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$BiBr_3$-Promoted Activation of Peracetylated Glycosyl Iodides: Straightforward Access to Synthetically Useful 2-*O*-Deprotected Allyl Glycosides

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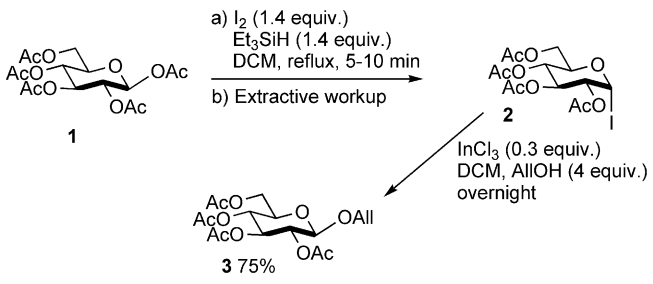
Substoichiometric amounts of $BiBr_3$ are able to promote anomeric activation of acetylated glycosyl iodides. This reactivity can be exploited for straightforward access to allyl glycosides unprotected at the O-2 position. The reported protocol appears to be convenient in comparison with the pre-existing ones in that shorter experimental times are needed and the use of strong acids is avoided. Suitable structural features of substrates (6-deoxy sugars or use of benzoyl or methoxycarbonyl 2-*O*-participating groups) switch the process to a preferential glycosidation without deprotection at the O-2 position.

Introduction

Chemical manipulation of monosaccharide functional groups is frequently the fundamental initial stage for accessing the building blocks needed for oligosaccharide synthesis or, more in general, for preparing useful precursors of chiral synthetic targets. The desired differentiation of the hydroxy groups of a sugar molecule often implies multiple synthetic steps in which the appropriate variety of protecting groups is installed and then suitably elaborated according to the synthetic requirement. These processes can be time consuming, as several synthetic operations and related purifications should be performed. Therefore, over the last year, some effort has been devoted towards the development of expeditious synthetic procedures providing the rapid differentiation of monosaccharide protecting groups through multiple stages performed sequentially without any purification of intermediates.[1] In this regard, herein we wish to report a simple and rapid protocol for accessing monosaccharides bearing the versatile allyl group at the anomeric position, a free hydroxy group at C-2, and acetyl groups at the other carbinolic positions. The approach relies on the feasible activation of glycosyl iodides with substoichiometric amounts of $BiBr_3$.

Results and Discussion

The procedure was disclosed in the course of an investigation aimed at finding catalytic activators of peracetylated glycosyl iodides to be employed in glycosidation reactions.[2] These precursors can be rapidly prepared within a few minutes from the corresponding peracetylated sugars[3] and can be employed as crude products after a simple extractive workup for a wide range of transformations.[4] As expected, substoichiometric amounts of $InCl_3$ (a known activator of glycosyl bromides)[5] are able to promote in high yield the anomeric allylation of glucosyl iodide with the predicted 1,2-*trans* selectivity arising from the vicinal participation effect (Scheme 1).



Scheme 1. $InCl_3$-promoted activation of glycosyl iodide **2**.

In searching for alternative catalytic reagents of higher reactivity, we examined several bismuth(III) salts, whose catalytic halophilic reactivity had been evidenced in some useful synthetic transformations such as Friedel–Crafts alkylation.[6] When $BiBr_3$ was used, the reaction outcome was rather different, and a mixture of products was recovered in which allyl glycoside **4**, deprotected at the O-2 position, predominated over minor, although not negligible, amounts of peracetylated allyl glycoside **3** (Scheme 2).

As shown in Scheme 2, the composition of the reaction mixture was examined under a variety of conditions (reactions at room temperature or in refluxing DCM, 2 or 4 equivalents of allyl alcohol used). The best yield of 2-*O*-deprotected compound **4** (57%) was achieved with 4 equiv.

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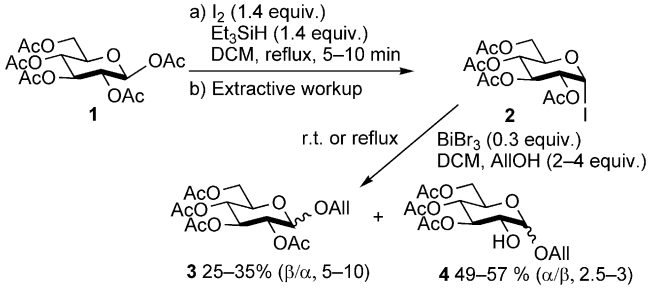


Scheme 2. $BiBr_3$-promoted activation of glycosyl iodide **2**.

of allyl alcohol in refluxing DCM and in the presence of freshly activated 4 Å molecular sieves. Remarkably, under these conditions the reaction is sufficiently fast (ca. 90 min) so that the whole synthetic sequence shown in Scheme 2 can be performed within a few hours. Other solvents (1,2-dichloroethane, toluene, dioxane, acetonitrile) were also tested, but lower yields were invariably obtained.

The anomeric profile of the obtained allylated products was also interesting: whereas compound **4** was obtained with some predominance of the α-anomer, peracetylated allyl glycoside **3** was obtained with predominant, though not exclusive, β-selectivity. Given that the allyl group is frequently used for anomeric transient protection, the described two-step sequence appeared of synthetic value, because it allowed the rapid chemical discrimination of the anomeric, the O-2 position, and the remaining oxygenated positions. From a literature survey it appeared that a similar transformation can be carried out with a slightly improved yield (63% of **4**; β/α, 3:1) by treating β-penta-*O*-acetyl glucose with allyl alcohol (4 equiv.) in the presence of a stoichiometric excess of $BF_3{\cdot}OEt_2$ (1.5 equiv.).[7] However, the overall reaction requires a much longer reaction time (overnight) than that required by the here-presented sequential procedure. Equally prolonged times (and high temperatures) were very recently reported to be required by several zeolites for inducing similar transformations (glycosidation with concomitant deprotection at the O-2 position) in the coupling of β-configured peracetylated sugars with either phenols or long-chain alcohols.[8] In contrast to the above-mentioned $BF_3{\cdot}OEt_2$-based procedure, the anomeric profile observed in this latter approach was analogous to that obtained under the here-described conditions. Further sparse examples of glycosidations proceeding with deacetylation at the O-2 position of the donor have been occasionally described as minor side processes.[9]

Once the best reaction conditions were established, the scope of the procedure was examined with a wide range of alternative saccharide precursors (Table 1). With peracetylated galactose and mannose precursors, the yields of the corresponding 2-OH allyl glycosides were again of synthetic interest, albeit lower than those obtained with glucose (Table 1, entries 5 and 8 vs. entry 1). Notably, a lower yield of 2-*O*-deprotected product was obtained when commercial acetobromogalactose was used in place of the corresponding iodinated precursor (Table 1, entries 6 and 5, respectively). Acetylated 6-deoxy sugars such as L-rhamnose or fucose were instead found to afford a large predominance of the peracetylated 1,2-*trans* allyl glycosides (Table 1, entries 9 and 10). Adoption of an alternative 2-*O*-acyl group such as benzoyl (Table 1, entry 4) or methoxycarbonyl[10] (Table 1, entry 7) suppressed, under otherwise identical conditions, the process of deprotection at the O-2 position and was effective in the exclusive generation of the corresponding 1,2-*trans* glycosides. These latter results indicate

Table 1. $BiBr_3$-promoted activation of glycosyl halides.[a]

Entry	Starting compound	Product, Yield (α/β)	
1	**1**	**3**, 35 % (1:10)	**4**, 57 % (3.0:1)
2[b]	**1**	**5**, 29 % (1:4.7)	**6**, 45 % (2.7:1)
3[c]	**1**	**7**, 35 % (only β)	**8**, 43 % (2.9:1)
4	**9**	**10**, 61 % (only β)	
5	**11**	**12**, 48 % (only β)	**13**, 45 % (1.3:1)
6[d]	**11**	**12**, 51 % (only β)	**13**, 35 % (1.6:1)
7	**14**	**15**, 66 % (only β)	
8	**16**	**17**, 25 % (3.7:1)	**18**, N. D.[e]
9	**19**	**20**, 68 % (only β)	**21**, 30 % (2.4:1)
10	**22**	**23**, 74 % (4.5:1)	
11	**24**	**25**, 29 % (1:6)	**26**, 48 % (only α)

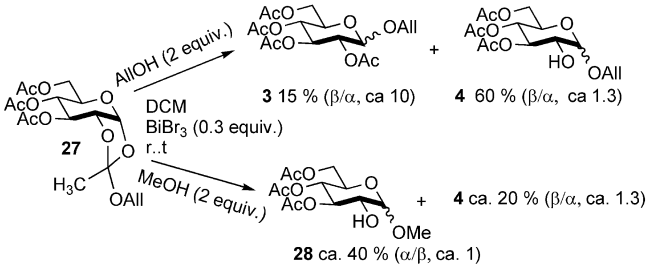
[a] General conditions: sugar, I_2 (1.4 equiv.), Et_3SiH (1.4 equiv.), refluxing DCM. Extractive workup, then glycosyl iodide, allyl alcohol (4 equiv.), 4 Å MS, $BiBr_3$ (0.3 equiv.), DCM, reflux. [b] *n*-Propanol was used in place of allyl alcohol. [c] *n*-Pentenyl alcohol was used in place of allyl alcohol. [d] Tetracetylbromogalactose was used in place of the corresponding iodide. [e] Isolated yield could not be determined, as the anomeric products were contaminated by inseparable 2,3,4,6-tetra-*O*-acetylmannopyranose. Estimated yield by NMR spectroscopy: ca 35% (α/β, ca. 1).

that $BiBr_3$-promoted anomeric allylation without deprotection at the O-2 position can also be usefully achieved under suitable structural conditions of the substrates, and this may offer an alternative to protocols based on Fischer glycosidations that require toxic and high-boiling allyl alcohol as the solvent.

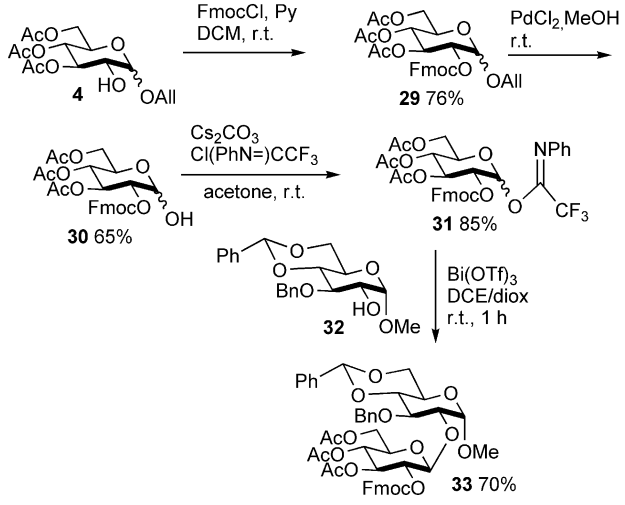
Use of alternative primary acceptors (*n*-propanol, *n*-pentenyl alcohol) in place of allyl alcohol was also tested with a *gluco*-configured acetylated precursor and did not result in a remarkable difference in the reaction mixture composition (Table 1, compare entries 2 and 3 with entry 1), although the best results in deprotection at the O-2 position were obtained with allyl alcohol. An especially interesting result was obtained with a disaccharide such as D-lactose, which afforded the 2-*O*-deprotected product in very good overall yield and α-selectivity (Table 1, entry 11). It should be noted that in previously reported approaches[7,8] of 2-*O*-deprotective glycosidation no disaccharide was surveyed. Additionally, only peracetylated β-configured *galacto* and *gluco* sugars, more prone to acid-promoted anomeric activation, were used in those procedures, whereas the present protocol can be generally independent of the anomeric configuration of the starting compound, as the initial iodination step is efficient with both anomers.[3]

After having established the scope and limitations of the protocol, some experiments were performed to gain some mechanistic information on the process. First, allyl 2,3,4,6-tetra-*O*-acetylgalactopyranoside was exposed to the typical reaction conditions above-described, and no appreciable amount of deacetylation at the O-2 position was detected, evidencing that the removal of the acetyl group does not occur after allylation of the anomeric position. In a second experiment, allyl orthoester **27** prepared via the corresponding iodide **2**[3] was exposed to $BiBr_3$ and allyl alcohol (Scheme 3). Interestingly, this treatment led to a mixture of allylated compounds **3** and **4** within a short time period even at room temperature with a larger relative predominance of deprotection at the O-2 position, but a lower α-selectivity. The outcome of this experiment is highly suggestive of an allylated orthoester as one of the feasible intermediates generated in the rate-determining step, in which $BiBr_3$ promotes the activation of the anomeric iodide. In order to ascertain the origin of the aglycon moiety in the final product, allyl orthoester **27** was treated under the same conditions previously adopted but in the presence of methanol rather than allyl alcohol as the external nucleophile. The profile of products (Scheme 3) displayed a predominant, albeit not exclusive, content of methyl glycosides, which implies that the aglycon can be provided from the reaction medium and it is not necessarily incorporated into the initial orthoester intermediate.

Due to our current interest in the search of 2-*O*-participating groups serving in $Bi(OTf)_3$-promoted 1,2-*trans* glycosidations[11] and amenable to selective removal in the presence of acetyls, we took advantage of the presented procedure for the straightforward access to **4**, a useful precursor of the 2-*O*-Fmoc trifluoroacetimidate donor **31** (Scheme 4).



Scheme 3. $BiBr_3$-promoted activation of orthoester **27**.



Scheme 4. Synthesis of donor **31** and its coupling with acceptor **32**.

The Fmoc group was initially installed in compound **4**, and resulting compound **29** was submitted to a sequence of anomeric deallylation and installation of the (*N*-phenyl)-trifluoroacetimidate leaving group.[12] $Bi(OTf)_3$-catalyzed coupling[11] with model acceptor **32** smoothly afforded disaccharide **33** in good yield (70%).

Conclusion

We have shown that the sequence of anomeric iodination and $BiBr_3$-promoted activation of the intermediate glycosyl iodides can afford, within short times, useful saccharidic building-blocks unprotected at the 2-OH position and bearing the selectively removable allyl anomeric group. Suitable structural conditions of substrates (6-deoxy sugars or use of benzoyl or methoxycarbonyl 2-*O*-participating groups) switch the preferential process to a glycosidation without concomitant deprotection at the O-2 position. Synthetically useful elaborations of the obtained derivatives are currently being investigated in our laboratory.

Experimental Section

General: ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ (internal standard $CHCl_3$ at δ = 7.26 ppm). Assignment of proton chemical shifts was based on decoupling experiments. Analytical thin-layer chromatography (TLC) was performed on aluminium

plates precoated with Silica Gel 60 F_{254} as the adsorbent. Column chromatography was performed on Kieselgel 60 (63–200 mesh).

Typical Procedure for $BiBr_3$-Promoted Allylation: To a solution of peracetylated glucose (110 mg, 0.28 mmol) in dichloromethane (4 mL) were sequentially added iodine (102 mg, 0.40 mmol) and triethylsilane (62.5 μL, 0.40 mmol; *caution*: exothermic reaction). After stirring for 5 min at reflux temperature, TLC analysis (petroleum ether/ethyl acetate, 6:4) displayed completion of the reaction. After cooling to room temperature, the mixture was diluted with dichloromethane and washed with a solution of saturated sodium hydrogen carbonate containing a minimal amount of sodium thiosulfate for reducing the residual amount of iodine. The aqueous phase was extracted with dichloromethane, and the collected organic phase was dried with sodium sulfate and concentrated in vacuo. Freshly activated 4 Å molecular sieves were added to the residue, and the mixture was suspended in anhydrous dichloromethane (4 mL). Allyl alcohol (4 equiv.) and $BiBr_3$ (37 mg, 0.084 mmol) were then added, and the mixture was heated at reflux until TLC analysis (petroleum ether/ethyl acetate, 4:6) displayed complete consumption of the UV/Vis detectable glycosyl iodide (ca. 80 min). Some drops of pyridine were added, and the mixture was filtered through a short pad of silica gel (ethyl acetate), and the residue from the filtered liquor was chromatographed by silica gel flash chromatography (petroleum ether/ethyl acetate, 6:4) to yield peracetylated allyl glycoside **3** (40 mg, 37%; α/β, 1:10), and 2-*O*-free allyl glycoside **4** (55 mg, 57%; α/β, 3:1).

Allyl 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranoside (3):[7] Foam, yield 35%, anomeric mixture (α/β, 1:10). Data for the β-anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.94–5.74 (m, 1 H, -CH_2CH=CH_2), 5.26 (dd, ^3J = 17.4 Hz, ^2J = 1.2 Hz, 1 H, -CH_2CH=$CH_{cis}H_{trans}$), 5.20 (t, $J_{3,4}$ = $J_{2,3}$ = 9.3 Hz, 1 H, 3-H), 5.19 (dd, ^3J = 10.4 Hz, ^2J = 1.2 Hz, 1 H, -CH_2CH=$CH_{cis}H_{trans}$), 5.08 (t, $J_{3,4}$ = $J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 5.01 (dd, $J_{1,2}$ = 7.8 Hz, 1 H, 2-H), 4.55 (d, 1 H, 1-H), 4.37–4.29 (dd, ^3J = 4.8 Hz, ^2J = 13.2 Hz, 1 H, -CH_aH_bCH=CH_2), 4.25 (dd, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6a}$ = 4.6 Hz, 1 H, 6_a-H), 4.13 (dd, $J_{5,6b}$ = 2.4 Hz, 1 H, 6_b-H), 4.12–4.03 (dd, ^3J = 6.0 Hz, ^2J = 13.2 Hz, 1 H, -CH_aH_bCH=CH_2), 3.72–3.64 (m, 1 H, 5-H), 2.08, 2.04, 2.01, 1.99 (4×s, 12 H, 4×-$COCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.5, 170.1, 169.2, 169.1, 133.2, 117.5, 99.4 (C-1), 72.7, 71.6, 71.1, 69.8, 68.3, 61.8, 20.4 ppm. $C_{17}H_{24}O_{10}$ (388.37): calcd. C 52.57, H 6.23; found C 52.40, H 6.10.

Allyl 3,4,6-Tri-*O*-acetyl-D-glucopyranoside (4):[7] Oil, yield 57%, anomeric mixture (α/β, 3.0:1). Data for the α-anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.00–5.80 (m, 1 H, -CH_2CH=CH_2), 5.30 (m, ^3J = 17.1 Hz, ^2J = 1.5 Hz, 1 H, -CH_2CH=$CH_{cis}H_{trans}$), 5.24 (m, ^3J = 10.2 Hz, ^2J = 1.5 Hz, 1 H, -CH_2CH=$CH_{cis}H_{trans}$), 5.22 (t, $J_{3,4}$ = $J_{2,3}$ = 9.7 Hz, 1 H, 3-H), 4.99 (t, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H), 4.95 (d, $J_{1,2}$ = 3.9 Hz, 1 H, 1-H), 4.36–4.01 (m, 2 H, -CH_2CH=CH_2), 4.24 (dd, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6a}$ = 4.5 Hz, 1 H, 6_a-H), 4.04 (dd, $J_{5,6b}$ = 2.1 Hz, 1 H, 6_b-H), 3.99–3.93 (m, 1 H, 5-H), 3.71–3.62 (m, 1 H, 2-H), 2.23 (d, $J_{2,OH}$ = 7.5 Hz, 1 H, OH-2), 2.06, 2.04, 2.00 (3×s, 9 H, 3×-$COCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.0, 170.5, 169.5, 132.9, 118.5, 97.3 (C-1), 73.3, 70.7, 69.0, 67.9, 67.6, 61.8, 20.7 ppm. Significant signals for the β-anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.09 (t, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 4.39 (d, $J_{1,2}$ = 8.1 Hz, 1 H, 1-H), 3.57 (m, 1 H, 2-H) ppm. $C_{15}H_{22}O_9$ (346.33): calcd. C 52.02, H 6.40; found C 51.80, H 6.31.

***n*-Propyl 2,3,4,6-Tetra-*O*-acetyl-D-glucopyranoside (5):**[13] Oil, yield 29%, anomeric mixture (α/β, 1:4.7). Data for the β-anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.16 (t, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 5.04 (t, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 4.94 (dd, $J_{1,2}$ = 8.1 Hz, $J_{2,3}$ = 9.6 Hz, 1 H, 2-H), 4.45 (d, 1 H, 1-H), 4.22 (dd, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6a}$ = 4.5 Hz, 1 H, 6_a-H), 4.08 (dd, $J_{5,6b}$ = 2.2 Hz, 1 H, 6_b-H), 3.85–3.74 (m, 1 H), 3.69–3.61 (m, 1 H, 5-H), 3.44–3.32 (m, 1 H), 2.04, 1.98, 1.97, 1.96 (4×s, 12 H, 4×-$COCH_3$), 1.6–1.4 (m, 2 H, -$OCH_2CH_2CH_3$), 0.85 (t, ^3J = 6.9 Hz, 3 H, -$OCH_2CH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.5, 170.1, 169.2, 169.1, 100.7 (C-1), 72.7, 71.6, 71.2, 70.2, 68.4, 61.9, 22.5, 20.5, 10.1 ppm. $C_{17}H_{26}O_{10}$ (390.39): calcd. C 52.30, H 6.71; found C 52.00, H 6.55.

***n*-Propyl 3,4,6-Tri-*O*-acetyl-D-glucopyranoside (6):** Oil, yield 45%, anomeric mixture (α/β, 2.7:1). Data for the α anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.18 (t, $J_{3,4}$ = $J_{2,3}$ = 9.6 Hz, 1 H, 3-H), 4.95 (t, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 4.87 (d, $J_{1,2}$ = 3.9 Hz, 1 H, 1-H), 4.21 (dd, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6a}$ = 4.5 Hz, 1 H, 6_a-H), 4.02 (dd, $J_{5,6b}$ = 2.1 Hz, 1 H, 6_b-H), 3.98–3.88 (m, 1 H, 5-H), 3.75–3.40 (m, 3 H, 2-H and -$OCH_2CH_2CH_3$), 2.41 (d, $J_{2,OH}$ = 7.4 Hz, 1 H, 2-OH), 2.04, 2.03, 1.98 (3×s, 9 H, 3×-$COCH_3$), 1.73–1.53 (m, 2 H, -$OCH_2CH_2CH_3$), 0.92 (t, ^3J = 7.5 Hz, 3 H, -$OCH_2CH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.0, 170.6, 169.6, 98.1 (C-1), 73.4, 70.7, 70.4, 68.1, 67.5, 62.0, 22.6, 20.5, 10.5 ppm. Significant signals for the β-anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.07 (t, $J_{3,4}$ = $J_{2,3}$ = 9.6 Hz, 1 H, 3-H), 4.97 (t, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 4.31 (d, $J_{1,2}$ = 7.8 Hz, 1 H, 1-H) ppm. $C_{15}H_{24}O_9$ (348.35): calcd. C 51.72, H 6.94; found C 51.45, H 6.75.

***n*-Pentenyl 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranoside (7):**[14] $[\alpha]_D^{25}$ = –17.2 (c = 0.6, $CHCl_3$), m.p. 47 °C (light petroleum/diethyl ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.86–5.67 (m, 1 H, -CH_2CH=CH_2), 5.18 (t, $J_{3,4}$ = $J_{2,3}$ = 9.4 Hz, 1 H, 3-H), 5.06 (t, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, 1 H, 4-H), 4.99 (dd, ^3J = 16.9 Hz, ^2J = 1.8 Hz, 1 H, -CH_2CH=$CH_{cis}H_{trans}$), 4.96 (dd, $J_{1,2}$ = 7.9 Hz, 1 H, 2-H), 4.95 (dd, ^3J = 9.9 Hz, ^2J = 1.8 Hz, 1 H, -CH_2CH=$CH_{cis}H_{trans}$), 4.47 (d, 1 H, 1-H), 4.24 (dd, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6a}$ = 4.8 Hz, 1 H, 6_a-H), 4.11 (dd, $J_{5,6b}$ = 2.5 Hz, 1 H, 6_b-H), 3.90–3.81 (dt, ^3J = 6.1 Hz, ^2J = 9.6 Hz, 1 H, -$OCH_aH_bCH_2CH_2CH$=CH_2), 3.71–3.63 (m, 1 H, 5-H), 3.53–3.43 (dt, ^3J = 6.6 Hz, ^2J = 9.6 Hz, 1 H, -OCH_aH_b-CH_2CH_2CH=CH_2), 2.06, 2.02, 2.00, 1.98 (4×s, 12 H, 4×-$COCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.5, 170.2, 169.3, 169.2, 137.7, 115.0, 100.8 (C-1), 72.9, 71.8, 71.4, 69.2, 68.6, 62.0, 29.8, 28.6, 20.5 ppm. $C_{19}H_{28}O_{10}$ (416.42): calcd. C 54.80, H 6.78; found C 54.53, H 6.65.

***n*-Pentenyl 3,4,6-Tri-*O*-acetyl-D-glucopyranoside (8):** Oil, yield 43%, anomeric mixture (α/β, 2.9:1). Data for the α-anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.87–5.70 (m, 1 H, -CH_2CH=CH_2), 5.19 (t, $J_{3,4}$ = $J_{2,3}$ = 9.6 Hz, 1 H, 3-H), 5.02 (dd, ^3J = 17.1 Hz, ^2J = 1.8 Hz, 1 H, -CH_2CH=$CH_{cis}H_{trans}$), 5.02–4.90 (m, 2 H, -CH_2CH=$CH_{cis}H_{trans}$ and 4-H), 4.87 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.23 (dd, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6a}$ = 4.5 Hz, 1 H, 6_a-H), 4.04 (dd, $J_{5,6b}$ = 2.4 Hz, 1 H, 6_b-H), 3.97–89 (m, 1 H, 5-H), 3.78–3.69 (dt, ^3J = 6.7 Hz, ^2J = 9.9 Hz, 1 H, -$CH_aH_bCH_2CH_2CH$=CH_2), 3.69–3.59 (m, 1 H, 2-H), 3.53–3.43 (dt, ^3J = 6.4 Hz, ^2J = 9.6 Hz, 1 H, -$CH_aH_bCH_2$-CH_2CH=CH_2), 2.60 (br. s, 1 H, 2-OH), 2.05 (×2), 2.00 (3×s, 9 H, 3×-$COCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.0, 170.5, 169.5, 137.6, 115.2, 98.3, 73.5, 70.8, 68.2 (×2), 67.7, 62.1, 30.2, 28.4, 20.6 ppm. Significant signals for the β-anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.09 (t, $J_{3,4}$ = $J_{2,3}$ = 9.9 Hz, 1 H, 3-H), 4.32 (d, $J_{1,2}$ = 7.8 Hz, 1 H, 1-H) ppm. $C_{17}H_{26}O_9$ (374.39): calcd. C 54.54, H 7.00; found C 54.32, H 6.87.

Allyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranoside (10):[15] Foam. $[\alpha]_D^{24}$ = +50.7 (c = 1.1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.30–7.20 (aromatic protons), 5.96 (t, $J_{3,4}$ = $J_{2,3}$ = 9.6 Hz, 1 H, 3-H), 5.80–5.66 (m, 2 H, -CH_2CH=CH_2 and 4-H), 5.62 (t, 1 H, 2-H), 5.24 (d, ^3J = 17.4 Hz, 1 H, CH_2CH=$CH_{cis}H_{trans}$), 5.14 (d, ^3J = 10.5 Hz, 1 H, -CH_2CH=$CH_{cis}H_{trans}$), 4.95 (d, $J_{1,2}$ = 8.1 Hz, 1 H,

1-H), 4.68 (dd, $J_{6a,6b}$ = 11.8 Hz, $J_{5,6b}$ = 2.8 Hz, 1 H, 6_b-H), 4.60–4.05 (4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.1, 165.8, 165.2, 165.1, 133.5, 133.3, 133.2 (×2), 133.1, 129.8–128.3, 117.9, 99.8 (C-1), 73.0, 72.2, 71.9, 70.1, 69.8, 63.2 ppm. $C_{37}H_{32}O_{10}$ (636.65): calcd. C 69.80, H 5.07; found C 69.65, H 5.21.

Allyl 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranoside (12):[16] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.90–5.70 (m, 1 H, -CH_2CH=CH_2), 5.35 (dd, $J_{3,4}$ = 3.3 Hz, $J_{4,5}$ = 1.0 Hz, 1 H, 4-H), 5.24 (dd, ^3J = 17.1 Hz, ^2J = 1.5 Hz, 1 H, -CH_2CH=$CH_{cis}H_{trans}$), 5.20 (dd, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 10.5 Hz, 1 H, 2-H), 5.17 (dd, ^3J = 10.5 Hz, ^2J = 1.5 Hz, 1 H, -CH_2CH=$CH_{cis}H_{trans}$), 4.99 (dd, 1 H, 3-H), 4.49 (d, 1 H, 1-H), 4.37–4.27 (m, 1 H), 4.15 (dd, $J_{6a,6b}$ = 12.6 Hz, 1 H, 6-H), 4.11–4.03 (m, 2 H), 3.87 (br. t, $J_{5,6a}$ = $J_{5,6b}$ = 6.6 Hz, 1 H, 5-H), 2.11, 2.02, 2.01, 1.94 (4×s, 12 H, 4×-$COCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.2, 170.1, 170.0, 169.3, 133.2, 117.4, 99.9 (C-1), 70.8, 70.5, 69.9, 68.7, 66.9, 61.2, 20.5 ppm. $C_{17}H_{24}O_{10}$ (388.37): calcd. C 52.57, H 6.23; found C 52.35, H 6.10.

Allyl 3,4,6-Tri-*O*-acetyl-D-galactopyranoside (13):[17] Oil, yield 45%, anomeric mixture (α/β, 1.3:1). Data for the α-anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.00–5.80 (m, 1 H, -CH_2CH=CH_2), 5.36 (dd, $J_{3,4}$ = 3.0 Hz, $J_{4,5}$ = 1.2 Hz, 1 H, 4-H), 5.29 (dd, ^3J = 17.1 Hz, ^2J = 1.2 Hz, 1 H, -CH_2CH=$CH_{cis}H_{trans}$), 5.22 (dd, ^3J = 10.5 Hz, ^2J = 1.2 Hz, 1 H, -CH_2CH=$CH_{cis}H_{trans}$), 5.11 (dd, $J_{2,3}$ = 10.5 Hz, 1 H, 3-H), 4.99 (d, $J_{1,2}$ = 3.9 Hz, 1 H, 1-H), 4.30–4.00 (m, 5 H, 5-H, 6-H_2 and -CH_2CH=CH_2), 3.80 (m, 1 H, 2-H), 2.70 (br. s, 1 H, 2-OH), 2.10, 2.01 (×2) (2×s, 9 H, 3×-$COCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.6, 170.3, 170.0, 133.0, 118.3, 97.6 (C-1), 70.6, 68.9, 68.1, 66.9, 66.7, 61.7 (C-6), 20.6, 20.5 ppm. Significant signals for the β-anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.89 (dd, $J_{3,4}$ = 3.3 Hz, $J_{2,3}$ = 10.5 Hz, 1 H, 3-H), 4.38 (d, $J_{1,2}$ = 7.5 Hz, 1 H, 1-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 101.9 (C-1) ppm. $C_{15}H_{22}O_9$ (346.33): calcd. C 52.02, H 6.40; found C 51.85, H 6.30.

Allyl 3,4,6-Tri-*O*-acetyl-2-*O*-methoxycarbonyl-β-D-glucopyranoside (15): Oil. $[\alpha]_D^{25}$ = +7.5 (c = 0.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.90–5.72 (m, 1 H, -CH_2CH=CH_2), 5.35 (br. s, 1 H, 4-H), 5.22 (m, ^3J = 17.4 Hz, ^2J = 1.2 Hz, 1 H, -CH_2CH=CH_{cis}-H_{trans}), 5.14 (m, ^3J = 10.5 Hz, ^2J = 1.2 Hz, 1 H, -CH_2CH=CH_{cis}-H_{trans}), 4.98–4.97 (m, overlapped signals, 2 H, 1-H and 3-H), 4.50 (dd, $J_{1,2}$ = $J_{2,3}$ = 3.9 Hz, 1 H, 1 H, 2-H), 4.35–4.00 (m, 4 H, 6-H_2 and -CH_2CH=CH_2), 3.86 (t, $J_{5,6a}$ = $J_{5,6b}$ = 6.9 Hz, 1 H, 5-H), 3.75 (s, 3 H, -OCH l_3), 2.08, 1.98, 1.93 (3×s, 9 H, 3×-$COCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.1, 170.0, 169.8, 154.7, 133.1, 117.4, 99.8 (C-1), 72.8, 70.6, 70.4, 70.0, 66.9, 61.0, 55.0, 20.4 ppm. $C_{17}H_{24}O_{11}$ (404.37): calcd. C 50.49, H 5.98; found C 50.25, H 6.04.

Allyl 2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranoside (17):[18] Oil, yield 25%, anomeric mixture (α/β, 3.7:1). Data for the α-anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.00–5.80 (m, 1 H, -CH_2CH=CH_2), 5.35 (dd, $J_{3,4}$ = 10.2 Hz, 1-H, 3-H), 5.29 (dd, ^3J = 17.1 Hz, ^2J = 1.2 Hz, 1 H, -CH_2CH=$CH_{cis}H_{trans}$), 5.27 (t, $J_{4,5}$ = 10.2 Hz, 1 H, 4-H), 5.24 (dd, $J_{2,3}$ = 3.1 Hz, 1 H, 2-H), 5.22 (dd, ^3J = 10.5 Hz, ^2J = 1.2 Hz, 1 H, CH_2CH=$CH_{cis}H_{trans}$), 4.85 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1-H), 4.27 (dd, $J_{6a,6b}$ = 12.1 Hz, $J_{5,6a}$ = 5.2 Hz, 1 H, 6_a-H), 4.22–4.12 (br. dd, ^3J = 5.4 Hz, ^2J = 13.2 Hz, 1 H, -CH_aH_bCH=CH_2), 4.11–3.95 (m, 3 H, 6_b-H, -CH_aH_bCH=CH_2 and 5-H), 2.13, 2.09, 2.02, 1.97 (4×s, 12 H, 4×-$COCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.6, 170.0, 169.7, 169.6, 132.9, 118.3, 96.5 (C-1), 69.6, 69.0, 68.6, 68.5, 66.2, 62.4, 20.6 ppm. Significant signals for the β-anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.48 (dd, $J_{1,2}$ = 0.9 Hz, $J_{2,3}$ = 3.6 Hz, 1 H, 2-H), 5.26 (t, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 5.04 (dd, 1-H, 3-H), 4.68 (d, 1 H, 1-H), 3.68–3.60 (m, 1 H, 5-H), 2.19, 2.09, 2.04, 1.99 (4×s, 12 H, 4×-$COCH_3$) ppm. $C_{17}H_{24}O_{10}$ (388.37): calcd. C 52.57, H 6.23; found C 52.35, H 6.15.

Allyl 2,3,4-Tri-*O*-acetyl-β-L-fucopyranoside (20): Oil, yield 68%, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.83–5.68 (m, 1 H, -CH_2CH=CH_2), 5.23–5.05 (m, 4 H, -CH_2CH=CH_2, 4-H and 2-H), 4.93 (dd, $J_{3,4}$ = 3.3 Hz, $J_{2,3}$ = 10.5 Hz, 1 H, 3-H), 4.41 (d, $J_{1,2}$ = 8.1 Hz, 1 H, 1-H), 4.32–4.20 (m, ^3J = 4.5 Hz, ^2J = 13.5 Hz, 1 H, -CH_aH_bCH=CH_2), 4.05–3.95 (m, ^3J = 6.0 Hz, ^2J = 13.5 Hz, 1 H, -CH_aH_bCH=CH_2), 3.73 (q, $J_{5,6}$ = 6.6 Hz, 1-H, 5-H), 2.08, 1.96, 1.88 (3×s, 9 H, 3×-$COCH_3$), 1.13 (d, 3 H, 6-CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.4, 169.9, 169.2, 133.4, 117.0, 99.6 (C-1), 71.1, 70.0, 69.5, 68.8, 68.7, 20.5, 20.4, 20.3, 15.8 ppm. $C_{15}H_{22}O_8$ (330.33): calcd. C 54.54, H 6.71; found C 54.35, H 6.65.

Allyl 3,4-Di-*O*-acetyl-L-fucopyranoside (21): Oil, yield 30%, anomeric mixture (α/β, 2.4:1). Data for the α-anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.95–5.80 (m, 1 H, -CH_2CH=CH_2), 5.35–5.20 (m, 3 H, -CH_2CH=CH_2 and 4-H), 5.11 (dd, $J_{3,4}$ = 3.3 Hz, $J_{2,3}$ = 10.5 Hz, 1 H, 3-H), 4.94 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4,25–3.95 (m, 3 H, -CH_2CH=CH_2 and 5-H), 3.91 (br. dd, 1 H, 2-H), 2.61 (br. s, 1 H, 2-OH), 2.12, 2.01 (2×s, 6 H, 2×-$COCH_3$), 1.10 (d, $J_{5,6}$ = 6.3 Hz, 3 H, 6-H_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.5 (×2), 133.3, 118.0, 97.7 (C-1), 71.2 (×2), 68.8, 66.9, 64.8, 20.8, 20.6, 15.8 ppm. Significant signals for the β-anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.89 (dd, $J_{3,4}$ = 3.3 Hz, $J_{2,3}$ = 10.5 Hz, 1 H, 3-H), 4.34 (d, $J_{1,2}$ = 8.1 Hz, 1 H, 1-H), 2.11, 2.01 (2×s, 6 H, 2×-$COCH_3$), 1.18 (d, $J_{5,6}$ = 6.3 Hz, 3 H, 6-H_3) ppm. $C_{13}H_{20}O_7$ (288.30): calcd. C 54.16, H 6.91; found C 54.21, H 6.80.

Allyl 2,3,4-Tri-*O*-acetyl-L-rhamnopyranoside (23):[19] Oil, yield 74%, anomeric mixture (α/β, 4.5:1). Data for the α-anomer: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.96–5.70 (m, 1 H, -CH_2CH=CH_2), 5.23 (dd, ^3J = 17.2 Hz, ^2J = 1.5 Hz, 1 H, -CH_2CH=$CH_{cis}H_{trans}$), 5.20 (dd, $J_{2,3}$ = 3.4 Hz, $J_{3,4}$ = 9.7 Hz, 1 H, 3-H), 5.18 (dd, $J_{1,2}$ = 1.8 Hz, 1 H, 2-H), 5.15 (dd, ^3J = 10.1 Hz, ^2J = 1.5 Hz, 1 H, -CH_2CH=$CH_{cis}H_{trans}$), 4.99 (t, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H), 4.70 (d, 1 H, 1-H), 4.18–3.88 (m, 2-H, -CH_2CH=CH_2), 3.88–3.74 (m, 1 H, 5-H), 2.07, 1.98, 1.91 (3×s, 9 H, 3×-$COCH_3$), 1.15 (d, $J_{5,6}$ = 6.2 Hz, 3 H, 6-CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 169.9, 169.8, 169.7, 133.1, 117.8, 96.3 (C-1), 70.9, 69.7, 68.9, 68.1, 66.2, 20.6 ppm. Data for the β-anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.92–5.77 (m, 1 H, -CH_2CH=CH_2), 5.44 (d, $J_{2,3}$ = 3.0 Hz, 1 H, 2-H), 5.24 (dd, ^3J = 17.5 Hz, ^2J = 1.5 Hz, 1 H, -CH_2CH=CH_{cis}-H_{trans}), 5.19 (dd, ^3J = 10.5 Hz, ^2J = 1.5 Hz, 1 H, -CH_2CH=CH_{cis}-H_{trans}), 5.03 (t, $J_{3,4}$ = $J_{4,5}$ = 10.2 Hz, 1 H, 4-H), 4.97 (dd, 1 H, 3-H), 4.63 (s, 1 H, 1-H), 4.32 (dd, ^3J = 4.8 Hz, ^2J = 12.9 Hz, 1 H, -CH_aH_bCH=CH_2), 4.07 (dd, ^3J = 6.3 Hz, ^2J = 12.9 Hz, 1 H, -CH_aH_bCH=CH_2), 3.55–3.42 (m, 1 H, 5-H), 2.16, 2.03, 1.96 (3×s, 9 H, 3×-$COCH_3$), 1.26 (d, $J_{5,6}$ = 6.0 Hz, 3 H, 6-CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.1 (×3), 133.2, 118.0, 96.9 (C-1), 71.1, 70.7, 70.5, 70.0, 69.1, 20.8, 20.7, 20.5, 17.4 ppm. $C_{15}H_{22}O_8$ (330.33): calcd. C 54.54, H 6.71; found C 54.40, H 6.60.

Allyl 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-D-glucopyranoside (25):[20] Foam, yield 29%, anomeric mixture (α/β, 1:6). Data for the β-anomer: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.93–5.70 (m, 1 H, -CH_2CH=CH_2), 5.31 (br. d, $J_{3,4}$ = 3.4 Hz, 1 H, 4′-H), 5.23 (dd, ^3J = 17.3 Hz, ^2J = 1.6 Hz, 1 H, -CH_2CH=$CH_{cis}H_{trans}$), 5.16 (t, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 5.15 (dd, ^3J = 10.6 Hz, ^2J = 1.6 Hz, 1 H, -CH_2CH=$CH_{cis}H_{trans}$), 5.07 (dd, $J_{1,2}$ = 7.9 Hz, $J_{2,3}$ = 10.4 Hz, 1 H, 2′-H), 4.92 (dd, 1 H, 3′-H), 4.89 (br. dd, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 9.6 Hz, 1 H, 2-H), 4.53–4.42 (2×d, 2 H, 1-H and 1′-H), 4.34–3.92 (m, 6 H), 3.84 (br. t, $J_{5,6a}$ = $J_{5,6b}$ = 6.8 Hz, 1 H, 5′-H), 3.77 (t, $J_{3,4}$ = $J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 3.63–3.50 (m, 1 H, 5-H), 2.11, 2.09, 2.02, 2.01 (×2), 2.00, 1.92 (7×s, 21 H, 7×-$COCH_3$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.2 (×2), 170.0, 169.8, 169.6, 169.4, 168.8, 133.2, 117.5, 100.9

(C-1′), 99.2 (C-1), 76.2, 72.8, 72.5, 71.6, 70.9, 70.6, 69.9, 69.1, 66.6, 62.0, 60.8, 20.6 ppm. $C_{29}H_{40}O_{18}$ (676.62): calcd. C 51.48, H 5.96; found C 51.13, H 5.78.

Allyl 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-acetyl-α-D-glucopyranoside (26): Oil. $[\alpha]_D^{25}$ = +62.3 (c = 1.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.97–5.80 (m, 1 H, -CH_2CH=CH_2), 5.37–5.15 (m, 4 H, 4′-H, -CH_2CH=CH_2, 3-H), 5.06 (dd, $J_{1,2}$ = 7.6 Hz, $J_{2,3}$ = 10.4 Hz, 1 H, 2′-H), 4.89 (dd, $J_{3,4}$ = 3.3 Hz, 1 H, 3′-H), 4.86 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1-H), 4.47 (d, 1 H, 1′-H), 4.40 (dd, $J_{5,6a}$ = 5.6 Hz, $J_{6a,6b}$ = 11.6 Hz, 1 H, 6a-H), 4.21–3.80 (m, 7 H, 6b-H, 6′-H_2, 5-H, OCH_2-CH=CH_2 and 2-H), 3.64 (t, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 3.56–3.47 (br. t, $J_{5,6a}$ = $J_{5,6b}$ = 7.8 Hz, 1 H, 5′-H), 2.74 (br. s, 1 H, 2-OH), 2.11, 2.08 (×2), 2.01 (×2), 1.92 (6×s, 18 H, 6×-$COCH_3$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.6, 170.2, 170.1, 170.0, 169.9, 168.9, 133.0, 118.3, 100.8 (C-1′), 97.0 (C-1), 76.1, 73.2, 70.9, 70.3, 68.9 (×2), 68.3, 66.5, 62.0, 60.7 (×2), 20.7, 20.5 ppm. $C_{27}H_{38}O_{17}$ (634.59): calcd. C 51.10, H 6.04; found C 50.95, H 5.83.

Allyl 2-(Fluorenyl)methyloxycarbonyl-3,4,6-tri-*O*-acetyl-D-glucopyranoside (29): To a solution of **4** (248 mg, 0.72 mmol) in anhydrous DCM (8 mL) was sequentially added pyridine (0.64 mL, 8.0 mmol) and FmocCl (259 mg, 1.0 mmol). When the reaction was complete (ca. 3 h), the mixture was diluted with DCM and washed with water. The aqueous phase was extracted with DCM, and the collected organic phase was dried and concentrated under vacuo. The residue was purified by silica-gel flash chromatography (petroleum ether/ethyl acetate mixtures) to yield **29** (oil, 311 mg, 76% yield) as an anomeric mixture (α/β, 6:1). Data for the α-anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80–7.28 (aromatic protons), 5.97–5.82 (m, 1 H, -CH_2CH=CH_2), 5.59 (t, $J_{2,3}$ = $J_{3,4}$ = 9.7 Hz, 1 H, 3-H), 5.34 (dq, ^3J = 17.2 Hz, ^2J = ^4J = 1.5 Hz, 1 H, -CH_2CH=$CH_{cis}H_{trans}$), 5.22 (dq, ^3J = 10.3 Hz, ^2J = ^4J = 1.5 Hz, 1 H, -CH_2CH=$CH_{cis}H_{trans}$), 5.17 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 5.09 (t, $J_{3,4}$ = $J_{4,5}$ = 9.7 Hz, 1 H, 4-H), 4.79 (dd, 1 H, 2-H), 4.44–4.01 (m, 8 H), 2.10, 2.04, 2.01 (3×s, 9 H, 3×-$COCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.3, 169.8, 169.6, 154.1, 143.0, 142.9, 141.1 (×2), 132.9, 127.8–119.9, 118.1, 94.6 (C-1), 73.8, 70.2, 69.9, 68.8, 68.5, 67.3, 61.7, 46.4, 20.5, 20.4 ppm. Significant signals for the β-anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.32 (t, $J_{2,3}$ = $J_{3,4}$ = 9.7 Hz, 1 H, 3-H), 5.11 (t, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H), 4.88 (br. dd, $J_{1,2}$ = 7.9 Hz, 1 H, 2-H), 4.64 (d, 1 H, 1-H), 3.76–3.68 (m, 1 H, 5-H), 2.09, 2.03, 1.97 (3×s, 9 H, 3×-$COCH_3$) ppm. $C_{30}H_{32}O_{11}$ (568.58): calcd. C 63.37, H 5.67; found C 63.14, H 5.75.

2-(Fluorenyl)methyloxycarbonyl-3,4,6-tri-*O*-acetyl-D-glucopyranose (30): To a solution of **29** (320 mg, 0.56 mmol) in DCM/MeOH (4:1, 5 mL) was added $PdCl_2$ (13 mg, 0.07 mmol). The mixture was stirred for 10 h at room temperature, concentrated, resuspended in DCM/MeOH (95:5), and then filtered through a short pad of silica gel. The filtered liquor was concentrated, and the residue was purified by silica-gel flash chromatography (petroleum ether/ethyl acetate mixtures) to yield **30** (oil, 193 mg, 65% yield) as an anomeric mixture (α/β 3.5). Data for the α-anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80–7.28 (aromatic protons), 5.61 (t, $J_{2,3}$ = $J_{3,4}$ = 9.7 Hz, 1 H, 3-H), 5.50 (br. s, 1 H, 1-H), 5.09 (t, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 4.78 (dd, $J_{1,2}$ = 3.6 Hz, 1 H, 2-H), 4.40–4.04 (m, 6 H), 2.07, 2.02, 1.99 (3×s, 9 H, 3×-$COCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.8, 170.1, 169.7, 154.2, 143.0, 142.9, 141.1 (×2), 127.8–120.0, 89.8 (C-1), 74.3, 70.2, 69.7, 68.4, 67.0, 61.8, 46.4, 20.6 ppm. Significant signals for the β-anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.32 (t, $J_{2,3}$ = $J_{3,4}$ = 9.7 Hz, 1 H, 3-H), 3.79–3.71 (m, 1 H, 5-H) ppm. $C_{27}H_{28}O_{11}$ (528.51): calcd. C 61.36, H 5.34; found C 61.12, H 5.18.

2-*O*-(Fluorenyl)methyloxycarbonyl-3,4,6-tri-*O*-acetyl-D-glucopyranosyl (*N*-Phenyl)trifluoroacetimidate (31): To a solution of **30** (106 mg, 0.20 mmol) in acetone (4 mL) was sequentially added at 0 °C Cs_2CO_3 (74 mg, 0.23 mmol) and (*N*-phenyl)trifluoroacetimidoyl chloride (50 mL, 0.40 mmol). The mixture was allowed to warm to room temperature and after 1 h from the start of the reaction the solvent was removed in vacuo. The residue was purified by column chromatography on neutral aluminium oxide (Brockman grade 2, petroleum ether/ethyl acetate mixtures) to yield **31** (oil, 119 mg, yield 85%) as an anomeric mixture (α/β, 2.5:1). Data for the α-anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80–6.75 (aromatic protons), 6.74 (br. s, 1 H, 1-H), 5.66 (t, $J_{2,3}$ = $J_{3,4}$ = 9.9 Hz, 1 H, 3-H), 5.23 (t, $J_{4,5}$ = 9.9 Hz, 1 H, 4-H), 5.05 (dd, $J_{1,2}$ = 3.3 Hz, 1 H, 2-H), 4.50–4.10 (m, 6 H), 2.14, 2.11, 2.09 (3×s, 9 H, 3×-$COCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.3, 169.7, 169.4, 154.0, 143.0, 142.8, 141.2, 128.7, 127.9, 127.1, 125.0, 124.5, 120.0, 119.1, 91.8 (C-1), 73.0, 70.6, 67.6, 61.2, 46.3, 20.5 ppm. Significant signals for the β-anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.90 (br. s, 1 H, 1-H), 5.39 (t, $J_{2,3}$ = $J_{3,4}$ = 9.9 Hz, 1 H, 3-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 94.2 (C-1) ppm. $C_{35}H_{32}F_3NO_{11}$ (699.63): calcd. C 60.09, H 4.61; found C 59.90, H 4.50.

Methyl 2-*O*-(Fluorenyl)methyloxycarbonyl-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (33): Donor **31** (35 mg, 0.05 mmol) and acceptor **32** (13 mg, 0.035 mmol) were coevaporated (3×) in anhydrous toluene and then dried in vacuo for 30 min. The mixture was then dissolved at 0 °C (ice bath) under an atmosphere of argon with anhydrous DCE (1 mL) in the presence of freshly activated 4 Å AW molecular sieves. After stirring for 15 min, a solution of $Bi(OTf)_3$ in dioxane (17 mg mL^{-1}, 135 μL, 3.5 μmol) was added. After a further 10 min the ice bath was removed and the mixture was left whilst stirring until TLC analysis displayed the consumption of the donor (ca. 90 min from the addition of the promoter). The reaction was quenched with pyridine, and the mixture was filtered through a short pad of silica gel. The residue from the filtered liquor was submitted to silica-gel flash chromatography (toluene/acetone, 7:1) to yield disaccharide **33** as a foam (21 mg, 70% yield). $[\alpha]_D^{25}$ = +29.3 (c = 1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.70–7.20 (aromatic protons), 5.56 (s, 1 H, benzylidene acetal CH), 5.27 (t, $J_{2,3}$ = $J_{3,4}$ = 9.7 Hz, 1 H, 3′-H), 5.09 (t, $J_{4,5}$ = 9.7 Hz, 1 H, 4′-H), 4.97 (d, $J_{1,2}$ = 7.5 Hz, 1 H, 1′-H), 4.93 (dd, 1 H, 2′-H), 4.83 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.72 (s, 2 H, benzyl CH_2), 4.40 (dd, ^3J = 7.8, 10.5 Hz, 1 H, Fmoc -OCH_2CH), 4.32–4.06 (m, 5 H, overlapped signals), 3.98 (t, $J_{2,3}$ = $J_{3,4}$ = 9.7 Hz, 1 H, 3-H), 3.86 (td, ^3J = 4.5, 9.7 Hz, 1 H, 5-H), 3.80–3.70 (m, 2 H, 2-H, 6ax-H), 3.70–3.65 (m, 1 H, 5′-H), 3.60 (t, 1 H, 4-H), 3.42 (s, 3 H, -OCH_3), 2.09, 2.03, 1.94 (3×s, 9 H, 3×-$COCH_3$) ppm. ^{13} C NMR ($CDCl_3$, 75 MHz): δ = 170.4, 170.0, 169.2, 169.4, 154.1, 133.1, 143.2, 142.9, 141.2, 138.3, 137.4, 128.9–127.2, 126.0, 125.0, 129.0, 101.3 (×2) (C-1′ and benzylidene acetal CH), 100.1 (C-1), 82.3, 79.5, 77.7, 77.2, 75.4, 75.2, 72.8, 71.9, 70.2, 69.1, 68.5, 62.2, 61.9, 55.4, 46.5, 20.6, 20.5 (×2) ppm. $C_{48}H_{50}O_{16}$ (882.91): calcd. C 65.30, H 5.71; found C 65.05, H 5.53.

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