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A highly efficient and convergent synthesis of a hexasaccharide, a dimer of the repeating unit of the antigen O2 polysaccharide of *Stenotrophomonas maltophilia*

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Abstract

A highly efficient and convergent synthesis of a hexasaccharide, which is a dimer of the repeating unit of the antigen O2 polysaccharide of *Stenotrophomonas maltophilia*, was achieved via coupling of 2,3,4-tri-*O*-acetyl-α-L-xylopyranosyl bromide with the tetrasaccharide, allyl 4-*O*-{3-*O*-[4-*O*-(3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-2,3,6-tri-*O*-benzoyl-α-D-mannopyranosyl]-4-benzoyl-α-L-rhamnopyranosyl}-2,3,6-tri-*O*-benzoyl-α-D-mannopyranoside (**18**) by the Koenigs–Knorr method followed by deacylation. Compound **18** was readily prepared from the coupling of the disaccharide trichloroacetimidate, 4-*O*-(2-*O*-acetyl-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-2,3,6-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (**8**) with the disaccharide acceptor, allyl 4-*O*-(2-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl)-2,3,6-tri-*O*-benzoyl-α-D-mannopyranoside (**16**), and both **8** and **16** were prepared via the trichloroacetimidate method from simple starting materials. The sole use of acyl protecting groups substantially simplified protection and deprotection, and the allyl group at the reducing end of allyl 4-*O*-{2-*O*-[2,3,4-tri-*O*-acetyl-β-L-xylopyranosyl]-3-*O*-[4-*O*-(2-*O*-(2,3,4-tri-*O*-acetyl-β-L-xylopyranosyl)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-2,3,6-tri-*O*-benzoyl-α-D-mannopyranosyl]-4-*O*-benzoyl-α-L-rhamnopyranosyl}-2,3,6-tri-*O*-benzoyl-α-D-mannopyranoside **19** allowed further chemical transformation.

Keywords: Synthesis of hexasaccharide; O2 antigen of *Stenotrophomonas maltophilia*; Glycosylation

1. Introduction

The organism known as *Stenotrophomonas* (*Xanthomonas* or *Pseudomonas*) *maltophilia* [1] is a free-living organism which is commonly present in clinical specimens. The organism has a growing reputation as an opportunistic pathogen, particularly as an agent of nosocomial infection, and a potential threat to the cystic fibrosis population, which is partly based on the multidrug resistance of many strains [2]. A polysaccharide consisting of $[(\text{-}3)\text{L-Xyl}p(\beta1\text{-}2)\text{L-Rha}p(\alpha1\text{-}4)\text{D-Man}p(\alpha1\text{-})]_n$ was isolated from the lipopolysaccharide (LPS) present in the reference strain for S*tenotrophomonas maltophilia* serogroup O2 by Winn and Wilkinson in 1997 [2]. We report here a facile synthesis of a hexasaccharide **20**, which is a dimer of the repeating unit of the antigen O2 polymer.

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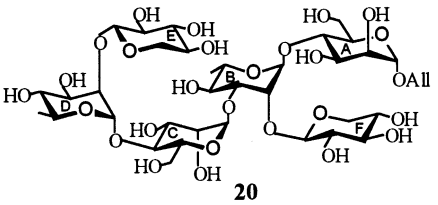

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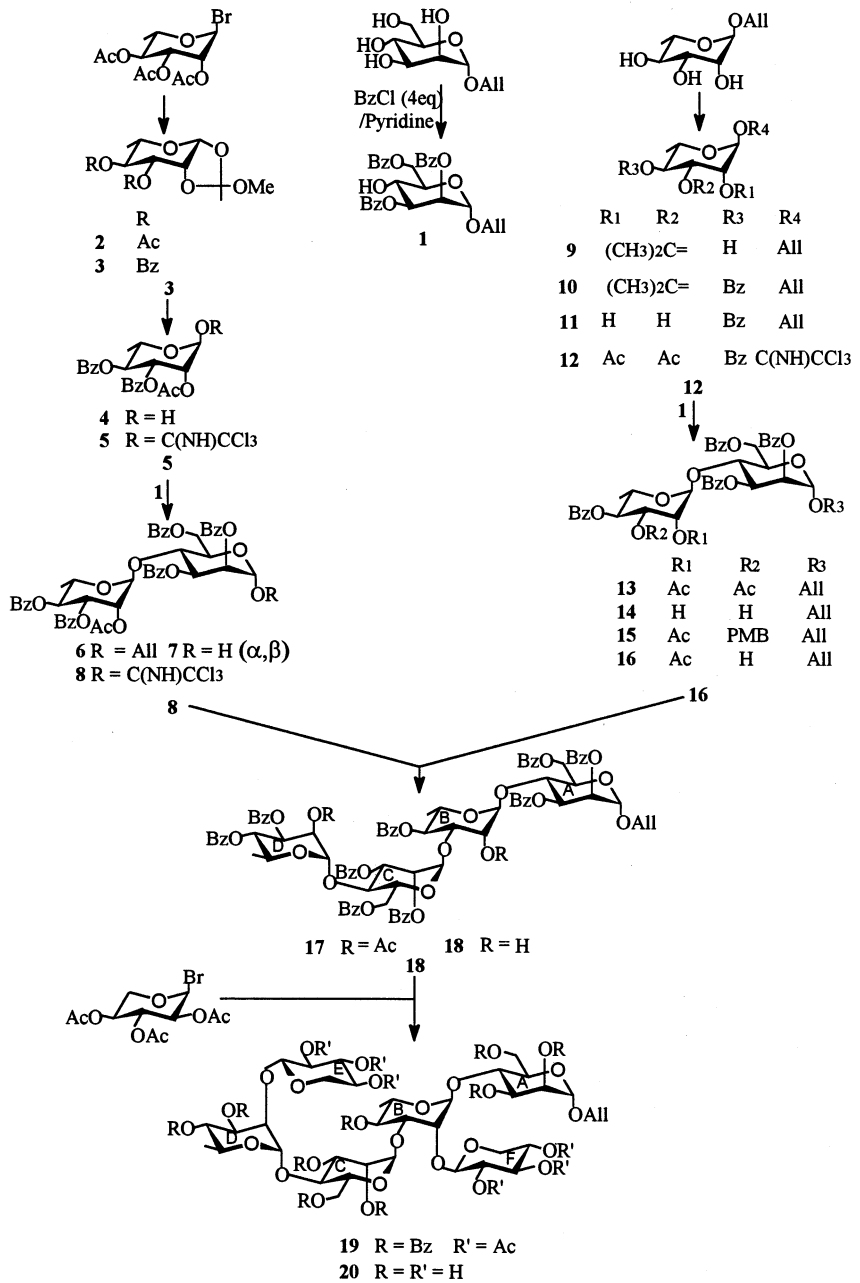
2. Results and discussion

Retrosynthetic analysis indicated that building a tetrasaccharide ABCD block first and then coupling the L-xylose unit at the B-2 and D-2 positions would be an effective and simple route, especially since the ABCD block can be readily constructed from two disaccharide blocks AB and CD. Thus, the glycoside acceptor **1**, allyl 2,3,6-tri-*O*-benzoyl-α-D-mannopyranoside, was obtained from allyl α-D-mannopyranoside [3] through selective tribenzoylation with benzoyl chloride in pyridine under the conditions designated for selective benzoylation of trehalose [4] (Scheme 1). The ^{1}H NMR of **1** gave H-4 as an upfield triplet (δ 4.3 ppm), a clear indication of a free OH hydroxyl. For the synthesis of disaccharide **6**,



Scheme 1.

an orthoester intermediate was used. Treatment of 'acetobromorhamnose' with MeOH in the presence of 2,4-lutidine/^{t}Bu$_4$NBr instead of sym-collidine/^{t}Bu$_4$NBr [5] gave orthoester **2** in high yield. Deacetylation of **2**, followed by benzoylation, gave orthoester **3** in quantitative yield. Hydrolysis of **3** in 70% AcOH solution under the conditions for the transformation of an orthoester to an acetate of an axial hydroxyl group [6] selectively afforded 2-*O*-acetyl-3,4-di-*O*-benzoyl-α,β-L-rhamnopyranose **4** with O-1 free, which was converted to the trichloroacetimidate glycosyl donor **5** on treatment with $CNCCl_3$/DBU [7]. Glycosylation [8] of the acceptor **1** with the trichloroacetimidate donor **5** was promoted with Me_3SiOTf, affording the disaccharide **6** in a high yield ($>90\%$). Deallylation [9] of **6** with palladium chloride in MeOH followed by treatment with trichloroacetonitrile in the presence of DBU afforded the disaccharide donor **8**, which was directly used in the next coupling reaction. The disaccharide acceptor **16** was prepared starting from allyl α-L-rhamnopyranoside [10]. Isopropylidenation of allyl rhamnopyranoside (giving **9**) followed by benzoylation afforded allyl 4-*O*-benzoyl-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (**10**) [11]. Hydrolysis of **10** followed by acetylation, then deallylation, and subsequent treatment with trichloroacetonitrile in the presence of DBU afforded the required donor **12**. Me_3SiOTf-promoted glycosylation of the acceptor **1** with the trichloroacetimidate **12** gave the disaccharide **13** in 86% yield. Selective deacetylation [12] of **13** with CH_3COCl–MeOH gave the disaccharide **16** as the major product (R_f 0.65, 2:1 petroleum ether–EtOAc) in 65% yield, which was easily separated from a minor product (R_f 0.29, 2:1 petroleum ether–EtOAc) and from the starting material **13** (R_f 0.82, 2:1 petroleum ether–EtOAc). To confirm the selective 3′-deacetylation, an unambiguous, alternative synthesis of **16** from **13** was carried out. Thus complete deacetylation of **13** with CH_3COCl–MeOH after extended reaction time gave allyl 4-*O*-(4-*O*-benzoyl-α-L-rhamnopyranosyl)-2,3,6-tri-*O*-benzoyl-α-D-mannopyranoside **14** (R_f 0.29, 2:1 petroleum ether–EtOAc). Selective 3′-*O*-4-methoxybenzylation via the corresponding dibutyltin complex intermediate [13] followed by acetylation afforded **15**, and subsequent selective 3′-deprotection with DDQ [14] furnished a product identical to that obtained from direct selective 3′-deacetylation of **13**, as indicated from TLC (R_f 0.65, 2:1 petroleum ether–EtOAc) and ^{1}H NMR.

Glycosylation of the disaccharide donor **8** with the disaccharide acceptor **16** in the presence of Me_3SiOTf afforded the tetrasaccharide **17** in 75% yield . The ^{1}H NMR spectrum of **17** showed two singlets at δ 2.26 and 2.02 (2 CH_3CO), and two doublets at δ 0.85 and 0.72 ($-CH_3$ of rhamnose), which came from the rhamnose moieties, and four broad singlets at δ 5.14, 5.08, 5.04 and 4.99 for H-1 of A, B, C, and D units. Selective B-2 and D-2 deacetylation of **17** with CH_3COCl–MeOH gave tetrasaccharide acceptor **18** in high yield.

Glycosylation of the acceptor **18** with 2,3,4-tri-*O*-acetyl-α-L-xylopyranosyl bromide [15] promoted by silver triflate gave the final hexasaccharide **19** in good yield. All of the tribenzoylated mannose-containing oligosaccharides, i.e., the disaccharides **6**, **7**, **8**, **14**, **15**, and **16**, the tetrasaccharides **17** and **18**, and the hexasaccharide **19**, showed the H-6 of rhamnose residues at δ 0.61–0.87 in their ^{1}H NMR spectra. These values differed from the normal region of around δ 1.3(e.g., δ 1.31 for **4**) and we rationalized that the unusual upfield shifting was the result of shielding by the benzene ring in the tribenzoylated mannose moieties. Deprotection [16] of **19** in MeOH–MeONa readily afforded the title hexasaccharide **20** in quantitative yield.

The allyl hexasaccharide glycoside consisting of the two trisaccharide units can be used not only for bioactivity study, but also for the preparation of glycoconjugates via conjugation to protein carriers. In addition, the designated strategy for the preparation of the hexasaccharide can be extended to the synthesis of higher oligosaccharides corresponding to the antigen O2 polymer.

3. Experimental

General methods.—Melting points were determined with a 'Mel-Temp' apparatus and optical rotations were determined with a Perkin–Elmer model 241-MC automatic po-

larimeter for solutions in a 1-dm, jacketed cell. ^{1}H NMR spectra were recorded with Varian XL-400 and Varian XL-200 spectrometers, for solutions in $CDCl_3$ with Me_4Si as the internal standard. Chemical shifts are expressed in ppm downfield from the internal Me_4Si absorption. Mass spectrometry was conducted on a JDS-D 3005 mass spectrometer using a direct-insertion technique to introduce the sample. Thin-layer chromatography (TLC) was performed on silica gel HF, detection being effected by charring with 30% (v/v) sulfuric acid in methanol or sometimes by UV detection. Column chromatography was conducted by elution of a column of silica gel (100–200 mesh) using EtOAc–petroleum ether (bp 60–90 °C) as the solvent. Solutions were concentrated at a temperature < 60 °C under diminished pressure. Analytical LC was performed with a Gilson HPLC consisting of a pump (model 306), a stainless steel column packed with silica gel (Spherisorb SiO_2, 10 × 300 mm or 4.6 × 250 mm), a differential refractometer (132-RI Detector), and a UV–Vis detector (model 118), and EtOAc–petroleum ether (bp 60–90 °C) was used as the solvent at a flow rate of 1–4 mL/min.

Allyl 2,3,6-tri-O-*benzoyl*-α-D-*mannopyranoside* (**1**).—Freshly distilled benzoyl chloride (11 mL, 92 mmol) was added dropwise to a solution of allyl α-D-mannopyranoside (5.0 g, 23 mmol) in dry pyridine (200 mL) at 0 °C. The mixture was allowed to warm to room temperature (rt) and was stirred overnight. The reaction was quenched with MeOH (10 mL), the mixture was concentrated, and the residual solution was poured into ice-water, extracted with CH_2Cl_2 (80 mL) and washed sequentially with N HCl (50 mL), satd aq $NaHCO_3$ (50 mL), and aq NaCl (50 mL). The aq phases were re-extracted with CH_2Cl_2 (40 mL), and the combined organic solutions were dried, concentrated, and purified by column chromatography with 1:1 petroleum ether–EtOAc as the eluent to give the title compound **1** as a colorless syrup (9.2 g, 76%); $[\alpha]_D^{20} + 1.85°$ (*c* 1.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.20–7.90 (m, 6 H, Bz–H), 7.70–7.23 (m, 9 H, Bz–H), 6.08–5.84 (m, 1 H, CH_2=C*H*–CH_2–), 5.65 (dd, 1 H, $J_{2,3}$ 2.6 Hz, $J_{3,4}$ 9.3 Hz, H-3), 5.63 (dd, 1 H, $J_{1,2}$ 1.0 Hz, $J_{2,3}$ 2.6 Hz, H-2), 5.41–5.20 (m, 2 H, CH_2=CH–CH_2–), 5.07 (d, 1 H, $J_{1,2}$ 1.0 Hz, H-1), 4.89 (dd, 1 H, $J_{5,6}$ 4.0 Hz, $J_{6,6'}$ 12.6 Hz, H-6), 4.66 (dd, 1 H, $J_{5,6'}$ 2.1 Hz, $J_{6,6'}$ 12.6 Hz, H-6′), 4.30 (t, 1 H, *J* 9.3 Hz, H-4), 4.38–4.15 (m, 3 H, H-5, CH_2=CH–C*H*$_2$–). Anal. Calcd for $C_{30}H_{28}O_9$: C, 67.66; H, 5.30. Found: C, 67.80; H, 5.36.

3,4-Di-O-*acetyl*-*1,2*-O-*methoxyethylidene*-β-L-*rhamnopyranose* (**2**).—A mixture of 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl bromide (2.0 g, 5.7 mmol), 2,4-lutidine (0.8 mL, 7.2 mmol), and tetrabutylammonium bromide (0.8 g, 2.4 mmol) in CH_2Cl_2 (15 mL) was stirred at rt for 3–5 min, then MeOH (anhyd, 0.5 mL, 12 mmol) was added. TLC (1:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was concentrated and subjected to column chromatography to give the title compound **2** (1.7 g, 97%). Compound **2** gave ^{1}H NMR data identical to those reported in the literature [5b]; mp 80–84 °C; $[\alpha]_D^{20} + 31°$ (*c* 1.0, $CHCl_3$); Ref. [5c] mp 84–86 °C; $[\alpha]_D^{20} + 34.7°$.

3,4-Di-O-*benzoyl*-*2*-O-*acetyl*-α,β-L-*rhamnopyranose* (**4**).—Compound **2** (1.5 g, 4.9 mmol) was deacetylated with MeOH–MeONa, and then benzoylated with BzCl–pyridine to furnish **3** in quantitative yield. Hydrolysis of **3** with 70% aq HOAc [6] at rt furnished **4** (1.6 g, 3.9 mmol) as a colorless syrup in 80% yield. Flash chromatography (2:1 petroleum ether–EtOAc) of the residue gave an anomeric mixture (α/β, 10/1); for α anomer: $[\alpha]_D^{20} + 63.9°$ (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ(α) 7.96, 7.85 (2 d, 4 H, *J* 7.6 Hz, Bz–H), 7.56–7.25 (m, 6 H, Bz–H), 5.81 (dd, 1 H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 9.8 Hz, H-3), 5.57 (t, 1 H, *J* 9.8 Hz, H-4), 5.52 (dd, 1 H, $J_{1,2}$ 1.5 Hz, $J_{2,3}$ 3.4 Hz, H-2), 5.31 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 4.49–4.31 (m, 1 H, H-5), 2.17 (s, 3 H, C*H*$_3$CO), 1.31 (d, 3 H, $J_{5,6}$ 6.7 Hz, C*H*$_3$). Anal. Calcd for $C_{22}H_{22}O_8$: C, 63.76; H, 5.35. Found: C, 63.90; H, 5.35.

Allyl 4-O-*(2*-O-*acetyl*-*3,4-di*-O-*benzoyl*-α-L-*rhamnopyranosyl)*-*2,3,6*-*tri*-O-*benzoyl*-α-D-*mannopyranoside* (**6**).—Treatment [7] of **4** (330 mg, 0.80 mmol) with trichloroacetonitrile (Cl_3CCN, 3 equiv) and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU, 0.25 equiv) at 0 °C in anhyd CH_2Cl_2 gave the glycoside donor, trichloroacetimidate **5** (370 mg, 72%)

after flash chromatography, which was used directly in the glycosylation reaction. A mixture of the donor **5** (370 mg, 0.66 mmol) and the acceptor **1** (266 mg, 0.50 mmol) in anhyd CH_2Cl_2 (20 mL) containing 4 Å activated molecular sieves (0.5 g) was stirred under N_2 for 1 h at rt and then cooled to −40 °C. Trimethylsilyl triflate (Me_3SiOTf, 20 μL, 0.2 equiv) was added and the mixture was stirred under N_2 below −30 °C for 40 min. TLC showed the starting material had disappeared. Triethylamine (15 μL) was added to the reaction solution and the solid was filtered off and washed with CH_2Cl_2 (30 mL). The combined filtrate and washings were washed sequentially with H_2O (30 mL), N HCl (30 mL), satd aq $NaHCO_3$ (30 mL), and satd aq NaCl (30 mL). The aq washings were re-extracted with CH_2Cl_2 (30 mL) and the combined organic solutions were dried and concentrated, and the residue was subjected to flash chromatography with 3:1 petroleum ether–EtOAc as the eluent to give **6** (420 mg, 0.45 mmol) in high yield (90%); $[\alpha]_D^{20}$ −40.4° (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.20–7.80 (m, 10 H, Bz–H), 7.67–7.24 (m, 15 H, Bz–H), 6.10–5.90 (m, 1 H, CH_2=C*H*–CH_2–), 5.91 (dd, 1 H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 9.5 Hz, H-3), 5.65(dd, 1 H, $J_{1,2}$ 1.5 Hz, $J_{2,3}$ 3.4 Hz, H-2), 5.60 (dd, 1 H, $J_{2',3'}$ 3.2 Hz, $J_{3',4'}$ 9.8 Hz, H-3′), 5.41 (dd, 1 H, $J_{1',2'}$ 1.7 Hz, $J_{2',3'}$ 3.2 Hz, H-2′), 5.45–5.25 (m, 3 H, H-4′, CH_2=CH–CH_2–), 5.11 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 5.05 (d, 1 H, $J_{1',2'}$ 1.7 Hz, H-1′), 5.00 (dd, 1 H, $J_{5,6a}$ 1.7 Hz, $J_{6a,6b}$ 12.7 Hz, H-6a), 4.67 (dd, 1 H, $J_{5,6b}$ 3.4 Hz, $J_{6a,6b}$ 12.7 Hz, H-6b), 4.57 (t, 1 H, $J_{3,4}$ 9.5 Hz, $J_{4,5}$ 9.5 Hz, H-4), 4.40–3.94 (m, 4 H, H-5, 5′, CH_2=CH–CH_2–), 2.03 (s, 3 H, CH_3CO), 0.74 (d, 3 H, $J_{5',6'}$ 6.5 Hz, CH_3). Anal. Calcd for $C_{52}H_{48}O_{16}$: C, 67.23; H, 5.21. Found: C, 67.12; H, 5.32.

4-O-*(2*-O-*Acetyl*-*3,4*-*di*-O-*benzoyl*-α-L-*rhamnopyranosyl)*-*2,3,6*-*tri*-O-*benzoyl*-α,β-D-*mannopyranose* (**7**).—Deallylation [9] of **6** (400 mg, 0.43 mmol) with $PdCl_2$ (1:20 g/g) in MeOH (10 mL) at rt furnished an amorphous solid **7** (320 mg, 0.36 mmol, 84%), presented mostly as α anomer; $[\alpha]_D^{20}$ −40.4° (*c* 0.7 $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.20–7.80 (m, 10 H, Bz–H), 7.68–7.20 (m, 15 H, Bz–H), 5.97 (dd, 1 H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 9.2 Hz, H-3), 5.67 (dd, 1 H, $J_{1,2}$ 1.9 Hz, $J_{2,3}$ 3.4 Hz, H-2), 5.60 (dd, 1 H, $J_{2',3'}$ 3.2 Hz, $J_{3',4'}$ 9.8 Hz, H-3′), 5.45 (d, 1 H, $J_{1,2}$ 1.9 Hz, H-1), 5.43 (dd, 1 H, $J_{1',2'}$ 1.7 Hz, $J_{2',3'}$ 3.2 Hz, H-2′), 5.40 (t, 1 H, *J* 9.8 Hz, H-4′), 5.14 (d, 1 H, $J_{1'2'}$ 1.7 Hz, H-1′), 5.06 (dd, 1 H, $J_{5,6a}$ 0.7 Hz, $J_{6a,6b}$ 12.4 Hz, H-6a), 4.65 (dd, 1 H, $J_{5,6b}$ 2.0 Hz, $J_{6a,6b}$ 12.4 Hz, H-6b), 4.60 (t, 1 H, *J* 9.2 Hz, H-4), 4.62–4.51 (m, 1 H, H-5), 4.12–3.96 (m, 1 H, H-5′), 2.07 (s, 3 H, CH_3CO), 0.78 (d, 3 H, *J* 6.2 Hz, CH_3). Anal. Calcd for $C_{49}H_{44}O_{16}$: C, 66.21; H, 4.99. Found: C, 66.14, H, 5.05.

4-O-*(2*-O-*Acetyl*-*3,4*-*di*-O-*benzoyl*-α-L-*rhamnopyranosyl)*-*2,3,6*-*tri*-O-*benzoyl*-α-D-*mannopyranosyl trichloroacetimidate* (**8**).—Trichloroacetonitrile (Cl_3CCN, 0.11 mL, 3 equiv) and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU, 14 μL, 0.25 equiv) were added to a solution of **7** (310 mg, 0.35 mmol) in anhyd CH_2Cl_2 (10 mL) and the mixture was stirred at 0 °C for 1 h, at the end of which time TLC showed the starting material had disappeared. The solvents were evaporated and flash chromatography (1:1 EtOAc–petroleum ether) of the residue gave the disaccharide donor **8** (300 mg, 0.29 mmol, 83%), which was used directly in the glycosylation reaction; ^{1}H NMR ($CDCl_3$): δ 8.68 (s, 1 H, N*H*), 8.12–7.16 (m, 25 H, Bz–H), 6.42 (d, $J_{1,2}$ 1.8 Hz, H-1), 6.02 (dd, 1 H, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 9.2 Hz, H-3), 5.87 (dd, 1 H, $J_{1,2}$ 1.8 Hz, $J_{2,3}$ 3.5 Hz, H-2), 5.67 (dd, 1 H, $J_{2',3'}$ 3.2 Hz, $J_{3',4'}$ 9.8 Hz, H-3′), 5.56 (dd, 1 H, $J_{1',2'}$ 1.7 Hz, $J_{2',3'}$ 3.2 Hz, H-2′), 5.45 (t, 1 H, *J* 9.8 Hz, H-4′), 5.20 (d, 1 H, $J_{1'2'}$ 1.7 Hz, H-1′), 5.02 (dd, 1 H, $J_{5,6a}$ 0.9 Hz, $J_{6a,6b}$ 12.4 Hz, H-6a), 4.66 (dd, 1 H, $J_{5,6b}$ 2.0 Hz, $J_{6a,6b}$ 12.4 Hz, H-6b), 4.60 (t, 1 H, *J* 9.2 Hz, H-4), 4.59–4.47 (m, 1 H, H-5), 4.12–3.96 (m, 1 H, H-5′), 2.10 (s, 3 H, CH_3CO), 0.87 (d, 3 H, *J* 6.2 Hz, CH_3).

Allyl 4-O-*benzoyl*-α-L-*rhamnopyranoside* (**11**).—Compound **11** was obtained as crystals from hydrolysis of **10**, which was prepared from benzoylation of **9**, according to the literature [11].

Allyl 4-O-*(2,3*-*di*-O-*acetyl*-*4*-O-*benzoyl*-α-L-*rhamnopyranosyl)*-*2,3,6*-*tri*-O-*benzoyl*-α-D-*mannopyranoside* (**13**).—Acetylation of compound **11** (6.5 g, 21 mmol) with Ac_2O (5 mL) in pyridine (10 mL) furnished allyl 2,3-di-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside

quantitatively. Deallylation with $PdCl_2$ (1/20 g/g) in MeOH furnished a mixture of 2,3-di-*O*-acetyl-4-*O*-benzoyl-α,β-L-rhamnopyranose. Subsequent treatment with trichloroacetonitrile (Cl_3CCN, 3 equiv) and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU, 0.25 equiv) at 0 °C in anhyd CH_2Cl_2 gave, after flash chromatography, the trichloroacetimidate donor **12** (595 mg, overall yield 72% for two steps), which was used directly in the glycosylation reaction [8]. A mixture of the donor **12** (595 mg, 1.19 mmol) and the acceptor **1** (535 mg, 1.0 mmol) in anhyd CH_2Cl_2 (20 mL) containing 4 Å activated molecular sieves (1 g) was stirred under N_2 for 1 h at rt and then cooled to −40 °C. Trimethylsilyl triflate (Me_3SiOTf, 20 μL, 0.1 equiv) was added and the mixture was stirred under N_2 below −30 °C for 40 min. TLC showed the starting material had disappeared. Triethylamine (25 μL) was added and the reaction mixture was handled as described for the preparation of **6**. Flash chromatography (1:2 EtOAc–petroleum ether) of the residue gave the disaccharide **13** (745 mg, 0.86 mmol, 86%) as a colorless syrup; $[\alpha]_D^{20}$ −24° (*c* 1.5, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.16–7.04 (m, 8 H, Bz–H), 7.69 (m, 12 H, Bz–H), 6.09–5.86 (m, 1 H, CH_2=C*H*–CH_2–), 5.85 (dd, 1 H, $J_{2,3}$ 3.7 Hz, $J_{3,4}$ 9.3 Hz, H-3), 5.62 (dd, 1 H, $J_{2,3}$ 3.7 Hz, $J_{1,2}$ 1.8 Hz, H-2), 5.42 (dd, 1 H, $J_{2',3'}$ 3.8 Hz, $J_{1',2'}$ 1.0 Hz, H-2′), 5.41 (dd, 1 H, $J_{2',3'}$ 3.5 Hz, $J_{3',4'}$ 9.8 Hz, H-3′), 5.35–5.22 (m, 2 H, CH_2=CH–CH_2–), 5.18 (t, 1 H, *J* 9.8 Hz, H-4′), 5.03 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 5.00 (d, 1 H, $J_{1',2'}$ 1.0 Hz, H-1′), 4.91 (dd, 1 H, $J_{5,6a}$ 2.0 Hz, $J_{6a,6b}$ 12.0 Hz, H-6a), 4.64 (dd, 1 H, $J_{5,6b}$ 3.6 Hz, $J_{6a,6b}$ 12.0 Hz, H-6b), 4.50 (t, 1 H, $J_{3,4}$ 9.3 Hz, $J_{4,5}$ 9.3 Hz, H-4), 4.39–4.06 (m, 3 H, H-5, CH_2=CH–CH_2–), 4.00–3.84 (m, 1 H, H-5′), 2.09, 1.88, (2 s, 6 H, 2 CH_3CO), 0.73 (d, 3 H, *J* 6.7 Hz, CH_3). Anal. Calcd for $C_{47}H_{46}O_{16}$: C, 65.12; H, 5.35. Found: C, 65.41; H, 5.27.

*Allyl 4-*O*-(4-*O*-benzoyl-α-*L*-rhamnopyranosyl)-2,3,6-tri-*O*-benzoyl-α-*D*-mannopyranoside* (**14**).—A methanolic solution [12] of HCl (1.04 N, 9 mL), prepared by adding acetyl chloride (0.8 mL) to freshly distilled MeOH (10 mL), was added to a solution of the disaccharide **13** (710 mg, 0.82 mmol) in freshly distilled MeOH (6 mL) and the solution was stirred at 48–54 °C. The reaction was quenched when TLC (2:1 petroleum ether–EtOAc) showed **14** (R_f 0.29) was the sole product. The solution was cooled to 0 °C and pyridine (1.5 mL) was added dropwise to neutralize the acid. The solution was concentrated to a semi-solid residue that was dissolved in CH_2Cl_2 (50 mL) and washed sequentially with M HCl (20 mL), satd aq $NaHCO_3$ (20 mL), and H_2O (20 mL). The aq washings were re-extracted with CH_2Cl_2 (30 mL) and the combined organic solutions were dried and concentrated. Gradient flash chromatography (1:1–1.5:1 EtOAc–petroleum ether) of the residue gave the diol **14** (540 mg, 0.69 mmol, 84%) as a colorless syrup; $[\alpha]_D^{20}$ −34.2° (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.16–7.79 (m, 8 H, *J* 8.4 Hz, Bz–H), 7.66–7.23 (m, 12 H, Bz–H), 6.07–5.86 (m, 1 H, CH_2=C*H*–CH_2–), 5.84 (dd, 1 H, $J_{2,3}$ 3.6 Hz, $J_{3,4}$ 9.7 Hz, H-3), 5.60 (dd, 1 H, $J_{1,2}$ 1.7 Hz, $J_{2,3}$ 3.6 Hz, H-2), 5.42–5.22 (m, 2 H, CH_2=CH–CH_2–), 5.06 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 5.01 (d, 1 H, $J_{1',2'}$ 0.8 Hz, H-1′), 4.93 (t, 1 H, *J* 9.7 Hz, H-4′), 4.77 (dd, 1 H, $J_{5,6a}$ 1.8 Hz, $J_{6a,6b}$ 12.3 Hz, H-6a), 4.16 (dd, 1 H, $J_{5,6b}$ 3.2 Hz, $J_{6a,6b}$ 12.3 Hz, H-6b), 4.50 (t, 1 H, *J* 9.7 Hz, H-4), 4.36–4.08 (m, 3 H, H-5, CH_2=CH–CH_2–), 4.04 (dd, 1 H, $J_{1'2'}$ 0.8 Hz, $J_{2',3'}$ 3.4 Hz, H-2′), 3.94 (dd, 1 H, $J_{2',3'}$ 3.4 Hz, $J_{3',4'}$ 9.7 Hz, H-4′), 3.93–3.78 (m, 1 H, H-5′), 0.74 (d, 3 H, *J* 6.7 Hz, CH_3). Anal. Calcd for $C_{43}H_{42}O_{14}$: C, 65.98; H, 5.41. Found: C, 65.70; H, 5.54.

*Allyl 4-*O*-[2-*O*-acetyl-3-*O*-(p-methoxybenzyl)-4-*O*-benzoyl-α-*L*-rhamnopyranosyl]-2,3,6-tri-*O*-benzoyl-α-*D*-mannopyranoside* (**15**).—To a solution of **14** (500 mg, 0.64 mmol) in MeOH (5 mL) was added dibutyltin oxide (160 mg, 1 equiv) and the mixture was refluxed. After the mixture became clear, heating was continued for 1 h, and the stannylene complex was obtained as a white foamy residue after evaporation of the methanol under diminished pressure. To the residue were added toluene (6 mL), tetrabutylammonium iodide (238 mg, 1 equiv), and *p*-methoxybenzyl chloride (120 μL, 1.5 equiv), and the mixture was stirred for 20 h at 60–70 °C. The reaction was monitored by TLC using 1:2 EtOAc–petroleum ether as the developing sol-

vent. After completion of the alkylation [13], the solvent was evaporated under diminished pressure, and the residue was subjected to column chromatography on silica gel with 1:2 EtOAc–petroleum ether as the eluent. Acetylation of the resulting compound was carried out quantitatively with Ac_2O–pyridine, and the reaction mixture was poured into ice water (10 mL) and extracted with CH_2Cl_2 (10 mL). The aq washings were re-extracted with CH_2Cl_2 (5 mL) and the combined organic solutions were washed sequentially with 5% aq HOAc (10 mL), satd aq $NaHCO_3$ (10 mL), and aq NaCl (10 mL). The organic phase was dried and concentrated under reduced pressure, and the pure, colorless syrupy product **15** (450 mg, 75%) was obtained after separation on a silica gel column with 1:3 EtOAc–petroleum ether as eluent; $[\alpha]_D^{20} - 54.1°$ (*c* 3.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.10–7.73 (4 d, 8 H, *J* 8.6 Hz, Bz–H), 7.68–7.24 (m, 12 H, Bz–H), 7.05, 6.64 (2 d, 4 H, *J* 9.1 Hz, pMB–H), 6.09–5.86 (m, 1 H, CH_2=C*H*–CH_2–), 5.84 (dd, 1 H, $J_{2,3}$ 2.3 Hz, $J_{3,4}$ 9.3 Hz, H-3), 5.61 (dd, 1 H, $J_{1,2}$ 1.7 Hz, $J_{2,3}$ 2.3 Hz, H-2), 5.44–5.24 (m, 2 H, CH_2=CH–CH_2–), 5.25 (dd, 1 H, $J_{1',2'}$ 1.2 Hz, $J_{2',3'}$ 3.6 Hz, H-2′), 5.13 (t, 1 H, *J* 9.8 Hz, H-4′), 5.05 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 5.03 (d, 1 H, $J_{1',2'}$ 1.2 Hz, H-1′), 4.94 (dd, 1 H, $J_{5,6a}$ 1.2 Hz, $J_{6a.6b}$ 12.3 Hz, H-6a), 4.52 (t, 1 H, *J* 9.3 Hz, H-4), 4.51 (dd, 1 H, $J_{5,6b}$ 5.6 Hz, $J_{6a,6b}$ 12.3 Hz, H-6b), 4.49, 4.37 (ABq, 2 H, ^2J 11.6 Hz, pMBCH_2), 4.38–4.07 (m, 4 H, H-5, 5′, CH_2=CH–CH_2–), 3.84 (dd, 1 H, $J_{2',3'}$ 3.6 Hz, $J_{3',4'}$ 9.8 Hz, H-3′), 3.74 (s, 3 H, OCH_3), 2.09 (s, 3H, CH_3CO), 0.74 (d, 3 H, *J* 6.8 Hz, CH_3). Anal. Calcd for $C_{53}H_{52}O_{16}$: C, 67.36; H, 5.55. Found: C, 67.50; H, 5.58.

*Allyl 4-*O*-(2-*O*-acetyl-4-*O*-benzoyl-α-*L*-rhamnopyranosyl)-2,3,6-tri-*O*-benzoyl-α-*D*-mannopyranoside* (**16**) *by direct selective 3′-deacetylation of* **13**.—A methanolic solution of HCl (1.04 N, 5 mL), prepared by adding acetyl chloride (0.8 mL) to freshly distilled MeOH (10 mL), was added to a solution of the disaccharide **13** (340 mg, 0.39 mmol) in freshly distilled MeOH (3.3 mL) and the solution was stirred at 45–50 °C for about 1 h. The reaction was monitored by TLC (2:1 petroleum ether–EtOAc), and the reaction was quenched when TLC showed that the maximum amount of major product (R_f 0.65) [minor product (R_f 0.29), starting material (R_f 0.82)] had been reached. The solution was cooled to 0 °C and pyridine (1 mL) was added dropwise to neutralize the acid. The solution was concentrated to a semi-solid residue that was dissolved in CH_2Cl_2 (10 mL) and washed sequentially with M HCl (10 mL), satd aq $NaHCO_3$ (10 mL), and H_2O (10 mL). The aq washings were re-extracted with CH_2Cl_2 (10 mL) and the combined organic solutions were dried and concentrated. Gradient flash chromatography (1:2–1:1–1.5:1 EtOAc–petroleum ether) of the residue gave **16** (206 mg, 0.25 mmol, 65%) as a colorless syrup; $[\alpha]_D^{20} -80°$ (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.20–7.80 (m, 8 H, Bz–H), 7.68–7.26 (m, 12 H, Bz–H), 6.07–5.87 (m, 1 H, CH_2=C*H*–CH_2–), 5.85 (dd, 1 H, $J_{3,4}$ 9.7 Hz, $J_{2,3}$ 3.6 Hz, H-3), 5.61 (dd, 1 H, $J_{1,2}$ 1.7 Hz, $J_{2,3}$ 3.2 Hz, H-2), 5.42–5.22 (m, 2 H, CH_2=CH–CH_2–), 5.09 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 5.05 (dd, 1 H, $J_{1',2'}$ 1.2 Hz, $J_{2',3'}$ 3.3 Hz, H-2′), 5.03 (d, 1 H, $J_{1',2'}$ 1.2 Hz, H-1′), 4.99 (dd, 1 H, $J_{5,6a}$ 1.2 Hz, $J_{6a,6b}$ 12.2 Hz, H-6a), 4.94 (t, 1 H, *J* 9.7 Hz, H-4′), 4.59 (dd, 1 H, $J_{5,6b}$ 3.1 Hz, $J_{6a,6b}$ 12.2 Hz, H-6b), 4.53 (t, 1 H, *J* 9.7 Hz, H-4), 4.36–4.05 (m, 4 H, H-3′,5, CH_2=CH–CH_2–), 3.95–3.78 (m, 1 H, H-5′), 2.08 (s, 3 H, CH_3CO), 0.73 (s, 3 H, *J* 6.8 Hz, CH_3). Anal. Calcd for $C_{45}H_{44}O_{15}$: C, 65.53; H, 5.38. Found: C, 65.40; H, 5.27.

*Allyl 4-*O*-(2-*O*-acetyl-4-*O*-benzoyl-α-*L*-rhamnopyranosyl)-2,3,6-tri-*O*-benzoyl-α-*D*-mannopyranoside* (**16**).—Solid 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 0.11 g, 0.48 mmol) [14] was added with stirring at rt to a mixture of compound **15** (420 mg, 0.44 mmol), CH_2Cl_2 (5 mL), and water (0.25 mL). Stirring was continued for 6 h, when TLC (1:2 EtOAc–petroleum ether) showed complete conversion of the starting material to a slower moving product. CH_2Cl_2 (5 mL) was added, the resulting solution was washed with aq $Na_2S_2O_3$, dried, and concentrated, and the residue was chromatographed to give **16** (318 mg, 88%). Its ^{1}H NMR spectrum was the same as that of the product obtained from the direct selective 3′-deacetylation of **13**.

Allyl 4-O-{3-O-[4-O-(2-O-*acetyl*-3,4-*di*-O-*benzoyl*-α-L-*rhamnopyranosyl*)-2,3,6-*tri*-O-*benzoyl*-α-D-*mannopyranosyl*]-2-O-*acetyl*-4-O-*benzoyl*-α-L-*rhamnopyranosyl*}-2,3,6-*tri*-O-*benzoyl*-α-D-*mannopyranoside* (**17**).—A mixture of the disaccharide donor **8** (289 mg, 0.28 mmol) and the disaccharide acceptor **16** (230 mg, 0.28 mmol) in anhyd CH_2Cl_2 (15 mL) containing 4 Å activated molecular sieves (1 g) was stirred under N_2 for 1 h at rt and then cooled to −40 °C. Trimethylsilyl triflate (Me_3SiOTf, 5 μL, 0.1 equiv) was added and the mixture was stirred under N_2 below −30 °C for another 40 min. TLC showed the starting material had disappeared. Triethylamine (5 μL) was added and the mixture was treated as described for the preparation of **6**. Flash chromatography (2:1 EtOAc–petroleum ether) of the residue gave the tetrasaccharide **17** (360 mg, 0.21 mmol, 75%) as a colorless syrup; $[\alpha]_D^{20}$ −42.6° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.20–7.74 (m, 18 H, Bz–H), 7.70–7.16 (m, 27 H, Bz–H), 6.08–5.86 (m, 1 H, CH_2=C*H*–CH_2–), 5.87 (dd, 1 H, $J_{2A,3A}$ 3.7 Hz, $J_{3A,4A}$ 9.8 Hz, H-3A), 5.64 (dd, 1 H, $J_{1A,2A}$ 1.7 Hz, $J_{2A,3A}$ 3.7 Hz, H-2A), 5.58–5.21 (m, 8 H, H-2B, 2C, 2D, 3C, 3D, 4D, CH_2=CH–CH_2–), 5.14, 5.08, 5.04, 4.99 (4 d, 4 H, H-1A, 1B, 1C, 1D), 4.83 (dd, 1 H, $J_{5A,6A}$ 0.7 Hz, $J_{6A,6A}$ 12.7 Hz, H-6A), 4.65–3.70 (m, 12 H, H-3B, 4A, 4C, 5A, 5B, 5C, 5D, 6A, 6C, 6C, CH_2=CH–CH_2–), 2.26, 2.02 (2 s, 6 H, 2 CH_3CO), 0.85, 0.72 (2 d, 6 H, *J* 6.2 Hz, 2 CH_3). Anal. Calcd for $C_{94}H_{86}O_{30}$: C, 66.58; H, 5.11. Found: C, 66.59; H, 5.20.

Allyl 4-O-{3-O-[4-O-(3,4-*di*-O-*benzoyl*-α-L-*rhamnopyranosyl*)-2,3,6-*tri*-O-*benzoyl*-α-D-*mannopyranosyl*]-4-*benzoyl*-α-L-*rhamnopyranosyl*}-2,3,6-*tri*-O-*benzoyl*-α-D-*mannopyranoside* (**18**).—A methanolic solution of HCl (1.04 N, 2.2 mL) prepared by adding acetyl chloride (0.8 mL) to freshly distilled MeOH (10 mL), was added to a solution of **17** (320 mg, 0.19 mmol) in freshly distilled MeOH (1.5 mL) and the solution was stirred at 48–52 °C for 1.5 h to give **18** as a syrup (260 mg, 0.16 mmol, 84%) after flash chromatography; $[\alpha]_D^{20}$ −49.4° (*c* 0.7 $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.17–7.80 (m, 18 H, Bz–H), 7.68–7.20 (m, 27 H, Bz–H), 6.07–5.82 (m, 1 H, CH_2=C*H*–CH_2–), 5.86 (dd, 1 H, $J_{2A,3A}$ 3.2 Hz, $J_{3A,4A}$ 9.8 Hz, H-3A), 5.68–5.02 (m, 8 H, H-2A, 2C, 3C, 3D, 4D, 6A, CH_2=CH–CH_2–), 5.22, 5.12, 5.05, 5.04 (4 d, 4 H, H-1A, 1B, 1C, 1D), 4.89–3.80 (m, 14 H, H-2B, 2D, 3B, 4A, 4C, 5A, 5B, 5C, 5D, 6A, 6C, 6C, CH_2=CH–CH_2–), 0.81, 0.76 (2 d, 6 H, *J* 6.2 Hz, 2 CH_3). Anal. Calcd for $C_{90}H_{82}O_{28}$: C, 67.07; H, 5.13. Found: C, 67.01; H, 5.15.

Allyl 4-O-{2-O-[2,3,4-*tri*-O-*acetyl*-β-L-*xylopyranosyl*]-3-O-[4-O-(2-O-(2,3,4-*tri*-O-*acetyl*-β-L-*xylopyranosyl*)-3,4-*di*-O-*benzoyl*-α-L-*rhamnopyranosyl*)-2,3,6-*tri*-O-*benzoyl*-α-D-*mannopyranosyl*]-4-O-*benzoyl*-α-L-*rhamnopyranosyl*}-2,3,6-*tri*-O-*benzoyl*-α-D-*mannopyranoside* (**19**).—Coupling of 2,3,4-tri-*O*-acetyl-α-L-xylopyranosyl bromide (128 mg, 0.3 mmol), obtained from L-xylose (purchased from Fluka) according to the standard method for the preparation of 'acetobromoglucose' [15], with the tetrasaccharide acceptor **18** (170 mg, 0.106 mmol), promoted by silver triflate (77 mg, 0.3 mmol), in dry CH_2Cl_2 (10 mL) containing 4 Å activated molecular sieves (0.5 g) under N_2 was carried out at −5 °C for 2 h, at the end of which time TLC showed the starting material had disappeared. Pyridine (150 μL) and 10% aq $Na_2S_2O_3$ (1 mL) were added to quench the reaction. The reaction mixture was dissolved in CH_2Cl_2 (10 mL) and washed sequentially with N HCl (10 mL), satd aq $NaHCO_3$ (10 mL), and H_2O (10 mL). The aq washings were re-extracted with CH_2Cl_2 (5 mL) and the combined organic solutions were dried and concentrated. After flash chromatography with 3:1 petroleum ether–EtOAc as the eluent, hexasaccharide **19** (152 mg, 0.071 mmol, 67%) was obtained; $[\alpha]_D^{20}$ +36.8° (*c* 1.8 $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.18–7.84 (m, 18 H, Bz–H), 7.72–7.22 (m, 27 H, Bz–H), 6.04–5.93 (m, 1 H, CH_2=C*H*–CH_2–), 5.85 (dd, 1 H, $J_{2A,3A}$ 3.4 Hz, $J_{3A,4A}$ 9.6 Hz, H-3A), 5.74 (dd, 1 H, $J_{1A,2A}$ 1.7 Hz, $J_{2A,3A}$ 3.4 Hz, H-2A), 5.63–5.59 (m, 2 H, H-2C, 3C), 5.39–5.20 (m, 2 H, CH_2=CH–CH_2–), 5.30–4.52 (m, 17 H, H-1A, 1B, 1C, 1D, 2E, 2F, 3D, 3E, 3F, 4B, 4D, 4E, 4F, 6A, 6C), 4.46–4.10 (m, 13 H, H-1E, 1F, 2B, 2D, 3B, 4A, 4C, 6E, 6F, CH_2=CH–CH_2–), 4.05–3.11 (m, 8 H, H-5A, 5B, 5C, 5D, 5E, 5F), 2.12, 2.03, 2.03, 2.02, 1.74, 1.57 (6 s, 18 H, 6 CH_3CO), 0.73 (d, 3 H, *J* 6.2 Hz, CH_3), 0.61 (d, 3 H, *J* 6.2 Hz, CH_3). Anal. Calcd for $C_{112}H_{110}O_{42}$: C, 63.21; H, 5.21. Found: C, 63.10; H, 5.25.

Allyl 4-O-{2-O-[β-L-xylopyranosyl]-3-O-[4-O-(2-O-(β-L-xylopyranosyl)-α-L-rhamnopyranosyl)-α-D-mannopyranosyl]-α-L-rhamnopyranosyl}-α-D-mannopyranoside (**20**).—The protected hexasaccharide **19** (120 mg, 0.056 mmol) was suspended in freshly distilled MeOH (10 mL), a solution of sodium methoxide (2 M, 0.5 mL) was added, and the mixture was stirred overnight at rt. More sodium methoxide (0.5 mL) was added, and the reaction was heated at 40 °C for another 8 h. TLC showed that the reaction was complete. The resulting solution was de-ionized with Amberlite IR-120 (H^+) anion-exchange resin, filtered, and evaporated. The hexasaccharide **20** was obtained after chromatography on Sephadex G-25 (H_2O solvent) as an amorphous powder (51 mg, 97%) after freeze-drying; $[\alpha]_D^{20} + 33.5°$ (*c* 1.8, MeOH); ESMS for $C_{37}H_{62}O_{27}$ (938.88): 937.7 $[M-1]^+$. ^{1}H NMR (D_2O): δ 6.00–5.85 (m, 1 H, CH_2=C*H*–CH_2–), 5.32–5.17 (m, 2 H, CH_2=CH–CH_2–), 5.00, 4.94, 4.94, 4.87 (4 s, 4 H, H-1A, 1B, 1C, 1D), 4.32, 4.30 (2 d, 2 H, $J_{1E,2F}$ 7.6 Hz, H-1E, 1F), 4.24–4.15 (m, 2 H, CH_2=CH–CH_2–), 1.23,1.23 (2 d, 6 H, *J* 4.3 Hz, CH_3).

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