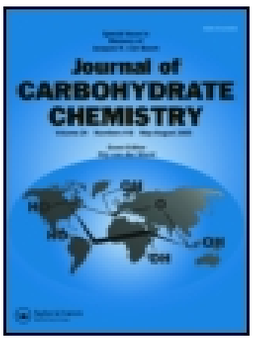

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Glycosylation employing glycopyranosyl fluorides promoted by TiF_4 under mild conditions

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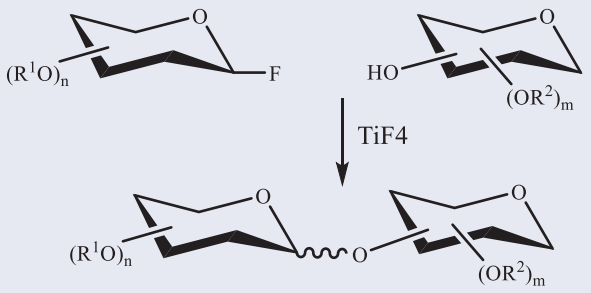
ABSTRACT

Glycopyranosyl fluorides are shown as efficient glycosyl donors by glycosylation of appropriate aglycon structures under mild conditions with Lewis acid catalysis in anhydrous ether or acetonitrile. Further direct reaction sequences gave naturally occurring disaccharide derivatives of biological interest.

GRAPHICAL ABSTRACT



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Glycopyranosyl fluorides; titanium tetrafluoride; boron trifluoride etherate; glycosylation; 1-4- and 1-3-linked-disaccharides

Introduction

The use of glycosyl fluorides as donor structures for glycosylation was previously considered inappropriate due to their reduced reactivity under silver salt catalysis. In basic media such as sodium methylate in methanol or barium hydroxide in water, unprotected glycosyl fluorides led to formation of methyl glycosides or anhydrides via epoxide-type intermediates.[1] With α-D-mannopyranosyl fluoride di- and oligosaccharides could be isolated, presumably formed again via epoxide intermediates.[2] Also, the reaction of 2,3,4,6-tetra-*O*-acetyl–α-D-glucopyranosyl fluoride with various reagents gave a mixture of products, among which trehalose could be isolated.[3] Phenyl β-D-glucopyranoside could be obtained from β-D-glucopyranosyl fluoride and barium phenolate in water.[4]

None of these reports qualified for synthetic requirements, until Mukaiyama et al. took up the employment of glycosyl fluorides for

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synthesis.[5] Indeed, more sophisticated glycosides could be prepared using $SnCl_2/AgClO_4$ leading with notable stereoselectivity to 1,2-*cis* glycosides. Further, a considerable number of tin(II)-catalyst systems were reported.[6–10] Extensive studies of Noyori et al. employing perbenzylated glycosyl fluorides under catalysis of SiF_4 and Me_3SiF with alcohols showed preferred formations in high yields of α-glycosides in ether and β-glycosides in acetonitrile.[11] Much easier was the use of BF_3-Et_2O as demonstrated in several synthetic studies.[12–15] Apparently, for glycosylations with perbenzylated as well as peracetylated glycosyl fluorides metal fluorides of the fourth and fifth group of the periodic table represented the most advantageous Lewis acids.[16] Thus, SnF_4 and TiF_4 proved to be effective heterogeneous catalysts in anhydrous polar (acetonitrile) or less polar (ether) solvents with convenient workup procedures.[16,17] Several surveys on the synthetic use of glycosyl fluorides were provided recently.[18–21,22]

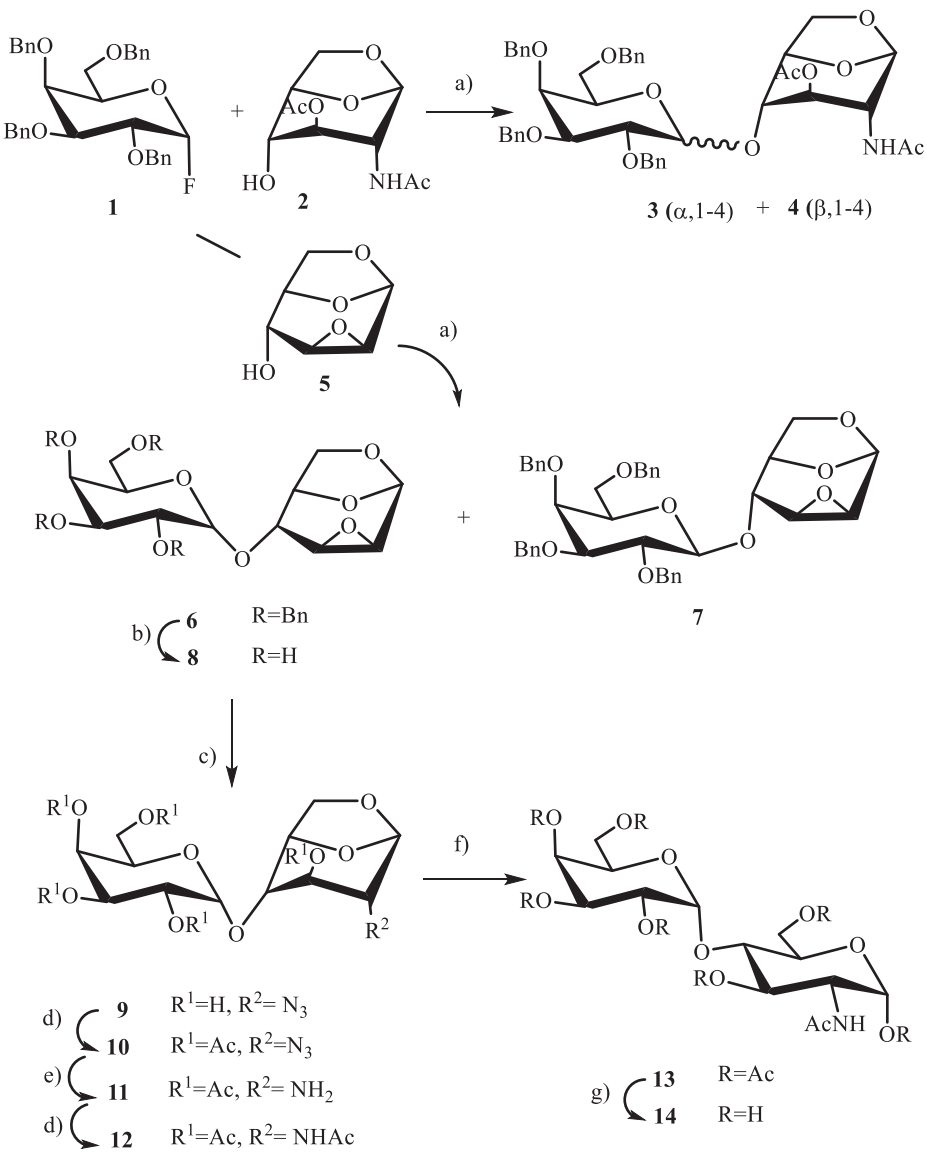
In general, for unprotected as well as peracetylated or perbenzylated glycosyl fluorides (e.g. Glc or Gal) the β-anomers proved to be less stable than the robust α-anomers. Since we were interested in using glycosyl fluorides as donor structures preferentially for synthetic purposes, several selectively prepared carbohydrate aglyconic molecules for formation of biologically relevant disaccharide derivatives were checked.

Results and discussion

Synthesis of 2-acetamido-2-deoxy-4-O-(α-D-galactopyranosyl)-D-glucopyranose (α-Gal-1 − 4-GlcNAc)

One of the important disaccharide derivatives of blood group antigens is *N*-acetyl-isolactosamine (α-Gal-1 − 4-GlcNAc), which was previously synthesized employing the orthoester method by Sinay et al.[23,24] Employing glycosyl fluorides, our attempt started with the perbenzylated galactopyranosyl fluoride (**1**)[25] and the 2-acetamido-1,6-anhydro *gluco* derivative **2**[26] as aglycon in anhydrous acetonitrile and with TiF_4 catalysis (Sch. 1). The disaccharide was formed in a yield of 79% with both the α-anomer (**3**) and β-anomer (**4**) in a favorite ratio of 83:17; however, since no chromatographic separation could be realized we had to change the approach.

Therefore, glycosyl fluoride **1** and 1,6:2,3-dianhydro-β-D-mannopyranose (**5**)[27] as aglycon structure and precursor were selected, which gave under similar conditions the α- and β-1-4-linked disaccharides (**6**) and (**7**) in 86% yield and a ratio of 74:26, which could be readily separated by chromatography. The α-component **6** was hydrogenolized to give compound **8**, in which opening of the 2,3-anhydro ring with sodium azide led to the 2-azido-*gluco* derivative **9**. Direct peracetylation gave the crystalline derivative **10**; however,



Scheme 1. Synthesis of 2-acetamido-2-deoxy-4-*O*-(α-D-galactopyranosyl)-D-glucopyranose (α-Gal-1-4-GlcNAc). Reaction conditions: (a) TiF_4/CH_3CN; (b) Pd-C/H_2/CH_3OH; (c) NaN_3/EtOH/H_2O; (d) Ac_2O/py; (e) Pd-C/H_2/HOAc; (f) Ac_2O/BF_3; (g) NaOMe/MeOH.

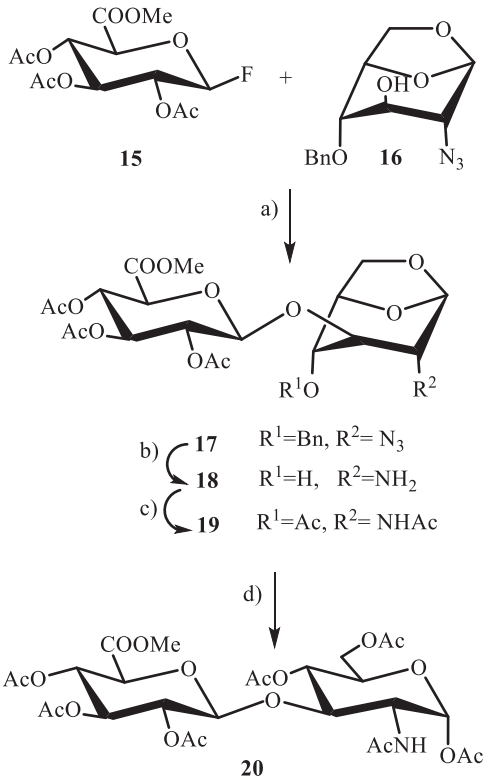
the yield of 28% was not convincing at all. Hydrogenation of the azide in **10** worked as expected and acetylation led to the crystalline compound **12**.

An explicitly preferred method[26] was heating epoxide **8** with aqueous ammonia under pressure, which after subsequent peracetylation gave the crystalline material **12** in 80% yield. Further, the 1,6-anhydro ring was opened with BF_3-Et_2O/acetic anhydride, which gave the crystalline compound **13** in 63% yield. Finally, *O*-deacetylation under Zemplén conditions[28] provided the target compound 2-acetamido-2-deoxy-4-*O*-(α-D-

galactopyranosyl)-D-glucopyranose (*N*-acetyl-isolactosamine, Gal-α,1 – 4-GlcNAc, **14)** (Sch. 1).

Synthesis of 2-acetamido-3-O-(β-D-glucopyranosyluronate)-2-deoxy-D-glucopyranose (hyalobiuronic acid, β-GlcUA-1-3-GlcNAc)

The dominant compound in connective tissues such as umbilical cord or vitreous body of the eye is the polysaccharide hyaluronic acid, and by acid hydrolysis[29,30] it gave a disaccharide identified as hyalobiuronic acid.[31] Previous syntheses of some derivatives of this repeating unit of the polysaccharide was reported by Koenigs-Knorr type condensation catalyzed by mercury cyanide.[32] Since acetylated β-glycosyl fluorides were reported to react stereospecifically via an acetoxonium intermediate to give 1,2-*trans* products, the glucopyranosyluronate fluoride **15**[33] was the ideal donor structure to react with the 1,6-anhydro-gluco derivative **16.**[33] By reaction with TiF_4 in anhydrous acetonitrile the yield of the β,1-3-linked disaccharide **17** was 55%; however, with BF_3 in dichloromethane the yield could be improved to 67%. Simultaneous de-benzylation and reduction of the azido group by hydrogenation in acetic acid at



Scheme 2. Synthesis of hyalobiuronic acid methyl ester. Reaction conditions: (a) BF_3-Et_2O; (b) Pd-C/H_2/HOAc; (c) Ac_2O, pyr; (d) BF_3-Et_2O/HOAc.

Table 1. Glycosylation reactions of various acceptors with glycoyl fluorides.

Glycosyl Fluoride	Aglycon	Disaccharides	Yield (%)	α,1-4 : β,1-4
21	**22**	**23** + **24**	85	55 : 45
1	**22**	**25** + **26**	81	65 : 35
1	**28**	**29** + **30**	85	62 : 38

TiF_4; anhydr. Et_2O, 3h, 0°C

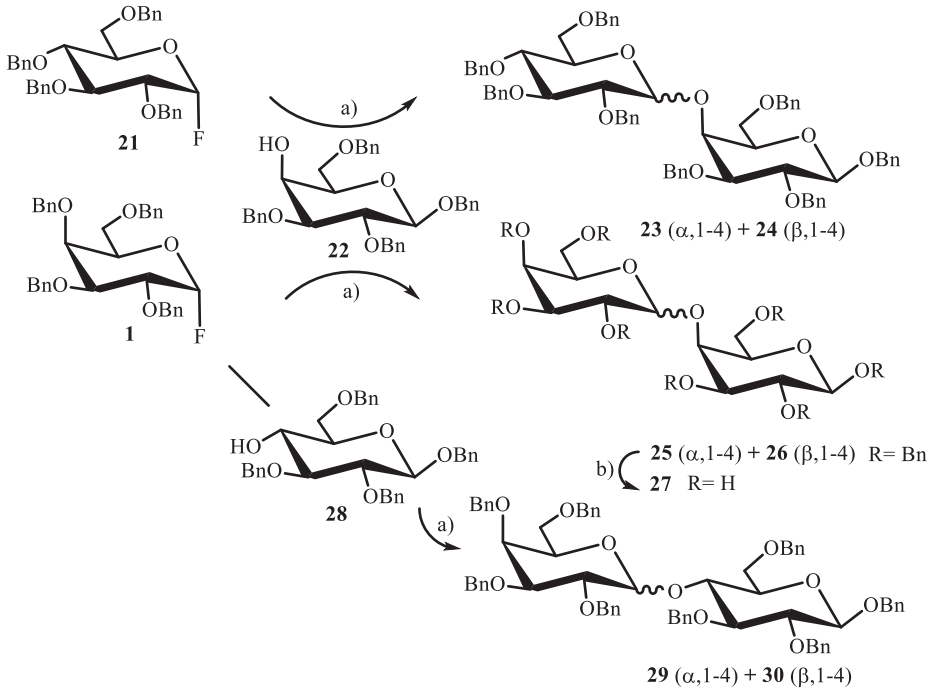
40 °C gave the intermediate **18**, which was peracetylated to result in formation of the crystalline compound **19** in 68% yield. Finally, the 1,6-anhydro ring was cleaved with BF_3-Et_2O/Ac_2O at room temperature to give the crystalline peracetate **20** in 75% yield. Deacetylation under Zemplén conditions[28] could not be realized due to extensive degradations. This compound is extremely base labile presumably because of the β-elimination tendency known for uronic acid derivatives (Sch. 2).

Synthesis of various α-1-4-linked disaccharides

Whereas bacterial infection of animal cells are common to start with attachment of mannose-rich oligo- and polysaccharides, properties of disaccharide derivatives with *gluco* and *galacto* units are unknown concerning potential inhibitory activities. Therefore, syntheses of predominantly α-1-4-linked disaccharides with Glc-Gal, Gal-Gal, and Gal-Glc arrangement were of interest. As donor structures perbenzylated α-D-glycopyranosyl fluorides of *gluco*-(**21**)[34] and *galacto*-(**1**)[25] configurations were easily obtained by perbenzylation of the unblocked fluorides.[25] Their treatment under TiF_4 catalysis with the C4-selectively unblocked tetra-*O*-benzyl derivatives of *galacto*-(**22**)[24] and *gluco*-(**28**)[26] configurations in anhydrous ether at 0 °C for 3 h gave the disaccharide derivatives in over 80% yield and an α:β ratio of about 60:40 (Table 1). Their separation by chromatography was feasible, however, reduced the overall yield considerably. In In case of disaccharide **25** hydrogenolysis in methanol led to the naturally occurring 4-*O*-(α-D-galactopyranosyl)-D-galactopyranose (**27**)[35–38] as amorphous material (Sch. 3).

Conclusion

This contribution reports on effective formations of disaccharide fragments by glycosylations employing glycopyranosyl fluorides under Lewis acid catalysis in anhydrous ether or acetonitrile. Further, straightforward reaction sequences leading to the naturally occurring disaccharide derivatives are described.



Scheme 3. Synthesis of various α-1-4-linked disaccharides. Reaction conditions: (a) TiF_4/Et_2O; (b) $Pd\text{-}C/H_2/CH_3OH$.

Experimental

General methods

All reactions were monitored by thin layer chromatography on silica gel foils GF_{254} (Merck). Detection was by UV or spraying with 20% ethanolic sulfuric acid and subsequent heating. Column chromatography was done on silica gel 60 (230-400 mesh, Merck) by the flash mode with the solvent mixture recorded. ^1H NMR (300 MHz) spectra were done on Bruker WM-300. Melting points are uncorrected and were taken with a Reichert heating table microscope. Optical rotations were measured with Perkin-Elmer polarimeter 241, cuvette length 10 cm, and temperature 20 °C. Solvents and reagents including TiF_4 were purchased from Sigma-Aldrich.

Acetylation (general procedure, GP1)

The starting material dissolved in anhydrous pyridine was treated with acetic anhydride (3 eq) for 1–3 h at 20 °C. The mixture was mixed with ice water and extracted with dichloromethane. The organic phase was washed with saturated sodium hydrogen carbonate and water, dried over $MgSO_4$, filtered, co-evaporated with toluene and purified by chromatography.

Glycosylation with TiF_4 (general procedure, GP2)

Glycosyl fluoride (1 mmol) and aglycon (1 mmol) dissolved in anhydrous solvent (3–5 mL) were stirred with activated molecular sieves 3 A (50 mg, dried for 24 h at 300 °C in high vacuo). TiF_4 (0.1–5.0 eq.) was added and stirring continued at 20 °C for the given time. For work up the mixture was filtered over silica gel, then poured into ice cold, aqueous saturated sodium hydrogen carbonate, extracted with ethyl acetate or dichloromethane, dried ($MgSO_4$) and evaporated to give the raw material to be purified further.

2-Acetamido-3-O-acetyl-4-O-(2,3,4,6-tetra-O-benzyl-α-D-galactopyranosyl)-1,6-anhydro-2-deoxy-β-D-glucopyranose (3)

2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl fluoride (**1**,[25] 170 mg, 0.31 mmol) and 2-acetamido-1,6-anhydro-2-deoxy-β-D-glucopyranose (**2**[26], 77 mg, 0.31 mmol) dissolved in anhydrous acetonitrile (5 mL) were treated with titanium tetrafluoride (40 mg, 0.32 mmol) for 2 h at 0 °C and worked up according to GP2. The raw material (187 mg, 78%) contained a mixture of anomers α(**3**): β(**4**) = 83: 17 according to ^{1}H NMR. By chromatography in various solvent mixtures only the α-anomer **3** could be obtained pure as amorphous material; mp 125–127 °C, $[\alpha]_D^{20} = +37.7$ ($c = 1.8$, $CHCl_3$); ^{1}H NMR (300 MHz, C_6D_6): δ = 6.99–7.38 (m, 20H, Aryl-H), 5.79 (s, 1H, H-1), 4.43 (d, 1H, $J_{2,NH}$ = 8.4 Hz, H-2), 4.95 (m, 1H, H-3), 3.42 (m, H-4), 4.25 (mc, 2H, H-5, −5′), 3.52 (dd, 1H, $J_{5,6a}$ = 0.7, $J_{6a,6b}$ = 7.7 Hz, H-6a), 3.39 (dd, 1H, $J_{5,6b}$ = 5.7, $J_{6a,6b}$ = 7.7 Hz, H-6b), 6.65 (d, 1H,$J_{2,NH}$= 8.4 Hz, NH), 5.42 (d, 1H, $J_{1',2'}$ = 3.5 Hz, H-1′), 4.22 (dd, 1H, $J_{1',2'}$ = 3.5, $J_{2',3'}$ = 10.1 Hz, H-2′), 3.96 (dd, 1H, $J_{2',3'}$ = 10.1, $J_{3',4'}$ = 2.9 Hz, H-3′), 3.91 (dd, 1H, $J_{3',4'}$ = 2.9, $J_{4',5'}$ = 1.1 Hz, H-4′), 3.77 (dd, 1H, $J_{5',6á}$ = 6.3, $J_{6á,6b'}$ = 9.4 Hz, H-6á), 3.70 (dd, 1H, $J_{5',6b'}$ = 6.5, $J_{6á,6b'}$ = 9.4 Hz, H-6b́), 4.30, 4.36, 4.47(2), 4.52, 4.56(2), 5.02 (4 AB, 8H, 4 x O*CH*$_2$Aryl), 1.47, 1.49 (2 s, each 3H, OAc, NAc). Calcd. for $C_{44}H_{49}NO_{11}$ (767.87): C, 68.82; H, 6.43; N, 1.82. Found: C, 68.80; H, 6.58; N, 1.21.

1,6:2,3-Dianhydro-4-O-(2,3,4,6-tetra-O-benzyl-α-D-galactopyranosyl)-β-D-mannopyranose (6) and 1,6:2,3-Dianhydro-4-O-(2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl)-β-D-mannopyranose (7)

2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl fluoride (**1**,[25] 1.1 g, 2.3 mmol) and 1,6:2,3-dianhydro-β-D-mannopyranose (**5**[27], 292 mg, 2.03 mmol) dissolved in anhydrous acetonitrile (20 mL) were treated with titanium tetrafluoride (251 mg, 2.03 mmol) for 2 h at 0 °C and worked up according to GP2. The raw material (1.14 g, 86%) contained a mixture of anomers α(**6**):

β(**7**) = 74: 26 according to ^{1}H NMR. Separation of the anomers was by chromatography (dichloromethane/ethyl ether 20: 1).

Compound **6**: colorless sirup, $[\alpha]_D^{20} = +32.1$ ($c = 1.1$, $CHCl_3$); ^{1}H NMR (300 MHz, C_6D_6): δ = 7.05–7.40 (m, 20H, Aryl-H), 5.40 (d, 1H, $J_{1,2}$ = 3.1 Hz, H-1), 2.80 (dd, 1H, $J_{1,2}$ = 3.1, $J_{2,3}$ = 3.8 Hz, H-2), 3.06 (d, 1H, $J_{2,3}$ = 3.8, $J_{3,4}$ = 0 Hz, H-3), 3.42 (s, 1H, $J_{3,4} = J_{4,5}$ = 0 Hz, H-4), 4.75 (dd, 1H, $J_{5,6a}$ = 2.0, $J_{5,6b}$ = 6.9 Hz, H-5), 3.47 (dd, 1H, $J_{5,6a}$ = 2.0, $J_{6a,6b}$ = 7.3 Hz, H-6a), 3.35 (dd, 1H, $J_{5,6b}$ = 6.9, $J_{6a,6b}$ = 7.3 Hz, H-6b), 4.99 (d, 1H, $J_{1',2'}$ = 3.7 Hz, H-1′), 4.23 (dd, 1H, $J_{1',2'}$ = 3.7, $J_{2',3'}$ = 10.4 Hz, H-2′), 4.04 (dd, 1H, $J_{2',3'}$ = 10.4, $J_{3',4'}$ = 2.9 Hz, H-3′), 3.72 (dd, 1H, $J_{3',4'}$ = 2.9, $J_{4',5'}$ = 1.0 Hz, H-4′), 4.33 (ddd, 1H, $J_{4',5'}$ = 1.0, $J_{5',6á}$ = 7.1, $J_{5',6b'}$ = 5.0 Hz, H-5′), 3.78 (dd, 1H, $J_{5',6á}$ = 7.1, $J_{6á,6b'}$ = 9.6 Hz, H-6á), 3.52 (dd, 1H, $J_{5',6b'}$ = 5.0, $J_{6á,6b'}$ = 9.6 Hz, H-6b́), 4.29(2), 4.43, 4.49, 4.53, 4.66(2), 5.03 (4 AB, 8H, 4 x OCH_2Aryl). Calcd. for $C_{40}H_{42}O_9$ (666.77): C, 72.06; H, 6.35. Found: C, 72.81; H, 6.42.

Compound **7**: colorless sirup, $[\alpha]_D^{20} = -5.5$ ($c = 1.7$, $CHCl_3$); ^{1}H NMR (300 MHz, C_6D_6): δ = 7.02–7.51 (m, 20H, Aryl-H), 5.36 (d, 1H, $J_{1,2}$ = 3.1 Hz, H-1), 2.80 (dd, 1H, $J_{1,2}$ = 3.1, $J_{2,3}$ = 3.8 Hz, H-2), 3.38 (m, 1H, H-3), 3.67 (m, 1H, H-4), 4.20 (dd, 1H, $J_{5,6a}$ = 2.1, $J_{5,6b}$ = 7.2 Hz, H-5), 3.47 (dd, 1H, $J_{5,6a}$ = 2.1, $J_{6a,6b}$ = 7.2 Hz, H-6a), 3.34 (dd, 1H, $J_{5,6b}$ = 7.2, $J_{6a,6b}$ = 7.2 Hz, H-6b), 4.35 (d, 1H, $J_{1',2'}$ = 7.7 Hz, H-1′), 4.12 (dd, 1H, $J_{1',2'}$ = 7.7, $J_{2',3'}$ = 9.8 Hz, H-2′), 3.43 (dd, 1H, $J_{2',3'}$ = 9.8, $J_{3',4'}$ = 3.0 Hz, H-3′), 3.86 (dd, 1H, $J_{3',4'}$ = 3.0, $J_{4',5'}$ = 0.7 Hz, H-4′), 3.50 (m, 1H, H-5′), 3.73 (dd, 1H, $J_{5',6á}$ = 7.2, $J_{6á,6b'}$ = 9.0 Hz, H-6á), 3.64 (dd, 1H, $J_{5',6b'}$ = 5.7, $J_{6á,6b'}$ = 9.0 Hz, H-6b́), 4.28, 4.34, 4.58, 4.62, 4.68,4.73, 5.06, 5.08 (4 AB, 8H, 4 x OCH_2Aryl). Calcd. for $C_{40}H_{42}O_9$ (666.77): C, 72.06; H, 6.35. Found: C, 72.18; H, 6.49.

1,6:2,3-Dianhydro-4-O-(α-D-galactopyranosyl)-β-D-mannopyranose (8)

Compound **6** (900 mg, 1.35 mmol) dissolved in methanol (15 mL) were hydrogenated with palladium/charcoal (100 mg, 10% Pd) for 12 h at 40 °C. Following filtration via celite and evaporation 376 mg (91%) of compound **8** were obtained as colorless sirup, $[\alpha]_D^{20} = +106.1$ ($c = 0.77$, CH_3OH), which was directly used for the subsequent reaction.

1,6-Anhydro-2-azido-3-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-α-D-galacto-pyranosyl)- 2-deoxy-β-D-glucopyranose (10)

Compound **8** (376 mg, 1.23 mmol) dissolved in ethanol/water (4:1, 10 mL) were refluxed with sodium azide (500 mg, 7.7 mmol) and ammonium chloride (500 mg, 9.4 mmol) for 6 h. The cold solution was filtered, evaporated and dried in vaccuo to give raw **9**. The material was peracetylated according to GP1 and worked up. Purification from considerable amount of

degradation products was by chromatography (toluene/ethyl acetate 1:1) to give 190 mg (28%) of **10** as colorless crystals, mp 147 °C, $[\alpha]_D^{20} = +106.9$ ($c = 1.76$, $CDCl_3$); ^1H NMR (300 MHz, C_6D_6): $\delta = 5.29$ (m, 1H, H-1), 2.70 (m, 1H, H-2), 4.98 (m, 1H, H-3), 3.04 (m, 1H, H-4), 4.48 (m, 1H, H-5), 3.39 (dd, 1H, $J_{5,6a} = 1.3$, $J_{6a,6b} = 7.7$ Hz, H-6a), 3.34 (dd, 1H, $J_{5,6b} = 5.7$, $J_{6a,6b} = 7.7$ Hz, H-6b), 5.57 (d, 1H, $J_{1',2'} = 3.9$ Hz, H-1′), 5.53 (dd, 1H, $J_{1',2'} = 3.9$, $J_{2',3'} = 10.9$ Hz, H-2′), 5.93 (dd, 1H, $J_{2',3'} = 10.9$, $J_{3',4'} = 3.3$ Hz, H-3′), 5.78 (dd, 1H, $J_{3',4'} = 3.3$, $J_{4',5'} = 1.1$ Hz, H-4′), 4.53 (m, 1H, H-5′), 4.24 (dd, 1H, $J_{5',6á} = 6.6$, $J_{6á,6b'} = 11.3$ Hz, H-6á), 4.13 (dd, 1H, $J_{5',6b'} = 6.0$, $J_{6á,6b'} = 11.3$ Hz, H-6b́), 1.50, 1.63(2), 1.75, 2.00 (each s, each 3H, 5 x OAc). Calcd. for $C_{22}H_{29}N_3O_{14}$ (559.48): C, 47.23; H, 5.22; N, 7.51. Found: C, 46.35; H, 5.36; N, 7.65.

2-Acetamido-3-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-α-D-galactopyranosyl)-1,6-anhydro-2-deoxy-β-D-glucopyranose (12)

Method A

Compound **10** (160 mg, 0.29 mmol) dissolved in acetic acid (5 mL) were hydrogenated with palladium/charcoal (100 mg, 10% Pd) for 12 h at 40 °C. Following filtration via celite and evaporation the raw material **11** was peracetylated according to GP1 and worked up. Purification was by chromatography (ethyl acetate) to give 127 mg (77%) of **12** as colorless crystals.

Method B

Compound **8** (320 mg, 1.04 mmol) dissolved concentrated aqueous ammonia solution (10 mL) were heated in an autoclave for 24 h at 100 °C. The solvent was evaporated and the residue peracetylated according to GP1 and worked up. The material was crystallized from ethyl acetate/petroleum ether to give 480 mg (80%) of **12** as colorless crystals, mp 86 °C, $[\alpha]_D^{20} = +40.6$ ($c = 0.85$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 5.41$ (s, 1H, H-1), 4.10 (d, 1H, $J_{2,NH} = 9.6$ Hz, H-2), 4.58 (m, 1H, H-3), 3.54 (m, 1H, H-4), 4.63 (dd, 1H, $J_{5,6a} = 0.5$, $J_{5,6b} = 5.7$ Hz, H-5), 4.05 (dd, 1H, $J_{5,6a} = 0.5$, $J_{6a,6b} = 7.7$ Hz, H-6a), 3.83 (dd, 1H, $J_{5,6b} = 5.7$, $J_{6a,6b} = 7.7$ Hz, H-6b), 6.04 (d, 1H, $J_{2,NH} = 9.6$ Hz, NH), 5.34 (d, 1H, $J_{1',2'} = 3.7$ Hz, H-1′), 5.20 (dd, 1H, $J_{1',2'} = 3.7$, $J_{2',3'} = 11.1$ Hz, H-2′), 5.41 (dd, 1H, $J_{2',3'} = 11.1$, $J_{3',4'} = 3.3$ Hz, H-3′), 5.48 (dd, 1H, $J_{3',4'} = 3.3$, $J_{4',5'} = 1.2$ Hz, H-4′), 4.53 (ddd, 1H, $J_{4',5'} = 1.2$, $J_{5',6á} = 6.0$, $J_{5',6b'} = 7.0$ Hz, H-5′), 4.14 (dd, 1H, $J_{5',6á} = 6.0$, $J_{6á,6b'} = 11.6$ Hz, H-6á), 4.08 (dd, 1H, $J_{5',6b'} = 7.0$, $J_{6á,6b'} = 11.6$ Hz, H-6b́), 2.01, 2.04, 2.05, 2.09, 2.11, 2.17 (each s, each 3H, 5 x OAc, NAc). Calcd. for $C_{24}H_{33}NO_{15}$ (575.52): C, 50.09; H, 5.78; N, 2.43. Found: C, 50.34; H, 6.01; N, 2.10.

2-Acetamido-1,3,6-tri-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-α-D-galacto-pyranosyl)-2-deoxy-α-D-glucopyranose (Octaacetyl-isolactosamine,13)

Compound **12** (420 mg, 0.73 mmol) dissolved in acetic anhydride (10 mL) was stirred with boron trifluoride-etherate (0.5 mL) for 3 h at 20 °C. The mixture was poured into ice-cold saturated aqueous sodium hydrogen carbonate, stirred for 30 min and extracted with ethyl acetate. The organic phase was washed with water, dried (MgSO4), evaporated and the raw material purified by chromato-graphy (toluene/ethyl acetate 4:1) to give 310 mg (63%) of **13** as colorless crystals, mp 188 °C, $[\alpha]_D^{20} = +112.9$ ($c = 2.14$, $CHCl_3$); ^{1}H NMR (300 MHz, $CHCl_3$): $\delta = 5.54$ (d, 1H, $J_{1,2}$ = 4.0 Hz, H-1), 4.39 (ddd, 1H, $J_{1,2} = 4.0$ $J_{2,3} = 11.1$, $J_{2,NH} = 9.6$ Hz, H-2), 4.58 (dd, 1H, $J_{2,3} = 11.1$, $J_{3,4} = 9.0$ Hz, H-3), 4.07 (m, 1H, $J_{3,4} = 9.0$, $J_{4,5}$ = 9.6 Hz H-4), 4.00 (m, 1H, H-5), 4.43 (dd, 1H, $J_{5,6a} = 2.4$, $J_{6a,6b} = 12.4$ Hz, H-6a), 4.19 (dd, 1H, $J_{5,6b} = 4.0$, $J_{6a,6b} = 12.4$ Hz, H-6b), 5.51 (d, 1H, $J_{2,NH}$ = 9.6 Hz, NH), 6.09 (d, 1H, $J_{1',2'} = 3.5$ Hz, H-1′), 5.15 (dd, 1H, $J_{1',2'} = 3.5$, $J_{2',3'} = 11.0$ Hz, H-2′), 5.28 (dd, 1H, $J_{2',3'} = 11.9$, $J_{3',4'} = 3.1$ Hz, H-3′), 5.44 (dd, 1H, $J_{3',4'} = 3.1$, $J_{4',5'} = 1.0$ Hz, H-4′), 4.17 (m, 1H, H-5′), 4.11 (dd, 1H, $J_{5',6á} = 1.5$, $J_{6á,6b'} = 12.6$ Hz, H-6á), 4.08 (dd, 1H, $J_{5',6b'} = 6.0$, $J_{6á,6b'} = 12.6$ Hz, H-6b́), 1.92, 1.99, 2.06(2), 2.07, 2.11, 2.14, 2.23 (each s, each 3H, 7 x OAc, NAc). Calcd. for $C_{28}H_{39}NO_{18}$ (677.61): C, 49.63; H, 5.80; N, 2.07. Found: C, 49.13; H, 5.71; N, 1.91.

2-Acetamido-2-deoxy-4-O-(α-D-galactopyranosyl)-α-D-glucopyranose (N-Acetyl-isolactosamine,14)

Compound **13** (200 mg, 0.30 mmol) dissolved in anhydrous methanol (10 mL) was treated with sodium methylate in anhydrous methanol (1%, 1 mL) for 4 h at 20 °C. Following neutralization with Amberlite IRA 120, H^+ the residue was freeze dried to give 105 mg (93%) of **14** as colorless amorphous material, softening interval 180–185 °C, $[\alpha]_D^{20} = +138.1$ (5 min) → + 125.9 (6 h) ($c = 0.82$, H_2O); lit.[24] mp 193–195 °C, $[\alpha]_D^{20} = +147$ (2 min) → + 131 (3 h) ($c = 0.5$, H_2O/CH_3OH 9:1).

1,6-Anhydro-2-azido-3-O-(methyl 2,3,4-tri-O-acetyl-β-D-glucopyranosyl-uronate)-4-O-benzyl-2-deoxy-β-D-glucopyranose (17)

Methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate fluoride (**15**,[39] 550 mg, 1.64 mmol) and 1,6-anhydro-2-azido-4-*O*-benzyl-2-deoxy-β-D-glucopyranose (**16**,[33] 454 mg, 1.64 mmol) dissolved in anhydrous dichloromethane (10 mL) were treated with boron trifluoride-etherate (0.83 mL, 6.5 mmol) and molecular sieve 3 A (59 mg) for 2 h at 20 °C. The mixture was poured onto ice water, extracted with dichloromethane, dried ($MgSO_4$), evaporated and purified by

chromatography (dichloromethane/ethyl acetate 20: 1) to give 650 mg (67%) of **17**, which crystallized from ethylacetate/*n*-hexane; mp 147–149 °C, $[\alpha]_D^{20} = +39.9$ ($c = 0.5$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.29$–7.41 (m, 5H, Aryl-H), 5.51 (m, 1H, H-1), 2.98 (m, 1H, H-2), 4.01 (m, 1H, H-3), 3.50 (m, 1H, H-4), 4.58 (dd, 1H, $J_{5,6a} = 0.8$, $J_{5,6b} = 6.0$ Hz, H-5), 3.89 (dd, 1H, $J_{5,6a} = 0.8$, $J_{6a,6b} = 7.6$ Hz, H-6a), 3.66 (dd, 1H, $J_{5,6b} = 6.0$, $J_{6a,6b} = 7.6$ Hz, H-6b), 4.55 (d, 1H, $J_{1',2'} = 8.0$ Hz, H-1′), 5.01(dd, 1H, $J_{1',2'} = 8.0$, $J_{2',3'} = 9.6$ Hz, H-2′), 5.16 (dd, 1H, $J_{2',3'} = 9.6$, $J_{3',4'} = 9.5$ Hz, H-3′), 5.27 (dd, 1H, $J_{3',4'} = 9.5$, $J_{4',5'} = 9.7$ Hz, H-4′), 4.53 (m, 1H, H-5′), 4.63, 4.72 (AB, 2H, OCH_2Aryl), 3.75 (s, 3H, OCH_3), 2.03, 2.04, 2.05 (each s, each 3H, 3 x OAc). Calcd. for $C_{26}H_{31}N_3O_{13}$ (593.54): C, 52.61; H, 5.26; N, 7.08. Found: C, 52.22; H, 5.13; N, 6.30.

2-Acetamido-3-O-(methyl 2,3,4-tri-O-acetyl-β-D-glucopyranosyluronate)-4-O-acetyl-1,6-anhydro-2-deoxy-β-D-glucopyranose (19)

Compound **17** (391 mg, 0.66 mmol) dissolved in acetic acid (10 mL) were hydrogenated with palla-dium/charcoal (100 mg, 10% Pd) for 15 h at 40 °C. Following filtration via celite and evaporation the raw material **18** was per-acetylated according to GP1 and worked up. Purification was by chroma-tography (ethyl acetate) and crystalli-sation from ethyl acetate/*n*-hexane to give 252 mg (68%) of **19** as colorless crystals; mp 224 °C, $[\alpha]_D^{20} = -70.0$ ($c = 1.41$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.341$ (m, 1H, H-1), 3.91 (m, 1H, H-2), 3.68 (m, 1H, H-3), 4.83 (m, 1H, H-4), 4.59 (dd, 1H, $J_{5,6a} = 0.8$, $J_{5,6b} = 6.0$ Hz, H-5), 4.10 (dd, 1H, $J_{5,6a} = 0.8$, $J_{6a,6b} = 8.0$ Hz, H-6a), 3.70 (dd, 1H, $J_{5,6b} = 6.0$, $J_{6a,6b} = 8.0$ Hz, H-6b), 5.87 (d, 1H, $J_{2,NH} = 9.3$ Hz, NH), 4.87 (d, 1H, $J_{1',2'} = 8.0$ Hz, H-1′), 5.07(dd, 1H, $J_{1',2'} = 8.0$, $J_{2',3'} = 9.6$ Hz, H-2′), 5.33 (dd, 1H, $J_{2',3'} = 9.6$, $J_{3',4'} = 9.6$ Hz, H-3′), 5.18 (dd, 1H, $J_{3',4'} = 9.6$, $J_{4',5'} = 10.0$ Hz, H-4′), 4.10 (d, 1H, $J_{4',5'} = 10.0$ Hz, H-5′), 3.74 (s, 3H, OCH_3), 2.02(2), 2.08, 2.12, 2.17 (each s, each 3H, 4 x OAc, NAc). Calcd. for $C_{23}H_{31}NO_{15}$ (561.49): C, 49.20; H, 5.57; N, 2.49. Found: C, 49.12; H, 5.44; N, 2.27.

2-Acetamido-1,4,6-tri-O-acetyl-3-O-(methyl 2,3,4-tri-O-acetyl-β-D-glucopyran-osyluronate)-2-deoxy-α-D-glucopyranose (20)

Compound **19** (220 mg, 0.39 mmol) dissolved in acetic anhydride (5 mL) was stirred with boron trifluoride-etherate (0.5 mL) for 2 h at 20 °C. The mixture was poured into ice-cold saturated aqueous sodium hydrogen car-bonate, stirred for 30 min and extracted with dichloromethane. The organic phase was washed with water, dried ($MgSO_4$) and evaporated. The raw material was purified by chromato-graphy (ethyl acetate) and crystallized from ethanol to give 195 mg (75%) of **20** as colorless crystals, mp

117–118 °C, $[\alpha]_D^{20}$= + 24.2 (c = 1.05, $CHCl_3$); lit.[31]: mp 120 °C, $[\alpha]_D^{24}$= + 24.5 (c = 2, $CHCl_3$); lit.[32]: mp 215–217 °C, $[\alpha]_D^{23}$= + 20 (c = 0.98, $CHCl_3$); ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ = 5.96 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.41 (ddd, 1H, $J_{1,2}$ = 3.7, $J_{2,3}$ = 10.8, $J_{2,NH}$ = 9.7 Hz, H-2), 4.17 (dd, 1H, $J_{2,3}$ = 10.8, $J_{3,4}$ = 9.3 Hz, H-3), 5.03 (dd, 1H, $J_{3,4}$ = 9.3, $J_{4,5}$ = 10.1 Hz, H-4), 4.07 (ddd, 1H, $J_{4,5}$ = 10.1, $J_{5,6a}$ = 4.1, $J_{5,6b}$ = 2.2 Hz, H-5), 4.18 (dd, 1H, $J_{5,6a}$ = 4.1, $J_{6a,6b}$ = 12.2 Hz, H-6a), 4.19 (dd, 1H, $J_{5,6b}$ = 2.2, $J_{6a,6b}$ = 12.2 Hz, H-6b), 7.34(d, 1H, $J_{2,NH}$ = 9.7 Hz, NH), 5.09 (d, 1H, $J_{1',2'}$ = 8.1 Hz, H-1′), 4.84 (dd, 1H, $J_{1',2'}$ = 8.1, $J_{2',3'}$ = 9.8 Hz, H-2′), 5.22 (dd, 1H, $J_{2',3'}$ = 9.8, $J_{3',4'}$ = 9.7 Hz, H-3′), 5.05 (dd, 1H, $J_{3',4'}$ = 9.7, $J_{4',5'}$ = 9.8 Hz, H-4′), 4.19 (d, 1H, $J_{4',5'}$ = 9.8 Hz, H-5′), 3.73 (s, 3H, OCH_3), 1.94, 1.96, 1.98, 2.00, 2.01, 2.09, 2.11 (each s, each 3H, 6 x OAc, NAc).

Benzyl 2,3,4-tri-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-β-D-galactopyranoside(23) and benzyl 2,3,4-tri-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-β-D-galactopyranoside(24)

Compound **21**[34] (550 mg, 1.01 mmol) and benzyl 2,3,6-tri-*O*-benzyl-β-D-galactopyranoside (**22**,[24] 548 mg, 1.01 mmol) dissolved in anhydrous ether (10 mL) were treated with titanium tetrafluoride (60 mg, 0.48 mmol) for 3 h at 0 °C and worked up according to GP2. The raw material (913 mg, 85%) contained a mixture of anomers α(**23**): β(**24**) = 55: 45 according to ^{1}H NMR. Separation was by chromatography (chloroform/ethyl acetate 100:1).

Compound **23**: 316 mg (29%), colorless sirup, $[\alpha]_D^{20}$= + 51.2 (c = 1.5, $CHCl_3$); ^{1}H NMR (300 MHz, C_6D_6): δ = 7.03–7.42 (m, 40H, Aryl-H), 4.43 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1), 4.11 (dd, 1H, $J_{1,2}$ =7.7, $J_{2,3}$ = 9.9 Hz, H-2), 3.31 (dd, 1H, $J_{2,3}$ =9.9, $J_{3,4}$ = 2.9 Hz, H-3), 4.10 (dd, 1H, $J_{3,4}$ =2.9, $J_{4,5}$ = 0.5 Hz, H-4), 4.18 (m, 1H, H-5), 3.72 (dd, 1H, $J_{5,6a}$ = 9.3, $J_{6a,6b}$ = 6.4 Hz, H-6a), 3.35 (dd, 1H, $J_{5,6b}$ = 7.2, $J_{6a,6b}$ = 6.4 Hz, H-6b), 5.19 (d, 1H, $J_{1',2'}$ = 3.5 Hz, H-1′), 3.61 (dd, 1H, $J_{1',2'}$ = 3.5, $J_{2',3'}$ = 9.9 Hz, H-2′), 4.38 (dd, 1H, $J_{2',3'}$ = 9.9, $J_{3',4'}$ = 9.2 Hz, H-3′), 4.06 (dd, 1H, $J_{3',4'}$ = 9.2, $J_{4',5'}$ = 10.1 Hz, H-4′), 4.57 (ddd, 1H, $J_{4',5'}$ = 10.1, $J_{5',6á}$ = 0.5, $J_{5',6b'}$ = 1.6 Hz, H-5′), 3.70 (dd, 1H, $J_{5',6á}$ = 0.5, $J_{6á,6b'}$ = 11.0 Hz, H-6á), 3.45 (dd, 1H, $J_{5',6b'}$ = 1.6, $J_{6á,6b'}$ = 11.0 Hz, H-6b́), 4.21, 4.25, 4.27, 4.29, 4.44, 4.54, 4.57, 4.72, 4.73, 4.74, 4.80, 4.82, 4.85, 4.89, 4.98, 4.99 (8 AB, 16H, 8 x OCH_2Aryl). Calcd. for $C_{68}H_{70}O_{11}$ (1063.3): C, 76.81; H, 6.64. Found: C, 76.40; H, 6.17.

Compound **24**: 259 mg (24%), colorless sirup, $[\alpha]_D^{20}$= + 13.5 (c = 1.42, $CHCl_3$); ^{1}H NMR (300 MHz, C_6D_6): δ = 7.00–7.56 (m, 40H, Aryl-H), 4.53 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1), 4.14 (dd, 1H, $J_{1,2}$ =7.7, $J_{2,3}$ = 9.8 Hz, H-2), 3.41 (dd, 1H, $J_{2,3}$ =9.8, $J_{3,4}$ = 2.8 Hz, H-3), 4.30 (dd, 1H, $J_{3,4}$ =2.8, $J_{4,5}$ = 0.7 Hz, H-4), 3.57 (m, 1H, H-5), 4.15 (dd, 1H, $J_{5,6a}$ = 4.7, $J_{6a,6b}$ = 10.3 Hz, H-6a), 4.07 (dd, 1H, $J_{5,6b}$ = 6.3, $J_{6a,6b}$ = 10.3 Hz, H-6b), 5.26 (d, 1H, $J_{1',2'}$ =

7.7 Hz, H-1′), 3.65 (dd, 1H, $J_{1',2'}$ = 7.7, $J_{2',3'}$ = 9.0 Hz, H-2′), 3.74 (m, 4H, H-3′, −4′, -6á, −6 b́), 3.52 (ddd, 1H, $J_{4',5'}$ = 9.6, $J_{5',6á}$ = 2.1, $J_{5',6b'}$ = 4.5 Hz, H-5′), 4.41, 4.47, 4.60, 4.63, 4.66(2), 4.69, 4.70, 4.73, 4.74, 4.8(2), 4.94, 5.00(2), 5.07, 5.39 (8 AB, 16H, 8 x OCH_2Aryl). Calcd. for $C_{68}H_{70}O_{11}$ (1063.3): C, 76.81; H, 6.64. Found: C, 76.21; H, 6.28.

Benzyl 2,3,4-tri-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl-α-D-galactopyranosyl)-β-D-galactopyranoside(25) and benzyl 2,3,4-tri-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl)-β-D-galactopyranoside(26)

Compound **1**[25] (420 mg, 0.77 mmol) and benzyl 2,3,6-tri-*O*-benzyl-β-D-galactopyranoside (**22**,[24] 420 mg, 0.77 mmol) dissolved in anhydrous ether (10 mL) were treated with titanium tetrafluoride (560 mg, 0.40 mmol) for 3 h at 0 °C and worked up according to GP2. The raw material (667 mg, 81%) contained a mixture of anomers α(**25**): β(**26**) = 65: 35 according to ^{1}H NMR. Separation was by chromatography (chloroform/ethyl acetate 50:1).

Compound **25**: 346 mg (42%), colorless sirup, $[\alpha]_D^{20}$= + 35.0 (c = 0.99, $CHCl_3$); lit.[35]: sirup, [α] = + 38 (c = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, C_6D_6): δ = 7.03–7.48 (m, 40H, Aryl-H), 4.44 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1), 4.15 (m, 3H, H-2, −4, −5), 3.34 (dd, 1H, $J_{2,3}$ =10.1, $J_{3,4}$ = 3.0 Hz, H-3), 3.69 (dd, 1H, $J_{5,6a}$ = 9.4, $J_{6a,6b}$ = 6.0 Hz, H-6a), 3.32 (dd, 1H, $J_{5,6b}$ = 8.0, $J_{6a,6b}$ = 6.03 Hz, H-6b), 5.26 (d, 1H, $J_{1',2'}$ = 3.4 Hz, H-1′), 4.37 (dd, 1H, $J_{1',2'}$ = 3.4, $J_{2',3'}$ = 10.1 Hz, H-2′), 4.27 (dd, 1H, $J_{2',3'}$ = 10.1, $J_{3',4'}$ = 2.7 Hz, H-3′), 4.20 (dd, 1H, $J_{3',4'}$ = 2.7, $J_{4',5'}$ = 0.8 Hz, H-4′), 4.81 (m, 1H, H-5′), 3.94 (dd, 1H, $J_{5',6á}$ = 9.0, $J_{6á,6b'}$ = 8.4 Hz, H-6á), 3.55 (dd, 1H, $J_{5',6b'}$ = 5.0, $J_{6á,6b'}$ = 8.4 Hz, H-6b́), 4.15(4), 4.42(2), 4.49, 4.55, 4.58, 4.65, 4.83, 4.90(2), 4.99, 5.05, 5.16 (8 AB, 16H, 8 x OCH_2Aryl).

Compound **26**: 185 mg (22%), colorless sirup, $[\alpha]_D^{20}$= + 5.4 (c = 2.59, $CHCl_3$); ^{1}H NMR (300 MHz, C_6D_6): δ = 7.03–7.57 (m, 40H, Aryl-H), 4.49 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 4.13 (dd, 1H, $J_{1,2}$ =7.8, $J_{2,3}$ = 9.9 Hz, H-2), 3.36 (dd, 1H, $J_{2,3}$ =9.9, $J_{3,4}$ = 2.7 Hz, H-3), 4.39 (dd, 1H, $J_{3,4}$ =2.7, $J_{4,5}$ = 0.8 Hz, H-4), 3.47 (ddd, 1H, $J_{4,5}$ = 0.8, $J_{5,6a}$ = 6.0, $J_{5,6b}$ =6.0 Hz, H-5), 4.01(dd, 1H, $J_{5,6a}$ = 6.0, $J_{6a,6b}$ = 10.0 Hz, H-6a), 3.88 (dd, 1H, $J_{5,6b}$ = 6.0, $J_{6a,6b}$ = 10.0 Hz, H-6b), 5.20 (d, 1H, $J_{1',2'}$ = 7.7 Hz, H-1′), 4.10 (dd, 1H, $J_{1',2'}$ = 7.7, $J_{2',3'}$ = 9.8 Hz, H-2′), 3.37 (dd, 1H, $J_{2',3'}$ = 9.8, $J_{3',4'}$ = 2.8 Hz, H-3′), 3.73 (dd, 1H, $J_{3',4'}$ = 2.8, $J_{4',5'}$ = 1.0 Hz, H-4′), 3.45 (m, 1H, H-5′), 3.71 (dd, 1H, $J_{5',6á}$ = 7.1, $J_{6á,6b'}$ = 9.1 Hz, H-6á), 3.65 (dd, 1H, $J_{5',6b'}$ = 5.9, $J_{6á,6b'}$ = 9.1 Hz, H-6b́), 4.30, 4.35, 4.47, 4.48, 4.49, 4.57, 4.58, 4.60, 4.61, 4.66, 4.67, 4.78, 4.94, 4.95, 5.07, 5.31 (8 AB, 16H, 8 x OCH_2Aryl). Calcd. for $C_{68}H_{70}O_{11}$ (1063.30): C, 76.81; H, 6.64. Found: C, 76.12; H, 5.22.

4-O-(α-D-Galactopyranosyl)-β-D-galactopyranose(27)

Compound **25** (322 mg, 0.30 mmol) dissolved in methanol (10 mL) were hydrogenated with palladium/charcoal (100 mg, 10% Pd) for 16 h at 40 °C.

Following filtration via celite and evaporation 95 mg (92%) of compound **27** were obtained as colorless amorphous material, softening point 100–105 °C $[\alpha]_D^{20} = +148.1$ ($c = 1.17$, H_2O); lit.[35]: $[\alpha] = +163$ ($c = 1$, H_2O); lit.[38]: $[\alpha]_D^{26} = +170$ ($c = 1$, H_2O).

Benzyl 2,3,4-tri-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl-α-D-galactopyranosyl)-β-D-glucopyranoside(29) and benzyl 2,3,4-tri-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl)-β-D-glucopyranoside (30)

Compound **1**[25] (515 mg, 0.95 mmol) and benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (**28**,[26] 514 mg, 0.95 mmol) dissolved in anhydrous ether (10 mL) were treated with titanium tetrafluoride (50 mg, 0.40 mmol) for 3 h at 0 °C and worked up according to GP2. The raw material (858 mg, 85%) contained a mixture of anomers α(**29**): β(**30**) = 62: 38 according to ^{1}H NMR. Separation was by chromatography (toluene/ethyl acetate 40:1).

Compound **29**: 282 mg (36%), colorless sirup, $[\alpha]_D^{20} = +15.2$ ($c = 2.11$, $CHCl_3$); ^{1}H NMR (300 MHz, C_6D_6): δ = 7.01–7.45 (m, 40H, Aryl-H), 4.42 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1), 3.63 (dd, 1H, $J_{1,2}$ =7.9, $J_{2,3}$ = 9.1 Hz, H-2), 4.95 (dd, 1H, $J_{2,3}$ =9.1, $J_{3,4}$ = 8.6 Hz, H-3), 4.31 (dd, 1H, $J_{3,4}$ =8.6, $J_{4,5}$ = 9.6 Hz, H-4), 3.47 (ddd, 1H, $J_{4,5}$ = 9.6, $J_{5,6a}$ = 4.3, $J_{5,6b}$ =2.4 Hz, H-5), 3.98 (dd, 1H, $J_{5,6a}$ = 4.3, $J_{6a,6b}$ = 11.0 Hz, H-6a), 3.92 (dd, 1H, $J_{5,6b}$ = 2.4, $J_{6a,6b}$ = 11.0 Hz, H-6b), 6.04 (d, 1H, $J_{1',2'}$ = 3.7 Hz, H-1′), 4.27 (m, 2H, H-2′, −5′), 4.16 (dd, 1H, $J_{2',3'}$ = 11.0, $J_{3',4'}$ = 2.8 Hz, H-3′), 4.16 (m, 1H, H-4′), 3.82 (dd, 1H, $J_{5',6á}$ = 7.8, $J_{6á,6b'}$ = 8.7 Hz, H-6á), 3.76 (dd, 1H, $J_{5',6b'}$ = 5.7, $J_{6á,6b'}$ = 8.7 Hz, H-6b′), 4.23, 4.30, 4.40, 4.51, 4.52, 4.56, 4.57, 4.61, 4.64, 4.66(2), 4.87, 4.95, 4.96, 5.03, 5.04 (8 AB, 16H, 8 x OCH_2Aryl). Calcd. for $C_{68}H_{70}O_{11}$ (1063.30): C, 76.81; H, 6.64. Found: C, 76.10; H, 6.31.

Compound **30**: 173 mg (17%), colorless sirup, $[\alpha]_D^{20} = +2.7$ ($c = 0.91$, $CHCl_3$); ^{1}H NMR (300 MHz, C_6D_6): δ = 7.07–7.52 and 7.68–7.73 (each m, 40H, Aryl-H), 4.47 (d, 1H, $J_{1,2}$ = 7.5 Hz, H-1), 3.66 (m, 3H, H-2, −3, -6á), 4.33 (dd, 1H, $J_{3,4}$ =9.0, $J_{4,5}$ = 10.0 Hz, H-4), 3.30 (m, 1H, H-5), 4.02 (dd, 1H, $J_{5,6a}$ = 3.7, $J_{6a,6b}$ = 11.4 Hz, H-6a), 3.78 (dd, 1H, $J_{5,6b}$ = 1.4, $J_{6a,6b}$ = 11.4 Hz, H-6b), 4.71 (d, 1H, $J_{1',2'}$ = 7.8 Hz, H-1′), 4.03 (dd, 1H, $J_{1',2'}$ = 7.8, $J_{2',3'}$ = 9.9 Hz, H-2′), 3.33 (dd, 1H, $J_{2',3'}$ = 9.9, $J_{3',4'}$ = 3.0 Hz, H-3′), 3.84 (dd, 1H, $J_{3',4'}$ = 3.0, $J_{4',5'}$ = 0.5 Hz, H-4′), 3.44 (m, 2H, H-5′, −6 b′), 4.18, 4.33, 4.39, 4.44, 4.51, 4.58(3), 4.79, 4.83, 4.87, 4.89, 4.91, 5.023, 5.03, 5.32 (8 AB, 16H, 8 x OCH_2Aryl). Calcd. for $C_{68}H_{70}O_{11}$ (1063.30): C, 76.81; H, 6.64. Found: C, 76.33; H, 6.32.

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