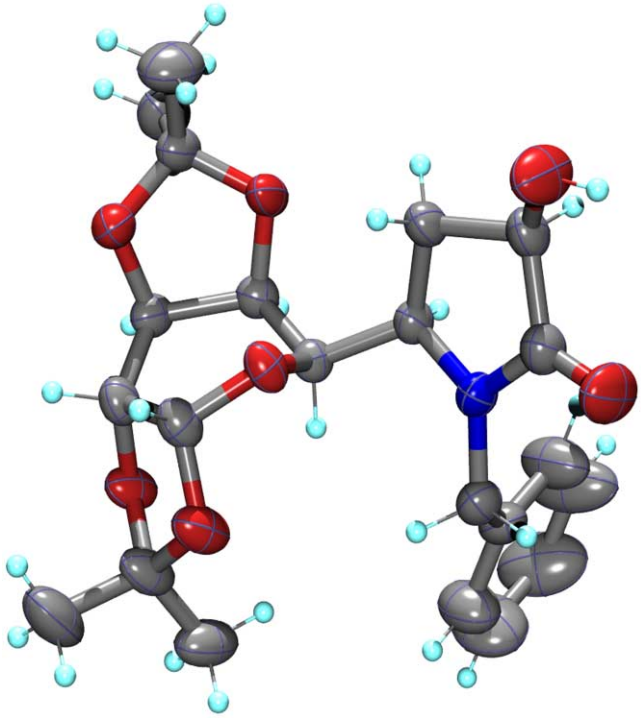


Figure 3. Perspective view (ORTEP) of **9a**. Non-hydrogen atoms are drawn as 50% thermal ellipsoids while hydrogens are drawn at an arbitrary size. Only the atoms refined with anisotropic thermal parameters are drawn with the principal axes indicated; the isotropic atoms are represented as simple circles.

4. Experimental

The reaction flasks and other glass equipment were heated in an oven at 130°C overnight and assembled in a stream of Ar. All reactions were monitored by TLC on silica gel 60 F254; the position of the spots were detected with 254 nm UV light or by spraying with one of the following staining systems: 50% methanolic sulfuric acid, 5% ethanolic phosphomolybdic acid and iodine. Preparative centrifugally accelerated radial thin-layer chromatography (radial chromatography) was performed with a Chromatotron® model 7924 T (Harrison Research, Palo Alto, CA, USA) and with solvents that were distilled prior to use; the rotors (1 or 2 mm layer thickness) were coated with silica gel Merck grade type 7749, TLC grade, with binder and fluorescence indicator (Aldrich 34,644-6) and the eluting solvents delivered by the pump at a flow-rate of 0.5–1.5 mL min^{-1}. Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian Unity or on a Bruker 300 instrument in $CDCl_3$. Chemical shifts are reported in ppm (δ) relative to $CHCl_3$ ($\delta = 7.26$) in $CDCl_3$. Optical rotations were taken at 25°C on a Perkin–Elmer 241 polarimeter. Elemental analyses were performed on a Perkin–Elmer 240B microanalyzer. Nitrones **1**, **2** and **3** were prepared from D-ribose, D-glucose and D-galactose, respectively, as described.[16]

4.1. 1,3-Dipolar cycloaddition of nitrones 1-3 with methyl acrylate. General procedure

The corresponding nitrone **1**–**3** (2 mmol) was dissolved in methyl acrylate (5.92 g, 80 mmol) and the resulting solution stirred at reflux until no more nitrone was observed (TLC). The reaction mixture was evaporated to dryness and the residue analyzed by NMR to determine the diastereomeric ratio. Purification by radial chromatography gave the pure adducts (eluent is given in brackets).

4.1.1. 4-[(3*R*,5*R*)-2-Benzyl-5-(methoxycarbonyl)-3-isoxazolidinyl]-2,3-*O*-isopropyliden-1-*O*-methyl-α-D-*lyxo*-tetrofuranose 4a. (Hexane/EtOAc, 80:20; $R_f = 0.30$); 0.268 g (34%); oil; $[\alpha]_D^{25} = +113$ (*c* 1.21, $CHCl_3$); IR ($\nu_{C=O}$) 1730 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.23 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 2.71 (td, 1H, $J = 7.7$, 12.9 Hz, H_{4b}), 2.80 (ddd, 1H, $J = 3.1$, 8.4, 12.9 Hz, H_{4a}), 3.30 (s, 3H, OCH_3), 3.76 (dt, 1H, $J = 3.1$, 8.5 Hz, H_3), 3.78 (s, 3H, OCH_3), 3.85 (dd, 1H, $J = 3.3$, 8.6 Hz, $H_{4'}$), 3.96 (d, 1H, $J = 13.3$ Hz, NCH_2Ph), 4.23 (d, 1H, $J = 13.3$ Hz, NCH_2Ph), 4.50 (d, 1H, $J = 5.8$ Hz, $H_{2'}$), 4.58 (t, 1H, $J = 8.1$ Hz, H_5), 4.69 (dd, 1H, $J = 3.3$, 5.8 Hz, $H_{3'}$), 4.83 (s, 1H, $H_{1'}$), 7.20–7.32 (m, 5H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.7, 25.9, 35.3, 37.6, 52.1, 54.4, 62.4, 63.3, 79.7, 79.8, 85.2, 107.4, 112.2, 127.1, 128.1, 129.4, 137.7, 172.9. Anal. calcd for $C_{20}H_{27}NO_7$: C, 61.06; H, 6.92; N, 3.56. Found: C, 61.30; H, 6.96; N, 3.70.

4.1.2. 4-[(3*R*,5*S*)-2-Benzyl-5-(methoxycarbonyl)-3-isoxazolidinyl]-2,3-*O*-isopropyliden-1-*O*-methyl-α-D-*lyxo*-tetrofuranose 4b. (Hexane/EtOAc, 80:20; $R_f = 0.28$); 0.196 g (25%); oil; $[\alpha]_D^{25} = +24$ (*c* 0.12, $CHCl_3$); IR ($\nu_{C=O}$) 1735 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.21 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 2.62 (ddd, 1H, $J = 3.4$, 5.9, 12.9 Hz, H_{4b}), 2.73 (ddd, 1H, $J = 7.8$, 9.2, 12.9 Hz, H_{4a}), 3.25 (s, 3H, OCH_3), 3.65 (ddd, 1H, $J = 3.4$, 7.8, 9.5 Hz, H_3), 3.72 (s, 3H, OCH_3), 3.89 (dd, 1H, $J = 3.4$, 9.5 Hz, $H_{4'}$), 3.97 (d, 1H, $J = 13.4$ Hz, NCH_2Ph), 4.02 (d, 1H, $J = 13.4$ Hz, NCH_2Ph), 4.46 (d, 1H, $J = 5.9$, $H_{2'}$), 4.69 (dd, 1H, $J = 3.4$, 5.9 Hz, $H_{3'}$), 4.70 (dd, 1H, $J = 5.9$, 9.2 Hz, H_5), 4.78 (s, 1H, $H_{1'}$), 7.15–7.45 (m, 5H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.7, 25.9, 30.6, 35.5, 52.0, 54.0, 61.2, 62.5, 79.5, 80.0, 85.2, 107.0, 112.1, 127.2, 128.1, 129.3, 137.0, 171.5. Anal. calcd for $C_{20}H_{27}NO_7$: C, 61.06; H, 6.92; N, 3.56. Found: C, 61.22; H, 6.85; N, 3.62.

4.1.3. 4-[(3*S*,5*R*)-2-Benzyl-5-(methoxycarbonyl)-3-isoxazolidinyl]-2,3-*O*-isopropyliden-1-*O*-methyl-α-D-*lyxo*-tetrofuranose 4c. (Hexane/EtOAc, 80:20; $R_f = 0.21$); 0.174 g (22%); oil; $[\alpha]_D^{25} = -35$ (*c* 0.75, $CHCl_3$); IR ($\nu_{C=O}$) 1732 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.27 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 2.33 (ddd, 1H, $J = 5.3$, 8.3, 13.1 Hz, H_{4b}), 2.86 (ddd, 1H, $J = 8.3$, 9.1, 13.1 Hz, H_{4a}), 3.21 (q, 1H, $J = 8.3$ Hz, H_3), 3.26 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.94 (d, 1H, $J = 15.2$ Hz, NCH_2Ph), 4.00 (dd, 1H, $J = 3.5$, 8.3 Hz, $H_{4'}$), 4.51 (d, 1H, $J = 5.8$ Hz, $H_{2'}$), 4.52 (d, 1H, $J = 15.2$ Hz, NCH_2Ph), 4.53 (dd, 1H, $J = 5.3$, 9.1 Hz, H_5), 4.67 (dd, 1H, $J = 3.5$, 5.8 Hz, $H_{3'}$), 4.90 (s, 1H, $H_{1'}$), 7.18–7.34 (m, 5H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.9, 26.1, 35.8, 38.2, 52.3, 54.6, 60.7, 64.1, 80.9, 81.2, 84.5, 107.4, 112.6, 126.9, 128.1, 128.8, 137.6,

172.8. Anal. calcd for $C_{20}H_{27}NO_7$: C, 61.06; H, 6.92; N, 3.56. Found: C, 60.99; H, 6.87; N, 3.51.

4.1.4. 4-[(3*S*,5*S*)-2-Benzyl-5-(methoxycarbonyl)-3-isoxazolidinyl]-2,3-*O*-isopropyliden-1-*O*-methyl-α-D-*lyxo*-tetrofuranose 4d. (Hexane/EtOAc, 80:20; $R_f=0.17$); 0.150 g (19%); oil; $[\alpha]_D^{25}=-168$ (*c* 0.35, $CHCl_3$); IR ($\nu_{C=O}$) 1730 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.28 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 2.41 (td, 1H, $J=8.9$, 12.6 Hz, H_{4a}), 2.71 (ddd, 1H, $J=5.3$, 7.4, 12.6 Hz, H_{4b}), 3.32 (s, 3H, OCH_3), 3.39 (q, 1H, $J=8.1$ Hz, H_3), 3.74 (s, 3H, OCH_3), 3.99 (dd, 1H, $J=3.6$, 7.8 Hz, $H_{4'}$), 4.08 (d, 1H, $J=14.3$ Hz, NCH_2Ph), 4.47 (d, 1H, $J=14.3$ Hz, NCH_2Ph), 4.50 (d, 1H, $J=5.8$ Hz, $H_{2'}$), 4.51 (dd, 1H, $J=5.3$, 8.9 Hz, H_5), 4.66 (dd, 1H, $J=3.6$, 5.8 Hz, $H_{3'}$), 4.92 (s, 1H, $H_{1'}$), 7.18–7.34 (m, 5H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.9, 26.1, 32.8, 36.5, 52.2, 53.7, 62.2, 64.0, 74.8, 80.7, 84.6, 107.3, 112.7, 127.0, 128.2, 129.1, 138.2, 172.6. Anal. calcd for $C_{20}H_{27}NO_7$: C, 61.06; H, 6.92; N, 3.56. Found: C, 61.19; H, 7.04; N, 3.49.

4.1.5. 4-[(3*R*,5*R*)-2-Benzyl-5-(methoxycarbonyl)-3-isoxazolidinyl]-3-*O*-benzyl-1,2-*O*-isopropyliden-α-D-*xylo*-tetrofuranose 5a. (Hexane/Et_2O, 60:40; $R_f=0.29$); 0.338 g (36%); oil; $[\alpha]_D^{25}=-21$ (*c* 1.25, $CHCl_3$); IR ($\nu_{C=O}$) 1725 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.29 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 2.73 (td, 1H, $J=7.6$, 13.1 Hz, H_{4b}), 2.92 (ddd, 1H, $J=1.7$, 8.5, 13.1 Hz, H_{4a}), 3.75 (d, 2H, $J=13.3$ Hz, NCH_2Ph), 3.76 (s, 3H, OCH_3), 3.91 (m, 1H, H_3), 4.07 (d, 1H, $J=3.0$ Hz, $H_{3'}$), 4.10 (dd, 1H, $J=3.0$, 9.1 Hz, $H_{4'}$), 4.20 (d, 2H, $J=13.3$ Hz, NCH_2Ph), 4.30 (d, 1H, $J=11.7$ Hz, OCH_2Ph), 4.49 (d, 1H, $J=11.7$ Hz, OCH_2Ph), 4.54 (d, 1H, $J=3.8$ Hz, $H_{2'}$), 4.61 (t, 1H, $J=8.4$ Hz, H_5), 5.88 (d, 1H, $J=3.8$ Hz, $H_{1'}$), 7.15–7.38 (m, 10H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 26.2, 26.8, 34.8, 52.4, 62.4, 63.0, 72.0, 77.2, 79.8, 81.7, 82.3, 105.0, 111.7, 127.3, 127.6, 127.9, 128.3, 128.5, 129.4, 137.5, 127.6, 173.2. Anal. calcd for $C_{26}H_{31}NO_7$: C, 66.51; H, 6.65; N, 2.98. Found: C, 66.36; H, 6.57; N, 2.95.

4.1.6. 4-[(3*R*,5*S*)-2-Benzyl-5-(methoxycarbonyl)-3-isoxazolidinyl]-3-*O*-benzyl-1,2-*O*-isopropyliden-α-D-*xylo*-tetrofuranose 5b. (Hexane/Et_2O, 60:40; $R_f=0.21$); 0.178 g (19%); oil; $[\alpha]_D^{25}=-4$ (*c* 0.75, $CHCl_3$); IR ($\nu_{C=O}$) 1732 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.27 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 2.67 (ddd, 1H, $J=2.5$, 5.6, 13.4 Hz, H_{4b}), 2.76 (ddd, 1H, $J=7.7$, 9.8, 13.4 Hz, H_{4a}), 3.71 (s, 3H, OCH_3), 3.75 (d, 1H, $J=13.6$ Hz, NCH_2Ph), 3.78 (ddd, 1H, $J=2.5$, 7.7, 9.9 Hz, H_3), 3.89 (d, 1H, $J=13.6$ Hz, NCH_2Ph), 4.09 (d, 1H, $J=3.1$ Hz, $H_{3'}$), 4.23 (dd, 1H, $J=3.1$, 9.9 Hz, $H_{4'}$), 4.30 (d, 1H, $J=11.7$ Hz, OCH_2Ph), 4.50 (d, 1H, $J=11.7$ Hz, OCH_2Ph), 4.52 (d, 1H, $J=3.7$ Hz, $H_{2'}$), 4.72 (dd, 1H, $J=5.6$, 9.8 Hz, H_5), 5.83 (d, 1H, $J=3.7$ Hz, $H_{1'}$), 7.16–7.30 (m, 10H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 26.5, 26.8, 35.4, 52.3, 61.1, 62.1, 71.9, 75.3, 80.6, 81.7, 82.3, 104.8, 111.9, 127.5, 127.5, 127.8, 128.3, 128.4, 129.0, 136.8, 137.6, 171.5. Anal. calcd for $C_{26}H_{31}NO_7$: C, 66.51; H, 6.65; N, 2.98. Found: C, 66.73; H, 6.79; N, 3.13.

4.1.7. 4-[(3*S*,5*R*)-2-Benzyl-5-(methoxycarbonyl)-3-isoxazolidinyl]-3-*O*-benzyl-1,2-*O*-isopropyliden-α-D-*xylo*-tetrofuranose 5c. (Hexane/Et_2O, 60:40; $R_f=0.15$); 0.196 g (21%); oil; $[\alpha]_D^{25}=-97$ (*c* 0.70, $CHCl_3$); IR ($\nu_{C=O}$) 1728 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.32 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 2.17 (ddd, 1H, $J=5.0$, 8.3, 12.6 Hz, H_{4b}), 2.58 (ddd, 1H, $J=8.3$, 9.1, 12.6 Hz, H_{4a}), 3.28 (q, 1H, $J=8.3$ Hz, H_3), 3.74 (s, 3H, OCH_3), 3.89 (d, 1H, $J=15.1$ Hz, NCH_2Ph), 3.92 (d, 1H, $J=3.3$ Hz, $H_{3'}$), 4.25 (dd, 1H, $J=3.3$, 8.6 Hz, $H_{4'}$), 4.46 (d, 1H, $J=11.6$ Hz, OCH_2Ph), 4.49 (dd, 1H, $J=5.0$, 9.1 Hz, H_5), 4.56 (d, 1H, $J=15.1$ Hz, NCH_2Ph), 4.61 (d, 1H, $J=3.9$ Hz, $H_{2'}$), 4.70 (d, 1H, $J=11.6$ Hz, OCH_2Ph), 5.97 (d, 1H, $J=3.9$ Hz, $H_{1'}$), 7.20–7.50 (m, 10H, ArH). ^{13}C NMR ($CDCl_3$) δ 26.3, 26.8, 35.5, 52.2, 60.8, 64.2, 71.8, 74.0, 81.2, 81.8, 83.5, 105.6, 111.8, 126.8, 127.8, 128.0, 128.2, 128.4, 128.6, 137.1, 137.8, 172.8. Anal. calcd for $C_{26}H_{31}NO_7$: C, 66.51; H, 6.65; N, 2.98. Found: C, 66.69; H, 6.58; N, 3.09.

4.1.8. 4-[(3*S*,5*S*)-2-Benzyl-5-(methoxycarbonyl)-3-isoxazolidinyl]-3-*O*-benzyl-1,2-*O*-isopropyliden-α-D-*xylo*-tetrofuranose 5d. (Hexane/Et_2O, 60:40; $R_f=0.10$); 0.226 g (24%); white solid; mp 106–108°C; $[\alpha]_D^{25}=-67$ (*c* 0.95, $CHCl_3$); IR ($\nu_{C=O}$) 1730 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.31 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 2.18 (td, 1H, $J=8.8$, 12.4 Hz, H_{4a}), 2.37 (ddd, 1H, $J=4.8$, 7.3, 12.4 Hz, H_{4b}), 3.44 (dt, 1H, $J=7.3$, 8.8 Hz, H_3), 3.71 (s, 3H, OCH_3), 3.87 (d, 1H, $J=3.3$ Hz, $H_{3'}$), 4.03 (d, 1H, $J=14.1$ Hz, NCH_2Ph), 4.41 (d, 1H, $J=14.1$ Hz, NCH_2Ph), 4.20 (dd, 1H, $J=3.3$, 8.6 Hz, $H_{4'}$), 4.42 (d, 1H, $J=11.7$ Hz, OCH$_2$Ph), 4.44 (dd, 1H, $J=4.8$, 8.8 Hz, H_5), 4.60 (d, 1H, $J=3.9$ Hz, $H_{2'}$), 4.69 (d, 1H, $J=11.7$ Hz, OCH$_2$Ph), 5.96 (d, 1H, $J=3.9$ Hz, $H_{1'}$), 7.17–7.43 (m, 10H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 26.3, 26.7, 36.1, 52.2, 62.4, 63.7, 71.8, 74.9, 81.2, 81.7, 82.9, 105.5, 111.8, 127.0, 128.0, 128.1, 128.2, 128.6, 129.1, 136.9, 138.2, 172.1. Anal. calcd for $C_{26}H_{31}NO_7$: C, 66.51; H, 6.65; N, 2.98. Found: C, 66.61; H, 6.52; N, 2.92.

4.1.9. 5-[(3*R*,5*R*)-2-Benzyl-5-(methoxycarbonyl)-3-isoxazolidinyl]-1,2:3,4-di-*O*-isopropyliden-α-D-*galacto*-pentopyranose 6a. (Hexane/Et_2O, 60:40; $R_f=0.41$); 0.664 g (74%); white solid; mp 117–119°C; $[\alpha]_D^{25}=-82$ (*c* 0.40, $CHCl_3$); IR ($\nu_{C=O}$) 1730 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.23 (s, 3H, CH_3), 1.31 (s, 6H, CH_3), 1.47 (s, 3H, CH_3), 2.64 (ddd, 1H, $J=7.0$, 8.4, 13.0 Hz, H_{4b}), 2.85 (ddd, 1H, $J=1.8$, 8.4, 13.0 Hz, H_{4a}), 3.56 (dd, 1H, $J=1.3$, 10.0 Hz, $H_{5'}$), 3.67 (ddd, 1H, $J=1.8$, 7.0, 10.0 Hz, H_3), 3.77 (s, 3H, OCH_3), 3.87 (d, 1H, $J=13.2$ Hz, NCH_2Ph), 4.24 (d, 1H, $J=13.2$ Hz, NCH_2Ph), 4.26 (dd, 1H, $J=2.1$, 4.9 Hz, $H_{2'}$), 4.43 (dd, 1H, $J=1.3$, 8.1 Hz, $H_{4'}$), 4.49 (t, 1H, $J=8.4$ Hz, H_5), 4.52 (dd, 1H, $J=2.1$, 8.1 Hz, $H_{3'}$), 5.48 (d, 1H, $J=4.9$ Hz, $H_{1'}$), 7.20–7.42 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$) δ 24.0, 24.9, 25.8, 26.2, 34.1, 52.1, 62.6, 64.1, 64.7, 67.1, 70.7, 70.8, 71.2, 96.6, 108.4, 108.7, 127.1, 128.1, 129.5, 137.6, 173.0. Anal. calcd for $C_{23}H_{31}NO_8$: C, 61.46; H, 6.95; N, 3.12. Found: C, 61.55; H, 7.03; N, 3.00.

4.1.10. 5-[(3*R*,5*S*)-2-Benzyl-5-(methoxycarbonyl)-3-isoxazolidinyl]-1,2:3,4-di-*O*-isopropyliden-α-D-*galacto*-pentopyranose 6b. (Hexane/Et_2O, 60:40; $R_f=0.35$); 0.046 g (5%); oil; $[\alpha]_D^{25}=-26$ (*c* 0.40, $CHCl_3$); IR ($\nu_{C=O}$) 1738 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.20 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.48 (s, 6H, CH_3), 2.54 (ddd, 1H, $J=2.8$, 6.6, 13.2 Hz, H_{4b}), 2.72 (ddd, 1H, $J=8.2$, 9.2, 13.2 Hz, H_{4a}), 3.54 (dt, 1H, $J=2.8$, 8.2 Hz, H_3), 3.67 (d, 1H, $J=8.2$, $H_{5'}$), 3.70 (s, 3H, OCH_3), 3.89 (d, 1H, $J=13.1$ Hz, NCH_2Ph), 4.02 (d, 1H, $J=13.1$ Hz, NCH_2Ph), 4.19 (dd, 1H, $J=1.9$, 4.9 Hz, $H_{2'}$), 4.43 (bd, 1H, $J=8.0$ Hz, $H_{4'}$), 4.49 (dd, 1H, $J=1.9$, 8.0 Hz, $H_{3'}$), 4.72 (dd, 1H, $J=6.6$, 9.2 Hz, H_5), 5.44 (d, 1H, $J=4.9$ Hz, $H_{1'}$), 7.20–7.40 (m, 5H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 23.8, 24.6, 25.7, 25.8, 35.3, 52.0, 57.7, 61.2, 63.5, 68.6, 70.7, 70.8, 71.0, 96.3, 108.4, 109.3, 127.2, 128.1, 129.4, 136.9, 171.0. Anal. calcd for $C_{23}H_{31}NO_8$: C, 61.46; H, 6.95; N, 3.12. Found: C, 61.32; H, 7.03; N, 3.21.

4.1.11. 5-[(3*S*,5*R*)-2-Benzyl-5-(methoxycarbonyl)-3-isoxazolidinyl]-1,2:3,4-di-*O*-isopropyliden-α-D-*galacto*-pentopyranose 6c. (Hexane/Et_2O, 60:40; $R_f=0.19$); 0.098 g (11%); oil; $[\alpha]_D^{25}=-55$ (*c* 0.90, $CHCl_3$); IR ($\nu_{C=O}$) 1736 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.30 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 2.43 (ddd, 1H, $J=5.5$, 7.7, 12.5 Hz, H_{4b}), 2.68 (ddd, 1H, $J=8.1$, 8.8, 12.5 Hz, H_{4a}), 3.20 (q, 1H, $J=8.0$ Hz, H_3), 3.69 (s, 3H, OCH_3), 3.88 (dd, 1H, $J=1.8$, 8.1 Hz, $H_{5'}$), 3.90 (d, 1H, $J=14.6$ Hz, NCH_2Ph), 4.23 (dd, 1H, $J=1.8$, 7.9 Hz, $H_{4'}$), 4.26 (dd, 1H, $J=2.5$, 5.0 Hz, $H_{2'}$), 4.46 (d, 1H, $J=14.6$ Hz, NCH_2Ph), 4.49 (dd, 1H, $J=5.5$, 8.8 Hz, H_5), 4.57 (dd, 1H, $J=2.5$, 7.9 Hz, $H_{3'}$), 5.78 (d, 1H, $J=5.0$ Hz, $H_{1'}$), 7.14–7.44 (m, 5H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.5, 25.1, 26.0, 26.0, 35.0, 52.2, 61.0, 64.1, 69.5, 70.3, 70.9, 72.3, 74.2, 96.3, 108.9, 109.4, 126.8, 127.9, 129.0, 137.8, 172.6. Anal. calcd for $C_{23}H_{31}NO_8$: C, 61.46; H, 6.95; N, 3.12. Found: C, 61.21; H, 7.08; N, 3.25.

4.1.12. 5-[(3*S*,5*S*)-2-Benzyl-5-(methoxycarbonyl)-3-isoxazolidinyl]-1,2:3,4-di-*O*-isopropyliden-α-D-*galacto*-pentopyranose 6d. (Hexane/Et_2O, 60:40; $R_f=0.16$); 0.090 g (10%); oil; $[\alpha]_D^{25}=-38$ (*c* 1.25, $CHCl_3$); IR ($\nu_{C=O}$) 1734 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.31 (s, 6H, CH_3), 1.43 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 2.53 (td, 1H, $J=8.8$, 12.5 Hz, H_{4a}), 2.61 (ddd, 1H, $J=5.1$, 7.3, 12.5 Hz, H_{4b}), 3.34 (q, 1H, $J=7.7$ Hz, H_3), 3.74 (s, 3H, OCH_3), 3.86 (dd, 1H, $J=1.8$, 7.4 Hz, $H_{5'}$), 4.06 (d, 1H, $J=14.0$ Hz, NCH_2Ph), 4.24 (dd, 1H, $J=1.8$, 8.1 Hz, $H_{4'}$), 4.26 (dd, 1H, $J=2.6$, 4.8 Hz, $H_{2'}$), 4.39 (d, 1H, $J=14.0$ Hz, NCH_2Ph), 4.52 (dd, 1H, $J=5.1$, 8.8 Hz, H_5), 4.58 (dd, 1H, $J=2.6$, 8.1 Hz, $H_{3'}$), 5.50 (d, 1H, $J=4.8$ Hz, $H_{1'}$), 7.10–7.40 (m, 5H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.4, 25.0, 25.9, 26.1, 35.6, 51.9, 62.4, 64.4, 69.5, 70.7, 71.0, 72.1, 75.2, 96.3, 108.8, 109.5, 126.8, 128.0, 129.1, 138.4, 172.3. Anal. calcd for $C_{23}H_{31}NO_8$: C, 61.46; H, 6.95; N, 3.12. Found: C, 61.64; H, 6.82; N, 3.23.

4.2. Reduction of ixoazolidines 4–6. Synthesis of pyrrolidin-2-ones 7–9. General procedure

A solution of the corresponding isoxazolidine (1 mmol) in THF (10 mL) was treated with glacial acetic acid (20 mL), water (10 mL) and Zn dust (0.200 g, 3.1 mmol); the resulting solution was heated at 60°C for 5 h. After cooling at ambient temperature, the reaction mixture was filtered through a plug of Celite. The filtrate was treated with a saturated aqueous solution of sodium carbonate and the resulting mixture extracted with CH_2Cl_2 (3×15 mL). The combined organic layers were washed with brine, dried over magnesium sulfate and evaporated to yield a residue which was purified by radial chromatography.

4.2.1. 4-[(3*R*,5*R*)-1-Benzyl-3-hydroxy-2-oxo-5-pyrrolidinyl]-2,3-*O*-isopropyliden-1-*O*-methyl-α-D-*lyxo*-tetrofuranose 7a. (Et_2O; $R_f=0.31$); 0.291 g (80%); white solid; mp 136–138°C; $[\alpha]_D^{25}=+88$ (*c* 0.25, $CHCl_3$); IR ($\nu_{C=O}$) 1680 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.24 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 2.22 (td, 1H, $J=5.4$, 14.0 Hz, H_{4b}), 2.49 (td, 1H, $J=7.6$, 14.0 Hz, H_{4a}), 3.23 (s, 3H, OCH_3), 3.79 (bs, 1H, O*H*), 3.83 (td, 1H, $J=5.0$, 7.6 Hz, H_5), 4.02–4.04 (bs, 1H, $H_{4'}$), 4.28 (d, 1H, $J=15.2$ Hz, NCH_2Ph), 4.33 (dd, 1H, $J=5.4$, 7.6 Hz, H_3), 4.46–4.50 (m, 2H, $H_{2'}$ and $H_{3'}$), 4.87 (d, 1H, $J=15.2$ Hz, NCH_2Ph), 4.89 (s, 1H, $H_{1'}$), 7.08–7.18 (m, 5H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.3, 25.7, 30.9, 45.3, 54.5, 54.8, 69.6, 78.0, 79.6, 85.3, 106.7, 112.8, 127.6, 127.7, 128.7, 136.6, 175.5. Anal. calcd for $C_{19}H_{25}NO_6$: C, 62.80; H, 6.93; N, 3.85. Found: C, 62.95; H, 6.97; N, 4.00.

4.2.2. 4-[(3*S*,5*R*)-1-Benzyl-3-hydroxy-2-oxo-5-pyrrolidinyl]-2,3-*O*-isopropyliden-1-*O*-methyl-α-D-*lyxo*-tetrofuranose 7b. (Et_2O; $R_f=0.20$); 0.254 g (70%); oil; $[\alpha]_D^{25}=+79$ (*c* 0.71, $CHCl_3$); IR ($\nu_{C=O}$) 1680 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.26 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 2.03 (td, 1H, $J=8.9$, 13.6 Hz, H_{4b}), 2.27 (ddd, 1H, $J=1.6$, 8.1, 13.6 Hz, H_{4a}), 3.25 (s, 3H, OCH_3), 3.70 (bs, 1H, O*H*), 3.76 (dt, 1H, $J=1.6$, 8.5 Hz, H_5), 3.85 (dd, 1H, $J=3.5$, 8.5 Hz, $H_{4'}$), 4.34 (d, 1H, $J=14.3$ Hz, NCH_2Ph), 4.50 (t, 1H, $J=8.6$ Hz, H_3), 4.51 (d, 1H, $J=5.8$ Hz, $H_{2'}$), 4.66 (dd, 1H, $J=3.5$, 5.8 Hz, $H_{3'}$), 4.93 (s, 1H, $H_{1'}$), 5.09 (d, 1H, $J=14.3$ Hz, NCH_2Ph), 7.20–7.27 (m, 5H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.9, 26.0, 31.6, 46.3, 53.3, 54.8, 68.9, 80.4, 83.5, 84.3, 107.7, 112.9, 127.6, 128.6, 128.8, 136.3, 175.2. Anal. calcd for $C_{19}H_{25}NO_6$: C, 62.80; H, 6.93; N, 3.85. Found: C, 62.88; H, 6.89; N, 4.72.

4.2.3. 4-[(3*R*,5*S*)-1-Benzyl-3-hydroxy-2-oxo-5-pyrrolidinyl]-2,3-*O*-isopropyliden-1-*O*-methyl-α-D-*lyxo*-tetrofuranose 7c. (Et_2O; $R_f=0.16$); 0.285 g (78%); oil; $[\alpha]_D^{25}=+176$ (*c* 0.62, $CHCl_3$); IR ($\nu_{C=O}$) 1690 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.25 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 2.03 (td, 1H, $J=8.5$, 13.6 Hz, H_{4b}), 2.26 (ddd, 1H, $J=1.5$, 8.5, 13.6 Hz, H_{4a}), 3.24 (s, 3H, OCH_3), 3.75 (dt, 1H, $J=1.5$, 8.5 Hz, H_5), 3.84 (dd, 1H, $J=3.3$, 8.5 Hz, $H_{4'}$), 4.15 (bs, 1H, O*H*), 4.32 (d, 1H, $J=14.3$ Hz, NCH_2Ph), 4.50 (d, 1H, $J=5.9$ Hz, $H_{2'}$), 4.50 (t, 1H, $J=8.5$ Hz, H_3), 4.67 (dd, 1H, $J=3.3$, 5.9 Hz, $H_{3'}$), 4.90 (s, 1H, $H_{1'}$), 5.08 (d, 1H, $J=14.3$ Hz, NCH_2Ph), 7.18–7.35 (m, 5H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.9, 25.9, 31.6, 46.3, 53.4, 54.8, 68.9, 80.4, 83.5, 84.3, 107.7, 112.9, 127.5, 128.6, 128.8, 136.3, 175.5. Anal. calcd for $C_{19}H_{25}NO_6$: C, 62.80; H, 6.93; N, 3.85. Found: C, 62.92; H, 6.86; N, 3.75.

4.2.4. 4-[(3*S*,5*S*)-1-Benzyl-3-hydroxy-2-oxo-5-pyrrolidinyl]-2,3-*O*-isopropyliden-1-*O*-methyl-α-D-*lyxo*-tetrofuranose 7d. (Et_2O; $R_f=0.32$); 0.327 g (90%); white solid; mp 76–78°C; $[\alpha]_D^{25}=+46$ (*c* 0.30, $CHCl_3$); IR ($\nu_{C=O}$) 1685 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.26 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.72 (td, 1H, $J=6.7$, 13.4 Hz, H_{4b}), 2.61 (ddd, 1H, $J=7.2$, 8.3, 13.4 Hz, H_{4a}), 3.14 (s, 3H, OCH_3), 3.74 (dt, 1H, $J=6.7$, 8.3 Hz, H_5), 3.95 (dd, 1H, $J=3.5$, 8.3 Hz, $H_{4'}$), 4.34 (t, 1H, $J=7.1$ Hz, H_3), 4.48 (d, 1H, $J=5.8$ Hz, $H_{2'}$), 4.49 (d, 1H, $J=14.4$ Hz, NCH_2Ph), 4.71 (dd, 1H, $J=3.5$, 5.8 Hz, $H_{3'}$), 4.91 (s, 1H, $H_{1'}$), 4.98 (d, 1H, $J=14.4$ Hz, NCH_2Ph), 4.60 (bs, 1H, O*H*), 7.07–7.19 (m, 5H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.9, 26.0, 30.8, 45.9, 54.7, 54.8, 69.3, 80.5, 84.8 (2C), 107.9, 112.7, 127.3, 128.3, 128.4, 137.1, 175.7. Anal. calcd for $C_{19}H_{25}NO_6$: C, 62.80; H, 6.93; N, 3.85. Found: C, 62.72; H, 6.95; N, 3.91.

4.2.5. 4-[(3*R*,5*R*)-1-Benzyl-3-hydroxy-2-oxo-5-pyrrolidinyl]-3-*O*-benzyl-1,2-*O*-isopropyliden-α-D-*xylo*-tetrofuranose 8a. (Et_2O; $R_f=0.27$); 0.334 g (76%); white solid; mp 152–154°C; $[\alpha]_D^{25}=-22$ (*c* 0.88, $CHCl_3$); IR ($\nu_{C=O}$) 1700 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.26 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 2.23 (td, 1H, $J=5.6$, 14.0 Hz, H_{4b}), 2.42 (td, 1H, $J=7.8$, 14.0 Hz, H_{4a}), 3.75 (ddd, 1H, $J=3.4$, 5.6, 7.4 Hz, H_5), 3.80 (d, 1H, $J=3.4$ Hz, $H_{3'}$), 4.09 (bs, 1H, O*H*), 4.19 (d, 1H, $J=15.6$ Hz, NCH_2Ph), 4.25–4.30 (m, 1H, H_3), 4.29 (t, 1H, $J=3.4$ Hz, $H_{4'}$), 4.32 (d, 1H, $J=11.7$ Hz, OCH_2Ph), 4.56 (d, 1H, $J=3.8$ Hz, $H_{2'}$), 4.58 (d, 1H, $J=11.7$ Hz, OCH_2Ph), 4.77 (d, 1H, $J=15.6$ Hz, NCH_2Ph), 5.90 (d, 1H, $J=3.8$ Hz, $H_{1'}$), 7.06–7.30 (m, 10H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 26.3, 26.8, 30.8, 45.0, 54.6, 69.4, 71.8, 77.8, 82.1, 82.7, 104.6, 111.9, 127.4, 127.5 (2C), 128.0, 128.4, 128.7, 136.3, 137.0, 175.0. Anal. calcd for $C_{25}H_{29}NO_6$: C, 68.32; H, 6.65; N, 3.19. Found: C, 68.42; H, 6.72; N, 3.23.

4.2.6. 4-[(3*S*,5*R*)-1-Benzyl-3-hydroxy-2-oxo-5-pyrrolidinyl]-3-*O*-benzyl-1,2-*O*-isopropyliden-α-D-*xylo*-tetrofuranose 8b. (Et_2O; $R_f=0.35$); 0.365 g (83%); oil; $[\alpha]_D^{25}=-86$ (*c* 0.64, $CHCl_3$); IR ($\nu_{C=O}$) 1695 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.29 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.79 (td, 1H, $J=9.0$, 13.0 Hz, H_{4b}), 2.84 (ddd, 1H, $J=1.0$, 8.3, 13.0 Hz, H_{4a}), 3.64 (bs, 1H, O*H*), 3.71 (bdd, 1H, $J=3.3$, 9.0, H_5), 3.80 (d, 1H, $J=3.3$ Hz, $H_{3'}$), 4.15 (d, 1H, $J=15.2$ Hz, NCH_2Ph), 4.23 (t, 1H, $J=3.3$ Hz, $H_{4'}$), 4.38 (d, 1H, $J=11.9$, OCH_2Ph), 4.59 (t, 1H, $J=8.8$ Hz, H_3), 4.59 (d, 1H, $J=3.8$ Hz, $H_{2'}$), 4.63 (d, 1H, $J=11.9$, OCH_2Ph), 4.82 (d, 1H, $J=15.2$ Hz, NCH_2Ph), 5.91 (d, 1H, $J=3.8$ Hz, $H_{1'}$), 7.10–7.35 (m, 10H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 26.2, 26.8, 31.3, 45.3, 54.6, 69.1, 71.8, 78.5, 82.1, 82.8, 104.9, 111.9, 127.4, 127.6, 127.7, 128.1, 128.6, 128.8, 135.9, 137.0, 176.0. Anal. calcd for $C_{25}H_{29}NO_6$: C, 68.32; H, 6.65; N, 3.19. Found: C, 68.14; H, 6.73; N, 3.27.

4.2.7. 4-[(3*R*,5*S*)-1-Benzyl-3-hydroxy-2-oxo-5-pyrrolidinyl]-3-*O*-benzyl-1,2-*O*-isopropyliden-α-D-*xylo*-tetrofuranose 8c. (Et_2O; $R_f=0.25$); 0.356 g (81%); oil; $[\alpha]_D^{25}=+24$ (*c* 0.34, $CHCl_3$); IR ($\nu_{C=O}$) 1686 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.32 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.86–1.93 (m, 2H, H_{4a} and H_{4b}), 3.70 (bs, 1H, O*H*), 3.85 (ddd, 1H, $J=3.6$, 7.2, 9.4 Hz, H_5), 3.91 (d, 1H, $J=3.3$ Hz, $H_{3'}$), 4.08 (dd, 1H, $J=3.3$, 9.4 Hz, $H_{4'}$), 4.36 and 5.05 (2d, 2H, $J=14.6$ Hz, NCH_2Ph), 4.39 (d, 1H, $J=11.8$ Hz, OCH_2Ph), 4.42 (t, 1H, $J=8.6$ Hz, H_3), 4.56 (d, 1H, $J=3.8$ Hz, $H_{2'}$), 4.63 (d, 1H, $J=11.8$ Hz, OCH_2Ph), 5.98 (d, 1H, $J=3.8$ Hz, $H_{1'}$), 7.16–7.36 (m, 10H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 26.2, 26.7, 31.5, 46.2, 53.4, 68.7, 71.8, 81.1, 82.5, 84.0, 105.6, 111.9, 127.3, 128.0, 128.3, 128.5, 128.5, 128.6, 134.2, 136.1, 174.9. Anal. calcd for $C_{25}H_{29}NO_6$: C, 68.32; H, 6.65; N, 3.19. Found: C, 68.56; H, 6.44; N, 3.11.

4.2.8. 4-[(3*S*,5*S*)-1-Benzyl-3-hydroxy-2-oxo-5-pyrrolidinyl]-3-*O*-benzyl-1,2-*O*-isopropyliden-α-D-*xylo*-tetrofuranose 8d. (Et_2O; $R_f=0.29$); 0.365 g (83%); white solid; mp 197–199°C; $[\alpha]_D^{25}=-29$ (*c* 0.81, $CHCl_3$); IR ($\nu_{C=O}$) 1700 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.29 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.52 (td, 1H, $J=7.6$, 13.1 Hz, H_{4b}), 2.00 (bs, 1H, O*H*), 2.42 (td, 1H, $J=7.6$, 13.1 Hz, H_{4a}), 3.77 (q, 1H, $J=8.1$ Hz, H_5), 3.95 (d, 1H, $J=3.1$ Hz, $H_{3'}$), 4.11 (dd, 1H, $J=3.1$, 8.3 Hz, $H_{4'}$), 4.31 (t, 1H, $J=7.6$ Hz, H_3), 4.40 (d, 1H, $J=11.4$, OCH_2Ph), 4.53 (d, 1H, $J=14.5$ Hz, NCH_2Ph), 4.56 (d, 1H, $J=3.8$ Hz, $H_{2'}$), 4.63 (d, 1H, $J=11.4$, OCH_2Ph), 4.88 (d, 1H, $J=14.5$ Hz, NCH_2Ph), 5.99 (d, 1H, $J=3.8$ Hz, $H_{1'}$), 7.06–7.43 (m, 10H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 26.3, 26.6, 29.7, 45.5, 54.7, 69.0, 71.9, 80.5, 82.7, 84.0, 105.6, 111.9, 127.2, 128.0, 128.3, 128.5, 128.6, 128.8, 136.6, 137.2, 175.4. Anal. calcd for $C_{25}H_{29}NO_6$: C, 68.32; H, 6.65; N, 3.19. Found: C, 68.21; H, 6.77; N, 3.07.

4.2.9. 5-[(3*R*,5*R*)-1-Benzyl-3-hydroxy-2-oxo-5-pyrrolidinyl]-1,2:3,4-di-*O*-isopropyliden-α-D-*galacto*-pentopyranose 9a. (Et_2O; $R_f=0.40$); 0.394 g (90%); white solid; mp 124–126°C; $[\alpha]_D^{25}=+47$ (*c* 0.40, $CHCl_3$); IR ($\nu_{C=O}$) 1688 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.29 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 2.25–2.42 (m, 2H, H_{4b} and H_{4a}), 3.27 (bs, 1H, O*H*), 3.62–3.67 (m, 1H, H_5), 4.00 (d, 1H, $J=15.3$ Hz, NCH_2Ph), 4.01 (bs, 1H, $H_{5'}$), 4.10 (dd, 1H, $J=1.6$, 8.0 Hz, $H_{4'}$), 4.25 (dd, 1H, $J=5.8$, 6.9 Hz, H_3), 4.31 (dd, 1H, $J=2.0$, 5.1 Hz, $H_{2'}$), 4.59 (dd, 1H, $J=2.0$, 8.0 Hz, $H_{3'}$), 5.20 (d, 1H, $J=15.3$ Hz, NCH_2Ph), 5.57 (d, 1H, $J=5.1$ Hz, $H_{1'}$), 7.14–7.35 (m, 5H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.1, 24.7, 25.8, 26.1, 30.2, 44.1, 55.6, 65.0, 70.0, 70.5, 71.2, 71.6, 96.7, 108.6, 109.5, 127.6, 127.8, 128.8, 136.2, 175.1. Anal. calcd for $C_{22}H_{29}NO_7$: C, 62.99; H, 6.97; N, 3.34. Found: C, 62.85; H, 7.15; N, 3.37.

4.2.10. 5-[(3*S*,5*R*)-1-Benzyl-3-hydroxy-2-oxo-5-pyrrolidinyl]-1,2:3,4-di-*O*-isopropyliden-α-D-*galacto*-pentopyranose 9b. (Et_2O; $R_f=0.39$); 0.381 g (91%); oil; $[\alpha]_D^{25}=-115$ (*c* 0.35, $CHCl_3$); IR ($\nu_{C=O}$) 1695 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 1.24 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 1.85 (td, 1H, $J=8.5$, 13.1 Hz, H_{4b}), 2.86 (dd, 1H, $J=8.8$, 13.1 Hz, H_{4a}), 3.00 (bs, 1H, O*H*), 3.58 (dd, 1H, $J=4.3$, 8.2 Hz, H_5), 3.76 (dd, 1H, $J=1.8$, 4.3 Hz, $H_{5'}$), 3.92 (d, 1H, $J=14.9$ Hz, NCH_2Ph), 4.10 (dd, 1H, $J=1.8$, 8.0 Hz, $H_{4'}$), 4.31 (dd, 1H, $J=2.3$, 5.1 Hz, $H_{2'}$), 4.52 (t, 1H, $J=9.0$ Hz, H_3), 4.59 (dd, 1H, $J=2.3$, 8.0 Hz, $H_{3'}$), 5.18 (d, 1H, $J=14.9$ Hz, NCH_2Ph), 5.51 (d, 1H, $J=5.1$ Hz,

$H_{1'}$), 7.18–7.34 (m, 5H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.1, 24.7, 27.8, 26.3, 31.0, 44.8, 54.5, 65.9, 69.0, 70.4, 71.0, 71.5, 96.4, 108.4, 109.5, 127.8, 128.1, 128.8, 135.7, 176.0. Anal. calcd for $C_{22}H_{29}NO_7$: C, 62.99; H, 6.97; N, 3.34. Found: C, 63.20; H, 6.87; N, 3.45.

4.2.11. 5-[(3*R*,5*S*)-1-Benzyl-3-hydroxy-2-oxo-5-pyrrolidinyl]-1,2:3,4-di-*O*-isopropyliden-α-D-*galacto*-pentopyranose 9c

(Et_2O; R_f=0.24); 0.369 g (88%); oil; $[\alpha]_D^{25}$=+35 (*c* 0.45, $CHCl_3$); IR ($\nu_{C=O}$) 1686 cm^{-1}; ^{1}H NMR ($CDCl_3$, 55°C) δ 1.27 (s, 3H, C*H*$_3$), 1.31 (s, 3H, C*H*$_3$), 1.32 (s, 3H, C*H*$_3$), 1.45 (s, 3H, C*H*$_3$), 1.92 (td, 1H, *J*=8.8, 13.9 Hz, H_{4b}), 2.34 (ddd, 1H, *J*=1.1, 7.9, 13.9 Hz, H_{4a}), 3.41 (bs, 1H, O*H*), 3.69–3.71 (m, 2H, $H_{5'}$ and H_5), 4.17 (dd, 1H, *J*=1.0, 7.8 Hz, $H_{4'}$), 4.29 (d, 1H, *J*=14.4 Hz, NC*H*$_2$Ph), 4.30 (dd, 1H, *J*=2.6, 5.0 Hz, $H_{2'}$), 4.45 (t, 1H, *J*=8.5 Hz, H_3), 4.56 (dd, 1H, *J*=2.6, 7.8 Hz, $H_{3'}$), 5.12 (d, 1H, *J*=14.4 Hz, NC*H*$_2$Ph), 5.56 (d, 1H, *J*=5.0 Hz, $H_{1'}$), 7.19–7.32 (m, 5H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.6, 24.8, 25.8, 26.1, 31.0, 46.6, 53.3, 68.9, 70.1, 70.8, 70.9, 71.2, 96.3, 108.9, 109.8, 127.5, 128.5, 128.7, 136.2, 175.2. Anal. calcd for $C_{22}H_{29}NO_7$: C, 62.99; H, 6.97; N, 3.34. Found: C, 63.27; H, 6.95; N, 3.28.

4.2.12. 5-[(3*S*,5*S*)-1-Benzyl-3-hydroxy-2-oxo-5-pyrrolidinyl]-1,2:3,4-di-*O*-isopropyliden-α-D-*galacto*-pentopyranose 9d

(Et_2O; R_f=0.50); 0.370 g (88%); oil; $[\alpha]_D^{25}$=−10 (*c* 1.02, $CHCl_3$); IR ($\nu_{C=O}$) 1702 cm^{-1}; ^{1}H NMR ($CDCl_3$, 55°C) δ 1.30 (s, 3H, C*H*$_3$), 1.34 (s, 6H, C*H*$_3$), 1.51 (s, 3H, C*H*$_3$), 1.72 (td, 1H, *J*=7.4, 13.0 Hz, H_{4b}), 2.53 (ddd, 1H, *J*=6.7, 8.0, 13.0 Hz, H_{4a}), 3.24 (bs, 1H, O*H*), 3.70 (q, 1H, *J*=7.6 Hz, H_5), 3.86 (dd, 1H, *J*=1.7, 8.0 Hz, $H_{5'}$), 4.27 (dd, 1H, *J*=1.7, 7.9 Hz, $H_{4'}$), 4.27 (t, 1H, *J*=7.0 Hz, H_3), 4.31 (dd, 1H, *J*=2.6, 5.0 Hz, $H_{2'}$), 4.49 (d, 1H, *J*=14.5 Hz, NC*H*$_2$Ph), 4.59 (dd, 1H, *J*=2.6, 7.9 Hz, $H_{3'}$), 5.08 (d, 1H, *J*=14.5 Hz, NC*H*$_2$Ph), 5.57 (d, 1H, *J*=5.0 Hz, $H_{1'}$), 7.15–7.35 (m, 5H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.5, 24.9, 25.8, 25.9, 30.7, 45.2, 54.2, 69.4, 70.0, 70.8, 71.0, 72.1, 96.4, 109.0, 109.6, 127.2, 128.5, 128.7, 137.1, 175.4. Anal. calcd for $C_{22}H_{29}NO_7$: C, 62.99; H, 6.97; N, 3.34. Found: C, 62.78; H, 6.82; N, 3.41.

4.3. *N*-Debenzylation of pyrrolidinones. General procedure

To a solution of lithium (75 mg, 3 mmol) in liquid ammonia (10 mL) cooled to −40°C was added dropwise a solution of the corresponding *N*-benzyl-2-pyrrolidinone (0.75 mmol) in THF (3 mL). The mixture was stirred for 2 h and then treated with solid ammonium chloride until the solution became colourless. The ammonia was allowed to evaporate at ambient temperature after which water (5 mL) was added. The aqueous solution was extracted with dichloromethane (3×10 ml), dried over $MgSO_4$ and evaporated under reduced pressure. The residue was filtered through a short pad of silica gel and eluted with ethyl acetate. Evaporation of the solvent afforded the crude product which was purified by radial chromatography.

4.3.1. 4-[(3*R*,5*R*)-3-Hydroxy-2-oxo-5-pyrrolidinyl]-2,3-*O*-isopropyliden-1-*O*-methyl-α-D-*lyxo*-tetrofuranose 10

(EtOAc; R_f=0.17); 0.265 g (97%); oil; $[\alpha]_D^{25}$=+18 (*c* 0.32, $CHCl_3$); IR ($\nu_{C=O}$) 1705 cm^{-1}; ^{1}H NMR ($CDCl_3$, 55°C) δ 1.29 (s, 3H, C*H*$_3$), 1.43 (s, 3H, C*H*$_3$), 1.65 (bs, 1H, O*H*), 1.98 (td, 1H, *J*=6.6, 13.4 Hz, H_{4b}), 2.71 (td, 1H, *J*=7.2, 13.4 Hz, H_{4a}), 3.29 (s, 3H, OC*H*$_3$), 3.79–3.86 (m, 2H, H_5 and $H_{4'}$), 4.31 (t, 1H, *J*=6.9 Hz, H_3), 4.56 (d, 1H, *J*=5.9, $H_{2'}$), 4.72 (dd, 1H, *J*=3.4, 5.9 Hz, $H_{3'}$), 4.90 (s, 1H, $H_{1'}$), 6.53 (bs, 1H, N*H*). ^{13}C NMR ($CDCl_3$) δ 24.6, 25.9, 34.2, 50.5, 54.6, 69.2, 79.3, 83.0, 84.9, 107.0, 112.9, 177.9. Anal. calcd for $C_{12}H_{19}NO_6$: C, 52.74; H, 7.01; N, 5.13. Found: C, 52.58; H, 6.97; N, 5.08.

4.3.2. 4-[(3*R*,5*R*)-3-Hydroxy-2-oxo-5-pyrrolidinyl]-3-*O*-benzyl-1,2-*O*-isopropyliden-α-D-*xylo*-tetrofuranose 11

(EtOAc/MeOH, 95:5; R_f=0.29); 0.234 g (90%); oil; $[\alpha]_D^{25}$=+53 (*c* 0.75, $CHCl_3$); IR ($\nu_{C=O}$) 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$, 55°C) δ 1.25 (s, 3H, C*H*$_3$), 1.31 (s, 3H, C*H*$_3$), 2.17–2.36 (m, 1H, H_{4b}), 2.57–2.71 (m, 2H, H_{4a}, O*H*), 3.56–3.68 (m, 2H, H_5 and $H_{4'}$), 3.94–3.96 (m, 2H, $H_{3'}$, O*H*), 4.22 (bs, 1H, H_3), 4.54 (d, 1H, *J*=3.6 Hz, $H_{2'}$), 5.70 (bs, 1H, N*H*), 5.93 (d, 1H, *J*=3.6 Hz, $H_{1'}$). ^{13}C NMR ($CDCl_3$) δ 26.1, 26.8, 29.7, 53.0, 67.1, 74.0, 83.2, 85.7, 105.2, 111.7, 180.0. Anal. calcd for $C_{11}H_{17}NO_6$: C, 50.96; H, 6.61; N, 5.40. Found: C, 51.28; H, 6.50; N, 5.30.

4.3.3. 5-[(3*R*,5*R*)-3-Hydroxy-2-oxo-5-pyrrolidinyl]-1,2:3,4-di-*O*-isopropyliden-α-D-*galacto*-pentopyranose 12

(EtOAc; R_f=0.22); 0.316 g (96%); white solid; mp 112–114°C; $[\alpha]_D^{25}$=−29 (*c* 0.65, $CHCl_3$); IR ($\nu_{C=O}$) 1712 cm^{-1}; ^{1}H NMR ($CDCl_3$, 55°C) δ 1.31 (s, 3H, C*H*$_3$), 1.34 (s, 3H, C*H*$_3$), 1.43 (s, 3H, C*H*$_3$), 1.51 (s, 3H, C*H*$_3$), 2.00 (ddd, 1H, *J*=4.7, 6.2, 13.7 Hz, H_{4b}), 2.62 (ddd, 1H, *J*=6.4, 7.8, 13.7 Hz, H_{4a}), 2.69 (bs, 1H, O*H*), 3.68–3.73 (m, 2H, H_5 and $H_{5'}$), 4.23 (dd, 1H, *J*=6.2, 7.8 Hz, H_3), 4.26 (dd, 1H, *J*=1.4, 7.9, $H_{4'}$), 4.33 (dd, 1H, *J*=2.6, 5.0 Hz, $H_{2'}$), 4.63 (dd, 1H *J*=2.6, 7.9 Hz, $H_{3'}$), 5.51 (d, 1H, *J*=5.0 Hz, $H_{1'}$), 5.69 (bs, 1H, N*H*). ^{13}C NMR ($CDCl_3$) δ 24.5, 25.0, 25.9 (2C), 33.7, 38.2, 51.3, 69.3, 70.3, 70.7, 70.9, 96.2, 109.0, 109.8, 177.6. Anal. calcd for $C_{15}H_{23}NO_7$: C, 54.70; H, 7.04; N, 4.25. Found: C, 54.87; H, 6.94; N, 4.32.

4.4. 5-[(3*R*,5*R*)-3-(*tert*-Butyldimethylsiloxy)-2-oxo-5-pyrrolidinyl]-1,2:3,4-di-*O*-isopropyliden-α-D-*galacto*-pentopyranose 13

A solution of **12** (0.165 g, 0.5 mmol) in DMF (5 mL) was treated with imidazol (0.189 g) and *tert*-butyldimethylsilyl chloride (0.113 g, 0.75 mmol). The resulting solution was stirred at 70°C until no more starting material was observed by TLC (ca. 1 h). Methanol (5 mL) and water (20 mL) were added and the resulting mixture extracted with EtOAc (3×25 mL). The organic layers were combined, dried over magnesium sulfate and evaporated under reduced pressure to give the crude material which was purified by radial chormatography (hexane/Et_2O, 40:60; R_f=0.21) to afford pure **13** (0.182 g, 82%) as an oil; $[\alpha]_D^{25}$=−52 (*c* 0.15, $CHCl_3$); IR ($\nu_{C=O}$) 1715 cm^{-1}; ^{1}H NMR ($CDCl_3$,

55°C) δ 0.00 (s, 3H, SiCH_3), 0.05 (s, 3H, SiCH_3), 0.83 (s, 9H, Si(CH_3)$_3$), 1.24 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.76 (td, 1H, J=6.9, 13.3 Hz, H_{4b}), 2.52 (ddd, 1H, J=6.9, 8.0, 13.3 Hz, H_{4a}), 3.52 (dd, 1H, J=1.4, 8.8 Hz, $H_{5'}$), 3.61 (td, 1H, J=6.9, 8.8 Hz, H_5), 4.18 (t, 1H, J=7.6 Hz, H_3), 4.22 (dd, 1H, J=2.2, 5.0 Hz, $H_{2'}$), 4.37 (dd, 1H, J=1.4, 7.9 Hz, $H_{4'}$), 4.52 (dd, 1H, J=2.2, 7.9 Hz, $H_{3'}$), 5.42 (d, 1H, J=5.0 Hz, $H_{1'}$), 5.60 (bs, 1H, NH). ^{13}C NMR ($CDCl_3$) δ −5.0, −4.6, 18.3, 24.5, 24.9, 25.8, 25.9, 26.2, 38.2, 50.6, 70.1, 70.4, 70.7, 70.8, 71.7, 96.2, 108.8, 109.7, 176.0. Anal. calcd for $C_{21}H_{37}NO_7Si$: C, 56.86; H, 8.41; N, 3.16. Found: C, 57.18; H, 8.35; N, 3.10.

4.5. 5-[(3*R*,5*R*)-1-(*tert*-Butoxycarbonyl)-3-(*tert*-butyldimethylsiloxy)-2-oxo-5-pyrrolidinyl]-1,2:3,4-di-*O*-isopropyliden-α-D-*galacto*-pentopyranose 14

A solution of **13** (0.177 g, 0.4 mmol) in CH_2Cl_2 (15 ml) was treated with Boc_2O (0.105 g, 0.48 mmol), Et_3N (61 mg, 0.6 mmol) and DMAP (7.2 mg, 0.06 mmol). The reaction mixture was stirred at ambient temperature for 18 h, at which time 1N $KHSO_4$ (10 mL) was added. The organic layer was separated, washed with water (1×15 ml) and brine (1×15 ml), dried over magnesium sulfate and evaporated. The residue was purified by radial chromatography (hexane/Et_2O, 40:60; R_f=0.32) to give pure **14** (0.194 g, 89%) as an oil; $[\alpha]_D^{25}$=−22 (*c* 0.10, $CHCl_3$); IR ($\nu_{C=O}$) 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$, 55°C) δ 0.08 (s, 3H, SiCH_3), 0.11 (s, 3H, SiCH_3), 0.88 (s, 9H, Si(CH_3)$_3$), 1.26 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.50 (s, 9H, C(CH_3)$_3$), 2.31 (ddd, 1H, J=8.4, 9.3, 13.6 Hz, H_{4b}), 2.38 (ddd, 1H, J=7.8, 9.3, 13.6 Hz, H_{4a}), 4.11 (dt, 1H, J=1.2, 8.0 Hz, H_5), 4.22 (t, 1H, J=9.3 Hz, H_3), 4.24 (dd, 1H, J=2.3, 5.1 Hz, $H_{2'}$), 4.27 (dd, 1H, J=2.3, 7.9 Hz, $H_{4'}$), 4.38 (bs, 1H, $H_{5'}$), 4.56 (dd, 1H, J=2.3, 7.9 Hz, $H_{3'}$), 5.50 (d, 1H, J=5.1 Hz, $H_{1'}$). ^{13}C NMR ($CDCl_3$) δ −5.1, −4.5, 18.1, 24.3, 24.8, 25.7, 26.0, 27.6, 28.1, 38.1, 55.0, 65.1, 70.5, 70.7, 71.4, 72.6, 83.0, 96.6, 108.4, 109.2, 151.2, 172.3. Anal. calcd for $C_{26}H_{45}NO_9Si$: C, 57.43; H, 8.34; N, 2.58. Found: C, 57.61; H, 8.29; N, 2.63.

4.6. 5-[(3*R*,5*R*)-1-(*tert*-Butoxycarbonyl)-3-(*tert*-butyldimethylsiloxy)-2-hydroxy-5-pyrrolidinyl]-1,2:3,4-di-*O*-isopropyliden-α-D-*galacto*-pentopyranose 15 (mixture of epimers at C-2′)

To a cooled (−78°C) solution of **14** (0.181 g, 0.33 mmol) in THF (10 mL) was added dropwise a solution of $LiEt_3BH$ (0.67 mL of a 1 M solution in hexanes, 0.67 mmol). The resulting solution was stirred at −78°C for 1 h at which time the reaction was quenched with water (0.5 mL) and allowed to warm to room temperature. The reaction mixture was diluted with EtOAc (10 mL) and brine (15 mL). The organic layer was separated, and the aqueous layer extracted with EtOAc (3×15 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered and evaporated. The residue was purified by radial chromatography (hexane/Et_2O, 20:80; R_f=0.30) to give **15** (0.134 g, 74%) as an oil. The NMR analysis of this product revealed that it was formed by a 3:1 mixture of epimers at C-2′. The signals of each isomer could be identified from the spectrum of the mixture.

Major isomer: ^{1}H NMR ($CDCl_3$, 55°C) δ 0.09 (s, 3H, SiCH_3), 0.10 (s, 3H, SiCH_3), 0.90 (s, 9H, Si(CH_3)$_3$), 1.28 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.45 (s, 9H, C(CH_3)$_3$), 1.47 (s, 3H, CH_3), 2.12–2.30 (m, 2H, H_{4b} and H_{4a}), 2.98 (bs, 1H, OH), 3.84–4.01 (m, 2H, H_2, H_3 and H_5), 4.19–4.28 (m, 3H, $H_{2'}$, $H_{4'}$ and $H_{5'}$), 4.56 (dd, 1H, J=2.3, 7.8 Hz, $H_{3'}$), 5.54 (d, 1H, J=5.1 Hz, $H_{1'}$). ^{13}C NMR ($CDCl_3$) δ −4.8 (2C), 18.4, 24.3, 25.0, 25.7, 25.8, 25.8, 28.4, 38.2, 56.0, 66.3, 70.9, 71.3, 71.9, 72.2, 80.3 (2C), 96.6, 108.9, 109.2, 153.9.

Minor isomer: ^{1}H NMR ($CDCl_3$, 55°C) δ 0.16 (s, 3H, SiCH_3), 0.21 (s, 3H, SiCH_3), 0.92 (s, 9H, Si(CH_3)$_3$), 1.27 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.45 (s, 9H, (CH_3)$_3$), 1.48 (s, 3H, CH_3), 1.80 (bs, 1H, OH), 2.12–2.30 (m, 2H, H_{4b} and H_{4a}), 3.84–4.01 (m, 2H, H_2, H_3, H_5), 4.19–4.28 (m, 3H, $H_{2'}$, $H_{4'}$, $H_{5'}$), 4.53 (dd, 1H, J=2.3, 6.3 Hz, $H_{3'}$), 5.46 (d, 1H, J=5.0 Hz, $H_{1'}$). ^{13}C NMR ($CDCl_3$) δ −4.5 (2C), 18.0, 24.4, 25.1, 25.9, 26.0, 26.1, 28.4, 42.8, 57.0, 66.8, 70.8, 71.3, 71.4, 72.7, 80.6, 80.8, 96.6, 108.4, 109.1, 154.3.

4.7. Synthesis of Mosher esters. General procedure

To a solution of the corresponding pyrrolidin-2-one (0.1 mmol) in CH_2Cl_2 (2 mL) was added the corresponding MTPA chloride (0.12 mmol), DCC (31 mg, 0.15 mmol) and DMAP (6 mg, 0.01 mmol). The resulting solution was stirred at ambient temperature for 12 h at which time the reaction mixture was treated with 1 M HCl (1 mL). The organic layer was separated and washed with a saturated aqueous solution of $NaHCO_3$. The organic layer was separated, dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was purified by radial chromatography to afford the pure Mosher esters.

4.7.1. 4-{(3*R*,5*R*)-1-Benzyl-3-[(1*R*)-1-methoxy-1-phenyl-1-(trifluoromethyl)acetoxy]-2-oxo-5-pyrrolidinyl}-2,3-*O*-isopropyliden-1-*O*-methyl-α-D-*lyxo*-tetrofuranose 16a.

(Hexane/Et_2O; R_f=0.22); 53 mg (92%); oil; $[\alpha]_D^{25}$=+26 (*c* 0.50, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 55°C) δ 1.23 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 2.22 (td, 1H, J=5.7, 14.0 Hz, H_{4b}), 2.63 (ddd, 1H, J=7.1, 8.8, 14.0 Hz, H_{4a}), 3.14 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 3.89 (td, 1H, J=5.3, 7.1 Hz, H_5), 3.94 (dd, 1H, J=3.3, 5.1 Hz, $H_{4'}$), 4.28 (d, 1H, J=15.2 Hz, NCH_2Ph), 4.40 (dd, 1H, J=3.3, 5.1 Hz, $H_{3'}$), 4.45 (d, 1H, J=5.9 Hz, $H_{2'}$), 4.70 (s, 1H, $H_{1'}$), 4.91 (d, 1H, J=15.2 Hz, NCH_2Ph), 5.70 (dd, 1H, J=5.9, 8.8 Hz, H_3), 7.20–7.40 (m, 8H, ArH), 7.40–7.45 (m, 1H, ArH), 7.63–7.68 (m, 1H, ArH). ^{13}C NMR ($CDCl_3$) δ 24.4, 25.7, 29.7, 34.0, 45.4, 54.3, 54.8, 55.6, 71.7, 78.0, 79.4, 85.3, 106.6, 112.8, 121.3, 127.6, 127.7, 127.7, 128.5, 128.8, 129.7, 132.0, 136.2, 166.1, 170.4. Anal. calcd for $C_{29}H_{32}F_3NO_8$: C, 60.10; H, 5.57; N, 2.42. Found: C, 60.30; H, 5.49; N, 2.33.

4.7.2. 4-{(3*R*,5*S*)-1-Benzyl-3-[(1*R*)-1-methoxy-1-phenyl-1-(trifluoromethyl)acetoxy]-2-oxo-5-pyrrolidinyl}-2,3-*O*-isopropyliden-1-*O*-methyl-α-D-*lyxo*-tetrofuranose 16b. (Hexane/Et_2O, 60:40; R_f = 0.22); 56 mg (97%); oil; $[\alpha]_D^{25}$ = +69 (*c* 0.72, $CHCl_3$); ^1H NMR ($CDCl_3$, 55°C) δ 1.25 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 2.08 (td, 1H, *J* = 8.6, 14.0 Hz, H_{4b}), 2.37 (ddd, 1H, *J* = 2.1, 8.6, 14.0 Hz, H_{4a}), 3.26 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 3.81 (dt, 1H, *J* = 2.1, 8.6 Hz, H_5), 3.91 (dd, 1H, *J* = 3.6, 8.6 Hz, $H_{4'}$), 4.38 (d, 1H, *J* = 14.3 Hz, NCH_2Ph), 4.52 (d, 1H, *J* = 6.0 Hz, $H_{2'}$), 4.67 (dd, 1H, *J* = 3.6, 6.0 Hz, $H_{3'}$), 4.94 (s, 1H, $H_{1'}$), 5.07 (d, 1H, *J* = 14.3 Hz, NCH_2Ph), 5.81 (t, 1H, *J* = 8.6 Hz, H_3), 7.20–7.95 (m, 10, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.8, 25.8, 29.4, 34.0, 46.4, 53.6, 54.9, 55.8, 71.5, 80.2, 83.1, 84.3, 107.7, 113.0, 121.3, 127.4, 127.6, 128.6, 128.7, 128.8, 129.7, 132.1, 136.1, 166.1, 169.4. Anal. calcd for $C_{29}H_{32}F_3NO_8$: C, 60.10; H, 5.57; N, 2.42. Found: C, 59.91; H, 5.68; N, 2.48.

4.7.3. 4-[(3*R*,5*R*)-1-Benzyl-3-[(1*R*)-1-methoxy-1-phenyl-1-(trifluoromethyl)acetoxy]-2-oxo-5-pyrrolidinyl]-3-*O*-benzyl-1,2-*O*-isopropyliden-α-D-*xylo*-tetrofuranose 16c. (Hexane/Et_2O, 60:40; R_f = 0.20); 61 mg (93%); oil; $[\alpha]_D^{25}$ = −9 (*c* 0.91, $CHCl_3$); ^1H NMR ($CDCl_3$, 55°C) δ 1.26 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 2.22 (td, 1H, *J* = 7.4, 14.3 Hz, H_{4b}), 2.58 (ddd, 1H, *J* = 7.4, 9.0, 14.3 Hz, H_{4a}), 3.65 (s, 3H, OCH_3), 3.72 (d, 1H, *J* = 3.6 Hz, $H_{3'}$), 3.83 (dt, 1H, *J* = 3.6, 7.4 Hz, H_5), 4.20 (d, 1H, *J* = 15.5 Hz, NCH_2Ph), 4.25 (t, 1H, *J* = 3.6 Hz, $H_{4'}$), 4.30 (d, 1H, *J* = 11.7 Hz, OCH_2Ph), 4.50 (d, 1H, *J* = 3.6 Hz, $H_{2'}$), 4.55 (d, 1H, *J* = 11.7 Hz, OCH_2Ph), 4.84 (d, 1H, *J* = 15.5 Hz, NCH_2Ph), 5.69 (dd, 1H, *J* = 7.4, 9.0 Hz, H_3), 5.72 (d, 1H, *J* = 3.6 Hz, $H_{1'}$), 7.10–7.46 (m, 13H, Ar*H*), 7.60–7.70 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 26.2, 26.7, 29.7, 45.2, 53.8, 55.7, 71.5, 71.6, 77.2, 77.6, 81.7, 82.3, 104.4, 111.7, 127.4, 127.5, 127.7, 128.2, 128.4, 128.6, 128.8, 129.6, 132.1, 135.7, 136.6, 166.2, 169.7. Anal. calcd for $C_{35}H_{36}F_3NO_8$: C, 64.11; H, 5.53; N, 2.14. Found: C, 63.86; H, 5.61; N, 2.02.

4.7.4. 5-[(3*R*,5*R*)-1-Benzyl-3-[(1*R*)-1-methoxy-1-phenyl-1-(trifluoromethyl)acetoxy]-2-oxo-5-pyrrolidinyl]-1,2:3,4-di-*O*-isopropyliden-α-D-*galacto*-pentopyranose 16d. (Hexane/Et_2O, 60:40; R_f = 0.24); 62 mg (98%); white solid; mp 167–169°C; $[\alpha]_D^{25}$ = −24 (*c* 0.55, $CHCl_3$); ^1H NMR ($CDCl_3$, 55°C) δ 1.25 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 2.26 (td, 1H, *J* = 7.2, 14.3 Hz, H_{4b}), 2.60 (ddd, 1H, *J* = 7.8, 9.0, 14.3 Hz, H_{4a}), 3.65 (s, 3H, OCH_3), 3.71 (dt, 1H, *J* = 2.3, 7.3 Hz, H_5), 3.95–4.05 (m, 2H, $H_{4'}$ and $H_{5'}$), 4.02 (d, 1H, *J* = 15.5 Hz, NCH_2Ph), 4.26 (dd, 1H, *J* = 1.8, 5.3 Hz, $H_{2'}$), 4.53 (dd, 1H, *J* = 1.8, 7.9, $H_{3'}$), 5.23 (d, 1H, *J* = 15.5 Hz, NCH_2Ph), 5.43 (d, 1H, *J* = 5.3, $H_{1'}$), 5.62 (dd, 1H, *J* = 7.2, 7.8 Hz, H_3), 7.14–7.42 (m, 8H, Ar*H*), 7.60–7.78 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.0, 24.5, 25.5, 26.2, 26.8, 44.1, 55.1, 55.5, 63.9, 70.4, 71.4, 71.6, 71.7, 89.6, 96.6, 108.1, 109.4, 121.3, 127.5, 127.7, 127.8, 128.2, 128.9, 129.4, 132.3, 135.8, 166.2, 169.6. Anal. calcd for $C_{32}H_{36}F_3NO_9$: C, 60.47; H, 5.71; N, 2.20. Found: C, 60.54; H, 5.79; N, 2.34.

4.7.5. 5-[(3*R*,5*S*)-1-Benzyl-3-[(1*R*)-1-methoxy-1-phenyl-1-(trifluoromethyl)acetoxy]-2-oxo-5-pyrrolidinyl]-1,2:3,4-di-*O*-isopropyliden-α-D-*galacto*-pentopyranose 16e. (Hexane/Et_2O, 60:40; R_f = 0.17); 59 mg (93%); oil; $[\alpha]_D^{25}$ = +5 (*c* 0.50, $CHCl_3$); ^1H NMR ($CDCl_3$, 55°C) δ 1.27 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 1.92 (td, 1H. *J* = 8.4, 13.6 Hz, H_{4b}), 2.52 (ddd, 1H, *J* = 1.8, 8.4, 13.6 Hz, H_{4a}), 3.66 (s, 3H, OCH_3), 3.77 (dt, 1H, *J* = 1.8, 8.4 Hz, H_5), 3.79 (dd, 1H, *J* = 1.8, 8.4 Hz, $H_{5'}$), 4.11 (dd, 1H, *J* = 1.8, 8.1 Hz, $H_{4'}$), 4.28 (d, 1H, *J* = 14.7 Hz, NCH_2Ph), 4.31 (dd, 1H, *J* = 2.6, 5.1 Hz, $H_{2'}$), 4.56 (dd, 1H, *J* = 2.6, 8.1 Hz, $H_{3'}$), 5.08 (d, 1H, *J* = 14.7 Hz, NCH_2Ph), 5.54 (d, 1H, *J* = 5.1 Hz, $H_{1'}$), 5.80 (t, 1H, *J* = 8.4 Hz, H_3), 7.20–7.24 (m, 5H, Ar*H*), 7.36–7.46 (m, 3H, Ar*H*), 7.56–7.62 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.4, 24.8, 25.8, 26.2, 29.7, 46.3, 54.0, 55.5, 64.7, 69.7, 70.2, 70.8, 72.5, 85.6, 96.3, 109.0, 109.9, 123.7, 127.7, 127.8, 128.5, 128.6, 128.7, 129.8, 131.6, 135.9, 166.0, 169.6. Anal. calcd for $C_{32}H_{36}F_3NO_9$: C, 60.47; H, 5.71; N, 2.20. Found: C, 60.69; H, 5.82; N,2.29.

4.7.6. 4-{(3*R*,5*R*)-1-Benzyl-3-[(1*S*)-1-methoxy-1-phenyl-1-(trifluoromethyl)acetoxy]-2-oxo-5-pyrrolidinyl}-2,3-*O*-isopropyliden-1-*O*-methyl-α-D-*lyxo*-tetrofuranose 17a. (Hexane/Et_2O, 60:40; R_f = 0.13); 55 mg (95%); oil; $[\alpha]_D^{25}$ = −4 (*c* 0.35, $CHCl_3$); ^1H NMR ($CDCl_3$, 55°C) δ 1.23 (s, 6H, CH_3), 2.36 (td, 1H, *J* = 5.7, 14.6 Hz, H_{4b}), 2.64 (td, 1H, *J* = 7.7, 14.6 Hz, H_{4a}), 3.18 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3), 3.89 (td, 1H, *J* = 5.6, 7.1 Hz, H_5), 3.97 (dd, 1H, *J* = 3.1, 5.3 Hz, $H_{4'}$), 4.27 (d, 1H, *J* = 15.6 Hz, NCH_2Ph), 4.39 (dd, 1H, *J* = 3.1, 6.0 Hz, $H_{3'}$), 4.47 (d, 1H, *J* = 6.0 Hz, $H_{2'}$), 4.82 (s, 1H, $H_{1'}$), 4.88 (d, 1H, *J* = 15.6 Hz, NCH_2Ph), 5.62 (dd, 1H, *J* = 5.7, 7.7 Hz, H_3), 7.20–7.36 (m, 5H, Ar*H*), 7.37–7.40 (m, 3H, Ar*H*), 7.58–7.62 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.3, 25.6, 29.7, 33.9, 45.4, 54.2, 54.8, 62.5, 72.1, 78.0, 79.4, 85.3, 106.6, 112.7, 125.1, 127.7, 127.8 (2C), 128.4, 128.7, 129.7, 131.7, 136.2, 165.9, 169.8. Anal. calcd for $C_{29}H_{32}F_3NO_8$: C, 60.10; H, 5.57; N, 2.42. Found: C, 60.32; H, 5.65; N, 2.36.

4.7.7. 4-{(3*R*,5*S*)-1-Benzyl-3-[(1*S*)-1-methoxy-1-phenyl-1-(trifluoromethyl)acetoxy]-2-oxo-5-pyrrolidinyl}-2,3-*O*-isopropyliden-1-*O*-methyl-α-D-*lyxo*-tetrofuranose 17b. (Hexane/Et_2O, 60:40; R_f = 0.16); 54 mg (94%); oil; $[\alpha]_D^{25}$ = +74 (*c* 0.33, $CHCl_3$); ^1H NMR ($CDCl_3$, 55°C) δ 1.25 (s, 6H, CH_3), 2.26 (td, 1H, *J* = 8.1, 14.0 Hz, H_{4b}), 2.40 (ddd, 1H, *J* = 2.4, 8.6, 14.0 Hz, H_{4a}), 3.26 (s, 3H, OCH_3), 3.51 (s, 3H, CH_3), 3.86 (dt, 1H, *J* = 2.4, 8.5 Hz, H_5), 3.91 (dd, 1H, *J* = 3.1, 9.2 Hz, $H_{4'}$), 4.36 (d, 1H, *J* = 14.3 Hz, NCH_2Ph), 4.52 (d, 1H, *J* = 6.0 Hz, $H_{2'}$), 4.67 (dd, 1H, *J* = 3.1, 6.0 Hz, $H_{3'}$), 4.95 (s, 1H, $H_{1'}$), 5.08 (d, 1H, *J* = 14.3 Hz, NCH_2Ph), 5.69 (t, 1H, *J* = 8.3 Hz, H_3), 7.24–7.29 (m, 5H, Ar*H*), 7.40–7.45 (m, 3H, Ar*H*), 7.60–7.64 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.8, 25.6, 28.6, 34.0, 46.3, 53.6, 54.9, 55.5, 72.1, 80.2, 83.1, 84.2, 107.7, 113.0, 121.8, 127.6, 127.8, 128.5, 128.6, 128.7, 129.8, 131.6, 136.1, 166.0, 169.2. Anal. calcd for $C_{29}H_{32}F_3NO_8$: C, 60.10; H, 5.57; N, 2.42. Found: C, 60.33; H, 5.42; N, 2.53.

4.7.8. 4-[(3*R*,5*R*)-1-Benzyl-3-[(1*S*)-1-methoxy-1-phenyl-1-(trifluoromethyl)acetoxy]-2-oxo-5-pyrrolidinyl]-3-*O*-benzyl-1,2-*O*-isopropyliden-α-D-*xylo*-tetrofuranose 17c. (Hexane/Et_2O, 60:40; $R_f=0.16$); 62 mg (95%); oil; $[\alpha]_D^{25}=-35$ (*c* 0.70, $CHCl_3$); ^1H NMR ($CDCl_3$, 55°C) δ 1.27 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 2.40 (td, 1H, $J=6.5$, 14.2 Hz, H_{4b}), 2.60 (ddd, 1H, $J=7.4$, 8.8, 14.2 Hz, H_{4a}), 3.56 (s, 3H, OCH_3), 3.73 (d, 1H, $J=3.3$ Hz, $H_{3'}$), 3.86 (ddd, 1H, $J=4.5$, 6.5, 7.4 Hz, H_5), 4.19 (d, 1H, $J=15.6$ Hz, NCH_2Ph), 4.26 (t, 1H, $J=3.9$ Hz, $H_{4'}$), 4.31 (d, 1H, $J=11.8$ Hz, OCH_2Ph), 4.55 (d, 1H, $J=3.8$ Hz, $H_{2'}$), 4.58 (d, 1H, $J=11.8$ Hz, OCH_2Ph), 4.77 (d, 1H, $J=15.6$ Hz, NCH_2Ph), 5.63 (dd, 1H, $J=6.9$, 8.8 Hz, H_3), 5.85 (d, 1H, $J=3.8$ Hz, $H_{1'}$), 7.06–7.09 (m, 2H, ArH), 7.15–7.33 (m, 8H, Ar*H*), 7.36–7.42 (m, 3H, Ar*H*), 7.57–7.62 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 26.2, 26.7, 27.9, 29.7, 45.2, 53.8, 55.6, 71.4, 71.8, 78.0, 81.7, 82.2, 85.0, 104.4, 111.8, 127.3, 127.6, 127.6, 127.8, 128.2, 128.4, 128.6, 128.8, 129.6, 131.6. 135.8, 136.8, 166.0, 169.6. Anal. calcd for $C_{35}H_{36}F_3NO_8$: C, 64.11; H, 5.53; N, 2.14. Found: C, 64.42; H, 5.42; N, 2.21.

4.7.9. 5-[(3*R*,5*R*)-1-Benzyl-3-[(1*S*)-1-methoxy-1-phenyl-1-(trifluoromethyl)acetoxy]-2-oxo-5-pyrrolidinyl]-1,2:3,4-di-*O*-isopropyliden-α-D-*galacto*-pentopyranose 17d. (Hexane/Et_2O, 60:40; $R_f=0.22$); 60 mg (95%); oil; $[\alpha]_D^{25}=+9$ (*c* 0.65, $CHCl_3$); ^1H NMR ($CDCl_3$, 55°C) δ 1.25 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 2.41 (td, 1H, $J=7.1$, 14.3, H_{4b}), 2.63 (ddd, 1H, $J=7.8$, 9.1, 14.3 Hz, H_{4a}), 3.55 (s, 3H, OCH_3), 3.69 (dt, 1H, $J=2.3$, 7.3 Hz, H_5), 3.99 (dd, 1H, $J=7.9$, 9.7 Hz, $H_{4'}$), 3.99 (d, 1H, $J=15.5$ Hz, NCH_2Ph), 4.03 (dd, 1H, $J=2.3$, 9.7 Hz, $H_{5'}$), 4.30 (dd, 1H, $J=2.0$, 5.0 Hz, $H_{2'}$), 4.55 (dd, 1H, $J=2.0$, 7.9 Hz, $H_{3'}$), 5.22 (d, 1H, $J=15.5$ Hz, NCH_2Ph), 5.54 (d, 1H, $J=5.0$ Hz, $H_{1'}$), 5.58 (dd, 1H, $J=7.1$, 9.1 Hz, H_3), 7.10–7.70 (m, 10H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.0, 24.5, 25.6, 26.2, 26.8, 43.9, 54.9, 55.5, 63.6, 70.1, 71.2, 71.5, 71.9, 85.0, 96.5, 108.2, 109.4, 123.2, 127.7, 127.8, 128.4, 128.9 (2C), 129.6, 131.6, 135.6, 166.2, 169.6. Anal. calcd for $C_{32}H_{36}F_3NO_9$: C, 60.47; H, 5.71; N, 2.20. Found: C, 60.35; H, 5.82; N, 2.28.

4.7.10. 5-[(3*R*,5*S*)-1-Benzyl-3-[(1*S*)-1-methoxy-1-phenyl-1-(trifluoromethyl)acetoxy]-2-oxo-5-pyrrolidinyl]-1,2:3,4-di-*O*-isopropyliden-α-D-*galacto*-pentopyranose 17e. (Hexane/Et_2O, 60:40; $R_f=0.24$); 60 mg (95%); oil; $[\alpha]_D^{25}=+85$ (*c* 0.25, $CHCl_3$); ^1H NMR ($CDCl_3$, 55°C) δ 1.23 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.55 (s, 3H, CH_3), 2.11 (ddd, 1H, $J=4.4$, 8.4, 13.6 Hz, H_{4b}), 2.54 (ddd, 1H, $J=1.8$, 8.1, 13.6 Hz, H_{4a}), 3.53 (s, 3H, OCH_3), 3.78 (dd, 1H, $J=1.8$, 4.4 Hz, H_5), 3.79 (s, 1H, $H_{5'}$), 4.12 (d, 1H, $J=7.9$ Hz, $H_{4'}$), 4.26 (d, 1H, $J=14.5$ Hz, NCH_2Ph), 4.31 (dd, 1H, $J=2.5$, 5.0 Hz, $H_{2'}$), 4.55 (dd, 1H, $J=2.5$, 7.9 Hz, $H_{3'}$), 5.10 (d, 1H, $J=14.5$ Hz, NCH_2Ph), 5.55 (d, 1H, $J=5.0$ Hz, $H_{1'}$), 5.69 (t, 1H, $J=8.2$ Hz, H_3), 7.18–7.29 (m, 5H, Ar*H*), 7.37–7.43 (m, 3H, Ar*H*), 7.57–7.64 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ 24.4, 24.8, 25.8, 26.2, 29.7, 46.3, 54.0, 55.5, 64.6, 69.7, 70.2, 70.8, 72.5, 84.9, 96.3, 109.0, 109.9, 121.3, 127.7, 127.8, 128.5, 128.6, 128.7, 129.8, 131.6, 135.9, 166.2, 169.6. Anal. calcd for $C_{32}H_{36}F_3NO_9$: C, 60.47; H, 5.71; N, 2.20. Found: C, 60.35; H, 5.77; N, 2.17.

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18. The authors have deposited the atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained on request from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The deposition number is CCDC 218370. The graphic view showed in Figure 2 was made with ORTEP3 software. Copyright by Farrugia, L. J., University of Glasgow, 1997–2000.