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Synthesis of chiral 2-furyl and 3-nitro-7-oxabicyclo[2.2.1]heptane derivatives from sugars

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ABSTRACT

Asymmetric Diels–Alder reactions between 2-methylfuran and chiral (*E*)-1,2-dideoxy-1-nitroalkenes derived from D-mannose and D-galactose were carried out at room temperature, under 13 kbar pressure. The processes were completely regioselective, and only the four adducts with penta-*O*-acetyl-1′-*C*-(4-methyl-3-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-yl)pentitols structures were formed in each case. These adducts, as well as those arising from cycloadditions of the same nitroalkenes and furan, have been converted into chiral derivatives, such as 2-furyl substituted 1-nitrosugars, 2-glyco-4-methyl-3-nitro-7-oxabicyclo[2.2.1]heptanes, and 5,6-*exo*-epoxy-2-glyco-3-nitro-7-oxabicyclo[2.2.1]hept-5-enes.

1. Introduction

Although chiral 7-oxabicyclo[2.2.1]heptenes are useful building blocks for the synthesis of natural products,[1] applications of this type of compounds are scarce[2] due to the difficulties associated with the use of furans as dienes (i.e., low reactivity, generally unstable cycloadducts, and easy cycloreversion to the reagents). Leaving aside previous work from our group,[3,4] to the best of our knowledge there are no references on the preparation of chiral 7-oxanitronorbornenes.[5] Moreover, they could not be synthesized from chiral nitroacrylates as dienophiles,[6] and only a few amines resulting from the reduction of racemic 7-oxanitronorbornenes have been resolved.[5] On the other hand, sugar derivatives with a furan ring in their structures have received attention as precursors in the preparation of biologically important compounds, such as tunicamines (main component of numerous antibiotics),[7] C-nucleosides,[8] peptidomimetics,[9] and spiro carbon linked disaccharides.[10] In most cases, furyl sugars can be prepared by either treatment of activated furans with the appropriate acceptors,[7,8a,10,11] or building the furan moiety from non-furylic precursors.[12,13]

Herein, we report new chiral 7-oxanitronorbornanes and 5,6-epoxy-7-oxanitronorbornenes from Diels–Alder reactions involving either 2-methylfuran or furan with D-mannose[14] or D-galactose[15] based nitroalkenes. Full details on the synthesis of 2-furyl sugars are provided.

2. Results and discussion

Diels–Alder reactions between **1a**[14] or **1b**[15] and 2-methylfuran **3** were performed in CH_2Cl_2, under high pressure (13 kbar) at room temperature (Scheme 1).[16] After five days, ^{1}H NMR spectra of the reaction mixtures showed complete disappearance of the starting materials, and their conversion into 7-oxanitronorbornene derivatives **9**–**12**, as indicated in Table 1.[17] It is noteworthy that none of these reactions occurred under atmospheric pressure, both at room temperature and at reflux, even for prolonged periods. As observed for cycloadditions between the same nitroalkenes and furan,[3] CH_2Cl_2 solutions of the crude mixtures **9**–**12** showed a slight cycloreversion at room temperature (this process was negligible at −18 °C) even after several weeks.

As shown in Table 1, the *endo*-nitro adducts were preponderant in the reactions with furan **2**[3] or 2-methylfuran **3**, while the *exo*-nitro adducts were favored with 2,5-dimethylfuran **4**.[4] In agreement with data reported by Franck et al.,[18] and with our previous observations for similar processes with furan[3] or cyclopentadiene,[19] the stereoselectivity in these cycloadditions seems to be dependent on the configuration of the adjacent stereogenic center to the dienophilic double bond. Thus, *endo*-nitro adducts **5b** and **9b** and *exo*-nitro adducts **8b** and **16b**, generated by the cycloaddition on the C1(*si*) face of the dienophile, are prevalent when the sugar fragment possesses a D-*galacto* configuration; on the contrary, *endo*-nitro **6a**, **10a**, and **14a** and *exo*-nitro **7a** and **11a** adducts, arising from the cycloaddition on the C1(*re*) face, are the major products when the configuration of the sugar side-chain is D-*manno*. This asymmetric induction works in a different sense in the cases of **15a**, **14b**, and **12b**, although the discrimination is almost negligible for the latter. Concerning either the facial diastereoselectivity or the *endo*/*exo* ratio, we observed a decrease when comparing the reactions of furan with those of 2-methylfuran; however, there is an increase in diastereoselectivity for the reaction of 2,5-dimethylfuran with **1b**, together with a clear decrease in the *endo*/*exo* ratio with both dienophiles.

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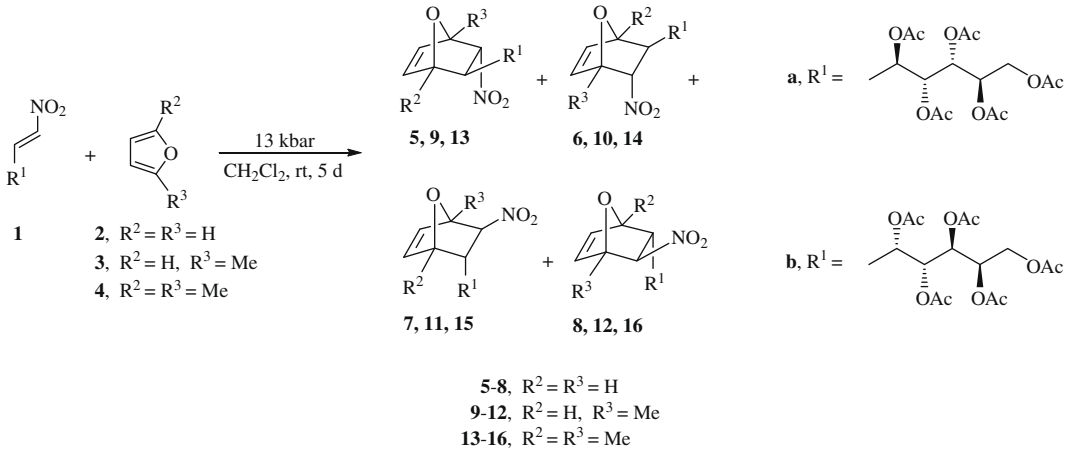


Scheme 1. Diels–Alder reactions between sugar-derived nitroalkene **1a** or **1b** with furan **2** (Ref. 3), 2-methylfuran **3**, and 2,5-dimethylfuran **4** (Ref. 4).

Table 1
Composition (%), diastereoselectivity and *endo*/*exo* ratios of the reaction mixtures from cycloadditions of **1a** and **1b** with furans **5–8**, 2-methylfurans **9–12**, and 2,5-dimethylfurans **13–16**

Compound	%	(2*S*,3*S*)/(2*R*,3*R*)	*endo*/*exo*
5a[a]	29.1	2.44	10.7
6a	62.4		
7a	8.5		
8a	–		
9a	26.7	1.65	2.1
10a	41.1		
11a	21.1		
12a	11.1		
13a	–	0.66[c]	0.10
14a	8.8		
15a	31.0		
16a	60.2		
5b[a]	69.1	0.35	18.6
6b	25.8		
7b	–		
8b	5.1		
9b	36.9	0.84	1.6
10b	24.6		
11b	21.0		
12b	17.5		
13b	–	0.23[c]	0.02
14b[b]	1.8		
15b	17.2		
16b	81.0		

[a] Data of **5a–8a** and **5b–8b** were taken from Ref. 3.
[b] Data of **14b–16b** were taken from Ref. 4.
[c] (2*R*,3*S*)/(2*S*,3*R*).

Table 2
^{1}H NMR shifts for H-2 and H-3 in compounds **5–16**

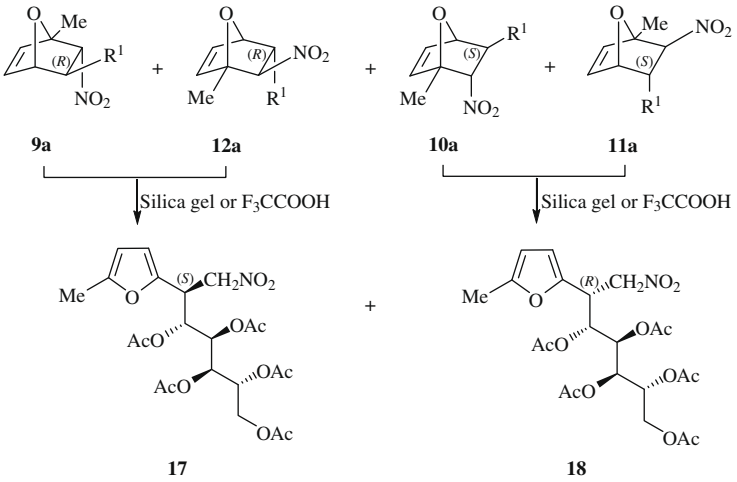
Compound	H-2	H-3
5a[a]	2.39	5.14
6a	2.54	5.10
7a	3.25	4.35
8a	–	–
9a	2.51	4.80
10a	2.61	4.76
11a	3.34	4.40
12a	3.43	4.44
13a	–	–
14a	2.61	4.92
15a	2.98	4.64
16a	3.25	4.51
5b[a]	2.27	4.95
6b	2.58	5.05
7b	–	–
8b	3.34	4.36
9b	2.38	4.59
10b	2.68	4.65
11b	3.01	4.40
12b	3.36	4.33
13b	–	–
14b	2.51	4.79
15b	2.80	4.70
16b[b]	2.97	4.35

[a] Data of **5a**, **6a**, **7a**, and **5b** were taken from Ref. 3.
[b] Data of **16b** were taken from Ref. 4.

In agreement with FMO theory predictions,[20] we found that the cycloadditions of 2-methylfuran with dienophiles **1a** or **1b** were completely regioselective; that is, only those adducts with methyl and nitro groups in vicinal positions were formed (**9–12**, Scheme 1). The regiochemistry and an increase in the amount of the *exo*-nitro adducts are in agreement with previous results[21] in reactions involving furan **2**, **3**, or **4** with 1,1,1-trichloro-3-nitro-2-propene.

As we shall see later, the bicyclic system in cycloadducts **9–12** undergoes ring opening on silica gel; as a result, they could not be isolated in pure form, and ^{1}H NMR data had to be obtained from crude or enriched mixtures in one of them. The configuration at the new stereogenic centers C-2 and C-3 in these compounds is based on the previously discussed facial selectivity,[3,18,19] as well as by comparison of their ^{1}H NMR data and those of cycloadducts derived from furan[3] or 2,5-dimethylfuran[4] **5**, **6** or **15**, **16** (see Table 2). An upfield shift of 0.34–0.40 ppm was observed for H-3 in the *endo* adducts **9** and **10** due to the presence of the vicinal methyl group, relative to the same proton in their analogues **5** and **6**. A similar shielding effect (0.18–0.39 ppm) for the H-2 proton was found when comparing **11** and **12** with **15** and **16**, respectively.

Preparative thin layer chromatography of the mixture containing **9a–12a** afforded only two bands, in which no Diels–Alder adducts, apart from 2-furyl derivatives **17** and **18** were identified (Scheme 2). These compounds, which should be formed during the chromatographic purification, were also isolated by column chromatography; we also detected a fraction containing a very small quantity of a non-isolated product, whose ^{1}H NMR spectrum was similar to that of oxime **21** (Fig. 1). For **17**, the presence of the nitromethylene group was deduced from the AB system of the two double doublets at 4.74 and 4.65 ppm; a similar pattern was found in compound **18**, at 4.70 and 4.62 ppm.



Scheme 2. Ring-opening reactions of 7-oxabicycles **9a**–**12a** by treatment with silica gel or chloroform–trifluoroacetic acid.

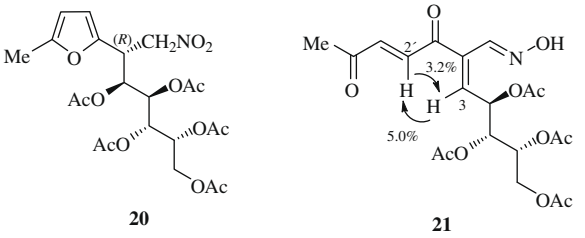


Figure 1. Structures of nitrofuryl derivative **20** and oxime **21** (with significant NOE observed).

The absolute configurations at C-2 in **17** and **18** are based on those of their 7-oxanorbornenic precursors; moreover, the ratio which appeared with the 2-furyl derivatives (**17**/**18** = 1.0/1.7) was almost identical to that of their respective starting cycloadducts (**9a** + **12a**/**10a** + **11a** = 1.0/1.65).

To demonstrate that **17** and **18** did not come from a Michael-type addition between 2-methylfuran **3** and nitroalkene **1a** arising from cycloreversion, we impregnated a mixture of these two compounds in silica gel; after 24 h at room temperature, the mixture remained unchanged, and the same result was obtained when **1a** and **3** were treated with chloroform–trifluoroacetic acid or refluxed for 1 h in the presence of pyrogallol (sometimes used as a catalyst in Michael additions[22a]). By contrast, when the mixture of **9a**–**12a** was treated either with silica gel for 5 h at room temperature, or with chloroform–trifluoroacetic acid[21] for 50 min at 50 °C, the ^{1}H NMR spectra of the respective crude mixtures showed the formation of compounds **17** and **18**, together with a slight cycloreversion in the reaction with chloroform–trifluoroacetic acid. On the other hand, the reaction of **9a**–**12a** with potassium carbonate led to a mixture of two non-isolated deacetylated furyl derivatives, which gave **17** and **18** after conventional acetylation.

From these results, we deduced that 2-furyl compounds **17** and **18** should be formed via ring-opening reactions of **9a**–**12a**, by heterolytic rupture[22e] of the bond between the carbon atoms bearing the nitro and methyl groups. This rupture should be facilitated by the strain in the 7-oxanorbornenic system, as well as by the resonance stabilization of the resulting carbocation and carbanion.[4] An alternative route through a Michael addition, involving electrophilic substitution, has been very controversial[6,21,22] for reactions of furan or 2-methylfuran with several nitroalkenes, and particularly with 3-nitroacrylates.

From a solution of the mixture of **9b**–**12b** in acetone, a small quantity of the major adduct **9b** could be obtained by crystallization, although it was slightly contaminated with the starting nitroalkene **1b**. The treatment of this crude product with chloroform–trifluoroacetic acid,[21] as indicated above, afforded compound **19** contaminated with **1b** (Scheme 3). According to the proposed mechanism for this transformation,[22e,f] the absolute configuration at C-2 in **19** should be (*S*).

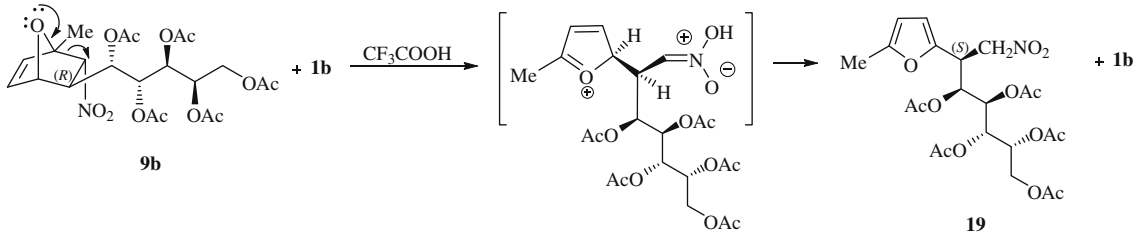
Either by contact with silica gel or by treatment with trifluoroacetic acid, a solution of the mixture of **9b**–**12b** in chloroform led to a mixture of **19** and **20** in a ratio (1.2/1.0) very similar to that of their starting adducts (**9b** + **12b**/**10b** + **11b** = 1.19/1.0), thus supporting the structural assignments. Compounds **19** and **20** were also obtained by treatment of **9b**–**12b** with potassium carbonate, followed by reaction of the resulting product with acetic anhydride in pyridine.

The ^{1}H NMR spectra of **19** showed a magnetic equivalence for the protons of the nitromethylene group, which appeared as a doublet at 4.51 ppm; for **20**, these protons appeared as an AB system with two double doublets at 4.78 and 4.69 ppm.

From a crude mixture of **19** and **20** we could also isolate, by PTLC, a small quantity of compound **21** with lower chromatographic mobility than **19** and **20**. The 2*E*-configuration of the double bond between C2 and C3 was supported by the marked NOE between the H-3 and H-2′ protons (Fig. 1). The formation of the oxime **21** can be justified through a cascade process, promoted by silica gel and favored by the extended conjugation of the product. This process would involve a ring-opening reaction of the furan cycle,[23] with reduction of the nitro group to an oxime,[24] followed by an antiperiplanar E2 elimination of acetic acid. In this way, the oxime **21** should be formed from the 2-furyl sugar **19**.

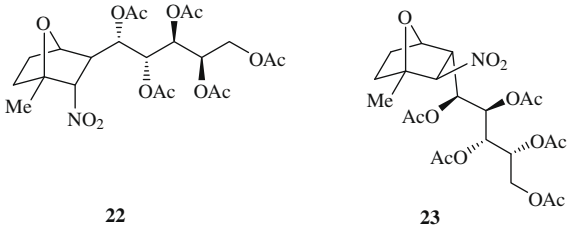
By standing **21** in $CDCl_3$ solution at room temperature, there was a gradual formation of new proton signals, whose origin was attributed to the *Z*/*E* isomerism of the C=N oxime bond. After 40 days, there was a stabilization of the signals, with the ratio being ca. 1:1 between such isomers. Since the new H-1 signal appeared more downfield shifted than the same proton in the starting material, we assigned[25] an *E*-configuration to **21**.

To preserve the 7-oxanorbornene system of the Diels–Alder adducts, and avoid ring-opening reactions, the mixture of **9b**–**12b** was hydrogenated on Pd/C. Compounds **22** and **23** (Fig. 2) were isolated pure by flash column chromatography, and were stable after several days at room temperature, even when in contact with silica gel. Their structural assignment was supported by correlation of the ^{1}H NMR shifts for H-2 protons; we deduced that **22** (2.70 ppm) should arise from **10b** (2.68 ppm), whereas **23** (3.39 ppm) should proceed from **12b** (3.36 ppm).



9b 19

Scheme 3. Ring-opening reaction of **9b**.

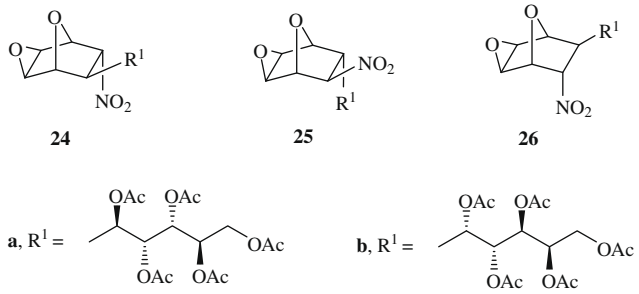


22 23

Figure 2. Structures of 7-oxanorbornanes **22** and **23**.

The ^{1}H NMR spectra of **22** and **23** did not show signals of olefinic protons, with those of H-6$_{endo}$, H-6$_{exo}$, H-5$_{endo}$, and H-5$_{exo}$ in the range 1.47–2.01 ppm. Unlike the expected signals,[25,26] it is noteworthy that the signal for H-5$_{endo}$ appeared in both cases more downfield shifted than that of H-5$_{exo}$, probably due to spatial proximity with the nitro group or the sugar side-chain.

In order to explore the problems associated with the cycloreversion[3] of the 7-oxanorbornenic system in synthetic processes, epoxidation reactions were carried out for some of the furan-derived cycloadducts. Thus, the treatment of **5b**, **6a**, **5b**+**6b**+**8b**, or **5a**–**7a** with *m*-chloroperoxybenzoic acid, resulted in the formation of the oxanorbornene-epoxides **24b**, **26a**, **25b**, or **24a**, respectively (Fig. 3).



24 25 26

Figure 3. Structures of epoxides **24**–**26**.

The structures of the new epoxides **24b** and **26a** were supported by their analytical and spectroscopic data and those of their respective starting materials. Thus, we have deduced that **25b** should arise from **8b**, since this is the only *exo*-nitro adduct in the mixture of **5b**+**6b**+**8b**. Compound **24a** would be formed from **5a**, since this is the other *endo*-nitro adduct in the **5a**–**7a** mixture. For the *endo*-nitro epoxides **24a**, **24b**, and **26a**, the H-5 and H-6 protons appeared between 3.4 and 3.6 ppm, and in the range 3.50–3.87 for the *exo*-nitro epoxide **25b**. In all cases, these protons appeared as doublets ($J_{5,6}$ = 2.8–3.6 Hz) because their couplings with H-4 and H-1 were almost zero.

3. Conclusions

In conclusion, the regioselective and asymmetric Diels–Alder reactions between 2-methylfuran and sugar-derived nitroalkenes have been achieved, using a high pressure methodology. The facial diastereoselectivities and *endo*/*exo* ratios for these cycloadditions have been compared with those previously described involving furan or 2,5-dimethylfuran.

Spontaneous ring-opening processes have been observed in the new adducts; however, we have shown that the 7-oxabicyclic system can be preserved by either hydrogenation or epoxidation of the double bond.

4. Experimental

4.1. General methods

All chemicals were purchased from commercial sources and were used directly, without further purification. Preparative TLC was performed using silica gel (Merck 60 GF$_{254}$). TLC was performed on precoated Merck Kieselgel 60 GF$_{254}$ aluminum backed plates; bands were visualized by UV light, iodine vapor, or *p*-anisaldehyde stain. NMR spectra were taken on a Bruker AC/PC (400 MHz for ^{1}H and 100 MHz for ^{13}C) instruments with $CDCl_3$ as solvent. All chemical shifts were expressed in ppm with respect to the residual solvent signal. Coupling constant values were recorded in hertz. Optical rotations were measured with a Perkin–Elmer 241 polarimeter in a 1 dm tube. HRMS were recorded on an AutoSpec spectrometer. High-pressure reactions were carried out by using a high-pressure apparatus U-101 (Unipress Equipment Division, High Pressure Research Center, Polish Academy of Sciences).

4.2. (2*R*,3*R*)-1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-(4-methyl-3-*endo*-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl)-D-*manno*-pentitol **9a**, (2*S*,3*S*)-1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-(4-methyl-3-*endo*-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl)-D-*manno*-pentitol **10a**, (2*S*,3*S*)-1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-(4-methyl-3-*exo*-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl)-D-*manno*-pentitol **11a** and (2*R*,3*R*)-1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-(4-methyl-3-*exo*-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl)-D-*manno*-pentitol **12a**

To a solution of (*E*)-3,4,5,6,7-penta-*O*-acetyl-D-*manno*-1-nitrohept-1-enitol[14] **1a**, (1.56 g, 3.60 mmol) in CH_2Cl_2 (2.5 mL) was added 2-methylfuran **3** (1.26 mL, 13.96 mmol). After 5 days at room temperature under 13 kbar pressure, the solvent was evaporated, leading quantitatively to an oil (1.84 g) that consisted, exclusively, of a 2.4:3.7:1.9:1.0 mixture of cycloadducts **9a**–**12a**, respectively. Compound **9a**: ^{1}H NMR δ: 6.60 (dd, $J_{1,6}$ = 1.9 Hz, $J_{5,6}$ = 5.7 Hz, 1H, H-6), 6.13 (d, 1H, H-5), 5.27 (dd, 1H, H-1′), 5.60–5.00 (m, 3H, H-2′,3′,4′), 4.95 (d, 1H, H-1), 4.80 (d, 1H, $J_{2,3}$ = 3.4 Hz, H-3), 4.21 (dd, 1H, H-5′a), 4.05 (dd, 1H, H-5′b), 2.51 (t, 1H, $J_{1,2} \sim 0$ Hz, $J'_{1,2}$ = 3.2 Hz, H-2), 1.77 (s, 3H, Me-4). Compound **10a**: ^{1}H NMR δ: 6.65 (dd, 1H, $J_{1,6}$ = 1.9 Hz, $J_{5,6}$ = 5.5 Hz, H-6), 6.06 (d, 1H, H-5), 5.27 (dd, 1H, H-1′), 5.60–5.00 (m, 3H, H-2′,3′,4′), 4.90 (d, 1H, H-1), 4.76 (d, 1H, $J_{2,3}$ = 3.0 Hz, H-3), 4.21 (dd, 1H, H-5′a), 4.05 (dd, 1H, H-5′b), 2.61 (t, 1H, $J_{1,2} \sim 0$ Hz, $J_{1',2}$ = 2.8 Hz, H-2), 1.78 (s, 3H, Me-4). Compound **11a**: ^{1}H NMR δ: 6.54 (dd, 1H, $J_{1,6}$ = 1.9 Hz, $J_{5,6}$ = 5.6 Hz, H-6), 6.27 (d, 1H, H-5), 5.60–5.00 (m,

3H, H-2′,3′,4′), 4.99 (m, 1H, H-1′), 4.90 (dd, 1H, H-1), 4.40 (d, 1H, H-3), 4.21 (dd, 1H, H-5′a), 4.05 (dd, 1H, H-5′b), 3.34 (ddd, 1H, $J_{1',2}$ = 7.6 Hz, $J_{1,2} \sim J_{2,3}$ 4.0 Hz, H-2), 1.55 (s, 3H, Me-4). Compound **12a**: ^{1}H NMR δ: 6.49 (dd, 1H, $J_{1,6}$ = 1.9 Hz, $J_{5,6}$ = 5.5 Hz, H-6), 6.23 (d, 1H, H-5), 5.60–5.00 (m, 3H, H-2′,3′,4′), 4.87 (m, 1H, H-1′), 4.83 (dd, 1H, H-1), 4.44 (d, 1H, H-3), 4.21 (dd, 1H, H-5′a), 4.05 (dd, 1H, H-5′b), 3.43 (ddd, 1H, $J_{1',2}$ = 8.4 Hz, $J_{1,2} \sim J_{2,3}$ 4.0 Hz, H-2), 1.56 (s, 3H, Me-4).

4.3. (2*R*,3*R*)-1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-(4-methyl-3-*endo*-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl)-D-*galacto*-pentitol 9b, (2*S*,3*S*)-1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-(4-methyl-3-*endo*-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl)-D-*galacto*-pentitol 10b, (2*S*,3*S*)-1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-(4-methyl-3-*exo*-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl)-D-*galacto*-pentitol 11b and (2*R*,3*R*)-1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-(4-methyl-3-*exo*-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl)-D-*galacto*-pentitol 12b

Following the same procedure described in 4.2, a mixture of (*E*)-3,4,5,6,7-penta-*O*-acetyl-D-*galacto*-1-nitrohept-1-enitol[15] **1b** (1.10 g, 2.54 mmol) and 2-methylfuran **3** (1.0 mL, 11.08 mmol) in CH_2Cl_2 (8 mL) led quantitatively (1.30 g) to an oily mixture of cycloadducts **9b**–**12b**, in 2.1:1.4:1.2:1.0 respective ratio. Pure **9b** (7 mg) crystallized from ethyl acetate: $[\alpha]_D^{25} = +27.3$ (*c* 1.33, $CHCl_3$). IR (NaCl): ν_{max} 3021 (=C–H), 1749 (C=O), 1548, 1371 (NO_2), 1216, 1029 (C–O–C) cm^{-1}. ^{1}H NMR δ: 6.56 (dd, 1H, $J_{1,6}$ = 2.0 Hz, $J_{5,6}$ = 5.6 Hz, H-6), 6.11 (d, 1H, H-5), 5.37 (dd, 1H, $J_{1',2'}$ = 1.6 Hz, $J_{2',3'}$ = 9.9 Hz, H-2′), 5.31 (m, 2H, H-1′,3′), 5.29 (m, 1H, H-4′), 4.97 (d, 1H, $J_{1,2} \sim 0$ Hz, H-1), 4.59 (d, 1H, $J_{2,3}$ = 3.3 Hz, H-3), 4.30 (dd, 1H, $J_{4',5'a}$ = 4.5 Hz, $J_{5'a,5'b}$ = 11.6 Hz, H-5′a), 3.79 (dd, 1H, $J_{4',5'b}$ = 7.4 Hz, H-5′b), 2.38 (dd, 1H, $J_{1',2}$ = 9.2 Hz, H-2), 2.13 (s, 3H, OAc), 2.10 (s, 6H, 2 × OAc), 2.08 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.77 (s, 3H, Me-4). ^{13}C NMR δ: 171.1, 171.0, 170.4, 170.3, 169.9 (O–*C*O–CH$_3$), 138.8 (C-6), 135.6 (C-5), 88.4 (C-1), 88.2 (C-4), 81.2 (C-3), 70.3, 68.5, 67.7, 67.5 (C-1′,2′,3′,4′), 62.2 (C-5′), 50.0 (C-2), 21.0, 20.7, 20.6, 20.5 (O–CO–*C*H$_3$), 17.2 (Me-4). Compound **10b**: ^{1}H NMR δ: 6.54 (dd, 1H, $J_{1,6}$ = 2.0 Hz, H-6), 6.08 (d, 1H, $J_{5,6}$ = 5.8 Hz, H-5), 5.50–5.00 (m, 4H, H-1′,2′,3′,4′), 4.72 (d, 1H, $J_{1,2} \sim 0$ Hz, H-1), 4.65 (d, 1H, $J_{2,3}$ = 3.1 Hz, H-3), 4.30 (dd, 1H, H-5′a), 3.79 (dd, 1H, H-5′b), 2.68 (dd, 1H, $J_{1',2}$ = 7.3 Hz, H-2), 1.82 (s, 3H, Me-4). Compound **11b**: ^{1}H NMR δ: 6.65 (dd, 1H, $J_{5,6}$ = 5.4 Hz, $J_{1,6}$ = 1.6 Hz, H-6), 6.35 (d, 1H, H-5), 5.50–5.00 (m, 3H, H-2′,3′,4′), 5.11 (dd, 1H, $J_{1,2}$ = 4.4 Hz, H-1), 4.79 (dd, 1H, $J_{1',2'}$ = 1.2 Hz, H-1′), 4.40 (d, 1H, $J_{2,3}$ = 3.7 Hz, H-3), 4.30 (dd, 1H, H-5′a), 3.79 (dd, 1H, H-5′b), 3.01 (dt, 1H, $J_{1',2}$ = 11.3 Hz, H-2), 1.55 (s, 3H, Me-4). Compound **12b**: ^{1}H NMR δ: 6.62 (dd, 1H, $J_{5,6}$ = 5.4 Hz, $J_{1,6}$ = 1.6 Hz, H-6), 6.27 (d, 1H, H-5), 5.50–5.00 (m, 3H, H-2′,3′,4′), 4.85 (dd, 1H, $J_{1,2}$ = 4.0 Hz, H-1), 4.73 (dd, 1H, $J_{1',2'}$ = 1.6 Hz, H-1′), 4.33 (d, 1H, $J_{2,3}$ = 4.0 Hz, H-3), 4.30 (dd, 1H, H-5′a), 3.79 (dd, 1H, H-5′b), 3.36 (dt, 1H, $J_{1',2}$ = 11.3 Hz, H-2), 1.54 (s, 3H, Me-4).

4.4. 3,4,5,6,7-Penta-*O*-acetyl-1,2-dideoxy-(2*S*)-(5′-methyl-2′-furyl)-1-nitro-D-*manno*-heptitol 17 and 3,4,5,6,7-penta-*O*-acetyl-1,2-dideoxy-(2*R*)-(5′-methyl-2′-furyl)-1-nitro-D-*manno*-heptitol 18

Method A. To a solution of a mixture of **9a**–**12a** (0.77 g, 1.50 mmol) in CH_2Cl_2 (2 mL) was added silica gel (3.1 g). After 5 h at room temperature, the solvent was evaporated, the residue was extracted with MeOH (10 mL), and then filtered and washed on a filter with the same solvent. Evaporation of the filtrate afforded an oil that consisted of a 1.0:1.65 mixture of **17** and **18** (0.62 g, 80%). *Method B*. A solution of a mixture of **9a**–**12a** (0.50 g, 0.97 mmol) in $CHCl_3$ (2.5 mL) was treated with trifluoroacetic acid (0.1 mL). After 50 min at 50 °C, the reaction mixture was washed with 5% $NaHCO_3$ (3 × 5 mL), dried over $MgSO_4$, and the solvent was evaporated, yielding 0.48 g (95%) of an oily 1.0:1.7 mixture of **17** and **18**. Flash column chromatography (AcOEt/hexane, 1:1) afforded pure samples of these two products (**17**, 0.09 g, 22%; **18**, 0.16 g, 38%). Compound **17**: Oil; $[\alpha]_D^{25} = +5.1$ (*c* 0.28, $CHCl_3$). IR (NaCl): ν_{max} 3020 (aromatic C–H), 2970, 2915 (C–H), 1742 (C=O), 1556, 1370 (NO_2), 1216, 1036 (C–O–C) cm^{-1}. ^{1}H NMR δ: 6.19 (d, 1H, $J_{3',4'}$ = 3.1 Hz, H-3′), 5.91 (dd, 1H, $J_{4',Me}$ = 1.0 Hz, H-4′), 5.36 (m, 2H, H-4,5), 5.10 (dd, 1H, $J_{2,3}$ = 1.7 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 4.98 (ddd, 1H, H-6), 4.74 (dd, 1H, $J_{1a,1b}$ = 13.8 Hz, $J_{1a,2}$ = 7.1 Hz, H-1a), 4.65 (dd, 1H, $J_{1b,2}$ = 8.0 Hz, H-1b), 4.17 (dd, 1H, $J_{6,7a}$ = 2.9 Hz, H-7a), 4.02 (dd, 1H, $J_{6,7b}$ = 4.8 Hz, $J_{7a,7b}$ = 12.5 Hz, H-7b), 3.81 (bt, 1H, H-2), 2.25 (s, 3H, Me-5′), 2.11 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.01 (s, 3H, OAc). ^{13}C NMR δ: 170.5, 170.4, 170.0, 169.9, 169.7 (O–*C*O–CH$_3$), 152.7 (C-2′), 145.4 (C-5′), 110.3 (C-4′), 106.5 (C-3′), 75.0 (C-1), 68.7, 68.3, 67.9, 67.4 (C-3,4,5,6), 61.7 (C-7), 38.7 (C-2), 20.9, 20.8, 20.7, 20.6 (O–CO–*C*H$_3$), 13.5 (Me-5′). FAB MS *m*/*z* (rel. int.): 538 (M+Na, 8), 457 (M−C_2H_2O–O, 10), 456 (M−OAc, 41), 409 (M−OAc–NO_2H, 17), 263 (12), 251 (12), 233 (15), 231 (73), 203 (16), 199 (14), 191 (20), 188 (M+H-4HOAc–NO_2–C_2H_2O, 10), 187 (M−4HOAc–NO_2–C_2H_2O, 25), 175 (13), 139 (21), 137 (100), 132 (28), 109 (38), 108 (M−$C_{15}H_{21}O_{10}$–NO_2, 36), 107 (M−$C_{15}H_{21}O_{10}$–NO_2H, 17). HRMS (FAB) calcd for $C_{22}H_{29}NO_{13}$+Na: 538.1536. Found 538.1549. Compound **18**: Oil; $[\alpha]_D^{25} = +40.4$ (*c* 0.52, $CHCl_3$). IR (NaCl): ν_{max} 2971, 2919 (C–H), 1749 (C=O), 1559, 1372 (NO_2), 1217, 1046 (C–O–C) cm^{-1}. ^{1}H NMR δ: 6.13 (d, 1H, $J_{3',4'}$ = 3.1 Hz, H-3′), 5.89 (d, 1H, $J_{4',Me}$ = 0.9 H, H-4′), 5.46 (dd, 1H, $J_{5,6}$ = 7.1 Hz, $J_{4,5}$ = 1.9 Hz, H-5), 5.43 (t, 1H, $J_{2,3}$ = 6.9 Hz, H-3), 5.15 (dd, 1H, $J_{3,4}$ = 7.3 Hz, H-4), 5.03 (ddd, 1H, H-6), 4.70 (dd, 1H, $J_{1a,1b}$ = 13.2 Hz, $J_{1a,2}$ = 5.5 Hz, H-1a), 4.62 (dd, 1H, $J_{1b,2}$ = 8.9 Hz, H-1b), 4.18 (dd, 1H, $J_{6,7a}$ = 2.6 Hz, $J_{7a,7b}$ = 12.5 Hz, H-7a), 4.04 (dd, 1H, $J_{6,7b}$ = 5.1 Hz, H-7b), 3.96 (ddd, 1H, H-2), 2.26 (s, 3H, Me-5′), 2.10 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.00 (s, 3H, OAc). ^{13}C NMR δ: 170.5, 170.1, 169.8, 169.7, 169.4 (O–*C*O–CH$_3$), 152.8 (C-2′), 146.6 (C-5′), 109.4 (C-4′), 106.4 (C-3′), 74.5 (C-1), 69.9, 68.3, 67.8, 66.8 (C-3,4,5,6), 61.7 (C-7), 38.3 (C-2), 20.7, 20.6, 20.5 (O–CO–*C*H$_3$), 13.4 (Me-5′). CI MS *m*/*z* (rel. int.): 516 (M+H, 2), 498 (M−OH, 13), 468 (M−NO_2H, 11), 457 (M−C_2H_2O–O, 35), 456 (M−OAc, 100), 410 (M−C_2H_2O–O–NO_2H, 11), 409 (M−OAc–NO_2H, 47), 408 (M−NO_2H–HOAc, 9), 391 (15), 307 (M−2HOAc–NO_2–C_2H_2O, 11), 247 (20), 246 (20), 229 (14), 209 (12), 295 (13), 188 (M+H–4HOAc–NO_2–C_2H_2O, 16), 187 (M−4HOAc–NO_2–C_2H_2O, 49), 167 (11), 149 (M−$C_{15}H_{21}O_{10}$–CH_3, 34), 139 (12), 115 (15), 108 (M−$C_{15}H_{21}O_{10}$–NO_2, 40), 95 (13). HRMS (CI) calcd for $C_{22}H_{29}NO_{13}$+H: 516.1717. Found 516.1717.

4.5. 3,4,5,6,7-Penta-*O*-acetyl-1,2-dideoxy-(2*S*)-(5′-methyl-2′-furyl)-1-nitro-D-*galacto*-heptitol 19, 3,4,5,6,7-penta-*O*-acetyl-1,2-dideoxy-(2*R*)-(5′-methyl-2′-furyl)-1-nitro-D-*galacto*-heptitol 20 and (2*E*)-2-[(2′*E*)-2′-penten-1′,4′-dione-1′-yl]-4,5,6,7-tetra-*O*-acetyl-D-*lyxo*-tetritol-2-heptenose oxime 21

Method A. To a solution of a mixture of **9b**–**12b** (0.21 g, 0.41 mmol) in CH_2Cl_2 (2 mL) was added silica gel (1.27 g). After 5 h at room temperature, the solvent was evaporated, and the residue was extracted with MeOH (5 mL) after which it was filtered and washed on the filter with the same solvent. Evaporation of the filtrate afforded an oil that consisted of a 1.2:1.0 mixture of **19** and **20** (0.16 g, 75%). *Method B*. A solution of a mixture of **9b**–**12b** (0.50 g, 0.97 mmol) in $CHCl_3$ (2.5 mL) was treated with trifluoroacetic acid (0.1 mL). After 50 min at 50 °C, the reaction mixture was washed with 5% $NaHCO_3$ (3 × 5 mL), dried over $MgSO_4$, and the solvent was evaporated, yielding 0.48 g (95%) of an oil that consisted of a 1.2:1.0 mixture of **19** and **20**. A portion of the product was subjected to preparative thin layer

chromatography (Et_2O/petroleum ether, 1:1; seven elutions), thus affording pure samples of **19** (0.025 g) and **20** (0.011 g); furthermore, from one yellow-colored band with lower R_f value was isolated an analytical sample of **21**. Compound **19**: Oil; $[\alpha]_D^{25} = -18.5$ (*c* 0.41, $CHCl_3$). IR (NaCl): ν_{max} 3020 (aromatic C–H), 2970, 2917 (C–H), 1748 (C=O), 1556, 1370 (NO_2), 1213, 1030 (C–O–C) cm^{-1}. ^1H NMR δ: 6.14 (br d, 1H, $J_{3',4'}$ = 3.1 Hz, H-3′) 5.92 (br d, 1H, $J_{4',Me}$ = 0.9 Hz, H-4′), 5.41 (dd, 1H, $J_{2,3}$ = 9.9 Hz, $J_{3,4}$ = 1.6 Hz, H-3), 5.23 (dd, 1H, $J_{4,5}$ = 9.6 Hz, $J_{5,6}$ = 2.3 Hz, H-5), 5.16 (dd, 1H, H-4), 5.14 (m, 1H, H-6), 4.51 (d, 2H, $J_{1,2}$ = 7.1 Hz, H-1a,1b), 4.23 (dd, 1H, $J_{6,7a}$ = 4.9 Hz, $J_{7a,7b}$ = 11.7 Hz, H-7a), 3.85 (dt, 1H, H-2), 3.79 (dd, 1H, $J_{6,7b}$ = 7.0 Hz, H-7b), 2.27 (s, 3H, Me-5′), 2.15 (s, 3H, OAc), 2.12 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.02 (s, 3H, OAc), 2.00 (s, 3H, OAc). ^{13}C NMR δ: 170.8, 170.4, 170.2, 169.8, 169.6 (O–*C*O–CH_3), 153.0 (C-2′), 145.8 (C-5′), 110.4 (C-4′), 106.5 (C-3′), 75.5 (C-1), 69.7, 67.9, 67.7 (C-3,4,5,6), 62.0 (C-7), 38.9 (C-2), 20.6 (O–CO–*C*H_3), 13.5 (Me-5′). CI MS *m/z* (rel. int.): 516 (M+H, 2), 498 (M−OH, 13), 468 (M−NO_2H, 11), 457 (M−C_2H_2O–O, 39), 456 (M−OAc, 100), 410 (M−C_2H_2O–O–NO_2H, 15), 409 (M−OAc–NO_2H, 56), 408 (M−NO_2H–AcOH, 14), 307 (M−2HOAc–NO_2–C_2H_2O, 13), 247 (20), 246 (18), 188 (M+H–4HOAc–NO_2–C_2H_2O, 10), 187 (M−4HOAc–NO_2–C_2H_2O, 36), 149 (M−$C_{15}H_{21}O_{10}$–CH_3, 13), 108 (M−$C_{15}H_{21}O_{10}$–NO_2, 37), 107 (M−$C_{15}H_{21}O_{10}$–NO_2H, 11), 95 (10). HRMS (CI) calcd for $C_{22}H_{29}NO_{13}$+H: 516.1717. Found 516.1727. Compound **20**: Oil; $[\alpha]_D^{25} = +10.2$ (*c* 0.43, $CHCl_3$). IR (NaCl): ν_{max} 3021 (aromatic C–H), 2969, 2920 (C–H), 1747 (C=O), 1558, 1372 (NO_2), 1216, 1034 (C–O–C) cm^{-1}. ^1H NMR δ: 6.06 (br d, 1H, $J_{3',4'}$ = 3.2 Hz, H-3′) 5.87 (m 1H, $J_{4',Me}$ = 0.4 Hz, H-4′), 5.42 (dd, 1H, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 3.0 Hz, H-3), 5.31 (m, 2H, H-4,5), 5.25 (m, 1H, H-6), 4.78 (dd, 1H, $J_{1a,1b}$ = 13.6 Hz, $J_{1a,2}$ = 6.0 Hz, H-1a), 4.69 (dd, 1H, $J_{1b,2}$ = 8.8 Hz, H-1b), 4.28 (dd, 1H, $J_{6,7a}$ = 4.8 Hz, $J_{7a,7b}$ = 11.6 Hz, H-7a), 3.82 (dd, 1H, $J_{6,7b}$ = 7.6 Hz, H-7b), 3.80 (ddd, 1H, H-2), 2.25 (s, 3H, Me-5′), 2.12 (s, 3H, OAc), 2.11 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.01 (s, 3H, OAc). ^{13}C NMR δ: 170.4, 170.3, 170.2, 169.9, 169.8 (O–*C*O–CH_3), 152.6 (C-2′), 146.0 (C-5′), 110.1 (C-4′), 106.3 (C-3′), 74.8 (C-1), 68.4, 68.3, 67.9, 67.5 (C-3,4,5,6), 62.1 (C-7), 39.3 (C-2), 20.8, 20.7, 20.6, 20.4 (O–CO–*C*H_3), 13.4 (Me-5′). FAB MS *m/z* (rel. int.): 538 (M+Na, 88), 456 (M−OAc, 58), 409 (M−OAc–NO_2H, 25), 188 (M+H–4HOAc–NO_2–C_2H_2O, 23), 187 (M−4HOAc–NO_2–C_2H_2O, 60), 154 (M−$C_{15}H_{21}O_{10}$, 19), 149 (M−$C_{15}H_{21}O_{10}$–CH_3, 23), 109 (M+H–$C_{15}H_{21}O_{10}$–NO_2, 28), 108 (M−$C_{15}H_{21}O_{10}$–NO_2, 100), 107 (M−$C_{15}H_{21}O_{10}$–NO_2H, 26), 95 (42), 73 (24). HRMS (FAB) calcd for $C_{22}H_{29}NO_{13}$+Na: 538.1536. Found 538.1570. Compound **21**: Oil; $[\alpha]_D^{25} = +17.5$ (*c* 0.40, $CHCl_3$). IR (NaCl): ν_{max} 3500–3300 (O–H), 3019 (=C–H), 2972, 2919 (C–H), 1749 (C=O), 1215, 1031 (C–O–C) cm^{-1}. ^1H NMR δ: 8.24 (s, 1H, H-1*syn*), 8.20 (s, 1H, H-1*anti*), 7.45 (d,1H, $J_{2',3'}$ = 16.0 Hz, H-2′*syn*), 7.00 (d, 1H, H-3′*syn*), 6.65 (d,1H, $J_{2',3'}$ = 12.9 Hz, H-2′*anti*), 6.43 (d, 1H, H-3′*anti*), 6.03 (d, 1H, $J_{3,4}$ = 2.8 Hz, H-3*syn*), 5.96 (d, 1H, $J_{3,4}$ = 3.3 Hz, H-3*anti*), 5.46 (dd, 1H, $J_{4,5}$ = 9.6 Hz, $J_{5,6}$ = 2.0 Hz, H-5), 5.39 (dd, 1H, H-4), 5.30 (m, 1H, H-6), 4.26 (dd, 1H, $J_{6,7a}$ = 5.2 Hz, $J_{7a,7b}$ = 11.6 Hz, H-7a), 3.85 (dd, 1H, $J_{6,7b}$ = 7.4 Hz, H-7b), 2.41 (s, 3H, Me-5′*syn*), 2.34 (s, 3H, Me-5′*anti*), 2.09 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.04 (s, 3H, OAc). ^{13}C NMR δ: 200.5, 200.4 (C-1′,4′), 170.4, 170.2, 169.7, 169.0 (O–*C*O–CH_3), 162.0 (C-1), 149.6 (C-3′), 135.6 (C-2′), 117.1 (C-3), 114.2 (C-2), 69.2, 67.9, 67.5 (C-4,5,6), 61.9 (C-7), 30.2 (C-5′), 20.8, 20.7, 20.6, 20.5 (O–CO–*C*H_3). CI MS *m/z* (rel. int.): 456 (M+H, 6), 439 (M+H−OH, 17), 438 (M−OH, 75), 396 (M−OAc, 29), 378 (M−OH–HOAc, 13), 354 (M−OAc–C_2H_2O, 5), 336 (M−OAc–AcOH, 11), 276 (M−OAc–2HOAc, 13), 234 (M−OAc–C_2H_2O–2HOAc, 13), 216 (M−OAc–3HOAc, 16), 187 (20), 166 (M−$C_{12}H_{17}O_8$, 15), 115 (21), 82 (100). HRMS (CI) calcd for $C_{20}H_{25}NO_{11}$+H: 456.1505. Found 456.1512.

4.6. (2*S*,3*S*)-1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-(4-methyl-3-*endo*-nitro-7-oxabicyclo[2.2.1]heptan-2-*exo*-yl)-D-*galacto*-pentitol (22) and (2*R*,3*R*)-1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-(4-methyl-3-*exo*-nitro-7-oxabicyclo[2.2.1]heptan-2-*endo*-yl)-D-*galacto*-pentitol 23

To a solution of a mixture of **9b**–**12b** (0.45 g, 0.87 mmol) in AcOEt (1.5 mL) was added 10% Pd–C catalyst (0.02 g), and the mixture was hydrogenated for 92 h at room temperature with 65 psig pressure. Next, filtration on Celite® and evaporation of the solvent, yielded an oily residue (0.39 g, 86%), that consisted of a mixture of the expected hydrogenated derivatives from adducts in the same ratio as the starting material. Flash column chromatography of the residue afforded pure samples of the more-mobile product **22** (0.07 g, 15%) and the less-mobile product **23** (0.09 g, 20%), together with a small quantity (0.01 g, 2%) of the hydrogenated starting nitroalkene **1b**. Compound **22**: Oil; $[\alpha]_D^{25} = +94.1$ (*c* 0.50, $CHCl_3$). IR (NaCl): ν_{max} 2975 (C–H), 1746 (C=O), 1548, 1371 (NO_2), 1218, 1028 (C–O) cm^{-1}. ^1H NMR δ: 5.36 (dd, 1H, $J_{1',2'}$ = 1.2 Hz, $J_{2',3'}$ = 10.0 Hz, H-2′), 5.26 (m, 1H, H-4′), 5.24 (dd, 1H, $J_{3',4'}$ = 1.6 Hz, H-3′), 5.20 (dd, 1H, $J_{1',2}$ = 9.6 Hz, H-1′), 4.55 (d, 1H, $J_{1,6exo}$ = 6.0 Hz, H-1), 4.44 (br d, 1H, $J_{2,3}$ = 4.4 Hz, H-3), 4.29 (dd, 1H, $J_{4',5'a}$ = 4.4 Hz, $J_{5'a,5'b}$ = 12.0 Hz, H-5′a), 3.80 (dd, 1H, $J_{4',5'b}$ = 7.6 Hz, H-5′b), 2.70 (dd, 1H, H-2), 2.12 (s, 3H, OAc), 2.11 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.98 (m, 1H, $J_{6endo,6exo}$ = 12.4 Hz, $J_{5endo,6exo}$ = 4.4 Hz, H-6*exo*), 1.79 (ddd, 1H, $J_{5endo,5exo}$ = 12.8 Hz, $J_{5endo,6endo}$ = 9.6 Hz, H-5*endo*), 1.64 (m, 1H, $J_{5exo,6endo}$ = 4.8 Hz, H-6*endo*), 1.63 (s, 3H, Me-4), 1.47 (m, 1H, $J_{5exo,6exo}$ = 12.0 Hz, $J_{3,5exo}$ = 1.6 Hz, H-5*exo*). ^{13}C NMR δ: 171.0, 170.4, 170.3, 170.2, 169.9 (O–*C*O–CH_3), 92.7 (C-3), 86.9 (C-4), 79.5 (C-1), 69.8, 68.4, 67.7, 67.5 (C-1′,2′,3′,4′), 62.3 (C-5′), 50.8 (C-2), 30.6, 29.9 (C-5,6) 20.7, 20.6, 20.5 (O–CO–*C*H_3), 19.5 (Me-4). CI MS *m/z* (rel. int.): 518 (M+H, 17), 501 (M−O, 23), 500 (M−OH, 67), 460 (M+H−C_2H_2O–O, 90), 458 (M−OAc, 100), 440 (M−OAc–H_2O, 30), 416 (M−OAc–C_2H_2O, 31), 398 (M−OAc–HOAc, 42), 309 (26), 293 (49), 251 (37), 233 (75), 191 (72), 189 (39), 173 (53). HRMS (CI): *m/z* calcd for $C_{22}H_{31}NO_{13}$+H: 518.1874. Found 518.1888. Compound **23**: Oil; $[\alpha]_D^{25} = -15.6$ (*c* 0.50, $CHCl_3$). IR (NaCl): ν_{max} 2963 (C–H), 1748 (C=O), 1555, 1370 (NO_2), 1214, 1049 (C–O) cm^{-1}. ^1H NMR δ: 5.27 (dd, 1H, $J_{1',2'}$ = 2.0 Hz, $J_{2',3'}$ = 9.6 Hz, H-2′), 5.16 (m, 2H, H-1′,3′), 5.10 (m, 1H, H-4′), 4.50 (t, 1H, $J_{1,2} = J_{1,6exo}$ = 5.6 Hz, H-1), 4.39 (d, 1H, $J_{2,3}$ = 5.6 Hz, H-3), 4.28 (dd, 1H, $J_{4',5'a}$ = 5.2 Hz, $J_{5'a,5'b}$ = 12.0 Hz, H-5′a), 3.78 (dd, 1H, $J_{4',5'b}$ = 7.2 Hz, H-5′b), 3.39 (dt, 1H, $J_{1',2}$ = 10.4 Hz, H-2), 2.13 (s, 3H, OAc), 2.12 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.02 (s, 3H, OAc), 2.01 (m, 1H, $J_{5endo,6endo}$ = 8.8 Hz, H-5*endo*), 1.79 (m, 1H, $J_{6endo,6exo}$ = 12.4 Hz, $J_{5exo,6exo}$ = 12.0 Hz, $J_{5endo,6exo}$ = 4.4 Hz, $J_{2,6exo}$ = 1.2 Hz, H-6*exo*), 1.70 (td, 1H, $J_{5exo,5endo}$ = 12.0 Hz, $J_{5exo,6endo}$ = 3.2 Hz, H-5*exo*), 1.60 (m, 1H, H-6*endo*), 1.41 (m, 3H, Me-4). ^{13}C NMR δ: 170.5, 170.4, 170.2, 169.9, 169.8 (O–*C*O–CH_3), 92.8 (C-3), 87.8 (C-4), 77.7 (C-1), 68.9, 68.2, 67.9, 67.6 (C-1′,2′,3′,4′), 62.1 (C-5′), 49.3 (C-2), 34.6, 25.9 (C-5,6) 20.7, 20.6, 20.3 (O–CO–*C*H_3), 17.1 (Me-4). CI MS *m/z* (rel. int.): 518 (M+H, 60), 501 (M−O, 40), 500 (M−OH, 86), 460 (M+H−C_2H_2O–O, 37), 459 (M−C_2H_2O–O, 89), 458 (M−OAc, 100), 440 (M−OAc–H_2O, 41), 416 (M−OAc–C_2H_2O, 37), 398 (M−OAc–HOAc, 63), 376 (31), 293 (48), 233 (55), 191 (40), 189 (37), 173 (42). HRMS (CI): *m/z* calcd for $C_{22}H_{31}NO_{13}$+H: 518.1874. Found 518.1867.

4.7. (2*R*,3*R*)-1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-(5,6-*exo*-epoxy-3-*endo*-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl)-D-*galacto*-pentitol 24b

To a stirred solution of **5b**[3] (0.12 g, 0.24 mmol) in CH_2Cl_2 (1 mL) were added $NaHCO_3$ (0.10 g, 1.19 mmol) and a solution of *m*-chloroperoxybenzoic acid (0.15 g, 0.47 mmol) in CH_2Cl_2 (7 mL). After stirring for 7 h at room temperature, the reaction mixture was

washed with aqueous 10% $Na_2S_2O_3$, aqueous 10% $NaHCO_3$, water, and then dried ($MgSO_4$). Evaporation of the solvent yielded the title compound as an oil that was purified by PTLC with 1:1 AcOEt–hexane as eluent. Yield: 0.1 g (79%); $[\alpha]_D^{25} = +56.4$ (*c* 0.22, $CHCl_3$). IR (NaCl): ν_{max} 1745 (C=O), 1551, 1371 (NO_2), 1216, 1030 (C–O–C) cm^{-1}. ^1H NMR δ: 5.33 (m, 1H, H-4′), 5.28 (s, 2H, H-2′,3′), 5.23 (br d, 1H, $J_{1',2}$ = 10 Hz, $J_{1',2'}$ <1.0 Hz, H-1′), 4.90 (dd, 1H, $J_{2,3}$ = 4.0 Hz, $J_{3,4}$ = 5.2 Hz, H-3), 4.85 (d, 1H, H-4), 4.67 (s, 1H, H-1), 4.30 (dd, 1H, $J_{4',5'a}$ = 4.8 Hz, $J_{5'a,5'b}$ = 11.6 Hz, H-5′a), 3.81 (dd, 1H, $J_{4',5'b}$ = 7.6 Hz, H-5′b), 3.54 (d, 1H, $J_{5,6}$ = 2.8 Hz, H-6), 3.42 (d, 1H, H-5), 2.49 (dd, 1H, H-2), 2.16 (s, 3H, OAc), 2.12 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.03 (s, 3H, OAc). ^{13}C NMR δ: 171.2, 170.8, 170.4, 170.2, 169.9 (O–*C*O–CH_3), 87.8 (C-3), 77.4 (C-4), 74.7 (C-1), 69.1, 68.5, 67.7, 67.4 (C-1′,2′,3′,4′), 62.5 (C-5′), 48.7, 47.4, 47.1 (C-2,5,6), 20.6 (O–CO–*C*H_3). CI MS *m/z* (rel. int.): 518 (M+H, 88), 500 (M−OH, 17), 458 (M−OAc, 100), 457 (74), 442 (M−OAc–O, 21), 429 (19), 416 (M−OAc–C_2H_2O, 23), 374 (M−OAc–$2C_2H_2O$, 66), 369 (31), 267 (26), 207 (25). HRMS (CI): *m/z* calcd for $C_{21}H_{27}NO_{14}$+H^+: 518.1510. Found 518.1498.

4.8. (2*R*,3*R*)-1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-(5,6-*exo*-epoxy-3-*exo*-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl)-D-*galacto*-pentitol 25b

Following the same procedure described in 4.7, a mixture of the adducts[3] **5b**, **6b**, and **8b** (0.35 g, 0.70 mmol), led to an oil from which the title compound was isolated by PTLC with 2:1 Et_2O/petroleum ether as eluent (0.023 g, 7%); IR (NaCl): ν_{max} 1747 (C=O), 1559, 1371 (NO_2), 1218, 1032 (C–O–C) cm^{-1}. ^1H NMR δ: 5.34 (dd, 1H, $J_{1',2'}$ = 2.4 Hz, $J_{2',3'}$ = 10.0 Hz, H-2′), 5.32 (dd, 1H, H-1′), 5.26 (dd, 1H, $J_{3',4'}$ = 2.0 Hz, H-3′), 5.16 (m, 1H, H-4′), 4.93 (s, 1H, H-4), 4.45 (d, 1H, $J_{2,3}$ = 4.8 Hz, H-3), 4.42 (s, 1H, $J_{1,2}$ = 4.4 Hz, H-1), 4.28 (dd, 1H, $J_{4',5'a}$ = 4.8 Hz, $J_{5'a,5'b}$ = 11.6 Hz, H-5′a), 3.87 (d, 1H, $J_{5,6}$ = 3.6 Hz, H-6), 3.79 (dd, 1H, $J_{4',5'b}$ = 7.2 Hz, H-5′b), 3.50 (d, 1H, H-5), 3.40 (ddd, 1H, $J_{1',2}$ = 8.4 Hz, H-2), 2.17 (s, 3H, OAc), 2.12 (s, 3H, OAc), 2.11 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.02 (s, 3H, OAc). ^{13}C NMR δ: 170.4, 170.3, 169.8 (O–*C*O–CH_3), 85.7 (C-3), 79.8 (C-4), 75.8 (C-1), 68.6, 67.6, 67.5, 67.4 (C-1′,2′,3′,4′), 62.0 (C-5′), 49.7, 48.7, 47.1 (C-2,5,6), 20.6 (O–CO–*C*H_3). FAB MS *m/z* (rel. int.): 518 (M+H, 1), 458 (M−OAc, 10), 416 (M−OAc–C_2H_2O, 1), 331 (4), 278 (7), 263 (11), 231 (55), 213 (3), 199 (8), 177 (6), 156 (10), 155 (16), 154 (100), 139 (11), 137 (76). HRMS (FAB): *m/z* calcd for $C_{21}H_{27}NO_{14}$+H^+: 518.1510. Found 518.1506.

4.9. (2*R*,3*R*)-1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-(5,6-*exo*-epoxy-3-*endo*-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl)-D-*manno*-pentitol 24a

Following the same procedure described in 4.7, a mixture of the adducts[3] **5a**–**7a** (0.17 g, 0.33 mmol), led to an oil from which the title compound was isolated by PTLC with 2:1 Et_2O/petroleum ether as eluent (0.017 g, 10%); $[\alpha]_D^{25} = +35.6$ (*c* 0.50, $CHCl_3$). IR (NaCl): ν_{max} 1747 (C=O), 1549, 1371 (NO_2), 1218, 1037 (C–O–C) cm^{-1}. ^1H NMR δ: 5.52 (dd, 1H, $J_{2',3'}$ = 2.0 Hz, $J_{3',4'}$ = 10.0 Hz, H-3′), 5.28 (dd, 1H, $J_{1',2'}$ = 9.6 Hz, H-2′), 5.16 (t, 1H, $J_{2,3} = J_{3,4}$ = 4.8 Hz, H-3), 5.14 (m, 1H, H-4′), 5.12 (dd, 1H, $J_{1',2}$ = 1.6 Hz, H-1′), 4.78 (d, 1H, H-4), 4.66 (s, 1H, H-1), 4.21 (dd, 1H, $J_{4',5'a}$ = 2.4 Hz, $J_{5'a,5'b}$ = 12.4 Hz, H-5′a), 4.07 (dd, 1H, $J_{4',5'b}$ = 4.8 Hz, H-5′b), 3.48 (d, 1H, $J_{5,6}$ = 3.6 Hz, H-6), 3.40 (d, 1H, H-5), 2.58 (dd, 1H, H-2), 2.16 (s, 3H, OAc), 2.12 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc). ^{13}C NMR δ: 170.9, 170.7, 170.5 169.7, 169.6 (O–*C*O–CH_3), 88.9 (C-3), 75.7 (C-4), 73.7 (C-1), 68.9, 68.8, 67.7, 66.9 (C-1′,2′,3′,4′), 61.7 (C-5′), 48.7, 47.3, 45.5 (C-2,5,6), 20.8, 20.7, 20.6, 20.5 (O–CO–*C*H_3). FAB MS *m/z* (rel. int.): 518 (M+H, 7), 458 (M−OAc, 14), 416 (M−OAc–C_2H_2O, 1), 374 (M−OAc–$2C_2H_2O$, 2), 341 (4), 281 (10), 267 (4), 264 (26), 231 (46), 221 (10), 218 (20), 155 (16), 154 (99), 147 (25), 139 (12), 137 (100), 135 (10). HRMS (FAB): *m/z* calcd for $C_{21}H_{27}NO_{14}$+H^+: 518.1510. Found 518.1509.

4.10. (2*S*,3*S*)-1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-(5,6-*exo*-epoxy-3-*endo*-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl)-D-*manno*-pentitol 26a

Following the same procedure described in 4.7, compound **6a**[3] (0.1 g, 0.2 mmol) led to **26a** as an oil (0.08 g, 78%); $[\alpha]_D^{25} = -31.1$ (*c* 0.52, $CHCl_3$). IR (NaCl): ν_{max} 1736 (C=O), 1545, 1369 (NO_2), 1205, 1035 (C–O–C) cm^{-1}. ^1H NMR δ: 5.40 (dd, 1H, $J_{2',3'}$ = 2.4 Hz, $J_{3',4'}$ = 8.8 Hz, H-3′), 5.36 (dd, 1H, $J_{1',2'}$ = 8.8 Hz, $J_{1',2}$ = 2.0 Hz, H-1′), 5.29 (dd, 1H, H-2′), 5.10 (dd, 1H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 5.2 Hz, H-3), 5.00 (m, 1H, H-4′), 4.83 (d, 1H, H-4), 4.65 (s, 1H, H-1), 4.21 (dd, 1H, $J_{4',5'a}$ = 2.8 Hz, $J_{5'a,5'b}$ = 12.8 Hz, H-5′a), 4.04 (dd, 1H, $J_{4',5'b}$ = 5.2 Hz, H-5′b), 3.51 (d, 1H, $J_{5,6}$ = 3.4 Hz, H-6), 3.41 (d, 1H, H-5), 2.82 (t, 1H, H-2), 2.10 (s, 6H, 2 × OAc), 2.06 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc). ^{13}C NMR δ: 170.5, 170.1, 169.9, 169.7 (O–*C*O–CH_3), 86.3 (C-3), 78.9 (C-4), 74.3 (C-1), 68.6, 68.2, 67.9, 67.2 (C-1′,2′,3′,4′), 61.5 (C-5′), 48.5, 47.3, 45.1 (C-2,5,6), 20.8, 20.6, 20.5, 20.4 (O–CO–*C*H_3). FAB MS *m/z* (rel. int.): 518 (M+H, 3), 458 (M−OAc, 6), 401 (10), 355 (M−2HOAc–C_2H_2O, 10), 341 (15), 326 (19), 324 (15), 282 (11), 281 (38), 267 (21), 265 (11), 231 (27), 221 (35), 208 (10), 207 (49), 193 (12), 154 (59), 147 (100), 137 (95). HRMS (FAB): *m/z* calcd for $C_{21}H_{27}NO_{14}$+H^+: 518.1510. Found 518.1511.

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16. Processes were carried out in sealed teflon ampoules with 10.2 mL capacity. Depending on the solubility of the starting sugar nitroalkenes in CH_2Cl_2, they could be charged with 8 g of **1a**, and with 2 g of **1b**.
17. For a comparative discussion, Scheme 1 and Table 1 also reflect data from previously reported reactions between chiral nitroalkenes **1a** or **1b** with furan, and **1b** with 2,5-dimethylfuran.
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