Supplementary materials

REVISED 10/10/00

Experimental Details and Compound Characterization

1. General procedures for the preparation of compounds **2-14**

To a solution of substrate (1 mmol) in pyridine was added 1.25 equiv of TrCl and catalytic amount of DMAP. The mixture was stirred at 80 °C for 16 h, then cooled down to 0 °C, 2 equiv of imidazole was added, and finally 1.1 equiv of TBDMSCl in DMF was added portion by portion during 2 h. The mixture was stirred at rt overnight, then a premixed benzoyl chloride (2.5 equiv, in entry 1 and 2) or acetic anhydride (3 equiv, in entry 3-7) and pyridine was added. The reaction mixture was stirred at 50 °C overnight, then poured into ice-cold water, extracted with EtOAc. The organic phase was concentrated to dryness with the help of toluene. The residue was subjected to column chromatography on silica gel with petroleum ether/EtOAc as the eluent (12/1) to give product.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) data: **2**. δ –0.15, 0.04 (2 s, 2 x 3 H, $Si(CH_3)_2$), 0.62, (s, 9 H, t-Bu), 3.75 (dd, 1 H, $J_{5,6a}$ 1.8, $J_{6a,6b}$ 11.2 Hz, H-6a), 3.84 (dd, 1 H, $J_{5,6b}$ 5.3 Hz, H-6b), 3.98 (ddd, 1 H, H-5), 4.09 (m, 1 H, CH_2=CH-CH_2-), 4.28 (m, 1 H, CH_2=CH-CH_2-), 4.38 (dd, 1 H, $J_{2,3}$ 3.5, $J_{3,4}$ 9.4 Hz, H-3), 5.03 (d, 1 H, $J_{1,2}$ 1.4 Hz, H-1), 5.24-5.36 (m, 2 H, CH_2=CH-CH_2-), 5.40 (dd, 1 H, H-2), 5.73 (t, 1 H, $J_{4,5}$ 9.9 Hz, H-4), 5.91-5.96 (m, 1 H, CH_2=CH-CH_2-), 7.20-8.30 (m, 25 H, Ph). Anal. Calcd for $C_{48}H_{52}O_8Si$: C, 73.47; H, 6.63. Found: C, 73.51; H, 6.58.

4. δ –0.15, 0.03 (2 s, 2 x 3 H, $Si(CH_3)_2$), 0.62, 1.02 (2 s, 2 x 9 H, t-Bu),3.46 (s, 3 H, OCH_3), 3.76 (dd, 1 H, $J_{5,6a}$ 1.6, $J_{6a,6b}$ 11.3 Hz, H-6a), 3.85 (dd, 1 H, $J_{5,6b}$ 5.2 Hz, H-6b), 4.09 (ddd, 1 H, H-5), 4.35 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 9.4 Hz, H-3), 4.91 (d, 1 H, $J_{1,2}$ 1.3 Hz, H-1), 5.37 (dd, 1 H, H-2), 5.72 (t, 1 H, $J_{4,5}$ 9.4 Hz, H-4), 7.17-8.15 (m, 20 H, Ph). Anal. Calcd for $C_{43}H_{54}O_8Si_2$: C, 68.43; H, 7.16. Found: C, 68.50; H, 7.17.

6. δ -0.04, 0.01 (2 s, 2 x 3 H, $Si(CH_3)_2$), 0.78 (s, 9 H, t-Bu), 1.70, 2.15 (2 s, 6 H, CH_3CO), 2.96 (dd, 1 H, $J_{5,6a}$ 2.0, $J_{6a,6b}$ 10.5 Hz, H-6a), 3.26 (dd, 1 H, $J_{5,6b}$ 6.86 Hz, H-6b), 3.50 (ddd, 1 H, $J_{4,5}$ 8.9 Hz, H-5), 3.78 (t, 1 H, $J_{2,3}$ 8.9 Hz, H-3), 4.69 (d, 1 H, $J_{1,2}$ 10.1 Hz, H-1), 4.84 (t, 1 H, $J_{3,4}$ 8.9 Hz, H-4), 4.99 (t, 1 H, H-2), 7.20-7.70 (m, 20 H,

Ph). Anal. Calcd for $C_{41}H_{48}O_7SiS$: C, 69.10; H, 6.74. Found: C, 69.14; H, 6.70.

8. δ -0.03, 0.02 (2 s, 2 x 3 H, Si(CH_3)$_2$), 0.79 (s, 9 H, t-Bu), 0.86 (t, 3 H, CH_3), 1.25-1.37 (m, 10 H, CH_2), 1.60-1.66 (m, 2 H, CH_2), 1.72, 2.09 (2 s, 2 x 3 H, CH_3CO), 3.04 (dd, 1 H, $J_{5,6a}$ 2.3, $J_{6a,6b}$ 10.4 Hz, H-6a), 3.18 (dd, 1 H, $J_{5,6b}$ 6.0 Hz, H-6b), 3.48 (ddd, 1 H, H-5), 3.57 (dt, 1 H, OCH_2), 3.79 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, H-3), 3.97 (dt, 1 H, OCH_2), 4.41 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.95 (t, 1 H, $J_{4,5}$ 9.2 Hz, H-4), 4.97 (dd, 1 H, H-2), 7.22-7.50 (m, 15 H, Ph). Anal. Calcd for $C_{43}H_{60}O_8Si$: C, 70.49; H, 8.20. Found: C, 70.55; H, 8.21.

10. δ 0.07, 0.11 (2 s, 2 x 3 H, Si(CH_3)$_2$), 0.88 (s, 9 H, t-Bu), 1.72, 2.00 (2 s, 6 H, 2 CH_3CO), 3.10 (dd, 1 H, $J_{5,6a}$ 5.4, $J_{6a,6b}$ 10.4 Hz, H-6a), 3.19 (dd, 1 H, $J_{5,6b}$ 2.0 Hz, H-6b), 3.48 (s, 3 H, OCH_3), 3.82 (dd, 1 H, $J_{2,3}$ 9.6 Hz, H-2), 3.90 (ddd, 1 H, H-5), 4.74 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.96 (t, 1 H, $J_{4,5}$ 9.6 Hz, H-4), 5.28 (t, 1 H, $J_{3,4}$ 9.6 Hz, H-3), 7.19-7.45 (m, 15 H, Ph). Anal. Calcd for $C_{36}H_{46}O_8Si$: C, 68.14; H, 7.25. Found: C, 68.20; H, 7.19.

12. δ 0.08, 0.12 (2 s, 2 x 3 H, Si(CH_3)$_2$), 0.86 (s, 9 H, t-Bu), 1.27, 1.30 (2 dd, 6 H, CH(CH_3)$_2$), 1.87, 2.06 (2 s, 6 H, CH_3CO), 3.05 (dd, 1 H, $J_{5,6a}$ 7.0, $J_{6a,6b}$ 9.2 Hz, H-6a), 3.19 (dq, 1 H, CH(CH_3)$_2$), 3.88 (dd, 1 H, $J_{5,6b}$ 6.2 Hz, H-6b), 3.65 (bt, 1 H, J 6.6 Hz, H-5), 3.79 (t, 1 H, $J_{2,3}$ 9.6, $J_{3,4}$ 3.4 Hz, H-3), 4.46 (d, 1 H, $J_{1,2}$ 10.1 Hz, H-1), 5.05 (t, 1 H, H-2), 5.41 (d, 1 H, H-4), 7.20-7.45 (m, 15 H, Ph). Anal. Calcd for $C_{38}H_{50}O_7SiS$: C, 67.26; H, 7.37. Found: C, 67.30; H, 7.36.

2. Preparation of allyl 2,4-di-*O*-benzoyl-α-D-mannopyranoside (**16**)

Compound **2** (2.5 g, 3.19 mmol) was dissolved into 90% aqueous TFA (15 mL) and the solution was stirred at rt for 4 h. Toluene (50 mL) was added and then the solvents were evaporated *in vacuo* to give a residue, which was purified by a silica gel column chromatography (petroleum ether-EtOAc, 1:1) to give **16** (1.24 g, 91%); ^{1}H NMR ($CDCl_3$) δ 3.74 (dd, 1 H, $J_{5,6a}$ 4.1, $J_{6a,6b}$ 12.6 Hz, H-6a), 3.81 (dd, 1 H, $J_{5,6b}$ 2.3 Hz, H-6b), 3.98 (ddd, 1 H, H-5), 4.09 (m, 1 H, CH_2=CH-CH_2-), 4.26 (m, 1 H, CH_2=CH-CH_2-), 4.46 (dd, 1 H, $J_{2,3}$ 3.5, $J_{3,4}$ 9.9 Hz, H-3), 5.10 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 5.25-5.34 (m, 2 H, CH_2=CH-CH_2-), 5.43 (dd, 1 H, H-2), 5.51 (t, 1 H, $J_{4,5}$ 9.9 Hz, H-4), 5.91-5.96 (m, 1 H, CH_2=CH-CH_2-), 7.25-8.10 (m, 10 H, Ph). Anal. Calcd for $C_{23}H_{24}O_8$:

C, 64.48; H, 5.61. Found: C, 64.40; H, 5.66.

3. Preparation of 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (**19**)

To a cooled solution (0 °C) of **16** (1.5 g, 3.5 mmol) and **17** (5.45 g, 7.36 mmol) in anhydrous CH_2Cl_2 (50 mL) was added TMSOTf (25 μL, 0.14 mmol). The mixture was stirred at this temperature for 2 h, and then quenched with Et_3N (2 drops). The solvents were evaporated *in vacuo* to give a residue, which was purified by a silica gel column chromatography (petroleum ether-EtOAc, 1.5:1) to give trisaccharide **18** (4.72 g, 85%).

A solution of **18** (850 mg, 0.54 mmol) in 90% aqueous acetic acid (10 mL) was added NaOAc (177 mg, 2.16 mmol) and $PdCl_2$ (191 mg, 1.08 mmol). The mixture was stirred at rt overnight and then neutralized with saturated aqueous $NaHCO_3$. The mixture was extract with CH_2Cl_2 (3 x 50 mL) and the organic phase was concentrated. The residue was purified by a silica gel column chromatography to give hemiacetal trisaccharide intermediate as syrup. A solution of the above syrup, CCl_3CN (4 equiv) and DBU (0.4 equiv) in dry CH_2Cl_2 (5 mL) was stirred at rt for 2 h. The solvents were removed *in vacuo*. The residue was purified by a silica gel flash column chromatography to give trichloroacetimidate **19** (725 mg, 80%) as a white foam; ^1H NMR (400 MHz, $CDCl_3$) δ 3.84 (dd, 1 H, J<1, J 9.2 Hz, H-6a), 4.15 (dd, 1 H, J 6.3, J 11.0 Hz, H-6b), 4.30-4.37 (m, 2 H), 4.48-4.58 (m, 5 H), 4.73 (dd, 1 H, J 3.4, J 9.8 Hz, H-3), 5.10 (d, 1 H, J 1.2 Hz, H-1), 5.38-5.41 (m, 2 H, H-1, H-2), 5.69-5.73 (m, 2 H, H-2, H-3), 5.90-5.95 (m, 2 H), 6.01 (t, 1 H, J 10.8 Hz, H-4), 6.07 (t, 1 H, J 10.0 Hz, H-4), 6.12 (t, 1 H, J 10.0 Hz, H-4), 6.59 (d, 1 H, J 1.5 Hz, H-1), 7.00-8.13 (m, 50 H, Ph), 9.00 (s, 1 H, N*H*). Anal. Calcd for $C_{90}H_{72}Cl_3NO_{26}$: C, 63.96; H, 4.26; Found: C, 63.88; H, 4.24.

4. Preparation of allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-D-mannopyranoside (**21**)

To a stirred solution of **2** (2 g, 2.55 mmol) in THF (50 mL) was added TBAF (800 mg, 2.55 mmol). The mixture was stirred at rt for 4 h, then evaporated to dryness (<

40 °C water both) under reduced pressure. The residue was purified by a silica gel column chromatography to give **20** as a white solid (1.13 g, 66%). To a cooled solution (-15 °C) of **20** (1.062 g, 1.58 mmol) and **17** (1.23 g, 1.66 mmol) in dry CH_2Cl_2 (15 mL) was added TMSOTf (15 μL, 0.08 mmol), and the mixture was stirred at this temperature for 40 min, another portion of TMSOTf (250 μL) was added. The reaction was warmed up to rt and stirred for 4 h further, then concentrated. The residue was purified by a silica gel column chromatography to give **21** (1.276 g, 80%); ^{1}H NMR ($CDCl_3$) δ 2.89 (bs, H, O*H*), 3.75-3.80 (m, 2 H, 2 H-6), 4.00 (ddd, 1 H, H-5), 4.07 (ddd, 1 H, H-5'), 4.18-4.25 (m, 1 H, CH_2=CH-CH_2-), 4.35 (dd, 1 H, $J_{5',6'a}$ 3.6, $J_{6'a,6'b}$ 12.3 Hz, H-6'a), 4.44-4.50 (m, 1 H, CH_2=CH-CH_2-), 4.61 (dd, 1 H, $J_{5',6'b}$ 2.4 Hz, H-6'b), 4.70 (dd, 1 H, $J_{2,3}$ 3.5, $J_{3,4}$ 9.8 Hz, H-3), 5.15 (d, 1 H, $J_{1,2}$ 1.4 Hz, H-1), 5.23-5.36 (m, 3 H, H-2 and CH_2=CH-CH_2-), 5.41 (d, 1 H, $J_{1',2'}$ 1.7 Hz, H-1'), 5.65-5.69 (m, 2 H, H-2', H-3'), 5.72 (t, 1 H, $J_{3,4}$ 10.0 Hz, H-4), 5.89 (m, 1 H, CH_2=C*H*-CH_2-), 6.02 (t, 1 H, $J_{3',4'}$ 10.0 Hz, H-4'), 7.19-8.25 (m, 30 H, Ph). Anal. Calcd for $C_{57}H_{50}O_{17}$: C, 67.99; H, 4.97. Found: C, 67.96; H, 4.99.

5. Preparation of allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-[2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→3)]-2,4-di-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-[2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→3)]-2,4-di-*O*-benzoyl-α-D-mannopyranoside (**22**)

To a cooled solution (0 °C) of **19** (2 g, 1.18 mmol) and **21** (1.13 g, 1.12 mmol) in dry CH_2Cl_2 (15 mL) was added TMSOTf (20 μL). The mixture was stirred at this temperature for 2 h, then neutralized with Et_3N (2 drops), and concentrated. The residue was purified by a silica gel column chromatography to give **22** (2.42 g, 85%); ^{1}H NMR ($CDCl_3$) δ 3.44 (bd, 1 H, H-6), 3.82 (dd, 1 H, H-6), 4.01 (dd, 1 H, H-6), 4.14 (ddd, 1 H, H-5), 4.20-4.53 (m, 12 H), 4.58 (dd, 1 H, H-6), 4.67 (dd, 1 H, H-3), 4.73 (dd, 1 H, H-3), 4.78 (d, 1 H, H-1), 5.17-5.19 (m, 2 H, H-1 and one proton of CH_2=CH-CH_2-), 5.21 (d, 1 H, H-1), 5.29-5.32 (m, 3 H, H-1, H-2, and one proton of CH_2=CH-CH_2-), 5.37 (d, 1 H, H-1), 5.44 (dd, 1 H, H-2), 5.57 (dd, 1 H, H-2), 5.65 (dd, 1 H, H-3), 5.69-5.74 (m, 2 H, H-2, H-3), 5.82 (dd, 1 H, H-2), 5.85-6.01 (m, 4 H, H-3, 2 H-4, CH_2=C*H*-CH_2-), 6.04 (t, 1 H, H-4), 6.07 (t, 1 H, H-4), 6.08 (t, 1 H, H-4), 7.18-

8.35 (m, 80 H, Ph). Anal. Calcd for $C_{145}H_{120}O_{42}$: C, 68.72; H, 4.74. Found: C, 68.79; H, 4.81.

6. Preparation of Octyl 2,4-di-*O*-acetyl-3-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside (**23**)

A solution of **8** (1 g, 1.37 mmol) and $FeCl_3 \cdot 6H_2O$ (737 mg, 2.73 mmol) in CH_2Cl_2 (20 mL) was stirred at rt for 3 h. The reaction mixture was diluted with CH_2Cl_2 (30 mL), washed with water, and the organic phase was concentrated. Purification on silica gel column gave **23** as a syrup (602 mg, 90%); ^{1}H NMR ($CDCl_3$) δ 0.04, 0.05 (2 s, 2 x 3 H, Si(CH_3)$_2$), 0.83 (s, 9 H, t-Bu), 0.88 (t, 3 H, CH_3), 1.12-1.32 (bs, 10 H, 5 CH_2), 1.52-1.55 (m, 2 H, CH_2), 2.08, 2.11 (2 s, 2 x 3 H, 2 CH_3CO), 3.36 (ddd, 1 H, H-5), 3.42 (dt, 1 H, one proton of OCH_2), 3.57 (dd, 1 H, $J_{5,6a}$ 5.2, $J_{6a,6b}$ 12.6 Hz, H-6a), 3.66 (dd, 1 H, $J_{5,6b}$ 2.4 Hz, H-6b), 3.82-3.89 (m, 2 H, $J_{2,3} = J_{3,4}$ = 9.1 Hz, H-3 and one proton of OCH_2), 4.36 (d, $J_{1,2}$ 8.1 Hz, H-1), 4.86 (t, 1 H, $J_{4,5}$ 9.3 Hz, H-4), 4.90 (dd, 1 H, H-2). Anal. Calcd for $C_{24}H_{46}O_8Si$: C, 58.78; H, 9.39. Found: C, 58.80; H, 9.37.

7. Preparation of Octyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopryansyl-(1→6)-2,4-di-*O*-acetyl-β-D-glucopyranoside (**25**)

To a cooled solution (0 °C) of **23** (1.4 g, 2.86 mmol) and **24** (1.48 g, 3.0 mmol) in anhydrous methylene chloride (20 mL) was added TMSOTf (20 μL, 0.11 mmol). The mixture was stirred at this temperature for 1 h and then extra TFA (90% in water, 1 mL) was added. The mixture was stirred at rt for 4 h then concentrated. The residue was purified by a silica gel column chromatography to give **25** (1.52 g, 75%); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3 H, CH_3), 1.25-1.37 (m, 10 H, CH_2), 1.56-1.63 (m, 2 H, CH_2), 2.00, 2.03, 2.04, 2.10, 2.11, 2.12 (6 s, 6 x 3 H, CH_3CO), 3.46 (dt, 1 H, one proton of OCH_2), 3.57-3.68 (m, 3 H, $J_{5,6a}$ 1.8, $J_{6a,6b}$ 11.8 Hz, H-5,6a,6b), 3.70 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.3 Hz, H-3), 3.84-3.90 (m, 2 H, H-5' and one proton of OCH_2), 4.20 (dd, 1 H, $J_{5',6'a}$ = 4.3, $J_{6'a,6'b}$ 12.9 Hz, H-6'a), 4.22 (dd, 1 H, $J_{5',6'b}$ 2.7 Hz, H-6'b), 4.40 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.60 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 4.80 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.3 Hz, H-4), 4.82 (t, 1 H, $J_{2,3}$ 9.3 Hz, H-2), 4.99 (dd, 1 H, $J_{2',3'}$ 9.5 Hz, H-2'), 5.08 (t, 1 H, $J_{3',4'} = J_{4',5'}$ = 9.5 Hz, H-4'), 5.18 (t, 1 H, H-3'). Anal. Calcd for $C_{32}H_{50}O_{17}$: C, 54.39; H, 7.08. Found: C, 54.33; H, 7.13.

8. Preparation of Octyl 2,4,6-tri-*O*-acetyl-3-*O*-benzyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranoside (**27**)

To a cooled solution (0 °C) of **25** (1.2 g, 1.7 mmol) and **26** (962 mg, 1.78 mmol) in anhydrous methylene chloride (20 mL) was added TMSOTf (20 μL, 0.11 mmol). The mixture was stirred at this temperature for 1 h, quenched by Et_3N (1 drop), then concentrated. The residue was purified by a silica gel column chromatography to give **27** (1.455 g, 79%); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3 H, C*H*$_3$), 1.25-1.35 (bs, 10 H, 5 C*H*$_2$), 1.45-1.55 (m, 2 H, C*H*$_2$), 2.00, 2.02, 2.02, 2.03, 2.04, 2.06, 2.09, 2.09, 2.09 (7 s, 27 H, 9 C*H*$_3$CO), 3.40 (dt, 1 H, one proton of OC*H*$_2$), 3.55-3.68 (m, 5 H, H-5^B, H-5^C, H-3^A, H-6a^A, H-6b^A), 3.80-3.90 (m, 3 H, H-3^C, H-5^A, one proton of OC*H*$_2$), 4.03 (dd, 1 H, J 2.2, J 12.4 Hz, H-6a^B/H-6a^C), 4.10 (dd, 1 H, J 2.1, J 12.3 Hz, H-6a^C/H-6a^B), 4.25-4.32 (m, 3 H, J 8.1 Hz, H-1^A, H-6b^B, H-6b^C), 4.50 (d, J 8.1 Hz, H-1^C), 4.55 (s, 2 H, PhC*H*$_2$), 4.57 (d, 1 H, J 8.1 Hz, H-1^B), 4.69 (t, 1 H, J 9.7 Hz, H-4^A), 4.88-5.00 (m, 3 H, H-2^{A,B,C}), 5.06 (t, J 9.7 Hz, H-4^C), 5.09 (t, 1 H, J 9.7 Hz, H-4^B), 5.18 (t, 1 H, J 9.5, H-3^B), 7.21-7,33 (m, 5 H, Ph). Anal. Calcd for $C_{51}H_{72}O_{25}$: C, 56.46; H, 6.64. Found: C, 56.50; H, 6.60.

9. Preparation of Octyl 2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranoside (**28**)

Compound **27** (325 mg, 0.3 mmol) was dissolved in EtOAc (6 mL) and then a solution of $NaBrO_3$ (136 mg, 0.9 mmol) in water (3 mL) was added. To the well stirred two-phase system an aqueous solution of $Na_2S_2O_4$ (85% pure, 157 mg, dissolved in 6 mL water) was added dropwise over 10 min at rt. After completion of the reaction (TLC) the mixture was diluted with EtOAc and the organic phase was washed with aqueous sodium thiosulfate. The crude product was then purified by silica gel chromatography to give **28** (277 mg, 93%); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3 H, C*H*$_3$), 1.25-1.35 (bs, 10 H, 5 C*H*$_2$), 1.45-1.55 (m, 2 H, C*H*$_2$), 2.00, 2.02, 2.02, 2.03, 2.08, 2.09, 2.09, 2.10, 2.11 (8 s, 27 H, 9 C*H*$_3$CO), 2.50 (bs, 1 H, O*H*), 3.40 (dt, 1 H, one proton of OC*H*$_2$), 3.55-3.70 (m, 5 H, H-5^B, H-5^C, H-3^A, H-6a^A, H-6b^A), 3.80-3.90 (m, 3 H, H-3^C, H-5^A, one proton of OC*H*$_2$), 4.07 (dd, 1 H, J 2.2, J 12.3 Hz, H-6a^B/H-

6a^{C}), 4.11 (dd, 1 H, J 2.6, J 12.0 Hz, H-6a^{C}/H-6a^{B}), 4.27 (dd, 1 H, J 4.7 Hz, H-6b^{B}/H-6b^{C}), 4.30 (d, 1 H, J 8.2 Hz, H-1^{A}), 4.35 (dd, 1 H, J 4.8 Hz, H-6b^{C}/H-6b^{B}), 4.51 (d, J 8.0 Hz, H-1^{C}), 4.57 (d, 1 H, J 8.0 Hz, H-1^{B}), 4.70 (t, 1 H, J 9.6 Hz, H-4^{A}), 4.72 (t, 1 H, J 8.2 Hz, H-2^{A}), 4.88-5.00 (m, 3 H, H-2^{B,C}, H-4^{C}), 5.07 (t, J 9.6 Hz, H-4^{B}), 5.18 (t, 1 H, J 9.5, H-3^{B}). Anal. Calcd for $C_{44}H_{66}O_{25}$: C, 53.12; H, 6.64. Found: C, 53.10; H, 6.70.

10. Preparation of phenyl 2,4-di-*O*-acetyl-1-thio-β-D-glucopyranoside (**29**)

Compound **6** (3 g, 4.21 mmol) was dissolved into 90% aqueous TFA (15 mL) and the solution was stirred at rt for 4 h. Toluene (50 mL) was added and then the solvents were evaporated *in vacuo* to give a residue, which was purified by a silica gel column chromatography (petroleum ether-EtOAc, 1:1) to give **29** (1.36 g, 91%); ^{1}H NMR ($CDCl_3$) δ 1.95, 2.10 (2 s, 6 H, C*H*$_3$CO), 2.85 (bs, 2 H, 2 O*H*), 3.22-3.26 (m, 2 H, H-6a, H-6b), 3.50 (ddd, 1 H, $J_{4,5}$ 9.6 Hz, H-5), 3.93 (t, 1 H, $J_{2,3}$ 9.6 Hz, H-3), 4.62 (d, 1 H, $J_{1,2}$ 8.8 Hz, H-1), 4.95 (t, 1 H, $J_{3,4}$ 9.6 Hz, H-4), 5.05 (t, 1 H, H-2). Anal. Calcd for $C_{16}H_{20}O_7S$: C, 53.93; H, 5.62. Found: C, 53.85; H, 5.68.

11. Preparation of Octyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranoside (**30**)

To a cooled solution (0 °C) of **24** (280 mg, 0.57 mmol) and **29** (100 mg, 0.28 mmol) in anhydrous methylene chloride (10 mL) was added TMSOTf (10 μL, 0.05 mmol). The mixture was stirred at this temperature for 1 h, then cooling the reaction temperature to −15 °C. To the above flask was added trisaccharide **28** (278 mg, 0.28 mmol), NIS (125 mg, 0.56 mmol) and TMSOTf (25 μL, 0.14 mmol) sequentially. The reaction mixture was stirred at 0 °C for 2 h, quenched by Et_3N (2 drop), then concentrated. The residue was purified by a silica gel column chromatography to give **30** (267 mg, 50.2%) as a white foam; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3 H), 1.24-1.27 (m, 10 H), 1.40-1.50 (m, 2 H), 1.94 (s, 3 H), 1.95 (s, 3 H), 1.96 (bs, 6 H), 1.98 (s, 3 H), 1.99 (s, 6 H), 2.01 (s, 9 H), 2.02 (s, 3 H), 2.03 (s, 3 H), 2.08 (s, 3 H), 2.09 (2 s, 6 H), 2.13 (s, 3 H), 2.14 (s, 3 H), 2.23 (s, 3 H), 2.24 (s, 3 H), 3.40 (dt, 1 H, one proton of OC*H*$_2$), 3.50-3.55 (m, 1 H), 3.56-3.72 (m, 6 H), 3.72-3.77 (m, 1 H), 3.78-3.91 (m, 5

H), 3.96 (dd, 1 H), 4.05 (dd, 1 H), 4.09-4.40 (m, 3 H), 4.43-4.58 (m, 6 H), 4.62-4.75 (m, 3 H), 4.86-4.94 (m, 2 H), 4.95-5.05 (m, 4 H), 5.10-5.22 (m, 6 H). Selected ^{13}C NMR ($CDCl_3$, 100 MHz) δ 95.48, 99.95, 100.24, 100.38, 100.75, 100.89 (6 C-1), 168.55, 168.73, 168.81, 169.20 (2 C), 169.24, 169.28, 169.39, 169.44 (2 C), 170.13 (2 C), 170.20, 170.24, 170.49, 170.60, 170.63, 171.10, 171.17 (19 CH_3CO). Anal. Calcd for $C_{82}H_{116}O_{50}$: C, 51.79; H, 6.10. Found: C, 51.70; H, 6.12.