Carbohydrate Research 404 (2015) 98–107

Contents lists available at ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

# Efficient synthesis of O-antigen fragments expressed by *Burkholderia anthina* by modular synthesis approach

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ARTICLE INFO

*Article history:*
Received 12 June 2014
Received in revised form 30 October 2014
Accepted 17 November 2014
Available online 29 November 2014

*Keywords:*
D-Galactose
L-Rhamnose
Oligosaccharides
O-Antigen
*Burkholderia anthina*
Glycosylation

ABSTRACT

To facilitate mapping of the interaction region of the O-chain of the lipopolysaccharide from *Burkholderia anthina* and of a lipopolysaccharide-specific monoclonal antibody, trisaccharide propyl α-L-rhamnopyranosyl-(1→2)-α-D-galactopyranosyl-(1→3)-α-L-rhamnopyranoside (**27**) and hexasaccharide propyl α-L-rhamnopyranosyl-(1→2)-α-D-galactopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→2)-α-D-galactopyranosyl-(1→3)-α-L-rhamnopyranoside (**33**) were synthesized. These oligosaccharides represent the repeating monomer and dimer of the O-antigen, respectively.



## 1. Introduction

Gram-negative bacteria like *Burkholderia anthina* belonging to the *Burkholderia cepacia* complex are human opportunistic pathogens responsible for lung infections in immunocompromised patients, such as those with cystic fibrosis.[1] Obviously, lipopolysaccharides (LPSs) of *B. cepacia* complex are pivotally involved in the mechanism of bacterial invasion and virulence.[2] As a rule such LPSs consist of a lipid A, a conserved core oligoheterosaccharide region, and an antigenic O-specific polysaccharide chain. The O-antigen structure of *B. anthina* has been determined by GC–MS and methylation analysis plus different NMR techniques as shown earlier:[3]

[→3)-α-L-Rha-(1→2)-α-L-Rha-(1→2)-α-D-Gal-(1→]$_n$

To understand more about the pathogenic mechanisms, the interaction between this O-polysaccharide chain and a lipopolysaccharide specific monoclonal antibody has been studied using high resolution NMR spectroscopy.[4] With in this framework, trisaccharide and hexasaccharide O-antigen repeating units have been synthesized as simpler carbohydrate ligands. In addition molecular dynamic simulations on the saccharides have been carried out. The synthesis and dynamics studies allow for more detailed information about the molecular recognition process to be obtained. In this multidisciplinary approach, the chemical synthesis of the oligosaccharides was our task.

## 2. Results and discussion

The target of this project was not to develop new synthetic methods but to apply the known chemistry for the efficient synthesis of oligosaccharides. Retrosynthetic analysis of the repeating unit described above illustrates that the key connection for a blockwise oligosaccharide synthesis is the glycosidic linkage between both of the L-rhamnose units. This strategy would require a trisaccharide module having D-galactose located in the center attached with two L-rhamnose units serving either as acceptor or as donor moieties at both ends of the molecule (Fig. 1).

Thus, higher oligosaccharides would be obtained by α-glycosylation of a *manno*-configured donor. The formation of this type of 1,2-*trans* glycosidic bond is characterized by high stereoselectivity caused by the anomeric effect and by using intramolecular neighboring group participation of acyl groups at the C-2 hydroxyl group, especially.

By taking advantage of difference in reactivities of acetyl and benzoyl esters we utilized benzoyl and benzyl functions as permanent and acetyl and allyl functions as temporary protecting groups.

Our initial task was the synthesis of suitable L-rhamnose units which allowed either as donor the stereoselective formation of the required α-(1→2)-glycosidic bond to D-galactose, or as

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http://dx.doi.org/10.1016/j.carres.2014.11.005
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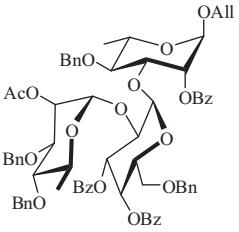



**Figure 1.**

acceptor the α-(1→3)-linkage by D-galactose. For the synthesis of a rhamnosyl acceptor, allyl α-L-rhamnopyranoside **1**[5] was regioselectively protected as an orthoester (**3**)[6] followed by benzylation of the C-4 hydroxyl group.[7] Treatment of the fully protected derivative **4** with dilute acid gave, regioselectively, the intermediate where the C-2 hydroxyl group was protected as a benzoyl ester while its C-3 hydroxyl group remained unprotected (**5**, Scheme 1). So, acceptor **5** was obtained in 86% overall yield, which is calculated based on compound **1**.

That regioselective ring opening of orthoester **4** had occurred was proven by $^1$H NMR data obtained. As expected, the benzoyl substituent at O-2 caused a considerable downfield shift of the H-2 signal from $\delta$ 3.94 ppm of compound **1** to $\delta$ 5.39 ppm in the spectrum of **5**. The stereochemistry at the anomeric center was evident from the $^{13}$C–$^1$H coupling constant $^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz confirming the proposed α configuration.

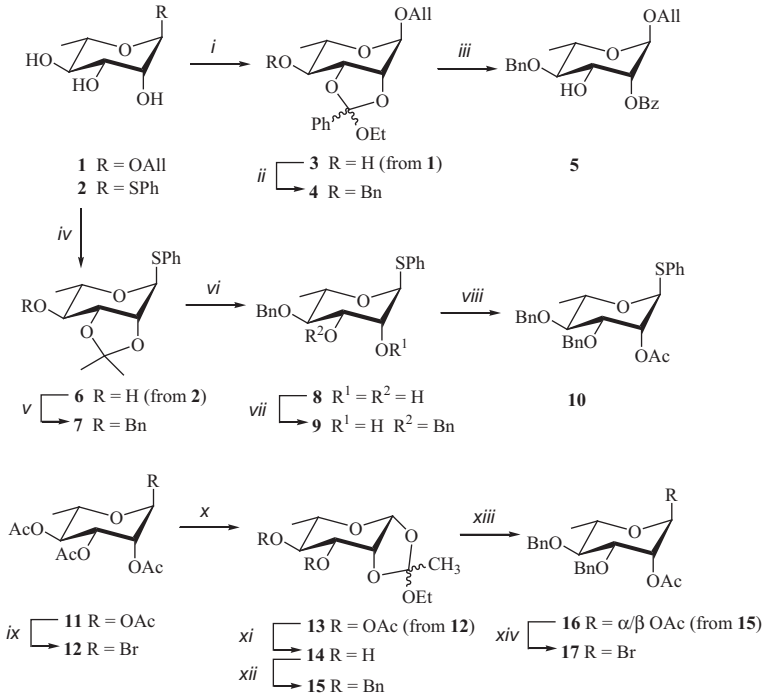
The L-rhamnose donor synthesis was based on procedures from the literature and began with thioglycoside **2**[8] by selective protection of the hydroxyl groups at C-2 and C-3 as the acetonide (**6**) followed again by benzylation of the C-4 hydroxyl group.[9] After removal of the isopropylidene group from **7**, regioselective mono-benzylation by the stannylation methodology provided 3,4-*O*-dibenzyl derivative **9**[10] which gave after acetylation of the C-2 hydroxyl group the glycosyl donor **10**.

The acetylation at the O-2 position of compound **9** caused a significant downfield shift of the H-2 signal from $\delta$ 4.19 to $\delta$ 5.61 ppm in the $^1$H NMR spectrum of compound **10**. Again, the observed $^{13}$C–$^1$H coupling constant $^1J_{C\text{-}1,H\text{-}1}$ = 169 Hz confirmed the assigned α configuration.

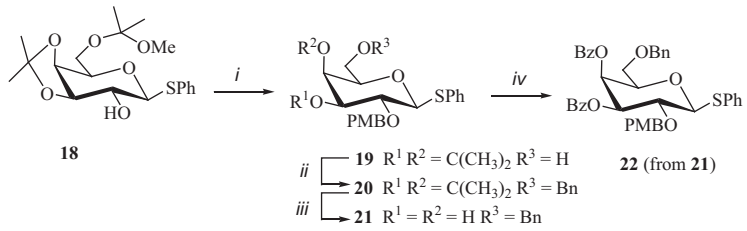
Basically, this pathway can also be applied to the synthesis of acceptor **5**. Thus, isopropylidenation of compound **1** followed by successive benzylation, deisopropylidenation, formation of cyclic orthoester and its regioselective opening provided acceptor **5** as described by Pinto et al.[11] But, compared to the former pathway the overall yield was significantly lower (57%) and the total number of synthetic steps twice as high.

Furthermore, the rhamnose donor **17**[12] was synthesized starting from tetraacetate **11** which was transformed via bromide **12** into the cyclic 1,2-orthoester **13**. Consecutive treatment of **13** with potassium hydroxide and benzyl chloride furnished 3,4-dibenzyl orthoester **15**.[13] Exposure of the cyclic orthoester to aqueous acetic acid, removal of the solvent from the reaction mixture, and treatment of the residue with acetic anhydride provided derivative **16** as α/β-mixture of O-acetates. This second glycosyl donor synthesis gave finally bromide **17** by treatment of **16** with oxalyl bromide in 49% yield over seven steps starting from L-rhamnose tetraacetate **11**.

The next task was to synthesize a D-galactose donor and assemble the galactose-rhamnose unit. After formation of the disaccharide, the deprotected C-2′ hydroxyl group of galactose residue should serve as an acceptor to furnish the desired trisaccharide module **25**. The galactose unit preparation began by reaction of known phenyl β-D-thiogalactopyranoside[14] with 2,2-dimethoxypropane to form the diacetal **18**[15] (Scheme 2) followed by protection of the C-2 hydroxyl group as *p*-methoxybenzyl ether. Exposure of the fully protected intermediate to camphorsulfonic acid




**Scheme 1.** (i) Camphorsulfonic acid, triethylorthobenzoate, DMF, 2 h, 0→20 °C; (ii) BnBr, NaH, DMF, 18 h, 0→20 °C; (iii) 50% aq acetic acid, 30 min, 20 °C (**5**, 86% over three steps); (iv) camphorsulfonic acid, 2,2-dimethoxypropane, acetone, 1 h, 20 °C; (v) BnBr, NaH, DMF, 16 h, 0→20 °C; (vi) 90% aq acetic acid, 3 h, 90 °C (**8**, 87% over three steps); (vii) dibutyltin oxide, benzene, 5 h, reflux; then CsF, BnBr, DMF, 2 h, 20 °C (**9**, 75%); (viii) $Ac_2O$, pyridine, 1 h, 0→20 °C (**10**, 91%); (ix) 40% HBr, $CHCl_3$, 1 h, 0→20 °C; (x) 2,6-lutidine, *n*-$Bu_4NBr$, EtOH, $CH_2Cl_2$, 18 h, 20 °C (**13**, 92% over two steps); (xi, xii) KOH, BnBr, toluene, 45 min, reflux (**15**, 82%); (xiii) 70% aq acetic acid, 10 min, 20 °C, ultrasonic bath; then $Ac_2O$, pyridine, 1 h, 0→20 °C (**16a**, 66%; **16b**, 15%); oxalyl bromide, $CH_2Cl_2$, 2 h, −40→20 °C, Ar atmosphere (**8**, 85%).




**Scheme 2.** (i) *p*-Methoxybenzyl bromide, NaH, DMF, 16 h, 0→20 °C; then camphorsulfonic acid, MeOH, 10 min, 20 °C (**19**, 80%); (ii) BnBr, NaH, DMF, 16 h, 0→20 °C (**20**, 81%); (iii) camphorsulfonic acid, MeOH, 14 h, 20 °C (**21**, 79%); (iv) BzCl, pyridine, 16 h, 0→20 °C (**22**, 98%).

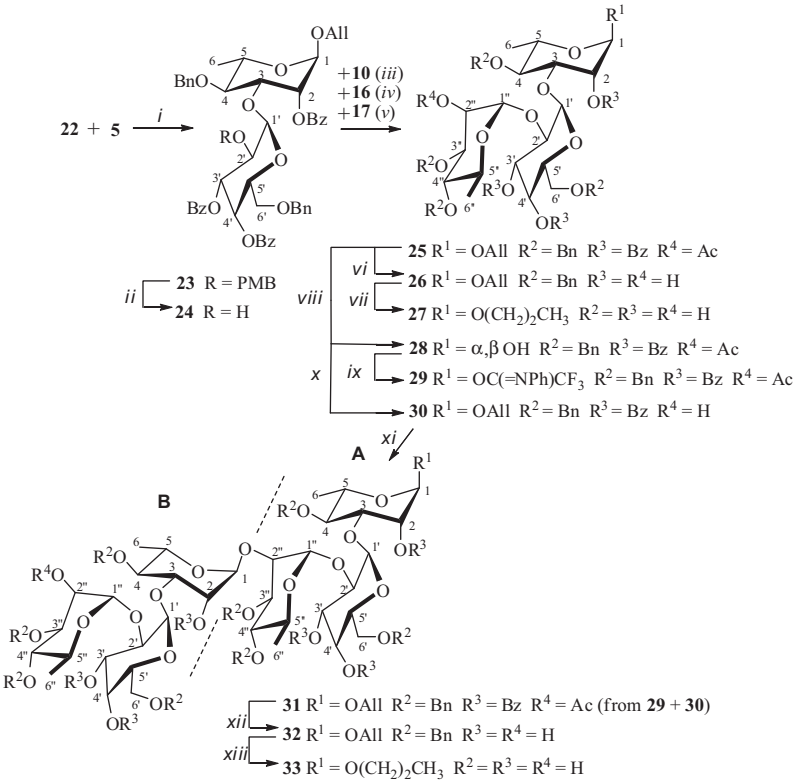
effected the removal of the aliphatic acetal at the C-6 hydroxyl group (**19**).[16] Consecutive benzylation (**20**), deisopropylidenation (**21**), and benzoylation gave the galactose module **22** in 50% yield over six steps.

Detailed NMR investigation of compounds **19**, **20**, **21**, and **22** verified the expected structures. First, the benzylation of the O-6 position caused a significant downfield shift of the C-6 signal in the $^{13}C$ NMR spectrum from $\delta$ 62.6 to $\delta$ 69.7 ppm in the spectrum of compound **20**. The deisopropylidenation of compound **20** led to an upfield shift of H-3 and H-4 signals in the $^{1}H$ NMR spectrum and C-3 and C-4 signals in the $^{13}C$ NMR spectrum, respectively. The benzoylation of O-3 and O-4 positions caused again a significant downfield shift of the H-3 and H-4 proton signals from 3.61 ppm (H-3) and 3.75 ppm (H-4) to 5.87 ppm (H-3) and 5.43 ppm (H-4) in the $^{1}H$ NMR spectrum of donor **22**. The vicinal coupling constant $^{3}J_{H\text{-}1,H\text{-}2}$ = 9.6 Hz is consistent with the β configuration.

For the synthesis of galactosyl-rhamnose disaccharide **23**, coupling of thioglycoside **22** and rhamnose acceptor **7** was promoted with NIS/AgOTf[17] in $CH_2Cl_2$ at −20→20 °C. The glycosylation reaction was complete within 30 min. Under these conditions disaccharide **23** was obtained in excellent 89% yield (Scheme 3). The acceptor disaccharide **24** was then prepared by oxidative cleavage of the *p*-methoxybenzyl ether linkage using cerium ammonium nitrate (CAN)[18] which gave quite a better yield (85%) than 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[19] (58%).

The coupling constant of $^{3}J_{H\text{-}1',H\text{-}2'}$ = 3.5 Hz in the $^{1}H$ NMR spectrum of disaccharide **23** indicated clearly the α linkage between the D-galactose and the L-rhamnose residue. After the debenzylation at the O-2′ position, the NMR data confirmed the proposed structure of compound **24**.

Although we expected a high stereoselectivity during the formation of the L-Rha-(1→2)-α-D-Gal linkage, we systematically examined the trisaccharide synthesis by applying the potential rhamnopyranosyl donors **10**, **16**, and **17**. Thus, disaccharide acceptor **24** was glycosylated with rhamnosyl bromide **17** in the presence of Helferich promotors[20] to give trisaccharide **25** in




**Scheme 3.** (i) NIS, AgOTf, mol. sieves, $CH_2Cl_2$, Ar atmosphere, 20 min, −10→20 °C (**23**, 89%); (ii) CAN, $CH_3CN$–$H_2O$, 3 h, 20 °C (85%); (iii) NIS, AgOTf, mol. sieves, Ar atmosphere, $CH_2Cl_2$, 1 h, −20→20 °C (**25**, 66%); (iv) TMSOTf, mol. sieves, Ar atmosphere, $CH_2Cl_2$, 36 h, 20 °C (**25**, 61%); (v) $Hg(CN)_2$, $HgBr_2$, $CH_3CN$, mol. sieves, Ar atmosphere, in the dark, 24 h, 20 °C (**25**, 35%); (vi) NaOMe, MeOH, 24 h, 20 °C (**26**, 74%); (vii) $Pd(OH)_2$/C, MeOH, $H_2$ atmosphere, 48 h, 20 °C (**27**, 94%); (viii) $PdCl_2$, MeOH–$CH_2Cl_2$, 16 h, 20 °C; (ix) $ClC(=NPh)CF_3$, $CsCO_3$, acetone, 3 h, 20 °C (**29**, 87% over two steps); (x) methanolic HCl, 18 h, 20 °C (**30**, 74%); (xi) TMSOTf, mol. sieves, Ar atmosphere, $CH_2Cl_2$, 30 min, −10 to 20 °C (**31**, 53%); (xii) NaOMe, MeOH, 43 h, 20 °C (**32**, 76%); (xiii) $Pd(OH)_2$/C, MeOH–$H_2O$, $H_2$ atmosphere, 72 h, 20 °C (**33**, 93%).

disappointing 35% yield. However, when 1-O-acetate **16** was used as donor promoted by trimethylsilyl trifluoromethanesulfonate,[21] **25** was obtained in promising 61% yield. The best result was observed when thioglycoside **10** was coupled with **24** by treatment with NIS/AgOTf[17] to provide the desired trisaccharide **25** in 66% yield. As anticipated, the *manno*-configuration and the neighboring effect of O-2 ester function directed the glycosylation to give only the α-linkage. The α configuration of the newly generated stereogenic center in the trisaccharide **25** was verified by 1D and 2D NMR spectroscopy. The $^{13}C$–$^{1}H$ coupling constant $^{1}J_{C\text{-}1'',H\text{-}1''}$ = 169 Hz is consistent with the proposed α linkage.

Synthesis of either trisaccharide donor **29** or trisaccharide acceptor **30** starting from module **25** was performed following procedures described previously by our group.[5] Accordingly deallylation[22] of **25** gave hemiacetal **28** which was treated with (*N*-phenyl)trifluoroacetimidate chloride[23] in the presence of $Cs_2CO_3$ in acetone to furnish (*N*-phenyl)trifluoroacetimidate **29**.

The anomeric proton signal of donor **29** appeared as broadened at ambient temperature due to a dynamic process, but the coupling constant $^{1}J_{C\text{-}1,H\text{-}1}$ = 174 Hz established the α configuration of the (*N*-phenyl)trifluoroacetimidate group at the anomeric center. On the other hand, deacetylation of **25** with 0.28 m methanolic HCl[5] provided acceptor **30** with only the O-2″ position being unsubstituted. The successful cleavage of the acetyl group was confirmed in the $^{1}H$ NMR spectrum by a significant upfield shift for the H-2″ ring proton signal from δ 5.09 ppm (**25**) to δ 3.71 ppm (**30**).

The final task was to couple donor **29** with acceptor **30** to get the hexasaccharide **31** and the global deprotection of both oligosaccharides **25** and **31** (Scheme 3). Using $CF_3SO_3SiMe_3$ as promoter, hexasaccharide **31** was obtained in 53% yield. Again, the stereochemistry of the new glycosidic linkage of hexasaccharide **31** was evident from the $^{13}C$–$^{1}H$ coupling constant $^{1}J_{C\text{-}1,H\text{-}1}$ = 169 Hz. Deprotection of oligosaccharides **25** and **31** was accomplished by Zemplén deacylation followed by catalytic hydrogenation to give the propyl glycosides **27** and **33** in good yield.

In summary, we have developed an efficient synthesis of trisaccharide module **25** which represents the repeating O-antigen structure of *B. anthina*. Applying the methodology of modular design principle[5] higher fragments of the O-chain are accessible. On this basis, hexasaccharide **31** was synthesized. After deprotection trisaccharide **27**and hexasaccharide **33** were used for mapping the interacting epitope with a monoclonal antibody and conformational studies on the bond state.[4]

## 3. Experimental

### 3.1. General methods

Melting points were determined with a Boetius micro-heating plate BHMK 05 (Rapido, Dresden) and were not corrected. Optical rotations were measured for solutions in a 2-cm cell with an automatic polarimeter GYROMAT (Dr. Kernchen Co.). $^{1}H$ NMR spectra (500.13 MHz, 300.13 MHz and 250.13 MHz) and $^{13}C$ NMR spectra (125.8 MHz, 75.5 MHz and 62.9 MHz) were recorded with Bruker instruments AVANCE 500, AVANCE 300, and AVANCE 250, with $CDCl_3$, $Me_2SO$-$d_6$, $CD_3OD$ or $D_2O$ as solvents. NMR spectra were calibrated using solvent signals ($CDCl_3$: δ $^{1}H$ = 7.26 ppm, δ $^{13}C$ = 77.00 ppm; $Me_2SO$-$d_6$: δ $^{1}H$ = 2.50 ppm, δ $^{13}C$ = 39.7 ppm; $CD_3OD$: δ $^{1}H$ = 3.31 ppm, δ $^{13}C$ = 49.0 ppm) or acetone as internal standard ($D_2O$: δ $^{1}H$ = 2.23 ppm, δ $^{13}C$ = 31.1 ppm). The $^{1}H$ and $^{13}C$ NMR signals were assigned by DEPT, two-dimensional $^{1}H$,$^{1}H$ COSY and NOESY and $^{1}H$,$^{13}C$ correlation spectra (HMBC and HSQC). For NMR numbering of atoms see Scheme 3. Mass spectra were recorded with a Finnigan MAT 95-XP (Thermo Electron). Elemental analysis was performed with a CHNS-Flash-EA-1112 instrument (Thermoquest). All washing solutions were cooled to ~5 °C. The $NaHCO_3$ and NaCl solutions were saturated. Reactions were monitored by thin-layer chromatography (TLC; Silica Gel 60, $F_{254}$, 0.25 mm, Merck KGaA). The following solvent systems (v/v) were used: ($A_1$) 2:1, ($A_2$) 1:1 *n*-heptane–EtOAc; ($B_1$) 50:1, ($B_2$) 15:1, ($B_3$) 1:1, ($B_4$) 18:1, ($B_5$) 2:3 toluene–EtOAc; ($C_1$) 2:1 $CHCl_3$–MeOH; ($D_1$) 4:0.5:0.5 acetonitrile–pyridine–$H_2O$. TLC spots were made visible by dipping the TLC plates into an ethanolic 10% $H_2SO_4$ solution and charring with a heat gun for 3–5 min. Detection of benzyl derivatives was effected by UV fluorescence. Preparative flash chromatography was performed by elution from columns of slurry-packed Silica Gel 60 (Merck, 40–63 μm). All solvents and reagents were purified and dried according to standard procedures.[24] After classical work-up of the reaction mixtures, the organic layers were dried over $MgSO_4$ and then concentrated under reduced pressure (rotary evaporator).

### 3.2. Allyl 2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (5)

Camphorsulfonic acid (117 mg, 0.5 mmol) and triethylorthobenzoate (0.86 mL, 3.8 mmol) were successively added to a solution of allyl α-L-rhamnopyranoside[5] (**1**, 613 mg, 3.0 mmol) in dry *N*,*N*-dimethylformamide (30 mL) at 0 °C under an argon atmosphere. The mixture was allowed to attain room temperature and stirring was continued for 2 h. After complete reaction (**3**, TLC: $R_f$ = 0.73, EtOAc), the reaction mixture was neutralized with triethylamine (1 mL) and then cooled to 0 °C, followed by addition of sodium hydride (178 mg, 7.4 mmol, 60% dispersion in oil) with vigorous stirring. The reaction mixture was stirred for 30 min at 0 °C, followed by dropwise addition of benzyl bromide (0.5 mL, 4.2 mmol) at 0 °C. The mixture was allowed to attain room temperature and stirring was continued for another 18 h. After complete reaction (**4**, TLC: $R_f$ = 0.76, solvent $A_1$), MeOH (10 mL) was added at 0 °C, and after stirring for additional 20 min, the reaction mixture was concentrated. The residue was dissolved in $CH_2Cl_2$ (50 mL) and the organic solution was washed with water (2 × 20 mL), dried and concentrated. The crude product was purified by flash chromatography (short column, Eluent EtOAc–heptane 1:4 with 1% $NEt_3$). The obtained syrup was dissolved in 50% aq acetic acid (45 mL) and stirred 30 min at room temperature (monitored by TLC). After complete reaction, satd $NaHCO_3$ (10 mL) solution was added to the reaction mixture. The solution was concentrated and repeatedly co-concentrated with toluene. The crude product was purified by flash chromatography (eluent solvent $A_1$) to give **5** (1.03 g, 86%) as a colorless syrup: $[\alpha]_D^{22}$ +5.3 (*c* 1.0, $CHCl_3$), Lit.[11] $[\alpha]_D^{25}$ +5.5 (*c* 0.9, $CH_2Cl_2$); $R_f$ = 0.55 (solvent $A_1$); NMR data see Ref. 11.

### 3.3. Phenyl 2-*O*-acetyl-3,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (10)

Acetyl anhydride (0.9 mL, 9.5 mmol) was added dropwise to a stirred solution of phenyl 3,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside[10] (**9**, 437 mg, 1.0 mmol) in dry pyridine (2 mL) under an argon atmosphere at 0 °C. Then the reaction mixture was allowed to attain room temperature and stirring was continued for 1 h. After complete reaction (monitored by TLC), MeOH (100 μL) was added at 0 °C, and after stirring for additional 20 min, the reaction mixture was poured into ice-water (80 mL). The aqueous phase was extracted with $CH_2Cl_2$ (4 × 20 mL), and the combined organic phases were washed successively with cold aq 15% $NaHSO_4$ (2 × 30 mL), aq $NaHCO_3$ (2 × 30 mL), water (1 × 50 mL), dried, and concentrated. Purification by flash chromatography (solvent $B_1$) afforded compound **10** (435 mg, 91%) as a colorless syrup: $[\alpha]_D^{22}$ −117.2 (*c* 1.1, $CHCl_3$); $R_f$ = 0.25 (solvent $B_1$); $^{1}H$ NMR (250.13 MHz, $CDCl_3$): δ 7.47–7.24 (m, 15H, 2 $CH_2C_6H_5$, $SC_6H_5$); 5.61 (dd, 1H, $^{3}J_{2,3}$ = 3.3 Hz, H-2); 5.41 (d, 1H, $^{3}J_{1,2}$ = 1.6 Hz, H-1);

4.94, 4.63 (2d, 2H, $^2J$ = 10.8 Hz), 4.72, 4.56 (2d, 2H, $^2J$ = 11.2 Hz), (2 C$H_2$C$_6$H$_5$); 4.23 (dq, 1H, $^3J_{4,5}$ = 9.5 Hz, $^3J_{5,6}$ = 6.2 Hz, H-5); 3.91 (dd, 1H, $^3J_{3,4}$ = 9.3 Hz, H-3); 3.52 ('t', 1H, $^3J_{4,5}$ = 9.5 Hz, H-4); 2.15 (s, 3H, COCH$_3$); 1.35 (d, 3H, $^3J_{5,6}$ = 6.2 Hz, H-6); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 170.2 (*C*OCH$_3$); 138.3 137.7 (2 *i*-CH$_2$C$_6$H$_5$); 133.9 (*i*-SC$_6$H$_5$); 131.7, 129.0, 128.4, 128.4, 128.1, 127.9 (2 *o*-, *m*-CH$_2$C$_6$H$_5$, *o*-, *m*-SC$_6$H$_5$); 127.8, 127.7, 127.6 (2 *p*-CH$_2$C$_6$H$_5$, *p*-SC$_6$H$_5$); 86.1 (C-1); 80.2 (C-4); 78.2 (C-3); 75.5, 71.8 (2× *C*H$_2$C$_6$H$_5$); 70.6 (C-2); 69.1 (C-5); 21.0 (*C*OCH$_3$); 17.8 (C-6). HRMS (ESI-TOF): calcd for $C_{28}H_{30}O_5S$ (M+Na$^+$): *m*/*z* 501.1706, found: *m*/*z* 501.1705. Anal. Calcd for $C_{28}H_{30}O_5S$ (478.60): C, 70.27; H, 6.32; S, 6.70. Found: C, 70.18; H, 6.38; S, 6.58.

### 3.4. Phenyl 3,4-*O*-isopropylidene-2-*O*-*p*-methoxybenzyl-1-thio-β-D-galactopyranoside (19)

A mixture of phenyl 1-thio-β-D-galactopyranoside[14] (1.09 g, 4.0 mmol), 2,2-dimethoxypropane (35 mL) and camphorsulfonic acid (40 mg, 0.2 mmol) was stirred for 48 h under an argon atmosphere at room temperature. After complete reaction (**18**, TLC: $R_f$ = 0.39, $A_2$ with 1% $NEt_3$), the reaction mixture was neutralized with triethylamine (1.4 mL) and concentrated. The residue was dissolved in dry *N*,*N*-dimethylformamide (27 mL) and cooled to 0 °C, followed by addition of sodium hydride (237 mg, 9.9 mmol, 60% dispersion in oil) with vigorous stirring. The reaction mixture was stirred for 30 min at 0 °C, followed by dropwise addition of *p*-methoxybenzyl bromide (0.82 mL, 5.6 mmol) at 0 °C. The mixture was allowed to attain room temperature and stirring was continued for another 16 h. After complete reaction (TLC: $R_f$ = 0.61, $A_2$ with 1% $NEt_3$), MeOH (5 mL) was added at 0 °C, and after stirring for additional 20 min, the reaction mixture was concentrated. The residue was dissolved in $CH_2Cl_2$ (50 mL) and the organic solution was washed with water (2 × 20 mL), dried, and concentrated. A solution of the raw material and camphorsulfonic acid (29 mg, 0.1 mmol) in methanol (25 mL) was stirred for 10 min at room temperature. After complete reaction (monitored by TLC), the reaction mixture was neutralized with triethylamine (0.6 mL) and concentrated. The crude product was purified by flash chromatography (eluent gradient ethyl acetate in heptane 20→50% with 1% $NEt_3$) to give **19** (1.39 g, 80%) as a colorless syrup: $[\alpha]_D^{23}$ +2.2 (*c* 1.0, $CHCl_3$); $R_f$ = 0.32 (solvent $A_2$ with 1% $NEt_3$); $^1$H NMR (250.13 MHz, $CDCl_3$): $\delta$ 7.52 (m, 2H), 7.42–7.20 (m, 5H), 6.89 (m, 2H), (CH$_2$C$_6$*H*$_4$, SC$_6$H$_5$); 4.77, 4.62 (2d, 2H, $^2J$ = 11.0 Hz, C*H*$_2$C$_6$H$_4$); 4.65 (d, 1H, $^3J_{1,2}$ = 9.3 Hz, H-1); 4.28 ('t', 1H, $^3J_{3,4}$ = 6.0 Hz, H-3), 4.20 (dd, 1H, H-4); 3.96 (ddd, 1H, H-5); 3.87–3.70 (m, 2H, H-6); 3.81 (s, 3H, OCH$_3$); 3.53 (dd, 1H, $^3J_{2,3}$ = 6.1 Hz, H-2); 1.43 (s, 3H), 1.36 (s, 3H), (C(CH$_3$)$_2$); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 159.3 (*p*-CH$_2$C$_6$H$_4$); 133.4 (*i*-SC$_6$H$_5$); 130.0 (*i*-CH$_2$C$_6$H$_4$); 131.9, 129.9, 128.9 (*o*-CH$_2$C$_6$H$_4$, *o*-, *m*-SC$_6$H$_5$); 127.5 (*p*-CH$_2$C$_6$H$_5$); 127.2 (*p*-SC$_6$H$_5$); 113.7 (*m*-CH$_2$C$_6$H$_4$); 110.3 (*C*(CH$_3$)$_2$); 85.9 (C-1); 79.8 (C-3); 77.9 (C-2); 76.7 (C-5); 73.9 (C-4); 73.1 (*C*H$_2$C$_6$H$_4$); 62.6 (C-6); 55.3 (OCH$_3$); 27.7, 26.3 (C(*C*H$_3$)$_2$). HRMS (ESI-TOF): calcd for $C_{23}H_{28}O_6S$ (M+H$^+$): *m*/*z* 433.5328, found: *m*/*z* 433.5329. Anal. Calcd for $C_{23}H_{28}O_6S$ (432.53): C, 63.87; H, 6.52; S, 7.41. Found: C, 63.78; H, 6.65; S, 7.29.

### 3.5. Phenyl 6-*O*-benzyl-3,4-*O*-isopropylidene-2-*O*-*p*-methoxybenzyl-1-thio-β-D-galactopyranoside (20)

Sodium hydride (178 mg, 7.4 mmol, 60% suspension in oil) was added to a stirred solution of compound **19** (1.3 g, 3.0 mmol) in dry *N*,*N*-dimethylformamide (20 mL) under an argon atmosphere at 0 °C. The reaction mixture was stirred for 30 min at that temperature, followed by dropwise addition of benzyl bromide (0.5 mL, 4.2 mmol) at 0 °C. The mixture was allowed to attain room temperature and stirring was continued for another 16 h. After complete reaction (monitored by TLC), MeOH (10 mL) was added at 0 °C, and after stirring for additional 20 min, the reaction mixture was concentrated. The residue was dissolved in $CH_2Cl_2$ (50 mL) and the organic solution was washed with water (2 × 20 mL), dried, and concentrated. The crude product was purified by column chromatography (eluent gradient ethyl acetate in heptane 33→50% with 1% $NEt_3$) to give **20** (1.27 g, 81%) as a colorless syrup: $[\alpha]_D^{23}$ −20.2° (*c* 1.0, $CHCl_3$); $R_f$ = 0.71 (solvent $A_2$ with 1% $NEt_3$); $^1$H NMR (250.13 MHz, $CDCl_3$): $\delta$ 7.55 (m, 2H), 7.38–7.20 (m, 10H), 6.88 (m, 2H), (CH$_2$C$_6$*H*$_5$, CH$_2$C$_6$*H*$_4$, SC$_6$H$_5$); 4.76, 4.63 (2d, 2H, $^2J$ = 11.0 Hz), 4.60, 4.53 (2d, 2H, $^2J$ = 11.8 Hz), (C*H*$_2$C$_6$H$_5$, C*H*$_2$C$_6$H$_4$); 4.65 (d, 1H, $^3J_{1,2}$ = 9.5 Hz, H-1); 4.28–4.20 (m, 2H, H-3, H-4); 3.94 (ddd, 1H, $^3J_{4,5}$ = 5.9 Hz, $^3J_{5,6a}$ = 5.9 Hz, $^3J_{5,6b}$ = 1.8 Hz, H-5); 3.82–3.78 (m, 2H, H-6); 3.81 (s, 3H, OCH$_3$); 3.53 (dd, 1H, $^3J_{1,2}$ = 9.5 Hz, $^3J_{2,3}$ = 5.7 Hz, H-2); 1.43 (s, 3H), 1.36 (s, 3H), (C(CH$_3$)$_2$); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 159.3 (*p*-CH$_2$C$_6$H$_4$); 138.2 (*i*-CH$_2$C$_6$H$_5$); 134.0 (*i*-SC$_6$H$_5$); 130.0 (*i*-CH$_2$C$_6$H$_4$); 131.7, 129.9, 128.7, 128.3, 127.6 (*o*-, *m*-CH$_2$C$_6$H$_5$, *o*-CH$_2$C$_6$H$_4$, *o*-, *m*-SC$_6$H$_5$); 127.6 (*p*-CH$_2$C$_6$H$_5$); 127.2 (*p*-SC$_6$H$_5$); 113.7 (*m*-CH$_2$C$_6$H$_4$); 110.0 (*C*(CH$_3$)$_2$); 86.3 (C-1); 79.6 (C-3); 77.9 (C-2); 75.7 (C-5); 73.8 (C-4); 73.1, 73.5 (*C*H$_2$C$_6$H$_5$, *C*H$_2$C$_6$H$_4$); 69.7 (C-6); 55.3 (OCH$_3$); 26.3, 27.8 (C(*C*H$_3$)$_2$). HRMS (ESI-TOF): calcd for $C_{30}H_{35}O_6S$ (M+H$^+$): *m*/*z* 523.2149, found: *m*/*z* 523.2144. Anal. Calcd for $C_{30}H_{34}O_6S$ (522.65): C, 68.94; H, 6.56; S, 6.14. Found: C, 68.71; H, 6.73; S, 6.18.

### 3.6. Phenyl 6-*O*-benzyl-2-*O*-*p*-methoxybenzyl-1-thio-β-D-galactopyranoside (21)

To a solution of compound **20** (540 mg, 1.0 mmol) in methanol (56 mL) ± 10-camphorsulfonic acid (120 mg, 0.5 mmol) was added. The mixture was stirred for 14 h at room temperature (monitored by TLC). Then the solution was neutralized with $NEt_3$ and concentrated. The residue was purified by flash chromatography (eluent gradient ethyl acetate in heptane 33→100%) to afford compound **21** (396 mg, 79%) as colorless crystals: mp 103–106 °C (EtOAc–heptane); $[\alpha]_D^{25}$ +9.5 (*c* 1.0, $CHCl_3$); $R_f$ = 0.46 (EtOAc); $^1$H NMR (250.13 MHz, DMSO-$d_6$): $\delta$ 7.48 (m, 2H), 7.37–7.17 (m, 10H), 6.87 (m, 2H), (CH$_2$C$_6$*H*$_5$, CH$_2$C$_6$*H*$_4$, SC$_6$H$_5$); 5.10 (d, 1H, $^3J_{3,OH}$ = 6.6 Hz, OH-3); 4.81 (d, 1H, $^3J_{4,OH}$ = 4.5 Hz, OH-4); 4.78 (d, 1H, $^3J_{1,2}$ = 9.5 Hz, H-1); 4.70, 4.55 (2d, 2H, $^2J$ = 10.6 Hz), 4.48 (s, 2H), (C*H*$_2$C$_6$H$_5$, C*H*$_2$C$_6$H$_4$); 3.82–3.68 (m, 2H, H-4, H-5); 3.73 (s, 3H, OCH$_3$); 3.66–3.55 (m, 3H, H-3, H-6); 3.48 ('t', 1H, $^3J_{2,3}$ = 9.3 Hz, H-2); $^{13}$C NMR (62.9 MHz, DMSO-$d_6$): $\delta$ 158.6 (*p*-CH$_2$C$_6$H$_4$); 138.5 (*i*-CH$_2$C$_6$H$_5$); 135.1 (*i*-SC$_6$H$_5$); 131.0 (*i*-CH$_2$C$_6$H$_4$); 129.6, 129.5, 129.0, 128.3, 127.5 (*o*-, *m*-CH$_2$C$_6$H$_5$, *o*-CH$_2$C$_6$H$_4$, *o*-, *m*-SC$_6$H$_5$); 127.5 (*p*-CH$_2$C$_6$H$_5$); 126.5 (*p*-SC$_6$H$_5$); 113.5 (*m*-CH$_2$C$_6$H$_4$); 86.0 (C-1); 77.8 (C-2); 77.3 (C-5); 74.5 (C-3); 73.9, 72.3 (*C*H$_2$C$_6$H$_5$, *C*H$_2$C$_6$H$_4$); 70.0 (C-6); 69.5 (C-4); 55.2 (OCH$_3$). HRMS (ESI-TOF): calcd for $C_{27}H_{30}O_6S$ (M+Na$^+$): *m*/*z* 505.1655, found: *m*/*z* 505.1658. Anal. Calcd for $C_{27}H_{30}O_6S$ (482.59): C, 67.20; H, 6.27; S, 6.64. Found: C, 67.04; H, 6.53; S, 6.68.

### 3.7. Phenyl 3,4-di-*O*-benzoyl-6-*O*-benzyl-2-*O*-*p*-methoxybenzyl-1-thio-β-D-galactopyranoside (22)

Benzoyl chloride (0.65 mL, 5.6 mmol) was added dropwise to a stirred solution of compound **21** (966 mg, 2.0 mmol) in dry pyridine (10 mL) under an argon atmosphere at 0 °C. The reaction mixture was stirred for 30 min at that temperature. The solution was then allowed to attain room temperature and stirring was continued for further 16 h. After complete reaction (monitored by TLC), MeOH (1 mL) was added at 0 °C, and after stirring for additional 20 min, the reaction mixture was poured into ice-water (100 mL). The aqueous phase was extracted with $CH_2Cl_2$ (4 × 50 mL), and the combined organic phases were washed successively with cold aq 15% $NaHSO_4$ (4 × 50 mL), aq $NaHCO_3$ (2 × 50 mL), water

(2 × 50 mL), dried and concentrated. Purification by flash chromatography (eluent gradient ethyl acetate in heptane 20→50%) afforded compound **22** (1.36 g, 98%) as a colorless syrup: $[\alpha]_D^{24}$ +107.8 (*c* 1.0, $CHCl_3$); $R_f$ = 0.49 (solvent $A_1$); $^1$H NMR (300.13 MHz, $CDCl_3$): $\delta$ 7.92 (m, 2H), 7.78 (m, 2H), 7.69 (m, 2H), 7.63 (m, 1H), 7.52–7.42 (m, 3H), 7.36–7.17 (m, 10H), 7.08 (m, 2H), 6.65 (m, 2H), (2 $COC_6H_5$, $CH_2C_6H_5$, $CH_2C_6H_4$, $SC_6H_5$); 5.87 (dd, 1H, $^3J_{3,4}$ = 3.3 Hz, $^3J_{4,5}$ = 1.0 Hz, H-4); 5.43 (dd, 1H, $^3J_{2,3}$ = 9.4 Hz, H-3); 4.84 (d, 1H, $^3J_{1,2}$ = 9.6 Hz, H-1); 4.73, 4.52 (2d, 2H, $^2J$ = 10.4 Hz), 4.53, 4.43 (2d, 2H, $^2J$ = 11.9 Hz), ($CH_2C_6H_5$, $CH_2C_6H_4$); 4.08 (d't', 1H, $^3J_{5,6a}$ = 6.3 Hz, $^3J_{5,6b}$ = 6.3 Hz, $^3J_{4,5}$ = 1.0 Hz, H-5); 3.96 ('t', 1H, H-2); 3.70 (dd, 1H, $^2J_{6a,6b}$ = 9.8 Hz, $^3J_{5,6a}$ = 6.3 Hz, H-6a); 3.69 (s, 3H, $OCH_3$); 3.61 (dd, 1H, $^2J_{6a,6b}$ = 9.8 Hz, $^3J_{5,6b}$ = 6.3 Hz, H-6b); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ 165.3, 165.3 (2 $COC_6H_5$); 159.2 (*p*-$CH_2C_6H_4$); 137.6 (*i*-$CH_2C_6H_5$); 133.3, 133.0 (*p*-$CH_2C_6H_5$); 133.0 (*i*-$SC_6H_5$); 132.5, 129.9, 129.8, 129.6, 129.0, 128.4, 128.3, 128.2, 127.7 (*o*-, *m*-$CH_2C_6H_5$, *o*-$CH_2C_6H_4$, 2 *o*-, *m*-$COC_6H_5$, *o*-, *m*-$SC_6H_5$); 129.5, 129.5 (2 *i*-$COC_6H_5$); 127.7 (*p*-$CH_2C_6H_5$); 127.7 (*p*-$SC_6H_5$); 113.6 (*m*-$CH_2C_6H_4$); 87.4 (C-1); 76.3 (C-5); 75.0 (C-3); 75.0, 73.6 ($CH_2C_6H_5$, $CH_2C_6H_4$); 74.8 (C-2); 69.1 (C-4); 68.2 (C-6); 55.1 ($OCH_3$). HRMS (ESI-TOF): calcd for $C_{41}H_{38}O_8S$ ($M+H^+$): *m*/*z* 713.2180, found: *m*/*z* 713.2188. Anal. Calcd for $C_{41}H_{38}O_8S$ (690.80): C, 71.29; H, 5.54; S, 4.64. Found: C, 71.23; H, 5.67; S, 4.59.

### 3.8. Allyl 3,4-di-*O*-benzoyl-6-*O*-benzyl-2-*O*-*p*-methoxybenzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (23)

Glycosyl acceptor **5** (398 mg, 1.0 mmol), donor **22** (829 mg, 1.2 mmol), and molecular sieves (4 Å, 7 g) were dried under high vacuum for 1 h at room temperature. The solids were then suspended in dry $CH_2Cl_2$ (75 mL), and the reaction mixture was stirred for 30 min under an argon atmosphere in the dark at room temperature. After cooling to −10 °C, NIS (515 mg, 2.3 mmol) and AgOTf (309 mg, 1.2 mmol, dissolved in 1 mL dry toluene) were added and the suspension was stirred for 10 min at −10 °C and then 20 min at room temperature. After complete reaction (monitored by TLC), the reaction mixture was neutralized with $NEt_3$ and filtered through Celite. The filtrate was washed with cold aq 1 M $Na_2S_2O_3$ (2 × 30 mL) and aq NaCl (1 × 30 mL), dried, and concentrated. Purification by flash chromatography (eluent gradient ethyl acetate in toluene 4→6%) gave compound **23** (870 mg, 89%) as a colorless syrup: $[\alpha]_D^{22}$ +151.6 (*c* 1.0, $CHCl_3$); $R_f$ = 0.38 (solvent $B_2$); $^1$H NMR (500.13 MHz, $CDCl_3$): $\delta$ 8.07 (m, 2H), 7.84 (m, 2H), 7.70 (m, 2H), 7.60–7.52 (m, 4H), 7.47–7.39 (m, 5H), 7.35 (m, 2H), 7.28–7.23 (m, 3H), 7.22–7.12 (m, 5H), 6.91 (m, 2H), 6.54 (m, 2H), (2 $CH_2C_6H_5$, $CH_2C_6H_4$, 3 $COC_6H_5$); 5.85 (m, 1H, $CH_2CH$=$CH_2$); 5.76 (dd, 1H, $^3J_{3',4'}$ = 3.4 Hz, H-3′); 5.68 (dd, 1H, $^3J_{2,3}$ = 3.3 Hz, H-2); 5.59 (dd, 1H, $^3J_{4',5'}$ = 1.0 Hz, H-4′); 5.42 (d, 1H, $^3J_{1',2'}$ = 3.5 Hz, H-1′); 5.31–5.16 (m, 2H, $CH_2CH$=$CH_2$); 5.02, 4.88 (2d, 2H, $^2J$ = 10.7 Hz), 4.33, 4.27 (2d, 2H, $^2J$ = 12.0 Hz), 4.22 (center of $q_{AB}$, 2H, $^2J$ = 12.3 Hz) (2 $CH_2C_6H_5$, $CH_2C_6H_4$); 4.93 (d, 1H, $^3J_{1,2}$ = 1.8 Hz, H-1); 4.52 (ddd, 1H, $^3J_{4',5'}$ = 1.0 Hz, H-5′); 4.45 (dd, 1H, $^3J_{3,4}$ = 9.7 Hz, H-3); 4.07 (dd, 1H, $J_{2',3'}$ 10.6 Hz, H-2′); 4.15 (m, 1H), 4.01 (m, 1H), ($CH_2CH$=$CH_2$); 3.90 (dq, 1H, $^3J_{4,5}$ = 9.7 Hz, $^3J_{5,6}$ = 6.3 Hz, H-5); 3.74 ('t', 1H, $^3J_{4,5}$ = 9.7 Hz, H-4); 3.69 (s, 3H, $OCH_3$); 3.46 (dd, 1H, $^3J_{5',6b'}$ = 6.8 Hz, H-6b′); 3.29 (dd, 1H, $^3J_{5',6a'}$ = 5.5 Hz, $^2J_{6a',6b'}$ = 10.4 Hz, H-6a′); 1.46 (d, 3H, $^3J_{5,6}$ = 6.2 Hz, H-6); $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ 166.1, 165.4, 165.4 (3 $COC_6H_5$); 159.0 (*p*-$CH_2C_6H_4$); 138.1, 137.9 (2 *i*-$CH_2C_6H_5$); 133.6 ($CH_2CH$=$CH_2$); 133.2, 133.1, 132.8 (3 *p*-$COC_6H_5$); 130.0, 129.7, 129.6, 129.6, 128.6, 128.4, 128.4, 128.3, 128.0, 127.5 (2) (2 *o*-, *m*-$CH_2C_6H_5$, *o*-$CH_2C_6H_4$, 3 *o*-, *m*-$COC_6H_5$); 129.9, 129.8, 129.7 (3 *i*-$COC_6H_5$); 128.0, 127.2 (2 *p*-$CH_2C_6H_5$); 117.6 ($CH_2CH$=$CH_2$); 113.5 (*m*-$CH_2C_6H_4$); 96.7 (C-1); 92.6 (C-1′); 79.7 (C-4); 72.3 (C-3); 71.9 (C-2′); 76.1, 72.6, 71.6 (2 $CH_2C_6H_5$, $CH_2C_6H_4$); 70.4 (C-3′); 69.9 (C-4′); 68.2 (C-6′); 68.2 (C-5); 68.1 ($CH_2CH$=$CH_2$); 68.0 (C-2); 67.1 (C-5′); 55.1 ($OCH_3$); 18.2 (C-6). HRMS (ESI-TOF): calcd for $C_{58}H_{58}O_{14}$ ($M+Na^+$): *m*/*z* 1001.3719, found: *m*/*z* 1001.3748. Anal. Calcd for $C_{58}H_{58}O_{14}$ (979.07): C, 71.15; H, 5.97. Found: C, 70.67; H, 6.34.

### 3.9. Allyl 3,4-di-*O*-benzoyl-6-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (24)

Cerium ammonium nitrate (CAN; 343 mg, 0.63 mmol) was added to a stirred solution of compound **23** (490 mg, 0.5 mmol) in acetonitrile–water (9:1, 10 mL). After stirring for 1 h at room temperature, additional CAN (274 mg, 0.5 mmol) was added to the solution. The mixture was stirred for additional 1 h and then diluted with $CH_2Cl_2$ (75 mL). The solution was washed with aq $NaHCO_3$ (2 × 25 mL). The aq phase was extracted with $CH_2Cl_2$ (2 × 30 ml). The combined organic phases were dried, concentrated, and the residue was purified by flash chromatography (eluent gradient ethyl acetate in toluene 4→6%) to give compound **24** (365 mg, 85%) as a colorless syrup: $[\alpha]_D^{23}$ +178.1 (*c* 1.1, $CHCl_3$); $R_f$ = 0.35 (solvent $B_2$); $^1$H NMR (500.13 MHz, $CDCl_3$): $\delta$ 8.09 (m, 2H), 7.99 (m, 2H), 7.84 (m, 2H), 7.62–7.57 (m, 2H), 7.50–7.43 (m, 6H), 7.34–7.24 (m, 5H), 7.22–7.13 (m, 6H), (2 $CH_2C_6H_5$, 3 $COC_6H_5$); 5.87 (m, 1H, $CH_2CH$=$CH_2$); 5.63 (dd, 1H, $^3J_{2,3}$ = 3.2 Hz, H-2); 5.59 (dd, 1H, $^3J_{3',4'}$ = 3.3 Hz, H-4′); 5.53 (dd, 1H, $^3J_{2',3'}$ = 10.4 Hz, H-3′); 5.46 (d, 1H, $^3J_{1',2'}$ = 3.8 Hz, H-1′); 5.32–5.18 (m, 2H, $CH_2CH$=$CH_2$); 4.94 (d, 1H, $^3J_{1,2}$ = 1.9 Hz, H-1); 4.89, 4.84 (2d, 2H, $^2J$ = 10.7 Hz, $CH_2C_6H_5$); 4.49–4.45 (m, 2H, H-3, H-5′); 4.27 (d't', 1H, H-2′); 4.20 (center of $q_{AB}$, 2H, $^2J$ = 12.1 Hz, $CH_2C_6H_5$); 4.18 (m, 1H), 4.02 (m, 1H), ($CH_2CH$=$CH_2$); 3.93 (dq, 1H, H-5); 3.65 ('t', 1H, $^3J_{3,4}$ = 9.8 Hz, $^3J_{4,5}$ = 9.5 Hz, H-4); 3.46 (dd, 1H, $^3J_{5',6a'}$ = 6.6 Hz, H-6a′); 3.29 (dd, 1H, $^3J_{5',6b'}$ = 6.0 Hz, $^2J_{6a',6b'}$ = 10.1 Hz, H-6b′); 2.16 (d, 1H, $^3J_{2',OH'}$ = 9.5 Hz, OH-2′); 1.48 (d, 3H, $^3J_{5,6}$ = 6.2 Hz, H-6); $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ 166.4, 166.2, 165.4 (3 $COC_6H_5$); 138.0, 137.7 (2 *i*-$CH_2C_6H_5$); 133.6, 133.2, 132.9 (3 *p*-$COC_6H_5$); 133.4 ($CH_2CH$=$CH_2$); 129.9, 129.8 (2), 128.6, 128.6, 128.5, 128.1, 128.0 (2), 127.5 (2 *o*-, *m*-$CH_2C_6H_5$, 3 *o*-, *m*-$COC_6H_5$); 129.7, 129.3 (2) (3 *i*-$COC_6H_5$); 128.2, 127.3 (2 *p*-$CH_2C_6H_5$); 117.9 ($CH_2CH$=$CH_2$); 96.7 (C-1); 95.2 (C-1′); 80.0 (C-4); 73.6 (C-3); 76.1, 72.8 (2 $CH_2C_6H_5$); 71.6 (C-3′); 69.5 (C-4′); 68.8 (C-2); 68.3 (C-5); 68.2 ($CH_2CH$=$CH_2$); 68.1 (C-6′); 67.8 (C-5′); 67.4 (C-2′); 18.2 (C-6). HRMS (ESI-TOF): calcd for $C_{50}H_{50}O_{13}$ ($M+Na^+$): *m*/*z* 881.3144, found: *m*/*z* 881.3139. Anal. Calcd for $C_{50}H_{50}O_{13}$ (858.92): C, 69.92; H, 5.87. Found: C, 69.63; H, 6.11.

### 3.10. Allyl 2-*O*-acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-6-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (25)

Via thioglycoside **10**: Glycosyl acceptor **24** (215 mg, 0.25 mmol), donor **10** (158 mg, 0.33 mmol), and molecular sieves (4 Å, 1 g) were dried under high vacuum for 1 h at room temperature. The solids were then suspended in dry $CH_2Cl_2$ (26 mL), and the reaction mixture was stirred for 30 min at room temperature under an argon atmosphere in the dark. After cooling to −10 °C, NIS (176 mg, 0.78 mmol) and AgOTf (68 mg, 0.26 mmol, dissolved in 1 mL dry toluene) were added and the suspension was stirred for 10 min at −10 °C and then 1 h at room temperature. After complete reaction (monitored by TLC), the reaction mixture was neutralized with $NEt_3$ and filtered through Celite. The filtrate was washed with cold aq 1 M $Na_2S_2O_3$ (2 × 30 mL) and aq NaCl (1 × 30 mL), dried, and concentrated. Purification by flash chromatography (eluent gradient ethyl acetate in toluene 4→6%) gave compound **25** (203 mg, 66%) as a colorless syrup.

Via 1-O-acetate **16**: Glycosyl acceptor **24** (215 mg, 0.25 mmol), donor **16** (141 mg, 0.33 mmol), and molecular sieves (4 Å, 1 g) were dried under high vacuum for 1 h at room temperature. The

solids were then suspended in dry $CH_2Cl_2$ (9 mL), and the reaction mixture was stirred for 1 h at room temperature under an argon atmosphere in the dark. After the addition of trimethylsilyl trifluoromethanesulfonate (144 μL, 0.8 mmol), the suspension was stirred 36 h at room temperature. After complete reaction (monitored by TLC), the reaction mixture was passed through a layer of alkaline alumina by elution with chloroform. The filtrate was washed with water (2 × 15 mL), dried, and concentrated. Purification by flash chromatography (eluent gradient ethyl acetate in toluene 4→6%) gave compound **25** (188 mg, 61%) as a colorless syrup.

Via glycosyl bromide **17**: Glycosyl acceptor **24** (217 mg, 0.25 mmol), mercury(II) cyanide (39 mg, 0.15 mmol), mercury(II) bromide (18 mg, 0.05 mmol), and molecular sieves (4 Å, 1 g) were dried under high vacuum for 1 h at room temperature. A solution of glycosyl donor **17** (157 mg, 0.35 mmol) in dry acetonitrile (10 mL) was added to the glycosyl acceptor, mercury(II) cyanide, mercury(II) bromide, and molecular sieves. The reaction mixture was then stirred for 24 h under an argon atmosphere at room temperature. After complete reaction (monitored by TLC), the reaction mixture was passed through a layer of Celite by elution with chloroform. The filtrate was washed with water (2 × 15 mL), 30% aq KI solution (2 × 15 mL) and water (2 × 15 mL), dried and concentrated. Purification by flash chromatography (eluent gradient ethyl acetate in toluene 4→6%) gave compound **25** (110 mg, 35%) as a colorless syrup: $[\alpha]_D^{24}$ +128.1 (*c* 1.0, $CHCl_3$); $R_f$ = 0.53 (solvent $B_2$); $^1$H NMR (500.13 MHz, $CDCl_3$): $\delta$ 8.09 (m, 2H), 7.97 (m, 2H), 7.80 (m, 2H), 7.60 (m, 2H), 7.49–7.43 (m, 3H), 7.40–7.13 (m, 22H), 7.07 (m, 2H), (4 $CH_2C_6H_5$, 3 $COC_6H_5$); 5.92 (dd, 1H, $^3J_{3',4'}$ = 3.5 Hz, H-3′); 5.82 (m, 1H, $CH_2CH$=$CH_2$); 5.61 (dd, 1H, $^3J_{2,3}$ = 2.9 Hz, $^3J_{1,2}$ = 1.9 Hz, H-2); 5.57 (dd, 1H, $^3J_{4',5'}$ = 1.3 Hz, H-4′); 5.40 (d, 1H, $^3J_{1',2'}$ = 3.5 Hz, H-1′); 5.27–5.12 (m, 2H, $CH_2CH$=$CH_2$); 5.09 (dd, 1H, $^3J_{2'',3''}$ = 3.4 Hz, H-2″); 5.05, 4.91 (2d, 2H, $^2J$ = 10.4 Hz, $CH_2C_6H_5$); 4.88 (d, 1H, $^3J_{1'',2''}$ = 1.9 Hz, H-1″); 4.87 (d, 1H, $^3J_{1,2}$ = 1.9 Hz, H-1); 4.74, 4.57 (2d, 2H, $^2J$ = 11.4 Hz, $CH_2C_6H_5$); 4.68 (m, 1H, H-5′); 4.49 (dd, 1H, $^3J_{3,4}$ = 9.8 Hz, H-3); 4.46 (dd, 1H, $^3J_{2',3'}$ = 10.7 Hz, H-2′); 4.22 (center of $q_{AB}$, 2H, $^2J$ = 12.0 Hz, $CH_2C_6H_5$); 4.16, 3.44 (2d, 2H, $^2J$ = 10.6 Hz) ($CH_2C_6H_5$); 4.14–4.10 (m, 1H, CHHCH=$CH_2$); 3.99–3.92 (m, 2H, H-5″, CHHCH=$CH_2$); 3.90 (dq, 1H, $^3J_{4,5}$ = 9.5 Hz, $^3J_{5,6}$ = 6.2 Hz, H-5); 3.79 ('t', 1H, $^3J_{4,5}$ = 9.5 Hz, H-4); 3.49 (dd, 1H, $^3J_{5',6a'}$ = 6.9 Hz, H-6a′); 3.28 (dd, 1H, $^3J_{5',6b'}$ = 5.4 Hz, $^2J_{6a',6b'}$ = 10.4 Hz, H-6b′); 3.27 (dd, 1H, $^3J_{3'',4''}$ = 9.0 Hz, H-3″); 3.21 ('t', 1H, $^3J_{4'',5''}$ = 9.0 Hz, H-4″); 1.64 (s, 3H, $COCH_3$); 1.48 (d, 3H, $^3J_{5,6}$ = 6.2 Hz, H-6); 1.38 (d, 3H, $^3J_{5'',6''}$ = 6.2 Hz, H-6″); $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ 168.8 ($COCH_3$); 165.5, 165.5, 165.2 (3 $COC_6H_5$); 138.9, 138.3, 138.1, 137.8 (4 *i*-$CH_2C_6H_5$); 133.6 ($CH_2CH$=$CH_2$); 133.2, 133.1, 132.9 (3 *p*-$COC_6H_5$); 130.5, 129.7, 129.7, 129.0, 128.6, 128.5, 128.3, 128.2, 128.2, 128.2, 128.2, 127.9, 127.7, 127.4 (4 *o*-, *m*-$CH_2C_6H_5$, 3 *o*-, *m*-$COC_6H_5$); 129.6, 129.5, 129.4 (3 *i*-$COC_6H_5$); 127.5, 127.3, 127.2 (3 *p*-$CH_2C_6H_5$); 117.6 ($CH_2CH$=$CH_2$); 100.1 (C-1″); 96.5 (C-1); 94.6 (C-1′); 80.0 (C-4); 79.9 (C-4″); 77.9 (C-3″); 72.4 (C-3); 72.1 (C-2′); 76.1, 74.9, 72.7, 71.2 (4 $CH_2C_6H_5$); 70.9 (C-3′); 70.0 (C-4′); 68.6, 68.5 (C-5, C-5″); 68.5 (C-2″); 68.4 (C-2); 68.3 (C-6′); 68.2 ($CH_2CH$=$CH_2$); 67.2 (C-5′); 20.3 ($COCH_3$); 18.3 (C-6); 18.2 (C-6″); one *p*-$CH_2C_6H_5$ not given. HRMS (ESI-TOF): calcd for $C_{72}H_{74}O_{18}$ (M+Na$^+$): *m*/*z* 1249.4767, found: *m*/*z* 1249.4792. Anal. Calcd for $C_{72}H_{74}O_{18}$ (1227.35): C, 70.46; H, 6.08. Found: C, 70.03; H, 6.55.

### 3.11. Allyl 3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-6-*O*-benzyl-α-D-galactopyranosyl-(1→3)-4-*O*-benzyl-α-L-rhamnopyranoside (26)

Compound **25** (95 mg, 0.08 mmol) was dissolved in dry MeOH (5 mL) and methanolic NaOMe (1 M, 1 mL) was added. The reaction mixture was stirred for 20 h at room temperature. After complete reaction (monitored by TLC), the reaction mixture was neutralized with Amberlite ($H^+$) resin and filtered through Celite. The filtrate was concentrated and the raw material was purified by flash chromatography (solvent $B_3$) to give compound **26** (50 mg, 74%) as a colorless syrup: $[\alpha]_D^{23}$ −9.2 (*c* 0.5, $CHCl_3$); $R_f$ = 0.54 (EtOAc); $^1$H NMR (500.13 MHz, $CDCl_3$): $\delta$ 7.36–7.20 (m, 20H, 4 $CH_2C_6H_5$); 5.87 (m, 1H, $CH_2CH$=$CH_2$); 5.38 (d, 1H, $^3J_{1'',2''}$ = 2.0 Hz, H-1″); 5.29–5.15 (m, 2H, $CH_2CH$=$CH_2$); 5.01 (d, 1H, $^3J_{1',2'}$ = 3.8 Hz, H-1′); 4.84, 4.62 (2d, 2H, $^2J$ = 11.4 Hz); 4.72, 4.59 (2d, 2H, $^2J$ = 11.4 Hz), 4.68 (center of $q_{AB}$, 2H, $^2J$ = 11.4 Hz), 4.49, 4.35 (2d, 2H, $^2J$ = 12.0 Hz), (4 $CH_2C_6H_5$); 4.79 (d, 1H, $^3J_{1,2}$ = 1.2 Hz, H-1); 4.18 (br m, 1H, H-2″); 4.13 (m, 1H, CHHCH=$CH_2$); 4.07 (dd, 1H, $^3J_{2',3'}$ = 9.8 Hz, $^3J_{1',2'}$ = 3.8 Hz, H-2′); 4.01–3.88 (m, 7H, H-2, H-3, H-3′, H-3″, H-4′, H-5′, CHHCH=$CH_2$); 3.78 (dq, 1H, $^3J_{4,5}$ = 9.8 Hz, $^3J_{5,6}$ = 6.3 Hz, H-5); 3.70 (dq, 1H, $^3J_{4'',5''}$ = 8.9 Hz, $^3J_{5'',6''}$ = 6.3 Hz, H-5″); 3.50–3.44 (m, 3H, H-4, H-4″, H-6a′); 3.22 (dd, 1H, $^2J$ = 10.7 Hz, $^3J_{5',6b'}$ = 3.5 Hz, H-6b′); 3.64 (d, 1H, $^3J_{H,OH}$ = 1.4 Hz, OH); 3.29 (d, 1H, $^3J_{H,OH}$ = 1.4 Hz, OH); 2.60 (d, 1H, $^3J_{H,OH}$ = 9.0 Hz, OH); 2.56 (d, 1H, $^3J_{2'',OH\text{-}2''}$ = 1.8 Hz, OH-2″); 1.35 (d, 3H, $^3J_{5,6}$ = 6.3 Hz, H-6); 1.30 (d, 3H, $^3J_{5'',6''}$ = 6.3 Hz, H-6″); $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ 138.4, 138.2, 138.0, 137.1 (4 *i*-$CH_2C_6H_5$); 133.8 ($CH_2CH$=$CH_2$); 128.5, 128.5, 128.4, 128.4, 127.8, 127.8, 127.8, 127.3 (4 *o*-, *m*-$CH_2C_6H_5$); 128.0, 127.8, 127.7, 127.7 (4 *p*-$CH_2C_6H_5$); 117.5 ($CH_2CH$=$CH_2$); 99.7 (C-1″); 98.3 (C-1); 94.9 (C-1′); 79.9 (C-3″); 79.6 (C-4); 79.4 (C-4″); 76.1 (C-3); 75.2, 74.7, 73.9, 72.2 (4 $CH_2C_6H_5$); 72.8 (C-2′); 71.4 (C-4′); 70.9 (C-3′); 70.8 (C-6′); 68.5 (C-5″); 68.4 (C-2″); 68.0 (C-5′); 68.0 ($CH_2CH$=$CH_2$); 67.5 (C-2); 67.4 (C-5); 18.0 (C-6″); 18.0 (C-6). HRMS (ESI-TOF): calcd for $C_{49}H_{60}O_{14}$ (M+Na$^+$): *m*/*z* 895.3875, found: *m*/*z* 895.3891. Anal. Calcd for $C_{49}H_{60}O_{14}$ (872.99): C, 67.41; H, 6.93. Found: C, 67.77; H, 6.94.

### 3.12. Propyl α-L-rhamnopyranosyl-(1→2)-α-D-galactopyranosyl-(1→3)-α-L-rhamnopyranoside (27)

To a solution of compound **26** (45 mg, 0.05 mmol) in methanol (6 mL) 20% palladium(II) hydroxide on carbon (75 mg) was added. The suspension was stirred for 43 h under a hydrogen atmosphere at room temperature (monitored by TLC). The mixture was then filtered over Celite by elution with methanol and the combined filtrates were concentrated. Purification by flash chromatography (solvent $C_1$) afforded compound **27** (25 mg, 94%) as a colorless powder: $[\alpha]_D^{23}$ −46.3 (*c* 1.0, $H_2O$); $R_f$ = 0.62 (solvent $D_1$); $^1$H NMR (300.13 MHz, $CD_3OD$): $\delta$ 5.04 (d, 1H, $^3J_{1'',2''}$ = 1.7 Hz, H-1″); 5.01 (d, 1H, $^3J_{1',2'}$ = 3.6 Hz, H-1′); 4.71 (d, 1H, $^3J_{1,2}$ = 1.7 Hz, H-1); 4.19 (ddd, 1H, $^3J_{5',6a'}$ = 6.4 Hz, $^3J_{5',6b'}$ = 5.8 Hz, $^3J_{4',5'}$ = 1.0 Hz, H-5′); 4.05–3.90 (m, 5H, H-2, H-2′, H-2″, H-3′, H-4′); 3.78–3.68 (m, 4H, H-3, H-3″, H-6′); 3.67–3.58 (m, 3H, H-5, H-5″, $CHHCH_2CH_3$); 3.49 ('t', 1H, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.4 Hz, H-4); 3.43–3.34 (m, 2H, H-4″, CHH$CH_2$ $CH_3$); 1.60 (m, 2H, $CH_2CH_2CH_3$); 1.30 (d, 3H, $^3J_{5,6(5'',6'')}$ = 6.2 Hz), 1.29 (d, 3H, $^3J_{5,6(5'',6'')}$ = 6.3 Hz), (H-6, H-6″); 0.95 (t, 3H, $^3J$ = 7.5 Hz, $CH_3$); $^{13}$C NMR (75.5 MHz, $CD_3OD$): $\delta$ 103.6 (C-1″); 101.2 (C-1); 98.0 (C-1′); 79.1 (C-3); 76.3 (C-2′); 73.9 (C-4″); 72.5 (C-4); 72.3 (C-5′); 72.2 (C-3″); 72.0 (C-2″); 71.6 (C-4′); 70.7 (C-3′); 70.4 (2) ($CH_2CH_2CH_3$, C-5 or C-5″); 69.5, 69.5 (C-2, C-5 or C-5″); 62.7 (C-6′); 23.8 ($CH_2CH_2CH_3$); 18.2, 18.1 (C-6, C-6″); 11.1 ($CH_3$). HRMS (ESI-TOF): calcd for $C_{21}H_{38}O_{14}$ (M+Na$^+$): *m*/*z* 537.2154, found: *m*/*z* 537.2167. Anal. Calcd for $C_{21}H_{38}O_{14}$ (514.52): C, 49.02; H, 7.44. Found: C, 49.00; H, 7.48.

### 3.13. 2-*O*-Acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-6-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl (*N*-phenyl)trifluoroacetimidate (29)

To a solution of compound **25** (245 mg, 0.2 mmol) in MeOH/$CH_2Cl_2$ (6.5 mL, 1.6:1) palladium chloride (8 mg, 0.05 mmol) was

added at room temperature. The reaction mixture was stirred for 16 h at room temperature. After complete reaction (monitored by TLC), the mixture was filtrated through Celite by elution with $CH_2Cl_2$ and concentrated to yield the hemiacetal intermediate **28** ($\alpha,\beta$ = 4:1.3) in a satisfying purity for the next step: $R_f$ = 0.16 (solvent $B_2$); α-anomer $^1$H NMR (500.13 MHz, $CDCl_3$): $\delta$ 8.10 (m, 2H), 7.97 (m, 2H), 7.82 (m, 2H), 7.62–7.56 (m, 3H), 7.49–7.43 (m, 4H), 7.40–7.07 (m, 22H) (4 $CH_2C_6H_5$, 3 $COC_6H_5$); 5.90 (dd, 1H, $^3J_{2',3'}$ = 10.6 Hz, $^3J_{3',4'}$ = 3.5 Hz, H-3′); 5.55–5.51 (m, 2H, H-2, H-4′); 5.41 (d, 1H, $^3J_{1',2'}$ = 3.5 Hz, H-1′); 5.18 (d, 1H, $^3J_{1,2}$ = 1.9 Hz, H-1); 5.11 (dd, 1H, $^3J_{2'',3''}$ = 3.5 Hz, $^3J_{1'',2''}$ = 1.9 Hz, H-2″); 5.07, 4.88 (2d, 2H, $^2J$ = 10.5 Hz, C$H_2C_6H_5$); 4.90 (d, 1H, $^3J_{1'',2''}$ = 1.9 Hz, H-1″); 4.76, 4.57 (2d, 2H, $^2J$ = 11.4 Hz, C$H_2C_6H_5$); 4.68 (m, 1H, H-5′); 4.53 (dd, 1H, $^3J_{3,4}$ = 9.8 Hz, $^3J_{2,3}$ = 2.8 Hz, H-3); 4.49 (dd, 1H, $^3J_{2',3'}$ = 10.6 Hz, H-2′); 4.23 (center of $q_{AB}$, 2H, $^2J$ = 12.0 Hz, C$H_2C_6H_5$); 4.20–3.59 (2d, 2H, $^2J$ = 10.9 Hz, C$H_2C_6H_5$); 4.07 (dq, 1H, $^3J_{4,5}$ = 9.5 Hz, $^3J_{5,6}$ = 6.2 Hz, H-5); 3.94 (dq, 1H, $^3J_{4'',5''}$ = 9.5 Hz, $^3J_{5'',6''}$ = 6.3 Hz, H-5″); 3.77 ('t', 1H, $^3J_{3,4}$ = 9.8 Hz, $^3J_{4,5}$ = 9.5 Hz, H-4); 3.50 (dd, 1H, $^2J_{6a',6b'}$ = 10.4 Hz, $^3J_{5',6a'}$ = 6.9 Hz, H-6a′); 3.77 (dd, 1H, $^3J_{3'',4''}$ = 8.9 Hz, H-3″); 3.32 (dd, 1H, $^3J_{5',6b'}$ = 5.4 Hz, H-6b′); 3.23 ('t', $^3J_{4'',5''}$ = 9.5 - Hz, H-4″); 2.85 (br s, 1H, OH); 1.67 (s, 3H, $COCH_3$); 1.44 (d, 3H, $^3J_{5,6}$ = 6.2 Hz, H-6); 1.37 (d, 3H, $^3J_{5'',6''}$ = 6.3 Hz, H-6″); $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ 168.9 ($COCH_3$); 165.5, 165.5, 165.2 (3 $COC_6H_5$); 138.8, 137.9, 137.8, 137.8 (4 *i*-$CH_2C_6H_5$); 129.5, 129.5, 129.4 (3 *i*-$COC_6H_5$); 133.2, 133.1, 132.9 (3 *p*-$COC_6H_5$); 130.7–127.2 (several signals of *o*-, *m*-$COC_6H_5$, *o*-, *m*-, *p*-$CH_2C_6H_5$); 100.1 (C-1″); 95.3 (C-1′); 92.1 (C-1); 80.0 (C-4); 79.8 (C-4″); 77.7 (C-3″); 72.5 (C-3); 72.4 (C-2′); 76.0, 74.9, 72.7, 71.1 (4 $CH_2C_6H_5$); 70.9 (C-3′); 69.9 (C-4′); 69.1 (C-2); 68.6 (C-5); 68.4 (C-5″); 68.4 (C-2″); 68.3 (C-6′); 67.4 (C-5′); 20.4 ($COCH_3$); 18.3 (C-6); 18.1 (C-6″). HRMS (ESI-TOF): calcd for $C_{69}H_{70}O_{18}$ (M+$Na^+$): *m*/*z* 1209.4454, found: *m*/*z* 1209.4454.

To a solution of the hemiacetal **28** in acetone (10 mL) and water (50 μL), $Cs_2CO_3$ (189 mg, 0.6 mmol) and (*N*-phenyl)trifluoroacetimidoyl chloride (56 μL, 0.4 mmol) were added at room temperature. The reaction mixture was stirred for 3 h at room temperature. After complete reaction (monitored by TLC), the mixture was filtered through Celite by elution with chloroform. The combined filtrates were concentrated and purified by flash chromatography (solvent D) to yield compound **29** (236 mg, 87%) as a colorless foam: $[\alpha]_D^{23}$ +164.2 (*c* 0.3, $CHCl_3$); $R_f$ = 0.57 (solvent $B_2$); $^1$H NMR (500.13 MHz, $CDCl_3$): $\delta$ 8.08 (m, 2H), 7.97 (m, 2H), 7.81 (m, 2H), 7.61–7.56 (m, 4H), 7.49–7.42 (m, 4H), 7.41–7.08 (m, 22H), 7.05 (m, 2H), 6.83 (m, 2H) (4 $CH_2C_6H_5$, 3 $COC_6H_5$, $NC_6H_5$); 6.27 (br, 1H, H-1); 5.93 (dd, 1H, $^3J_{2',3'}$ = 10.7 Hz, $^3J_{3',4'}$ = 3.5 Hz, H-3′); 5.78 (dd, 1H, $^3J_{2,3}$ = 3.0 Hz, $^3J_{1,2}$ = 2.0 Hz, H-2); 5.58 (dd, 1H, $^3J_{3',4'}$ = 3.5 Hz, $^3J_{4',5'}$ = 1.4 Hz, H-4′); 5.46 (d, 1H, $^3J_{1',2'}$ = 3.3 Hz, H-1′); 5.07 (dd, 1H, $^3J_{2'',3''}$ = 3.3 Hz, $^3J_{1'',2''}$ = 1.9 Hz, H-2″); 5.08, 4.94 (2d, 2H, $^2J$ = 10.4 Hz, C$H_2C_6H_5$); 4.89 (d, 1H, $^3J_{1'',2''}$ = 1.9 Hz, H-1″); 4.74, 4.58 (2d, 2H, $^2J$ = 11.4 Hz, C$H_2C_6H_5$); 4.68 (m, 1H, H-5′); 4.55 (dd, 1H, $^3J_{3,4}$ = 9.8 Hz, $^3J_{2,3}$ = 3.0 Hz, H-3); 4.50 (dd, 1H, $^3J_{2',3'}$ = 10.7 Hz, H-2′); 4.24 (center of $q_{AB}$, 2H, $^2J$ = 12.2 Hz), 4.15, 3.43 (2d, 2H, $^2J$ = 10.7 Hz), (2 C$H_2C_6H_5$); 4.03 (dq, 1H, $^3J_{4,5}$ = 9.2 Hz, $^3J_{5,6}$ = 6.1 Hz, H-5); 3.98 (dq, 1H, $^3J_{4'',5''}$ = 9.1 Hz, $^3J_{5'',6''}$ = 6.3 Hz, H-5″); 3.98 ('t', 1H, $^3J_{3,4}$ = 9.8 Hz, $^3J_{4,5}$ = 9.5 Hz, H-4); 3.43 (dd, 1H, $^3J_{5',6a'}$ = 6.3 Hz, H-6a′); 3.31 (dd, 1H, $^2J_{6a',6b'}$ = 10.2 Hz, $^3J_{5',6b'}$ = 5.7 Hz, H-6b′); 3.26 (dd, 1H, $^3J_{3'',4''}$ = 8.8 Hz, $^3J_{2'',3''}$ = 3.3 Hz, H-3″); 3.23 ('t', 1H, $^3J_{4'',5''}$ = 9.1 Hz, H-4″); 1.63 (s, 3H, $COCH_3$); 1.54 (d, 3H, $^3J_{5,6}$ = 6.1 Hz, H-6); 1.39 (d, 3H, $^3J_{5'',6''}$ = 6.3 Hz, H-6″); $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ 168.8 ($COCH_3$); 165.1, 165.2, 165.5 (3 $COC_6H_5$); 143.2 (*i*-$NC_6H_5$); 137.4, 137.8, 138.2, 138.9 (4 *i*-$CH_2C_6H_5$); 133.4, 133.3, 133.0 (3 *p*-$COC_6H_5$); 130.6–127.2 (several signals of *o*-, *m*-$COC_6H_5$, *o*-, *m*-, *p*-$CH_2C_6H_5$, *m*-$NC_6H_5$); 129.5, 129.3, 128.8 (3 *i*-$COC_6H_5$); 124.4 (*p*-$NC_6H_5$); 119.4 (*o*-$NC_6H_5$); 115.9 (q, $^1J_{C,F}$ = 287 Hz, $CF_3$); 100.0 (C-1″); 94.4 (C-1′); 93.7 (br, C-1); 79.9 (C-4″); 79.0 (C-4); 77.8 (C-3″); 76.3, 75.0, 72.8, 71.2 (4 $CH_2C_6H_5$); 71.7 (C-2′); 71.5 (C-3); 71.3 (C-5); 70.8 (C-3′); 69.8 (C-4′); 68.5 (C-5″); 68.4 (C-2″); 67.8 (C-6′); 67.3 (C-5′); 66.7 (C-2); 20.3 ($COCH_3$); 18.4 (C-6); 18.1 (C-6″); $CCF_3$ signal not given; $^{19}$F NMR (282.4 MHz, $CDCl_3$): $\delta$ −75.7 ($CF_3$). HRMS (ESI-TOF): calcd for $C_{77}H_{74}F_3NO_{18}$ (M+$Na^+$): *m*/*z* 1380.4750, found: *m*/*z* 1380.4751.

### 3.14. Allyl 3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-6-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (30)

Compound **25** (245 mg, 0.2 mmol) was added to a stirred methanolic HCl solution [0.28 M, 10 mL, prepared by adding 0.2 mL acetyl chloride to 10 mL ice-cold dry MeOH], and the mixture was kept for 18 h under an argon atmosphere at room temperature (monitored by TLC). The reaction mixture was then filtered through a layer of alkaline alumina by elution with chloroform. The combined filtrates were dried and concentrated. Purification by flash chromatography (solvent $B_4$) gave compound **30** (175 mg, 74%) as a colorless foam: $[\alpha]_D^{23}$ +146.1 (*c* 0.5, $CHCl_3$); $R_f$ = 0.29 (solvent $B_2$); $^1$H NMR (500.13 MHz, $CDCl_3$): $\delta$ 8.08 (m, 2H), 7.95 (m, 2H), 7.86 (m, 2H), 7.58 (m, 3H), 7.48 (m, 1H), 7.43 (m, 3H), 7.40–7.10 (m, 23H), (4 $CH_2C_6H_5$, 3 $COC_6H_5$); 5.86 (dd, 1H, $^3J_{3',4'}$ = 3.5 Hz, H-3′); 5.83 (m, 1H, $CH_2CH{=}CH_2$); 5.66 (dd, 1H, $^3J_{3',4'}$ = 3.5 Hz, $^3J_{4',5'}$ = 1.5 Hz, H-4′); 5.58 (dd, 1H, $^3J_{2,3}$ = 3.0 Hz, $^3J_{1,2}$ = 1.8 Hz, H-2); 5.37 (d, 1H, $^3J_{1',2'}$ = 2.8 Hz, H-1′); 5.27–5.12 (m, 2H, $CH_2CH{=}CH_2$); 5.06, 4.88 (2d, 2H, $^2J$ = 10.4 Hz, C$H_2C_6H_5$); 4.98 (d, 1H, $^3J_{1'',2''}$ = 1.5 Hz, H-1″); 4.91 (d, 1H, $^3J_{1,2}$ = 1.8 Hz, H-1); 4.71, 4.61 (2d, 2H, $^2J$ = 11.0 Hz, C$H_2C_6H_5$); 4.69 (m, 1H, H-5′); 4.49 (dd, 1H, $^3J_{3,4}$ = 10.0 Hz, $^3J_{2,3}$ = 3.0 Hz, H-3); 4.49 (dd, 1H, $^3J_{2',3'}$ = 10.0 Hz, $^3J_{1',2'}$ = 2.8 Hz, H-2′); 4.22 (center of $q_{AB}$, 2H, $^2J$ = 12.0 Hz), 4.07, 3.88 (2d, 2H, $^2J$ = 10.7 Hz), (2 C$H_2C_6H_5$); 4.11 (m, 1H), 4.97 (m, 1H), (C$H_2CH{=}CH_2$); 3.92–3.86 (m, 1H, H-5); 3.83 (dd, 1H, $^3J_{4'',5''}$ = 9.1 Hz, H-5″); 3.78 ('t', 1H, $^3J_{3,4}$ = 10.0 Hz, $^3J_{4,5}$ = 9.5 Hz, H-4); 3.71 (br, 1H, H-2″); 3.48 (dd, 1H, $^2J_{6a',6b'}$ = 10.4 Hz, $^3J_{5',6a'}$ = 6.9 Hz, H-6a′); 3.32–3.28 (m, 2H, H-4″, H-6b′); 3.25 (dd, 1H, $^3J_{3'',4''}$ = 8.8 Hz, $^3J_{2'',3''}$ = 2.8 Hz, H-3″); 2.22 (br s, 1H, OH); 1.45 (d, 3H, $^3J_{5,6}$ = 6.2 Hz, H-6); 1.35 (d, 3H, $^3J_{5'',6''}$ = 6.0 Hz, H-6″); $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ 165.5, 165.5, 165.5 (3 $COC_6H_5$); 138.7, 138.1, 138.0, 137.7 (4 *i*-$CH_2C_6H_5$); 133.5 ($CH_2CH{=}CH_2$); 133.2, 133.1, 133.0 (3 *p*-$COC_6H_5$); 130.5, 129.7, 129.6, 128.6, 128.5, 128.4, 128.3 (2), 128.3, 128.2, 128.0, 128.0, 127.4, 127.3 (4 *o*-, *m*-$CH_2C_6H_5$, 3 *o*-, *m*-$COC_6H_5$); 129.6, 129.5, 129.3 (3 *i*-$COC_6H_5$); 128.1, 127.6, 127.5, 127.2 (4 *p*-$CH_2C_6H_5$); 117.6 ($CH_2CH{=}CH_2$); 101.4 (C-1″); 96.3 (C-1); 95.2 (C-1′); 80.1 (C-4); 79.8 (C-3″); 79.7 (C-4″); 76.1, 75.1, 72.7, 71.6 (4 $CH_2C_6H_5$); 72.7, 72.5 (C-3, C-2′); 71.0 (C-3′); 69.9 (C-4′); 68.9 (C-2); 68.5 (C-5); 68.3 (C-2″); 68.3 (C-6′); 68.2 (C-5″); 68.2 ($CH_2CH{=}CH_2$); 67.4 (C-5′); 18.2 (C-6); 17.9 (C-6″). HRMS (ESI-TOF): calcd for $C_{70}H_{72}O_{17}$ (M+$Na^+$): *m*/*z* 1207.4662, found: *m*/*z* 1207.4666. Anal. Calcd for $C_{70}H_{72}O_{17}$ (1185.31): C, 70.93; H, 6.12. Found: C, 71.16: H, 6.29.

### 3.15. Allyl 2-*O*-acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-6-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-6-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (31)

Glycosyl acceptor **30** (179 mg, 0.15 mmol), donor **29** (217 mg, 0.16 mmol), and molecular sieves (4 Å, 1 g) were dried under high vacuum for 1 h at room temperature. The solids were then suspended in dry $CH_2Cl_2$ (10 mL), and the reaction mixture was stirred for 1 h under an argon atmosphere in the dark at room temperature. After cooling to −20 °C, trimethylsilyl trifluoromethanesulfonate (38 μL, 0.21 mmol) was added. The suspension was stirred for 10 min at that temperature and then 15 min at room temperature. After complete reaction (monitored by TLC), the reaction mixture

was neutralized by the addition of $NEt_3$ and filtered through Celite. The filtrate was concentrated and purified by flash chromatography (eluent gradient ethyl acetate in heptane 33→50%) to provide compound **31** (187 mg, 53%) as a colorless syrup: $[\alpha]_D^{23}$ +187.1 (*c* 1.0, $CHCl_3$); $R_f$ = 0.22 (solvent $A_1$); $^1$H NMR (500.13 MHz, $CDCl_3$): $\delta$ 8.02 (m, 4H), 7.94 (m, 4H), 7.84–7.77 (m, 4H), 7.60–7.54 (m, 6H), 7.48–6.95 (m, 51H), 6.75 (m, 1H), (8 $CH_2C_6H_5$, 6 $COC_6H_5$); 5.91 (dd, 1H, $^3J_{2',3'}$ = 10.7 Hz, $^3J_{3',4'}$ = 3.5 Hz, H-3′B); 5.83 (m, 1H, $CH_2CH{=}CH_2$); 5.82 (dd, 1H, $^3J_{2',3'}$ = 10.7 Hz, $^3J_{3',4'}$ = 3.5 Hz, H-3′A); 5.68 (dd, 1H, $^3J_{4',5'}$ = 1.3 Hz, H-4′A); 5.61 (dd, 1H, $^3J_{4',5'}$ = 1.3 Hz, H-4′B); 5.50–5.47 (m, 2H, H-2A, H-2B); 5.35 (d, 1H, $^3J_{1',2'}$ = 3.2 Hz, H-1′A); 5.33 (d, 1H, $^3J_{1',2'}$ = 3.5 Hz, H-1′B); 5.26–5.11 (m, 2H, $CH_2CH{=}CH_2$); 5.06, 4.88 (2d, 2H, $^2J$ = 10.5 Hz, $CH_2C_6H_5$); 5.03 ('t', 1H, $^3J_{2'',3''}$ = 2.8 Hz, $^3J_{1'',2''}$ = 1.9 Hz, H-2″B); 5.01, 4.79 (2d, 2H, $^2J$ = 10.5 Hz, $CH_2C_6H_5$); 4.97 (d, 1H, $^3J_{1,2}$ = 1.3 Hz, H-1″A); 4.95 (d, 1H, $^3J_{1,2}$ = 1.6 Hz, H-1A); 4.84 (d, 1H, $^3J_{1'',2''}$ = 1.9 Hz, H-1″B); 4.72, 4.54 (2d, 2H, $^2J$ = 11.4 Hz, $CH_2C_6H_5$); 4.70, 4.49 (2d, 2H, $^2J$ = 11.4 Hz, $CH_2C_6H_5$); 4.70 (m, 1H, H-5′A); 4.61 (m, 1H, H-5′B); 4.50 (dd, 1H, $^3J_{3,4}$ = 9.5 Hz, $^3J_{2,3}$ = 3.0 Hz, H-3A); 4.41 (dd, 1H, $^3J_{2',3'}$ = 10.7 Hz, $^3J_{1',2'}$ = 3.2 Hz, H-2′B); 4.37 (dd, 1H, $^3J_{2',3'}$ = 10.7 Hz, $^3J_{1',2'}$ = 3.2 Hz, H-2′A); 4.33 (dd, 1H, $^3J_{3,4}$ = 9.8 Hz, $^3J_{2,3}$ = 2.8 Hz, H-3B); 4.27 (d, 1H, $^3J_{1'',2''}$ = 1.6 Hz, H-1B); 4.22 (center of $q_{AB}$, 2H, $^2J$ = 12.0 Hz, $CH_2C_6H_5$); 4.14–4.07 (m, 4H, $CH_2C_6H_5$, $CH$HCH=$CH_2$, $CH$HC$_6$H$_5$); 4.03 (d, 1H, $^2J$ = 11.7 Hz, CH$H$C$_6$H$_5$); 3.99–3.92 (m, 3H, H-5″B, CH$H$CH=$CH_2$, CH$H$C$_6$H$_5$); 3.88 (dq, 1H, $^3J_{4,5}$ = 9.5 Hz, $^3J_{5,6}$ = 6.0 Hz, H-5A); 3.84–3.77 (m, 2H, H-4A, H-5B); 3.69 (dq, 1H, $^3J_{4'',5''}$ = 8.5 Hz, $^3J_{5'',6''}$ = 6.3 Hz, H-5″A); 3.61 ('t', 1H, $^3J_{3,4}$ = 9.8 Hz, $^3J_{4,5}$ = 9.5 Hz, H-4B); 3.52 ('t', 1H, $^3J_{2'',3''}$ = 2.8 Hz, $^3J_{3'',4''}$ = 1.9 Hz, H-2″A); 3.48 (dd, 1H, $^2J_{6a',6b'}$ = 10.2 Hz, $^3J_{5',6a'}$ = 6.9 Hz, H-6a′A); 3.37–3.25 (m, 6H, H-3″A, H-4″A, H-6a′B, H-6b′A, H-6b′B, CHHC$_6$H$_5$); 3.19–3.14 (m, 2H, H-3″B, H-4″B); 1.59 (s, 3H, $COCH_3$); 1.43 (d, 3H, $^3J_{5,6}$ = 6.2 Hz, H-6A); 1.29 (d, 3H, $^3J_{5'',6''}$ = 6.3 Hz, H-6″B); 1.21 (d, 3H, $^3J_{5'',6''}$ = 6.3 Hz, H-6″A); 0.97 (d, 3H, $^3J_{5,6}$ = 6.2 Hz, H-6B); $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ 168.7 ($COCH_3$); 165.5, 165.5, 165.5, 165.4, 165.2, 164.6 (6 $COC_6H_5$); 139.1, 139.1, 138.7, 138.3, 138.1, 137.8, 137.8, 137.7 (8 *i*-$CH_2C_6H_5$); 133.7 ($CH_2CH{=}CH_2$); 133.1 (2), 133.0 (2), 132.9, 132.8 (6 *p*-$COC_6H_5$); 130.5, 130.4, 129.7 (2), 129.7, 129.6, 128.5–127.1 (signals of *o*-, *m*-$COC_6H_5$, *o*-, *m*-, *p*-$CH_2C_6H_5$); 129.8, 129.7 (2), 129.6, 129.5, 129.2 (6 *i*-$COC_6H_5$); 117.5 ($CH_2CH{=}CH_2$); 101.8 (C-1″A); 100.0 (C-1″B); 99.4 (C-1B); 96.1 (C-1A); 95.6 (C-1′A); 93.6 (C-1′B); 80.2 (C-4″A); 80.1 (C-4A); 80.0 (C-4″B); 79.7 (C-4B); 79.1 (C-3″A); 78.0 (C-2″A); 77.8 (C-3″B); 76.2, 76.0, 75.3, 74.9 (4 $CH_2C_6H_5$); 74.3 (C-2′A); 72.9 (C-3A); 72.8, 72.7 (2 $CH_2C_6H_5$); 71.9 (C-2′B); 71.7 ($CH_2C_6H_5$); 71.5 (C-3B); 72.7 (2 $CH_2C_6H_5$); 71.1 (C-3′B); 70.4 (C-3′A); 70.0 (C-4′A); 69.8 (C-4′B); 69.4 (C-2B); 68.9 (C-5″A); 68.8 (C-5B); 68.5 (C-2″B); 68.5 (C-5A); 68.4 (C-5″B); 68.3 (C-6′A); 68.3 ($CH_2CH{=}CH_2$); 67.6 (C-2A); 67.5 (C-6′B); 67.5 (C-5′A); 66.8 (C-5′B); 20.3 ($COCH_3$); 18.2, 18.1, 18.1, 17.8 (C-6A, C-6B, C-6″A, C-6″B). HRMS (ESI-TOF): calcd for $C_{139}H_{140}O_{34}$ (M+$Na^+$): *m*/*z* 2376.9152, found: *m*/*z* 2376.9114. Anal. Calcd for $C_{139}H_{140}O_{34}$ (2354.58): C, 70.90; H, 5.99. Found: C, 71.16; H, 6.21.

### 3.16. Allyl 3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-6-*O*-benzyl-α-D-galactopyranosyl-(1→3)-4-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-6-*O*-benzyl-α-D-galactopyranosyl-(1→3)-4-*O*-benzyl-α-L-rhamnopyranoside (32)

To a solution of compound **31** (221 mg, 0.1 mmol) in dry MeOH (10 mL) methanolic NaOMe (1 M, 1 mL) was added. The reaction mixture was then stirred for 43 h at room temperature. After complete reaction (monitored by TLC), the reaction mixture was neutralized with Amberlite ($H^+$) resin and filtered through Celite. The filtrate was concentrated and purified by flash chromatography (solvent $B_5$) to give compound **32** (101 mg, 76%) as a colorless syrup: $[\alpha]_D^{24}$ +8.3 (*c* 0.5, $CHCl_3$); $R_f$ = 0.35 (solvent G); $^1$H NMR (500.13 MHz, $CDCl_3$): $\delta$ 7.37–7.20 (m, 40H, 8 $CH_2C_6H_5$); 5.88 (m, 1H, $CH_2CH{=}CH_2$); 5.34 (d, 1H, $^3J_{1'',2''}$ = 2.4 Hz), 5.33 (d, 1H, $^3J_{1'',2''}$ = 2.2 Hz), (H-1″A, H-1″B); 5.30–5.17 (m, 2H, $CH_2CH{=}CH_2$); 5.11 (d, 1H, $^3J_{1',2'}$ = 3.8 Hz, H-1′B); 5.09 (d, 1H, $^3J_{1,2}$ = 1.6 Hz, H-1B); 5.04 (d, 1H, $^3J_{1',2'}$ = 3.8 Hz, H-1′A); 4.76 (d, 1H, $^3J_{1,2}$ = 1.4 Hz, H-1A); 4.85–4.57 (m, 12H), 4.50 (2d, 2H, $^2J$ = 12.0 Hz), 4.37 (d, 1H, $^2J$ = 12.0 Hz), 4.35 (d, 1H, $^2J$ = 12.0 Hz), (8 $CH_2C_6H_5$); 4.20–4.12 (m, 4H, H-2, H-2″A, H-2″B, CHHCH=$CH_2$); 4.08–4.00 (m, 5H, H-2, H-2′A, H-2′B, H-3A, H-3B); 3.98–3.86 (m, 10H, H-3′A, H-3′B, H-3″A, H-3″B, H-4′A, H-4′B, H-5, H-5′A, H-5′B, CH$H$CH=$CH_2$); 3.82–3.76 (m, 3H, H-5A, H-5″, OH); 3.71 (dq, 1H, $^3J_{4'',5''}$ = 8.6 Hz, $^3J_{5'',6''}$ = 6.3 Hz, H-5″); 3.56 (br s, 1H, OH); 3.57–3.44 (m, 6H, H-4A, H-4B, H-4″A, H-4″B, H-6a′A, H-6a′B); 3.31 (br s, 1H, OH); 3.30–3.25 (m, 3H, H-6b′A, H-6b′B, OH); 3.00 (br s, 1H, OH); 2.87 (br s, 1H, OH); 2.78 (d, 1H, $^3J_{H,OH}$ = 8.0 Hz, OH); 1.38 (d, 3H, $^3J_{5,6(5'',6'')}$ = 6.3 Hz), 1.36 (d, 3H, $^3J_{5,6(5'',6'')}$ = 6.3 Hz), 1.32 (d, 3H, $^3J_{5,6(5'',6'')}$ = 6.2 Hz), 1.26 (d, 3H, $^3J_{5,6(5'',6'')}$ = 6.3 Hz), (H-6A, H-6B, H-6″A, H-6″B); $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ 138.4, 138.3, 138.2, 138.1, 138.1, 137.9, 137.2, 137.1 (8 *i*-$CH_2C_6H_5$); 133.8 ($CH_2CH{=}CH_2$); 128.4 (2), 128.4, 128.3 (2), 128.3, 128.3, 128.2, 127.9, 127.8 (2), 127.8, 127.7, 127.7 (2), 127.5, 127.3, 127.2 (*o*-, *m*-$CH_2C_6H_5$); 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 127.4, 127.2 (*p*-$CH_2C_6H_5$); 117.4 ($CH_2CH{=}CH_2$); 101.3 (C-1B); 99.9 (C-1″B); 99.5 (C-1″A); 98.3 (C-1A); 94.7 (C-1′A); 94.2 (C-1′B); 79.8, 79.6, 79.5 (2), 79.1 (2) (C-3″A, C-3″B, C-4A, C-4B, C-4″A, C-4″B); 76.1 (C-3A); 75.3, 75.2 ($CH_2C_6H_5$); 75.1 (C-3B); 74.5 (2) ($CH_2C_6H_5$); 73.9 (C-2″A); 73.8 (C-2′B); 73.7, 73.7 (2 $CH_2C_6H_5$); 73.1 (C-2′A); 72.3, 72.2 ($CH_2C_6H_5$); 71.2, 71.2 (C-4′); 70.7, 70.5 ($CH_2C_6H_5$); 70.6 (C-3′A, C-3′B); 69.0 (C-5″A); 68.6 (C-5″B); 68.4 (C-2″B); 67.9 (2), 67.8 (C-5B, C-5′A, C-5′B); 67.9 ($CH_2CH{=}CH_2$); 67.4 (C-5A); 67.3, 67.0 (C-2A, C-2B); 18.0, 17.9, 17.8, 17.8 (C-6A, C-6B, C-6″A, C-6″B). HRMS (ESI-TOF): calcd for $C_{95}H_{114}O_{27}$ (M+$Na^+$): *m*/*z* 1710.7474, found: *m*/*z* 1710.7486. Anal. Calcd for $C_{95}H_{114}O_{27}$ (1687.91): C, 67.60; H, 6.81. Found: C, 67.48; H, 6.97.

### 3.17. Propyl α-L-rhamnopyranosyl-(1→2)-α-D-galactopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→2)-α-D-galactopyranosyl-(1→3)-α-L-rhamnopyranoside (33)

To a solution of compound **32** (54 mg, 0.03 mmol) in methanol–water (6 mL, 5:1) 20% palladium(II) hydroxide on carbon (84 mg) was added. The suspension was stirred for 74 h under a hydrogen atmosphere at room temperature (monitored by TLC). The mixture was then filtered over Celite by elution with methanol. The combined filtrates were concentrated and purified by flash chromatography (solvent $C_1$) to provide compound **33** (28 mg, 93%) as a colorless powder: $[\alpha]_D^{23}$ −57.5 (*c* 0.5, $H_2O$); $R_f$ = 0.21 (solvent $D_1$); $^1$H NMR (500.13 MHz, $D_2O$): $\delta$ 5.20 (d, 1H, $^3J_{1'',2''}$ = 1.6 Hz, H-1″B); 5.17 (d, 1H, $^3J_{1',2'}$ = 3.8 Hz, H-1′B); 5.11 (d, 1H, $^3J_{1',2'}$ = 3.8 Hz, H-1′A); 5.02 (d, 1H, $^3J_{1'',2''}$ = 1.7 Hz, H-1″A); 5.00 (d, 1H, $^3J_{1,2}$ = 1.9 Hz, H-1B); 4.81 (d, 1H, $^3J_{1,2}$ = 2.0 Hz, H-1A); 4.27 (dd, 1H, $^3J_{2,3}$ = 3.2 Hz, $^3J_{1,2}$ = 1.9 Hz, H-2B); 4.22–4.18 (m, 2H, H-5′A, H-5′B); 4.10–4.05 (m, 5H, H-2A, H-2″A, H-2″B, H-3′A, H-3′B); 4.03 (m, 2H, H-4′A, H-4B); 3.93, 3.93 (2dd, 2H, $^3J_{2',3'}$ = 10.3 Hz, $^3J_{1',2'}$ = 3.8 Hz, H-2′A, H-2′B); 3.89–3.83 (m, 3H, H-3A, H-3B, H-3″B); 3.79 (dd, 1H, $^3J_{3'',4''}$ = 9.8 Hz, $^3J_{2'',3''}$ = 3.5 Hz, H-3″A); 3.77–3.70 (m, 8H, H-5A, H-5B, H-5′A, H-5″B, H-6a′A, H-6b′A, H-6a′B, H-6b′B); 3.64 (m, 1H), 3.49 (m, 1H), ($CH_2CH_2CH_3$); 3.59, 3.57 (2't', 2H, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.8 Hz, H-4A, H-4B); 3.49, 3.46 (2't', 2H, $^3J_{3'',4''}$ = $^3J_{4'',5''}$ = 9.6 Hz, H-4″A, H-4″B); 1.60 (m, 2H, $CH_2CH_2CH_3$); 1.30 (m, 12H, H-6A, H-6B, H-6″A, H-6″B); 0.91 (t, 3H, $^3J$ = 7.5 Hz, $CH_2CH_2$-$CH_3$); $^{13}$C NMR (125.8 MHz, $D_2O$): $\delta$ = 103.0 (C-1B); 102.9 (C-1″A); 101.2 (C-1″B); 100.3 (C-1A); 95.6, 95.4 (C-1′A, C-1′B); 78.9 (C-2″A); 76.1, 75.5 (C-3A, C-3B); 75.6, 75.1 (C-2′A, C-2′B); 72.7, 72.6 (C-4″A, C-4″B); 71.6, 71.6 (C-5′A, C-5′B); 71.2, 71.2 (C-4A, C-4B);

70.9 (C-3″A); 70.8 (C-2″B); 70.7 (C-3″B); 70.4, 70.2 (C-4′A, C-4′B); 70.5 ($CH_2CH_2CH_3$); 70.3, 70.1, 70.0, 69.4 (C-5A, C-5B, C-5″A, C-5″B); 70.1, 69.8 (C-3′A, C-3′B); 67.7 (C-2A); 67.4 (C-2B); 61.7, 61.6 (C-6′A, C-6′B); 22.8 ($CH_2CH_2CH_3$); 17.6, 17.6, 17.5, 17.5 (C-6A, C-6B, C-6″A, C-6″B); 10.7 ($CH_2CH_2CH_3$). HRMS (ESI-TOF): calcd for $C_{39}H_{68}O_{27}$ ($M+Na^+$): *m*/*z* 991.3840, found: *m*/*z* 991.3838. Anal. Calcd for $C_{39}H_{68}O_{27}$ (968.94): C, 48.34; H, 7.07. Found: C, 48.53; H, 7.21.

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