Supporting Information

Stereoselective Palladium-Catalyzed *O*-Glycosylation Using Glycals

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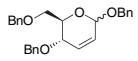
Representative Experimental Procedure (Table 2, Entry 10)

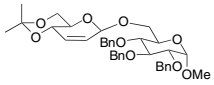
To a solution of acceptor **10** (390 mg, 1.5 mmol) in THF (1.0 mL) was added dropwise a solution of Et_2Zn (1.0 M in Hexanes, 0.8 mL, 0.8 mmol) at 25 °C. After stirring for 4 h, donor **6** (545 mg, 1.0 mmol) in THF (1.0 mL) was added to the mixture via syringe followed by $Pd(OAc)_2$ (22.4 mg, 0.1 mmol) and DTBBP ligand (45 mg, 0.15 mmol). The reaction mixture was stirred at 25 °C for 48 h and then directly loaded onto a silica gel column. Purification by flash chromatography (Hexanes-EtOAc 8:1) gave **22β** (507 mg, 0.68 mmol, 68%) as a white foam.



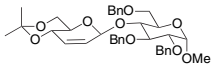
3,6-Bis-benzyloxy-2-benzyloxymethyl-3,6-dihydro-2*H*-pyran (**2**)

For the characterization data of the α-isomer, see: Wieczorek, E.; Thiem, J. *Carbohydr. Res.* **1998**, *307*, 263.

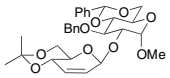
β-isomer : ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.24 (m, 15H), 6.08 (dq, *J* = 10.3, 1.5 Hz, 1H), 5.90 (dt, *J* = 10.3, 1.2 Hz, 1H), 5.22 (d, *J* = 1.5 Hz, 1H), 4.89 (d, *J* = 11.8Hz, 1H), 4.63 (d, *J* = 11.8 Hz, 1H), 4.60-4.57 (m, 4H), 4.07-4.00 (m, 2H), 3.73 (d, J = 4.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2, 137.9, 137.6, 128.9, 128.3, 128.0, 127.9, 127.7, 127.65, 127.56, 94.8, 75.2, 73.2, 70.9, 70.4, 69.7, 69.4.



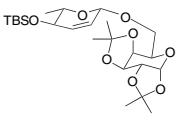
Methyl 2,3-dideoxy-4,6-*O*-isopropylidene-β-D-hex-2-enopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**13**): R_f = 0.34 (Hexanes-EtOAc 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.17 (m, 15H), 6.00 (d, *J* = 10.3 Hz, 1H), 5.60 (ddd, *J* = 10.3, 2.5, 1.5 Hz, 1H), 5.27 (m, 1H), 5.00 (d, *J* = 10.9 Hz, 1H), 4.91 (d, *J* = 11.1 Hz, 1H), 4.84 (d, *J* = 11.0 Hz, 1H), 4.81 (d, *J* = 12.2 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 2H), 4.62 (d, *J* = 3.5 Hz, 1H), 4.32 (m, 1H), 4.01 (t, *J* = 9.2 Hz, 1H), 3.94 (d, *J* = 8.6 Hz, 1H), 3.85-3.69 (m, 4H), 3.63-3.51 (m, 3H), 3.38 (s, 3H), 1.48 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 138.6, 138.3, 132.6, 128.62, 128.59, 128.3, 128.2, 128.1, 127.9, 127.80, 127.78, 100.0, 98.7, 98.4, 82.3, 79.8, 77.5, 75.9, 75.0, 73.6, 71.6, 69.8, 65.4, 62.8, 55.4, 29.4, 19.2; HRMS calc'd for $C_{37}H_{44}O_9Na$ [M^+Na]: 655.2878 found 655.2909.



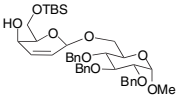
Methyl 2,3-dideoxy-4,6-*O*-isopropylidene-β-D-hex-2-enopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (**14**): R_f = 0.41 (Hexanes-EtOAc 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.15 (m, 15H), 5.87 (d, *J* = 10.2 Hz, 1H), 5.38 (ddd, *J* = 10.2, 2.5, 1.5 Hz, 1H), 5.33 (m, 1H), 4.97 (d, *J* = 10.9 Hz, 1H), 4.89 (d, *J* = 10.2 Hz, 1H), 4.80 (d, *J* = 12.2 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.66 (d, *J* = 12.2 Hz, 1H), 4.61 (d, *J* = 3.6 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.25 (m, 1H), 3.89 (dd, *J* = 8.6, 4.9 Hz, 1H) 3.78-3.60 (m, 5H), 3.56-3.53 (m, 3H) 3.39 (s, 3H), 1.42 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 138.4, 137.7, 131.7, 128.6, 128.55, 128.33, 128.26, 128.10, 128.05, 127.99, 127.5, 99.9, 99.8, 98.4, 80.8, 79.3, 77.2, 75.5, 73.7, 71.9, 69.9, 68.3, 67.4, 62.6, 55.4, 29.3, 19.1; HRMS calc'd for $C_{37}H_{44}O_9Na$ [M^+Na]: 655.2878 found 655.2884.



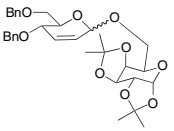
Methyl 2,3-dideoxy-4,6-*O*-isopropylidene-β-D-hex-2-enopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**15**): R_f = 0.40 (Hexanes-EtOAc 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.50 (m, 2H), 7.45-7.30 (m, 8H), 5.98 (d, *J* = 10.1 Hz, 1H), 5.74 (d, *J* = 10.1 Hz, 1H), 5.56 (d, *J* = 1.0 Hz, 1H), 5.55 (s, 1H), 4.80 (d, *J* = 12.1 Hz, 1H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.59 (d, *J* = 3.0 Hz, 1H), 4.42 (d, *J* = 8.7 Hz, 1H), 4.26 (dd, *J* = 10.0, 4.4 Hz, 1H), 4.21 (t, *J* = 9.5 Hz, 1H), 3.85-3.78 (m, 3H), 3.71 (t, *J* =10.1 Hz, 1H), 3.58-3.52 (m, 3H), 3.39 (s, 3H), 1.47 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 137.6, 132.0, 129.0, 128.8, 128.4, 128.3, 128.2, 126.2, 101.1, 100.5, 100.0, 99.1, 80.2, 79.4, 78.3, 73.9, 72.0, 69.1, 67.6, 63.0, 55.5, 29.9, 29.4, 19.2; HRMS calc'd for $C_{30}H_{36}O_9Na$ [M^+Na]: 563.2252 found 563.2284.



4-*O*-(tert-Butyldimethylsilyl)-2,3,6-trideoxy-β-L-hex-2-enopyranosyl-(1→6)-1,2;3,4-di-*O*-isopropylidene-α-D-galactopyranoside (**16**): R_f = 0.54 (Hexanes-EtOAc 3:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80 (dd, *J* = 10.2, 1.1 Hz, 1H), 5.68 (ddd, *J* = 10.2, 2.6, 2.0 Hz, 1H), 5.51 (d, *J* = 5.0 Hz, 1H), 4.97 (t, *J* = 1.0 Hz, 1H), 4.58 (dd, *J* = 8.0, 2.4 Hz, 1H), 4.29 (dd, *J* = 4.9, 2.4 Hz, 1H), 4.27 (dd, *J* = 8.0, 1.6 Hz, 1H), 3.98-3.90 (m, 2H), 3.86 (dq, *J* = 8.8, 1.6 Hz, 1H), 3.79-3.72 (m, 1H), 3.66-3.59 (m, 1H), 1.52 (s, 3H), 1.43 (s, 3H), 1.31 (s, 6H), 1.22 (d, J = 6.2 Hz, 3H), 0.88 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.4, 125.6, 109.0, 108.4, 96.2, 94.3, 71.0, 70.5, 70.2, 67.6, 67.0, 66.1, 26.04, 25.95, 25.7, 24.9, 24.3, 18.0, 17.9, -4.2, -4.8; HRMS calc'd for $C_{24}H_{42}O_8SiNa$ [M^+Na]: 509.2547 found 509.2539.



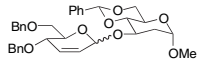
Methyl 6-*O*-(tert-butyldimethylsilyl)-2,3-dideoxy-4-hydroxy-β-D-hex-2-enopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**17**): R_f = 0.23 (Hexanes-EtOAc 2:1); ^{1}H NMR (300 MHZ, $CDCl_3$) δ 7.37-7.25 (m, 15H), 6.11 (dq, *J* = 10.1, 1.3 Hz, 1H), 5.75 (d, *J* = 10.1 Hz, 1H), 4.99 (d, *J* = 10.8 Hz, 1H), 4.94 (d, *J* = 1.3 Hz, 1H), 4.88 (d, *J* = 10.1 Hz, 1H), 4.82 (d, *J* = 10.8 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 10.1 Hz, 1H), 4.60 (d, *J* = 3.5 Hz, 1H), 4.05-3.91 (m, 3H), 3.86 (dd, *J* = 10.3, 7.2 Hz, 1H), 3.78-3.70 (m, 3H), 3.67-3.51 (m, 3H), 3.36 (s, 3H), 2.00 (d, *J* = 9.9 Hz, 1H), 0.88 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 138.3, 138.1, 131.1, 130.4, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 100.0, 98.1, 97.0, 82.2, 79.7, 77.3, 75.8, 74.9, 73.4, 69.6, 66.4, 62.3, 55.1, 25.8, 18.2, -5.4, -5.5; HRMS calc'd for $C_{40}H_{54}O_9SiNa$ [M^+Na]: 729.3429 found 729.3433.



4,6-Di-*O*-benzyl-2,3-dideoxy-α/β-D-hex-2-enopyranosyl-(1→6)-1,2;3,4-di-*O*-isopropylidene-α-D-galactopyranoside (**18β**): R_f = 0.43 (Hexanes-EtOAc 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.20 (m, 10H), 5.95 (dd, *J* = 10.2, 1.6 Hz, 1H), 5.85 (dd, *J* = 10.2, 1.2 Hz, 1H), 5.48 (d, *J* = 5.0 Hz, 1H), 5.14 (s, 1H), 4.54-4.44 (m, 5H), 4.25 (dd, *J* = 5.0, 1.4 Hz, 1H), 4.13 (d, *J* = 7.9 Hz, 1H), 3.97-3.89 (m, 4H), 3.69-3.61 (m, 3H), 1.47 (s, 3H), 1.38 (s, 3H), 1.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 129.1, 128.4, 127.9, 128.3, 127.9, 127.7, 127.6, 127.5, 109.2, 108.5,

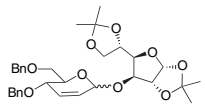
96.34, 96.27, 75.1, 73.2, 71.2, 70.9, 70.6, 70.4, 69.8, 69.4, 67.4, 67.1, 26.0, 25.9, 24.9, 24.4. HRMS calc'd for $C_{32}H_{40}O_9Na$ [M^+Na] 591.2570 found 591.2595.

(18α): R_f = 0.23 (Hexanes-EtOAc 4:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.20 (m, 10H), 6.08 (d, *J* = 10.2 Hz, 1H), 5.80 (ddd, *J* = 10.2, 2.7, 2.0 Hz, 1H), 5.53 (d, *J* = 5.0 Hz, 1H), 5.11 (s, 1H), 4.67 (d, *J* = 12.3 Hz, 1H), 4.62-4.59 (m, 2H), 4.50 (d, *J* = 12.2 Hz, 1H), 4.44 (d, *J* = 11.5 Hz, 1H), 4.32 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.29 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.24 (ddd, *J* = 9.4, 3.1, 1.7 Hz, 1H), 4.04-3.99 (m, 1H), 3.97-3.93 (m, 1H), 3.88 (dd, *J* = 10.2, 6.0 Hz, 1H), 3.82-3.76 (m, 2H), 3.70 (dd, *J* = 10.5, 2.2 Hz, 1H), 1.53 (s, 3H), 1.46 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 130.7, 128.3, 127.9, 127.8, 127.7, 127.6, 126.4, 109.1, 108.5, 96.3, 95.0, 73.3, 71.1, 70.7, 70.6, 70.5, 70.1, 69.3, 68.5, 66.7, 65.9, 26.0, 25.9, 24.9, 24.5. HRMS calc'd for $C_{32}H_{40}O_9Na$ [M^+Na] 591.2570 found 591.2581.



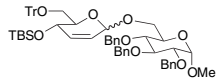
Methyl 4,6-di-*O*-benzyl-2,3-dideoxy-α/β-D-hex-2-enopyranosyl-(1→3)-4,6-*O*-benzylidene-3-deoxy-α-D-glucopyranoside (19β): R_f = 0.12 (Hexanes-EtOAc 4:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.0, 1.8 Hz, 2H), 7.35-7.23 (m, 11H), 7.14 (dd, *J* = 7.5, 1.0 Hz, 2H), 6.05 (ddd, *J* = 10.3, 3.8, 1.6 Hz, 1H), 5.83 (m, 1H), 5.57 (s, 1H), 5.30 (s, 1H), 4.80 (d, *J* = 3.0 Hz, 1H), 4.67-4.56 (m, 1H), 4.56 (s, 2H), 4.52-4.48 (m, 1H), 4.41-4.32 (m, 1H), 4.26 (dd, *J* = 10.2, 4.5 Hz, 1H), 4.05-4.01 (m, 1H), 3.98-3.96 (m, 1H), 3.89-3.80 (m, 1H), 3.76 (t, *J* = 10.2 Hz, 1H), 3.70 (dd, *J* = 10.5, 4.6 Hz, 1H), 3.61 (t, *J* = 9.2 Hz, 1H), 3.56 (dd, *J* = 10.5, 6.7 Hz, 1H), 3.34 (s, 3H), 2.37 (dd, *J* = 13.4 Hz, 1H), 1.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 138.1, 137.7, 129.0, 128.8, 128.6, 128.4, 128.3, 128.2, 128.0, 127.9, 127.6, 127.4, 127.3, 126.4, 101.9, 99.0, 92.1, 81.5, 74.8, 72.7, 70.8, 70.0, 69.1, 68.9, 68.7, 67.9, 63.1, 54.7, 36.0; HRMS calc'd for $C_{34}H_{38}O_8Na$ [M^+Na]: 597.2464 found 597.2465.

(19α): R_f = 0.19 (Hexanes-EtOAc 4:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.48-7.25 (m, 15H), 6.06 (d, *J* = 10.2 Hz, 1H), 5.81 (ddd, *J* = 10.2, 2.8, 1.9 Hz, 1H), 5.58 (s, 1H), 5.37 (d, *J* = 2.4 Hz, 1H), 4.71 (d, *J* = 2.9 Hz, 1H), 4.66 (d, *J* = 12.6 Hz, 1H), 4.62 (d, *J* = 11.4 Hz, 1H), 4.54 (d, *J* = 12.1 Hz, 1H), 4.45 (d, *J* = 11.4 Hz, 1H), 4.37-4.31 (m, 1H), 4.25 (dd, *J* = 9.8, 4.5 Hz, 1H), 4.15-4.10 (m, 1H), 4.02-3.98 (m, 1H), 3.87-3.70 (m, 4H), 3.60 (t, *J* = 9.2 Hz, 1H), 3.32 (s, 3H), 2.36-2.32 (m, 1H), 1.83-1.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 138.0, 137.6, 130.3, 128.8, 128.30, 128.25, 128.2, 127.8, 127.7, 127.5, 126.6, 126.0, 101.4, 99.1, 95.4, 83.2, 77.2, 73.4, 71.7, 71.0, 70.4, 69.2, 69.14, 69.08, 62.9, 54.6, 37.2; HRMS calc'd for $C_{34}H_{38}O_8Na$ [M^+Na]: 597.2464 found 597.2445.



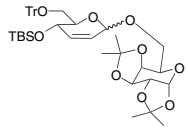
4,6-Di-*O*-benzyl-2,3-dideoxy-α/β-D-hex-2-enopyranosyl-(1→3)-1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranoside (20β): R_f = 0.17 (Hexanes-EtOAc 4:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.27 (m, 10H), 6.14 (d, *J* = 10.3 Hz, 1H), 5.90 (d, *J* = 3.7 Hz, 1H), 5.80 (d, *J* = 9.7 Hz, 1H), 5.38 (s, 1H), 4.66 (d, *J* = 3.6 Hz, 1H), 4.62 (d, *J* = 11.5 Hz, 1H), 4.59 (d, J = 10.3 Hz, 1H), 4.54 (d, J = 11.4 Hz, 1H), 4.65-4.50 (m, 1H), 4.36 (m, 2H), 4.21 (dd, *J* = 6.7, 3.0 Hz, 1H), 4.12-4.08 (m, 1H), 4.06-3.97 (m, 2H), 3.89-3.85 (m, 1H), 3.78 (dd, *J* = 10.8, 4.9 Hz, 1H), 3.71 (dd, *J* = 10.8, 3.6 Hz, 1H), 1.50 (s, 3H), 1.43 (s, 3H), 1.34 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 137.8, 130.9, 128.4, 128.3, 128.1, 127.9, 127.8, 127.6, 111.7, 108.7, 105.1, 95.3, 83.6, 80.5, 77.1, 76.1, 73.3, 72.7, 71.4, 69.5, 66.7, 26.8, 26.7, 26.2, 25.4; HRMS calc'd for $C_{32}H_{40}O_9Na$ [M^+Na]: 591.2570 found 591.2550.

(**20α**): R_f = 0.23 (Hexanes-EtOAc 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.24 (m, 10H), 6.09 (d, *J* = 10.1 Hz, 1H), 5.85 (d, *J* = 3.4 Hz, 1H), 5.77 (m, 1H), 5.25 (s, 1H), 4.76 (d, *J* = 3.6 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 11.1 Hz, 1H), 4.55 (d, *J* = 12.2 Hz, 1H), 4.60-4.47 (m, 1H), 4.44 (d, *J* = 11.4 Hz, 1H), 4.25-4.20 (m, 1H), 4.12-4.03 (m, 3H), 4.00-3.96 (m, 2H), 3.76 (dd, *J* = 10.7, 1.9 Hz, 1H), 3.69 (dd, *J* = 10.6, 5.2 Hz, 1H), 1.49 (s, 3H), 1.41 (s, 3H), 1.33 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 137.8, 130.5, 128.40, 128.36, 127.83, 127.79, 127.6, 126.1, 111.8, 109.0, 105.4, 95.8, 84.0, 81.3, 81.2, 73.5, 72.6, 71.1, 70.4, 69.7, 69.1, 67.8, 26.9, 26.8, 26.1, 25.4; HRMS calc'd for $C_{32}H_{40}O_9Na$ [M^+Na]: 591.2570 found 591.2547.



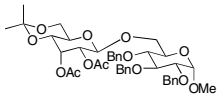
Methyl 4-*O*-(tert-butyldimethylsilyl)-2,3-dideoxy-6-*O*-trityl-α/β-D-hex-2-enopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**21β**): R_f = 0.47 (Hex-EtOAc 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.17 (m, 30H), 5.80 (dt, *J* = 10.2, 1.8 Hz, 1H), 5.67 (dt, *J* = 10.2, 1.3 Hz, 1H), 5.15 (d, *J* = 1.2 Hz, 1H), 5.02 (d, *J* = 10.8, Hz, 1H), 4.91 (d, *J* = 11.1 Hz, 1H), 4.85 (d, *J* = 10.8 Hz, 1H), 4.82 (d, *J* = 12.2 Hz, 1H), 4.69 (d, *J* = 12.1 Hz, 1H), 4.66 (d, *J* = 11.0 Hz, 1H), 4.63 (d, *J* = 3.5 Hz, 1H), 4.24 (d, *J* = 8.7 Hz, 1H), 4.18 (dq, *J* = 8.0, 2.0 Hz, 1H), 4.04 (t, *J* = 9.2 Hz, 1H), 3.85-3.80 (m, 2H), 3.72-3.66 (m, 2H), 3.59 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.40 (s, 3H), 3.28-3.20 (m, 2H), 0.72 (s, 9H), –0.04 (s, 3H), –0.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 138.8, 138.3, 138.1, 133.8, 128.8, 128.42, 128.37, 128.1, 128.0, 127.9, 127.74, 127.65, 127.56, 126.8, 98.1, 97.6, 79.7, 78.1, 75.7, 74.9, 69.6, 66.4, 64.2, 63.7, 55.1, 25.6, 17.7, -4.4, -5.1; HRMS calc'd for $C_{59}H_{68}O_9SiNa$ [M^+Na]: 971.4525 found 971.4481.

(**21α**): R_f = 0.37 (Hex-EtOAc 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.1 (m, 30H), 5.82 (d, *J* = 10.3 Hz, 1H), 5.75 (dt, *J* = 10.2, 2.1 Hz, 1H), 5.17 (s, 1H), 4.97 (d, *J* = 11.0 Hz, 1H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.81 (d, *J* = 10.6 Hz, 1H), 4.78 (d, *J* = 11.6 Hz, 1H), 4.68-4.64 (m, 3H), 4.22 (dd, *J* = 11.4, 4.0 Hz, 1H), 4.16 (dd, *J* = 9.1, 1.3 Hz, 1H), 4.00 (t, *J* = 9.4 Hz, 1H), 3.88-3.78 (m, 3H), 3.64 (t, *J* = 9.4 Hz, 1H), 3.54 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.39 (s, 3H), 3.25 (dd, *J* = 9.8, 1.7 Hz, 1H), 3.03 (dd, *J* = 9.9, 5.9 Hz, 1H), 0.66 (s, 9H), -0.05 (s, 3H), -0.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 138.8, 138.2, 134.4, 128.8, 128.4, 128.3, 128.1, 128.0, 127.8, 127.65, 127.60, 127.5, 126.8, 125.5, 98.0, 94.6, 86.2, 82.0, 79.8, 77.9, 75.6, 75.0, 73.3, 71.5, 70.2, 66.4, 64.5, 63.1, 55.1, 25.6, 17.7, -4.3, -5.1; HRMS calc'd for $C_{59}H_{68}O_9SiNa$ [M^+Na]: 971.4525 found 971.4511.



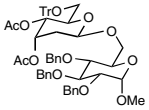
Methyl 4-*O*-(tert-butyldimethylsilyl)-2,3-dideoxy-6-*O*-trityl-α/β-D-hex-2-enopyranosyl-(1→6)-1,2;3,4-di-*O*-isopropylidene-α-D-glucopyranoside (**22β**): R_f = 0.40 (Hexanes-EtOAc 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 3H), 7.47-7.17 (m, 12H), 5.80 (s, 2H), 5.57 (d, *J* = 5.0 Hz, 1H), 5.45 (d, *J* = 2.0 Hz, 1H), 4.60 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.31 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.28 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.22 (dd, *J* = 8.2, 2.1 Hz, 1H), 4.17 (dd, *J* = 10.8, 4.1 Hz, 1H), 4.06-4.03 (m, 1H), 3.84 (dd, *J* = 10.8, 7.2 Hz, 1H), 3.71-3.67 (m, 1H), 3.29 (dd, *J* = 9.9, 2.5 Hz, 1H), 3.21 (dd, *J* = 9.9, 6.0 Hz, 1H), 1.52 (s, 3H), 1.43 (s, 3H), 1.321 (s, 3H), 1.317 (s, 3H), 0.69 (s, 9H), –0.05 (s, 3H), –0.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 133.7, 128.8, 127.9, 127.8, 127.6, 126.8, 109.2, 108.5, 97.8, 96.3, 86.2, 78.0, 71.4, 70.6, 70.4, 67.6, 67.2, 64.2, 63.6, 60.3, 26.06, 25.98, 25.6, 24.9, 24.4, 17.7, 14.4, -4.4, -5.2; HRMS calc'd for $C_{43}H_{56}O_9SiNa$ [M^+Na]: 767.3586 found 767.3566.

(**22α**): R_f = 0.47 (Hexanes-EtOAc 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.46 (m, 6H), 7.29-7.16 (m, 9H), 5.81 (d, *J* = 10.4 Hz, 1H), 5.75 (dt, *J* = 10.3, 2.4 Hz, 1H), 5.56 (d, *J* = 5.0 Hz, 1H), 5.19 (s, 1H), 4.59 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.32 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.27 (dd, *J* = 7.9, 1.7 Hz, 1H), 4.17-4.04 (m, 3H), 3.98 (dd, *J* = 6.6, 1.4 Hz, 1H), 3.89 (dd, *J* = 9.7, 6.6 Hz, 1H), 3.31 (dd, *J* = 9.8, 1.6 Hz, 1H), 3.10 (dd, *J* = 9.8, 6.8 Hz, 1H), 1.50 (s, 3H), 1.44 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H), 0.66 (s, 9H), –0.07 (s, 3H), –0.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 124.3, 128.8, 127.7, 126.8, 125.6, 109.2, 108.5, 96.4, 93.1, 86.4, 71.4, 71.0, 70.7, 65.51, 65.46, 64.7, 63.8, 26.1, 26.0, 25.6, 24.9, 17.7, 14.4, -4.4, -5.2; HRMS calc'd for $C_{43}H_{56}O_9SiNa$ [M^+Na]: 767.3586 found 767.3573.



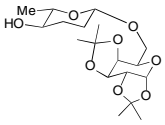
Methyl 2,3-di-*O*-acetoxy-4,6-*O*-isopropylidene-β-D-allopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**23**). A mixture of OsO_4 (4 wt% in H_2O, 0.020 mL, 0.0032 mmol), *N*-methyl morpholine *N*-oxide (50% in H_2O, 0.049 mL, 0.24 mmol) and **13** (100 mg, 0.158 mmol) in acetone (1 mL) was stirred at room temperature for 18 h. The reaction was quenched with saturated aqueous Na_2SO_3 solution, and the resulting mixture was stirred for 0.5 h and extracted with ethyl acetate (3 x 30 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash silica gel column chromatography (Hexanes-EtOAc 1:4) gave the corresponding diol (92.7 mg, 0.139 mmol, 88%). To a solution of the diol (30 mg, 0.045 mmol) in pyridine (0.5 mL) were added acetic anhydride (0.021 mL, 0.225 mmol) and a crystal of DMAP (4-dimethylaminopyridine). After stirred at 25 °C for 18 h, the reaction mixture was moved directly onto a silica gel column. Purification by flash chromatography (Hexanes-EtOAc 2:1) afforded **23** (34 mg, 0.045 mmol, 100%) as a clear oil: R_f = 0.56 (Hexanes-EtOAc 1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.26 (m, 15H), 5.60 (s, 1H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.87 (d, *J* = 10.8 Hz, 1H), 4.84-4.79 (m, 4H), 4.65 (d, *J* = 12.1 Hz, 1H), 4.59 (d, *J* = 11.1 Hz, 1H), 4.58 (d, *J* = 3.5 Hz, 1H), 4.08 (m, *J* = 9.3 Hz, 1H), 3.98 (t, *J* = 9.4 Hz, 1H), 3.94 (dd, *J* = 7.5, 2.9 Hz, 1H), 3.85-3.74 (m, 5H), 3.56 (d, *J* = 8.2 Hz, 1H), 3.52 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.36 (s, 3H), 2.11 (s, 3H), 1.91 (s, 3H), 1.45 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 169.2, 138.6, 138.3, 138.0, 128.46, 128.37, 128.2, 127.9, 127.8, 127.61, 127.55, 99.6, 99.0, 98.2, 82.0, 79.6, 75.8, 74.9, 73.4, 70.4, 69.4, 69.1, 68.5, 68.0, 65.0, 62.2, 55.1, 28.8, 20.8, 20.6, 18.8; HRMS calcd' for $C_{40}H_{47}O_{13}$ [M^+ -CH_3]: 735.3017 found 735.3042.

The configuration of the new stereogenic centers were assigned based on the chemical shift and coupling patterns of C1, C2, and C3 methine protons of the allose unit in the debenzylated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.323 (t, J = 2.9 Hz, 1H, H_3'), 4.806 (d, *J* = 8.3 Hz, 1H, H_1'), 4.544 (dd, *J* = 8.3, 3.0 Hz, 1H, H_2').



Methyl 3,4-di-*O*-acetoxy-2-deoxy-6-*O*-trityl-β-D-hexopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**24**). A solution of TBAF (1 M in THF, 0.4 mL, 0.4 mmol) was added to **21β** (290 mg, 0.300 mmol) in THF (2 mL). After stirred for 2 h at 25 C, the reaction mixture was moved directly onto silica gel column. Purification by flash silica gel column chromatography (Hexanes-EtOAc 2:1) afforded the corresponding alcohol (0.243 mg, 0.292 mmol, 97%). To a solution of the alcohol (80 mg, 0.096mmol) in aqueous THF (1:1, 2 mL) was added $Hg(OTf)_2$ (57 mg, 0.12 mmol) in one portion. After stirring in the dark for 24 h, a solution of $NaBH_4$ in 2*N* NaOH (3M, 3 mL) was added dropwise to the reaction mixture. The resulting suspension was

stirred for 15 min and extracted with diethyl ether (3 x 10 mL). Organic extract was washed with brine and water, dried over $MgSO_4$, and concentrated. Purification by flash silica gel column chromatography (Hexanes-EtOAc 1:1) gave the corresponding diol (65 mg, 0.077 mmol, 80%). To the diol (33 mg, 0.039 mmol) in dichloromethane (1 mL) were added triethylamine (0.08 mL, 0.58 mmol), acetic anhydride (0.04 mL, 0.42 mmol) and a crystal of 4-DMAP. After stirred at 25 °C for 24 h, the reaction mixture was directly moved onto a silica gel column and purified by flash silica gel chromatography (Hexanes-EtOAc 2:1) to yield **24** (36 mg, 0.039 mmol, 100%) as a clear oil: R_f = 0.24 (Hexanes-EtOAc 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47-7.15 (m, 30H), 5.46 (ddd, *J* = 6.6, 3.5, 3.1 Hz, 1H, **H_3'**), 5.05 (dd, *J* = 9.7, 3.1 Hz, 1H, **H_4'**), 5.00 (d, *J* = 10.8 Hz, 1H), 4.90 (d, *J* = 11.3 Hz, 1H), 4.81 (d, *J* = 10.8 Hz, 1H), 4.80 (d, *J* = 12.3 Hz, 1H), 4.76 (m, 1H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.62 (d, *J* = 3.5 Hz, 1H), 4.56 (d, *J* = 11.2 Hz, 1H), 4.18 (dd, *J* = 10.7, 1.9 Hz, 1H), 4.02 (t, *J* = 9.3 Hz, 1H), 3.90 (ddd, *J* = 10.0, 4.6, 2.7 Hz, 1H), 3.83-3.78 (m, 1H), 3.67 (dd, *J* = 10.6, 4.1 Hz, 1H), 3.58 (t, *J* = 9.7 Hz, 1H). 3.56 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.39 (s, 3H), 3.28 (dd, *J* = 10.2, 2.6 Hz, 1H), 3.07 (dd, *J* = 10.2, 4.6 Hz, 1H), 2.02 (s, 3H), 2.0-1.97 (m, 2H), 1.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8, 169.4, 143.8, 138.7, 138.4, 138.1, 128.45, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 127.6, 127.6, 126.9, 98.6, 98.1, 86.2, 82.2, 79.8, 75.8, 74.8, 73.4, 71.8, 69.6, 67.8, 67.5, 67.3, 62.6, 55.2, 35.1, 20.9, 20.5; HRMS calc'd for $C_{57}H_{60}O_{12}Na$ [M^+Na]: 959.3977 found 959.3934.



2,3,6-Trideoxy-4-hydroxy-β-L-hexopyranosyl-(1→6)-1,2;3,4-di-*O*-isopropylidene-α-D-glucopyranoside (**25**). A solution of TBAF (1 M in THF, 0.25 mL, 0.25 mmol) was added dropwise to **16** (110 mg, 0.22 mmol) in THF (2 mL). After stirred for 2 h, the reaction mixture was moved directly onto silica gel column and purified by flash chromatography (Hexanes-EtOAc 2:1) to afford the corresponding alcohol (82 mg, 0.22 mmol). To the alcohol (27 mg, 0.072 mmol) in DME (2.5 mL) were added an aqueous solution of sodium acetate (90 mg, 1.08 mmol, 2.5 mL H_2O) and p-toluenesulfonylhydrazide (135 mg, 0.72 mmol). After refluxed for 4 h and then cooled to room temperature, the reaction was diluted with diethyl ether (50 mL), washed with H_2O, dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash silica gel column chromatography gave **25** (24 mg, 0.063 mmol, 88%) as a clear oil: R_f = 0.50 (Hexanes-EtOAc 1.5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 (d, *J* = 5.0 Hz, 1H), 4.79 (d, *J* = 1.8 Hz, 1H), 4.61 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.32 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.28 (dd, *J* = 7.9, 1.9 Hz, 1H), 3.98 (dt, *J* = 6.2, 1.8 Hz, 1H), 3.84 (dd, *J* = 10.2, 5.9 Hz, 1H), 3.65 (m, 1H), 3.58 (dd, *J* = 10.2, 6,8 Hz, 1H), 3.26 (m, *J* = 5.0 Hz, 1H), 1.89-1.82 (m, 2H), 1.79-1.72 (m, 2H), 1.55 (s, 3H), 1.45 (s, 3H), 1.34 (s, 6H), 1.24 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.2, 108.5, 96.3, 96.1, 72.1, 71.1, 70.6, 70.56, 69.4, 67.0, 65.1, 29.5, 27.6, 26.1, 25.96, 24.9, 24.4, 17.8; HRMS calc'd for $C_{17}H_{27}O_8$ [M^+-CH_3]: 359.1706 found 359.1694.