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Concise synthesis of a heptasaccharide antigen found in the cell-wall lipopolysaccharide of *Mycobacterium gordonae* strain 990

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Abstract A straight forward synthesis of a heptasaccharide part of the cell-wall lipopolysaccharide of *Mycobacterium gordonae* strain 990, known to have antigenicity, has been achieved in excellent yield. Judicious choice of protecting groups in the intermediates played a significant role throughout the synthesis. Most of the intermediate steps furnished satisfactory yield.

Keywords Oligosaccharides · Glycosylations · Antigens · Vaccines · *Mycobacterium gordonae* 990

Introduction

Since the emergence of acquired immunodeficiency syndrome (AIDS), mycobacterial infection has become a serious concern [1, 2]. In AIDS patients, infections due to non-tubercular mycobacteria (NTM) other than tuberculosis are gradually increasing causing severe problems associated with unnecessary treatments with therapeutics [3, 4]. Among several NTM species isolated from soil and water [5], *Mycobacterium gordonae* (*M. gordonae*) is one of the important organisms, which requires extra attention. Other than soil and water *M. gordonae* can be found in the sputum, urine and gastric juice in human [6]. Earlier it was considered as a friendly organism and often called as "*Mycobacterium aque* or tap-water bacillus" [7]. Afterwards, a number of infections in the skin, soft tissues, respiratory tract, liver and immunosuppression associated with this species have been reported [8, 9]. In HIV infected patients this particular species causes serious pulmonary infections, which are indistinguishable from the tuberculosis. As a result, treatment with currently available antitubercular drugs e.g. isoniazid, pyrazinamide, ethambutol and cycloserine can not cure the patient as *M. gordonae* is resistant to these drugs [8, 9]. Therefore, urgent attention is essential to identify such atypical *Mycobacteria* from other species of *Mycobacteria* for the proper drug administration and thereby AIDS management.

M. gordonae 990 strain is a member of atypical NTM, which causes several pulmonary infections in AIDS patients. The cell-wall of this particular strain contains a large number of glycolipids and some of them are antigenic in nature. Brennan *et al*. have isolated and determined the structure of a unique trehalose linked heptasaccharide moiety having antigenic activity (Fig. 1) [10]. As an antigenic oligosaccharide can produce specific immune response in the host by developing specific antibodies, this particular heptasaccharide moiety could also provide useful serodiagnosis of the mycobacterial infection by developing specific antibodies and thus help to design an antibacterial vaccine candidate against this strain.

Although, glycoconjugate vaccines are highly effective to control several bacterial infections, numbers of chemically synthesized carbohydrate vaccines are limited. In most of the glycoconjugate vaccines, the oligosaccharide parts were isolated from natural sources. However, a number of reports appeared in the literature for the development of the synthetic glycoconjugate vaccines against several bacterial infections [11–21]. As cell-wall oligosaccharides having antigenicity are attractive targets for the development of glycoconjugate vaccine candidates, their limited availability

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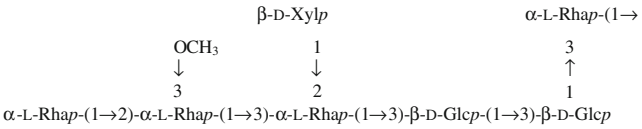


Fig. 1 Structure of the heptasaccharide antigen found in the cell-wall of *M. gordonae* 990

from the natural source set the challenges to the organic chemists to develop concise synthetic protocols for their large scale preparation. In order to develop a specific immune response in the host with the synthetic glycoconjugate vaccine candidate, it is essential to link the synthetic oligosaccharide moiety with a protein through a spacer linkage. Therefore, it is recommended that the reducing end of the synthetic oligosaccharide moiety should contain a temporary protecting group, which can be removed during the process of conjugation with the protein. Although, synthesis of a tetrasaccharide methyl glycoside related to the heptasaccharide moiety was reported earlier [22], total synthesis of the full heptasaccharide with temporary anomeric protecting group was not attempted. In this communication, we present a concise chemical synthesis of the full heptasaccharide antigen found in the cell-wall lipopolysaccharide of *M. gordonae* strain 990 as its 4-methoxyphenyl glycoside (Fig. 2).

Results and discussion

The synthesis of the target heptasaccharide **1** was achieved by judicious functional group manipulations and stereoselective glycosylations. Several differentially protected monosaccharide derivatives (Fig. 3), prepared from commercially available sugars using reported methodologies [23] have been used to construct the target molecule **1**.

Ethyl 4-*O*-benzyl-2-*O*-(4-methoxybenzyl)-3-*O*-methyl-1-thio-α-L-rhamnopyranoside **(6)** was prepared from ethyl 4-*O*-benzyl-1-thio-α-L-rhamnopyranoside **(8)** [24] in excellent yield following a tin mediated selective methylation followed by 4-methoxybenzylation under alkaline conditions (Scheme 1).

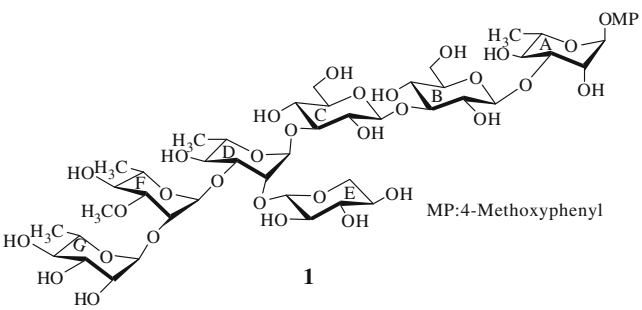


Fig. 2 Chemical structure of the synthesized heptasaccharide as its 4-methoxyphenyl glycoside (1)

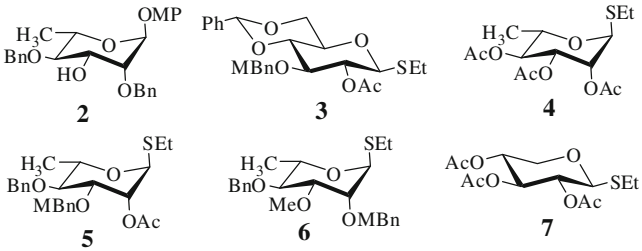
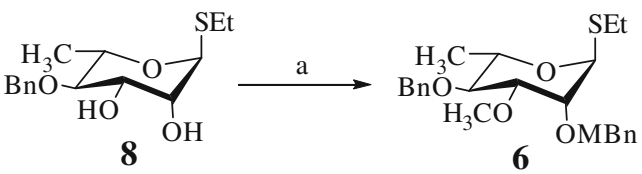
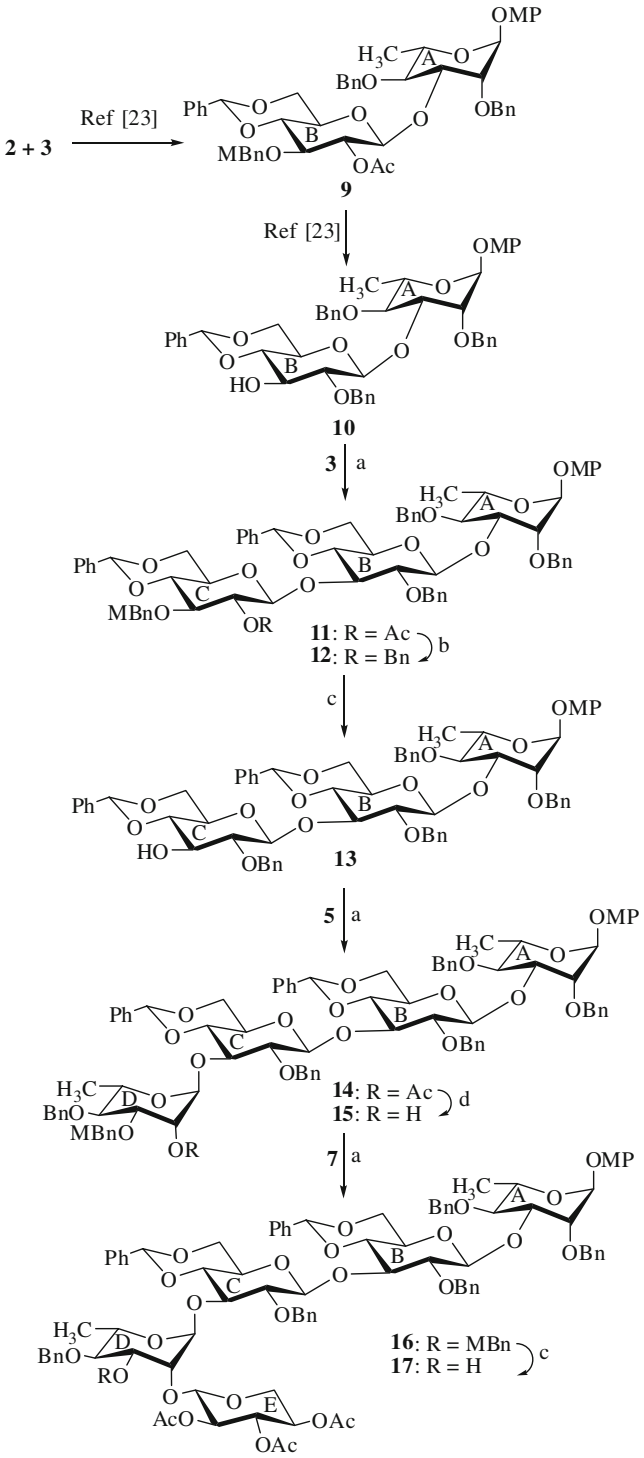


Fig. 3 Suitably protected monosaccharide building blocks used for the construction of heptasaccharide (1) as its 4-methoxyphenyl glycoside

Sequential stereoselective glycosylations and protecting group manipulations for the synthesis of target heptasaccharide 1 is presented in Scheme 1 and 2. Compounds **2** and **3** were coupled together stereoselectively to furnish disaccharide derivative **9**, which was transformed into the disaccharide acceptor **10** following an earlier reported reaction conditions [23]. *N*-Iodosuccinimide (NIS)-trimethylsilyl trifluoromethanesulfonate (TMSOTf) [25, 26] mediated β-selective glycosylation of disaccharide derivative **10** with thioglycoside **3** afforded trisaccharide derivative **11** in 80% yield, which was benzylated to furnish trisaccharide derivative **12** under a one-pot deacetylation-benzylation protocol reported earlier [27]. Exclusive formation of β-glycosidic linkage in the compound **11** was achieved, due to the presence of an *O*-acetyl group at the C-2 position of the thioglycoside donor **3**, which was confirmed by the signature peaks that appeared in its NMR spectra e. g. δ [5.49 (s, PhC*H*), 5.27 (br s, H-1_A), 5.17 (s, PhC*H*), 4.88 (d, *J*=8.0 Hz, H-1_B), 4.91 (d, *J*=8.0 Hz, H-1_C) in ^{1}H NMR and δ [103.6 (C-1_C), 101.6 (Ph*C*H), 100.8 (Ph*C*H), 100.6 (C-1_B), 97.3 (C-1_A)] in ^{13}C NMR spectra. Oxidative removal of 4-methoxybenzyl group in compound **12** using DDQ [28] afforded the trisaccharide acceptor **13**, which was coupled with 2-*O*-acetylated thioglycoside donor **5** to furnish tetrasaccharide derivative **14** in 77% yield exploiting neighboring group participation. Signals in the NMR spectra of compound **14** confirmed the α-selective 1,2-*trans* glycosylation [δ 5.30 (br s, 1 H, H-1_A), 4.97 (br s, 1 H, H-1_D) in ^{1}H NMR and δ 103.4 (C-1_C), 102.1 (C-1_B), 101.5 (Ph*C*H), 101.2 (Ph*C*H), 97.8 (C-1_D), 97.3 (C-1_A) in ^{13}C NMR spectra]. Saponification of compound **14** gave tetrasaccharide acceptor **15**, which on NIS-TMSOTf mediated glycosylation with the D-xylose

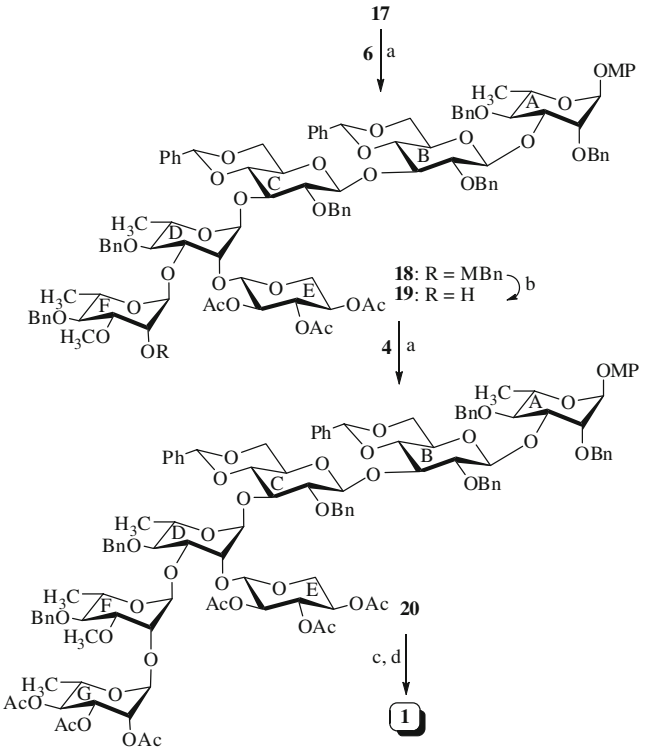


Scheme 1 Reagents: *a* (1) Bu_2SnO, toluene, 110°C, 4 h, then iodomethane, TBAB, r t, 48 h; (2) 4-methoxybenzyl chloride, NaOH, DMF, r t, 3 h, 75% in two steps



Scheme 2 Reagents: *a* *N*-Iodosuccinimide, TMSOTf, CH_2Cl_2, MS-4 Å, −40°C, 80% for 11, 77% for 14, 78% for 16; *b* benzyl bromide, NaOH, TBAB, DMF, r t, 3 h, 85%; *c* DDQ, CH_2Cl_2-H_2O, r t, 2 h, 77% for 13 and 80% for 17; *d* CH_3ONa, CH_3OH, r t, 2 h, quantitative

derived thioglycoside donor **7** furnished pentasaccharide derivative **16** in 78% yield. As mentioned earlier stereoselective 1,2-*trans* glycosylation was achieved, due to the presence of an *O*-acetyl group at the C-2 position of compound **7**, which was confirmed from the 1D and 2D NMR spectra of compound 16 [δ 4.10 (d, J=7.2 Hz, H-1_E, β-D-Xylp) in ^{1}H NMR and 103.4 (C-1_C), 102.5 (C-1_B), 101.9 (C-1_E), 101.5 (Ph*C*H), 101.3 (Ph*C*H), 99.2 (C-1_D), 97.2 (C-1_A) in ^{13}C NMR]. Compound **16** was allowed to react with DDQ to furnish pentasaccharide acceptor **17** via oxidative removal of 4-methoxybenzyl group (Scheme 2). Compound **17** was allowed to couple with thioglycoside donor 6 under NIS-TMSOTf mediated glycosylation conditions to afford hexasaccharide **18**. Although in this case, due to the presence of the 4-methoxybenzyl group, a non-participating functional group at the C-2 position of L-rhamnosyl donor, there was a chance of formation of some β-L-rhamnose linked hexasaccharide derivative together with required compound 18, spectral data of compound **18** confirmed the formation of only the α-linked required product [signals at δ 5.51 (s, PhC*H*), 5.30 (d, J=1.7 Hz, H-1_A), 5.28 (s, PhC*H*), 5.08 (br s, H-1_D), 5.05 (br s, H-1_F), 4.97 (d, J=7.8 Hz, H-1_B), 4.90 (d, J=8.1 Hz, H-1_C), 4.70 (d, J=7.2 Hz, H-1_E) in ^{1}H NMR, signals at δ 103.3 (C-1_C), 102.0 (C-1_B), 101.2 (2 C, 2 Ph*C*H), 100.7 (C-1_E), 99.4 (C-1_F), 98.7 (C-1_D), 97.1 (C-1_A) in ^{13}C NMR and proton coupled ^{13}C NMR spectra [($J_{C\text{-}1/H\text{-}1}$ 160 Hz, 160 Hz (2 β-D-Glc*p*), 164 Hz (β-D-Xyl*p*), 172 Hz, 172 Hz and 170 Hz (3 α-L-Rha*p*)]. The values of the coupling constants ($J_{C\text{-}1/H\text{-}1}$) being above 165 Hz for L-rhamnose moieties confirmed their α-linkages [22, 29]. Compound **18** was treated with DDQ under similar reaction conditions mentioned earlier to generate hexasaccharide acceptor **19** in 80% yield. Finally, iodonium ion catalyzed α-selective glycosylation of compound **19** with per-*O*-acetylated thioglycoside donor **4** furnished heptasaccharide derivative **20** in 85% yield, which on global deprotection of functional groups involving saponification and hydrogenolysis [30] resulted the target heptasaccharide **1** as its 4-methoxyphenyl glycoside. Formation of the required glycosyl linkage in compound **20** was confirmed from its spectral data [signals at δ 102.2 (C-1_C), 101.1 (C-1_B), 100.2 (2 C, Ph*C*H), 99.6 (C-1_F), 99.4 (C-1_E), 97.7 (2 C, C-1_D and C-1_G), 96.1 (C-1_A) in ^{13}C NMR spectrum]. Compound **1** was characterized by its 1D and 2D spectral analysis [signals at δ 5.39 (br s, 1 H, H-1_G), 5.33 (br s, 1 H, H-1_A), 5.26 (br s, 1 H, H-1_D), 4.92 (br s, 1 H, H-1_F), 4.70 (d, J=7.5 Hz, 1 H, H-1_B), 4.63 (d, J= 7.5 Hz, 1 H, H-1_C), 4.54 (d, J=7.2 Hz, 1 H, H-1_E) in the ^{1}H NMR and at δ 105.0 (C-1_E), 103.9 (C-1_B), 103.5 (C-1_C), 101.7 (C-1_F), 100.7 (C-1_D), 100.0 (C-1_G), 99.0 (C-1_A) in the ^{13}C NMR spectra] (Scheme 3). Use of functional groups with participating ability (*O*-acetyl) at C-2 positions of the glycosyl donors resulted in the required stereooutcome in all 1,2-*trans* glycosylation products. General glycosylation conditions and a similar kind of protecting group strategy were adopted to make this synthetic strategy useful for a scale-up preparation.



Scheme 3 Reagents: *a* *N*-Iodosuccinimide, TMSOTf, CH_2Cl_2, MS-4 Å, −30°C, 30 min, 74% for 18, 85% for 20; *b* DDQ, CH_2Cl_2-H_2O, r t, 2 h, 80%; *c* CH_3ONa, CH_3OH, r t, 2 h; *d* H_2, 20% $Pd(OH)_2$-C, CH_3OH, r t, 24 h, 76% in two steps

Conclusion

In summary, a concise chemical synthesis of the heptasaccharide motif as its 4-methoxyphenyl glycoside found in the cell-wall of *Mycobacterium gordonae* strain 990 has been achieved using general glycosylation conditions and a similar type of protecting group manipulations. This synthetic sequence can also be applied to a scale-up preparation on demand. All glycosylation steps are reasonably fast, stereoselective, high yielding and highly reproducible. Most of the intermediates were solid and characterized with the help of NMR and mass spectral analysis. 4-Methoxy phenyl group can serve as a temporary anomeric protecting group, which can be oxidatively removed using ammonium ceric nitrate (CAN) to couple the heptasaccharide moiety to a carrier protein for the preparation of glycoconjugate antigens.

Experimental section

General methods All the 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. ^1H and ^{13}C NMR (^1H coupled and decoupled), 2D COSY, and HSQC 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 values are 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.

Ethyl 4-O-benzyl-2-O-(4-methoxybenzyl)-3-O-methyl-1-thio-α-L-rhamnopyranoside ***(6)*** To a solution of compound **8** (7.5 g, 25.1 mmol) in toluene (200 mL) was added dibutyltin oxide (7.5 g, 30.1 mmol) and the reaction mixture was allowed to stir at 110°C with azeotropic removal of water for 4 h. The solvents were reduced to half of the volume and iodomethane (6.3 mL, 101.2 mmol) and tetrabutylammonium bromide (1 g) were added to it and the reaction mixture was stirred at room temperature for 48 h. The solvents were removed under reduced pressure and crude product was diluted with CH_2Cl_2 (150 mL). The organic layer was washed with 1 N aq. HCl, satd. $NaHCO_3$ and water in succession, dried (Na_2SO_4) and concentrated under reduced pressure. To a solution of the crude product in DMF (50 mL) were added powdered NaOH (3 g, 75 mmol), 4-methoxybenzyl chloride (6 mL, 44.2 mmol) and the reaction mixture was allowed to stir at room temperature for 3 h. The reaction mixture was diluted with water (150 mL) and extracted with CH_2Cl_2 (150 mL). The organic layer was washed with water, dried (Na_2SO_4) and evaporated to dryness. The crude product was purified over SiO_2 using hexane-EtOAc (5:1) as eluant to furnish pure compound **6** (8.2 g, 75%); colorless oil; $[\alpha]_D^{25}$ −47.1 (*c* 1.5, $CHCl_3$); IR (neat): 2925, 2361, 1612, 1512, 1457, 1219, 1099, 1032, 758 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.35–7.26 (m, 7 H, Ar-H), 6.90 (d, *J*=8.6 Hz, 2 H, Ar-H), 5.24 (br s, 1 H, H-1), 4.94 (d, *J*=11.2 Hz, 1 H, PhC*H*$_2$), 4.71–4.60 (m, 3 H, PhC*H*$_2$), 3.99 (t, *J*=7.0 Hz, 1 H, H-4), 3.86–3.85 (m, 1 H, H-5), 3.83 (s, 3 H, OC*H*$_3$), 3.56–3.47 (m, 2 H, H-2 and H-3), 3.38 (s, 3 H, OC*H*$_3$), 2.66–2.52 (m, 2 H, SC*H*$_2$CH$_3$), 1.33 (d, *J*=6.2 Hz, 3 H, CC*H*$_3$), 1.27 (t, *J*=7.4 Hz, 3 H, SCH$_2$C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.3–113.8 (Ar-C), 82.3 (C-1), 81.9 (C-4), 80.6 (C-2), 75.4, 75.1 (2 Ph*C*H$_2$), 71.8 (C-3), 68.2 (C-5), 57.4 (O*C*H$_3$), 55.1 (O*C*H$_3$), 25.4 (S*C*H$_2$CH$_3$), 17.9 (C*C*H$_3$), 15.1 (SCH$_2$*C*H$_3$); ESI-MS: *m/z*=455.2 $[M+Na]^+$; Anal. Calcd. for $C_{24}H_{32}O_5S$ (432.20): C, 66.64; H, 7.46; found: C, 66.43; H, 7.70.

4-Methoxyphenyl [2-O-acetyl-4,6-O-benzylidene-3-O-(4-methoxybenzyl)-β-D-glucopyranosyl]-(1→3)-(2-O-benzyl-4,6-O-benzylidine-β-D-glucopyranosyl)-(1→3)-2,

4-di-O-benzyl-α-L-rhamnopyranoside ***(11)*** To a solution of compound **10** (4 g, 5 mmol) and compound **3** (2.9 g, 6.1 mmol) in dry CH_2Cl_2 (30 mL) was added MS 4 Å (3 g) and the reaction mixture was allowed to stir at room temperature for 30 min under argon. After cooling the reaction mixture to −40°C, *N*-iodosuccinimide (1.7 g, 7.5 mmol) and TMSOTf (50 μL, 0.27 mmol) were added to it. The reaction mixture was stirred at −40°C for 30 min and quenched with Et_3N (0.2 mL). The reaction mixture was filtered and washed with CH_2Cl_2 (30 mL). The organic layer was washed successively with aq. $Na_2S_2O_3$ and water, dried (Na_2SO_4) and concentrated under reduced pressure to give the crude product, which was purified over SiO_2 using hexane-EtOAc (6:1) as eluant to furnish pure **11** (4.8 g, 80%); colorless solid; m.p. 86–87°C; $[\alpha]_D^{25}$ −42.7 (*c* 1.5, $CHCl_3$); IR (KBr): 2924, 1749, 1608, 1504, 1407, 1232, 1091, 1030, 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.48–7.07 (m, 27 H, Ar-H), 6.88 (d, *J*=9.0 Hz, 2 H, Ar-H), 6.79–6.74 (m, 4 H, Ar-H), 5.49 (s, 1 H, PhC*H*), 5.27 (br s, 1 H, H-1_A), 5.17 (s, 1 H, PhC*H*), 4.99 (t, *J*=8.0 Hz, 1 H, H-2_C), 4.93 (d, *J*=11.6 Hz, 1 H, PhCH_2), 4.91 (d, *J*=8.0 Hz, 1 H, H-1_C), 4.88 (d, *J*=8.0 Hz, 1 H, H-1_B), 4.85 (d, *J*= 12.1 Hz, 1 H, PhCH_2), 4.75 (d, *J*=12.1 Hz, 1 H, PhCH_2), 4.73–4.68 (m, 3 H, PhCH_2), 4.59 (d, *J*= 11.8 Hz, 1 H, PhCH_2), 4.36–4.28 (m, 3 H, H-3_A, H-6_{aC} and PhCH_2), 4.14–4.09 (m, 1 H, H-6_{aB}), 3.96–3.95 (m, 1 H, H-2_A), 3.90–3.77 (m, 3 H, H-3_B, H-3_C and H-6_{bC}), 3.76, 3.74 (2 s, 6 H, 2 OCH_3), 3.71–3.51 (m, 5 H, H-4_A, H-4_B, H-5_B, H-5_C and H-6_{bB}), 3.43 (t, *J*=8.1 Hz, 1 H, H-2_B), 3.36–3.28 (m, 2 H, H-4_C and H-5_A), 1.78 (s, 3 H, COCH_3), 1.27 (d, *J*=6.3 Hz, 3 H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.0 (*C*OCH_3), 159.2–113.6 (Ar-C), 103.6 (C-1_C), 101.6 (PhCH), 100.8 (PhCH), 100.6 (C-1_B), 97.3 (C-1_A), 82.7 (C-2_B), 81.5 (C-5_C), 80.7 (C-5_B), 79.7 (C-3_C), 78.9 (C-4_B), 78.4 (C-3_B), 78.1 (C-2_A), 77.0 (C-2_C), 75.4 (PhCH_2), 74.5 (PhCH_2), 73.7 (PhCH_2), 73.4 (C-3_A), 72.9 (PhCH_2), 68.7 (C-6_B), 68.6 (C-6_C), 68.5 (C-4_A), 66.3 (C-5_A), 65.9 (C-4_C), 55.5 (OCH_3), 55.1 (OCH_3), 20.7 (COCH_3), 18.0 (CCH_3); ESI-MS: *m/z*= 1225.6 $[M+Na]^+$; Anal. Calcd. for $C_{70}H_{74}O_{18}$ (1202.48): C, 69.87; H, 6.20; found: C, 69.70; H, 6.46.

4-Methoxyphenyl [2-O-benzyl-4,6-O-benzylidene-3-O-(4-methoxybenzyl)-β-D-glucopyranosyl]-(1→3)-(2-O-benzyl-4,6-O-benzylidine-β-D-glucopyranosyl)-(1→3)-2,4-di-O-benzyl-α-L-rhamnopyranoside ***(12)*** To a solution of compound **11** (4.5 g, 3.74 mmol) in DMF (50 mL) were added benzyl bromide (0.9 mL, 7.6 mmol), TBAB (0.2 g), powdered NaOH (450 mg, 11.2 mmol) and the reaction mixture was allowed to stir at room temperature for 3 h. The reaction mixture was diluted with water (150 mL) and extracted with CH_2Cl_2 (100 mL). The organic layer was washed with water, dried (Na_2SO_4) and concentrated to give the crude product, which was purified over SiO_2 using hexane-EtOAc (4:1) as eluant to furnish pure **12** (4 g, 85%); colorless solid; m.p. 67–69°C; $[\alpha]_D^{25}$ −31.3 (*c* 1.5, $CHCl_3$); IR (KBr): 2926, 1720, 1613, 1508, 1456, 1367, 1247, 1219, 1080, 827, 739, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.51–7.17 (m, 32 H, Ar-H), 6.95 (d, *J*=9.0 Hz, 2 H, Ar-H), 6.80–6.77 (m, 4 H, Ar-H), 5.55 (s, 1 H, PhC*H*), 5.33 (d, *J*=1.7 Hz, 1 H, H-1_A), 5.31 (s, 1 H, PhC*H*), 5.07–4.95 (m, 2 H, PhCH_2), 4.93 (d, *J*= 8.0 Hz, 1 H, H-1_C), 4.84 (d, *J*=7.7 Hz, 1 H, H-1_B), 4.82–4.63 (m, 7 H, PhCH_2), 4.39–4.34 (m, 3 H, H-3_A, H-6_{aC} and PhCH_2), 4.27–4.20 (m, 1 H, H-6_{aB}), 4.02 (t, *J*=8.5 H, 1 H, H-3_C), 3.99–3.97 (m, 1 H, H-2_A), 3.86–3.78 (m, 2 H, H-3_B and H-4_A), 3.79 (s, 6 H, 2 OCH_3), 3.76–3.72 (m, 1 H, H-6_{bC}), 3.70–3.63 (m, 4 H, H-4_B, H-4_C, H-5_B and H-6_{bB}), 3.54 (t, *J*=8.0 Hz, H-2_C), 3.51 (t, *J*=7.6 Hz, 1 H, H-2_B), 3.48–3.40 (m, 1 H, H-5_A), 3.38–3.30 (m, 1 H, H-5_C), 1.28 (d, *J*=6.0 Hz, 3 H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.4–113.6 (Ar-C), 103.5 (C-1_C), 102.2 (PhCH), 101.5 (PhCH), 100.8 (C-1_B), 97.4 (C-1_A), 83.3 (C-2_B), 82.2 (C-5_C), 81.5 (C-5_B), 81.2 (C-3_A), 80.2 (C-3_C), 79.7 (C-4_B), 78.5 (C-3_B), 78.2 (C-2_A), 77.0 (C-2_C), 75.1 (PhCH_2), 74.5 (2 C, PhCH_2), 74.0 (PhCH_2), 73.7 (PhCH_2), 68.9 (2 C, C-6_B and C-6_C), 68.6 (C-4_A), 66.2 (C-5_A), 65.7 (C-4_C), 55.5 (OCH_3), 55.0 (OCH_3), 17.9 (CCH_3); ESI-MS: *m/z*=1268.5 $[M+NH_4]^+$; Anal. Calcd. for $C_{75}H_{78}O_{17}$ (1250.52): C, 71.98; H, 6.28; found: C, 71.78; H, 6.54.

4-Methoxyphenyl (2-O-benzyl-4,6-O-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-O-benzyl-4,6-O-benzylidine-β-D-glucopyranosyl)-(1→3)-2,4-di-O-benzyl-α-L-rhamnopyranoside ***(13)*** To a solution of compound **12** (3.8 g, 3 mmol) in CH_2Cl_2 and water (50 mL, 1:1), was added DDQ (820 mg, 3.6 mmol) and the reaction mixture was allowed to stir at room temperature for 2 h. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and the organic layer was washed successively with satd. aq $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated under reduced pressure to give the crude product, which was purified over SiO_2 using hexane-EtOAc (4:1) to furnish pure **13** (2.6 g, 77%); colorless solid; m.p. 96–98°C; $[\alpha]_D^{25}$ −40.3 (*c* 1.5, $CHCl_3$); IR (KBr): 2874, 1632, 1506, 1457, 1378, 1220, 1091, 1033, 998, 745, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.50–7.07 (m, 30 H, Ar-H), 6.92 (d, *J*=9.0 Hz, 2 H, Ar-H), 6.78 (d, *J*=9.0 Hz, 2 H, Ar-H), 5.52 (s, 1 H, PhC*H*), 5.32 (s, 1 H, PhC*H*), 5.30 (d, *J*=1.6 Hz, 1 H, H-1_A), 5.01 (d, *J*=8.0 Hz, 1 H, H-1_C), 4.99 (d, *J*=7.9 Hz, 1 H, H-1_B), 4.96 (d, *J*=11.7 Hz, 1 H, PhCH_2), 4.89 (d, *J*=11.7 Hz, 1 H, PhCH_2), 4.85 (d, *J*=12.0 Hz, 1 H, PhCH_2), 4.78 (d, *J*= 11.7 Hz, 1 H, PhCH_2), 4.71–4.65 (m, 3 H, PhCH_2), 4.37–4.32 (m, 3 H, H-3_A, H-6_{aC} and PhCH_2), 4.24–4.19 (m, 1 H, H-6_{aB}), 4.01 (t, *J*=8.9 Hz, 1 H, H-3_C), 3.97–3.95 (m, 1 H, H-2_A), 3.85–3.76 (m, 1 H, H-4_A), 3.75 (s, 3 H, OCH_3), 3.73–3.69 (m, 1 H, H-3_B), 3.67–3.57 (m, 3 H, H-4_C, H-6_{bB}

and H-6_{bC}), 3.55–3.48 (m, 3 H, H-2_C, H-4_B and H-5_B), 3.47–3.28 (m, 3 H, H-2_B, H-5_A and H-5_C), 1.27 (d, *J*= 6.0 Hz, 3 H, CC*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.2–114.5 (Ar-C), 103.5 (C-1_C), 102.4 (C-1_B), 101.5 (PhC*H*), 101.4 (PhC*H*), 97.2 (C-1_A), 83.1 (C-5_B), 82.2 (C-2_B), 81.5 (C-5_C), 80.5 (C-4_B), 79.5 (C-3_A), 78.5 (C-2_A), 78.4 (C-3_C), 76.8 (C-2_C), 75.1 (PhC*H*$_2$), 74.4 (2 C, 2 PhC*H*$_2$), 73.6 (PhC*H*$_2$), 73.3 (C-3_B), 68.7 (2 C, C-6_B and C-6_C), 68.5 (C-4_A), 66.2 (C-5_A), 65.7 (C-4_C), 55.4 (OC*H*$_3$), 17.9 (CC*H*$_3$); ESI-MS: *m/z*=1153.5 $[M+Na]^+$; Anal. Calcd. for $C_{67}H_{70}O_{16}$ (1130.46): C, 71.13; H, 6.24; found: C, 70.92; H, 6.50.

4-Methoxyphenyl [2-O-acetyl-4-O-benzyl-3-O-(4-methoxybenzyl)-α-L-rhamnopyranosyl]-(1→3)-(2-O-benzyl-4,6-O-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-O-benzyl-4,6-O-benzylidine-β-D-glucopyranosyl)-(1→3)-2,4-di-O-benzyl-α-L-rhamnopyranoside ***(14)*** To a solution of compound **13** (2.5 g, 2.2 mmol) and compound **5** (1.2 g, 2.6 mmol) in dry CH_2Cl_2 (25 mL) was added MS 4 Å (2 g) and the reaction mixture was stirred at room temperature for 30 min under argon. The reaction mixture was cooled to −40°C and *N*-iodosuccinimide (700 mg, 3.1 mmol) and TMSOTf (20 μL, 0.12 mmol) were added to it. The mixture was stirred at −40°C for 30 min and quenched with Et_3N (0.1 mL). The reaction mixture was filtered and washed with CH_2Cl_2 (50 mL). The filtrate was successively washed with 10% aq $Na_2S_2O_3$ and water, dried (Na_2SO_4) and concentrated under reduced pressure to give crude product, which was purified over SiO_2 using hexane-EtOAc (4:1) as eluant to furnish pure **14** (2.6 g, 77%); colorless solid; m.p. 100–101°C; $[\alpha]_D^{25}$ −38.6 (*c* 1.5, $CHCl_3$); IR (KBr): 2926, 2361, 1741, 1705, 1510, 1459, 1374, 1238, 1090, 754, 697 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46–7.09 (m, 37 H, Ar-H), 6.89 (d, *J*=9.0 Hz, 2 H, Ar-H), 6.78–6.74 (m, 4 H, Ar-H), 5.49 (s, 1 H, PhC*H*), 5.38–5.36 (m, 1 H, H-2_D), 5.30 (br s, 1 H, H-1_A), 5.25 (s, 1 H, PhC*H*), 5.02–4.98 (m, 3 H, H-1_B, H-1_C and PhC*H*$_2$), 4.97 (br s, 1 H, H-1_D), 4.94–4.77 (m, 5 H, PhC*H*$_2$), 4.70–4.58 (m, 4 H, PhC*H*$_2$), 4.51 (d, *J*=11.2 Hz, 1 H, PhC*H*$_2$), 4.38–4.31 (m, 4 H, H-3_A, H-4_D, H-6_{aC} and PhC*H*$_2$), 4.24–4.17 (m, 1 H, H-6_{aB}), 4.08–4.0 (m, 2 H, H-3_C and H-4_C), 3.97–3.95 (m, 1 H, H-2_A), 3.85–3.79 (m, 3 H, H-3_B, H-3_D and H-6_{bC}), 3.74, 3.72 (2 s, 6 H, 2 OC*H*$_3$), 3.70–3.59 (m, 4 H, H-4_A, H-5_B, H-5_D and H-6_{bB}), 3.58–3.40 (m, 3 H, H-2_B, H-2_C and H-4_B), 3.35–3.20 (m, 2 H, H-5_A and H-5_C), 2.03 (s, 3 H, COC*H*$_3$), 1.27 (d, *J*=6.0 Hz, 3 H, CC*H*$_3$), 0.93 (d, *J*= 6.0 Hz, 3 H, CC*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.7 (*C*OCH$_3$), 159.2–113.7 (Ar-C), 103.4 (C-1_C), 102.1 (C-1_B), 101.5 (PhC*H*), 101.2 (PhC*H*), 97.8 (C-1_D), 97.3 (C-1_A), 83.3 (C-2_B), 82.6 (C-2_C), 81.5 (C-5_B), 80.1 (C-3_C), 79.6 (C-5_C), 79.0 (C-5_D), 78.5 (C-2_A), 77.8 (2 C, C-3_B and C-3_D), 76.9 (C-3_A), 76.3 (C-4_B), 75.1 (PhC*H*$_2$), 74.9 (PhC*H*$_2$), 74.6 (PhC*H*$_2$), 74.5 (PhC*H*$_2$), 73.7 (PhC*H*$_2$), 71.4 (PhC*H*$_2$), 68.9 (2 C, C-6_B and C-6_C), 68.7 (C-2_D), 68.6 (C-4_A), 67.5 (C-4_C), 66.2 (C-5_A), 66.0 (C-4_D), 55.4 (OC*H*$_3$), 55.0 (OC*H*$_3$), 20.9 (COC*H*$_3$), 17.9 (CC*H*$_3$), 17.5 (CC*H*$_3$); ESI-MS: *m/z*=1546.7 $[M+NH_4]^+$; Anal. Calcd. for $C_{90}H_{96}O_{22}$ (1528.64): C, 70.66; H, 6.33; found: C, 70.48; H, 6.55.

4-Methoxyphenyl [4-O-benzyl-3-O-(4-methoxybenzyl)-α-L-rhamnopyranosyl]-(1→3)-(2-O-benzyl-4,6-O-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-O-benzyl-4,6-O-benzylidine-β-D-glucopyranosyl)-(1→3)-2,4-di-O-benzyl-α-L-rhamnopyranoside ***(15)*** A solution of the compound **14** (2.5 g, 1.6 mmol) in 0.1 M CH_3ONa in CH_3OH (50 mL) was allowed to stir at room temperature for 2 h, neutralized with Amberlite IR-120 (H^+) resin, filtered and concentrated. The crude product was passed through a short pad of SiO_2 using hexane-EtOAc (3:1) to give pure compound **15** (2.4 g, quantitative); colorless solid; m.p. 92–94°C; $[\alpha]_D^{25}$ −55.6 (*c* 1.5, $CHCl_3$); IR (KBr): 2927, 1620, 1508, 1457, 1377, 1220, 1093, 1036, 744, 697 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47–7.01 (m, 37 H, Ar-H), 6.93 (d, *J*=9.0 Hz, Ar-H), 6.81–6.76 (m, 4 H, Ar-H), 5.50 (s, 1 H, PhC*H*), 5.31 (d, *J*=1.7 Hz, 1 H, H-1_A), 5.28 (s, 1 H, PhC*H*), 5.06 (br s, 1 H, H-1_D), 4.98 (2 d, *J*=7.7 Hz, 2 H, H-1_B and H-1_C), 4.95–4.75 (m, 5 H, PhC*H*$_2$), 4.70 (d, *J*=12.0 Hz, 1 H, PhC*H*$_2$), 4.63–4.47 (m, 5 H, PhC*H*$_2$), 4.37–4.31 (m, 3 H, H-3_A, H-6_{aC} and PhC*H*$_2$), 4.24–4.19 (m, 1 H, H-6_{aB}), 4.03–3.94 (m, 3 H, H-2_A, H-3_C and H-3_D), 3.82–3.76 (m, 2 H, H-3_B and H-4_D), 3.75, 3.73 (2 s, 6 H, 2 OC*H*$_3$), 3.72–3.70 (m, 1 H, H-6_{bC}), 3.69–3.60 (m, 3 H, H-2_D, H-4_A and H-6_{bB}), 3.58–3.32 (m, 6 H, H-2_B, H-4_B, H-4_C, H-5_A, H-5_B and H-5_D), 3.30–3.22 (m, 2 H, H-2_C and H-5_C), 1.27 (d, *J*=6.0 Hz, 3 H, CC*H*$_3$), 0.87 (d, *J*=6.0 Hz, 3 H, CC*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.2–113.8 (Ar-C), 103.4 (C-1_C), 102.5 (C-1_B), 101.3 (2 C, 2 PhC*H*), 99.5 (C-1_D), 97.1 (C-1_A), 83.2 (C-2_B), 82.5 (C-2_C), 81.5 (C-5_B), 80.1 (C-3_C), 79.5 (C-5_C), 79.4 (C-4_A), 79.2 (C-2_A), 78.4 (C-3_D), 78.2 (C-3_B), 76.8 (2 C, C-3_A and C-4_B), 75.2, 74.9, 74.6, 74.5, 73.6 (5 PhC*H*$_2$), 68.8 (2 C, C-6_B and C-6_C), 68.5 (C-2_D), 68.4 (C-5_D), 67.2 (C-4_C), 66.2 (C-5_A), 66.0 (C-4_D), 55.4 (OC*H*$_3$), 55.0 (OC*H*$_3$), 17.9, 17.3 (2 CC*H*$_3$); ESI-MS: *m/z*=1504.6 $[M+NH_4]^+$; Anal. Calcd. for $C_{88}H_{94}O_{21}$ (1486.63): C, 71.05; H, 6.37; found: C, 70.84; H, 6.62.

4-Methoxyphenyl (2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-(1→2)-[4-O-benzyl-3-O-(4-methoxybenzyl)-α-L-rhamnopyranosyl]-(1→3)-(2-O-benzyl-4,6-O-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-O-benzyl-4,6-O-benzylidine-β-D-glucopyranosyl)-(1→3)-2,4-di-O-benzyl-α-L-rhamnopyranoside ***(16)*** To a solution of compound **15** (2.3 g, 1.5 mmol) and compound 7 (0.6 g, 1.9 mmol) in dry CH_2Cl_2 (20 mL) was added MS 4 Å (1 g) and the reaction

mixture was stirred at room temperature for 30 min under argon. The reaction mixture was cooled to −40°C and *N*-iodosuccinimide (500 mg, 2.2 mmol) and TMSOTf (15 μL, 0.08 mmol) were added to it. The mixture was stirred at the same temperature for 30 min and quenched with Et_3N (0.1 mL). The reaction mixture was filtered and washed with CH_2Cl_2 (50 mL). The organic layer was washed successively with 10% aq $Na_2S_2O_3$ and water, dried (Na_2SO_4) and concentrated under reduced pressure to give crude product, which was purified over SiO_2 using hexane-EtOAc (5:1) as eluant to furnish pure **16** (2 g, 78%); colorless solid; m.p. 86–88°C; $[\alpha]_D^{25}$ −53.6 (*c* 1.5, $CHCl_3$); IR (KBr): 2927, 2859, 1754, 1509, 1457, 1371, 1247, 1222, 1179, 1092, 1040, 1000, 828, 749, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.47–7.01 (m, 37 H, Ar-H), 6.90 (d, *J*=9.0 Hz, 2 H, Ar-H), 6.82–6.75 (m, 4 H, Ar-H), 5.50 (s, 1 H, PhC*H*), 5.32 (S, 1 H, PhC*H*), 5.30 (d, *J*=1.6 Hz, 1 H, H-1_A), 5.10 (br s, 1 H, H-1_D), 5.02 (2 d, *J*=7.7 Hz, 2 H, H-1_B and H-1_C), 4.97 (d, *J*=11.7 Hz, 1 H, PhCH_2), 4.93–4.90 (m, 2 H, H-2_E and PhCH_2), 4.88–4.68 (m, 6 H, PhCH_2), 4.65–4.58 (m, 2 H, H-3_E and PhCH_2), 4.55–4.44 (m, 3 H, PhCH_2), 4.41 (d, *J*=7.2 Hz, 1 H, H-1_E), 4.35–4.23 (m, 4 H, H-3_A, H-3_D, H-4_E and H-6_{aC}), 3.97 (t, *J*=8.0 Hz, 1 H, H-3_C), 3.96–3.88 (m, 2 H, H-2_A and H-5_{aE}), 3.85–3.77 (m, 3 H, H-2_D, H-4_A and H-5_{bE}), 3.75 (s, 6 H, 2 OCH_3), 3.74–3.70 (m, 2 H, H-5_A and H-6_{bC}), 3.68–3.58 (m, 3 H, H-3_B, H-4_D and H-6_{aB}), 3.57–3.50 (m, 1 H, H-4_B), 3.49–3.35 (m, 4 H, H-2_B, H-4_C, H-5_D and H-6_{bB}), 3.32–22 (m, 2 H, H-2_C and H-5_C), 2.82–2.72 (m, 1 H, H-5_B), 2.03, 2.01 (2 s, 9 H, 3 COCH_3), 1.25 (d, *J*=9.0 Hz, 3 H, CCH_3), 0.85 (d, *J*=9.0 Hz, 3 H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.9, 169.8 (2 C) (3 *C*OCH$_3$), 159.5–113.7 (Ar-C), 103.4 (C-1_C), 102.5 (C-1_B), 101.9 (C-1_E), 101.5 (PhCH), 101.3 (PhCH), 99.2 (C-1_D), 97.2 (C-1_A), 83.2 (C-2_B), 82.5 (C-5_C), 81.5 (C-5_B), 80.5 (C-2_C), 79.4 (2 C, C-4_A and C-4_B), 78.5 (C-2_A), 78.0 (C-4_D), 76.9 (C-3_A), 75.0 (2 C, PhCH_2), 74.4 (PhCH_2), 74.2 (PhCH_2), 73.6 (PhCH_2), 72.2 (PhCH_2), 71.2 (C-4_E), 71.0 (C-2_E), 70.6 (C-3_E), 69.5 (C-2_D), 69.3 (C-3_B), 69.0 (2 C, C-5_E and C-6_C), 68.8 (C-5_D), 68.6 (C-3_D), 67.8 (C-3_C), 66.2 (C-5_A), 66.0 (C-4_C), 61.3 (C-6_B), 55.5, 55.0 (2 OCH$_3$), 20.6 (3 C, 3 COCH$_3$), 17.9, 17.3 (2 CCH$_3$); ESI-MS: *m/z*= 1762.8 $[M+NH_4]^+$; Anal. Calcd. for $C_{99}H_{108}O_{28}$ (1744.70): C, 68.11; H, 6.24; found: C, 67.92; H, 6.46.

4-Methoxyphenyl (2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-(1→2)-(4-O-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2-O-benzyl-4,6-O-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-O-benzyl-4,6-O-benzylidine-β-D-glucopyranosyl)-(1→3)-2,4-di-O-benzyl-α-L-rhamnopyranoside (17) To a solution of compound **16** (1.8 g, 1 mmol) in CH_2Cl_2 and water (30 mL, 1:1), was added DDQ (270 mg, 1.2 mmol) and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with CH_2Cl_2 (30 mL) and the organic layer was washed in succession with satd. aq $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated under reduced pressure to give the crude product, which was purified over SiO_2 using hexane-EtOAc (3:1) as eluant to furnish pure **17** (1.3 g, 80%); colorless solid; m.p. 104–106°C; $[\alpha]_D^{25}$ −36.9 (*c* 1.5, $CHCl_3$); IR (KBr): 2925, 1749, 1605, 1375, 1224, 1086, 761 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.47–7.02 (m, 35 H, Ar-H), 6.88 (d, *J*=9.0 Hz, 2 H, Ar-H), 6.78 (d, *J*=9.0 Hz, 2 H, Ar-H), 5.50 (s, 1 H, PhC*H*), 5.30 (s, 1 H, PhC*H*), 5.29 (br s, 1 H, H-1_A), 5.05 (br s, 1 H, H-1_D), 5.02–4.88 (m, H-1_B, H-1_C and PhCH_2), 4.85–4.72 (m, 3 H, H-2_E and PhCH_2), 4.70–4.66 (m, 2 H, PhCH_2), 4.64–4.50 (m, 4 H, H-3_E and PhCH_2), 4.35–4.27 (m, 3 H, H-3_A, H-3_D and H-4_E), 4.25–4.17 (m, 1 H, H-6_{aC}), 4.10 (d, *J*=7.2 Hz, 1 H, H-1_E), 4.00 (t, *J*=7.9 Hz, 1 H, H-3_C), 3.94–3.92 (m, 1 H, H-2_A), 3.87–3.76 (m, 5 H, H-3_B, H-4_A, H-4_C, H-5_D and H-5_{aE}), 3.74 (s, 3 H, OCH_3), 3.70–3.60 (m, 4 H, H-2_D, H-5_B, H-5_{bE} and H-6_{bC}), 3.58–3.50 (m, 2 H, H-4_B and H-6_{aB}), 3.48–3.35 (m, 3 H, H-2_B, H-2_C and H-5_A), 3.32–3.23 (m, 1 H, H-5_C), 3.07 (t, *J*=7.9 Hz, 1 H, H-4_D), 2.68–2.58 (m, 1 H, H-6_{bB}), 2.06, 2.05, 2.03 (3 s, 9 H, 3 COCH_3), 1.24 (d, *J*=6.0 Hz, 3 H, CCH_3), 0.80 (d, *J*=6.0 Hz, 3 H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.6, 169.5, 169.2 (3 *C*OCH$_3$), 154.8–114.4 (Ar-C), 103.2 (C-1_C), 102.4 (C-1_B), 102.1 (C-1_E), 101.5 (PhCH), 101.2 (PhCH), 98.7 (C-1_D), 97.1 (C-1_A), 83.0 (C-2_B), 82.8 (C-5_C), 81.9 (C-4_D), 81.3 (C-2_C), 80.3 (C-5_B), 79.3 (C-4_A), 79.2 (C-4_B), 78.4 (C-2_A), 78.1 (C-2_D), 77.2 (C-3_A), 74.9 (PhCH_2), 74.4 (2 C, PhCH_2), 74.3 (PhCH_2), 73.5 (PhCH_2), 71.3 (C-4_E), 71.2 (C-3_C), 70.9 (C-2_E), 70.7 (C-3_E), 69.3 (C-3_B), 69.2 (C-5_D), 68.9 (2 C, C-5_E and C-6_C), 68.4 (C-3_D), 66.9 (C-5_A), 66.0 (C-4_C), 61.4 (C-6_B), 55.3 (OCH$_3$), 20.5 (3 C, 3 COCH$_3$), 17.8, 17.2 (2 CCH$_3$); ESI-MS: *m/z*=1642.7 $[M+NH_4]^+$; Anal. Calcd. for $C_{91}H_{100}O_{27}$ (1624.64): C, 67.23; H, 6.20; found: C, 67.02; H, 6.44.

4-Methoxyphenyl [4-O-benzyl-3-O-methyl-2-O-(4-methoxybenzyl)-α-L-rhamnopyranosyl]-(1→3)-[(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-(1→2)]-(4-O-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2-O-benzyl-4,6-O-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-O-benzyl-4,6-O-benzylidine-β-D-glucopyranosyl)-(1→3)-2,4-di-O-benzyl-α-L-rhamnopyranoside ***(18)***
To a solution of compound **17** (1.2 g, 0.74 mmol) and compound **6** (390 mg, 0.9 mmol) in dry CH_2Cl_2 (20 mL) was added MS 4 Å (1 g) and the reaction mixture was stirred at room temperature for 30 min under argon. The reaction mixture was cooled to −30°C and *N*-iodosuccinimide (225 mg, 1 mmol) and TMSOTf (10 μL, 0.05 mmol) were added to it. The mixture was stirred at the same temperature for 30 min and quenched with Et_3N (0.1 mL). The reaction mixture was filtered and washed with CH_2Cl_2 (50 mL). The organic layer was washed successively with 10% aq $Na_2S_2O_3$ and water, dried

(Na_2SO_4) and concentrated under reduced pressure to give crude product, which was purified over SiO_2 using hexane-EtOAc (5:1) as eluant to furnish pure 18 (1.1 g, 74%); colorless solid; m.p. 78–80°C; $[\alpha]_D^{25}$ −35.6 (*c* 1.5, $CHCl_3$); IR (KBr): 2926, 2363, 1752, 1707, 1652, 1510, 1458, 1374, 1223, 1090, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.39–7.15 (m, 40 H, Ar-H), 7.06–7.02 (m, 2 H, Ar-H), 6.90 (d, *J*=9.0 Hz, 2 H, Ar-H), 6.78–6.70 (m, 4 H, Ar-H), 5.51 (s, 1 H, PhC*H*), 5.30 (d, *J*=1.7 Hz, 1 H, H-1_A), 5.28 (s, 1 H, PhC*H*), 5.08 (br s, 1 H, H-1_D), 5.05 (br s, 1 H, H-1_F), 5.04–5.0 (m, 2 H, H-2_E and PhCH_2), 4.97 (d, *J*= 7.8 Hz, 1 H, H-1_B), 4.94–4.91 (m, 1 H, H-3_E), 4.90 (d, *J*= 8.1 Hz, 1 H, H-1_C), 4.89–4.76 (m, 6 H, PhCH_2), 4.70 (d, *J*=7.2 Hz, 1 H, H-1_E), 4.67–4.61 (m, 3 H, H-4_E and PhCH_2), 4.60–4.43 (m, 4 H, PhCH_2), 4.38–4.20 (m, 6 H, H-3_A, H-3_B, H-3_D, H-3_F, H-6_{aC}, PhCH_2), 4.06–3.92 (m, 3 H, H-2_A, H-3_C, H-4_F), 3.88–3.72 (m, 3 H, H-2_D, H-5_A and H-6_{bC}), 3.74 (s, 3 H, OCH_3), 3.69 (s, 3 H, OCH_3), 3.67–3.57 (m, 6 H, H-2_F, H-4_B, H-5_D, H-5_{aE}, H-5_F and H-6_{aB}), 3.55–3.38 (m, 5 H, H-2_B, H-2_C, H-4_A, H-4_D and H-5_{bE}), 3.35 (s, 3 H, OCH_3), 3.34–3.23 (m, 2 H, H-4_C and H-5_B), 3.22–3.14 (m, 1 H, H-5_C), 2.96–2.88 (m, 1 H, H-6_{bB}), 2.04, 2.01, 2.0 (3 s, 9 H, 3 COCH_3), 1.30 (d, *J*=6.1 Hz, 3 H, CCH_3), 1.25 (d, *J*=6.1 Hz, 3 H, CCH_3), 0.81 (d, *J*=6.0 Hz, 3 H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.4, 169.1, 168.6 (3 *C*OCH_3), 159.6–113.4 (Ar-C), 103.3 (C-1_C), 102.0 (C-1_B), 101.2 (2 C, 2 Ph*C*H), 100.7 (C-1_E), 99.4 (C-1_F), 98.7 (C-1_D), 97.1 (C-1_A), 83.2 (C-2_F), 81.8 (C-5_F), 81.6 (C-2_C), 81.3 (2 C, C-4_A and C-4_D), 80.9 (C-2_B), 80.2 (C-5_C), 79.3 (C-4_B), 78.9 (C-2_D), 78.4 (C-2_A), 77.4 (C-5_B), 77.2 (C-3_B), 76.7 (2 C, C-3_A and C-3_C), 76.1 (C-5_D), 74.8 (3 C, Ph*C*H_2), 74.3 (C-3_F), 74.2 (Ph*C*H_2), 73.8 (Ph*C*H_2), 73.5 (Ph*C*H_2), 71.9 (Ph*C*H_2), 70.9 (C-3_D), 70.7 (C-4_E), 68.6 (2 C, C-5_E and C-6_C), 68.5 (2 C, C-2_E and C-5_A), 68.4 (C-3_E), 66.1 (C-4_F), 65.8 (C-4_C), 61.2 (C-6_B), 57.3 (O*C*H_3), 55.3, 54.8 (2 O*C*H_3); ESI-MS: *m/z*=2012.8 $[M+NH_4]^+$; Anal. Calcd. for $C_{113}H_{126}O_{32}$ (1994.82): C, 67.99; H, 6.36; found: C, 67.78; H, 6.60.

4-Methoxyphenyl (4-O-benzyl-3-O-methyl-α-L-rhamnopyranosyl)-(1→3)-[(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-(1→2)]-(4-O-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2-O-benzyl-4,6-O-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-O-benzyl-4,6-O-benzylidine-β-D-glucopyranosyl)-(1→3)-2,4-di-O-benzyl-α-L-rhamnopyranoside ***(19)*** To a solution of compound **18** (1 g, 0.5 mmol) in CH_2Cl_2 and water (20 mL, 1:1), was added DDQ (140 mg, 0.6 mmol) and the reaction mixture was stirred at room temperature for 2 h and diluted with CH_2Cl_2 (30 mL). The organic layer was washed successively with satd. aq $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated under reduced pressure to give the crude product, which was purified over SiO_2 using hexane-EtOAc (5:1) as eluant to furnish pure **19** (750 mg, 80%); colorless solid; m.p. 98–100°C; $[\alpha]_D^{25}$ −51.6 (*c* 1.5, $CHCl_3$); IR (KBr): 3021, 2363, 1757, 1593, 1372, 1216, 1087, 760, 670 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.49–7.06 (m, 40 H, Ar-H), 6.90 (d, *J*=9.0 Hz, 2 H, Ar-H), 6.77 (d, *J*=9.0 Hz, 2 H, Ar-H), 5.50 (s, 1 H, PhC*H*), 5.29 (br s, 1 H, H-1_A), 5.24 (s, 1 H, PhC*H*), 5.08 (br s, 2 H, H-1_D and H-1_F), 5.04–4.99 (m, 3 H, H-1_B, H-1_C and PhCH_2), 4.98–4.94 (m, 1 H, H-2_E), 4.90–4.80 (m, 5 H, PhCH_2), 4.77–4.60 (m, 4 H, H-1_E and PhCH_2), 4.58–4.45 (m, 4 H, H-3_E, H-4_E and PhCH_2), 4.38–4.30 (m, 4 H, H-3_A, H-3_D, H-3_F and PhCH_2), 4.28–4.19 (m, 1 H, H-6_{aC}), 4.05–3.90 (m, 5 H, H-2_A, H-2_F, H-3_B, H-3_C and H-4_B), 3.88–3.76 (m, 4 H, H-2_D, H-4_F, H-5_A, H-6_{bC}), 3.74 (s, 3 H, O*C*H_3), 3.72–3.52 (m, 4 H, H-5_D, H-5_F, H-5_{aE} and H-6_{aB}), 3.50–3.40 (m, 4 H, H-2_B, H-2_C, H-4_A and H-5_{bE}), 3.39 (s, 3 H, O*C*H_3), 3.38–3.26 (m, 3 H, H-4_C, H-4_D and H-5_B), 3.25–3.16 (m, 1 H, H-5_C), 2.97–2.86 (m, 1 H, H-6_{bB}), 2.01, 1.96 (2 s, 9 H, 3 COCH_3), 1.30 (d, *J*=6.0 Hz, 3 H, CCH_3), 1.25 (d, *J*= 6.0 Hz, 3 H, CCH_3), 0.85 (d, *J*=6.0 Hz, 1 H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.2, 169.0, 168.6 (3 *C*OCH_3), 154.8–117.5 (Ar-C), 103.2 (C-1_C), 102.0 (C-1_B), 101.3 (Ph*C*H), 101.2 (Ph*C*H), 100.7 (2 C, C-1_E and C-1_F), 98.7 (C-1_D), 97.1 (C-1_A), 83.5 (C-5_C), 83.2 (C-2_F), 81.9 (C-2_C), 81.5 (C-4_A), 81.4 (C-4_D), 81.0 (C-2_B), 79.6 (C-5_F), 79.3 (C-4_B), 79.0 (C-2_D), 78.4 (C-2_A), 77.5 (2 C, C-3_B and C-5_B), 76.9 (C-3_C), 76.2 (C-3_A), 74.8 (2 C, Ph*C*H_2), 74.7 (Ph*C*H_2), 74.3 (Ph*C*H_2), 73.8 (Ph*C*H_2), 73.5 (Ph*C*H_2), 70.7 (C-5_D), 70.6 (C-3_F), 68.7 (2 C, C-5_E and C-6_C), 68.5 (2 C, C-3_D and C-4_E), 68.0 (C-2_E), 67.7 (C-3_E), 67.6 (C-5_A), 66.0 (C-4_F), 65.8 (C-4_C), 61.2 (C-6_B), 57.1 (O*C*H_3), 55.3 (O*C*H_3), 20.7, 20.5 (2 C) (3 COCH_3), 18.2, 17.8, 17.2 (3 CCH_3); ESI-MS: *m/z*=1897.8 $[M+Na]^+$; Anal. Calcd. for $C_{105}H_{118}O_{31}$ (1874.76): C, 67.22; H, 6.34; found: C, 67.0; H, 6.58.

4-Methoxyphenyl (2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-(1→2)-(4-O-benzyl-3-O-methyl-α-L-rhamnopyranosyl)-(1→3)-[(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-(1→2)]-(4-O-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2-O-benzyl-4,6-O-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-O-benzyl-4,6-O-benzylidine-β-D-glucopyranosyl)-(1→3)-2,4-di-O-benzyl-α-L-rhamnopyranoside ***(20)*** To a solution of compound 19 (700 mg, 0.37 mmol) and compound **4** (190 mg, 0.57 mmol) in dry CH_2Cl_2 (20 mL) was added MS 4 Å (3 g) and the reaction mixture was stirred at room temperature for 30 min under argon. The reaction mixture was cooled to −30°C and *N*-iodosuccinimide (150 mg, 0.66 mmol) and TMSOTf (5 μL, 0.03 mmol) were added to it. The reaction mixture was stirred at the same temperature for 30 min and quenched with Et_3N (50 μL). The reaction mixture was filtered and washed with CH_2Cl_2 (30 mL). The organic layer was successively washed with 10% aq $Na_2S_2O_3$ and water,

dried (Na_2SO_4) and concentrated under reduced pressure to give crude product, which was purified over SiO_2 using hexane-EtOAc (5:1) as eluant to furnish pure **20** (675 mg, 85%); colorless solid; m.p. 95–97°C; $[\alpha]_D^{25}$ −45 (*c* 1.5, $CHCl_3$); IR (KBr): 3021, 2925, 2365, 1753, 1662, 1600, 1369, 1219, 1085, 761 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.48–7.02 (m, 40 H, Ar-H), 6.89 (d, *J*=9.0 Hz, 2 H, Ar-H), 6.78 (d, *J*=9.0 Hz, 2 H, Ar-H), 5.30 (s, 1 h, PhC*H*), 5.40–5.20 (m, 4 H, H-1_A, H-2_G, H-3_G and PhC*H*), 5.14–4.78 (m, 10 H, H-1_B, H-1_C, H-1_D, H-1_F, H-1_G, H-2_E, H-4_G and PhCH_2), 4.75–4.60 (m, 7 H, H-1_E, H-3_E, H-4_E and PhCH_2), 4.58–4.43 (m, 4 H, PhCH_2), 4.40–4.20 (m, 5 H, H-3_A, H-3_D, H-3_F, H-6_{aC} and PhCH_2), 4.13–4.07 (m, 1 H, H-3_B), 4.05–3.90 (m, 5 H, H-2_A, H-2_D, H-2_F, H-3_C and H-4_B), 3.88–3.70 (m, 4 H, H-4_F, H-5_A, H-5_G and H-6_{bC}), 3.75 (s, 3 H, (OCH_3), 3.68–3.50 (m, 6 H, H-4_A, H-4_D, H-5_D, H-5_F, H-5_{aE} and H-6_{aB}), 3.46 (s, 3 H, OCH_3), 3.44–3.10 (m, 6 H, H-2_B, H-2_C, H-4_C, H-5_B, H-5_C and H-5_{bE}), 2.98–2.88 (m, 1 H, H-6_{bB}), 2.05, 2.04, 2.02, 2.01, 2.00, 1.98 (6 s, 18 H, 6 COCH_3), 1.31–1.20 (m, 9 H, 3 CCH_3), 0.87 (d, *J*=6.0 Hz, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.9–168.4 (6 *C*OCH$_3$), 154.8–114.5 (Ar-C), 102.2 (C-1_C), 101.1 (C-1_B), 100.2 (2 C, Ph*C*H), 99.6 (C-1_F), 99.4 (C-1_E), 97.7 (2 C, C-1_D and C-1_G), 96.1 (C-1_A), 83.2 (C-5_C), 82.2 (C-2_F), 81.4 (3 C, C-2_C, C-4_A and C-4_D), 81.0 (C-5_G), 80.0 (C-2_B), 79.4 (C-5_F), 79.1 (C-4_B), 78.5 (C-2_D), 77.7 (C-2_A), 77.6 (C-3_B), 77.2 (C-5_B), 76.8 (C-3_C), 76.4 (C-3_A), 75.2 (C-3_F), 75.1 (Ph*C*H$_2$), 75.9 (Ph*C*H$_2$), 74.7 (Ph*C*H$_2$), 74.4 (Ph*C*H$_2$), 74.0 (Ph*C*H$_2$), 73.6 (Ph*C*H$_2$), 70.9 (3 C, C-3_D, C-4_E and C-5_D), 70.8 (C-4_G), 69.7 (C-2_G), 68.9 (C-3_G), 68.8 (2 C, C-5_E and C-6_C), 68.5 (2 C, C-2_E and C-3_E), 67.8 (C-5_A), 66.8 (C-4_F), 66.2 (C-4_C), 61.5 (C-6_B), 57.9 (O*C*H$_3$), 55.4 (O*C*H$_3$), 20.8–20.6 (6 CO*C*H$_3$), 18.3, 17.9, 17.2, 17.1 (4 C*C*H$_3$); ESI-MS: *m/z*=2165.0 $[M+NH_4]^+$; Anal. Calcd. for $C_{117}H_{134}O_{38}$ (2146.85): C, 65.41; H, 6.29; found: C, 65.22; H, 6.55.

4-Methoxyphenyl (α-L-rhamnopyranosyl)-(1→2)-(3-O-methyl-α-L-rhamnopyranosyl)-(1→3)-[(β-D-xylopyranosyl)-(1→2)]-(α-L-rhamnopyranosyl)-(1→3)-(β-D-glucopyranosyl)-(1→3)-(β-D-glucopyranosyl)-(1→3)-α-L-rhamnopyranoside ***(1)*** A solution of compound **20** (650 mg, 0.3 mmol) in 0.1 M CH_3ONa in CH_3OH (10 mL) was allowed to stir at room temperature for 2 h. The reaction mixture was neutralized with Dowex 50 W X-8 (H^+) resin, filtered and concentrated. To a solution of the crude product in CH_3OH (10 mL) was added 20% $Pd(OH)_2$/C (150 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 evaporated to dryness to give heptasaccharide **1**, which was purified through a Sephadex LH-20 column using CH_3OH-water (8:1) as eluant (270 mg, 76%); white powder; $[\alpha]_D^{25}$ −52.3 (*c* 1.0, H_2O); IR (KBr): 2926, 2373, 1759, 1658, 1550, 1467, 1429, 1370, 1045, 679 cm^{-1}; ^1H NMR (300 MHz, D_2O): δ 7.0 (d, *J*=9.0 Hz, 2 H, Ar-H), 6.88 (d, *J*=9.0 Hz, 2 H, Ar-H), 5.39 (br s, 1 H, H-1_G), 5.33 (br s, 1 H, H-1_A), 5.26 (br s, 1 H, H-1_D), 4.92 (br s, 1 H, H-1_F), 4.70 (d, *J*=7.5 Hz, 1 H, H-1_B), 4.63 (d, *J*=7.5 Hz, 1 H, H-1_C), 4.54 (d, *J*=7.2 Hz, 1 H, H-1_E), 4.30 (br s, 1 H, H-2_A), 4.23 (br s, 1 H, H-2_D), 4.07–4.03 (m, 2 H, H-2_G and H-3_A), 4.0–3.82 (m, 6 H, H-2_F, H-4_B, H-4_G, H-5_{aE} and H-$6_{a,bB}$), 3.80–3.78 (m, 1 H, H-3_F), 3.76 (s, 3 H, OCH_3), 3.70–3.61 (m, 5 H, H-3_E, H-3_G, H-4_F and H-$6_{a,bC}$), 3.60–3.51 (m, 7 H, H-2_B, H-3_B, H-3_C, H-3_D, H-4_A, H-4_D, H-5_G), 3.50 (s, 3 H, OCH_3), 3.45–3.30 (m, 10 H, H-2_C, H-2_E, H-4_C, H-4_E, H-5_A, H-5_B, H-5_C, H-5_D, H-5_{bE}, H-5_F), 1.36–1.27 (m, 9 H, 3 CCH_3), 0.91 (d, *J*=6.0 Hz, 3 H, CCH_3); ^{13}C NMR (75 MHz, D_2O): δ 155.0–114.2 (Ar-C), 105.0 (C-1_E), 103.9 (C-1_B), 103.5 (C-1_C), 101.7 (C-1_F), 100.7 (C-1_D), 100.0 (C-1_G), 99.0 (C-1_A), 85.9 (C-3_G), 82.1 (C-3_D), 81.2 (C-2_G), 80.4 (C-5_G), 78.8 (C-3_A), 76.5 (C-4_C), 76.0 (2 C, C-2_C, C-4_G), 75.9 (C-4_E), 74.7 (C-5_F), 73.6 (C-4_A), 73.3 (C-2_D), 73.1 (C-3_C), 72.4 (2 C, C-2_B, C-4_B), 71.8 (C-5_B), 71.2 (C-2_A), 70.8 (C-2_E), 70.7 (C-5_A), 70.0 (C-4_F), 69.7 (C-3_B), 69.2 (C-3_E), 68.8 (2 C, C-5_C, C-5_D), 68.7 (C-3_F), 68.5 (C-4_D), 68.1 (C-2_F), 65.4 (C-5_E), 61.1 (C-6_B), 60.6 (C-6_C), 56.7 (O*C*H$_3$), 54.6 (O*C*H$_3$), 16.8, 16.6, 16.4, 16.3 (4 C*C*H$_3$); ESI-MS: *m/z*=1201.5 $[M+Na]^+$; Anal. Calcd. for $C_{49}H_{78}O_{32}$ (1178.45): C, 49.91; H, 6.67; found: C, 49.67; H, 6.96.

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