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Synthetic oligorhamnans related to the most common O-chain backbone from phytopathogenic bacteria

Emiliano Bedini,* Antonella Carabellese, Daniela Comegna, Cristina De Castro and Michelangelo Parrilli

Dipartimento di Chimica Organica e Biochimica, Università di Napoli 'Federico II', Complesso Universitario Monte Santangelo, Via Cintia 4, 80126 Napoli, Italy

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Abstract—The synthesis of the tetrasaccharide rhamnanic motif α-L-Rha-(1→3)-α-L-Rha-(1→2)-α-L-Rha-(1→2)-α-L-Rha and its dimerization to octasaccharide have been developed. Three different pathways toward the dimerization have been investigated; the best one was based on a [4+2]+2 stepwise condensation of a rhamnose tetrasaccharide with two rhamnosyl *N*-phenyl trifluoroacetimidates as glycosyl donors and on an orthogonal set of protecting groups consisting of benzoyl, levulinoyl, and allyl groups.

1. Introduction

The mechanism of pathogenic agent recognition by plants is still unknown, even if many efforts toward understanding are currently underway.[1] It has been recently suggested that the recognition is analogous to the innate immunity system of animals,[2] which is based on the perception of pathogen-associated molecular patterns (PAMPs), characteristic structures of the pathogen indispensable for its growth within the host.[3] Since lipopolysaccharides (LPS) cover almost 80% of the cell surface, they are one of a group of general elicitors that can be recognized by plants to trigger a defense response; this role is induced especially by lipid-A and core[4] that are the most highly conserved regions of LPS in different Gram negative bacteria.[5] A recent study showed that some synthetic oligorhamnans are also able to trigger defense responses in plants and therefore they are PAMP.[6] The oligosaccharides used in that work were the rhamnose trisaccharide **A** and its dimer and trimer; they were chosen as first compounds for phytopathogenic tests, since **A** represents the motif of the most general backbone of the LPS *O*-antigenic region (O-chain) from phytopathogenic bacteria. Nevertheless, only a few bacterial strains present **A** as a repeating unit of their O-chain backbone; the most common O-chain backbones are characterized by motifs such as **B** or **C** that differ from **A** by the addition of a 3-linked- or 2-linked-rhamnose unit (Fig. 1).[7] So far, tetrasaccharide

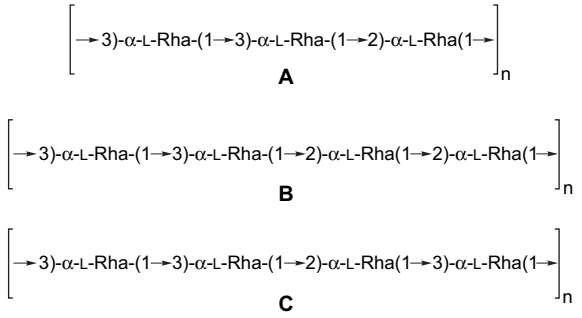

Figure 1. Common rhamnanic backbones of *O*-antigen polysaccharides from phytopathogenic bacteria.

motif **B** has been most frequently found in the O-chains of LPS from phytopathogenic bacteria. In this paper, the synthesis of **B** and its oligomerization is described; the synthetic oligorhamnans obtained will be the object of molecular mechanics calculations and phytopathogenic tests, in order to compare their 3D-structures and their eventual biological activities with the oligorhamnans related to motif **A**.

2. Results and discussion

The synthesis of α-linked oligorhamnans was the target of several reports in the last two decades;[8] recently, a methyl and an octyl glycoside bearing a tetrasaccharide corresponding to motif **B** were also synthesized,[9] nevertheless their oligomerization was not attempted. The synthetic approach described in this paper aimed at the synthesis

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* Corresponding author. Tel.: +39 81 674146; fax: +39 81 674393; e-mail: ebedini@unina.it

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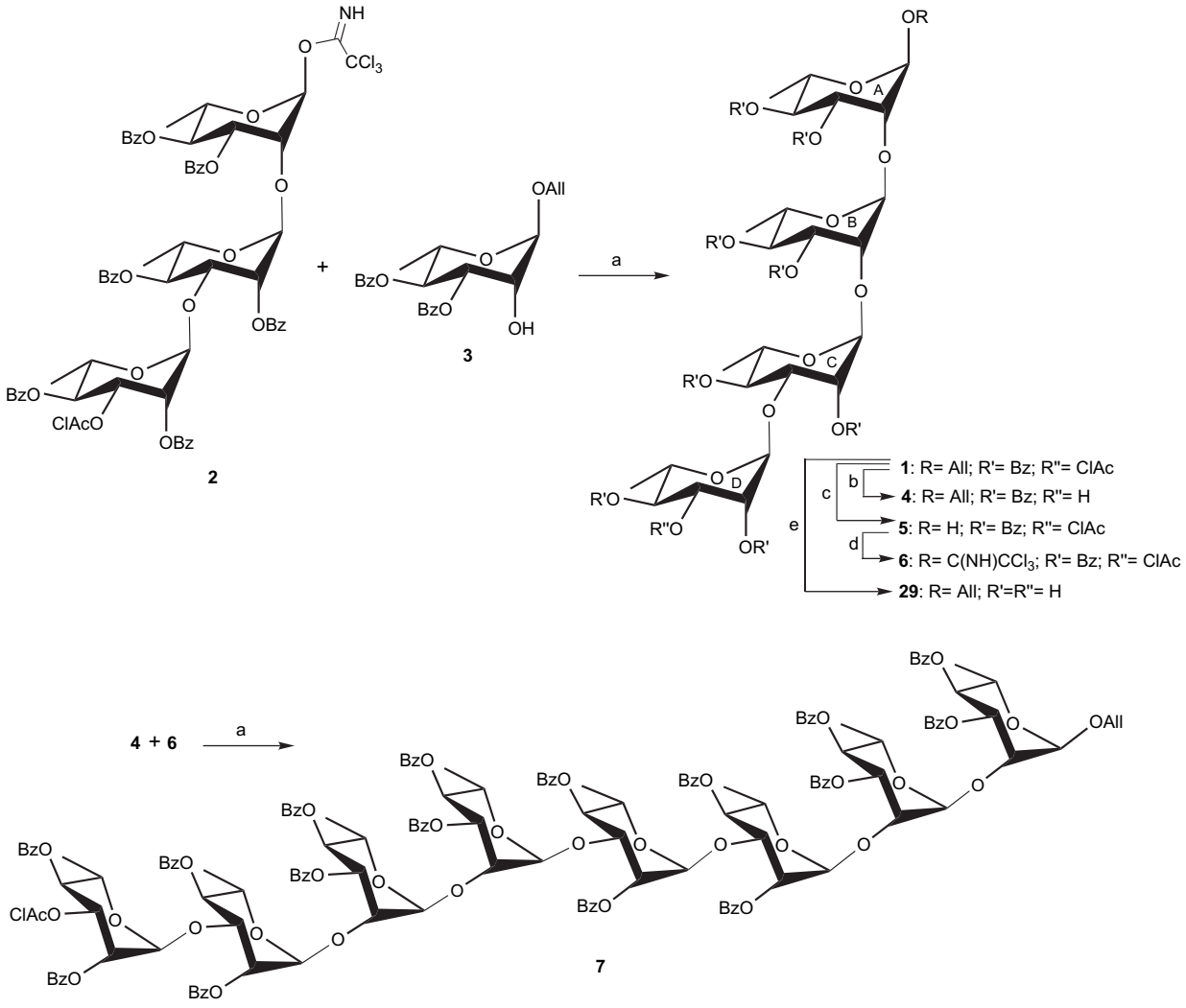
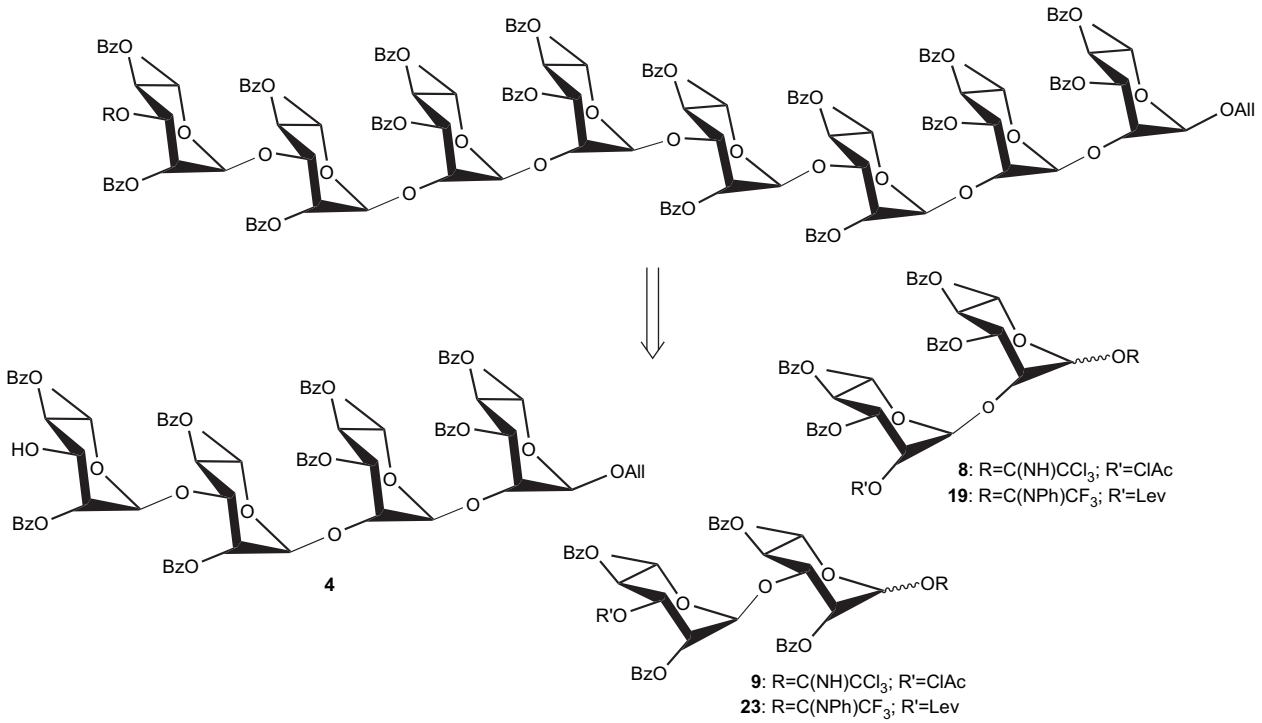
of a tetrasaccharide building-block that would be easily functionalized both as a glycosyl donor and a glycosyl acceptor, thus permitting stepwise condensation to higher oligosaccharides. Therefore, the protection pattern of this tetrasaccharide should have two orthogonal temporary protecting groups at positions O-1_A and O-3_D and a permanent protecting group at the other positions; an allyl group was chosen for the anomeric position, a chloroacetyl for position O-3_D, and benzoyls for the other positions. Tetrasaccharide **1** with this protection pattern was obtained by condensing trisaccharide donor **2**[10] with acceptor **3**[11] in CH_2Cl_2 at −50 °C with $BF_3\cdot OEt_2$ as activator (72% yield) (Scheme 1). The α-configuration of the newly formed glycosidic linkage was ascertained by the heteronuclear C_1–H_1 coupling constant of 172 Hz measured in a *J*-coupled HSQC experiment. Selective removal of the chloroacetyl moiety was easily achieved by treating an aliquot of **1** with thiourea; the tetrasaccharide acceptor **4** was obtained in 71% yield. Another aliquot of **1** was de-O-allylated with $PdCl_2$ in 1:1 CH_2Cl_2/MeOH to obtain a tetrasaccharide glycosyl donor, the resulting hemiacetal **5** (80%) was subsequently activated by treatment with Cl_3CCN and DBU to give the trichloroacetimidate **6** in 61% yield. Unfortunately, the glycosylation of **6** with **4** was unsuccessful; octasaccharide **7** was obtained in very low yield (<15%) by activating **6** with $BF_3\cdot OEt_2$ at −50 °C. No better yield was observed even by changing several reaction conditions. Interestingly, the glycosylation of trisaccharide trichloroacetimidate **2**, that is related to **6**, with rhamnose oligosaccharides had been already successfully accomplished.[10] Thus, we hypothesized that the upper limit for such couplings between rhamnose oligosaccharides was the use of a trisaccharide donor and a new strategy for the dimerization of **1** was planned. This new approach was to dimerize **1** by stepwise condensation of tetrasaccharide acceptor **4** with two different disaccharide donors that would have a temporary protecting group at positions O-2_B and O-3_B, respectively. In analogy to the [4+4] strategy, a chloroacetyl was chosen as temporary protecting group; compounds **8** and **9** was therefore, designed as suitable disaccharide donors (Scheme 2).

The synthesis of compound **8** was started by treating the known diol **10**[12] with BzCl in 2:1 CH_2Cl_2/Py at −30 °C to give selectively 3,4-di-*O*-benzoylated alcohol **11** in 88%



Scheme 1. Reagents and conditions: (a) $BF_3\cdot OEt_2$, AW-300 4 Å MS, CH_2Cl_2, −50 °C, to **1**: 75 min, 72%; to **7**: 2 h, <15%; (b) NH_2CSNH_2, 1:1 EtOH/DMF, rt, 2 days, 71%; (c) $PdCl_2$, 1:1 CH_2Cl_2/MeOH, rt, 2 days, 80%; (d) Cl_3CCN, DBU, 0 °C, 3 h, 61%; (e) NaOMe, MeOH, 40 °C, overnight, 78%.

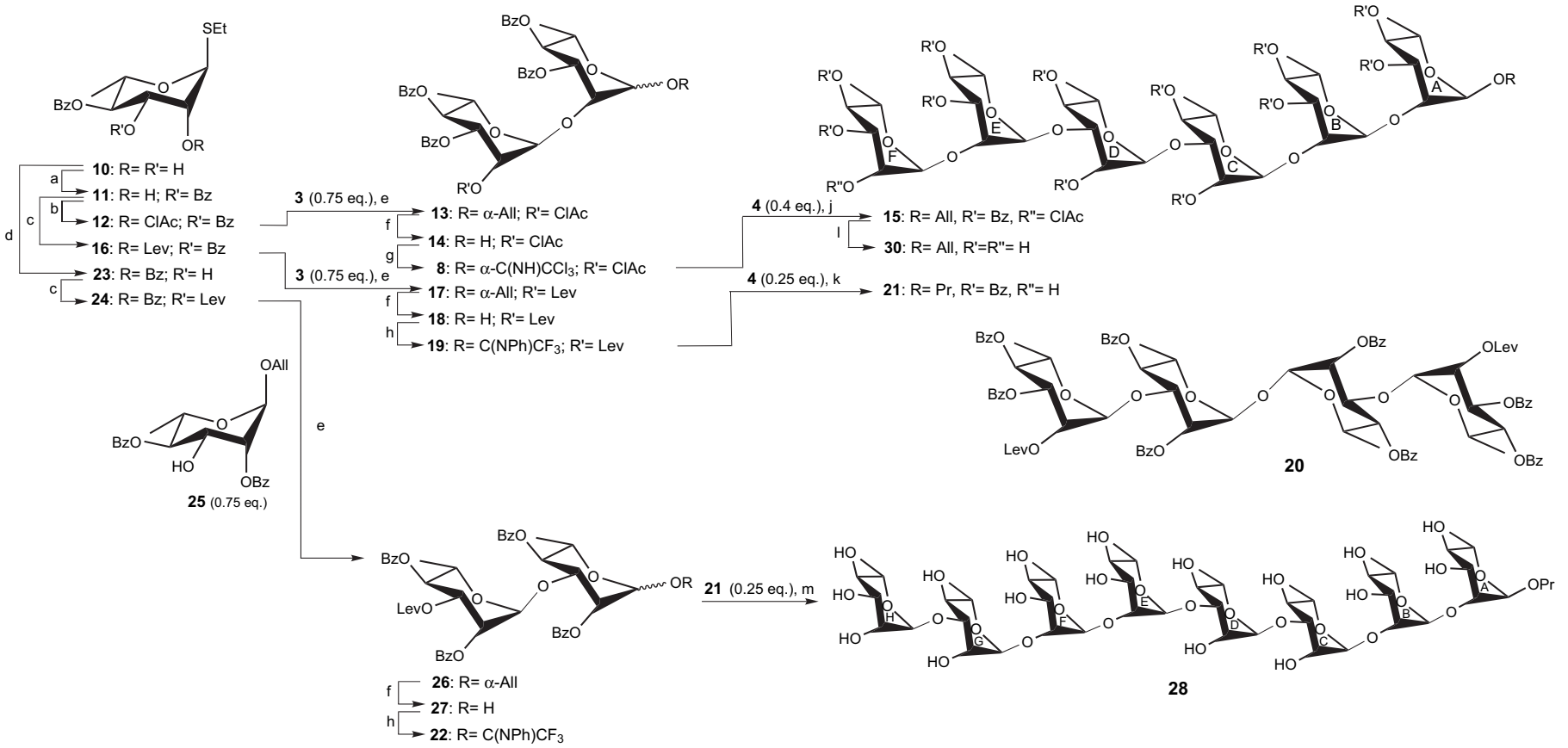


Scheme 2. [4+2]+2 Strategy for the dimerization of the rhamnanic motif **B**.

yield (Scheme 3). Compound **11** was chloroacetylated (56%) and the resulting fully-protected thioglycoside **12** was coupled with **3** by activation with NIS/TfOH at −30 °C. Disaccharide **13** was obtained in unsatisfactory yield (45%); this result was consistent with a recent report on the poor outcome of a condensation reaction involving a 2-chloroacetylated trichloroacetimidate as rhamnosyl donor.[13] In spite of the limited yield of the coupling, compound **13** was de-O-allylated with $PdCl_2$ to give hemi-acetal **14** (53%) that was converted in turn to trichloroacetimidate **8** (80%). Condensation of **8** with tetrasaccharide acceptor **4** at −50 °C with $BF_3 \cdot OEt_2$ as activator gave hexasaccharide **15** in moderate yield (48%).

The low global yield of the synthetic path from diol **10** to hexasaccharide **15** (5%) necessitated the re-designing of this synthetic path. The chloroacetyl temporary protecting group was replaced with a levulinoyl group; in addition the trichloroacetimidate leaving group on the disaccharide donor was replaced by a *N*-phenyltrifluoroacetimidate,[14] because the latter was recently shown to be very effective in glycosylation reactions involving deoxysugars (Scheme 2).[15] Thus, alcohol **11** was treated with levulinic acid (LevOH) in the presence of *N*,*N*′-diisopropylcarbodiimide (DIPC) and DMAP to give the 2-*O*-levulinoylated thioglycoside **16** (91%) that was coupled with **3** by activation with NIS/TfOH at −30 °C to afford disaccharide **17** in 83% yield. Hemi-acetal **18** was obtained from **17** with $PdCl_2$ (83%) and then converted into *N*-phenyltrifluoroacetimidate **19** (72%) by treatment with $CF_3C(NPh)Cl$ and NaH (Scheme 3).[16] Coupling of disaccharide donor **19** with tetrasaccharide acceptor **4** by activation with TMSOTf in CH_2Cl_2 at 0 °C proceeded very satisfyingly. Actually, an exact yield of this condensation was not obtained, since, after column chromatography, the resulting hexasaccharide was contaminated by traces of tetrasaccharide **20**, a side product due to self-condensation of **19**. Treatment with hydrazinium acetate in 7:1 CH_2Cl_2/MeOH cleaved the Lev group and reduced the allyl aglycon to propyl by the diimide generated in situ,[17] affording pure hexasaccharide acceptor **21** in 77% yield (calculated from **3**). A *J*-coupled HSQC experiment on **21** confirmed the α-configuration of the newly formed glycosidic linkage ($^1J_{C,H}$=172 Hz). The global yield of the synthetic path from **10** to **21** was much better with Lev than ClAc as O-2 temporary protecting group (30% vs 5%).

This result prompted us to re-design also the second disaccharide donor with a Lev temporary group. Thus, the synthesis of donor **22** (to replace **9**) was undertaken. Diol **10** was regioselectively 2-O-benzoylated via *ortho*-ester as already reported[13] and the resulting alcohol **23** was converted to 3-*O*-levulinoylated thioglycoside **24** (89%). Coupling of **24** with acceptor **25**[18] proceeded in high yield (87%) by activation of **24** with NIS/TfOH at −30 °C. Disaccharide **26** was de-O-allylated (60%) and the resulting hemi-acetal **27** was converted into *N*-phenyltrifluoroacetimidate **22** (58%). Elongation of hexasaccharide **21** by condensation with disaccharide donor **22** gave, after column chromatography, an octasaccharide contaminated by tetrasaccharide **20**. Benzoyl and levulinoyl deprotection by Zemplén transesterification of the mixture afforded pure propyl octasaccharide **28** (49% calculated from **21**) after size exclusion chromatography, the ^1H NMR spectrum of which is reported in Figure 2. Similarly, ester deprotection of **1** and **15** gave tetrasaccharide **29** (78%) and hexasaccharide **30** (90%) (Schemes 1 and 3). Compounds **28**, **29**, and **30** are currently the object of molecular mechanics calculations and phytopathogenic tests.



Scheme 3. Reagents and conditions: (a) BzCl, 2:1 CH_2Cl_2/Py, −30 °C, 2.5 h, 88%; (b) $ClCH_2COCl$, 1:1 Py/DMF, rt, 4 h, 56%; (c) LevOH, DIPC, DMAP, rt, to **16**: 1 h, 91%; to **24**: 30 min, 89%; (d) see Ref. 12; (e) NIS, TfOH, AW-300 4 Å MS, CH_2Cl_2, −30 °C, to **13**: 90 min, 45%; to **17**: 90 min, 83%; to **26**: 3 h, 87%; (f) $PdCl_2$, 3:1 CH_2Cl_2/MeOH, rt, overnight, to **14**: 53%; to **18**: 83%; to **27**: 60%; (g) Cl_3CCN, DBU, CH_2Cl_2, 0 °C, 2 h, 80% (α/β=6:1); (h) $CF_3C(NPh)Cl$, NaH, 4 Å MS, CH_2Cl_2, 0 °C to rt, 4 h, to **19**: 72% (α/β=1:1); to **22**: 58% (α/β=1:1); (j) $BF_3 \cdot OEt_2$, AW-300 4 Å MS, CH_2Cl_2, −50 °C, 4 h, 48%; (k) (i) TMSOTf, AW-300 4 Å MS, CH_2Cl_2, 0 °C, 3 h; (ii) N_2H_4, AcOH, 7:1 CH_2Cl_2/MeOH, rt, 2 h, 77% over two steps; (l) NaOMe, 3:1 MeOH/CH_2Cl_2, 40 °C, overnight, 77%; (m) (i) TMSOTf, AW-300 4 Å MS, CH_2Cl_2, 0 °C, overnight, (ii) NaOMe, 3:1 MeOH/CH_2Cl_2, 40 °C, 2 days, 49% over two steps.

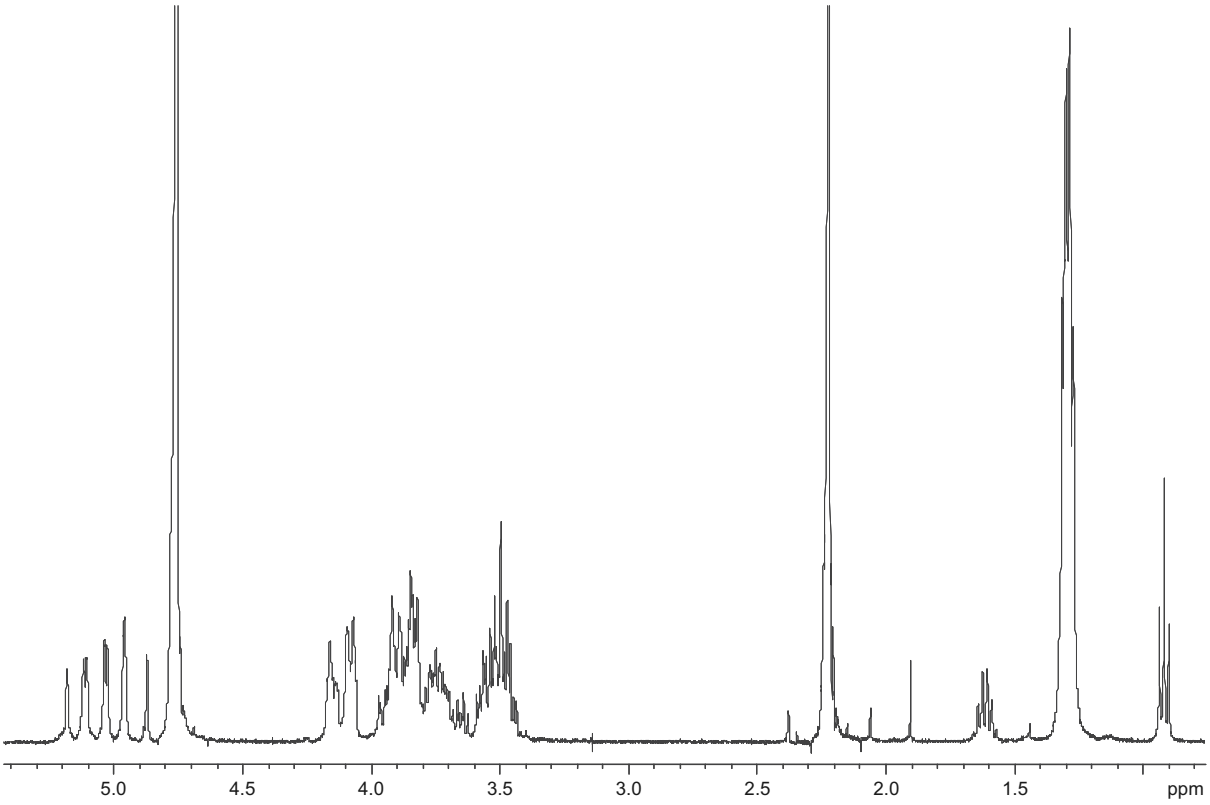


Figure 2. ^{1}H NMR spectrum (D_2O, 400 MHz; acetone as internal standard) of the octasaccharide **28**.

3. Experimental

3.1. General methods

^{1}H and ^{13}C NMR spectra were recorded on Varian XL-200 (^{1}H: 200 MHz; ^{13}C: 50 MHz), Varian Gemini-300 (^{1}H: 300 MHz; ^{13}C: 75 MHz) or Bruker DRX-400 (^{1}H: 400 MHz; ^{13}C: 100 MHz) instruments in $CDCl_3$ ($CHCl_3$ as internal standard, ^{1}H: C*H*Cl_3 at δ 7.26; ^{13}C: *C*DCl_3 at δ 77.0) and in D_2O (acetone as internal standard, ^{1}H: $(CH_3)_2CO$ at δ 2.22; ^{13}C: $(CH_3)_2CO$ at δ 31.5). Assignment of proton and carbon chemical shifts of the deprotected oligosaccharides was based on 2D NMR experiments such as COSY, TOCSY, NOESY, and HSQC. Heteronuclear C_1–H_1 coupling constants were measured with *J*-coupled HSQC experiments. Positive ESI-MS spectra were recorded on a Finnigan LCQ-DECA ion trap mass spectrometer. Positive MALDI-MS spectra were recorded on an Applied Biosystem Voyager DE-PRO MALDI-TOF mass spectrometer in the positive mode; compounds were dissolved in the appropriate solvent at a concentration of 1 mg/mL and 1 μL of these solutions were mixed with 1 μL of a 20 mg/mL solution of 2,5-dihydroxybenzoic acid in 7:3 CH_3CN/0.1 M aqueous TFA. IR spectra were recorded on a JASCO-FTIR-430 spectrometer. Optical rotations were measured on a JASCO P-1010 polarimeter. Analytical thin layer chromatography (TLC) was performed on aluminum plates precoated with Merck silica gel 60 F_{254} as the adsorbent. The plates were developed with 5% H_2SO_4 ethanolic solution and then heated to 130 °C. Column chromatography was performed on Merck Kieselgel 60 (63–200 mesh), except where differently specified. Gel-filtration chromatographies were performed on a Sephadex G-10 column (2.0×90 cm) with water as eluant.

3.1.1. Allyl (2,4-di-*O*-benzoyl-3-*O*-chloroacetyl-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)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (1). A mixture of **3** (179 mg, 0.43 mmol) and **2** (734 mg, 0.56 mmol) was coevaporated three times with toluene, the residue was dried, and then mixed with freshly activated AW-300 4 Å molecular sieves, suspended under argon in CH_2Cl_2 (15 mL), and stirred at −50 °C. $BF_3{\cdot}OEt_2$ (35 μL, 0.28 mmol) was then added. After 75 min the reaction mixture was quenched with some drops of Et_3N. After filtration over a Celite pad, the mixture was concentrated to give a residue that after column chromatography (5:1 to 3:1 petroleum ether/ethyl acetate) afforded **1** (480 mg, 72%) as a white foam. $[\alpha]_D$ +95.8 (*c* 1.0, CH_2Cl_2). IR (thin film, NaCl) 3030, 2913, 1720, 1458, 1275 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.15–7.09 (m, 40H), 5.98 (m, 1H), 5.83 (dd, *J*=9.9, 3.1 Hz, 1H), 5.68–5.57 (m, 3H), 5.54 (br s, 1H), 5.43–5.27 (m, 5H), 5.18 (br s, 1H), 5.17 (br s, 1H), 5.12 (br s, 1H), 5.01 (br s, 1H), 4.80 (br s, 1H), 4.50 (dd, *J*=10.0, 3.4 Hz, 1H), 4.40 (br s, 1H), 4.36 (br s, 1H), 4.30 (dd, *J*=9.7, 3.6 Hz, 1H), 4.23 (dq, *J*=9.6, 6.1 Hz, 1H), 4.13 (m, 3H), 4.00 (dq, *J*=10.0, 6.1 Hz, 1H), 3.72 (AB d, *J*=14.9 Hz, 1H), 3.68 (AB d, *J*=14.9 Hz, 1H), 1.41 (d, *J*=6.1 Hz, 3H), 1.35 (d, *J*=6.1 Hz, 3H), 1.20 (d, *J*=6.1 Hz, 3H), 1.01 (d, *J*=6.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 165.8–165.3 (CO), 133.8–133.3 (C_{ipso}, $OCH_2CH{=}CH_2$),

129.8–128.3 (C-Ar), 118.1 ($OCH_2CH{=}\mathit{C}H_2$), 100.8, 99.3, 99.0, 97.9 (C_1^A, C_1^B, C_1^C, C_1^D), 78.0, 77.5, 75.1 (C_2^A, C_2^B, C_3^C), 72.8, 71.8, 71.7, 71.6, 71.5, 71.3, 70.6, 70.5, 70.3, 68.1, 67.5, 67.4, 67.3, 66.9 (C_2^C, C_2^D, C_3^A, C_3^B, C_3^D, C_4^A, C_4^B, C_4^C, C_4^D, C_5^A, C_5^B, C_5^C, C_5^D, $OCH_2CH{=}CH_2$), 40.3 ($\mathit{C}H_2Cl$), 17.6–17.2 (C_6^A, C_6^B, C_6^C, C_6^D). MALDI-MS for $C_{85}H_{79}ClO_{26}$ (*m*/*z*): M_r (calcd) 1550.45; M_r (found) 1573.27 $(M+Na)^+$. Anal. Calcd: C 65.78, H 5.13. Found: C 65.97, H 5.10.

3.1.2. Allyl (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)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (4). A solution of **1** (189 mg, 0.12 mmol) was dissolved in 1:1 EtOH/DMF (12 mL) and then thiourea was added (93 mg, 1.29 mmol). After 2 days stirring at rt, the solution was diluted with CH_2Cl_2, washed with 1 M HCl, 1 M $NaHCO_3$, and water. The organic layer was collected, dried, and concentrated to give a residue that, after column chromatography (4:1 petroleum ether/ethyl acetate) afforded **4** (128 mg, 71%) as a white foam. $[\alpha]_D$ +116.9 (*c* 1.7, CH_2Cl_2). IR (thin film, NaCl) 3053, 3031, 2925, 1723, 1460 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.17–7.07 (m, 40H), 5.98 (m, 1H), 5.85 (dd, *J*=9.9, 3.1 Hz, 1H), 5.64 (m, 2H), 5.58 (t, *J*=9.8 Hz, 1H), 5.53 (br s, 1H), 5.39 (m, 2H), 5.29 (d, *J*=10.8 Hz, 1H), 5.21 (br s, 1H), 5.13–5.05 (m, 4H), 5.02 (br s, 1H), 4.80 (br s, 1H), 4.48 (dd, *J*=9.6, 3.1 Hz 1H), 4.41 (br s, 1H), 4.37 (br s, 1H), 4.30 (dd, *J*=9.7, 3.6 Hz, 1H), 4.23 (dq, *J*=9.6, 6.1 Hz, 1H), 4.13 (m, 2H), 4.03 (m, 2H), 2.17 (br s, 1H), 1.39 (d, *J*=6.1 Hz, 3H), 1.34 (d, *J*=6.1 Hz, 3H), 1.16 (d, *J*=6.1 Hz, 3H), 1.01 (d, *J*=6.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.8–165.3 (CO), 133.9–133.3 (C_{ipso}, $OCH_2\mathit{C}H{=}CH_2$), 130.0–128.2 (C-Ar), 118.1 ($OCH_2CH{=}\mathit{C}H_2$), 100.8, 99.2, 99.0, 98.3 (C_1^A, C_1^B, C_1^C, C_1^D), 77.9, 77.0, 75.3, 75.1, 73.3–71.7, 70.6, 68.4, 68.3, 68.0, 67.4, 66.9 (C_2^A, C_2^B, C_2^C, C_2^D, C_3^A, C_3^B, C_3^C, C_3^D, C_4^A, C_4^B, C_4^C, C_4^D, C_5^A, C_5^B, C_5^C, C_5^D, $OCH_2CH{=}CH_2$), 17.6–17.3 (C_6^A, C_6^B, C_6^C, C_6^D). MALDI-MS for $C_{63}H_{78}O_{25}$ (*m*/*z*): M_r (calcd) 1474.48; M_r (found) 1497.42 $(M+Na)^+$. Anal. Calcd: C 67.56, H 5.33. Found: C 67.67, H 5.30.

3.1.3. (2,4-Di-*O*-benzoyl-3-*O*-chloroacetyl-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)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (6). Compound **1** (299 mg, 0.19 mmol) was dissolved in 1:1 MeOH/CH_2Cl_2 (8.0 mL), $PdCl_2$ (8.6 mg, 95 μmol) was then added, and the mixture was vigorously stirred at rt for 2 days, after that it was filtered over a Celite pad, diluted with CH_2Cl_2, and washed with 5 M NaCl. The organic layer was collected, dried, and concentrated to give **5** (227 mg, 80%) that was then dissolved in CH_2Cl_2 (15 mL) under Ar atmosphere. The solution was cooled to 0 °C and then treated with Cl_3CCN (76 μL, 0.76 mmol) and DBU (6.7 μL, 45 μmol). After 3 h the solution was concentrated at 30 °C. The residue was subjected to neutral alumina (Brockman grade 1) column chromatography (9:2 petroleum ether/ethyl acetate) to give **6** (152 mg, 61%) as a white foam. $[\alpha]_D$ +101.5 (*c* 1.0, CH_2Cl_2). IR (thin film, NaCl) 3023, 2970, 1741, 1650 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.39 (s, 1H), 8.15–7.11 (m, 40H), 6.47 (br s, 1H), 5.84 (dd, *J*=9.8, 3.2 Hz, 1H), 5.72 (t, *J*=9.8 Hz, 1H), 5.68 (dd, *J*=9.6, 3.2 Hz, 1H), 5.60 (t, *J*=9.8 Hz, 1H), 5.55 (br s, 1H), 5.42 (m, 2H), 5.31 (t, *J*=9.5 Hz, 1H), 5.19 (br s, 2H), 5.17 (br s, 1H), 4.88 (br s, 1H), 4.63 (br s, 1H), 4.51 (dd, *J*=9.5, 3.3 Hz, 1H), 4.40 (br s, 1H), 4.33 (m, 2H), 4.13 (dq, *J*=9.5, 6.1 Hz, 1H), 4.01 (dq, *J*=9.5, 6.1 Hz, 1H), 3.72 (AB d, *J*=14.9 Hz, 1H), 3.68 (AB d, *J*=14.9 Hz, 1H), 1.43 (d, *J*=6.1 Hz, 3H), 1.39 (d, *J*=6.1 Hz, 3H), 1.30 (d, *J*=6.1 Hz, 3H), 0.93 (d, *J*=6.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.0–165.4 (CO), 161.4 ($Cl_3C\mathit{C}{=}NH$), 133.8–133.4 (C_{ipso}), 130.0–128.3 (C-Ar), 100.9, 100.2, 100.1, 97.2 (C_1^A, C_1^B, C_1^C, C_1^D), 78.1, 75.1, 74.9, 72.9–71.1, 70.5, 70.2, 69.8, 69.7, 67.7–67.5 (C_2^A, C_2^B, C_2^C, C_2^D, C_3^A, C_3^B, C_3^C, C_3^D, C_4^A, C_4^B, C_4^C, C_4^D, C_5^A, C_5^B, C_5^C, C_5^D), 40.3 (CH_2Cl), 17.7–17.3 (C_6^A, C_6^B, C_6^C, C_6^D). Anal. Calcd: C 60.91, H 4.56, N 0.85. Found: C 61.09, H 4.45, N 0.88.

3.1.4. Ethyl 3,4-di-*O*-benzoyl-1-thio-α-L-rhamnopyranoside (11). A solution of **10** (2.935 g, 9.40 mmol) in 2:1 CH_2Cl_2/Py (12 mL) was cooled to −30 °C and then treated with a 1.1 M solution (2.25 mL) of BzCl in 2:1 CH_2Cl_2/Py. After stirring for 2.5 h, the mixture was treated with some drops of water, heated to rt, and then diluted with CH_2Cl_2. The mixture was washed with water, 1 M HCl, and water again. The organic layer was collected, dried, and concentrated to give a residue that, after column chromatography (7:1 petroleum ether/ethyl acetate) afforded **11** (3.446 g, 88%) as a white foam. $[\alpha]_D$ +8 (*c* 0.5, CH_2Cl_2). IR (thin film, NaCl) 3063, 3025, 2926, 1707, 1605 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ 7.99–7.30 (m, 10H), 5.62 (t, *J*=9.8 Hz, 1H), 5.53 (dd, *J*=9.8, 2.6 Hz, 1H), 5.37 (br s, 1H), 4.48 (dq, *J*=9.8, 6.2 Hz, 1H), 4.39 (br s, 1H), 2.71 (app oct, *J*=8.4 Hz, 2H), 2.04 (br s, 1H), 1.35 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.6 (CO), 132.9, 132.8 (C_{ipso}), 129.4–128.0 (C-Ar), 84.1 (C_1), 72.7, 71.6, 70.5, 66.7 (C_2, C_3, C_4, C_5), 24.8 ($S\mathit{C}H_2CH_3$), 17.1 (C_6), 14.5 ($SCH_2\mathit{C}H_3$). ESIMS for $C_{22}H_{24}O_6S$ (*m*/*z*): M_r (calcd) 416.13; M_r (found) 439.33 $(M+Na)^+$. Anal. Calcd: C 63.44, H 5.81. Found: C 63.66, H 5.88.

3.1.5. Ethyl 3,4-di-*O*-benzoyl-2-*O*-chloroacetyl-1-thio-α-L-rhamnopyranoside (12). A solution of **11** (100 mg, 0.24 mmol) 1:1 pyridine/DMF (2.0 mL) was treated with $ClCH_2COCl$ (86 μL, 1.08 mmol) and then stirred at rt for 4 h. The mixture was coevaporated several times with toluene, then diluted with CH_2Cl_2, and washed with water. The organic layer was dried and concentrated to give a residue that was subjected to column chromatography (7:1 petroleum ether/ethyl acetate) to afford **12** (66 mg, 56%) as a yellowish oil. $[\alpha]_D$ −17.4 (*c* 2.1, CH_2Cl_2). IR (thin film, NaCl) 3060, 3025, 2959, 1721, 1596 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ 7.99–7.30 (m, 10H), 5.68–5.52 (m, 3H), 5.36 (br s, 1H), 4.50 (dq, *J*=9.8, 6.2 Hz, 1H), 4.18 (s, 2H), 2.70 (m, 2H), 1.34 (m, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 166.5, 165.6, 165.3 (CO), 133.3 ($2C_{ipso}$), 129.7–128.3 (C-Ar), 81.7 (C_1), 73.7, 71.5, 70.0, 67.3 (C_2, C_3, C_4, C_5), 40.6 (CH_2Cl), 25.6 ($S\mathit{C}H_2CH_3$), 17.5 (C_6), 14.9 ($SCH_2\mathit{C}H_3$). ESIMS for $C_{24}H_{25}ClO_7S$ (*m*/*z*): M_r (calcd) 492.10; M_r (found) 513.39 $(M+Na)^+$. Anal. Calcd: C 58.47, H 5.11. Found: C 58.77, H 5.02.

3.1.6. Allyl (3,4-di-*O*-benzoyl-2-*O*-chloroacetyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (13). A mixture of **3** (50 mg, 0.12 mmol) and **12** (79 mg, 0.16 mmol) was coevaporated three times with

toluene, the residue was dried, and then mixed with freshly activated AW-300 4 Å molecular sieves and NIS (45 mg, 0.20 mmol). The mixture was suspended in CH_2Cl_2 (4.0 mL) under an Ar atmosphere and rapidly cooled to −30 °C. A 115 mg/mL solution of TfOH in CH_2Cl_2 (54 μL, 40 μmol) was then added. After 90 min the reaction mixture was rapidly filtered over a Celite pad, diluted with CH_2Cl_2, and washed with 10% $Na_2S_2O_3$ and 1 M $NaHCO_3$. The organic layer was collected, dried and concentrated to give a foamy residue. After column chromatography (7:1 petroleum ether/ethyl acetate), **13** (46 mg, 45%) was recovered as a white foam. $[\alpha]_D$ +45.1 (*c* 1.0, CH_2Cl_2). IR (thin film, NaCl) 3055, 3026, 2948, 1726, 1600, 1255 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ 8.02–7.30 (m, 20H, H-Ar), 5.98 (m, 1H), 5.87 (dd, *J*=10.0, 3.2 Hz, 1H), 5.80 (dd, *J*=10.0, 3.2 Hz, 1H), 5.70 (dd, *J*=3.2, 1.8 Hz, 1H), 5.62 (t, *J*=10.0 Hz, 1H), 5.50 (t, *J*=10.0 Hz, 1H), 5.39 (d, *J*=17.0 Hz, 1H), 5.28 (d, *J*=10.4 Hz, 1H), 5.00 (br s, 2H), 4.34–4.12 (m, 5H), 4.08 (AB d, *J*=14.9 Hz, 1H), 3.98 (AB d, *J*=14.9 Hz, 1H), 1.39 (d, *J*=6.1 Hz, 3H), 1.30 (d, *J*=6.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 166.0, 165.7, 165.6, 165.4, 165.1 (CO), 133.4–133.1 (C_{ipso}, $OCH_2CH{=}CH_2$), 129.8–128.4 (C-Ar), 117.9 ($OCH_2CH{=}CH_2$), 99.0, 97.6 (C_1^A, C_1^B), 76.7, 71.7, 71.6, 71.4, 71.1, 69.3, 68.2, 67.5, 67.0 (C_2^A, C_2^B, C_3^A, C_3^B, C_4^A, C_4^B, C_5^A, C_5^B, $OCH_2CH{=}CH_2$), 40.5 (CH_2Cl), 17.6 (C_6^A, C_6^B). ESIMS for $C_{45}H_{43}ClO_{14}$ (*m/z*): M_r (calcd) 842.23; M_r (found) 865.49 $(M+Na)^+$. Anal. Calcd: C 64.09, H 5.14. Found: C 64.18, H 5.07.

3.1.7. (3,4-Di-*O*-benzoyl-2-*O*-chloroacetyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzoyl-L-rhamnopyranosyl trichloroacetimidate (8). Compound **13** (130 mg, 0.15 mmol) was dissolved in 3:1 CH_2Cl_2/MeOH (4.0 mL), $PdCl_2$ (5.4 mg, 60 μmol) was then added, and the mixture was vigorously stirred overnight. It was then filtered over a Celite pad, diluted with CH_2Cl_2, and washed with 5 M NaCl. The organic layer was dried and concentrated to give **14** (65 mg, 53%) that was then dissolved in CH_2Cl_2 (3.0 mL) under Ar atmosphere. The solution was cooled to 0 °C and then treated with Cl_3CCN (33 μL, 0.33 mmol) and DBU (4.3 μL, 29 μmol). After 2 h the solution was concentrated at 30 °C. The residue was subjected to neutral alumina (Brockman grade 1) column chromatography (6:1 petroleum ether/ethyl acetate) to give **8** (61 mg, 80%; α/β= 6:1) as a white foam. $[\alpha]_D$ +34.5 (*c* 1.0, CH_2Cl_2). IR (thin film, NaCl) 3048, 3020, 2970, 1738, 1655 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) (α-anomer) δ 8.76 (s, 1H), 8.02–7.33 (m, 20H, H-Ar), 6.46 (d, *J*=1.8 Hz, 1H), 5.86 (dd, *J*=10.0, 3.3 Hz, 1H), 5.81 (dd, *J*=10.0, 3.3 Hz, 1H), 5.73 (t, *J*=10.0 Hz, 1H), 5.70 (dd, *J*=3.3, 1.5 Hz, 1H), 5.53 (t, *J*=10.0 Hz, 1H), 5.07 (d, *J*=1.5 Hz, 1H), 4.55 (dd, *J*=3.3, 1.8 Hz 1H), 4.35 (m, 2H), 4.09 (AB d, *J*=15.0 Hz, 1H), 4.00 (AB d, *J*=15.0 Hz, 1H), 1.45 (d, *J*=6.2 Hz, 3H), 1.37 (d, *J*=6.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) (α-anomer) δ 165.9, 165.7, 165.4, 165.3 (CO), 161.4 ($Cl_3CC{=}NH$), 133.4–133.1 (C_{ipso}), 129.9–128.4 (C-Ar), 99.9, 95.8 (C_1^A, C_1^B), 77.2, 74.3, 72.5, 71.8, 71.6, 71.5, 71.0, 70.6, 69.3, 68.6 (C_2^A, C_2^B, C_3^A, C_3^B, C_4^A, C_4^B, C_5^A, C_5^B), 40.3 (CH_2Cl), 17.7, 17.3 (C_6^A, C_6^B). Anal. Calcd: C 55.77, H 4.15, N 1.48. Found: C 56.01, H 4.11, N 1.45.

3.1.8. Allyl (3,4-di-*O*-benzoyl-2-*O*-chloroacetyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-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-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (15). A mixture of **4** (30 mg, 20 μmol) and **8** (57 mg, 60 μmol) was coevaporated three times with toluene, the residue was dried, and then mixed with freshly activated AW-300 4 Å molecular sieves, suspended under argon in CH_2Cl_2 (2.0 mL) and stirred at −50 °C. An 85 mg/mL solution of $BF_3{\cdot}OEt_2$ in CH_2Cl_2 (50 μL, 30 μmol) was then added. After 3 h the reaction mixture was quenched with some drops of Et_3N. After filtration over a Celite pad, the mixture was concentrated. The residue was subjected to column chromatography (11:1 to 6:1 toluene/ethyl acetate) to give **15** (22 mg, 48%) as a white foam. $[\alpha]_D$ +92 (*c* 0.5, CH_2Cl_2). IR (thin film, NaCl) 3024, 2927, 2857, 1722, 1604, 1449, 1272 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.15–7.24 (m, 60H, H-Ar), 6.00 (m, 1H), 5.85 (dd, *J*=9.9, 3.1 Hz, 1H), 5.74 (dd, *J*=9.9, 3.4 Hz, 1H), 5.65–5.51 (m, 4H), 5.44–5.30 (m, 7H), 5.23 (br s, 1H), 5.19 (br s, 1H), 5.14 (br s, 1H), 5.03 (br s, 1H), 4.94 (br s, 1H), 4.81 (br s, 1H), 4.71 (br s, 1H), 4.59 (br s, 1H), 4.49 (dd, *J*=9.6, 3.2 Hz, 1H), 4.38–4.32 (m, 3H), 4.22–4.14 (m, 3H), 4.03–3.91 (m, 3H), 3.82 (dq, *J*=9.8, 6.2 Hz, 1H), 3.73 (dq, *J*=9.9, 6.2 Hz, 1H), 3.70 (AB d, *J*=14.9 Hz, 1H), 3.65 (AB d, *J*=14.9 Hz, 1H), 3.61 (dq, *J*=9.9, 6.2 Hz, 1H), 1.42 (d, *J*=6.2 Hz, 3H), 1.37 (d, *J*=6.2 Hz, 3H), 1.15 (d, *J*=6.2 Hz, 3H), 1.00 (d, *J*=6.2 Hz, 3H), 0.85 (d, *J*=6.2 Hz, 3H), 0.79 (d, *J*=6.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.8–165.0 (Ph*C*O), 133.8–133.3 (C_{ipso}, $OCH_2CH{=}CH_2$), 130.3–128.2 (C-Ar), 117.9 ($OCH_2CH{=}CH_2$), 100.9, 100.8, 100.4, 99.6, 99.5, 98.9 (C_1^A, C_1^B, C_1^C, C_1^D, C_1^E, C_1^F), 77.8, 76.9, 76.2, 75.4, 73.2, 73.1, 73.0, 72.2–71.5, 70.5, 70.0, 69.9, 68.2–67.0 (C_2^A, C_2^B, C_2^C, C_2^D, C_2^E, C_2^F, C_3^A, C_3^B, C_3^C, C_3^D, C_3^E, C_3^F, C_4^A, C_4^B, C_4^C, C_4^D, C_4^E, C_4^F, C_5^A, C_5^B, C_5^C C_5^D, C_5^E, C_5^F, $OCH_2CH_2{=}CH_2$), 40.3 (CH_2Cl), 17.5–17.0 (C_6^A, C_6^B, C_6^C, C_6^D, C_6^E, C_6^F). MALDI-MS for $C_{125}H_{115}ClO_{38}$ (*m/z*): M_r (calcd) 2258.68; M_r (found) 2281.40 $(M+Na)^+$. Anal. Calcd: C 66.41, H 5.13. Found: C 66.66, H 5.00.

3.1.9. Ethyl 3,4-di-*O*-benzoyl-2-*O*-levulinoyl-1-thio-α-L-rhamnopyranoside (16). Compound **11** (1.541 g, 3.70 mmol) was dissolved in CH_2Cl_2 (15 mL) and levulinic acid (1.89 mL, 18.5 mmol), DMAP (271 mg, 2.20 mmol), and DIPC (2.90 mL, 18.5 mmol) were added in succession. The mixture was stirred for 1 h at rt, then filtered over a Celite pad, diluted with CH_2Cl_2, and washed with water. The organic layer was dried and concentrated to afford a residue that after column chromatography (4:1 petroleum ether/ethyl acetate) gave **12** (1.735 g, 91%) as a yellowish oil. $[\alpha]_D$ −7 (*c* 0.5, CH_2Cl_2). IR (thin film, NaCl) 3060, 3020, 2985, 2930, 1726, 1601, 1452 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ 8.00–7.30 (m, 10H), 5.61–5.51 (m, 3H), 5.30 (br s, 1H), 4.46 (dq, *J*=8.8, 6.4 Hz, 1H), 2.71–2.63 (m, 6H), 2.03 (s, 3H), 1.26 (t, *J*=6.2 Hz, 3H), 1.21 (d, *J*=6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 205.8 (CH_2COCH_3), 171.3 ($OCOCH_2CH_2$), 165.9–165.6 (Ph*C*O), 133.6, 133.4 (C_{ipso}), 130.0–128.4 (C-Ar), 81.6 (C_1), 71.5, 71.4, 69.9, 66.6 (C_2, C_3, C_4, C_5), 37.2, 29.1, 27.5, 25.1 ($COCH_2CH_2COCH_3$), 17.0 (C_6), 14.4 (SCH_2CH_3). ESIMS for $C_{27}H_{30}O_8S$ (*m/z*): M_r (calcd) 514.17; M_r (found) 537.41 $(M+Na)^+$. Anal. Calcd: C 63.02, H 5.88. Found: C 63.26, H 5.65.

3.1.10. Allyl (3,4-di-*O*-benzoyl-2-*O*-levulinoyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (17). A mixture of **3** (544 mg, 1.32 mmol) and **16** (1.018 g, 1.98 mmol) was coevaporated three times with toluene, the residue was dried, and then mixed with freshly activated AW-300 4 Å molecular sieves and NIS (282 mg, 2.43 mmol). The mixture was suspended in CH_2Cl_2 (4.0 mL) under an Ar atmosphere, rapidly cooled to −30 °C, and treated with TfOH (43 μL, 0.49 mmol). After 90 min the reaction mixture was rapidly filtered over a Celite pad, diluted with CH_2Cl_2, and washed with 10% $Na_2S_2O_3$ and 1 M $NaHCO_3$. The organic layer was collected, dried, and concentrated to give a residue that after column chromatography (7:2 petroleum ether/ethyl acetate) afforded **17** (946 mg, 83%) as a white foam. $[\alpha]_D$ +60.9 (*c* 1.0, CH_2Cl_2). IR (thin film, NaCl) 3050, 3026, 1731, 1604, 1263 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ 8.03–7.28 (m, 20H), 5.97 (m, 1H), 5.82 (dd, *J*=10.0, 3.4 Hz, 1H), 5.78 (dd, *J*=10.0, 3.0 Hz, 1H), 5.63 (m, 2H), 5.50 (t, *J*=10.0 Hz, 1H), 5.38 (d, *J*=17.2 Hz, 1H), 5.27 (d, *J*=10.6 Hz, 1H), 5.02 (d, *J*=1.6 Hz, 1H), 4.96 (d, *J*=1.4 Hz, 1H), 4.34–4.06 (m, 5H), 2.60 (s, 4H), 2.08 (s, 3H), 1.38 (d, *J*=6.2 Hz, 3H), 1.30 (d, *J*=6.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 205.8 (CH_2COCH_3), 171.3 ($OCOCH_2$), 165.9, 165.6, 165.5, 165.3 (Ph*C*O), 133.6–133.2 (C_{ipso}, $OCH_2CH{=}CH_2$), 130.1–128.4 (C-Ar), 117.9 ($OCH_2CH{=}CH_2$), 99.6, 97.8 (C_1^A, C_1^B), 76.9, 72.1, 71.8, 71.2, 70.3, 69.7, 68.4, 67.6, 67.1 (C_2^A, C_2^B, C_3^A, C_3^B, C_4^A, C_4^B, C_5^A, C_5^B, $OCH_2CH{=}CH_2$), 37.9, 29.8, 28.0 ($COCH_2CH_2COCH_3$), 17.7, 17.6 (C_6^A, C_6^B). ESIMS for $C_{48}H_{48}O_{15}$ (*m*/*z*): M_r (calcd) 864.30; M_r (found) 887.41 $(M+Na)^+$. Anal. Calcd: C 66.66, H 5.59. Found: C 66.86, H 5.50.

3.1.11. (3,4-Di-*O*-benzoyl-2-*O*-levulinoyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzoyl-L-rhamnopyranosyl *N*-phenyl-trifluoroacetimidate (19). Compound **17** (838 mg, 0.97 mmol) was dissolved in 3:1 CH_2Cl_2/MeOH (4.0 mL), $PdCl_2$ (103 mg, 0.58 mmol) was then added, and the mixture was vigorously stirred overnight. It was then filtered over a Celite pad, diluted with CH_2Cl_2, and washed with 5 M NaCl. The organic layer was dried and concentrated to give **14** (664 mg, 83%) that was then mixed with freshly powdered 4 Å MS and suspended in CH_2Cl_2 (12 mL) under Ar atmosphere. The mixture was cooled to 0 °C and then treated with $CF_3C(NPh)Cl$ (148 μL, 1.26 mmol) and NaH (60% dispersion in mineral oil; 58 mg, 1.45 mmol). After 4 h the solution was concentrated at 30 °C. The residue was subjected to neutral alumina (Brockman grade 1) column chromatography (6:1 petroleum ether/ethyl acetate) to give **19** (577 mg, 72%; α/β=1:1) as a white foam. IR (thin film, NaCl) 3026, 3012, 2917, 1732, 1600, 1452 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 8.08–6.84 (m, 50H), 6.40 (br s, 1H), 5.99 (br s, 1H), 5.88–5.43 (m, 11H), 5.13 (br s, 1H), 5.07 (br s, 1H), 5.04 (br s, 1H), 4.60–4.52 (m, 2H), 4.22–4.13 (m, 2H), 2.57 (s, 4H), 2.56 (s, 4H), 2.01 (s, 6H), 1.45 (d, *J*=6.0 Hz, 3H), 1.22 (d, *J*=6.0 Hz, 3H), 1.18 (d, *J*=6.0 Hz, 3H), 1.15 (d, *J*=6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 205.8 (CH_2COCH_3), 171.2 ($OCOCH_2$), 165.8, 165.7, 165.4, 165.3 (Ph*C*O), 143.2 (C=N), 133.4–133.1 (C_{ipso}), 130.0–115.3 (C-Ar), 99.3, 98.3, 95.5, 93.9 ($2C_1^A$, $2C_1^B$), 76.9, 76.8, 74.1, 73.3, 72.5, 72.0, 71.5, 71.4, 71.0, 70.5, 69.9, 69.8, 69.7, 69.5, 67.8, 67.1 ($2C_2^A$, $2C_2^B$, $2C_3^A$, $2C_3^B$, $2C_4^A$, $2C_4^B$, $2C_5^A$, $2C_5^B$), 37.8, 29.7, 27.9 ($COCH_2CH_2COCH_3$), 17.7, 17.3 ($2C_6^A$, $2C_6^B$). ESIMS for $C_{53}H_{48}F_3NO_{15}$ (*m*/*z*): M_r (calcd) 995.30; M_r (found) 1018.40 $(M+Na)^+$. Anal. Calcd: C 63.92, H 4.86, N 1.41. Found: C 63.67, H 4.72, N 1.38.

3.1.12. Propyl (3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-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-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (21). A mixture of **4** (73 mg, 49 μmol) and **2** (195 mg, 0.20 mmol) was coevaporated three times with toluene, the residue was dried, and then mixed with freshly activated AW-300 4 Å molecular sieves, suspended under argon in CH_2Cl_2 (6.0 mL), and stirred at 0 °C. A 10 mg/mL solution of TMSOTf in CH_2Cl_2 (50 μL, 2.2 μmol) was then added. After 3 h the reaction mixture was quenched with some drops of Et_3N. After filtration over a Celite pad, the mixture was concentrated. The residue was subjected to column chromatography (5:1 to 3:2 petroleum ether/ethyl acetate) to give a foamy residue that was dissolved in CH_2Cl_2 (7.0 mL) and then treated with a 26 mg/mL solution of hydrazinium acetate in MeOH (1.0 mL, 0.28 mmol). After 2 h stirring at rt, the mixture was concentrated; a column chromatography (7:1 toluene/ethyl acetate) on the residue afforded **21** (82 mg, 77%) as a white foam. $[\alpha]_D$ +100.8 (*c* 2.0, CH_2Cl_2). IR (thin film, NaCl) 3019, 2924, 1729, 1600, 1269 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.11–7.25 (m, 60H, H-Ar), 5.82 (dd, *J*=10.0, 3.2 Hz, 1H), 5.61–5.52 (m, 5H), 5.41–5.34 (m, 4H), 5.29 (t, *J*=9.6 Hz, 1H), 5.26 (br s, 1H), 5.15 (br s, 1H), 5.10 (br s, 1H), 5.00 (br s, 1H), 4.93 (br s, 1H), 4.91 (br s, 1H), 4.76 (br s, 1H), 4.57 (br s, 1H), 4.48 (dd, *J*=9.6, 3.2 Hz, 1H), 4.36 (m, 2H), 4.22 (m, 3H), 4.11 (m, 1H), 3.99–3.88 (m, 3H), 3.73 (m, 2H), 3.48 (dq, *J*=9.4, 6.2 Hz, 1H), 1.70 (app sextet, *J*=7.4 Hz, 2H), 1.37 (d, *J*=6.2 Hz, 3H), 1.33 (d, *J*=6.0 Hz, 3H), 1.11 (d, *J*=6.1 Hz, 3H), 0.99 (t, *J*=7.4 Hz, 3H), 0.96 (d, *J*=6.1 Hz, 3H), 0.84 (d, *J*=6.2 Hz, 3H), 0.75 (d, *J*=6.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.8–165.0 (Ph*C*O), 133.9–133.3 (C_{ipso}), 130.0–128.0 (C-Ar), 100.8, 100.7, 100.4, 99.3, 99.2, 98.9 (C_1^A, C_1^B, C_1^C, C_1^D, C_1^E, C_1^F), 77.6, 76.9, 76.3, 75.4, 74.8, 73.3, 73.0, 72.0–71.4, 70.6, 70.0, 69.8, 68.4–67.3 (C_2^A, C_2^B, C_2^C, C_2^D, C_2^E, C_2^F, C_3^A, C_3^B, C_3^C, C_3^D, C_3^E, C_3^F, C_4^A, C_4^B, C_4^C, C_4^D, C_4^E, C_4^F, C_5^A, C_5^B, C_5^C, C_5^D, C_5^E, C_5^F, $OCH_2CH_2CH_3$), 22.7 ($OCH_2CH_2CH_3$), 17.4–16.9 (C_6^A, C_6^B, C_6^C, C_6^D, C_6^E, C_6^F), 10.5 ($OCH_2CH_2CH_3$). MALDI-MS for $C_{123}H_{116}O_{37}$ (*m*/*z*): M_r (calcd) 2184.72; M_r (found) 2207.49 $(M+Na)^+$. Anal. Calcd: C 67.57, H 5.35. Found: C 67.80, H 5.22.

3.1.13. Ethyl 2,4-di-*O*-benzoyl-3-*O*-levulinoyl-1-thio-α-L-rhamnopyranoside (24). Compound **23** (86 mg, 0.21 mmol) was dissolved in CH_2Cl_2 (1.0 mL) and levulinic acid (172 μL, 2.07 mmol), DMAP (13 mg, 0.10 mmol), and DIPC (326 μL, 2.07 mmol) were added in succession. The mixture was stirred for 30 min at rt, then diluted with CH_2Cl_2, and washed with water. The organic layer was dried and concentrated to afford a residue that after column chromatography (4:1 petroleum ether/ethyl acetate) gave **24** (96 mg, 89%) as a colorless oil. $[\alpha]_D$ +11.5 (*c* 1.0, CH_2Cl_2). IR (thin film, NaCl) 3058, 3020, 2928, 1726, 1599, 1452 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ 8.12–7.41

(m, 10H), 5.62 (br s, 1H), 5.51 (m, 2H), 5.39 (br s, 1H), 4.43 (dq, J=9.0, 6.4 Hz, 1H), 2.71 (dt, J=7.6, 3.8 Hz, 2H), 2.63 (dt, J=7.6, 3.8 Hz, 2H), 2.48 (dq, J=7.2, 3.2 Hz, 1H), 2.33 (dq, J=7.2, 3.2 Hz, 1H), 2.00 (s, 3H), 1.30 (m, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 205.7 (CH_2COCH_3), 171.5 ($OCOCH_2CH_2$), 165.6, 165.4 (Ph*C*O), 133.4, 133.3 (C_{ipso}), 129.8–128.4 (C-Ar), 82.0 (C_1), 72.1, 71.8, 69.7, 67.1 (C_2, C_3, C_4, C_5), 37.5, 29.2, 27.7, 25.4 ($COCH_2CH_2COCH_3$, SCH_2CH_3), 17.4 (C_6), 14.7 (SCH_2CH_3). ESIMS for $C_{27}H_{30}O_8S$ (*m/z*): M_r (calcd) 514.17; M_r (found) 537.29 $(M+Na)^+$. Anal. Calcd: C 63.02, H 5.88. Found: C 62.95, H 5.96.

3.1.14. Allyl (2,4-di-*O*-benzoyl-3-*O*-levulinoyl-α-L-rhamnopyranosyl)-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (26). A mixture of **25** (53 mg, 0.13 mmol) and **24** (86 mg, 0.17 mmol) was coevaporated three times with toluene, the residue was dried, and then mixed with freshly activated AW-300 4 Å molecular sieves and NIS (47 mg, 0.21 mmol). The mixture was suspended in CH_2Cl_2 (4.0 mL) under an Ar atmosphere, rapidly cooled to −30 °C, and treated with TfOH (5.5 μL, 63 μmol). After 3 h the reaction mixture was rapidly filtered over a Celite pad, diluted with CH_2Cl_2, and washed with 10% $Na_2S_2O_3$ and 1 M $NaHCO_3$. The organic layer was collected, dried, and concentrated to give a residue that after column chromatography (10:1 to 8:1 toluene/ethyl acetate) afforded **26** (97 mg, 87%) as a white foam. $[\alpha]_D$ +84.4 (*c* 1.0, CH_2Cl_2). IR (thin film, NaCl) 3052, 3026, 1733, 1604, 1263 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.23–7.32 (m, 20H), 5.92 (m, 1H), 5.57 (t, J=9.8 Hz, 1H), 5.52 (m, 2H), 5.42–5.21 (m, 3H), 5.16 (br s, 2H), 5.05 (br s, 1H), 4.48 (dd, J=10.0, 3.4 Hz, 1H), 4.24 (ddt, J=12.8, 5.0, 1.2 Hz, 1H), 4.14–4.00 (m, 3H), 2.37 (dt, J=7.4, 3.8 Hz, 2H), 2.23 (dt, J=7.4, 3.8 Hz, 2H), 1.86 (s, 3H), 1.35 (d, J=6.2 Hz, 3H), 1.16 (d, J=6.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 205.6 (CH_2COCH_3), 170.6 ($OCOCH_2CH_2$), 166.0, 165.6, 165.4, 164.8 (Ph*C*O), 133.4, 133.1 (C_{ipso}, $OCH_2CH{=}CH_2$), 129.8–128.3 (C-Ar), 117.8 ($OCH_2CH{=}CH_2$), 99.1, 96.3 (C_1^A, C_1^B), 75.9, 73.0, 72.2, 71.3, 70.2, 68.7, 68.4, 67.2, 66.7 (C_2^A, C_2^B, C_3^A, C_3^B, C_4^A, C_4^B, C_5^A, C_5^B, $OCH_2CH{=}CH_2$), 37.5, 29.2, 27.6 ($COCH_2CH_2COCH_3$), 17.5, 17.2 (C_6^A, C_6^B). ESIMS for $C_{48}H_{48}O_{15}$ (*m/z*): M_r (calcd) 864.30; M_r (found) 887.48 $(M+Na)^+$. Anal. Calcd: C 66.66, H 5.59. Found: C 66.95, H 5.65.

3.1.15. (2,4-Di-*O*-benzoyl-3-*O*-levulinoyl-α-L-rhamnopyranosyl)-(1→2)-2,4-di-*O*-benzoyl-L-rhamnopyranosyl *N*-phenyl-trifluoroacetimidate (22). Compound **26** (178 mg, 0.21 mmol) was dissolved in 3:1 CH_2Cl_2/MeOH (4.0 mL), $PdCl_2$ (19 mg, 0.11 mmol) was then added, and the mixture was vigorously stirred overnight. It was then filtered over a Celite pad, diluted with CH_2Cl_2, and washed with 5 M NaCl. The organic layer was dried and concentrated to give **27** (104 mg, 60%) that was then mixed with freshly powdered 4 Å MS and suspended in CH_2Cl_2 (6.0 mL) under Ar atmosphere. The mixture was cooled to 0 °C and then treated with $CF_3C(NPh)Cl$ (19 μL, 0.16 mmol) and NaH (60% dispersion in mineral oil; 7.6 mg, 0.19 mmol). After 4 h the solution was concentrated at 30 °C. The residue was subjected to neutral alumina (Brockman grade 1) column chromatography (10:1 to 5:1 petroleum ether/ethyl acetate) to give **22** (73 mg, 58%; α/β=1:1) as a white foam. IR (thin film, NaCl) 3028, 3012, 2925, 1728, 1595, 1452 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.25–6.80 (m, 50H), 6.43 (br s, 1H), 6.08 (br s, 1H), 5.70–5.57 (m, 3H), 5.40–5.12 (m, 11H), 4.52 (dd, J=10.0, 3.4 Hz, 1H), 4.16–4.07 (m, 3H), 2.38 (m, 4H), 2.25 (m, 4H), 1.88 (s, 3H), 1.40 (d, J=6.0 Hz, 3H), 1.27 (d, J=6.0 Hz, 3H), 1.20 (d, J=6.0 Hz, 3H), 1.18 (d, J=6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 206.1 (CH_2COCH_3), 170.9 ($OCOCH_2$), 165.8, 165.6, 165.5, 164.8 (Ph*C*O), 143.0 (C=N), 133.7–133.3 (C_{ipso}), 130.0–115.3 (C-Ar), 99.3, 94.1, 93.6 ($2C_1^A$, $2C_1^B$), 75.1, 72.4, 72.0, 71.3, 70.6, 70.1, 69.4, 68.9, 68.7, 67.6 ($2C_2^A$, $2C_2^B$, $2C_3^A$, $2C_3^B$, $2C_4^A$, $2C_4^B$, $2C_5^A$, $2C_5^B$), 37.6, 29.3, 27.7 ($COCH_2CH_2COCH_3$), 17.7, 17.3 ($2C_6^A$, $2C_6^B$). ESIMS for $C_{53}H_{48}F_3NO_{15}$ (*m/z*): M_r (calcd) 995.30; M_r (found) 1018.29 $(M+Na)^+$. Anal. Calcd: C 63.92, H 4.86, N 1.41. Found: C 63.59, H 4.74, N 1.38.

3.1.16. Propyl α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranoside (28). A mixture of **21** (40 mg, 18 μmol) and **22** (72 mg, 72 μmol) was coevaporated three times with toluene, the residue was dried, and then mixed with freshly activated AW-300 4 Å molecular sieves, suspended under argon in CH_2Cl_2 (3.0 mL), and stirred at 0 °C. An 8.2 mg/mL solution of TMSOTf in CH_2Cl_2 (50 μL, 1.8 μmol) was then added. After stirring the reaction mixture at 0 °C overnight, some drops of Et_3N were added. The mixture was filtered over a Celite pad and concentrated. The residue was subjected to column chromatography (10:1 to 8:1 toluene/ethyl acetate) to give a foamy residue that was dissolved in 3:1 MeOH/CH_2Cl_2 (2.0 mL) and then treated with a 3.5 M methanolic solution of NaOMe (90 μL, 0.31 mmol). The solution was heated to 40 °C and stirred at this temperature over 2 days; it was then neutralized with Amberlist-15 H^+, filtered, and concentrated. The residue was subjected to a gel-filtration chromatography to give **28** (10.8 mg, 49%) as a white wax. $[\alpha]_D$ +81 (*c* 0.6, H_2O). ^{1}H NMR (D_2O, 400 MHz) δ 5.19 (br s, 1H, H_1^E), 5.12 (br s, 1H, H_1^F), 5.11 (br s, 1H, H_1^B), 5.04 (br s, 1H, H_1^H), 5.02 (br s, 1H, H_1^D), 4.96 (br s, 2H, H_1^C, H_1^G), 4.87 (br s, 1H, H_1^A), 4.15 (m, 3H, H_2^C, H_2^D, H_2^G), 4.08 (m, 4H, H_2^B, H_2^E, H_2^F, H_2^H), 3.96 (dd, $J_{3,4}$=9.8 Hz, $J_{3,2}$=3.2 Hz, 1H, H_3^E), 3.92–3.82 (m, 9H, H_2^A, H_3^A, H_3^B, H_3^C, H_3^D, H_3^F, H_3^G, H_3^H, H_5^E), 3.77–3.72 (m, 8H, H_5^A, H_5^B, H_5^C, H_5^D, H_5^F, H_5^G, H_5^H), 3.65 (dt, J_{gem}=13.9 Hz, J_{vic}=6.5 Hz, 1H, $OCHHCH_2CH_3$), 3.56–3.46 (m, 9H, H_4^A, H_4^B, H_4^C, H_4^D, H_4^E, H_4^F, H_4^G, H_4^H, $OCHHCH_2CH_3$), 1.61 (app sextet, J=7.0 Hz, 2H, $OCH_2CH_2CH_3$), 1.29 (m, 24H, H_6^A, H_6^B, H_6^C, H_6^D, H_6^E, H_6^F, H_6^G, H_6^H), 0.91 (t, J=7.0 Hz, 3H, $OCH_2CH_2CH_3$); ^{13}C NMR (D_2O, 100 MHz) δ 103.0 (C_1^D, C_1^H), 102.7 (C_1^C, C_1^G), 101.6 (C_1^E), 101.5 (C_1^B, C_1^F), 98.9 (C_1^A), 79.0 (C_2^A), 78.9 (C_2^B, C_2^E, C_2^F), 78.8 (C_3^C, C_3^G), 78.3 (C_3^D), 72.9 (C_4^A, C_4^B, C_4^E, C_4^F, C_4^H), 72.0 (C_4^C, C_4^D, C_4^G), 70.6 (C_3^E), 70.4 (C_3^A, C_3^H, C_5^E), 70.3 (C_3^B, C_3^H, $OCH_2CH_2CH_3$), 70.1 (C_5^B, C_5^C, C_5^D, C_5^F, C_5^G, C_5^H), 69.8 (C_5^A), 22.5 ($OCH_2CH_2CH_3$), 17.4 (C_6^A, C_6^B, C_6^C, C_6^D, C_6^E, C_6^F, C_6^G, C_6^H), 10.4 ($OCH_2CH_2CH_3$). MALDI-MS for $C_{51}H_{88}O_{33}$ (*m/z*): M_r (calcd) 1228.52; M_r (found) 1251.15 $(M+Na)^+$. Anal. Calcd: C 49.83, H 7.22. Found: C 49.59, H 7.44.

3.1.17. Allyl α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranoside (29). A solution of **1** (24 mg, 15.5 μmol)

in MeOH (1.0 mL) was treated with a 0.7 M methanolic solution of NaOMe (500 μL, 0.35 mmol). The solution was heated to 40 °C and stirred at this temperature overnight; it was then neutralized with Amberlist-15 H^+, filtered, and concentrated. The residue was subjected to a gel-filtration chromatography to give **29** (7.8 mg, 78%) as a white wax. $[\alpha]_D$ +25 (*c* 0.5, H_2O). ^1H NMR (D_2O, 400 MHz) δ 6.12 (m, 1H, $OCH_2CH{=}CH_2$), 5.52 (d, J=17.2 Hz, 1H, *trans* $OCH_2CH{=}CHH$), 5.47 (d, J=10.4, 1H, *cis* $OCH_2CH{=}CHH$), 5.25 (br s, 1H, H-1_B), 5.20 (br s, 1H, H-1_D), 5.12 (br s, 1H, H-1_C), 5.08 (br s, 1H, H-1_A), 4.40 (br d, J=5.1 Hz, 1H, $OCHHCH{=}CH_2$), 4.37 (br d, J=5.1 Hz, 1H, $OCHHCH{=}CH_2$), 4.31 (br s, 1H, H_2^C), 4.25 (br s, 1H, H_2^B), 4.22 (br s, 1H, H_2^D), 4.09 (br s, 1H, H_2^A), 4.07–3.96 (m, 5H, H_3^A, H_3^B, H_3^C, H_3^D, H_5^D), 3.93–3.86 (m, 3H, H_5^A, H_5^B, H_5^C), 3.70 (t, J=9.8 Hz, 1H, H_4^C), 3.63 (m, 3H, H_4^A, H_4^B, H_4^D), 1.45 (m, 12H, H_6^A, H_6^B, H_6^C, H_6^D); ^{13}C NMR (D_2O, 100 MHz) δ 133.5 ($OCH_2CH{=}CH_2$), 119.1 ($OCH_2CH{=}CH_2$), 102.8 (C_1^D), 102.4 (C_1^C), 101.4 (C_1^B), 97.7 (C_1^A), 78.9 (C_2^A), 78.5 (C_2^B), 78.4 (C_2^C), 72.5–72.4 (C_4^A, C_4^B, C_4^D), 71.6 (C_4^C), 70.5–70.1 (C_2^C, C_2^D, C_3^A, C_3^B, C_3^D, C_5^D), 69.7 (C_5^C), 69.6 (C_5^A), 69.5 (C_5^B), 68.6 ($OCH_2CH{=}CH_2$), 17.0–16.9 (C_6^A, C_6^B, C_6^C, C_6^D). MALDI-MS for $C_{27}H_{46}O_{17}$ (*m/z*): M_r (calcd) 642.27; M_r (found) 643.49 $(M+Na)^+$. Anal. Calcd: C 50.46, H 7.21. Found: C 50.20, H 7.36.

3.1.18. Allyl α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranoside (30). A solution of **15** (22 mg, 9.7 μmol) in 3:1 $MeOH/CH_2Cl_2$ (2.0 mL) was treated with a 3.5 M methanolic solution of NaOMe (90 μL, 0.31 mmol). The solution was heated to 40 °C and stirred at this temperature overnight; it was then neutralized with Amberlist-15 H^+, filtered, and concentrated. The residue was subjected to a gel-filtration chromatography to give **30** (7.0 mg, 77%) as a white wax. $[\alpha]_D$ +47 (*c* 0.5, H_2O). ^1H NMR (D_2O, 400 MHz) δ 5.96 (m, 1H, $OCH_2CH{=}CH_2$), 5.36 (d, J=17.2, 1H, *trans* $OCH_2CH{=}CHH$), 5.31 (d, J=10.4 Hz, 1H, *cis* $OCH_2CH{=}CHH$), 5.22 (br s, 1H, H_1^E), 5.10 (br s, 1H, H_1^B), 5.02 (br s, 1H, H_1^D), 4.96 (br s, 2H, H_1^C, H_1^F), 4.92 (br s, 1H, H_1^A), 4.24 (br d, J=5.1 Hz, 1H, $OCHHCH{=}CH_2$), 4.21 (br d, J=5.1 Hz, 1H, $OCHHCH{=}CH_2$), 4.17 (br s, 1H, H_2^C), 4.14 (br s, 1H, H_2^D), 4.11 (br s, 1H, H_2^B), 4.08 (br s, 2H, H_2^E, H_2^F), 4.01–3.77 (m, 13H, H_2^A, H_3^A, H_3^B, H_3^C, H_3^D, H_3^E, H_3^F, H_5^A, H_5^B, H_5^C, H_5^D, H_5^E, H_5^F), 3.58 (m, 2H, H_4^C, H_4^D), 3.51–3.44 (m, 4H, H_4^A, H_4^B, H_4^E, H_4^F), 1.29 (m, 18H, H_6^A, H_6^B, H_6^C, H_6^D, H_6^E, H_6^F); ^{13}C NMR (D_2O, 100 MHz) δ 133.9 ($OCH_2CH{=}CH_2$), 119.5 ($OCH_2CH{=}CH_2$), 103.0 (C_1^D), 102.9 (C_1^C, C_1^F), 101.7 (C_1^B, C_1^E), 98.0 (C_1^A), 79.3 (C_2^A), 79.0 (C_2^E), 78.9 (C_2^B), 78.8 (C_2^C), 78.5 (C_3^D), 72.8–72.2 (C_4^A, C_4^B, C_4^C, C_4^D, C_4^E, C_4^F), 70.7–70.5 (C_2^C, C_2^D, C_2^F, C_3^A, C_3^B, C_3^E C_3^F, C_5^C), 70.0–69.8 (C_5^A, C_5^B, C_5^D, C_5^E, C_5^F), 68.9 ($OCH_2CH{=}CH_2$), 17.4–17.3 (C_6^A, C_6^B, C_6^C, C_6^D, C_6^E, C_6^F). MALDI-MS for $C_{39}H_{66}O_{25}$ (*m/z*): M_r (calcd) 934.39; M_r (found) 935.41 $(M+H)^+$. Anal. Calcd: C 50.10, H 7.12. Found: C 49.91, H 7.29.

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