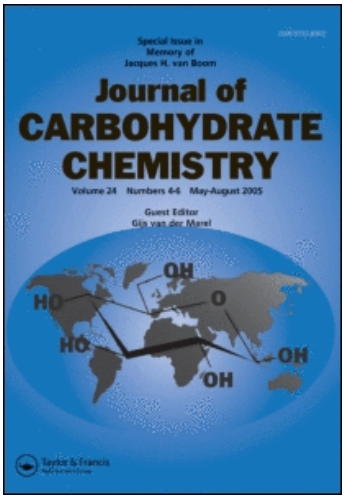

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FACILE SYNTHESIS OF A BRANCHED TRISACCHARIDE— THE REPEATING UNIT OF ANTIGEN O2 POLYMER USING ORTHOESTER FORMATION - REARRANGEMENT STRATEGY

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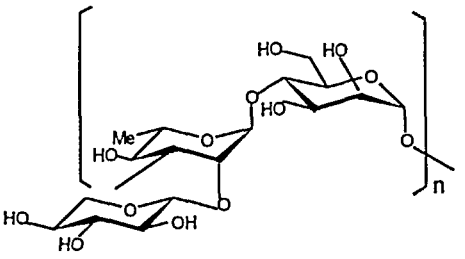
ABSTRACT

The synthesis of a branched trisaccharide, the repeating unit of the antigen O2 polymer containing L-rhamnose, D-mannose, and L-xylose, was achieved using orthoester formation - rearrangement strategy.

INTRODUCTION

Since its introduction by Ogawa's group in 1981,[1a] the use of TMSOTf catalyzed rearrangement for building glycosidic linkages has not received much attention, and very few examples[1] have been reported. We found that under suitable conditions, both orthoester formation and subsequent rearrangemnt are carried out readily forming a glycosidic linkage stereoselectively in high yields. Here we present the synthesis of a branched trisaccharide using orthoester formation - rearrangement strategy.

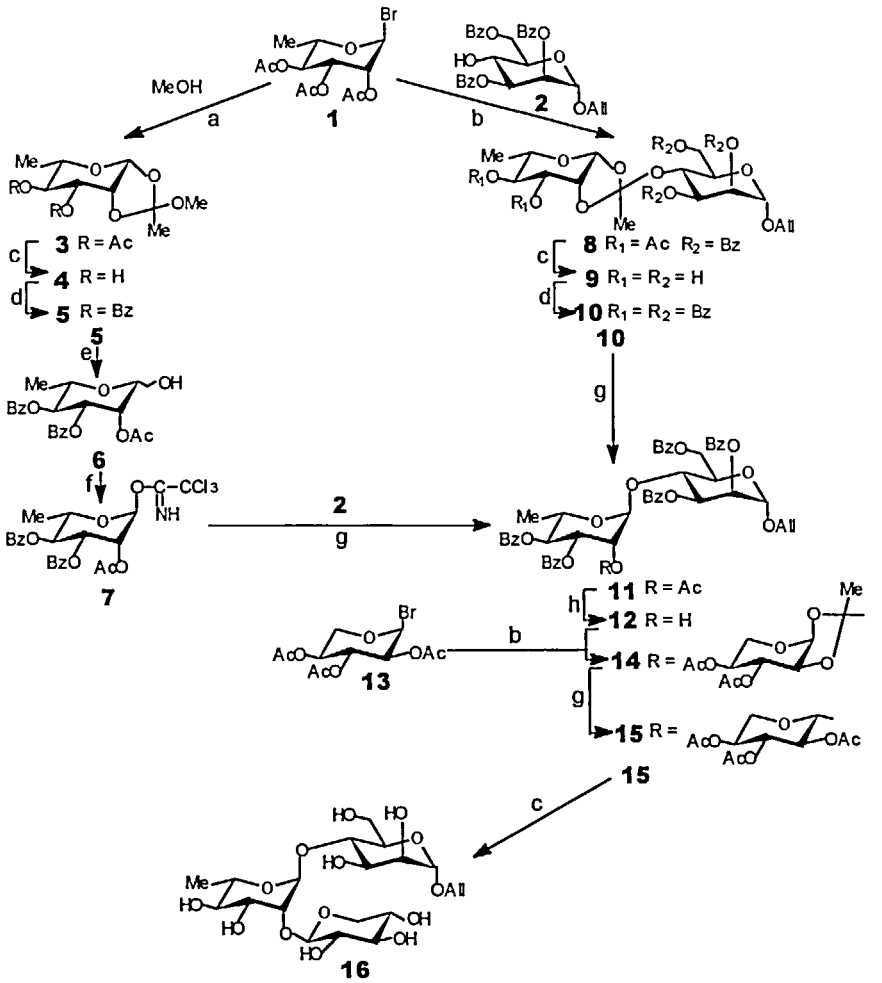


Scheme 1

RESULTS AND DISCUSSION

The organism known as *Stenotrophomonas* (*Xanthomonas* or *Pseudomonas*) *maltophilia* is an agent of nosocomial infection and a potential threat to the cystic fibrosis population. The antigen O2 polymer containing L-rhamnose, D-mannose, and L-xylose was isolated from the lipopolysaccharide (LPS) occurring in the reference strain for *Stenotrophomonas maltophilia* serogroup O2, and its structure was elucidated to be composed of a branched trisaccharide repeating unit,[2] as shown in Scheme 1.

The following reaction pathway was designated for the synthesis of the described trisaccharide. Selective benzoylation[3] of allyl α-D-mannopyranoside, afforded allyl 2,3,6-tri-*O*-benzoyl-α-D-mannopyranoside **2**. Coupling[4] of **2** with acetobromorhamnose in dichloromethane in the presence of equivalent AgOTf and 2,4-lutidine, gave orthoester **8** as the sole product in nearly quantitative yield. Deacetylation of **8** followed by benzoylation gave orthoester **10** in very high yield. Rearrangement[4] of **10** with a catalytic amount of TMSOTf gave the desired disaccharide **11** in satisfactory yield (86%). Selective deacetylation[5] of **11** with CH_3COCl/MeOH readily furnished disaccharide **12** (96%), its coupling with acetobromo-L-xylose **13**, prepared easily from L-xylose according to the method for acetobromination of glucose,[6] in the presence of equivalent AgOTf and 2,4-lutidine gave orthoester **14** as the sole product in very high yield (96%). Rearrangement of **14** with a catalytic amount of TMSOTf gave trisaccharide **15** (85%), and subsequent deprotection with catalytic MeONa in MeOH easily afforded the final trisaccharide **16** in quantitative yield.



Scheme 2

a: MeOH/lutidine/*t*-Bu_4NBr (92%); b: AgOTf/lutidine (>95%); c: MeONa/MeOH (quant); d: BzCl/pyridine (quant); e: 70%AcOH (90%); f: CCl_3CN/DBU (83%); g: TMSOTf/CH_2Cl_2 (>80%); h: CH_3COCl/MeOH (96%);

To confirm the structure of **11**, an alternative synthesis was conducted. Thus methyl orthoester **3** was prepared in a high yield from reaction of acetobromorhamnose with MeOH in the presence of lutidine/*t*-Bu_4NBr. Deacetylation of **3** followed by benzoylation gave orthoester **5** in nearly quantitative yield. Hydrolysis of **5** in 70% AcOH solution afforded 2-*O*-acetyl-3,4-di-*O*-benzoyl-α,β-L-rhamnopyranose **6** with C-1 hydroxyl free,

which was converted to the trichloroacetimidate glycosyl donor **7** on treatment with CCl_3CN/DBU (overall yield 74%, for two steps). Glycosylation[7] of the acceptor **2** with the trichloroacetimidate **7** promoted by TMSOTf gave disacchride (85%) identical to **11**.

The key intermediates involved in the synthesis were characterized by ^1H NMR spectroscopy, optical rotation, and elemental analysis, the deprotected trisaccharide **16** gave ^1H NMR data similar to those reported in the literature.[2]

In summary, we have presented an orthoester formation - rearrangement strategy that can be a useful and general method for building glycosidic linkages. Its advantages include the high stereoselectivity and yield, the use of easily prepared acetobromoglycose as the starting material, the use of sole acyl protective groups which are easily removed by base, and the potential for building the 1→2 glycosyl linkage.

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 NMR spectra were recorded with Varian XL-400 and XL-200 spectrometers, for solutions in $CDCl_3$ with tetramethylsilane (Me_4Si) 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 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 (8/100 mm, 16/240 mm, 18/300 mm, and 35/400 mm) of silica gel (100-200 mesh) with EtOAc/petroleum ether (bp 60-90 °C) as the eluent. Solutions were concentrated at a temperature < 60 °C under diminished pressure.

Allyl 2,3,6-Tri-*O*-benzoyl-α-D-mannopyranoside (2). 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 up to room temperature and 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 aqueous phases were re-extracted with CH_2Cl_2 (40 mL), and the combined organic solutions were dried, concentrated, and the resultant residue was purified by column chromatography with 1/1 petroleum ether/EtOAc as the eluent to give compound **2** 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, 6H, Bz-H), 7.70-7.23 (m, 9H, Bz-H), 6.08-5.84 (m, 1H, CH_2=C*H*-CH_2-), 5.65 (dd, 1H, $J_{2,3}$ = 2.6 Hz, $J_{3,4}$ = 9.3 Hz, H-3), 5.63 (dd, 1H, $J_{1,2}$ = 1.0 Hz, $J_{2,3}$ = 2.6 Hz, H-2), 5.41-5.20 (m, 2H, C*H*$_2$=CH-CH_2-), 5.07 (d, 1H, $J_{1,2}$ = 1.0 Hz, H-1), 4.89 (dd, 1H, $J_{5,6}$ = 4.0 Hz, $J_{6,6'}$ = 12.6 Hz, H-6), 4.66 (dd, 1H, $J_{5,6'}$ = 2.1 Hz, $J_{6,6'}$ = 12.6 Hz, H-6'), 4.30 (t, 1H, J = 9.3 Hz, H-4), 4.38-4.15 (m, 3H, 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 (3). 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 room temperature, and MeOH (anhydrous, 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 compound **3** (1.7 g, 97%): mp 80-84 °C; $[\alpha]_D^{20}$ +31° (*c* 1.0, $CHCl_3$); lit.[8] mp 84-86 °C; $[\alpha]_D$ +34.7°.

Anal. Calcd for $C_{13}H_{20}O_8$: C, 51.31; H, 6.63. Found: C, 51.14; H, 6.80.

2-*O*-Acetyl-3,4-di-*O*-benzoyl-α,β-L-rhamnopyranose (6). According to the standard method,[9] compound **3** (1.5 g, 4.9 mmol) was deacetylated with MeONa in MeOH, and then benzoylated with BzCl in pyridine to furnish **5** in quantitative yield. Hydrolysis of **5** with 70% aqueous HOAc at room temperature furnished **6** (1.8 g) as a colorless syrup in a yield of 89%. Flash chromatography (2/1 petroleum ether/EtOAc) of the residue gave an anomeric mixture **6** (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 (2d, 4H, J = 7.6 Hz, Bz-H), 7.56-7.25 (m, 6H, Bz-H), 5.81 (dd, 1H, $J_{2,3}$ = 3.4 Hz, $J_{3,4}$ = 9.8 Hz, H-3), 5.57 (t, 1H, J = 9.8 Hz, H-4), 5.52 (dd, 1H, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3.4 Hz, H-2), 5.31 (d, 1H, $J_{1,2}$ = 1.5 Hz, H-1), 4.49-4.31 (m, 1H,

H-5), 2.17 (s, 3H, CH_3CO), 1.31 (d, 3H, $J_{5,6}$ = 6.7 Hz, CH_3); β isomer was not isolated in pure form and it was used as an α, β mixture for further reaction.

Anal. Calcd for $C_{22}H_{22}O_8$: C, 63.76; H, 5.35. Found: C, 63.90; H, 5.35.

3,4-Di-*O*-acetyl-β-L-rhamnopyranose 1,2-(Allyl 2,3,6-tri-*O*-benzoyl-α-D-mannopyranosid-4-yl orthoacetate) (8). To a stirred solution 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 allyl 2,3,6-tri-*O*-benzoyl-α-D-mannopyranoside (2.9 g, 5.5 mmol) in dichloromethane (30 mL) under nitrogen atmosphere was added silver triflate (1.48 g, 5.8 mmol) in a dark room. The reaction was carried out at room temperature and monitored by TLC (2:1 petroleum ether/EtOAc). After completion of the reaction, the mixture was partitioned between dichloromethane and water, the organic phase was concentrated under reduced pressure. The residual oil was purified by silica gel column chromatography with 2:1 petroleum ether/EtOAc as the eluent giving **8** as the sole product in a yield of 95% (4.8 g) capable of being used for further rearrangement: $[\alpha]_D^{20}$ +16.2° (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$, 200 MHz) δ 8.22-8.00 (m, 6H, Bz-H), 7.70-7.30 (m, 9H, Bz-H), 6.05-5.83 (m, 1H, CH_2=C*H*-CH_2-), 5.71 (dd, 1H, $J_{1,2}$ = 1.7 Hz, $J_{2,3}$ = 3.2 Hz, H-2), 5.63 (dd, 1H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 5.40-5.19 (m, 2H, CH_2=CH-CH_2-), 5.07 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 4.98 (t, 1H, $J_{3',4'}$ = $J_{4',5'}$ = 9.1 Hz, H-4'), 4.99 (d, 1H, $J_{1',2'}$ = 2.2 Hz, H-1'), 4.88 (dd, 1H, $J_{2',3'}$ = 3.6 Hz, $J_{3',4'}$ = 9.1 Hz, H-3'), 4.72-4.62 (m, 3H, H-2', 6), 4.55 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 4.32-4.02 (m, 3H, H-5, CH_2=CH-CH_2-), 3.38-3.22 (m, 1H, H-5'), 2.02, 1.62, 1.59 (3s, 9H, CH_3-), 1.13 (d, 3H, $J_{5',6'}$ = 6.5 Hz, H-6').

Anal. Calcd for $C_{42}H_{44}O_{16}$: C, 62.68; H, 5.51. Found: C, 62.82; H, 5.26.

3,4-Di-*O*-benzoyl-β-L-rhamnopyranose 1,2-(Allyl 2,3,6-tri-*O*-benzoyl-α-D-mannopyranosid-4-yl orthoacetate) (10). As described in the preparation of compound **6**, compound **8** (1.6 g, 2 mmol) was deacylated with MeONa in MeOH, and then benzoylated with BzCl in pyridine to furnish **10** (1.8 g) in quantitative yield: $[\alpha]_D^{20}$ +3.2° (*c* 0.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 200 MHz) δ 8.22-7.88 (m, 10H, Bz-H), 7.72-6.97 (m, 15H, Bz-H), 6.04-5.80 (m, 1H, CH_2=C*H*-CH_2-), 5.68 (dd, 1H, $J_{2,3}$ = 2.9 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 5.63 (dd, 1H, $J_{1,2}$ = 1.7 Hz, $J_{2,3}$ = 2.9 Hz, H-2), 5.38 (t, 1H, $J_{3',4'}$ = $J_{4',5'}$ = 9.4 Hz, H-4'), 5.37-5.14 (m, 4H, H-1', 3', CH_2=CH-CH_2-), 5.01 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 4.93 (dd,

1H, $J_{1',2'}$ = 3.5 Hz, $J_{2',3'}$ = 2.1 Hz, H-2'), 4.76 (dd, 1H, $J_{5,6}$ = 2.0 Hz, $J_{6,6}$ = 12.2 Hz, H-6), 4.63 (dd, 1H, $J_{5,6}$ = 3.8 Hz, $J_{6,6}$ = 12.2 Hz, H-6), 4.60 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 4.30-3.98 (m, 3H, H-5, CH_2=CH-CH_2-), 3.62-3.44 (m, 1H, H-5'), 1.77 (s, 3H, CH_3-), 1.22 (d, 3H, $J_{5',6'}$ = 6.1 Hz, H-6').

Anal. Calcd for $C_{52}H_{48}O_{16}$: C, 67.23; H, 5.21. Found: C, 67.40; H, 5.32.

Allyl 4-*O*-(2-*O*-Acetyl-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-2,3,6-tri-*O*-benzoyl-α-D-mannopyranoside (11). Method A: To a stirred solution of sugar-sugar orthoester **10** (360 mg, 0.39 mmol) in dichloromethane (10 mL) under nitrogen atmosphere was added TMSOTf (7 μL, 0.1 equiv) at –20 °C, and the reaction was monitored by TLC (2:1 petroleum ether/EtOAc). After completion of the reaction, triethylamine (10 μL) was added, then the solid was filtered off and washed with CH_2Cl_2 (3 × 10 mL). The combined filtrate and washings were washed sequentially with H_2O (20 mL), N HCl (20 mL), satd aq $NaHCO_3$ (20 mL), and satd aq NaCl (20 mL). The aqueous washings were re-extracted with CH_2Cl_2 (10 mL), the combined organic solutions were dried and concentrated, and the residue was subjected to flash chromatography with 2/1 petoleum ether/EtOAc as the eluent to give **11** (316 mg, 0.34 mmol) in a high yield (86%); Method B: Compound **6** (596 mg, 1.44 mmol) was treated 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 for 1 h, at which time TLC (2/1 petroleum ether/EtOAc) indicated completion of the trichloroacetimidation reaction. Concentration of the reaction mixture followed by purification with flash chromatography (1.5/1 petoleum ether/EtOAc) gave the glycoside donor, trichloroacetimidate **7** (666 mg, 83%), which was used directly in the glycosylation reaction. A mixture of the donor **7** (660 mg, 1.18 mmol) and the acceptor **2** (535 mg, 1.0 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 room temperature and then cooled to –40 °C. Trimethylsilyl triflate (TMSOTf, 43 μL, 0.2 equiv) was added, the mixture was stirred under N_2 below –30 °C for 40 min., then TLC showed the starting material disappeared. Triethylamine (30 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 handled as described in method A and the organic solution was dried and concentrated, and the

residue was subjected to flash chromatography with 2/1 petoleum ether/EtOAc as the eluent to give **11** (789 mg, 85%): $[\alpha]_D^{20}$ -40.4° (*c* 0.6, $CHCl_3$); ^1H NMR ($CDCl_3$, 200 MHz) δ 8.20-7.80 (m, 10H, Bz-H), 7.67-7.24 (m, 15H, Bz-H), 6.10-5.90 (m, 1H, CH_2=C*H*-CH_2-), 5.91 (dd, 1H, $J_{2,3}$ = 3.4 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 5.65 (dd, 1H, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3.4 Hz, H-2), 5.60 (dd, 1H, $J_{2',3'}$ = 3.2 Hz, $J_{3',4'}$ = 9.8 Hz, H-3'), 5.41 (dd, 1H, $J_{1',2'}$ = 1.7 Hz, $J_{2',3'}$ = 3.2 Hz, H-2'), 5.45-5.25 (m, 3H, H-4', C*H*$_2$=CH-CH_2-), 5.11 (d, 1H, $J_{1,2}$ = 1.5 Hz, H-1), 5.05 (d, 1H, $J_{1',2'}$ = 1.7 Hz, H-1'), 5.00 (dd, 1H, $J_{5,6a}$ = 1.7 Hz, $J_{6a,6b}$ = 12.7 Hz, H-6_a), 4.67 (dd, 1H, $J_{5,6b}$ = 3.4 Hz, $J_{6a,6b}$ = 12.7 Hz, H-6_b), 4.57 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 4.40-3.94 (m, 4H, H-5, 5', CH_2=CH-C*H*$_2$-), 2.03 (s, 3H, C*H*$_3$CO), 0.74 (d, 3H, $J_{5',6'}$ = 6.5 Hz, H-6').

Anal. Calcd for $C_{52}H_{48}O_{16}$: C, 67.23; H, 5.21. Found: C, 67.02; H, 5.30.

Allyl 4-*O*-(3,4-Di-*O*-benzoyl-α-L-rhamnopyranosyl)-2,3,6-tri-*O*-benzoyl-α-D-mannopyranoside (12). A methanolic solution of HCl (1.04 N, 3 mL), prepared by adding acetyl chloride (0.8 mL) to freshly distilled MeOH (10 mL), was added to a solution of the disaccharide **11** (260 mg, 0.28 mmol) in freshly distilled MeOH (2 mL) and the solution was stirred at 48-54 °C. When TLC (2/1, petroleum/EtOAc) showed completion of the reaction, the solution was cooled to 0 °C and pyridine (0.5 mL) was added dropwise to neutralize the acid. The solution was concentrated to a semi-solid residue that was dissolved in CH_2Cl_2 (10 mL) and washed sequentially with N HCl (10 mL), satd aq $NaHCO_3$ (10 mL), and H_2O (10 mL). The aqueous washings were re-extracted with CH_2Cl_2 (3 × 5 mL) and the combined organic solutions were dried and concentrated. Gradient flash chromatography (EtOAc/petroleum ether 1/1 to 1.5/1) of the residue gave **12** (238 mg, 0.27 mmol, 96%) as a colorless syrup: $[\alpha]_D^{20}$ -39.8° (*c* 2.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 200 MHz) δ 8.19-7.80 (m, 10H, Bz-H), 7.63-7.22 (m, 15H, Bz-H), 6.10-5.89 (m, 1H, CH_2=C*H*-CH_2-), 5.89 (dd, 1H, $J_{1,2}$ = 1.9 Hz, $J_{2,3}$ = 3.4 Hz, H-2), 5.54-5.24 (m, 4H, H-3', 4', C*H*$_2$=CH-CH_2-), 5.08 (d, 1H, $J_{1,2}$ = 1.9 Hz, H-1), 5.05 (d, 1H, $J_{1',2'}$ = 1.5 Hz, H-1'), 4.77 (d, 2H, $J_{5,6}$ = 2.2 Hz, H-6), 4.52 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, H-4), 4.42-3.87 (m, 5H, H-2', 5, 5', CH_2=CH-C*H*$_2$-), 0.76 (d, 3H, $J_{5',6'}$ = 6.4 Hz, H-6').

Anal. Calcd for $C_{50}H_{46}O_{15}$: C, 67.71; H, 5.23. Found: C, 67.44; H, 5.08.

3'',4''-Di-*O*-acetyl-α-L-xylopyranose 1'',2''-{allyl 4-*O*-(3',4'-Di-*O*-benoyl-α-L-rhamnopyranosyl)-2,3,6-tri-*O*-benzoyl-α-D-mannopyranosid}-2'-yl Orthoactate (14).

To a stirred mixture of **12** (200 mg, 0.22 mmol), acetobromo-L-xylose[6] (85 mg, 0.24 mmol), 2,4-lutidine (30 μL, 0.25 mmol), and 4 Å molecular sieves (0.5 g) in CH_2Cl_2 (dry, 10 mL) was added silver triflate (62 g, 0.24 mmol) under nitrogen atmosphere in a dark room, and the reaction was carried out at room temperature and monitored by TLC (1/1 petroleum ether/EtOAc). After completion of the reaction, the mixture was partitioned between CH_2Cl_2 (10 mL) and H_2O (10 mL), the organic phase was washed with 10% aq $Na_2S_2O_3$ (20 mL) and aq NaCl (20 mL), then concentrated under reduced pressure. The residual oil was purified by column chromatography with 1/1 petroleum ether/EtOAc as the eluent giving the product **14** as an amorphous solid in a yield of 94% (240 mg), capable of being used directly for further rearrangement: $[\alpha]_D^{20}$ -19.2° (*c* 1.8, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.36-7.84 (5d, J = 7.8 Hz, 10H, Bz-H), 7.70-7.26 (m, 15H, Bz-H), 5.59-6.07 (m, 1H, CH_2=C*H*-CH_2-), 5.88 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 5.64 (dd, 1H, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 3.3 Hz, H-2), 5.48-5.28 (m, 4H, H-4', 4'', CH_2=CH-CH_2-), 5.35 (d, 1H, $J_{1'',2''}$ = 3.4 Hz, H-1''), 5.24 (dd, 1H, $J_{2',3'}$ = 3.3 Hz, $J_{3',4'}$ = 9.7 Hz, H-3'), 5.08 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 5.01 (d, 1H, $J_{1',2'}$ = 3.4 Hz, H-1'), 4.90 (dd, 1H, $J_{5,6}$ = 1.9 Hz, $J_{6,6}$ = 12.3 Hz, H-6), 4.73 (t, 1H, $J_{2'',3''}$ = 2.8 Hz, $J_{3'',4''}$ = 2.8 Hz, H-3''), 4.55 (dd, 1H, $J_{5,6}$ = 3.7 Hz, $J_{6,6}$ = 12.3 Hz, H-6), 4.54 (t, 1H, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.6 Hz, H-4), 4.50-4.30 (m, 2H, CH_2=CH-CH_2-), 4.18-3.63 (m, 6H, H-2',2'',5, 5' ,5''), 2.02, 1.83, 1.62 (3s, 9H, 3CH_3), 0.74 (d, 3H, $J_{5',6'}$ = 6.4 Hz, H-6').

Anal. Calcd for $C_{61}H_{60}O_{22}$: C, 63.98; H, 5.28. Found: C, 64.12; H, 5.11.

Allyl 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-mannopyranoside (15). As described in the preparation of **11**, to a stirred solution of **14** (200 mg, 0.17 mmol) in dichloromethane (10 mL) under nitrogen atmosphere was added TMSOTf (3 μL, 0.1 equiv) at –20 °C, and the reaction was monitored by TLC (1/1 petroleum ether/EtOAc). After completion of the reaction, triethylamine (5 μL) was added, then the solid was filtered off and washed with CH_2Cl_2 (3×10 mL). The combined filtrate and washings were washed sequentially with H_2O (10 mL), N HCl (10 mL), satd aq $NaHCO_3$ (10 mL), and satd aq NaCl (10 mL). The aqueous washings were re-extracted with CH_2Cl_2 (10 mL) and the combined organic solutions were dried and concentrated, and the residue was subjected to flash chromatography with 1/1 petoleum ether/EtOAc as the eluent to give **15** (170 mg, 0.15

mmol, 85%): $[\alpha]_D^{20}$ +14.5° (*c* 2.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.19-7.89 (m, 10H, Bz-H), 7.70-7.26 (m, 15H, Bz-H), 6.05-5.96 (m, 1H, CH_2=C*H*-CH_2-), 5.90 (dd, 1H, $J_{2,3}$ = 3.4 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 5.64 (dd, 1H, $J_{1,2}$ = 1.9 Hz, $J_{2,3}$ = 3.4 Hz, H-2), 5.44-5.38 (m, 2H, C*H*$_2$=CH-CH_2-), 5.33 (t, 1H, $J_{3',4'}$ = $J_{4',5'}$ = 9.6 Hz, H-4'), 5.31 (dd, 1H, $J_{2',3'}$ = 2.6 Hz, $J_{3',4'}$ = 9.6 Hz, H-3'), 5.10 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 5.06 (t, 1H, $J_{2'',3''}$ = $J_{3'',4''}$ = 7.2 Hz, H-3''), 4.87 (dd, 1H, $J_{5,6}$ = 1.7 Hz, $J_{6,6}$ = 12.7 Hz, H-6), 4.86 (dd, 1H, $J_{1'',2''}$ = 6.4 Hz, $J_{2',3'}$ = 7.2 Hz, H-2''), 4.84 (d, 1H, $J_{1',2'}$ = 1.7 Hz, H-1'), 4.80-4.73 (m, 1H, H-4''), 4.67 (d, 1H, $J_{1'',2''}$ = 6.4 Hz, H-1''), 4.58 (dd, 1H, $J_{5,6}$ = 1.5 Hz, $J_{6,6}$ = 12.7 Hz, H-6), 4.48 (dd, 1H, $J_{1',2'}$ = 1.7 Hz, $J_{2',3'}$ = 2.6 Hz, H-2'), 4.38 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, H-4), 4.40-4.24 (m, 2H, CH_2=CH-C*H*$_2$-), 4.15 (dd, 1H, $J_{4'',5''}$ = 7.0 Hz, $J_{5'',6''}$ = 12.1 Hz, H-5''), 3.94-3.87 (m, 2H, H-5, 5'), 2.06, 2.01, 1.68 (3s, 9H, 3 CH_3CO), 0.69 (d, 3H, $J_{5',6'}$ = 6.2 Hz, H-6').

Anal. Calcd for $C_{61}H_{60}O_{22}$: C, 63.98; H, 5.28. Found: C, 64.27; H, 5.12.

Allyl 4-*O*-(2-*O*-(β-L-Xylopyranosyl)-α-L-rhamnopyranosyl)-α-D-mannopyranoside (16). A solution of compound **15** (120 mg, 0.1 mmol) in MeONa/MeOH was stirred at 35-40 °C for 5 h. TLC showed that the reaction was complete, and the resulting solution was de-ionized with Amberlite IR-120 (H^+) ion-exchange resin, the mixture was filtered, and concentrated. The trisaccharide **16** (48 mg, 96%) was finally obtained after chromatography on sephadex G-25 column (H_2O) as a syrup: $[\alpha]_D^{20}$ +6.4° (*c* 0.5, MeOH); ESMS for $C_{20}H_{34}O_{14}$ (498.48): 497 $[M-H]^+$; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.98-5.82 (m, 1H, CH_2=C*H*-CH_2-), 5.30 (d, 1H, J = 17.2 Hz, C*H*$_2$=CH-CH_2-), 5.21 (d, 1H, J = 10.4 Hz, C*H*$_2$=CH-CH_2-), 4.91(s, 1H, H-1), 4.85 (s, 1H, H-1'), 4.32 (d, 1H, $J_{1'',2''}$ = 7.6 Hz, H-1''), 4.18-3.2 (m, 19H, H-2, 2', 2'', 3, 3', 3'', 4, 4', 4'', 5, 5', 5'', 6, 6', CH_2=CH-C*H*$_2$-), 1.20 (d, 3H, $J_{5'',6''}$ = 6.0 Hz, CH_3). *Lit.*[2] ^1H NMR data for the native O2 polymer δ 5.06 (H-1), 5.01 (H-1'), 4.36 (H-1''), 1.30 (CH_3).

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