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Note

Synthesis of the 6-deoxytalose-containing tri- and hexasaccharides of the O-antigen polysaccharide from *Mesorhizobium huakuii* IFO15243T

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ABSTRACT

The synthesis of a trisaccharide and a hexasaccharide, the monomer and dimer of the repeating unit of O-antigen polysaccharide from *Mesorhizobium huakuii* IFO15243, has been accomplished through suitable protecting group manipulations and stereoselective glycosylation reactions starting from commercially available L-rhamnose. The target oligosaccharides in the form of their *p*-methoxyphenyl glycosides are suitable for further glycoconjugate formation via selective cleavage of this group.

In Japan and the southern part of China, the winter growing, green manure legumes renge-sou (*Astragalus sinicus* cv. Japan) and Chinese milk vetch (*A. sinicus* cv. China), respectively, are widely used as natural fertilizers of rice fields during the idle period. *Mesorhizobium huakuii*, a member of the *Rhizobiaceae* family isolated from nodules of *A. sinicus*, is able to form nitrogen-fixing symbiotic relationships with *A. sinicus* on the host roots and is of vital importance to the process of biological nitrogen fixation (BNF).[1–3] As Gram-negative bacteria, their components, especially polysaccharides, such as exopolysaccharides (EPSs), lipopolysaccharides (LPSs), capsular polysaccharides (CPSs) and cyclic β-glucans, play an important role during the free-living stage in soil environment and especially during the development of symbiosis.[4,5] The involvement of the carbohydrate-rich molecules in establishing the interaction between the BNF bacterium and the host has been reported,[6,7] and it has been revealed that environmental conditions (in planta and ex planta), as well as plant-derived molecular signals, are able to induce entire LPS modifications in *Rhizobium*.[8]

The O-antigenic polysaccharides (OPSs), which are present at the distal part of LPSs, are in direct contact with the environment and are closely involved in the process of exchanging signals between rhizobia and legumes.[9] Mutants having lipopolysaccharides that lack their OPSs, or have modified core components, either are defective in the formation of infection threads or have the nodules unoccupied.[10–13] The structures of OPSs show a high variability from genus to genus of rhizobia and even from strain to strain within one genus.[14] Generally, they are often composed of deoxysugars, methylated deoxysugars, uronic acids and heptosyl residues and some of them may be highly acetylated. In certain rhizobial strains there are polymers of repeating units.[14–17] Whereas in other strains they are homopolymers.[14,18,19] These facts are of interest from the viewpoints of the biological roles of carbohydrates, and to get a better understanding of these plant–microbe interactions, synthetic studies on the LPSs will be useful. Choma et al.[20] reported that the OPS of *M. huakuii* IFO15243T was a linear polymer constituted of a trisaccharide-repeating unit composed of the rare sugar of 6-deoxy-L-talose and L-rhamnose (**I** in Fig. 1). Here we report the total synthesis of the trisaccharide-repeating unit and its dimer (**II** and **III**, respectively) of the OPS in the form of their *p*-methoxyphenyl glycosides.

The synthesis of the target oligosaccharides followed a convergent, blockwise approach, relying on monosaccharide intermediates either described by us earlier or developed in this study. As outlined in Scheme 1, known *p*-methoxylphenyl 3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**1**)[21] was an ideal C-2-OH rhamnose glycosyl acceptor. In addition, it was used as the starting material for the preparation of the rhamnose glycosyl donor **3**. Thus, compound **1** was first reacted with AllocCl in the presence of pyridine to afford the C-2-OH allyloxycarbonylated derivative **2** in 90% yield. Next, removal of the anomeric methoxylphenyl group of **2** with ceric ammonium nitrate (CAN) in 80% CH_3CN–H_2O, followed by trichloroacetimidate formation, provided trichloroacetimidate **3** in 75% yield over the two steps.

In our previous study we had developed an efficient procedure for the preparation of *p*-methoxylphenyl 4-*O*-benzoyl-6-deoxy-α-L-talopyranoside (**4**) from L-rhamnose.[22] Starting from this

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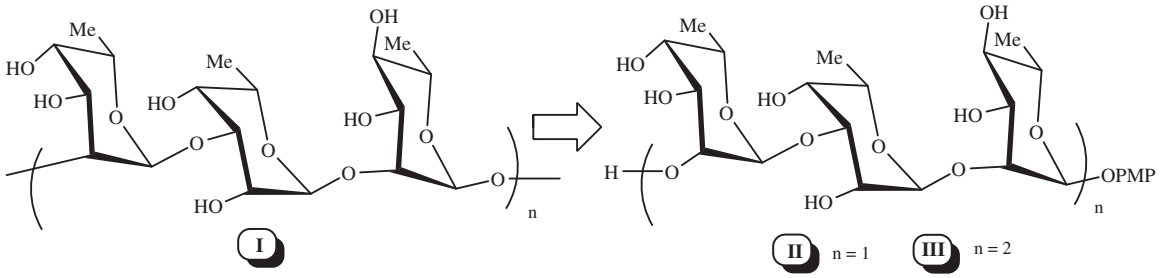
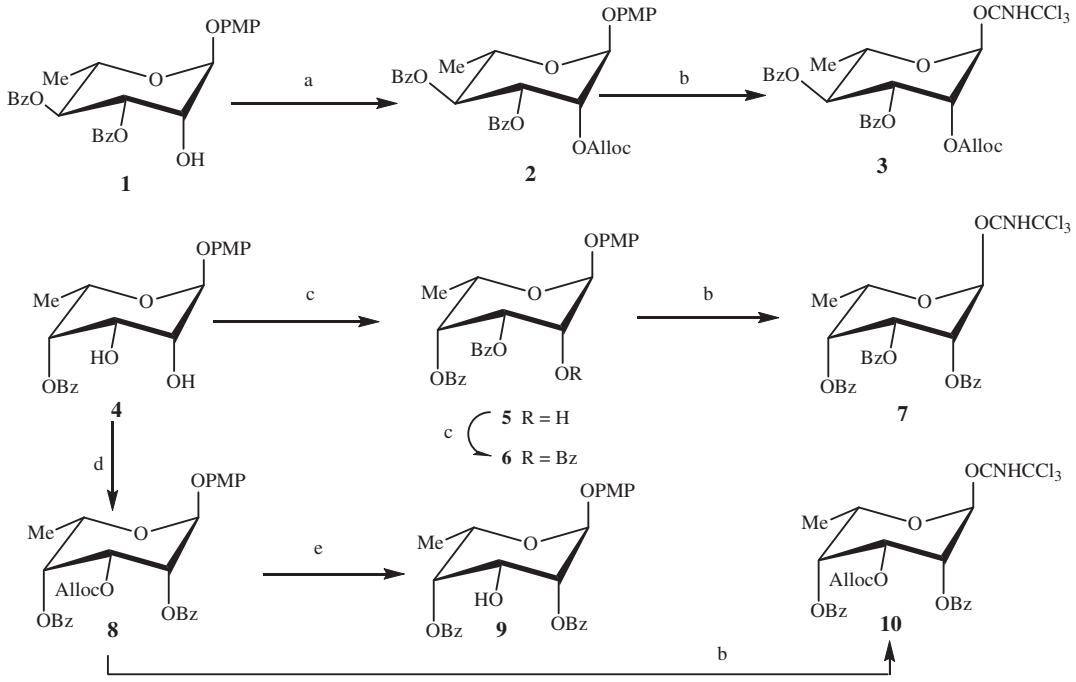


Figure 1. Structure of the OPS of *M. huakuii* **IFO15243T** (**I**) and the synthesized tri- and hexasaccharide (**II** and **III**, respectively).

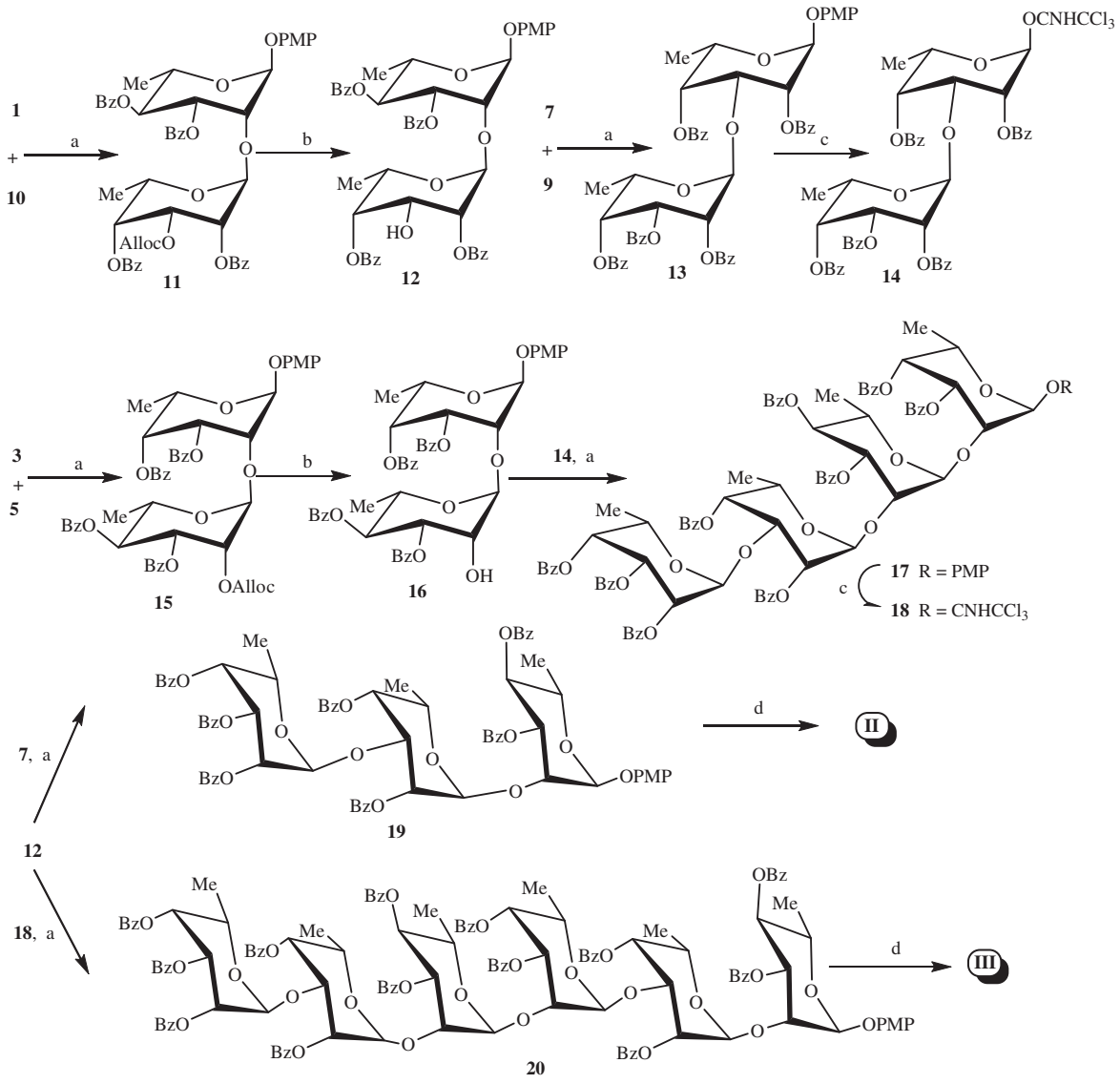


Scheme 1. Reagents and conditions: (a) AllocCl, Py, DMAP, CH_2Cl_2, −10 °C, 3 h, 90%; (b) 4:1 CH_3CN–H_2O, CAN, 30 °C, then Cl_3CCN, DBU, CH_2Cl_2, rt, 0.5 h, 75% for two steps for **3**; 76% for two steps for **7**; 88% for two steps for **10**; (c) BzCl, Py, CH_2Cl_2, −10 °C, 3 h, 95% for **5**; 94% for **6**; (d) (i) AllocCl, Py, CH_2Cl_2, −10 °C, 0.5 h; (ii) BzCl, Py, CH_2Cl_2, −10 °C, 3 h, 82% over two steps; (e) CH_3COONH_4, $Pd[P(C_6H_5)_3]_4$, $NaBH_4$, MeOH–THF, −10 °C, 4 min, 93% for **9**.

material, a series of suitably protected 6-deoxy-L-talopyranose glycosyl acceptors or donors were constructed. Thus, **4** was treated with 1.1 equiv of benzoyl chloride (the chloride was diluted with dichloromethane and the solution was added slowly) in dichloromethane at −10 °C in the presence of 20 equiv of pyridine and catalytic amounts of DMAP, the C-3 hydroxyl group was then selectively blocked to give 4-methoxyphenyl 3,4-di-*O*-benzoyl-6-deoxy-α-L-talopyranoside (**5**)[22] in excellent yield (95%). Under the same reaction conditions, if more benozyl chloride (another 1.5 equiv) was added to the reaction mixture, 4-methoxyphenyl 2,3,4-tri-*O*-benzoyl-6-deoxy-α-L-talopyranoside (**6**) was obtained. Cleavage of the 4-methoxyphenyl group of **6** with CAN, followed by the reaction with trichloroacetonitrile and DBU,[23] gave the 6-deoxy-α-L-talopyranose glycosyl trichloroacetimidate **7**.

Meanwhile, treatment of **4** with allyloxycarbonyl chloride in dichloromethane at −10 °C in the presence of 10 equiv of pyridine and catalytic amounts of DMAP resulted in selective acylation of the C-3 hydroxyl group to give *p*-methoxyphenyl 3-*O*-allyloxycarbonyl-6-deoxy-α-L-talopyranoside, which was benzoylated with 1.5 equiv of benzoyl chloride to provide *p*-methoxyphenyl 3-*O*-allyloxycarbonyl-2,4-di-*O*-benzoyl-6-deoxy-α-L-talopyranoside (**8**) in 82% yield. The ^{1}H NMR spectrum of compound **8** was in accordance with our previously reported data.[24,25] Because the equatorially oriented C-3-OH is more reactive than the axial C-2-OH, the regioselectivity was not unexpected. Dibenzoate **8** was transformed into the corresponding glycosyl acceptor and donor as follows: the allyloxycarbonyl group of **8** was successfully removed in MeOH–THF[26] in the presence of CH_3COONH_4, $Pd[P(C_6H_5)_3]_4$ and $NaBH_4$, within 4 min without affecting any of the other protecting groups, giving the desired acceptor **9** in 93% yield. The ^{1}H NMR spectrum of compound **9** agreed with our previously reported data.[24] Cleavage of the *p*-methoxyphenyl group of **8** followed by conversion of the anomeric hydroxyl group to the corresponding trichloroacetimidate derivative provided 3-*O*-allyloxycarbonyl-2,4-di-*O*-benzoyl-α-L-talopyranosyl trichloroacetimidate (**10**, 88%)[25] conveniently.

With the monosaccharide-building blocks in hand, synthesis of the target tri- and hexasaccharide was achieved as shown in Scheme 2. Glycosylation between rhamnosyl acceptor **1** and 6-deoxytalosyl donor **10** was accomplished by using TMSOTf as the catalyst in the presence of 4 Å molecular sieves to afford disaccharide **11** in 92% yield. The disaccharide **11** was reacted with palladium catalyst ($Pd[P(C_6H_5)_3]_4$), $NaBH_4$ and CH_3COONH_4 in MeOH–THF[26] to afford the disaccharide acceptor **12** in 88% yield. Meanwhile, the coupling between 6-deoxytalosyl donor **7** and acceptor **9** smoothly gave disaccharide **15**, which was transformed to the corresponding glycosyl donor **16** by CAN-promoted 4-methoxyphenyl deprotection and then conversion of the product



Scheme 2. Reagents and conditions: (a) TMSOTf, CH_2Cl_2, −10 °C to rt, 2 h, 92% for **11**; 79% for **13**; 81% for **15**; 75% for **17**; 77% for **19**; 79% for **20**; (b) CH_3COONH_4, $Pd[P(C_6H_5)_3]_4$, $NaBH_4$, MeOH–THF, −10 °C, 4 min, 88% for **12**; 89% for **16**; (c) 4:1 CH_3CN–H_2O, CAN, then Cl_3CCN, DBU, CH_2Cl_2, rt, 72% for two steps for **14**; 65% for two steps for **18**; (d) satd NH_3–MeOH, rt, 96 h, 84% for **II**; 81% for **III**.

hemiacetal to the trichloroacetimidate.[23] Similar to the preparation of **12**, condensation of **3** with **5**, followed by deallyloxycarbonylation of the resulting **15**, successfully provided the disaccharide acceptor **16**. This disaccharide was further glycosylated with donor **14** to furnish the tetrasaccharide **17** in 75% yield. Cleavage of the 4-methoxyphenyl group of **17** with CAN followed by reaction with trichloroacetonitrile and DBU provided the tetrasaccharide donor **18** in satisfactory overall yield (65%). Due to the poor solubility of **17** in 4:1 CH_3CN–H_2O, cleavage of the 4-methoxyphenyl group of **17** with CAN in this solvent system initially failed. To overcome this problem, THF was added to the reaction mixture to increase the solubility of the starting material and satisfactory results were obtained in CH_3CN–THF–H_2O 5:5:2, giving 2,3,4-tri-*O*-benzoyl-α-L-6-deoxy-talopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-6-deoxy-talopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-6-deoxy-talopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-6-deoxy-talopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α,β-L-rhamnopyranose as the sole product as indicated on TLC detection.

Finally, condensation of the acceptor **12** with the donor **7** (or **18**) following the same glycosylation strategy as mentioned above yielded the fully protected trisaccharide **19** in 77% yield (or hexasaccharide **20**, 79%, respectively). Deacylation of trisaccharide **19** or hexasaccharide **20** with ammonia-saturated methanol afforded the target trisaccharide **II** (84%), or hexasaccharide **III** (81%), respectively.

In conclusion, the synthesis of a trisaccharide-repeating unit of the LPS isolated from *M. huakuii* IFO15243T and its dimer has been accomplished. Because the protecting group manipulation strategies and glycosylation steps were selective and high-yielding, the present synthetic strategy is capable of being carried out on reasonably large scale. Bioactivity investigations of trisaccharide **II** and hexasaccharide **III** are in progress and the results will be reported in due course.

1. Experimental

1.1. General methods

Optical rotations were determined with a Perkin–Elmer model 241-MC automatic polarimeter for solution in a 1-dm, jacketed

cell. ^{1}H and ^{13}C NMR spectra were recorded with Bruker DPX300 and Bruker AVANCE600 spectrometers in $CDCl_3$ or D_2O solutions. Internal references: TMS (δ 0.000 ppm for ^{1}H), $CDCl_3$ (δ 77.00 ppm for ^{13}C), HOD (δ 4.700 for ^{1}H). Elemental analysis was performed on a Yanaco CHN Corder MF-3 automatic elemental analyzer. Matrix-assisted laser-desorption ionization mass spectra (MALDI MS) and electrospray-ionization mass spectra (ESIMS) were performed by the Institute of Chemistry, Chinese Academy of Sciences. Thin-layer chromatography (TLC) was performed on silica gel HF with detection by charring with 30% (v/v) H_2SO_4 in MeOH or by UV detection. Column chromatography was conducted by elution of a column of silica gel (200–300 mesh) with EtOAc/PE (bp 60–90 °C) as the eluent. Solutions were concentrated at a temperature <60 °C under diminished pressure.

1.2. *p*-Methoxylphenyl 2,3,4-tri-*O*-benzoyl-α-L-6-deoxy-talopyranoside (6)

Compound **5**[22] (6.2 g, 13 mmol) was dissolved in pyridine (20 mL), then benzoyl chloride (1.8 mL, 16 mmol) in CH_2Cl_2 (10 mL) was added dropwise to the solution over 30 min at −10 °C. The reaction mixture was slowly raised to room temperature and stirred for 2 h, at the end of which time TLC (petroleum ether–EtOAc, 3:1) indicated that the reaction was complete. The reaction mixture was diluted with CH_2Cl_2 (100 ml), washed with 1 M HCl (50 mL), water (2 × 50 mL) and dried (Na_2SO_4). The solvent was evaporated under vacuum and the residue was purified by column chromatography (petroleum ether–EtOAc 4:1) to afford compound **6** (7.1 g, 94%) as a white solid. $[\alpha]_D^{25}$ −84 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.12–7.18 (m, 15H, Bz*H*), 7.12–7.09 (m, 2H, Mp*H*), 6.89–6.86 (m, 2H, Mp*H*), 5.98 (t, 1H, $J_{2,3} = J_{3,4} = 4.0$ Hz, H-3), 5.76 (d, 1 H, $J_{1,2} = 1.3$ Hz, H-1), 5.73 (m, 1H, H-2), 5.67 (m, 1H, H-4), 4.55 (m, 1H, H-5), 3.79 (s, 3H, $C_6H_4OCH_3$), 1.33 (d, 3H, $J_{5,6} = 6.5$ Hz, C-C*H*$_3$). Anal. Calcd for $C_{34}H_{30}O_9$: C, 70.09; H, 5.19. Found: C, 70.22; H, 5.35.

1.3. 2,3,4-Tri-*O*-benzoyl-α-L-6-deoxy-talopyranosyl trichloroacetimidate (7)

Cleavage of the PMP group in **6** (6.2 g, 11 mmol) and conversion to the trichloroacetimidate derivative were accomplished by following the same reaction protocol as described above for the preparation of monosaccharide donor **3**. After purification, donor **7** (5.0 g, 76% over 2 steps) was obtained as a white foam. $[\alpha]_D^{25}$ −70 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.82 (s, 1H, CN*H*CCl$_3$), 8.10–7.21 (m, 15H, Bz*H*), 6.61 (d, 1H, $J_{1,2} = 1.4$ Hz, H-1), 5.86 (dd, 1H, $J_{2,3} = J_{3,4} = 4.0$ Hz, H-3), 5.76 (d, 1H, $J_{1,2} = J_{2,3} = 3.8$ Hz, H-2), 5.71 (m, 1H, H-4), 4.63 (m, 1H, H-5), 1.39 (d, 3H, $J_{5,6} = 6.5$ Hz, C-C*H*$_3$). Anal. Calcd for $C_{29}H_{24}Cl_3NO_8$: C, 56.10; H, 3.90; N, 2.26. Found: C, 55.82; H, 4.11; N, 2.46.

1.4. 3-*O*-Allyloxycarbonyl 2,4-di-*O*-benzoyl-α-L-6-deoxy-talopyranosyl trichloroacetimidate (10)

Cleavage of the PMP group in **8**[24,25] (4.3 g, 7.6 mmol) and conversion to the trichloroacetimidate derivative were accomplished by following the same reaction protocol as described in our previous work.[25] After purification, the disaccharide donor **12** (4.0 g, 88% over two steps) was obtained as a white foam. $[\alpha]_D^{25}$ −51 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.81 (s, 1H, CN*H*CCl$_3$), 8.15–7.20 (m, 10H, Bz*H*), 6.56 (d, 1H, $J_{1,2} = 1.5$ Hz, H-1), 5.91 (m, 1H, CH_2=C*H*CH$_2$OCO), 5.70 (m, 1H, H-2), 5.63 (m, 1H, H-4), 5.45 (t, 1H, $J_{2,3} = J_{3,4} = 3.7$ Hz, H-3), 5.36–5.22 (m, 2H, C*H*$_2$=CHCH$_2$OCO), 4.68–4.64 (m, 2H, CH_2=CHC*H*$_2$OCO), 4.54 (m, 1H, H-5), 1.35 (d, 3H, $J_{5,6} = 6.5$ Hz, C-C*H*$_3$). Anal. Calcd for $C_{26}H_{24}Cl_3NO_9$: C, 51.97; H, 4.03; N, 2.33. Found: C, 51.74; H, 4.21; N, 2.78.

1.5. *p*-Methoxylphenyl 3-*O*-allyloxycarbonyl 2,4-di-*O*-benzoyl-α-L-6-deoxy-talopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (11)

To a cooled (−10 °C) solution of **1** (1.6 g, 3.3 mmol) and **10** (2.4 g, 4.0 mmol) in anhydrous, redistilled CH_2Cl_2 (40 mL) was added 4 Å molecular sieves (3.0 g) and the mixture was stirred under a nitrogen atmosphere for 0.5 h. Then TMSOTf (27 μL, 0.15 mmol) was added and the mixture was stirred at −10 °C for another 0.5 h, during which time the mixture was allowed to gradually warm to ambient temperature. TLC (petroleum ether–EtOAc; 5:1, eluted twice) indicated that the reaction was complete. Then the reaction mixture was neutralized with Et_3N (two drops) and filtrated. The filtrate was evaporated under vacuum to give a residue that was purified by column chromatography (petroleum ether–EtOAc 6:1) to give disaccharide **11** as a white solid (2.8 g, 92%). $[\alpha]_D^{25}$ −41 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.11–7.12 (m, 20H, Bz*H*), 7.12–7.09 (m, 2H, Mp*H*), 6.91–6.88 (m, 2H, Mp*H*), 6.02–5.89 (m, 2H, CH_2=C*H*CH$_2$OCO, H-3), 5.70–5.61 (m, 3H, H-2′, H-4, H-4′), 5.53 (d, 1H, $J_{1,2} = 1.8$ Hz, H-1), 5.47 (dd, 1H, $J_{2',3'} = J_{3',4'} = 3.8$ Hz, H-3′), 5.39–5.23 (m, 3H, C*H*$_2$=CHCH$_2$OCO, H-1′), 4.71–4.68 (m, 2H, CH_2=CHC*H*$_2$OCO), 4.52–4.47 (m, 2H, H-2, H-5′), 4.24 (m, 1H, H-5), 3.80 (s, 3H, $C_6H_4OCH_3$), 1.34, 1.29 (2d, 6H, $J_{5,6} = 6.5$ Hz, 2 × C-C*H*$_3$). Anal. Calcd for $C_{51}H_{48}O_{16}$: C, 66.80; H, 5.28. Found: C, 66.96; H, 5.06.

1.6. *p*-Methoxylphenyl 2,4-di-*O*-benzoyl-α-L-6-deoxy-talopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (12)

Compound **11** (2.0 g, 2.2 mmol) was de-*O*-allyloxycarbonylated by following the same procedure as described for the preparation of compound **9** to afford the disaccharide acceptor **12** (1.6 g, 88%) as a foamy solid. $[\alpha]_D^{25}$ −42 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.09–7.18 (m, 20H, Bz*H*), 7.12–7.09 (m, 2H, Mp*H*), 6.90–6.87 (m, 2H, Mp*H*), 5.94 (dd, 1H, $J_{2,3} = 3.2$ Hz, $J_{3,4} = 10.0$ Hz, H-3), 5.63 (dd, 1H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4), 5.56 (d, 1H, $J_{1,2} = 1.8$ Hz, H-1), 5.52–5.48 (m, 2H, H-2′, H-4′), 5.28 (s, 1H, H-1′), 4.62 (m, 1H, H-5′), 4.49–4.43 (m, 2H, H-2, H-3′), 4.24 (m, 1H, H-5), 3.80 (s, 3H, $C_6H_4OCH_3$), 3.01 (d, 1H, J = 6.4 Hz, O*H*), 1.32, 1.29 (2d, 6H, $J_{5,6} = 6.5$ Hz, 2 × C-C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 167.3, 166.4, 165.9, 165.6 (4 × *C*OPh), 155.3, 150.2 (Mp*C*), 133.2(3), 133.1, 130.0(2), 129.9(2), 129.8(2), 129.7(2), 129.6, 129.4, 129.3, 129.1, 128.4(2), 128.3(4), 128.1(2), 117.6(2), 114.8(2) (Mp*C*),100.5, 97.8 (2 × C-1), 72.2, 71.8, 70.9, 70.2, 67.9, 67.5, 66.1, 65.7, 55.7 ($C_6H_4OCH_3$), 17.7, 16.6 (2 × C-*C*H$_3$). Anal. Calcd for $C_{47}H_{44}O_{14}$: C, 67.78; H, 5.33. Found: C, 67.98; H, 5.40.

1.7. *p*-Methoxylphenyl 2,3,4-tri-*O*-benzoyl-α-L-6-deoxy-talopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-6-deoxy-talopyranoside (13)

Glycosylation between monosaccharide acceptor **9** (2.1 g, 4.4 mmol) and donor **7** (3.3 g, 5.2 mmol) was accomplished by following the same reaction protocol as described above for the preparation of disaccharide **11**. After purification by column chromatography (petroleum ether–EtOAc 5:1) **13** was obtained as a white solid (3.3 g, 79%). $[\alpha]_D^{25}$ −168 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.22–7.19 (m, 25H, Bz*H*), 7.10–7.07 (m, 2H, Mp*H*), 6.89–6.86 (m, 2H, Mp*H*), 5.74 (d, 1H, $J_{1,2} = 1.4$ Hz, H-1), 5.67 (m, 1H, H-4′), 5.61–5.57 (m, 3H, H-2, H-1′, H-2′), 5.52 (dd, 1H, $J_{2',3'} = J_{3',4'} = 4.0$ Hz, H-3′), 5.38 (m, 1H, H-4), 4.74 (dd, 1H, $J_{2,3} = J_{3,4} = 3.9$ Hz, H-3), 4.52–4.42 (m, 2H, H-5, H-5′), 3.79 (s, 3H, $C_6H_4OCH_3$), 1.32, 1.29 (2d, 6H, $J_{5,6} = 6.5$ Hz, 2 × C-C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.7, 166.6, 166.3, 165.7, 164.6 (5 × *C*OPh), 155.3, 150.1(Mp*C*), 133.2, 133.0, 132.9(2), 132.8, 130.2(2),

130.1(2), 130.0(2), 129.9(2), 129.8(2), 129.6(4), 129.5, 128.4(2), 128.3(4), 128.2(2), 128.1(2), 117.7(2), 114.7(2) (MpC), 97.5(2) (2 × C-1), 69.5, 69.4, 68.9, 68.2, 67.7, 66.4, 66.1, 65.9, 55.6 ($C_6H_4OCH_3$), 16.5, 16.4 (2 × C-CH_3). Anal. Calcd for $C_{54}H_{48}O_{15}$: C, 69.22; H, 5.16. Found: C, 68.99; H, 5.04.

1.8. 2,3,4-Tri-*O*-benzoyl-α-L-6-deoxy-talopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-6-deoxy- talopyranosyl trichloroacetimidate (14)

Cleavage of the PMP group in **13** (3.1 g, 3.3 mmol) and conversion to the trichloroacetimidate derivative were accomplished by following the same reaction protocol as described above for the preparation of **3**. After purification by column chromatography (petroleum ether–EtOAc 4:1) **14** (2.3 g, 72% over two steps) was obtained as a white foam. $[\alpha]_D^{25}$ −124 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.82 (s, 1H, CN*H*CCl_3), 8.22–7.18 (m, 25 H, Bz*H*), 6.60 (d, 1H, $J_{1,2}$ = 1.4 Hz, H-1), 5.67 (m, 1H, H-4′), 5.62-5.57 (m, 3H, H-2, H-1′, H-2′), 5.52 (t, 1H, $J_{2',3'} = J_{3',4'}$ = 4.0 Hz, H-3′), 5.36 (m, 1H, H-4), 4.68 (dd, 1H, $J_{2,3} = J_{3,4}$ = 3.9 Hz, H-3), 4.55–4.49 (m, 2H, H-5, H-5′), 1.39, 1.28 (2d, 6H, $J_{5,6}$ = 6.5 Hz, 2 × C-CH_3). Anal. Calcd for $C_{49}H_{42}Cl_3NO_{14}$: C, 60.35; H, 4.34; N, 1.44. Found: C, 60.02; H, 4.32; N, 1.78.

1.9. *p*-Methoxylphenyl 2-*O*-allyloxycarbonyl-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-O-benzoyl-α-L-6-deoxy-talopyranoside (15)

Glycosylation between monosaccharide acceptor **5** (2.6 g, 5.6 mmol) and donor **3** (4.0 g, 6.7 mmol) was accomplished by following the same reaction protocol as described above for the preparation of disaccharide **11**. After purification, the disaccharide **15** (4.2 g, 81%) was obtained as a white solid. $[\alpha]_D^{25}$ +4.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.18–7.25 (m, 20H, Bz*H*), 7.13–7.10 (m, 2H, Mp*H*), 6.91–6.88 (m, 2H, Mp*H*), 5.91–5.87 (m, 2H, H-3, H-3′), 5.78 (m, 1H, CH_2=C*H*CH_2OCO), 5.71–5.69 (m, 2H, H-1′, H-4), 5.54 (dd, 1H, $J_{3',4'} = J_{4',5'}$ = 9.9 Hz, H-4′), 5.29–5.15 (m, 2H, CH_2=CHCH_2OCO), 5.20 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 4.51–4.38 (m, 3H, CH_2=CHCH_2OCO, H-5), 4.34 (m, 1H, H-2), 4.27 (m, 1H, H-5′), 3.80 (s, 3H, $C_6H_4OCH_3$), 1.32, 1.29 (2d, 6H, $J_{5,6}$ = 6.6 Hz, 6.2 Hz, 2 × C-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.5, 165.6, 165.4, 165.1 (4 × *C*OPh), 155.2 (Alloc*C*), 153.7, 150.1(Mp*C*), 133.3, 133.2, 133.1, 133.0, 131.1(Alloc*C*), 130.0(2), 129.8(4), 129.7(2), 129.6, 129.4, 129.3, 129.2, 128.6(2), 128.4(4), 128.3(2), 119.1 (Alloc*C*), 117.5(2), 114.8(2) (Mp*C*), 98.9, 98.6 (2 × C-1), 73.4, 72.5, 71.6, 69.5, 69.1 (Alloc*C*), 68.7, 67.8, 67.6, 65.9, 55.7 ($C_6H_4OCH_3$), 17.5, 16.3 (2 × C-CH_3). Anal. Calcd for $C_{51}H_{48}O_{16}$: C, 66.80; H, 5.28. Found: C, 66.62; H, 5.40.

1.10. *p*-Methoxylphenyl 3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-6-deoxy-talopyranoside (16)

De-*O*-allyloxycarbonylation of compound **15** (3.2 g, 3.5 mmol) was accomplished by following the same procedure as described above for the preparation of compound **9** to afford the disaccharide acceptor **16** (2.6 g, 89%) as a foamy solid. $[\alpha]_D^{25}$ +3.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.16–7.26 (m, 20H, Bz*H*), 7.13–7.10 (m, 2H, Mp*H*), 6.91–6.88 (m, 2H, Mp*H*), 5.86 (dd, 1H, $J_{2,3} = J_{3,4}$ = 3.8 Hz, H-3), 5.79 (dd, 1H, $J_{2',3'}$ = 3.2 Hz, $J_{3',4'}$ = 9.9 Hz, H-3′), 5.71 (d, 1H, $J_{1',2'}$ = 1.6 Hz, H-1′), 5.69 (m, 1H, H-4), 5.55 (t, 1H, $J_{3',4'} = J_{4',5'}$ = 9.9 Hz, H-4′), 5.21 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1), 4.47 (m, 1H, H-5), 4.38 (m, 1H, H-2), 4.28 (m, 1H, H-5′), 4.17 (m, 1H, H-2′), 3.80 (s, 3H, $C_6H_4OCH_3$), 1.31, 1.27 (2d, 6H, $J_{5,6}$ = 6.6 Hz, 2 × C–CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3, 165.8, 165.4, 165.2 (4 × *C*OPh), 155.2, 150.1 (Mp*C*), 133.2(3), 133.0, 129.8(2), 129.7(4), 129.6(2), 129.4(4), 128.6(2), 128.5(2), 128.4(4), 117.5(2), 114.8(2) (Mp*C*), 101.1, 98.7 (2 × C-1), 72.3, 72.1, 71.7, 69.6, 69.3, 68.3, 67.5, 65.8, 55.7 ($C_6H_4OCH_3$), 17.5, 16.2 (2 × C–CH_3). Anal. Calcd for $C_{47}H_{44}O_{14}$: C, 67.78; H, 5.33. Found: C, 68.03; H, 5.50.

1.11. *p*-Methoxylphenyl 2,3,4-tri-*O*-benzoyl-α-L-6-deoxy-talopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-6-deoxy-talopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-6-deoxy-talopyranoside (17)

Compound **16** (1.2 g, 1.5 mmol) and **14** (1.7 g, 1.7 mmol) were glycosylated by following the same procedure as described above for the preparation of disaccharide **11** to afford the tetrasaccharide **17** (1.8 g, 75%) as a white foam after purification by column chromatography (petroleum ether–EtOAc 3:1). $[\alpha]_D^{25}$ −25 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.04–7.22 (m, 45H, Bz*H*), 7.16–7.13 (m, 2H, Mp*H*), 6.93–6.90 (m, 2H, Mp*H*), 5.89–5.84 (m, 2H, H-3, H-3′), 5.72 (m, 2H, H-1, H-4), 5.60 (m, 1H, H-4), 5.58 (t, 1H, $J_{3',4'} = J_{4',5'}$ = 10.0 Hz, H-4′), 5.52 (s, 1H, H-1‴), 5.49 (t, 1H, $J_{2''',3'''} = J_{3''',4'''}$ = 3.9 Hz, H-3‴), 5.44 (m, 1H, H-2″), 5.39 (m, 1H, H-4″), 5.35 (d, 1H, $J_{1'',2''}$ = 1.4 Hz, H-1″), 5.32 (m, 1H, H-2‴), 4.70 (d, 1H, $J_{1',2'}$ = 1.2 Hz, H-1′), 4.57 (t, 1H, $J_{2'',3''} = J_{3'',4''}$ = 3.8 Hz, H-3″), 4.53–4.88 (m, 2H, 2 × H-5), 4.42 (m, 1H, H-2), 4.31–4.21 (m, 2H, 2 × H-5), 4.14 (m, 1H, H-2′), 3.80 (s, 3H, $C_6H_4OCH_3$), 1.35, 1.32 (2d, 12H, $J_{5,6}$ = 6.5 Hz, 4 × C-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.5, 166.4, 166.3, 165.8, 165.7, 165.6, 165.5, 165.4, 164.6 (9 × *C*OPh), 155.2, 150.2 (Mp*C*), 133.3, 133.2, 133.1(2), 133.0, 132.9(2), 132.8, 132.7, 130.0(10), 129.9(2), 129.8(2), 129.7(4), 129.6(6), 129.5, 129.4, 129.3, 128.6(2), 128.5(2), 128.4(2), 128.3(2), 128.2(6), 128.1(2), 128.0(2), 117.5(2), 114.8(2) (Mp*C*), 100.3, 99.8, 98.7, 96.9 (4 × C-1), 78.1, 72.3, 71.7, 70.8, 69.5, 69.3, 68.6, 68.5, 68.3, 68.0, 67.7, 67,4, 66.5, 66,1, 66.0, 65.9, 55.7 ($C_6H_4OCH_3$), 17.7, 16.2, 16.2, 16.1 (4 × C-CH_3). Anal. Calcd for $C_{94}H_{84}O_{27}$: C, 68.61; H, 5.14. Found: C, 68.94; H, 5.35.

1.12. 2,3,4-Tri-*O*-benzoyl-α-L-6-deoxy-talopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-6-deoxy- talopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-6-deoxy-talopyranosyl trichloroacetimidate (18)

Cleavage of the PMP group in **17** (1.4 g, 0.85 mmol) in 5:5:2 CH_3CN–THF–H_2O (48 mL) and then conversion of the product to the trichloroacetimidate derivative were accomplished by following the same reaction protocol as described above for the preparation of monosaccharide donor **3**. After purification by column chromatography (petroleum ether–EtOAc 4:1) **18** (0.93 g, 65% over two steps) was obtained as a white foam. $[\alpha]_D^{25}$ −34 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.76 (s, 1H, CN*H*CCl_3), 8.13–7.18 (m, 45H, Bz*H*), 6.60 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1), 5.86 (dd, 1H, $J_{2',3'}$ = 3.1 Hz, $J_{3',4'}$ = 10.2 Hz, H-3′), 5.78–5.71 (m, 2H, H-3, H-4), 5.59 (t, 1H, $J_{3',4'} = J_{4',5'}$ = 10.0 Hz, H-4′), 5.57 (m, 1H, H-4‴), 5.50 (s, 1H, H-1‴), 5.48 (t, 1H, $J_{2''',3'''} = J_{3''',4'''}$ = 4.0 Hz, H-3‴), 5.40 (m, 2H, H-2″, H-4″), 5.32 (m, 2H, H-1″, H-2‴), 4.74 (d, 1H, $J_{1',2'}$ = 1.1 Hz, H-1′), 4.63 (m, 1H, H-5), 4.56 (dd, 1H, $J_{2'',3''} = J_{3'',4''}$ = 3.8 Hz, H-3″), 4.52–4.47 (m, 2H, H-2, H-5), 4.35 (m, 1H, H-5), 4.19 (m, 1H, H-5), 4.11 (m, 1H, H-2′), 1.42, 1.37, 1.32, 0.81 (4d, 12H, $J_{5,6}$ = 6.5 Hz, 4 × C-CH_3). Anal. Calcd for $C_{89}H_{78}Cl_3NO_{26}$: C, 63.48; H, 4.67; N, 0.83. Found: C, 63.24; H, 4.96; N, 0.98.

1.13. *p*-Methoxylphenyl 2,3,4-tri-*O*-benzoyl-α-L-6-deoxy-talopyranosyl-(1→3)-2,4-di-*O*- benzoyl-α-L-6-deoxy-talopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (19)

Glycosylation between disaccharide acceptor **12** (0.57 g, 0.69 mmol) and monosaccharide donor **7** (0.50 g, 0.81 mmol) was accomplished by following the same reaction protocol as described above for the preparation of disaccharide **11**. After purification by

column chromatography (petroleum ether–toluene–EtOAc 8:3:1) **19** was obtained as a white solid (0.68 g, 77%). $[\alpha]_D^{25}$ −63 (*c* 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ: 8.11–7.16 (m, 35H, Bz*H*), 7.13-6.88 (m, 4H, Mp*H*), 5.95 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 10.2 Hz, H-3), 5.67 (t, 1H, $J_{3,4} = J_{4,5}$ = 9.9 Hz, H-4), 5.65–5.58 (m, 5H, H-1′, H-1″, H-2′, H-2″, H-4″), 5.55 (t, 1H, $J_{2'',3''} = J_{3'',4''}$ = 4.0 Hz, H-3″), 5.36 (m, 1H, H-4′), 5.30 (d, 1H, $J_{1,2}$ = 1.1 Hz, H-1), 4.73 (t, 1H, $J_{2',3'} = J_{3',4'}$ = 3.9 Hz, H-3′), 4.64–4.24 (m, 4H, H-2, H-5, H-5′, H-5″), 3.80 (s, 3H, $C_6H_4OCH_3$), 1.41, 1.33 (2d, 9H, $J_{5,6}$ = 6.5 Hz, 3 × C–CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.6, 166.3, 166.0, 165.9, 165.6, 165.4, 164.6 (7 × *C*OPh), 155.3, 150.2(Mp*C*), 133.3, 133.1, 132.9(2), 132.8(2), 132.7, 130.0(6), 129.9(4), 129.8(3), 129.7(2), 129.6(3), 129.5, 129.4, 129.0, 128.5(2), 128.3(4), 128.2(2), 128.1(4), 128.0(2), 117.6(2), 114.8(2) (Mp*C*), 100.6, 97.7, 97.0 (3 × C-1), 77.2, 77.1, 71.6, 71.0, 69.6, 68.6, 68.5, 68.1, 67.5, 66.5, 66.2, 66.1, 55.6 ($C_6H_4OCH_3$), 17.7, 16.5, 16.3 (3 × C-CH_3). Anal. Calcd for $C_{74}H_{66}O_{21}$: C, 68.83; H, 5.15. Found: C, 68.55; H, 5.34.

1.14. *p*-Methoxylphenyl α-L-6-deoxy-talopyranosyl-(1→3)-α-L-6-deoxy talopyranosyl-(1→2)-α-L-rhamnopyranoside (II)

Trisaccharide **19** (0.41 g, 0.32 mmol) was dissolved in satd NH_3–MeOH (150 mL). After 96 h at rt, the reaction mixture was concentrated and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **II** (0.15 g, 84%) as a white solid. $[\alpha]_D^{25}$ −81 (*c* 0.5, H_2O). ^1H NMR (300 MHz, D_2O) δ: 6.96, 6.85 (2d, 4H, Mp*H*), 5.35, 5.08, 5.05 (3s, 3 × H-1), 3.41–3.68 (m, 14H, $C_6H_4OCH_3$), 3.45 (t, 1H, $J_{3,4} = J_{4,5}$ = 9.6 Hz, H-4), 1.20, 1.17, 1.14 (3d, 9H, $J_{5,6}$ = 6.5 Hz, 3 × C–CH_3); ^{13}C NMR (75 MHz, D_2O) δ: 154.9, 149.7, 119.0(2), 115.2(2) (Ar*C*), 102.9, 98.6, 98.5 (3 × C-1), 78.6, 72.4, 72.1, 70.5, 69.9, 69.8, 69.6, 69.4, 69.0, 67.9, 67.8, 65.6, 55.8 ($C_6H_4OCH_3$), 16.8, 16.7, 15.7 (3 × C–CH_3). HRMS calcd for $C_{25}H_{38}O_{14}Na$ $(M+Na)^+$: 585.2159, found: 585.2142.

1.15. *p*-Methoxylphenyl 2,3,4-tri-*O*-benzoyl-α-L-6-deoxy-talopyranosyl-(1→3)-2,4-di-*O*- benzoyl-α-L-6-deoxy-talopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-6-deoxy-talopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-6-deoxy-talopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (20)

Glycosylation between disaccharide acceptor **12** (0.2 g, 0.24 mmol) and tetrasaccharide donor **18** (0.45 g, 0.27 mmol) was accomplished by following the same reaction protocol as described above for the preparation of disaccharide **11**. After purification by column chromatography (petroleum ether–EtOAc 3:1) **20** was obtained as a white foam (0.44 g, 79%). $[\alpha]_D^{25}$ −32 (*c* 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ: 8.07–7.21 (m, 65H, Bz*H*), 7.15–7.12 (m, 2H, Mp*H*), 6.92–6.89 (m, 2H, Mp*H*), 5.95 (dd, 1H, $J_{2,3}$ = 3.1 Hz, $J_{3,4}$ = 10.0 Hz, H-3 of Rha*p*), 5.91 (dd, 1H, $J_{2,3}$ = 3.1 Hz, $J_{3,4}$ = 10.0 Hz, H-3 of Rha*p*), 5.76 (m, 1H, H-2′), 5.70 (t, 1H, $J_{3,4} = J_{4,5}$ = 10.0 Hz, H-4 of Rha*p*), 5.66-5.60 (m, 5H, H-1″, H-1‴, 3 × H-4 of Tal*p*), 5.57 (t, 1H, $J_{3,4} = J_{4,5}$ = 10.0 Hz, H-4 of Rha*p*), 5.51–5.47 (m, 3H, H-1, 2 × H-3 of Tal*p*), 5.41 (m, 1H, H-2⁗), 5.38 (d, 1H, H-1⁗), 5.35 (m, 1H, H-4⁗), 5.30–5.28 (m, 2H, H-1, H-2⁗), 4.82 (t, 1H, $J_{2',3'} = J_{3',4'}$ = 3.8 Hz, H-3′), 4.71 (m, 1H, H-5), 4.58–4.52 (m, 5H, H-1‴, H-2″, H-3⁗, 2 × H-5), 4.40–4.21 (m, 3H, 3 × H-5), 4.04, 4.01 (2 m, 2H, 2 × H-2), 3.80 (s, 3H, $C_6H_4OCH_3$), 1.53, 1.47, 1.35, 1.33, 1.32, 0.77 (6d, 18H, $J_{5,6}$ = 6.5 Hz, 6 × C–CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.5(2), 166.4, 166.3, 165.9(2), 165.8, 165.6, 165.5, 165.5, 165.3, 165.2, 164.6 (13 × *C*OPh), 155.3, 150.3 (Mp*C*), 133.4, 133.2(2), 133.1, 132.9(3), 132.8(5), 132.7, 130.1(3), 130.0(8), 129.9(10), 129.8(8), 129.7(4), 129.6(4), 129.4, 129.0, 128.5(6), 128.3(4), 128.2(7), 128.1(3), 128.0(6), 117.6(2), 114.8(2) (Mp*C*), 100.8, 100.1, 98.6, 97.7, 97.3, 96.8 (6 × C-1), 78.4, 77.3, 72.0, 71.5, 71.1, 70.9, 70.6, 69.8, 69.6, 68.8, 68.6, 68.4, 68.2, 68.1, 67.9, 67.8, 67.5, 67.4, 67.0, 66.6, 66.3, 66.1, 66.0, 65.8, 55.7 ($C_6H_4OCH_3$), 18.0, 17.7, 16.6, 16.2, 16.1(2) (6 × C-CH_3). Anal. Calcd for $C_{134}H_{120}O_{39}$: C, 68.36; H, 5.14. Found: C, 68.11; H, 5.32.

1.16. *p*-Methoxylphenyl α-L-6-deoxy-talopyranosyl-(1→3)-α-L-6-deoxy talopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→2)-α-L-6-deoxy-talopyranosyl-(1→3)-α-L-6-deoxy-talopyranosyl-(1→2)-α-L-rhamnopyranoside (III)

Compound **20** (230 mg, 0.098 mmol) was dissolved in satd NH_3–MeOH (150 ml). After 96 h at rt, the reaction mixture was concentrated and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **III** (79 mg, 81%) as a white solid. $[\alpha]_D^{25}$ −45 (*c* 0.5, H_2O). ^1H NMR (300 MHz, D_2O) δ: 6.96, 6.85 (2d, 4H, Mp*H*), 5.34 (s, 1H, H-1), 5.12–5.02 (3s, 5H, 5 × H-1), 4.13–3.68 (m, 25H), 3.47–3.40 (m, 2H), 1.22, 1.19 (2d, 12H, $J_{5,6}$ = 6.9 Hz, 4 × C-CH_3), 1.16, 1.14 (2d, 6H, $J_{5,6}$ = 5.9 Hz, 2 × C–CH_3); ^{13}C NMR (75 MHz, D_2O) δ: 154.9, 149.7, 118.9(2), 115.2(2) (Mp*C*), 102.8, 102.7, 101.4, 98.5, 98.4, 97.3 (6 × C-1), 72.4, 72.2, 72.1(2), 71.6, 70.9, 70.5, 69.9(2), 69.8, 69.6, 69.5, 69.4, 69.3, 69.2, 69.0, 67.9(2), 67.8(2), 67.6, 65.9, 65.6(2), 55.8 ($C_6H_4OCH_3$), 16.9, 16.8, 15.7(2), 15.6(2) (6 × C-CH_3). HRMS calcd for $C_{43}H_{68}O_{26}Na$ $(M+Na)^+$: 1023.3896, found: 1023.3875.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2010.07.023.

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