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Note

# Rearrangement of sugar 1,2-orthoesters to glycosidic products: a mechanistic implication

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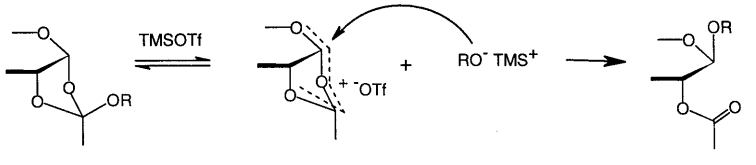
**Abstract**

The identification of cross-over products in the rearrangement of two structurally similar sugar 1,2-orthoesters to glycosidic products is reported. 

*Keywords:* Sugar 1,2-orthoester; Rearrangement; Mechanism

Sugar 1,2-orthoesters are classic glycosyl donors used in the construction of 1,2-*trans*-glycosidic linkages, which, in particular, have been studied by Kochetkov and co-workers [1]. On the other hand, sugar 1,2-orthoesters are often undesired side products in glycosylation with donors carrying C-2 acetyl protecting groups [2]. The undesired orthoesters can then be converted into the corresponding glycosidic products under the action of protic or Lewis acids [2b–d,3], a transformation that has recently been put to good use [4]. Several experiments further demonstrated that the normal glycosidic products in the glycosylation reactions were actually derived from the corresponding orthoester intermediates [5]. The mechanism of the rearrangement of the orthoester to the glycosidic product has been postulated, as shown in Scheme 1. The mechanism involves the dissociation of the orthoester to a 1,2-acyloxonium ion and glycosidation of the transient oxocarbenium species [6].




Scheme 1.

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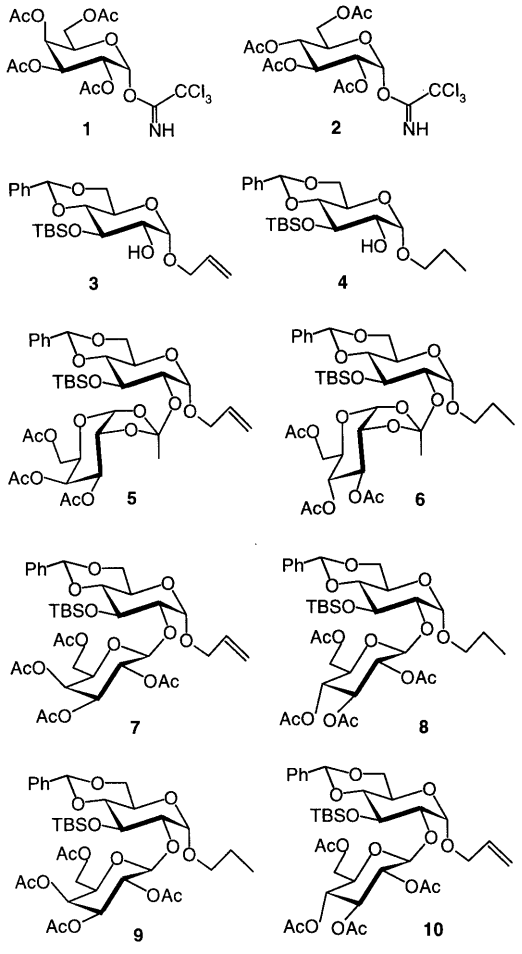
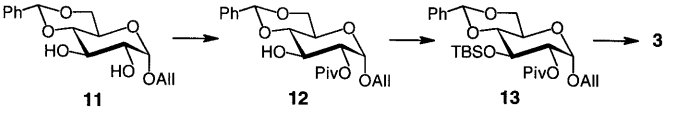


When we attempted to glycosylate sugar alcohol **3** with 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl trichloroacetimidate (**1**) under the action of usual promoters for trichloroacetimidate donors (0.1 equivalent), i.e., using TMSOTf [7], $BF_3{\cdot}OEt_2$ [7], TfOH [8], and AgOTf [9] under normal conditions ($CH_2Cl_2$, 4 Å MS, −78 °C to rt), orthoester **5** was isolated as the major product (83–100%). Orthoester **5** was then converted into glycosidic product **7** under the action of a promoter (TMSOTf or AgOTf, 0.25 equivalents). By using >0.25 equivalents of promoter (TMSOTf or AgOTf) in the absence of 4 Å MS in the glycosylation reaction, the normal glycosidic product **7** was directly produced in >80% yield. High-performance liquid chromatography (HPLC) monitoring of the course of the reaction demonstrated that glycosidic product **7** was generated in situ from orthoester **5** (Table 1). The kinetics of this rearrangement process have not been determined. This transformation was found to be sensitive to the reaction conditions and to be further complicated by several side reactions, such as acetyl group transfer, as well as benzylidene and TBS group cleavage.

The requisite allyl 4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-α-D-glucopyranoside (**3**) was prepared according to the process in Scheme 2. Thus **11** [12] was selectively pivaloylated at O-2, and the intermediate **12** was then protected with *tert*-butylchlorodimethylsilane/imidazole/DMAP to give **13**, which yielded the desired **3** upon removal of the pivaloyl group.



Scheme 2.

Table 1
Reaction of **1** and **3** to give products **5** and **7** [a]

| AgOTf (equivalent) | 5:7 (peak area) [b] | | | | | | |
|---|---|---|---|---|---|---|---|
| | 5 min | 15 min | 30 min | 60 min | 90 min | 140 min | 280 min |
| 0.1 | 13.0:1.0 | 4.3:1.0 | 2.5:1.0 | 1.6:1.0 | | | 1:20 |
| 0.25 | 3.0:1.0 | 2.7:1.0 | 2.1:1.0 | 1.0:1.7 | 1.0:9.9 | 1.0:20 | |
| 0.5 | 2.7:1.0 | 2.1:1.0 | 1.0:1.2 | 1.0:3.8 | 1.0:20 | | |

[a] Reaction conditions: **1** (1.2 equiv), **3** (1.0 equiv), AgOTf, $CH_2Cl_2$, 17 °C. HPLC conditions: Column, Nova-Pak® $C_{18}$ (3.9×1500 mm); eluent, 4:1 MeOH–water; flow rate, 1.2 mL/min; detector, UV 256 nm.

[b] Because both compounds **5** and **7** bear one benzene ring as the UV chromophore, the ratio of their peak area should be equal to the ratio of their amounts.

Table 2
Reaction of **5** and **6** to give products **7**–**10**[a]

| Entry | Equivalent of TMSOTf | **7**:**8**:**9**:**10** (peak area)[d,e] |
|---|---|---|
| 1 | 0.04 | 1.0:0.8:1.1:1.0 |
| 2 | 0.08 | 1.3:1.1:1.4:1.0 |
| 3[b] | 0.08 | 1.9:1.4:1.9:1.0 |
| 4 | 0.1 | 1.6:1.0:1.5:1.0 |
| 5[c] | 0.1 | 4.3:1.6:5.9:1.0 |
| 6 | 0.25 | 1.1:1.4:1.1:1.0 |

[a] Reaction conditions: **5** (1.0 equiv, 0.01 M), **6** (1.0 equiv), $Me_3SiOTf$, 4 Å MS, $CH_2Cl_2$, 11 °C, 2 h. HPLC conditions: Column, Nova-Pak® $C_{18}$ (3.9 × 1500 mm); eluent, 3:1 MeOH–water; flow rate, 1.0 mL/min; detector, UV 256 nm.

[b] The concentration of **5** or **6** was diluted to 0.0048 M.

[c] Carried out at −78 °C.

[d] Because products **7**–**10** bear one benzene ring as the UV chromophore, the ratio of their peak area should be equal to the ratio of their amounts.

[e] Compounds **7**–**10** were synthesized accordingly as standard samples.

Orthoester **6** was prepared from the 2-OH sugar **4** and 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (**2**) under similar conditions for the preparation of orthoester **5** (0.14 equiv. of AgOTf, $CH_2Cl_2$, 4Å MS, rt, 100%). Treatment of equimolar quantities of orthoester **5** and **6** with TMSOTf under the rearrangement conditions produced, not only the corresponding glycosidic products **7** and **8**, but also cross- over glycosidic products **9** and **10** in comparable amounts (Table 2). The disproportionation of glycosides **7**–**10** under similar reaction conditions was not detected. These results support the proposed mechanism as shown in Scheme 1. Galactopyranosides **7** and **9** were produced (in almost equal amounts) in higher amounts compared with that of the glucopyranosides **8** and **10** (in almost equal amounts), especially when the reaction was carried out at −78 °C (Table 2, entry 5). These results seem to reflect the difference between the coupling ability of galactopyranosyl and glucopyranosyl cation intermediates and are in accordance with the rationale that galactopyranosyl donors are more active than their glucopyranosyl counterparts [10].

## 1. Experimental

*General methods — see Ref. [11]*

*Allyl 4,6-O-benzylidene-2-O-pivaloyl-α-D-glucopyranoside* (**12**). To a stirred solution of **11** [12] (7.30 g, 24.0 mmol) in dry pyridine (90 mL) at −17 °C was added trimethylacetyl chloride (93.56 mL, 28.8 mmol) dropwise during 10 min. The mixture was stirred at −17 to −2 °C for 3 h, then quenched with water and diluted with EtOAc. The organic phase was washed with aq HCl (10%), satd aq NaCl, and water, respectively, and then dried over sodium sulfate and concentrated in vacuo. Column chromatography of the residue on silica gel (3:1 petroleum ether–EtOAc) gave **12** (7.57 g, 80%) as a syrup: $R_f$ 0.55 (3:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +112.4° (*c* 1.40, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.50–7.35 (m, 5 H, Ph), 5.86 (m, 1 H, $OCH_2CHCH_2$), 5.56 (s, 1 H, PhC*H*), 5.34–5.18 (m, 2 H, $OCH_2CHCH_2$); 5.09 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 4.75 (dd, $J_{2,3}$ 9.7, $J_{2,1}$ 3.8 Hz, H-2), 4.28 (dd, 1 H, $J_{6,6'}$10.0, $J_{6,5}$ 4.8 Hz, H-6), 4.24 (t, 1 H, $J_{3,2} = J_{3,4}$ 9.4 Hz, H-3), 4.15–4.22 (m, 1 H, $OCH_aH_bCHCH_2$), 3.99–3.92 (m, 1 H, $OCH_aH_bCHCH_2$), 3.89 (m, 1 H, H-5), 3.76 (t, 1 H, $J_{6',6} = J_{6',5}$ 10.2 Hz, H-6′), 3.57 (t, 1 H, $J_{4,5} = J_{4,3}$ 9.4 Hz, H-4), 2.05 (s, 1 H, OH), 1.24 (s, 9 H, *t*-Bu). EIMS (*m*/*z*, %): 392 [$M^+$, 43], 391 [$M^+ - 1$, 100], 335 [$M^+ - OAll$, 57]. Anal. Calcd for $C_{21}H_{28}O_7$: C, 64.27; H, 7.19. Found: C, 64.28; H, 7.29.

*Allyl 4,6-O-benzylidene-3-O-tert-butyldimethylsilyl-2-O-pivaloyl-α-D-glucopyranoside* (**13**). To a solution of **12** (17.19 g, 43.8 mmol), imidazole (5.79 g, 87.6 mmol) and DMAP (2.1 g, 17.5 mmol) in dry DMF (70 mL) was added *tert*-butylchlorodimethylsilane (9.9 g, 65.7 mmol). The mixture was stirred at 50 °C for 2 h, then quenched with water and diluted with EtOAc. The organic phase was washed with satd aq NaCl, dried over sodium sulfate, and then concentrated in vacuo. Column chromatography of the residue on silica gel (30:1 petroleum ether–EtOAc) gave **13** (20 g, 90%) as white solid: $R_f$ 0.74 (8:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +88.1° (*c* 1.27, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.50–7.30 (m, 5 H, Ph), 5.86 (m, 1 H, $OCH_2CHCH_2$), 5.50 (s, 1 H, PhC*H*), 5.32–5.18 (m, 2 H, $OCH_2CHCH_2$), 5.05 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 4.72 (dd, $J_{2,3}$

9.3, $J_{2,1}$ 3.9 Hz, H-2), 4.20 (m, 3 H, H-3, H-6, OC$H_a$H$_b$CHCH$_2$), 3.90 (m, 2 H, OCH$_a$$H_b$CHCH$_2$, H-5), 3.71 (t, 1 H, $J_{6',6} = J_{6',5}$ 10.3 Hz, H-6′), 3.50 (t, 1 H, $J_{4,5} = J_{4,3}$ 9.3 Hz, H-4), 1.22 (s, 9 H, *t*-BuCO), 0.79 (s, 9 H, *t*-BuSi), 0.00 (2s, 2 Me). EIMS (*m*/*z*, %): 505 [M$^+$ − 1, 1], 449 [M$^+$ − OAll, 33], 391 [M]$^+$ − TBDMS, 7]. Anal. Calcd for $C_{27}H_{42}O_7Si$: C, 64.00; H, 8.35. Found: C, 63.66; H, 8.60.

*Allyl 4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-α-*D*-glucopyranoside* (**3**). To a solution of **13** (24.8 g, 48.9 mmol) in dry $CH_2Cl_2$ (50 mL) was added DIBAL-H (99 mL, 97.7 mmol, 1.0 M in hexanes) at − 78 °C. The solution was stirred at − 78 to − 10 °C for 3 h, then quenched with MeOH (20 mL) and diluted with EtOAc. The organic phase was washed sequentially with aq HCl (5%), satd aq $NaHCO_3$, and brine, and then dried over $Na_2SO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (15:1 petroleum ether–EtOAc) to give **3** (19.6 g, 95%) as a syrup: $R_f$ 0.43 (8:1 petroleum ether–EtOAc); $[\alpha]_D^{22}$ + 74.8° (*c* 0.82, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.51–7.33 (m, 5 H), 5.94 (m, 1 H), 5.50 (s, 1 H, PhC*H*), 5.36–5.22 (m, 2 H), 4.95 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 4.26 (dd, $J_{6,6'}$ 9.9, $J_{6,5}$ 4.5 Hz, H-6), 4.22 (m, 1 H), 4.10–4.03 (m, 1 H), 3.90 (t, 1 H, $J_{3,2}$ 8.6 Hz, H-3), 3.82 (m, 1 H, H-5), 3.72 (t, 1 H, $J_{6',6} = J_{6',5}$ 10.1 Hz, H-6′), 3.58 (dd, 1 H, $J_{2,3}$ 8.8, $J_{2,1}$ 3.9 Hz, H-2), 3.43 (t, 1 H, $J_{4,3}$ 9.1 Hz, H-4), 0.87 (s, 9 H), 0.10 and 0.03 (2s, 6 H); Anal. Calcd for $C_{22}H_{34}O_6Si$: C, 62.50; H, 8.11. Found: C, 62.53; H, 8.34.

*Propyl 4,6-*O*-benzylidene-3-*O*-tert-butyldimethylsilyl-α-*D*-glucopyranoside* (**4**). A procedure similar to the preparation of allyl glycoside **3** was employed. Data for **4**: $R_f$ 0.43 (8:1 petroleum ether–EtOAc); $[\alpha]_D^{22}$ + 70.6° (*c* 1.05, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.48–7.35 (m, 5 H, Ph), 5.51 (s, 1 H, Ph*H*), 4.88 (d, 1 H, $J_{1,2}$ 4.12 Hz, H-1), 4.26 (dd, 1 H, *J* 4.40, *J* 9.61), 3.86 (t, 1 H, *J* 8.93), 3.82–3.64 (m, 3 H), 3.59–3.38 (m, 3 H), 2.06 (s, 1 H, OH), 1.65 (m, 2 H, OCH$_2$C$H_2$CH$_3$), 0.96 (t, 3 H, OCH$_2$CH$_2$C$H_3$); 0.89 (s, 9 H, *t*-BuSi), 0.11, 0.04 (2s, each 3 H, Me$_2$Si). EIMS (*m*/*z*, %): 425 [M$^+$, 1.2]. Anal. Calcd for $C_{22}H_{36}O_6Si$: C, 62.23; H, 8.55. Found: C, 62.11; H, 8.51.

*3,4,6-Tri-*O*-acetyl-1,2-(allyl 4,6-*O*-benzylidene-3-*O*-tert-butyldimethylsilyl-2-yl-α-*D*-glucopyranosid-2-yloxy-1-ethylidene)-α-*D*-galactopyranose* (**5**). To a stirred suspension of sugar alcohol **3** (22 mg, 0.052 mmol), imidate **1** (28 mg, 0.057 mmol) and 4 Å MS ( ~ 40 mg) in dry $CH_2Cl_2$ (2 mL) at − 78 °C, was added $Me_3SiOTf$ (0.1 equiv) for 0.5 h. The mixture was quenched with $Et_3N$ and then filtered and concentrated. The residue was applied to a silica gel column (10:1–3:1 petroleum ether–EtOAc) to give **5** (35 mg, 89%) as a white solid: $R_f$ 0.53 (2:1 petroleum ether–EtOAc); $[\alpha]_D^{22}$ + 68.4° (*c* 1.05, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.45–7.33 (m, 5 H), 5.94 (m, 1 H), 5.77 (d, 1 H, $J_{1,2}$ 4.7 Hz), 5.49 (s, 1 H, PhC*H)*, 5.42 (t, 1 H, *J* 2.6), 5.36–5.19 (m, 2 H), 5.02 (m, 2 H), 4.34–3.98 (m, 8 H), 3.82 (m, 1 H), 3.69 (t, 1 H, *J* 10.2 Hz), 3.58 (dd, 1 H, *J* 3.6, *J* 8.8 Hz), 3.43 (t, 1 H, *J* 9.5 Hz), 2.10, 2.07, 2.05, 1.70 (each s, each 3 H), 0.82 (s, 9 H), 0.06, 0.00 (each s, each 3 H). EIMS (*m*/*z*, %): 423 [M$^+$ − Gal, 3], 331 (Gal, 93). Anal. Calcd for $C_{36}H_{52}O_{15}Si$: C, 57.43; H, 6.96. Found: C, 57.43; H, 7.00.

*3,4,6-Tri-*O*-acetyl-1,2-(propyl 4,6-*O*-benzylidene-3-*O*-tert-butyldimethylsilyl-α-*D*-glucopyranosid-2-yloxy-1-ethylidene)-α-*D*-glucopyranose* (**6**). A procedure similar to the preparation of orthoester **5** was employed. **6**: $R_f$ 0.43 (2:1 petroleum ether–EtOAc); $[\alpha]_D^{22}$ + 35.9° (*c* 1.00, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.52–7.32 (m, 5 H), 5.53 (d, 1 H, $J_{1',2}$ 5.1 Hz, H-1′), 5.49 (s, 1 H, PhC*H*), 5.22–5.21 (m, 1 H), 4.98 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.93–4.89 (m, 1 H), 4.49–4.46 (m, 1 H), 4.37–4.11 (m, 3 H), 3.97–3.89 (m, 2 H), 3.81–3.62 (m, 3 H), 3.60–3.50 (m, 1 H), 3.40 (t, 1 H, *J* 8.92), 3.32–3.23 (m, 1 H), 2.12 (s, 9 H), 1.78 (s, 3 H), 1.62 (m, 2 H), 0.98 (t, 3 H), 0.82 (s, 9 H), 0.06, 0.00 (each s, each 3 H). ESIMS (*m*/*z*): 778 [M$^+$ + Na]. Anal. Calcd for $C_{36}H_{54}O_{15}Si$: C, 57.28; H, 7.21. Found: C, 57.24; H, 7.25.

*Allyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl-(1→2)-4,6-*O*-benzylidene-3-*O*-tert-butyldimethylsilyl-α-*D*-glucopyranoside* (**7**). To a stirred suspension of sugar alcohol **3** (39 mg, 0.092 mmol), imidate **1** (55 mg, 0.11 mmol), and 4 Å MS ( ~ 50 mg) in dry $CH_2Cl_2$ (3 mL) at rt, was added a toluene solution of AgOTf (0.25 equiv). After being stirred overnight, the

mixture was quenched with $Et_3N$ and then filtered and concentrated. The residue was applied to a silica gel column (petroleum ether–EtOAc) to give **7** (66 mg, 95%) as a white solid: $R_f$ 0.51 (2:1 petroleum ether–EtOAc); $[\alpha]_D^{22}$ +28.7° (*c* 1.00, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.45–7.33 (m, 5 H), 5.95 (m, 1 H), 5.45 (s, 1 H, PhC*H*), 5.42–5.35 (m, 2 H), 5.24 (t, 1 H, *J* 10.5 Hz), 5.22 (m, 1 H), 4.97 (dd, 1 H, *J* 10.4, 3.4 Hz), 4.93 (d, 1 H, *J* 3.6 Hz), 4.84 (d, 1 H, $J_{1',2'}$ 7.9 Hz, H-1′), 4.24 (dd, 1 H, *J* 10.2, 4.9 Hz), 4.20–4.04 (m, 5 H), 3.89 (m, 2 H), 3.70 (dd, 1 H, *J* 9.1, 3.6 Hz), 3.68 (t, 1 H, *J* 10.1 Hz), 3.38 (t, 1 H, *J* 9.3 Hz), 2.17, 2. 05, 2.03, 1.97 (each s, each 3 H), 0.71 (s, 9 H), 0.04, −0.04 (each s, each 3 H). ESIMS (*m*/*z*): $[M^+ + Na]$. Anal. Calcd for $C_{36}H_{52}O_{15}Si$: C, 57.43; H, 6.96. Found: C, 57.02; H, 6.99.

*Propyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl-(1→2)-4,6-*O*-benzylidene-3-*O*-tert-butyldimethylsilyl-α-*D*-glucopyranoside* (**8**). A procedure similar to the preparation of disaccharide **7** was employed to prepare **8** from imidate **2** and sugar alcohol **4**. Data for **8**: $[\alpha]_D^{22}$ +18.5° (*c* 1.02, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.52–7.32 (m, 5 H), 5.44 (s, 1 H, PhC*H*), 5.19–5.02 (m, 3 H), 4.86 (d, 1 H, *J* 3.65 Hz, H-1), 4.84 (d, 1 H, *J* 7.53 Hz, H-1′), 4.28–4.04 (m, 4 H), 3.88 (m, 1 H), 3.72–3.56 (m, 4 H), 3.48–3.34 (m, 2 H), 2.16–1.96 (each s, each 3 H), 1.62 (m, 2 H), 0.98 (t, 3 H), 0.82 (s, 9 H), 0.06, −0.04 (each s, each 3 H). ESIMS (*m*/*z*): 777 $[M^+ + Na\text{-}1]$. Anal. Calcd for $C_{36}H_{54}O_{15}Si$: C, 57.28; H, 7.21. Found: C, 57.42; H, 7.34.

*Propyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl-(1→2)-4,6-*O*-benzylidene-3-*O*-tert-butyldimethylsilyl-α-*D*-glucopyranoside* (**9**). A procedure similar to the preparation of disaccharide **7** was employed to prepare **8** from imidate **1** and sugar alcohol **4**. Data for **9**: $[\alpha]_D^{22}$ +23.8° (*c* 1.05, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.52–7.32 (m, 5 H), 5.44 (s, 1 H, PhC*H*), 5.38 (d, 1 H, *J* 3.2 Hz, H-4′), 5.22 (dd, 1 H, *J* 10.4, *J* 8.0 Hz, H-2′), 4.98 (dd, 1 H, *J* 10.4, *J* 3.2 Hz, H-3′), 4.88 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.83 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 4.30–4.16 (m, 2 H), 4.14–4.06 (m, 2 H), 3.90–3.82 (m, 2 H), 3.70–3.60 (m, 3 H), 3.50–3.32 (m, 2 H), 2.18, 2.00, 2.04, 1.96 (each s, each 3 H), 1.62 (m, 2 H), 0.98 (t, 3 H), 0.82 (s, 9 H), 0.06, 0.00 (each s, each 3 H). ESIMS (*m*/*z*): 778 $[M^+ + Na]$. Anal. Calcd for $C_{36}H_{54}O_{15}Si$: C, 57.28; H, 7.21. Found: C, 57.38; H, 7.25.

*Allyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl-(1→2)-4,6-*O*-benzylidene-3-*O*-tert-butyldimethylsilyl-α-*D*-glucopyranoside* (**10**). A procedure similar to the preparation of disaccharide **7** was employed to prepare **10** from imidate **2** and sugar alcohol **3**. Data for **10**: $[\alpha]_D^{22}$ +18.9° (*c* 1.03, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.52–7.32 (m, 5 H), 6.00–5.88 (m, 1 H), 5.44 (s, 1 H, PhC*H*), 5.40–5.32 (m, 1 H), 5.24–5.19 (m, 1 H), 5.17–5.02 (m, 3 H), 4.92 (d, 1 H, *J* 3.7 Hz), 4.85 (d, 1 H, *J* 7.5 Hz), 4.28–4.03 (m, 6 H), 3.92–3.80 (m, 1 H), 3.70–3.62 (m, 3 H), 3.38 (t, 1 H, *J* 9.2 Hz), 2.16–1.96 (each s, each 3 H), 0.82 (s, 9 H), 0.06, −0.04 (each s, each 3 H). ESIMS (*m*/*z*): 776 $[M^+ + Na]$. Anal. Calcd for $C_{36}H_{54}O_{15}Si$: C, 57.28; H, 7.21. Found: C, 57.42; H, 7.34.

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