Regiospecific 4,6-Functionalization of Pyranosides via Dimethylboron Bromide-Mediated Cleavage of Phthalide Orthoesters

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Abstract: An efficient strategy for regiocontrolled differentiation of the 4,6-positions of pyranosides has been developed using dimethylboron bromide-mediated cleavage of phthalide orthoesters. The reaction proceeds under mild conditions, is tolerant of additional acetal functionality, and produces a benzoate bearing suitable functionality for intramolecular assisted cleavage in the presence of SAc, OAc, and NHAc groups.

Introduction

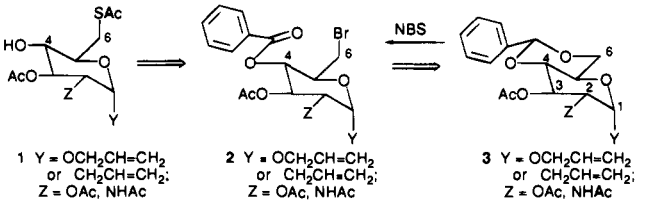
Regiocontrolled manipulation of a specific hydroxyl group in polyols is a unique and challenging problem in synthesis. Existing methods require initial protection/activation followed by regiocontrolled transformation to effect differentiation of similar hydroxyl groups in polyols.[1] Once regiospecific differentiation has been achieved, chemospecific removal of the resultant functionality in the presence of similar group(s) can be problematic. Herein we wish to report a new method which solves both the problems in an efficient manner.

In conjunction with a project to prepare various pyranoside-derived targets bearing a sulfur moiety at C-6 for evaluation as potential agents in an anti-retroviral screen, we needed to selectively differentiate C-4 and C-6 in a substrate bearing carboxylate functionality at C-3 in addition to having appended allyloxy or allyl moieties (cf. **1**). While the venerable Hanessian–Hullar reaction[2] has often been used for selective functionalization of C-6 in carbohydrate substrates, application in this instance would appear to be doubly problematic in that competitive halogenation of the allyl(oxy) moiety seems likely and liberation of the C-4 alcohol would require selective deprotection of the benzoate ester in the presence of substantially more reactive carboxylate functionality (3 → 2 → 1, Scheme 1).

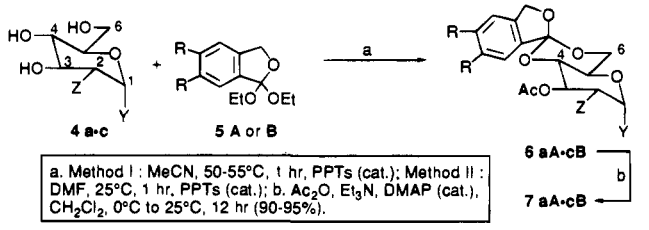
Results and Discussion

In order to address the above objective, an alternative protocol has been developed based upon the selective functionalization

Scheme 1



Scheme 2



of phthalide orthoesters. Reaction of glycosides **4a–c**[3] with the readily available orthoesters **5A** or **5B**[4] in acetonitrile or DMF in the presence of catalytic pyridinium *p*-toluenesulfonate (PPTs) resulted in 4,6-O-protected orthoesters **6aA–cB** in excellent yield (Scheme 2) as single diastereomers (Table 1). The stereochemistry of the C-2,3 diol **6cA** has been unambiguously confirmed by X-ray.[5] Subsequent acylation provides **7aA–cB** as the first examples of functionalized phthalide orthoesters ("4,6-POE" group) in near quantitative yield.

Selective differentiation of C-4 and C-6 was investigated with dimethylboron bromide, a reagent well explored in the cleavage

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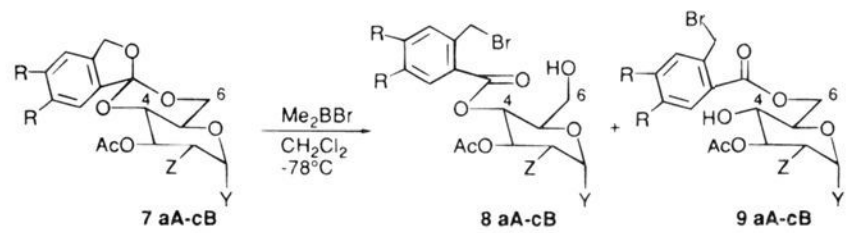
0002-7863/95/1517-0177$09.00/0

Table 1

SM	Z	Y	R	method	yield (%)	product
4a	NHAc	*O*-allyl	H	**I**	95	**6aA**
4a	NHAc	*O*-allyl	OMe	**I**	80	**6aB**
4b[a]	OH	*O*-allyl	H	**II**	89	**6bA**
4c	OH	allyl	H	**I**	80	**6cA**
4c	OH	allyl	OMe	**II**	64	**6cB**

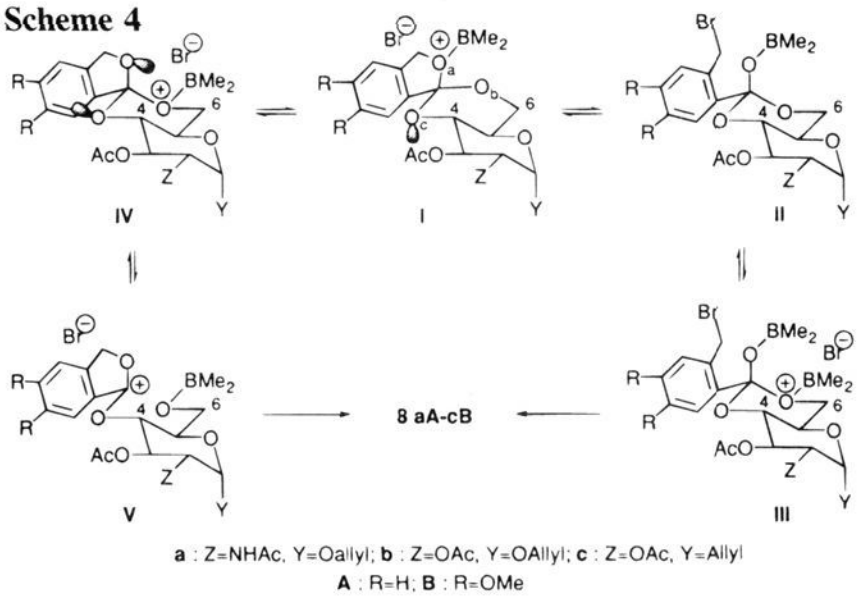
[a] A 10:1 mixture of α:β anomers was employed.

Scheme 3



a : Z=NHAc, Y=Oallyl; **b** : Z=OAc, Y=OAllyl; **c** : Z=OAc, Y=Allyl
A : R=H; **B** : R=OMe

Scheme 4



of acetals.[6] Instantaneous reaction occurred on *rapid* addition of dimethylboron bromide (1 M in dichloromethane) to the pyranosides **7aA−cB** at −78 °C in dichloromethane (Scheme 3). The reactions were typically quenched by quickly adding the cold mixture to a well-stirred solution of aqueous sodium bicarbonate at 25 °C. Essentially identical results were obtained by quenching after warming the reaction mixture to 25 °C. Time and temperature of quench has no influence on the product ratio. The major determinants of product selectivity are phthalide substitution pattern and the number of equivalents of boron reagent. High selectivity for generation of the C-4 benzoate was achieved by employing 2.3 equiv of dimethylboron bromide, the products **8aA−cB/9aA−cB** being isolated in excellent yield.[7] Two important features to be noted are (i) the reaction proceeds smoothly with absolutely *no complications from competitive cleavage of the acetal moiety* (**7aA−bA**), and (ii) the reaction results in *complete reversal of chemoselectivity*; the sterically demanding secondary (C-4) hydroxyl group is protected over a free primary (C-6) hydroxyl group.

A preliminary mechanistic hypothesis can be advanced to explain the stoichiometric and substitution effects upon the regiospecificity of the orthoester cleavage process (Scheme 4). Molecular mechanics calculations suggest that coordination of dimethylboron bromide at the benzylic oxygen and C-6 oxygens (O_a, O_b) are of approximate equal energy affording intermediates **I** and **IV**, while coordination of dimethylboron bromide with the C-4 oxygen (O_c) is far less favorable. **I** is calculated to reside in a boat conformation, with only one lone pair appropriately positioned[8] to facilitate fragmentation of the O_a orthoester bond; furthermore, O_a is approximately in the plane of the arene and should not enjoy significant benzylic activation. In contrast, intermediate **IV** has two potential participatory lone pairs[9] and is also geometrically positioned for π activation by the arene ring. We were therefore initially quite surprised to obtain approximately equal amounts of both *o*-(bromomethyl)-benzoates **8/9** (Table 2 entries 1, 2, 9, 11, 12, 15, 16). This finding implies rapid and irreversible production of intermediate **II** which generates approximately a 1:1 mixture of **8/9** upon hydrolysis of the borinate intermediate.

(7) All new compounds were fully-characterized. Copies of proton and carbon NMR spectra may be found in the supplementary information.

Table 2

entry	compd (**7xx**)	equiv. of reagent	quench *T* (°C)	time	product ratio **8xX**:**9xX**	yield (%)
1	**7aA**	1.2	−78	5 min	1:1.5	98[a]
2	**7aA**	1.2	25	1 h	1:1.5	98[a]
3	**7aA**	2.3	−78	5 min	10:1	95[a]
4	**7aA**	2.3	25	1 h	10:1	95[a]
5	**7aA**	3.5	25	1 h	10:1	90
6	**7aB**	1.2	25	1 h	12:1	98
7	**7aB**	2.3	25	1 h	25:1	86
8	**7aB**	2.3	80	24 h	25:1	94
9	**7bA**	1.2	25	1 h	2:1	98
10	**7bA**	2.3	25	1 h	14:1	95
11	**7cA**	1.2	−78	5 min	1:1	86[a]
12	**7cA**	1.2	25	1 h	1:1	86[a]
13	**7cA**	2.3	−78	5 min	2:1	95[a]
14	**7cA**	2.3	25	1 h	2:1	95[a]
15	**7cA**	1.2[b]	−78	5 min	2:1	95[a]
16	**7cA**	1.2[b]	25	1 h	2:1	95[a]
17	**7cA**	2.3[b]	−78	5 min	2.3:1	91[a]
18	**7cA**	2.3[b]	25	1 h	2.3:1	91[a]
19	**7cB**	1.2	25	1 h	14:1	90
20	**7cB**	2.3	25	2 h	14:1	96
21	**7cB**	2.3[b]	25	1 h	13:1	90

[a] Combined yield of −78 and 25 °C quench experiments. [b] 9-Br-9-BBN was used instead of Me_2BBr.

On the basis of this model we added a second equivalent of the boron reagent to convert intermediate **II** to **III** which substantially improved the regiospecificity for cleavage of **7aA**, **7bA** but not **7cA** (Table 2, entries 3, 4, 10, 13, 14, 17, 18). We next investigated the chemistry of the dimethoxy orthoesters **7a−cB** with a view to promoting intramolecular oxygen alkylation[10] of borinate **II** by the *p*-methoxybenzyl halide, thus reestablishing intermediates **I** and **IV** as active participants in the equilibrium. In addition, the dimethoxy substitution should strongly facilitate the transformation of **IV** to **V**, by virtue of resonance effects imparted by the second methoxy group *meta* to the benzylic oxygen O_a. In the event, compounds **7aB** and **7cB** are best converted to C-4 substituted benzoates by the synergistic interplay of both the methoxy substitution and the

(8) For stereoelectronic effects see: (a) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon Press: Oxford, 1983. (b) *Reactivity and Structure. Concepts in Organic Chemistry*; Hafner, K., Rees, C. W., Trost, B. M., Lehn, J.-M., Schleyer, P. R., Zahradnik, R., Eds.; Springer-Verlag: Berlin, 1983; pp 81−84.

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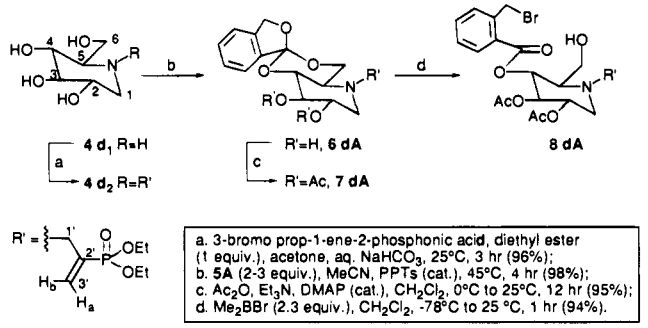
(10) Evidence in support of the concept of reversible alkylation is found in the work of Guindon (refs 6b,e,f) who has shown that dimethylboron bromide cleaves the endocyclic bond of THP acetals *and sugar-derived pyranosides* under kinetic conditions to rapidly provide α-bromo ether. Under more forcing conditions the α-bromo ether undergoes intramolecular oxygen alkylation of the borinate moiety to ultimately generate α-bromopyranyl ether as the thermodynamic product.

Scheme 5

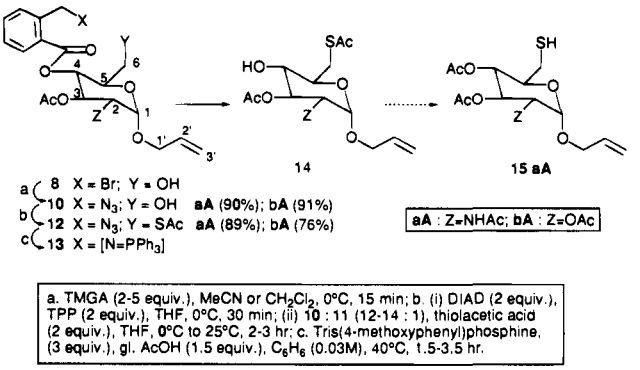


use of 2.3 equivalents of dimethylboron bromide (Table 2 entries 6, 7, 20, 21).

The phthalide orthoester strategy was also employed (Scheme 5) for functionalization of the azasugar deoxynojirimycin (DNJ, $\mathbf{4d_1}$).[11] Numerous derivatives of this interesting class of compounds, in which the ring oxygen of sugars are replaced by an amino group, possess excellent biological activity including anti-HIV activity.[12] Treatment of DNJ $\mathbf{4d_1}$ with 3-bromoprop-1-ene-2-phosphonic acid, diethyl ester,[13] in acetone and aqueous sodium bicarbonate at 25 °C for 3 h, followed by lyophylization, afforded vinyl phosphonate $\mathbf{4d_2}$ in 96% yield. Acid−catalyzed reaction of $\mathbf{4d_2}$ with phthalide orthoester **5A** in warm acetonitrile resulted in 4,6-O protected derivative **6dA** in near quantitative yield as a single diastereomer. Acylation to provide **7dA** followed by regiospecific orthoester cleavage using the conditions described above (2.3 equiv of dimethylboron bromide at −78 °C) resulted in an instantaneous reaction. The required product **8dA** was isolated as a *single* isomer in excellent yield (94%).[14]

Attention was next focused on exploiting the *o*-(bromomethyl)benzoate moiety as a means of directed benzoate cleavage. Chemospecific deprotection of the substituted benzoate in the presence of additional acyl functionalities was carried out for both series **aA** and **bA**. Suitable functionalization of the benzylic position was necessary for chemospecific removal of the benzoate moiety at C-4.[15] Conversion of the inseparable 12−14:1 mixture of *o*-(bromomethyl)benzoates **8** and **9** to a 12−14:1 inseparable mixture of C-4 *o*-(azidomethyl)benzoate

Scheme 6



10 and C-6 *o*-(azidomethyl)benzoate **11** (not shown) was accomplished in excellent yield by employing tetramethylguanidinium azide (TMGA, Scheme 6).[16] Temperature and time are key factors in this reaction; higher temperatures or longer reaction times result in base-catalyzed migration of the C-4 benzoate to the C-6 position. Initial attempts at converting the C-6 OH **10** to the corresponding tosylate followed by displacement with KSAc were unsuccessful. Successful introduction of sulfur residue at C-6 was achieved by the application of the Mitsunobu protocol.[17] Addition of the 12−14:1 mixture of **10**/**11** and thiolacetic acid in THF to the preformed adduct of diisopropyl azodicarboxylate (DIAD) and triphenylphosphine (TPP) in THF at 0 °C followed by slow warming to 25 °C resulted in a high-yielding clean conversion; only the primary C-6 **OH** was displaced by thioacetic acid (Scheme 6) to give **12** while the sterically more hindered C-4 OH remained intact, thus facilitating chromatographic removal of the unwanted minor benzoate.

Chemospecific cleavage of the benzoate moiety *in the presence of the three additional acyl functionalities* was accomplished in high isolated yield (**14aA**, 81% and **14bA**, 80%) by using tris(4-methoxyphenyl)phosphine in warm benzene (0.03 M) in the presence of glacial acetic acid. Presumably this reaction involves intramolecular transacylation[15] of phosphoranylideneamine[18] intermediate **13**. Higher concentration or omission of the proton source resulted in partial rearrangement of **14aA** to mercaptan **15aA** (~3:1) in which the acyl group has migrated from C-6 to C-4, along with other unidentified products. This migration was not observed in the case of **14bA**. While TPP and tributylphosphine gave similar results, tris(4-methoxyphenyl)phosphine is currently the reagent of choice which best simplifies purification.

Conclusion

In summary, an efficient strategy for regiocontrolled differentiation of the 4,6-positions of pyranosides has been developed using dimethylboron bromide-mediated cleavage of phthalide orthoesters. The reaction proceeds under mild conditions, is tolerant of additional acetal functionality, and produces a benzoate bearing suitable functionality for intramolecular assisted cleavage in the presence of SAc, OAc, and NHAc groups. Studies are underway to determine the scope, limitations, and mechanistic features of this strategy.

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(13) 3-Bromoprop-1-ene-2-phosphonic acid, diethyl ester, was prepared as a colorless liquid from the corresponding alcohol (Rambaud, M.; Vecchio, A.; Villieras, J. *Synth. Commun.* **1984**, *14*, 833) using PBr_3 in ether (Villieras, J.; Rambaud, M. *Synthesis* **1982**, 924): ^1H NMR ($CDCl_3$) δ 1.31 (t, 6H, 2 × CH_3), 4.05−4.12 (m, 6H, 2 × OCH_2, H-$3_{a,b}$), 6.17 (dd, 1H, H-1_{trans}, $J_{P,H}$ = 44.5 Hz), 6.24 (d, 1H, H-1_{cis}, $J_{P,H}$ = 21.2 Hz); ^{13}C NMR ($CDCl_3$) δ 16.14 (o), 16.23 (o), 29.61 (e, C-3, $J_{P,C}$ = 16.8 Hz), 62.23 (e), 62.31 (e), 134.45 (e, C-1, $J_{P,C}$ = 8.4 Hz), 135.63 (e, C-2, $J_{P,C}$ = 171.0 Hz).

(14) The 300 MHz ^1H NMR of the crude reaction material shows only one isomer.

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Experimental Section

General Methods. Melting points were determined on a Meltemp apparatus and are uncorrected. Unless otherwise stated, reactions were performed under argon in flame/oven dried glassware. Tetrahydrofuran (THF) was distilled from sodium–benzophenone ketyl. Acetonitrile, dichloromethane, and benzene were distilled from calcium hydride. Dimethylformamide (DMF) was distilled from calcium hydride and stored over molecular sieves. Dimethylboron bromide was purchased from Aldrich Chemical Co. and used as a 1 M solution in dichloromethane. All other reagents were used as purchased. Flash chromatography was carried out as described by Still[19] using 230–400 mesh silica gel. ^{1}H and ^{13}C NMR spectra were obtained using a GE QE-300 NMR spectrometer at 300 and 75 MHz, respectively. ^{1}H NMR chemical shifts are reported in ppm relative to residual protonated solvent resonance: $CHCl_3$, δ 7.26; C_6D_5H, δ 7.15. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; ap t, apparent triplet; q, quartet, m, multiplet; br, broadened; ABq, ABquartet. Coupling constants (J) are reported in Hertz. ^{13}C NMR chemical shifts are reported in ppm relative to solvent resonance: $CDCl_3$, δ 77.00; C_6D_6, δ 128.00. Peaks in ^{13}C NMR spectra are denoted as "e" for carbons with zero or two attached protons or "o" for carbons with one or three attached protons as determined from APT pulse sequence. For numbering of compounds see **4d$_2$** (azasugar derivatives, Scheme 5) and **8aA** (sugar derivatives, Scheme 6). Optical rotations were taken on a Rudolph Research Autopol III instrument. Mass spectral data were obtained from Purdue University Campus-wide Mass Spectral Facility. X-ray data were obtained from Purdue Chemistry Department X-ray Crystallography Laboratory. Labconco Freeze Dry System was used for lyophilizing the reactions carried out in aqueous medium.

Deoxynojirimycin Derivative 4d$_2$. To deoxynojirimycin (55 mg, 0.34 mmol, 1.0 equiv) dissolved in a minimum amount of saturated aqueous sodium bicarbonate was added 3-bromoprop-1-ene-2-phosphonic acid, diethyl ester (86 mg, 0.34 mmol, 1.0 equiv), in acetone (1 mL). Instantaneous reaction occurred as indicated by TLC (20/80 MeOH/EtOAc) and a fine white solid precipitated. The reaction mixture was stirred at 25 °C for 3 h. After removing the acetone *in vacuo*, the reaction mixture was lyophilized for 24 h. The resulting white solid was stirred with portions of warm EtOAc repeatedly till all the product was extracted into the organic layer. The organic phases were mixed and dried over Na_2SO_4. Removal of the solvent *in vacuo* resulted in 4d$_2$ as a colorless foam (110 mg, 96% yield) which was homogeneous by TLC and NMR. **4d$_2$**: ^{1}H NMR ($CDCl_3$) δ 1.31 (t, 3H), 1.94 (ap t, 1H), 2.08 (d, 1H), 2.65 (dd, 1H), 3.05 (dd, 1H), 3.29 (ap t, 1H) 3.43 (m, 1H), 3.60 (ap t, 1H), 3.91–4.13 (m, 8H), 4.84–4.86 (br, 3H), 5.86 (d, 1H), 5.90 (d, 1H); ^{13}C NMR ($CDCl_3$) δ 16.25 (o), 16.41 (o), 55.46 (e), 57.41 (e), 62.26 (e), 62.45 (e), 66.67 (o), 69.06 (o), 69.70 (o), 79.34 (o), 131.20 (e), 138.37 (e); HRMS (CI, isobutane) calcd for $C_{13}H_{26}NO_7P$ 340.1525 $(M + H)^+$, found 340.1514.

General Procedure for 4,6-POE Derivatives. Method I. To the anhydrous pyranoside derivative **4** (1.0 equiv) was added phthalide orthoester **5**[4] (1.5–2.0 equiv) in dry acetonitrile. A crystal of anhydrous PPTs was then added and the reaction mixture was heated to 50–55 °C for 1 h. At this time the reaction mixture was almost homogeneous. The reaction was quenched by addition of solid sodium carbonate (50 mg) followed by aqueous sodium carbonate solution. The mixture was extracted with dichloromethane (four times). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel using 2% Et_3N in ethyl acetate.

Method II. To a mixture of the anhydrous pyranoside derivative (1.0 equiv) and the phthalide orthoester (1.5–2.0 equiv) was added dry DMF. A crystal of anhydrous PPTs was then added and the reaction mixture was stirred at 25 °C for 1 h. On completion, the reaction was quenched by addition of solid sodium carbonate (50 mg) followed by aqueous sodium carbonate solution. The mixture was worked-up as above.

6aA (method I, 95% yield): colorless oil; ^{1}H NMR (C_6D_6) δ 1.70 (s, 3H), 3.70–3.75 (m, 1H, H-1′$_a$), 3.90–4.22 (m, 4H, H-1′$_b$, H-3, H-5, H-6$_a$), 4.42–4.62 (m, 4H, H-2, H-4, H-6$_b$, OH), 4.79–5.20 (m, 5H, H-1, H-3′$_{a,b}$, $ArCH_2$), 5.70–5.82 (m, 1H, H-2′), 6.43 (d, 1H, NH), 6.73–6.78 (m, 1H, ArH), 7.01–7.10 (m, 2H, ArH), 7.60–7.66 (m, 1H, ArH); ^{13}C NMR (C_6D_6) δ 22.77 (o), 54.97 (o), 63.71 (o), 63.90 (e, C-6), 68.58 (e, C-1′), 69.79 (o), 71.28 (e, $ArCH_2$), 76.19 (o), 98.00 (o, C-1), 117.36 (e, C-3′), 121.14 (e), 121.27 (o), 123.06 (o), 127.83 (o), 129.91 (o), 134.32 (o, C-2′), 137.29 (e), 140.14 (e), 171.33 (e); HRMS (CI, isobutane) calcd for $C_{19}H_{23}NO_7$ 378.1553 $(M + H)^+$, found 378.1553.

6aB (method I, 80% yield): colorless oil; ^{1}H NMR (C_6D_6) δ 1.44 (s, 3H), 3.29 (s, 3H), 3.32 (s, 3H), 3.59–3.66 (m, 1H, H-1′$_a$), 3.89–3.96 (m, 1H, H-1′$_b$), 4.06–4.13 (m, 2H, H-3, H-6$_a$), 4.19–4.28 (m, 1H, H-5), 4.46 (ddd, 1H, H-2), 4.56 (ap t, 2H, H-4, H-6$_b$), 4.77 (d, J = 3.7, 1H, H-1), 4.90 (ABq, 2H, $ArCH_2$), 4.95–4.99 (m, 1H, H-3′$_a$), 5.04–5.11 (m, 1H, H-3′$_b$), 5.42 (d, 1H, NH), 5.60–5.73 (m, 1H, H-2′), 6.15 (s, 1H, ArH), 7.17 (s, 1H, ArH); ^{13}C NMR (C_6D_6) δ 22.75 (o), 55.07 (o), 55.54 (o), 55.71 (o), 63.81 (o), 64.01 (e), 68.57 (e), 70.13 (o), 71.47 (e), 76.40 (o), 97.97 (o, C-1), 104.23 (o), 106.16 (o), 117.37 (e), 121.58 (e), 128.95 (e), 131.88 (e), 134.30 (o), 150.32 (e), 171.19 (e); HRMS (EI) calcd for $C_{21}H_{27}NO_9$ 437.1685 $(M)^+$, found 437.1695.

6bA (method II, 89% yield): colorless oil; ^{1}H NMR (C_6D_6) δ 3.54 (dd, 1H, H-2), 3.64–3.70 (m, 1H, H-1′$_a$), 3.89–3.96 (m, 2H, H-1′$_b$, H-3), 4.00 (dd, 1H, H-6$_a$), 4.09–4.17(m, 1H, H-5), 4.34 (ap t, 1H, H-4), 4.42 (ap t, 1H, H-6$_b$), 4.69 (d, J = 3.9, 1H, H-1), 4.80 (ABq, 2H, $ArCH_2$), 4.96–4.99 (m, 1H, H-3′$_a$), 5.08–5.15 (m, 1H, H-3′$_b$), 5.61–5.74 (m, 1H, H-2′), 6.69–6.72 (m, 1H, ArH), 7.03–7.06 (m, 2H, ArH), 7.62–7.65 (m, 1H, ArH); ^{13}C NMR (C_6D_6) δ 63.38 (o, C-5), 64.01 (e, C-6), 68.80 (e, C-1′), 71.37 (e, $ArCH_2$), 71.57 (o, C-3), 73.31 (o, C-2), 75.24 (o, C-4), 98.89 (o, C-1), 117.36 (e, C-3′) 121.06 (e), 121.25 (o), 123.14 (o), 127.87 (o), 129.97 (o), 134.41 (o, C-2′), 137.15 (e), 140.03 (e); HRMS (CI, isobutane) calcd for $C_{17}H_{20}O_7$ 337.1287 $(M + H)^+$, found 337.1270.

6cA (method I, 80% yield): colorless crystals; 187–188 °C (CH_2Cl_2); $[\alpha]^{25}_D$ +63.5 (c 0.01, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.42–2.48 (m, 2H, H-1′$_{a,b}$), 3.64–4.15 (m, 7H, H-1 to H-6$_{a,b}$), 5.08–5.20 (m, 4H, H-3′a,b, $ArCH_2$), 5.76–5.85 (m, 1H, H-2′), 7.22–7.49 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$) δ 29.57 (e), 63.36 (o), 63.90 (e), 71.32 (e), 71.43 (o), 72.15 (o), 75.36 (o), 76.13 (o), 117.18 (e), 120.35 (e), 121.20 (o), 122.41 (o), 128.00 (o), 130.30 (o), 134.39 (o), 135.87 (e), 139.37 (e); HRMS (CI, isobutane) calcd for $C_{17}H_{20}O_6$ 321.1338 $(M + H)^+$, found 321.1324.

6cB (method II, 64% yield): colorless oil; ^{1}H NMR (C_6D_6) δ 2.34–2.57 (m, 2H, H-1′$_{a,b}$), 3.34 (s, 3H), 3.39 (s, 3H), 3.70 (ap t, 1H, H-3), 3.82–3.99 (m, 2H, H-2, H-5), 4.01–4.06 (m, 2H, H-1, H-6$_a$), 4.31 (ap t, 1H, H-4), 4.39 (ap t, 1H, H-6$_b$), 4.83–5.08 (m, 4H, H-3′$_{a,b}$, $ArCH_2$), 5.71–5.85 (m, 1H, H-2′), 6.18 (s, 1H, ArH), 7.14 (s, 1H, ArH); ^{13}C NMR (C_6D_6) δ 29.97 (e, C-1′), 55.60 (o), 55.70 (o), 64.09 (o, C-2), 64.52 (e, C-6), 71.61 (e, $ArCH_2$), 71.99 (o, C-3), 72.69 (o, C-5), 76.16 (o, C-4), 76.67 (o, C-1), 104.06 (o), 106.01 (o), 116.69 (e, C-3′), 121.49 (e), 131.76 (e), 135.49 (o, C-2′), 150.41 (e), 152.22 (e); HRMS (EI) calcd for $C_{19}H_{24}O_8$ 380.1471 $(M)^+$, found 380.1457.

6dA (method I with modifications, see Scheme 5, 98% yield): foam; ^{1}H NMR ($CDCl_3$) δ 1.33 (dt, 6H, 2xCH_3), 2.07 (ap t, 1H, H-1$_{ax}$), 2.54 (ddd, 1H, H-5), 2.86 (ap t, 1H, H-1′$_a$), 3.08 (dd, 1H, H-1$_{eq}$), 3.14 (br, 1H, OH), 3.25 (br, 1H, OH), 3.40–3.47 (m, 2H, H-1′$_b$, H-3), 3.66 (dd, 1H, H-2), 4.02–4.18 (m, 7H, H-4, H-6$_{a,b}$, 2xOCH_2), 5.10 (ABq, 2H, $ArCH_2$), 6.02 (dd, 1H, H-3′$_b$), 6.10 (d, 1H, H-3′$_a$), 7.21–7.47 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$) δ 16.33 (o), 16.41 (o), 53.46 (e, C-1′), 56.73 (e, C-1), 58.38 (o, C-5), 62.10 (e), 62.09 (e), 63.88 (e, C-6), 69.99 (o, C-2), 71.08 (e, $ArCH_2$), 75.14 (o, C-4), 76.24 (o, C-3), 120.08 (e), 121.12 (o), 122.50 (o), 127.89 (o), 130.51 (o), 136.24 (e), 137.86 (e), 139.46 (e); HRMS (CI, isobutane) calcd for $C_{21}H_{30}NO_8P$ 456.1787 $(M + H)^+$, found 456.1778.

General Procedure for Acylation. To a well-stirred solution of the pyranoside alcohol **6aA–cB** (1.0 equiv) in dichloromethane at 0 °C was added Et_3N (5–8 equiv) followed by acetic anhydride (4–6 equiv). A crystal of (dimethylamino)pyridine (DMAP) was then added and the reaction mixture slowly warmed to 25 °C over 12 h. The reaction mixture was diluted with dichloromethane (3–4 volumes) and washed with aqueous sodium bicarbonate (two times). The organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. The oily residue was purified by flash chromatography on silica gel using 2% Et_3N in a 50/50 mixture of hexanes/ethyl acetate.

7aA (95% yield): colorless oil; $[\alpha]^{25}_D$ +61.5 (c 0.01, $CHCl_3$); ^{1}H NMR (C_6D_6) δ 1.53 (s, 3H), 1.58 (s, 3H), 3.68–3.75 (m, 1H, H-1′$_a$),

(19) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

3.94−4.04 (m, 2H, H-1′$_b$, H-6$_a$), 4.26−4.35 (m, 1H, H-5), 4.44 (ap t, 1H, H-6$_b$), 4.65−4.84 (m, 4H, H-2, H-4, ArCH$_2$), 4.86 (d, J = 3.7, 1H, H-1), 4.97−5.01 (m, 1H, H-3′$_a$), 5.08−5.14 (m, 1H, H-3′$_b$), 5.63−5.75 (m, 2H, H-2′, H-3), 5.97 (d, 1H, NH), 6.62−6.64 (m, 1H, ArH), 6.90−7.00 (m, 2H, ArH), 7.53−7.56 (m, 1H, ArH); ^{13}C NMR (C_6D_6) δ 20.49 (o), 22.57 (o), 53.33 (o, C-2), 63.70 (e, C-6), 63.78 (o, C-5), 68.62 (e, C-1′), 70.64 (o, C-3), 71.46 (e, ArCH$_2$), 73.44 (o, C-4), 97.84 (o, C-1), 117.72 (e, C-3′), 121.05 (o), 121.21 (e), 123.17 (o), 127.84 (o), 130.01 (o), 133.90 (o, C-2′), 136.80 (e), 139.66 (e), 169.30 (e), 171.28 (e); HRMS (CI, isobutane) calcd for $C_{21}H_{25}NO_8$ 420.1658 (M + H)$^+$, found 420.1654.

7aB (93% yield): colorless oil; $[\alpha]^{25}_D$ +37.8 (c 0.013, $CHCl_3$); ^{1}H NMR (C_6D_6) δ 1.61 (s, 3H), 1.63 (s, 3H), 3.19 (s, 3H), 3.28 (s, 3H), 3.73−3.80 (m, 1 H, H-1′$_a$), 3.99−4.06 (m, 1H, H-1′$_b$), 4.11 (dd, 1H, H-6$_a$), 4.34−4.43 (m, 1H, H-5), 4.54 (ap t, 1H, H-6$_b$), 4.73−4.82 (m, 2H, H-2, H-4), 4.84−4.94 (m, 3H, H-1, ArCH$_2$), 4.97−5.01 (m, 1H, H-3′$_a$), 5.09−5.16 (m, 1H, H-3′$_b$), 5.65−5.79 (m, 2H, H-2′, H-3), 6.06 (s, 1H, ArH), 6.10 (d, 1H, NH), 7.06 (s, 1H, ArH); ^{13}C NMR (C_6D_6) δ 20.59 (o), 22.59 (o), 53.33 (o, C-2), 55.35 (o), 55.66 (o), 63.84 (e, C-6), 63.92 (o, C-5), 68.65 (e, C-1′), 70.65 (o, C-3), 71.63 (e, ArCH$_2$), 73.57 (o, C-4), 97.92 (o, C-1), 104.07 (o), 105.95 (o), 117.72 (e, C-3′), 121.64 (e), 131.48 (e), 133.92 (o, C-2′), 150.51 (e), 152.21 (e), 169.47 (e), 171.32 (e); HRMS (EI) calcd for $C_{23}H_{29}NO_{10}$ 479.1791 (M)$^+$, found 479.1776.

7bA (95% yield): colorless oil; ^{1}H NMR (C_6D_6) δ 1.51 (s, 3H), 1.64 (s, 3H), 3.66−3.73 (m, 1H, H-1′$_a$), 3.90−4.00 (m, 2H, H-1′$_b$, H-6$_a$), 4.28−4.45 (m, 2H, H-5, H-6$_b$), 4.60 (ap t, 1H, H-4), 4.78 (s, 2H, ArCH$_2$), 4.94−4.99 (m, 1H, H-3′$_a$), 5.10−5.17 (m, 3H, H-1, H-2, H-3′$_b$), 5.60−5.73 (m, 1H, H-2′), 6.08−6.15 (m, 1H, H-3), 6.62−6.65 (m, 1H, ArH), 6.95−7.00 (m, 2H, ArH), 7.51−7.54 (m, 1H, ArH); ^{13}C NMR (C_6D_6) δ 20.19 (o), 20.38 (o), 63.31 (o, C-5), 63.53 (e, C-6), 68.58 (e, C-1′), 69.31 (o, C-3), 71.45 (e, ArCH$_2$), 72.41 (o, C-2), 73.45 (o, C-4), 96.35 (o, C-1), 117.35 (e, C-3′), 120.94 (o), 121.15 (e), 123.27 (o), 128.16 (o), 130.03 (o), 133.76 (o, C-2′), 136.69 (e), 139.45 (e), 169.36 (e), 169.89 (e); HRMS (CI, isobutane) calcd for $C_{21}H_{24}O_9$ 421.1420 (M + H)$^+$, found 421.1441.

7cA (90% yield): colorless oil; $[\alpha]^{25}_D$ +42.1 (c 0.012, $CHCl_3$); ^{1}H NMR (C_6D_6) δ 1.51 (s, 3H), 1.57 (s, 3H), 2.13−2.21 (m, 1H, H-1′$_a$) 2.33−2.44 (m, 1H, H-1′$_b$), 3.93−4.04 (m, 2H, H-5, H-6$_a$), 4.22 (m, J = 6.0, 1H, H-1), 4.32−4.41 (m, 1H, H-6$_b$), 4.58 (ap t, 1H, H-4), 4.76 (s, 2H, ArCH$_2$), 4.89−4.99 (m, 2H, H-3′$_{a,b}$), 5.33 (dd, 1H, H-2), 5.53−5.66 (m, 1H, H-2′), 5.79 (ap t, 1H, H-3), 6.62−6.65 (m, 1H, ArH), 6.96−6.99 (m, 2H, ArH), 7.65−7.68 (m, 1H, ArH); ^{13}C NMR (C_6D_6) δ 20.13 (o), 20.36 (o), 31.21 (e, C-1′), 63.96 (e, C-6), 64.23 (o, C-5), 70.09 (o, C-3), 71.41 (e, ArCH$_2$), 72.17 (o, C-2), 73.69 (o, C-1), 73.82 (o, C-4), 117.23 (e, C-3′) 121.05 (o), 121.19 (e), 123.07 (o), 128.09 (o), 130.05 (o), 134.00 (o, C-2′), 136.79 (e), 139.61 (e), 169.15 (e), 169.71 (e); HRMS (EI) calcd for $C_{21}H_{24}O_8$ 404.1471 (M)$^+$, found 404.1468.

7cB (90% yield): colorless oil; ^{1}H NMR (C_6D_6) δ 1.57 (s, 6H), 2.14−2.22 (m, 1H, H-1′$_a$), 2.38−2.49 (m, 1H, H-1′$_b$), 3.22 (s, 3H), 3.28 (s, 3H), 4.00−4.12 (m, 2H, H-5, H-6$_a$), 4.25 (m, J = 6.0, 1H, H-1), 4.42−4.50 (m, 1H, H-6$_b$), 4.66 (ap t, 1H, H-4), 4.83 (s, 2H, ArCH$_2$), 4.91−5.01 (m, 2H, H-3′$_{a,b}$), 5.37 (dd, 1H, H-2), 5.55−5.68 (m, 1H, H-2′), 5.84 (ap t, 1H, H-3), 6.06 (s, 1H, ArH), 7.18 (s, 1H, ArH); ^{13}C NMR (C_6D_6) δ 20.13 (o), 20.42 (o), 31.30 (e, C-1′), 55.33 (o), 55.66 (o), 64.11 (e, C-6), 64.37 (o, C-5), 70.17 (o, C-3), 71.61 (e, ArCH$_2$), 72.19 (o, C-2), 73.61 (o, C-1), 73.94 (o, C-4), 104.07 (o), 105.87 (o), 117.26 (e, C-3′), 121.64 (e), 131.34 (e), 133.90 (o, C-2′), 150.61 (e), 152.20 (e), 169.16 (e), 169.81 (e); HRMS (EI) calcd for $C_{23}H_{28}O_{10}$ 464.1682 (M)$^+$, found 464.1677.

7dA (95% yield): foam; ^{1}H NMR (C_6D_6) δ 1.10 (dt, 6H, 2xCH$_3$), 1.55 (s, 3H), 1.64 (s, 3H), 2.00 (ap t, 1H, H-1$_{ax}$), 2.48−2.60 (m, 2H, H-1′$_a$, H-5), 3.15 (dd, 1H, H-1$_{eq}$), 3.32 (dd, 1H, H-1′$_b$), 3.91−4.03 (m, 4H, 2xOCH$_2$), 4.09 (dd, 1H, H-6$_a$), 4.43 (ap t, 1H, H-6$_b$), 4.66 (ap t, 1H, H-4), 4.78 (s, 2H, ArCH$_2$), 5.31 (ddd, 1H, H-2), 5.54 (ap t, 1H, H-3), 5.60 (dd, 1H, H-3′$_b$), 6.07 (d, 1H, H-3′$_a$), 6.62−6.65 (m, 1H, ArH), 6.95−7.02 (m, 2H, ArH), 7.64−7.66 (m, 1H, ArH); ^{13}C NMR (C_6D_6) δ 16.45 (o), 16.53 (o), 20.36 (o), 20.49 (o), 53.86 (e, C-1′), 54.50 (e, C-1), 58.97 (o, C-5), 61.67 (e), 61.75 (e), 63.78 (e, C-6), 70.24 (o, C-2), 71.23 (e, ArCH$_2$), 73.77 (o, C-4), 73.89 (o, C-3), 120.88 (e), 121.04 (o), 123.19 (o), 128.53 (o), 129.98 (o), 130.75 (e, C-3′), 137.16 (e), 138.12 (e, C-2′), 139.69 (e), 169.53 (e), 169.82 (e); HRMS (CI, isobutane) calcd for $C_{25}H_{34}NO_{10}P$ 540.1999 (M + H)$^+$, found 540.1971.

General Procedure for Me_2BBr Reaction. To the 4,6-POE derivative (1.0 equiv) in dichloromethane at −78 °C was added dimethylboron bromide or 9-Br-9-BBN (see Table 2 for amounts) *very rapidly*. Instantaneous reaction had occured as indicated by TLC. The reaction mixture was quenched with aqueous sodium bicarbonate (see below for mode of quench) at the proper time and temperature indicated in Table 2. After quenching the organic phase was separated and the aqueous phase was extracted with dichloromethane (three times). The combined organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel using 2% Et_3N in hexanes/ethyl acetate.

Procedure for −78 °C Quench. The cold reaction mixture was added very rapidly to a well-stirred solution of aqueous sodium bicarbonate using a double-ended needle.

Procedure for 25 °C Quench. To the well-stirred reaction mixture was added aqueous sodium bicarbonate at 25°C.

8aA (eluent for flash chromatography, 2% Et_3N in 50/50 hexanes/ethyl acetate): colorless oil; ^{1}H NMR (C_6D_6) δ 1.56 (s, 3H), 1.74 (s, 3H), 3.41 (t, 1H, OH), 3.84−3.90 (m, 3H, H-1′$_a$, H-6$_{a,b}$), 4.09−4.16 (m, 2H, H-1′$_b$, H-5), 4.79−4.87 (m, 3H, H-2, ArCH$_2$), 5.01 (d, J = 3.6, 1H, H-1), 5.04−5.08 (m, 1H, H-3′$_a$), 5.18−5.26 (m, 1H, H-3′$_b$), 5.74−5.85 (m, 3H, H-2′, H-3, H-4), 6.02 (d, 1H, NH), 6.91−6.93 (m, 3H, ArH), 7.88−7.90 (m, 1H, ArH); ^{13}C NMR (C_6D_6) δ 20.53 (o), 22.56 (o), 31.40 (e, ArCH$_2$), 52.49 (o, C-2), 61.60 (e, C-6), 68.49 (e, C-1′), 70.02 (o, C-4), 71.19 (o, C-5), 71.82 (o, C-3), 96.80 (o, C-1) 117.90 (e, C-3′), 128.67 (o), 128.73 (e), 131.41 (o), 131.92 (o), 132.82 (o), 133.94 (0, C-2′), 140.29 (e), 165.52 (e), 169.92 (e), 171.42 (e); HRMS (CI, isobutane) calcd for $C_{21}H_{26}BrNO_8$ 500.0920 (M + H)$^+$, found 500.0915.

8aB (eluent for flash chromatography, 2% Et_3N in 30/70 hexanes/ethyl acetate): colorless oil; ^{1}H NMR (C_6D_6) δ 1.50 (s, 3H), 1.72 (s, 3H), 3.19 (s, 3H), 3.25 (t, 1H, OH), 3.50 (s, 3H), 3.77−3.83 (m, 1H, H-1′$_a$), 3.96 (br d, 2H, H-6$_{a,b}$), 4.01−4.08 (m, 1H, H-1′$_b$), 4.09−4.15 (m, 1H, H-5), 4.79−5.04 (m, 5H, H-1 [J = 3.6], H-2, H-3′$_a$, ArCH$_2$), 5.12−5.20 (m, 1H, H-3′$_b$), 5.67−5.80 (m, 3H, H-2′, H-4, NH), 5.86 (ap t, 1H, H-3), 6.48 (s, 1H, ArH), 7.60 (s, 1H, ArH); ^{13}C NMR (C_6D_6) δ 20.52 (o), 22.52 (o), 32.31 (e, ArCH$_2$), 52.23 (o, C-2), 55.34 (o), 55.66 (o), 61.75 (e, C-6), 68.44 (e, C-1′), 70.26 (o, C-4), 71.29 (o, C-5), 71.81 (o, C-3), 96.81 (o, C-1), 114.48 (o), 114.72 (o), 117.90 (e, C-3′), 120.37 (e), 133.86 (o, C-2′), 134.48 (e), 149.53 (e), 153.25 (e), 165.56 (e), 169.50 (e), 171.46 (e); HRMS (EI) calcd for $C_{23}H_{30}BrNO_{10}$ 559.1053 (M)$^+$, found 559.1036.

8bA (eluent for flash chromatography, 2% Et_3N in 60/40 hexanes/ethyl acetate): colorless oil; ^{1}H NMR (C_6D_6) δ 1.65 (s, 3H), 1.66 (s, 3H), 2.37 (br t, 1H, OH), 3.70−3.79 (m, 3H, H-1′$_a$, H-6$_{a,b}$), 3.96−4.03 (H-1′$_b$, H-5), 4.76 (ABq, 2H, ArCH$_2$), 4.97−5.01 (m, 1H, H-3′$_a$), 5.13−5.23 (m, 3H, H-1, H-2, H-3′$_b$), 5.61 (ap t, 1H, H-4), 5.65−5.78 (m, 1H, H-2′), 6.16 (ap t, 1H, H-3), 6.86−6.90 (m, 3H, ArH), 7.94−7.97 (m, 1H, ArH); ^{13}C NMR (C_6D_6) δ 20.18 (o), 20.39 (o), 31.32 (e, ArCH$_2$), 61.39 (e, C-6), 68.57 (e, C-1′), 70.19 (o, C-4), 70.39 (o, C-3, C-5, overlapped), 71.58 (o, C-2), 95.34 (o, C-1), 117.41 (e, C-3′), 128.79 (o), 131.72 (o), 131.80 (o), 132.93 (o), 133.96 (o, C-2′), 140.27 (e), 165.83 (e), 169.81 (e), 169.98 (e); HRMS (CI, isobutane) calcd for $C_{21}H_{25}BrO_9$ 501.0760 (M + H)$^+$, found 501.0783.

8cA (eluent for flash chromatography, 2% Et_3N in 75/25 hexanes/ethyl acetate): colorless oil; $[\alpha]^{25}_D$ +38.5 (c 0.013, $CHCl_3$); ^{1}H NMR (C_6D_6) δ 1.61 (s, 3H), 1.68 (s, 3H), 2.14−2.23 (m, 1H, H-1′$_a$), 2.36−2.45 (m, 1H, H-1′$_b$), 2.49 (br t, 1H, OH), 3.67−3.79 (m, 3H, H-5, H-6$_{a,b}$), 4.29 (m, J = 5.9, 1H, H-1), 4.77 (ABq, 2H, ArCH$_2$), 4.97−5.03 (m, 2H, H-3′$_{a,b}$), 5.33 (dd, 1H, H-2), 5.52 (ap t, 1H, H-4), 5.60−5.73 (m, 1H, H-2′), 5.81 (ap t, 1H, H-3), 6.91−6.95 (m, 3H, ArH), 7.99−8.02 (m, 1H, ArH); ^{13}C NMR (C_6D_6) δ 20.17 (o), 20.41 (o), 30.66 (e, C-1′), 31.27 (e, ArCH$_2$), 61.86 (e, C-6), 70.47 (o, C-4), 70.87 (o, C-3), 71.11 (o, C-2), 71.42 (o, C-5), 72.37 (o, C-1), 117.60 (e, C-3′), 128.71 (o), 131.44 (o), 131.91 (o), 132.92 (o), 133.79 (o, C-2′), 140.18 (e), 165.67 (e), 169.23 (e), 170.20 (e); HRMS (CI, isobutane) calcd for $C_{21}H_{25}BrO_8$ 485.0811 (M + H)$^+$, found 485.0785.

9cA (eluent for flash chromatography, 2% Et_3N in 75/25 hexanes/ethyl acetate): colorless oil; ^{1}H NMR (C_6D_6) δ 1.60 (s, 3H), 1.76 (s,

3H), 2.14−2.22 (m, 1H, H-1′$_a$), 2.36−2.47 (m, 1H, H-1′$_b$), 3.04 (d, 1H, OH), 3.58−3.66 (m, 1H, H-4), 3.71−3.77 (m, 1H, H-5), 4.25 (m, J = 5.9, 1H, H-1), 4.55 (ap t, 2H, H-6$_{a,b}$), 4.80 (ABq, 2H, ArCH$_2$), 4.93−5.01 (m, 2H, H-3′$_{a,b}$), 5.26 (dd, 1H, H-2), 5.46 (ap t, 1H, H-3), 5.57−5.68 (m, 1H, H-2′), 6.86−6.96 (m, 3H, ArH), 7.98 (d, 1H, ArH); ^{13}C NMR (C_6D_6) δ 20.21 (o), 20.56 (o), 30.74 (e, C-1′), 31.63 (e, ArCH$_2$), 64.43 (e, C-6), 70.03 (o, C-4), 71.11 (o, C-2), 71.42 (o, C-5), 72.54 (o, C-1), 73.51 (o, C-3), 117.34 (e, C-3′), 128.53 (o), 129.19 (e), 131.78 (o), 131.89 (o), 132.59 (o), 134.04 (o, C-2′), 139.90 (e), 166.84 (e), 169.30 (e), 170.86 (e); HRMS (CI, isobutane) calcd for $C_{21}H_{25}BrO_8$ 485.0811 (M + H)$^+$, found 485.0792.

8cB (eluent for flash chromatography, 2% Et$_3$N in 50/50 hexanes/ethyl acetate): colorless oil; ^{1}H NMR (C_6D_6) δ 1.57 (s, 3H), 1.63 (s, 3H), 2.08−2.17 (m, 1H, H-1′$_a$), 2.29−2.38 (m, 1H, H-1′$_b$), 2.43 (br t, 1H, OH), 3.18 (s, 3H), 3.62 (s, 3H), 3.70−3.85 (m, 3H, H-5, H-6$_{a,b}$), 4.28 (m, J = 6.1, 1H, H-1), 4.91 (ABq, 2H, ArCH$_2$), 4.91−5.02 (m, 2H, H-3′$_{a,b}$), 5.33 (dd, 1H, H-2), 5.49 (ap t, 1H, H-4), 5.53−5.67 (m, 1H, H-2′), 5.87 (ap t, 1H, H-3), 6.46 (s, 1H, ArH), 7.68 (s, 1H, ArH); ^{13}C NMR (C_6D_6) δ 20.10 (o), 20.38 (o), 30.51 (e, C-1′), 32.17 (e, ArCH$_2$), 55.33 (o), 55.77 (o), 62.10 (e, C-6), 70.73 (o, C-3), 70.97 (o, C-4), 71.16 (o, C-2), 71.51 (o, C-5), 72.45 (o, C-1), 114.50 (o), 114.70 (o), 117.52 (e, C-3′), 120.22 (e), 133.75 (o, C-2′), 134.56 (e), 149.62 (e), 153.32 (e), 165.59 (e), 169.04 (e), 170.48 (e); HRMS (EI) calcd for $C_{23}H_{29}BrO_{10}$ 544.0944 (M)$^+$, found 544.0928.

8dA (eluent for flash chromatography, 2% Et$_3$N in 50/50 hexanes/ethyl acetate): colorless oil; ^{1}H NMR (C_6D_6) δ 0.99 (t, 3H, CH$_3$), 1.18 (t, 3H, CH$_3$), 1.60 (s,3H), 1.72 (s, 3H), 1.94 (ap t, 1H, H-1$_{ax}$), 2.27−2.39 (m, 2H, H-1′$_a$, H-5), 3.28 (dd, 1H, H-1$_{eq}$), 3.70−3.98 (m, 5H, H-1′$_b$, H-6$_{a,b}$, OCH$_2$), 4.04−4.14 (m, 2H, OCH$_2$), 4.82 (ABq, 2H, ArCH$_2$), 5.30 (d, 1H, H-3′$_b$), 5.33 (ddd, 1H, H-2), 5.45 (br dd, 1H, OH), 5.61 (ap t, 1H, H-3), 5.65 (d, 1H, H-3′$_a$), 6.07 (ap t, 1H, H-4), 6.89−6.92 (m, 3H, ArH), 8.06−8.08 (m, 1H, ArH); ^{13}C NMR (C_6D_6) δ 16.49 (o), 16.56 (o), 20.28 (o), 20.55 (o), 31.31 (e, ArCH$_2$), 52.25 (e, C-1), 54.51 (e, C-1′), 57.18 (e, C-6), 61.98 (e), 62.61 (e), 65.43 (o, C-5), 68.87 (o, C-2), 70.37 (o, C-4), 75.51 (o, C-3), 129.21 (e), 129.77 (e, C-3′), 131.38 (o), 131.44 (o), 132.02 (o), 132.59 (o), 138.65 (e, C-2′), 140.21 (e), 165.17 (e), 169.42 (e), 170.33 (e); HRMS (FAB, DTT/DTE) calcd for $C_{25}H_{35}BrNO_{10}P$ 620.1260, found 620.1262.

4-*O*-[*o*-(Azidomethyl)benzoyl]pyranoside 10aA. To the inseparable mixture of *o*-(bromomethyl)benzoates **8aA/9aA** (12/1 mixture, 271 mg, 0.54 mmol, 1.0 equiv) in dry acetonitrile or dichloromethane (0.2M) was added TMGA (2−5 equiv) in one portion at 0 °C. The reaction mixture was slowly warmed to no higher than 10 °C over 1 h. Longer reaction time and/or higher temperature resulted in migration of the benzoate functionality to the C-6 position. On completion, dry ether (6 volumes) was added to the reaction mixture to produce a thick white precipitate. The reaction mixture with the precipitate was poured into a separatory funnel and washed with water till the organic phase was clear (2−3 times). The organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. The resultant mixture of *o*-(azidomethyl)-benzoates **10aA/11aA** (12/1 mixture, 226 mg, 90% yield) was homogeneous by NMR and TLC for further transformation. **10aA**: colorless oil; ^{1}H NMR (C_6D_6) δ 1.61 (s, 3H), 1.73 (s, 3H), 3.85−3.97 (m, 4H, H-1′$_a$, H-6$_{a,b}$, OH), 4.12−4.21 (m, 2H, H-1′$_b$, H-5), 4.66 (ABq, 2H, ArCH$_2$), 4.81−4.89 (m, 1H, H-2), 5.06 (d, J = 3.3, 1H, H-1), 5.06−5.10 (m, 1H, H-3′$_a$), 5.22−5.28 (m, 1H, H-3′$_b$), 5.77−5.89 (m, 3H, H-2′, H-3, H-4), 6.24 (d, 1H, NH), 6.95−7.12 (m, 3H, ArH), 7.94 (dd, 1H, ArH); ^{13}C NMR (C_6D_6) δ 20.36 (o), 22.56 (o), 52.46 (o, C-2), 53.06 (e, ArCH$_2$), 61.53 (e, C-6), 68.52 (e, C-1′), 70.07 (o, C-3), 71.32 (o, C-5), 71.84 (o, C-4), 96.81 (o, C-1), 117.93 (e, C-3′), 128.47 (e), 128.53 (o), 130.07 (o), 131.20 (o), 133.05 (o), 134.01 (o, C-2′), 138.22 (e), 165.66 (e), 170.28 (e), 171.38 (e); HRMS (CI, isobutane) calcd for $C_{21}H_{26}N_4O_8$ 463.1828 (M + H)$^+$, found 463.1823. **11aA**:[20] colorless oil; ^{1}H NMR (C_6D_6) δ 1.59 (s, 3H), 1.88 (s, 3H), 3.74−3.80 (m, 1H, H-1′$_a$), 3.87 (br t, 1H, H-4), 4.00−4.06 (m, 1H, H-1′$_b$), 4.09−4.14 (m, 1H, H-5), 4.20 (br, 1H, OH), 4.54−4.64 (m, 3H, H-2, ArCH$_2$), 4.66−4.75 (m, 2H, H-6$_{a,b}$), 4.88 (d, J = 3.6, 1H, H-1), 4.97−5.01 (m, 1H, H-3′$_a$), 5.09−5.16 (m, 1H, H-3′$_b$), 5.49 (dd, 1H, H-3), 5.66−5.79 (m, 1H, H-2′), 5.98 (d, 1H, NH), 6.95−7.12 (m, 3H, ArH), 8.05 (dd, 1H, ArH); ^{13}C NMR (C_6D_6) δ 20.77 (o), 22.57 (o), 52.54 (o, C-2), 53.15 (e, ArCH$_2$), 64.52 (e, C-6), 68.51 (e, C-1′), 69.42 (o, C-4), 70.76 (o, C-5), 74.41 (o, C-3), 96.97 (o, C-1), 117.74 (e,C-3′), 128.53 (o), 129.02 (e), 129.90 (o), 131.40 (o), 132.81 (o), 133.87 (o, C-2′), 137.92 (e), 166.78 (e), 170.02 (e), 171.88 (e); HRMS (CI, isobutane) calcd for $C_{21}H_{26}N_4O_8$ 463.1828 (M + H)$^+$, found 463.1808.

4-*O*-[*o*-(Azidomethyl)benzoyl]pyranoside 10bA. An inseparable mixture of *o*-(bromomethyl)benzoates **8bA/9bA** (14/1 mixture, 44 mg, 0.088 mmol, 1.0 equiv) in dry dichloromethane was processed as above. The crude product was purified by flash chromatography using 2% Et$_3$N in 50/50 hexanes/ethyl acetate to afford 37 mg (91% yield) of **10bA/11bA** (14/1mixture). **10bA**: colorless oil; ^{1}H NMR (C_6D_6) δ 1.64 (s, 3H), 1.65 (s, 3H), 2.26 (t, 1H, OH), 3.57−3.69 (m, 2H, H-6$_{a,b}$), 3.71−3.77 (m, 1H, H-1′$_a$), 3.93−4.02 (m, 2H, H-1′$_b$, H-5), 4.53 (ABq, 2H, ArCH$_2$), 4.99 (ddd, 1H, H-3′$_a$), 5.11−5.22 (m, 3H, H-1, H-2, H-3′$_b$), 5.56 (ap t, 1H, H-4), 5.65−5.78 (m, 1H, H-2′), 6.15 (ap t, 1H, H-3), 6.91−7.05 (m, 3H, ArH), 7.99 (dd, 1H, ArH); ^{13}C NMR (C_6D_6) δ 20.17 (o), 20.28 (o), 53.04 (e, ArCH$_2$), 61.39 (e, C-6), 68.63 (e, C-1′), 70.19 (o, C-4), 70.33 (o, C-5), 70.37 (o, C-3), 71.58 (o, C-2), 95.37 (o, C-1), 117.45 (e, C-3′), 128.17 (e), 128.43 (o), 130.17 (o), 131.51 (o), 133.17 (o), 133.73 (o, C-2'), 138.18 (e), 165.99 (e), 169.85 (e), 169.94 (e).

6-(Acetylthio)-4-*O*-[*o*-(azidomethyl)benzoyl]pyranoside 12aA. To triphenylphosphine (227 mg, 0.866 mmol, 2.0 equiv) in dry THF (1 mL) was added DIAD (175 mg, 0.866 mmol, 2.0 equiv) at 0 °C. The reaction mixture turned into a pale yellow semisolid after 1 min. Stirring was continued for additional 30 min at 0 °C. Then a mixture of **10aA/11aA** (12/1 ratio, 200 mg, 0.433 mmol, 1.0 equiv) and thioacetic acid (66 mg, 0.866 mmol, 2.0 equiv) in dry THF (2 mL) was added dropwise. The reaction mixture turned dark and it was warmed to 25 °C over 3 h. On completion, aqueous sodium bicarbonate was added to the reaction mixture and extracted with ether (three times). The combined organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. The brown residue was purified by flash chromatography using 2% Et$_3$N in 50/50 hexanes/ethyl acetate to afford 200 mg (89% yield) of **12aA**: colorless oil; $[\alpha]^{24}_D$ +48.4 (*c* 0.026, $CHCl_3$); ^{1}H NMR (C_6D_6) δ 1.57 (s, 3H), 1.68 (s, 3H), 1.85 (s, 3H), 3.06 (dd, 1H, H-6$_a$), 3.37 (dd, 1H, H-6$_b$), 3.72−3.78 (m, 1H, H-1′$_a$), 4.02−4.08 (m, 1H, H-1′$_b$), 4.11−4.17 (m, 1H, H-5), 4.67 (ABq, 2H, ArCH$_2$), 4.67−4.75 (m, 1H, H-2), 4.82 (d, J = 3.6, 1H, H-1), 4.98−5.02 (m, 1H, H-3′$_a$), 5.11−5.18 (m, 1H, H-3′$_b$), 5.50 (ap t, 1H, H-4), 5.65−5.76 (m, 2H, H-2′, H-3), 5.97 (d, 1H, NH), 6.96−7.13 (m, 3H, ArH), 8.10 (dd, 1H, ArH); ^{13}C NMR (C_6D_6) δ 20.31 (o), 22.53 (o), 29.89 (o), 30.69 (e, C-6), 52.35 (o, C-2), 52.96 (e, ArCH$_2$), 68.47 (e, C-1′), 69.60 (o, C-5), 71.45 (o, C-3), 72.17 (o, C-4), 96.67 (o, C-1), 117.95 (e, C-3′), 128.75 (e), 130.15 (o), 131.27 (o), 132.98 (o), 133.63 (o, C-2′), 137.99 (e), 165.66 (e), 169.31 (e), 171.11 (e), 193.83 (e); HRMS (CI, isobutane) calcd for $C_{23}H_{28}N_4O_8S$ 521.1706 (M + H)$^+$, found 521.1711.

6-(Acetylthio)-4-*O*-[*o*-(azidomethyl)benzoyl]pyranoside 12bA. An inseparable mixture of *o*-(azidomethyl)benzoates **10bA/11bA** (14/1 mixture, 35 mg, 0.08 mmol, 1.0 equiv) was processed as above. A clear homogeneous solution resulted after 2 h at 25 °C, at which time TLC indicated reaction completion. The crude product was purified by careful flash chromatography (twice) using 2% Et$_3$N in 80/20 hexanes/ethyl acetate to afford 30 mg (76% yield) of **12bA**: colorless oil; ^{1}H NMR (C_6D_6) δ 1.61 (s, 3H), 1.65 (s, 3H), 1.82 (s, 3H), 3.11 (dd, 1H, H-6$_a$), 3.30 (dd, 1H, H-6$_b$), 3.68−3.75 (m, 1H, H-1′$_a$), 3.96−4.03 (m, 1H, H-1′$_b$), 4.13−4.20 (m, 1H, H-5), 4.69 (ABq, 2H, ArCH$_2$), 4.95 (d, 1H, H-3′$_a$), 5.08−5.17 (m, 3H, H-1, H-2, H-3′$_b$), 5.47 (ap t, 1H, H-4), 5.60−5.72 (m, 1H, H-2′), 6.06−6.14 (m, 1H, H-3), 6.97−7.11 (m, 3H, ArH), 8.13−8.16 (m, 1H, ArH); ^{13}C NMR (C_6D_6) δ 20.11 (o), 20.24 (o), 29.87 (o), 30.44 (e, C-6), 52.97 (e, ArCH$_2$), 68.50 (e, C-1′), 69.08 (o, C-5), 70.26 (o, C-3), 71.45 (o, C-2), 72.12 (o, C-4), 95.10 (o, C-1), 117.63 (e, C-3′), 128.54 (o), 128.57 (e), 130.10 (o), 131.52 (o), 133.04 (o), 133.49 (o, C-2′), 138.10 (e), 165.73 (e), 169.66 (e), 169.80 (e), 193.55 (e).

6-(Acetylthio)pyranoside 14aA. To the benzoate **12aA** (50 mg, 0.096 mmol, 1.0 equiv) in dry benzene (0.03M) at 25 °C was added tris(4−methoxyphenyl)phosphine (101 mg, 0.288 mmol, 3.0 equiv) in one portion followed by immediate addition of glacial acetic acid (8.6 μL, 0.15 mmol, 1.5 equiv). The reaction mixture was slowly heated to 40 °C over 1.5 h. At this time the starting material had completely

(20) Treatment of **10aA/11aA** (12/1 mixture, 1.0 equiv) using tosyl chloride (2.0 equiv) and Et$_3$N (5.0 equiv) in dichloromethane at 25 °C for 6 h resulted in tosylation of C-6 OH only. The unreacted C-4 OH (**11aA**) was easily separated from the C-6 tosylate by flash chromatography.

disappeared by TLC and the reaction was quenched with 5% HCl. The mixture was extracted with dichloromethane (three times). The combined organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by careful flash chromatography using 30/70 hexanes/ethyl acetate to afford 28 mg (81% yield) of **14aA**: colorless oil; ^{1}H NMR (C_6D_6) δ 1.57 (s, 3H), 1.83 (s, 3H), 1.84 (s, 3H), 3.23 (dd, 1H, H-6$_a$), 3.41 (dd, 1H, H-6$_b$), 3.61 (ddd, 1H, H-4), 3.70−3.77 (m, 1H, H-1′$_a$), 3.91−3.97 (m, 1H, H-5), 3.99−4.05 (m, 2H, H-1′$_b$, OH), 4.56 (ddd, 1H, H-2), 4.83 (d, J = 3.6, 1H, H-1), 4.97−5.01 (m, 1H, H-3′$_a$), 5.09−5.16 (m, 1H, H-3′$_b$), 5.46 (dd, 1H, H-3), 5.63−5.76 (m, 1H, H-2′), 5.91 (d, 1H, NH); ^{13}C NMR (C_6D_6) δ 20.74 (o), 22.57 (o), 29.93 (o), 31.23 (e, C-6), 52.67 (o, C-2), 68.25 (e, C-1′), 71.17 (o, C-5), 71.40 (o, C-4), 73.78 (o, C-3), 96.80 (o, C-1), 117.69 (e, C-3′), 133.88 (o, C-2′), 169.71 (e), 171.79 (e), 196.28 (e); HRMS (CI, isobutane) calcd for $C_{15}H_{23}NO_7S$ 362.1273 (M + H)$^+$, found 362.1258.

6-(Acetylthio)pyranoside 14bA. The benzoate **12bA** (24 mg, 0.046 mmol, 1.0 equiv) in dry benzene (0.03 M) was processed as above. TLC indicated reaction completion after slow warming to 40 °C over 3.5 h. The crude product was purified by careful flash chromatography using 30/70 hexanes/ethyl acetate to afford 13 mg (80% yield) of **14bA**: colorless oil; ^{1}H NMR (C_6D_6) δ 1.64 (s, 3H), 1.72 (s, 3H), 1.77 (s, 3H), 3.07 (br, 1H, OH), 3.17 (br d, 2H, H-6$_{a,b}$), 3.44 (br t, 1H, H-4), 3.65−3.72 (m, 1H, H-1′$_a$), 3.80−3.86 (m, 1H, H-5), 3.92−4.00 (m, 1H, H-1′$_b$), 4.96 (ddd, 1H, H-3′$_a$), 5.02−5.07 (m, 2H, H-1, H-2), 5.15 (ddd, 1H, H-3′$_b$), 5.60−5.73 (m, 1H, H-2′), 5.77 (ap t, 1H, H-3); ^{13}C NMR (C_6D_6) δ 20.23 (o), 20.51 (o), 29.83 (o), 30.86 (e, C-6), 68.30 (e, C-1′), 70.65 (o), 71.65 (o), 71.77 (o), 72.33 (o), 95.35 (o, C-1), 117.31 (e, C-3′), 133.74 (o, C-2′), 169.92 (e), 170.40 (e), 196.53 (e); HRMS (CI, isobutane) calcd for $C_{15}H_{22}O_8S$ 363.1114 (M + H)$^+$, found 363.1099.

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Supplementary Material Available: Copies of proton and carbon spectra for all new compounds (56 pages). This material is contained in many 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. X-ray information of compound **6cA** can be obtained from the Cambridge Crystallographic Data Centre.[5]

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