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Regio- and stereoselective synthesis of 3- and 5-(*C*-glycosyl)-4-nitroisoxazolidines by nitrone–nitroalkene [3+2] cycloaddition reactions

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Abstract

Cycloaddition reactions of nitrones, including sugar nitrones, with nitroalkenes, including sugar nitroolefins, led with complete regioselectivity and stereospecificity to 4,5-*trans*-4-nitroisoxazolidines in 51–78% global yields. The *endo/exo* stereoselectivity depends on the type of sugar derivative used. As expected, the best π-diastereofacial selectivity was observed when both partners were sugar derivatives. Isomerisation of the first formed diastereomers by the action of silica gel was observed in some cases. Absolute configurations for two crystalline products were assigned by X-ray diffraction methods.

1. Introduction

1,3-Dipolar cycloaddition reactions[1] have been widely used in the last two decades as the first step in strategies for the synthesis of diverse natural products and analogues. Nitrones, easily available from aldehydes or ketones and *N*-monosubstituted hydroxylamines, are one kind of 1,3-dipoles that undergo [3+2] cycloaddition reactions with alkenes to afford isoxazolidine derivatives having a masked 1,3-aminoalcohol functionality.[2] Three new stereogenic centres are generated in the reaction. Sugar derivatives have been considered as suitable target molecules since cycloaddition reactions of nitrones with certain dipolarophiles show, besides stereospecificity, good regio- and stereoselectivities.[3] Thus, the regio- and stereochemistry of reactions between *N*- or *C*-glycosyl nitrones and olefins leading to

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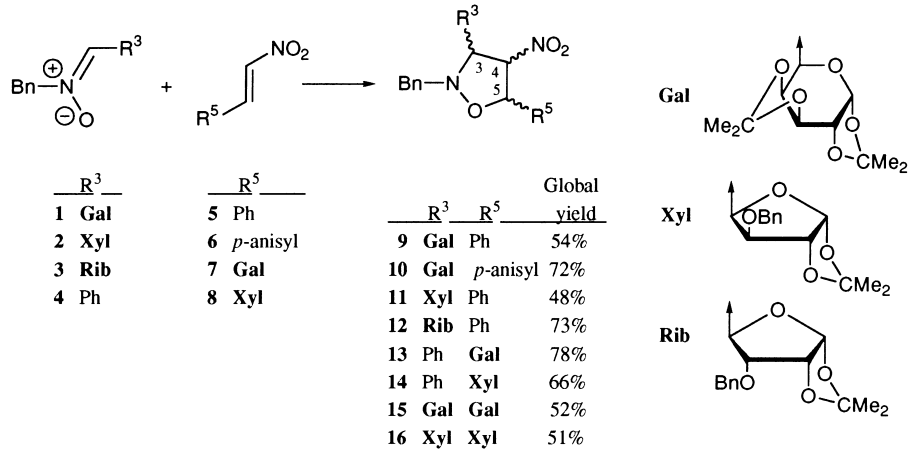
diversely substituted glycosyl isoxazolidines have been studied,[4–6] and applications to the synthesis of aminohexoses starting from *C*-glycosyl nitrones are known.[7,8] The intramolecular version of the nitrone–alkene cycloaddition reaction has been applied to sugar nitrones and the stereochemical course has been studied, for instance in the case[9] of nitrones of 3-*O*-allyl-D-hexoses. Reactions of alkenes having heterotopic faces with sugar nitrones, like other chiral nitrones,[10] are expected to proceed showing not only *endo/exo* stereoselectivity, but also π-diastereofacial selectivity (asymmetric induction). This possibility also arises when the chiral component is the dipolarophile[11] instead of the nitrone. Moreover, when both partners are enantiomerically pure, the diastereofacial selectivity will reach a much higher value if they constitute a *matched pair*. Stereochemical control of the reaction is then necessary for obtaining one of the eight possible diastereomers as the predominant product. We now report on the stereochemical course of cycloaddition reactions of three *C*-glycosylnitrones with β-nitrostyrene and *p*-methoxy-β-nitrostyrene, two sugar nitroolefins with *N*-benzyl-*C*-phenylnitrone, and two *C*-glycosylnitrones with nitroolefins derived from the same sugars, respectively.

2. Results and discussion

The (*Z*)-*N*-benzyl-*C*-glycosylnitrones **1**–**3** (Scheme 1), easily obtained by reaction of *N*-benzyl-hydroxylamine with 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose, 1,2-*O*-isopropylidene-α-D-*xylo*-, and -α-D-*ribo*-pentodialdo-1,4-furanose, respectively, underwent regioselective [3+2] cycloaddition reaction with excess β-nitrostyrene **5** in toluene at 50–110°C, to afford diastereomeric mixtures of 2-benzyl-3-(glycopyranos-5-yl or glycofuranos-4-yl)-4-nitro-5-phenylisoxazolidines **9**, **11**, and **12** in 54%, 48%, and 73% global yields, respectively. The presence of an electron-donor group, such as the *p*-methoxy group, on the aromatic ring of β-nitrostyrene seems to raise the reactivity of the dipolarophile, since the nitrone **1** reacted with *p*-methoxy-β-nitrostyrene **6** under similar conditions to afford a diastereomeric mixture of the corresponding isoxazolidine derivative **10** in a higher yield (72%). Starting from *N*-benzyl-*C*-phenylnitrone **4** and the sugar nitroolefins **7** and **8**, derived from nitromethane and the two dialdo-sugars cited first and second above, resulted in diastereomeric mixtures of the isoxazolidines **13** (global yield, 78%) and **14** (66%), respectively. Reaction of equimolar amounts of the nitrone **1** and the nitroolefin **7**, both derived from D-galactose, afforded 52% of a mixture of cycloadducts **15**, whereas the D-xylose derivatives **2** and **8** gave rise to one predominant diastereomer (>90:10) of **16** in 51% yield.

The regioselectivity of these reactions, as deduced from the ^{1}H and ^{13}C NMR spectra of **9**–**16** (Tables 1 and 2, respectively), was that expected from antecedents for reactions of nitroalkenes, such as β-nitrostyrene itself[12] or nitroethylene[13,14] with other nitrones, that is, the nitro group is oriented to position 4 of the isoxazolidine ring. COSY and HETCOR experiments confirmed the assignments given in Tables 1 and 2.

More problematic is the assignment of absolute configuration to the new stereogenic centres. It is known[15] that the coupling constant values measured on the signals of H-3, H-4, and H-5 of the isoxazolidine ring are not clearly correlated with their *cis* or *trans* relative disposition, since different ring conformations are possible. NOE experiments are normally needed for ascertaining the spatial relationships in isoxazolidine derivatives.[16] Some stereochemical features may be predicted; thus, starting from a *trans*-1,2-disubstituted alkene, the formation of a *trans*-3,4-disubstituted isoxazolidine is expected, due to the stereospecificity of the cycloaddition reactions. If it is assumed that this rule is followed, the number of possible diastereomeric products will be limited to four (**a**, **b**, **c**, **d**, Scheme 2). The stereoselective formation of **a** and **c** through *endo* transition states, over **b** and **d**, coming from



R3		R5		Global yield
1	Gal	5	Ph	
2	Xyl	6	*p*-anisyl	
3	Rib	7	Gal	
4	Ph	8	Xyl	
9	Gal	Ph		54%
10	Gal	*p*-anisyl		72%
11	Xyl	Ph		48%
12	Rib	Ph		73%
13	Ph	Gal		78%
14	Ph	Xyl		66%
15	Gal	Gal		52%
16	Xyl	Xyl		51%

Scheme 1.

exo approaches, should be expected. However, this second rule is not always obeyed. It is known that certain aldonitrones undergo *Z–E* isomerisation under the reaction conditions,[17] and the presence of both isomers of *C*-glycosyl nitrones in the reaction mixtures could not be ruled out[5,11] in spite of the high energy differences calculated by semiempirical methods.[5] In the cases discussed here, we have not found any evidence for the presence of *E*-isomers of **1**–**4**, in agreement with other authors,[18,19] but we cannot completely exclude their formation in the course of the reactions.

In the reactions of **1** with **5** and **6**, the formation of two diastereomers was observed (65:35 by ^{1}H NMR), which underwent a partial isomerisation when in contact with the silica gel used in the subsequent chromatographic separation, to give a new diastereomer **9b** as the main component of the new mixture of products (72:18:10; global yield, 54%); a similar isomerisation by silica gel had earlier[13] been observed for an isoxazolidine obtained in the reaction of nitroethylene with *N*-methyl-*C*-phenylnitrone, and had been described as a 3,4-*cis*-to-*trans* isomerisation. In our case, the major isolated diastereomer **9b** could be crystallised and its absolute configuration was unambiguously determined by X-ray diffraction analysis as 2*S*,3*S*,4*S*,5*R*, that is, its structure corresponds to one of the two possible invertomers at the isoxazolidine nitrogen (2*S*)-**9b** (Fig. 1, Table 3). The two minor products were identical (by ^{1}H NMR) to the components of the original reaction mixture, respectively; the more abundant among these two crystallised from the mother liquors of (2*S*)-**9b**, and was characterised as **9d** from the following evidence: (i) 1D NOESY experiments, carried out on a sample in DMSO-d_6 at 40°C, clearly showed the 3,4-*cis* and 4,5-*trans* configurations (H-3/H-4 contacts, absence of H-3/H-5 contact); (ii) it slowly isomerises to **9b** in the same solvent, to give, after 5 days at room temperature, a ~89:11 mixture of **9b** and **9d**. Apart from that, compound **9d** showed in solution the behaviour of a system in relatively slow equilibrium, as suggested by the ^{1}H NMR spectra in $CDCl_3$ at room temperature or in DMSO-d_6, where H-3, H-5 and the benzylic methylene protons appeared as broadened signals. However, lowering the temperature of the solution in $CDCl_3$ down to −25°C resulted in the separation in the spectra of two isomers (86% and 14%), although neither was superimposable to that of **9b**; hence, the equilibrating system is a mixture of invertomers (2*R*)- and (2*S*)-**9d**. For the minor component of the diastereomer mixture, the *endo* structure **9a** (or **9c**) is tentatively assigned. Thus, an explanation for the foregoing results may be that the products **9d** and **9a** of the kinetic mixture isomerise over the course of chromatography to give the thermodynamic mixture, from which the main product **9b** crystallises; the isomerisation might occur through a silica gel catalysed equilibration by cycloreversion of the former products and a new cycloaddition by attack of the nitroalkene on the opposite face of the nitrone.

Table 1
Selected ^{1}H NMR data for compounds **9–16** at 500 MHz[a]

Compd	Chemical shifts (δ in ppm)					
	Isoxazolidine protons			Sugar moiety protons		
	H-3	H-4	H-5	H-1'/H-1"	H-4'/H-4"	H-5'/H-5"
9 d[b]	3.65-3.20br	5.25dd	5.37-5.25br	5.61d		4.37dd
idem[c]	3.60-3.40br	5.29dd	5.40-5.30br	5.59d		4.26dd
idem[b] (at -25 °C)						
Major (86%) invertomer	3.37brdd	5.21dd[e]	5.21d[e]	5.65d		4.30dd
Minor (14%) invertomer	4.62dd[e]	5.41dd	5.80d	5.68d		4.15dd
9c or **a**[bd]	≈ 4.35dd[e]	5.40dd	5.78d	5.48d		3.76dd
9b[b]	4.19dd	5.80dd	5.53d	5.50d		3.77dd
9b[c]	4.08dd	5.95dd	5.31d	5.54d		3.89dd
10d[bd]	≈ 4.3[e]	5.22brdd	≈ 5.2[e]	5.59d		3.83dd
10c or **a**[bd]	5.38dd	5.72dd	5.63d	5.49d		3.78dd
10b[bf]	4.17dd	5.73dd	5.46d	5.50d		3.76dd
11b[b]	4.52dd	5.52dd	5.75d	5.87d	4.35dd	
11d[bd]	4.22dd	5.13dd	5.59d	5.97d	≈ 4.35[e]	
12b[b]	4.13dd	5.49dd	5.74d	5.66d	4.39dd	
12d[b]	4.10dd	5.48dd	5.71d	5.88d	4.15dd	
13c[bf]	4.08d	5.63dd	5.10dd	5.58d		4.05dd
13a[bf]	4.28d	5.39dd	4.93dd	5.57d	←4.19-4.14m→	
13b or **d**[bf]	4.29d	5.34dd	4.93dd	5.58d		4.23dd
14b or **d**[b]	4.13d	5.60dd	5.08dd	6.00d	4.47dd	
14a or **c**[b]	4.29d	5.45dd	5.01dd	5.93d	4.58dd	
14(**c** or **a**)[b]	4.31d	5.05dd	4.92dd	5.90d	4.67dd	
14(**d** or **b**)[bf]	4.12d	5.55dd	5.25dd	5.96d	4.47dd	
15b[cg]	3.61-3.53br	5.80dd	4.53-4.47br	5.56d/5.47d[h]		3.98dd/3.93dd
idem[b] (at -25 °C)						
Major (77%) invertomer	3.62dd	5.75dd	≈4.59dd[e]	5.64d/5.48d		3.90dd[e]/3.89dd[e]
Minor (23%) invertomer	4.66dd	6.08dd	5.27dd	≈5.64d[e]/5.53d		≈4.10dd[e]/n.o.[ei]
15(**d**)[bk]	3.42-3.40br	5.31dd	n.o.[ei]	5.53d/5.51d[e]		3.90dd/3.85dd
16b or **d**[b]	4.01dd	5.28dd	4.83dd	5.89d/5.92d[h]	4.43dd/4.39dd	

table continues

Compd	Selected coupling constants (J in Hz)						
	$J_{3,4}$	$J_{4,5}$	$J_{1',2'}/J_{1'',2''}$	$J_{3,5'}$	$J_{3,4'}$	$J_{5,5'}/J_{5,5''}$	$J_{4',5}/J_{4'',5}$
9d[b]	4.7	6.6	5.0	8.5	--	--	--
idem[c]	4.5	6.4	5.1	8.5	--	--	--
idem[b] (at -25 °C)							
Major invertomer	3.5	6.5	5.1	8.4	--	--	--
Minor invertomer	7.5	5.7	5.1	10.1	--	--	--
9c or **a**[bd]	2.3	6.6	5.1	10.1	--	--	--
9b[b]	3.5	5.8	4.9	7.0	--	--	--
10d[bd]	3.5	n.m.[j]	5.1	2.3	--	--	--
10c or **a**[bd]	≈ 6.7	≈ 7.0	5.0	≈ 2.4	--	--	--
10b[bf]	3.6	5.9	4.9	7.1	--	--	--
11b[b]	2.3	6.3	3.7	--	8.7	--	--
11d[bd]	4.9	6.0	4.0	--	7.6	--	--
12b[b]	4.9	5.6	3.6	--	3.0	--	--
12d[b]	3.8	6.4	3.8	--	4.2	--	--
13c[bf]	8.0	4.6	4.9	--	--	1.5	--
13a[bf]	6.9	2.7	5.1	--	--	8.4	--
13b or **d**[bf]	7.0	3.8	4.9	--	--	8.2	--
14b or **d**[b]	8.0	4.6	3.8	--	--	--	1.5
14a or **c**[b]	6.4	2.8	3.6	--	--	--	7.0
14(**c** or **a**)[b]	7.1	4.6	4.0	--	--	--	6.6
14(**d** or **b**)[bf]	7.8	5.1	3.6	--	--	--	6.4
15b[cg]	6.5	4.4	5.0/ 4.9[h]	9.0	--	--/ 6.8	--
idem[b] (at -25 °C)							
Major invertomer	6.0	3.2	5.0/ 4.8	9.4	--	--/ 5.6	--
Minor invertomer	7.1	4.4	n.o.[ei]/ 5.0	10.9	--	--/ 5.9	--
15(**d**)[bk]	6.0	2.8	5.0/ 5.0	7.8	--	--/ 8.0	--
16b or **d**[b]	5.0	3.4	3.8/ 3.8	--	9.2	--	--/ 7.0

[a]Unless otherwise noted.
[b]In $CDCl_3$.
[c]In DMSO-d_6.
[d]From the reaction mixture.
[e]Overlapped signal.
[f]At 300 MHz.
[g]At 50 °C.
[h]Notations H-n' and H-n'' apply, respectively, to protons of the sugar moiety at the 3- and 5-positions of the isoxazolidine ring.
[i]Not observed.
[j]Not measured (complex multiplet).
[k]From a mixed fraction.

The reaction of **1** with **6** proceeded in a similar manner, ^{1}H NMR of the mixture showing the presence of only two diastereomers of **10** (67:33); isomerisation of these products took place during column chromatography, and the new diastereomer could be isolated pure as an oil, to which the absolute

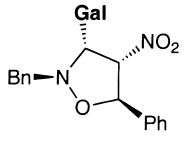
Table 2
Selected ^{13}C NMR data for compounds **9–16** in $CDCl_3$

Selected ^{13}C NMR data for compounds **9-16** in $CDCl_3$

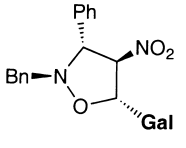
Compd	Chemical shifts (δ in ppm)					
	C-3	C-4	C-5	C-1'/C-1"	C-4'/C-4"	C-5'/C-5"
9d[a]	71.0	96.2[b]	83.7	96.3[b]		65.7
9b[c]	71.3	94.1	81.4	96.2		66.4
10b[a]	71.2	94.1	81.2	96.1		66.4
11b[a]	68.0	97.2	83.9	105.0	80.0	---
11d[ad]	68.0	96.8	82.9	105.3	80.7	---
12b[c]	69.9	94.7	82.1	103.9	78.5	---
12d[c]	69.3	96.9	83.7	104.4	79.5	---
13c[a]	74.3	92.6	80.1	96.2		65.5
13a[a]	76.1	96.5	78.2	96.3		66.5
13b or **d**[a]	76.1	95.4	80.1	96.3		66.9
14b or **d**[c]	74.9	93.0	79.3	105.3	78.3	---
14a or **c**[c]	76.1	96.6	77.7	105.3	79.8	---
14(**c** or **a**)[a]	74.6	96.0	79.7	105.4	80.1	---
14(**d** or **b**)[a]	74.9	93.5	78.4	105.1	78.2	---
15b[c]	60.1[e]	91.2	80.5[e]	96.3/96.2		64.6/66.2
15(**d**)[c]	71.5	91.3	79.7	96.4/96.3		64.6/64.9
16b or **d**[c]	70.4	92.5	78.9	105.2/105.4	80.7/78.9	---

[a] At 75.5 MHz.
[b] These assignments may be interchanged.
[c] At 125.8 MHz.
[d] From the reaction mixture.
[e] Broad signal.

configuration 3*S*,4*S*,5*R* (**10b**) was assigned on the basis of the similarity found between its ^{1}H and ^{13}C NMR spectra and those of **9b** (Tables 1 and 2). For the main primitive diastereomer, the structure **10d** is assigned by analogy with the respective diastereomer of **9**.

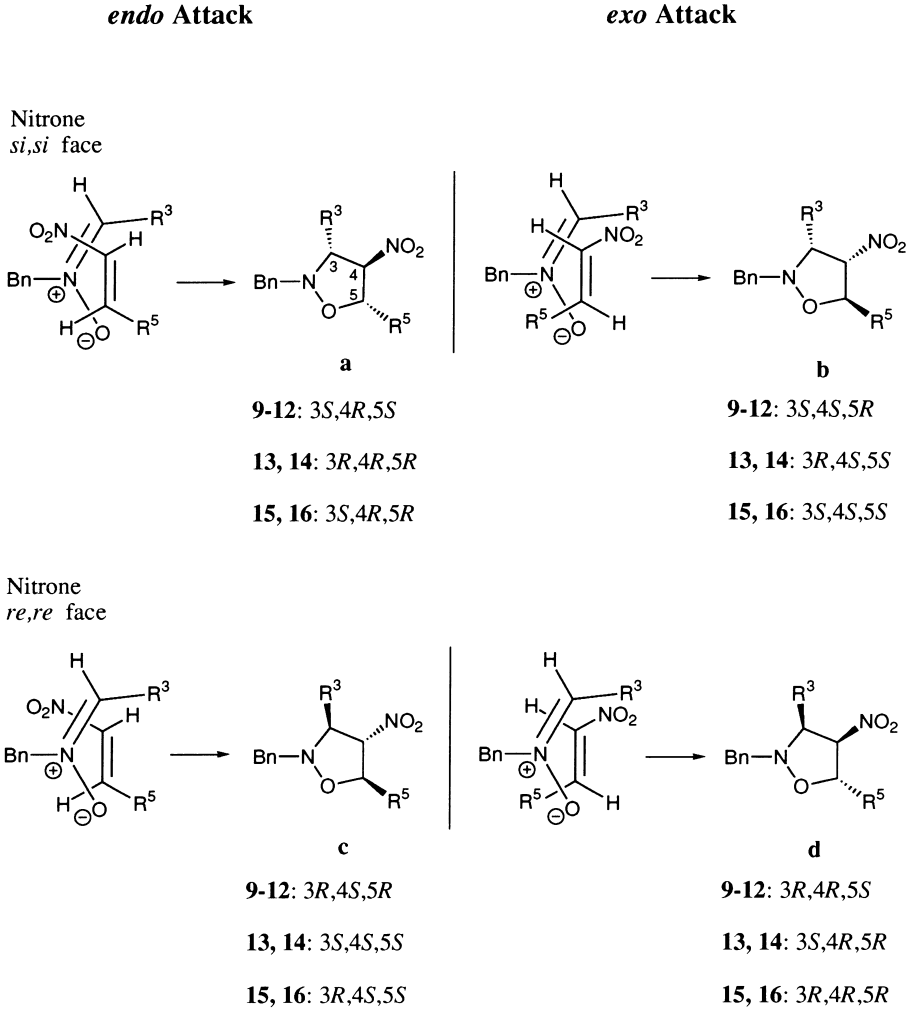


(2*S*)-**9b**



(2*S*)-**13a**

The reactions of the nitrones **2** and **3** with **5** led to 65:35 and 61:39 mixtures of diastereomers of **11** and **12**, respectively. No isomerisation provoked by silica gel was observed in the chromatographic purification. The absolute configuration of the major diastereomer of **11** was tentatively assigned by 1D NOESY, which evidenced the 3,4-*cis* and 4,5-*trans* configurations (H-4/H-3 contact; absence of contacts H-4/H-5 and H-3/H-5) and the *cis* disposition between the *N*-benzyl group and the sugar moiety (H-5/NC*H*HPh and H-5/H-1′ contacts), in agreement with the expected H-4/H-4′ contact also observed.



Scheme 2.

These facts are compatible with **11b** or **11d**. Molecular models seem to indicate that **11d** is sterically more hindered than **11b** due to the presence of the 3′-*O*-benzyl group in the same configured sugar moiety for both diastereomers; the **11b** structure is thus tentatively assigned for the major isomer, to which the 3*S*,4*S*,5*R* configuration should correspond. Moreover, in this case, the more stable invertomer in solution seems to be the 2*R* configured one, as deduced from the NOE contact between H-5 and one of the benzylic methylene protons mentioned above. For the minor diastereomer, the alternative **11d** structure is assigned on the assumption that the *exo* attack, as for its isomer, is predominant. With respect to the configuration of the major isomer of the ribose derivative **12**, it was also determined on the basis of 1D NOESY experiments, from which the 3,4-*cis* and 4,5-*trans* relationships were deduced (H-4/H-3 contact; absence of contact between H-4 and H-5). By comparison of models of **12b** and **12d**, it appears that the H-4/H-4′ and H-4/H-3′ contacts observed are more compatible for the former than for the latter. The contact between H-5 and one of the methylene hydrogen atoms of *N*-benzyl again agrees here with the assignment of the (2*R*)-**12b** structure for the major isomer. The **12d** configurational structure is tentatively assigned for the minor isomer.

Products **13** and **14**, formed in the reactions of the nitrone **4** with the sugar nitroolefins **7** and **8**,

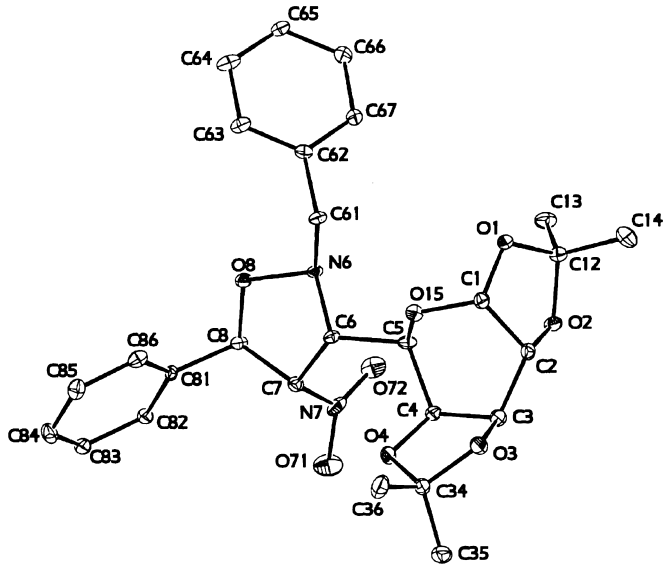


Figure 1. A PLATON view of (2*S*)-**9b** showing the atomic labelling. Thermal ellipsoids enclose 30% probability. C–H bonds are omitted for clarity

Table 3
Selected bond distances (Å) and torsion angles (°) for (2*S*)-**9b**

Bond lengths		Torsion angles		e.s.d.
O8-N6	1.473(10)	C8-O8-N6-C6	-48.94	0.79
N6-C6	1.495(12)	O8-N6-C6-C7	45.26	0.77
C6-C7	1.524(14)	H6-C6-C7-H7	-25.06	1.09
C7-C8	1.528(14)	N6-C6-C7-C8	-26.48	0.88
O8-C8	1.430(12)	C5-C6-C7-N7	-34.05	1.24
N6-C61	1.495(12)	H7-C7-C8-H8	-121.23	0.99
C5-C6	1.547(14)	N7-C7-C8-O8	-123.60	0.82
O15-C5	1.441(11)	H6-C6-C5-H5	-162.56	0.82
O15-C1	1.417(12)	N6-C6-C5-O15	86.42	0.84
C1-C2	1.489(14)	N6-C6-C5-C4	-154.64	0.78
C2-C3	1.500(15)	C7-C6-C5-C4	-35.80	1.23
C3-C4	1.523(14)	C7-C6-C5-O15	-154.74	0.81
C4-C5	1.529(14)	C6-N6-C61-C62	177.56	0.75
N7-C7	1.504(14)	C82-C81-C8-C7	-91.68	1.02
C8-C81	1.524(13)	O71-N7-C7-C6	142.11	1.04
O71-N7	1.239(17)	N7-C7-C8-C81	118.96	0.87
O72-N7	1.197(15)	C61-N6-C6-C5	-74.11	0.94

respectively, were also separated into pure diastereomers by chromatography on silica gel. For **13**, three diastereomers were detected in the reaction mixture (55:36:9 by ^{1}H NMR). After column chromatography, the two major products were isolated as pure diastereomers (44% and 25%, respectively); the second one was crystalline and could be unambiguously characterized by X-ray diffraction methods as the (2*S*,3*R*,4*R*,5*R*) diastereomer [(2*S*)-**13a**, Fig. 2, Table 4], formation of which is explained as coming from the *endo* attack of the sugar nitroalkene to the *si*,*si* face of the nitrone (Scheme 2). The configurational assignment for the major diastereomer is based only on NMR data and mechanistic considerations; thus, the higher values of $J_{3,4}$ and $J_{4,5}$ (8.0 and 4.6 Hz) as compared, respectively, with those for **13a** (6.9 and 2.7 Hz), and particularly the much lower value of $J_{5,5'}$ for the former (1.5 Hz) than for the latter (8.4 Hz) are in fair agreement with those expected for the structure **13c** (3*S*,4*S*,5*S*, probably 2*R* as the more

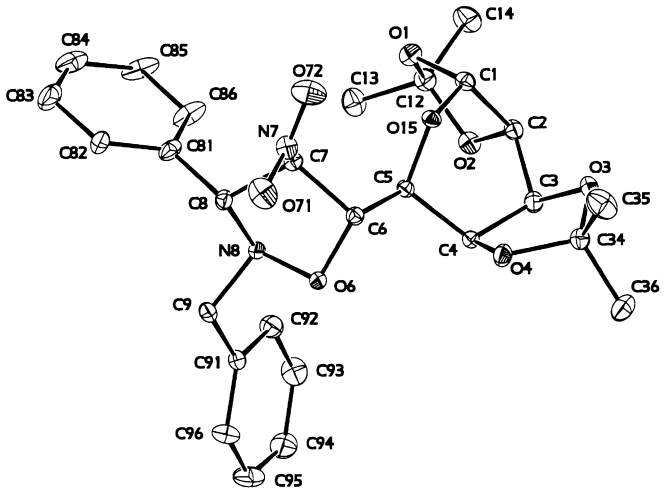


Figure 2. A PLATON view of (2*S*)-**13a** showing the atomic labelling. Thermal ellipsoids enclose 30% probability. C–H bonds are omitted for clarity

stable invertomer). In a first approach, molecular models show that the sugar moiety in **13a** would adopt in solution a preferred conformation around the C-5–C-5′ bond having a dihedral H–C–C–H angle of ~180°, similar to that adopted in the crystalline state (172.04°, see Table 4 and Fig. 2), but in **13c** this value would be incompatible with the $J_{5,5'}$ value (1.5 Hz) cited above, a rotation down at ~110° (or ~70°) being in better agreement; the models reveal that a value of ~180° in **13c** (*but not in* **13a**) would cause an unfavourable dipolar interaction between the nitro group and the C-4′–O bond of the sugar moiety. The major diastereomer **13c** would come from the *endo* attack of the sugar nitroalkene to the *re,re* face of the nitrone, the π-diastereofacial selectivity being 55:36 (60:40). A mixed fraction from the chromatography contained a small amount of **13a** (2.4%) and the minor diastereomer (6%), a configurational assignment for which could not be ascertained from the ^{1}H NMR of this mixture, the remaining possibilities being **13b** or **13d**. With respect to the xylose derivative **14**, the major isomer shows the 3,4-*cis* and the 4,5-*trans* relationships as deduced from its 1D NOESY spectrum (H-4/H-3 contact, low intensity H-5/H-4 contact, absence of H-5/H-3 contact), compatible with the structures **14b** or **14d**; the second main diastereomer is tentatively formulated as the **14a** or **14c** isomer, since NOE experiments (1D NOESY) revealed the *trans* relationship for both H-3/H-4 and H-4/H-5 proton pairs on the isoxazolidine ring (low intensity contacts between them in each pair and also between H-3 and H-5). Two minor diastereomers (12% and 2%) were also isolated, although the experimental data obtained for them were insufficient to assign any configuration.

The reaction of **1** with **7** led to **15** as a ~70:30 mixture of two isomers (by ^{13}C NMR), among which only the major one (41% after column chromatography) could be studied as a pure substance. Its ^{1}H NMR spectrum, recorded in DMSO-d_6 at 50°C, showed broadened H-3 and H-5 signals (Table 1), which suggested a slowly equilibrating system similar to that found for **9d** (see above). When the spectrum was recorded in $CDCl_3$ at −25°C, signals for two invertomers (77:23) were again observed here; for the major invertomer under these last conditions, the *cis*-relationship between H-3 and H-4 and the *trans*-disposition between H-4 and H-5 were deduced from 1D NOESY experiments (H-3/H-4 contact; absence of H-4/H-5 and H-3/H-5 contacts). From these facts and by analogy with **9b** (particularly the chemical shift of H-4) the structure **15b** is assigned for the isolated diastereomer; the major invertomer has probably the (2*S*) configuration as deduced from the NOE contact also observed between H-3 and

Table 4
Selected bond distances (Å) and torsion angles (°) for (2*S*)-**13a**

Bond lengths		Torsion angles		e.s.d.
O6-N8	1.468(06)	C6-O6-N8-C8	-52.86	0.46
N8-C8	1.480(08)	C6-C7-C8-N8	-23.11	0.52
C7-C8	1.538(09)	H7-C7-C8-H8	-137.48	0.54
C6-C7	1.536(07)	C6-C7-C8-C81	-141.36	0.50
O6-C6	1.433(08)	N7-C7-C8-C81	99.48	0.59
C6-C5	1.518(07)	O6-C6-C7-C8	-8.11	0.54
O15-C5	1.431(07)	H6-C6-C7-H7	108.22	0.56
O15-C1	1.405(06)	C5-C6-C7-N7	-131.31	0.48
C1-C2	1.540(09)	N8-O6-C6-C7	36.70	0.48
C3-C2	1.517(07)	C9-N8-C8-C81	-80.48	0.59
C4-C3	1.543(08)	C7-C8-C81-C82	-117.98	0.71
C5-C4	1.526(07)	H6-C6-C5-H5	172.04	0.45
N8-C9	1.461(09)	C7-C6-C5-C4	174.58	0.44
C8-C81	1.511(08)	O6-C6-C5-O15	169.71	0.40
N7-C7	1.512(09)	O71-N7-C7-C8	44.08	0.79
N7-O71	1.204(07)	O72-N7-C7-C6	104.67	0.70
N7-O72	1.168(09)	C8-N8-C9-C91	172.45	0.47

one of the benzylic methylene protons. A mixed fraction from the chromatography contained the minor isomer (11% yield by ^{1}H NMR), to which the structure **15d** is tentatively assigned.

Finally, in the reaction of **2** with **8** a main product was formed accompanied by <10% of a diastereomer (by ^{1}H NMR). Only the major product was isolated after column chromatography (**16**, 51%), for which the configurational structures **16b** (3*S*,4*S*,5*S*) or **16d** (3*R*,4*R*,5*R*) might be assigned on the basis of some similarities of its NMR spectra with those of **11b** and **11d**, and mechanistic considerations, but the available data are not conclusive.

*2.1. X-Ray structure analysis of (2*S*)-**9b***

A PLATON view[20] of the molecule along the *c* axis together with the atomic labelling is shown in Fig. 1. Selected bond lengths and torsion angles are shown in Table 3. The pyranose endocyclic bond lengths are O15–C1=1.417(11) and O15–C5=1.441(11) Å showing some anomeric effect. The two phenyl groups are planar (max. s.d. 0.015 Å). The geometry observed for the pyranose ring shows a heavily distorted conformation[21] between twist-boat (skew-boat) $^{O}T_2$ and screw-boat $^{O}S_5$ deviated towards $B_{2,5}$. In terms of ring-puckering coordinates,[22] amplitudes and phase magnitudes are Q=0.66(1) Å, φ=−36(1)°, and θ=82(1)° for the sequence O15–C1–C2–C3–C4–C5, and the asymmetry parameters[23] are ΔC_2[C1]=0.059 and ΔC_2[O15–C5]=0.042. The two dioxolane rings have different conformations. The geometry observed for one dioxolane ring with sequence O1–C12–O2–C2–C1 is intermediate between *T* and *E* with puckering coordinates Q=0.32(1) Å, φ=−99(2)°. The asymmetry parameters are ΔC_2[O11]=0.031 and ΔC_s[O2]=0.040. The other dioxolane group, sequence O3–C34–O4–C4–C3 shows a slightly distorted *E* conformation, Q=0.29(1) Å and φ=5(1)°, asymmetry parameters ΔC_2[C4]=0.0038 and ΔC_s[O3]=0.023. The isoxazolidine ring conformation is slightly distorted *E*, of which puckering and asymmetry parameters are Q=0.467(7) Å, φ=34(1)°, ΔC_s[N6]=0.017, and ΔC_2[C7]=0.074 for the sequence O8–N6–C6–C7–C8. The isoxazolidine substituents C61 and C81 are on one side at −0.407(10) and −0.828(9) Å and N7 and C5 are on the other side of the least-squares best plane at 1.448(10) and 0.877(10) Å. The dihedral angles formed by least-squares planes are: isopropylidene–pyranose 78.3(3) and 86.1(3)° and isoxazolidine–pyranose 79.3(4)°. The packing of molecules is

governed by van der Waals forces. There are three intramolecular short contacts: C63···O8=3.215(13), C61···O15=3.016(12), and C7···O4=3.076(13) Å.

2.2. X-Ray structure analysis of (2S)-13a

A PLATON view[20] of the molecule along the *c* axis together with the atomic labelling is shown in Fig. 2. Selected bond lengths and torsion angles are shown in Table 4. The typical asymmetry of endocyclic bonds for the pyranose ring O15–C1 and O15–C5 [1.405(6) and 1.431(7) Å, respectively] caused by the anomeric effect, is observed. The two phenyl groups are planar and the C9 (benzyl methylene) is slightly distorted (0.066 Å) from the least-squares phenyl plane. The pyranose geometry observed for this compound agrees with a heavily distorted conformation between twist-boat (skew-boat) $^{O}T_2$ and screw-boat $^{O}S_5$ deviated towards $B_{2,5}$, in agreement with the foregoing compound and other 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose derivatives.[21] The ring-puckering coordinates[22] and asymmetry parameters are Q=0.65(1) Å, φ=−35(1)°, and θ=79(1)° for the sequence O15–C1–C2–C3–C4–C5, and ΔC_2[C1]=0.070 and ΔC_2[O15–C5]=0.033. The geometries observed for the two dioxolane rings are also different, in agreement with (2*S*)-**9b**. The conformation for one of them with sequence O3–C34–O4–C4–C3 is intermediate between *T* and *E*, with puckering coordinates and asymmetry parameters Q=0.27(1) Å, φ=−12(1)°, ΔC_2[C4]=0.015 and ΔC_s[O3]=0.048. The other dioxolane group sequence O1–C12–O2–C2–C1 shows a slightly distorted *E* conformation, Q=0.31(1) Å, φ=−114(1)°, and ΔC_s[O2]=0.027 and ΔC_2[C1]=0.038. The isoxazolidine ring shows a geometry different to (2*S*)-**9b**, the conformation for the sequence O6–N8–C8–C7–C6 being intermediate between *T* and *E* with parameters Q=0.49(1) Å, φ=−28(1)°, and ΔC_s[N8]=0.059, ΔC_2[C7]=0.049. The isoxazolidine substituents C81 and C5 are on one side at 0.310(8) and 1.663(5) Å and the C9 and N7 on the other side of the least-squares best plane at −0.283(6) and −1.125(5) Å. The dihedral angles between the least-squares planes of the pyranose and isopropylidene groups are 103.5(2) and 98.9(2)°, and between those of isoxazolidine and pyranose 69.6(3)°. Crystal cohesion by van der Waals interactions: there is one intramolecular short contact C5···O2=3.101(7) Å.

3. Conclusion

The reactions studied here proceeded with complete regioselectivity to give isoxazolidines with the nitro group at position 4. All the products **9**–**16** exhibited the 4,5-*trans* relationship, in agreement with the stereospecificity rule of cycloaddition reactions. Table 5 summarizes the formed diastereomeric ratios in the reaction mixtures and the global and isolated diastereomer yields after chromatography. Only two diastereomers were formed when the glycosyl substituent is at position 3 **9**–**12**; for the D-galactose derivatives **9** and **10**, these isomers are *exo/endo* diastereomers, the *exo* one (**d**) undergoing isomerisation in contact with silica gel to its more stable π-facial diastereomer **b**; for the pentose derivatives **11** and **12**, the initially formed *exo* adducts suffered no isomerisation by silica gel and seem to be the isomers **b** and **d**, the π-diastereofacial selectivity (expressed as formed diastereomeric ratio) rising to ~3:2. Starting from the sugar nitroalkenes **7** and **8** and the *C*-phenyl nitrone **4**, the stereoselectivity is low, as three isomers of **13** and four of **14** were formed (Table 5). Therefore, the *exo/endo* and/or the π-facial stereoselectivities seem to be generally better for reactions of *C*-glycosyl nitrones than for those of sugar nitroalkenes. The reactions between reagents both containing a sugar moiety gave the cycloadducts **15** and **16** with complete *exo* stereoselectivity, leading to **b** and **d** with better π-diastereofacial selectivity values (~7:3 for **15** and ~9:1 for **16**), as a consequence of the double asymmetric induction exerted by

Table 5
Diastereomeric ratios in the reaction mixtures (by ^{1}H NMR) and global[a] and isolated diastereomer yields[a]

Compd	Formed diastereomer ratios		Global yields	%	Isolated yields, %
9	**d**:**c**[b](**a**[b])	65:35	**b**[c]+**d**+**c**	54	**b** 19, **d**[d]
10	**d**:**c**[b](**a**[b])	67:33	**b**[c]+**c**	72	**b**[e] 35, **c**[f]
11	**b**:**d**	65:35	(Only **b**)	48	**b** 48
12	**b**:**d**	61:39	**b**+**d**	73	**b** 46, **d** 27
13	**c**:**a**:**b**[b](**d**[b])	55:36:9	**c**+**a**+**b**(**d**)	78	**c** 44, **a** 28, **b**(**d**) 6
14	**b**[b](**d**[b]):**a**[b](**c**[b]):**c**[g]:**d**[g]	45:34:14:7	**b**+**a**+**c**+**d**	66	**b** 27, **a** 25, **c** 12, **d** 2
15	**b**:**d**[b]	≈70:30	**b**+**d**	52	**b** 41, **d** 11
16	**b**[b]:**d**[b]	>90:10	(Only **b**)	51	**b** 51

[a] After chromatography on silica gel.
[b] These configurational assignments are tentative.
[c] Formed during the chromatography.
[d] Not determined.
[e] An additional amount (22%) was present in other two fractions, but mixed with **c**.
[f] 15% in two mixed fractions with **b**.
[g] For these minor isomers any configurational assignment could not be ascertained.

both sugar derivatives used as the reagents, which form a *matched pair*. With respect to isolated products, the major one agrees with the major formed product, except for **9** and **10**, where a partial isomerisation of the adducts **d** and **c** (or **a**) to **b** occurs during the chromatographic separation; this fact is explained assuming a silica gel catalysed cycloreversion of the kinetic adduct followed by a new cycloaddition to the thermodynamically more stable one.

4. Experimental

4.1. General

TLC was performed on silica gel 60 plates (DC-Alufolien F_{254}, E. Merck, or Alugram Sil G/UV_{254}, Macherey–Nagel), with detection by UV light (254 nm) or by charring with H_2SO_4. Silica gel 60 (E. Merck) was used for column chromatography. Solutions were concentrated under reduced pressure. Optical rotations were measured in $CHCl_3$ with a Perkin–Elmer 241 MC polarimeter. IR spectra (films on KBr discs) were recorded with an FTIR Bomem Michelson MB-120 spectrometer. UV spectra were obtained on a Philips PU 8710 spectrophotometer. ^{1}H NMR spectra (500 MHz) and ^{13}C NMR spectra (125.8 or 75.5 MHz) were recorded from solutions in $CDCl_3$ or DMSO-d_6 with a Bruker AMX-500 or a Bruker AMX-300 spectrometer. Assignments were confirmed by decoupling and/or homonuclear 2D COSY, 1D NOESY, and heteronuclear 2D correlated (HETCOR) experiments. HR-EI mass spectra (70 eV) were measured with a Kratos MS-80RFA instrument, with an ionising current of 100 μA, an accelerating voltage of 4 kV, and a resolution of 10 000 (10% valley definition). Fast-atom bombardment mass spectrometry (FABMS) was performed on the same instrument; ions were produced by a beam of xenon atoms (6–7 keV) using a matrix consisting of *m*-nitrobenzyl alcohol or thioglycerol and NaI as salt. FAB-HRMS was performed on a VG Autospec spectrometer (Fisons Instruments) (30 keV). Crystalline compounds were studied by X-ray diffraction; intensity data were

collected from a single crystal on an Enraf-CAD4 diffractometer with an ω–2θ scan technique at 295 K using a Mo-Kα radiation graphite monochromator, with scattering angles in the range $4<2\theta<50°$. Three standard reflections measured every hour during the entire collection period showed no significant trend. The raw step–scan data were converted into intensities and corrected for Lorentz and polarisation factors, extinction factors were ignored. The structures were solved by direct methods using SIR92[24] and refinement based on *F* of the non-H atoms by full matrix least-squares methods. The function minimised was $\sum w(|F_O|-|F_C|)^2$ with $w=1/\sigma^2(F_O)$. All heavy atoms were refined with anisotropic parameters and all hydrogen atoms were placed in geometrically calculated positions with C–H=1.00 Å and included as fixed contributors in the structure factor calculations with isotropic thermal parameters as the atom to which they were bonded but not refined. Atomic scattering factors were taken from *International Tables for X-Ray Crystallography*[25] and all calculations were carried out with the X-ray system of crystallographic programs.[26] The geometrical analysis was performed using PARST.[27]

*4.2. (Z)-*N*-Benzyl-(1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranos-6-ylidene)amine* N*-oxide **1***

A solution of 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose[28] (1.29 g, 5 mmol) in dichloromethane (20 mL) was added, with stirring, to a suspension of sodium hydrogencarbonate (0.48 g), magnesium sulphate (0.80 g), 4 Å molecular sieve, and *N*-benzyl-hydroxylamine hydrochloride (0.85 g, 5.3 mmol) in dichloromethane (35 mL) at room temperature, and the stirring was maintained for 5 h (monitoring by TLC). The mixture was then filtered and the filtrate was concentrated to give an amorphous product (1.74 g, 96% of conversion by ^{1}H NMR), column chromatography of which (2:3 hexane:EtOAc) afforded pure **1** (1.16 g, 60%); after recrystallisation (EtOH), **1** showed mp 105–107°C; $[\alpha]_D^{24}$ −111 (*c* 1); (lit.[18] mp 106°C; $[\alpha]_D^{20}$ −120.5); UV (96% EtOH) λ_{max} 240 nm (ε_{mM} 4.60); IR (KBr) ν_{max} 1616 (C=N) and 862 cm^{-1} (NO); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44–7.37 (m, 5H, Ph), 6.72 (d, 1H, $J_{5,6}$=5.1, H-6), 5.50 (d, 1H, $J_{1,2}$=5.0, H-1), 5.01 (dd, 1H, $J_{4,5}$=2.0, H-5), 4.91 (s, 2H, C*H*$_2$Ph), 4.74 (dd, 1H, $J_{3,4}$=7.9, H-4), 4.61 (dd, 1H, $J_{2,3}$=2.4, H-3), 4.31 (dd, 1H, H-2), 1.56, 1.42, 1.33, 1.32 (each s, each 3H, 4Me); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 136.6 (C-6), 132.1 (*ipso*-C of Ph), 129.3, 128.8, 128.7 (the other 5C of Ph), 109.2, 108.9 (2*C*Me$_2$), 95.9 (C-1), 70.2, 70.1 (C-2 and C-3), 69.6 (C-4), 69.1 (*C*H$_2$Ph), 65.4 (C-5), 25.9, 25.8, 24.7, 24.1 (4Me); HRMS *m/z* 363.1686 (calcd for $C_{19}H_{25}NO_6$: 363.1682). Anal. calcd for $C_{19}H_{25}NO_6$: C, 62.80; H, 6.93; N, 3.85. Found: C, 62.70; H, 7.00; N, 3.89.

*4.3. (Z)-*N*-Benzyl-(3-*O*-benzyl-1,2-*O*-isopropylidene-α-*D*-xylofuranos-5-ylidene)amine* N*-oxide **2***

A solution of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose[29] (1.90 g, 6.82 mmol) in dichloromethane (29 mL) was added, with stirring, to a suspension of sodium hydrogencarbonate (0.65 g), magnesium sulphate (1.14 g), 4 Å molecular sieve, and *N*-benzyl-hydroxylamine hydrochloride (1.15 g, 7.2 mmol) in dichloromethane (48 mL) at room temperature, and the stirring was maintained for 3 h (monitoring by TLC). The solids were filtered off and the filtrate was concentrated at reduced pressure to give a solid residue that, after recrystallisation from 96% EtOH afforded pure **2** (1.83 g, 70%); mp 98–100°C; $[\alpha]_D^{25}$ −137 (*c* 1); (lit.[18] mp 96°C; $[\alpha]_D^{20}$ −135.7); IR (KBr) ν_{max} 1613 (C=N) and 860 cm^{-1} (NO); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.18 (m, 10H, 2Ph), 6.86 (d, 1H, $J_{4,5}$=4.4, H-5), 5.96 (d, 1H, $J_{1,2}$=3.7, H-1), 5.28 (dd, 1H, $J_{3,4}$=3.3, H-4), 4.91, 4.84 (each d, each 1H, J_{gem}=13.6, NC*H*$_2$Ph), 4.60 (d, 1H, $J_{2,3}\approx$0, H-2), 4.56 (d, 1H, H-3), 4.51, 4.42 (each d, each 1H, J_{gem}=11.7, OC*H*$_2$Ph), 1.49, 1.30 (each s, each 3H, 2Me); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 136.0 (C-5), 137.5, 132.0 (2 *ipso*-C of 2Ph), 129.5, 129.1, 128.9, 128.4, 127.8, 127.4 (the other 10C of 2Ph), 112.2 (*C*Me$_2$), 104.9 (C-1), 82.8 (C-2), 82.3 (C-3), 77.9 (C-4), 72.6 (O*C*H$_2$Ph), 69.2 (N*C*H$_2$Ph), 26.9, 26.3

(2Me); HRMS *m/z* 383.1736 (calcd for $C_{22}H_{25}NO_5$: 383.1733). Anal. calcd for $C_{22}H_{25}NO_5$: C, 68.91; H, 6.57; N, 3.65. Found: C, 68.91; H, 6.54; N, 3.69.

*4.4. (Z)-*N*-Benzyl-(3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-ribofuranos-5-ylidene)amine* N-*oxide* ***3***

A solution of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*ribo*-pentodialdo-1,4-furanose[30] (0.78 g, 2.81 mmol) in dichloromethane (11 mL) was added, with stirring, to a suspension of sodium hydrogencarbonate (0.26 g), magnesium sulphate (0.47 g), 4 Å molecular sieve, and *N*-benzyl-hydroxylamine hydrochloride (0.475 g, 2.97 mmol) in dichloromethane (20 mL) at room temperature, and the stirring was maintained for 5 h (monitoring by TLC). The solids were filtered off and the filtrate was concentrated at reduced pressure to give a solid residue that, after column chromatography (4:1 ether:hexane) afforded pure **3** (0.345 g, 32%); $[\alpha]_D^{22}$ +14 (*c* 1); IR (KBr) ν_{max} 1595 (C=N) and 866 cm^{-1} (NO); ^1H NMR (500 MHz, $CDCl_3$) δ 7.41–7.19 (m, 10H, 2Ph), 6.55 (d, 1H, $J_{4,5}$=6.8, H-5), 5.72 (d, 1H, $J_{1,2}$=3.5, H-1), 5.25 (dd, 1H, $J_{3,4}$=8.7, H-4), 4.88, 4.85 (each d, each 1H, J_{gem}=13.6, NCH_2Ph), 4.60 (dd, 1H, $J_{2,3}$=4.4, H-2), 4.61, 4.51 (each d, each 1H, J_{gem}=12.4, OCH_2Ph), 3.82 (dd, 1H, H-3), 1.62, 1.31 (each s, each 3H, 2Me); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 134.0 (C-5), 137.3, 132.1 (2 *ipso*-C of Ph), 129.3, 129.0, 128.8, 128.2 (the other 10C of Ph), 113.5 (*C*Me_2), 103.8 (C-1), 79.6 (C-3), 78.4 (C-2), 72.8 (C-4), 71.9 (O*C*H_2Ph), 70.3 (N*C*H_2Ph), 26.7, 26.4 (2Me); HRMS *m/z* 383.17338 (calcd for $C_{22}H_{25}NO_5$: 383.17327). Anal. calcd for $C_{22}H_{25}NO_5$: C, 68.91; H, 6.57; N, 3.65. Found: C, 68.98; H, 6.47; N, 3.55.

*4.5. Reaction of (Z)-*N*-benzyl-(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-ylidene)amine* N-*oxide* ***1*** *with β-nitrostyrene* ***5****. Preparation of 2-benzyl-3-(1,2:3,4-di-*O*-isopropylidene-α-D-galacto-pentopyranos-5-yl)-4-nitro-5-phenylisoxazolidines* ***9***

A solution of **1** (0.235 g, 0.65 mmol) and **5** (0.385 g, 2.60 mmol) in toluene (0.5 mL) was stirred at 50°C. After 24 h, the conversion was complete, as indicated by ^1H NMR, which showed the formation of two diastereomers of **9** (65:35); for the major component **9d**: (500 MHz, $CDCl_3$) δ 7.49–7.26 (m, 10H, 2Ph), 5.60 (d, 1H, $J_{1',2'}$=5.1, H-1′), 5.35–5.25 (br, 1H, H-5), 5.25 (dd, 1H, $J_{3,4}$=4.7, $J_{4,5}$=6.6, H-4), 4.78, 4.00 (each d, each 1H, J_{gem}=14.6, CH_2Ph), 4.58 (dd, 1H, $J_{2',3'}$=2.7, $J_{3',4'}$=7.8, H-3′), 4.38 (dd, 1H, $J_{4',5'}$=1.5, $J_{3,5'}$=8.5, H-5′), 4.36 (dd, 1H, H-2′), 4.05 (dd, 1H, H-4′), 3.6–3.3 (br, 1H, H-3), 1.63, 1.45, 1.34, 1.28 (each s, each 3H, 4Me); for the minor component **9a** or **9c**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.48–7.26 (m, aromatics), 5.78 (d, 1H, $J_{4,5}$=6.6, H-5), 5.48 (d, 1H, $J_{1',2'}$=5.1, H-1′), 5.40 (dd, 1H, $J_{3,4}$=2.3, H-4), 4.55 (dd, 1H, $J_{2',3'}$=2.3, $J_{3',4'}$=8.0, H-3′), 4.45, 4.32 (each d, each 1H, J_{gem}=12.7, CH_2Ph), ~4.35 (dd, overlapped signal, H-3), 4.27 (dd, 1H, H-2′), ~4.25 (overlapped signal, H-4′), 3.76 (dd, 1H, $J_{4',5'}$=1.7, $J_{3,5'}$=10.1, H-5′), 1.63 (overlapped with one Me signal of the major component), 1.38, 1.28 (overlapped with other Me signal of the major component) and 1.18 (each s, each 3H, 2Me). Preparative TLC (12:1 hexane:EtOAc) of the reaction mixture allowed us to discard the excess of **5** and afforded 0.181 g (54%) of a 72:18:10 (^1H NMR) diastereomeric mixture; the major component was a new diastereomer **9b**, different (^1H NMR) from any of the components in the original mixture before chromatography, but the other two agreed with the former two. Treatment of this mixture with boiling abs. EtOH gave a crystalline product (65 mg, 19.4%), mp 145–149°C, which proved (^1H NMR) to be a 63:37 mixture of the new and the original major components. Further recrystallisation afforded pure the new major diastereomer (mp 143–144°C), crystallographic analysis of which allowed the unequivocal assignment of its (2*S*,3*S*,4*S*,5*R*) absolute configuration, corresponding to the structure (2*S*)-**9b**; $[\alpha]_D^{27}$ −112 (*c* 1); UV (CH_2Cl_2) λ_{max} 229 nm (ε_{mM} 2.26); IR (KBr) ν_{max} 1562 and 1383 cm^{-1} (NO_2); ^1H NMR (500 MHz, $CDCl_3$) δ 7.48–7.30 (m, 10H, 2Ph), 5.80 (dd, 1H, $J_{3,4}$=3.5, $J_{4,5}$=5.8, H-4), 5.53 (d, 1H, H-5),

5.50 (d, 1H, $J_{1',2'}$=4.9, H-1′), 4.60 (dd, 1H, $J_{2',3'}$=2.3, $J_{3',4'}$=8.0, H-3′), 4.50 (dd, 1H, $J_{4',5'}$=1.8, H-4′), 4.48, 4.37 (each d, each 1H, J_{gem}=13.4, C*H*$_2$Ph), 4.29 (dd, 1H, H-2′), 4.19 (dd, 1H, $J_{3,5'}$=7.0, H-3), 3.77 (dd, 1H, H-5′), 1.52, 1.36, 1.35, 1.30 (each s, each 3H, 4Me); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 132.4, 129.3, 128.8, 128.4, 128.3, 127.7, 126.2 (2Ph), 109.4, 108.6 (2*C*Me$_2$), 96.2 (C-1′), 94.1 (C-4), 81.4 (C-5), 71.3 (C-3), 70.7 (C-3′), 70.7 (C-4′), 70.5 (C-2′), 66.4 (C-5′), 62.5 (*C*H$_2$Ph), 26.1, 25.8, 24.7, 24.1 (4Me); HRMS *m/z* 512.2172 (calcd for $C_{27}H_{32}N_2O_8$: 512.2159). Anal. calcd for $C_{27}H_{32}N_2O_8$: C, 63.27; H, 6.29; N, 5.47. Found: C, 63.16; H, 6.37; N, 5.45.

From the mother liquors slowly crystallised the other component, mp 170–173°C, which proved to be identical (by ^{1}H NMR in $CDCl_3$) to **9d**; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.39–7.25 (m, 10H, 2Ph), 5.59 (d, 1H, $J_{1',2'}$=5.1, H-1′), 5.40–5.30 (br, 1H, H-5), 5.29 (dd, 1H, $J_{3,4}$=4.5, $J_{4,5}$=6.4, H-4), 4.68 (dd, 1H, $J_{2',3'}$=2.7, $J_{3',4'}$=7.8, H-3′), 4.67, 3.87 (each d, each 1H, J_{gem}=13.8, C*H*$_2$Ph), 4.45 (dd, 1H, H-2′), 4.26 (dd, 1H, $J_{4',5'}$=1.6, $J_{3,5'}$=8.5, H-5′), 4.02 (dd, 1H, H-4′), 3.60–3.40 (br, 1H, H-3), 1.53, 1.39, 1.31, 1.27 (each s, each 3H, 4Me); NOE contacts (1D NOESY, DMSO-d_6, 40°C): H-3, H-4 (strong), NC*H*$_2$Ph (weak); H-4, H-3, H-4′; H-5′, H-4′, Me; [after 5 days, the spectrum of this sample in DMSO-d_6 showed the presence of both diastereomers **9b** and **9d**, in a ~89:11 ratio]; pure **9d** was stable in $CDCl_3$: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.34 (m, 10H, 2Ph), 5.61 (d, 1H, $J_{1',2'}$=5.0, H-1′), 5.37–5.25 (br, 1H, H-5), 5.25 (dd, 1H, $J_{3,4}$=4.7, $J_{4,5}$=6.6, H-4), 4.80, 4.00 (each brd, each 1H, J_{gem}=14.0, C*H*$_2$Ph), 4.58 (dd, 1H, $J_{2',3'}$=2.7, $J_{3',4'}$=7.8, H-3′), 4.37 (dd, 1H, $J_{4',5'}$=1.5, $J_{3,5'}$=8.5, H-5′), 4.36 (dd, 1H, H-2′), 4.05 (dd, 1H, H-4′), 3.65–3.20 (br, 1H, H-3), 1.63, 1.45, 1.34, 1.28 (each s, each 3H, 4Me); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 136.9, 136.8 (2 *ipso*-C of Ph), 128.9, 128.7, 127.9, 127.0, 126.2 (the other 10C of Ph), 109.9, 109.4 (2*C*Me$_2$), 96.3, 96.2 (C-1′ and C-4), 83.7 (C-5), 71.0, 70.8 (C-3 and C-4′), 69.8 (C-2′), 67.5 (C-3′), 65.7 (C-5′), 60.2 (*C*H$_2$Ph), 25.8, 25.7, 25.0, 24.3 (4Me); ^{1}H NMR (500 MHz, $CDCl_3$, −25°C), major invertomer (86%): δ 7.50–7.24 (m, 10H, 2Ph), 5.65 (d, 1H, $J_{1',2'}$=5.1, H-1′), 5.21 (overlapped d, 1H, H-5), 5.21 (overlapped dd, 1H, $J_{4,5}$=6.5, $J_{3,4}$=not measured, H-4), 4.79, 4.07 (each d, each 1H, J_{gem}=14.5, C*H*$_2$Ph), 4.56 (dd, 1H, $J_{2',3'}$=2.6, $J_{3',4'}$=7.9, H-3′), 4.38 (dd, 1H, H-2′), 4.30 (dd, 1H, $J_{4',5'}$=1.3, $J_{3,5'}$=8.4, H-5′), 3.98 (dd, 1H, H-4′), 3.37 (brdd, $J_{3,4}$≈3.5, 1H, H-3), 1.63, 1.44, 1.34, 1.25 (each s, each 3H, 4Me); minor invertomer (14%): δ 7.50–7.24 (m, 10H, 2Ph), 5.68 (d, 1H, $J_{1',2'}$=5.1, H-1′), 5.80 (d, 1H, $J_{4,5}$=5.7, H-5), 5.41 (dd, 1H, $J_{3,4}$=7.5, H-4), 4.62 (overlapped dd, 1H, H-3), 4.61 (overlapped dd, 1H, $J_{2',3'}$=2.6, $J_{3',4'}$=7.9, H-3′), 4.49, 4.01 (each d, each 1H, J_{gem}=13.7, C*H*$_2$Ph), 4.40 (dd, 1H, H-2′), 4.37 (overlapped dd, 1H, H-4′), 4.15 (dd, 1H, $J_{3,5'}$=10.1, $J_{4',5'}$≈0.5, H-5′), 1.54, 1.49, 1.32, 1.30 (each s, each 3H, 4Me).

*4.6. Reaction of (*Z*)-*N*-benzyl-(1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranos-6-ylidene)amine* N-*oxide* ***1*** *with* p-*methoxy-β-nitrostyrene* ***6***. *Preparation of 2-benzyl-3-(1,2:3,4-di-*O*-isopropylidene-α-*D*-galacto-pentopyranos-5-yl)-4-nitro-5-*p*-methoxyphenylisoxazolidines* ***10***

A solution of **1** (0.300 g, 0.83 mmol) and **6** (0.594 g, 3.32 mmol) in toluene (0.6 mL) was stirred at 70°C. After 24 h, the conversion was complete, as indicated by ^{1}H NMR, which showed the formation of **10** as a 67:33 diastereomeric mixture; for the major diastereomer **10d**: (500 MHz, $CDCl_3$) δ 7.54–6.84 (m, 9H, Ph and –C$_6$H$_4$–, both isomers), 5.59 (d, 1H, $J_{1',2'}$=5.1, H-1′), 5.22 (brdd, 1H, $J_{3,4}$=3.5, H-4), ~5.2 (overlapped with the H-4 signal, 1H, H-5), 4.77, 3.98 (each d, each 1H, J_{gem}=14.0, C*H*$_2$Ph), 4.57 (dd, 1H, $J_{2',3'}$=2.6, $J_{3',4'}$=7.8, H-3′), 4.35 (dd, 1H, H-2′), ~4.3 (overlapped with the H-2′ signal, H-3), 4.04 (dd, 1H, $J_{4',5'}$=1.6, H-4′), 3.83 (dd, 1H, $J_{3,5'}$=2.3, H-5′), 3.79 (s, 3H, OMe), 1.59, 1.45, 1.34, 1.28 (each s, each 3H, 2CMe$_2$); for the minor component **10a** or **10c**: (500 MHz, $CDCl_3$) δ 7.54–6.84 (m, 9H, Ph and –C$_6$H$_4$–, both isomers), 5.72 (dd, 1H, $J_{3,4}$≈$J_{4,5}$≈6.8, H-4), 5.63 (d, 1H, $J_{4,5}$≈7.0, H-5), 5.49 (d, 1H, $J_{1',2'}$=5.0, H-1′), 5.38 (dd, 1H, $J_{3,4}$≈6.7, $J_{3,5'}$≈2.4, H-3), ~4.35 (overlapped with the other isomer) and 4.11 (each d, each 1H, J_{gem}≈14.5, C*H*$_2$Ph), 4.55 (dd, 1H, $J_{2',3'}$=2.4, $J_{3',4'}$=7.9, H-3′), 4.27 (dd, 1H,

H-2′), 3.80 (s, 3H, OMe), 4.34 (partially overlapped with the other isomer) (dd, 1H, $J_{4',5'}$=1.5, H-4′), 3.78 (dd, 1H, H-5′), 1.59, 1.44, 1.30, 1.27 (each s, each 3H, 2CMe$_2$). Column chromatography (12:1 to 3:1 gradient of hexane:EtOAc containing 2% of Et$_3$N) of the reaction mixture afforded 0.512 g of pure recovered **6**, and three fractions containing isoxazolidine derivatives (global yield: 0.325 g, 72.1%), two of which being mixed fractions (overall yield, 0.167 g) of the minor component (15%) with a new diastereomer (22%), and the third consisting only of this last (**10b**, 0.158 g, 35%; overall yield for this: 57%); oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.50–7.30 (m, 5H, Ph), 7.19 (d, 2H, $J_{o,m}$=8.7, H-2 and H-6 of 4-MeO-C$_6$H$_4$-), 6.84 (d, 2H, H-3 and H-5 of 4-MeO-C$_6$H$_4$-), 5.73 (dd, 1H, $J_{3,4}$=3.6, $J_{4,5}$=5.9, H-4), 5.50 (d, 1H, $J_{1',2'}$=4.9, H-1′), 5.46 (d, 1H, H-5), 4.59 (dd, 1H, $J_{2',3'}$=2.3, $J_{3',4'}$=8.0, H-3′), 4.48 (dd, 1H, $J_{4',5'}$=1.8, H-4′), 4.45, 4.36 (each d, each 1H, J_{gem}=13.4, C*H*$_2$Ph), 4.28 (dd, 1H, H-2′), 4.17 (dd, 1H, $J_{3,5'}$=7.1, H-3), 3.77 (s, 3H, OMe), 3.76 (dd, 1H, H-5′), 1.50, 1.36, 1.34, 1.30 (each s, each 3H, 2CMe$_2$); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 159.9, 136.4, 129.2, 128.4, 127.6, 127.5, 124.2, 113.7 (Ph and *C*$_6$H$_4$), 109.4, 108.6 (2*C*Me$_2$), 96.1 (C-1′), 94.1 (C-4), 81.2 (C-5), 71.2 (C-3), 70.7 (C-4′), 70.6 (C-3′), 70.4 (C-2′), 66.4 (C-5′), 62.5 (*C*H$_2$Ph), 55.0 (OMe), 26.1, 25.7, 24.6, 24.0 (2C*Me*$_2$); HRMS *m/z* 542.2264 (calcd for $C_{28}H_{34}N_2O_9$: 522.2264). Anal. calcd for $C_{28}H_{34}N_2O_9$: C, 61.98; H, 6.32; N, 5.16. Found: C, 61.94; H, 6.30; N, 5.55.

*4.7. Reaction of (*Z*)-*N*-benzyl-(3-*O*-benzyl-1,2-*O*-isopropylidene-α-*D*-xylofuranos-5-ylidene)amine* N-*oxide* ***2*** *with β-nitrostyrene* ***5****. Preparation of 2-benzyl-3-(3-*O*-benzyl-1,2-*O*-isopropylidene-α-*D*-xylo-tetrofuranos-4-yl)-4-nitro-5-phenylisoxazolidines* ***11***

Nitrone **2** (0.287 g, 0.75 mmol) was added to a solution of **5** (0.447 g, 3.00 mmol) in toluene (2 mL) and the mixture was heated to reflux until the reaction was complete (20 h, ^{1}H NMR). The ^{1}H NMR spectrum showed the presence of two diastereomeric adducts (65:35). Evaporation of the solvent at reduced pressure and subsequent column chromatography (1:6 ether:hexane) led to separate the excess of **5** and to isolate pure the major component **11b** as an oil (0.191 g, 48%); $[\alpha]_D^{25}$ +2 (*c* 1); IR (KBr) ν_{max} 1555 and 1373 cm^{-1} (NO$_2$); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.42–7.17 (m, 15H, 3Ph), 5.87 (d, 1H, $J_{1',2'}$=3.7, H-1′), 5.75 (d, 1H, $J_{4,5}$=6.3, H-5), 5.52 (dd, 1H, $J_{3,4}$=2.3, H-4), 4.54 (d, 1H, $J_{2',3'}\approx$0, H-2′), 4.52 (dd, 1H, $J_{3,4'}$=8.7, H-3), 4.35 (dd, 1H, $J_{3',4'}$=3.2, H-4′), 4.48, 4.26 (each d, each 1H, J_{gem}=11.8, OC*H*$_2$Ph), 4.43, 4.09 (each d, each 1H, J_{gem}=13.5, NC*H*$_2$Ph), 4.05 (d, 1H, H-3′), 1.45, 1.29 (each s, each 3H, 2Me); NOE contacts (1D NOESY): H-5, H-1′, NC*H*$_2$Ph; H-4, H-3, H-4′; ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 136.8, 136.4, 135.4 (3 *ipso*-C of Ph), 128.9, 128.8, 128.7, 128.5, 128.4, 128.2, 128.0, 127.9, 127.7, 127.6, 126.7, 126.2 (the other 15C of Ph), 112.0 (*C*Me$_2$), 105.0 (C-1′), 97.2 (C-4), 83.9 (C-5), 81.9 (C-2′), 81.2 (C-3′), 80.0 (C-4′), 71.7 (O*C*H$_2$Ph), 68.0 (C-3), 60.3 (N*C*H$_2$Ph), 26.9, 26.1 (2Me); HRMS *m/z* 532.22131 (calcd for $C_{30}H_{32}N_2O_7$: 532.22095). Anal. calcd for $C_{30}H_{32}N_2O_7$: C, 67.65; H, 6.06; N, 5.26. Found: C, 67.73; H, 6.15; N, 5.06. The minor diastereomer **11d** had (from the reaction mixture) ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.56–7.17 (m, aromatics), 5.97 (d, 1H, $J_{1',2'}$=4.0, H-1′), 5.59 (d, 1H, $J_{4,5}$=6.0, H-5), 5.13 (dd, 1H, $J_{3,4}\approx$5.0, H-4), 4.62 (dd, 1H, $J_{2',3'}\approx$0.8, H-2′), 4.22 (dd, 1H, $J_{3,4'}$=7.6, $J_{3,4}$=4.9, H-3), 4.35 (overlapped with the major isomer, H-4′), 4.71, 3.92 (each d, each 1H, J_{gem}=14.8, NC*H*$_2$Ph), 4.51 (d, 1H, J_{gem}=11.4) and ∼4.0 (overlapped with the major isomer, 1H, both: OC*H*$_2$Ph), 4.02 (dd, 1H, $J_{3',4'}$=4.4, H-3′), 1.47, 1.31 (each s, each 3H, 2Me); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 136.8–126.2 (18 aromatic C, overlapped with signals of the major isomer), 112.0 (*C*Me$_2$), 105.3 (C-1′), 96.8 (C-4), 82.9 (C-5), 82.6 (C-2′), 82.4 (C-3′), 80.7 (C-4′), 70.3 (O*C*H$_2$Ph), 68.0 (C-3), 61.2 (N*C*H$_2$Ph), 26.9, 26.1 (2Me).

*4.8. Reaction of (Z)-*N*-benzyl-(3-*O*-benzyl-1,2-*O*-isopropylidene-α-*D*-ribofuranos-5-ylidene)amine* N*-oxide **3** with β-nitrostyrene (**5**). Preparation of 2-benzyl-3-(3-*O*-benzyl-1,2-*O*-isopropylidene-α-*D*-ribo-tetrofuranos-4-yl)-4-nitro-5-phenylisoxazolidines **12***

Compound **5** (0.233 g, 1.56 mmol) was added to a solution of nitrone **3** (0.150 g, 0.39 mmol) in toluene (3.8 mL) and the mixture was heated to reflux for 24 h. ^{1}H NMR of the mixture showed the presence of two diastereomers (61:39). Evaporation of the solvent at reduced pressure and subsequent column chromatography (1:8 ether:hexane) led to the separation of the excess **5** and to the isolation of the two new products. The major component (**12b**) was an oil (0.096 g, 46%); $[\alpha]_D^{20}$ +116 (*c* 1); IR (KBr) ν_{max} 1553 and 1375 cm^{-1} (NO_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.17 (m, 15H, 3Ph), 5.74 (d, 1H, $J_{4,5}$=5.6, H-5), 5.66 (d, 1H, $J_{1',2'}$=3.6, H-1′), 5.49 (dd, 1H, $J_{3,4}$=4.9, H-4), 4.45 (dd, 1H, $J_{2',3'}$=4.4, H-2′), 4.45, 4.21 (each d, each 1H, J_{gem}=11.6, OC*H*$_2$Ph), 4.39 (dd, 1H, $J_{3',4'}$=8.8, $J_{3,4'}$=3.0, H-4′), 4.32 (s, 2H, NC*H*$_2$Ph), 4.13 (dd, 1H, H-3), 3.85 (dd, 1H, H-3′), 1.57, 1.31 (each s, each 3H, 2Me); NOE contacts (1D NOESY): H-4, H-3, H-3′, H-4′; H-5, NC*H*$_2$Ph; ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 137.1, 136.3, 136.2 (3 *ipso*-C of Ph), 129.3, 128.7, 128.4, 128.3, 127.9, 127.8, 127.7, 126.5 (the other 15C of Ph), 113.4 (*C*Me$_2$), 103.9 (C-1′), 94.7 (C-4), 82.1 (C-5), 78.5 (C-4′), 78.3 (C-3′), 77.3 (C-2′), 71.8 (O*C*H$_2$Ph), 69.9 (C-3), 61.7 (N*C*H$_2$Ph), 26.8, 26.6 (2Me); HRMS *m/z* 532.22126 (calcd for $C_{30}H_{32}N_2O_7$: 532.22095). Anal. calcd for $C_{30}H_{32}N_2O_7$: C, 67.65; H, 6.06; N, 5.26. Found: C, 67.57; H, 5.84; N, 5.04. The minor isomer **12d** was an oil (0.056 g, 27%); $[\alpha]_D^{18}$ +3 (*c* 1); IR (KBr) ν_{max} 1553 and 1373 cm^{-1} (NO_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.17 (m, 15H, 3Ph), 5.88 (d, 1H, $J_{1',2'}$=3.8, H-1′), 5.71 (d, 1H, $J_{4,5}$=6.4, H-5), 5.48 (dd, 1H, $J_{3,4}$=3.8, H-4), 4.54 (dd, 1H, $J_{2',3'}$=4.6, H-2′), 4.35, 4.02 (each d, each 1H, J_{gem}=11.0, OC*H*$_2$Ph), 4.33, 4.31 (each d, each 1H, J_{gem}=12.6, NC*H*$_2$Ph), 4.15 (dd, 1H, $J_{3',4'}$=8.5, $J_{3,4'}$=4.2, H-4′), 4.10 (dd, 1H, H-3), 3.69 (dd, 1H, H-3′), 1.54, 1.34 (each s, each 3H, 2Me); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 137.0, 135.8, 135.5 (3 *ipso*-C of Ph), 129.8, 129.0, 128.7, 128.5 128.2, 128.0, 127.9, 127.8, 127.0, 126.4 (the other 15C of Ph), 113.0 (*C*Me$_2$), 104.4 (C-1′), 96.9 (C-4), 83.7 (C-5), 79.5 (C-4′), 78.9 (C-3′), 77.2 (C-2′), 71.7 (O*C*H$_2$Ph), 69.3 (C-3), 61.2 (N*C*H$_2$Ph), 26.6, 26.5 (2Me); HRMS *m/z* 532.22369 (calcd for $C_{30}H_{32}N_2O_7$: 532.22095). Anal. calcd for $C_{30}H_{32}N_2O_7$: C, 67.65; H, 6.06; N, 5.26. Found: C, 67.66; H, 6.03; N, 5.03.

*4.9. Reaction of (E)-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-7-nitro-α-*D*-galacto-hept-6-eno-1,5-pyranose **7** with (Z)-*N*-benzyl-benzylideneamine* N*-oxide **4**. Preparation of 2-benzyl-5-(1,2:3,4-di-*O*-isopropylidene-α-*D*-galacto-pentopyranos-5-yl)-4-nitro-3-phenylisoxazolidines **13***

Nitrone **4** (0.143 g, 0.68 mmol), prepared following a procedure similar to that used for the *N*-methyl analogue,[31] was added to a solution of **7** (0.205 g, 0.68 mmol) in toluene (3.4 mL) and the mixture was heated to reflux for 24 h. ^{1}H NMR of the mixture showed the presence of three diastereomers (55:36:9). Evaporation of the solvent at reduced pressure and subsequent column chromatography (14:1 hexane:EtOAc) led to three fractions (global yield: 0.273 g, 78%). First eluted was a pure compound (0.088 g, 25%), but the second fraction contained an additional amount of the same compound (total: 0.097 g, 28%); it crystallised from EtOH, mp 145–147°C, and was unambiguously characterised by X-ray diffraction analysis as the (2*S*,3*R*,4*R*,5*R*) diastereomer (2*S*)-**13a**; $[\alpha]_D^{21}$ −10 (*c* 1); IR (KBr) ν_{max} 1561 and 1383 cm^{-1} (NO_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54–7.27 (m, 10H, 2Ph), 5.57 (d, 1H, $J_{1',2'}$=5.1, H-1′), 5.39 (dd, 1H, $J_{3,4}$=6.9, $J_{4,5}$=2.7, H-4), 4.93 (dd, 1H, $J_{5,5'}$=8.4, H-5), 4.59 (dd, 1H, $J_{2',3'}$=2.4, $J_{3',4'}$=7.7, H-3′), 4.35 (dd, 1H, H-2′), 4.28 (d, 1H, H-3), 4.19–4.14 (m, 2H, H-4′ and H-5′), 4.00, 3.84 (each d, each 1H, J_{gem}=14.6, C*H*$_2$Ph), 1.60, 1.40, 1.36, 1.29 (each s, each 3H, 4Me); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 136.7, 135.1, 129.0, 128.1, 128.0, 127.9, 127.1 (2Ph), 109.5, 108.6 (2*C*Me$_2$), 96.5 (C-

4), 96.3 (C-1′), 78.2 (C-5), 76.1 (C-3), 70.5 (C-3′), 70.5 (C-2′), 70.3 (C-4′), 66.5 (C-5′), 58.7 (*C*H_2Ph), 25.9, 25.7, 24.8, 24.2 (4Me); HRMS *m/z* 512.2168 (calcd for $C_{27}H_{32}N_2O_8$: 512.2159). Anal. calcd for $C_{27}H_{32}N_2O_8$: C, 63.27; H, 6.29; N, 5.47. Found: C, 63.21; H, 6.35; N, 5.46. The second fraction was an oil (0.030 g), a mixture of a small amount of **13a** and the minor component of the reaction mixture (**13b** or **13d**, 6% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51–7.30 (m, 10H, 2Ph), 5.58 (d, 1H, $J_{1',2'}$=4.9, H-1′), 5.34 (dd, 1H, $J_{3,4}$=7.0, $J_{4,5}$=3.8, H-4), 4.93 (dd, 1H, $J_{5,5'}$=8.2, H-5), 4.63 (dd, 1H, $J_{2',3'}$=2.5, $J_{3',4'}$=7.8, H-3′), 4.34 (dd, 1H, H-2′), 4.33 (dd, $J_{4',5'}$=1.8, H-4′), 4.29 (d, 1H, H-3), 4.23 (dd, 2H, H-5′), 4.06, 3.93 (each d, each 1H, J_{gem}=15.1, C*H*$_2$Ph), 1.57, 1.40, 1.36, 1.31 (each s, each 3H, 4Me); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 136.6, 135.1, 129.1, 128.1, 128.0, 127.6, 127.1, 127.0 (2Ph), 109.9, 108.8 (2*C*Me$_2$), 96.3 (C-1′), 95.4 (C-4), 80.1 (C-5), 76.1 (C-3), 70.8 (C-2′), 70.3 (C-3′), 70.2 (C-4′), 66.9 (C-5′), 58.4 (*C*H_2Ph), 26.0, 25.7, 24.9, 24.3 (4Me). Last eluted was the pure major compound (**13c**, 0.155 g, 44%); oil; IR (KBr) ν_{max} 1579 and 1377 cm^{-1} (NO_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48–7.33 (m, 10H, 2Ph), 5.63 (dd, 1H, $J_{3,4}$=8.0, $J_{4,5}$=4.6, H-4), 5.58 (d, 1H, $J_{1',2'}$=4.9, H-1′), 5.10 (dd, 1H, $J_{5,5'}$=1.5, H-5), 4.60 (dd, 1H, $J_{2',3'}$=2.5, $J_{3',4'}$=8.0, H-3′), 4.33 (dd, 1H, H-2′), 4.19 (dd, 1H, $J_{4',5'}$=1.9, H-4′), 4.08 (d, 1H, H-3), 4.05 (dd, 1H, H-5′), 4.00, 3.69 (each d, each 1H, J_{gem}=14.6, C*H*$_2$Ph), 1.61, 1.42, 1.42, 1.30 (each s, each 3H, 4Me); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 136.8, 132.6, 129.1, 128.8, 128.1, 127.2 (2Ph), 109.6, 108.9 (2*C*Me$_2$), 96.2 (C-1′), 92.6 (C-4), 80.1 (C-5), 74.3 (C-3), 71.2 (C-4′), 70.4 (C-3′), 70.1 (C-2′), 65.5 (C-5′), 59.0 (*C*H_2Ph), 26.0, 25.1, 24.8, 23.7 (4Me); HRMS *m/z* 512.2168 (calcd for $C_{27}H_{32}N_2O_8$: 512.2159). Anal. calcd for $C_{27}H_{32}N_2O_8$: C, 63.27; H, 6.29; N, 5.47. Found: C, 62.99; H, 6.42; N, 5.25.

*4.10. Reaction of (*E*)-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-nitro-α-*D*-xylo-hex-5-eno-1,4-furanose **8** with (Z)-*N*-benzyl-benzylideneamine *N*-oxide **4**. Preparation of 2-benzyl-5-(3-*O*-benzyl-1,2-*O*-isopropylidene-α-*D*-xylo-tetrofuranos-4-yl)-4-nitro-3-phenylisoxazolidines **14***

Nitrone **4** (0.101 g, 0.477 mmol) was added to a solution of the nitroalkene **8** (0.153 g, 0.477 mmol) in toluene (2.5 mL), and the mixture was heated to reflux for 18 h. ^{1}H NMR of the mixture showed the presence of four diastereomers (45:34:14:7). Column chromatography (1:8 ether:hexane) afforded separately the isomers (global yield: 0.168 g, 66%) as oils. The major isomer (**14b** or **14d**, 0.069 g, 27%) had $[\alpha]_D^{19}$ +60 (*c* 1); IR (KBr) ν_{max} 1557 and 1377 cm^{-1} (NO_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.10 (m, 15H, 3Ph), 6.00 (d, 1H, $J_{1',2'}$=3.8, H-1′), 5.60 (dd, 1H, $J_{3,4}$=8.0, $J_{4,5}$=4.6, H-4), 5.08 (dd, 1H, $J_{4',5}$=1.5, H-5), 4.55 (d, 1H, $J_{2',3'}\approx$0, H-2′), 4.47 (dd, 1H, $J_{3',4'}$=3.8, H-4′), 4.45, 4.33 (each d, each 1H, J_{gem}=12.0, OC*H*$_2$Ph), 4.13 (d, 1H, $J_{3,4}$=8.0, H-3), 3.97, 3.66 (each d, each 1H, J_{gem}=14.6, NC*H*$_2$Ph), 3.91 (d, 1H, H-3′), 1.47, 1.32 (each s, each 3H, 2Me); NOE contacts (1D NOESY): H-5, H-4′, H-3′, (H-4: low intensity); H-4, H-3; ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 137.1, 135.8, 132.5 (3 *ipso*-C of Ph), 129.2, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.0, 127.2 (the other 15C of Ph), 112.1 (*C*Me$_2$), 105.3 (C-1′), 93.0 (C-4), 81.3 (C-2′), 80.7 (C-3′), 79.3 (C-5), 78.3 (C-4′), 74.9 (C-3), 71.6 (O*C*H$_2$Ph), 59.3 (N*C*H$_2$Ph), 26.8, 26.2 (2Me); HRMS *m/z* 532.22240 (calcd for $C_{30}H_{32}N_2O_7$: 532.22095). Anal. calcd for $C_{30}H_{32}N_2O_7$: C, 67.65; H, 6.06; N, 5.26. Found: C, 67.53; H, 5.85; N, 4.88. The second main isomer (**14a** or **14c**, 0.064 g, 25%) had $[\alpha]_D^{19}$ −71 (*c* 1); IR (KBr) ν_{max} 1555 and 1373 cm^{-1} (NO_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.19 (m, 15H, 3Ph), 5.93 (d, 1H, $J_{1',2'}$=3.6, H-1′), 5.45 (dd, 1H, $J_{3,4}$=6.4, $J_{4,5}$=2.8, H-4), 5.01 (dd, 1H, $J_{4',5}$=7.0, H-5), 4.58 (dd, 1H, $J_{3',4'}$=3.3, H-4′), 4.52 (d, 1H, $J_{2',3'}\approx$0, H-2′), 4.45, 4.39 (each d, each 1H, J_{gem}=11.8, OC*H*$_2$Ph), 4.29 (d, 1H, H-3), 4.03, 3.84 (each d, each 1H, J_{gem}=14.4, NC*H*$_2$Ph), 3.88 (d, 1H, H-3′), 1.52, 1.32 (each s, each 3H, 2Me); NOE contacts (1D NOESY): H-5, (H-4: low intensity); H-4, H-4′, (H-5 and H-3: low intensity); H-3, NC*H*$_2$Ph, (H-4: low intensity); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 136.8, 136.7, 135.5 (3 *ipso*-C of Ph), 130.0, 129.9, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.3, 127.2 (the other 15C of Ph), 112.0 (*C*Me$_2$), 105.3

(C-1′), 96.6 (C-4), 82.4 (C-2′), 81.0 (C-3′), 79.8 (C-4′), 77.7 (C-5), 76.1 (C-3), 72.3 (O*C*H$_2$Ph), 59.0 (N*C*H$_2$Ph), 26.9, 26.3 (2Me); HRMS *m/z* 532.21744 (calcd for $C_{30}H_{32}N_2O_7$: 532.22095). Anal. calcd for $C_{30}H_{32}N_2O_7$: C, 67.65; H, 6.06; N, 5.26. Found: C, 67.85; H, 6.08; N, 5.05. The third diastereomer in order of decreasing yield (**14c** or **14a**, 0.030 g, 12%) had ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.18 (m, 15H, 3Ph), 5.90 (d, 1H, $J_{1',2'}$=4.0, H-1′), 5.05 (dd, 1H, $J_{3,4}$=7.1, $J_{4,5}$=4.6, H-4), 4.92 (dd, 1H, $J_{4',5}$=6.6, H-5), 4.67 (dd, 1H, $J_{3',4'}$=4.6, H-4′), 4.54, 4.42 (each d, each 1H, J_{gem}=11.4, OC*H*$_2$Ph), 4.44 (d, 1H, $J_{2',3'}\approx$0, H-2′), 4.31 (d, 1H, H-3), 4.08, 3.90 (each d, each 1H, J_{gem}=14.2, NC*H*$_2$Ph), 4.07 (d, 1H, H-3′), 1.52, 1.31 (each s, each 3H, 2Me); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 136.6, 135.8, 135.0 (3 *ipso*-C of Ph), 129.2, 128.9, 128.4, 128.1, 128.0, 127.8, 127.7, 127.6, 127.4 (the other 15C of Ph), 112.6 (*C*Me$_2$), 105.4 (C-1′), 96.0 (C-4), 82.6 (C-2′), 82.5 (C-3′), 80.1 (C-4′), 79.7 (C-5), 74.6 (C-3), 71.6 (O*C*H$_2$Ph), 58.5 (N*C*H$_2$Ph), 27.2, 26.7 (2Me). The minor diastereomer (**14d** or **14b**, 0.005 g, 2%) had ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.04 (m, 15H, 3Ph), 5.96 (d, 1H, $J_{1',2'}$=3.6, H-1′), 5.55 (dd, 1H, $J_{3,4}$=7.8, $J_{4,5}$=5.1, H-4), 5.25 (dd, 1H, $J_{4',5}$=6.4, H-5), 4.62 (d, 1H, $J_{2',3'}\approx$0, H-2′), 4.47 (dd, 1H, $J_{3',4'}$=3.6, H-4′), 4.43, 4.32 (each d, each 1H, J_{gem}=11.8, OC*H*$_2$Ph), 3.97, 3.66 (each d, each 1H, J_{gem}=14.0, NC*H*$_2$Ph), 4.12 (d, 1H, H-3), 4.06 (d, 1H, H-3′), 1.50, 1.33 (each s, each 3H, 2Me); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 137.0, 135.5, 131.9 (3 *ipso*-C of Ph), 129.1, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8 (the other 15C of Ph), 112.1 (*C*Me$_2$), 105.1 (C-1′), 93.5 (C-4), 82.8 (C-3′), 81.4 (C-2′), 78.2 (C-4′), 78.4 (C-5), 74.9 (C-3), 71.9 (O*C*H$_2$Ph), 58.4 (N*C*H$_2$Ph), 29.6 (double intensity, 2Me).

*4.11. Reaction of (Z)-*N*-benzyl-(1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranos-6-ylidene)amine* N*-oxide **1** with (*E*)-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-7-nitro-α-*D*-galacto-hept-6-eno-1,5-pyranose **7**. Preparation of 2-benzyl-3,5-bis-(1,2:3,4-di-*O*-isopropylidene-α-*D*-galacto-pentopyranos-5-yl)-4-nitroisoxazolidines **15***

Nitroalkene **7** (0.186 g, 0.615 mmol) was added to a solution of **1** (0.223 g, 0.615 mmol) in toluene (4.4 mL), and the mixture was heated to reflux for 18 h. After elimination of the solvent at reduced pressure, the residue was subjected to column chromatography (1:6 ether:hexane). A portion of **7** was recovered unreacted (38.5 mg, 21%). The major product (**15b**, 0.169 g, 41%) had mp 185–187°C; $[\alpha]_D^{26}$ −104 (*c* 1); IR (KBr) ν_{max} 1555 and 1377 cm^{-1} (NO_2); ^{1}H NMR (500 MHz, DMSO-d_6, at 50°C) (protons of the sugar moiety on 3-position of the isoxazolidine ring are noted H-n′; those of the sugar moiety on 5-position are noted H-n′′) δ 7.40–7.20 (m, 5H, Ph), 5.80 (dd, 1H, $J_{3,4}$=6.5, $J_{4,5}$=4.4, H-4), 5.56 (d, 1H, $J_{1',2'}$=5.0, H-1′), 5.47 (d, 1H, $J_{1'',2''}$=4.9, H-1′′), 4.65 (dd, 1H, $J_{2',3'}$=2.5, $J_{3',4'}$=7.7, H-3′), 4.57, 3.85 (each d, each 1H, J_{gem}=14.6, C*H*$_2$Ph), 4.56 (dd, 1H, $J_{2'',3''}$=2.2, $J_{3'',4''}$=8.0, H-3′′), 4.53–4.47 (brm, 1H, H-5), 4.40 (dd, 1H, H-2′), 4.32 (dd, 1H, H-2′′), 4.30 (dd, 1H, $J_{4'',5''}$=1.5, H-4′′), 4.05 (dd, 1H, $J_{4',5'}$=1.3, H-4′), 3.98 (dd, 1H, $J_{3,5'}$=9.0, H-5′), 3.93 (dd, 1H, $J_{5,5''}$=6.8, H-5′′), 3.61–3.53 (brm, 1H, H-3), 1.45, 1.42, 1.40, 1.36, 1.31, 1.29, 1.27, 1.20 (each s, each 3H, 8Me); ^{1}H NMR (500 MHz, $CDCl_3$, −25°C), major invertomer (77%): δ 7.45–7.26 (m, 5H, Ph), 5.75 (dd, 1H, $J_{3,4}$=6.0, $J_{4,5}$=3.2, H-4), 5.64 (d, 1H, $J_{1',2'}$=5.0, H-1′), 5.48 (d, 1H, $J_{1'',2''}$=4.8, H-1′′), ~4.59 (dd, 1H, H-5), 4.55 (dd, 1H, $J_{2',3'}$=2.6, $J_{3',4'}$=7.8, H-3′), 4.61, 4.28 (each d, each 1H, J_{gem}=15.2, C*H*$_2$Ph), 4.39 (dd, 1H, $J_{2'',3''}$=2.1, $J_{3'',4''}$=8.1, H-3′′), 4.34 (dd, 1H, H-2′), 4.22 (dd, 1H, H-2′′), 4.11 (dd, 1H, $J_{4'',5''}\approx$0.5, H-4′′), 3.96 (dd, 1H, $J_{4',5'}\approx$0.5, H-4′), 3.90 (dd, 1H, $J_{3,5'}$=9.4, H-5′), 3.89 (dd, 1H, $J_{5,5''}$=5.6, H-5′′), 3.62 (dd, 1H, H-3), 1.51, 1.49, 1.45, 1.31, 1.29, 1.28, 1.24, 1.17 (each s, each 3H, 8Me); minor invertomer (23%): δ 7.40–7.20 (m, 5H, Ph), 6.08 (dd, 1H, $J_{3,4}$=7.1, $J_{4,5}$=4.4, H-4), ~5.64 (d, 1H, overlapped, H-1′), 5.53 (d, 1H, $J_{1'',2''}$=5.0, H-1′′), 4.48 (dd, 1H, overlapped, H-3′), ~4.59, 4.16 (each d, each 1H, J_{gem}=13.6, C*H*$_2$Ph), ~4.35 (dd, 1H, $J_{3'',4''}$=8.3, H-3′′), 5.27 (dd 1H, H-5), ~4.26 (dd, 1H, H-2′), ~4.22 (dd, 1H, H-2′′), ~4.10 (dd, 1H, overlapped, H-4′′), ~4.00 (dd, 1H, overlapped, H-4′), ~4.10 (dd, 1H, $J_{3,5'}$=10.9, H-5′), ~3.90 (dd, 1H, $J_{5,5''}$=5.9,

H-5′′), 4.66 (dd, 1H, H-3), 1.51, 1.49, 1.45, 1.31, 1.29, 1.28, 1.24, 1.17 (each s, each 3H, 8Me); NOE contacts (1D NOESY, at −25°C; for the major invertomer): H-3, H-4, C*H*$_2$Ph (one of the protons), H-5′′; ^{13}C NMR (125.8 MHz, $CDCl_3$) δ ~136.3br, 130.3, 128.7, 127.7, 127.0 (Ph), 109.6, 109.4, 109.2, 108.7 (4*C*Me$_2$), 96.3 (C-1′), 96.2 (C-1′′), 91.2 (C-4), 80.5br (C-5), 71.1 (C-4′), 70.8 (C-3′), 70.8 (C-2′′), 70.5 (C-3′′), 70.0 (C-4′′), 69.8 (C-2′), 66.2 (C-5′′), 64.9 (*C*H$_2$Ph), 64.6 (C-5′), ~60.1br (C-3), 26.1, 26.0, 25.7, 25.4, 25.0, 24.7, 24.4, 24.0 (8Me); HRMS *m/z* 664.2842 (calcd for $C_{32}H_{44}N_2O_{13}$: 664.2843). Anal. calcd for $C_{32}H_{44}N_2O_{13}$: C, 57.82; H, 6.67 N, 4.21. Found: C, 57.78; H, 6.66; N, 4.15. For the minor component, present in a mixed fraction (44.7 mg, 11% yield, by ^{1}H NMR), the structure **15d** was tentatively assigned; it had (only distinct signals) ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.53 (d, 1H, $J_{1',2'}$=5.0, H-1′), 5.51 (d, 1H, $J_{1'',2''}$=5.0, H-1′′), 5.31 (dd, 1H, $J_{3,4}$=6.0, $J_{4,5}$=2.8, H-4), ~4.50 (overlapped dd, 1H, $J_{2'',3''}$=2.2, H-3′′), 4.39 (dd, 1H, $J_{4',3'}$=7.9, $J_{4',5'}$=1.3, H-4′), 3.90 (dd, 1H, $J_{3,5'}$=7.8, H-5′), 3.85 (dd, 1H, $J_{5,5''}$=8.0, H-5′′), 3.42–3.40 (brm, 1H, H-3), 1.55, 1.52, 1.43, 1.39, 1.36, 1.32, 1.29, 1.25 (each s, each 3H, 8Me); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 109.9, 109.5, 108.9, 108.6 (4*C*Me$_2$), 96.4 (C-1′), 96.3 (C-1′′), 91.3 (C-4), 79.7 (C-5), 71.5 (C-3), 70.7, 70.6, 70.4, 70.2, 70.2, 68.7 (C-4′, C-3′, C-2′, C-4′′, C-3′′, C-2′′), 66.4br (C-5′′), 64.6 (C-5′), 60.8 (*C*H$_2$Ph), 26.2, 26.0, 25.7, 25.6, 24.9, 24.9, 24.2, 24.1 (8Me).

*4.12. Reaction of (*Z*)-*N*-benzyl-(3-*O*-benzyl-1,2-*O*-isopropylidene-α-*D*-xylopyranos-5-ylidene)amine N-oxide **2** with (*E*)-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-nitro-α-*D*-xylo-hex-5-eno-1,4-furanose **8**. Preparation of (3*S*,4*S*,5*S*)- **16b** or (3*R*,4*R*,5*R*)-2-benzyl-3,5-di-(3-*O*-benzyl-1,2-*O*-isopropylidene-α-*D*-xylo-tetrofuranos-4-yl)-4-nitroisoxazolidine **16d***

Nitrone **2** (0.205 g, 0.536 mmol) was added to a solution of **8** (0.172 g, 0.536 mmol) in toluene (3.7 mL) and the mixture was heated to reflux for 18 h. ^{1}H NMR of the reaction mixture showed resonances for a main product accompanied by small signals of an isomer (<10%). After evaporation of the solvent, the residue was subjected to column chromatography (1:2 ether:hexane) to give a major compound (**16b** or **16d**, 0.192 g, 51%); oil; $[\alpha]_D^{25}$ −90 (*c* 1); IR (KBr) ν_{max} 1559 and 1379 cm^{-1} (NO_2); ^{1}H NMR (500 MHz, $CDCl_3$) (protons of the sugar moiety on 3-position of the isoxazolidine ring are noted H-n′; those of the sugar moiety on 5-position are noted H-n′′) δ 7.40–7.17 (m, 15H, 3Ph), 5.92 (d, 1H, $J_{1'',2''}$=3.8, H-1′′), 5.89 (d, 1H, $J_{1',2'}$=3.8, H-1′), 5.28 (dd, 1H, $J_{3,4}$=5.0, $J_{4,5}$=3.4, H-4), 4.83 (dd, 1H, $J_{4'',5}$=7.0, H-5), 4.60 (d, 1H, $J_{2'',3''}\approx$0, H-2′′), 4.50 (d, 1H, $J_{2',3'}\approx$0, H-2′), 4.52, 4.49 (each d, each 1H, J_{gem}=11.7, OC*H*$_2$Ph), 4.41, 4.37 (each d, each 1H, J_{gem}=11.4, OC*H*$_2$Ph), 4.50, 4.13 (each d, each 1H, J_{gem}=14.5, NC*H*$_2$Ph), 4.43 (dd, 1H, $J_{3',4'}$=3.4, H-4′), 4.39 (dd, 1H, $J_{3'',4''}$=3.4, H-4′′), 4.14 (d, 1H, H-3′), 4.01 (dd, 1H, $J_{3,4'}$=9.2, H-3), 3.81 (d, 1H, H-3′′), 1.50, 1.46, 1.32, 1.29 (each s, each 3H, 4Me); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 137.4, 136.7, 136.7 (3 *ipso*-C of Ph), 129.1, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 126.9, 126.8 (the other 15C of Ph), 112.0, 111.9 (2*C*Me$_2$), 105.4 (C-1′′), 105.2 (C-1′), 92.5 (C-4), 82.9 (C-3′), 82.6 (C-2′), 81.3 (C-2′′), 80.7 (C-4′), 80.6 (C-3′′), 78.9 (C-4′′), 78.9 (C-5), 72.2, 71.5 (2O*C*H$_2$Ph), 70.4 (C-3), 60.8 (N*C*H$_2$Ph), 26.8, 26.7, 26.2, 26.1 (4Me); HRMS *m/z* 704.29118 (calcd for $C_{38}H_{44}N_2O_{11}$: 704.29451). Anal. calcd for $C_{38}H_{44}N_2O_{11}$: C, 64.76H, H, 6.29; N, 3.98. Found: C, 64.81; H, 6.40; N, 3.70.

*4.13. Crystallographic analysis for (2*S*)-**9b***[†]

The compound crystallised as colourless rectangular parallelpipeds. A crystal of dimensions 0.20×0.36×0.45 mm was used for X-ray investigations; it belonged to the orthorhombic system with

[†] Lists of the atomic coordinates, hydrogen coordinates, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

systematic absences consistent with the space group $P2_12_12_1$. Accurate cell dimensions and crystal orientation matrix, determined on an Enraf-CAD4 diffractometer by least-squares treatment of the setting angles of 25 reflections in the range $2<\theta<25°$, were a=11.086(10), b=24.755(4), and c=9.577(2) Å, $\alpha=\beta=\gamma=90°$, V=2626(2) Å^3, d_{calc}=1.30 g cm^{-3} for Z=4, F(000)=1088 and the absorption coefficient μ=0.096 mm^{-1}. A total of 2670 independent reflections were collected, 1825 intensities greater than $2\sigma(I_0)$ were used as observed for the structure determination. The final discrepancy factors were R=0.060 and Rw=0.071 for 334 variables, average shift/e.s.d. was 0.002, maximum and minimum electron densities were 0.29 and −0.30 e Å^{-3}, respectively.

*4.14. Crystallographic analysis for (2S)-**13a***[‡]

The compound crystallised as colourless prisms. A crystal of dimensions 0.40×0.48×0.52 mm was used for X-ray study; it belonged to the monoclinic space group $P2_1$. Accurate cell dimensions and crystal orientation matrix, determined on an Enraf-CAD4 diffractometer by least-squares treatment of the setting angles of 25 reflections in the range $2<\theta<25°$, were a=11.331(8), b=12.841(1), and c=9.709(8) Å, α=90, β=102.54(1), γ=90°, V=1379(2) Å^3, d_{calc}=1.23 g cm^{-3} for Z=2, F(000)=544 and the absorption coefficient μ=0.091 mm^{-1}. A total of 3156 independent reflections were collected, 2110 observed for I greater than $2\sigma(I_0)$. The final discrepancy factors were R=0.050 and Rw=0.046 for 333 variables (y coordinate for O1 was held fixed), maximum and minimum electron densities were 0.41 and −0.21 e Å^{-3}, respectively.

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References

1. Torssell, K. B. G. *Nitrile Oxides, Nitrones, and Nitronates in Organic Synthesis*; VCH: New York, 1988.
2. Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon Press: Oxford, 1990; pp. 298–331.
3. Confalone, P. N.; Huie, E. M. *Org. React.* **1988**, *36*, 1–173.
4. Huber, R.; Vasella, A. *Tetrahedron* **1990**, *46*, 33–58.
5. For a review, see: Fisera, L.; Al-Timari, U. A. R.; Ertl, P. In *Cycloaddition Reactions in Carbohydrate Chemistry*; ACS Symposium Series 494; Giuliano, R. M., Ed.; American Chemical Society: Washington, DC, 1992; pp. 158–171.
6. Al-Timari, U. A. R.; Fisera, L.; Goljer, I.; Ertl, P. *Carbohydr. Res*. **1992**, *226*, 49–56.
7. DeShong, P.; Dicken, C. M.; Leginus, J. M.; Whittle, R. R. *J. Am. Chem. Soc*. **1984**, *106*, 5598–5602.
8. Schiehser, G. A.; White, J. D. *Tetrahedron Lett*. **1986**, *27*, 5587–5590.
9. Shing, T. K. M.; Zhong, Y.-L.; Mak, T. C. W.; Wang, R.-j.; Xue, F. *J. Org. Chem.* **1998**, *63*, 414–415.
10. See, for example: Wovkulich, P. M.; Barcelos, F.; Batcho, A. D.; Sereno, J. F.; Baggiolini, E. G.; Hennesy, B. M.; Uskokovic, M. R. *Tetrahedron* **1984**, *40*, 2283–2296.
11. Rispens, M. T.; Keller, E.; de Lange, B.; Zijlstra, R. W. J.; Feringa, B. L. *Tetrahedron: Asymmetry* **1994**, *5*, 607–624.
12. Joucla, M.; Grée, D.; Hamelin, J. *Tetrahedron* **1973**, *29*, 2315–2322.
13. Sims, J.; Houk, K. N. *J. Am. Chem. Soc*. **1973**, *95*, 5798–5800.

[‡] Lists of the atomic coordinates, hydrogen coordinates, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

14. Houk, K. N.; Bimanand, A.; Mukherjee, D.; Sims, J.; Chang, Y.-M.; Kaufman, D.; Domelsmith, L. *Heterocycles* **1977**, *7*, 293–299.
15. See, for instance: Hossain, N.; Papchikhin, A.; Plavec, J.; Chattopadhyaya, J. *Tetrahedron* **1993**, *49*, 10133–10156.
16. DeShong, P.; Dicken, C. M.; Staib, R. R.; Freyer, A. J.; Weinreb, S. M. *J. Org. Chem.* **1982**, *47*, 4397–4403.
17. Vasella, A. *Helv. Chim. Acta* **1977**, *60*, 427–446, 1273–1295.
18. Dondoni, A.; Franco, S.; Junquera, F.; Merchán, F.; Merino, P.; Tejero, T. *Synth. Commun*. **1994**, *24*, 2537–2550.
19. Gothelf, K. V.; Thomsen, I.; Jørgensen, K. A. *J. Am. Chem. Soc*. **1996**, *118*, 59–64.
20. Spek, A. L. *PLATON. Molecular Geometry Program*; University of Utrecht, The Netherlands, 1994.
21. Köll, P.; Saak, W.; Pohl, S.; Steiner, B.; Koós, M. *Carbohydr. Res*. **1994**, *265*, 237–248.
22. Cremer, D.; Pople, J. A. *J. Am. Chem. Soc*. **1975**, *97*, 1354–1358.
23. Nardelli, M. *Acta Crystallogr*. **1983**, *C39*, 1141–1142.
24. Altomare, A.; Cascarano, C.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Cryst*. **1994**, *27*, 435.
25. *International Tables for X-Ray Crystallography, Vol. C*; Kluwer Academic Publishers: Dordrecht, 1992.
26. Stewart, J. M.; Machin, P. A.; Dickinson, C. W.; Ammon, H. L.; Heck, H.; Flack, H. *The X-Ray System 76*; Computer Science Center, University of Maryland, College Park, 1976.
27. Nardelli, M. *J. Comp. Chem*. **1983**, *7*, 95–98.
28. Roldán, F.; González, A.; Palomo, C. *Carbohydr. Res*. **1986**, *149*, C1–C4.
29. Horton, D.; Swanson, F. O. *Carbohydr. Res*. **1970**, *14*, 159–171.
30. Matulic-Adamic, J.; Haeberli, P.; Usman, N. *J. Org. Chem*. **1995**, *60*, 2563–2569.
31. DeShong, P.; Li, W.; Kennington Jr., J. W.; Ammon, H. L. *J. Org. Chem*. **1991**, *56*, 1364–1373.