Diastereoselective Synthesis of Branched-Chain Cyanonitrosugar Derivatives by Michael Addition/MMPP Oxidation Using Formaldehyde SAMP- and RAMP-Hydrazones as New Chiral Cyanide Equivalents

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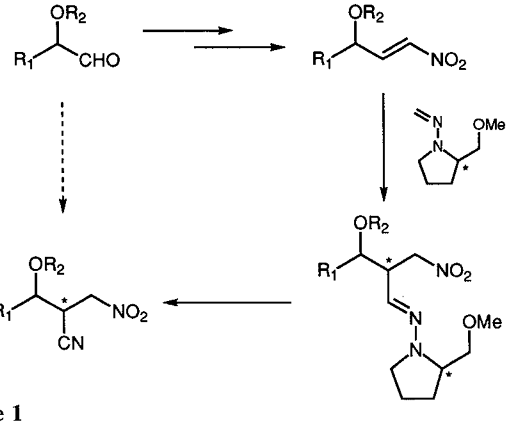
Dedicated to Prof. Richard R. Schmidt on the occasion of his 60th birthday

The diastereoselective synthesis of sugar derived β-nitro nitriles through double asymmetric induction experiments involving Michael addition of formaldehyde SAMP- and RAMP-hydrazones [(*S*)-**1** and (*R*)-**1**] to sugar nitroolefins **2** in excellent overall yields and high diastereoselective excesses is described. The absolute configuration of the RAMP-hydrazone 1,4-adduct **3c** was determined by chemical correlation of its corresponding β-nitro nitrile **4c**.

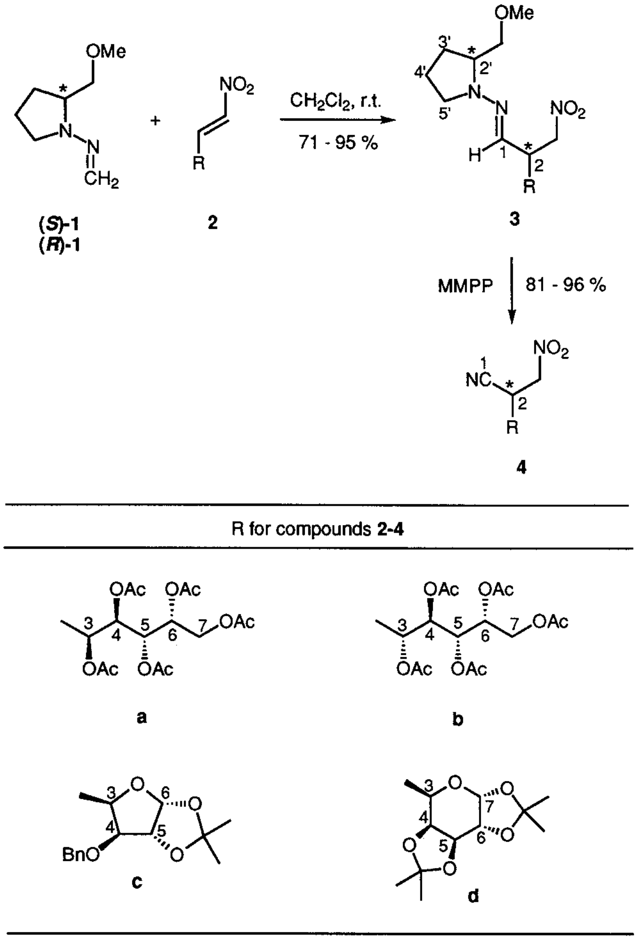
An impressive array of carbohydrate molecules have been synthesized in recent years using nitrosugar intermediates.[1] Moreover, the activating effect of the nitro group and its facile transformation into a variety of organic functional groups[2] have broadened the importance of nitro compounds in carbohydrate chemistry. The construction of complex molecular arrays in this field usually involves stereoselective carbon-carbon bond-forming reactions. In connection with this, we have reported our results on the Michael addition of formaldehyde dialkylhydrazones with nitroolefins.[3,4] These compounds readily add to nitroolefins, without any need of base or catalyst, acting as a sort of low energy carbanion. The corresponding Michael adducts, which were obtained in excellent yields, were successfully transformed into aldehydes and β-cyanonitro derivatives.[3-5] Both asymmetric variants of these Michael additions, employing either the chiral formaldehyde SAMP-hydrazone and achiral nitroolefins as acceptors,[4] or vice versa, the achiral formaldehyde dimethylhydrazone and sugar nitroolefins, have been reported.[3,6] We now wish to report on the useful extension of this approach in carbohydrate chemistry to obtain, in a diastereoselective way, potentially versatile compounds for the synthesis of optically pure sugars of interest. Thus, reactions of formaldehyde SAMP- and RAMP-hydrazones with sugar nitroolefins have now been studied.

We intended to develop a stereocontrolled dialkylhydrazone-based route to both α-epimeric β-nitro nitriles from various sugar aldehydes, outlined in Scheme 1. The procedure takes advantage of the well established versatility and usefulness of sugar nitroolefins,[1] easily accessible in a two step synthesis starting from the corresponding *aldehydo*-sugar. The key steps of the protocol proposed here consist of two efficient operations: i) stereospecific Michael addition of formaldehyde SAMP- and RAMP-hydrazones; ii) oxidation with magnesium monoperoxyphthalate (MMPP) to the corresponding cyano derivatives (Scheme 1).

As depicted in Scheme 2, nitroolefins **2a–d** were made to react with formaldehyde SAMP- and RAMP-hydrazones [(*S*)-**1** and (*R*)-**1**]. The reaction takes place in di-



Scheme 1



Scheme 2

Table 1. β-Nitrohydrazones **3** Prepared

Starting Materials	Reaction Time (h)	Yield of **3**[a] (%)	de (%)[b]	Yield of Pure Epimer at C-2	$[\alpha]_D^{20}$ (c, $CHCl_3$)
(*S*)-**1** + **2a**	12	71	44	(*S*,*S*)-**3a**,[c] 50	– 29.0 (1.01)
				(*S*,*R*)-**3a**, 11	– 52.1 (1.12)
(*R*)-**1** + **2a**	12	83	> 96	(*R*,*R*)-**3a**,[d] 83	+ 31.6 (1.20)
(*S*)-**1** + **2b**	2	83	> 96	(*S*,*S*)-**3b**,[e] 83	– 20.0 (0.91)
(*R*)-**1** + **2b**	5	80	68	(*R*,*R*)-**3b**, 60	+ 90.1 (0.82)
				–[f]	
(*S*)-**1** + **2c**	4	77	64	(*S*,*S*)-**3c**,[g] 60	– 130.0 (1.02)
				(*S*,*R*)-**3c**, 10	– 91.0 (0.71)
(*R*)-**1** + **2c**	4	77	> 96	(*R*,*R*)-**3c**, 77	+ 16.7 (1.10)
(*S*)-**1** + **2d**	3	90	38	(*S*,*S*)-**3d**, 64	– 95.1 (1.10)
				(*S*,*R*)-**3d**, 26	– 100.8 (0.97)
(*R*)-**1** + **2d**	3	95	> 96	(*R*,*R*)-**3d**, 95	+ 13.8 (1.06)

[a] Yield of isolated product.
[b] Measured from the intensities of ^{13}C NMR signals.
[c] Colourless solid, mp 106–108 °C.
[d] Colourless solid, mp 81–83 °C.
[e] Colourless solid, mp 84–85 °C.
[f] (*R*,*S*)-**3b** could not be isolated pure.
[g] Colourless solid, mp 53–55 °C.

chloromethane at room temperature by simply stirring both reagents, and is complete in short time (3–12 h, TLC control). Column chromatography afforded the corresponding 1,4-adducts **3a–d** in good to excellent overall yields (72–95 %) (Table 1).

The diastereomeric excesses were determined by ^{13}C NMR spectroscopy of the crude 1,4-adducts, and ranged from 38–68 % for the mismatched pairs, whereas for the matched pairs the asymmetric inductions were virtually complete (de ≥ 96 %) (Table 1), indicating the effective double asymmetric induction of this carbon-carbon bond-forming process. Fortunately, in the case of the mismatched pairs, where both epimers were formed, they could be separated by column chromatography.

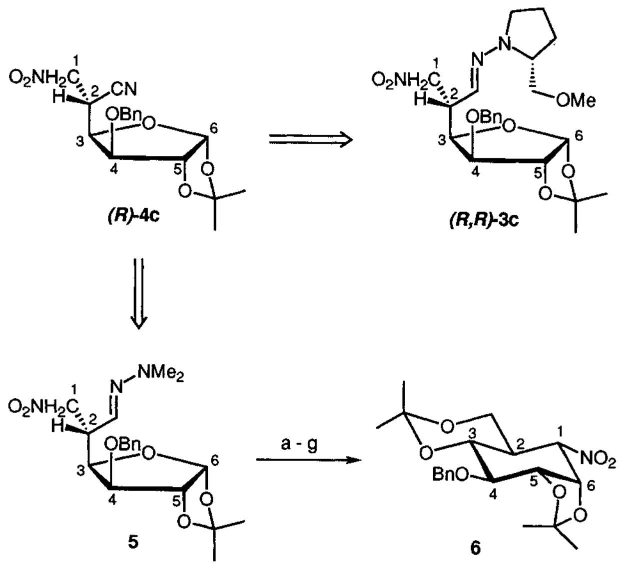
Oxidative cleavage of the C = N bond of the hydrazone moiety performed for the major isomers of **3** by treatment with MMPP in methanol at 0 °C[4,5] afforded the sugar β-nitro nitriles **4a–d** in excellent yields (81–96 %). No epimerization was observed and the cyano derivatives **4** were obtained with high diastereomeric excesses (de ≥ 96 %) (Table 2) as determined by ^{13}C NMR spectroscopy.

Table 2. β-Nitro Nitriles **4** Prepared

Starting Material	Product	Yield[a,b] (%)	$[\alpha]_D^{20}$ (c, $CHCl_3$)
(*S*,*S*)-**3a**	(*S*)-**4a**[c]	92	+ 24.8 (0.91)
(*R*,*R*)-**3a**	(*R*)-**4a**[d]	90	+ 18.4 (1.10)
(*S*,*S*)-**3b**	(*S*)-**4b**	86	+ 2.0 (1.02)
(*R*,*R*)-**3b**	(*R*)-**4b**[e]	94	+ 13.4 (0.91)
(*S*,*S*)-**3c**	(*S*)-**4c**	83	– 45.0 (0.82)
(*R*,*R*)-**3c**	(*R*)-**4c**	81	– 59.6 (1.20)
(*S*,*S*)-**3d**	(*S*)-**4d**[f]	96	– 57.5 (0.74)
(*R*,*R*)-**3d**	(*R*)-**4d**[g]	94	– 66.6 (0.92)

[a] Yield of isolated product.
[b] de > 96 %, measured from the intensities of ^{13}C NMR signals.
[c] Colourless solid, mp 177–180 °C.
[d] Colourless solid, mp 122–124 °C.
[e] Colourless solid, mp 161–163 °C.
[f] Colourless solid, mp 145–147 °C.
[g] Colourless solid, mp 154–155 °C.

The stereochemistry at the new stereogenic center for RAMP-hydrazone 1,4-adduct (*R*,*R*)-**3c** is determined, based on the identity of its corresponding nitrile (*R*)-**4c** obtained by treatment of the 1,4-adduct **5** with MMPP. The stereochemistry of **5** has been previously established[6] by chemical correlation with the known[7] nitrofuranose derivative **6** (Scheme 3).



a) O_3, Me_2S. b) $NaBH_4$, MeOH. c) BzCl, Py. d) 80 % AcOH (80 °C). e) KF, 18-crown-6, DMF. f) 1 % NaOMe-MeOH. g) 2,2-dimethoxypropane, *p*-TsOH, $CuSO_4$, acetone.

Scheme 3

The (*R*)-configuration found for the new stereogenic center for this RAMP-hydrazone product confirms the postulated mechanism for nucleophilic addition of formaldehyde SAMP- and RAMP-hydrazones to nitroolefins.[4] A model based on the electrostatic stabilization of the developing charges in the transition state was proposed to explain the observed stereoselectivity. Assuming that the stereochemical outcome of the above reactions is uniform for all examples presented and similar to that observed with simple nitroolefins and (*S*)-**1**, the assignment of the absolute configuration of the new stereocenter for the major diastereoisomers of **3** [(*S*,*S*) for SAMP-hydrazones adducts and (*R*,*R*) for RAMP-hydrazones adducts] (Table 1) can be made with great reliability.

The matched pairs found for nitroolefins **2a** and **2b** [(*R*)-**1** for **2a**, (*S*)-**1** for **2b**)] are in agreement with the reported stereoselective addition of different nucleophiles to open-chain sugar nitroolefins containing a terminal nitromethylene group, where the preponderant stereoisomers produced are those expected on the basis of Cram's rule.[1,6,8] For nitroolefins **2c** and **2d**, bearing a neighboring cyclic

Table 3. Stereoscopic Data of β-Nitrohydrazones **3**

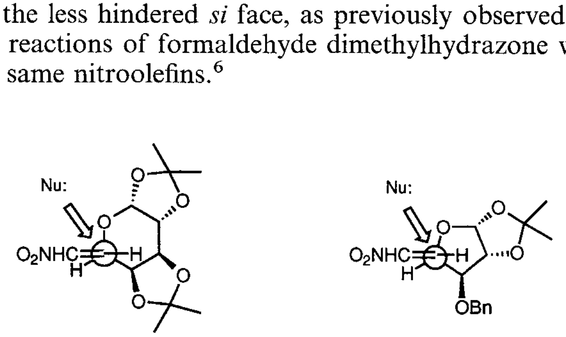
Product[a]	^1H NMR ($CDCl_3$, 500 MHz) δ, J (Hz)	^{13}C NMR ($CDCl_3$, 125.5 MHz) δ
(*S*,*S*)-**3a**	1.79–2.00 (m, 4 H, H-3′a, H-3′b, H-4′a, H-4′b), 2.03, 2.08, 2.10, 2.11, 2.13 (5 s, 15 H, 5 $OCOH_3$), 2.71–2.76 (m, 1 H, H-5′b), 3.24–3.30 (m, 1 H, H-5′a), 3.35 (s, 3 H, OCH_3), 3.37–3.45 (m, 3 H, H-2, H-2′, C*H*bOMe), 3.48 (dd, $J_{gem} = 8.9$, $J_{2',CH} = 3.5$, 1 H, C*H*aOMe), 3.83 (dd, $J_{7a,7b} = 11.7$, $J_{6,7b} = 7.4$, 1 H, H-7b), 4.29 (dd, $J_{6,7a} = 4.9$, 1 H, H-7a), 4.57 (dd, $J_{gem} = 13.4$, $J_{2,CH} = 5.3$, 1 H, $CHbNO_2$), 4.70 (dd, $J_{2,CH} = 8.1$, 1 H, $CHaNO_2$), 5.24 (ddd, $J_{5,6} = 1.9$, 1 H, H-6), 5.32 (dd, $J_{4,5} = 9.6$, 1 H, H-5), 5.27 (dd, $J_{2,3} = 6.5$, $J_{3,4} = 2.1$, 1 H, H-3), 5.43 (dd, 1 H, H-4), 6.26 (d, $J_{1,2} = 4.9$, 1 H, H-1)	20.4, 20.5, 20.5, 20.7 (CO*C*H$_3$), 22.0 (C-4′), 26.4 (C-3′), 42.2 (C-2), 49.0 (C-5′), 59.0 (OCH_3), 62.0 (C-7), 62.9 (C-2′), 67.5, 67.8, 68.3, 68.7 (C-3, C-4, C-5, C-6), 74.2, 74.4 (CH_2NO_2, *C*H$_2$OMe), 126.7 (C-1), 169.7, 169.7, 170.2, 170.3 (*C*OCH$_3$)
(*S*,*R*)-**3a**	1.82–2.00 (m, 4 H, H-3′a, H-3′b, H-4a′, H-4′b), 2.02, 2.07, 2.10, 2.11, 2.15 (5 s, 15 H, 5 $OCOCH_3$), 2.74–2.79 (m, 1 H, H-5′b), 3.29–3.33 (m, 1 H, H-5′a), 3.35–3.44 (m, 2 H, H-2, H-2′), 3.40 (s, 3 H, OCH_3), 3.50 (dd, $J_{gem} = 9.5$, $J_{2',CH} = 5.9$, 1 H, C*H*bOMe), 3.54 (dd, $J_{2',CH} = 3.5$, 1 H, C*H*aOMe), 3.82 (dd, $J_{7a,7b} = 11.7$, $J_{6,7b} = 7.3$, 1 H, H-7b), 4.29 (dd, $J_{6,7a} = 4.9$, 1 H, H-7a), 4.32 (dd, $J_{gem} = 13.5$, $J_{2,CH} = 6.1$, 1 H, $CHbNO_2$), 4.70 (dd, $J_{2,CH} = 7.5$, 1 H, $CHaNO_2$), 5.22 (ddd, $J_{5,6} = 1.9$, 1 H, H-6), 5.25 (dd, $J_{4,5} = 9.9$, 1 H, H-5), 5.28 (dd, $J_{2,3} = 9.8$, $J_{3,4} = 1.5$, 1 H, H-3), 5.42 (dd, 1 H, H-4), 6.43 (d, $J_{1,2} = 4.2$, 1 H, H-1)	20.6, 20.6, 20.6, 20.7 (CO*C*H$_3$), 22.0 (C-4′), 26.3 (C-3′), 41.2 (C-2), 48.9 (C-5′), 59.2 (OCH_3), 62.2 (C-7), 63.1 (C-2′), 67.6, 67.7, 67.8 (C-4, C-5, C-6), 70.05 (C-3), 73.9, 74.8 (CH_2NO_2, *C*H$_2$OMe), 127.3 (C-1), 169.8, 169.8, 170.2, 170.4, 170.7 (*C*OCH$_3$)
(*R*,*R*)-**3a**	1.83–1.99 (m, 4 H, H-3′a, H-3′b, H-4′a, H-4′b), 2.02, 2.06, 2.09, 2.10, 2.14 (5 s, 15 H, 5 $OCOCH_3$), 2.84–2.89 (m, 1 H, H-5′b), 3.22–3.27 (m, 1 H, H-5′a), 3.36 (s, 3 H, OCH_3), 3.37–3.45 (m, 3 H, H-2, H-2′, C*H*bOMe), 3.48 (dd, $J_{gem} = 9.0$, $J_{2',CH} = 3.5$, 1 H, C*H*aOMe), 3.82 (dd, $J_{7a,7b} = 11.7$, $J_{6,7b} = 7.2$, 1 H, H-7b), 4.28 (dd, $J_{6,7a} = 4.8$, 1 H, H-7a), 4.32 (dd, $J_{gem} = 13.5$, $J_{2,CH} = 6.0$, 1 H, $CHbNO_2$), 4.69 (dd, $J_{2,CH} = 7.8$, 1 H, $CHaNO_2$), 5.21 (ddd, $J_{5,6} = 2.0$, 1 H, H-6), 5.25 (dd, $J_{4,5} = 9.7$, 1 H, H-5), 5.26 (dd, $J_{2,3} = 9.5$, $J_{3,4} = 1.6$, 1 H, H-3), 5.44 (dd, 1 H, H-4), 6.38 (d, $J_{1,2} = 4.3$, 1 H, H-1)	20.5, 20.6, 20.6, 20.7 (CO*C*H$_3$), 22.0 (C-4′), 26.7 (C-3′), 41.0 (C-2), 48.9 (C-5′), 59.1 (OCH_3), 62.1 (C-7), 62.8 (C-2′), 67.7, 67.7, 67.8 (C-4, C-5, C-6), 70.2 (C-3), 74.1 (*C*H$_2$OMe), 74.7 (CH_2NO_2), 126.7 (C-1), 169.7, 169.8, 170.1, 170.3, 170.7 (*C*OCH$_3$)
(*S*,*S*)-**3b**	1.75–2.00 (m, 4 H, H-3′a, H 3′b, H-4′a, H-4′b), 2.01, 2.06, 2.08, 2.12, 2.15 (s, 15 H, 5 $OCOCH_3$), 2.71–2.75 (m, 1 H, H-5′b), 3.22–3.26 (m, 1 H, H-5′a), 3.31–3.42 (m, 3 H, H-2, H-2′, C*H*bOMe), 3.35 (s, 3 H, OCH_3), 3.49 (dd, $J_{gem} = 12.5$, $J_{2',CH} = 6.8$, 1 H, C*H*aOMe), 4.05 (dd, $J_{7a,7b} = 12.6$, $J_{6,7b} = 5.2$, 1 H, H-7b), 4.21 (dd, $J_{6,7a} = 2.7$, 1 H, H-7a), 4.59 (dd, $J_{gem} = 13.6$, $J_{2,CHb} = 3.7$, 1 H, $CHbNO_2$), 4.83 (dd, $J_{2,CHa} = 10.0$, 1 H, $CHaNO_2$), 5.09 (ddd, $J_{5,6} = 9.2$, 1 H, H-6), 5.31 (dd, $J_{2,3} = 3.2$, $J_{3,4} = 9.2$, 1 H, H-3), 5.37 (dd, $J_{4,5} = 2.1$, 1 H, H-4), 5.42 (dd, 1 H, H-5), 6.37 (d, $J_{1,2} = 3.6$, 1 H, H-1)	20.6, 20.7, 20.7, 20.8 (CO*C*H$_3$), 21.9 (C-4′), 26.5 (C-3′), 40.7 (C-2), 48.6 (C-5′), 59.2 (OCH_3), 61.8 (C-7), 63.1 (C-2′), 67.1, 67.8, 67.8 (C-4, C-5, C-6), 68.6 (C-3), 74.1 (*C*H$_2$OMe), 72.2 (CH_2NO_2), 128.3 (C-1), 169.8, 169.8, 169.8, 170.1, 170.5 (*C*OCH$_3$)
(*R*,*R*)-**3b**	1.78–2.03 (m, 4 H, H-3′a, H-3′b, H-4′a, H-4′b), 2.05, 2.06, 2.09, 2.09, and 2.10 (5 s, 15 H, $OCOCH_3$), 2.85–2.90 (m, 1 H, H-5′b), 3.23–3.27 (m, 1 H, H-5′a), 3.33 (dd, $J_{gem} = 9.0$, $J_{2',CH} = 6.3$, 1 H, C*H*bOMe), 3.35 (s, 3 H, OCH_3), 3.40–3.47 (m, 2 H, H-2, H-2′), 3.47 (dd, $J_{2',CH} = 3.5$, 1 H, C*H*aOMe), 4.04 (dd, $J_{7a,7b} = 12.6$, $J_{6,7b} = 5.1$, 1 H, H-7b), 4.20 (dd, $J_{6,7a} = 2.7$, 1 H, H-7a), 4.45 (dd, $J_{gem} = 13.9$, $J_{2,CHb} = 5.8$, 1 H, $CHbNO_2$), 4.78 (dd, $J_{2,CHa} = 8.6$, 1 H, $CHaNO_2$), 5.03 (ddd, $J_{5,6} = 9.2$, 1 H, H-6), 5.11 (dd, $J_{2,3} = 2.1$, $J_{3,4} = 10.1$, 1 H, H-3), 5.41 (dd, $J_{4,5} = 2.0$, 1 H, H-5), 5.46 (dd, 1 H, H-4), 6.42 (d, $J_{1,2} = 3.7$, 1 H, H-1)	20.5, 20.6, 20.7, 20.8 (CO*C*H$_3$), 21.9 (C-4′), 26.6 (C-3′), 41.2 (C-2), 48.7 (C-5′), 59.0 (OCH_3), 61.7 (C-7), 62.6 (C-2′), 67.7, 67.3, 67.7 (C-4, C-5, C-6), 68.1 (C-3), 73.9 (CH_2NO_2), 74.1 (*C*H$_2$OMe), 125.7 (C-1), 169.6, 169.7, 169.8, 170.1 (*C*OCH$_3$)
(*S*,*S*)-**3c**	1.33, 1.49 [2 s, 6 H, 2 $C(CH_3)_2$], 1.51–1.95 (m, 4 H, H-3′a, H-3′b, H-4′a, H-4′b), 2.44–2.52 (m, 1 H, H-5′b), 3.01–3.09 (m, 1 H, H-5′a), 3.31 (s, 3 H, OCH_3), 3.32–3.38 (m, 2 H, H-2′, C*H*bOMe), 3.45 (dd, $J_{gem} = 12.2$, $J_{2'CH} = 6.8$, 1 H, C*H*aOMe), 3.69 (m, 1 H, H-2), 3.96 (d, $J_{3,4} = 3.1$, 1 H, H-4), 4.10 (dd, $J_{2,3} = 9.9$, 1 H, H-3), 4.48, 4.73 (2 d, $J_{gem} = 11.7$, 2 H, OC*H*$_2$Ph), 4.66 (d, $J_{5,6} = 3.8$, 1 H, H-5), 4.72 (dd, $J_{gem} = 13.4$, $J_{2,CH} = 4.3$, 1 H, $CHbNO_2$), 4.81 (dd, $J_{2,CH} = 9.5$, $CHaNO_2$), 5.93 (d, 1 H, H-6), 6.19 (d, $J_{1,2} = 4.1$, 1 H, H-1), 7.33–7.39 (m, 5 H, C_6H_5)	21.8 (C-4′), 26.1, 26.6 [C(*C*H$_3$)$_2$], 26.4 (C-3′), 39.4 (C-2), 48.8 (C-5′), 59.0 (OCH_3), 62.8 (C-2′), 71.7 (O*C*H$_2$Ph), 74.1 (*C*H$_2$OMe), 75.2 (CH_2NO_2), 79.8 (C-3), 80.8 (C-4), 81.6 (C-5), 104.7 (C-6), 111.7 [*C*(CH$_3$)$_2$], 128.1, 128.2, 128.3, 128.5, 136.8 (C-1, C_6H_5)
(*S*,*R*)-**3c**	1.34, 1.49 [2 s, 6 H, $C(CH_3)_2$], 1.75–1.98 (m, 4 H, H-3′a, H-3′b, H-4′a, H-4′b), 2.62–2.67 (m, 1 H, H-5′b), 3.21–3.28 (m 1 H, H-5′a), 3.32–3.36 (m, 1 H, H-2′), 3.35 (s, 3 H, OCH_3), 3.43 (dd, $J_{gem} = 9.3$, $J_{2'CH} = 6.3$, 1 H, C*H*bOMe), 3.50 (dd, $J_{2'CH} = 3.8$, 1 H, C*H*aOMe), 3.69 (m, 1 H, H-2), 3.92 (d, $J_{3,4} = 2.9$, 1 H, H-4), 4.26 (dd, $J_{2,3} = 8.1$, 1 H, H-3), 4.30 (dd, $J_{gem} = 13.2$, $J_{2,CH} = 4.0$, 1 H, $CHbNO_2$), 4.45, 4.70 (2 d, $J_{gem} = 12.0$, 2 H, OC*H*$_2$Ph), 4.64 (d, $J_{5,6} = 3.7$, 1 H, H-5), 4.72 (dd, $J_{2,CH} = 8.7$, 1 H, $CHaNO_2$), 5.94 (d, 1 H, H-6), 6.53 (d, $J_{1,2} = 3.9$, 1 H, H-1), 7.32–7.37 (m, 5 H, C_6H_5)	21.8 (C-4′), 26.1, 26.2 [C(*C*H$_3$)$_2$], 26.6 (C-3′), 39.9 (C-2), 49.0 (C-5′), 59.0 (OCH_3), 63.0 (C-2′), 71.4 (O*C*H$_2$Ph), 73.9, 74.0 (*C*H$_2$OMe, CH_2NO_2), 79.4 (C-3), 81.2 (C-4), 81.5 (C-5), 104.5 (C-6), 111.6 [*C*(CH$_3$)$_2$], 128.1, 128.2, 128.5, 136.5 (C_6H_5), 130.6 (C-1)
(*R*,*R*)-**3c**	1.33, 1.48 [2 s, 6 H, $C(CH_3)_2$], 1.75–1.98 (m, 4 H, H-3′a, H-3′b, H-4′a, H-4′b), 2.68–2.78 (m, 1 H, H-5′b), 3.12–3.22 (m, 1 H, H-5′a), 3.32–3.36 (m, 3 H, H-2′, C*H*$_2$OMe), 3.34 (s, 3 H, OCH_3), 3.69 (m, 1 H, H-2), 3.91 (d, $J_{3,4} = 3.2$, 1 H, H-4), 4.25 (dd, $J_{2,3} = 7.9$, 1 H, H-3), 4.31 (dd, $J_{gem} = 13.3$, $J_{2,CH} = 4.1$, 1 H, $CHbNO_2$), 4.43, 4.69 (2 d, $J_{gem} = 11.7$, 2 H, OC*H*$_2$Ph), 4.63 (d, $J_{5,6} = 3.9$, 1 H, H-5), 4.73 (dd, $J_{2,CH} = 9.0$, 1 H, $CHaNO_2$), 5.93 (d, 1 H, H-6), 6.48 (d, $J_{1,2} = 4.2$, 1 H, H-1), 7.31–7.38 (m, 5 H, C_6H_5)	21.8 (C-4′), 26.0, 26.5 [C(*C*H$_3$)$_2$], 26.4 (C-3′), 39.9 (C-2), 48.9 (C-5′), 59.0 (OCH_3), 62.8 (C-2′), 71.5 (O*C*H$_2$Ph), 73.9 (CH_2NO_2), 74.1 (*C*H$_2$OMe), 79.5 (C-3), 81.3 (C-4), 81.5 (C-5), 104.5 (C-6), 111.6 [*C*(CH$_3$)$_2$], 128.0, 128.2, 128.5, 136.5 (C_6H_5), 130.0 (C-1)

Table 3. (continued)

Product[a]	^{1}H NMR (CDCl$_3$, 500 MHz) δ, J (Hz)	^{13}C NMR (CDCl$_3$, 125.5 MHz) δ
(S,S)-**3d**	1.30, 1.32, 1.46, 1.49 [4 s, 12 H, 2 C(CH$_3$)$_2$], 1.75–1.95 (m, 4 H, H-3′a, H-3′b, H-4′a, H-4′b), 2.78–2.83 (m, 1 H, H-5′a), 3.17–3.26 (m, 1 H, H-5′b), 3.32 (s, 3 H, OCH$_3$), 3.34 (dd, J_{gem} = 9.0, $J_{2',CH}$ = 6.3, 1 H, CHbOMe), 3.40–3.44 (m, 1 H, H-2′), 3.46 (dd, $J_{2',CH}$ = 3.6, 1 H, CHaOMe), 3.48–3.54 (m, 1 H, H-2), 3.73 (dd, $J_{2,3}$ = 9.7, $J_{3,4}$ = 1.7, 1 H, H-3), 4.25 (dd, $J_{4,5}$ = 7.9, 1 H, H-4), 4.29 (dd, $J_{5,6}$ = 2.4, $J_{6,7}$ = 5.0, 1 H, H-6), 4.58 (dd, 1 H, H-5), 4.71 (dd, J_{gem} = 13.6, $J_{2,CHa}$ = 4.6, 1 H, CHaNO$_2$), 4.85 (dd, $J_{2,CHb}$ = 7.8, 1 H, CHbNO$_2$), 5.48 (d, 1 H, H-7), 6.48 (d, $J_{1,2}$ = 4.3, 1 H, H-1)	22.0 (C-4′), 24.5, 24.9, 25.9, 26.0, 26.6 [2 C(CH$_3$)$_2$, C-3′], 40.6 (C-2), 59.2 (OCH$_3$), 62.8 (C-2′), 67.9, 70.5, 70.9, 71.1 (C-3, C-4, C-5, C-6), 74.3, 74.8 (CH$_2$NO$_2$, CH$_2$OMe), 96.4 (C-7), 108.8, 109.5 2 C(CH$_3$)$_2$], 128.8 (C-1)
(S,R)-**3d**	1.29, 1.30, 1.43, 1.48 [4 s, 12 H, 2 C(CH$_3$)], 1.75–1.94 (m, 4 H, H-3′a, H-3′b, H-4′a, H-4′b), 2.74–2.80 (m, 1 H, H-5′a), 3.23–3.28 (m, 1 H, H-5′b), 3.33 (s, 3 H, OCH$_3$), 3.34–3.52 (m, 4 H, H-2, H-2′, CH_2OMe), 4.02 (dd, $J_{2,3}$ = 6.6, $J_{3,4}$ = 1.7, 1 H, H-3), 4.26 (dd, $J_{4,5}$ = 8.0, 1 H, H-4), 4.28 (dd, $J_{5,6}$ = 2.3, $J_{6,7}$ = 5.0, 1 H, H-6), 4.58 (dd, 1 H, H-5), 4.69 (dd, J_{gem} = 13.8, $J_{2,CHa}$ = 4.7, 1 H, CHaNO$_2$), 4.83 (dd, $J_{2,CHb}$ = 7.5, 1 H, CHbNO$_2$), 5.51 (d, 1 H, H-7), 6.58 (d, $J_{1,2}$ = 4.2, 1 H, H-1)	21.9 (C-4′), 24.2, 24.9, 25.9, 26.0, 26.5 2 C(CH$_3$)$_2$, C-3′], 42.2 (C-2), 59.2 (OCH$_3$), 63.9 (C-2′), 67.0, 70.4, 71.0, 71.5 (C-3, C-4, C-5, C-6), 74.2, 74.5 (CH$_2$NO$_2$, CH$_2$OMe), 96.5 (C-7), 108.7, 109.4 [2 C(CH$_3$)$_2$], 130.9 (C-1)
(R,R)-**3d**	1.32, 1.33, 1.45, 1.50 [4 s, 12 H, 2 C(CH$_3$)$_2$, 1.75–1.98 (m, 4 H, H-3′a, H-3′b, H-4′a, H-4′b), 2.73–2.79 (m, 1 H, H-5′a), 3.26–3.31 (m, 1 H, H-5′b), 3.35 (s, 3 H, OCH$_3$), 3.35–3.53 (m, 4 H, H-2, H-2′, CH_2OMe), 4.03 (dd, $J_{2,3}$ = 6.7, $J_{3,4}$ = 1.7, 1 H, H-3), 4.28 (dd, $J_{4,5}$ = 8.0, 1 H, H-4), 4.30 (dd, $J_{5,6}$ = 2.4, $J_{6,7}$ = 5.0, 1 H, H-6), 4.60 (dd, 1 H, H-5), 4.69 (dd, J_{gem} = 13.7, $J_{2,CHa}$ = 4.7, 1 H, CHaNO$_2$), 4.85 (dd, $J_{2,CHb}$ = 7.8, 1 H, CHbNO$_2$), 5.52 (d, 1 H, H-7), 6.62 (d, $J_{1,2}$ = 4.1, 1 H, H-1)	21.7 (C-4′), 24.1, 24.7, 25.7, 25.7, 26.3 [2 C(CH$_3$)$_2$, C-3′], 42.0 (C-2), 58.9 (OCH$_3$), 62.9 (C-2′), 67.3, 70.4, 70.9, 71.4 (C-3, C-4, C-5, C-6), 74.1, 74.2 (CH$_2$NO$_2$, CH$_2$OMe), 96.4 (C-7), 108.5, 109.3 [2 C(CH$_3$)$_2$], 131.1 (C-1)

[a] Satisfactory microanalyses and/or HRMS obtained: C ± 0.22, H ± 0.28, N ± 0.33 and/or 0.002 amu.

sugar moiety, the observed matched pairs [(R)-**1** in both cases)] could be explained by the models shown in the Figure. This considers the asymmetric induction by the chiral nitroolefin, in which the nucleophile would attack on the less hindered *si* face, as previously observed for the reactions of formaldehyde dimethylhydrazone with the same nitroolefins.[6]



2c **2d**

Figure. Asymmetric Induction of Chiral Nitroolefins **2c**, **d**.

Furthermore, the stereochemical results and the de values indicate that in all cases the facial diastereoselectivity induced by the chiral hydrazones is far superior to that induced by the sugar nitroolefin. Thus, using this methodology, both α-epimeric nitriles **4** can be effectively obtained as desired by use of SAMP or RAMP, even when the desired configuration is the opposite to that induced by the sugar moiety.

In conclusion, a methodology has been displayed that, starting from readily available sugar aldehydes and employing formaldehyde SAMP- and RAMP-hydrazones as chiral equivalents of the cyano group, offers a new route for the effective one-C elongation with simultaneous stereoselective introduction of a nitromethyl group. Adequate manipulation of the various functionalities present in the resulting products should allow their use in the stereoselective synthesis of higher nitro-, amino-, and aldehydo-sugars of biological or pharmaceutical interest.

Melting and boiling points were determinated with a Gallenkamp MFB-595 melting point apparatus and are uncorrected. Elemental analyses were carried out at the Instituto Químico de Sarriá, Barcelona, and the Departamento de Química Analítica, Universidad de Sevilla. Optical rotations were measured with a Perkin-Elmer 241 MC polarimeter. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AMX 500 instrument in CDCl$_3$ with either TMS or CHCl$_3$ as an internal reference. EI mass spectra were obtained at 70 eV, using a MS-80 RFA Kratos instrument, an ionising current of 100 μA, an accelerating voltage of 4 KV, and a resolution of 1000 or 10000 (10 % valley definition). The reactions were monitored by ^{1}H 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. The starting materials (S)-1-amino-2-methoxymethylpyrrolidine (SAMP),[9] (R)-1-amino-2-methoxymethylpyrrolidine (RAMP),[9] (S)-(−)-2-methoxymethyl-1-methylideneaminopyrrolidine [(S)-**1**],[4] 3,4,5,6,7-penta-*O*-acetyl-1,2-dideoxy-1-nitro-D-*galacto*-hept-1-enitol (**2a**),[10] 3,4,5,6,7-penta-*O*-acetyl-1,2-dideoxy-1-nitro-D-*manno*-hept-1-enitol (**2b**),[11] and 3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-nitro-α-D-*xylo*-hex-5-enofuranose (**2c**),[12] were prepared according to literature procedures.

(R)-(+)-2-Methoxymethyl-1-methylideneaminopyrrolidine [(R)-1]: To a stirred suspension of paraformaldehyde (0.83 g, 27 mmol) in anhyd pentane (50 mL) cooled at 0 °C was added dropwise (R)-1-amino-2-methoxymethylpyrrolidine (RAMP) (3.00 g, 23 mmol). The mixture was stirred overnight at r.t., dried (Na$_2$SO$_4$), and the solvent was removed under reduced pressure. The crude hydrazone was purified by bulb-to-bulb distillation to afford 3.0 g (92 %) of a colourless oil; bp 50 °C/0.2 Torr; $[\alpha]_D^{22}$ + 127.9 (c = 1, CHCl$_3$).

^{1}H NMR (CDCl$_3$): δ = 1.75–2.05 (m, 4 H, H-3, H-3′, H-4, H-4′), 2.80–2.86 (m, 1 H, H-5b), 3.31–3.36 (m, 1 H, H-5a), 3.38 (s, 3 H, OCH$_3$), 3.42–3.47 (m, 1 H, H-2), 3.54–3.58 (m, 2 H, CH$_2$O), 6.02 (d, J_{gem} = 11.6 Hz, 1 H, CHa=N), 6.13 (d, 1 H, CHb=N).

^{13}C NMR (CDCl$_3$): δ = 22.0 (C-4), 26.7 (C-3), 48.4 (C-5), 59.1 (OCH$_3$), 62.8 (C-2), 74.6 (CH$_2$O), 121.7 (C=N).

Table 4. Spectroscopic Data of β-Nitro Nitriles **4**

Product[a]	^{1}H NMR ($CDCl_3$, 500 MHz) δ, J (Hz)	^{13}C NMR ($CDCl_3$, 125.5 MHz) δ
(*S*)-**4a**	2.03, 2.09, 2.11, 2.22 (4s, 15H, 5$OCOCH_3$), 3.76 (dt, $J_{2,\mathrm{CHaN}} = J_{2,\mathrm{CHbN}} = 7.2$, $J_{2,3} = 2.5$, 1H, H-2), 3.83 (dd, $J_{\mathrm{gem}} = 11.6$, $J_{6,7b} = 7.4$, 1H, H-7b), 4.26 (dd, $J_{6,7a} = 4.9$, 1H, H-7a), 4.57 (dd, $J_{\mathrm{gem}} = 14.1$, 1H, $CHbNO_2$), 4.64 (dd, 1H, $CHaNO_2$), 5.21 (dd, $J_{3,4} = 1.1$, 1H, H-3), 5.33–5.38 (m, 3H, H-4, H-5, H-6)	20.3, 20.4, 20.5, 20.5, 20.6 (CO*C*H_3), 33.0 (C-2), 61.7 (C-7), 65.6 (CH_2NO_2), 67.1, 67.2, 68.9, 71.8 (C-3, C-4, C-5, C-6), 114.1 (C-1), 169.6, 170.0, 170.2, 170.8, 170.9 (*C*OCH_3)
(*R*)-**4a**	2.03, 2.11, 2.12, 2.18, 2.20 (5s, 15H, 5$OCOCH_3$), 3.83 (dd, $J_{\mathrm{gem}} = 11.6$, $J_{6,7b} = 7.4$, 1H, H-7b), 3.84 (dt, $J_{2,\mathrm{CHaN}} = J_{2,3} = 7.4$, $J_{2,\mathrm{CHbN}} = 6.2$, 1H, H-2), 4.27 (dd, $J_{6,7a} = 5.1$, 1H, H-7a), 4.62 (dd, $J_{\mathrm{gem}} = 14.7$, 1H, $CHbNO_2$), 4.76 (dd, 1H, $CHaNO_2$), 5.11 (dd, $J_{3,4} = 1.3$, 1H, H-3), 5.29–5.43 (m, 3H, H-4, H-5, H-6)	20.5, 20.6, 20.7 (CO*C*H_3), 30.8 (C-2), 61.7 (C-7), 66.2, 66.5, 67.1, 67.2, 70.9 (C-3, C-4, C-5, C-6, CH_2NO_2), 114.6 (C-1), 169.5, 170.0, 170.1, 170.3, 170.8 (*C*OCH_3)
(*S*)-**4b**	2.07, 2.09, 2.12, 2.13, 2.19 (5s, 15H, 5$OCOCH_3$), 3.73 (dt, $J_{2,3} = J_{2,\mathrm{CHbN}} = 5.3$, $J_{2,\mathrm{CHaN}} = 8.1$, 1H, H-2), 4.05 (dd, $J_{\mathrm{gem}} = 12.6$, $J_{6,7b} = 5.0$, 1H, H-7b), 4.22 (dd, $J_{6,7a} = 2.8$, 1H, H-7a), 4.63 (dd, $J_{\mathrm{gem}} = 14.4$, 1H, $CHaNO_2$), 4.73 (dd, 1H, $CHbNO_2$), 5.09 (m, 1H, H-6), 5.35–5.48 (m, 3H, H-3, H-4, H-5)	20.3, 20.4, 20.5, 20.7 (CO*C*H_3), 31.3 (C-2), 61.5 (C-7), 66.5, 66.6, 67.6, 68.4, 71.2 (C-3, C-4, C-5, C-6, CH_2NO_2), 115.3 (C-1), 168.9, 169.7, 169.8, 170.4, 170.4 (*C*OCH_3)
(*R*)-**4b**	2.11, 2.17, 2.21, 2.22 (4s, 15H, 5$OCOCH_3$), 3.78 (dt, $J_{2,\mathrm{CHaN}} = J_{2,\mathrm{CHbN}} = 7.0$, $J_{2,3} = 2.0$, 1H, H-2), 4.06 (dd, $J_{\mathrm{gem}} = 12.6$, $J_{6,7b} = 4.7$, 1H, H-7b), 4.22 (dd, $J_{6,7a} = 2.8$, 1H, H-7a), 4.64–4.66 (m, 2H, CH_2NO_2), 5.06–5.12 (m, 2H, H-3, H-6), 5.45 (dd, $J_{4,5} = 2.3$, $J_{5,6} = 9.3$, 1H, H-5), 5.52 (dd, $J_{3,4} = 8.7$, 1H, H-4)	20.4, 20.5, 20.5, 20.6, 20.7 (CO*C*H_3), 31.6 (C-2), 61.4 (C-7), 66.6, 67.2, 67.5, 68.0, 71.6 (C-3, C-4, C-5, C-6, CH_2NO_2), 114.2 (C-1), 169.6, 169.8, 169.8, 170.2, 170.4 (*C*OCH_3)
(*S*)-**4c**	1.32, 1.49 [2s, 6H, $C(CH_3)_2$], 3.78 (ddd, $J_{2,3} = 9.7$, $J_{2,\mathrm{CHaN}} = 8.3$, $J_{2,\mathrm{CHbN}} = 4.3$, 1H, H-2), 4.18 (d, $J_{3,4} = 3.4$, 1H, H-4), 4.45 (dd, 1H, H-3), 4.62–4.81 (m, 5H, CH_2NO_2, OC*H*$_2$Ph, H-5), 5.89 (d, $J_{5,6} = 3.6$, 1H, H-6), 7.34–7.39 (m, 5H, C_6H_5)	26.0, 26.7 [C(*C*H_3)$_2$],. 29.5 (C-2), 72.1 (CH_2NO_2), 73.0 (C-3), 77.0 (O*C*H_2Ph), 81.3 (C-5), 81.5 (C-4), 105.4 (C-6), 112.6 [*C*(CH_3)$_2$], 115.9 (C-1), 128.1, 128.4, 128.6, 136.1 (C_6H_5)
(*R*)-**4c**	1.34, 1.50 [s, 6H, $C(CH_3)_2$], 3.90 (ddd, $J_{2,3} = 6.5$, $J_{2,\mathrm{CHaN}} = 8.0$, $J_{2,\mathrm{CHbN}} = 4.9$, 1H, H-2), 4.11 (d, $J_{3,4} = 3.6$, 1H, H-4), 4.49 (dd, 1H, H-3), 4.60–4.82 (m, 5H, CH_2NO_2, OC*H*$_2$Ph, H-5), 5.97 (d, $J_{5,6} = 3.7$, 1H, H-6), 7.34–7.45 (m, 5H, C_6H_5)	26.1, 26.7 [C(*C*H_3)$_2$], 29.8 (C-2), 71.6 (CH_2NO_2), 72.5 (C-3), 76.7 (O*C*H_2Ph), 81.4 (C-5), 81.7 (C-4), 105.3 (C-6), 112.6 [*C*(CH_3)$_2$], 116.3 (C-1), 128.2, 128.6, 128.8, 135.9 (C_6H_5)
(*S*)-**4d**	1.37, 1.42, 1.50, 1.56 [4s, 12H, $C(CH_3)_2$], 3.67 (ddd, $J_{2,3} = 10.1$, $J_{2,\mathrm{CHbN}} = 6.3$, $J_{2,\mathrm{CHaN}} = 4.4$, 1H, H-2), 4.09 (dd, $J_{3,4} = 1.7$, 1H, H-3), 4.37 (dd, $J_{5,6} = 2.6$, $J_{6,7} = 4.9$, 1H, H-6), 4.45 (dd, $J_{4,5} = 7.8$, 1H, H-4), 4.71 (dd, 1H, H-5), 4.71 (dd, $J_{\mathrm{gem}} = 15.0$, 1H, $CHbNO_2$), 4.78 (dd, 1H, $CHaNO_2$), 5.48 (d, H-7)	24.1, 24.6, 25.7, 25.8 [C(*C*H_3)$_2$], 30.3 (C-2), 65.3 (C-3), 70.2, 70.4, 70.6 (C-4, C-5, C-6), 71.2 (CH_2NO_2), 96.2 (C-7), 109.4, 110.2 [*C*(CH_3)$_2$], 115.9 (C-1)
(*R*)-**4d**	1.34, 1.36, 1.50, 1.57 [4s, 12H, $C(CH_3)_2$], 3.76 (ddd, $J_{2,3} = J_{2,\mathrm{CHbN}} = 5.6$, $J_{2,\mathrm{CHaN}} = 7.0$, 1H, H-2), 4.08 (dd, $J_{3,4} = 1.8$, 1H, H-3), 4.36 (dd, $J_{5,6} = 2.5$, $J_{6,7} = 4.9$, 1H, H-6), 4.36 (dd, $J_{4,5} = 7.9$, 1H, H-4), 4.68 (dd, 1H, H-5), 4.78 (dd, $J_{\mathrm{gem}} = 14.9$, 1H, $CHbNO_2$), 4.84 (dd, 1H, $CHaNO_2$), 5.56 (d, H-7)	24.0, 24.5, 25.5, 25.7 [C(*C*H_3)$_2$], 31.8 (C-2), 64.9 (C-3), 70.0, 70.6, 70.8 (C-4, C-5, C-6), 71.6 (CH_2NO_2), 96.3 (C-7), 109.2, 110.5 [*C*(CH_3)$_2$], 115.9 (C-1)

[a] Satisfactory microanalyses and/or HRMS obtained: C ± 0.18, H ± 0.29, N ± 0.31 and/or 0.002 amu.

$C_7H_{14}N_2O$	calc.	C 59.12	H 9.92	N 19.70
(142.2)	found	58.90	10.03	19.53

6,7-Dideoxy-1,2:3,4-di-*O*-isopropylidene-7-nitro-α-D-*galacto*-hept-1-enopyranose (2d):

To a solution of 6-*O*-acetyl-7-deoxy-1,2:3,4-di-*O*-isopropylidene-7-nitro-D,L-glicero-α-D-*galacto*-1,5-heptopyranose[13] (7.22 g, 0.02 mol) in benzene (250 mL) was added K_2CO_3 (5.53 g, 0.04 mol) with stirring. The mixture was refluxed for 1.5 h, and then allowed to reach r.t. and filtered. The solvent was removed and the residue purified by column chromatography (Et_2O/hexane, 1:5) to afford 4.88 g (81%) of a crystalline solid; mp 140–142°C; $[\alpha]_D^{20}$ -143 ($c = 0.73$, $CHCl_3$).

^{1}H NMR ($CDCl_3$): $\delta = 1.34, 1.36, 1.42, 1.52$ (4s, 12H, CCH_3), 4.33 (dd, $J_{3,4} = 7.7$ Hz, $J_{4,5} = 2.2$ Hz, 1H, H-4), 4.39 (dd, $J_{1,2} = 5.0$ Hz, $J_{2,3} = 2.6$ Hz, 1H, H-2), 4.60 (m, $J_{5,6} = 1.7$ Hz, 1H, H-5), 4.69 (dd, 1H, H-3), 5.59 (d, $J_{1,2} = 5.0$ Hz, 1H, H-1), 7.22 (m, 2H, H-6, H-7).

^{13}C NMR ($CDCl_3$): $\delta = 24.3, 24.6, 25.7, 25.9$ [C(*C*H_3)$_2$], 65.6 (C-6), 70.2 (C-2), 70.7 (C-3), 71.9 (C-4), 96.2 (C-1), 108.9, 110.0 [*C*(CH_3)$_2$], 137.1 (C-6), 140.8 (C-7).

$C_7H_{14}N_2O$	calc.	C C51.82	H 6.36	N 4.65
(301.1)	found	52.02	6.37	4.65

β-Nitrohydrazones 3; General Procedure:

To a solution of the nitroolefin **2** (1 mmol) in anhyd CH_2Cl_2 (1 mL) was added formaldehyde SAMP- or RAMP-hydrazones (**1**; 1.71 g, 1.2 mmol). The mixture was kept at r.t. under Ar atmosphere until the nitroolefin had completely reacted (TLC control). Evaporation of the solvent and the excess of **1** and column chromatography of the residue (Et_2O/hexane 1:1 to 1:8) afforded **3**.

β-Nitro Nitriles 4; General Procedure:

To a suspension of MMPP · $6H_2O$ (0.62 g, 1.25 mmol) in MeOH (4 mL) cooled to 0°C was added dropwise a solution of the β-nitrohydrazone **3** (0.5 mmol) in MeOH (2 mL). The mixture was stirred at 0°C until the hydrazone had completely reacted (~ 5 min, TLC control). CH_2Cl_2 (15 mL) and water (15 mL) were added, the organic layer was separated and washed with brine (15 mL). The organic phase was dried ($MgSO_4$) and evaporated at reduced pressure. The crude product was purified by column chromatography (Et_2O/hexane, 1:4) to give pure **4**.

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