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Synthesis of oligosaccharide fragments corresponding to the exopolysaccharide released by *Streptococcus macedonicus* Sc 136

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Abstract Hexa-, penta- and tetrasaccharide fragments related to the repeating unit of the exopolysaccharide secreted by *Streptococcus macedonicus* Sc 136 were synthesized in a very efficient manner involving minimum number of steps. A general glycosylation condition has been applied for all glycosylation steps and yields were excellent.

Keywords Carbohydrates · Glycosides · Glycosylations · Anomeric control · Exopolysaccharides

Introduction

Lactic acid bacteria (LAB) possess a large number of metabolic properties, for instance, they ferment lactose to lactic acid, which in turn inhibits the growth of pathogenic bacteria. LAB are the organisms that beneficially affect the host animal by improving the intestinal microbial balance [1, 2] by producing an abundant variety of exopolysaccharides (EPS), which provide an important contribution to human health by acting as prebiotic substrates [3]. In general EPS have excellent water-binding properties and so protect the bacterial cells in low moisture environment [4]. EPSs secreted by LAB play a significant role in the protection of microbial cells against phagocytosis, phage attacks, antibiotics, toxic compounds (*e.g.* toxic metal ions, sulfur dioxide, and ethanol), osmotic stress and bacteriocins such as nisin [5]. Due to their excellent adhesion properties EPS play key role in biofilm formation and dental caries pathogenesis [6, 7]. In the dairy industry, and particularly, yogurt industry, in which the addition of stabilizers is prohibited, LAB have been studied for their ability to influence both the texture and viscosity of fermented milk products [3]. Most of the LAB are nonpathogenic and a number of EPSs secreted by LAB has antigenic properties, which cause modulation of the immune system of the host and/or host-pathogen interactions [8]. In general, yoghurts are used to develop immunogenicity and so the strains used as starter cultures may indirectly be immunostimulators. Various studies directing to the immunomodulatory effects of EPSs have established that EPS produced by *Lactobacillus* and *Streptococcus* strains have considerable immunomodulatory effects in the host. Besides acting as immunomodulators [9], EPSs secreted by LAB have several other medicinal activities, which include their use as antihyperlipidemic [10, 11], antitumor [12], antimutagenic [13], antiulcer [14] and antibacterial agents [15].

Streptococcus macedonicus is a Gram-positive lactic acid bacteria, present in the starter flora of the Greek cheese and goat cheese. Several *Streptococcus macedonicus* strains are used as cultures and natural food preservatives and are found to have several antimicrobial activities especially in cheese [16]. Recently, the structure of a hexasaccharide repeating unit of the exopolysaccharide secreted by *Streptococcus macedonicus* Sc136, isolated from cheese has been demonstrated, containing a unique galactofuranose moiety at the non-reducing terminus [17] (Fig. 1). In order to study the rheological, pharmaceutical and physicochemical properties of EPS produced by *Streptococcus macedonicus*, it is essential to have a larger quantity of the

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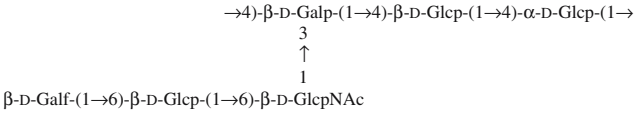


Fig. 1 Structure of the extracellular hexasaccharide produced by *Streptococcus macedonicus* Sc136

hexasaccharide and their close analogs. Whilst oligosaccharides can sometimes be isolated from natural sources, efficient chemical synthetic strategies offer the advantage of having access to large quantities of oligosaccharides as well as analogues of the natural oligosaccharides. We report herein concise chemical syntheses of hexa-, penta- and tetrasaccharide fragments corresponding to the exopolysaccharide secreted by *Streptococcus macedonicus* Sc136.

Results and discussion

The synthesis of compounds **1**, **2** and **3** (Fig. 2) from suitably functionalized mono- and disaccharide intermediates are presented in Schemes 1, 2, 3, 4 and 5. Compounds **4**–**10** [18–24] were synthesized following earlier literature reports (Fig. 3).

The synthesis of compound **1** started with the glycosylation of the glycosyl acceptor **10** [24], prepared from D-glucose in three steps, with ethyl thioglycoside donor **4** [18], prepared from D-lactose octaacetate, in the presence of *N*-iodosuccinimide-methyltrifluoromethanesulfonate (NIS-TMSOTf) [25] to furnish trisaccharide derivative **11** in 78% yield. The compound **11** was converted to the trisaccharide derivative **12** in 60% over all yield following a sequence of reactions involving deacetylation, 3,4-*O*-isopropylidenation [26] and benzylation [27]. Removal of isopropylidene group [28] from compound **12** using 80% aq. acetic acid afforded trisaccharide diol **13** in 90% yield, which was selectively acetylated [29] using triethyl orthoacetate to furnish trisaccharide acceptor **14** in 85% yield. Glycosylation of compound **14** with ethyl thioglycoside donor **6** [20], prepared from D-glucosamine hydrochloride in six steps, in the presence of NIS-TMSOTf [25] furnished tetrasaccharide derivative **15** in 82% yield. Removal of the benzylidene acetal [30] from the compound **15** using $HClO_4$–SiO_2 afforded tetrasaccharide diol **16** in 90% yield (Scheme 1). Selective glycosylation of tetrasaccharide diol acceptor **16** with ethyl thioglycoside donor **8** [22], prepared from D-glucose in five steps, in the presence of NIS-TMSOTf [25] furnished pentasaccharide derivative **17** in 78% yield. Conventional acetylation followed by removal of benzylidene acetal [30] from the compound **17** using $HClO_4$–SiO_2 afforded pentasaccharide acceptor **18** in 95% yield, which was selectively glycosylated with ethyl thioglycoside donor **9** [23], prepared from D-galactose, in the presence of NIS–TMSOTf [25] to give hexasaccharide derivative **19** in 81% yield. Conversion of *N*-phthalimido group to *N*-acetyl group of compound **19** was achieved in two steps involving the treatment with hydrazine hydrate, followed by *N*-acetylation [31]. Global deprotection of the resulting acetylated hexasaccharide derivative involving deacetylation and hydrogenolysis [32] furnished target hexasaccharide **1** as its methyl glycoside in 69% yield (Scheme 2). The structure of the hexasaccharide **1** was confirmed from its 1 D, 2 D NMR and mass spectral data. Presence of six anomeric signals in the ^{1}H NMR spectrum [δ 5.02 (d, J=1.2 Hz, H-1$_F$), 4.82 (d, J=8.4 Hz, H-1$_D$), 4.77

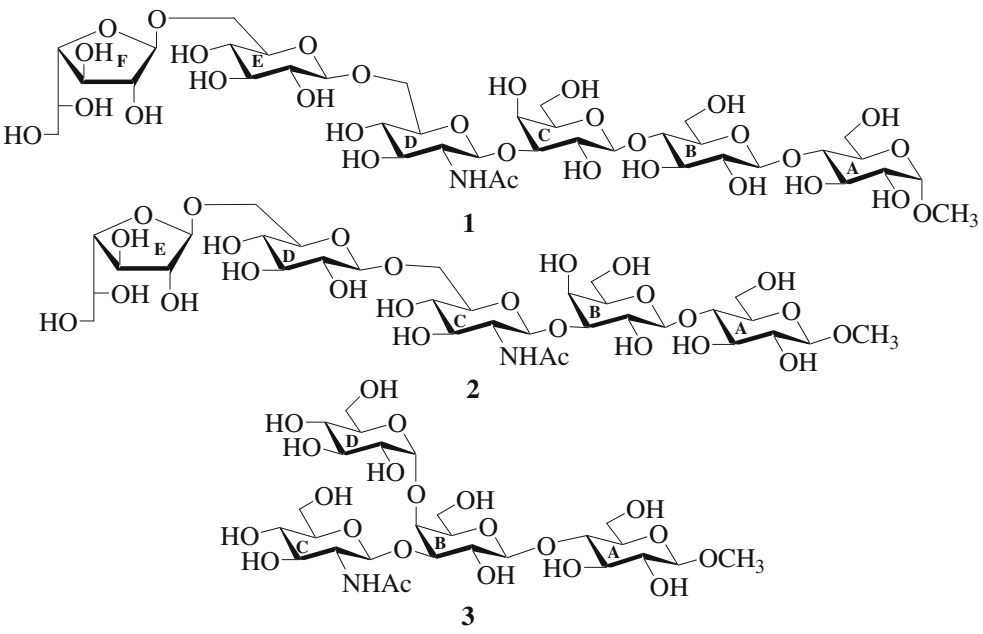


Fig. 2 Structures of synthesized hexa- and penta- and tetrasaccharides (**1**, **2** and **3**) corresponding to the exopolysaccharide produced by *Streptococcus macedonicus* Sc136

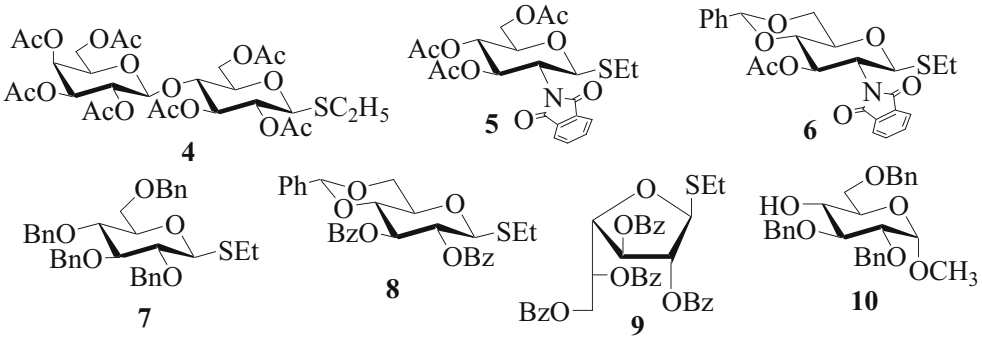
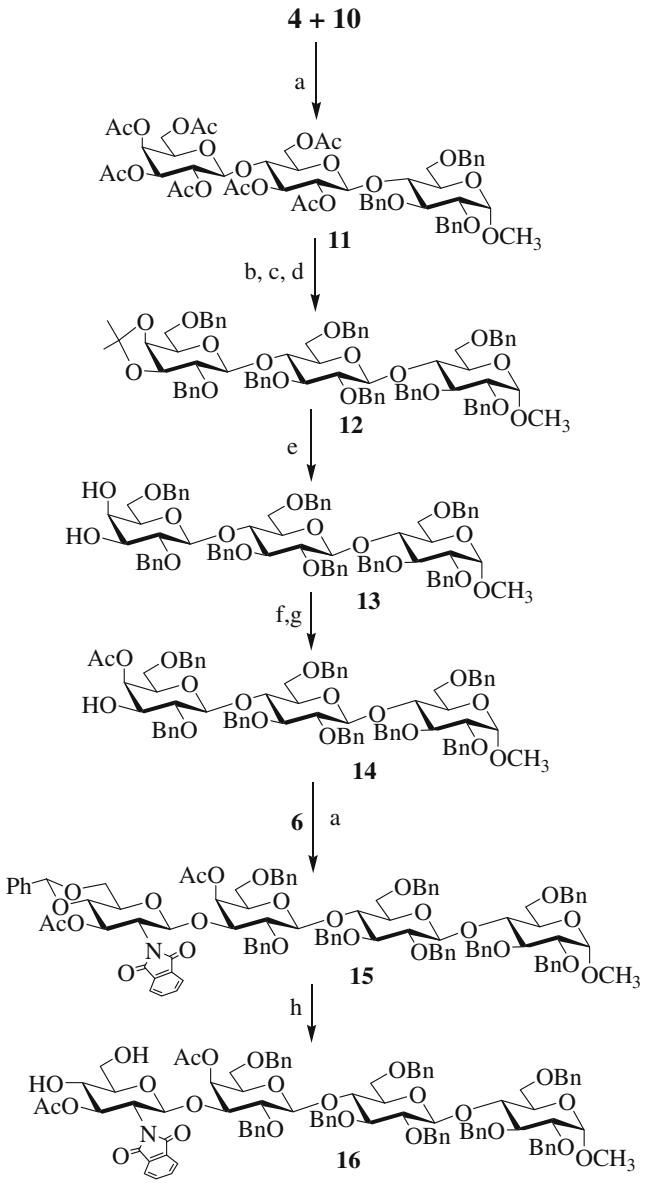


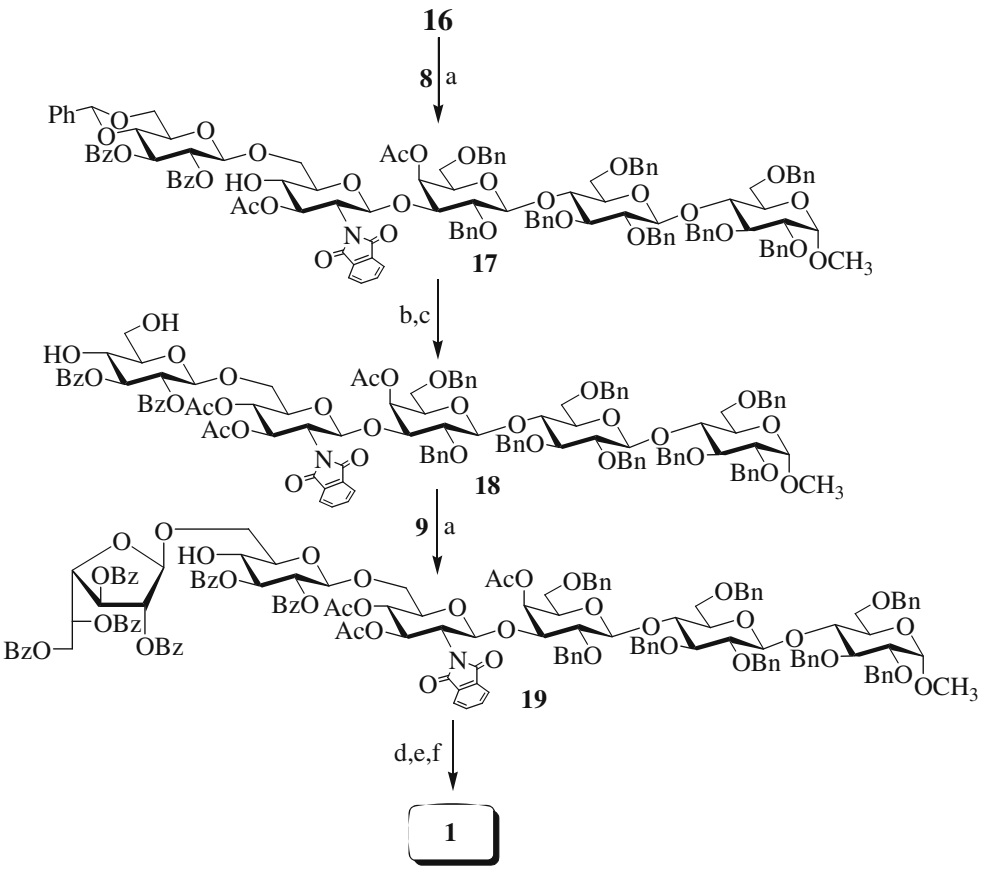
Fig. 3 Mono- and disaccharide intermediates for the synthesis of compounds **1**, **2** and **3**



Scheme 1 Reagents: *a* NIS, TMSOTf, CH_2Cl_2, −10°C, 2 h, 78% for **11** and 82% for **15**; *b* CH_3ONa, CH_3OH, r t, 5 h; *c* 2,2-dimethoxypropane, *p*-TsOH, DMF, r t, 5 h; *d* BnBr, solid NaOH, *n*-Bu_4NBr, THF, r t, 5 h, 60% in three steps; *e* 80% aq. AcOH, 80°C, 1 h, 90%; *f* triethyl orthoacetate, *p*-TsOH, r t, 4 h; *g* 80% aq. AcOH, r t, 1 h, 85% in two steps; *h* $HClO_4$–SiO_2, CH_3CN, r t, 20 min, 90%

(d, J=4.0 Hz, H-1_A), 4.50 (d, J=8.0 Hz, H-1_C), 4.48 (d, J= 8.0 Hz, H-1_B), 4.42 (d, J=7.6 Hz, 1 H, H-1_E)] and ^{13}C NMR spectrum [δ 107.5 (C-1_F), 102.7 (C-1_B), 102.3 (C-1_D), 101.8 (C-1_C), 101.7 (C-1_E) and 98.4 (C-1_A)] supported the formation of the hexasaccharide **1**.

In separate experiments, target pentasaccharide **2** was synthesized following Schemes 3 and 4. The disaccharide derivative **23** was prepared from per-*O*-acetylated methyl D-lactoside (**20**) [33] following a three-step reaction sequence. Conventional saponification of compound **20**, isopropylidenation [26] in the presence of 2,2-dimethoxypropane and *p*-TsOH followed by benzylation [27] afforded disaccharide derivative **21** in 78% overall yield. Removal of isopropylidene group [28] from compound **21** using 80% aq. AcOH at elevated temperature resulted in the formation of disaccharide diol **22** in 87% yield. Compound **22** was selectively 4-*O*-acetylated [29] via the orthoester formation followed by its hydrolysis under acidic condition to give the disaccharide acceptor **23** in 86% overall yield. Glycosylation of **23** with the ethyl thioglycoside donor **6**, in the presence of NIS-TMSOTf [25] furnished trisaccharide derivative **24** in 84% yield. Removal of the benzylidene acetal [30] from compound **24** using $HClO_4$-SiO_2 in acetonitrile furnished trisaccharide diol **25** in 92% yield. Selective glycosylation of diol acceptor **25** with ethyl thioglycoside donor **8** in the presence of NIS-TMSOTf [25] furnished tetrasaccharide derivative **26** in 82% yield. Removal of the benzylidene acetal [30] from compound **26** using $HClO_4$-SiO_2 in acetonitrile afforded the tetrasaccharide diol **27** in 89% yield. Selective 6-*O*-glycosylation of compound **27** with ethyl thioglycoside donor **9** in the presence of NIS-TMSOTf [25] furnished the pentasaccharide derivative **28** in 79% yield. Conversion of *N*-phthalimido group to *N*-acetyl group of compound **28** was achieved in two steps involving the treatment with hydrazine hydrate, followed by *N*-acetylation [31]. Global deprotection of the resulting pentasaccharide derivative involving deacetylation and hydrogenolysis [32] furnished target pentasaccharide **2** as its methyl glycoside in 66% yield. Presence of five anomeric signals in the ^1H NMR spectrum [δ 4.98 (d, J=1.2 Hz, H-1_E), 4.77 (d, J= 8.4 Hz, H-1_C), 4.46 (d, J=8.0 Hz, H-1_D), 4.44 (d, J=8.0



Scheme 2 Reagents: *a* NIS–TMSOTf, −30°C, 2 h, 78% for **17** and 81% for **19**; *b* acetic anhydride, pyridine, r t, 1 h; *c* $HClO_4$–SiO_2, CH_3CN, r t, 20 min, 95% in two steps; *d* (1) $NH_2NH_2.H_2O$, C_2H_5OH, 80°C, 6 h; (2) Ac_2O, Pyridine, r t, 2 h; *e* CH_3ONa, CH_3OH, r t, 5 h; *f* H_2, 20% $Pd(OH)_2$–C, CH_3OH, r t, 12 h, 69% in three steps

Hz, H-1_B) and 4.38 (d, J=7.6 Hz, H-1_A)] and ^{13}C NMR spectrum [δ 107.0 (C-1_E), 102.2 (C-1_A and C-1_B), 101.8 (C-1_C), 100.3 (C-1_D)] confirmed the formation of the required pentasaccharide **2**.

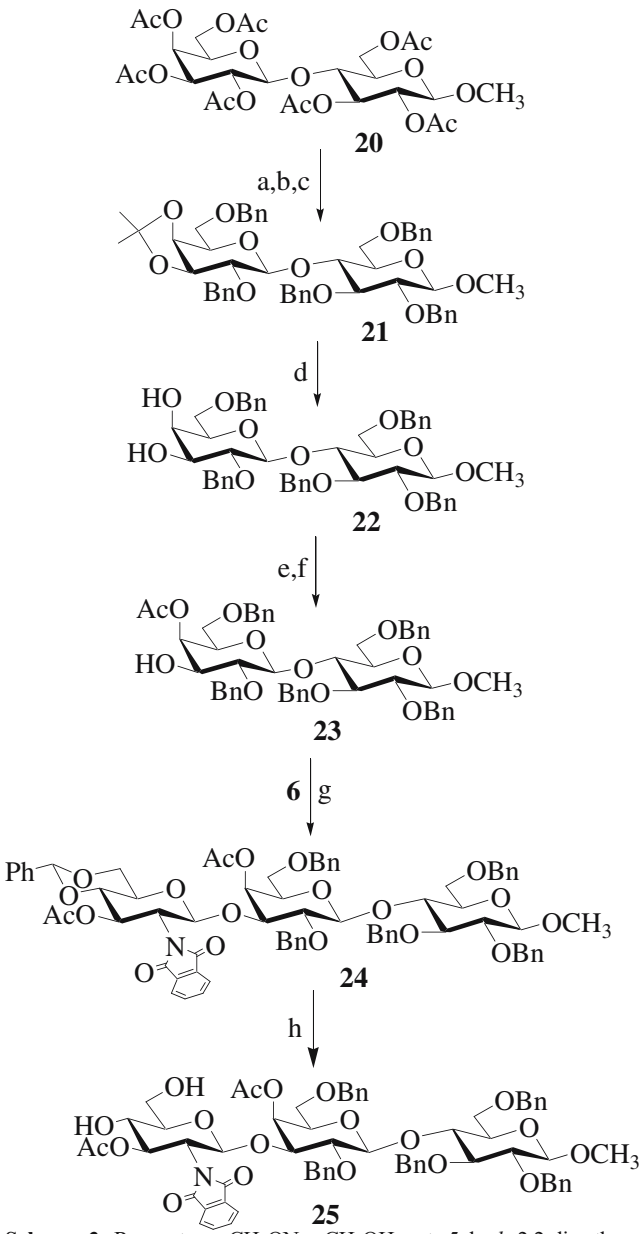
In another set of experiments presented in Scheme 5, the preparation of tetrasaccharide **3** started with the selective glycosylation of disaccharide diol **22** with ethyl thioglycoside donor **5** [19] in the presence of NIS-TMSOTf [25] to furnish trisaccharide derivative **29** in 47% yield together with some undesired di-glycosylated product (~25%). The compound **29** was separated and used for the next step glycosylation reaction using ethyl thioglycoside donor **7** [21]. Condensation of compound **7** with compound **29** in the presence of NIS–TMSOTf [25] furnished tetrasaccharide derivative **30** in 35% yield. Conversion of *N*-phthalimido group to *N*-acetyl group of compound **30** was achieved in two steps involving the treatment with hydrazine hydrate, followed by *N*-acetylation [31]. Global deprotection of the resulting tetrasaccharide derivative involving deacetylation and hydrogenolysis [32] furnished target tetrasaccharide **3** as its methyl glycoside in 70% yield. Presence of four anomeric signals in the ^1H NMR spectrum [δ 4.80 (d, J=8.1 Hz, H-1_C), 4.73 (d, J=4.0 Hz, H-1_D), 4.62 (d, J=8.2 Hz, H-1_B), 4.32 (d, J=7.5 Hz, H-1_A)] and ^{13}C NMR spectrum [δ 101.9 (C-1_B), 101.7 (C-1_A), 100.8 (C-1_C), 100.0 (C-1_D)] confirmed the formation of the required tetrasaccharide **3**.

Conclusion

In summary, concise synthesis of hexa-, penta- and a tetrasaccharide fragments corresponding to the exopolysaccharide secreted by *Streptococcus macedonicus* Sc 136 as their methyl glycosides were achieved using thioglycosides as glycosyl donors and a generalized glycosylation conditions. In the course of synthesis of target molecules (**1**, **2** and **3**), a number of novel methodologies developed from our laboratory have been applied. These synthesized oligosaccharide fragments could be evaluated for their use as prebiotic substances to control metabolic disorders [34].

Experimental section

General methods All reactions were monitored by thin layer chromatography over silica gel coated TLC plates. The spots on TLC were visualized by warming ceric sulphate (2% Ce $(SO_4)_2$ in 2N H_2SO_4) sprayed plates on a hot plate. Silica gel 230–400 mesh was used for column chromatography.

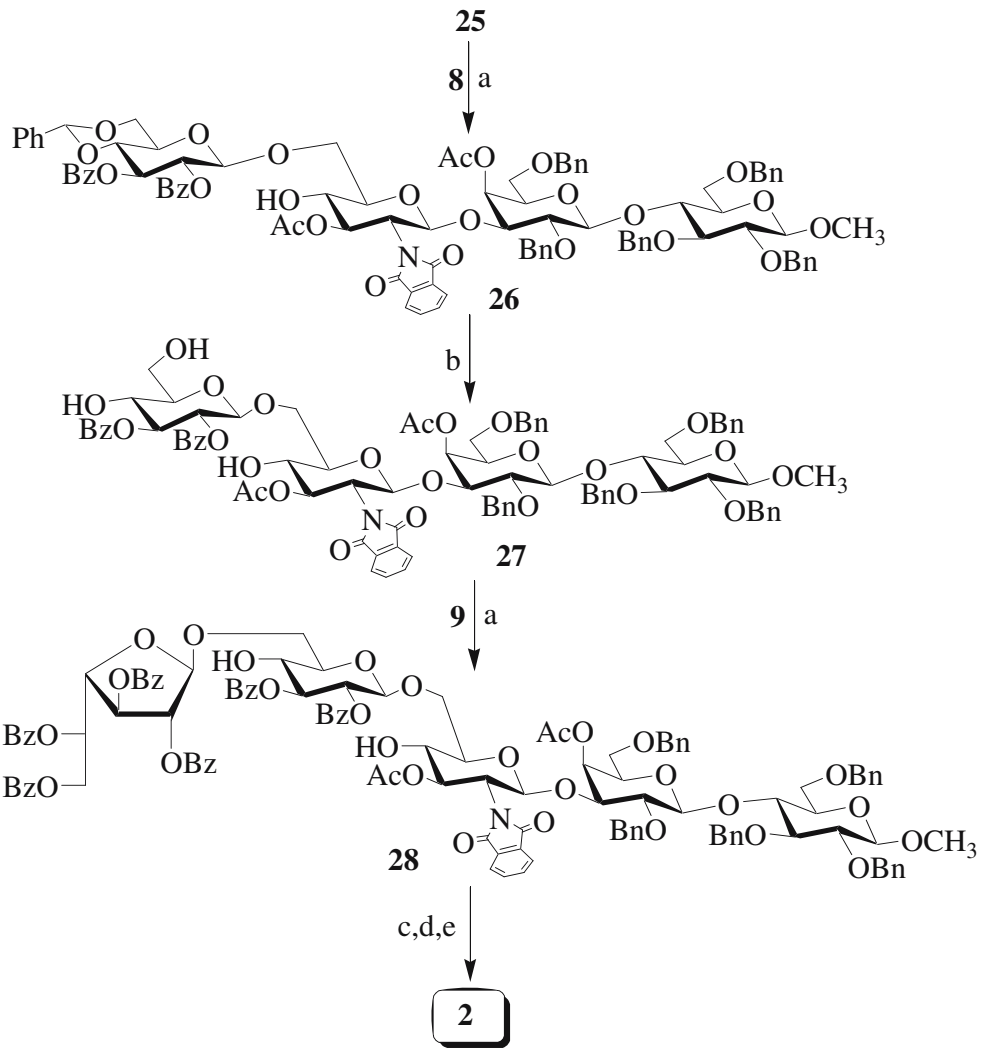


Scheme 3 Reagents: *a* CH_3ONa, CH_3OH, r t, 5 h; *b* 2,2-dimethoxypropane, *p*-TsOH, DMF, r t, 5 h; *c* BnBr, NaOH, *n*-Bu_4NBr, THF, r t, 5 h, 78% in three steps; *d* 80% aq. AcOH, 80°C, 1 h, 87% *e* triethyl orthoacetate, *p*-TsOH, r t, 4 h; *f* 80% aq. AcOH, r t, 1 h, 86% after two steps; *g* NIS–TMSOTf, −30°C, 1 h, 84%; *h* $HClO_4$–SiO_2, CH_3CN, r t, 20 min, 92%

^1H and ^{13}C NMR, 2DCOSY, HMQC spectra were recorded on Brucker Advance DPX 300 MHz using $CDCl_3$ and D_2O as solvents and TMS as internal reference unless stated otherwise. Chemical shift value is expressed in δ ppm. ESI-MS were recorded on a MICROMASS QUTTRO II triple quadrupole mass spectrometer. Elementary analysis was carried out on Carlo ERBA-1108 analyzer. Optical rotations were measured at 25°C on a Rudolf Autopol III polarimeter. Commercially available grades of organic solvents of adequate purity are used in many reactions.

Methyl (2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1→4)-(2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (11) To a solution of compound **10** (1.0 g, 2.1 mmol) and ethyl thioglycoside donor **4** (1.8 g, 2.6 mmol) in anhydrous CH_2Cl_2 (20 ml) was added powdered MS 4 Å (1.0 g) and the reaction mixture was allowed to stir at room temperature under argon for 1 h. *N*-iodosuccinimide (880 mg, 3.9 mmol) was added to the reaction mixture and it was cooled to −10°C. To the cold reaction mixture was added TMSOTf (15 μl) and the reaction mixture was allowed to stir at −10°C for 2 h. After completion (TLC; hexane-EtOAc 3:1), the reaction mixture was quenched by adding 5% aq. $Na_2S_2O_3$ and diluted with CH_2Cl_2 (100 ml). The organic layer was washed successively with aq. $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane-EtOAc (6:1) as eluant to afford pure trisaccharide derivative **11** (1.7 g, 78%) as yellow oil; $[\alpha]_D^{25}$ − 15.6(*c* 1.0, $CHCl_3$); IR (neat) 2365, 1752, 1712, 1370, 1221, 1052, 771 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.62–7.59 (m, 1 H, aromatic protons), 7.36–7.25 (m, 12 H, aromatic protons), 7.10–7.07 (m, 2 H, aromatic protons), 5.33 (br s, 1 H), 5.12–5.09 (m, 1 H), 4.99–4.92 (m, 3 H), 4.79–4.72 (m, 3 H), 4.67–4.65 (m, 1 H), 4.58–4.54 (m, 2 H), 4.48–4,34 (m, 3 H), 4.25–4.18 (m, 1 H), 4.13–4.08 (m, 2 H), 4.00–3.92 (m, 1 H), 3.84–3.73 (m, 4 H), 3.68–3.58 (m, 3 H), 3.48–3.39 (m, 1 H), 3.36 (s, 3 H, OC*H*$_3$), 3.24–3.18 (m, 1 H), 2.15, 2.06, 2.04, 2.01, 1.96, 1.95 (6 s, 21 H, 7 COC*H*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.5, 170.4, 170.2, 170.1, 169.9, 169.5, 169.1, 139.1–127.0 (aromatic carbons), 101.1 (C-1_B), 99.7 (C-1_C), 98.2 (C-1_A), 79.8, 78.7, 77.0, 75.9, 74.7, 73.6, 73.3, 73.2, 72.2 (2 C), 70.9, 70.5, 69.6, 69.0, 67.5, 66.7, 62.1, 60.8, 55.3 (O*C*H$_3$), 21.0, 20.8 (2 C), 20.7, 20.6, 20.5 (2 C); ESI–MS: *m/z*=1,105.4 $[M+Na]^+$; Anal. Calcd. for $C_{54}H_{66}O_{23}$ (1,082.4): C, 59.88; H, 6.14; found: C, 59.65; H, 6.40.

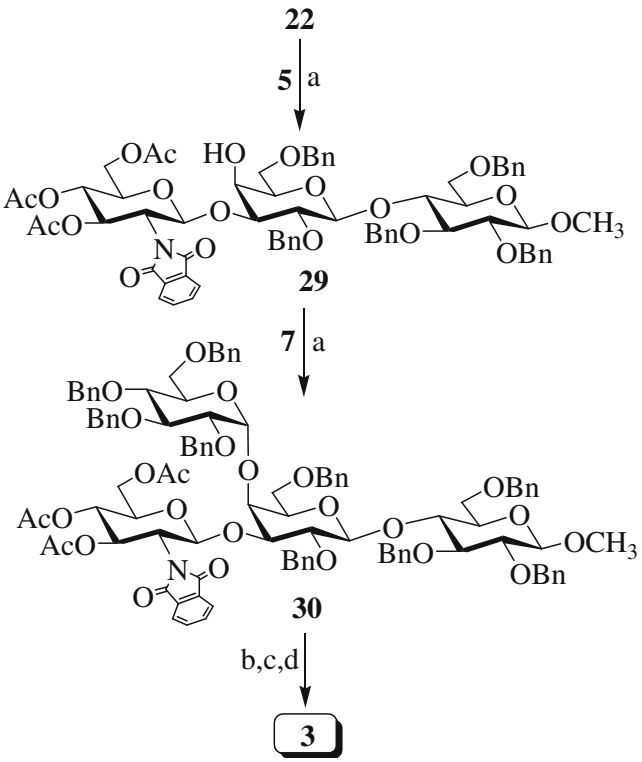
Methyl (2,6-di-O-benzyl-3,4-O-isopropylidene-β-D-galactopyranosyl)-(1→4)-(2,3,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (12) To a solution of trisaccharide derivative **11** (1.5 g, 1.4 mmol) in CH_3OH (20 ml) was added solid CH_3ONa until the pH of the solution became ~10. The reaction mixture was allowed to stir at room temperature for 5 h. After neutralization with Amberlite IR-120 (H^+) resin, the reaction mixture was filtered and evaporated to dryness. To a solution of the crude mass in DMF (5.0 ml) was added 2,2-dimethoxypropane (210 μl, 1.7 mmol) and *p*-toluenesulfonic acid (100 mg) and the reaction mixture was allowed to stir at 60°C for 4 h. The reaction was quenched with triethylamine (0.2 ml) and the solvents were removed under reduced pressure. To a solution of the crude mass in THF (20 ml) were added powdered NaOH (650 mg, 16.2 mmol), benzyl



Scheme 4 Reagents: *a* NIS–TMSOTf, −30°C, 1 h, (82% for **26** and 79% for **28)**; *b* $HClO_4$–SiO_2, CH_3CN, r t, 20 min, 89%; *c* (1) $NH_2NH_2{\cdot}H_2O$, C_2H_5OH, 80°C, 6 h; (2) Ac_2O, Pyridine, rt, 2 h; *d* CH_3ONa, CH_3OH, r t, 5 h; *e* H_2, 20% $Pd(OH)_2$-C, CH_3OH, r t, 12 h, 66% in three steps

bromide (1.6 ml, 13.8 mmol) and tetrabutylammonium bromide (100 mg) in succession and the reaction mixture was allowed to stir vigorously at room temperature for 8 h. After completion (TLC; hexane-EtOAc 6:1), the reaction mixture was diluted with water (100 ml) and extracted with CH_2Cl_2 (150 ml). The organic layer was washed with water, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane-EtOAc (9:1) as eluant to furnish pure compound **12** (1.1 g, 60%) as yellow oil; $[\alpha]_D^{25} - 23.2 (c\ 1.0, CHCl_3)$; IR (neat): 2,927, 1,636, 1,217, 1,054, 770 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.36–7.14 (m, 40 H, aromatic protons), 5.12–5.09 (d, *J*=10.5 Hz, 1 H), 4.97–4.93 (d, *J*=10.5 Hz, 1 H), 4.80–4.79 (d, *J*=2.7 Hz, 1 H), 4.75–4.68 (m, 6 H), 4.63–4.49 (m, 4 H), 4.42–4.38 (d, *J*=11.1 Hz, 1 H), 4.38–4.36 (d, *J*= 7.5 Hz, 1 H, H-1_B), 4.34–4.33 (d, *J*=3.9 Hz, 1 H, H-1_A), 4.31–4.27 (m, 3 H), 4.07–4.05 (d, *J*=5.4 Hz, 1 H), 3.99–3.94 (m, 2 H), 3.91–3.83 (m, 3 H), 3.70 (br s, 2 H), 3.63–3.58 (m, 3 H), 3.50–3.44 (m, 3 H), 3.39 (s, 3 H, OCH_3), 3.34–3.26 (m, 3 H), 3.18–3.16 (m, 1 H), 1.40, 1.36 (2 s, 6 H, $C(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 139.6–138.0 (aromatic carbons), 128.3–126.9 (aromatic carbons), 109.6, 102.6 (C-1_B), 101.8 (C-1_C), 98.4 (C-1_A), 83.2, 82.3, 80.5 (2 C), 79.4, 78.9, 76.2, 75.4, 75.3, 75.2 (2 C), 73.7, 73.6, 73.3 (2 C), 73.2 (2 C), 72.9, 72.1, 70.1, 68.9, 68.1, 67.9, 55.2 (OCH_3), 28.0, 26.5; ESI-MS: *m/z*=1301.6 $[M+Na]^+$; Anal. Calcd. for $C_{78}H_{86}O_{16}$ (1278.6): C, 73.22; H, 6.77; found: C, 73.0; H, 7.00.

Methyl (2,6-di-O-benzyl-β-D-galactopyranosyl)-(1→4)-(2,3,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→4)-2,3,6- tri-O-benzyl-α-D-glucopyranoside (13) A solution of compound **12** (1.0 g, 0.8 mmol) in 80% aq. acetic acid (50 ml) was stirred at 80°C for 1 h. After completion (TLC; hexane-EtOAc 3:1), the reaction mixture was concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane-EtOAc (4:1) as eluant to furnish pure compound **13** (870 mg; 90%) as yellow oil; $[\alpha]_D^{25} - 18.9 (c\ 1.0, CHCl_3)$; IR (neat): 3,447, 3,030, 2,922, 1,722, 1,454, 1,363, 1,058, 745, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz):



Scheme 5 Reagents: *a* NIS–TMSOTf, CH_2Cl_2, −30°C, 2 h, (47% for **29** and 35% for **30**); *b* (1) $NH_2NH_2{\cdot}H_2O$, C_2H_5OH, 80°C, 6 h; (2) Ac_2O, Pyridine, r t, 2 h; *c* CH_3ONa, CH_3OH, r t, 5 h; *d* H_2, 20% Pd $(OH)_2$-C, CH_3OH, r t, 12 h, 70% in three steps

δ 7.43–7.08 (m, 40 H, aromatic protons), 5.10–5.03 (dd, *J*= 10.5 each Hz, 1 H), 5.04 (d, *J*=10.5 Hz, 1 H), 4.86–4.81 (m, 2 H), 4.78–4.69 (m, 4 H), 4.66–4.62 (m, 2 H), 4.60–4.58 (m, 2 H), 4.48–4.36 (m, 5 H), 4.35–4.33 (m, 2 H), 4.12–3.99 (t, *J*=9.3 each Hz, 1 H), 3.93–3.79 (m, 3 H), 3.73–3.70 (m, 2 H), 3.61–3.58 (m, 3 H), 3.52–3.46 (m, 3 H), 3.44–3.37 (m, 2 H), 3.36 (s, 3 H, OCH_3), 3.34–3.30 (m, 3 H), 3.20–3.16 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.4–135.7 (aromatic carbons), 128.5–125.4 (aromatic carbons), 101.3 (2 C, C-1_B and C-1_C), 97.1 (C-1_A), 81.8, 80.9, 79.1, 78.7, 77.6, 75.1, 74.0, 73.9 (2 C), 73.8, 73.6, 72.3, 72.1 (3 C), 71.9, 71.8, 71.6, 68.8, 67.4 (2 C), 66.9, 66.7, 53.9 (O*C*H_3); ESI–MS: *m*/*z*=1261.5 $[M+Na]^+$; Anal. Calcd. for $C_{75}H_{82}O_{16}$ (1,238.5): C, 72.68; H, 6.67; found: C, 72.45; H, 6.95.

Methyl (4-O-acetyl-2,6-di-O-benzyl-β-D-galactopyranosyl)-(1→4)-(2,3,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (14) To a solution of compound **13** (850 mg, 0.7 mmol) in DMF (3 ml) was added triethyl orthoacetate (630 μl, 3.4 mmol) followed by *p*-toluenesulfonic acid (50 mg) and the reaction mixture was allowed to stir at room temperature for 2 h. After completion, the reaction mixture was neutralized with triethylamine (0.1 ml) and the solvents were removed under reduced pressure. A solution of the crude mass in 80% aq. acetic acid (20 ml) was allowed to stir at room temperature for 1 h. After completion (TLC; hexane-EtOAc 3:1), the reaction mixture was concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane-EtOAc (5:1) as eluant to furnish pure compound **14** (760 mg, 85%) as yellow oil; $[\alpha]_D^{25}$ − 23.4(*c* 1.0, $CHCl_3$); IR (neat): 3,018, 2,926, 1,740, 1,455, 1,366, 1,218, 1,067, 767, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.45–7.15 (m, 40 H, aromatic protons), 5.31 (br s, 1 H), 5.11 (d, *J*=11.7 Hz, 1 H), 5.02 (d, *J*= 10.2 Hz, 1 H), 4.84–4.68 (m, 6 H), 4.64–4.60 (m, 3 H), 4.59 (d, *J*=4.2 Hz, 1 H, H-1_A), 4.50–4.46 (m, 1 H), 4.45 (d, *J*= 8.0 Hz, 1 H, H-1_C), 4.39 (d, *J*=7.8 Hz, 1 H, H-1_B), 4.38–4.35 (m, 2 H), 4.30–4.26 (m, 2 H), 4.05–4.02 (t, *J*=9.9 Hz each, 1 H), 3.92–3.84 (m, 3 H,), 3.70–3.69 (m, 2 H), 3.62–3.57 (m, 2 H), 3.52–3.46 (m, 3 H), 3.40 (s, 3 H, OCH_3), 3.36–3.31 (m, 5 H), 3.16–3.14 (m, 1 H), 2.04 (s, 3 H, COCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.5, 139.5–136.9 (aromatic carbons), 129.6–126.9 (aromatic carbons), 102.5 (C-1_B), 102.2 (C-1_C), 98.3 (C-1_A), 82.9, 82.1, 80.3, 79.5, 78.8, 76.1, 75.2, 75.0 (2 C), 74.9 (2 C), 73.5, 73.2, 73.1, 72.8, 72.2, 71.9, 69.8, 69.5, 68.0, 667.9 (2 C), 67.1, 55.1 (O*C*H_3), 20.1; ESI–MS: *m*/*z*=1,303.5 $[M+Na]^+$; Anal. Calcd. for $C_{77}H_{84}O_{17}$ (1,280.6): C, 72.17; H, 6.61; found: C, 71.92; H, 6.90.

Methyl (3-O-acetyl-4,6-O-benzylidene-2-deoxy-2-N-phthalimido-β-D-glucopyranosyl)-(1→3)-(4-O-acetyl-2,6-di-O-benzyl-β-D-galactopyranosyl)-(1→4)-(2,3,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (15) To a solution of compound **14** (750 mg, 0.6 mmol) and ethyl thioglycoside donor **6** (340 mg, 0.7 mmol) in anhydrous CH_2Cl_2 (10 ml) was added powdered MS 4 Å (1 g) and the reaction mixture was allowed to stir at room temperature under argon for 1 h. *N*-iodosuccinimide (240 mg, 1.0 mmol) was added to the reaction mixture and it was cooled to −10°C. To the cold reaction mixture was added TMSOTf (10 μl) and allowed to stir at −10°C for 2 h. After completion (TLC; hexane-EtOAc 3:1), the reaction mixture was quenched by adding 5% aq. $Na_2S_2O_3$ and diluted with CH_2Cl_2 (50 ml). The organic layer was washed successively with aq. $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane-EtOAc (4:1) as eluant to afford pure tetrasaccharide derivative **15** (840 mg, 82%) as yellow oil; $[\alpha]_D^{25}$ − 11.5(*c* 1.0, $CHCl_3$); IR (neat): 2,928, 2,870, 1,495, 1,454, 1,366, 1,217, 1,090, 758, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.57–6.92 (m, 49 H, aromatic protons), 5.97–5.91 (t, *J*=9.6 each, 1 H), 5.65–5.59 (t, *J*=9.6 each, 1 H), 5.59 (br s, 1 H, PhC*H*), 5.44 (br s, 1 H), 5.10 (d, *J*=11.4 Hz, 1 H), 4.95 (d, *J*=10.5 Hz, 1 H), 4.80–4.73 (m, 4 H), 4.68–4.55 (m, 5 H), 4.50–4.42 (m, 3 H), 4.37–4.29 (m, 5 H), 4.26–4.15 (m, 3 H), 3.94–3.77 (m, 8 H), 3.63–3.56 (m, 3 H), 3.47–3.41 (m, 5 H), 3.38 (s, 3 H, OCH_3), 3.24–3.22

(m, 2 H), 2.93–2.90 (m, 1 H), 2.12, 1.89 (2 s, 6 H, 2 COCH_3), ^{13}C NMR ($CDCl_3$, 75 MHz) : δ 170.1, 169.9, 167.6 (2 C), 139.6–134.1 (aromatic carbons), 131.0–123.3 (aromatic carbons), 102.6 (C-1_B), 101.8 (PhCH), 101.6 (C-1_D), 98.8 (C-1_C), 98.4 (C-1_A), 82.8, 82.1, 80.5, 79.7, 78.8 (2 C), 75.5, 75.3, 75.1 (2 C), 74.7, 74.3, 73.6 (2 C), 73.5 (2 C), 73.3, 72.9, 72.4, 69.9 (2 C), 69.6, 68.6, 68.1, 67.8, 67.7, 66.0, 55.7 (C-2_D), 55.3 (OCH_3), 20.9, 20.6; ESI-MS: *m/z*=1,724.6 $[M+Na]^+$; Anal. Calcd. for $C_{100}H_{103}NO_{24}$ (1701.7): C, 70.53; H, 6.10; found: C, 70.27; H, 6.30.

Methyl (3-O-acetyl-2-deoxy-2-N-phthalimido-β-D-glucopyranosyl)-(1→3)-(4-O-acetyl-2,6-di-O-benzyl-β-D-galacto-pyranosyl)-(1→4)-(2,3,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (16) To a solution of compound **15** (800 mg, 0.5 mmol) in CH_3CN (15 ml) was added $HClO_4$–SiO_2 (90 mg) and the reaction mixture was allowed to stir at room temperature for 20 min. After completion (TLC; hexane-EtOAc 2:1), the reaction mixture was filtered through a Celite® bed and evaporated to dryness under reduced pressure. The crude compound was passed through a short pad of SiO_2 using hexane-EtOAc (1:1) as eluant to furnish pure compound **16** (685 mg, 90%) as yellow oil; $[\alpha]_D^{25} - 21.4(c\,1.0, CHCl_3)$; IR (neat): 3,443, 2,926, 1,718, 1,638, 1,219, 1,080, 770 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.46–7.44 (m, 4 H, aromatic protons), 7.33–7.27 (m, 34 H, aromatic protons), 7.11–7.03 (m, 4 H, aromatic protons), 6.75–6.73 (m, 2 H, aromatic protons), 5.69–5.64 (t, *J*=9.6 Hz each, 1 H), 5.58 (d, *J*=9.4, 1 H, H-1_D), 5.57 (br s, 1 H), 5.06 (d, *J*=11.4 Hz, 1 H), 4.94 (d, *J*=10.5 Hz, 1 H), 4.76–4.71 (m, 3 H), 4.65–4.58 (m, 2 H), 4.56 (d, *J*=3.9 Hz, 1 H, H-1_A), 4.54–4.51 (m, 2 H), 4.41 (d, *J*=8.7 Hz, 1 H), 4.35 (d, *J*=8.1 Hz, 1 H, H-1_C), 4.34 (d, *J*=7.9 Hz, 1 H, H-1_B), 4.31–4.27 (m, 3 H), 4.19–4.10 (m, 4 H), 4.05–3.96 (m, 1 H), 3.95–3.87 (m, 1 H), 3.85–3.74 (m, 5 H), 3.68–3.60 (m, 1 H) 3.58–3.48 (m, 3 H), 3.45–3.37 (m, 4 H), 3.35 (s, 3 H, OCH_3), 3.35–3.33 (m, 3 H) 3.21–3.17 (m, 1 H), 2.93–2.90 (m, 1 H), 2.95–2.90 (m, 1 H), 2.10, 1.88 (2 s, 6 H, 2 COCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) : δ 171.1, 171.0, 168.0 (2 C), 139.6–136.9 (aromatic carbons), 128.4–126.8 (aromatic carbons), 102.5 (C-1_B), 101.7 (C-1_D), 99.1 (C-1_C), 98.4 (C-1_A), 82.8, 82.0, 81.1, 80.5, 78.7, 78.2, 77.0, 75.9, 75.6, 75.3, 75.0, 74.6, 74.2, 73.6 (3 C), 73.5, 73.4, 72.8, 71.9, 70.4, 69.9, 68.6, 67.9, 67.7, 67.6, 61.3, 55.2 (C-2_D), 54.9 (OCH_3), 21.1, 20.6; ESI-MS: *m/z*=1,636.6 $[M+Na]^+$; Anal. Calcd. for $C_{93}H_{99}NO_{24}$ (1613.6): C, 69.17; H, 6.18; found: C, 69.0; H, 6.40.

Methyl (2,3-di-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl)-(1→6)-(3-O-acetyl-2-deoxy-2-N-phthalimido-β-D-glucopyranosyl)-(1→3)-(4-O-acetyl-2,6-di-O-benzyl-β-D-galactopyranosyl)-(1→4)-(2,3,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (17) To a solution of compound **16** (650 mg, 0.4 mmol) and ethyl thioglycoside donor **8** (250 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (10 ml) was added powdered MS 4 Å (500 mg) and the reaction mixture was allowed to stir at room temperature under argon for 1 h. *N*-iodosuccinimide (180 mg, 0.8 mmol) was added to the reaction mixture and it was cooled to −30°C. TMSOTf (5 μl) was added to the cold reaction mixture and it was allowed to stir at −30°C for 1 h. After completion (TLC; hexane-EtOAc 5:2), the reaction mixture was quenched by adding 5% aq. $Na_2S_2O_3$, diluted with CH_2Cl_2 (50 ml). The organic layer was washed successively with aq. $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane-EtOAc (2:1) as eluant to afford pure pentasaccharide derivative **17** (650 mg, 78%) as yellow oil; $[\alpha]_D^{25} - 28.5(c\,1.0, CHCl_3)$; IR (neat): 2,930, 2,880, 1,510, 1,457, 1,369, 1,090, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.05–8.00 (m, 5 H, aromatic proton), 7.32–7.15 (m, 52 H, aromatic protons), 6.95–6.93 (m, 2 H, aromatic protons), 5.96–5.90 (t, *J*=9.9 Hz each, 1 H), 5.60 (br s, 1 H, PhC*H*), 5.57–5.48 (m, 3 H), 5.42 (br s, 1 H), 5.09 (d, *J*=11.2 Hz, 1 H), 5.02–4.96 (m, 2 H), 4.81–4.71 (m, 4 H), 4.66–4.50 (m, 7 H), 4.43–4.31 (m, 5 H), 4.30–4.14 (m, 4 H), 4.04–3.80 (m, 9 H), 3.64–3.59 (m, 3 H), 3.54–3.40 (m, 8 H), 3.38 (s, 3 H, OCH_3), 3.24–3.23 (m, 2 H), 2.95–2.90 (m, 1 H), 2.09, 1.86 (2 s, 6 H, 2COCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 171.0, 170.2, 167.9 (2 C), 165.7, 165.5, 139.6–132.8 (aromatic carbons), 129.9–126.1 (aromatic carbons), 102.5 (C-1_B), 101.9 (PhCH), 101.8 (C-1_D), 101.5 (C-1_C), 98.4 (C-1_E), 98.3 (C-1_A), 82.8, 82.2, 80.4, 79.1, 78.8 (2 C), 76.7, 75.6, 75.3, 75.1 (2 C), 74.9, 74.3, 73.6, 73.5 (2 C), 73.3 (2 C), 73.2, 72.9 (2 C), 72.8, 72.6, 72.0, 70.0, 69.9, 69.6, 69.4, 68.7, 68.4, 67.8, 66.6, 55.3 (C-2_D), 54.8 (OCH_3), 20.9, 20.6; ESI–MS: *m/z*=2,094.8 $[M+Na]^+$; Anal. Calcd. for $C_{120}H_{121}NO_{31}$ (2,071.8): C, 69.52; H, 5.88; found: C, 69.25; H, 6.0.

Methyl (2,3-di-O-benzoyl-β-D-glucopyranosyl)-(1→6)-(3,4-di-O-acetyl-2-deoxy-2-N-phthalimido-β-D-glucopyranosyl)-(1→3)-(4-O-acetyl-2,6-di-O-benzyl-β-D-galactopyranosyl)-(1→4)-(2,3,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (18) A solution of compound **17** (600 mg, 0.3 mmol) in pyridine and acetic anhydride (10 ml; 1:1 *v/v*) was allowed to stir at room temperature for 5 h. The solvents were removed and co-evaporated with toluene (3×10 ml) under reduce pressure. To a solution of the acetylated product in CH_3CN (15 ml) was added $HClO_4$–SiO_2 (50 mg) and the reaction mixture was allowed to stir at room temperature for 20 min. After completion (TLC; hexane-EtOAc 2:1), the reaction mixture was filtered through a Celite® bed and evaporated to dryness under reduced pressure. The crude product was passed through a short pad of SiO_2 using hexane-EtOAc

(1:1) as eluant to furnish pure compound **18** (580 mg, 95%) as yellow oil; $[\alpha]_D^{25} - 26.8(c\ 1.0, CHCl_3)$; IR (neat): 3,460, 2,941, 2,890, 1,506, 1,461, 1,375, 1,092, 715 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 8.0–7.90 (m, 6 H, aromatic protons), 7.48–7.38 (m, 7 H, aromatic protons), 7.35–7.11 (m, 39 H, aromatic protons), 6.85–6.83 (m, 2 H, aromatic protons), 5.75–5.72 (t, *J*=9.9 Hz each, 1 H), 5.58 (d, *J*=8.9 Hz, 1 H, H-1_D), 5.50–5.30 (m, 3 H), 5.20–5.08 (m, 1 H), 5.03 (d, *J*=11.5 Hz, 1 H), 4.90 (d, *J*=11.2 Hz, 1 H), 4.84–4.72 (m, 1 H), 4.70–4.65 (m, 1 H), 4.63 (d, *J*=4.1 Hz, 1 H, H-1_A), 4.61–4.59 (m, 1 H), 4.56 (d, *J*=8.3 Hz, 1 H, H-1_E), 4.54–4.51 (m, 1 H), 4.49 (d, *J*=8.1 Hz, 1 H, H-1_C), 4.46–4.37 (m, 2 H), 4.34 (d, *J*=7.8 Hz, 1 H, H-1_B) 4.32–4.19 (m, 4 H), 4.18–4.06 (m, 4 H), 4.01–3.91 (m, 3 H), 3.88–3.70 (m, 7 H), 3.65–3.50 (m, 5 H), 3.48–3.33 (m, 7 H), 3.32 (s, 3 H, OC*H*$_3$), 3.20–3.12 (m, 2 H), 2.88–2.80 (m, 1 H), 2.05, 1.92, 1.76 (3 s, 9 H, 3 COC*H*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.5, 170.1, 169.9, 167.4 (2 C), 165.9, 165.2, 139.5-137.8 (aromatic carbons), 133.9–123.2 (aromatic carbons), 102.3 (C-1_B), 101.7 (C-1_D), 99.8 (C-1_C), 98.7 (C-1_E), 98.2 (C-1_A), 82.6, 81.9, 80.3, 79.4, 78.6, 78.5, 76.6, 76.0, 75.4, 75.2, 74.9, 74.7, 74.1, 73.6, 73.4 (2 C), 73.1, 72.7, 72.4, 72.2, 72.0, 71.5, 71.4, 70.3, 70.1, 70.0, 69.8, 69.1, 68.1, 67.6, 62.0, 61.5, 55.2 (C-2_D), 54.7 (O*C*H$_3$), 20.7, 20.6, 20.3; ESI–MS: *m/z*=2,048.7 $[M+Na]^+$; Anal. Calcd. for $C_{115}H_{119}NO_{32}$ (2025.7): C, 68.14; H, 5.92; found: C, 68.02; H, 6.11.

Methyl (2,3,5,6-tetra-O-benzoyl-β-D-galactofuranosyl)-(1→6)-(2,3-di-O-benzoyl-β-D-glucopyranosyl)-(1→6)-(3,4-di-O-acetyl-2-deoxy-2-N-phthalimido-β-D-glucopyranosyl)-(1→3)-(4-O-acetyl-2,6-di-O-benzyl-β-D-galactopyranosyl)-(1→4)-(2,3,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (19) To a solution of compound **18** (550 mg, 0.3 mmol) and ethyl thioglycoside donor **9** (210 mg, 0.3 mmol) in anhydrous CH_2Cl_2 (10 ml) was added powdered MS 4 Å (300 mg) and the reaction mixture was allowed to stir at room temperature under argon for 1 h. *N*-Iodosuccinimide (100 mg, 0.4 mmol) was added to the reaction mixture and it was cooled to −30°C. To the cold reaction mixture was added TMSOTf (3 μl) and the reaction mixture was allowed to stir at −30°C for 1 h. After completion (TLC; hexane-EtOAc 1:1), the reaction mixture was quenched by adding 5% aq. $Na_2S_2O_3$ and diluted with CH_2Cl_2 (50 ml). The organic layer was washed successively with aq. $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane-EtOAc (1:1) as eluant to afford pure hexasaccharide derivative **19** (635 mg, 81%) as yellow oil; $[\alpha]_D^{25} - 32.4(c\ 1.0, CHCl_3)$; IR (neat): 2,929, 2,876, 1,498, 1,453, 1,365, 1,217, 1,088, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 8.20–8.07 (m, 4 H, aromatic protons), 8.00–7.88 (m, 9 H, aromatic protons), 7.50–7.42 (m, 13 H, aromatic protons), 7.38–7.05 (m, 48 H, aromatic protons), 6.10–6.09 (m, 1 H), 5.76–5.64 (m, 2 H), 5.69–5.57 (m, 2 H), 5.52 (br s, 1 H), 5.41–5.38 (m, 3 H), 5.05–4.85 (m, 6 H), 4.80–4.69 (m, 4 H), 4.59–4.47 (m, 5 H), 4.41–4.30 (m, 4 H), 4.26–4.05 (m, 8 H), 4.02–3.82 (m, 7 H), 3.80–3.71 (m, 2 H), 3.68–3.57 (m, 3 H), 3.48–3.37 (m, 7 H), 3.33 (s, 3 H, OCH_3), 3.20–3.18 (m, 2 H), 2.98–2.80 (m, 1 H), 2.06, 1.95, 1.72 (3 s, 9 H, 3COC*H*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 169.9 (2 C), 169.5, 167.2 (2 C), 166.6, 166.0, 165.7, 165.6 (2 C), 165.3, 139.4–132.8 (aromatic carbons), 129.8–123.2 (aromatic carbons), 106.2 (C-1_F), 102.2 (C-1_B), 101.7 (C-1_D), 100.9 (C-1_C), 98.2 (2 C, C-1_A and C-1_E), 82.6, 82.0, 81.9, 81.1, 80.1, 78.7, 78.6 (2 C), 77.0 (2 C), 76.6, 75.6, 75.1, 74.9 (3 C), 74.1, 73.3 (2 C), 73.1 (3 C), 72.7, 72.3, 71.8, 70.3, 70.1, 69.9, 69.7, 69.6 (2 C), 68.2, 68.0, 67.6 (2 C), 66.5, 63.7, 55.1 (C-2_D), 54.8 (O*C*H$_3$), 20.6, 20.5, 20.2; ESI–MS: *m/z*=2,626.9 $[M+Na]^+$; Anal. Calcd. for $C_{149}H_{145}NO_{41}$ (2603.9): C, 68.68; H, 5.61; found: C, 68.45; H, 5.90.

Methyl (3,4-O-isopropylidene-2,6-di-O-benzyl-β-D-galacto-pyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (21) To a solution of disaccharide derivative **20** (1.0 g, 1.5 mmol) in CH_3OH (20 ml) was added solid CH_3ONa until the pH of the solution became ~10. The reaction mixture was allowed to stir at room temperature for 5 h. After neutralization with Amberlite IR-120 (H^+) resin, the reaction mixture was filtered and evaporated to dryness. To a solution of the crude mass in DMF (5.0 ml) were added 2,2-dimethoxypropane (220 μl, 1.8 mmol) and *p*-toluenesulfonic acid (100 mg) and the reaction mixture was allowed to stir at 60°C for 4 h. The reaction was quenched with triethylamine (0.5 ml) and the solvents were removed under reduced pressure. To a solution of the crude mass in THF (30 ml) were added powdered NaOH (640 mg, 15.9 mmol), benzyl bromide (1.6 ml, 13.8 mmol) and tetrabutylammonium bromide (50 mg) in succession and the reaction mixture was allowed to stir vigorously at room temperature for 8 h. After completion (TLC; hexane-EtOAc 6:1), the reaction mixture was diluted with water (100 ml) and extracted with CH_2Cl_2 (150 ml). The organic layer was washed with water, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane-EtOAc (9:1) as eluant to furnish pure compound **21** (990 mg, 78%) as yellow oil; $[\alpha]_D^{25} + 4.8(c\ 1.0, CHCl_3)$; IR (neat): 3,018, 2,926, 1,740, 1,366, 1,218, 1,067, 769 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.36–7.27 (m, 25 H, aromatic protons), 5.07–5.05 (m, 1 H), 5.04–5.02 (dd, *J*=5.9 Hz, 1 H), 4.99 (d, *J*=5.9 Hz, 1 H), 4.91–4.86 (dd, *J*=9.6 and 6.9 Hz, 2 H), 4.78–4.73 (m, 2 H), 4.59–4.53 (m, 2 H), 4.50–4.10 (m, 2 H), 4.21 (d, *J*=12.0 Hz, 1 H), 4.22–4.07 (m, 3 H), 3.84 (d, *J*=2.4 Hz, 1 H), 3.80–3.69 (m, 3 H), 3.63–3.54 (m, 2 H), 3.54–3.37 (t, *J*=7.2 Hz each, 1 H), 3.38 (s, 3 H, OC*H*$_3$), 3.01–2.99 (m, 1 H), 2.88–2.81 (m, 1 H), 1.44 (s, 3 H,

(CH_3)$_2$C), 1.39 (s, 3 H, (CH_3)$_2$C); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.9–138.2 (aromatic carbons), 128.7–126.7 (aromatic carbons), 109.8 ((CH_3)$_2$*C*), 102.8 (C-1$_B$), 102.0 (C-1$_A$), 82.9, 81.6, 80.6, 79.3, 76.4, 75.5, 75.2 (2 C), 73.6, 73.4 (2 C), 73.2, 73.1, 68.9, 68.2, 55.6 (O*C*H$_3$), 28.0, 26.4 (*C*H$_3$)$_2$C); ESI-MS: *m/z*=869.4 [M+Na]$^+$; Anal. Calcd. for $C_{51}H_{58}O_{11}$ (846.4): C, 72.32; H, 6.90; found: C, 72.14; H, 7.11.

Methyl (2,6-di-O-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (22) A solution of compound **21** (950 mg, 1.1 mmol) in 80% aq. acetic acid (30 ml) was stirred at 80°C for 1 h. After completion (TLC; hexane-EtOAc 3:1), the reaction mixture was concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane-EtOAc (4:1) as eluant to furnish pure compound **22** (785 mg; 87%) as yellow oil; $[\alpha]_D^{25} + 3.2$ (*c* 1.0, $CHCl_3$); IR (neat): 3,018, 2,926, 1,740, 1,366, 1,218, 1,067, 769 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.40–7.38 (m, 2 H, aromatic protons), 7.32–7.23 (m, 23 H, aromatic protons), 5.03–4.97 (m, 2 H), 4.87 (d, *J*=8.0 Hz, 1 H, H-1$_B$), 4.83–4.78 (m, 3 H), 4.69 (d, *J*=12.0 Hz, 1 H), 4.55 (d, *J*=12.0 Hz, 1 H), 4.47–4.41 (m, 4 H, H-1$_A$ and 2 PhC*H*$_2$), 4.06–4.02 (t, *J*=8.0 Hz each, 1 H), 3.94 (br s, 1 H), 3.81 (br s, 1 H), 3.76 (br s, 1 H), 3.68–3.61 (m, 3 H), 3.53–3.49 (m, 2 H), 3.46–3.45 (m, 2 H), 3.44 (s, 3 H, OC*H*$_3$) 3.40–3.37 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 139.1–138.1 (aromatic carbons), 128.5–127.4 (aromatic carbons), x102.8 (2 C, C-1$_A$ and C-1$_B$), 82.8, 81.6, 80.1, 76.7, 75.3 (3 C), 75.1, 75.0, 73.5 (2 C), 73.2, 73.0, 68.8 (2 C), 55.6 (O*C*H$_3$); ESI-MS: *m/z*=829.4 [M+Na]$^+$; Anal. Calcd. for $C_{48}H_{54}O_{11}$ (806.4): C, 71.44; H, 6.75; found: C, 70.98; H, 6.90.

Methyl (4-O-acetyl-2,6-di-O-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (23) To a solution of compound **22** (750 mg, 0.9 mmol) in DMF (5 ml) were added triethyl orthoacetate (920 μl, 5.0 mmol) and *p*-toluenesulfonic acid (50 mg) and the reaction mixture was allowed to stir at room temperature for 2 h. After completion (TLC; hexane-EtOAc 5:1), the reaction mixture was neutralized with triethylamine (0.1 ml) and evaporated to dryness. A solution of the crude mass in 80% aq. acetic acid (15 ml) was allowed to stir at room temperature for 1 h. The reaction mixture was concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane-EtOAc (7:1) as eluant to furnish pure compound **23** (660 mg, 86%) as yellow oil; $[\alpha]_D^{25} + 11.2$(*c* 1.0, $CHCl_3$); IR (neat): 3,018, 2,926, 1,740, 1,366, 1,218, 1,067, 769 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.43–7.21 (m, 25 H, aromatic protons), 5.33–5.32 (m, 1 H), 5.07–5.01 (m, 2 H), 4.88–4.73 (m, 5 H), 4.58 (d, *J*=12.0 Hz, 1 H), 4.53–4.43 (m, 3 H), 4.28 (d, *J*=12.0 Hz, 1 H), 4.08–4.02 (t, *J*=9.0 Hz each, 1 H), 3.77–3.75 (m, 2 H), 3.70–3.65 (m, 3 H), 3.57–3.41 (m, 3 H), 3.37 (br s, 3 H, OC*H*$_3$), 3.36–3.34 (m, 2 H), 2.06 (s, 3 H, COC*H*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.7, 139.1–127.3 (aromatic carbons), 102.9 (C-1$_B$), 102.5 (C-1$_A$), 82.6, 81.5, 80.2, 76.5, 75.3 (2 C), 75.1 (2 C), 73.4, 73.2, 72.5, 72.1, 69.8, 68.2, 67.3, 55.4; ESI-MS: *m/z*=871.3 [M+Na]$^+$; Anal. Calcd. for $C_{50}H_{56}O_{12}$ (848.4): C, 70.74; H, 6.65; found: C, 70.56; H, 6.90.

Methyl (3-O-acetyl-4,6-O-benzylidene-2-deoxy-2-N-phthalimido-β-D-glucopyranosyl)-(1→3)-(4-O-acetyl-2,6-di-O-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (24) To a solution of compound **23** (650 mg, 0.8 mmol) and ethyl thioglycoside donor **6** (435 mg, 0.9 mmol) in anhydrous CH_2Cl_2 (10 ml) was added powdered MS 4 Å (300 mg) and the reaction mixture was allowed to stir at room temperature under argon for 1 h. *N*-iodosuccinimide (300 mg, 1.3 mmol) was added to the reaction mixture and it was cooled to −10°C. TMSOTf (5 μl) was added to the cold reaction mixture and it was allowed to stir at −10°C for 1 h. After completion (TLC; hexane-EtOAc 3:1), the reaction mixture was quenched by adding 5% aq. $Na_2S_2O_3$, diluted with CH_2Cl_2 (50 ml). The organic layer was washed successively with aq. $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane-EtOAc (5:1) as eluant to afford pure tetrasaccharide derivative **24** (855 mg, 84%) as yellow oil; $[\alpha]_D^{25} + 14.3$(*c* 1.0, $CHCl_3$); IR (neat): 3,012, 2,870, 1,459, 1,370, 1,220, 1,090, 758 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.55–6.95 (m, 34 H, aromatic protons), 5.95–5.89 (t, *J*=9.9 and 9.9 Hz, 1 H, H-3$_C$), 5.60 (d, *J*=8.1 Hz, 1 H, H-1$_C$), 5.57 (br s, 1 H, PhC*H*), 5.45 (br s, 1 H), 4.95 (d, *J*=11.1 Hz, 1 H), 4.81–4.72 (m, 3 H), 4.48–4.43 (m, 3 H), 4.38–4.20 (m, 6 H), 3.95–3.92 (m, 1 H), 3.90–3.72 (m, 4 H), 3.69–3.64 (m, 2 H), 3.52–3.46 (m, 5 H), 3.45–3.38 (m, 2 H), 3.36 (s, 3 H, OC*H*$_3$), 3.18–3.12 (m, 1 H), 2.06, 1.87 (2 s, 6 H, 2 COC*H*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.1, 169.9, 167.6 (2 C), 139.0–123.4 (aromatic carbons), 102.8 (Ph*C*H), 102.0 (C-1$_B$), 101.6 (C-1$_C$), 98.9 (C-1$_A$), 82.7, 81.5, 78.9, 78.7, 75.8, 75.4, 75.2 (2 C), 74.9, 74.5, 73.6, 73.1, 72.4, 69.8, 69.6, 68.7, 68.1, 67.8, 66.1, 55.6 (2 C, O*C*H$_3$ and C-2$_C$), 20.8, 20.5 (2 CO*C*H$_3$); ESI–MS: *m/z*=1,292.5 [M+Na]$^+$; Anal. Calcd. for $C_{73}H_{75}NO_{19}$ (1,269.5): C, 69.02; H, 5.95; found: C, 68.79; H, 6.20.

Methyl (3-O-acetyl-2-deoxy-2-N-phthalimido-β-D-glucopyranosyl)-(1→3)-(4-O-acetyl-2,6-di-O-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (25) To a solution of compound **24** (800 mg, 0.6 mmol) in CH_3CN (10 ml) was added $HClO_4$–SiO_2 (50 mg) and the reaction mixture was allowed to stir at room temperature for 20 min. After completion (TLC; hexane-EtOAc 2:1), the

reaction mixture was filtered through a Celite® bed and evaporated to dryness under reduced pressure. The crude product was passed through a short pad of SiO_2 using hexane-EtOAc (1:1) as eluant to furnish pure compound **25** (690 mg, 92%) as yellow oil; $[\alpha]_D^{25} + 6.5$(c 1.0, $CHCl_3$); IR (neat): 3,449, 2,930, 1,725, 1,646, 1,225, 1,090, 779 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.45–7.05 (m, 29 H, aromatic protons), 5.66–5.56 (m, 3 H), 4.94–4.90 (m, 2 H), 4.77–4.66 (m, 3 H), 4.41–4.33 (m, 2 H), 4.29 (br s, 1 H), 4.27–4.26 (m, 1 H), 4.22–4.18 (m, 2 H), 4.15–4.08 (m, 2 H), 4.03–4.01 (m, 1 H), 3.86–3.73 (m, 4 H), 3.63–3.59 (m, 1 H), 3.56–3.51 (m, 2 H), 3.44 (s, 3 H, OCH_3), 3.41–3.32 (m, 6 H), 3.09–3.06 (m, 1 H), 2.10, 1.87 (2 s, 6 H, 2 COCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 169.5, 169.4, 167.5 (2 C), 137.8–136.7 (aromatic carbons), 132.2–124.8 (aromatic carbons), 101.5 (C-1_B), 100.6 (C-1_C), 97.8 (C-1_A), 81.3, 80.1, 79.9, 77.1, 75.0, 74.5, 73.7, 73.6, 73.0, 72.3, 72.2, 71.7, 70.8, 69.2, 67.5, 66.7, 66.4, 60.1, 58.8, 54.0 (C-2_C), 53.8 (OCH_3), 19.7, 19.2 (2 COCH_3); ESI–MS: m/z= 1,204.4 $[M+Na]^+$; Anal. Calcd. for $C_{66}H_{71}NO_{19}$ (1181.5): C, 67.05; H, 6.05; found: C, 66.82; H, 6.30.

Methyl (2,3-di-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl)-(1→6)-(3-O-acetyl-2-deoxy-2-N-phthalimido-β-D-glucopyranosyl)-(1→3)-(4-O-acetyl-2,6-di-O-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (26) To a solution of compound **25** (600 mg, 0.5 mmol) and ethyl thioglycoside donor **8** (315 mg, 0.6 mmol) in anhydrous CH_2Cl_2 (10 ml) was added powdered MS 4 Å (300 mg) and the reaction mixture was allowed to stir at room temperature under argon for 1 h. *N*-Iodosuccinimide (200 mg, 0.9 mmol) was added to the reaction mixture and it was cooled to −30°C. To the cold reaction mixture was added TMSOTf (5 μl) and it was allowed to stir at −30°C for 1 h. After completion (TLC; hexane-EtOAc 2:1), the reaction mixture was quenched by adding 5% aq. $Na_2S_2O_3$, diluted with CH_2Cl_2 (25 ml). The organic layer was washed successively with aq. $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane-EtOAc (2:1) as eluant to afford pure tetrasaccharide derivative **26** (675 mg, 82%) as yellow oil; $[\alpha]_D^{25}$+ 9.7(c 1.0, $CHCl_3$); IR (neat): 2,926, 1,730, 1,650, 1,625, 1,219, 1,096, 779 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 8.02–7.96 (m, 4 H, aromatic protons), 7.55–6.19 (m, 40 H, aromatic protons), 5.60–5.57 (t, J=8.7 Hz each, 1 H), 5.57–5.54 (m, 2 H), 5.53–5.45 (m, 2 H), 5.41–5.40 (m, 1 H), 4.97 (br s, 1 H), 4.95–4.93 (m, 1 H), 4.92–4.82 (ABq, J= 11.4 Hz, 2 H), 4.80–4.70 (m, 2 H), 4.51–4.47 (m, 2 H), 4.35–4.24 (m, 4 H), 4.23–4.13 (m, 5 H), 3.97–3.89 (m, 5 H), 3.88–3.75 (m, 2 H), 3.61–3.47 (m, 5 H), 3.46 (br s, 3 H, OCH_3), 3.38–3.34 (m, 3 H), 3.15–3.14 (m, 1 H), 2.06, 1.85 (2 s, 6 H, 2 COCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 171.1, 170.2, 168.2 (2 C), 165.6, 165.5, 138.8-123.3 (aromatic carbons), 102.5 (PhCH), 102.0 (C-1_B), 101.9 (C-1_A), 101.5 (C-1_C), 98.2 (C-1_D), 85.5, 82.5, 81.4, 79.3, 78.9, 78.7, 77.3, 75.7, 75.2, 74.9, 74.6, 74.2, 73.5, 73.1, 73.0, 72.7, 72.5, 71.8, 70.3, 69.5, 68.5, 68.1, 67.7, 66.6, 56.8 (C-2_C), 54.7 (OCH_3), 20.9, 20.8 (2 COCH_3); ESI–MS: m/z=1662.6 $[M+Na]^+$; Anal. Calcd. for $C_{93}H_{93}NO_{26}$ (1,639.6): C, 68.08; H, 5.71; found: C, 67.85; H, 6.00.

Methyl (2,3-di-O-benzoyl-β-D-glucopyranosyl)-(1→6)-(3-O-acetyl-2-deoxy-2-N-phthalimido-β-D-glucopyranosyl)-(1→3)-(4-O-acetyl-2,6-di-O-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (27) To a solution of compound **26** (600 mg, 0.4 mmol) in CH_3CN (10 ml) was added $HClO_4$-SiO_2 (50 mg) and the reaction mixture was allowed to stir at room temperature for 20 min. After completion (TLC; hexane-EtOAc 1:1), the reaction mixture was filtered through a Celite® bed and evaporated to dryness under reduced pressure. The crude product was passed through a short pad of SiO_2 to furnish pure compound **27** (555 mg, 89%) as yellow oil; $[\alpha]_D^{25} + 18.7$(c 1.0, $CHCl_3$); IR (neat): 3,443, 2,930, 2,875, 1,710, 1,652, 1,454, 1,370, 1,226, 1,100, 775 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.99–7.96 (m, 4 H, aromatic protons), 7.51–7.16 (m, 32 H, aromatic protons), 6.90–6.88 (m, 3 H, aromatic protons), 5.87–5.80 (m, 1 H), 5.61–5.58 (m, 1 H), 5.55–5.48 (m, 2 H), 5.43–5.40 (m, 2 H), 4.95–4.84 (m, 4 H), 4.75 (d, J= 10.8 Hz, 1 H), 4.68–4.63 (m, 2 H), 4.46–4.39 (m, 1 H), 4.35–4.27 (m, 3 H), 4.21–4.12 (m, 4 H), 4.05–4.02 (m, 2 H), 3.92–3.86 (m, 2 H), 3.81–3.78 (m, 2 H), 3.70–3.60 (m, 3 H), 3.56–3.50 (m, 2 H), 3.46–3.41 (m, 3 H), 3.36 (s, 3 H, OCH_3), 3.35–3.31 (m, 2 H), 3.09–3.06 (m, 1 H), 2.04, 1.82 (2 s, 6 H, 2 COCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.1, 170.0, 168.0 (2 C), 167.0, 165.8, 139.0–123.2 (aromatic carbons), 102.5 (C-1_B), 101.8 (C-1_A), 100.7 (C-1_C), 98.6 (C-1_D), 82.4, 81.3, 79.2, 78.9, 76.1, 75.6, 75.1 (2 C), 74.9, 74.7, 74.5, 73.5, 73.1, 73.0 (2 C), 72.5, 72.1, 70.1, 69.7, 69.4, 68.5, 68.2, 67.6, 62.0, 56.7 (C-2_C), 54.3 (OCH_3), 20.8, 20.5 (2 COCH_3); ESI–MS: m/z=1,574.5 $[M+Na]^+$; Anal. Calcd. for $C_{86}H_{89}NO_{26}$ (1,551.5): C, 66.53; H, 5.78; found: C, 66.25; H, 6.00.

Methyl (2,3,5,6-tetra-O-benzoyl-β-D-galactofuranosyl)-(1→6)-(2,3-di-O-benzoyl-β-D-glucopyranosyl)-(1→6)-(3-O-acetyl-2-deoxy-2-N-phthalimido-β-D-glucopyranosyl)-(1→3)-(4-O-acetyl-2,6-di-O-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (28) To a solution of tetrasaccharide acceptor **27** (500 mg, 0.3 mmol) and ethyl thioglycoside donor **9** (230 mg, 0.4 mmol) in anhydrous CH_2Cl_2 (10 ml) was added powdered MS 4 Å (500 mg) and the reaction mixture was allowed to stir at

room temperature under argon for 1 h. *N*-Iodosuccinimide (230 mg, 0.4 mmol) was added to the reaction mixture and it was cooled to −30°C. To the cold reaction mixture was added TMSOTf (3 μl) and it was allowed to stir at −30°C for 1 h. After completion (TLC; hexane-EtOAc 1:1), the reaction mixture was quenched by adding 5% aq. $Na_2S_2O_3$, diluted with CH_2Cl_2 (25 ml). The organic layer was washed successively with aq. $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane-EtOAc (1:1) to afford pure pentasaccharide derivative **28** (510 mg, 79%) as yellow oil; $[\alpha]_D^{25} + 12.9 (c\,1.0,\ CHCl_3)$; IR (neat): 2,929, 2,376, 1,765, 1,723, 1,660, 1,370, 1,229, 1,082, 770 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 8.08–7.72 (m, 12 H, aromatic protons), 7.53–6.90 (m, 47 H, aromatic protons), 5.84–5.78 (m, 1 H), 5.62–5.52 (m, 3 H), 5.48–5.32 (m, 4 H), 4.95–4.82 (m, 4 H), 4.77–4.63 (m, 4 H), 4.55–4.18 (m, 8 H), 4.17–4.11 (m, 4 H), 4.02–3.86 (m, 4 H), 3.79–3.75 (m, 1 H), 3.68–3.47 (m, 7 H), 3.43 (s, 3 H, OC*H*$_3$), 3.37–3.32 (m, 4 H), 3.12–3.09 (m, 1 H), 1.98, 1.83 (2 s, 6 H, 2 COC*H*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.3, 170.0, 167.8 (2 C), 165.4 (2 C), 165.1 (2 C), 165.0 (2 C), 138.8–122.8 (aromatic carbons), 105.7 (C-1_E), 102.1 (C-1_B), 101.5 (C-1_A), 100.5 (C-1_C), 97.7 (C-1_D), 85.0, 82.2, 82.1, 81.8, 80.9, 78.7, 78.6, 75.6, 75.2, 74.7 (2 C), 74.5, 74.2, 73.8, 73.0, 72.6 (2 C), 72.1, 71.7, 71.0, 70.8, 70.6, 69.7, 69.1, 67.9, 67.8, 67.3, 63.3, 63.1, 56.3 (C-2_C), 54.5 (O*C*H$_3$), 20.3, 20.1; ESI-MS: *m*/*z*=2,152.7 $[M+Na]^+$; Anal. Calcd. for $C_{120}H_{115}NO_{35}$ (2129.7): C, 67.63; H, 5.44; found: C, 67.40; H, 5.75.

Methyl (3,4,6-tri-O-acetyl-2-deoxy-2-N-phthalimido-β-D-glucopyranosyl)-(1→3)-(2,6-di-O-benzyl-β-D-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (29) To a solution of compound **22** (700 mg, 0.9 mmol) and ethyl thioglycoside donor **5** (480 mg, 1.0 mmol) in anhydrous CH_2Cl_2 (10 ml) was added powdered MS 4 Å (500 mg) and the reaction mixture was allowed to stir at room temperature under argon for 1 h. *N*-iodosuccinimide (270 mg, 1.2 mmol) was added to the reaction mixture and it was cooled to −30°C. To the cold reaction mixture was added TMSOTf (5 μl) and it was allowed to stir at −30°C for 1 h. After completion (TLC; hexane-EtOAc 4:1), the reaction mixture was quenched by adding 5% aq. $Na_2S_2O_3$ and diluted with CH_2Cl_2 (50 ml). The organic layer was washed successively with aq. $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane-EtOAc (5:1) as eluant to afford pure trisaccharide derivative **29** (520 mg, 47%) as yellow oil; $[\alpha]_D^{25} + 23.4 (c\,1.0,\ CHCl_3)$; IR (neat): 2,928, 2,870, 1,705, 1,495, 1,454, 1,366, 1,217, 1,090, 758, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.70–7.68 (m, 29 H, aromatic protons), 5.83–5.76 (t, *J*=9.3 and 1.5 Hz, 1 H, H-3_C), 5.63 (d, *J*=8.4 Hz, 1 H, H-1_C), 5.34–5.27 (t, *J*=9.9 Hz each, 1 H, H-4_C), 5.03 (d, *J*=10.8 Hz, 1 H), 4.97 (d, *J*=11.1 Hz, 1 H), 4.82 (d, *J*=11.1 Hz, 1 H), 4.74–4.69 (m, 2 H), 4.48–4.36 (m, 4 H), 4.34–4.23 (m, 3 H), 4.07 (br s, 1 H), 3.97–3.92 (t, *J*=8.4 Hz each, 1 H), 3.84–3.72 (m, 3 H), 3.68–3.63 (m, 1 H), 3.60–3.52 (m, 7 H), 3.48 (s, 3 H, OC*H*$_3$), 3.47–3.44 (m, 2 H), 3.19–3.16 (m, 1 H), 2.06, 1.92, 1.87 (3 s, 9 H, 3 COC*H*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.2 (2 C), 169.1, 167.8 (2 C), 139.5–123.8 (aromatic carbons), 103.2 (C-1_B), 102.3 (C-1_A), 99.1 (C-1_C), 84.2, 83.2, 81.9, 78.5, 76.2, 75.9, 75.7, 75.4, 75.1, 74.9, 74.6, 74.5, 73.8, 73.4, 71.2, 69.6, 69.1, 64.5, 62.8, 55.7 (C-2″), 55.2 (O*C*H$_3$), 20.9, 20.8, 19.6; ESI–MS: *m*/*z*=1,246.5 $[M+Na]^+$; Anal. Calcd. for $C_{68}H_{73}NO_{20}$ (1,223.5): C, 66.71; H, 6.01; found: C, 66.48; H, 6.30.

Methyl [(3,4,6-tri-O-acetyl-2-deoxy-2-N-phthalimido-β-D-glucopyranosyl)-(1→3)]-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-(1→4)-(2,6-di-O-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (30) To a solution of compound **29** (500 mg, 0.4 mmol) and ethyl thioglycoside donor **7** (290 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 ml) was added powdered MS 4 Å (500 mg) and the reaction mixture was allowed to stir at room temperature under argon for 1 h. *N*-Iodosuccinimide (170 mg, 0.8 mmol) was added to the reaction mixture and it was cooled to −30°C. To the cold reaction mixture was added TMSOTf (3 μl) and it was allowed to stir at −30°C for 1 h. After completion (TLC; hexane-EtOAc 4:1), the reaction mixture was quenched by adding 5% aq. $Na_2S_2O_3$, diluted with CH_2Cl_2 (30 ml). The organic layer was washed successively with aq. $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane-EtOAc (2:1) as eluant to afford pure tetrasaccharide derivative **30** (250 mg, 35%) as yellow oil; $[\alpha]_D^{25} + 9.3 (c\,1.0,\ CHCl_3)$; IR (neat): 2,928, 2,870, 1,705, 1,495, 1,454, 1,366, 1,217, 1,090, 758, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 7.44–7.42 (m, 5 H, aromatic protons), 7.35–7.22 (m, 32 H, aromatic protons), 7.09–7.06 (m, 8 H, aromatic protons), 6.92–6.89 (m, 2 H, aromatic protons), 5.65–5.62 (m, 2 H, aromatic protons), 5.69–5.60 (m, 2 H, H-1_C and H-3_C), 5.13 (d, *J*=3.0 Hz, 1 H, H-1_D), 4.98–4.95 (d, *J*=11.4 Hz, 1 H), 4.88–4.84 (d, *J*=11.1 Hz, 1 H), 4.81–4.77 (d, *J*=10.5 Hz, 1 H, H-1_B), 4.70 (br s, 1 H), 4.69–4.57 (m, 6 H), 4.54–4.42 (m, 5 H), 4.37–4.24 (m, 6 H), 4.23–4.17 (m, 3 H), 4.15–4.06 (m, 1 H), 3.95–3.79 (m, 6 H), 3.78–3.65 (m, 2 H), 3.60–3.47 (m, 6 H), 3.46 (s, 3 H, OC*H*$_3$), 3.44–3.42 (m, 3 H), 3.10–3.02 (m, 1 H), 1.93, 1.91, 1.81 (3 s, 9 H, 3 COC*H*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.1 (3 C), 167.2 (2 C), 138.5–122.9 (aromatic carbons), 102.7 (C-1_B),

102.4 (C-1_A), 101.0 (C-1_C), 99.2 (C-1_D), 83.0, 82.3, 82.1, 81.2, 80.6, 78.7, 78.1, 78.0, 77.8, 76.4, 75.3, 75.2, 75.1, 74.8, 74.7, 74.1, 73.7, 73.7, 73.4, 73.1, 73.0, 71.0, 70.0, 68.7, 68.6, 67.6, 66.9, 65.8, 56.7 (O*C*H_3), 55.4 (C-2_C), 20.5 (3 C); ESI-MS: *m/z*=1,768.7 $[M+Na]^+$; Anal. Calcd. for $C_{102}H_{107}NO_{25}$ (1745.7): C, 70.13; H, 6.17; found: C, 69.91; H, 6.39.

Methyl (β-D-galactofuranosyl)-(1→6)-(β-D-glucopyranosyl)-(1→6)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-(β-D-galactopyranosyl)-(1→4)-(β-D-glucopyranosyl)-(1→4)-α-D-glucopyranoside (1) To a solution of the hexasaccharide derivative **19** (600 mg, 0.2 mmol) in EtOH (5.0 ml) was added hydrazine hydrate (1.0 ml) and the reaction mixture was allowed to stir at 80°C for 8 h. The solvents were removed and the crude mass was treated with pyridine (2.0 ml) and acetic anhydride (2.0 ml) for 2 h at room temperature, concentrated and purified over SiO_2 using toluene-EtOAc (1:1) as eluant. To a solution of the *N*-acetylated hexasaccharide derivative in CH_3OH (10 ml) was added solid CH_3ONa until the pH of the solution reached ~10. The reaction mixture was allowed to stir at room temperature for 5 h and neutralized with Amberlite IR-120 (H^+) resin. The reaction mixture was filtered and evaporated to dryness. To a solution of the crude product in CH_3OH (5 ml) was added 20% Pd $(OH)_2$-C (100 mg) and the reaction mixture was allowed to stir at room temperature under a positive pressure of hydrogen for 12 h. After completion (TLC; CH_3CN-AcOH-H_2O 10:5:1), the reaction mixture was filtered through a Celite® bed and concentrated to a white powder, which was further purified through a Sephadex LH-20 column using CH_3OH-H_2O (4:1) as eluant to furnish pure hexasaccharide **1** (170 mg, 69%) as an amorphous powder; $[\alpha]_D^{25} - 35.6(c\,1.0,\ H_2O)$; IR (KBr): 3,447, 3,062, 3,030, 2,922, 2,365, 1,363, 1,055, 699 cm^{-1}; ^1H NMR (D_2O, 400 MHz): δ 5.02 (d, *J*=1.2 Hz, 1 H, H-1_F), 4.82 (d, *J*=8.4 Hz, 1 H, H-1_D), 4.77 (d, *J*=4.0 Hz, 1 H, H-1_A), 4.50 (d, *J*=8.0 Hz, 1 H, H-1_C), 4.48 (d, *J*=8.0 Hz, 1 H, H-1_B), 4.42 (d, *J*=7.6 Hz, 1 H, H-1_E), 4.22–4.13 (m, 2 H, H-2_F and H-3_D), 4.11–4.00 (m, 3 H, H-3_F, H-4_E and H-6_{aF}), 3.98–3.95 (m, 1 H, H-4_A), 3.94–3.86 (m, 4 H, H-2_E, H-3_A, H-4_B and H-6_{bB}), 3.84–3.77 (m, 3 H, H-3_B, H-4_D and H-6_{aB}), 3.76–3.65 (m, 10 H, H-2_A, H-3_C, H-4_C, H-4_F, H-5_A, H-$6_{a,bA}$, H-$6_{a,bD}$ and H-6_{bF}), 3.64–3.53 (m, 10 H, H-3_E, H-5_B, H-5_C, H-5_D, H-5_E, H-5_F, H-$6_{a,bC}$ and H-$6_{a,bE}$), 3.38 (s, 3 H, O*CH*$_3$), 3.33–3.28 (m, 3 H, H-2_C, H-2_B and H-2_D), 1.87 (s, 3 H, NHCOC*H*$_3$); ^{13}C NMR (D_2O, 100 MHz): δ 172.6 (NH*C*OCH$_3$), 107.5 (C-1_F), 102.7 (C-1_B), 102.3 (C-1_D), 101.8 (C-1_C), 101.7 (C-1_E), 98.4 (C-1_A), 82.4 (C-3_F), 81.7 (C-4_B), 80.4 (C-3_D), 78.0 (C-5_A), 77.7 (C-5_C), 76.2 (C-4_E), 75.1 (C-4_F), 74.5 (C-2_A), 74.4 (C-5_B), 74.3 (C-5_D), 74.2 (C-5_E), 73.5 (C-5_F), 72.6 (C-2_C), 72.3 (C-2_B), 70.4 (2 C, C-3_E and C-3_C), 70.3 (C-4_D), 69.7 (C-3_B), 69.3, (C-4_A), 69.2 (C-3_A), 69.0 (C-2_E), 68.0 (C-4_C), 67.8 (C-2_F), 66.5 (C-6_E), 62.2 (2 C, C-6_A and C-6_D), 60.5 (C-6_F), 59.4 (C-6_C), 59.3 (C-6_B), 55.9 (C-2_D), 54.6 (O*C*H$_3$), 19.5 (NHCO*C*H$_3$); ESI–MS: *m/z*=1,068.3 $[M+Na]^+$; Anal. Calcd. for $C_{39}H_{67}NO_{31}$ (1,045.4): C, 44.78; H, 6.46; found: C, 44.60; H, 6.80.

Methyl (β-D-galactofuranosyl)-(1→6)-(β-D-glucopyranosyl)-(1→6)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-(β-D-galactopyranosyl)-(1→4)-β-D-glucopyranoside (2) To a solution of pentasaccharide derivative **28** (500 mg, 0.2 mmol) in EtOH (5.0 ml) was added hydrazine hydrate (1.0 ml) and the reaction mixture was stirred at 80°C for 8 h. The solvents were removed and the crude mass was treated with pyridine (2 ml) and acetic anhydride (2 ml) at room temperature for 2 h. The reaction mixture was concentrated and purified over SiO_2 using toluene-EtOAc (1:1) as eluant. To a solution of the *N*-acetylated pentasaccharide derivative in CH_3OH (10 ml) was added solid CH_3ONa until the pH of the solution reached ~10. The reaction mixture was allowed to stir at room temperature for 5 h and neutralized with Amberlite IR-120 (H^+) resin. The reaction mixture was filtered and evaporated to dryness. To a solution of the crude product in CH_3OH (10 ml) was added 20% $Pd(OH)_2$-C (100 mg) and the reaction mixture was allowed to stir at room temperature under a positive pressure of hydrogen for 12 h. After completion (TLC; CH_3CN-AcOH-H_2O 10:5:1), the reaction mixture was filtered through a Celite® bed and concentrated to a white mass, which was further purified through a Sephadex LH-20 column using CH_3OH-H_2O (4:1) as eluant to furnish pure pentasaccharide **2** (110 mg, 66%) as an amorphous powder; $[\alpha]_D^{25} + 32.3(c\,1.0,\ H_2O)$); IR (KBr): 3,018, 2,926, 1,740, 1,366, 1,218, 1,067, 769 cm^{-1}; ^1H NMR (D_2O, 400 MHz): δ 4.98 (d, *J*=1.2 Hz, 1 H, H-1_E), 4.77 (d, *J*=8.4 Hz, 1 H, H-1_C), 4.46 (d, *J*=8.0 Hz, 1 H, H-1_D), 4.44 (d, *J*=8.0 Hz, 1 H, H-1_B), 4.38 (d, *J*=7.6 Hz, 1 H, H-1_A), 4.07–3.96 (m, 2 H, H-2_E and H-3_C), 3.90–3.87 (m, 1 H, H-3_E), 3.85–3.77 (m, 3 H, H-4_D and H-6_{abE}), 3.76–3.70 (m, 2 H, H-2_D and H-6_{aA}), 3.68–3.60 (m, 9 H, H-3_A, H-3_B, H-4_A, H-4_B, H-4_C, H-4_E, H-6_{bA} and H-6_{abC}), 3.58–3.45 (m, 11 H, H-2_A, H-3_D, H-5_A, H-5_B, H-5_C, H-5_D, H-5_E, H-6_{abB} and H-6_{abD}), 3.29 (s, 3 H, O*CH*$_3$), 3.20-3.12 (m, 1 H, H-2_C), 3.10-3.02 (m, 1 H, H-2_B), 1.77 (s, 3 H, NHCOC*H*$_3$); ^{13}C NMR (D_2O, 100 MHz): δ 172.5 (NH*C*OCH$_3$), 107.0 (C-1_E), 102.2 (2 C, C-1_A and C-1_B), 101.8 (C-1_C), 100.3 (C-1_D), 82.2, 80.3, 77.6, 76.1, 75.6, 75.3, 75.0, 74.3, 74.2, 74.0, 73.5, 73.4, 72.5 (2 C), 72.0, 71.5, 71.4, 70.9, 69.9, 69.1, 68.9, 68.8, 62.2, 61.9, 55.3 (C-2_C), 55.2 (O*C*H$_3$), 19.6 (NHCO*C*H$_3$); ESI–MS: *m/z*=906.3 $[M+Na]^+$; Anal. Calcd. for $C_{33}H_{57}NO_{26}$ (883.3): C, 44.85; H, 6.50; found: C, 44.65; H, 6.88.

Methyl [(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)]-(α-D-glucopyranosyl)-(1→4)-(β-D-galactopyranosyl)-(1→4)-β-D-glucopyranoside (3) To a solution of tetrasaccharide derivative **30** (220 mg, 0.1 mmol) in EtOH (5.0 ml) was added hydrazine hydrate (700 μl) and the reaction mixture was stirred at 80°C for 8 h. The solvents were removed and the crude mass was treated with pyridine (2.0 ml) and acetic anhydride (2.0 ml) at room temperature for 2 h, concentrated and purified over SiO_2 using toluene-EtOAc (1:1) as eluant. To a solution of the *N*-acetylated tetrasaccharide derivative in CH_3OH (5 ml) was added solid CH_3ONa until the pH of the solution reached ~10. The reaction mixture was allowed to stir at room temperature for 5 h, and neutralized with Amberlite IR-120 (H^+) resin. The reaction mixture was filtered and evaporated to dryness. To a solution of the crude product in CH_3OH (5 ml) was added 20% $Pd(OH)_2$-C (80 mg) and the reaction mixture was allowed to stir at room temperature under a positive pressure of hydrogen for 12 h. After completion (TLC; CH_3CN-AcOH-H_2O 10:5:1), the reaction mixture was filtered through a Celite® bed and concentrated to a white powder, which was further purified through a Sephadex LH-20 column using CH_3OH-H_2O (4:1) as eluant to furnish pure tetrasaccharide **3** (52 mg, 70%) as amorphous powder; $[\alpha]_D^{25} + 13.5(c\,1.0,\ H_2O)$; IR (KBr): 3,018, 2,926, 1,740, 1,366, 1,218, 1,067, 769 cm^{-1}; ^1H NMR (D_2O, 300 MHz): δ 4.80 (d, *J*=8.1 Hz, 1 H, H-1_C), 4.73 (d, *J*=4.0 Hz, 1 H, H-1_D), 4.62 (d, *J*=8.2 Hz, 1 H, H-1_B), 4.32 (d, *J*=7.5 Hz, 1 H, H-1_A), 3.79–3.72 (m, 4 H), 3.70–3.52 (m, 14 H), 3.37–3.35 (m, 4 H), 3.33 (s, 3 H, OC*H*$_3$), 3.32–3.30 (m, 2 H), 1.87 (s, 3 H, NHCOC*H*$_3$); ^{13}C NMR (D_2O, 75 MHz): δ 170.9, 101.9 (C-1_B), 101.7 (C-1_A), 100.8 (C-1_C), 100.0 (C-1_D), 82.3, 79.2, 76.9, 76.5 (2 C), 76.3, 75.6, 75.1, 73.6, 72.4, 71.3, 71.2, 70.8, 70.5, 70.2, 61.6, 61.2, 60.9, 60.8, 56.9 (O*C*H$_3$), 56.5 (C-2″), 21.6 (NHCO*C*H$_3$); ESI–MS: *m/z*=744.2 $[M+Na]^+$; Anal. Calcd. for $C_{27}H_{47}NO_{21}$ (721.3): C, 44.94; H, 6.56; found: C, 44.81; H, 6.72.

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