General considerations. CH$_2$Cl$_2$ was purified and dried from a safe purification system filled with anhydrous Al$_2$O$_3$. Dry CH$_3$CN was freshly distilled from CaH$_2$ under N$_2$ atmosphere. All other reagents were obtained from commercial sources and used without further purification. Water was either distilled or Milli-Q-purified. Flash column chromatography was carried out on Silica Gel 60 (230–400 mesh, E. Merck). TLC was performed on glass plates pre-coated with Silica Gel 60 F254 (0.25 mm, E. Merck); detection was executed by spraying with a solution of Ce(NH$_4$)$_2$(NO$_3$)$_6$, (NH$_4$)$_6$Mo$_7$O$_{24}$, and H$_2$SO$_4$ in water followed subsequent heating on a hot plate. Specific rotations were taken at ambient conditions and reported in $10^{-1}$·deg·cm$^2$·g$^{-1}$; the sample concentrations are in g·dL$^{-1}$. $^1$H and $^{13}$C NMR spectra were recorded on 400 and 600 MHz spectrometers. Proton peaks were assigned with the aid of 2D NMR techniques ($^1$H-$^1$H COSY, HMQC and NOESY). Coupling constants are given in Hz. The hydrogen multiplicities of carbon peaks were determined using DEPT-90 and DEPT-135 experiments.
4-Methylphenyl 3,4-di-\textit{O}-benzyl-1-thio-\textit{\textbeta}\text-d-glucopyranoside (2). TMSOTf (5 \( \mu \text{L} \), 26 \( \mu \text{mol} \)) was added to a solution of compound 1 (100 mg, 174 \( \mu \text{mol} \)) and benzaldehyde (19 \( \mu \text{L} \), 190 \( \mu \text{mol} \)) in CH\(_2\)Cl\(_2\) (1 mL) with freshly dried 3 \( \AA \) molecular sieves (120 mg) at –78 °C under N\(_2\) atmosphere. The mixture was kept stirring at same temperature for 2 h. Et\(_3\)SiH (31 \( \mu \text{L} \), 190 \( \mu \text{mol} \)), benzaldehyde (18 \( \mu \text{L} \), 183 \( \mu \text{mol} \)) and TMSOTf (5 \( \mu \text{L} \), 26 \( \mu \text{mol} \)) were sequentially added to the reaction solution. After stirring for 2.5 h at –78 °C, the reaction flask was moved to 0 °C, and BH\(_3\)-THF (1 m solution in THF, 0.87 mL, 0.87 mmol) was added to the reaction mixture, followed by addition of TMSOTf (16 \( \mu \text{L} \), 0.087 mmol). The solution was kept stirring for another 5 h at 0 °C. The reaction was slowly quenched with MeOH (5 mL) and Et\(_3\)N (1 mL) at 0 °C. The mixture was filtered through a pad of Celite, and the filtrate was coevaporated with MeOH under reduced pressure. The residue was partitioned between ethyl acetate and H\(_2\)O and the combined organic layer was washed with brine, dried over anhydrous MgSO\(_4\), filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography (ethyl acetate/hexanes = 1/2) gave the 2,6-diol 2 (70 mg, 86%) as a white solid. m.p. 115–118 °C; \([\alpha]^\text{D}_{28} \) –29.5 (c 0.9 in CHCl\(_3\)); IR (thin film): \( \nu \) 3391, 3031, 2875, 1495, 1454, 1090, 807, 733, 697 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.43 (2 H, d, \( J \) 8.1, Ar-H), 7.38–7.28 (10 H, m, Ar-H), 7.12 (2 H, d, \( J \) 8.1, Ar-H), 4.94 (1 H, d, \( J \) 11.3, ArCH\(_2\)), 4.86 (1 H, d, \( J \) 11.3, ArCH\(_2\)), 4.85 (1 H, d, \( J \) 11.0, ArCH\(_2\)), 4.64 (1 H, d, \( J \) 11.0, ArCH\(_2\)), 4.50 (1 H, d, \( J \) 9.3, 1-H), 3.89 (1 H, d, \( J \) 11.8, 6-H\(_a\)), 3.72–3.69 (1 H, m, 6-H\(_b\)), 3.61 (1 H, t, \( J \) 9.3, 2-H), 3.52 (1 H, t, \( J \) 9.3, 3-H), 3.50–3.39 (2 H, m, 4-H, 5-H), 2.71 (1H, d, \( J \) 1.9, 2-OH), 2.33 (3 H, s, CH\(_3\)), 2.27 (1 H, br s, 6-OH); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 138.5 (C), 138.4 (C), 137.8 (C), 133.3 (CH), 129.8 (CH),
128.4 (CH), 127.9 (CH), 127.87 (CH), 127.83 (CH), 127.7 (CH), 127.6 (C), 88.2 (CH), 85.7 (CH), 79.5 (CH), 77.1 (CH), 75.2 (CH2), 75.0 (CH2), 72.6 (CH), 61.9 (CH2), 21.1 (CH3); HRMS (ESI): m/z calcd for C27H30O5SNa ([M + Na]+): 489.1712, found: 489.1711.

4-Methylphenyl 3,6-di-O-benzyl-1-thio-β-D-glucopyranoside (3). TMSOTf (5 μL, 26 μmol) was added to a solution of compound 1 (100 mg, 174 μmol) and benzaldehyde (19 μL, 190 μmol) in CH2Cl2 (1 mL) with freshly dried 3 Å molecular sieves (120 mg) at −78 °C under N2 atmosphere. The mixture was stirred at same temperature for 2 h. Et3SiH (31 μL, 190 μmol), benzaldehyde (18 μL, 183 μmol) and TMSOTf (5 μL, 26 μmol) were sequentially added to the reaction solution. After stirring for another 2.5 h at −78 °C, the reaction flask was moved to 0 °C, and Me2EtSiH (70 μL, 522 μmol) and CH3CN (3 mL) were added to the reaction mixture followed by addition of TMSOTf (6 μL, 35 μmol), and the solution was kept stirring for another 1 h at 0 °C. The reaction was slowly quenched with Et3N (2 mL) at 0 °C, the mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. Purification of the residue by flash column chromatography (ethyl acetate/hexanes = 1/2) supplied the 2,4-diol 3 (58mg, 72%) as a white solid. m.p. 95–97 °C; [α]28D -35.8 (c 0.66 in CHCl3); IR (thin film): ν 3442, 2919, 1494, 1453, 1361, 1071, 809, 736, 698 cm⁻¹; ¹H NMR (400 MHz, CDCl3): δ 7.45–7.42 (2 H, m, Ar-H), 7.38–7.25 (10 H, m, Ar-H), 7.06 (2 H, d, J 7.9, Ar-H), 4.93 (1 H, d, J 11.6, ArCH2), 4.79 (1 H, d, J 11.6, ArCH2), 4.59 (1 H, d, J 12.0, ArCH2), 4.55 (1 H, d, J 12.0, ArCH2), 4.45 (1 H, d, J 9.3, 1-H), 3.78–3.75 (2 H, m, 6-Ha, 6-Hb), 3.60–3.55 (1 H, m, 2-H), 3.51–3.38 (3 H, m, 3-H, 4-H, 5-H), 2.69 (1 H, d, J 2.2, OH), 2.52 (1 H, d, J 1.6,
OH), 2.33 (3 H, s, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 138.44 (C), 138.41 (C), 137.9 (C), 133.5 (CH), 129.7 (CH), 128.6 (CH), 128.4 (CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 127.6 (CH), 80.4 (CH), 85.1 (CH), 78.5 (CH), 74.8 (CH₂), 73.6 (CH₂), 72.1 (CH), 71.1 (CH), 70.2 (C), 21.1 (CH₃); HRMS (ESI): m/z calcd for C₂₇H₃₀O₅SNa ([M + Na]⁺) 489.1712, found 489.1711.

4-Methylphenyl 2-O-acetyl-4-O-benzyl-1-thio-β-D-glucopyranoside (4). A solution of compound 1 (100 mg, 174 µmol) and benzaldehyde (19 µL, 190 µmol) in CH₂Cl₂ (1 mL) with freshly dried 3 Å molecular sieves (120 mg) was stirred at −78 °C under N₂ atmosphere. TMSOTf (5 µL, 26 µmol) was added to the solution, and the mixture was kept stirring at the same temperature for 2 h. Et₃SiH (31 µL, 191 µmol), 2-NaphCHO (29 mg, 183 µmol) and TMSOTf (5 µL, 26 µmol) were consecutively added to the reaction solution. The resultant mixture was stirred for another 3 h. Ac₂O (25 µL, 261 µmol) and TMSOTf (5 µL, 26 µmol) were consecutively added to the solution. The reaction flask was moved to 0 °C, and the mixture was stirred for 1 h. BH₃·THF (1 M solution in THF, 0.52 mL, 0.52 mmol) was added to the reaction mixture followed by addition of TMSOTf (16 µL, 87 µmol). The solution was kept stirring for another 5 h at 0 °C. H₂O (5 mL) was slowly added to the solution, the whole mixture was vigorously stirred for 5 min, and the aqueous layer was removed from the reaction bottle by using a pipette. DDQ (119 mg, 522 µmol) was then added to the solution. The mixture was stirred at room temperature for another 3 h. The reaction mixture was quenched by saturated NaHCO₃(aq) (5 mL) and 10% Na₂S₂O₃(aq) (5 mL), followed by filtration through a pad of Celite. The desired material was extracted with ethyl acetate, and the combined organic layer was
washed with brine, dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. Purification of this residue via flash column chromatography (ethyl acetate/hexanes = 1/2) furnished the desired 3,6-diol 4 (30 mg, 41%) as a white solid. m.p. 106–111 °C; [α]₂⁸⁻²₀ (c 0.4 in CHCl₃); IR (thin film): ν 3438, 2922, 1749, 1493, 1371, 1231, 1043, 752 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.35–7.24 (7 H, m, Ar-H), 7.10 (2 H, d, J 8.4, Ar-H), 4.79 (1 H, d, J 11.3, ArCH₂), 4.77 (1 H, t, J 9.6, 2-H), 4.69 (1 H, d, J 11.3, ArCH₂), 4.58 (1 H, d, J 9.6, 1-H), 3.88 (1 H, d, J 11.8, 6-Hₐ), 3.78–3.69 (2 H, m, 3-H, 6-Hₖ), 3.47 (1 H, t, J 9.6, 4-H), 3.36 (1 H, ddd, J 9.6, 4.4, 2.6, 5-H), 2.66 (1 H, s, 3-OH), 2.31 (3 H, s, CH₃), 2.14 (3 H, s, CH₃), 1.83 (1 H, s, 6-OH); ¹³C NMR (100 MHz, CDCl₃): δ 170.6 (C), 138.4 (C), 137.8 (C), 133.0 (CH), 129.8 (CH), 128.6 (CH), 128.4 (C), 128.1 (CH), 85.8 (CH), 79.2 (CH), 77.6 (CH), 76.9 (CH), 74.9 (CH₂), 72.6 (CH), 61.9 (CH₂), 21.1 (CH₃), 21.0 (CH₃); HRMS (ESI): m/z calcd for C₂₂H₂₆O₆SNa ([M + Na]⁺): 441.1348, found: 441.1342.

4-Methylphenyl 2-O-acetyl-6-O-benzyl-1-thio-β-D-glucopyranoside (5). TMSOTf (5 µL, 26 µmol) was added to a solution of compound 1 (100 mg, 174 µmol), benzaldehyde (19 µL, 190 µmol) in CH₂Cl₂ (1 mL) with freshly dried 3 Å molecular sieves (120 mg) at −78 °C under N₂ atmosphere. The mixture was kept stirring at the same temperature for 2 h. Et₃SiH (31 µL, 190 µmol), 2-NaphCHO (29 mg, 183 µmol) and TMSOTf (5 µL, 26 µmol) were consecutively added to the reaction solution and the mixture was stirred at −78 °C for another 3 h. Ac₂O (18 µL, 261 µmol) and TMSOTf (5 µL, 26 µmol) were consecutively added to the solution, the reaction flask
was moved to 0 °C, and the mixture was stirred at the same temperature 1 h. Me₂EtSiH (46 µL, 0.348 mmol) and CH₃CN (3 mL) were added to the reaction mixture followed by TMSOTf (6 µL, 35 µmol), and the solution was kept stirring for another 1 h at 0 °C. DDQ (119 mg, 522 µmol) and H₂O (0.1 mL) were added to the solution, and the mixture was stirred at room temperature for 3 h. The reaction mixture was quenched by saturated NaHCO₃(aq) (5 mL) and 10% Na₂S₂O₃(aq) (5 mL), then filtered through a pad of Celite. The desired material was extracted with ethyl acetate and the combined organic layer was washed with brine, dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography (ethyl acetate/hexanes = 1/2) furnished the 3,4-diol 5 (34 mg, 47%) as a white solid. m.p. 155–157 °C; [α]²⁸_D +40.7 (c 0.36 in CHCl₃); IR (thin film): ν 3491, 2920, 2872, 1723, 1495, 1375, 1268, 1077, 1049, 743, 695 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.38–7.26 (7 H, m, Ar-H), 7.04 (2 H, d, J 8.3, Ar-H), 4.75 (1 H, t, J 9.2, 2-H), 4.57 (1 H, d, J 11.8, ArCH₂), 4.56 (1 H, d, J 9.2, 1-H), 4.53 (1 H, d, J 11.8, ArCH₂), 3.76 (2 H, d, J 4.5, 6-H × 2), 3.59 (1 H, t, J 9.2, 3-H), 3.53 (1 H, t, J 9.2, 4-H), 3.48–3.43 (1 H, m, 5-H), 3.26 (1 H, br s, OH), 3.00 (1 H, br s, OH), 2.29 (3 H, s, CH₃), 2.14 (3 H, s, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 170.7 (C), 138.3 (C), 137.7 (C), 133.2 (CH), 129.6 (CH), 128.4 (CH), 127.8 (C), 127.7 (CH), 85.9 (CH), 78.1 (CH), 76.7 (CH), 73.7 (CH₂), 72.2 (CH), 72.0 (CH), 70.1 (CH₂), 21.1 (CH₃), 21.0 (CH₃); HRMS (ESI): m/z calcd for C₂₂H₂₆O₆SNa ([M + Na]^+): 441.1348, found: 441.1341.

4-Methylphenyl 2-O-Benzoyl-3-O-benzyl-1-thio-β-D-glucopyranoside (6). TMSOTf (6.2 µL, 34 µmol) was added to solution of compound 1 (106 mg, 185 µmol), benzaldehyde (19 µL,
190 \( \mu \text{mol} \) in \( \text{CH}_2\text{Cl}_2 \) (1.6 mL) with freshly dried 3 Å molecular sieves (160 mg) at 0 °C under \( \text{N}_2 \) atmosphere. The mixture was kept stirring at the same temperature for 2 h. After cooling to to \(-78 \text{ °C} \), \( \text{Et}_3\text{SiH} \) (33 \( \mu \text{L, 207 } \mu \text{mol} \)), benzaldehyde (19 \( \mu \text{L, 190 } \mu \text{mol} \)) and TMSOTf (3.4 \( \mu \text{L, 19 } \mu \text{mol} \)) were sequentially added, and the resulting mixture was stirred at \(-78 \text{ °C} \) for another 3 h. The reaction flask was moved to 0 °C, and \( \text{Bz}_2\text{O} \) (130 mg, 0.56 mmol), and TMSOTf (3.4 \( \mu \text{L, 19 } \mu \text{mol} \)) were then added. The reaction flask was gradually warmed up to room temperature and the mixture was stirred at the same temperature for 18 h. 70% TFA\((\text{aq}) \) (3 mL) was added to the resulting solution and the mixture was continuously stirred at room temperature for another 1 h. The reaction was quenched by saturated \( \text{NaHCO}_3(\text{aq}) \), and the desired material was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over \( \text{MgSO}_4 \), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (ethyl acetate/hexanes = 1/1) to afford the 4,6-diol 6 (67 mg, 75%). mp 117–118 °C; \([\alpha]^{22}_D +12.9 \ (c 1.0 \text{ in CHCl}_3); \text{IR (thin film): } \nu 3630, 3100, 1724, 1267, 1254, 1094, 1070 \text{ cm}^{-1}; \text{H NMR (400 MHz, CDCl}_3): \delta 8.07–8.05 \ (2 \text{ H, Ar-H}), 7.61–7.57 \ (1 \text{ H, m, Ar-H}), 7.49–7.44 \ (2 \text{ H, m, Ar-H}), 7.30 \ (2 \text{ H, d, J 8.1, Ar-H}), 7.21–7.15 \ (5 \text{ H, m, Ar-H}), 7.06 \ (2 \text{ H, d, J 7.9, Ar-H}), 5.20 \ (1 \text{ H, dd, J 10.0, 9.0, 2-H}), 4.75 \ (1 \text{ H, d, J 10.0, 1-H}), 4.70 \ (1 \text{ H, d, J 11.4, ArCH}_2), 4.55 \ (1 \text{ H, d, J 11.4, ArCH}_2), 3.90 \ (1 \text{ H, ddd, J 12.0, 6.6, 3.4, 6-H}_a), 3.81–3.75 \ (1 \text{ H, m, 6-H}_b), 3.71–3.66 \ (2 \text{ H, m, 3-H, 4-H}), 3.46–3.42 \ (1 \text{ H, m, 5-H}), 2.37 \ (1 \text{ H, d, J 2.2, 4-OH}), 2.30 \ (3 \text{ H, s, ArCH}_3), 2.11 \ (1 \text{ H, t, J 6.6, 6-OH}); \text{C NMR (100 MHz, CDCl}_3): \delta 165.2 \ (\text{C}), 138.4 \ (\text{C}), 137.6 \ (\text{C}), 133.3 \ (\text{CH}), 133.1 \ (\text{CH}), 129.9 \ (\text{CH}), 129.7 \ (\text{CH}), 128.6 \ (\text{C}), 128.51 \ (\text{CH}), 128.49 \ (\text{CH}), 128.0 \ (\text{CH}), 86.6 \ (\text{CH}), 83.9 \ (\text{CH}), 79.4 \ (\text{CH}), 74.8 \ (\text{CH}_2), 72.4 \ (\text{CH}), 70.3 \ (\text{CH}), 62.6 \ (\text{CH}_2), 21.1 \ (\text{CH}_3); \text{HRMS (FAB): } m/z \text{ calcd for C}_{27}\text{H}_{29}\text{O}_6\text{S ([M + H]}^+\text{): 481.1685, found: 481.1696.}
4-Methylphenyl 2,3-di-O-acetyl-1-thio-β-D-glucopyranoside (7). TMSOTf (5 µL, 26 µmol) was added to a solution of compound 1 (100 mg, 174 µmol) and benzaldehyde (19 µL, 190 µmol) in CH₂Cl₂ (1 mL) with freshly dried 3 Å molecular sieves (120 mg) at 0 °C under N₂ atmosphere. The mixture was stirred at same temperature for 2 h. Ac₂O (40 µL, 418 µmol) and TMSOTf (10 µL, 52 µmol) were consecutively added to the solution, and the mixture was stirred at the same temperature. After stirring for 1 h, 70% TFAₐq (1 mL) was added to the resulting solution, ice-bath was removed, and the reaction was continuously stirred at room temperature for another 1 h. The reaction was quenched by saturated NaHCO₃ₐq (5 mL), and the desired material was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over MgSO₄, filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography (ethyl acetate/hexanes = 2/1) to acquire the 2,3-diacetate 7 (45 mg, 70%) as a colorless oil. [α]²⁸ D –28.4 (c 0.88, CHCl₃); IR (thin film): ν 3441, 2930, 1752, 1374, 1044, 900, 808, 759 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.32 (2 H, d, J 8.1, Ar-H), 7.08 (2 H, d, J 8.1, Ar-H), 5.03 (1 H, t, J 9.6, 2-H), 4.84 (1 H, t, J 9.6, 3-H), 4.65 (1 H, d, J 9.6, 1-H), 3.87 (1 H, dd, J 12.1, 3.3, 6-Ha), 3.77 (1 H, dd, J 12.1, 4.3, 6-Hb), 3.66 (1 H, t, J 9.6, 4-H), 3.6 (1 H, br s, OH), 3.38 (1 H, ddd, J 9.6, 4.3, 3.3, 5-H), 2.69 (1 H, br s, OH), 2.3 (3 H, s, CH₃), 2.05 (3 H, s, CH₃), 2.02 (3 H, s, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 171.3 (C), 169.6 (C), 133.1 (CH), 129.8 (CH), 128.1 (C), 85.9 (CH), 79.6 (CH), 76.8 (CH2), 70.15 (CH), 68.7 (CH), 61.9 (CH₂), 21.1 (CH₃), 20.8 (CH₃), 20.8 (CH₃); HRMS (ESI): m/z calcd for C₂₂H₂₆O₆SNa ([M + Na]⁺): 393.0984, found: 393.0992.
4-Methylphenyl 2,6-di-O-acetyl-3,4-di-O-benzyl-1-thio-β-D-glucopyranoside (8).

TMSOTf (5 µL, 26 µmol) was added to a solution of compound 1 (100 mg, 174 µmol) and benzaldehyde (19 µL, 190 µmol) in CH₂Cl₂ (1 mL) with freshly dried 3 Å molecular sieves (160 mg) at −78 °C under N₂ atmosphere. The mixture was stirred at same temperature for 2 h. Et₃SiH (31 µL, 190 µmol), benzaldehyde (18 µL, 183 µmol) and TMSOTf (5 µL, 26 µmol) were sequentially added to the reaction solution. After stirring at −78 °C for another 2.5 h, the reaction flask was moved to 0 °C. BH₃·THF (1 M solution in THF, 0.87 mL, 0.87 mmol) was added to the reaction mixture followed by TMSOTf (16 µL, 87 µmol), and the solution was kept stirring for another 5 h at 0 °C. Borane was slowly quenched with MeOH (70 µL, 1.74 mmol) at 0 °C, followed by further stirring for 30 min. Et₃N (1.4 mL, 8.7 mmol), Ac₂O (0.66 mL, 6.96 mmol) and DMAP (2 mg, 17.4 µmol) were added to the reaction mixture and the solution was stirred at room temperature for another 12 h. The whole mixture was filtered through a pad of Celite. H₂O was added to the filtrate followed by extraction with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography (ethyl acetate/hexanes = 1/4) to afford the diacetate 8 (74 mg, 77%) as a white solid. m.p. 132–136 °C; [α]²⁸D +10.9 (c 0.76 in CHCl₃); IR (thin film): ν 2901, 1742, 1453, 1358, 1238, 1126, 1043, 808, 743, 696 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ 7.36 (2 H, d, J 8.1, Ar-H), 7.34–7.24 (8 H, m, Ar-H), 7.23–7.22 (2 H, m, Ar-H ), 7.07 (2 H, d, J 7.8, Ar-H ), 4.94 (1 H, t, J 9.8, 2-H), 4.80–4.76 (2 H, m, ArCH₂), 4.66 (1 H, d, J 11.3, ArCH₂), 4.54 (1 H, d, J 11.6, ArCH₂), 4.51 (1 H, d, J 9.8, 1-H), 4.38 (1 H, dd, J 11.9, 1.8, 6-Hₐ), 4.15 (1 H, dd, J 11.9, 4.7, 6-Hₐ), 3.67 (1 H, t, J
8.7, 3-H), 3.56–3.52 (2 H, m, 4-H, 5-H), 2.31 (3 H, s, CH₃), 2.02 (3 H, s, CH₃), 2.00 (3 H, s, CH₃); ¹³C NMR (150 MHz, CDCl₃): δ 170.5 (C), 169.4 (C), 138.1 (C), 137.8 (C), 137.4 (C), 133.18 (CH), 129.4 (CH), 128.5 (C), 128.4 (CH), 128.3 (CH), 127.9 (CH), 128.0 (CH), 127.9 (CH), 127.8(CH), 86.0 (CH), 84.4 (CH), 77.3 (CH), 76.9 (CH), 75.3 (CH₂), 75.0 (CH₂), 71.6 (CH), 62.8 (CH₂), 21.0 (CH₃), 20.9 (CH₃), 20.7 (CH₃); HRMS (ESI): m/z calcd for C₃₁H₃₄O₇SNa ([M + Na]⁺): 573.1923, found: 573.1924.

4-Methylphenyl 2,4-di-O-acetyl-3,6-di-O-benzyl-1-thio-β-D-glucopyranoside (9). TMSOTf (5 µL, 26 µmol) was added to a solution of compound 1 (100 mg, 174 µmol) and benzaldehyde (19 µL, 190 µmol) in CH₂Cl₂ (1 mL) with freshly dried 3 Å molecular sieves (150 mg) at −78 °C under N₂ atmosphere. The mixture was stirred for 2 h at the same temperature. Et₃SiH (31 µL, 190 µmol), benzaldehyde (18 µL, 183 µmol) and TMSOTf (5 µL, 26 µmol) were sequentially added to the reaction solution. After stirring for another 2.5 h at −78 °C, the reaction flask was moved to 0 °C. Me₂EtSiH (69 µL, 522 µmol) and CH₃CN (3 mL) were added to the reaction mixture followed by addition of TMSOTf (5 µL, 26 µmol). The solution was kept stirring for another 1 h at 0 °C. Then, Ac₂O (75 µL, 783 µmol) and TMSOTf (15 µL, 78 µmol) were consecutively added to the mixture, which stirred further for 12 h at the same temperature. The reaction was slowly quenched by Et₃N (2 mL) at 0 °C, the mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (ethyl acetate/hexanes = 1/4) to obtain the desired fully protected thioglucoside 9 (40 mg, 42%) as a white solid. m.p. 110–112 °C; [α]²⁸D −12.2 (c
0.76 in CHCl₃); IR (thin film): ν 2868, 1749, 1372, 1220, 1061, 737, 698 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.40 (2 H, d, J 8.1, Ar-H), 7.37–7.20 (10 H, m, Ar-H), 7.03 (2 H, d, J 8.1, Ar-H), 5.04–5.00 (2 H, m, 4-H), 4.62–4.55 (3 H, m, 1-H, ArCH₂), 4.53–4.47 (2 H, m, ArCH₂), 3.70 (1 H, t, J 9.2, 3-H), 3.63–3.54 (3 H, m, 5-H, 6-H × 2), 2.29 (3 H, s, CH₃), 2.04 (3 H, s, CH₃), 1.88 (3 H, s, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 169.4 (C), 169.2 (C), 138.1 (C), 137.9 (C), 137.8 (C), 132.9 (CH), 129.6 (CH), 128.7 (C), 128.3 (CH), 128.2 (CH), 127.7 (CH), 127.6 (CH), 86.3 (CH), 81.6 (CH), 77.8 (CH), 73.9 (CH₂), 73.6 (CH₂), 71.4 (CH), 70.6 (CH), 69.7 (CH₂), 21.0 (CH₃), 20.9 (CH₃), 20.7 (CH₃); HRMS (ESI): m/z calcd for C₃₁H₃₄O₇SNa ([M + Na]+): 573.1923, found: 573.1926.

4-Methylphenyl 4-O-benzyl-1-thio-β-D-glucopyranoside (10). TMSOTf (5 µL, 26 µmol) was added to a mixture of compound 1 (100 mg, 174 µmol) and benzaldehyde (19 µL, 190 µmol) in CH₂Cl₂ (1 mL) with freshly dried 3 Å molecular sieves (120 mg) at 0 °C under N₂ atmosphere. After 2 h of stirring at 0 °C, BH₃·THF (1 M solution in THF, 0.87 mL, 0.87 mmol) was added to the reaction mixture followed by addition of TMSOTf (16 µL, 87 µmol). The solution was kept stirring for another 5 h at 0 °C. The reaction was slowly quenched with MeOH (5 mL) and Et₃N (1 mL) at 0 °C, the mixture was filtered through a pad of Celite, and the filtrate was coevaporated with MeOH under reduced pressure. Ethyl acetate and H₂O were added to the residue followed by extraction with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. Purification by flash column chromatography (CHCl₃/MeOH = 20/1) provided the 2,3,6-triol 10.
(53 mg, 81%) as a white solid. m.p. 113–116 °C; \([\alpha]^{28}\)D –41.7 (c 0.26 in CHCl₃); IR (thin film): \(\nu\) 3419, 1493, 1028, 807, 751, 699 cm⁻¹; \(^1\)H NMR (400 MHz, CDCl₃): \(\delta\) 7.38 (2 H, d, \(J\) 8, Ar-H), 7.31–7.23 (5 H, m, Ar-H), 7.07 (2 H, d, \(J\) 8, Ar-H), 4.83 (1 H, d, \(J\) 11.3, ArCH₂), 4.65 (1 H, d, \(J\) 11.3, ArCH₂), 4.47 (1 H, d, \(J\) 9.7, 1-H), 3.86 (1 H, d, \(J\) 11.8, 6⁻Hₐ), 3.71–3.67 (2 H, m, 2-H, 6⁻Hₐ), 3.48 (1 H, br s, OH), 3.44–3.30 (4 H, m, 3-H, 4-H, 5-H, OH), 2.41 (1 H, d, \(J\) 1.9, 6-OH), 2.30 (3 H, s, CH₃); \(^{13}\)C NMR (100 MHz, CDCl₃): \(\delta\) 138.4 (C), 138.0 (C), 133.0 (CH), 129.8 (CH), 128.5 (CH), 127.9 (CH), 127.8 (CH), 87.9 (CH), 79.2 (CH), 78 (CH), 76.9 (CH), 74.7 (CH₂), 72.3 (CH), 62.0 (CH₂), 21.1 (CH₃); HRMS (ESI): \(m/z\) calcd for C₂₀H₂₄O₅SNa ([M + Na]⁺): 399.1242, found: 399.1246.

4-Methylphenyl 6-O-benzyl-1-thio-β-D-glucopyranoside (11). TMSOTf (5 \(\mu\)L, 26 \(\mu\)mol) was added to a solution of compound 1 (100 mg, 174 \(\mu\)mol) and benzaldehyde (19 \(\mu\)L, 190 \(\mu\)mol) in CH₂Cl₂ (1 mL) with freshly dried 3 Å molecular sieves (120 mg) at 0 °C under N₂ atmosphere. The mixture was stirred at same temperature for 2 h; then moved to 0 °C afterwards. Me₂EtSiH (46 \(\mu\)L, 0.522 mmol) and CH₃CN (3 mL) were added to the reaction mixture followed by addition of TMSOTf (6 \(\mu\)L, 35 \(\mu\)mol), and the solution was kept stirring for 1 h at 0 °C. TBAF (1.74 mL, 1.74 mmol) was added to the mixture, the reaction flask was gradually warmed up to room temperature, and the solution was kept stirring overnight. The whole mixture was filtered through a pad of Celite, and the filtrate was mixed with saturated NaHCO₃(aq) (10 mL). The desired material was extracted with ethyl acetate, and the combined organic layer was washed with brine, dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The
residue was purified by flash column chromatography (ethyl acetate/hexanes = 2/1) to obtain the
2,3,4-triol 11 (32 mg, 51%) as a white solid. m.p. 79–81 °C; [α]$_D^{28}$ –47.3 (c 0.4 in CHCl$_3$); IR
(thin film): ν 3375, 2919, 1493, 1366, 1045, 808, 733, 696 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.38 (2 H, d, $J$ 8.1, Ar-H), 7.30–7.21 (5 H, m, Ar-H), 6.97 (2 H, d, $J$ 8.1, Ar-H), 4.87
(1 H, br s, OH), 4.35–4.43 (3 H, m, 1-H, ArCH$_2$), 4.28 (1 H, br s, OH), 4.12 (1 H, br s, OH), 3.72
(1 H, dd, $J$ 10.9, 2.8, 6-H$_a$), 3.64 (1 H, dd, $J$ 10.9, 4.9, 6-H$_b$), 3.53–3.38 (3 H, m, 2-H, 3-H, 5-H),
3.3 (1 H, t, $J$ 9.1, 4-H), 2.23 (3 H, s, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 138.0 (C), 137.9 (C),
133.0 (CH), 129.7 (CH), 128.5 (CH), 128.4 (CH), 127.8 (CH), 127.67 (CH), 87.9 (CH), 78.7
(CH), 77.9 (CH), 73.6 (CH$_2$), 71.9 (CH), 70.7(CH), 69.9 (CH$_2$), 21.1 (CH$_3$); HRMS (ESI): $m$/z
calcd for C$_{20}$H$_{24}$O$_5$SNa ([M + Na]$^+$): 399.1242, found: 399.1248.

4-Methylphenyl 3-O-benzyl-1-thio-β-D-glucopyranoside (12). TMSOTf (5 µL, 26 µmol)
was added to a solution of compound 1 (100 mg, 174 µmol) and benzaldehyde (19 µL, 190 µmol)
in CH$_2$Cl$_2$ (1 mL) with freshly dried 3 Å molecular sieves (120 mg) at –78 °C under N$_2$
atmosphere. The mixture was stirred for 2 h at the same temperature. Et$_3$SiH (31 µL, 190 µmol),
benzaldehyde (18 µL, 183 µmol) and TMSOTf (5 µL, 26 µmol) were successively added to the
solution. After stirring for another 2.5 h at –78 °C, the reaction flask was moved to 0 °C. A 70%
aqueous TFA solution (1 mL) was added to the resultant mixture. The reaction was continuously
stirred at room temperature for 1 h. The reaction was quenched by saturated NaHCO$_3$(aq),
followed by extraction with ethyl acetate. The combined organic layer was washed with brine,
dried over MgSO$_4$, filtered and concentrated under reduced pressure. The residue was purified
by flash column chromatography (ethyl acetate/hexanes = 1/1) to afford the 2,4,6-triol 12 (40 mg, 62%) as a white solid. m.p. 136–140 °C; $\left[\alpha\right]_{D}^{28} -72.4$ (c 0.6 in CHCl$_3$); IR (thin film): $\nu$ 3325, 1493, 1367, 1121, 1035, 808, 751, 701 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.41–7.37 (2 H, m, Ar-H), 7.10 (2 H, d, J 7.9, Ar-H), 4.97 (1 H, d, J 11.6, ArCH$_2$), 4.74 (1 H, d, J 11.6, ArCH$_2$), 4.47 (1 H, d, J 9.3, 1-H), 3.87–3.84 (1 H, m, 6-H$_a$), 3.76–3.70 (1 H, m, 6-H$_b$), 3.44–3.32 (3 H, m, 3-H, 4-H, 5-H), 2.67 (1 H, d, J 2.6, OH), 2.61 (1 H, d, J 1.6, OH), 2.32 (3 H, s, CH$_3$), 2.30–2.27 (1 H, m, OH); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.7 (C), 138.4 (C), 133.3 (CH), 129.9 (CH), 128.6 (CH), 128.0 (CH), 127.5 (C), 88.7 (CH), 85.1 (CH), 79.4 (CH), 74.8 (CH$_2$), 72.5 (CH), 69.9 (CH), 62.6 (CH$_2$), 21.1 (CH$_3$); HRMS (ESI): $m/z$ calcd for C$_{20}$H$_{24}$O$_5$SNa ([M + Na]$^+$): 399.1242, found: 399.1235.

![Image](image.png)

4-Methylphenyl 2-O-acetyl-1-thio-β-D-glucopyranoside (13). TMSOTf (5 $\mu$L, 26 $\mu$mol) was added to a solution of compound 1 (100 mg, 174 $\mu$mol) and benzaldehyde (19 $\mu$L, 190 $\mu$mol) CH$_2$Cl$_2$ (1 mL) with freshly dried 3 Å molecular sieves (120 mg) at –78 °C under N$_2$ atmosphere. The mixture was kept stirring at the same temperature for 2 h. Et$_3$SiH (31 $\mu$L, 228 $\mu$mol), 2-NaphCHO (29 mg, 183 $\mu$mol) and TMSOTf (5 $\mu$L, 26 $\mu$mol) were consecutively added to the reaction solution. After stirring at –78 °C for 3 h, Ac$_2$O (25 $\mu$L, 261 $\mu$mol) and TMSOTf (5 $\mu$L, 26 $\mu$mol) were consecutively added to the solution, the reaction flask was moved to 0 °C, and the mixture was stirred at the same temperature for 1 h. A 70% aqueous TFA (1 mL) was added to the resulting solution, the ice-bath was removed, and the reaction was continuously stirred at room temperature for another 1 h. The reaction was quenched by saturated NaHCO$_3$(aq),
followed by extraction with ethyl acetate. The combined organic layer was washed with brine, dried over MgSO₄, filtered and concentrated under reduced pressure. Purification by flash column chromatography (CHCl₃/MeOH = 15/1) gave the 3,4,6-triol product 13 (30 mg, 53%) as a white solid. m.p. 201–205 °C; [α]₂⁰⁸D −63.2 (c 0.3 in ethyl acetate); IR (thin film): ν 3510, 3234, 2923, 1721, 1456, 1040, 810, 720, 668 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.40–7.37 (2 H, m, Ar-H), 7.11 (2 H, d, J 7.9, Ar-H), 4.73–4.64 (2 H, m, 1-H, 2-H), 3.86 (1 H, dd, J 12.1, 2.1, 6-Hₐ), 3.67 (1 H, dd, J 12.1, 5.4, 6-Hₐ), 3.53 (1 H, t, J 8.6, 3-H), 3.38–3.29 (2 H, m, 4-H, 5-H), 2.30 (3 H, s, CH₃), 2.10 (3 H, s, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 171.8 (C), 139.0 (CH), 133.4 (CH), 133.1 (C), 130.6 (CH), 87.7 (CH), 82.2 (CH), 77.5 (CH), 74.0 (CH), 71.4 (CH), 62.8 (CH₂), 21.1(CH₃); HRMS (ESI): m/z calcd for C₁₅H₂₀O₆SNa ([M + Na⁺]: 351.0878, found: 351.0876.

![Chemical Structure](image)

**4-Methylphenyl 2,3,6-tri-O-acetyl-4-O-benzyl-1-thio-β-D-glucopyranoside (14).**

TMSOTf (5 µL, 26 µmol) was added to a solution of compound 1 (100 mg, 174 µmol) and benzaldehyde (19 µL, 190 µmol) in CH₂Cl₂ (1 mL) with freshly dried 3 Å molecular sieves (120 mg) at 0 °C under N₂ atmosphere. The mixture was stirred for 2 h at same temperature. BH₃·THF (1 M solution in THF, 0.9 mL, 0.9 mmol) was added to the reaction mixture followed by addition of TMSOTf (16 µL, 87 µmol). After 5 h of stirring at 0 °C, BH₃ was slowly quenched by MeOH (70 µL, 1.74 mmol) at 0 °C, and the mixture was stirred for 30 min. Et₃N (3.6 mL, 26.1 mmol), Ac₂O (1.6 mL, 17.4 mmol) and DMAP (2 mg, 17.4 µmol) were added to the reaction mixture, followed by 12 h of stirring at room temperature. The whole mixture was
filtered through a pad of Celite. H₂O was added to the filtrate and the desired material was
extracted with ethyl acetate. The combined organic layer was washed with brine, dried over
anhydrous MgSO₄, filtered and concentrated under reduced pressure. Purification of the residue
by flash column chromatography (ethyl acetate/hexanes = 1/3) supplied the triacetate 14 (67 mg,
77%) as a white solid. m.p. 95–98 °C; [α]²⁸ D –26.9 (c 0.96 in CHCl₃); IR (thin film): ν 2945,
1751, 1366, 1231, 1046, 809, 752, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.34 (2 H, d, J 8.1, Ar-H), 7.31–7.19 (5 H, m, Ar-H), 7.07 (2 H, d, J 8.1, Ar-H), 5.23 (1 H, t, J 9.6, 2-H), 4.82
(1 H, t, J 9.6 Hz, 3-H), 4.59 (1 H, d, J 9.6, 1-H), 4.55 (1 H, d, J 11.3, ArCH₂), 4.51 (1 H, d, J 11.3, ArCH₂), 4.38 (1 H, d, J 11.9, 6-H₆), 4.14 (1 H, dd, J 11.9, 3.4, 6-H₆), 3.59–3.53 (2 H, m, 4-H, 5-H), 2.30 (3 H, s, CH₃), 2.04 (3 H, s, CH₃), 2.01 (3 H, s, CH₃), 1.91 (3 H, s, CH₃); ¹³C NMR
(100 MHz, CDCl₃): δ 170.5 (C), 169.7 (C), 169.0 (C), 137.3 (C), 137.3 (C), 133.8 (CH), 129.7
(CH), 128.7 (CH), 128.2 (CH), 128.1 (CH), 127.9 (C), 85.6 (CH), 77.0 (CH), 76.3 (CH), 75.7
(CH), 74.8 (CH₂), 70.6 (CH), 62.8 (CH₂), 21.3 (CH₃), 20.9 (CH₃ × 3); HRMS (ESI): m/z calcd

4-Methylphenyl 2,3,4-tri-O-acetyl-6-O-benzyl-1-thio-β-D-glucopyranoside (15).

TMSOTf (5 µL, 26 µmol) was added to a solution of compound 1 (100 mg, 174 µmol) and
benzaldehyde (19 µL, 190 µmol) in CH₂Cl₂ (1 mL) with freshly dried 3 Å molecular sieves (120
mg) at 0 °C under N₂ atmosphere. The mixture was stirred at same temperature for 2 h, then
Me₂EtSiH (69 µL, 0.522 mmol) and acetonitrile (3 mL) were added to the reaction mixture
followed by addition of TMSOTf (5 µL, 26 µmol). After stirring for 1 h at 0 °C, Ac₂O (66 µL,
696 \mu\text{mol}) and TMSOTf (15 \mu\text{L}, 78 \mu\text{mol}) were consecutively added to the solution. Stirring was continued at 0 °C for 12 h. The reaction was slowly quenched by Et$_3$N (2 mL), the mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. Purification by flash column chromatography (ethyl acetate/hexanes = 1/3) furnished the triacetate 15 (41 mg, 47%) as a white solid. m.p. 92–95 °C; [\alpha]$_{28}^D$ –8.8 (c 0.55 in CHCl$_3$); IR (thin film): ν 2922, 1755, 1494, 1373, 1243, 1219, 1048, 912, 808, 699 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.39–7.27 (7 H, m, Ar-H), 7.04 (2 H, d, $J$ 8.4, Ar-H ), 5.18 (1 H, t, $J$ 9.7, 2-H), 5.00 (1 H, t, $J$ 9.7, 3-H), 4.92 (1 H, dd, $J$ 9.9, 9.7, 4-H), 4.63 (1 H, d, $J$ 9.7, 1-H), 4.52 (1 H, d, $J$ 11.8 Hz, ArCH$_2$), 4.47 (1 H, d, $J$ 11.8, ArCH$_2$), 3.69–3.64 (1 H, m, 5-H), 3.57 (2 H, m, 6-H × 2), 2.30 (3 H, s, CH$_3$), 2.06 (3 H, s, CH$_3$), 1.96 (3 H, s, CH$_3$), 1.90 (3 H, s, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 170.2 (C), 169.5 (C), 169.2 (C), 138.5 (C), 137.8 (C), 133.5 (CH), 129.7 (CH), 128.3 (CH), 127.8 (CH), 127.7 (CH), 85.8 (CH), 77.5 (CH), 74.2 (CH), 73.6 (CH), 70.1 (CH$_2$), 69.1 (CH), 69.0 (CH$_2$), 21.1 (CH$_3$), 20.6 (CH$_3$ × 3); HRMS (ESI): $m/z$ calcd for C$_{26}$H$_{30}$O$_8$SNa ([M + Na]$^+$): 525.1559, found: 525.1563.

**Methyl 6-O-(2-O-acetyl-3-O-benzyl-4,6-O-benzylidene-β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (18).** TMSOTf (9 \mu\text{L}, 52 \mu\text{mol}) was added to a solution of compound 1 (200 mg, 348 \mu\text{mol}) and benzaldehyde (39 \mu\text{L}, 383 \mu\text{mol}) in CH$_2$Cl$_2$ (3 mL) with freshly dried 3 Å molecular sieves (400 mg) at –78 °C under N$_2$ atmosphere. The mixture was kept stirring at the same temperature for 2 h. Et$_3$SiH (61 \mu\text{L}, 383 \mu\text{mol}), benzaldehyde (37 \mu\text{L,
366 µmol) and TMSOTf (9 µL, 52 µmol) were consecutively added to the reaction solution. After stirring at –78 °C for 2.5 h, Ac₂O (40 µL, 365 µmol) and TMSOTf (9 µL, 52 µmol) were consecutively added to the solution, the reaction flask was moved to 0 °C, and the mixture was stirred at the same temperature 1 h. The solution of glycosyl acceptor 17 (156 mg, 522 µmol) in CH₂Cl₂ (1 ml), NIS (97 mg, 420 µmol) and TfOH (6 µL, 70 µmol) were sequentially added to the solution at –78 °C. The reaction temperature gradually raised to 0 °C for a period of 2 h. Saturated NaHCO₃(aq) (5 mL) and 10% Na₂S₂O₃(aq) (5 mL) were added to quench the reaction, the mixture was filtered through Celite followed by extraction with CH₂Cl₂, and the combined organic layer was dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography (ethyl acetate/hexanes = 1/3) furnished the desired adduct 18 (121 mg, 41%) as a white foam. [α]²⁷D +10.7 (c 3.4 in CHCl₃); IR (thin film): ν 2927, 1752, 1230, 1095, 1070, 698 cm⁻¹, ¹H NMR (600 MHz, CDCl₃): δ 7.48–7.47 (2 H, m, Ar-H), 7.41–7.25 (23 H, m, Ar-H), 5.46 (1 H, s, ArCH), 4.91–4.88 (2 H, m, 2-H’, ArCH₂), 4.85 (1 H, d, J 12.1, ArCH₂), 4.80–4.76 (2 H, m, ArCH₂), 4.72 (1 H, d, J 12.0, ArCH₂), 4.63–4.60 (2 H, m, ArCH₂), 4.57 (1 H, d, J 3.6, 1-H), 4.40 (1 H, d, J 8.1, 1-H’), 4.37 (1 H, d, J 12.0, ArCH₂), 4.11 (1 H, dd, J 10.5, 4.9, 6-H₄a), 3.86–3.80 (2 H, m, 3-H, 4-H), 3.73 (1 H, dd, J 10.5, 2.7, 6-H₄a), 3.63 (1 H, t, J 9.3, 3-H), 3.73 (1 H, dd, J 10.5, 2.7, 6-H₄a), 3.59–3.55 (2 H, m, 5-H, 6-H₆b), 3.50–3.44 (2 H, m, 2-H, 3-H’), 3.40 (1 H, t, J 10.3, 6-H₆b), 3.36 (3 H, s, OCH₃), 3.12 (1 H, td, J 9.7, 5.0, 5-H’), 1.91 (3 H, s, CH₃); ¹³C NMR (150 MHz, CDCl₃): δ 169.0 (C), 139.3 (C), 138.3 (C), 137.6 (C), 137.2 (C), 129.0 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.26 (CH), 128.22 (CH), 128.20 (CH), 128.1 (CH), 128.0 (CH), 127.7 (CH), 127.67 (CH), 127.60 (CH), 127.4 (CH), 127.2 (CH), 126.0 (CH), 101.1 (CH), 100.7 (CH), 98.4 (CH), 81.6 (CH), 79.8 (CH), 78.8 (CH), 78.5 (CH), 75.3 (CH₂), 73.9 (CH₂), 73.6 (CH₂), 73.5 (CH₂), 73.2
(CH), 69.8 (CH), 68.5 (CH₂), 67.4 (CH₂), 65.8 (CH), 55.3 (CH₃), 20.9 (CH₃); HRMS (ESI): m/z calcd for C₅₀H₅₄O₁₂Na ([M + Na⁺]: 869.3513, found: 869.3499.

Methyl 4-O-(2-O-acetyl-3-O-benzyl-4,6-O-benzylidene-β-D-glucopyranosyl)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (20). TMSOTf (5 µL, 32 µmol) was added to a solution of compound 1 (120 mg, 215 µmol) and benzaldehyde (24 µL, 237 µmol) in CH₂Cl₂ (2 mL) with freshly dried 3 Å molecular sieves (240 mg) at −78 °C under N₂ atmosphere. The mixture was kept stirring at the same temperature for 2 h. Et₃SiH (37 µL, 237 µmol), benzaldehyde (22 µL, 226 µmol) and TMSOTf (5 µL, 32 µmol) were consecutively added to the reaction solution. After stirring at −78 °C for 2.5 h, Ac₂O (20 µL, 226 µmol) and TMSOTf (5 µL, 32 µmol) were consecutively added to the mixture, and the reaction flask was moved to 0 °C, where the mixture was stirred for 1 h. Then, the vessel was cooled again to −78 °C, and a solution of the glycosyl acceptor 19 (120 mg, 323 µmol) in CH₂Cl₂ (1 mL), NIS (60 mg, 258 µmol) and TfOH (4 µL, 43 µmol) were sequentially added to the mixture. Reaction temperature was gradually raised up to 0 °C for a period of 2 h. Saturated NaHCO₃(aq) (5 mL) and 10% Na₂S₂O₃(aq) (5 mL) were added to quench the reaction. The mixture was filtered through Celite, and the desired material was extracted with CH₂Cl₂. The combined organic layer was dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography (ethyl acetate/hexanes = 1/3) furnished the adduct 20 (95 mg, 52%) as a white foam. [α]²⁷D +4.33 (c 3.5 in CHCl₃); IR (thin film): ν 2871, 1752, 1493, 1229, 1096, 1062, 738, 697 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ 7.49–7.48 (2 H, m, Ar-H), 7.40–7.23 (23 H, m, Ar-H),
5.55 (1 H, s, PhCH), 5.08 (1 H, t, J 8.3, 2-H'), 4.97 (1 H, d, J 11.0, ArCH2), 4.87–4.77 (4 H, m, ArCH2), 4.66–4.63 (2 H, m, ArCH2), 4.57 (1 H, d, J 3.3, 1-H), 4.51 (1 H, d, J 11.0, ArCH2), 4.47 (1 H, d, J 8.3, 1-H'), 4.32 (1 H, dd, J 10.5, 5.0, 6-Ha), 4.04 (1 H, d, J 10.3, 6-Ha), 3.96 (1 H, t, J 9.3, 3-H), 3.81–3.67 (5 H, m, 5-H, 6-Hb, 3-H', 4-H', 6-H'b), 3.52 (1 H, dd, J 9.8, 3.5, 2-H), 3.45 (1 H, t, J 9.5, 4-H), 3.40 (1 H, td, J 9.7, 5.0, 5-H'), 3.34 (3 H, s, OCH3), 1.88 (3 H, s, CH3); 13C NMR (150 MHz, CDCl3): δ 169.0 (C), 138.7 (C), 138.2 (C), 138.1 (C), 138.0 (C), 137.1 (C), 129.0 (CH), 128.4 (CH), 128.3 (CH), 128.25 (CH), 128.23 (CH), 128.1 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 125.9 (CH), 101.4 (CH), 101.2 (CH), 98.1 (CH), 81.9 (CH), 81.3 (CH), 79.7 (CH), 78.5 (CH), 77.5 (CH), 75.6 (CH2), 74.8 (CH2), 74.0 (CH2), 73.4 (CH2), 72.6 (CH2), 69.5 (CH), 68.5 (CH2), 68.0 (CH2), 66.3 (CH), 55.1 (CH3), 20.8 (CH3); HRMS (ESI): m/z calcd for C50H54O12Na ([M + Na]+): 869.3513, found: 869.3547.

4-Methylphenyl 2-O-(6-O-tert-butyldiphenylsilyl-2,3,4-tri-O-benzyl-α-D-mannopyranosyl)-3-O-benzyl-4,6-O-benzylidene-1-thio-β-D-glucopyranoside (23). TMSOTf (9 µL, 52 µmol) was added to a solution of compound 1 (200 mg, 348 µmol) and benzaldehyde (39 µL, 383 µmol) in CH2Cl2 (3 mL) with freshly dried 3 Å molecular sieves (400 mg) at –78 °C under N2 atmosphere. The mixture was stirred at same temperature for 2 h. Et3SiH (61 µL, 383 µmol), benzaldehyde (37 µL, 366 µmol) and TMSOTf (9 µL, 52 µmol) were sequentially added to the reaction solution. After stirring at –78 °C for 2.5 h, a solution of glycosyl donor 22 (406 mg, 520 µmol) in CH2Cl2 (7.5 ml), NIS (129 mg, 560 µmol), AW-300 molecular sieves (700 mg)
and TfOH (16 µL, 104 µmol) were sequentially added to the mixture at –78 °C. The reaction temperature was gradually raised to –40 °C for a period of 3 h. Saturated NaHCO₃(aq) (10 mL) and 10% Na₂S₂O₃(aq) (10 mL) were added to quench the reaction. The mixture was filtered through Celite followed by extraction with CH₂Cl₂. The combined organic layer was dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography (ethyl acetate/hexanes = 1/4) furnished the adduct 23 (286 mg, 72%) as a white foam. [α]²⁶⁰D +11.04 (c 1.2 in CHCl₃); IR (thin film): ν 2857, 1494, 1454, 1028, 697 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ 7.74–7.72 (2 H, m, Ar-H), 7.64–7.62 (2 H, m, Ar-H), 7.46–7.38 (8 H, m, Ar-H), 7.34–7.22 (20 H, m, Ar-H), 7.17–7.16 (2 H, m, Ar-H), 7.09–7.07 (2 H, m, Ar-H), 7.03–7.00 (1 H, m, Ar-H), 6.94–6.91 (2 H, m, Ar-H), 5.63 (1 H, d, J 0.7, 1-H'), 5.52 (1 H, s, ArCH), 5.01 (1 H, d, J 10.9, ArCH₂), 4.84 (1 H, d, J 12.7, ArCH₂), 4.85–4.78 (3 H, m, ArCH₂), 4.71–4.67 (3 H, m, ArCH₂), 4.57–4.54 (2 H, m, 1-H, ArCH₂), 4.38–4.34 (2 H, m, 6-Hₐ, 3-H), 3.98–3.96 (2 H, m, 3-H, 2-H'), 3.92 (1 H, d, J 9.7, 4-H'), 3.75 (1 H, t, J 10.3, 6-H₉), 3.66–3.62 (4 H, m, 2-H, 4-H, 5-H', 6-H₉'), 3.51 (1 H, dd, J 11.3, 1.0, 6-H₉), 3.51 (1 H, dt, J 9.6, 5.1, 5-H), 2.35 (3 H, s, CH₃), 1.04 (9 H, s, t-Bu); ¹³C NMR (150 MHz, CDCl₃): δ 139.1 (C), 138.7 (C), 138.6 (C), 138.2 (C), 137.5 (C), 137.1 (C), 136.0 (CH), 135.6 (CH), 134.1 (C), 133.6 (C), 132.8 (CH), 129.8 (CH), 129.3 (CH), 129.27 (CH), 128.9 (CH), 128.7 (C), 128.5 (CH), 128.3 (CH), 128.23 (CH), 128.21 (CH), 128.16 (CH), 128.10 (CH), 127.9 (CH), 127.7 (CH), 127.53 (CH), 127.52 (CH), 127.49 (CH), 127.44 (CH), 127.38 (CH), 127.31 (CH), 125.9 (CH), 101.1 (CH), 98.0 (CH), 88.6 (CH), 81.7 (CH), 81.2 (CH), 79.8 (CH), 76.0 (CH), 75.14 (CH), 75.13 (CH₂), 75.0 (CH₂), 74.3 (CH), 73.2 (CH), 72.2 (CH₂), 72.1 (CH₂), 70.1 (CH), 68.6 (CH₂), 62.4 (CH₂), 26.8 (CH₃), 21.1 (CH₃), 19.3 (C); HRMS (ESI): m/z calcd for C₇₀H₇₄O₁₀SSiNa ([M + Na]⁺): 1157.4670, found 1157.4663.
Methyl (6-O-tert-butyldiphenylsilyl-2,3,4-tri-O-benzyl-α-D-mannopyranosyl)-(1→2)-3-O-benzyl-4,6-O-benzylidene-α/β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (24). TMSOTf (4 µL, 23 µmol) was added to a solution of compound 1 (87 mg, 152 µmol) and benzaldehyde (17 µL, 166 µmol) in CH₂Cl₂ (1.5 mL) with freshly dried 3 Å molecular sieves (200 mg) at –78 °C under N₂ atmosphere. The mixture was stirred at same temperature for 2 h. Et₃SiH (27 µL, 166 µmol), benzaldehyde (16 µL, 160 µmol) and TMSOTf (4 µL, 23 µmol) were sequentially added to the reaction solution. After stirring at –78 °C for 2.5 h, a solution of glycosyl donor 22 (176 mg, 226 µmol) in CH₂Cl₂ (3.5 mL), NIS (63 mg, 270 µmol), AW-300 molecular sieves (300 mg) and TfOH (3 µL, 35 µmol) were sequentially added to the mixture at –78 °C. The reaction temperature was gradually raised to –40 °C for a period of 3 h. Then, a solution of glycosyl acceptor 17 (101 mg, 270 µmol) in CH₂Cl₂ (1.5 ml), NIS (56 mg, 240 µmol) and TfOH (7 µL, 75 µmol) were sequentially added to the solution at –40 °C, and the reaction temperature was gradually raised to 0 °C for a period of 2 h. Saturated NaHCO₃(aq) (5 mL) and 10% Na₂S₂O₃(aq) (5 mL) were added to quench the reaction, the mixture was filtered through Celite followed by extraction with CH₂Cl₂, and the combined organic layer was dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography (ethyl acetate/hexanes = 1/6) furnished the trisaccharide 24 (117 mg, 52%, crude α/β = 2/1). ¹H NMR (600 MHz, CDCl₃): δ 7.69–7.61 (10.1 H, m, Ar-H), 7.45–7.41 (5.5 H, m, Ar-H), 7.38–7.25 (68.2 H, m, Ar-H), 7.23–7.15 (29.7 H, m, Ar-H), 7.10–7.01 (15.5 H, m, Ar-H), 7.04–6.95 (11.1 H, m, Ar-H), 6.91–6.81 (13.1 H, m, Ar-H), 6.77–6.63 (13.1 H, m, Ar-H), 6.59–6.47 (13.1 H, m, Ar-H), 6.23–6.10 (13.1 H, m, Ar-H), 3.81–3.71 (23.3 H, m, Ar-H), 2.60–2.40 (13.1 H, m, Ar-H), 2.32–2.15 (13.1 H, m, Ar-H), 1.25–1.15 (13.1 H, m, Ar-H), 0.90–0.80 (13.1 H, m, Ar-H).
m, Ar-H), 7.12–7.04 (1.5 H, m, Ar-H), 7.01–6.96 (3.9 H, m, Ar-H), 6.89–6.86 (3 H, m, Ar-H), 5.62 (1 H, d, J 1.1), 5.50 (1.3 H, s, ArCH), 5.45 (1 H, s, ArCH), 5.06 (1 H, d, J 2.8), 5.04 (1 H, d, J 1.3), 4.99–4.89 (7.4 H, m), 4.84–4.81 (2.2 H, m), 4.77–4.73 (4 H, m), 4.71–4.60 (13.1 H, m), 4.58–4.55 (4.2 H, m), 4.52–4.47 (3.9 H, m), 4.40–4.35 (4.2 H, m), 4.31–4.26 (2.8 H, m), 4.19–4.16 (1 H, m), 4.12–4.06 (2.4 H, m), 4.02–3.94 (6.1 H, m), 3.91–3.78 (12.9 H, m), 3.74–3.71 (3 H, m), 3.68–3.45 (12.5 H, m), 3.40–3.38 (1.5 H, m), 3.36–3.27 (6 H, m), 3.32 (4 H, s), 1.03 (25.9 H, m); HRMS (ESI): m/z calcd for C_{91}H_{98}O_{16}SiNa ([M + Na]^+) 1497.6522, found: 1497.6523.

4-Methylphenyl 2-O-(2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-3-O-benzyl-4,6-O-benzylidene-1-thio-β-D-glucopyranoside (26). TMSOTf (4 µL, 23 µmol) was added to a solution of compound 1 (87 mg, 152 µmol) and benzaldehyde (17 µL, 166 µmol) in CH_{2}Cl_{2} (1.5 mL) with freshly dried 3 Å molecular sieves (200 mg) at –78 °C under N\textsubscript{2} atmosphere. The mixture was stirred at same temperature for 2 h. Et\textsubscript{3}SiH (27 µL, 165 µmol), benzaldehyde (16 µL, 160 µmol) and TMSOTf (4 µL, 23 µmol) were sequentially added to the reaction solution. After stirring at –78 °C for 2.5 h, a solution of glycosyl donor 25 (110 mg, 166 µmol) in CH\textsubscript{2}Cl\textsubscript{2} (3 mL), NIS (46 mg, 198 µmol), AW-300 molecular sieves (300 mg) and Tf\textsubscript{OH} (3 µL, 30 µmol) were sequentially added to the solution at –78 °C. The reaction temperature was gradually raised to –60 °C for 3 h. Saturated NaHCO\textsubscript{3}(aq) (10 mL) and 10\% Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}(aq) (10 mL) were added to quench the reaction, and the mixture was filtered through Celite followed by extraction with CH\textsubscript{2}Cl\textsubscript{2}. The combined organic layer was dried over anhydrous MgSO\textsubscript{4}, filtered, and
concentrated under reduced pressure. Purification of the residue via flash column chromatography (ethyl acetate/hexanes = 1/5) furnished the adduct 26 (105 mg, 70%) as a white foam. $[\alpha]^{27}_D -6.9$ (c 1.4 in CHCl$_3$); IR (thin film): $\nu$ 2866, 1730, 1453, 1266, 1092, 1027, 697 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.91 (1 H, d, $J$ 7.2, Ar-H), 7.52–7.49 (1 H, m, Ar-H), 7.45–7.43 (2 H, m, Ar-H), 7.39–7.37 (4 H, m, Ar-H), 7.34–7.29 (15 H, m, Ar-H), 7.27–7.23 (3 H, m, Ar-H), 7.14–7.11 (5 H, m, Ar-H), 7.09–7.07 (2 H, m, Ar-H), 7.03–7.00 (1 H, m, Ar-H), 5.48 (1 H, s, ArCH), 5.40 (1 H, dd, $J$ 9.4, 8.1, 2-H'), 5.26 (1 H, d, $J$ 8.1, 1-H'), 4.80–4.78 (2 H, m, ArCH$_2$), 4.76 (1 H, d, $J$ 11.2, ArCH$_2$), 4.67–4.65 (4 H, m, 1-H, ArCH$_2$), 4.51 (1 H, d, $J$ 11.1, ArCH$_2$), 4.30 (1 H, dd, $J$ 10.6, 5.1, 6-H$_a$), 3.94–3.90 (2 H, m, 2-H, 4-H'), 3.87 (1 H, dd, $J$ 11.4, 6-H', 6-H$_b$), 3.71 (1 H, t, $J$ 10.4, 6-H$_b$), 3.66–3.61 (2 H, m, 3-H, 4-H), 3.51 (1 H, dddd, $J$ 9.8, 4.0, 1.7, 5-H'), 3.36 (1 H, dt, $J$ 9.5, 5.1, 5-H), 2.33 (3 H, s, CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 165.1 (C), 138.4 (C), 138.3 (C), 137.9 (C), 137.8 (C), 137.6 (C), 137.1 (C), 133.0 (CH), 129.8 (C), 129.7 (CH), 129.6 (C), 129.5 (CH), 128.9 (CH), 128.43 (CH), 128.40 (CH), 128.35 (CH), 128.32 (CH), 128.2 (CH), 128.16 (CH), 128.12 (CH), 127.9 (CH), 127.8 (CH), 127.68 (CH), 127.65 (CH), 127.56 (CH), 127.4 (CH), 127.3 (CH), 125.9 (CH), 101.1 (CH), 100.5 (CH), 87.2 (CH), 83.5 (CH), 82.8 (CH), 81.5 (CH), 78.0 (CH), 76.1 (CH), 75.5 (CH$_2$), 75.1 (CH$_2$), 74.9 (CH$_2$), 74.7 (CH$_2$), 73.9 (CH), 73.87 (CH$_2$), 69.7 (CH), 68.6 (CH$_2$), 68.58 (CH$_2$), 21.1 (CH$_3$); HRMS (ESI): $m/z$ calcd for C$_{61}$H$_{60}$O$_{11}$SNa ([M + Na]$^+$): 1023.3754, found: 1023.3745.
Methyl (2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→2)-3-O-benzyl-4,6-O-benzylidene-α/β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (27).

TMSOTf (4 µL, 23 µmol) was added to a solution of compound 1 (87 mg, 152 µmol) and benzaldehyde (17 µL, 166 µmol) in CH₂Cl₂ (1.5 mL) with freshly dried 3 Å molecular sieves (200 mg) at −78 °C under N₂ atmosphere. The mixture was stirred at same temperature for 2 h. Et₃SiH (27 µL, 166 µmol), benzaldehyde (16 µL, 160 µmol) and TMSOTf (4 µL, 23 µmol) were sequentially added to the reaction solution. After stirring −78 °C for 2.5 h, a solution of glycosyl donor 25 (110 mg, 167 µmol) in CH₂Cl₂ (3 ml), NIS (46 mg, 200 µmol), AW-300 molecular sieves (300 mg) and TfOH (3 µL, 30 µmol) were sequentially added to the solution at −78 °C. The reaction temperature was gradually raised to −60 °C for a period of 3 h. Then, a solution of the glycosyl acceptor 17 (84 mg, 228 µmol) in CH₂Cl₂ (1.5 ml), NIS (42 mg, 182 µmol) and TfOH (7 µL, 75 µmol) were sequentially added to the mixture at −60 °C. The reaction temperature was gradually raised to 0 °C for a period of 2 h. Saturated NaHCO₃(aq) (5 mL) and 10% Na₂S₂O₃(aq) (5 mL) were added to quench the reaction, the mixture was filtered through Celite followed by extraction with CH₂Cl₂, and the combined organic layer was dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography (ethyl acetate/hexanes = 1/3) furnished the trisaccharide 27 (131 mg, 65%, crude α/β = 3/1). For the α-isomer: [α]²⁷D +63.1 (c 1.2 in CHCl₃); IR (thin film): ν 2859, 1731, 1453, 1365, 1266, 1089, 1027, 736 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ 7.88 (2 H, d, J 8.3, Ar-H), 7.42 (1 H, t, J 7.4, Ar-H), 7.39–7.34 (6 H, m, Ar-H), 7.32–7.25 (20 H, m, Ar-H), 7.23–7.15 (9 H, m, Ar-H), 7.13–7.10 (5 H, m, Ar-H), 7.06–7.04 (2 H, m, Ar-H), 5.47 (1 H, s, ArCH), 5.38 (1 H, t, J 8.5, 2-H”), 5.13 (1 H, d, J 3.5, 1-H”), 5.00 (1 H, d, J 11.0, ArCH₂), 4.96 (1 H, d, J 8.5, 1-H”), 4.91 (1 H, d, J 11.2, ArCH₂), 4.84 (1 H, d, J 11.0,
ArCH$_2$), 4.79 (1 H, d, $J$ 12.0, ArCH$_2$), 4.76 (1 H, d, $J$ 10.8, ArCH$_2$), 4.73–4.69 (2 H, m, ArCH$_2$), 4.66–4.64 (2 H, m, ArCH$_2$), 4.60 (1 H, d, $J$ 11.2, ArCH$_2$), 4.57 (1 H, d, $J$ 11.7, ArCH$_2$), 4.54 (1 H, d, $J$ 12.2, ArCH$_2$), 4.51–4.48 (2 H, m, ArCH$_2$), 4.38 (1 H, d, $J$ 11.6, ArCH$_2$), 4.20 (1 H, dd, $J$ 10.2, 4.9, 6-H$_a$), 4.02 (1 H, t, $J$ 9.3, 3-H), 3.88–3.63 (12 H, m, 2-H, 4-H, 6-H $\times$ 2, 2-H', 3-H', 4-H', 6-H''$_a$, 3-H''$_a$, 4-H''$_b$, 6-H'' $\times$ 2), 3.57–3.52 (3 H, m, 5-H, 5-H', 5-H''), 3.35 (3 H, s, CH$_3$); 13C NMR (150 MHz, CDCl$_3$): $\delta$ 164.7 (C), 139.1 (C), 138.6 (C), 138.5 (C), 138.4 (C), 137.9 (C), 137.8 (C), 137.7 (C), 137.4 (C), 132.8 (CH), 129.8 (C), 129.7 (CH), 128.1 (CH), 128.4 (CH), 128.34 (CH), 128.30 (CH), 128.28 (CH), 128.21 (CH), 128.1 (CH), 128.08 (CH), 128.05 (CH), 127.97 (CH), 127.93 (CH), 127.8 (CH), 127.78 (CH), 127.70 (CH), 127.65 (CH), 127.60 (CH), 127.5 (CH), 127.3 (CH), 127.21 (CH), 127.18 (CH), 126.0 (CH), 101.8 (CH), 101.3 (CH), 99.6 (CH), 97.7 (CH), 82.9 (CH), 82.2 (CH), 80.3 (CH), 78.4 (CH), 78.2 (CH), 77.9 (CH), 77.8 (CH), 75.6 (CH$_2$), 75.1 (CH$_2$), 75.0 (CH$_2$), 74.8 (CH$_2$), 74.5 (CH$_2$), 73.7 (CH), 73.3 (CH$_2$), 70.0 (CH), 69.1 (CH$_2$), 68.8 (CH$_2$), 67.0 (CH$_2$), 62.4 (CH), 55.1 (CH$_3$); HRMS (ESI): $m/z$ calcd for C$_{82}$H$_{84}$O$_{17}$Na ([M + Na]$^+$): 1363.5606, found: 1363.5602. For the $\beta$-isomer: IR (thin film): $\nu$ 2925, 1731, 1453, 1266, 1093, 737, 697 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.81 (2 H, d, $J$ 7.3, Ar-H), 7.46–7.41 (3 H, m, Ar-H), 7.34–7.31 (6 H, m, Ar-H), 7.30–7.21 (26 H, m, Ar-H), 7.17–7.14 (1 H, m, Ar-H), 7.10–7.02 (7 H, m, Ar-H), 5.42 (1 H, s, ArCH), 5.17 (1 H, t, $J$ 8.2, 2-H''$_a$), 5.11 (1 H, d, $J$ 8.2, 1-H''$_a$), 5.00–4.97 (2 H, m, ArCH$_2$), 4.85–4.81 (2 H, m, ArCH$_2$), 4.70–4.67 (2 H, m, ArCH$_2$), 4.61–4.51 (4 H, m, 1-H, ArCH$_2$), 4.52–4.48 (4 H, m, 1-H', ArCH$_2$), 4.39 (1 H, d, $J$ 11.4, ArCH$_2$), 4.26–4.24 (2 H, m, 6-H''$_a$, ArCH$_2$), 4.05 (1 H, d, $J$ 10.3, 6-H''$_a$), 3.98 (1 H, t, $J$ 9.1, 3-H), 3.85 (1 H, t, $J$ 7.8, 2-H'), 3.80 (1 H, dd, $J$ 10.4, 3.2, 6-H''$_a$), 3.77–3.76 (2 H, m, 4-H, 4-H''), 3.71–3.60 (5 H, m, 6-H $\times$ 2, 4-H', 6-H''$_b$, 3-H''), 3.57–3.48 (3 H, m, 2-H, 3-H', 5-H''), 3.36 (3 H, s, CH$_3$), 3.34–3.40 (2 H, m, 5-H, 5-H'); 13C NMR (150 MHz, CDCl$_3$): $\delta$ 164.9 (C), 139.0 (C),
138.8 (C), 138.4 (C), 138.3 (C), 138.2 (C), 137.8 (C), 137.1 (C), 132.9 (CH), 129.8 (C), 129.7 (CH), 128.9 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.22 (CH), 128.20 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.88 (CH), 127.83 (CH), 127.78 (CH), 127.5 (CH), 127.49 (CH), 127.45 (CH), 127.2 (CH), 125.9 (CH), 102.1 (CH), 101.0 (CH), 100.7 (CH), 97.9 (CH), 82.8 (CH), 82.1 (CH), 82.05 (CH), 81.3 (CH), 80.0 (CH), 78.7 (CH), 78.3 (CH), 77.6 (CH), 75.8 (CH2), 75.2 (CH2), 75.1 (CH), 75.0 (CH2), 74.7 (CH2), 74.5 (CH2), 74.0 (CH), 73.3 (CH2), 73.2 (CH2), 69.9 (CH), 69.2 (CH2), 68.7 (CH2), 68.5 (CH2), 65.6 (CH), 55.2 (CH3); HRMS (ESI): m/z calcd for C82H84O17Na ([M + Na]+): 1363.5606, found: 1363.5601.

4-Methylphenyl 2-O-(2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-galactopyranosyl)-3-O-benzyl-4,6-O-benzylidene-1-thio-β-D-glucopyranoside (29). TMSOTf (4 µL, 23 µmol) was added to a solution of compound 1 (87 mg, 152 µmol) and benzaldehyde (17 µL, 166 µmol) in CH2Cl2 with freshly dried 3 Å molecular sieves (200 mg) at −78 °C under N2 atmosphere. The mixture was stirred at same temperature for 2 h. Et3SiH (27 µL, 165 µmol), benzaldehyde (16 µL, 160 µmol) and TMSOTf (4 µL, 23 µmol) were sequentially added to the reaction mixture. After stirring at −78 °C for 2.5 h, a solution of glycosyl donor 28 (110 mg, 166 µmol) in CH2Cl2 (3 mL), NIS (46 mg, 198 µmol), AW-300 molecular sieves (300 mg) and TfOH (3 µL, 30 µmol) were sequentially added again to the solution at −78 °C. The reaction temperature was gradually raised up to −60 °C for 3 h. Saturated NaHCO3(aq) (10 mL) and 10% Na2S2O3(aq) (10 mL) were added to quench the reaction, the mixture was filtered through Celite followed by extraction with
CH$_2$Cl$_2$, and the combined organic layer was dried over anhydrous MgSO$_4$, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography (ethyl acetate/hexanes = 1/5) furnished the adduct 29 (94 mg, 63%) as a white foam. $[\alpha]_D^{27} - 11.9$ (c 0.9 in CHCl$_3$); IR (thin film): $\nu$ 1731, 1454, 1269, 1095, 751, 698 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.93 (2 H, d, $J$ 8.1, Ar-H), 7.52 (1 H, t, $J$ 7.0, Ar-H), 7.45 (2 H, d, $J$ 8.1, Ar-H), 7.40 (2 H, d, $J$ 7.0, Ar-H), 7.38–7.31 (14 H, m, Ar-H), 7.28–7.20 (7 H, m, Ar-H), 7.18–7.16 (4 H, m, Ar-H), 7.01 (2 H, d, $J$ 8.1, Ar-H), 5.71 (1 H, t, $J$ 8.1, 2-H'), 5.47 (1 H, s, ArCH), 5.19 (1 H, d, $J$ 8.1, 1-H'), 5.03 (1 H, d, $J$ 11.7, ArCH$_2$), 4.68 (1 H, d, $J$ 11.8, ArCH$_2$), 4.64–4.61 (2 H, m, 1-H, ArCH$_2$), 4.51 (1 H, d, $J$ 11.1, ArCH$_2$), 4.48–4.45 (2 H, m, ArCH$_2$), 4.30 (1 H, dd, $J$ 10.6, 5.1, 6-H$_a$), 4.05 (1 H, d, $J$ 2.4, 4-H'), 3.86 (1 H, t, $J$ 8.8, 2-H), 3.75 (1 H, t, $J$ 8.4, 6-H'$_a$), 3.69 (1 H, t, $J$ 10.4, 6-H$_b$), 3.65 (1 H, t, $J$ 9.2, 3-H), 3.60–3.55 (4 H, m, 3-H', 4-H', 5-H', 6-H'$_b$), 3.35 (1 H, dt, $J$ 9.8, 5.1, 5-H), 2.31 (3 H, s, CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 165.3 (C), 138.6 (C), 138.3 (C), 137.8 (C), 137.7 (C), 137.5 (C), 137.1 (C), 133.7 (CH), 132.9 (CH), 130.0 (C), 129.8 (CH), 129.4 (CH), 128.9 (C), 128.8 (CH), 128.5 (CH), 128.3 (CH), 128.26 (CH), 128.20 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.66 (CH), 127.50 (CH), 127.49 (CH), 127.44 (CH), 125.9 (CH), 101.0 (CH), 100.5 (CH), 86.6 (CH), 83.4 (CH), 81.4 (CH), 79.7 (CH), 76.0 (CH), 74.7 (CH$_2$), 74.4 (CH$_2$), 73.6 (CH$_2$), 73.5 (CH), 72.4 (CH), 72.2 (CH), 71.4 (CH), 69.6 (CH), 68.6 (CH$_2$), 68.3 (CH$_2$), 21.1 (CH$_3$); HRMS (ESI): $m/z$ calcd for C$_{61}$H$_{60}$O$_{11}$Na ([M + Na]$^+$): 1023.3754, found: 1023.3733.
Methyl (2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-galactopyranosyl)-(1→2)-(3-O-benzyl-4,6-O-benzylidene-α/β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (30).

TMSOTf (4 µL, 23 µmol) was added to a solution of compound 1 (87 mg, 152 µmol) and benzaldehyde (17 µL, 166 µmol) in CH₂Cl₂ (1.5 mL) with freshly dried 3 Å molecular sieves (200 mg) at –78 °C under N₂ atmosphere. The mixture was kept stirring at same temperature for 2 h. Et₃SiH (27 µL, 166 µmol), benzaldehyde (16 µL, 160 µmol) and TMSOTf (4 µL, 23 µmol) were sequentially added to the reaction solution. After 2.5 h of stirring at –78 °C, a solution of the glycosyl donor 28 (110 mg, 167 µmol) in CH₂Cl₂ (3 mL), NIS (46 mg, 200 µmol), AW-300 molecular sieves (300 mg) and TfOH (3 µL, 30 µmol) were sequentially added to the mixture. The reaction temperature was gradually raised to –60 °C for 3 h. Then, a solution of the glycosyl acceptor 17 (84 mg, 228 µmol) in CH₂Cl₂ (1.5 ml), NIS (42 mg, 182 µmol) and TfOH (7 µL, 75 µmol) were sequentially added to the solution at –60 °C. The reaction temperature was gradually raised to 0 °C for 2 h. Saturated NaHCO₃(aq) (5 mL) and 10% Na₂S₂O₃(aq) (5 mL) were added to quench the reaction, the mixture was filtered through Celite, and the desired material was extracted with CH₂Cl₂. The combined organic layer was dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography (ethyl acetate/hexanes = 1/3) provided the trisaccharide 30 (124 mg, 61%, crude α/β = 2/1) as a white foam. ¹H NMR (600 MHz, CDCl₃): δ 7.94–7.92 (2.4 H, m, Ar-H), 7.87–7.86 (2 H, m, Ar-H), 7.51–7.45 (4.5 H, m, Ar-H), 7.43–7.29 (45.8 H, m, Ar-H), 7.26–7.18 (25.5 H, m, Ar-H), 7.17–7.05 (20.4 H, m, Ar-H), 5.69 (1.2 H, t, J 8.9), 5.66 (1 H, t, J 8.9), 5.48 (1.2 H, s, PhCH), 5.45 (1 H, s, PhCH), 5.10–4.96 (9.1 H, m), 4.92–4.87 (4.1 H, m), 4.84–4.77 (4.2 H, m), 4.73–4.68 (6.1 H, m), 4.65–4.57 (7 H, m), 4.53 (1 H, d, J 7.4), 4.48–4.35 (9.4 H, m), 4.29 (1 H, dd, J 10.6, 5.1), 4.24–4.19 (2.2 H, m), 4.06–4.00 (4.5 H, m), 3.96 (1 H, d, J 2.5), 3.90–3.80 (8.6
H, m), 3.78–3.74 (3.1 H, m), 3.73–3.68 (5.8 H, m), 3.67–3.59 (8.6 H, m), 3.56–3.53 (2.1 H, m),

![Structural formula](image)

**Methyl 3-O-tert-butyl-(2R)-2-O-[3-O-benzyl-2-O-(2,3,4-tri-O-benzyl-6-O-tert-butylidiphenylsilyl-α-D-mannopyranosyl)-4,6-O-benzylidene-α-D-glucopyranosyl]-2,3-dihydroxypropanoate (32).** TMSOTf (4 µL, 23 µmol) was added to a solution of compound 1 (87 mg, 152 µmol) and benzaldehyde (17 µL, 166 µmol) in CH₂Cl₂ (1.5 mL) with freshly dried 3 Å molecular sieves (200 mg) at −78 °C under N₂ atmosphere. The mixture was stirred at same temperature for 2 h. Et₃SiH (27 µL, 166 µmol), benzaldehyde (16 µL, 160 µmol) and TMSOTf (4 µL, 23 µmol) were sequentially added to the reaction solution. After 2.5 h of stirring at −78 °C, a solution of the glycosyl donor 22 (176 mg, 176 µmol) in CH₂Cl₂ (3.5 ml), NIS (61 mg, 270 µmol), AW-300 molecular sieves (300 mg) and TfOH (3 µL, 35 µmol) were sequentially added to the solution at −78 °C. The reaction temperature was gradually raised to −40 °C for a period of 3 h. Then, a solution of the glycerate 31 (97 mg, 270 µmol) in CH₂Cl₂ (1.5 ml), NIS (34 mg, 146 µmol) and TfOH (7 µL, 75 µmol) were sequentially added to the mixture at −40 °C, and the reaction temperature was gradually raised to 0 °C for a period of 2 h. Saturated NaHCO₃(aq) (5 mL) and 10% Na₂S₂O₃(aq) (5 mL) were added to quench the reaction. The mixture was filtered through Celite, followed by extraction with CH₂Cl₂. The combined organic layer was dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. Purification of the residue
via flash column chromatography (ethyl acetate/hexanes = 1/6) delivered the MMG backbone (70 mg, 34%). \([\alpha]^{24}_D +24.4 \ (c \ 3.1 \ \text{in CHCl}_3)\); IR (thin film): \(\delta 2930, 2857, 1752, 1427, 1112, 1044, 737, 698 \ \text{cm}^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta 7.79–7.70 \ (8 \ \text{H, m, Ar-H}), 7.48–7.46 \ (4 \ \text{H, m, Ar-H}), 7.43–7.35 \ (11 \ \text{H, m, Ar-H}), 7.33–7.25 \ (13 \ \text{H, m, Ar-H}), 7.24–7.18 \ (6 \ \text{H, m, Ar-H}), 7.11–7.09 \ (1 \ \text{H, m, Ar-H}), 7.03–7.01 \ (2 \ \text{H, m, Ar-H}), 5.59 \ (1 \ \text{H, s, 1'-H}), 5.49 \ (1 \ \text{H, s, ArCH}), 5.35 \ (1 \ \text{H, s, 1-H}), 4.99 \ (1 \ \text{H, d, J 11.1, ArCH}_2), 4.90 \ (1 \ \text{H, d, J 12.2, ArCH}_2), 4.85 \ (1 \ \text{H, d, J 12.2, ArCH}_2), 4.78 \ (1 \ \text{H, d, J 10.9, ArCH}_2), 4.74 \ (1 \ \text{H, d, J 10.9, ArCH}_2), 4.63 \ (1 \ \text{H, d, J 11.1, ArCH}_2), 4.54–4.48 \ (3 \ \text{H, m, glycerate-CH, ArCH}_2), 4.20 \ (1 \ \text{H, dd, J 10.3, 4.8, 6-Ha}), 4.16–4.15 \ (5 \ \text{H, m, 2'-H, 3'-H, 4'-H, 5-H, glycerate-CH}_2), 4.04–4.03 \ (2 \ \text{H, m, 2-H, 3-H}), 4.00 \ (1 \ \text{H, dd, J 10.8, 2.4, glycerate-CH}_2), 3.91–3.84 \ (3 \ \text{H, m, 5-H, 6'-H × 2}), 3.77 \ (3 \ \text{H, s, OCH}_3), 3.68 \ (1 \ \text{H, t, J 10.3, 6-Hb}), 3.60 \ (1 \ \text{H, t, J 8.9, 4-H}), 1.07–1.06 \ (18 \ \text{H, m, t-Bu}); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta 170.0 \ (\text{C}), 139.14 \ (\text{C}), 139.11 \ (\text{C}), 138.6 \ (\text{C}), 138.3 \ (\text{C}), 137.4 \ (\text{C}), 135.9 \ (\text{CH}), 135.7 \ (\text{CH}), 135.5 \ (\text{CH}), 133.9 \ (\text{C}), 133.6 \ (\text{C}), 133.1 \ (\text{C}), 132.8 \ (\text{C}), 129.8 \ (\text{CH}), 129.4 \ (\text{CH}), 129.3 \ (\text{CH}), 128.8 \ (\text{CH}), 128.2 \ (\text{CH}), 128.1 \ (\text{CH}), 128.09 \ (\text{CH}), 128.06 \ (\text{CH}), 128.04 \ (\text{CH}), 127.8 \ (\text{CH}), 127.79 \ (\text{CH}), 127.75 \ (\text{CH}), 127.6 \ (\text{CH}), 127.5 \ (\text{CH}), 127.45 \ (\text{CH}), 127.43 \ (\text{CH}), 127.3 \ (\text{CH}), 127.2 \ (\text{CH}), 127.1 \ (\text{CH}), 127.0 \ (\text{CH}), 126.0 \ (\text{CH}), 101.3 \ (\text{CH}), 94.5 \ (\text{CH}), 93.9 \ (\text{CH}), 81.9 \ (\text{CH}), 80.1 \ (\text{CH}), 75.4 \ (\text{CH}_2), 75.2 \ (\text{CH}_2), 74.9 \ (\text{CH}_2), 74.6 \ (\text{CH}), 74.3 \ (\text{CH}), 73.0 \ (\text{CH}), 72.4 \ (\text{CH}), 72.3 \ (\text{CH}_2), 71.5 \ (\text{CH}_2), 68.8 \ (\text{CH}_2), 64.9 \ (\text{CH}_2), 63.3 \ (\text{CH}_2), 62.8 \ (\text{CH}), 51.9 \ (\text{CH}_3), 26.9 \ (\text{CH}_3), 26.7 \ (\text{CH}_3), 19.3 \ (\text{C}), 19.2 \ (\text{C}); \mathrm{HRMS} \ (\mathrm{ESI}): \text{m/z} \ \text{calcd for C}_{83}\text{H}_{92}\text{O}_{14}\text{Si}_2\text{Na} ([\text{M + Na}]^+): 1391.5923, \text{found: } 1391.5970.
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PL1: 1.00 dB
SFO1: 100.6288660 MHz

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F2 - Processing parameters
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Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Current Data Parameters
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F2 - Processing parameters
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Current Data Parameters
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SFO1  100.6288660 MHz

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PCPD2  90.00 usec
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F2 - Processing Parameters
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- GB: 0
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Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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PROCNO: 1

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 PROBHD: 5 mm CPDCH 13C
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 PLL2: 0.33 dB
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23
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- **TD0:** 1

**======== CHANNEL f1 ========**

- **NUC1:** 1H
- **P1:** 10.20 usec
- **PL1:** -0.80 dB
- **PL1W:** 18.11971092 W
- **SFO1:** 600.1536010 MHz

**F2 - Processing parameters**

- **SI:** 16384
- **SF:** 600.1500278 MHz
- **WDW:** EM
- **SSB:** 0
- **LB:** 0 Hz
- **GB:** 0
- **PC:** 1.00

**Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry**

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Current Data Parameters
NAME: TYH-1337-1
EXPNO: 2
PROCNO: 1

F2 - Acquisition Parameters
Date: 20130619
Time: 2.03
INSTRUM: spect
PROBHD: 5 mm CPDCH 13C
PULPROG: zgpg30
TD: 131072
SOLVENT: CDCl3
NS: 1500
DS: 0
SWH: 39062.500 Hz
FIDRES: 0.298023 Hz
AQ: 1.6777716 sec
RG: 3640
DW: 12.800 usec
DE: 21.00 usec
TE: 298.0 K
D1: 2.00000000 sec
D11: 0.03000000 sec

======== CHANNEL f1 ========
NUC1: 13C
P1: 10.35 usec
PL1: 2.80 dB
SFO1: 150.9251886 MHz

======== CHANNEL f2 ========
CPDPRG2: waltz16
NUC2: 1H
PCPD2: 80.00 usec
PL2: 0.33 dB
PL2W: 13.96854782 W

F2 - Processing parameters
SI: 65536
SF: 150.907649 MHz
SM: 0
LB: 2.00 Hz
PC: 1.00
Current Data Parameters
NAME         TYH-1337-3
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20130618
Time              19.36
INSTRUM           spect
PROBHD   5 mm CPDCH 13C
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   64
DS                    0
SWH            8389.262 Hz
FIDRES         0.256020 Hz
AQ            1.9530228 sec
RG                   57
DW               59.600 usec
DE                21.00 usec
TE                298.1 K
D1           2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.20 usec
PL1               -0.80 dB
PL1W        18.11971092 W
SFO1        600.1536010 MHz

F2 - Processing parameters
SI                16384
SF          600.1500278 MHz
WDW                  EM
SSB      0
LB       0 Hz
GB       0
PC                 1.00

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Current Data Parameters
NAME: T18-1337-1
EXPT: PROC30

F2 - Acquisition Parameters
Date: 20130618
Time: 21:12
INSTRUM: spect
PROBHD: 5 mm CPDCH 13C
PRECUR: zgpg30
TD: 131072
SOLVENT: CDCl3
NS: 1500
DS: 0
SN: 39.062.500 Hz
FIDRES: 0.298023 Hz
AQ: 1.6777716 sec
RG: 1290
DW: 12.800 usec
DE: 21.00 usec
TE: 297.9 K
D1: 2.0000000 sec
D11: 0.30000000 sec
T00: 1

====== CHANNEL f1 ======
NUC1: 13C
P1: 10.35 usec
PL1: 2.80 dB
PL1W: 49.17097855 W
SFO1: 150.9251886 MHz

====== CHANNEL f2 ======
CPDPGR: waltz16
NUC2: 1H
PCPD2: 80.00 usec
PL2: 0.33 dB
PL12: 16.50 dB
PL13: 19.50 dB
PL2W: 13.6854782 W
PL12W: 0.33740479 W
PL13W: 0.16910298 W
SFO2: 600.1524006 MHz

F2 - Processing parameters
SI: 65536
SF: 150.907685 MHz
WDW: EM
SSB: 0
LB: 2.00 Hz
GB: 0
PC: 1.00
Current Data Parameters
NAME  TYH-1332-C
EXPNO  2
PROCNO  1

F2 - Acquisition Parameters
Date_  20130614
Time  20.21
INSTRUM  spect
PROBHD  5 mm CPDCH 13C
PULPROG  zgpg30
TD  131072
SOLVENT  CDCl3
NS  2000
DS  2000
SW  39962.500 Hz
TDPRCS  0.29803 Hz
A0  1.6777716 sec
BG  1030
DN  12.800 usec
DE  21.000 usec
TE  298.0 K
D1  2.00000000 sec
D11  0.00000000 sec
TD0  1

======== CHANNEL f1 ========
NUC1  13C
P1  10.35 usec
PL1  2.80 dB
PL1W  49.17097855 W
SFO1  150.9297855 MHz

======== CHANNEL f2 ========
CPDPRG2  waltz16
NUC2  1H
P12  80.00 usec
P12  0.33 dB
P113  19.50 dB
P12M  13.36584582 W
P12W  0.33740479 W
SFO2  600.15406 MHz

F2 - Processing parameters
SI  65536
SF  150.9297855 MHz
WDM  EM
SLM  0
LB  2.00 Hz
GB  0
FC  1.00
Current Data Parameters

NAME        TYH-1336-1
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20130619
Time               6.18
INSTRUM           spect
PROBHD   5 mm CPDCH 13C
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   64
DS                    0
SWH            8389.262 Hz
FIDRES         0.256020 Hz
AQ            1.9530228 sec
RG                   57
DW               59.600 usec
DE                21.00 usec
TE                297.9 K
D1           2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.20 usec
PL1               -0.80 dB
PL1W        18.11971092 W
SFO1        600.1536010 MHz

F2 - Processing parameters
SI                16384
SF          600.1500000 MHz
WDW                  EM
SSB      0
LB       0 Hz
GB       0
PC                 1.00

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Current Data Parameters
NAME    TYH-1340-18
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20130629
Time     19.24
INSTRUM  spect
PROBHD   5 mm CPDCH 13C
PULPROG  zg30
TD       32768
SOLVENT  CDCl3
NS       47
DS       0
SWH      8389.262 Hz
FIDRES   0.256020 Hz
AQ       1.9530228 sec
RG       16
DW       59.600 usec
DE       21.00 usec
TE       297.9 K
D1       2.00000000 sec
TD0      1

======== CHANNEL f1 ========
NUC1     1H
P1       10.20 usec
PL1      -0.80 dB
PL1W     18.11971092 W
SFO1     600.1536010 MHz

F2 - Processing parameters
SI       16384
SF       600.1500283 MHz
WDW      EM
SSB      0
LB       0 Hz
GB       0
PC       1.00

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Ph
BnO
BnO
OTBDPS
CO_2Me

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Current Data Parameters
NAME: T3H-1340-1B
EXPNO: 2
PROCNO: 1

F2 - Acquisition Parameters
Date: 20130629
Time: 19:26
INSTRUM: spect
PROBHD: 5 mm CPDCH 13C
PULPROG: zgpg30
TD: 131072
SOLVENT: CDCl3
NS: 5000
DS: 0
SMH: 39.062.500 Hz
FIDRES: 0.298023 Hz
AQ: 1.6777116 sec
RG: 3640
DW: 12.800 usec
TE: 297.9 K
D1: 2.0000000 sec
D11: 0.0300000 sec
TD0: 1

======== CHANNEL f1 ========
NUC1: 13C
P1: 11.00 usec
PL1: 2.80 dB
SFO1: 150.9251886 MHz

======== CHANNEL f2 ========
CPDPRG2: waltz16
NUC2: 1H
PCPD2: 80.00 usec
PL2: 2.80 dB
SFO2: 600.1524006 MHz

F2 - Processing parameters
SI: 65536
SF: 150.9078511 MHz
WD: EM
SSB: 0
LB: 2.00 Hz
GB: 1.00