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Total synthesis of an antigenic heptasaccharide motif found in the cell-wall lipooligosaccharide of *Mycobacterium gordonae* strain 989

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Abstract An antigenic heptasaccharide motif of the cell-wall glycolipid of *Mycobacterium gordonae* strain 989 has been synthesized in a linear fashion by using a general glycosylation condition and minimum number of protecting group manipulation. All suitably protected monosaccharide intermediates were prepared from commercially available reducing sugars following some novel methodologies recently developed in our laboratory. Most of the synthetic intermediates were obtained as solid compounds in excellent yields.

Keywords Carbohydrates · Oligosaccharides · Glycosylations · Vaccines · *Mycobacterium gordonae* 989

Introduction

False infections or artifactual clustering of real infections caused by non-tubercular mycobacteria (NTM) are known for several years and continue to be a serious concern, because of the problems associated with the unnecessary administration of therapeutics [1–4]. A number of NTM species have been isolated from water and soil, which include *Mycobacterium gordonae*, *Mycobacteriaum avium* complex, *Mycobacterium fortuitum*, *Mycobacterium kansasii*, *Mycobacterium xenopi*, *Mycobacterium terrae etc.* [5]. The mycobacterial infections have been seriously revived since the outbreak of acquired immunodeficiency syndrome (AIDS) [6, 7]. Recently, infections due to *mycobacteria*, apart from tuberculosis, are on the rise particularly in patients with AIDS. Among several species of NTM, *Mycobacterium gordonae* (*M. gordonae*) is widely distributed in soil and water [8]. In humans, *M. gordonae* can be found in sputum, gastric fluid and urine [9]. Although, earlier *M. gordonae* was considered as a benign commensal, and sometimes termed as *Mycobacterium aque* or "tap-water bacillus" [10], recently a number of infections involving skin and soft tissues, cornea, liver and lower respiratory tract, trauma and immunosuppression have been reported [11, 12]. Particularly, in patients suffering from AIDS, *M. gordonae* behaves as an opportunistic pathogen causing pulmonary diseases, which are quite indistinguishable from that caused by *M. tuberculosis*. Administration of antituberculosis therapy such as isoniazid, pyrazinamide, ethambutol and cycloserine can not cure the patients because *M. gordonae* is resistant to these drugs [12]. In order to provide the required chemotherapy avoiding such confusion, it is essential to identify atypical *Mycobacteria* from other species of *Mycobacteria*.

M. gordonae strain 989 belongs to atypical nontuberculotic *Mycobacteria,* which contains a large number of trehalose-containing glycolipids in its cell wall, some of which possess antigenicity [13–15]. Isolation and structural elucidation of a unique trehalose linked heptasaccharide motif known to have antigenic activity from the cell wall of *M. gordonae* strain 989 has been reported by Brennan *et al*. (Fig. 1) [16]. It is well established that specific oligosaccharide antigen can produce specific immune response through the development of antibodies against it. This antigenic heptasaccharide motif could be useful to generate corresponding antibodies for the serodiagnosis of the individual mycobacterial infection and to design an antibacterial vaccine against this particular strain.

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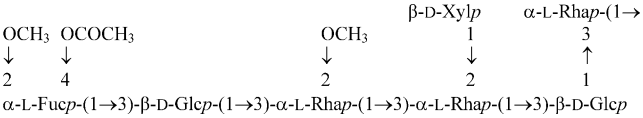


Fig. 1 Structure of heptasaccharide motif of the glycolipid found in the cell-wall of *M. gordonae* strain 989

In the medicinal chemistry, carbohydrate based vaccines are well known for their effectiveness against pathogenic bacterial infections. A number of carbohydrate vaccines used in the clinics are prepared from the polysaccharides obtained from the natural sources. Recently, Roy *et al.* reported a synthetic version of the *Haemophilus influenzae* type b (Hib) vaccine [17]. In the recent past several reports have appeared in the literature aiming to develop synthetic version of the polysaccharide-based carbohydrate vaccine candidates against Shigella, Cholera, pneumoccaus, cancer, anthrax, malaria, leishmania *etc.* [18–34]. In order to induce a specific immune response in the host using a carbohydrate vaccine candidate, antigenic oligosaccharides are attractive targets. Although, oligosaccharides can be isolated from the respective natural sources, large quantities of the oligosaccharides can only be accessed from the efficient chemical synthetic strategies. Essentially, the synthetic oligosaccharide motif is required to conjugate with a carrier protein through a spacer arm to be used as an antigen for the production of a specific immune response. Therefore, the synthetic oligosaccharide motif should contain a temporary protecting group at the reducing terminus, which can be removed to attach the oligosaccharide unit with the carrier protein. However, the first step for the preparation of a glycoconjugate is to develop a concise chemical synthetic strategy for the synthesis of a target oligosaccharide moiety containing a temporary protecting group at the reducing terminus. We report herein the first total synthesis of the heptasaccharide motif of the lipooligosaccharide found in the cell wall of *M. gordonae* strain 989 as its 4-methoxyphenyl glycoside (Fig. 2) with preserved natural structure for its use to evoke antibodies, necessary for serodiagnosis of the individual strain.

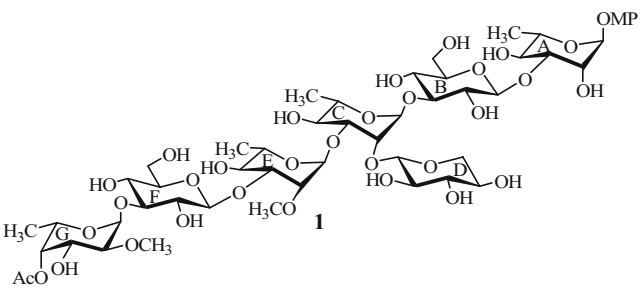


Fig. 2 Chemical structure of the synthesized heptasaccharide as its 4-methoxyphenyl glycoside (**1**)

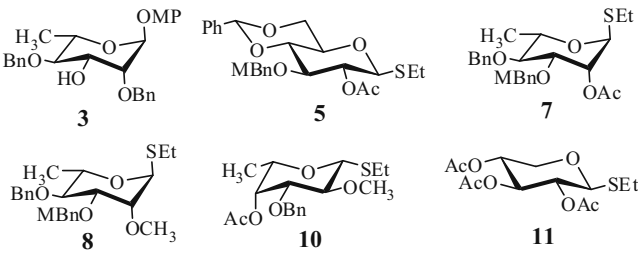


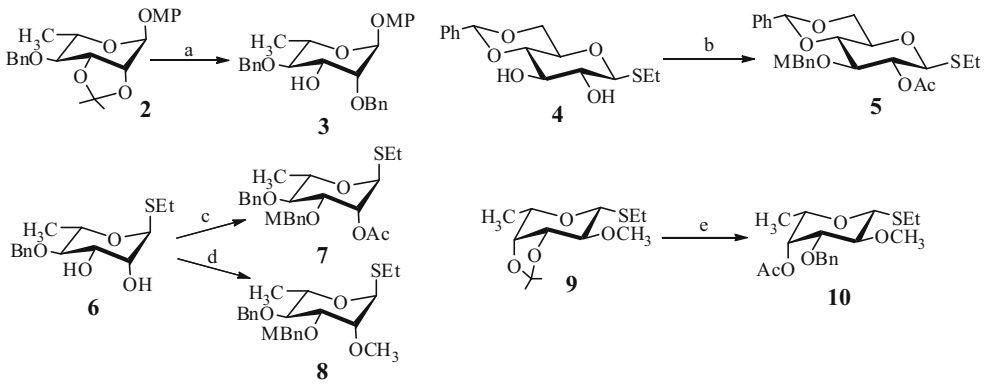
Fig. 3 Suitably protected monosaccharide derivatives used for the synthesis of heptasaccharide as its 4-methoxyphenyl glycoside (**1**)

Results and discussion

The synthesis of the target heptasaccharide as its 4-methoxyphenyl glycoside (**1**) was achieved by a series of stereoselective glycosylation and judicious functional group manipulations. A series of suitably functionalized monosaccharide derivatives (Fig. 3) used in the construction of the target molecule, were prepared from commercially available reducing sugars using several novel methodologies developed in our laboratory and reported in the literature.

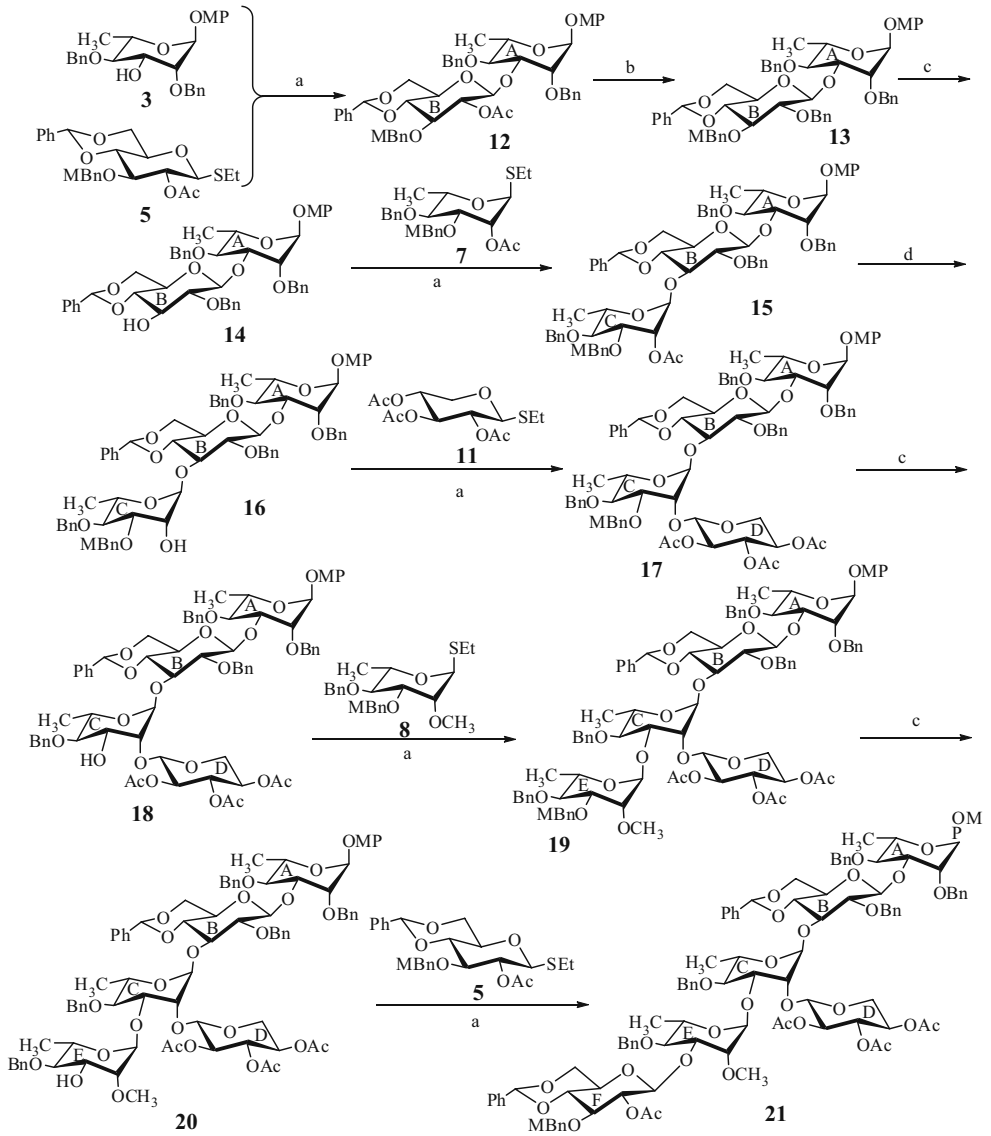
Synthesis of the protected monosaccharide synthons are presented in Scheme 1. 4-Methoxyphenyl 2,4-di-*O*-benzyl-α-L-rhamnopyranoside (**3**) was prepared from 4-methoxyphenyl 4-*O*-benzyl-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (**2**) [35] using a sequence of reactions involving acidic hydrolysis of isopropylidene group followed by selective benzylation under phase transfer reaction conditions. Selective 4-methoxybenzylation of ethyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (**4**) [36] via stannylidene acetal formation [37] followed by conventional acetylation furnished ethyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(4-methoxybenzyl)-1-thio-β-D-glucopyranoside (**5**). Tin mediated [37] selective 4-methoxybenzylation of ethyl 4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (**6**) [38] followed by acetylation furnished compound 7 in excellent yield. Compound **8** was also prepared from compound **6** in excellent yield following the similar reaction sequences except a base mediated methylation [39] in stead of acetylation. Removal of isopropylidene group from ethyl 3,4-*O*-isopropylidene-2-*O*-methyl-1-thio-β-L-fucopyranoside (**9**) [40] followed by tin mediated selective benzylation [37] and acetylation furnished compound **10** in excellent yield. Preparation of ethyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside (**11**) [41] is well documented in the literature. Yields are excellent in most of the reactions (Scheme 1). After having the suitably functionalized monosaccharide intermediates at hand, construction of the target heptasaccharide was attempted by stereoselective glycosylations of monosaccharide intermediates and functionalization of the glycoside intermediates.

Iodonium ion promoted β-selective glycosylation of compound **3** with the thioglycoside donor **5** in the presence



Scheme 1 Reagents: *a* (1) 80% aq. AcOH, 75°C, 1.5 h; (2) benzyl bromide, 5% aq. NaOH, Bu_4NBr, CH_2Cl_2, 80% in two steps; *b* (1) Bu_2SnO, CH_3OH, 80°C, 2 h, then 4-methoxybenzyl chloride, CsF, DMF, 80°C, 16 h, 72%; (2) acetic anhydride, pyridine, r t, 2 h, quantitative; *c* (1) Bu_2SnO, toluene, 110°C, 4 h, then 4-methoxybenzyl chloride, 80°C, 16 h, 75%; (2) acetic anhydride, pyridine, r t, 2 h, quantitative; *d* (1) Bu_2SnO, toluene, 110°C, 4 h, then 4-methoxybenzyl chloride, 80°C, 16 h, 75%; (2) CH_3I, NaOH, DMF, 5°C, 3 h, 86%; *e* (1) 80% aq. AcOH, 80°C, 1.5 h; (2) Bu_2SnO, toluene, 110°C, 4 h, then benzyl bromide, Bu_4NBr, 80°C, 12 h; (3) acetic anhydride, pyridine, r t, 1.5 h, 76% in three steps

of a combination of *N*-iodosuccinimide (NIS) and trimethylsilyl trifluoromethanesulfonate (TMSOTf) [42, 43] furnished the disaccharide derivative **12** in 81% yield. Conversion of the acetyl group to the benzyl group of compound **12** in one step [39] using benzyl bromide and sodium hydroxide furnished compound **13** in 84% yield. Oxidative removal of 4-methoxybenzyl group using dichloro-dicyano-benzoquinone (DDQ) [44] in a bi-phasic reaction condition resulted in the formation of disaccharide acceptor **14** in 86% yield. α-Selective condensation of disaccharide derivative **14** with thioglycoside **7** in the presence of NIS-TMSOTf [42, 43] afforded trisaccharide derivative **15** in 85% yield, which was deacetylated using sodium methoxide to give trisaccharide acceptor **16** in quantitative yield. Formation of exclusive α-glycosidic linkage in the trisaccharide derivative **15** was confirmed from its ^{1}H NMR [δ 5.33 {d, *J*=1.7 Hz, H-1_A (α-D-Rha*p*)}, 5.21 {d, *J*=1.1 Hz, H-1_C (α-D-Rha*p*)}, 4.98 {d, *J*=7.8 Hz, H-1_B (β-D-Glc*p*)}] and ^{13}C NMR spectra [δ 103.7 {($J_{C\text{-}1/H\text{-}1}$ 164.2 Hz, C-1_B (β-D-Glc*p*)}, 98.4 {$J_{C\text{-}1/H\text{-}1}$ 172.0 Hz, C-1_C (α-D-Rha*p*)}, 97.3 {($J_{C\text{-}1/H\text{-}1}$ 172.5 Hz, C-1_A (α-D-Rha*p*)}] [45–47]. Compound **16** was allowed to condense with thioglycoside donor **11** in the presence of NIS-TMSOTf [42, 43] to furnish the tetrasaccharide derivative **17** in 82% yield. Presence of signals at [δ 5.32 {d, *J*=1.7 Hz, H-1_A (α-D-Rha*p*)}, 5.26 {d, *J*=1.2 Hz, H-1_C (α-D-Rha*p*)}, 4.99 {d, *J*=7.5 Hz, H-1_B (β-D-Glc*p*)} and 4.50 {d, *J*=7.7 Hz, H-1_D (β-D-Xylp)}] in the ^{1}H NMR and δ 103.7 {C-1_B (β-D-Glc*p*)}, 101.9 {C-1_D (β-D-Xylp)}, 99.6 {C-1_C (α-D-Rha*p*)} 97.2 {C-1_A (α-D-Rha*p*)} in the ^{13}C NMR spectrum of compound **17** supported the formation of β-linkage of the D-xylose moiety. Oxidative removal of 4-methoxybenzyl group in compound **17** using DDQ [44] afforded the tetrasaccharide acceptor **18** in 86% yield. Further, α-selective coupling of compound **18** with thioglycoside **8** in the presence of NIS-TMSOTf [42, 43] gave pentasaccharide derivative **19** in 84%, which was treated with DDQ [44] to produce pentasaccharide acceptor **20** in 88% yield. Presence of signals at [δ 5.32 {d, *J*=1.7 Hz, H-1_A (α-D-Rha*p*)}, 5.26 {brs, H-1_C (α-D-Rha*p*)}, 5.08 {brs, H-1_E (α-D-Rha*p*)}, 4.95 {d, *J*=7.7 Hz, H-1_B (β-D-Glc*p*)}, 4.73 {d, *J*=7.0 Hz, H-1_D (β-D-Xylp)}] in the ^{1}H NMR and [δ 103.8 {$J_{C\text{-}1/H\text{-}1}$ 163.5 Hz, C-1_B (β-D-Glc*p*)}, 100.5 {$J_{C\text{-}1/H\text{-}1}$ 159.7 Hz, C-1_D (β-D-Xylp)}, 99.5 {2 C, $J_{C\text{-}1/H\text{-}1}$ 171.0 Hz each, C-1_C and C-1_E (2 α-D-Rha*p*)}, 97.2 {$J_{C\text{-}1/H\text{-}1}$ 169.5 Hz, C-1_A (α-D-Rha*p*)}] in the ^{13}C NMR spectra confirmed the formation of compound **19**. NIS-TMSOTf [42, 43] promoted glycosylation of pentasaccharide acceptor **20** with thioglycoside donor **5** furnished hexasaccharide derivative **21** in 82% yield. Presence of signals [δ 103.9 {C-1_B (β-D-Glc*p*)}, 101.2 {C-1_D (β-D-Xylp)}, 100.4 {C-1_F (β-D-Glc*p*)}, 99.9 {C-1_E (α-D-Rha*p*)}, 99.4 {C-1_C (α-D-Rha*p*)}, 97.2 {C-1_A (α-D-Rha*p*)}] in the ^{13}C NMR spectrum supported the formation of compound **21** (Scheme 2). Following a one-pot, two-step reaction protocol [39] compound **21** was treated with benzyl bromide in the presence of solid sodium hydroxide to give benzylated hexasaccharide derivative **22** in 90% yield. Oxidative removal of 4-methoxybenzyl group in hexasaccharide derivative **22** using DDQ [44] afforded the hexasaccharide acceptor **23** in 86% yield. Final α-selective glycosylation of hexasaccharide acceptor **23** with thioglycoside donor **10** in the presence of NIS-TMSOTf [42, 43] furnished heptasaccharide derivative **24** in 76% yield. Formation of the compound **24** was supported by the appearance of a signature peak at δ 5.50 {d, *J*=4.0 Hz, 1 H, H-1_G (α-D-Fucp)} in the ^{1}H NMR and presence of signals at δ [104.4 (C-1_D), 103.7 (C-1_B), 103.4 (C-1_F), 101.7 (Ph*C*H), 101.6 (Ph*C*H), 100.4 (C-1_E), 100.1 (C-1_C), 98.0 (C-1_G), 97.3 (C-1_A)] in the ^{13}C NMR spectrum.

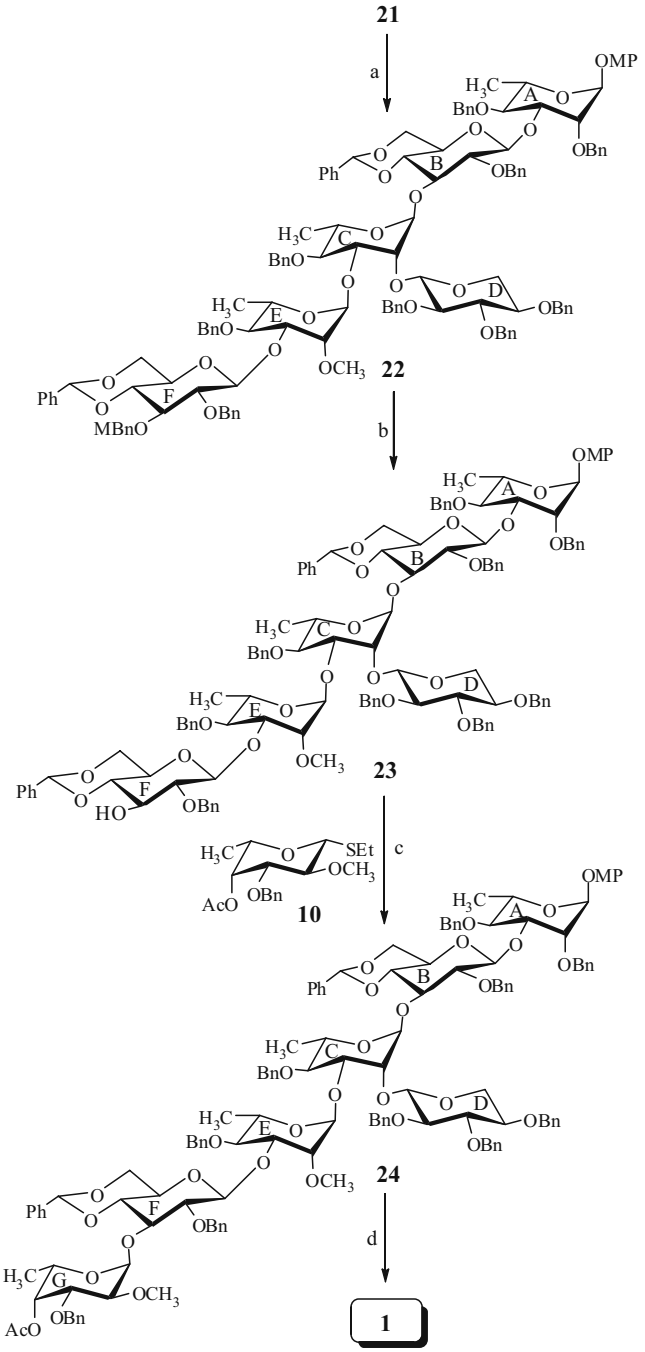


Scheme 2 Reagents: *a* *N*-Iodosuccinimide, TMSOTf, MS 4 Å, CH_2Cl_2, −40°C, 30 min, (81% for **12**, 85% for **15**, 82% for **17**, 84% for **19**, 82% for **21**); *b* benzyl bromide, NaOH, Bu_4NBr, THF, r t, 3 h, 84%; *c* DDQ, CH_2Cl_2–H_2O (1:1), r t, 2 h, (86% for **14**, 86% for **18**, 88% for **20**); *d* 0.1 M CH_3ONa, CH_3OH–CH_2Cl_2 (4:1), r t, 3 h, quantitative

Removal of benzylidene acetals and benzyl groups of heptasaccharide derivative **24** under a global deprotection condition using hydrogenolysis over Pearlman's catalyst [48] afforded target heptasaccharide **1** as its 4-methoxyphenyl glycoside in 81% yield, which was further purified through Sephadex LH-20 column using methanol–water as eluant. The formation of the compound **1** was confirmed from its 1D and 2D NMR and mass spectral analysis. Characteristic signals at δ [5.65 (brs, H-1_C), 5.50 (brs, 2 H, H-1_A and H-1_G), 5.31 (brs, H-1_E), 4.71 (d, J=7.9 Hz, 2 H, H-1_B and H-1_F), 4.56 (d, J=7.5 Hz, H-1_D)] in the ^{1}H NMR and at δ [105.4 (C-1_D), 103.9 (C-1_B), 103.7 (C-1_F), 99.9 (C-1_G), 98.9 (C-1_A), 98.5 (C-1_E), 96.3 (C-1_C)] in the ^{13}C NMR spectra supported its formation (Scheme 3). Most of the synthetic intermediates are obtained as solid compounds in high yields. Use of a general glycosylation condition and similar kind of protecting group strategy makes the synthetic scheme viable for a scale-up preparation. A series of modified reaction protocols recently developed by us and found in the literature have been applied successfully for the synthesis of the target heptasaccharide **1**.

Conclusion

In summary, a straightforward linear synthesis of a heptasaccharide motif with intact natural structure, found in the cell-wall of *Mycobacterium gordonae* strain 989 has been achieved using sequential glycosylations and minimum number of protecting group manipulations. A com-



Scheme 3 Reagents: *a* Benzyl bromide, NaOH, Bu_4NBr, THF, r t, 5 h, 90%; *b* DDQ, CH_2Cl_2–H_2O (1:1), 2 h, 86%; *c* *N*-iodosuccinimide, TMSOTf, MS 4 Å, CH_2Cl_2, −40°C, 30 min, 76%; *d* H_2, 20% $Pd(OH)_2$–C, CH_3OH–toluene (1:1), 24 h, 81%

mon glycosylation condition has been used throughout the synthesis and similar protecting group (4-methoxybenzyl group) has been used to make the synthetic strategy more general for a scale-up synthesis, if necessary. All glycosylation steps are reasonably fast, highly reproducible and high yielding. The structure of the naturally found heptasaccharide is preserved in the synthetic heptasaccharide **1** (*i.e.* presence of an acetyl group and a methoxy group at the non-reducing L-fucose terminus and a methoxy group at the middle L-rhamnose moiety). 4-Methoxy phenyl group can serve as a temporary anomeric protecting group. It can be removed under standard reaction conditions whenever it is necessary to couple the heptasaccharide moiety to a carrier protein for the preparation of glycoconjugates to raise antibody against the synthetic hapten.

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 in hot plate. Silica gel 230–400 mesh was used for column chromatography. ^1H and ^{13}C NMR, 2DCOSY, HSQC spectra were recorded on Brucker Advance DPX 200 and 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.

*4-Methoxyphenyl 2,4-di-O-benzyl-α-L-rhamnopyranoside (**3**)* A solution of compound **2** (10 g, 25 mmol) in 80% aq. acetic acid (200 ml) was allowed to stir at 75°C for 1.5 h. The solvents were evaporated and co-evaporated with toluene (3×50 ml) under reduced pressure. To a solution of the diol derivative in CH_2Cl_2 (150 ml) were added 5% aq. NaOH (80 ml), benzyl bromide (3.5 ml, 29.5 mmol) and Bu_4NBr (200 mg) and the reaction mixture was allowed to stir at room temperature for 5 h. The reaction mixture was diluted with CH_2Cl_2 (100 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 (2:1) as eluant to give pure compound **3** (9 g, 80%); colorless oil; $[\alpha]_D^{25}$ −51.6 (*c* 1.5, $CHCl_3$), IR (neat): 2,926, 2,365, 1,649, 1,510, 1,460, 1,392, 1,221, 1,105, 1,033, 754, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.42–7.28 (m, 10 H, Ar-H), 6.97 (d, *J*=9.1 Hz, 2 H, Ar-H), 6.83 (d, *J*=9.1 Hz, 2 H, Ar-H), 5.43 (d, *J*=1.2 Hz, 1 H, H-1), 4.95 (d, *J*=11.2 Hz, 1 H, PhCH_2), 4.82 (d, *J*=11.8 Hz, 1 H, PhCH_2), 4.72 (d, *J*=11.2 Hz, 1 H, PhCH_2), 4.70 (d, *J*=11.8 Hz, 1 H, PhCH_2), 4.17 (dd, *J*=9.2 and 3.7 Hz, 1 H, H-3), 3.95–3.93 (m, 1 H, H-2), 3.90–3.82 (m, 1 H, H-5), 3.80 (s, 3 H, OCH_3), 3.43 (t, *J*=9.3 Hz, 1 H, H-4), 1.35 (d, *J*=6.3 Hz, 3 H, CCH_3); ^{13}C NMR (75 MHz,

$CDCl_3$): δ 154.8 (Ar-C), 150.3 (Ar-C), 138.5 (Ar-C), 137.6 (Ar-C), 128.6–127.7 (10 C, Ar-C), 117.4 (2 C, Ar-C), 114.5 (2 C, Ar-C), 95.9 (C-1), 82.2 (C-4), 78.4 (C-2), 75.0, 73.2 (2 Ph*C*H_2), 71.5 (C-3), 67.9 (C-5), 55.5 (O*C*H_3), 18.1 (C*C*H_3); ESI-MS: *m*/*z*=468.1 $[M+NH_4]^+$; Anal. Calcd. for $C_{27}H_{30}O_6$ (450.20): C, 71.98; H, 6.71; found: C, 71.72; H, 6.96.

*Ethyl 2-O-acetyl-4,6-O-benzylidene-3-O-(4-methoxybenzyl)-1-thio-β-D-glucopyranoside (**5**)* To a solution of compound **4** (6.5 g, 20.8 mmol) in anhydrous CH_3OH (150 ml) was added dibutyltin oxide (6.2 g, 24.9 mmol) and the reaction mixture was allowed to stir at 80°C for 2 h. The solvents were evaporated and co-evaporated with toluene (3×100 ml) under reduced pressure. To a solution of the crude mass in dry DMF (50 ml) were added cesium fluoride (3.5 g, 23 mmol) and 4-methoxybenzylchloride (5.7 ml, 42 mmol) and the reaction mixture was allowed to stir at 80°C for 16 h. The reaction mixture was diluted with water (200 ml) and extracted with CH_2Cl_2 (150 ml). The organic layer was washed with aq. $NaHCO_3$ and water in succession, dried (Na_2SO_4) and evaporated to dryness. The crude product was conventionally acetylated using acetic anhydride (15 ml) and pyridine (15 ml) to give compound **5**, which was purified over SiO_2 using hexane–EtOAc (3:1) as eluant to give pure compound **5** (7.1 g, 72%); colorless solid; m.p. 84°C; $[\alpha]_D^{25}$ −26.7 (*c* 1.5, $CHCl_3$); IR (KBr): 2,926, 2,367, 1,745, 1,649, 1,516, 1,461, 1,378, 1,236, 1,093, 1,031, 757, 693 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.51–7.18 (m, 5 H, Ar-H), 7.20 (d, *J*=8.6 Hz, 2 H, Ar-H), 6.83 (d, *J*=8.6 Hz, 2 H, Ar-H), 5.58 (s, 1 H, PhC*H*), 5.02 (dd, *J*=10.0 and 8.6 Hz, 1 H, H-2), 4.80 (d, *J*=11.7 Hz, 1 H, PhCH_2), 4.62 (d, *J*=11.7 Hz, 1 H, PhCH_2), 4.43 (d, *J*=10.1 Hz, 1 H, H-1), 4.38 (dd, *J*=10.5 and 5.0 Hz, 1 H, H-4), 3.81 (s, 3 H, OCH_3), 3.78–3.70 (m, 3 H, H-3, H-6_{ab}), 3.51–3.48 (m, 1 H, H-5), 2.71 (ddd, *J*=9.9, 7.4 and 2.5 Hz, 2 H, SCH_2CH$_3$), 2.03 (s, 3 H, OCOCH_3), 1.27 (t, *J*=7.5 Hz, 3 H, SCH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.1 (*C*OCH$_3$), 159.2 (Ar-C), 137.2–113.6 (Ar-C), 101.1 (Ph*C*H), 84.0 (C-1), 81.5 (C-3), 79.0 (C-5), 73.8 (MeOPh*C*H_2), 71.1 (C-2), 70.6 (C-4), 68.5 (C-6), 55.1 (O*C*H_3), 23.6 (S*C*H_2CH$_3$), 20.8 (CO*C*H_3), 14.7 (SCH_2CH_3); ESI-MS: *m*/*z*=497.2 $[M+Na]^+$; Anal. Calcd. for $C_{25}H_{30}O_7S$ (474.17): C, 63.27; H, 6.37; found: C, 63.06; H, 6.60.

*Ethyl 2-O-acetyl-4-O-benzyl-3-O-(4-methoxybenzyl)-1-thio-α-L-rhamnopyranoside (**7**)* To a solution of compound **6** (7.5 g, 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 4-methoxybenzyl chloride (7 ml, 51.6 mmol) was added to it and the reaction mixture was stirred at 80°C for 16 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. The crude product was conventionally acetylated using acetic anhydride (15 ml) and pyridine (20 ml) at room temperature. The solvents were removed under reduced pressure to give the crude product, which was purified over SiO_2 using hexane–EtOAc (5:1) as eluant to furnish pure compound 7 (8.6 g, 75%); colorless oil; $[\alpha]_D^{25}$ −66.6 (*c* 1.5, $CHCl_3$); IR (neat): 2,928, 2,380, 1,743, 1,612, 1,513, 1,455, 1,370, 1,238, 1,102, 1,040, 828, 746 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.33–7.28 (m, 5 H, Ar-H), 7.20 (d, *J*=8.5 Hz, 2 H, Ar-H), 6.80 (d, *J*=8.5 Hz, 2 H, Ar-H), 5.41 (t, *J*=1.4 Hz, 1 H, H-2), 5.16 (brs, 1 H, H-1), 4.87 (d, *J*=10.9 Hz, 1 H, PhCH_2), 4.56 (dd, *J*=10.8 and 4.4 Hz, 2 H, MeOPhCH_2), 4.40 (d, *J*=10.9 Hz, 1 H, PhCH_2), 4.10–4.00 (m, 1 H, H-5), 3.82 (dd, *J*=9.3 and 3.1 Hz, 1 H, H-3), 3.75 (s, 3 H, OCH_3), 3.41 (t, *J*=9.4 Hz, 1 H, H-4), 2.64–2.47 (m, 2 H, SCH_2CH$_3$), 2.12 (s, 3 H, OCOCH_3), 1.29 (d, *J*=6.2 Hz, 3 H, CCH_3), 1.24 (t, *J*=7.4 Hz, SCH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2 (*C*OCH$_3$), 159.2 (Ar-C), 138.4 (Ar-C), 129.8 (3 C, Ar-C), 128.2 (2 C, Ar-C), 127.7 (2 C, Ar-C), 127.5 (Ar-C), 113.7 (2 C, Ar-C), 82.2 (C-1), 80.1 (C-4), 77.9 (C-2), 75.2 (MeOPh*C*H_2), 71.3 (Ph*C*H_2), 70.8 (C-3), 68.2 (C-5), 55.1 (O*C*H_3), 25.4 (S*C*H_2CH$_3$), 21.0 (CO*C*H_3), 17.8 (C*C*H_3), 14.8 (SCH_2CH_3); ESI-MS: *m*/*z*=499.2 $[M+K]^+$; Anal. Calcd. for $C_{25}H_{32}O_6S$ (460.19): C, 65.19; H, 7.00; found: C, 65.0; H, 7.26.

*Ethyl 4-O-benzyl-3-O-(4-methoxybenzyl)-2-O-methyl-1-thio-α-L-rhamnopyranoside (**8**)* To a solution of ethyl y44-*O*-benzyl-3-*O*-(4-methoxybenzyl)-1-thio-α-L-rhamnopyranoside (5 g, 11.9 mmol) (prepared from compound **6** following similar reaction conditions as described in the preparation of compound 7), in dry DMF (20 ml) were added crushed NaOH (1.5 g, 37.5 mmol) and iodomethane (3 ml, 48.2 mmol) and Bu_4NBr (100 mg) at 0°C and the reaction mixture was allowed to stir at 5°C for 3 h. The reaction mixture was diluted with water and extracted with CH_2Cl_2 (150 ml). The organic layer was washed with water, dried (Na_2SO_4) and evaporated to dryness to give the crude product, which was purified over SiO_2 using hexane–EtOAc (7:1) as eluant to furnish pure compound **8** (4.4 g, 86%); colorless oil; $[\alpha]_D^{25}$ −126.6 (*c* 1.5, $CHCl_3$); IR (neat): 2,364, 1,590, 1,351, 1,083, 769, 669 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.32–7.28 (m, 5 H, Ar-H), 7.23 (d, *J*=8.5 Hz, 2 H, Ar-H), 6.80 (d, *J*=8.6 Hz, 2 H, Ar-H), 5.24 (brs, 1 H, H-1), 4.88 (d, *J*=11.0 Hz, 1 H, PhCH_2), 4.57 (brs, 2 H, MeOPhCH_2), 4.53 (d, *J*=11.0 Hz, 1 H, PhCH_2), 3.95 (dd, *J*=9.3 and 6.2 Hz, 1 H, H-2), 3.77 (s, 3 H, OCH_3), 3.72

(dd, *J*=9.4 and 3.1 Hz, 1 H, H-3), 3.51–3.41 (m, 2 H, H-4, H-5), 3.45 (s, 3 H, OCH_3), 2.64–2.55 (m, 2 H, SCH_2CH$_3$), 1.27 (t, *J*=7.5 Hz, 3 H, SCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.3 (Ar-C), 138.7 (Ar-C), 130.3 (Ar-C), 129.6 (2 C, Ar-C), 128.2 (2 C, Ar-C), 127.8 (2 C, Ar-C), 127.5 (Ar-C), 113.8 (2 C, Ar-C), 81.2 (C-1), 80.5 (C-4), 79.8 (2 C, C-2, C-3), 75.3 (MeOPhCH_2), 71.9 (PhCH_2), 68.3 (C-5), 58.5 (OCH_3), 55.1 (OCH_3), 25.3 (SCH_2CH$_3$), 17.8 (CCH_3), 15.0 (SCH$_2$CH_3); ESI-MS: *m*/*z*=471.2 [M+K]$^+$; Anal. Calcd. for $C_{24}H_{32}O_5S$ (432.20): C, 66.64; H, 7.46; found: C, 66.48; H, 7.62.

*Ethyl 4-O-acetyl-3-O-benzyl-2-O-methyl-1-thio-β-L-fucopyranoside (***10***)* A solution of compound **9** (2 g, 7.6 mmol) in 80% aq. acetic acid (50 ml) was allowed to stir at 80°C for 1.5 h. The solvents were removed under reduced pressure to give the diol derivative. To a solution of the diol derivative in dry toluene (100 ml) was added dibutyltin oxide (2.3 g, 9.2 mmol) and the reaction mixture was allowed to stir at 110°C for 4 h with azeotropic removal of water. The solvents were reduced by distillation. To the reaction mixture were added Bu_4NBr (500 mg) and benzyl bromide (2.7 ml, 22.7 mmol) and the reaction mixture was allowed to stir at 80°C for 12 h. The solvents were removed under reduced pressure and the crude mass was dissolved in CH_2Cl_2 (100 ml). The organic layer was washed with 1 N aq. HCl, satd. aq. $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated to give the crude product, which was conventionally acetylated using acetic anhydride (5 ml) and pyridine (5 ml) at room temperature. The solvents were removed under reduced pressure to give the crude product, which was purified over SiO_2 using hexane–EtOAc (6:1) to furnish pure compound **10** (2 g, 74%); colorless oil; $[\alpha]_D^{25}$ −10.2 (*c* 1.5, $CHCl_3$); IR (neat): 2,364, 1,740, 1,453, 1,374, 1,237, 1,127, 1,099, 1,020, 987, 744, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32–7.25 (m, 5 H, Ar-H), 5.30 (d, *J*= 2.8 Hz, 1 H, H-4), 4.69 (d, *J*=11.4 Hz, 1 H, PhCH_2), 4.51 (d, *J*=11.4 Hz, 1 H, PhCH_2), 4.28 (d, *J*=9.7 Hz, 1 H, H-1), 3.61–3.59 (m, 1 H, H-5), 3.58 (s, 3 H, OCH_3), 3.46 (dd, *J*= 9.1 and 3.5 Hz, 1 H, H-3), 3.23 (t, *J*=9.4 Hz, 1 H, H-2), 2.72 (ddd, *J*=12.1, 7.5 and 4.6 Hz, 2 H, SCH_2CH$_3$), 2.15 (s, 3 H, COCH_3), 1.30 (t, *J*=7.5 Hz, 3 H, SCH$_2$CH_3), 1.18 (d, *J*=6.4 Hz, 3 H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6 (*C*OCH$_3$), 137.8 (Ar-C), 128.3 (2 C, Ar-C), 127.8 (2 C, Ar-C), 127.6 (Ar-C), 84.8 (C-1), 80.8 (C-4), 79.4 (C-3), 72.8 (C-2), 71.7 (PhCH$_2$), 69.8 (C-5), 61.2 (OCH$_3$), 24.7 (SCH$_2$CH$_3$), 20.8 (CO*C*H$_3$), 16.7 (C*C*H$_3$), 14.9 (SCH$_2$*C*H$_3$); ESI-MS: *m*/*z*=393.1 [M+K]$^+$; Anal. Calcd. for $C_{18}H_{26}O_5S$ (354.15): C, 60.99; H, 7.39; found: C, 60.76; H, 7.65.

*4-Methoxyphenyl [2-O-acetyl-4,6-O-benzylidine-3-O-(4-methoxybenzyl)-β-D-glucopyranosyl]-(1→3)-2,4-di-O-benzyl-α-L-rhamnopyranoside (***12***)* To a solution of compound **3** (5 g, 11.1 mmol) and compound **5** (6.32 g, 13.3 mmol) in dry CH_2Cl_2 (70 ml) was added MS 4 Å (4 g) and the mixture was stirred at room temperature for 20 min under argon. The reaction mixture was cooled to −40°C and *N*-iodosuccinimide (3.6 g, 16 mmol) and TMSOTf (90 μl, 0.48 mmol) were added to it. After stirring the reaction mixture at same temperature for 30 min, Et_3N (0.5 ml) was added to it. The reaction mixture was diluted with CH_2Cl_2 (40 ml), filtered and washed with aq. $Na_2S_2O_3$ and water. The organic layer was 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 **12** (7.8 g, 81%); colorless solid; m.p. 62°C; $[\alpha]_D^{25}$ −52.2 (*c* 1.5, $CHCl_3$); IR (KBr): 2,368, 1,750, 1,610, 1,508, 1,457, 1,375, 1,228, 1,095, 826, 745, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46–7.23 (m, 15 H, Ar-H), 7.15 (d, *J*=8.3 Hz, 2 H, Ar-H), 6.87 (d, *J*=9.0 Hz, 2 H, Ar-H), 6.78 (d, *J*=8.0 Hz, 2 H, Ar-H), 6.73 (d, *J*=8.5 Hz, 2 H, Ar-H), 5.52 (s, 1 H, PhC*H*), 5.22 (brs, 1 H, H-1$_A$), 5.09 (t, *J*= 8.2 Hz, 1 H, H-2$_B$), 4.88–4.86 (m, 1 H, PhCH_2), 4.81 (d, *J*=11.4 Hz, 1 H, PhCH_2), 4.77 (d, *J*=9.8 Hz, 1 H, H-1$_B$), 4.74 (d, *J*=11.0 Hz, 1 H, PhCH_2), 4.70 (d, *J*=12.1 Hz, 1 H, PhCH_2), 4.58 (d, *J*=11.7 Hz, 1 H, PhCH_2), 4.52 (d, *J*= 11.0 Hz, 1 H, PhCH_2), 4.29 (dd, *J*=10.2 and 4.8 Hz, 1 H, H-4$_B$), 4.16 (dd, *J*=9.5 and 2.6 Hz, 1 H, H-2$_A$), 3.93–3.86 (m, 1 H, H-5$_A$), 3.76 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 3.73–3.52 (m, 5 H, H-3$_A$, H-3$_B$, H-4$_A$ and H-6$_{abB}$), 3.46–3.35 (m, 1 H, H-5$_B$), 1.78 (s, 3 H, COCH_3), 1.21 (d, *J*= 6.1 Hz, 3 H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.2 (*C*OCH$_3$), 159.2–113.7 (Ar-C), 102.1 (C-1$_B$), 101.2 (PhCH), 97.4 (C-1$_A$), 81.6 (C-4$_A$), 80.2 (C-3$_B$), 79.3 (C-2$_A$), 78.1 (C-3$_A$), 77.7 (C-5$_A$), 74.9 (PhCH$_2$), 73.7 (PhCH$_2$), 73.5 (PhCH$_2$), 73.2 (C-2$_B$), 68.6 (2 C, C-4$_B$ and C-6$_B$), 66.1 (C-5$_B$), 55.6 (OCH$_3$), 55.2 (OCH$_3$), 20.8 (COCH$_3$), 17.8 (CCH$_3$); ESI-MS: *m*/*z*=880.5 [M+NH$_4$]$^+$; Anal. Calcd. for $C_{50}H_{54}O_{13}$ (862.36): C, 69.59; H, 6.31; found: C, 69.42; H, 6.50.

*4-Methoxyphenyl [2-O-benzyl-4,6-O-benzylidine-3-O-(4-methoxybenzyl)-β-D-glucopyranosyl]-(1→3)-2,4-di-O-benzyl-α-L-rhamnopyranoside (***13***)* To a solution of compound **12** (7.4 g, 8.6 mmol) in THF (50 ml), were added crushed NaOH (1 g, 25 mmol), benzyl bromide (2 ml, 16.8 mmol) and Bu_4NBr (200 mg) and the reaction mixture was allowed to stir vigorously 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 concentrated under reduced pressure to give the crude product, which was purified over SiO_2 using hexane–EtOAc (7:1) as eluant to give pure **13** (6.5 g, 84%); colorless solid; m.p. 54°C; $[\alpha]_D^{25}$ −46.8 (*c* 1.5, $CHCl_3$); IR (KBr): 2,368, 1,611, 1,507,

1,457, 1,372, 1,220, 1,174, 1,088, 1,034, 1,000, 825, 748, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.49–7.12 (m, 22 H, Ar-H), 6.91–6.88 (m, 2 H, Ar-H), 6.80–6.75 (m, 4 H, Ar-H), 5.55 (s, 1 H, PhC*H*), 5.30 (d, *J*=1.4 Hz, 1 H, H-1_A), 5.00 (d, *J*=11.3 Hz, 1 H, PhCH_2), 4.94 (d, *J*=7.7 Hz, 1 H, H-1_B), 4.90–4.68 (m, 6 H, 3 PhCH_2 and MeOPhCH_2), 4.39 (d, *J*=10.7 Hz, 1 H, PhCH_2), 4.36–4.27 (m, 2 H, H-2_A and H-4_B), 3.96–3.95 (m, 1 H, H-5_A), 3.87–3.61 (m, 5 H, H-3_A, H-3_B, H-4_A, and H-6_{abB}), 3.76 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 3.47 (t, *J*=7.8 Hz, 1 H, H-2_B), 3.42–3.32 (m, 1 H, H-5_B), 1.28 (d, *J*=6.1 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.2–113.7 (Ar-C), 103.9 (C-1_B), 101.2 (Ph*C*H), 97.4 (C-1_A), 82.6 (C-4_A), 82.0 (C-3_B), 81.3 (C-2_A), 80.5 (C-3_A), 78.4 (C-5_A), 77.6 (C-2_B), 75.5 (Ph*C*H_2), 74.7 (2 Ph*C*H_2), 73.6 (Ph*C*H_2), 68.9 (C-6_B), 68.6 (C-4_B), 66.0 (C-5_B), 55.5 (O*C*H_3), 55.1 (O*C*H_3), 18.1 (C*C*H_3); ESI-MS: *m/z*=933.7 $[M+Na]^+$; Anal. Calcd. for $C_{55}H_{58}O_{12}$ (910.39): C, 72.51; H, 6.42; found: C, 72.28; H, 6.60.

*4-Methoxyphenyl (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** (6.3 g, 6.9 mmol) in CH_2Cl_2 and water (60 ml, 1:1), was added DDQ (1.9 g, 8.3 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. The organic layer was 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) as eluant to furnish pure **14** (4.7 g, 86%); colorless solid; m.p. 64°C; $[\alpha]_D^{25}$ −50.4 (*c* 1.5, $CHCl_3$); IR (KBr): 2,371, 1,601, 1,505, 1,456, 1,380, 1,219, 1,086, 1,031, 741, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.54–7.12 (m, 20 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), 5.49 (s, 1 H, PhC*H*), 5.30 (brs, 1 H, H-1_A), 5.08–4.75 (m, 6 H, H-1_B, and PhCH_2), 4.48 (d, *J*=10.5 Hz, 1 H, PhCH_2), 4.35–4.26 (m, 2 H, H-2_A and H-4_B), 4.00–3.92 (m, 1 H, H-5_A), 3.88–3.62 (m, 4 H, H-3_A, H-3_B and H-6_{abB}), 3.75 (s, 3 H, OCH_3), 3.49 (t, *J*=9.2 Hz, 1 H, H-4_A), 3.45–3.33 (m, 2 H, H-2_B and H-5_B), 1.31 (d, *J*=5.9 Hz, 3 H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.9–114.6 (Ar-C), 103.8 (C-1_B), 101.8 (Ph*C*H), 97.3 (C-1_A), 82.2 (C-4_A), 81.2 (C-3_B), 80.8 (C-2_A), 78.5 (C-3_A), 77.7 (C-5_A), 75.0 (Ph*C*H_2), 74.7 (Ph*C*H_2), 73.6 (Ph*C*H_2), 73.4 (C-2_B), 68.8 (C-6_B), 68.6 (C-4_B), 66.1 (C-5_B), 55.5 (O*C*H_3), 18.1 (C*C*H_3); ESI-MS: *m/z*= 808.2 $[M+NH_4]^+$; Anal. Calcd. for $C_{47}H_{50}O_{11}$ (790.34): C, 71.38; H, 6.37; found: C, 71.20; H, 6.55.

*4-Methoxyphenyl [2-O-acetyl-4-O-benzyl-3-O-(4-methoxybenzyl)-α-L-rhamnopyranosyl]-(1→3)-(2-O-benzyl-4,6-O-benzylidine-β-D-glucopyranosyl)-(1→3)-2,4-di-O-benzyl-α-L-rhamnopyranoside (***15***)* To a solution of compound **14** (4.4 g, 5.5 mmol) and compound 7 (3.1 g, 6.7 mmol) in dry CH_2Cl_2 (40 ml) was added MS 4 Å (3.5 g) and the reaction mixture was allowed to stir at room temperature for 20 min under argon. After cooling the reaction mixture to −40°C, *N*-iodosuccinimide (1.8 g, 8.0 mmol) and TMSOTf (45 μl, 0.24 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 **15** (5.6 g, 85%); colorless solid; m.p. 58°C; $[\alpha]_D^{25}$ −43.5 (*c* 1.5, $CHCl_3$); IR (KBr): 2,932, 2,364, 1,743, 1,594, 1,509, 1,457, 1,370, 1,240, 1,092, 826, 745, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.51–7.14 (m, 27 H, Ar-H), 6.93–6.89 (m, 2 H, Ar-H), 6.82–6.76 (m, 4 H, Ar-H), 5.50 (s, 1 H, PhC*H*), 5.46 (dd, *J*=3.3 Hz and 1.7 Hz, 1 H, H-2_C), 5.33 (d, *J*=1.7 Hz, 1 H, H-1_A), 5.21 (d, *J*=1.1 Hz, 1 H, H-1_C), 5.08 (d, *J*= 11.0 Hz, 1 H, PhCH_2), 4.98 (d, *J*=7.8 Hz, 1 H, H-1_B), 4.92 (d, *J*=12.0 Hz, 1 H, PhCH_2), 4.85–4.71 (m, 4 H, PhCH_2), 4.64 (d, *J*=10.4 Hz, 1 H, PhCH_2), 4.50 (d, *J*=11.0 Hz, 1 H, PhCH_2), 4.46–4.28 (m, 4 H, H-2_A and H-4_B, MeOPhCH_2), 4.12 (dd, *J*=9.2 and 3.1 Hz, 1 H, H-5_C), 4.00–3.96 (m, 1 H, H-5_A), 3.95–3.82 (m, 3 H, H-3_C and H-6_{abB}), 3.76 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 3.73–3.67 (m, 2 H, H-3_A and H-3_B), 3.52 (2 t, *J*=9.0 Hz, 2 H, H-2_B and H-4_A), 3.46–3.35 (m, 1 H, H-5_B), 3.29 (t, *J*=9.4 Hz, 1 H, H-4_C), 2.03 (s, 3 H, COCH_3), 1.30 (d, *J*=6.1 Hz, 3 H, CCH_3), 0.94 (d, *J*= 6.1 Hz, 3 H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.9 (*C*OCH_3), 159.2–113.7 (Ar-C), 103.7 (C-1_B), 101.6 (Ph*C*H), 98.4 (C-1_C), 97.3 (C-1_A), 83.4 (C-4_A), 81.4 (C-3_A), 80.1 (C-2_B), 79.5 (C-3_B), 78.3 (C-3_C), 77.9 (C-5_A), 77.0 (C-4_C), 76.5 (C-4_B), 75.3 (Ph*C*H_2), 74.9 (Ph*C*H_2), 74.6 (Ph*C*H_2), 73.6 (Ph*C*H_2), 71.4 (Ph*C*H_2), 68.7 (2 C, C-6_B and C-2_C), 68.6 (C-2_A), 67.6 (C-5_C), 66.3 (C-5_B), 55.6 (O*C*H_3), 55.1 (O*C*H_3), 20.9 (CO*C*H_3), 18.0 (C*C*H_3), 17.4 (C*C*H_3); ESI-MS: *m/z*=1,211.5 $[M+Na]^+$; Anal. Calcd. for $C_{70}H_{76}O_{17}$ (1,188.51): C, 70.69; H, 6.44; found: C, 70.51; H, 6.60.

*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)-2,4-di-O-benzyl-α-L-rhamnopyranoside (***16***)* A solution of compound **15** (5.40 g, 4.54 mmol) in 0.1 M CH_3ONa in MeOH:CH_2Cl_2 (70 ml, 4:1) was allowed to stir at room temperature for 3 h and neutralized with Amberlite IR-120 (H^+). The reaction mixture was filtered, washed with CH_3OH and the filtrate was evaporated to dryness to give crude product, which was purified over SiO_2 using hexane–EtOAc (4:1) as eluant to furnish pure **16** (5.2 g, quantitative); colorless solid; m.p.

63°C; $[\alpha]_D^{25}$ −68.1 (*c* 1.5, $CHCl_3$); IR (KBr): 2,932, 2,364, 2,340, 1,592, 1,509, 1,457, 1,383, 1,353, 1,248, 1,219, 1,096, 1,033, 749, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.49–7.12 (m, 27 H, Ar-H), 6.93–6.88 (m, 2 H, Ar-H), 6.86–6.76 (m, 4 H, Ar-H), 5.46 (s, 1 H, PhC*H*), 5.32 (d, *J*=1.7 Hz, 1 H, H-1_A), 5.23 (brs, 1 H, H-1_C), 5.03 (d, *J*=11.2 Hz, 1 H, PhCH_2), 4.95 (d, *J*=7.6 Hz, 1 H, H-1_B), 4.92 (d, *J*=10.8 Hz, 1 H, PhCH_2), 4.88–4.69 (m, 4 H, PhCH_2), 4.56–4.48 (m, 3 H, PhCH_2, MeOPhCH_2), 4.40 (d, *J*=10.4 Hz, 1 H, PhCH_2), 4.38–4.26 (m, 2 H, H-2_A and H-4_B), 4.07–3.95 (m, 2 H, H-5_A, H-5_C), 3.92–3.80 (m, 2 H, H-3_C and H-6_{aB}), 3.78–3.64 (m, 4 H, H-2_C, H-3_A, H-3_B, and H-6_{bB}), 3.75 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 3.52–3.28 (m, 4 H, H-2_B, H-4_A, H-4_C and H-5_B), 1.30 (d, *J*=6.2 Hz, 3 H, CCH_3), 0.87 (d, *J*=6.2 Hz, 3 H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.3–113.8 (Ar-C), 103.8 (C-1_B), 101.6 (Ph*C*H), 100.0 (C-1_C), 97.2 (C-1_A), 83.2 (C-4_A), 81.4 (C-3_A), 80.1 (C-2_B), 79.6 (2 C, C-3_B and C-5_A), 78.3 (C-3_C), 77.1 (C-4_B), 76.9 (C-4_C), 75.3 (Ph*C*H_2), 74.9 (Ph*C*H_2), 74.6 (Ph*C*H_2), 73.6 (Ph*C*H_2), 71.6 (Ph*C*H_2), 68.7 (C-6_B), 68.5 (2 C, C-2_A and C-2_C), 67.2 (C-5_C), 66.3 (C-5_B), 55.5 (O*C*H_3), 55.1 (O*C*H_3), 17.9 (C*C*H_3), 17.3 (C*C*H_3); ESI-MS: *m/z*=1,164.8 $[M+NH_4]^+$; Anal. Calcd. for $C_{68}H_{74}O_{16}$ (1,146.5): C, 71.19; H, 6.50; found: C, 71.0; H, 6.74.

*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)-2,4-di-O-benzyl-α-L-rhamnopyranoside (***17***)* To a solution of compound **16** (5 g, 4.36 mmol) and compound **11** (1.7 g, 5.23 mmol) in dry CH_2Cl_2 (50 ml) was added MS 4 Å (3.5 g) and the reaction mixture was allowed to stir at room temperature for 20 min under argon. The reaction mixture was cooled to −40°C and *N*-iodosuccinimide (1.4 g, 6.3 mmol) and TMSOTf (35 μl, 0.2 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 (100 ml). The organic layer was washed successively with 10% $Na_2S_2O_3$ 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 **17** (5 g, 82%). colorless solid; m.p. 68°C; $[\alpha]_D^{25}$ −49.5 (*c* 1.5, $CHCl_3$); IR (KBr): 2,931, 2,362, 2,339, 1,754, 1,592, 1,510, 1,458, 1,354, 1,223, 1,097, 1,037, 738, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.50–7.10 (m, 27 H, Ar-H), 6.91 (d, *J*=9.1 Hz, 2 H, Ar-H), 6.84 (d, *J*=8.7 Hz, 2 H, Ar-H), 6.79 (d, *J*=9.2 Hz, 2 H, Ar-H), 5.48 (s, 1 H, PhC*H*), 5.32 (d, *J*=1.7 Hz, 1 H, H-1_A), 5.26 (d, *J*=1.2 Hz, 1 H, H-1_C), 5.06 (t, *J*=8.9 Hz, 1 H, H-3_D), 4.99 (d, *J*=7.5 Hz, 1 H, H-1_B), 4.98–4.87 (m, 3 H, H-2_D, H-4_D and PhCH_2), 4.85–4.59 (m, 5 H, PhCH_2), 4.58–4.45 (m, 3 H, PhCH_2), 4.50 (d, *J*=7.7 Hz, 1 H, H-1_D), 4.39–4.25 (m, 3 H, H-2_A, H-4_B and PhCH_2), 4.05–3.94 (m, 2 H, H-5_A and H-5_C), 3.93–3.79 (m, 4 H, H-3_C, H-5_{abD} and H-6_{aB}), 3.76 (brs, 6 H, 2 OCH_3), 3.73–3.57 (m, 2 H, H-3_B and H-6_{bB}), 3.54–3.36 (m, 4 H, H-3_A, H-4_A, H-4_C and H-5_B), 3.29 (t, *J*=9.5 Hz, 1 H, H-2_B), 2.84 (dd, *J*=11.9 and 8.5 Hz, 1 H, H-2_C), 2.01 (s, 3 H, COCH_3), 2.00 (s, 3 H, COCH_3), 1.83 (s, 3 H, COCH_3), 1.26 (d, *J*=6.1 Hz, 3 H, CCH_3), 0.87 (d, *J*=6.2 Hz, 3 H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.0, 169.4, 169.2 (3 *C*OCH_3), 159.1–113.6 (Ar-C), 103.7 (C-1_B), 101.9 (C-1_D), 101.6 (Ph*C*H), 99.6 (C-1_C), 97.2 (C-1_A), 83.1 (C-4_A), 81.3 (C-3_A), 80.5 (C-2_B), 79.7 (C-3_B), 79.4 (C-5_A), 78.3 (C-3_C), 76.9 (C-4_C), 76.8 (C-4_B), 76.7 (C-4_D), 75.0 (Ph*C*H_2), 74.7 (Ph*C*H_2), 74.5 (Ph*C*H_2), 73.5 (Ph*C*H_2), 72.1 (Ph*C*H_2), 71.0 (C-3_D), 70.6 (C-2_D), 68.9 (C-2_C), 68.7 (C-6_B), 68.4 (C-2_A), 67.8 (C-5_C), 66.2 (C-5_B), 61.3 (C-5_D), 55.5 (O*C*H_3), 55.1 (O*C*H_3), 20.6 (2 C, 2 CO*C*H_3), 20.5 (CO*C*H_3), 17.9 (C*C*H_3), 17.3 (C*C*H_3); ESI-MS: *m/z*=1,424.1 $[M+NH_4+1]^+$; Anal. Calcd. for $C_{79}H_{88}O_{23}$ (1,405.53): C, 67.51; H, 6.31; found: C, 67.34; H, 6.50.

*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-benzylidine-β-D-glucopyranosyl)-(1→3)-2,4-di-O-benzyl-α-L-rhamnopyranoside (***18***)* To a solution of compound **17** (4.8 g, 3.4 mmol) in CH_2Cl_2 and water (50 ml, 1:1), was added DDQ (930 mg, 4.1 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 **18** (3.8 g, 86%); colorless solid; m.p. 84°C; $[\alpha]_D^{25}$ −70.8 (*c* 1.5, $CHCl_3$); IR (KBr): 2,930, 2,364, 2,251, 1,752, 1,593, 1,507, 1,456, 1,377, 1,223, 1,085, 737, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.48–7.15 (m, 25 H, Ar-H), 6.91 (d, *J*=9.1 Hz, 2 H, Ar-H), 6.79 (d, *J*=9.1 Hz, 2 H, Ar-H), 5.46 (s, 1 H, PhC*H*), 5.32 (d, *J*=1.7 Hz, 1 H, H-1_A), 5.22 (brs, 1 H, H-1_C), 5.11 (d, *J*=11.5 Hz, 1 H, PhCH_2), 5.02 (t, *J*=8.9 Hz, 1 H, H-3_D), 4.98 (d, *J*=8.4 Hz, 1 H, H-1_B), 4.91–4.81 (m, 3 H, H-2_D, H-4_D and PhCH_2), 4.80–4.64 (m, 4 H, PhCH_2), 4.54 (d, *J*=11.1 Hz, 1 H, PhCH_2), 4.42–4.28 (m, 3 H, H-2_A, H-4_B and PhCH_2), 4.19 (d, *J*=7.1 Hz, 1 H, H-1_D), 4.04–3.96 (m, 2 H, H-5_A and H-5_C), 3.95–3.80 (m, 3 H, H-5_{abD} and H-6_{aB}), 3.75 (s, 3 H, OCH_3), 3.74–3.52 (m, 4 H, H-3_A, H-3_B, H-3_C and H-6_{bB}), 3.51–3.36 (m, 3 H, H-4_A, H-4_C and H-5_B), 3.13 (t, *J*=9.5 Hz, 1 H, H-2_B), 2.71 (dd, *J*=11.9 and 8.5 Hz, 1 H, H-2_C), 2.04, 2.01, 1.99 (3 s, 9 H, 3 COCH_3), 1.26 (d, *J*=5.3 Hz, 3 H, CCH_3), 0.85 (d, *J*=6.2 Hz, 3 H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.8, 169.7, 169.4 (3 *C*OCH_3), 154.8–114.5 (Ar-C), 103.7 (C-1_B), 102.2 (C-1_D), 101.8

(Ph*C*H), 99.1 (C-1_C), 97.3 (C-1_A), 83.5 (C-4_A), 82.0 (C-3_A), 81.2 (C-2_B), 80.4 (C-3_B), 79.6 (C-5_A), 78.3 (C-4_C), 77.1 (C-4_B), 77.0 (C-4_D), 75.0 (Ph*C*H_2), 74.5 (2 C, 2 Ph*C*H_2), 73.5 (Ph*C*H_2), 71.4 (C-3_D), 71.1 (C-2_D), 70.9 (C-3_C), 68.7 (2 C, C-2_C and C-6_B), 68.4 (C-2_A), 67.1 (C-5_C), 66.3 (C-5_B), 61.6 (C-5_D), 55.5 (O*C*H_3), 20.6 (CO*C*H_3), 20.5 (2 C, 2 CO*C*H_3), 17.9 (C*C*H_3), 17.3 (C*C*H_3); ESI-MS: *m*/*z*=1,308.2 $[M+Na]^+$; Anal. Calcd. for $C_{71}H_{80}O_{22}$ (1,285.38): C, 66.34; H, 6.27; found: C, 66.18; H, 6.45.

*4-Methoxyphenyl [4-O-benzyl-3-O-(4-methoxybenzyl)-2-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)-2,4-di-O-benzyl-α-L-rhamnopyranoside (***19***)* To a solution of compound **18** (3.5 g, 2.7 mmol) and compound **8** (1.4 g, 3.3 mmol) in dry CH_2Cl_2 (35 ml) was added MS 4 Å (3 g) and the reaction mixture was stirred at room temperature for 20 min under argon. The reaction mixture was cooled to −40°C and *N*-iodosuccinimide (880 mg, 3.9 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 **19** (3.8 g, 84%); colorless solid; m.p. 80°C; $[\alpha]_D^{25}$ −53.1 (*c* 1.5, $CHCl_3$); IR (KBr): 2,937, 2,362, 1,755, 1,588, 1,509, 1,456, 1,371, 1,223, 1,078, 1,036, 737, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.49–7.10 (m, 32 H, Ar-H), 6.91 (d, *J*=9.1 Hz, 2 H, Ar-H), 6.81 (d, *J*=8.6 Hz, 2 H, Ar-H), 6.79 (d, *J*=9.1 Hz, 2 H, Ar-H), 5.51 (s, 1 H, PhC*H*), 5.32 (d, *J*=1.7 Hz, 1 H, H-1_A), 5.26 (brs, 1 H, H-1_C), 5.12–4.99 (m, 3 H, H-3_D, H-1_E and PhCH_2), 4.95 (d, *J*=7.7 Hz, 1 H, H-1_B), 4.95–4.91 (m, 2 H, H-2_D and H-4_D), 4.91–4.77 (m, 3 H, PhCH_2), 4.73 (d, *J*=7.0 Hz, 1 H, H-1_D), 4.73–4.68 (m, 2 H, PhCH_2), 4.67–4.50 (m, 5 H, PhCH_2), 4.39–4.26 (m, 3 H, H-2_A, H-4_B and PhCH_2), 4.11–4.00 (m, 2 H, H-2_E and H-5_E), 3.90–3.86 (m, 3 H, H-5_A, H-5_C and H-6_{aB}), 3.85–3.78 (m, 2 H, H-5_{abD}), 3.75 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 3.73–3.59 (m, 3 H, H-3_A, H-3_E and H-6_{bB}), 3.58–3.47 (m, 3 H, H-3_B, H-3_C and H-4_E), 3.46–3.35 (m, 3 H, H-4_A, H-4_C and H-5_B), 3.28 (t, *J*=9.5 Hz, 1 H, H-2_B), 3.18 (s, 3 H, OCH_3), 2.97 (dd, *J*=11.9 and 8.5 Hz, 1 H, H-2_C), 2.02, 1.98, 1.95, (3 s, 9 H, 3 COCH_3), 1.30 (d, *J*=6.2 Hz, 3 H, CCH_3), 1.27 (d, *J*=6.1 Hz, 3 H, CCH_3), 0.83 (d, *J*=6.1 Hz, 3 H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.7, 169.5, 168.9 (3 *C*OCH$_3$), 159.0–113.6 (Ar-C), 103.8 (C-1_B), 101.6 (Ph*C*H), 100.5 (C-1_D), 99.5 (2 C, C-1_C and C-1_E), 97.2 (C-1_A), 82.7 (C-4_A), 81.2 (C-3_A), 80.8 (C-2_B), 80.2 (C-3_B), 79.5 (C-5_A), 79.4 (C-5_E), 78.1 (C-4_C), 78.0 (C-4_E), 77.8 (C-4_B), 77.4 (C-4_D), 76.8 (C-3_C), 76.4 (C-3_E), 75.0 (Ph*C*H_2), 74.6 (Ph*C*H_2), 74.4 (Ph*C*H_2), 74.3 (Ph*C*H_2), 73.4 (Ph*C*H_2), 72.0 (Ph*C*H_2), 70.7 (C-3_D), 70.6 (C-2_D), 68.6 (C-6_B), 68.5 (C-2_E), 68.4 (C-2_C), 68.3 (C-2_A), 67.8 (C-5_C), 66.2 (C-5_B), 61.0 (C-5_D), 58.8 (O*C*H_3), 55.4 (O*C*H_3), 55.0 (O*C*H_3), 20.7 (CO*C*H_3), 20.6 (2 C, 2 CO*C*H_3), 18.2 (C*C*H_3), 17.9 (C*C*H_3), 17.2 (C*C*H_3); ESI-MS: *m*/*z*=1,673.8 $[M+NH_4]^+$; Anal. Calcd. for $C_{93}H_{106}O_{27}$ (1,655.82): C, 67.46; H, 6.45; found: C, 67.29; H, 6.67.

*4-Methoxyphenyl (4-O-benzyl-2-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-benzylidine-β-D-glucopyranosyl)-(1→3)-2,4-di-O-benzyl-α-L-rhamnopyranoside (***20***)* To a solution of compound **19** (3.5 g, 2.14 mmol) in CH_2Cl_2 and water (40 ml, 1:1), was added DDQ (590 mg, 2.6 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 **20** (2.9 g, 88%); colorless solid; m.p. 83°C; $[\alpha]_D^{25}$ −65.7 (*c* 1.5, $CHCl_3$); IR (KBr): 2,936, 2,363, 1,756, 1,590, 1,508, 1,381, 1,353, 1,224, 1,094, 1,042, 752, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.49–7.08 (m, 30 H, Ar-H), 6.90 (d, *J*=9.1 Hz, 2 H, Ar-H), 6.77 (d, *J*=9.1 Hz, 2 H, Ar-H), 5.51 (s, 1 H, PhC*H*), 5.30 (d, *J*=1.6 Hz, 1 H, H-1_A), 5.24 (brs, 1 H, H-1_C), 5.08 (brs, 1 H, H-1_E), 5.03 (t, *J*=8.2 Hz, 1 H, H-3_D), 5.02–4.98 (m, 1 H, PhCH_2), 4.96 (d, *J*=7.9 Hz, 1 H, H-1_B), 4.97–4.92 (m, 1 H, H-2_D), 4.92–4.76 (m, 4 H, H-4_D and PhCH_2), 4.76–4.65 (m, 3 H, PhCH_2), 4.63 (d, *J*=7.0 Hz, 1 H, H-1_D), 4.61–4.55 (m, 2 H, PhCH_2), 4.38–4.26 (m, 3 H, H-2_A, H-4_B and PhCH_2), 4.10–4.00 (m, 2 H, H-2_C and H-2_E), 3.97–3.92 (m, 1 H, H-5_A), 3.91–3.82 (m, 3 H, H-5_C and H-5_{abD}), 3.81–3.77 (m, 1 H, H-6_{aB}), 3.75 (s, 3 H, OCH_3), 3.72–3.57 (m, 3 H, H-3_A, H-3_C and H-6_{bB}), 3.56–3.44 (m, 2 H, H-3_E and H-4_E), 3.43–3.35 (m, 2 H, H-4_A and H-4_C), 3.34–3.28 (m, 2 H, H-3_B and H-5_E), 3.22 (t, *J*=9.4 Hz, 1 H, H-2_B), 3.03 (s, 3 H, OCH_3), 2.92 (dd, *J*=12.0 and 8.2 Hz, 1 H, H-5_B), 2.06, 2.03, 1.94 (3 s, 9 H, 3 COCH_3), 1.33–1.24 (m, 6 H, 2 CCH_3), 0.83 (d, *J*=6.1 Hz, 3 H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.7, 169.2, 168.9 (3 *C*OCH$_3$), 154.8–114.4 (Ar-C), 103.8 (C-1_B), 101.7 (Ph*C*H), 100.8 (C-1_D), 99.4 (C-1_C), 97.9 (C-1_E), 97.1 (C-1_A), 82.8 (C-4_A), 81.8 (C-3_A), 81.4 (C-2_B), 81.1 (C-3_B), 80.6 (C-5_A), 79.5 (C-5_E), 78.4 (C-4_C), 77.8 (C-4_E), 76.8 (2 C, C-4_B and C-4_D), 76.2 (C-3_C), 74.8 (Ph*C*H_2), 74.6 (Ph*C*H_2), 74.5 (Ph*C*H_2), 74.4 (Ph*C*H_2), 73.5 (Ph*C*H_2), 71.3 (C-3_D), 70.9 (C-2_D), 70.7 (C-3_E), 68.7 (C-6_B), 68.6 (C-2_C), 68.5 (C-2_A), 67.9 (2 C, C-5_C and C-2_E), 66.3 (C-5_B), 61.1 (C-5_D), 58.1

(OCH_3), 55.4 (OCH_3), 20.7 ($COCH_3$), 20.6 ($COCH_3$), 20.5 ($COCH_3$), 18.2 (CCH_3), 18.0 (CCH_3), 17.3 (CCH_3); ESI-MS: m/z=1,553.4 $[M+NH_4]^+$; Anal. Calcd. for $C_{85}H_{98}O_{26}$ (1,534.63): C, 66.48; H, 6.43; found: C, 66.30; H, 6.64.

*4-Methoxyphenyl [2-O-acetyl-4,6-O-benzylidene-3-O-(4-methoxybenzyl)-β-D-glucopyranosyl]-(1→3)-(4-O-benzyl-2-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)-2,4-di-O-benzyl-α-L-rhamnopyranoside (***21***)* To a solution of compound **20** (2.7 g, 1.76 mmol) and compound **5** (1 g, 2.1 mmol) in dry CH_2Cl_2 (30 ml) was added MS 4 Å (3 g) and the reaction mixture was stirred at room temperature for 20 min under argon. The reaction mixture was cooled to −40°C and *N*-iodosuccinimide (570 g, 2.5 mmol) and TMSOTf (15 μl, 0.08 mmol) were added to it. The mixture was stirred at 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 **21** (2.8 g, 82%); colorless solid; m.p. 95°C; $[\alpha]_D^{25}$ −55.2 (*c* 1.5, $CHCl_3$); IR (KBr): 2,934, 2,365, 2,339, 1,753, 1,595, 1,509, 1,457, 1,355, 1,226, 1,096, 748, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.50–7.09 (m, 37 H, Ar-H), 6.90 (d, *J*=9.1 Hz, 2 H, Ar-H), 6.78 (d, *J*= 8.5 Hz, 2 H, Ar-H), 6.76 (d, *J*=9.1 Hz, 2 H, Ar-H), 5.49 (brs, 2 H, 2 PhC*H*), 5.29 (d, *J*=1.5 Hz, 1 H, H-1_A), 5.24 (brs, 1 H, H-1_C), 5.10–5.02 (m, 1 H, H-2_F), 5.01 (brs, 1 H, H-1_E), 5.00–4.85 (m, 5 H, H-1_B and PhCH_2), 4.84–4.76 (m, 4 H, H-1_D, H-2_D, H-3_D and H-4_D), 4.75–4.62 (m, 4 H, H-1_F and PhCH_2), 4.61–4.48 (m, 4 H, PhCH_2), 4.36–4.27 (m, 3 H, H-2_A, H-4_B and PhCH_2), 4.12 (dd, *J*=10.0 and 3.2 Hz, 1 H, H-2_E), 4.06–3.97 (m, 2 H, H-2_C and H-5_E), 3.96–3.85 (m, 4 H, H-5_A, H-5_C and H-5_{abD}), 3.83–3.77 (m, 2 H, H-3_A and H-6_{aB}), 3.75 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 3.73–3.57 (m, 6 H, H-3_C, H-6_{bB}, H-3_F, H-4_F and H-6_{abF}), 3.57–3.47 (m, 2 H, H-4_C and H-4_E), 3.46–3.35 (m, 3 H, H-4_A, H-3_B and H-5_F), 3.34–3.22 (m, 2 H, H-2_B and H-3_E), 3.19 (s, 3 H, OCH_3), 3.01–2.91 (m, 1 H, H-5_B), 2.04, 2.00, 1.95 (3 s, 9 H, 3 COCH_3), 1.71 (s, 3 H, COCH_3), 1.30–1.22 (m, 6 H, 2 CCH_3), 0.83 (d, *J*=6.1 Hz, 3 H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.5, 169.2, 168.9, 168.8, (4 *C*OCH$_3$), 159.1–113.6 (Ar-C), 103.9 (C-1_B), 101.8 (2 C, 2 PhCH), 101.2 (C-1_D), 100.4 (C-1_F), 99.9 (C-1_E), 99.4 (C-1_C), 97.2 (C-1_A), 82.8 (C-4_A), 81.5 (C-3_A), 81.4 (C-2_B), 80.7 (C-3_B), 80.0 (2 C, C-5_A and C-5_E), 79.9 (C-4_C), 79.6 (C-4_E), 78.5 (C-4_B), 78.4 (C-4_D), 77.9 (C-3_C), 77.5 (C-3_E), 76.9 (C-3_F), 76.5 (C-4_F), 74.7 (PhCH$_2$), 74.6 (2 C, 2 PhCH$_2$), 74.5 (PhCH$_2$), 73.5 (PhCH$_2$), 73.4 (PhCH$_2$), 73.0 (C-2_F), 70.4 (3 C, C-2_C, C-2_D and C-3_D), 68.8 (C-6_B), 68.6 (C-2_A), 68.5 (C-2_E), 68.4 (C-6_F), 67.9 (C-5_C), 66.4 (C-5_B), 66.0 (C-5_F), 61.0 (C-5_D), 59.1 (OCH_3), 55.4 (OCH_3), 55.0 (OCH_3), 20.8 (COCH_3), 20.7 (COCH_3), 20.6 (2 C, 2 COCH_3), 18.1 (CCH_3), 18.0 (CCH_3), 17.3 (CCH_3); ESI-MS: m/z=1,964.5 $[M+NH_4]^+$; Anal. Calcd. for $C_{108}H_{122}O_{33}$ (1,946.79): C, 66.59; H, 6.31; found: C, 66.42; H, 6.55.

*4-Methoxyphenyl [2-O-benzyl-4,6-O-benzylidene-3-O-(4-methoxybenzyl)-β-D-glucopyranosyl]-(1→3)-(4-O-benzyl-2-O-methyl-α-L-rhamnopyranosyl)-(1→3)-[(2,3,4-tri-O-benzyl-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)-2,4-di-O-benzyl-α-L-rhamnopyranoside (***22***)* To a solution of compound **21** (2.5 g, 1.3 mmol) in THF (20 ml) were added crushed NaOH (250 mg), benzyl bromide (730 μl, 6.14 mmol) and Bu_4NBr (100 mg) and the reaction mixture was stirred briskly at room temperature for 5 h. The reaction mixture was diluted with water (100 ml) and extracted with CH_2Cl_2 (100 ml). The organic layer was washed with water, dried (Na_2SO_4) and concentrated under reduced pressure to give the crude product, which was purified over SiO_2 using hexane–EtOAc (7:1) to give pure **22** (2.5 g, 90%); colorless solid; m.p. 68°C; $[\alpha]_D^{25}$ −35.7 (*c* 1.5, $CHCl_3$); IR (KBr): 2,929, 2,362, 2,339, 1,594, 1,508, 1,456, 1,382, 1,353, 1,086, 996, 737, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.51–7.07 (m, 57 H, Ar-H), 6.92 (d, *J*=9.1 Hz, 2 H, Ar-H), 6.79 (d, *J*= 9.3 Hz, 2 H, Ar-H), 6.75 (d, *J*=8.7 Hz, 2 H, Ar-H), 5.53 (s, 1 H, PhC*H*), 5.37 (brs, 2 H, H-1_C and PhC*H*), 5.33 (d, *J*= 1.6 Hz, 1 H, H-1_A), 5.16 (d, *J*=12.0 Hz, 1 H, PhCH_2), 5.12 (brs, 1 H, H-1_E), 5.01 (d, *J*=11.8 Hz, 1 H, PhCH_2), 4.99–4.93 (m, 3 H, H-1_B and PhCH_2), 4.92–4.75 (m, 7 H, PhCH_2), 4.74–4.59 (m, 4 H, PhCH_2), 4.71 (d, *J*=7.2 Hz, 1 H, H-1_F), 4.63 (d, *J*=7.0 Hz, 1 H, H-1_D), 4.55–4.43 (m, 3 H, PhCH_2), 4.42–4.27 (m, 5 H, H-3_A, H-3_E, H-4_B and PhCH_2), 4.26–4.03 (m, 6 H, H-2_A, H-5_A, H-2_C, H-5_C, H-2_E and H-5_E), 4.02–3.89 (m, 3 H, H-6_{aB} and H-5_{abD}), 3.87–3.79 (m, 1 H, H-3_C), 3.73 (brs, 6 H, 2 OCH_3), 3.72–3.59 (m, 2 H, H-6_{bB} and H-6_{aF}), 3.58–3.49 (m, 5 H, H-4_A, H-4_C, H-3_D, H-4_E and H-6_{bF}), 3.48–3.31 (m, 7 H, H-2_B, H-3_B, H-2_D, H-4_D, H-2_F, H-3_F and H-4_F), 3.24 (s, 3 H, OCH_3), 3.03–2.88 (m, 2 H, H-5_B and H-5_F), 1.33 (d, *J*=6.2 Hz, 3 H, CCH_3), 1.26 (d, *J*=6.1 Hz, 3 H, CCH_3), 0.87 (d, *J*= 5.6 Hz, 3 H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0–113.6 (Ar-C), 104.3 (C-1_D), 103.7 (C-1_B), 103.6 (C-1_F), 101.7 (PhCH), 100.9 (PhCH), 100.1 (C-1_C), 99.8 (C-1_E), 97.3 (C-1_A), 83.9 (C-4_A), 83.1 (C-3_A), 82.4 (C-2_B), 81.9 (C-3_B), 81.5 (C-5_A), 81.4 (2 C, C-4_E and C-5_E), 80.9 (C-4_C), 80.6 (C-2_D), 80.5 (C-3_D), 79.6 (C-4_B), 78.3 (C-4_D), 77.9 (C-3_C), 77.7 (2 C, C-3_E and C-3_F), 76.9 (C-4_F), 76.8 (C-2_C), 76.4 (C-2_F), 74.8–72.8 (10 C, 10 PhCH$_2$), 68.8 (C-

6_B), 68.7 (C-2_A), 68.5 (C-2_E), 68.4 (C-6_F), 67.9 (C-5_C), 66.3 (C-5_B), 65.8 (C-5_F), 63.2 (C-5_D), 59.2 (O*C*H_3), 55.6 (O*C*H_3), 55.2 (O*C*H_3), 18.1 (C*C*H_3), 17.9 (C*C*H_3), 17.4 (C*C*H_3); ESI-MS: *m/z*=2,162.0 $[M+Na]^+$; Anal. Calcd. for $C_{128}H_{138}O_{29}$ (2,138.93): C, 71.82; H, 6.50; found: C, 71.65; H, 6.70.

*4-Methoxyphenyl (2-O-benzyl-4,6-O-benzylidene-β-D-glucopyranosyl)-(1→3)-(4-O-benzyl-2-O-methyl-α-L-rhamnopyranosyl)-(1→3)-[(2,3,4-tri-O-benzyl-β-D-xylopyranosyl)-(1→2)-4-O-benzyl-α-L-rhamnopyranosyl]-(1→3)-(2-O-benzyl-4,6-O-benzylidine-β-D-glucopyranosyl)-(1→3)-2,4-di-O-benzyl-α-L-rhamnopyranoside (***23***)* To a solution of compound **22** (2.1 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 and diluted with CH_2Cl_2 (50 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 **23** (1.7 g, 86%); colorless solid; m.p. 95°C; $[\alpha]_D^{25}$ −41.4 (*c* 1.5, $CHCl_3$); IR (KBr): 2,930, 2,363, 2,339, 1,591, 1,505, 1,456, 1,354, 1,214, 1,100, 738, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.49–7.05 (m, 55 H, Ar-H), 6.90 (d, *J*=9.1 Hz, 2 H, Ar-H), 6.77 (d, *J*=9.1 Hz, 2 H, Ar-H), 5.52 (s, 1 H, PhC*H*), 5.34 (brs, 1 H, H-1_C), 5.31 (brs, 2 H, H-1_A and PhC*H*), 5.14 (d, *J*=12.0 Hz, 1 H, PhCH_2), 5.10 (brs, 1 H, H-1_E), 4.99 (d, *J*=11.4 Hz, 1 H, PhCH_2), 4.95 (d, *J*=7.3 Hz, 1 H, H-1_B), 4.94–4.79 (m, 6 H, PhCH_2), 4.78–4.72 (m, 3 H, PhCH_2), 4.71–4.57 (m, 4 H, H-1_D, H-1_F and PhCH_2), 4.55–4.45 (m, 3 H, PhCH_2), 4.40–4.28 (m, 3 H, H-3_A and PhCH_2), 4.27–4.04 (m, 6 H, H-2_A, H-4_B, H-2_C, H-2_E, H-3_E and H-5_E), 4.01–3.88 (m, 3 H, H-5_A, H-6_{aB} and H-5_C), 3.85–3.66 (m, 2 H, H-6_{bB} and H-6_{aF}), 3.75 (s, 3 H, O*C*H_3), 3.64–3.49 (m, 5 H, H-3_C, H-3_D, H-5_{abD} and H-6_{bF}), 3.48–3.24 (m, 10 H, H-4_A, H-2_B, H-3_B, H-4_C, H-2_D, H-4_D, H-4_E, H-2_F, H-3_F and H-4_F), 3.21 (s, 3 H, O*C*H_3), 2.99–2.85 (m, 2 H, H-5_B and H-5_F), 1.35 (d, *J*=6.1 Hz, 3 H, C*C*H_3), 1.26 (d, *J*=6.0 Hz, 3 H, C*C*H_3), 0.84 (d, *J*=6.1 Hz, 3 H, C*C*H_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.8–114.5 (Ar-C), 104.4 (C-1_D), 103.7 (C-1_B), 103.4 (C-1_F), 101.7 (Ph*C*H), 101.5 (Ph*C*H), 100.0 (C-1_C), 99.6 (C-1_E), 97.3 (C-1_A), 83.9 (C-4_A), 83.1 (C-3_A), 82.0 (C-2_B), 81.9 (C-3_B), 81.3 (2 C, C-5_A and C-5_E), 80.8 (C-4_E), 80.6 (C-4_C), 80.3 (C-2_D), 79.6 (C-3_D), 78.3 (C-4_B), 78.1 (C-4_D), 77.7 (C-3_C), 77.6 (C-3_E), 76.9 (2 C, C-2_C and C-2_F), 76.4 (C-4_F), 75.6–72.8 (9 C, 9 Ph*C*H_2), 73.1 (C-3_F), 68.7 (C-6_B), 68.6 (C-2_A), 68.5 (C-2_E), 68.4 (C-6_F), 67.9 (C-5_C), 66.3 (C-5_B), 65.7 (C-5_F), 63.2 (C-5_D), 59.1 (O*C*H_3), 55.6 (O*C*H_3), 18.1 (C*C*H_3), 17.9 (C*C*H_3), 17.4 (C*C*H_3); ESI-MS: *m/z*=2,043.0 $[M+Na]^+$; Anal. Calcd. for $C_{120}H_{130}O_{28}$ (2,020.30): C, 71.34; H, 6.49; found: C, 71.18; H, 6.70.

*4-Methoxyphenyl (4-O-acetyl-3-O-benzyl-2-O-methyl-α-L-fucopyranosyl)-(1→3)-(2-O-benzyl-4,6-O-benzylidene-β-D-glucopyranosyl)-(1→3)-(4-O-benzyl-2-O-methyl-α-L-rhamnopyranosyl)-(1→3)-[(2,3,4-tri-O-benzyl-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)-2,4-di-O-benzyl-α-L-rhamnopyranoside (***24***)* To a solution of compound **23** (1.5 g, 0.74 mmol) and compound **10** (320 mg, 0.9 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 20 min under argon. The reaction mixture was cooled to −40°C and *N*-iodosuccinimide (240 mg, 1.1 mmol) and TMSOTf (6 μl, 0.03 mmol) were added to it. The reaction mixture was stirred at 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 **24** (1.3 g, 76%); colorless solid; m.p. 92°C; $[\alpha]_D^{25}$ −61.8 (*c* 1.5, $CHCl_3$); IR (KBr): 2,929, 2,364, 1,740, 1,593, 1,505, 1,456, 1,377, 1,236, 1,097, 737, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.51–7.05 (m, 60 H, Ar-H), 6.91 (d, *J*=9.1 Hz, 2 H, Ar-H), 6.78 (d, *J*=9.1 Hz, 2 H, Ar-H), 5.52 (s, 1 H, PhC*H*), 5.50 (d, *J*=4.0 Hz, 1 H, H-1_G), 5.37 (brs, 1 H, H-1_C), 5.33 (brs, 1 H, H-1_A), 5.28 (s, 1 H, PhC*H*), 5.20 (d, *J*=2.9 Hz, 1 H, H-4_G), 5.23–5.17 (m, 1 H, PhCH_2), 5.17–5.10 (m, 1 H, PhCH_2), 5.08 (brs, 1 H, H-1_E), 5.05–4.83 (m, 5 H, PhCH_2), 4.96 (d, *J*=7.9 Hz, 1 H, H-1_B), 4.82–4.58 (m, 8 H, H-1_D, H-1_F and PhCH_2), 4.53–4.42 (m, 3 H, PhCH_2), 4.40–4.24 (m, 6 H, H-3_A, H-3_E and PhCH_2), 4.22–4.06 (m, 5 H, H-2_A, H-4_B, H-2_C, H-2_E and H-5_E), 4.05–3.90 (m, 4 H, H-5_A, H-6_{aB}, H-5_C and H-6_{aF}), 3.87–3.78 (m, 3 H, H-6_{bB} and H-5_{abD}), 3.75–3.71 (m, 1 H, H-6_{bF}), 3.74 (s, 3 H, O*C*H_3), 3.70–3.50 (m, 6 H, H-4_A, H-3_C, H-3_D, H-4_E, H-2_G and H-3_G), 3.48–3.36 (m, 7 H, H-2_B, H-3_B, H-4_C, H-2_D, H-4_D, H-2_F and H-3_F), 3.32 (s, 3 H, O*C*H_3), 3.29 (s, 3 H, O*C*H_3), 3.27–3.18 (m, 2 H, H-4_F and H-5_G), 3.04–2.83 (m, 2 H, H-5_B and H-5_F), 1.31 (d, *J*=6.1 Hz, 3 H, C*C*H_3), 1.26 (d, *J*=6.0 Hz, 3 H, C*C*H_3), 0.87 (d, *J*=6.1 Hz, 3 H, C*C*H_3), 0.67 (d, *J*=6.4 Hz, 3 H, C*C*H_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.7 (*C*O*C*H_3), 154.8–114.5 (Ar-C), 104.4 (C-1_D), 103.7 (C-1_B), 103.4 (C-1_F), 101.7 (Ph*C*H), 101.6 (Ph*C*H), 100.4 (C-1_E), 100.1 (C-1_C), 98.0 (C-1_G), 97.3 (C-1_A), 83.8 (2 C, C-4_A and C-3_G), 83.2 (C-3_A), 81.9 (C-3_F), 81.3 (2 C, C-2_B and C-3_B), 81.2 (C-5_A), 80.9 (C-5_E), 79.6 (C-2_D), 79.2 (C-4_C), 78.3 (C-4_E), 78.2 (C-2_G), 77.6 (C-3_D), 77.4 (C-4_B), 77.2 (C-4_D), 77.0 (C-3_C), 76.9 (2 C, C-2_C and C-2_F), 76.5 (C-3_E), 76.0 (C-4_F), 75.6–71.6 (10 C, 10 PhCH_2), 70.7 (C-4_G), 68.8 (C-6_B), 68.6 (C-2_A), 68.5 (2 C, C-2_E and C-6_F), 67.9 (C-5_C), 66.3 (C-5_B), 66.0 (C-5_F), 64.3 (C-5_G), 63.2 (C-5_D), 60.5

(OCH_3), 59.7 (OCH_3), 55.6 (OCH_3), 20.8 ($COCH_3$), 18.0 (CCH_3), 17.9 (CCH_3), 17.4 (CCH_3), 15.6 (CCH_3); ESI-MS: m/z=2,330.0 $[M+NH_4]^+$; Anal. Calcd. for $C_{136}H_{150}O_{33}$ (2,312.63): C, 70.63; H, 6.54; found: C, 70.44; H, 6.70.

*4-Methoxyphenyl (4-O-acetyl-2-O-methyl-α-L-fucopyranosyl)-(1→3)-(β-D-glucopyranosyl)-(1→3)-(2-O-methyl-α-L-rhamnopyranosyl)-(1→3)-[(β-D-xylopyranosyl)-(1→2)-α-L-rhamnopyranosyl]-(1→3)-(β-D-glucopyranosyl)-(1→3)-α-L-rhamnopyranoside (***1***)* To a solution of compound **24** (1 g, 0.43 mmol) in CH_3OH:toluene (3:1, 25 ml) was added 20% $Pd(OH)_2$/C (500 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 (4:1) as eluant (430 mg, 81%); white powder; $[\alpha]_D^{25}$ −71.0 (*c* 1.0, H_2O); IR (KBr): 2,920, 2,367, 1,741, 1,650, 1,542, 1,512, 1,457, 1,425, 1,377, 1,271, 1,035, 672 cm^{-1}; ^1H NMR (300 MHz, D_2O): δ 7.17 (d, J=8.9 Hz, 2 H, Ar-H), 7.05 (d, J=8.8 Hz, 2 H, Ar-H), 5.65 (brs, 1 H, H-1_C), 5.50 (brs, 2 H, H-1_A and H-1_G), 5.31 (brs, 1 H, H-1_E), 5.29 (brs, 1 H, H-4_G), 4.71 (d, J=7.9 Hz, 2 H, H-1_B and H-1_F), 4.63–4.57 (m, 1 H, H-5_A), 4.56 (d, J=7.5 Hz, 1 H, H-1_D), 4.47 (brs, 1 H, H-2_A), 4.23 (brs, 1 H, H-2_G), 4.21–4.10 (m, 3 H, H-3_A, H-4_C and H-3_E), 4.09–3.90 (m, 10 H, H-4_B, H-6_{aB}, H-2_D, H-4_D, H-5_{abD}, H-2_E, H-4_F, H-6_{aF} and H-3_G), 3.87 (s, 3 H, OCH_3), 3.86–3.79 (m, 2 H, H-3_B and H-3_F), 3.78–3.47 (m, 12 H, H-4_A, H-2_B, H-6_{bB}, H-2_C, H-3_C, H-5_C, H-3_D, H-4_E, H-5_E, H-2_F, H-6_{bF} and H-5_G), 3.58 (s, 3 H, OCH_3), 3.50 (s, 3 H, OCH_3), 3.46–3.30 (m, 2 H, H-5_B and H-5_F), 1.39 (d, J=5.9 Hz, 3 H, CCH_3), 1.33 (d, J=5.7 Hz, 3 H, CCH_3), 1.31 (d, J=5.8 Hz, 3 H, CCH_3), 1.15 (d, J=6.4 Hz, 3 H, CCH_3); ^{13}C NMR (75 MHz, D_2O): δ 174.0 ($COCH_3$), 154.7 (Ar-C), 149.4 (Ar-C), 118.8 (2 C, Ar-C), 115.1 (2 C, Ar-C), 105.4 (C-1_D), 103.9 (C-1_B), 103.7 (C-1_F), 99.9 (C-1_G), 98.9 (C-1_A), 98.5 (C-1_E), 96.3 (C-1_C), 82.2 (H-3_E), 80.9 (H-3_A), 80.3 (C-2_E), 80.0 (C-2_G), 79.9 (C-4_C), 79.2 (C-3_G), 77.4 (C-4_D), 76.8 (C-2_D), 75.8 (C-4_G), 75.7 (2 C, C-4_B and C-5_E), 74.4 (C-4_F), 74.1 (2 C, C-3_B and C-3_F), 73.1 (C-3_C), 72.1 (C-4_A), 71.1 (C-2_C), 71.0 (C-2_A), 69.7 (C-3_D), 69.3 (2 C, C-4_E and C-2_F), 69.1 (C-2_B), 68.9 (C-5_G), 68.0 (C-5_F), 67.7 (C-5_C), 67.0 (C-5_A), 65.3 (C-5_B), 65.1 (C-5_D), 60.9 (C-6_B), 60.5 (C-6_F), 57.9 (OCH_3), 57.4 (OCH_3), 55.8 (OCH_3), 20.3 ($COCH_3$), 16.8 (CCH_3), 16.7 (CCH_3), 16.4 (CCH_3), 15.1 (CCH_3); ESI-MS: m/z=1,252.2 $[M+NH_4]^+$; Anal. Calcd. for $C_{52}H_{82}O_{33}$ (1,234.47): C, 50.56; H, 6.69; found: C, 50.38; H, 6.95.

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