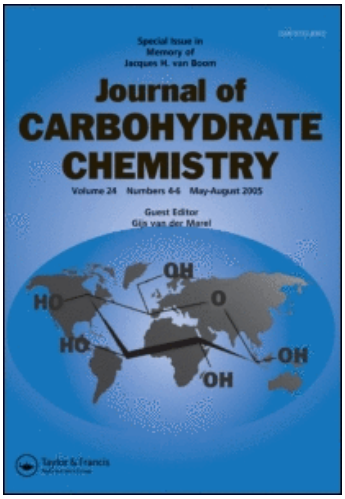

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SYNTHESIS AND APPLICATION OF SPACER-MODIFIED L-FUCOSE ANALOGUES[1]

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SYNTHESIS AND APPLICATION OF SPACER-MODIFIED L-FUCOSE ANALOGUES[1]

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Dedicated to Professor Joachim Thiem on the occasion of his 60th birthday.

ABSTRACT

Starting from 6-*O*-*tert*-butyldimethylsilyl-2,3;4,5-di-*O*-isopropylidenealdehydo-D-galactose (**1**), the carbon backbone elongated GDP-L-fucose analogue **15** bearing a chromophore tag at the end of a spacer was synthesized. Additionally, the analogues of 3-L-fucosyllactose (**29**) and 2′-L-fucosyllactose (**36**), where the fucosyl moiety is marked by a five atom alkyl chain at C-5, were prepared as labeled oligosaccharides of human milk.

INTRODUCTION

As part of a program[2] directed towards the synthesis of human milk oligosaccharides containing fucose residues with various markers, we herein attempt to improve the synthesis of a carbon backbone elongated L-fucose derivative bearing a carboxy group at the end of the alkyl chain. Compound **8** was the base for the preparation of a spacer-modified GDP-L-fucose analogue carrying a chromophore marker. In addition, the glycosylation of various lactose derivatives with carbon backbone elongated L-fucoses was investigated in order to obtain labeled oligosaccharides of human milk. In connection with this, the first biological experiments using these oligosaccharides will be discussed.

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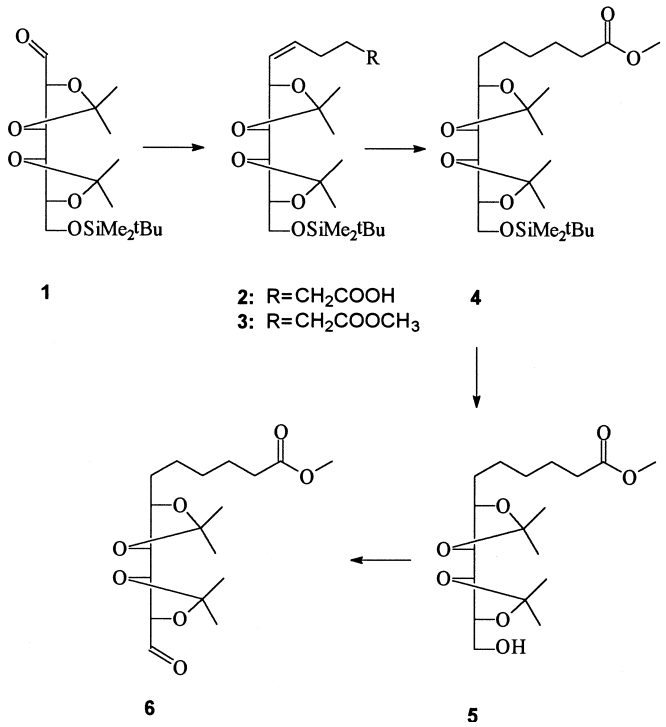
RESULTS AND DISCUSSION

The carbon backbone elongated L-fucose derivatives **9** and **10** are key intermediates in our overall synthetic strategy for the preparation of GDP-L-fucose analogues of human milk oligosaccharides bearing a chromophore tag (Scheme 2). Previously, we were able to synthesize the protected D-galactose aldehyde **1** in three steps from D-galactose diethyl dithioacetal in an overall yield of 65%.[2] The Wittig reaction with 4-carboxybutyl triphenylphosphonium bromide in the presence of lithium-*bis*-(trimethylsilyl) amide followed by esterification of the carboxy function provided the alkene **3** in 58% yield (Scheme 1). Subsequent hydrogenation (**4**, 94%), followed by cleavage of the TBDMS protecting group with tetra-*n*-butylammonium fluoride (**5**, 98%), and oxidation by the Swern procedure gave the carbon backbone elongated L-fucose derivative **6** (89%).

Removal of the isopropylidene group from **6** was accompanied by partial cleavage of the ester bond (Scheme 2). Thus, after acetylation the α/β mixtures of separated compounds **9** and **10** (ratio 1 : 1.5, 75%) were obtained in an overall yield of 23% from D-galactose diethyl dithioacetal. An alternative route recently described by us[3] was comparatively successful, giving the target compound **9** in a 20% yield after the same number of synthetic steps. The free acid **10** was then used for the synthesis of a chromophore labeled GDP-L-fucose analogue, whereas the



Scheme 1.

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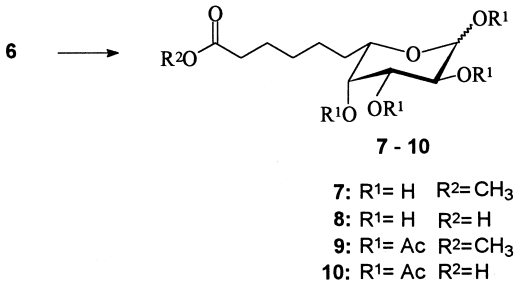
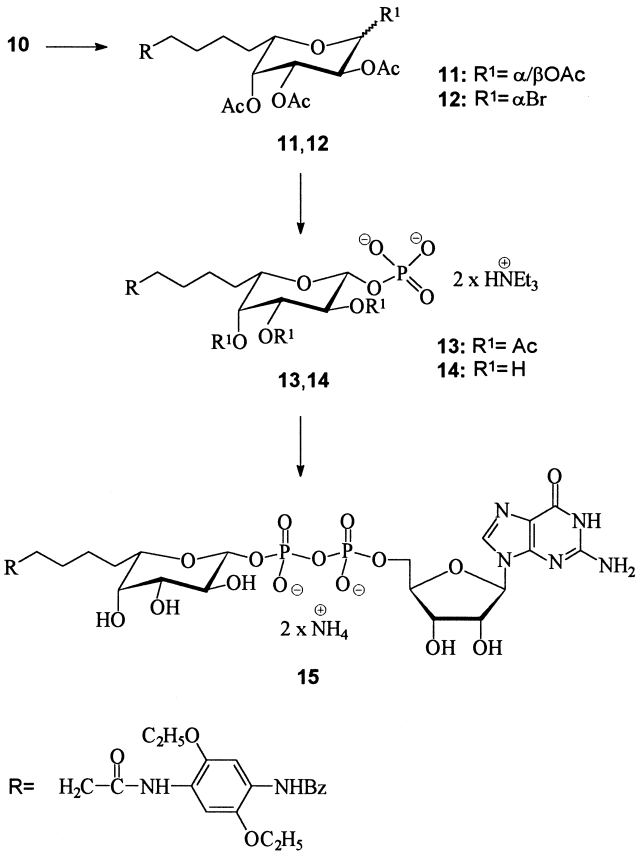


Scheme 2.

ester **9** was converted into a glycosyl donor for the preparation of marked oligosaccharides.

Compound **10** was therefore coupled with 4-amino-2,5-diethoxybenzanilide (Fast Blue BB base) using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI)[4] and 1-hydroxybenzotriazole (HOBt), giving the target compound **11** in 81% yield (Scheme 3).[5,6] The α/β acetate **11** was treated with hydrogen bromide



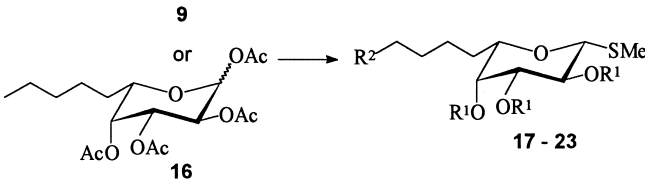
Scheme 3.

in dichloromethane to give the glycosyl bromide **12** in 93% yield. Replacement of bromine by phosphate was achieved using tetrabutylammonium phosphate.[2,7] After purification by column chromatography the acetylated phosphate **13** was isolated in 43% yield. Without further characterization compound **13** was deacetylated and converted into the triethylammonium salt **14** in 60% yield (based on **13**). In the ^{1}H NMR spectrum of **14** the vicinal coupling constant value $J_{1,2} = 7.7$ Hz indicates clearly the β-glycosidic linkage of the pyranosyl phosphate which is a requirement for biochemical activity.

To avoid the formation of a guanosine-5′-monophosphate dimer which cannot be separated from the target compound **15**, GMP-morpholidate[9] was added in portions to an excess of the fucosyl phosphate **14**, providing the sugar nucleotide **15** in 28% yield. The analytical data of **15** are in complete agreement with the structure proposed. Thus, the coupling constant values $^3J_{1,P} = J_{1,2} = 7.6$ Hz of galactosyl H-1 in the ^{1}H NMR spectrum and the resonances of Gal-P at δ −12.11 (d, J = 19.5 Hz) Gal-P) and Rib-P at δ −10.21 (d, J = 19.5 Hz) in the ^{31}P NMR spectrum indicate clearly the stereochemistry at the diphosphate bridge. The enzymatically catalyzed transfer of the chromophore labeled fucosyl moiety of **15** to a suitable glycosyl acceptor is currently under investigation.

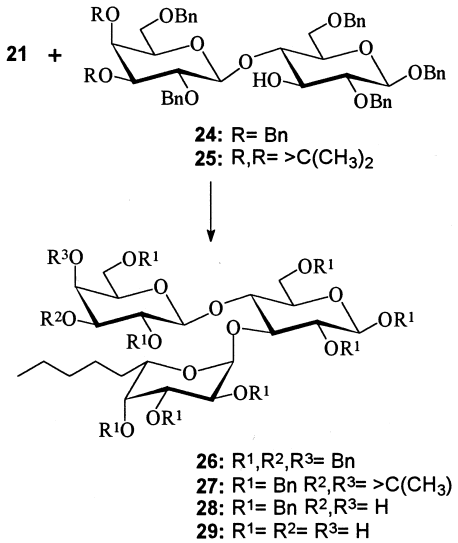
For the synthesis of labeled oligosaccharides of human milk, the peracetylated L-fucose derivatives **9** and **16**, bearing a simple carbon chain of five atoms at C-5,[2] were converted into the thioglycosides **17** and **18** in an analogous fashion as described by R.K. Jain and K. L. Matta[10] (Scheme 4). After deacetylation the resulting compounds **19** and **20** were benzylated to provide the tri-*O*-benzyl thioglycosides **21** and **22** in moderate yields (ca. 45%). Owing to these low yields, the trimethylsilylation of **20** was used as a simple alternative for hydroxyl group protection[11] to give **23** in 68% yield.

For the synthesis of a labeled 3-fucosyllactose (Scheme 5) the glycosylation of the partially benzylated lactoside **24**[12] with glycosyl donor **21** was promoted by freshly prepared[13] iodonium di-*sym*-collidine perchlorate (IDCP)[14] or dimethyl-



17: R¹= Ac R²=CH_3
18: R¹= Ac R²=CH_2COOCH_3
19: R¹= H R²=CH_3
20: R¹= H R²=CH_2COOCH_3
21: R¹= Bn R²=CH_3
22: R¹= Bn R²=CH_2COOCH_3
23: R¹= $Si(CH_3)_3$ R²=CH_2COOCH_3

Scheme 4.

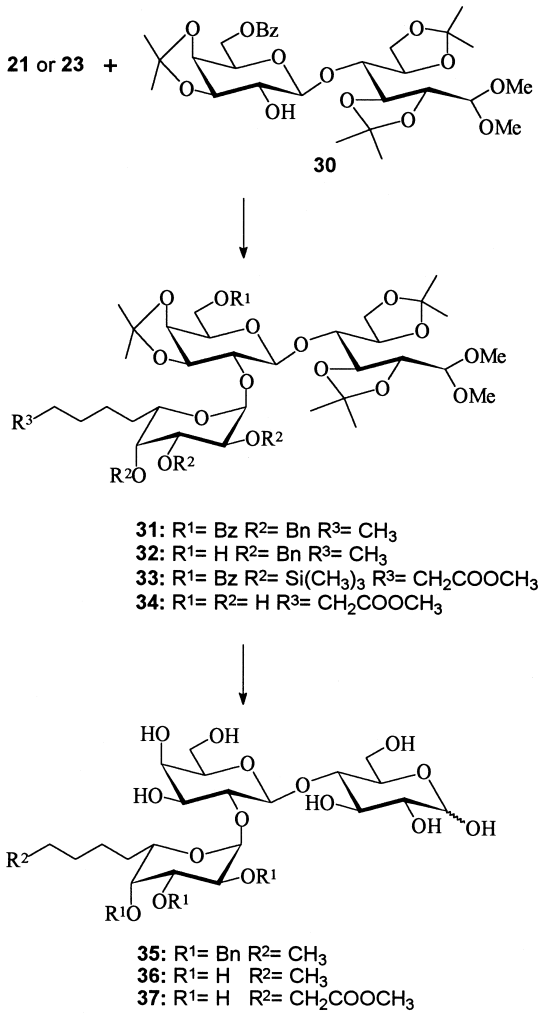


Scheme 5.

(methylthio)sulfonium triflate (DMTST)[15,16] to give the desired fully protected trisaccharide **26** in comparable yields of 33% and 38%, respectively. The vicinal coupling constant value $J_{1,2} = 3.5$ Hz in the ^{1}H NMR spectrum and the C-1 signal at δ 96.93 in the ^{13}C NMR spectrum of the fucosyl moiety proved the 1,2-*cis*-glycosidic linkage. An exchange of the acceptor **24** by the partially benzylated benzyl 3′,4′-*O*-isopropylidene-β-lactoside **25**[17] and its glycosylation with **21** in a ratio of one to one, promoted by DMTST, gave the trisaccharide **27** in a comparable 30% yield or an 84% yield based on the recovered acceptor **25**. The trisaccharides **26** and **27** were then taken through the requisite deprotection steps. The isopropylidene group of **27** was removed by 80% acetic acid (60%). Catalytic hydrogenolysis of **26** or **28** in ethanol/acetic acid in the presence of palladium-on-charcoal afforded the free trisaccharide **29** as an amorphous colorless solid in 90% yield.

For the synthesis of labeled 2′-fucosyllactoses (Scheme 6) an approach originally described by K. L. Matta and coworkers was used.[18] After selective benzoylation[18] of the 2,3;5,6;3′,4′-tri-*O*-isopropylidenelactose dimethyl acetal,[19,20] glycosylation of resulting acceptor **30** with glycosyl donor **21**, promoted by IDCP,[21] provided the trisaccharide **31** in 46% yield after purification by MPLC. The stereochemistry of the glycosidic linkage between the fucosyl residue and the lactose was assigned based on the small coupling constant $J_{1,2} = 3.2$ Hz in the ^{1}H NMR spectrum and the signal for C-1 occurring at δ 94.83 in the ^{13}C NMR spectrum.

In the ^{13}C NMR spectrum of a mixture of **31** and a slightly faster moving (TLC) compound, probably the β-fucosyl isomer, additional signals in the anomeric region were observed [δ 102.56 (Fuc: C-1), 103.05 (Gal: C-1) and 105.25 (Glc: C-1)].



Scheme 6.

After debenzoylation of **31** with methanolic sodium methoxide, the trisaccharide **32** (84%) was deacetalated in aq 60% acetic acid at 60 °C to afford the tri-*O*-benzyl trisaccharide **35** in 72% yield. Finally, catalytic hydrogenolysis of **35** in glacial acetic acid and chromatographic purification provided the free trisaccharide **36** in a yield of 87% as a colorless powder.

Analogously the freshly prepared glycosyl donor **23** was coupled with acceptor **30** in the presence of IDCP to afford the partially trimethylsilylated trisaccharide **33** in an excellent 78% yield (Scheme 6). Characteristic signals in the ^{1}H NMR spectrum appeared at δ 5.29 (d, 1H, $J_{1,2}$ = 3.7 Hz, Fuc: H-1) and in the ^{13}C NMR spectrum at δ 97.41 (Fuc: C-1), which confirm the assigned structure of **33**. Treatment of **33** with methanolic sodium methoxide led to a simultaneous cleavage of the benzoyl ester and the trimethylsilyl ether linkages in 81% yield. Finally,

the deisopropylidenation of resulting **34** afforded an analog (**37**) of 2′-fucosyllactose, where C-5 of the fucosyl moiety is derivatized with a five-atom spacer terminating in a methoxycarbonyl group. In further experiments, we will use the trisaccharide **37** for fluorescence marked fucosyllactose.

Recent results in a biological study[22] indicated that 2′-fucosyllactose labeled with an alkyl chain elongated fucose residue (**36**) was almost completely degraded, most likely in the intestinal tract, when administered orally to three weeks old suckling rats. No traces of this compound nor of the modified L-fucose were detected in the faeces and only small amounts of **36** could be characterized in the urine by high-pH anion-exchange chromatography with pulsed amperometric detection.[23] Surprisingly, a higher concentration of **36** in the rat milk does not lead to a higher content in the urine of suckling rats. Nevertheless, this animal experiment emphasized the supposition of an absorption pathway for human milk oligosaccharides in breast-fed infants.[24]

EXPERIMENTAL

General methods. Melting points were determined with a Boetius micro apparatus BHMK 05 (Rapido, Dresden) and are uncorrected. Optical rotations were measured in a 2 cm cell with an automatic polarimeter "GYROMAT" (Dr. Kernchen Co.). A Perkin-Elmer Model "Lambda 2" spectrometer was used for measurement of UV-VIS spectra. NMR spectra were recorded with Bruker AC-250 or ARX-300 spectrometers, at 250 MHz or 300 MHz for ^{1}H and 62.9 MHz or 75.5 MHz for ^{13}C, respectively. Chemical shifts are recorded relative to tetramethylsilane ($\delta = 0$) as an internal standard. First order chemical shifts and coupling constants were obtained from one-dimensional spectra, and assignment of proton resonances was based on COSY experiments. Thin-layer chromatography (TLC) was performed on precoated plates of silica gel (Merck, Silica Gel 60, F_{254}, 0.25 mm) with the following solvent systems (v/v): (A) 10:1, (B) 9:1, (C) 5:1, (D) 4:1, (E) 3:1, (F) 5:2, (G) 2:1, (H) 1:1, (I) 1:2 heptane-ethyl acetate, (J) 12:1, (K) 8:1, (L) 4:1 ethyl acetate-methanol, (M) 5:2:1 ethyl acetate-methanol-water, (N) 5:1, (O) 1:1, (P) 1:2 chloroform-methanol, (Q) 9:1 acetonitrile-water, and 2:1 2-propanol-water. The spots were made visible by spraying with a methanolic 10% H_2SO_4 solution and charring them for 3–5 min with a heat gun. Detection of benzyl derivatives was effected by UV fluorescence. Preparative flash chromatography, MPLC and HPLC was performed by elution from columns of slurry-packed Silica Gel 60 (Merck, 40–63 μm) or Nucleosil 100–7 (Knauer, 7.0 μm), respectively, using the above solvent systems. All solvents and reagents were purified and dried according to standard procedures.[25] After classical work up of the reaction mixtures, the organic layers were dried over $MgSO_4$, and then concentrated under reduced pressure (rotary evaporator).

1-*O*-*tert*-Butyldimethylsilyl-2,3;4,5-di-*O*-isopropylidene-10-methoxycarbonyl-6,7,8,9,10-pentadeoxy-L-*galacto*-dec-6-enitol (3). To a stirred suspen-

sion of (4-carboxybutyl)triphenylphosphonium bromide (50g, 113 mmol) in dry tetrahydrofuran (100 mL) was added dropwise a 1 M solution of lithium bis(trimethylsilyl)amide in dry tetrahydrofuran (200 mL, FLUKA) under argon at room temperature. After stirring for 15 min, a solution of **1** (42.2 g, 110 mmol)[2] in dry tetrahydrofuran (60 mL) was slowly added and the yellow colored reaction mixture was stirred for a further 30 min. The colorless mixture was then diluted with water (300 mL) and concentrated under vacuum to a volume of 250 mL. To the solution was added heptane (100 mL) and the precipitated salts were filtered off. The phases were separated, the aqueous layer was washed with heptane (2 × 50 mL), and the organic layer and washings were combined. For esterification of the carboxylic group, to the solution of **2** was added heptane (200 mL), chloroform (100 mL), methyl iodide (20 mL, 320 mmol), tetrabutylammonium bromide (16 g, 50 mmol), and sodium hydrogen carbonate (8.3 g, 100 mmol). The suspension was then vigorously stirred for 48 h at ambient temperature (TLC, solvent C, R_f 0.40). The phases were separated and the aqueous phase was extracted with chloroform (2 × 50 mL). The combined organic layers were washed with water (3 × 100 mL), dried, and concentrated. The crude ester **3** (30 g, 58%) was used for the next step without further purification. An analytical sample of **3** was obtained by HPLC (eluent solvent C) as a colorless syrup: $[\alpha]_D^{27}$ +6.0° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 0.06 [s, 6H, $(CH_3)_2Si$], 0.88 [s, 9H, $(CH_3)_3C$], 1.26, 1.28, 1.30 [3s, 12H, 2 × $(CH_3)_2C$], 1.64 (m, 2H, H-9, H-9′), 2.13 (m, 2H, H-8, H-8′), 2.24 (t, 2H, H-10, H-10′), 3.56 (s, 3H, CO_2CH_3), 3.64 (dd, 1H, $J_{1,1'}$ = 10.9 Hz, H-1), 3.68 (m, 1H, H-4), 3.74 (dd, 1H, H-1′), 3.83 (m, 1H, H-2), 3.91 (m, 1H, H-5), 4.67 (m, 1H, H-3), 5.37 (m, 1H, H-7), 5.52 (m, 1H, H-6); ^{13}C NMR ($CDCl_3$) δ −5.48, −5.56 [$(CH_3)_2Si$], 18.20 [$(CH_3)_3C$], 24.85 (C-9), 26.77 [$(CH_3)_3C$], 26.95, 26.98, 27.01, 27.08 [2 × $(CH_3)_2C$], 27.07 (C-8), 33.16 (C-10), 51.14 (CO_2CH_3), 63.35 (C-1), 74.75 (C-3), 77.30 (C-5), 79.71 (C-2), 81.64 (C-4) 109.28, 109.33 [2 × $(CH_3)_2C$], 128.06(C-7), 131.96 (C-6); 173.53 (CO_2CH_3).

Anal. Calcd for $C_{24}H_{44}O_7Si$ (472.69): C, 60.98; H, 9.38. Found: C, 61.06; H, 9.38.

1-*O*-*tert*-Butyldimethylsilyl-2,3;4,5-di-*O*-isopropylidene-10-methoxycarbonyl-6,7,8,9,10-pentadeoxy-L-*galacto*-decitol (4). The crude alkene **3** (25.1 g, 53 mmol) was dissolved in heptane (100 mL) and hydrogenated with H_2 in the presence of 10% Pd/C (1.2 g) at room temperature under atmospheric pressure. After shaking overnight [TLC solvent C; during charring, the spot of the unsaturated compound **3** (R_f 0.40) became black at once, whereas the spot of the saturated compound **4** (R_f 0.50) changed more slowly from red-brown to black], the catalyst was removed by centrifugation, and the solution was concentrated. The crude product **4** (23.7 g, 94%) was sufficiently pure for the next step. Processing by HPLC (eluent solvent G) gave an analytical sample of **4** as a colorless syrup: $[\alpha]_D^{24}$ −4.1° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 0.00 [s, 6H, $(CH_3)_2Si$], 0.82 [s, 9H, $(CH_3)_3C$], 1.30, 1.33, 1.34, 1.35 [4s, 12H, 2 × $(CH_3)_2C$], 1.33–1.72 (6m, 8H, H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 2.27 (t, 2H, H-10, H-10′), 3.57 (t, 1H,

H-4), 3.62 (s, 3H, CO_2CH_3), 3.68 (dd, 1H, $J_{1,1'}$ = 11.3 Hz, H-1), 3.82 (m, 1H, H-3), 3.85 (dd, 1H, H-1′), 3.90 (m, 1H, H-2), 3.98 (m, 1H, H-5); ^{13}C NMR ($CDCl_3$) δ −5.30, −5.45 [$(CH_3)_2Si$], 18.36 [$(CH_3)_3C$], 24.81 (C-9), 25.61 (C-7), 25.91 [$(CH_3)_3C$], 27.00, 27.06, 27.13, 27.38 [2 × $(CH_3)_2C$], 29.11 (C-8), 33.38 (C-6), 33.95 (C-10), 51.29 ($COCH_3$), 63.35 (C-1), 74.48 (C-3), 80.48 (C-2), 81.31 (C-5), 81.89 (C-4) 108.77, 109.48 [2 × $(CH_3)_2C$], 173.03 (CO_2CH_3).

Anal. Calcd for $C_{24}H_{46}O_7Si$ (474.71): C, 60.72; H, 9.77. Found: C, 60.93; H, 9.64.

2,3;4,5-Di-*O*-isopropylidene-10-methoxycarbonyl-6,7,8,9,10-pentadeoxy-L-*galacto*-decitol (5). To a vigorously stirred solution of the *tert*-butyldimethylsilyl derivative **4** (23.7 g, 50 mmol) in acetone (100 mL) was added tetra-*n*-butylammonium fluoride trihydrate (24.0 g, 76 mmol). After 4 h at ambient temperature (TLC, solvent H, R_f 0.45), the solution was diluted with heptane (200 mL), concentrated to a volume of about 100 mL to remove acetone, and then diluted with chloroform (50 mL). The organic layer was washed successively with water (50 mL), aq sat $NaHCO_3$ (2 × 50 mL), water (2 × 50 mL), dried, and concentrated. The residue was purified by column chromatography (eluent solvent G) to provide **5** (17.7 g, 98%) as a colorless syrup: $[\alpha]_D^{23}$ −13.5° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.17, 1.19 1.21, 1.23 [4s, 12H, 2 × $(CH_3)_2C$], 1.25–1.58 (6m, 8H, H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 2.14 (t, 2H, H-10, H-10′), 2.82 (dd, 1H, OH), 3.40 (dd, 1H, H-4), 3.48 (s, 3H, CO_2CH_3), 3.53 (m, 1H, H-1), 3.55 (m, 1H, H-3), 3.64 (m, 1H, H-1′), 3.77 (m, 1H, H-5), 3.87 (m, 1H, H-2); ^{13}C NMR ($CDCl_3$) δ 24.43 (C-9), 25.20 (C-7), 26.54 (two signals are isochronic), 26.81, 27.00 [2 × $(CH_3)_2C$], 28.67 (C-8) 32.76 (C-6), 33..53 (C-10), 51.99 (CO_2CH_3), 62.33 (C-1), 78.49 (C-3), 80.53 (C-5), 80.92 (C-2), 81.21 (C-4), 108.70, 109.43 [2 x$(CH_3)_2C$], 173.69 (CO_2CH_3).

Anal. Calcd for $C_{18}H_{32}O_7$ (360.45): C, 59.98; H, 8.95. Found: C, 60.07; H, 9.01.

2,3;4,5-Di-*O*-isopropylidene-10-methoxycarbonyl-6,7,8,9,10-pentadeoxy-L-*galacto*-decose (6). Dimethyl sulfoxide (9.5 mL, 134 mmol) was added dropwise to a stirred solution of oxalyl chloride (4.8 mL, 56 mmol) in dry dichloromethane (40 mL) at −78°C, under an argon atmosphere. After the mixture had been stirred for 30 min, a solution of the sugar alcohol **5** (18.0 g, 50 mmol) in dry dichlormethane (50 mL) was added dropwise at −78°C. Stirring was continued for another 30 min before triethylamine (17 mL, 122 mmol) was added dropwise. The mixture was warmed to room temperature and the solution was then diluted by addition of heptane (280 mL). The organic solution was washed with ice-water (2 × 80 mL), cold aq 1 M hydrochloric acid (2 × 80 mL), ice-water (80 mL), cold aq sat $NaHCO_3$ (2 × 80 mL), ice-water (2 × 80 mL), dried, and concentrated. An analytical sample was obtained by HPLC (eluent solvent G), whereas the main part of **6** (16.0 g, 89%, TLC, solvent H, R_f 0.50) was used without further purification, colorless syrup: $[\alpha]_D^{21}$ −36.3° (*c* 2.0, chloroform); ^{1}H NMR ($CDCl_3$)

δ 1.20, 1.22 1.33, 1.40 [4s, 12H, 2 × $(CH_3)_2C$], 1.32–1.60 (6m, 8H, H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 2.25 (t, 2H, H-10, H-10′), 3.58 (s, 3H, CO_2CH_3), 3.65 (t, 1H, H-4), 3.90 (m, 1H, H-5), 4.03 (dd, 1H, H-3), 4.40 (dd, 1H, H-2), 9.69 (d, H-1); ^{13}C NMR ($CDCl_3$) δ 24.72 (C-9), 25.46 (C-7), 26.20, 27.00, 27.15, 28.96 [2 × $(CH_3)_2C$], 28.96 (C-8), 33.14 (C-6), 33.86 (C-10), 51.20 (CO_2CH_3), 77.79 (C-3), 79.80 (C-5), 80.81 (C-4), 83.14 (C-2), 109.13, 111.71 [2 × $(CH_3)_2C$], 173.89 (CO_2CH_3), 199.72 (C-1).

Anal. Calcd for $C_{18}H_{30}O_7$ (358.43): C, 60,32; H, 8,44. Found: C, 60.59, H, 8.46.

Deisopropylidenation and acetylation of compounds 6. Dowex 50 [H^+] (20 g) was added to a solution of **6** (17.9 g, 50 mmol) in acetonitrile (200 mL) and water (20 mL) and the mixture was stirred for 3 h at 70 °C. After filtration the filtrate was concentrated to a volume of 15 mL, aq 90% trifluoroacetic acid (40 mL) was then added, and the solution was kept for 30 min at ambient temperature. When the reaction was complete (TLC, solvent N), the solution was diluted with toluene (50 mL) and concentrated. Traces of trifluoroacetic acid were removed by repeated coevaporation with toluene (3 × 100 mL), and the residue was finally lyophilized to provide **7** and **8** (13.0 g). Without further characterization a solution of compounds **7** and **8** (the whole amount of the preceding step) in dry acetonitrile (30 mL) was added dropwise to a solution of acetic anhydride (90 mL) and aq 70% perchloric acid (0.9 mL) at 0°C. The solution was kept for 40 min at room temperature and then slowly poured under vigorous stirring into ice-water (2 L). After stirring for 2 h the aqueous layer was extracted with solvent heptane - ethyl acetate 2 : 1 (2 × 150 mL). The combined organic layers were washed with water (4 × 50 mL), dried and concentrated. The residue was purified by MPLC (eluent ethyl acetate gradient 25% → 100% in heptane). Analytical samples of **9** and **10** were obtained by HPLC using again ethyl acetate gradient 25% → 100% in heptane as eluent.

1,2,3,4-Tetra-*O*-acetyl-10-methoxycarbonyl-6,7,8,9,10-α-L-*galacto*-decopyranose (9α). (4.5 g, 20%, TLC, solvent G, R_f 0.42), colorless syrup: $[\alpha]_D^{27}$ −111.3° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.24–1.59 (6m, 8H, H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 1.96, 1.98, 2.11, 2.13 (4s, 12H, 4 × $OCOCH_3$), 2.24 (t, 2H, H-10, H-10′), 3.62 (s, 3H, CO_2CH_3), 3.99 (m, 1H, H-5); 5.26 (m, 1H, H-4), 5.27 (m, 1H, H-3), 5.34 (m, 1H, H-2), 6.30 (d, 1H, $J_{1,2}$ = 0.1 Hz, H-1); ^{13}C NMR ($CDCl_3$) δ 20.44, 20.54, 20.64, 20.78 (4 × $OCOCH_3$), 24.54 (C-9), 24.74 (C-7), 28.75 (C-8) 29.78 (C-6), 33.78 (C-10), 51.33 (CO_2CH_3), 68.13 (C-4), 69.25 (C-3), 70.92 (C-2, C-5, two signals are isochronic), 89.90 (C-1), 168.96, 169.31, 170.03, 170.31 (4 × $OCOCH_3$), 173.86 (CO_2CH_3).

Anal. Calcd for $C_{20}H_{30}O_{11}$ (446.45): C, 53.81; H, 6.77. Found: C, 53.69; H, 6.56.

1,2,3,4-Tetra-*O*-acetyl-10-methoxycarbonyl-6,7,8,9,10-β-L-*galacto*-decopyranose (9β). (2.2 g, 10%, TLC, solvent G, R_f 0.40), colorless crystals: mp

75 °C (from ethyl acetate - heptane); $[\alpha]_D^{22}$ −24.0° (*c* 1.5, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.28–1.60 (6m, 8H, H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 1.94, 1.99, 2.07, 2.13 (4s, 12H, 4 × $OCOCH_3$), 2.24 (t, 2H, H-10, H-10′), 3.61 (s, 3H, $COCH_3$), 3.68 (m, 1H, H-5), 5.01 (m, 1H, $J_{3,4}$ = 3.6 Hz, H-3), 5.26 (m, 1H, H-4), 5.27 (dd, 1H, $J_{2,3}$ =10.4 Hz, H-2), 5.60 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1); ^{13}C NMR ($CDCl_3$) δ 20.45, 20.54, 20.64, 20.73 (4 × $OCOCH_3$), 24.56 (C-9), 24.83 (C-7), 28.64 (C-8), 29.84 (C-6), 33.81 (C-10), 51.34 (CO_2CH_3), 68.16(C-2), 69.04 (C-4), 71.33 (C-3), 74.16 (C-5), 92.34 (C-1), 168.99, 169.32, 169.87, 170.31 (4 × $OCOCH_3$), 173.89 (CO_2CH_3).

Anal. Calcd for $C_{20}H_{30}O_{11}$ (446.45): C, 53.81; H, 6.77. Found: C, 53.82; H, 6.49.

1,2,3,4-Tetra-*O*-acetyl-10-carboxy-6,7,8,9,10-α-L-*galacto*-decopyranose (10α). (6.5 g, 30%, TLC, solvent G, R_f 0.17), colorless syrup: $[\alpha]_D^{25}$ −106.7° (*c* 0.8, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.31–1.56 (6m, 8H, H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 1.93, 1.94, 2.04, 2.10 (4s, 12H, 4 × $OCOCH_3$), 2.25 (t, 2H, H-10, H-10′), 3.89 (m, 1H, H-5); 5.23 (m, 1H, H-3), 5.25 (m, 1H, H-4), 5.31 (m, 1H, H-2), 6.27 (d, 1H, $J_{1,2}$ =1.8 Hz, H-1); ^{13}C NMR ($CDCl_3$) δ 20.44, 20.52, 20.62, 20.72 (4 × $OCOCH_3$), 24.30 (C-9), 24.71 (C-7), 28.66 (C-8) 29.77 (C-6), 33.68 (C-10), 66.88 (C-3), 67.94 (C-4), 69.61 (C-2), 70.92 (C-5), 89,91 (C-1), 169.05, 169.95, 170.12, 170.43 (4 × $OCOCH_3$), 178.84 (CO_2H).

Anal. Calcd for $C_{19}H_{28}O_{11}$ (432.42): C, 52.77; H, 6.53. Found: C, 52.63; H, 6.31.

1,2,3,4-Tetra-*O*-acetyl-10-carboxy-6,7,8,9,10-β-L-*galacto*-decopyranose (10β). (3.3 g, 15%, TLC, solvent G, R_f 0.15), colorless crystals: mp 136 °C (from ethyl acetate - heptane); $[\alpha]_D^{22}$ −20.4° (*c* 1.8, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.27–1.55 (6m, 8H, H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 1.92, 1.96, 2.04, 2.10 (4s, 12H, 4 × $OCOCH_3$), 2.25 (t, 2H, H-10, H-10′), 3.67 (m, 1H, H-5), 5.01 (dd, 1H, $J_{3,4}$ = 3.4 Hz, H-3), 5.23 (dd, 1H, $J_{2,3}$ = 10.4 Hz, H-2), 5.24 (m, 1H, H-4), 5.59 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1); ^{13}C NMR ($CDCl_3$) δ 20.43, 20.54 (two signals are isochronic), 20.71 (4 × $OCOCH_3$), 24.28 (C-9), 24.80 (C-7), 28.53 (C-8) 29.79 (C-6), 33.68 (C-10), 68.17 (C-2), 69.08 (C-4), 71.31 (C-3), 74.12 (C-5), 92.31 (C-1), 169.06, 169.41, 169.94, 170.40 (4 × $OCOCH_3$), 178.96 (CO_2H).

Anal. Calcd for $C_{19}H_{28}O_{11}$ (432.42): C, 52.77; H, 6.53. Found: C, 52.84; H, 6.24.

1,2,3,4-Tetra-*O*-acetyl-10-(4-benzamido-2,5-diethyloxyphenylaminocarbonyl)-6,7,8,9,10-pentadeoxy-α,β-L-*galacto*-decopyranose (11α,β). Molecular sieves (4 Å, 10 g) were added to a stirred solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI, 3.3 g, 17 mmol) and 1-hydroxybenzotriazole (2.7 g, 17 mmol) in dry dichloromethane (48 mL) and dry *N,N*-dimethylformamide (12 mL). After 30 min a solution of **10α,β** (3.5g 8 mmol) and 4-amino-2,5-diethoxybenzanilide (6.0 g, 20 mmol) in dry dichloromethane (32 mL) and dry *N,N*-dimethylformamide (8 mL) was added. After stirring overnight at room tempera-

ture (TLC, solvent I, R_f 0.40), the mixture was diluted with heptane (400 mL) and chloroform (200 mL) and the organic layer washed successively with ice-water (2 × 200 mL), cold aq 1 M hydrochloric acid (2 × 200 mL), ice-water (200 mL), cold aq sat $NaHCO_3$ (2 × 200 mL), ice-water (2 × 200 mL), dried, and concentrated. The crude product was purified by column chromatography (eluent ethyl acetate gradient 50% → 75% in heptane) to yield **11α,β** (81%). An analytical sample was obtained by HPLC using ethyl acetate gradient 50% → 75% in heptane as eluent.

1,2,3,4-Tetra-*O*-acetyl-10-(4-benzamido-2,5-diethyloxyphenylaminocarbonyl)-6,7,8,9,10-pentadeoxy-α-L-*galacto*-decopyranose (11α). Colorless crystals: mp 110°C (from ethyl acetate - heptane),$[\alpha]_D^{19}$ −84.0° (*c* 2.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.40, 1.68 (2m, 8H, H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 1.43 (t, 6H, 2 × C*H*$_3$CH$_2$O), 1.97, 1.99, 2.10, 2.13 (4s, 12H, 4 × OCOCH$_3$), 2.35 (t, 2H, H-10, H-10′), 4.02 (m, 1H, H-5), 4.14 (dq, 4H, CH$_3$C*H*$_2$O), 5.28 (m, 1H, H-3), 5.31 (m, 1H, H-2), 5.37 (m, 1H, H-4), 6.33 (d, 1H, $J_{1,2}$ =1.7 Hz, H-1), 7.48, 7.52, 7.86, 8.25, [3m, 1s, 7H, C_6H_5CO, $C_6H_2(OC_2H_5)_2$], 7.76, 8.58 (2s, 2H, 2 × NH); ^{13}C NMR ($CDCl_3$) δ 14.92, 14.95 (2 × OCH$_2$*C*H$_3$), 20.51, 20.60, 20.85 (4 × OCO*C*H$_3$, two signals are isochronic), 24.94 (C-9), 25.12 (C-7), 28.80 (C-8), 29.88 (C-6), 37.67 (C-10), 64.99, 65.05 (2 × CH$_3$*C*H$_2$O), 66.72 (C-3), 67.98 (C-4), 69.62 (C-2), 71.05 (C-5), 89.96 (C-1), 104.26, 104.35, 123.35, 123.62, 126.85, 128.81, 131.68, 135.19, 140.67, 141.15 [*C*$_6$H$_5$CO, *C*$_6$H$_2$(OC$_2$H$_5$)$_2$, 4 signals are isochronic], 164.81 (C$_6$H$_5$*C*O), 169.02 (*C*ONH), 169.87, 170.10, 170.40, 170.77 (4 × O*C*OCH$_3$).

Anal. Calcd for $C_{36}H_{46}N_2O_{13}$ (714.77): C, 60.49; H, 6.49; N, 3.92. Found: C, 60.49; H, 6.50; N, 3.84.

1,2,3,4-Tetra-*O*-acetyl-10-(4-benzamido-2,5-diethyloxyphenylaminocarbonyl)-6,7,8,9,10-pentadeoxy-β-L-*galacto*-decopyranose (11β). Colorless crystals: mp 133°C (from ethyl acetate - heptane),$[\alpha]_D^{19}$ −20.0° (*c* 2.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.39, 1.69 (2m, 8H, H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 1.39 (t, 6H, 2 × C*H*$_3$CH$_2$O), 1.96, 2.00, 2.08, 2.14 (4s, 12H, 4 × OCOCH$_3$), 2.35 (t, 2H, H-10, H-10′), 3.70 (m, 1H, H-5), 4.13 (dq, 4H, CH$_3$C*H*$_2$O), 5.03 (dd, 1H, $J_{3,4}$ = 3.4 Hz, H-3), 5.27 (m, 1H, H-4), 5.29 (dd, 1H, $J_{2,3}$ = 10.4 Hz, H-2), 5.63 (d, 1H, $J_{1,2}$ =8.2 Hz, H-1), 7.48, 7.86, 8.20, 8.30, [2m, 2s, 7H, C_6H_5CO, $C_6H_2(OC_2H_5)_2$], 7.75, 8.58 (2s, 2H, 2 × NH); ^{13}C NMR ($CDCl_3$) δ 14.96 (2 × *C*H$_3$CH$_2$O, two signals are isochronic), 20.77, 20.87, 20.94 (4 × OCO*C*H$_3$, two signals are isochronic), 24.30 (C-9), 24.71 (C-7), 28.79 (C-8), 29.90 (C-6), 37.68 (C-10), 64.90, 64.97 (2 × CH$_3$*C*H$_2$O), 68.05 (C-4), 68.99 (C-2), 71.16 (C-5), 71.34 (C-3), 92.32 (C-1), 104.07, 104.19, 123.21, 123.54, 126.86, 128.84, 131.73, 135.12, 140.07, 140.59 [*C*$_6$H$_5$CO, *C*$_6$H$_2$(OC$_2$H$_5$)$_2$, 4 signals are isochronic], 164.82 (C$_6$H$_5$*C*O), 169.14 (*C*ONH), 169.45, 170.03, 170.44, 170.88 (4 × O*C*OCH$_3$).

Anal. Calcd for $C_{36}H_{46}N_2O_{13}$ (714.77): C, 60.49; H, 6.49; N, 3.92. Found: C, 60.74; H, 6.52; N, 3.97.

2,3,4-Tri-*O*-acetyl-10-(4-benzamido-2,5-diethyloxyphenylaminocarbonyl)-6, 7, 8,9,10-pentadeoxy-α-L-*galacto*-decopyranosyl bromide (12). A solution of water (0.33 mL, 18.2 mmol) in glacial acetic acid (1.6 mL) was added dropwise to a stirred solution of **11** (4.5 g, 6.2 mmol) in dry dichloromethane (10 mL), acetic anhydride (0.6 mL, 6.2 mmol), glacial acetic acid (1.6 mL) and acetyl bromide (1.4 mL, 18.2 mmol) at 5 °C. After stirring for two hours at ambient temperature (TLC, solvent I, R_f 0.50), heptane (60 mL) and chloroform (30 mL) were added, and the organic layer was successively washed with ice-water (40 mL), cold sat aq $NaHCO_3$ (2 × 40 mL), ice-water (2 × 40 mL), dried, and concentrated. The bromide **20** (4.3 g, 93%; syrup) was immediately used for the next step without further purification: ^{1}H NMR ($CDCl_3$), δ 1.41, 1.69 (2m, 8H, H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 1.43 (t, 6H, 2 × C*H*$_3$CH$_2$O), 1.99, 2.09, 2.14 (3s, 9H, 3 × OCOCH$_3$), 2.37 (t, 2H, H-10, H-10′), 4.15 (dq, 4H, CH$_3$C*H*$_2$O), 4.16 (m, 1H, H-5), 5.01 (m, 1H, H-2), 5.38 (dd, 1H, $J_{3,4}$ = 3.4 Hz, H-3), 5.39 (m, 1H, H-4), 6.69 (d, 1H, $J_{1,2}$ = 4.0 Hz, H-1), 7.50, 7.86, 8.20, 8.30, [2m, 2s, 7H, C_6H_5CO, $C_6H_2(OC_2H_5)_2$], 7.76, 8.59 (2s, 2H, 2 × NH); ^{13}C NMR ($CDCl_3$) δ 14.94 (2 × *C*H$_3$CH$_2$O, two signals are isochronic), 20.53, 20.58, 20.70 (3 × OCO*C*H$_3$), 24.74, 25.11, 28.63, 29.49 (C-6, C-7, C-8, C-9), 37.69 (C-10), 65.07 (2 × CH$_3$*C*H$_2$O, two signals are isochronic), 68.01 (C-2), 68.54 (C-3), 69.19 (C-4), 73.42 (C-5), 89.40 (C-1), 104.27, 104.38, 123.50, 124.00, 126.85, 128.80, 131.66, 135.00, 140.50, 141.15 [*C*$_6$H$_5$CO, *C*$_6$H$_2$(OC$_2$H$_5$)$_2$, 4 signals are isochronic], 164.90 (C$_6$H$_5$*C*O), 169.90 (*C*ONH), 170.00, 170.50, 171.30 (3 × O*C*OCH$_3$).

Bis(triethylammonium) 10-(4-benzamido-2,5-diethyloxyphenylaminocarbonyl)-6,7,8,9, 10-pentadeoxy-β-L-*galacto*-decopyranos-1-yl phosphate (14). A solution of glycosyl bromide **12** (4.35 g, 5.9 mmol) in dry acetonitrile (30 mL) was added to a stirred mixture of tetrabutylammonium phosphate (4.0 g, 11.8 mmol) and ground molecular sieves (4Å) in dry acetonitrile (60 mL) at 0 °C under an argon atmosphere in the dark. After 30 min at 0°C stirring was continued for a further 1.5 h at ambient temperature (TLC, solvent Q, R_f 0.40). The molecular sieves were then filtered off and the filtrate was concentrated. The purification of the crude material by column chromatography (3.0 × 40 cm; eluent linear gradient ethyl acetate-methanol-triethylamine 100:0:1→70:30:1 v,v,v) provided **13** (2.3 g, 43%). Freshly distilled cyclohexylamine (30 mL) was added to a solution of the triacetate **13** (2.3 g, 2.4 mmol) in dry methanol (30 mL), without the triacetate being characterized further. The reaction mixture was refluxed for two hours under argon, cooled and concentrated. The residue was dissolved in water (600 mL), the aqueous layer washed with heptane-chloroform (2:1, 5 × 50 mL), concentrated to a volume of about 150 mL and lyophilized. The galactodecopyranosyl phosphate was converted to the triethylammonium salt by loading onto Dowex 50-X8 (3 × 45 cm; 200–400 mesh, Et_3NH^+) ion-exchange resin in water and eluting with water (2 mL/min). Fractions containing the product were pooled and lyophilized to provide **14** (1.2 g, 60%, based on **13**), colorless powder: $[\alpha]_D^{27}$ −17.6° (*c* 0.6, methanol); ^{1}H NMR (CD_3OD) δ 1.30 [m, 18H, N(CH$_2$C*H*$_3$)$_3$], 1.43 [m, 6H, 2 × C*H*$_3$CH$_2$O], 1.47, 1.72 (2m, 8H, H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′),

2.45 (t, 2H, H-10, H-10′), 3.19 [m, 12H, 2 × N(CH_2CH$_3$)$_3$], 3.45 (m, 1H, H-5), 3.50 (m, 1H, H-3), 3.53 (m, 1H, H-2), 3.67 (d, 1H, $J_{3,4}$ = 3.0 Hz, $J_{4,5}$ ≈0.0 Hz, H-4), 4.09 (m, 4H, CH$_3$CH_2O), 4.85 (t, 1H, $^3J_{1,P}$ = $J_{1,2}$ = 7.7 Hz, H-1), 7.52, 7.58, 7.78, 7.86, 7.90 [3m, 2s, 7H, C$_6$H$_5$CO, C$_6$$H_2$(OC$_2H_5$)$_2$]; ^{13}C NMR (CD$_3$OD) δ 9.19 [N(CH$_2$$CH_3$)$_3$], 15.23 (2 × CH$_3CH_2$O, two signals are isochronic), 26.58, 26.85, 30.30, 31.59 (C-6, C-7, C-8, C-9), 37.83 (C-10), 47.11 [N(CH$_2$CH$_3$)$_3$], 66.21 (2 × CH$_3$$CH_2$O, two signals are isochronic), 71.60 (C-4), 74.30 ($J_{2,P}$ = 3.7 Hz, C-2), 75.44 (C-3), 76.50 (C-5), 99.84 ($J_{1,P}$ = 2.1 Hz, C-1), 108.39, 108.49, 124.84, 125.40, 128.20, 129.88, 136.05, 138.95, 145.15, 145.42 [$C$$_6H_5$CO, $C$$_6H_2$(OC$_2H_5$)$_2$, 4 signals are isochronic], 171.00 (C$_6$H$_5$$C$O), 177.44 ($C$ONH); ^{31}P NMR (CD$_3$OD) δ 3.53.

For this ionic compound no microanalysis was performed, because the concentration of the counterions was not exactly defined.

Bis(ammonium) 10-(4-benzamido-2,5-diethyloxyphenylaminocarbonyl)-6,7,8,9,10-pentadeoxy-β-L-*galacto*-decopyranos-1-yl guanosine 5-diphosphate (15). After stirring a suspension of galactodecopyranosyl phosphate **14** (829 mg, 1.0 mmol) and molecular sieves (4 Å,1.0 g) in dry pyridine (20 mL) under an argon atmosphere for 30 min, guanosine 5′-monophosphomorpholidate 4-morpholine-*N,N*-dicyclohexylcarboxamidine salt was added in three portions (200 mg, 150 mg and 120 mg, total 0.65 mmol) combined in each case with the addition of molecular sieves (500 mg) at room temperature in an interval of 20 h. After the last addition the reaction mixture was stirred for a further 20 h (TLC, solvent R, R_f 0.20–0.50), filtered, coconcentrated with water to remove pyridine, concentrated to a volume of 120 mL and lyophilized. A part of the crude product **15** (200 mg of a total of 1.8 g) was passed through a column of Biogel P-2 (3.5 × 90 cm; Bio Rad, 45–90 μm; 0.5 mL/min; 6 mL fractions) using aq 0.25 M NH_4HCO_3 as the eluent. The carbohydrate fractions were pooled and lyophilized. The treatment of the whole amount of the crude diphosphate as described above provided analytically pure **15** (183 mg, 28% yield based on guanosine 5′-monophosphomorpholidate 4-morpholine-*N,N*-dicyclohexylcarboxamidine salt) as a colorless powder: $[\alpha]_D^{23}$ −19.8° (*c* 0.33, water); UV λ 310 nm (ε 6400 L mol^{-1} cm^{-1}, water); ^{1}H NMR (D$_2$O) δ 1.44 [m, 6H, 2 × CH_3CH$_2$O], 1.45, 1.70 (2m, 8H, H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 2.42 (t, 2H, H-10, H-10′), 3.62 (m, 1H, H-5), 3.68 (t, 1H, $J_{2,3}$ = 7.6 Hz, H-2) 3.72 (dd, 1H, $J_{3,4}$ = 3.1 Hz, H-3), 3.86 (m, 1H, H-4), 4.02 (m, 4H, CH$_3$CH_2O), 4.26 (m, 2H, Rib: H-5), 4.36 (m, Rib: H-4), 4.54 (dd, 1H, $J_{3,4}$ = 3.5 Hz, Rib: H-3), 4.74 (m, 1H, Rib: H-2), 4,91 (t, 1H, $^3J_{1,P}$ = $J_{1,2}$ = 7.6 Hz, H-1), 5.88 (d, 1H, $J_{1,2}$ = 6.4 Hz, Rib: H-1), 7.40, 7.58, 7.64, 7.70, 7.86 [3m, 2s, 7H, C$_6$H$_5$CO, C$_6$$H_2$(OC$_2H_5$)$_2$], 8.08 (s, 1H, G: H-8); ^{13}C NMR (D$_2$O) δ 15.21, 15.24 (2 × CH$_3$CH$_2$O), 25.68, 26.19, 29.28, 30.56 (C-6, C-7, C-8, C-9), 37.37 (C-10), 66.35 (Rib: C-5), 66.62 (2 × CH$_3$$CH_2$O, two signals are isochronic), 70.87 (C-4), 71.48 (Rib: C-3), 72.56 (J = 7.6 Hz, C-2), 73.78 (C-3), 75.04 (Rib: C-2), 76.36 (C-5), 84.79 (d, J = 9.3 Hz, Rib: C-4), 88,08 (Rib: C-1), 99.67 (C-1), 108.80, 109.39, 124.31, 124.45, 128.00, 129.92, 133.51, 144.28, 144.48 [$C$$_6H_5$CO, $C$$_6H_2$(OC$_2H_5$)$_2$, 6 signals are isochronic], 134.30, 138.20, 152.50, 154.69, 159,63

(G: C-2, C-4, C-5, C-6, C-8), 168.30 (*C*ONH), 176.22 (C_6H_5CO); ^{31}P NMR (D_2O) δ −12.11 (d, J = 19.5 Hz, Gal-P), −10.21 (d, J = 19.5 Hz, Rib-P).

Anal. Calcd for $C_{38}H_{57}N_9O_{19}P_2$ (1005.87): C, 45.38; H, 5.71, N, 12.53; P, 6.16. Found: C, 45.11; H, 5.97; N, 13.00; P, 6.05.

Transformation of 9 and 16 into the acetylated methyl thioglycosides 17 and 18. To a solution of **9** (5.8 g, 15 mmol) or 1,2,3,4-tetra-*O*-acetyl-6,7,8,9,10-pentadeoxy-L-*galacto*-decopyranose (**16**, 5.8 g, 15 mmol) in dry dichloromethane (25 mL) were added *S*-trimethylsilylmethylmercaptan (5 mL, 34.4 mmol) and trimethylsilyltriflate (2.5 mL, 13.8 mmol). After stirring for 24 h under argon atmosphere followed by TLC, the reaction mixture was treated with *N*-ethyldiisopropylamine (3 mL), diluted with chloroform (35 mL) and heptane (120 mL), and the organic layer washed with water (3 × 90 mL), dried and concentrated. The crude products were purified by MPLC (eluent ethyl acetate gradient 10% → 20% in heptane).

Methyl 2,3,4-tri-*O*-acetyl-6,7,8,9,10-pentadeoxy-1-thio-β-L-*galacto*-decopyranoside (17). (4.7 g, 83%, TLC, solvent H, R_f 0.46), colorless syrup:$[\alpha]_D^{22}$ −15.2° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H, H-10, H-10′, H-10″), 1.25, 1.40, 1.60 (3m, 8H, H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 1.96, 2.04, 2.15, 2.18 (4s, 12H, 3 × $OCOCH_3$, SCH_3), 3.59 (m, 1H, H-5), 4.35 (d, 1H, $J_{1,2}$ = 9.8 Hz, H-1), 5.02 (dd, 1H, $J_{3,4}$ = 3.3 Hz, H-3), 5.20 (t, 1H, H-2), 5.30 (dd, 1H, $J_{4,5}$ = 2.2 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 11.74 (SCH_3), 13.88 (C-10), 20.58, 20.65, 20.77 (3 × $OCOCH_3$), 22.36, 25.01, 30.43, 31.47 (C-6, C-7, C-8, C-9), 67.20 (C-2), 69.53 (C-4), 72.44 (C-3), 77.33 (C-5), 83.51 (C-1), 169.67, 170.08, 170.48 (3 × $OCOCH_3$).

Anal. Calcd $C_{17}H_{28}O_7S$ (376.46): C, 54.23; H, 7.49; S, 8.51. Found: C, 54.34; H, 7.59; S, 8.65.

Methyl 2,3,4-tri-*O*-acetyl-10-methoxycarbonyl-6,7,8,9,10-pentadeoxy-1-thio-β-L-*galacto*-decopyranoside (18). (5.7 g, 87%, TLC, solvent H, R_f 0.53), colorless crystals: mp 52–55 °C; $[\alpha]_D^{22}$ −14.5° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.26–1.71 (3m, 8H, H-6, H-6′, H-7,H-7′, H-8, H-8′, H-9, H-9′), 1.95, 2.04, 2.13, 2.16 (4s, 12H, 3 × $OCOCH_3$, SCH_3), 2.26 (t, 2H, H-10, H-10′), 3.58 (m, 1H, H-5), 3.63 (s, 3H, CO_2CH_3), 4.32 (d, 1H, $J_{1,2}$ = 9.7 Hz, H-1), 5.01 (dd, 1H, $J_{3,4}$ = 3.9 Hz, H-3), 5.19 (t, 1H, $J_{2,3}$ = 9.9 Hz, H-2), 5.29 (dd, 1H, $J_{4,5}$ = 0.7 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 11.67 (SCH_3), 20.52, 20.59, 20.71 (3 × $OCOCH_3$), 24.57, 25.01, 28.72, 30.27, 33.79 (C-6, C-7, C-8, C-9, C-10), 51.35 (CO_2CH_3), 67.09 (C-2), 69.49 (C-4), 72.34 (C-3), 77.14 (C-5), 83.47 (C-1), 169.64, 170.03, 170.45 (3 × $OCOCH_3$), 173.93 (CO_2CH_3).

Anal. Calcd for $C_{19}H_{30}O_9S$ (434.50): C, 52.52; H, 6.96; S, 7.38. Found: C, 52.65; H, 6.93; S, 7.17.

Deacetylation of **17** and **18**. Methanolic 0.5 M sodium methoxide (6 mL) was added to a stirred solution of **17** (3.4g, 9 mmol) or **18** (3.9 g, 9 mmol) in dry methanol (60 mL) at ambient temperature. When the reaction was complete fol-

lowed by TLC, the mixture was passed through a layer of Dowex 50 (H^+ form), and the filtrate was concentrated.

Methyl 6,7,8,9,10-pentadeoxy-1-thio-β-L-*galacto*-decopyranoside (19). (1.8 g, 80%, TLC, solvent J, R_f 0.48), colorless crystals: mp 93–94°C (from ethyl acetate); $[\alpha]_D^{22}$ +4.5° (*c* 1.0, chloroform); ^{1}H NMR (CD_3OD) δ 0.90 (t, 3H, H-10, H-10′, H-10″), 1.35, 1.50, 1.75 (3m, 8H, H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 2.30 (s, 3H, SCH_3), 3.42 (m, 1H, H-5), 3.48 (dd, 1H, $J_{3,4}$ = 3.2 Hz, H-3), 3.55 (t, 1H, H-2), 3.72 (dd, 1H, $J_{4,5}$ = 0.8 Hz, H-4), 4.19 (d, 1H, $J_{1,2}$ = 9.1 Hz, H-1); ^{13}C NMR (CD_3OD) δ 15.32 (SCH_3), 17.36 (C-10), 26.61, 29.56, 34.79, 35.89 (C-6, C-7, C-8, C-9), 74.11 (C-2), 75.15 (C-4), 79.49 (C-3), 83.11 (C-5), 90.76 (C-1).

Anal. Calcd $C_{11}H_{22}O_4S$ (250.35): C, 52.77; H, 8.85; S, 12.80. Found: C, 52.47; H, 8.66; S, 12.71.

Methyl 10-methoxycarbonyl-6,7,8,9,10-pentadeoxy-1-thio-β-L-*galacto*-decopyranoside (20). (2.5g, 89%, TLC, solvent K, R_f 0.42), the resulting syrup crystallized after a few days in the refrigerator: mp 73–75 °C; $[\alpha]_D^{23}$–6.4° (*c* 1.0, chloroform); ^{1}H NMR (CD_3OD) δ 1.31–1.84 (m, 8H, H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 2.21 (s, 3H, SCH_3), 2.36 (t, 2H, H-10, H-10′), 3.46 (m, 1H, H-5), 3.49 (dd, 1H, $J_{3,4}$ = 3.3 Hz, H-3), 3.56 (t, 1H, $J_{2,3}$ = 9.3 Hz, H-2), 3.68 (s, 3H, CO_2CH_3), 3.74 (dd, 1H, $J_{4,5}$ = 0.8 Hz, H-4), (d, 1H, $J_{1,2}$ = 9.3 Hz, H-1); ^{13}C NMR (CD_3OD) δ 12.20 (SCH_3), 25.78, 26.38, 29.91, 31.53, 34.59 (C-6, C-7, C-8, C-9, C-10), 51.85 (CO_2CH_3), 71.01 (C-2), 72.09 (C-4), 76.39 (C-3), 79.89 (C-5), 87.67 (C-1), 175.96 (CO_2CH_3).

Anal. Calcd for $C_{13}H_{24}O_6S$ (308.39): C, 50.63; H, 7.84; S 10.40. Found: C, 50.64; H, 7.74; S, 10.25.

Benzylation of 19 and 20. Sodium hydride (600 mg, 75% of sodium hydride by weight, 18.5 mmol) was added to a stirred solution of **19** (1.5 g, 6 mmol) or 20 (1.85 g, 6 mmol) and benzyl bromide (2.6 mL, 22 mmol) in dry *N,N*- dimethylformamide (20 mL) under an argon atmosphere at −60 °C. After 15 min at that temperature, the reaction mixture was allowed to warm up to ambient temperature and stirring was continued for a further 4 h followed by TLC. Methanol (3 mL) was then added and after 15 min, the mixture was diluted with chloroform (70 ml) and heptane (140 mL). The organic layer was washed successively with ice-water (2 × 70 mL), cold aq 1 M hydrochloric acid (2 × 70 mL), ice-water (70 mL), cold sat aq $NaHCO_3$ (2 × 70 mL), ice-water (2 × 70 mL), dried and concentrated. The crude products were purified by column chromatography (eluent ethyl acetate gradient 0% → 10% in heptane).

Methyl 2,3,4-tri-*O*-benzyl-6,7,8,9,10-pentadeoxy-1-thio-β-L-*galacto*-decopyranoside (21). (1.5 g, 47 %, TLC, solvent E, R_f 0.58), colorless syrup:$[\alpha]_D^{23}$ −6.8° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 0.86 (t, 3H, H-10, H-10′, H-10″), 1.24, 1.50, 1.80 (3m, 8H, H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 2.22 (s, 3H, SCH_3), 3.25 (m, 1H, H-5), 3.57 (dd, 1H, $J_{3,4}$ = 2.8 Hz, H-3), 3.70 (d, 1H, $J_{4,5}$ ≈0

Hz, H-4), 3.86 (t, 1H, $J_{2,3}$ = 9.4 Hz, H-2), 4.31 (d, 1H, $J_{1,2}$ = 9.4 Hz, H-1), 4.66–5.15 (m, 6H, $CH_2C_6H_5$), 7.15–7.42 (m, 15H, $CH_2C_6H_5$); ^{13}C NMR ($CDCl_3$) δ 12.92 (SCH_3), 14.03 (C-10), 22.54, 25.56, 31.14, 31.75 (C-6, C-7, C-8, C-9), 72.92, 74.38, 75.66 (3 × $CH_2C_6H_5$), 75.31 (C-4), 78.43 (C-2), 78.90 (C-5), 84.78 (C-3), 85.68 (C-1), 127.50, 127.55, 127.65, 127.70, 128.17, 128.20, 129.43, 138.33, 138.45, 138.75 ($CH_2C_6H_5$, 4 × 2 signals are isochronic).

Anal. Calcd $C_{32}H_{40}O_4S$ (520.72): C, 73.81; H, 7.74; S, 6.15. Found: C, 73.85; H, 7.86; S, 5.98.

Methyl 2,3,4-tri-*O*-benzyl-10-methoxycarbonyl-6,7,8,9,10-pentadeoxy-1-thio-β-L-*galacto*-decopyranoside (22). (1.4 g, 40%, TLC, solvent D, R_f 0.54), colorless crystals: mp 40–43 °C (from ethyl acetate - heptane),$[\alpha]_D^{23}$ −0.6° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.11–1.65 (3m, 8H, H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 2.23 (s, 3H, SCH_3), 2.30 (t, 2H, H-10, H-10′), 3.25 (m, 1H, H-5), 3.58 (dd, 1H, $J_{3,4}$ = 2.9 Hz, H-3), 3.67 (s, 3H, CO_2CH_3), 3.70 (d, 1H, $J_{4,5}$ ≈0 Hz, H-4), 3.87 (t, 1H, $J_{2,3}$ = 9.3 Hz, H-2), 4.32 (d, 1H, $J_{1,2}$ = 9.3 Hz, H-1), 4.70, 5.02 (2d, 2H, J = 12.0 Hz, $CH_2C_6H_5$), 4.79 (s, 2H, $CH_2C_6H_5$), 4.84, 4.90 (2d, 2H, J = 10.4 Hz, $CH_2C_6H_5$), 7.26–7.44 (m, 15H, 3 × $CH_2C_6H_5$); ^{13}C NMR ($CDCl_3$) δ 13.02 (SCH_3), 24.81, 25.54, 29.02, 31.0, 34,03 (C-6, C-7, C-8, C-9, C-10), 51.52 (CO_2CH_3), 72.94, 74.42 (2 × $CH_2C_6H_5$), 75.30 (C-4), 75.71 ($CH_2C_6H_5$), 78.40 (C-2), 78.72 (C-5), 84.73 (C-3), 85.71 (C-1), 127.52, 127.51, 127.60, 127.69, 128.18, 128.24, 129.47, 138.36, 138.49, 138.74 ($CH_2C_6H_5$, 4 × 2 signals are isochronic), 174.92 (CO_2CH_3).

Anal. Calcd for $C_{34}H_{42}O_6S$ (578.77): C, 70.56; H, 7.31; S 5.54. Found: C, 70.24; H, 7.14; S, 5.58.

Methyl 10-methoxycarbonyl-6,7,8,9,10-pentadeoxy-1-thio-2,3,4-tris-*O*-trimethylsilyl-β-L-*galacto*-decopyranoside (23). Trimethylsilyl chloride (0.76 mL, 6.0 mmol) was added dropwise to a solution of **20** (308 mg, 1.0 mmol) in dry pyridine (4.5 ml) at ambient temperature. After stirring for two hours under an argon atmosphere followed by TLC (solvent A, R_f 0.34), dry ether (30 mL) was added and the precipitated pyridinium salts were separated by filtration. The filtrate was concentrated and then coconcentrated with toluene (3 × 50 mL). The residue was again dissolved in dry ether (30 mL), the solution filtered, concentrated and coconcentrated with toluene. The syrup obtained was then purified by HPLC (eluent solvent A) to provide 23 (357 mg, 68%) as a colorless syrup: $[\alpha]_D^{23}$ +12.3° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.11, 0.15, 0.16 [3s, 27H, 3 × $Si(CH_3)_3$], 1.24–1.75 (m, 8H, H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 2.14 (s, 3H, SCH_3), 2.29 (t, 2H, H-10, H-10′), 3.28 (m, 1H, H-5), 3.39 (dd, 1H, $J_{3,4}$ = 2.7 Hz, H-3), 3,62 (d, 1H, $J_{4,5}$ ≈0.0 Hz, H-4), 3.64 (s, 3H, CO_2CH_3), 3.74 (t, 1H, $J_{2,3}$ = 9.2 Hz, H-2), 4.19 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1); ^{13}C NMR ($CDCl_3$): δ 0.43, 0.80, 1.08 [3 × $Si(CH_3)_3$], 13.14 (SCH_3), 24.89, 25.42, 29.08, 31.02 (C-6, C-7, C-8, C-9), 34.00 (C-10), 51.42 (CO_2CH_3), 71.05 (C-2), 74.40 (C-4), 77.15 (C-3), 78.91 (C-5), 87.26 (C-1), 175.14 (CO_2CH_3).

Anal. Calcd for $C_{22}H_{48}O_6SSi_3$ (524.93): C, 50.33; H, 9.55; S, 6.11. Found: C, 50.21; H, 9.49; S 6.23.

Benzyl 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl-(1→4)-[2,3,4-tri-*O*-benzyl-6,7,8,9,10-pentadeoxy-α-L-*galacto*-decopyranosyl-(1→3)]-2,6-di-*O*-benzyl-β-D-glucopyranoside (26). Promotion by IDCP: Powdered molecular sieves (4Å, 1.0 g) were added to a solution of benzyl 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl-(1→4)-2,6-di-*O*-benzyl-β-D-glucopyranoside (**24**, 889 mg, 0.91 mmol) and glycosyl donor **21** (547 mg, 1.05 mmol) in dry diethyl ether (15 mL) and dry dichloromethane (3 mL), and the mixture was stirred under an argon atmosphere for one hour at room temperature. After cooling to 0°C, iodonium di-*sym*-collidine perchlorate (IDCP, 939 mg, 2.00 mmol) was added. After 15 min at that temperature, the reaction mixture was stirred for a further 3.5 h at ambient temperature (TLC, solvent F, R_f 0.47). Chloroform (250 mL) was then added and the solids were filtered off. The filtrate was washed with cold aq 10% sodium thiosulfate (2 × 100 mL), ice-water (2 × 75 mL), cold aq 1M hydrochloric acid (2 × 50 mL), ice-water (2 × 75 mL), dried and concentrated. The crude product was purified by MPLC (eluent ethyl acetate gradient 0% → 14% in heptane) to furnish the trisaccharide **26** (439 mg, 33%) as a colorless syrup.

Promotion by DMTST: To a solution of acceptor **24** (227 mg, 0.23 mmol) and donor **21** (84 mg, 0.16 mmol) in dry toluene (5 mL) were added powdered molecular sieves (4Å, 400 mg), and the mixture was stirred under argon for one hour at room temperature. After cooling to 0°C, dimethyl(methylthio)sulfonium triflate (DMTST, 102 mg, 0.4 mmol) was added and stirring was continued for a further 20 h at that temperature (TLC, solvent F, R_f 0.47). Triethylamine (0.1 ml), methanol (0.1 ml), and chloroform (100 mL) were then added and the mixture was filtered. The filtrate was washed with ice-water (2 × 50 mL), sat aq $NaHCO_3$ (2 × 50 mL), ice-water (2 × 50 mL), dried, and concentrated. The crude product was purified by MPLC (eluent ethyl acetate gradient 0% → 14% in heptane) to yield **26** (89 mg, 38%) as a colorless syrup: $[\alpha]_D^{24}$ −55.5° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 0.94 (t, 3H, J = 6.4 Hz, Fuc: H-10, H-10′, H-10″), 1.30–1.71 (m, 8H, Fuc: H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 3.38–4.35 (3m, 16H, Gal: H-2, H-3, H-4, H-5, H-6, H-6′, Glc: H-2, H-3, H-4, H-5, H-6, H-6′, Fuc: H-2, H-3, H-4, H-5), 4.38–5.16 (m, 20H, 10 × $CH_2C_6H_5$), 4.58, 4.59 (2d, 2H, $J_{1,2}$ = 7.3 Hz and 7.6 Hz, Gal: H-1, Glc: H-1), 5.81 (d, 1H, $J_{1,2}$ = 3.5 Hz, Fuc: H-1), 7.20–7.57 (m, 50H, 10 × $CH_2C_6H_5$); ^{13}C NMR ($CDCl_3$) δ 14.28 (Fuc: C-10), 22.61, 25.17, 30.90, 32.79 (Fuc: C-6, C-7, C-8, C-9), 67.86, 67.95 (Gal: C-6, Glc: C-6), 69.88, 72.58, 73.87, 74.16, 74.85, 75.68, 77.88, 79.46, 80.04, 82.56, 83.02 (Fuc, Gal, Glc: C-2, C-3, C-4, C-5; two signals are isochronic), 70.79, 72.38, 72.68, 73.02, 73.13, 73.37, 75.04, 75.30, 75.42 (10 × $CH_2C_6H_5$, two signals are isochronic), 96.93 (Fuc: C-1), 102.55, 102.60 (Gal: C-1, Glc: C-1), 126.53–139.22 (10 × $CH_2C_6H_5$).

Anal. Calcd for $C_{92}H_{100}O_{15}$ (1445.78): C, 76.43; H, 6.97. Found: C, 76.27; H, 6.85.

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Benzyl 2,6-di-*O*-benzyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl-(1→4)-[2,3,4-tri-*O*-benzyl-6,7,8,9,10-pentadeoxy-α-L-*galacto*-decopyranosyl-(1→3)]-2,6-di-*O*-benzyl-β-D-glucopyranoside (27). Powdered molecular sieves (4Å, 1.5 g) were added to a solution of benzyl 2,6-di-*O*-benzyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl-(1→4)-2,6-di-*O*-benzyl-β-D-glucopyranoside (**25**, 0.49 g, 0.6 mmol) and glycosyl donor **21** (0.31 g, 0.6 mmol) in dry toluene (7 mL) and the mixture was stirred under argon for one hour at room temperature. Dimethyl(methylthio)sulfonium triflate (DMTST, 0.46 g, 1.78 mmol) was added after cooling to 0°C and stirring was continued for further 10 h at 0 °C (TLC, solvent G, R_f 0.51). The reaction mixture was then filtered, diluted with heptane (140 mL) and chloroform (70 mL), and the organic layer washed with water (2 × 50 mL), sat aq $NaHCO_3$ (3 × 50 mL), water (2 × 50 mL), dried, and concentrated. The residue was purified by column chromatography (eluent solvent B) giving the starting material **25** (320 mg) and the trisaccharide **27** (230 mg, 30%, or 84% based on recovered acceptor **25**) as a light-yellow syrup:$[\alpha]_D^{22}$ −33.1° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 0.91 (t, 3H, Fuc: H-10, H-10′, H-10″), 1.22–1.42 (3m, 8H, Fuc: H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 1.50, 1.54 [2s, 6H, $C(CH_3)_2$], 3.26 (dd, 1H, Gal: H-2), 3.32–4.17 (3m, 13H, Glc, Fuc: H-2, H-3, H-4, H-5; Gal: H-3, H-4, H-5, H-6, H-6′), 4.38–5.17 (m, 18H, 8 × C*H*$_2$C$_6$H$_5$ and Glc: H-6, H-6′), 4.54 (d, 1H, $J_{1,2}$ = 7.8 Hz, Gal: H-1), 4.63 (d, 1H, $J_{1,2}$ = 7.2 Hz, Glc: H-1), 5.78 (d, 1H, $J_{1,2}$ = 3.2 Hz, Fuc: H-1), 7.24–7.52 (m, 40H, 8 × $CH_2C_6H_5$); ^{13}C NMR ($CDCl_3$) δ 14.26 (Fuc: C-10), 22.59, 25.66, 31.52, 32.63 (Fuc: C-6, C-7, C-8, C-9), 26.35, 28.23 [C(*C*H$_3$)$_2$], 67.82 (Gal: C-6), 68.93 (Glc: C-6), 69.84, 71.67, 72.74, 73.61, 74.48, 75.40, 76.12, 77.34, 79.62, 79.75, 81.84, 83.26 (Glc, Gal, Fuc: C-2, C-3, C-4, C-5), 70.93, 72.90, 73.26, 73.32, 73.47, 73.80, 74.85 (8 × *C*H$_2$C$_6$H$_5$, two signals are isochronic), 96.72 (Fuc: C-1), 102.15 (Gal: C-1), 102.57 (Glc: C-1), 109.60 [*C*(CH$_3$)$_2$], 126.51–139.30 (8 × CH$_2$*C*$_6$H$_5$).

Anal. Calcd $C_{81}H_{92}O_{15}$ (1305.61): C, 74.52; H, 7.10. Found: C, 74.25; H, 7.08.

Benzyl 2,6-di-*O*-benzyl-β-D-galactopyranosyl-(1→4)-[2,3,4-tri-*O*-benzyl-6,7,8,9,10-pentadeoxy-α-L-*galacto*-decopyranosyl-(1→3)]-2,6-di-*O*-benzyl-β-D-glucopyranoside (28). A solution of **27** (261 mg, 0.2 mmol) in aq 80% acetic acid (35 mL) was heated overnight at 50°C. When the reaction was complete (TLC, solvent H, R_f 0,53), the solution was diluted with toluene (70 mL) and concentrated. Traces of acetic acid were removed by repeated coconcentration with toluene (3 × 30 mL). The residue was purified by column chromatography (eluent solvent E) to provide **28** (152 mg, 60%) as a syrup: $[\alpha]_D^{23}$ −41,5° (c 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 0.81 (t, 3H, Fuc: H-10, H-10′, H-10″), 1.16–1.62, (3m, 8H, Fuc: H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 3.28–5.04 (4m, 32H, 8 × C*H*$_2$C$_6$H$_5$; Glc, Gal, Fuc: H-2, H-3, H-4, H-5; Glc, Gal: H-6, H-6′), 4.47 (d, 1H, $J_{1,2}$ = 8.5 Hz, Gal: H-1), 4.49 (d, 1H, $J_{1,2}$ = 7.8 Hz, Glc: H-1), 5.74 (d, 1H, $J_{1,2}$ = 3.3 Hz, Fuc: H-1), 7.04–7.40 (m, 40H, 8 × $CH_2C_6H_5$); ^{13}C NMR ($CDCl_3$) δ 14.25 (Fuc: C-10), 22.73, 25.19, 29.73, 32.75 (Fuc: C-6, C-7, C-8, C-9), 67.90 (Gal: C-

6), 68.15 (Glc: C-6), 69.95, 70.79, 72.44, 72.87, 74.87, 75.17, 75.34, 75.95, 77.11, 79.77, 80.45, 82.98 (Glc, Gal, Fuc: C-2, C-3, C-4, C-5), 70.87, 72.69, 72.96, 73.18, 73.29, 73.37, 74.96, 75.07 ($8 \times CH_2C_6H_5$), 97.06 (Fuc: C-1), 102.45 (Gal: C-1), 102.65 (Glc: C-1), 126.41–139.23 ($8 \times CH_2C_6H_5$).

Anal. Calcd $C_{78}H_{88}O_{15}$ (1265.54): C, 74.03; H, 7.01. Found: C, 74.18; H, 7.25.

β-D-Galactopyranosyl-(1→4)-[6,7,8,9,10-pentadeoxy-α-L-*galacto*-decopyranosyl-(1→3)-α,β-D-glucopyranose (29). To a solution of **26** (145 mg, 0.1 mmol) or **28** (127 mg, 0.1 mmol) in ethanol (15 mL) and acetic acid (2 mL) palladium-on-charcoal (70 mg) was added. The suspension was stirred under an atmosphere of hydrogen for 24 h at room temperature. When the reaction was complete (TLC, solvent P, R_f 0.20), the mixture was filtered over Celite, successively eluted with ethanol, and the combined filtrates were concentrated. The residue was purified by column chromatography (eluent solvent O) or RP-HPLC (eluent water gradient 0% → 67% in methanol) to provide **29** (49 mg, 90%) as an amorphous colorless solid: ^{13}C NMR (D_2O) δ 14.20 (Fuc: C-10), 22.25, 25.28, 30.66, 32.37 (Fuc: C-6, C-7, C-8, C-9), 60.63, 60.65 (Glc: C-6α,β), 62.19 (Gal: C-6), 69.19, 69.94, 71.30, 71.74, 71.74, 72.09, 73.40, 72.79, 73.98, 74.18, 75.83, 76.16, 76.32, 76.62 (Gal, Glc, Fuc: C-2, C-3, C-4, C-5), 92.91 (Glc: C-1β), 96.57 (Glc: C-1α), 98.10, 98.34 (Fuc: C-1), 103.00 (Gal: C-1).

Anal. Calcd $C_{22}H_{40}O_{15}$ (544.55): C, 48.52; H, 7.40. Found: C, 48.22; H, 7.28.

2,3,4-Tri-*O*-benzyl-6,7,8,9,10-pentadeoxy-α-L-*galacto*-decopyranosyl-(1→2)-6-*O*-benzoyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl-(1→4)-2,3;4,6-di-*O*-isopropylidene-D-glucose dimethyl acetal (31). A suspension of 6-*O*-benzoyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl-(1→4)-2,3;4,6-di-*O*-isopropylidene-D-glucose dimethyl acetal (**30**, 4.57 g, 7.5 mmol)[18–20] and molecular sieves (4Å, 10 g) in dry ethyl ether (20 mL) and dry dichloromethane (4 mL) was stirred for one hour under an atmosphere of argon at ambient temperature. After cooling to 4°C, iodonium di-*sym*-collidine perchlorate (IDCP, 3.01 g, 6.4 mmol) and, after an additional 15 min, the glycosyl donor **21** (2.01 g, 3.86 mmol) were added. The mixture was then allowed to react for 90 min at room temperature (TLC, solvent G, R*f* 0.42). The resulting suspension was diluted with chloroform (250 mL) and filtered through a layer of Celite. The filtrate was washed with cold aq 10% sodium thiosulfate (2 × 100 mL), ice-water (2 × 100 mL), dried and concentrated. The crude product was purified by MPLC (eluent ethyl acetate gradient 0% → 25% in heptane) to provide **31** (1.92 g, 46%,) as a colorless foam: $[\alpha]_D^{23}$ −69.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.86 (t, 3H, Fuc: H-10, H-10′, H-10″), 1.20–1.63 (m, 8H, Fuc: H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 1.27, 1.33, 1.37, 1.43, 1.50 [5s, 18H, $3 \times C(CH_3)_2$], 3.35, 3.37 [2s, 6H, $C(OCH_3)_2$], 3.76 (m, 2H, Gal: H-2, Fuc: H-4), 3.84 (m, 1H, Fuc: H-5), 3.94 (dd, 1H, $J_{5,6} = 6.4$ Hz, $J_{6,6'} = 8.3$ Hz, Glc: H-6), 3.99 (dd, 1H, $J_{4,5} = 5.4$ Hz, Glc: H-4), 4.03–4.15 (m, 5H, Fuc: H-2, H-3, Gal: H-4, H-5, Glc: H-6′), 4.17 (dd, 1H, $J_{3,4} = 2.0$ Hz, Glc: H-3), 4.20

(t, 1H, $J_{2,3} = J_{3,4} = 5.7$ Hz, Gal: H-3), 4.27 (m, 1H, Glc: H-5), 4.45 (d, 1H, $J_{1,2} = 6.0$ Hz, Glc: H-1), 4.48 (dd, 1H, $J_{2,3} = 7.5$ Hz, Glc: H-2), 4.56 (d, 2H, $J_{5,6} = 6.0$ Hz, Gal: H-6, H-6′), 4.76 (s, 2H, $CH_2C_6H_5$), 4.75 (d, 1H, $J_{1,2} = 7.6$ Hz, Gal: H-1), 4.64, 4.78, 4.91, 4.99 (4d, 4H, J = 11.6 Hz, 2 × $CH_2C_6H_5$), 5.63 (d, 1H, $J_{1,2} = 3.2$ Hz, Fuc: H-1), 7.29–8.10 (m, 20 H, $CH_2C_6H_5$); ^{13}C NMR ($CDCl_3$) δ 14.10 (Fuc: C-10), 22.57, 25.32 (Fuc: C-8, C-9), 25.39, 26.42, 26.72, 26.94, 27.09, 27.84 [Gal, Glc: 3 × $C(CH_3)_2$], 30.86, 32.22 (Fuc: C-6, C-7), 53.15, 55.95 [Glc: $C(OCH_3)_2$], 63.82 (Gal: C-6), 65.54 (Glc: C-6), 70.94 (Fuc: C-2, C-5, two signals are isochronic), 72.74, 73.26, 74.50 (3 × $CH_2C_6H_5$), 73.79 (Glc: C-3), 74.68 (Glc: C-4), 74.97 (Glc: C-2), 75.13 (Fuc: C-4), 76.56 (Gal: C-2), 76.80 (Fuc: C-3), 77.26 (Glc: C-5), 77.60 (Gal: C-5), 79.48 (Gal: C-4), 80.09 (Gal: C-3), 94.83 (Fuc: C-1), 101.26 (Gal: C-1), 105.33 (Glc: C-1), 108.72, 109.78, 110.35 [3 × $C(CH_3)_2$], 127.29–139.38 (3 × $CH_2C_6H_5$, $OCOC_6H_5$), 166.32 ($OCOC_6H_5$); FAB^+ mass spectrum matrix nitrobenzyl alcohol: *m/z* 1084 [$C_{61}H_{80}O_{17}$, 9%], 779 [M-Glc$^+$, 21%], 335 [100%].

Anal. Calcd for $C_{61}H_{80}O_{17}$ (1085.28): C, 67.50; H, 7.42. Found: C, 67.29; H, 7.41.

The proposed β-Fuc isomer (180 mg, 5%, in an 1 : 1 mixture together with **31**, TLC, solvent G, R_f 0.44); gave additional signals in the anomeric region: ^{13}C NMR ($CDCl_3$) δ 102.56 (Fuc: C-1), 103.05 (Gal: C-1), 105.25 (Glc: C-1).

2,3,4-Tri-*O*-benzyl-6,7,8,9,10-pentadeoxy-α-L-*galacto*-decopyranosyl-(1→2)-3,4-*O*-isopropylidene-β-D-galactopyranosyl-(1→4)-2,3;4,6-di-*O*-isopropylidene-D-glucose dimethyl acetal (32). A methanolic sodium methoxide solution (0.4 M, 4 mL) was added to a solution of **31** (1.63 g, 1.5 mmol) in dry methanol (40 ml) and the mixture was stirred under an atmosphere of argon overnight at ambient temperature (TLC, solvent H, R_f 0.44). The solution was then passed through a layer of DOWEX 50 × 4 [H^+] and concentrated. The residue was purified by MPLC (eluent ethyl acetate gradient 30% → 50% in heptane) to provide **32** (1.24 g, 84%,) as a colorless syrup: $[\alpha]_D^{23}$ −39.7° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H, Fuc: H-10, H-10′, H-10″), 1.18–1.63 (m, 8H, Fuc: H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 1.30, 1.36, 1.38, 1.45 [4s, 18H, $C(CH_3)_2$, 2 signals are isochronic], 3.48 [s, 6H, $C(OCH_3)_2$], 3.61 (m, 1H, Fuc: H-4), 3.66 (dd, 1H, $J_{4,5} = 1.5$ Hz, Gal: H-4), 3.70 (dd, 1H, $J_{2,3} = 6.2$ Hz, Gal: H-2), 3.74–3.85 (m, 3H, Fuc: H-5, Gal: H-6, H-6′), 3.86 (dd, 1H, $J_{5,6} = 6.0$ Hz, $J_{6,6'} = 8.1$ Hz, Glc: H-6), 3.94 (dd, 1H, $J_{4,5} = 5.6$ Hz, Glc: H-4), 3.96–4.11 (m, 5H, Fuc: H-2, H-3, Gal: H-5, Glc: H-3, H-6′), 4.17 (t, 1H, $J_{3,4} = 6.0$ Hz, Gal: H-3), 4.24 (m, 1H, Glc: H-5), 4.36 (d, 1H, $J_{1,2} = 6.8$ Hz, Glc: H-1), 4.54 (dd, 1H, $J_{1,2} = 8.0$ Hz, Gal: H-1), 4.61 (d, 1H, $J_{2,3} = 8.0$ Hz, Glc: H-2), 4.63, 5.00 (2d, 2H, J = 11.7 Hz, $CH_2C_6H_5$), 4.76 (s, 2H, $CH_2C_6H_5$), 4.85 (d, 2H, J = 11.9 Hz, $CH_2C_6H_5$), 5.60 (d, 1H, $J_{1,2} = 3.6$ Hz, Fuc: H-1), 7.29–7.46 (m, 15 H, $CH_2C_6H_5$); ^{13}C NMR ($CDCl_3$) δ 14.11 (Fuc: C-10), 22.57, 25.27, (Fuc: C-8, C-9), 25.35, 26.45, 26.47, 27.03, 27.05, 27.90 [3 × $C(CH_3)_2$], 30.72, 32.27 (Fuc: C-6, C-7), 53.93, 57.61 [$C(OCH_3)_2$], 62.50 (Gal: C-6), 65.23 (Glc: C-6), 72.83, 73.19, 74.63 (3

× $CH_2C_6H_5$), 70.93, 73.97, 74.67, 74.72, 75.79, 76.68, 76.37, 76.75, 77.19, 77.87, 79.42, 80.70 (Glc, Gal, Fuc: C-2, C-3, C-4, C-5), 94.86 (Fuc: C-1), 101.78 (Gal: C-1), 107.55 (Glc: C-1), 108.80, 109.56, 110.48 [3 × $C(CH_3)_2$], 127.38, 127.45, 127.75, 128.13, 128.32, 128.38, 138.92, 139.01, 139.27 (3 × $CH_2C_6H_5$, 9 signals are isochronic); FAB^+ mass spectrum, matrix nitrobenzylalcohol: *m/z* 981 [$C_{54}H_{76}O_{16}^+$, 20%], 675 [M-Glc^+, 14%], 272 [100%], 241 [100%].

Anal. Calcd for $C_{54}H_{76}O_{16}$ (981.18): C, 66.10; H, 7.80. Found: C, 65.85; H, 7.92.

10-Methoxycarbonyl-2,3,4-tri-*O*-trimethylsilyl-6,7,8,9,10-pentadeoxy-α-L-*galacto*-decopyranosyl-(1→2)-6-*O*-benzoyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl-(1→4)-2,3;4,6-di-*O*-isopropylidene-D-glucose dimethyl acetal (33). The glycosyl acceptor **30** (613 mg, 1.0 mmol) and molecular sieves (4 Å, 2.0 g) were added to a solution of freshly prepared glycosyl donor **23** (630 mg, 1.2 mmol) in dry diethyl ether (30 mL) and dry dichloromethane (6 mL). After stirring under an atmosphere of argon for 30 min at 4 °C, iodonium di-*sym*-collidine perchlorate (IDCP, 761 mg, 1.6 mmol) was added and stirring was continued for one hour at room temperature (TLC, solvent H, R*f* 0.44). The reaction mixture was then diluted with chloroform (100 mL) and passed through a layer of Celite. The filtrate was washed with cold aq 10% sodium thiosulfate (2 × 30 mL), ice-water (2 × 30 mL), dried and concentrated. The residue was purified by column chromatography (eluent solvent D) to give **33** (850 mg, 78%,) as a syrup: $[\alpha]_D^{23}$ −65.3° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 0.03, 0.09, 0.11 [3s, 27H, 3 × $Si(CH_3)_3$], 1.24–1.65 (m, 8H, Fuc: H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 1.25, 1.27, 1.34, 1.35, 1.40, 1.43 [6s, 18H, 3 × $C(CH_3)_2$], 2.26 (t, 2H, Fuc: H-10, H-10′), 3.30, 3.33 [2s, 6H, $C(OCH_3)_2$], 3.64 (s, 3H, CO_2CH_3), 3.65 (d, 1H, Fuc: H-4), 3.70 (dd, 1H, $J_{2,3}$ = 5,6 Hz, Gal: H-2), 3.77 (dd, 1H, $J_{3,4}$ = 2.7 Hz, Fuc: H-3), 3.79 (m, 1H, Fuc: H-5), 3.87 (dd, 1H, $J_{2,3}$ = 9.5 Hz, Fuc: H-2), 3.96 (dd, 1H, $J_{3,4}$ = 5.9 Hz, $J_{4,5}$ = 1.9 Hz, Gal: H-4), 3.98 (dd, 1H, $J_{5,6}$ = 6.5 Hz, $J_{6,6'}$ = 8.5 Hz, Glc: H-6), 4.06 (m, 1H, Gal: H-5), 4.08 (dd, 1H, $J_{3,4}$ = 1.4 Hz, Glc: H-3), 4.14 (dd, 1H, $J_{5,6'}$ = 5.5 Hz, Glc: H-6′), 4.21–4.24 (m, 3H, Glc: H-4, H-5, Gal: H-3), 4.34 (d, 1H, $J_{1,2}$ = 5.9 Hz, Glc: H-1), 4.49 (dd, 1H, $J_{2,3}$ = 7.6 Hz, Glc: H-2), 4.53 (d, 1H, $J_{5,6}$ = 5.7 Hz, Gal: H-6), 4.54 (d, 1H, $J_{5,6'}$ = 6.8 Hz, Gal: H-6′), 4.75 (d, 1H, $J_{1,2}$ = 7.8 Hz, Gal: H-1), 5.29 (d, 1H, $J_{1,2}$ = 3.7 Hz, Fuc: H-1), 7.37–8.02 (2m, 5H, $OCOC_6H_5$); ^{13}C NMR ($CDCl_3$) δ 0.09, 0.46, 0.70 [3 × $Si(CH_3)_3$, 3 signals are isochronic], 24.89, 25.13 (Fuc: C-7, C-8), 25.40, 26.17, 26.71, 26.92, 27.14, 27.73 [3 × $C(CH_3)_2$], 29.57, 30.8 (Fuc: C-6, C-9), 34.07 (Fuc: C-10), 51.32 (CO_2CH_3), 52.98, 55.82 [$C(OCH_3)_2$], 63.62 (Gal: C-6), 65.47 (Glc: C-6), 68.99 (Fuc: C-2), 70.75 (Fuc: C-5), 70.80 (Gal: C-5), 70.92 (Fuc: C-3), 73.55 (Glc: C-5), 74.35 (Fuc: C-4), 74.43 (Gal: C-4), 74.81 (Glc: C-2), 75.82 (Gal: C-2), 77.28 (Gal, Glc: C-3, two signals are isochronic), 79.67 (Glc: C-4), 97.41 (Fuc: C-1), 101.41 (Gal: C-1), 105.26 (Glc: C-1), 108.62, 109.77, 110.10 [$C(CH_3)_2$)], 128.35, 129.64, 129.96, 133.05 ($OCOC_6H_5$), 166.24 ($OCOC_6H_5$), 174.02 (CO_2CH_3).

Anal. Calcd for $C_{51}H_{88}O_{19}Si_3$ (1089.47): C, 56.22; H, 8.14. Found: C, 56.09; H, 8.10.

10-Methoxycarbonyl-6,7,8,9,10-pentadeoxy-α-L-*galacto*-decopyranosyl-(1→2)-3,4-*O*-isopropylidene-β-D-galactopyranosyl-(1→4)-2,3;4,6-di-*O*-isopropylidene-D-glucose dimethyl acetal (34). A methanolic sodium methoxide solution (0.5 N, 1.3 mL) was added to a solution of **33** (163 mg, 0.15 mmol) in dry methanol (6 ml) and the mixture was stirred under an atmosphere of argon for 48 h at room temperature (TLC, solvent L, R_f 0.37). The solution was then passed through a layer of DOWEX 50 × 4 [H^+] and concentrated. The residue was purified by column chromatography (eluent solvent N) to give **34** (93 mg, 81%) as a colorless syrup: $[\alpha]_D^{23}$ −95.7° (*c* 1.0, methanol); ^{1}H NMR (CD_3OD) δ 1.28–1.67 (m, 8H, Fuc: H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 1.30, 1.32, 1.36, 1.42, 1.45 [5s, 18H, 3 × $C(CH_3)_2$, two signals are isochronic], 2.30 (t, 2H, Fuc: H-10, H-10′), 3.45, 3.47 [2s, 6H, $C(OCH_3)_2$], 3.64 (s, 3H, CO_2CH_3), 3.67 (dd, 1H, $J_{3,4}$ = 3.2 Hz, Fuc: H-3), 3.69 (dd, 1H, $J_{2,3}$ = 6.1 Hz, Gal: H-2), 3.71 (m, 1H, Fuc: H-5), 3.74 (dd, 1H, $J_{2,3}$ = 9.0 Hz, Fuc: H-2), 3.77 (d, 1H, Fuc: H-4), 3.83 (m, 2H, Gal: H-6, H-6′), 3.86 (dd, 1H, $J_{4,5}$ = 6.6 Hz, Glc: H-4), 3.88 (m, 1H, Gal: H-5), 4.01 (dd, 1H, $J_{5,6}$ = 6.3 Hz, $J_{6,6'}$ = 8.4 Hz, Glc: H-6), 4.13 (dd, 1H, $J_{5,6'}$ = 4.8 Hz, Glc: H-6′), 4.14 (dd, 1H, $J_{3,4}$ = 1.4 Hz, Glc H-3), 4.19 (dd, 1H, $J_{4,5}$ = 1.7 Hz, Gal: H-4), 4.26 (m, 1H, Glc: H-5), 4.31 (t, 1H, $J_{3,4}$ = 6.1 Hz, Gal: H-3), 4.40 (d, 1H, $J_{1,2}$ = 6.4 Hz, Glc: H-1), 4.53 (dd, 1H, $J_{2,3}$ = 8.1 Hz, Glc: H-2), 4.59 (d, 1H, $J_{1,2}$ = 8.1 Hz, Gal: H-1), 5.35 (d, 1H, $J_{1,2}$ = 3.0 Hz, Fuc: H-1); ^{13}C NMR (CD_3OD) δ 25.30, 26.51, 27.15, 27.31, 27.32, 28.27, [3 × $C(CH_3)_2$], 25.99, 26.45, 30.54, 31.47 (Fuc: C-6, C-7, C-8, C-9), 34.72 (Fuc: C-10), 51.92 (CO_2CH_3), 55.22, 57.29 [$C(OCH_3)_2$], 62.69 (Gal: C-6), 66.85 (Glc: C-6), 70.10 (Fuc: C-5), 71.47 (Fuc: C-2), 71.76 (Glc: C-5), 72.10 (Gal: C-2), 75.08 (Gal: C-4), 75.36 (Fuc: C-4), 76.76, 76.82 (Fuc: C-3, Glc: C-2), 76.96 (Glc: C-4), 77.89 (Glc: C-5), 78.72 (Glc: C-3), 81.42 (Gal: C-3), 97.52 (Fuc: C-1), 102.95 (Gal: C-1), 108.23 (Glc: C-1), 110.13, 110.61, 111.33 [3 × $C(CH_3)_2$], 175.89 (CO_2CH_3).

Anal. Calcd for $C_{35}H_{60}O_{18}$ (768.83): C, 54.67; H, 7.87. Found: C, 54.53; H, 7.91.

2,3,4-Tri-*O*-benzyl-6,7,8,9,10-pentadeoxy-α-L-*galacto*-decopyranosyl-(1→2)-4-*O*-β-D-galactopyranosyl-(1→4)-α/β-D-glucopyranose (35). A solution of **32** (1.18 g, 1.2 mmol) in 30 mL aq 60% acetic acid was heated for 6 h at 60°C (TLC, solvent L, R_f 0.19). The reaction mixture was then diluted with toluene (60 mL) and concentrated. The residue was coconcentrated with toluene (3 × 60 mL) in order to remove traces of acetic acid. Finally, the crude product was purified by MPLC (eluent solvent N) to yield **35** (704 mg, 72%) as a colorless syrup: Partially interpreted ^{1}H NMR (CD_3OD) δ 0.87 (m, 3H, Fuc: H-10, H-10′, H-10″), 1.16–1.59 (m, 8H, Fuc: H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 4.44 (d, 0.4H, $J_{1,2}$ = 7.7 Hz, Glc: H-1β), 4.46 (d, 1H, $J_{1,2}$ = 7.0 Hz, Gal: H-1), 5.09 (d, 0.6H, $J_{1,2}$ = 3.7 Hz, Glc: H-1α), 5.72 (d, 1H, $J_{1,2}$ = 3.6 Hz, Fuc: H-1), 7.24–7.46 (m, 15H, $CH_2C_6H_5$); partially interpreted ^{13}C NMR (CD_3OD) δ 14.53 (Fuc: C-10), 23.50, 23.61, 26.58, 26.76, 31.98, 32.06, 33.38, 33.51 (Fuc: C-6, C-7, C-8, C-9), 61.65, 61.90 (Glc: C-6α, C-6β), 62.48 (Gal: C-6), 73.42, 73.99, 76.00 (3 × $CH_2C_6H_5$), 70.96, 71.87, 72.14, 73.00, 73.65, 75.58, 75.91, 76.39, 76.42, 76.50, 76.92, 77.27, 77.54, 77.85,

77.91, 79.01, 79.34, 80.20 (Gal, Glc, Fuc: C-2, C-3, C-4, C-5), 93.69 (Glc: C-1α), 98.09 (Fuc: C-1), 98.14 (Glc: C-1β), 102.66, 102.70 (Gal: C-1), 128.57, 128.62, 128.69, 128.78, 129.20, 129.31, 129.39, 139.64, 140.07, 140.29 ($3 \times CH_2C_6H_5$, 8 signals are isochronic); FAB^+ mass spectrum, matrix NaCl ($C_{43}H_{58}O_{15}$ + Na): *m/z* 837 [$(M + Na)^+$, 100%].

Anal. Calcd for $C_{43}H_{58}O_{15}$ (814.92): C, 63.37; H, 7.17. Found: C, 63.18; H, 7.31.

6,7,8,9,10-Pentadeoxy-α-L-*galacto*-decopyranosyl-(1→2)-β-D-galactopyranosyl-(1→4)-α/β-D-glucopyranose (36). To a solution of **35** (815 mg, 1.0 mmol) in glacial acetic acid (25 mL) palladium-on-charcoal (700 mg) was added. The suspension was stirred under an atmosphere of hydrogen for 20 h at ambient temperature. When the reaction was complete (TLC, solvent M, R_f 0.42), the mixture was filtered over Celite and concentrated. The residue was coconcentrated with toluene (3×30 mL) and purified by column chromatography (eluent solvent M) to afford **36** (474 mg, 87%), as a colorless powder: Partially interpreted ^1H NMR (D_2O) δ 0.96 (m, 3H, Fuc: H-10, H-10′, H-10″), 1.34–1.72 (m, 8H, Fuc: H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 4.57 (d, 1H, $J_{1,2}$ = 7.8 Hz, Gal: H-1), 4.67 (d, 0.4H, $J_{1,2}$ = 7.9 Hz, Glc: H-1β), 5.29 (d, 0.6H, $J_{1,2}$ = 3.6 Hz, Glc: H-1α), 5.49, 5.51 (2d, 1H, $J_{1,2}$ = 3.6 Hz, Fuc: H-1); partially interpreted ^{13}C NMR (D_2O) δ 14.20 (Fuc: C-10), 22.74, 22.83, 25.57, 25.72, 30.57, 30.64, 32.22, 32.28 (Fuc: C-6, C-7, C-8, C-9), 60.78, 60.93 (Glc: C-6), 61.92 (Gal: C-6), 69.16, 70.09, 70.49, 70.98, 71.07, 71.29, 71.79, 72.09, 72.20, 74.71, 74.84, 75.26, 75.74, 75.93, 76.04, 76.23, 77.00, 77.37 (Gal, Glc, Fuc: C-2, C-3, C-4, C-5), 92.69 (Glc: C-1α), 96.82 (Glc: C-1β), 99.32, 99.43 (Fuc: C-1), 101.35 (Gal: C-1); FAB^+ mass spectrum, matrix NaCl ($C_{22}H_{40}O_{15}$ + Na): *m/z* 567 [$(M + Na)^+$ 48%], 177 (100%).

Anal. Calcd for $C_{22}H_{40}O_{15}$ (544.55): C, 48.52; H, 7.40. Found: C,48.28; H, 7.16.

10-Methoxycarbonyl-6,7,8,9,10-pentadeoxy-α-L-*galacto*-decopyranosyl-(1→ 2)-β-D-galactopyranosyl-(1→4)-α/β-D-glucopyranose (37). A stirred solution of **34** (77 mg, 0.1 mmol) in aq 80% acetic acid (5.0 mL) was heated for 6 h at 80°C. TLC analysis (eluent solvent M) indicated the formation of a unidentified byproduct (R_f 0.52) besides the desired compound **37** (R_f 0.37). The solution was concentrated and the residue coconcentrated with toluene (3×10 mL). Finally, crude **37** was purified by preparative TLC (eluent solvent M, R_f 0.37) in which the isolated silica gel fractions were extracted with methanol. The extracts were concentrated to provide **37** (28 mg, 47%) as a colorless powder: Partially interpreted ^1H NMR (D_2O) δ 1.21–1.82 (m, 8H, Fuc: H-6, H-6′, H-7, H-7′, H-8, H-8′, H-9, H-9′), 2.43 (t, 2H, Fuc: H-10, H-10′), 3.81 (s, 3H, CO_2CH_3), 4.57 (d, 1H, $J_{1,2}$ = 7.4 Hz, Gal: H-1), 4.66 (d, 0.53 H, $J_{1,2}$ = 7.7 Hz, Glc: H-1β), 5.28 (d, 0.47 H, $J_{1,2}$ = 3.4 Hz, Glc: H-1α), 5.49, 5.51 (2 d, 1H, $J_{1,2}$ = 3.3 Hz, Fuc: H-1); partially interpreted ^{13}C NMR (D_2O) δ 25.14, 25.20, 25.66, 25.88, 29.49, 29.56, 30.61, 34.53 (Fuc: C-6, C-7, C-8, C-9, C-10), 53.02 (CO_2CH_3), 60.88, 61.03 (Glc: C-6), 62.04 (Gal: C-6), 69.20, 70.20, 70.55, 71.10, 71.28, 71.41, 71.78, 72.27, 74.81, 74.95,

75.42, 75.68, 75.92, 76.17, 76.36, 77.13, 77.40 (Gal, Glc, Fuc: C-2, C-3, C-4, C-5), 92.79 (Glc: C-1α), 96.93 (Glc: C-1β), 99.34, 99.49 (Fuc: C-1), 101.44 (Gal: C-1), 178.64 (CO_2CH_3); Fab^+ mass spectrum, matrix nitrobenzyl alcohol/NaCl ($C_{24}H_{42}O_{17}$ + Na): *m/z* 625 [$(M + Na)^+$, 100%].

Anal. Calcd for $C_{24}H_{42}O_{17}$ (602.59): C, 47.84; H, 7.03. Found: C, 47.59; H, 6.83.

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