Synthetic Study on *Campylobacter jejuni* Lipopolysaccharides: An Improved Synthesis of a Branched, Heptose-Containing Trisaccharide Core Structure and Its Conversion into Ganglioside GD3 Related Hexasaccharide[‡]

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The first synthesis of the oligosaccharide skeleton of the *Campylobacter jejuni* lipooligosaccharide composed of a branched, heptose-containing trisaccharide core structure and, including a substantially improved preparation of the core structure, the ganglioside GD3 related trisaccharide epitope is reported.

Introduction

Miller−Fischer syndrome (MFS) is a neuropathy associated with ataxia, areflexia, and opthalmoplegia and is considered to be an infrequently occurring variation of the more common form known as Guillain-Barré syndrome (GBS).[2] Renewed interest in the etiology of these neuropathies has stemmed from the finding that the onset of both MFS and GBS in some patients is preceded by intestinal infections with *Campylobacter jejuni*. It is known that lipopolysaccharides (LPSs) from some strains of *C. jejuni* mimic the structures of human gangliosides (Figure 1),[3] and attention has focused on the possibility that molecular mimicry might be a factor in the pathogenesis of human neurological disease.[4−6] The ganglioside-mimicking structures have been found to be located at the terminal regions of the core oligosaccharides (OSs) of the LPS molecules. OS structures mimicking human gangliosides GM2, GM1, GD1a,[3,7] and GQ1b[6] have been found.

In this study we describe an efficient construction of the *C. jejuni* LPS mimicking the human ganglioside GD3, which was recovered from a patient who developed MFS,[8] as a part of the study to corroborate the molecular mimicry hypothesis proposed for the onset of MFS and GBS.

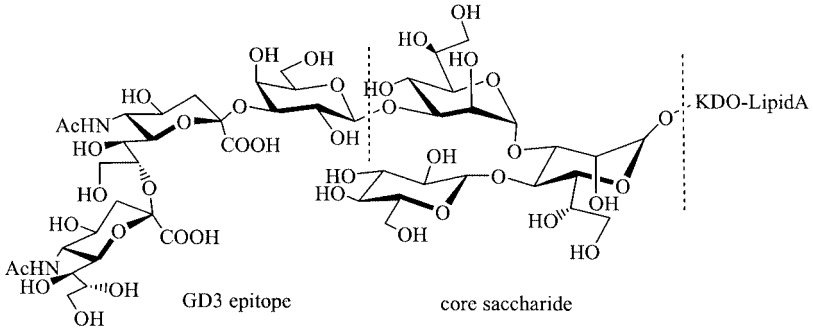

Figure 1. Structure of lipooligosaccharide of *Campylobacter jejuni* PEN19 OH4382

Results and Discussion

The main problems needing to be faced in the construction of the title compound **28** are: (i) the development of a facile synthesis of L-*glycero*-D-*manno*-heptose (LD-Hep; **8**), (ii) efficient construction of the branched, heptose-contain-

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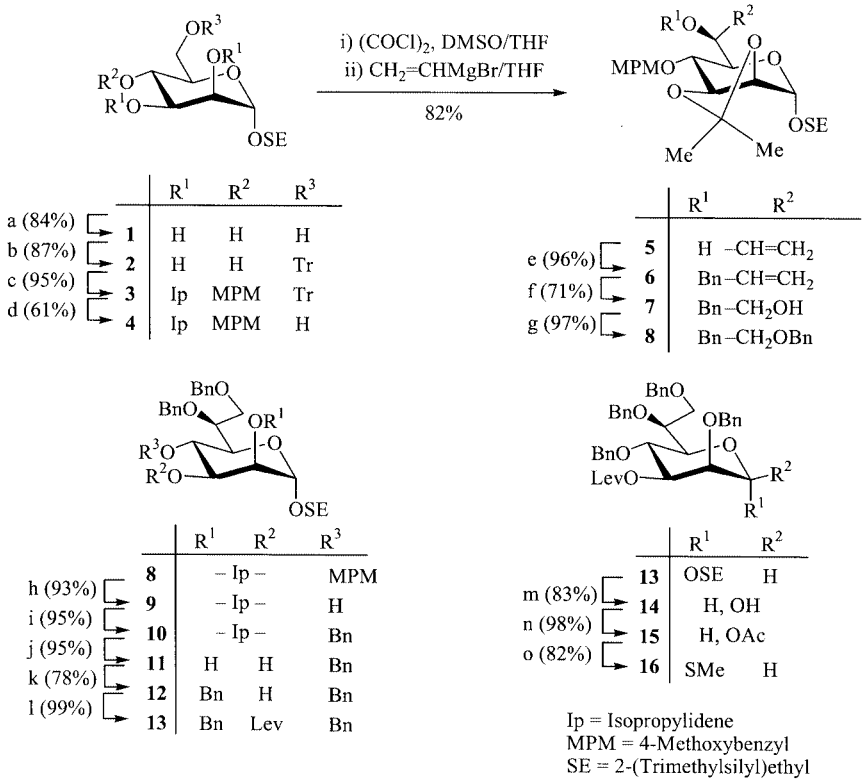
ing trisaccharide core structure **26**, and (iii) coupling of the core trisaccharide and GD3-related trisaccharide (see Figure 2).

A suitably protected LD-Hep derivative, in which the hydroxy groups at C-1,3,4 are protected with different species, was synthesized by the procedure described by Dasser et al.[9] Starting from known[10] 2-(trimethylsilyl)ethyl β-D-mannopyranoside, 6-*O*-triphenylmethylation (94%), 2,3-*O*-isopropylidenation (87%), 4-*O*-*p*-methoxybenzylation (95%), and the acidic hydrolysis of the triphenylmethyl group with acetic acid/methanol (63%) gave the desired 6-OH derivative **4**. Partial hydrolysis of the isopropylidene group, affording the corresponding 2,3,6-OH derivative (37%), was observed under these conditions. This by-product could be transformed into **4** (71%) after further isopropylidenation, however. Swern oxidation[11] of the alcohol **4** gave the corresponding aldehyde, which was immediately condensed with commercially available vinylmagnesium bromide in tetrahydrofuran at −60 °C to afford alcohol **5** (82% in two steps). The stereochemistry at the new chiral center was determined by comparison of the NMR spectroscopic data with those reported.[9] The allylic alcohol **5** was then protected as the benzyl ether **6** in 96% yield. The double bond of **6** was oxidatively cleaved with sodium periodate in the presence of osmium tetraoxide in aqueous diethyl ether. The intermediate aldehyde was immediately reduced with sodium borohydride (71% in three steps). Subsequent benzylation of alcohol **7** gave the suitably protected derivative of LD-Hep **8** (Scheme 1).

Our next objective was the efficient construction of the LD-Hep-containing trisaccharide core structure. Bernlind and Oscarson[12] found that the preparation of branched trisaccharides with an α-D-linked moiety at an equatorial *O*-3 position and a β-D-moiety at an equatorial *O*-4 position was a difficult task, mainly due to steric crowding. They solved this problem by forming a 1,6-anhydro ring to change the conformation of the heptose ring of the acceptor from C_1 to ^1C. This approach succeeded in increasing the yield for the construction of the desired trisaccharide, but additional steps are required both to form the 1,6-anhydro bridge and later to cleave it. Our strategy is based on the use of the acetyl-protected disaccharide acceptor **20** as the key intermediate for the construction of the trisaccharide structure, avoiding the presence of the bulkier benzoyl groups used in the above work. Benzylation of **7** gave **8** (97%), which was treated with DDQ[13] to give the desired LD-Hep acceptor **9** (93%). The LD-Hep donor **16**, in which the hydroxy group at *O*-3 was protected as the corresponding levulonate ester, was obtained from **9** in seven steps. Compound **9** was benzylated (95%) and then treated with 85% aq. acetic acid to give the 2,3-diol derivative **11** (95%). Phase-transfer-catalyzed benzylation[14] of **11** preferentially afforded the 2-*O*-benzylated derivative **12** (78%), which was treated with levulinic acid, 4-(dimethylamino)pyridine, and



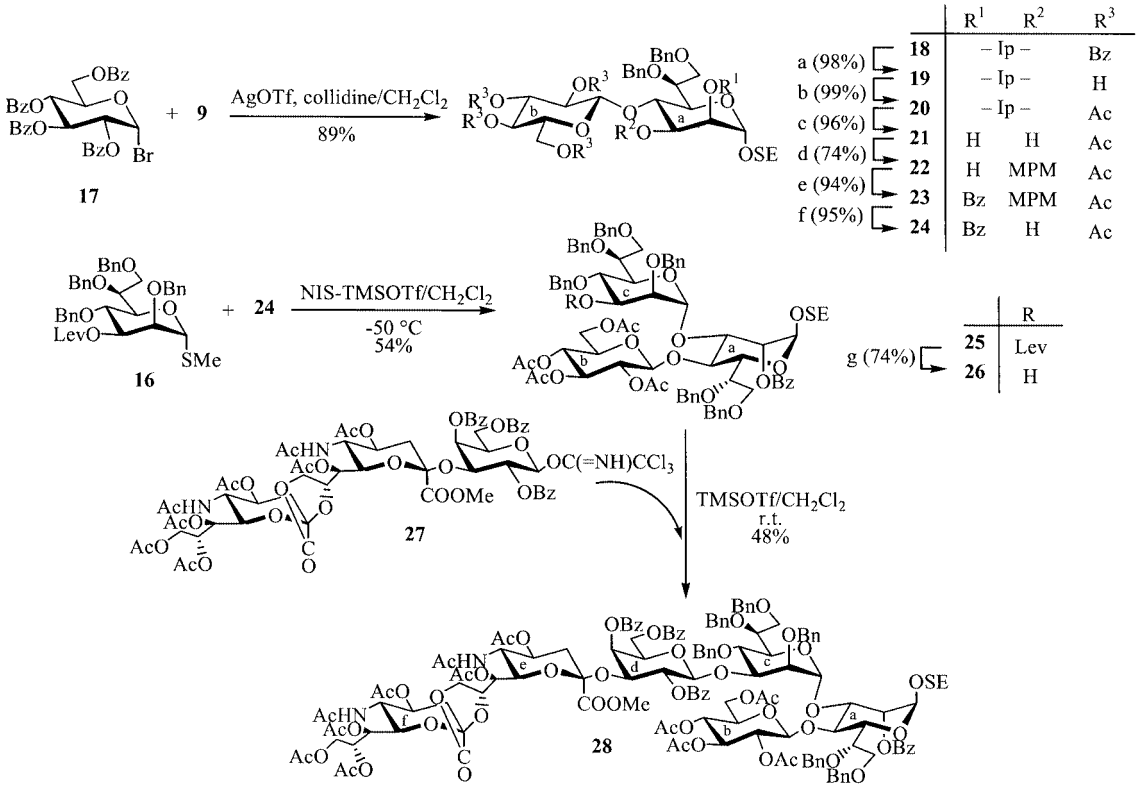
Scheme 1. Reagents: a) TrCl, DMAP/Pyr.; b) DMP, *p*-TsOH; c) MPMCl, NaH/DMF; d) AcOH; e) BnBr, NaH/DMF; f) (i) OsO_4, $NaIO_4$/*t*BuOH, (ii) $NaBH_4$/CH_3OH, H_2O; g) BnBr, NaH/DMF; h) DDQ, H_2O/CH_2Cl_2; i) BnBr, NaH/DMF; j) 85% aq. AcOH; k) BnBr, TBAB/10% aq. NaOH, (CH_2Cl_2); l) LevOH, DCC, DMAP/CH_2Cl_2; m) TFA/CH_2Cl_2; n) Ac_2O/Pyr.; o) TMS·SMe, TMSOTf/CH_2Cl_2

DCC to give 3-*O*-levulinoylated derivative **13** (99%). The position protected with the levulinoyl group was confirmed to be *O*-3 by NMR spectroscopic data [δ = 5.31 ppm (dd, $J_{2,3}$ = 3.3, $J_{3,4}$ = 9.2 Hz, 1 H, 3-H)]. Compound **13** was converted into the methylthio derivative **16** by selective cleavage of the 2-(trimethylsilyl)ethyl group (to give **14**; 83%),[15] acetylation (to give **15**; 98%), and treatment with trimethyl(methylthio)silane (TMS·SMe; 1:1 equiv.) and trimethylsilyl trifluoromethanesulfonate at −10 °C (82%). It is worth mentioning that an increase in the amount of TMS·SMe or the reaction temperature resulted in decreased yields, due to a concomitant side reaction involving the oxo function in the levulinoyl group and the methylthio group (Scheme 1). Alternatively, we also prepared the corresponding trichloroacetimidate donor from **14**, but this was too labile to be used as a glycosyl donor in our hands.

Coupling of **9** with perbenzoylated glucosyl bromide **17**[16] stereoselectively gave the β(1→4)-linked disaccharide **18** (89%), the benzoyl group of which was replaced with acetyl group by Zemplén transesterification (to give **19**; 99%) and conventional acetylation with acetic anhydride and pyridine (96%) to give **20**. Removal of the isopropylidene acetal in **20** afforded the 2,3-diol **21** (96%), which was then glycosylated with **16** to give mainly the 2-*O*-glycosylated derivative (about 60%; data not shown). Tin activation[17] of **21**, followed by *p*-methoxybenzylation, gave **22** (74%) as the major reaction product. After benzoylation of **22** at O-2 (to give **23**; 94%), the MPM group was removed by treatment with ceric ammonium nitrate (CAN) to afford the desired Glcβ(1−4)LD-Hep glycosyl acceptor **24** (95%). The position protected with the benzoyl group was confirmed to be O-2 by NMR spectroscopic data [δ = 5.39 ppm (m, 1 H, 2a-H)]. NIS/TMSOTf-promoted coupling of **24** with suitably protected LD-Hep donor **16** gave the desired α-linked trisaccharide **25** (54%). This result, in comparison with the work of Bernlind and Oscarson commented on above, underlines the importance of the choice of the protecting groups, even in the residue next to the residue to be glycosylated, for the outcome of glycosylation reactions.

The levulinoyl group in **25** was selectively removed by treatment with hydrazine monoacetate,[18] and the resulting compound **26** was glycosylated with the trichloroacetimidate[19] of the suitably protected disialylgalactose **27**[20] in the presence of trimethylsilyl trifluoromethanesulfonate to afford the desired hexasaccharide **28**, in fully protected form (48%). Hexasaccharide **28** is a suitable precursor, after conversion into the corresponding glycosyl donor, for further coupling with KDO derivatives. Work in that direction is currently underway in our laboratory.

In conclusion, an improved synthesis of a branched, LD-Hep-containing trisaccharide core structure was accomplished by appropriate manipulation of the protecting groups in Glcβ(1−4)LD-Hep glycosyl acceptor, and the ob-



	R1	R2	R3
18	– Ip –		Bz
19	– Ip –		H
20	– Ip –		Ac
21	H	H	Ac
22	H	MPM	Ac
23	Bz	MPM	Ac
24	Bz	H	Ac

	R
25	Lev
26	H

Scheme 2. Reagents: a) CH_3ONa/CH_3OH; b) Ac_2O/Pyr.; c) 80% aq. AcOH; d) (i) Bu_2SnO/benzene, (ii) MPMCl, TBAB/benzene; e) BzCl/Pyr.; f) CAN/CH_3CN, H_2O; g) NH_2NH_2·AcOH/CH_3CH_2OH

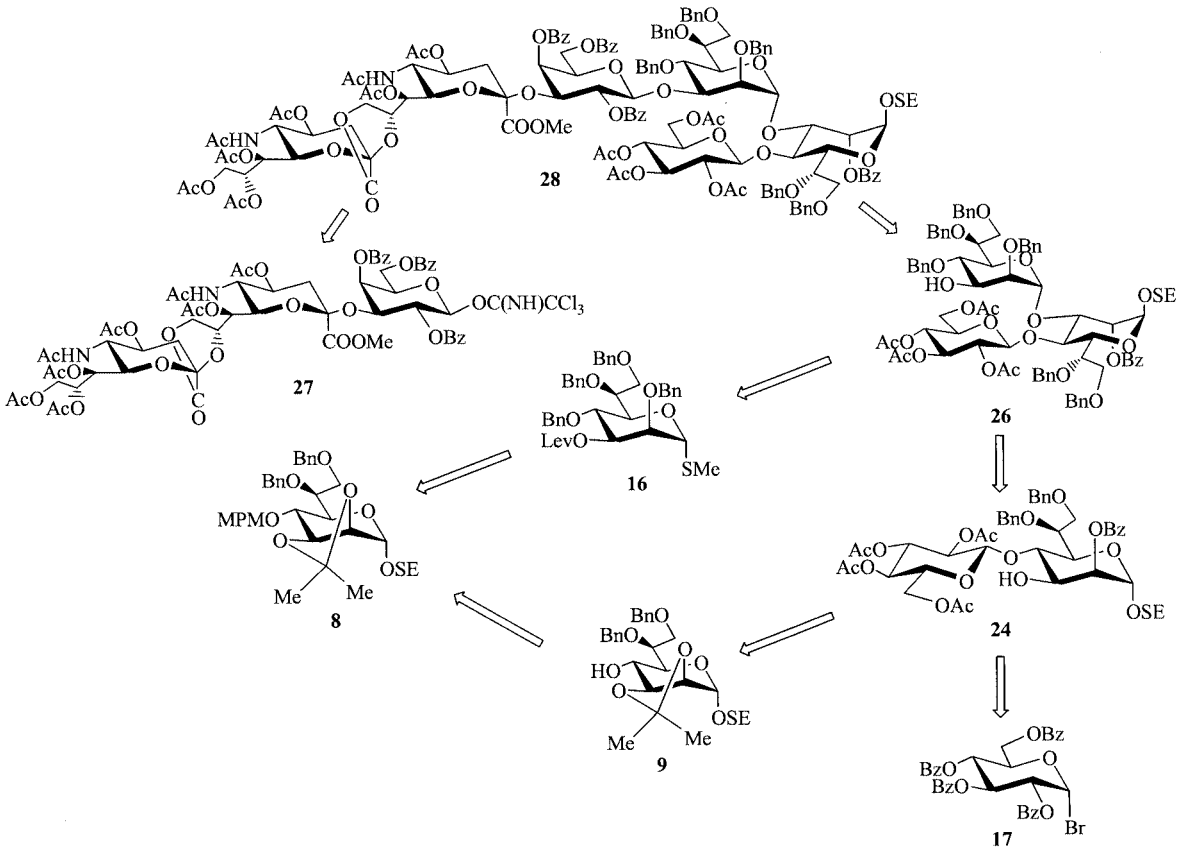


Figure 2. Synthetic plan for the title compound

tained trisaccharide was used as an efficient building block in the construction of a ganglioside GD3 related hexasaccharide.

Experimental Section

General Remarks: Specific rotations were determined with a Horiba SEPA-300 high-sensitivity polarimeter at ambient temperature (25±1 °C). ^{1}H NMR spectra were recorded with Varian Gemini 2000 (200 MHz) and Varian Unity Inova (400 and 500 MHz) spectrometers with $CDCl_3$ as solvent and TMS as the internal standard. Preparative thin-layer chromatography (TLC) was performed on silica gel 60 (E. Merck). Column chromatography on silica gel (Fuji Silysia Co., 300 mesh) was performed with the solvent systems specified (v/v). Concentrations and evaporations were conducted in vacuo.

2-(Trimethylsilyl)ethyl 6-*O*-Trityl-α-D-mannopyranoside (1): Trityl chloride (1.3 g, 4.7 mmol) and 4-(dimethylamino)pyridine (50 mg) were added to a solution of 2-(trimethylsilyl)ethyl α-D-mannopyranoside (1.1 g, 3.9 mmol) in pyridine (5 mL), and the mixture was stirred at 40 °C for 24 h. After addition of methanol, the mixture was stirred at room temperature for 30 min to quench the reaction and concentrated. The residue was extracted with chloroform, and the organic layer was washed with 2 M HCl and sat. Na_2CO_3, and dried with anhydrous Na_2SO_4. The solvent was evaporated, and the residue was chromatographed on a column of silica gel (ethyl acetate) to give **1** (1.8 g, 89%). $[\alpha]_D$ = +15.60 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.00 (s, 9 H, $Me_3SiCH_2CH_2$), 0.95 (m, 2 H, $Me_3SiCH_2CH_2$), 3.50−3.90 (m, 8 H, $Me_3SiCH_2CH_2$, 2,3,4,5,6,6′-*H*), 4.82 (d, $J_{1,2}$ = 1.4 Hz, 1 H, 1-*H*), 7.20−7.50 (m, 15 H, 3 Ph). $C_{30}H_{38}O_6Si$ (522.71): calcd. C 68.93, H 7.33; found C 68.69, H 7.31.

2-(Trimethylsilyl)ethyl 2,3-*O*-Isopropylidene-6-*O*-trityl-α-D-mannopyranoside (2): A solution of **1** (1.83 g, 3.5 mmol) in 2,2-dimethoxypropane (11 mL) was treated with *p*-toluenesulfonic acid monohydrate (24 mg) and then stirred at room temperature. After 45 min, the solution was neutralized with triethylamine and extracted with chloroform. The organic layer was dried with anhydrous Na_2SO_4 and concentrated. The residue was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:5) to give **2** (1.72 g, 87%). $[\alpha]_D$ = +0.74 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.02 (s, 9 H, $Me_3SiCH_2CH_2$), 0.96 (m, 2 H, $Me_3SiCH_2CH_2$), 1.33, 1.47 (2 s, 6 H, 2 CMe), 3.37 (m, 2 H, 6-*H*, 6′-*H*), 3.5−4.0 (m, 4 H, $Me_3SiCH_2CH_2$, 4-*H*, 5-*H*), 4.10 (m, 2 H, 2-*H*, 3-*H*), 5.01 (s, 1 H, 1-*H*), 7.1−7.5 (m, 15 H, 3 Ph). $C_{33}H_{42}O_6Si$ (562.78): calcd. C 70.43, H 7.52; found C 70.16, H 7.26.

2-(Trimethylsilyl)ethyl 2,3-*O*-Isopropylidene-4-*O*-(*p*-methoxybenzyl)-6-*O*-trityl-α-D-mannopyranoside (3): A solution of **2** (1.21 g, 2.1 mmol) in DMF (9 mL) was treated with sodium hydride (65%; 135 mg, 3.6 mmol) at 0 °C for 30 min. *p*-Methoxybenzyl chloride (0.32 mL, 2.3 mmol) was added at 0 °C to the mixture, which was stirred at room temperature for 2 h. After addition of methanol, the mixture was stirred for 30 min at room temperature and concentrated. The residue was extracted with diethyl ether, and the organic layer was washed with water, dried with anhydrous Na_2SO_4, and concentrated. The residue was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:20) to give **3** (1.39 g, 95%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.00 (s, 9 H, Me_3-

$SiCH_2CH_2$), 0.96 (m, 2 H, $Me_3SiCH_2CH_2$), 1.33, 1.47 (2 s, 6 H, 2 CMe), 3.17 (dd, J = 5.9, J = 9.8 Hz, 1 H, 6-*H*), 3.3−4.0 (m, 8 H, $Me_3SiCH_2CH_2$, 4-*H*, 5-*H*, 6′-*H*, OMe), 3.77 (s, 3 H, OMe), 4.20 (m, 1 H, 2-*H*), 4.26 (t, 1 H, 3-*H*), 4.26, 4.63 (d, 2 H, $PhCH_2$), 5.19 (s, 1 H, 1-*H*), 6.8−7.0 (m, 4 H, ArH), 7.1−7.5 (m, 15 H, 3 Ph). $C_{41}H_{50}O_7Si$ (682.93): calcd. C 72.11, H 7.38; found C 71.86, H 7.26.

2-(Trimethylsilyl)ethyl 2,3-*O*-Isopropylidene-4-*O*-(*p*-methoxybenzyl)-α-D-mannopyranoside (4): A solution of **3** (109 mg, 0.15 mmol) in acetic acid (11 mL) was stirred at 60 °C for 11 h, and then concentrated. The residue was diluted with chloroform, and the organic layer was washed with sat. Na_2CO_3, dried with anhydrous Na_2SO_4, and concentrated. The residue was chromatographed on a column of silica gel (ethyl acetate) to give **4** (43 mg, 61%). $[\alpha]_D$ = +55.7 (c = 0.4, $CHCl_3$). IR: $\tilde{\nu}$ = 3500 (OH), 2950 (CH), and 860 and 840 (C−Si) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.00 (s, 9 H, $Me_3SiCH_2CH_2$), 0.89 (m, 2 H, $Me_3SiCH_2CH_2$), 1.37, 1.51 (2 s, 6 H, 2 CMe), 3.4−3.9 (m, 6 H, $Me_3SiCH_2CH_2$, 4-*H*, 5-*H*, 6-*H*, 6′-*H*), 3.80 (s, 3 H, OMe), 4.12 (d, $J_{2,3}$ = 5.8 Hz, 1 H, 2-*H*), 4.31 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 6.2 Hz, 3-*H*), 4.55, 4.82 (d, 2 H, $PhCH_2$), 5.20 (s, 1 H, 1-*H*), 6.8−7.3 (m, 4 H, ArH), 7.1−7.5 (m, 15 H, 3 Ph). $C_{22}H_{36}O_7Si$ (440.61): calcd. C 59.97, H 8.24; found C 59.88, H 8.12.

2-(Trimethylsilyl)ethyl 7,8-Dideoxy-2,3-*O*-isopropylidene-4-*O*-(*p*-methoxybenzyl)-L-*glycero*-α-D-*manno*-oct-7-enopyranoside (5): A solution of oxalyl chloride (225 μL, 2.5 mmol) in THF (7 mL) was cooled to −60 °C, and a solution of dimethyl sulfoxide (367 μL, 5.1 mmol) in THF (3 mL) was added. The reaction mixture was stirred at room temperature for 5 min. A solution of **4** (950 mg, 2.1 mmol) in THF (7 mL) was added dropwise at −60 °C, and the mixture was stirred at −60 °C for 15 min. A solution of triethylamine (1.5 mL, 10 mmol) in THF (3 mL) was added at −60 °C and the reaction mixture was allowed to warm to room temperature. After completion of the reaction, the mixture was cooled to −60 °C again. Vinylmagnesium bromide (1.0 M in THF, 10.7 mL, 10 mmol) was added, and the mixture was stirred at −60 °C for 24 h and then allowed to warm to room temperature. After addition of ethanol and sat. NH_4Cl, the mixture was extracted with diethyl ether. The organic layer was washed with water, dried with anhydrous Na_2SO_4, and concentrated. The residue was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:10) to give **5** (820 mg, 82%). $[\alpha]_D$ = +27.0 (c = 0.8, $CHCl_3$). IR: $\tilde{\nu}$ = 3500 (OH), 2950 (CH), and 860 and 840 (C−Si) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.00 (s, 9 H, $Me_3SiCH_2CH_2$), 0.89 (m, 2 H, $Me_3SiCH_2CH_2$), 1.36, 1.51 (2 s, 6 H, 2 CMe), 3.30−3.90 (m, 7 H, $Me_3SiCH_2CH_2$, 4-*H*, 5-*H*), 3.78 (s, 3 H, OMe), 4.09 (d, $J_{2,3}$ = 5.8 Hz, 1 H, 2-*H*), 4.32 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 6.2 Hz, 3-*H*), 4.43 (m, 1 H, 6-*H*), 4.55, 4.85 (d, 2 H, $PhCH_2$), 5.02 (s, 1 H, 1-*H*), 5.18 (m, 1 H, 8-*H*), 5.34 (m, 1 H, 8′-*H*), 5.95 (m, 1 H, 7-*H*), 6.80−7.40 (m, 4 H, ArH). $C_{22}H_{36}O_7Si$ (440.61): calcd. C 61.77, H 8.21; found C 61.53, H 8.16.

2-(Trimethylsilyl)ethyl 6-*O*-Benzyl-7,8-dideoxy-2,3-*O*-isopropylidene-4-*O*-(*p*-methoxybenzyl)-L-*glycero*-α-D-*manno*-oct-7-enopyranoside (6): A solution of **5** (118 mg, 0.25 mmol) in DMF (3 mL) was treated with sodium hydride (65%, 15 mg, 0.42 mmol) and benzyl bromide (39 μL, 0.32 mmol) as described for the *p*-methoxybenzylation of **2**, to give **3**. After the workup, the residue was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:20) to give **6** (136 mg, 96%). $[\alpha]_D$ = +70.2 (c = 1.0, $CHCl_3$). IR: $\tilde{\nu}$ = 2950 (CH), 860 and 840 (C-Si), and 740 and 700 (phenyl) cm^{-1}. ^1H NMR (400 MHz): δ = 0.00 (s, 9 H, $Me_3SiCH_2CH_2$), 0.88 (m, 2 H, $Me_3SiCH_2CH_2$), 1.38, 1.56 (2 s, 6 H, 2 CMe), 3.45 (m, 1 H, $Me_3SiCH_2CH_2$), 3.56 (dd, $J_{4,5}$ = 9.8, $J_{5,6}$ = 1.6 Hz, 1 H, 5-*H*), 3.75 (m, 1 H, $Me_3SiCH_2CH_2$), 3.75 (s, 3 H, OMe), 3.86 (dd, $J_{3,4}$ = 6.9, $J_{4,5}$ = 9.8 Hz, 1 H, 4-*H*), 4.05−4.35 (m, 5 H, 2-*H*, 3-*H*, 6-*H*, $PhCH_2$), 4.68, 4.76 (2 d, 2 H, $PhCH_2$), 5.11 (s, 1 H, 1-*H*), 5.32 (m, 2 H, 8-*H*, 8′-*H*), 6.7−7.4 (m, 9 H, ArH). $C_{31}H_{44}O_7Si$ (556.77): calcd. C 66.87, H 7.97; found C 66.62, H 7.88.

2-(Trimethylsilyl)ethyl 6-*O*-Benzyl-2,3-*O*-isopropylidene-4-*O*-(*p*-methoxybenzyl)-L-*glycero*-α-D-*manno*-heptopyranoside (7): Water (8 mL), osmium tetraoxide (2.5 wt% in *tert*-butyl alcohol, 1.59 mL), and sodium periodate (1.71 g, 8.0 mmol) were added to a solution of **6** (890 mg, 1.6 mmol) in diethyl ether (8 mL), and the mixture was stirred at room temperature for 24 h. After evaporation of the solvent, the residue was dissolved in methanol (32 mL) and water (16 mL). The solution was treated with sodium borohydride (242 mg, 6.4 mmol) at room temperature for 1 h, neutralized with 2 M HCl, and then concentrated. The residue was extracted with chloroform, and the organic layer was washed with water, dried with anhydrous Na_2SO_4, and concentrated. The residue was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:5) to give **7** (640 mg, 71%). $[\alpha]_D$ = +58.7 (c = 1.0, $CHCl_3$). IR: $\tilde{\nu}$ = 3500 (OH), 2950 (CH), 860 and 840 (C−Si), and 740 and 700 (phenyl) cm^{-1}. ^1H NMR (200 MHz): δ = 0.00 (s, 9 H, $Me_3SiCH_2CH_2$), 0.91 (m, 2 H, $Me_3SiCH_2CH_2$), 1.38, 1.56 (2 s, 6 H, 2 CMe), 3.4−3.9 (m, 7 H, $Me_3SiCH_2CH_2$, 4-*H*, 5-*H*, 6-*H*, 7-*H*, 7′-*H*), 3.75 (s, 3 H, OMe), 4.11 (d, $J_{2,3}$ = 5.8 Hz, 1 H, 2-*H*), 4.33 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 5.8 Hz, 3-*H*), 4.25−4.9 (4 d, 4 H, 2 $PhCH_2$), 5.09 (s, 1 H, 1-*H*), 5.32 (m, 2 H, 8-*H*, 8′-*H*), 6.7−7.3 (m, 9 H, ArH). $C_{30}H_{44}O_8Si$ (560.76): calcd. C 64.26, H 7.91; found C 64.11, H 7.74.

2-(Trimethylsilyl)ethyl 6,7-Di-*O*-benzyl-2,3-*O*-isopropylidene-4-*O*-(*p*-methoxybenzyl)-L-*glycero*-α-D-*manno*-heptopyranoside (8): A solution of **7** (612 mg, 1.1 mmol) in DMF (12 mL) was treated with sodium hydride (65%, 68 mg, 1.8 mmol) and benzyl bromide (168 μL, 1.4 mmol) as described for the *p*-methoxybenzylation of **2** to give **3**. After the workup, the residue was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:10) to give **8** (689 mg, 97%). $[\alpha]_D$ = +51.9 (c = 1.8, $CHCl_3$). IR: $\tilde{\nu}$ = 2950 (CH), 860 and 840 (C−Si), and 740 and 700 (phenyl) cm^{-1}. ^1H NMR (200 MHz): δ = 0.00 (s, 9 H, $Me_3SiCH_2CH_2$), 0.90 (m, 2 H, $Me_3SiCH_2CH_2$), 1.41, 1.59 (2 s, 6 H, 2 CMe), 3.40−4.20 (m, 8 H, $Me_3SiCH_2CH_2$, 2-*H*, 4-*H*, 5-*H*, 6-*H*, 7-*H*, 7′-*H*), 3.78 (s, 3 H, OMe), 4.20−4.90 (6 d, 6 H, 3 $PhCH_2$), 5.13 (s, 1 H, 1-*H*), 6.80−7.40 (m, 14 H, ArH). $C_{37}H_{50}O_8Si$ (650.88): calcd. C 68.28, H 7.74; found C 68.21, H 7.61.

2-(Trimethylsilyl)ethyl 6,7-Di-*O*-benzyl-2,3-*O*-isopropylidene-L-*glycero*-α-D-*manno*-heptopyranoside (9): Water (0.45 mL) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ; 470 mg, 2.0 mmol) were added at 0 °C to a solution of **8** (900 mg, 1.3 mmol) in dichloromethane (9 mL), and the mixture was stirred at room temperature for 1.5 h. Insoluble materials were removed by filtration (Celite) and washed with chloroform. The filtrate and washings were combined, washed with sat. Na_2CO_3, dried with Na_2SO_4, and concentrated. The residue was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:5) to give **9** (685 mg, 93%). $[\alpha]_D$ = +35.8 (c = 1.2, $CHCl_3$). IR: $\tilde{\nu}$ = 3600−3500 (OH), 3100−2950 (CH), 860 and 840 (C−Si), and 740 and 700 (phenyl) cm^{-1}. ^1H NMR (400 MHz): δ = 0.00 (s, 9 H, $Me_3SiCH_2CH_2$), 0.81−0.98 (m, 2 H, $Me_3SiCH_2CH_2$), 1.36, 1.53 (2s, 6 H, Me_2C), 2.13 (b, 1 H, OH-4), 3.49 (m, 1 H, $Me_3SiCH_2CH_2$), 3.65 (dd, $J_{4,5}$ = 10.3, $J_{5,6}$ = 2.2 Hz, 1 H, 5-*H*), 3.73−3.82 (m, 4 H, $Me_3SiCH_2CH_2$, 4-*H*, 7-*H*, 7′-*H*), 3.96 (dt, 1 H, $J_{5,6}$ = 2.2, $J_{6,7}$ = $J_{6,7'}$ = 5.5 Hz, 6-*H*), 4.08 (m, 2 H, 2-*H*, 3-*H*), 4.54−4.86 (4 d, 4 H, 2 $PhCH_2$), 5.08 (s, 1 H,

1-*H*), 7.28−7.41 (m, 10 H, ArH). $C_{29}H_{42}O_7Si$ (530.733): calcd. C 65.63, H 7.98; found C 65.37, H 7.68.

2-(Trimethylsilyl)ethyl 4,6,7-Tri-*O*-benzyl-2,3-*O*-isopropylidene-L-*glycero*-α-D-*manno*-heptopyranoside (10): A solution of **9** (5.5 g, 10 mmol) in DMF (9 mL) was treated with sodium hydride (65%; 650 mg, 17 mmol) at 0 °C for 30 min. Benzyl bromide (2.0 mL, 17 mmol) was added at 0 °C to the mixture, which was stirred at room temperature for 3 h. After addition of water, the mixture was stirred at room temperature for 30 min. It was then diluted with toluene and the organic layer was washed with water, dried with anhydrous Na_2SO_4, and concentrated. The residue was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:10) to give **10** (6.1 g, 95%). $[\alpha]_D$ = +45.4 (*c* = 0.9, $CHCl_3$). IR: $\tilde{\nu}$ = 3100−2800 (CH), 860 and 840 (C−Si), and 740 and 700 (phenyl) cm^{-1}. ^1H NMR (400 MHz): δ = 0.00 (s, 9 H, $Me_3SiCH_2CH_2$), 0.91 (m, 2 H, $Me_3SiCH_2CH_2$), 1.40, 1.58 (2 s, 6 H, 2 CMe), 3.50 (m, 1 H, $Me_3SiCH_2CH_2$), 3.72−3.86 (m, 5 H, $Me_3SiCH_2CH_2$, 4-*H*, 5-*H*, 7-*H*, 7′-*H*), 4.14 (m, 2 H, 2-*H*, 6-*H*), 4.38 (t, 1 H, $J_{2,3} = J_{3,4}$ = 5.8 Hz, 3-*H*), 4.30, 4.50−4.91 (6 d, 6 H, $PhCH_2$), 5.14 (s, 1 H, 1-*H*), 7.22−7.37 (m, 15 H, ArH). $C_{36}H_{48}O_7Si$ (620.857): calcd. C 69.65, H 7.79; found C 69.57, H 7.50.

2-(Trimethylsilyl)ethyl 4,6,7-Tri-*O*-benzyl-L-*glycero*-α-D-*manno*-heptopyranoside (11): A solution of **10** (6.1 g, 9.8 mmol) in acetic acid (60 mL) and water (10 min) was stirred at 50 °C for 24 h. After concentration in vacuo, the residue was diluted with chloroform and the organic layer was washed with sat. Na_2CO_3, dried with anhydrous Na_2SO_4, and concentrated. The residue was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:3) to give **11** (5.5 g, 96%). $[\alpha]_D$ = +80.5 (*c* = 1.3, $CHCl_3$). IR: $\tilde{\nu}$ = 3600−3200 (OH), 3100−2800 (CH), 860 and 840 (C−Si), and 740 and 700 (phenyl) cm^{-1}. ^1H NMR (400 MHz): δ = 0.00 (s, 9 H, $Me_3SiCH_2CH_2$), 0.88 (m, 2 H, $Me_3SiCH_2CH_2$), 2.81 (broad s, 1 H, OH-3), 3.23 (broad s, 1 H, OH-2), 3.43 (m, 1 H, $Me_3SiCH_2CH_2$), 3.68−3.87 (m, 6 H, $Me_3SiCH_2CH_2$, 2-*H*, 4-*H*, 5-*H*, 7-*H*, 7′-*H*), 3.85 (broad s, 1 H, 3-*H*), 4.14 (t, 1 H, $J_{6,7} = J_{6,7'}$ = 5.8 Hz, 6-*H*), 4.41−4.87 (d and m, 6 H, $PhCH_2$), 4.83 (s, 1 H, 1-*H*), 7.24−7.38 (m, 15 H, ArH). $C_{33}H_{44}O_7Si$ (580.79): calcd. C 68.25, H 7.64; found C 68.16, H 7.45.

2-(Trimethylsilyl)ethyl 2,4,6,7-Tetra-*O*-benzyl-L-*glycero*-α-D-*manno*-heptopyranoside (12): NaOH (10% aq., 30 mL), benzyl bromide (2.4 mL, 20 mmol), and tetrabutylammonium bromide (1.3 g, 4.0 mmol) were added to a solution of **11** (5.9 g, 10 mmol) in 1,2-dichloroethane (36 mL), and the mixture was stirred at 50 °C for 24 h. The mixture was extracted with chloroform, and the organic layer was washed with water, dried with anhydrous Na_2SO_4, and concentrated. The residue was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:5) to give **12** (5.3 g, 78%). $[\alpha]_D$ = +20.6 (*c* = 1.8, $CHCl_3$). IR: $\tilde{\nu}$ = 3600−3300 (OH), 3100−2800 (CH), 860 and 840 (C−Si), and 740 and 700 (phenyl) cm^{-1}. ^1H NMR (400 MHz): δ = 0.05 (s, 9 H, $Me_3SiCH_2CH_2$), 0.88 (m, 2 H, $Me_3SiCH_2CH_2$), 2.39 (d, $J_{OH,3}$ = 9.9 Hz, 1 H, OH-3), 3.47 (m, 1 H, $Me_3SiCH_2CH_2$), 3.71−3.78 (m, 4 H, $Me_3SiCH_2CH_2$, 2-*H*, 5-*H*, 7′-*H*), 3.86−3.92 (m, 2 H, 4-*H*, 7-*H*), 4.04 (m, 1 H, 3-*H*), 4.17 (m, 1 H, 6-*H*), 4.36−4.91 (8 d, 8 H, 4 $PhCH_2$), 5.03 (d, $J_{1,2}$ = 1.1 Hz, 1 H, 1-*H*), 7.25−7.41 (m, 20 H, ArH). $C_{40}H_{50}O_7Si$ (670.92): calcd. C 71.61, H 7.51; found C 71.40, H 7.36.

2-(Trimethylsilyl)ethyl 2,4,6,7-Tetra-*O*-benzyl-3-*O*-levulinoyl-L-*glycero*-α-D-*manno*-heptopyranoside (13): Levulinic acid (1.5 mL, 14 mmol), 4-(dimethylamino)pyridine (DMAP; 175 mg, 1.4 mmol), and 1,3-dicyclohexylcarbodiimide (DCC; 2.9 g, 14 mmol) were added to a solution of **12** (4.8 g, 7.1 mmol) in dichloromethane (48 mL), and the mixture was stirred at room temperature for 1 h. After addition of methanol, the mixture was stirred at room temperature for 30 min, and then concentrated. The residue was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:5) to give **13** (5.5 g, 99%). $[\alpha]_D$ = +24.0 (*c* = 1.6, $CHCl_3$). IR: $\tilde{\nu}$ = 3100−2800 (CH), 1730 (carbonyl), 860 and 840 (C−Si), and 740 and 700 (phenyl) cm^{-1}. ^1H NMR (400 MHz): δ = 0.03 (s, 9 H, $Me_3SiCH_2CH_2$), 0.91 (m, 2 H, $Me_3SiCH_2CH_2$), 2.12 (s, 3 H, $MeCOCH_2CH_2$), 2.34−2.68 (m, 4 H, $MeCOCH_2CH_2$), 3.47 (m, 1 H, $Me_3SiCH_2CH_2$), 3.72−3.79 (m, 2 H, $Me_3SiCH_2CH_2$, 7′-*H*), 3.84−3.92 (m, 3 H, 2-*H*, 5-*H*, 7-*H*), 4.10 (t, $J_{6,7} = J_{6,7'}$ = 5.5 Hz, 1 H, 6-*H*), 4.21 (t, $J_{3,4} = J_{4,5}$ = 9.2 Hz, 1 H, 4-*H*), 4.32−4.91 (8 d, 8 H, 4 $PhCH_2$), 4.94 (d, $J_{1,2}$ = 1.8 Hz, 1 H, 1-*H*), 5.31 (dd, $J_{2,3}$ = 3.3, $J_{3,4}$ = 9.2 Hz, 1 H, 3-*H*), 7.20−7.42 (m, 20 H, ArH). $C_{45}H_{56}O_9Si$ (769.018): calcd. C 70.28, H 7.34; found C 70.24, H 7.08.

2,4,6,7-Tetra-*O*-benzyl-3-*O*-levulinoyl-L-*glycero*-D-*manno*-heptopyranose (14): Trifluoroacetic acid (28 mL) was added at 0 °C to a solution of **13** (5.6 g, 7.2 mmol) in dichloromethane (56 mL), which was stirred at 0 °C. After 3 h, the solution was concentrated. The residue was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:2) to give **14** (4.0 g, 83%, α:β = 10:1). IR: $\tilde{\nu}$ = 3600−3200 (OH), 3100−2800 (CH), 1730 (carbonyl), and 740 and 700 (phenyl) cm^{-1}. ^1H NMR (400 MHz) of α-form: δ = 2.07 (s, 3 H, $MeCOCH_2CH_2$), 2.29−2.66 (m, 4 H, $MeCOCH_2CH_2$), 3.66−3.83 (m, 3 H, 2-*H*, 7-*H*, 7′-*H*), 3.97 (d, $J_{4,5}$ = 9.5 Hz, 1 H, 5-*H*), 4.02 (dd, $J_{6,7}$ = 6.2, $J_{6,7'}$ = 5.9 Hz, 1 H, 6-*H*), 4.16 (dd, $J_{3,4}$ = 9.2, $J_{4,5}$ = 9.5 Hz, 1 H, 4-*H*), 4.28−4.82 (8 d, 8 H, 4 $PhCH_2$), 5.19 (d, $J_{1,2}$ = 1.1 Hz, 1 H, 1-*H*), 5.31 (dd, $J_{2,3}$ = 2.9, $J_{3,4}$ = 8.8 Hz, 1 H, 3-*H*), 7.13−7.39 (m, 20 H, ArH). $C_{40}H_{44}O_9$ (668.78): calcd. C 71.84, H 6.63; found C 71.75, H 6.37.

1-*O*-Acetyl-2,4,6,7-tetra-*O*-benzyl-3-*O*-levulinoyl-L-*glycero*-α,β-D-*manno*-heptopyranose (15): Acetic anhydride (1 mL) was added to a solution of **14** (470 mg, 0.7 mmol) in pyridine (5 mL) at 0 °C, and the mixture was then stirred at room temperature for 24 h. After addition of methanol at 0 °C, the solution was stirred for 30 min at room temperature, and then concentrated with toluene. The residue was extracted with chloroform, and the organic layer was washed with 2 M HCl and water, dried with anhydrous Na_2SO_4, and concentrated. The residue was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:3) to give **15** (490 mg, 98%, α/β = 10:1). IR: $\tilde{\nu}$ = 3100−2800 (CH), 1730 (carbonyl), and 740 and 700 (phenyl) cm^{-1}. ^1H NMR (500 MHz) of α-form: δ = 1.95 (s, 3 H, AcO), 2.10 (s, 3 H, $MeCOCH_2CH_2$), 2.34−2.65 (m, 4 H, $MeCOCH_2CH_2$), 3.64 (dd, $J_{6,7'}$ = 6.6, $J_{7,7'}$ = 9.6 Hz, 1 H, 7-*H*), 3.81 (dd, $J_{6,7'}$ = 6.2, $J_{7,7'}$ = 9.6 Hz, 1 H, 7′-*H*), 3.85 (m, 1 H, 2-*H*), 3.93 (d, $J_{4,5}$ = 9.8 Hz, 1 H, 5-*H*), 4.05 (t, $J_{6,7} = J_{6,7'}$ = 6.2 Hz, 1 H, 6-*H*), 4.25 (dd, $J_{3,4}$ = 9.2, $J_{4,5}$ = 9.6 Hz, 1 H, 4-*H*), 4.34−4.81 (8 d, 8 H, 4 $PhCH_2$), 5.25 (dd, $J_{2,3}$ = 3.2, $J_{3,4}$ = 9.2 Hz, 1 H, 3-*H*), 6.18 (d, $J_{1,2}$ = 1.8 Hz, 1 H, 1-*H*), 7.12−7.42 (m, 20 H, ArH). $C_{42}H_{46}O_{10}$ (710.82): calcd. C 70.97, H 6.52; found C 70.72, H 6.42.

Methyl 2,4,6,7-Tetra-*O*-benzyl-3-*O*-levulinoyl-1-thio-L-*glycero*-α-D-*manno*-heptopyranoside (16): Trimethyl(methylthio)silane (26 μL, 0.18 mmol) and trimethylsilyl trifluoromethanesulfonate (TMSOTf; 32 μL, 0.16 mmol) were added at −10 °C to a solution of **15** (119 mg, 0.16 mmol) in dichloromethane (2 mL). The reaction mixture was diluted with chloroform, and the organic layer was washed with sat. Na_2CO_3, dried with anhydrous Na_2SO_4, and concentrated. The residue was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:3) to give **16** (96 mg, 82%). $[\alpha]_D$ = +43.1 (*c* = 1.0, $CHCl_3$). IR: $\tilde{\nu}$ = 3100−2800 (CH), 1730 (carbonyl), and 740 and 700 (phenyl) cm^{-1}. ^1H NMR (500 MHz): δ =

2.05 (s, 3 H, MeS), 2.10 (s, 3 H, *Me*COCH$_2$CH$_2$), 2.36−2.64 (m, 4 H, MeCO*CH$_2$CH$_2$*), 3.70 (dd, $J_{6,7}$ = 5.9, $J_{7,7'}$ = 9.6 Hz, 1 H, 7-*H*), 3.82 (dd, $J_{6,7'}$ = 6.4, $J_{7,7'}$ = 9.8 Hz, 1 H, 7′-*H*), 3.91 (dd, $J_{1,2}$ = 2.7, $J_{2,3}$ = 2.9 Hz, 1 H, 2-*H*), 4.07 (dt, $J_{5,6}$ = 1.4, $J_{6,7}$ = $J_{6,7'}$ = 6.2 Hz, 1 H, 6-*H*), 4.12 (dd, $J_{4,5}$ = 9.6, $J_{5,6}$ = 1.1 Hz, 1 H, 5-*H*), 4.19 (dd, $J_{3,4}$ = 8.7, $J_{4,5}$ = 9.4 Hz, 1 H, 4-*H*), 4.29−4.84 (d and m, 8 H, Ph*CH$_2$*), 5.19 (dd, $J_{2,3}$ = 3.2, $J_{3,4}$ = 8.5 Hz, 1 H, 3-*H*), 5.28 (d, $J_{1,2}$ = 2.9 Hz, 1 H, 1-*H*), and 7.17−7.38 (m, 20 H, ArH). $C_{41}H_{46}O_8S$ (698.87): calcd. C 70.46, H 6.63; found C 70.40, H 6.52.

2-(Trimethylsilyl)ethyl (2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→4)-6,7-di-*O*-benzyl-2,3-*O*-isopropylidene-L-*glycero*-α-D-*manno*-heptopyranoside (18): A solution of **17** (1.39 g, 2.1 mmol) and **9** (625 mg, 1.1 mmol) in dichloromethane (15 mL) was stirred in the presence of 2,4,6-trimethylpyridine (248 μL, 1.8 mmol) and molecular sieves (4 Å; 2.0 g) at room temperature for 1 h and then cooled to 0 °C. Silver trifluoromethanesulfonate (595 mg, 2.3 mmol) was added to the mixture at 0 °C in the dark, and the system was stirred in the dark at 0 °C for 24 h. After addition of triethylamine for neutralization, insoluble materials were removed by filtration (Celite) and washed with chloroform. The filtrate and washings were combined and concentrated to a syrup, which was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:3) to give **18** (1.1 g, 89%). $[\alpha]_D$ = +24.7 (*c* = 1.34, $CHCl_3$). IR: $\tilde{\nu}$ = 3100−2800 (CH), 1730 and 1260 (ester), 860 and 840 (C−Si), and 740 and 700 (phenyl) cm^{-1}. ^{1}H NMR (400 MHz): δ = 0.00 (s, 9 H, *Me$_3$*SiCH$_2$CH$_2$), 0.79−0.98 (m, 2 H, Me$_3$Si*CH$_2$*CH$_2$), 1.29, 1.55 (2 s, 6 H, Me$_2$C), 3.47 (m, 2 H, Me$_3$SiCH$_2$*CH$_2$*, 5b-*H*), 3.66 (dd, $J_{6,7}$ = 5.5, $J_{7,7'}$ = 9.5 Hz, 1 H, 7a-*H*), 3.69−3.80 (m, 3 H, Me$_3$SiCH$_2$*CH$_2$*, 5a-*H*, 7′a-*H*), 4.03 (t, $J_{6,7}$ = $J_{6,7'}$ = 5.5 Hz, 1 H, 6a-*H*), 4.07−4.13 (m, 2 H, 2a-*H*, 4a-*H*), 4.37−4.50 (m, 5 H, 3a-*H*, 6b-*H*, Ph*CH$_2$*), 4.56 (dd, $J_{6,6'}$ = 11.7 Hz, 1 H, 6b-*H*), 4.83 (d, $J_{1,2}$ = 8.1 Hz, 1 H, 1b-*H*), 4.82−4.86 (4 d, 3 H, 2 Ph*CH$_2$*), 5.11 (s, 1 H, 1a-*H*), 5.60 (dd, $J_{1,2}$ = 8.1, $J_{2,3}$ = 9.9 Hz, 1 H, 2b-*H*), 5.65 (t, $J_{3,4}$ = 9.5, $J_{4,5}$ = 9.9 Hz, 1 H, 4b-*H*), 5.78 (t, $J_{2,3}$ = 9.9, $J_{3,4}$ = 9.5 Hz, 1 H, 3b-*H*), 7.25−8.06 (m, 30 H, ArH). $C_{63}H_{68}O_{16}Si$ (1109.37): calcd. C 68.21, H 6.18; found C 68.06, H 5.98.

2-(Trimethylsilyl)ethyl (β-D-Glucopyranosyl)-(1→4)-6,7-di-*O*-benzyl-2,3-*O*-isopropylidene-L-*glycero*-α-D-*manno*-heptopyranoside (19): Sodium methoxide was added to a solution of **18** (1.1 g, 0.99 mmol) until pH = 12, and the mixture was stirred at room temperature for 24 h. After neutralization with Amberlite IR 120 (H^+), the resin was removed by filtration and washed with methanol. The filtrate and washings were combined and concentrated to syrup, which was chromatographed on a column of silica gel (ethyl acetate/hexane, 5:1) to give **19** (673 mg, 98%). $[\alpha]_D$ = +7.1 (*c* = 1.0, $CHCl_3$). IR: $\tilde{\nu}$ = 3700−3100 (OH), 3100−2800 (CH), 860 and 840 (C-Si), and 740 and 700 (phenyl) cm^{-1}. ^{1}H NMR (500 MHz): δ = 0.00 (s, 9 H, *Me$_3$*SiCH$_2$CH$_2$), 0.88 (m, 2 H, Me$_3$Si*CH$_2$*CH$_2$), 1.35, 1.50 (2 s, 6 H, Me$_2$C), 2.92 (t, $J_{5,6}$ = 6.9 Hz, 1 H, 5b-*H*), 3.48 (m, 1 H, Me$_3$SiCH$_2$*CH$_2$*), 3.58 (dd, $J_{5,6}$ = 6.9, $J_{6,6'}$ = 11.4 Hz, 1 H, 6b-*H*), 4.07 (d, $J_{2,3}$ = 6.2 Hz, 1 H, 2a-*H*), 4.13 (m, 1 H, 6a-*H*), 4.36 (t, $J_{2,3}$ = $J_{3,4}$ = 6.2 Hz, 1 H, 3a-*H*), 4.49−4.89 (4 d, 4 H, 2 Ph*CH$_2$*), 7.25−7.38 (m, 10 H, ArH). $C_{35}H_{52}O_{12}Si$ (692.88): calcd. C 60.67, H 7.56; found C 60.51, H 7.57.

2-(Trimethylsilyl)ethyl (2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-6,7-di-*O*-benzyl-2,3-*O*-isopropylidene-L-*glycero*-α-D-*manno*-heptopyranoside (20): Compound **19** (685 mg, 0.95 mmol) was treated with pyridine (7 mL) and acetic anhydride (0.8 mL, 7.7 mmol) as described for the synthesis of **15**. After the workup, the residue was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:3) to give **20** (817 mg, 99%). $[\alpha]_D$ = +15.6 (*c* = 1.0, $CHCl_3$). IR: $\tilde{\nu}$ = 3100−2800 (CH), 1760 and 1220 (ester), 860 and 840 (C−Si), and 740 and 700 (phenyl) cm^{-1}. ^{1}H NMR (400 MHz): δ = 0.00 (s, 9 H, *Me$_3$*SiCH$_2$CH$_2$), 0.88 (m, 2 H, Me$_3$Si*CH$_2$*CH$_2$), 1.34, 1.52 (2 s, 6 H, Me$_2$C), 1.98−2.07 (4 s, 12 H, 4 AcO), 2.86 (m, 1 H, 5b-*H*), 3.49 (m, 1 H, Me$_3$SiCH$_2$*CH$_2$*), 3.70−3.79 (m, 3 H, Me$_3$SiCH$_2$*CH$_2$*, 5a-*H*, 7a-*H*), 3.88−4.04 (m, 4 H, 4a-*H*, 6a-*H*, 6b-*H*, 7a-*H*), 4.08 (d, $J_{2,3}$ = 5.5 Hz, 1 H, 2a-*H*), 4.13 (dd, $J_{5,6'}$ = 4.4, $J_{6,6'}$ = 12.1 Hz, 1 H, 6′b-*H*), 4.30 (d, $J_{1,2}$ = 7.3 Hz, 1 H, 1b-*H*), 4.31 (t, $J_{2,3}$ = $J_{3,4}$ = 5.5 Hz, 1 H, 3a-*H*), 4.52−4.59 (3 d, 3 H, Ph*CH$_2$*), 4.92 (m, 4 H, 2b-*H*, 3b-*H*, 4b-*H*, Ph*CH$_2$*), 5.10 (s, 1 H, 1a-*H*), 7.28−7.45 (m, 10 H, ArH). $C_{43}H_{60}O_{16}Si$ (861.02): calcd. C 59.98, H 7.02; found C 59.85, H 6.83.

2-(Trimethylsilyl)ethyl (2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-6,7-di-*O*-benzyl-L-*glycero*-α-D-*manno*-heptopyranoside (21): Compound **20** (810 mg, 0.94 mmol) was treated with acetic acid (8 mL) and water (2 mL) as described for the synthesis of **11**. After the workup, the residue was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:2) to give **21** (741 mg, 96%). $[\alpha]_D$ = +61.9 (*c* = 1.2, $CHCl_3$). IR: $\tilde{\nu}$ = 3650−3200 (OH), 3100−2800 (CH), 1760 and 1240 (ester), 860 and 840 (C-Si), and 740 and 700 (phenyl) cm^{-1}. ^{1}H NMR (500 MHz): δ = 0.00 (s, 9 H, *Me$_3$*SiCH$_2$CH$_2$), 0.86, 0.94 (m, 2 H, Me$_3$Si*CH$_2$*CH$_2$), 2.01−2.11 (4 s, 12 H, 4 AcO), 3.24 (m, 1 H, 5b-*H*), 3.47 (m, 1 H, Me$_3$SiCH$_2$*CH$_2$*), 3.66−3.94 (m, 8 H, Me$_3$SiCH$_2$*CH$_2$*, 2a-*H*, 3a-*H*, 4a-*H*, 5a-*H*, 6a-*H*, 7a-*H*, 7′a-*H*), 4.07 (dd, $J_{5,6}$ = 5.5, $J_{6,6'}$ = 12.4 Hz, 1 H, 6b-*H*), 4.18 (dd, $J_{5,6'}$ = 2.9, $J_{6,6'}$ = 12.4 Hz, 1 H, 6′b-*H*), 4.30 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1b-*H*), 4.52−4.57 (3 d, 3 H, Ph*CH$_2$*), 4.85−5.01 (m, 5 H, 1a-*H*, 2b-*H*, 3b-*H*, 4b-*H*, Ph*CH$_2$*), 7.28−7.48 (m, 10 H, ArH). $C_{40}H_{56}O_{16}Si$ (820.96): calcd. C 58.52, H 6.88; found C 58.46, H 6.81.

2-(Trimethylsilyl)ethyl (2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-6,7-di-*O*-benzyl-3-*O*-(*p*-methoxybenzyl)-L-*glycero*-α-D-*manno*-heptopyranoside (22): A solution of **21** (358 mg, 0.43 mmol) in benzene (7 mL) was stirred in the presence of molecular sieves (4 Å; 0.7 g) at room temperature for 1 h, and dibutyltin oxide (217 mg, 0.86 mmol) was added. After the system had been stirred under reflux for 12 h, tetrabutylammonium bromide (140 mg, 0.43 mmol) and *p*-methoxybenzyl chloride (118 μL, 0.86 mmol) were added, and the mixture was stirred under reflux for an additional 6 h. Insoluble materials were removed by filtration (Celite), and washed with chloroform. The filtrate and washings were combined and concentrated to a syrup, which was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:3) to give **22** (307 mg, 74%). $[\alpha]_D$ = +45.6 (*c* = 1.8, $CHCl_3$). IR: $\tilde{\nu}$ = 3650−3200 (OH), 3100−2800 (CH), 1760 and 1240 (ester), 860 and 840 (C−Si), and 740 and 700 (phenyl) cm^{-1}. ^{1}H NMR (500 MHz): δ = 0.00 (s, 9 H, *Me$_3$*SiCH$_2$CH$_2$), 0.87 (m, 2 H, Me$_3$Si*CH$_2$*CH$_2$), 1.96−2.00 (4 s, 12 H, 4 AcO), 2.79 (m, 1 H, 5b-*H*), 3.43 (m, 1 H, Me$_3$SiCH$_2$*CH$_2$*), 3.64−3.73 (m, 4 H, Me$_3$SiCH$_2$*CH$_2$*, 3a-*H*, 5a-*H*, 7′a-*H*), 3.79 (s, 3 H, MeO), 3.83 (broad d, 1 H, 2a-*H*), 3.87−3.94 (m, 2 H, 6′b-*H*, 7a-*H*), 4.04−4.13 (m, 4 H, 1b-*H*, 4a-*H*, 6a-*H*, 6b-*H*), 4.48−4.74 (5 d, 5 H, Ph*CH$_2$*), 4.84−4.99 (m, 5 H, 1a-*H*, 2b-*H*, 3b-*H*, 4b-*H*, Ph*CH$_2$*), 6.82−7.44 (m, 14 H, ArH). $C_{48}H_{64}O_{17}Si$ (941.11): calcd. C 61.26, H 6.85; found C 61.12, H 6.72.

2-(Trimethylsilyl)ethyl (2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-2-*O*-benzoyl-6,7-di-*O*-benzyl-3-*O*-(*p*-methoxybenzyl)-L-*glycero*-α-D-*manno*-heptopyranoside (23): Benzoyl chloride (26 μL, 0.22 mmol) was added at 0 °C to a solution of **22** (110 mg, 0.11 mmol) in pyridine (2 mL), and the mixture was stirred for 8 h at room temperature. After addition of methanol at 0 °C, the mixture was concentrated with toluene. The residue was extracted with chloroform, and the organic layer was washed with 2 M HCl and

water, dried with anhydrous Na_2SO_4, and concentrated. The residue was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:2) to give **23** (114 mg, 94%). $[\alpha]_D = -22.4$ (c = 1.8, $CHCl_3$). IR: $\tilde{\nu}$ = 3100−2800 (CH), and 1760 and 1240 (ester), 860 and 840 (C−Si), and 740 and 700 (phenyl) cm^{-1}. ^1H NMR (400 MHz): δ = 0.00 (s, 9 H, $Me_3SiCH_2CH_2$), 0.89 (m, 2 H, $Me_3SiCH_2CH_2$), 1.75−1.99 (4 s, 12 H, 4 AcO), 2.89 (m, 1 H, 5b-*H*), 3.47 (m, 1 H, $Me_3SiCH_2CH_2$), 3.68−3.82 (m, 7 H, $Me_3SiCH_2CH_2$, 5a-*H*, 6′b-*H*, 7′a-*H*, *Me*O), 3.89 (m, 2 H, 3a-*H*, 7a-*H*), 4.00 (dd, 1 H, 6b-*H*), 4.11−4.19 (m, 2 H, 1b-*H*, 6a-*H*), 4.29 (t, 1 H, 4a-*H*), 4.50−4.63 (6 d, 6 H, 3 $PhCH_2$), 4.90−4.96 (m, 4 H, 1a-*H*, 2b-*H*, 3b-*H*, 4b-*H*), 5.46 (m, 1 H, 2a-*H*), 6.77−8.06 (m, 19 H, ArH). $C_{55}H_{68}O_{18}Si$ (1045.22): calcd. C 63.20, H 6.56; found C 62.99, H 6.34.

2-(Trimethylsilyl)ethyl (2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-2-*O*-benzoyl-6,7-di-*O*-benzyl-L-*glycero*-α-D-*manno*-heptopyranoside (24): Diammonium cerium(IV) nitrate (CAN; 151 mg, 0.27 mmol) was added to a solution of **23** (96 mg, 91 μmol) in a mixture of acetonitrile (2.7 mL) and water (0.3 mL), and the mixture was stirred at room temperature for 1 h. The mixture was extracted with chloroform, and the organic layer was washed with sat. $NaHCO_3$ and water, dried with anhydrous Na_2SO_4, and concentrated. The residue was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:3) to give **24** (80 mg, 95%). $[\alpha]_D = +9.7$ (c = 1.8, $CHCl_3$). IR: $\tilde{\nu}$ = 3600−3400 (OH), 3100−2800 (CH), 1760 and 1220 (ester), 860 and 840 (C−Si), and 740 and 700 (phenyl) cm^{-1}. ^1H NMR (500 MHz): δ = 0.00 (s, 9 H, $Me_3SiCH_2CH_2$), 0.99 (m, 2 H, $Me_3SiCH_2CH_2$), 1.71−2.03 (4 s, 12 H, 4 AcO), 3.23 (m, 1 H, 5b-*H*), 3.47 (m, 1 H, $Me_3SiCH_2CH_2$), 3.60 (s, 1 H, OH-3), 3.67−3.75 (m, 3 H, $Me_3SiCH_2CH_2$, 3a-*H*, 7′a-*H*), 3.84 (t, $J_{3,4} = J_{4,5}$ = 9.4 Hz, 4a-*H*), 3.88−3.93 (m, 3 H, 6a-*H*, 6b-*H*, 7a-*H*), 4.01−4.07 (m, 2 H, 3a-*H*, 6b-*H*), 4.50−4.58, 5.04 (4 d, 4 H, 2 $PhCH_2$), 4.80−4.87 (m, 2 H, 2b-*H*, 4b-*H*), 4.93−4.96 (m, 2 H, 1a-*H*, 3b-*H*), 5.39 (m, 1 H, 2a-*H*), 7.24−8.08 (m, 15 H, ArH). $C_{47}H_{60}O_{17}Si$ (925.07): calcd. C 61.02, H 6.54; found C 60.77, H 6.46.

2-(Trimethylsilyl)ethyl (2,4,6,7-Tetra-*O*-benzyl-3-*O*-levulinoyl-L-*glycero*-α-D-*manno*-heptopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)]-2-*O*-benzoyl-6,7-di-*O*-benzyl-L-*glycero*-α-D-*manno*-heptopyranoside (25): A solution of **16** (222 mg, 0.31 mmol) and **24** (178 mg, 0.19 mmol) in dichloromethane (2 mL) was stirred at room temperature for 2 h in the presence of molecular sieves (4 Å; 1 g). After the mixture had been cooled to −50 °C, *N*-iodosuccinimide (NIS; 86 mg, 0.38 mmol) and TMSOTf (4 μL, 19 μmol) were added, and the mixture was stirred at −50 °C for 24 h. Insoluble materials were removed by filtration (Celite) and washed with chloroform. The filtrate and washings were combined and diluted with chloroform, and the organic layer was washed with sat. Na_2CO_3 and sat. $Na_2S_2O_3$, dried with anhydrous Na_2SO_4, and concentrated. The residue was chromatographed on a column of silica gel (ethyl acetate/hexane, 2:3) to give **25** (116 mg, 54%). $[\alpha]_D = -19.2$ (c = 1.2, $CHCl_3$). IR: $\tilde{\nu}$ = 3100−2800 (CH), 1760 and 1220 (ester), 860 and 840 (C−Si), and 740 and 700 (phenyl) cm^{-1}. ^1H NMR (500 MHz): δ = 0.07 (s, 9 H, $Me_3SiCH_2CH_2$), 0.89 (m, 2 H, $Me_3SiCH_2CH_2$), 1.54−2.04 (5 s, 15 H, 4 AcO, *Me*C-OCH_2CH_2), 2.21−2.53 (m, 4 H, $MeCOCH_2CH_2$), 2.58 (m, 1 H, 5b-*H*), 3.43, 3.67 (m, 2 H, $Me_3SiCH_2CH_2$), 3.72−4.14 (m, 12 H, 1b-*H*, 2c-*H*, 5a-*H*, 5c-*H*, 6a-*H*, 6b-*H*, 6′b-*H*, 6c-*H*, 7a-*H*, 7′a-*H*, 7c-*H*, 7′c-*H*), 4.22−4.36 (m, 3 H, 3a-*H*, 4a-*H*, 4c-*H*), 4.39 (d, 1 H, $PhCH_2$), 4.50−4.74 (m, 11 H, 2b-*H*, 4b-*H*, $PhCH_2$), 4.84−4.88 (m, 2 H, 3b-*H*, $PhCH_2$) 4.89 (d, $J_{1,2}$ = 1.6 Hz, 1 H, 1a-*H*), 5.10 (d, 1 H, $PhCH_2$), 5.18 (dd, $J_{2,3}$ = 2.9, $J_{3,4}$ = 10.1 Hz, 3c-*H*), 5.29 (s, 1 H, 1c-*H*), 5.42 (dd, $J_{1,2}$ = 1.8, $J_{2,3}$ = 2.9 Hz, 2a-*H*), 7.15−8.11 (m, 35 H, ArH). $C_{87}H_{102}O_{25}Si$ (1575.83): calcd. C 66.31, H 6.52; found C 66.15, H 6.48.

2-(Trimethylsilyl)ethyl (2,4,6,7-Tetra-*O*-benzyl-L-*glycero*-α-D-*manno*-heptopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)]-2-*O*-benzoyl-6,7-di-*O*-benzyl-L-*glycero*-α-D-*manno*-heptopyranoside (26): Hydrazine acetate (69 mg, 0.72 mmol) was added to a solution of **25** (115 mg, 72 μmol) in ethanol (2 mL), which was stirred at room temperature for 2 h and concentrated. The residue was extracted with chloroform, and the organic layer was washed with water, dried with anhydrous Na_2SO_4, and concentrated. The residue was chromatographed on a column of silica gel (ethyl acetate/hexane, 1:2) to give **26** (80 mg, 74%). $[\alpha]_D = -16.5$ (c = 1.6, $CHCl_3$). IR: $\tilde{\nu}$ = 3650−3400 (CH), 3100−2800 (CH), 1760 and 1220 (ester), 860 and 840 (C−Si), and 740 and 700 (phenyl) cm^{-1}. ^1H NMR (500 MHz): δ = 0.00 (s, 9 H, $Me_3SiCH_2CH_2$), 0.94 (m, 2 H, $Me_3SiCH_2CH_2$), 1.69−2.03 (4 s, 12 H, 4 AcO), 2.31 (d, $J_{OH,3}$ = 9.2 Hz, 1 H, OH-3), 2.58 (m, 1 H, 5b-*H*), 3.48 (m, 1 H, $Me_3SiCH_2CH_2$), 3.69−4.24 (m, 15 H, 1b-*H*, 2c-*H*, 3c-*H*, 4c-*H*, 5a-*H*, 5c-*H*, 6a-*H*, 6b-*H*, 6′b-*H*, 6c-*H*, 7a-*H*, 7′a-*H*, 7c-*H*, 7′c-*H*), 4.23 (dd, $J_{2,3}$ = 2.9, $J_{3,4}$ = 9.4 Hz, 3a-*H*), 4.37 (t, $J_{3,4}$ = 9.8, $J_{4,5}$ = 9.6 Hz, 4a-*H*), 4.42 (d, 1 H, $PhCH_2$), 4.54−4.61 (6 d, 6 H, 3 $PhCH_2$), 4.69−4.92 (m, 7 H, 2b-*H*, 3b-*H*, 4b-*H*, $PhCH_2$), 4.93 (d, $J_{1,2}$ = 1.4 Hz, 1 H, 1a-*H*), 5.14 (d, 1 H, $PhCH_2$), 5.33 (s, 1 H, 1c-*H*), 5.42 (dd, $J_{1,2}$ = 1.8, $J_{2,3}$ = 2.9 Hz, 2a-*H*), 7.22−8.09 (m, 35 H, ArH). $C_{82}H_{96}O_{23}Si$ (1477.73): calcd. C 66.65, H 6.55; found C 66.50, H 6.29.

2-(Trimethylsilyl)ethyl [Methyl 5-acetamido-8-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylono-1,9-lactone)-4,7-di-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-(2,4,6,7-tetra-*O*-benzyl-L-*glycero*-α-D-*manno*-heptopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)]-2-*O*-benzoyl-6,7-di-*O*-benzyl-L-*glycero*-α-D-*manno*-heptopyranoside (28): A solution of **26** (61 mg, 41 μmol) and **27** (106 mg, 72 μmol) in dichloromethane (2 mL) was stirred at room temperature for 2 h in the presence of molecular sieves (4 Å; 0.8 g). TMSOTf (2.6 μL, 14 μmol) was added to the mixture, which was stirred at room temperature for 24 h. Insoluble materials were removed by filtration (Celite) and washed with chloroform. The filtrate and washings were combined and washed with sat. $NaHCO_3$, dried with anhydrous Na_2SO_4, and concentrated. The residue was chromatographed on a column of silica gel (chloroform/methanol, 50:1) to give **28** (55 mg, 48%). $[\alpha]_D = -23.6$ (c = 1.3, $CHCl_3$). IR: $\tilde{\nu}$ = 3700−3100 (NH), 3100−2800 (CH), 1740 and 1240 (ester), 1680−1540 (amide), 860 and 840 (C−Si), and 740 and 700 (phenyl) cm^{-1}. ^1H NMR (500 MHz): δ = 0.07 (s, 9 H, $Me_3SiCH_2CH_2$), 0.89 (m, 2 H, $Me_3SiCH_2CH_2$), 1.61 (m, 1 H, 3fax-*H*), 1.70−2.11 (12 s, 36 H, 10 AcO, 2 AcN), 1.87 (m, 1 H, 3eax-*H*), 2.02 (m, 1 H, 3eeq-*H*), 2.45 (dd, J_{gem} = 13.5, $J_{3,4}$ = 5.3 Hz, 1 H, 3feq-*H*), 2.86 (m, 1 H, 5b-*H*), 3.25 (s, 3 H, MeO), 3.40 (m, 1 H, $Me_3SiCH_2CH_2$), 3.51 (bd, 1 H, 9′e-*H*), 3.64 (m, 1 H, $Me_3SiCH_2CH_2$), 3.83 (dd, $J_{5,6}$ = 10.5, $J_{6,7}$ = 2.9 Hz, 1 H, 6f-*H*), 4.36 (m, 1 H, 4a-*H*), 4.43 (d, 1 H, $PhCH_2$), 4.49−4.67 (m, 11 H, 2b-*H*, 3d-*H*, 4b-*H*, $PhCH_2$), 4.74−4.81 (m, 4 H, 1a-*H*, 1d-*H*, 7e-*H*, $PhCH_2$), 4.94 (t, $J_{2,3} = J_{3,4}$ = 9.4 Hz, 3b-*H*), 5.06 (m, 1 H, 4e-*H*), 5.11−5.16 (m, 3 H, 8f-*H*, $PhCH_2$), 5.27−5.33 (m, 4 H, 1c-*H*, 7f-*H*, 5e-*NH*, 5f-*NH*), 5.40 (s, 1 H, 2a-*H*), 5.53−5.59 (m, 2 H, 2d-*H*, 4f-*H*), 5.63(d, $J_{3,4}$ = 2.7 Hz, 4d-*H*), 6.83−8.08 (m, 50 H, ArH). $C_{144}H_{164}N_2O_{52}Si$ (2782.95): calcd. C 62.15, H 5.94; found C 61.98, H 5.80.

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