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A general method for the synthesis of oligosaccharides consisting of α-(1→2)- and α-(1→3)-linked rhamnan backbones and GlcNAc side chains

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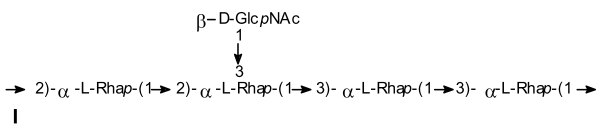
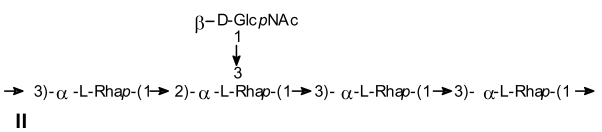
Abstract—A general method has been developed for the synthesis of oligosaccharides consisting of (1→2)- and (1→3)-linked rhamnans with GlcNAc side chains. As examples, highly effective and convergent syntheses of two decasaccharides in the O polysaccharide moiety of the lipopolysaccharide of the phytopathogenic bacterium *Pseudomonas syringae* pv. ribicola NCPPB 1010 were achieved. The two decasaccharides consist of O polysaccharide repeating units **I**+**II** and **II**+**I**, respectively. Allyl 3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside, allyl 2-*O*-benzoyl-3-*O*-chloroacetyl-α-L-rhamnopyranoside, 2,4-di-*O*-benzoyl-3-*O*-chloroacetyl-α-L-rhamnopyranosyl trichloroacetimidate, and 3-*O*-acetyl-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate, which were obtained by highly regioselective 3-O-acylations, were used as the key synthons to obtain the required α-(1→2)- and α-(1→3)-linked rhamnoocta saccharide acceptors with 3^3- and 3^7-free hydroxyl groups. Therefore, several disaccharides were synthesized, from which tetrasaccharides and hexasaccharides were then synthesized. Coupling of the hexasaccharide donors with the disaccharide acceptors gave the octasaccharide acceptors. Finally, the coupling of 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate with the octasaccharide acceptors, followed by deprotection, afforded the two target decasaccharides. A repeating hexasaccharide unit of the cell wall polysaccharide of β-hemolytic *Streptococci* Group A was also synthesized in a similar way.

1. Introduction

The phytopathogenic bacterium *Pseudomonas syringae* causes diseases in nearly all cultivated plants and in an unknown number of wild plant species. Recently, Knirel et al. reported that the O polysaccharide (OPS) moiety of the lipopolysaccharide (LPS) of *P. syringae* pv. ribicola NCPPB 1010 was composed of branched pentasaccharide repeating units (O repeats) of two types, major **I** and minor **II**, differing in the position of substitution of one of the rhamnose residues.[1]

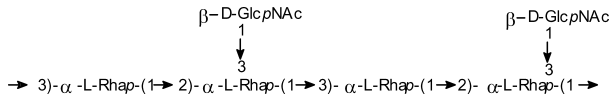


I



II

A similar structure (**III**) with alternate (1→2)- and (1→3)-linked rhamnan backbone and 3-*O*-GlcNAc side chains on the →2)-rhamnose residues occur in the cell wall polysaccharide of the β-hemolytic *Streptococci* Group A, which is one of the primary infective agents in humans, causing streptococcal pharyngitis, known as strep throat, and sometimes rheumatic fever.[2]



III

Synthetic samples of higher-order rhamnan structures spanning two or more branch points would be very valuable in the research of plant pathology and in the design of immunodiagnostic reagents. However, the efficient synthesis of complex rhamnans with a backbone of different linkages, and multiple sugar side chains represents a challenge task, since it is difficult to finish the synthesis with a simple process. The synthesis of structure **III**[3] and its frame-shifted analogue,[4] has been reported by Pinto's group using a procedure involving orthogonal masking groups and multiple protection–deprotection steps. We present herein a general and facile method for construction of (1→2)- and (1→3)-linked rhamnans with GlcNAc side chains.

Keywords: *Pseudomonas syringae*; rhamnose; glycosylation.

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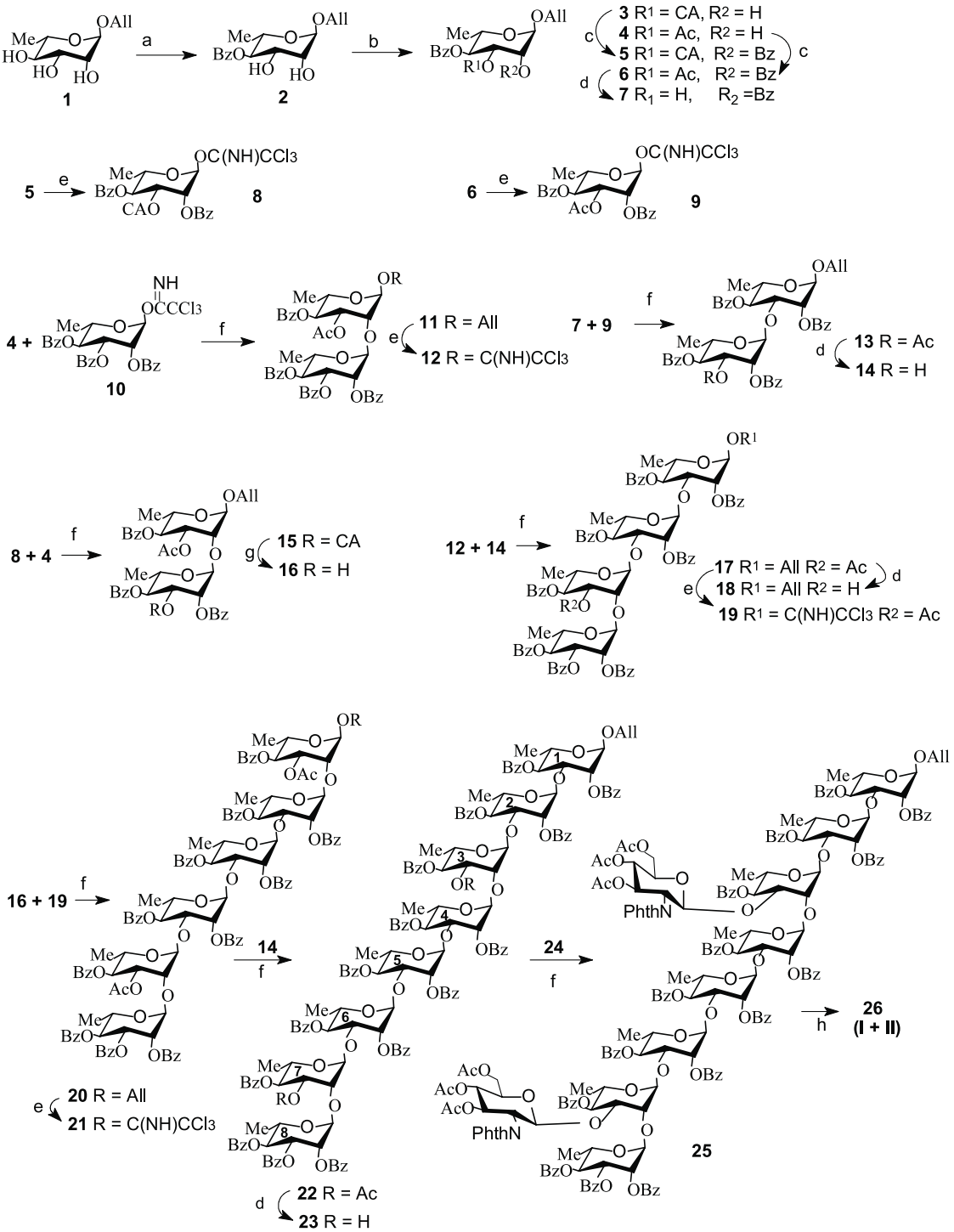
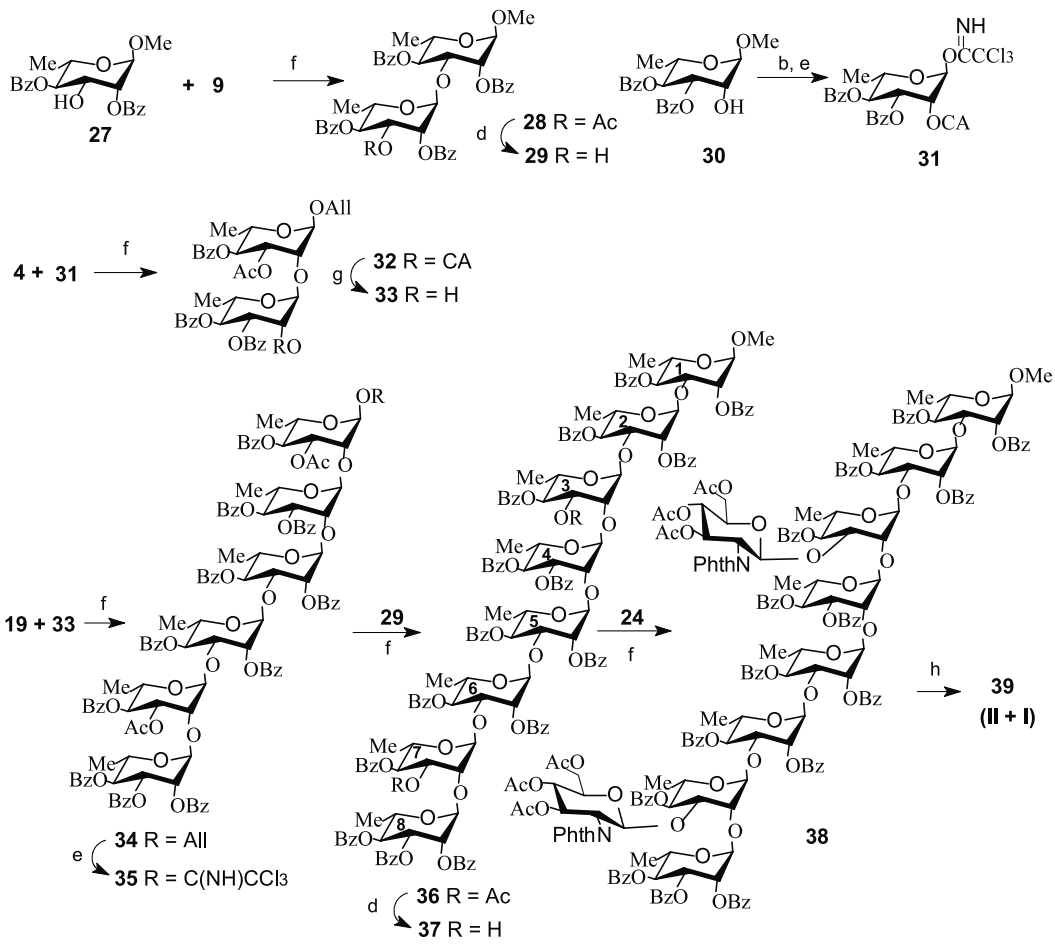
2. Results and discussion

As a typical example of the method, the synthesis of the decasaccharide consisting of two pentasaccharide repeating units **I**+**II** of the O polysaccharide moiety of *P. syringae* pv. ribicola NCPPB 1010 was carried out as outlined in Scheme 1. Allyl α-L-rhamnoside (**1**) was converted to allyl 4-*O*-benzoyl-α-L-rhamnopyranoside (**2**) by 2,3-*O*-isopropylidenation with 2,2-dimethoxypropane, 4-*O*-benzoylation, and removal of 2,3-*O*-isopropylidene. Selective chloroacetylation and acetylation with chloroacetyl chloride and acetyl chloride, respectively, in pyridine proceeded smoothly to give allyl 4-*O*-benzoyl-3-*O*-chloroacetyl- (**3**) and 3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (**4**) in high yields (88 and 93%, respectively). The selective 3-*O*-chloroacetylation and 3-*O*-acetylation were



Scheme 1. *Conditions and reagents*: (also suitable for Scheme 2 and Scheme 3) (a) (i) 2,2-Dimethoxypropane, DMF, toluenesulfonic acid; (ii) BzCl–pyridine; (iii) 90% HOAc. (b) For **3**: $ClCH_2COCl$, CH_2Cl_2, pyridine; for **4**: CH_3COCl, CH_2Cl_2, pyridine. (c) BzCl–pyridine. (d) 1–5% CH_3COCl/CH_3OH, 0°C to room temperature. (e) $PdCl_2$, CH_3COOH/CH_3COONa, then CCl_3CN, CH_2Cl_2, DBU, room temperature. (f) TMSOTf, CH_2Cl_2, 0°C to room temperature. (g) Thiourea in EtOH–CH_2Cl_2 (1:4), reflux. (h) (i) EtOH/10% hydrazine hydrate, reflux, 48 h; (ii) Ac_2O–pyridine (dry), room temperature, 12 h; (iii) satd NH_3/MeOH, room temperature, 72 h.



Scheme 2.

the key steps in the synthesis, because the resulting 3-*O*-chloroacetyl rhamnoside **3** and the 3-*O*-acetyl rhamnoside **4** were not only the required acceptors for construction of (1→2)-linked disaccharides, but could also be transformed to the related donors. These rhamnose donors and acceptors could then be assembled and transformed in an appropriate way to build a (1→2)- and (1→3)-linked long chain with acetyl groups as temporary hydroxyl protecting groups at the branched points. Thus, **3** and **4** were benzoylated to produce the corresponding allyl 2,4-di-*O*-benzoyl-3-*O*-chloroacetyl- (**5**) and 3-*O*-acetyl-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**6**), respectively in quantitative yields. Deallylation of **5** and **6** with $PdCl_2$,[5] followed by trichloroacetimidation with trichloroacetonitrile[6] gave the donors **8** (83% for 2 steps) and **9** (87% for 2 steps), respectively. Selective deacetylation[7] of **6** gave acceptor **7**. Condensation of **4** with 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (**10**) furnished the (1→2)-linked disaccharide, **11**. Subsequent deallylation and trichloroacetimidation yielded the disaccharide donor, **12**. Glycosylation of acceptor **7** with imidate **9** gave disaccharide **13**. Subsequent deacetylation of **13** gave disaccharide acceptor **14**. Condensation of **12** with **14** offered the tail (nonreducing end) tetrasaccharide **17**. Deacetylation followed to give the tetrasaccharide acceptor **18**, which was the key precursor for the construction of the pentasaccharide structure **I** or **II**. Disaccharide **15**, an inner moiety of the backbone, was built by the coupling of **8** with **4**. Dechloroacetylation of **15** gave the disaccharide acceptor **16**, while deallylation of **17** followed by trichloroacetimidation gave the tetrasaccharide donor **19**. Coupling of **16** with **19** furnished hexasaccharide **20**, and reiteration of deallylation and trichloroacetimidation transformed **20** to the hexasaccharide donor, **21**. Octasaccharide **22** was obtained by glycosylation of **14** with **21**. All of the glycosylation reactions described above gave satisfactory yields (84–92% for the disaccharides, 86% for the tetrasaccharide, 81% for the hexasaccharide, and 83% for the octasaccharide), making large-scale preparation possible. Selective deacetylation of **22** gave the octasaccharide acceptor **23** with 3^3- and 3^7- hydroxyl groups free, and subsequent coupling with 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-D-glucopyranosyl trichloroacetimidate (**24**) gave decasaccharide **25**. Compound **25** was identified by its ^1H and ^{13}C NMR spectra which showed 8 rhamnose H-6 signals at δ 1.25, 1.17, 0.99, 0.71, 0.67, 0.62, 0.47, and 0.40 ppm, 8 rhamnose C-1 signals at 99.44, 99.27, 98.98, 98.81, 98.50, 98.46, 96.24, 96.02 ppm, and two C-1 signals for glucosamines at 100.31 and 100.16 ppm. Decasaccharide **39** consisting of two pentasaccharide repeating units **II**+**I** was synthesized in a similar way (Scheme 2). Thus, the disaccharide acceptor methyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**29**) was obtained by the coupling of **9** with methyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**27**), followed by deacetylation. The other disaccharide acceptor allyl 3,4-di-*O*-benzoyl-α-L-

rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (**33**) was obtained by the coupling of **4** with 3,4-di-*O*-benzoyl-2-*O*-chloroacetyl-α-L-rhamnopyranoside (**31**). Condensation of the tetrasaccharide donor **19** with disaccharide acceptor **33** gave hexasaccharide **34**. Deallylation of **34**, followed by trichloroacetimidation, produced hexasaccharide donor **35**, whose coupling with disaccharide acceptor **29** and subsequent selective deacetylation afforded the octasaccharide acceptor **37**. The final two steps to obtain **39** were exactly the same as those in the preparation of decasaccharide **26** from **23**. Protected decasaccharide **38** clearly had all of the characteristic peaks in its ^{1}H NMR (δ 1.39, 1.31, 1.11, 1.05, 0.72, 0.69, 0.59 and 0.55 ppm for 8 rhamnose H-6 signals) and ^{13}C NMR (100.05, 99.91, 99.59, 99.32, 99.32, 99.32, 99.16, 98.59, 98.13, 91.97 ppm for 10 C-1 signals) spectra.

With the disaccharide synthons **12** and **16** in hand, hexasaccharide **III** can also be synthesized in a facile manner. Thus, the coupling of donor **12** with acceptor **16** gave tetrasaccharide **40**, and its subsequent deacetylation furnished tetrasaccharide diol acceptor **41**. Condensation of **24** with **41** produced the protected hexasaccharide, **42** (Scheme 3).

Conventional removal of phthalimido group from **25**, **38**, and **42** using hydrazine worked well; however, the reaction of **25** and **42** was accompanied by simultaneous reduction of the allyl group to propyl.[4] Subsequent acetylation of the amino groups and deacylation of the protective hydroxyl groups with sodium methoxide–methanol gave unprotected decasaccharides **26** and **39**, and hexasaccharide **43** (**III**), respectively. The decasaccharides were characterized by mass and ^{1}H NMR spectroscopy, and the hexasaccharide showed spectral data similar to those reported in the literature.[3]

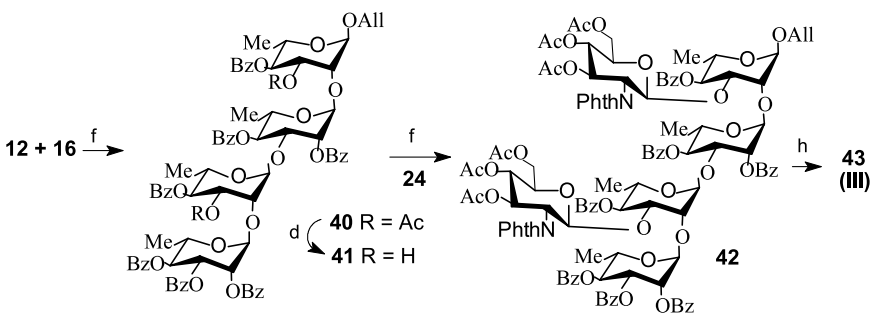
In summary, we have presented herein a general and convergent method that can be applied to the synthesis of (1→2)- and (1→3)-linked rhamnans with arbitrary sugar side chains on the 3-OH of the rhamnose residues.

3. Experimental

3.1. General methods

Melting points were determined using a 'Mel-Temp' apparatus. Optical rotations were determined using a Perkin–Elmer model 241-MC automatic polarimeter for solutions in a 1-dm jacketed cell. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian XL-400 and Varian XL-200 spectrometers, for solutions in $CDCl_3$ or in D_2O as indicated. Chemical shifts are expressed in ppm downfield from the Me_4Si absorption. Mass spectra were recorded on 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) sulfuric acid in methanol or by UV detection. Column chromatography was conducted by the elution of columns (8×100 mm, 16×240 mm, 18×300 mm, 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 mm 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 reduced pressure.

3.1.1. 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*-TsOH·H_2O (38 mg, 0.2 mmol) was added 2,2-dimethoxypropane (2.5 mL, 20 mmol). The mixture was stirred for 12 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. Then a solution of pyridine (20 mL) containing benzoyl chloride (4.7 mL, 40 mmol) was added dropwise to the reaction mixture. After stirring for 24 h at room temperature, the mixture was diluted with CH_2Cl_2, and washed sequentially with 1 M HCl, water, and satd $NaHCO_3$ (aq). The organic layers were combined, dried, and concentrated to give a residue. The residue was dissolved in 90% acetic acid and refluxed for 1 h. The solution was concentrated. Purification of the residue by flash column chromatography on silica gel (1:1 petroleum ether–EtOAc) gave compound **2** (2.63 g, 85%) as a syrup; $[\alpha]_D^{25}=-71.3$ (*c* 1.3, $CHCl_3$); ν_{max} (KBr) 3439, 2980, 1736, 1267, 1050, 826, 710; δ_H (400 MHz, $CDCl_3$) 8.06–7.42 (m, 5H, Ph), 5.93 (m, 1H, $OCH_2CH{=}CH_2$), 5.32–5.21 (m, 2H, $OCH_2CH{=}CH_2$), 5.07 (dd, 1H, $J_{3,4}$=9.9 Hz, $J_{4,5}$=9.9 Hz, H-4), 4.92 (d, 1H, $J_{1,2}$=0.8 Hz, H-1), 4.24–3.98 (m, 5H), 3.07–2.90 (bs, 2H, 2 O*H*), 1.24 (d, 3H, $J_{5,6}$=6.4 Hz, H-6); δ_C (100 MHz, $CDCl_3$) 165.4 (Ph*C*O), 117.8 ($OCH_2CH{=}CH_2$), 98.6 (C-1), 71.6, 70.1, 67.7, 66.9, 17.3. Anal. calcd for $C_{16}H_{20}O_6$: C, 62.32; H, 6.54. Found: C, 62.49; H, 6.76.



Scheme 3.

3.1.2. Allyl 4-*O*-benzoyl-3-*O*-chloroacetyl-α-L-rhamnopyranoside (3). Compound **2** (3.08 g, 10 mmol) was dissolved in dry CH_2Cl_2 (40 mL) containing pyridine (8.1 mL, 100 mmol), then under N_2, chloroacetyl chloride (0.7 mL, 11 mmol) in anhydrous CH_2Cl_2 (10 mL) was added dropwise to the solution over 30 min at 0°C. The reaction mixture was slowly raised to room temperature and stirred for 2 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with water, 1 M HCl, and dried (Na_2SO_4). The solution was concentrated, and purification of the residue by column chromatography on silica gel (3:1 petroleum ether–EtOAc) gave compound **3** (3.20 g, 83%) as a syrup; $[\alpha]_D^{25}=-39.2$ (*c* 0.7, $CHCl_3$); ν_{max} (KBr) 3443, 2970, 1733, 1271, 1079, 1026, 711; δ_H (400 MHz, $CDCl_3$) 8.05–7.43 (m, 5H, Ph), 5.93 (m, 1H, CH_2=C*H*–CH_2O), 5.50 (dd, 1H, $J_{2,3}$=3.1 Hz, $J_{3,4}$=10.0 Hz, H-3), 5.40 (dd, 1H, $J_{3,4}$=10.0 Hz, $J_{4,5}$=10.0 Hz, H-4), 5.37–5.24 (m, 2H, CH_2=CH–CH_2O), 4.91 (d, 1H, $J_{1,2}$=1.6 Hz, H-1), 4.24 (m, 1H, CH_2=CH–C*H*$_2$O), 4.18 (dd, 1H, $J_{1,2}$=1.6 Hz, $J_{2,3}$=3.1 Hz, H-2), 4.08–4.02 (m, 2H, CH_2=CH–C*H*$_2$O, H-5), 3.97 (d, 1H, ^2J=17.5 Hz, ClC*H*$_2$CO), 3.93 (d, 1H, ^2J=17.5 Hz, ClC*H*$_2$CO), 1.28 (d, 3H, $J_{5,6}$=6.4 Hz, H-6); δ_C (100 MHz, $CDCl_3$) 170.6 (ClCH$_2$*C*O), 166.2 (Ph*C*O), 117.8 (OCH$_2$CH=*C*H$_2$), 97.4 (C-1), 71.4, 70.6, 68.1, 66.7, 40.2 (Cl*C*H$_2$CO), 17.3. Anal. calcd for $C_{18}H_{21}ClO_7$: C, 56.15; H, 5.50. Found: C, 56.03; H, 5.69.

3.1.3. Allyl 3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (4). Compound **2** (3.08 g, 10 mmol) was dissolved in dry CH_2Cl_2 (40 mL) containing pyridine (8.1 mL, 100 mmol), then under N_2, acetyl chloride (0.8 mL, 11 mmol) in anhydrous CH_2Cl_2 (10 mL) was added dropwise to the solution over 30 min at 0°C. The reaction mixture was slowly raised to room temperature and stirred for 2 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with water, 1 M HCl, and dried (Na_2SO_4). The solution was concentrated, and purification of the residue by column chromatography on silica gel (3:1 petroleum ether–EtOAc) gave compound **4** (3.24 g, 93%) as a syrup; $[\alpha]_D^{25}=-53.2$ (*c* 1.1, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 8.02–7.43 (m, 5H, Ph), 5.93 (m, 1H, CH_2=C*H*–CH_2O), 5.46 (dd, 1H, $J_{2,3}$=3.2 Hz, $J_{3,4}$=10.0 Hz, H-3), 5.37 (dd, 1H, $J_{3,4}$=10.0 Hz, $J_{4,5}$=10.0 Hz, H-4), 5.37–5.23 (m, 2H, CH_2=CH–CH_2O), 4.90 (d, 1H, $J_{1,2}$=1.6 Hz, H-1), 4.23 (m, 1H, CH_2=CH–C*H*$_2$O), 4.12 (dd, 1H, $J_{1,2}$=1.6 Hz, $J_{2,3}$=3.2 Hz, H-2), 4.08–4.01 (m, 2H, CH_2=CH–C*H*$_2$O, H-5), 1.97 (s, 3H, C*H*$_3$CO), 1.27 (d, 3H, $J_{5,6}$=6.3 Hz, H-6). Anal. calcd for $C_{18}H_{22}O_7$: C, 61.70; H, 6.33. Found: C, 61.96; H, 6.24.

3.1.4. Allyl 2,4-di-*O*-benzoyl-3-*O*-chloroacetyl-α-L-rhamnopyranoside (5). To the solution of compound **3** (3.85 g, 10 mmol) in pyridine (20 mL) was added benzoyl chloride (2.4 mL, 20 mmol) dropwise, and the mixture was stirred overnight at room temperature. Ice water was added, and the mixture was diluted with CH_2Cl_2, washed with 1 M HCl, water, and satd Na_2CO_3 (aq) sequentially. The organic layers were combined, dried (Na_2SO_4), and concentrated. Purification of the crude product by column chromatography (4:1 petroleum ether–EtOAc) gave **5** (4.52 g, 92%) as a syrup; $[\alpha]_D^{25}=+75.7$ (*c* 1.3, $CHCl_3$); ν_{max} (KBr) 2974, 1729, 1274, 1079, 1022, 713; δ_H (400 MHz, $CDCl_3$) 7.97–7.26 (m, 10H, Ph), 5.95 (m, 1H, OCH$_2$C*H*=CH$_2$), 5.77 (dd, 1H, $J_{2,3}$=3.4, $J_{3,4}$=10.2 Hz, H-3), 5.55–5.50 (m, 2H, H-2, H-4), 5.40–5.26 (m, 2H, OCH$_2$CH=C*H*$_2$), 4.94 (d, 1H, $J_{1,2}$=1.7 Hz, H-1), 4.26 (m, 1H, OC*H*$_2$CH=CH$_2$), 4.20 (d, 1H, ^2J=8.9 Hz, ClC*H*$_2$CO), 4.16 (d, 1H, ^2J=8.9 Hz, ClC*H*$_2$CO), 4.16–4.07 (m, 2H, H-5, OC*H*$_2$CH=CH$_2$), 1.32 (d, 3H, $J_{5,6}$=6.3 Hz, H-6); δ_C (100 MHz, $CDCl_3$) 170.6 (ClCH$_2$*C*O), 166.3, 165.7 (Ph*C*O), 117.8 (OCH$_2$-CH=*C*H$_2$), 98.6 (C-1), 71.8, 70.4, 68.7, 68.6, 40.0 (Cl*C*H$_2$CO), 17.7. Anal. calcd for $C_{25}H_{25}ClO_8$: C, 61.41; H, 5.15. Found: C, 61.22; H, 5.10.

3.1.5. Allyl 3-*O*-acetyl-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (6). Compound **4** (3.50 g, 10 mmol) was benzoylated under the same conditions as those used for the preparation of **5** from **3**, giving **6** (4.30 g, 95%) as a foamy solid; $[\alpha]_D^{25}=+76.3$ (*c* 1.0, $CHCl_3$); ν_{max} (KBr) 1730, 1270, 1112, 1073, 716; δ_H (400 MHz, $CDCl_3$) 8.13–7.26 (m, 10H, Ph), 5.98 (m, 1H, OCH$_2$C*H*=CH$_2$), 5.65 (dd, 1H, $J_{2,3}$=3.4 Hz, $J_{3,4}$=10.1 Hz, H-3), 5.54 (dd, 1H, $J_{1,2}$=1.7 Hz, $J_{2,3}$=3.4 Hz, H-2), 5.47 (t, 1H, $J_{3,4}$=10.1 Hz, $J_{4,5}$=10.1 Hz, H-4), 5.39–5.25 (m, 2H, OCH$_2$CH=C*H*$_2$), 4.98 (d, 1H, $J_{1,2}$=1.7 Hz, H-1), 4.21–4.06 (m, 3H, H-5, OC*H*$_2$-CH=CH$_2$), 1.86 (s, 3H, C*H*$_3$CO), 1.32 (d, 3H, $J_{5,6}$=6.2 Hz, H-6); δ_C (100 MHz, $CDCl_3$) 169.7 (CH$_3$*C*O), 167.0, 166.3 (Ph*C*O), 117.9 (OCH$_2$CH=*C*H$_2$), 97.4 (C-1), 70.9, 70.4, 69.3, 68.0, 20.6 (*C*H$_3$CO), 17.8. Anal. calcd for $C_{25}H_{26}O_8$: C, 66.07; H, 5.77. Found: C, 66.19; H, 5.50.

3.1.6. Allyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (7). To a solution of **6** (2.27 g, 5 mmol) in anhydrous MeOH (50 mL) was added acetyl chloride (1.5 mL) at 0°C. The solution was stirred at room temperature until TLC (3:1 petroleum ether–EtOAc) showed that the starting material had been consumed. The solution was neutralized with Et_3N, then concentrated to dryness. The residue was passed through a short silica gel column to give **7** (1.81 g, 88%) as a syrup; $[\alpha]_D=+46.7$ (*c* 1.1, $CHCl_3$); ν_{max} (KBr) 3443, 1736, 1269, 1110, 1025, 713; δ_H (400 MHz, $CDCl_3$) 8.12–7.45 (m, 10H, Ph), 5.97 (m, 1H, OCH$_2$C*H*=CH$_2$), 5.41 (dd, 1H, $J_{1,2}$=1.7 Hz, $J_{2,3}$=3.5 Hz, H-2), 5.39–5.25 (m, 2H, OCH$_2$-CH=C*H*$_2$), 5.28 (dd, 1H, $J_{3,4}$=10.0 Hz, $J_{4,5}$=10.0 Hz, H-4), 5.02 (d, 1H, $J_{1,2}$=1.7 Hz, H-1), 4.34 (dd, 1H, $J_{2,3}$=3.5 Hz, $J_{3,4}$=10.0 Hz, H-3), 4.27–4.05 (m, 3H, H-5, OC*H*$_2$-CH=CH$_2$), 1.33 (d, 3H, $J_{5,6}$=6.3 Hz, H-6); δ_C (100 MHz, $CDCl_3$) 166.8, 165.6 (Ph*C*O), 117.8 (OCH$_2$CH=*C*H$_2$), 98.0 (C-1), 70.6, 70.0, 69.1, 68.4, 17.7. Anal. calcd for $C_{23}H_{24}O_7$: C, 66.98; H, 5.87. Found: C, 66.81; H, 5.68.

3.1.7. 2,4-Di-*O*-benzoyl-3-*O*-chloroacetyl-α-L-rhamnopyranosyl trichloroacetimidate (8). To a solution of compound **5** (2.44 g, 5 mmol) in 90% acetic acid (50 mL) containing sodium acetate (1.46 g, 15 mmol) was added $PdCl_2$ (270 mg, 2.5 mmol). The mixture was stirred 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 diluted with CH_2Cl_2 (150 mL), washed with water and satd Na_2CO_3 (aq). 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 2,4-di-*O*-benzoyl-3-*O*-chloroacetyl-α,β-L-rhamnopyranose as a syrup. A solution of the above syrup in dry CH_2Cl_2 (30 mL), CCl_3CN (1.0 mL, 10 mmol) and DBU (135 μL, 0.9 mmol) was stirred at room temperature for 2 h. The solvents were removed in vacuo. The residue was purified by silica gel flash column chromatography to give trichloroacetimidate **8** (2.46 g, 83%) as a white foam; $[\alpha]_D^{25}$=+49.3 (*c* 1.1, $CHCl_3$); ν_{max} (KBr) 3344, 1730, 1270, 1064, 711; δ_H (400 MHz, $CDCl_3$) 8.80 (s, 1H, CN*H*CCl_3), 8.14–7.25 (m, 10H, Ph), 6.42 (d, 1H, $J_{1,2}$=1.9 Hz, H-1), 5.77 (dd, 1H, $J_{1,2}$=1.9 Hz, $J_{2,3}$=3.2 Hz, H-2), 5.71 (dd, 1H, $J_{2,3}$=3.2 Hz, $J_{3,4}$=10.2 Hz, H-3), 5.94 (dd, 1H, $J_{3,4}$=10.2 Hz, $J_{4,5}$=10.2 Hz, H-4), 4.30 (m, 1H, H-5), 3.93 (d, 1H, ^2J=15.2 Hz, ClCH_2CO), 3.87 (d, 1H, ^2J=15.2 Hz, ClCH_2CO), 1.40 (d, 3H, $J_{5,6}$=6.2 Hz, H-6). Anal. calcd for $C_{24}H_{21}Cl_4NO_8$: C, 48.59; H, 3.57. Found: C, 48.71; H, 3.50.

3.1.8. 3-*O*-Acetyl-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (9). Compound **6** (4.54 g, 10 mmol) was deallylated and subsequently converted to the trichloroacetimidate under the same conditions as that used for the preparation of **8** from **5**, giving **9** (4.84 g, 87%) as a foamy solid; $[\alpha]_D^{25}$=+50.8 (*c* 0.5, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 8.77 (s, 1H, CN*H*CCl_3), 8.10–7.27 (m, 10H, Ph), 6.42 (d, 1H, $J_{1,2}$=1.6 Hz, H-1), 5.60 (dd, 1H, $J_{2,3}$=3.2 Hz, $J_{3,4}$=10.0 Hz, H-3), 5.57 (dd, 1H, $J_{1,2}$=1.6 Hz, $J_{2,3}$=3.2 Hz, H-2), 5.42 (t, 1H, $J_{3,4}$=10.0 Hz, $J_{4,5}$=10.0 Hz, H-4), 4.32 (m, 1H, H-5), 1.97 (s, 3H, COCH_3), 1.44 (d, 3H, $J_{5,6}$=6.2 Hz, H-6). Anal. calcd for $C_{24}H_{22}Cl_3NO_8$: C, 51.59; H, 3.96. Found: C, 51.40; H, 3.74.

3.1.9. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (11). To a cooled solution (0°C) of **4** (1.75 g, 5 mmol) and 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (**10**) (3.25 g, 5.3 mmol) in anhydrous CH_2Cl_2 (30 mL) was added TMSOTf (36 μL, 0.2 mmol). The mixture was stirred at this temperature for 2 h, then neutralized with Et_3N, and concentrated. The residue was purified by silica gel column chromatography to give **11** (3.41 g, 84%) as a foamy solid; $[\alpha]_D^{25}$=+118.4 (*c* 1.0, $CHCl_3$); ν_{max} (KBr) 1730, 1267, 1112, 714; δ_H (400 MHz, $CDCl_3$) 8.11–7.41 (m, 20H, Ph), 5.98 (m, 1H, OCH$_2$C*H*=CH$_2$), 5.92 (dd, 1H, $J_{2',3'}$=3.2 Hz, $J_{3',4'}$=9.8 Hz, H-3′), 5.74 (dd, 1H, $J_{1',2'}$=1.4 Hz, $J_{2',3'}$=3.5 Hz, H-2′), 5.70 (t, 1H, $J_{3',4'}$=9.8 Hz, $J_{4',5'}$=9.8 Hz, H-4′), 5.54 (dd, 1H, $J_{2,3}$=3.2 Hz, $J_{3,4}$=10.1 Hz, H-3), 5.47 (dd, 1H, $J_{3,4}$=10.1 Hz, $J_{4,5}$=10.1 Hz, H-4), 5.38–5.25 (m, 2H, OCH$_2$CH=CH_2), 5.14 (d, 1H, $J_{1',2'}$=1.4 Hz,H-1′), 4.98 (d, 1H, $J_{1,2}$=1.5 Hz, H-1), 4.32–4.24 (m, 2H, H-5′, OCH_2CH=CH$_2$), 4.19 (dd, 1H, $J_{1,2}$=1.5 Hz, $J_{2,3}$=3.2 Hz, H-2), 4.11–4.04 (m, 2H, H-5, OCH_2CH=CH$_2$), 2.04 (s, 3H, CH_3CO), 1.34 (d, 3H, $J_{5,6}$=6.3 Hz, H-6/H-6′), 1.15 (d, 3H, $J_{5,6}$=6.2 Hz, H-6/H-6′); δ_C (100 MHz, $CDCl_3$) 170.6 (CH$_3$*C*O), 165.8, 165.3, 165.2, 165.1 (4Ph*C*O), 117.8 (OCH$_2$CH=*C*H$_2$), 99.5, 97.5 (2C-1), 20.7 (*C*H$_3$CO), 17.6, 17.5 (2C-6). Anal. calcd for $C_{45}H_{44}O_{14}$: C, 66.82; H, 5.48. Found: C, 67.01; H, 5.74.

3.1.10. 2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (12). Compound **11** (4.04 g, 5 mmol) was deallylated and subsequently converted to the trichloroacetimidate under the same conditions as those used for the preparation of **8** from **5**, giving **12** (3.90 g, 85%) as a foamy solid; $[\alpha]_D$=+113.6 (*c* 0.6, $CHCl_3$); ν_{max} (KBr) 3339, 1730, 1270, 1107, 712; ^{1}H NMR δ 8.74 (s, 1H, CN*H*CCl_3), 8.11–7.26 (m, 20H, Ph), 6.44 (d, 1H, $J_{1,2}$=1.6 Hz, H-1), 5.94 (dd, 1H, $J_{2',3'}$=3.4 Hz, $J_{3',4'}$=10.0 Hz, H-3′), 5.76 (dd, 1H, $J_{1',2'}$=1.0 Hz, $J_{2',3'}$=3.4 Hz, H-2′), 5.71 (t, 1H, $J_{3',4'}$=10.0 Hz, $J_{4',5'}$=10.0 Hz, H-4′), 5.62–5.55 (m, 2H, H-3, H-4), 5.23 (d, 1H, $J_{1,2}$=1.0 Hz, H-1′), 4.44 (dd, 1H, $J_{1,2}$=1.6 Hz, $J_{2,3}$=3.1 Hz, H-2), 4.38 (m, 1H, H-5), 4.28 (m, 1H, H-5′), 2.06 (s, 3H, CH_3CO), 1.43 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 1.40 (d, 3H, $J_{5',6'}$=6.3 Hz, H-6′). Anal. calcd for $C_{44}H_{40}Cl_3NO_{14}$: C, 57.87; H, 4.42. Found: C, 57.72; H, 4.31.

3.1.11. Allyl 3-*O*-acetyl-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (13). Compounds **7** (2.06 g, 5.0 mmol) and **9** (2.80 g, 5.0 mmol) were coupled under the same conditions as those used for the preparation of **11** from **4** and **10**, giving **13** (3.38 g, 84%) as a foamy solid; $[\alpha]_D^{25}$=+105.8 (*c* 1.3, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 8.23–7.37 (m, 20H, Ph), 5.95 (m, 1H, OCH$_2$C*H*=CH$_2$), 5.46 (dd, 1H, $J_{3,4}$=9.8 Hz, $J_{4,5}$=9.8 Hz, H-4), 5.51 (dd, 1H, $J_{1,2}$=1.8 Hz, $J_{2,3}$=3.5 Hz, H-2), 5.37 (dd, 1H, $J_{2',3'}$=3.1 Hz, $J_{3',4'}$=9.7 Hz, H-3′), 5.33 (m, 1H, OCH$_2$CH=CH_2), 5.29 (t, 1H, $J_{3',4'}$=9.7 Hz, $J_{4',5'}$=9.7 Hz, H-4′), 5.25 (m, 1H, OCH$_2$CH=CH_2), 5.15–5.13 (m, 2H, H-1′, H-2′), 5.05 (d, 1H, $J_{1,2}$=1.8 Hz, H-1), 4.47 (dd, 1H, $J_{2,3}$=3.5 Hz, $J_{3,4}$=9.8 Hz, H-3), 4.22–4.04 (m, 4H, H-5′, H-5, OCH_2CH=CH$_2$), 1.71 (s, 3H, CH_3CO), 1.34 (d, 3H, $J_{5,6}$=6.3 Hz, H-6/H-6′), 1.15 (d, 3H, $J_{5,6}$=6.2 Hz, H-6/H-6′); δ_C (100 MHz, $CDCl_3$) 169.1 (CH$_3$*C*O), 166.1, 165.6, 165.5, 164.9 (4Ph*C*O), 117.9 (OCH$_2$CH=*C*H$_2$), 99.3, 96.4 (2C-1), 20.4 (*C*H$_3$CO), 17.6, 17.3 (2C-6). Anal. calcd for $C_{45}H_{44}O_{14}$: C, 66.82; H, 5.48. Found: C, 66.70; H, 5.53.

3.1.12. Allyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (14). Compound **13** (3.00 g, 3.7 mmol) was deacetylated under the same conditions as those used for the preparation of **7** from **6**, giving **14** (2.33 g, 82%) as a foamy solid; $[\alpha]_D^{25}$=+92.2 (*c* 0.5, $CHCl_3$); ν_{max} (KBr) 3447, 1275, 1266, 1110, 712; δ_H (400 MHz, $CDCl_3$) δ 8.21–7.38 (m, 20H, Ph), 5.93 (m, 1H, CH$_2$=C*H*–CH$_2$), 5.56 (t, 1H, $J_{3',4'}$=9.9 Hz, $J_{4',5'}$=9.9 Hz, H-4′), 5.51 (dd, 1H, $J_{1',2'}$=1.8 Hz, $J_{2',3'}$=3.5 Hz, H-2′), 5.38–5.25 (m, 2H, CH_2=CH–CH$_2$), 5.18 (d, 1H, $J_{1',2'}$=1.8 Hz, H-1′), 5.07 (t, 1H, $J_{3,4}$=9.8 Hz, $J_{4,5}$=9.8 Hz, H-4), 5.04 (d, 1H, $J_{1,2}$=1.7 Hz, H-1), 5.00 (dd, 1H, $J_{1,2}$=1.7 Hz, $J_{2,3}$=3.5 Hz, H-2), 4.47 (dd, 1H, $J_{2,3}$=3.5 Hz, $J_{3,4}$=9.8 Hz, H-3), 4.23 (m, 1H, CH$_2$=CH–CH_2), 4.10–4.04 (m, 3H, H-3′, H-5, CH$_2$=CH–CH_2), 3.98 (m, 1H, H-5′), 1.34 (d, 3H, $J_{5',6'}$=6.4 Hz, H-6′), 1.12 (d, 3H, $J_{5,6}$=6.4 Hz, H-6); δ_C (100 MHz, $CDCl_3$) 166.6, 166.3, 165.7, 165.0 (4Ph*C*O), 117.8 (OCH$_2$CH=*C*H$_2$), 98.9, 97.4 (2C-1), 17.7, 17.3 (2C-6). Anal. calcd for $C_{43}H_{42}O_{13}$: C, 67.35; H, 5.52. Found: C, 67.44; H, 5.40.

3.1.13. Allyl 2,4-di-*O*-benzoyl-3-*O*-chloroacetyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (15). Compound **4** (1.75 g, 5.0 mmol) and **8** (2.97 g, 5.0 mmol) were coupled under the same conditions as those used for the preparation of **11** from **4** and

10, giving **15** as a foamy solid (3.44 g, 88%); $[\alpha]_D^{25}$=+66.2 (*c* 1.9, $CHCl_3$); ν_{max} (KBr) 1736, 1270, 1074, 1026, 713; δ_H (400 MHz, $CDCl_3$) 8.10–7.45 (m, 15H, Ph), 5.94 (m, 1H, OCH_2CH=CH_2), 5.78 (dd, 1H, $J_{2',3'}$=3.4 Hz, $J_{3',4'}$=10.1 Hz, H-3′), 5.63 (dd, 1H, $J_{1',2'}$=1.8 Hz, $J_{2',3'}$=3.4 Hz, H-2′), 5.53 (t, 1H, $J_{3',4'}$=10.1 Hz, $J_{4',5'}$=10.1 Hz, H-4′), 5.51 (dd, 1H, $J_{2,3}$=3.2 Hz, $J_{3,4}$=9.7 Hz, H-3), 5.42 (dd, 1H, $J_{3,4}$=9.7 Hz, $J_{4,5}$=9.7 Hz, H-4), 5.37–5.08 (m, 2H, OCH_2-CH=CH_2), 5.08 (d, 1H, $J_{1',2'}$=1.8 Hz, H-1′), 4.95 (d, 1H, $J_{1,2}$=1.6 Hz, H-1), 4.26–4.22 (m, 2H, H-5′, OCH_2-CH=CH_2), 4.16 (dd, 1H, $J_{1,2}$=1.6 Hz, $J_{2,3}$=3.2 Hz, H-2), 4.09–4.04 (m, 2H, H-5, OCH_2CH=CH_2), 3.92 (d, 1H, ^2J=14.9 Hz, $ClCH_2CO$), 3.84 (d, 1H, ^2J=14.9 Hz, $ClCH_2$-CO), 2.03 (s, 3H, CH_3CO), 1.36 (d, 3H, $J_{5,6}$=6.2 Hz, H-6/H-6′), 1.29 (d, 3H, $J_{5,6}$=6.2 Hz, H-6/H-6′); δ_C (100 MHz, $CDCl_3$) 170.5 (CH_3CO), 166.3 ($ClCH_2CO$), 165.7, 165.4, 165.3 (3Ph*C*O), 117.9 (OCH_2CH=CH_2), 99.4, 97.4 (2C-1), 40.4 ($ClCH_2CO$), 20.7 (CH_3CO), 17.6, 17.4 (2C-6). Anal. calcd for $C_{40}H_{41}ClO_{14}$: C, 61.50; H, 5.30. Found: C, 61.31; H, 5.42.

3.1.14. Allyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (16). To a solution of **15** (3.20 g, 4.1 mmol) in EtOH (25 mL) CH_2Cl_2 (100 mL) was added thiourea (0.36 g), and the mixture was refluxed for 16 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated. The residue was passed through a silica-gel column with 3:1 petroleum ether–EtOAc as the eluent to give **16** (2.33 g, 81%) as a foamy solid; $[\alpha]_D^{25}$=+52.7 (*c* 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 8.13–7.46 (m, 15H, Ph), 5.92 (m, 1H, OCH_2CH=CH_2), 5.52 (dd, 1H, $J_{2,3}$=3.2 Hz, $J_{3,4}$=9.8 Hz, H-3), 5.48 (dd, 1H, $J_{1',2'}$=1.4 Hz, $J_{2',3'}$=3.3 Hz, H-2′), 5.40 (t, 1H, $J_{3',4'}$=9.8 Hz, $J_{4',5'}$=9.8 Hz, H-4′), 5.33 (m, 1H, OCH_2CH=CH_2), 5.32 (t, 1H, $J_{3,4}$=9.9 Hz, $J_{4,5}$=9.9 Hz, H-4), 5.25 (m, 1H, OCH_2CH=CH_2), 5.07 (d, 1H, $J_{1',2'}$=1.4 Hz, H-1′), 4.95 (d, 1H, $J_{1,2}$=1.6 Hz, H-1), 4.25 (m, 1H, H-5/H-5′), 4.23–4.19 (m, 2H, H-5/H-5′, OCH_2-CH=CH_2), 4.16 (dd, 1H, $J_{1,2}$=1.6 Hz, $J_{2,3}$=3.2 Hz, H-2), 4.09–4.02 (m, 2H, H-3′, OCH_2CH=CH_2), 2.04 (s, 3H, CH_3CO), 1.31 (d, 3H, $J_{5,6}$=6.3 Hz, H-6/H-6′), 1.29 (d, 3H, $J_{5,6}$=6.1 Hz, H-6/H-6′). Anal. calcd for $C_{38}H_{40}O_{13}$: C, 64.76; H, 5.72. Found: C, 64.70; H, 5.45.

3.1.15. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (17). Compounds **12** (3.0 g, 3.3 mmol) and **14** (2.50 g, 3.3 mmol) were coupled under the same conditions as those used for the preparation of **11** from **4** and **10**, giving **17** as a foamy solid (4.32 g, 86%); $[\alpha]_D^{25}$=+126.6 (*c* 1.1, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 8.20–7.20 (m, 40H, Ph), 5.95 (m, 1H, OCH_2CH=CH_2), 5.78 (dd, 1H, $J_{2,3}$=3.3 Hz, $J_{3,4}$=10.1 Hz, H-3), 5.59–5.52 (m, 4H), 5.37–5.23 (m, 4H), 5.15 (s, 1H, H-1), 5.13 (dd, 1H, $J_{3,4}$=9.7 Hz, $J_{4,5}$=9.7 Hz, H-4), 5.08 (dd, $J_{1,2}$=1.0 Hz, $J_{2,3}$=2.9 Hz, H-2), 5.04 (d, $J_{1,2}$=0.8 Hz, H-1), 4.89 (d, $J_{1,2}$=1.0 Hz, H-1), 4.64 (d, $J_{1,2}$=1.0 Hz, H-1), 4.47 (dd, 1H, $J_{2,3}$=3.1 Hz, $J_{3,4}$=9.8 Hz, H-3), 4.24 (m, 1H, OCH_2CH=CH_2), 4.18 (dd, 1H, $J_{2,3}$=3.2 Hz, $J_{3,4}$=9.8 Hz, H-3), 4.10–3.94 (m, 4H), 3.74 (dd, $J_{1,2}$=1.0 Hz, $J_{2,3}$=3.1 Hz, H-2), 3.64 (m, 1H, H-5), 1.86 (s, 3H, CH_3CO), 1.32 (d, 3H, $J_{5,6}$=6.4 Hz, H-6), 1.09 (d, 3H, $J_{5,6}$=6.4 Hz, H-6), 0.94 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 0.70 (d, 3H, $J_{5,6}$=6.3 Hz, H-6); δ_C (100 MHz, $CDCl_3$) 169.7 (CH_3CO), 165.9 (2C), 165.8, 165.6, 165.2, 165.1 (2C), 165.0 (8Ph*C*O), 118.0 (OCH_2CH=CH_2), 100.2, 99.3, 99.0, 96.3 (4C-1), 20.6 (CH_3CO), 17.7, 17.3, 17.2, 16.8 (4C-6). Anal. calcd for $C_{85}H_{80}O_{26}$: C, 67.27; H, 5.31. Found: C, 67.42; H, 5.51.

3.1.16. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (18). To a solution of **17** (455 mg, 0.3 mmol) in anhydrous MeOH (50 mL) was added acetyl chloride (1.0 mL) at 0°C. The solution was stirred at room temperature until TLC (3:1 petroleum ether–EtOAc) showed that the starting material had been consumed. The solution was neutralized with Et_3N, then concentrated to dryness. The residue was passed through a short silica gel column to give **18** (410 g, 93%) as a syrup; $[\alpha]_D^{25}$=+107.3 (*c* 1.1, $CHCl_3$); ν_{max} (KBr) 3443, 1731, 1265, 1101, 1024, 711; δ_H (400 MHz, $CDCl_3$) 8.19–7.21 (m, 40H, Ph), 5.96 (m, 1H, OCH_2CH=CH_2), 5.72 (dd, 1H, $J_{2,3}$=3.1 Hz, $J_{3,4}$=9.9 Hz, H-3), 5.59–5.52 (m, 4H), 5.39 (m, 1H, OCH_2CH=CH_2), 5.31 (dd, 1H, $J_{3,4}$=9.8 Hz, $J_{4,5}$=9.8 Hz, H-4), 5.25 (m, 1H, OCH_2CH=CH_2), 5.20 (d, 1H, $J_{1,2}$=1.0 Hz, H-1), 5.11 (dd, $J_{1,2}$=0.8 Hz, $J_{2,3}$=3.0 Hz, H-2), 5.03 (d, 1H, $J_{1,2}$=0.8 Hz, H-1), 5.00 (d, 1H, $J_{1,2}$=1.1 Hz, H-1), 4.90 (t, 1H, $J_{3,4}$=9.8 Hz, $J_{4,5}$=9.8 Hz, H-4), 4.59 (d, $J_{1,2}$=1.0 Hz, H-1), 4.48 (dd, 1H, $J_{2,3}$=3.4 Hz, $J_{3,4}$=9.8 Hz, H-3), 4.25–3.98 (m, 6H), 3.60–3.54 (m, 3H), 1.32 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 1.10 (d, 6H, $J_{5,6}$=6.1 Hz, H-6), 0.72 (d, 3H, $J_{5,6}$=6.3 Hz, H-6); δ_C (100 MHz, $CDCl_3$) 166.5, 165.9 (2C), 165.8, 165.4 (2C), 165.3, 164.9 (8Ph*C*O), 118.0 (OCH_2CH=CH_2), 100.3, 99.5, 99.2, 96.3 (4C-1), 17.6, 17.4, 17.3, 16.9 (4C-6). Anal. calcd for $C_{83}H_{78}O_{25}$: C, 67.56; H, 5.33. Found: C, 67.44; H, 5.18.

3.1.17. 2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (19). Compound **17** (3.34 g, 2.2 mmol) was deallylated and subsequently converted to the trichloroacetimidate under the same conditions as those used for the preparation of **8** from **5**, giving **19** (2.93 g, 82%) as a foamy solid; $[\alpha]_D$=+116.0 (*c* 1.0, $CHCl_3$); ν_{max} (KBr) 3374, 1740, 1256, 1093, 1035, 716; δ_H (400 MHz, $CDCl_3$) 8.80 (s, 1H, C=NH), 8.19–7.23 (m, 40H, Ph), 6.47 (d, 1H, $J_{1,2}$=1.7 Hz, H-1), 5.77 (dd, 1H, $J_{2,3}$=3.1 Hz, $J_{3,4}$=9.7 Hz, H-3), 5.70 (dd, 1H, $J_{1,2}$=1.5 Hz, $J_{2,3}$=3.3 Hz, H-2), 5.67 (t, 1H, $J_{3,4}$=9.8 Hz, $J_{4,5}$=9.8 Hz, H-4), 5.56–5.51 (m, 3H), 5.34 (t, 1H, $J_{3,4}$=9.6 Hz, $J_{4,5}$=9.6 Hz, H-4), 5.24 (d, 1H, $J_{1,2}$=1.6 Hz, H-1), 5.17–5.13 (m, 3H), 4.93 (d, 1H, $J_{1,2}$=0.8 Hz, H-1), 4.63 (d, 1H, $J_{1,2}$=1.3 Hz, H-1), 4.54 (dd, 1H, $J_{2,3}$=3.4 Hz, $J_{3,4}$=9.9 Hz, H-3), 4.26 (m, 1H, H-5), 4.20 (dd, 1H, $J_{2,3}$=3.4 Hz, $J_{3,4}$=9.5 Hz, H-3), 4.05–4.01 (m, 2H), 3.75 (dd, 1H, $J_{1,2}$=0.8 Hz, $J_{2,3}$=3.3 Hz, H-2), 3.66 (m, 1H, H-5), 1.86 (s, 3H, CH_3CO), 1.37 (d, 3H, $J_{5,6}$=6.2 Hz), 1.12 (d, 3H, $J_{5,6}$=6.3 Hz), 0.97 (d, 3H, $J_{5,6}$=6.3 Hz), 0.74 (d, 3H, $J_{5,6}$=6.3 Hz). Anal. calcd for $C_{84}H_{76}Cl_3NO_{26}$: C, 62.20; H, 4.72. Found: C, 62.29; H, 4.70.

3.1.18. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosy-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (20). Compounds **19** (1.45 g, 0.9 mmol) and **16** (750 mg, 1.05 mmol) were dried together under high vacuum for 2 h, then dissolved in anhydrous CH_2Cl_2 (20 mL). TMSOTf (18 μL, 0.1 mmol) was added dropwise at 0°C under 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 Et_3N, and concentrated to dryness. Purification of the residue by column chromatography (1:1 petroleum ether–EtOAc) gave **20** (1.57 g, 81%) as a foamy solid; $[\alpha]_D^{25}$=+122.8 (*c* 0.6, $CHCl_3$); ν_{max} (KBr) 1736, 1269, 1110, 1024, 712; δ_H (400 MHz, $CDCl_3$) 8.03–7.21 (m, 55H, Ph), 5.60 (m, 1H, OCH_2CH=CH_2), 5.29 (d, 1H, $J_{1,2}$=1.5 Hz, H-1), 5.09 (d, $J_{1,2}$=1.4 Hz, H-1), 4.91 (d, $J_{1,2}$=1.4 Hz, H-1), 4.85 (d, $J_{1,2}$=1.4 Hz, H-1), 4.84 (d, $J_{1,2}$=1.5 Hz, H-1), 4.59 (d, $J_{1,2}$=1.4 Hz, H-1), 2.03 (s, 3H, CH_3CO), 1.86 (s, 3H, CH_3CO), 1.32 (d, 3H, $J_{5,6}$=6.4 Hz, H-6), 1.25 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 1.09 (d, 3H, $J_{5,6}$=6.4 Hz, H-6), 0.87 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 0.71 (d, 3H, $J_{5,6}$=6.4 Hz, H-6), 0.68 (d, 3H, $J_{5,6}$=6.3 Hz, H-6). δ_C (100 MHz, $CDCl_3$) 170.6, 169.8 ($2CH_3CO$), 165.9, 165.8, 165.7, 165.4 (3C), 165.3, 165.2 (2C), 165.0, 163.4 (11Ph*C*O), 117.9 (OCH_2-CH=CH_2), 100.1, 99.6, 99.0 (2C), 98.7, 97.6 (6C-1), 20.7, 20.5 ($2CH_3CO$), 17.6 (2C), 17.3, 17.1, 16.9, 16.8 (6C-6). Anal. calcd for $C_{120}H_{114}O_{38}$: C, 66.60; H, 5.31. Found: C, 66.57; H, 5.02.

3.1.19. 2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosy-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (21). Compound **20** (1.08 g, 0.5 mmol) was deallylated and subsequently converted to the trichloroacetimidate under the same conditions as those used for the preparation of **8** from **5**, giving **21** (840 mg, 74%) as a foamy solid; $[\alpha]_D$=+144.3 (*c* 0.7, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 8.71 (s, 1H, C=NH), 8.03–7.20 (m, 55H, Ph), 6.37 (d, 1H, $J_{1,2}$=0.8 Hz, H-1), 5.73 (dd, 1H, $J_{2,3}$=3.4 Hz, $J_{3,4}$=10.1 Hz, H-3), 5.64 (dd, 1H, $J_{1,2}$=1.0 Hz, $J_{2,3}$=3.1 Hz, H-2), 5.60 (t, 1H, $J_{3,4}$=9.9 Hz, $J_{4,5}$=9.9 Hz, H-4), 5.51–5.54 (m, 4H), 5.40 (dd, 1H, $J_{3,4}$=9.8 Hz, $J_{4,5}$=9.8 Hz, H-4), 5.30 (d, 1H, $J_{1,2}$=1.3 Hz, H-1), 5.20–5.12 (m, 5H), 4.99 (dd, 1H, $J_{1,2}$=1.2 Hz, $J_{2,3}$=2.9 Hz, H-2), 4.86 (d, 1H, $J_{1,2}$=0.8 Hz, H-1), 4.84 (d, 1H, $J_{1,2}$=0.7 Hz, H-1), 4.59 (d, 1H, $J_{1,2}$= 1.0 Hz, H-1), 4.52 (dd, 1H, $J_{2,3}$=3.4 Hz, $J_{3,4}$=9.7 Hz, H-3), 4.37 (dd, 1H, $J_{1,2}$=0.8 Hz, $J_{2,3}$=3.0 Hz, H-2), 4.25–4.21 (m, 3H), 4.07 (dd, 1H, $J_{2,3}$=3.1 Hz, $J_{3,4}$=9.8 Hz, H-3), 4.01–3.97 (m, 2H), 3.71–3.63 (m, 3H), 2.04 (s, 3H, CH_3CO), 1.57 (s, 3H, CH_3CO), 1.38 (d, 3H, $J_{5,6}$=6.2 Hz), 1.36 (d, 3H, $J_{5,6}$=6.2 Hz), 1.08 (d, 3H, $J_{5,6}$=6.1 Hz), 0.89 (d, 3H, $J_{5,6}$=6.2 Hz), 0.72 (d, 3H, $J_{5,6}$=6.2 Hz), 0.70 (d, 3H, $J_{5,6}$=6.3 Hz). Anal. calcd for $C_{119}H_{110}Cl_3NO_{38}$: C, 63.00; H, 4.89. Found: C, 63.21; H, 4.79.

3.1.20. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosy-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (22). Compounds **21** (568 mg, 0.25 mmol) and **14** (250 mg, 0.31 mmol) were coupled under the same conditions as those used for the preparation of **20** from **19** and **16**, giving **22** as a foamy solid (593 mg, 83%); $[\alpha]_D$=+117.8 (*c* 0.5, $CHCl_3$); ν_{max} (KBr) 1740, 1266, 1110, 714; δ_H (400 MHz, $CDCl_3$) 8.10–7.20 (m, 75H, Ph), 5.95 (m, 1H, CH_2=C*H*–CH_2), 5.25 (d, 1H, $J_{1,2}$=0.8 Hz, H-1), 5.08 (d, 1H, $J_{1,2}$=1.0 Hz, H-1), 5.03 (d, 1H, *J*=1.4 Hz, H-1), 4.85 (d, 1H, $J_{1,2}$=1.0 Hz, H-1), 4.84 (s, 2H, H-1), 4.58 (d, 1H, $J_{1,2}$=1.0 Hz, H-1), 4.56 (d, 1H, $J_{1,2}$=0.8 Hz, H-1), 1.84 (s, 6H, CH_3CO), 1.31 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 1.09 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 1.05 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 0.92 (d, 3H, $J_{5,6}$=6.4 Hz, H-6), 0.89 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 0.76 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 0.73 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 0.68 (d, 3H, $J_{5,6}$=6.2 Hz, H-6); δ_C (100 MHz, $CDCl_3$) 169.7, 169.6 ($2CH_3CO$), 118.0 (OCH_2CH=CH_2), 100.3, 100.1, 99.3, 99.1, 99.0, 98.9, 98.7, 96.3 (8C-1), 20.5, 20.4 ($2CH_3CO$), 17.7, 17.6, 17.3, 17.2, 17.1, 16.9, 16.8, 16.7 (8C-6). Anal. calcd for $C_{160}H_{150}O_{50}$: C, 66.89; H, 5.26. Found: C, 66.70; H, 5.17.

3.1.21. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosy-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (23). To a solution of **22** (575 mg, 0.2 mmol) in anhydrous MeOH (100 mL) was added acetyl chloride (4.0 mL) at 0°C. The solution was stirred at room temperature for 24 h. The solution was neutralized with Et_3N, then concentrated to dryness. The residue was passed through a short silica gel column to give **23** (476 g, 85%) as a syrup; $[\alpha]_D^{25}$=+113.4 (*c* 0.5, $CHCl_3$); ν_{max} (KBr) 3441, 1739, 1270, 1112, 712; δ_H (400 MHz, $CDCl_3$) 5.94 (m, 1H, CH_2=C*H*–CH_2), 5.12 (d, 1H, $J_{1,2}$=0.9 Hz, H-1), 5.04 (s, 2H, H-1), 4.99 (d, 2H, H-1), 4.83 (d, 1H, $J_{1,2}$=0.9 Hz, H-1), 4.55 (s, 2H, H-1), 1.32 (d, 3H, $J_{5,6}$=6.4 Hz, H-6), 1.13 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 1.09 (d, 6H, $J_{5,6}$=6.3 Hz, 2H-6), 0.86 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 0.78 (d, 6H, $J_{5,6}$=6.4 Hz, 2H-6), 0.73 (d, 3H, $J_{5,6}$=6.2 Hz, H-6). δ_C (100 MHz, $CDCl_3$) 118.0 (OCH_2CH=CH_2), 100.2, 100.1, 99.5, 99.3, 99.2, 98.8, 98.7, 96.3 (8C-1), 17.7, 17.5, 17.4, 17.3 (2C), 16.9 (2C), 16.8 (8C-6). Anal. calcd for $C_{156}H_{146}O_{48}$: C, 67.18; H, 5.28. Found: C, 67.32; H, 5.40.

3.1.22. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→3)-]4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosy-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→3)-]4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (25). Compounds **23**

(420 mg, 0.15 mmol) and 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate (**24**) (250 mg, 0.4 mmol) and were dried together under high vacuum for 2 h, then dissolved in anhydrous CH_2Cl_2 (10 mL). TMSOTf (3 μL, 0.02 mmol) was added at −25°C under 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 Et_3N, and concentrated to dryness. Purification of the residue on a silica gel column with 1:1 petroleum ether–EtOAc as the eluent, furnished **25** (208 mg, 38%) as a syrup; $[\alpha]_D$=+102.2 (*c* 0.5, $CHCl_3$); ν_{max} (KBr) 3440, 1733, 1274, 1108, 710; δ_H (400 MHz, $CDCl_3$) 8.07–7.02 (m, 83H, Ph), 5.86 (m, 1H, CH_2=C*H*–CH_2), 5.76 (dd, 1H, $J_{2,3}$=3.2 Hz, $J_{3,4}$=9.9 Hz, H-3), 5.56–5.50 (m, 2H), 5.47 (dd, 1H, $J_{1,2}$=1.2 Hz, $J_{2,3}$=3.1 Hz, H-2), 5.43–5.35 (m, 6H), 5.28–5.15 (m, 6H), 5.09–5.05 (m, 6H), 5.02 (dd, 1H, $J_{1,2}$=1.4 Hz, $J_{2,3}$=3.2 Hz, H-2), 4.97 (dd, 1H, $J_{1,2}$=1.6 Hz, $J_{2,3}$=3.0 Hz, H-2), 4.94 (d, 1H, $J_{1,2}$=1.5 Hz, H-1), 4.85–4.70 (m, 5H), 4.61 (dd, 1H, $J_{1,2}$=1.0 Hz, $J_{2,3}$=2.8 Hz, H-2), 4.36 (dd, 1H, $J_{2,3}$=3.4 Hz, $J_{3,4}$=9.8 Hz, H-3), 4.19–4.12 (m, 3H), 4.05–3.94 (m, 9H), 3.87–3.83 (m, 4H), 3.77–3.62 (m, 4H), 3.52–3.26 (m, 5H), 1.89 (s, 3H, C*H*$_3$CO), 1.88 (s, 3H, C*H*$_3$CO), 1.65 (s, 6H, C*H*$_3$CO), 1.45 (s, 3H, C*H*$_3$CO), 1.44 (s, 3H, C*H*$_3$CO), 1.25 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 1.17 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 0.99 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 0.71 (d, 3H, $J_{5,6}$=6.4 Hz, H-6), 0.67 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 0.62 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 0.47 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 0.40 (d, 3H, $J_{5,6}$=6.4 Hz, H-6); δ_C (100 MHz, $CDCl_3$) 170.5, 170.4, 170.2, 170.1, 169.0, 168.9 (6CH_3*C*O), 117. 9, (*C*H_2=CH–CH_2), 100.3, 100.2, 99.4, 99.3, 99.0, 98.8, 98.5, 98.4, 96.2, 96.0 (10C-1), 20.6, 20.5, 20.4, 20.0, 19.9, 19.1 (6*C*H_3CO), 17.6, 17.3, 17.2, 17.0 (2C), 16.9, 16.7, 16.6 (8C-6). Anal. calcd for $C_{196}H_{184}N_2O_{66}$: C, 64.96; H, 5.12. Found: C, 65.03; H, 5.10.

3.1.23. Propyl α-L-rhamnopyranosyl-(1→2)-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-]α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosy-(1→3)-α-L-rhamnopyranosyl-(1→2)-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-]α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranoside (26) (I+II). Decasaccharide **25** (180 mg, 0.05 mmol) was dissolved in EtOH (36 mL). Hydrazine hydrate (100%, 4 mL) was added, and the solution was refluxed for 48 h. The solution was then concentrated and co-evaporated several times with toluene. The residue was taken up in pyridine (20 mL), and acetic anhydride (15 mL) was added. The solution was allowed to stand for 12 h at room temperature and then evaporated to dryness. Purification of the residue by flash column chromatography (EtOAc) gave a foamy solid intermediate, which was taken up in a saturated solution of ammonia in MeOH (30 mL). After 96 h at room temperature, the reaction mixture was concentrated and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **26** as a foamy solid (52 mg, 64%); $[\alpha]_D$=−14.2 (*c* 0.2, H_2O); δ_H (400 MHz, D_2O) 5.22 (d, 1H, $J_{1,2}$=1.1 Hz, H-1), 5.16 (s, 2H, 2H-1), 5.13 (d, 1H, $J_{1,2}$=1.4 Hz, H-1), 5.06 (m, 3H, 3H-1), 4.83 (d, 1H, $J_{1,2}$=1.5 Hz, H-1), 4.74 (d, 1H, $J_{1,2}$=7.6 Hz, H-1), 4.70 (d, 1H, $J_{1,2}$=8.1 Hz, H-1), 2.03 (s, 3H, C*H*$_3$CONH), 1.98 (s, 3H, C*H*$_3$CONH), 1.61 (m, 2H, $OCH_2CH_2CH_2CH_3$), 1.37 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 1.29–1.19 (m, 12H, 4H-6), 1.15–1.12 (m, 6H, 2H-6), 1.08 (d, 3H, $J_{5,6}$=6.4 Hz, H-6), 0.83 (t, 3H, *J*=7.3 Hz, $OCH_2CH_2CH_3$). MALDI-TOF MS calcd for $C_{67}H_{114}N_2O_{43}$: 1635.6 [M^+]. Found: 1658.6 [M+Na^+].

3.1.24. Methyl 3-*O*-acetyl-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (28). Condensation of methyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**27**) (1.98 g, 5.0 mmol) and **9** (2.80 g, 5.0 mmol) under the same conditions as those used for the preparation of **11** from **4** and **10**, gave **28** as a foamy solid (3.12 g, 80%); $[\alpha]_D^{25}$=+114.7 (*c* 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 8.22–7.36 (m, 20H, Ph), 5.54 (dd, 1H, $J_{3',4'}$=9.9 Hz, $J_{4',5'}$=9.9 Hz, H-4′), 5.59 (dd, 1H, $J_{1',2'}$=1.2 Hz, $J_{2',3'}$=3.1 Hz, H-2′), 5.84 (dd, 1H, $J_{2',3'}$=3.1 Hz, $J_{3',4'}$=9.9 Hz, H-3′), 5.43 (dd, 1H, $J_{3,4}$=9.8 Hz, $J_{4,5}$=9.8 Hz, H-4), 5.14 (dd, $J_{1,2}$=1.5 Hz, $J_{2,3}$=3.2 Hz, H-2), 5.11 (d, 1H, $J_{1',2'}$=1.2 Hz, H-1′), 4.89 (d, 1H, $J_{1,2}$=1.5 Hz, H-1), 4.43 (dd, 1H, $J_{2,3}$=3.2 Hz, $J_{3,4}$=9.8 Hz, H-3), 4.07–4.00 (m, 2H, H-5, H-5′), 3.45 (s, 3H, OC*H*$_3$), 1.70 (s, 3H, C*H*$_3$CO), 1.34 (d, 3H, $J_{5',6'}$=6.3 Hz, H-6′), 1.17 (d, 3H, $J_{5,6}$=6.4 Hz, H-6); δ_C (100 MHz, $CDCl_3$) 169.1 (CH_3*C*O), 166.1, 165.6, 165.4, 164.9 (4Ph*C*O), 99.3, 98.3 (2C-1), 20.3 (*C*H_3CO), 17.6, 17.3 (2C-6). Anal. calcd for $C_{43}H_{42}O_{14}$: C, 65.98; H, 5.41. Found: C, 65.80; H, 5.13.

3.1.25. Methyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (29). Compound **28** (2.90 g, 3.7 mmol) was deacetylated under the same conditions as those used for the preparation of **7** from **6**, giving **29** (2.40 g, 88%) as a foamy solid; $[\alpha]_D^{25}$=+93.2 (*c* 0.5, $CHCl_3$); ν_{max} (KBr) 3440, 1723, 1261, 1070, 977, 712; δ_H (400 MHz, $CDCl_3$) 8.20–7.39 (m, 20H, Ph), 5.60 (dd, 1H, $J_{3',4'}$=9.7 Hz, $J_{4',5'}$=9.7 Hz, H-4′), 5.50 (dd, 1H, $J_{1',2'}$=0.8 Hz, $J_{2',3'}$=3.0 Hz, H-2′), 5.17 (d, 1H, $J_{1',2'}$=0.8 Hz, H-1′), 5.08 (dd, 1H, $J_{3,4}$=9.8 Hz, $J_{4,5}$=9.8 Hz, H-4), 5.00 (dd, $J_{1,2}$=1.0 Hz, $J_{2,3}$=3.1 Hz, H-2), 4.90 (d, 1H, $J_{1,2}$=1.0 Hz, H-1), 4.44 (dd, 1H, $J_{2,3}$=3.1 Hz, $J_{3,4}$=9.8 Hz, H-3), 4.07–3.98 (m, 3H, H-3′, H-5, H-5′), 3.47 (s, 3H, OC*H*$_3$), 1.34 (d, 3H, $J_{5',6'}$=6.2 Hz, H-6′), 1.13 (d, 3H, $J_{5,6}$=6.4 Hz, H-6); δ_C (100 MHz, $CDCl_3$) 166.7, 165.9, 165.0, 164.9 (4Ph*C*O), 98.8, 98.4 (2C-1), 17.5, 17.2 (2C-6). Anal. calcd for $C_{41}H_{40}O_{13}$: C, 66.48; H, 5.44. Found: C, 66.76; H, 5.40.

3.1.26. 3,4-Di-*O*-benzoyl-2-*O*-chloroacetyl-α-L-rhamnopyranosyl trichloroacetimidate (31). Allyl 3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**30**) (2.06 g, 5 mmol) was dissolved in dry CH_2Cl_2 (20 mL) containing pyridine (4.0 mL, 50 mmol). Under N_2 protection, chloroacetyl chloride (0.7 mL, 11 mmol) in anhydrous CH_2Cl_2 (10 mL) was added dropwise to the solution over 30 min at 0°C. The reaction mixture was stirred for 2 h at room temperature, at the end of which time TLC (4:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with water, 1 M HCl, and dried (Na_2SO_4). The solution was concentrated, and purification of the residue by flash column chromatography on silica gel (4:1 petroleum ether–EtOAc) gave allyl 3,4-di-*O*-benzoyl-2-*O*-chloroacetyl-α-L-rhamnopyranoside as a colorless syrup, which was deallylated and converted to the trichloroacetimidate under the same

conditions as those used for the preparation of **8** from **5**, giving **31** (2.18 g, 73% for 3 steps) as a foamy solid; $[\alpha]_D^{25}$=+20.2 (*c* 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 8.84 (s, 1H, CN*H*CCl_3), 8.14–7.25 (m, 10H, Ph), 6.60 (d, 1H, $J_{1,2}$=1.5 Hz, H-1), 5.83 (dd, 1H, $J_{1,2}$=1.5 Hz, $J_{2,3}$=3.0 Hz, H-2), 5.67 (dd, 1H, $J_{2,3}$=3.0 Hz, $J_{3,4}$=9.7 Hz, H-3), 5.90 (dd, 1H, $J_{3,4}$=9.7 Hz, $J_{4,5}$=9.7 Hz, H-4), 4.30 (m, 1H, H-5), 3.86 (q, 2H, *J*=14.1 Hz, ClCH_2CO), 1.44 (d, 3H, $J_{5,6}$=6.2 Hz, H-6). Anal. calcd for $C_{24}H_{21}Cl_4NO_8$: C, 48.59; H, 3.57. Found: C, 48.43; H, 3.44.

3.1.27. Allyl 3,4-di-*O*-benzoyl-2-*O*-chloroacetyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (32). Compounds **4** (1.75 g, 5.0 mmol) and **31** (2.97 g, 5.0 mmol) were coupled under the same conditions as those used for the preparation of **11** from **4** and **10**, giving **32** as a foamy solid (3.41 g, 87%); $[\alpha]_D^{25}$=+50.5 (*c* 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 8.04–7.35 (m, 15H, Ph), 5.95 (m, 1H, CH_2=C*H*CH_2O), 5.84 (dd, 1H, $J_{2',3'}$= 3.3 Hz, $J_{3',4'}$=9.8 Hz, H-3′), 5.59 (dd, 1H, $J_{1',2'}$=1.1 Hz, $J_{2',3'}$=3.3 Hz, H-2′), 5.54 (dd, 1H, $J_{3',4'}$=9.8 Hz, $J_{4',5'}$= 9.8 Hz, H-4′), 5.51 (dd, 1H, $J_{2,3}$=3.2 Hz, $J_{3,4}$=9.8 Hz, H-3), 5.43 (dd, 1H, $J_{3,4}$=9.8 Hz, $J_{4,5}$=9.8 Hz, H-4), 5.38–5.25 (m, 2H, CH_2=CHCH_2O), 5.02 (d, 1H, $J_{1',2'}$=1.1 Hz, H-1′), 4.95 (d, 1H, $J_{1,2}$=1.1 Hz, H-1), 4.27–4.22 (m, 2H, H-5, CH_2=CH–CH_2O), 4.18 (s, 2H, ClCH_2CO), 4.16 (dd, $J_{1,2}$=1.1 Hz, $J_{2,3}$=3.2 Hz, H-2), 4.10–4.03 (m, 2H, H-5, CH_2=CH–CH_2O), 2.00 (s, 3H, CH_3CO), 1.35 (d, 3H, $J_{5',6'}$=6.4 Hz, H-6′), 1.27 (d, 3H, $J_{5,6}$=6.4 Hz, H-6); δ_C (100 MHz, $CDCl_3$) 170.4 (CH_3CO), 166.3 ($ClCH_2CO$), 165.7, 165.4, 165.1 (3Ph*C*O), 117.8 (OCH_2CH=CH_2), 98.9, 97.5 (2C-1), 40.4 ($ClCH_2CO$), 20.6 (CH_3CO), 17.5, 17.3 (2C-6). Anal. calcd for $C_{40}H_{41}ClO_{14}$: C, 61.50; H, 5.30. Found: C, 61.58; H, 5.09.

3.1.28. Allyl 3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (33). Compound **32** (3.90 g, 5 mmol) was deprotected under the same conditions as those used for the preparation of **16** from **15**, giving **33** as a foamy solid (2.80 g, 80%); $[\alpha]_D^{25}$=19.6 (*c* 1.0, $CHCl_3$); ν_{max} (KBr) 3446, 1727, 1274, 1110, 1072, 1026, 713; δ_H (400 MHz, $CDCl_3$) 8.03–7.37 (m, 15H, Ph), 5.94 (m, 1H, CH_2=C*H*–CH_2), 5.68 (dd, 1H, $J_{2',3'}$=3.2 Hz, $J_{3',4'}$=9.8 Hz, H-3′), 5.59 (dd, 1H, $J_{3',4'}$= 9.8 Hz, $J_{4',5'}$=9.8 Hz, H-4′), 5.54 (dd, 1H, $J_{2,3}$=3.4 Hz, $J_{3,4}$=9.9 Hz, H-3), 5.41 (dd, 1H, $J_{3,4}$=9.9 Hz, $J_{4,5}$=9.9 Hz, H-4), 5.37–5.25 (m, 2H, CH_2=CH–CH_2), 5.07 (d, 1H, $J_{1',2'}$=1.6 Hz, H-1′), 4.96 (d, 1H, $J_{1,2}$=1.7 Hz, H-1), 4.47 (dd, 1H, $J_{1',2'}$=1.6 Hz, $J_{2',3'}$=3.2 Hz, H-2′), 4.27 (m, 1H, CH_2=CH–CH_2O), 4.20–4.16 (m, 2H, H-2, H-5′), 4.09–4.01 (m, 2H, H-5, CH_2=CH–CH_2O), 1.95 (s, 3H, CH_3CO), 1.34 (d, 3H, $J_{5',6'}$=6.3 Hz, H-6′), 1.27 (d, 3H, $J_{5,6}$=6.4 Hz, H-6); δ_C (100 MHz, $CDCl_3$) 170.0 (CH_3CO), 165.8, 165.5, 165.3 (3Ph*C*O), 117.7 (OCH_2CH=CH_2), 101.3, 97.7 (2C-1), 20.6 (CH_3CO), 17.5, 17.4 (2C-6). Anal. calcd for $C_{38}H_{40}O_{13}$: C, 64.76; H, 5.72. Found: C, 64.53; H, 5.60.

3.1.29. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosy-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (34). Compounds **19** (1.45 g, 0.9 mmol) and **33** (750 mg, 1.05 mmol) were coupled under the same conditions as those used for the preparation of **20** from **16** and **19**, giving **34** (1.71 g, 88%) as a foamy solid; $[\alpha]_D^{25}$=+112.6 (*c* 1.0, $CHCl_3$); ν_{max} (KBr) 1733, 1270, 1039, 712; δ_H (400 MHz, $CDCl_3$) 8.11–7.23 (m, 55H, Ph), 5.95 (m, 1H, OCH_2CH=CH_2), 5.82 (dd, 1H, $J_{2,3}$=3.1 Hz, $J_{3,4}$=9.8 Hz, H-3), 5.75 (dd, 1H, $J_{2,3}$=3.3 Hz, $J_{3,4}$=9.9 Hz, H-3), 5.67 (dd, 1H, $J_{1,2}$=1.3 Hz, $J_{2,3}$=3.2 Hz, H-2), 5.29 (d, 1H, $J_{1,2}$=1.4 Hz, H-1), 5.19 (d, $J_{1,2}$=1.5 Hz, H-1), 5.14 (d, $J_{1,2}$=1.6 Hz, H-1), 4.94 (d, $J_{1,2}$=1.2 Hz, H-1), 4.92 (d, $J_{1,2}$=1.5 Hz, H-1), 4.62 (d, $J_{1,2}$=1.4 Hz, H-1), 4.59 (dd, 1H, $J_{2,3}$=3.1 Hz, $J_{3,4}$=9.7 Hz, H-3), 4.44 (dd, 1H, $J_{1,2}$=1.5 Hz, $J_{2,3}$=3.1 Hz, H-2), 1.93 (s, 3H, CH_3CO), 1.86 (s, 3H, CH_3CO), 1.35 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 1.33 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 1.29 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 1.12 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 0.94 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 0.73 (d, 3H, $J_{5,6}$=6.4 Hz, H-6); δ_C (100 MHz, $CDCl_3$) 170.1, 169.6 ($2CH_3CO$), 165.9, 165.8, 165.5, 165.4 (3C), 165.3, 165.2, 165.1, 165.0, 164.9 (11Ph*C*O), 117.9 (CH_2=CH–CH_2O), 100.6, 100.2, 99.6, 99.1, 99.0, 97.6 (6C-1), 20.7, 20.5 ($2CH_3CO$), 17.5 (3C), 17.3, 17.2, 16.9 (6C-6). Anal. calcd for $C_{120}H_{114}O_{38}$: C, 66.60; H, 5.31. Found: C, 66.74; H, 5.13.

3.1.30. 2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosy-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (35). Compound **34** (1.08 g, 0.5 mmol) was deallylated and converted to the trichloroacetimidate under the same conditions as those used for the preparation of **8** from **5**, giving **35** (861 mg, 76%) as a foamy solid; $[\alpha]_D$=+94.3 (*c* 0.7, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 8.73 (s, 1H, C=NH), 8.03–7.22 (m, 55H, Ph), 6.36 (s, 1H, $J_{1,2}$=0.8 Hz, H-1), 5.81 (dd, 1H, $J_{2,3}$=3.1 Hz, $J_{3,4}$=9.7 Hz, H-3), 5.76 (dd, 1H, $J_{2,3}$=3.2 Hz, $J_{3,4}$=10.1 Hz, H-3), 5.68 (dd, 1H, $J_{1,2}$=0.9 Hz, $J_{2,3}$=3.2 Hz, H-2), 5.60 (t, 1H, $J_{3,4}$=10.4 Hz, $J_{4,5}$=10.4 Hz, H-4), 5.53 (t, 1H, $J_{3,4}$=10.0 Hz, $J_{4,5}$=10.0 Hz, H-4), 5.52–5.48 (m, 4H), 5.34 (t, 1H, $J_{3,4}$=9.7 Hz, $J_{4,5}$=9.7 Hz, H-4), 5.28 (s, 1H, $J_{1,2}$=1.5 Hz, H-1), 5.22 (s, 1H, $J_{1,2}$=1.2 Hz, H-1), 5.20 (s, 1H, $J_{1,2}$=1.4 Hz, H-1), 5.17–5.13 (m, 3H), 4.92 (s, 1H, $J_{1,2}$=1.3 Hz, H-1), 4.62 (s, 1H, $J_{1,2}$=1.3 Hz, H-1), 4.60 (dd, 1H, $J_{2,3}$=3.0 Hz, $J_{3,4}$=9.9 Hz, H-3), 4.47–4.44 (m, 2H), 4.27–4.03 (m, 6H), 3.76–3.70 (m, 2H), 1.95 (s, 3H, CH_3CO), 1.86 (s, 3H, CH_3CO), 1.40–1.37 (t, 6H, $J_{5,6}$=6.1 Hz, 2H-6), 1.29 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 1.11 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 0.94 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 0.75 (d, 3H, $J_{5,6}$=6.2 Hz, H-6). Anal. calcd for $C_{119}H_{110}Cl_3NO_{38}$: C, 63.00; H, 4.89. Found: C, 63.12; H, 5.01.

3.1.31. Methyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*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→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (36). Compounds **35** (600 mg, 0.26 mmol) and **29** (300 mg, 0.40 mmol) were

coupled under the same conditions as those used for the preparation of **20** from **19** and **16**, giving **36** as a foamy solid (640 mg, 85%); $[\alpha]_D^{25}$=+91.0 (*c* 0.5, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) δ 8.10–7.24 (m, 75H, Ph), 5.75 (dd, 1H, $J_{2,3}$= 3.4 Hz, $J_{3,4}$=10.2 Hz, H-3), 5.66 (dd, 1H, $J_{2,3}$=3.2 Hz, $J_{3,4}$=9.9 Hz, H-3), 5.61 (dd, 1H, $J_{1,2}$=1.6 Hz, $J_{2,3}$=3.2 Hz, H-2), 5.57–5.48 (m, 5H), 5.43 (dd, 1H, $J_{3,4}$=9.8 Hz, $J_{4,5}$=9.8 Hz, H-4), 5.34 (dd, 1H, $J_{3,4}$=9.7 Hz, $J_{4,5}$= 9.7 Hz, H-4), 5.30 (dd, 1H, $J_{3,4}$=9.7 Hz, $J_{4,5}$=9.7 Hz, H-4), 5.28 (d, 1H, $J_{1,2}$=1.3 Hz, H-1), 5.21 (d, 1H, $J_{1,2}$=1.6 Hz, H-1), 5.17–5.05 (m, 7H), 4.91 (d, 1H, $J_{1,2}$=1.2 Hz, H-1), 4.89 (d, 1H, $J_{1,2}$=1.5 Hz, H-1), 4.82 (s, 2H, 2H-1), 4.62 (d, 1H, $J_{1,2}$=1.4 Hz, H-1), 4.50 (dd, 1H, $J_{2,3}$=3.3 Hz, $J_{3,4}$=9.9 Hz, H-3), 4.45 (dd, 1H, $J_{2,3}$=3.2 Hz, $J_{3,4}$=9.8 Hz, H-3), 4.28 (dd, 1H, $J_{1,2}$=1.8 Hz, $J_{2,3}$=3.2 Hz, H-2), 4.22–4.18 (m, 2H), 4.07–3.86 (m, 6H), 3.79 (dd, 1H, $J_{1,2}$=1.5 Hz, $J_{2,3}$=3.0 Hz, H-2), 3.75 (dd, 1H, $J_{1,2}$=1.0 Hz, $J_{2,3}$=2.9 Hz, H-2), 3.72–3.62 (m, 2H), 3.45 (s, 3H, OCH_3), 1.86 (s, 3H, CH_3CO), 1.75 (s, 3H, CH_3CO), 1.35 (d, 3H, $J_{5,6}$=6.4 Hz, H-6), 1.15 (d, 3H, $J_{5,6}$=6.4 Hz, H-6), 1.12 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 1.09 (d, 3H, $J_{5,6}$=6.4 Hz, H-6), 0.93 (d, 3H, $J_{5,6}$=6.4 Hz, H-6), 0.88 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 0.75 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 0.69 (d, 3H, $J_{5,6}$=6.2 Hz, H-6); δ_C (100 MHz, $CDCl_3$) 170.0, 169.8 ($2CH_3CO$), 117.8 (CH_2=CH–CH_2), 100.3, 100.2, 100.1, 99.3, 99.2, 99.0, 98.2, 91.9 (8C-1), 20.6, 20.6 (2 CH_3CO), 17.7, 17.4, 17.4, 17.3, 17.2, 17.1, 16.9, 16.7 (8C-6). Anal. calcd for $C_{158}H_{148}O_{50}$: C, 66.66; H, 5.24. Found: C, 66.48; H, 5.12.

3.1.32. Methyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosy-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (37). To a solution of **36** (570 mg, 0.2 mmol) in anhydrous MeOH (100 mL) was added acetyl chloride (4.0 mL) at 0°C. The solution was stirred at room temperature for 24 h. The solution was neutralized with Et_3N, then concentrated to dryness. The residue was passed through a short silica gel column to give **37** (510 g, 92%) as a syrup; $[\alpha]_D^{25}$=+117.6 (*c* 1.0, $CHCl_3$); ν_{max} (KBr) 3442, 1740, 1268, 1070, 714; δ_H (400 MHz, $CDCl_3$) 8.11–7.21 (m, 75H, Ph), 5.72 (dd, 1H, $J_{2,3}$=3.1 Hz, $J_{3,4}$=9.7 Hz, H-3), 5.69–5.66 (m, 2H, H-2, H-3), 5.57 (dd, 1H, $J_{1,2}$=1.4 Hz, $J_{2,3}$=3.3 Hz, H-2), 5.55 (dd, 1H, $J_{3,4}$=9.8 Hz, $J_{4,5}$=9.8 Hz, H-4), 5.52 (dd, 1H, $J_{3,4}$=9.8 Hz, $J_{4,5}$=9.8 Hz, H-4), 5.51 (dd, 1H, $J_{1,2}$=1.0 Hz, $J_{2,3}$=3.1 Hz, H-2), 5.49 (dd, 1H, $J_{3,4}$=9.7 Hz, $J_{4,5}$=9.7 Hz, H-4), 5.44 (dd, 1H, $J_{3,4}$=9.8 Hz, $J_{4,5}$=9.8 Hz, H-4), 5.36 (dd, 1H, $J_{3,4}$=9.8 Hz, $J_{4,5}$=9.8 Hz, H-4), 5.29 (dd, 1H, $J_{3,4}$=9.8 Hz, $J_{4,5}$=9.8 Hz, H-4), 5.25 (d, 1H, $J_{1,2}$=1.5 Hz, H-1), 5.17 (dd, 1H, $J_{1,2}$=1.5 Hz, $J_{2,3}$= 3.2 Hz, H-2), 5.10 (dd, 1H, $J_{1,2}$=1.3 Hz, $J_{2,3}$=3.0 Hz, H-2), 5.09 (d, 1H, $J_{1,2}$=1.0 Hz, H-1), 5.06 (d, 1H, $J_{1,2}$=1.0 Hz, H-1), 4.93 (dd, 1H, $J_{3,4}$=9.7 Hz, $J_{4,5}$=9.7 Hz, H-4), 4.88 (d, 1H, $J_{1,2}$=1.5 Hz, H-1), 4.86 (d, 1H, $J_{1,2}$=1.4 Hz, H-1), 4.81 (dd, 1H, $J_{3,4}$=9.0 Hz, $J_{4,5}$=9.0 Hz, H-4), 4.55 (d, 1H, $J_{1,2}$=1.3 Hz, H-1), 4.51 (dd, 1H, $J_{2,3}$=3.3 Hz, $J_{3,4}$=9.9 Hz, H-3), 4.51 (dd, 1H, $J_{2,3}$=3.4 Hz, $J_{3,4}$=9.8 Hz, H-3), 4.30 (dd, 1H, $J_{1,2}$=1.3 Hz, $J_{2,3}$=3.3 Hz, H-2), 3.45 (s, 3H, OCH_3), 1.34 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 1.19 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 1.14 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 1.12 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 1.09 (d, 3H, $J_{5,6}$=6.4 Hz, H-6), 0.97 (d, 3H, $J_{5,6}$=6.4 Hz, H-6), 0.76 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 0.69 (d, 3H, $J_{5,6}$=6.4 Hz, H-6). δ_C (100 MHz, $CDCl_3$) 166.9, 166.6, 166.1, 166.0, 165.9, 165.8, 165.6, 165.5 (3C), 165.4, 165.3 (3C), 165.0 (15Ph*C*O), 100.9, 100.6, 100.3, 99.6, 99.3, 99.1, 99.0, 98.3 (8C-1), 17.8, 17.6, 17.4 (3C), 17.3, 17.0, 16.8 (8C-6). Anal. calcd for $C_{154}H_{144}O_{48}$: C, 66.94; H, 5.25. Found: C, 66.73; H, 5.44.

3.1.33. Methyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→3)-]4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosy-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→3)-]4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (38). Compounds **37** (497 mg, 0.18 mmol) and 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate (**24**) (300 mg, 0.5 mmol) were coupled under the same conditions as those used for the preparation of **25** from **23** and **24**, giving **38** (223 mg, 35%) as a syrup; $[\alpha]_D$=+102.2 (*c* 0.5, $CHCl_3$); ν_{max} (KBr) 1728, 1265, 1109, 712; δ_H (400 MHz, $CDCl_3$) 8.12–7.24 (m, 83H, Ph), 5.80 (dd, 1H, $J_{2,3}$=3.0 Hz, $J_{3,4}$=9.8 Hz, H-3), 5.72 (dd, 1H, $J_{1,2}$=1.4 Hz, $J_{2,3}$=2.8 Hz, H-2), 5.65 (dd, 1H, $J_{2,3}$=2.9 Hz, $J_{3,4}$=9.6 Hz, H-3), 5.60–5.46 (m, 7H), 5.39 (dd, 1H, $J_{3,4}$=9.7 Hz, $J_{4,5}$=9.7 Hz, H-4), 5.32 (dd, 1H, $J_{3,4}$=9.8 Hz, $J_{4,5}$= 9.8 Hz, H-4), 5.29–4.70 (m, 17H), 4.57 (dd, 1H, $J_{1,2}$=1.5 Hz, $J_{2,3}$=3.0 Hz, H-2), 4.41 (dd, 1H, $J_{1,2}$= 1.5 Hz, $J_{2,3}$=3.1 Hz, H-2), 4.30–3.49 (m, 21H), 3.43 (s, 3H, OCH_3), 334–3.25 (m, 2H), 1.96 (s, 3H, CH_3CO), 1.93 (s, 3H, CH_3CO), 1.89 (s, 6H, $2CH_3CO$), 1.72 (s, 3H, CH_3CO), 1.55 (s, 3H, CH_3CO), 1.39 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 1.31 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 1.11 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 1.05 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 0.72 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 0.69 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 0.59 (d, 3H, $J_{5,6}$=6.3 Hz, H-6), 0.55 (d, 3H, $J_{5,6}$=6.4 Hz, H-6); δ_C (100 MHz, $CDCl_3$) 170.5, 170.3, 170.1, 169.8, 169.0, 168.9 ($6CH_3CO$), 100.1, 99.9, 99.6, 99.3, 99.3, 99.2, 99.2, 98.6, 98.1, 98.1 (10C-1), 20.6, 20.5, 20.3, 20.2, 19.9, 19.0 (6 CH_3CO), 18.0, 17.6, 17.4, 17.2, 17.1, 16.9, 16.7, 16.6 (8C-6). Anal. calcd for $C_{194}H_{182}N_2O_{66}$: C, 64.77; H, 5.10. Found: C, 64.99; H, 5.41.

3.1.34. Methyl α-L-rhamnopyranosyl-(1→2)-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-]α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosy-(1→2)-α-L-rhamnopyranosyl-(1→2)-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-]α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranoside (39) (II+I). Decasaccharide **38** (215 mg, 0.06 mmol) was dissolved in EtOH (36 mL). Hydrazine hydrate (100%, 4 mL) was added, and the solution was refluxed for 48 h. The solution was then concentrated and co-evaporated several times with toluene. The residue was taken up in pyridine (20 mL), and acetic anhydride (15 mL) was added. The solution was allowed to stand for 12 h at room temperature and then evaporated to dryness. Purification of the residue by flash column chromatography (EtOAc) gave a foamy solid intermediate,

which was taken up in a saturated solution of ammonia in MeOH (30 mL). After 96 h at room temperature, the reaction mixture was concentrated and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **39** as a foamy solid (57 mg, 59%); $[\alpha]_D=-17.3$ (*c* 0.2, H_2O); δ_H (400 MHz, D_2O) 5.18–5.15 (m, 3H, 3H-1), 5.09 (d, 1H, $J_{1,2}=1.4$ Hz, H-1), 5.03–5.01 (m, 3H, 3H-1), 4.84 (d, 1H, $J_{1,2}=1.1$ Hz, H-1), 4.77 (d, 1H, $J_{1,2}=8.0$ Hz, H-1), 4.75 (d, 1H, $J_{1,2}=8.1$ Hz, H-1), 3.39 (s, 3H, OCH_3), 1.97 (s, 3H, CH_3CONH), 1.90 (s, 3H, CH_3CONH), 1.26 (d, 3H, $J_{5,6}=6.2$ Hz, H-6), 1.29–1.14 (m, 18H, 6H-6), 1.10 (d, 3H, $J_{5,6}=6.4$ Hz, H-6). MALDI-TOF MS calcd for $C_{65}H_{110}N_2O_{43}$: 1607.5 [M^+]. Found: 1630.7 [M+Na^+].

3.1.35. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (40). Compounds **12** (912 mg, 1.0 mmol) and **16** (704 mg, 1.0 mmol) were coupled under the same conditions as those used for the preparation of **20** from **16** and **19**, giving **40** as a foamy solid (1.21 g, 83%); $[\alpha]_D^{25}=+103.5$ (*c* 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 8.20–7.23 (m, 35H, Ph), 5.94 (m, 1H, $OCH_2CH{=}CH_2$), 5.22 (d, $J_{1,2}=1.0$ Hz, H-1), 5.13 (d, $J_{1,2}=0.9$ Hz, H-1), 4.95 (d, $J_{1,2}=1.0$ Hz, H-1), 4.74 (d, $J_{1,2}=0.8$ Hz, H-1), 2.04 (s, 3H, CH_3CO), 1.90 (s, 3H, CH_3CO), 1.32 (d, 3H, $J_{5,6}=6.2$ Hz, H-6), 1.30 (d, 3H, $J_{5,6}=6.3$ Hz, H-6), 1.26 (d, 3H, $J_{5,6}=6.2$ Hz, H-6), 1.11 (d, 3H, $J_{5,6}=6.4$ Hz, H-6); δ_C (100 MHz, $CDCl_3$) 170.5, 169.9 ($2CH_3CO$), 165.9, 165.8, 165.6, 165.4, 165.3, 165.2, 165.1 (7Ph*C*O), 118.0 ($OCH_2CH{=}CH_2$), 100.2, 99.5, 99.2, 97.6 (4C-1), 20.6, 20.5 ($2CH_3CO$) 17.6, 17.5, 17.4, 17.3 (4C-6). Anal. calcd for $C_{80}H_{78}O_{26}$: C, 61.77; H, 5.05. Found: C, 62.01; H, 5.16.

3.1.36. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-4-*O*-benzoyl-α-L-rhamnopyranoside (41). Compound **40** (1.16 g, 0.8 mmol) was deacetylated under the same conditions as those used for the preparation of **23** from **22**, giving **41** (820 mg, 75%) as a foamy solid; $[\alpha]_D^{25}=+77.5$ (*c* 1.0, $CHCl_3$); ν_{max} (KBr) 3440, 1730, 1263, 1107, 709; δ_H (400 MHz, $CDCl_3$) 8.18–7.24 (m, 35H, Ph), 5.92 (m, 1H, $OCH_2CH{=}CH_2$), 5.74 (dd, 1H, $J_{2,3}=3.3$ Hz, $J_{3,4}=9.8$ Hz, H-3), 5.65 (dd, 1H, $J_{1,2}=1.2$ Hz, $J_{2,3}=3.3$ Hz, H-2), 5.62 (dd, 1H, $J_{1,2}=1.1$ Hz, $J_{2,3}=3.2$ Hz, H-2), 5.60 (dd, 1H, $J_{3,4}=9.7$ Hz, $J_{4,5}=9.7$ Hz, H-4), 5.52 (dd, 1H, $J_{3,4}=9.9$ Hz, $J_{4,5}=9.9$ Hz, H-4), 5.33 (m, 1H, $OCH_2CH{=}CH_2$), 5.32 (d, $J_{1,2}=1.0$ Hz, H-1), 5.26 (d, $J_{1,2}=1.1$ Hz, H-1), 5.24 (m, 1H, $OCH_2CH{=}CH_2$), 5.16 (dd, 1H, $J_{3,4}=9.8$ Hz, $J_{4,5}=9.8$ Hz, H-4), 5.08 (dd, 1H, $J_{3,4}=9.8$ Hz, $J_{4,5}=9.8$ Hz, H-4), 5.01 (d, $J_{1,2}=1.2$ Hz, H-1), 4.67 (d, $J_{1,2}=1.4$ Hz, H-1), 4.47 (dd, 1H, $J_{2,3}=3.4$ Hz, $J_{3,4}=9.8$ Hz, H-3), 3.91 (dd, 1H, $J_{2,3}=3.2$ Hz, $J_{3,4}=9.9$ Hz, H-3), 1.32–1.24 (m, 12H, 4H-6); δ_C (100 MHz, $CDCl_3$) 166.9, 166.6, 165.8, 165.8, 165.6, 165.3, 164.9 (7Ph*C*O), 117.7 ($OCH_2CH{=}CH_2$), 100.3, 99.9, 99.6, 97.5 (4C-1), 17.6, 17.6, 17.5, 17.5 (4C-6). Anal. calcd for $C_{76}H_{74}O_{24}$: C, 66.56; H, 5.44. Found: C, 66.70; H, 5.31.

3.1.37. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→3)-]4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→3)-]4-*O*-benzoyl-α-L-rhamnopyranoside (42). Compounds **41** (685 mg, 0.5 mmol) and 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate (**24**) (900 mg, 1.5 mmol) were coupled under the same conditions as those used for the preparation of **25** from **23** and **24**, giving **42** (455 mg, 41%) as a syrup; $[\alpha]_D^{25}=+43.2$ (*c* 0.5, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 8.03–7.02 (m, 35H, Ph), 5.85 (m, 1H, $CH_2{=}CH{-}CH_2O$), 5.82 (dd, 1H, $J_{2,3}=3.4$ Hz, $J_{3,4}=9.8$ Hz, H-3), 5.52 (d, 1H, $J_{1,2}=7.6$ Hz, H-1), 5.48 (d, 1H, $J_{1,2}=8.0$ Hz, H-1), 5.29 (d, 1H, $J_{1,2}=1.1$ Hz, H-1), 5.23 (d, 1H, $J_{1,2}=1.3$ Hz, H-1), 5.05 (d, 1H, $J_{1,2}=1.3$ Hz, H-1), 4.73 (d, 1H, $J_{1,2}=1.0$ Hz, H-1), 4.46 (dd, 1H, $J_{2,3}=3.3$ Hz, $J_{3,4}=9.7$ Hz, H-3), 4.21 (dd, 1H, $J_{1,2}=1.5$ Hz, $J_{2,3}=3.1$ Hz, H-2), 1.93 (s, 3H, CH_3CO), 1.91 (s, 3H, CH_3CO), 1.74 (s, 3H, CH_3CO), 1.67 (s, 6H, $2CH_3CO$), 1.57 (s, 3H, CH_3CO), 1.18 (d, 3H, $J_{5,6}=6.1$ Hz, H-6), 1.15 (d, 3H, $J_{5,6}=6.3$ Hz, H-6), 1.03 (d, 3H, $J_{5,6}=6.0$ Hz, H-6), 0.80 (d, 3H, $J_{5,6}=6.4$ Hz, H-6); δ_C (100 MHz, $CDCl_3$) 170.7, 170.6, 170.1, 170.1, 169.2, 169.1 ($6CH_3CO$), 166.0, 165.7, 165.2, 164.9, 164.8, 164.5, 164.3 ($7C_6H_5CO$), 117.9 ($CH_2{=}CH{-}CH_2$), 100.2, 99.4, 99.4, 99.3, 98.7, 98.00 (6C-1), 20.6, 20.5, 20.4, 20.4, 20.2, 20.1 ($6CH_3CO$), 17.5, 17.4, 17.2, 17.2 (4C-6). Anal. calcd for $C_{116}H_{112}N_2O_{42}$: C, 63.15; H, 5.12. Found: C, 63.32; H, 5.21.

3.1.38. Propyl α-L-rhamnopyranosyl-(1→2)-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-]α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-]α-L-rhamnopyranoside (43). Compound **42** (220 mg, 0.1 mmol) was deprotected under conditions similar to those used for the preparation of **26** from **25**, giving **43** (66 mg, 63%) as a foamy solid; $[\alpha]_D=-23.6$ (*c* 0.2, H_2O); the ^1H NMR data of compound **43** were identical to those reported in the literature.[3]

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