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C-Glycosylmethylene carbenes: synthesis of anhydro-aldose tosylhydrazones as precursors; generation and a new synthetic route to *exo*-glycals

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Acylated anhydro-aldononitriles (glycosyl cyanides) were transformed into anhydro-aldose tosylhydrazones by Raney–nickel reduction in the presence of tosylhydrazine in a one-pot reaction. The configuration of the C=N double bond in these hydrazones was *E* as proven by ^{15}N–^{1}H coupling constants as well as X-ray crystallography. Thermolysis in refluxing 1,4-dioxane of the sodium salts of the tosylhydrazones obtained by sodium hydride (generally 10 eq.) resulted in the formation of anhydro-1-deoxy-ald-1-enitols (*exo*-glycals). "Dimeric" *N*-glycosylmethyl anhydro-aldose tosylhydrazones could also be isolated when the use of less base caused incomplete deprotonation of the starting compounds. This two-step procedure constitutes a novel, reasonably short synthetic pathway to acylated *exo*-glycals from the readily available glycosyl cyanides.

Introduction

Recognition of the essential roles of carbohydrates in various biological events has brought about an enormous development in synthetic carbohydrate chemistry.[1] To get a better insight into the action of carbohydrate derivatives in living organisms, molecules of natural origin as well as their counterparts with similar biological effects and/or chemical structure (the so-called mimetics) need to be prepared in large amounts by chemical synthesis. The design of glycomimetics[2] comprises a variety of structural modifications, among others introduction of double bonds into carbohydrate derivatives to modify conformation, replacement of either or both oxygens in the ring or attached to the anomeric carbon by other atoms to modify chemical properties or stability and changing the ring size, just to mention a few.

Unsaturated carbohydrates, especially glycals (1,4- or 1,5-anhydro-2-deoxypent- or hex-1-enitols, Chart 1 **A** and **B**) and *exo*-glycals (2,5- or 2,6-anhydro-1-deoxyhex- or hept-1-enitols, Chart 1 **D**) play a central role in the aforementioned efforts being themselves glycomimetics on one hand, and offering many elegant synthetic possibilities for further transformations on the other. Syntheses and synthetic uses of glycals[3] are well documented and reviewed, however, seven-membered ring glycals (1,6-anhydro-2-deoxy-hex- or hept-1-enitols, Chart 1 **C**) are scarcely mentioned in the literature.[4] Several synthetic protocols are known for the preparation of *exo*-glycals[5]: olefination of sugar lactones by using the Tebbe reagent,[5a,b] dimethyltitanocene,[5c–e] the Wittig methodology,[5f,g] or addition of *C*-nucleophiles followed by dehydration;[5h] Ramberg–Bäcklund rearrangement of glycosylsulfonyl methanes;[5i–k] oxidation of *C*-glycosyl phenylselenyl methane followed by elimination;[5l] Keck-reaction of glycosylidene dihalides[5m] and hydrogen halogenide eliminations from *C*-glycosyl iodomethanes.[5n–p] With the exception of the last two methods the applied (generally strongly basic) reaction conditions require *O*-benzyl (or other base stable) protecting groups. On the other hand, *O*-acylated *exo*-glycals, which can be more advantageous *e.g.* for radical-mediated transformations, are accessible only *via* laborious preparation of precursors.[5m–p]

A not yet studied possibility for the formation of septanose glycals/*exo*-glycals may be the rearrangement of a carbene attached to the anomeric carbon of a sugar derivative (Scheme 1, **I**). To this end one has to find access to suitable precursors of such intermediates and to study the possibilities of their transformations outlined in Scheme 1. 1,2-*O* and 1,2-*C* shifts might result in seven-membered ring glycals **III** and **IV**, and the products of the two routes would be indistinguishable from each other if $R^1 = R^2$. Shift of the R^2 substituent (1,2-*H* shift if R^2 = H) should lead to *exo*-glycal derivatives **II**. Other pathways than substituent shifts may also be operative and should be considered depending on the structure of the products.[6]

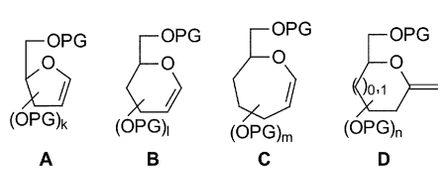
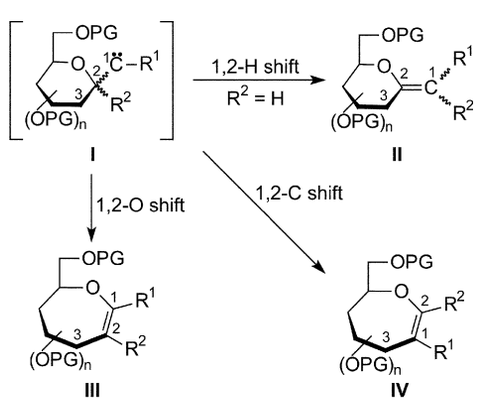


Chart 1



Scheme 1

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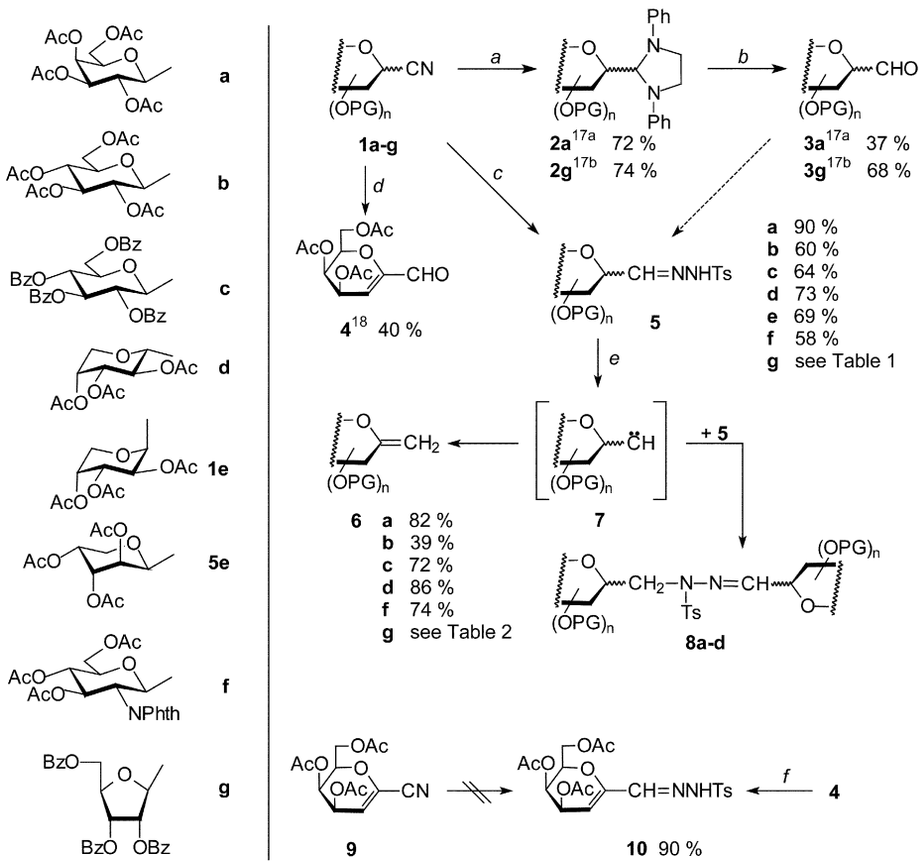

Scheme 2 *a*: Raney-Ni, NaH_2PO_2, $PhNHCH_2CH_2NHPh$, pyridine, AcOH, H_2O; *b*: *p*-TsOH·H_2O, acetone, CH_2Cl_2; *c*: Raney-Ni, NaH_2PO_2, $TsNHNH_2$, pyridine, AcOH, H_2O; *d*: Raney-Ni, NaH_2PO_2, pyridine, AcOH, H_2O; *e*: NaH, abs. 1,4-dioxane, reflux; *f*: $TsNHNH_2$, *p*-TsOH, molecular sieves (3 Å) abs. 1,4-dioxane.

In this paper we present a full account of our investigations into the preparation of 2,5- and 2,6-anhydro-aldose tosylhydrazones as precursors of *C*-glycosylmethylene carbenes (**I**, $R^1 = R^2 = H$) whose generation and ensuing transformation lead to *exo*-glycals **II**.[7]

Results and discussion

Precursors

From the classes of compounds known to be suitable for carbene generation[8] *C*-glycosyl derivatives of diazomethane,[9] monohalomethanes,[5n–p,10] oxirane,[11] and tetrazole[12] have so far been described in the literature. Since *C*-glycosyl diazomethanes are extremely labile,[13] and the preparation of *C*-glycosyl halomethanes[14] as well as oxiranes is rather lengthy, and because carbene generation from the latter can be expected to occur at the least substituted carbon, only 5-glycosyl tetrazoles have been investigated as precursors of *C*-glycosylmethylene carbenes. As these experiments were rather discouraging (under several thermolytic or photolytic conditions either decomposition or no reaction was observed) other precursors have been sought for.

A widely used method for the generation of carbenes is the aprotic Bamford–Stevens reaction: thermo- or photolysis of tosylhydrazone salts.[15] The corresponding precursors of *C*-glycosylmethylene carbenes, *i.e.* anhydro-aldose tosylhydrazones (**5** in Scheme 2) can expectedly be prepared from anhydro-aldoses **3**, however, these "*C*-glycosyl aldehydes", although known, are not readily accessible especially with pyranoid rings mainly because of the lengthiness of the preparative procedures.[16] One of the most straightforward ways to obtain *C*-glycosyl aldehydes is reduction of the nitrile moiety in anhydro-aldononitriles (glycosyl cyanides) **1** by Raney-nickel and sodium hypophosphite in aqueous acetic acid and pyridine.[17] Under these conditions the product should be trapped as an imidazolidine derivative **2** by 1,2-dianilinoethane, because, in the absence of a trapping agent, the reaction gave *e.g.* 2,6-anhydro-ald-2-enose **4** (1-formyl-galactal) as the ultimate product.[18] *C*-Glycosyl aldehyde **3** can be obtained from **2** by acid catalyzed hydrolysis in moderate yields.

The conversion of nitriles to aldehydes with Raney-nickel in aqueous alcohols under hydrogen atmosphere was studied in some details and trapping the intermediate with a carbonyl reagent proved advantageous to prevent formation of the corresponding methylamine derivative.[19] While 1,2-dianilinoethane mentioned above and semicarbazide were very effective, phenylhydrazine was less efficient, and tosyl- and benzoylhydrazine as well as hydroxylamine were reported to give no useful results.[20]

In keeping with the above reports we have found that the reduction of **1** with Raney-nickel and sodium hypophosphite in aqueous acetic acid and pyridine in the presence of semicarbazide gave anhydro-aldose semicarbazones.[21] In our hands, contrary to the reported failure, tosylhydrazine proved also effective and besides several non-sugar aldehyde tosylhydrazones[22] anhydro-aldose tosylhydrazones **5** were isolated in acceptable to good yields (Table 1).

As little as 10% excess reagent tosylhydrazine was sufficient to obtain the expected hydrazone (entry 2), and the crude products were generally pure enough for further transformations. The reaction of **1c** led to a complex mixture at room temperature, however, at 40 °C **5c** could be isolated in an acceptable yield (entry 6). Under the same conditions unsaturated nitrile **9** gave a mixture of products which were not separated. The corresponding tosylhydrazone **10** was obtained by a conventional condensation of 1-formyl-galactal **4** with tosylhydrazine.

Table 1 Preparation of 2,5- and 2,6-anhydro-aldose tosylhydrazones at room temperature

Entry	Starting compound 1	mmol	$TsNHNH_2$/mmol (eq.)	React. time[a]/h	Product	Isolated yield[b](%)
1	**a**	8.40	14.28 (1.7)	4	**5a**	87[c]
2	**a**	11.19	12.31 (1.1)	7	**5a**	90[c]
3	**a**	0.14	0.24 (1.7)	3	**5a**	55
4	**b**	0.98	1.67 (1.7)	6	**5b**	60[d]
5	**c**	0.17	0.29 (1.7)	6	[e]	
6	**c**	0.86	1.46 (1.7)	2[f]	**5c**	64
7	**d**	3.50	4.20 (1.2)	4	**5d**	73[g]
8	**e**	0.70	0.84 (1.2)	5	**5e**	69
9	**f**	1.13	1.36 (1.2)	5	**5f**	58
10	**g**	0.21	0.36 (1.7)	4	**5g**	[h]

[a] The reaction time may depend on the quality of the Raney-nickel. [b] By column chromatography. [c] Crude product. [d] 94% conversion. [e] Complex reaction mixture. [f] Reaction temperature: 40 °C. [g] By crystallization. [h] This product could not be isolated in pure state.

The ^{1}H NMR spectra of compounds **5** exhibited resonances for the 4-methylbenzenesulfonyl moiety (δ 2.2–2.4 ppm, 3H singlets for CH_3; 6.9–7.8 ppm, two 2H doublets, J = 7.9–8.1 Hz, for the aromatic protons), the NH proton (δ 8.1–11.6 ppm, 1H broad singlets), and H-1 (δ 7.0–7.3 ppm, 1H doublets, $J_{1,2}$ = 6.3–6.8 Hz for the 2,3-*trans* configurated **5a**–**d**, 4.8 Hz for **5e**, 5.5 Hz for **5f**, and 6.0 Hz for **5g**). The vicinal couplings indicated that the sugar moieties existed in the conformations depicted for **5a**–**d**,**f**, with **5e** undergoing a conformational change as compared to the parent compound **1e** to accommodate the bulky tosylhydrazone moiety in an equatorial position. In the ^{13}C NMR spectra characteristic signals appeared for the 4-methylbenzenesulfonyl groups (δ 144–145, 135–137, 127–131 ppm for the aromatic carbons, 21.4–21.8 ppm for CH_3), for C-1 (δ 143–146 ppm), and for the sugar carbons as expected.

Each of these spectra exhibited one set of resonances showing that one diastereomer of **5** was present in the samples. From the gradient enhanced ^{15}N–^{1}H long-range correlation experiments (G-HSQMBC)[23] all of the chemical shifts and coupling constants of ^{15}N have been obtained (Fig. 1). On the basis of the sign and magnitude of two- and three-bond ^{15}N–^{1}H coupling constants,[24] the configuration of the carbon–nitrogen double bond in the $-CH_b{=}N_b{-}N_aH_a$ moiety could unambiguously be assigned. The value of 3.7 Hz measured for $^2J_{NbHb}$ suggests an *anti* orientation of the lone-pair electrons on nitrogen (δ_{Nb} = 325.21 ppm) to the methine proton attached to the adjacent carbon, *i.e. E* configuration around the C=N double bond. The value of three-bond coupling constants, $^3J_{NaHb}$ = 7.9 Hz (where δ_{Na} = 167.24 ppm), indicates a *cis*-arrangement of the relevant atoms as well. This conclusion was corroborated by a single crystal X-ray investigation of **5d** (Fig. 2).

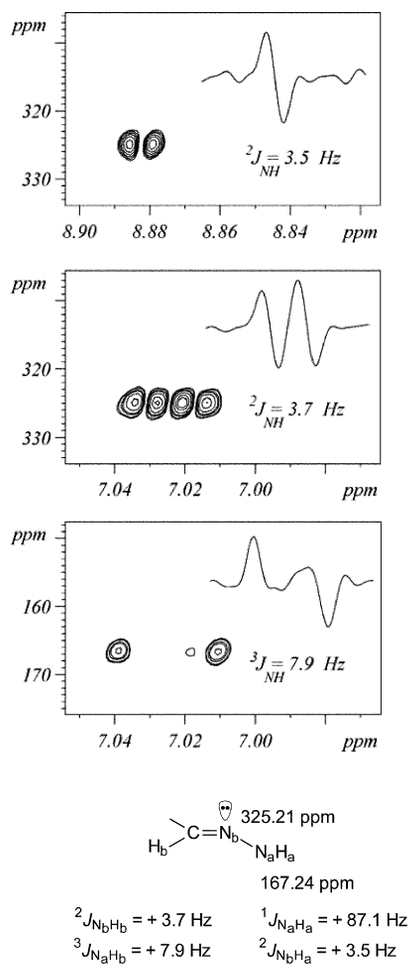

Fig. 1 Expansion of the relevant parts of the ^{15}N–^{1}H HSQMBC spectrum of **5d** used to establish the configuration of the C=N double bond.

Generation of *C*-glycosylmethylene carbenes and isolation of their ensuing products

According to the Bamford–Stevens protocol, generation of carbenes can be effected by photo- or thermolysis of (usually sodium) salts of tosylhydrazones in an aprotic solvent.[15] Because of milder conditions photolysis of the sodium salt of **5a** obtained with sodium hydride in 1,4-dioxane was tried first. After 4.5 hours irradiation with a 150 W mercury lamp in a quartz tube the starting material disappeared, and a complex reaction mixture was obtained. The only product to be isolated was **6a** (8%). Use of other conditions, like *t*BuOK in *t*BuOH did not give better results.

Thermolytic reactions (Table 2) were carried out by placing a base into a solvent, which was heated to reflux and a solution of **5** in the same solvent was added dropwise to the vigorously stirred refluxing mixture. A comparison of the conditions in entries 1–5 indicates that NaH in 1,4-dioxane gave the best isolated yields. Increasing the excess of the base enhanced the proportion of **6a** over **8a** (Entries 6 and 7) and similar observations were made in other cases, as well (Entries 8–13). The formation of compounds **8** suggested that with incomplete deprotonation of **5** the formed carbene (**7**) could insert into the NH bond of **5** (or, alternatively, the probable intermediate *C*-glycosyl diazomethane alkylated **5**) as it was observed with other substrates as well.[25] Since compounds **6** formed in rather clean reactions (in reactions of entries 7, 11, 13, and 15 TLC showed only the product) and were isolated in fairly good yields, it can be concluded that the main pathway for the transformation of carbenes **7** is the 1,2-*H* shift and the other possibilities shown in Scheme 1 play only a subordinate role if any.

The Bamford–Stevens reaction of **10** gave isolable products under neither photolytic nor thermolytic conditions.

Table 2 Generation of *C*-glycosylmethylene carbenes by thermolysis and isolation of their ensuing products

	Starting compound				Isolated yield[a] (%)	
Entry	**5**	mmol	Base (eq.)	Solvent	**6**	**8**
1	**a**	0.57	*t*BuOK (2.0)	*t*BuOH	7	Not isolated
2	**a**	0.38	NaOMe (3.0)	Diglyme	15	14
3	**a**	0.57	NaH (2.4)	Diglyme	8	18
4	**a**	0.57	NaOMe (2.0)	1,4-Dioxane	26	19
5	**a**	0.57	NaH (1.2)	1,4-Dioxane	52	17
6	**a**	0.38	NaH (5.0)	1,4-Dioxane	59	Not isolated
7	**a**	0.76	NaH (10.0)	1,4-Dioxane	82	Not formed
8	**b**	0.38	NaH (1.7)	1,4-Dioxane	11	59
9	**b**	0.12	NaH (10.0)	1,4-Dioxane	39	22
10	**c**	0.33	NaH (2.2)	1,4-Dioxane	16	45
11	**c**	0.26	NaH (10.0)	1,4-Dioxane	72	Not formed
12	**d**	0.66	NaH (1.2)	1,4-Dioxane	25	30
13	**d**	0.44	NaH (10.0)	1,4-Dioxane	86	Not formed
14	**e**	0.22	NaH (2.0)	1,4-Dioxane	18	Not observed
15	**f**	0.26	NaH (10.0)	1,4-Dioxane	74	Not formed
16	**g**	[b]	NaH (~2.0)	1,4-Dioxane	25[c]	Not observed

[a] By column chromatography. [b] From the crude product. [c] Yield from **1g**.

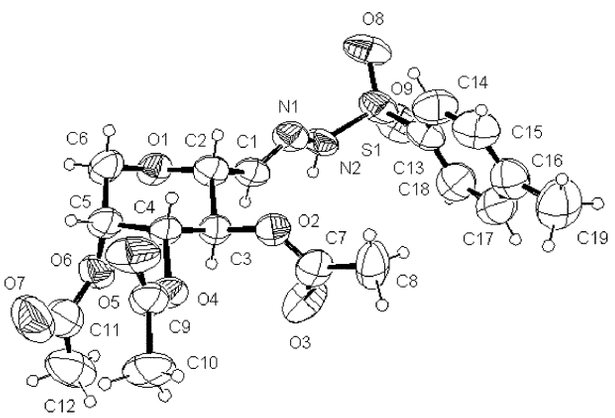

Fig. 2 ORTEP drawing of **5d**. Selected bond length (Å), angle (°) and torsion angle (°) data: C1–C2 1.474(8), C1–N1 1.243(7), N1–N2 1.390(7), N2–S1 1.615(6), S1–O8 1.443(5), S1–O9 1.444(5), S1–C13 1.741(8); C2–C1–N1 120.9(7), C1–N1–N2 116.2(8), N1–N2–S1 118.8(6), N2–S1–O8 106.6(4), N2–S1–O9 104.8(4); O1–C2–C1–N1 125.2, C2–C1–N1–N2 −175.4.

Exo-glycals **6** exhibited characteristic resonances in their ^{1}H NMR spectra[26] for H-1 (δ 4.6–5.0 ppm) and H-1′ (δ 4.2–4.7 ppm) which appeared as triplets ($J_{1,1'}$ = 1.5–2.1 Hz, $J_{1,3}$ < 1 to 1.5 Hz, $J_{1',3}$ < 1 to 1.8 Hz). Signals for C-1 and C-2 were observed around 95–97 ppm and 152–155 ppm for **6a**–**f** and at 87.1 and 157.7 ppm for **6g**, respectively. All other protons and carbons resonated as expected. For **8d** a complete assignment of proton resonances was accomplished by COSY experiments.

In summary, the Raney-nickel–sodium-hypophosphite reduction of the nitrile group in anhydro-aldononitriles (glycosyl cyanides) in the presence of tosylhydrazine constitutes a simple method to obtain anhydro-aldose tosylhydrazones. The scope and limitations of this reductive transformation as to the preparation of other azomethine derivatives of anhydro-aldoses have been described elsewhere.[21] Aprotic Bamford–Stevens reaction of these tosylhydrazones opens a new way to *exo*-glycals which have thus become easily accessible with acyl protecting groups as well.

Experimental

General experimental methods

Melting points were measured on a Kofler hot-stage apparatus and are uncorrected. Optical rotations were determined with a Perkin-Elmer 241 polarimeter at room temperature. $[a]_D$ values are given in 10^{-1}deg cm^2 g^{-1}. IR spectra were taken with a Perkin-Elmer 16 PC FT-IR spectrometer. Routine NMR spectra were recorded with Bruker WP 360 SY (360/90 MHz for ^{1}H/^{13}C) and Avance DRX 500 (500/125/50 MHz for ^{1}H/^{13}C/^{15}N) spectrometers, *J* values are quoted in Hz. Chemical shifts are referenced to Me_4Si (^{1}H), to the residual solvent signals (^{13}C), or to NH_4Cl as external standard (^{15}N). TLC was performed on DC-Alurolle Kieselgel 60 F_{254} (Merck); the plates were visualized by gentle heating or with UV light. For column chromatography Kieselgel 60 (Merck) was used. Organic solutions were dried on $MgSO_4$, and concentrated *in vacuo* at 40–50 °C (water bath).

^{15}N NMR experimental

NMR experiments were performed on a Bruker DRX 500 spectrometer equipped with a triple resonance (^{1}H/^{13}C/^{15}N) x,y,z-gradient probe. The temperature for all measurements was set to 300 K. All spectra were processed with XWINNMR 2.6. Samples of 5–10 mg in 600 µl $CDCl_3$ or C_6D_6 were used for all experiments, except for the long range ^{1}H–^{15}N correlation spectra of **5d** (~40–60 mg in 500 µl $CDCl_3$).

^{1}H NMR assignments were established on the basis of gradient enhanced DQF-COSY spectra.[27] Proton chemical shifts (referenced to internal TMS) and scalar coupling constants were extracted from the resolution enhanced 1D proton spectra. COSY spectra were recorded with 512 × 2k data points, spectral widths 4000 Hz, number of transients 4 and recycle delay of 1.8 s.

Proton–nitrogen coupling constants were measured by the recently proposed gradient enhanced HSQMBC experiment[23] (heteronuclear single quantum multiple bond correlation) with selective excitation of CH_b and N_aH_a protons. Selective excitation of proton resonances was achieved by a Gaussian pulse of 35 ms. Two HSQMBC spectra were acquired with 150 × 512 data points, spectral width of 100000 Hz in ^{15}N and 500 Hz in ^{1}H dimension, number of transients 16 and recycle delay of 2.0 s. The relevant two- and three-bond proton–nitrogen coupling constants (Fig. 1) were determined from the pure absorption phase multiplets after sufficient zero-filling during processing to establish 0.3 Hz resolution in the F2 dimension. In-phase splitting of the multiplets is due to proton–proton coupling, while the heteronuclear coupling yields antiphase multiplet structure (see Fig. 1).

General procedure for the synthesis of anhydro-aldose tosylhydrazones 5

(For the actually used amounts of reagents see Table 1): Raney-nickel (1.5 g per 1 mmol substrate, from an aqueous suspension,

Merck) was added at room temperature to a vigorously stirred solution of pyridine (5.7 mL per 1 mmol substrate), acetic acid (3.4 mL per mmol substrate), and water (3.4 mL per 1 mmol substrate). Then sodium hypophosphite (0.74 g, 8.4 mmol), tosylhydrazine (0.20 g–0.32 g, 1.1–1.7 mmol), and the corresponding anhydro-aldononitrile **1** (1 mmol) were added to the mixture. When the reaction was complete (TLC, eluent: ethyl acetate–hexane 1 : 1) the insoluble materials were filtered off with suction, and washed with dichloromethane (10 mL). The organic layer of the filtrate was separated, washed with water (3 mL), 10% aqueous hydrogen chloride solution (2 × 3 mL), cold, saturated sodium hydrogencarbonate solution (2 × 3 mL), water (3 mL), and then dried on anhydrous magnesium sulfate. The solution was concentrated under reduced pressure, and traces of pyridine were removed by repeated co-evaporations with toluene. The residue was purified by column chromatography (eluent: ethyl acetate–hexane 1 : 1 or 1 : 2) to give **5a**–**c**,**e**, and **f**, while **5d** was obtained by crystallization from a mixture of ethyl acetate and hexane.

General method for the synthesis of *exo*-glycals 6

(For the actual amounts of reagents see Table 2): Sodium hydride (0.24 g, 10 mmol, or the amount indicated in Table 2) was added to dry 1,4-dioxane (25 mL). The suspension was stirred and heated to reflux, and then a solution of a tosylhydrazone **5** (1 mmol) in dry 1,4-dioxane (25 mL) was added dropwise. When the reaction was complete (TLC, eluent: ethyl acetate–hexane 1 : 1), the mixture was cooled down, and the insoluble material filtered off. The solvent was removed under diminished pressure, and the residue was purified by column chromatography (eluent: gradient of ethyl acetate–hexane 1 : 2 to 1 : 1) to give *exo*-glycals **6a**–**d**,**f**, and **g**.

Isolation of compounds 8

These compounds were obtained from reactions conducted under conditions given above for *exo*-glycals **6** modified according to the data shown in Table 2. Isolation of **8** was effected by column chromatography (eluent: gradient of ethyl acetate–hexane 1 : 2 to 1 : 1).

3,4,5,7-Tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-L-*manno*-heptose tosylhydrazone (5a). Colourless syrup; $[a]_D$ + 6 (*c* 0.97 in $CHCl_3$); δ_H (360 MHz; DMSO-d_6) 11.62 (1 H, br s, NH), 7.67 (2 H, d, *J* 7.9, Ts), 7.42 (2 H, d, *J* 7.9, Ts), 7.00 (1 H, d, $J_{1,2}$ 6.7, H-1), 5.29 (1 H, d, $J_{5,6}$ < 1.0, H-5), 5.22 (1 H, dd, $J_{4,5}$ 3.1, H-4), 4.95 (1 H, dd, $J_{3,4}$ 10.4, H-3), 4.24–4.20 (1 H, m, H-6), 4.14 (1 H, dd, $J_{2,3}$ 9.8, H-2), 4.00 (1 H, dd, $J_{6,7'}$ 4.9, $J_{7,7'}$ 11.6, H-7′), 3.93 (1 H, dd, $J_{6,7}$ 7.4, H-7), 2.37 (3 H, s, CH_3-Ts), 2.11, 1.98, 1.90, 1.66 (12 H, 4 s, 4 × OAc); δ_C (90 MHz; $CDCl_3$) 170.6, 170.5, 170.2, 170.1 (C=O), 144.1 (C-1), 144.1, 135.5 (Ts quaternary), 129.6, 127.9 (Ts), 78.2, 74.3, 71.0, 67.6, 66.9 (C-2, C-3, C-4, C-5, C-6), 61.7 (C-7), 21.4 (CH_3-Ts), 20.6, 20.2 (CH_3); IR ν_{max}/cm^{-1} 3208, 1752, 1372, 1228, 1166, 1054 (Found: C, 49.91; H, 5.45; N, 5.42. Calc. for $C_{22}H_{28}N_2O_{11}S$: C, 50.00; H, 5.34; N, 5.30%).

3,4,5,7-Tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-D-*gulo*-heptose tosylhydrazone (5b). Colourless syrup; $[a]_D$ − 8 (*c* 1.33 in $CHCl_3$); δ_H (360 MHz; $CDCl_3$) 9.16 (1 H, br s, NH), 7.80 (2 H, d, *J* 7.9, Ts), 7.34 (2 H, d, *J* 7.9, Ts), 7.00 (1 H, d, $J_{1,2}$ 6.3, H-1), 5.26 (1 H, dd, $J_{3,4}$ 9.4, H-3), 5.05 (1 H, dd, $J_{4,5}$ 10.0, H-4), 5.01–4.94 (1 H, m, H-5), 4.24 (1 H, dd, $J_{7,7'}$ 12.2, H-7), 4.07 (1 H, dd, H-7′), 3.99 (1 H, dd, $J_{2,3}$ 9.5, H-2), 3.72 (1 H, ddd, $J_{5,6}$ 9.5, $J_{6,7}$ 5.3, $J_{6,7'}$ 1.8, H-6), 2.42 (3 H, s, CH_3-Ts), 2.07, 2.03, 2.01, 1.72 (12 H, 4 s, 4 × OAc); δ_C (90 MHz; $CDCl_3$) 170.8, 170.6, 170.2, 169.6 (C=O), 144.3, 135.5 (Ts quaternary), 143.7 (C-1), 129.8, 128.0 (Ts), 77.8, 75.9, 73.1, 69.6, 68.3 (C-2, C-3, C-4, C-5, C-6), 62.1 (C-7), 21.6 (CH_3-Ts), 20.8, 20.7, 20.3 (CH_3); IR ν_{max}/cm^{-1} 3186, 1754, 1368, 1226, 1166, 1036 (Found: C, 50.15; H, 5.48; N, 5.21. Calc. for $C_{22}H_{28}N_2O_{11}S$: C, 50.00; H, 5.34; N, 5.30%).

3,4,5,7-Tetra-*O*-benzoyl-2,6-anhydro-D-*glycero*-D-*gulo*-heptose tosylhydrazone (5c). Colourless syrup; $[a]_D$ + 4 (*c* 1.00 in $CHCl_3$); δ_H (360 MHz; $CDCl_3$) 8.12 (1 H, br s, NH), 8.04–7.74 (8 H, m, OBz), 7.58 (2 H, d, *J* 7.9, Ts), 7.57–7.21 (12 H, m, OBz), 7.16 (1 H, d, $J_{1,2}$ 6.3, H-1), 6.90 (2 H, d, *J* 7.9, Ts), 5.93, 5.67, 5.41 (3 H, 3 pseudo t, *J* 9.5, H-3, H-4, H-5), 4.58 (1 H, dd, $J_{7,7'}$ 12.1, H-7′), 4.43 (1 H, dd, H-7), 4.36 (1 H, dd, $J_{2,3}$ 9.5, H-2), 4.15 (1 H, ddd, $J_{6,7}$ 5.3, $J_{6,7'}$ 2.1, H-6), 2.19 (3 H, s, CH_3); δ_C (90 MHz; $CDCl_3$) 166.3, 165.9, 165.6, 165.3 (C=O), 144.1 (C-1), 143.7, 135.2 (Ts quaternary), 133.6, 133.4, 133.2, 129.8, 129.6, 129.3, 128.4, 127.3 (Ts, OBz), 128.7, 128.6 (OBz quaternary), 78.1, 76.2, 73.7, 70.7, 69.3 (C-2, C-3, C-4, C-5, C-6), 63.2 (C-7), 21.6 (CH_3); IR ν_{max}/cm^{-1} 3200, 1732, 1452, 1268, 1166, 1094, 710 (Found: C, 64.82; H, 4.74; N, 3.72. Calc. for $C_{42}H_{36}N_2O_{11}S$: C, 64.94; H, 4.67; N, 3.61%).

3,4,5-Tri-*O*-acetyl-2,6-anhydro-D-*manno*-hexose tosylhydrazone (5d). White crystals; mp 83–86 °C; $[a]_D$ − 35 (*c* 1.01 in $CHCl_3$); δ_H (360 MHz; $CDCl_3$) 8.93 (1 H, br s, NH), 7.81 (2 H, d, *J* 7.9, Ts), 7.33 (2 H, d, *J* 7.9, Ts), 7.03 (1 H, d, $J_{1,2}$ 6.8, H-1), 5.33 (1 H, br s, H-5), 5.18 (1 H, dd, $J_{3,4}$ 10.0, H-3), 5.09 (1 H, dd, $J_{4,5}$ 3.1, H-4), 3.99 (1 H, d, $J_{5,6}$ < 1, $J_{6,6'}$ 13.1, H-6), 3.89 (1 H, dd, $J_{2,3}$ 9.5, H-2), 3.68 (1 H, d, $J_{5,6'}$ < 1, H-6′), 2.42 (CH_3-Ts), 2.15, 2.01, 1.75 (9 H, 3 s, 3 × OAc); δ_C (90 MHz; $CDCl_3$) 170.6, 170.2, 170.0 (C=O), 144.3 (C-1), 144.0, 135.3 (Ts quaternary), 129.5, 127.9 (Ts), 78.5, 70.5, 68.4, 67.1 (C-2, C-3, C-4, C-5), 67.8 (C-6), 21.4 (CH_3-Ts), 20.8, 20.5, 20.2 (CH_3); IR ν_{max}/cm^{-1} 3202, 1748, 1372, 1224, 1166, 1050 (Found: C, 50.07; H, 5.39; N, 6.05. Calc. for $C_{19}H_{24}N_2O_9S$: C, 49.99; H, 5.30; N, 6.14%).

3,4,5-Tri-*O*-acetyl-2,6-anhydro-D-*gluco*-hexose tosylhydrazone (5e). Colourless syrup; $[a]_D$ − 4 (*c* 1.00 in $CHCl_3$); δ_H (360 MHz; acetone-d_6) 10.1 (1 H, br s, NH), 7.75 (2 H, d, *J* 8.1, Ts), 7.39 (2 H, d, *J* 8.1, Ts), 7.25 (1 H, d, $J_{1,2}$ 4.8, H-1), 5.31 (1 H, dd, $J_{4,5}$ 3.8, H-4), 5.07 (1 H, ddd, $J_{5,6}$ 10.0, $J_{5,6'}$ 3.3, H-5), 4.99 (1 H, dd, $J_{2,3}$ 2.2, H-2), 4.44 (1 H, dd, $J_{3,4}$ 4.5, H-3), 3.83 (1 H, dd, $J_{6,6'}$ 11.0, H-6′), 3.71 (1 H, dd, H-6), 2.41 (3 H, s, CH_3-Ts), 2.11, 1.96, 1.94 (9 H, 3 s, 3 × OAc); δ_C (90 MHz; acetone-d_6) 170.1, 169.8 (C=O), 146.2 (C-1), 144.7, 137.2 (Ts quaternary), 130.4, 128.5 (Ts), 74.1, 69.9, 66.9, 66.3 (C-2, C-3, C-4, C-5), 64.0 (C-6), 21.4 (CH_3-Ts), 20.7, 20.6, 20.5 (CH_3); IR ν_{max}/cm^{-1} 3208, 1750, 1372, 1222, 1066 (Found: C, 49.88; H, 5.39; N, 6.22. Calc. for $C_{19}H_{24}N_2O_9S$: C, 49.99; H, 5.30; N, 6.14%).

4,5,7-Tri-*O*-acetyl-2,6-anhydro-3-deoxy-3-phthalimido-D-*glycero*-D-*gulo*-heptose tosylhydrazone (5f). White crystals; mp 207 °C dec.; $[a]_D$ + 65 (*c* 1.01 in $CHCl_3$); δ_H (360 MHz; DMSO-d_6) 11.48 (1 H, br s, NH), 7.90–7.80 (4 H, m, Phth), 7.34 (2 H, d, *J* 7.9, Ts), 7.10 (1 H, d, $J_{1,2}$ 5.5, H-1), 7.07 (2 H, d, *J* 7.9, Ts), 5.62, 5.02, 4.30 (3 H, 3 pseudo t, *J* 9.5–10.0, H-3, H-4, H-5), 4.87 (1 H, dd, $J_{2,3}$ 10.4, H-2), 4.16 (1 H, dd, $J_{7,7'}$ 12.5, H-7), 4.07–4.03 (2 H, m, H-6, H-7′), 2.27 (3 H, s, CH_3-Ts), 2.02, 1.99, 1.76 (9 H, 3 s, 3 × OAc); δ_C (90 MHz; $CDCl_3$) 170.8, 170.3, 169.7, 168.0, 167.5 (C=O), 144.0 (C-1), 144.2, 135.1 (Ts quaternary), 131.6, 131.5 (Phth quaternary), 134.4, 123.9 (Phth), 129.6, 127.8 (Ts), 76.1, 73.9, 71.3, 68.9 (C-2, C-4, C-5, C-6), 62.3 (C-7), 52.3 (C-3), 21.8 (CH_3-Ts), 20.9, 20.7, 20.6 (CH_3); IR ν_{max}/cm^{-1} 3194, 1750, 1718, 1384, 1230, 1166, 1042 (Found: C, 54.72; H, 4.92; N, 6.95. Calc. for $C_{28}H_{29}N_3O_{11}S$: C, 54.63; H, 4.75; N, 6.83%).

3,4,6-Tri-*O*-benzoyl-2,5-anhydro-D-*allo*-hexose tosylhydrazone (5g). Crude product, colourless syrup; δ_H (360 MHz; $CDCl_3$) 8.35 (1 H, br s, NH), 8.08–7.27 (15 H, m, Bz), 7.74 (2 H, d, *J* 8.2, Ts), 7.16 (1 H, d, $J_{1,2}$ 6.0, H-1), 7.11 (2 H, d, *J* 8.2, Ts), 5.69 (1 H, dd, $J_{4,5}$ 3.8, H-4), 5.64 (1 H, dd, $J_{3,4}$ 5.5, H-3), 4.83 (1 H, t, $J_{2,3}$ 6.0, H-2), 4.64 (1 H, dd, $J_{6,6'}$ 11.4, H-6′), 4.58 (1 H, dd, $J_{5,6}$ 3.8, $J_{5,6'}$ 3.2, H-5), 4.47 (1 H, dd, H-6), 2.27 (3 H, s, CH_3); δ_C (90 MHz; $CDCl_3$) 166.3, 165.4, 165.2 (C=O), 145.7 (C-1), 144.0, 135.2 (Ts quaternary), 135.5, 129.8, 129.6, 128.6,

128.5 (Ts, OBz), 128.9 (OBz quaternary), 80.5, 80.0, 73.4, 72.8 (C-2, C-3, C-4, C-5), 64.4 (C-6), 21.5 (CH_3); IR ν_{max}/cm^{-1} 3208, 1728, 1452, 1270, 1168, 710.

4,5,7-Tri-*O*-acetyl-2,6-anhydro-3-deoxy-D-*lyxo*-hept-2-enose tosylhydrazone (10). Formyl galactal **4** (200 mg, 0.66 mmol) was dissolved in dry 1,4-dioxane (2 mL), molecular sieves (3 Å) and then a solution of tosylhydrazine (150 mg, 0.78 mmol) in dry 1,4-dioxane (2 mL) were added in one portion, followed by 4-methylbenzenesulfonic acid (12 mg, 0.066 mmol). The mixture was stirred at room temp. until disappearance of the starting material (1–2 days). After filtration and evaporation of the solvent the residue was dissolved in diethyl ether, washed with water, dried, and the solvent removed. Attempted purification by silica gel column chromatography resulted in partial decomposition, therefore the crude product (282 mg, 90%) was used for further experiments. Colourless syrup; δ_H (360 MHz; acetone-d_6) 10.26 (1 H, br s, NH), 7.81 (2 H, d, *J* 7.9, Ts), 7.40 (2 H, d, *J* 7.9, Ts), 7.39 (1 H, br s, H-1), 5.69 (1 H, dd, $J_{4,5}$ 3.0, H-4), 5.45 (1 H, d, $J_{3,4}$ 4.3, H-3), 5.15 (1 H, br s, H-5), 4.54 (1 H, m, H-6), 4.32 (1 H, dd, $J_{6,7}$ 7.0, $J_{7,7'}$ 11.3, H-7), 4.22 (1 H, dd, $J_{6,7'}$ 5.8, H-7′), 2.40 (3 H, s, CH_3-Ts), 2.06, 2.05, 1.96 (9 H, 3 s, 3 × OAc); δ_C (90 MHz; acetone-d_6) 170.6, 170.3 (C=O), 150.3 (C-2), 144.7, 137.2 (Ts quaternary), 142.1 (C-1), 130.3, 128.6, 128.4 (Ts), 105.4 (C-3), 74.2, 65.5, 63.8 (C-4, C-5, C-6), 62.3 (C-7), 21.4 (CH_3-Ts), 20.6, 20.5 (CH_3).

3,4,5,7-Tetra-*O*-acetyl-2,6-anhydro-1-deoxy-D-*galacto*-hept-1-enitol (6a). Colourless syrup; $[\alpha]_D$ + 74 (*c* 1.45 in $CHCl_3$); (lit.,[10a] $[\alpha]_D^{25}$ + 70 (*c* 1.10 in $CHCl_3$); δ_H (360 MHz; $CDCl_3$) 5.69 (1 H, ddd, $J_{3,4}$ 10.5, H-3), 5.52 (1 H, dd, $J_{5,6}$ 1.5, H-5), 5.06 (1 H, dd, $J_{4,5}$ 3.1, H-4), 4.82 (1 H, dd, $J_{1,1'}$ 2.1, $J_{1,3}$ 1.5, H-1), 4.51 (1 H, dd, $J_{1',3}$ 1.6, H-1′), 4.21 (1 H, dd, $J_{7,7'}$ 11.5, H-7), 4.15 (1 H, dd, H-7′), 4.02 (1 H, ddd, $J_{6,7}$ 6.8, $J_{6,7'}$ 6.4, H-6), 2.17, 2.14, 2.07, 2.01 (12 H, 4 s, 4 × OAc); δ_C (90 MHz; $CDCl_3$) 170.5, 170.2, 170.0, 169.6 (C=O), 154.1 (C-2), 96.1 (C-1), 75.7, 71.3, 67.7, 67.0 (C-3, C-4, C-5, C-6), 61.7 (C-7), 20.8, 20.7 (CH_3); IR ν_{max}/cm^{-1} 2942, 1748, 1666, 1372, 1216, 1084 (Found: C, 52.39; H, 5.98. Calc. for $C_{15}H_{20}O_9$: C, 52.33; H, 5.85%).

3,4,5,7-Tetra-*O*-acetyl-2,6-anhydro-1-deoxy-D-*gluco*-hept-1-enitol (6b). Colourless syrup; $[\alpha]_D$ + 41 (*c* 1.02 in $CHCl_3$); δ_H (360 MHz; $CDCl_3$) 5.47 (1 H, d, $J_{3,4}$ 8.4, H-3), 5.22 (1 H, dd, $J_{5,6}$ 9.4, H-5), 5.16 (1 H, pseudo t, $J_{4,5}$ 8.5, H-4), 4.84 (1 H, br s, $J_{1,1'} < 1.0$, $J_{1,3} < 1.0$, H-1), 4.56 (1 H, br s, $J_{1',3} < 1.0$, H-1′), 4.29 (1 H, dd, $J_{7,7'}$ 12.6, H-7), 4.20 (1 H, dd, H-7′), 3.84 (1 H, ddd, $J_{6,7}$ 4.2, $J_{6,7'}$ 2.1, H-6), 2.13, 2.11, 2.05, 2.04 (12 H, 4 s, 4 × OAc); δ_C (90 MHz; $CDCl_3$) 170.8, 170.1, 169.5, 169.3 (C=O), 153.2 (C-2), 96.7 (C-1), 76.4, 73.4, 69.3, 68.2 (C-3, C-4, C-5, C-6), 62.0 (C-7), 20.9, 20.8, 20.7 (CH_3); IR ν_{max}/cm^{-1} 1748, 1668, 1372, 1216, 1038 (Found: C, 52.44; H, 5.72. Calc. for $C_{15}H_{20}O_9$: C, 52.33; H, 5.85%).

3,4,5,7-Tetra-*O*-benzoyl-2,6-anhydro-1-deoxy-D-*gluco*-hept-1-enitol (6c). Colourless syrup; $[\alpha]_D$ + 43 (*c* 0.98 in $CHCl_3$); δ_H (360 MHz; $CDCl_3$) 8.08–8.03 (4 H, m, OBz), 7.93–7.87 (4 H, m, OBz), 7.59–7.26 (12 H, m, Bz), 5.98–5.80 (3 H, m, H-3, H-4, H-5 strongly coupled), 4.96 (1 H, pseudo t, $J_{1,1'}$ 1.5, $J_{1,3}$ 1.5, H-1), 4.71 (1 H, pseudo t, $J_{1',3}$ 1.5, H-1′), 4.71 (1 H, dd, $J_{6,7'}$ 3.1, $J_{7,7'}$ 12.1, H-7′), 4.53 (1 H, dd, $J_{6,7}$ 4.7, H-7), 4.32–4.27 (1 H, m, H-6); δ_C (90 MHz; $CDCl_3$) 166.3, 165.7, 165.2, 165.1 (C=O), 153.3 (C-2), 133.7, 133.5, 133.3, 130.1, 129.9, 128.7, 128.6, 128.5 (OBz), 129.7, 129.1, 129.0, 128.9, (OBz quaternary), 97.3 (C-1), 77.0, 73.3, 69.9, 69.1 (C-3, C-4, C-5, C-6), 63.0 (C-7); IR ν_{max}/cm^{-1} 1732, 1602, 1452, 1270, 1094, 708 (Found: C, 71.08; H, 4.89. Calc. for $C_{35}H_{28}O_9$: C, 70.94; H, 4.76%).

3,4,5-Tri-*O*-acetyl-2,6-anhydro-1-deoxy-D-*manno*-hex-1-enitol (6d). White crystals; mp 98–100 °C; $[\alpha]_D$ − 94 (*c* 0.99 in $CHCl_3$); δ_H (360 MHz; DMSO-d_6) 5.42 (1 H, ddd, $J_{3,4}$ 10.0, H-3), 5.30 (1 H, ddd, $J_{5,6}$ 3.2, $J_{5,6'}$ 1.6, H-5), 5.10 (1 H, dd, $J_{4,5}$ 3.2, H-4), 4.69 (1 H, pseudo t, $J_{1,1'}$ 1.6, $J_{1,3}$ 1.6, H-1), 4.49 (1 H, pseudo t, $J_{1',3}$ 1.6, H-1′), 4.02 (1 H, dd, $J_{6,6'}$ 12.6, H-6), 3.92 (1 H, dd, H-6′), 2.12, 2.10, 1.99 (9 H, 3 s, 3 × OAc); δ_C (90 MHz; $CDCl_3$) 170.3, 170.0, 169.5 (C=O), 154.5 (C-2), 96.9 (C-1), 70.3, 67.8, 67.7 (C-3, C-4, C-5), 68.3 (C-6), 21.0, 20.9, 20.8 (CH_3); IR ν_{max}/cm^{-1} 1748, 1662, 1372, 1218, 1070 (Found: C, 53.11; H, 5.84. Calc. for $C_{12}H_{16}O_7$: C, 53.01; H, 5.92%).

4,5,7-Tri-*O*-acetyl-2,6-anhydro-1,3-dideoxy-3-phthalimido-D-*glycero*-D-*gluco*-hept-1-enitol (6f). Colourless syrup; $[\alpha]_D$ + 29 (*c* 1.08 in $CHCl_3$); δ_H (360 MHz; $CDCl_3$) 7.88 (2 H, dd, Phth), 7.76 (2 H, dd, Phth), 5.92 (1 H, pseudo t, $J_{4,5}$ 9.7, H-4), 5.30 (1 H, pseudo t, $J_{5,6}$ 9.8, H-5), 5.07 (1 H, ddd, $J_{3,4}$ 9.8, H-3), 4.80 (1 H, dd, $J_{1,1'}$ 1.8, $J_{1,3}$ 1.5, H-1), 4.42 (1 H, dd, $J_{7,7'}$ 12.3, H-7), 4.24 (1 H, pseudo t, $J_{1',3}$ 1.8, H-1′), 4.22 (1 H, dd, H-7′), 4.01 (1 H, ddd, $J_{6,7}$ 4.2, $J_{6,7'}$ 1.8, H-6), 2.06, 2.04, 1.87 (9 H, 3 s, 3 × OAc); δ_C (90 MHz; $CDCl_3$) 170.7, 170.0, 169.5, 167.0 (C=O), 151.9 (C-2), 131.4 (Phth quaternary), 134.6, 123.8 (Phth), 95.7 (C-1), 75.8, 70.8, 68.3 (C-4, C-5, C-6), 61.8 (C-7), 51.4 (C-3), 20.7, 20.6, 20.5 (CH_3); IR ν_{max}/cm^{-1} 1748, 1732, 1380, 1222, 1048, 722 (Found: C, 58.32; H, 5.04; N, 3.12. Calc. for $C_{21}H_{21}NO_9$: C, 58.47; H, 4.91; N, 3.25%).

3,4,6-Tri-*O*-benzoyl-2,5-anhydro-1-deoxy-D-*ribo*-hex-1-enitol (6g). Colourless syrup; $[\alpha]_D$ + 24 (*c* 0.90 in $CHCl_3$); δ_H (360 MHz; $CDCl_3$) 8.09–7.89 (6 H, m, OBz), 7.60–7.31 (9 H, m, OBz), 6.20 (1 H, ddd, $J_{3,4}$ 5.3, H-3), 5.73 (1 H, t, $J_{4,5}$ 5.3, H-4), 4.89 (1 H, ddd, $J_{5,6}$ 4.2, $J_{5,6'}$ 3.7, H-5), 4.72 (1 H, dd, $J_{6,6'}$ 12.1, H-6′), 4.67 (1 H, pseudo t, $J_{1,1'}$ 1.5, $J_{1,3}$ 1.5, H-1), 4.57 (1 H, dd, H-6), 4.44 (1 H, pseudo t, $J_{1',3}$ 1.5, H-1′); δ_C (90 MHz; $CDCl_3$) 165.4, 166.2 (C=O), 157.7 (C-2), 133.6, 133.5, 133.4, 133.3, 129.9, 128.6 (OBz), 129.3, 128.9 (OBz quaternary), 87.1 (C-1), 80.6, 72.0, 70.9 (C-3, C-4, C-5), 63.9 (C-6); IR ν_{max}/cm^{-1} 1728, 1266, 1118, 708 (Found: C, 70.80; H, 4.94. Calc. for $C_{27}H_{22}O_7$: C, 70.74; H, 4.84%).

3,4,5,7-Tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-L-*manno*-heptose-[*N*-(4-methylbenzenesulfonyl)-*N*-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-galactopyranosylmethyl)] hydrazone (8a). Colourless syrup; $[\alpha]_D$ + 25 (*c* 0.87 in $CHCl_3$); δ_H (360 MHz; C_6D_6) 7.92 (2 H, d, *J* 8.4, Ts), 7.33 (1 H, d, $J_{1,2}$ 6.3, H-1), 6.79 (2 H, d, *J* 7.8, Ts), 5.62–5.44 (4 H, m), 5.29–5.16 (2 H, m), 4.32–4.23 (2 H, m), 4.19–4.02 (2 H, m), 4.01–3.84 (2 H, m), 3.68–3.60 (2 H, m), 3.51–3.39 (1 H, m), 3.25 (1 H, t), 2.05 (3 H, s, CH_3-Ts) 1.94, 1.85, 1.83, 1.76, 1.70, 1.67, 1.64, 1.55 (24 H, 8 s, 8 × OAc); δ_C (90 MHz; $CDCl_3$) 170.6, 170.3, 170.2, 170.1 (C=O), 144.4, 134.8 (Ts quaternary), 140.9 (C-1), 129.7, 128.3 (Ts), 79.2, 77.5, 74.4, 74.1, 72.1, 71.0, 67.8, 67.6, 67.4, 67.1 (C-2, C-3, C-4, C-5, C-6, C-1′, C-2′, C-3′, C-4′, C-5′), 61.7, 60.9 (C-7, C-6′), 48.4 (CH_2-N), 21.7 (CH_3-Ts), 21.0, 20.8, 20.7, 20.6 (CH_3); IR ν_{max}/cm^{-1} 1748, 1372, 1228, 1050 (Found: C, 51.18; H, 5.67, N, 3.11. Calc. for $C_{37}H_{48}N_2SO_{20}$: C, 50.91; H, 5.54; N, 3.21%).

3,4,5,7-Tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-D-*gulo*-heptose-[*N*-(4-methylbenzenesulfonyl)-*N*-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosylmethyl)] hydrazone (8b). Colourless syrup; $[\alpha]_D$ + 8 (*c* 1.02 in $CHCl_3$); δ_H (360 MHz; $CDCl_3$) 7.72 (2 H, d, *J* 7.9, Ts), 7.31 (2 H, d, *J* 7.9, Ts), 7.05 (1 H, d, $J_{1,2}$ 6.4, H-1), 5.33–5.15 (2 H, m), 5.13–4.85 (4 H, m), 4.27–4.01 (4 H, m), 3.99–3.50 (6 H, m), 2.42 (3 H, s, CH_3-Ts), 2.15–2.01 (21 H, m, 7 × OAc), 1.82 (3 H, s, OAc); δ_C (90 MHz; $CDCl_3$) 170.6, 170.4, 170.3, 170.1, 169.5 (C=O), 144.4, 134.6 (Ts quaternary), 141.0 (C-1), 129.7, 128.4 (Ts), 78.7, 76.9, 75.9, 75.7, 74.2, 73.1, 70.3, 69.8, 68.4, 68.1 (C-2, C-3, C-4, C-5, C-6, C-1′, C-2′, C-3′, C-4′, C-5′), 62.2, 61.6 (C-7, C-6′), 48.3 (CH_2-N), 21.6 (CH_3-Ts), 20.9, 20.8, 20.7, 20.4 (CH_3); IR ν_{max}/cm^{-1} 1748, 1366, 1226, 1034 (Found: C, 51.02; H, 5.69; N, 3.35. Calc. for $C_{37}H_{48}N_2SO_{20}$: C, 50.91; H, 5.54; N, 3.21%).

3,4,5,7-Tetra-*O*-benzoyl-2,6-anhydro-D-*glycero*-D-*gulo*-heptose-[*N*-(4-methylbenzenesulfonyl)-*N*-(2′,3′,4′,6′-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl)] hydrazone (8c). Colourless syrup; δ_H (360 MHz; $CDCl_3$) 8.14–7.75 (14 H, m), 7.60–7.27 (29 H, m), 6.80 (2 H, d, *J* 7.9, Ts), 5.95–5.83 (2 H, m), 5.66 (1 H, t), 5.53–5.43 (2 H, m), 5.12–5.03 (2 H, m), 4.74 (1 H, dd), 4.56 (1 H, dd), 4.45–4.31 (2 H, m), 4.28 (1 H, dd), 4.21–4.00 (2 H, m), 3.95–3.71 (2 H, m), 2.12 (3 H, s, CH_3); δ_C (90 MHz; $CDCl_3$) 166.3, 166.1, 166.0, 165.8, 165.6, 165.4, 165.3 (C=O), 143.9, 134.1 (Ts quaternary), 142.3 (C-1), 78.6, 77.3, 76.2, 74.5, 73.6, 71.0, 69.5 (C-2, C-3, C-4, C-5, C-6, C-1′, C-2′, C-3′, C-4′, C-5′), 63.6, 63.0 (C-7, C-6′), 49.3 (CH_2-N), 21.6 (CH_3); IR ν_{max}/cm^{-1} 1732, 1452, 1270, 1094, 710.

3,4,5-Tri-*O*-acetyl-2,6-anhydro-D-*manno*-hexose-[*N*-(4-methylbenzenesulfonyl)-*N*-(2′,3′,4′-tri-*O*-acetyl-α-D-arabinopyranosylmethyl)] hydrazone (8d). White crystals; mp 182–185 °C dec.; $[\alpha]_D$ − 65 (*c* 0.90 in $CHCl_3$); δ_H (HSQMBC) (500 MHz; C_6D_6) 8.00 (2 H, d, *J* 8.2, Ts), 7.44 (1 H, d, $J_{1,2}$ 6.6, H-1), 6.86 (2 H, d, *J* 8.2, Ts), 5.64 (1 H, dd, $J_{3,4}$ 10.2, H-3), 5.60 (1 H, t, $J_{2',3'}$ 9.9, H-2′), 5.32 (2 H, br s, H-5, H-4′), 5.28 (1 H, dd, $J_{4,5}$ 3.7, H-4), 5.22 (1 H, dd, $J_{3',4'}$ 3.7, H-3′), 4.20 (1 H, d, $J_{CH2a,1'}$ 14.2, CH_{2a}–N), 3.90 (1 H, dd, $J_{2,3}$ 9.4, H-2), 3.77 (1 H, dd, $J_{4',5'eq}$ 2, $J_{5'eq,5'ax}$ 13.3, H-5′$_{eq}$), 3.65 (1 H, dd, $J_{CH2b,1'}$ 5.8, CH_{2b}–N), 3.63 (1 H, dd, $J_{1',2'}$ 9.0, H-1′), 3.58 (1 H, dd, $J_{5,6eq}$ 1.8, $J_{6eq,6ax}$ 13.3, H-6$_{eq}$), 3.16 (1 H, d, $J_{4',5'ax}$ 13.3, H-5′$_{ax}$), 2.88 (1 H, d, $J_{5,6ax}$ 13.3, H-6$_{ax}$), 2.16 (CH_3-Ts), 1.96, 1.93, 1.86, 1.82, 1.76, 1.69 (18 H, 6 s, 6 × OAc); δ_C (90 MHz; $CDCl_3$) 170.6, 170.5, 170.3, 170.2, 170.1 (C=O), 144.3, 134.8 (Ts quaternary), 140.9 (C-1), 129.6, 128.2 (Ts), 79.6, 77.6, 71.7, 70.7, 68.7, 68.6, 68.2, 67.3 (C-2, C-3, C-4, C-5, C-1′, C-2′, C-3′, C-4′), 68.1, 67.8 (C-6, C-5′), 48.6 (CH_2–N), 21.6 (CH_3-Ts), 21.1, 21.0, 20.9, 20.7, 20.5 (CH_3); IR ν_{max}/cm^{-1} 1748, 1372, 1222. (Found: C, 51.22, H, 5.64, N, 3.72. Calc. for: $C_{31}H_{40}N_2O_{16}S$: C, 51.10; H, 5.53; N, 3.84%).

X-Ray crystallographic structure determination of 5d †

Colourless block crystals (0.66 × 0.55 × 0.4 mm) of $C_{19}H_{24}N_2O_9S$, $M = 456.46$, orthorhombic, $a = 9.939(7)$ Å, $b = 12.907(5)$ Å, $c = 20.160(3)$ Å, $V = 2586(2)$ Å^3, $Z = 4$, space group: $P2_12_12_1$, $\rho_{calc} = 1.172$ g cm^{-3}. Data were collected at 293(1) K, Enraf Nonius MACH3 diffractometer, Mo Kα radiation $\lambda = 0.71073$ Å, ω-2θ motion, $\theta_{max} = 25.3°$, 5867 measured reflections of which 2786 reflections were unique with $I > 2\sigma(I)$, decay: 38%. The structure was solved using the SIR-92 software[28] and refined on F^2 using SHELX-97 program,[29] publication material was prepared with the WINGX-97 suite,[30] $R(F) = 0.0533$ and $wR(F^2) = 0.1828$ for 5867 reflections, 288 parameters. H atoms were placed into geometric positions except N–H and hydrogen on C1 which were found at the difference electron density map and refined isotropically. Residual electron density: 0.269/−0.196 e/Å^3.

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† CCDC reference number 213880. See http://www.rsc.org/suppdata/ob/b3/b307378e/ for crystallographic data in .cif or other electronic format.

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