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Synthesis of a trisaccharide repeating unit of the O-antigen from *Burkholderia cenocepacia* and its dimer

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ABSTRACT

The trisaccharide repeating unit of an O-antigen derived from *Burkholderia cenocepacia* and its dimer, i.e., α-L-Rha*p*-(1 → 3)-α-D-Gal*p*NAc-(1 → 3)-β-D-Gal*p*NAc-O$(CH_2)_3N_3$ (**1**) and α-L-Rha*p*-(1 → 3)-α-D-Gal*p*-NAc-(1 → 3)-β-D-Gal*p*NAc-(1 → 4)-α-L-Rha*p*-(1 → 3)-α-D-Gal*p*NAc-(1 → 3)-β-D-Gal*p*NAc-O$(CH_2)_3N_3$ (**2**), respectively, were synthesized via a highly convergent strategy. Glycosylation of galactosaminyl acceptor **4** with galactosaminyl trichloroacetimidate donor **5** was followed by condensation of resulting disaccharide acceptor **12** with rhamnosyl imidate donor **6** to furnish stereoselectively trisaccharyl thioglycoside **3**, which was used as a key and common glycosyl donor for the construction of both **1** and **2**. Title molecule **1** was prepared by glycosylation of 3-azidopropanol with **3** and subsequently global deprotection, whereas coupling reaction of **3** with a trisaccharide acceptor **21** containing an 2,3-*O*-position acetonide-modified rhamnose residue, followed by global deprotection, generated the dimer **2** in a convergent [3 + 3] manner.

1. Introduction

Polysaccharides on the bacterial cell surface, such as lipopolysaccharides (LPSs) [1], capsular polysaccharides (CPSs) [2], extracellular polysaccharides (EPSs) [3] and so on, play an important role in various biological events [4,5]. For example, many of the polysaccharides are important virulence factors for bacterial pathogenicity [1,6,7] and are crucial immunomodulators useful for the development of new carbohydrate-based diagnostic agents and vaccines [8–12].

The *Burkholderia cepacia* complex (Bcc) represents a group of phenotypically similar but genotypically diverse Gram-negative bacteria [13,14] that are opportunistic human pathogens [15–17]. Bcc bacteria can occasionally cause serious lung infections in patients with cystic fibrosis (CF), resulting in a high mortality due to clinically uncontrollable "cepacia syndrome", such as necrotizing pneumonia and septicemia [15]. However, the pathogenic mechanism of Bcc infection still remains unclear, and therefore, detailed studies of Bcc, and the development of effective strategies to control Bcc infection are in urgent demand.

B. cenocepacia is one of the two predominant Bcc species found in CF patients, accounting for approximate 46% of Bcc infections in the United States [18]. *B. cenocepacia* infection is frequently connected with poor clinical recovery and high rate of mortality [19]. It has been reported that the LPS O-polysaccharides, also known as O-antigens, of *B. cenocepacia* K56-2 were associated with bacterial invasion and virulence [20,21]. It not only induced inflammatory cytokine IL-1β production [20] but also modulated phagocytosis and interfered with bacterial adhesion to bronchial epithelial cells [21]. Therefore, the O-antigen of *B. cenocepacia* might be a useful target in studying pathogenic mechanism of Bcc and developing carbohydrate-based therapeutic agents against Bcc diseases.

An O-antigen from *B. cenocepacia* K56-2, which is composed of a trisaccharide repeating unit →4)-α-L-Rha*p*-(1 → 3)-α-D-Gal*p*NAc-(1 → 3)-β-D-Gal*p*NAc-(1→ (Fig. 1), was recently characterized [22]. As a part of our ongoing research effort to develop vaccines against Bcc [23–25], we described herein the first chemical synthesis of the

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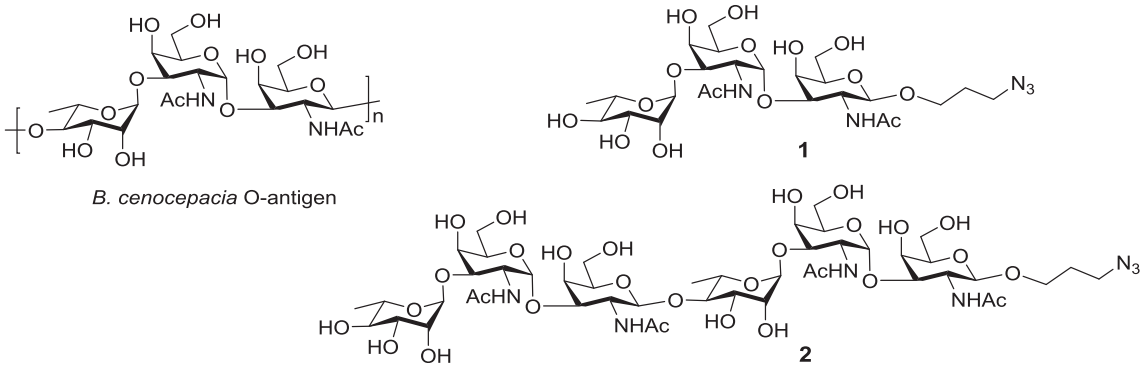


Fig. 1. Structures of the O-antigen from *B. cenocepacia* and the synthetic targets **1** and **2.**

repeating unit of this O-antigen **1** and its dimer **2** (Fig. 1). These synthetic targets were designed to carry an azido group at their reducing end, which would enable their regioselective modification, such as conjugation with carrier molecules to generate glycoconjugates that are useful for various biological and immunological studies.

2. Results and discussion

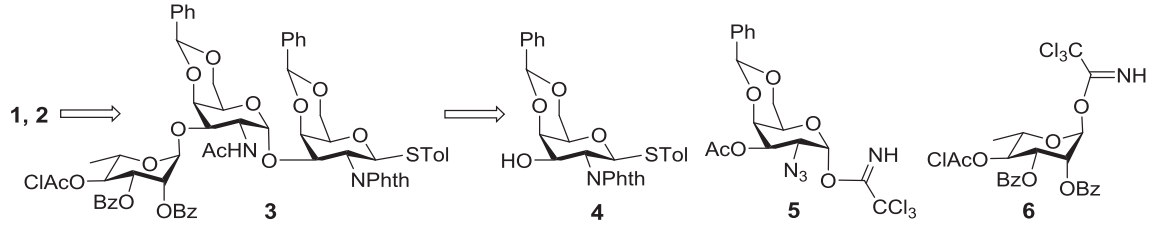
As shown in Scheme 1, retrosynthetic analysis of the synthetic targets **1** and **2** resulted in a key trisaccharyl donor **3**, which could act as a common building block for the introduction of a 3-azidopropyl group at the reducing end and for oligomerization as well. In turn, **3** could be assembled from three monosaccharides, namely, galactosaminyl acceptor **4** [26], galactosaminyl trichloroacetimidate donor **5** [27] and rhamnosyl trichloroacetimidate donor **6**. We planned to use phathalyl and benzoyl groups to protect the 2-*N* and 2-*O*-positions in **4** and **6** to boost 1,2-*trans* glycosylation reactions based on neighboring group participation. Alternatively, an azido group at the C-2 position in **5** was chosen to prevent neighboring group participation and thereby facilitate stereoselective formation of 1,2-*cis* glycosidic bond [28,29].

The synthesis commenced with the preparation of **4** [26] and **5** [27] according to reported procedures. Thereafter, **6** was prepared from reported rhamnoside **7** [30] in four steps (Scheme 2). Removal of the isopropylidene group in **7** with 80% aqueous acetic acid followed by benzoylation of the resultant 2,3-diol with benzoyl chloride in pyridine provided **8** in a 66% overall yield. Next, **8** was converted into hemiacetal by reaction with *N*-iodosuccinamide (NIS) and silver triflate (AgOTf) in wet CH_2Cl_2 [25], which was followed by trichloroacetimidation [31] under basic conditions using trichloroacetonitrile and 1,8-diazabicydo[5.4.0]undec-7-ene (DBU) [32] to give glycosyl donor **6** in a 67% yield (two steps).

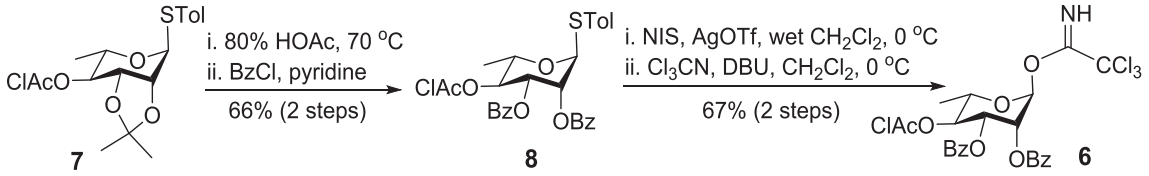
The key trisaccharyl thioglycoside **3** was assembled by a stepwise glycosylation strategy as outlined in Scheme 3. Interestingly, glycosylation of **4** with trichloroacetimidate **5** under the conventional condition with trimethylsilyl triflate (TMSOTf) as a promoter yielded **9** (62%) as the major product, which was a thio transfer product [33,34] probably because of the relatively low reactivity of the 3-OH group in **4**. To solve the problem, inverse glycosylation strategy [35] was employed, in which **4** was premixed with the promotor at −15 °C for 1 h, followed by the addition of **5** (1.2 equiv) at 0 °C. In this way, α-linked disaccharide **10** was furnished as the main product (α/β 2:1) in a 63% yield. When employing a mixture of toluene and 1,4-dioxane (v/v 1:1) as the solvent [36], the reaction gave **10** as the only anomer in a good yield (65%). The stereoselectivity of the newly formed α-glycosidic bond was verified by the small coupling constant ($J_{1',2'} = 3.6$ Hz) of its H-1′ signal at δ 4.98 ppm in the ^{1}H NMR spectrum of **10**. At this stage, the 2′-azido group in **10** was converted into acetamido group using thioacetyl acid (AcSH) in pyridine [37], affording **11** in a high yield (85%). Basic selective deacetylation of **11** in methanol afforded **12**, which served as a glycosyl acceptor glycosylated with **6** under the promotion of TMSOTf to furnish fully protected trisaccharide **3** in a 65% overall yield. The α-rhamnosidic bond in **3** was characterized by its $^1J_{C\text{-}1,H\text{-}1}$ coupling constant (171.6 Hz) for its ^{1}H-coupled gHSQC spectrum [38].

Starting from **3**, the synthetic target **1** was readily assembled according to Scheme 4. The reaction between **3** and 3-azido-1-propanol proceeded smoothly in the presence of NIS and TMSOTf to produce **13** in a 76% yield. It was then subjected to global deprotection in four steps. First, **13** was treated with hydrazine hydrate in refluxing ethanol [39] to remove the acyl and Phth groups. Then, the exposed amino and hydroxyl groups were acetylated with acetic anhydride in pyridine. This was followed by the cleavage of benzylidene groups using 80% aqueous acetic acid. Finally, any remaining *O*-acetyl groups in the product were selectively removed with sodium methoxide in methanol to afford **1** in a 75% overall yield (four steps) after purification by size-exclusion chromatography on a Sephadex G-10 column. Compound **1** was fully characterized by various NMR and MS data.

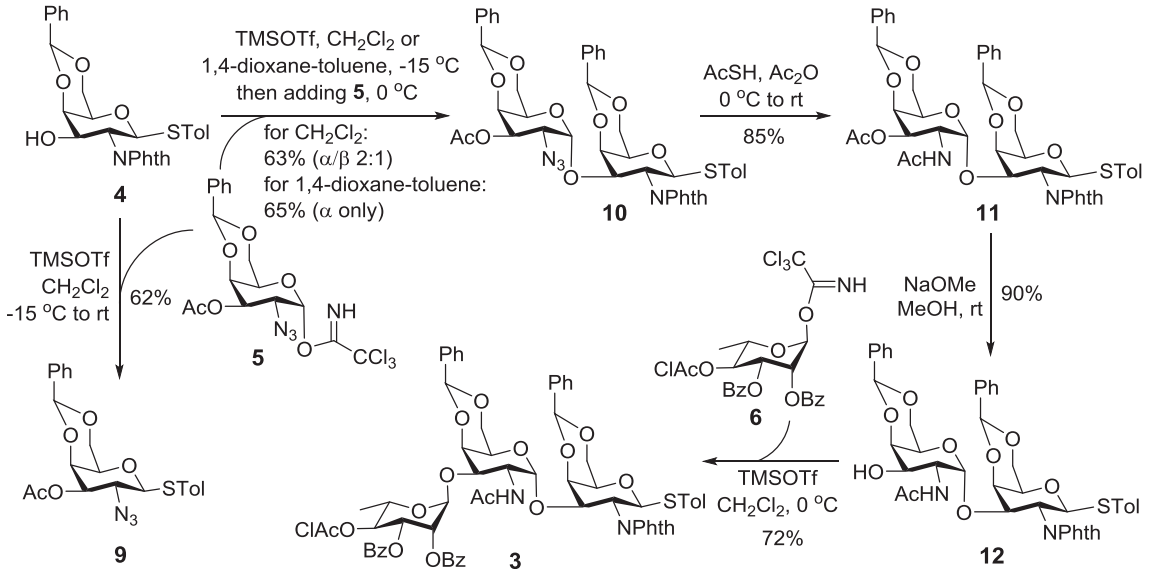
On the other hand, **13** was selectively dechloroacetylated with thiourea [40] to generate **14** (80% yield) as a glycosyl acceptor



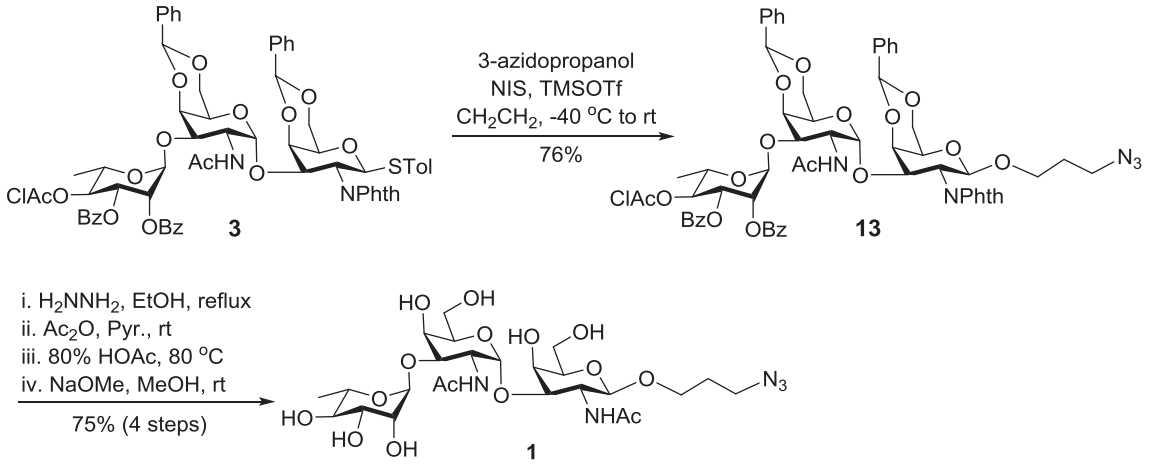
Scheme 1. Retrosynthetic analysis of synthetic targets **1** and **2.**



Scheme 2. Synthesis of rhamnosyl donor **6.**



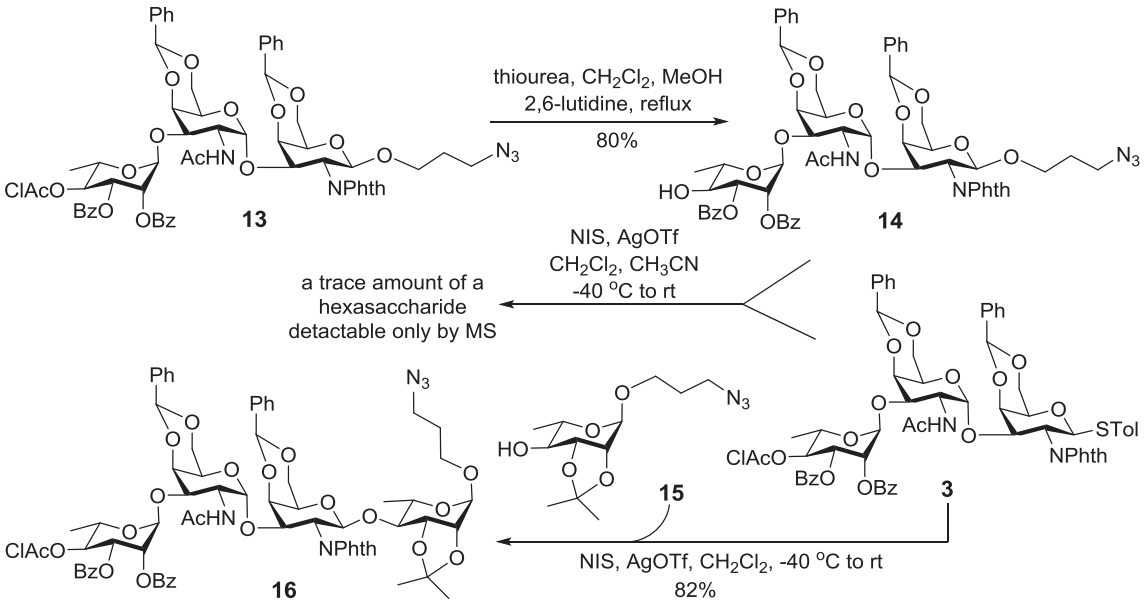
Scheme 3. Synthesis of trisaccharide **3** as a glycosyl donor.



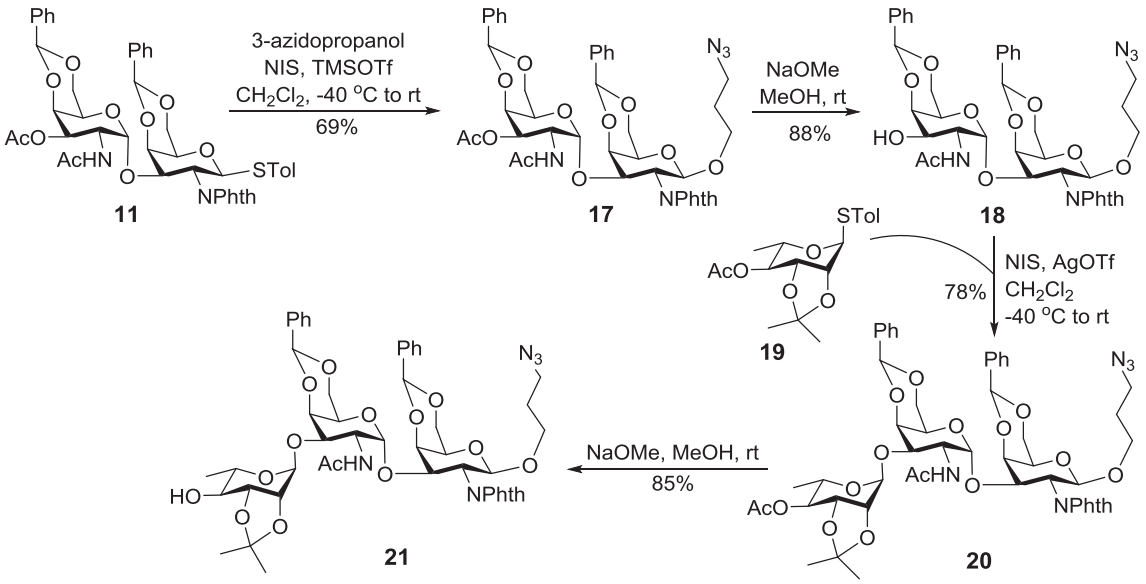
Scheme 4. Synthesis of target molecule **1**.

(Scheme 5). The upfield shift of the rhamnosyl H-4 signal at δ 3.72 ppm in the ^{1}H NMR spectrum of **14** confirmed the correct regiochemistry. Next, a convergent [3 + 3] gylocsylation strategy was attempted to construct **2** through the coupling of **3** and **14**. Unfortunately, this reaction was very sluggish and gave only a trace amount of the hexasaccharide detectable by MS. Varied reaction conditions, including different solvents, catalysts and temperatures or utilizing more reactive trichloroacetimidate and phosphate as glycosyl donors were attempted but failed to accomplish the desired result. We assumed that this might be because of the low reactivity of the 4^{Rha}-OH group in **14** due to the presence of electron-withdrawing benzoyl groups on C-2^{Rha} and C-3^{Rha} positions. To verify the hypothesis, a rhamnosyl acceptor **15** containing a 2,3-*O*-acetonide group was prepared and glycosylated with **3** (Scheme 5). Under the same conditions, the reaction proceeded smoothly to furnish **16** in an 82% yield. The newly formed β–glycosidic bond was confirmed by the large coupling constant (9.0 Hz) of the galctosaminyl H-1 signal at δ 5.37 ppm in the ^{1}H NMR spectrum of **16**.

Encouraged by these results, we redesigned and synthesized another trisaccharide **21** as a glycosyl acceptor, as outline in Scheme 6, to achieve the [3 + 3] assembly of hexasaccharide **2**. In **21**, the



Scheme 5. Glycosylations between **3** with different glycosyl acceptors.



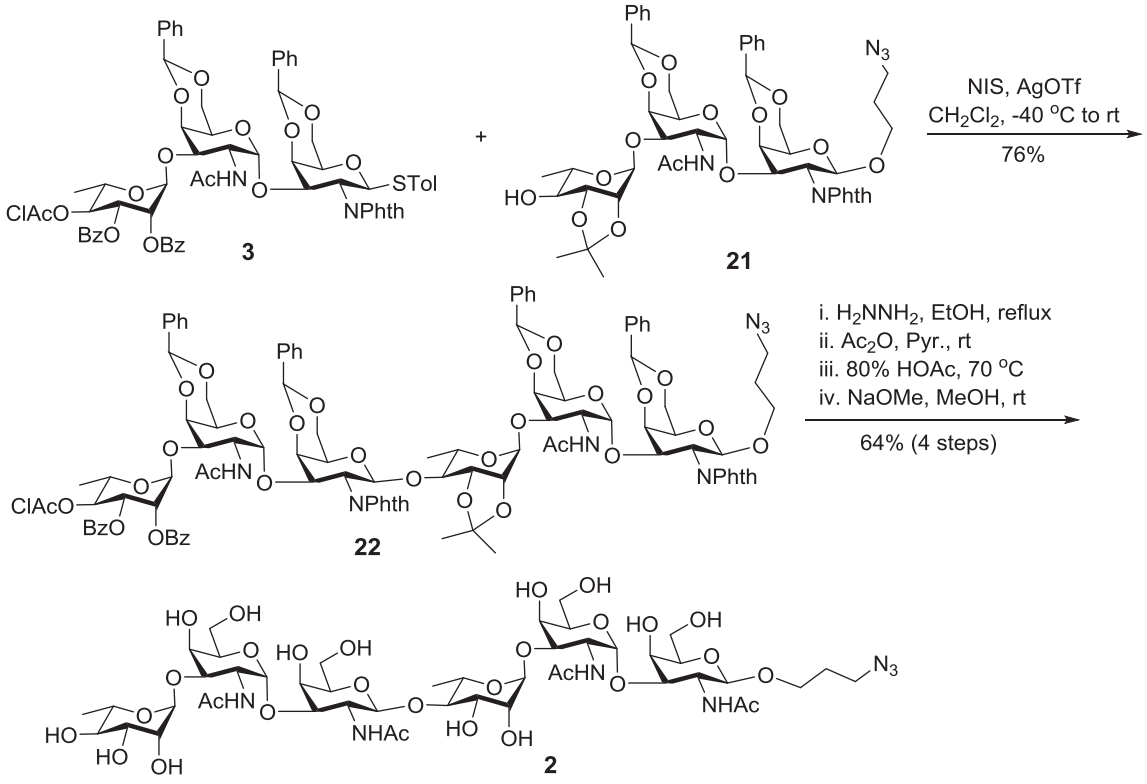
Scheme 6. Synthesis of trisaccharide acceptor **21.**

rhamnose 2- and 3-*O*-positions were protected with an acetonide group. Therefore, **11** was coupled with 3-azido-1-propanol under the promotion of NIS and TMSOTf to furnish **17**, which was selectively de-*O*-acetylated with sodium methoxide in methanol to afford **18** (in an overall yield of 61%) as a glycosyl acceptor. Again, the upfield shift of the H-3′ signal at δ 3.51 ppm in the ^{1}H NMR spectrum of **18** confirmed the correct regiochemistry. Glycosylation of **18** with **19** [41] was also carried out with NIS and AgOTf as promoters to afford predominantly the α-linked **20** in a high yield (78%). The ^{1}H-coupled gHSQC spectrum of **20** showed that the C-1^{Rha}/H-1^{Rha} coupling constant was 169.2 Hz, confirming the α configuration of the new glycosidic bond in **20**. Finally, selective removal of the 2-*O*-acetyl group in **20** with sodium methoxide in methanol gave **21** in an 85% yield.

Eventually, the synthetic target **2** was assembled by a procedure shown in Scheme 7. The coupling reaction between **21** and **3** was promoted with NIS-AgOTf to smoothly produce the fully protected hexasaccharide **22** in a 76% yield. The newly formed β-glycosidic bond was again verified by the large coupling constant (J = 8.4 Hz) of galactosaminyl H-1″ signal at δ 5.35 ppm in the ^{1}H NMR spectrum of **22**. Global deprotection of **22** in four steps by the same sequence as described for **1** produced **2** in a 64% overall yield. Synthetic target and all of the synthetic intermediates were fully characterized by various NMR and MS data.

3. Conclusions

In conclusion, we have described here an efficient synthesis of the trisaccharide repeating unit of *B. cenocepacia* O-antigen and its dimer. In this synthesis, trisaccharyl thioglycoside **3** was used as a common glycosyl donor not only for the glycosylation of 3-azido-1-propanol to achieve **1** but also for elongating the carbohydrate



Scheme 7. Synthesis of target hexasaccharide **2.**

chain of **21** to achieve hexasaccharide **2** via a highly convergent [3 + 3] strategy. Trisaccharide **1** was smoothly prepared from stepwise glycosylation reactions of monosaccharide building blocks. In this process, the α-glycosidic linked was accomplished using donor **5** with the galactosamine 2-amino group protected as a non-participating azido group. For the synthesis of **2**, trisaccharide **14**, in which the rhamnose 2- and 3-*O*-positons were protected with benzoyl groups, was proved to be a torpid glycosyl acceptor. To solve the problem, trisaccharide **21** containing a 2,3-*O*-isopropylidene group on the rhamnose residue was designed and then successfully glycosylated with **3** to afford the desired molecule. In addition, both synthetic targets **1** and **2** carried a 3-azidopropyl linker at their reducing end, allowing for their convenient attachment to functionalized biomolecules for the exploration of various biological problems, such as *B. cenocepacia* immunology and development of O-antigen-based vaccines against Bcc infections.

4. Experimental section

4.1. General methods

Optical rotations were determined at 25 °C with a Rudolph Autopol I automatic polarimeter. ^{1}H and ^{13}C NMR spectra were recorded with an Agilent 600 MHz spectrometer for solutions in $CDCl_3$, CD_3CN, CD_3OD, or D_2O. Chemical shifts (δ) are given in ppm downfield from internal Me_4Si or with the DHO signal as reference when D_2O was used as the solvent. Positive-mode electrospray ionization (ESI) high-resolution mass spectroscopy (HRMS) was recorded on an IT-TOF spectrometer. Thin layer chromatography (TLC) was performed on silica gel HF_{254} plates, detected by charring using 30% (v/v) H_2SO_4 in MeOH or by means of a UV detector. Silica gel column chromatography was conducted with mixtures of ethyl acetate and hexane as the eluents. Solution concentration was performed at < 60 °C under diminished pressure.

4.2. *para*-Tolyl 2,3-di-*O*-benzoyl-4-*O*-chloroacetyl-1-thio-α-L-rhamnopyranoside **(8)**

A solution of **7** (3.02 g, 7.82 mmol) in 80% HOAc (10 mL) was stirred at 70 °C for 3 h, and then co-evaporated with toluene (2 × 15 mL) under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexane–ethyl acetate 2:1 to 1:2) to give *para*-tolyl 4-*O*-chloroacetyl-1-thio-α-L-rhamnopyranoside (2.11 g, 78%) as a white foamy solids. ^{1}H NMR (600 MHz, CD_3OD): δ 7.34 (d, J = 8.4 Hz, 2 H, Ar*H*), 7.13 (d, J = 7.8 Hz, 2 H, Ar*H*), 5.32 (s, 1 H, H-1), 5.04 (t, J = 9.6 Hz, 1 H, H-4), 4.29, 4.24 (2 d, J = 15.0 Hz, 2 H, -OCOC*H*$_2$Cl), 4.25–4.20 (m, 1 H, H-5), 4.11 (dd, J = 3.0, 1.8 Hz, 1 H, H-2), 3.82 (dd, J = 9.6, 3.0 Hz, 1 H, H-3), 2.30 (s, 3 H, -SPhC*H*$_3$), 1.15 (d, J = 6.0 Hz, 3 H, H-6); ^{13}C NMR (150 MHz, CD_3OD): δ 167.4, 137.6, 131.9, 130.2, 129.3, 88.9, 76.0, 72.3, 69.3, 67.0, 40.4, 19.7, 16.2; ESI-TOF HRMS *m/z*: Calcd for $C_{15}H_{19}ClO_5SNa$ [M + Na^+] 369.0539; found, 369.0525. To a solution of the above product (1.99 g, 5.75 mmol) in pyridine (10 mL) was added BzCl (2 mL, 17.25 mmol) at 0 °C. The mixture was stirred at rt for 2 h and then diluted with CH_2Cl_2 (60 mL). The organic phase washed with 1 M HCl (2 × 30 mL) and brine (30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (hexane–ethyl acetate 8:1) to give **8** (2.7 g, 85%) as a white foamy solid. $[\alpha]_D^{25}$ +15 (*c* 0.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, J = 7.8 Hz, 2 H, Ar*H*), 7.88 (d, J = 8.4 Hz, 2 H, Ar*H*), 7.56 (t, J = 7.8 Hz, 1 H, Ar*H*), 7.51 (t, J = 7.8 Hz, 1 H, Ar*H*), 7.46 (t, J = 7.8 Hz, 2 H, Ar*H*), 7.41 (d, J = 8.4 Hz, 2 H, Ar*H*), 7.35 (t, J = 7.8 Hz, 2 H, Ar*H*), 7.14 (d, J = 7.8 Hz, 2 H, Ar*H*), 5.86 (dd, J = 3.6, 1.2 Hz, 1 H, H-2), 5.65 (dd, J = 10.2, 3.6 Hz, 1 H, H-3), 5.56 (d, J = 1.2 Hz, 1 H, H-1), 5.51 (t, J = 10.2 Hz, 1 H, H-4), 4.62–4.55 (m, 1 H, H-5), 4.02, 3.96 (2 d, J = 14.4 Hz, 2 H, -OCOC*H*$_2$Cl), 2.33 (s, 3 H,

-SPhCH_3), 1.35 (d, J = 6.6 Hz, 3 H, H-6); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.7, 165.3 (2C), 138.3, 133.5, 133.4, 132.6, 130.2, 130.0, 129.8, 129.7, 129.2, 128.8, 128.6, 128.5, 86.1, 73.3, 72.2, 70.1, 67.4, 40.5, 21.1, 17.4; ESI-TOF HRMS *m/z*: Calcd for $C_{29}H_{27}ClO_7SNa$ $[M + Na]^+$ 577.1064; found, 577.1033.

4.3. 2,3-Di-O-benzoyl-4-O-chloroacetyl-α-L-rhamnopyranosyl trichloroacetimidate **(6)**

After **8** (2.5 g, 4.51 mmol) was dissolved in CH_2Cl_2 and CH_3CN (v/v 1:1, 40 mL) containing two drops of H_2O (100 μL), NIS (1.21 g, 5.41 mmol) and AgOTf (0.1 g, 0.39 mmol) were added at 0 °C. The reaction mixture was stirred at same temperature for 4 h, and then neutralized with Et_3N and concentrated, and the residue was briefly purified by flash column chromatography (hexane–ethyl acetate 4:1 to 1:1). The resultant hemiacetal was then dissolved in CH_2Cl_2 (10 mL) at 0 °C, and trichloroacetonitrile (1.8 mL, 12.5 mmol) and DBU (100 μL) was added. The reaction mixture was stirred at 0 °C for 1 h, and then concentrated. The residue was subjected to flash column chromatography (hexane–ethyl acetate 4:1) to give **6** (1.78 g, 67% for 2 steps) as a white foamy solid. $[\alpha]_D^{25}$ +54 (*c* 0.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.80 (s, 1 H, -N*H*), 8.06 (d, J = 8.4 Hz, 2 H, Ar*H*), 7.87 (d, J = 7.2 Hz, 2 H, Ar*H*), 7.62 (t, J = 7.8 Hz, 1 H, Ar*H*), 7.54–7.45 (m, 3 H, Ar*H*), 7.35 (t, J = 7.8 Hz, 2 H, Ar*H*), 6.43 (d, J = 1.8 Hz, 1 H, H-1), 5.83 (dd, J = 3.6, 1.8 Hz, 1 H, H-2), 5.73 (dd, J = 10.2, 3.6 Hz, 1 H, H-3), 5.54 (t, J = 10.2 Hz, 1 H, H-4), 4.33–4.26 (m, 1 H, H-5), 4.00, 3.95 (2 d, J = 14.4 Hz, 2 H, -OCOCH_2Cl), 1.39 (d, J = 6.0 Hz, 3 H, H-6); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.6, 165.4, 165.2, 159.9, 133.7, 133.5, 129.9, 129.7, 128.8, 128.7, 128.6, 128.5, 94.5, 90.6, 72.4, 69.5, 68.97, 68.96, 40.4, 17.6.

4.4. para-Tolyl 3-O-acetyl-2-azido-4,6-O-benzylidene-2-deoxy-β-D-galactopyranoside **(9)**

To a stirred mixture of **4** (150 mg, 0.30 mmol), **5** (172 mg, 0.36 mmol) and activated MS 4 Å (300 mg) in anhydrous CH_2Cl_2 at −15 °C was added TMSOTf (15 μL, 68 μmol) under a N_2 atmosphere. The mixture reaction was stirred at this condition for 40 min, and then neutralized with Et_3N. The mixture was diluted with CH_2Cl_2 (5 mL), filtered through a pad of Celite, and the filtrate was concentrated. The residue was purified by silica gel column chromatography (hexane–ethyl acetate 10:1 to 2:1) to yield **9** (204 mg, 62%) as a white foamy solid. $[\alpha]_D^{25}$ -11 (*c* 0.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 (d, J = 7.8 Hz, 2 H, Ar*H*), 7.43–7.35 (m, 5 H, Ar*H*), 7.07 (d, J = 7.8 Hz, 2 H, Ar*H*), 5.47 (s, 1 H, C*H*Ph), 4.80 (dd, J = 10.2, 3.0 Hz, 1 H, H-3), 4.46 (d, J = 9.6 Hz, 1 H, H-1), 4.38 (d, J = 12.0 Hz, 1 H, H-6a), 4.32 (d, J = 3.0 Hz, 1 H, H-4), 4.01 (d, J = 12.0 Hz, 1 H, H-6b), 3.80 (t, J = 10.2 Hz, 1 H, H-2), 3.55 (s, 1 H, H-5), 2.34 (s, 3 H, -SPhCH_3), 2.09 (s, 3 H, -OCCH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.4 (*C*=O), 138.8, 137.5, 134.8, 129.8, 129.2, 128.2, 126.5, 101.0, 85.3, 74.0, 72.6, 69.5, 69.2, 58.1, 29.7, 21.3, 21.0; ESI-TOF HRMS *m/z*: Calcd for $C_{22}H_{23}N_3O_5SK$ $[M + K]^+$ 480.0990; found, 480.1045.

4.5. para-Tolyl 3-O-acetyl-2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-galactopyranoside **(10)**

To a stirred mixture of **4** (340 mg, 0.68 mmol), and activated MS 4 Å (500 mg) in anhydrous toluene and 1,4-dioxane (v/v 1:1, 5 mL) at −15 °C was added TMSOTf (15 μL, 82 μmol) under a N_2 atmosphere. After the mixture was stirred at these temperature for 1 h, a solution of **5** (390 mg, 0.82 mmol) in anhydrous toluene and 1,4-dioxane (v/v 1:1, 5 mL) was added dropwise at 0 °C under a N_2 atmosphere. The mixture reaction was stirred at these conditions for another 1 h, and then neutralized with Et_3N. The mixture was diluted with CH_2Cl_2 (20 mL), filtered through a pad of Celite, and the filtrate was concentrated. The residue was purified by silica gel column chromatography (hexane–ethyl acetate 10:1 to 2:1) to yield **10** (360 mg, 65%) as a white foamy solid. $[\alpha]_D^{25}$ +96 (*c* 0.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89 (d, J = 6.6 Hz, 1 H, Ar*H*), 7.83 (d, J = 7.2 Hz, 1 H, Ar*H*), 7.79–7.72 (m, 2 H, Ar*H*), 7.52 (d, J = 6.6 Hz, 2 H, Ar*H*), 7.44–7.37 (m, 5 H, Ar*H*), 7.36–7.31 (m, 2 H, Ar*H*), 7.30–7.28 (m, 3 H, Ar*H*), 7.00 (d, J = 7.8 Hz, 2 H, Ar*H*), 5.62 (s, 1 H, C*H*Ph), 5.52 (d, J = 9.6 Hz, 1 H, H-1^{GalN}), 5.28 (s, 1 H, C*H*Ph), 5.07 (dd, J = 10.8, 3.6 Hz, 1 H, H-3$^{GalN'}$), 4.98 (d, J = 3.6 Hz, 1 H, H-1$^{GalN'}$), 4.74 (t, J = 10.2 Hz, 1 H, H-2^{GalN}), 4.70 (dd, J = 10.2, 3.0 Hz, 1 H, H-3^{GalN}), 4.45 (d, J = 3.0 Hz, 1 H, H-4^{GalN}), 4.43 (d, J = 12.0 Hz, 1 H, H-6a^{GalN}), 4.22 (d, J = 3.0 Hz, 1 H, H-4$^{GalN'}$), 4.10 (d, J = 12.0 Hz, 1 H, H-6b^{GalN}), 3.85 (dd, J = 10.8, 3.6 Hz, 1 H, H-2$^{GalN'}$), 3.67 (s, 1 H, H-5^{GalN}), 3.55 (d, J = 12.6 Hz, 1 H, H-6a$^{GalN'}$), 3.42 (s, 1 H, H-5$^{GalN'}$), 3.19 (d, J = 12.6 Hz, 1 H, H-6b$^{GalN'}$), 2.30 (s, 3 H, -SPhCH_3), 2.07 (s, 3 H, -OCOCH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.0 (*C*=O), 168.8 (*C*=O), 167.2 (*C*=O), 138.1, 137.8, 137.2, 134.5, 134.4, 133.6, 131.7, 131.5, 129.5, 129.0, 128.8, 128.1, 128.0, 127.4, 126.5, 125.9, 123.53, 123.49, 100.9 (*C*HPh), 100.40 (*C*HPh), 100.3 (C-1$^{GalN'}$), 82.9 (C-1^{GalN}), 77.8 (C-3^{GalN}), 73.8 (C-4^{GalN}), 72.9 (C-4$^{GalN'}$), 70.2 (C-5^{GalN}), 69.3 (C-6^{GalN}), 69.2 (C-3$^{GalN'}$), 68.5 (C-6$^{GalN'}$), 63.3 (C-5$^{GalN'}$), 57.4 (C-2$^{GalN'}$), 51.2 (C-2^{GalN}), 21.2 (-SPhCH$_3$), 20.9 (-OCOCH_3); ESI-TOF HRMS *m/z*: Calcd for $C_{43}H_{44}N_5O_{11}S$ $[M + NH_4]^+$ 838.2753; Found 838.2717.

4.6. para-Tolyl 2-acetamido-3-O-acetyl-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-galactopyranoside **(11)**

To a solution of **10** (230 mg, 0.28 mmol) in pyridine (2 mL) was added AcSH (4 mL, 202 mmol) at 0 °C. The mixture was allowed to warm up to rt and stirred for 6 h, and then diluted with ethyl acetate (50 mL) and washed with saturated aq. $NaHCO_3$ (2 × 25 mL) and brine (25 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (hexane–ethyl acetate 5:1 to 1:2) to give **11** (200 mg, 85%) as a white foamy solid. $[\alpha]_D^{25}$ +112 (*c* 0.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98 (d, J = 7.2 Hz, 1 H, Ar*H*), 7.87 (d, J = 7.2 Hz, 1 H, Ar*H*), 7.85–7.78 (m, 2 H, *ArH*), 7.47–7.35 (m, 9 H, Ar*H*), 7.32–7.28 (m, 3 H, Ar*H*), 7.08 (d, J = 7.8 Hz, 2 H, Ar*H*), 5.64 (d, J = 9.6 Hz, 1 H, H-1^{GalN}), 5.54 (d, J = 9.0 Hz, 1 H, -N*H*Ac), 5.50 (s, 1 H, C*H*Ph), 5.25 (s, 1 H, C*H*Ph), 5.07 (d, J = 3.0 Hz, 1 H, H-1$^{GalN'}$), 4.701–4.58 (m, 4 H, H-2^{GalN}, H-3^{GalN}, H-2$^{GalN'}$, H-3$^{GalN'}$), 4.42 (dd, J = 12.0, 1.8 Hz, 1 H, H-6a^{GalN}), 4.33 (d, J = 2.4 Hz, 1 H, H-4^{GalN}), 4.08 (dd, J = 12.0, 1.2 Hz, 1 H, H-6b^{GalN}), 3.85 (d, J = 1.2 Hz, 1 H, H-4$^{GalN'}$), 3.68 (s, 1 H, H-5^{GalN}), 3.62 (dd, J = 12.6, 1.2 Hz, 1 H, H-6a$^{GalN'}$), 3.34 (dd, J = 12.6, 1.2 Hz, 1 H, H-6b$^{GalN'}$), 3.00 (s, 1 H, H-5$^{GalN'}$), 2.36 (s, 3 H, -SPhCH_3), 1.93 (s, 3 H, -OCOCH_3), 1.36 (s, 3 H, -NHCOCH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.9 (*C*=O), 170.0 (*C*=O), 168.3 (*C*=O), 167.2 (*C*=O), 138.6, 137.4, 137.2, 134.7, 134.6, 134.5, 131.4, 131.2, 129.6, 129.5, 129.0, 128.4, 128.1, 126.6, 126.5, 126.2, 124.2, 123.1, 101.4 (*C*HPh), 100.7 (*C*HPh), 95.3 (C-1$^{GalN'}$), 82.2 (C-1^{GalN}), 72.8 (C-4$^{GalN'}$), 72.6 (C-3^{GalN}), 71.3 (C-4^{GalN}), 69.7 (C-5^{GalN}), 69.6 (C-6^{GalN}), 69.3 (C-3$^{GalN'}$), 68.4 (C-6$^{GalN'}$), 63.1 (C-5$^{GalN'}$), 50.5 (C-2^{GalN}), 46.4 (C-2$^{GalN'}$), 22.6 (-NHCOCH_3) 21.3 (-SPhCH_3), 20.9 (-COCH_3); ESI-TOF HRMS *m/z*: Calcd for $C_{45}H_{45}N_2O_{12}S$ $[M+H]^+$ 837.2688; Found 837.2648; Calcd for $C_{45}H_{44}N_2O_{12}SNa$ $[M+Na]^+$ 859.2507; Found 859.2538.

4.7. para-Tolyl 2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-galactopyranoside **(12)**

To a solution of **11** (200 mg, 0.24 mmol) in MeOH (5 mL) was added NaOMe (0.5 M in MeOH) dropwise until the pH value

reached 10. The mixture was stirred at rt for 30 min and neutralized with Amberlite IR 120 (H^+). The solution was filtered, and the filtrate was concentrated. The residue was purified by silica gel column chromatography (hexane–ethyl acetate 1:2) to give **12** (170 mg, 90%) as a white foamy solid. $[\alpha]_D^{25}$ +145 (*c* 0.2, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 7.93–7.70 (m, 4 H, Ar*H*), 7.46–7.41 (m, 4 H, Ar*H*), 7.40–7.36 (m, 5 H, Ar*H*), 7.32–7.28 (m, 3 H, Ar*H*), 7.09 (t, *J* = 10.4 Hz, 2 H, Ar*H*), 5.81 (d, *J* = 9.0 Hz, 1 H, -N*H*Ac), 5.60 (d, *J* = 9.6 Hz, 1 H, H-1^{GalN}), 5.53 (s, 1 H, C*H*Ph), 5.29 (s, 1 H, C*H*Ph), 5.03 (d, *J* = 3.6 Hz, 1 H, H-$1^{GalN'}$), 4.70 (dd, *J* = 10.8, 3.0 Hz, 1 H, H-3^{GalN}), 4.67 (dd, *J* = 10.8, 9.6 Hz, 1 H, H-2^{GalN}), 4.40 (d, *J* = 12.6 Hz, 1 H, H-$6a^{GalN}$), 4.34 (d, *J* = 3.0 Hz, 1 H, H-4^{GalN}), 4.30 (ddd, *J* = 10.8, 9.0, 3.6 Hz, 1 H, H-$2^{GalN'}$), 4.07 (d, *J* = 12.6 Hz, 1 H, H-$6b^{GalN}$), 3.71 (d, *J* = 3.6 Hz, 1 H, H-$4^{GalN'}$), 3.65 (s, 1 H, H-5^{GalN}), 3.62 (d, *J* = 12.0 Hz, 1 H, H-$6a^{GalN'}$), 3.44 (dt, *J* = 10.2, 3.0 Hz, 1 H, H-$3^{GalN'}$), 3.30 (d, *J* = 12.0 Hz, 1 H, H-$6b^{GalN'}$), 2.95–2.89 (m, 2 H, H-$5^{GalN'}$, -O*H*), 2.36 (s, 3 H, -SPhCH_3), 1.39 (s, 3 H, -NHCOCH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.9 (*C*=O), 168.192 (*C*=O), 167.1 (*C*=O), 138.6, 137.3, 137.2, 134.73, 134.67, 134.4, 131.4, 131.2, 129.7, 129.6, 129.1, 128.5, 128.2, 126.7, 126.6, 126.2, 123.9, 123.2, 101.5 (*C*HPh), 101.0 (*C*HPh), 95.1 (C-$1^{GalN'}$), 82.40 (C-1^{GalN}) 75.0 (C-$4^{GalN'}$), 72.2 (C-3^{GalN}), 71.3 (C-4^{GalN}), 69.7 (C-5^{GalN}), 69.6 (C-6), 69.2 (C-$3^{GalN'}$), 68.4 (C-6′), 63.6 (C-$5^{GalN'}$), 50.6 (C-2^{GalN}), 49.7 (C-$2^{GalN'}$), 22.5 (-NHCOCH_3), 21.3 (-SPhCH_3); ESI-TOF HRMS *m/z*: Calcd for $C_{43}H_{43}N_2O_{11}S$ $[M+H]^+$ 795.2582; Found 795.2561.

4.8. para-Tolyl 2,3-di-O-benzoyl-4-O-chloroacetyl-α-L-rhamnopyranosyl-(1 → 3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-galactopyranoside **(3)**

TMSOTf (10 μL, 55 μmol) was added to a stirred mixture of **12** (152 mg, 0.19 mmol), **6** (132 mg, 0.22 mmol), and activated MS 4 Å (300 mg) in anhydrous CH_2Cl_2 (5 mL) at 0 °C under a N_2 atmosphere. The mixture was stirred at 0 °C for 1 h, and then neutralized with Et_3N. The mixture was diluted with CH_2Cl_2 (15 mL), filtered through a pad of Celite, and the filtrate was concentrated. The resulting residue was purified by silica gel chromatography (hexane–ethyl acetate 2:1 to 1:2) to yield **3** (168 mg, 72%) as a white foamy solid. $[\alpha]_D^{25}$ +8 (*c* 0.25, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.4 Hz, 2 H Ar*H*), 7.94 (d, *J* = 6.6 Hz, 1 H, Ar*H*), 7.87 (d, *J* = 7.2 Hz, 1 H, Ar*H*), 7.82–7.76 (m, 4 H, Ar*H*), 7.60 (t, *J* = 7.2 Hz, 1 H, Ar*H*), 7.50–7.38 (m, 12 H, Ar*H*), 7.34–7.27 (m, 5 H, Ar*H*), 7.10 (d, *J* = 7.8 Hz, 2 H, Ar*H*), 5.68–5.61 (m, 2 H, H-1^{GalN}, -N*H*Ac), 5.53 (s, 1 H, C*H*Ph), 5.43–5.38 (m, 2 H, H-2^{Rha}, H-3^{Rha}), 5.27 (d, *J* = 10.2 Hz, 1 H, H-4^{Rha}), 5.26 (s, 1 H, C*H*Ph), 5.11 (d, *J* = 4.2 Hz, 1 H, H-$1^{GalN'}$), 4.88 (s, 1 H, H-1^{Rha}), 4.70 (dt, *J* = 10.2, 4.2 Hz, 1 H, H-$2^{GalN'}$), 4.69–4.65 (m, 2 H, H-2^{GalN}, H-3^{GalN}), 4.42 (d, *J* = 12.0 Hz, 1 H, H-$6a^{GalN}$), 4.33 (d, *J* = 3.0 Hz, 1 H, H-4^{GalN}), 4.21–4.14 (m, 1 H, H-5^{Rha}), 4.09 (d, *J* = 12.0 Hz, 1 H, H-$6b^{GalN}$), 3.92 (d, *J* = 3.0 Hz, 1 H H-$4^{GalN'}$), 3.86, 3.82 (2 d, *J* = 14.4 Hz, 2 H, -OCOCH_2Cl), 3.69 (s, 1 H, H-5^{GalN}), 3.53 (d, *J* = 12.0 Hz, 1 H, H-$6a^{GalN'}$), 3.49 (dd, *J* = 10.8, 3.0 Hz, 1 H, H-$3^{GalN'}$), 3.23 (d, *J* = 12.0 Hz, 1 H, H-$6b^{GalN'}$), 2.91 (s, 1 H, H-$5^{GalN'}$), 2.36 (s, 3 H, -SPhCH_3), 1.63 (s, 3 H, -NHCOCH_3), 0.94 (d, *J* = 6.6 Hz, 3 H, H-6^{Rha}); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.5 (*C*=O), 168.0 (*C*=O), 167.2 (*C*=O), 166.7 (*C*=O), 165.3 (*C*=O), 164.8 (C=O), 138.5, 137.3, 137.0, 134.69, 134.65, 134.5, 133.5, 133.1, 131.4, 131.2, 129.8, 129.64, 129.58, 129.21, 129.16, 129.15, 128.6, 128.5, 128.3, 128.2, 126.7, 126.4, 126.1, 123.9, 123.3, 101.6 (*C*HPh), 101.0 (*C*HPh), 98.5 (C-1^{Rha}), 96.1 (C-$1^{GalN'}$), 82.1 (C-1^{GalN}), 77.8 (C-$3^{GalN'}$), 74.4 (C-$4^{GalN'}$), 73.1 (C-3^{GalN}), 72.7 (C-4^{Rha}), 71.6 (C-4^{GalN}), 70.5 (C-2^{Rha}), 69.8 (C-5^{GalN}), 69.7 (C-3^{Rha}), 69.5 (C-6^{GalN}), 68.5 (C-$6^{GalN'}$), 66.5 (C-5^{Rha}), 63.1 (C-$5^{GalN'}$), 50.6 (C-2^{GalN}), 46.9 (C-$2^{GalN'}$), 40.5 (-OCOCH_2Cl), 22.8 (-NHCOCH_3), 21.3 (-SPhCH_3), 17.4 (C-6^{Rha}); ESI-TOF HRMS *m/z*: Calcd for $C_{65}H_{62}ClN_2O_{18}S$ $[M+H]^+$ 1225.3401; Found 1225.3376.

4.9. 3-Azidopropyl 2,3-di-O-benzoyl-4-O-chloroacetyl-α-L-rhamnopyranosyl-(1 → 3)- 2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-galactopyranoside **(13)**

To a stirred mixture of **3** (105 mg, 0.085 mmol), 3-azidopropanol (50 μL, 0.49 mmol), and activated MS 4 Å (200 mg) in anhydrous CH_2Cl_2 (4 mL) were added NIS (30 mg, 0.13 mmol) and TMSOTf (15 μL, 0.06 mmol) at −40 °C under a N_2 atmosphere. The mixture was stirred at −40 °C for 30 min and then slowly warmed up to rt and stirred for another 1 h. The mixture was neutralized with Et_3N, and then diluted with CH_2Cl_2 (20 mL) and washed with saturated aq. $Na_2S_2O_3$ (10 mL) and brine (10 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (hexane–ethyl acetate 5:1 to 1:2) to give **13** (78 mg, 76%) as a white syrup solid. $[\alpha]_D^{25}$ +12 (*c* 0.2, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.2 Hz, 2 H, Ar*H*), 7.94 (d, *J* = 6.6 Hz, 1 H, Ar*H*), 7.86 (d, *J* = 7.2 Hz, 1 H, Ar*H*), 7.80 (d, *J* = 7.2 Hz, 2 H, Ar*H*), 7.79–7.74 (m, 2 H, Ar*H*), 7.61–7.56 (m, 3 H, Ar*H*), 7.48–7.40 (m, 7 H, Ar*H*), 7.37 (t, *J* = 7.2 Hz, 1 H, Ar*H*), 7.34–7.27 (m, 5 H, Ar*H*), 5.69 (d, *J* = 9.0 Hz, 1 H, -N*H*Ac), 5.58 (s, 1 H, C*H*Ph), 5.46–5.41 (m, 2 H, H-2^{Rha}, H-3^{Rha}), 5.31–5.26 (m, 3 H, C*H*Ph, H-1^{GalN}, H-4^{Rha}), 5.15 (d, *J* = 3.6 Hz, 1 H, H-$1^{GalN'}$), 4.92 (s, 1 H, H-1^{Rha}), 4.75 (dt, *J* = 9.6, 3.6 Hz, 1 H, H-$2^{GalN'}$), 4.71–4.68 (m, 2 H, H-2^{GalN}, H-3^{GalN}), 4.37 (d, *J* = 11.4 Hz, 1 H, H-$6a^{GalN}$), 4.33 (br s, 1 H, H-4^{GalN}), 4.23–4.16 (m, 1 H, H-5^{Rha}), 4.14 (d, *J* = 11.4 Hz, 1 H, H-$6b^{GalN}$), 3.98 (d, *J* = 3.0 Hz, 1 H, H-$4^{GalN'}$), 3.98–3.93 (m, 1 H, -OCH_2CH_2-), 3.86, 3.82 (2 d, *J* = 14.4 Hz, 2 H, -OCOCH_2Cl), 3.64 (d, *J* = 12.0 Hz, 1 H, H-$6a^{GalN'}$), 3.61 (s, 1 H, H-5^{GalN}), 3.59–3.50 (m, 2 H, H-$3^{GalN'}$, -OCH_2CH_2-), 3.32 (d, *J* = 12.0 Hz, 1 H, H-$6b^{GalN'}$), 3.23–3.11 (m, 2 H, -CH_2C$H_2$$N_3$), 3.00 (s, 1 H, H-$5^{GalN'}$), 1.81–1.74 (m, 1 H, -OCH$_2$CH_2CH$_2$$N_3$), 1.73–1.66 (m, 1 H, -OCH$_2$CH_2CH$_2$$N_3$), 1.64 (s, 3 H, -NHCOC$H_3$), 0.95 (d, *J* = 6.6 Hz, 3 H, H-6^{Rha}); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.5 (*C*=O), 168.2 (*C*=O), 167.7 (*C*=O), 166.7 (*C*=O), 165.3 (*C*=O), 164.8 (*C*=O), 137.3, 137.0, 134.69, 134.67, 133.5, 133.1, 131.28, 131.26, 129.8, 129.6, 129.5, 129.22, 129.18, 129.1, 128.6, 128.5, 128.3, 128.2, 126.5, 126.1, 123.9, 123.2, 101.5 (*C*HPh), 101.0 (*C*HPh), 98.6 (C-1^{Rha}), 98.2 (C-1^{GalN}), 96.2 (C-$1^{GalN'}$), 77.9 (C-$3^{GalN'}$), 74.4 (C-$4^{GalN'}$), 72.7 (C-4^{Rha}), 72.3 (C-3^{GalN}), 71.7 (C-4^{GalN}), 70.5 (C-2^{Rha}), 69.7 (C-3^{Rha}), 69.3 (C-6^{GalN}), 68.6 (C-$6^{GalN'}$), 66.6 (C-5^{Rha}), 66.5 (C-5^{GalN}), 66.0 (-OCH_2CH_2-), 63.2 (C-$5^{GalN'}$), 52.1 (C-2^{GalN}), 48.1 (-CH_2C$H_2$$N_3$), 47.0 (C-$2^{GalN'}$), 40.5 (-OCOC$H_2$Cl), 28.8 (-OCH$_2CH_2CH_2$$N_3$), 22.8 (-NHCOC$H_3$), 17.4 (C-$6^{Rha}$); ESI-TOF HRMS *m/z*: Calcd for $C_{61}H_{61}ClN_5O_{19}$ $[M+H]^+$ 1202.3644; Found 1202.3631; Calcd for $C_{61}H_{60}ClN_5O_{19}Na$ $[M+Na]^+$ 1224.3463; Found 1224.3421; Calcd for $C_{61}H_{60}ClN_5O_{19}K$ $[M+K]^+$ 1240.3203; Found 1240.3205.

4.10. 3-Azidopropyl α-L-rhamnopyranosyl-(1 → 3)-2-acetamido-2-deoxy-α-D-galactopyranosyl-(1 → 3)-2-acetamido-2-deoxy-β-D-galactopyranoside **(1)**

A solution of **13** (20 mg, 16.6 μmol) in ethanol (4 mL) and 80% hydrazine hydrate (1 mL) was refluxed for 6 h. The reaction mixture was then concentrated and purified by size exclusion chromatography on a Bio-Gel LH-20 column with methanol as the eluent to get a white solid. The product was dissolved in pyridine (5 mL) containing acetic anhydride (2 mL). The reaction mixture was stirred at rt for 4 h and then concentrated to give a pale yellow solid, which was then dissolved in 80% HOAc (5 mL) and stirred at 80 °C for overnight. The reaction mixture was then co-evaporated with toluene (2 × 5 mL), and the resulting product was then dissolved MeOH (4 mL) followed by addition of NaOMe (0.5 M) in MeOH until the pH value reached 10. The mixture was stirred at rt for 3 h, and neutralized with Amberlite IR 120 (H^+). The solution was filtered, and the filtrate was concentrated. The resulting

residue was purified by size exclusion chromatography on a Sephadex G-10 column with distilled water as the eluent and then lyophilized to give **1** (8.4 mg, 75%) as a white solid. $[\alpha]_D^{25}$ +13 (*c* 0.2, H_2O); ^1H NMR (600 MHz, D_2O): δ 4.90 (d, J = 3.0 Hz, 1 H, H-$1^{GalN'}$), 4.67 (s, 1 H, H-1^{Rha}), 4.35 (d, J = 8.4 Hz, 1 H, H-1^{GalN}), 4.20 (dd, J = 10.8, 3.6 Hz, 1 H, H-$2^{GalN'}$), 3.97 (d, J = 3.0 Hz, 1 H, H-4^{GalN}), 3.90–3.86 (m, 2 H), 3.84–3.80 (m, 1 H), 3.69–3.55 (m, 10 H), 3.55–3.49 (m, 1 H), 3.48–3.44 (m, 1 H), 3.25 (t, J = 9.6 Hz, 1 H), 3.21 (t, J = 6.6 Hz, 2 H, -$CH_2CH_2N_3$), 1.90, 1.85 (2 s, 2 × 3 H, 2 × -NHCOCH_3), 1.71–1.64 (m, 2 H, -$OCH_2CH_2CH_2N_3$), 1.08 (d, J = 6.0 Hz, 3 H, H-6^{Rha}); ^{13}C NMR (150 MHz, D_2O): δ 174.33, 174.30, 102.2 (C-1^{Rha}), 101.0 (C-1^{GalN}), 93.1 (C-$1^{GalN'}$), 76.0, 74.9, 74.2, 71.8, 71.4, 70.2, 69.8, 69.1, 68.0, 67.0, 63.1, 60.9, 60.7, 50.6, 48.1, 47.7, 28.0, 22.1, 21.8, 16.5; ESI-TOF HRMS *m/z*: Calcd for $C_{25}H_{44}N_5O_{15}$ $[M+H]^+$ 654.2828; Found 654.2876; Calcd for $C_{25}H_{43}N_5O_{15}Na$ $[M+Na]^+$ 676.2648; Found 676.2686.

4.11. 3-Azidopropyl 2,3-di-O-benzoyl-α-L-rhamnopyranosyl-(1 → 3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-galactopyranoside ***(14)***

To a solution of **13** (70 mg, 0.058 mmol) in CH_2Cl_2/CH_3OH (v/v 1:4, 5 mL) at rt were added thiourea (13 mg, 0.17 mmol) and 2,6-lutidine (2 μL). The reaction mixture was refluxed for 6 h, at which point TLC (hexane–ethyl acetate 1:2) showed the complete disappearance of **13**, and the solvent was then removed under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (20 mL) and washed successively with 1M HCl, water and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated. Purification of the residue on size exclusion chromatography on a Bio-Gel LH-20 column with methanol as the eluent to generate a colorless syrup, which was further purified on a silica gel column chromatography (hexane–ethyl acetate 1:2) gave **14** (52 mg, 80%) as a white foamy solid. $[\alpha]_D^{25}$ +148 (*c* 0.2, $CHCl_3$); ^1H NMR (600 MHz, CD_3CN): δ 7.98 (d, J = 8.4 Hz, 2 H, Ar*H*), 7.92 (t, J = 6.6 Hz, 1 H, Ar*H*), 7.90 (d, J = 7.2 Hz, 1 H, Ar*H*), 7.89–7.84 (m, 2 H, Ar*H*), 7.83 (d, J = 7.8 Hz, 2 H, Ar*H*), 7.72 (dd, J = 6.0, 3.6 Hz, 1 H, Ar*H*), 7.69 (t, J = 7.2 Hz, 1 H, Ar*H*), 7.62 (dd, J = 6.0, 3.6 Hz, 1 H, Ar*H*), 7.58–7.52 (m, 4 H, Ar*H*), 7.46–7.33 (m, 9 H, Ar*H*), 6.10 (d, J = 9.0 Hz, 1 H, -N*H*Ac), 5.73 (s, 1 H, C*H*Ph), 5.43 (s, 1 H, C*H*Ph), 5.34 (br dd, J = 3.6, 1.8 Hz, 1 H, H-2^{Rha}), 5.22 (d, J = 8.4 Hz, 1 H, H-1^{GalN}), 5.12 (d, J = 4.2 Hz, 1 H, H-$1^{GalN'}$), 5.08 (dd, J = 9.6, 3.6 Hz, 1 H, H-3^{Rha}), 4.90 (br s, 1 H, H-1^{Rha}), 4.79 (dd, J = 11.4, 3.6 Hz, 1 H, H-3^{GalN}), 4.49 (d, J = 3.6 Hz, 1 H, H-4^{GalN}), 4.45 (dd, J = 11.4, 8.4 Hz, 1 H, H-2^{GalN}), 4.40–4.35 (m, 1 H, H-$2^{GalN'}$), 4.22, 4.18 (2 d, J = 12.0 Hz, 2 × 1 H, H-6a,b^{GalN}), 4.12 (d, J = 3.0 Hz, 1 H, H-$4^{GalN'}$), 3.92–3.84 (m, 2 H, -OCH_2CH_2-, H-5^{Rha}), 3.76–3.70 (m, 2 H, H-4^{Rha}, H-5^{GalN}), 3.63 (dd, J = 11.4, 3.0 Hz, 1 H, H-$3^{GalN'}$), 3.56–3.51 (m, 1 H, -OCH_2CH_2-), 3.47 (d, J = 4.8 Hz, 1 H, -O*H*), 3.44–3.37 (m, 2 H, H-6a,b$^{GalN'}$), 3.19–3.07 (m, 3 H, -$CH_2CH_2N_3$, H-$5^{GalN'}$), 1.75–1.65 (m, 2 H, -$OCH_2CH_2CH_2N_3$), 1.65 (s, 3 H, -COCH_3), 1.22 (d, J = 6.0 Hz, 3 H, H-6^{Rha}); ^{13}C NMR (150 MHz, CD_3CN): δ 169.8 (*C*=O), 168.3 (*C*=O), 168.0 (*C*=O), 165.4 (*C*=O), 165.1 (*C*=O), 138.4, 138.3, 134.9, 134.8, 133.6, 133.2, 131.4, 131.3, 131.2, 129.8, 129.6, 129.5, 129.3, 129.00, 128.97, 128.8, 128.7, 128.4, 128.2, 126.3, 126.1, 123.6, 123.2, 100.5 (*C*HPh), 100.4 (*C*HPh), 99.6 (C-1^{Rha}), 98.3 (C-1^{GalN}), 97.3 (C-$1^{GalN'}$), 76.0 (C-$3^{GalN'}$), 74.8 (C-$4^{GalN'}$), 73.1 (C-3^{GalN}), 72.5 (C-3^{Rha}), 72.2 (C-4^{GalN}), 70.3 (C-2^{Rha}), 70.2 (C-4^{Rha}), 68.91 (C-5^{Rha}), 68.88 (C-6^{GalN}), 68.1 (C-$6^{GalN'}$), 66.4 (C-5^{GalN}), 66.2 (-OCH_2CH_2-), 63.3 (C-$5^{GalN'}$), 52.2 (C-2^{GalN}), 47.8 (-$CH_2CH_2N_3$), 47.6 (C-$2^{GalN'}$), 28.4 (-$OCH_2CH_2CH_2N_3$), 22.2 (-COCH_3), 17.1 (C-6^{Rha}); ESI-TOF HRMS *m/z*: Calcd for $C_{59}H_{60}N_5O_{18}$ $[M+H]^+$ 1126.3928; Found 1126.3914; Calcd for $C_{59}H_{59}N_5O_{18}Na$ $[M+Na]^+$ 1148.3747; Found 1148.3711; Calcd for $C_{59}H_{59}N_5O_{18}K$ $[M+K]^+$ 1164.3487; Found 1164.3503.

4.12. 3-Azidopropyl 2,3-O-isopropylidene-α-L-rhamnopyranoside ***(15)***

To a stirred mixture of **7** (108 mg, 0.28 mmol), 3-azidopropanol (140 μL, 1.40 mmol), and activated MS 4 Å (250 mg) in anhydrous CH_2Cl_2 (4 mL) were added NIS (75 mg, 0.34 mmol) and TMSOTf (5 μL, 0.03 mmol) at −40 °C under a N_2 atmosphere. The reaction mixture was stirred for 1 h, and neutralized with Et_3N. The mixture was diluted with CH_2Cl_2 (10 mL), filtered through a pad of Celite, and the filtrate was washed with saturated aq. $Na_2S_2O_3$ (10 mL) and brine (10 mL), respectively. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated. The above obtained residue was dissolved into methanol (4 mL), and NaOMe (0.5 M) in MeOH was added until the pH value reached 10. The resulting mixture was stirred for 30 min and then neutralized with Amberlite IR 120 (H^+). The solution was filtered, and the filtrate was concentrated. The residue was purified by silica gel column chromatography (hexane–ethyl acetate 3:1) to give **15** (42 mg, 53%) as a white foamy solid. $[\alpha]_D^{25}$ -27 (*c* 0.4, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 4.95 (s, 1 H, H-1), 4.12 (d, J = 5.4 Hz, 1 H, H-2), 4.09–4.04 (t, J = 6.6 Hz, 1 H, H-3), 3.82–3.77 (m, 1 H, -OCH_2CH_2-), 3.66–3.59 (m, 1 H, H-5), 3.53–3.48 (m, 1 H, -OCH_2CH_2-), 3.42–3.36 (m, 3 H, H-4, -$CH_2CH_2N_3$), 2.40 (d, J = 4.2 Hz, 1 H, -O*H*), 1.92–1.80 (m, 2 H, -$OCH_2CH_2CH_2N_3$), 1.52 [s, 3 H, -$C(CH_3)_2$], 1.35 [s, 3 H, -$C(CH_3)_2$], 1.29 (d, J = 6.6 Hz, 3 H, H-6); ^{13}C NMR (150 MHz, $CDCl_3$): δ 109.5, 97.1, 78.3, 75.8, 74.5, 65.8, 64.2, 48.34, 28.8, 28.0, 26.2, 17.4.

4.13. 3-Azidopropyl 2,3-di-O-benzoyl-4-O-chloroacetyl-α-L-rhamnopyranosyl-(1 → 3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1 → 4)-2,3-O-isopropylidene-α-L-rhamnopyranoside ***(16)***

After a mixed solution of **3** (20 mg, 0.016 mmol), **15** (13 mg, 0.045 mmol), and activated MS 4 Å (200 mg) in anhydrous CH_2Cl_2 (5 mL) was stirred at rt for 1 h under a N_2 atmosphere, it was cooled to −40 °C, and NIS (5 mg, 0.02 mmol) and AgOTf (2 mg, 7.7 μmol) were then added. The reaction mixture was stirred −40 °C for 30 min and slowly warmed to 0 °C and stirred for another 1 h, and then neutralized with Et_3N. The resulting mixture was diluted with CH_2Cl_2 (10 mL), filtered through a pad of Celite, and the filtrate was washed with saturated aq. $Na_2S_2O_3$ (10 mL) and brine (10 mL). The organic phase was dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (hexane–ethyl acetate 1:2) to give **16** (19 mg, 82%) as a white foamy solid. $[\alpha]_D^{25}$ +141 (*c* 0.2, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 7.99 (d, J = 7.8 Hz, 2 H, Ar*H*), 7.91 (d, J = 7.8 Hz, 1 H, Ar*H*), 7.84 (d, J = 6.0 Hz, 1 H, Ar*H*), 7.80 (d, J = 8.4 Hz, 2 H, Ar*H*), 7.78–7.72 (m, 2 H, Ar*H*), 7.58 (d, J = 7.8 Hz, 3 H, Ar*H*), 7.48–7.41 (m, 7 H, Ar*H*), 7.38 (t, J = 7.2 Hz, 1 H, Ar*H*), 7.33–7.27 (m, 5 H, Ar*H*), 5.78 (d, J = 9.6 Hz, 1 H, -N*H*Ac), 5.57 (s, 1 H, C*H*Ph), 5.45–5.40 (m, 2 H, H-$2^{Rha'}$, H-$3^{Rha'}$), 5.37 (d, J = 9.0 Hz, 1 H, H-1^{GalN}), 5.29 (s, 1 H, C*H*Ph), 5.28 (d, J = 10.2 Hz, 1 H, H-$4^{Rha'}$), 5.16 (d, J = 3.6 Hz, 1 H, H-$1^{GalN'}$), 4.95 (s, 1 H, H-$1^{Rha'}$), 4.91 (dd, J = 11.4, 3.6 Hz, 1 H, H-3^{GalN}), 4.83 (s, 1 H, H-1^{Rha}), 4.74 (dt, J = 10.2, 3.6 Hz, 1 H, H-$2^{GalN'}$), 4.62 (dd, J = 11.4, 8.4 Hz, 1 H, H-2^{GalN}), 4.34–4.30 (m, 2 H, H-4^{GalN}, H-6a^{GalN}), 4.23–4.17 (m, 1 H, H-$5^{Rha'}$), 4.14 (d, J = 11.4 Hz, 1 H, H-6b^{GalN}), 4.01 (d, J = 3.0 Hz, 1 H, H-$4^{GalN'}$), 3.88–3.80 (m, 3 H, -OCOCH_2Cl, H-2^{Rha}), 3.74 (t, J = 3.0 Hz, 1 H, H-3^{Rha}), 3.72–3.67 (m, 1 H, -OCH_2CH_2-), 3.65–3.61 (m, 2 H, H-$3^{GalN'}$, H-5^{GalN}), 3.58 (m, 2 H, H-6a$^{GalN'}$, H-5^{Rha}), 3.44–3.38 (m, 1 H, -OCH_2CH_2-), 3.35–3.28 (m, 4 H, H-4^{Rha}, H-6b$^{GalN'}$, -$CH_2CH_2N_3$), 3.04 (s, 1 H, H-$5^{GalN'}$), 1.82–1.75 (m, 2 H, -$OCH_2CH_2CH_2N_3$), 1.65 (s, 3 H, -COCH_3), 1.36 [s, 3 H, -$C(CH_3)_2$], 1.34 (d, J = 6.6 Hz, 3 H, H-6^{Rha}), 0.96 (d, J = 6.0 Hz, 3 H, H-$6^{Rha'}$), 0.83 [s, 3 H, -$C(CH_3)_2$]; ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.6 (*C*=O), 168.3 (*C*=O), 168.0 (*C*=O), 166.8

(*C*=O), 165.3 (*C*=O), 164.8 (*C*=O), 137.4, 137.0, 134.1, 134.1, 133.5, 133.1, 132.2, 131.5, 129. 8, 129.7, 129.6, 129.2, 129.2, 129.1, 128.6, 128.5, 128.3, 128.2, 126.5, 126.1, 123.7, 122.6, 109.0 [-*C*$(CH_3)_2$], 101.6 (-*C*HPh), 101.0 (-*C*HPh), 100.2 (C-1^{GalN}), 98.6 (C-$1^{Rha'}$), 96.7 (C-1^{Rha}), 96.5 (C-$1^{GalN'}$), 84.2 (C-4^{Rha}), 77.8 (C-$3^{GalN'}$), 77.5 (C-3^{GalN}), 75.7 (C-2^{Rha}), 74.5 (C-$4^{GalN'}$), 72.7 (C-$4^{Rha'}$), 72.1 (C-3^{GalN}), 71.7 (C-4^{GalN}), 70.6 (C-2^{Rha}), 69.7 (C-3^{Rha}), 69.4 (C-6^{GalN}), 68.6 (C-$6^{GalN'}$), 66.5 (C-$5^{Rha'}$), 66.1 (C-5^{GalN}), 64.5 (C-5^{Rha}), 64.1 (-O*C*H_2CH_2-), 63.0 (C-$5^{GalN'}$), 52.8 (C-2^{GalN}), 48.3 (-$CH_2CH_2N_3$), 47.1 (C-$2^{GalN'}$), 40.5 (-OCO*C*H_2Cl), 28.8 (-$OCH_2CH_2CH_2N_3$), 27.7 [-C(*C*$H_3)_2$], 25.7 [-C(*C*$H_3)_2$], 22.8 (-CO*C*H_3), 17.6 (C-6^{Rha}), 17.4 (C-$6^{Rha'}$); ESI-TOF HRMS m/z: Calcd for $C_{70}H_{75}ClN_5O_{23}$ $[M+H]^+$ 1388.4536; Found 1388.4514.

4.14. 3-Azidopropyl 3-O-acetyl-4,6-O-benzylidene-2-acetamido-2-deoxy-α-D-galactopyranosyl-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-galactopyranoside **(17)**

To a stirred mixture of **11** (110 mg, 0.13 mmol), 3-azidopropanol (79 μL, 0.78 mmol), and activated MS 4 Å (200 mg) in anhydrous CH_2Cl_2 (5 mL) were added NIS (35 mg, 0.15 mmol) and TMSOTf (20 μL, 0.09 mmol) at −40 °C under a N_2 atmosphere. The reaction mixture was stirred at −40 °C for 1 h, and slowly warmed up to rt with stirring for another 1 h, and then neutralized with Et_3N. The mixture was then diluted with CH_2Cl_2 (20 mL), filtered through a pad of Celite, and the filtrate was washed successively with saturated aq. $Na_2S_2O_3$ (20 mL) and brine (15 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel column chromatography (hexane−ethyl acetate 10:1 to 1:2) to give **17** (74 mg, 69%) as a white foamy solid. $[\alpha]_D^{25}$ +116 (*c* 0.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.97 (d, *J* = 7.2 Hz, 1 H, Ar*H*), 7.87 (d, *J* = 7.2 Hz, 1 H, Ar*H*), 7.84−7.77 (m, 2 H, Ar*H*), 7.56 (d, *J* = 7.2 Hz, 2 H, Ar*H*), 7.44−7.36 (m, 5 H, Ar*H*), 7.34−7.29 (m, 3 H, Ar*H*), 5.66 (d, *J* = 9.0 Hz, 1 H, -N*H*Ac), 5.56 (s, 1 H, C*H*Ph), 5.31 (d, *J* = 7.8 Hz, 1 H, H-1^{GalN}), 5.28 (s, 1 H, C*H*Ph), 5.12 (d, *J* = 3.6 Hz, 1 H, H-$1^{GalN'}$), 4.754−4.63 (m, 4 H, H-2^{GalN}, H-3^{GalN}, H-$2^{GalN'}$, H-$3^{GalN'}$), 4.38 (d, *J* = 12.0 Hz, 1 H, H-$6a^{GalN}$), 4.35 (d, *J* = 2.4 Hz, 1 H, H-4^{GalN}), 4.16−4.12 (dd, *J* = 12.0, 1.2 Hz, 1 H, H-$6b^{GalN}$), 3.99−3.94 (m, 1 H, -OC*H*$_2$CH$_2$-), 3.93 (d, *J* = 3.0 Hz, 1 H, H-$4^{GalN'}$), 3.67 (dd, *J* = 12.6, 1.2 Hz, 1 H, H-$6a^{GalN'}$), 3.62 (s, 1 H, H-5^{GalN}), 3.59−3.53 (m, 1 H, -OC*H*$_2$CH$_2$-), 3.42 (dd, *J* = 12.6, 1.2 Hz, 1 H, H-$6b^{GalN'}$), 3.24−3.14 (m, 2 H, -$CH_2CH_2N_3$), 3.10 (s, 1 H, H-$5^{GalN'}$), 1.95 (s, 3 H, -CO*C*H_3), 1.83−1.75 (m, 1 H, -$OCH_2CH_2CH_2N_3$), 1.74−1.66 (m, 1 H, -$OCH_2CH_2CH_2N_3$), 1.44 (s, 3 H, -NHCO*C*H_3); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* 171.0 (*C*=O), 170.0 (*C*=O), 168.5 (*C*=O), 167.8 (*C*=O), 137.24, 137.20, 134.7, 134.6, 131.3, 131.2, 129.4, 129.0, 128.5, 128.1, 126.4, 126.2, 124.1, 123.1, 101.4 (*C*HPh), 100.7 (*C*HPh), 98.2 (C-1^{GalN}), 95.7 (C-$1^{GalN'}$), 72.9 (C-$4^{GalN'}$), 71.9 (C-3^{GalN}), 71.5 (C-4^{GalN}), 69.4 (C-6^{GalN}), 69.2 (C-$3^{GalN'}$), 68.4 (C-$6^{GalN'}$), 66.4 (C-5^{GalN}), 66.0 (-O*C*H_2CH$_2$-), 63.1 (C-$5^{GalN'}$), 52.1 (C-2^{GalN}), 48.1 (-$CH_2CH_2N_3$), 46.6 (C-$2^{GalN'}$), 28.8 (-$OCH_2CH_2CH_2N_3$), 22.7 (-OCO*C*H_3), 20.9 (-NHCO*C*H_3); ESI-TOF HRMS *m/z*: Calcd for $C_{41}H_{44}N_5O_{13}$ $[M+H]^+$ 814.2930; Found 814.2900; Calcd for $C_{41}H_{43}N_5O_{13}Na$ $[M+Na]^+$ 836.2750; Found 836.2727.

4.15. 3-Azidopropyl 4,6-O-benzylidene-2-acetamido-2-deoxy-α-D-galactopyranosyl-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-galactopyranoside **(18)**

To a solution of **17** (70 mg, 0.086 mmol) in MeOH (3 mL) was added NaOMe (0.5 M) in MeOH until the pH value reached 10. The mixture was stirred at rt for 1 h, and then neutralized with Amberlite IR 120 (H^+). The solution was filtered, and the filtrate was concentrated. The residue was purified by silica gel column chromatography (hexane−ethyl acetate 1:2) to give **18** (58 mg, 88%) as a white foamy solid. $[\alpha]_D^{25}$ +96 (*c* 0.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.95−7.76 (m, 4 H, Ar*H*), 7.57−7.53 (m, 2 H, Ar*H*), 7.44−7.36 (m, 5 H, Ar*H*), 7.33−7.29 (m, 3 H, Ar*H*), 5.88 (d, *J* = 8.4 Hz, 1 H, -N*H*Ac), 5.57 (s, 1 H, C*H*Ph), 5.32 (s, 1 H, C*H*Ph), 5.26 (d, *J* = 8.4 Hz, 1 H, H-1^{GalN}), 5.07 (d, *J* = 3.6 Hz, 1 H, H-$1^{GalN'}$), 4.73 (dd, *J* = 10.8, 3.6 Hz, 1 H, H-3^{GalN}), 4.67 (dd, *J* = 10.8, 8.4 Hz, 1 H, H-2^{GalN}), 4.39−4.31 (m, 3 H, H-$2^{GalN'}$, H-4^{GalN}, H-$6a^{GalN}$), 4.14 (dd, *J* = 12.6, 1.8 Hz, 1 H, H-$6b^{GalN}$), 3.99−3.93 (m, 1 H, -OC*H*$_2$CH$_2$-), 3.78 (d, *J* = 3.0 Hz, 1 H, H-$4^{GalN'}$), 3.74 (dd, *J* = 12.6, 1.2 Hz, 1 H, H-$6a^{GalN'}$), 3.60 (d, *J* = 1.2 Hz, 1 H, H-5^{GalN}), 3.58−3.53 (m, 1 H, -OC*H*$_2$CH$_2$-), 3.51 (dt, *J* = 9.6, 3.0 Hz, 1 H, H-$3^{GalN'}$), 3.41 (dd, *J* = 12.6, 1.8 Hz, 1 H, H-$6b^{GalN'}$), 3.23−3.14 (m, 2 H, -$CH_2CH_2N_3$), 3.02 (s, 1 H, H-$5^{GalN'}$), 2.97 (d, *J* = 9.6 Hz, 1 H, -O*H*), 1.83−1.74 (m, 1 H, -$OCH_2CH_2CH_2N_3$), 1.73−1.65 (m, 1 H, -$OCH_2CH_2CH_2N_3$), 1.42 (s, 3 H, -NHCOCH_3); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* 171.9 (*C*=O), 168.3 (*C*=O), 167.6 (*C*=O), 137.2, 134.74, 134.67, 131.24, 131.20, 129.6, 129.1, 128.6, 128.2, 126.4, 126.2, 123.9, 123.1, 101.5 (*C*HPh), 101.0 (*C*HPh), 98.2 (C-1^{GalN}), 95.2 (C-$1^{GalN'}$), 75.0 (C-$4^{GalN'}$), 71.3 (C-4^{GalN}), 71.2 (C-3^{GalN}), 69.4 (C-6^{GalN}), 69.3 (C-$3^{GalN'}$), 68.5 (C-$6^{GalN'}$), 66.4 (C-5^{GalN}), 66.0 (-O*C*H_2CH$_2$-), 63.6 (C-$5^{GalN'}$), 52.0 (C-2^{GalN}), 49.7 (C-$2^{GalN'}$), 48.0 (-$CH_2CH_2N_3$), 28.8 (-$OCH_2CH_2CH_2N_3$), 22.5 (-NHCO*C*H_3); ESI-TOF HRMS *m/z*: Calcd for $C_{39}H_{42}N_5O_{12}$ $[M+H]^+$ 772.2824; Found 772.2822; Calcd for $C_{39}H_{41}N_5O_{12}Na$ $[M+Na]^+$ 794.2644; Found 794.2610.

4.16. 3-Azidopropyl 4-O-acetyl-2,3-O-isopropylidene-α-L-rhamnopyranosyl-(1 → 3)- 2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-galactopyranoside **(20)**

After a mixed solution of **18** (45 mg, 0.058 mmol), **19** (25 mg, 0.071 mmol), and activated 4 Å MS (100 mg) in anhydrous CH_2Cl_2 (4 mL) was stirred at rt for 2 h under a N_2 atmosphere, it was cooled to −40 °C, and then NIS (16 mg, 0.07 mmol) and AgOTf (4 mg, 0.015 mmol) were added. The reaction mixture was stirred −40 °C for 30 min and slowly warmed to 0 °C and stirred for another 1 h, and then neutralized with Et_3N. The mixture was diluted with CH_2Cl_2 (20 mL), filtered through a pad of Celite, and the filtrate was washed successively with saturated aq. $Na_2S_2O_3$ (20 mL) and brine (15 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (hexane−ethyl acetate 2:1 to 1:2) to give **20** (45 mg, 78%) as a white foamy solid. $[\alpha]_D^{25}$ +15 (*c* 0.15, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.98−7.79 (m, 4 H, Ar*H*), 7.56 (d, *J* = 7.8 Hz, 2 H, Ar*H*), 7.45−7.37 (m, 5 H, Ar*H*), 7.34−7.30 (m, 3 H, Ar*H*), 5.65 (d, *J* = 9.6 Hz, 1 H, -N*H*Ac), 5.55 (s, 1 H, C*H*Ph), 5.33 (d, *J* = 7.8 Hz, 1 H, H-1^{GalN}), 5.27 (s, 1 H, C*H*Ph), 5.08 (d, *J* = 3.6 Hz, 1 H, H-$1^{GalN'}$), 4.91 (s, 1 H, H-1^{Rha}), 4.72 (dd, *J* = 9.6, 7.8 Hz, 1 H, H-4^{Rha}), 4.69 (dd, *J* = 10.8, 7.8 Hz, 1 H, H-2^{GalN}), 4.65 (dd, *J* = 10.8, 3.6 Hz, 1 H, H-3^{GalN}), 4.58 (dt, *J* = 10.8, 3.6 Hz, 1 H, H-$2^{GalN'}$), 4.37 (d, *J* = 12.0 Hz, 1 H, H-$6a^{GalN}$), 4.34 (br d, *J* = 3.0 Hz, 1 H, H-4^{GalN}), 4.14 (dd, *J* = 12.0, 1.2 Hz, 1 H, H-$6b^{GalN}$), 4.09 (dd, *J* = 7.8, 5.4 Hz, 1 H, H-3^{Rha}), 4.00−3.94 (m, 1 H, -OC*H*$_2$CH$_2$-), 3.91 (d, *J* = 5.4 Hz, 1 H, H-2^{Rha}), 3.85 (d, *J* = 3.0 Hz, 1 H, H-$4^{GalN'}$), 3.80−3.73 (m, 2 H, H-$6a^{GalN'}$, H-5^{Rha}), 3.61 (s, 1 H, H-5^{GalN}), 3.60−3.54 (m, 1 H, -OC*H*$_2$CH$_2$-), 3.42 (dd, *J* = 10.8, 3.0 Hz, 1 H, H-$3^{GalN'}$), 3.38 (dd, *J* = 12.0, 1.2 Hz, 1 H, H-$6b^{GalN'}$), 3.25−3.15 (m, 2 H, -$CH_2CH_2N_3$), 2.97 (s, 1 H, H-$5^{GalN'}$), 2.00 (s, 3 H, -OCOCH_3), 1.84−1.76 (m, 1 H, -$OCH_2CH_2CH_2N_3$), 1.75−1.66 (m, 1 H, -$OCH_2CH_2CH_2N_3$), 1.51 [s, 3 H, -C(C$H_3)_2$], 1.42 (s, 3 H, -NHCOCH_3), 1.26 [s, 3 H, -C(C$H_3)_2$], 0.88 (d, *J* = 6.0 Hz, 3 H, H-6^{Rha}); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* 170.2 (*C*=O), 170.0 (*C*=O), 168.3 (*C*=O), 167.9 (*C*=O), 137.3, 137.2, 134.9, 134.7, 131.3, 131.2, 129.6, 129.1, 128.5, 128.2, 126.5, 126.1, 124.1, 123.1, 109.6 [-*C*$(CH_3)_2$], 101.6 (*C*HPh), 100.9 (*C*HPh), 99.9 (C-1^{Rha}), 98.1 (C-1^{GalN}), 95.2 (C-$1^{GalN'}$), 77.5 (C-$3^{GalN'}$), 75.9 (C-2^{Rha}), 75.3 (C-3^{Rha}), 75.0 (C-$4^{GalN'}$), 74.1 (C-4^{Rha}), 71.3 (2C, C-3^{GalN}, C-4^{GalN}), 69.3 (C-

6^{GalN}), 68.6 (C-6$^{GalN'}$), 66.4 (C-5^{GalN}), 66.1 (-O*C*H_2CH$_2$-), 64.5 (C-5^{Rha}), 63.2 (C-5$^{GalN'}$), 52.1 (C-2^{GalN}), 48.1 (-CH$_2$*C*H$_2$N$_3$), 47.1 (C-2$^{GalN'}$), 28.7 (-OCH$_2$*C*H$_2$CH$_2$N$_3$), 27.6 [-C(*C*H$_3$)$_2$], 26.3 [-C(*C*H$_3$)$_2$], 22.7 (-NHCO*C*H$_3$), 21.0 (-OCO*C*H$_3$), 17.0 (C-6^{Rha}); ESI-TOF HRMS *m/z*: Calcd for $C_{50}H_{58}N_5O_{17}$ [M+H]$^+$ 1000.3822; Found 1000.3800; Calcd for $C_{50}H_{57}N_5O_{17}Na$ [M+Na]$^+$ 1022.3642; Found 1022.3626.

4.17. 3-Azidopropyl 2,3-O-isopropylidene-α-L-rhamnopyranosyl-(1 → 3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-galactopyranoside (21)

To a solution of **20** (40 mg, 0.04 mmol) in MeOH (2 mL) was added NaOMe (0.5 M) in MeOH dropwise until the pH value reached 10. The mixture was stirred at rt for 5 h and neutralized with Amberlite IR 120 (H$^+$). The solution was filtered, and the filtrate was concentrated. The residue was purified by silica gel column chromatography (hexane–ethyl acetate 1:4) to give **21** (33 mg, 85%) as a white foamy solid. $[\alpha]_D^{25}$ +65 (*c* 0.2, CHCl$_3$); ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.99–7.78 (m, 4 H, Ar*H*), 7.56 (br d, *J* = 7.2 Hz, 2 H, Ar*H*), 7.45–7.36 (m, 5 H, Ar*H*), 7.33–7.28 (m, 3 H, Ar*H*), 5.69 (d, *J* = 9.6 Hz, 1 H, -N*H*Ac), 5.55 (s, 1 H, C*H*Ph), 5.33 (d, *J* = 7.8 Hz, 1 H, H-1^{GalN}), 5.28 (s, 1 H, C*H*Ph), 5.07 (d, *J* = 4.2 Hz, 1 H, H-1$^{GalN'}$), 4.84 (s, 1 H, H-1^{Rha}), 4.72–4.63 (m, 2 H, H-2^{GalN}, H-3^{GalN}), 4.56 (dt, *J* = 10.2, 3.6 Hz, 1 H, H-2$^{GalN'}$), 4.37 (d, *J* = 12.0 Hz, 1 H, H-6a^{GalN}), 4.34 (d, *J* = 3.0 Hz, 1 H, H-4^{GalN}), 4.14 (d, *J* = 12.0 Hz, 1 H, H-6b^{GalN}), 4.03 (t, *J* = 6.0 Hz, 1 H, H-3^{Rha}), 4.00–3.95 (m, 1 H, -OC*H*$_2$CH$_2$-), 3.92 (d, *J* = 6.0 Hz, 1 H, H-2^{Rha}), 3.87 (d, *J* = 3.0 Hz, 1 H, H-4$^{GalN'}$), 3.76 (d, *J* = 11.4 Hz, 1 H, H-6a$^{GalN'}$), 3.74–3.69 (m, 1 H, H-5^{Rha}), 3.61 (s, 1 H, H-5^{GalN}), 3.59–3.54 (m, 1 H, -OC*H*$_2$CH$_2$-), 3.44 (dd, *J* = 10.2, 3.0 Hz, 1 H, H-3$^{GalN'}$), 3.37 (d, *J* = 11.4 Hz, 1 H, H-6b$^{GalN'}$), 3.28 (q, *J* = 6.0 Hz, 1 H, H-4^{Rha}), 3.25–3.15 (m, 2 H, -CH$_2$C*H*$_2$N$_3$), 2.97 (s, 1 H, H-5$^{GalN'}$), 2.39 (d, *J* = 6.0 Hz, 1 H, -O*H*), 1.84–1.76 (m, 1 H, -OCH$_2$C*H*$_2$CH$_2$N$_3$), 1.75–1.66 (m, 1 H, -OCH$_2$C*H*$_2$CH$_2$N$_3$), 1.46 [s, 3 H, -C(*CH*$_3$)$_2$], 1.42 (s, 3 H, -NHCOC*H*$_3$), 1.26 [s, 3 H, -C(*CH*$_3$)$_2$], 1.08 (d, *J* = 6.0 Hz, 3 H, H-6^{Rha}); ^{13}C NMR (150 MHz, CDCl$_3$): δ 170.1 (*C*=O), 168.3 (*C*=O), 167.8 (*C*=O), 137.3, 137.1, 134.8, 134.7, 131.3, 131.2, 129.6, 129.1, 128.6, 128.2, 126.5, 126.1, 124.1, 123.1, 109.2 [-*C*(CH$_3$)$_2$], 101.6 (*C*HPh), 101.0 (*C*HPh), 100.0 (C-1^{Rha}), 98.2 (C-1^{GalN}), 95.3 (C-1$^{GalN'}$), 77.5 (C-3^{Rha}), 76.9 (C-3$^{GalN'}$), 75.3 (C-2^{Rha}), 74.9 (C-4$^{GalN'}$), 73.4 (C-4^{Rha}), 71.34 (C-3^{GalN}), 71.32 (C-4^{GalN}), 69.4 (C-6^{GalN}), 68.5 (C-6$^{GalN'}$), 67.5 (C-5^{Rha}), 66.4 (C-5^{GalN}), 66.1 (-O*C*H$_2$CH$_2$-), 63.39 (C-5$^{GalN'}$), 52.1 (C-2^{GalN}), 48.1 (-CH$_2$*C*H$_2$N$_3$), 47.3 (C-2$^{GalN'}$), 28.8 (-OCH$_2$*C*H$_2$CH$_2$N$_3$), 27.7 [-C(*C*H$_3$)$_2$], 25.8 [-C(*C*H$_3$)$_2$], 22.7 (-NHCO*C*H$_3$), 18.1 (C-6^{Rha}); ESI-TOF HRMS *m/z*: Calcd for $C_{48}H_{55}N_5O_{16}Na$ [M+Na]$^+$ 980.3536; Found 980.3547; Calcd for $C_{48}H_{55}N_5O_{16}K$ [M+K]$^+$ 996.3275; Found 996.3286.

4.18. 3-Azidopropyl 2,3-di-O-benzoyl-4-O-chloroacetyl-α-L-rhamnopyranosyl-(1 → 3)- 2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1 → 4)-2,3-isopropylidene-α-L-rhamnopyranosyl-(1 → 3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-galactopyranoside (22)

After a mixed solution of **3** (20 mg, 0.016 mmol), **21** (13 mg, 0.013 mmol), and activated MS 4 Å (200 mg) in anhydrous CH_2Cl_2 (3 mL) was stirred at rt for 2 h under a N_2 atmosphere, it was cooled to −40 °C, and NIS (5 mg, 0.02 mmol) and AgOTf (2 mg, 7.7 μmol) were then added. The reaction mixture was stirred −40 °C for 30 min and slowly warmed to 0 °C and stirred for another 1 h, and then neutralized with Et_3N. The resulting mixture was diluted with CH_2Cl_2 (20 mL), filtered through a pad of Celite, and the filtrate was washed successively with saturated aq. $Na_2S_2O_3$ (20 mL) and brine (15 mL). The organic phase was dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (hexane–ethyl acetate 1:4) to give **22** (21 mg, 76%) as a white foamy solid. $[\alpha]_D^{25}$ +98 (*c* 0.2, CHCl$_3$); ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.98 (d, *J* = 8.4 Hz, 2 H, Ar*H*), 7.95–7.92 (m, 1 H, Ar*H*), 7.88–7.84 (m, 2 H, Ar*H*), 7.82–7.76 (m, 5 H, Ar*H*), 7.73–7.68 (m, 2 H, Ar*H*), 7.59 (t, *J* = 7.8 Hz, 1 H, Ar*H*), 7.56–7.50 (m, 4 H, Ar*H*), 7.45 (t, *J* = 7.8 Hz, 3 H, Ar*H*), 7.43–7.34 (m, 10 H, Ar*H*), 7.34–7.26 (m, 8 H, Ar*H*), 5.72 (d, *J* = 9.6 Hz, 1 H, -N*H*Ac), 5.60 (d, *J* = 10.2 Hz, 1 H, -N*H*Ac), 5.54 (s, 1 H, C*H*Ph), 5.51 (s, 1 H, C*H*Ph), 5.44–5.39 (m, 2 H, H-2,3$^{Rha'}$), 5.35 (d, *J* = 8.4 Hz, 1 H, H-1$^{GalN''}$), 5.33 (d, *J* = 8.4 Hz, 1 H, H-1^{GalN}), 5.28 (s, 1 H, C*H*Ph), 5.27 (t, *J* = 9.6 Hz, 1 H, H-4$^{Rha'}$), 5.24 (s, 1 H, C*H*Ph), 5.12 (d, *J* = 3.6 Hz, 1 H, H-1$^{GalN'''}$), 5.03 (d, *J* = 3.6 Hz, 1 H, H-1$^{GalN'}$), 4.92 (d, *J* = 1.2 Hz, 1 H, H-1$^{Rha'}$), 4.86 (dd, *J* = 10.8, 3.6 Hz, 1 H, H-3$^{GalN''}$), 4.78 (s, 1 H, H-1^{Rha}), 4.71 (dt, *J* = 10.2, 3.6 Hz, 1 H, H-2$^{GalN'''}$), 4.66 (dd, *J* = 11.4, 8.4 Hz, 1 H, H-2^{GalN}), 4.62 (dd, *J* = 11.4, 3.6 Hz, 1 H, H-3^{GalN}), 4.54 (dd, *J* = 11.4, 8.4 Hz, 1 H, H-2$^{GalN''}$), 4.48 (dt, *J* = 10.2, 3.6 Hz, 1 H, H-2$^{GalN'}$), 4.37 (d, *J* = 12.6 Hz, 1 H, H-6a), 4.32 (d, *J* = 3.6 Hz, 1 H, H-4^{GalN}), 4.30–4.26 (m, 2 H, H-4$^{GalN''}$, H-6a$^{GalN''}$), 4.22–4.16 (m, 1 H, H-5$^{Rha'}$), 4.14–4.09 (m, 2 H, H-6b, H-6b$^{GalN''}$), 4.01–3.93 (m, 2 H, H-4$^{GalN'''}$, -OC*H*$_2$CH$_2$-), 3.86, 3.82 (2 d, *J* = 14.4 Hz, 2 H, -OCOC*H*$_2$Cl), 3.77 (d, *J* = 11.4 Hz, 1 H, H-6a$^{GalN'}$), 3.73 (d, *J* = 3.0 Hz, 1 H, H-4$^{GalN'}$), 3.70–3.50 (m, 8 H, H-2^{Rha}, H-3^{Rha}, H-3$^{GalN'''}$, H-5^{GalN}, H-5$^{GalN''}$, H-5^{Rha}, H-6a$^{GalN'''}$, -OC*H*$_2$CH$_2$-), 3.37 (d, *J* = 11.4 Hz, 1 H, H-6b$^{GalN'}$), 3.34 (dd, *J* = 10.8, 3.0 Hz, 1 H, H-3$^{GalN'}$), 3.27 (d, *J* = 12.0 Hz, 1 H, H-6b$^{GalN'''}$), 3.23 (dd, *J* = 10.8, 7.2 Hz, 1 H, H-4^{Rha}), 3.23–3.14 (m, 2 H, -CH$_2$C*H*$_2$N$_3$), 3.00 (s, 1 H, H-5$^{GalN'''}$), 2.92 (s, 1 H, H-5$^{GalN'}$), 1.83–1.67 (m, 2 H, -OCH$_2$C*H*$_2$CH$_2$N$_3$), 1.61 (s, 3 H, -NHCOC*H*$_3$), 1.35 [s, 3 H, -C(*CH*$_3$)$_2$], 1.33 (s, 3 H, -NHCOC*H*$_3$), 1.12 (d, *J* = 6.6 Hz, 3 H, H-6^{Rha}), 0.94 (d, *J* = 6.0 Hz, 3 H, H-6$^{Rha'}$), 0.81 [s, 3 H, -C(*CH*$_3$)$_2$]; ^{13}C NMR (150 MHz, CDCl$_3$): δ 170.5 (*C*=O), 169.9 (*C*=O), 168.3 (*C*=O), 168.2 (*C*=O), 167.84 (*C*=O), 167.77 (*C*=O), 166.7 (*C*=O), 165.3 (*C*=O), 164.8, (*C*=O) 137.4, 137.3, 137.1, 134.8, 134.7, 134.1, 133.5, 133.1, 132.1, 1313, 131.2, 131.1, 129.8, 129.64, 129.60, 129.5, 129.21, 129.18, 129.1, 128.9, 128.6, 128.54, 128.49, 128.3, 128.2, 128.1, 126.5, 126.2, 126.1, 124.1, 124.0, 123.1, 122.5, 108.8 [-*C*(CH$_3$)$_2$], 101.6 (*C*HPh), 101.5 (*C*HPh), 101.1 (*C*HPh), 101.0 (*C*HPh), 99.7 (C-1^{Rha}), 99.6 (C-1$^{GalN''}$), 98.6 (C-1$^{Rha'}$), 98.2 (C-1^{GalN}), 96.3 (C-1$^{GalN'''}$), 95.0 (C-1$^{GalN'}$), 82.9 (C-4^{Rha}), 77.8 (C-3$^{GalN'''}$), 77.1 (C-3^{Rha}), 76.3 (C-3$^{GalN'}$), 75.8 (C-2^{Rha}), 75.1 (C-4$^{GalN'}$), 74.5 (C-4$^{GalN'''}$), 72.8 (C-4$^{Rha'}$), 71.9 (C-3$^{GalN''}$), 71.6 (C-4$^{GalN''}$), 71.2 (C-4^{GalN}), 71.1 (C-3^{GalN}), 70.5 (C-2$^{Rha'}$), 69.7 (C-3$^{Rha'}$), 69.40 (C-6$^{GalN''}$), 69.36 (C-6^{GalN}), 68.6 (C-6$^{GalN'''}$), 68.5 (C-6$^{GalN'}$), 66.5 (C-5$^{Rha'}$), 66.4 (C-5^{GalN}), 66.1 (-O*C*H$_2$CH$_2$-), 66.0 (C-5$^{GalN''}$), 64.7 (C-5^{Rha}), 63.4 (C-5$^{GalN'}$), 63.0 (C-5$^{GalN'''}$), 52.5 (C-2$^{GalN''}$), 52.1 (C-2^{GalN}), 48.0 (-CH$_2$*C*H$_2$N$_3$), 47.2 (C-2$^{GalN'}$), 47.0 (C-2$^{GalN'''}$), 40.5 (-OCO*C*H$_2$Cl), 28.8 (-OCH$_2$*C*H$_2$CH$_2$N$_3$), 27.7 [-C(*C*H$_3$)$_2$], 25.7 [-C(*C*H$_3$)$_2$], 22.8 (-NHCO*C*H$_3$), 22.6 (-NHCO*C*H$_3$), 17.7 (C-6^{Rha}), 17.4 (C-6$^{Rha'}$); ESI-TOF HRMS *m/z*: Calcd for $C_{106}H_{109}ClN_7O_{34}$ [M+H]$^+$ 2058.6698; Found 2058.6721.

4.19. 3-Azidopropyl α-L-rhamnopyranosyl-(1 → 3)-2-acetamido-2-deoxy-α-D-galactopyranosyl-(1 → 3)-2-acetamido-2-deoxy-β-D-galactopyranosyl-(1 → 4)-α-L-rhamnopyranosyl-(1 → 3)-2-acetamido-2-deoxy-α-D-galactopyranosyl-(1 → 3)-2-acetamido-2-deoxy-β-D-galactopyranoside (2)

After a solution of **22** (15 mg, 7.3 μmol) in ethanol (4 mL) and 80% hydrazine hydrate (1 mL) was refluxed for 6 h, the solvent was then concentrated and the resulting residue was purified by size exclusion chromatography on a Bio-Gel LH-20 column with methanol as the eluent to get a white solid. The product was dissolved in pyridine (6 mL) containing acetic anhydride (2 mL). The reaction mixture was stirred at rt for 8 h and then concentrated to give a pale yellow solid, which was then dissolved in 80% HOAc (6 mL) and stirred at 70 °C for overnight. The reaction mixture was

then co-evaporated with toluene (2 × 5 mL), and the resulting product was then dissolved MeOH (4 mL) followed by addition of NaOMe (0.5 M) in MeOH until the pH value reached 10. The mixture was stirred at rt for overnight, and then neutralized with Amberlite IR 120 (H^+). The solution was filtered, and the filtrate was concentrated. The resulting residue was purified by size exclusion chromatography on a Sephadex G-10 column with distilled water as the eluent and then lyophilized to give **2** (5.6 mg, 64%) as a white solid. $[\alpha]_D^{25}$ +105 (*c* 0.1, H_2O); ^{1}H NMR (600 MHz, D_2O): δ 4.91 (d, J = 3.0 Hz, 2 H, 2 × H-1^{GalN}), 4.68 (s, 2 H, 2 × H-1^{Rha}), 4.61 (d, J = 9.6 Hz, 1 H, H-1^{GalN}), 4.35 (d, J = 8.4 Hz, 1 H, H-1^{GalN}), 4.20 (dd, J = 10.8, 3.0 Hz, 2 H, 2 × H-2^{GalN}), 3.97 (br d, J = 6.6 Hz, 2 H), 3.90–3.79 (m, 5 H), 3.75–3.40 (m, 24 H), 3.26 (t, J = 9.6 Hz, 1 H), 3.22 (t, J = 6.6 Hz, 2 H, -$CH_2CH_2N_3$), 1.90, 1.85 (2 s, 4 × 3 H, 4 × -NHCOCH_3), 1.73–1.64 (m, 2 H, -$OCH_2CH_2CH_2N_3$), 1.16 (d, J = 6.0 Hz, 3 H, H-6^{Rha}), 1.09 (d, J = 6.0 Hz, 3 H, H-6^{Rha}); ^{13}C NMR (150 MHz, D_2O): δ 174.5, 174.4, 174.31, 174.30, 102.2, 101.9, 101.5, 101.0, 93.2, 93.1, 79.8, 76.0 (2C), 74.9, 74.7, 74.4, 74.2, 71.8, 71.40, 71.39, 70.4, 70.2, 70.1, 69.8, 69.1, 68.1, 68.0, 67.5, 67.0, 63.1 (2C), 60.9, 60.8, 60.7 (2C), 51.0, 50.6, 48.1 (2C), 47.7, 28.0, 22.2, 22.1, 21.8 (2C), 16.9, 16.5; ESI-TOF HRMS *m/z*: Calcd for $C_{47}H_{80}N_7O_{29}$ $[M+H]^+$ 1206.4995; Found 1206.5015; Calcd for $C_{47}H_{79}N_7O_{29}Na$ $[M+Na]^+$ 1228.4814; Found 1228.4809.

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Appendix A. Supplementary data

Supplementary data including ^{1}H NMR, ^{13}C NMR, and ESI-HRMS spectra of all final products and intermediates are available at http://dx.doi.org/10.1016/j.carres.2017.09.001.

References

[1] C.R. Raetz, C. Whitfield, Annu. Rev. Biochem. 71 (2002) 635–700.
[2] K. Miyake, S. Iijima, Adv. Biochem. Eng. Biotechnol. 90 (2004) 89–111.
[3] K. Bazaka, R.J. Crawford, E.L. Nazarenko, E.P. Ivanova, Adv. Exp. Med. Biol. 715 (2011) 213–226.
[4] J.W. Costerton, R.T. Irvin, K.J. Cheng, Annu. Rev. Microbiol. 35 (1981) 299–324.
[5] J.M. Tarbell, L.M. Cancel, J. Intern. Med. 280 (2016) 97–113.
[6] E.R. Moxon, J.S. Kroll, Curr. Top. Microbiol. Immunol. 150 (1990) 65–85.
[7] R.F. Maldonado, I. Sa-Correia, M.A. Valvano, FEMS Microbiol. Rev. 40 (2016) 480–493.
[8] A. Weintraub, Carbohydr. Res. 338 (2003) 2539–2547.
[9] C. Alexander, E.T. Rietschel, J. Endotoxin Res. 7 (2001) 167–202.
[10] S.A. Plotkin, Nat. Med. 11 (2005) S5–S11.
[11] A. Zariri, P. van der Ley, Expert Rev. Vaccines 14 (2015) 861–876.
[12] S. Zielen, J. Trischler, R. Schubert, Expert Rev. Clin. Immunol. 11 (2015) 409–418.
[13] P. Vandamme, P. Dawyndt, Syst. Appl. Microbiol. 34 (2011) 87–95.
[14] T. Coenye, P. Vandamme, J.R. Govan, J.J. LiPuma, J. Clin. Microbiol. 39 (2001) 3427–3436.
[15] A. Isles, I. Maclusky, M. Corey, R. Gold, C. Prober, P. Fleming, H. Levison, J. Pediatr. 104 (1984) 206–210.
[16] J.J. Lipuma, Curr. Opin. Pulm. Med. 11 (2005) 528–533.
[17] E. Mahenthiralingam, A. Baldwin, P. Vandamme, J. Med. Microbiol. 51 (2002) 533–538.
[18] R. Reik, T. Spilker, J.J. Lipuma, J. Clin. Microbiol. 43 (2005) 2926–2928.
[19] T. Coenye, T. Spilker, A. Martin, J.J. LiPuma, J. Clin. Microbiol. 40 (2002) 3300–3307.
[20] S. Kotrange, B. Kopp, A. Akhter, D. Abdelaziz, A. Abu Khweek, K. Caution, B. Abdulrahman, M.D. Wewers, K. McCoy, C. Marsh, S.A. Loutet, X. Ortega, M.A. Valvano, A.O. Amer, J. Leukoc. Biol. 89 (2011) 481–488.
[21] M.S. Saldias, X. Ortega, M.A. Valvano, J. Med. Microbiol. 58 (2009) 1542–1548.
[22] X. Ortega, T.A. Hunt, S. Loutet, A.D. Vinion-Dubiel, A. Datta, B. Choudhury, J.B. Goldberg, R. Carlson, M.A. Valvano, J. Bacteriol. 187 (2005) 1324–1333.
[23] X. Zhang, G. Gu, Z. Guo, Eur. J. Org. Chem. (2015) 7075–7085.
[24] X. Geng, L. Wang, G. Gu, Z. Guo, Carbohydr. Res. 427 (2016) 13–20.
[25] D. Wang, W. Zhuge, Z. Guo, G. Gu, Carbohydr. Res. 442 (2017) 41–51.
[26] S.S. Mandal, G. Liao, Z. Guo, RSC Adv. 5 (2015) 23311–23319.
[27] G. Grundler, R.R. Schmidt, Liebigs Ann. Chem. 1984 (1984) 1826–1847.
[28] K. Kakita, T. Tsuda, N. Suzuki, S. Nakamura, H. Nambu, S. Hashimoto, Tetrahedron 68 (2012) 5005–5017.
[29] H. Tanaka, R. Takeuchi, M. Jimbo, N. Kuniya, T. Takahashi, Chem. Eur. J. 19 (2013) 3177–3187.
[30] G. Gu, M. Fang, Y. Du, Carbohydr. Res. 346 (2011) 2801–2804.
[31] R.R. Schmidt, J. Michel, Angew. Chem. Int. Ed. 19 (1980) 731–732.
[32] M. Numata, M. Sugimoto, K. Koike, T. Ogawa, Carbohydr. Res. 163 (1987) 209–225.
[33] F. Belot, J.-C. Jacquinet, Carbohydr. Res. 290 (1996) 79–86.
[34] H.M. Christensen, S. Oscarson, H.H. Jensen, Carbohydr. Res. 408 (2015) 51–95.
[35] R.R. Schmidt, A. Toepfer, Tetrahedron Lett. 32 (1991) 3353–3356.
[36] A.V. Demchenko, E. Rousson, G.J. Boons, Tetrahedron Lett. 40 (1999) 6523–6526.
[37] C.E. Martin, F. Broecker, S. Eller, M.A. Oberli, C. Anish, C.L. Pereira, P.H. Seeberger, Chem. Commun. 49 (2013) 7159–7161.
[38] K. Bock, C. Pedersen, J. Chem. Soc. Perk. Trans. 2 (1974) 293–299.
[39] A. Maranduba, A. Veyrieres, Carbohydr. Res. 151 (1986) 105–119.
[40] M. Bertolini, C.P.J. Glaudemans, Carbohydr. Res. 15 (1970) 263–270.
[41] B. Mukhopadhyay, D.A. Russell, R.A. Field, Carbohydr. Res. 340 (2005) 1075–1080.