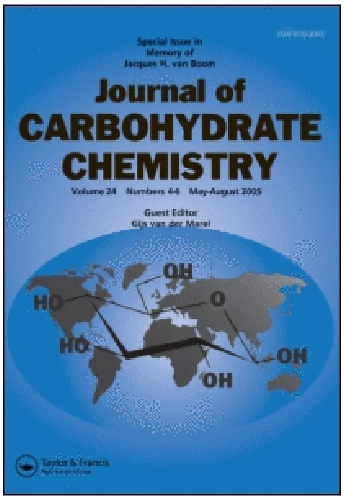

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Synthesis and Reactions of *C*-Hetaryl Substituted Ketoses

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SYNTHESIS AND REACTIONS OF *C*-HETARYL SUBSTITUTED KETOSES

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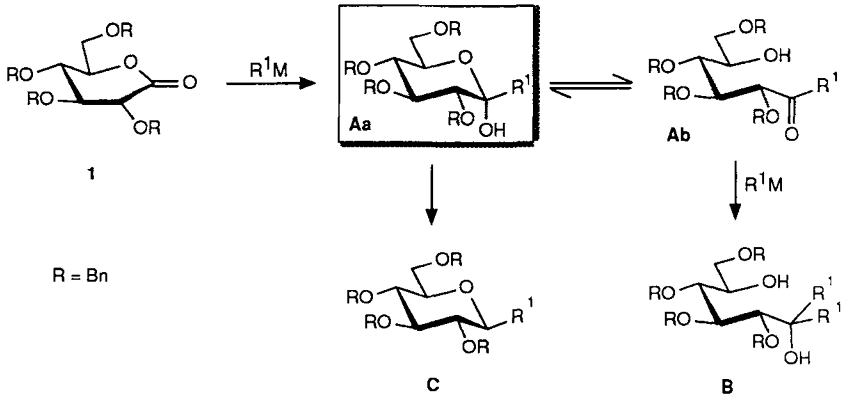
ABSTRACT

O-Benzyl protected gluconolactone **1** reacts readily with 2-lithio derivatives of quinaldine, 2-methylquinoxaline, 2-methylbenzimidazole and *N*-protected derivatives, and 1-benzyloxymethyl-2-methylimidazole at low temperatures to afford as monoaddition products the corresponding D-*gluco*-2-heptuloses **2-5**. The benzyl protective groups can be readily removed by hydrogenolysis as shown for the transformation of **4a** into **8**. Acylation reactions with **4a** exhibited an interesting interplay between *O*- and *N*-acylation which is dependent on the nature of the acylating agent and on the reaction conditions. Reductive removal of the anomeric hydroxy group in **4a**-**c** and **5** was readily performed via elimination products **18a-c** and **23**; their hydrogenation with Pd/C gave directly the *O,N*-deprotected C-β-D-glucopyranosylmethyl derivatives **21** and **25**, respectively.

INTRODUCTION

The manifold occurrence of complex oligosaccharide structures as epitopes at the cell surface[1-3] and the various biological functions attributed to these molecules[3,4] has led to a great interest in their availability by chemical and enzymatic methodologies.[1,2,5,6] For an understanding of these functions, structural analogues, for instance those stable to glycosidase action, are required for biological testings. Amongst these analogues carbon-bridged derivatives[7,8] could play an important role because they are thought to affect the activity of glycosidases mainly via competitive inhibition.[8-10] The potential access to planar geometry at the anomeric center and the presence of basic



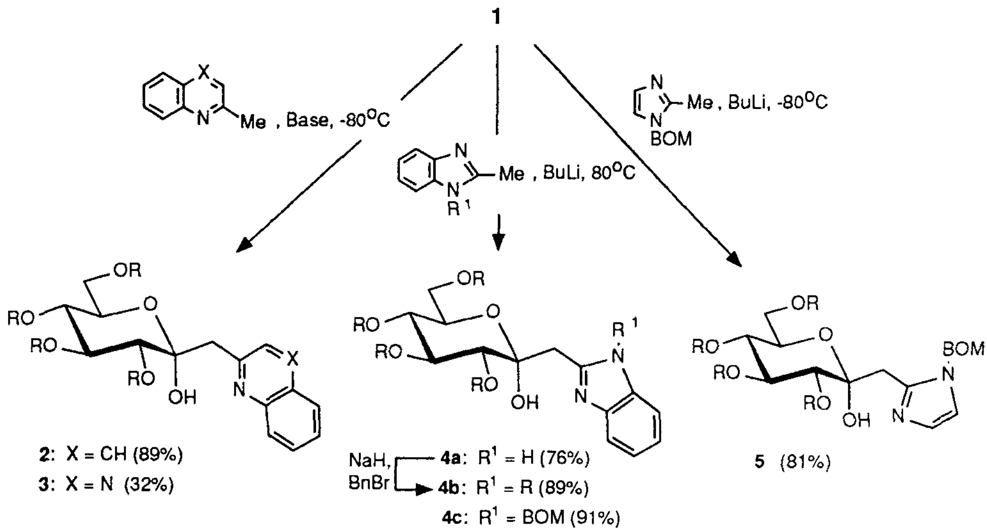
Scheme 1

groups close to it will eventually increase this inhibition effect.[11] Additionally, the ligation of sugars via carbon to heterocyclic systems may have also interesting pharmacological implications.[12-14]

Therefore, we investigated the reaction of 2,3,4,6-tetra-*O*-benzyl-protected gluconolactone (Scheme 1, **1**) as electrophile with CH-acidic heterocyclic bases. As shown, the addition of a C-nucleophile R^1M to **1** affording at low temperatures adduct **Aa** is already known.[7,15-18] At higher temperatures or prolonged reaction times ring-opening to **Ab** and then a second addition of C-nucleophile R^1M affording **B** is generally an undesired ensuing reaction in this work. However, this reaction course may be successfully employed for the introduction of two different nucleophiles at the anomeric center, as recently demonstrated.[18] For the formation of the desired heterocyclic *C*-glycosides **C**, replacement of the anomeric hydroxy group by hydrogen is required. Such reductions have been successfully performed for simple alkyl derivatives with triethylsilane/Lewis Acid as a reducing agent.[15]

RESULTS AND DISCUSSION

Readily accessible, 2-methyl-substituted nitrogen heterocycles were investigated in this study. Thus, 2-methylquinoline (quinaldine) was treated with *n*-butyllithium in THF at -80 °C and then **1** was added (Scheme 2). The desired monoaddition product **2** was obtained in high yield; only one anomer was isolated; because ketopyranoses are preferentially found as α-anomers, the structure is drawn accordingly. Reaction of the strongly electron deficient 2-methylquinoxaline with **1** required a nonnucleophilic base;

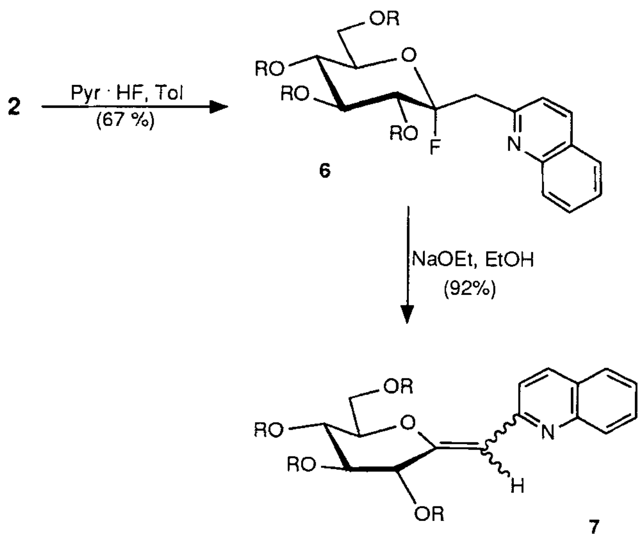


Scheme 2 (R = Bn)

thus, with potassium hexamethyldisilylamide as base at -70 °C addition product **3** was obtained in 32% yield. However, reaction with the relatively electron rich 2-methylbenzimidazole gave with two equivalents of *n*-butyllithium at -85 °C addition product **4a** in 76% yield. Thus, obviously a wide scope for such addition reactions to glyconolactones is available. Similar results were obtained for reactions with 1-benzyl- and 1-benzyloxymethyl-2-methylbenzimidazole, affording compounds **4b** and **4c**, respectively, in high yields. *N*-Benzylation of **4a** with NaH and benzyl bromide in DMF led also to **4b**. Reaction of **1** with 1-benzyloxymethyl-2-methylimidazole afforded the corresponding ketopyranose **5**.

Compounds **2** and **4** were subjected to various transformations. Treatment of quinaldine derivative **2** with the pyridine/HF complex in toluene furnished glycosyl fluoride **6** which may serve as glycosyl donor (Scheme 3). Reaction with sodium ethanolate in ethanol afforded a single elimination product. Based on the ^{1}H NMR shift for H-1 (δ = 6.13) and comparison with previous *E*/*Z*-assignments for simple 1-enitols[19] the *E*-configuration was tentatively assigned to **7**.[20] However, the ^{1}H NMR shift data do not seem to yield reliable *E*/*Z*-assignments (see below).

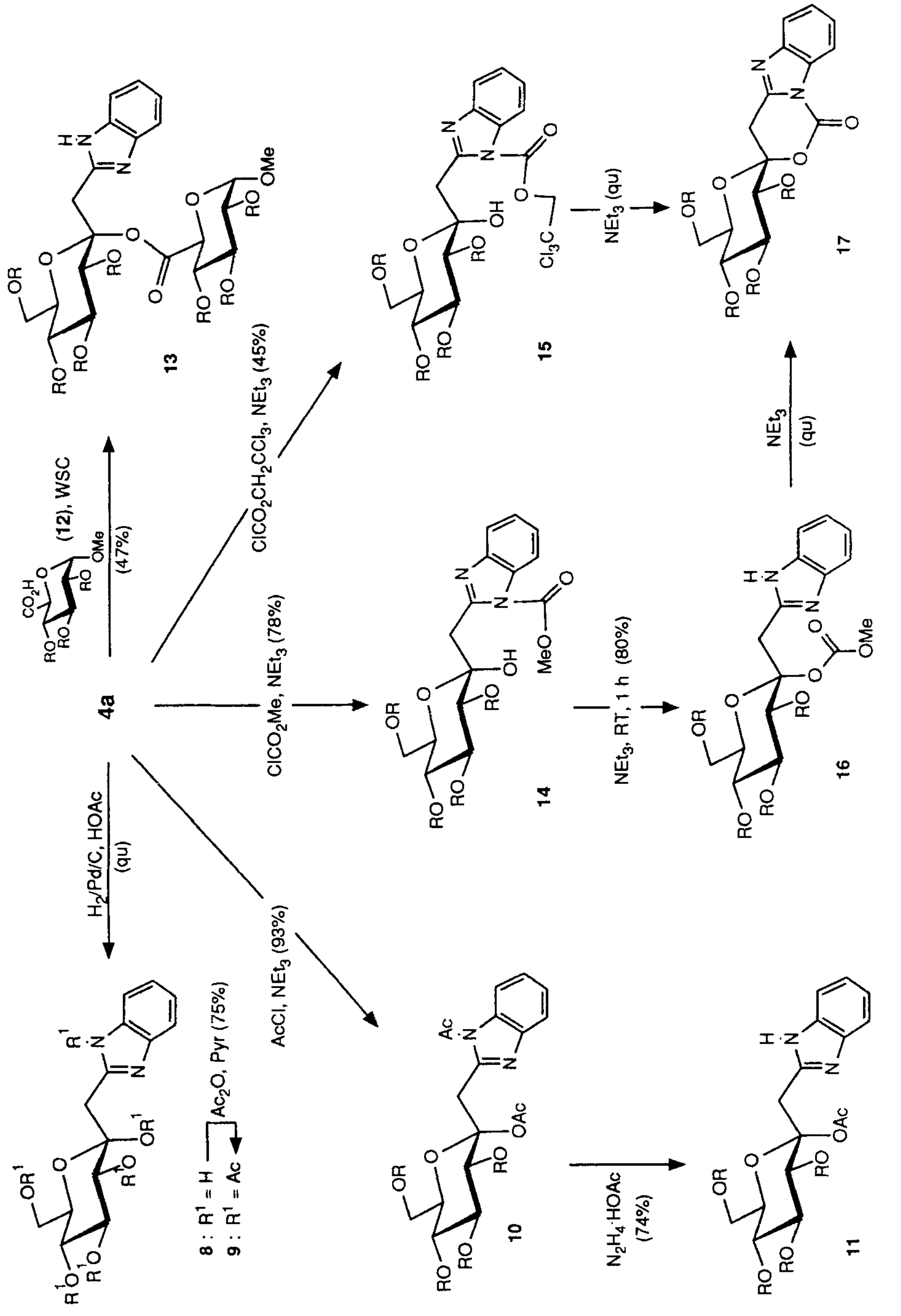
An important prerequisite for biological studies is deprotection. Therefore, benzimidazole derivative **4a** was hydrogenated with palladium on carbon as catalyst; in acetic acid fully deprotected **8** was readily obtained (Scheme 4). For the structural



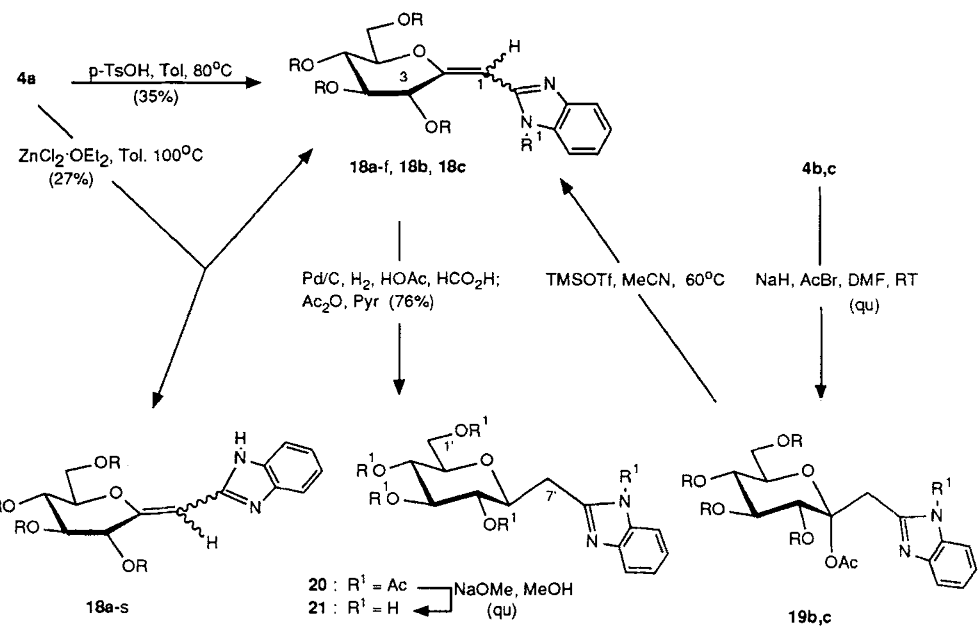
Scheme 3 (R = Bn)

assignment, **8** was reacted with acetic anhydride in pyridine to afford the desired fully protected compound **9** in high yield.

Of special interest were acylation reactions of **4a**, which possesses an imidazole residue close to the sterically hindered ketopyranose anomeric hydroxy group thus functioning as a relay system for acyl migrations. Treatment of **4a** with two equivalents of acetyl chloride in the presence of triethylamine afforded *N,O*-diacetyl derivative **10** in high yield; addition of one equivalent of hydrazinium acetate to this compound led to selective *N*-deacetylation yielding compound **11**. This reaction is presumably due to activation of the imidazole moiety by hydrazinium ion protonation. Reaction of **4a** with only one equivalent of acetyl chloride in the presence of triethylamine afforded a mixture of **10** and **11**. These results were reason to investigate other acylation reactions. From the reaction of **4a** with uronic acid **12**[21] in the presence of water soluble carbodiimide (WSC) as condensing agent only *O*-acyl derivative **13** could be isolated. With methyl chloroformate and trichloroethyl chloroformate in the presence of triethylamine only *N*-alkoxycarbonyl derivatives **14** and **15**, respectively, were found. However, due to their different reactivity, further treatment with triethylamine exhibited quite different behavior; **14** led to *N*/*O*-methoxycarbonyl migration yielding compound **16**, whereas the more reactive **15** resulted immediately in cyclic urethane **17**, which was obtained from **16** only after prolonged triethylamine treatment. Thus, the kind of activating system and


4a
H2/Pd/C, HOAc
(qu)
8 : R1 = H
9 : R1 = Ac
Ac2O, Pyr (75%)
AcCl, NEt3 (93%)
10
N2H4·HOAc
(74%)
11
ClCO2Me, NEt3 (78%)
14
NEt3, RT, 1 h (80%)
16
(12), WSC
(47%)
13
ClCO2CH2CCl3, NEt3 (45%)
15
NEt3 (qu)
NEt3
(qu)
17

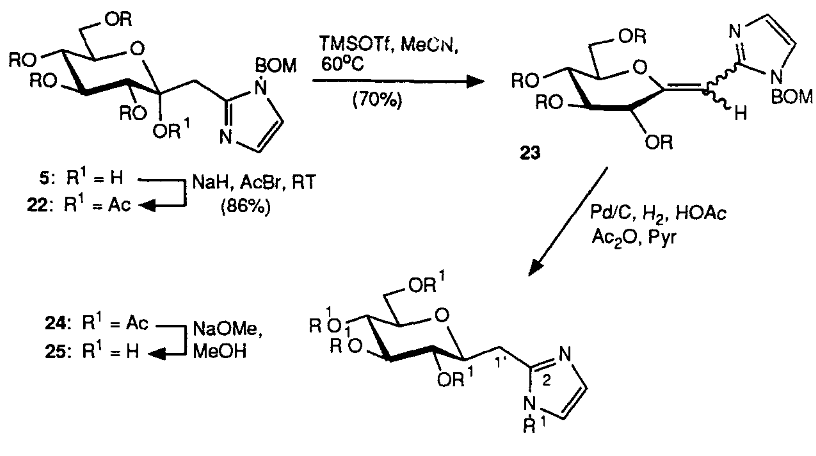
Scheme 4 (R = Bn)



Scheme 5 (R = Bn)

the reactivity of the acyl donor seem to have a strong influence on (kinetic) product formation.

Investigation towards direct transformation of **4a** into the corresponding 2-(*C*-β-D-glucopyranosylmethyl)benzimidazole failed with triethylsilane/Lewis acid as reducing agent,[22] though this has been successfully applied to simple ketopyranoses.[15] Also other related reducing agents proved to be unsuccessful. Therefore, hydrogenation of the derived enitol system was attempted. To this aim, glycosyl fluoride formation and then elimination could be carried out, as shown for the transformation of **2** via **6** into **7** (Scheme 3). Alternatively, direct acid catalyzed dehydration of **4a** with *p*-toluenesulfonic acid (*p*-TsOH) at elevated temperature gave directly elimination product **18a** (Scheme 5); of the two possible *E*/*Z*-diastereoisomers only the faster moving on TLC (= **18a**-*f*) was obtained (for details, see Experimental). With $ZnCl_2$·ether as dehydrating agent at 75 °C both diastereoisomers **18a**-*f*/*s* were isolated. A simpler approach to these compounds was – as shown for **4b,c** – *O*-acetylation with acetyl bromide in the presence of sodium hydride as base (→ **19b,c**) and then treatment with TMSOTf, thus affording **18b,c**; again only one isomer was obtained. Based on the ^{1}H NMR shifts of H-1 of **18a-c** and on H-1/H-3 correlations (obtained by ROESY and HMBC experiments)[23] either *E*- or *Z*-configuration cannot be unequivocally assigned to these compounds.[24]



Scheme 6 (R = Bn)

Hydrogenation of **18a-c** with palladium on carbon as catalyst in a mixture of HOAc/HCO_2H and then acetylation with acetic anhydride in pyridine afforded practically exclusively the desired *C*-β-D-glucopyranosyl-methyl derivative **20**; the β-configuration could be readily derived from the ^{1}H NMR data (δ 5.10, $J_{4,5}$ 9.2, $J_{5,6}$ 9.5 Hz, H-5). Treatment of **20** with sodium methanolate in methanol gave target molecule **21**. The same reaction sequence applied to imidazole derivative **5** (Scheme 6), i.e., *O*-acetylation (→ **22**), acid catalyzed acetic acid elimination (→ **23**), hydrogenation and ensuing acetylation (→ **24**, ^{1}H NMR: δ 5.04, $J_{4,5}$ 9.2 Hz, $J_{5,6}$ 9.5 Hz, H-5) and then complete deacetylation afforded as target molecule the corresponding *C*-β-D-glucopyranosylmethyl-imidazole **25**.

Glycosidase inhibition studies with compounds **21** and **25** were carried out with β-glucosidase (cellobiase) from almonds; measurements against *O*-nitrophenyl β-D-glucopyranoside as substrate exhibited only low competitive inhibition (**21**: $K_i = 3.8 \cdot 10^{-2}$ M; **25**: $K_i = 7.0 \cdot 10^{-3}$ M).[25] Further structural modifications in order to improve the inhibitory activity of these type of compounds are on the way.

EXPERIMENTAL

General methods. Solvents were purified in the usual way, the petroleum ether had a boiling range of 30-70 °C. The reactions were carried out under an atmosphere of dry nitrogen. NMR spectra: Bruker AC-250 Cryospec and DRX 600 (150.4 MHz for ^{13}C NMR). Flash chromatography: silica gel 60 (particle size 40 μm, J. T. Baker). Thin layer chromatography (TLC): TLC plastic sheets, silica gel 60 F_{254} (layer thickness 0.2 mm, E. Merck). Melting points (uncorrected): metal block. Elemental analyses: Heraeus CHN-O-Rapid. Optical rotations: Perkin-Elmer polarimeter 241/MS; 1 dm cell. FAB MS spectra: Finnigan MAT 312; 70 eV, 70 °C.

3,4,5,7-Tetra-*O*-benzyl-1-(2-quinolinyl)-1-deoxy-α-D-*gluco*-2-heptulopyranose (2). To a solution of 2-methylquinoline (2.51 mL, 18.56 mmol) in dry tetrahydrofuran (50 mL) *n*-butyllithium (11.6 mL, 1.6 M in hexane) was added with stirring at -80 °C. After 20 min the mixture was slowly added at -80 °C to a solution of 2,3,4,6-tetra-*O*-benzyl-D-glucono-1,5-lactone (**1**)[26] (10 g, 18.56 mmol) in tetrahydrofuran (100 mL) and the reaction mixture was stirred for additional 30 min. After quenching by addition of saturated NH_4Cl solution (200 mL), the mixture was warmed up to room temperature and extracted with ethyl acetate (3 x 100 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography (4:1→1:1 toluene/ethyl acetate) to give **2** (11.2 g, 89%) as yellow crystals; mp 118 °C; R_f 0.45 (9:1 toluene/ethyl acetate); $[\alpha]_D^{20}$ -62° (*c* 1, chloroform); ^1H NMR (250 MHz, $CDCl_3$) δ 2.95 (m, 1H, H-1a), 3.40-3.75 (m, 5H, H-1b, H-3, H-5, H-7a, H-7b), 4.03 (m, 1H, H-6), 4.12-4.42 (m, 3H, H-4, $PhCH_2$), 4.52-5.08 (m, 6H, $3PhCH_2$), 7.00-8.15 (m, 26H, $4C_6H_5$, C_9H_6N); MS (FAB positive mode, matrix: NBOH) *m/z* 682 $(MH)^+$, 664 $(MH-H_2O)^+$, 590 $(MH-C_7H_8)^+$, 574 $(MH-C_7H_8O)^+$, 556 $(MH-C_7H_8O-H_2O)^+$, 466 $(MH-2C_7H_8O)^+$, 448 $(MH-2C_7H_8O-H_2O)^+$, 358 $(MH-3C_7H_8O)^+$.

Anal. Calcd for $C_{44}H_{43}NO_6$ (681.83): C, 77.51; H, 6.36; N, 2.05. Found: C, 77.72; H, 6.47; N, 1.87.

3,4,5,7-Tetra-*O*-benzyl-1-(2-quinoxalinyl)-1-deoxy- α- D- *gluco*- 2- heptulopyranose (3). To a solution of potassium bis(trimethylsilyl)amide (3.7 mL, 0.5 M in toluene) in dry tetrahydrofuran (20 mL) methylquinoxaline[27] (0.265 mL, 2.04 mmol) was added at -70 °C. After stirring for 5 min, a solution **1**[26] (1 g, 1.86 mmol) was added dropwise and the mixture was stirred for additional 10 min. Saturated NH_4Cl solution (20 mL) was added, the mixture was warmed to room temperature and extracted with ethyl acetate (2 x 20 mL). The combined organic solutions were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography (4:1 toluene/ethyl acetate) to yield **3** (0.35 g, 32%) as colourless crystals; mp 105 °C; R_f 0.38 (toluene/ethyl acetate 4:1); $[\alpha]_D^{20}$ -52.2° (c 1, chloroform); ^1H NMR (250 MHz, $CDCl_3$) δ 3.00 (d, $J_{1a,1b}$ = 14.5 Hz, 1H, H-1a), 3.38-3.71 (m, 5H, H-1b, H-3, H-5, H-7a, H-7b), 3.95 (mc, H-6), 4.17 (dd, $J_{3,4}$ = 9.3 Hz, $J_{4,5}$ = 9.3 Hz, 1H, H-4), 4.25-5.07 (m, 8H, $4PhCH_2$), 6.41 (s, 1H, OH), 7.08-7.42 (m, 20H, $4C_6H_5$), 7.69-8.09 (m, 4H, C_6H_4), 8.68 [s, 1H, H-3(quin.)].

Anal. Calcd for $C_{43}H_{42}N_2O_6$ (682.82): C, 75.64; H, 6.20; N, 4.10. Found: C, 75.49; H, 6.24; N, 3.97.

1-(2-Benzimidazolyl)-3,4,5,7-tetra-*O*-benzyl-1-deoxy-α-D-*gluco*-2-heptulopyranose (4a). To a solution of 2-methylbenzimidazole (5g, 37.85 mmol) in dry tetrahydrofuran *n*-butyllithium (47.5 mL, 1.6 M in hexane) was added. After stirring for 1 h, the colourless suspension was cooled to -85 °C and a solution of **1**[26] (11.5 g, 21.34 mmol) in dry tetrahydrofuran (150 mL) was added. After stirring for 1 h, the reaction was quenched by addition of saturated NH_4Cl solution (150 mL) and warmed up to room temperature. The mixture was diluted with water (200 mL) and extracted with ethyl acetate (3 x 100 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography (1:1 toluene/ethyl acetate) to give **4a** (12.5 g, 76%) as colourless crystals; mp 130 °C; R_f 0.43 (toluene/ethyl acetate 1:1); $[\alpha]_D^{20}$ +13.9° (*c* 1, chloroform); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.23 (d, 1H, $J_{3,4}$ = 9.3 Hz, H-3), 3.30 (s, 2H, H-1a, H-1b), 3.60 (dd, 1H, $J_{4,5}$ = 9.7 Hz, $J_{5,6}$ = 9.7 Hz, H-5), 3.71 (mc, 2H, H-7a, H-7b), 3.91 (dd, $J_{3,4}$ = 9.3 Hz, $J_{4,5}$ = 9.7 Hz, 1H, H-4), 4.00 (mc, 1H, H-6), 4.42-4.79 (m, 8H, 4 $PhCH_2$), 6.50, 6.98, 7.05, 7.59 (4m, 4H, C_6H_4), 7.10-7.30 (m, 20H, $4C_6H_5$), 10.14 (br. s, 1H, NH); MS (FAB positive mode, matrix: NBOH) *m/z* 672 $(MH)^+$, 654 $(MH-H_2O)^+$, 580 $(MH-C_7H_8)^+$, 546 $(MH-C_7H_8O-H_2O)^+$.

Anal. Calcd for $C_{42}H_{42}N_2O_6$ (670.81): C, 75.20; H, 6.31; N, 4.18. Found: C, 74.77; H, 6.35; N, 4.19.

3,4,5,7-Tetra-*O*-benzyl-1-[2-(1-benzyl)benzimidazolyl]-1- deoxy -α- D- *gluco* -2-heptulopyranose (4b). (a) From **1**: *Synthesis of 1-Benzyl-2-methylbenzimidazole:* To a solution of 2-methylbenzimidazole (5 g, 37.9 mmol) and benzyl chloride (6.55 mL, 56.7 mmol) in dry dimethylformamide (50 mL) was added at 0 °C sodium hydride (1.7 g, 55% in mineral oil). After 15 min methanol (10 mL) and then saturated aqueous NH_4Cl (40 mL) were added. The mixture was extracted with ethyl acetate (250 mL). The combined organic solutions were dried ($MgsO_4$) and concentrated *in vacuo*. Flash chromatography (1:1 toluene/EtOAc) gave (7.6 g, 90%) as a colourless solid; mp 69 °C; R_f 0.20 (1:1 toluene/ethyl acetate). The ^{1}H NMR data agree with the reported data.[28]

Transformation into **4b**: To a solution of 1-benzyl-2-methylbenzimidazole (1.64 g, 7.43 mmol) in dry tetrahydrofuran (30 mL) *n*-butyllithium (4.64 mL, 1.6 M in hexane) was added at -80 °C. After stirring for 20 min the orange solution was added dropwise at -80 °C to a solution of **1**[26] (4.0 g, 7.43 mmol) in dry tetrahydrofuran (50 mL). The mixture was stirred for 30 min. After quenching by the addition saturated aqueous NH_4Cl solution (100 mL) the mixture was extracted with ethyl acetate (3 x 50 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography (12:1 toluene/ethyl acetate) of the residue yielded **4b** (5.00 g, 89%) as a white solid; mp 124 °C; R_f 0.51 (4:1 toluene/ethyl acetate); $[\alpha]_D^{20}$ -16.6° (*c* 1, chloroform). ^{1}H NMR (250 MHz, $CDCl_3$): δ

2.62 (d, $J_{1a,1b}$ = 15.3 Hz, 1H, H-1a), 3.13 (d, $J_{1b,1a}$ = 15.3 Hz, 1H, H-1b), 3.42 (d, $J_{3,4}$ = 9.5 Hz, 1H, H-3), 3.50 (dd, $J_{7a,7b}$ = 10.9 Hz, $J_{6,7a}$ = 1.7 Hz, 1H, H-7a), 3.67 (dd, $J_{6,7b}$ = 3.6 Hz, $J_{7a,7b}$ = 10.9 Hz, 1H, H-7b), 3.70 (dd, $J_{4,5}$ = 9.3 Hz, $J_{5,6}$ = 9.7 Hz, 1H, H-5), 4.03 (ddd, $J_{5,6}$ = 9.7 Hz, $J_{6,7a}$ = 1.7 Hz, $J_{6,7b}$ = 3.6 Hz, 1H, H-6), 4.22 (dd, $J_{4,5}$ = 9.3 Hz, $J_{3,4}$ = 9.5 Hz, 1H, H-4), 4.28-5.02 (m, 8H, 4 $PhCH_2O$), 5.15 (m, 2H, $PhCH_2N$), 6.93, 6.95, 7.71 (3 mc, 3H, C_6H_4), 7.11-7.36 (m, 26H, 5 Ph, Benzim.).

Anal. Calcd for $C_{49}H_{48}N_2O_6$ (760.93): C, 77.39; H, 6.36; N, 3.68. Found: C, 77.03; H, 6.38; N, 3.75.

(b) *From* **4a**: To a solution of **4a** (1.50 g, 2.25 mmol) in dimethylformamide (20 mL) were added benzyl bromide (0.4 mL, 3.3 mmol) and sodium hydride (57 mg, 2.36 mmol). The reaction was quenched after 15 min by the addition of methanol (5 mL) and satd. ammonium chloride solution (15 mL). Extraction with ethyl acetate (70 mL) and drying of the extract ($MgSO_4$) afforded after evaporation of the solvent a residue which was chromatographed on silica gel (12:1 toluene/ethyl acetate) to afford **4a** (1.04 g, 61%) as a colourless solid, which had physical data in agreement with those reported above.

3,4,5,7-Tetra-*O*-benzyl-1-[2-(1-benzyloxymethyl)benzimidazolyl]-1-deoxy-α-D-*gluco*-2-heptulopyranose (4c): *Synthesis of 1-benzyloxymethyl-2-methylbenzimidazole:* A mixture of 2-methylbenzimidazole (2.5 g, 19.8 mmol) and benzyl chloromethyl ether (60%, 3.5 mL, 14.0 mmol) in acetonitrile (125 mL) was heated under reflux for 3 h. After addition of water (25 mL) and brine (50 mL) the mixture was extracted with ethyl acetate (3 x 30 mL). The combined organic solutions were dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography (3:2 toluene/ethyl acetate) of the residue yielded 1-benzyloxymethyl-2-methylbenzimidazole (2.85 g, 80%) as colourless crystals; mp 110 °C; R_f 0.16 (1:1 toluene/ethyl acetate). ^1H NMR (250 MHz, $CDCl_3$): δ 2.60 (s, 3H, CH_3), 4.44 (s, 2H, OCH_2Ph), 5.48 (s, 2H, NCH_2O), 7.21-7.75 (m, 9H, Ph, Benzim.).

Anal. Calcd for $C_{16}H_{16}N_2O$ (252.32): C, 76.16; H, 6.39; N, 11.10. Found: C, 76.01; H, 6.67; N, 10.81.

Transformation into **4c**: To a solution of 1-benzyloxymethyl-2-methylbenzimidazole (2.70 g. 10.7 mmol) in dry tetrahydrofuran (50 mL) *n*-butyllithium (6.7 mL, 1.6 M in hexane) was added at -85 °C. After stirring for 20 min a cooled solution (-85 °C) of **1**[26] (5.76 g, 10.7 mmol) in dry tetrahydrofuran (50 mL) was added dropwise. After stirring for 30 min at -85 °C satd. aqueous NH_4Cl solution (100 mL) was added. The mixture was extracted with ethyl acetate (3 x 50 mL). The combined organic solutions were dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography (12:1 toluene/ethyl acetate) of the residue yielded **4c** (7.69 g, 91%) as a colourless solid; mp 80 °C, R_f 0.41 (4:1 toluene/ethyl acetate); [α] -14.5° (*c* 1, chloroform). ^1H NMR (250 MHz, $CDCl_3$): δ 2.73 (d, $J_{1a,1b}$ = 15.1 Hz, 1H, H-1a), 3.17 (d, $J_{1a,1b}$ = 15.1 Hz, 1H, H-

1b), 3.40-3.45 (m, 2H, H-3, -7a), 3.62 (dd, $J_{6,7b}$ = 3.5 Hz, $J_{7a,7b}$ = 10.8 Hz, 1H, H-7b), 3.72 (dd, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 9.6 Hz, 1H, H-5), 3.99 (ddd, $J_{5,6}$ = 9.6 Hz, $J_{6,7a}$ = 1.8 Hz, $J_{6,7b}$ = 3.5 Hz, 1H, H-6), 4.17-5.06 (m, 11H, H-4, 5 OCH_2Ph), 5.11, 5.21 (2 d, J_{gem} = 11.5 Hz, 2H, NCH_2Ph), 6.98 (s, 1H, OH), 7.05-7.72 (m, 29H, Ph, Benzim.).

Anal. Calcd for $C_{49}H_{48}N_2O_6$ (760.93): C, 75.93; H, 6.37; N, 3.54. Found: C, 76.32; H, 6.48; N, 3.66.

3,4,5,7-Tetra-*O*-benzyl-1-[2- (1-benzyloxymethyl) imidazolyl]- 1- deoxy- α- D-*gluco*-2-heptulopyranose (5): *Synthesis of 1-benzyloxymethyl-2-methylimidazole:* A mixture of 2-methylimidazole (6.0 g, 73.1 mmol) and benzyl chloromethyl ether (60%, 9.6 mL, 40.6 mmol) in acetonitrile (150 mL) was heated under reflux for 3 h. After addition of water (25 mL) and brine (50 mL) the mixture was extracted with ethyl acetate (3 x 30 mL). The combined organic solutions were dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography (ethyl acetate) of the residue yielded 1-benzyloxymethyl-2-methylimidazole (5.25 g, 64%) as a colourless oil; R_f 0.49 (3:1 ethyl acetate/methanol). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.33 (s, 3 H, CH_3), 4.34 (s, 2H, OCH_2Ph), 5.14 (s, 2H, NCH_2O), 6.81-6.84 (m, 2H, Im.), 7.16-7.31 (m, 5H, Phenyl). MS (EI, 70 eV, T = RT), *m/z* (%): 202 (28, $[M]^+$), 91 (100, $[C_7H_7]^+$).

Transformation into **5**: To a solution of 1-benzyloxymethyl-2-methylimidazole (3.60 g, 17.9 mmol) in dry tetrahydrofuran (70 mL) *n*-butyllithium (11.2 mL, 1.6 M in hexane) was added at -80 °C. After stirring for 15 min a cooled solution (-80 °C) of **1**[26] (8.0 g, 14.9 mmol) in dry tetrahydrofuran (70 mL) was added. After 30 min satd. aqueous NH_4Cl solution (100 mL) was added and the mixture was extracted with ethyl acetate (3 x 70 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography (4:1 toluene/ethyl acetate) of the residue yielded **5** (8.9 g, 81%) of a colourless solid; mp 102 °C; R_f 0.51 (1:1 toluene/ethyl acetate); $[\alpha]_D$ +5.3° (*c* 1, chloroform). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.63 (d, $J_{1a,1b}$ = 15.1 Hz, 1H, H-1a), 3.03 (d, $J_{1a,1b}$ = 15.1 Hz, 1H, H-1b), 3.39 (d, $J_{3,4}$ = 9.4 Hz, 1H, H-3), 3.46 (dd, $J_{7a,7b}$ = 10.8, $J_{6,7a}$ = 1.7 Hz, 1H, H-7a), 3.63 (dd, $J_{7a,7b}$ = 10.8 Hz, $J_{6,7b}$ = 3.9 Hz, 1H, H-7b), 3.68 (dd, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 9.7 Hz, 1H, H-5), 3.98 (ddd, $J_{5,6}$ = 9.7 Hz, $J_{6,7a}$ = 1.7 Hz, $J_{6,7b}$ = 3.9 Hz, 1 H, H-6), 4.17 (dd, $J_{3,4}$ = 9.4 Hz, $J_{4,5}$ = 9.4 Hz, 1H, H-4), 4.25-5.03 (m, 10H, 5 OCH_2Ph), 5.00, 5.23 (2 d, J_{gem} = 11.1 Hz, 2H, NCH_2O), 6.89, 6.96 (2d, J = 1.4 Hz, 2 H, Im.), 7.15-7.41 (m, 25H, Ph).

Anal. Calcd for $C_{46}H_{48}N_2O_7$ (740.90): C, 74.57; H, 6.53; N, 3.78. Found: C, 74.48; H, 6.52; N, 3.76.

3,4,5,7-Tetra-*O*-benzyl-1-(2-quinolinyl)-1-deoxy-α-D-*gluco*-2-heptulopyranosyl fluoride (6). Pyridine-hydrogen fluoride complex (~60% HF, 2 mL) was added to a solution of compound **2** (1.94 g, 2.84 mmol) in dry toluene (20 mL) in a teflon flask with cooling. After stirring for 1 h at room temperature, saturated $NaHCO_3$ solution (50 mL) was added. The mixture was stirred for 10 min and extracted with ethyl acetate (2 x 30 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash chromatography of the residue (toluene/ethyl acetate 9:1) gave **6** (1.3 g, 67%) as a colourless oil; R_f 0.6 (9:1 toluene/ethyl acetate); $[\alpha]_D^{20}$ +34° (*c* 1, chloroform); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.42-3.70 (m, 6H, H-1a, H-1b, H-3, H-5, H-7a, H-7b), 3.89 (mc, 1H, H-6), 3.98 (dd, 1H, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.6 Hz, H-4), 4.24-5.15 (m, 6H, 3 $PhCH_2$), 4.82 (s, 2H, $PhCH_2$), 7.02-7.96 (m, 26H, $4C_6H_5$, C_9H_6N); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 43.2 (d, 1C, $J_{1,F}$ = 32 Hz, C-1), 68 (1C, C-7), 73, 74.5, 75.5, 77 (4C, 4 $PhCH_2$), 73.8 (d, 1C, $J_{4,F}$ = ~10 Hz, C-4), 77.4, 83.3, (2C, C-5, C-6), 79.5 (d, 1C, $J_{3,F}$ = 32 Hz, C-3), 114 (d, 1C, $J_{2,F}$ = 240 Hz, C-2), 123-156 ($4C_6H_5$, C_9H_6N).

Anal. Calcd for $C_{44}H_{42}FNO_5$ (683.82): C, 77.28; H, 6.19; N, 2.05. Found: C, 77.82; H,6.37; N, 2.00.

(1*E*)-2,6-Anhydro-3,4,5,7-tetra-*O*-benzyl-1- (2-quinolinyl)- 1- deoxy - D - *gluco*-hept-1-enitol (7). To a solution of compound **6** (0.3 g, 0.44 mmol) in dry ethanol (10 mL) sodium ethanolate (4.4 mL, 0.1 M in ethanol) was added. The mixture was refluxed until TLC indicated the absence of starting material. After cooling to room temperature NH_4Cl (100 mg) was added, the mixture was filtered, and the filtrate was concentrated *in vacuo*. Flash chromatography of the residue (toluene/ethyl acetate 4:1) gave **7** (0.27 g, 92%) as a colourless oil; R_f 0.36 (4:1 toluene/ethyl acetate); $[\alpha]_D^{20}$ +15.1° (*c* 1, chloroform); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.76-3.94 (m, 4H, H-4, H-5, H-7a, H-7b), 4.11 (d, 1H, $J_{3,4}$ = 3.7 Hz, H-3), 4.39 (mc, 1H, H-6), 4.49-4.85 (m, 8H, $4PhCH_2$), 6.13 (s, 1H, H-1), 7.16-8.35 (m, 26H, $4C_6H_5$, C_9H_6N).

Anal. Calcd for $C_{44}H_{41}NO_5$ (663.81): C, 79.61; H, 6.23; N, 2.11. Found: C, 79.50; H, 6.34; N, 2.28.

1-(2-Benzimidazolyl)-1-deoxy-α-D-*gluco*-2-heptulopyranose (8). A suspension of **4a** (300 mg, 0.45 mmol) and palladium on carbon (100 mg) in acetic acid (10 mL) was stirred overnight under hydrogen atmosphere. After filtration through Celite the filtrate was concentrated *in vacuo* and repeatedly coconcentrated with toluene. For structural analysis, unprotected ketose **8** was directly acetylated. ^{1}H NMR (250 MHz, D_2O) δ 3.35-3.95 (m, 8H, H-1a, H-1b, H-3, H-4, H-5, H-6, H-7a, H-7b), 7.50-7.83 (2m, 4H, C_6H_4).

2,3,4,5,7-Penta-*O*-acetyl-1-[2-(1-acetyl)-benzimidazolyl]-α-D-*gluco*-2-heptulopyranose (9). Compound **8** (100 mg, 0.32 mmol) was dissolved in pyridine/acetic anhydride (1:1, 5 mL). After 15 h the solvent was evaporated *in vacuo*, and the residue was purified by flash chromatography (toluene/ethyl acetate 2:1) to yield **9** (135 mg, 75%) as colourless crystals; mp 68-69 °C; R_f 0.63 (toluene/acetone 1:1); $[\alpha]_D^{20}$ +21.5° (*c* 1, chloroform); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.92-1.99 (4s, 12H, 4OAc), 2.21 (s, 3H, OAc), 2.82 (s, 3H, NAc), 3.87 (mc, 1H, H-6), 3.94 (d, 1H, $J_{1a,1b}$ = 15.4 Hz, H-1a), 4.06-4.09 (m, 2H, H-7a, H-7b), 4.52 (d, $J_{1a,1b}$ = 15.4 Hz, 1H, H-1b), 5.03 (dd, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 9.4 Hz, H-5), 5.09 (d, 1H, $J_{3,4}$ = 9.8 Hz, H-3), 5.37 (dd, $J_{3,4}$ = 9.8 Hz, $J_{4,5}$ = 9.4 Hz, 1H, H-4), 7.29-7.34 (m, 4H, C_6H_4), 7.66-7.78 (m, 2H, C_6H_4).

Anal. Calcd for $C_{26}H_{30}N_2O_{12}$ (562.53): C, 55.52; H, 5.38; N, 4.98. Found: C, 55.42; H, 5.38; N, 5.18.

2-*O*-Acetyl-1-[2-(1-acetyl)-benzimidazolyl]-3,4,5,7-tetra-*O*-benzyl-1-deoxy-α-D-*gluco*-2-heptulopyranose (10). To a solution of **4a** (0.2 g, 0.3 mmol) in dry dichloromethane (5 mL), triethylamine (83 μL, 0.64 mmol) and acetyl chloride (43 μL, 0.6 mmol) were added. After stirring for 10 min saturated NH_4Cl solution was added and the mixture was extracted with ethyl acetate The combined organic solutions were dried (Na_2SO_4) and concentrated *in vacuo*. Flash chromatography (4:1 toluene/ethyl acetate) of the residue yielded **10** (195 mg, 92%) as a colourless oil; R_f 0.55 (4:1 toluene/ethyl acetate); $[\alpha]_D^{20}$ -12.2° (*c* 1, chloroform); ^1H NMR (250 MHz, $CDCl_3$) δ 2.09 (s, 3H, OAc), 2.85 (s, 3H, NAc), 3.41-3.60 (m, 4H, H-5, H-6, H-7a, H-7b), 3.66 (d, 1H, $J_{3,4}$ = 9.5 Hz, H-3), 3.88 (d, 1H, $J_{1a,1b}$ = 14.6 Hz, H-1b), 3.93 (dd, 1H, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 9.2 Hz, H-4), 4.26-5.35 (m, 8H, 4 $PhCH_2$), 4.69 (d, $J_{1a,1b}$ = 14.6 Hz, 1H, H-1a), 7.01-7.86 (m, 24H, 4 C_6H_5, C_6H_4).

Anal. Calcd for $C_{46}H_{46}N_2O_8$ (754.88): C, 73.19; H, 6.14; N, 3.71. Found: C, 72.75; H, 6.23; N, 3.59.

2-*O*-Acetyl-1-(2-benzimidazolyl)-3,4,5,7- tetra- *O*- benzyl- 1- deoxy-α-D-*gluco*-2-heptulopyranose (11). A mixture of compound **10** (0.3 g, 0.4 mmol) and hydrazinium acetate (40 mg, 0.44 mmol) in dry dimethylformamide (5 mL) was stirred for 10 min. The mixture was diluted with ethyl acetate (20 mL) and extracted with water (2 x 10 mL). The combined organic layers were concentrated *in vacuo* and residual dimethylformamide was removed by repeated coevaporation with toluene. Flash chromatography (toluene/ethyl acetate 4:1) of the residue yielded **11** (0.21 g, 74%) as a colourless oil; R_f 0.2 (4:1 toluene/ethyl acetate); $[\alpha]_D^{20}$ +21.5° (*c* 1, chloroform); ^1H NMR (250 MHz, $CDCl_3$) δ 2.16 (s, 3H, OAc), 3.18 (d, 1H, $J_{1a,1b}$ = 9.5 Hz, H-1a), 3.72-3.94 (m, 5H, H-3, H-5, H-6, H-7a, H-7b), 4.00 (dd, 1H, $J_{3,4}$ = 8.9 Hz, $J_{4,5}$ = 9.0 Hz, H-4), 4.40-4.91 (m, 9H, H-1b, 4$PhCH_2$), 6.37-7.65 (m, 3H, C_6H_4), 7.16-7.42 (m, 21H, 4C_6H_5, C_6H_4), 10.17 (br. s, 1H, NH).

Anal. Calcd for $C_{44}H_{44}N_2O_7 \cdot 0.5\ H_2O$ (721.85): C, 73.20; H, 6.28; N, 3.88. Found: C, 73.18; H, 6.32; N, 4.00.

(Methyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosid)uronic acid (12). To a solution of methyl (methyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosid)uronate[21] (150 mg, 0.3 mmol) in acetone (10 mL) 0.1 M KOH (5.7 mL) was added at 0 °C with stirring. The mixture was stirred for 1 h and then neutralized with Amberlite IR-120 resin (H^+ form). The resin was filtered off, washed carefully with acetone and water. The combined solutions were concentrated *in vacuo*. The residue was repeatedly coevaporated with toluene to yield crude **12** (143 mg, qu) which was sufficiently pure to be used in the next step.

1-(2-Benzimidazolyl)-3,4,5,7-tetra-*O*-benzyl-1-deoxy-α-D-*gluco*-2-heptulopyranosyl(methyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosid)uronate (13). To a solution of compound **12** (50 mg, 0.104 mmol) and ketose **4a** (70 mg, 0.105 mmol) in dichloromethane (3 mL) 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (WSC, 20 mg, 0.105 mmol) was added. After stirring for 1 h the mixture was diluted with dichloromethane (10 mL) and extracted with water (2 x 5 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash chromatography (toluene/ethyl acetate 6:1) of the residue yielded **13** (55 mg, 47%) as a colourless syrup; R_f 0.29 (6:1 toluene/ethyl acetate); $[\alpha]_D^{20}$ +22.5° (*c* 1, chloroform); ^1H NMR (250 MHz, $CDCl_3$) δ 3.13 (d, 1H, $J_{1b,1b'}$ = 9.4 Hz, H-1b), 3.33 (s, 3H, OMe), 3.48 (dd, 1H, $J_{1a,2a}$ = 3.5 Hz, $J_{2a,3a}$ = 9.6 Hz, H-2a), 3.62-3.97 (m, 9H, H-3a, H-4a, H-1b', H-3b, H-4b, H-5b, H-6b, H-7b, H-7b'), 4.16 (d, 1H, $J_{4a,5a}$ = 9.9 Hz, H-5a), 4.25-4.90 (m, 15H, H-1a, 7PhCH$_2$), 6.28, 7.57 (2m, 2H, C_6H_4), 6.90-7.35 (m, 37H, 7C_6H_5, C_6H_4), 10.09 (s, 1H, NH).

Anal. Calcd for $C_{70}H_{70}N_2O_{12}$ (1131.33): C, 74.31; H, 6.24; N, 2.48. Found: C, 74.00; H, 6.28; N, 2.59.

3,4,5,7-Tetra-*O*-benzyl-1-deoxy-1-[2-(1-methyloxycarbonyl)benzimidazolyl]-α-D-*gluco*-2-heptulopyranose (14). To a solution of compound **4a** (100 mg, 0.15 mmol) and triethylamine (16 μL) in dichloromethane (3 mL) methyl chloroformate (13 μL) was added with cooling. After stirring for 20 min the reaction was quenched with saturated NH_4Cl solution. The mixture was extracted with dichloromethane. The combined organic solutions were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography (toluene/ethyl acetate 4:1) to yield **14** (85 mg, 78%) as colourless crystals; mp 122 °C; R_f 0.65 (2:1 toluene/ethyl acetate); $[\alpha]_D^{20}$ -8° (*c* 1, chloroform); ^1H NMR (250 MHz, $CDCl_3$) δ 3.39-3.47 (m, 4H, H-1b, H-3, H-7a, H-7b), 3.58-3.69 (m, 2H, H-1a, H-5), 3.91 (s, 3H, OMe), 4.00 (mc, 1H, H-6), 4.15 (dd, 1H, $J_{3,4}$ = 9.3 Hz, $J_{4,5}$ = 9.3 Hz, 1H, H-4), 4.22-4.99 (m, 8H, 4PhCH$_2$), 6.98 (d, 1H, $J_{3,OH}$ = 1.1 Hz, OH), 7.11-7.86 (m, 24H, 4C_6H_5, C_6H_4).

Anal. Calcd for $C_{44}H_{44}N_2O_8$ (728.84): C, 72.51; H, 6.09; N, 3.84. Found: C, 72.73; H, 6.03; N, 4.05.

3,4,5,7-Tetra-*O*-benzyl-1-deoxy-1-[2-(1-trichlorethoxycarbonyl)benzimidazolyl]-α-D-*gluco*-2-heptulopyranose (15). Acylation of compound **4a** with trichloroethyl chloroformate was carried out at -20 °C as described for **14** to give **15** (yield 45%) as a colourless oil. The compound was very sensitive to moisture. R_f 0.58 (2:1 toluene/ethyl acetate); $[\alpha]_D^{20}$ +4° (*c* 1, chloroform); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.38-3.70 (m, 6H, H-1a, H-1b, H-3, H-5, H-7a, H-7b), 3.96 (m, 1H, H-6), 4.12 (dd, $J_{3,4}$ = 9.3 Hz, $J_{4,5}$ = 9.3 Hz, 1H, H-4), 4.23-4.99 (m, 10H, $4PhCH_2$, CH_2CCl_3), 6.24 (d, $J_{3,OH}$ = 1 Hz, 1H, OH), 7.07-7.99 (m, 24H, $4C_6H_5$, C_6H_4).

1-(2-Benzimidazolyl)-3,4,5,7-tetra-*O*-benzyl-2-methyloxycarbonyl-α-D-*gluco*-2-heptulopyranose (16). Compound **14** was treated with triethylamine (1 equiv) in dichloromethane for 2h. Isolation and purification were carried out as described for **14** to give **16** as a colourless oil; R_f 0.45 (2:1 toluene/ethyl acetate); $[\alpha]_D^{20}$ +24.5° (*c* 1, chloroform); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.15 (d, $J_{1a,1b}$ = 9.2 Hz, 1H, H-1a), 3.71 (s, 3H, OMe), 3.70-4.05 (m, 7H, H-1b, H-3, H-4, H-5, H-6, H-7a, H-7b), 4.25-4.75 (m, 8H, $4PhCH_2$), 6.28-7.57 (m, 3H, C_6H_4), 7.02-7.35 (m, 21H, $4C_6H_5$, C_6H_4), 10.08 (br. s, 1H, NH).

1-(2-Benzimidazolyl)-3,4,5,7-tetra-*O*-benzyl -2- *O,N*- carbonyl -1- deoxy- α- D-*gluco*-2-heptulopyranose (17). (a) *From* **14** or **16**: A solution of compound **14** or **16**, respectively, in dichloromethane was stirred with an excess of triethylamine for several hours to give **17** (qu) as a colourless oil.

(b) *From* **15**: To a solution of compound **15** in dichloromethane triethylamine (1 equiv) was added. The mixture was stirred until TLC indicated complete conversion to the spiro compound **17**. Purification by flash chromatography (4:1 toluene/ethyl acetate) yielded **17** (qu) as a colourless oil; R_f 0.39 (4:1 toluene/ethyl acetate); $[\alpha]_D^{20}$ +54.5° (*c* 1, chloroform); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.07 (d, 1H, $J_{1a,1b}$ = 17.5 Hz, H-1a), 3.43 (dd, 1H, $J_{7a,7b}$ = 11.2 Hz, $J_{6,7b}$ = 1.6 Hz, H-7b), 3.75 (d, $J_{1a,1b}$ = 17.5 Hz, 1H, H-1b), 3.53 (d, 1H, $J_{3,4}$ = 9.7 Hz, H-3), 3.63 (dd, 1H, $J_{7a,7b}$ = 11.2 Hz, $J_{6,7a}$ = 3.2 Hz, H-7a), 3.79 (dd, 1H, $J_{4,5}$ = 9.7 Hz, $J_{5,6}$ = 9.7 Hz, H-5), 4.00 (ddd, $J_{5,6}$ = 9.7 Hz, $J_{6,7a}$ = 3.2 Hz, $J_{6,7b}$ = 1.6 Hz, 1H, H-6), 4.24 (dd, $J_{3,4}$ = 9.7 Hz, $J_{4,5}$ = 9.7 Hz, 1H, H-4), 4.24-4.92 (m, 8H, $4PhCH_2$), 7.04-8.00 (m, 24H, $4C_6H_5$, C_6H_4).

Anal. Calcd for $C_{43}H_{40}N_2O_7$ (696.80): C, 74.12; H, 5.79; N, 4.02. Found: C, 73.92; H, 5.82; N, 4.12.

2,6-Anhydro-1- (2-benzimidazolyl) -3,4,5,7- tetra-*O*- benzyl-1- deoxy -D- *gluco*-hept-1-enitol (18a-*f/s*). (a) *With* $ZnCl_2$: To a solution of **4a** (150 mg, 0.22 mmol) in dry toluene (10 mL) 2.2 M zinc chloride-diethyl ether in dichloromethane (0.153 mL, 0.337 mmol) was added. After heating to 100 °C for 2 h the reaction mixture was neutralized with saturated aqueous $NaHCO_3$ solution and extracted with ethyl acetate (40 mL). The combined organic solutions were dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography (12 : 1, toluene/ethyl acetate, 1% triethylamine) of the residue gave **18a**-*f* (30 mg, 20.1 %) and **18a**-*s* (11 mg, 7.7%) as colourless oils.

(b) *With p*-TsOH: To a solution of **4a** (500 mg, 0.75 mmol) in toluene (10 mL) was added *p*-toluenesulphonic acid monohydrate (290 mg, 1.5 mmol). After stirring for 2 h at 80 °C the mixture was poured into a saturated aqueous $NaHCO_3$ solution (10 mL) and extracted with ethyl acetate (100 mL). The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by flash chromatography (8:1 toluene/ethyl acetate, 1% triethylamine) to yield **18a-*f*** (170 mg, 35%) as a colourless oil. **18a-*f***: R_f 0.31 (4:1 toluene/ethyl acetate): $[\alpha]_D^{20}$ +82° (*c* 1, chloroform); ^1H NMR (250 MHz, $CDCl_3$) δ 3.60-3.72 (m, 2H H-5, H-7a), 3.84-3.91 (m, 2H, H-4, H-7b), 4.08-4.16 (m, 2H, H-3, H-6), 4.51-4.88 (m, 8H, 4 $PhCH_2$), 6.30 (s, 1H, H-1), 6.54, 7.04, 7.14, 7.66 (4 mc, 4H, Benzim.), 7.18-7.41 (m, 20H, Ph), 10.83 (br.s, 1H, NH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 69.5 (1C, C-7), 72.9-74.4 (4C, 4 CH_2Ph), 77.7 (1C, C-5), 77.92 (1C, C-6), 78.4 (1C, C-3), 84.6 (1C, C-4), 102.0 (1C, C-1), 110.5-148.7 (31C, 4 Phenyl, Benzim.), 154.4 (1C, C-2). MS (EI, 70 eV, T = 230 °C); *m/z* (%): 652 (17, $[M]^+$), 561 (60, $[M-C_7H_7]^+$), 544 (17, $[M-C_7H_8O]^+$), 453 (95, $[M-C_7H_8O-C_7H_7]^+$).

Anal. Calcd for $C_{42}H_{40}N_2O_5$ (652.8): C, 77.28; H 6.18; N, 4.29. Found: C, 76.92; H 6.39; N, 4.19.

18a-*s*: R_f 0.21; (4:1 toluene/ethyl acetate); $[\alpha]_D^{20}$ +6.2° (*c* 1, chloroform); ^1H NMR (250 MHz, $CDCl_3$): δ 3.75 (dd, $J_{3,4}$ = 3.3 Hz, $J_{4,5}$ = 8.4 Hz, 1H, H-4), 3.81-3.97 (m, 3H, H-7a, H-7b, H-6), 4.00 (dd, $J_{4,5}$ = 8.4 Hz, $J_{5,6}$ = 8.7 Hz, 1H, H-5), 4.21 (d, $J_{3,4}$ = 3.3 Hz, 1H, H-3), 4.43-5.02 (m, 8H, $PhCH_2$), 6.13 (s, 1H, H-1), 6.30, 7,66 (2mc, 2H, H-4 Benzim., H-7 Benzim.), 7.00, 7.15 (2mc, 2H, H-5 Benzim., H-6 Benzim.), 7.24-7.45 (m, 20H, Phenyl), 10.89 (br.s, 1H, NH).- ^{13}C NMR (150 MHz, $CDCl_3$): δ 70.0, 71.7, 74.0, 75.1 (4 C, 4 CH_2Ph), 70.5 (1C, C-7), 73.2 (1C, C-3), 74.5 (1C, C-5), 79.9 (1C, C-6), 81.1 (1C, C-4), 106.2 (1C, C-1), 127.8-147.9 (31C, 4 Phenyl, Benzim.), 153.5 (1C, C-2). MS (EI, 70 eV, T = 240 °C); m/z (%): 652 (17, $[M]^+$), 561 (40, $[M-C_7H_7]^+$), 544 (43, $[M-C_7H_8O]^+$), 453 (17, $[M-C_7H_8O-C_7H_7]^+$).

Anal. Calcd for $C_{42}H_{40}N_2O_5$ (652.79): C, 77.28; H, 6.18; N, 4.29. Found: C, 77.57; H, 6.23; N, 4.21.

2,6-Anhydro-3,4,5,7-tetra-*O*-benzyl-1-[2-(1-benzyl)benzimidazolyl]-1-deoxy-D-*gluco*-hept-1-enitol (18b). To a solution of **19b** (560 mg, 0.70 mmol) in dry acetonitrile (10 mL) trimethylsilyl trifluoromethanesulfonate (127 μL, 0.70 mmol) was added. After stirring at 60 °C for 30 min saturated aqueous $NaHCO_3$ solution (10 mL) was added and the mixture was extracted with ethyl acetate (150 mL). The organic solution was dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography (6:1 toluene/ethyl acetate, 1% triethylamine) of the residue yielded **18b** (332 mg, 64%) as a colourless oil; R_f 0.35 (4:1 toluene/ethyl acetate, 1% triethylamine); $[\alpha]_D$ 53° (*c* 1, chloroform); ^1H NMR (250 MHz, $CDCl_3$): δ 3.76-3.94 (m, 4H, H-7a, H-7b, H-4, H-5), 4.03 (d, $J_{3,4}$ = 4.2 Hz, 1H, H-

3), 4.31 (ddd, 1H, H-6), 4.49-4.74 (m, 8H, 4 $PhCH_2O$), 5.29, 5.36 (2 d, J_{gem} = 15 Hz, 2H, $PhCH_2N$), 5.74 (s, 1H, H-1), 6.95-7.80 (m, 29 H, Phenyl, Benzim.). MS (EI, 70 eV): 742 $(M)^+$, 651 $(M-C_7H_7)^+$, 543 $(M-C_7H_7-C_7H_7O)^+$.

Anal. Calcd for $C_{49}H_{46}N_2O_5$ (742.92): C, 79.22; H, 6.24; N, 3.77. Found: C, 79.48; H, 6.49; N, 3.8.

2,6-Anhydro-3,4,5,7-tetra-*O*-benzyl-1-[2-(1-benzyloxymethyl)benzimidazolyl]-1-deoxy-D-*gluco*-hept-1-enitol (18c). To a solution of **19c** (1.05 g, 1.26 mmol) in dry acetonitrile (20 mL) at 60 °C trimethylsilyl trifluoromethanesulfonate (0.34 mL, 1.90 mmol) was added dropwise. After stirring at 60 °C for 30 min saturated aqueous $NaHCO_3$ (15 mL) was added and the mixture was added with ethyl acetate (100 mL). The organic solution was dried ($MgSO_4$) and concentrated *in vacuo.* Flash chromatography (6:1 toluene/ethyl acetate, 1% triethylamine) of the residue yielded **18c** (666 mg, 69%) as a colourless oil; R_f 0.36 (4:1 toluene/ethyl acetate, 1% triethylamine); $[\alpha]_D$ +41.5° (*c* 1, chloroform). ^1H NMR (250 MHz, $CDCl_3$): δ 3.76 (dd, $J_{6,7a}$ = 3.6 Hz, $J_{7a,7b}$ = 11.3 Hz, 1H, H-7a), 3.82 (dd, $J_{6,7b}$ = 1.9 Hz, $J_{7a,7b}$ = 11.3 Hz, 1H, H-7b), 3.85-3.93 (m, 2H, H-4, H-5), 4.08 (d, $J_{3,4}$ = 4.0 Hz, 1 H, H-3), 4.30 (s, 2H, OCH_2Ph), 4.32 (ddd, $J_{6,7a}$ = 3.6 Hz, $J_{6,7b}$ = 1.9 Hz, $J_{5,6}$ = 8.2 Hz, 1H, H-6), 4.49-4.80 (m, 8H, 4 OCH_2Ph), 5.53, 5.58 (2 d, J_{gem} = 11.5 Hz, 2H, NCH_2O), 5.88 (s, 1H, H-1), 7.13-7.78 (m, 29H, Ph, Benzim.). ^{13}C NMR (150.4 MHz, $CDCl_3$): δ 68.20 (1 C, C-7), 73.15 (1 C, NCH_2O), 70.07, 71.38, 72.85, 73.42, 73.56, (5 C, 5 OCH_2Ph), 77.01 (1 C, C-6), 77.47 (1 C, C-5), 77.94 (1 C, C-3), 83.21 (1 C, C-4), 96.66 (1 C, C-2), 109.93-143.61 (36 C, Ph, Benzim.), 148.82 [1 C, C-2 (Benzim.)], 155.15 (1 C, C-2).

Anal. Calcd for $C_{50}H_{48}N_2O_6$ (772.94): C, 77.70; H, 6.26; N, 3.62. Found: C, 77.43; H, 6.40; N, 4.04.

Acetyl-3,4,5,7-tetra-*O*-benzyl-1-[2-(1-benzyl)benzimidazolyl]-1-deoxy-α-D-*gluco*-2-heptulopyranoside (19b). To a solution of **4b** (1.02 g, 1.34 mmol) and acetyl bromide (0.15 mL, 2.01 mmol) in dry dimethylformamide (15 mL) sodium hydride (33 mg, 1.38 mmol) was added at 0 °C. After stirring for 30 min methanol (5 mL) and then saturated aqueous NH_4Cl solution (30 mL) were added and the mixture was extracted with ethyl acetate (200 mL). The organic solution was dried ($MgSO_4$) and concentrated *in vacuo.* Chromatography (7:2 petroleum ether/ethyl acetate, 1% triethylamine) of the residue yielded **19b** (1.0 g, 93%) as a colourless oil; R_f 0.47 (6:1 toluene/ethyl acetate, 1% triethylamine); $[\alpha]_D^{20}$ +42.3° (*c* 1, chloroform). ^1H NMR (250 MHz, $CDCl_3$): δ 2.14 (s, 3H, OAc), 3.56-3.79 (m, 5H, H-5, H-6, H-7a, H-1a, H-7b), 3.99-4.08 (m, 2H, H-3, H-4), 4.27 (d, $J_{1a,1b}$ = 14.0 Hz, 1H, H-1b), 4.18, 4.26, 4.51, 4.75-6.04 (m, 10H, 5 $PhCH_2$), 6.91-7.76 (m, 29 H, 5 Ph, C_6H_4).

Anal. Calcd for $C_{51}H_{50}N_2O_7$ (802.97): C, 76.29; H, 6.28; N, 3.49. Found: C, 76.35; H, 6.37; N, 3.80.

Acetyl- 3,4,5,7- tetra-*O*- benzyl -1- [2- (1-benzyloxymethyl) benzimidazolyl] -1-deoxy-α-D-*gluco*-2-heptulopyranoside (19c). To a solution of **4c** (4.60 g, 5.82 mmol) and acetyl bromide (0.64 mL, 5.95 mmol) in dry dimethylformamide (50 mL) sodium hydride (146 mg, 6.11 mmol) was added at 0 °C. After stirring for 30 min methanol (15 mL) and then saturated aqueous NH_4Cl solution (50 mL) were added and the mixture was extracted with ethyl acetate (300 mL). The organic solution was dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography (4:1 petroleum ether/ethyl acetate, 1% triethylamine) of the residue yielded **19c** (1.0 g, 93%) as a colourless oil; R_f 0.62 (4:1 toluene/ethyl acetate, 1% triethylamine); $[\alpha]_D$ +12.7 (*c* 1, chloroform). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.15 (s, 3H, OAc), 3.45-3.55 (m, 3H, H-5, H-6, H-7a), 3.66 (dd, $J_{6,7b}$ = 2.1 Hz, $J_{7a,b}$ = 10.7 Hz, 1H, H-7b), 3.76 (d, $J_{1a,1b}$ = 14.1 Hz, 1H, H-1a), 3.91 (dd, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 9.8 Hz, 1H, H-4), 4.00 (d, $J_{3,4}$ = 9.5 Hz, 1H, H-3), 4.15 (s, 2H, OCH_2Ph), 4.44 (d, $J_{1a,1b}$ = 14.1 Hz, 1H, H-1b), 4.42, 4.45, 4.47, 4.68, 4.84, 4.91, 5.03, 5.56 (mc, 8H, 4 OCH_2Ph), 5.46, 6.16 (2 d, J_{gem} = 11.4 Hz, 2H, NCH_2Ph), 6.86-7.72 (m, 29 H, Ph, Benzim.). ^{13}C NMR (150.4 MHz, $CDCl_3$): δ 22.28 (1 C, methyl), 30.54 (1 C, C-1), 68.35 (1 C, C-7), 73.10 (1 C, N*C*H_2O), 70.21, 73.31, 75.15, 75.47, 75.45 (5 C, 5 O*C*H_2Ph), 73.40 (1 C, C-6), 77.20, (1 C, C-5), 79.43 (1 C, C-3), 82.90 (1 C, C-4), 104.96, (1 C, C-2), 110.24-142.85 (36 C, Ph, Benzim.), 149.84 [1 C, C-2 (Benzim.)], 169.27 (1 C, CH_3*C*O).

Anal. Calcd for $C_{52}H_{52}N_2O_8$ (832.99): C, 74.98; H, 6.29; N, 3.36. Found: C, 74.80; H, 6.35; N, 3.55.

1,3,4,5-Tetra-*O*-acetyl-7-[2-(1-acetyl)benzimidazolyl]-2,6-anhydro-7-deoxy-L-*glycero*-L-*gulo*-heptitol (20). Method A: A solution of **18a-*f*** (70 mg, 107 μmol) in acetic acid (3 mL) was stirred with palladium on carbon (25 mg, 10% Pd) for 24 h at room temperature under hydrogen (1 bar). Then formic acid (1 mL) was added and stirring was continued for another 24 h under hydrogen (1 bar). Then the mixture was filtered through Celite and concentrated *in vacuo*. The residue was treated with pyridine/acetic anhydride (2:1, 9 mL) at room temperature for 15 h. Then the solution was concentrated *in vacuo*. Flash chromatography (2:1 toluene/ethyl acetate) of the residue gave **20** (41 mg, 76%) as a colourless oil.

Method B: A solution of **18b** (200 mg, 0.27 mmol) in acetic acid (10 mL) was stirred with palladium on carbon (75 mg, 10% Pd) for 24 h at room temperature under hydrogen (1 bar). Then formic acid (3 mL) and additional palladium on carbon (100 mg) were added. This mixture was shaken for 3 d under hydrogen (6 bar). After addition of methanol (10 mL), the mixture was filtered through Celite, and the solution was concentrated *in vacuo*. The residue was treated with pyridine/acetic anhydride (2:1, 16 mL) at room temperature for 15 h. Flash chromatography (2:1 toluene/ethyl acetate) of the residue gave **20** (83 mg, 61%) as a colourless oil. R_f 0.31 (1:1 toluene/ethyl acetate); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.92, 1.94, 2.01, 2.02 (s, 12H, 4 OAc), 2.82 (s, 3H, NAc), 3.42 (dd, $J_{7a,7b}$ = 15.6 Hz, $J_{6,7a}$ = 4.0 Hz, 1H, H-7a), 3.57 (dd, $J_{7a,7b}$ = 15.6 Hz, $J_{6,7b}$ = 8.3 Hz, 1H, H-7b), 3.67 (ddd, $J_{2,3}$ = 9.8 Hz, $J_{1a,2}$ = 2.2 Hz, $J_{1b,2}$ = 5.2 Hz, 1 H, H-2), 3.99 (dd, $J_{1a,2}$ = 2.2 Hz, $J_{1a,1b}$ = 12.3 Hz, 1H, H-1a), 4.15-4.23 (m, 2H, H-6, H-1b), 5.01 (dd, $J_{3,4}$ = 9.2 Hz, $J_{2,3}$ = 9.8 Hz, 1H, H-3), 5.07 (dd, $J_{3,4}$ = 9.2 Hz, $J_{4,5}$ = 9.2 Hz, 1H, H-5), 5.23 (dd, $J_{4,5}$ = 9.2 Hz, $J_{3,4}$ = 9.2 Hz, 1H, H-4), 7.36, 7.70 (mc, 4 H, Benzim.). MS (FAB, positive mode, matrix: NBOH): *m/z* (%): 505 (95, $[MH]^+$), 463 (100, $[MH-C_2H_2O]^+$), 445 (7, $[MH-C_2H_4O_2]^+$).

Anal. Calcd for $C_{24}H_{28}O_{11}N_2$ (320.44): C, 55.40; H, 5.42; N, 5.38. Found: C, 55.71; H, 5.62; N, 5.48.

2,6-Anhydro-7-(2-benzimidazolyl)-7-deoxy-L-*glycero*-L-*gulo*-heptitol (21). To a solution of **20** (41 mg, 81 µmol) in dry methanol (5 mL) 0.5 M sodium methanolate in methanol (1.0 mL, 500 µmol) was added. After 3 h the reaction mixture was directly applied to short column chromatography (silica gel, eluent methanol) to yield **21** (24 mg, qu) as colourless crystals; mp 199 °C; R_f 0.52 (1:1 ethyl acetate/methanol); $[\alpha]_D^{20}$ -2.9° (*c* 0.5, CH_3OH). ^{1}H NMR (250 MHz, D_2O): δ 2.76 (dd, $J_{7a,7b}$ = 15.4 Hz, $J_{6,7a}$ = 8.6 Hz, 1H, H-7a), 3.01 (dd, $J_{5,6}$ = 9.3 Hz, $J_{4,5}$ = 9.0 Hz, 1H, H-5), 3.07-3.18 (m, 3H, H-2, H-3, H-7b), 3.27 (dd, $J_{3,4}$ = 8.6 Hz, $J_{4,5}$ = 9.0 Hz, 1H, H-4), 3.39-3.50 (m, 2H, H-1a, H-6), 3.55 (dd, $J_{1a,1b}$ = 12.2 Hz, $J_{1b,2}$ = 1.6 Hz, 1H, H-1b), 7.00, 7.28 (mc, 4H, Benzim.). ^{13}C NMR (62.9 MHz, D_2O): δ 32.8 (1C, C-1), 62.2, 71.2, 74.5, 78.8, 80.8 (6C, C-1, C-2, C-3, C-4, C-5, C-6), 115.9 (2C, C-4 Benzim., C-7 Benzim.), 123.9 (2C, C-5 Benzim., C-6 Benzim.), 139.0 (2C, C-8 Benzim., C-9 Benzim.), 154.3 (1C, C-2 Benzim.); MS (FAB, positive Mode, matrix: NBOH); *m/z* (%) 611 (3, $[2M-Na]^+$), 589 (4, $[2 M+H]^+$), 317 (20, $[M+Na]^+$), 295 (100, $[MH]^+$), 154 (40, $[(NBOH)H]^+$ + $[M-C_6H_{11}O_6+Na]^+$), 132 (19, $[MH-C_6H_{11}O_6]^+$).

Anal. Calcd for $C_{14}H_{18}N_2O_5 \cdot 0.5\ H_2O$ (303.31): C, 55.43; H, 6.31; N, 9.23. Found: C, 55.08; H, 6.45; N, 9.11.

Acetyl-3,4,5,7-tetra-*O*-benzyl-1-[2-(1-benzyloxymethyl)imidazolyl]-1-deoxy-α-D-*gluco*-2-heptulopyranoside (22). To a solution of **5** (4.6 g, 6.22 mmol) and acetyl bromide (0.47 mL, 9.38 mmol) in dry dimethylformamide (50 mL) sodium hydride (157 mg, 6.53 mmol) was added at room temperature. After stirring for 15 min methanol (5 mL) and then saturated aqueous NH_4Cl solution was added and the mixture was extracted with ethyl acetate (200 mL). The organic solution was dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography (5:2 petroleum ether/ethyl acetate, 1% triethylamine) of the residue yielded **22** (4.2 g, 86%) as a colorless oil; R_f 0.64 (2:1 toluene/ethyl acetate); $[\alpha]_D$ +23.1° (*c* 1, chloroform). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.14 (s, 3H, OAc), 3.54-3.62 (m, 4H, H-1a, H-5, H-6, H-7a), 3.71 (dd, $J_{6,7b}$ = 2.8 Hz, $J_{7a,7b}$ = 11.0 Hz, 1H, H-7b), 3.79 (d, $J_{3,4}$ = 9.6 Hz, 1H, H-3), 3.98 (dd, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 8.8 Hz, 1H, H-4), 4.22 (d, $J_{1a,1b}$ = 14.5 Hz, 1H, H-1a), 4.28-5.91 (m, 12H, 5 OCH_2Ph, NCH_2Ph), 6.89, 6.99 (2 d, J = 1.3 Hz, 2H, Im.), 7.13-7.47 (m, 25H, Ph). MS (FAB, positive Mode, Matrix: 3-Nitrobenzylalkohol, NaJ): *m/z* (%): 783 (33, $[(M)H]^+$, 724 (77, $[(M - C_2H_3O_2)H]^+$, 154 (33, $[(NBOH)H]^+$, 136 (30 $[(NBOH - H_2O)H]^+$), 91 (100, $[C_7H_7]^+$).

Anal. Calcd for $C_{48}H_{50}N_2O_8$ (782.93): C, 73.64; H, 6.44; N, 3.58. Found: C, 73.82; H, 6.02; N, 3.44.

2,6-Anhydro- 3,4,5,7- tetra-*O*- benzyl-1- [2- (1-benzyloxymethyl)imidazolyl]-1-deoxy-D-*gluco*-hept-enitol (23). To a solution of **22** (2.5 g, 3.2 mmol) in dry acetonitrile (100 mL) trimethylsilyl trifluoromethanesulfonate (1.0 mL, 5.5 mmol) was added dropwise at 60 °C. After stirring at 60 °C for 20 min saturated aqueous $NaHCO_3$ solution (50 mL) and water (50 mL) were added and the mixture was extracted with ethyl acetate (3 x 70 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography (3:2 petroleum ether/ethyl acetate, 1% triethylamine) of the residue yielded **23** (1.62 g, 70%) as a colourless oil; R_f 0.42 (2:1 toluene/ethyl acetate, 1% triethylamine); $[\alpha]_D$ +28.8° (*c* 0.5, chloroform). ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.74 (dd, $J_{6,7a}$ = 3.3 Hz, $J_{7a,7b}$ = 11.4 Hz, 1 H, H-7a), 3.82 (dd, $J_{6,7b}$ = 2.0 Hz, $J_{7a,7b}$ = 11.4 Hz, 1 H, H-7b), 3.84-3.88 (m, 2H, H-4, H-5), 4.03 (d, $J_{3,4}$ = 3.9 Hz, 1H, H-3), 4.22 (ddd, $J_{6,7a}$ = 3.3 Hz, $H_{6,7b}$ = 2.0 Hz, $J_{5,6}$ = 8 Hz, 1H, H-6), 4.29 (s, 2H, OCH_2Ph), 4.49-4.76 (m, 8H, 4 OCH_2Ph), 5.26, 5.32 (2 d, J_{gem} = 11.4 Hz, 2H, NCH_2O), 5.77 (s, 1H, H-1), 6.97, 7.13 (2 d, J = 1.3 Hz, 2H, Im.), 7.13-7.78 (m, 25 H, Ph). ^{13}C NMR (150.4 MHz, $CDCl_3$): δ 68.39 (2 C, C-7a, C-7b), 69.94, 71.37, 72.95, 73.26, 73.55 (5 C, 5 OCH_2Ph), 75.31 (1 C, NCH_2O), 76.78 (1 C, C-6), 77.46 (1 C, C-4), 78.01 (1 C, C-3), 83.41 (1 C, C-5), 97.23 (1 C, C-1), 119.17-138.15 [32 C, Ph, C-4, C-5 (Im.)], 143.00 [1 C, C-2 (Im.)], 151.96 (1 C, C-2). MS (FAB, positive Mode, matrix: NBOH, NaJ): *m/z* (%): 895 (3, $[(M + NaJ)Na]^+$), 745 (40, $[(M)Na]^+$), 723 (72, $[(M)H]^+$), 329 (30, $[(2\ NBOH)Na]^+$), 307 (12, $[(2\ NBOH)H]^+$), 289 (5, $[2\ NBOH\text{-}H_2O)H]^+$), 176 (78, $[(NBOH)Na]^+$), 154 (52, $[(NBOH)H]^+$), 136 (37, $[(NBOH\text{-}H_2O)H]^+$), 91 (100, $[C_7H_7]^+$).

Anal. Calcd for $C_{46}H_{46}N_2O_6$ (722.88): C, 76.43; H, 6.41; N, 3.88. Found: C, 76.31; H, 6.38; N, 4.12.

1,3,4,5- Tetra -*O*- acetyl-7- [2-(1-acetyl)imidazolyl]- 2,6- anhydro-7-deoxy-L-*glycero*-L-*gulo*-heptitol (24). A solution of **23** (0.50 g, 0.69 mmol) in ethyl acetate (20 mL) was shaken with palladium on carbon (50 mg, 10% Pd) for 24 h at room temperature under hydrogen (1 bar). Then the mixture was filtered through Celite, and the solution was concentrated *in vavuo*. The residue was dissolved in acetic acid (10 mL) and water (2 mL), and the solution was added to palladium on carbon (100 mg, 10% Pd) which was previously shaken in acetic acid (10 mL) under hydrogen (6 bar) for 2 h. After shaking under hydrogen (6 bar) for 3 d the solution was filtered through Celite, and the solution was evaporated *in vacuo*. The residue was treated with pyridine/acetic anhydride (2:1, 20 mL) at room temperature for 15 h. Flash chromatography (1:4 toluene/ethyl acetate) of the residue yielded **24** (0.23 g, 71%) as a colourless oil; R_f 0.36 (ethyl acetate); $[\alpha]_D$ +8.8° (*c* 1, chloroform). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.98, 1.99, 2.00, 2.01 (4 s, 12H, 4 OAc), 2.57 (s, 3H, NAc), 3.25 (dd, $J_{7a,7b}$ = 15.8 Hz, $J_{6,7a}$ = 4.1 Hz, 1H, H-7a), 3.42 (dd, $J_{7a,7b}$ = 15.8 Hz, $J_{6,7b}$ = 8.0 Hz, 1H, H-7b), 3.65 (ddd, $J_{2,3}$ = 9.7 Hz, $J_{1a,2}$ = 2.4 Hz, $J_{1b,2}$ = 5.0 Hz, 1H, H-2), 4.04 (dd, $J_{1a,2}$ = 2.4 Hz, $J_{1a,1b}$ = 12.3 Hz, 1H, H-1a), 4.10 (ddd, $J_{6,7a}$ = 4.1 Hz, $J_{6,7b}$ = 8.0 Hz, $J_{5,6}$ = 9.5 Hz, 1H, H-6), 4.19 (dd, $J_{1a,1b}$ = 12.3 Hz, $J_{1b,2}$ = 5.0 Hz, 1H, H-1b), 5.04 (dd, $J_{4,5}$ = 9.2 Hz, $J_{5,6}$ = 9.5 Hz, 1H, H-5), 5.09 (dd, $J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 9.2 Hz, 1H, H-3), 5.20 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.2 Hz, 1H, H-4), 6.95 7.22 (2 mc, 2H, Im.). MS (EI, 70 eV, T = 115 °C), *m/z* (%): 454 (40, $[M]^+$), 412 (12, $[M-C_2H_2O]^+$), 109 (53, $[C_5H_7N_2O]^+$).

2,6-Anhydro-7-deoxy-7-(2-imidazolyl)-L-*glycero*-L-*gulo*-heptitol (25). To a solution of **24** (0.15 g, 0.32 mmol) in dry methanol (25 mL) was added 0.5 M soldium methanolate in methanol (4 mL, 2.0 mmol). After stirring at room temperature for 2 h the solution was applied directly to a short silica gel column. Elution with methanol yielded **25** (78 mg, 100%) as a colourless solid; R_f 0.25 (1:1 ethyl acetate/methanol); $[\alpha]_d$ -4.3° (*c* 1, methanol). ^{1}H NMR (250 MHz, D_2O): δ 2.72 (dd, $J_{7a,7b}$ = 15.5 Hz, $J_{6,7a}$ = 8.5 Hz, 1H, H-7a), 3.97-3.57 (m, 7H, H-1a, H-2, H-3, H-4, H-5, H-6, H-7b), 3.55 (dd, $J_{1a,1b}$ = 11.9 Hz, $J_{1b,2}$ = 1.5 Hz, 1H, H-1b), 6.84 (s, 2H, Im.). ^{13}C NMR (62.9 MHz, D_2O): δ 32.8 (1 C, C-7), 62.2-80.8 (6 C, C-1, C-2, C-3, C-4, C-5, C-6), 115.9 [2 C, C-4, C-5 (Im.)].

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