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Formaldehyde Dimethylhydrazone: A New Neutral Reagent for Nucleophilic Hydroformylation and Hydrocyanation

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Abstract: The readily available title compound smoothly adds to nitroolefins without any need of base or catalysis, giving β-nitrodimethylhydrazones **3** in high yields. Michael adducts **3** have been successfully transformed into β-nitroaldehydes by ozonolysis and in β-nitronitriles in excellent yields by treatment with MMPP. Therefore, formaldehyde dimethylhydrazone behaves as a new neutral formyl anion and cyanide equivalent, introducing a functionalized carbon unit β to the nitro group of a nitroolefin. Good yields and high stereoselectivities were obtained in the addition of **1** to a nitroolefin group within sugar derivatives, and no epimerization was observed in the cleavage of the dimethylhydrazone group. Copyright © 1996 Elsevier Science Ltd

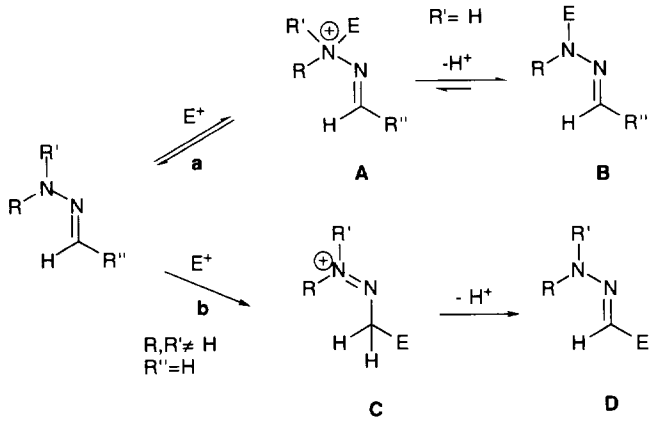
INTRODUCTION

The development of new or improved methods for one-carbon extension reactions has been and continues to be a major objective in organic chemistry, since they constitute one of the most important building blocks for the construction of molecular skeletons. Among the potentially most useful and versatile functional groups to be introduced is the formyl group, as carbonyl groups are commonly encountered reactive sites for carbon-carbon bond formation processes leading to extended carbon frameworks. Although the high-energy species formyl anion ($^-$CH=O) is known, its high reactivity imposes many limitations on its direct use in synthesis. Thus, much research has been done for the development of functional group equivalents which provide an umpolung of the normal pattern of reactivity of the carbonyl group, and specially reagents which act as equivalents of formyl anion.[1-3]

Important formyl anion equivalents are of the type X-$^-$CH-Y, X and Y being anion stabilizing auxiliary groups. Among the stabilized formyl anion equivalents where X and Y are heteroatoms, the most extended is the cyclic 2-lithio-1,3-dithiane,[4,5] generated by treatment of 1,3-dithiane with *n*-butyllithium. More recently, the use of 1-(carbazol-9-ylmethyl)benzotriazole[3] and 4-isopropyl-2-oxazolin-5-one[6] has been reported. Another class of formyl anion equivalents also proposed, X(Y:)C$^-$, requires a subsequent reduction step, as is the case of substituted imines,[7] 3-methylthio-1,4-diphenyl-*s*-triazolium iodide,[8] and different thiazole derivatives.[9] All these reagents for nucleophilic formylation react through their stabilized carbanions, usually generated *in situ* by deprotonation with alkyllithium reagents. On the other hand, 2-(trimethylsilyl)thiazole[1b] reacts with various carbon electrophiles without the need for any added activating species, but the aldehyde liberation in the resulting 2-substituted thiazoles employs a laborious multi-step process including *N*-methylation, reduction with $NaBH_4$, and mercury-assisted hydrolysis.

In general, these methods are subject to various limitations: the need of a strong base to generate the nucleophile, the incompatibility or lack of selectivity in their reactions with the appropriate electrophile, and the difficulty to eliminate X and Y to release the carbonyl function. As an alternative to the existing methods, which might avoid some of these problems, we wish to report here the use of formaldehyde dimethylhydrazone as a new convenient masked synthon of formyl anion.[10]

The versatility and usefulness of *N,N*-dialkylhydrazones as intermediates in organic synthesis have been shown in a number of reactions for carbon-carbon bond formation.[11,12] Hydrazones are ambident nucleophiles, which can react with electrophiles either at the amine nitrogen or at the azomethine carbon. The former is usually the most nucleophilic center (Scheme 1, equilibrium a), and the primary products of their reactions with electrophiles are of those of type **A**, in which a new nitrogen-carbon bond has been formed.



Scheme 1

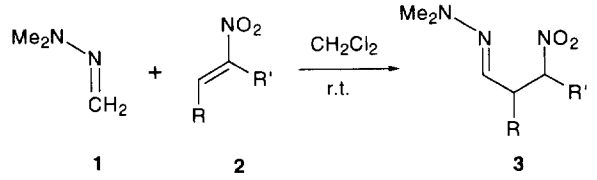
When at least one of the substituents of the amine nitrogen is a hydrogen, the loss of a proton in **A** would yield adducts of type **B**. This route is not feasible in the case of *N,N*-disubstituted hydrazones. This fact, together with the expected minimization of the steric hindrance around the azomethinic carbon in formaldehyde dialkylhydrazones, make it reasonable to suppose that in these compounds this second center might exhibit an enhanced nucleophilic character (Scheme 1, equilibrium b). Additionally, the energy associated to the formation of a new C-C bond in **C** will make of its formation an essentially irreversible process, which after the loss of a proton would yield the final adduct **D**. Surprisingly, in spite of the vast amount of accumulated information on the rich and varied chemistry of *N,N*-dialkylhydrazones, to the best of our knowledge the synthetic potential of these compounds in this context has been scarcely investigated.[13-15]

The new formylation protocol here reported is based on the use of formaldehyde dimethylhydrazone as nucleophile in Michael addition reactions, for which there is no precedent. As a first example of Michael acceptors we have studied nitroolefins, powerful electrophiles which, through different processes,[16] afford nitrocompounds of high synthetic potential because of their versatile functional group transformations.[17] We wish now to demonstrate the actual equivalence of formaldehyde dimethylhydrazone (FDMH, **1**) with the formyl anion through a sequence consisting of two efficient steps: a) Michael addition of **1** to nitroolefins to give β-nitrodimethylhydrazones and b) liberation of the carbonyl function by ozonolysis leading to β-

nitroaldehydes. Additionally, the high yielding oxidative deprotection with MMPP of the hydrazone moiety in the Michael adducts to give β-nitronitriles demonstrates the ability of FDMH to function also as a new equivalent of cyanide. Considering the rich chemistry of the cyano group,[18] this result gives additional worth to this reagent.

RESULTS AND DISCUSSION

The reaction of nitroolefins **2** with formaldehyde *N,N*-dimethylhydrazone (FDMH, **1**) in dichloromethane leads to the corresponding Michael adducts **3** (Scheme 2). Reaction conditions have been set



1 **2** **3**

Scheme 2

up for simple aliphatic and aromatic nitroolefins **2a-f**. The reaction proceeds at room temperature without any need of base or catalyst just by mixing the reagents, and β-nitrodimethylhydrazones **3** are formed in some cases almost quantitatively and can be isolated in excellent yields (Table 1). Comparing the reactivity of the

Table 1. β-Nitrodimethylhydrazones 3a-f.

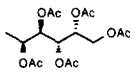
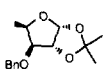
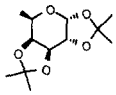
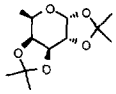
Entry	R	R'	Reaction time	Product, yield %[a]
a	Me	H	15m	**3a**, 90[b]
b	^{i}Pr	H	20h	**3b**, 92[b]
c	Ph	H	24h	**3c**, 75[c]
d	*p*-C$_6$H$_4$-Me	H	18h	**3d**, 70[c]
e	*p*-C$_6$H$_4$-OMe	H	4d	**3e**, 45[c]
f	Ph	Me	48h	**3f**, 80[c,d]

[a]Values referred to isolated total yield. [b]After bulb-to-bulb distillation. [c] After column chromatography. [d]As a mixture of *u* and *l* isomers (63/37).

ring-substituted arene nitroolefins **2d** and **2e** with that of the unsubstituted parent **2c**, it can be seen that the *p*-Me derivative reacted as rapidly as **2c**, with similar yield of **3c**. The *p*-OMe-substituted compound was more sluggish, requiring 4d for reaction and giving the lowest yield for **3d**; this can be explained considering that its *push-pull* character makes of it a poorer electrophile.

Taking into account the great number of synthetic approaches based on nitrosugars reported for the synthesis of branched-chain, extended chain, unsaturated and unusually functionalized carbohydrate compounds,[17] we have carried out the addition of FDMH to sugar nitroolefins. Results on the reactivity and stereoselectivity of **1** toward nitroolefins **2g-j** are collected in Table 2. The addition occurred smoothly under

Table 2. β-Nitrodimethylhydrazones 3g-j.

Entry	R	R'	Reaction time	Product, yield %[a]	Diastereo-isomeric ratio[b]	Yield of pure epimers at C-2 %
g		H	6h	**3g**, 95	78:22	(*R*)-**3g**, 71 (*S*)-**3g**, 20
h		H	3h	**3h**, 90	82:18	(*R*)-**3h**, 73 (*S*)-**3h**, 15
i		H	4h	**3i**, 92	75:25	(*R*)-**3i**, 59 (*S*)-**3i**, 16
j		Et	16h	**3j**, 84	91[c]:9	(*R*)-**3j**, 62[c] (*S*)-**3j**, 6

[a]Values referred to isolated total yield of the mixture of diastereoisomers. [b]Product ratios from integrated methine signals of *R* and *S* isomers in the crude reaction mixture. [c]As a mixture of epimers at C-3.

mild conditions to give the β-nitrodimethylhydrazones **3g-j** in very good yields. Additionally, the presence of an α-chiral center exerts an effective asymmetric control on the generation of the new stereogenic center, and nitrosugar derivatives **3g-h** are obtained with high levels of diastereofacial selectivity. The diastereomeric excesses were determined by ^{1}H-NMR spectroscopy on the crude 1,4-adducts, and in all cases both epimers could be separated by column chromatography. Interestingly, in the reported conjugate addition of 2-lithio-1,3-dithiane to a nitroolefin group within sugar derivatives the reaction proceeds to give the 1,4-addition products with poor yields and low stereoselectivity.[5b-d]

It is worth mentioning that a study of the solvent effect carried out for the reaction of **1** with **2g** showed that the stereoselectivities were not much affected by the change of polarity, being only significantly increased in the mixture MeOH-H_2O 1:1 (Table 3). On the other hand, higher reactivities were found for polar aprotic solvents, whereas in apolar aprotic or polar protic solvents the reaction was slower, and in some cases

Table 3. Influence of the Solvent in the Addition of 1 to Nitroolefin 2g.

Solvent	Conversion %[a] (Diastereoisomeric ratio)[a]		
	6h	4d	10d
MeOH-H_2O 1:1	< 20 (86:14)	50 (92:8)	50 (92:8)
^{i}PrOH	<10 (81:19)	25 (88:12)	64 (88:12)
MeCN	100 (75:25)		
$HCONMe_2$	100 (77:23)		
CH_2Cl_2	100 (78:22)		
THF	<10 (80:20)	88 (74:26)	100 (74:26)
PhMe	< 10 (76:24)	45 (73:27)	46 (73:27)

[a]Determined by integration of ^{1}H-NMR spectra of the reaction mixture.

the starting nitroolefin was largely recovered. These results can be explained considering a closed, chair-like transition state,[19] most probably favored by the electrostatic attractive interaction of the developing charges $N^{\delta+}/NO_2^{\delta-}$ (Figure 1). The negative influence of protic solvents is explained by the formation of hydrogen bonds, which would inhibit this intramolecular stabilization. Moreover, a rigid transition state would take account of the higher stereoselectivities observed in the addition of **1** to sugar nitroolefins, when compared to the same reactions using more hindered nucleophiles, such as 2-lithio-1,3-dithiane.[5] Assuming this model, for

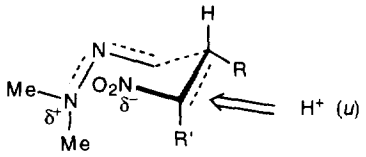
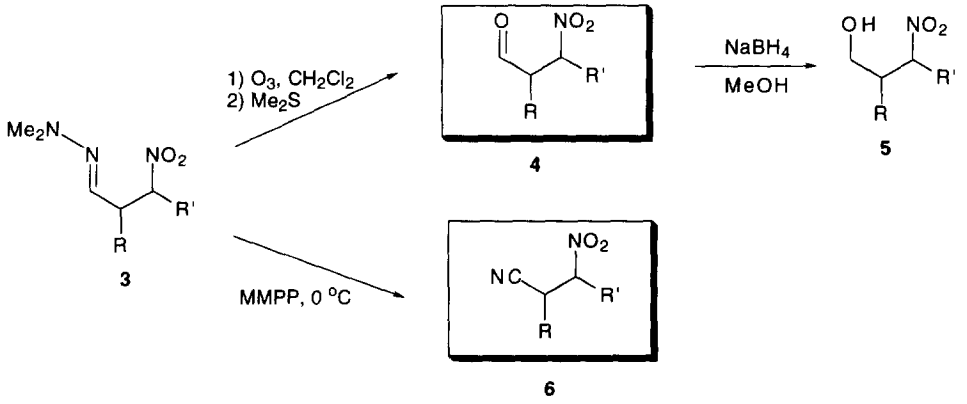


Figure 1

compound **3f**, in which two new chiral centers are created, the configuration of the major isomer (racemic) obtained has been tentatively assigned as *u*, considering the most probable *pseudo*-equatorial protonation (Figure 1, R'=Me).

β-Nitrodimethylhydrazones **3** are interesting polyfunctional molecules, which could be used as starting materials to synthesize more complex compounds through different selective and controlled transformations of their two differentially masked carbonyl groups. Our first interest was the aldehydic release in compounds **3** from the dimethylhydrazone moiety, for which a number of procedures are available.[20] It is evident that the methodology required here must be efficient and leave intact the chirality at the various centers. After several attempts, the best results for β-nitroaldehydes **4** were obtained by ozonolysis[12,21,22] (Scheme 3, Table 4).



Scheme 3

Although the purity of the isolated compounds **4** proved to be 95% or more by NMR analyses, in some cases the attempts of purification by column chromatography on silica gel led to partial decomposition. Further $NaBH_4$ reduction of **4** afforded β-nitroalcohols **5** in high overall yields. The analysis of the NMR

spectra showed that β-nitroaldehydes **4g-j** were diastereomerically pure, thus proving that no substantial racemization occurs at the chiral C-2 in the course of the aldehyde-releasing sequence.

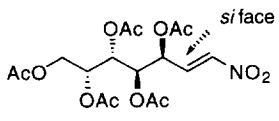
Table 4. Synthesis of β-Nitroaldehydes 4, β-Nitroalcohols 5, and β-Nitronitriles 6.

Compound **3**	Yield of **4** %	Yield of **5** %[a]	Yield of **6** %[a]
3b	**4b**, 82		
3c			**6c**, 90
(*R*)-**3g**	(*S*)-**4g**, 90[a]		(*R*)-**6g**, 90
(*S*)-**3g**	(*R*)-**4g**, 85[a]		(*S*)-**6g**, 92
(*R*)-**3h**	(*S*)-**4h**, 98[b]	(*R*)-**5h**, 78	(*R*)-**6h**, 92
(*S*)-**3h**	(*R*)-**4h**, 99[b]	(*S*)-**5h**, 68	(*S*)-**6h**, 93
(*R*)-**3i**	(*S*)-**4i**, 99[b]	(*R*)-**5i**, 76	(*R*)-**6i**, 87
(*S*)-**3i**	(*R*)-**4i**, 99[b]	(*S*)-**5i**, 70	(*S*)-**6i**, 89
(*R*)-**3j**	(*S*)-**4j**, 95[b]	(*R*)-**5j**, 88	
(*S*)-**3j**	(*R*)-**4j**, 99[b]	(*S*)-**5j**, 88	

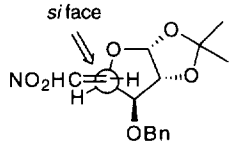
[a]Of isolated pure product. [b]Purity >95% estimated by ^{1}H-NMR.

Additionally, aldehyde dimethylhydrazones **3** have been converted into the corresponding nitriles **6** by our recently reported facile oxidative cleavage of aldehyde dimethylhydrazones with magnesium monoperoxyphtalate hexahydrate (MMPP) (Scheme 3).[23] Using this procedure, compounds **3** gave rise to the cyanoderivatives **6** after a simple work-up. The reaction is complete in an extremely short time and nitriles **6** are formed in almost quantitative yield (Table 4). Transformation of sugar hydrazone derivatives **3g-i** demonstrates the chemoselectivity of the process and interestingly compounds **6g-i** are isolated without racemization (NMR analysis).

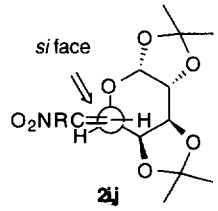
Concerning the stereochemical outcome of the addition of **1** to nitroolefins **2**, the configuration of the major isomers at the newly formed diastereogenic center in compounds **3g-j**, included in Table 2, has been assigned on the basis of several arguments. First, the addition of different nucleophiles to acyclic sugar derivatives containing a terminal nitro olefin group appears to be stereoselective, and the preponderant stereoisomers produced are those expected on the basis of Cram's rule.[17,24] The (*R*)-configuration assigned for the major isomer of **3g** is the one anticipated if the sugar nitroolefin **2g** in the conformation shown in Figure 2 was attacked by **1** at the less hindered *si* face.



2g



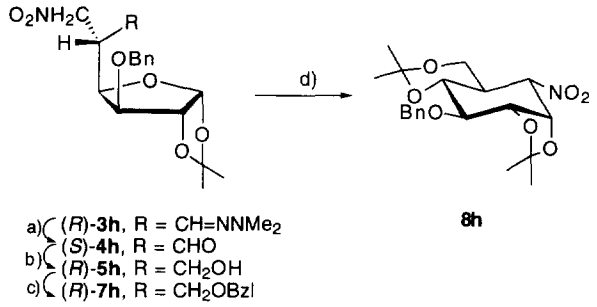
2h



2j

Figure 2

The stereochemistry of the major isomer of **3h** was confirmed to be (*R*) on the basis of a chemical correlation with the known 6-nitro-*pseudo*-α-D-glucopyranose **8h.**[25] This compound was prepared from (*R*)-**5h** by a sequence involving benzoylation, removal of the isopropylidene group, Henry reaction, deacylation, and isopropylidenation (Scheme 4). The conformation of **2h** shown in Figure 2, and the preferred



a) O_3, Me_2S. b) $NaBH_4$. c) BzlCl, Py. d) 80% aq. AcOH , 80 °C; KF/18-crown-6/DMF; 1% NaOMe-MeOH; 2,2-dimethoxypropane/*p*-TsOH/$CuSO_4$/acetone

Scheme 4

attack of **1** by its less hindered si *face* would account for this observed selectivity. Assuming a similar reaction pathway for the addition to **2i** and **2j** (Figure 2), the configuration of the major isomers of **3i** and **3j** has been tentatively assigned as (*R*).

CONCLUSION

In conclusion, through the sequence, a) high yielding Michael addition of **1** to nitroolefins and b) chemically efficient and racemization-free cleavage of the dimethylhydrazone group, FDMH appears to be a convenient alternative to other precursor for the formyl and cyano groups. FDMH, which is a neutral and stable reagent that can be easily and economically prepared, provides the additional advantage of being eliminated from the reaction mixture after completion simply by evaporation under reduced pressure, which notably simplifies the work-up of the reaction. In the carbohydrate field the procedure here described can be envisaged as a new and versatile approach to functionalized long branched-chain nitrosugars. A synthetic value of this method is evident when considering further applications by conversion of the carbonyl, nitro, and cyano group into other functionalities, such as hydroxy, aldehyde and amino. Thus, FDMH constitutes a new neutral reagent which, operating under very mild conditions, appears to be a highly efficient nucleophile, being compatible with a great range of functional groups. Recent investigations of our group show that FDMH also reacts with other electrophiles, such as α,β-unsaturated ketones[26] and α-alkoxyaldehydes,[27] indicating a broad scope for the new method.

EXPERIMENTAL

General Experimental Data.

Melting and boiling points were determinated with a Gallenkamp MFB-595 melting-points apparatus and are uncorrected. Elemental analyses were carried out at the Instituto Químico de Sarriá (Barcelona, Spain). Optical rotations were measured at room temperature with a Perkin-Elmer 241 MC polarimeter. ^1H and ^{13}C NMR spectra were obtained on Varian XL-200, on Bruker AMX 500, and on Bruker AMX 300 spectrometers in $CDCl_3$ with either TMS (0.00 ppm ^1H, 0.00 ppm ^{13}C) or $CDCl_3$ (7.26 ppm ^1H, 77.00 ppm ^{13}C) as an internal reference. E.i.-mass spectra were obtained at 70 eV, using a MS-80 RFA Kratos instrument, an ionizing current of 100 μA, an accelerating voltage of 4 KV, and a resolution of 1000 or 10000 (10% valley definition). Ozonolysis were performed with a Fischer 502 apparatus. The reactions were monitored by ^1H-NMR and TLC. (Kieselgel 60 F_{254}, Merck). Purifications of the products were carried out by column chromatography (Silica Gel 60, 0.063-0.200 nm, Merck) or by bulb-to-bulb distillation using a Büchi GKR-51 apparatus and boiling points referred to air bath temperatures. All experiments were carried out with freshly distilled and dried solvents.

Starting materials.

Formaldehyde dimethylhydrazone[13a] (**1**), 1-nitropropene[28] (**2a**), 3-methyl-1-nitro-1-butene[29] (**2b**), β-nitrostyrene[29] (**2c**), 2-nitro-1-(*p*-tolyl)ethylene[29] (**2d**), 1-(*p*-methoxyphenyl)-2-nitroethylene[29] (**2e**), 2-nitro-1-phenylpropene (**2f**)[30], 3,4,5,6,7-penta-*O*-acetyl-1,2-dideoxy-1-nitro-D-*galacto*-hept-1-enitol[31] (**2g**), 3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-nitro-α-D-*xylo*-hex-5-enofuranose[5b] (**2h**), and (*E*)-6,7-Dideoxy-1,2:3,4-di-*O*-isopropylidene-7-nitro-α-D-*galacto*-hept-6-enopyranose[32] (**2i**), were prepared according to literature procedures.

(E)-6,7,8,9-Tetradeoxy-1,2:3,4-di-O-isopropylidene-7-nitro-α-D-galacto-non-6-enopyranose (2j).

To a cooled (0 °C) solution of 7,8,9-trideoxy-1,2:3,4-di-*O*-isopropylidene-7-nitro-L-*threo*,D-*erythro*-α-D-*galacto*-nonealdo-1,5-pyranose[33] (3.0 g, 8.7 mmol) in $CHCl_3$ (30 mL) was added acetic anhydride (4.25 mL, 45.0 mmol) and pyridine (2.83 mL, 35 mmol). The mixture was stirred at room temperature until total consumption of the starting material (TLC, 8h), washed with water, and satd. $NaHCO_3$. The organic layer was separated, concentrated, and the resulting residue (3.48 g) was dissolved in dry benzene (110 mL). To this solution was added potassium carbonate (3.7 g) with stirring. The mixture was refluxed for 8 h, and then allowed to reach r.t. and filtered. The solvent was removed *in vacuo* and the residue was recrystallized from MeOH to afford **2j** (1.98 g ,70%); mp 109-110 °C; $[\alpha]_D^{22}$ -116.0° (*c* 1, CH_2Cl_2). ^1H-NMR (200 MHz, $CDCl_3$) δ 7.08 (d, 1 H, $J_{5,6}$ 7.8, H–6), 5.56 (d, 1 H, $J_{1,2}$ 5.0, H-1), 4.65 (dd, 1 H, $J_{3,4}$ 7.8, H-3), 4.53 (dd, 1 H, $J_{2,3}$ 2.6, H-2), 4.37 (dd, 1 H, H-5), 4.20 (dd, 1 H, $J_{4,5}$ 2.0, H-4), 2.68 (q, 2 H, $J_{8,9}$ 7.4, H-8), 1.55, 1.48, 1.35, 1.34 [each s, each 3H, 2 $C(CH_3)_2$], 1.16 (t, 3 H, H-9). ^{13}C-NMR (50 MHz, $CDCl_3$) δ 155.5 (C-7), 129.5 (C-6), 109.8, 108.7 [2 $C(CH_3)_2$], 96.3 (C-1), 72.6 (C-4), 70.5 (C-3), 69.9 (C-2), 64.4 (C-5), 25.9, 25.8, 24.6, 24.2 [2 $C(CH_3)_2$], 20.7 (C-8), 12.7 (C-9). Anal. Calcd for $C_{15}H_{23}NO_7$: C, 54.70; H, 7.04; N, 4.25. Found: C, 55.10; H, 7.20; N, 4.24.

β-Nitrodimethylhydrazones 3a-f; General procedure:

To a solution of the nitroolefin **2** (5 mmol) in dry CH_2Cl_2 (20 mL) was added formaldehyde dimethylhydrazone **1** (0.64 mL, 7.5 mmol). The mixture was kept at r.t. until the nitroolefin had completely reacted (TLC control). Evaporation of the solvent and excess of **1** and purification of the residue by bulb-to-bulb distillation or column chromatography afforded **3a-f**.

2-Methyl-3-nitropropionaldehyde N,N-dimethylhydrazone (3a). Obtained from **2a** after distillation. Yield: 0.72 g (90%); bp 58-59 °C/0.2 mm Hg; ^1H-NMR (200 MHz, $CDCl_3$) δ 6.43 (d, 1 H, $J_{1,2}$ 4.3, H-1), 4.61 (dd, 1 H, $J_{2,3}$ 6.9, $J_{3,3'}$ 12.4, H-3), 4.27 (dd, 1 H, $J_{2,3'}$ 7.4, H-3'), 3.16 (m, 1 H, H-2), 2.68 [s, 6 H, $N(CH_3)_2$], 1.17 (d, 3 H, J_{2,CH_3} 7.1,

CH_3-2). ^{13}C-NMR (50 MHz, $CDCl_3$) d 134.5 (C-1), 78.8 (C-3), 42.5 [$N(CH_3)_2$], 35.1 (C-2), 16.1 (CH_3-2); HRMS m/z calcd for $C_6H_{13}N_3O_2$ 159.1008, found 159.1002.

3-Methyl-2-nitromethylbutyraldehyde* N,N-*dimethylhydrazone (3b). Obtained from **2b** after distillation. Yield: 0.85 g (92%); bp 98-99 °C/0.9 mm Hg. ^{1}H-NMR (200 MHz, $CDCl_3$) δ 6.50 (d, 1 H, $J_{1,2}$ 5.0, H-1), 4.72 (dd, 1 H, $J_{2,CHa}$ 8.7, J_{gem} 12.8, $CHaNO_2$), 4.42 (dd, 1 H, $J_{2,CHb}$ 5.8, $CHbNO_2$), 3.04 (m, 1 H, H-2), 2.74 [s, 6 H, $N(CH_3)_2$], 1.89 (m, 1 H, $J_{2,3}$ 5.2, H-3), 0.99 (d, 3 H, $J_{3,4}$ 6.9, H-4), 0.95 (d, 3 H, $J_{3,CH3}$ 6.8, CH_3-3). ^{13}C-NMR (50 MHz, $CDCl_3$) δ 132.5 (C-1), 75.7 (CH_2NO_2), 45.8 (C-2), 42.6 [$N(CH_3)_2$], 29.0 (C-3), 19.7, 18.5 (C-4, CH_3-3). HRMS m/z calcd for $C_8H_{17}N_3O_2$ 185.1164, found 185.1207.

2-Phenyl-3-nitropropionaldehyde* N,N-*dimethylhydrazone (3c). Obtained from **2c** after column chromatography (Et_2O/hexane, 1:4) as an oil. Yield: 0.81 g (75 %). ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.21-7.35 (m, 5 H, Ph), 6.59 (d, 1 H, $J_{1,2}$ 3.6, H-1), 5.06 (dd, 1 H, $J_{2,3}$ 7.5, $J_{3,3'}$ 12.9, H-3), 4.56 (dd, 1 H, $J_{2,3'}$ 7.5, H-3'), 4.40 (td, 1 H, H-2), 2.76 [s, 6 H, $N(CH_3)_2$]. ^{13}C-NMR (50 MHz, $CDCl_3$) δ 137.4, 132.3, 128.9, 128.1, 127.8 (Ph, C-1), 77.7 (C-3), 46.1 (C-2), 42.5 [$N(CH_3)_2$]. HRMS m/z calcd for $C_{11}H_{15}N_3O_2$ 221.1164, found 221.1137. Anal. Calcd for $C_{11}H_{15}N_3O_2$: C, 59.71; H, 6.83; N, 18.99. Found: C, 59.74; H, 6.88; N, 18.73.

3-Nitro-2-(p-tolyl)propionaldehyde* N,N-*dimethylhydrazone (3d). Obtained from **2d** after column chromatography (Et_2O/hexane, 1:6) as an oil. Yield: 0.82 g (70 %). ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.25-7.12 (m, 4 H, C_6H_4), 6.58 (d, 1 H, $J_{1,2}$ 3.6, H-1), 5.03 (dd, 1 H, $J_{2,3}$ 7.5, $J_{3,3'}$ 12.9, H-3), 4.53 (dd, 1 H, $J_{2,3'}$ 7.5, H-3'), 4.36 (td, 1 H, H-2), 2.75 [s, 6 H, $N(CH_3)_2$], 2.33 (s, 3H, H_3C-C_6H_4). ^{13}C-NMR (50 MHz, $CDCl_3$) δ 137.6, 134.3, 129.6, 127.9 (C_6H_4), 132.7 (C-1), 77.8 (C-3), 45.7 (C-2), 42.7 [$N(CH_3)_2$], 20.9 (H_3C-C_6H_4). HRMS m/z calcd for $C_{12}H_{17}N_3O_2$ 235.1321, found 235.1305.

2-(p-Methoxyphenyl)-3-nitropropionaldehyde* N,N-*dimethylhydrazone (3e). Obtained from **2e** after column chromatography (Et_2O/hexane, 1:6) as an oil. Yield: 0.50 g (40 %). ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.17-6.84 (m, 4 H, C_6H_4), 6.58 (d, 1 H, $J_{1,2}$ 3.7, H-1), 5.01 (dd, 1 H, $J_{2,3}$ 7.4, $J_{3,3'}$ 12.9, H-3a), 4.52 (dd, 1 H, $J_{2,3'}$ 7.7, H-3b), 4.34 (ddd, 1 H, H-2), 3.77 (s, 3H, H_3CO-C_6H_4), 2.75 [s, 6 H, $N(CH_3)_2$]. ^{13}C-NMR (50 MHz, $CDCl_3$) δ 159.0, 129.1, 129.0, 114.1 (C_6H_4), 132.7 (C-1), 77.8 (C-3), 55.0 (H_3CO-C_6H_4), 45.2 (C-2), 42.6 [$N(CH_3)_2$]. HRMS m/z calcd for $C_{12}H_{17}N_3O_3$ 251.1270, found 251.1199.

3-Nitro-2-phenylbutyraldehyde* N,N-*dimethylhydrazone (3f). Obtained from **2f** after column chromatography (Et_2O/hexane, 1:4). First eluted was *u*-**2f** as a white solid. Yield: 0.59 g (50%); mp 30-31 °C. ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.38-7.21 (m, 5 H, Ph), 6.63 (d, 1 H, $J_{1,2}$ 4.6, H-1), 5.17 (dq, 1 H, H-3), 4.10 (dd, 1 H, $J_{2,3}$ 9.8, H-2), 2.75 [s, 6 H, $N(CH_3)_2$], 1.36 (d, 3H, $J_{3,4}$ 6.8, H-4). ^{13}C-NMR (50 MHz, $CDCl_3$) δ 136.9, 128.9, 128.7, 127.7 (Ph), 132.7 (C-1), 84.7 (C-3), 52.2 (C-2), 42.6 [$N(CH_3)_2$], 18.1 (C-4). Anal. Calcd for $C_{12}H_{17}N_3O_2$: C, 61.26; H, 7.28; N, 17.86. Found: C, 60.94; H, 7.35; N, 17.80. Further elution gave *l*-**2f** as a white solid. Yield: 0.35 g (30%); mp 56-57 °C. ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.31-7.22 (m, 5 H, Ph), 6.54 (d, 1 H, $J_{1,2}$ 5.9, H-1), 5.14 (dq, 1 H, H-3), 4.00 (dd, 1 H, $J_{2,3}$ 9.9, H-2), 2.78 [s, 6 H, $N(CH_3)_2$], 1.68 (d, 3H, $J_{3,4}$ 6.5, H-4). ^{13}C-NMR (50 MHz, $CDCl_3$) δ 137.6, 132.0, 128.8, 128.2, 127.7 (Ph, C-1), 86.7 (C-3), 53.2 (C-2), 42.8 [$N(CH_3)_2$], 18.4 (C-4). Anal. Calcd for $C_{12}H_{17}N_3O_2$: C, 61.26; H, 7.28; N, 17.86. Found: C, 61.15; H, 7.40; N, 17.71.

β-Nitrodimethylhydrazones 3g-j; General procedure:

To a solution of the nitroolefin **2** (3 mmol) in dry CH_2Cl_2 (12 mL) was added formaldehyde dimethylhydrazone **1** (0.77 mL, 9 mmol). The mixture was kept at r.t. until the nitroolefin had completely reacted (TLC control). Evaporation of the solvent and excess of **1** and purification of the residue by column chromatography afforded **3g-j**.

***3,4,5,6,7-Penta-O-acetyl-2-deoxy-2-nitromethyl*-D-glycero-L-gluco-*heptose* N,N-*dimethylhydrazone* [(R)-3g] and *3,4,5,6,7-Penta-O-acetyl-2-deoxy-2-nitromethyl*-D-glycero-L-manno-*heptose* N,N-*dimethylhydrazone* [(S)-3g].** Obtained from **2f** after column chromatography (Et_2O/hexane, 3:2). First eluted was (*R*)-**3g** as a white solid. Yield: 1.07 g (71%); mp 54-55 °C; $[\alpha]_D^{22}$ -6.2° (*c* 1, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.39 (d, 1 H, $J_{1,2}$ 4.6, H-1), 5.40-5.13 (m, 4 H, H-3, H-4, H-5, H-6), 4.67 (dd, 1 H, $J_{2,CHa}$ 7.7, J_{gem} 13.6, $CHaNO_2$), 4.30 (dd, 1 H, $J_{2,CHb}$ 5.9, $CHbNO_2$), 4.25 (dd, 1 H, $J_{6,7}$ 4.8, $J_{7,7'}$ 11.6, H-7), 3.80 (dd, 1 H, $J_{6,7'}$ 7.2, H-7'), 3.34 (m, 1 H, H-2), 2.76 [s, 6 H, $N(CH_3)_2$], 2.12, 2.08, 2.07, 2.05, 2.00 (each s, each 3 H, 5 CH_3CO). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 170.6, 170.3, 170.1, 169.7, 169.6 (5 $COCH_3$), 127.2 (C-1), 74.7 (CH_2NO_2), 70.0, 67.5 (C-3, C-4, C-5, C-6), 62.0 (C-7), 42.3 [$N(CH_3)_2$], 40.9 (C-2), 20.6, 20.5 (5 CH_3CO). Anal. Calcd for $C_{20}H_{31}N_3O_{12}$: C, 47.52; H, 6.18; N, 8.31. Found: C, 47.71; H, 6.24; N, 7.98. Second eluted was a mixture of (*R*)-**3g** and (*S*)-**3g**. Yield: 0.26 g (17%) [(*R*)-**3g**/(*S*)-**3g**, 77/23). Third eluted was (*S*)-**3g** as a white solid. Yield: 0.26 g (17%); mp 121-122 °C; $[\alpha]_D^{22}$ +0.9° (*c* 1, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.24 (d, 1 H, $J_{1,2}$ 5.8, H-1), 5.45-5.20 (m, 4 H, H-3, H-4, H-5, H-6), 4.69 (dd, 1 H, $J_{2,CHa}$ 7.7, J_{gem} 13.2, $CHaNO_2$), 4.56 (dd, 1 H, $J_{2,CHb}$ 5.4, $CHbNO_2$), 4.28 (dd, 1 H, $J_{6,7}$ 4.9, $J_{7,7'}$ 11.6, H-7), 3.81 (dd, 1 H, $J_{6,7'}$ 7.4, H-7'), 3.35 (m, 1 H, H-2), 2.73 [s, 6 H, $N(CH_3)_2$], 2.12, 2.10, 2.09, 2.06, 2.02 (each s, each 3 H, 5 CH_3CO). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 170.3, 170.2, 169.8, 169.7 (5 $COCH_3$), 127.1 (C-1), 74.7 (CH_2NO_2), 68.4, 68.1, 67.7, 67.4 (C-3, C-4, C-5, C-6), 62.0 (C-7), 42.4 [$N(CH_3)_2$], 42.2 (C-2), 20.5, 20.4 (5 CH_3CO). Anal. Calcd for $C_{20}H_{31}N_3O_{12}$: C, 47.52; H, 6.18; N, 8.31. Found: C, 47.38; H, 6.30; N, 8.10.

***3-O-Benzyl-5-deoxy-1,2-O-isopropylidene-5-nitromethyl*-α-D-gluco-*hexodialdo-1,4-furanose* N,N-*dimethylhydrazone* [(R)-3h] and *3-O-Benzyl-5-deoxy-1,2-O-isopropylidene-5-nitromethyl*-β-L-ido-*hexodialdo-1,4-furanose* N,N-*dimethylhydrazone* [(S)-3h].** Obtained from **2h** after column chromatography (Et_2O/hexane/CH_2Cl_2 1:6:1 to 1:2:1). First eluted was (*S*)-**3h** as a white solid. Yield: 0.18 g (15%); mp 79-80 °C; $[\alpha]_D^{22}$ -56.0° (*c* 0.58, CH_2Cl_2). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.36-7.32 (m, 5H, Ph), 6.18 (d, 1 H, $J_{5,6}$ 4.3, H-6), 5.91 (d, 1 H, $J_{1,2}$ 3.9, H-1), 4.78 (dd, 1 H, $J_{5,CHa}$ 9.3, J_{gem} 13.2, $CHaNO_2$), 4.74 (d, 1 H, J_{gem} 11.5, CH_2Ph), 4.72 (dd, 1 H, $J_{5,CHb}$ 4.7, $CHbNO_2$), 4.64 (d, 1 H, H-2), 4.44 (d, 1 H, CH_2Ph), 4.11 (dd, 1 H, $J_{3,4}$ 3.1, $J_{4,5}$ 9.9, H-4), 3.94 (d, 1 H, H-3), 3.66 (m, 1 H, H-5), 2.60 [s, 6 H, $N(CH_3)_2$], 1.48, 1.32 [each s, each 3 H, $C(CH_3)_2$]. ^{13}C-NMR (75 MHz, $CDCl_3$) δ 136.5, 130.6, 128.5, 128.2, 128.0 (Ph), 111.6 (C-6), 104.6 [C-1, $C(CH_3)_2$], 81.6, 80.6, 79.7 (C-2, C-3, C-4), 75.3, 71.6 (CH_2NO_2, CH_2Ph), , 42.4 [$N(CH_3)_2$], 39.1 (C-5), 26.6, 26.0 [$C(CH_3)_2$]. Anal. Calcd for $C_{19}H_{27}N_3O_6$: C, 58.00; H, 6.92; N, 10.68. Found: C, 58.21; H, 6.76; N, 10.71. Second eluted was a mixture of (*S*)-**3h** and (*R*)-**3h**. Yield: 0.02 g (2%) [(*S*)-**3h**/(*R*)-**3h**, 40/60). Third eluted was (*R*)-**3h** as an oil. Yield: 0.86 g (73%); $[\alpha]_D^{22}$ -48.5° (*c* 0.66, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.35-7.30 (m, 5H, Ph), 6.50 (d, 1 H, $J_{5,6}$ 4.3, H-6), 5.92 (d, 1 H, $J_{1,2}$ 3.8, H-1), 4.72 (dd, 1 H, $J_{5,CHa}$ 4.2, J_{gem} 13.3, $CHaNO_2$), 4.68 (d, 1 H, J_{gem} 12.0, CH_2Ph), 4.62 (d, 1 H, H-2), 4.42 (d, 1 H, CH_2Ph), 4.32 (dd, 1 H, $J_{5,CHb}$ 8.3, $CHbNO_2$), 4.25 (dd, 1 H, $J_{3,4}$ 3.2, $J_{4,5}$ 8.0, H-4), 3.90 (d, 1 H, H-3), 3.66 (m, 1 H, H-5), 2.69 [s, 6 H, $N(CH_3)_2$], 1.48, 1.32 [each s, each 3 H, $C(CH_3)_2$]. ^{13}C-NMR (75 MHz, $CDCl_3$) δ 136.7, 128.8, 128.5, 128.2, 128.1 (Ph), 111.6 (C-6), 104.5 [C-1, $C(CH_3)_2$], 81.4, 81.2, 79.4 (C-2, C-3, C-4), 73.9, 71.5 (CH_2NO_2, CH_2Ph), 42.6 [$N(CH_3)_2$], 39.8 (C-5), 26.5, 26.0 [$C(CH_3)_2$]. HRMS m/z calcd for $C_{19}H_{27}N_3O_6$ 393.1899, found 393.1899.

***6-Deoxy-1,2:3,4-di-O-isopropylidene-6-nitromethyl*-D-glycero-α-D-galacto-*heptodialdo-1,5-pyranose* N,N-*dimethylhydrazone* [(R)-3i] and *6-Deoxy-1,2:3,4-di-O-isopropylidene-6-nitromethyl*-L-glycero-α-D-galacto-*heptodialdo-1,5-pyranose* N,N-*dimethylhydrazone* [(S)-3i].** Obtained from **2i** after column chromatography (Et_2O/hexane/CH_2Cl_2 1:6:2). First eluted was (*S*)-**3i** as a white solid. Yield: 0.19 g (17%); mp 90-92 °C; $[\alpha]_D^{22}$ -33.0° (*c* 0.94, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.54 (d, 1 H, $J_{6,7}$ 4.4, H-7), 5.48 (d, 1 H, $J_{1,2}$, 5.0, H-1), 4.75-4.73 (m, 2 H, CH_2NO_2), 4.58 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 7.9, H-3), 4.30 (dd, 1 H, H-2), 4.23 (dd, 1 H, $J_{4,5}$ 1.8, H-4), 3.78 (dd, 1 H, $J_{5,6}$ 9.5, H-5), 3.51 (m, 1 H, H-6), 2.73 [s, 6 H, $N(CH_3)_2$], 1.54, 1.51, 1.38, 1.35 [each s, each 3 H, 2 $C(CH_3)_2$]. ^{13}C-NMR (75 MHz, $CDCl_3$) δ 129.6 (C-7), 109.4, 108.7 [$C(CH_3)_2$], 96.3 (C-1), 75.0 (CH_2NO_2), 71.0, 70.7, 70.3 (C-2, C-3, C-4), 67.8 (C-5), 42.6 [$N(CH_3)_2$], 40.2 (C-6), 25.9, 25.8, 24.8, 24.4 [$C(CH_3)_2$]. Anal. Calcd for $C_{16}H_{27}N_3O_7$: C, 51.46; H,

7.29; N, 11.25. Found: C, 51.67; H, 7.28; N, 10.95. Second eluted was a mixture of (*S*)-**3i** and (*R*)-**3i**. Yield: 0.21 g (19%) [(*S*)-**3i**/(*R*)-**3i**, 32:68). Third eluted was (*R*)-**3i** as an oil. Yield: 0.63 g (56%); $[\alpha]_D^{22}$ -60.0° (*c* 0.70 $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.64 (d, 1 H, $J_{6,7}$ 4.3, H-7), 5.52 (d, 1 H, $J_{1,2}$, 5.1, H-1), 4.84 (dd, 1 H, $J_{6,CHa}$ 7.2, J_{gem} 13.6, $CHaNO_2$), 4.69 (dd, 1 H, $J_{6,CHb}$ 5.0, $CHbNO_2$), 4.60 (dd, 1 H, $J_{2,3}$ 2.3, $J_{3,4}$ 8.0, H-3), 4.30 (dd, 1 H, H-2), 4.27 (dd, 1 H, $J_{4,5}$ 1.7, H-4), 4.01 (dd, 1 H, $J_{5,6}$ 6.6, H-5), 3.43 (m, 1 H, H-6), 2.74 [s, 6 H, $N(CH_3)_2$], 1.44, 1.34, 1.32 [each s, 12 H, 2 $C(CH_3)_2$]. ^{13}C-NMR (75 MHz, $CDCl_3$) δ 131.7 (C-7), 109.8, 108.7 [$C(CH_3)_2$], 96.4 (C-1), 74.5 (CH_2NO_2), 71.5, 70.9, 70.3 (C-2, C-3, C-4), 67.0 (C-5), 42.8 [$N(CH_3)_2$], 41.9 (C-6), 25.8, 24.8, 24.2 [$C(CH_3)_2$]. HRMS m/z calcd for $C_{16}H_{27}N_3O_7$ 373.1849, found 373.1853.

***6-Deoxy-1,2:3,4-di-O-isopropylidene-6-(1-nitropropyl)*-D-glycero-α-D-galacto-*heptodialdo-1,5-pyranose* N,N-*dimethylhydrazone* [(R)-3j] and *6-deoxy-1,2:3,4-di-O-isopropylidene-6-(1-nitropropyl)*-L-glycero-α-D-galacto-*heptodialdo-1,5-pyranose* N,N-*dimethylhydrazone* [(S)-3j].** Obtained from **2j** after column chromatography (Et_2O/hexane, 1:4 to 1:3) by the general procedure described above, but in this case using 8 equiv of **1**. First eluted was unreacted **2j** (14%). Second eluted was (*S*)-**3j** as an oil. Yield: 0.07 g (6%); $[\alpha]_D^{22}$ -5.9° (*c* 1, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.39 (d, 1 H, $J_{6,7}$ 5.4, H-7), 5.51 (d, 1 H, $J_{1,2}$, 5.1, H-1), 4.80 (ddd, 1 H, $J_{6,CH}$ 5.1, $J_{CH,Et}$ 3.4, 10.4, $CHNO_2$), 4.57 (dd, 1 H, $J_{2,3}$ 2.6, $J_{3,4}$ 7.9, H-3), 4.31 (dd, 1 H, H-2), 4.28 (dd, 1 H, $J_{4,5}$ 1.5, H-4), 4.08 (dd, 1 H, $J_{5,6}$ 10.2, H-5), 3.48 (m, 1 H, H-6), 2.76 [s, 6 H, $N(CH_3)_2$], 1.95-1.65 (m, 2H, CH_2CH_3), 1.54, 1.46, 1.32, 1.30 [each s, each 3 H, 2 $C(CH_3)_2$], 0.93 (t, 3H, $J_{CH2,CH3}$ 7.2, CH_2CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 128.6 (C-7), 109.2, 108.5 [$C(CH_3)_2$], 96.5 (C-1), 90.0 ($CHNO_2$), 70.9, 70.8 (C-3, C-4), 70.3 (C-2), 66.4 (C-5), 43.4 (C-6), 42.6 [$N(CH_3)_2$], 25.8, 25.6, 24.8, 24.5 [$C(CH_3)_2$], 21.1 (CH_2CH_3), 10.5 (CH_2CH_3). HRMS m/z calcd f or $C_{18}H_{31}N_3O_7$ 401.2162, found 401.2169. Second eluted was a mixture of (*S*)-**3j** and (*R*)-**3j**. Yield: 0.19 g (16%) [(*S*)-**3j**/(*R*)-**3j**, 10:90). Third eluted was (*R*)-**3j** as a mixture of two diastereoisomers (60/40). Yield: 0.75 g (62%). Spectral data of the major isomer of (*R*)-**3j**: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.44 (d, 1 H, $J_{6,7}$ 6.7, H-7), 5.48 (d, 1 H, $J_{1,2}$, 5.1, H-1), 4.75 (dt, 1 H, $J_{CH,Et}$ 9.3, 4.6, $CHNO_2$), 4.62 (dd, 1 H, $J_{2,3}$ 2.4, $J_{3,4}$ 7.9, H-3), 4.42 (dd, 1 H, $J_{4,5}$ 1.9, H-4), 4.29 (dd, 1 H, H-2), 3.92 (dd, 1 H, $J_{5,6}$ 7.8, H-5), 3.02 (td, 1 H, $J_{6,CH}$ 4.2, H-6), 2.76 [s, 6 H, $N(CH_3)_2$], 2.14-1.86 (m, 2H, CH_2CH_3), 1.52, 1.45, 1.36, 1.33 [each s, each 3 H, 2 $C(CH_3)_2$], 0.90 (t, 3H, $J_{CH2,CH3}$ 7.3, CH_2CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 132.2 (C-7), 109.3, 108.6 [$C(CH_3)_2$], 96.5 (C-1), 89.6 ($CHNO_2$), 72.6, 71.0, 70.1 (C-2, C-3, C-4), 65.7 (C-5), 45.5 (C-6), 42.9 [$N(CH_3)_2$], 25.9, 25.7, 25.2, 24.6 [$C(CH_3)_2$], 24.0 (CH_2CH_3), 10.0 (CH_2CH_3). Spectral data of the minor isomer of (*R*)-**3j**: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.53 (d, 1 H, $J_{6,7}$ 7.2, H-7), 5.51 (d, 1 H, $J_{1,2}$ 5.2, H-1), 4.76 (ddd, 1 H, $J_{CH,Et}$ 6.7, $CHNO_2$), 4.57 (dd, 1 H, $J_{2,3}$ 2.1, $J_{3,4}$ 7.9, H-3), 4.25 (dd, 1 H, H-2), 4.20 (dd, 1 H, $J_{4,5}$ 2.2, H-4), 3.75 (dd, 1 H, $J_{5,6}$ 2.6, H-5), 3.24 (ddd, 1 H, $J_{6,CH}$ 9.5, H-6), 2.76 [s, 6 H, $N(CH_3)_2$], 2.14-1.86 (m, 2H, CH_2CH_3), 1.50, 1.41, 1.33, 1.31 [each s, each 3 H, 2 $C(CH_3)_2$], 1.00 (t, 3H, $J_{CH2,CH3}$ 7.3, CH_2CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 132.5 (C-7), 109.3, 108.6 [$C(CH_3)_2$], 96.4 (C-1), 89.5 ($CHNO_2$), 71.4, 70.9, 70.1 (C-2, C-3, C-4), 66.2 (C-5), 47.2 (C-6), 42.9 [$N(CH_3)_2$], 25.9, 25.2, 24.8, 24.5 [$C(CH_3)_2$], 24.3 (CH_2CH_3), 10.3 (CH_2CH_3). HRMS m/z calcd for $C_{18}H_{31}N_3O_7$ 401.2162, found 401.2165.

β-Nitroaldehydes 4 and β-nitroalcohols 5; General procedure:

Dry ozone was bubbled through a solution of hydrazone **3** (1 mmol) in CH_2Cl_2 (30 mL) at -78 °C until complete consumption of hydrazone **3** (TLC control). Then a precooled (- 78 °C) solution of dimethylsulfide (1 mL, 13.6 mmol) in CH_2Cl_2 (1.1 mL) was added. The solution was allowed to warm to r.t. Evaporation of the solvent gave aldehydes **4** of purity 95% or more proved by NMR analyses. To a stirred solution of this crude **4** in a mixture of MeOH (32 mL) and water (5 mL) at 0 °C was slowly added $NaBH_4$ (0.038 g, 1 mmol). After completion of the reaction (TLC), the solvent was removed under reduced pressure, the residue was dissolved in CH_2Cl_2 (10 mL), and the solution was washed with water (3x10 ml). The organic layer was separated, the solvent removed under reduced pressure, and the residue was purified by column chromatography to give pure **5**.

3-Methyl-2-nitromethylbutyraldehyde (4b). Obtained from **3b** after column chromatography (Et_2O/hexane, 3:1) as an oil.Yield: 0.12 g (82%). ^{1}H-NMR (200 MHz, $CDCl_3$) δ 9.79 (s, 1 H, H-1), 4.84 (dd, 1 H, $J_{2,CHa}$ 8.6, J_{gem} 14.4, $CHaNO_2$), 4.37 (dd, 1 H, $J_{2,CHb}$ 4.4, $CHbNO_2$), 3.25 (ddd, 1 H, $J_{2,3}$ 4.9, H-2), 2.26 (m, 1 H, H-3), 1.09 (d, 3H, $J_{3,4}$ 6.9 Hz), 1.03 (d, 3H, $J_{3,CH}$ 6.9 Hz). ^{13}C-NMR (50 MHz, $CDCl_3$) δ 200.1 (C-1), 70.9 (CH_2NO_2), 54.4 (C-2), 26.9 (C-3), 19.8 (C-4), 19.3 (CH_3-3). HRMS m/z calcd for $C_6H_9NO_3$ (M^+-1) 144.0661, found 144.0702.

3,4,5,6,7-Penta-O-acetyl-2-deoxy-2-nitromethyl-*D-*glycero-*L-*gluco-heptose [(S)-4g]. Obtained from (*R*)-**3g** after column chromatography (Et_2O/hexane, 3:2) as an oil. Yield: 0.37 g (90%). ^{1}H-NMR (200 MHz, $CDCl_3$) δ 9.77 (s, 1 H, H-1), 5.46 (dd, 1 H, $J_{2,3}$ 6.7, $J_{3,4}$ 1.5, H-3), 5.39-5.29 (m, 2 H, H-4, H-5), 5.26 (ddd, 1 H, $J_{6,7}$ 4.9, $J_{6,7'}$ 7.4, H-6), 4.80 (dd, 1 H, $J_{2,CHa}$ 6.9, J_{gem} 14.9, $CHaNO_2$), 4.42 (dd, 1 H, $J_{2,CHb}$ 5.4, $CHbNO_2$), 4.29 (dd, 1 H, $J_{7,7'}$ 11.6, H-7), 3.82 (dd, 1 H, H-7'), 3.56 (td, 1 H, H-2), 2.13, 2.10, 2.07, 2.06, 2.00 (each s, each 3 H, 5 CH_3CO). ^{13}C-NMR (50 MHz, $CDCl_3$) δ 195.9 (C-1), 170.3, 170.2, 170.0, 169.9, 169.6 (5 $COCH_3$), 69.6 (CH_2NO_2), 67.8, 67.4, 67.3, 67.1 (C-3, C-4, C-5, C-6), 61.8 (C-7), 49.7 (C-2), 20.6, 20.5, 20.4, 20.3, 20.2 (5 CH_3CO). Anal. Calcd for $C_{18}H_{25}NO_{13}$: C, 46.65; H, 5.44; N, 3.02. Found: C, 46.37; H, 5.23; N, 2.98.

3,4,5,6,7-Penta-O-acetyl-2-deoxy-2-nitromethyl-*D-*glycero-*L-*manno-heptose [(R)-4g]. Obtained from (*S*)-**3g** after column chromatography (Et_2O/hexane, 3:2) as an oil. Yield: 0.30 g (85%). ^{1}H-NMR (200 MHz, $CDCl_3$) δ 9.66 (s, 1 H, H-1), 5.39 (dd, 1 H, $J_{2,3}$ 6.6, $J_{3,4}$ 1.7, H-3), 5.38-5.30 (m, 3 H, H-4, H-5, H-6), 4.81 (dd, 1 H, $J_{2,CHa}$ 7.5, J_{gem} 14.9, $CHaNO_2$), 4.65 (dd, 1 H, $J_{2,CHb}$ 5.2, $CHbNO_2$), 4.29 (dd, 1 H, $J_{6,7}$ 4.8, $J_{7,7'}$ 11.7, H-7), 3.85 (dd, 1 H, $J_{6,7'}$ 7.4, H-7'), 3.46 (m, 1 H, H-2), 2.16, 2.10, 2.09, 2.08, 2.02 (each s, each 3 H, 5 CH_3CO). ^{13}C-NMR (50 MHz, $CDCl_3$) δ 195.7 (C-1), 170.4, 170.3, 170.2, 170.1 (5 $COCH_3$), 71.1 (CH_2NO_2), 69.0, 67.5, 67.4, 67.2 (C-3, C-4, C-5, C-6), 61.9 (C-7), 49.9 (C-2), 20.6, 20.5, 20.4, 20.3 (5 CH_3CO). Anal. Calcd for $C_{18}H_{25}NO_{13}$: C, 46.65; H, 5.44; N, 3.02. Found: C, 46.84; H, 5.35; N, 3.10.

3-O-Benzyl-5-deoxy-1,2-O-isopropylidene-5-nitromethyl-α-*D-*gluco-hexodialdo-1,4-furanose [(S)-4h]. Obtained from (*R*)-**3h** as an oil. Yield: 0.36 g (99%); $[\alpha]_D^{22}$ -35.2° (*c* 1, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 9.88 (s, 1 H, H-6), 7.40-7.28 (m, 5H, Ph), 5.99 (d, 1 H, $J_{1,2}$ 3.8, H-1), 4.72 (dd, 1 H, $J_{5,CHa}$ 7.1, $CHaNO_2$), 4.72 (d, 1 H, J_{gem} 11.8, CH_2Ph), 4.69 (d, 1 H, H-2), 4.45 (d, 1 H, CH_2Ph), 4.43 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 7.1, H-4), 3.98 (dd, 1 H, $J_{5,CHb}$ 4.8, J_{gem} 14.9, $CHbNO_2$), 3.98 (d, 1 H, H-3), 3.68 (td, 1 H, H-5), 1.48, 1.33 [each s, each 3 H, $C(CH_3)_2$]. ^{13}C-NMR (75 MHz, $CDCl_3$) δ 198.9 (C-6), 136.0, 128.6, 128.3, 127.8 (Ph), 112.1 [$C(CH_3)_2$], 104.8 (C-1), 81.4, 81.2, 77.4 (C-2, C-3, C-4), 71.8 (CH_2Ph), 70.8 (CH_2NO_2), 48.0 (C-5), 26.6, 26.0 [$C(CH_3)_2$]. HRMS m/z calcd for $C_{16}H_{17}O_5$ (M^+-NO_2H-CH_3) 289.1076, found 289.1077. MS-FAB: 374 (MNa^+).

3-O-Benzyl-5-deoxy-1,2-O-isopropylidene-5-nitromethyl-α-*D-*glucofuranose [(R)-5h]. Obtained from (*S*)-**4h** after column chromatography (Et_2O/hexane/$CHCl_3$, 2:5:2) as a white solid. Yield: 0.28 g (78%); mp 94-95 °C; $[\alpha]_D^{22}$ -44.6° (*c* 0.90, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.37-7.32 (m, 5H, Ph), 5.92 (d, 1 H, $J_{1,2}$ 3.9, H-1), 4.70 (d, 1 H, J_{gem} 11.7, CH_2Ph), 4.65 (d, 1 H, H-2), 4.45 (d, 1 H, CH_2Ph), 4.41 (dd, 1 H, $J_{5,CHa}$ 7.5, J_{gem} 12.7, $CHaNO_2$), 4.26 (dd, 1 H, $J_{5,CHb}$ 4.8, $CHbNO_2$), 4.19 (dd, 1 H, $J_{3,4}$ 3.2, $J_{4,5}$ 8.7, H-4), 3.91 (d, 1 H, H-3), 3.89 (dd, 1 H, $J_{5,6}$ 4.0, $J_{6,6'}$ 11.4, H-6), 3.80 (dd, 1 H, $J_{5,6'}$ 4.2, H-6'), 2.89 (m, 1 H, H-5), 1.62 (s, 1 H, OH), 1.48, 1.33 [each s, each 3 H, $C(CH_3)_2$]. ^{13}C-NMR (125 MHz, $CDCl_3$) δ 136.6, 128.7, 128.4, 128.1 (Ph), 111.9 [$C(CH_3)_2$], 104.5 (C-1), 81.6, 81.1 (C-2, C-3), 78.2 (CH_2Ph), 73.9 (C-4), 71.6 (CH_2NO_2), 60.9 (C-6), 38.8 (C-5), 26.6, 26.1 [$C(CH_3)_2$]. Anal. Calcd for $C_{17}H_{23}NO_7$: C, 57.78; H, 6.56; N, 3.96. Found: C, 58.06; H, 6.74; N, 3.84.

3-O-Benzyl-5-deoxy-1,2-O-isopropylidene-5-nitromethyl-β-*L-* ido-hexodialdo-1,4-furanose [(R)-4h]. Obtained from (*S*)-**3h** as an oil. Yield: 0.36 g (99%); $[\alpha]_D^{22}$ -34.8° (*c* 0.89, CH_2Cl_2). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 9.68 (s, 1 H, H-6), 7.40-7.26 (m, 5H, Ph), 5.94 (d, 1 H, $J_{1,2}$ 3.8, H-1), 4.86 (dd, 1 H, $J_{5,CHa}$ 6.8, J_{gem} 14.9, $CHaNO_2$), 4.69 (d, 1 H,

H-2), 4.68 (d, 1 H, J_{gem} 11.9, CH_2Ph), 4.57 (dd, 1 H, $J_{5,CHb}$ 4.8, CHbNO$_2$), 4.45 (d, 1 H, CH_2Ph), 4.43 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 7.3, H-4), 4.09 (d, 1 H, H-3), 3.64 (td, 1 H, H-5), 1.47, 1.33 [each s, each 3 H, C(CH$_3$)$_2$]. ^{13}C-NMR (75 MHz, CDCl$_3$) δ 197.1 (C-6), 136.1, 128.6, 128.5, 128.2, 128.1 (Ph), 112.1 [*C*(CH$_3$)$_2$], 104.4 (C-1), 81.7, 80.8, 77.3 (C-2, C-3, C-4), 71.9, 71.1 (*C*H$_2$Ph, (CH$_2$NO$_2$), 48.0 (C-5), 26.6, 26.0 [C(*C*H$_3$)$_2$]. HRMS m/z calcd for C$_{16}$H$_{17}$O$_5$ (M$^+$-NO$_2$H-CH$_3$) 289.1076, found 289.1078. MS-FAB: 374 (MNa$^+$).

3-O-Benzyl-5-deoxy-1,2-O-isopropylidene-5-nitromethyl-β-L-idofuranose [(S)-5h]. Obtained from (*R*)-**4h** after column chromatography (Et$_2$O/hexane/CHCl$_3$, 2:5:2) as a white solid. Yield: 0.24 g (68%); mp 103-105 °C; $[\alpha]_D^{22}$ -58.8° (*c* 0.80, CHCl$_3$). ^{1}H-NMR (500 MHz, CDCl$_3$) δ 7.40-7.32 (m, 5H, Ph), 5.92 (d, 1 H, $J_{1,2}$ 3.9, H-1), 4.81 (dd, 1 H, $J_{5,CHa}$ 4.1, J_{gem} 13.3, CHaNO$_2$), 4.73 (d, 1 H, J_{gem} 11.8, CH_2Ph), 4.66 (d, 1 H, H-2), 4.49 (d, 1 H, CH_2Ph), 4.63 (dd, 1 H, $J_{5,CHb}$ 9.2, CHbNO$_2$), 4.23 (dd, 1 H, $J_{3,4}$ 3.2, $J_{4,5}$ 8.3, H-4), 3.98 (d, 1 H, H-3), 3.65 (td, 1 H, $J_{6,OH}$ 5.1, $J_{6,5}$ 5.1, $J_{6,6'}$ 10.8, H-6), 3.56 (dt, 1 H, $J_{6',OH}$ 5.1, $J_{5,6'}$ 5.1, H-6'), 2.93 (m, 1 H, H-5), 1.71 (t, 1 H, OH), 1.50, 1.34 [each s, each 3 H, C(CH$_3$)$_2$]. ^{13}C-NMR (125 MHz, CDCl$_3$) δ 136.7, 128.6, 128.3, 128.0 (Ph), 111.8 [*C*(CH$_3$)$_2$], 104.5 (C-1), 81.7 (C-2), 81.5 (C-3), 77.9 (*C*H$_2$Ph), 74.1 (C-4), 71.7 (CH$_2$NO$_2$), 60.5 (C-6), 38.8 (C-5), 26.6, 26.1 [C(*C*H$_3$)$_2$]. Anal. Calcd for C$_{17}$H$_{23}$NO$_7$: C, 57.78; H, 6.56; N, 3.96. Found: C, 57.34; H, 6.62; N, 3.64.

6-Deoxy-1,2:3,4-di-O-isopropylidene-6-nitromethyl-D-glycero-α-D-galacto-heptodialdopyranose [(S)-4i]. Obtained from (*R*)-**3i** as an oil. Yield: 0.33 g (99%). $[\alpha]_D^{22}$ -31.4° (*c* 0.70 CHCl$_3$). ^{1}H-NMR (500 MHz, CDCl$_3$) δ 9.96 (s, 1 H, H-7), 5.54 (d, 1 H, $J_{1,2}$ 5.0, H-1), 4.85 (dd, 1 H, $J_{6,CHa}$ 5.7, J_{gem} 15.2, CHaNO$_2$), 4.72 (dd, 1 H, $J_{6,CHb}$ 6.3, CHbNO$_2$), 4.69 (dd, 1 H, $J_{2,3}$ 2.5, H-3), 4.37 (dd, 1 H, H-2), 4.28 (dd, 1 H, $J_{3,4}$ 7.9, $J_{4,5}$ 1.6, H-4), 3.85 (dd, 1 H, $J_{5,6}$ 5.9, H-5), 3.37 (m, 1 H, H-6), 1.51, 1.47, 1.37, 1.35 [each s, each 3 H, 2 C(CH$_3$)$_2$]. ^{13}C-NMR (125 MHz, CDCl$_3$) δ 199.3 (C-7), 109.9, 109.1 [*C*(CH$_3$)$_2$], 96.3 (C-1), 71.6, 71.5, 70.8, 70.0 (C-2, C-3, C-4, CH$_2$NO$_2$), 66.0 (C-5), 49.8 (C-6), 25.8, 25.7, 24.7, 24.1 [C(*C*H$_3$)$_2$]. HRMS m/z calcd for C$_{14}$H$_{21}$NO$_8$ 331.1267, found 331.1274.

6-Deoxy-1,2:3,4-di-O-isopropylidene-6-nitromethyl-D-glycero-α-D-galacto-hepto-1,5-pyranose [(R)-5i]. Obtained from (*S*)-**4i** after column chromatography (Et$_2$O/hexane, 1:2) as an amorphous solid. Yield: 0.23 g (70%); $[\alpha]_D^{22}$ -51.1° (*c* 0.88, CHCl$_3$). ^{1}H-NMR (500 MHz, CDCl$_3$) δ 5.58 (d, 1 H, $J_{1,2}$ 5.1, H-1), 4.69 (dd, 1 H, $J_{6,CHa}$ 6.6, J_{gem} 13.2, CHaNO$_2$), 4.68 (dd, 1 H, H-3), 4.64 (dd, 1 H, $J_{6,CHb}$ 5.5, CHbNO$_2$), 4.38 (dd, 1 H, $J_{2,3}$ 2.4, H-2), 4.33 (dd, 1 H, $J_{4,5}$ 1.8, $J_{3,4}$ 7.9, H-4), 4.00 (dd, 1 H, $J_{5,6}$ 7.3, H-5), 3.99 (ddd, 1 H, $J_{6,7}$ 4.3, $J_{7,7'}$ 11.5, $J_{7,OH}$ 5.8, H-7), 3.86 (ddd, 1 H, $J_{6,7'}$ 4.7, $J_{7',OH}$ 6.6, H-7'), 2.77 (m, 1 H, H-6), 2.21-2.17 (m, 1 H, OH), 1.55, 1.51, 1.40, 1.37 [each s, each 3 H, 2 C(CH$_3$)$_2$]. ^{13}C-NMR (75 MHz, CDCl$_3$) δ 109.5, 108.9 [2 *C*(CH$_3$)$_2$], 96.4 (C-1), 74.2 (CH$_2$NO$_2$), 71.4, 70.9, 70.3 (C-2, C-3, C-4), 65.6 (C-5), 60.3 (C-7), 40.6 (C-6), 25.8, 25.7, 24.8, 24.2 [2 C(*C*H$_3$)$_2$]. Anal. Calcd for C$_{14}$H$_{23}$NO$_8$: C, 50.44; H, 6.95; N, 4.20. Found: C, 50.68; H, 7.19; N, 3.93.

6-Deoxy-1,2:3,4-di-O-isopropylidene-6-nitromethyl-L-glycero-α-D-galacto-heptodialdopyranose [(R)-4i]. Obtained from (*S*)-**3i**. Yield: 0.31 g (94%); $[\alpha]_D^{22}$ -59.4° (*c* 0.80 CHCl$_3$). ^{1}H-NMR (500 MHz, CDCl$_3$) δ 9.85 (s, 1 H, H-7), 5.53 (d, 1 H, $J_{1,2}$, 5.0, H-1), 4.94 (dd, 1 H, $J_{6,CHa}$ 6.4, J_{gem} 15.0, CHaNO$_2$), 4.79 (dd, 1 H, $J_{6,CHb}$ 5.2, CHbNO$_2$), 4.69 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 7.9, H-3), 4.37 (dd, 1 H, H-2), 4.36 (dd, 1 H, H-4), 4.18 (dd, 1 H, $J_{4,5}$ 1.8, $J_{5,6}$ 7.0, H-5), 3.57 (m, 1 H, H-6), 1.52, 1.46, 1.35, 1.34 [each s, each 3 H, 2 C(CH$_3$)$_2$]. ^{13}C-NMR (125 MHz, CDCl$_3$) δ 197.6 (C-7), 110.0, 109.2 [*C*(CH$_3$)$_2$], 96.3 (C-1), 71.3,70.7, 70.6, 70.2 (C-2, C-3, C-4, CH$_2$NO$_2$), 65.1 (C-5), 50.0 (C-6), 25.9, 25.7, 24.8, 24.2 [C(*C*H$_3$)$_2$]. HRMS m/z calcd for C$_{13}$H$_{18}$NO$_8$ (M$^+$-CH$_3$) 316.1032, found 316.1037. MS-FAB: 354 (MNa$^+$). HRMS-FAB: m/z calcd for (MRb$^+$) 416.0384, found 416.0376.

6-Deoxy-1,2:3,4-di-O-isopropylidene-6-nitromethyl-D-glycero-α-D-galacto-hepto-1,5-pyranose [(S)-5i]. Obtained from (*R*)-**4i** after column chromatography (Et$_2$O/hexane, 1:2) as a white solid. Yield: 0.25 g (76%); mp 108-110 °C; $[\alpha]_D^{22}$ -28.7° (*c* 0.88, CHCl$_3$). ^{1}H-NMR (500 MHz, CDCl$_3$) δ 5.51 (d, 1 H, $J_{1,2}$ 5.1, H-1), 4.84 (dd, 1 H, $J_{6,CHa}$

4.5, J_{gem} 13.4, $CHaNO_2$), 4.63 (dd, 1 H, $J_{2,3}$ 2.4, $J_{3,4}$ 7.9, H-3), 4.56 (dd, 1 H, $J_{6,CHb}$ 8.0, $CHbNO_2$), 4.32 (dd, 1 H, H-2), 4.30 (dd, 1 H, H-4), 3.93 (dd, 1 H, $J_{4,5}$ 1.8, $J_{5,6}$ 7.7, H-5), 3.84 (td, 1 H, $J_{6,7}$ 4.8, $J_{7,7'}$ 11.3, $J_{7,OH}$ 4.8, H-7), 3.79 (dt, 1 H, $J_{6,7'}$ 5.4, $J_{7',OH}$ 5.4, H-7'), 2.76 (m, 1 H, H-6), 1.91 (t, 1 H, OH),1.51, 1.45, 1.34, 1.32 (each s, each 3 H, 2 $C(CH_3)_2$]. ^{13}C-NMR (125 MHz, $CDCl_3$) δ 109.5, 108.9 [2 $C(CH_3)_2$], 96.4 (C-1), 73.6 (CH_2NO_2), 71.4 , 70.8, 70.4 (C-2, C-3, C-4), 65.4 (C-5), 60.2 (C-7), 40.4 (C-6), 25.8, 25.7, 24.8, 24.2 [2 $C(CH_3)_2$]. Anal. Calcd for $C_{14}H_{23}NO_8$: C, 50.44; H, 6.95; N, 4.20. Found: C, 50.72; H, 6.88; N, 4.08.

6-Deoxy-1,2:3,4-di-O-isopropylidene-6-(1-nitropropyl)-D-glycero-α-D-galacto-heptodialdo-1,5-pyranose [(S)-4j]. Obtained from a mixture 40/60 of two diastereoisomers of (*S*)-**3j**. Yield: 0.34 g of a mixture 40/60 of two diastereoisomers (95%). Spectral data of the major isomer: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 9.79 (d, 1 H, $J_{6,7}$ 3.2, H-7), 5.53 (d, 1 H, $J_{1,2}$, 5.1, H-1), 4.95 (dt, 1 H, $J_{6,CH}$ 9.8, $J_{CH,Et}$ 4.3, 9.8, $CHNO_2$), 4.64 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 7.8, H-3), 4.36 (dd, 1 H, H-2), 4.25 (dd, 1 H, $J_{4,5}$ 2.0, H-4), 3.86 (t, 1 H, $J_{5,6}$ 2.0, H-5), 3.16 (ddd, 1 H, H-6), 2.18-1.81 (m, 2 H, CH_2CH_3), 1.36, 1.35, 1.33, 1.26 [each s, 9 H, 2 $C(CH_3)_2$], 0.96 (t, 3 H, $J_{CH2,CH3}$ 7.3, CH_2CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$) δ 197.9 (C-7), 109.7, 108.8 [$C(CH_3)_2$], 96.3 (C-1), 86.6 ($CHNO_2$), 72.0 (C-3), 70.8, 69.9 (C-2, C-4), 65.2 (C-5), 54.7 (C-6), 25.8, 24.9 [$C(CH_3)_2$], 24.6 (CH_2CH_3), 9.9 (CH_2CH_3). Spectral data of the minor isomer: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 9.83 (d, 1 H, $J_{6,7}$ 1.9, H-7), 5.56 (d, 1 H, $J_{1,2}$ 5.0, H-1), 4.88 (dt, 1 H, $J_{6,CH}$ 4.6, $J_{CH,Et}$ 4.6, 9.4, $CHNO_2$), 4.64 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 7.9, H-3), 4.33 (dd, 1 H, H-2), 4.32 (dd, 1 H, $J_{4,5}$ 2.2, H-4), 4.24 (dd, 1 H, $J_{5,6}$ 4.5, H-5), 3.06 (td, 1 H, H-6), 2.18-1.841(m, 2 H, CH_2CH_3), 1.56, 1.48, 1.43, 1.40 [each s, each 3 H, 2 $C(CH_3)_2$], 1.00 (t, 3 H, $J_{CH2,CH3}$ 7.3, CH_2CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$) δ 198.7 (C-7), 109.8, 109.7 [$C(CH_3)_2$], 96.5 (C-1), 87.7 ($CHNO_2$), 72.4 (C-3), 70.7, 69.8 (C-2, C-4), 66.7 (C-5), 52.5 (C-6), 24.9, 25.8 [$C(CH_3)_2$], 24.7 (CH_2CH_3), 10.3 (CH_2CH_3). HRMS m/z calcd for $C_{15}H_{22}NO_8$ (M^+-CH_3) 344.1345, found 344.1351.

6-Deoxy-1,2:3,4-di-O-isopropylidene-6-(1-nitropropyl)-D-glycero-α-D-galacto-hepto-1,5-pyranose [(R)-5j]. Obtained from a mixture 40/60 of two diastereoisomers of (*S*)-**4j**. Yield: 0.32 g of a mixture 38/62 of two diastereoisomers (88%). Spectral data of the major isomer: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.55 (d, 1 H, $J_{1,2}$ 5.1, H-1), 4.64 (dd, 1 H, $J_{6,CH}$ 4.3, $J_{CH,Et}$ 9.7, $CHNO_2$), 4.60 (dd, 1 H, $J_{2,3}$ 2.0, $J_{3,4}$ 7.9, H-3), 4.32 (dd, 1 H, H-2), 4.30 (dd, 1 H, H-4), 4.06 (dd, 1 H, $J_{4,5}$ 1.1, $J_{5,6}$ 8.0, H-5), 3.84 (dt, 1 H, $J_{6,7}$ 5.3, $J_{7,7'}$ 11.9, $J_{7,OH}$ 5.3, H-7), 3.75 (m, 1 H, H-7'), 2.52 (dd, 1 H, $J_{7',OH}$ 7.7, OH), 2.25 (m, 1 H, H-6), 2.15-1.70 (m, 2H, CH_2CH_3),1.37, 1.35, 1.34, 1.33 (each s, each 3 H, 2 $C(CH_3)_2$], 0.98 (t, 3 H, $J_{CH2,CH3}$ 7.2, CH_2CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 109.3, 108.9 [2 $C(CH_3)_2$], 96.4 (C-1), 88.4 ($CHNO_2$), 70.8, 70.2 (C-2, C-3), 67.0, 66.8 (C-7, C-5), 59.9 (C-4), 44.0 (C-6), 25.8, 25.5, 24.8, 24.3 [2 $C(CH_3)_2$], 23.9 (CH_2CH_3), 10.1 (CH_2CH_3). Spectral data of the minor isomer: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.56 (d, 1 H, $J_{1,2}$ 5.2, H-1), 4.78 (dd, 1 H, $J_{6,CH}$ 3.1, $J_{CH,Et}$ 9.8, $CHNO_2$), 4.68 (dd, 1 H, $J_{2,3}$ 2.3, $J_{3,4}$ 7.9, H-3), 4.46 (dd, 1 H, $J_{4,5}$ 1.6, H-4), 4.36 (dd, 1 H, H-2), 4.16 (dd, 1 H, $J_{5,6}$ 8.0, H-5), 3.95 (ddd, 1 H, $J_{6,7}$ 8.0, $J_{7,7'}$ 11.8, $J_{7,OH}$ 3.5, H-7), 3.75 (m, 1 H, H-7'), 2.58 (dd, 1 H, $J_{7',OH}$ 10.0, OH), 2.35 (m, 1 H, H-6), 2.15-1.70 (m, 2H, CH_2CH_3), 1.54, 1.52, 1.49, 1.46 (each s, each 3 H, 2 $C(CH_3)_2$], 1.00 (t, 3 H, $J_{CH2,CH3}$ 7.3, CH_2CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 109.5, 109.0 [2 $C(CH_3)_2$], 96.5 (C-1), 90.7 ($CHNO_2$), 73.1 (C-5), 71.5 (C-4), 70.9 (C-3), 70.3 (C-2), 59.4 (C-7), 44.0 (C-6), 25.7, 25.6, 24.8, 24.2 [2 $C(CH_3)_2$], 24.1 (CH_2CH_3), 10.6 (CH_2CH_3). CIMS: 362 (M^++1). HRMS m/z calcd for $C_{15}H_{24}NO_8$ (M^+-CH_3) 346.1502, found 346.1518.

6-Deoxy-1,2:3,4-di-O-isopropylidene-6-(1-nitropropyl)-L-glycero-α-D-galacto-heptodialdo-1,5-pyranose [(R)-4j]. Obtained from (*S*)-**3j** as an oil. Yield: 0.36 g (99%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 9.87 (s, 1 H, H-7), 5.53 (d, 1 H, $J_{1,2}$, 5.1, H-1), 4.89 (ddd, 1 H, $J_{6,CH}$ 6.4, $J_{CH,Et}$ 3.7, 10.3, $CHNO_2$), 4.62 (dd, 1 H, $J_{2,3}$ 2.6, $J_{3,4}$ 7.8, H-3), 4.35 (dd, 1 H, H-2), 4.25 (dd, 1 H, $J_{4,5}$ 1.8, H-4), 4.05 (dd, 1 H, $J_{5,6}$ 8.3, H-5), 3.47 (dd, 1 H, H-6), 2.12-1.93 (m, 2 H, $J_{CH2,CH3}$ 7.3, CH_2CH_3), 1.52, 1.44, 1.34, 1.32 [each s, each 3 H, 2 $C(CH_3)_2$], 1.01 (t, 3 H, CH_2CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 198.6 (C-7), 109.7, 108.9 [$C(CH_3)_2$], 96.2 (C-1), 87.6 ($CHNO_2$), 70.7, 70.5, 69.9 (C-2, C-3, C-4), 65.4 (C-5),

52.5 (C-6), 25.6, 25.5, 24.7, 24.2 [C(CH_3)$_2$], 24.1 (CH_2CH_3), 10.4 (CH_2CH_3). HRMS m/z calcd for $C_{16}H_{25}NO_8$ 359.1580, found 359.1560.

6-Deoxy-1,2:3,4-di-O-isopropylidene-6-(1-nitropropyl)-L-glycero-α-D-galacto-hepto-1,5-pyranose [(S)-5j]. Obtained from (*R*)-**4j** after column chromatography (Et_2O/hexane, 1:3) as a white solid. Yield: 0.32 g (88%); mp 131-132 °C; $[\alpha]_D^{22}$ -84.0° (*c* 1, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.51 (d, 1 H, $J_{1,2}$ 5.1, H-1), 4.76 (q, 1 H, $J_{6,CH}$ 7.2, $J_{CH,Et}$ 7.2, $CHNO_2$), 4.64 (dd, 1 H, $J_{2,3}$ 2.4, $J_{3,4}$ 7.9, H-3), 4.35 (dd, 1 H, $J_{4,5}$ 1.6, H-4), 4.31 (dd, 1 H, H-2), 3.95 (td, 1 H, $J_{6,7}$ 3.5, $J_{7,7'}$ 12.1, $J_{7,OH}$ 3.5, H-7), 3.83 (dd, 1 H, $J_{5,6}$ 7.6, H-5), 3.73 (ddd, 1 H, $J_{6,7'}$ 4.6, $J_{7',OH}$ 7.7, H-7'), 2.59 (dd, 1 H, OH), 2.56 (m, 1 H, H-6), 2.05 (m, 2H, CH_2CH_3), 1.48, 1.47, 1.36, 1.31 (each s, each 3 H, 2 C(CH_3)$_2$], 0.97 (t, 3 H, $J_{CH2,CH3}$ 7.3, CH_2CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 109.5, 108.8 [2 C(CH_3)$_2$], 96.5 (C-1), 89.6 ($CHNO_2$), 71.0 (C-3), 70.6, 70.3 (C-2, C-4), 65.2 (C-5), 57.4 (C-7), 44.8 (C-6), 25.7, 25.6, 24.8, 24.2 [2 C(CH_3)$_2$], 23.3 (CH_2CH_3), 10.6 (CH_2CH_3). Anal. Calcd for $C_{16}H_{27}NO_8$: C, 53.18; H, 7.53; N, 3.88. Found: C, 53.21; H, 7.66; N, 3.79.

β-Nitronitriles 6; General Procedure:

To a cooled (0 °C) suspension of MMPP (5 mmol) in MeOH (16 mL) was added dropwise a solution of the hydrazone **3** (2 mmol) in MeOH (2 mL). The mixture was stirred for 5-10 min (TLC control) and then poured into a mixture of CH_2Cl_2 (50 mL) and water (50 mL). The organic layer was separated, washed with brine (50 mL) and water (2x50 mL), and dried ($MgSO_4$). The solvent was removed and the residue purified by column chromatography to afford pure compounds **6**.

3-Nitro-2-phenylpropanenitrile (6c). Obtained from **3c** after column chromatography (Et_2O/hexane, 1:2) as a white solid. Yield: 0.16 g (90%); mp 63-65 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.49-7.37 (m, 5 H, Ph), 4.85 (dd, 1 H, $J_{2,3}$ 10.1, $J_{3,3'}$ 15.4, H-3), 4.68 (dd, 1 H, $J_{2,3'}$ 6.2, H-3'), 4.67 (dd, 1 H, H-2). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 129.8, 129.7, 129.6, 127.5 (Ph), 116.8 (C-1), 76.4 (C-3), 35.3 (C-2). Anal. Calcd for $C_9H_8N_2O_2$: C, 61.36; H, 4.55; N, 15.90. Found: C, 61.21; H, 4.53; N, 15.63.

3,4,5,6,7-Penta-O-acetyl-2-deoxy-2-nitromethyl-D-glycero-L-gluco-heptanenitrile [(R)-6g]. Obtained from (*R*)-**3g** after column chromatography (Et_2O/hexane, 1:1) as a white solid. Yield: 0.42 g (91%); mp 122-124 °C; $[\alpha]_D^{22}$ +18.4° (*c* 0.76, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.36 (t, 1 H, $J_{4,5}$ 6.0, H-4), 5.34-5.29 (m, 2 H, H-5, H-6), 5.11 (dd, 1 H, $J_{2,3}$ 7.2, $J_{3,4}$ 1.3, H-3), 4.76 (dd, 1 H, $J_{2,CHa}$ 7.6, J_{gem} 14.7, $CHaNO_2$), 4.62 (dd, 1 H, $J_{2,CHb}$ 6.2, $CHbNO_2$), 4.27 (dd, 1 H, $J_{6,7}$ 5.1, $J_{7,7'}$ 11.6, H-7), 3.83 (dd, $J_{6,7'}$ 7.4, 1 H, H-7'), 3.84 (m, 1 H, H-2), 2.20, 2.18,, 2.11, 2.10, 2.03 (each s, 15 H, 5 CH_3CO). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 170.8, 170.3, 170.1, 170.0, 169.5 (5 $COCH_3$), 114.6 (C-1), 70.9 (CH_2NO_2), 67.2, 67.0, 66.5, 66.2 (C-3, C-4, C-5, C-6), 61.7 (C-7), 30.8 (C-2), 20.7, 20.6, 20.5, 20.3 (5 CH_3CO). Anal. Calcd for $C_{18}H_{24}N_2O_{12}$: C, 46.96; H, 5.25; N, 6.08. Found: C, 47.14; H, 5.10; N, 5.75.

3,4,5,6,7-Penta-O-acetyl-2-deoxy-2-nitromethyl-D-glycero-L-manno-heptanenitrile [(S)-6g]. Obtained from (*S*)-**3g** after column chromatography (Et_2O/hexane, 1:1) as a white solid. Yield: 0.43 g (92%); mp 177-180 °C; $[\alpha]_D^{22}$ +24.8° (*c* 0.77, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.38-5.33 (m, 3 H, H-4, H-5, H-6), 5.21 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 1.1, H-3), 4.64 (dd, 1 H, $J_{2,CHa}$ 6.4, J_{gem} 14.1, $CHaNO_2$), 4.57 (dd, 1 H, $J_{2,CHb}$ 5.8, $CHbNO_2$), 4.26 (dd, 1 H, $J_{6,7}$ 4.9, $J_{7,7'}$ 11.6, H-7), 3.83 (dd, $J_{6,7'}$ 7.4, 1 H, H-7'), 3.76 (td, 1 H, H-2), 2.22, 2.11, 2.09, 2.03 (each s, 15 H, 5 CH_3CO). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 170.9, 170.8, 170.2, 170.0, 169.5 (5 $COCH_3$), 114.1 (C-1), 71.8, 68.9, 67.2, 67.1 (C-3, C-4, C-5, C-6,), 65.6 (CH_2NO_2), 61.7 (C-7), 33.0 (C-2), 20.6, 20.5, 20.5, 20.4, 20.3 (5 CH_3CO). Anal. Calcd for $C_{18}H_{24}N_2O_{12}$: C, 46.96; H, 5.25; N, 6.08. Found: C, 46.85; H, 4.96; N, 5.87.

3-O-Benzyl-5-deoxy-1,2-O-isopropylidene-5-nitromethyl-α-D-glucofuranuronenitrile [(R)-6h]. Obtained from (*R*)-**3h** after column chromatography (Et_2O/hexane, 1:4) as an oil. Yield: 0.32 g (92%); $[\alpha]_D^{22}$ -59.6° (*c* 0.75, CH_2Cl_2).

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.40-7.36 (m, 5H, Ph), 5.97 (d, 1 H, $J_{1,2}$ 3.7, H-1), 4.72 (d, 1 H, J_{gem} 11.2, CH_2Ph), 4.65 (d, 1 H, H-2), 4.64 (dd, 1 H, $J_{5,CHa}$ 8.4, J_{gem} 15.0, CHaNO$_2$), 4.55 (d, 1 H, CH_2Ph), 4.55 (dd, 1 H, $J_{5,CHb}$ 4.6, CHbNO$_2$), 4.49 (dd, 1 H, $J_{3,4}$ 3.6, $J_{4,5}$ 6.5, H-4), 4.11 (d, 1 H, H-3), 3.90 (ddd, 1 H, H-5), 1.49, 1.33 [each s, each 3 H, C(CH$_3$)$_2$]. ^{13}C-NMR (75 MHz, $CDCl_3$) δ 135.9, 128.8, 128.6, 128.2 (Ph), 116.3 (C-6), 112.6 [*C*(CH$_3$)$_2$], 105.3 (C-1), 81.7, 81.4 (C-2, C-3), 76.7 (*C*H$_2$Ph), 72.5, 71.6 (C-4, CH$_2$NO$_2$), 29.8 (C-5), 26.7, 26.1 [C(*C*H$_3$)$_2$]. HRMS m/z calcd for $C_{17}H_{20}N_2O_6$ 348.1321, found 348.1321.

3-O-Benzyl-5-deoxy-1,2-O-isopropylidene-5-nitromethyl-β-L-idofuranuronenitrile [(S)-6h]. Obtained from (*S*)-**3h** after column chromatography (Et$_2$O/hexane, 1:4). Yield: 0.29 g (83%); $[\alpha]_D^{22}$ -45.0° (*c* 1, CH_2Cl_2). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.34-7.39 (m, 5H, Ph), 5.89 (d, 1 H, $J_{1,2}$ 3.6, H-1), 4.78 (dd, 1 H, $J_{5,CHa}$ 4.3, J_{gem} 14.7, CHaNO$_2$), 4.72 (d, 1 H, J_{gem} 11.1, CH_2Ph), 4.69 (dd, 1 H, $J_{5,CHb}$ 8.2, CHbNO$_2$), 4.64 (d, 1 H, H-2), 4.64 (d, 1 H, CH_2Ph), 4.45 (dd, 1 H, $J_{3,4}$ 3.3, $J_{4,5}$ 9.7, H-4), 4.18 (d, 1 H, H-3), 3.78 (ddd, 1 H, H-5), 1.49, 1.32 [each s, each 3 H, C(CH$_3$)$_2$]. ^{13}C-NMR (75 MHz, $CDCl_3$) δ 136.1, 128.6, 128.4, 128.1 (Ph), 115.9 (C-6), 112.6 [*C*(CH$_3$)$_2$], 105.4 (C-1), 81.5, 81.3 (C-2, C-3), 77.0 (*C*H$_2$Ph), 73.0, 72.1 (C-4, CH$_2$NO$_2$), 29.5 (C-5), 26.7, 26.0 [C(*C*H$_3$)$_2$]. HRMS m/z calcd for $C_{17}H_{20}N_2O_6$ 348.1321, found 348.1326.

6-Deoxy-1,2:3,4-di-O-isopropylidene-6-nitromethyl-D-glycero-α-D-galacto-hepto-1,5-pyranuronenitrile [(R)-6i]. Obtained from (*R*)-**3i** after column chromatography (Et$_2$O/hexane, 1:2) as a white solid. Yield: 0.31 g (95%); mp 145-147 °C; $[\alpha]_D^{22}$ -66.6° (*c* 0.92, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.56 (d, 1 H, $J_{1,2}$ 5.0, H-1), 4.84 (dd, 1 H, $J_{6,CHa}$ 7.0, J_{gem} 14.9, CHaNO$_2$), 4.78 (dd, 1 H, $J_{6,CHb}$ 5.6, CHbNO$_2$), 4.68 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 7.9, H-3), 4.36 (dd, 1 H, H-2), 4.36 (dd, 1 H, H-4), 4.08 (dd, 1 H, $J_{4,5}$ 1.8, $J_{5,6}$ 5.6, H-5), 3.76 (td, 1 H, H-6), 1.52, 1.46, 1.35, 1.34 (each s, each 3 H, 2 C(CH$_3$)$_2$]. ^{13}C-NMR (125 MHz, $CDCl_3$) δ 115.9 (C-7), 110.5, 109.2 [*C*(CH$_3$)$_2$], 96.3 (C-1), 71.6 (CH$_2$NO$_2$), 70.8 (C-4), 70.6 (C-3), 70.0 (C-2), 64.9 (C-5), 31.8 (C-6), 25.7, 25.5, 24.5, 24.0 [C(*C*H$_3$)$_2$]. Anal. Calcd for $C_{14}H_{20}N_2O_7$: C, 51.22; H, 6.14; N, 8.53. Found: C, 51.37; H, 5.91; N, 8.12.

6-Deoxy-1,2:3,4-di-O-isopropylidene-6-nitromethyl-L-glycero-α-D-galacto-hepto-1,5-pyranuronenitrile [(S)-6i]. Obtained from (*S*)-**3i** after column chromatography (Et$_2$O/hexane, 1:2) as a white solid. Yield: 0.32 g (96%); mp 154-155 °C; $[\alpha]_D^{22}$ -57.5° (*c* 0.74, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.48 (d, 1 H, $J_{1,2}$ 4.9, H-1), 4.78 (dd, 1 H, $J_{6,CHa}$ 4.4, J_{gem} 15.0, CHaNO$_2$), 4.71 (dd, 1 H, $J_{6,CHb}$ 6.3, CHbNO$_2$), 4.71 (dd, 1 H, $J_{2,3}$ 2.6, $J_{3,4}$ 7.8, H-3), 4.37 (dd, 1 H, H-2), 4.45 (dd, 1 H, $J_{4,5}$ 1.7, H-4), 4.09 (dd, 1 H, $J_{5,6}$ 10.1, H-5), 3.67 (td, 1 H, H-6), 1.56, 1.50, 1.42, 1.37 [each s, each 3 H, 2 C(CH$_3$)$_2$]. ^{13}C-NMR (75 MHz, $CDCl_3$) δ 115.9 (C-7), 110.2, 109.4 [*C*(CH$_3$)$_2$], 96.2 (C-1), 71.2 (CH$_2$NO$_2$), 70.6, 70.4, 70.2 (C-2, C-3, C-4), 65.3 (C-5), 30.3 (C-6), 25.8, 25.7, 24.6, 24.1 [C(*C*H$_3$)$_2$]. Anal. Calcd for $C_{14}H_{20}N_2O_7$: C, 51.22; H, 6.14; N, 8.53. Found: C, 51.25; H, 6.43; N, 8.22.

1,2:4,5-di-O-Isopropylidene-3-O-benzyl-6-nitro-pseudo-α-D-glucopyranose (8h).
To a solution of (*R*)-**5h** (0.42 g, 1.18 mmol) in CH_2Cl_2 (4 mL) was added benzoyl chloride (0.27 mL, 2.36 mmol) and pyridine (0.68 mL). After completion of the reaction (30 min, TLC) the mixture was poured into ice-water and extracted three times with CH_2Cl_2 (4 mL). The organic layer was dried ($MgSO_4$), concentrated, and the residue was purified by column chromatography (Et$_2$O/hexane, 1:3) to afford 0.44 g (81%) of (*R*)-**7h**. This product was dissolved in AcOH 80% (10 mL) and refluxed for 10h. After removal of the solvent, the residue was coevaporated several times with toluene and purified by column chromatography (Et$_2$O/hexane, 2:1 to 4:1) to afford 0.29 g (72%) of the deisopropylidenated product. To a cooled (0°C) solution of this compound (0.29 g, 0.69 mmol) in DMF (20 mL) was added KF (20 mg, 0.34 mmol) and 18-crown-6 (18 mg, 0.07 mmol) under an argon atmosphere. After completion of the reaction (18h, TLC), the solvent was removed, and the residue was dissolved in MeOH (15 mL), and treated with NaOMe (90 mg). After 50 min the solution was neutralized with Amberlite IR-120(H$^+$), filtered and the solvent removed *in vacuo*. To a solution of the resulting residue in dry acetone (15 mL) was added $CuSO_4$ (0.32 g, 2 mmol),

2,2-dimethoxypropane (2.45 mL, 20 mmol) and *p*-TsOH (0.02 g, 0.1 mmol). After completion of the reaction (7d, TLC) the solution was filtered, neutralized with CaH_2 and filtered again. Evaporation of the solvent and column chromatography afforded **8h** (0.28 g, 72%) as a white solid of physical constants identical to those described in the literature.[25] ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.68 (t, 1 H, $J_{1,2}$ 5.0, $J_{1,6}$ 5.0, H-1), 4.40 (dd, 1 H, $J_{5,6}$ 12.0, H-6), 4.18 (dd, 1 H, $J_{2,3}$ 7.0, H-2), 4.10 (dd, 1 H, $J_{5,7}$ 6.0, $J_{5,7'}$ 10.0, H-7), 3.61 (t, 1 H, $J_{3,4}$ 10.0, $J_{4,5}$ 10.0, H-4), 3.66 (dd, 1 H, $J_{7,7'}$ 11.0, H-7'), 3.56 (dd, 1 H, H-3), 2.71 (m, 1 H, H-5),

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