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Synthesis of O- and C-glycosides derived from β-(1,3)-D-glucans

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ABSTRACT

A series of β-(1,3)-D-glucans have been synthesized incorporating structural variations specifically on the reducing end of the oligomers. Both O- and C-glucosides derived from di- and trisaccharides have been obtained in good overall yields and with complete selectivity. Whereas the O-glycosides were obtained via a classical Koenigs–Knorr glycosylation, the corresponding C-glycosides were obtained through allylation of the anomeric carbon and further cross-metathesis reaction. Finally, the compounds were evaluated against two glycosidases and two *endo*-glucanases and no inhibitory activity was observed.

1. Introduction

Fungal cells possess a thick cell-wall mainly constituted by a linear chain of β-(1,3)-D-glucan linked to chitin via β-(1,4) linkage with ca. 3–4% of interchain β-(1,6) glucosidic bonds (Fig. 1).[1] Synthesis, degradation, and remodeling of polysaccharides forming the fungal cell wall are dynamic processes important for growth, budding, branching, or cell lysis.[2] The major component of the cell wall, β-(1,3)-D-glucan **1** units, are not present in human cells, and therefore the enzymes responsible for the synthesis and remodeling of fungal cell walls are suitable targets for the treatment of fungal infections. Among these enzymes β-(1,3)-D-glucan synthase (EC 2.4.1.34), that makes β-(1,3)-D-glucan from UDP-D-glucose, is one of the best drug targets.[3] Indeed, β-(1,3)-D-glucan synthase inhibitors have shown promising biological activities for the treatment of important fungal infections such as Candidiasis and Aspergillosis.[4]

In addition to β-(1,3)-D-glucan synthase, glucanases play an active role in the metabolism of β-(1,3)-D-glucans.[5] In this context, the activities of three endo-β-(1,3) glucanases that exclusively hydrolyze linear β-(1,3)-D-glucans have been recently studied.[6] Similarly, β-(1,3)-D-transglycosylases are also important enzymes in fungal cell wall assembly and rearrangement.[7] These enzymes are classified as GH72 family in the CAZy database and are named differently depending on the organism from which they come from.[8] These proteins have been also shown to be essential in organisms like *Aspergillus fumigatus* and *Schizosaccharomyces*

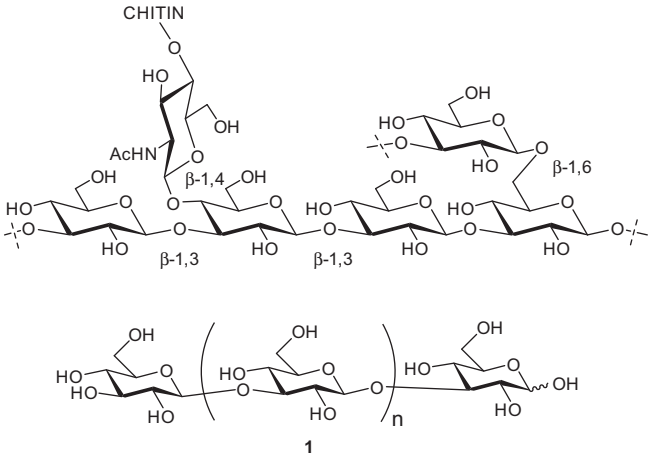

Figure 1. β-(1,3)-D-Glucans in the fungal cell wall.

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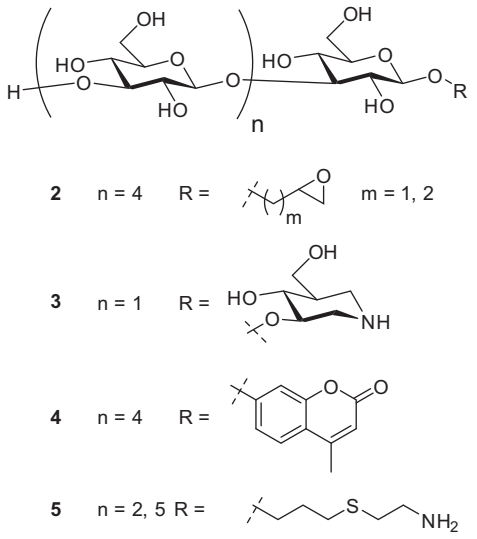


Figure 2. O-Glycoside analogues of β-(1,3)-D-glucans.

pombe suggesting that the development of inhibitors against them might be a new approach to tackle fungal diseases.[9]

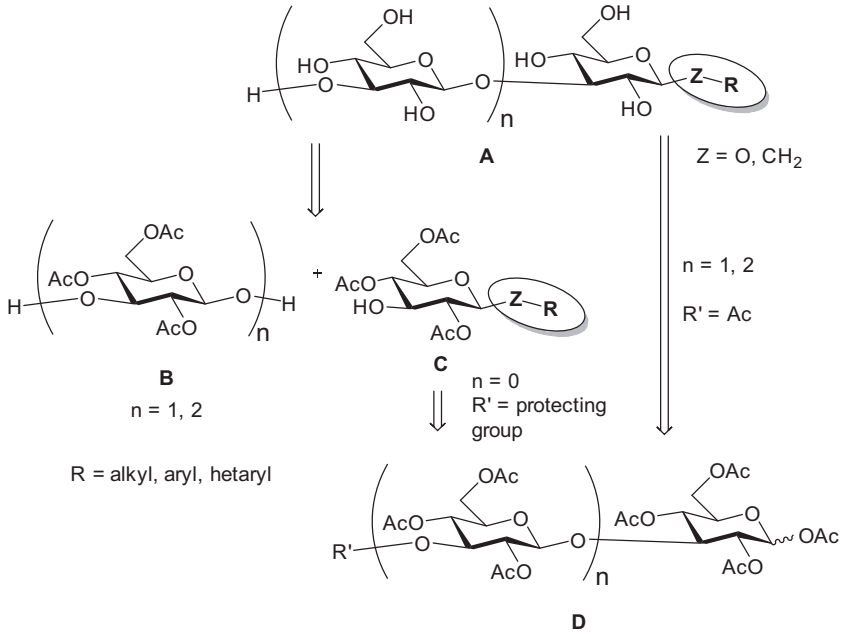
Other important aspects of β-(1,3)-D-glucans include the immunological and pharmacological effects of natural and synthetic analogues of this polysaccharide.[10] The synthesis of epoxyalkyl β-(1,3)-D-glucans **2** has attracted some attention owing to their implication in a variety of biological events including phagocytosis, hydrogen peroxide and citokine synthesis,[11] scavenging ability toward superoxide anion,[12] and as elicitors.[13] Stick and co-workers prepared β-(1,3)-di- and trisaccharides like **3** containing an isofagomine unit, which showed to be potent inhibitors of a β-(1,3)-glucan *endo*-hydrolase.[14] The 1-*O*-methylumbelliferyl β-(1,3)-D-pentaglucoside **4** has shown to be very stable toward fungal glucosidases with respect to the natural pentasaccharide (**1**, $n = 3$).[15] Very recently, Constantino and co-workers reported the synthesis of the β-(1,3)-glucan hexasaccharide **5** as a vaccine candidate against *Candida albicans* (see Fig. 2).[16]

In this paper we report an efficient synthesis of a variety of O- and C-glycosides related to laminaribiose and laminaritriose of general formula **A** (Scheme 1). The glycosides contain hydrophobic units at the reducing end of the oligosaccharides. The presence of a hydrophobic pocket in GH+1 subsite is well-known and it is admitted that additional mimicking of the transition state is required for inhibiting these enzymes.[17] However, in the case of compounds **A** the presence of additional carbohydrate units linked by 1,3-bonds can help to the recognition by the enzyme thus facilitating the interaction of the hydrophobic residue. Modified β-(1,3)-D-glucans **A** could also provide crucial information regarding the mechanism of action of the above mentioned enzymes, particularly transglycosylases which also have a hydrophobic pocket suitable of interacting with hydrophobic results.[8] Biological tests with a series of glycosidases and *endo*-glucanases are also reported.

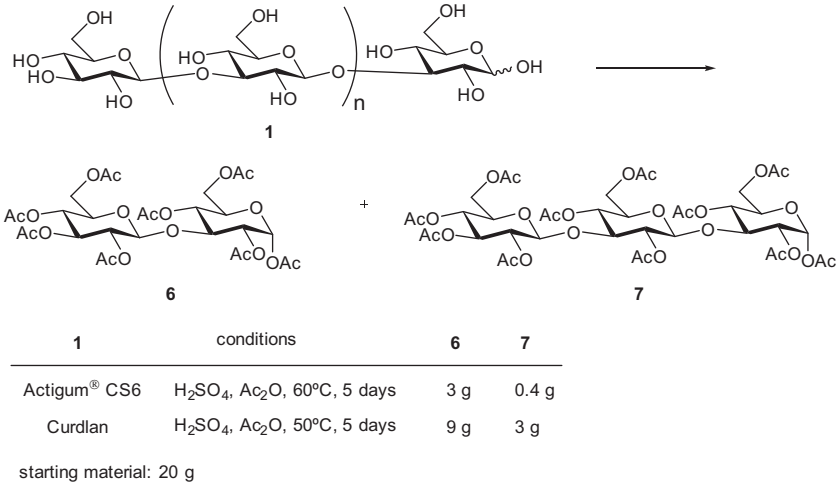
2. Results and discussion

In principle, two approaches are possible for the synthesis of 1-O- and 1-C-glycosides **A**. Glycosylation of **B** with a suitable derivative **C**, in which the desired unit has been incorporated into the anomeric center could be considered a convergent approach (Scheme 1). Compound **C** should be prepared by the corresponding O- and C-glycosylation procedures from a D-glucose derivative **D** ($n = 0$, R′ = protecting group). This route, however, involves the regioselective protection of the first glucose unit at position 3 and two glycosylation reactions. On the other hand, the direct incorporation, by means of convenient O- and C-glycosylation reactions, of the hydrophobic residues at the anomeric center could be made in a straightforward way from peracetylated laminaribiose **D** ($n = 1$, R′ = Ac) and laminaritriose **D** ($n = 2$, R′ = Ac).

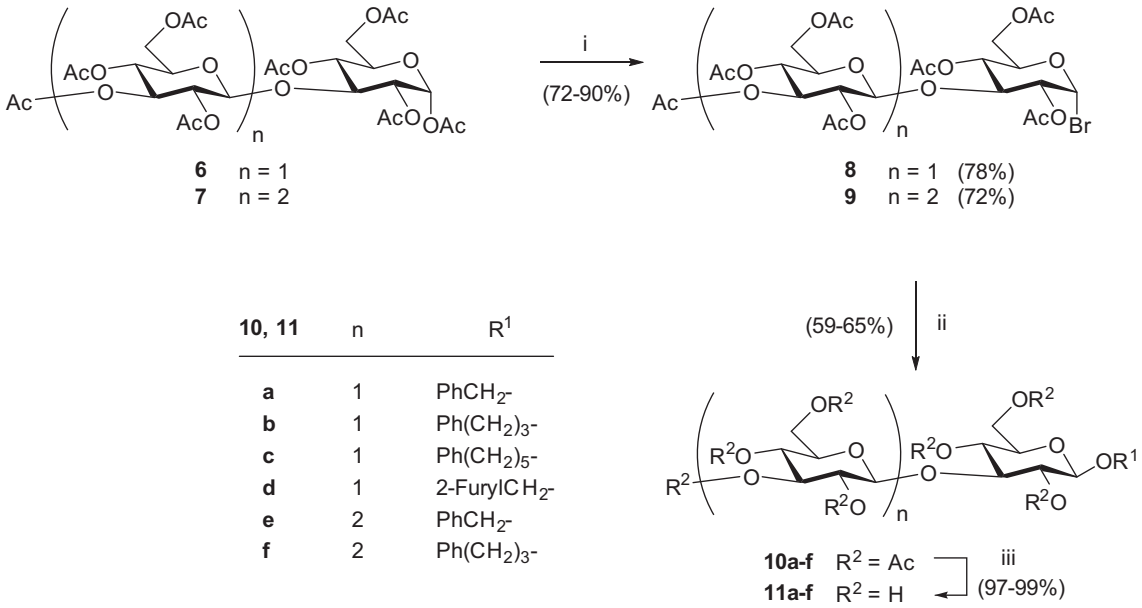
Even though both laminaribiose (**1**, $n = 0$) and laminaritriose (**1**, $n = 1$) are commercially available, the requirement of multigram quantities makes necessary to consider their preparation as peracetylated derivatives in multigram scale. The synthesis of laminaribiose and its peracetylated derivative has been reported through a typical Koenigs–Knorr condensation of two glucose units adequately functionalized.[18] Different protection with acetyl and benzyl groups in the two glucose moieties is also possible.[19] A large scale synthesis of laminaribiose has been optimized starting from



Scheme 1. Retrosynthetic analysis.



Scheme 2. Hydrolysis of scleroglucans.



Scheme 3. Synthesis of O-glycosides. Reagents and conditions: (i) 30% HBr, AcOH, rt, 15 min; (ii) R^1OH, $AgCO_3$, CH_2Cl_2, rt, 20 h; (iii) NaOMe, MeOH, rt, 4 h.

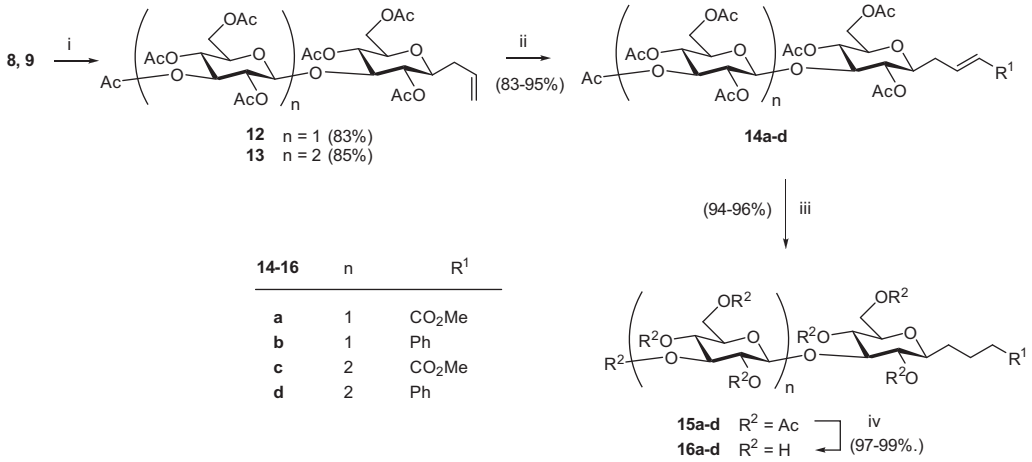
peracetylated donors and diacetone-D-glucose. The procedure allows the preparation of up to 300 g of compound **1**.[20] An alternative to the glycosylation methods is the controlled hydrolysis of scleroglucans, a method that has been widely used with other polysaccharides such as hemicelluloses.[21] The controlled hydrolysis of 20 g of Actigum CS6 following a slightly modified methodology described by Driguez and co-workers[22] afforded 3 g of laminaribiose octacetate **2** and, more interestingly, 0.4 g of laminaritriose undecacetate **3**. A more efficient hydrolysis was achieved by using the linear scleroglucan Curdlan.[23] Following the conditions reported by Kuzuhara and co-workers,[24] the hydrolysis of 20 g of crude material provided 9 g of compound **6** and 3 g of compound **7**, which were used for their further transformations into the targeted di- and trisaccharides (see Scheme 2).

2.1. Synthesis of O-glycosides

The laminarine analogues containing *O*-alkyl units were synthesized from the corresponding glycosyl bromides **8** and **9**, prepared from the *O*-acetyl precursors **6** and **7**, respectively (Scheme 3). Bromination of peracetylated derivatives was carried out with a 30% solution of hydrogen bromide in acetic acid, in a similar way to that reported for peracetyl glucose.[25] In the case of compounds **6** and **7**, however, the reaction time, not exceeding of 15 min, was crucial to obtain good chemical yields because of the partial hydrolysis of the glycosydic bond. The next glycosylation step was performed under typical Koenigs–Knorr conditions; preliminary chromatographic purification of the glycosyl bromides **8** and **9** was necessary to achieve good results. Treatment of **8** and **9** with the corresponding alcohol in the presence of silver carbonate furnished compound **10** in good yields. Complete O-deacetylation of **10** afforded a series of O-glycosides **11** in quantitative yields (Scheme 3).

2.2. Synthesis of C-glycosides

The synthesis of C-glycosides has received considerable attention during the last decade and several reviews cover a variety of



Scheme 4. Synthesis of C-glycosides. Reagents and conditions: (i) AllylMgBr, Et_2O, reflux, then Ac_2O, Py, DMAP, rt, 12 h; (ii) Methyl acrylate or styrene, 2nd gen. Grubbs catalyst, CH_2Cl_2, reflux, 3 h; (iii) H_2, MeOH, $Pd(OH)_2$-C, rt, 100 bar, 1.5 h. (iv) NaOMe, MeOH, rt, 4 h.

synthetic approaches[26] including the use of *exo*-glycals.[27] Most of these approaches are focused on the preparation of monosaccharides and with the exception of imino-*C*-disaccharides[28] are not very reliable for the preparation of oligosaccharide derivatives. One of the more attractive strategies for the obtention of C-glycosides derived from complex carbohydrates is the use of cross-coupling reactions.[29] Although these reactions are mostly dedicated to the preparation of aryl-C-glycosides,[30] Gagne and co-workers reported[31] the synthesis of alkyl-C-glycosides through a Negishi cross-coupling using the corresponding alkylzinc derivatives and glycosyl bromides. Unfortunately, even though we verified that the reaction could be used with monosaccharides, when compounds **8** and **9** were employed as substrates only decomposition products were obtained.

We then turned our attention to the addition of Grignard derivatives, which had also been successfully reported for the preparation of alkyl-C-glycosides.[32] Again, unsuccessful results were obtained with a series of phenyl alkylmagnesium halides and compounds **8** and **9**; only the addition of allylmagnesium bromide furnished C-glycosides **12** and **13** in good yields (Scheme 4). In both cases the β-anomers were obtained as the only product of the reaction as expected by the presence of an acetoxy group at position 2. Thus, we decided to elongate the anomeric chain by a metathesis reaction following a strategy that had been successfully applied to monosaccharides.[33]

Cross-metathesis of compounds **12** and **13** with methyl acrylate and styrene in the presence of 2nd generation Grubbs catalyst afforded compounds **14** in very good yields. Hydrogenation of **14** over Pearlman's catalyst in MeOH gave compounds **15**, which were then treated with sodium methoxide in methanol to provide C-glycosides **16** in excellent yields. For compounds **16b** and **16c** the process was carried out in a one-pot procedure from allylic derivatives **12** and **13**, respectively without isolating **14b,c** and **15b,c** thus demonstrating that no intermediate purification is necessary. Thus, the final C-glycosides can be obtained in two steps starting from the corresponding glycosyl bromides **8** and **9**.

3. Biological assays

Compounds **11a–f** and **16a,d** were tested on several glycoside hydrolases to assess the effect of introducing alkyl chains with a hydrophobic terminus at the anomeric position. Commercial α-glucosidase from *Saccharomyces cerevisae* and α-galactosidase from *green coffee bean* were used as enzymes and 2,4-dinitrophenyl glucose and galactose were used, respectively, as substrates. Unfortunately, all the compounds have negligible inhibitory activity toward the studied enzymes.

The oligosaccharides **11a–f** and **16a,d** have also been evaluated for their inhibitory activities toward endo-β-1,3-glucanase (*Barley*) and endo-β-1,3(4)-D-glucanase from *Clostridum thermocellum*. A commercial kit for evaluating glucanase activity containing AZCL-Pachyman (Glucazyme® from Megazyme) was used. Also in this case a complete absence of inhibitory activity was observed.

4. Conclusions

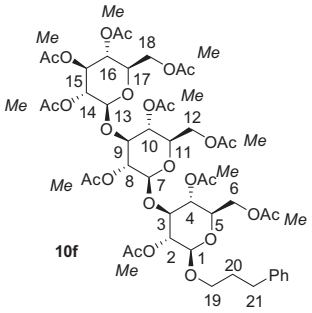
In conclusion, a series of novel *O*-alkyl and *C*-alkyl β-(1,3)-di- and triglucosides containing a hydrophobic moiety at the end of the allylic chain have systematically synthesized as potential glycoside hydrolases inhibitors. The approach described in this paper combines efficiency and flexibility since it allows the preparation of a variety of di- and trisaccharides. The glycosyl bromides **8** and **9** used as starting materials are prepared in good chemical yields from peracetylated laminaribiose and laminaritriose. The synthesis of C-glycosides can be carried out in two steps and excellent selectivity by grouping in a one-pot procedure the final metathesis, hydrogenation, and deacetylation reactions, which are made from common allyl derivatives **12** and **13**. The biological activity of the synthesized glycomimetics has been evaluated toward 4 commercially available glycosidases and *endo*-glucanases. The observed lack of activities can probably be related to the spatial disposition of the chains located at the anomeric position. Nevertheless, the synthetic strategy described here is facile and general, and could be extended to increase the diversity of the glycosidase and transglycosylase inhibitors obtained since this diversity is introduced very efficiently. Thus, the extension of this methodology for the preparation of other members of the same family to be used as glycomimetics is underway.

5. Experimental part

5.1. General methods

The reaction flasks and other glass equipment were heated in an oven at 130 °C overnight and assembled in a stream of Ar. All reactions were monitored by TLC on silica gel 60 F254; the position of the spots was detected with 254 nm UV light or by spraying with either 5% ethanolic phosphomolybdic acid or Mostain solution. Column chromatography was carried out in a Buchi 800 MPLC

system or a Combiflash apparatus, using silica gel 60 microns and with solvents distilled prior to use. Melting points were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 400 instrument in the stated solvent. Purification by semipreparative HPLC (column Atlantis® DC18 5 μm, 19 × 100 mm, flow: 12.5 mL/min) was carried out in a Waters 515 pump with PDA and ELSD detection. Chemical shifts are reported in ppm (δ) relative to $CHCl_3$ (δ = 7.26) in $CDCl_3$. Optical rotations were taken on a JASCO DIP-370 polarimeter. Elemental analyses were performed on a Perkin Elmer 240B microanalyzer or with a Perkin-Elmer 2400 instrument. Laminaribiose octaacetate **6** and laminaritriose undecaacetate **7** were prepared as described.[22] The numbering scheme in NMR assignments for the prepared compounds follows the following scheme illustrated for compound **10f**:



5.2. General procedure for the synthesis of glycosyl bromides

A solution of the corresponding peracetylated laminarin derivative (**6** or **7**, 1 mmol) in 30% hydrogen bromide in acetic acid (10 mL) was stirred at ambient temperature for 15 min at which time the reaction mixture was poured into 50 mL of ice-water. The resulting white solid was extracted with dichloromethane (3 × 30 mL). The combined organic extracts were dried over magnesium sulfate and the solvent was eliminated under reduced pressure to give the crude product which was purified by column chromatography.

5.2.1. 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-1-bromo-2,4,6-tri-*O*-acetyl-α-D-glucopyranose (8)

Following the general procedure, the reaction of **6** (0.679 g, 1 mmol) afforded **8** (0.562 g, 81%) as a sticky foam; R_f = 0.23 (hexane/EtOAc, 3:2); +39 (*c* 1.10, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.96 (s, 3H, *Me*), 1.98 (s, 3H, *Me*), 2.01 (s, 3H, *Me*), 2.05 (s, 3H, *Me*), 2.08 (s, 3H, *Me*), 2.09 (s, 3H, *Me*), 2.19 (s, 3H, *Me*), 3.74 (ddd, 1H, *J* = 2.3, 4.2, 9.8 Hz, H_{11}), 4.28-4.04 (m, 5H, H_3, H_5, H_6, H_{12a}), 4.38 (dd, 1H, *J* = 4.3, 12.5 Hz, H_{12b}), 4.68 (d, 1H, *J* = 8.1 Hz, H_7), 4.81 (dd, 1H, *J* = 4.0, 9.7 Hz, H_2), 4.90 (dd, 1H, *J* = 8.2, 9.4 Hz, H_8), 5.03–5.19 (m, 3H, H_4, H_9, H_{10}), 6.51 (d, 1H, *J* = 4.03 Hz, H_1); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.3 (Me), 20,4 (Me), 20.5 (2C, Me), 20.6 (Me), 20.7 (Me), 20.8 (Me), 61.1 (C_6), 61.6 (C_{12}), 66.5 (C_4), 67.9 (C_9), 71.4 (C_8), 71.7 (C_{11}), 72.3 (C_2), 72.24 (C_5), 72.9 (C_{10}), 76.4 (C_3), 87.3 (C_1), 100.7 (C_7), 169.0 (2C, C=O), 169.3 (C=O), 169.5 (C=O), 170.3 (C=O), 170.5 (C=O), 170.6 (C=O). Anal. Calcd for C_{26} $H_{35}BrO_{17}$: C, 44.65; H, 5.04; Br, 11.42. Found: C, 44.38; H, 5.11; Br, 11.56.

5.2.2. 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-1-bromo-2,4,6-tri-*O*-acetyl-β-D-glucopyranose (9)

Following the general procedure, the reaction of **7** (0.967 g, 1 mmol) afforded **9** (0.467 g, 76%) as a white solid. mp 116–118 °C; R_f = 0.56 (hexane/EtOAc, 7:3); $[\alpha]_D^{25}$ +33 (*c* 1.00, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.97 (s, 3H, *Me*), 1.99 (s, 3H, *Me*), 2.01 (s, 3H, *Me*), 2.01 (s, 3H, *Me*), 2.04 (s, 3H, *Me*), 2.04 (s, 3H, *Me*), 2.06 (s, 3H, *Me*), 2.07 (s, 3H, *Me*), 2.08 (s, 3H, *Me*), 2.21 (s, 3H, *Me*), 3.66–3.73 (m, 2H, H_{11}, H_{17}), 3.82 (t, 1H, *J* = 9.4 Hz, H_9), 4.00–4.32 (m, 6H, H_3, H_5, H_6, H_{12a}, H_{18a}), 4.32 (dd, 1H, *J* = 4.5, 12.5 Hz, H_{12b}), 4.37 (dd, 1H, *J* = 4.1, 12.4 Hz, H_{18b}), 4.53 (d, 1H, *J* = 8.06 Hz, H_{13}), 4.56 (d, 1H, *J* = 8.1 Hz, H_7), 4.77 (dd, 1H, *J* = 4.0, 9.7 Hz, H_2), 4.86–4.95 (m, 3H, H_8, H_{10}, H_{14}), 5.02–5.14 (m, 3H, H_4, H_{15}, H_{16}), 6.51 (d, 1H, *J* = 4.0 Hz, H_1); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.4 (2C, Me), 20.5 (Me), 20.6 (Me), 20.7 (Me), 20.7 (Me), 20.9 (Me), 61.1 (C_{18}), 61.7 (C_{12}), 61.8 (C_6), 66.5 (C_4), 68.0 (2C, C_{14}, C_{16}), 70.9 (C_8), 71.6 (C_{11}), 71.6 (C_{17}), 72.4 (C_5), 72.5 (C_2), 72.7 (C_{10}), 72.8 (C_{15}), 76.1 (C_3), 78.0 (C_9), 87.4 (C_1), 100.7 (C_7), 101.0 (C_{13}), 168.4 (C=O), 168.9 (C=O), 169.1 (C=O), 169.2 (C=O), 169.4 (C=O), 170.3 (C=O), 170.5 (C=O), 170.6 (C=O). Anal. Calcd for C_{38} $H_{51}BrO_{25}$: C, 46.21; H, 5.20; Br, 8.09. Found: C, 46.35; H, 5.05; Br, 8.14.

5.3. General procedure for the glycosylation of glycosyl bromides

A solution of the corresponding glycosyl bromide (1 mmol) and alcohol (1 mmol) in anhydrous dichloromethane (8 mL) was treated in the darkness and under an argon atmosphere with silver carbonate (1.18 mmol) and a catalytic amount (a small crystal) of iodine. The resulting solution was stirred at ambient temperature for 20 h and diluted with dichloromethane (10 mL). The reaction mixture was filtered through a pad of Celite® and the filtrate was evaporated under reduced pressure to give the crude product which was purified by column chromatography.

5.3.1. Benzyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranoside (10a)

Following the general procedure, the reaction of **8** (0.700 g, 1 mmol) and benzyl alcohol (0.108 g, 1 mmol) afforded **10a** (0.356 g, 62%) as a white solid. Mp 169–171 °C; R_f = 0.42 (hexane/EtOAc, 2:3); $[\alpha]_D^{25}$ −44 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.97 (s, 3H, *Me*), 2.00 (s, 3H, *Me*), 2.01 (s, 3H, *Me*), 2.01 (s, 3H, *Me*), 2.06 (s, 3H, *Me*), 2.08 (s, 3H, *Me*), 2.10 (s, 3H, *Me*), 3.61–3.66 (m, 2H, H_5, H_{11}), 3.84 (t, 1H, *J* = 9.5 Hz, H_3), 4.01 (dd, 1H, *J* = 2.3, 12.4 Hz, H_{12a}), 4.19–4.21 (m, 2H, H_6), 4.34 (dd, 1H, *J* = 4.3, 12.4 Hz, H_{12b}), 4.39 (d, 1H, *J* = 8.1 Hz, H_1), 4.55–4.60 (m, 2H, H_7, H_{13}), 4.86–4.91 (m, 2H, H_8, H_{13}), 4.97 (t, 1H, *J* = 9.7 Hz, H_4), 5.02–5.08 (m, 2H, H_2, H_{10}), 5.11 (t, 1H, *J* = 9.4 Hz, H_9), 7.24–7.29 (m, 2H, *ArH*), 7.29–7.37 (m, 3H, *ArH*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.3 (Me), 20.5 (2C, Me), 20.6 (Me), 20.8 (Me), 20.9 (Me), 61.7 (C_{12}), 62.1 (C_6), 68.0 (C_{10}), 68.2 (C_4), 70.2 (CH_2Ph), 71.0 (C_8), 71.6 (C_5), 71.8 (C_{11}), 72.7 (C_2), 72.9 (C_9), 78.9 (C_3), 99.0 (C_1), 100.9 (C_1), 127.7 (Ar), 127.9 (Ar), 128.4 (Ar), 136.8 (Ar), 168.8 (C=O), 169.1 (C=O), 169.2 (C=O), 169.4 (C=O), 170.3 (C=O), 170.5 (C=O), 170.7 (C=O). Anal. Calcd for $C_{33}H_{42}O_{18}$: C, 54.54; H, 5.83. Found: C, 54.65; H, 5.71.

5.3.2. 3-Phenylpropyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranoside (10b)

Following the general procedure, the reaction of **8** (0.700 g, 1 mmol) and 3-phenylpropan-1-ol (0.137 g, 1 mmol) afforded **10b** (0.456 g, 65%) as a yellow oil; R_f = 0.50 (hexane/EtOAc, 3:7); $[\alpha]_D^{25}$ −32 (*c* 1.11 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.80–1.95 (m, 2H, H_{14}), 1.98 (s, 3H, *Me*), 2.01 (s, 3H, *Me*), 2.02 (s, 3H, *Me*), 2.03 (s, 3H, *Me*), 2.04 (s, 6H, *Me*), 2.08 (s, 3H, *Me*), 2.14 (s, 3H, *Me*), 2.58–2.73 (m, 2H, H_{15}), 3.43 (ddd, 1H, *J* = 5.8, 7.4, 9.6 Hz, H_{13a}), 3.63–3.71 (m, 2H, H_5, H_{11}), 3.84–3.90 (m, 2H, H_3, H_{13b}), 4.05 (dd, 1H, *J* = 4.7, 12.4 Hz, H_{12a}), 4.13–4.18 (m, 1H, H_{6a}), 4.20 (dd, 1H, *J* = 4.7, 12.4 Hz, H_{6b}), 4.36–4.39 (m, 2H, H_1, H_{12b}), 4.61 (d, 1H, *J* = 8.1 Hz, H_7), 4.90 (dd, 1H, *J* = 8.2, 9.5 Hz, H_8), 4.96 (t, 1H,

J = 9.6 Hz, H_4), 5.03 (dd, 1H, J = 8.1, 9.7 Hz, H_2), 5.07 (t, 1H, J = 9.7 Hz, H_{10}), 5.14 (t, 1H, J = 9.5 Hz, H_9), 7.15–7.21 (m, 3H, *ArH*), 7.26–7.30 (m, 2H, *ArH*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.3 (Me), 20.4 (Me), 20.5 (Me), 20.6 (Me), 20.7 (Me), 20.8 (Me), 21.0 (Me), 31.1 (C_{14}), 31.8 (C_{15}), 61.6 (C_{12}), 62.2 (C_6), 68.0 (C_{10}), 68.4 (C_4), 68.7 (C_{13}), 71.1 (C_8), 71.6 (C_{11}), 71.8 (C_5)5, 72.8 (C_2), 79.0 (C_9), 100.8 (C_1), 101.1 (C_7), 125.8 (Ar), 128.3 (Ar), 128.4 (Ar), 142.0 (Ar), 168.7 (C=O), 169.1 (C=O), 169.2 (C=O), 169.2 (C=O), 169.2 (C=O), 169.2 (C=O), 169.4 (C=O), 170.3 (C=O), 170.5 (C=O), 170.6 (C=O), 170.8 (C=O). Anal. Calcd for $C_{35}H_{46}O_{18}$: C, 55.70; H, 6.14. Found: C, 55.59; H, 6.30.

5.3.3. 5-Phenylpentyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranoside (10c)

Following the general procedure, the reaction of **8** (0.700 g, 1 mmol) and 3-phenylpentan-1-ol (0.164 g, 1 mmol) afforded **10c** (0.209 g, 61%) as a yellow oil; R_f = 0.48 (hexane/EtOAc, 2:3); $[\alpha]_D^{25}$ −29 (*c* 1.00 CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.35–1.40 (m, 2H, H_{15}), 1.51–1.65 (m, 4H, H_{14}, H_{16}), 1.97 (s, 3H, *Me*), 2.00 (s, 3H, *Me*), 2.01 (s, 3H, *Me*), 2.02 (s, 3H, *Me*), 2.04 (s, 3H, *Me*), 2.06 (s, 3H, *Me*), 2.07 (s, 3H, *Me*), 2.08 (s, 3H, *Me*), 2.57–2.61 (m, 2H, H_{17}), 3.41 (td, 1H, J = 6.8,.5 Hz, H_{13a}), 3.62–3.69 (m, 2H, H_5, H_{11}), 3.81–3.88 (m, 2H, H_3, H_{13b}), 4.04 (dd, 1H, J = 2.3, 12.4 Hz, H_{12a}), 4.13–4.21 (m, 2H, H_6), 4.33 (d, 1H, J = 8.1 Hz, H_1), 4.36 (dd, 1H, J = 4.3, J = 12.4 Hz, H_{12b}), 4.58 (d, 1H, J = 8.1 Hz, H_7), 4.86–4.99 (m, 3H, H_2, H_4, H_8), 5.06 (t, 1H, J = 9.6 Hz, H_{10}), 5.13 (t, 1H, J = 9.4 Hz, H_9), 7.15–7.19 (m, 3H, *ArH*), 7.25–7.29 (m, 2H, *ArH*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.2 (Me), 20.3 (Me), 20.4 (Me), 20.4 (Me), 20.5 (Me), 20.6 (Me), 20.7 (Me), 25.3 (C_{15}), 29.1 (C_{14}), 30.9 (C_{16}), 35.7 (C_{17}), 61.5 (C_{12}), 62.0 (C_6), 67.9 (C_{10}), 68.1 (C_4), 69.5 (C_{13}), 70.9 (C_8), 71.5 (C_{11}), 71.6 (C_5), 72.5 (C_2), 72.8 (C_9), 78.8 (C_3), 100.6 (C_1), 100.7 (C_7), 125.5 (Ar), 128.1 (Ar), 128.2 (Ar), 142.3 (Ar), 168.6 (C=O), 169.1 (C=O), 169.1 (C=O), 169.2 (C=O), 170.2 (C=O), 170.3 (C=O), 170.6 (C=O). Anal. Calcd for $C_{37}H_{50}O_{18}$: C, 56.77; H, 6.44. Found: C, 56.64; H, 6.31.

5.3.4. Furylmethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranoside (10d)

Following the general procedure, the reaction of **8** (0.700 g, 1 mmol) and furfuryl alcohol (0.098 g, 1 mmol) afforded **10d** (0.332 g, 59%) as a white solid; mp 148–150 °C; R_f = 0.52 (hexane/EtOAc, 2:3); $[\alpha]_D^{25}$ −47 (*c* 1.02, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.97 (s, 3H, *Me*), 1.99 (s, 3H, *Me*), 2.00 (s, 3H, *Me*), 2.02 (s, 3H, *Me*), 2.04 (s, 3H, *Me*), 2.07 (s, 3H, *Me*), 2.09 (s, 3H, *Me*), 3.62–3.69 (m, 2H, H_5, H_{11}), 3.85 (t, 1H, J = 9.4 Hz, H_3), 4.02 (dd, 1H, J = 2.3, 12.4 Hz, H_{12a}), 4.15–4.22 (m, 2H, H_6), 4.35 (dd, 1H, J = 4.3, 12.4 Hz, H_{12b}), 4.42 (d, 1H, J = 8.1 Hz, H_1), 4.56 (d, 1H, J = 8.1 Hz, H_7), 4.59 (d, 1H, J = 13.3 Hz, H_{13a}), 4.72 (d, 1H, J = 13.3 Hz, H_{13b}), 4.87 (dd, 1H, J = 8.2, 9.3 Hz, H_8), 4.95 (t, 1H, J = 9.6 Hz, H_4), 4.99 (dd, 1H, J = 13.3 Hz, H_2), 5.04 (t, 1H, J = 9.6 Hz, H_{10}), 5.11 (t, 1H, J = 9.4 Hz, H_9), 6.32 (d, 1H, J = 3.1 Hz, H_{15}), 6.35 (d, 1H, J = 1.9, 3.2 Hz, H_{14}), 7.41 (dd, 1H, J = 0.8, 1.8 Hz, H_{16}); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.2 (Me), 20.3 (Me), 20.4 (Me), 20.5 (Me), 20.6 (Me), 61.5 (C_{12}), 62.0 (C_6), 62.1 (C_{13}), 67.9 (C_{10}), 68.1 (C_4), 70.9 (C_8), 71.5 (C_5 or C_{11}), 71.7 (C_5 or C_{11}), 72.4 (C_2), 72.8 (C_9), 78.8 (C_3), 98.6 (C_1), 100.7 (C_7), 110.1 (Ar), 110.3 (Ar), 143.0 (Ar), 150.3 (Ar), 168.8 (C=O), 169.1 (C=O), 169.2 (C=O), 169.3 (C=O), 170.2 (C=O), 170.3 (C=O), 170.6 (C=O). Anal. Calcd for $C_{31}H_{40}O_{19}$: C, 51.96; H, 5.63. Found: C, 52.11; H, 5.48.

5.3.5. Benzyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (10e)

Following the general procedure, the reaction of **9** (0.987 g, 1 mmol) and 3-phenylpropan-1-ol (0.137 g, 1 mmol) afforded **10e** (0.198 g, 65%) as a white solid. Mp 100–102 °C; R_f = 0.34 (hexane/EtOAc, 3:7); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.96 (s, 3H, *Me*), 1.99 (s, 3H, *Me*), 2.00 (s, 3H, *Me*), 2.01 (s, 3H, *Me*), 2.02(s, 3H, *Me*), 2.05(s, 3H, *Me*), 2.06(s, 3H, *Me*), 2.09 (s, 3H, *Me*), 2.10 (s, 3H, *Me*), 3.59–5.68 (m, 3H, H_5, H_{11}, H_{17}), 3.78 (t, 1H, J = 9.4 Hz, H_9), 3.83 (t, 1H, J = 9.3 Hz, H_3), 4.02 (d, 2H, J = 12.0 Hz, H_{12a}, H_{18a}), 4.18 (d, 2H, J = 3.6 Hz, H_6), 4.28 (dd, 1H, J = 4.5, 12.4 Hz, H_{12b}), 4.35–4.45 (m, 3H, H_1, H_7, H_{18b}), 4.49 (d, 1H, J = 8.1 Hz, H_{13}), 4.57 (d, 1H, J = 12.4 H, H_{19a}), 4.84–4.95 (m, 5H, H_4, H_8, H_{10}, H_{14}, H_{19b}), 5.00–5.13 (m, 3H, H_2, H_{15}, H_{16}), 7.25–7.37 (m, 5H, *ArH*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.3 (Me), 20.4 (Me), 20.5 (2C, Me), 20.6 (Me), 20.7 (2C, Me), 20.8 (Me), 21.0 (Me), 61.6 (C_{18}), 61.9 (C_{12}), 62.2 (C_6), 68.0 (C_{16}), 68.3 (C_8), 68.5 (C_4), 70.2 (C_{19}), 70.8 (C_{14}), 71.5 (C_{17}), 71.6 (C_5), 71.8 (C_{11}), 72.6 (C_{10}), 72.8 (C_{15}), 72.9 (C_2), 78.2 (C_3), 78.9 (C_9), 99.0 (C_1), 100.6 (C_7), 101.0 (C_{13}), 127.7 (Ar), 127.9 (Ar), 128.4 (Ar), 136.8 (Ar), 168.8 (C=O), 169.1 (2C, C=O), 169.2 (C=O), 169.4 (C=O), 170.3 (C=O), 170.5 (C=O), 170.6 (C=O), 170 (C=O). Anal. Calcd for $C_{45}H_{58}O_{26}$: C, 53.25; H, 5.76. Found: C, 53.07; H, 5.52.

5.3.6. 3-Phenylpropyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (10f)

Following the general procedure, the reaction of **9** (0.987 g, 1 mmol) and 3-phenylpropan-1-ol (0.137 g, 1 mmol) afforded **10f** (0.218 g, 63%); white solid. Mp 95–97 °C; R_f = 0.29 (hexane/EtOAc, 3:7); $[\alpha]_D^{25}$ −43 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.79–1.94 (m, 2H, H_{20}), 1.97 (s, 3H, *Me*), 1.99 (s, 3H, *Me*), 2.00 (s, 3H, *Me*), 2.01 (s, 3H, *Me*), 2.02 (s, 3H, *Me*), 2.04 (s, 3H, *Me*), 2.05 (s, 3H, *Me*), 2.06 (s, 3H, *Me*), 2.07 (s, 3H, *Me*), 2.10 (s, 3H, *Me*), 2.15 (s, 3H, *Me*), 2.57–2.70 (m, 2H, H_{21}), 3.39–3.44 (m, 1H, H_{19a}), 3.64–3.69 (m, 3H, H_5, H_{11}, H_{17}), 3.80 (t, 1H, J = 9.3 Hz, H_9), 3.83–3.89 (m, 2H, H_3, H_{19b}), 4.01–4.06 (m, 2H, H_{12a}, H_{18a}), 4.13–4.19 (m, 2H, H_6), 4.31 (dd, 1H, J = 4.4, 12.4 Hz, H_{12b}), 4.35 (d, 1H, J = 8.0 Hz, H_1), 4.38 (dd, 1H, J = 3.9, 12.5 Hz, H_{18b}), 4.46 (d, 1H, J = 8.1 Hz, H_7), 4.50 (d, 1H, J = 8.1 Hz, H_{13}), 4.85–4.93 (m, 4H, H_4, H_8, H_{10}, H_{14}), 4.99 (dd, 1H, J = 8.2, 9.3 Hz, H_2), 5.05 (t, 1H, J = 9.6 Hz, H_{16}), 5.11 (t, 1H, J = 9.4 Hz, H_{15}), 7.17–7.20 (m, 3H, *ArH*), 7.26–7.30 (m, 2H, *ArH*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.3 (Me), 20.4 (Me), 20.5 (2C, Me), 20.6 (Me), 20.7 (Me), 20.8 (Me), 21.0 (Me), 31.1 (C_{20}), 31.8 (C_{21}), 61.6 (C_{18}), 62.0 (C_{12}), 62.2 (C_6), 68.0 (C_{16}), 68.4 (C_4), 68.6 (C_{19}), 70.8 (C_{14}), 71.6 (2C, C_5 or C_{11} or C_{17}), 71.7 (C_5 or C_{11} or C_{17}), 72.6 (C_{10}), 72.8 (C_{15}), 73.1 (C_2), 78.2 (C_3), 78.9 (C_9), 100.7 (2C, C_1, C_7), 101.0 (C_{13}), 125.9 (Ar), 128.3 (Ar), 128.4 (Ar), 141.5 (Ar), 168.8 (2C, C=O), 169.1 (C=O), 169.2 (C=O), 169.3 (C=O), 169.5 (C=O), 170.3 (C=O), 170.5 (C=O), 170.6 (C=O), 170.8 (C=O). Anal. Calcd for $C_{47}H_{62}O_{26}$: C, 54.13; H, 5.99. Found: C, 54.34; H, 6.17.

5.4. General procedure for the allylation of glycosyl bromides

A solution of the glycosyl bromide (0.266 g, 0.38 mmol of **8** and 0.27 mmol of **9**) was treated dropwise with a solution of allylmagnesium bromide (6 mL of a 1 M solution in diethy ether, 6 mmol) under an argon atmosphere and the resulting solution was stirred at reflux for 5 h. The reaction mixture was then poured into ice-water (20 mL). The aqueous layer was separated, washed with ethyl acetate (2 × 10 mL), and lyophilized. The resulting solid was taken up in pyridine (25 mL) and treated with acetic anhydride (25 mL) and a catalytic amount of *N,N*-dimethylaminopyridine (DMAP). The reaction mixture was stirred for additional 12 h at which time was diluted with water (40 mL) and extracted with diethyl ether (3 × 40 mL). The combined organic extracts were washed sequentially with 1 N sodium hydroxide (1 × 25 mL), saturated aqueous sodium bicarbonate (1 × 25 mL), saturated aqueous copper sulfate (2 × 25 mL), and brine (1 × 25 mL). The organic layer was separated, dried over magnesium sulfate, filtered, and evaporated under reduced pres-

sure to give the crude product which was purified by column chromatography.

5.4.1. 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-1-allyl-1-deoxy-2,4,6-tri-*O*-acetyl-β-D-glucopyranose (12)

Following the general procedure, the reaction of **8** (0.266 g, 0.38 mmol) with allylmagnesium bromide (6 mL of a 1 M solution in diethy ether, 6 mmol) afforded **12** (0.398 g, 83%) as a white solid. Mp 148–150 °C; R_f = 0.19 (hexane/EtOAc, 7:3); $[\alpha]_D^{25}$ −22 (*c* 1.03, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.97 (s, 3H, *Me*), 2.00 (s, 3H, *Me*), 2.02 (s, 3H, *Me*), 2.02 (s, 3H, *Me*), 2.06 (s, 3H, *Me*), 2.07 (s, 3H, *Me*), 2.12 (s, 3H, *Me*), 2.21–2.25 (m, 2H, H_{13}), 3.34 (ddd, 1H, *J* = 5.1, 6.7, 9.9 Hz, H_1), 3.58 (ddd, 1H, *J* = 2.3, 4.9, 10.0 Hz, H_5), 3.67 (ddd, 1H, *J* = 2.4, 4.2, 9.7 Hz, H_{11}), 3.82 (t, 1H, *J* = 9.4 Hz, H_3), 4.04 (dd, 1H, *J* = 2.3, 12.4 Hz, H_{12a}), 4.09–4.14 (m, 1H, H_{6a}), 4.16 (dd, 1H, *J* = 5.0, 12.2 Hz, H_{6b}), 4.38 (dd, 1H, *J* = 4.3, 12.4 Hz, H_{12b}), 4.57 (d, 1H, *J* = 7.0 Hz, H_7), 4.88–4.94 (m, 3H, H_2, H_4, H_8), 5.03–5.13 (m, 4H, H_9, H_{10}, H_{15}, H_{15}), 5.74–5.84 (m, 1H, H_{14}); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.3 (Me), 20.5 (Me), 20.5 (Me), 20.5 (Me), 20.6 (Me), 20.8 (Me), 21.1 (Me), 35.7 (C_{13}), 61.7 (C_{12}), 62.5 (C_6), 68.0 (C_{10}), 68.4 (C_4), 71.0 (C_8), 71.7 (C_{11}), 73.0 (C_9), 73.6 (C_2), 75.7 (C_5), 77.4 (C_1), 80.4 (C_3), 101.0 (C_7), 117.3 (C_{14}), 133.2 (C_{15}), 169.3 (C═O), 169.3 (C═O), 169.3 (C═O), 170.4 (C═O), 170.5 (C═O), 170.8 (C═O). Anal. Calcd for $C_{29}H_{40}O_{17}$: C, 52.73; H, 6.10. Found: C, 52.873; H, 6.01.

5.4.2. 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-1-allyl-1-deoxy-2,4,6-tri-*O*-acetyl-β-D-glucopyranose (13)

Following the general procedure, the reaction of **9** (0.266 g, 0.27 mmol) with allylmagnesium bromide (6 mL of a 1 M solution in diethy ether, 6 mmol) afforded **13** (0.489 g, 83%) as a white solid. Mp 88–90 °C; R_f = 0.45 (hexane/EtOAc, 3:7); $[\alpha]_D^{25}$ −38 (*c* 1.01, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.97 (s, 3H, *Me*), 1.99 (s, 3H, *Me*), 2.00 (s, 3H, *Me*), 2.01 (s, 3H, *Me*), 2.02 (s, 3H, *Me*), 2.04 (s, 3H, *Me*), 2.06 (s, 3H, *Me*), 2.10 (s, 3H, *Me*), 2.13 (s, 3H, *Me*), 2.19–2.24 (m, 2H, H_{19}), 3.33 (td, 1H, *J* = 5.8, 9.9 Hz, H_1), 3.58 (ddd, 1H, *J* = 2.6, 4.7, 9.9 Hz, H_5), 3.63–3.69 (m, 2H, H_{11}, H_{17}), 3.75–3.83 (m, 2H, H_3, H_9), 4.00–4.06 (m, 2H, H_{12a}, H_{18a}), 4.08–4.16 (m, 2H, H_6), 4.32 (dd, 1H, *J* = 4.5, 12.4 Hz, H_{12b}), 4.39 (dd, 1H, *J* = 3.9, 12.4 Hz, H_{18b}), 4.42 (d, 1H, *J* = 8.1 Hz, H_7), 4.49 (d, 1H, *J* = 8.1 Hz, H_{13}), 4.86–4.93 (m, 5H, H_2, H_4, H_8, H_{10}, H_{14}), 5.03–5.13(m, 4H, H_{15}, H_{16}, H_{21}), 5.78 (tdd, 1H, *J* = 6.7, 9.7, 16.3 Hz, H_{20}); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.3 (Me), 20.4 (Me), 20.5 (Me), 20.6 (Me), 20.7 (Me), 20.7 (Me), 20.8 (Me), 21.2 (Me), 35.8 (C_{19}), 61.6 (C_{18}), 61.9 (C_{12}), 62.5 (C_6), 68.0 (C_{16}), 68.2 (C_{10}), 68.5 (C_4), 70.8 (C_2), 71.6 (2C, C_{11}, C_{17}), 72.6 (C_8), 72.8 (C_{15}), 73.7 (C_{14}), 75.7 (C_5), 77.3 (C_1), 79.1 (C_9), 79.8 (C_3), 100.8 (C_7), 101.1 (C_{13}), 117.3 (C_{20}), 133.2 (C_{21}), 168.7 (C═O), 169.1 (C═O), 169.2 (C═O), 169.2 (C═O), 169.4 (C═O), 170.3 (C═O), 170.5 (C═O), 170.6 (C═O), 170.8 (C═O). Anal. Calcd for $C_{41}H_{56}O_{25}$: C, 51.90; H, 5.95. Found: C, 51.72; H, 6.17.

5.5. General procedure for the metathesis reaction

A solution of the corresponding allyl derivative (1 mmol) and styrene (or methyl acrylate) (14 mmol) was treated with 2nd generation Grubbs catalyst (12.5 mol %) and the resulting mixture was stirred at reflux for 116 h. The reaction mixture was filtered and the filtrate evaporated under reduced pressure to give a residue that was purified by column chromatography to furnish the pure product.

5.5.1. 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-1-deoxy-1-((*E*)-4-methoxy-4-oxobut-2-en-1-yl)-2,4,6-tri-*O*-acetyl-β-D-glucopyranose (14a)

Following the general procedure, the reaction of **12** (0.661 g, 1 mmol) with methyl acrylate (1.21 g, 14 mmol) afforded **14a** (0.195 g, 90%) as a white soild; mp 84–86 °C; R_f = 0.46 (hexane/EtOAc, 7:3); $[\alpha]_D^{25}$ −13 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.97 (s, 3H, *Me*), 2.00 (s, 3H, *Me*), 2.01 (s, 3H, *Me*), 2.03 (s, 3H, *Me*), 2.04 (s, 3H, *Me*) 2.07 (s, 3H, *Me*), 2.07 (s, 3H, *Me*), 2.32–2.43 (m, 2H, H_{13}), 3.38–3.43 (m, 1H, H_1), 3.60 (ddd, 1H, *J* = 2.3, 5.2, 10.1 Hz, H_5), 3.68 (ddd, 1H, *J* = 2.4, 4.1, 9.7 Hz, H_{11}), 3.72 (s, 3H, *OMe*), 3.84 (t, 1H, *J* = 9.3 Hz, H_3), 4.04 (dd, 1H, *J* = 2.3, 12.4 Hz, H_{12a}), 4.08–4.13 (m, 1H, H_{6a}), 4.16 (dd, 1H, *J* = 5.3, 12.3 Hz, H_{6b}), 4.38 (dd, 1H, *J* = 4.3, 12.4 Hz, H_{12b}), 4.57 (d, 1H, *J* = 8.1 Hz, H_7), 4.88–4.95 (m, 3H, H_2, H_4, H_8), 5.06 (t, 1H, *J* = 9.6 Hz, H_{10}), 5.11 (t, 1H, *J* = 9.4 Hz, H_9), 5.87 (td, 1H, *J* = 1.3, 15.7 Hz, H_{15}), 6.90 (td, 1H, *J* = 6.9, 15.7 Hz, H_{14}); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.3 (Me), 20.4 (Me), 20.5 (Me), 20.6 (Me), 20.7 (Me), 21.0 (Me), 34.1 (C_{13}), 51.5 (OMe), 61.6 (C_{12}), 62.4 (C_6), 67.9 (C_{10}), 68.2 (C_4), 71.0 (C_8), 71.7 (C_{11}), 73.0 (C_9), 73.6 (C_2), 75.8 (C_5), 76.4 (C_1), 80.2 (C_3), 101.0 (C_7), 123.4 (C_{15}), 143.4 (C_{14}), 166.6 (C═O), 169.2 (C═O), 169.4 (C═O), 170.4 (C═O), 170.5 (C═O), 170.7 (C═O). Anal. Calcd for $C_{31}H_{42}O_{19}$: C, 51.81; H, 5.89. Found: C, 51.75; H, 5.97.

5.5.2. 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-1-((*E*)-3-phenylprop-2-en-1-yl)-1-deoxy-2,4,6-tri-*O*-acetyl-β-D-glucopyranose (14d)

Following the general procedure, the reaction of **13** (0.949 g, 1 mmol) with styrene (1.46 g, 14 mmol) afforded **14d** (0.221 g, 92%) as an oil; R_f = 0.26 (hexane/EtOAc, 2:3); $[\alpha]_D^{25}$ −34 (*c* 0.5, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.97 (s, 3H, *Me*), 1.99 (s, 3H, *Me*), 2.01 (s, 3H, *Me*), 2.02 (s, 3H, *Me*), 2.02 (s, 3H, *Me*),2.03 (s, 3H, *Me*), 2.06 (s, 3H, *Me*), 2.07 (s, 3H, *Me*), 2.10 (s, 3H, *Me*), 2.11 (s, 3H, *Me*), 2.33–2.45 (m, 2H, H_{19}), 3.40 (ddd, 1H, *J* = 4.8, 7.0, 9.8 Hz, H_1), 3.61 (ddd, 1H, *J* = 2.3, 4.9, 10.0 Hz, H_5), 3.65–3.69 (m, 2H, H_{11}, H_{17}), 3.78 (t, 1H, *J* = 9.3 Hz, H_9), 3.83 (t, 1H, *J* = 9.3 Hz, H_3), 4.01–4.08 (m, 2H, H_{12a}, H_{18a}), 4.08–4.13 (m, 1H, H_{6a}), 4.16 (dd, 1H, *J* = 5.1, 12.3 Hz, H_{6b}), 4.33 (dd, 1H, *J* = 4.4, 12.4 Hz, H_{12b}), 4.40 (dd, 1H, *J* = 3.8, 12.4 Hz, H_{18b}), 4.44 (d, 1H, *J* = 8.1 Hz, H_7), 4.50 (d, 1H, *J* = 8.1 Hz, H_{13}), 4.86–4.96 (m, 5H, H_2, H_4, H_8, H_{10}, H_{14}), 5.06 (t, 1H, *J* = 9.6 Hz, H_{16}), 5.11 (t, 1H, *J* = 9.4 Hz, H_{15}), 6.19 (ddd, 1H, *J* = 6.2, 7.8, 15.8 Hz, H_{20}), 6.39 (d, 1H, *J* = 15.9 Hz, H_{21}), 7.18–7.24 (m, 1H, *ArH*), 7.28–7.32 (m, 2H, *ArH*), 7.31–7.34 (m, 2H, *ArH*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.2 (Me), 20.3 (Me), 20.4 (Me), 20.5 (Me), 20.6 (Me), 20.6 (Me), 20.7 (Me), 21.0 (Me), 35.2 (C_{19}), 61.5 (C_{18}), 61.9 (C_{12}), 62.4 (C_6), 67.9 (C_{16}), 68.1 (C_{10}), 68.4 (C_4), 70.7 (C_{14}), 71.5 (C_{11} or C_{17}), 71.5 (C_{11} or C_{17}), 72.5 (C_8), 72.7 (C_{15}), 73.8 (C_2), 75.6 (C_5), 77.4 (C_1), 79.0 (C_3), 79.7 (C_9), 100.7 (C_7), 100.9 (C_{13}), 124.8 (C_{20}), 125.9 (Ar), 127.2 (Ar), 128.4 (Ar), 132.3 (C_{21}), 137.1 (Ar), 168.6 (C═O), 169.0 (C═O), 169.1 (C═O), 169.2 (C═O), 169.3 (C═O), 170.2 (C═O), 170.4 (C═O), 170.4 (C═O), 170.7 (C═O). Anal. Calcd for $C_{47}H_{60}O_{25}$: C, 55.08; H, 5.90. Found: C, 54.93; H, 6.16.

5.6. General procedure for the hydrogenation

A solution of alkene (1 mmol) in methanol (6 mL) was treated with Pearlman's catalyst (15 mol %) and the resulting mixture was stirred under hydrogen (100 bar) at ambient temperature for 2 h. The reaction mixture was filtered through a pad of Celite and the filtrate evaporated under reduced pressure. The resulting crude product was purified by column chromatography.

5.6.1. 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-1-deoxy-1-(4-methoxy-4-oxobutyl)-2,4,6-tri-*O*-acetyl-β-D-glucopyranose (15a)

Following the general procedure, the hydrogenation of **14a** (0.719 g, 1 mmol) afforded **15a** (0.186 g, 94%) as a white solid; mp 71–73 °C; R_f = 0.42 (hexane/EtOAc, 7:3); $[\alpha]_D^{25}$ −15 (*c* 1.00, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 1.38–1.53 (m, 2H, H_{13}, H_{13}), 1.57–1.72 (m, 1H, H_{14a}), 1.76–1.89 (m, 1H, H_{14b}), 1.97 (s, 3H, *Me*), 2.00 (s, 3H, *Me*), 2.01 (s, 3H, *Me*), 2.02 (s, 3H, *Me*), 2.07 (s, 6H, *Me*), 2.13 (s, 3H, *Me*), 2.23–2.38 (m, 2H, H_{15}), 3.23–3.29 (m, 1H, H_1), 3.56 (ddd, 1H, *J* = 2.3, 5.0, 10.0 Hz, H_5), 3.65 (s, 3H, *OMe*), 3.66–3.69 (m, 1H, H_{11}), 3.82 (t, 1H, *J* = 9.4 Hz, H_3), 4.01–4.13 (m, 2H, H_{6a}, H_{12a}), 4.16 (dd, 1H, *J* = 5.1, 12.2 Hz, H_{6b}), 4.38 (dd, 1H, *J* = 4.3, 12.4 Hz, H_{12b}), 4.57 (d, 1H, *J* = 8.1 Hz, H_7), 4.83–4.93 (m, 3H H_2, H_4, H_8), 5.06 (t, 1H, *J* = 9.3 Hz, H_{10}), 5.11 (t, 1H, *J* = 9.4 Hz, H_9); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.3 (Me), 20.5 (Me), 20.5 (Me), 20.6 (C_{14}), 20.8 (Me), 21.0 (Me), 30.3 (C_{13}), 33.5 (C_{15}), 51.5 (OMe), 61.7 (C_{12}), 62.5 (C_6), 68.0 (C_{10}), 71.0 (C_8), 71.7 (C_{11}), 73.0 (C_9), 73.6 (C_2), 75.7 (C_5), 77.7 (C_1), 80.4 (C_3), 101.0 (C_7), 169.3 (C═O), 169.3 (C═O), 169.4 (C═O), 170.4 (C═O), 170.5 (C═O), 170.8 (C═O), 173.8 (C═O). Anal. Calcd for $C_{31}H_{44}O_{19}$: C, 51.67; H, 6.15. Found: C, 51.78; H, 5.97.

5.6.2. 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-1-(3-phenylpropyl)-1-deoxy-2,4,6-tri-*O*-acetyl-β-D-glucopyranose (15d)

Following the general procedure, the hydrogenation of **14d** (1.03 g, 1 mmol) afforded **15d** (0.198 g, 96%) as a white solid; mp 90–92 °C; R_f = 0.27 (hexane/EtOAc, 2:3); $[\alpha]_D^{25}$ −39 (*c* 0.51 $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 1.39–1.49 (m, 2H, H_{19}), 1.53–1.67 (m, 1H, H_{20a}), 1.85–1.90 (m, 1H, H_{20b}), 1.97 (s, 3H, *Me*), 1.99 (s, 3H, *Me*), 2.01 (s, 3H, *Me*), 2.01 (s, 3H, *Me*), 2.03 (s, 3H, *Me*), 2.05 (s, 3H, *Me*), 2.07 (s, 3H, *Me*), 2.09 (s, 3H, *Me*), 2.10 (s, 3H, *Me*), 2.53–2.63 (m, 2H, H_{21}), 3.21–3.28 (m, 1H, H_1), 3.55 (ddd, 1H, *J* = 2.2, 4.8, 10.0 Hz, H_5), 3.62–3.69 (m, 2H, H_{11}, H_{17}), 3.74–3.84 (m, 2H, H_3, H_9), 4.00–4.12 (m, 3H, H_{6a}, H_{12a}, H_{1a8}), 4.15 (dd, 1H, *J* = 5.1, 12.3 Hz, H_{6b}), 4.32 (dd, 1H, *J* = 4.5, 12.4 Hz, H_{12b}),4.39 (dd, 1H, *J* = 3.9, 12.4 Hz, H_{18b}), 4.42 (d, 1H, *J* = 8.1 Hz, H_7), 4.49 (d, 1H, *J* = 8.1 Hz, H_{13}), 4.82–4.94 (m, 5H, H_2, H_4, H_8, H_{10}, H_{14}), 5.06 (t, 1H, *J* = 9.6 Hz, H_{16}), 5.11 (t, 1H, *J* = 9.4 Hz, H_{15}), 7.12–7.20 (m, 3H, *ArH*), 7.24–7.30 (m, 2H, *ArH*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.3 (Me), 20.4 (Me), 20.5 (Me), 20.6 (Me), 20.7 (Me), 20.7 (Me), 20.8 (Me), 21.0 (Me), 26.7 (C_{20}), 30.4 (C_{19}), 35.4 (C_{21}), 61.6 (C_{18}), 62.0 (C_{12}), 62.6 (C_6), 68.0 (C_{16}), 68.2 (C_{10} or C_{14}), 68.6 (C_{10} or C_{14}), 70.8 (C_4), 71.6 (2C, C_{11},C_{17}), 72.8 (C_8), 73.8 (C_2), 75.7 (C_5), 77.1 (C_1), 79.1 (C_9), 79.9 (C_3), 100.7 (C_7), 101.1 (C_{13}), 125.8 (Ar), 128.3 (Ar), 128.4 (Ar), 142.0 (Ar), 168.7 (C═O), 169.1 (C═O), 169.2 (C═O), 169.2 (C═O), 169.2 (C═O), 169.4 (C═O), 170.3 (C═O), 170.5 (C═O), 170.6 (C═O), 170.8 (C═O). Anal. Calcd for $C_{47}H_{62}O_{25}$: C, 54.97; H, 6.09. Found: C, 55.13; H, 6.21.

5.7. General procedure for deacetylation

A solution of the peracetylated derivative (0.14 mmol) in methanol (10 mL) was treated with sodium methoxyde (10 mg, 0.19 mmol) and stirred at ambient temperature for 1.5 h. The reaction mixture is then treated with dry Amberlyst 15 and the resulting suspension is stirred for additional 25 min. The reaction mixture is filtered through a pad of Celite® and the filtrate was evaporated under reduced pressure to give the crude product which was purified by semipreparative HPLC (eluent: water–methanol) using a column Atlantis® DC18 5 μm, 19 × 100 mm, flow: 12.5 mL/min. Detection: ELSD.

5.7.1. Benzyl β-D-Glucopyranosyl-(1→3)-β-D-glucopyranoside (11a)

Following the general procedure, the deacetylation of **10a** (0.102 g, 0.14 mmol) afforded **11a** (71 mg, 98%) as an oil; HPLC: *t* = 2.5 min (water/MeOH, 1:1); $[\alpha]_D^{25}$ −46 (*c* 0.53, H_2O); ^1H NMR (D_2O, 400 MHz): δ 3.21–3.42 (m, 7H, H_2, H_4, H_5, H_8, H_9, H_{10}, H_{11}), 3.57–3.66 (m, 3H, H_3, H_{6a}, H_{12a}), 3.81 (ddd, 2H, *J* = 2.2, 10.6, 12.7 Hz, H_{6b}, H_{12b}), 4.45 (d, 1H, *J* = 8.2 Hz, H_1), 4.60 (d, 1H, *J* = 7.9 Hz, H_7), 4.66 (d, 1H, *J* = 11.8 Hz, H_{13}), 4.84 (d, 1H, *J* = 11.7 Hz, H_{13}), 7.28–7.38 (m, 5H); ^{13}C NMR (D_2O, 100 MHz): δ 60.6, 60.7, 68.2 (C_4), 69.5 (C_{10}), 71.5 (C_{13}), 72.8 (C_9), 73.4 (C_8), 75.5 (C_5), 75.5 (C_2), 75.9 (C_{11}), 84.5 (C_3), 100.9 (C_1), 102.8 (C_7), 128.5 (Ar), 128.7 (Ar), 128.7 (Ar), 136.5 (Ar). Anal. Calcd for $C_{23}H_{32}O_{13}$: C, 53.49; H, 6.25. Found: C, 53.62; H, 6.08.

5.7.2. 3-Phenylpropyl β-D-glucopyranosyl-(1→3)-β-D-glucopyranoside (11b)

Following the general procedure, the deacetylation of **10b** (0.106 g, 0.14 mmol) afforded **11b** (64 mg, 99%) as an oil; HPLC: *t* = 4.3 min (water/MeOH, 1:1); $[\alpha]_D^{25}$ −31 (*c* 1, H_2O); ^1H NMR (D_2O, 400 MHz): δ 1.80–1.89 (m, 2H, H_{14}), 2.60–2.66 (m, 2H, H_{15}), 3.23–3.43 (m, 8H, H_2, H_4, H_5, H_8, H_9, H_{10}, H_{11}, H_{13a}), 3.49–3.66 (m, 4H, H_3, H_{6a}, H_{12a}, H_{13b}), 3.78–3.83 (m, 2H, H_{6b}, H_{12b}), 4.35 (d, 1H, *J* = 8.1 Hz, H_1), 4.63 (d, 1H, *J* = 7.9 Hz, H_7), 7.14–7.29 (m, 5H, ArH); ^{13}C NMR (D_2O, 100 MHz): δ 30.5 (C_{15}), 31.2 (C_{14}), 60.6 (2C, C_6, C_{12}), 68.1 (C_4), 69.5 (C_{10}), 69.6 (C_{13}), 72.8 (C_9), 73.4 ($C8_7$), 75.5 (C_5), 75.5 (C_2), 76.0 (C_{11}), 84.5 (C_3), 101.9 (C_1), 102.8 (C_7), 126.0 (Ar), 128.6 (Ar), 142.2 (Ar). Anal. Calcd for $C_{21}H_{32}O_{11}$: C, 54.78; H, 7.00. Found: C, 54.63; H, 6.87.

5.7.3. 5-Phenylpentyl β-D-glucopyranosyl-(1→3)-β-D-glucopyranoside (11c)

Following the general procedure, the deacetylation of **10c** (0.110 g, 0.14 mmol) afforded **11c** (67 mg, 98%) as an oil; HPLC: *t* = 5.1 min (water/MeOH, 2:3); $[\alpha]_D^{25}$ −24 (*c* 1.13, H_2O); ^1H NMR (D_2O, 400 MHz): δ 1.21–1.06 (m, 2H, H_{15a}, H_{15b}), 1.51–1.35 (m, 4H, H_{14a}, H_{14b}, H_{16a}, H_{16b}), 2.39 (t, *J* = 7.5 Hz, 2H, H_{17a}, H_{17b}), 3.50–3.20 (m, 7H, H_2, H_4, H_5, H_8, H_{10}, H_{11}, H_{13a}), 3.84–3.53 (m, 7H, H_3, H_{6a}, H_{6b}, H_9, H_{12a}, H_{12b}, H_{13b}), 4.23 (d, *J* = 8.0 Hz, 1H, H_1), 4.61 (d, *J* = 7.9 Hz, 1H, H_7), 7.04–6.93 (m, 3H, *ArH*), 7.11–7.04 (m, 2H, *ArH*); ^{13}C NMR (D_2O, 100 MHz): δ 24.9 (C_{15}), 28.9 (C_{14}), 30.7 (C_{16}), 35.3 (C_{17}), 60.7 (2C, C_6, C_{12}), 68.1 (C_4), 69.5 (C_{10}), 70.3 (C_{13}), 72.8 (C_2), 73.5 (C_8), 75.4 (C_9), 75.6 (C_5 or C_{11}), 76.0 (C_5 or C_{11}), 85.0 (C_3), 102.0 (C_1), 102.9 (C_7), 125.6 (Ar), 128.3 (Ar), 128.4 (Ar), 142.8 (Ar). Anal. Calcd for $C_{23}H_{36}O_{11}$: C, 56.55; H, 7.43. Found: C, 56.75; H, 7.24.

5.7.4. Furylmethyl β-D-glucopyranosyl-(1→3)-β-D-glucopyranoside (11d)

Following the general procedure, the deacetylation of **10d** (0.1 g, 0.14 mmol) afforded **11d** (58 mg, 98%) as an oil; HPLC: *t* = 2.6 min (water/MeOH, 7:3); $[\alpha]_D^{25}$ −41 (c 0.69, H_2O); ^1H NMR (D_2O, 400 MHz): δ 3.22–3.44 (m, 7H, H_2, H_4, H_5, H_8, H_9, H_{10}, H_{11}), 3.59–3.67 (m, 3H, H_3, H_6, H_{12}), 3.79–3.83 (m, 2H, H_6, H_{12}), 4.45 (d, 1H, *J* = 8.1 Hz, H_1), 4.61 (d, 1H, *J* = 7.9 Hz, H_7), 4.66 (d, 1H, *J* = 12.9 Hz, H_{13}), 4.73 (d, 1H, *J* = 12.9 Hz, *Ar*H), 6.37 (dd, 1H, *J* = 1.9, 3.2 Hz, *Ar*H), 6.44 (d, 1H, *J* = 3.2 Hz, *Ar*H), 7.46 (dd, 1H, *J* = 0.8, 1.9 Hz, H_{16}); ^{13}C NMR (D_2O, 100 MHz): δ 63.2 (2C, C_6, C_{12}), 65.5 (C_{13}), 70.7 (C_4), 72.1 (C_{10}), 75.2 (C_8), 75.9 (C_9), 78.0 (C_5 or C_{11}), 78.5 (C_5 or C_{11}), 87.1 (C_3), 103.0 (C_1), 105.3 (2C, C_6, C_{12}), 113.2 (Ar), 113.4 (Ar), 146.4 (Ar), 152.6 (Ar). Anal. Calcd for $C_{17}H_{26}O_{12}$: C, 48.34; H, 6.20. Found: C, 48.50; H, 6.36.

5.7.5. Benzyl β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranoside (11e)

Following the general procedure, the deacetylation of **10e** (0.142 g, 0.14 mmol) afforded **11e** (81 mg, 97%); oil; HPLC: t = 3.0 min (water/MeOH, 1:1); $[\alpha]_D^{25}$ −36 (c 0.51, H_2O); ^1H NMR (D_2O, 400 MHz): δ 3.20–3.40 (m, 10H, H_2, H_4, H_5, H_8, H_{10}, H_{11}, H_{14}, H_{15}, H_{16}, H_{17}), 3.51–3.64 (m, 5H, H_3, H_{6a}, H_9, H_{12a}, H_{18a}), 3.78–3.82 (m, 3H, H_{6b}, H_{12b}, H_{18b}), 4.43 (d, 1H, J = 8.1 Hz, H_1), 4.54 (d, 1H, J = 8.0 Hz, H_7), 4.57 (d, 1H, J = 7.8 Hz, H_{13}), 4.64 (d, 1H, J = 11.5 Hz, H_{19a}), 4.81 (d, 1H, J = 11.6 Hz, H_{19b}), 7.26–7.38 (m, 5H, *ArH*); ^{13}C NMR (D_2O, 100 MHz): δ 60.6 (C_6 or C_{12} or C_{18}), 60.6 (C_6 or C_{12} or C_{18}), 60.7 (C_6 or C_{12} or C_{18}), 68.1 (C_4 or C_{10}), 68.2 (C_4 or C_{10}), 69.5 (C_{16}), 71.5 (C_{13}), 72.9 (C_2), 73.2 (C_8), 73.4 (C_{14}), 75.5 (C_5 or C_{11} or C_{17}), 75.5 (C_5 or C_{11} or C_{17}), 75.6 (C_5 or C_{11} or C_{17}), 76.0 (C_{15}), 84.2 (C_9), 84.4 (C_3), 100.9 (C_1), 102.5 (C_7), 102.8 (C_{13}), 128.5 (Ar), 128.7 (Ar), 128.7 (Ar), 136.5 (Ar). Anal. Calcd for $C_{25}H_{38}O_{16}$: C, 50.50; H, 6.44. Found: C, 50.67; H, 6.29.

5.7.6. 3-Phenylpropyl β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranoside (11f)

Following the general procedure, the deacetylation of **10f** (0.146 g, 0.14 mmol) afforded **11f** (92 mg, 99%); oil; HPLC: t = 7.7 min (water/MeOH, 1:1); $[\alpha]_D^{25}$ −28 (c 0.56, H_2O); ^1H NMR (D_2O, 400 MHz): δ 1.80–1.86 (m, 2H, H_{20a}, H_{20b}), 2.62 (t, 2H, J = 7.6 Hz, H_{21}), 3.25 (dd, 1H, J = 8.0, 9.4 Hz, H_8), 3.22–3.5 (m, 9H, H_2, H_4, H_5, H_{10}, H_{11}, H_{14}, H_{15}, H_{16}, H_{17}), 3.55 (td, 1H, J = 6.6, 10.1 Hz, H_{19a}), 3.59–3.68 (m, 5H, H_3, H_{6a}, H_9, H_{12a}, H_{18a}), 3.78–3.84 (m, 4H, H_{6b}, H_{12b}, H_{18b}, H_{19b}), 4.34 (d, 1H, J = 8.1 Hz, H_1), 4.64 (d, 1H, J = 7.9 Hz, H_{13}), 4.67 (d, 1H, J = 8.1 Hz, H_7), 7.14–7.18 (m, 1H, *ArH*), 7.20–7.22 (m, 2H, *ArH*), 7.25–7.28 (m, 2H, *ArH*); ^{13}C NMR (D_2O, 100 MHz): δ 30.5 (C_{20}), 31.2 (C_{21}), 60.7 (3C, C_6, C_{12}, C_{18}), 68.1 (C_4 or C_{10}), 68.2 (C_4 or C_{10}), 69.5 (C_{16}), 69.6 (C_{19}), 72.9 (C_2), 73.5 (C_8), 73.7 (C_{14}), 75.5 (C_5 or C_{11} or C_{17}), 75.7 (C_5 or C_{11} or C_{17}), 75.7 (C_5 or C_{11} or C_{17}), 76.0 (C_{15}), 85.0 (C_9), 85.3 (C_3), 102.0 (C_1), 103.2 (C_7), 103.3 (C_{13}), 125.3 (Ar), 126.0 (Ar), 128.6 (Ar), 129.4 (Ar), 142.7 (Ar). Anal. Calcd for $C_{29}H_{44}O_{17}$: C, 52.41; H, 6.67. Found: C, 52.63; H, 6.78.

5.7.7. β-D-Glucopyranosyl-(1→3)-1-deoxy-1-(4-methoxy-4-oxobutyl)-β-D-glucopyranoside (16a)

Following the general procedure, the deacetylation of **15a** (0.101 g, 0.14 mmol) afforded **16a** (58 mg, 97%); oil; HPLC: t = 5.0 min (water/MeOH, 4:1); $[\alpha]_D^{25}$ −20 (c 0.74, H_2O); ^1H NMR (D_2O, 400 MHz): δ 1.33–1.42 (m, 1H, H_{13a}), 1.57–1.68 (m, 1H, H_{14a}), 1.71–1.81 (m, 2H, H_{13b}, H_{14b}), 2.31–2.42 (m, 2H, H_{15}), 3.22–3.47 (m, 8H, H_1, H_2, H_4, H_5, H_8, H_9, H_{10}, H_{11}), 3.57–3.66 (m, 6H, H_3, H_{6a}, H_{12a}, *OMe*), 3.79–3.85 (m, 2H, H_{6b}, H_{12b}), 4.66 (d, 1H, J = 7.9 Hz, H_7); ^{13}C NMR (D_2O, 100 MHz): δ 20.2 (C_{14}), 30.0 (C_{13}), 33.3 (C_{15}), 52.1 (OMe), 60.7 (C_6 or C_{12}), 60.9 (C_6 or C_{12}), 68.5 (C_4), 69.5 (C_2), 72.9 (C_5), 73.4 (C_8), 75.5 (C_{10}), 75.9 (C_{11}), 78.7 (C_1), 79.3 (C_9), 86.2 (C_3), 102.8 (C_7), 177.2 (C=O). Anal. Calcd for $C_{17}H_{30}O_{12}$: C, 47.88; H, 7.09. Found: C, 47.73; H, 6.87.

5.7.8. β-D-Glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-1-deoxy-1-(3-phenylpropyl)-β-D-glucopyranose (16d)

Following the general procedure, the deacetylation of **15d** (0.144 g, 0.14 mmol) afforded **16d** (83 mg, 98%); oil; HPLC: t = 1.5 min (water/MeOH, 1:9); $[\alpha]_D^{25}$ −14 (c 1.35, H_2O); ^1H NMR (D_2O, 400 MHz): δ 1.10–1.24 (m, 2H, H_{19a}, H_{20a}), 1.26–1.38 (m, 1H, H_{20b}), 1.54–1.67 (m, 1H, H_{19b}), 1.73–1.78 (m, 1H, H_{21a}), 2.48–2.60 (m, 1H, H_{21b}), 3.22–3.35 (m, 11H, H_1, H_2, H_4, H_5, H_8, H_{10}, H_{11}, H_{14}, H_{15}, H_{16}, H_{17}), 3.49–3.60 (m, 5H, H_3, H_{6a}, H_9, H_{12a}, H_{18a}), 3.75–3.82 (m, 3H, H_{6b}, H_{12b}, H_{18b}), 4.51 (d, 1H, J = 7.7 Hz, H_7), 4.55 (d, 1H, J = 7.6 Hz, H_{13}), 7.10–7.34 (m, 5H, *ArH*); ^{13}C NMR (D_2O, 100 MHz): δ 26.5 (C_{20}), 30.6 (C_{19}), 34.9 (C_{21}), 61.0 (C_6 or C_{12} or C_{18}), 61.1 (C_6 or C_{12} or C_{18}), 61.2 (C_6 or C_{12} or C_{18}), 68.8 (C_4 or C_{10} or C_{16}), 68.9 (C_4 or C_{10} or C_{16}), 70.0 (C_4 or C_{10} or C_{16}), 73.2 (C_2 or C_8 or C_{14}), 74.2 (C_2 or C_8 or C_{14}), 74.3 (C_2 or C_8 or C_{14}), 76.2 (C_5 or C_{11} or C_{17}), 76.5 (C_5 or C_{11} or C_{17}), 76.7 (C_5 or C_{11} or C_{17}), 79.0 (C_1), 79.7 (C_{15}), 87.9 (C_3 or C_9), 88.5 (C_3 or C_9), 104.5 (C_7), 105.0 (C_{13}), 125.6 (Ar), 128.6 (2C, Ar), 143.1 (Ar). Anal. Calcd for $C_{27}H_{42}O_{15}$: C, 53.46; H, 6.98. Found: C, 53.65; H, 7.23.

5.8. General procedure for the one-pot preparation of free oligosaccharides from 1-deoxy-1-allylglucosides

A solution of the corresponding allyl derivative (0.25 mmol) and styrene (or methyl acrylate) (3.5 mmol) was treated with 2nd generation Grubbs catalyst (12.5 mol %) and the resulting mixture was stirred at reflux for 116 h. The reaction mixture was filtered and the filtrate evaporated under reduced pressure to give a residue that was taken up in methanol (2 mL) and treated with Pearlman's catalyst (15 mol %). The resulting mixture was stirred under hydrogen (100 bar) at ambient temperature for 2 h at which time the reaction mixture was filtered through a pad of Celite. The filtrate was treated with sodium methoxide (2.5 mg, 0.19 mmol) and stirred at ambient temperature for 1.5 h. The reaction mixture is then treated with dry Amberlyst 15 and the resulting suspension is stirred for additional 25 min. The reaction mixture is filtered through a pad of Celite® and the filtrate was evaporated under reduced pressure to give the crude product which was purified by semipreparative HPLC (eluent: water–methanol) using a column Atlantis® DC 18 5 μm, 19 × 100 mm, flow: 12.5 mL/min. Detection: ELSD.

5.8.1. β-D-Glucopyranosyl-(1→3)-1-deoxy-1-(3-phenylpropyl)-β-D-glucopyranose (16b)

Following the general procedure, the one-pot procedure for **12** (0.165 g, 0.25 mmol) afforded **16b** (44 mg, 40%) as a white foam; HPLC: t = 2.0 min (MeOH); $[\alpha]_D^{25}$ −18 (c 0.57, H_2O); ^1H NMR (D_2O, 400 MHz): δ 1.38 (dd, 1H, J = 9.0, 18.2 Hz, H_{13}), 1.59–1.69 (m, 1H, H_{14}), 1.70–1.82 (m, 2H, H_{13}, H_{14}), 2.58 (m, 2H, H_{15}, H_{15}), 3.21–3.47 (m, 8H, H_1, H_2, H_4, H_5, H_8, H_9, H_{10}, H_{11}), 3.55–3.65 (m, 3H, H_3, H_6, H_{12}), 3.79 (dd, 1H, J = 1.8, 12.2 Hz, H_6), 3.83 (dd, 1H, J = 2.1, 12.3 Hz, H_{12}), 4.64 (d, 1H, J = 7.9 Hz, H_7), 7.15–7.18 (m, 1H, *ArH*), 7.21–7.22 (m, 2H, *ArH*), 7.26–7.29 (m, 2H, *ArH*); ^{13}C NMR (D_2O, 100 MHz): δ 26.4 (C_{14}), 30.4 (C_{13}), 34.9 (C_{15}), 60.7 (C_{12}), 61.0 (C_6), 68.6 (C_4), 69.6 (C_2), 73.1 (C_8), 73.5 (C_8), 75.6 (C_{10}), 76.0 (C_{11}), 78.9 (C_1), 79.4 (C_9), 86.4 (C_3), 102.9 (C_7), 125.9 (Ar), 128.5 (Ar), 128.6 (Ar), 143.0 (Ar). Anal. Calcd for $C_{21}H_{32}O_{10}$: C, 56.75; H, 7.26. Found: C, 56.88; H, 7.41.

5.8.2. β-D-Glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-1-deoxy-1-(4-methoxy-4-oxobutyl)-β-D-glucopyranoside (16c)

Following the general procedure, the one-pot procedure for **13** (0.237 g, 0.25 mmol) afforded **16c** (93 mg, 52%) as an oil; HPLC: t = 1.1 min (water/MeOH, 1:9); $[\alpha]_D^{25}$ −12 (c 1.16 H_2O); ^1H NMR (D_2O, 400 MHz): δ 1.27–1.36 (m, 1H, H_{20}), 1.47–1.57 (m, 1H, H_{19}), 1.61–1.75 (m, 2H, H_{19}, H_{20}), 2.04–2.16 (m, 2H, H_{21a}, H_{21b}), 3.18–3.43 (m, 14H, H_1, H_2, H_4, H_5, H_8, H_{10}, H_{11}, H_{14}, H_{15}, H_{16}, H_{17}, *OMe*), 3.49–3.62 (m, 5H, H_3, H_6, H_9, H_{12}, H_{18}), 3.77–3.83 (m, 3H, H_6, H_{12}, H_{18}), 4.54 (d, 1H, J = 8.1 Hz, H_7), 4.56 (d, 1H, J = 7.9 Hz, H_{13}); ^{13}C NMR (D_2O, 100 MHz): δ 21.8 (C_{20}), 30.7 (C_{19}), 37.3 (C_{21}), 61.0 (C_6 or C_{12} or C_{18}), 61.1 (C_6 or C_{12} or C_{18}), 61.3 (C_6 or C_{12} or C_{18}), 68.7 (C_4 or C_{10} or C_{16}), 68.8 (C_4 or C_{10} or C_{16}), 69.9 (C_4 or C_{10} or C_{16}), 73.1 (C_2 or C_8 or C_{14}), 74.2 (C_2 or C_8 or C_{14}), 74.2 (C_2 or C_8 or C_{14}), 76.2

(C_5 or C_{11} or C_{17}), 76.5 (C_5 or C_{11} or C_{17}), 76.6 (C_5 or C_{11} or C_{17}), 79.0 (C_1), 79.7 (C_5), 87.7 (C_3 or C_9), 88.2 (C_3 or C_9), 104.4 (C_{13}), 104.8 (C_7), 183.6 (C=O). Anal. Calcd for $C_{29}H_{46}O_{20}$: C, 48.74; H, 6.49. Found: C, 48.98; H, 6.26.

5.9. Biological assays

5.9.1. Glycosidases

Two commercially available (Sigma Aldrich Chemical Co.) glycosidases (α-glucosidase from *Saccharomyces cerevisae* and α-galactosidase from *green coffee bean*) were assayed following the method of Saul et al.[34] A typical enzymatic assay (final volume 0.1 mL) contains 0.33 units/mL of the enzyme and 1 mM aqueous solution of the appropriate *p*-nitrophenyl glycoside substrate buffered to the optimum pH of the enzyme. The incubations were performed for 40 min at 37 °C and the reaction was stopped by addition of 0.25 mL 0.2 M sodium borate buffer pH 9. The released *p*-nitrofenol was measured at 410 nm.

Enzyme and glycomimetic (**11a–f** and **16a–d**) were preincubated for 5 min at 20 °C, and the reaction started by addition of the substrate. After 40 min incubation at 37 °C, the reaction was stopped by addition of 0.25 mL 0.2 M sodium borate buffer pH 9.8. The *p*-nitrophenolate formed was measured by visible absorption spectroscopy at 410 nm. Under these conditions of the assay, the *p*-nitrophenolate released led to optical densities linear with both time of the reaction and concentration of the enzyme. Several measures of glycosidase activities were made in the presence of various concentrations (1, 10, 50 and 100 mM) of compounds **11a–f** and **16a–d** and in all cases the observed activity was identical to that in their absence indicating the complete absence of inhibitory activity.

5.9.2. Glucanases

Two commercially available (Megazyme) glucanases (*endo*-β-1,3-glucanase (*Barley*) and *endo*-β-1,3(4)-D-glucanase from *Clostridum thermocellum*) were assayed. An aliquot (0.5 mL, 1 unit/mL of enzyme) is pre-equilibrated at 30 °C in the case of *endo*-β-1,3-glucanase (*Barley*) or 60 °C in the case of *endo*-β-1,3(4)-D-glucanase from *Clostridum thermocellum* for 5 min. A 1,3-beta-Glucazyme® tablet (containing azurine-crosslinked pachyman) is added without stirring and incubation is maintained at the corresponding temperature for 10 min in the case of *endo*-β-1,3-glucanase (*Barley*) and 3 h in the case of *endo*-β-1,3(4)-D-glucanase from *Clostridum thermocellum*, at which time the reaction mixture is treated with 10 mL of 100 mM TRIS buffer at pH 8 with stirring. The resulting mixture is maintained at room temperature and is stirred again for 5 min. The resulting slurry is filtered through a Whatman No. 1 (9 cm) filter circle the absorbance of the filtrate is measured at 590 nm against a substrate blank. The substrate blank is prepared by adding a 1,3-beta-Glucazyme® tablet to 0.5 mL of extraction buffer, incubating at 30 °C for 10 min, adding 10.0 mL of Trizma Base (2% w/v) and filtering after 5 min.

Several measures of glucanase activities were made in the presence of various concentrations (10, 50 and 100 mM) of compounds **11a–f** and **16a–d** and in all cases the observed activity was identical to that in their absence indicating the complete absence of inhibitory activity.

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