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Synthesis of two trisaccharides related to the triterpenoid saponin eryloside isolated from the sponge *Erylus nobilis*

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Dedicated to Professor Rabindranath Mukherjee, Department of Chemistry, Indian Institute of Technology Kanpur.

ABSTRACT

The chemical synthesis of two trisaccharides related to the triterpenoid saponin eryloside from commercially available D-galactose, L-arabinose and D-glucosamine hydrochloride via rational protecting group manipulations is reported. The required glycosylations were carried out by the extensive use of thioglycoside chemistry where the activations were achieved by using NIS in the presence of $La(OTf)_3$.

1. Introduction

The abundance of steroidal and triterpenoid saponins in starfish and sea cucumbers provides representative groups of echinoderm metabolites.[1] This group of biomolecules are of great medicinal interest as they exhibit diverse bioactivities, such as antiviral, antifungal, cytotoxic and haemolytic activities. These metabolites are rare in other marine organisms that include the most studied marine organisms, sponges. In sponges, the saponins are generally regarded as a minor structural group of metabolites. However, a growing number of saponins have recently been isolated from these animals.[2] Recently, Shin et al.[3] have reported the isolation of saponins, erylosides from the sponge *Erylus nobilis* Thiele collected from the Jaeju Island, Korea. Erylosides have shown moderate cytotoxicity (LC_{50} 317 μg/mL) against the human leukaemia cell line K562. Structural elucidation revealed that erylosides posses a lanostane-based carbon framework as an aglycone with a branched oligosaccharide having *N*-acetyl D-glucosamine, D-galactose and L-arabinose residues or, two L-arabinose residues with an *N*-acetyl glucosamine moiety. As the formation of the oligosaccharide framework is an integral part of the saponin biosynthesis and the role of the oligosaccharide towards the bioactivity of the saponin is not clearly understood, a systematic chemical approach for the synthesis of the sugar part is highly relevant. Herein, we report the chemical synthesis of two trisaccharides related to the saponins erylosides from commercially available D-glucosamine hydrochloride, D-galactose and L-arabinose through rational protecting group manipulation strategies and stereoselective glycosylations (Fig. 1).

2. Results and discussion

The selection of the *p*-methoxyphenyl glycoside as the final reducing end glycoside was triggered by the fact that it can be selectively cleaved to open up the scope for further glycoconjugate formation through trichloroacetimidate chemistry. Further study of the retrosynthetic scheme revealed that a 3,4,6-protected *p*-methoxyphenyl galactopyronoside or a 3,4-protected *p*-methoxyphenyl arabinopyranoside could be used as the reducing end acceptor. For the *N*-acetyl glucosamine moiety, the corresponding *N*-phthalimido thioglycoside would be the best choice, as it would confirm the exclusive formation of the β-linkage as required. After the formation of the disaccharide, the 3,4-protection of either galactose or arabinose moieties can be cleaved; further protection of the 4-position will furnish the desired disaccharide acceptor. Finally, the non-reducing end of the arabinopyranosyl moiety can be glycosylated by using thioglycoside chemistry. The hydrazine mediated cleavage of the *N*-phthalimido group followed by acetylation and global de-*O*-acylation will provide the target trisaccharides (Scheme 1).

At first, the 6-*O*-position of the known *p*-methoxyphenyl 3,4-isopropylidene-β-D-galactopyranoside **3**[4] was benzoylated by using a molar equivalent of benzoyl cyanide (BzCN)[5] in the presence of catalytic Et_3N to afford the acceptor, *p*-methoxyphenyl 6-*O*-benzoyl-3,4-isopropylidene-β-D-galactopyranoside **4** in 87% yield. Acceptor **4** was glycosylated with the known *p*-tolyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside **5**[6] using *N*-iodosuccinimide (NIS) in the presence of $La(OTf)_3$[7] to afford the disaccharide, *p*-methoxyphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-6-*O*-benzoyl-3,4-*O*-isopropylidene-β-D-galactopyranoside **6** in 82% yield. The use of TMSOTf instead of $La(OTf)_3$ resulted in only 68% yield of

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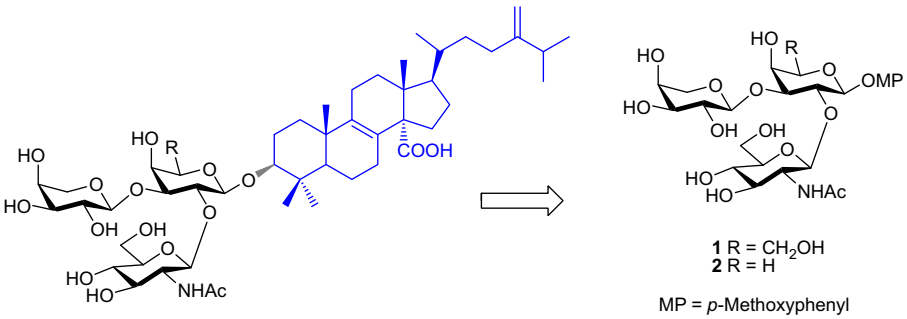
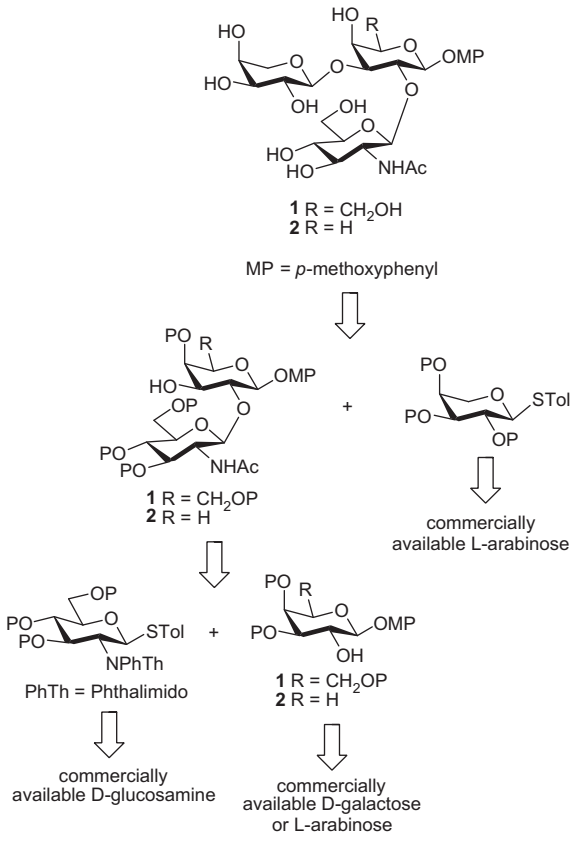
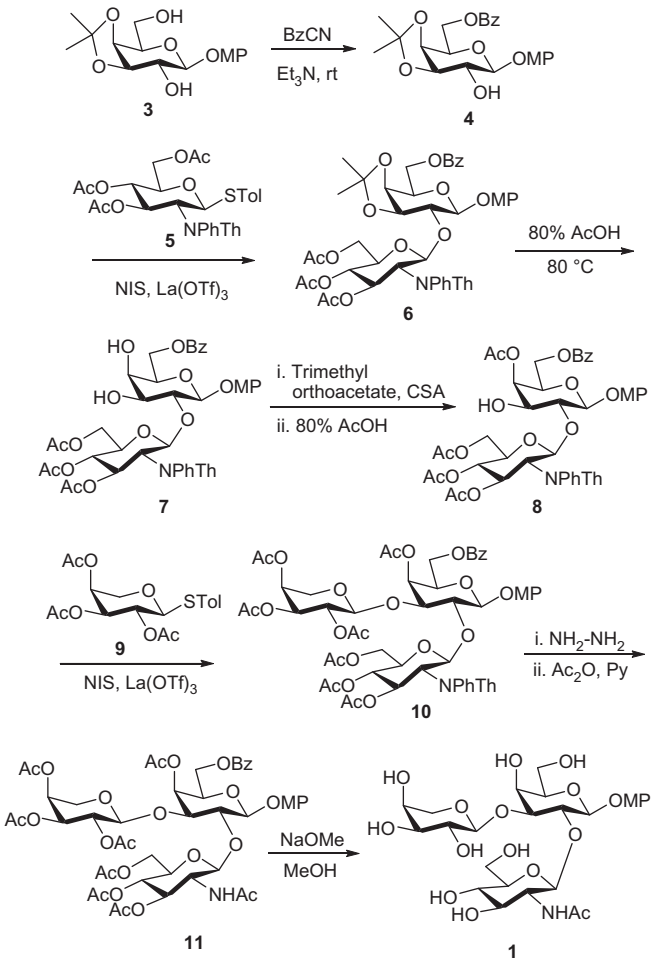


Figure 1. Structure of the triterpenoid saponin and the synthetic targets.



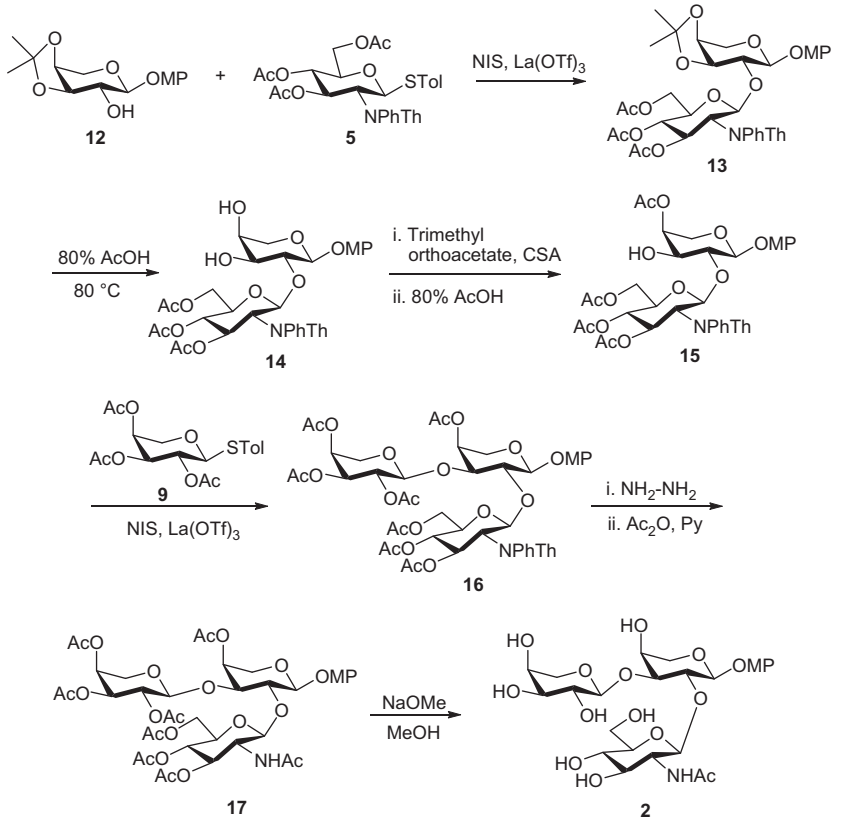
Scheme 1. Retrosynthetic analysis for the target oligosaccharides.



Scheme 2. Synthesis of the target trisaccharide **1**.

the disaccharide. Therefore, $La(OTf)_3$ was proved to be the better choice as a promoter for the NIS-mediated activation of thioglycosides in this particular case. Hydrolysis of the isopropylidene using 80% aq AcOH at 80 °C[8] afforded diol **7** in 85% yield. The reaction of compound **7** with trimethyl orthoacetate in the presence of CSA[9] followed by the rearrangement of the orthoester using 80% aq AcOH at rt furnished the disaccharide acceptor **8** in 81% yield. Further glycosylation of the disaccharide acceptor **8** with the known *p*-tolyl 2,3,4-tri-*O*-acetyl-1-thio-β-L-arabinopyranoside **9**[10] was accomplished by using NIS in the presence of $La(OTf)_3$ to furnish the trisaccharide, *p*-methoxyphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-4-*O*-acetyl-6-*O*-benzoyl-3-*O*-(2,3,4-tri-*O*-acetyl-β-L-arabinopyranosyl)-β-D-galactopyranoside **10** in 84% yield. The hydrazine mediated cleavage of the phthalimido group[11] followed by acetylation using Ac_2O and pyridine afforded the trisaccharide **11** in 82% yield. Finally, Zemplen de-*O*-acylation[12] using NaOMe in MeOH afforded the target trisaccharide, *p*-methoxyphenyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-3-*O*-(β-L-arabinopyranosyl)-β-D-galactopyranoside **1** in 78% yield (Scheme 2).

The synthesis of the target trisaccharide **2** was started with the glycosylation between the known acceptor, *p*-methoxyphenyl 3,4-*O*-isopropylidene-β-L-arabinopyranoside **12**[13] and donor **5** using NIS in the presence of $La(OTf)_3$. The reaction resulted in the formation of disaccharide **13** in 88% yield. The 3,4-*O*-isopropylidene moiety was then hydrolysed by 80% aq AcOH at 80 °C to afford diol **14** in 91% yield. The reaction of diol **14** with trimethyl orthoacetate in the presence of catalytic CSA followed by a rearrangement induced by 80% aq AcOH at rt furnished the disaccharide acceptor, *p*-methoxyphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-4-*O*-acetyl-β-L-arabinopyranoside **15**



Scheme 3. Synthesis of the target trisaccharide **2**.

in 86% yield. Glycosylation between the disaccharide acceptor **15** and donor **9** using NIS in the presence of $La(OTf)_3$ resulted in the formation of trisaccharide **16** in 81% yield. Hydrazine mediated cleavage of the *N*-phthalimido group and subsequent acetylation of the free amine using Ac_2O in pyridine afforded the corresponding acetamido trisaccharide **17** in 85% yield. Global deprotection of the acetate groups using NaOMe in MeOH furnished the target trisaccharide, *p*-methoxyphenyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-3-*O*-(β-L-arabinopyranosyl)-β-L-arabinopyranoside **2** in 80% yield (Scheme 3).

3. Conclusion

In conclusion, the chemical synthesis of two trisaccharides related to the triterpenoid saponin eryloside isolated from the sponge, *Erylus nobilis* has been accomplished. The derived trisaccharides in the form of their *p*-methoxyphenyl glycoside open up the scope for further glycoconjugates formations by selective cleavage of the OMP followed by trichloroacetimidate chemistry with a suitable aglycon. Furthermore $La(OTf)_3$ has been successfully used for the NIS-mediated activation of thioglycosides. The Lewis acid catalyst was found to be a better alternative than the traditional TfOH or TMSOTf.

4. Experimental

4.1. General

All reagents and solvents were dried prior to use according to standard methods.[14] Commercial reagents were used without further purification unless otherwise stated. Analytical TLC was performed on Silica Gel 60-F_{254} (Merck or Whatman) with detection by fluorescence and/or by charring following immersion in a 10% ethanolic solution of sulfuric acid. An orcinol dip, prepared by the careful addition of concentrated sulfuric acid (20 cm^3) to an ice-cold solution of 3,5-dihydroxytoluene (360 mg) in EtOH (150 cm^3) and water (10 cm^3), was used to detect deprotected compounds by charring. Flash chromatography was performed with silica gel 230–400 mesh (Merck, India). Optical rotations were measured at the sodium D-line at ambient temperature, with a Perkin Elmer 141 polarimeter. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance spectrometer at 500 and 125 MHz, respectively, using Me_4Si or CH_3OH as internal standards, as appropriate.

4.1.1. *p*-Methoxyphenyl 6-*O*-benzyl-3,4-*O*-isopropylidene-β-D-galactopyranoside 4

To a solution of **3** (3.1 g, 9.5 mmol) in CH_2Cl_2 (30 mL), BzCN (1.2 mL, 9.7 mmol) was added followed by Et_3N (200 μL) and the mixture was stirred at 0–5 °C for 10 min until the starting material had completely disappeared (TLC). The excess BzCN was neutralized with MeOH and the solvents were evaporated to give the crude product as a syrup. It was purified by flash chromatography using *n*-hexane–EtOAc (1.5:1) to afford pure **4** (3.6 g, 87%) as a colourless glass. $[\alpha]_D^{25} = +79$ (*c* 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 8.08–6.67 (m, 9H, Ar*H*), 4.72 (dd, 1H, $J_{6a,6b}$ 11.5 Hz, $J_{5,6a}$ 3.0 Hz, H-6a), 4.67 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 4.62 (m, 1H, H-6b), 4.24 (m, 2H, H-3, H-4), 3.89 (t, 1H, $J_{1,2}$, $J_{2,3}$ 8.5 Hz, H-2), 3.73 (s, 3H, C_6H_4–OCH_3), 3.72 (m, 1H, H-5), 1.59, 1.43 (2s, 6H, 2 × isopropylidene-CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.2 (*C*OPh), 155.4, 151.0, 133.1, 129.8, 129.7(2), 128.4(2), 118.6(2), 114.4(2) (Ar*C*), 110.8 [$C(CH_3)_2$], 101.6 (C-1), 78.9, 73.3, 73.2, 71.4, 63.6, 55.5 (C_6H_4–OCH_3), 26.3, 22.6 (2 × isopropylidene CH_3). HRMS calcd. for $C_{23}H_{26}O_8Na$ $(M+Na)^+$: 453.1525, found: 453.1521.

4.1.2. *p*-Methoxyphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-6-*O*-benzoyl-3,4-*O*-isopropylidene-β-D-galactopyranoside 6

A mixture of compound **4** (2.0 g, 4.6 mmol), compound **5** (3.3 g, 6.0 mmol) and MS 4 Å (2.0 g) in dry CH_2Cl_2 (30 mL) was stirred under nitrogen for 30 min. Next, NIS (1.75 g, 7.8 mmol) was added and the mixture was cooled to 10 °C using ice-water bath. After stirring for 15 min, La(OTf)$_3$ (25 mg) was added and the mixture was allowed to stir at 10 °C until complete consumption of acceptor **4** was evident by TLC (45 min). The mixture was immediately filtered through a pad of Celite and the filtrate was washed successively with $Na_2S_2O_3$ (2 × 30 mL), $NaHCO_3$ (2 × 30 mL) and brine (30 mL). The organic phase was collected, dried (Na_2SO_4) and evaporated to a syrup. The crude product thus obtained was purified by flash chromatography using *n*-hexane–EtOAc (1:1) to afford pure compound **6** (3.2 g, 82%) as a white foam. $[\alpha]_D^{25} = +91$ (*c* 1.1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.00–6.63 (m, 13H, Ar*H*), 5.91 (dd, 1H, $J_{2',3'}$ 10.5 Hz, $J_{3',4'}$ 9.0 Hz, H-3′), 5.57 (d, 1H, $J_{1',2'}$ 8.5 Hz, H-1′), 5.16 (dd, 1H, $J_{3',4'}$ 9.0 Hz, $J_{4',5'}$ 10.5 Hz, H-4′), 4.67 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.56 (dd, 1H, $J_{5,6a}$ 5.5 Hz, $J_{6a,6b}$ 13.0 Hz, H-6a), 4.47 (dd, 1H, $J_{5,6b}$ 8.0 Hz, $J_{6a,6b}$ 13.0 Hz, H-6b), 4.36 (dd, 1H, $J_{1',2'}$ 8.5 Hz, $J_{2',3'}$ 10.5 Hz, H-2′), 4.28 (dd, 1H, $J_{6a',6b'}$ 10.5 Hz, $J_{6a',5'}$ 3.0 Hz, H-6a′), 4.00 (m, 3H, H-4, H-5, H-5′), 3.92 (m, 2H, H-3, H-6b′), 3.70 (s, 3H, C_6H_4–OC*H*$_3$), 3.69 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 9.5 Hz, H-2), 2.06, 2.02, 1.86 (3s, 9H, 3 × COC*H*$_3$), 1.14, 0.81 (2s, 6H, 2 × isopropylidene-C*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.7, 170.0, 169.5 (3 × *C*OCH$_3$), 167.6, 167.5 (2 × phthalimido *C*=O), 166.1 (*C*OPh), 155.4, 151.2, 133.9, 133.1, 131.9, 131.8, 131.7, 131.6, 129.7, 129.6(2), 128.3(2), 123.3, 118.8(2), 114.3(2) (Ar*C*), 110.4 [*C*(CH$_3$)$_2$], 100.7 (C-1), 100.4 (C-1′), 83.5, 78.3, 73.0, 71.9, 70.9, 70.5, 68.8, 63.5, 62.0, 55.5 ($C_6H_4OCH_3$), 55.2, 27.2, 25.6 (2 × isopropylidene-*C*H$_3$), 20.6, 20.5, 20.4 (3 × COC*H*$_3$). HRMS calcd for $C_{43}H_{45}O_{17}NNa$ (M+Na)$^+$: 870.2585, found: 870.2582.

4.1.3. *p*-Methoxyphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-6-*O*-benzoyl-β-D-galactopyranoside 7

Compound **6** (3.0 g, 3.5 mmol) was dissolved in AcOH–H_2O (9:1, 30 mL) and the solution was stirred at 80 °C for 2 h until the starting material was completely converted to a slower running spot (TLC). After evaporating the solvents and co-evaporating with toluene, the crude product was purified by flash chromatography using *n*-hexane–EtOAc (1:2) to afford pure disaccharide **7** (2.4 g, 85%) as a white foam. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.98–6.59 (m, 13H, Ar*H*), 5.82 (dd, 1H, $J_{2',3'}$ 9.0 Hz, $J_{3',4'}$ 9.5 Hz, H-3′), 5.74 (d, 1H, $J_{1',2'}$ 8.5 Hz, H-1′), 5.18 (dd, 1H, $J_{3',4'}$ 9.5 Hz, $J_{4',5'}$ 10.0 Hz, H-4′), 4.80 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.57 (dd, 1H, $J_{5',6a'}$ 5.5 Hz, $J_{6a',6b'}$ 12.0 Hz, H-6a′), 4.44 (dd, 1H, $J_{5',6b'}$ 8.0 Hz, $J_{6a',6b'}$ 12.0 Hz, H-6b′), 4.38 (dd, 1H, $J_{1',2'}$ 8.5 Hz, $J_{2',3'}$ 9.0 Hz, H-2′), 4.24 (dd, 1H, $J_{5,6a}$ 4.5 Hz, $J_{6a,6b}$ 12.5 Hz, H-6a), 3.97 (dd, 1H, $J_{5,6b}$ 2.0 Hz, $J_{6a,6b}$ 12.5 Hz, H-6b), 3.89 (m, 1H, H-5), 3.84 (m, 2H, H-4, H-5′), 3.79 (t, 1H, $J_{1,2}$, $J_{2,3}$ 7.5 Hz, H-2), 3.71 (s, 3H, $C_6H_4OCH_3$), 3.57 (dd, 1H, $J_{2,3}$ 7.5 Hz, $J_{3,4}$ 1.5 Hz, H-3), 2.91, 2.79 (2br s, 2H, 2 × O*H*), 2.04, 2.02, 1.85 (3s, 9H, 3 × COC*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.7, 170.1, 169.5 (3 × *C*OCH$_3$), 166.4 (*C*OPh), 155.2, 150.8, 134.1, 133.3, 131.4, 129.7(2), 129.5, 128.9, 128.4(2), 123.5(2), 118.1(2), 114.3(2), 114.0 (Ar*C*), 100.1 (C-1), 98.4 (C-1′), 80.2, 72.2, 72.1, 72.0, 70.7, 68.7, 68.4, 62.9, 61.6, 55.6 ($C_6H_4OCH_3$), 54.6, 20.6, 20.5, 20.4 (3 × COC*H*$_3$).

4.1.4. *p*-Methoxyphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-4-*O*-acetyl-6-*O*-benzoyl-β-D- galactopyranoside 8

To a solution of compound **7** (2.0 g, 2.5 mmol) in dry CH_3CN (20 mL) was added trimethylorthoacetate (480 μL, 3.8 mmol) followed by CSA (25 mg) and the solution was stirred at room temperature for 1 h. After neutralizing with Et_3N, the solvents were evaporated in vacuo and the crude product was suspended in 80% aq AcOH (20 mL) and stirred at room temperature for 45 min. After removing the solvents in vacuo, the crude product was purified by flash chromatography using *n*-hexane–EtOAc (2:1) as eluent to afford the pure compound **8** (1.7 g, 81%) as a colourless gel. $[\alpha]_D^{25} = +98$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.97–6.62 (m, 13H, Ar*H*), 5.83 (dd, 1H, $J_{2',3'}$ 9.0 Hz, $J_{3',4'}$ 10.5 Hz, H-3′), 5.73 (d, 1H, $J_{1',2'}$ 8.5 Hz, H-1′), 5.25 (d, 1H, $J_{3,4}$ 3.0 Hz, H-4), 5.19 (dd, 1H, $J_{3',4'}$ 10.5 Hz, $J_{4',5'}$ 10.5 Hz, H-4′), 4.84 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.36 (m, 2H, H-2′, H-6a′), 4.29 (m, 2H, H-6a, H-6b′), 3.98 (dd, 1H, $J_{5,6b}$ 2.0 Hz, $J_{6a,6b}$ 12.0 Hz, H-6b), 3.91 (m, 2H, H-5, H-5′), 3.81 (dd, 1H, $J_{1,2}$ 7.5 Hz, $J_{2,3}$ 10.5 Hz, H-2), 3.75 (dd, 1H, $J_{2,3}$ 10.5 Hz, $J_{3,4}$ 2.0 Hz, H-3), 3.72 (s, 3H, $C_6H_4OCH_3$), 2.91, 2.79 (2br s, 2H, 2 × O*H*), 2.03, 2.02, 2.01, 1.85 (4s, 12H, 4 × COC*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.0, 170.7, 170.1, 169.5 (4 × *C*OCH$_3$), 165.9 (*C*OPh), 155.3, 150.9, 134.2, 133.3, 131.4, 129.8, 129.7(2), 129.5, 128.4(2), 123.7, 123.6, 123.4, 118.5(2), 114.3(2) (Ar*C*), 100.4 (C-1), 98.5 (C-1′), 79.9, 72.0, 71.2, 70.9, 70.6, 69.3, 68.7, 62.1, 61.7, 55.6 ($C_6H_4OCH_3$), 54.8, 20.8, 20.7, 20.6, 20.4 (4 × COC*H*$_3$). HRMS calcd for $C_{42}H_{43}O_{18}NNa$ (M+Na)$^+$: 872.2378, found: 872.2381.

4.1.5. *p*-Methoxyphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-4-*O*-acetyl-6-*O*-benzoyl-3-*O*-(2,3,4-tri-*O*-acetyl-β-L-arabinopyranosyl)-β-D-galactopyranoside 10

A mixture of compound **8** (1.5 g, 1.8 mmol), compound **9** (765 mg g, 2.0 mmol) and MS 4 Å (2.0 g) in dry CH_2Cl_2 (25 mL) was stirred under nitrogen for 45 min. Next, NIS (527 mg, 2.3 mmol) was added and the mixture was cooled to 15 °C followed by the addition of La(OTf)$_3$ (20 mg) and the mixture was allowed to stir at the same temperature for 1 h when all acceptor disaccharide **8** was consumed (R_f 0.4, *n*-hexane–EtOAc; 1:1). The mixture was immediately filtered through a pad of Celite and the filtrate was washed successively with $Na_2S_2O_3$ (2 × 30 mL), $NaHCO_3$ (2 × 30 mL) and brine (30 mL). The organic layer was separated, dried (Na_2SO_4) and concentrated in vacuo. The crude product thus obtained was purified by flash chromatography using *n*-hexane–EtOAc (1:1.5) to give the pure trisaccharide **10** (1.6 g, 84%) as a white foam. $[\alpha]_D^{25} = +101$ (*c* 1.1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.97–6.73 (m, 13H, Ar*H*), 5.95 (d, 1H, $J_{1'',2''}$ 8.5 Hz, H-1″), 5.77 (dd, 1H, $J_{2',3'}$ 9.0 Hz, $J_{3',4'}$ 10.5 Hz, H-3′), 5.38 (d, 1H, $J_{3,4}$ 3.0 Hz, H-4), 5.16 (t, 1H, $J_{3',4'}$, $J_{4',5'}$ 10.0 Hz, H-4′), 5.07 (dd, 1H, $J_{2'',3''}$ 7.5 Hz, $J_{3'',4''}$ 3.5 Hz, H-3″), 5.02 (d, 1H, $J_{1',2'}$ 8.5 Hz, H-1′), 4.98 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.94 (m, 1H, H-4″), 4.38 (dd, 1H, $J_{5',6a'}$ 7.5 Hz, $J_{6a',6b'}$ 11.5 Hz, H-6a′), 4.34–4.23 (m, 4H, H-2′, H-2″, H-6a, H-6b′), 4.17–4.10 (m, 2H, H-5, H-6b), 4.06 (dd, 1H, $J_{1,2}$ 7.5 Hz, $J_{2,3}$ 10.5 Hz, H-2), 3.94 (m, 2H, H-3, H-5a″), 3.78 (m, 1H, H-5′), 3.74 (s, 3H, $C_6H_4OCH_3$), 3.70 (m, 1H, H-5b″), 2.21, 2.11, 2.06, 2.01, 1.99, 1.84, 1.83 (7s, 21H, 7 × COC*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.6(2), 170.4, 170.1, 170.0, 169.5, 169.4 (7 × *C*OCH$_3$), 167.3, 167.2 (2 × phthalimido *C*O), 165.9 (*C*OPh), 155.5, 150.7, 134.3, 134.0, 133.3, 131.3, 129.7(2), 129.6, 129.5, 128.4(2), 128.3, 123.7, 118.0(2), 114.5(2) (Ar*C*), 102.8 (C-1′), 100.8 (C-1), 97.0 (C-1″), 80.8, 78.6, 76.1, 75.3, 74.2, 72.1, 70.8, 70.7, 68.5, 64.9, 62.2, 62.1, 61.3, 55.6 ($C_6H_4OCH_3$), 55.4, 20.9, 20.8(2), 20.7(2), 20.6(2) (7 × COC*H*$_3$). HRMS calcd for $C_{53}H_{57}O_{25}NNa$ (M+Na)$^+$: 1130.3117, found: 1130.3112.

4.1.6. *p*-Methoxyphenyl 3,4,6-tri-*O*-acetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-4-*O*-acetyl-6-*O*-benzoyl-3-*O*-(2,3,4-tri-*O*-acetyl-β-L-arabinopyranosyl)-β-D-galactopyranoside 11

To a solution of compound **10** (1.5 g, 1.35 mmol) in EtOH (50 mL) was added hydrazine monohydrate (1 mL) and the reaction mixture was allowed to stir at 80 °C for 12 h. The solvents were removed under reduced pressure and the residue was

dissolved in pyridine (10 mL) followed by Ac_2O (7 mL) and the solution was stirred at room temperature for 12 h. The solvents were evaporated in vacuo and the crude product thus obtained was purified by flash chromatography using *n*-hexane–EtOAc (1:6) to give the pure trisaccharide **11** (1.1 g, 82%) as a white foam. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.98, 6.80 (2d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 6.31 (d, 1H, *J* 8.5 Hz, NHAc), 5.50 (dd, 1H, $J_{2',3'}$ 8.5 Hz, $J_{3',4'}$ 10.5 Hz, H-3′), 5.48 (m, 1H, H-4″), 5.22 (d, 1H, $J_{1',2'}$ 8.0 Hz, H-1′), 5.20 (d, 1H, $J_{1'',2''}$ 8.0 Hz, H-1″), 5.10 (m, 2H, H-3″, H-4), 5.07 (t, 1H, $J_{3',4'}$, $J_{4',5'}$ 10.5 Hz, H-4′), 4.90 (d, 1H, $J_{1,2}$ 7.0 Hz, H-1), 4.43 (m, 2H, H-5a″, H-2″), 4.28–4.23 (m, 2H, H-5b″, H-6a′), 4.15–4.09 (m, 3H, H-3, H-6a, H-6b), 3.97 (m, 1H, H-2), 3.87–3.83 (m, 2H, H-5, H-6b′), 3.74 (m, 1H, H-5′), 3.77 (s, 3H, $C_6H_4OCH_3$), 3.63 (m, 1H, H-2′), 2.17, 2.14, 2.13, 2.12, 2.05, 2.00, 1.99, 1.98 (8s, 24H, 8 × $COCH_3$), 1.94 (s, 3H, $NHCOCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.6 (NHAc), 170.6, 170.5, 170.4, 170.3, 170.0, 169.9, 169.7, 169.5 (8 × $COCH_3$), 155.6, 151.2, 118.4(2), 114.5(2) (ArC), 106.2 (C-1″), 101.2 (C-1), 100.2 (C-1′), 81.8, 81.2, 72.4, 71.9, 70.7, 68.6, 66.3, 63.0, 61.7, 61.6, 56.1, 55.7, 22.7 ($NHCOCH_3$), 20.7(8) (8 × $COCH_3$). HRMS calcd for $C_{47}H_{57}O_{24}NNa$ $(M+Na)^+$: 1042.3168, found: 1042.3163.

4.1.7. *p*-Methoxyphenyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-3-*O*-(β-L-arabinopyranosyl)-β-D-galactopyranoside 1

Compound **11** (500 mg, 0.5 mmol) was dissolved in dry MeOH (10 mL) and then NaOMe (1 mL, 0.5 M in MeOH) was added and the solution was stirred at room temperature for 5 h. After neutralizing with DOWEX 50W H^+ resin and filtration, the solvents were evaporated in vacuo to afford pure compound **1** (238 mg, 78%) as white amorphous powder. $[\alpha]_D^{25} = +72$ (*c* 0.9, MeOH). ^{1}H NMR (500 MHz, D_2O) δ: 6.97, 6.84 (2d, 4H, *J* 9.0 Hz, $C_6H_4OCH_3$), 5.38 (d, 1H, $J_{1'',2''}$ 7.5 Hz, H-1″), 5.01 (d, 1H, $J_{1',2'}$ 8.5 Hz, H-1′), 4.73 (d, 1H, $J_{1,2}$ 9.5 Hz, H-1), 3.77 (s, 3H, $C_6H_4OCH_3$), 1.51 (s, 3H, $NHCOCH_3$). ^{13}C NMR (125 MHz, D_2O) δ: 173.6 ($NHCOCH_3$), 154.6, 150.5, 117.1(2), 115.7(2) (ArC), 107.9 (C-1″), 102.3 (C-1), 100.2 (C-1′), 84.2, 81.5, 77.7, 77.3, 76.2, 75.4, 73.6, 69.7, 68.3, 66.2, 62.1, 61.6, 61.1, 56.3, 55.7, 21.7 ($NHCOCH_3$). $C_{26}H_{39}O_{16}NNa$ $(M+Na)^+$: 644.2167, found: 644.2162.

4.1.8. *p*-Methoxyphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-3,4-*O*-isopropylidene-β-D-arabinopyranoside 13

A mixture of donor **5** (3.6 g, 6.6 mmol), acceptor **12** (1.5 g, 5.1 mmol) and MS 4 Å (2.0 g) in dry CH_2Cl_2 (30 mL) was stirred under nitrogen for 30 min. Next, NIS (1.9 g, 8.6 mmol) was added followed by La(OTf)$_3$ (50 mg) and the mixture was allowed to stir for 45 min at 5–10 °C when TLC (*n*-hexane–EtOAc, 4:1) showed complete conversion of the acceptor. The mixture was filtered through a pad of Celite® and the filtrate was washed successively with aq $Na_2S_2O_7$ (2 × 30 mL), aq $NaHCO_3$ (2 × 30 mL) and brine (30 mL). The organic layer was separated, dried (Na_2SO_4), filtered, and evaporated in vacuo. The residue was purified by flash chromatography using *n*-hexane–EtOAc (1:1) as the eluent to give pure disaccharide **13** (3.2 g, 88%) as a white foam. $[\alpha]_D^{25} = +108$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.53 (m, 4H), 6.56 (m, 4H) (ArH), 5.89 (dd, 1H, $J_{2',3'}$ 10.0 Hz, $J_{3',4'}$ 9.0 Hz, H-3′), 5.66 (d, 1H, $J_{1',2'}$ 8.5 Hz, H-1′), 5.20 (dd, 1H, $J_{3',4'}$ 9.0 Hz, $J_{4',5'}$ 10.0 Hz, H-4′), 4.62 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.39 (dd, 1H, $J_{1',2'}$ 8.5 Hz, $J_{2',3'}$ 10.0 Hz, H-2′), 4.34 (dd, 1H, $J_{6a',6b'}$ 12.0 Hz, $J_{6a',5'}$ 5.0 Hz, H-6a′), 4.21 (m, 3H, H-3, H-4, H-6b′), 4.02 (dd, 1H, $J_{4,5a}$ 3.5 Hz, $J_{5a,5b}$ 13.0 Hz, H-5a), 3.95 (m, 1H, H-5′), 3.89 (dd, 1H, $J_{1,2}$ 7.5 Hz, $J_{2,3}$ 7.5 Hz, H-2), 3.72 (s, 3H, C_6H_4–OCH_3), 3.68 (dd, 1H, $J_{4,5b}$ 3.5 Hz, $J_{5a,5b}$ 13.0 Hz, H-5b), 2.10, 2.03, 1.84 (3s, 9H, 3 × $COCH_3$), 1.56, 1.32 (2s, 6H, 2 × isopropylidene-CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.7, 170.1, 169.5 (3 × $COCH_3$), 167.7, 167.5 (2 × phthalimido C=O), 155.0, 149.9, 134.0, 133.3, 133.0, 124.3, 124.1, 123.1, 118.2(2), 114.2(2) (ArC), 110.3 [$C(CH_3)_2$], 99.6 (C-1′), 98.6 (C-1), 80.0, 76.8, 72.8, 72.0, 70.6, 69.1, 62.9, 62.4, 55.6 ($C_6H_4OCH_3$), 54.7, 27.8, 25.9 (2 × isopropylidene-CH_3), 20.8, 20.6, 20.4 (3 × $COCH_3$). $C_{35}H_{39}O_{15}NNa$ $(M+Na)^+$: 736.2217, found: 736.2213.

4.1.9. *p*-Methoxyphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-β-D-arabinopyranoside 14

A solution of compound **13** (3.0 g, 4.2 mmol) in 80% aq AcOH (30 mL) was stirred at 80 °C for 3 h. Then the solvents were evaporated and co-evaporated with toluene to remove residual AcOH. The residue was purified by flash chromatography using *n*-hexane–EtOAc (1:4) as the eluent to give pure disaccharide diol **14** (2.6 g, 91%) as a white foam. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.47 (m, 4H), 6.42 (m, 4H) (ArH), 5.85 (dd, 1H, $J_{2',3'}$ 10.5 Hz, $J_{3',4'}$ 9.0 Hz, H-3′), 5.55 (d, 1H, $J_{1',2'}$ 9.0 Hz, H-1′), 5.13 (dd, 1H, $J_{3',4'}$ 9.0 Hz, $J_{4',5'}$ 10.0 Hz, H-4′), 4.60 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.37–4.30 (m, 2H, H-2′, H-6a′), 4.21 (dd, 1H, $J_{6a',6b'}$ 12.0 Hz, $J_{6a',5'}$ 5.5 Hz, H-6b′), 4.01 (m, 1H, H-5′), 3.94 (m, 2H, H-4, H-5a), 3.78 (dd, 1H, $J_{1,2}$ 7.5 Hz, $J_{2,3}$ 8.5 Hz, H-2), 3.67 (m, 1H, H-3), 3.66 (s, 3H, C_6H_4–OCH_3), 3.37 (dd, 1H, $J_{4,5b}$ 1.5 Hz, $J_{5a,5b}$ 13.0 Hz, H-5b), 2.12, 2.03, 1.83 (3s, 9H, 3 × $COCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.6, 169.9, 169.4 (3 × $COCH_3$), 167.9, 167.7 (2 × phthalimido C=O), 154.9, 149.9, 134.8, 133.9, 133.7, 132.6, 124.3, 124.1, 118.4(2), 114.1(2) (ArC), 100.1 (C-1′), 99.4 (C-1), 82.5, 72.0, 71.8, 70.2, 68.8, 67.8, 65.7, 61.8, 55.5 ($C_6H_4OCH_3$), 54.3, 20.6, 20.5, 20.3 (3 × $COCH_3$). $C_{32}H_{35}O_{15}NNa$ $(M+Na)^+$: 696.1904, found: 696.1901.

4.1.10. *p*-Methoxyphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-4-*O*-acetyl-β-D-arabinopyranoside 15

To a solution of **14** (2.5 g, 3.7 mmol) in dry CH_3CN (20 mL), trimethyl orthoacetate (715 μL, 5.6 mmol) was added followed by CSA (20 mg). The mixture was stirred at room temperature until complete conversion of the starting material to a faster moving spot on TLC (~45 min). The solvents were evaporated in vacuo and the residue was dissolved in AcOH–H_2O (9:1, 25 mL) and stirred at room temperature for 1 h. Next, the solvents were evaporated in vacuo and the residue was purified by flash chromatography using *n*-hexane–EtOAc (1:2) as the eluent to give pure compound **15** (2.3 g, 86%) as a colourless gel. $[\alpha]_D^{25} = +93$ (*c* 1.1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.48 (m, 4H), 6.43 (m, 4H) (ArH), 5.85 (dd, 1H, $J_{2',3'}$ 10.5 Hz, $J_{3',4'}$ 9.0 Hz, H-3′), 5.60 (d, 1H, $J_{1',2'}$ 8.5 Hz, H-1′), 5.16 (m, 1H, H-4), 5.14 (dd, 1H, $J_{3',4'}$ 9.0 Hz, $J_{4',5'}$ 10.0 Hz, H-4′), 4.65 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.37 (dd, 1H, $J_{1',2'}$ 8.5 Hz, $J_{2',3'}$ 10.5 Hz, H-2′), 4.30 (dd, 1H, $J_{5',6a'}$ 2.5 Hz, $J_{6a',6b'}$ 12.5 Hz, H-6a′), 4.23 (dd, 1H, $J_{6a',6b'}$ 12.0 Hz, $J_{6a',5'}$ 6.0 Hz, H-6b′), 4.05 (m, 1H, H-5′), 3.92 (dd, 1H, $J_{4,5a}$ 2.0 Hz, $J_{5a,5b}$ 13.5 Hz, H-5a), 3.79 (m, 2H, H-2, H-3), 3.68 (s, 3H, C_6H_4–OCH_3), 3.42 (dd, 1H, $J_{4,5b}$ 0.5 Hz, $J_{5a,5b}$ 13.5 Hz, H-5b), 2.14, 2.12, 2.05, 1.84 (4s, 12H, 4 × $COCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.7, 170.5, 169.9, 169.5 (4 × $COCH_3$), 167.8, 167.6 (2 × phthalimido C=O), 155.0, 149.8, 134.7, 133.8, 133.5, 132.4, 124.5, 124.3, 118.2(2), 114.2(2) (ArC), 100.2 (C-1′), 99.4 (C-1), 82.9, 72.0, 70.5, 70.3, 69.5, 68.9, 64.5, 61.9, 55.5 ($C_6H_4OCH_3$), 54.4, 21.1, 20.6, 20.5, 20.4 (4 × $COCH_3$). $C_{34}H_{37}O_{16}NNa$ $(M+Na)^+$: 738.2010, found: 738.2002.

4.1.11. *p*-Methoxyphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-4-*O*-acetyl-3-*O*-(2,3,4-tri-*O*-acetyl-β-L-arabinopyranosyl)-β-D-arabinopyranoside 16

A mixture of compound **15** (2.0 g, 2.8 mmol), compound **9** (1.4 g, 3.6 mmol) and MS 4 Å (2 g) in dry CH_2Cl_2 (30 mL) was stirred under nitrogen for 1 h. NIS (1.1 g, 4.7 mmol) was added and the mixture was cooled to 10 °C using an ice-water bath. After stirring for 15 min, La(OTf)$_3$ (25 mg) was added and the mixture was allowed to stir at 10 °C until complete consumption of acceptor

15 was evident by TLC (45 min). The mixture was immediately filtered through a pad of Celite and the filtrate was washed successively with $Na_2S_2O_3$ (2 × 30 mL), $NaHCO_3$ (2 × 30 mL) and brine (30 mL). The organic phase was collected, dried (Na_2SO_4) and evaporated to a syrup. The crude product thus obtained was purified by flash chromatography using *n*-hexane–EtOAc (1:1.5) to afford pure compound **16** (2.2 g, 81%) as a white foam. $[\alpha]_D^{25} = +91$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.66–7.46 (m, 4H, Ar*H*), 6.61–6.56 (2d, 4H, *ArH*), 5.88 (dd, 1H, $J_{2',3'}$ 9.0 Hz, $J_{3',4'}$ 10.5 Hz, H-3′), 5.40 (dd, 1H, $J_{2'',3''}$ 7.5 Hz, $J_{3'',4''}$ 3.5 Hz, H-3″), 5.63 (d, 1H, $J_{1',2'}$ 8.5 Hz, H-1′), 5.20 (m, 1H, H-4″), 5.17 (m, 1H, H-4), 5.13 (t, 1H, $J_{3',4'}$, $J_{4',5'}$ 10.0 Hz, H-4′), 4.91 (d, 1H, $J_{1'',2''}$ 7.5 Hz, H-1″), 4.59 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.47 (dd, 1H, $J_{5',6a'}$ 7.5 Hz, $J_{6a'',6b'}$ 11.5 Hz, H-6a′), 4.29–4.18 (m, 4H, H-2, H-2″, H-5a″, H-6b′), 4.12 (m, 1H, H-2″), 3.93 (m, 1H, H-5′), 3.84 (dd, 1H, $J_{4,5b}$ 1.5 Hz, $J_{5a,5b}$ 13.0 Hz, H-5a), 3.74 (m, 1H, H-3), 3.71 (s, 3H, $C_6H_4OCH_3$), 3.46 (dd, 1H, $J_{4,5b}$ 0.5 Hz, $J_{5a,5b}$ 13.0 Hz, H-5b), 2.19, 2.10, 2.09, 2.08, 2.07, 1.99, 1.81 (7s, 21H, 7 × $COCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.6, 170.4, 170.1, 169.9, 169.6, 169.3, 169.2 (7 × $COCH_3$), 167.4, 167.3 (2 × phthalimido *C*O), 155.5, 149.7, 134.3, 134.0, 133.3, 124.8, 124.6, 123.5, 123.3, 118.0(2), 114.3(2) (ArC), 106.9 (C-1″), 100.4 (C-1′), 98.0 (C-1), 81.5, 80.7, 77.6, 74.3, 71.5, 70.4, 69.8, 69.7, 64.3, 63.3, 62.6, 55.5 ($C_6H_4OCH_3$), 54.9, 53.4, 22.6, 20.9, 20.8(2), 20.7, 20.6(2) (7 × $COCH_3$). $C_{46}H_{55}O_{23}NNa$ (M+Na)$^+$: 1012.3063, found: 1012.3058.

4.1.12. *p*-Methoxyphenyl 3,4,6-tri-*O*-acetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-4-*O*-acetyl-3-*O*-(2,3,4-tri-*O*-acetyl-β-L-arabinopyranosyl)-β-D-arabinopyranoside 17

To a solution of compound **16** (2.0 g, 2.0 mmol) in EtOH (30 mL) was added hydrazine monohydrate (1 mL) and the reaction mixture was allowed to stir at 80 °C for 12 h. The solvents were removed under reduced pressure after which the residue was dissolved in pyridine (15 mL) followed by Ac_2O (7.5 mL) and the solution was allowed to stir at room temperature for 12 h. After removing the solvents in vacuo, the crude product was purified by flash chromatography using *n*-hexane–EtOAc (1:6) to give the pure trisaccharide **17** (1.0 g, 85%) as a white foam. $[\alpha]_D^{25} = +98$ (*c* 1.1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.95, 6.83 (2d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 5.43 (d, 1H, $J_{1'',2''}$ 7.5 Hz, H-1″), 5.29–5.22 (m, 2H, H-4, H-4″), 5.14 (m, 1H, H-2‴), 5.03 (dd, 1H, $J_{2',3'}$ 8.5 Hz, $J_{3',4'}$ 10.5 Hz, H-3′), 5.01 (m, 1H, H-3″), 4.86 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 5.07 (m, 1H, H-4′), 4.81 (d, 1H, $J_{1',2'}$ 8.5 Hz, H-1′), 4.45 (dd, 1H, $J_{5',6a'}$ 7.5 Hz, $J_{6a',6b'}$ 11.5 Hz, H-6a′), 4.22–4.06 (m, 5H, H-2, H-3, H-5′, H-5a″, H-6b′), 3.98–3.92 (m, 3H, H-2′, H-5a, H-5b″), 3.76 (s, 3H, $C_6H_4OCH_3$), 3.63 (dd, 1H, $J_{4,5b}$ 1.0 Hz, $J_{5a,5b}$ 12.5 Hz, H-5b), 2.13, 2.12, 2.09, 2.08, 2.07, 2.01, 1.95 (7s, 24H, 8 × $COCH_3$), 1.41 (s, 3H, $NHCOCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.1, 170.6, 170.5, 170.1, 170.0, 169.9, 169.4, 169.2 (8 × $COCH_3$), 155.4, 150.4, 117.0(2), 115.0(2) (ArC), 106.6 (C-1″), 101.4 (C-1′), 100.2 (C-1), 81.6, 81.5, 77.7, 77.6, 73.4, 73.1, 71.7, 69.6, 69.0, 64.4, 63.3, 62.8, 55.7, 53.8, 22.6, 22.5, 20.9, 20.8, 20.6(2), 20.5(2) (8 × $COCH_3$). $C_{39}H_{51}O_{22}NNa$ (M+Na)$^+$: 908.2800, found: 908.2795.

4.1.13. *p*-Methoxyphenyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-3-*O*-(β-L-arabinopyranosyl)-β-D-arabinopyranoside 2

A solution of compound **17** (450 mg, 0.5 mmol) was dissolved in dry MeOH (10 mL) after which NaOMe (1.0 mL, 0.5 M in MeOH) was added and the solution was stirred at room temperature for 3 h. After neutralizing the solution with DOWEX 50W H^+ and filtration, the solvents were evaporated in vacuo to afford pure compound **2** (240 mg, 80%) as a white amorphous powder. $[\alpha]_D^{25} = +67$ (*c* 0.9, MeOH). ^{1}H NMR (500 MHz, D_2O) δ: 6.94, 6.87 (2d, 4H, *J* 9.0 Hz, $C_6H_4OCH_3$), 5.33 (d, 1H, $J_{1'',2''}$ 7.5 Hz, H-1″), 4.93 (d, 1H, $J_{1',2'}$ 7.5 Hz, H-1′), 4.68 (d, 1H, $J_{1,2}$ 9.0 Hz, H-1), 3.67 (s, 3H, $C_6H_4OCH_3$), 1.31 (s, 3H, $NHCOCH_3$). ^{13}C NMR (125 MHz, D_2O) δ: 174.4 ($NHCOCH_3$), 154.4, 150.4, 116.9(2), 115.3(2) (ArC), 108.8 (C-1″), 102.0 (C-1′), 99.9 (C-1), 84.3, 81.4, 77.6, 77.2, 76.5, 75.6, 73.4, 69.8, 68.1, 66.1, 61.4, 61.0, 56.0, 55.8, 21.5 ($NHCOCH_3$). $C_{25}H_{37}O_{15}NNa$ (M+Na)$^+$: 614.2061, found: 614.2057.

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