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Synthesis of the Rhamnosyl Trisaccharide Repeating Unit To Mimic the Antigen Determinant of *Pseudomonas syringae* Lipopolysaccharide

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Abstract: The trisaccharide 2,3,4-*O*-tribenzyl-α-L-rhamnosyl-(1→3)-4-*O*-acetyl-2-*O*-benzoyl-(1→2)-4-*O*-acetyl-3-*O*-benzoyl-α-L-rhamnosyl-1-(4-tolyl)thio-α-L-rhamnopyranoside was prepared from the thio-sugar 1-(4-tolyl)thio-α,β-L-rhamnopyranoside from the nonreducing end to the reducing end. The two acceptors possessing 2- and 3-OH groups for the construction of the trisaccharide were obtained from a 2,3-benzylidine-protected thio-sugar in a one-pot deprotection manner in a respective ratio of 1:2.5. As donors for glycosylation, the thio-sugars of both mono- and disaccharides were converted to trichloroacetimido rhamnosides. Through this chemoselective strategy, a trisaccharide was obtained that retained an anomeric thio group for coupling with ceramide moieties. Bioassays are in progress.

Key words: cancer vaccine, imidate, rhamnose, trisaccharide, glycosylation

Lipopolysaccharide (LPS), also called endotoxin, is found in Gram-negative bacteria in which it forms the major anchoring component of the membrane surface.[1] LPS is comprised of two components, namely, lipid A and polysaccharide.[2] The exterior polysaccharide portion is composed of three types of saccharide moieties termed the inner core, outer core and O-specific chain. Of these, the O-specific chain is an invariant repeating unit of oligosaccharides. When mammalians ingest a small amount of LPS, their immune system will respond to this foreign molecule by stimulating slight inflammatory effects, the symptoms of which are negligible, however, in cases when large amounts of LPS is taken in, this may result in high fever, septic shock or even death. The saccharide portion has been recognized to be a key player in triggering this immune response. Through the recent study of this specific glycan–glycan interaction between pathogens and their hosts, glycoconjugates have acquired a new terminology: glycosynapse.[3]

LPS was believed to exert its damaging bioactivity through a two-step process: inducing a general immune response by the lipid A portion, and targeting cells expressing biomolecules bearing a structural resemblance to the saccharide portion of LPS. Thus, modification of the structure of LPS to redirect the intrinsic immune responses specifically against some diseases such as cancer cells has become an emerging interest in recent glycobiology field. The synthesis of such molecules, with characteristics that could initiate immuno-recognition, is of critical importance for the study of possible cancer vaccines. For example, the synthetic alpha-gal ceramide has been extensively investigated for its ability to induce prominent immune response of natural killer T cells, mediated by signaling CD1d molecules.[4,5]

Among these glycoconjugates, the repeating units are thought to play a central role in tuning the immune specificity. We are interested in the development of glycoceramide derivatives and have focused especially on the assembly of the glyco portion of the trisaccharide moiety of rhamnose. While rhamnose has been reported to be a rare sugar component found in natural LPS or in some herbs such as Reishi,[6] some strains of bacteria, such as *Pseudomonas syringae* pv. *coronafaciens* IMV 9030 and *atrofaciens* IMV 8281 were found to possess this specific sequence of α-L-rha(1→3)α-L-rha(1→2)α-L-rha.[7,8] Furthermore, a tetrasaccharide comprising these three rhamnose residues has been recognized as the antigen determinant responsible for the toxin of *Bacillus anthracis*.[9,10]

Herein, we report the facile preparation of a trisaccharide of rhamnose **26** bearing a thio group ready for subsequent glycosylation with ceramide.[11] As the ceramide moiety was synthesized via a multi-step synthesis, our trisaccharide portion **1** was assembled first. The retrosynthetic analysis of this trisaccharide moiety is shown in Scheme 1.

Encouraged by the recent success of constructing oligosialic acids via chemoselective glycosylation with alternate thio and phosphite glycosides,[12] we attempted to assemble the trisaccharide unit from the nonreducing end to the reducing end. Due to the importance of protecting groups with respect to tuning the reactivity of glycosylation, we initially synthesized and compared both ether- and ester-type protecting groups. Preparation of the three thio donors **8**, **10** and **11** was achieved via peracetylation[13] of the four hydroxyl groups of rhamnose **6**, introduction of a 4-thiotolyl group,[14] deprotection of the hydroxyl groups[14] and, finally, protection with benzyl[15] and benzoyl groups (Scheme 2).

After removal of the thio groups, the three hemiacetals **12**,[13,16] **13**[17] and **14**,[18] were obtained in high yields. Upon introduction of the trichloroacetamido groups, the three

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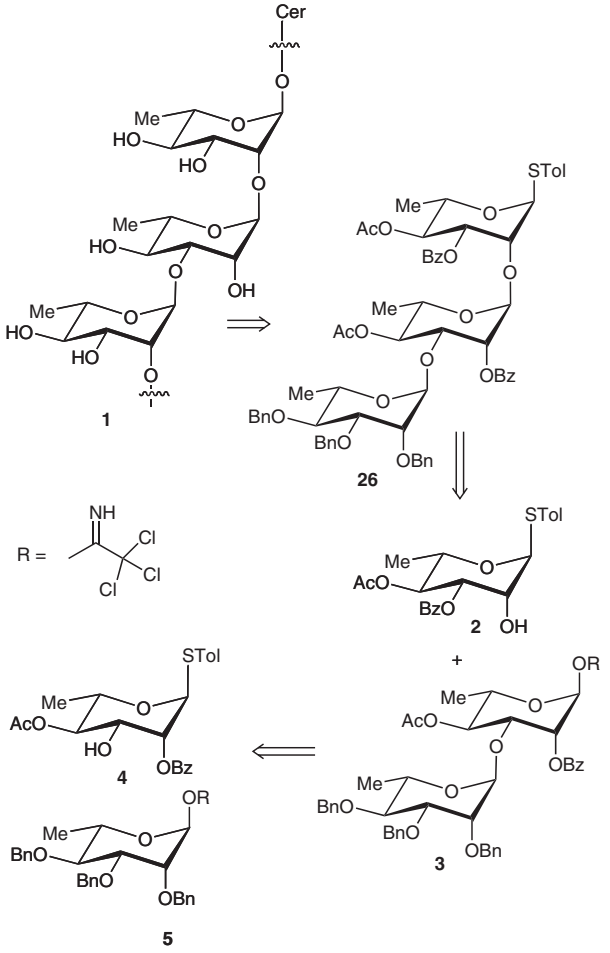
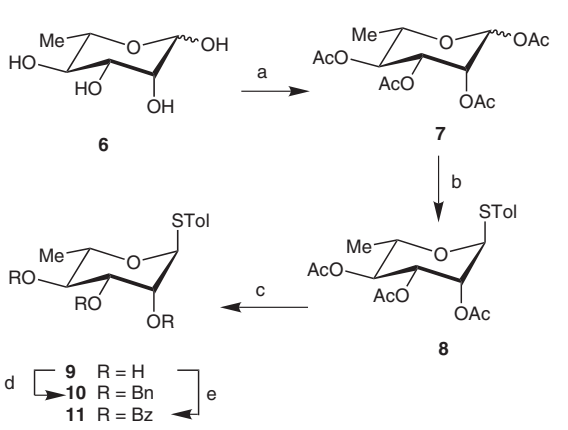
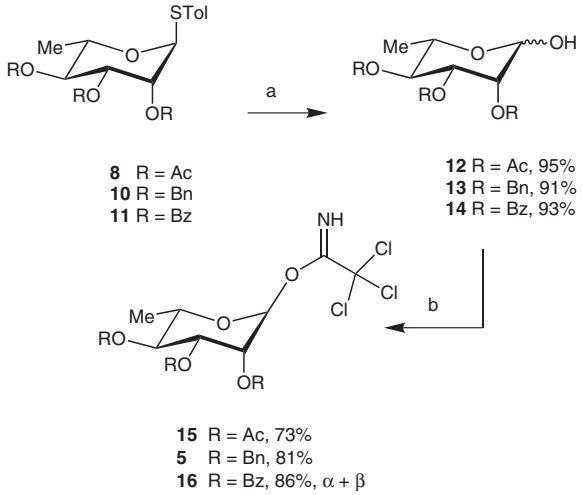


Scheme 1 Retrosynthetic analysis of the preparation of the rhamnose trisaccharide repeating unit; Cer = ceramide.

imidates **5**,[16c] **15**,[17a] and **16**,[19] were obtained (Scheme 3). Though no NMR spectrum was available for compound **16**, the presence of a sole α-anomer was suggested by the observation of a single spot by TLC analysis. Adjusting of the basicity of the system is a common method for controlling the stereoselectivity of the imidates in benzyl-protected rhamnose.[17a] For example, α- and β-imidates could be independently prepared by using either a strong base (e.g. NaH) or a weak base (e.g. K_2CO_3), respectively. However, no analogous rules for either acetyl- or benzoyl-protected rhamnose could be found in the literature. Common bases used for the preparation of acetyl- and benzoyl-protected imidates have been cesium carbonate or a combination of potassium carbonate and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), respectively. The α-configurational assignments of the three imidates **15**, **5** and **16** were made on the basis of empirical data.[16c,19,20]



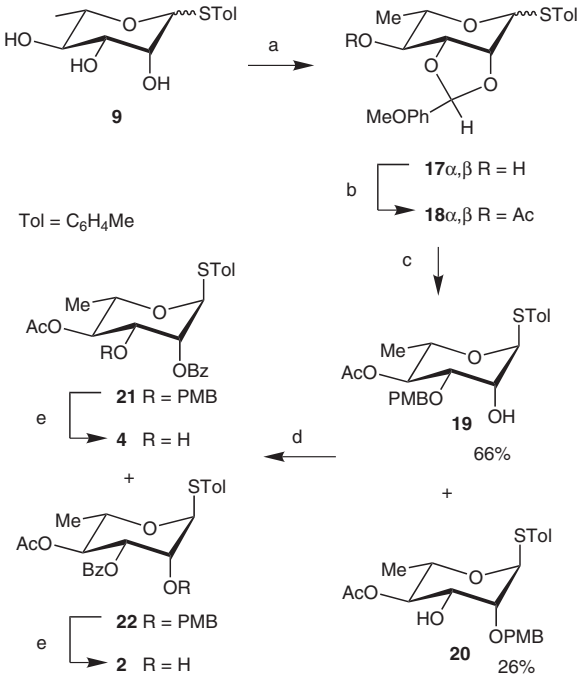
Scheme 2 *Reagents and conditions*: (a) Ac_2O, DMAP, pyridine, 30 min, 95%; (b) *p*-thiocresol, $BF_3{\cdot}Et_2O$, CH_2Cl_2, 0 °C→r.t., 1 h, 81%; (c) MeONa, MeOH, H^+, 20 min, 99%; (d) NaH, 0 °C, 20 min, BnBr, r.t., 1 h, 89%; (e) BzCl, DMAP, pyridine, 30 min, 95%.



Scheme 3 *Reagents and conditions*: (a) NBS, acetone–H_2O, r.t., 1 h, 90%; (b) CH_2Cl_2, r.t.; (i) for Ac: K_2CO_3 (1.1 equiv), CCl_3CN (20 equiv), 2.5 h; (ii) for Bn: NaH (1.1 equiv), CCl_3CN (10 equiv), 2.5 h; (iii) for Bz: DBU (0.5 equiv), CCl_3CN (10 equiv), 2 h.

While an efficient preparation of an acceptor bearing a 3-OH group has been reported, a corresponding, facile procedure for the preparation of the 2-OH isomer remains a challenge.[21,22] The typical four-step synthesis of the 2-OH acceptor, starting from acetyl-protected 1-bromorhamnoside via reaction with sym-collidine and subsequent deprotection, was relatively lengthy and low-yielding (24%). Our preparation of both acceptors **19** and **20**, simultaneously, was achieved in three steps (Scheme 4).

Attempts at coupling the donor **5** with acceptor **19** failed to provide the corresponding disaccharide due to the propensity of the *p*-methoxyphenyl (PMB) group to be eliminated. This group was therefore replaced by a more stable ester-type protecting group. For convenience, a mixture of compounds **19** and **20** was protected with the benzoyl group to provide a mixture of **21** and **22**; however, these compounds could not be separated by column chromatography. Following deprotection with cerium(IV) ammonium nitrate (CAN), the mixture of compounds **4** and **2** obtained could only be partially (~30%) purified by chromatography. For analytical purposes, further purification of samples of the isolated compounds **4** and **2** by HPLC was performed. Due to the problems with purification, the two isomers were chromatographically separated at an earlier stage of the preparation; taking advantage of the

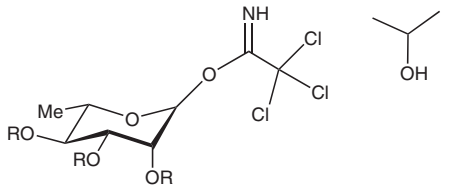


Scheme 4 *Reagents and conditions*: (a) CSA, DMF, *p*-anisaldehyde dimethyl acetal, 78%; (b) DMAP, pyridine, Ac_2O, 97% (**18α**–**18β**, 2:3); (c) Na_2CNBH_3, 4Å MS, CH_2Cl_2, TFA, r.t., 16 h, 92% (from **18α**); (d) DMAP, pyridine, BzCl, r.t., 30 min, 97% (**21**–**22**, 2.5:1), obtained from a mixture of **19**,**20**; (e) CAN, MeCN–H_2O (9:1), r.t., 1 h, 72% (**4**–**2**, 2.5:1), obtained from a mixture of **21**,**22**.

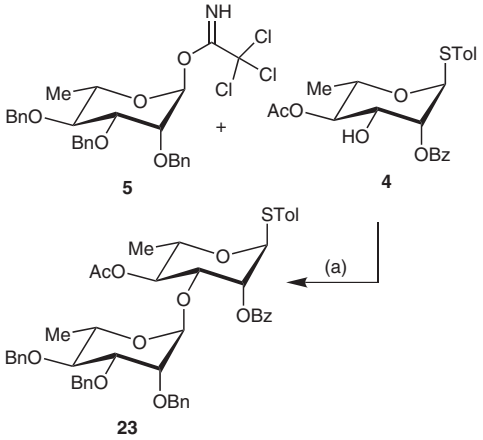
subtle R_f differences (6%), compounds **19** and **20** could be separated by chromatography. As indicated in Table 1, the glycosylation yield of the three donors was satisfactory, particularly in the case of the ester-protected sugar **15**.

Disaccharide **23** was also obtained (Scheme 5) which, through application of the method shown in Scheme 2, was used to form the imidate of disaccharide **25** (76% yield from **23**; Scheme 6). Coupling of **25** with the 2-OH acceptor **2** gave the trisaccharide **26** in high yield.

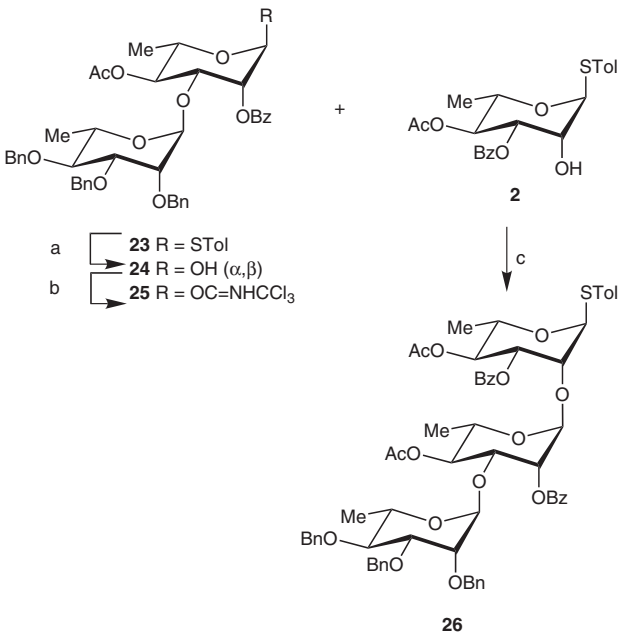
Table 1 Effect of Protecting Groups on Glycosylation Yield[a]

Donor (1 equiv)	Acceptor (2 equiv)	TMSOTf (equiv)	Yield (%)
			
5 (R = Bn)		0.3	70
16 (R = Bz)		0.2	80
15 (R = Ac)		0.3	90

[a] In CH_2Cl_2 at –20 °C.



Scheme 5 *Reagents and conditions*: (a) 4Å MS, CH_2Cl_2, TMSOTf, 0 °C (30 min)→r.t., 78%.



Scheme 6 *Reagents and conditions*: (a) NBS, acetone–H_2O, r.t., 1 h, 92%; (b) DBU (0.5 equiv), CCl_3CN (10 equiv), CH_2Cl_2, 1.5 h, 83%; (c) 4Å MS, CH_2Cl_2, TMSOTf, 0 °C (15 min)→r.t., 84%.

In brief, the current method provides a facile route for the preparation of two acceptors **4** and **2**, simultaneously, which can be easily separated by column chromatography. The glycosylation yield was improved when more reactive, ester-protected donors **15** and **16** were added. The glycosylation of trisaccharide donor **26** with ceramide acceptors is in progress.

NMR spectroscopy was performed at the department of chemistry of National Tsing-Hua University (NTHU). ^1H NMR and ^{13}C NMR spectra (including DEPT-135) were recorded using 500 MHz Varian Unity INOVA instruments. ESI-QTOF mass spectroscopy was performed at the department of applied chemistry of the National Chiao Tung University (NCTU). ESI-MS spectra were recorded using a Micromass Q-Tof liquid chromatograph tandem mass spectrometer. Analytical TLC was performed using Macherey–Nagel

silica gel 60 F254 precoated plates, which were examined by UV absorption at 254 nm and visualized by staining with a solution prepared from 5% *p*-anisaldehyde, sulfuric acid, acetic acid and EtOH under heating. Column chromatography employed Merck Geduran Si 60 silica gel (230–400 mesh). Solvents of either industrial grade or reagent grade (EtOAc, acetone and *n*-hexane) were distilled prior to column chromatography. Solvents of reagent grade were dried before use. DMF was distilled over CaH_2 under reduced pressure and stored over 4Å MS. CH_2Cl_2 and pyridine were distilled over CaH_2. THF was distilled over Na after repeated treatment with $FeSO_4$ and KOH for the removal of peroxide. MeOH was distilled over Mg. Normal-phase HPLC (Agilent 1100) was equipped with a sample loop (500 μL) and a semipreparative column (9.4 × 250 mm ZORBAX SIL, 5 μm material). Constant conditions were used [*n*-hexane–EtOAc, 3:1; flow rate 3 mL/min; UV detection (260 nm)].

2,3,4-Tri-*O*-acetyl-1-(4-tolyl)thio-α-L-rhamnopyranoside (8)

A mixture of L-rhamnose (7.6 g, 22.8 mmol), DMAP (0.55 g, 4.5 mmol) and pyridine (40 mL) was stirred at r.t. under N_2 for 10 min. Ac_2O (23 mL) was added and the mixture was stirred for 30 min. The reaction was followed by monitoring formation of the product 1,2,3,4-*O*-tetraacetyl-α,β-L-rhamnopyranoside (**7**; R_f = 0.86) by TLC (*n*-hexane–EtOAc, 1:1). Upon completion, the solvent was removed under reduced pressure and the crude mixture was purified by column chromatography (*n*-hexane–EtOAc, 1:1) to provide a mixture of the products in 95% yield (14.3 g). A portion of this mixture (2.42 g, 7.27 mmol) and *p*-thiocresol (1.24 g, 8.42 mmol) was dissolved in CH_2Cl_2 (5 mL) and the solution was cooled to 0 °C. To the solution was added $BF_3{\cdot}Et_2O$ (2.06 mL, 14.6 mmol) slowly under N_2. The reaction mixture was warmed to r.t. and stirred for 60 min until the starting material (R_f = 0.22; *n*-hexane–EtOAc, 7:3) was consumed and the products **8** (R_f = 0.55 and R_f = 0.45) were formed. After the removal of the volatile solvents, the residue was partitioned between CH_2Cl_2 (30 mL) and sat. aq solutions of $NaHCO_3$ (15 mL), NaCl (15 mL) and H_2O (10 mL) sequentially. The organic layer was then dried (Na_2SO_4), concentrated and the residue was purified by column chromatography on silica gel (*n*-hexane–EtOAc, 3:1) to give **8**.

Yield: 81% (2.33 g).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.22 (d, $J_{5,6}$ = 6.0 Hz, 3 H, H-6), 1.99 (s, 3 H, CH_3), 2.06 (s, 3 H, CH_3), 2.11 (s, 3 H, CH_3), 2.31 (s, 3 H, $SPhCH_3$), 4.35 (dq, $J_{5,4}$ = 9.5 Hz, $J_{5,6}$ = 6.0 Hz, 1 H, H-5), 5.11 (dd, $J_{4,3}$ = 10.5 Hz, $J_{4,5}$ = 9.5 Hz, 1 H, H-4), 5.27 (dd, $J_{3,4}$ = 10.5 Hz, $J_{3,2}$ = 3.5 Hz, 1 H, H-3), 5.30 (br s, 1 H, H-1), 5.46 (dq, $J_{2,3}$ = 3.5 Hz, $J_{2,1}$ = 1.5 Hz, 1 H, H-2), 7.10 (d, *J* = 8.0 Hz, 2 H, H_{arom}), 7.33 (d, *J* = 8.0 Hz, 2 H, H_{arom}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.30 (C-6), 20.68 ($OCCH_3$), 20.81 ($OCCH_3$), 20.91 ($OCCH_3$), 21.11 ($SPhCH_3$), 67.67 (CH), 69.36 (CH), 71.18 (CH), 71.28 (CH), 86.02 (CH), 129.36 (arom., $SPhCH_3$), 129.95 (arom., $SPhCH_3$), 132.45 (arom., $SPhCH_3$), 138.21 (arom., $SPhCH_3$), 169.93 ($OCCH_3$), 170.01 ($OCCH_3$) 170.03 ($OCCH_3$).

MS (ESI+Q-TOF): *m*/*z* = 419.1 $[M + Na]^+$, 273.1 $[M - SPhCH_3 + H]$.

1-(4-Tolyl)thio-α-L-rhamnopyranoside (9)

A mixture of compounds **8** (2.64 g, 9.8 mmol), MeONa (0.36 g, 9.8 mmol) and MeOH (20 mL) was stirred at r.t. for 20 min. The products **9** (R_f = 0.13 and R_f = 0.06) were detected on TLC (*n*-hexane–EtOAc, 1:1). After completion of the reaction, the reaction mixture was treated with Amberlite IR-120 (H^+ form) and filtered. After concentration, the residue was purified by column chromatography on silica gel (*n*-hexane–EtOAc, 3:7) to give **9**.

Yield: 99% (1.8 g).

^{1}H NMR (500 MHz, CD_3OD): δ = 1.26 (d, $J_{6,5}$ = 6.5 Hz, 3 H, H-6), 2.31 (s, 3 H, $SPhCH_3$), 3.44 (dd, $J_{4,3}$ = 10.0 Hz, $J_{4,5}$ = 9.5 Hz, 1 H, H-4), 3.64 (dd, $J_{3,4}$ = 10.0 Hz, $J_{3,2}$ = 3.5 Hz, 1 H, H-3), 4.05 (dq, $J_{5,4}$ = 9.5 Hz, $J_{5,6}$ = 6.0 Hz, 1 H, H-5), 4.56 (dd, $J_{2,3}$ = 3.5 Hz, $J_{2,1}$ = 1.0 Hz, 1 H, H-2), 5.28 (d, $J_{1,2}$ = 1.0 Hz, 1 H, H-1), 7.13 (d, *J* = 8.5 Hz, 2 H, H_{arom}), 7.34 (d, *J* = 8.5 Hz, 2 H, H_{arom}).

^{13}C NMR (125 MHz, CD_3OD): δ = 17.83 (C-6), 21.08 ($SPhCH_3$), 70.88 (CH), 72.91 (CH), 73.82 (CH), 74.17 (CH), 90.56 (C-1), 130.78 (arom., 2 × C), 132.22 (arom.), 133.28 (arom., 2 × C), 138.85 (arom.).

MS (ESI+Q-TOF): *m*/*z* = 541.2 $[2 \times M + H]^+$, 293.1 $[M + Na]^+$, 271.1 $[M + H]^+$.

2,3-*O*-Di(4-methoxy)benzylidene-1-(4-tolyl)thio-α,β-L-rhamnopyranoside (17α,β)

A mixture of compounds **9** (0.67 g, 2.48 mmole), CSA (175 mg, 0.74 mmol), DMF (8 mL) and *p*-anisaldehyde dimethyl acetal (0.5 mL, 3 mmol) was stirred at 50 °C under N_2 for 3 h. The starting materials **9** (R_f = 0.13 and R_f = 0.06) were consumed, while products **17** (R_f = 0.44) were detected on TLC (*n*-hexane–EtOAc, 1:1). After removal of the volatile solvents, the residue was partitioned between EtOAc (10 mL) and sat. aq $NaHCO_3$ (3 mL) and NaCl (3 mL) sequentially. The organic layer was dried (Na_2SO_4), filtered and concentrated to give a residue which was purified by column chromatography on silica gel (*n*-hexane–EtOAc, 1:1) to give **17**.

Yield: 78% (755 mg).

^{1}H NMR (500 MHz, benzene-d_6): δ = 1.22 (d, $J_{6,5}$ = 6.5 Hz, 3 H, H-6), 1.29 (d, $J_{5,6}$ = 6.0 Hz, 3 H, H-6), 1.99 (s, 3 H, $SPhCH_3$), 3.26 (s, 3 H, $PhOCH_3$), 3.29 (s, 3 H, $PhOCH_3$), 3.47 (dq, $J_{5,6}$ = 6.5 Hz, $J_{5,4}$ = 7.5 Hz, 1 H, H-5), 3.56 (dq, $J_{5,6}$ = 6.0 Hz, $J_{5,4}$ = 7.5 Hz, 1 H, H-5), 4.16 (dd, $J_{4,3}$ = 7.5 Hz, $J_{4,5}$ = 7.5 Hz, 1 H, H-4), 4.24 (d, $J_{2,3}$ = 6.0 Hz, 1 H, H-2), 4.27 (dd, $J_{4,3}$ = 7.0 Hz, $J_{4,5}$ = 7.5 Hz, 1 H, H-4), 4.27 (dd, $J_{3,2}$ = 6.0 Hz, $J_{3,4}$ = 7.0 Hz, 1 H, H-3), 4.33 (dd, $J_{3,2}$ = 5.5 Hz, $J_{3,4}$ = 7.0 Hz, 1 H, H-3), 4.41 (d, $J_{2,3}$ = 5.5 Hz, 1 H, H_2), 4.49 (dd, $J_{3,4}$ = 7.5 Hz, $J_{3,2}$ = 5.0 Hz, 1 H, H-3), 5.76 (s, 1 H, O_2CHPh or H-1), 5.94 (s, 1 H, O_2CHPh or H-1), 6.00 (s, 1 H, O_2CHPh or H-1), 6.10 (s, 1 H, O_2CHPh or H-1), 6.73 (d, *J* = 9.0 Hz, 2 H, H_{arom}), 6.84 (d, *J* = 8.0 Hz, 2 H, H_{arom}), 7.30 (d, *J* = 8.0 Hz, 2 H, H_{arom}), 7.33 (d, *J* = 7.5 Hz, 2 H, H_{arom}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.05 (C-6), 17.07 (C-6), 21.01 ($SPhCH_3$), 55.16 ($O_2CHPhOCH_3$), 55.45 ($O_2CHPhOCH_3$), 66.91 ($O_2CHPhOCH_3$), 69.10 (C-4), 71.97 (C-3), 72.10, 72.39, 75.43, 76.01 (C-2), 76.43 (C-2), 77.00, 86.02 (C-1), 129.36 (arom.), 129.95 (arom., 2 × C), 132.45 (arom., 2 × C), 138.21 (arom.), 169.93 ($OCCH_3$), 170.01 ($OCCH_3$), 170.03 ($OCCH_3$).

MS (ESI+Q-TOF): *m*/*z* = 389.2 $[M + H]^+$.

2,3-*O*-Di(4-methoxy)benzylidene-4-*O*-acetyl-1-(4-tolyl)thio-α-L-rhamnopyranoside (18α)

A mixture of compound **17α,β** (157 mg, 0.4 mmol), DMAP (13.8 mg, 0.1 mmol) and pyridine (0.8 mL) was stirred for 20 min. Ac_2O (0.5 mL) was added and the reaction was stirred at r.t. for 30 min. Products **18α** and **18β** (both R_f = 0.61) were detected on TLC (*n*-hexane–EtOAc, 7:3). After removal of the volatile solvents, the crude product was purified by column chromatography on silica gel (*n*-hexane–EtOAc, 4:1) to give a mixture of **18α** and **18β** in 97% yield (147 mg) in a ratio of 2:3 respectively. An analytical sample was further purified with normal phase HPLC to provide pure **18α** and **18β**.

^{1}H NMR (500 MHz, benzene-d_6): δ = 1.19 (d, $J_{6,5}$ = 6.5 Hz, 3 H, H-6), 1.68 (s, 3 H, CH_3), 2.00 (s, 3 H, $SPhCH_3$), 3.24 (s, 3 H, $PhOCH_3$), 4.38 (dq, $J_{5,4}$ = 10.0 Hz, $J_{5,6}$ = 6.5 Hz, 1 H, H-5), 4.45 (d, $J_{2,3}$ = 5.0 Hz, 1 H, H-2), 4.49 (dd, $J_{3,4}$ = 7.5 Hz, $J_{3,2}$ = 5.0 Hz, 1 H, H-3), 5.46 (dd, $J_{4,5}$ = 10.0 Hz, $J_{4,3}$ = 8.5 Hz, 1 H, H-4), 5.94 (s, 1 H, O_2CHPh or H-1), 6.31 (s, 1 H, H-1 or O_2CHPh), 6.73 (d, *J* = 9.0 Hz,

2 H, H_{arom}), 6.84 (d, J = 8.5 Hz, 2 H, H_{arom}), 7.30 (d, J = 8.5 Hz, 2 H, H_{arom}), 7.33 (d, J = 8.5 Hz, 2 H, H_{arom}).

^{13}C NMR (125 MHz, benzene-d_6): δ = 17.21 (C-6), 20.40 ($OCCH_3$), 20.94 ($SPhCH_3$), 54.71 ($O_2CHPhOCH_3$), 65.60 (CH), 72.07 (CH), 76.69 (CH), 77.21 (CH), 84.94 (C-1), 103.70 ($O_2CHPhOCH_3$), 113.94 (arom., CH, 2 × C), 128.29 (arom., CH, 2 × C), 130.09 (arom., CH, 2 × C), 131.32 (arom.), 132.92 (arom., CH, 2 × C), 137.87 (arom.), 160.76 (arom.), 169.59 ($OCCH_3$).

4-*O*-Acetyl-2,3-*O*-di-(4-methoxybenzylidene)-1-(4-tolyl)thio-β-L-rhamnopyranoside (18β)

^{1}H NMR (500 MHz, benzene-d_6): δ = 1.13 (d, $J_{6,5}$ = 6.0 Hz, 3 H, H-6), 1.64 (s, 3 H, H_{Ac}), 2.00 (s, 3 H, $SPhCH_3$), 3.20 (s, 3 H, $PhOCH_3$), 4.25 (d, $J_{2,3}$ = 5.5 Hz, 1 H, H-2), 4.33 (dd, $J_{3,4}$ = 7.0 Hz, $J_{3,2}$ = 5.5 Hz, 1 H, H-3), 4.35 (dq, $J_{5,4}$ = 10.0 Hz, $J_{5,6}$ = 6.0 Hz, 1 H, H-5), 5.44 (dd, $J_{4,5}$ = 10.0 Hz, $J_{4,3}$ = 7.5 Hz, 1 H, H-4), 5.76 (s, 1 H, H-1 or O_2CHPh), 5.97 (s, 1 H, O_2CHPh or H-1), 6.81 (d, J = 9.0 Hz, 2 H, H_{arom}), 6.84 (d, J = 8.0 Hz, 2 H, H_{arom}), 7.35 (d, J = 8.0 Hz, 2 H, H_{arom}), 7.66 (d, J = 8.5 Hz, 2 H, H_{arom}).

^{13}C NMR (125 MHz, benzene-d_6): δ = 17.17 (C-6), 20.44 ($OCCH_3$), 20.93 ($SPhCH_3$), 54.67 ($O_2CHPhOCH_3$), 66.00 (CH), 75.46 (CH), 75.77 (CH), 78.91 (CH), 84.21 (C-1), 105.07 ($O_2CHPhOCH_3$), 114.17 (arom., 2 × C), 128.87 (arom., 2 × C), 129.41 (arom.), 130.04 (arom.), 130.11 (arom., 2 × C), 132.92 (arom., 2 × C), 137.93 (arom.), 161.09 (arom.), 169.41 ($OCCH_3$).

4-*O*-Acetyl-3-*O*-(4-methoxy)benzyl-1-(4-tolyl)thio-α-L-rhamnopyranoside (19)

A mixture of compound **16α** (42 mg, 0.1 mmol), 4Å molecular sieves (128 mg) and CH_2Cl_2 (4 mL) was stirred for 20 min. To the solution was added sodium cyanoborohydride (81 mg, 1 mmol), THF (3 mL) and TFA (0.15 mL, 1.92 mmol) sequentially and the reaction was stirred at r.t. for 16 h. The starting material **18α** (R_f = 0.61) was consumed, while the products **19** (R_f = 0.31) and **20** (R_f = 0.25) were formed [monitored by TLC (*n*-hexane–EtOAc, 7:3)]. After the removal of the volatile solvents, the residue was partitioned between CH_2Cl_2 (10 mL) and sat. aq $NaHCO_3$ (3 mL), NaCl (3 mL) and H_2O (3 mL) sequentially. The organic layer was then dried (Na_2SO_4), filtered and concentration to give a residue which was purified by column chromatography on silica gel (*n*-hexane–EtOAc, 4:1) to give **19** (66%, 28 mg) and **20** (26%, 11 mg).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.18 (d, $J_{6,5}$ = 6.5 Hz, 3 H, H-6), 2.10 (s, 3 H, $OCCH_3$), 2.32 (s, 3 H, $SPhCH_3$), 3.79 (s, 3 H, $PhOCH_3$), 3.80 (dd, $J_{3,4}$ = 10.0 Hz, $J_{3,2}$ = 4.0 Hz, 1 H, H-3), 3.95 (dd, $J_{2,3}$ = 4.0 Hz, $J_{2,1}$ = 1.0 Hz, 1 H, H-2), 4.20 (dq, $J_{5,4}$ = 10.0 Hz, $J_{5,6}$ = 6.5 Hz, 1 H, H-5), 4.43 (d, J_{gem} = 12.5 Hz, 1 H, OCH_2Ph), 4.63 (d, J_{gem} = 11.5 Hz, 1 H, OCH_2Ph), 4.89 (dd, $J_{4,3}$ = 10.0 Hz, $J_{4,5}$ = 10.0 Hz, 1 H, H-4), 5.41 (br s, 1 H, H-1), 6.85 (d, J = 8.5 Hz, 2 H, H_{arom}), 7.10 (d, J = 7.5 Hz, 2 H, H_{arom}), 7.21 (d, J = 8.5 Hz, 2 H, H_{arom}), 7.29 (d, J = 8.5 Hz, 2 H, H_{arom}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.28 (C-6), 21.06 ($OCCH_3$), 21.10 ($SPhCH_3$), 55.27 ($PhOCH_3$), 67.17 (CH), 70.00 (CH), 72.10 (OCH_2Ph), 74.98 (CH), 79.25 (CH), 85.37 (C-1), 114.02 (arom., 2 × C), 129.19 (arom.), 129.73 (arom., 2 × C), 129.88 (arom., 2 × C), 130.21 (arom.), 132.12 (arom., 2 × C), 137.83 (arom.), 159.56 (arom.), 170.99 ($OCCH_3$).

MS (ESI+Q-TOF): m/z = 887.4 [2 × M + Na]$^+$, 455.1 [M + Na]$^+$, 433.2 [M + H]$^+$.

4-*O*-Acetyl-2-*O*-(4-methoxy)benzyl-1-(4-tolyl)thio-α-L-rhamnopyranoside (20)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.16 (d, $J_{6,5}$ = 7.0 Hz, 3 H, H-6), 2.03 (s, 3 H, CH_3), 2.31 (s, 3 H, $SPhCH_3$), 3.72 (dd, $J_{3,4}$ = 9.5 Hz, $J_{3,2}$ = 4.0 Hz, 1 H, H-3), 3.80 (s, 3 H, $PhOCH_3$), 4.18 (dd, $J_{2,3}$ = 4.0 Hz, $J_{2,1}$ = 1.0 Hz, 1 H, H-2), 4.20 (dq, $J_{5,4}$ = 9.5 Hz, $J_{5,6}$ = 7.0 Hz, 1 H, H-5), 4.49 (d, J_{gem} = 12.5 Hz, 1 H, OCH_2Ph), 4.58 (d, J_{gem} = 11.5 Hz, 1 H, OCH_2Ph), 5.05 (dd, $J_{4,3}$ = 9.5 Hz, $J_{4,5}$ = 9.5 Hz, 1 H, H-4), 5.45 (d, $J_{1,2}$ = 1.0 Hz, 1 H, H-1), 6.88 (d, J = 8.5 Hz, 2 H, H_{arom}), 7.10 (d, J = 7.5 Hz, 2 H, H_{arom}), 7.22 (d, J = 8.5 Hz, 2 H, H_{arom}), 7.31 (d, J = 8.5 Hz, 2 H, H_{arom}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.25 (C-6), 20.98 ($OCCH_3$), 21.07 ($SPhCH_3$), 55.28 ($PhOCH_3$), 67.43 (CH), 69.66 (CH), 71.46 (OCH_2Ph), 72.53 (CH), 76.46 (CH), 85.10 (C-1), 113.96 (arom., 2 × C), 129.45 (arom.), 129.49 (arom., 2 × C), 129.87 (arom., 2 × C), 129.89 (arom.), 131.93 (arom., 2 × C), 137.73 (arom.), 159.52 (arom.), 170.05 ($OCCH_3$).

MS (ESI+Q-TOF): m/z = 887.4 [2 × M + Na]$^+$, 455.1 [M + Na]$^+$, 433.2 [M + H]$^+$.

2,3,4-*O*-Tribenzyl-1-(4-tolyl)thio-α-L-rhamnopyranoside (10α)

A mixture of compounds **19** (218 mg, 0.8 mmol), DMF (4 mL), THF (4 mL) and NaH (60 % in oil; 114 mg, 2.83 mmol) was stirred under N_2 for 20 min and then cooled to 0 °C. BnBr (317 μL, 2.7 mmol) was added and the reaction mixture was warmed to r.t. and stirred for 1 h. The starting materials (R_f = 0.06) was consumed, while the products **10α** (R_f = 0.67) was formed [monitored by TLC (*n*-hexane–EtOAc, 1:1)]. The reaction was quenched with MeOH (1 mL) and, after removal of the volatile solvents, the crude product was purified by column chromatography on silica gel (*n*-hexane–EtOAc, 9:1→4:1) to give **10α** (89%, 388 mg).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.33 (d, $J_{6,5}$ = 6.0 Hz, 3 H, H-6), 2.31 (s, 3 H, $SPhCH_3$), 3.66 (dd, $J_{4,3}$ = 9.5 Hz, $J_{4,5}$ = 9.5 Hz, 1 H, H-4), 3.82 (dd, $J_{3,4}$ = 9.5 Hz, $J_{3,2}$ = 3.0 Hz, 1 H, H-3), 3.95 (dd, $J_{2,3}$ = 3.0 Hz, $J_{2,1}$ = 1.5 Hz, 1 H, H-2), 4.13 (dq, $J_{5,4}$ = 9.5 Hz, $J_{5,6}$ = 6.0 Hz, 1 H, H-5), 4.56 (d, J_{gem} = 12.5 Hz, 1 H, OCH_2Ph), 4.59 (d, J_{gem} = 12.5 Hz, 1 H, OCH_2Ph), 4.62 (d, J_{gem} = 12.0 Hz, 1 H, OCH_2Ph), 4.63 (d, J_{gem} = 11.0 Hz, 1 H, OCH_2Ph), 4.69 (d, J_{gem} = 12.5 Hz, 1 H, OCH_2Ph), 4.95 (d, J_{gem} = 10.5 Hz, 1 H, OCH_2Ph), 5.40 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1), 7.07 (d, J = 8.5 Hz, 2 H), 7.21–7.39 (m, 17 H, H_{arom}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.88 (C-6), 21.09 ($SPhCH_3$), 69.221 (CH), 72.02 (OCH_2Ph), 72.05 (OCH_2Ph), 75.45 (OCH_2Ph), 76.37 (CH), 79.95 (CH), 80.51 (CH), 86.07 (C-1), 127.66 (arom., 2 × C), 127.73 (arom.), 127.78 (arom.), 127.80 (arom., 2 × C), 128.00 (arom., 4 × C), 128.37 (arom., 4 × C), 128.50 (arom.), 129.79 (OCH_2Ph, 2 × C), 130.78 (arom.), 131.93 (OCH_2Ph, 2 × C), 137.51 (arom.), 137.89 (arom.), 138.22 (arom.), 138.52 (arom.).

MS (ESI+Q-TOF): m/z = 563.1 [M + Na]$^+$, 417.1 [M – $SPhCH_3$ + H].

2,3,4-*O*-Tribenzoyl-1-(4-tolyl)thio-α-L-rhamnopyranoside (11α)

A mixture of compounds **9** (96 mg, 0.35 mmol), DMAP (17 mg, 0.14 mmol) and pyridine (1 mL) was stirred for 10 min. BzCl (185 μL, 1.32 mmol) was then added and the reaction was stirred at r.t. under N_2 for 30 min. The products **11α** (R_f = 0.73) was detected by TLC (*n*-hexane–EtOAc. 7:3). After the removal of the volatile solvents, the residue was partitioned between EtOAc (10 mL) and sat. aq NaCl (5 mL) and H_2O (5 mL) sequentially. The organic layer was then dried (Na_2SO_4), filtered and, after concentration, the residue was purified by column chromatography on silica gel (*n*-hexane–EtOAc, 4:1) to give **11α** (95%, 197 mg).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (d, $J_{6,5}$ = 6.0 Hz, 3 H, H-6), 2.32 (s, 3 H, $SPhCH_3$), 4.68 (dq, $J_{5,4}$ = 10.0 Hz, $J_{5,6}$ = 6.0 Hz, 1 H, H-5), 5.60 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1), 5.72 (dd, $J_{4,3}$ = 10.0 Hz, $J_{4,5}$ = 10.0 Hz, 1 H, H-4), 5.80 (dd, $J_{3,4}$ = 10.0 Hz, $J_{3,2}$ = 3.0 Hz, 1 H, H-3), 5.90 (dq, $J_{2,3}$ = 3.0 Hz, $J_{2,1}$ = 1.5 Hz, 1 H, H-2), 7.14 (d, J = 8.5 Hz, 2 H, H_{arom}), 7.26 (d, J = 8.0 Hz, 2 H, H_{arom}), 7.36–7.48 (m, 7 H, H_{arom}), 7.52 (d, J = 7.5 Hz, 1 H, H_{arom}), 7.58 (d, J = 7.5 Hz,

1 H, H_{arom}), 7.82 (d, J = 7.5 Hz, 2 H, H_{arom}), 7.99 (d, J = 7.0 Hz, 2 H, H_{arom}), 8.06 (d, J = 7.5 Hz, 2 H, H_{arom}).

MS (ESI+Q-TOF): m/z = 583.1 [M + H^+], 459.1 [M – $SPhCH_3$ + H].

2,3,4-*O*-Tribenzyl-L-rhamnopyranoside (13α,β)

A mixture of compounds **10α** (844 mg, 1.6 mmol), NBS (565 mg, 3.2 mmol) and acetone–H_2O (1:1, 10 mL) was stirred at r.t. for 1 h. The reaction was monitored by TLC (*n*-hexane–EtOAc, 7:3). NBS (282 mg, 1.6 mmol) was added and the solution was stirred for a further 1 h. The starting material (R_f = 0.67) was consumed, while the products **10α**,**β** (R_f = 0.32) formed. After the removal of the volatile solvents, the crude product was purified by column chromatography on silica gel (*n*-hexane–EtOAc, 1:3) to give **10α**,**β** (91%, 620 mg).

MS (ESI+Q-TOF): m/z = 457.1 [M + $Na]^+$.

2,3,4-*O*-Tribenzoyl-α,β-L-rhamnopyranoside (14α,β)

A mixture of compounds **11α**,**β** (169 mg, 0.29 mmol), NBS (107 mg, 0.6 mmol) and acetone–H_2O (1:2, 4 mL) was stirred at r.t. for 1 h. The reaction was monitored by TLC (*n*-hexane–EtOAc, 7:3). NBS (51 mg, 0.29 mmol) was added and stirring was continued for 1 h. The starting material (R_f = 0.72) was consumed, while the products **14α**,**β** (R_f = 0.36) was formed. After the removal of the volatile solvents, the crude products were purified by column chromatography on silica gel (*n*-hexane–EtOAc, 9:2) to give **14α**,**β** (93%, 129 mg).

MS (ESI+Q-TOF): m/z = 499.1 [M + $Na]^+$.

2,3,4-*O*-Triacetyl-α,β-L-rhamnopyranoside (12)

Compound **12** was prepared using the procedure described above. Compound **8** (144 mg, 0.4 mmol), NBS (108 mg, 0.6 mmol) and acetone–H_2O (9:1, 6 mL) were employed. Purification by column chromatography (*n*-hexane–EtOAc, 7:4) gave pure **12**.

Yield: 95% (100 mg); R_f = 0.2 (*n*-hexane–EtOAc, 3:7).

MS (ESI+Q-TOF): m/z = 313.3 [M + $Na]^+$.

2,3,4-*O*-Tribenzyl-1-*O*-trichloroacetimido-α-L-rhamnopyranoside (5)

A mixture of compounds **13α**,**β** (100 mg, 0.23 mmol) and CH_2Cl_2 (2 mL) was stirred under N_2 for 20 min. After addition of NaH (60% in oil; 11 mg, 0.27 mmol) the solution was stirred for 30 min then CCl_3CN (235 μL, 2.3 mmol) was added. The reaction mixture was stirred at r.t. for 1.5 h, during which the product **5** (R_f = 0.57) was detected on TLC (*n*-hexane–EtOAc, 7:3). After the removal of the volatile solvents, the crude residue was purified by column chromatography on silica gel (*n*-hexane–EtOAc, 9:1) to give **5** (81%, 108 mg).

^{1}H NMR (500 MHz, benzene-d_6): δ = 1.37 (d, $J_{6,5}$ = 6.5 Hz, 3 H, H-6), 3.93 (dd, $J_{4,3}$ = 9.0 Hz, $J_{4,5}$ = 9.0 Hz, 1 H, H-4), 3.98 (dd, $J_{2,3}$ = 3.5 Hz, $J_{2,1}$ = 2.0 Hz, 1 H, H-2), 4.09 (dd, $J_{3,4}$ = 9.0 Hz, $J_{3,2}$ = 3.0 Hz, 1 H, H-3), 4.21 (dq, $J_{5,4}$ = 10.0 Hz, $J_{5,6}$ = 6.0 Hz, 1 H, H-5), 4.49 (br s, 2 H, OCH_2Ph), 4.50 (d, J = 11.5 Hz, 1 H, OCH_2Ph), 4.60 (br s, 2 H, OCH_2Ph), 4.96 (d, J = 11.5 Hz, 1 H, OCH_2Ph), 6.67 (d, $J_{1,2}$ = 2.0 Hz, 1 H, H-1), 7.04–7.19 (m, 9 H, H_{arom}), 7.28 (d, J = 7.0 Hz, 4 H, H_{arom}), 7.39 (d, J = 7.2 Hz, 2 H, H_{arom}), 8.43 (s, 1 H, NH).

MS (ESI+Q-TOF): m/z = 595.2 [M + $NH_4]^+$, 417.2 [M – imidate – H + H].

2,3,4-*O*-Tribenzoyl-1-*O*-trichloroacetimido-α-L-rhamnopyranoside (16)

A mixture of compounds **14α**,**β** (75 mg, 0.16 mmol) and CH_2Cl_2 (3 mL) was stirred for 20 min. To the solution was added CCl_3CN (0.18 mL, 1.79 mmol) and the mixture was vigorously stirred for 30 min. A catalytic amount of DBU (11.8 μL, 0.08 mmol) was added and the reaction mixture was stirred at r.t. under N_2 for 1 h. The product **16** (R_f = 0.6; *n*-hexane–EtOAc, 3:7) was formed. After the removal of the volatile solvents, the crude residue was purified by column chromatography on silica gel (*n*-hexane–EtOAc, 7:3) to give **16** (86%, 84 mg).

MS (ESI+Q-TOF): m/z = 459.2 [M – imidate – H + H].

2,3,4-*O*-Triacetyl-1-*O*-trichloroacetimido-α-L-rhamnopyranoside (15)

A mixture of compound **12** (27 mg, 0.1 mmol), K_2CO_3 (148 mg, 1.1 mmol) and CH_2Cl_2 (2 mL) was vigorously stirred for 30 min. After addition of CCl_3CN (190 μL, 1.9 mmol), the mixture was stirred for 2 h. After removal of the volatile solvents, the crude residue was purified by column chromatography on silica gel (*n*-hexane–EtOAc, 9:2) to give **15**.

Yield: 73% (30 mg); R_f = 0.6 (*n*-hexane–EtOAc, 6:4).

^{1}H NMR (500 MHz, benzene-d_6): δ = 1.23 (d, $J_{6,5}$ = 6.0 Hz, 3 H, H-6), 1.55 (s, 3 H, $OCCH_3$), 1.62 (s, 3 H, $OCCH_3$), 1.71 (s, 3 H, $OCCH_3$), 4.32 (dq, $J_{5,4}$ = 9.5 Hz, $J_{5,6}$ = 6.5 Hz, 1 H, H-5), 5.60 (dd, $J_{4,3}$ = 10.5 Hz, $J_{4,5}$ = 9.5 Hz, 1 H, H-4), 5.79 (dd, $J_{3,4}$ = 10.5 Hz, $J_{3,2}$ = 3.5 Hz, 1 H, H-3), 5.85 (dd, $J_{2,3}$ = 3.5 Hz, $J_{2,1}$ = 2.5 Hz, 1 H, H-2), 6.50 (d, $J_{2,1}$ = 2.5 Hz, 1 H, H-1), 8.47 (s, 1 H, NH).

^{13}C NMR (125 MHz, benzene-d_6): δ = 17.60 (C-6), 19.99 ($OCCH_3$), 20.17 ($OCCH_3$), 20.23 ($OCCH_3$), 68.38 (CH), 69.48 (CH), 69.96 (CH), 70.59 (CH), 95.55 (C-1), 159.86 ($OCNHCCl_3$), 169.31 ($OCNHCCl_3$), 169.36 ($OCNHCCl_3$), 169.51 ($OCNHCCl_3$).

4-*O*-Acetyl-2-*O*-benzoyl-3-*O*-(4-methoxy)benzyl-1-(4-tolyl)thio-α-L-rhamnopyranoside (21)

A mixture of compounds **19** and **20** (134 mg, 0.31 mmol), DMAP (23 mg, 0.19 mmol) and pyridine (4 mL) was stirred for 10 min. To the solution was added BzCl (45 μL, 0.32 mmol) and the reaction mixture was stirred at r.t. under N_2 for 30 min. The products **21** and **22** (both R_f = 0.53) were detected by TLC (*n*-hexane–EtOAc, 7:3). After removal of the volatile solvents, the residue was partitioned between EtOAc (10 mL) and sat. aq NaCl (5 mL) and H_2O (5 mL), sequentially. The organic layer was dried (Na_2SO_4) and filtered. After concentration, the residue was purified by column chromatography on silica gel (*n*-hexane–EtOAc, 9:1) to give **21** and **22** (total yield: 97%, 161 mg) in a ratio of 2.5:1. No further purification with HPLC was pursued. The peaks corresponding to compound **21** in the NMR spectra of the mixture was elucidated and could be assigned as follows.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.24 (d, $J_{6,5}$ = 6.5 Hz, 3 H, H-6), 2.04 (s, 3 H, $OCCH_3$), 2.30 (s, 3 H, $SPhCH_3$), 3.78 (s, 3 H, $PhOCH_3$), 3.86 (dd, $J_{3,4}$ = 9.5 Hz, $J_{3,2}$ = 3.0 Hz, 1 H, H-3), 4.28 (dq, $J_{5,4}$ = 10.0 Hz, $J_{5,6}$ = 6.0 Hz, 1 H, H-5), 4.42 (d, J_{gem} = 12.0 Hz, 1 H, OCH_2Ph), 4.61 (d, J_{gem} = 12.0 Hz, 1 H, OCH_2Ph), 5.18 (dd, $J_{4,3}$ = 9.5 Hz, $J_{4,5}$ = 10.0 Hz, 1 H, H-4), 5.47 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1), 5.75 (dd, $J_{2,3}$ = 2.5 Hz, $J_{2,1}$ = 1.5 Hz, 1 H, H-2), 6.83 (d, J = 8.5 Hz, 2 H, H_{arom}), 7.10 (d, J = 7.5 Hz, 2 H, H_{arom}), 7.19 (d, J = 8.0 Hz, 2 H, H_{arom}), 7.34 (d, J = 8.5 Hz, 2 H, H_{arom}), 7.43 (d, J = 7.5 Hz, 2 H, H_{arom}), 7.54 (d, J = 8.0 Hz, 1 H, H_{arom}), 8.05 (d, J = 7.5 Hz, 2 H, H_{arom}).

MS (ESI+Q-TOF): m/z = 1095.4 [2 × M + $Na]^+$, 559.1 [M + $Na]^+$.

4-*O*-Acetyl-3-*O*-benzoyl-2-*O*-(4-methoxy)benzyl-1-(4-tolyl)thio-α-L-rhamnopyranoside (22)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.26 (d, $J_{6,5}$ = 6.5 Hz, 3 H, H-6), 1.97 (s, 3 H, $OCCH_3$), 2.33 (s, 3 H, $SPhCH_3$), 3.67 (s, 3 H, $PhOCH_3$), 4.21 (dd, $J_{2,3}$ = 3.0 Hz, $J_{2,1}$ = 1.5 Hz, 1 H, H-2), 4.34 (dq, $J_{5,4}$ = 10.0 Hz, $J_{5,6}$ = 6.5 Hz, 1 H, H-5), 4.40 (d, J_{gem} = 12.0 Hz, 1 H, OCH_2Ph), 4.55 (d, J_{gem} = 12.5 Hz, 1 H, OCH_2Ph), 5.31 (dd, $J_{3,4}$ = 10.0 Hz, $J_{3,2}$ = 3.0 Hz, 1 H, H-3), 5.41 (s, 1 H, H-1), 5.43 (dd, $J_{4,3}$ = 10.0 Hz, $J_{4,5}$ = 10.0 Hz, 1 H, H-4), 6.58 (d, J = 8.0 Hz, 2 H, H_{arom}), 7.08 (d, J = 8.5 Hz, 2 H, H_{arom}), 7.11 (d, J = 8.5 Hz, 2 H,

H_{arom}), 7.33 (d, J = 8.0 Hz, 2 H, H_{arom}), 7.45 (d, J = 7.0 Hz, 2 H, H_{arom}), 7.56 (d, J = 7.0 Hz, 1 H, H_{arom}), 7.98 (d, J = 7.0 Hz, 2 H, H_{arom}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.41 (C-6), 17.52 (C-6), 20.81 ($OCCH_3$), 20.97 ($OCCH_3$), 21.09 ($SPhCH_3$), 55.07 ($PhOCH_3$), 55.24 ($PhOCH_3$), 67.76 (CH), 67.86 (CH), 70.622 (CH), 70.773 (OCH_2Ph), 71.30 (CH), 72.14 (OCH_2Ph), 72.26 (CH), 72.72 (CH), 74.23 (CH), 76.22 (CH), 85.99 (C-1), 86.47 (C-1), 113.65, 113.78 (arom., 2 × C), 128.44, 129.31, 129.52, 129.58 (arom.), 129.63 (arom.), 129.74 (arom.), 129.81, 129.88, 129.94, 131.97, 132.28, 133.29, 138.08 (arom.), 159.32 (arom.), 165.74 (OCPh), 169.96 ($OCCH_3$).

4-*O*-Acetyl-2-*O*-benzoyl-1-(4-tolyl)thio-α-L-rhamnopyranoside (4)

A mixture of compounds **22**, **21** (158 mg, 0.29 mmol) and CAN (327 mg, 0.6 mmol) in MeCN–H_2O (9:1, 4 mL) was stirred for 60 min. To the solution was added CAN (122 mg, 0.22 mmol) and the reaction mixture was stirred at r.t. for 1 h. The products **4** (R_f = 0.41) and **2** (R_f = 0.39) were detected by TLC (*n*-hexane–EtOAc, 7:3). After the removal of the volatile solvents, the residue was partitioned between EtOAc (10 mL) and sat. aq Na_2CO_3 (5 mL) and H_2O (5 mL), sequentially. The organic layer was dried (Na_2SO_4) and filtered. After concentration, the residue was purified by column chromatography on silica gel (*n*-hexane–EtOAc, 7:3) to give **4** (52%, 64 mg) and **2** (20%, 25 mg). For analytical purposes, a small amount of each sample was further purified with HPLC (*n*-hexane–EtOAc, 7:3).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.26 (d, $J_{6,5}$ = 6.0 Hz, 3 H, H-6), 2.16 (s, 3 H, $OCCH_3$), 2.30 (s, 3 H, $SPhCH_3$), 4.36 (dd, $J_{3,4}$ = 9.5 Hz, $J_{3,2}$ = 3.0 Hz, 1 H, H-3), 4.38 (dq, $J_{5,4}$ = 9.5 Hz, $J_{5,6}$ = 6.0 Hz, 1 H, H-5), 5.04 (dd, $J_{4,3}$ = 9.5 Hz, $J_{4,5}$ = 9.5 Hz, 1 H, H-4), 5.51 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1), 5.75 (d, $J_{2,1}$ = 1.5 Hz, 1 H, H-2), 7.10 (d, J = 8.0 Hz, 2 H, H_{arom}), 7.36 (d, J = 8.0 Hz, 2 H, H_{arom}), 7.45 (d, J = 7.0 Hz, 2 H, H_{arom}), 8.04 (d, J = 7.5 Hz, 2 H, H_{arom}), 8.08 (d, J = 7.0 Hz, 1 H, H_{arom}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.42 (C-6), 21.04 ($OCCH_3$), 21.10 ($SPhCH_3$), 67.29 (CH), 69.56 (CH), 74.77 (CH), 76.74 (CH), 86.14 (C-1), 128.56 (arom., 2 × C), 129.26 (arom.), 129.64 (arom.), 129.87 (arom., 2 × C), 129.94 (arom., 2 × C), 130.16 (arom.), 132.38 (arom., 2 × C), 133.57 (arom.), 138.13 (arom.), 165.90 (OCPh), 171.65 ($OCCH_3$).

MS (ESI+Q-TOF): m/z = 855.4 [2 × M + Na]$^+$, 439.2 [M + Na]$^+$, 317.1 [M – $SPhCH_3$ + Na]$^+$, 295.2 [M – $SPhCH_3$ + H]$^+$.

4-*O*-Acetyl-3-*O*-benzoyl-1-(4-tolyl)thio-α-L-rhamnopyranoside (2)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.26 (d, $J_{6,5}$ = 6.0 Hz, 3 H, H-6), 1.98 (s, 3 H, $OCCH_3$), 2.32 (s, 3 H, $SPhCH_3$), 4.43 (dq, $J_{5,4}$ = 9.5 Hz, $J_{5,6}$ = 6.0 Hz, 1 H, H-5), 4.47 (dd, $J_{2,3}$ = 2.5 Hz, $J_{2,1}$ = 1.5 Hz, 1 H, H-2), 5.36 (dd, $J_{4,3}$ = 10.0 Hz, $J_{4,5}$ = 9.5 Hz, 1 H, H-4), 5.40 (dd, $J_{3,4}$ = 10.0 Hz, $J_{3,2}$ = 2.5 Hz, 1 H, H-3), 5.44 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1), 7.12 (d, J = 7.5 Hz, 2 H, H_{arom}), 7.37 (d, J = 8.5 Hz, 2 H, H_{arom}), 7.44 (d, J = 8.0 Hz, 2 H, H_{arom}), 7.57 (d, J = 7.0 Hz, 1 H, H_{arom}), 8.01 (d, J = 7.0 Hz, 2 H, H_{arom}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.33 (C-6), 20.79 ($OCCH_3$), 21.12 ($SPhCH_3$), 67.63 (CH), 70.87 (CH), 71.05 (CH), 72.77 (CH), 87.85 (C-1), 128.63 (arom., 2 × C), 129.23 (arom.), 129.82 (arom., 3 × C), 129.96 (arom., 2 × C), 132.16 (arom., 2 × C), 133.54 (arom.), 137.97 (arom.), 165.57 (OCPh), 170.11 ($OCCH_3$).

MS (ESI+Q-TOF): m/z = 855.4 [2 × M + Na]$^+$, 439.2 [M + Na]$^+$, 317.1 [M – $SPhCH_3$ + H + Na]$^+$, 295.2 [M – $SPhCH_3$ + 2H]$^+$.

2,3,4-*O*-Tribenzyl-α-L-rhamnosyl-(1→3)-4-*O*-acetyl-2-*O*-benzoyl-1-(4-tolyl)thio-α-L-rhamnopyranoside (23)

A mixture of compound **4** (90 mg, 0.22 mmol), 4 Å molecular sieves (220 mg) and compound **5** (130 mg, 0.23 mmol) in CH_2Cl_2 (5 mL) was stirred at r.t. for 30 min then cooled to 0 °C. TMSOTf (19 μL, 0.11 mmol) was added and the reaction mixture was stirred for 30 min and then warmed to r.t.. The product **21** (R_f = 0.65) was detected on TLC (*n*-hexane–EtOAc, 7:3). After completion of the reaction, the reaction mixture was quenched with Et_3N (0.5 mL), diluted with CH_2Cl_2 (15 mL) and filtered. After concentration, the residue was purified by column chromatography on silica gel (*n*-hexane–EtOAc, 9:2) to give **21** (78%, 64 mg).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.18 (d, $J_{6,5}$ = 6.0 Hz, 3 H, H-6), 1.21 (d, $J_{6',5'}$ = 6.0 Hz, 3 H, H-6′), 1.88 (s, 3 H, $OCCH_3$), 2.30 (s, 3 H, $SPhCH_3$), 3.51 (dd, $J_{4',5'}$ = 9.0 Hz, $J_{4',3'}$ = 9.0 Hz, 1 H, H-4′), 3.59 (dd, $J_{2',3'}$ = 3.0 Hz, $J_{2',1'}$ = 2.0 Hz, 1 H, H-2′), 3.63 (dq, $J_{5',4'}$ = 9.0 Hz, $J_{5',6'}$ = 6.5 Hz, 1 H, H-5′), 3.64 (dd, $J_{3',4'}$ = 9.0 Hz, $J_{3',2'}$ = 3.0 Hz, 1 H, H-3′), 4.12 (dd, $J_{3,4}$ = 10.0 Hz, $J_{3,2}$ = 3.5 Hz, 1 H, H-3), 4.30 (dq, $J_{5,4}$ = 9.5 Hz, $J_{5,6}$ = 6.0 Hz, 1 H, H-5), 4.45 (d, J_{gem} = 11.5 Hz, 1 H, OCH_2Ph), 4.48 (d, J_{gem} = 11.5 Hz, 1 H, OCH_2Ph), 4.48 (d, J_{gem} = 12.0 Hz, 1 H, OCH_2Ph), 4.63 (d, J_{gem} = 13.0 Hz, 1 H, OCH_2Ph), 4.69 (d, J_{gem} = 12.5 Hz, 1 H, OCH_2Ph), 4.73 (d, J_{gem} = 12.0 Hz, 1 H, OCH_2Ph), 4.91 (d, $J_{1',2'}$ = 1.5 Hz, 1 H, H-1′), 5.18 (dd, $J_{4,5}$ = 9.5 Hz, $J_{4,3}$ = 9.5 Hz, 1 H, H-4), 5.48 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1), 5.58 (d, $J_{2,3}$ = 2.5 Hz, 1 H, H-2), 7.10 (d, J = 8.0 Hz, 2 H, H_{arom}), 7.13 (d, J = 8.5 Hz, 2 H), 7.20–7.32 (m, 13 H, H_{arom}), 7.35 (d, J = 8.5 Hz, 2 H, H_{arom}), 7.41 (dd, J = 8.0 Hz, J = 8.0 Hz, 2 H, H_{arom}), 7.54 (dd, J = 8.0 Hz, J = 8.0 Hz, 1 H, H_{arom}), 8.03 (d, J = 7.0 Hz, 2 H, H_{arom}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.48 (C-6), 17.87 (C-6′), 20.76 ($OCCH_3$), 21.11 ($SPhCH_3$), 67.78 (CH), 69.04 (CH), 72.51 (OCH_2Ph), 72.79 (OCH_2Ph), 73.15 (CH), 73.89 (CH), 74.16 (OCH_2Ph), 74.83 (CH), 76.74 (CH), 77.25 (CH), 79.25 (CH), 85.90 (C-1), 100.42 (C-1′), 127.29 (arom.), 127.48 (arom., 3 × C), 127.68 (arom., 3 × C), 127.76 (arom., 2 × C), 128.13 (arom., 2 × C), 128.29 (arom., 2 × C), 128.39 (arom., 2 × C), 128.50 (arom., 2 × C), 129.52 (arom.), 129.60 (arom.), 129.89 (arom., 2 × C), 129.92 (arom., 2 × C), 132.41 (arom., 2 × C), 133.34 (arom.), 138.10 (arom.), 138.24 (arom.), 138.44 (arom.), 138.68 (arom.), 165.70 (OCPh), 169.75 ($OCCH_3$).

MS (ESI+Q-TOF): m/z = 833.5 [M + H]$^+$, 856.5 [M + Na]$^+$, 709.4 [M – $SPhCH_3$ + H].

2,3,4-*O*-Tribenzyl-α-L-rhamnosyl-(1→3)-4-*O*-acetyl-2-*O*-benzoyl-α,β-L-rhamnopyranoside (24α,β)

A mixture of compound **23** (86 mg, 0.1 mmol) and NBS (29 mg, 0.2 mmol) in acetone–H_2O (1:1, 8 mL) was stirred at r.t. for 1 h. NBS (33 mg, 0.18 mmol) was added and stirring was continued for 1 h. The products **24α,β** (R_f = 0.25) were detected on TLC (*n*-hexane–EtOAc, 7:3). After concentration, the crude residue was purified by column chromatography on silica gel (*n*-hexane–EtOAc, 7:3) to give **24α,β** (92%, 69 mg).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.16 (d, $J_{5,6}$ = 6.0 Hz, 3 H, H-6), 1.19 (d, $J_{5',6'}$ = 6.0 Hz, 3 H, H-6′), 1.85 (s, 3 H, $OCCH_3$), 3.49 (dd, $J_{4',5'}$ = 9.0 Hz, $J_{4',3'}$ = 9.0 Hz, 1 H, H-4′), 3.58 (dd, $J_{2',3'}$ = 2.5 Hz, $J_{2',1'}$ = 2.5 Hz, 1 H, H-2′), 3.64 (dd, $J_{3',4'}$ = 9.0 Hz, $J_{3',2'}$ = 2.5 Hz, 1 H, H-3′), 3.65 (dq, $J_{5',4'}$ = 9.0 Hz, $J_{5',6'}$ = 6.0 Hz, 1 H, H-5′), 4.05 (dq, $J_{5,4}$ = 10.0 Hz, $J_{5,6}$ = 6.0 Hz, 1 H, H-5), 4.21 (dd, $J_{3,4}$ = 9.5 Hz, $J_{3,2}$ = 3.5 Hz, 1 H, H-3), 4.43 (d, J_{gem} = 11.5 Hz, 1 H, OCH_2Ph), 4.47 (d, J_{gem} = 11.5 Hz, 1 H, OCH_2Ph), 4.48(d, J_{gem} = 11.5 Hz, 1 H, OCH_2Ph), 4.62 (d, J_{gem} = 12.0 Hz, 1 H, OCH_2Ph), 4.68 (d, J_{gem} = 12.5 Hz, 1 H, OCH_2Ph), 4.73 (d, J_{gem} = 11.5 Hz, 1 H, OCH_2Ph), 4.90 (d, $J_{1',2'}$ = 2.0 Hz, 1 H, H-1′), 5.13 (dd, $J_{4,5}$ = 9.0 Hz, $J_{4,3}$ = 9.0 Hz, 1 H, H-4), 5.30 (br s, 1 H, H-1), 5.37 (dd, $J_{2,3}$ = 3.5 Hz, $J_{2,3}$ = 2.5 Hz, 1 H, H-2), 7.12 (d, J = 8.0 Hz, 2 H, H_{arom}), 7.14–

7.34 (m, 14 H_{arom}), 7.42 (dd, J = 8.0 Hz, J = 8.0 Hz, 2 H, H_{arom}), 7.55 (dd, J = 7.5 Hz, 2 H, H_{arom}), 7.55 (d, J = 6.5 Hz, 2 H, H_{arom}).

MS (ESI+Q-TOF): m/z = 749.3 $[M + Na]^+$.

2,3,4-*O*-Tribenzyl-α-L-rhamnosyl-(1→3)-4-*O*-acetyl-2-*O*-benzoyl-1-*O*-trichloroacetimido-α-L-rhamnopyranoside (25)

A mixture of compound **24α,β** (47 mg, 0.07 mmol), CH_2Cl_2 (2 mL) and CCl_3CN (65 μL, 0.65 mmol) was stirred at r.t. for 20 min. A solution of DBU [0.72 μL, 0.01 mmol; taken from a stock solution of DBU (0.1 mL) in CH_2Cl_2 (1 mL)] was added and the stirring was continued for 1 h. The product **25** (R_f = 0.69) was detected on TLC (*n*-hexane–EtOAc, 3:2). After the removal of the volatile solvents, the crude residue was purified by column chromatography on silica gel (*n*-hexane–EtOAc, 4:1) to give **25** (83%, 47 mg).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.16 (d, $J_{6,5}$ = 6.0 Hz, 3 H, H-6), 1.24 (d, $J_{6',5'}$ = 6.0 Hz, 3 H, H-6′), 1.90 (s, 3 H, $OCCH_3$), 3.50 (dd, $J_{4',5'}$ = 9.0 Hz, $J_{4',3'}$ = 9.0 Hz, 1 H, H-4′), 3.61 (dd, $J_{2',3'}$ = 2.5 Hz, $J_{2',1'}$ = 2.5 Hz, 1 H, H-2′), 3.65 (dd, $J_{3',4'}$ = 9.0 Hz, $J_{3',2'}$ = 2.5 Hz, 1 H, H-3′), 3.69 (dq, $J_{5',4'}$ = 9.0 Hz, $J_{5',6'}$ = 6.0 Hz, 1 H, H-5′), 4.02 (dq, $J_{5,4}$ = 9.5 Hz, $J_{5,6}$ = 6.0 Hz, 1 H, H-5), 4.27 (dd, $J_{3,4}$ = 9.5 Hz, $J_{3,2}$ = 3.0 Hz, 1 H, H-3), 4.45 (d, J_{gem} = 12.0 Hz, 1 H, OCH_2Ph), 4.50 (d, J_{gem} = 11.5 Hz, 2 H, OCH_2Ph), 4.61 (d, J_{gem} = 12.0 Hz, 1 H, OCH_2Ph), 4.68 (d, J_{gem} = 12.0 Hz, 1 H, OCH_2Ph), 4.69 (d, J_{gem} = 11.0 Hz, 1 H, OCH_2Ph), 4.92 (d, $J_{1',2'}$ = 2.5 Hz, 1 H, H-1′), 5.23 (dd, $J_{4,5}$ = 9.5 Hz, $J_{4,3}$ = 9.5 Hz, 1 H, H-4), 5.53 (dd, $J_{2,3}$ = 3.0 Hz, $J_{2,1}$ = 1.5 Hz, 1 H, H-2), 6.34 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1), 7.16 (d, J = 6.5 Hz, 2 H, H_{arom}), 7.20–7.31 (m, 13 H, H_{arom}), 7.45 (dd, J = 7.5 Hz, J = 7.5 Hz, 2 H, H_{arom}), 7.58 (dd, J = 8.0 Hz, J = 8.0 Hz, 1 H, H_{arom}), 8.07 (d, J = 7.0 Hz, 2 H, H_{arom}), 8.73 (s, 1 H, NH).

^{1}H NMR (500 MHz, benzene-d_6): δ = 1.29 (d, $J_{6,5}$ = 6.0 Hz, 3 H, H-6), 1.39 (d, $J_{6',5'}$ = 6.5 Hz, 3 H, H-6′), 1.61 (s, 3 H, $OCCH_3$), 3.80 (dd, $J_{4',5'}$ = 9.0 Hz, $J_{4',3'}$ = 9.0 Hz, 1 H, H-4′), 3.81 (dd, $J_{2',3'}$ = 3.0 Hz, $J_{2',1'}$ = 2.0 Hz, 1 H, H-2′), 3.99 (dd, $J_{3',4'}$ = 9.0 Hz, $J_{3',2'}$ = 3.0 Hz, 1 H, H-3′), 4.20 (dq, $J_{5',4'}$ = 9.0 Hz, $J_{5',6'}$ = 6.0 Hz, 1 H, H-5′), 4.32 (dq, $J_{5,4}$ = 10.0 Hz, $J_{5,6}$ = 6.5 Hz, 1 H, H-5), 4.34 (d, J_{gem} = 12.0 Hz, 1 H, OCH_2Ph), 4.42 (d, J_{gem} = 11.0 Hz, 1 H, OCH_2Ph), 4.45 (d, J_{gem} = 11.0 Hz, 1 H, OCH_2Ph), 4.54 (d, J_{gem} = 12.0 Hz, 1 H, OCH_2Ph), 4.65 (d, J_{gem} = 12.0 Hz, 1 H, OCH_2Ph), 4.68 (dd, $J_{3,4}$ = 10.0 Hz, $J_{3,2}$ = 3.5 Hz, 1 H, H-3), 4.82 (d, J_{gem} = 11.5 Hz, 1 H, OCH_2Ph), 5.26 (d, $J_{1',2'}$ = 2.0 Hz, 1 H, H-1′), 5.75 (dd, $J_{4,5}$ = 10.0 Hz, $J_{4,3}$ = 10.0 Hz, 1 H, H-4), 6.10 (dd, $J_{2,1}$ = 2.0 Hz, $J_{2,3}$ = 3.5 Hz, 1 H, H-2), 6.79 (d, $J_{1,2}$ = 2.0 Hz, 1 H, H-1), 6.92 (dd, J = 7.5 Hz, J = 7.5 Hz, 2 H, H_{arom}), 7.00–7.20 (m, 12 H, H_{arom}), 7.24 (d, J = 7.5 Hz, 2 H, H_{arom}), 7.32 (d, J = 8.0 Hz, 2 H, H_{arom}), 8.21 (d, J = 7.0 Hz, 2 H, H_{arom}), 8.57 (s, 1 H, NH).

^{13}C NMR (125 MHz, benzene-d_6): δ = 17.79 (C-6), 18.41 (C-6′), 20.35 ($OCCH_3$), 69.85 (CH), 69.97 (CH), 71.204 (CH), 72.63 (OCH_2Ph), 73.06 (CH), 73.34 (OCH_2Ph), 73.86 (CH), 74.45 (OCH_2Ph), 76.77 (CH), 80.24 (CH), 80.73 (CH), 95.49 (C-1), 100.91 (C-1′), 127.34, 127.58, 127.70, 127.73, 127.87, 127.91, 128.28, 128.32, 128.46, 128.54, 128.71, 130.26, 133.35, 139.05 ($OCNHCCl_3$), 139.25 ($OCNHCCl_3$), 139.50 ($OCNHCCl_3$), 159.78 ($OCNHCCl_3$), 165.63 (OCPh), 169.25 ($OCCH_3$).

MS (ESI+Q-TOF): m/z = 749.4 $[M$ – imidate + OH + $Na]^+$.

2,3,4-*O*-Tribenzyl-α-L-rhamnosyl-(1→3)-4-*O*-acetyl-2-*O*-benzoyl-(1→2)-4-*O*-acetyl-3-*O*-benzoyl-α-L-rhamnosyl-1-(4-tolyl)thio-α-L-rhamnopyranoside (26)

A mixture of compound **25** (23 mg, 0.03 mmol), CH_2Cl_2 (3 mL), compound **2** (7 mg, 0.02) and 4 Å molecular sieves (30 mg) was stirred at r.t. for 30 min then cooled to 0 °C. To the solution was added TMSOTf (0.3 μL, 0.01 mmol), prepared by the addition of TMSOTf (100 μL) to CH_2Cl_2 (5 mL). After stirring at 0 °C for 15 min, the mixture was warmed to r.t. and formation of the product **26** was monitored by TLC (R_f = 0.5; *n*-hexane–EtOAc, 7:3). The mixture was quenched with Et_3N (0.5 mL), diluted with CH_2Cl_2 (10 mL) and filtered. After removal of the volatile solvents, the crude residue was purified by column chromatography on silica gel (*n*-hexane–EtOAc, 8:3) to give **26** (84%, 15 mg).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.08 (d, $J_{6,5}$ = 7.0 Hz, 3 H, H-6), 1.17 (d, $J_{6',5'}$ = 6.0 Hz, 3 H, H-6′), 1.29 (d, $J_{6'',5''}$ = 6.0 Hz, 3 H, H-6″), 1.86 (s, 3 H, $OCCH_3$, $H_{Ac'}$), 1.96 (s, 3 H, $OCCH_3$, H_{Ac}), 2.32 (s, 3 H, $SPhCH_3$), 3.50 (dd, $J_{4'',5''}$ = 8.5 Hz, $J_{4'',3''}$ = 9.0 Hz, 1 H, H-4″), 3.58 (br s, 1 H, H-2″), 3.63 (dd, $J_{3'',4''}$ = 9.0 Hz, $J_{3'',2''}$ = 3.0 Hz, 1 H, H-3″), 3.67 (dq, $J_{5'',4''}$ = 8.5 Hz, $J_{5'',6''}$ = 6.0 Hz, 1 H, H-5″), 3.91 (dq, $J_{5,4}$ = 9.0 Hz, $J_{5,6}$ = 6.0 Hz, 1 H, H-5), 4.23 (dd, $J_{3,4}$ = 9.5 Hz, $J_{3,2}$ = 3.5 Hz, 1 H, H-3′), 4.40 (dq, $J_{5',4'}$ = 9.5 Hz, $J_{5',6'}$ = 6.5 Hz, 1 H, H-5′), 4.40 (d, $J_{2,3}$ = 3.5 Hz, 1 H, H-2), 4.41 (d, J_{gem} = 11.0 Hz, 1 H, OCH_2Ph), 4.43 (d, J_{gem} = 11.5 Hz, 1 H, OCH_2Ph), 4.49 (d, J_{gem} = 11.5 Hz, 1 H, OCH_2Ph), 4.63 (d, J_{gem} = 13.0 Hz, 1 H, OCH_2Ph), 4.67 (d, J_{gem} = 12.5 Hz, 1 H, OCH_2Ph), 4.75 (d, J_{gem} = 11.5 Hz, 1 H, OCH_2Ph), 4.96 (br s, 1 H, H-1″), 5.00 (d, $J_{1',2'}$ = 1.0 Hz, 1 H, H-1′), 5.09 (dd, $J_{4',5'}$ = 9.5 Hz, $J_{4',3'}$ = 9.5 Hz, 1 H, H-4′), 5.33 (dd, $J_{4,5}$ = 9.5 Hz, $J_{4,3}$ = 9.5 Hz, 1 H, H-4), 5.44 (br s, 1 H, H-2′), 5.48 (br s, 1 H, H-1), 5.53 (dd, $J_{3,4}$ = 9.5 Hz, $J_{3,2}$ = 3.5 Hz, 1 H, H-3), 7.12 (d, J = 8.0 Hz, 2 H, H_{arom}), 7.14 (d, J = 7.5 Hz, 2 H, H_{arom}), 7.18–7.42 (m, 19 H, H_{arom}), 7.45 (dd, J = 7.0 Hz, J = 7.0 Hz, 1 H, H_{arom}), 7.51 (dd, J = 7.5 Hz, J = 7.5 Hz, 1 H, H_{arom}), 7.96 (d, J = 7.0 Hz, 2 H, H_{arom}), 8.03 (d, J = 7.0 Hz, 2 H, H_{arom}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.45 (C-6), 17.48 (C-6′), 17.76 (C-6″), 20.76 ($OCCH_3$), 20.76 ($OCCH_3$), 21.13 ($SPhCH_3$), 67.35 (CH), 67.97 (CH), 68.99 (CH), 71.08 (CH), 71.44 (CH), 72.02 (CH), 72.44 (OCH_2Ph), 72.68 (OCH_2Ph), 72.93 (CH), 73.56 (CH), 74.11 (OCH_2Ph), 75.38 (CH), 78.43 (CH), 79.53 (CH), 80.23 (CH), 87.49 (C-1), 99.34 (C-1″), 99.93 (C-1′), 127.22 (arom.), 127.49 (arom., 3 × C), 127.63 (arom., 3 × C), 127.74 (arom., 2 × C), 128.09 (arom., 2 × C), 128.25 (arom., 2 × C), 128.35 (arom., 2 × C), 128.43 (arom., 2 × C), 128.66 (arom., 2 × C), 128.98 (arom.), 129.50 (arom.), 129.84 (arom., 2 × C), 130.03 (arom., 2 × C), 130.19 (arom.), 132.34 (arom., 2 × C), 133.19 (arom.), 133.40 (arom.), 138.12 (arom.), 138.32 (arom.), 138.52 (arom.), 138.86 (arom.), 165.71 (OCPh), 165.71 (OCPh), 169.70 ($OCCH_3$).

MS (ESI+Q-TOF): m/z = 1125.7 $[M + H]^+$, 1147.7 $[M + Na]^+$.

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