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Synthesis of a tetrasaccharide corresponding to the teichoic acid from the cell wall of *Streptomyces* sp. VKM Ac-2275

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ABSTRACT

A concise chemical synthesis of a tetrasaccharide found in the teichoic acid from the cell wall of *Streptomyces* sp. VKM Ac-2275 was achieved in high yield. A [2+2] block synthetic strategy has been adopted for the construction of the target tetrasaccharide by exploiting the orthogonal property of a thioglycoside. For the first time, the 2-(4-methoxyphenoxy) ethyl group has been used as the anomeric protecting group to make the glycone moiety with a readily available linker for its conjugation to a protein without destroying the cyclic structure at the reducing end. Yields were high in all of the intermediate steps.

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1. Introduction

Potato scab, a commonly found infectious disease in potato, causes serious damage in the agriculture industry.[1] A group of bacteria, for example, *Streptomyces* sp., infect the potato and cause parts of the vegetable to turn from a delicious vegetable into a dry, corky substance that looks unpleasant and tastes worse. *Streptomyces scabiei* is the most frequently known bacterial species for causing potato scab.[2] Among other potato scab-forming bacterial species, *Streptomyces* sp. VKM-2275 is unique in nature as it does not produce thaxtomin, a phytotoxin responsible for the inhibition of cellulose biosynthesis in plants like others.[3] In general, the cell wall of plant pathogenic *Streptomycetes* species consists of different polymers related to teichoic acids, such as teichuronic acids, poly glycerol phosphates, poly ribitol phosphates, and Kdn polymers[4] Very often, these cell wall polymers are responsible for the pathogenicity of the *Streptomyces* species.[5] Recently, the structural elucidation of the teichoic acid from the cell wall of *Streptomyces* sp. VKM Ac-2275, isolated from the potato tubers infected by scab lesions, has been reported by Streshinskaya et al. (Fig. 1).[6] The cell wall of *Streptomyces* sp. VKM Ac-2275 differs from that of other scab-forming bacterial species, as it only contains anionic polymeric teichoic acid.

The development of anti-infective agents for controlling the microbial infections in the crops has been an important concern in the recent scenario. Since the pathogenicity emerges from the bacterial cell wall teichoic acids, it is reasonable to synthesize oligosaccharides related to them in order to study their role in the pathogenicity. As a part of our program for the synthesis of complex oligosaccharides for their use in the preparation of glycoconjugates,[7] we herein report a concise chemical synthesis of a branched tetrasaccharide as its 2-(4-methoxyphenoxy) ethyl glycoside corresponding to the teichoic acid found in the cell wall of the *Streptomyces* sp. VKM Ac-2275 (Fig. 2). The 2-(4-methoxyphenoxy) ethyl group at the anomeric position has been chosen for the ready availability of an ethylene linker for its conjugation with a suitable protein without destroying the cyclic structure at the reducing end. A number of noteworthy features present in the synthetic strategy, such as the use of (a) 2-(4-methoxyphenoxy) ethyl group at the anomeric protecting group for the first time, (b) thioglycoside as an acceptor in the presence of thioglycoside as a glycosyl donor under thioglycoside activation condition, (c) a block synthetic strategy, and (d) one-pot multistep-protecting group manipulation.

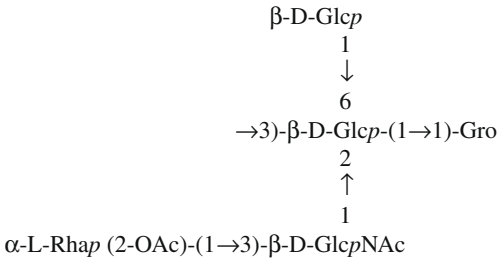

Figure 1. Structure of the repeating unit of the teichoic acid of the cell wall of *Streptomyces* sp. VKM Ac-2275.

2. Results and discussion

In order to synthesize the target tetrasaccharide as its 2-(4-methoxyphenoxy) ethyl glycoside **1,** a block synthetic strategy has been adopted. A disaccharide thioglycoside donor **14** was

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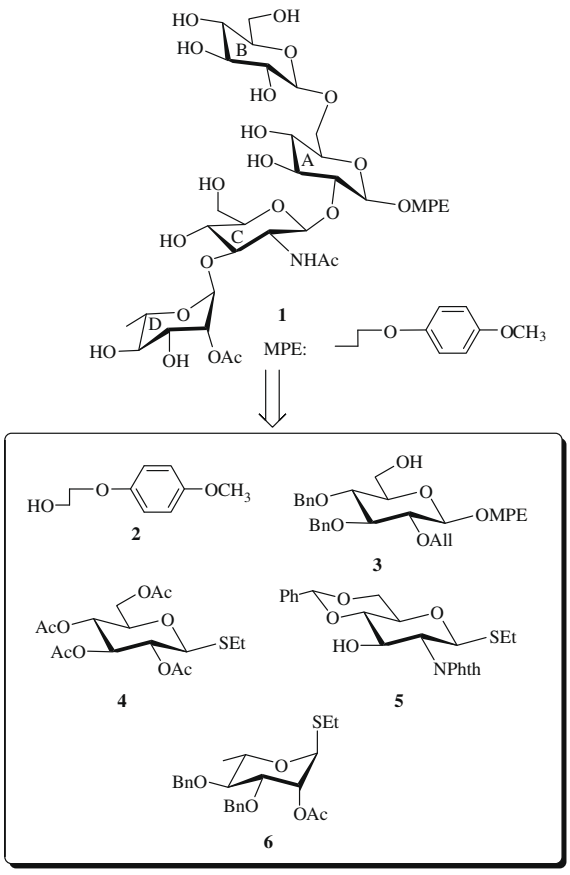
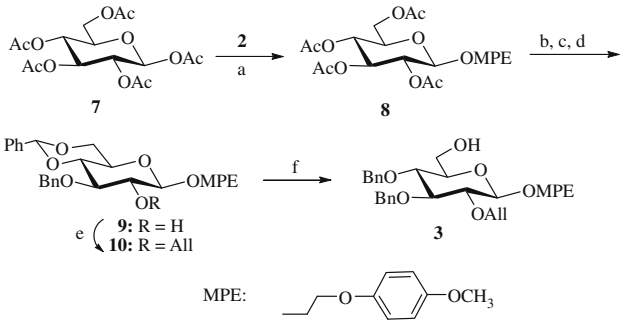


Figure 2. Structure of the synthesized tetrasaccharide as its 2-(4-methoxyphenoxy) ethyl glycoside corresponding to the teichoic acid of the cell wall of *Streptomyces* sp. VKM Ac-2275.

prepared using the two thioglycosides **5** and **6** by selective activation of compound **6** in the presence of compound **5** tuning the reactivity differences of the two thioglycosides under iodonium ion-mediated glycosylation conditions. Compound **5** behaves as an orthogonal thioglycoside donor by acting as a glycosyl acceptor. Another disaccharide derivative **13** was prepared with a 2-(4-methoxyphenoxy) ethyl group at the anomeric position. Finally the stereoselective condensation of two disaccharide derivatives **13** and **14** furnished tetrasaccharide derivative **15**, which was deprotected to give the target tetrasaccharide as its 2-(4-methoxyphenoxy) ethyl glycoside **1**. For this purpose, suitably protected 2-(4-methoxyphenoxy) ethyl glucoside derivative **3** was prepared from D-glucose penta-*O*-acetate **7** via a number of steps. Three other monosaccharide derivatives **4**,[8] **5**[9], and **6**[10] were prepared following the literature-reported synthetic methodologies. Treatment of penta-*O*-acetyl-β-D-glucopyranose **7** with 2-(4-methoxyphenoxy) ethanol **2**[11] in the presence of borontrifluoride etherate furnished 2-(4-methoxyphenoxy) ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside **8** in 82% yield. Compound **8** was converted to compound **9** in 72% overall yield following a sequence of reactions involving (a) saponification, (b) benzylidene acetal formation,[12] and (c) selective benzylation[13] via stannylidene acetal formation. Allylation of compound **9** using allyl bromide in the presence of sodium hydroxide followed by regioselective ring opening of the benzylidene acetal[14] using lithium aluminim hydride–aluminim chloride combination furnished compound **3** in 76% yield. Iodonium ion-promoted stereoselective glycosylation of compound **3** with thioglycoside derivative **4** in the presence of *N*-iodosuccinimide (NIS) and trifluoromethanesulfonic acid (TfOH)[15] afforded disaccharide derivative **11** in 88% yield. Characteristic signals in the NMR spectra confirmed the formation of compound **11**. By applying a one-pot deacetylation–benzylation protocol,[16] compound **11** was transformed into disaccharide derivative **12**, which on treatment with palladium chloride[17] furnished disaccharide acceptor **13** in 78% yield.

In another experiment, L-rhamnose-derived thioglycoside **6** was allowed to glycosylate with D-glucosamine-derived thioglycoside **5** in the presence of a NIS–TfOH combination exploiting the orthogonal properties of compound **5** to give disaccharide thioglycoside derivative **14** in 80% yield. It is worth mentioning that the simultaneous use of thioglycosides as donors and acceptors minimized the protecting group manipulations. The presence of signals in the NMR spectra [δ 5.39 (d, J = 10.6 Hz, H-1_C), 4.54 (d, J = 1.5 Hz, H-1_D), 2.72–2.62 (m, 2H, SCH_2CH$_3$), 1.21 (t, J = 7.4 Hz, 3H, SCH$_2$CH_3) in the ^{1}H NMR and δ 102.4 (PhCH), 98.5 (C-1_D), 82.4 (C-1_C) in the ^{13}C NMR spectra] supported the formation of compound **14**.

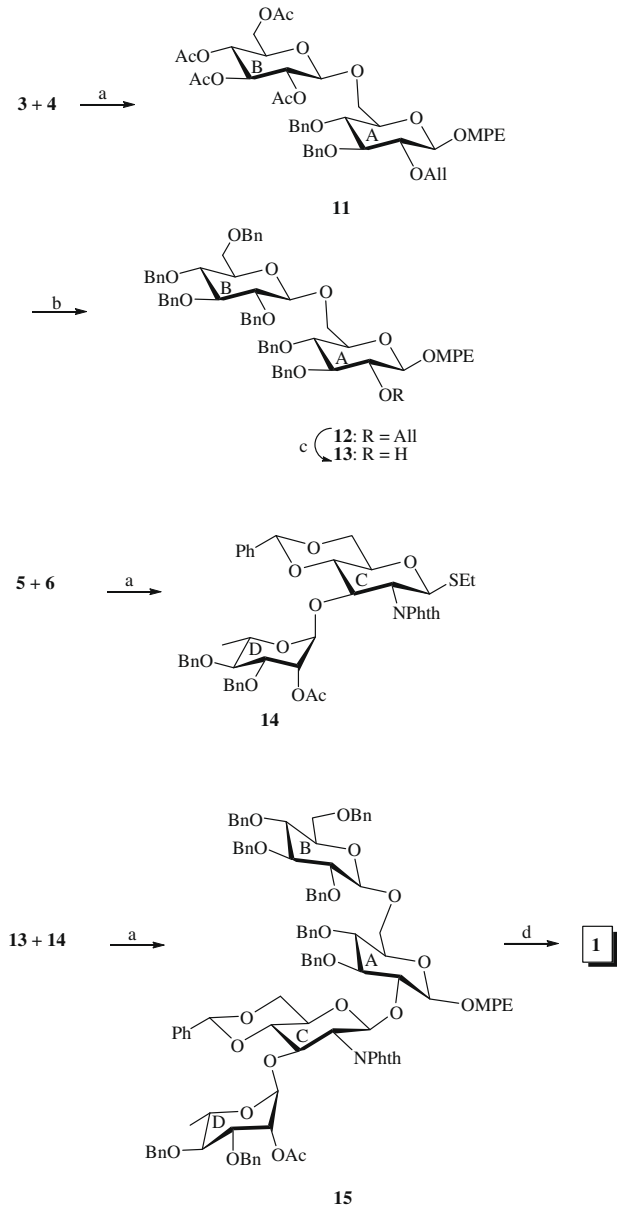
The stereoselective glycosylation of disaccharide acceptor **13** and thioglycoside disaccharide donor **14** in the presence of a NIS–TfOH combination furnished the tetrasaccharide derivative **15** in 75% yield. The appearance of signature signals in the NMR spectra supported the formation of compound **15**. Compound **15** was subjected to a series of functional group transformations involving hydrazinolysis of the *N*-phthalimido group; acetylation and hydrogenolysis over Pearlman's catalyst[17] furnished the target tetrasaccharide as its 2-(4-methoxyphenoxy) ethyl glycoside in 71% yield. The structure of compound **1** was unambiguously supported by its 1D and 2D NMR spectroscopic analysis [δ 4.92–4.87 (m, 1H, H-2_D), 4.86 (d, J = 8.0 Hz, H-1_C), 4.81 (br s, 1H, H-1_D), 4.51 (d, J = 7.43 Hz, H-1_A), 4.36 (d, J = 7.8 Hz, H-1_B) in the ^{1}H NMR and δ 103.9 (C-1_B), 102.4 (C-1_A), 101.1 (C-1_C), 99.4 (C-1_D) in the ^{13}C NMR spectra]. The 4-methoxyphenyl group of the anomeric linker of compound **1** can be removed by treatment with ammonium ceric nitrate (CAN) in methanol to produce the tetrasaccharide with a hydroxyethyl linker at the reducing end without destroying the cyclic structure of the reducing end (see Schemes 1 and 2).



Scheme 1. Reagents and conditions: (a) 2-(4-methoxyphenoxy) ethanol, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 5 °C, 12 h, 82%; (b) 0.1 N CH_3ONa, CH_3OH, room temperature, 4 h; (c) $PhCH(OCH_3)_2$, *p*-TsOH, CH_3CN, room temperature, 12 h; (d) (i) Bu_2SnO, CH_3OH, 80 °C, 2 h; (ii) benzyl bromide, CsF, DMF, room temperature, 16 h, 72% in three steps; (e) allyl bromide, NaOH, DMF, room temperature, 4 h, 93%; (f) $LiAlH_4$, $AlCl_3$, CH_2Cl_2, Et_2O, 1.5 h, 76%.

3. Conclusion

In conclusion, the chemical synthesis of a tetrasaccharide related to the teichoic acid of the cell wall of *Streptomyces* sp. VKM Ac-2275 as its 2-(4-methoxyphenoxy) ethyl glycoside was achieved in excellent yield. The 2-(4-methoxyphenoxy) ethyl group, which was used as the anomeric protecting group was introduced for the first time to provide the oligosaccharide moiety readily attached to an ethylene linker useful for the preparation of



Scheme 2. Reagents and conditions: (a) *N*-iodosuccinimide (NIS), trifluoromethanesulfonic acid (TfOH), CH_2Cl_2, −40 °C, 1 h, 88% for **11**, 80% for **14** and 75% for **15**; (b) benzyl bromide, NaOH, TBAB, THF, room temperature, 4 h, 86%; (c) $PdCl_2$, CH_3OH, room temperature, 2 h, 78%; (d) (i) $NH_2NH_2{\cdot}H_2O$, C_2H_5OH, 80 °C, 4 h; (ii) acetic anhydride, pyridine, room temperature, 2 h; (iii) H_2, 20% $Pd(OH)_2$–C, CH_3OH, room temperature, 24 h, 71% in three steps.

glycoconjugates without destroying the cyclic structure of the monosaccharide of the reducing end. The use of a thioglycoside as an orthogonal glycosyl acceptor under the thioglycoside activation conditions allowed us to obtain the target compound in the minimum number of steps. Finally a block synthetic strategy has been adopted for the preparation of a tetrasaccharide derivative. Yields were excellent in all intermediate steps and reproducible.

4. Experimental

4.1. 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 sulfate (2% $Ce(SO_4)_2$ in 2 N H_2SO_4)-sprayed plates on a hot plate. Silica gel 230–400 mesh was used for column chromatography. ^1H and ^{13}C NMR, 2D COSY, HMQC spectra were recorded on Bruker Avance DRX 500 MHz using $CDCl_3$ and D_2O as solvents and TMS as an internal reference unless stated otherwise. Chemical shift value is expressed in δ ppm. ESI-MS were recorded on a Micromass Quttro II triple quadrupole mass spectrometer. Elementary analysis was carried out on Carlo ERBA-1108 analyzer. Optical rotations were measured at 25 °C on a Perkin–Elmer 341 polarimeter. Commercially available grades of organic solvents of adequate purity were used in many reactions.

4.1.1. 2-(4-Methoxyphenoxy) ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside 8

To a solution of compound **7** (10 g, 25.64 mmol) and 2-(4-methoxyphenoxy) ethanol (7 g, 41.62 mmol) in anhydrous CH_2Cl_2 (100 mL) was added MS 4 Å (5 g) and the reaction mixture was allowed to stir at room temperature for 1 h. To the reaction mixture was added $BF_3{\cdot}OEt_2$ (6.5 mL, 52.66 mmol) and it was allowed to stir at 5 °C for 12 h. The reaction mixture was filtered through a Celite® bed and washed with CH_2Cl_2 (200 mL). The organic layer was successively washed with satd $NaHCO_3$ and H_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane/EtOAc (5:1) as eluant to give pure **8** (10.5 g, 82%). White solid; mp 99–100 °C; $[\alpha]_D^{25} = -20.4$ (*c* 1.0, $CHCl_3$); IR (KBr): 3468, 2918, 2849, 1741, 1755, 1513, 1453, 1385, 1370, 1260, 1247, 1226, 1172, 1058, 1035, 901, 822 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 6.82–6.81 (m, 4H, Ar–H), 5.22 (t, *J* = 9.5 Hz, 1H, H-3), 5.10 (t, *J* = 9.8 Hz, 1H, H-2), 5.04–5.00 (m, 1H, H-4), 4.68 (d, *J* = 8.0 Hz, 1H, H-1), 4.28–4.24 (dd, *J* = 4.7, 12.3 Hz, 1H, H-6a), 4.14–4.06 (m, 4H, H-6b, 2H–OCH_2, H–OCH_{2a}), 3.94–3.90 (m, 1H, H–OCH_{2b}), 3.76 (s, 3H, OCH_3), 3.73–3.70 (m, 1H, H-5), 2.10 (s, 3H, COCH_3), 2.03 (s, 3H, COCH_3), 2.00 (s, 3H, COCH_3), 1.94 (s, 3H, COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.1, 170.7, 169.8, 169.8 (4C, *C*OCH$_3$), 154.5–115.1 (Ar–C), 101.5 (C-1), 73.2 (C-2), 72.3 (C-3), 71.6 (C-5), 68.8 (2C, C-6, C-4), 68.4 (O*C*H$_2$), 62.3 (O*C*H$_2$), 56.1 (O*C*H$_3$), 21.1, 21.0, 21.0, 20.9 (4C, 4CO*C*H$_3$); ESI-MS: 521.1 $[M+Na]^+$. Anal. Calcd for $C_{23}H_{30}O_{12}$ (498.17): C, 55.42; H, 6.07. Found: C, 55.25; H, 6.30.

4.1.2. 2-(4-Methoxyphenoxy) ethyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside 9

A solution of compound **8** (10 g, 20.06 mmol) in 0.1 M CH_3ONa (150 mL) was allowed to stir at room temperature for 4 h and neutralized with Amberlite IR-120 (H^+) resin. The reaction mixture was filtered and evaporated to dryness. To a solution of the crude mass in CH_3CN (50 mL) were added benzaldehyde dimethylacetal (6 mL, 40 mmol) and *p*-TsOH (500 mg) and the reaction mixture was allowed to stir at room temperature for 12 h. The reaction was quenched with Et_3N (2 mL) and the solvents were removed under reduced pressure. To a solution of the crude product in CH_3OH (100 mL) was added dibutyltin oxide (7.5 g, 30.13 mmol) and the reaction mixture was allowed to stir at 80 °C for 2 h. The solvents were removed under reduced pressure and the crude stannylidene acetal derivative was dissolved in anhydrous DMF (50 mL). To the reaction mixture were added CsF (3.1 g, 20.4 mmol) and benzyl bromide (4.8 mL, 40.36 mmol) and it was allowed to stir at room temperature for 16 h. The solvents were removed under reduced pressure and the crude mass was dissolved in EtOAc (200 mL). The organic layer was washed with satd $NaHCO_3$ and H_2O, dried (Na_2SO_4), and concentrated. The crude product was purified over SiO_2 using hexane/EtOAc (4:1) as eluant to give pure **9** (7.3 g, 72%). White solid; mp 106–108 °C; $[\alpha]_D^{25} = -31.1$ (*c* 1.0, $CHCl_3$); IR (KBr): 3496, 2922, 2853, 1511, 1455, 1367, 1235, 1101, 1066, 1029, 822, 744, 735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.50–6.82 (m, 14H, Ar–H), 5.57 (s, 1H, PhC*H*), 4.95 (d, *J* = 11.7 Hz, 1H, PhCH_2), 4.83 (d, *J* = 11.7 Hz, 1H, PhCH_2), 4.50 (d, *J* = 7.6 Hz, 1H,

H-1), 4.33–4.31 (dd, J = 4.9, 10.5 Hz, 1H, H-6_a), 4.20–4.10 (m, 3H, H-6_b, OC$H_{2a,b}$), 3.98–3.94 (m, 1H, OCH_{2a}), 3.79 (t, J = 10.2 Hz, 1H, H-4), 3.76 (s, 3H, OCH_3), 3.70–3.68 (m, 2H, H-3, H–OCH_{2b}), 3.62 (t, J = 7.9, 7.9 Hz, 1H, H-2), 3.48–3.43 (m, 1H, H-5); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.8–115.1 (Ar–C), 104.3 (C-1), 101.7 (PhCH), 81.7 (C-2), 80.6 (PhCH_2), 75.0 (C-3), 74.8 (C-5), 69.2 (C-6), 69.1 (C-4), 68.3 (OCH_2), 67.0 (OCH_2), 56.1 (OCH_3); ESI-MS: 531.2 $[M+Na]^+$. Anal. Calcd for $C_{29}H_{32}O_8$ (508.21): C, 68.49; H, 6.34. Found: C, 68.30; H, 6.50.

4.1.3. 2-(4-Methoxyphenoxy) ethyl 2-*O*-allyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside 10

To a solution of compound **9** (5 g, 9.83 mmol) in THF (20 mL) were added allyl bromide (1.7 mL, 19.64 mmol), powdered NaOH (1.2 g, 30 mmol), and TBAB (200 mg, 0.62 mmol) and the reaction mixture was allowed to stir at room temperature for 4 h. The reaction mixture was diluted with CH_2Cl_2 (100 mL) and the organic layer was washed with H_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane/EtOAc (6:1) as eluant to give pure **10** (5 g, 93%). White solid; mp 95–97 °C; $[\alpha]_D^{25} = -40.8$ (c 1.0, $CHCl_3$); IR (KBr): 3446, 2917, 2873, 1510, 1365, 1235, 1096, 1073, 811, 744, 693 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50–6.81 (m, 14H, Ar–H), 5.96–5.90 (m, 1H, –CH_2–CH=CH_2), 5.55 (s, 1H, PhCH), 5.27–5.13 (m, 2H, –CH_2–CH=CH_2), 4.89 (d, J = 11.5 Hz, 1H, PhCH_2), 4.81 (d, J = 11.5 Hz, 1H, PhCH_2), 4.54 (d, J = 7.7 Hz, 1H, H-1), 4.41–4.39 (m, 1H, CH_{2a}–CH=CH_2), 4.33–4.30 (dd, J = 5.0, 10.5 Hz, 1H, H-6_a), 4.25–4.22 (m, 1H, CH_{2b}–CH=CH_2), 4.12–4.10 (m, 3H, H-6_b, OC$H_{2a,b}$), 3.95–3.92 (m, 1H, OCH_{2a}), 3.77 (t, J = 10.4 Hz, 1H, H-4), 3.76 (s, 3H, OCH_3), 3.69–3.64 (m, 2H, H-3, OCH_{2b}), 3.41–3.36 (m, 2H, H-5, H-2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.8–115.1 (Ar–C), 129.6 (CH_2–CH=CH_2), 117.4 (CH_2–CH=CH_2), 104.8 (C-1), 101.6 (PhCH), 82.2 (C-2), 81.6 (PhCH_2), 81.1 (C-3), 75.5 (C-4), 74.4 (C-5), 69.3 (C-6), 69.2 (CH_2–CH=CH_2), 68.1 (OCH_2), 66.5 (OCH_2), 56.1 (OCH_3); ESI-MS: 571.2 $[M+Na]^+$. Anal. Calcd for $C_{32}H_{36}O_8$ (548.24): C, 70.06; H, 6.61. Found: C, 69.84; H, 6.85.

4.1.4. 2-(4-Methoxyphenoxy) ethyl 2-*O*-allyl-3,4-di-*O*-benzyl-β-D-glucopyranoside 3

To a solution of compound **10** (3 g, 5.47 mmol) in CH_2Cl_2/Et_2O (60 mL, 1:1 v/v) was added $LiAlH_4$ (1 g, 26.35 mmol) portionwise and the reaction mixture was allowed to stir at 40 °C. To the stirred reaction mixture was slowly added $AlCl_3$ (3 g, 22.5 mmol) suspended in Et_2O (50 mL) for30 min and the reaction mixture was allowed to stir at the same temperature for 1.5 h. The reaction mixture was cooled and excess $LiAlH_4$ was decomposed by EtOAc (10 mL) and extracted with Et_2O (100 mL). The organic layer was washed with H_2O, dried (Na_2SO_4), and evaporated to dryness. The crude product was purified over SiO_2 using hexane/EtOAc (4:1) to give pure **3** (2.3 g, 76%). Colorless oil; $[\alpha]_D^{25} = -9.6$ (c 1.0, $CHCl_3$); IR (neat): 3572, 3462, 3030, 2928, 2895, 2851, 1738, 1633, 1509, 1464, 1453, 1361, 1291, 1281, 1234, 1149, 1114, 1070, 1047, 1016, 1001, 914, 820, 754, 736, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–6.81 (m, 14H, Ar–H), 5.94–5.86 (m, 1H, CH_2=CH–CH_2), 5.26–5.12 (m, 2H, CH_2=CH–CH_2), 4.95 (d, J = 10.9 Hz, 1H, PhCH_2), 4.86 (d, J = 10.9 Hz, 1H, PhCH_2), 4.80 (d, J = 10.9 Hz, 1H, PhCH_2), 4.63 (d, J = 10.9 Hz, 1H, PhCH_2), 4.47 (d, J = 7.8 Hz, 1H, H-1), 4.45–4.41 (m, 1H, CH_{2a}–CH=CH_2), 4.41–4.14 (m, 2H, CH_{2b}–CH=CH_2, OCH_{2a}), 4.12–4.10 (m, 2H, OC$H_{2a,b}$), 3.93–3.91 (m, 1H, OCH_{2b}), 3.85–3.82 (m, 1H, H-6_a), 3.76 (s, 3H, OCH_3), 3.71–3.70 (m, 1H, H-6_b), 3.63 (t, J = 9.1 Hz, 1H, H-3), 3.54 (t, J = 9.4 Hz, 1H, H-4), 3.38–3.21 (m,, 2H, H-5, H-2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.5–115.1 (Ar–C), 128.9 (CH_2–CH=CH_2), 117.4 (CH_2–CH=CH_2), 104.3 (C-1), 84.8 (C-2), 82.3 (PhCH), 77.8 (PhCH_2), 76.1 (C-3), 75.5 (2C, C-5, C-4), 74.1 (C-6), 69.1 (CH_2–CH=CH_2), 68.3 (OCH_2), 62.4 (OCH_2), 56.1 (OCH_3); ESI-MS: 573.2 $[M+Na]^+$. Anal. Calcd for $C_{32}H_{38}O_8$ (550.26): C, 69.80; H, 6.96. Found: C, 69.62; H, 7.20.

4.1.5. 2-(4-Methoxyphenoxy) ethyl (2,3,4,6-tera-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2-*O*-allyl-3,4-di-*O*-benzyl-β-D-glucopyranoside 11

To a solution of compound **3** (1.5 g, 2.72 mmol) and compound **4** (1.3 g, 3.31 mmol) in CH_2Cl_2 (15 mL) was added MS 4 Å (3 g) and the reaction mixture was allowed to stir under argon at room temperature for 1 h. The reaction mixture was cooled to −40 °C and to the cooled reaction mixture were added *N*-iodosuccinimide (NIS; 900 mg, 4 mmol) and trifluoromethanesulfonic acid (TfOH; 10 μL) and the reaction mixture was allowed to stir at the same temperature for 1 h. The reaction mixture was filtered through a Celite® bed and washed with CH_2Cl_2 (100 mL). The organic layer was washed with 5% $Na_2S_2O_3$, satd $NaHCO_3$ and H_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane/EtOAc (4:1) to give pure **11** (2.1 g, 88%). White solid; mp 105–107 °C; $[\alpha]_D^{25} = -15.2$ (c 1.0, $CHCl_3$); IR (KBr): 3473, 2932, 1747, 1510, 1381, 1234, 1178, 1060, 914, 821, 749, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35–6.82 (m, 14H, Ar–H), 5.94–5.89 (m, 1H, CH_2=CH–CH_2), 5.26–5.22 (m, 2H, CH_2=CH–CH_2), 5.16 (t, J = 9.1 Hz, 1H, H-3_B), 5.10 (t, J = 9.6 Hz, 1H, H-2_B), 5.02 (m, 1H, H-4_B), 4.94 (d, J = 10.9 Hz, 1H, PhCH_2), 4.85 (d, J = 10.9 Hz, 1H, PhCH_2), 4.76 (d, J = 10.9 Hz, 1H, PhCH_2), 4.63 (d, J = 8.0 Hz, 1H, H-1_B), 4.53 (d, J = 10.9 Hz, 1H, PhCH_2), 4.45–4.43 (m, 1H, CH_{2a}–CH=CH_2) 4.41 (d, J = 7.7 Hz, 1H, H-1_A), 4.22–4.10 (m, 7H, OCH_2, OCH_{2a}, H-6_{aB}, CH_{2b}–CH=CH_2, H-6_{abA}), 3.91–3.89 (m, 1H, OCH_{2b}), 3.76 (s, 3H, OCH_3), 3.67–3.59 (m, 3H, H-5_A, H-6_{bB}, H-4_A), 3.48 (m, 1H, H-5_B), 3.39–3.31 (m, 2H, H-3_A, H-2_A), 2.04, 2.01, 1.99, 1.98 (4s, 12H, 4COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.1, 170.7, 169.8, 169.5 (4C, 4COCH$_3$), 154.4–115.1 (Ar–C), 128.9 (CH_2–CH=CH_2), 117.4 (CH_2–CH=CH_2), 104.1 (C-1_A), 101.3 (C-1_B), 84.9 (C-4_A), 82.2 (C-2_A), 78.1 (C-3_A), 76.1 (PhCH_2), 75.3 (PhCH_2), 75.2 (C-5_B), 73.9 (CH_2–CH=CH_2), 73.4 (C-3_B), 72.2 (C-4_B), 71.7 (C-5_A), 68.9 (C-6_B), 68.8 (C-6_A), 68.7 (C-2_B), 68.2 (OCH_2), 62.3 (OCH_2), 56.1 (OCH_3), 21.1, 21.1, 21.0, 20.9 (4C, 4COCH_3); ESI-MS: 903.3 $[M+Na]^+$. Anal. Calcd for $C_{46}H_{56}O_{17}$ (880.35): C, 62.72; H, 6.41. Found: C, 62.55; H, 6.27.

4.1.6. 2-(4-Methoxyphenoxy) ethyl (2,3,4,6-tera-*O*-benzyl-β-D-glucopyranosyl)-(1→6)-2-*O*-allyl-3,4-di-*O*-benzyl-β-D-glucopyranoside 12

To a solution of compound **11** (2 g, 2.27 mmol) in THF (30 mL) were added powdered NaOH (1 g, 25 mmol), benzyl bromide (2 mL, 16.81 mmol), and *n*-Bu_4NBr (200 mg, 0.62 mmol) and the reaction mixture was allowed to stir at room temperature for 4 h. The reaction mixture was diluted with H_2O (100 mL) and extracted with CH_2Cl_2 (100 mL). The organic layer was washed with H_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane/EtOAc (7:1) to give pure **12** (2.1 g, 86%). Yellow oil; $[\alpha]_D^{25} = +6.5$ (c 1.0, $CHCl_3$); IR (neat): 3449, 3063, 3031, 2907, 1509, 1454, 1358, 1237, 1069, 913, 825, 747, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33–6.78 (m, 34H, Ar–H), 5.95–5.87 (m, 1H, CH_2=CH–CH_2), 5.27–5.10 (m, 2H, CH_2=CH–CH_2), 4.97 (d, J = 11.1 Hz, 1H, PhCH_2), 4.94 (d, J = 10.9 Hz, 1H, PhCH_2), 4.89 (d, J = 10.9 Hz, 1H, PhCH_2), 4.80 (d, J = 10.4 Hz, 1H, PhCH_2), 4.77–4.71 (m, 4H, PhCH_2), 4.60 (d, J = 12.0 Hz, 1H, PhCH_2), 4.54–4.51 (m, 3H, PhCH_2), 4.47 (d, J = 7.8 Hz, 1H, H-1_B), 4.43–4.39 (m, 1H, CH_{2a}=CH–CH_2), 4.34 (d, J = 7.8 Hz, 1H, H-1_A), 4.21–4.18 (m, 1H, H-6_{aA}), 4.17–4.13 (m, 1H, CH_{2b}=CH–CH_2), 4.06–4.02 (m, 1H, OCH_{2a}), 3.95–3.87 (m, 2H, OCH_{2ab}), 3.72 (s, 3H, OCH_3), 3.71–3.67 (m, 4H, H-6_{bA}, H-6_{abB}, OCH_{2b}), 3.66–3.57 (m, 4H, H-2_B, H-3_B, H-4_A, H-5_A), 3.46–3.42 (m, 2H, H-5_B, H-4_B), 3.38 (m, 1H, H-3_A), 3.32 (m, 1H, H-2_A); ^{13}C NMR

(125 MHz, $CDCl_3$): δ 154.3–115.0 (Ar–C), 128.8 (CH_2–CH=CH_2), 117.4 (CH_2–CH=CH_2), 104.5 (C-1_B), 103.9 (C-1_A), 85.2 (C-2_B), 85.0 (C-3_B), 82.6 (C-2_A), 82.4 (C-3_A), 78.5 (C-4_A), 78.2 (C-5_A), 76.1 (PhCH$_2$), 76.0 (PhCH$_2$), 75.4 (C-5_B), 75.4 (2C, 2 PhCH$_2$), 75.3 (C-4_B), 75.1 (CH_2–CH=CH_2), 74.0 (PhCH$_2$), 73.9 (PhCH$_2$), 69.3 (C-6_A), 69.2 (C-6_B), 68.8 (OCH$_2$), 68.0 (OCH$_2$), 56.1 (OCH$_3$); ESI-MS: 1095.5 $[M+Na]^+$. Anal. Calcd for $C_{66}H_{72}O_{13}$ (1072.50): C, 73.86; H, 6.76. Found: C, 73.65; H, 7.0.

4.1.7. 2-(4-Methoxyphenoxy) ethyl (2,3,4,6-tera-*O*-benzyl-β-D-glucopyranosyl)-(1→6)-3,4-di-*O*-benzyl-β-D-glucopyranoside 13

To a solution of compound **12** (2 g, 1.86 mmol) in CH_3OH (30 mL) was added $PdCl_2$ (200 mg, 1.13 mmol) and the reaction mixture was allowed to stir at room temperature for 2 h. The solvent was removed and the reaction mixture was diluted with CH_2Cl_2 (100 mL). The organic layer was washed with satd $NaHCO_3$, dried (Na_2SO_4), and evaporated to dryness. The crude product was purified over SiO_2 using hexane/EtOAc (5:1) to give pure **13** (1.5 g, 78%). Colorless oil; $[\alpha]_D^{25} = +8.5$ (*c* 1.0, $CHCl_3$); IR (neat): 3581, 3494, 3060, 3031, 2907, 2861, 1509, 1454, 1382, 1358, 1234, 1178, 1069, 919, 826, 752, 735, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.33–6.79 (m, 34H, Ar–H), 4.97 (d, *J* = 11.1 Hz, 1H, PhCH$_2$), 4.96 (d, *J* = 11.2 Hz, 1H, PhCH$_2$), 4.89 (d, *J* = 10.9 Hz, 1H, PhCH$_2$), 4.80 (d, *J* = 10.4 Hz, 1H, PhCH$_2$), 4.79 (d, *J* = 11.2 Hz, 1H, PhCH$_2$), 4.77–4.72 (m, 3H, PhCH$_2$), 4.60 (d, *J* = 12.0 Hz, 1H, PhCH$_2$), 4.55–4.51 (m, 3H, PhCH$_2$), 4.46 (d, *J* = 7.8 Hz, 1H, H-1_B), 4.26 (d, *J* = 7.5 Hz, 1H, H-1_A), 4.22–4.20 (m, 1H, H-6_{aA}), 4.03–3.99 (m, 1H, OCH$_{2a}$), 3.96–3.93 (m, 1H, OCH$_{2a}$), 3.90–3.88 (m, 1H, OCH$_{2b}$), 3.72 (s, 3H, OCH$_3$), 3.71–3.66 (m, 4H, H-6_{bA}, H-6_{abB}, OCH$_{2b}$), 3.63–3.54 (m, 5H, H-2_B, H-3_B, H-4_A, H-5_A, H-5_B), 3.48–3.41 (m, 3H, H-2_A H-3_A, H-4_B); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.5–115.1 (Ar–C), 103.4 (C-1_B), 102.2 (C-1_A), 85.2 (C-2_B), 84.9 (C-3_B), 82.6 (C-3_A), 78.3 (C-4_A), 78.2 (C-5_A), 76.1 (PhCH$_2$), 75.8 (C-5_B), 75.5 (PhCH$_2$), 75.4 (2C, PhCH$_2$), 75.3 (C-2_A), 75.2 (C-4_B), 75.1 (PhCH$_2$), 73.9 (PhCH$_2$), 69.3 (C-4_B), 69.2 (C-6_A), 68.8 (OCH$_2$), 68.2 (OCH$_2$), 56.1 (OCH$_3$); ESI-MS: 1055.4 $[M+Na]^+$. Anal. Calcd for $C_{63}H_{68}O_{13}$ (1032.47): C, 73.24; H, 6.63. Found: C, 73.05; H, 6.90.

4.1.8. Ethyl (2-*O*-acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalimido-1-thio-β-D-glucopyranoside 14

To a solution of compound **5** (1.5 g, 3.39 mmol) and compound **6** (1.6 g, 3.72 mmol) in anhydrous CH_2Cl_2 (25 mL) was added MS 4 Å (3 g) and the reaction mixture was allowed to stir at room temperature for 1 h. The reaction mixture was cooled to −40 °C and NIS (850 mg, 3.77 mmol) and TfOH (10 μL) were added to it. After stirring at the same temperature for 1 h, the reaction mixture was filtered through a Celite® bed and washed with CH_2Cl_2 (100 mL). The organic layer was washed with 5% $Na_2S_2O_3$, satd $NaHCO_3$ and H_2O, dried (Na_2SO_4), and concentrated. The crude product was purified over SiO_2 using hexane/EtOAc (5:1) as eluant to give pure **14** (2.2 g, 80%). White solid; mp 143–145 °C; $[\alpha]_D^{25} = -7.1$ (*c* 1.0, $CHCl_3$); IR (KBr): 3474, 3376, 2977, 2930, 2869, 1775, 1746, 1713, 1468, 1456, 1389, 1232, 11445, 1096, 1060, 1011, 994, 963, 917, 873, 745, 723, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.50–7.21 (m, 19H, Ar–H), 5.54 (s, 1H, PhCH), 5.39 (d, *J* = 10.6 Hz, 1H, H-1_C), 4.88–4.79 (m, 1H, H-2_D), 4.78 (d, *J* = 10.9 Hz, 1H, PhCH$_2$), 4.62 (t, *J* = 9.4 Hz, 1H, H-3_C), 4.54 (d, *J* = 1.5 Hz, 1H, H-1_D), 4.50–4.49 (m, 2H, 2-PhCH$_2$), 4.42–4.39 (m, 2H, H-6_{aC}, PhCH$_2$), 4.36 (t, *J* = 10.3 Hz, 1H, H-2_C), 3.90–3.88 (m, 1H, 6_{bC}), 3.83–3.80 (m, 2H, H-3_D, H-5_D), 3.76–3.73 (m, 1H, H-5_C), 3.65 (t, *J* = 9.1 Hz, 1H, H-4_C), 3.23 (t, *J* = 9.6 Hz, 1H, H-4_D), 2.72–2.62 (m, 2H, SCH$_2$CH$_3$), 1.78 (s, 3H, COCH$_3$), 1.21 (t, *J* = 7.4 Hz, 3H, SCH$_2$CH$_3$), 0.77 (d, *J* = 6.2 Hz, 3H, CCH$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.0 (COCH$_3$), 138.9–126.9 (Ar–C), 102.4 (PhCH), 98.5 (C-1_D), 82.4 (C-1_C), 80.8 (C-4_D), 80.4 (C-3_D), 77.9 (C-3_C), 76.3 (C-5_D), 75.5 (PhCH$_2$), 72.0 (PhCH$_2$), 71.3 (C-4_C), 69.4 (C-2_D), 69.1 (C-6_C), 68.4 (C-5_C), 55.8 (C-2_C), 24.7 (SCH$_2$CH$_3$), 21.1 (COCH$_3$), 17.6 (SCH$_2$CH$_3$), 15.3 (CCH$_3$); ESI-MS: 832.2 $[M+Na]^+$. Anal. Calcd for $C_{45}H_{47}NO_{11}S$ (809.29): C, 66.73; H, 5.85. Found: C, 66.55; H, 6.10.

4.1.9. 2-(4-Methoxyphenoxy) ethyl (2-*O*-acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalimido-β-D-glucopyranosyl)-(1→2)-[(2,3,4,6-tera-*O*-benzyl-β-D-glucopyranosyl)-(1→6)]-3,4-di-*O*-benzyl-β-D-glucopyranoside 15

To a solution of compound **13** (1 g, 0.97 mmol) and compound **14** (940 mg, 1.16 mmol) in anhydrous CH_2Cl_2 (15 mL) was added MS 4 Å (2 g) and the reaction mixture was allowed to stir under argon at room temperature for 1 h. The reaction mixture was cooled to −40 °C and NIS (300 g, 1.33 mmol) and TfOH (5 μL) were added to it. After stirring at the same temperature for 1 h, the reaction mixture was filtered through a Celite® bed and washed with CH_2Cl_2 (50 mL). The organic layer was washed with 5% $Na_2S_2O_3$, satd $NaHCO_3$ and H_2O, dried (Na_2SO_4), and concentrated. The crude product was purified over SiO_2 using hexane/EtOAc (5:1) as eluant to give pure **15** (1.3 g, 75%). White solid; mp 126–127 °C; $[\alpha]_D^{25} = +6.9$ (*c* 1.0, $CHCl_3$); IR (KBr): 3460, 3031, 2924, 1775, 1745, 1717, 1508, 1454, 1387, 1234, 1070, 1028, 737, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.46–6.80 (m, 53H, Ar–H), 5.71 (d, *J* = 8.6 Hz, 1H, H-1_C), 5.47 (s, 1H, PhCH), 4.93 (d, *J* = 11.0 Hz, 1H, PhCH$_2$), 4.88 (d, *J* = 10.9 Hz, 1H, PhCH$_2$), 4.81–4.80 (m, 1H, H-2_D), 4.78–4.70 (m, 4H, 4 PhCH$_2$), 4.64 (d, *J* = 12.0 Hz, 1H, PhCH$_2$), 4.59 (d, *J* = 12.1 Hz, 1H, PhCH$_2$), 4.54–4.49 (m, 3H, 3 PhCH$_2$), 4.45–4.39 (m, 8H, H-1_A, H-1_B, H-1_D, H-3_C, 4 PhCH$_2$), 4.34 (d, *J* = 11.2 Hz, 1H, PhCH$_2$), 4.31 (t, *J* = 10.1 Hz, 1H, H-2_C), 4.12–4.10 (m, 1H, H-6_{aA}), 4.05–4.02 (m, 2H, OCH$_2$), 3.84–3.82 (m, 2H, OCH$_2$), 3.78–3.76 (m, 3H, H-6_{bA}, H-6_{abC}), 3.70–3.65 (m, 3H, H-4_B, H-3_D, H-5_D), 3.69 (s, 3H, OCH$_3$), 3.59–3.51 (m, 7H, H-2_B, H-3_B, H-4_A, H-5_B, H-3_A, H-6_{abB}), 3.43–3.40 (m, 2H, H-2_A, H-5_A), 3.31 (t, *J* = 9.1 Hz, 1H, H-4_C), 3.17 (t, *J* = 9.5 Hz, 1H, H-4_D), 1.73 (s, 3H, COCH$_3$), 0.71 (d, *J* = 6.2 Hz, 3H, CCH$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.8 (COCH$_3$), 154.4–115.1 (Ar–C), 104.4 (C-1_D), 102.4 (2C, PhCH, C-1_C), 98.6 (2C, C-1_B, C-1_A), 85.1 (C-4_A), 84.3 (C-5_B), 82.5 (C-2_A), 82.2 (C-5_A), 80.9 (C-2_B), 80.3 (C-3_B), 78.5 (C-5_C), 78.2 (C-4_C), 78.0 (C-4_D), 76.1 (PhCH$_2$), 75.9 (C-5_D), 75.4 (PhCH$_2$), 75.3 (PhCH$_2$), 75.2 (3C, 3 PhCH$_2$), 75.1 (C-3_A), 75.0 (C-4_B), 73.9 (PhCH$_2$), 71.8 (PhCH$_2$), 69.3 (C-6_C), 69.2 (C-3_D), 69.1 (C-3_C), 69.0 (C-6_A), 68.5 (C-6_B), 68.3 (2C, 2OCH$_2$), 66.7 (C-2_D), 57.3 (C-2_C), 56.1 (OCH$_3$), 21.0 (COCH$_3$), 17.6 (CCH$_3$); MALDI-TOF: 1802.7 $[M+Na]^+$. Anal. Calcd for $C_{106}H_{109}NO_{24}$ (1779.73): C, 71.48; H, 6.17. Found: C, 71.26; H, 6.40.

4.1.10. 2-(4-Methoxyphenoxy) ethyl (α-L-rhamnopyranosyl)-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-[β-D-glucopyranosyl)-(1→6)]-β-D-glucopyranoside 1

To a solution of compound **15** (1 g, 0.56 mmol) in C_2H_5OH (20 mL) was added $NH_2NH_2{\cdot}H_2O$ (150 μL, 3.1 mmol) and the reaction mixture was allowed to stir at 80 °C for 4 h. The solvents were removed under reduced pressure and a solution of the crude product in acetic anhydride–pyridine (5 mL, 1:1, v/v) was kept at room temperature for 2 h. The solvents were removed under reduced pressure and the crude product was passed through a short pad of SiO_2 using EtOAc as an eluant. To a solution of the crude product in CH_3OH (10 mL) was added 20% $Pd(OH)_2$–C (200 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. The crude product was purified by passing through a column of Sephadex LH-20 using CH_3OH as an eluant to give pure **1** (350 mg, 71%). White powder; $[\alpha]_D^{25} = -38$ (*c* 1.0, CH_3OH); IR

(KBr): 3407, 2926, 1736, 1649, 1554, 1510, 1459, 1377, 1236, 1057, 832, 609 cm^{-1}; ^1H NMR (500 MHz, CD_3OD): δ 6.92–6.83 (m, 4H, Ar–H), 4.92–4.87 (m, 1H, H-2_D), 4.86 (d, J = 8.0 Hz, 1H, H-1_C), 4.81 (br s, 1H, H-1_D), 4.51 (d, J = 7.43 Hz, 1H, H-1_A), 4.36 (d, J = 7.8 Hz, 1H, H-1_B), 4.17–4.11 (m, 4H, H-6_{abA}, H-6_{aC}, H-3_A), 4.05–3.92 (m, 2H, H-6_{bC}, H-5_D), 3.88–3.80 (m, 2H, H-4_B, H-6_{aB}), 3.78–3.73 (m, 2H, H-2_C, H-6_{bB}), 3.74 (s, 3H, OCH_3), 3.69–3.64 (m, 3H, H-3_C, H-3_D, H-4_A), 3.48–3.43 (m, 2H, H-3_A, H-4_C), 3.38–3.28 (m, 6H, H-2_A, H-3_B, H-4_D, H-5_A, H-5_B, H-5_C), 3.23–3.20 (m, 1H, H-2_B), 2.07, 2.03 (2s, 6H, 2COCH_3), 1.26 (d, J = 6.1 Hz, 3H, CCH_3); ^{13}C NMR (125 MHz, CD_3OD): δ 173.8 (NHCOCH_3), 171.1 (COCH_3) 154.6–114.8 (Ar–C), 103.9 (C-1_B), 102.4 (C-1_A), 101.1 (C-1_C), 99.4 (C-1_D), 81.1 (C-3_C), 77.0 (4C, C-3_A, C-3_B, C-5_B, C-5_C), 76.7 (C-2_A), 75.8 (C-2_B), 74.1 (2C, C-2_D, C-5_A), 73.5 (C-4_D), 73.1 (C-4_C), 70.6 (C-4_A), 70.3 (C-4_B), 69.5 (C-5_D), 69.2 (C-3_D), 68.9 (C-6_A), 68.7 (C-6_C), 68.5 (C-6_B), 61.8 (2C, OCH_2), 56.4 (C-2_C), 55.4 (OCH_3), 20.1 (NHCOCH_3), 19.9 (COCH_3), 16.8 (CCH_3); ESI-MS: 906.3 $[M+Na]^+$. Anal. Calcd for $C_{37}H_{57}NO_{23}$ (883.33): C, 50.28; H, 6.50. Found: C, 50.05; H, 6.76.

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