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Synthesis of the hexasaccharide repeating unit corresponding to the cell wall lipopolysaccharide of *Azospirillum irakense* KBC1

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ABSTRACT

A convenient chemical synthesis of the hexasaccharide repeating unit of the cell wall lipopolysaccharide of *Azospirillum irakense* KBC1 has been successfully achieved. A stereo- and regioselective [4 + 2] block glycosylation strategy has been used to obtain the target hexasaccharide as its octyl glycoside. All synthetic intermediates have been prepared in high yields from commercially available reducing sugars following a series of protection–deprotection reactions. An oxidation–reduction methodology has been applied to convert β-D-glucosidic unit to a β-D-mannosidic moiety.

1. Introduction

Bacteria belonging to the genus *Azospirillum* are known as plant growth promoting rhizobacteria (PGPR) for their active role to promote plant growth by associating them with different plants in the rhizosphere.[1] *Azospirilla* are gram-negative, motile, free-living nitrogen fixing rhizobacteria that exert beneficial effects on plant growth and crop productions by producing several phytohormones, vitamins, and bioactive substances.[2] In general, PGPR establish association with roots of cereals and other non-legumes by symbiotic relationships.[3] Macromolecules, such as exopolysaccharides (EPS), lipopolysaccharides (LPS), and capsular polysaccharides (CPS) present in the cell-wall of *Azospirilla* regulate their interactions with the leguminous and non-leguminous roots of plants.[4] Among cell-wall polysaccharides, the role of LPS in the plant-bacterial interactions is considered to be very important for their survival in challenging environmental conditions. Although the usefulness of the LPSs has been well documented, only a few structures of the LPS have been reported from *Azospirillum* strains.[1b,5] Fedonenko et al. reported the structure of a hexasaccharide repeating unit found in the LPS of *Azospirillum irakense* KBC1 (Fig. 1).[1c]

α-D-Gal*f*-(1→2)-α-L-Rha*p*-(1→3)-β-D-Man*p*-(1→3)-α-L-Rha*p*
1
↓
3
→4)-α-L-Rha*p*-(1→3)-β-D-Gal*p*-(1→

Figure 1. Hexasaccharide repeating unit corresponding to the cell-wall lipopolysaccharide of *Azospirillum irakense* KBC1.

In the current scenario, the development of plant growth-promoting agents is highly essential to enhance the crop production. In this context it is quite reasonable to understand the role of the LPS of *Azospirillum irakense* KBC1 in the interaction of the bacteria with plant roots. In order to carry out different biological experiments, sufficient quantities of the hexasaccharide repeating unit are required, which are not accessible from its natural source. Therefore, the development of a convenient chemical synthetic strategy is essential to provide the required quantity of the hexasaccharide repeating unit as well as its several analogs. Herein we report a convenient chemical synthesis of the hexasaccharide as its octyl glycoside found in the cell-wall lipopolysaccharide of *Azospirillum irakense* KBC1 (Fig. 2). The presence of an octyl group at the reducing end makes the purification of the target hexasaccharide easier following solid phase extraction using reverse phase C_{18} column.[6]

2. Results and discussion

The synthesis of the target hexasaccharide containing a β-D-mannose unit and an α-D-galactofuranose moiety at the non-reducing end, as its octyl glycoside (Fig. 2) has been accomplished by exploiting a [4 + 2] block glycosylation strategy. Since, β-selective glycosylation of D-mannose derivatives is considered as troublesome, a D-glucose derivative **6** has been used as the precursor of the D-mannose moiety. A tetrasaccharide diol derivative **16** has been used as the glycosyl acceptor in the block glycosylation step. Regio- and steroselective glycosylation of a tetrasaccharide diol derivative **16** with a disaccharide thioglycoside derivative **17** furnished hexasaccharide derivative **18**. Dess–Martin oxidation followed by sodium borohydride reduction of the free hydroxyl group of compound **18** gave hexasaccharide derivative **19**, which was finally deprotected to give target hexasaccharide **1**. The key

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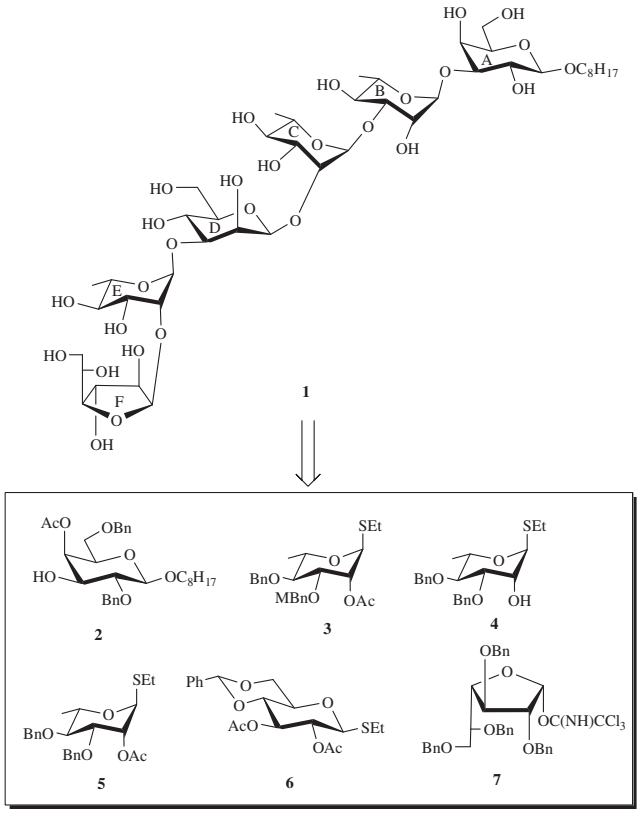
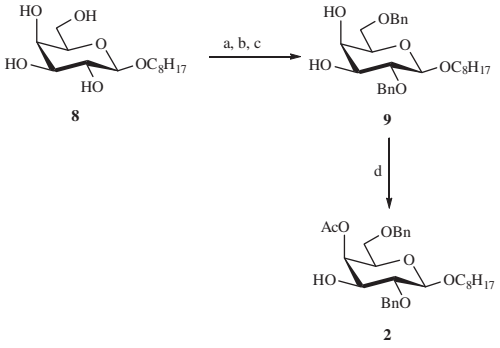


Figure 2. Structure of the synthesized hexasaccharide as its octyl glycoside **1** corresponding to the cell-wall lipopolysaccharide of *Azospirillum irakense* KBC1.

features of the synthetic strategy are: (a) a late-stage conversion of the β-D-glucose to the β-D-mannose moiety after completion of the glycosylation steps; (b) a highly regio- and stereoselective glycosylation of a disaccharide thioglycoside **17** with a tetrasaccharide diol **16**; (c) the formation of α-glycoside using C-2 glycosylated L-rhamnosyl thioglycoside donor **17**; (d) use of a thioglycoside derivative **4** as an orthogonal glycosyl acceptor; (e) the use of a per-O-benzylated D-galactofuranosyl trichloroacetimidate derivative for the preparation of the α-linked D-galactofuranosylated compound; and (f) the use of an octyl group as an anomeric protecting group makes the purification of unprotected hexasaccharide **1** easier using solid phase extraction over reverse-phase C_{18} silica gel.

A dihydroxyl groups containing tetrasaccharide acceptor **16** and a disaccharide thioglycoside derivative **17** have been synthesized from suitably derivatized monosaccharide intermediates **2**, **3**,[7] **4**,[8] **5**,[8] **6**[9] and **7**.[10] Octyl β-D-galactopyranoside **8**[11] was subjected to a series of reactions consisting of the acetonide formation using 2,2-dimethoxypropane and *p*-toluenesulfonic acid,[12] benzylation of the remaining hydroxyl groups using benzyl bromide and sodium hydroxide[13] and finally acidic hydrolysis of the acetonide ring to give octyl 2,6-di-*O*-benzyl-β-D-galactopyranoside **9** in 72% yield. Compound **9** was selectively acetylated via orthoesterification[14] to give octyl 4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside **2** in 76% yield (Scheme 1).

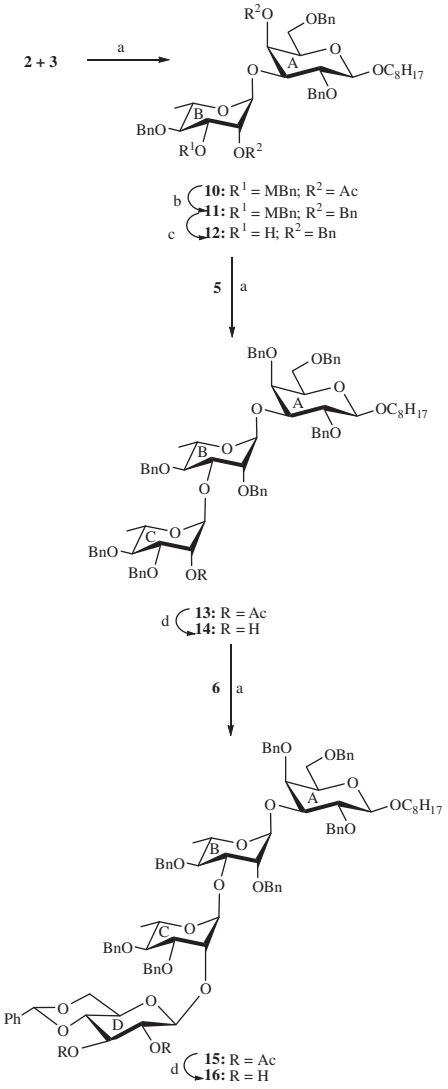
The stereoselective 1,2-*trans* glycosylation of L-rhamnose derived thioglycoside **3** with compound **2** in the presence of a combination of *N*-iodosuccinimide (NIS) and trimethylsilyl trifluomethanesulfonate (TMSOTf)[15] furnished the disaccharide derivative **10** in 79% yield. Appearance of signals in the NMR spectra [δ 5.05 (br s, H-1_B), 4.35 (d, J = 7.0 Hz, H-1_A) in ^{1}H NMR and δ 103.9 (C-1_A), 99.2 (C-1_B) in ^{13}C NMR spectra] confirmed its formation. The presence of a 2-*O*-acetyl group in the thioglycoside donor **3**



Scheme 1. Reagents and conditions: (a) 2,2-dimethoxypropane, *p*-TsOH, DMF, room temperature, 12 h; (b) benzyl bromide, NaOH, DMF, room temperature, 6 h; (c) 80% aq AcOH, 80 °C, 1.5 h, 72% overall; (d) triethylorthoacetate, *p*-TsOH, DMF, 2 h then H_2O, room temperature, 30 min, 76%.

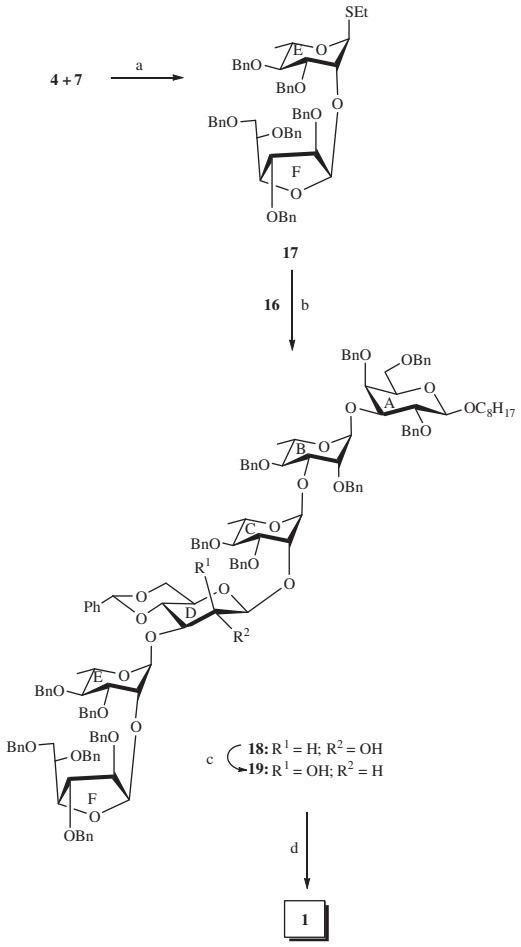
directed the formation of 1,2-*trans* glycosylated product **10** by a neighboring participation effect. One-pot deacetylation–benzylation[13] of compound **10** using benzyl bromide and sodium hydroxide afforded compound **11** in 80% yield. Oxidative removal of the 4-methoxybenzyl group of compound **11** using DDQ[16] produced compound **12** in 77% yield. The stereoselective glycosylation of compound **12** with thioglycoside derivative **5** in the presence of NIS-TMSOTf[15] furnished trisaccharide derivative **13** in 77% yield, which on deacetylation gave compound **14** in 95% yield. The presence of an 2-*O*-acetyl group in the thioglycoside donor **5** directed the formation of the 1,2-*trans* glycosylated product **13** by neighboring group participation. The structure of compound **13** was confirmed through spectral analysis [δ 5.24 (br s, H-1_B), 5.00 (br s, 1_C), 4.33 (d, J = 7.2 Hz, H-1_A) in ^{1}H NMR and δ 104.1 (C-1_A), 98.8 (C-1_B), 96.2 (C-1_C) in ^{13}C NMR spectra]. β-Selective glycosylation of compound **14** with thioglycoside derivative **6** in the presence of NIS-TMSOTf[15] furnished tetrasaccharide derivative **15** in 71% yield, which was deacetylated to give compound **16** in 92% yield. In this case, the 1,2-*trans* glycosylated product **15** was obtained by applying the neighboring participation effect of 2-*O*-acetyl group present in the thioglycoside donor **6**. The appearance of signals corresponding to compound **15** confirmed its formation [δ 104.1 (C-1_A), 102.9 (C-1_D), 101.3 (PhCH), 101.2 (C-1_C), 98.7 (C-1_B) in the ^{13}C NMR spectrum] (Scheme 2).

In a separate experiment, L-rhamnose derived thioglycoside **4** was allowed to couple with the galactofuranosyl trichloroacetimidate donor **7** under Schmidt's glycosylation conditions[17] to give disaccharide thioglycoside derivative **17** in 73% yield together with some of the β-isomer (~10%), which was separated by flash column chromatography. The formation of the α-linked galactofuranosyl disaccharide thioglycoside **17** was unambiguously confirmed from its NMR spectroscopic analysis. The presence of signals at δ 5.32 (br s, H-1_E, α-L-Rha*p*) and 5.23 (d, J = 4.3 Hz, H-1_F, α-D-Gal*f*) in the ^{1}H NMR and δ 98.0 ($J_{C\text{-}1/H\text{-}1}$ = 170 Hz, C-1_F, α-D-Gal*f*) and 84.4 ($J_{C\text{-}1/H\text{-}1}$ = 171 Hz, C-1_E, α-L-Rha*p*) in the ^{13}C NMR supported its structure. In earlier reports,[18] it has been established that the β-galactofuranosyl linkage has $J_{H1/H2}$ = 0–2 Hz, whereas the α-galactofuranosyl residue has $J_{H1/H2}$ = 4–5 Hz. In the ^{1}H NMR spectrum of compound **17**, the appearance of the $J_{H1,H2}$ = 4.3 Hz for the galactofuranosyl moiety confirmed it as an α-linkage. Regio- and stereoselective glycosylation of compound **16** with compound **17** in the presence of NIS-TMSOTf[15] combination furnished hexasaccharide derivative **18** in 70% yield together with a minor quantity of (1→3)-linked β-glycosylation product (~10%), which was separated by flash column chromatography. The formation of compound **18** was unambiguously confirmed from NMR spectroscopic analysis. Appearance of signals at δ 5.40 (br s, H-1_B), 5.37 (s, 1H, PhC*H*), 5.28 (d, J = 3.8 Hz, H-1_E), 5.23 (br s,



Scheme 2. Reagents and conditions: (a) *N*-iodosuccinimide (NIS), TMSOTf, CH_2Cl_2, MS 4 Å, −40 °C, 1 h, 79% for **10**, 77% for **13** and 71% for **15**; (b) benzyl bromide, NaOH, TBAB, DMF, room temperature, 4 h, 80%; (c) DDQ, CH_2Cl_2, H_2O, room temperature, 3 h, 77%; (d) 0.1 M CH_3ONa, CH_3OH, room temperature, 2 h, 95% for **14** and 92% for **16**.

H-1_C), 5.05 (br s, H-1_F), 4.30 (d, J = 9.1 Hz, H-1_A), 4.18 (d, J = 7.5 Hz, H-1_D) in the ^{1}H NMR and δ 106.7 ($J_{C\text{-}1/H\text{-}1}$ = 158.5 Hz, C-1_A, β-D-Gal*p*), 104.5 ($J_{C\text{-}1/H\text{-}1}$ = 155.9 Hz, C-1_D, β-D-Glc*p*), 101.7 (PhCH), 101.2 ($J_{C\text{-}1/H\text{-}1}$ = 171 Hz, C-1_E, α-L-Rha*p*), 99.4 ($J_{C\text{-}1/H\text{-}1}$ = 172.3 Hz, C-1_C, α-L-Rha*p*), 98.3 ($J_{C\text{-}1/H\text{-}1}$ = 168.5 Hz, C-1_F, α-D-Gal*f*), 97.4 ($J_{C\text{-}1/H\text{-}1}$ = 170 Hz, C-1_B, α-L-Rha*p*) in the ^{13}C NMR and gated ^{1}H coupled ^{13}C NMR spectra[19] of compound **18** confirmed the stereoselective [4 + 2] glycosylation to obtain compound **18**. The formation of regioselective (1→3)-glycosylation product **18** was confirmed from its 2D HMBC NMR spectral analysis. The appearance of three bond correlation peak (H-1_E/C-3_D) in the 2D HMBC spectrum of compound **18** and also spectroscopic analysis of the acetylated product of compound **18** (data not included) strongly confirmed the formation of the regioselective (1→3)-glycosylation product **18**. Oxidation of the free hydroxyl group at the C-2_D position in compound **18** using Dess–Martin periodinane[20] followed by sodium borohydride reduction[21] of the resulting ketone furnished hexasaccharide derivative **19** containing a β-D-mannosidic moiety, which was conventionally hydrogenolized over Pearlman's catalyst to give target hexasaccharide **1** in 62% overall yield as its octyl glycoside. Spectroscopic analysis of compound **1** confirmed its formation. The presence of signals at δ 5.30 (br s, H-1_C), 5.07 (br s, H-1_E), 4.94 (br s, H-1_B), 4.83 (d, J = 4.8 Hz, H-1_F), 4.46 (br s, H-1_D), 4.36 (d, J = 7.8 Hz, H-1_F), 4.14 (d, J = 4.8 Hz, H-1_F) in the ^{1}H NMR and δ 105.5 ($J_{C\text{-}1/H\text{-}1}$ = 158.5 Hz, C-1_A, β-D-Gal*p*), 104.0 ($J_{C\text{-}1/H\text{-}1}$ = 156 Hz, C-1_D, β-D-Man*p*), 102.8 ($J_{C\text{-}1/H\text{-}1}$ = 171 Hz, C-1_B, α-L-Rha*p*), 102.4 ($J_{C\text{-}1/H\text{-}1}$ = 173.5 Hz, C-1_C, α-L-Rha*p*), 101.8 ($J_{C\text{-}1/H\text{-}1}$ = 169 Hz, C-1_F, α-D-Gal*f*), 100.1 ($J_{C\text{-}1/H\text{-}1}$ = 172.3 Hz, C-1_E, α-L-Rha*p*) in the ^{13}C NMR supported its formation (Scheme 3). The appearance of coupling constants ($J_{C\text{-}1/H\text{-}1}$) in the gated ^{1}H coupled ^{13}C NMR spectrum of compound **1** confirmed the presence of two equatorial (β-D-Gal*p* and β-D-Man*p*) and three axial glycopyranosyl linkages (three α-L-Rha*p*).[19] The presence of an α-D-galactofuranosyl linkage was confirmed from the ^{1}H NMR ($J_{H\text{-}1/H\text{-}2}$ = 4.8 Hz) and $J_{C\text{-}1/H\text{-}1}$ = 169 Hz value.[18]



Scheme 3. Reagents and conditions: (a) TMSOTf, CH_2Cl_2, −15 °C, 1 h, 73%; (b) NIS, TMSOTf, CH_2Cl_2, MS 4 Å, −40 °C, 70%; (c) (i) Dess–Martin periodinane, CH_2Cl_2, room temperature, 18 h; (ii) $NaBH_4$, CH_3OH, room temperature, 4 h; (d) H_2, 20% $Pd(OH)_2$–C, CH_3OH, room temperature, 24 h, 62% overall.

3. Conclusion

In conclusion, an efficient synthetic strategy has been successfully developed for the preparation of the hexasaccharide repeating unit of the lipopolysaccharide found in the cell wall of *Azospirillum irakense* KBC1. Regio- and stereoselective [4 + 2] glycosylation allowed us to achieve the target hexasaccharide in minimum number of steps. The generation of β-D-mannosyl moiety from a β-D-glucosyl moiety in the late stage minimized the difficulties

for its formation. All intermediate steps were reasonably high yielding and reproducible for a scale-up preparation.

4. Experimental

4.1. 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 sulfate [2% $Ce(SO_4)_2$ in 2 N H_2SO_4]-sprayed plates in a hot plate. Silica gel 230–400 mesh was used for column chromatography. ^1H and ^{13}C NMR, 2D COSY, and HMQC spectra were recorded on Brucker Avance DPX 500 MHz using $CDCl_3$ and CD_3OD as solvents and TMS as internal reference unless stated otherwise. Chemical shift values are expressed in δ ppm. ESI-MS were recorded on a Micromass Quttro II mass spectrometer. Elementary analysis was carried out on Carlo Erba-1108 analyzer. Optical rotations were measured at 25 °C on a Jasco P-2000 polarimeter. Commercially available grades of organic solvents of adequate purity are used in all reactions.

4.2. Octyl 2,6-di-*O*-benzyl-β-D-galactopyranoside (9)

To a solution of compound **8** (3.0 g, 10.26 mmol) in dry DMF (10 mL) were added 2,2-dimethoxypropane (4 mL, 32.53 mmol) followed by *p*-TsOH (150 mg) and the reaction mixture was allowed to stir at room temperature for 12 h. To the reaction mixture were added powdered NaOH (4.0 g, 100 mmol) and benzyl bromide (5.0 mL, 42.05 mmol) and it was allowed to stir at room temperature for 6 h. The reaction mixture was poured into water (200 mL) and extracted with EtOAc (100 mL). The organic layer was washed with satd $NaHCO_3$, dried (Na_2SO_4), and concentrated. A solution of the crude product in 80% aq AcOH (100 mL) was allowed to stir at 80 °C for 1.5 h. The solvents were removed under reduced pressure and the crude product was purified over SiO_2 using hexane–EtOAc (4:1) as eluant to give pure **9** (3.5 g, 72%). Colorless oil; $[\alpha]_D^{25} = -6.4$ (*c* 1.2, $CHCl_3$); ν_{max} (neat): 3418, 2927, 2857, 1722, 1603, 1585, 1453, 1374, 1316, 1275, 1115, 1069, 1028, 756, 712 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.33–7.25 (m, 10H, Ar-H), 4.94 (d, *J* = 11.5 Hz, 1H, PhC*H*$_2$), 4.65 (d, *J* = 11.5 Hz, 1H, PhC*H*$_2$), 4.57 (br s, 2H, PhC*H*$_2$), 4.32 (d, *J* = 7.4 Hz, 1H, H-1), 4.03–3.90 (m, 2H, H-3, H-4), 3.78–3.63 (m, 2H, H-5, H-OC*H*$_{2a}$), 3.59–3.34 (m, 4H, 2H-6$_{ab}$, H-OC*H*$_{2b}$, H-2), 2.59 (br s, 2H, 2 O*H*), 1.66–1.59 (m, 2H, C*H*$_2$), 1.38–1.08 [m, 10H, $(CH_2)_5$], 0.87–0.85 (m, 3H, C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.2–126.4 (Ar-C), 102.4 (C-1), 77.8 (C-2), 73.2 (C-3), 72.4 (C-5), 72.1 (PhCH_2), 71.9 (PhCH_2), 69.9 (OCH_2), 68.6 (C-4), 67.6 (C-6), 30.6 (CH_2), 28.5 (CH_2), 28.1 (CH_2), 28.0 (CH_2), 24.9 (CH_2), 21.4 (CH_2), 12.8 (CH_3); ESI-MS: *m/z* 495.2 $[M+Na]^+$; Anal. Calcd for $C_{28}H_{40}O_6$ (472.28): C, 71.16; H, 8.53. Found: C, 71.0; H, 8.75.

4.3. Octyl 4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside (2)

To a solution of compound **9** (3.0 g, 6.34 mmol) in dry DMF (10 mL) were added triethyl orthoacetate (8.0 mL, 43.64 mmol) followed by *p*-TsOH (100 mg) and the reaction mixture was allowed to stir at room temperature for 2 h. To the reaction mixture was added water (100 mL) and then was extracted with EtOAc (100 mL) after stirring at room temperature for 30 min. The organic layer was dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 using hexane–EtOAc (5:1) as eluant to give pure **2** (2.5 g, 76%). Colorless oil; $[\alpha]_D^{25} = -9.1$ (*c* 1.2, $CHCl_3$); ν_{max} (neat): 3469, 3031, 2927, 2857, 1744, 1455, 1373, 11238, 1173, 1102, 1079, 752, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.33–7.25 (m, 10H, Ar-H), 5.36 (d, *J* = 3.2 Hz, 1H, H-4), 4.96 (d, *J* = 11.3 Hz, 1H, PhC*H*$_2$), 4.65 (d, *J* = 11.5 Hz, 1H, PhC*H*$_2$), 4.54 (d, *J* = 11.9 Hz, 1H, PhC*H*$_2$), 4.45 (d, *J* = 11.9 Hz, 1H, PhC*H*$_2$), 4.36 (d, *J* = 7.7 Hz, 1H, H-1), 3.97–3.93 (m, 1H, OC*H*$_{2a}$), 3.74–3.71 (m, 2H, H-6$_{ab}$), 3.56–3.48 (m, 3H, H-3, H-5, OC*H*$_{2b}$), 3.47–3.44 (dd, *J* = 7.8, 7.8 Hz, 1H, H-2), 2.05 (s, 3H, COC*H*$_3$), 1.30–1.25 [m, 12H, $(CH_2)_6$], 0.87 (t, *J* = 6.5 Hz, 3H, C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.1 (*C*OCH$_3$), 138.7–128.2 (Ar-C), 104.1 (C-1), 79.6 (C-2), 75.1 (C-3), 74.0 (PhCH_2), 72.9 (PhCH_2), 72.4 (C-5), 70.7 (OCH_2), 70.0 (C-6), 68.7 (C-4), 32.2 (CH_2), 30.1 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 26.6 (CH_2), 23.1 (CH_2), 21.2 (COCH_3), 14.5 (CH_3); ESI-MS: *m/z* 537.2 $[M+Na]^+$; Anal. Calcd for $C_{30}H_{42}O_7$ (514.29): C, 70.01; H, 8.23. Found: C, 69.78; H, 8.45.

4.4. Octyl [2-*O*-acetyl-4-*O*-benzyl-3-*O*-(4-methoxybenzyl)-α-L-rhamnopyranosyl]-(1→3)-4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside (10)

To a solution of compound **2** (2.0 g, 3.88 mmol) and compound **3** (2.1 g, 4.56 mmol) in anhydrous CH_2Cl_2 (20 mL) were added MS 4 Å (3 g) and reaction mixture was allowed to stir at room temperature for 30 min under argon. The reaction mixture was cooled to −40 °C and *N*-iodosuccinimide (NIS; 1.2 g, 5.33 mmol) followed by TMSOTf (20 μL) were added to it. The reaction mixture was allowed to stir at same temperature for 1 h, filtered through a Celite bed®, and washed with CH_2Cl_2 (100 mL). The organic layer was washed with 5% aq $Na_2S_2O_3$, 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 **10** (2.8 g, 79%). Colorless oil; $[\alpha]_D^{25} = +1.1$ (*c* 1.2, $CHCl_3$); ν_{max} (neat): 3031, 2929, 2858, 1746, 1613, 1514, 1455, 1370, 1237, 1174, 1140, 1099, 1078, 1060, 985, 823, 754, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.31–7.23 (m, 15H, Ar-H), 7.20 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.79 (d, *J* = 8.6 Hz, 2H, Ar-H), 5.42–5.40 (m, 1H, H-2$_B$), 5.31 (d, *J* = 3.1 Hz, 1H, H-4$_A$), 5.05 (br s, 1H, H-1$_B$), 4.89 (d, *J* = 10.9 Hz, 1H, PhC*H*$_2$), 4.85 (d, *J* = 11.7 Hz, 1H, PhC*H*$_2$), 4.62 (d, *J* = 10.9 Hz, 1H, PhC*H*$_2$), 4.58 (d, *J* = 11.0 Hz, 2H, PhC*H*$_2$), 4.54 (d, *J* = 11.8 Hz, 1H, PhC*H*$_2$), 4.45 (d, *J* = 11.8 Hz, 1H, PhC*H*$_2$), 4.36 (d, *J* = 10.9 Hz, 1H, PhC*H*$_2$), 4.35 (d, *J* = 7.0 Hz, 1H, H-1$_A$), 3.98–3.91 (m, 1H, OC*H*$_{2a}$), 3.89–3.79 (m, 1H, H-5$_B$), 3.76 (s, 3H, OC*H*$_3$), 3.77–3.69 (m, 3H, H-3$_A$, H-3$_B$, H-5$_A$), 3.63–3.56 (dd, *J* = 7.8 Hz each, 1H, H-2$_A$), 3.53–3.47 (m, 3H, H-6$_{abA}$, OC*H*$_{2b}$), 3.32 (t, *J* = 9.4 Hz each, 1H, H-4$_B$), 2.07 (s, 3H, COC*H*$_3$), 2.00 (s, 3H, COC*H*$_3$), 1.65–1.61 (m, 2H, C*H*$_2$), 1.28–1.23 [m, 13H, $(CH_2)_5$, C*H*$_3$], 0.87 (t, *J* = 4.0 Hz, 3H, C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.7 (2C, 2*C*OCH$_3$), 159.2–113.7 (Ar-C), 103.9 (C-1$_A$), 99.2 (C-1$_B$), 79.5 (C-4$_B$), 79.4 (C-2$_A$), 77.2 (C-3$_A$), 75.4 (C-3$_B$), 74.9 (PhCH_2), 74.5 (PhCH_2), 73.7 (PhCH_2), 72.6 (C-5$_A$), 71.4 (PhCH_2), 70.3 (OCH_2) 69.7 (C-5$_B$), 68.9 (C-2$_B$), 68.5 (C-4$_A$), 68.4 (C-6$_A$), 55.1 (OCH_3), 31.8 (CH_2), 29.8 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 26.2 (CH_2), 22.7 (CH_2), 21.0 (COCH_3), 20.7 (COCH_3), 18.1 (CH_3), 14.2 (CH_3); ESI-MS: *m/z* 935.4 $[M+Na]^+$; Anal. Calcd for $C_{53}H_{68}O_{13}$ (912.46): C, 69.71; H, 7.51. Found: C, 69.50; H, 7.75.

4.5. Octyl [2,4-di-*O*-benzyl-3-*O*-(4-methoxybenzyl)-α-L-rhamnopyranosyl]-(1→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (11)

To a solution of compound **10** (2.6 g, 2.85 mmol) in dry DMF (10 mL) were added powdered NaOH (1.0 g, 25.0 mmol), tetrabutylammonium bromide (200 mg) and benzyl bromide (1.2 mL, 10.09 mmol) and the reaction mixture was allowed to stirred at room temperature for 4 h. The reaction mixture was poured into water and extracted with EtOAc (100 mL). The organic layer was washed with water, dried (Na_2SO_4), and concentrated. The crude product was purified over SiO_2 using hexane–EtOAc (7:1) as eluant to give pure **11** (2.3 g, 80%). Colorless oil; $[\alpha]_D^{25} = -7$ (*c* 1.2, $CHCl_3$); ν_{max} (neat): 3031, 2929, 2858, 1746, 1613, 1514, 1455, 1370, 1237, 1174, 1099, 1078, 1060, 985, 823, 754, 699 cm^{-1}; ^1H NMR

(300 MHz, $CDCl_3$): δ 7.34–7.18 (m, 25H, Ar-H), 7.15 (d, J = 8.5 Hz, 2H, Ar-H), 6.73 (d, J = 8.5 Hz, 2H, Ar-H), 5.27 (br s, 1H, H-1_B), 4.98 (d, J = 12.0 Hz, 1H, PhCH_2), 4.94 (d, J = 11.4 Hz, 1H, PhCH_2), 4.83 (d, J = 11.7 Hz, 1H, PhCH_2), 4.67–4.39 (m, 7H, PhCH_2), 4.37–4.32 (m, 3H, H-1_A, PhCH_2), 3.97–3.87 (m, 1H, OCH_{2a}), 3.84–3.74 (m, 6H, H-2_A, H-2_B, H-4_A, H-5_B, H-6_{abA}), 3.69 (s, 3H, OCH_3), 3.61–3.51 (m, 4H, H-3_A, H-3_B, H-4_B, H-5_A), 3.49–3.42 (m, 1H, OCH_{2b}), 1.60–1.56 (m, 2H, CH_2), 1.33 (d, J = 6.1 Hz, 3H, CCH_3), 1.32–1.20 [m, 10H, (CH_2)$_5$], 0.85 (t, J = 6.5 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.1–113.7 (Ar-C), 104.1 (C-1_A), 99.4 (C-1_B), 80.2 (C-4_B), 79.7 (C-2_A), 79.3 (C-3_A), 78.0 (C-3_B),76.1 (C-2_B), 75.5 (C-5_B), 75.1 (PhCH$_2$), 74.7 (PhCH$_2$), 74.3 (PhCH$_2$), 73.6 (C-5_A), 73.5 (PhCH$_2$), 72.3 (PhCH$_2$), 71.5 (PhCH$_2$), 70.1 (OCH$_2$), 69.0 (C-4_A), 68.9 (C-6_A), 55.1 (OCH$_3$), 31.8 (CH$_2$), 29.7 (CH$_2$), 29.4 (CH$_2$), 29.2 (CH$_2$), 26.1 (CH$_2$), 22.6 (CH$_2$), 18.2 (CH$_3$), 14.1 (CH$_3$); ESI-MS: m/z 1031.5 [M+Na]$^+$; Anal. Calcd for $C_{63}H_{76}O_{11}$ (1008.54): C, 74.97; H, 7.59. Found: C, 74.80; H, 7.85.

4.6. Octyl [2,4-di-*O*-benzyl-3-*O*-(4-methoxybenzyl)-α-L-rhamnopyranosyl]-(1→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (12)

To a solution of compound **11** (2.2 g, 2.18 mmol) in CH_2Cl_2 (50 mL) was added a solution of DDQ (1.0 g, 4.40 mmol) in H_2O (20 mL) and the reaction mixture was allowed to stir at room temperature for 3 h. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and the organic layer was washed with satd $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated. The crude product was purified over SiO_2 using hexane–EtOAc (5:1) as eluant to give pure **12** (1.5 g, 77%). Colorless oil; $[\alpha]_D^{25} = -1.4$ (c 1.2, $CHCl_3$); ν_{max} (neat): 3556, 3064, 3031, 2927, 2857, 1497, 1455, 1371, 1209, 1101, 1029, 993, 912, 808, 753, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36–7.10 (m, 25H, Ar-H), 5.30 (br s, 1H, H-1_B), 5.07 (d, J = 11.5 Hz, 1H, PhCH_2), 4.89 (d, J = 12.5 Hz, 1H, PhCH_2), 4.88 (d, J = 12.5 Hz, 1H, PhCH_2), 4.64–4.56 (m, 3H, PhCH_2), 4.47 (d, J = 11.9 Hz, 1H, PhCH_2), 4.42 (d, J = 11.9 Hz, 1H, PhCH_2), 4.36 (d, J = 7.0 Hz, 1H, H-1_A), 4.22 (d, J = 11.7 Hz, 1H, PhCH_2), 4.00 (d, J = 11.7 Hz, 1H, PhCH_2), 3.96–3.86 (m, 2H, H-3_A, OCH_{2a}), 3.83–3.77 (m, 4H, H-2_A, H-3_B, H-6_{abA}), 3.69–3.68 (m, 1H, H-2_B), 3.61–3.58 (m, 3H, H-4_A, H-5_A, H-5_B), 3.51–3.43 (m, 1H, OCH_{2b}), 3.29 (t, J = 9.4 Hz, 1H, H-4_B), 1.62–1.59 (m, 2H, CH_2), 1.32 (d, J = 6.2 Hz, 3H, CCH_3), 1.30–1.20 [m, 10H, (CH_2)$_5$], 0.86 (t, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.9–127.3 (Ar-C), 104.1 (C-1_A), 98.4 (C-1_B), 82.1 (C-4_B), 80.0 (C-3_A), 78.8 (C-4_A), 78.4 (C-2_A), 76.1 (C-3_B), 74.9 (PhCH$_2$), 74.7 (PhCH$_2$), 74.6 (PhCH$_2$), 73.6 (C-2_B), 73.5 (PhCH$_2$), 72.2 (PhCH$_2$), 71.5 (C-5_B), 70.0 (OCH$_2$), 68.8 (C-6_A), 68.0 (C-5_A), 31.7 (CH$_2$), 29.6 (CH$_2$), 29.3 (CH$_2$), 29.2 (CH$_2$), 26.1 (CH$_2$), 22.6 (CH$_2$), 18.1 (CCH$_3$), 14.0 (CH$_3$); ESI-MS: m/z 911.4 [M+Na]$^+$; Anal. Calcd for $C_{55}H_{68}O_{10}$ (888.48): C, 74.30; H, 7.71. Found: C, 74.17; H, 7.95.

4.7. Octyl (2-*O*-acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (13)

To a solution of compound **12** (1.2 g, 1.35 mmol) and compound **5** (700 mg, 1.62 mmol) in anhydrous CH_2Cl_2 (10 mL) were added MS 4 Å (2 g) and reaction mixture was allowed to stir at room temperature for 30 min under argon. The reaction mixture was cooled to −40 °C and NIS (440 mg, 1.95 mmol) followed by TMSOTf (5 μL) were added to it. The reaction mixture was allowed to stir at same temperature for 1 h, filtered through a Celite bed®, and washed with CH_2Cl_2 (100 mL). The organic layer was washed with 5% aq $Na_2S_2O_3$, 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 **13** (1.3 g, 77%). Colorless oil; $[\alpha]_D^{25} = -5.9$ (c 1.2, $CHCl_3$); ν_{max} (neat): 3089, 3064, 3031, 2926, 2858, 1744, 1606, 1497, 1454, 1369, 1235, 1079, 913, 840, 740, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31–7.11 (m, 35H, Ar-H), 5.45–5.43 (m, 1H, H-2_C), 5.24 (br s, 1H, H-1_B), 5.00 (br s, 1H, 1_C), 4.97–4.85 (m, 3H, PhCH_2), 4.77 (d, J = 11.1 Hz, 1H, PhCH_2), 4.61–4.56 (m, 5H, PhCH_2), 4.48–4.36 (m, 3H, PhCH_2), 4.33 (d, J = 7.2 Hz, 1H, H-1_A), 4.20 (br s, 2H, PhCH_2), 4.08–4.04 (dd, J = 9.2, 2.6 Hz, 1H, H-3_A), 3.92–3.84 (m, 2H, H-3_C, OCH_{2a}), 3.82–3.74 (m, 5H, H-3_B, H-4_A, H-5_A, H-6_{abA}), 3.68 (br s, 1H, H-2_B), 3.62–3.57 (m, 4H, H-2_A, H-4_B, H-5_B, H-5_C), 3.49–3.41 (m, 1H, OCH_{2b}), 3.36 (t, J = 9.4 Hz, 1H, H-4_C), 2.07 (s, 3H, COCH_3), 1.58–1.53 (m, 2H, CH_2), 1.28 (d, J = 6.1 Hz, 3H, CCH_3), 1.27–1.20 (m, 10H, (CH_2)$_5$], 0.85 (t, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.7 (COCH$_3$), 138.8–127.2 (Ar-C), 104.1 (C-1_A), 98.8 (C-1_B), 96.2 (C-1_C), 80.9 (C-4_B), 80.0 (C-3_A), 79.8 (C-4_A), 78.3 (C-3_B), 78.2 (C-3_C), 77.9 (C-2_A), 77.2 (C-4_C), 76.0 (C-2_C), 75.2 (PhCH$_2$), 75.1 (PhCH$_2$), 74.7 (PhCH$_2$), 74.5 (PhCH$_2$), 73.7 (C-2_B), 73.5 (PhCH$_2$), 72.1 (PhCH$_2$), 71.6 (PhCH$_2$), 69.9 (OCH$_2$), 69.0 (C-5_B), 68.9 (C-5_C), 68.8 (C-6_A), 68.3 (C-5_A), 31.8 (CH$_2$), 29.7 (CH$_2$), 29.4 (CH$_2$), 29.2 (CH$_2$), 26.1 (CH$_2$), 22.7 (CH$_2$), 20.9 (COCH$_3$), 18.2 (CCH$_3$), 18.1 (CCH$_3$), 14.2 (CH$_3$); ESI-MS: m/z 1279.6 [M+Na]$^+$; Anal. Calcd for $C_{77}H_{92}O_{15}$ (1256.64): C, 73.54; H, 7.37. Found: C, 73.35; H, 7.60.

4.8. Octyl (3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (14)

A solution of compound **13** (1.2 g, 0.95 mmol) in 0.1 M CH_3ONa in CH_3OH (15 mL) was allowed to stir at room temperature for 2 h, neutralized with Dowex 50W X8 (H^+) resin. The reaction mixture was filtered and the filtrate was concentrated to give crude product, which was passed through a short pad of SiO_2 using hexane–EtOAc (3:1) as eluant to give pure **14** (1.1 g, 95%). Colorless oil; $[\alpha]_D^{25} = -15.1$ (c 1.2, $CHCl_3$); ν_{max} (neat): 3478, 3064, 3031, 2927, 2858, 1497, 1454, 1365, 1213, 1099, 1078, 1057, 1029, 994, 752, 735, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30–7.13 (m, 35H, Ar-H), 5.24 (br s, 1H, H-1_B), 5.06 (br s, 1H, H-1_C), 4.99 (d, J = 11.5 Hz, 1H, PhCH_2), 4.90–4.84 (m, 2H, PhCH_2), 4.70 (d, J = 11.1 Hz, 1H, PhCH_2), 4.63–4.53 (m, 6H, PhCH_2), 4.47 (d, J = 12.1 Hz, 1H, PhCH_2), 4.42 (d, J = 12.1 Hz, 1H, PhCH_2), 4.31 (d, J = 7.0 Hz, 1H, H-1_A), 4.25–4.17 (m, 2H, PhCH_2), 4.06–4.02 (dd, J = 9.3, 2.7 Hz, H-3_A), 3.93–3.86 (m, 2H, H-3_C, OCH_{2a}), 3.84–3.71 (m, 7H, H-2_A, H-2_C, H-3_B, H-4_A, H-4_B, H-5_B, H-6_{abA}), 3.60–3.52 (m, 4H, H-2_B, H-2_C, H-4_A, H-5_B), 3.49–3.37 (m, 2H, H-4_C, H-OCH_{2b}), 1.58–1.56 (m, 2H, CH_2), 1.28–1.19 [m, 13H, (CH_2)$_5$, CCH_3], 0.86 (t, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.8–127.1 (Ar-C), 104.1 (C-1_A), 100.6 (C-1_C), 98.9 (C-1_B), 80.8 (C-4_B), 78.0 (C-4_A), 79.9 (C-3_A), 79.8 (C-3_C), 78.3 (C-3_B), 78.2 (C-2_A), 77.5 (C-2_B), 76.2 (C-4_C), 75.1 (PhCH$_2$), 75.0 (PhCH$_2$) 74.8 (PhCH$_2$), 74.5 (PhCH$_2$), 73.7 (C-2_C), 73.5 (PhCH$_2$), 72.0 (PhCH$_2$), 71.9 (PhCH$_2$), 69.9 (OCH$_2$), 69.0 (C-5_C), 68.8 (C-6_A), 68.7 (C-5_B), 68.0 (C-5_A), 31.8 (CH$_2$), 29.7 (CH$_2$), 29.4 (CH$_2$), 29.2 (CH$_2$), 26.1 (CH$_2$), 22.6 (CH$_2$), 18.2 (CH$_3$), 18.1 (CH$_3$), 14.1 (CH$_3$); ESI-MS: m/z 1237.6 [M+Na]$^+$; Anal. Calcd for $C_{75}H_{90}O_{14}$ (1214.63): C, 74.11; H, 7.46. Found: C, 74.27; H, 7.70.

4.9. Octyl (2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (15)

To a solution of compound **14** (1.0 g, 0.82 mmol) and compound **6** (390 mg, 0.98 mmol) in anhydrous CH_2Cl_2 (5 mL) were added MS 4 Å (1 g) and the reaction mixture was allowed to stir at room temperature for 30 min under argon. The reaction mixture was cooled

to −40 °C and NIS (260 mg, 1.15 mmol) followed by TMSOTf (3 μL) were added to it. The reaction mixture was allowed to stir at same temperature for 1 h, filtered through a Celite bed® and washed with CH_2Cl_2 (50 mL). The organic layer was washed with 5% aq $Na_2S_2O_3$, 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 tetrasaccharide derivative **15** (900 mg, 71%). Colorless oil; $[\alpha]_D^{25} = -16$ (*c* 1.2, $CHCl_3$); ν_{max} (neat): 3485, 3089, 3064, 3031, 2925, 2856, 1753, 1497, 1455, 1370, 1239, 1218, 1082, 911, 819, 740, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.38–7.12 (m, 40H, Ar-H), 5.27 (s, 1H, PhC*H*), 5.22 (br s, 1H, H-1_B), 5.21 (t, *J* = 9.4 Hz, H-3_D), 5.04 (br s, 1H, H-1_C), 5.03 (d, *J* = 11.2 Hz, 1H, PhCH_2), 4.99 (t, *J* = 9.4 Hz, H-2_D), 4.89 (d, *J* = 11.5 Hz, 1H, PhCH_2), 4.80 (d, *J* = 11.1 Hz, 1H, PhCH_2), 4.68 (d, *J* = 11.5 Hz, 1H, PhCH_2), 4.60–4.51 (m, 5H, PhCH_2), 4.48–4.40 (m, 4H, H-1_D, PhCH_2), 4.32 (d, *J* = 7.0 Hz, 1H, H-1_A), 4.18–4.11 (m, 2H, PhCH_2), 4.03–3.99 (dd, *J* = 9.4, 2.7 Hz, H-3_A), 3.93–3.87 (m, 1H, OCH_{2a}), 3.81–3.63 (m, 9H, H-2_A, H-2_C, H-3_B, H-3_C, H-4_A, H-4_B, H-5_A, H-6_{abA}), 3.57–3.53 (m, 3H, H-2_B, H-6_{abD}), 3.51–3.41 (m, 3H, H-5_B, H-5_C, OCH_{2b}), 3.34 (t, *J* = 9.4 Hz, 1H, H-4_D), 3.22–3.10 (m, 2H, H-4_C, H-5_D), 2.04 (s, 3H, COCH_3), 1.84 (s, 3H, COCH_3), 1.60–1.56 (m, 2H, CH_2), 1.25–1.20 [m, 13H, (CH_2)$_5$, CCH_3], 0.85 (t, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.8 (*C*OCH$_3$), 169.4 (*C*OCH$_3$), 138.8–126.1 (Ar-C), 104.1 (C-1_A), 102.9 (C-1_D), 101.3 (PhCH), 101.2 (C-1_C), 98.7 (C-1_B), 80.5 (C-4_B), 80.3 (C-4_A), 79.9 (C-3_B), 79.5 (C-3_C), 78.5 (C-3_A), 78.4 (C-2_A), 78.1 (C-2_B), 77.9 (C-4_D), 75.9 (C-5_B), 75.1 (PhCH$_2$), 75.0 (PhCH$_2$), 74.6 (2C, 2 PhCH$_2$), 73.6 (C-2_C), 73.5 (PhCH$_2$), 72.8 (PhCH$_2$), 72.1 (C-2_D), 72.0 (PhCH$_2$), 71.4 (C-3_D), 69.9 (OCH$_2$), 68.8 (3C, C-5_A, C-5_C, C-6_A), 68.6 (C-4_C), 69.0 (C-6_D), 66.0 (C-5_D), 31.8 (CH$_2$), 29.7 (CH$_2$), 29.4 (CH$_2$), 29.2 (CH$_2$), 26.1 (CH$_2$), 22.6 (CH$_2$), 20.8 (COCH$_3$), 20.6 (COCH$_3$), 18.1 (2C, 2CH$_3$), 14.1 (CH$_3$); MALDI-MS: *m/z* 1571.7 $[M+Na]^+$; Anal. Calcd for $C_{92}H_{108}O_{21}$ (1548.73): C, 71.30; H, 7.02. Found: C, 71.12; H, 7.30.

4.10. Octyl (4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (16)

A solution of compound **15** (800 mg, 0.52 mmol) in 0.1 M CH_3O-Na in CH_3OH (10 mL) was allowed to stir at room temperature for 2 h, neutralized with Dowex 50W X8 (H^+) resin. The reaction mixture was filtered and the filtrated was concentrated to give a crude product, which was passed through a short pad of SiO_2 using hexane–EtOAc (3:1) as eluant to give pure **16** (700 mg, 92%). Colorless oil; $[\alpha]_D^{25} = -9$ (*c* 1.2, $CHCl_3$); ν_{max} (neat): 3478, 3469, 3031, 2925, 2858, 1606, 1496, 1454, 1365, 1213, 1099, 1056, 1030, 751, 736, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.27–7.14 (m, 40H, Ar-H), 5.30 (s, 1H, PhC*H*) 5.20 (br s, 1H, H-1_B), 4.99 (br s, 1H, H-1_C), 4.94 (d, *J* = 11.5 Hz, 1H, PhCH_2), 4.79 (d, *J* = 11.6 Hz, 1H, PhCH_2), 4.76 (d, *J* = 11.2 Hz, 1H, PhCH_2), 4.60–4.44 (m, 7H, PhCH_2), 4.39 (d, *J* = 11.9 Hz, 1H, PhCH_2), 4.33 (d, *J* = 11.9 Hz, 1H, PhCH_2), 4.25 (d, *J* = 7.0 Hz, 1H, H-1_A), 4.13–4.05 (m, 2H, PhCH_2), 4.08 (d, *J* = 9.5 Hz, 1H, H-1_D), 3.95–3.92 (dd, *J* = 9.4, 2.8 Hz, 1H, H-3_A), 3.84–3.82 (m, 1H, OCH_{2a}), 3.79–3.77 (dd, *J* = 9.4, 3.0 Hz, 1H, H-3_C), 3.73–3.65 (m, 8H, H-2_A, H-2_D, H-3_B, H-4_A, H-4_B, H-5_A, H-6_{abA}), 3.63 (br s, 1H, H-2_B), 3.57 (t, *J* = 9.1 Hz each, 1H, H-3_D), 3.52–3.48 (m, 3H, H-2_C, H-6_{abD}), 3.46–3.38 (m, 3H, H-4_D, H-5_B, OCH_{2b}), 3.35–3.31 (m, 2H, H-4_C, H-5_C), 2.95–2.91 (m, 1H, H-5_D), 1.54–1.49 (m, 2H, CH_2), 1.26–1.14 [m, 16H, (CH_2)$_5$, 2CH_3], 0.77 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.9–126.7 (Ar-C), 106.3 (C-1_D), 104.5 (C-1_A), 102.1 (2C, C-1_C, PhCH), 99.2 (C-1_B), 81.1 (C-4_B), 80.8 (C-4_A), 80.5 (C-3_B), 80.3 (2C, C-3_A, C-3_C), 79.9 (C-2_A), 79.0 (C-2_B), 78.9 (C-4_D), 76.5 (C-5_B), 75.5 (2C, C-2_C, PhCH$_2$), 75.3 (C-5_C), 75.1 (PhCH$_2$), 75.0 (PhCH$_2$), 74.1 (C-4_D), 74.0 (2C, 2 PhCH$_2$), 73.7 (C-3_D), 72.4 (PhCH$_2$), 70.4 (PhCH$_2$), 69.3 (C-6_A), 69.2 (2C, C-5_A, OCH$_2$), 68.8 (C-4_C), 68.7 (C-6_D), 66.9 (C-5_D), 32.2 (CH$_2$), 30.1 (CH$_2$), 29.8 (CH$_2$), 29.6 (CH$_2$), 26.5 (CH$_2$), 23.1 (CH$_2$), 18.5 (CCH$_3$), 18.4 (CCH$_3$), 14.5 (CH$_2$CH$_3$); ESI-MS: *m/z* 1487.7 $[M+Na]^+$; Anal. Calcd for $C_{88}H_{104}O_{19}$ (1464.71): C, 72.11; H, 7.15. Found: C, 71.88; H, 7.40.

4.11. Ethyl (2,3,5,6-tetra-*O*-benzyl-α-D-galactofuranosyl)-(1→2)-3,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (17)

A solution of compound **4** (500 mg, 1.29 mmol) and compound **7** (1.1 g, 1.60 mmol) in anhydrous CH_2Cl_2 (10 mL) was cooled to −15 °C. To the cooled reaction mixture was added TMSOTf (25 μL) and it was allowed to stir at same temperature for 1 h. The reaction mixture was diluted with CH_2Cl_2 (100 mL) and the organic layer was washed with satd $NaHCO_3$, water, dried (Na_2SO_4), and concentrated. The crude product was purified over SiO_2 using hexane–EtOAc (5:1) as eluent to give pure **17** (860 mg, 73%). Colorless oil; $[\alpha]_D^{25} = +16$ (*c* 1.2, $CHCl_3$); ν_{max} (neat): 3087, 3032, 2856, 1742, 1739, 1615, 1560, 1475, 1372, 1239, 1173, 1097, 1072, 1059, 989, 911, 823, 755, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.24–7.11 (m, 30H, Ar-H), 5.32 (br s, 1H, H-1_E), 5.23 (d, *J* = 4.3 Hz, 1H, H-1_F), 4.72 (d, *J* = 11.0 Hz, 1H, PhCH_2), 4.70 (d, *J* = 11.4 Hz, 1H, PhCH_2), 4.65 (d, *J* = 11.6 Hz, 1H, PhCH_2), 4.55 (d, *J* = 11.9 Hz, 1H, PhCH_2), 4.50–4.31 (m, 8H, PhCH_2), 4.29–4.24 (m, 1H, H-3_F), 4.20–4.18 (m, 1H, H-2_E), 4.05–4.02 (m, 1H, H-2_F), 3.95–3.91 (m, 2H, H-4_F, H-5_F), 3.73–3.69 (m, 2H, H-3_E, H-5_E), 3.55–3.44 (m, 3H, H-4_E, H-6_{abF}), 2.54–2.49 (m, 2H, SCH_2CH$_3$), 1.19 (t, *J* = 7.4 Hz, 3H, SCH$_2$CH_3), 1.11 (d, *J* = 6.2 Hz, 3H, CCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.3–127.7 (Ar-C), 98.0 ($J_{C\text{-}1/H\text{-}1}$ = 170 Hz, C-1_F, α-D-Gal*f*), 84.4 (C-1_E, $J_{C\text{-}1/H\text{-}1}$ = 171 Hz, α-L-Rha*p*), 81.4 (C-2_F), 81.3 (C-4_E), 81.2 (C-3_F), 81.1 (C-4_F), 79.7 (C-5_E), 79.4 (C-3_E), 74.1 (C-2_E), 73.7 (2C, 2 PhCH$_2$), 72.9 (PhCH$_2$), 72.5 (PhCH$_2$), 72.3 (PhCH$_2$), 71.9 (PhCH$_2$), 70.4 (C-6_F), 68.9 (C-5_F), 26.1 (SCH$_2$CH$_3$), 18.5 (CCH$_3$), 15.6 (SCH$_2$CH$_3$); ESI-MS: *m/z* 933.4 $[M+Na]^+$; Anal. Calcd for $C_{56}H_{62}O_9S$ (910.41): C, 73.82; H, 6.86. Found: C, 73.61; H, 7.10.

4.12. Octyl (2,3,5,6-tetra-*O*-benzyl-α-D-galactofuranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (18)

To a solution of compound **16** (600 mg, 0.41 mmol) and compound **17** (400 mg, 0.44 mmol) in anhydrous CH_2Cl_2 (10 mL) were added MS 4 Å (2 g) and reaction mixture was allowed to stir at room temperature for 30 min under argon. The reaction mixture was cooled to −40 °C and NIS (120 mg, 0.53 mmol) followed by TMSOTf (2 μL) were added to it. The reaction mixture was allowed to stir at same temperature for 1 h, filtered through a Celite bed®, and washed with CH_2Cl_2 (50 mL). The organic layer was washed with 5% aq $Na_2S_2O_3$, 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 hexasaccharide derivative **18** (660 mg, 70%). Colorless oil; $[\alpha]_D^{25} = -7.2$ (*c* 1.2, $CHCl_3$); ν_{max} (neat): 3666, 3064, 3030, 2926, 2857, 1951, 1728, 1611, 1585, 1511, 11496, 1454, 1371, 1311, 1238, 1175, 1081, 911, 818, 740, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.32–7.20 (m, 70H, Ar-C), 5.40 (br s, 1H, H-1_B), 5.37 (s, 1H, PhC*H*), 5.28 (d, *J* = 3.8 Hz, 1H, H-1_E), 5.23 (br s, 1H, H-1_C), 5.05 (br s, 1H, H-1_F), 5.19–4.29 (m, 27H, H-3_F, PhCH_2), 4.30 (d, *J* = 9.1 Hz, 1H, H-1_A), 4.20–4.19 (m, 1H, H-2_E), 4.18 (d, *J* = 7.5 Hz, 1H, H-1_D), 4.13–4.07 (m, 2H, H-2_F, H-3_A), 4.02–3.98 (m, 2H, H-4_F, H-5_F), 3.91–3.87 (m, 2H, H-3_C, OCH_{2a}), 3.82–3.67 (m, 11H, H-2_A, H-2_D, H-3_B, H-3_D, H-3_E, H-4_A, H-4_B, H-5_A, H-5_E, H-6_{abA}), 3.66–3.36

(m, 12H, H-2_B, H-2_C, H-4_C, H-4_D, H-4_E, H-5_B, H-2_C, H-6_{abD}, H-6_{abF}, OCH_{2b}), 3.08–3.04 (m, 1H, H-5_D), 1.60–1.54 (m, 2H, CH_2), 1.31–1.20 (m, 16H, (CH_2)$_5$, 2CH_3), 0.92 (d, J = 6.2 Hz, 1H, CH_3), 0.85 (t, J = 6.9 Hz, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.9–127.8 (Ar-C), 106.7 ($J_{C\text{-}1/H\text{-}1}$ = 158.5 Hz, C-1_A, β-D-Gal$p$), 104.5 ($J_{C\text{-}1/H\text{-}1}$ = 155.9 Hz, C-1_D, β-D-Glc$p$), 101.7 (PhCH), 101.2 ($J_{C\text{-}1/H\text{-}1}$ = 171 Hz, C-1_E, α-L-Rha$p$), 99.4 ($J_{C\text{-}1/H\text{-}1}$ = 172.3 Hz, C-1_C, α-L-Rha$p$), 98.3 ($J_{C\text{-}1/H\text{-}1}$ = 168.5 Hz, C-1_F, α-D-Gal$f$), 97.4 ($J_{C\text{-}1/H\text{-}1}$ = 170 Hz, C-1_B, α-L-Rha$p$), 84.3 (C-4_A), 82.9 (C-4_B), 81.8 (C-3_B), 81.2 (C-2_A), 80.9 (2C, C-3_A, C-3_C), 80.5 (C-2_F), 80.4 (C-4_E), 80.3 (C-3_F), 79.7 (C-4_F), 79.1 (C-3_D), 79.0 (C-2_B), 78.9 (C-5_E), 78.6 (C-3_E), 77.0 (C-5_B), 76.8 (C-2_C), 76.5 (C-5_A), 75.6 (PhCH_2), 75.3 (C-2_D), 75.1 (PhCH_2), 75.0 (PhCH_2), 74.1 (C-4_D), 74.0 (2C, 2 PhCH_2), 73.9 (PhCH_2), 73.8 (C-2_E), 73.6 (PhCH_2), 73.0 (PhCH_2), 72.8 (PhCH_2), 72.5 (PhCH_2), 72.4 (PhCH_2), 72.1 (PhCH_2), 72.0 (PhCH_2), 70.4 (OCH_2), 70.3 (C-6_F), 69.3 (C-6_A), 69.3 (C-5_C), 68.9 (C-6_D), 68.2 (C-5_F), 67.3 (C-4_C), 66.2 (C-5_D), 32.4 (CH_2), 30.1 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 26.5 (CH_2), 23.1 (CH_2), 18.6 (CH_3), 18.5 (CH_3), 18.4 (CH_3), 14.5 (CH_3); MALDI-MS: m/z 2336.1 [M+Na]$^+$; Anal. Calcd for $C_{142}H_{160}O_{28}$ (2313.11): C, 73.68; H, 6.97. Found: C, 73.46; H, 7.20.

4.13. Octyl (α-D-galactofuranosyl)-(1→2)-(α-L-rhamnopyranosyl)-(1→3)-(β-D-mannopyranosyl)-(1→2)-(α-L-rhamnopyranosyl)-(1→3)-(α-L-rhamnopyranosyl)-(1→3)-β-D-galactopyranoside (1)

To a solution of compound **18** (550 mg, 0.24 mmol) in dry CH_2Cl_2 (5 mL) was added Dess–Martin periodinane (200 mg, 0.47 mmol) and the reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and the organic layer was washed with 5% $Na_2S_2O_3$ and water in succession. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude ketone, which was used in the next step without purification. To a solution of the crude ketone in CH_3OH (10 mL) was slowly added $NaBH_4$ (100 mg, 2.64 mmol) portionwise at 0 °C. The reaction mixture was allowed to stir at room temperature for 12 h and concentrated under reduced pressure. The crude product was dissolved in CH_2Cl_2 (50 mL) and successively washed with 1 M HCl, satd $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated. The crude product was purified over SiO_2 using hexane–EtOAc (4:1) as eluant to afford pure hexasaccharide derivative **19** (390 mg). To a solution of the crude product (390 mg, 0.17 mmol) 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 24 h. The reaction mixture was filtered through a Celite® bed and then washed with CH_3OH–H_2O (60 mL; 4:1 v/v). The combined filtrate was evaporated under reduced pressure to furnish compound **1**, which was purified through a Sep-Pak® C_{18} column using water and CH_3OH sequentially as eluant to give pure compound **1** (110 mg, 62%). White powder; $[\alpha]_D^{25} = -27$ (c 1.0, CH_3OH); ν_{max} (KBr): 3401, 2925, 2854, 1736, 1649, 1460, 1379, 1121, 1073, 1044, 985, 915, 805, 725 cm^{-1}; ^{1}H NMR (500 MHz, CD_3OD): δ 5.30 (br s, 1H, H-1_C), 5.07 (br s, 1H, H-1_E), 4.94 (br s, 1H, H-1_B), 4.83 (d, J = 4.8 Hz, 1H, H-1_F), 4.46 (br s, 1H, H-1_D), 4.36 (d, J = 7.8 Hz, 1H, H-1_F), 4.14 (d, J = 4.8 Hz, 1H, H-1_F), 3.97–3.96 (m, 2H, H-2_B, H-2_D), 3.91–3.87 (m, 2H, H-2_C, H-3_F), 3.84–3.81 (m, 2H, H-3_C, H-3_D), 3.80–3.74 (m, 4H, H-2_E, H-3_B, H-3_E, H-6_{aD}), 3.73–3.69 (m, 3H, H-4_D, H-5_E, H-6_{aA}), 3.64–3.61 (m, 3H, H-5_B, H-6_{abF}), 3.56–3.49 (m, 5H, H-3_A, H-5_C, H-6_{bA}, H-6_{bD}, OCH_{2a}), 3.45–3.38 (m, 6H, H-4_A, H-4_F, H-5_A, H-5_D, H-5_F, OCH_{2b}), 3.29–3.23 (m, 4H, H-2_A, H-4_B, H-4_C, H-4_E), 1.54–1.50 (m, 2H, CH_2), 1.21–1.15 (m, 19H, (CH_2)$_5$, 3CH_3), 0.80 (t, J = 6.7 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, CD_3OD): δ 105.5 ($J_{C\text{-}1/H\text{-}1}$ = 158.5 Hz, C-1_A, β-D-Gal$p$), 104.0 ($J_{C\text{-}1/H\text{-}1}$ = 156 Hz, C-1_D, β-D-Man$p$), 102.8 ($J_{C\text{-}1/H\text{-}1}$ = 171 Hz, C-1_B, α-L-Rha$p$), 102.4 ($J_{C\text{-}1/H\text{-}1}$ = 173.5 Hz, C-1_C, α-L-Rha$p$), 101.8 ($J_{C\text{-}1/H\text{-}1}$ = 169 Hz, C-1_F, α-D-Gal$f$), 100.1 ($J_{C\text{-}1/H\text{-}1}$ = 172.3 Hz, C-1_E, α-L-Rha$p$), 83.5 (C-4_F), 81.5 (C-4_A), 81.4 (C-5_F), 80.6 (C-5_D), 79.8 (C-3_D), 78.9 (C-4_D), 77.6 (C-4_E), 77.1 (C-2_A), 75.4 (C-5_A), 75.1 (C-4_B), 73.7 (C-4_C), 73.5 (C-2_F), 73.2 (C-3_B), 72.5 (C-3_A), 71.1 (C-3_F), 71.0 (C-3_E), 70.8 (C-2_C), 70.5 (C-2_E), 70.4 (C-2_D), 69.9 (OCH_2), 69.4 (C-5_C), 69.3 (C-2_B), 69.1 (C-5_E), 69.0 (C-5_B), 68.8 (C-3_C), 63.4 (C-6_A), 61.7 (C-6_F), 61.2 (C-6_D), 32.0 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 26.1 (CH_2), 22.7 (CH_2), 17.0 (2C, 2CH_3), 16.8 (CH_3), 13.4 (CH_3); ESI-MS: m/z 1077.4 [M+Na]$^+$; Anal. Calcd for $C_{44}H_{78}O_{28}$ (1054.46): C, 50.09; H, 7.45. Found: C, 49.86; H, 7.72.

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