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1,2-*Trans*-Selective Synthesis of Glycosyl Boranophosphates and Their Utility as Building Blocks for the Synthesis of Phosphodiester-Linked Disaccharides

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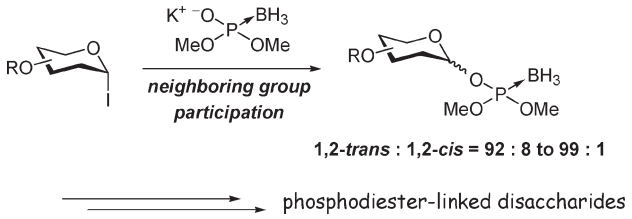

A highly 1,2-*trans*-selective synthesis of glycosyl boranophosphate derivatives by glycosylation of dimethyl boranophosphate with glycosyl iodides was developed. A study on the reaction mechanism indicated that the stereoselectivity of the reactions is controlled by neighboring group participation. The resultant glycosyl boranophosphate triesters were converted into the corresponding boranophosphate diesters and condensed with appropriately protected monosaccharides to give disaccharides linked with an anomeric boranophosphate linkage. Furthermore, the disaccharides worked as precursors of the corresponding phosphodiester-linked disaccharides. The whole synthesis of boranophosphate-linked disaccharides and their conversion to the phosphodiester-linked disaccharides were accomplished in good yields without loss of stereopurity at the anomeric position, indicating that the method is useful to synthesize diastereopure glycosyl phosphate-containing biomolecules.

Introduction

Glycosyl phosphate repeating units are found in capsular polysaccharides of bacteria, including most pathogenic species, such as *Neisseria meningitidis* and *Streptococcus pneumoniae*.[1,2] These units also exist in glycocalyx lipophosphoglycans and secreted proteophosphoglycans of protozoan parasites.[1,3] It has been reported that these glycoconjugates work as antigens and also play important roles in infection processes of the pathogenic organisms and their evasion of host immune defense.[1−3] In addition, glycosyl phosphates are the main units of biological glycosyl donors, such as sugar nucleotides[4] and dolichol phosphate sugars.[5]

Since the biological processes mediated by these biomolecules are important subjects of research, particularly for drug discovery, chemical synthesis of the glycosyl phosphate-containing biomolecules and their chemically modified analogues has been intensively studied, and synthesized molecules have been used as probes to explore the biological processes mentioned above or directly applied to therapeutic studies as drug candidates.[6,7]

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Currently, the chemical synthesis of these molecules, particularly those containing glycosyl phosphate repeating units, is carried out via the *H*-phosphonate method almost exclusively.[1,2a,6,8] In this method, a glycosyl *H*-phosphonate monoester and a hydroxy group of another molecule are condensed to create an *H*-phosphonate diester linkage, which is then immediately oxidized to form a phosphate diester linkage. By using this method, molecules containing 2−4 glycosyl phosphate repeating units have been synthesized to date. In addition, the method can produce *P*-modified glycosyl phosphate analogues, such as phosphorothioate, phosphoramidate, alkylphosphonate, etc.[9]

However, this method has some limitations. First, *H*-phosphonate diester linkages are unstable and often cleaved by hydrolysis during the synthesis. Second, for the first reason, the *H*-phosphonate diesters should be immediately oxidized to phosphate diesters having a nucleophilic P-O^- group, which would undergo undesirable side reactions. The synthetic intermediates having multiple phosphate diesters are also highly polar, and their purification is often troublesome. Probably for these reasons, decrease in yield is observed as the number of glycosyl phosphate repeating units increases.[8b,c,e,f] Thus, the development of a new efficient method to synthesize glycosyl phosphate-containing molecules is strongly required.

Under these circumstances, we have recently proposed a new strategy that uses glycosyl boranophosphates to synthesize glycosyl phosphate-containing molecules.[10] Glycosyl boranophosphate is one of the *P*-modified glycosyl phosphate analogues, in which the P═O group of the parent glycosyl phosphate is replaced by a BH_3 group.[6a,11] These compounds are chemically stable compared to the *H*-phosphonate counterparts, and their triester intermediates do not have a negative charge and are not as reactive as phosphate diesters. In addition, the boranophosphate diester linkages can be quantitatively converted into the *H*-phosphonate diester linkages.[10a,12] Therefore, the glycosyl boranophosphates can be used as stable precursors of *H*-phosphonate diesters or "protected" *H*-phosphonates.[12a]

Since the naturally occurring glycosyl phosphate units are stereopure at their anomeric position, diastereopure α- or β-glycosyl boranophosphates are also required for their synthesis. Although we have developed a method to synthesize α-glycosyl boranophosphates via glycosyl phosphites,[10b] only a limited number of diastereopure glycosyl boranophosphates are available by this method. In order to develop a more versatile method to synthesize glycosyl boranophosphates stereoselectively, we focused on a reaction reported by Imamoto et al.[11a] They used dimethyl boranophosphate diester as a nucleophile and allowed it to directly react with various *C*-electrophiles including 2,3,4,6-tetra-*O*-acetyl-α-D-glucosyl bromide to synthesize various boranophosphate triesters. However, we found that the direct reaction between dimethyl boranophosphate and 2,3,4,6-tetra-*O*-acetyl-α-D-glucosyl bromide in MeCN was sluggish, and the desired product was obtained in only ca. 40% even after 48 h. Given this result, we aimed to employ more reactive glycosyl iodides as glycosyl donors to develop a more efficient and practical method to synthesize glycosyl boranophosphates in a stereocontrolled manner.

Results and Discussion

First, the influence of hydroxy protecting groups on the reactivity and chemo- and stereoselectivity of the substrates was studied (Table 1, entries 1−6). When 2,3,4,6-tetra-*O*-benzyl-α-D-glucosyl iodide[13] (**1**, R = Bn) was allowed to react with potassium dimethyl boranophosphate **2**[11a] in MeCN at rt, the *O*-glycosylation of **2** proceeded rapidly to afford the desired glycosyl boranophosphate (**3**, R = Bn) in modest yield with poor stereoselectivity (entry 1).

In sharp contrast, the reaction between 2,3,4,6-tetra-*O*-acetyl-α-D-glucosyl iodide[14] (**1**, R = Ac) and **2** was completely β-selective, though a small amount of a glycal (**4**) and a large amount of an acetal (**5**) were generated as byproducts (entry 2). The acetal **5** was probably generated by the reduction of a positively charged 1,2-cyclic intermediate **7** by dimethyl boranophosphate **2** (Scheme 1). The reducing power of dimethyl boranophosphate **2** is very weak but has been shown to be strong enough to reduce relatively stable carbocations, such as triphenylmethyl cations.[10a,12] The generation of acetal **5** as well as the complete β-selectivity of the reaction indicate that the reaction proceeded via neighboring group participation. Since glycosyl iodides are relatively unstable and can undergo an E1 reaction to lose the anomeric iodo group, the neighboring group participation could happen even though a pure α-glycosyl iodide was used as the starting material (Scheme 1). Equilibrium between the α-glycosyl iodide and its β-isomer via repetitive nucleophilic attacks of a trace amount of iodide ion in the reaction mixture and neighboring group participation on the β-isomer may also be involved.[13−15]

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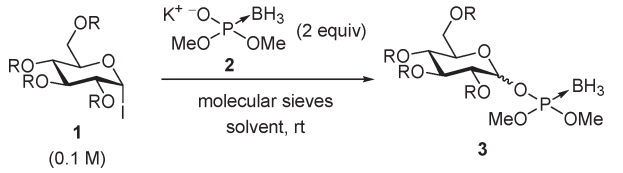
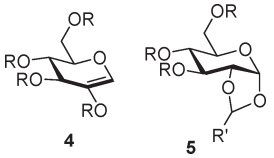
TABLE 1. Synthesis of Glucosyl Boranophosphates 3[a]

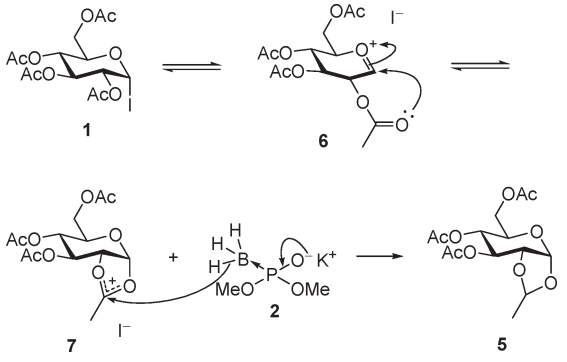


entry	R	solvent	time (h)	**3**:**4**:**5**[b]	yield of **3** (%)[c]
1	Bn	MeCN	0.6	1:>0.01:>0.01	53 (31:69)
2	Ac	MeCN	4	1:0.05:1.18	−(>1:99)[d]
3	Piv	MeCN	5	1:0.10:1.29	33 (>1:99)
4	Bz	MeCN	8.5	1:0.07:0.04	73 (1:99)
5	*o*-ClBz	MeCN	39	1:0.28:0.26	59 (4:96)
6	An	MeCN	13	1:0.03:0.03	85 (1:99)
7	Bz	$MeNO_2$	48	1:0.02:0.23	60 (>1:99)
8[e]	Bz	DME	57	1:0.09:0.16	40 (3:97)
9	Bz	DMF	1	1:0.16:>0.01	46 (5:95)
10[f]	Bz	MeCN	7.5	1:0.07:0.13	59 (3:97)
11[g]	Bz	MeCN	6.5	1:0.12:0.09	73 (2:98)
12[e,h]	Bz	MeCN	22	1:0.11:0.05	30 (1:99)
13[i]	Bz	MeCN	1.5	1:0.16:>0.01	71 (3:97)
14[i]	*o*-ClBz	MeCN	3	1:0.42:0.02	47 (4:96)
15[i]	An	MeCN	2	1:0.10:>0.01	76 (1:99)

[a]MS 3Å was used for MeCN. MS 4Å was used for the other solvents. [b]Determined by ^{1}H NMR. [c]α:β ratios of isolated **3** are given in parentheses. [d]Not isolated. [e]Reaction was not completed. [f]0.25 M **1** was used. [g]5 equiv of **2** was used. [h]Reaction was conducted at 0 °C. [i]2 equiv of 18-crown-6 was used as additive.

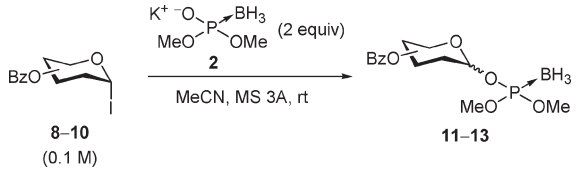


SCHEME 1. Plausible Mechanism for Formation of Acetal 5



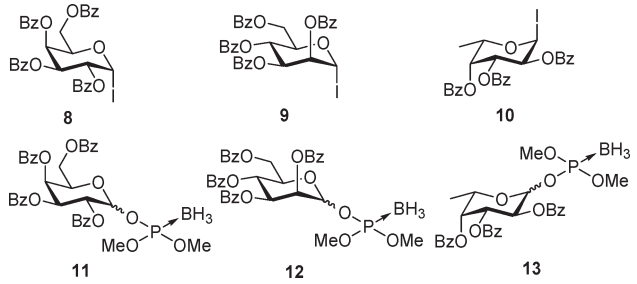
2,3,4,6-Tetra-*O*-pivaloyl-α-D-glucosyl iodide (**1**, R = Piv) gave a similar result (Entry 3). In contrast, the use of 2,3,4,6-tetra-*O*-benzoyl-α-D-glucosyl iodide (**1**, R = Bz) significantly limited the formation of acetal **5**, and the desired boranophosphate triester **3** was obtained in good yield and excellent β-selectivity (entry 4). The use of *o*-chlorobenzoyl groups (**1**, R = *o*-ClBz, entry 5) in the place of the benzoyl groups increased the formation of the acetal **5** and the glycal **4**, whereas the use of anisoyl groups (**1**, R = An, entry 6) suppressed the formation of **4** and **5**. It is surprising that 2,3,4,6-tetra-*O*-(*o*-chlorobenzoyl)-α-D-glucosyl iodide gave a fair amount of the acetal **5** (entry 5), as an *o*-chlorobenzoyl group should have the least participation ability. It indicates that all of the per-*O*-acyl protected glucosyl iodides used in this study underwent the glycosylation via neighboring group participation, and the chemoselectivity of the desired *O*-glycosylation over the reduction depends on the stereoelectronic effects of the acyl group.

TABLE 2. Synthesis of Glycosyl Boranophosphates 11−13



entry	glycosyl iodide	equiv of 18-crown-6	time (h)	product	yield (%)[a]
1	**8**		3	**11**	83 (12:88)
2	**9**		48	**12**	74 (98:2)
3	**10**		0.5	**13**	82 (7:93)
4	**8**	2	0.5	**11**	91 (8:92)
5	**9**	2	6	**12**	84 (93:7)

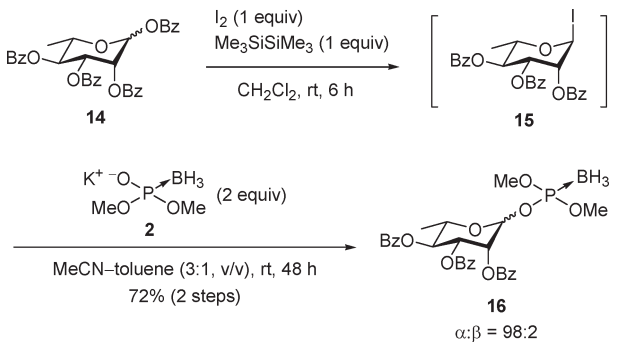
[a]α:β ratios of isolated **11**−**13** were given in parentheses.



Next, optimization of the reaction conditions was carried out by using per-*O*-benzoyl-glucosyl iodide **1** (R = Bz). Our preliminary attempts to suppress the side reactions with **1** (R = Ac) by changing the countercation of dimethyl boranophosphate revealed that the potassium salt **2** was the most effective for the boranophosphorylation.[16] Since **2** is poorly soluble in less polar solvents, such as toluene, relatively polar solvents (MeCN, $MeNO_2$, DME, and DMF) were used for the reaction (entries 4, 7, 8, 9). The reaction was extremely slower in $MeNO_2$ and DME compared to the reaction in MeCN (entries 7, 8 vs 4). In contrast, the reaction was accelerated in DMF (entry 9). The increase in the nucleophilicity of **2** in the highly coordinating solvent also improved the chemoselectivity of glycosylation over reduction, resulting in the suppression of the formation of the acetal **5**. In this case, however, the amount of the glycal **4** increased. It indicates that the basicity of **2** also increases in DMF and the glycosyl iodide **1** underwent an E2 reaction with **2**. Reaction was much slower at 0 °C compared to that conducted at rt (entries 12 vs 4). Addition of 18-crown-6 suppressed the formation of the acetal **5** but accelerated the formation of the glycal **4** (entries 4 vs 13, 5 vs 14, and

(16) The use of tetrabutylammonium dimethyl boranophosphate increased the formation of the glycal **4**, while the reaction of the triethylammonium salt with the glycosyl iodide **1** was much slower than that of the potassium salt **2**.

SCHEME 2. One-Pot Synthesis of Rhamnosyl Boranophosphate 16



6 vs 15). This can be attributed to the effects of 18-crown-6 to increase both the nucleophilicity and basicity of **2** as in the case of DMF.

The optimized reaction conditions were then applied to other substrates. Per-*O*-benzoyl-α-D-galactosyl iodide (**8**), α-D-mannosyl iodide (**9**), and α-L-fucosyl iodide (**10**)[17] were allowed to react with **2** (Table 2). All of these glycosyl iodides gave the corresponding 1,2-*trans*-glycosyl boranophosphates in good yields and stereoselectivity (entries 1−3), indicating that the stereochemistry of the reaction was controlled by neighboring group participation. The formation of glycals and acetals was not observed except for the reaction of the mannosyl iodide **9**, in which ca. 5% of the acetal was generated as a byproduct. Addition of 18-crown-6 accelerated the reactions and improved the yields of the galactosyl and mannosyl boranophosphates **11** and **12** (entries 1 vs 4, 2 vs 5). It also improved the *β*-selectivity of **11** (entries 1 vs 4), whereas the α-selectivity of **12** was slightly lowered (entries 2 vs 5)

Since 2,3,4-tri-*O*-benzoyl-α-L-rhamnosyl iodide **15** could not be isolated by silica gel column chromatography because of its instability on silica gel, we used a one-pot reaction from 1,2,3,4-tetra-*O*-benzoyl-L-rhamnose **14** to synthesize the L-rhamnosyl boranophosphate **16** (Scheme 2). This reaction proceeded without observable formation of the glycal and the acetal to afford **16** in good yield with excellent α-selectivity.

Next, we attempted to synthesize disaccharides linked with an anomeric phosphodiester linkage from the thus obtained 1,2-*trans*-glycosyl boranophosphate triesters in a stereospecific manner. *β*-D-Glc-(1-PO_3H-6)-D-Glc derivative (**22**, Scheme 3) was chosen as the first model compound. Although *β*-D-glucosyl phosphodiester repeating units have not been found in nature, some biomolecules consisting of a *β*-D-glucosyl phosphodiester linkage have been reported.[18] It should also be noted that reports on the chemical synthesis of *β*-D-glucosyl phosphodiester linkages are scarce because it is difficult in general to synthesize the thermodynamically less stable *β*-isomers of the D-glucosyl *H*-phosphonates and other synthetic precursors.[1,8g,8h]

First, dimethyl 2,3,4,6-tetra-*O*-benzoyl-*β*-D-glucosyl boranophosphate (**3**, α:*β* = 1:99) was treated with PhSH and Et_3N to remove one of the methyl groups. In our previous report, the demethylation was performed by treatment of 1,4-diazabicyclo[2.2.2]octane (DABCO), though it gave a small amount of the corresponding phosphite.[10a] This side reaction was suppressed by using PhS^- as a nucleophile, and the demethylation reaction proceeded almost quantitatively. The resultant diester **17** was then allowed to condense with the 6-OH of an appropriately protected methyl glucoside **18**[19] by using 3-nitro-1,2,4-triazol-1-yl-tris(pyrrolidin-1-yl)-phosphonium hexafluorophosphate (PyNTP)[20] to give the boranophosphotriester-linked disaccharide **19**. The methyl group of the boranophosphate triester linkage of **19** was then selectively removed by treatment with PhSH and Et_3N to give the boranophosphodiester-linked disaccharide **20** in excellent yield. Finally, we attempted to convert **20** to the corresponding phosphodiester-linked disaccharide (**22**). When the compound **20** was treated with 4,4′-dimethoxytrityl (DMTr) cation generated *in situ* from DMTrOMe and dichloroacetic acid (DCA) in CH_2Cl_2 at 0 °C for 10 min,[12] the desired disaccharide linked with an anomeric *H*-phosphonate diester linkage (**21**) was generated. However, a partial cleavage of the glycosyl bond of **21** (ca. 7%) and a slight anomerization to the α-isomer (ca. 4%) were observed by ^{31}P NMR. These side reactions can be attributed to the relatively high Brønsted acidity of DCA and/or the Lewis acidity of DMTr cation in CH_2Cl_2. In fact, the conversion of **20** to **21** was accomplished without any side reactions when Lewis basic dioxane was added as a cosolvent to reduce the acidity of the reaction medium.[21] The resultant *H*-phosphonate diester was oxidized *in situ* with I_2-H_2O−pyridine to give the desired *β*-D-Glc-(1-PO_3H-6)-D-Glc derivative **22** (α:*β* = 2:98) in excellent yield.

Next, the method was applied to the synthesis of α-D-Man-(1-PO_3H-6)-D-Gal derivative (**28**, Scheme 4), the repeating unit of immunologically important *Leishmania* glycocalyx lipophosphoglycans.[3] The reaction of 2,3,4,6-tetra-*O*-benzoyl-α-D-mannosyl iodide **9** with potassium dimethyl boranophosphate **2** gave the α-D-mannosyl boranophosphate triester derivative **12**, which was then converted to the diester **23** without purification. Condensation reaction of **23** with the appropriately protected galactoside **24**[22] was carried out under the same conditions as for **17** and **18** in Scheme 3. The boranophosphotriester-linked disaccharide **25** was isolated by silica gel column chromatography in an almost quantitative yield. The subsequent demethylation, conversion to the *H*-phosphonate diester-linked disaccharide **27**, and oxidation with I_2-H_2O gave the desired **28** (α:*β* = 97:3) in good yield. ^{31}P NMR analysis showed that the conversion of **26** to **27** proceeded almost quantitatively without addition of dioxane.[21]

Conclusion

The reactions between per-*O*-acyl-glycosyl iodides with potassium dimethyl boranophosphate afforded the

(17) The fucosyl iodide **10** was relatively unstable and used right after the purification by silica gel column chromatography.

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(21) See Supporting Information.

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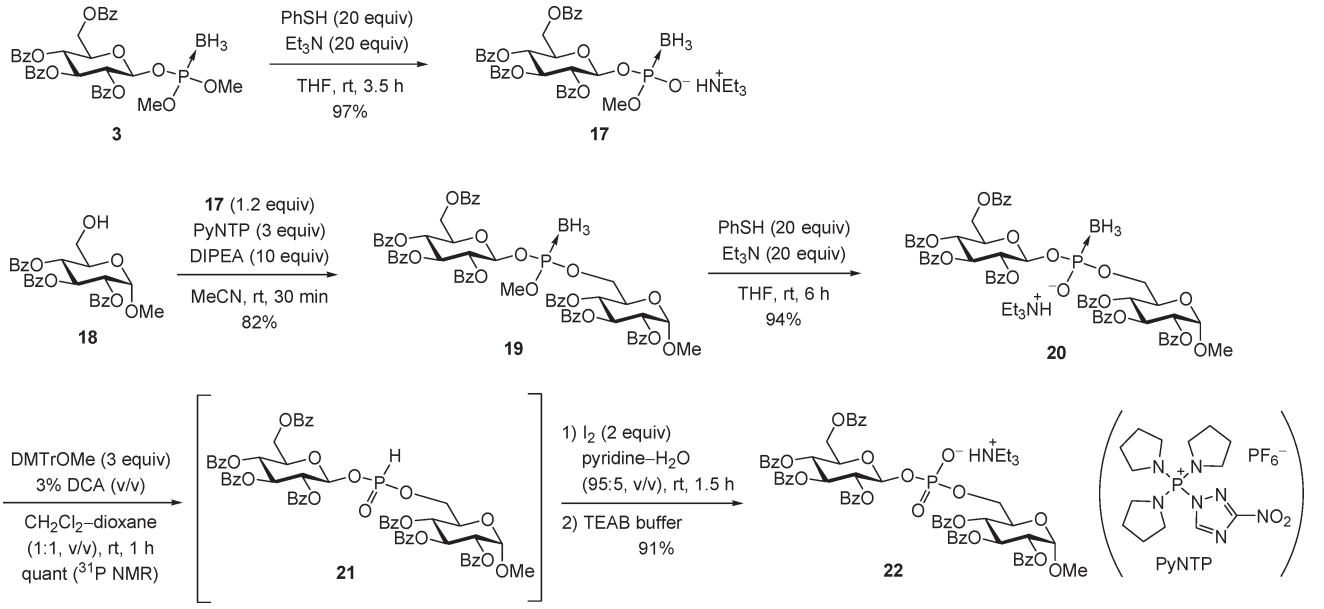
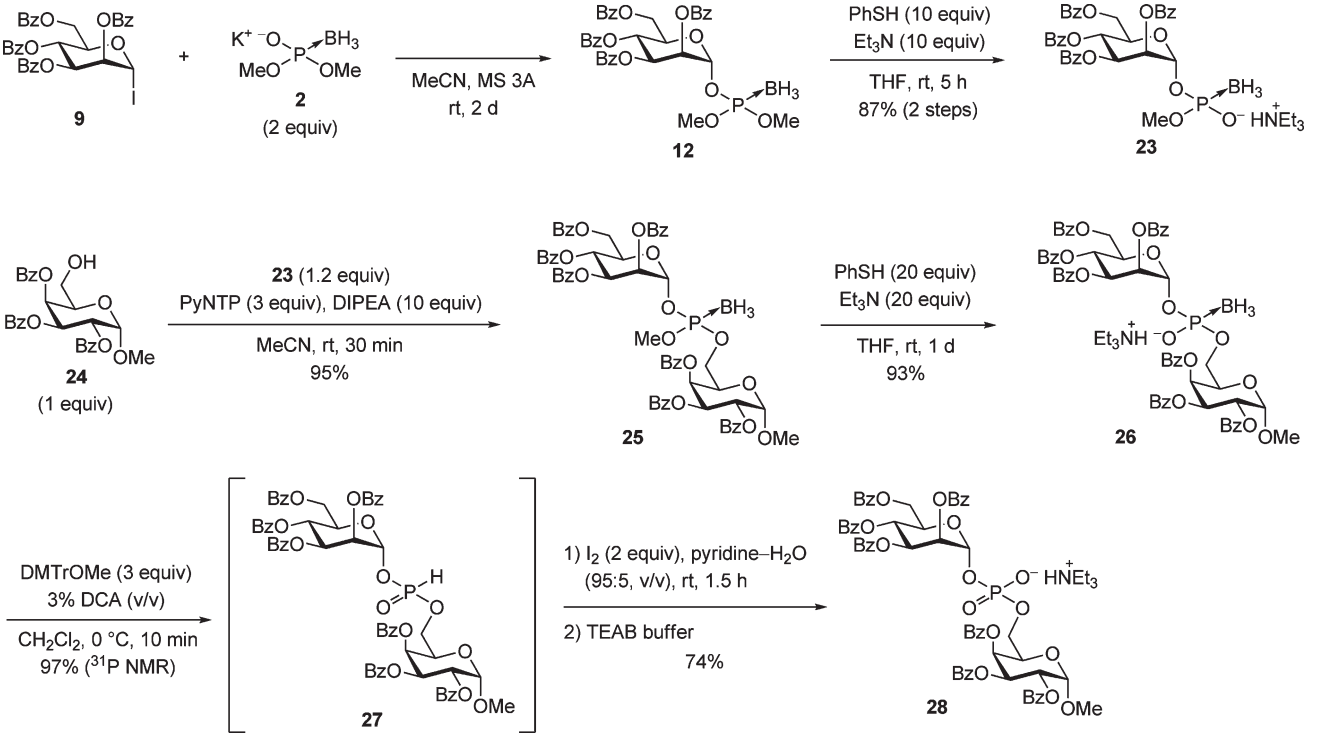
SCHEME 3. Synthesis of β-D-Glc-(1-PO$_3$H-6)-D-Glc Derivative 22[a]



[a]TEAB = triethylammonium bicarbonate.

SCHEME 4. Synthesis of α-D-Man-(1-PO$_3$H-6)-D-Gal Derivative 28



corresponding 1,2-*trans*-glycosyl boranophosphate triesters in good yields and stereoselectivity. The data obtained in this study indicate that the stereochemistry of the reaction is controlled by neighboring group participation. It has also been demonstrated that the resultant glycosyl boranophosphates are applicable to the synthesis of disaccharides linked with an anomeric phosphodiester linkage of high diastereopurity via the *in situ* formation of the corresponding *H*-phosphonate diester-linked disaccharides. Considering that many 1,2-*trans*-glycosyl boranophosphates have become available by the method developed in this study, the use of the glycosyl boranophosphates as "protected" glycosyl *H*-phosphonates is now a useful option to synthesize biomolecules containing glycosyl phosphate units as well as their *P*-modified analogues.

Experimental Section

2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl iodide (**1**, R = Bn) and 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl iodide (**1**, R = Ac) were prepared according to the literature.[13c,23]

2,3,4,6-Tetra-*O*-pivaloyl-α-D-glucopyranosyl Iodide (1, R = Piv). 1,2,3,4,6-Penta-*O*-pivaloyl-D-glucopyranoside (2.01 g, 3.6 mmol) was dissolved in dry CH_2Cl_2 (7 mL). TMSI (500 μL) was added to the solution at 0 °C while stirring. After being stirred for 90 min at rt, additional TMSI (500 μL) was added, and the mixture was stirred for 18 h at rt. Then, a saturated $NaHCO_3$ aqueous solution (25 mL), a 10% $Na_2S_2O_3$ aqueous solution (25 mL), and CH_2Cl_2 (30 mL) were added to the mixture at 0 °C. The organic layer was separated, washed quickly with a saturated $NaHCO_3$ aqueous solution (30 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt−hexane (1:6, v/v) as an eluent to give **1** as a colorless foam (1.70 g, 2.7 mmol, 81%). IR (KBr, cm^{-1}) 2976, 2873, 1741, 1481, 1460, 1398, 1369, 1281, 1135, 942, 896, 763, 735, 618, 564, 488, 453. ^1H NMR ($CDCl_3$) δ 6.99 (d, J = 4.5 Hz, 1H, H-1), 5.54 (t, J = 9.6 Hz, 1H, H-3), 5.24 (t, J = 9.9 Hz, 1H, H-4), 4.22 (dd, J = 4.5, 9.9 Hz, 1H, H-2), 4.20−4.15 (m, 2H, H-6), 4.12−4.04 (m, 1H, H-5), 1.22, 1.20, 1.18, 1.13 (s, 4 × 9H, C-CH_3). ^{13}C NMR ($CDCl_3$) δ 177.9, 177.1, 176.7, 176.4 (C=O), 75.4 (C-5), 73.3 (C-1), 71.1 (C-3), 70.4 (C-2), 66.3 (C-4), 60.8 (C-6), 38.9, 38.8, 38.7, 38.6 (Me_3CCO), 27.1, 27.0 (C-CH_3). HRMS (ESI): calcd for $C_{26}H_{43}IO_9Na$ $[M + Na]^+$ 649.1850; found 649.1857.

2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl Iodide (1, R = Bz). I_2 (0.408 g, 1.6 mmol) and hexamethyldisilane (0.33 mL, 1.6 mmol) were added successively to a solution of 1,2,3,4,6-penta-*O*-benzoyl-D-glucopyranoside (1.41 g, 2.0 mmol) in dry CH_2Cl_2 (4 mL) at rt while stirring.[23] After 9 h, $CHCl_3$ (18 mL), a 10% $Na_2S_2O_3$ aqueous solution (12 mL), and a saturated $NaHCO_3$ aqueous solution (8 mL) were added successively. The organic layer was separated and washed successively with a 10% $Na_2S_2O_3$ aqueous solution (10 mL), a saturated $NaHCO_3$ aqueous solution (10 mL), and saturated $NaHCO_3$ aqueous solutions (2 × 20 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (20 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt−hexane (2:7, v/v) as an eluent to give the desired product as a colorless foam (0.847 g, 1.2 mmol, 60%). The ^1H NMR spectrum was identical to the reported data.[24]

2,3,4,6-Tetra-*O*-(2-chlorobenzoyl)-α-D-glucopyranosyl Iodide (1, R = *o*-ClBz). I_2 (0.203 g, 0.80 mmol) and hexamethyldisilane (0.16 mL, 0.80 mmol) were added successively to a solution of 1,2,3,4,6-penta-*O*-(2-chlorobenzoyl)-D-glucopyranoside (0.874 g, 1.0 mmol) in dry CH_2Cl_2 (2 mL) at rt while stirring.[23] The mixture was allowed to stir overnight. $CHCl_3$ (20 mL), a 10% $Na_2S_2O_3$ aqueous solution (5 mL), and a saturated $NaHCO_3$ aqueous solution (10 mL) were successively added to the mixture. The organic layer was separated and washed with saturated $NaHCO_3$ aqueous solutions (3 × 15 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (20 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt−hexane (1:3, v/v) as an eluent to give the desired product as a colorless foam (0.807 g, 0.96 mmol, 96%). IR (KBr, cm^{-1}) 2957, 1744, 1592, 1474, 1437, 1293, 1246, 1108, 1048, 858, 789, 745, 650, 578, 515. ^1H NMR ($CDCl_3$) δ 8.03−7.21 (m, 17H, Ar, H-1), 6.15 (t, J = 9.6 Hz, 1H, H-3), 5.83 (t, J = 9.9 Hz, 1H, H-4), 4.72 (dd, J = 4.3, 9.8 Hz, 1H, H-2), 4.66−4.62 (m, 2H, H-6), 4.51−4.43 (m, 1H, H-5). ^{13}C NMR ($CDCl_3$) δ 165.0, 164.4, 164.1, 163.3, 134.9, 134.0, 133.9, 133.7, 133.2, 133.1, 132.9, 132.6, 131.8, 131.5, 131.4, 131.1, 129.2, 128.7, 128.5, 127.1, 126.9, 126.8 (C=O, Ar), 75.0 (C-5), 72.3, 72.2 (C-1,3), 71.1 (C-2), 67.8 (C-4), 62.1 (C-6). HRMS (ESI): calcd for $C_{34}H_{23}Cl_4IO_9K$ $[M + K]^+$ 880.8778; found 880.8789.

2,3,4,6-Tetra-*O*-(4-methoxybenzoyl)-α-D-glucopyranosyl Iodide (1, R = An). I_2 (0.153 g, 0.60 mmol) and hexamethyldisilane (0.12 mL, 0.60 mmol) were added successively to a solution of 1,2,3,4,6-penta-*O*-(4-methoxybenzoyl)-D-glucopyranoside (0.852 g, 1 mmol) in dry CH_2Cl_2 (2 mL) at rt while stirring.[23] The mixture was allowed to stir overnight. I_2 (75 mg, 0.30 mmol) and hexamethyldisilane (62 μL, 0.30 mmol) were added to the mixture. After being stirred for 1.5 h, the mixture was diluted with $CHCl_3$ (20 mL), a 10% $Na_2S_2O_3$ aqueous solution (10 mL), and a saturated $NaHCO_3$ aqueous solution (10 mL). The organic layer was separated and washed successively with a 10% $Na_2S_2O_3$ aqueous solution (10 mL), a saturated $NaHCO_3$ aqueous solution (10 mL), and saturated $NaHCO_3$ aqueous solutions (2 × 20 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (2 × 20 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt−hexane (9:16−2:3, v/v) as an eluent to give the desired product as a colorless foam (0.678 g, 0.82 mmol, 82%). IR (KBr, cm^{-1}) 3080, 2958, 2935, 2839, 1727, 1605, 1512, 1460, 1421, 1258, 1169, 1098, 1029, 846, 767, 694, 614, 566, 482. ^1H NMR ($CDCl_3$) δ 8.05−7.81 (m, 8H, Ar), 7.23 (d, J = 4.2 Hz, 1H, H-1), 6.95−6.74 (m, 8H, Ar), 6.11 (t, J = 9.8 Hz, 1H, H-3), 5.79 (t, J = 9.6 Hz, 1H, H-4), 4.71−4.58 (m, 2H, H-2, 6), 4.51−4.42 (m, 2H, H-5,6), 3.85, 3.81, 3.75 (s, 4 × 3H, Ar-OCH_3). ^{13}C NMR ($CDCl_3$) δ 165.7, 164.7, 163.9, 163.8, 163.5, 132.2, 132.0, 131.8, 121.8, 121.1, 120.8, 120.7, 113.8, 113.7, 113.6, 113.5 (C=O, Ar), 75.5 (C-5), 73.8 (C-1), 71.9 (C-3), 70.8 (C-2), 67.4 (C-4), 61.6 (C-6), 55.4, 55.3 (Ar-OCH_3). HRMS (ESI): calcd for $C_{38}H_{35}IO_{13}Na$ $[M + Na]^+$ 849.1020; found 849.1003.

Dimethyl Boranophosphate Monopotassium Salt (2). This material was prepared according to the literature with minor modifications.[11a] A 0.99 M BH_3·THF solution in THF (48 mL, 48 mmol) was added dropwise at 0 °C to a solution of trimethyl phosphite (4.70 mL, 40 mmol) in dry THF (40 mL) while stirring. After being kept at 0 °C for 30 min, the mixture was allowed to warm to rt, and the reaction was monitored by ^{31}P NMR. Upon complete consumption of trimethyl phosphite, the mixture was concentrated under reduced pressure. The residue was dissolved in dry methanol (40 mL), and KOH (purity 85%, 2.0 g, 31 mmol) was added to the mixture at 0 °C. After stirring for 30 min, the mixture was allowed to warm to rt and stirred for 60 h. The mixture was concentrated under reduced pressure, and the residue was recrystallized from acetonitrile (15 mL) to give **2** as colorless crystals (4.26 g, 26 mmol, 84%). The ^1H and ^{31}P NMR spectra were identical to the reported data.[11a]

2,3,4,6-Tetra-*O*-benzoyl-α-D-galactopyranosyl Iodide (8). I_2 (0.61 g, 2.4 mmol) and hexamethyldisilane (0.495 mL, 2.4 mmol) were added successively to a solution of 1,2,3,4,6-penta-*O*-benzoyl-D-galactopyranoside (2.11 g, 3.0 mmol) in dry CH_2Cl_2 (6 mL) at rt while stirring.[23] The mixture was allowed to stir overnight and diluted with $CHCl_3$ (15 mL), a saturated $NaHCO_3$ aqueous solution (15 mL), and a 10% $Na_2S_2O_3$ aqueous solution (15 mL). The organic layer was separated and washed with saturated $NaHCO_3$ aqueous solutions (2 × 30 mL). The aqueous layers were combined and back-extracted with $CHCl_3$

(23) Mukhopadhyay, B.; Kartha, K. P. R.; Russell, D. A.; Field, R. A. *J. Org. Chem.* **2004**, *69*, 7758–7760.
(24) Caputo, R.; Kunz, H.; Mastroianni, D.; Palumbo, G.; Pedatella, S.; Solla, F. *Eur. J. Org. Chem.* **1999**, 3147–3150.

(30 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt−hexane (2:7, v/v) as an eluent to give **8** as a colorless foam (2.12 g, 3.0 mmol, quant). The ^{1}H NMR spectrum was identical to the reported data.[24]

2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl Iodide (9). I_2 (1.4 g, 5.6 mmol) and hexamethyldisilane (1.15 mL, 5.6 mmol) were added successively to a solution of 1,2,3,4,6-penta-*O*-benzoyl-D-mannopyranoside (4.91 g, 7.0 mmol) in dry CH_2Cl_2 (7 mL) at rt while stirring.[23] The mixture was allowed to stir overnight. $CHCl_3$ (20 mL), a saturated $NaHCO_3$ aqueous solution (20 mL), and a 10% $Na_2S_2O_3$ aqueous solution (20 mL) were successively added to the mixture. The organic layer was separated and washed with saturated $NaHCO_3$ aqueous solutions (2 × 30 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (2 × 30 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on NH silica gel (100−200 mesh) using AcOEt−hexane (1:3, v/v) as an eluent to give **9** as a colorless foam (4.29 g, 6.1 mmol, 87%). The ^{1}H NMR spectrum was identical to the reported data.[24]

2,3,4-Tri-*O*-benzoyl-α-L-fucopyranosyl Iodide (10). 1,2,3,4-Tetra-*O*-benzoyl-L-fucopyranoside (1.71 g, 2.9 mmol) was dissolved in dry CH_2Cl_2 (30 mL). TMSI (750 μL) was added to the solution at rt while stirring. After 6 h, a saturated $NaHCO_3$ aqueous solution (25 mL) and a 10% $Na_2S_2O_3$ aqueous solution (25 mL) were added to the mixture at 0 °C. The organic layer was separated, washed quickly with a saturated $NaHCO_3$ aqueous solution (30 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt−hexane (1:7, v/v) as an eluent to give **10** as a colorless foam (1.05 g, 1.8 mmol, 61%). IR (KBr, cm^{-1}) 1728, 1602, 1451, 1315, 1281, 1083, 1026, 909, 709, 478. ^{1}H NMR ($CDCl_3$) δ 8.09 (d, J = 7.5 Hz, 2H, COPh), 8.02 (d, J = 7.5 Hz, 2H, COPh), 7.80 (d, J = 7.2 Hz, 2H, COPh), 7.66−7.23 (m, 10 H, COPh, H-1), 5.90 (dd, J = 3.3 Hz, 11.0 Hz, 1H, H-3), 5.82 (d, J = 3.3 Hz, 1H, H-4), 4.95 (d, J = 3.9 Hz, 11.0 Hz, 1H, H-2), 4.30 (q, J = 6.3 Hz, 1H, H-5), 1.37 (d, J = 6.3 Hz, 3H, H-6). ^{13}C NMR ($CDCl_3$) δ 165.7, 165.4, 165.3 (C=O), 133.7, 133.6, 133.3, 130.0−128.3 (Ar), 76.7 (CH, C-1), 73.2 (CH, C-5), 71.1 (CH, C-3), 70.4 (CH, C-4), 68.2 (CH, C-2), 15.7 (CH_3, C-6). HRMS (ESI): calcd for $C_{27}H_{24}IO_7$ $[M + H]^+$ 587.0561; found 587.0544.

1,2,3,4-Tetra-*O*-benzoyl-L-rhamnopyranoside (14). α-L-Rhamnose monohydrate (0.91 g, 5.0 mmol) was dried by repeated coevaporation with dry pyridine and dissolved in dry pyridine (25 mL). Benzoyl chloride (3.5 mL, 30 mmol) was added dropwise to the solution at 0 °C while stirring. After being kept at 0 °C for 30 min, the mixture was allowed to warm to rt. After being stirred for 4.5 h at rt, ethanol (4 mL) and $CHCl_3$ (40 mL) were added successively. The solution was washed with saturated $NaHCO_3$ aqueous solutions (3 × 40 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (40 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt−hexane (1:3, v/v) as an eluent to give **14** as a colorless foam (2.79 g, 4.8 mmol, α:β = 77:23, 96%). The ^{1}H NMR spectrum was identical to the reported data.[25]

General Procedure for Synthesis of Dimethyl Glycopyranosyl Boranophosphates 3, 11−13. (Tables 1, 2). Glycosyl iodide **1**, **8**, **9**, or **10** (0.10 mmol) was dried by repeated coevaporation with dry toluene and dissolved in dry solvent (1.0 mL) under argon. Molecular sieves 3Å, 18-crown-6 (52.9 mg, 0.20 mmol, for Table 1, entries 13−15, Table 2, entries 4, 5), and potassium dimethyl boranophosphate **2** (32 mg, 0.20 mmol), which was dried *in vacuo* overnight, were added successively to the reaction mixture. The reaction was monitored by TLC. Upon complete consumption of the glycosyl iodide, a saturated $NaHCO_3$ aqueous solution (4 mL) and toluene (7 mL) were added successively to the mixture. The organic layer was separated and washed with saturated $NaHCO_3$ aqueous solutions (3 × 7 mL). The aqueous layers were combined and back-extracted with toluene (2 × 20 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt−hexane as an eluent to give the dimethyl glycopyranosyl boranophosphate (**3**, **11**−**13**).

Dimethyl 2,3,4,6-Tetra-*O*-pivaloyl-β-D-glucopyranosyl Boranophosphate (3, R = Piv). IR (KBr, cm^{-1}) 2971, 2873, 2408, 1747, 1481, 1460, 1398, 1368, 1281, 1134, 1031, 850, 762, 669, 618, 585. ^{1}H NMR ($CDCl_3$) δ 5.37 (t, J = 9.3 Hz, 1H, H-3), 5.26 (t, J = 7.4 Hz, 1H, H-1), 5.19−5.08 (m, 2H, H-2, 4), 4.27 (dd, J = 1.4, 12.2 Hz, 1H, H-6), 4.04 (dd, J = 6.0, 12.3 Hz, 1H, H-6), 3.89−3.81 (m, 1H, H-5), 3.77−3.62 (m, 6H, P-OCH_3), 1.22, 1.17, 1.16, 1.12 (s, 4 × 9H, C-CH_3), 1.2 to −0.1 (br, 3H, -BH_3). ^{13}C NMR ($CDCl_3$) δ 178.0, 176.9, 176.6, 176.5 (C=O), 96.2 (C-1), 73.1 (C-5), 71.7 (C-3), 71.1 (C-2), 67.4 (C-4), 61.5 (C-6), 53.4, 53.3 (P-OCH_3), 38.8, 38.7 (Me_3CCO), 27.1, 27.0 (C-CH_3). ^{31}P NMR ($CDCl_3$) δ 122.2−119.0 (m). HRMS (ESI): calcd for $C_{28}H_{52}BO_{12}PK$ $[M + K]^+$ 661.2927; found 661.2915.

Dimethyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl Boranophosphate (3, R = Bz) (Containing 3% α-Isomer). IR (KBr, cm^{-1}) 3064, 2957, 2923, 2852, 2404, 1734, 1602, 1584, 1492, 1452, 1267, 1179, 1094, 1070, 1026, 840, 757, 710, 645. ^{1}H NMR ($CDCl_3$) δ 8.11−7.23 (m, 20H, Ar), 5.96 (t, J = 9.0 Hz, 1H, H-3), 5.74−5.56 (m, 3H, H-1,2,4), 4.66 (dd, J = 2.6, 12.2 Hz, 1H, H-6), 4.51 (dd, J = 5.9, 12.2 Hz, 1H, H-6), 4.34−4.27 (m, 1H, H-5), 3.67 (d, J = 11.4 Hz, 3H, P-OCH_3), 3.47 (d, J = 10.8 Hz, 3H, P-OCH_3), 1.2 to −0.1 (br, 3H, -BH_3). ^{13}C NMR ($CDCl_3$) δ 166.0, 165.5, 165.1, 165.0 (C=O), 133.6, 133.4, 133.3, 129.8, 129.7, 129.3, 128.6, 128.5, 128.4, 128.3 (Ar), 96.2 (J_{C-H} = 160 Hz, C-1), 73.2 (C-5), 72.3 (C-3), 71.7 (C-2), 69.0 (C-4), 62.6 (C-6), 53.4, 53.3 (P-OCH_3). ^{31}P NMR ($CDCl_3$) δ 122.2−119.0 (m). HRMS (ESI): calcd for $C_{36}H_{36}BO_{12}PNa$ $[M + Na]^+$ 725.1935; found 725.1942.

Dimethyl 2,3,4,6-Tetra-*O*-(2-chlorobenzoyl)-β-D-glucopyranosyl Boranophosphate (3, R = *o*-ClBz) (Containing 4% α-Isomer). IR (KBr, cm^{-1}) 3070, 2956, 2922, 2851, 2405, 1731, 1592, 1473, 1437, 1294, 1248, 1120, 1039, 867, 837, 745, 693, 664, 651, 536, 474. ^{1}H NMR ($CDCl_3$) δ 8.00−7.21 (m, 16H, Ar), 5.95 (t, J = 9.5 Hz, 1H, H-3), 5.77−5.51 (m, 3H, H-1,2,4), 4.69 (dd, J = 2.6, 12.5 Hz, 1H, H-6), 4.59 (dd, J = 5.1, 12.3 Hz, 1H, H-6), 4.30−4.22 (m, 1H, H-5), 3.72 (d, J = 11.7 Hz, 3H, P-OCH_3), 3.61 (d, J = 11.1 Hz, 3H, P-OCH_3), 1.2 to −0.2 (br, 3H, -BH_3). ^{13}C NMR ($CDCl_3$) δ 164.8, 164.4, 164.1, 163.6, 134.2, 134.0, 133.9, 133.4, 133.3, 133.1, 133.0, 131.9, 131.8, 131.7, 131.6, 131.2, 131.1, 131.0, 130.6, 129.0, 128.4, 128.2, 126.8, 126.7 (C=O, Ar), 95.9 (C-1), 72.8 (C-5), 72.5 (C-3), 71.9 (C-2), 69.0 (C-4), 62.6 (C-6), 53.6 (P-OCH_3). ^{31}P NMR ($CDCl_3$) δ 122.0−118.5 (m). HRMS (ESI): calcd for $C_{36}H_{32}BCl_4O_{12}PK$ $[M + K]^+$ 877.0116; found 877.0081.

Dimethyl 2,3,4,6-Tetra-*O*-(4-methoxybenzoyl)-β-D-glucopyranosyl Boranophosphate (3, R = An) (Containing 1% α-Isomer). IR (KBr, cm^{-1}) 3080, 3009, 2958, 2841, 2404, 1718, 1604, 1513, 1461, 1421, 1246, 1165, 1021, 844, 767, 695, 668, 634, 615, 509. ^{1}H NMR ($CDCl_3$) δ8.04−6.73 (m, 16H, Ar), 5.88 (t, J = 9.5 Hz, 1H, H-3), 5.66−5.52 (m, 3H, H-1,2,4), 4.60 (dd, J = 2.6, 12.2 Hz, 1H, H-6), 4.45 (dd, J = 6.1, 12.1 Hz, 1H, H-6), 4.30−4.22 (m, 1H, H-5), 3.85, 3.82, 3.80, 3.76 (s, 4 × 3H, Ar-OCH_3), 3.66 (d, J = 11.4 Hz, 3H, P-OCH_3), 3.47 (d, J = 11.1 Hz, 3H, P-OCH_3), 1.2 to −0.2 (br, 3H, -BH_3). ^{13}C NMR ($CDCl_3$) δ 165.7,

(25) Zhang, H.; Reddy, M. S.; Phoenix, S.; Deslongchamps, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 1272–1275.

165.2, 164.8, 164.7, 163.7, 163.5, 132.0, 131.9, 131.8, 121.8, 121.0, 120.8, 113.7, 113.6, 113.5 (C=O, Ar), 96.3 (C-1), 73.3 (C-5), 72.0 (C-3), 71.5 (C-2), 68.8 (C-4), 62.5 (C-6), 55.4, 55.3 (Ar-O$\underline{C}H_3$), 53.4, 53.3 (P-O$\underline{C}H_3$). ^{31}P NMR ($CDCl_3$) δ 122.0−118.7 (m). HRMS (ESI): calcd for $C_{40}H_{44}BO_{16}PNa$ $[M + Na]^+$ 845.2358; found 845.2334.

Dimethyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl Boranophosphate (11) (Containing 8% α-Isomer). IR (KBr, cm^{-1}) 3064, 2957, 2852, 2404, 1726, 1602, 1584, 1492, 1452, 1274, 1178, 1028, 841, 712, 615. ^{1}H NMR ($CDCl_3$) δ 8.14−7.22 (m, 20H, Ar), 6.04−6.02 (m, 1H, H-4), 5.91 (dd, J = 8.0, 10.2 Hz, 1H, H-2), 5.66 (dd, J = 3.3, 10.5 Hz, 1H, H-3), 5.59 (t, J = 7.8 Hz, 1H, H-1), 4.72−4.62 (m, 1H, H-6), 4.53−4.41 (m, 2H, H-5, 6), 3.70 (d, J = 11.4 Hz, 3H, P-OC$\underline{H}_3$), 3.50 (d, J = 10.8 Hz, 3H, P-OC$\underline{H}_3$), 1.2 to −0.1 (br, 3H, -B$\underline{H}_3$). ^{13}C NMR ($CDCl_3$) δ 165.9, 165.4, 165.3, 165.2 (C=O), 133.7, 133.6, 133.4, 133.3, 130.0, 129.9, 129.8, 129.7, 129.2, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3 (Ar), 96.5 (J_{C-H} = 162 Hz, C-1), 72.6 (C-5), 71.3 (C-3), 69.7 (C-2), 67.8 (C-4), 62.1 (C-6), 53.5, 53.4 (P-O$\underline{C}H_3$). ^{31}P NMR ($CDCl_3$) δ 122.6−119.5 (m). HRMS (ESI): calcd for $C_{36}H_{36}BO_{12}PNa$ $[M + Na]^+$ 725.1935; found 725.1947.

Dimethyl 2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl Boranophosphate (12) (Containing 2% β-Isomer). IR (KBr, cm^{-1}) 3065, 2956, 2852, 2405, 1731, 1602, 1584, 1492, 1452, 1266, 1177, 1107, 1070, 1028, 960, 709. ^{1}H NMR ($CDCl_3$) δ 8.14−7.25 (m, 20H, Ar), 6.19 (t, J = 10.2 Hz, 1H, H-4), 5.96−5.90 (m, 2H, H-1, 3), 5.79−5.75 (m, 1H, H-2), 4.73 (dd, J = 2.3, 12.2 Hz, 1H, H-6), 4.68−4.60 (m, 1H, H-5), 4.51 (dd, J = 4.2, 12.0 Hz, 1H, H-6), 3.85 (t, J = 11.1 Hz, 6H, P-OC$\underline{H}_3$), 1.2 to −0.1 (br, 3H, -B$\underline{H}_3$). ^{13}C NMR ($CDCl_3$) δ 166.0, 165.5, 165.3, 165.1 (C=O), 133.7, 133.6, 133.4, 133.1, 129.9, 129.8, 129.7, 128.8, 128.7, 128.6, 128.5, 128.4 (Ar), 94.1 (J_{C-H} = 181 Hz, C-1), 70.6 (C-5), 69.8 (C-2), 69.2 (C-3), 65.9 (C-4), 62.3 (C-6), 54.2, 53.8 (P-O$\underline{C}H_3$). ^{31}P NMR ($CDCl_3$) δ 122.6−119.2 (m). HRMS (ESI): calcd for $C_{36}H_{36}BO_{12}PNa$ $[M + Na]^+$ 725.1935; found 725.1936.

Dimethyl 2,3,4-Tri-*O*-benzoyl-β-L-fucopyranosyl Boranophosphate (13) (Containing 7% α-Isomer). IR (KBr, cm^{-1}) 3065, 2957, 2851, 2405, 1730, 1603, 1452, 1263, 1178, 1094, 1026, 862, 764, 709, 687, 617. ^{1}H NMR ($CDCl_3$) δ 8.14−7.25 (m, 15H, Ar), 5.85 (dd, J = 7.8, 10.2 Hz, 1H, H-2), 5.77−5.74 (m, 1H, H-4), 5.59 (dd, J = 3.3, 10.5 Hz, 1H, H-3), 5.52 (t, J = 7.8 Hz, 1H, H-1), 4.25−4.17 (m, 1H, H-5), 3.77 (d, J = 11.4 Hz, 3H, P-OC$\underline{H}_3$), 3.49 (d, J = 11.1 Hz, 3H, P-OC$\underline{H}_3$), 1.38 (d, J = 6.3 Hz, 3H, H-6), 1.1 to −0.2 (br, 3H, -B$\underline{H}_3$). ^{13}C NMR ($CDCl_3$) δ 165.8, 165.4, 165.3 (C=O), 133.5, 133.3, 133.0, 129.9, 129.8, 129.7, 129.1, 128.9, 128.7, 128.6, 128.4, 128.3 (Ar), 96.5 (J_{C-H} = 168 Hz, C-1), 71.6 (C-3), 70.9 (C-5), 70.6 (C-4), 69.7 (C-2), 53.5, 53.3 (P-O$\underline{C}H_3$), 16.1 (C-6). ^{31}P NMR ($CDCl_3$) δ 122.4−118.5 (m). HRMS (ESI): calcd for $C_{29}H_{32}BO_{10}PNa$ $[M + Na]^+$ 605.1724; found 605.1695.

One-Pot Synthesis of Dimethyl 2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl Boranophosphate (16). 1,2,3,4-Tetra-*O*-benzoyl-L-rhamnopyranoside (**14**) (59 mg, 0.10 mmol) was dried by repeated coevaporation with dry toluene and dissolved in dry CH_2Cl_2 (1.0 mL) under argon. I_2 (25 mg, 0.098 mmol) and hexamethyldisilane (20 μL, 0.098 mmol) were added successively to the solution, and the mixture was stirred at rt. The reaction was monitored by TLC. Upon complete consumption of **14**, the mixture was concentrated under reduced pressure under argon. Any volatile reagents were removed by repeated coevaporation with dry toluene under argon. The residue was then dissolved in dry toluene (0.25 mL). A solution of potassium dimethyl boranophosphate **2** (32 mg, 0.20 mmol), which was dried *in vacuo* overnight, in dry acetonitrile (0.75 mL) was added to the residue, and the mixture was stirred at rt for 48 h. A saturated $NaHCO_3$ aqueous solution (4 mL), a 10% $Na_2S_2O_3$ aqueous solution (3 mL), and toluene (7 mL) were then added successively to the mixture. The organic layer was separated and washed with saturated $NaHCO_3$ aqueous solutions (3 × 7 mL). The aqueous layers were combined and back-extracted with toluene (2 × 20 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt−hexane (1:4, v/v) as an eluent to give **16** as a colorless foam (42 mg, 0.072 mmol, 72%, α:β = 98:2). IR (KBr, cm^{-1}) 3065, 2956, 2852, 2404, 1732, 1602, 1492, 1452, 1280, 1177, 1095, 1070, 1028, 957, 710, 629. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.14−7.23 (m, 15H, Ar), 5.87−5.82 (m, 2H, H-1,3), 5.77−5.68 (m, 2H, H-2,4), 4.46 (dq, J = 6.2, 9.6 Hz, 1H, H-5), 3.91−3.85 (m, 6H, P-OC$\underline{H}_3$), 1.41 (d, J = 6.3, 3H, H-6), 1.2 to −0.1 (br, 3H, -B$\underline{H}_3$). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 165.6, 165.5, 165.3 (C=O), 133.7, 133.5, 133.3, 129.9, 129.7, 129.0, 128.9, 128.6, 128.5, 128.3 (Ar), 94.2 (J_{C-H} = 178 Hz, C-1), 70.9 (C-4), 70.2 (C-2), 69.2 (C-3), 68.7 (C-5), 54.1, 53.7 (P-O$\underline{C}H_3$), 17.5 (C-6). ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ 122.0−118.8 (m). HRMS (ESI): calcd for $C_{29}H_{32}BO_{10}PNa$ $[M + Na]^+$ 605.1724; found 605.1697.

Methyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl Boranophosphate Triethylammonium Salt (17). Triethylamine (5.6 mL, 40 mmol) and benzenethiol (4.1 mL, 40 mmol) were added successively to a solution of dimethyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl boranophosphate (**3**, R = Bz, α:β = 1:99, 1.41 g, 2.0 mmol) in dry THF (20 mL), and the mixture was allowed to stir for 3.5 h at rt. A 1 M TEAB aqueous solution (30 mL) and $CHCl_3$ (30 mL) were added successively to the mixture. The organic layer was separated and washed with 1 M TEAB aqueous solutions (2 × 30 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (2 × 30 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2−Et_3N−MeOH (100:1:0−100:1:1, v/v/v) as an eluent to give **17** as a colorless foam (1.54 g, 1.95 mmol, 97%, α:β = 1:99). IR (KBr, cm^{-1}) 2947, 2368, 1732, 1602, 1584, 1452, 1316, 1269, 1069, 1027, 838, 796, 712. ^{1}H NMR ($CDCl_3$) δ 12.4 (br, 1H), 8.13−7.78, 7.59−7.24 (m, 20H, Ar), 5.98−5.88 (m, 1H), 5.76−5.53 (m, 3H), 4.62 (dt, J = 3.1, 12.2 Hz, 1H), 4.45 (ddd, J = 5.4, 12.6 Hz, 1H), 4.32−4.23 (m, 1H), 3.51 (d, J = 10.5 Hz, 1.5 H), 3.22 (d, J = 11.1 Hz, 1.5 H), 2.93−2.81 (m, 6H), 1.15 (t, J = 7.4 Hz, 9H), 1.0 to −0.1 (br, 3H). ^{13}C NMR ($CDCl_3$) δ 166.1, 165.6, 165.4, 165.3, 165.2 (C=O), 133.4, 133.1, 130.1, 129.8, 129.7, 129.5, 129.4, 129.3, 129.2, 128.8, 128.7, 128.4, 128.3, 128.2 (Ar), 95.2 (CH), 94.9 (CH), 73.2 (CH), 73.1 (CH), 72.5 (CH), 72.4 (CH), 72.3 (CH), 69.7 (CH), 69.4 (CH), 63.2 (CH_2), 63.0 (CH_2), 50.4 (CH_3), 50.3 (CH_3), 50.0 (CH_3), 49.9 (CH_3), 45.2 (CH_2), 8.3 (CH_3). ^{31}P NMR ($CDCl_3$) δ 101.6−95.2 (m). HRMS (ESI): calcd for $C_{35}H_{34}BO_{12}PNa$ $[M + Na]^+$ 711.1779; found 711.1788.

Boranophosphotriester-Linked β-D-Glc-(1-*P*-6)-D-Glc Derivative (19). Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl boranophosphate triethylammonium salt (**17**, 1.22 g, 1.5 mmol) and methyl 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (**18**,[19] 0.657 g, 1.3 mmol) were dried by repeated coevaporation with dry toluene and dissolved in dry MeCN (15 mL) under argon. DIPEA (2.2 mL, 13 mmol) and PyNTP (1.93 g, 3.9 mmol) were added successively, and the mixture was allowed to stir for 30 min at rt. A saturated $NaHCO_3$ aqueous solution (20 mL) and $CHCl_3$ (30 mL) were added successively to the mixture. The organic layer was separated and washed with saturated $NaHCO_3$ aqueous solutions (2 × 30 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (2 × 30 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography on NH silica gel (100−200 mesh) using AcOEt−hexane (1:3−1:2, v/v) as an eluent to give **19** as a colorless foam (1.25 g, 1.1 mmol, 82%, α:β = 1:99). IR

(KBr, cm^{-1}) 3064, 2957, 2405, 1731, 1602, 1584, 1492, 1452, 1316, 1278, 1178, 1093, 872, 712. ^1H NMR ($CDCl_3$) δ 8.11−7.81, 7.68−7.24 (m, 35H, Ar), 6.15−6.00 (m, 1H), 5.92 (t, J = 9.6 Hz, 1H), 5.70−5.54 (m, 2.5H), 5.51−5.39 (m, 1H), 5.27 (t, J = 9.5 Hz, 0.5H), 5.22−5.14 (m, 1H), 5.09−5.03 (m, 1H), 4.66−4.56 (m, 1H), 4.46 (dd, J = 5.9, 12.2 Hz, 1H), 4.31−4.21 (m, 1H), 4.20−4.11 (m, 1.5H), 4.09−3.96 (m, 1.5H), 3.65 (d, J = 11.4 Hz, 1.5 H), 3.47 (d, J = 11.4 Hz, 1.5H), 3.40 (s, 1.5 H), 3.30 (s, 1.5H), 1.0 to −0.1 (br, 3H). ^{13}C NMR ($CDCl_3$) δ 165.9, 165.7, 165.6, 165.5, 165.1, 164.9 (C═O), 133.5, 133.4, 133.3, 133.2, 133.1, 129.9, 129.8, 129.7, 129.6, 129.3, 129.1, 129.0, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2 (Ar), 96.8 (CH), 96.6 (CH), 96.1 (CH), 73.2 (CH), 73.1 (CH), 72.4 (CH), 71.8 (CH), 71.7 (CH), 71.6 (CH), 70.3 (CH), 69.0 (CH), 68.9 (CH), 68.6 (CH), 68.1 (CH), 68.0 (CH), 67.9 (CH), 65.4 (CH_2), 65.2 (CH_2), 62.6 (CH_2), 55.6 (CH_3), 55.4 (CH_3), 53.6 (CH_3), 53.5 (CH_3), 53.4 (CH_3). ^{31}P NMR ($CDCl_3$) δ 122.4−118.3 (m). HRMS (ESI): calcd for $C_{63}H_{58}BO_{20}PNa$ $[M + Na]^+$ 1199.3250; found 1199.3226.

Boranophosphodiester-Linked β-D-Glc-(1-*P*-6)-D-Glc Derivative (20). Triethylamine (1.4 mL, 10 mmol) and benzenethiol (1.0 mL, 10 mmol) were added successively to a solution of the compound **19** (0.591 g, 0.50 mmol) in dry THF (5 mL), and the mixture was allowed to stir for 6 h at rt. A 1 M TEAB aqueous solution (20 mL) and $CHCl_3$ (20 mL) were added successively to the mixture. The organic layer was separated and washed with 1 M TEAB aqueous solutions (2 × 20 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (2 × 20 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2−Et_3N (100:1, v/v) as an eluent to give **20** as a colorless foam (0.597 g, 0.47 mmol, 94%, α:β = 1:99). IR (KBr, cm^{-1}) 3064, 2947, 2369, 1732, 1602, 1584, 1452, 1315, 1272, 1096, 838, 804, 711. ^1H NMR ($CDCl_3$) δ 12.3 (br, 1H), 8.16−7.22 (m, 35H, Ar), 6.09−5.84 (m, 2H), 5.71−5.46 (m, 3H), 5.27 (t, J = 9.8 Hz, 0.5H), 5.20−5.09 (m, 1.5H), 4.99−4.91 (m, 1H), 4.70−4.33 (m, 2H), 4.28−4.09 (m, 2H), 4.03−3.76 (m, 2H), 3.43 (s, 1.5H), 3.29 (s, 1.5H), 2.87−2.73 (m, 6H), 1.09 (t, J = 7.4 Hz, 9H), 1.0 to −0.2 (br, 3H). ^{13}C NMR ($CDCl_3$) δ 166.1, 166.0, 165.7, 165.6, 165.4, 165.2, 165.1, 165.0 (C═O), 133.4, 133.2, 133.0, 132.9, 130.2, 130.1, 130.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.4, 129.3, 129.1, 128.9, 128.8, 128.4, 128.2 (Ar), 96.4 (CH), 96.2 (CH), 95.3 (CH), 94.9 (CH), 73.2 (CH), 73.1 (CH), 72.4 (CH), 72.2 (CH), 72.1 (CH), 70.7 (CH), 69.6 (CH), 69.5 (CH), 69.2 (CH), 69.1 (CH), 68.6 (CH), 63.0 (CH_2), 62.3 (CH_2), 61.7 (CH_2), 55.4 (CH_3), 55.2 (CH_3), 45.1 (CH_2), 8.2 (CH_3). ^{31}P NMR ($CDCl_3$) δ 101.0−95.6 (m). HRMS (ESI): calcd for $C_{62}H_{56}BO_{20}PNa$ $[M + Na]^+$ 1185.3093; found 1185.3126.

Phosphodiester-Linked β-D-Glc-(1-*P*-6)-D-Glc Derivative (22). A solution of DMTrOMe (50 mg, 0.15 mmol) and DCA (30 μL) in dry CH_2Cl_2 (0.5 mL) was added to the compound **20** (63 mg, 50 μmol) in dry dioxane (0.5 mL), and the mixture was allowed to stir for 1 h at rt. Et_3SiH (0.1 mL) and $CHCl_3$ (5 mL) were added successively to the mixture and the mixture was washed with 5% $NaHCO_3$ aqueous solutions (3 × 5 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (3 × 15 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give of the *H*-phosphonate diester intermediate **21**. A solution of I_2 (25 mg, 99 μmol) in dry pyridine (0.95 mL) and H_2O (50 μL) was then added and the mixture was allowed to stir for 1.5 h at rt. The mixture was diluted with $CHCl_3$ (5 mL) and washed with a 10% $Na_2S_2O_3$ aqueous solution (5 mL) and 1 M TEAB aqueous solutions (2 × 5 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (2 × 15 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2−Et_3N−MeOH (100:1:0−100:1:2, v/v/v) as an eluent. The fractions containing **22** were collected and concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (5 mL) and washed with a 1 M TEAB aqueous solution (5 mL). The aqueous layer was back-extracted with $CHCl_3$ (3 × 5 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give **22** as a yellow foam (58 mg, 46 μmol, 91%, α:β = 2:98). IR (KBr, cm^{-1}) 3065, 2943, 1732, 1602, 1584, 1492, 1452, 1316, 1267, 1177, 1095, 852, 711. ^1H NMR ($CDCl_3$) δ 11.9 (br, 1H), 8.13−7.18 (m, 35H, Ar), 5.98 (t, J = 9.5 Hz, 1H), 5.87 (t, J = 9.8 Hz, 1H), 5.76−5.66 (m, 2H), 5.55 (dd, J = 8.0, 9.5 Hz, 1H), 5.23 (t, J = 9.8 Hz, 1H), 5.03−4.95 (m, 2H), 4.61 (dd, J = 3.2, 12.2 Hz, 1H), 4.40 (dd, J = 5.6, 12.3 Hz, 1H), 4.26−4.18 (m, 1H), 4.05−3.87 (m, 3H), 3.33 (s, 3H), 2.95−2.84 (m, 6H), 1.17 (t, J = 7.5 Hz, 9H). ^{13}C NMR ($CDCl_3$) δ 166.0, 165.7, 165.6, 165.2, 165.1 (C═O), 133.3, 133.1, 132.9, 130.0, 129.8, 129.7, 129.6, 129.4, 129.2, 129.1, 128.9, 128.8, 128.4, 128.3, 128.2 (Ar), 96.3 (CH), 73.2 (CH), 72.1 (CH), 72.0 (CH), 70.8 (CH), 69.4 (CH), 69.1 (CH), 68.7 (CH), 68.6 (CH), 64.2 (CH_2), 62.8 (CH_2), 55.3 (CH_3), 45.3 (CH_2), 8.3 (CH_3). ^{31}P NMR ($CDCl_3$) δ −2.57. HRMS (ESI): calcd for $C_{62}H_{53}O_{21}PNa$ $[M + Na]^+$ 1187.2715; found 1187.2758.

Methyl 2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl Boranophosphate Triethylammonium Salt (23). 2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl iodide **9** (5.63 g, 8.0 mmol) was dried by repeated coevaporation with dry toluene and dissolved in dry acetonitrile (80 mL) under argon. Molecular sieves 3Å and potassium dimethyl boranophosphate **2** (2.60 g, 16 mmol), which was dried *in vacuo* overnight, were added successively, and the mixture was stirred for 2 d at rt. The mixture was then concentrated under reduced pressure. The residue was dissolved in toluene (50 mL), and the solution was filtered to remove molecular sieves. The filtrate was washed with saturated $NaHCO_3$ aqueous solutions (3 × 50 mL). The aqueous layers were combined and back-extracted with toluene (2 × 100 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude **12** (5.22 g). Triethylamine (11.0 mL, 79 mmol) and benzenethiol (8.1 mL, 79 mmol) were added successively to a solution of crude **12** (5.15 g) in dry THF (79 mL) at rt. The mixture was allowed to stir for 5 h and concentrated under reduced pressure. CH_2Cl_2 (50 mL) was added to the residue, and the solution was washed with 1 M TEAB aqueous solutions (3 × 50 mL). The aqueous layers were combined and back-extracted with CH_2Cl_2 (2 × 50 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2−Et_3N−MeOH (100:1:0−100:1:0.3, v/v/v) as an eluent to give **23** as a colorless foam (5.39 g, 6.8 mmol, 87% from **9**, α:β = 98:2). IR (KBr, cm^{-1}) 2985, 2369, 1729, 1602, 1452, 1315, 1267, 1108, 1070, 1027, 848, 790, 711. ^1H NMR ($CDCl_3$) δ 12.3 (br, 1H), 8.19−7.80, 7.62−7.22 (m, 20H, Ar), 6.24−6.13 (m, 1H), 6.02 (dd, J = 2.4, 10.2 Hz, 1H), 5.92−5.85 (m, 1H), 5.81−5.75 (m, 1H), 4.84−4.66 (m, 2H), 4.46 (ddd, J = 3.6, 13.0 Hz, 1H), 3.70 (dd, J = 0.9, 10.8 Hz, 3H), 3.16−3.04 (m, 6H), 1.34 (t, J = 7.4 Hz, 9H), 1.1 to −0.1 (br, 3H). ^{13}C NMR ($CDCl_3$) δ 166.2, 165.4, 165.2, 165.1 (C═O), 133.3, 133.0, 132.9, 130.0, 129.9, 129.8, 129.7, 129.4, 129.2, 129.0, 128.5, 128.4, 128.2 (Ar), 92.1 (CH), 91.1 (CH), 91.0 (CH), 71.0 (CH), 70.8 (CH), 70.2 (CH), 70.1 (CH), 69.3 (CH), 66.6 (CH_2), 62.8 (CH_3), 62.6 (CH_3), 45.5 (CH_2), 8.6 (CH_3). ^{31}P NMR ($CDCl_3$) δ 99.2−93.6 (m). HRMS (ESI): calcd for $C_{35}H_{34}BO_{12}PNa$ $[M + Na]^+$ 711.1779; found 711.1780.

Boranophosphotriester-Linked α-D-Man-(1-*P*-6)-D-Gal Derivative (25). The compound **23** (2.85 g, 3.6 mmol) and methyl 2,3,4-tri-*O*-benzoyl-α-D-galactopyranoside (**24**,[22] 1.52 g, 3.0

mmol) were dried by repeated coevaporation with dry toluene and dissolved in dry MeCN (30 mL) under argon. DIPEA (5.1 mL, 30 mmol) and PyNTP (4.49 g, 9.0 mmol) were added successively to the mixture at rt. The mixture was allowed to stir for 30 min and diluted with $CHCl_3$ (75 mL). The mixture was washed with saturated $NaHCO_3$ aqueous solutions (3 × 75 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (2 × 75 mL). The organic layers were combined and concentrated under reduced pressure. $CHCl_3$ (50 mL) was added to the residue, and the solution was washed with 0.1 M pH 7.0 phosphate buffer solutions (3 × 50 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (2 × 50 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt−hexane (2:5−2:3, v/v) as an eluent to give **25** as a colorless foam (3.37 g, 2.9 mmol, 95%, α:β = 98:2). IR (KBr, cm^{-1}) 3065, 2958, 2406, 1731, 1602, 1585, 1452, 1316, 1268, 1177, 1095, 1069, 1027, 957, 709. ^{1}H NMR ($CDCl_3$) δ 8.18−7.14 (m, 35H, Ar), 6.25−6.09 (m, 1H), 6.05−5.84 (m, 4H), 5.79−5.75 (m, 1H), 5.72−5.62 (m, 1H), 5.30 (t, J = 3.2 Hz, 1H), 4.76−4.49 (m, 3.5H), 4.45−4.20 (m, 2.5H), 3.82 (d, J = 11.7 Hz, 1.5H), 3.75 (d, J = 11.1 Hz, 1.5H), 3.49 (s, 2 × 1.5H), 1.1 to 0.0 (br, 3H). ^{13}C NMR ($CDCl_3$) δ 166.0, 165.9, 165.6, 165.4, 165.3, 164.9 (C═O), 133.6, 133.5, 133.3, 133.1, 129.9, 129.8, 129.7, 129.6, 129.1, 129.0, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2 (Ar), 97.5 (CH), 94.2 (CH), 94.1 (CH), 70.7 (CH), 70.6 (CH), 69.8 (CH), 69.7 (CH), 69.6 (CH), 69.3 (CH), 69.2 (CH), 68.8 (CH), 68.2 (CH), 68.1 (CH), 67.5 (CH), 67.4 (CH), 67.3 (CH), 65.9 (CH), 65.8 (CH), 65.2 (CH_2), 64.9 (CH_2), 62.3 (CH_2), 62.2 (CH_2), 55.8 (CH_3), 54.4 (CH_3), 54.3 (CH_3), 54.1 (CH_3), 54.0 (CH_3). ^{31}P NMR ($CDCl_3$) δ 121.1−117.4 (m). HRMS (ESI): calcd for $C_{63}H_{58}BO_{20}PNa$ $[M + Na]^+$ 1199.3250; found 1199.3218.

Boranophosphodiester-Linked α-D-Man-(1-*P*-6)-D-Gal Derivative (26). Triethylamine (4.6 mL, 30 mmol) and benzenethiol (3.1 mL, 30 mmol) were added successively to a solution of the compound **25** (1.76 g, 1.5 mmol) in dry THF (15 mL), and the mixture was allowed to stir for 1 d at rt. The mixture was then diluted with $CHCl_3$ (30 mL) and washed with 1 M TEAB aqueous solutions (3 × 30 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (2 × 30 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2−Et_3N−MeOH (100:1:0−100:1:1, v/v/v) as an eluent to give **26** as a colorless foam (1.76 g, 1.4 mmol, 93%, α:β = 98:2). IR (KBr, cm^{-1}) 3064, 2982, 2369, 1730, 1602, 1584, 1492, 1452, 1316, 1266, 1096, 1027, 848, 804, 711. ^{1}H NMR ($CDCl_3$) δ 12.1 (br, 1H), 8.22−7.14 (m, 35H, Ar), 6.20 (t, J = 10.1, 0.5H), 6.09−5.87 (m, 4H), 5.83−5.72 (m, 1.5H), 5.68−5.59 (m, 1H), 5.26 (dd, J = 3.6, 14.7 Hz, 1H), 4.81−4.39 (m, 3.5H), 4.33−4.05 (m, 2.5H), 3.51 (s, 2 × 1.5H), 3.06 (q, J = 5.3 Hz, 6H), 1.31 (t, J = 7.4 Hz, 9H), 1.1 to −0.1 (br, 3H). ^{13}C NMR ($CDCl_3$) δ 166.1, 166.0, 165.6, 165.4, 165.3, 165.2, 165.1, 165.0, 133.2, 133.1, 132.9, 130.1, 130.0, 129.9, 129.8, 129.6, 129.4, 129.3, 129.2, 129.1, 129.0, 128.4, 128.3, 128.2, 128.1 (Ar), 97.3 (CH), 91.9 (CH), 91.1 (CH), 91.0 (CH), 70.9 (CH), 70.2 (CH), 70.0 (CH), 69.6 (CH), 69.4 (CH), 69.3 (CH), 69.0 (CH), 68.9 (CH), 68.8 (CH), 68.7 (CH), 68.1 (CH), 67.8 (CH), 67.7 (CH), 66.6 (CH), 66.5 (CH), 62.8 (CH_2) 62.5 (CH_2), 61.8 (CH_2), 61.6 (CH_2), 55.7 (CH_3), 55.6 (CH_3), 45.5 (CH_2), 8.5 (CH_3). ^{31}P NMR ($CDCl_3$) δ 98.8−93.7 (m). HRMS (ESI): calcd for $C_{62}H_{56}BO_{20}PNa$ $[M + Na]^+$ 1185.3093; found 1185.3058.

Phosphodiester-Linked α-D-Man-(1-*P*-6)-D-Gal Derivative (28). A solution of DMTrOMe (50 mg, 0.15 mmol) and DCA (30 μL) in dry CH_2Cl_2 (0.5 mL) was added to a solution of the compound **26** (64 mg, 50 μmol) in dry CH_2Cl_2 (0.5 mL) at 0 °C, and the mixture was allowed to stir for 10 min at 0 °C. Et_3SiH (0.1 mL) and $CHCl_3$ (5 mL) were added successively to the mixture, and the mixture was washed with 5% $NaHCO_3$ aqueous solutions (3 × 5 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (3 × 15 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give of the *H*-phosphonate diester intermediate **27**. A solution of I_2 (25 mg, 99 μmol) in dry pyridine (0.95 mL) and H_2O (50 μL) was added to the compound **27**, and the mixture was allowed to stir for 1.5 h at rt. The mixture was diluted with $CHCl_3$ (5 mL) and washed with a 10% $Na_2S_2O_3$ aqueous solution (5 mL) and 1 M TEAB aqueous solutions (2 × 5 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (2 × 15 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2−Et_3N−MeOH (100:1:0−100:1:2, v/v/v) as an eluent. The fractions containing **28** were collected and concentrated under reduced pressure. $CHCl_3$ (5 mL) was added to the residue, and the solution was washed with a 1 M TEAB aqueous solution (5 mL). The aqueous layer was back-extracted with $CHCl_3$ (3 × 5 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give **28** as a yellow foam (48 mg, 38 μmol, 74%, α:β = 97:3). IR (KBr, cm^{-1}) 2922, 1728, 1602, 1452, 1316, 1265, 1108, 1070, 1027, 712. ^{1}H NMR ($CDCl_3$) δ 11.4 (br, 1H), 8.16−7.16 (m, 35H, Ar), 6.13−5.89 (m, 4H), 5.78 (t, J = 2.6 Hz, 1H), 5.70 (dd, J = 2.1, 8.1 Hz, 1H), 5.64 (dd, J = 3.4, 10.4 Hz, 1H), 5.26 (d, J = 3.6 Hz, 1H), 4.71 (dt, J = 2.9, 9.8 Hz, 1H), 4.63−4.55 (m, 2H), 4.35−4.22 (m, 2H), 4.19−4.08 (m, 1H), 3.49 (s, 3H), 3.17−3.06 (m, 6H), 1.35 (t, J = 7.2 Hz, 9H). ^{13}C NMR ($CDCl_3$) δ 166.0, 165.6, 165.5, 165.3, 165.1 (C═O), 133.3, 133.2, 133.0, 132.9, 129.9, 129.8, 129.6, 129.5, 129.4, 129.3, 129.1, 128.9, 128.5, 128.4, 128.3, 128.2, 128.1 (Ar), 97.4 (CH), 93.6 (CH), 70.5 (CH), 69.9 (CH), 69.5 (CH), 69.4 (CH), 68.8 (CH), 67.8 (CH), 67.7 (CH), 66.5 (CH), 63.3 (CH_2), 62.7 (CH_2), 55.7 (CH_3), 45.8 (CH_2), 8.6 (CH_3). ^{31}P NMR ($CDCl_3$) δ −2.90. HRMS (ESI): calcd for $C_{62}H_{53}O_{21}PNa$ $[M + Na]^+$ 1187.2715; found 1187.2668.

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Supporting Information Available: Experimental details and characterizing data, including ^{1}H, ^{13}C, and ^{31}P spectra. This material is available free of charge via the Internet at http://pubs.acs.org.