Synthesis and Glycosylation of 2'-(Benzyloxycarbonyl)benzyl Glycosides as Glycosyl Donors

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Recent advances in glycobiology have directed an increased attention to efficient and stereoselective glycosylation of oligosaccharides.[1] Devising new glycosyl donors and developing new activation systems for existing donors have led to major advances in this field. Nevertheless, there still remains a need for more efficient and generally applicable new glycosyl donors although several glycosyl donors are presently available.[2] In fact, there have been recent reports on new glycosyl donors and new activation systems.[3] We have also recently reported a novel type of glycosyl donors, the 2'-carboxybenzyl (CB) glycoside **B**, as shown in Figure 1 for stereoselective β-mannopyranosylation[4] and 2-deoxyglycosylation[5] and applied this methodology to the synthesis of a tetrasaccharide.[6] The CB glycoside **B** was prepared from the 2'-(benzyloxycarbonyl)benzyl (BCB) glycoside **A** by the selective removal of its benzyl ester functionality.[4] Treatment of the CB glycoside **B** with triflic anhydride followed by spontaneous lactonization of the resulting glycosyl triflate **C** afforded the oxocarbenium ion **D** by extrusion of stable phthalide. Reaction of the oxocarbenium ion **D** with the glycosyl acceptor (Sugar-OH) gave the desired glycoside **E** as shown in Figure 1. The direct generation of the oxocarbenium ion **D** from the BCB glycoside **A** would be more convenient than that from the CB glycoside **B** through the triflate **C**. Thus, we envisaged that Lewis acid-mediated lactonization of the BCB glycoside **A** would liberate stable phthalide to generate the oxocarbenium ion **D** as shown in Figure 1. Herein we report the glycosylation of the BCB glycoside **A** with glycosyl acceptors in the presence of TMSOTf as a promoter.

Coupling of the tetrabenzoylglucosyl bromide **1**[7] and benzyl 2-(hydroxymethyl)benzoate (**2**)[4] in the presence of mercury salts at 0 °C in acetonitrile gave the BCB tetrabenzoylglucoside **3** in 84% yield. The BCB tetrabenzylglucoside **5**, on the other hand, was prepared by the benzylation of the known BCB glucopyranoside **4**[4] as shown in Scheme 1. The BCB 2,3-di-*O*-benzoylcyclohexylideneglucoside **7** was also prepared from the compound **4** by the two-step sequence: (i) selective cyclohexylidenation of the compound **4** with 1,1-dimethoxycyclohexane in the presence of *p*-TsOH to afford the diol **6** in 82% yield and (ii) benzoylation of the resulting diol **6** with benzoyl chloride to give the compound **7** in 90% yield as shown in Scheme 1.

Glycosylation of the BCB tetrabenzoylglucoside **3** with the glycosyl acceptor **8** was carried out in acetonitrile by addition of TMSOTf at 0 °C and allowing the reaction mixture to warm over 3 h to room temperature to afford only the β-disaccharide **9** in 71% yield as shown in Scheme 2. The fact that the β-disaccharide **9** was obtained exclusively without formation the α-disaccharide indicates that the participating group at C-2 is working well in the glycosylation with the BCB glycoside. Trimethylsilyl triflate was found to be a good promoter but other Lewis acids, such as $BF_3{\cdot}OEt_2$ and $SnCl_4$, did not activate the glycosyl donor **3**. The same glycosylation reaction in methylene chloride instead of acetonitrile resulted in a little lower yield of the disaccharide **9** while Et_2O and THF were found to be not proper solvents for the present glycosylation. The 'armed' BCB tetrabenzylglucoside **5** was a more reactive glycosyl donor than the 'disarmed' BCB tetrabenzoylglucoside **3** as expected[8] and the glycosylation of **5** proceeded at lower temperature than that of **3**. Thus, glycosylation of the

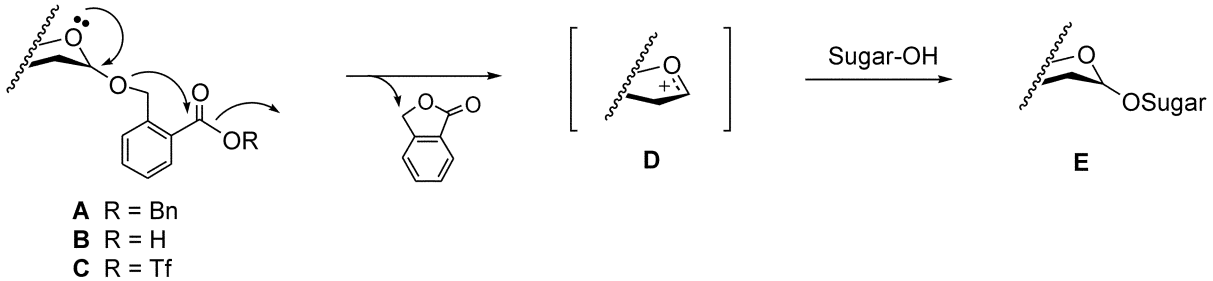

Figure 1

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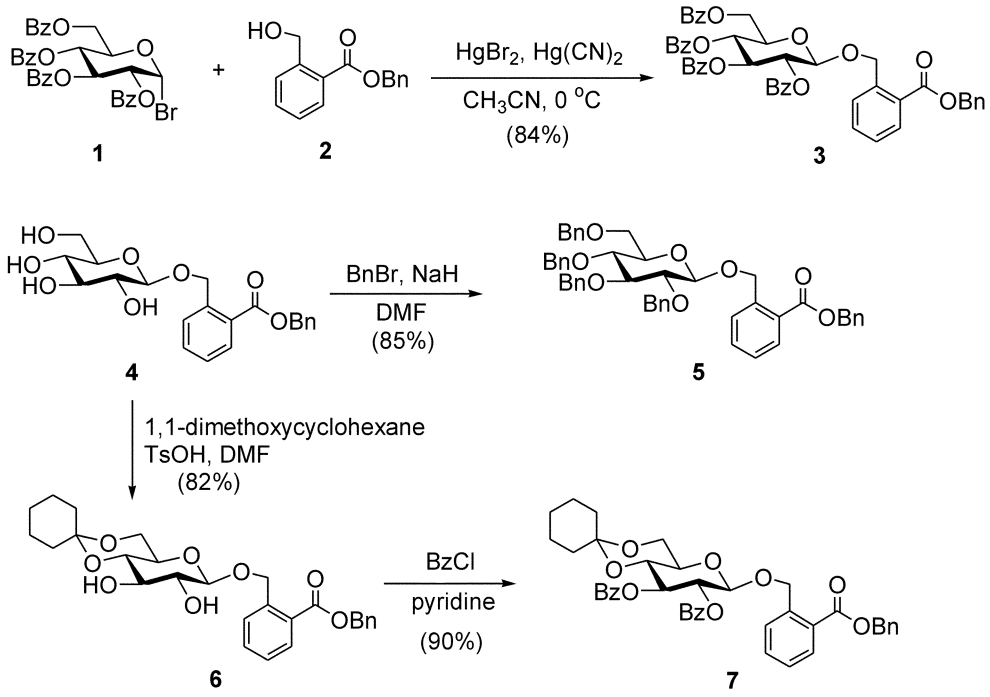


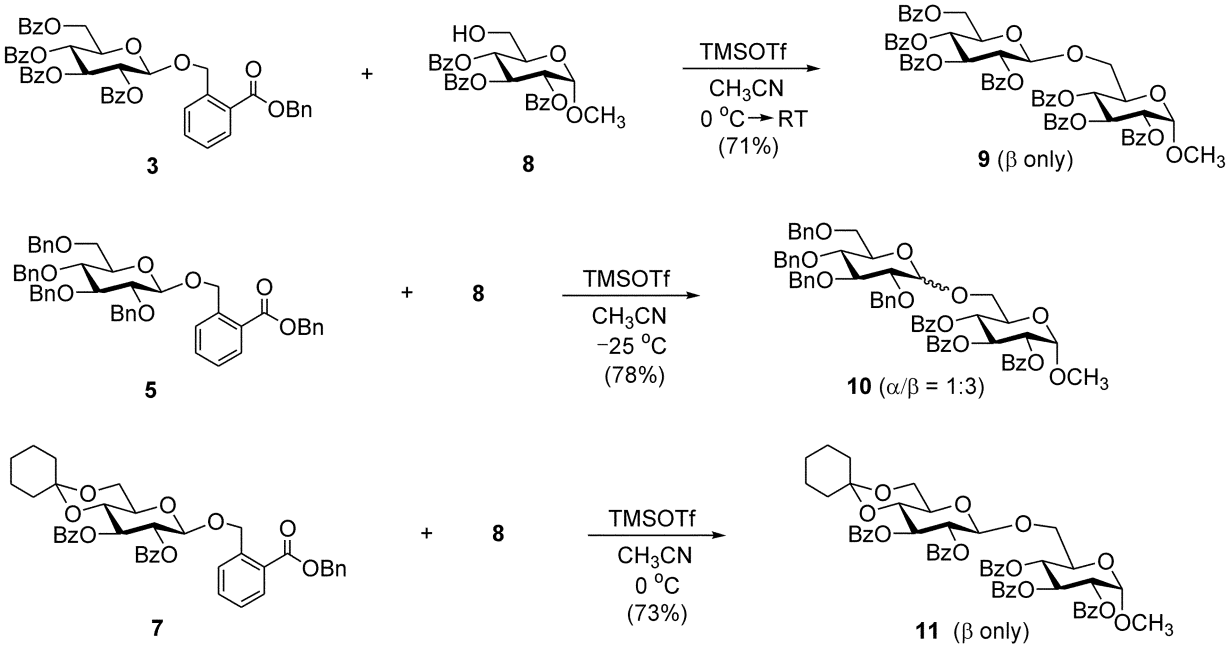
Scheme 1

glycosyl donor **5** with the glycosyl acceptor **8** at -25 °C in the presence of TMSOTf in aceronitrile provided a separable mixture of disaccharides **10α** and **10β** (1 : 3) in 78% yield. On the other hand, the BCB 4,6-cyclohexylideneglucoside 7 showed intermediate reactivity in the glycosylation. Glycosylation of the glycosyl donor 7 with the acceptor **8** in the presence of TMSOTf in acetonitrile proceeded at 0 °C to afford only β-disaccharide **11** in 73% yield.

In summary, BCB glycosides, which had been used as the precursor to a novel type of glycosyl donors, CB glycosides, were also found to be good glycosyl donors. Glycosylation of BCB glycosides with glycosyl acceptors employing TMSOTf as a promoter readily afforded disaccharides.

Experimental Section

Synthesis of 2-(Benzyloxycarbonyl)benzyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (3). To a stirred solution of 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl bromide (**1**)[7] (1.86 g, 2.8 mmol) and benzyl 2-(hydroxymethyl)-



Scheme 2

benzoate (**2**)[4] (0.82 g, 3.4 mmol, 1.2 equiv) in CH_3CN (5 mL) in the presence of 4 Å molecular sieves were added mercury (II) bromide (1.22 g, 3.4 mmol, 1.2 equiv) and mercury (II) cyanide (0.85 g, 3.4 mmol, 1.2 equiv) at 0 °C. After stirring at 0 °C for further 10 min, the reaction mixture was filtered and the filtrate was concentrated. The resulting oil was dissolved in EtOAc (50 mL) and the solution was washed with saturated aqueous $NaHCO_3$ (2 × 50 mL) and brine (50 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo and the residue was purified by silica gel flash column chromatography (*n*-hexane/EtOAc, 2 : 1, v/v) to afford the compound **3** (1.94 g, 84%) as white solids: mp 47-50 °C; R_f = 0.45 (*n*-hexane/EtOAc, 2 : 1, v/v); $[\alpha]_D^{20}$ = +9.6 (c = 2.7, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.11-4.18 (m, 1H), 4.49 (dd, *J* = 5.2, 12.2 Hz, 1H), 4.65 (dd, *J* = 3.1, 12.1 Hz, 1H), 4.97 (d, *J* = 7.8 Hz, 1H), 5.19 (d, *J* = 14.7 Hz, 1H), 5.21 (s, 2H), 5.34 (d, *J* = 14.7 Hz, 1H), 5.65-5.77 (m, 2H), 5.92 (t, *J* = 9.6 Hz, 1H), 7.21-8.05 (m, 29H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 63.1, 66.7, 69.5, 69.9, 72.1, 72.4, 73.1, 100.9, 127.2, 127.5, 127.7, 128.3, 128.4, 128.5, 128.7, 128.9, 129.4, 129.8, 129.9, 130.7, 132.7, 133.2, 139.8, 165.3(2), 165.9, 166.5; IR (NaCl) 1256, 1453, 1604, 1736 cm^{-1}. Anal. Calcd for $C_{49}H_{40}O_{12}$: C, 71.70; H, 4.91. Found: C, 71.67; H, 4.83.

2-(Benzyloxycarbonyl)benzyl 2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranoside (5). To a solution of 2-(benzyloxycarbonyl)benzyl-β-D-glucopyranoside (**4**)[4] (3.28 g, 8.1 mmol, 1.0 equiv) and benzyl bromide (3.87 mL, 32.5 mmol, 4.0 equiv) in DMF (30 mL) was added sodium hydride (1.3 g, 32.5 mmol, 4.0 equiv) at 0 °C and then the ice bath was removed. After stirring at room temperature for 1 h, the reaction mixture was quenched with water (50 mL) and extracted with EtOAc (2 × 100 mL). The combined organic layer was washed with saturated aqueous NH_4Cl (50 mL) and brine (50 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (*n*-hexane/EtOAc, 4 : 1, v/v) to afford the compound **5** (7.48 g, 85%): R_f = 0.50 (*n*-hexane/EtOAc, 4 : 1, v/v); $[\alpha]_D^{20}$ = -1.72 (c = 3.3, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.43-3.46 (m, 1H), 3.55-3.74 (m, 5H), 4.50-4.65 (m, 4H), 4.75-4.85 (m, 3H), 4.93-5.02 (m, 2H), 5.15 (d, *J* = 14.8 Hz, 1H), 5.30 (s, 2H), 5.40 (d, *J* = 14.8 Hz, 1H), 7.15-7.48 (m, 27H), 7.79 (d, *J* = 7.7 Hz, 1H), 8.03 (dd, *J* = 13, 7.8 Hz, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 66.8, 68.8, 69.4, 73.6, 75.1(2), 75.8, 78.0, 82.5, 84.9, 103.2, 127.1, 127.6, 127.7(2), 127.8, 127.9, 128.0(2), 128.1, 128.2, 128.4(2), 128.5(2), 128.7, 130.8, 132.7, 136.0, 138.2, 138.5, 138.8, 140.8, 166.7; IR ($CHCl_3$ film) 1077, 1266, 1729 cm^{-1}. Anal. Calcd for $C_{49}H_{48}O_8$: C, 76.94; H, 6.33. Found: C, 76.98; H, 6.35.

2-(Benzyloxycarbonyl)benzyl 4,6-*O*-Cyclohexylidene-β-D-glucopyranoside (6). A solution of 2-(benzyloxycarbonyl)benzyl-β-D-glucopyranoside (**4**)[4] (934 mg, 2.31 mmol, 1.0 equiv), 1,1-dimethoxycyclohexane (666 mg, 4.62 mmol, 2.0 equiv), and *p*-TsOH (8 mg, 0.46 mmol, 0.2 equiv) in DMF (10 mL) was stirred at 60 °C for 4 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (30 mL), and extracted with EtOAc (3 × 30 mL). The combined organic layer was washed with saturated aqueous NH_4Cl (2 × 30 mL) and brine (30 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography (*n*-hexane/EtOAc, 1 : 2, v/v) to afford the compound **6** (917 mg, 82%) as white solids: mp 58-60 °C; R_f = 0.6 (*n*-hexane/EtOAc, 1 : 2, v/v); $[\alpha]_D^{20}$ = -34.9 (c = 1.3, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.43-2.02 (m, 10H), 2.87 (s, 1H), 3.06 (s, 1H), 3.22-3.32 (m, 1H), 3.48-3.81 (m, 5H), 3.91 (dd, *J* = 5.5, 10.7 Hz, 1H), 4.78 (d, *J* = 7.6 Hz, 1H), 5.09 (d, *J* = 13.0 Hz, 1H), 5.19 (d, *J* = 13.0 Hz, 1H), 5.34 (s, 1H), 7.32-7.64 (m, 8H), 7.99 (dd, *J* = 1.1, 7.7 Hz, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 22.7, 22.9, 25.7, 27.9, 38.0, 61.5, 67.1, 67.7, 70.2, 72.4, 73.9, 74.8, 100.0, 103.1, 127.9, 128.3, 128.4, 128.7, 128.8, 129.0, 130.9, 132.7, 135.9, 139.4, 167; IR ($CHCl_3$ film) 1084, 1269, 1729 cm^{-1}. Anal. Calcd for $C_{27}H_{32}O_8$: C, 66.93; H, 6.66. Found: C, 66.93; H, 6.68.

2-(Benzyloxycarbonyl)benzyl 2,3-Di-*O*-benzoyl-4,6-*O*-cyclohexylidene-β-D-glucopyranoside (7). A solution of 2-(benzyloxycarbonyl)benzyl 4,6-*O*-cyclohexylidene-β-D-glucopyranoside (**6**) (400 mg, 0.83 mmol, 1.0 equiv) and benzoyl chloride (350 mg, 2.49 mmol, 3.0 equiv) in pyridine (5 mL) was stirred at room temperature for 2 h. The reaction mixture was quenched with saturated aqueous NH_4Cl (10 mL), and extracted with EtOAc (3 × 15 mL). The combined organic layer was washed with saturated aqueous NH_4Cl (2 × 15 mL) and brine (15 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (*n*-hexane/EtOAc, 2 : 1, v/v) to afford the compound 7 (516 mg, 90%) as white solids: mp 66-68 °C; R_f = 0.6 (*n*-hexane/EtOAc, 2 : 1, v/v); $[\alpha]_D^{20}$ = +15.6 (c = 1.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.27-2.09 (m, 10H), 3.48-3.58 (m, 1H), 3.85-4.06 (m, 3H), 4.87 (d, *J* = 7.3 Hz, 1H), 5.16 (d, *J* = 15.0 Hz, 1H), 5.25 (s, 2H), 5.33 (d, *J* = 15.0 Hz, 1H), 5.50-5.68 (m, 2H), 7.15-7.99 (m, 19H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 22.5, 22.7, 25.5, 27.6, 37.8, 61.5, 66.7, 67.7, 69.5, 71.1, 72.7(2), 99.9, 101.4, 127.0, 127.2, 127.3, 127.8, 128.2, 128.4, 128.7, 129.5, 129.6, 129.7, 129.9(2), 130.6, 132.7, 133.1, 133.2, 135.9, 140.1, 165.3, 165.7, 166.4; IR ($CHCl_3$ film) 1111, 1275, 1407, 1637, 1743 cm^{-1}. Anal. Calcd for $C_{41}H_{40}O_{10}$: C, 71.08; H, 5.82. Found: C, 71.06; H, 5.79.

Methyl (2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (9).[9] A solution of 2-(benzyloxycarbonyl)benzyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (**3**) (31 mg, 0.038 mmol, 1.0 equiv), methyl 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (**8**) (59 mg, 0.11 mmol, 3.0 equiv) and TMSOTf (42 mg, 0.19 mmol, 5.0 equiv.) in CH_3CN (3 mL) was stirred at 0 °C for 10 min, and allowed to warm over 3 h to room temperature. The reaction mixture was quenched by addition of saturated aqueous $NaHCO_3$ solution (2 mL) and then extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layer was washed with brine (15 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (toluene/EtOAc, 10 : 1, v/v) to

afford the β-disaccharide **9** (29 mg, 71%) as white solids: mp 91-93 °C; R_f = 0.30 (toluene/EtOAc, 10 : 1, v/v); $[\alpha]_D^{20}$ = +39.0 (c = 4.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 3.11 (s, 3 H), 3.78 (dd, *J* = 7.5, 11.5 Hz, 1H), 4.08-4.16 (m, 2H), 4.20-4.24 (m, 1H), 4.45 (dd, *J* = 5.5, 12.0 Hz, 1H), 4.60 (dd, *J* = 3.0, 12.0 Hz, 1H), 4.94 (d, *J* = 3.5 Hz, 1H), 4.97 (d, *J* = 8.0 Hz, 1H), 5.09 (dd, *J* = 3.5, 10.0 Hz, 1H), 5.31 (t, *J* = 10.0 Hz, 1H), 5.56 (dd, *J* = 8.5, 18.5 Hz, 1H), 5.65 (t, *J* = 10.0 Hz, 1H), 5.59 (t, *J* = 9.5 Hz, 1H), 6.07 (t, *J* = 10.0 Hz, 1H), 7.23-8.00 (m, 35H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.2, 63.2, 68.8, 69.1, 69.9(2), 70.5, 72.1, 72.2, 72.5, 73.0, 96.6, 101.9, 128.5, 129.0, 129.3, 129.8, 130.0, 133.3, 133.6, 165.3(2), 165.6, 165.8(2), 165.9, 166.3; IR ($CHCl_3$ film) 1216, 1455, 1606, 1731 cm^{-1}.

Methyl (2,3,4,6-Tetra-*O*-benzyl-α,β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (10). A solution of 2-(benzyloxycarbonyl)benzyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (**5**) (92 mg, 0.12 mmol, 1.0 equiv), methyl 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (**8**) (182 mg, 0.36 mmol, 3.0 equiv), and TMSOTf (65 μL, 0.36 mmol, 3.0 equiv.) in CH_3CN (5 mL) was stirred at -25 °C for 3 h and the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (2 mL) and then extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was washed with brine (20 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (toluene/EtOAc, 10 : 1, v/v) to afford the disaccharide **10** (97 mg, 78%, α : β = 1 : 3). **10α**: colorless oil, R_f = 0.60 (*n*-hexane/EtOAc, 2 : 1, v/v); $[\alpha]_D^{20}$ = +54.0 (c = 1.1, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 3.43 (s, 3H), 3.48-3.66 (m, 5H), 3.81 (m, 2H), 3.96 (dd, *J* = 9.3, 9.3 Hz, 1H), 4.24-4.28 (m, 1H), 4.37 (d, *J* = 12.3 Hz, 1H), 4.44 (d, *J* = 11.0 Hz, 1H), 4.55 (d, *J* = 12.3 Hz, 1H), 4.62 (d, *J* = 12.5 Hz, 1H), 4.73 (s, 2H), 4.79 (s, 1H), 4.81 (d, *J* = 12.5 Hz, 1H), 4.91 (d, *J* = 11.0 Hz, 1H), 5.19-5.24 (m, 2H), 5.52 (dd, *J* = 9.7, 9.7 Hz, 1H), 6.13 (dd, *J* = 9.7, 9.7 Hz, 1H), 7.11-7.57 (m, 29H), 7.80-8.09 (m, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 55.7, 66.8, 68.4, 68.7, 69.8, 70.4, 70.8, 72.4, 73.3, 73.5(2), 74.9, 75.7, 80.1, 82.0, 96.9, 97.4, 127.6, 127.8(2), 128.0, 128.1, 128.4(2), 128.5(2), 128.7, 129.3, 129.5, 129.9, 130.0, 130.1, 133.2, 133.5(2), 138.0, 138.5, 138.7, 139.0, 165.4, 166.0(2); IR (NaCl) 1101, 1278, 1736 cm^{-1}; Anal. Calcd for $C_{62}H_{60}O_{14}$: C, 72.36; H, 5.88. Found: C, 72.31; H, 5.87. **10β**: colorless oil, R_f = 0.65 (*n*-hexane/EtOAc, 2 : 1, v/v); $[\alpha]_D^{20}$ = +3.48 (c = 1.4, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 3.37 (s, 3H), 3.43-3.71 (m, 6H), 3.80 (dd, *J* = 7.5, 10.8 Hz, 1H), 4.10-4.14 (m, 1H), 4.35-4.55 (m, 5H), 4.66-4.82 (m, 3H), 4.91 (d, *J* = 10.9 Hz, 1H), 5.06 (d, *J* = 10.9 Hz, 1H), 5.20-5.32 (m, 2H), 5.47 (dd, *J* = 9.7, 9.7 Hz, 1H), 6.17 (dd, *J* = 9.7, 9.7 Hz, 1H), 7.13-7.53 (m, 29H), 7.83-7.98 (m, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 55.6, 68.8, 69.0, 69.1, 70.0, 70.6, 72.3, 73.6, 74.9, 75.0, 75.1, 75.8, 77.8, 82.5, 84.7, 96.9, 104.1, 127.7, 127.8, 127.9, 128.0, 128.1, 128.3, 128.4, 128.5(2), 129.1, 129.2, 129.4, 129.8, 130.0, 130.1, 133.2, 133.5(2), 138.3, 138.6, 138.8, 165.6, 165.9, 166.0; IR ($CHCl_3$ film) 2931, 1729, 1281, 1103 cm^{-1}. Anal. Calcd for $C_{62}H_{60}O_{14}$: C, 72.36; H, 5.88. Found: C, 72.34; H, 5.88.

Methyl (2,3-Di-*O*-benzoyl-4,6-*O*-cyclohexylidene-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (11). A solution of 2-(benzyloxycarbonyl)-benzyl 2,3-di-*O*-benzoyl-4,6-*O*-cyclohexylidene-β-D-glucopyranoside (**7**) (50 mg, 0.072 mmol, 1.0 equiv), methyl 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (**8**) (110 mg, 0.22 mmol, 3.0 equiv), and TMSOTf (80 mg, 0.36 mmol, 5.0 equiv.) in CH_2Cl_2 (5 mL) was stirred at 0 °C for 3 h and the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (2 mL) and then extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layer was washed with brine (15 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (*n*-hexane/EtOAc, 2 : 1, v/v) to afford the disaccharide **11** (51 mg, 73%) as white solids: mp 79-82 °C; R_f = 0.68 (*n*-hexane/EtOAc, 1 : 2, v/v); $[\alpha]_D^{20}$ = +33.5 (c = 1.0, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.23-1.69 (m, 10H), 3.39 (s, 3H), 3.74 (dd, *J* = 6.0, 11.3 Hz, 1H), 3.94-4.04 (m, 2H), 4.24-4.30 (m, 1H), 4.39-4.51 (m, 1H), 4.53 (dd, *J* = 5.4, 7.9 Hz, 1H), 5.19-5.32 (m, 3H), 5.54-5.61 (m, 2H), 5.81 (dd, *J* = 1.1, 5.3 Hz, 1H), 6.12-6.20 (m, 1H), 7.23-8.01 (m, 25H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 23.6, 24.0, 25.2, 34.6, 36.5, 55.7, 66.8, 66.9, 69.2, 69.5, 70.7, 72.3, 73.7, 74.8, 81.0, 82.7, 97.0, 106.7, 110.0, 128.4, 128.5, 128.6, 129.1, 129.2, 129.4, 129.8, 130.0(2), 133.2, 133.5, 133.6, 165.0, 165.2, 165.3, 165.9(2); IR ($CHCl_3$ film) 1104, 1275, 1460, 1736 cm^{-1}. Anal. Calcd for $C_{54}H_{52}O_{16}$: C, 67.77; H, 5.48. Found: C, 67.76; H, 5.44.

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