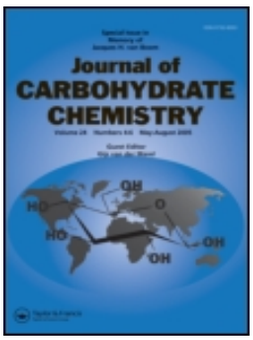

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SYNTHESIS OF β-d-Glcp-(1→2)-[β-d-Ribf-(1→3)-]α-l-Rhap-(1→3)-α-l-Rhap-(1→2)-α-l-Rhap, THE REPEATING UNIT OF THE LIPOPOLYSACCHARIDE OF Acetobacter diazotrophicus PAL 5

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SYNTHESIS OF β-D-Glc*p*-(1→2)-[β-D-Rib*f*-(1→3)-]α-L-Rha*p*-(1→3)-α-L-Rha*p*-(1→2)-α-L-Rha*p*, THE REPEATING UNIT OF THE LIPOPOLYSACCHARIDE OF *ACETOBACTER DIAZOTROPHICUS* PAL 5

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ABSTRACT

A pentasaccharide, the major repeating unit of the lipopolysaccharide (LPS) of the nitrogen fixing bacterium *Acetobacter diazotrophicus* PAL 5 was efficiently synthesized as its allyl glycoside using a regio- and stereoselective strategy. The key acceptor, allyl 3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (**3**), was prepared by selective 3-*O*-acetylation of allyl 4-*O*-benzoyl-α-L-rhamnopyranoside. Condensation of **3** with 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate furnished the disaccharide **5**. Deallylation and subsequent trichloroacetimidation of **5** afforded 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (**10**). Selective 3-*O*-glycosylation of allyl α-L-rhamnopyranoside (**1**) with **10** followed by benzoylation gave trisaccharide (**12**), which could be conveniently converted to a donor (**14**). Condensation of **14** with allyl 3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**15**) gave tetrasaccharide **16**. Selective deacetylation of **16** gave the acceptor **17** which was ribosylated to furnish the protected pentasaccharide, and finally deprotection led to the title compound.

Key Words: Regio- and stereoselective synthesis; Rhamnan; Trichloroacetimidate

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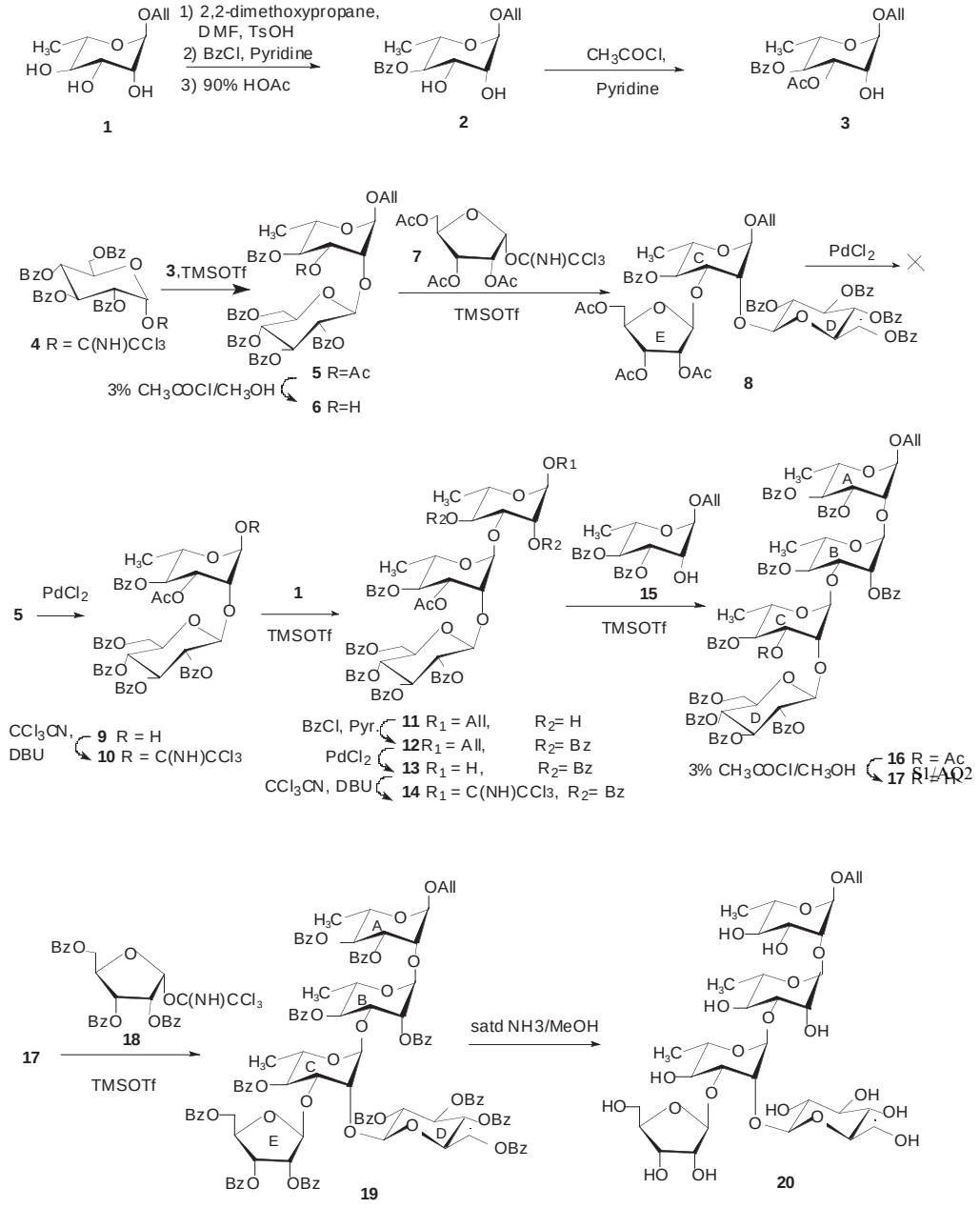
INTRODUCTION

The pentasaccharide, β-D-Glc*p*-(1→2)-[β-D-Rib*f*-(1→3)-]α-L-Rha*p*-(1→3)-α-L-Rha*p*-(1→2)-α-L-Rha*p*, is the major repeating unit of the lipopolysaccharide (LPS) of the nitrogen fixing bacterium *Acetobacter diazotrophicus* PAL 5 occurring in sugar cane in Brazil and Australia.[1] Field experiments suggest that up to 80% of the N incorporated into Brazilian sugar cane may be obtained from biological nitrogen fixation (BNF). The involvement of the carbohydrate-rich molecules in establishing the interaction between the BNF bacterium and the host has been reported.[2,3] These facts are of interest from the viewpoints of the biological roles of carbohydrates.

Rhamnans with a long backbone consisting of α-(1→2) and α-(1→3) linked L-rhamnose units to which are attached various kinds of side chains are widely distributed in nature. These target compounds are structurally very similar, but the synthetic approaches used are quite different. A stepwise synthesis of the hexasaccahride with rhamnotetraose as the backbone and two glucosamine units as the side chains has been reported.[4] Our previous work described highly regio- and stereoselective syntheses of oligosaccharides via orthoester formation-rearrangement strategy using glycosyl trichloroacetimidates as the donors and lightly protected sugars as the acceptors were achieved in a one-pot manner.[5–7] As part of our ongoing research project on the synthesis of rhamnans, we present herein the synthesis of the well-defined ribosylated glucorhamnan pentasaccharide.

RESULTS AND DISCUSSION

As outlined in Scheme 1, allyl α-L-rhamnopyranoside was converted to allyl 4-*O*-benzoyl-α-L-rhamnopyranoside (**2**) through 2,3-*O*-isopropylidenation with 2,2-dimethoxypropane in DMF in the presence of catalytic TsOH, 4-*O*-benzoylation with benzoyl chloride in pyridine, and deisopropylidenation with 90% acetic acid. These three steps were performed continuously without separation, giving 85.3% overall yield. Subsequent acetylation of **2** with 1.05 equiv of acetyl chloride in pyridine-dichloromethane selectively gave allyl 3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (**3**) as the only product in 91.5% yield. Its structure was confirmed by its ^{1}H NMR spectrum which showed a characteristic upfield signal at δ 4.11 ppm (dd, $J_{1,2}=1.6$ Hz, $J_{2,3}=3.2$ Hz) for H-2. Coupling of the glucose donor **4** with the acceptor **3** in the presence of catalytic TMSOTf furnished the (1→2)-linked disaccharide **5**. The 3-*O*-acetyl group of the disaccharide **5** was successfully removed without affecting any of the benzoyl groups in CH_3COCl-methanol[8] (3%) to give the desired acceptor **6** in 84.5% yield. Thus coupling of **6** with 2,3,4-tri-*O*-acetyl-α-D-ribofuranosyl trichloroacetimidate[9] (**7**) gave trisaccharide **8** in satisfactory yield (79.5%). However, perhaps because of the presence of peracetylated ribofuranosyl group, an attempt to deallylate **8** with $PdCl_2$ was not successful and gave a very complex product. Later on, we tried to first construct the glucorhamnose tetrasaccharide acceptor **17**, and then successively made the target pentasaccharide. Thus, deallylation of **5** with $PdCl_2$, followed by trichloroacetimidation[10] with CCl_3CN in the presence of DBU or K_2CO_3 gave the disaccharide donor **10**. Coupling of the donor **10** with the acceptor allyl α-L-rhamnopyranoside (**1**) in the presence of catalytic TMSOTf selectively gave the (1→3)-linked trisaccharide **11**. Benzoylation of **11** gave allyl 2,3,4,6-tetra-*O*-benzoyl-β-D-



Scheme 1. Synthesis of the target pentasaccharide.

glucopyranosyl-(1 →2)-3-*O*-acetyl-4-*O*-benzoy-α-L-rhamnopyranosyl-(1 →3)-2,4-di-*O*-benzoy-α-L-rhamnopyranoside (**12**, 68.1% for 2 steps). The ^{1}H NMR spectrum of **12** showed characteristic upfield signals at δ 4.45 ppm (dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.8 Hz) for H-3 and δ 3.75 ppm (dd, $J_{1,2}$ = 1.3 Hz, $J_{2,3}$ = 3.2 Hz) for H-2 respectively. It was noted that the temperature during addition of TMSOTf had to be maintained below −20°C

to ensure formation of the orthoester intermediate, otherwise, for example at room temperature, the regioselectivity was poor. Condensation of the rhamnose donor **14**, readily prepared from **12** through deallylation and trichloroacetimidation, with the acceptor **15** furnished the tetrasaccharide **16**. Subsequent selective deacetylation of **16** with CH_3COCl-methanol (3%) afforded the tetrasaccharide acceptor, allyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1 →2)-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1 →3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1 →2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**17**). Coupling of the tetrasaccharide **17** with 2,3,4-tri-*O*-benzoyl-α-D-ribofuranosyl trichloroacetimidate[9] (**18**) proceeded smoothly in dichloromethane in the presence of TMSOTf, giving the pentasaccharide (**19**). The structure of **19** was specified by its ^1H, ^{13}C NMR, and $^1H-^1H$ COSY NMR spectra. Deacylation of **19** in ammonium-saturated methanol gave the target pentasaccharide **20**. The bioassay of **20** is in progress.

In summary, a very concise and efficient synthesis of allyl β-D-glucopyranosyl-(1 →2)-[β-D-ribofuranosyl-(1 →3)-]α-L-rhamnopyranosyl-(1 →3)-α-L-rhamnopyranosyl-(1 →2)-α-L-rhamnopyranoside was achieved through a regio- and stereoselective process. In terms of the simplicity and efficiency, this method can be used for construction of higher oligosaccharides with similar structures.

EXPERIMENTAL

General methods. Melting points were determined with a 'Mel-Temp' apparatus. Optical rotations were determined with a Perkin-Elmer model 241-MC automatic polarimeter for solutions in a 1-dm, jacketed cell. ^1H and ^{13}C NMR spectra were recorded with Varian XL-400 and Varian XL-200 spectrometers, for solutions in $CDCl_3$ with tetramethylsilane (Me_4Si) as the internal standard or in D_2O with acetone as the internal standard. Chemical shifts are expressed in ppm downfield from the internal Me_4Si absorption. Mass spectra were recorded with a VG PLATFORM mass spectrometer using the ESI mode. Thin-layer chromatography (TLC) was performed on silica gel HF, detection being affected by charring with 30% (v/v) sulfuric acid in methanol or sometimes by UV detection. Column chromatography was conducted by elution of a column (16×240, 18×300, 35×400 mm) of silica gel (100–200 mesh) with EtOAc–petroleum ether (60–90°C) as the eluent. Analytical LC was performed with a Gilson HPLC consisting of a pump (model 306), stainless steel packed with silica gel (Spherisorb SiO_2, 10×300 mm or 4.6×250 mm), differential refractometer (132-RI Detector), UV/VIS detector (model 118), and EtOAc/petroleum ether (bp 60–90°C) was used as the eluent at a flow rate of 1–4 mL/min. Solutions were concentrated at a temperature <60°C under diminished pressure.

Allyl 4-*O*-benzoyl-α-L-rhamnopyranoside (2). To a solution of allyl α-L-rhamnopyranoside (**1**) (2.04 g, 10 mmol) in DMF (10 mL) containing *p*-toluenesulfonic acid monohydrate (38 mg, 0.2 mmol) was added 2,2-dimethoxypropane (2.5 mL, 20 mmol) and the mixture was stirred for 12 h, at the end of which time TLC (3/1 petroleum ether/ethyl acetate) indicated that the reaction was complete. Then the reaction mixture was added dropwise to a solution of pyridine (20 mL) containing benzoyl chloride (4.7 mL, 40 mmol). After stirring for 24 h at room temperature, the mixture was diluted

with dichloromethane, washed with 1 N hydrochloric acid, water, and satd aq solution of sodium bicarbonate subsequently. The organic layer was combined, dried, and concentrated to a residue. The residue was dissolved in 90% acetic acid and refluxed for 1 h. The solution was concentrated, and purification of the residue by flash column chromatography on a silica gel column (1:1 petroleum ether–EtOAc) gave compound **2** (2.63 g, 85.4%) as a syrup; $[\alpha]_D - 71.3°$ (*c* 1.3, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.06–7.42 (m, 5 H, Bz-H), 5.93 (m, 1 H, OCH_2CHCH_2), 5.32–5.21 (m, 2 H, OCH_2CHCH_2), 5.07 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4), 4.92 (d, 1 H, $J_{1,2} = 0.8$ Hz, H-1), 4.24–3.98 (m, 5 H), 3.07–2.90 (bs, 2 H, 2 OH), 1.24 (d, $J_{5,6} = 6.4$ Hz, 3 H, H-6).

Anal. Calcd for $C_{16}H_{20}O_6$: C, 62.32; H, 6.54. Found: C, 64.49; H, 6.76.

Allyl 3-*O*-Acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (3). A solution of acetyl chloride (0.8 mL, 11 mmol) in anhyd dichloromethane (10 mL) was added dropwise to a solution of allyl 4-*O*-benzoyl-α-L-rhamnopyranoside (**2**, 3.08 g, 10 mmol) in anhyd dichloromethane (100 mL) containing 5 mL pyridine at 0°C within 10 min, and the mixture was stirred at room temperature for 2 h, at the end of which time TLC (3/1 petroleum ether/ethyl acetate) indicated that the reaction was complete. The mixture was washed with 1 N hydrochloric acid, water, and satd aq solution of sodium bicarbonate subsequently. The organic layer was combined, dried, and concentrated to a residue. Purification of the residue on a silica gel column with 3:1 petroleum ether–ethyl acetate as the eluent gave **3** (3.20 g, 91.5%) as a syrup; $[\alpha]_D - 53.2°$ (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.06–7.42 (m, 5 H, Bz-H), 5.93 (m, 1 H, OCH_2CHCH_2), 5.48 (dd, 1 H, $J_{2,3} = 3.2$ Hz, $J_{3,4} = 9.8$ Hz, H-3), 5.37 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 5.36–5.23 (m, 2 H, OCH_2CHCH_2), 4.90 (d, 1 H, $J_{1,2} = 1.6$ Hz, H-1), 4.24 (m, 1 H, OCH_2CHCH_2), 4.11 (dd, 1 H, $J_{1,2} = 1.6$ Hz, $J_{2,3} = 3.2$ Hz, H-2), 4.07–4.01 (m, 2 H, H-5, OCH_2CHCH_2), 1.99 (s, 3 H, CH_3CO), 1.25 (d, $J_{5,6} = 6.3$ Hz, 3 H, H-6).

Anal. Calcd for $C_{18}H_{22}O_7$: C, 61.70; H, 6.33. Found: C, 61.86; H, 6.30.

Allyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (5). 2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate (**4**) (3.70 g, 5 mmol) and allyl 3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (**3**) (1.75 g, 5 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (20 mL). TMSOTf (45 μL, 0.05 equiv) was added dropwise at −10°C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually warmed to ambient temperature. Then the mixture was neutralized with triethylamine and concentrated to dryness. Purification by column chromatography (3:1 petroleum ether–EtOAc) gave **5** (3.92 g, 84.5%) as a foamy solid; $[\alpha]_D - 5.8°$ (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.15–7.43 (m, 25 H, 5 PhH), 5.96 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.8$ Hz, H-3′), 5.80 (m, 1 H, OCH_2CHCH_2), 5.66 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4′), 5.61 (dd, 1 H, $J_{1,2} = 7.8$ Hz, $J_{2,3} = 9.8$ Hz, H-2′), 5.38 (dd, 1 H, $J_{2,3} = 3.2$ Hz, $J_{3,4} = 9.7$ Hz, H-3), 5.39–5.21 (m, 3 H, H-4, OCH_2CHCH_2), 5.04 (d, 1 H, $J_{1,2} = 1.4$ Hz, H-1), 4.88 (d, 1 H, $J_{1,2} = 7.8$ Hz, H-1′), 4.60–4.46 (m, 2 H, H-6′), 4.15–3.88 (m, 5 H, H-2, H-5, H-5′, OCH_2CHCH_2), 1.26 (s, 3 H, $COCH_3$), 1.22 (d, 3 H, $J_{5,6} = 6.4$ Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2 ($COCH_3$), 165.9, 165.8, 165.1, 164.9, 164.8 (5 C, 5 COPh), 117.4 (OCH_2CHCH_2), 102.8, 98.1 (2 C, C-1, 1′), 78.3, 72.4, 72.2, 71.9, 71.8, 70.4, 69.5, 68.2, 66.7, 63.0, 19.7, 16.5.

Anal. Calcd for $C_{52}H_{48}O_{16}$: C, 67.23; H, 5.21. Found: C, 67.09; H, 5.40.

Allyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)-4-*O*-benzoyl-α-L-rhamnopyranoside (6). To a solution of **5** (1.86 g, 2 mmol) in anhyd MeOH (50 mL) was added CH_3COCl (1.5 mL) at 0°C. The solution was stoppered in a flask and stirred at room temperature until TLC (3:1 petroleum ether–EtOAc) showed that the starting material disappeared. The solution was neutralized with Et_3N, then concentrated to dryness. The residue was passed through a short silica gel column to give **6** (1.69 g, 94.9%) as a white solid; $[\alpha]_D + 18.5°$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.03–7.27 (m, 25 H, 5 Ph*H*), 5.95 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.6$ Hz, H-3′), 5.80 (m, 1 H, OCH_2CHCH_2), 5.70–5.63 (m, 2 H, H-2′, H-4′), 5.25–5.13 (m, 3 H, H-1′, OCH_2CHCH_2), 5.04 (d, 1 H, $J_{1,2} = 0.8$ Hz, H-1), 4.90 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 4.67–4.50 (m, 2 H, H-6′), 4.20 (m, 1 H, H-5), 4.10 (m, 1 H, OCH_2CHCH_2), 4.03 (dd, 1 H, $J_{1,2} = 0.8$ Hz, $J_{2,3} = 3.1$ Hz, H-2), 4.00 (dd, 1 H, $J_{2,3} = 3.1$ Hz, $J_{3,4} = 9.8$ Hz, H-3), 3.92–3.84 (m, 2 H, H-5′, OCH_2CHCH_2), 1.21 (d, 3 H, $J_{5,6} = 6.3$ Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 166.0, 165.7, 165.2, 165.1 (5 C, 5 *C*OPh), 117.1 (OCH_2CHCH_2), 102.9, 98.1 (2 C, C-1, 1′), 80.3, 75.4, 72.6, 72.3, 72.1, 70.0, 69.5, 68.1, 66.0, 63.1, 17.4.

Anal. Calcd for $C_{50}H_{46}O_{15}$: C, 67.71; H, 5.23. Found: C, 67.53; H, 5.42.

Allyl 2,3,4-Tri-*O*-acetyl-β-D-ribofuranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)]-α-L-rhamnopyranoside (8). 2,3,4-Tri-*O*-acetyl-α-D-ribofuranosyl trichloroacetimidate (**7**, 421 mg, 1.0 mmol) and allyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)-4-*O*-benzoyl-α-L-rhamnopyranoside (**6**, 886 mg, 1.0 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (10 mL). TMSOTf (18 μL, 0.10 mmol) was added dropwise at −20°C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually warmed to ambient temperature. Then the mixture was neutralized with triethylamine and concentrated to dryness. Purification of the residue by column chromatography (1:1 petroleum ether–EtOAc) gave **8** (910 mg, 79.5%) as a foamy solid. $[\alpha]_D + 9.3°$ (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.17–7.28 (m, 25 H, 5 Ph*H*), 5.95 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4_C), 5.83 (m, 1 H, OCH_2CHCH_2), 5.69 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4_D), 5.60 (dd, 1 H, $J_{2,3} = 9.6$ Hz, $J_{3,4} = 9.7$ Hz, H-3_D), 5.36 (d, 1 H, $J_{2,3} = 3.7$ Hz, H-2_E), 5.26 (m, 1 H, OCH_2CHCH_2), 5.21 (d, 1 H, $J_{1,2} = 7.7$ Hz, H-1_D), 5.16–5.08 (m, 3 H, H-1_C, H-2_D, OCH_2CHCH_2), 4.96–4.92 (m, 2 H, H-1_E, H-3_E), 4.66–4.67 (m, 2 H, H-6_D), 4.30–3.70 (m, 8 H), 2.09 (s, 3 H, $COCH_3$), 2.04 (s, 3 H, $COCH_3$), 1.40 (s, 3 H, $COCH_3$), 1.08 (d, 3 H, $J_{5,6} = 6.3$ Hz, H-6_C); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 169.8, 169.6 (3 C, 3 $COCH_3$), 166.0, 165.8, 165.3, 165.3, 165.1, 165.0 (5 C, 5 *C*OPh), 116.9 (OCH_2CHCH_2), 102.0, 98.4, 97.6 (3 C, C-1_C, 1_D, 1_E), 78.3, 73.9, 72.6, 72.1, 72.0, 71.9, 70.0, 69.8, 68.0, 67.2, 66.8, 65.0, 63.1, 62.1, 20.9, 20.8, 20.6, 17.5.

Anal. Calcd for $C_{61}H_{60}O_{22}$: C, 63.98; H, 5.28. Found: C, 63.95; H, 5.51.

2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (10). To a solution of allyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (**5**, 928 mg, 1 mmol) in 90% acetic acid (10 mL) containing sodium acetate (293 mg, 3 mmol) was added $PdCl_2$ (89 mg, 0.5 mmol), and the mixture was stirred for 12 h,

at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was diluted with dichloromethane (30 mL), washed with water and satd aq sodium bicarbonate. The organic layer was concentrated, and the residue was passed through a short silica gel column with 2:1 petroleum ether–EtOAc as the eluent to give crude 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1 →2)-3-*O*-acetyl-4-*O*-benzoyl-α,β-L-rhamnopyranose (**9**, 844 mg, 95.0%). Compound **9** was dissolved in dichloromethane (10 mL), and CCl_3CN (0.2 mL, 2 mmol) and DBU (27 μL, 0.18 mmol) were added. The reaction mixture was stirred for 2 h, at the end of which time TLC (3:1 petroleum ether–ethyl acetate) indicated that the reaction was complete. Concentration of the reaction mixture followed by purification on a silica gel column with 3:1 petroleum ether–EtOAc as the eluent, furnished the disaccharide donor **10** (876 mg, 89.4%) as a foamy solid; $[\alpha]_D - 11.6°$ (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1 H, CN*H*CCl_3), 8.17–7.28 (m, 25 H, 5 Ph*H*), 6.52 (d, 1 H, $J_{1,2} = 1.6$ Hz, H-1), 5.99 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3′), 5.70–5.59 (m, 2 H, H-4′, H-2′), 5.37 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 4.93 (d, 1 H, $J_{1,2} = 7.7$ Hz, H-1′), 4.63–4.53 (m, 2 H, H-3, H-6′), 4.32 (dd, 1 H, $J_{1,2} = 1.6$ Hz, $J_{2,3} = 3.1$ Hz, H-2), 4.24–4.12 (m, 2 H, H-5, H-6′), 1.30 (d, 3 H, $J_{5,6} = 6.4$ Hz, H-6), 1.22 (s, 3 H, CO*C*H_3).

Anal. Calcd for $C_{51}H_{44}Cl_3NO_{16}$: C, 59.28; H, 4.29. Found: C, 59.50; H, 4.44.

Allyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1 →2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1 →3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (12). 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1 →2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (**10**, 1.03 g, 1 mmol) and allyl α-L-rhamnopyranoside (**1**, 204 mg, 1 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (40 mL). TMSOTf (18 μL, 0.1 mmoL) was added dropwise at −25°C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually warmed to ambient temperature. Then the mixture was neutralized with triethylamine, and concentrated to dryness under reduced pressure to afford the crude allyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1 →2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1 →3)-α-L-rhamnopyranoside (**11**). To the solution of crude **11** in pyridine (20 mL) was added benzoyl chloride (3.5 mL, 30 mmol) dropwise, and the mixture was stirred overnight at room temperature. TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. Ice water was added, and the mixture was diluted with dichloromethane, washed with 1 N hydrochloric acid, water, and satd aq sodium bicarbonate. The organic layer was combined, dried, and concentrated. Purification of the crude product by column chromatography (3:1 petroleum ether–EtOAc) gave **12** (810 mg, 68.1% for 2 steps) as a syrup: $[\alpha]_D + 42.6°$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15–7.27 (m, 35 H, 7 Ph*H*), 5.95 (m, 1 H, OCH_2CHCH_2), 5.71 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.6$ Hz, H-3″), 5.56–5.46 (m, 2 H, H-4″, H-2″), 5.44 (dd, 1 H, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3.1$ Hz, H-2), 5.42–5.25 (m, 3 H, H-4, OCH_2CHCH_2), 5.13 (dd, 1 H, $J_{2,3} = 3.2$ Hz, $J_{3,4} = 9.6$ Hz, H-3′), 5.11 (d, 1 H, $J_{1,2} = 1.5$ Hz, H-1/H-1′), 5.06 (d, 1 H, $J_{1,2} = 1.0$ Hz, H-1/H-1′), 5.05 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4′), 4.48 (d, 1 H, $J_{1,2} = 7.7$ Hz, H-1″), 4.45 (dd, 1 H, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.8$ Hz, H-3), 4.37–4.08 (m, 5 H, H-5/H-5′, H-6″, OCH_2CHCH_2), 3.76 (m, 1 H, H-5/H-5′), 3.75 (dd, 1 H, $J_{1,2} = 1.3$ Hz, $J_{2,3} = 3.2$ Hz, H-2′), 3.54 (m, 1 H, H-5″), 1.29 (d, 3 H, $J_{5,6} = 6.2$ Hz, H-6/H-6′), 1.16 (s, 3 H, CO*C*H_3), 1.01 (d, 3 H, $J_{5,6} = 6.2$ Hz, H-6/H-6′); ^{13}C NMR (100

MHz, $CDCl_3$): δ 168.9 (*C*OCH_3), 165.7, 165.6, 165.4, 165.0 164.6, 164.4, 164.3 (7 C, 7 *C*OPh), 117.5 (OCH_2CH*C*H_2), 101.6, 100.5, 96.2 (3 C, C-1, 1′, 1″), 77.2, 76.0, 73.0, 72.3, 72.1, 71.6, 71.4, 71.1, 69.7, 69.0, 68.3, 68.2, 67.0, 66.1, 19.2, 17.2, 16.7.

Anal. Calcd for $C_{72}H_{66}O_{22}$: C, 67.38; H, 5.18. Found: C, 67.46; H, 5.03.

2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1 →2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1 →3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (14). To a solution **12** (1.2 g, 1 mmol) in 90% acetic acid (10 mL) containing sodium acetate (293 mg, 3 mmol) was added $PdCl_2$ (89 mg, 0.5 mmol), and the mixture was stirred for 12 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was diluted with dichloromethane (30 mL), washed with water and satd aq sodium bicarbonate. The organic layer was concentrated, and the residue was passed through a short silica gel column with 2:1 petroleum ether–EtOAc as the eluent to give crude 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1 →2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1 →3)-2,4-di-*O*-benzoyl-α,β-L-rhamnopyranose (**13**, 1.05 g, 91.3%). Compound **13** was dissolved in dichloromethane (10 mL), and CCl_3CN (0.2 mL, 2 mmol) and DBU (27 μL, 0.18 mmol) were added. The reaction mixture was stirred for 2 h, at the end of which time TLC (3:1 petroleum ether–ethyl acetate) indicated that the reaction was complete. Concentration of the reaction mixture followed by purification on a silica gel column with 3:1 petroleum ether–EtOAc as the eluent, furnished the trisaccharide donor **14** (1.01 g, 86.0%) as a foamy solid: $[\alpha]_D + 37.8°$ (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (s, 1 H, CN*H*CCl_3), 8.19–7.27 (m, 35 H, 7 Ph*H*), 6.47 (d, 1 H, $J_{1,2} = 1.9$ Hz, H-1), 5.75 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3″), 5.66 (dd, 1 H, $J_{1,2} = 1.9$ Hz, $J_{2,3} = 3.3$ Hz, H-2), 5.61 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4″), 5.51 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 5.40 (dd, 1 H, $J_{1,2} = 7.7$ Hz, $J_{2,3} = 9.7$ Hz, H-2″), 5.20 (d, 1 H, $J_{1,2} = 1.6$ Hz, H-1′), 5.18 (dd, 1 H, $J_{2,3} = 3.2$ Hz, $J_{3,4} = 9.6$ Hz, H-3′), 5.08 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4′), 4.60 (d, 1 H, $J_{1,2} = 7.7$ Hz, H-1″), 4.54 (dd, 1 H, $J_{2,3} = 3.3$ Hz, $J_{3,4} = 9.8$ Hz, H-3), 4.30–4.24 (m, 2 H, H-5″, H-6″), 4.04–3.91 (m, 2 H, H-5/H-5′, H-6″), 3.86 (dd, 1 H, $J_{1,2} = 1.6$ Hz, $J_{2,3} = 3.2$ Hz, H-2′), 3.61 (m, 1 H, H-5/H-5′), 1.43 (d, 3 H, $J_{5,6} = 6.3$ Hz, H-6/H-6′), 1.25 (s, 3 H, CO*C*H_3), 1.02 (d, 3 H, $J_{5,6} = 6.4$ Hz, H-6/H-6′).

Anal. Calcd for $C_{71}H_{62}Cl_3NO_{22}$: C, 61.45; H, 4.50. Found: C, 61.26; H, 4.41.

Allyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1 →2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1 →3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1 →2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (16). Compound **14** (693 mg, 0.5 mmol) and allyl 3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**15**, 206 mg, 0.5 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (40 mL). TMSOTf (18 μL, 0.1 mmoL) was added dropwise at −5°C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually raised to ambient temperature. Then the mixture was neutralized with triethylamine, and concentrated. Purification of the residue by column chromatography (2:1 petroleum ether–EtOAc) gave **16** (684 mg, 83.6%) as a syrup: $[\alpha]_D + 71.2°$ (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10–7.25 (m, 45 H, 9 Ph*H*), 5.90 (m, 1 H, OCH_2C*H*CH_2), 5.77 (dd, 1 H, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.8$ Hz, H-3_A), 5.73 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3_D), 5.67 (dd, 1 H, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3.1$ Hz, H-2_B), 5.60 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4_A), 5.50–5.28 (m, 5 H, H-2_D, H-4_B, H-4_D, OCH_2CHC*H*$_2$), 5.25 (d, 1 H, $J_{1,2} = 1.6$ Hz, H-1_C), 5.23 (dd, 1

H, $J_{2,3}$ = 3.1 Hz, $J_{3,4}$ = 9.7 Hz, H-3_C), 5.14 (d, 1 H, $J_{1,2}$ = 1.5 Hz, H-1_B), 5.11 (dd, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.7 Hz, H-4_C), 5.03 (d, 1 H, $J_{1,2}$ = 1.3 Hz, H-1_A), 4.64 (d, 1 H, $J_{1,2}$ = 7.7 Hz, H-1_D), 4.61 (dd, 1 H, $J_{2,3}$ = 3.1 Hz, $J_{3,4}$ = 9.8 Hz, H-3_B), 4.31 (dd, 1 H, $J_{1,2}$ = 1.3 Hz, $J_{2,3}$ = 3.0 Hz, H-2_A), 4.30–4.07 (m, 6 H), 3.92 (m, 1 H, H-5_C), 3.90 (dd, 1 H, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 3.1 Hz, H-2_C), 3.60 (m, 1 H, H-5_A), 1.32 (d, 3 H, $J_{5,6}$ = 6.2 Hz), 1.28 (s, 3 H, CO*CH*$_3$), 1.26 (d, 3 H, $J_{5,6}$ = 6.4 Hz), 1.07 (d, 3 H, $J_{5,6}$ = 6.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8 (*C*OCH$_3$), 165.5, 165.4, 165.3, 165.1, 165.0, 164.9, 164.6, 164.5, 164.3 (9 C, 9 *C*OPh), 117.3 (OCH$_2$CH*C*H$_2$), 101.3, 99.8, 99.1, 97.3 (4 C, C-1_A, 1_B, 1_C, 1_D), 73.8, 73.1, 72.2, 71.7, 71.6, 71.6, 71.5, 71.5, 71.4, 70.7, 69.8, 69.3, 67.9, 67.8, 67.3, 67.0, 66.6, 62.4 (18 C, C-2_A, 2_B,2_C, 2_D, 3_A, 3_B, 3_C, 3_D, 4_A, 4_B, 4_C, 4_D, 5_A, 5_B, 5_C, 5_D, 6_D, O*C*H$_2$CHCH$_2$), 19.4, 17.2, 17.2, 16.8 (4 C, C-6_A, 6_B, 6_C, CO*C*H$_3$).

Anal. Calcd for $C_{92}H_{84}O_{28}$: C, 67.47; H, 5.17. Found: C, 67.54; H, 5.33.

Allyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (17). To a solution of **16** (654 mg, 0.4 mmol) in anhyd MeOH (50 mL) was added acetyl chloride (1.5 mL) at 0°C. The solution was stoppered in a flask and stirred at room temperature until TLC (3:1 petroleum ether–EtOAc) showed that the starting material disappeared. The solution was neutralized with Et_3N, then concentrated to dryness. The residue was passed through a short silica gel column to give **17** (603 mg, 94.6%) as a white solid: $[\alpha]_D$ + 75.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11–7.32 (m, 45 H, 9 Ph*H*), 5.91 (m, 1 H, OCH$_2$C*H*CH$_2$), 5.79 (dd, 1 H, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.8 Hz, H-3_A), 5.68 (dd, 1 H, $J_{1,2}$ = 0.8 Hz, $J_{2,3}$ = 3.1 Hz, H-2_B), 5.67 (dd, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, H-3_D), 5.62 (dd, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.8 Hz, H-4_A), 5.53 (dd, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4_D), 5.48 (dd, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.7 Hz, H-4_B), 5.45 (dd, 1 H, $J_{1,2}$ = 7.7 Hz, $J_{2,3}$ = 9.6 Hz, H-2_D), 5.40–5.26 (m, 2 H, OCH$_2$CHC*H*$_2$), 5.22 (d, 1 H, $J_{1,2}$ = 0.8 Hz, H-1_B), 5.13 (d, 1 H, $J_{1,2}$ = 1.6 Hz, H-1_C), 5.03 (d, 1 H, $J_{1,2}$ = 1.6 Hz, H-1_A), 4.80 (dd, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.9 Hz, H-4_C), 4.66 (d, 1 H, $J_{1,2}$ = 7.7 Hz, H-1_D), 4.58 (dd, 1 H, $J_{2,3}$ = 3.1 Hz, $J_{3,4}$ = 9.7 Hz, H-3_B), 4.32–4.11 (m, 7 H), 3.92 (m, 1 H), 3.78–3.74 (m, 2 H), 3.45 (m, 1 H), 1.33 (d, 3 H, $J_{5,6}$ = 6.4 Hz), 1.27 (d, 3 H, $J_{5,6}$ = 6.4 Hz), 1.10 (d, 3 H, $J_{5,6}$ = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 165.5, 165.4, 165.3, 165.3, 165.1, 165.0, 164.9, 164.8, 164.5 (9 C, 9 *C*OPh), 117.5 (OCH$_2$CH*C*H$_2$), 102.0, 99.5, 99.1, 97.3 (4 C, C-1_A, 1_B, 1_C, 1_D), 79.3, 73.8, 73.1, 72.1, 71.7, 71.6, 71.6, 71.5, 71.5, 71.4, 70.7, 69.8, 69.2, 68.9, 67.8, 66.9, 66.6, 62.3 (18 C, C-2_A, 2_B,2_C, 2_D, 3_A, 3_B, 3_C, 3_D, 4_A, 4_B, 4_C, 4_D, 5_A, 5_B, 5_C, 5_D, 6_D, O*C*H$_2$CHCH$_2$), 17.2, 17.1, 16.8 (3 C, C-6_A, 6_B, 6_C).

Anal. Calcd for $C_{90}H_{82}O_{27}$: C, 67.74; H, 5.18. Found: C, 67.63; H, 5.26.

Allyl 2,3,4-Tri-*O*-benzoyl-β-D-ribofuranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)-]4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (19). 2,3,4-Tri-*O*-benzoyl-α-D-ribofuranosyl trichloroacetimidate (**18**, 243 mg, 0.4 mmol) and **17** (590 mg, 0.37 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (40 mL). TMSOTf (18 μL, 0.10 mmol) was added dropwise at −10°C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually warmed to ambient temperature. Then the mixture was neutralized with triethylamine and concentrated to dryness. Purification

of the residue by column chromatography (1:1 petroleum ether–EtOAc) gave **19** (536 mg, 71.1%) as a foamy solid: $[\alpha]_D + 37.1°$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.10–7.19 (m, 60 H, 12 Ph*H*), 6.00 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.5$ Hz, H-3_D), 5.94 (m, 1 H, OCH_2CHCH_2), 5.78 (dd, 1 H, $J_{2,3} = 3.2$ Hz, $J_{3,4} = 9.8$ Hz, H-3_A), 5.67 (dd, 1 H, $J_{1,2} = 1.7$ Hz, $J_{2,3} = 3.3$ Hz, H-2_B), 5.61–5.52 (m, 3 H, H-4_A, H-4_B, H-4_D), 5.47–5.43 (m, 2 H, H-2_D, H-4_E), 5.37 (m, 1 H, OCH_2CHCH_2), 5.35 (d, 1 H, $J_{1,2} = 7.7$ Hz, H-1_D), 5.26 (m, 1 H, OCH_2CHCH_2), 5.22–5.21(m, 2 H, H-1_C, H-1_E), 5.15 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4_C), 5.12 (d, 1 H, $J_{1,2} = 1.5$ Hz, H-1_B), 5.00 (d, 1 H, $J_{1,2} = 1.5$ Hz, H-1_A), 4.95 (dd, 1 H, $J_{2,3} = J_{3,4} = 4.0$ Hz, H-3_E), 4.84 (d, 1 H, $J_{2,3} = 4.0$ Hz, H-2_E), 4.61 (dd, 1 H, $J_{2,3} = 3.4$ Hz, $J_{3,4} = 9.9$ Hz, H-3_B), 4.32–4.06 (m, 10 H), 3.82 (m, 1 H), 3.54–3.39 (m, 2 H), 1.33 (d, 3 H, $J_{5,6} = 6.3$ Hz), 1.29 (d, 3 H, $J_{5,6} = 6.4$ Hz), 0.75 (d, 3 H, $J_{5,6} = 6.3$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 165.4, 165.3, 165.1, 165.0, 164.9, 164.9, 164.9, 164.8, 164.5, 164.3, 163.9 (12 C, 12 *C*OPh), 117.5 (OCH_2CHCH_2), 100.0 (1 C, C-$1_{A/B/C}$, $J_{C1\text{-}H1} = 173$ Hz), 99.5 (1 C, C-1_E, $J_{C1\text{-}H1} = 162$ Hz), 99.1 (2 C, C-$1_{A/B/C}$, $J_{C1\text{-}H1} = 171$ Hz), 97.2 (1 C, C-1_D, $J_{C1\text{-}H1} = 164$ Hz), 17.2, 17.2, 16.5 (3 C, C-6_A, 6_B, 6_C).

Anal. Calcd for $C_{116}H_{102}O_{34}$: C, 68.29; H, 5.09. Found: C, 68.41; H, 5.03.

Allyl β-D-Ribofuranosyl-(1→3)-[β-D-glucopyranosyl-(1→2)]-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranoside (20). Pentasaccharide **19** (500 mg, 0.25 mmol) was dissolved in a saturated solution of ammonia in MeOH (10 mL). After 4 days at rt, the reaction mixture was concentrated and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **20** as a foamy solid (151 mg, 77.8%); $[\alpha]_D - 46.1°$ (*c* 1.0, D_2O); ^1H NMR (400 MHz, D_2O): δ 5.95 (m, 1 H, OCH_2CHCH_2), 5.43 (s, 1 H, H-1), 5.41–5.30 (m, 2 H, OCH_2CHCH_2), 5.05 (d, 1 H, $J_{1,2}$ 5.1 Hz, H-1), 4.94 (s, 2 H, H-1), 4.62 (d, 1 H, $J_{1,2}$ 10.3 Hz, H-1); ^{13}C NMR (100 MHz, D_2O): δ 105.8, 104.8, 104.4, 102.9, 101.9 (5C, C-1); MS (*m*/*z*) Calcd for $C_{32}H_{54}O_{22}$: 790.31 $[M]^+$. Found: 813.52$[M + Na]^+$.

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