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Synthesis of Tri-, Hexa-, and Nonasaccharide Subunits of the Atypical O-Antigen Polysaccharide of the Lipopolysaccharide from Danish *Helicobacter pylori* Strains

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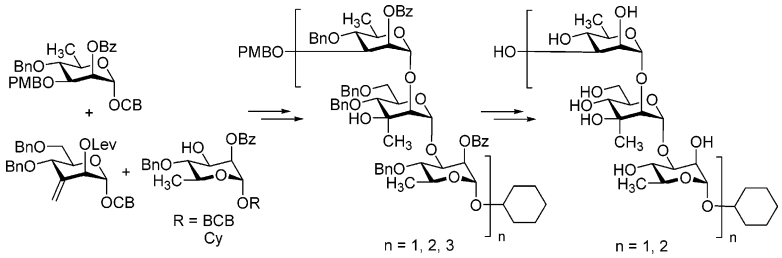

Synthesis of trisaccharide repeating unit, →3)-α-D-Rha*p*-(1→2)-α-D-Man*p*3CMe-(1→3)-α-L-Rha *p*-(1→, and its dimeric hexa- and trimeric nonasaccharide subunits of the atypical O-antigen polysaccharide of the lipopolysaccharide from Danish *H. pylori* strains D1, D3, and D6 has been accomplished. Successful synthesis of the hexasaccharide and the nonasaccharide was possible by dimerization and trimerization of the suitably protected trisaccharide repeating unit, in which three monosaccharide moieties were arranged in a proper order by placing the sterically demanding 3-*C*-methyl-D-mannose moiety in between D- and L-rhamnoses. Key steps include the coupling of three monosaccharide moieties and dimerization and trimerization of the trisaccharide unit by glycosylations employing the 2′-carboxybenzyl glycoside method. Also presented is a method for the synthesis of the novel branched sugar, 3-*C*-methyl-D-mannose moiety by elaboration of its equatorial hydroxyl and axial methyl groups at C-3′ in the disaccharide stage.

Since the first isolation of *Helicobacter pylori*,[1] extensive studies have led to recognition of this bacterium as the major cause of chronic gastritis and gastric and duodenal ulcers.[2] Moreover, persistent infection with *H. pylori* is strongly associated with the risk of development of gastric cancer.[2,3] *H. pylori* is estimated to infect over one-half of the world's population and thus has been classified as a category 1 (definite) human carcinogen.[4] Although the antibiotic therapy is currently used to manage *H. pylori* infections, this strategy has several drawbacks as antibiotic-resistant strains have emerged.[5] Like the cell envelope of other gram-negative bacteria, that of *H. pylori* contains lipopolysaccharides (LPS), which is known to contribute to the pathogenesis. It has also been reported that LPS from some *H. pylori* strains can act as antagonists for Toll-like receptor 4.[6] The O-antigen polysaccharide is a part of the LPS, which interacts with the bacterial microenvironment and the infected host. Structural studies on the LPS of a number of *H. pylori* strains have shown that the O-antigen polysaccharide exhibits mimicry of Lewis blood group antigens by expression of the corresponding determinants in the O-chain or located at nonreducing end of the O-chain polysaccharide.[7] Consequently,

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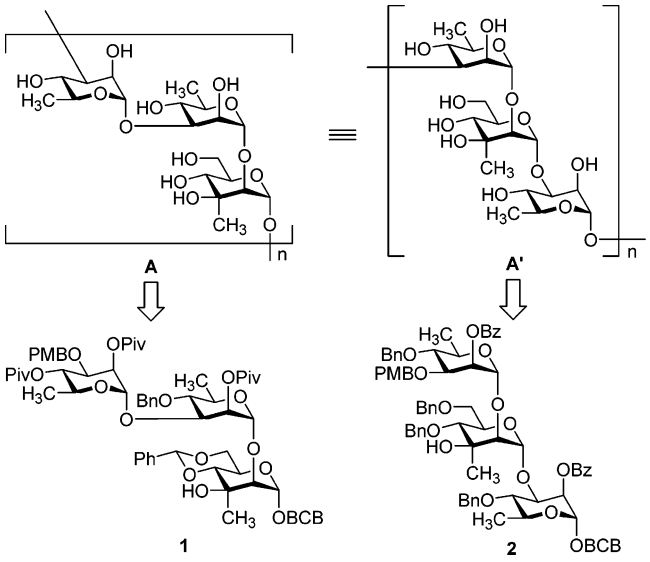
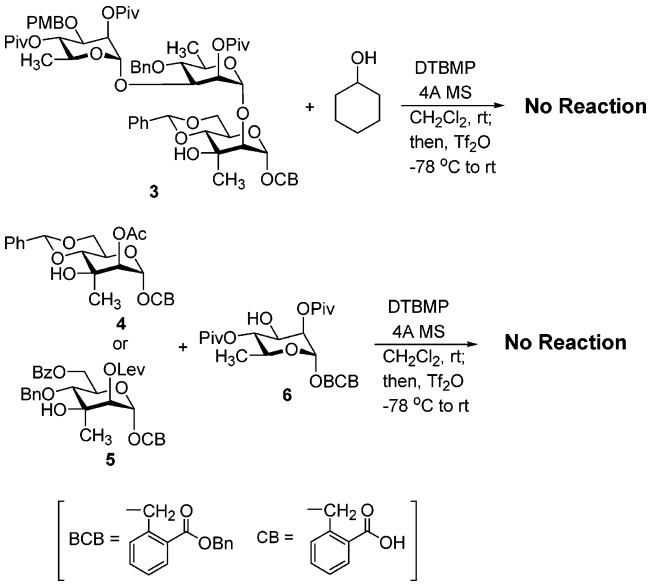


FIGURE 1. The repeat unit of the O-antigen polysaccharide of LPS from Danish *H. pylori* strains.

a number of studies have been performed to account for the pathogenic relevance of Lewis antigen mimicry by *H. pylori*.[8] And there have also been immunization studies with inactivated *H. pylori* whole-cell vaccines having homologous and heterologous LPS O-antigens expressing different Lewis antigens[9] and with *H. pylori* outer membrane vesicles, which is enriched with LPS.[10] It has also been reported that *H. pylori* LPS in a whole cell sonicate vaccine promotes a Th1 immune response that may aid in protection or clearance of *H. pylori* infections.[11] Recently, however, an atypical O-antigen polysaccharide of LPS from Danish *H. pylori* strains D1, D3, and D6 was isolated and the following structure of the trisaccharide repeating unit of the O-polysaccharide was established: →3)-α-L-Rha*p*-(1→3)-α-D-Rha*p*-(1→2)-α-D-Man*p*3CMe-(1→ (**A**) (Figure 1).[12] Unusual feature of this *O*-polysaccharide is the occurrence of a novel branched sugar, 3-*C*-methyl-D-mannose, which has not been found in Nature before and the simultaneous occurrence of both L-rhamnose and D-rhamnose. Owing to its structural uniqueness and biological and medical potential, not only the trisaccharide repeating unit **A** but also its dimeric hexasaccharide and trimeric nonasaccharide subunits are attractive synthetic targets. A few years ago, therefore, we reported the synthesis of trisaccharide **1** as a protected form of the repeating unit **A** by coupling of three monosaccharide building blocks[13] employing the 2′-carboxybenzyl (CB) glycoside method.[14] However, we have found that the trisaccharide **1** was not the proper monomeric unit for the synthesis of its oligomeric subunits. Herein we report the synthesis of newly designed trisaccharide **2**, in a suitably protected form of repeating unit **A**′ and the synthesis of its dimeric hexasaccharide and trimeric nonasaccharide as well.

SCHEME 1. Model Study for the Glycosylation with CB C-3-Methyl-glycosides 3, 4, and 5 as Glycosyl Donors



In order to achieve our goal for the synthesis of oligosaccharide subunits of the O-antigen polysaccharide of LPS from Danish *H. pylori* strains, it was essential to establish the efficient procedure for oligomerizations of the trisaccharide **1** by glycosylation reactions. Before dimerization and trimerization of **1**, we carried out a model study for the glycosylation with CB trisaccharide **3** as the glycosyl donor, which was obtained from **1** by selective hydrogenolysis. The CB trisaccharide **3** found to be unreactive as the glycosyl donor, and thus the coupling reaction of **3** with cyclohexanol did not provide a desired cyclohexyl glycoside (Scheme 1). We also found that CB monosaccharide donors **4** and **5** both having an axial C-3 methyl group were quite unreactive as glycosyl donors. Thus, the glycosylation of L-rhamnoside **6** with CB monosaccharide **4** or **5** did not proceed under the general reaction condition of the CB glycoside method[14,15] but rather provided a mixture of unknown products upon warming or for prolonged reaction time. Unreactivities of **3**, **4**, and **5** as glycosyl donors in the coupling reactions with cyclohexanol or **6** might be attributed to the steric hindrance imposed by the C-3 axial methyl group to the C-1 reactive site. Therefore, we changed our synthetic strategy by planning to synthesize new trisaccharide repeating unit **A**′, →3)-α-D-Rha*p*-(1→2)-α-D-Man*p*3CMe-(1→3)-α-L-Rha*p*-(1→, in which the sterically demanding α-D-Man*p*3CMe moiety was placed in between two other monosaccharide moieties, D- and L-rhamnose so that the axial 3-*C*-methyl group in the 3-*C*-methyl-D-mannose would not interfere with dimerization and

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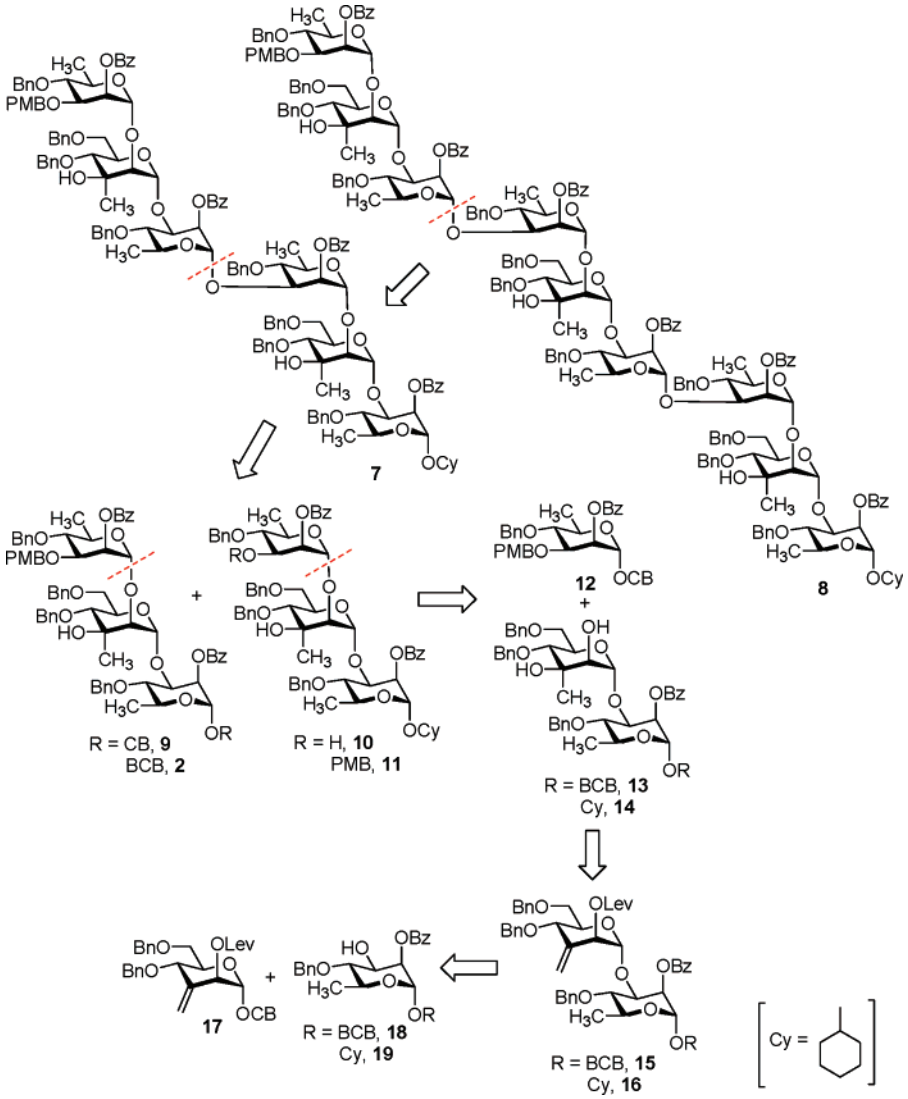
SCHEME 2. Retrosynthesis of Trisaccharides 2 and 11, Hexasaccharide 7, and Nonasaccharide 8

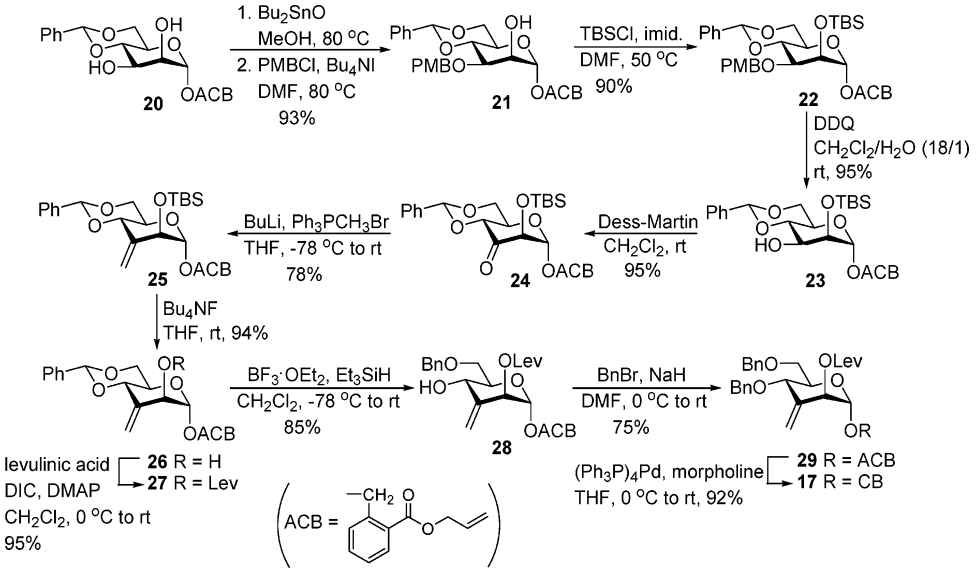


trimerization of the trisaccharide unit. The trisaccharide repeating unit **A′** would eventually give same oligosaccharides as the trisaccharide repeat unit **A** after oligomerization, and thus we designed new target trisaccharide **2** as a suitably protected form of the repeating unit **A′**.

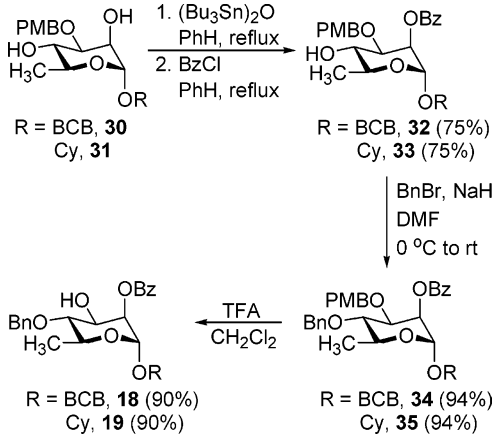
Retrosynthesis of the trisaccharide **2** and its dimeric hexasaccharide **7** and trimeric nonasaccharide **8** leads to three monosaccharide building blocks **12**, **17**, and **18** or **19** (Scheme 2). The CB glycoside method would be here used extensively for the coupling of all three monosaccharide components of trisaccharides **2** and **11** as well as for the assembly of trisaccharide units of hexasaccharide **7** and nonasaccharide **8**. The protective groups were carefully chosen for the synthesis of the first target trisaccharides **2** and **11** since they should be selectively removed in the next stage for the synthesis of hexasaccharide **7** and nonasaccharide **8** by dimerization and trimerization of **2** and **11**. Thus, the latent 2′-(benzyloxycarbonyl)benzyl (BCB) group[13−15] at C-1 in the reducing end of the trisaccharide **2** would be readily converted into the active 2′-carboxybenzyl (CB) group to give trisaccharide donor **9**. The *p*-methoxybenzyl (PMB) group at C-3 in the nonreducing end of **11** would also be selectively cleaved to provide trisaccharide acceptor **10**. Retrosynthesis of **2** leads to CB D-rhamnoside donor **12** and disaccharide acceptor **13**. At this juncture it was assumed that the disaccharide **13** could not be obtained directly by coupling of completely elaborated monosaccharide building blocks, namely, a 3-*C*-methyl mannoside donor and an L-rhamnoside acceptor, based on the consideration of the model study shown in Scheme 1. So we envisaged that the axial methyl and equatorial hydroxyl groups at C-3′ in **13** would be elaborated in the disaccharide stage from the C-3′ methylene group of disaccharide **15**. Synthesis of **15** would be possible by the glycosylation of acceptor **18** with donor **17**, of which the C-3 methylene group is less sterically demanding than the C-3 axial methyl group and thus would not interfere with the glycosylation. Trisaccharide **11** having cyclohexyl L-rhamnoside moiety at reducing end would be also synthesized in a manner similar to the synthesis of the BCB trisaccharide **2**.

Synthesis of the C-3-methylene-D-mannose building block **17** started with the known 2′-(allyloxycarbonyl)benzyl (ACB) mannoside **20**[15c] (Scheme 3). Introduction of the ACB group in the place of the previously used BCB group was necessary because the alkene functionality at C-3 in **29** was also reduced during conversion of the BCB group into the CB group under the hydrogenolysis condition. The hydroxy group at C-3 of the diol **20** was selectively protected with the *p*-methoxybenzyl

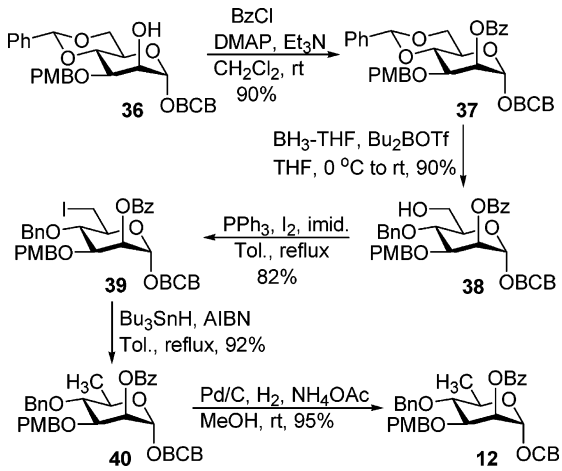
SCHEME 3. Synthesis of CB 3-*C*-Methylene-mannoside 17



SCHEME 4. Synthesis of l-Rhamnosides 18 and 19



SCHEME 5. Synthesis of CB d-Rhamnoside 12



(PMB) group by using the dibutyltin oxide method[16] to give C-3 PMB ether **21** in 93% yield in two steps with complete regioselectivity. Treatment of **21** with TBSCl afforded fully protected sugar **22**, and the deprotection of PMB group in **22** with DDQ provided C-3 hydroxyl sugar **23** in high yield. Oxidation of **23** with Dess−Martin periodinane[17] gave ketosugar **24** in 95% yield, while that with PDC afforded **24** in 70% yield. Wittig reaction of **24** with triphenylphosphonium methylide, formed *in situ*, smoothly gave olefin **25** in 78% yield. The TBS group in **25** was removed by Bu_4NF, and the subsequent protection of resulting C-2 hydroxy sugar **26** with levulinic acid in the presence of diisopropylcarbodiimide (DIC) afforded C-2 Lev-protected sugar **27**. We decided in this stage to change the 4,6-*O*-benzylidene protective group of **27** to the benzyl group because the benzylidene group of the CB glycoside, derived from the ACB glycoside **27**, was cleaved even at low temperature during the glycosylation, in which a slight excess of Tf_2O over DTBMP has been used in order to suppress the generation of an orthoester. The unusual instability of the benzylidene group might be attributable to the effect of the nearby C-3 methylene group since the usual 4,6-*O*-benzylidene group having no C-3 methylene group is stable under the acidic CB glycosylation condition. When excess of DTBMP was employed to prevent the cleavage of the benzylidene group during the glycosylation, indeed, the orthoester was generated exclusively. Therefore, the 4,6-*O*-benzylidene sugar **27** was transformed to 4,6-di-*O*-benzyl sugar **29**. However, cleavage of the benzylidene group of **27** under acidic condition and the subsequent benzylation of the resulting diol under basic condition did not provide a desired product but rather afforded an undesired 6-*O*-levulinyl sugar by migration of the levulinyl group from O-2 to O-6 under the basic condition. Migration of the TBS group from O-2 to O-6 also occurred in the same reaction with compound **25**. To prevent the migration of the levulinyl group during benzylation, C-6 benzyl ether **28** was prepared directly from **27** by the reductive cleavage of the benzylidene acetal of **27** with $BF_3 \cdot OEt_2$ and Et_3SiH[18] in 85% yield, and the subsequent benzylation of the C-4 hydroxyl group of **28** gave desired dibenzyl ether **29**. Then, the latent ACB glycoside **29** was readily converted into active CB glycoside **17** in 92% yield by deallylation with a catalytic amount of $Pd(Ph_3P)_4$ in the presence of morpholine.[19]

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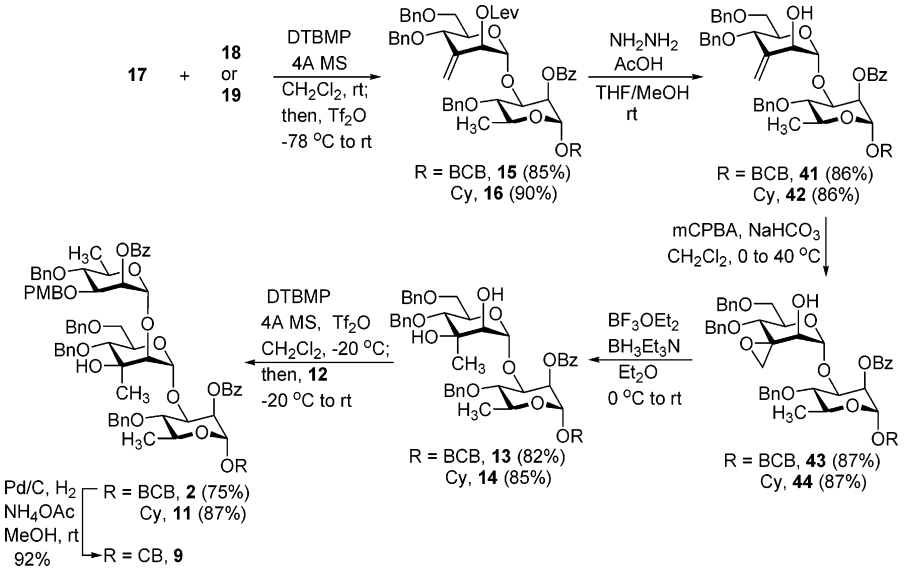
SCHEME 6. Synthesis of Trisaccharides 2 and 11



This result indicates that ACB glycosides are the useful precursor for CB glycosides especially in the presence of the alkene functionality, which could not survive during conversion of BCB glycosides into CB glycosides by hydrogenolysis.

Synthesis of BCB L-rhamnoside **18**, which would become the reducing terminal of the trisaccharide **2**, started from known BCB L-rhamnoside **30**[13] as shown in Scheme 4. Treatment of diol **30** with $(Bu_3Sn)_2O$ in refluxing benzene and the subsequent reaction of resulting stannylene acetal with benzoyl chloride afforded C-2 benzoate **32** in 75% yield. Benzylation of **32** followed by the deprotection of PMB group in resultant fully protected sugar **34** with trifluoroacetic acid provided C-3 hydroxyl sugar **18** in high yield. Cyclohexyl L-rhamnoside **19**, which would become the permanent reducing end of the tri-, hexa-, and nonasaccharide, was also readily obtained from **31**[20] in a manner similar to the synthesis of **18** from **30**.

D-Rhamnose moiety **12** was prepared starting from known BCB mannoside **36**[13] (Scheme 5). Benzoylation of **36** followed by the reductive cleavage of the benzylidene group in resulting benzoate **37** with borane in the presence of Bu_2BOTf[21] afforded C-4 benzyl ether **38** having a free hydroxyl group at C-6 in high yield. Iodination of the primary alcohol **38** with Ph_3P and I_2 provided iodide **39** without difficulty. Free radical-mediated reduction of the iodide **39** with Bu_3SnH in the presence of AIBN resulted in the formation of 6-deoxy sugar **40** in high yield. Hydrogenolysis of the latent BCB D-rhamnoside **40** in the presence of ammonium acetate afforded active CB D-rhamnoside **12** in excellent yield.

The stage was set for the assembly of properly protected monosaccharide building blocks **12**, **17**, **18**, and **19** to make trisaccharides **2** and **11** (Scheme 6). Coupling of the CB C-3-methylene-mannoside **17** with the BCB L-rhamnoside **18** or with the cyclohexyl L-rhamnoside **19** was achieved by the addition of Tf_2O to the mixture of **17** and **18** or **19** in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) and 4 Å MS in CH_2Cl_2 at −78 °C followed by warming up the reaction mixture to room temperature. The desired α-disaccharides **15** and **16** were obtained in 85% and 90% yield, respectively. The levulinyl group in **15** was removed by hydrazine, and the epoxidation of resulting allylic alcohol **41** with mCPBA at 40 °C afforded desired spiroepoxide **43** in high yield with complete stereoselectivity. The exclusive *β*-face delivery of oxygen by mCPBA to the C-3′ double bond of the disaccharide **41** could be attributed to a steric effect and to the hydrogen bond between mCPBA and the C-2′ OH of **41**. Reductive ring opening of the spiroepoxy sugar **43** with Bu_3SnH in the presence of NaI and AIBN,[22] which we used previously for the same purpose in the synthesis of the trisaccharide **1**,[13] gave desired 3′-*C*-methyl-mannosyl disaccharide **13** in only 31% yield (entry 1 in Table 1) while the same reaction with Bu_3SnH/LiI/AIBN gave **13** in 58% yield (entry 2). A satisfactory result was obtained by reduction of the spiroepoxy disaccharide **43** with $BH_3{\cdot}Et_3N$ in the presence of a Lewis acid. Thus, chemoselective reduction of the epoxide **43** with $BH_3{\cdot}Et_3N/BF_3{\cdot}Et_2O$ in CH_2Cl_2 afforded desired disaccharide **13** in 82% yield (entry 5) whereas the same reaction did not proceed with $BH_3{\cdot}Et_3N/LiClO_4$ in Et_2O and with $BH_3{\cdot}Et_3N/ZnCl_2$ in CH_2Cl_2[23] (entries 3 and 4). The stereochemistry at C-3′ of **13** was confirmed by its NOESY spectrum, which showed correlations between the methyl group at C-3′ with H-2′ and with H-5′ but not with H-4′. Glycosylation of the BCB disaccharide acceptor **13** with CB D-rhamnoside donor **12** using Tf_2O in the presence of DTBMP afforded desired α-trisaccharide **2** as a single isomer in 75% yield. The stereochemistry at the newly generated anomeric center of **2** was unequivocally determined on the basis of their ^1H and ^{13}C NMR spectral data, especially one-bond C1−H1 coupling

TABLE 1. Chemoselective Reduction of Epoxide 43 to 13 under Various Conditions

entry	reagents	solvent	reaction temp (°C)	yield (%)
1	NaI, AIBN, Bu_3SnH[21]	DME	rt to 90	31
2	LiI, AIBN, Bu_3SnH	DME	reflux	58
3	$LiClO_4$, $BH_3{\cdot}Et_3N$[22]	Et_2O	0 to rt	No rxn.
4	$ZnCl_2$, $BH_3{\cdot}Et_3N$	CH_2Cl_2	rt	No rxn.
5	$BF_3{\cdot}Et_2O$, $BH_3{\cdot}Et_3N$	CH_2Cl_2	rt	82

(20) Compound **31** was readily prepared from cyclohexyl 2,3,4 tri-*O*-acetyl-α-L-rhamnopyranoside (**C-1**), see Supporting Information.

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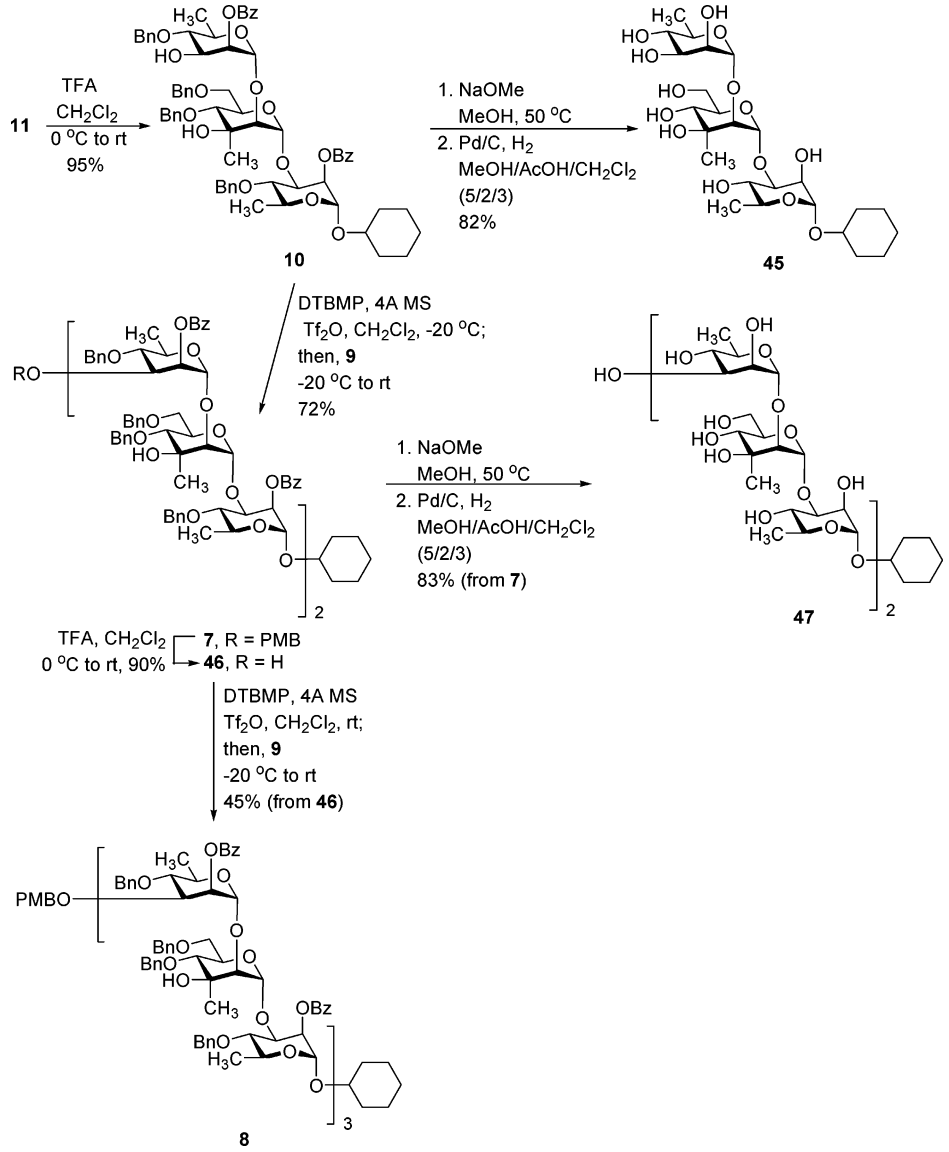
SCHEME 7. Synthesis of Nonasaccharide 8, Deprotected Trisaccharide 45, and Deprotected Hexasaccharide 47



constants: $^1J_{C1'-H1'}$ = 171 Hz in Man, $^1J_{C1-H1}$ = 171 Hz in L-Rha, and $^1J_{C1''-H1''}$ = 173 Hz in D-Rha.[24] Hydrogenolysis of the BCB trisaccharide **2** in the presence of ammonium acetate afforded CB trisaccharide **9** in 92% yield. Trisaccharide **11** as a cyclohexyl glycoside was also obtained from cyclohexyl disaccharide **16** in a manner similar to the synthesis of **2** from **15**.

Deprotection of the PMB group in the fully protected trisaccharide **11** with trifluoroacetic acid gave C-3″ hydroxyl sugar **10** as the trisaccharide acceptor for the hexasaccharide synthesis (Scheme 7). Dimerization of the trisaccharide to the hexasaccharide was carried out by glycosylation of the cyclohexyl trisaccharide acceptor **10** with the CB trisaccharide donor **9**. Thus, slow addition of **9** to the solution of **10** in the presence of Tf_2O and DTBMP in CH_2Cl_2 at −20 °C followed by warming up the reaction mixture to room temperature afforded desired α-hexasaccharide **7** as a single isomer in 72% yield. The protected trisaccharide **10** and hexasaccharide **7** were converted into fully deprotected trisaccharide **45** and hexasaccharide **47**, respectively. Saponification of the benzoyl ester functionality of **10** with sodium methoxide in methanol and subsequent hydrogenolysis over Pd/C catalyst to remove all benzyl protecting groups afforded fully deprotected trisaccharide **45** as a cyclohexyl glycoside in 82% yield. NMR spectral data, especially one-bond C1−H1 coupling constants of **45**, 171, 171, and 172 Hz, clearly indicated that the deprotection procedure did not affect the stereochemistry at all three anomeric centers. Saponification of the protected hexasaccharide **7** and subsequent hydrogenolysis, as described for **10**, also provided fully deprotected hexasaccharide **47** as a cyclohexyl glycoside in high yield without difficulty. One-bond C1−H1 coupling constants of **47** indicated that all six glycosyl bonds had α-configurations.[25] The nonasaccharide, meanwhile, was synthesized by coupling of the CB trisaccharide donor **9** and cyclohexyl hexasaccharide acceptor **46**, which was obtained by deprotection of the PMB group of the hexasaccharide **7** with trifluoroacetic acid. Thus, the coupling was carried out by addition of the donor **9** to the solution of the acceptor **46** in the presence of Tf_2O and DTBMP in CH_2Cl_2 to afford desired α-nonasaccharide **8** in 45% yield.

(24) For C-H coupling constants in pyranoses, see: Bock, K.; Pedersen, C. *J. Chem. Soc., Perkin Trans. 2* **1974**, 293−297.

(25) See one-bond C1−H1 coupling constants in experimental section.

The stereochemistry at the newly generated glycosyl bond in **8** was unambiguously determined on the basis of the one-bond C1−H1 coupling constant.[25]

We have described synthesis of trisaccharides **2** and **11**, the suitably protected form of the trisaccharide repeating unit of an atypical O-antigen polysaccharide of the LPS from Danish *H. pylori* strains D1, D3, and D6. Synthesis of protected hexasaccharide **7** and nonasaccharide **8** was also accomplished by dimerization and trimerization of the trisaccharide, in which the sterically demanding 3-*C*-methyl-D-mannose moiety was placed in between two other sugars, D- and L-rhamnoses. The axial methyl and equatorial hydroxyl groups at C-3 of 3-*C*-methyl-D-mannose were elaborated in disaccharide stage, in compounds **13** and **14**, by epoxidation of the C-3′ double bond of disaccharides **41** and **42** and followed by reduction of resultant epoxides **43** and **44**, respectively. In addition, we have described the synthesis of fully deprotected trisaccharide **45** and hexasaccharide **47** as cyclohexyl glycosides. The 2′-carboxybenzyl (CB) glycoside method proved to be effective in the coupling of three monosaccharide components for the trisaccharide and the coupling of the trisaccharide repeating unit for hexasaccharide **7** and nonasaccharide **8**.

Experimental Section

2′-(Benzyloxycarbonyl)benzyl (4,6-Di-*O*-benzyl-2-*O*-levulinyl-3-deoxy-3-methylene-α-D-*arabino*-hexopyranosyl)-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (15). A solution of CB glycoside **17** (417 mg, 0.71 mmol), BCB glycoside **18** (495 mg, 0.85 mmol, 1.2 equiv), and 2,6-di-*tert*-butyl-4-methylpyridine (262 mg, 1.27 mmol) in CH_2Cl_2 (20 mL) in the presence of 4 Å molecular sieves was stirred for 20 min at room temperature and then cooled down to −78 °C. After addition of Tf_2O (240 μL, 0.85 mmol) to the above solution, the reaction mixture was stirred at −78 °C for 30 min, allowed to warm up over 30 min to room temperature, stirred for further 1.5 h, filtered through Celite, and quenched with saturated aqueous $NaHCO_3$. Organic phase was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 7:2, v/v) to give compound **15** (614 mg, 0.60 mmol, 85%) as a white foam. R_f = 0.13 (hexane/EtOAc, 7:2); $[\alpha]_D$ +61.2 (*c* 0.50, $CHCl_3$); IR ($CHCl_3$ film) 3022, 2939, 2850, 1716, 1454, 1407, 1362, 1257, 1082, 1047, 741, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.39 (d, *J* = 6.0 Hz, 3H), 2.13 (s, 3H), 2.60−2.65 (m, 2H), 2.72−2.76 (m, 2H), 3.48 (t, *J* = 9.6 Hz, 1H), 3.55 (dd, *J* = 6.4, 1.6 Hz, 1H), 3.66 (dd, *J* = 11.0, 3.2 Hz, 1H), 3.83−3.87 (m, 1H), 4.02 (d, *J* = 8.8 Hz, 1H), 4.32 (s, 1H), 4.35 (s, 1H), 4.39−4.47 (m, 3H), 4.61−4.67 (m, 2H), 4.77 (d, *J* = 10.4 Hz, 1H), 4.96 (s, 1H), 4.98 and 5.09 (ABq, *J* = 12.4 Hz, 2H), 5.17 (s, 1H), 5.20 (s, 1H), 5.24 (s, 1H), 5.32 (s, 1H), 5.44 (s, 1H), 5.64 (t, *J* = 1.4 Hz, 1H), 7.05−7.09 (m, 2H), 7.15−7.50 (m, 22H), 7.57−7.63 (m, 2H), 8.00 (dd, *J* = 7.6, 1.2 Hz, 1H), 8.10 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 28.3, 29.9, 38.0, 66.8, 67.4, 68.2, 68.4, 68.7, 72.8, 72.99, 73.02, 73.3, 73.5, 75.3, 75.9, 79.5, 94.5, 97.6, 114.4, 127.2, 127.5, 127.6, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 128.6, 128.7, 129.0, 129.9, 130.0, 130.8, 132.7, 133.3, 136.0, 137.7, 138.3, 139.81, 139.83, 165.8, 166.6, 171.2, 206.4. Anal. calcd for $C_{61}H_{62}O_{14}$: C, 71.89; H, 6.13. Found: C 71.69; H, 6.46

2′-(Benzyloxycarbonyl)benzyl (4,6-Di-*O*-benzyl-3-deoxy-3-methylene-α-D-*arabino*-hexopyranosyl)-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (41). A solution of compound **15** (300 mg, 0.29 mmol), NH_2NH_2 (1.0 M in THF, 1.0 mL), and acetic acid (2.0 mL) in THF/MeOH (5:1, 6.0 mL) was stirred in THF/MeOH (4:1, 25.0 mL). The reaction mixture was stirred at room temperature for 2 h, quenched with saturated $NaHCO_3$, and extracted with ethyl acetate. The organic layer was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (CH_2Cl_2/EtOAc, 10:1, v/v) to give compound **41** (233 mg, 0.25 mmol, 86%) as a colorless viscous oil. R_f = 0.38 (CH_2Cl_2/EtOAc, 10:1); $[\alpha]_D$ +43.8 (*c* 0.50, $CHCl_3$); IR ($CHCl_3$ film) 3400, 2939, 2850, 1716, 1454, 1407, 1362, 1267, 1257, 1093, 1082, 1047, 741, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.37 (d, *J* = 6.4 Hz, 3H), 2.67 (brs, 1H, OH), 3.42−3.58 (m, 3H), 3.83−3.87 (m, 1H), 3.98−4.00 (m, 1H), 4.10 (s, 1H), 4.30−4.39 (m, 4H), 4.46 (d, *J* = 10.0 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 11.2 Hz, 1H), 4.80 (d, *J* = 10.4 Hz, 1H), 4.94−4.96 (m, 2H), 5.06−5.10 (m, 2H), 5.17 (s, 1H), 5.27 (s, 1H), 5.33 (s, 2H), 5.64 (t, *J* = 3.2 Hz, 1H), 7.19−7.64 (m, 26H), 8.00 (dd, *J* = 7.6, 1.2 Hz, 1H), 8.10 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.2, 66.9, 67.5, 68.4, 68.7, 69.3, 72.4, 73.3, 73.6, 74.1, 74.4, 75.9, 79.5, 97.7, 98.4, 112.4, 127.4, 127.6, 127.8, 128.0, 128.1, 128.4, 128.7, 128.8, 128.9, 129.9, 130.1, 130.8, 132.7, 133.6, 136.0, 137.9, 138.2, 138.4, 139.7, 143.0, 166.3, 166.7. HRMS (FAB): $[M + Na]^+$ calcd for $C_{56}H_{56}O_{12}Na$: 943.3669; found: 943.3663.

2′-(Benzyloxycarbonyl)benzyl (3,3′-Anhydro-4,6-di-*O*-benzyl-3-*C*-hydroxymethyl-α-D-*manno*-hexopyranosyl)-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (43). A solution of compound **41** (260 mg, 0.28 mmol), mCPBA (150 mg, 0.87 mmol), and $NaHCO_3$ (104 mg, 1.24 mmol) in CH_2Cl_2 (25 mL) was stirred at 0 °C for 30 min and warmed up to 40 °C. After being stirred for further 4 h at 40 °C, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (CH_2Cl_2/EtOAc, 10:1, v/v) to afford compound **43** (230 mg, 0.25 mmol, 87%) as a white foam. R_f = 0.38 (CH_2Cl_2/EtOAc, 50:1); $[\alpha]_D$ +38.8 (*c* 0.50, $CHCl_3$); IR ($CHCl_3$ film) 3507, 3030, 2926, 2850, 1716, 1601, 1496, 1453, 1267, 1095, 1059, 914, 742, 713, 697 cm^{-1}. ^1H NMR (400 MHz $CDCl_3$) δ 1.38 (d, *J* = 6.0 Hz, 3H), 2.50 (d, *J* = 5.6 Hz, 1H), 3.20 (d, *J* = 5.2 Hz, 1H), 3.44−3.60 (m, 3H), 3.85−3.93 (m, 1H), 4.08−4.12 (m, 1H), 4.24−4.33 (m, 3H), 4.43 (dd, *J* = 9.6, 3.2 Hz, 1H), 4.52−4.66 (m, 4H), 4.96 (s, 1H), 5.00 and 5.08 (ABq, *J* = 13.6 Hz, 2H), 5.30 (s, 1H), 5.32 (s, 2H), 5.67 (brs, 1H), 7.02−7.62 (m, 26H), 8.00 (d, *J* = 7.6 Hz, 1H), 8.06 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.2, 29.9, 49.4, 61.3, 66.9, 67.6, 68.3, 68.4, 68.8, 69.7, 71.8, 73.4, 73.5, 74.0, 75.2, 76.0, 77.4, 79.9, 96.9, 97.7, 127.5, 127.66, 127.69, 127.90, 127.95, 127.99, 128.0, 128.1, 128.3, 128.4, 128.41, 128.45, 128.49, 128.7, 128.8, 129.8, 130.0, 130.9, 132.8, 133.6, 136.0, 137.4, 138.2, 138.4, 139.7, 165.9, 166.8. Anal. calcd for $C_{56}H_{56}O_{13}$: C, 71.78; H, 6.02. Found: C, 71.51; H, 6.11.

2′-(Benzyloxycarbonyl)benzyl (4,6-Di-*O*-benzyl-3-*C*-methyl-α-D-*manno*-hexopyranosyl)-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (13). A solution of compound **43** (377 mg, 0.40 mmol), $BH_3{\cdot}NEt_3$ (214 mg, 1.86 mmol), and $BF_3{\cdot}OEt_2$ (264 mg, 1.86 mmol) in Et_2O (20 mL) was stirred at 0 °C for 20 min and allowed to warm up over 40 min to room temperature. After being stirred for further 1 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with Et_2O. The combined organic phase was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 2:1, v/v) to give compound **13** (310 mg, 0.33 mmol, 82%) as a white foam. R_f = 0.35 (CH_2Cl_2/EtOAc, 6:1); $[\alpha]_D$ +42.7 (*c* 0.70, $CHCl_3$); IR ($CHCl_3$ film) 3507, 3030, 2926, 2850, 1716, 1601, 1496, 1453, 1267, 1095, 1059, 914, 742, 713, 697 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.22 (s, 3H), 1.41 (d, *J* = 6.4 Hz, 3H), 1.76 (brs, 1H), 2.77 (s, 1H), 3.30−3.39 (m, 3H), 3.48 (t, *J* = 9.4 Hz, 1H), 3.70 (d, *J* = 9.6 Hz, 1H), 3.80−3.83 (m, 1H), 3.89−3.93 (m, 1H), 4.25 and 4.51 (ABq, *J* = 12.0 Hz, 2H), 4.31 (dd, *J* = 9.2, 3.2 Hz, 1H), 4.43 and 4.76 (ABq, *J* = 11.6 Hz, 2H), 4.66 (s, 2H), 4.96 (s, 1H), 5.00 and 5.09 (ABq, *J* = 14.4 Hz, 2H), 5.15 (s, 1H), 5.34 (s, 2H), 5.62 (dd, *J* = 4.2, 1.6 Hz, 1H), 7.10−7.63 (m, 26H), 8.01 (d, *J* = 8.8 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.5, 19.8, 66.9, 67.6, 68.5, 68.8, 69.4, 70.7, 73.5, 73.8, 74.3, 74.6,

75.0, 75.3, 77.9, 80.0, 97.8, 98.0, 128.3, 128.36, 128.41, 128.44, 128.6, 128.7, 128.8, 129.9, 130.0, 130.9, 132.8, 133.6, 136.0, 137.7, 138.2, 139.1, 139.7, 166.2, 166.8. HRMS (FAB): $[M + Na]^+$ calcd for $C_{56}H_{58}O_{13}Na$: 961.3775; found: 961.3771.

2′-(Benzyloxycarbonyl)benzyl (2-*O*-Benzoyl-4-*O*-benzyl-3-*O*-*p*-methoxybenzyl-α-D-rhamnopyranosyl)-(1→2) -(4,6-Di-*O*-benzyl-3-*C*-methyl-α-D-*manno*-hexopyranosyl)-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (2). A solution of compound **13** (230 mg, 0.24 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (91 mg, 0.44 mmol) in CH_2Cl_2 (20 mL) in the presence of 4 Å molecular sieves was stirred for 20 min at room temperature and cooled to −20 °C. After addition of Tf_2O (97 μL, 0.34 mmol), the resulting solution was stirred at −20 °C for 10 min and then compound **12** (195 mg, 0.32 mmol) was added to this solution by using syringe pump over 30 min. The reaction mixture was allowed to warm up over 30 min to room temperature and stirred for further 1.5 h, filtered through Celite, and quenched with saturated aqueous $NaHCO_3$. Collected organic phase was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/CH_2Cl_2/EtOAc, 10:4:1, v/v) to give compound **2** (257 mg, 0.18 mmol, 75%) as a white foam. R_f = 0.20 (hexane/CH_2Cl_2/EtOAc, 10:4:1); $[\alpha]_D$ +24.3 (*c* 0.65, $CHCl_3$); IR ($CHCl_3$ film) 3320, 3013, 2930, 1722, 1602, 1514, 1453, 1268, 1113, 1060, 917, 751, 712, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (s, 3H), 1.39(s, 3H), 1.41 (s, 3H), 3.34−3.66 (m, 6H), 3.69 (s, 3H), 3.73−3.80 (m, 2H), 3.87−3.92 (m, 1H), 3.99 (dd, *J* = 9.2, 3.2 Hz, 1H), 4.06−4.09 (m, 1H), 4.27−4.31 (m, 1H), 4.44−4.50 (m, 2H), 4.56−4.69 (m, 5H), 4.83−5.02 (m, 4H), 5.13 (d, *J* = 14.8 Hz, 1H), 5.21 (d, *J* = 1.6 Hz, 1H), 5.33 (s, 3H), 5.53 (dd, *J* = 2.8, 2.0 Hz, 1H), 5.62 (dd, *J* = 2.8, 2.0 Hz, 1H), 6.75 (d, *J* = 8.8 Hz, 2H), 7.12−7.65 (m, 38H), 8.00 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.05−8.11 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.3, 18.5, 19.5, 55.3, 66.9, 67.5, 68.6, 69.0, 69.1, 69.3, 70.0, 70.9, 71.6, 73.2, 73.8, 74.6, 75.0, 75.2, 75.3, 78.4, 80.0, 80.2, 83.4, 96.9 ($J_{C'-H'}$ = 171 Hz), 97.8 (J_{C-H} = 171 Hz), 100.0 ($J_{C''-H''}$ = 173 Hz), 113.9, 127.7, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.47, 128.52, 128.6, 128.8, 129.9, 130.0, 130.2, 130.9, 132.8, 133.3, 136.1, 137.7, 138.8, 138.9, 139.3, 139.9, 159.3, 165.7, 165.9, 166.7. MALDI-TOF: $[M + Na]^+$ calcd for $C_{84}H_{86}O_{19}Na$: 1421.5661; found: 1421.5663.

2′-Carboxybenzyl (2-*O*-Benzoyl-4-*O*-benzyl-3-*O*-*p*-methoxybenzyl-α-D-rhamnopyranosyl)-(1→2) -(4,6-di-*O*-benzyl-3-*C*-methyl-α-D-*manno*-hexopyranosyl)-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (9). A solution of compound **2** (250 mg, 0.18 mmol) in MeOH (10 mL) was stirred under hydrogen atmosphere using a balloon in the presence of Pd/C (10%, 20 mg) and ammonium acetate (7.5 mg, 0.096 mmol) at room temperature for 30 min. The reaction mixture was filtered through Celite, and the filtrate was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (CH_2Cl_2/EtOAc, 10:1, v/v) to give compound **9** (215 mg, 0.16 mmol, 92%) as a white foam. R_f = 0.22 (CH_2Cl_2/EtOAc, 5:1); $[\alpha]_D$ +40.0 (*c* 0.30, $CHCl_3$); IR ($CHCl_3$ film) 3020, 2928, 2890, 1767, 1722, 1602, 1514, 1453, 1361, 1268, 1060, 738, 712, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (s, 3H), 1.37 (d, *J* = 6.4 Hz, 3H), 1.47 (d, *J* = 6.4 Hz, 3H), 3.41−3.57 (m, 7H), 3.69 (s, 3H), 3.86−3.88 (m, 1H), 3.96−4.13 (m, 3H), 4.19 (d, *J* = 12.8 Hz, 1H), 4.31 (dd, *J* = 9.6, 3.2 Hz, 1H), 4.42−4.50 (m, 2H), 4.62−4.70 (m, 5H), 4.78−4.90 (m, 3H), 4.97 (d, *J* = 1.2 Hz, 1H), 5.12 (d, *J* = 12.0 Hz, 1H), 5.20 (s, 1H), 5.37 (s, 1H), 5.54 (t, *J* = 2.6 Hz, 1H), 5.61 (t, *J* = 2.4 Hz, 1H), 6.76 (d, *J* = 11.6 Hz, 2H), 7.09−7.36 (m, 23H), 7.42−7.49 (m, 6H), 7.54−7.60 (m, 2H), 7.90 (d, *J* = 7.6 Hz, 1H), 8.04−8.10 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 18.5, 19.6, 55.3, 68.4, 69.1, 69.2, 69.9, 70.2, 71.6, 72.7, 73.9, 74.1, 75.0, 75.3, 75.4, 77.2, 78.7, 79.8, 80.2, 83.2, 96.3, 98.0, 99.7, 113.9, 127.4, 127.5, 127.6, 127.7, 127.7, 127.8, 127.9, 128.2, 128.3, 128.4, 128.50, 128.53, 128.6, 129.1, 129.8, 129.96, 129.99, 130.0, 130.12, 130.15, 130.7, 132.4, 133.3, 133.4, 137.7, 138.4, 138.6, 139.0, 139.1, 159.3, 165.8, 165.9, 170.2. HRMS (FAB): $[M + Na]^+$ calcd for $C_{77}H_{80}O_{19}Na$: 1331.5192; found, 1331.5187.

Cyclohexyl (2-*O*-Benzoyl-4-*O*-benzyl-3-*O*-*p*-methoxybenzyl-α-D-rhamnopyranosyl)-(1→2) -(4,6-di-*O*-benzyl-3-*C*-methyl-α-D-*manno*-hexopyranosyl)-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (11). A solution of compound **14** (160 mg, 0.20 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (90 mg, 0.44 mmol) in CH_2Cl_2 (20 mL) in the presence of 4 Å molecular sieves was stirred for 20 min at room temperature and cooled down to −20 °C. After addition of Tf_2O (85 μL, 0.30 mmol), the resulting solution was stirred at −20 °C for 10 min and compound 12 (195 mg, 0.32 mmol) was added to this solution by using syringe pump over 30 min. The reaction mixture was allowed to warm up over 30 min to room temperature, stirred for further 1.5 h, filtered through Celite, and quenched with saturated aqueous $NaHCO_3$. Collected organic phase was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/CH_2Cl_2/EtOAc, 10:4:1, v/v) to give compound **11** (220 mg, 0.17 mmol, 87%) as a white foam. R_f = 0.25 (hexane/CH_2Cl_2/EtOAc, 10:4:1); $[\alpha]_D$ +35.4 (*c* 0.85, $CHCl_3$); IR ($CHCl_3$ film) 3031, 2929, 2855, 1725, 1613, 1585, 1514, 1452, 1361, 1268, 1114, 1065, 837, 749, 713, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.22−1.28 (m, 8H), 1.35−1.43 (m, 6H), 1.52 (brs, 1H), 1.68−1.72 (m, 2H), 1.80−1.84 (m, 2H), 3.37−3.49 (m, 4H), 3.52−3.64 (m, 3H), 3.69 (s, 3H), 3.74−3.80 (m, 1H), 3.90−4.00 (m, 2H), 4.05−4.08 (m, 1H), 4.23 (dd, *J* = 9.6, 2.8 Hz, 1H), 4.31 (d, *J* = 12.0 Hz, 1H), 4.43−4.51 (m, 2H), 4.58−4.69 (m, 5H), 4.84−4.96 (m, 3H), 5.20 (d, *J* = 1.6 Hz, 1H), 5.29 (brs, 2H), 5.45 (t, *J* = 2.4 Hz, 1H), 5.54 (t, *J* = 2.4 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 2H), 7.13−7.32 (m, 18H), 7.42−7.59 (m, 8H), 7.64−7.68 (m, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 8.04−8.11 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.2, 18.4, 19.4, 23.9, 24.1, 25.7, 31.5, 33.3, 55.2, 68.2, 68.9, 69.0, 69.7, 69.9, 70.0, 70.8, 71.6, 73.2, 73.7, 74.6, 75.0, 75.2, 75.3, 75.8, 78.4, 80.0, 80.1, 83.5, 95.9 (J_{C-H} = 170 Hz), 96.8 (J_{C-H} = 169 Hz), 100.0 (J_{C-H} = 172 Hz), 113.8, 122.2, 125.9, 127.3, 127.4, 127.5, 127.6, 127.8, 128.0, 128.1, 128.2, 128.3, 128.43, 128.46, 128.5, 129.1, 129.86, 129.89, 129.9, 130.02, 130.05, 130.09, 130.1, 133.25, 133.28, 134.1, 137.7, 138.7, 138.9, 139.2, 146.6, 159.3, 165.8. MALDI-TOF: $[M + Na]^+$ calcd for $C_{75}H_{84}O_{17}Na$: 1279.5606; found: 1279.5607.

Cyclohexyl (2-*O*-Benzoyl-4-*O*-benzyl-α-D-rhamnopyranosyl)-(1→2)-(4,6-di-*O*-benzyl-3-*C*-methyl-α-D-*manno*-hexopyranosyl)-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (10). A solution of compound **11** (150 mg, 0.12 mmol) and TFA (54 μL, 0.48 mmol) in CH_2Cl_2 (25 mL) was stirred at 0 °C for 15 min and allowed to warm up over 15 min to room temperature. After being stirred for further 30 min, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 3:1, v/v) to give compound **10** (129 mg, 0.11 mmol, 95%) as a colorless viscous oil. R_f = 0.30 (hexane/EtOAc, 3:1); $[\alpha]_D$ +46.6 (*c* 0.45, $CHCl_3$); IR ($CHCl_3$ film) 3473, 2932, 2850, 1723, 1452, 1359, 1269, 1113, 1066, 1058, 750, 713, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.21−1.29 (m, 8H), 1.40 (d, *J* = 6.4 Hz, 3H), 1.46 (d, *J* = 6.4 Hz, 3H), 1.51 (brs, 1H), 1.69−1.74 (m, 2H), 1.80−1.85 (m, 2H), 2.30 (s, 1H), 2.51 (s, 1H), 3.36−3.60 (m, 5H), 3.70−3.81 (m, 2H), 3.91−3.98 (m, 1H), 4.07−4.15 (m, 1H), 4.23−4.32 (m, 3H), 4.47 (d, *J* = 11.2 Hz, 2H), 4.58 (d, *J* = 12.4 Hz, 1H), 4.65 (d, *J* = 5.6 Hz, 2H), 4.73−4.86 (m, 3H), 4.97 (s, 1H), 5.23−5.28 (m, 2H), 5.46 (s, 1H), 5.48 (d, *J* = 1.6 Hz, 1H), 7.12−7.35 (m, 20H), 7.41−7.49 (m, 4H), 7.51−7.61 (m, 2H), 8.05−8.08 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.2, 18.4, 19.4, 23.9, 24.1, 25.7, 31.5, 33.4, 68.2, 68.6, 68.9, 70.0, 70.4, 70.8, 73.1, 73.2, 73.8, 74.6, 74.96, 74.98, 75.2, 75.8, 78.4, 80.1, 81.6, 83.7, 95.9, 96.9, 99.9, 127.30, 127.34, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 129.8, 129.90, 129.95, 129.99, 130.1, 133.3, 133.4, 137.7,

138.4, 138.8, 139.2, 165.8, 166.3. Anal. calcd for $C_{67}H_{76}O_{16}$: C, 70.76; H, 6.74. Found: C 70.39; H, 6.71.

Cyclohexyl (α-D-Rhamnopyranosyl)-(1→2)-(3-*C*-methyl-α-D-*manno*-hexopyranosyl)-(1→ 3)-α-L-rhamnopyranoside (45). A solution of compound **10** (96 mg, 0.08 mmol) and NaOMe (4.6 mg, 0.08 mmol) in MeOH (10 mL) was stirred at 50 °C for 10 h. After being cooled down to room temperature, the reaction mixture was neutralized with DOEX CCR-3 (H^+ mode) resin and filtered through Celite, and the filtrate was concentrated in vacuo. The residue, without further purification, was dried under vacuum and dissolved in MeOH/AcOH/CH_2Cl_2 (5:2:3, 5 mL). The resulting solution was stirred under hydrogen atmosphere using a balloon in the presence of Pd/C (10%, 10.80 mg) at room temperature overnight. The reaction mixture was filtered through Celite, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on Iatrobeads 6RS-8060 (CH_2Cl_2/MeOH/H_2O, 3:1.5:0.1, v/v) to afford compound **45** (39 mg, 0.07 mmol, 82%) as an amorphous solid. R_f = 0.60 (CH_2Cl_2/MeOH/H_2O, 30:15:1); $[\alpha]_D$ +44.2 (*c* 0.95, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 1.25−1.31 (m, 10H), 1.67 (brs, 1H), 1.41 (s, 3H), 1.55 (brs, 1H), 1.91−1.97 (brs, 2H), 1.88−2.00 (brs, 2H), 3.48−3.51 (m, 2H), 3.66 (brs, 1H), 3.72−3.89 (m, 11H), 4.08 (d, J = 1.6 Hz, 1H), 4.12 (d, J = 1.6 Hz, 1H), 4.97 (s, 1H), 5.01 (s, 1H), 5.11 (s, 1H); ^{13}C NMR (100 MHz, D_2O) δ 16.7, 16.8, 18.1, 23.8, 24.0, 25.1, 31.0, 32.9, 61.2, 66.6, 68.9, 69.3, 69.4, 70.0, 70.1, 70.5, 71.5, 72.0, 73.2, 73.8, 76.3, 82.9, 95.4 (J_{C-H} = 171 Hz), 97.5 (J_{C-H} = 171 Hz), 102.9 (J_{C-H} = 172 Hz). MALDI-TOF: $[M + Na]^+$ calcd for $C_{25}H_{44}O_{14}$: 591.2628; found: 591.2623.

Cyclohexyl (2-*O*-Benzoyl-4-*O*-benzyl-3-*O*-*p*-methoxybenzyl-α-D-rhamnopyranosyl)-(1→2)-(4,6-di-*O*-benzyl-3-*C*-methyl-α-D-*manno*-hexopyranosyl)-(1→3)-(2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2-*O*-benzoyl-4-*O*-benzyl-α-D-rhamnopyranosyl)-(1→2)-(4,6-di-*O*-benzyl-3-*C*-methyl-α-D-*manno*-hexopyranosy l)-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (7). A solution of compound **10** (40 mg, 0.04mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (13 mg, 0.06mmol) in CH_2Cl_2 (20 mL) in the presence of 4 Å molecular sieves was stirred for 20 min at room temperature and cooled down to −20 °C. After addition of Tf_2O (13 μL, 0.05 mmol), the resulting solution was stirred at −20 °C for 10 min, and compound 9 (55 mg, 0.04 mmol) was added to this solution by using syringe pump over 30 min. The reaction mixture was allowed to warm up over 30 min to room temperature, stirred for further 1.5 h, filtered through Celite, and quenched with saturated aqueous $NaHCO_3$. Organic phase was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/CH_2Cl_2/EtOAc, 10:4:1, v/v) to give compound **7** (58 mg, 0.03 mmol, 72%) as a colorless viscous oil. R_f = 0.43 (hexane/CH_2Cl_2/EtOAc, 3:1:1); $[\alpha]_D$ +37.5 (*c* 1.60, $CHCl_3$); IR ($CHCl_3$ film) 3655, 3031, 2930, 2855, 1725, 1613, 1585, 1514, 1452, 1361, 1268, 1113, 1069, 749, 713, 711, 698 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (d, J = 6.0 Hz, 3H), 1.22−1.44 (m, 18H), 1.50 (d, J = 6.0 Hz, 3H), 1.72 (brs, 2H), 1.83 (brs, 2H), 3.01 (d, J = 10.8 Hz, 1H), 3.20 (d, J = 10.8 Hz, 1H), 3.33−3.53 (m, 7H), 3.56−3.65 (m, 5H), 3.68 (s, 3H), 3.76−3.85 (m, 2H), 3.91−4.05 (m, 6H), 4.08−4.12 (m, 2H), 4.22−4.30 (m, 3H), 4.35−4.48 (m, 5H), 4.51−4.67 (m, 8H), 4.77−4.91 (m, 4H), 5.00 (s, 1H), 5.17 (s, 1H), 5.22 (s, 1H), 5.26 (s, 1H), 5.30 (s, 1H), 5.41 (brs, 1H), 5.46 (t, J = 2.4 Hz, 1H), 5.49 (t, J = 2.4 Hz, 1H), 5.65 (brs, 1H), 6.73 (d, J = 8.8 Hz, 2H), 6.97−7.33 (m, 42H), 7.35−7.59 (m, 12H), 8.04−8.11 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7, 18.0, 18.4, 18.55, 19.53, 23.9, 24.2, 25.7, 29.8, 31.5, 33.3, 55.2, 67.9, 68.2, 68.5, 68.6, 68.7, 68.96, 69.0, 70.0, 70.5, 70.7, 71.6, 72.2, 73.21, 73.23, 73.5, 73.7, 73.9, 74.4, 74.8, 74.9, 75.1, 75.2, 75.3, 75.8, 76.5, 77.6, 78.1, 78.3, 79.7, 79.9, 80.1, 82.7, 83.6, 93.8, 95.9, 96.3, 96.81, 99.7, 100.0, 113.8, 127.54, 127.56, 127.64, 127.68, 127.8, 128.1, 128.21, 128.26, 128.27, 128.33,128.38, 128.45, 128.49, 128.54, 128.59, 128.6, 128.7, 129.6, 129.8, 129.9, 130.01, 130.08, 130.13, 130.18, 130.2, 133.1, 133.2, 133.3, 137.6, 137.70, 137.77, 138.6, 138.74, 138.8, 139.1, 139.3, 159.2, 165.3, 165.84, 165.87,165.9. MALDI-TOF: $[M + Na]^+$ calcd for $C_{136}H_{148}O_{32}Na$: 2315.9851; found: 2315.9859.

Cyclohexyl (2-*O*-Benzoyl-4-*O*-benzyl-3-hydroxy-α-D-rhamnopyranosyl)-(1→2)-(4,6-di-*O*-benzyl-3-*C*-methyl-α-D-*manno*-hexopyranosyl)-(1→3)-(2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2-*O*-benzoyl-4-*O*-benzyl-α-D-rhamnopyranosyl)-(1→2)-(4,6-di-*O*-benzyl-3-*C*-methyl-α-D-*manno*-hexopyranosyl)-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (46). A solution of compound **7** (53 mg, 0.02 mmol) and TFA (13 μL 0.11 mmol) in CH_2Cl_2 (15 mL) was stirred at 0 °C for 30 min and allowed to warm up over 30 min to room temperature. After being stirred for further 4 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 2:1, v/v) to give compound **46** (45 mg, 0.02 mmol, 90%) as a colorless viscous oil. R_f = 0.17 (hexane/EtOAc, 2:1); $[\alpha]_D$ +55.2 (*c* 0.40, $CHCl_3$); IR ($CHCl_3$ film) 3498, 3031, 2930, 2855, 1727, 1613, 1585, 1514, 1452, 1361, 1269, 1114, 1069, 749, 712, 698 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (d, J = 6.4 Hz, 3H), 1.21−1.28 (m, 11H), 1.39 (d, J = 6.0 Hz, 3H), 1.50 (d, J = 6.4 Hz, 3H), 1.65 (s, 4H), 1.71 (brs, 2H), 1.83 (brs, 2H), 2.12 (d, J = 4.4 Hz, 1H), 2.29 (d, J = 4.4 Hz, 1H), 3.00 (d, J = 10.0 Hz, 1H), 3.20 (dd, J = 8.8, 2.4 Hz, 1H), 3.34−3.46 (m, 7H), 3.56−3.61 (m, 2H), 3.65−3.69 (m, 2H), 3.73−3.77 (m, 2H), 3.91−4.02 (m, 3H), 4.09−4.18 (m, 3H), 4.22−4.30 (m, 3H), 4.36−4.47 (m, 4H), 4.53−4.56 (m, 4H), 4.64−4.70 (m, 3H), 4.75−4.83 (m, 3H), 4.89 (d, J = 10.4 Hz, 2H), 5.15 (s, 1H), 5.19 (s, 1H), 5.22 (s, 1H), 5.26 (s, 1H), 5.30 (s, 1H), 5.39−5.41 (m, 2H), 5.46 (t, J = 2.4 Hz, 1H), 5.60 (brs, 1H), 7.04−7.09 (m, 6H), 7.11−7.21 (m,18H), 7.22−7.28 (m, 9H), 7.30−7.35 (m, 7H), 7.41−7.49 (m, 9H), 7.55−7.62 (m, 3H), 8.04−8.12 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7, 18.1, 18.4, 18.5, 19.52, 19.55, 23.9, 24.2, 25.7, 31.5, 33.4, 68.2, 68.4, 68.5, 68.9, 69.1, 70.0, 70.4, 70.5, 70.7, 72.3, 73.21, 73.21, 73.23, 73.4, 73.7, 74.0, 74.4, 74.8, 74.9, 75.0, 75.1, 75.2, 75.8, 76.5, 78.0, 78.3, 79.8, 79.9, 80.1, 81.7, 82.8, 83.5, 93.9, 95.9, 96.3, 96.8, 99.6, 100.0, 127.2, 127.3, 127.4, 127.61, 127.65, 127.69, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.22, 128.25, 128.28, 128.3, 128.4, 128.50, 128.55, 128.61, 128.64, 128.7, 129.6, 129.8, 129.9, 130.02, 130.09, 130.1, 130.2, 133.2, 133.3, 133.4, 138.5, 138.7, 139.1, 139.2, 165.3, 165.8, 165.8, 166.3. MALDI-TOF: $[M + Na]^+$ calcd for $C_{128}H_{140}O_{31}Na$: 2195.9276; found: 2195.9263.

Cyclohexyl (α-D-Rhamnopyranosyl)-(1→2)-(3-*C*-methyl-α-D-*manno*-hexopyranosyl)-(1→ 3)-(α-L-rhamnopyranosyl)-(1→3)-(α-D-rhamnopyranosyl)-(1→2)-(3-*C*-methyl-α-D-*manno*-hexopyranosyl)-(1→3)-α-L-rhamnopyranoside (47). A solution of compound **7** (80 mg, 0.04 mmol) and NaOMe (7.5 mg, 0.01 mmol) in MeOH (10 mL) was stirred at 50 °C for 10 h. After being cooled down to room temperature, the reaction mixture was neutralized with DOEX CCR-3 (H^+ mode) resin and filtered through Celite, and the filtrate was concentrated in vacuo. The residue, without further purification, was dried under vacuum and dissolved in MeOH/AcOH/CH_2Cl_2 (5:2:3, 5 mL). The resulting solution was stirred under hydrogen atmosphere using a balloon in the presence of Pd/C (10%, 10 mg) at room temperature overnight. The reaction mixture was filtered through Celite, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on Iatrobeads 6RS-8060 (CH_2Cl_2/MeOH/H_2O, 25:15:1, v/v) to give compound **47** (30 mg, 0.03 mmol, 83%) as a white solid. R_f = 0.62 (CH_2Cl_2/MeOH/H_2O, 2.5:1.5:0.1); $[\alpha]_D$ +34.0 (*c* 0.65, H_2O). ^{1}H NMR (400 MHz, D_2O) δ 1.14−1.33 (m, 18H), 1.39 (d, J = 3.2 Hz, 6H), 1.51 (brs, 1H), 1.70 (brs, 2H), 1.86−1.95 (brs, 2H), 3.42−3.54 (m, 4H), 3.62−3.63 (brs, 1H), 3.69−3.84 (m, 18H), 3.89−4.01 (m, 2H), 4.05 (brs, 1H), 4.09 (brs, 1H), 4.18 (brs, 1H), 4.30 (brs, 1H), 4.95 (s, 1H), 4.98 (s, 2H), 5.01 (s, 1H), 5.08 (s, 1H), 5.11 (s, 1H); ^{13}C NMR (100 MHz, D_2O) δ 16.72, 16.73, 16.8, 16.9, 18.1, 18.2, 23.8, 24.0, 25.1, 31.0, 32.9, 61.1, 61.2, 66.0, 66.3, 66.6,

68.9, 68.9, 69.2, 69.3, 69.42, 69.45, 69.7, 70.0, 70.1, 70.2, 70.3, 70.5, 71.64, 71.65, 72.0, 73.2, 73.7, 74.0, 74.2, 76.3, 82.8, 83.2, 95.3 (J_{C-H} = 170 Hz), 95.4 (J_{C-H} = 170 Hz), 96.1 (J_{C-H} = 172 Hz), 97.5 (J_{C-H} = 171 Hz), 102.7 (J_{C-H} = 172 Hz), 102.8 (J_{C-H} = 174 Hz). MALDI-TOF: $[M + Na]^+$ calcd for $C_{44}H_{76}O_{27}Na$: 1059.4471; found: 1059.4478.

Cyclohexyl (2-*O*-Benzoyl-4-*O*-benzyl-3-*O*-*p*-methoxybenzyl-α-D-rhamnopyranosyl)-(1→2)-(4,6-di-*O*-benzyl-3-*C*-methyl-α-D-*manno*-hexopyranosyl)-(1→3)-(2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2-*O*-benzoyl-4-*O*-benzyl-α-D-rhamnopyranosyl)-(1→2)-(4,6-di-*O*-benzyl-3-*C*-methyl-α-D-*manno*-hexopyranosyl)-(1→3)-(2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2-*O*-benzoyl-4-*O*-benzyl-α-D-rhamnopyranosyl)-(1→2)-(4,6-di-*O*-benzyl-3-*C*-methyl-α-D-*manno*-hexopyranosyl)-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (8). A solution of compound **46** (52 mg, 0.02 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (7.30 mg, 0.03 mmol) in CH_2Cl_2 (20 mL) in the presence of 4 Å molecular sieves was stirred for 20 min at room temperature and cooled down to −20 °C. After addition of Tf_2O (7.30 μL, 0.03 mmol), the resulting solution was stirred at −20 °C for 10 min and compound 9 (26 mg, 0.02 mmol) was added to this solution by using syringe pump over 20 min. The reaction mixture was allowed to warm up over 30 min to room temperature, stirred for further 1.5 h, filtered through Celite, and quenched with saturated aqueous $NaHCO_3$. Collected organic phase was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/CH_2Cl_2/EtOAc, 2:1:1, v/v) to give compound **8** (30 mg, 0.01 mmol, 45%) as a white viscous oil. R_f = 0.65 (hexane/CH_2Cl_2/EtOAc, 2:1:1); $[\alpha]_D$ +30.1 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$ film) 3600, 3062, 3030, 2930, 2856, 1727, 1602, 1585, 1513, 1496, 1452, 1360, 1316, 1269, 1176, 1114, 1017980, 918, 839, 751, 712, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (d, J = 6.4 Hz, 3H), 1.90−1.27 (m, 27H), 1.37 (d, J = 12.4 Hz, 3H), 1.49 (d, J = 6.0 Hz, 3H), 1.72 (brs, 2H), 1.84 (d, J = 10.0 Hz, 2H), 2.14 (d, J = 4.8 Hz, 2H), 2.25 (s, 1H), 2.99 (t, J = 9.8 Hz, 2H), 3.15 (d, J = 8.8 Hz, 1H), 3.22 (d, J = 8.8 Hz, 1H), 3.34−3.79 (m, 23H), 3.91−4.08 (m, 10H), 4.21−4.30 (m, 6H), 4.32−4.41 (m, 5H), 4.44−4.50 (m, 3H), 4.53−4.65 (m, 7H), 4.71−4.82 (m, 3H), 4.86−4.90 (m, 3H), 4.96 (d, J = 1.2 Hz, 1H), 5.14−5.17 (m, 4H), 5.22 (s, 1H), 5.26 (s, 2H), 5.30 (s, 1H), 5.40 (s, 1H), 5.42 (s, 1H), 5.46 (s, 1H), 5.48 (s, 1H), 5.54 (s, 1H), 5.59 (s, 1H), 6.73 (d, J = 8.4 Hz, 2H), 7.01−7.14 (m, 43H), 7.16−7.33 (m, 20H), 7.40−7.47 (m, 19H), 8.06−8.11 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.6, 17.7, 18.1, 18.4, 18.50, 18.58, 19.5, 19.6, 24.0, 24.2, 25.7, 29.5, 29.8, 31.5, 32.0, 33.4, 55.2, 68.06, 68.08, 68.2, 68.5, 68.5, 68.6, 68.76, 68.76, 68.9, 69.0, 69.1, 70.03, 70.09, 70.4, 70.5, 70.8, 71.6, 72.3, 73.22, 73.26, 73.4, 73.5, 73.7, 73.9, 73.9, 74.5, 74.82, 74.89, 75.0, 75.1, 75.2, 75.3, 75.8, 76.5, 77.6, 78.0, 78.1, 78.4, 79.8, 80.0, 80.1, 82.7, 83.0, 83.6, 93.8 (J_{C-H} = 173 Hz), 93.9 (J_{C-H} = 171 Hz), 95.9 (J_{C-H} = 169 Hz), 96.3 (J_{C-H} = 171 Hz), 96.3 (J_{C-H} = 171 Hz), 96.8 (J_{C-H} = 171 Hz), 99.7 (J_{C-H} = 175 Hz), 99.9 (J_{C-H} = 171 Hz), 100.1 (J_{C-H} = 175 Hz), 113.8, 128.4, 128.51, 128.54, 128.61, 128.67, 128.7, 129.71, 129.76, 129.8, 129.9, 130.0, 130.13, 130.16, 130.23, 130.27, 133.1, 133.2, 133.3, 137.6, 137.6, 137.7, 137.8, 138.5, 138.7, 138.7, 138.8, 139.1, 139.2, 139.3, 159.2, 165.3, 165.3, 165.83, 165.88, 165.9. MALDI-TOF: $[M + Na]^+$ calcd for $C_{197}H_{212}O_{47}Na$: 3352.4100; found: 3352.4094.

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Supporting Information Available: General experimental procedures, spectral/analytical data, and copies of ^1H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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