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Temperature-Controlled Regioselectivity in the Reductive Cleavage of *p*-Methoxybenzylidene Acetals

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Received June 14, 2004

The regioselective ring opening of pyranosidic 4,6-*p*-methoxybenzylidene acetals with BH_3/Bu_2BOTf in THF can be tuned by adjusting the reaction temperature and reagent concentrations. Reductive cleavage at 0 °C resulted in the exclusive formation of 4-*O*-*p*-methoxybenzyl (PMB) ethers, whereas reaction at −78 °C produced 6-*O*-PMB ethers in high yields. The latter condition was observed to be compatible with a variety of acid-sensitive functional groups, including allyl and enol ethers. The presence of water does not interfere with reductive ring opening and may contribute toward in situ generation of H^+ as a catalyst for 6-*O*-PMB ether formation. Reductive cleavage under rigorously aprotic conditions is greatly decelerated, and yields only the 4-*O*-PMB ether. The temperature-dependent reductive cleavage of the 4,6-acetal can be described in terms of kinetic versus thermodynamic control: Lewis-acid coordination of the more accessible O-6 is favored at higher temperatures, whereas protonation of the more basic but sterically encumbered O-4 predominates at low temperatures.

Introduction

Benzylidene and *p*-methoxybenzylidene (anisylidene) acetals are widely employed as protecting groups for intermediates possessing 1,2- and 1,3-diols.[1] An especially appealing feature of these acetals is their readiness to undergo reductive cleavage to regioselectively protected alcohols. Reaction conditions have been developed to favor the formation of either regioisomer: for example, reduction of 4,6-anisylidene-protected glucopyranosides with $NaCNBH_3$ under protic conditions produces 6-*O*-*p*-methoxybenzyl (PMB) ethers in high yield,[2] whereas reductive cleavage with iBu_2AlH[3] or $NaCNBH_3$ and TMSCl[4] yields 4-*O*-PMB ethers. Regioselectivity is thought to be determined in the first case by differences in Lewis basicity of the acetal oxygens (O-4 > O-6) and in the second case by accessibility to the bulky Lewis acid (O-6 > O-4). The choice of solvent has also been shown to play a role in some instances.[5] However, despite the variety of methods available for reductive cleavage of acetals,[5−10] this transformation is at times limited by unpredictable yields or regioselectivities, as well as by the sensitivities of acid-labile or easily reducible functional groups.

A mild condition for the reductive cleavage of 4,6-benzylidene-protected pyranosides was recently reported by Jiang and Chan, using BH_3 in THF at 0 °C as the hydride source and Bu_2BOTf as a Lewis acid.[11] This reaction afforded 4-*O*-benzyl ethers in good to excellent yields and with complete regioselectivity in most cases. We have recently used similar conditions to prepare 4-*O*-PMB ethers of orthogonally protected glucosamines from their corresponding 4,6-anisylidene acetals, without detriment to the remaining functional groups.[12] However, at 0 °C the BH_3/Bu_2BOTf conditions were found not to be compatible with alkenes, such as allyl ethers.[13]

Here we report that the reductive cleavage of anisylidene acetals by BH_3/Bu_2BOTf can selectively produce either regioisomer, simply by adjusting the reaction temperatures and reagent concentrations. Strictly anhydrous conditions are not required because any traces of water are consumed by excess borane, obviating the need for molecular sieves. Furthermore, reductive ring opening at low temperatures was determined to be compatible with sensitive functional groups such as allyl and enol ethers and other ketals, considerably expanding the scope of this transformation. In addition to demonstrating the practical benefits of this method for protecting group

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(9) DeNinno, M. P.; Etienne, J. B.; Duplainter, K. C. *Tetrahedron Lett.* **1995**, *36*, 669.

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10.1021/jo048999m CCC: $27.50
Published on Web 09/18/2004

manipulations, our studies include some mechanistic explanations for the regioselectivity of reductive cleavage.

Results and Discussion

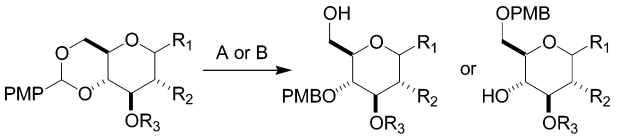
Several anisylidene-protected pyranosides were subjected to reductive ring opening with the conditions outlined below, to obtain 4-*O*- and 6-*O*-PMB ethers in high yields and regioselectivities. Treatment of the anisylidene acetals with excess borane at high concentrations (10 equiv, 1 M in THF) followed by the addition of commercially available Bu_2BOTf (2 equiv) at 0 °C produced exclusively the corresponding 4-*O*-PMB ethers, in accord with previous reports (see Table 1, condition A).[11] On the other hand, treating the anisylidene acetals with BH_3 and Bu_2BOTf under more dilute conditions (5 equiv of BH_3, 0.2 M in THF) and at low temperatures (−78 to −50 °C) produced the 6-*O*-PMB ethers in excellent yields (see Table 1, condition B). Hydrogen evolution was often observed upon addition of BH_3 prior to the addition of Bu_2BOTf at 0 °C, indicating consumption of adventitious water. The reactions were quenched with Et_3N followed by the slow addition of MeOH at 0 °C, and could be concentrated without aqueous workup. The regioselectivities were confirmed by acetylation of the alcohols and characterization by ^1H NMR spectroscopy.

The temperature-dependent reductive ring openings proceeded with complete regioselectivity in nearly every situation save for acetal **1g**, which produced a 3.5:1 mixture of 6-*O*- to 4-*O*- PMB ethers under the low-temperature conditions. The reaction pathways are likely to be influenced by local steric crowding (see below); in the case of **1g**, the phthalimide at C-2 may force the bulky *tert*-butyldimethylsilyl (TBS) ether at C-3 toward O-4 and hinder its activation.[14] The azide group on disaccharide **1h** also survived the reduction conditions yielding the desired PMB ethers in good yields. It is worth mentioning that no 4,6-diol was observed, a side product that is often produced by other reductive cleavage conditions.[1−3]

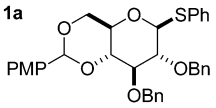
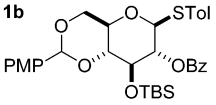
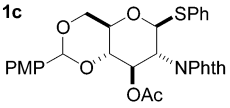
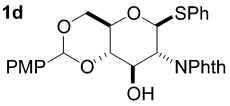
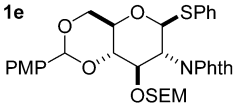
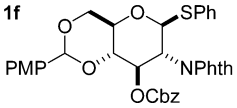
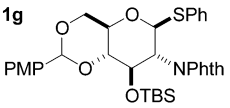
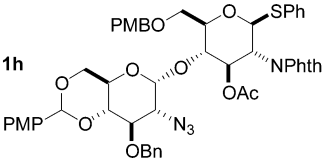
In addition to the protecting groups above, reductive cleavage with BH_3/Bu_2BOTf was determined to be compatible with several other functional groups at −78 °C. In particular, the allyl ether of **1i**, the allyloxycarbonyl (AOC) ester of **1j**, and the dimethyl ketal of **1k** all remained intact during the reductive cleavage of the anisylidene acetals to their corresponding 6-*O*-PMB ethers (see Table 2). Glycals (1,2-unsaturated pyranosides) were also found to be compatible with the low-temperature reaction conditions: reductive cleavage of glucal **1*l*** afforded 6-*O*-PMB ether **3*l*** in 85% isolated yield. Reactions at higher temperatures or reagent concentrations were not well-suited with these more reactive functional groups. For example, in the case of dimethyl ketal **1k** the temperature was kept strictly at −78 °C to minimize reductive ring opening of the 2,3-acetonide.[15]

We suspected that more than one acid catalyst was responsible for the observed regioselectivities. In particular, we considered that the low-temperature reductive cleavage might be catalyzed by the in situ generation of H^+, formed by the hydrolysis of Bu_2BOTf. Low-temperature reductive cleavage of benzylidene acetals to the O-6 ether has been reported previously with use of TfOH.[8] Our initial attempts at reductive cleavage under aprotic conditions did not appear to affect the reaction outcome: for example, reduction of anisylidene acetal **4** at −78 °C in base-washed glassware with molecular sieves and freshly prepared Bu_2BOTf[16] yielded 6-*O*-PMB ether **5a** as the sole product (see Scheme 1). However, when 2,6-

TABLE 1. Regioselective Ring Opening of 4,6-Anisylidene Acetals[a,b]



1 2 3

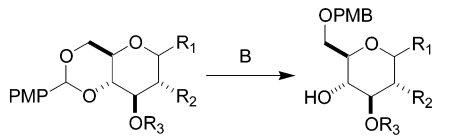
Entry	react cond A[c]	react cond B[d,e]
1a 	**2a** (84%)	**3a** (98%)
1b 	**2b** (95%)	**3b** (90%)
1c 	**2c** (89%)	**3c** (98%)
1d 	**2d** (77%)	**3d** (98%)
1e 	**2e** (86%)	**3e** (95%)
1f 	**2f** (82%)	**3f** (85%)
1g 	**2g** (93%)	**3g** (69%) **2g** (20%)
1h 	**2h** (85%)	**3h** (93%)

[a] Isolated yields. [b] Selected acronyms: Bz = benzoyl; Cbz = benzyloxycarbonyl; Phth = phthaloyl; PMB = *p*-methoxybenzyl; PMP = *p*-methoxyphenyl; SEM = (2-trimethylsilyl)ethoxymethyl; TBS = *tert*-butyldimethylsilyl. [c] Reaction condition A: BH_3 (1 M in THF, 10 equiv), Bu_2BOTf (2 equiv), 0 °C. [d] Reaction condition B: BH_3 (0.2 M in THF, 5 equiv), Bu_2BOTf (2.5 equiv), −78 °C. [e] For entries **1c**, **1e**, and **1g**, the reactions were run at −50 °C.

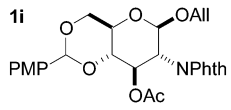
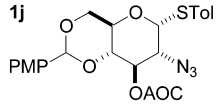
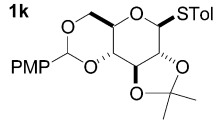
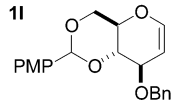
(14) It should be noted that the 3-*O*-TBS ether does not compromise the regioselectivity in the reductive cleavage of compound **1b**.

(15) The reductive cleavage of acetonides to isopropyl ethers by BH_3/Bu_2BOTf at 0 °C has been previously described; see ref 11.

TABLE 2. Reductive Ring Opening of 4,6-Anisylidene Acetals with Acid- or Borane-Sensitive Groups[a,b]

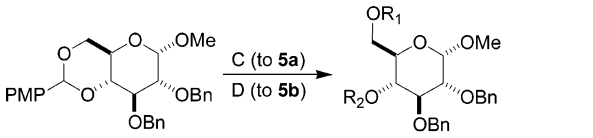


1 3

Entry	React cond B[c]
1i 	**3i** (95%)
1j 	**3j** (66%)
1k 	**3k** (85%)[d]
1l 	**3l** (85%)

[a] Isolated yields. [b] Selected acronyms: All = allyl; AOC = allyloxycarbonyl; Phth = phthaloyl; PMB = *p*-methoxybenzyl; PMP = *p*-methoxyphenyl. [c] Reaction condition B: BH_3 (0.2 M in THF, 5 equiv), Bu_2BOTf (2.5 equiv), −78 °C. [d] A small amount (<5%) of side product with cleaved acetonide was also observed.

SCHEME 1. Reductive Cleavage with Freshly Prepared Bu_2BOTf[a,b]



4

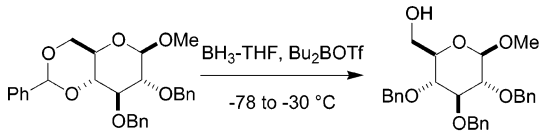
5a: R_1 = PMB, R_2 = H (95% yield)
5b: R_1 = H, R_2 = PMB (79% yield)

[a] Isolated yields. [b] All reactions were performed in base-washed glassware. Reaction condition C: BH_3 (0.2 M in THF, 5 equiv), Bu_2BOTf (2.5 equiv), 4A mol sieves, −78 °C, 1.5 h. Reaction condition D: BH_3 (0.2 M in THF, 5 equiv), Bu_2BOTf (2.5 equiv), 4A mol sieves, DTBMP (2.5 equiv), −78 to −45 °C, 36 h. See ref 16 for the preparation of Bu_2BOTf.

di-*tert*-butyl-4-methylpyridine (DTBMP) was added as an acid scavenger the rate of reduction was greatly decelerated, with no discernible ring opening after several hours at −78 °C. Slowly warming the reaction mixture to −45 °C resulted in the exclusive formation of 4-*O*-PMB ether **5b**. The formation of the 6-*O*-PMB ether is thus due to the remarkably high catalytic activity of the trace Bronsted acid.

The regioselectivity of the reductions presented here can be readily described in terms of kinetic versus thermodynamic control.[17] The O-6 acetal oxygen is sterically more accessible for coordinating with Bu_2BOTf or H^+, leading to rapid acetal cleavage at 0 °C. Lowering the temperature reduces both the rate of Lewis-acid complexation and the rate of hydride delivery to the

SCHEME 2. Reductive Cleavage of Benzylidene Acetal 6



6 7 (82% yield)

activated complex, with a negative effect on the formation of the 4-*O*-PMB ether. In comparison, protonation of the acetal is expected to be diffusion controlled and thus presumably dictated by thermodynamics, which would favor activation of the more basic O-4 oxygen and cleavage to the 6-*O*-PMB ether.

Further support for this notion can be drawn from investigations on the effect of reagent concentration in the regioselectivity of acetal cleavage. Reduction of acetals **1c** and **4** at −78 °C with higher reagent concentrations (cf. reaction condition A) also produced 6-*O*-PMB ethers (**3c** and **5a**, respectively) in high yield (>95%), whereas reductions conducted at 0 °C with lower reagent concentrations (cf. reaction condition B) produced a mixture of regioisomers, again favoring the 6-*O*-PMB ether (**3c**:**2c** = 2.5:1; **5a**:**5b** = 11:1). These results suggest that protonation is faster than the rate of acetal−Bu_2BOTf complex formation at low temperatures or under the more dilute conditions, and provide additional testimony to the high catalytic activity of the Bronsted acid.

Finally, it is worth mentioning that while 4,6-anisylidene acetals could be reductively cleaved at low temperatures to produce 6-*O*-PMB ethers, the less reactive 4,6-benzylidene acetals were inert under these conditions. Benzylidene acetal **6** was initially subjected to BH_3/Bu_2BOTf at −78 °C (reaction condition B), then slowly warmed over a period of hours until reductive cleavage was observed at −30 °C, yielding exclusively 4-*O*-benzyl ether **7** in 82% yield (see Scheme 2). As it is already known that excess TfOH can activate the cleavage of benzylidene acetals at −78 °C to yield 6-*O*-benzyl ethers,[8] our result indicates that catalytic quantities of acid are not sufficient to activate the reductive cleavage of benzylidene acetals at low temperatures.

Experimental Section

General Procedures for Reductive Ring Opening of *p*-Methoxybenzylidene Acetals. The borane−THF complex (1 M in THF), Bu_2BOTf (1 M in CH_2Cl_2), and reagents for the preparation of neat Bu_2BOTf were obtained from Aldrich and used as received. *Note*: Neat Bu_2BOTf is highly pyrophoric and must be distilled and stored under an inert atmosphere (it can be kept as a solid at −20 °C). In addition, methane is generated during the preparation of Bu_2BOTf, resulting in a highly combustible mixture that must be vented with caution.

Reaction condition A: An oven-dried, 10-mL round-bottomed reaction flask containing acetal **1a** (50 mg, 0.09 mmol) was cooled to −10 °C under Ar and treated with borane−THF complex (0.9 mL of a 1 M solution in THF). The mixture was stirred at −10 °C for 15 min, then treated with Bu_2BOTf (176 μL of a 1 M solution in CH_2Cl_2) and warmed to 0 °C over a period of 10 min. The mixture was stirred at 0 °C

(16) Mukaiyama, T.; Inoue, T. *Chem. Lett.* **1976**, 559. See note in the Experimental Section.

(17) For a closely related discussion in an earlier work, see: Garegg, P. J.; Hultberg, H.; Wallin, S. *Carbohydr. Res.* **1982**, *108*, 97.

for an additional 2 h, cooled to −10 °C, and treated with Et_3N (0.1 mL), then quenched by the dropwise addition of MeOH (3.0 mL) until effervescence ceased. The mixture was warmed to room temperature and stirred for 30 min, then concentrated by rotary evaporation. Volatile components in the reaction mixture were removed by azeotropic distillation with MeOH (2 × 5 mL) and toluene (5 mL). The product was purified by silica gel flash chromatography, using a 20−50% EtOAc−hexanes gradient to yield the desired 4-*O*-PMB ether.

Reaction condition B: An oven-dried, 10-mL round-bottomed reaction flask containing acetal **1a** (50 mg, 0.09 mmol) was dissolved in freshly distilled THF (1.8 mL) and cooled to −78 °C under argon, then treated with borane−THF complex (0.4 mL of a 1 M solution in THF). After 15 min, the mixture was treated with Bu_2BOTf (225 μL of a 1 M solution in CH_2Cl_2) and stirred at −78 °C for up to 8 h or at −50 °C for up to 6 h. The reaction was then quenched with Et_3N (0.1 mL), followed by the dropwise addition of MeOH (3.0 mL) until effervescence ceased. The mixture was warmed to room temperature and stirred for 30 min, then concentrated by rotary evaporation and purified as described previously to yield the desired 6-*O*-PMB ether.

Reaction condition C: A base-washed and oven-dried, 10-mL round-bottomed reaction flask containing acetal **4** (40 mg, 0.08 mmol) and 4A molecular sieves (200 mg) was charged with freshly distilled THF (1.6 mL) and stirred for 30 min at room temperature under argon. The reaction mixture was cooled to −78 °C and treated with borane−THF complex (0.41 mL of a 1 M solution in THF). After 15 min, the mixture was treated with freshly prepared Bu_2BOTf [16] (200 μL of a 1 M solution in CH_2Cl_2) and stirred at −78 °C for an additional 3 h. The reaction was then quenched with Et_3N (0.1 mL), followed by the dropwise addition of MeOH (3 mL) until effervescence ceased. The mixture was warmed to room temperature and stirred for 30 min, then filtered through Celite, concentrated by rotary evaporation, and purified as described in procedure A to yield the desired 6-*O*-PMB ether.

Reaction condition D: As in reaction condition C, but with the addition of 2,6-di-*tert*-butyl-4-methylpyridine (2.5 equiv) prior to treatment with BH_3−THF. Following addition of the freshly prepared Bu_2BOTf, the mixture was stirred at −78 °C for 3 h, at −60 °C for 17 h, and finally at −45 °C for 16 h. The reaction mixture was quenched and purified as described in reaction condition A to yield the desired 4-*O*-PMB ether.

The regioselectivity of the reductive ring opening was confirmed by acetylation of the free hydroxyl and characterization by ^{1}H NMR spectroscopy. Reduction products were dissolved in pyridine (0.5 mL) and treated with acetic anhydride (250 μL) at 0 °C, stirred overnight at room temperature, then quenched at 0 °C with EtOH and concentrated to dryness followed by azeotropic distillation with toluene (3 × 2 mL). Purification by silica gel flash chromatography with an EtOAc−hexanes gradient afforded the acetate in nearly quantitative yield.

Thiophenyl 6-*O*-Acetyl-2,3-*O*-dibenzyl-4-*O*-(*p*-methoxybenzyl)-β-D-glucopyranoside (6-*O*-acetyl 2a). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47−7.52 (m, 2 H), 7.19−7.34 (m, 13 H), 7.09 (d, 2 H, *J* = 8.1 Hz), 6.76 (d, 2 H, *J* = 8.1 Hz), 4.84 (d, 1 H, *J* = 10.5 Hz), 4.83 (d, 1 H, *J* = 10.2 Hz), 4.77 (d, 1 H, *J* = 11.1 Hz), 4.69 (d, 1 H, *J* = 11.7 Hz), 4.65 (d, 1 H, *J* = 10.5 Hz), 4.56 (d, 1 H, *J* = 9.9 Hz), 4.42 (d, 1 H, *J* = 10.5 Hz), 4.26 (d, 1 H, *J* = 11.7 Hz), 4.14 (dd, 1 H, *J* = 4.2 Hz, 11.7 Hz,), 3.72 (s, 3 H), 3.64 (m, 1 H), 3.39−3.47 (m, 3 H), 2.00 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 159.5, 138.2, 137.9, 133.6, 132.0, 129.8, 129.7, 128.8, 128.5, 128.4, 128.2, 127.9, 127.8, 127.7, 127.6, 113.9, 87.5, 86.7, 80.9, 77.1, 76.9, 75.8, 75.5, 74.7, 63.2, 55.2, 20.8; IR (thin film) 1742, 1613, 1514, 1455, 1362, 1249, 1066, 1030, 822, 741, 698 cm^{-1}; $[\alpha]^{20}_D$ +5.0 (*c* 1.02, $CHCl_3$); ESI-MS *m*/*z* 637 $[M + Na]^+$.

Thiophenyl 4-*O*-Acetyl-2,3-*O*-dibenzyl-6-*O*-(*p*-methoxybenzyl)-β-D-glucopyranoside (4-*O*-acetyl 3a). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56−7.59 (m, 2 H), 7.23−7.41 (m, 15 H), 6.59 (d, 2 H, *J* = 8.1 Hz), 5.01 (t, 1 H, *J* = 8.7 Hz), 4.87 (d, 1 H, *J* = 9.9 Hz), 4.80 (d, 1 H, *J* = 11.7 Hz), 4.70 (d, 1 H, *J* = 9.9 Hz), 4.68 (d, 1 H, *J* = 9.9 Hz), 4.63 (d, 1 H, *J* = 11.7 Hz), 4.45 (s, 2 H), 3.82 (s, 3 H), 3.67 (t, 1 H, *J* = 8.7 Hz), 3.52−3.60 (m, 4 H), 1.90 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 159.2, 138.1, 137.8, 133.5, 131.9, 130.1, 129.4, 128.9, 128.4, 128.3, 127.9, 127.7, 127.6, 127.5, 113.7, 87.5, 84.0, 80.6, 77.6, 75.5, 75.4, 73.2, 70.8, 69.5, 55.2, 20.8; IR (thin film) 1746, 1613, 1584, 1513, 1455, 1362, 1231, 1175, 1050, 821, 744, 689 cm^{-1}; $[\alpha]^{20}_D$ −15.5 (*c* 1.02, $CHCl_3$); ESI-MS *m*/*z* 637 $[M + Na]^+$.

Thiotolyl 6-*O*-Acetyl-2-*O*-benzoyl-3-*O*-(*tert*-butyldimethylsilyl)-4-*O*-(*p*-methoxybenzyl)-β-D-glucopyranoside (6-*O*-acetyl 2b). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, 2 H, *J* = 7.5 Hz), 7.60 (m, 1 H), 7.46 (m, 2 H), 7.30 (d, 2 H, *J* = 8.1 Hz), 7.22 (d, 2 H, *J* = 8.1 Hz), 7.04 (d, 2 H, *J* = 7.8 Hz), 6.86 (d, 2 H, *J* = 8.1 Hz), 5.16 (t, 1 H, *J* = 9.4 Hz), 4.77 (d, 1 H, *J* = 10.5 Hz), 4.64 (d, 1 H, *J* = 9.9 Hz), 4.45 (d, 1 H, *J* = 11.1 Hz), 4.40 (dd, 1 H, *J* = 1.8 Hz, 12.9 Hz), 4.06 (dd, 1 H, *J* = 4.8 Hz, 11.7 Hz), 3.92 (t, 1 H, *J* = 8.5 Hz), 3.80 (s, 3 H), 3.58 (m, 1 H), 3.47 (t, 1 H, *J* = 9.1 Hz), 2.31 (s, 3H), 2.06 (s, 3 H), 0.80 (s, 9 H), 0.37 (s, 3 H), −0.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 165.3, 159.3, 138.0, 133.0, 130.2, 129.9, 129.6, 129.4, 129.2, 128.3, 113.8, 99.5, 68.8, 78.0, 77.1, 76.8, 74.9, 72.3, 63.1, 55.2, 29.6, 25.6, 21.1, 20.8, 1.0; $[\alpha]^{20}_D$ +22.8 (*c* 0.64, $CHCl_3$); ESI-MS *m*/*z* 689 $[M + Na]^+$.

Thiotolyl 4-*O*-Acetyl-2-*O*-benzoyl-3-*O*-(*tert*-butyldimethylsilyl)-6-*O*-(*p*-methoxybenzyl)-β-D-glucopyranoside (4-*O*-acetyl 3b). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, 2 H, *J* = 8.4 Hz), 7.59 (m, 1 H), 7.46 (m, 2 H), 7.32 (d, 2 H, *J* = 7.2 Hz), 7.24 (d, 2 H, *J* = 7.2 Hz), 6.99 (d, 2 H, *J* = 7.8 Hz), 6.86 (d, 2 H, *J* = 7.2 Hz), 5.18 (t, 1 H, *J* = 9.3 Hz), 4.96 (t, 1 H, *J* = 9.3 Hz), 4.70 (d, 1 H, *J* = 10.2 Hz), 4.44 (d, 2 H, *J* = 11.7 Hz), 4.40 (d, 2 H, *J* = 12.3 Hz), 3.98 (t, 1 H, *J* = 8.7 Hz), 3.81 (s, 3 H), 3.53−3.63 (m, 3 H), 2.29 (s, 3 H), 1.97 (s, 3 H), 0.71 (s, 9 H), −0.03 (s, 3 H), −0.20 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7 165.1, 159.2, 137.9, 133.1, 132.8, 130.2, 130.0, 129.9, 129.6, 129.5, 129.2, 128.4, 113.7, 96.5, 86.8, 77.7, 74.6, 73.3, 73.2, 72.4, 70.0, 55.3, 29.7, 21.2, 21.1, 17.7, −4.1, −4.6; IR (thin film) 1734, 1613, 1514, 1493, 1373, 1250, 1228, 1176, 1146, 1092, 1057, 841, 810, 779, 710 cm^{-1}; $[\alpha]^{20}_D$ +17.0 (*c* 1.00, $CHCl_3$); ESI-MS *m*/*z* 689 $[M + Na]^+$.

Thiophenyl 3,6-*O*-Diacetyl-2-deoxy-4-*O*-(*p*-methoxybenzyl)-2-phthalimido-β-D-glucopyranoside (6-*O*-acetyl 2c). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84−7.88 (m, 2 H), 7.73−7.75 (m, 2 H), 7.38−7.40 (m, 2 H), 7.25−7.27 (m, 3 H), 7.15 (d, 2 H, *J* = 8.4 Hz), 6.83 (d, 2 H, *J* = 8.1 Hz), 5.80 (t, 1 H, *J* = 9.5 Hz), 5.70 (d, 1 H, *J* = 10.5 Hz), 4.54 (d, 1 H, *J* = 10.8 Hz), 4.47 (d, 1 H, *J* = 11.1 Hz), 4.41 (dd, 1 H, *J* = 2.1, 12.3 Hz), 4.24 (t, 1 H, *J* = 10.3 Hz), 4.21 (dd, 1 H, *J* = 5.1, 12.3 Hz), 3.79 (m, 1 H), 3.78 (s, 3 H), 3.67 (t, 1 H, *J* = 9.4 Hz), 2.07 (s, 3 H), 1.82 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 169.9, 159.5, 134.4, 134.1, 133.1, 131.3, 129.5, 129.4, 128.8, 128.2, 123.7, 123.4, 113.9, 99.9, 82.7, 75.7, 74.2, 62.9, 55.2, 54.0, 20.8, 20.6; IR (thin film) 1777, 1745, 718, 1612, 1514, 1385, 1225, 1088, 1034, 751, 720 cm^{-1}; $[\alpha]^{20}_D$ +34.0 (*c* 1.00, $CHCl_3$); ESI-MS *m*/*z* 628 $[M + Na]^+$.

Thiophenyl 3,4-*O*-Diacetyl-2-deoxy-6-*O*-(*p*-methoxybenzyl)-2-phthalimido-β-D-glucopyranoside (4-*O*-acetyl 3c). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87−7.90 (m, 2 H), 7.75−7.78 (m, 2 H), 7.42−7.45 (m, 2 H), 7.24−7.29 (m, 5 H), 6.89 (d, 2 H, *J* = 8.7 Hz), 5.82 (t, 1 H, *J* = 9.6 Hz), 5.74 (d, 1 H, *J* = 10.5 Hz), 5.16 (t, 1 H, *J* = 9.6 Hz), 4.52 (d, 1 H, *J* = 11.4 Hz), 4.45 (d, 1 H, *J* = 11.7 Hz), 4.38 (t, 1 H, *J* = 10.5 Hz), 3.89 (m, 1 H), 3.84 (s, 3 H), 3.63 (d, 2 H, *J* = 4.2 Hz), 1.92 (s, 3 H), 1.83 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 169.6, 159.2, 134.3, 132.8, 131.4, 129.9, 129.4, 128.9, 128.1, 123.6, 113.7, 83.1, 77.5, 73.2, 71.8, 69.6, 68.8, 55.3, 53.7, 20.6, 20.4; IR (thin film) 1777, 1751, 1718, 1612, 1514, 1384, 1235, 1070, 1038, 752, 720 cm^{-1}; $[\alpha]^{20}_D$ +43.1 (*c* 1.00, $CHCl_3$); ESI-MS *m*/*z* 628 $[M + Na]^+$.

Thiophenyl 6-*O*-Acetyl-2-deoxy-4-*O*-(*p*-methoxybenzyl)-3-*O*-(2-(trimethylsilyl)ethoxymethyl)-2-phthalimido-β-D-

glucopyranoside (6-*O*-acetyl 2e). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82−7.94 (m, 2 H), 7.73−7.77 (m, 2 H), 7.38−7.42 (m, 2 H), 7.20−7.24 (m, 5 H), 6.85 (d, 2 H, J = 8.7 Hz), 5.52 (d, 1 H, J = 10.5 Hz), 4.68−4.71 (m, 3 H), 4.38−4.53 (m, 3 H), 4.26 (t, 1 H, J = 10.2 Hz), 4.20 (dd, 1 H, J = 5.1, 12.0 Hz), 3.80 (s, 3 H), 3.70 (m, 1 H), 3.55 (t, 1 H, J = 9.3 Hz), 3.06−3.13 (m, 2 H), 2.06 (s, 3 H), 0.31−0.42 (m, 1 H), −0.05 (m, 1 H), −0.22 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.6, 132.1, 132.0, 129.7, 128.7, 127.8, 123.4, 113.9, 97.2, 83.4, 81.0, 78.2, 74.7, 65.9, 63.0, 55.3, 54.8, 29.7, 20.9, 17.2, −1.5; IR (thin film) 1777, 1742, 1716, 1613, 1514, 1388, 1249, 1088, 1037, 859, 834, 749, 720, 691 cm^{-1}; $[\alpha]^{20}_D$ +32.5 (*c* 0.80, $CHCl_3$); ESI-MS *m*/*z* 716 $[M + Na]^+$.

Thiophenyl 4-*O*-Acetyl-2-deoxy-6-*O*-(*p*-methoxybenzyl)-3-*O*-(2-(trimethylsilyl)ethoxymethyl)-2-phthalimido-*β*-D-glucopyranoside (4-*O*-acetyl 3e). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82−7.92 (m, 2 H), 7.73−7.77 (m, 2 H), 7.39−7.42 (m, 2 H), 7.18−7.23 (m, 5 H), 6.86 (d, 2 H, J = 8.1 Hz), 5.55 (d, 1 H, J = 10.2 Hz), 5.01 (t, 1 H, J = 9.3 Hz), 4.56 (d, 1 H, J = 6.9 Hz), 4.55 (d, 1 H, J = 6.6 Hz), 4.53 (t, 1 H, J = 9.3 Hz), 4.46 (s, 2 H), 4.34 (t, 1 H, J = 10.2 Hz), 3.81 (s, 3 H), 3.78 (m, 1 H), 3.59 (d, 2 H, J = 4.2 Hz), 3.08−3.15 (m, 2 H), 1.98 (s, 3 H), 0.41 (m, 1 H), 0.11 (m, 1 H), −0.21 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 159.3, 132.1, 131.9, 129.5, 128.9, 127.8, 123.7, 123.5, 113.8, 99.0, 96.6, 83.7, 78.6, 77.8, 73.3, 72.2, 69.6, 55.4, 54.8, 29.8, 20.9, 17.3, −1.5; IR (thin film) 1777, 1748, 1716, 1613, 1513, 1388, 1225, 1227, 1173, 1108, 1037, 860, 835, 749, 720, 691 cm^{-1}; $[\alpha]^{20}_D$ +67.3 (*c* 1.01, $CHCl_3$); ESI-MS *m*/*z* 716, $[M + Na]^+$.

Thiophenyl 6-*O*-Acetyl-3-*O*-benzyloxycarbonyl-2-deoxy-4-*O*-(*p*-methoxybenzyl)-2-phthalamido-*β*-D-glucopyranoside (6-*O*-acetyl 2f). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70−7.88 (m, 4 H), 7.37−7.40 (m, 2 H), 7.09−7.24 (m, 10 H), 6.79 (d, 2 H, J = 8.7 Hz), 5.68 (t, 1 H, J = 9.3 Hz), 5.64 (d, 1 H, J = 10.5 Hz), 4.90 (s, 2 H), 4.54 (d, 1 H, J = 10.8 Hz), 4.42 (d, 1 H, J = 10.5 Hz), 4.39 (d, 1 H, J = 9.9 Hz), 4.33 (t, 1 H, J = 10.3 Hz), 4.22 (dd, 1 H, J = 4.8, J = 11.7 Hz), 3.77−3.82 (m, 1 H), 3.77 (s, 3 H), 3.71 (t, 1 H, J = 9.6 Hz), 2.05 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 159.4, 154.5, 134.8, 134.2, 134.1, 133.1, 131.3, 129.7, 129.2, 128.8, 128.4, 128.3, 128.2, 127.9, 123.6, 113.8, 82.8, 78.3, 76.84, 75.4, 74.4, 69.8, 62.8, 55.2, 53.8, 20.8; IR (thin film) 1777, 1750, 1718, 1613, 1513, 1385, 1248, 1089, 1034, 750, 720, 693 cm^{-1}; $[\alpha]^{20}_D$ +19.5 (*c* 0.77, $CHCl_3$); ESI-MS *m*/*z* 720 $[M + Na]^+$.

Thiophenyl 4-*O*-Acetyl-3-*O*-benzyloxycarbonyl-2-deoxy-6-*O*-(*p*-methoxybenzyl)-2-phthalamido-*β*-D-glucopyranoside (4-*O*-acetyl 3f). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82−7.90 (m, 2 H), 7.75−7.80 (m, 2 H), 7.42 (dd, 2 H, J = 1.5, 8.1 Hz), 7.17−7.29 (m, 10 H), 6.89 (d, 2 H, J = 8.7 Hz), 5.71 (t, 1 H, J = 9.7 Hz), 5.69 (d, 1 H, J = 10.5 Hz), 5.17 (t, 1 H, J = 9.7 Hz), 4.95 (d, 1 H, J = 12.3 Hz), 4.89 (d, 1 H, J = 12.3 Hz), 4.50 (d, 1 H, J = 11.4 Hz), 4.46 (t, 1 H, J = 10.5 Hz), 4.45 (d, 1 H, J = 11.4 Hz), 3.89 (m, 1 H), 3.84 (s, 3 H), 3.63 (d, 2 H, J = 4.2 Hz), 1.80 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.4, 159.2, 154.4, 134.8, 134.2, 132.7, 131.4, 129.9, 129.4, 128.9, 128.4, 128.3, 128.1, 127.9, 123.7, 123.6, 113.7, 83.2, 77.5, 75.4, 73.2, 69.7, 69.6, 68.9, 55.3, 53.5, 20.4; IR (thin film) 1755, 1718, 1613, 1513, 1385, 1251, 1221, 1067, 1036, 751, 720, 695 cm^{-1}; $[\alpha]^{20}_D$ +38.0 (*c* 1.00, $CHCl_3$); ESI-MS *m*/*z* 720 $[M + Na]^+$.

Thiophenyl 6-*O*-Acetyl-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-4-*O*-(*p*-methoxybenzyl)-2-phthalimido-*β*-D-glucopyranoside (6-*O*-acetyl 2g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79−7.98 (m, 4 H), 7.39−7.42 (m, 2 H), 7.27−7.31 (m, 5 H), 6.90 (d, 2 H, J = 8.4 Hz), 5.60 (d, 1 H, J = 10.5 Hz), 4.80 (d, 1 H, J = 11.1 Hz), 4.53 (t, 1 H, J = 9.7 Hz), 4.49 (d, 1 H, J = 11.1 Hz), 4.46 (d, 1 H, J = 11.4 Hz), 4.30 (t, 1 H, J = 10.2 Hz), 4.16 (dd, 1 H, J = 5.4, 11.7 Hz), 3.84 (s, 3 H), 3.76 (m, 1 H), 3.51 (t, 1 H, J = 9.0 Hz), 2.11 (s, 3 H), 0.79 (s, 9 H), 0.04 (s, 3 H), −0.38 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 159.2, 134.3, 132.4, 132.3, 129.7, 129.0, 128.7, 127.8, 113.8, 83.3, 79.7, 77.2, 74.7, 73.6, 63.2, 56.5, 55.2, 25.7, 20.9, 17.6, −4.1, −4.6; IR (thin film) 1777, 1743, 1716, 1613, 1514, 1471, 1387, 1249, 1109, 1089, 1034, 839, 720, 691 cm^{-1}; $[\alpha]^{20}_D$ +40.2 (*c* 1.02, $CHCl_3$); ESI-MS *m*/*z* 700 $[M + Na]^+$.

Thiophenyl 4-*O*-Acetyl-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-6-*O*-(*p*-methoxybenzyl)-2-phthalimido-*β*-D-glucopyranoside (4-*O*-acetyl 3g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74−7.92 (m, 4 H), 7.36−7.38 (m, 2 H), 7.18−7.23 (m, 5 H), 6.86 (d, 2 H, J = 8.1 Hz), 5.55 (d, 1 H, J = 10.5 Hz), 4.96 (t, 1 H, J = 9.3 Hz), 4.60 (t, 1 H, J = 9.1 Hz), 4.44 (d, 1 H, J = 12.3 Hz), 4.40 (d, 1 H, J = 11.7 Hz), 4.31 (t, 1 H, J = 10.2 Hz), 3.81 (s, 3 H), 3.75 (m, 1 H), 3.52−3.63 (m, 2 H), 1.97 (s, 3 H), 0.66 (s, 9 H), −0.06 (s, 3 H), −0.42 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 159.2, 134.3, 132.4, 132.1, 130.1, 129.5, 128.8, 127.7, 113.7, 83.6, 77.6, 73.5, 73.2, 71.3, 70.0, 56.5, 55.3, 25.3, 21.3, 17.6, −4.5, −4.7; IR (thin film) 1777, 1746, 1716, 1613, 1514, 1470, 1387, 1249, 1227, 1109, 1086, 1060, 1037, 840, 757, 721 cm^{-1}; $[\alpha]^{20}_D$ +54.0 (*c* 1.00, $CHCl_3$); ESI-MS *m*/*z* 700 $[M + Na]^+$.

Thiophenyl 3-*O*-Acetyl-4-*O*-(6-*O*-acetyl-2-azido-2-deoxy-3-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-α-D-glucopyranosyl)-2-deoxy-6-*O*-(*p*-methoxybenzyl)-2-phthalimido-*β*-D-glucopyranoside (6-*O*-acetyl 2h). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83−7.90 (m, 2 H), 7.73−7.75 (m, 2 H), 7.41−7.44 (m, 2 H), 7.17−7.35 (m, 12 H), 6.85−6.89 (m, 4 H), 5.81 (t, 1 H, J = 9.6 Hz), 5.74 (d, 1 H, J = 11.1 Hz), 5.10 (d, 1 H, J = 3.6 Hz), 4.84 (d, 1 H, J = 11.1 Hz), 4.79 (d, 1 H, J = 11.1 Hz), 4.73 (d, 1 H, J = 10.5 Hz), 4.53 (s, 2 H), 4.45 (d, 1 H, J = 11.4 Hz), 4.24 (t, 1 H, J = 10.6 Hz), 4.18 (dd, 1 H, J = 4.2, 11.7 Hz), 4.08 (d, 1 H, J = 10.5 Hz), 3.94 (t, 1 H, J = 8.7 Hz), 3.81 (s, 3 H), 3.78 (s, 3 H), 3.75−3.87 (m, 5 H), 3.48 (t, 1 H, J = 9.3 Hz), 3.34 (dd, 1 H, J = 3.6, 10.5 Hz), 2.00 (s, 3 H), 1.88 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.0, 167.9, 167.3, 159.5, 159.2, 137.6, 134.4, 134.1, 133.1, 131.8, 131.3, 131.2, 130.1, 129.7, 129.5, 129.2, 128.9, 128.5, 128.2, 128.0, 127.9, 123.6, 123.5, 113.8, 99.3, 82.6, 80.1, 78.7, 77.3, 76.1, 75.5, 74.7, 74.1, 73.1, 70.2, 68.7, 63.7, 62.5, 55.3, 55.2, 54.0, 29.7, 20.7, 20.5; IR (thin film) 2109, 1777, 1744, 1718, 1612, 1513, 1385, 1245, 10.73, 1031, 822, 753, 720 cm^{-1}; $[\alpha]^{20}_D$ +41.8 (*c* 1.03, $CHCl_3$); ESI-MS *m*/*z* 1025 $[M + Na]^+$.

Thiophenyl 3-*O*-Acetyl-4-*O*-(4-*O*-acetyl-2-azido-2-deoxy-3-*O*-benzyl-6-*O*-(*p*-methoxybenzyl)-α-D-glucopyranosyl)-2-deoxy-6-*O*-(*p*-methoxybenzyl)-2-phthalimido-*β*-D-glucopyranoside (4-*O*-acetyl 3h). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84−7.90 (m, 2 H), 7.73−7.76 (m, 2 H), 7.41 (m, 2 H), 7.20−7.32 (m, 12 H), 6.86 (m, 4 H), 5.82 (t, 1 H, J = 9.5 Hz), 5.78 (d, 1 H, J = 10.5 Hz), 5.12 (s, 1 H), 5.05 (t, 1 H, J = 9.3 Hz), 4.72 (d, 1 H, J = 11.1 Hz), 4.53 (d, 1 H, J = 11.1 Hz), 4.47 (s, 2 H), 4.39 (d, 1 H, J = 10.5 Hz), 4.30 (d, 1 H, J = 10.5 Hz), 4.26 (t, 1 H, J = 10.5 Hz), 4.95 (t, 1 H, J = 9.2 Hz), 3.81 (s, 3 H), 3.78 (s, 3 H), 3.78−3.89 (m, 5 H), 3.42 (d, 1 H, J = 9.9 Hz), 3.52 (s, 2 H), 1.89 (s, 3 H), 1.83 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 169.5, 167.9, 167.2, 159.2, 158.6, 137.5, 134.3, 134.1, 133.1, 131.7, 131.3, 131.0, 130.4, 129.7, 129.5, 129.1, 128.8, 128.4, 128.1, 127.9, 127.8, 123.6, 123.5, 113.8, 99.5, 99.0, 82.6, 78.9, 77.8, 74.9, 73.9, 73.2, 73.9, 70.6, 70.1, 68.9, 68.3, 63.3, 55.2, 53.9, 29.7, 20.7, 20.6; IR (thin film) 2110, 1777, 1745, 1718, 1613, 1513, 1385, 1227, 1034, 820, 751, 720, 699 cm^{-1}; $[\alpha]^{20}_D$ +33.8 (*c* 1.01, $CHCl_3$); ESI-MS *m*/*z* 1025 $[M + Na]^+$.

Allyl 2-Deoxy-3,4-*O*-diacetyl-6-*O*-(*p*-methoxybenzyl)-2-phthalimido-*β*-D-glucopyranoside (4-*O*-acetyl 3i). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83−7.86 (m, 2 H), 7.71−7.74 (m, 2 H), 7.25 (d, 2 H, J = 8.4 Hz), 6.89 (d, 2 H, J = 8.4 Hz), 5.78 (t, 1 H, J = 9.9 Hz), 5.67 (m, 1 H), 5.38 (d, 1 H, J = 8.7 Hz), 5.15 (t, 1 H, J = 9.9 Hz), 5.09 (d, 1 H, J = 16.8 Hz), 5.03 (d, 1 H, J = 10.5 Hz), 4.52 (d, 1 H, J = 11.4 Hz), 4.44 (d, 1 H, J = 11.7 Hz), 4.33 (t, 1 H, J = 9.6 Hz), 4.28 (dd, 1 H, J = 4.8, 12.9 Hz), 4.04 (dd, 1 H, J = 6.3, 12.9 Hz), 3.79 (m, 1 H), 3.81 (s, 3 H), 3.59 (d, 2 H, J = 3.9 Hz), 1.92 (s, 3 H), 1.83 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 169.6, 159.2, 134.2, 133.4, 131.4, 129.8, 129.5, 123.5, 117.6, 113.7, 97.0, 73.3, 73.2, 70.9, 70.0, 69.9, 68.6, 55.3, 54.7, 20.7, 20.5; IR (thin film) 1777, 1752, 1718, 1612, 1513, 1387, 1236, 1173, 1042, 722 cm^{-1}; $[\alpha]^{20}_D$ +55.0 (*c* 0.74, $CHCl_3$); ESI-MS *m*/*z* 576 $[M + Na]^+$.

Thiotolyl 3-*O*-Allyloxycarbonyl-4-*O*-acetyl-2-azido-2-deoxy-6-*O*-(*p*-methoxybenzyl)-*β*-D-glucopyranoside (4-*O*-acetyl 3j). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, 2 H, J = 7.8 Hz), 7.20 (d, 2 H, J = 8.4 Hz), 7.05 (d, 2 H, J = 7.5 Hz), 6.85 (d, 2 H, J = 8.4 Hz), 5.93 (m, 1 H), 5.56 (d, 1 H, J = 5.4 Hz), 5.34 (d, 1 H, J = 17.4 Hz), 5.27 (d, 1 H, J = 10.5 Hz), 5.18 (t, 1 H, J = 9.5 Hz), 5.08 (t, 1 H, J = 9.5 Hz), 4.66 (d, 2 H, J = 4.8 Hz), 4.54 (m, 1 H), 4.46 (d, 1 H, J = 11.4 Hz), 4.32 (d, 1 H, J = 11.7 Hz), 4.06 (dd, 1 H, J = 5.7, 10.2 Hz), 3.80 (s, 3 H), 3.51 (d, 2 H, J = 3.6 Hz), 2.32 (s, 3 H), 1.96 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 159.2, 154.1, 138.2, 132.8, 131.1, 129.8, 129.4, 118.9, 113.6, 86.9, 76.2, 73.0, 69.5, 68.9, 68.8, 67.6, 61.6, 55.2, 29.6, 21.0, 20.5; IR (thin film) 2109, 1777, 1744, 1719, 1612, 1514, 1467, 1385, 1302, 1249, 1073, 1032, 753, 720, 699 cm^{-1}; $[\alpha]^{20}_D$ +65.4 (*c* 0.55, $CHCl_3$); ESI-MS *m*/*z* 581 [M + Na]$^+$.

Thiotolyl 4-*O*-Acetyl-2,3-*O*-isopropylidene-6-*O*-(*p*-methoxybenzyl)-*β*-D-glucopyranoside (4-*O*-acetyl 3k). ^{1}H NMR (300 MHz, C_6D_6) δ 7.65 (d, 2 H, J = 8.1 Hz), 7.24 (d, 2 H, J = 8.1 Hz), 6.83 (d, 2 H, J = 7.8 Hz), 6.78 (d, 2 H, J = 8.7 Hz), 5.40 (t, 1 H, J = 9.5 Hz), 4.60 (d, 1 H, J = 9.3 Hz), 4.37 (d, 1 H, J = 11.7 Hz), 4.32 (d, 1 H, J = 11.7 Hz), 3.53−3.66 (m, 3 H), 3.44 (t, 1 H, J = 9.2 Hz), 3.41 (m, 1 H), 3.29 (s, 3 H), 1.99 (s, 3 H), 1.53 (s, 3 H), 1.33 (s, 3 H), 1.20 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) δ 168.9, 159.8, 138.3, 134.4, 130.7, 129.8, 129.7, 114.0, 111.2, 85.1, 80.8, 78.8, 75.7, 73.4, 70.3, 69.3, 54.7, 26.7, 26.6, 21.0, 20.3; IR (thin film) 1748, 1613, 1514, 1493, 1456, 1372, 1240, 1173, 1151, 1038, 833, 782 cm^{-1}; $[\alpha]^{20}_D$ −11.8 (*c* 0.67, C_6H_6); ESI-MS *m*/*z* 511 [M + Na]$^+$.

4-*O*-Acetyl-3-*O*-benzyl-6-*O*-(*p*-methoxybenzyl)-*β*-D-glucal (4-*O*-acetyl 3l). ^{1}H NMR (300 MHz, C_6D_6) δ 7.28 (m, 2 H), 7.07−7.19 (m, 5 H), 6.74 (d, 2 H, J = 8.7 Hz), 6.27 (d, 1 H, J = 6.3 Hz), 5.54 (t, 1 H, J = 4.1 Hz), 4.71 (t, 1 H, J = 5.1 Hz), 4.49 (d, 1 H, J = 12.6 Hz), 4.45 (d, 1 H, J = 12.6 Hz), 4.38 (dd, 1 H, J = 5.1, 10.5 Hz), 4.30 (d, 1 H, J = 11.7 Hz), 4.26 (d, 1 H, J = 11.7 Hz), 3.90 (t, 1 H, J = 3.9 Hz), 3.77 (dd, 1 H, J = 6.0, 10.5 Hz), 3.73 (dd, 1 H, J = 5.7, 10.2 Hz), 3.28 (s, 3 H), 1.58 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) δ 169.3, 159.7, 144.8, 139.0, 130.6, 129.5, 114.0, 75.5, 73.1, 70.3, 69.9, 68.3, 68.1, 54.7, 20.5; IR (thin film) 1740, 1650, 1613, 1514, 1456, 1369, 1245, 1102, 1036, 819, 739, 699 cm^{-1}; $[\alpha]^{20}_D$ −11.7 (*c* 0.63, C_6H_6); ESI-MS *m*/*z* 421 [M + Na]$^+$.

Methyl 4-*O*-Acetyl-2,3-*O*-dibenzyl-6-*O*-(*p*-methoxybenzyl)-α-D-glucopyranoside (4-*O*-acetyl 5a). ^{1}H NMR (300 MHz, C_6D_6) δ 7.27 (m, 6 H), 7.01−7.12 (m, 6 H), 6.77 (m, 2 H), 5.40 (t, 1 H, J = 9.8 Hz), 4.86 (d, 1 H, J = 12.0 Hz), 4.63 (d, 1 H, J = 12.0 Hz), 5.59 (d, 1 H, J = 3.3 Hz), 4.44 (d, 1 H, J = 12.0 Hz), 4.36 (s, 2 H), 4.32 (d, 1 H, J = 12.6 Hz), 4.15 (t, 1 H, J = 9.5 Hz), 4.00 (m, 1 H), 3.62 (dd, 1 H, J = 3.3, 10.2 Hz), 3.56 (dd, 1 H, J = 5.4, 10.5 Hz), 3.47 (dd, 1 H, J = 3.3, 9.6 Hz), 3.30 (s, 3 H), 3.15 (s, 3 H), 1.60 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) δ 169.3, 159.7, 139.5, 139.1, 130.8, 129.1, 128.5, 128.4, 127.9, 127.8, 127.5, 114.0, 98.2, 80.8, 79.5, 75.1, 73.4, 73.0, 71.6, 70.1, 69.5, 54.9, 54.7, 20.4; IR (thin film) 1744, 1613, 1514, 1497, 1455, 1369, 1234, 1163, 1101, 1046, 739, 698 cm^{-1}; $[\alpha]^{20}_D$ +54.1 (*c* 1.03, C_6H_6); ESI-MS *m*/*z* 559 [M + Na]$^+$.

Methyl 6-*O*-Acetyl-2,3-*O*-dibenzyl-4-*O*-(*p*-methoxybenzyl)-α-D-glucopyranoside (6-*O*-acetyl 5b). ^{1}H NMR (300 MHz, C_6D_6) δ 7.36 (m, 2 H), 7.05−7.23 (m, 10 H), 6.75 (m, 2 H), 5.03 (d, 1 H, J = 11.7 Hz), 4.86 (d, 1 H, J = 11.1 Hz), 4.82 (d, 1 H, J = 11.7 Hz), 4.60 (s, 1 H), 4.56 (d, 1 H, J = 10.5 Hz), 4.49 (d, 1 H, J = 12.3 Hz), 4.44 (dd, 1 H, J = 2.1, 11.7 Hz), 4.40 (d, 1 H, J = 11.7 Hz), 4.33 (dd, 1 H, J = 4.8, 11.7 Hz), 4.23 (t, 1 H, J = 9.2 Hz), 3.89 (m, 1 H), 3.57 (t, 1 H, J = 9.6 Hz), 3.51 (dd, 1 H, J = 3.3, 9.6 Hz), 3.27 (s, 3 H), 3.09 (s, 3 H), 1.60 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) δ 169.9, 159.8, 139.7, 139.0, 130.9, 130.0, 128.5, 128.4, 114.0, 98.2, 82.4, 81.0, 77.4, 75.6, 74.6, 72.9, 69.2, 63.4, 54.9, 54.7, 30.2, 20.4; IR (thin film) 1741, 1612, 1514, 1497, 1455, 1364, 1249, 1071, 1030, 739, 698 cm^{-1}; $[\alpha]^{20}_D$ +34.1 (*c* 1.02, C_6H_6); ESI-MS *m*/*z* 559 [M + Na]$^+$.

Methyl 6-*O*-Acetyl-2,3,4-*O*-tribenzyl-*β*-D-glucopyranoside (6-*O*-acetyl 7). ^{1}H NMR (300 MHz, C_6D_6) δ 7.33 (m, 4 H), 7.24 (m, 2 H), 7.02−7.19 (m, 9 H), 5.01 (d, 1 H, J = 11.1 Hz), 4.97 (d, 1 H, J = 11.4 Hz), 4.80 (d, 1 H, J = 10.5 Hz), 4.77 (d, 1 H, J = 10.2 Hz), 4.68 (d, 1 H, J = 11.4 Hz), 4.47 (d, 1 H, J = 11.1 Hz), 4.42 (dd, 1 H, J = 2.4, 12.0 Hz), 4.28 (dd, 1 H, J = 4.8, 12.0 Hz), 4.13 (d, 1 H, J = 7.5 Hz), 3.64 (t, 1 H, J = 9.0 Hz), 3.54 (t, 1 H, J = 7.9 Hz), 3.52 (t, 1 H, J = 9.3 Hz), 3.28 (s, 3 H), 3.27 (m, 1 H), 1.60 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) δ 169.9, 139.4, 139.3, 138.7, 128.6, 128.5, 105.0, 85.0, 82.6, 77.7, 75.5, 74.9, 74.6, 73.2, 63.2, 56.5, 20.3; IR (thin film) 1743, 1497, 1454, 1364, 1237, 1070, 1029, 737, 699 cm^{-1}; $[\alpha]^{20}_D$ +25.4 (*c* 0.95, C_6H_6); ESI-MS *m*/*z* 529 [M + Na]$^+$.

Acknowledgment. The authors gratefully acknowledge financial support from the American Cancer Society (03-135-01-CDD), the American Heart Association (30399Z), and the National Institutes of Health (EB-001777-01). Support from the Purdue Cancer Center is gratefully acknowledged. We thank Dr. Fabien Boulineau for providing several of the anisylidene acetals for our studies.

Supporting Information Available: ^{1}H NMR spectra of acetylated 4-*O*- and 6-*O*-PMB ethers **2a**−***l***, **3a**−***l***, **5a**, **5b**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO048999M