DDQ-Mediated Oxidation of 4,6-*O*-Methoxybenzylidene-Protected Saccharides in the Presence of Various Nucleophiles: Formation of 4-OH, 6-Cl, and 6-Br Derivatives

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Treatment of 4,6-*O*-*p*-methoxybenzylidene-protected pyranosidic mono- and disaccharides with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), in the presence of a few equivalents of water, gave the corresponding 6- and 4-*O*-*p*-methoxybenzoates with unprotected hydroxyl groups in the 4- and 6-position in the ratio ∼4:1 and in 85−98% yield. Dry conditions in the presence of halide salts gave the 6-deoxychloro and -bromo 4-*O*-*p*-methoxybenzoates exclusively, in >90% yield.

Introduction

Cyclic acetals are versatile protecting groups for diols and have found widespread use in carbohydrate synthesis.[1] Well-known examples include 3,4-*O*-isopropylidene and 4,6-*O*-benzylidene protection in hexopyranosides and 1,2;5,6-di-*O*-isopropylidene-protection in hexofuranosides. In addition to protection/deprotection, regioselective cleavage of benzylidene acetals by both reductive and oxidative procedures gives access to partly protected sugars with only one unprotected hydroxyl group, suitable as e.g. glycosyl acceptors.

Hanessian,[2] and Hullar and Siskin,[3] independently found in 1966 that 4,6-*O*-benzylidene acetals could be transformed into the corresponding 4-*O*-benzoyl-6-deoxybromo derivatives, by treatment with *N*-bromosuccinimide (NBS) in tetrachloromethane. This procedure has developed into one of the standard reactions for regioselective functionalization of carbohydrates. Following these initial examples, further search for effective methods for regioselective ring-opening of sugar acetals has yielded other valuable procedures for the preparation of partially protected sugars.[4]

Reductive cleavage of sugar benzylidene acetals, using reagents such as $LiAlH_4/AlCl_3$,[5] $NaCNBH_3/HCl$,[6] and i-Bu_2AlH,[7] gives benzyl ether sugars with one unprotected hydroxyl group. The regioselectivity varies between these methods. Generally speaking, $LiAlH_4/AlCl_3$ and $NaCNBH_3/HCl$ give products with unprotected 6-OH and 4-OH, respectively. The latter reagent is now generally accepted for reliable regioselective preparation of pyranosidic glycosyl acceptors.

In contrast to the reductive cleavage reactions that give benzyl ethers, oxidative cleavage gives benzoyl esters. The latter are labile under alkaline conditions and can therefore be simply and selectively removed in later stages of a synthetic route. In order to enhance the ease of oxidation, *p*-methoxybenzylidene acetals were chosen as protecting groups. With non-saccharidic acetals, a number of oxidants have thus been evaluated, including ozone,[8] pyridinium dichromate/t-BuOOH,[9] $NaBO_3 \cdot 4H_2O/Ac_2O$,[10] and t-BuOOH/$Pd(OCOCF_3)$(t-BuOOH).[11] However, the regioselectivity obtained with most of these reagents was rather poor. Treatment of some *p*-methoxybenzylidene acetals of furanoses with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) gave the two expected regioisomeric *p*-methoxybenzoyl esters in the ratio 7:3.[12] Oxidative cleavage of 4,6-*O*-benzylidene acetals of pyranosides, using $Pd(OAc)_2$ or $CuCl_2$/t-BuOOH, gave the benzoyl esters in high yield, but low regioselectivity.[13]

To the best of our knowledge, oxidative cleavage of 4,6-*O*-*p*-methoxybenzylidene acetals of pyranosidic sugars has not been reported. We now disclose our results from an investigation of DDQ-promoted cleavage of such acetals. Using different reaction conditions (Tables 1 and 2), the 4-hydroxy, 6-deoxychloro, and 6-deoxybromo derivatives, carrying a *p*-methoxybenzoyl group (MBz) in the 6- or 4-position, respectively, were formed as the main products.

Results and Discussion

The acetals **2**−**10**, depicted in Chart 1, were used as starting materials in the DDQ-mediated cleavage reactions discussed below. Treatment of 2-(trimethylsilyl)-ethyl β-D-galactopyranoside[14] with *p*-methoxybenzaldehyde dimethyl acetal and *p*-toluenesulfonic acid gave **1** (98%). Benzoylation and benzylation of **1** gave **2** (95%) and **3** (90%), respectively. Acetals **4**−**10** were prepared according to published procedures.[14−17]

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1996.

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Chart 1

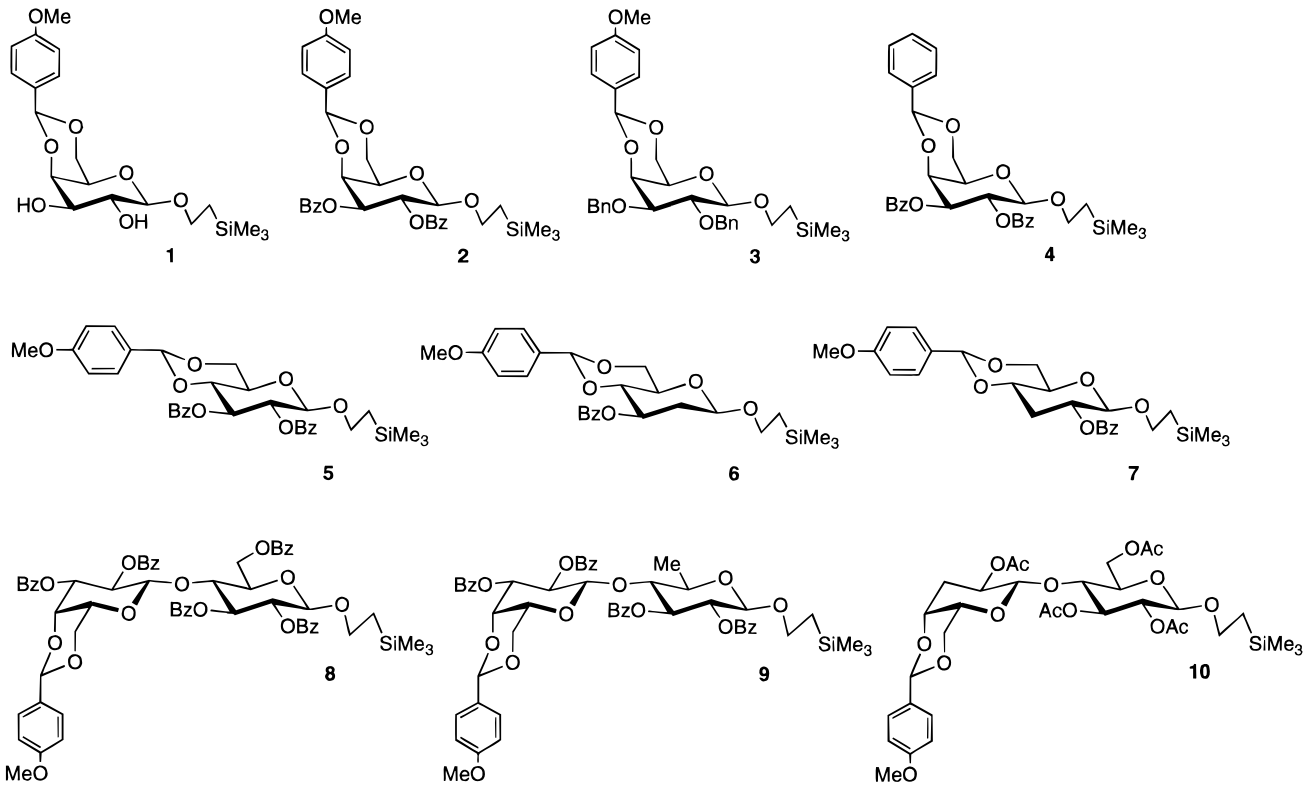
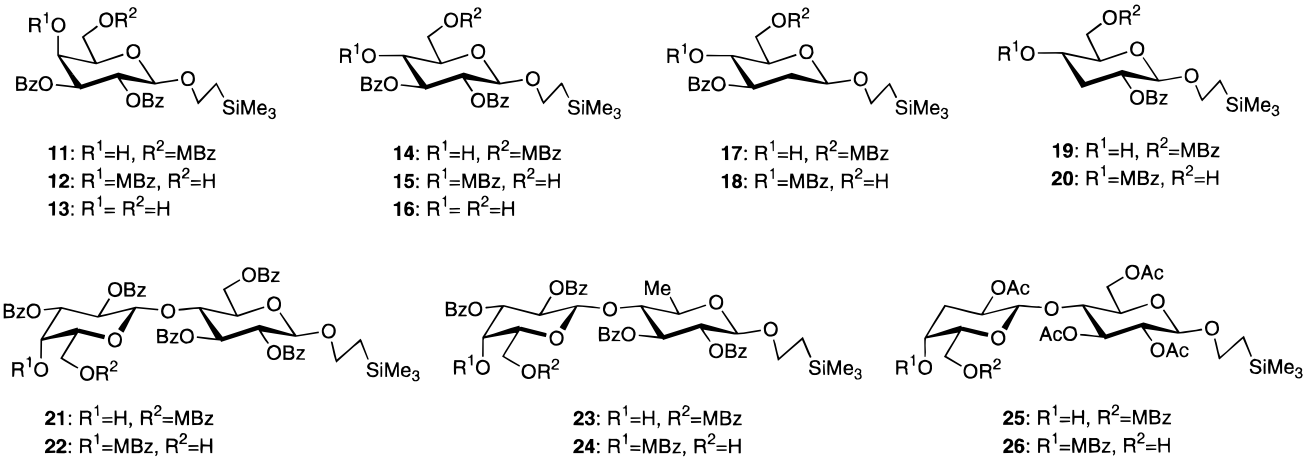


Chart 2



11: R^1=H, R^2=MBz
12: R^1=MBz, R^2=H
13: R^1= R^2=H
14: R^1=H, R^2=MBz
15: R^1=MBz, R^2=H
16: R^1= R^2=H
17: R^1=H, R^2=MBz
18: R^1=MBz, R^2=H
19: R^1=H, R^2=MBz
20: R^1=MBz, R^2=H

21: R^1=H, R^2=MBz
22: R^1=MBz, R^2=H
23: R^1=H, R^2=MBz
24: R^1=MBz, R^2=H
25: R^1=H, R^2=MBz
26: R^1=MBz, R^2=H

Synthesis of 4-*O*- and 6-*O*-*p*-Methoxybenzoyl-Protected Saccharides (Chart 2). An initial attempt, based on a published procedure,[12] to regioselectively cleave the acetal ring of **2** with DDQ in dichloromethane/water (17:1) resulted in hydrolysis of the acetal to give the corresponding 4,6-diol **13**. Similar DDQ-induced hydrolysis of other acetals has been reported recently.[18] It seems as if excess water in the reaction mixture leads to hydrolysis rather than the desired oxidative cleavage to MBz-esters. When the reaction was run with **2** in acetonitrile or dioxane (without previous drying of the solvent; supposed to contain excess water) only diol **13** was formed. Using essentially the published conditions[18] [DDQ (0.2 equiv), MeCN/H_2O, 9:1, 2−6 h, 45 °C], compounds **2** and **5**[17] were hydrolyzed to give the corresponding diols **13** and **16** in 97 and 95% isolated yield, respectively.

When the solvent (toluene or 1,2-dichloroethane) was predried and a controlled amount of water was added (preabsorbed in molecular sieves), only the desired 4-*O*- and 6-*O*-MBz-esters **11** and **12** were obtained from **2** (Chart 2 and Table 1). Addition of a small amount of acetic acid increased the **11**/**12** ratio.

In addition to compound **2** we tested the 4,6-*O*-*p*-methoxybenzylidene acetals **5**−**10**. The glucoside **5** was more sensitive than **2** toward hydrolysis. Thus, when water was added to the reaction mixture containing **5** (same conditions as method A in Table 1), a substantial amount of diol **16** was formed. However, by omitting the addition of water and lowering the amount of acetic acid

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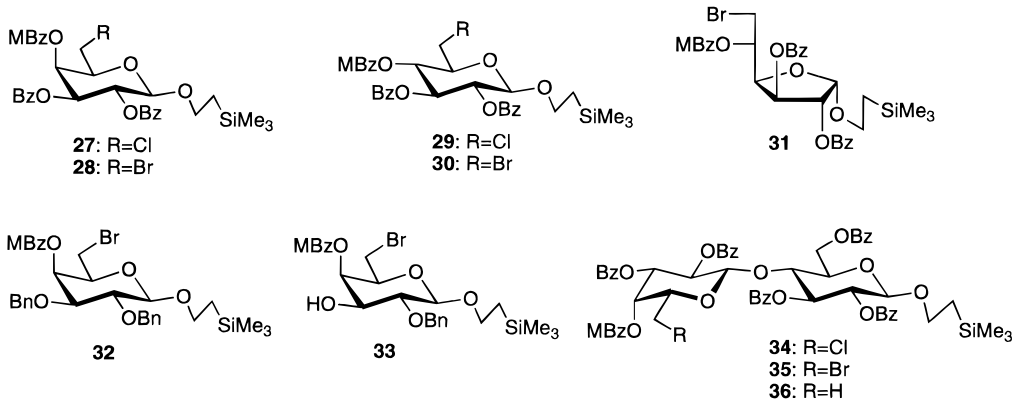
Chart 3



to 1.5 equiv (method B), **14** and **15** were isolated in 76 and 13% yield, respectively, and no diol **16** was formed. Presumably, the nondried solvent and nonactivated molecular sieves contained enough water for the reaction to proceed to completion.

The 2- and 3-deoxyglucosides[17] **6** and **7** were, as expected, more sensitive toward hydrolysis than **5**. Decreasing the amount of acetic acid to 0.2 equiv (method C) gave with **6** the desired **17** (66%) and **18** (19%), together with a small amount of diol (3%). The 3-deoxyglucoside **7** was even more acid sensitive, decomposing in the presence of silica gel. Omitting the addition of acetic acid (method D) permitted the transformation of **7** into a mixture of **19** and **20**. However, the regioselectivity was low in the absence of acid (**19**/**20** 3:2). We have previously shown that *p*-methoxybenzoyl groups migrate from the 4- to the 6-position by treatment with silver nitrate/potassium fluoride.[17,19] Under these conditions, the **19**/**20** ratio was shifted from 3:2 to 14:1 and pure **19** was obtained in 85% yield.

The lactoside[15] **8** was treated under the same conditions as galactoside **2** (method A) to give **21** and **22** in 79 and 20% yield, respectively. These conditions worked equally well with the 6-deoxylactoside[17] **9**, giving **23** and **24** in 83 and 16% yield, respectively. The 3′-deoxylactoside[16] **10** was transformed into **25** and **26** in 65 and 31% yield, respectively, in the presence of added water and sodium hydrogen sulfate (method E), indicating once more that galactosides are less prone to hydrolysis than glucosides (cf. **10** and **7**).

Treatment of the 2,3-*O*-benzylated galactoside **3** under the conditions of method E gave a complex mixture of debenzylated products, indicating that electron-withdrawing protecting groups (such as benzoyl groups) stabilize the compounds much better than benzyl protecting groups.

Finally, the 4,6-*O*-benzylidene acetal[14] **4** was virtually stable under the conditions that converted **2** into **11** and **12**. Thus, when a mixture of compounds **2** and **4** was treated according to method A, compound **2** was consumed but **4** remained unchanged and 92% of **4** was recovered from the reaction mixture.

Synthesis of 4-*O*-*p*-Methoxybenzoyl-6-deoxychloro and -bromo Saccharides (Chart 3). As depicted in Scheme 1, a benzyloxonium ion is considered to be an early intermediate in DDQ-oxidation of 4,6-*O*-*p*-methoxybenzylidene acetals. Such intermediates should in principle be amenable to nucleophilic attack at position 4 and 6. In an initial attempt along these lines, compound **2** was treated with DDQ (2 equiv), potassium chloride (3 equiv), and 18-crown-6 (0.5 equiv) in dry 1,2-dichloroethane. The 6-deoxychloro galactoside **27** was formed together with a small amount of compound **11**; compound **27** was isolated in 85% yield. The same result was obtained when toluene was used as solvent (method F, Table 2).

To our surprise, attempted formation of the corresponding deoxyfluoro galactoside from **2** in the presence of potassium fluoride instead of potassium chloride, also gave the deoxychloro galactoside **27**. In order to investigate the nature of the chloride-ion source, the 1,2-dichloroethane solvent was substituted by toluene, but **27** was also here the main product formed. The same results were obtained when potassium bromide, potassium azide, and lithium tosylate were used as the potential nucleophiles. In an experiment where **2** was treated with 1.3 equiv of DDQ and only 0.3 equiv of potassium chloride, the 6-deoxychloro compound **27** was isolated in 72% yield. The logical conclusion is that DDQ, or its reaction products, reacts with nucleophiles present in solution (including water) thus liberating chloride ions, which can then react with the activated *p*-methoxybenzylidene acetal (Scheme 1). Substitution of chloride ion by fluoride ion was reported to occur when 2,3,5,6-tetrachloro-*p*-benzoquinone was treated with potassium fluoride.[20] Consequently, a halogen source different from

Table 1. Synthesis of 4-*O*- and 6-*O*-*p*-Methoxybenzoyl-Protected Saccharides by DDQ-Mediated Oxidative Cleavage of 4,6-*O*-*p*-Methoxybenzylidene Acetals

starting mtrl[a]	method[b]	product[c]	yield[d] (%)
2	A	**11**/**12**	79/19
5	B	**14**/**15**	76/13
6	C	**17**/**18**/diol	66/19/3
7	D	**19**/**20**	85/6[e]
8	A	**21**/**22**	79/20
9	A	**23**/**24**	83/16
10	E	**25**/**26**	65/31
2 + **4**	A	**11**/**12** + **4**	92[f]

[a] See Chart 1. [b] A: DDQ (1.5 equiv), AcOH (5 equiv), H_2O (2 equiv), nonactivated molecular sieves (4 Å), toluene, 80 °C; B: DDQ (1.5 equiv), AcOH (1.5 equiv), nonactivated molecular sieves (4 Å), toluene, 80 °C; C: DDQ (2 equiv), AcOH (0.2 equiv), nonactivated molecular sieves (4 Å), toluene, 80 °C (ref 17); D: DDQ (2 equiv), nonactivated molecular sieves (4 Å), toluene, 80 °C (ref 17); E: DDQ (1.5 equiv), $NaHSO_4$ (4.5 equiv), H_2O (5 equiv), 18-crown-6 (cat.), nonactivated molecular sieves (4 Å), toluene, 70 °C (ref 16). [c] See Chart 2. [d] Isolated yields of the 4OH-6OMBz/4OMBz-6OH products. [e] After rearrangement and chromatography of the original mixture (ref 17). [f] Yield of unreacted **4**.

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Scheme 1

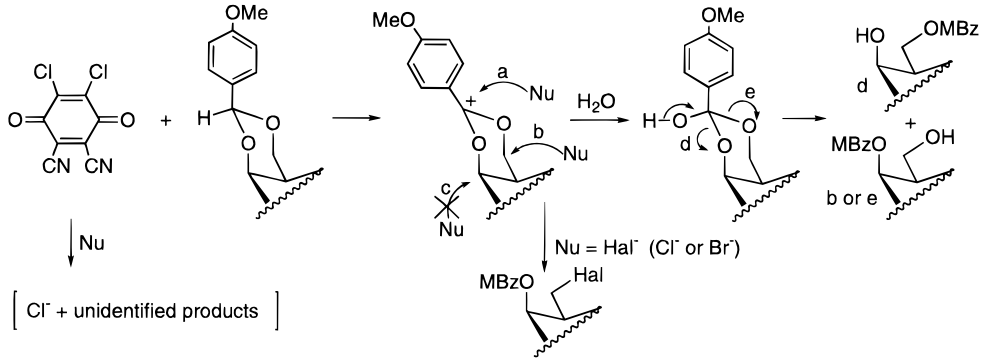

Table 2. Synthesis of 6-Deoxychloro- and 6-Deoxybromo-4-*O*-*p*-methoxybenzoyl-Protected Saccharides by DDQ-Mediated Oxidative Cleavage of 4,6-*O*-*p*-Methoxybenzylidene Acetals in the Presence of Halide Donors

starting mtrl[a]	method[b]	product[c]	yield[d] (%)
2	F	**27** (Cl)	85
2	G	**27** (Cl)	88
2	H	**27** (Cl)	96
2	I	**28** (Br)	90
2	J	**28** (Br)	93
5	G	**29** (Cl)	71
5	H	**29** (Cl)	91
5	I	**30**/**31** (Br)	75/20
5	J	**30** (Br)	88
3	K	**32**/**33** (Br)	33/53
8	H	**34** (Cl)	97
8	I	**35** (Br)	83
8	J	**35** (Br)	93
8	L	**35** (Br)	95

[a] See Chart 1. [b] F: DDQ, KCl, 18-crown-6 (cat.), molecular sieves (4 Å), toluene, 80 °C; G: DDQ, TMS-Cl, molecular sieves (4 Å), 1,2-dichloroethane 50 °C; H: DDQ, $CuCl_2$/Bu_4NCl, molecular sieves (4 Å), 1,2-dichloroethane, reflux; I: DDQ, TMS-Br, molecular sieves (4 Å), 1,2-dichloroethane, 50 °C; J: DDQ, $CuBr_2$/Bu_4NBr, molecular sieves (4 Å), 1,2-dichloroethane, reflux; K: DDQ, TMS-Br, molecular sieves (4 Å), chloroform, 50 °C; L: NBS, CCl_4, reflux. [c] See Chart 3. [d] Isolated yields.

potassium halide had to be found when halosugars other than chlorides are desired.

Treatment of **2** and **5** with DDQ and trimethylsilyl chloride in 1,2-dichloromethane (method G) gave **27** and **29** in 88 and 71% yield, respectively. Similarly, when trimethylsilyl bromide was used with **2** and **8** (method I), the deoxybromo galacto- and lactosides **28** and **35** were obtained in 90 and 83% yield, respectively. However, with glucoside **5**, the yield of the desired deoxybromo glucoside **30** was only 75% and the deoxybromo furanoside **31** was formed as a byproduct (20%). Another disadvantage with trimethylsilyl bromide was found on attempted bromination of the 2,3-di-*O*-benzyl galactoside **3** (method K). Both the desired bromodeoxy compound **32** (33%) and the partially debenzylated derivative **33** (53%) were obtained. Finally, attempted conversion of **2** using DDQ and trimethylsilyl iodide gave a very complex reaction mixture. It was concluded that trimethylsilyl chloride and bromide are acceptable reagents when stable starting materials, such as **2** and **8**, are used. However, with less stable compounds, such as **3** and **5**, a less aggressive reagent is desired.

Preliminary experiments with **2** and DDQ/tetrabutylammonium chloride and bromide did not produce the desired deoxyhalo sugars. We assume that a Lewis acid is needed in addition to the halide source, in order to expedite the nucleophilic attack on the activated 4,6-*O*-*p*-methoxybenzylidene acetal. Copper(II) halides were found to function well as Lewis acids in these reactions. Thus, the combination DDQ/$CuCl_2$/Bu_4NCl (1:1:2; method H) gave with **2**, **5**, and **8** the desired 6-deoxychloro derivatives **27**, **29**, and **34** in 96, 91, and 97% isolated yield. Using the same starting materials with DDQ/$CuBr_2$/Bu_4NBr (1:1:2, method J) gave **28**, **30**, and **35** in 93, 88, and 93% yield. Compound **35** was treated with tributyltin hydride to give the corresponding 6′-deoxylactoside **36**, clearly demonstrating that the bromine atom was present in the 6′-position of **35**.

In analogy with the experiment described in Table 1 (**2** + **4**) the stability of the 4,6-*O*-benzylidene derivative **4** was investigated with the DDQ/$CuBr_2$/Bu_4NBr reagent. After 2 days under the conditions of method J, approximately 90% of **4** was recovered intact, showing that combined *p*-methoxybenzylidene and benzylidene protection of pyranosides can be used to advantage when selective deprotection or halogenation is desired with larger oligosaccharides that contain both protecting groups.

Mechanistic Considerations. Oxidation of allylic alcohols by DDQ was suggested to occur via an ionic rather than a radical mechanism.[21] It seems reasonable to assume that the DDQ-oxidations of *p*-methoxybenzylidene acetals reported here also proceed via ionic intermediates, as depicted in Scheme 1. Attack by nucleophiles (H_2O, Cl^-, or Br^-) on the initially formed *p*-methoxybenzyloxonium ion can in principle take place at three different positions. The benzylic position, carrying the highest positive charge density, probably undergoes the most rapid nucleophilic attack (a, Scheme 1). Reaction with water gives a hemi-orthoester intermediate, which can react further by cleavage of the dioxine ring to form the desired *p*-methoxybenzoyl ester with unprotected HO-4 (d) or HO-6 (e), as shown in Table 1. Alternatively, the HO-6 compound may be formed via direct attack by water at C-6 (b). Yet another possibility includes migration of the *p*-methoxybenzoyl group from the 4- to the 6-position after initial formation of the HO-6 compound, although this is considered to be less likely.

In contrast to the water case above, attack at the benzylic carbenium ion by Cl^- or Br^- is nonproductive and the carbenium ion is recreated due to the good leaving group characteristics of the halogenide ions. Attack at C-6 leads on the other hand to the desired

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6-deoxyhalo products, as shown in Table 2. It is noteworthy that no 4-deoxyhalo compounds were found in the reaction mixtures, which means that route c (Scheme 1) is strongly disfavored compared to route b. This is in agreement with Hanessian's results with NBS-mediated tranformation of 4,6-*O*-benzylidene acetals into the corresponding 4-*O*-benzoyl-6-deoxybromo compounds.[2b]

Experimental Section

General Methods. NMR spectra were recorded in $CDCl_3$; chemical shifts are relative to Me_4Si. TLC was performed on Kieselgel 60 F_{254} (Merck). Products were chromatographed on Kieselgel 60 (Merck, 35−70 mesh). Melting points are uncorrected. Solvents were freshly distilled over drying agents under N_2 (toluene/Na, 1,2-dichloroethane/CaH_2, chloroform/CaH_2). Powdered molecular sieves were activated at 180 °C and then with a flame under vacuum for 5 min and kept under vacuum for 1 h before use. Tetrabutylammonium halides and cupric halides were treated in the same way. Compounds **4** and **6**−**10** have been described.[14−17]

2-(Trimethylsilyl)ethyl 4,6-*O*-*p*-Methoxybenzylidene-*β*-D-galactopyranoside (1). To a mixture of 2-(trimethylsilyl)ethyl *β*-D-galactopyranoside[14] (8.00 g, 28.6 mmol), *p*-methoxybenzaldehyde dimethyl acetal (8.60 mL, 57.3 mmol), and dry acetonitrile (170 mL) was added toluenesulfonic acid monohydrate (320 mg) at room temperature. After 1 h, the mixture was neutralized with triethylamine (1.0 mL) and concentrated. The residue was chromatographed (SiO_2, EtOAc/heptane 3:1 → 4:1) to give **1** (11.14 g, 98%); Recrystallization (EtOAc−heptane) gave an analytical sample: mp 155−156 °C; $[\alpha]^{22}_D$ −47.8° (*c* 1.0, $CHCl_3$); ^{1}H-NMR *δ* 7.42 (d, 2 H, *J* = 8.7 Hz), 6.88 (d, 2 H, *J* = 8.7 Hz), 5.50 (s, 1 H), 4.33 (dd, 1 H, *J* = 12.5, 1.5 Hz), 4.28 (d, 1 H, *J* = 7.3 Hz), 4.18 (dd, 1 H, *J* = 3.5, 1.0 Hz), 3.80 (s, 3 H), 3.67 (dd, 1 H, *J* = 3.5, 9.7 Hz), 1.05 (m, 2 H), 0.03 (s, 9 H); HRMS calcd for $C_{19}H_{30}O_7SiNa$ (M + Na) 421.1659, found 421.1674.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-4,6-*O*-*p*-methoxybenzylidene-*β*-D-galactopyranoside (2). Compound **1** (8.00 g, 20.1 mmol) was dissolved in pyridine (120 mL), the mixture was cooled (ice-water bath), and benzoyl chloride (6.4 mL, 55 mmol) was added dropwise. After 19 h, the mixture was diluted with CH_2Cl_2 (500 mL), washed with 2 M H_2SO_4 (2 × 200 mL), water (2 × 200 mL), saturated aqueous $NaHCO_3$ (200 mL), and water (200 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was recrystallized (EtOAc/heptane) to give **2** (7.41 g, 61%). The mother liquor was concentrated, and the residue was chromatographed (SiO_2, heptane/EtOAc 5:1 → 2:1) to give an additional crop of **2** (3.82 g, 31%): mp 117−118 °C; $[\alpha]^{22}_D$ +130.2° (*c* 1.0, $CHCl_3$); ^{1}H-NMR *δ* 7.98 (d, 2 H, *J* = 8.6 Hz), 6.88 (d, 2 H, *J* = 8.6 Hz), 5.85 (dd, 1 H, *J* = 10.4, 7.9 Hz), 5.50 (s, 1 H), 5.35 (dd, 1 H, *J* = 10.5, 3.6 Hz), 4.77 (d, 1 H, *J* = 8.1 Hz), 4.57 (d, 1 H, *J* = 3.4 Hz), 4.40 (dd, 1 H, *J* = 12.3, 1.4 Hz), 3.81 (s, 3 H), 0.90 (m, 2 H), −0.07 (s, 9 H); HRMS calcd for $C_{33}H_{38}O_9SiNa$ (M + Na) 629.2183, found 629.2169.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzyl-4,6-*O*-*p*-methoxybenzylidene-*β*-D-galactopyranoside (3). Compound **1** (1.16 g, 2.9 mmol) was dissolved in DMF (18 mL), NaH (80%, 262 mg, 8.7 mmol) was added, the mixture was stirred for 40 min, benzyl bromide (1.76 mL, 14.6 mmol) was added, and the mixture was stirred overnight. MeOH (0.5 mL) was added, and the mixture was stirred for 15 min to destroy unreacted NaH. The mixture was coconcentrated with toluene−H_2O (2: 1, 4 × 5 mL), and the residue was diluted with CH_2Cl_2 (100 mL). The mixture was washed with saturated aqueous $NaHCO_3$ (40 mL) and saturated aqueous NaCl (40 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was recrystallized (EtOAc/heptane) to give **3** (1.05 g, 62%). The mother liquor was concentrated, and the residue was chromatographed (SiO_2, heptane/EtOAc 6:1 → 4:1) to give an additional crop of **3** (472 mg, 29%): mp 138−140 °C; $[\alpha]^{22}_D$ +30.7° (*c* 1.0, $CHCl_3$); ^{1}H-NMR *δ* 5.47 (s, 1 H), 5.35 (dd, 1 H, *J* = 10.5, 3.6 Hz), 4.90−4.75 (m, 4 H), 4.39 (d, 1 H, *J* = 7.7 Hz), 4.30 (dd, 1 H, *J* = 12.2, 1.5 Hz), 3.99 (dd, 1 H, *J* = 12.5, 1.7 Hz), 3.81 (s, 3 H), 3.30 (bs, 1 H), 1.05 (m, 2 H), 0.03 (s, 9 H); HRMS calcd for $C_{33}H_{42}O_7SiNa$ (M + Na) 601.2598, found 601.2583.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-4,6-*O*-*p*-methoxybenzylidene-*β*-D-glucopyranoside[17] (5). 2-(Trimethylsilyl)ethyl 4,6-*O*-*p*-methoxybenzylidene-*β*-D-glucopyranoside[17] (1.93 g, 4.9 mmol) was benzoylated as described in the preparation of **2**. The crude product was chromatographed (SiO_2, heptane/EtOAc 5:1 → 2:1) to give **5** (2.67 g, 91%). The physical data for **5** were as described.[17]

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-6-*O*-*p*-methoxybenzoyl-*β*-D-galactopyranoside (11) and 2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-4-*O*-*p*-methoxybenzoyl-*β*-D-galactopyranoside (12). Method A: H_2O (5.9 *μ*L, 0.3 mmol) and AcOH (28.3 *μ*L, 0.8 mmol) were absorbed in crushed (nonactivated) molecular sieves (100 mg). The sieves were added to a solution of compound **2** (100 mg, 0.17 mmol) in toluene (5 mL). The mixture was stirred for 5 min, DDQ (58 mg, 0.25 mmol) was added, and the temperature was raised to 80 °C. After 20 h, TLC (toluene/EtOAc 4:1) showed that **2** had been consumed. The mixture was diluted with EtOAc (50 mL), filtered through Celite, washed with saturated aqueous $NaHCO_3$ (2 × 25 mL) and water (25 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 3:1 → 2:1) to give **11** (80.5 mg, 79%) and **12** (19.1 mg, 19%). Compound **11** had mp 113−115 °C; $[\alpha]^{22}_D$ +39.7° (*c* 1.0, $CHCl_3$); ^{1}H-NMR *δ* 5.75 (dd, 1 H, *J* = 10.3, 7.9 Hz), 5.34 (dd, 1 H, *J* = 10.3, 3.2 Hz), 4.74 (d, 1 H, *J* = 7.9 Hz), 4.68, 4.58 (dd, 1 H each, *J* = 11.4, 6.7, 6.5 Hz), 4.34 (d, 1 H, *J* = 2.7 Hz), 3.86 (s, 3 H), −0.08 (s, 9 H). Anal. Calcd for $C_{33}H_{38}O_{10}Si$: C, 63.6; H, 6.2. Found: C, 63.7; H, 6.2. Compound **12** had mp 162−163 °C; $[\alpha]^{22}_D$ +221.5° (*c* 1.0, $CHCl_3$); ^{1}H-NMR *δ* 5.84 (dd, 1 H, *J* = 10.4, 7.9 Hz), 5.76 (d, 1 H, *J* = 3.4 Hz), 5.57 (dd, 1 H, *J* = 10.4, 3.4 Hz), 4.81 (d, 1 H, *J* = 8.0 Hz), 3.89 (s, 3 H), −0.08 (s, 9 H); HRMS calcd for $C_{33}H_{38}O_{10}SiNa$ (M + Na): 645.2132, found 645.2128.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-*β*-D-galactopyranoside (13). To a mixture of compound **2** (50 mg, 0.083 mmol) and CH_3CN/H_2O (1.5 mL, 9:1) was added DDQ (3.8 mg, 0.017 mmol). The mixture was stirred at 45 °C for 2 h, diluted with EtOAc (30 mL), washed with aqueous 10% $NaHCO_3$/NaCl (15 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 2:1 → 1:1) to give **13** (38.1 mg, 97%); $[\alpha]^{22}_D$ +74.0° (*c* 1.0, $CHCl_3$); ^{1}H-NMR *δ* 5.76 (dd, 1 H, *J* = 10.3, 7.9 Hz), 5.30 (dd, 1 H, *J* = 10.3, 3.1 Hz), 4.74 (d, 1 H, *J* = 8.0 Hz), 4.41 (d, 1 H, *J* = 2.7 Hz), 3.78 (bt, 1 H, *J* = 5.1 Hz), −0.09 (s, 9 H); ^{13}C-NMR *δ* 166.0, 165.4, 133.4, 133.1, 101.0, 74.6, 74.1, 69.8, 68.2, 67.7, 62.4, 18.0, −1.5; HRMS calcd for $C_{25}H_{32}O_8SiNa$ (M + Na): 511.1764, found 511.1764.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-6-*O*-*p*-methoxybenzoyl-*β*-D-glucopyranoside (14) and 2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-4-*O*-*p*-methoxybenzoyl-*β*-D-glucopyranoside (15). Method B: Compound **5** (100 mg, 0.17 mmol) was treated with DDQ (58 mg, 0.25 mmol) and AcOH (14 *μ*L, 0.25 mmol) in the presence of molecular sieves (nonactivated; no H_2O added), as described in the preparation of **11** and **12**. The crude product was chromatographed (SiO_2, heptane/EtOAc 6:1 → 4:1) to give **14** (78 mg, 76%) and **15** (13.7 mg, 13%). Compound **14** had mp 139−140 °C; $[\alpha]^{22}_D$ +57.2° (*c* 1.0, $CHCl_3$); ^{1}H-NMR *δ* 8.06, 6.95 (d, 2 H each, *J* = 9.0 Hz), 5.50−5.39 (m, 2 H), 4.78 (dd, 1 H, *J* = 12.1, 4.2 Hz), 4.74 (d, 1 H, *J* = 7.7 Hz), 4.61 (dd, 1 H, *J* = 12.2, 2.1 Hz), 3.88 (s, 3 H), 3.78 (ddd, 1 H, *J* = 9.7, 4.1, 2.2 Hz), 3.50 (d, 1 H, *J* = 4.1 Hz), −0.08 (s, 9 H); HRMS calcd for $C_{33}H_{38}O_{10}SiNa$ (M + Na): 645.2132, found 645.2144. Compound **15** had $[\alpha]^{22}_D$ +45.6° (*c* 0.9, $CHCl_3$); ^{1}H-NMR *δ* 6.86 (d, 2 H, *J* = 9.0 Hz), 5.91 (t, 1 H, *J* = 9.7 Hz), 5.49 (dd, 1 H, *J* = 9.9, 7.9 Hz), 5.44 (t, 1 H, *J* = 9.7 Hz), 4.84 (d, 1 H, *J* = 7.9 Hz), 3.83 (s, 3 H), −0.06 (s, 9 H); HRMS calcd for $C_{33}H_{38}O_{10}SiNa$ (M + Na): 645.2132, found 645.2108.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-*β*-D-glucopyranoside (16). A mixture of compound **5** (50 mg, 0.083 mmol), DDQ (3.8 mg, 0.017 mmol), and CH_3CN/H_2O (1.5 mL, 9:1) was stirred at 45 °C for 6 h and worked up as described in the preparation of **13**. The residue was chromatographed (SiO_2, heptane/EtOAc 2:1 → 1:1) to give **16** (37.5 mg, 96%); $[\alpha]^{22}_D$

+61.0° (*c* 1.0, $CHCl_3$); ^{1}H-NMR δ 5.46−5.36 (m, 2 H), 4.75 (bd, 1 H, J = 7.8 Hz), −0.08 (s, 9 H); ^{13}C-NMR 167.6, 165.3, 133.6, 133.2, 100.6, 77.3, 75.7, 71.6, 70.0, 67.8, 62.3, 18.0, −1.5; HRMS calcd for $C_{25}H_{32}O_8SiNa$ (M + Na): 511.1764, found 511.1779.

2-(Trimethylsilyl)ethyl 3-*O*-Benzoyl-2-deoxy-6-*O*-*p*-methoxybenzoyl-β-D-glucopyranoside (17) and 2-(Trimethylsilyl)ethyl 3-*O*-Benzoyl-2-deoxy-4-*O*-*p*-methoxybenzoyl-β-D-glucopyranoside (18). Method C: Compound **6** (779 mg, 1.60 mmol) was treated with DDQ (751 mg, 3.21 mmol) and AcOH (17 μL, 0.48 mmol) in the presence of molecular sieves (nonactivated; no H_2O added), as described in the preparation of **11** and **12**. The crude product was chromatographed (SiO_2, heptane/EtOAc 6:1 → 4:1) to give **17** (553 mg, 66%) and **18** (220 mg, 19%). The physical data for **17** and **18** were as described.[17]

2-(Trimethylsilyl)ethyl 2-*O*-Benzoyl-3-deoxy-6-*O*-*p*-methoxybenzoyl-β-D-glucopyranoside (19) and 2-(Trimethylsilyl)ethyl 2-*O*-Benzoyl-3-deoxy-4-*O*-*p*-methoxybenzoyl-β-D-glucopyranoside (20). Method D: Compound **7** (150 mg, 0.31 mmol) was treated with DDQ (192 mg, 0.82 mmol) in the presence of molecular sieves (nonactivated; no AcOH or H_2O added), as described in the preparation of **11** and **12**. The crude product was treated with $AgNO_3$/KF to change the **19**/**20** ratio from 3:2 to 14:1. Chromatography (SiO_2, toluene/CH_2Cl_2/THF 20:10:3) of the rearranged mixture gave **19** (132 mg, 85%) and **20** (10 mg, 6%). The physical data for **19** and **20** were as described.[17]

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzoyl-4-*O*-(2,3-di-*O*-benzoyl-6-*O*-*p*-methoxybenzoyl-β-D-galactopyranosyl)-β-D-glucopyranoside (21) and 2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzoyl-4-*O*-(2,3-di-*O*-benzoyl-4-*O*-*p*-methoxybenzoyl-β-D-galactopyranosyl)-β-D-glucopyranoside (22). Method A: Compound **8**[15] (150 mg, 0.14 mmol) was treated with DDQ (49.5 mg, 0.21 mmol), H_2O (5.1 μL, 0.28 mmol), AcOH (24.2 μL, 0.71 mmol), and nonactivated molecular sieves (100 mg), as described in the preparation of **11** and **12**. The crude product was chromatagraphed (SiO_2, heptane/EtOAc 6:1 → 4:1) to give **21** (121 mg, 79%) and **22** (30 mg, 20%). Compound **21** had $[\alpha]^{22}_D$ +50.6° (*c* 1.0, $CHCl_3$); ^{1}H-NMR δ 5.80−5.69 (m, 2 H), 5.43 (dd, 1 H, J = 9.6, 7.9 Hz), 5.13 (dd, 1 H, J = 10.4, 3.2 Hz), 4.77, 4.70 (d, 1 H each, J = 8.1, 7.9 Hz), 4.60, 4.45 (dd, 1 H each, J = 12.0, 1.5, 4.7 Hz), 4.20 (t, 1 H, J = 9.3 Hz), 3.88 (s, 3 H), −0.13 (s, 9 H); HRMS calcd for $C_{60}H_{60}O_{18}SiNa$ (M + Na): 1119.3447, found 1119.3474. Compound **22** had $[\alpha]^{22}_D$ +112.9° (*c* 1.0, $CHCl_3$); ^{1}H-NMR δ 5.77 (dd, 1 H, J = 10.2, 7.9 Hz), 5.70 (t, 1 H, J = 9.1 Hz), 5.50 (d, 1 H, J = 3.4 Hz), 5.44 (dd, 1 H, J = 9.6, 8.0 Hz), 5.33 (dd, 1 H, J = 10.5, 3.4 Hz), 4.81, 4.70 (d, 1 H each, J = 7.8, 7.8 Hz), 4.59 (bd, 1 H, J = 12.0 Hz), 4.45 (dd, 1 H, J = 12.1, 5.0 Hz), 4.18 (t, 1 H, J = 9.5 Hz), 3.92 (s, 3 H), 2.93, 2.66 (dABq, 1 H each, J = 11.8, 6.3 Hz), −0.13 (s, 9 H); HRMS calcd for $C_{60}H_{60}O_{18}SiNa$ (M + Na): 1119.3447, found 1119.3423.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-6-deoxy-4-*O*-(2,3-di-*O*-benzoyl-6-*O*-*p*-methoxybenzoyl-β-D-galactopyranosyl)-β-D-glucopyranoside (23) and 2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-6-deoxy-4-*O*-(2,3-di-*O*-benzoyl-4-*O*-*p*-methoxybenzoyl-β-D-galactopyranosyl)-β-D-glucopyranoside (24). Method A: Compound **9** (259 mg, 0.27 mmol) was treated with DDQ (134 mg, 0.57 mmol), AcOH (81.5 μL, 1.43 mmol), molecular sieves (250 mg), and H_2O (10 μL, 0.57 mmol), as described in the preparation of **11** and **12**. The crude product was chromatographed (SiO_2, heptane/EtOAc 3:1 → 1:1) to give **23** (218 mg, 83%) and **24** (43.9 mg, 16%). The physical data for **23** and **24** were as described.[17]

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2-*O*-acetyl-3-deoxy-6-*O*-*p*-methoxybenzoyl-β-D-*xylo*-hexopyranosyl)-β-D-glucopyranoside (25) and 2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2-*O*-acetyl-3-deoxy-4-*O*-*p*-methoxybenzoyl-β-D-*xylo*-hexopyranosyl)-β-D-glucopyranoside (26). Method E: A mixture of **10** (80 mg, 0.112 mmol), DDQ (40 mg, 0.169 mmol), 18-crown-6 ether (3 mg), $NaHSO_4$ (69 mg, 0.507 mmol), molecular sieves (4 Å) (0.01 mL H_2O added to 200 mg of sieves), and $ClCH_2CH_2Cl$ (5 mL) was stirred at 70 °C overnight and then diluted with CH_2Cl_2/H_2O (70 mL, 5:2) and filtered (Celite). The organic phase was washed with saturated aqueous $NaHCO_3$ (2 × 20 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, toluene/CH_3CN 9:1 → 7:1) to give **25** (53 mg, 65%) and **26** (25 mg, 31%). The physical data for **25** and **26** were as described.[16]

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-6-chloro-6-deoxy-4-*O*-*p*-methoxybenzoyl-β-D-galactopyranoside (27). Method F: A mixture of **2** (200 mg, 0.33 mmol), 18-crown-6 ether (37.2 mg, 0.14 mmol), KCl/4 Å molecular sieves (2.77 mmol/g, 379 mg, ∼1.05 mmol), and dry toluene (5 mL) was stirred under Ar for 10 min. DDQ (164 mg, 0.70 mmol) was added, and the mixture was heated at 80 °C overnight. The mixture was diluted with EtOAc (75 mL), filtered through Celite, washed with saturated aqueous $NaHCO_3$ (2 × 40 mL) with vigorous shaking, dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 4:1) to give **27** (179.5 mg, 85%). An analytical sample was obtained by recrystallization from MeOH; mp 148−149 °C; $[\alpha]^{22}_D$ +207.0° (*c* 1.0, $CHCl_3$); ^{1}H-NMR δ 8.04, 6.95 (d, 2 H each, J = 9.0 Hz), 5.96 (dd, 1 H, J = 3.4, 1.0 Hz), 5.77 (dd, 1 H, J =10.5, 8.0 Hz), 5.57 (dd, 1 H, J = 10.4, 3.4 Hz), 4.83 (d, 1 H, J = 7.9 Hz), 3.88 (s, 3 H), 3.74−3.64 (m, 3 H), −0.04 (s, 9 H); ^{13}C-NMR δ 165.6, 165.22, 165.17, 163.9, 121.3, 113.9, 101.0, 74.2, 72.0, 69.8, 67.9, 55.5, 41.5, 18.0, −1.5; HRMS calcd for $C_{33}H_{37}O_9ClSiNa$ (M + Na) 663.1793, found 663.1779.

Method G: A mixture of **2** (500 mg, 0.82 mmol), DDQ (375 mg, 1.7 mmol), molecular sieves (4 Å, 600 mg), and dry $ClCH_2CH_2Cl$ (10 mL) was stirred for 20 min under Ar, and then trimethylsilyl chloride (0.209 mL, 1.7 mmol) was added. The mixture was left at 50 °C overnight and then diluted with EtOAc (200 mL), filtered throught Celite, washed with saturated aqueous $NaHCO_3$ (2 × 40 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc/CH_2Cl_2 7:1:1) to give **27** (464 mg, 88%).

Method H: A mixture of **2** (100 mg, 0.17 mmol), Bu_4NCl/$CuCl_2$ (2:1, 175.8 mg), activated molecular sieves (200 mg), and dry $ClCH_2CH_2Cl$ (4 mL) was stirred for 20 min under Ar and then at 90 °C for 15 h. General workup and purification as above gave **2** (101 mg, 96%).

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-6-bromo-6-deoxy-4-*O*-*p*-methoxybenzoyl-β-D-galactopyranoside (28). Method I: A mixture of **2** (200 mg, 0.33 mmol), DDQ (112 mg, 0.50 mmol), molecular sieves (4 Å, 200 mg), and dry $ClCH_2CH_2Cl$ (10 mL) was stirred for 20 min, and then trimethylsilyl bromide (0.067 mL, 0.50 mmol) was added. The mixture was left at 40 °C for 20 h and then diluted with EtOAc (100 mL), filtered throught Celite, washed with saturated aqueous $NaHCO_3$ (2 × 40 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, toluene/EtOAc 80:1 → 10:1) to give **28** (203 mg, 90%). An analytical sample was obtained by recrystallization from ether/heptane: mp 143−144 °C; $[\alpha]^{22}_D$ +201.2° (*c* 1.0, $CHCl_3$); ^{1}H-NMR δ 8.04, 6.95 (d, 2 H each, J = 9.0 Hz), 5.96 (dd, 1 H, J = 3.4, 1.1 Hz), 5.75 (dd, 1 H, J = 10.4, 7.8 Hz), 5.54 (dd, 1 H, J = 9.4, 3.4 Hz), 4.81 (d, 1 H, J = 7.9 Hz), 3.89 (s, 3 H), 3.52 (dd, 2 H, J = 6.5, 1.2 Hz), −0.04 (s, 9 H); ^{13}C-NMR δ 165.6, 165.23, 165.18, 163.9, 121.2, 113.9, 101.0, 100.9, 74.14, 74.10, 72.0, 69.83, 69.77, 68.4, 67.9, 55.5, 28.8, 18.0, −1.5; HRMS calcd for $C_{33}H_{37}O_9SiBrNa$ (M + Na) 707.1288, found 707.1304.

Method J: A mixture of **2** (200 mg, 0.33 mmol), Bu_4NBr/$CuBr_2$ (2:1, 220 mg), activated molecular sieves (4 Å, 200 mg), and dry $ClCH_2CH_2Cl$ (4 mL) was stirred for 20 min under Ar. DDQ (164 mg, 0.70 mmol) was added, and the mixture was stirred at 90 °C for 15 h. Workup and purification as above gave **28** (210 mg, 93%).

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-6-chloro-6-deoxy-4-*O*-*p*-methoxybenzoyl-β-D-glucopyranoside (29). Method G: Compound **5** (200 mg, 0.33 mmol) was treated with DDQ (112 mg, 0.50 mmol) and trimethylsilyl chloride (0.063 mL, 0.50 mmol) as described in the preparation of **27** according to method G. The crude product was chromatographed (SiO_2, toluene/EtOAc 80:1 → 40:1) to give **29** (166 mg, 79%). An analytical sample was obtained by recrystallization from ether/heptane: mp 149−151 °C; $[\alpha]^{22}_D$ −2.9° (*c* 1.0, $CHCl_3$); ^{1}H-NMR δ 5.86 (t, 1 H, J = 9.6 Hz), 5.50 (dd, 1 H, J = 9.8, 7.9 Hz), 5.43 (t, 1 H, J = 9.6 Hz), 4.86 (d, 1 H, J = 7.9 Hz), 4.02−

3.95 (m, 1 H), 3.82 (s, 3 H), −0.05 (s, 9 H); HRMS calcd for $C_{33}H_{37}O_9SiClNa$ (M + Na) 663.1793, found 663.1802.

Method H: Compound **5** (100 mg, 0.17 mmol) was treated with DDQ (58 mg, 0.25 mmol), $Bu_4NCl/CuCl_2$ (2:1, 176 mg) and molecular sieves (3 Å, 100 mg) as described in the preparation of **27** according to method H. Workup and purification as above gave **9** (96.5 mg, 91%).

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-6-bromo-6-deoxy-4-*O*-*p*-methoxybenzoyl-*β*-D-glucopyranoside (30) and 2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-6-bromo-6-deoxy-5-*O*-*p*-methoxybenzoyl-α-D-glucofuranoside (31). Method I: Compound **5** (100 mg, 0.17 mmol) was treated with DDQ (58 mg, 0.25 mmol) and trimethylsilyl bromide (98%, 0.033 mL, 0.25 mmol) as described in the preparation of **28** according to method I. Workup and purification as above gave **31** (22.1 mg, 20%) and **30** (85.2 mg, 75%). Compound **30**: $[\alpha]^{22}_D$ −40.0° (*c* 1.0, $CHCl_3$); ^{1}H-NMR δ 5.86 (t, 1 H, J = 9.7 Hz), 5.50 (dd, 1 H, J = 9.7, 7.9 Hz), 5.40 (t, 1 H, J = 9.6 Hz), 4.86 (d, 1 H, J = 7.8 Hz), 3.98 (m, 1 H), 3.82 (s, 3 H), 3.58 (dd, 1 H, J = 11.2, 3.4 Hz), 3.53 (dd, 1 H, J = 11.4, 7.6 Hz), −0.04 (s, 9 H); ^{13}C-NMR δ 165.8, 165.0, 163.9, 120.9, 113.8, 100.4, 74.3, 72.9, 72.1, 71.6, 67.7, 55.4, 31.2, 17.9, −1.5; HRMS calcd for $C_{33}H_{37}O_9BrSiNa$ 707.1288, found 707.1309. Compound **31**: $[\alpha]^{22}_D$ −35.4° (*c* 1.0, $CHCl_3$); ^{1}H-NMR δ 5.88 (dd, 1 H, J = 5.6, 1.0 Hz), 5.51 (dt, 1 H, J = 9.2, 2.8 Hz), 5.43 (d, 1 H, J = 1.2 Hz), 5.26 (s, 1 H), 5.01 (dd, 1 H, J = 9.2, 5.5 Hz), 4.03 (dd, 1 H, J = 11.5, 3.0 Hz), 3.83 (s, 3 H), 3.64 (m, 1 H), 0.04 (s, 9 H); ^{13}C-NMR 165.1, 165.0, 164.7, 163.6, 121.5, 113.5, 106.0, 81.3, 79.0, 74.5, 69.6, 66.3, 55.4, 33.9, 18.0, −1.3; HRMS calcd for $C_{33}H_{37}O_9SiBrNa$ (M + Na) 707.1288, found 707.1309.

Method J: Compound **5** (100 mg, 0.17 mmol) was treated with DDQ (58 mg, 0.25 mmol) and $Bu_4NBr/CuBr_2$ (2:1, 220 mg) as described in the preparation of **28** according to method J. Workup and purification as above gave **30** (99.3 mg, 88%).

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzyl-6-bromo-6-deoxy-4-*O*-*p*-methoxybenzoyl-*β*-D-galactopyranoside (32) and 2-(Trimethylsilyl)ethyl 2-*O*-Benzyl-6-bromo-6-deoxy-4-*O*-*p*-methoxybenzoyl-*β*-D-galactopyranoside (33). Compound **3** (100 mg, 0.17 mmol) was treated with DDQ (80 mg, 0.35 mmol) and trimethylsilyl bromide (0.040 mL, 0.31 mmol) in dry chloroform (8 mL) at 60 °C for 2 h, essentially as described in the preparation of **28** according to method B. The crude product was chromatographed (SiO_2, heptane/EtOAc 4:1) to give **32** (38 mg, 33%) and **33** (52 mg, 53%). Compound **32**: $[\alpha]^{22}_D$ +55.1° (*c* 1.0, $CHCl_3$); ^{1}H-NMR δ 8.06, 6.93 (d, 2 H each, J = 9.0 Hz), 5.83 (t, 1 H, J = 1.3 Hz), 4.94−4.57 (m, 4 H), 4.48 (bd, 1 H, J = 7.6 Hz), 4.10 (m, 1 H), 3.81 (dt, 1 H, J = 6.6, 1.0 Hz), 3.44 (dd, 2 H, J = 6.7, 1.3 Hz), 0.05 (s, 9 H); ^{13}C-NMR δ 165.5, 163.7, 138.6, 137.8, 121.8, 113.7, 103.3, 79.3, 78.8, 75.3, 73.8, 72.0, 67.9, 67.4, 55.5, 29.4, 18.5, −1.4. Anal. Calcd for $C_{33}H_{41}O_7BrSi$: C, 60.4; H, 6.3. Found: C, 60.7; H, 6.3. Compound **33**: $[\alpha]^{22}_D$ +46.5° (*c* 1.5, $CHCl_3$); ^{1}H-NMR δ 8.05, 6.92 (d, 2 H each, J = 9.0 Hz), 5.85 (bd, 1 H, J = 3.2 Hz), 4.88, 4.54 (d, 1 H each, J = 11.5 Hz), 4.39 (d, 1 H, J = 7.8 Hz), 4.08 (m, 1 H), 3.86 (s, 3 H), 3.57 (dd, 1 H, J = 9.7, 3.3 Hz), 3.45 (d, 1 H, J = 6.7 Hz), 0.04 (s, 9 H); ^{13}C-NMR δ 165.5, 163.8, 137.4, 121.6, 113.7, 102.5, 79.1, 74.1, 71.7, 70.7, 67.69, 66.7, 55.5, 29.3, 18.2, −1.4; HRMS calcd for $C_{26}H_{35}O_7SiBrNa$ (M + Na) 589.1233, found 589.1233.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzoyl-4-*O*-(2,3-di-*O*-benzoyl-6-chloro-6-deoxy-4-*O*-*p*-methoxybenzoyl-*β*-D-galactopyranosyl)-*β*-D-glucopyranoside (34). Method H: Compound **8** (150 mg, 0.14 mmol) was treated with DDQ (49 mg, 0.22 mmol) and trimethylsilyl chloride (0.0277 mL, 0.22 mmol) in dry chloroform (4 mL) at 55 °C, as described in the preparation of **27** according to method B. The crude product was chromatographed (SiO_2, heptane/EtOAc 8:3) to give **34** (151 mg, 97%). An analytical sample was obtained by recrystallization from ether/heptane: mp 100−102 °C; $[\alpha]^{22}_D$ +113° (*c* 0.7, $CHCl_3$); ^{1}H-NMR δ 5.77 (t, 1 H, J = 9.6 Hz), 5.70−5.64 (m, 2 H), 5.45 (dd, 1 H, J = 9.7, 8.0 Hz), 5.30 (dd, 1 H, J = 10.3, 3.3 Hz), 4.85 (d, 1 H, J = 8.0 Hz), 4.71 (d, 1 H, J = 7.9 Hz), 4.63, 4.44 (dd, 1 H each, J = 12.2, 1.5, 4.4 Hz), 4.27 (t, 1 H, J = 9.5 Hz), 3.90 (s, 3 H), 3.66 (t, 1 H, J = 6.6 Hz), 2.92, 2.74 (dd, 1 H each J = 11.4, 6.4, 6.8 Hz), −0.13 (s, 9 H); ^{13}C-NMR δ 165.9, 165.4, 165.2, 164.8, 163.9, 121.1, 113.9, 100.7, 100.4, 75.9, 74.3, 73.3, 72.9, 71.9, 71.8, 69.9, 67.5, 67.3, 62.5, 55.6, 40.5, 17.9, −1.5; HRMS calcd for $C_{60}H_{59}O_{17}SiClNa$ (M + Na) 1137.3108, found 1137.3126.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzoyl-4-*O*-(2,3-di-*O*-benzoyl-6-bromo-6-deoxy-4-*O*-*p*-methoxybenzoyl-*β*-D-galactopyranosyl)-*β*-D-glucopyranoside (35). Method I: Compound **8** (150 mg, 0.14 mmol) was treated with DDQ (49 mg, 0.22 mmol) and trimethylsilyl bromide (98% 0.0186 mL, 0.14 mmol) in dry chloroform (3 mL) at 50 °C as described in the preparation of **28** according to method I. The crude product was chromatographed (SiO_2, heptane/EtOAc 3:1) to give **35** (134 mg, 83%). An analytical sample was obtained by recrystallization from ether/heptane: mp 109−110 °C; $[\alpha]^{22}_D$ +101.0° (*c* 1.0, $CHCl_3$); ^{1}H-NMR δ 5.79 (t, 1 H, J = 9.5 Hz), 5.71 (d, 1 H, J = 2.9 Hz), 5.68 (dd, 1 H, J = 10.4, 8.0 Hz), 5.47 (dd, 1 H, J = 9.7, 8.0 Hz), 5.33 (dd, 1 H, J = 10.3, 3.4 Hz), 4.87 (d, 1 H, J = 8.0 Hz), 4.72 (d, 1 H, J = 7.9 Hz), 4.66 (bd, 1 H, J = 10.7 Hz), 4.46 (dd, 1 H, J = 12.2, 4.4 Hz), 4.32 (t, 1 H, J = 9.5 Hz), 3.89 (s, 3 H), 3.74 (t, 1 H, J = 6.6 Hz), 2.83, 2.58 (dd, 1 H each J = 10.7, 6.1, 7.1 Hz), −0.12 (s, 9 H). Anal. Calcd for $C_{60}H_{59}O_{17}BrSi$: C, 62.1; H, 5.1. Found: C, 61.8; H, 5.5.

Method J: Compound **8** (100 mg, 0.093 mmol) was treated with DDQ (33 mg, 0.14 mmol) and $Bu_4NBr/CuBr_2$ (2:1, 123 mg) in dry $ClCH_2CH_2Cl$ (4 mL) as described in the preparation of **28** according to method J. Workup and purification as above gave **35** (100 mg, 93%)

Method L:[2] A mixture of compound **8** (50 mg, 0.046 mmol), NBS (15.6 mg, 0.069 mmol), and tetrachloromethane (20 mL) was heated until ∼2 mL of the solvent was distilled off. The mixture was refluxed overnight, diluted with chloroform (10 mL), washed with 10% aqueous $Na_2S_2O_3$ (10 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 3:1) to give **35** (51 mg, 95%).

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzoyl-4-*O*-(2,3-di-*O*-benzoyl-6-deoxy-4-*O*-*p*-methoxybenzoyl-*β*-D-galactopyranosyl)-*β*-D-glucopyranoside (36). Tributyltin hydride (0.030 mL, 0.11 mmol) was dissolved in dry toluene (3 mL) and the mixture was brought to reflux. A solution of compound **35** (50 mg, 0.043 mmol) and azobis(isobutyronitrile) (AIBN, 1 mg) in dry toluene (1 mL) was added under Ar. The mixture was refluxed for 5 h and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc/acetone 8:2:1) to give **36** (46 mg, 99%): $[\alpha]^{22}_D$ +123.1° (*c* 1.0, $CHCl_3$); ^{1}H-NMR δ 5.77 (t, 1 H, J = 9.3 Hz), 5.67 (dd, 1 H, J = 10.3, 7.8 Hz), 5.45−5.38 (m, 2 H), 5.31 (dd, 1 H, J = 10.3, 3.3 Hz), 4.80 (d, 1 H, J = 7.9 Hz), 4.71 (d, 1 H, J = 7.8 Hz), 4.59, 4.45 (dd, 1 H each, J = 11.9, 1.6, 4.6 Hz), 4.19 (t, 1 H, J = 9.2 Hz), 3.89 (s, 3 H), 0.64 (d, 3 H, J = 6.4 Hz); HRMS calcd for $C_{60}H_{60}O_{17}SiNa$ (M + Na) 1103.3497, found 1103.3466.

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Supporting Information Available: ^{1}H NMR spectra and ^{1}H NMR data with peak assignments for all title compounds described in the Experimental Section (34 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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