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Synthesis of a Tetrasaccharide Building Block of the O-Specific Polysaccharide of *Shigella dysenteriae* Type 1*

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Abstract: A glycosyl trichloroacetimidate derivative (**1**) of the tetrasaccharide α-D-Gal*p*-(1→3)-α-D-Glc*p*NAc-(1→3)-α-L-Rha*p*-(1→3)-α-L-Rha*p* was synthesized in a highly stereoselective, stepwise manner, using methyl 1-thioglycosides of L-rhamnose, 2-azido-2-deoxy-D-glucose and D-galactose, as major intermediates. The protecting group scenario in compound **1** permits regioselective deblocking at its "non-reducing end" unit. Therefore **1** is a suitable intermediate for the preparation of extended fragments of the title polysaccharide.

Shigella dysenteriae type 1 is a Gram-negative pathogen causing dysentery in humans only, with a high incidence of mortality.[2] The O-specific polysaccharide (O-SP) of its lipopolysaccharide (LPS) envelope is a regular heteropolysaccharide composed[3] of the tetrasaccharide repeating unit **A**. Serum antibodies to the O-

2)-α-D-Gal*p*-(1→3)-α-D-Glc*p*NAc-(1→3)-α-L-Rha*p*-(1→3)-α-L-Rha*p*-(1→ **A**

SP may provide the basis for the protection against such infections through vaccination.[2] Host-protective antibodies can be elicited by synthetic antigens in which the native O-SP is covalently linked to a carrier protein.[2,4,5] It is generally agreed upon, that the immunogenecity of the carbohydrate-protein conjugates depends on the carrier protein, the type of attachment, which influences the net charge, the degree of crosslinking, and the carbohydrate-protein ratio.[4] However, there is a considerable degree of controversy concerning the minimal length of the carbohydrate part required for eliciting *protective* antibodies, directed to the carbohydrates of the bacterial cell-surface. There is evidence that the immunogenic properties of the bacterial, cell-surface polysaccharides can also be expressed by carbohydrate structures smaller than the native polysaccharides.[6] Recently, protein-conjugates of synthetic oligosaccharides, corresponding to the inner core regions of *meningococcal* LPSs were shown to induce immunotype-specific antibodies in rabbits.[7] On the other hand, the failure of complete, tetra- and pentasaccharide repeating unit fragments of the capsular polysaccharides of *Pneumococcus* Type 14[8] and Type III Group B *Streptococcus*[9], respectively, to be antigenic indicates, that the recognition by antibodies generated against native polysaccharides requires extended carbohydrate structures.

*For a preliminary publication see Ref. 1.

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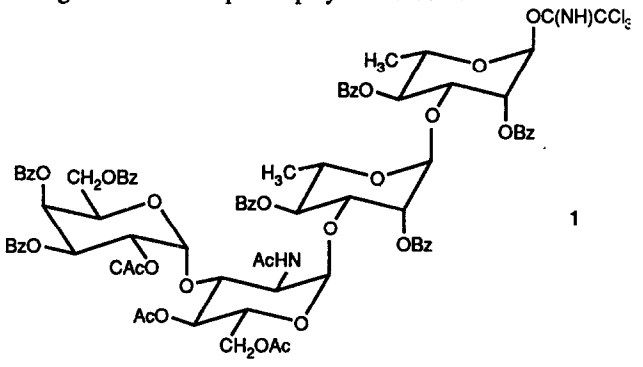
The induction of *protective* antibodies will require, in general, oligo- or polysaccharides which resemble the average conformation of the native polysaccharides.[10] Indeed, host-protective antibodies could be elicited by a synthetic antigen in which the protein-bound carbohydrate moieties represented an *extended fraction* of the native, type III Group B *streptococcal* polysaccharide.[6]

As part of our project aimed at developing a conjugate vaccine against shigellosis we are investigating the molecular specificities of the interaction between the O-SP and antibodies raised against *Shigella dysenteriae* type 1.[11] In these explorations we use synthetic oligosaccharides[12] as molecular probes, which correspond to the O-SP (A).[1,13-15] It is anticipated that these studies, in combination with nuclear magnetic resonance measurements, will define fragments which express characteristic features of the O-SP. Such oligosaccharides may possess haptenic properties suitable for eliciting protective antibodies, and will be covalently coupled to a carrier protein for studying their immunogenic characteristics.

In this paper we describe the synthesis of the fully protected tetrasaccharide **1** which permits access to higher oligosaccharide fragments of the O-specific polysaccharide **A**.

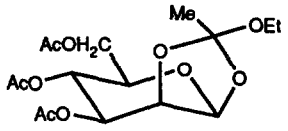


1

Results and Discussion

The approach adopted in this study is based on the synthesis of heterofunctional, monosaccharide intermediates. These blocks were combined in a stepwise manner to construct the tetrasaccharide **1**.

D-Glucosamine Units. Our approach for the attachment of an *N*-acetyl-D-glucosaminyl residue having a 1,2-*cis* stereochemistry is based on Paulsen's azido-glycose technology[16,17] which exploits the non-participating properties of the azido group[18] at C-2. The acetate[19] **5** was the starting material for the synthesis of the glucosamine donor **11**. In this study we followed a recently published synthesis[19b] of **5** which was modeled after the concept of van Boom and co-workers.[20] As the precursor to **5** we used the orthoester[21] **2** which was subjected to controlled acetolysis[23] to provide the tetraacetate[22] **3** in 32 % yield. Other, reported routes[22] to tetraacetate **3** proceed in erratic yields that are difficult to reproduce.[22a] Compound **3** was converted to the azide **5** *via* the triflate **4** essentially as described,[19b] except for experimental improvements involving



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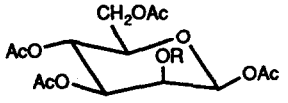
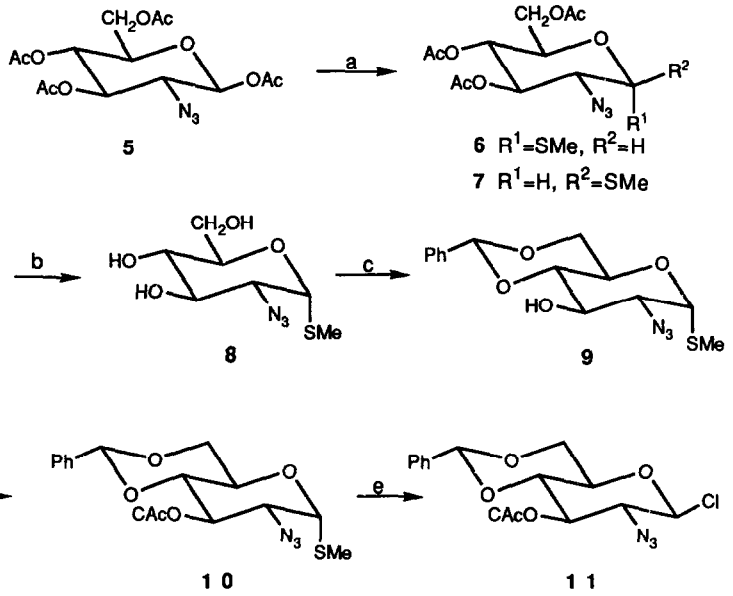


3 R=H
4 R=Tf

the use of only 1 instead of 2 molar equivalents of the expensive reagent trifluoromethanesulfonic anhydride and keeping the temperature during all operations of the **4**→**5** conversion below 30°.

The thioglycoside **6** was chosen as the major intermediate. (Scheme I) Compound **6** is a useful α-D-glucosaminyl donor, since it allows a wide range of protecting group manipulations.[24] The reaction[25] of acetate **5** with (methylthio)trimethylsilane in the presence of TMSOTf gave the crystalline thioglycosides **6** and

Scheme I[a]



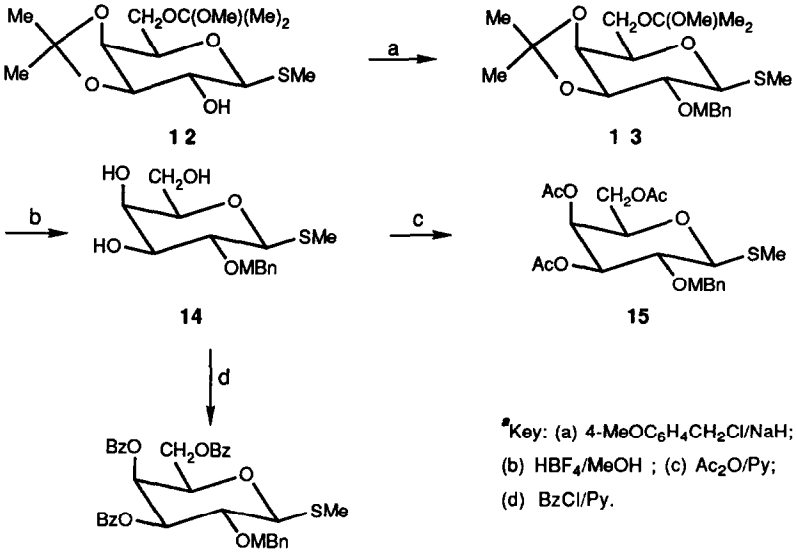
[a]Key: (a) $CH_3SSi(CH_3)_3$, TMSOTf, $(CH_2Cl)_2$; (b) NaOMe/MeOH; (c) $C_6H_5CH(OMe)_2$, CSA; (d) CAcCl/Py; (e) Cl_2.

7 in a ratio of 4:1, in 93 % yield. The anomeric configuration of the thioglycosides **6** and **7** was ascertained by their $^1J_{C\text{-}1,H\text{-}1}$ coupling constants (167 Hz and 156 Hz, respectively), which are characteristically lower than those of the *O*-glycosides.[25b] The major, α-isomer **6** was obtained in pure form by crystallization, without the need of chromatography, and was exposed to NaOMe in methanol to provide the triol **8**. Treatment of **8** with benzaldehyde dimethylacetal in the presence of 10-camphorsulfonic acid gave **9** which was chloroacetylated to

give **10** (88 % yield). Reaction of the thioglycoside **10** with chlorine gave the crystalline chloride **11** in 96 % yield. The 1,2-*trans* configuration in **11** was confirmed by the $^3J_{H\text{-}1,H\text{-}2}$ coupling constant being 7.8 Hz.

D-Galactose Units. Thiogalactoside **16** was selected as the galactosyl donor. In **16** the 4-methoxybenzyl group at *O*-2 serves a dual function. As a non-participating group[16] it allows the stereoselective formation of a 1,2-*cis* interglycosidic linkage upon activation of the anomeric center by thiophilic reagents. The sensitivity of the 4-methoxybenzyl group to oxidation[26] permits selective unmasking of the *HO*-2 group for subsequent chain-elongation. Treatment of the known alcohol[25c] **12** with 4-methoxybenzyl chloride/NaH (Scheme II) gave the crystalline **13** (73 %) which was de-acetalated[27] (HBF_4/MeOH, 92 %) to give **14**. The position of the 4-methoxybenzyl group in **14** was further confirmed by the ^1H and ^{13}C NMR data of its triacetate **15** (Experimental). Conventional benzoylation (BzCl/Py) of the triol **14** gave the fully protected, crystalline **16.**

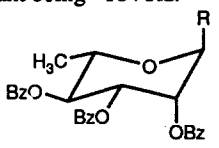
Scheme II[a]



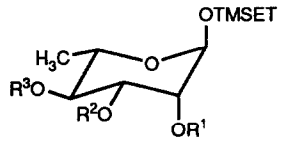
[a]Key: (a) 4-$MeOC_6H_4CH_2Cl$/NaH; (b) HBF_4/MeOH ; (c) Ac_2O/Py; (d) BzCl/Py.

L-Rhamnose Units. Acetolysis of the methyl glycoside[28] **17** followed by treatment with α,α-dichloromethyl methyl ether gave the crystalline chloride[28] **18** (96 %) which was coupled with 2-(trimethylsilyl)ethanol (AgOTf, DTBMP) to provide the glycoside **19** (86 %). We note that attempted coupling of 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl chloride or bromide with 2-(trimethylsilyl)ethanol under Koenigs Knorr-type conditions (AgOTf/base, or $Hg(CN)_2$) failed to afford the required glycoside in an acceptable yield. Transesterification (NaOMe/MeOH) of compound **19** provided the triol **20** (92 %). Treatment[29] of the triol **20** with trimethyl orthobenzoate *under vacuum* followed in succession by *in situ* benzoylation and acid

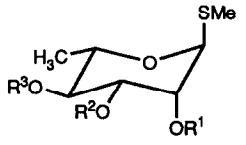
hydrolysis[30,31b] afforded the dibenzoate **21** in 69 % yield. The donor **25** was prepared as follows. The thiorhamnoside[25b] **22** was regioselectively di-*O*-benzoylated [→ **23** (79 %)] in analogy to the preparation of compound **21**. Subsequent chloroacetylation at *HO*-3 provided compound **24**. Treatment of **24** with chlorine afforded the rhamnosyl chloride **25** (84 %). The α anomeric configuration in **25** was ascertained by its $^1J_{C\text{-}1,H\text{-}1}$ coupling constant being 184 Hz.



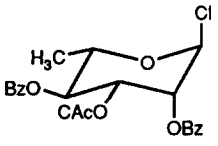
17 R = OMe
18 R = Cl
19 R = OTMSET



	R^1	R^2	R^3
20	H	H	H
21	Bz	H	Bz



	R^1	R^2	R^3
22	H	H	H
23	Bz	H	Bz
24	Bz	CAc	Bz



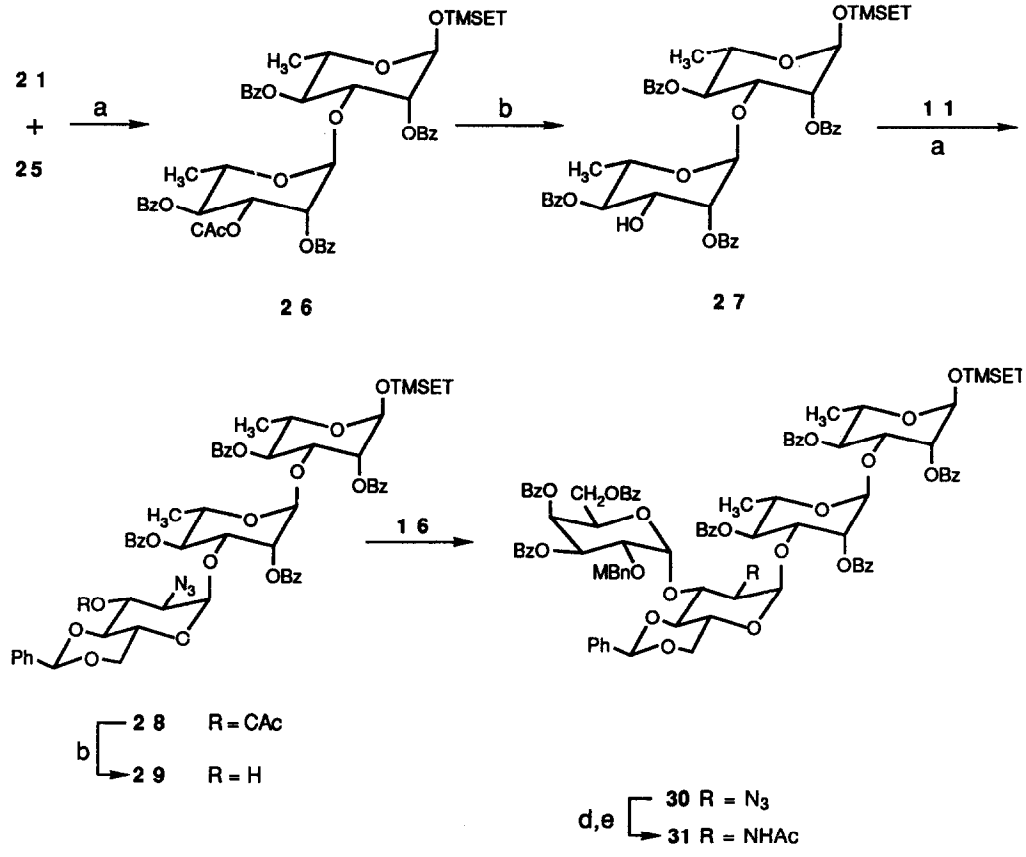
25

Bz = benzoyl
CAc = chloroacetyl
TMSET = 2-(trimethylsilyl)ethyl

Assembly of the tetrasaccharide. Rhamnosyl chloride **25** was coupled with the acceptor **21** using AgOTf as the promoter and the base 2,6-di-*tert*-butyl-4-methylpyridine. (Scheme III) The disaccharide **26** was obtained in 64 % yield. The α interglycosidic linkage in **26** was ascertained by the $^1J_{C\text{-}1,H\text{-}1}$ coupling constant (172 Hz). Removal of the chloroacetyl group (thiourea in EtOH[32]) afforded the disaccharide alcohol **27**. Our preliminary studies indicated, that the direct activation of the azido-thioglucoside **10** with MeOTf[33] in diethyl ether, in the presence of glycosyl acceptors of moderate nucleophilicity leads to 1,2-*cis*-linked disaccharides in a highly stereocontrolled manner. However, the reactions were sluggish and the yields unsatisfactory. On the other hand, the high reactivity of 2-azido-2-deoxy-glycosyl halides in Koenings-Knorr-type reactions is amply documented.[16,17] Therefore, in these studies the heterofunctional azido-glucosyl chloride **11**, instead of its precursor thioglucoside **10** was used, as the glucosamine unit. We used glycosyl halides, which were isolated and characterized prior to the glycosylation reactions. This is, however, not always necessary since thioglycosides can be converted *in situ* into the corresponding glycosyl halides. This technology was first reported by Weygand and Ziemann[34] in 1962 and adopted by Bundle's group[35] in 1990 for the synthesis of

1,2-*trans*-linked oligosaccharides. We note, that thioglycoside conversion into a 1,2-*cis*-linked disaccharide

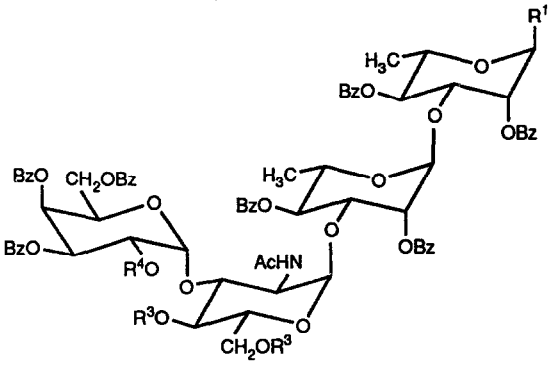
Scheme III[a]



[a]Key: (a) AgOTf, DTBMP, CH_2Cl_2; (b) $CS(NH_2)_2$, EtOH; (c) MeOTf, ether; (d) $NiCl_2$-H_3BO_3-$NaBH_4$, EtOH; (e) Ac_2O.

through the intermediacy of an *in situ*, reagent-generated, glycosyl bromide was also described.[36] Combination of the azido-chloride **11** with the disaccharide nucleophile **27** under AgOTf promotion afforded the trisaccharide **28** (69 %). In this reaction formation of the 1,2-*trans* linked isomer was not observed. The moderate yield of this reaction was due to partial decomposition of the donor **11**. Dechloroacetylation of **28** (thiourea[32]) gave the trisaccharide alcohol **29** (90 %). Compound **29** was galactosylated using the thiogalactoside donor **16** under activation by MeOTf[33] to provide the protected tetrasaccharide **30**. The proper choice of the solvent was critical to the stereochemical outcome of this reaction. No product containing a 1,2-*trans* interglycosidic linkage could be isolated when diethyl ether was used as the solvent whereas dichloromethane promoted the formation of the

unwanted isomer. For the galactose residue the $^1J_{C\text{-}1,H\text{-}1}$ coupling constant equalled 170 Hz confirming the α anomeric linkage for this glycon. Reduction[18b] ($NiCl_2$-H_3BO_3-$NaBH_4$) of the azido group in **30** followed by *in situ* *N*-acetylation (Ac_2O) afforded the acetamido derivative **31**. Replacement of the 4-methoxybenzyl by a chloroacetyl group by way of the intermediate **32** in a two-step sequence [(i) oxidation[26a] with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, (ii) chloroacetylation (chloroacetyl chloride, pyridine)] provided compound **33** (90 % yield for two steps). This change of selectively removable protecting groups was necessary to avoid side-reactions during the subsequent acidolytic steps. Treatment of the benzylidene derivative **33** with aqueous acetic acid provided the diol **34** which was acetylated (Ac_2O/Py) to afford the diacetate **35**. Treatment of **35** with trifluoroacetic acid removed the 2-(trimethylsilyl)ethyl aglycon[37] to provide the corresponding hemiacetal which was then treated with trichloroacetonitrile and 1,8-diazabicyclo[5.4.0]undec-7-ene in dichloromethane[38] to give the tetrasaccharide donor **1** (73 % yield). In **1** the α configuration at the "reducing" end was assigned on the basis of the $^1J_{C\text{-}1,H\text{-}1}$ coupling constant (179 Hz).



	R^1	R^2	R^3	R^4
32	OTMSET	CHPh		H
33	OTMSET	CHPh		CAc
34	OTMSET	H	H	CAc
35	OTMSET	Ac	Ac	CAc

Compound **1**, being a glycosyl trichloroacetimidate, permits glycosylation reactions under Lewis-acid catalysis. Since the chloroacetyl group can be selectively removed in glycosides formed from **1**, the synthesis of extended oligosaccharide fragments corresponding to the O-specific polysaccharide A becomes now possible. These experiments are currently under way in these laboratories.

EXPERIMENTAL SECTION*

General. Melting points are uncorrected. Optical rotations were measured at 22°C with a Perkin-Elmer Type 241MC polarimeter in $CHCl_3$, except where indicated otherwise. Column chromatography was performed on silica gel 60 (0.040-0.063 mm). The NMR spectra were recorded on a Gemini-300 spectrometer (300 MHz for ^1H, 75 MHz for ^{13}C) at 23-25°C. Internal references: TMS (0.000 ppm for ^1H for solutions in organic solvents), acetone (2.225 ppm for ^1H and 31.00 ppm for ^{13}C for solutions in D_2O), $CDCl_3$ (77.00 ppm for ^{13}C for solutions in $CDCl_3$), CD_3OD (49.90 ppm for ^{13}C for solutions in CD_3OD), $(CD_3)_2SO$ (39.5 ppm for ^{13}C for solutions in $(CD_3)_2SO$). Subscripts A-D refer to the individual sugar residues, with A standing for the reducing-end unit. The ^{13}C NMR assignments were aided by two-dimensional, ^{13}C,^1H correlation spectroscopy. Low resolution mass spectra were obtained by the chemical ionization technique (CIMS), using

*Compounds **2**-**5** and **18** are known. The protocols included here are improvements from the literature procedures.

NH_3 as the ionizing gas and by the positive-ion fast atom-bombardment technique performed in the low (FABMS) and high resolution mode (HRFAB), using 3-nitrobenzyl alcohol as the matrix.

3,4,6-Tri-*O*-acetyl-1,2-*O*-(1-ethoxyethylidene)-β-D-mannopyranose (2). A solution of 1,2,3,4,6-penta-*O*-acetyl-α,β-D-mannopyranose (135 g) in a mixture of glacial AcOH (100 mL) and Ac_2O (10 mL) was treated with 30 % HBr in AcOH (140 mL) at 0°C. The solution was allowed to reach room temperature. After 4 h TLC (1:1 EtOAc-hexane) indicated complete conversion to a faster-moving product. The solution was diluted with $CHCl_3$ (500 mL) and the mixture was successively extracted with ice-water (5 x 800 mL), 1 % aq. $NaHCO_3$, ice-water (500 mL), dried (Na_2SO_4) and concentrated. A solution of the syrupy product in MeCN (50 mL) was treated with anhydrous EtOH (80 mL) and 2,4,6-trimethylpyridine (70 mL). After 14 h at room temperature the mixture was diluted with $CHCl_3$ (500 mL). The mixture was extracted with water (3 x 400 mL). The organic phase was dried (Na_2SO_4) and concentrated. The semisolid obtained was crystallized from EtOH to give **2** (82 g, 63 %): mp 101-103°C, lit.[21] mp 102.5-104°C; $[\alpha]_D$ -19° (c 0.8), lit.[21] $[\alpha]_D$ -15°.

1,3,4,6-Tetra-*O*-acetyl-β-D-mannopyranose (3). A solution of **2** (50 g) in acetone (300 mL) was treated with 1 N aq. HCl (30 mL) for 5 min at 20°C then was concentrated at 20°C at 20 mmHg. The residue was dissolved in $CHCl_3$ (300 mL) and the solution was washed with H_2O (2 x 100 mL). The organic layer was dried (Na_2SO_4), and concentrated to a *thin* syrup. The residue crystallized upon addition of diethyl ether to give **3** (15 g, 32.4 %). A portion was recrystallyzed from EtOH. Mp 164-166°C, lit.[22] mp 164-165°C; $[\alpha]_D$ -19° (c 0.8), lit.[22] $[\alpha]_D$ -24°.

1,3,4,6-Tetra-*O*-acetyl-2-*O*-trifluoromethanesulfonyl-β-D-mannopyranose (4). To a stirred solution of **3** (55 g) in CH_2Cl_2 (600 mL) and pyridine (28 mL) was added trifluoromethanesulfonic anhydride (27 mL) dropwise, at -15°C, during 1 h. The mixture was allowed to reach 5°C then was successively extracted with ice-cold, aq. $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated. Crystallization from EtOH gave **4** (71.5 g, 97.5 %), mp 118-120°C, lit.[39] mp 120°C.

1,3,4,6-Tetra-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranose (5). A solution of **4** (40.5 g) and sodium azide (11 g) in DMF (250 mL) was stirred for 40 min. Concentration of the solution *below* 30°C gave a syrup which was dissolved in $CHCl_3$ (200 mL). Extraction with water (3 x 50 mL) followed by drying (Na_2SO_4) and concentration gave a syrup which was crystallized from isopropyl ether to give **5** (25 g, 77 %), mp 94-95°C, lit.[19c] mp 97°C; $[\alpha]_D$ +3° (c 1.2), lit.[19c] $[\alpha]_D$ +8°.

Methyl 2-azido-2-deoxy-3,4,6-tri-*O*-acetyl-1-thio-α- (6) and β-D-glucopyranoside (7). A solution of **5** (45 g), (methylthio)trimethylsilane (45 mL), and trimethylsilyl trifluoromethanesulfonate (4 mL) in anhydrous $(CH_2Cl)_2$ (180 mL) was stirred under reflux for 12 h. The solution was concentrated to a syrup. A solution of the residue in $CHCl_3$ (200 mL) was extracted with cold, 5 % aq. $NaHCO_3$, H_2O, dried (Na_2SO_4), and concentrated. Crystallization of the residue from EtOH gave **6** (29.1 g, 66.7 %), mp 96-98°C, $[\alpha]_D$ +167° (c 0.91). Column chromatography of the mother liquor (5:1 hexane-EtOAc) afforded **7** (4.46 g, 10.2 %), mp 73-74°C, $[\alpha]_D$ -41° (c 1.4) and a mixture of **6** and **7** (7.2 g, containing *ca.* 3 % **5**, 16 %). Total yield of **6** and **7**: 93 %. NMR data ($CDCl_3$): **6** ^{1}H, δ 5.341 (d, 1H, $J_{1,2}$ 5.5 Hz, H-1), 5.305 (dd, 1H, $J_{2,3}$ 10.0 Hz, H-3), 5.017 (t, 1H, $J_{3,4}$=$J_{4,5}$ =10.1 Hz, H-4), 4.402 (ddd, 1H, H-5), 4.315 (dd, 1H $J_{5,6}$ 4.8 Hz, $J_{6,6'}$ 12.2 Hz, H-6), 4.090 (dd, 1H $J_{5,6'}$ 2.0 Hz, H-6'); ^{13}C, δ 170.4 and 169.7 (*C*=O), 84.1 (C-1, $J_{C\text{-}1,H\text{-}1}$ 167 Hz), 72.1 (C-4), 68.8 (C-3), 67.9 (C-5), 61.9 (C-6), 61.6 (C-2), 20.6 (CH_3CO), 12.8 (CH_3S); **7** ^{1}H, δ 5.113 (t, 1H $J_{2,3}$=$J_{3,4}$=9.4 Hz, H-3), 5.043 (t, 1H, H-4), 4.348 (d, 1H, $J_{1,2}$ 10.2 Hz, H-1), 4.288 (dd, 1H, $J_{5,6}$ 4.8 Hz, $J_{6,6'}$ 12.3 Hz, H-6), 4.163 (dd, 1H $J_{5,6'}$ 2.2 Hz, H-6'); ^{13}C δ 170.4, 169.7, 169.5 (*C*=O), 84.4 $J_{C\text{-}1,H\text{-}2}$ 156 Hz, C-1), 75.8 (C-5, 74.3 (C-3), 68.2 (C-4), 63.1 (C-2), 62.0 (C-6), 20.6, 20.4 (CH_3CO), 12.4 (CH_3S). CIMS: **6** and **7** m/z 379 $[M+18]^+$. Anal. Calcd for $C_{13}H_{19}N_3O_7S$: C, 43.20; H, 5.30; N, 11.63; S, 8.87. Found: **6** C, 43.75; H, 5.38; N, 11.74; S, 8.98; **7** C, 43.86; H, 5.42; N, 11.68; S, 9.06.

Methyl 2-azido-2-deoxy-1-thio-α-D-glucopyranoside (8). A solution of **6** (5.0 g) in anhydrous MeOH (40 mL) was treated with a catalytic amount of MeONa at room temperature for 3 h. The solution was neutralized (Dowex 50X2-200, H^+), and concentrated. Trituration of the residue in ether gave **8** (2.68g, 82 %), mp 123-124°C, $[\alpha]_D$ +221° (c 1.2, MeOH). NMR data (D_2O): ^{1}H, δ 5.436 (d, 1H, $J_{1,2}$ 5.5 Hz, H-1), 4.015 (ddd, 1H, $J_{4,5}$ 9.7 Hz, H-5), 3.895 (dd, 1H, H-2), 3.874 (dd, 1H, $J_{5,6}$ 2.3 Hz, H-6), 3.780 (dd, 1H, $J_{5,6'}$ 5.6 Hz, $J_{6,6'}$ 12.3 Hz, H-6'), 3.686 (dd, 1H, $J_{2,3}$ 10.1, H-3), 3.463 (t, 1H, $J_{3,4}$ 9.7 Hz, H-4), 2.130 (CH_3); ^{13}C, δ 84.9 (C-1), 73.3 (C-3), 73.1 (C-5), 70.7 (C-4), 64.4 (C-2), 61.3 (C-6), 13.0 (CH_3). CIMS: m/z 253 $[M+18]^+$, 236 $[M+1]^+$. HRFAB: Found m/z 236.0706, $C_7H_{14}N_3O_4S$ requires 236.0705.

Methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-1-thio-α-D-glucopyranoside (9). A solution of compound **8** (2.3 g) in MeCN (20 mL) was treated with benzaldehyde dimethylacetal (5 mL) and a catalytic

amount of 10-camphorsulfonic acid at room temperature for 3 h. The mixture was treated with triethylamine and concentrated to a syrup. Trituration in hexane afforded crystalline **9** (2.65g, 84 %), mp 160-161°C, $[\alpha]_D$ +160° (c 0.58). NMR data ($CDCl_3$): ^1H, δ 7.3-7.55 (m, 5H, aromatic protons), 5.525 (s, 1H, *H*CPh), 5.250 (d, 1H, $J_{1,2}$ 5.3 Hz, H-1), 4.15-4.27 (m, 2H, H-6,6'), 3.976 (t, 1H, $J_{2,3}$=$J_{3,4}$=9.3 Hz, H-3), 3.828 (dd, 1H, H-2), 3.73-3.82 (m, 1H, H-5), 3.509 (t, 1H, H-4), 2.11 (s, 3H, C*H*$_3$S); ^{13}C, δ 136.8, 129.4, 128.3, 126.2 (aromatic carbons), 102.1 (*C*HPh), 85.1 (C-1), 81.7 (C-4), 70.6 (C-3), 68.6 (C-6), 63.7 (C-2), 62.7 (C-5), 13.2 (*C*H$_3$S). CIMS: m/z 341 $[M+18]^+$, 324 $[M+1]^+$. Anal. Calcd for $C_{14}H_{17}N_3O_4S$: C, 52.00; H, 5.30; N, 13.00; S, 9.91. Found: C, 52.57; H, 5.44; N, 12.65; S, 9.76.

Methyl 2-azido-4,6-*O*-benzylidene-3-*O*-chloroacetyl-2-deoxy-1-thio-α-D-glucopyranoside (10). To a stirred solution of **9** (11.6 g) in a mixture of pyridine (50 mL) and DMF (50 mL) at -50°C was added chloroacetyl chloride (8.3 mL) during 15 min. The mixture was allowed to reach *ca* 0°C in 20 min then was concentrated under vacuum. A solution of the residue in $CHCl_3$ (200 mL) was extracted with ice-cold aq. $NaHCO_3$, ice-water, was dried (Na_2SO_4) and concentrated. The residue was crystallized from EtOAc to give **10** (6.6 g). Column chromatography (4:1 hexane-EtOAc) of the mother liquor afforded an additional amount of **10** (6.0 g, total yield 88 %), mp 160-162°C, $[\alpha]_D$ +86° (c 1.03). NMR data ($CDCl_3$): ^1H, δ 7.35-7.45 (m, 5H, aromatic resonances), 5.499 (s, 1H, *H*CPh), 5.447 (t, 1H, $J_{2,3}$=$J_{3,4}$=9.8 Hz, H-3), 5.365 (d, 1H, $J_{1,2}$ 5.7 Hz, H-1), 4.25-4.35 (m, 2H, H-5,6), 4.108 (s, 2H, C*H*$_2$Cl), 4.035 (dd, 1H, H-2), 3.800 (m, 1H, H-6'), 3.670 (t, 1H, H-4), 2.351 (s, 3H C*H*$_3$S); ^{13}C, δ 166.0 (*C*=O), 126.1, 128.2, 129.1, 136.6 (aromatic carbons), 101.6 (*C*HPh), 85.0 (C-1), 79.2 (C- 4), 72.3 (C-3), 68.5 (C-6), 63.0 (C-2), 62.2 (C-5), 40.5 (*C*H$_2$Cl), 13.1 (*C*H$_3$S). CIMS: m/z 417 $[M+18]^+$. HRFAB: Found m/z 400.0716, $C_{16}H_{19}ClN_3O_5S$ requires 400.0734.

2-Azido-4,6-*O*-benzylidene-3-*O*-chloroacetyl-2-deoxy-β-D-glucopyranosyl chloride (11). A solution of **10** (2.1 g) in anhydrous CH_2Cl_2 (20 mL) was treated at 0°C with chlorine dissolved in CCl_4. After 10 min 1-hexene was added until the yellow color disappeared. Concentration of the solution afforded a syrupy residue which crystallized from hexane to give **11** (1.95 g, 96 %), mp 81-83°C, $[\alpha]_D$ -80° (c 0.82). ^1H NMR data ($CDCl_3$): δ 7.9–7.3 (aromatic protons), 5.51 (s, 1H, C*H*Ph), 5.220 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.395 (dd, 1H, $J_{5,6}$ 4.9 Hz, $J_{6,6'}$ 10.4 Hz, H-6), 4.138 (s, 2H, C*H*$_2$Cl), 3.616 (dd, 1H, $J_{5,6'}$ 4.9 Hz). CIMS: m/z 405 $[M+18]^+$.

Methyl 2,3-*O*-isopropylidene-2-*O*-(4-methoxybenzyl)-6-O-(2-methoxy-2-methylethyl)-β-D-galactopyranoside (13). A solution of methyl 2,3-*O*-isopropylidene-6-*O*-(2-methoxy-2-methylethyl)-β-D-galactopyranoside[25c] (33 g) in DMF (100 mL) was treated with NaH (4.1 g, 60 % dispersion in oil) at 0°C, under stirring. 4-Methoxybenzyl chloride (15 mL) was added dropwise. Stirring was continued for 3 h at 0°C. MeOH (5 mL) was added dropwise, followed by H_2O (500 mL). The mixture was extracted with $CHCl_3$ (3x100 mL). The combined $CHCl_3$ extracts were washed with H_2O (5x100 mL) and dried (Na_2SO_4). Crystallization from hexane afforded **13** (21.5 g). Column chromatography of the mother liquor (4:1 hexane-ethyl acetate containing 1 % Et_3N) gave an additonal amount of **13** (10.5 g, total yield 73 %), mp 79-81°C, $[\alpha]_D$ -9° (c 0.9). NMR data (C_6D_6-$CHCl_3$, 100:5): ^1H, δ 6.8-7.5 (aromatic protons), 4.870 and 4.760 [2d, 2H, *J* 11.2 Hz, C*H*$_2$ (benzyl)], 4.226 (d, 1H, $J_{1,2}$ 10.5 Hz, H-1), 4.056 (dd, 1H, H-3), 3.911 (dd, 1H, $J_{3,4}$ 5.7 Hz, $J_{4,5}$ 2.2 Hz, H-4), 3.858 (dd, 1H, $J_{5,6}$ 6.8 Hz, $J_{6,6'}$ 9.7 Hz, H-6), 3.727 (dd, 1H, $J_{5,6'}$ 5.3Hz, H-6'), 3.633 (ddd, 1H, H-5), 3.607 (dd, 1H, $J_{2,3}$ 6.4 Hz, H-2), 3.348 [s, 3H, C*H*$_3$O (MBn)], 3.167 (*C*H$_3$OC(CH$_3$)$_2$), 2.031 (*C*H$_3$S), 1.373 and 1.234 (2s, 2x3H, (*C*H$_3$)$_2$CO$_2$), 1.283 (s, 6H, (*C*H$_3$)$_2$COCH$_3$); ^{13}C, δ 159.3, 130.3-127.2, 113.5 (aromatic carbons), 109.3 [*C*(CH$_3$)$_2$], 99.68 (CH$_3$O*C*(CH$_3$)$_2$), 84.1 (C-1), 79.7 (C-3), 78.4 (C-2), 75.5 (C-5), 73.9 (C-4), 72.8 [*C*H$_2$ (MBn)], 60.5 (C-6), 54.4 *C*H$_3$O [(MBn)], 47.9 (*C*H$_3$OC(CH$_3$)$_2$), 27.7 and 26.0 (*C*H$_3$)$_2$CO$_2$), 24.1 [(*C*H$_3$)$_2$COCH$_3$], 11.8 (*C*H$_3$S). CIMS: m/z 460 $[M+18]^+$. Anal. Calcd for $C_{22}H_{34}O_7S$: C, 59.71; H, 7.74; S, 7.24. Found: C, 59.90; H, 7.77; S, 7.29.

Methyl 2-*O*-(4-methoxybenzyl)-1-thio-β-D-galactopyranoside (14). A solution of **13** (32 g) in MeOH (220 mL) was treated with 50 %, aq. HBF_4 (3 mL) at 0°C for 1 h. The resulting crystalline mass was treated with ether (50 mL). Filtration afforded **14** (19.3 g). The filtrate was treated with triethylamine and was concentrated. The residue was triturated with ether (100 mL). Filtration afforded a second crop of **14** (3.5 g, total yield 92 %), mp 173-175°C, $[\alpha]_D$ -3° (c 0.34, MeOH). NMR data (DMSO-d_6): ^1H NMR, δ 6.85-7.33 (m, 4H, aromatic protons), 4.700, 4.610 [2d, 2H, *J* 10 Hz, C*H*$_2$ (MBn)], 4.238 (d, 1H, $J_{1,2}$ 9.3 Hz, H-1), 3.736 (s, 3H, C*H*$_3$O), 3.71 (m, 1H, H-4), 3.46-3.54 (m, 3H, H-3,6,6'), 3.36-3.43 (m, 2H, H-2,5), 2.108 (s, 3H, C*H*$_3$S); ^{13}C, δ 158.4, 130.8, 129.1, 113.2 (aromatic carbons), 84.2 (C-1), 78.9 (C-5), 77.8 (C-2), 74.4 (C-3), 73.5 [*C*H$_2$ (MBn)], 68.7 (C-4), 60.4 (C-6), 54.9 (*C*H$_3$O), 11.8 (*C*H$_3$S). CIMS: m/z 348 $[M+18]^+$. Anal. Calcd for C, 59.71; H, 7.74; S, 7.24. Found: C, 59.81, H, 7.73; S, 7.33.

Methyl 3,4,6-tri-*O*-acetyl-2-*O*-(4-methoxybenzyl)-1-thio-β-D-galactopyranoside (15). A solution of **14** (500 mg) in anhydrous pyridine (5 mL) at 0°C was treated with Ac_2O (4 mL). The solution was allowed to reach room temperature in 2 h. Concentration to a syrup under vacuum followed by crystallization from hexane afforded **15** (635 mg, 92 %), mp 96-98°C, $[\alpha]_D$ +10° (c 1.1). NMR data ($CDCl_3$): ^1H, δ 6.83-6.9 and 7.22-7.28 (m, 4H, aromatic protons), 5.405 (dd, 1H, $J_{3,4}$ 4 Hz, $J_{4,5}$ 1 Hz, H-4), 4.996 (dd, 1H $J_{2,3}$ 9.7 Hz, H-3), 4.76 and 4.56 [2d, 2H, J 10.4 Hz, CH_2 (MBn)], 4.441 (d, 1H, $J_{1,2}$ 10.5 Hz, H-1), 4.161 (dd, 1H, $J_{5,6}$ 6.6 Hz, $J_{6,6'}$ 11.2 Hz, H-6). 4.087 (dd, 1H, $J_{5,6'}$ 6.6 Hz, H-6'), 3.864 (dt, 1H, H-5), 3.793 (s, 1H, CH_3O), 3.659 (t, 1H, H-2); ^{13}C, δ 170.2, 170.0, 169.7 (*C*=O), 158.3, 129.7, 129.6, 113.7 (aromatic carbons), 85.9 (C-1), 75.3 (C-2), 75.1 [CH_2 (MBn)], 74.0 (C-3,5), 67.7 (C-4), 61.5 (C-6), 55.3 (CH_3O), 20.7 (CH_3CO), 13.2 (CH_3S). CIMS: m/z 474 $[M+18]^+$, 457 $[M+1]^+$. Anal. Calcd for $C_{21}H_{28}O_9S$: C, 55.25; H, 6.18; S, 7.02. Found: C, 55.34; H, 6.22; S, 7.08.

Methyl 3,4,6-tri-*O*-benzoyl-2-*O*-(4-methoxybenzyl)-1-thio-β-D-galactopyranoside (16). A solution of **14** (3 g) in pyridine (20 mL) at 0°C was treated with benzoyl chloride (5 mL). The mixture was kept at 25°C for 2 h. Methanol (10 mL) was added under cooling with ice. The solution was concentrated to a syrup which was dissolved in $CHCl_3$ (50 mL). The $CHCl_3$ solution was extracted with H_2O (5x20 mL), dried (Na_2SO_4) and concentrated. Column chromatography of the residue (8:1 → 4:1 hexane-EtOAc) gave **16** (5.29 g, 90 %), which was crystallized from diisopropyl ether, mp 150-151°C, $[\alpha]_D$ +71° (c 1.45). NMR data ($CDCl_3$): ^1H, δ 6.62-8.06 (m, 19H, aromatic protons), 5.924 (bd, 1H, H-4), 5.458 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 3.4 Hz, H-3), 4.59 and 4.77 [2d, 2H, CH_2 (MBn)], 4.638 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1), 4.625 (dd, 1H, H-6), 4.341 (dd, 1H, $J_{5,6'}$ 6.6 Hz, $J_{6,6'}$ 11.2 Hz, H-6'), 4.225 (bt, 1H, H-5), 3.963 (t, 1H H-2), 3.689 (s, 3H, CH_3O), 2.340 (s, 3H, CH_3S); ^{13}C, δ 165.8, 165.2 (*C*=O), 159.2, 133.0-133.4, 129.3-129.9, 128.1-128.5-113.6 (aromatic carbons), 86.1 (C-1), 75.3 (C-2), 75.1 [CH_2 (MBn)], 74.6 (C-3,5), 68.8 (C-4), 62.2 (C-6), 55.2 (CH_3O), 13.3 (CH_3S). CIMS: m/z 660 $[M+18]^+$. Anal. Calcd for $C_{36}H_{34}O_9S$: C, 67.27; H, 5.33; S, 4.99. Found: C, 66.90; H, 5.47; S, 4.81.

2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl chloride (18). A solution of methyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranoside[28] (20 g) in Ac_2O (80 mL) was treated with 100 μL of cc. H_2SO_4 for 4 h at 25°C. $NaHCO_3$ (1 g) was added and the solution was concentrated.The residual syrup was dissolved in $CHCl_3$. The $CHCl_3$ solution was extracted with aq. $NaHCO_3$, water, was dried (Na_2SO_4) and concentrated. A solution of the residue in CH_2Cl_2 (150 mL) was treated with α,α-dichloromethyl methyl ether (10 mL), and freshly fused $ZnCl_2$ (*ca.* 0.2 g) for 3 h at 25°C. The mixture was cooled to 0°C then was poured into ice-cold, aq. $NaHCO_3$. The aqueous solution was extracted with $CHCl_3$. The organic phase was washed with H_2O, was dried (Na_2SO_4) and concentrated. Crystallization of the residue from EtOAc afforded **18** (19.5 g, 96 %), mp 165-166°C, lit.[28] mp 165-166°C, $[\alpha]_D$ +129° (c 0.77), lit.[28] $[\alpha]_D$ +136°. NMR data ($CDCl_3$): ^1H, δ 7.22-8.12 (aromatic protons), 6.231(d, 1H, $J_{1,2}$ 1.4 Hz, H-1), 6.096 (dd, 1H, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 10.3 Hz, H-3), 5.815 (dd, 1H, H-2), 5.752 (t, 1H, H-4), 4.491 (dq, 1H, H-5), 1.417 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6); ^{13}C, δ 165.6 (*C*=O), 128.3-133.7 (aromatic carbons), 89.2 (C-1), 72.8 (C-2), 71.0 (C-4), 69.8 (C-5), 68.7 (C-3), 17.3 (C-6). CIMS: m/z512 $[M+18]^+$, 459 $[M-35]^+$. Anal. Calcd for $C_{27}H_{23}O_7Cl$: C, 65.52; H, 4.68; Cl, 7.16. Found: C, 65.27; H, 4.69; Cl, 7.32.

2-(Trimethylsilyl)ethyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranoside (19). A mixture of **18** (19 g), 2,6-di-*tert*-butyl-4-methylpyridine (7 g), 2-(trimethylsilyl)ethanol (8 mL), powdered, 4A molecular sieves (10 g), and anhydrous CH_2Cl_2 (100 mL) was stirred for 1 h then cooled to -20°C. AgOTf (10 g) was added in one portion. The reaction mixture was stirred for 2 h at 0°C. More AgOTf (8 g) was added and stirring was continued at 0°C for 3 h. The mixture was treated with ice cold, aq. $NaHCO_3$ (5 %) and was then filtered. The filtrate was extracted with H_2O, dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (4:1 hexane-EtOAc) to give **19** as a syrup (19 g, 86 %), $[\alpha]_D$ +122° (c 0.8). NMR data ($CDCl_3$): ^1H, δ 7.22-8.14 (aromatic protons), 5.851 (dd, 1H, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 10.0 Hz, H-3), 5.668 (t, 1H, $J_{4,5}$ 10.0 Hz, H-4), 5.627 (dd, 1H, H-2), 5.032 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1), 4.209 (dq, 1H, H-5), 3.907, 3.646 (2x1H, OCH_2CH_2), 1.366 (d, 3H, H-6), 1.00-1.12 (2H, CH_2Si), 0.093 (s, 9H, $SiMe_3$); ^{13}C, δ 165.7, 165.6, 165.4 (*C*=O), 128.2-133.3 (aromatic carbons), 97.0 (C-1), 71.9 (C-4), 71.2 (C-2), 70.1 (C-3), 66.6 (C-5), 65.8 (OCH_2), 18.8 ($SiCH_2$), 17.7 (C-6), -1.3 ($CH_3)_3Si$. CIMS: m/z 594 $[M+18]^+$, 459 $[M-C_5H_{13}OSi]^+$. Anal. Calcd for $C_{32}H_{36}O_8Si$: C, 66.64; H, 6.29. Found: C, 66.68; H, 6.34.

2-(Trimethylsilyl)ethyl α-L-rhamnopyranoside (20). A solution of **19** (15 g) in anhydrous MeOH (100 mL) was treated with a catalytic amount of MeONa for 24 h. The solution was neutralized [Dowex 50x2 (H^+)] and concentrated. Column chromatography of the residue (EtOAc) afforded **20** as a syrup (6.3 g, 92

%), $[\alpha]_D$ -75° (c 1.5). NMR data (MeOH-d_4): ^{1}H, δ 4.680 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1), 3.775 (dd, 1H, H-2), 3.655 (dd, 1H, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 9.4 Hz, H-3), 3.588 (dq, 1H, H-5), 3.371 (t, 1H, $J_{4,5}$ 9.4 Hz, H-4), 1.261 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6); ^{13}C, δ 101.2 (C-1), 73.9 (C-4), 72.4 (C-3), 72.3 (C-2), 69.6 (C-5), 65.8 (OCH_2), 18.6 (CH_2Si), 17.9 (C-6), -1.3 [$(CH_3)_3Si$]. CIMS: m/z 282 $[M+18]^+$. Anal. Calcd for $C_{11}H_{24}O_5Si$: C, 49.97; H, 9.15. Found: C, 49.36; H, 8.91.

2-(Trimethylsilyl)ethyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (21). A solution of compound **20** (3.5 g) in EtOAc (30 mL) was mixed with trimethyl orthobenzoate (4.5 mL) at 25°C, then most of EtOAc was removed under vacuum. The mixture was treated with 10-camphorsulfonic acid (40 mg) followed by evacuation of the reaction flask. After 10 min pyridine (5 mL) was added, the solution was cooled to 0°C and treated with benzoyl chloride (2.5 mL) for 1 h at 0°C. MeOH (5 mL) was added under stirring, then the mixture was concentrated and treated with aq. 80 % AcOH (30 mL). After 5 min the solution was concentrated and the residue was partitioned between $CHCl_3$ and H_2O. The organic phase was concentrated. Column chromatography (8:1 hexane-EtOAc) of the residue afforded **21** (4.3 g, 69 %) as a syrup which crystallized on standing, mp 133-134°C, $[\alpha]_D$ +31° (c 0.9). NMR data ($CDCl_3$): ^{1}H, δ 8.05-8.15, 7.56-7.64, 7.43-7.52 (aromatic protons), 5.358 (dd, 1H, $J_{1,2}$ 1.7 Hz, $J_{2,3}$ 3.5 Hz, H-2), 5.263 (t, 1H, $J_{3,4}$=$J_{4,5}$=9.7 Hz, H-4), 4.985 (d, 1H, H-1), 4.320 (ddd, 1H, H-3), 4.078 (dq, 1H, H-5), 2.424 (d, 1H, $J_{H\text{-}3,OH}$ 8.2 Hz, *H*O-3), 1.320 (d, 1H, H-6); ^{13}C, δ 167.0, 166.0 (*C*=O), 128.4-133.4 (aromatic carbons), 96.9 (C-1), 75.7 (C-4), 73.6 (C-2), 69.1 (C-3), 66.2 (C-5), 65.7 (OCH_2CH_2Si), 18.0 (OCH_2CH_2Si), 17.7 (C-6), -1.2 [$Si(CH_3)_3$]. Anal. Calcd for $C_{25}H_{32}O_7Si$: C, 63.53; H, 6.83. Found: C, 63.44; H,6.85.

Methyl 2,4-di-*O*-benzoyl-1-thio-α-L-rhamnopyranoside (23). 10-Camphorsulfonic acid (40 mg) was added to a stirred mixture of methyl 1-thio-α-L-rhamnopyranoside[25b] (1 g), DMF (0.5 mL) and trimethyl orthobenzoate (3 mL) followed, *immediately*, by exposure of the reaction flask to vacuum. After 5 min pyridine (2 mL) was added and the mixture was cooled to 0°C. Benzoyl chloride (2 mL) was added under stirring and the reaction mixture was allowed to reach 25°C in *ca.* 30 min. The mixture was then cooled to 0°C and was treated with MeOH (5 mL) followed by removal of the volatiles in vacuum. The residue was treated with aq. 80 % AcOH (10 mL). After 10 min the mixture was concentrated. Column chromatography of the residue (7:1 hexane-EtOAc) afforded **23** as an amorphous solid (1.64 g, 79 %), $[\alpha]_D$ -21° (c 1.2), lit.[29] $[\alpha]_D$ -21°. For NMR data see Ref. 29. CIMS: m/z 420 $[M+18]^+$, 403 $[M+1]^+$.

Methyl 2,4-di-*O*-benzoyl-3-*O*-chloroacetyl-1-thio-α-L-rhamnopyranoside (24). A solution of **23** (15 g) in a 1:1 mixture of pyridine and DMF (100 mL) was treated at -45°C with chloroacetyl chloride (4.5 mL) under stirring. After 5 min the reaction mixture was concentrated under reduced pressure at 30°C. Column chromatography (7:1 hexane-EtOAc) of the residue afforded **24** as an amorphous solid (16.2 g, 91%), $[\alpha]_D$ +23° (c 1.3). NMR data ($CDCl_3$): ^{1}H, δ 8.1-7.3 (aromatic protons), 5.681 (dd, 1H, $J_{1,2}$ 1.4 Hz, $J_{2,3}$ 3.2 Hz, H-2), 5.630 (dd, 1H, $J_{3,4}$ 9.9 Hz, H-3), 5.527 (t, 1H, $J_{4,5}$ 9.9 Hz, H-4), 5.316 (d, 1H, H-1), 4.446 (dq, 1H. H-5), 3.887 and 3.817 (2d 2x1H, *J* for each 15 Hz, CH_2Cl), 2.219 (s, 3H, CH_3S), 1.363 (d, 3H, H-6); ^{13}C, δ 166.5, 165.6 (*C*=O), 128.5-133.6 (aromatic carbons), 83.4 (C-1), 71.6 (C-2,3,4), 67.2 (C-5), 40.4 (CH_2Cl), 17.6 (C-6), 13.8 (CH_3S). CIMS: m/z 496 $[M+18]^+$. Anal. Calcd for $C_{23}H_{23}ClO_7S$: C, 57.68; H, 4.84; Cl, 7.40; S, 6.69. Found: C, 57.78; H, 4.92; Cl, 7.31; S, 6.63.

2,4-Di-*O*-benzoyl-3-*O*-chloroacetyl-α-L-rhamnopyranosyl chloride (25). A solution of **24** (10 g) in CH_2Cl_2 (50 mL) was treated with a solution of Cl_2 in CCl_4 at 0°C until the mixture remained yellow. After 10 min the solution was concentrated. Column chromatography (7:1 hexane-EtOAc) of the residue afforded **25** as a syrup (8.2 g, 84 %), $[\alpha]_D$ +52° (c 1). NMR data ($CDCl_3$): ^{1}H, δ 8.1-7.4 (aromatic protons), 6.160 (d, 1H, H-1), 5.941 (dd, 1H, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 10.2 Hz, H-3), 5.710 (dd, 1H, $J_{1,2}$ 1.7 Hz, H-2), 5.569 (t, 1H, $J_{4,5}$ 10.2 Hz, H-4), 4.413 (dq, 1H, H-5), 3.896 and 3.832 (2d, 2x1H, *J* for each 15 Hz, CH_2Cl), 1.39 (d, 1H, $J_{5,6}$ 6.3 Hz, H-6); ^{13}C, δ 166.5, 165.5, 165.3 (*C*=O), 128.6-133.9 (aromatic carbons), 89.0 (C-1, $^1J_{C\text{-}1,H\text{-}1}$ 184 Hz), 72.3 (C-2), 70.7 (C-4), 69.8 (C-3,5), 40.3 (CH_2Cl), 17.3 (C-6). CIMS: m/z 484 $[M+18]^+$.

2-(Trimethylsilyl)ethyl 2,4-di-*O*-benzoyl-3-*O*-(2,4-di-*O*-benzoyl-3-*O*-chloroacetyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (26). Silver trifluoromethanesulfonate (3.9 g) was added to a stirred mixture of **21** (2.2 g), **25** (3.8 g), 2,6-di-*tert*-butyl-4-methylpyridine (1.6 g) and powdered 4A molecular sieves (5 g) in CH_2Cl_2 (45 mL) at -40°C. The stirring was continued for 1 h during which the reaction mixture reached room temperature. Ice-cold, 5 % aq. $NaHCO_3$ was added and the mixture was filtered. The mixture was diluted with $CHCl_3$ (50 mL) and was extracted with water. The organic layer was concentrated. Column chromatography (7:1 hexane-EtOAc) of the residue afforded **26** as an amorphous solid (2.7 g, 64 %), $[\alpha]_D$

+99° (c 0.8). NMR data ($CDCl_3$): ^1H, δ 8.26-7.33 (aromatics), 5.560 (t, 1H, $J_{3,4}$=$J_{4,5}$= 9.8 Hz, H-4_A), 5.467 (dd, 1H, $J_{1,2}$ 1.6 Hz, $J_{2,3}$ 3.3 Hz, H-2_A), 5.428 (dd, 1H, $J_{2,3}$ 3.3 Hz, H-3_B), 5.305 (t, 1H, $J_{3,4}$=$J_{4,5}$=9.7 Hz, H-4_B), 5.164 (dd, 1H, $J_{1,2}$ 1.7 Hz, $J_{2,3}$ 3.4 Hz, H-2_B), 5.135 (d, 1H, H-1_B), 5.013 (d, 1H, H-1_A), 4.470 (dd, 1H, H-3_A), 4.105 (dq, 1H, H-5_B), 4.062 (dq, 1H, H-5_A), 3.776 and 3.672 (2d, 2x1H, *J* 15.6 Hz, CH_2Cl), 1.340 (d, 3H, H-6_A), 1.160 (d, 3H, H-6_B), 0.07 (s, 9H, $(CH_3)_3Si$); ^{13}C, δ 166.2-194.9 (5 *C*=O), 133.5-128.4 (aromatic carbons), 99.2 (C-1_B, $^1J_{C\text{-}1,H\text{-}1}$ 172 Hz), 96.9 (C-1_A, $^1J_{C\text{-}1,H\text{-}1}$ 171 Hz), 76.0 (C-3_A), 73.4 (C-4_A), 72.5 (C-2_A), 71.3, 70.5, 70.1 (C-2_B, 3_B, 4_B) 67.4 (C-5_B), 66.6 (C-5_A), 65.7 (OCH_2CH_2), 40.3 (CH_2Cl), 17.9 (CH_2Si), 17.7 (C-6_A), 17.3 (C- 6_B), -1.3 [$CH_3)_3Si$]. CIMS: m/z 921 $[M+18]^+$. Anal. Calcd for $C_{47}H_{57}ClO_{14}Si$: C, 62.48; H, 5.69, Cl, 3.92. Found: C, 63.31; H, 5.98; Cl, 3.79.

2-(Trimethylsilyl)ethyl 2,4-di-*O*-benzoyl-3-*O*-(2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (27). A solution of **26** (2.5 g) and thiourea (1.5 g) in EtOH (50 mL) was stirred at 25°C for 36 h. The solution was concentrated and the residue was triturated with $CHCl_3$ (50 mL). The mixture was filtered, and the filtrate was extracted with ice-cold, 5 % aq. HCl, H_2O, 5 % aq. $NaHCO_3$, dried (Na_2SO_4) and concentrated. Column chromatography (4:1 hexane-EtOAc) of the residue afforded **27** as an amorphous solid (2.25 g, 90 %), $[\alpha]_D$ +83° (c 1.1). NMR data ($CDCl_3$): ^1H, δ 8.24–7.33 (aromatic protons), 5.553 (t, 1H, $J_{3,4}$=$J_{4,5}$=9.8 Hz, H-4_A), 5.476 (dd, 1H, $J_{1,2}$ 1.7 Hz, $J_{2,3}$ 3.2 Hz, H-2_A), 5.176 (d, 1H, $J_{1,2}$ 1.4 Hz, H-1_B), 5.087 (t, 1H, $J_{3,4}$=$J_{4,5}$=9.8 Hz, H-4_B), 5.020 (dd, 1H, H-2_B), 5.012 (dd, 1H, H-1_A), 4.450 (dd, 1H, H-3_A), 4.076 (ddd, 1H, H-3_B), 4.062 (dq, 1H, H-5_A), 4.006 (dq, 1H, H-5_B), 2.221 (d, 1H, $J_{3,HO}$ 7.7 Hz, *HO*), 1.335 (d, 3H, H-6_A), 1.138 (d, 3H, H-6_B), 0.070 (s, 9H, $(CH_3)_3Si$); ^{13}C, δ 166.7, 166.0, 165.3 (*C*=O), 133.5-128.3 (aromatic carbons), 99.2 (C-1_B), 96.8 (C-1_A), 76.3 (C-3_A), 75.1 (C-4_B), 73.2 (C-4_A), 72.9 (C-2_B), 72.7 (C-2_A), 68.5 (C-3_B), 66.9 (C-5_B), 66.6 (C-5_A), 65.7 (OCH_2CH_2), 17.9 (CH_2Si), 17.7, 17.3 (C-6_A, 6_B), -1.3 [$(CH_3)_3Si$). CIMS: m/z 844 $[M+18]^+$. Anal. Calcd for $C_{45}H_{50}O_{13}Si$: C, 65.36; H, 6.09. Found: C, 65.78; H, 6.50.

2-(Trimethylsilyl)ethyl 3-*O*-[3-*O*-(2-azido-4,6-*O*-benzylidene-3-*O*-chloroacetyl-2-deoxy-α-D-glucopyranosyl)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl]-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (28). To a stirred solution of **11** (2.1 g), **27** (2.2 g) and 2,6-di-*tert*-butyl-4-methylpyridine (1.1 g) in CH_2Cl_2 (40 mL) containing powdered, 4A molecular sieves (3 g) at -50°C was added AgOTf (1.5 g) and the mixture was stirred for 2 h during which time the temperature of the mixture was allowed to reach 0°C. Processing as described for **27**, using 4:1 hexane-EtOAc as chromatographic eluent, afforded **28** as an amorphous solid (1.95 g, 69 %), $[\alpha]_D$ +141° (c 0.5). NMR data ($CDCl_3$): ^1H, δ 8.25-6.87 (aromatic protons), 5.549 (t, 1H, $J_{3,4}$=$J_{4,5}$=10 Hz, H-4_A), 5.506 (dd, 1H, $J_{1,2}$ 1.6 Hz, $J_{2,3}$ 3.4 Hz, H-2_A), 5.402 (t, 1H, $J_{3,4}$=$J_{4,5}$=9.7 Hz, H-4_B), 5.225 (dd, 1H, H-2_B), 5.181 (s, 1H, *H*CPh), 5.150 (d, 1H $J_{1,2}$ 1.6 Hz, H-1_B), 5.087 (t, 1H, $J_{3,4}$=$J_{4,5}$=9.8 Hz, H-3_C), 4.985 (d, 1H, H-1_A), 4.769 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1_C), 4.472 (dd, 1H, $J_{2,3}$ 9.8 Hz, $J_{3,4}$ 3.4 Hz, H-3_A), 4.143 (dd, 1H, $J_{2,3}$ 3.3 Hz, H-3_B), 4.7 (2dq, 2H, H-5_A, 5_B), 3.92 (s, 2H, CH_2Cl), 3.722 (dd, 1H, $J_{5,6}$ 4.7 Hz, $J_{6,6'}$ 9.8 Hz, H-6_C), 3.484 (ddd, 1H, H-5_C), 3.39-3.30 (m, 2H, H-4_C, $6'_C$), 2.948 (dd, 1H, H-2_C), 1.346 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6_A), 1.171 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6_B), 0.06 (s, 9H, $(CH_3)_3Si$); ^{13}C, δ 165.9, 165.6, 165.3, 165.1 (*C*=O), 136.6, 133.5-133.1, 129.8-127.8, 126.2 (aromatic carbons), 101.2 (*C*HPh), 99.1 (C-1_B), 96.9 (C-1_A), 94.7 (C-1_C), 78.5 (C-4_C), 75.6 (C-3_A), 73.6 (C-4_A), 72.3 (C-2_A), 71.6 (C-4_B), 71.5 (C-3_B), 70.6 (C-3_C), 68.0 (C-6_C), 67.7 (C-5_B), 67.5 (C-2_B), 66.5 (C-5_A), 65.7 (OCH_2CH_2), 62.5 (C-5_C), 60.9 (C-2_C), 40.4 (CH_2Cl), 17.9 (CH_2Si), 17.7 (C-6_A), 17.4 (C-6_B), -1.3 [$CH_3)_3Si$]. HRFAB: Found m/z 1176.3572, $C_{60}H_{63}{}^{35}CN_3O_{18}Si$ ($M+H^+-H_2$) requires 1176.3564.

2-(Trimethylsilyl)ethyl 3-*O*-[3-*O*-(2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranosyl)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl]-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (29). A solution of **28** (1.7 g) and thiourea (2.0 g) in EtOH (50 mL) was stirred at 25°C for 36 h. Work-up as described for **27** afforded **29** as an amorphous solid (1.46 g, 90 %), $[\alpha]_D$ +117° (c 0.6). NMR data ($CDCl_3$): ^1H, δ 8.22-6.99 (aromatics), 5.546 (t, 1H, $J_{3,4}$=$J_{4,5}$=9.9 Hz, H-4_A), 5.499 (dd, 1H, $J_{1,2}$ 1.6 Hz, $J_{2,3}$ 3.4 Hz, H-2_A), 5.369 (t, 1H, $J_{3,4}$=$J_{4,5}$=9.8 Hz, H-4_B), 5.215 (s, 1H, *H*CPh), 5.195 (dd, 1H, H-2_B), 5.146 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1_B), 4.983 (d, 1H H-1_A), 4.586 (d, 1H, $J_{1,2}$ 4.6 Hz, H-1_C), 4.463 (dd, 1H, $J_{3,4}$ 9.8 Hz, H-3_A), 4.110 (dd, 1H, $J_{2,3}$ 3.2 Hz, $J_{3,4}$ 9.9 Hz, H-3_B), 4.073 (dq, 1H, H-5_B), 4.030 (dq, 1H, H-5_A),3.414 (ddd, 1H, H-5_C), 3.754 (dt, $J_{2,3}$=$J_{3,4}$=10 Hz, $J_{3,OH}$ 3.4 Hz, H-3_C), 3.679 (dd, 1H, $J_{5,6}$ 4.0 Hz, $J_{6,6'}$ 9.4 Hz, H-6_C), 3.332 (t, $J_{5,6'}$ 9.4 Hz, H-$6'_C$), 3.175 (t, 1H H-4_C), 2.916 (dd, 1H, $J_{2,3}$ 10 Hz, H-2_C), 1.348, 1.135 (2d, 2x3H, H-6_A, H-6_B), 0.070 [$(CH_3)_3Si$], ^{13}C, δ 166.0-165.2 (*C*=O), 136.7-126.4 (aromatic carbons), 101.7 (*C*HPh), 99.1 (C-1_B), 96.9 (C-1_A), 94.9 (C-1_C), 81.2 (C-4_C), 75.8 (C-3_A), 73.5 (C-4_A), 72.3 (C-2_A), 72.0 (C-4_B), 71.7 (C-3_B), 68.4 (C-3_C), 68.2 (CH_2CH_2Si), 68.0 (C-2_B), 67.4 (C-5_A), 66.6 (C-5_B), 65.7 (C-6_C), 62.6 (C-2_C), 62.4 (C-5_C), 17.9 (CH_2Si), 17.7, 17.35 (C-6_A, 6_B), -1.3 [$(CH_3)_3Si$]. FABMS: m/z 1074

$[M-N_2+1]^+$. Anal. Calcd for $C_{58}H_{63}N_3O_{17}Si$: C, 63.20; H, 5.76; N, 3.81. Found: C, 63.28; H, 5.80, N, 3.80.

2-(Trimethylsilyl)ethyl 3-*O*-{3-*O*-[2-azido-4,6-*O*-benzylidene-3-*O*-(3,4,6-tri-*O*-benzoyl-2-*O*-/4-methoxybenzyl/-α-D-galactopyranosyl)-2-deoxy-α-D-glucopyranosyl]-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl}-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (30). To a solution of **16** (1.7 g), **29** (1.39 g), 2,6-di-*tert*-butyl-4-methylpyridine (1.5 g) in ether (40 mL), containing powdered, 4A molecular sieves (4 g) was added methyl triflate[33] (MeOTf) (300 μL). Stirring was continued for 24 h. Triethylamine (1 mL) was added and the mixture was filtered. The solids were washed with $CHCl_3$. The filtrated was concentrated. Column chromatography (3:1 hexane-EtOAc) of the residue afforded **30** as an amorphous solid (1.9 g, 89 %), $[\alpha]_D$ +136° (c 0.7). NMR data ($CDCl_3$): ^1H, δ 8.22-6.41 (aromatic protons), 5.752 (dd, $J_{3,4}$ 3.2 Hz, H-4_D), 5.607 (dd, 1H, $J_{2,3}$ 10.7 Hz, H-3_D), 5.562 (t, 1H, $J_{3,4}=J_{4,5}$=9.8 Hz, H-4_A), 5.514 (dd, 1H, $J_{1,2}$ 1.6 Hz, $J_{2,3}$ 3.4 Hz, H-2_A), 5.417 (t, 1H, $J_{3,4}=J_{4,5}$=9.9 Hz, H-4_B), 5.383 (d, 1H, $J_{1,2}$ 3.4 Hz, H-1_D), 5.248 (dd, 1H, H-2_B), 5.219 (s, 1H *H*CPh), 5.160 (d, 1H, H-1_B), 4.990 (d, 1H, H-1_A), 4.652 (d, 1H, $J_{1,2}$ 3.9 Hz, H-1_C), 4.468 (dd, 1H, H-3_A), 4.270 and 3.944 [2d, 2H, CH_2 (MBn)], 3.651 (s, 3H, CH_3O), 3.032 (dd, 1H, $J_{2,3}$ 10.Hz, H-3), 1.358 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6_A), 1.139 (d, 3H, $J_{5,6}$ 6.1 Hz, H-6_B), 0.07 (s, 9H, $(CH_3)_3Si$); ^{13}C, δ 165.9, 165.5, 165.3, 165.1 (*C*=O), 102.1 (*C*HPh), 99.1 (C-1_B, $^1J_{C-1,H-1}$ 168 Hz), 97.0 , (C-1_A, $^1J_{C-1,H-1}$ 171 Hz), 96.9 (C-1_D, $^1J_{C-1,H-1}$ 171 Hz), 94.8 , (C-1_C $^1J_{C-1,H-1}$ 170 Hz), 82.0 (C-4_C), 76.1 (C-3_A), 73.4 (C-4_B), 72.4, 72.3, 71.9, 71.5, 70.9, (C-2_A, 2_B, 2_D, 3_C, 4_A), 70.5 [CH_2 (MBn)], 69.0, 68.9, 67.8, 67.5, 66.6(2C) (C-3_B, 3_D, 4_D, 5_A, 5_B, 5_D), 68.4 (C-6_C), 65.7 (OCH_2CH_2), 62.1, 61.4 (C-2_C, 5_C), 61.1 (C-6_D), 17.9 (CH_2Si), 17.7, 17.4 (C-6_A, 6_B), -1.3 [$(CH_3)_3Si$]. FABMS: m/z 1668 [M-N_2+1]$^+$. Anal. Calc for $C_{93}H_{93}N_3O_{26}Si$: 65.83; H, 5.52; N, 2.48. Found: C, 66.30; H, 6.02; N, 2.34.

2-(Trimethylsilyl)ethyl 3-*O*-{3-*O*-[2-acetamido-4,6-*O*-benzylidene-3-*O*-(3,4,6-tri-*O*-benzoyl-2-*O*-/4-methoxybenzyl/-α-D-galactopyranosyl)-2-deoxy-α-D-glucopyranosyl]-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl}-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (31). To a solution containing **30** (1.8 g), $NiCl_2$ (0.8 g), and H_3BO_3 (0.5 g) in EtOH was added a 1 % solution of $NaBH_4$ in EtOH dropwise until the black color persisted. More $NiCl_2$ (1.6 g), H_3BO_3 (1.0 g) was added followed by $NaBH_4$ in EtOH until the starting material disappeared. The mixture was concentrated to *ca* half its original volume then cooled to 0°C. Acetic anhydride (10 mL) was added. After 15 min the solution was concentrated. The residue was equilibrated between $CHCl_3$ and H_2O, the organic phase was dried and concentrated. Column chromatography (3:1 hexane-EtOAc) of the residue afforded **31** as an amorphous solid (780 mg, 43 %), $[\alpha]_D$ +128° (c 0.5). NMR data ($CDCl_3$): ^1H, δ 8.22-7.08, 6.59-6.43 (aromatic resonances), 6.65 (d, 1H, *H*NAc), 5.84 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4_D), 5.60 (dd, 1H, $J_{2,3}$ 10.5 Hz, H-3_D), 5.52 (t, 1H, $J_{3,4}=J_{4,5}$=10.0 Hz, H-4_A), 5.48 (dd, 1H, $J_{1,2}$ 1.5 Hz, $J_{2,3}$ 3.5 Hz, H-2_A), 5.28 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1_D), 5.23 (t, 1H, $J_{3,4}=J_{4,5}$=9.9 Hz, H-4_B), 5.17 (s, 1H, *H*CPh), 5.16 (dd, 1H, H-2_B), 5.09 (d, 1H, H-1_B), 4.99 (d, 1H, H-1_A), 3.65 (s, 3H, CH_3O), 1.68 (s, 3H, CH_3CON) 1.32 (d, 3H, $J_{5,6}$ 6.2 Hx, H-6_A), 1.25 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6_B), 0.07 (s, 9H, $[(CH_3)_3Si]$. ^{13}C, δ 169.9 [*C*=O (AcNH)], 102.0 (*C*HPh), 100.2, 99.5, 96.9(2C) (C-1_A, 1_B, 1_C, 1_D), 82.1 (C-4_C), 70.3 [CH_2 (MBn)], 68.4 (C-6_C), 65.7 (OCH_2CH_2), 61.1 (C-5_C), 60.4 (C-6_D), 55.0 (OCH_3), 51.4 (C-2_C), 22.3 (CH_3CON), 17.9 (CH_2Si), 17.6 (C-6_A), 17.4 (C-6_B), -1.3 [$(CH_3)Si$]. FABMS: m/z 1712 $[M+1]^+$. Anal. Calcd for $C_{95}H_{97}NO_{27}Si$: 66.62; H, 5.71; N, 0.82. Found: C, 67.01; H, 6.10; N, 0.82.

2-(Trimethylsilyl)ethyl 3-*O*-{3-*O*-[2-acetamido-4,6-*O*-benzylidene-3-*O*-(3,4,6-tri-*O*-benzoyl-α-D-galactopyranosyl)-2-deoxy-α-D-glucopyranosyl]-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl}-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (32). A mixture of **31** (700 mg), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (200 mg), CH_2Cl_2 (10 mL), and H_2O (2 mL) was stirred at 25°C for 12 h. The mixture was extracted with aq. 5 % $NaHCO_3$. The organic phase was concentrated. Column chromatography (2:1 hexane-EtOAc) of the residue afforded **32** as an amorphous solid (640 mg, 98 %), $[\alpha]_D$ +107 (c 0.8). NMR data ($CDCl_3$): ^1H, δ 8.22-7.2 (aromatic protons), 6.49 (d, 1H, $J_{H\text{-}2,NH}$ 9.9 Hz, *H*N), 5.875 (bd, 1H, H-4_D), 5.544 (t, 1H, $J_{3,4}=J_{4,5}$=9.8 Hz, H-4_A), 5.515 (dd, 1H, H-2_A), 5.508 (dd, 1H, $J_{3,4}$ 3.3 Hz, H-3_D), 5.294 (s, 1H, *H*CPh), 5.239 (t, 1H, $J_{3,4}=J_{4,5}$=9.6 Hz, H-4_B), 5.156 (dd, 1H, $J_{1,2}$ 1.7 Hz, $J_{2,3}$ 3.3 Hz, H-2_B), 5.093 (d, 1H, H-1_B), 5.072 (d, 1H $J_{1,2}$ 3.6 Hz, H-1_D), 4.996 (d, 1H $J_{1,2}$ 1.5 Hz, H-1_A), 4.462 (dd, 1H, H-3_A), 3.960 (dd, 1H, H-3_B), 2.66 (d, 1H, *H*O), 1.66 (s, 3H, CH_3CON), 1.339 (d 3H, $J_{5,6}$ 6.2 Hz, H-6_A), 1.220 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6_B), 0.070 (s, 9H, $(CH_3)_3Si$); ^{13}C, δ 170.2 (CH_3CON), 166.1-165.4 [*C*=O (Bz)], 136.4, 133.8-132.8, 129.8-127.8, 126.0 (aromatic carbons), 101.1 (*C*HPh), 100.8, 99.2 (2C), 96.9 (C-1_A, 1_B, 1_C, 1_D), 81.0 (C-4_C), 75.8 (C-3_A), 73.6 (C-4_B), 68.0 (C-6_C), 65.7 (OCH_2CH_2), 63.2 (C-5_C), 61.2 (C-6_D), 51.7 (C-2_C), 22.4 (CH_3CO), 17.9 (CH_2Si), 17.6 (C-6_A), 17.4 (C-6_B), -1.3 [$(CH_3)_3Si$]. FABMS: m/z 1592 $[M+1]^+$. Anal. Calcd for $C_{87}H_{89}NO_{26}Si$: 65.61; H, 5.63; N, 0.88. Found: C, 65.88; H, 5.87; N, 0.88.

2-(Trimethylsilyl)ethyl 3-*O*-{3-*O*-[2-acetamido-4,6-*O*-benzylidene-3-*O*-(3,4,6-tri-*O*-benzoyl-2-*O*-chloroacetyl-α-D-galactopyranosyl)-2-deoxy-α-D-glucopyranosyl]-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl}-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (33). To a solution of **32** (610 mg) in pyridine (3 mL) at 0°C was added under stirring chloroacetyl chloride (150 μL). After 15 min the misture was diluted with $CHCl_3$, and the resulting solution was extracted with ice-cold, aq. 5 % $NaHCO_3$.The organic phase was concentrated. Column chromatography (2:1 hexane-EtOAc) of the residue afforded **33** as an amorphous solid (600 mg, 92 %): $[\alpha]_D$ +114° (c 0.6). NMR data ($CDCl_3$): ^1H, δ 8.22-7.08 (aromatic protons), 6.74 (d, 1H, $J_{H\text{-}2,NH}$ 9.8 Hz, *H*N), 5.978 (bd, 1H $J_{3,4}$ 3.4 Hz, H-4_D), 5.669 (dd, 1H, $J_{1,2}$ 4.4 Hz, $J_{2,3}$ 10.8 Hz, H-2_D), 5.529 (t, 1H, $J_{3,4}$=$J_{4,5}$=9.8 Hz, H-4_A), 5.497 (dd, 1H, H-2_A), 5.496 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.8 Hz, H-3_D), 5.227 (dd, 1H, $J_{1,2}$ 3.8 Hz, H-2_D), 5.213 (s, 1H, *H*CPh), 5.204 (t, 1H, $J_{3,4}$=$J_{4,5}$=9.8 Hz, H-4_B), 5.154 (dd, 1H, $J_{1,2}$ 1.7 Hz, $J_{2,3}$ 3.4 Hz, H-2_B), 5.086 (d, 1H, H-1_B), 4.991 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1_A), 3.322, 3.317 (2d, 2H, *J* 15 Hz, H_2CCl), 1.711 (s, 3H, C*H*$_3$CON), 1.324 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6_A), 1.205 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6_B), 0.07 (s, 9H, (C*H*$_3$)$_3$Si). ^{13}C, δ 170.1 (CH_3C=O), 166.4-164.9 [C=O (Bz)], 101.3 (*C*HPh), 100.1, 99.4, 97.1, 96.9 (C-1_A, 1_B, 1_C, 1_D), 81.6 (C-4_C), 75.8 (C-3_A), 73.7 (C-4_B), 68.1 (C-6_C), 65.7 (OCH_2CH_2), 63.0 (C-5_C), 60.1 (C-6_D), 51.6 (C-2_C), 39.9 (CH_2Cl), 22.4 (CH_3CO), 17.9 (CH_2Si), 17.6 (C-6_A), 17.4 (C-6_B), -1.3 [(CH_3)$_3$Si]. FABMS: m/z 1668 $[M+1]^+$. Anal. Calcd for $C_{89}H_{90}ClNO_{27}Si$: C, 64.04; H, 5.43; N, 0.84; Cl, 2.12. Found: C, 63.61; H, 5.66; N, 0.95; Cl, 2.37.

2-(Trimethylsilyl)ethyl 3-*O*-{3-*O*-[2-acetamido-4,6-di-*O*-acetyl-3-*O*-(3,4,6-tri-*O*-benzoyl-2-*O*-chloroacetyl-α-D-galactopyranosyl)-2-deoxy-α-D-glucopyranosyl]-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl}-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (35). A solution of **33** (520 mg) in AcOH (5 mL) was warmed to 70°C. Water (1 mL) was added and the solution was stirred at 70°C for 6 h. The solution was concentrated. Residual solvents were removed by addition and distillation of toluene (3 x 5 mL). Column chromatography (2:1 hexane-EtOAc) of the residue afforded the diol **34** (280 mg) (FABMS: m/z 1580 $[M+1]^+$) which was treated with pyridine (1 mL) and Ac_2O (1 mL) at 25°C for 3 h. Removal of the solvents followed by column chromatography (3:1 hexane-EtOAc) afforded **35** (205 mg, 70 %), $[\alpha]_D$ +127°. NMR data ($CDCl_3$: ^1H, δ 8.22-7.22 (aromatic protons), 5.959 (bd, 1H, $J_{3,4}$ 3.2 Hz, H-4_D), 5.618 (dd, 1H, $J_{2,3}$ 10.6 Hz, H-3_D), 5.52 (t, 1H, $J_{3,4}$=$J_{4,5}$=9.8 Hz, H-4_A), 5.500 (dd, 1H, H-2_A), 5.460 (dd, 1H, $J_{1,2}$ 3.8 Hz, H-2_D), 5.220 (t, 1H, $J_{3,4}$=$J_{4,5}$=9.6 Hz, H-4_B), 5.140 (dd, 1H, $J_{1,2}$ 1.6 Hz, $J_{2,3}$ 3.2 Hz, H-2_B), 5.089 (d, 1H, H-1_D), 4.99 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1_A), 4.970 (t, 1H, $J_{3,4}$=$J_{4,5}$=9.3 Hz, H-4_C), 4.55, 8.82 (2d, 2H, *J* 15 Hz, H_2CCl), 1.936, 1.709, 1. 609 (3s, 3H each, 3C*H*$_3$CO), 1.327 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6_A), 1.204 (d, 3H, $J_{5,6}$ 6.1 Hz, H-6.1 Hz, H-6_B), 0.07 (s, 9H, (C*H*$_3$)$_3$Si); ^{13}C, δ 170.4-164.8 (11 lines, *C*=O), 99.2, 98.7, 96.9, 96.3 (C-1_A, 1_B, 1_C, 1_D), 76.0 (C-3_A), 73.5 (C-4_A), 65.7 (O*C* H_2CH_2)], 60.7, 60.6 (C-6_C, 6_D), 51.2 (C-2_C), 40.7 (CH_2Cl), 22.3 (CH_3CON), 20.5 (2C) (CH_3CO), 17.9 (CH_2Si), 17.5 (C-6_A), 17.4 (C-6_B), -1.3 [(CH_3)$_3$Si]. FABMS: m/z 1664 $[M+1]^+$. Anal. Calcd for $C_{86}H_{90}ClNO_{29}Si$: C, 62.03; H, 5.45; N, 0.84. Found: C, 61.77; H, 5.55; N, 0.85.

***O*-(3,4,6-Tri-*O*-benzoyl-2-*O*-chloroacetyl-α-D-galactopyranosyl)-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-α-D-glucopyranosyl)-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (1).** A solution of **35** (160 mg) in a 1:1 mixture of CH_2Cl_2 and trifluoroacetic acid (2 mL) was kept at 25°C for 4 h then the volatiles were removed. Toluene (3 x 5 mL) was added and evaporated from the residue. The solid residue was dissolved in CH_2Cl_2 (2 mL) and the solution was cooled to -20°C. CCl_3CN (0.4 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (10 μL) were added. The solution was stirred at - 20°C for 1 h then was allowed to reach *ca* 20°C in 1 h. Removal of the volatiles was followed by column chromatography (2:1 hexane-EtOAc) to give **1** as an amorphous solid (120 mg, 73 %), $[\alpha]_D$ +124° (c 0.4). NMR data ($CDCl_3$): ^1H, δ 6.48 (d, 1H, $J_{H\text{-}2,NH}$ 8 Hz, N*H*), 6.467 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1_A), 5.958 (bd, 1H, H-4_D), 5.732 (dd, 1H, $J_{2,3}$ 2.9 Hz, H-2_A), 5.647 (t, 1H, $J_{3,4}$=$J_{4,5}$=9.9 Hz, H-4_A), 5.614 (dd, 1H, $J_{3,4}$ 3.2 Hz, H-3_D), 5.452 (dd, 1H, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 10.8 Hz, H-2_D), 5.258 (t, 1H, $J_{3,4}$=$J_{4,5}$=9.7 Hz, H-4_B), 5.166 (dd, 1H, H-2_B), 5.122 (d, 1H, H-1_B), 5.102 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1_D), 4.985 (t, 1H, $J_{3,4}$=$J_{4,5}$=9.5 Hz, H-4_C), 4.06, 3.82 (2d, H_2CCl), 1.948, 1.706, 1.590 (CH_3CO), 1.383 (d, 3H, H-6_A), 1.210 (d, 1H, H-6_B). ^{13}C, δ 99.2 ($^1J_{C\text{-}1,H\text{-}1}$ 174 Hz), 98.3 ($^1J_{C\text{-}1,H\text{-}1}$ 172 Hz), 96.3 ($^1J_{C\text{-}1,H\text{-}1}$ 173 Hz), (C-1_B, 1_C, 1_D), 94.7 ($^1J_{C\text{-}1,H\text{-}1}$ 179 Hz) (C-1_A), 60.7, 60.6 (C-6_C, 6_D), 52.1 (C-2_C), 40.7 (CH_2Cl), 22.2 (CH_3CON), 20.5 (CH_3COO), 17.6, 17.4 (C-6_A, 6_B). FABMS: m/z 1546 [M-C_2HCl_3NO]$^+$. Anal. Calcd for $C_{83}H_{78}O_{29}Cl_4N_2$: C, 58.32; H, 4.60; N, 1.64; Cl, 8.30. Found: C, 58.08; H, 4.69; N, 1.62; Cl, 8.22.

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