Available online at www.sciencedirect.com
SCIENCE DIRECT®
Carbohydrate Research 338 (2003) 1023–1031
CARBOHYDRATE RESEARCH
www.elsevier.com/locate/carres

Efficient synthesis of a heptasaccharide, the repeating unit of the O-chain lipopolysaccharide produced by *Xanthomonas campestris* strain 642

Jianjun Zhang, Jun Ning, Fanzuo Kong*

Research Center for Eco-Environmental Sciences, Academia Sinica, P.O. Box 2871, Beijing 100085, China

Received 17 December 2002; accepted 12 February 2003

Abstract

α-L-Rha*p*-(1→3)-α-L-Rha*p*-(1→2)-α-L-Rha*p*-(1→3)-[β-D-Xyl*p*-(1→2)-][β-D-Xyl*p*-(1→4)-]α-L-Rha*p*-(1→3)-α-L-Rha*p*, the repeating unit of the O-chain lipopolysaccharide produced by *Xanthomonas campestris* strain 642 was synthesized as its methyl glycoside via 3-*O*-selective glycosylation of methyl α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**9**) with 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (**8**), followed by dixylosylation with 2,3,4-tri-*O*-benzoyl-α,β-D-xylopyranosyl trichloroacetimidate (**12**) and subsequent deacylation.

Keywords: Oligosaccharide; Rhamnose; Xylose

1. Introduction

Rhamnose-containing oligosaccharides are widely distributed in natural products,[1–3] and they usually consist of an α-(1→2)- and α-(1→3)-linked backbone with xylose, glucose, ribose, or GlcNAc side chains. *Xanthomonas campestris* is a phytopathogenic bacterium recognized to cause a serious disease in strawberries.[4] Recently, a new O-polysaccharide chain has been isolated and identified from the LPS fraction of the *X. campestris* strain 642, whose repeating unit is a xylosylated rhamnan heptasaccharide as shown below:[5]

β-D-Xyl*p*
1
↓
2
→2)-α-L-Rha*p*-(1→3)-α-L-Rha*p*-(1→2)-α-L-Rha*p*-(1→3)-α-L-Rha*p*-(1→3)-α-L-Rha*p*-(1→
4
↑
1
β-D-Xyl*p*

Synthesis of these compounds will need orthogonal masking groups and multiple protection–deprotection steps if a traditional stepwise method[6,7] is used. Our previous work described a highly regio- and stereoselective synthesis using glycosyl trichloroacetimidates as the donors and partially protected sugars as the acceptors, and a variety of branched rhamnans was obtained.[8–11] Synthetic samples of new rhamnan structures would be very valuable in research in plant pathology and in the design of immunodiagnostic reagents. We present herein a highly efficient synthesis of the title heptasaccharide.

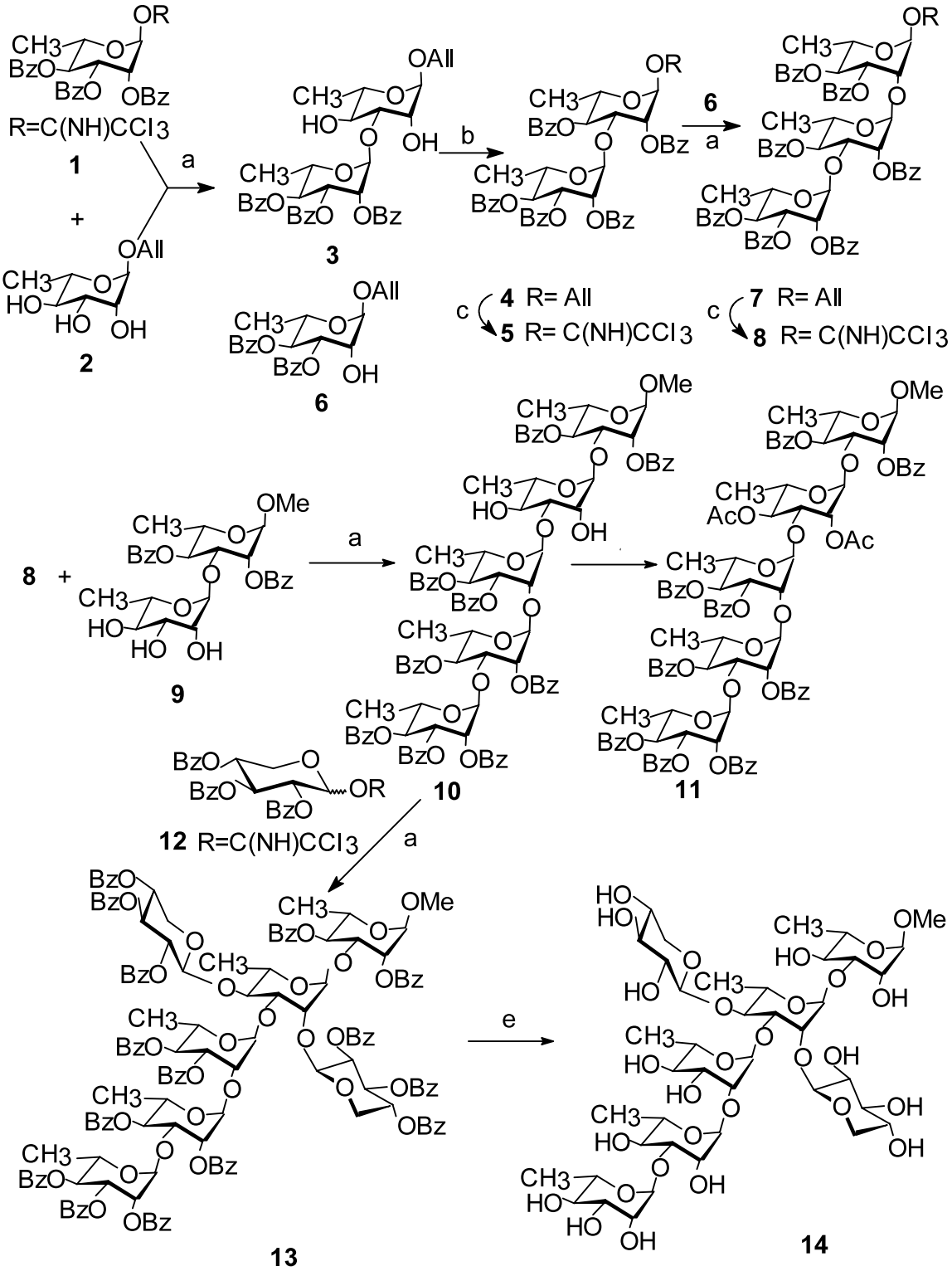
2. Results and discussion

As outlined in Scheme 1, condensation of 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (**1**) with unprotected allyl α-L-rhamnopyranoside (**2**) selec-

* Corresponding author. Tel.: +86-10-62936613; fax: +86-10-62923563
E-mail address: fzkong@mail.rcees.ac.cn (F. Kong).

0008-6215/03/$ - see front matter
doi:10.1016/S0008-6215(03)00080-6

tively gave allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranoside (**3**)[8] in satisfactory yield (63.2%). Keeping the temperature below −20 °C during the addition of TMSOTf was necessary in order to avoid byproduct formation. The (1→3)-linkage was confirmed by benzoylation of **3** to give **4**, and the ^{1}H NMR spectrum of **4** showed two newly emerged downfield signals at δ 5.51 (dd, $J_{3,4} = J_{4,5} = 9.8$ Hz) for H-4 and δ 5.28 (dd, $J_{1,2}$ 1.4, $J_{2,3}$ 3.5) for H-2, respectively, compared to **3**. Deallylation with $PdCl_2$, fol-



Scheme 1. (a) TMSOTf, CH_2Cl_2; (b) BzCl–pyridine (dry); (c) $PdCl_2$, 90% HOAc–NaOAc, rt, 12 h; then Cl_3CN, DBU, CH_2Cl_2 8 h; (d) Ac_2O–pyridine (dry); (e) satd NH_3–MeOH, rt, 72 h.

lowed by trichloroacetimidation with CCl_3CN in the presence of DBU or K_2CO_3,[12] gave the disaccharide donor **5**. Coupling of compound **5** with allyl 3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**6**)[10] in the presence of catalytic TMSOTf gave trisaccharide **7** in high yield (88.2%), which could be activated by deallylation and trichloroacetimidation to furnish the trisaccharide donor **8**. 3-*O*-Selective glycosylation of methyl α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**9**)[8] with the donor **8**, promoted by catalytic TMSOTf, gave pentasaccharide **10** in satisfactory yield (57.3%). The structure of **10** was confirmed by acetylation to give methyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**11**). The ^{1}H NMR spectrum of **11** showed newly emerged downfield signals at δ 4.99 (dd, H, $J_{3,4} = J_{4,5} = 10.0$ Hz) for H-4′ and 4.93 (dd, $J_{1,2}$ 0.8, $J_{2,3}$ 2.9 Hz) for H-2′, respectively, compared to **10**. With the pentasaccharide diol **10** at hand, the heptasaccharide **13** was readily obtained in high yield (71.3%) by coupling of **10** with the xylose donor **12** in dichloromethane in the presence of TMSOTf. The ^{13}C NMR spectrum of **13** showed all of the characteristic peaks, i.e., δ 104.8, 104.8, 104.6, 104.0, 103.3, 103.2, 103.2 for seven C-1s and 18.1, 17.9, 17.5, 17.4, 17.3 for five rhamnose C-6s. Finally deacylation of **13** in ammonia–methanol gave the target heptasaccharide **14**.

Before the successful synthesis of the target heptasaccharide by the route described above, we also tried another route using a 4 + 3 (**20** + **8**) or 4 + 1 + 2 (**20** + **22** + **5**) strategy (A) (Scheme 2). Although the target compound was not obtained by the strategy, an interesting effect of steric factors on the glycosylation was observed as described below. Isopropylidenation of compound **15** in DMF with 2,2-dimethoxypropane in the presence of TsOH readily gave allyl 2,3-*O*-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**16**) in high yield (87.3%). The structure of **16** was confirmed by acetylation to give allyl 4-*O*-acetyl-2,3-*O*-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**17**), showing characteristic signals in its ^{1}H NMR spectrum at δ 5.48 (dd, $J_{3,4} = J_{4,5} = 9.9$ Hz) for H-4, and 4.71 (dd, $J_{3',4'} = 8.0$ Hz, $J_{4',5'} = 10.0$ Hz) for H-4′, respectively. Coupling of **16** with 2,3,4-tri-*O*-benzoyl-α,β-D-xylopyranosyl trichloroacetimidate (**12**) in the presence of catalytic TMSOTf gave the trisaccharide **18** (88.5%), and O-deisopropylidenation of **18** in 9:1 trifluoroacetic acid (TFA)–water at room temperature furnished the diol acceptor **19** (90.7%). Condensation of the diol acceptor **19** with **12** in dichloromethane in the presence of TMSOTf at −20 °C selectively gave 2-*O*-glycosylated tetrasaccharide **20** (79.9%). Acetylation of **20** with acetic anhydride in pyridine gave **21**, and the ^{1}H NMR spectrum of **21** confirmed the regioselectivity by showing characteristic peaks at δ 4.85 ($J_{2,3}$ 2.9, $J_{3,4}$ 9.2 Hz) for H-3′, and 4.48 ($J_{2,3}$ 3.4, $J_{3,4}$ 9.8 Hz) for H-3, respectively.

Condensation of tetrasaccharide **20** with trisaccharide donor **8** did not give the expected heptasaccharide, but afforded only a byproduct and unreacted starting materials. This indicated that the trisaccharide donor was too big to get close to the 3′-OH that was severely shielded by the two xylosyl residues at the 2′- and 4′-positions. However, when the tetrasaccharide **20** was coupled with monosaccharide donor **22**, pentasaccharide **23** was obtained in 41.3% yield, revealing that a smaller size of donor was allowed to react with **20**, albeit to a limited extent. However, subsequent selective 2″-*O*-deacetylation of **23** in 2–3% CH_3COCl–MeOH did not work, even at elevated temperature (50 °C), and only unchanged starting material was obtained. Here, severe steric hindrance at the 2″-OAc of the pentasaccharide **23** rejected the deacetylation under normal conditions. It seemed that the target heptasaccharide was not readily obtained by any other methods, and construction of the pentasaccharide backbone, followed by attaching the side chains was the best choice.

In summary, a branched xylosylated rhamnan heptasaccharide was synthesized in a highly regioselective way with a simple procedure. Large-scale preparations should be possible with this method.

3. Experimental

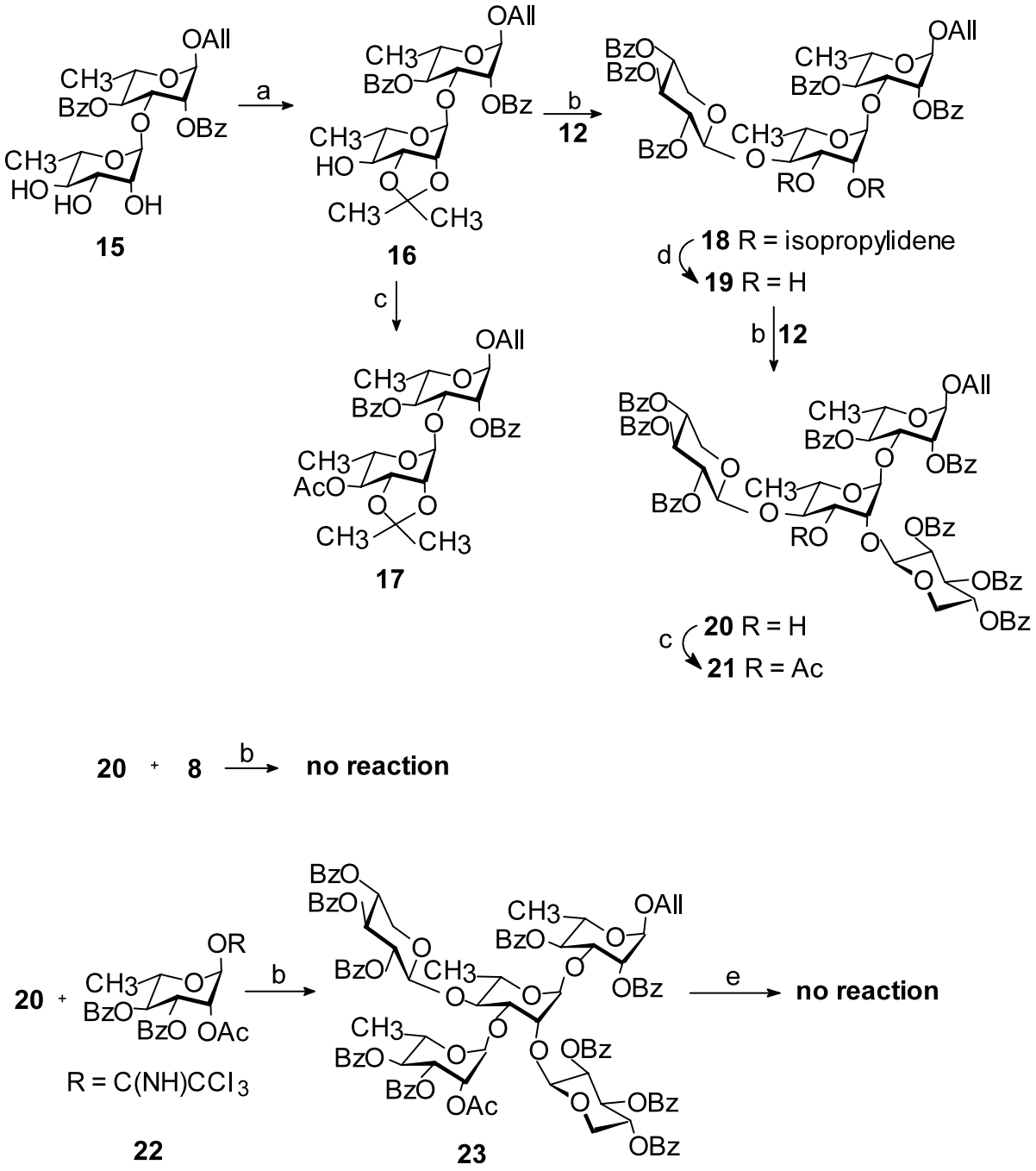
3.1. General methods

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. ^{1}H, ^{13}C, and 2D NMR spectra were recorded with Varian XL-400 spectrometers, for solutions in $CDCl_3$ or in D_2O as indicated. Chemical shifts are expressed in δ (ppm) downfield from the Me_4Si resonance. Mass spectra were recorded with a VG PLATFORM mass spectrometer using the ESI mode. 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 (8 × 100, 16 × 240, 18 × 300, 35 × 400 mm) of silica gel (100–200 mesh) with EtOAc–petroleum ether (bp 60–90 °C) as the eluent. Analytical LC was performed with a Gilson HPLC consisting of a pump (model 306), stainless steel column packed with silica gel (Spherisorb SiO_2, 10 × 300 or 4.6 × 250 mm), differential refractometer (132-RI Detector), UV–Vis detector (model 118). 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.

3.2. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (4)

2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (**1**) (6.20 g, 10.0 mmol) and allyl α-L-rhamnopyranoside (**2**) (2.04 g, 10.0 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (40 mL). TMSOTf (36 μL, 0.2 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 Et_3N and concentrated to dryness to afford the crude allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranoside (**3**). To the solution of crude **3** in pyridine (20 mL), benzoyl chloride (3.5 mL, 30



Scheme 2. 2,2-Di-methoxypropene, *p*-TsOH, DMF, rt, 2 h; (b) TMSOTf, CH_2Cl_2; (c) Ac_2O–pyridine (dry); (d) 90% TFA, rt, 2 h; (e) 3–5% CH_3COCl–methanol, rt, 14–24 h.

mmol) was added dropwise, and the mixture was stirred overnight at room temperature (rt). TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. Ice-water was added, and the mixture was diluted with CH_2Cl_2, subsequently washed with M HCl, water, and satd aq $NaHCO_3$. The organic layers were combined, dried, and concentrated. Purification by column chromatography (3:1 petroleum ether–EtOAc) gave **4** (5.50 g, 63.2% for two steps) as a syrup: $[\alpha]_D + 122.3°$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.25–7.19 (m, 25 H, 5 Ph*H*), 6.01–5.93 (m, 1 H, CH_2=C*H*CH_2O), 5.61 (dd, 1 H, $J_{3',4'} = J_{4',5'} = 9.7$ Hz, H-4′), 5.58 (dd, 1 H, $J_{2',3'}$ 3.1 Hz, $J_{3',4'}$ 9.7 Hz, H-3′), 5.54 (dd, 1 H, $J_{1',2'}$ 1.5 Hz, $J_{2',3'}$ 3.1 Hz, H-2′), 5.51 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 5.38–5.34 (m, 1 H, C*H*$_2$=CHCH_2O), 5.28 (dd, 1 H, $J_{1,2}$ 1.4 Hz, $J_{2,3}$ 3.5 Hz, H-2), 5.29–5.25 (m, 1 H, C*H*$_2$=CHCH_2O), 5.23 (d, 1 H, $J_{1',2'}$ 1.5 Hz, H-1′), 5.07 (d, 1 H, $J_{1,2}$ 1.4 Hz, H-1), 4.50 (dd, 1 H, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 9.8 Hz, H-3), 4.26–4.22 (m, 1 H, CH_2=CHC*H*$_2O$), 4.15–4.07 (m, 3 H, H-5, H-5′, CH_2=CHC*H*$_2O$), 1.35 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6), 1.16 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6). Anal. Calcd for $C_{50}H_{46}O_{14}$: C, 68.95; H, 5.32. Found: C, 69.24; H, 5.21.

3.3. 2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (5)

To a solution of allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**4**) (4.35 g, 5 mmol) in 90% HOAc (50 mL) containing NaOAc (1.46 g, 15 mmol) was added $PdCl_2$ (270 mg, 2.5 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 CH_2Cl_2 (150 mL), washed with water and satd aq $NaHCO_3$. 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-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-L-rhamnopyranose as a foamy solid. Dried under high vacuum for 2 h, the solid was was dissolved in CH_2Cl_2 (30 mL), and CCl_3CN (1.0 mL, 10 mmol) and DBU (135 μL, 0.9 mmol) were added. The reaction mixture was stirred for 2 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. Concentration of the reaction mixture, followed by purification of the crude product on a silica gel column with 2:1 petroleum ether–EtOAc as the eluent, furnished the disaccharide donor **5** (4.10 g, 84.1%) as a syrup: $[\alpha]_D + 114.7°$ (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 1 H, CNHCCl_3), 8.27–7.19 (m, 25 H, 5 Ph*H*), 6.51 (d, 1 H, $J_{1,2}$ 1.9 Hz, H-1), 5.73 (dd, 1 H, $J_{1,2}$ 1.9 Hz, $J_{2,3}$ 3.5 Hz, H-2), 5.71 (dd, 1 H, $J_{3',4'} = J_{4',5'} = 9.8$ Hz, H-4′), 5.60 (dd, 1 H, $J_{2',3'}$ 3.2 Hz, $J_{3',4'}$ 9.8 Hz, H-3′), 5.52 (dd, 1 H, $J_{3,4} = J_{4,5} =$ 10.0 Hz, H-4), 5.33 (dd, 1 H, $J_{1',2'}$ 1.6 Hz, $J_{2',3'}$ 3.2 Hz, H-2′), 5.24 (d, 1 H, $J_{1',2'}$ 1.6 Hz, H-1′), 4.60 (dd, 1 H, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 10.0 Hz, H-3), 4.29–4.20 (m, 2 H, H-5, H-5′), 1.38 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6), 1.16 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6). Anal. Calcd for $C_{49}H_{42}Cl_3NO_{14}$: C, 60.35; H, 4.34. Found: C, 60.50; H, 4.39.

3.4. Allyl 2,3,4-tri-*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 (7)

Compound **5** (3.96 g, 3.0 mmol) and allyl 3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**6**) (1.25 g, 3.0 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (20 mL). TMSOTf (18 μL, 0.1 mmol) was added dropwise at 0 °C with N_2 protection. The reaction mixture was stirred for 3 h at rt, and then neutralized with Et_3N. Concentration of the reaction mixture and purification of the crude product on a silica gel column with 2:1 petroleum ether–EtOAc as the eluent, furnished the trisaccharide **7** (3.24 g, 88.2%) as a foamy solid: $[\alpha]_D + 124.0°$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.16–7.19 (m, 35 H, 7 Ph*H*), 5.99–5.91 (m, 1 H, CH_2=C*H*CH_2O), 5.80 (dd, 1 H, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 10.1 Hz, H-3), 5.72 (dd, 1 H, $J_{1,2}$ 1.8 Hz, $J_{2,3}$ 3.3 Hz, H-2), 5.62 (dd, 2 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, 2 H-4), 5.60 (dd, 1 H, $J_{2,3}$ 3.2 Hz, $J_{3,4}$ 9.8 Hz, H-3), 5.52 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.41–5.37 (m, 1 H, C*H*$_2$=CHCH_2O), 5.34 (dd, 1 H, $J_{1,2}$ 1.7 Hz, $J_{2,3}$ 3.3 Hz, H-2), 5.30 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 5.28–5.24 (m, 1 H, C*H*$_2$=CHCH_2O), 5.19 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 5.04 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 4.65 (dd, 1 H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 9.8 Hz, H-3), 4.32 (dd, 1 H, $J_{1,2}$ 1.6 Hz, $J_{2,3}$ 3.2 Hz, H-2), 4.31–4.27 (m, 1 H, CH_2=CHC*H*$_2O$), 4.26–4.08 (m, 4 H, 3 H-5, CH_2=CHC*H*$_2O$), 1.37 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6), 1.31 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6), 1.22 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 165.6, 165.5, 165.5, 165.4, 164.7, 164.6 (7 C, 7 *C*OPh), 99.4, 99.1, 97.6 (3 C, 3 C-1), 77.2, 74.9, 73.1, 71.9, 71.8, 71.6, 71.0, 70.4, 69.3, 68.2, 67.6, 67.4, 66.9, 17.6, 17.5, 17.3. Anal. Calcd for $C_{70}H_{64}O_{20}$: C, 68.62; H, 5.27. Found: C, 68.48; H, 5.55.

3.5. 2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (8)

Compound **7** (2.45 g, 2.0 mmol) was deallylated and then trichloroacetimidated under the same conditions as those used for the preparation of **5** from **4**, giving **8** (2.11 g, 79.6% for two steps) as a foamy solid: $[\alpha]_D +$ 99.8° (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1 H, CN*H*CCl_3), 8.16–7.19 (m, 35 H, 7 Ph*H*),

6.48 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 5.83 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 10.0 Hz, H-3), 5.72 (dd, H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4), 5.70 (dd, 1 H, $J_{1,2}$ 1.4 Hz, $J_{2,3}$ 3.4 Hz, H-2), 5.62 (dd, H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 5.60 (dd, 1 H, $J_{2,3}$ 3.1 Hz, $J_{3,4}$ 9.8 Hz, H-3), 5.54 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 5.35 (dd, 1 H, $J_{1,2}$ 1.5 Hz, $J_{2,3}$ 3.2 Hz, H-2), 5.31 (d, 1 H, $J_{1,2}$ 1.0 Hz, H-1), 5.26 (d, 1 H, $J_{1,2}$ 1.3 Hz, H-1), 4.64 (dd, 1 H, $J_{2,3}$ 3.1 Hz, $J_{3,4}$ 9.8 Hz, H-3), 4.55 (dd, 1 H, $J_{1,2}$ 1.6 Hz, $J_{2,3}$ 3.4 Hz, H-2), 4.39–4.36 (m, 1 H, H-5), 4.27–4.24 (m, 1 H, H-5), 4.21–4.18 (m, 1 H, H-5), 1.43 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 1.34 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6), 1.19 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6). Anal. Calcd for $C_{69}H_{60}Cl_3NO_{20}$: C, 62.33; H, 4.55. Found: C, 62.60; H, 4.31.

3.6. Methyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (10)

Compound **8** (1.33 g, 1.0 mmol) and methyl α-L-rhamnopyranosyl - (1→3) - 2,4 - di - *O* - benzoyl - α - L-rhamnopyranoside (**9**) (530 mg, 1.0 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (20 mL). TMSOTf (18 μL, 0.1mmol) was added dropwise at −25 °C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the mixture was gradually warmed to ambient temperature. Then the mixture was neutralized with Et_3N and concentrated to dryness. Purification of the residue by column chromatography (1:1 petroleum ether–EtOAc) gave **10** (974 mg, 57.3%) as a syrup: $[\alpha]_D + 131.5°$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15–7.19 (m, 45 H, 9 Ph*H*), 5.64 (dd, 1 H, $J_{1,2}$ 1.6 Hz, $J_{2,3}$ 3.3 Hz, H-2), 5.59–5.46 (m, 7 H), 5.33 (dd, 1 H, $J_{1,2}$ 1.4 Hz, $J_{2,3}$ 3.2 Hz, H-2), 5.26 (s, 2 H, 2 H-1), 5.11 (d, 1 H, $J_{1,2}$ 1.3 Hz, H-1), 4.95 (s, 1 H, H-1), 4.83 (d, 1 H, $J_{1,2}$ 1.4 Hz, H-1), 4.57 (dd, 1 H, $J_{2,3}$ 3.1 Hz, $J_{3,4}$ 9.6 Hz, H-3), 4.41 (dd, 1 H, $J_{2,3}$ 3.2 Hz, $J_{3,4}$ 9.8 Hz, H-3), 4.28 (dd, 1 H, $J_{1,2}$ 1.3 Hz, $J_{2,3}$ 3.0 Hz, H-2), 4.26–4.23 (m, 1 H, H-5), 4.17–4.14 (m, 1 H, H-5), 4.05–4.02 (m, 1 H, H-5), 3.93–3.90 (m, 1 H, H-5), 3.74–3.70 (m, 3 H, H-2, H-3, H-5), 3.56 (dd, H, $J_{3,4} = J_{4,5} = 9.3$ Hz, H-4) 3.45 (s, 3 H, OC*H*$_3$), 1.30 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 1.25–1.19 (m, 9 H, 3 H-6), 1.01 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 165.8, 165.7, 165.5, 165.5, 165.5, 165.3, 164.7, 164.7 (9 C, 9 *C*OPh), 101.4, 99.8, 99.2, 99.1, 98.3 (5 C, 5 C-1), 78.0, 76.7, 75.1, 74.9, 73.5, 73.0, 72.3, 72.2, 71.9, 71.7, 71.6, 70.9, 70.8, 70.4, 69.3, 69.2, 67.7, 67.4, 67.2, 66.4, 55.2, 17.6, 17.4, 17.3, 17.2, 17.1. Anal. Calcd for $C_{94}H_{90}O_{30}$: C, 66.42; H, 5.34. Found: C, 66.48; H, 5.25.

3.7. Methyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (11)

To a solution of **10** (85 mg, 0.05 mmol) in pyridine (5 mL) was added Ac_2O (2.0 mL, 2 mmol). The reaction mixture was stirred at rt for 12 h, at the end of which time TLC (4:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was concentrated, and then the residue was purified by flash column chromatography on a silica gel column (2:1 petroleum ether–EtOAc) to give compound **11** (80 mg, 89.8%) as a foamy solid: $[\alpha]_D + 120.7°$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16–7.20 (m, 45 H, 9 Ph*H*), 5.60–5.57 (m, 3 H), 5.53 (dd, H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.47 (dd, H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4), 5.45 (dd, 1 H, $J_{1,2}$ 1.2 Hz, $J_{2,3}$ 3.1 Hz, H-2), 5.41 (dd, 1 H, $J_{2,3}$ 3.2 Hz, $J_{3,4}$ 9.8 Hz, H-3), 5.39 (dd, H, $J_{3,4} = J_{4,5} =$ 9.7 Hz, H-4), 5.35 (dd, 1 H, $J_{1,2}$ 1.5 Hz, $J_{2,3}$ 3.0 Hz, H-2), 5.29 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 5.03 (d, 1 H, $J_{1,2}$ 1.4 Hz, H-1), 4.99 (dd, H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4′), 4.96 (d, 1 H, $J_{1,2}$ 0.7 Hz, H-1), 4.94 (d, 1 H, $J_{1,2}$ 0.9 Hz, H-1), 4.93 (dd, 1 H, $J_{1,2}$ 0.8 Hz, $J_{2,3}$ 2.9 Hz, H-2′), 4.84 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 4.59 (dd, 1 H, $J_{2,3}$ 3.2 Hz, $J_{3,4}$ 9.7 Hz, H-3), 4.38 (dd, 1 H, $J_{2,3}$ 3.2 Hz, $J_{3,4}$ 9.8 Hz, H-3), 4.21–4.17 (m, 2 H, 2 H-5), 4.03 (dd, 1 H, $J_{1,2}$ 1.0 Hz, $J_{2,3}$ 3.1 Hz, H-2), 3.99 (m, 1 H, H-5), 3.96 (dd, 1 H, $J_{2,3}$ 3.1 Hz, $J_{3,4}$ 9.9 Hz, H-3), 3.85–3.81 (m, 1 H, H-5), 3.80–3.76 (m, 1 H, H-5), 3.44 (s, 3 H, OC*H*$_3$), 2.03 (s, 3 H, C*H*$_3$CO), 1.97 (s, 3 H, C*H*$_3$CO), 1.30 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6), 1.26 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 1.18 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 1.05 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6), 0.88 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6). Anal. Calcd for $C_{98}H_{94}O_{32}$: C, 65.98; H, 5.31. Found: C, 65.69; H, 5.50.

3.8. Methyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-[2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→2)-][2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→4)]-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (13)

Compound **10** (765 mg, 0.45 mmol) and 2,3,4-tri-*O*-benzoyl-α,β-D-xylopyranosyl trichloroacetimidate (**12**) (606 mg, 1.0 mmol) were coupled under the same conditions as those used for the preparation of **7** from **5** and **6**, giving **13** (830 g, 71.3%) as a foamy solid: $[\alpha]_D + 97.3°$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, characteristic signals are given): δ 5.92 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4-Rha*p*), 5.53 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4-Rha*p*), 5.48 (dd, 1 H, $J_{1,2}$ 1.3 Hz, $J_{2,3}$ 3.2 Hz, H-2-Rha*p*), 5.44 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4-Rha*p*), 5.36 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4-Rha*p*), 5.29 (dd, 1 H, $J_{1,2}$ 1.5 Hz, $J_{2,3}$ 3.4 Hz, H-2-

Rha*p*), 5.20 (s, 1 H, H-1-Rha*p*), 5.11 (s, 1 H, H-1-Rha*p*), 5.04 (d, 1 H, $J_{1,2}$ 6.1 Hz, H-1-Xyl*p*), 5.01 (s, 1 H, H-1-Rha*p*), 4.81 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1-Rha*p*), 4.74 (d, 1 H, $J_{1,2}$ 5.8 Hz, H-1-Xyl*p*), 4.63 (s, 1 H, H-1-Rha*p*), 3.45 (s, 3 H, OCH_3), 1.35 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 1.29 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6), 1.22 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6), 1.05 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 1.04 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 166.5, 165.6, 165.5, 165.4, 165.3, 165.3, 165.2, 165.1, 165.1, 165.1, 164.9, 164.6, 164.5, 164.5 (15 C, 15 *C*OPh), 100.9, 100.9, 100.2, 98.9, 98.8, 98.8, 98.5 (7 C, 7 C-1), 18.1, 17.9, 17.5, 17.4, 17.3 (5 C, 5 C-6-Rha*p*). Anal. Calcd for $C_{146}H_{130}O_{44}$: C, 67.74; H, 5.06. Found: C, 67.68; H, 5.35.

3.9. Methyl α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-[β-D-xylopyranosyl-(1→2)-][β-D-xylopyranosyl-(1→4)]-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranoside (14)

Heptasaccharide **13** (520 mg, 0.20 mmol) was dissolved in a saturated solution of NH_3–MeOH (30 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 **14** (143 mg, 69.8%) as a foamy solid: $[\alpha]_D$ −52.8° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.05 (s 1 H, H-1), 5.03 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 5.02 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 4.67 (d, 2 H, $J_{1,2}$ 1.6 Hz, 2 H-1), 4.61 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 4.47 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 3.40 (s, 3 H, OCH_3), 1.35 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 1.32–1.29 (m, 12 H, 4 H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 104.8, 104.8, 104.6, 104.0, 103.3, 103.2, 103.2 (7 C, 7 C-1), 19.3, 19.3, 19.1, 19.1, 19.1 (5 C, 5 C-6); MS (*m*/*z*) Calcd for $C_{41}H_{70}O_{29}$: 1026.97 $[M]^+$. Found: 1050.09 $[M+Na]^+$.

3.10. Allyl 2,3-*O*-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (16)

To a solution of allyl α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**15**) (5.58 g, 10 mmol) in anhyd DMF (50 mL) was added *p*-TsOH·H_2O (190 mg, 1.0 mmol) and 2,2-dimethoxypropane (3.7 mL, 30 mmol) under N_2 protection. The mixture was stirred at rt for 12 h, and TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. Sodium bicarbonate (5.00 g, 60 mmol) was added to the reaction mixture, and the mixture was stirred for additional 1 h. After filtration, the mixture was concentrated in vacuo to give a residue that was subjected to silica gel column chromatography (2:1 petroleum ether–EtOAc) to give **16** (5.22 g, 87.3%) as a syrup: $[\alpha]_D$ + 52.1° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12–7.45 (m, 10 H, 2 Ph*H*), 6.03–5.95 (m, 1 H, $OCH_2CH{=}CH_2$), 5.48 (dd, 1 H, $J_{1,2}$ 0.7 Hz, $J_{2,3}$ 3.0 Hz, H-2), 5.47 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4), 5.38–5.25 (m, 2 H, $OCH_2CH{=}CH_2$), 5.07 (s, 1 H, H-1′), 4.97 (s, 1 H, $J_{1,2}$ 0.7 Hz, H-1), 4.42 (dd, 1 H, $J_{2,3}$ 3.0 Hz, $J_{3,4}$ 9.9 Hz, H-3), 4.26–4.22 (m, 1 H, $OCH_2CH{=}CH_2$), 4.10–4.04 (m, 2 H, H-4′, $OCH_2CH{=}CH_2$), 3.82–3.75 (m, 2 H, H-2′, H-3′), 3.65–3.61 (m, 1 H, H-5), 3.24–3.20 (m, 1 H, H-5), 1.35 (s, 3 H, isopropylidene), 1.31 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 1.20 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6), 0.96 (s, 3 H, isopropylidene). Anal. Calcd for $C_{32}H_{38}O_{11}$: C, 64.20; H, 6.40. Found: C, 64.08; H, 6.51.

3.11. Allyl 4-*O*-acetyl-2,3-*O*-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (17)

To a solution of **16** (180 mg, 0.3 mmol) in pyridine (5 mL) was added Ac_2O (2.0 mL, 2 mmol). The reaction mixture was stirred at rt for 12 h, at the end of which time TLC (4:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was concentrated, and the residue was purified by flash column chromatography on a silica gel column (3:1 petroleum ether–EtOAc) to give compound **17** (158 mg, 82.4%) as a syrup: $[\alpha]_D$ +40.3° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14–7.45 (m, 10 H, 2 Ph*H*), 6.01–5.93 (m, 1 H, $OCH_2CH{=}CH_2$), 5.48 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4), 5.40 (dd, 1 H, $J_{1,2}$ 1.0 Hz, $J_{2,3}$ 2.9 Hz, H-2), 5.38–5.25 (m, 2 H, $OCH_2CH{=}CH_2$), 5.11 (s, 1 H, H-1′), 4.97 (s, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 4.71 (dd, 1 H, $J_{3',4'} = 8.0$ Hz, $J_{4',5'} = 10.0$ Hz, H-4′), 4.41 (dd, 1 H, $J_{2,3}$ 3.0 Hz, $J_{3,4}$ 9.9 Hz, H-3), 4.25–4.21 (m, 1 H, $OCH_2CH{=}CH_2$), 4.10–4.05 (m, 2 H, H-5, $OCH_2CH{=}CH_2$), 3.89 (dd, 1 H, $J_{2',3'}$ 5.4 Hz, $J_{3',4'}$ 8.0 Hz, H-3′), 3.74 (d, 1 H, $J_{2',3'}$ 5.4 Hz, H-2′), 3.69–3.66 (m, 1 H, H-5), 2.00 (s, 3 H, CH_3CO), 1.39 (s, 3 H, isopropylidene), 1.32 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6), 1.08 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6), 0.93 (s, 3 H, isopropylidene). Anal. Calcd for $C_{34}H_{40}O_{12}$: C, 63.74; H, 6.29. Found: C, 63.57; H, 6.13.

3.12. Allyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (18)

2,3,4-Tri-*O*-benzoyl-α,β-D-xylopyranosyl trichloroacetimidate (**12**) (3.03 g, 5.0 mmol) and allyl 2,3-*O*-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**16**) (3.0 g, 5.0 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (30 mL). TMSOTf (18.0 μL, 0.10 mmol) was added dropwise at −0 °C with N_2 protection. The reaction mixture was stirred for 2 h and then neutralized with Et_3N. Concentration of the reaction mixture and purification of the residue on a silica gel column (3:1 petroleum ether–EtOAc) afforded com-

pound **18** (4.61 g, 88.5%) as a foamy solid: $[\alpha]_D$ +41.2° (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–7.31 (m, 25 H, 5 Ph*H*), 6.01–5.93 (m, 1 H, $OCH_2CH{=}CH_2$), 5.71 (dd, 1 H, $J_{2'',3''} = J_{3'',4''} = 7.8$ Hz, H-3″), 5.45 (dd, 1 H, $J_{1,2}$ 1.2 Hz, $J_{2,3}$ 3.2 Hz, H-2), 5.40 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 5.36–5.30 (m, 1 H, $OCH_2CH{=}CH_2$), 5.30–5.23 (m, 3 H, H-2″, H-4″, $OCH_2CH{=}CH_2$), 5.22 (d, 1 H, $J_{1,2}$ 6.1 Hz, H-1″), 5.04 (s, 1 H, H-1′), 4.97 (s, 1 H, $J_{1,2}$ 1.2 Hz, H-1), 4.40–4.32 (m, 2 H, H-3′, H-3), 4.25–4.21 (m, 1 H, $OCH_2CH{=}CH_2$), 4.10–4.02 (m, 2 H), 3.84 (dd, 1 H, $J_{3',4'} = 8.6$ Hz, $J_{4',5'} = 9.7$ Hz, H-4′), 43.66–3.62 (m, 2 H), 3.56–3.44 (m, 2 H), 1.36 (s, 3 H, isopropylidene), 1.30 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 1.25 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6), 0.87 (s, 3 H, isopropylidene); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 165.6, 165.5, 165.4, 165.0 (5 C, 5 *C*OPh), 117.8, 108.7 (2 C, $OCH_2CH{=}CH_2$ and Me_2CO_2), 99.8, 99.2, 96.6 (3 C, 3 C-1), 27.6, 25.6 (2 C, Me_2CO_2), 17.6, 17.2 (2 C, 2 C-6). Anal. Calcd for $C_{58}H_{58}O_{18}$: C, 66.78; H, 5.61. Found: C, 66.64; H, 5.45.

3.13. Allyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 4)-α-L-rhamnopyranosyl-(1 → 3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (19)

Compound **18** (4.17 g, 4 mmol) was dissolved in 9:1 TFA–water (50 mL) and stirred for 2 h, at the end of which time the reaction mixture was poured directly into toluene (200 mL), and then the mixture was concentrated. The residue was purified by flash chromatography (1:1 petroleum ether–EtOAc) to give **19** (3.63 g, 90.7%) as a syrup: $[\alpha]_D$ +32.6° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18–7.34 (m, 25 H, 5 Ph*H*), 6.03–5.97 (m, 1 H, $OCH_2CH{=}CH_2$), 5.69 (dd, 1 H, $J_{2'',3''} = J_{3'',4''} = 8.8$ Hz, H-3″), 5.52 (dd, 1 H, $J_{1,2}$ 1.6 Hz, $J_{2,3}$ 3.2 Hz, H-2), 5.47 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4), 5.39–5.29 (m, 3 H, H-2″, $OCH_2CH{=}CH_2$), 5.24–5.20 (m, 1 H, H-4″), 4.98 (d, 1 H, $J_{1',2'}$ 1.1 Hz, H-1′), 4.88 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 4.85 (d, 1 H, $J_{1,2}$ 6.9 Hz, H-1″), 4.40 (dd, 1 H, $J_{2,3}$ 3.2 Hz, $J_{3,4}$ 9.9 Hz, H-3), 4.29–4.25 (m, 1 H, $OCH_2CH{=}CH_2$), 4.19 (dd, 1 H, $J_{2',3'}$ 3.9 Hz, $J_{3',4'}$ 9.8 Hz, H-3′), 4.07–4.03 (m, 1 H, $OCH_2CH{=}CH_2$), 4.04–4.01 (m, 1 H, H-5′), 3.84–3.80 (m, 1 H, H-5), 3.69–3.65 (m, 1 H, H-5″$_a$), 3.61 (dd, 1 H, $J_{1',2'}$ 1.1 Hz, $J_{2',3'}$ 3.9 Hz, H-2′), 3.55 (dd, 1 H, $J_{3',4'} = J_{4',5'} = 9.8$ Hz, H-4′), 3.19 (dd, 1 H, *J* 9.0, 11.7 Hz, H-5″$_b$), 1.31 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 1.07 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 165.6, 165.5, 165.3, 164.9 (5 C, 5 *C*OPh), 117.9, (1 C, $OCH_2CH{=}CH_2$), 101.2, 98.6, 96.7 (3 C, 3 C-1), 17.5, 17.3 (2 C, 2 C-6). Anal. Calcd for $C_{55}H_{54}O_{18}$: C, 65.86; H, 5.43. Found: C, 66.00; H, 5.71.

3.14. Allyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 2)-[2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 4)]-α-L-rhamnopyranosyl-(1 → 3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (20)

Compound **19** (3.00 g, 3 mmol) and 2,3,4-tri-*O*-benzoyl-α,β-D-xylopyranosyl trichloroacetimidate (**12**) (1.91 g, 3.15 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (50 mL). TMSOTf (18.0 μL, 0.10 mmol) was added dropwise at −20 °C with N_2 protection. The reaction mixture was stirred for 2 h, during which time the temperature was gradually warmed to ambient temperature. Then the mixture was neutralized with Et_3N and concentrated to dryness under reduced pressure. Purification of the residue by column chromatography on a silica gel column (2:1 petroleum ether–EtOAc) furnished the tetrasaccharide **20** (3.47 mg, 79.9%) as a syrup: $[\alpha]_D$ −2.3° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05–7.32 (m, 40 H, 8 Ph*H*), 6.01–5.95 (m, 1 H, $OCH_2CH{=}CH_2$), 5.57 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.0$ Hz, H-3-Xyl*p*), 5.56 (dd, 1 H, $J_{2,3} = J_{3,4} = 8.9$ Hz, H-3-Xyl*p*), 5.47 (dd, 1 H, $J_{1,2}$ 1.4 Hz, $J_{2,3}$ 3.1 Hz, H-2-Rha*p*), 5.44 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4-Rha*p*), 5.36–5.32 (m, 1 H, $OCH_2CH{=}CH_2$), 5.29–5.20 (m, 3 H, 2 H-2-Xyl*p*, $OCH_2CH{=}CH_2$), 5.18–5.15 (m, 1 H, H-4-Xyl*p*), 4.97 (d, 1 H, $J_{1,2}$ 1.0 Hz, H-1-Rha*p*), 4.95 (d, 1 H, $J_{1,2}$ 1.4 Hz, H-1-Rha*p*), 4.94–4.91 (m, 1 H, H-4-Xyl*p*), 4.60 (d, 1 H, $J_{1,2}$ 6.0 Hz, H-1-Xyl*p*), 4.52 (d, 1 H, $J_{1,2}$ 7.1 Hz, H-1-Xyl*p*), 4.44 (dd, 1 H, $J_{2,3}$ 3.1 Hz, $J_{3,4}$ 9.8 Hz, H-3-Rha*p*), 4.24–4.20 (m, 1 H, $OCH_2CH{=}CH_2$), 4.12–4.03 (m, 3 H), 3.77–3.75 (m, 1 H, H-5-Rha*p*), 3.63 (dd, 1 H, $J_{1,2}$ 1.0 Hz, $J_{2,3}$ 3.1 Hz, H-2-Rha*p*), 3.58–3.55 (m, 1 H), 3.44 (dd, 1 H, $J_{2,3}$ 3.0 Hz, $J_{3,4}$ 9.9 Hz, H-3-Rha*p*), 3.34 (dd, 1 H, $J_{3,4} = J_{4,5} =$ 9.9 Hz, H-4-Rha*p*), 3.02 (dd, 1 H, *J* 9.1, 11.0 Hz, H-5$_b$-Xyl*p*), 2.78 (dd, 1 H, *J* 9.3, 11.7 Hz, H-5$_b$-Xyl*p*), 1.26 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 1.17 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 165.5, 165.4, 165.3, 165.3, 165.2, 165.0, 164.7 (8 C, 8 *C*OPh), 117.8, (1 C, $OCH_2CH{=}CH_2$), 101.6, 100.5, 100.1, 96.7 (4 C, 4 C-1), 17.4, 17.4 (2 C, 2 C-6). Anal. Calcd for $C_{81}H_{74}O_{25}$: C, 67.21; H, 5.15. Found: C, 67.40; H, 5.07.

3.15. Allyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 2)-[2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 4)]-3-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (21)

To a solution of **20** (145 mg, 0.1 mmol) in pyridine (5 mL) was added Ac_2O (2.0 mL, 2 mmol). The reaction mixture was stirred at rt for 12 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was concentrated, and then the residue was purified by flash column chromatography on a silica gel

column (3:1 petroleum ether–EtOAc) to give compound **21** (113 mg, 75.8%) as a syrup: $[\alpha]_D -11.4°$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.05–7.33 (m, 40 H, 8 Ph*H*), 6.00 (m, 1 H, $OCH_2CH{=}CH_2$), 5.57 (dd, 1 H, $J_{2,3} = J_{3,4} = 8.3$ Hz, H-3-Xyl*p*), 5.53 (dd, 1 H, $J_{1,2}$ 1.7 Hz, $J_{2,3}$ 3.1 Hz, H-2-Rha*p*), 5.48 (dd, 1 H, $J_{2,3} = J_{3,4} = 8.7$ Hz, H-3-Xyl*p*), 5.47 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4-Rha*p*), 5.38–5.34 (m, 1 H, $OCH_2CH{=}CH_2$), 5.27–5.17 (m, 3 H, 2 H-2-Xyl*p*, $OCH_2CH{=}CH_2$), 5.14–5.10 (m, 1 H, H-4-Xyl*p*), 5.01 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1-Rha*p*), 4.98 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1-Rha*p*), 4.85 (dd, 1 H, $J_{2,3}$ 2.9 Hz, $J_{3,4}$ 9.2 Hz, H-3-Rha*p*), 4.82–4.78 (m, 1 H, H-4-Xyl*p*), 4.63 (d, 1 H, $J_{1,2}$ 6.0 Hz, H-1-Xyl*p*), 4.48 (dd, 1 H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 9.8 Hz, H-3-Rha*p*), 4.28–4.24 (m, 1 H, $OCH_2CH{=}CH_2$), 4.24 (d, 1 H, $J_{1,2}$ 6.1 Hz, H-1-Xyl*p*), 4.12–3.87 (m, 4 H), 3.77 (dd, 1 H, $J_{1,2}$ 2.0 Hz, $J_{2,3}$ 3.1 Hz, H-2-Rha*p*), 3.59 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4-Rha*p*), 3.36–3.21 (m, 2 H), 1.45 (s, 3 H, CH_3CO), 1.29 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6), 1.27 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6). Anal. Calcd for $C_{83}H_{76}O_{26}$: C, 66.93; H, 5.14. Found: C, 66.70; H, 5.33.

3.16. Allyl 2-*O*-acetyl-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-[2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→2)-][2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→4)]-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (23)

Compound **20** (2.89 g, 2.0 mmol) and allyl 2-*O*-acetyl-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (**22**) (1.17 g, 2.1 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (50 mL). TMSOTf (18 μL, 0.1 mmol) was added dropwise at −20 °C with N_2 protection. The reaction mixture was stirred for 2 h, during which time the temperature was gradually warmed to rt. Then the mixture was neutralized with Et_3N and concentrated to dryness under reduced pressure. Purification of the residue by column chromatography on a silica gel column (2:1 petroleum ether–EtOAc) furnished the pentasaccharide **23** (1.52 g, 41.3%) as a foamy solid: $[\alpha]_D +32.4°$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, characteristic signals are given): δ 6.02 (m, 1 H, $OCH_2CH{=}CH_2$), 5.93 (dd, 1 H, $J_{2,3} = J_{3,4} = 8.9$ Hz, H-3-Xyl*p*), 5.61 (dd, 1 H, $J_{2,3} = J_{3,4} = 8.4$ Hz, H-3-Xyl*p*), 5.08 (d, 1 H, $J_{1,2}$ 1.1 Hz, H-1-Rha*p*), 5.06 (d, 1 H, $J_{1,2}$ 6.7 Hz, H-1-Xyl*p*), 5.02 (s, 1 H, H-1-Rha*p*), 4.95 (d, 1 H, $J_{1,2}$ 6.6 Hz, H-1-Xyl*p*), 4.93 (s, 1 H, H-1-Rha*p*), 2.06 (s, 3 H, CH_3CO), 1.32 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6), 1.25 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3 (1 C, 1 CH_3CO), 165.7, 165.4, 165.4, 165.2, 165.1, 165.1, 165.1, 165.0, 164.9, 164.7 (10 C, 10 *C*OPh), 117.9 (1 C, $OCH_2CH{=}CH_2$), 100.2, 99.8, 99.1, 98.4, 96.8 (5 C, 5 C-1), 20.5 (1 C, 1 CH_3CO), 17.7, 17.5, 17.4 (3 C, 3 C-6). Anal. Calcd for $C_{103}H_{94}O_{32}$: C, 67.09; H, 5.14. Found: C, 67.20; H, 5.26.

Acknowledgements

This work was supported by The Chinese Academy of Sciences (KZCX3-J-08) and by The National Natural Science Foundation of China (Projects 30070185 and 39970864).

References

1. Tommasi, N. D.; Piacente, S.; Gacs-Baitz, E.; De Simone, F.; Pizza, C.; Aquino, R. *J. Nat. Prod.* **1998**, *323*, 61–66.
2. Jackson, G. E.; Ravenscroft, N.; Stephen, A. M. *Carbohydr. Res.* **1990**, *200*, 409–418.
3. Mcneil, M.; Chatterjee, D.; Hunter, S. W.; Brenna, P. J. *Methods Enzymol.* **1989**, *179*, 215–228.
4. Mass, J. L.; Pooler, M. R.; Gallette, G. J. *Adv. Straberry Res.* **1995**, *14*, 18–24.
5. Molinaro, A.; Evidente, A.; Fiore, S.; Lacobellis, N. S.; Lanzetta, R.; Parrilli, M. *Carbohydr. Res.* **2000**, *325*, 222–229.
6. Reimer, K. B.; Harris, S. L.; Varma, V.; Pinto, B. M. *Carbohydr. Res.* **1992**, *228*, 399–414.
7. Albernas, J. M.; Harris, S. L.; Varma, V.; Pinto, B. M. *Carbohydr. Res.* **1993**, *245*, 245–257.
8. Zhang, J.; Kong, F. *J. Carbohydr. Chem.* **2002**, *21*, 79–87.
9. Zhang, J.; Kong, F. *Carbohydr. Res.* **2002**, *337*, 391–396.
10. Zhang, J.; Zhu, Y.; Kong, F. *Carbohydr. Res.* **2001**, *336*, 329–335.
11. Zhang, J.; Kong, F. *J. Carbohydr. Chem.* **2002**, *21*, 575–585.
12. Schmidt, R. R.; Kinzy, W. *Adv. Carbohydr. Chem. Biochem.* **1994**, *50*, 21–125.