Flexible 1,2-cis α-Glycosylation Strategy Based on \textit{in situ} Adduct Transformation

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1 General Experimental

Reagent-grade chemicals were purchased from commercial vendors and used without further purification. Dichloromethane (CH₂Cl₂) was dried by Asianwong solvent purification system (AWS-1000). N-Formyl morpholine (NFM) and 2,6-lutidine was purchased from vendor and was treated with activated molecular sieves (MS) under N₂ before use. Progress of reactions was monitored by thin layer chromatography on silica gel 60 F-254 plate and visualized under UV illumination and/or by staining with acidic ceric ammonium molybdate or p-anisaldehyde. HPLC analysis was performed over Mightysil Si 60 (250 mm L × 4.6 mm I.D.) obtained from KANTO CHEMICAL CO. INC. and eluted with EtOAc/hexanes/CH₂Cl₂ or EtOAc/hexanes mixture at a 1 mL/min flow rate. Gradient pump (L-2130) and UV detector (L-2400) from Hitachi were employed for solvent elution and detection respectively. 0.063-0.200 mm Silica gel for column chromatography was obtained from Merck (Geduran Si-60). NMR spectroscopy analysis of saccharide building blocks and glycosylation products were recorded by 300 (Büchi console), 400 (Varian console), 500 (Varian console), or 600 (Varian console) MHz NMR spectrometers. The proton chemical shifts (in ppm) of reported were calibrated against the proton signal of TMS standard and the carbon chemical shift was calibrated against the ¹³C signals of deuterated chloroform (CDCl₃). Coupling constants (in Hz) was calculated from chemical shifts of ¹H NMR spectra. Diacetonide protected galactosyl acceptor 15, cholesterol 33, and diosgenine 17 are commercially available. Preparation of glycosyl donors/acceptors 1, 2, 3, 4, 9, 11, 16, 18, 30, 31, and 42 followed the literature procedures. On some occasions, low concentration glycosylation method is applied to obtain the β-anomers of the glycosylation product as standard for determination of α:β ratio.
2 Experimental procedures and spectroscopic data

2.1 One-pot *in situ* adduct transformation and glycosylation protocol for thioglycosyl donors (1, 2, 9-14, 30, and 32).

Thioglycoside donor (1.0 equiv), *N*-formylmorpholine (2.0 equiv), and activated 4Å molecular sieve (MS) were added to dried CH$_2$Cl$_2$ such that final concentration of the donor was 50 mM. Resulting mixture was stirred at room temperature for 10 min and at 0 °C (for 1, 2, 9-13, 30) or at -20 °C (for 14, 32) for additional 20-30 min. Subsequently, NIS (1.5 equiv.) and TMSOTf (1.0 equiv.) were added, and the reaction progress was monitored by TLC. Upon the complete formation of the NFM imidinium ion (by TLC examination), TBAI (5.0 equiv.) was added. The mixture was stirred at 0 °C for 0.5 to 2 h. Glycosyl iodides from donors 1, 2, 9-12 were detectable by TLC, but glycosyl iodides from 13, 14, 30 and 32 were not detectable. After 0.5 - 2 h, an acceptor (1.5 equiv.) and a base (DTBP, DIEA, or lutidine) (2.0 equiv.) were added to the reaction mixture. The reaction temperature was then raised to 30 °C and the resulting mixture was continuously stirred for ~ 18 - 24 h (for 14, a lower 15 °C was applied), followed by the addition of satd. NaHCO$_3$ and Na$_2$S$_2$O$_3$(s). The mixture was vigorously stirred until the red color of the solution changed to the pale yellow. The mixture was diluted with CH$_2$Cl$_2$, followed by filtration, and concentrated for flash chromatography purification over silica gel to furnish the glycosylation product.

2.2 One-pot *in situ* adduct transformation and glycosylation procedure for 2-azido-2-deoxythioglucoside donor (31)

Mixture of 2-azido-2-deoxythioglucoside donor 31 (2.0 equiv.), *N*-formylmorpholine (4.0 equiv.), and activated 4Å molecular sieve (MS) was suspended in dried CH$_2$Cl$_2$ ([31] = 50 mM). Then, the resulting mixture was stirred at room temperature for 10 min and at 0 °C for an additional 20 min, followed by addition of NIS (3.0 equiv.) and TMSOTf (2.6 equiv.). The formation of the NFM imidinium ion intermediate was monitored by TLC. Upon complete formation of the imidinium ion, TBAI (10.0 equiv.) was added and the mixture was stirred ng mixture was stirred at room temperature for 10 min and at 0 °C until the formation of glycosyl iodide (detectable by TLC). At this stage, acceptor (1.0 equiv.) and lutidine (5.2 equiv.) were
added and the reaction temperature was raised to 30 °C. After 24 h reaction, satd. NaHCO₃ and Na₂S₂O₃(s) were added to the mixture, followed by vigorous stirring until the color of the solution changed from the deep red to pale yellow. The resulting mixture was dried (over MgSO₄), filtered, and concentrated for flash chromatography purification over silica gel to furnish the glycosylation product.

2.3 Preparation of thioglycosyl substrates

2.3.1 p-Tolyl 2,3,4-Tri-O-benzyl-1-thio-α-D-xylopyranoside (14)

\[
\begin{align*}
\text{HO} & \quad \text{O} \quad \text{STol} \\
\text{OH} & \quad \text{BnO} \quad \text{BnO} \quad \text{OBn}
\end{align*}
\]

To a solution of thioxylopyranoside 14a (2 g, 7.8 mmol) in dried DMF (5 mL), NaH (1.2 g, 31 mmol) was added at ice bath temperature and the mixture was stirred under N₂ atmosphere. And then benzyl bromide (BnBr) (3.36 mL, 28 mmol) was added and the stirring was continued for 2 h. The reaction was quenched with ice water and diluted with CH₂Cl₂ (20 mL). The CH₂Cl₂ solution was washed with water (20 mL × 2), brine, dried over MgSO₄, filtered, and concentrated for flash chromatography (Hexanes/EtOAc 9:1). Desired thioxylopyranoside 14 (3.9 g) was afforded in 98% yield as a yellowish liquid. For thioxylopyranoside 14: Rf 0.30 (Hexanes/EtOAc 9:1); [α]D²⁰ +20.4 (c 0.22, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.43 (dd, J = 17.3, 8.6 Hz, 4H), 7.39 – 7.27 (m, 13H), 7.13 (d, J = 7.9 Hz, 2H), 4.97 – 4.82 (m, 3H), 4.83 – 4.70 (m, 2H), 4.64 (dt, J = 9.4, 6.7 Hz, 2H), 4.14 – 4.01 (m, 1H), 3.70 – 3.59 (m, 2H), 3.48 – 3.38 (m, 1H), 3.29 – 3.16 (m, 1H), 2.35 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 138.49, 138.15, 138.09, 137.84, 132.64, 132.25, 129.79, 129.76, 129.73, 128.49, 128.42, 128.41, 128.35, 128.19, 128.09, 128.06, 127.96, 127.89, 127.83, 127.71, 127.61, 88.75 (C-1), 85.44, 80.43, 76.74, 75.67, 75.44, 73.23, 67.51, 21.35 (CH₃). HRMS (ESI): calcd for C₃₃H₃₄NaO₄S⁺ requires 549.2070; found: m/z 549.2068 [M + Na]⁺.
2.4.2  

\[ p\text{-Tolyl 4-Azido-2,3-di-O-benzyl-4,6-dideoxy-1-thio-\(\beta\)-D-galactopyranoside (32)} \]

\[
\begin{align*}
32a &\xrightarrow{1) \text{TsCl, Et\textsubscript{3}N, DMAP, 0 }^\circ\text{C to rt}} \xrightarrow{2) \text{LAH, THF, 0 }^\circ\text{C to rt}} 32b \\
32b &\xrightarrow{1) \text{TsCl, Et\textsubscript{3}N, DMAP, 40 }^\circ\text{C}} \xrightarrow{2) \text{NaN\textsubscript{3}, DMF}} 32
\end{align*}
\]

73%  

\[
\begin{align*}
\text{32a}^{10} &\text{ (7.8 g, 16.7 mmol), NEt\textsubscript{3} (5.77 mL, 41.75 mmol), and DAMP (0.2 g, 1.67 mmol) in dried CH\textsubscript{2}Cl\textsubscript{2} (33 mL) was added tosyl chloride (TsCl) (4.77 g, 25.1 mmol) at 0 }^\circ\text{C. The reaction mixture was stirred at RT for 6 h, and then diluted with EtOAc (100 mL). The mixture was washed with 10% HCl}\text{(aq) (100 mL }\times 2\text{), brine, dried (over MgSO\textsubscript{4}), concentrated, and dried under vacuo to give crude C6-tosylated derivative. The crude tosylated derivative was dissolved in dried THF (65 mL) and to which lithium aluminum hydride (LiAlH\textsubscript{4}) (1.26 g, 33.4 mmol) was added at 0 }^\circ\text{C. The reaction mixture was stirred at RT for overnight and then quenched with EtOAc. The mixture was filtered and the filtrate obtained was diluted with EtOAc (200 mL), which was washed with H\textsubscript{2}O (100 mL }\times 2\text{), brine, dried (over MgSO\textsubscript{4}), and concentrated for flash chromatography (Hexanes/EtOAc = 10/1) to give 32b (5.3 g, 73%) as a white glassy solid. For 32b, } R\text{r 0.42 (Hexane/EtOAc = 3/1); } [\alpha]^{35}_D \text{ } -2.1 \text{ (c 0.9, CHCl}_3\text{); } ^1\text{H NMR (500 MHz, CDCl}_3\text{): } \delta 7.47 - 7.39 \text{ (m, 4H, } \text{ArH}), 7.36 - 7.26 \text{ (m, 8H, ArH), 7.10 (d, } J = 7.9 \text{ Hz, 2H, ArH}), 4.95 \text{ (d, } J = 10.5 \text{ Hz, 1H, benzyl-H), 4.93 \text{ (d, } J = 11.5 \text{ Hz, 1H, benzyl-H}), 4.71 \text{ (d, } J = 14.5 \text{ Hz, 1H, benzyl-H}), 4.68 \text{ (d, } J = 15.0 \text{ Hz, 1H, benzyl-H}), 4.59 \text{ (d, } J = 9.0 \text{ Hz, 1H, H-1}), 3.48 - 3.40 \text{ (m, 2H, H-4, H-2), 3.29 (dq, } J = 9.5, 6.0 \text{ Hz, 1H, H-5), 3.22 (t, } J = 8.5 \text{ Hz, 1H, H-3), 2.32 (s, 3H, } \text{CH}_3\text{), 2.22 (br-s, 1H, OH), 1.31 (d, } J = 6.0 \text{ Hz, 1H, H-6); } ^{13}\text{C NMR (125 MHz, CDCl}_3\text{): } \delta 138.3, 137.9, 137.6, 132.3, 129.9, 129.6, 128.6, 128.4, 128.2, 127.9, 127.8, 87.9 (C-1), 86.0, 81.0, 75.6, 75.2, 75.2, 74.8, 21.0, 17.9; } \text{HRMS (ESI): calcd for C}_{27}\text{H}_{30}\text{O}_4\text{SNa}^+ [M + Na]^+ \text{ requires 473.1757, found 473.1762 } m/z.}
\end{align*}
\]

To a solution of 32b (0.5g, 1.11 mmol), NEt\textsubscript{3} (0.46 mL, 3.33 mmol) and DAMP (0.67g, 0.555 mmol) in dried CH\textsubscript{2}Cl\textsubscript{2} (5 mL) was added tosylchloride (TsCl) (0.42 g, 2.22 mmol) at 0 °C. The reaction mixture was stirred at 40 °C for 24 h, and then diluted with EtOAc (10 mL). The
mixture was washed with 10% HCl(aq) (10 mL × 2), brine, dried (over MgSO₄), concentrated, and dried under vacuo to give crude C4-tosylated derivative. The crude tosylated derivative was dissolved in dried DMF (10 mL), followed by sodium nitrate (NaNO₃) (0.65 g, 9.99 mmol) was added at 110 °C and the reaction mixture was stirred for 22h. After completion reaction mixture was diluted with EtOAc (10 mL) and water (10mL). Organic layer was washed with saturated NaHCO₃(aq) (10 mL × 2) and brine (10 mL), dried (over MgSO₄), and concentrated for flash chromatography (Hexane/EtOAc = 9/1) to give 32 (0.86 g, 85%) as a white glassy solid. For 32, Rf 0.25 (Hexanes/EtOAc = 6/1); [α]D³⁵ −8.19 (c 0.39, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, J = 8.1 Hz, 2H, ArH), 7.41 – 7.24 (m, 10H, ArH), 7.09 (d, J = 7.9 Hz, 2H, ArH), 4.80 (d, J = 10.0 Hz, 1H, benzyl-H), 4.74–4.72 (m, 3H, benzyl-H), 4.48 (dd, J = 6.7, 2.7 Hz, 1H, H-1), 3.71–3.67 (m, 3H, H-2, H-3, H-4), 3.52 (q, J = 6.3 Hz, 1H, H-5), 2.31 (s, 3H, CH₃), 1.32 (d, J = 6.4 Hz, 3H, H-6); ¹³C NMR (100 MHz, CDCl₃) δ 138.1, 137.6, 137.5, 132.6, 129.7, 129.6, 129.5, 128.5, 128.3, 128.2, 127.9, 127.8, 127.7, 126.9, 87.9 (C-1), 83.1 (C-2), 77.3, 77.0, 76.8 (C-3), 76.7, 75.7 (C-5), 73.0, 72.7, 63.6 (C-4), 21.1, 17.8; HRMS (ESI): calcd for C₂₇H₂₉N₃O₃SNa⁺ [M + Na⁺] requires 498.1822, found 498.1822 m/z.

### 2.4.3 Methyl 4-O-Benzyl-2,6-dideoxy-α-D-ribo-hexopyranoside (34)

To a solution of α/β anomers of 34a¹¹ (0.848 g, 2.47 mmol) in dry CH₂Cl₂ (10 mL) containing pyridine (0.89 mL), triflic anhydride (TeO) (0.14 mL, 3.69 mmol) was added dropwise at -20 °C. The reaction mixture was stirred at -20 °C for 2 h and then diluted in EtOAc (30 mL) followed by washing with water (30 mL). The organic layer was further washed with satd. NaHCO₃ (30 mL) and brine, dried (over MgSO₄), filtered, concentrated, and dried under
vacuo to give crude 3-O-triflyl intermediate. The triflyl intermediate in dry toluene was added DBU (1.1 mL, 7.40 mmol) and benzoic acid (2.70 g, 22.17 mmol) and the mixture was stirred at room temperature for 30 min. The reaction mixture was stirred at 60 °C for 9 h. After then, the reaction mixture was cooled down to rt and diluted with EtOAc (10 mL). The EtOAc solution was washed satd. NaHCO₃ (30 mL × 3), brine, dried (over MgSO₄), and concentrated for flash chromatography (Hexanes/EtOAc = 20/1) to give 3-O-benzoyl intermediate 34b (0.71 g, 64%, α/β = 1:1 based on checking TLC) as an oily yellow liquid. For α anomer of 34b, Rf 0.35 (Hexanes/CH₂Cl₂/EtOAc = 10/1/1); [α]D³⁵ +288.0 (c 1.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.32 (dd, J = 8.1, 1.1 Hz, 2H, ArH), 7.56 – 7.51 (m, 1H, ArH), 7.48 – 7.37 (m, 4H, ArH), 7.30 – 7.21 (m, 5H, ArH), 7.09 (d, J = 7.9 Hz, 2H, ArH), 5.84 (d, J = 2.8 Hz, 1H, H-3), 5.43 – 5.39 (t, 1H, H-1), 4.74 (d, J = 11.5 Hz, 1H, benzyl-H), 4.69 (m, 1H, H-5), 4.45 (d, J = 11.5 Hz, 1H, benzyl-H), 3.26 (dd, J = 9.6, 2.8 Hz, 1H, H-4), 2.44-2.42 (m, 2H, H-2), 2.30 (s, 3H, CH₃), 1.32 (d, J = 6.4 Hz, 3H, H-6); ¹³C NMR (100 MHz, CDCl₃): δ 165.9 (C=O), 137.6, 137.0, 132.9, 131.6, 130.2, 129.5, 128.3, 128.2, 128.1, 127.7, 83.3 (C-1), 78.4 (C-4), 70.9, 65.1 (C-3), 64.1 (C-5), 35.4 (C-2), 21.0 (CH₃), 17.9 (C-6). For β anomer of 34b, Rf 0.45 (Hexanes/CH₂Cl₂/EtOAc = 10/1/1); [α]D³⁵ +9.74 (c 1.08, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.04 (dd, J = 4.5, 3.8 Hz, 2H, ArH), 7.53 (ddd, J = 6.9, 4.1, 1.3 Hz, 1H, ArH), 7.45 – 7.38 (m, 4H, ArH), 7.28 – 7.23 (m, 5H, ArH), 7.11 (d, J = 8.0 Hz, 2H, ArH), 5.80 (d, J = 2.8 Hz, 1H, H-3), 5.12 (d, J = 10.4 Hz, 1H, H-1), 4.70 (d, J = 11.5 Hz, 1H, benzyl-H), 4.42 (d, J = 11.5 Hz, 1H, benzyl-H), 4.05 – 3.97 (dq, J = 9.6 , 6.4 Hz, 1H, H-5), 3.24 (dd, J = 9.6, 2.8 Hz, 1H, H-4), 2.32 (s, 3H, CH₃ including H-2eq), 2.00 (ddd, J = 12.0, 14.4, 2.8 Hz, 1H, H-2ax), 1.34 (d, J = 6.4 Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 165.6 (C=O), 137.7, 137.5, 133.1, 132.5, 129.7, 129.5, 128.3, 128.3, 128.1, 127.7, 80.1 (C-1), 78.2 (C-4), 72.4 (C-5), 71.1, 66.6 (C-3), 36.3, 21.1 (CH₃), 18.5 (C-6); HRMS (ESI): calcd for C₂₇H₂₈O₄SNa⁺ [M + Na⁺] requires 471.1601, found 471.1620 m/z.

A suspension of 34b (0.46 g, 1.03 mmol) and activated molecular sieve (4Å) in dried CH₂Cl₂ (4.0 mL) was treated with DMF (0.33 mL, 4.1 mmol). The resulting mixture was stirred at rt for 10 min and then at −70 °C for 30 min. Subsequently, N-iodosuccinimide (NIS) (0.277 g, 1.23 mmol) and trimethylsilyl triflate (TMSOTf) (0.22 mL, 1.23 mmol) were added. Progress of
the reaction was monitored by TLC (EtOAc/Hexanes/CH2Cl2 = 1/10/1). After activation of 34b activation, additional DMF (0.63 mL, 8.21 mmol) and MeOH (0.2 mL, 5.13 mmol) was added to the donor activation mixture, which was then stirred at −50 °C under N2 till the formation of the product. The reaction was quenched with addition of satd. NaHCO3 and small lumps of Na2S2O3(s), followed by vigorous stirring until the color of the reaction mixture turned from dark red to pain yellow. The resulting mixture was dried (over MgSO4(s)), filtered, and concentrated for flash chromatography (Hexanes/EtOAc = 20/1) to give 34b (0.31 g, 85%, α/β = 1/1 based on checking TLC) as an oily yellow liquid. For α anomer of 34b, Rf 0.23 (Hexanes/CH2Cl2/EtOAc = 10/1/1); [α]D35 +184.85 (c 4.55, CHCl3); 1H NMR (400 MHz, CDCl3): δ 8.11 (d, J = 7.2 Hz, 2H), 7.56 – 7.50 (m, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.30 – 7.23 (m, 5H), 5.71 (q, J = 3.2 Hz, 1H, H-3), 4.73 (d, J = 11.6 Hz, H, benzyl-H), 4.71 (s, H-1 ), 4.45 (d, J = 11.6 Hz, 1H, benzyl-H), 4.32 – 4.23 (dq, J = 11.5, 6.0, 1H, H-5), 3.38 (s, 3H, OCH3), 3.25 (dd, J = 9.2, 2.8 Hz, 1H, H-4), 2.25 (dd, J = 15.2, 3.2 Hz, 1H, H-2α), 1.99 (dt, J = 15.2, 4.0 Hz, 1H, H-2ax), 1.29 (d, J = 6.0 Hz, 3H, H-6); 13C NMR (100 MHz, CDCl3): δ 166.2, 137.7, 132.7, 130.6, 129.8, 128.3, 128.2, 128.1, 127.7, 96.9(C-1), 78.1 (C-4), 70.8, 65.1 (C-3), 62.9 (C-5), 55.0 (OCH3), 33.6 (C-2), 17.9 (C-6). For β anomer of 34b, Rf 0.28 (Hexanes/CH2Cl2/EtOAc = 10/1/1); [α]D35 +91.49 (c 2.95, CHCl3); 1H NMR (400 MHz, CDCl3): δ 8.07 (dd, J = 8.1, 1.0 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.48 – 7.42 (m, 2H), 7.29 – 7.23 (m, 5H), 5.83 (dd, J = 6.4, 2.8 Hz, 1H, H-3), 4.80 (dd, J = 9.6, 2.0 Hz, 1H, H-1), 4.72 (d, J = 11.4 Hz, 1H, benzyl-H), 4.43 (d, J = 11.4 Hz, 1H, benzyl-H), 4.01 (dq, J = 9.2, 6.4 Hz, 1H, H-5), 3.51 (s, 3H, OCH3), 3.26 (dd, J = 9.2, 2.8 Hz, 1H, H-4), 2.24 (ddd, J = 14.2, 6.0, 2.0 Hz, 1H, H-2α), 1.84 (ddd, J = 14.2, 9.6, 2.8 Hz, 1H, H-2ax), 1.33 (d, J = 6.4 Hz, 3H, H-6); 13C NMR (100 MHz, CDCl3): δ 165.6 (C=O), 137.5, 133.0, 130.2, 129.7, 128.4, 128.3, 128.1, 127.8, 99.0 (C-1), 78.6, 71.3, 69.5, 66.7, 56.4, 35.8, 18.3; HRMS (ESI): calcd for C21H24O5Na+ [M + Na]+ requires 379.1518, found 379.1529 m/z.

To a solution of 34b (0.31 g, 0.87 mmol) in MeOH (5 mL), potassium carbonate (0.06 g, 0.87 mmol) was added at 0 °C. The reaction mixture was stirred at rt for 6 h and neutralized with resin IR-120 H+. The neutralization solution was filtered and concentrated for flash chromatography (Hexanes/EtOAc = 9/1) to give 34 (0.178 g, 81%, α/β = 1/1 based on checking
TLC) as an oily yellow liquid. For α anomer of 34, Rf 0.28 (Hexanes/ EtOAc = 3/1); [α]_{D}^{35} +75.10 (c 4.76, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.35 – 7.23 (m, 5H, ArH), 4.71 (d, J = 11.8 Hz, 2H, benzyl-H), 4.70 (d, J = 4.0 Hz, 1H, H-1) 4.49 (d, J = 11.8 Hz, 2H, benzyl-H), 4.15 (d, J = 3.0 Hz, 1H, H-3), 4.00 (dq, J = 9.6, 6.4 Hz, 1H, H-5), 3.33 (s, 3H, OCH₃), 3.27 (br-s, 1H, OH), 3.04 (dd, J = 9.6, 3.2 Hz, 1H, H-4), 2.12 (dd, J = 14.8, 3.6 Hz, 1H, H-2eq), 1.80 (dt, J = 14.8, 3.6 Hz, 1H, H-2ax), 1.28 (d, J = 6.0 Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 137.9, 128.3, 127.8, 127.7, 98.1 (C-1), 79.7, 70.4, 63.8, 62.1, 55.0, 35.0, 17.9. For β anomer of 34, Rf 0.38 (Hexanes/ EtOAc = 3/1); [α]_{D}^{35} +23.80 (c 2.11, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.38 – 7.28 (m, 5H, ArH), 4.72 (dd, J = 9.2, 1.6 Hz, 1H, H-1), 4.61 (d, J = 11.4 Hz, 1H, benzyl-H), 4.51 (d, J = 11.5 Hz, 1H, benzyl-H), 4.19 (d, J = 2.0 Hz, 1H, H-3), 3.82 (dq, J = 9.4, 6.2 Hz, 1H, H-5), 3.46(s, 1H, OCH₃), 3.13 – 3.09 (dq, 1H, J = 9.2, 3.2, 1.6 Hz, H-4), 2.55 (br-s, 1H, OH), 2.15 (d, J = 14.0 Hz, 1H, H-2eq), 1.65 – 1.56 (ddd, 1H, J = 9.6, 3.2, H-2ax), 1.29 (d, J = 6.4 Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 137.4, 128.4, 128.0, 127.8, 98.7 (C-1), 80.48, 71.6, 68.0, 64.4, 56.3, 36.5, 18.1; HRMS (ESI): calcd for C₁₄H₂₀O₄Na⁺ [M + Na]⁺ requires 275.1254, found 275.1245 m/z.

2.4 HPLC chromatograms and α/β ratio determination for glycosylations of Table 1

2.4.1 Amount of TBAI

Glycosylation without TBAI and base addition (Table 1, entry 1 in article): HPLC conditions - flow rate 1.0 mL/min and elution with 3/1 hexanes/EtOAc. Retention time for α anomer of 5 = 9.3 min and for β anomer of 5 = 7.7 min, thus α/β = 2/1 (Figure S1).
**Figure S1.** Partial HPLC chromatogram for 5 obtained from glycosylation without iodide substitution.

Glycosylation with addition of 2.0 equiv. TBAI (Table 1, entry 2 in article): HPLC conditions - flow rate 1.0 mL/min and 3/1 hexanes/EtOAc elution. Retention time for \( \alpha \) anomer of 5 = 9.0 min and \( \beta \) anomer of 5 = 7.4 min, thus \( \alpha/\beta = 5/1 \) (Figure S2).

**Figure S2.** HPLC chromatogram for sample 5 obtained from glycosylation with 2.0 equiv of TBAI.

Glycosylation with addition of 5.0 equiv. TBAI (Table 1, entry 3 in article): HPLC conditions: flow rate 1.0 mL/min and 3/1 hexanes/EtOAc elution. Retention time for \( \alpha \) anomer of 5 = 8.9 min and \( \beta \) anomer of 5 = 7.4, thus \( \alpha/\beta = 11/1 \) (Figure S3).

**Figure S3.** HPLC chromatogram for crude sample 5 obtained from glycosylation with 5.0 equiv of TBAI.
Glycosylation with addition of 10 equiv. TBAI (Table 1, entry 4 in article): HPLC conditions: flow rate 1.0 mL/min and 3/1 hexanes/EtOAc elution. Retention time for α anomer of 5 = 9.1 min and β anomer of 5 = 7.6 min, thus α/β = 13/1 (Figure S4).

**Figure S4.** HPLC chromatogram for crude sample 5 from glycosylation with 10.0 equiv. of TBAI.

### 2.4.2 Effect of temperature in glycosylation

Glycosylation at 15 ºC (Table 1, entry 6 in article): HPLC conditions: flow rate 1.0 mL/min and 4/1 hexanes/EtOAc elution. Retention time for β anomer of 6 obtained from low concentration glycosylation = 10.7 min (Figure S6-1). Retention time for α-anomer of 6 = 12.5 min and no β-anomer of 6 was detected at 10.7 min, thus α/β = >19/1(Figure S6-2).
Glycosylation at 30 °C (Table 1, entry 7 in article): HPLC conditions: flow rate 1.0 mL/min and 4/1 hexanes/EtOAc elution. Retention time for β anomer 6 obtained from low concentration glycosylation = 10.7 min (Figure S7-1). For crude product obtained from one-pot in situ adduct transformation and glycosylation procedure, retention time for α-anomer of 6 = 12.8 min and no β-anomer of 6 was detected at 10.7 min, thus $\alpha/\beta = >19/1$ (Figure S7-2).
Glycosylation at 50 °C (Table 1, entry 8 in article): HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 4/1. For crude product obtained from one-pot in situ adduct transformation and glycosylation procedure, retention time of β anomer of 6 = 11.3 min (Figure S8-1). Retention time for α anomer of 6 = 13.5 min and for β anomer of 6 = 11.6 min, thus α/β = 3/1 (Figure S8-2).
2.4.3 Effect of base in glycosylation

Glycosylation without base addition (Table 1, entry 9 in article): HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 4/1. Retention time for β-anomer 6 from low concentration glycosylation = 14.4 min (Figure S9-1). For crude product obtained from one-pot in situ adduct
transformation and glycosylation procedure in the absence of base, retention time for \( \alpha \) anomer of \( 6 \) = 16.7 min and \( \beta \) anomer of \( 6 \) = 14.7 min, thus \( \alpha/\beta = 5/1 \) (Figure S9-2).

**Figure S9-1.** HPLC chromatogram of \( \beta \) anomer of \( 6 \).

**Figure S9-2.** HPLC chromatogram for crude sample \( 6 \) from one-pot *in situ* adduct transformation and glycosylation procedure in the absence of base.

Glycosylation with 2,6-lutidine addition (Table 1, entry 10 in article): HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 4/1. Retention time for \( \beta \) anomer standard \( 6 \) obtained from low concentration glycosylation = 12.6 min (Figure S11-1). For sample obtained from one-pot *in situ* adduct transformation and glycosylation procedure with 2,6-Lutidine addition, retention time for \( \alpha \) anomer of \( 6 \) = 14.8 min; \( \beta \) anomer of \( 6 \) = 12.3 min, thus \( \alpha/\beta > 19/1 \) (Figure S11-2).
Glycosylation with DIEA addition (Table 1, entry 11 in article): HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 4/1. Retention time for β anomer standard of 6 obtained from low concentration glycosylation = 12.6 min (Figure S12-1). For sample obtained from one-pot in situ adduct transformation and glycosylation procedure with DIEA addition, retention time for α anomer of 6 = 15.0 min; β anomer of 6 = 12.4 min, thus α/β > 19/1 (Figure S12-1).
Figure S12-1. HPLC chromatogram of β anomer standard of 6.

Figure S12-2. HPLC chromatogram for crude product 6 obtained from one-pot in situ adduct transformation and glycosylation with DIEA addition.

2.5 Glycosylation products (5, 6, 19-29, 35-41, 43, 45)

2.5.1 3-O-[3,4,6-tri-O-benzyl-2-O-(2-naphthylmethyl)-α-D-glucopyranosyl]-1,2-O-cyclohexyldene-sn-glycerol (5)

\[
\begin{align*}
\alpha\text{-Glucoside } 5^1 \text{ was (126 mg, 60%) prepared from and glycosylation of } sn\text{-glycerol acceptor } 3 \text{ (72 mg, 0.42 mmol)}^1 \text{ with thioglucoside } 1 \text{ (200 mg, 0.28 mmol)}^1 \text{ according to one-pot }
\end{align*}
\]
in situ adduct transformation and glycosylation procedure (with DTBP as the base). For 5, ¹H NMR (500 MHz, CDCl₃): δ 7.84 – 7.73 (m, 4H), 7.51 – 7.44 (m, 3H), 7.39 – 7.21 (m, 13H), 7.16 – 7.12 (m, 2H), 5.00 (d, J = 10.9 Hz, 1H, OCHPh), 4.93 – 4.89 (m, 2H, including H-1’), 4.86 – 4.80 (m, 3H), 4.58 (d, J = 12.1 Hz, 1H, OCHPh), 4.49 – 4.44 (m, 2H), 4.40 – 4.34 (m, 1H), 4.06 (dd, J = 8.3, 6.4 Hz, 1H), 3.98 (t, J = 9.3 Hz, 1H), 3.81 – 3.76 (m, J = 8.9 Hz, 1H), 3.75 – 3.68 (m, 2H), 3.66 – 3.55 (m, 5H), 1.64 – 1.56 (m, 10H ); ¹³C NMR (125 MHz, CDCl₃): δ 138.8, 138.3, 137.9, 135.6, 133.2, 133.1, 128.4, 128.3, 128.2, 127.90, 127.86, 127.8, 127.7, 127.6, 127.5, 126.8, 126.1, 126.0, 125.9, 110.1, 97.3 (C-1’, J_CH = 167.8 Hz), 81.9, 79.9, 77.6, 75.7, 75.0, 74.3, 73.5, 73.1, 70.4, 69.0, 68.5, 66.6, 36.5, 35.0, 25.1, 24.0, 23.9. The α:β ratio of 5 was determined to be 11:1 by HPLC analysis (Table 1, entry 3). HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 3:1. Retention time of α anomer of 5 = 8.9 min and β anomer of 5 = 7.4 min (Figure S13).

![HPLC Chromatogram](image)

**Figure S13.** HPLC chromatogram for sample 5 obtained from one-pot in situ adduct transformation and glycosylation procedure.

### 2.5.2 Methyl 2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (6)
α-Anomer of disaccharide 6\textsuperscript{12} was (78 mg, 55%) synthesized from Glc donor \textit{2} (100 mg, 0.15 mmol) and Glc acceptor \textit{4} (105 mg, 0.23 mmol) using the one-pot in situ adduct transformation and glycosylation procedure (with DTBP as the base) (76% yield was achieved from DIEA or lutidine as the base). For α-anomer of 6, \textit{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ 7.37 – 7.20 (m, 33H, Ar\textit{H}), 7.15 – 7.10 (m, 2H, Ar\textit{H}), 5.00 – 4.89 (m, 4H, including H-1’), 4.85 – 4.75 (m, 3H), 4.70 (d, \textit{J} = 12.1 Hz, 1H, OCH\textit{Ph}), 4.68 – 4.62 (m, 3H), 4.58 (d, \textit{J} = 3.7 Hz, 1H), 4.55 (d, \textit{J} = 3.7 Hz, 2H, including H-1), 4.45 (d, \textit{J} = 11.0 Hz, 1H), 4.41 (d, \textit{J} = 12.1 Hz, 1H, OCH\textit{Ph}), 4.02 – 3.93 (m, 2H), 3.82 (dd, \textit{J} = 11.5, 4.4 Hz, 1H), 3.80 – 3.76 (m, 2H), 3.71 (d, \textit{J} = 11.1 Hz, 1H, OCH\textit{Ph}), 3.68 – 3.59 (m, 3H), 3.57 – 3.52 (m, 2H, including H-2’), 3.44 (dd, \textit{J} = 9.6, 3.5 Hz, 1H, H-2), 3.35 (s, 3H, OCH\textit{3}); \textit{13}C NMR (125 MHz, CDCl\textsubscript{3}) δ 138.8, 138.7, 138.41, 138.37, 138.36, 138.1, 137.9, 128.38, 128.35, 128.30, 128.26, 128.24, 128.21, 128.0, 127.94, 127.91, 127.88, 127.81, 127.78, 127.66, 127.65, 127.57 127.56, 127.54, 127.52, 127.49, 127.47, 127.4, 97.9 (C-1, \textit{J}\textit{CH} = 166.3 Hz), 97.2 (C-1’, \textit{J}\textit{CH} = 167.8 Hz), 82.1, 81.6, 80.1, 79.9, 77.9, 77.6, 75.7, 75.4, 74.9, 74.8, 73.3, 73.3, 72.3, 70.3, 70.2, 68.4, 66.0, 55.1 (OCH\textit{3}). The α/β ratio of 6\textit{a} was determined to be >19/1 by HPLC analysis (Table 1, entries 7, 10, and 11). HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 4/1. For sample obtained from one-pot in situ adduct transformation and glycosylation procedure, retention time for α anomer = 12.8 min and no β anomer was detected (Figure S14-2). β-Anomer of disaccharide 6 was synthesized from 2 and 4 using low concentration glycosylation procedure.\textsuperscript{7}

![Figure S14-1. HPLC chromatogram for β anomer of 6.](20)
2.5.3 Methyl 2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl(1→4)-2,3-O-isopropylidene-α-L-rhamnopyranoside (19)

α-Anomer of disaccharide 19\(^{13}\) was (78 mg, 70%) synthesized from donor 2 (100 mg, mmol) and acceptor 16 (46 mg, 0.23 mmol) according to one-pot in situ adduct transformation and glycosylation procedure (Table 2, entry 1 in article). For α-anomer of 19, \(^1\)H NMR (600 MHz, CDCl\(_3\)): δ 7.36 – 7.23 (m, 18H, ArH), 7.19 – 7.15 (m, 2H, ArH), 4.97 (d, J = 3.5 Hz, 1H, H-1′), 4.95(d, J = 10.09 Hz, 1H) 4.88 – 4.81 (m, 3H, including H-1), 4.79 (d, J = 11.6 Hz, 1H), 4.70 (d, J = 11.7 Hz, 1H), 4.61 (d, J = 12.1 Hz, 1H), 4.53 (d, J = 10.7 Hz, 1H), 4.49 (d, J = 12.1 Hz, 1H), 4.12 – 4.08 (m, 1H), 4.08 – 4.04 (m, 2H), 3.98 (t, J = 9.4 Hz, 1H), 3.82 – 3.71 (m, 3H), 3.67 – 3.62 (m, 1H), 3.59 (dd, J = 9.8, 3.6 Hz, 1H), 3.33 (m, 4H), 1.43 (s, 3H, isopropylidene-CH\(_3\)), 1.31 (d, J = 6.3 Hz, 3H, CH\(_3\)), 1.25 (s, 3H, isopropylidene-CH\(_3\)); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) δ 138.8, 138.4, 138.0, 137.9, 128.4, 128.9, 128.4, 128.3, 128.2, 127.9, 127.9, 127.9, 127.9, 127.8, 127.6, 127.6, 127.5, 108.9, 98.3 (C-1′, J\(_{\text{CF}} = 167.9\) Hz.), 97.8 (C-1, J\(_{\text{CH}} = 167.4\) Hz), 82.2, 80.9, 79.9, 77.9, 76.8, 75.9, 75.5, 75.1, 74.2, 73.5, 70.3, 68.0, 64.7, 54.6, 28.1, 26.3, 17.4; HRMS-ESI (m/z): [M + Na]\(^+\) calcd for C\(_{44}\)H\(_{52}\)NaO\(_{10}\)\(^+\), 763.3453; found 763.3450. The α/β ratio of 19 was
determined to be 19:1 by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 23/7. Retention time for β anomer standard sample of 19 obtained from low concentration glycosylation = 11.8 min (Figure S15-1). For 19 obtained from one-pot in situ adduct transformation and glycosylation procedure, retention for α anomer = 17.0 min; β anomer = 12.1 min (Figure S15-2).

Figure S15-1. HPLC chromatogram for β-anomer of disaccharide 19.

Figure S15-2. HPLC chromatogram for crude product 19 obtained from one-pot in situ adduct transformation and glycosylation procedure.
Diogeninyl α-glucoside 20 was synthesized from glycosylation of diosgenine acceptor 17 (94 mg, 0.225 mmol) with Glc donor 2 (100 mg, 0.15 mmol) using one-pot *in situ* adduct transformation and glycosylation procedure (Table 2, entry 2 in article). For α-glucoside 20, Rf 0.54 (hexanes/EtOAc 3/1); [α]D\textsubscript{35} +150 (c 0.08, CHCl\textsubscript{3}); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ 7.34 – 7.25 (m, 18H, Ar-H), 7.13 (dd, J = 2.0, 7.5 Hz, 2H, Ar-H), 5.28 (d, J = 5.0 Hz, 1H), 5.00 (d, J = 11.0 Hz, 1H), 4.93 (d, J = 3.5 Hz, 1H, H-1), 4.82 (dd, J = 8.0, 10.5 Hz, 2H), 4.76 (d, J = 12.0 Hz, 1H), 4.65 (d, J = 12.0 Hz, 1H), 4.60 (d, J = 12.0 Hz, 1H), 4.47 (d, J = 6.5 Hz, 1H), 4.44 (d, J = 8.0 Hz, 1H), 4.41 (q, J = 15.5 Hz, 1H), 3.99 (t, J = 9.5 Hz, 1H), 3.87 (d, J = 10.5 Hz, 1H), 3.73 (dd, J = 4.0, 11.0 Hz, 1H), 3.64 – 3.61 (m, 2H), 3.55 (dd, J = 4.0, 10.0 Hz, 1H), 3.48 – 3.43 (m, 2H), 3.37 (t, J = 10.5 Hz, 1H), 2.42 (t, J = 11.0 Hz, 1H), 2.28 (dd, J = 3.0, 13.0 Hz, 1H), 2.00 – 1.95 (m, 2H), 1.88 – 1.84 (m, 3H), 1.79 – 1.72 (m, 2H), 1.68 – 1.60 (m, 5H), 1.54 – 1.50 (m, 3H), 1.48 – 1.42 (m, 2H), 1.31 – 1.27 (m, 2H), 1.20 – 1.07 (m, 3H), 1.04 – 1.01 (m, 4H), 0.97 (d, J = 7.0 Hz, 3H), 0.93 (dd, J = 5.0, 11.5 Hz, 1H), 0.78 (t, J = 3.5 Hz, 6H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): δ 140.95, 139.04, 138.35, 138.33, 138.05, 128.49, 128.46, 128.45, 128.41, 128.22, 128.05, 127.99, 127.93, 127.89, 127.84, 127.78, 127.71, 127.63, 127.61, 121.51, 109.36, 94.74, 82.20, 80.91, 80.03, 77.97, 76.57, 75.75, 75.21, 73.51, 73.17, 70.15, 68.69, 66.93, 62.20, 56.61, 50.12, 41.70, 40.36, 39.95, 39.87, 37.16, 37.02, 32.17, 31.94, 31.52, 31.48, 30.39, 29.78, 28.89, 27.57, 20.94, 19.50, 17.22, 16.37, 14.61; HRMS-ESI (m/z): [M + Na]\textsuperscript{+} calcd for C61H76NaO8+, 959.5438; found, 959.5437.

The α/β ratio of 20 was determined to be 14/1 by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 85/15. Retention time of β anomer standard of 20 = 5.4
min (Figure S16-1). For 20 obtained from one-pot *in situ* adduct transformation and glycosylation procedure, retention time of α anomer = 6.1 min (Figure S16-2).

Figure S16-1. HPLC chromatogram of β-anomer of 20.

Figure S16-2. HPLC chromatogram for crude 20 obtained from one-pot *in situ* adduct transformation and glycosylation procedure.

2.5.5 \( p \)-Tolyl 2,3,4,6-Tetra-\( O \)-benzyl-\( \alpha \)-d-glucopyranosyl-(1→6)-2,3-di-\( O \)-benzoyl- 4-\( O \)-benzyl-thio-\( \beta \)-d-glucopyranoside (21)
α-Anomer of disaccharide 21 was (101 mg, 68%) synthesized from Glc 2 (100 mg, 0.15 mmol) and thiogluoside acceptor 18 (132 mg, 0.23 mmol) using one-pot in situ adduct transformation and glycosylation procedure (Table 2, entry 3 in article). For α-anomer of 21, Rf 0.35 (hexanes/EtOAc 3/1); [α]D35 +49.8 (c 0.610, CHCl3); 1H NMR (500 MHz, CDCl3): δ 7.95 (d, J = 7.2 Hz, 2H), 7.77 (d, J = 7.2 Hz, 2H), 7.52 – 7.46 (m, J = 13.7, 7.4 Hz, 2H), 7.40 – 7.24 (m, 25H), 7.15 – 7.12 (m, 2H), 7.11 – 7.08 (m, 2H), 7.06 – 7.03 (m, 4H), 5.65 (t, J = 9.4 Hz, 1H), 5.29 (t, J = 9.7 Hz, 1H), 5.11 (d, J = 3.5 Hz, 1H, H-1′), 5.01 (d, J = 10.9 Hz, 1H), 4.86 (d, J = 10.9 Hz, 1H), 4.83 (d, J = 10.9 Hz, 1H), 4.80 (d, J = 10.0 Hz, 1H), 4.73 – 4.68 (m, 2H), 4.65 (d, J = 12.2 Hz, 1H), 4.54 – 4.49 (m, 4H), 4.02 (t, J = 9.3 Hz, 1H), 3.92 – 3.87 (m, 4H), 3.75 – 3.66 (m, 4H), 3.62 (dd, J = 9.6, 3.5 Hz, 1H, H-2′), 2.20 (s, 3H); 13C NMR (125 MHz, CDCl3): δ 165.6, 165.2, 138.8, 138.5, 138.4, 138.2, 138.0, 137.3, 134.0, 133.1, 133.0, 129.83, 129.77, 129.75, 129.5, 129.4, 128.5, 128.4, 128.29, 128.27, 128.19, 128.17, 127.91, 127.90, 127.84, 127.79, 127.71, 127.70, 127.63, 127.55, 97.1 (C-1′, JCH = 168.8), 86.6, 81.9, 80.3, 79.6, 77.7, 76.3, 75.7, 75.6, 75.1, 74.6, 73.4, 72.9, 71.0, 70.3, 68.6, 65.2, 21.1 (CH3); HRMS-ESI (m/z): [M + Na]+ calcd for C₆₈H₆₆NaO₁₂S⁺, 1129.4167; found, 1129.4162.

The α/β ratio of 21 was 9:1 determined by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc gradient from 4/1 to 11/9. Retention time of β anomer of 21 (from low concentration glycosylation) = 15.1 min (Figure S17-1). For disaccharide 21 obtained from one-pot in situ adduct transformation and glycosylation procedure, retention time for α anomer = 17.4 min; β anomer = 15.1 min (Figure S17-2). β-Anomer of disaccharide 21 was synthesized from donor 2 and acceptor 18 using the low concentration glycosylation.7
Figure S17-1. HPLC chromatogram for β-anomer of 21.

Figure S17-2. HPLC chromatogram for crude product 21 obtained from one-pot *in situ* adduct transformation and glycosylation procedure.

2.5.6 6-O-Acetyl-2,3,4-tri-O-benzyl-α-D-glucopyranosyl-(1→6)-1,2:3,4-O-diisopropylidene-α-D-galactopyranose (22)

α-Anomer of disaccharide 22\textsuperscript{15} was (41 mg, 70%) synthesized from glycosylation of galactosyl acceptor 15 (31 mg, 0.12 mmol with glucosyl donor 9 (50 mg, 0.08 mmol) using one-pot *in situ* adduct transformation and glycosylation procedure (Table 2, entries 4 and 5 in article).
For α-anomer of 22, ¹H NMR (500 MHz, CDCl₃): δ 7.39 – 7.24 (m, 15H, ArH), 5.52 (d, J = 5.0 Hz, 1H, H-1), 5.00 (d, J = 10.8 Hz, 1H), 4.94 (d, J = 3.6 Hz, 1H, H-1′), 4.86 (d, J = 10.9 Hz, 1H), 4.81 (d, J = 10.8 Hz, 1H), 4.72 (q, J = 11.9 Hz, 2H), 4.60 (dd, J = 7.9, 2.4 Hz, 1H), 4.56 (d, J = 10.9 Hz, 1H), 4.35 – 4.29 (m, 3H), 4.23 (dd, J = 12.0, 2.1 Hz, 1H), 4.06 – 3.99 (m, 2H), 3.94 (ddd, J = 10.1, 4.1, 2.1 Hz, 1H), 3.80-3.70 (m, 2H), 3.55 (dd, J = 9.6, 3.6 Hz, 1H), 3.49 (dd, J = 9.9, 9.1 Hz, 1H), 2.02 (s, 3H, COCH₃), 1.54 (s, 3H, isopropylidene-CH₃), 1.45 (s, 3H, isopropylidene-CH₃), 1.33 (s, 3H, isopropylidene-CH₃), 1.31 (s, 3H, isopropylidene-CH₃); ¹³C NMR (125 MHz, CDCl₃): δ 170.8 (C=O), 138.7, 138.1, 137.9, 128.41, 128.37, 128.36, 128.1, 127.9, 127.83, 127.78, 127.75, 127.6, 109.2, 108.6, 97.0 (C-1′, JCH = 168.0 Hz), 96.3 (C-1, JCH = 178.4 Hz), 81.8, 79.8, 77.2, 75.6, 74.8, 72.4, 70.9, 70.6, 68.6, 66.6, 65.9, 63.1, 26.1, 26.0, 24.9, 24.6, 20.8 (CH₃CO); HRMS-ESI (m/z): [M + Na]⁺ calcd for C₄₁H₅₀NaO₁₂⁺, 757.3195; found, 757.3197.

The α/β ratio of 22 was determined to be >19/1 by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 3/1 gradient to 7/3. Retention time for β anomer of 22 obtained from low concentration glycosylation = 13.4 (Figure S18-1). For sample obtained from one-pot in situ adduct transformation and glycosylation procedure using DIEA, retention time for α anomer of 22 = 12.7 min and no β anomer of 22 detected at 13.4 min (Figure S18-2). For sample obtained from one-pot in situ adduct transformation and glycosylation procedure using LTD, retention time for α anomer of 22 (with LTD as the base) = 12.3 min and β anomer of 22 = 13.6 min (Figure S18-3). β-Anomer of disaccharide 22 was (92 mg, 74%) synthesized from 9 and 15 according to low concentration glycosylation procedure.⁷
Figure S18-1. HPLC chromatogram of β-anomer standard 22.

Figure 18-2. HPLC chromatogram for crude disaccharide product 22 obtained from one-pot in situ adduct transformation and glycosylation procedure with DIEA.

Figure S18-3. Partial HPLC chromatogram for crude disaccharide product 22 obtained from one-pot in situ adduct transformation and glycosylation procedure with LTD.

2.5.7 Methyl 6-O-Acetyl-2,3,4-tri-O-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (23)
α-Anomer of disaccharide 235 was (1.1 g, 70%) prepared from glucosyl acceptor 4 (1.2 g, 2.51 mmol) with thioglucoside donor 9 (1.0 g, 1.67 mmol) using one-pot in situ adduct transformation and glycosylation procedure (Table 2, entry 6 in article). For α-anomer of 23, 1H NMR (500 MHz, CDCl3): δ 7.34 – 7.23 (m, 30H, ArH), 4.98 (d, J = 1.4 Hz, 1H), 4.96 – 4.94 (m, 2H, including H-1′), 4.93 (d, J = 11.4 Hz, 1H), 4.87 (d, J = 11.0 Hz, 1H), 4.81 (d, J = 10.8 Hz, 1H), 4.78 (d, J = 10.9 Hz, 1H), 4.71 (d, J = 12.0 Hz, 1H), 4.67 – 4.62 (m, 3H), 4.60 – 4.52 (m, 3H, including H-1), 4.19 (d, J = 3.1 Hz, 2H), 3.98 (td, J = 9.2, 6.2 Hz, 2H), 3.85 (dt, J = 10.1, 3.0 Hz, 1H), 3.82 – 3.76 (m, 2H), 3.70 (d, J = 10.4 Hz, 1H), 3.64 (t, J = 9.4 Hz, 1H), 3.51 (dd, J = 9.6, 3.4 Hz, 1H, H-2′), 3.48 – 3.42 (m, 2H, including H-2), 3.36 (s, 3H, OCH3), 1.96 (s, 3H, COCH3); 13C NMR (125 MHz, CDCl3): δ 170.6 (C=O), 138.7, 138.5, 138.3, 138.2, 138.1, 138.0, 128.4 128.3, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 97.9 (C-1, JCH = 168.5 Hz), 97.0 (C-1′, JCH = 167.1 Hz), 82.1, 81.5, 80.1, 79.9, 77.7, 77.1, 75.7, 75.5, 74.9, 74.8, 73.3, 72.3, 70.3, 68.7, 66.0, 63.0, 55.1 (OCH3), 20.76 (COCH3). HRMS-ESI (m/z): [M + Na]+ calcd for C57H62NaO12+, 961.4134; found, 961.4135.

The α/β ratio of 23 was determined to be >19/1 by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc/CH2Cl2 7/2/1 gradient to 6/3/1. Retention time for β anomer standard 23 obtained from low concentration glycosylation = 11.9 min (Figure S19-1). For 23 obtained from one-pot in situ adduct transformation and glycosylation procedure, retention time of α anomer = 15.0 min; β anomer = 12.2 min (Figure S19-2). β-Anomer of disaccharide 235 was synthesized from Glc acceptor 4 with Glc donor 9 according to low concentration glycosylation procedure.7
Figure S19-1. HPLC chromatogram of β-anomer of 23.

Figure S19-2. HPLC chromatogram for crude 23 obtained from one-pot in situ adduct transformation and glycosylation procedure.

2.5.8 Methyl 6-\textit{O}-Benzoyl-2,3,4-tri-\textit{O}-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-\textit{O}-benzyl-α-D-glucopyranoside (24)

\[ \text{24} \]

α-Anomer of disaccharide 24 was (75 mg, 60%) synthesized from glucoside acceptor 4 (105 mg, 0.225 mmol) with thioglucoside donor 10 (100 mg, 0.125 mmol) using one-pot in situ adduct transformation and glycosylation procedure (Table 2, entry 7 in article). The resulting mixture
was dried (over MgSO₄), filtered, and concentrated for flash chromatography purification over silica gel (Elution: hexanes/EtOAc 1/0 to 7/1) to furnish the glycosylation product. For α-disaccharide 24, Rf 0.34 (hexanes/EtOAc 3/1); [α]D²⁵ +59.75 (c 0.569, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.90 – 7.88 (m, 2H, Ar-H), 7.45 (t, J = 7.6 Hz, 1H, Ar-H), 7.32 – 7.22 (m, 13H, Ar-H), 7.20 – 7.15 (m, 19H, Ar-H), 4.90 (d, J = 3.2 Hz, 1H), 4.87 (t, J = 2.8 Hz, 2H), 4.84 (d, J = 5.6 Hz, 1H), 4.82 (d, J = 5.2 Hz, 1H), 4.72 (dd, J = 3.2, 10.8 Hz, 2H), 4.59 (t, J = 13.6 Hz, 4H), 4.53 (s, 1H), 4.50 (d, J = 2.0 Hz, 1H), 4.47 (d, J = 3.2 Hz, 1H), 4.42 (dd, J = 2.0, 12.0 Hz, 1H), 4.30 (dd, J = 4.4, 12.0 Hz, 1H), 3.96 – 3.88 (m, 3H), 3.75 – 3.69 (m, 2H), 3.62 (d, J = 10.0 Hz, 1H), 3.54 – 3.45 (m, 3H), 3.32 (dd, J = 3.6, 9.6 Hz, 1H), 3.27 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 166.2 (C=O), 138.9, 138.6, 138.38, 138.37, 138.2, 138.0, 133.1, 130.0, 129.7, 128.47, 128.46, 128.41, 128.39, 128.2, 128.04, 128.03, 127.97, 127.90, 127.84, 127.78, 127.75, 127.72, 127.65, 127.63, 98.0 (¹JCH = 165.4 Hz), 97.0 (¹JCH = 168.4 Hz), 82.2, 81.8, 80.24, 80.20, 77.9, 77.6, 75.8, 75.1, 73.4, 72.5, 70.4, 68.9, 66.1, 63.5, 55.2; HRMS -ESI (m/z): [M + Na]⁺ calcd for C₆₂H₆₄NaO₁₂⁺, 1023.4290; found, 1023.4332. The α:β ratio of the product was estimated by ¹H NMR spectroscopy.

2.5.9 Methyl 6-O-tert-Butyl-diphenylsilyl-2,3,4-tri-O-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (25)

α-Anomer of disaccharide 25 was (80 mg, 55%) synthesized from glucosyl acceptor 4 (87 mg, 0.188 mmol) with thioglucoside donor 11 (100 mg, 0.125 mmol) using one-pot in situ adduct transformation and glycosylation procedure (Table 2, entry 8 in article). For α-disaccharide 25, Rf 0.42 (hexanes/EtOAc 3/1); [α]D²⁸ +52.1 (c 2.07, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.70 – 7.63 (m, 4H, Ar-H), 7.38 – 7.23 (m, 34H, Ar-H), 7.15 – 7.12 (m, 2H, Ar-H), 5.01 (t, J = 3.6 Hz, 1H; H-1’), 4.95 – 4.87 (m, 4H), 4.83 – 4.77 (m, 2H), 4.71 – 4.53 (m, 7H; including H-1),
4.02 – 3.95 (m, 2H), 3.82 – 3.64 (m, 9H), 3.57 – 3.52 (m, 1H), 3.44 – 3.40 (m, 1H), 3.35 (s, 3H; CH₃), 1.02 (s, 9H; tbutyl-H); ¹³C NMR (100 MHz, CDCl₃) δ 138.9, 138.8, 138.64, 138.57, 138.4, 138.3, 135.9, 135.7, 133.7, 133.4, 129.62, 129.58, 128.5, 128.43, 128.41, 128.35, 128.2, 128.06, 128.03, 127.9, 127.8, 127.73, 127.69, 127.66, 127.60, 127.57, 98.02 (¹JCH = 168.5 Hz), 97.00 (¹JCH = 167.1 Hz), 82.2, 81.9, 80.5, 80.2, 77.84, 77.79, 75.75, 75.7, 75.1, 75.0, 73.4, 72.4, 71.7, 70.6, 65.7, 63.0, 55.2, 26.9, 19.4; HRMS-ESI (m/z): [M + Na]^+ calcd for C₇₁H₇₈NaO₁₁Si^+, 1157.5206; found, 1157.5227.

The α/β ratio of 25 was determined to be 10/1 by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 80/20. Retention time of β anomer standard of 25 = 7.6 min (Figure S20-1). For 25 obtained from one-pot in situ adduct transformation and glycosylation procedure, retention time of α anomer = 8.2 min (Figure S20-2).

![Figure S20-1. HPLC chromatogram of β-anomer of 25.](image1)

![Figure S20-2. HPLC chromatogram for crude 25 obtained from one-pot in situ adduct transformation and glycosylation procedure.](image2)
2.5.10 Methyl 4-O-Acetyl-2,3,6-tri-O-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (26)

α-Anomer of disaccharide 26 was (1.02 g, 65%) synthesized from acceptor 4 (1.17 g, 2.51 mmol) with donor 12 (1.0 g, 1.67 mmol) using one-pot in situ adduct transformation and glycosylation procedure (Table 2, entry 9 in article). For α-disaccharide 26, Rf 0.16 (hexanes/EtOAc 3/1); [α]_{D}^{35} +76.2 (c 0.315, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 7.34 – 7.22 (m, 30H, Ar-H), 5.02 (d, J = 10.0 Hz, 1H), 4.99 (d, J = 5.0 Hz, 1H), 4.95 (d, J = 3.5 Hz, 2H, including H-1’), 4.92 (d, J = 10.5 Hz, 1H), 4.82 (t, J = 11.5 Hz, 2H), 4.71 (d, J = 12.5 Hz, 1H), 4.66 (d, J = 5.0 Hz, 2H), 4.63 (d, J = 8.0 Hz, 1H), 4.59 (d, J = 1.5 Hz, 1H), 4.57 (d, J = 3.0 Hz, 1H; H-1), 4.45 (q, J = 12.0 Hz, 2H), 3.99 (t, J = 9.0 Hz, 1H), 3.87 (t, J = 12.5 Hz, 1H), 3.84 – 3.77 (m, 3H), 3.71 (d, J = 11.5 Hz, 1H), 3.65 (t, J = 9.5 Hz, 1H), 3.56 (dd, J = 3.0, 9.5 Hz, 1H), 3.45 (dd, J = 3.5, 9.5 Hz, 1H), 3.41 (dd, J = 3.0, 11.0 Hz, 1H), 3.37 (d, J = 5.0 Hz, 1H), 3.35 (s, 3H, CH₃), 1.80 (s, 3H, CH₃); ¹³C NMR (125 MHz, CDCl₃): δ 169.7 (C=O), 138.9, 138.7, 138.5, 138.3, 138.2, 137.9, 128.51, 128.47, 128.46, 128.36, 128.34, 128.11, 128.07, 128.03, 127.94, 127.91, 127.77, 127.76, 127.73, 127.69, 127.65, 127.58, 98.1 (C-1, ¹J_CH = 165.0 Hz), 97.2 (C-1’), ¹J_CH = 168.6 Hz), 82.22 80.3, 79.7, 78.6, 77.9, 75.8, 75.1, 74.9, 73.6, 73.5, 72.6, 70.5, 70.4, 68.94, 68.89, 66.3, 55.2, 20.9. HRMS-ESI (m/z): [M + Na]⁺ calcd for C₅₇H₆₂NaO₁₂⁺, 961.4133; found, 961.4150. The α:β ratio of 26 was 12:1 as estimated by ¹H NMR spectroscopy.
2.5.11 Methyl 2,3,4,6-tetra-O-benzyl-α-D-galactopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (27)

α-Anomer of disaccharide 27\textsuperscript{16} (54.4 mg, 69%) was synthesized from donor 13 (50 mg, 0.08 mmol) and acceptor 4 (56 mg, 0.12 mmol) using one-pot \textit{in situ} adduct transformation and glycosylation procedure (Table 2, entry 10 in article). For α-anomer of 27, \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 7.38 – 7.17 (m, 35H, Ar-H), 4.99 (d, \(J = 3.5\) Hz, 1H, H-1), 4.95 (d, \(J = 8.7\) Hz, 1H), 4.93 (d, \(J = 9.2\) Hz, 1H), 4.84 (d, \(J = 11.0\) Hz, 1H), 4.80 (d, \(J = 4.8\) Hz, 1H, H-1’), 4.78 (d, \(J = 5.9\) Hz, 1H), 4.72 – 4.67 (m, 4H), 4.60 – 4.56 (m, 2H), 4.54 (d, \(J = 4.2\) Hz, 1H), 4.53 (d, \(J = 3.5\) Hz, 1H, H-1), 4.42 (d, \(J = 11.8\) Hz, 1H), 4.36 (d, \(J = 11.8\) Hz, 1H), 4.03 (dd, \(J = 3.5, 9.5\) Hz, 1H), 3.99 – 3.93 (m, 2H), 3.93 – 3.88 (m, 2H), 3.82 – 3.70 (m, 3H), 3.59 (t, \(J = 9.3\) Hz, 1H), 3.54 – 3.46 (m, 2H), 3.41 (dd, \(J = 3.6, 9.6\) Hz, 1H, H-2’), 3.29 (s, 3H, OCH\textsubscript{3}); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \(\delta\) 138.9, 138.8, 138.71, 138.67, 138.4, 138.2, 138.1, 138.4, 138.32, 138.30, 128.25, 128.20, 128.15, 128.14, 128.09, 128.07, 128.01, 128.00, 127.93, 127.91, 127.8, 127.7, 127.60, 127.58, 127.5, 127.4, 127.3, 97.90 (C-1, \(J_{\text{CH}} =168.3\) Hz), 97.85 (C-1’, \(J_{\text{CH}} =168.3\) Hz), 82.0, 80.2, 78.2, 78.0, 76.51, 75.6, 75.1, 75.0, 74.7, 73.3, 73.3, 72.8, 72.5, 70.3, 69.4, 68.9, 66.4, 55.0 (OCH\textsubscript{3}). The α/β ratio of 27 was determined to be >19/1 by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 4/1 to 7/3. Retention time for β anomer of 27 = 15.1 min (Figure S21-1). For 27 obtained from one-pot \textit{in situ} adduct transformation and glycosylation procedure, retention time for α anomer = 13.4 min; no β anomer was detected at 15.1 min (Figure S21-2). β-Anomer of disaccharide 27\textsuperscript{16} was synthesized from 13 and 4 using low concentration glycosylation procedure.\textsuperscript{7}
Figure S21-1. HPLC chromatogram of β-anomer of 27.

Figure S21-2. HPLC chromatogram for crude product 27 from one-pot in situ adduct transformation and glycosylation procedure.

2.5.12 2,3,4,6-tetra-O-benzyl-α-D-galactopyranosyl-(1→6)-1,2:3,4-di-O-isopropylidene-α-D-galactose (28)

α-Anomer of disaccharide 28\textsuperscript{17} was (135 mg, 63%, 13:1 α:β) synthesized from acceptor 15 (117 mg, 0.45 mmol) and donor 13 (200 mg, 0.30 mmol) with the one-pot in situ adduct transformation and glycosylation procedure (Table 2, entry 11 in main text). For α-anomer of 28,
$R_{f} 0.28$ (hexanes/EtOAc 3/1); $[\alpha]^{35}_{D} +48.0 \ (c \ 0.248, \ \text{CHCl}_3);$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta 7.83 – 7.78 \ (m, \ 3H, \ \text{Ar-H}), \ 7.75 – 7.72 \ (m, \ 1H, \ \text{Ar-H}), \ 7.50 – 7.44 \ (m, \ 3H, \ \text{Ar-H}), \ 7.39 – 7.38 \ (m, \ 2H, \ \text{Ar-H}), \ 7.35 – 7.22 \ (m, \ 11H, \ \text{Ar-H}), \ 5.52 \ (d, \ J = 4.8 \ Hz, \ 1H, \ H-1'), \ 5.03 \ (d, \ J = 3.6 \ Hz, \ 1H, \ H-1'), \ 4.97 \ (dd, \ J = 4.8, \ 12.0 \ Hz, \ 2H), \ 4.87 \ (d, \ J = 12.0 \ Hz, \ 1H), \ 4.78 \ (s, \ 2H), \ 4.61 \ (d, \ J = 11.6 \ Hz, \ 1H), \ 4.57 \ (dd, \ J = 2.4, \ 8.0 \ Hz, \ 1H), \ 4.49 \ (d, \ J = 12.8 \ Hz, \ 1H), \ 4.43 \ (d, \ J = 12.8 \ Hz, \ 2H), \ 4.34 – 4.29 \ (m, \ 2H), \ 4.12 \ (dd, \ J = 1.6, \ 10.8 \ Hz, \ 1H), \ 4.07 – 4.01 \ (m, \ 3H), \ 3.83 – 3.73 \ (m, \ 2H), \ 3.62 – 3.52 \ (m, \ 2H), \ 1.50 \ (s, \ 3H, \ \text{CH}_3), \ 1.44 \ (s, \ 3H, \ \text{CH}_3), \ 1.32 \ (s, \ 3H, \ \text{CH}_3), \ 1.30 \ (s, \ 3H, \ \text{CH}_3); \ ^{13}$C NMR (100 MHz, CDCl$_3$): $\delta 138.79, \ 138.77, \ 138.1, \ 136.5, \ 133.5, \ 132.9, \ 128.4, \ 128.30, \ 128.23, \ 128.17, \ 128.0, \ 127.94, \ 127.85, \ 127.8, \ 127.7, \ 127.54, \ 127.53, \ 126.03, \ 126.00, \ 125.8, \ 125.7, \ 109.2, \ 108.6, \ 97.6 \ (C-1, \ ^1J_{CH} = 168.5 \ Hz), \ 96.4 \ (C-1', \ ^1J_{CH} = 176.2 \ Hz), \ 79.0, \ 76.5, \ 75.1, \ 74.9, \ 73.4, \ 73.1, \ 72.7, \ 70.9, \ 70.71, \ 70.67, \ 69.2, \ 68.7, \ 66.4, \ 65.9, \ 26.2, \ 26.1, \ 24.5, \ 24.6.$

The $\alpha/\beta$ ratio of 28 was determined to be $10/1$ by HPLC analysis. HPLC conditions: flow rate $1.0 \ \text{mL/min};$ elution: hexanes/EtOAc 75/25. Retention time of $\beta$ anomer of 28 = 9.7 min (Figure S22-1). For 28 obtained from one-pot in situ adduct transformation and glycosylation procedure, retention time of $\alpha$ anomer = 7.9 min (Figure S22-2).

![Figure S22-1. HPLC chromatogram of $\beta$-anomer of 28.](image-url)
2.5.13 2,3,4-Tri-O-benzyl-α-D-xylopyranosyl-(1→6)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (29)

α-Anomer of disaccharide 29\(^{18}\) was (45 mg, 75%) synthesized from the reaction of acceptor 15 (36 mg, 0.14 mmol) with xylosyl donor 14 (50 mg, 0.09 mmol) using one-pot \textit{in situ} adduct transformation and glycosylation procedure (Table 2, entry 12 in main text). For α-anomer of disaccharide 29, \(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)): δ 7.38 – 7.26 (m, 15H), 5.53 (d, \(J = 5.0\) Hz, 1H, H-1), 4.92 (d, \(J = 10.9\) Hz, 1H), 4.89 – 4.86 (m, 2H, including H-1’), 4.75 – 4.70 (m, 3H), 4.64 – 4.59 (m, 2H), 4.36 (dd, \(J = 7.9, 1.8\) Hz, 1H), 4.31 (dd, \(J = 5.0, 2.3\) Hz, 1H), 4.07 – 4.03 (m, 1H), 3.93 – 3.87 (m, 1H), 3.77 (dd, \(J = 10.2, 6.0\) Hz, 1H), 3.71 (dd, \(J = 10.2, 7.7\) Hz, 1H), 3.62-3.55 (m, 3H), 3.46 (dd, \(J = 3.6, 9.5\) Hz, 1H), 1.54 (s, 3H, isopropylidene-CH\(_3\)), 1.45 (s, 3H, isopropylidene-CH\(_3\)), 1.33 (s, 3H, isopropylidene-CH\(_3\)), 1.31 (s, 3H, isopropylidene-CH\(_3\)); \(^{13}\text{C NMR}\) (125 MHz, CDCl\(_3\)): δ 139.0, 138.4, 138.3, 128.39, 128.37, 128.30, 128.27, 128.25, 128.17, 127.94, 127.91, 127.80, 127.78, 127.75, 127.71, 127.6, 127.48, 127.46, 127.43, 109.1,
108.6, 97.2 (C-1', $J_{CH} = 167.6$ Hz), 96.3 (C-1, $J_{CH} = 178.6$ Hz), 81.2, 79.6, 78.0, 75.6, 73.4, 72.5, 70.8, 70.7, 70.6, 66.3, 65.8, 60.0, 26.1, 26.0, 24.9, 24.6.

The $\alpha/\beta$ ratio of 29 was determined by HPLC analysis (Elution: hexanes/EtOAc 4/1 gradient to 7/3). Retention time of $\beta$ anomer of 29 = 16.4 min (Figure S23-1). For 29 obtained from one-pot $in situ$ adduct transformation and glycosylation procedure, retention time for $\alpha$ anomer = 12.1 min and $\beta$ anomer = 16.6 min, thus $\alpha/\beta = 5/1$ (Figure S23-2). $\beta$-Anomer of disaccharide 29 was synthesized from 14 and 15 according to the low concentration glycosylation procedure.

![Figure S23-1. HPLC chromatogram of $\beta$-anomer 29.](image1)

![Figure S23-2. Partial HPLC chromatogram of crude product 29 from one-pot $in situ$ adduct transformation and glycosylation procedure.](image2)
2.5.14 Methyl 2-Azido-3,4,6-tri-\textit{O}-benzyl-2-deoxy-\alpha-D-galactopyranosyl-(1→6)-2,3,4- \textit{O}-benzyl-\alpha-D-glucopyranoside (35)

α-Anomer of disaccharide 35 was (102 mg, 65%) synthesized from glucosyl acceptor 4 (121 mg, 0.26 mmol) with 2-azido-2-deoxythiogalactoside donor 30 (100 mg, 0.17 mmol) using one-pot \textit{in situ} adduct transformation and glycosylation procedure (Table 3, entry 1 in article). For α-anomer of disaccharide 35, \textit{Rf} 0.4 (hexanes/EtOAc 2.5/1); [\textit{α}]_{D}^{25} +60.4 (c 0.345, CHCl\textsubscript{3}); \textit{1H NMR} (500 MHz, CDCl\textsubscript{3}): δ 7.43 – 7.20 (m, 30H), 5.01 – 4.96 (m, 2H, including H-1'), 4.90 – 4.84 (m, 2H), 4.83 – 4.75 (m, 2H), 4.72 (d, \textit{J} = 10.8 Hz, 1H), 4.65 (d, \textit{J} = 10.7 Hz, 2H), 4.60 – 4.50 (m, 3H, including H-1), 4.44 (d, \textit{J} = 11.8 Hz, 1H, OCH\textsubscript{Ph}), 4.37 (d, \textit{J} = 11.1 Hz, 1H, OCH\textsubscript{Ph}), 4.03 – 3.96 (m, 2H), 3.96 – 3.91 (m, 1H), 3.91 – 3.86 (m, 1H), 3.85 – 3.73 (m, 3H), 3.69 (d, \textit{J} = 11.1 Hz, 1H, H-6), 3.59 – 3.48 (m, 4H), 3.33 (s, 3H, OCH\textsubscript{3}); \textit{13C NMR} (125 MHz, CDCl\textsubscript{3}): δ 138.7, 138.2, 138.2, 138.1, 137.8, 137.4, 128.5, 128.4, 128.3, 128.2, 128.0, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6, 98.5 (C-1', \textit{J}\textsubscript{CH} = 171.0 Hz), 97.8 (C-1, \textit{J}\textsubscript{CH} = 166.9 Hz), 81.9, 80.0, 77.8, 76.5, 75.7, 74.9, 74.7, 73.4, 73.3, 71.9, 69.9, 69.6, 68.5, 66.6, 59.8, 55.0; HRMS-ESI (m/z): [M + Na]\textsuperscript{+} calcd for C\textsubscript{55}H\textsubscript{59}N\textsubscript{3}NaO\textsubscript{10}, 944.4093; found, 944.4097.

The α/β ratio of 35 was determined by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 3/1. For β anomer standard of 35, retention time = 12.4 min (Figure S24-1). For 35 obtained from one-pot \textit{in situ} adduct transformation and glycosylation procedure, retention time of α anomer = 10.2 min and β anomer = 12.8 min, thus α/β ratio >19/1 (Figure S24-2). β-Anomer of disaccharide 35\textsuperscript{19} was synthesized from 30 and 4 using the low concentration glycosylation procedure.\textsuperscript{7}
2.5.15 Cholesteryl 2-Azido-3,4,6-tri-O-benzyl-2-deoxy-α-D-galactopyranoside (36)

α-Anomer of cholesteryl galactoside 36 was (55 mg, 54%) synthesized from cholesterol 33 (70 mg, 0.18 mmol) and GalN₃ donor 30 (70 mg, 0.12 mmol) according to one-pot *in situ* adduct transformation and glycosylation procedure (Table 3, entry 2 in article) and was obtained as a white amorphous solid upon column chromatography purification (Elution: hexanes/EtOAc/
CH₂Cl₂ 30/1/1 to 26/1/1). For α-anomer of 36, \( R_t \) 0.7 (hexanes/EtOAc 5/1); [\( \alpha \)]\( _D^{25} \) +51.0 (c 0.8, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 7.43 – 7.22 (m, 15H), 5.28 (d, \( J = 5.0 \) Hz, 1H), 5.05 (d, \( J = 3.6 \) Hz, 1H, H-1’), 4.88 (d, \( J = 11.3 \) Hz, 1H), 4.72 (q, \( J = 11.3 \) Hz, 2H), 4.53 (d, \( J = 11.0 \) Hz, 1H), 4.50 (d, \( J = 12.0 \) Hz, 1H), 4.43 (d, \( J = 11.7 \) Hz, 2H), 4.10 – 4.03 (m, 2H), 3.98 (dd, \( J = 2.6, 10.7 \) Hz, 1H), 3.79 (dd, \( J = 3.6, 10.7 \) Hz, 1H, H-2), 3.63 – 3.53 (m, 2H), 3.51 – 3.43 (m, 1H), 2.41 – 2.28 (m, 2H), 2.06 – 1.89 (m, 3H), 1.90 – 1.78 (m, 2H), 1.63 – 0.84 (m, 33H), 0.68 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 140.6, 138.4, 137.9, 137.7, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 121.9, 96.8 (C-1, \( J_{CH} = 168.5 \) Hz), 78.2, 77.4, 74.8, 73.6, 73.5, 72.2, 69.6, 68.8, 59.7 (C-2’), 56.8, 56.1, 50.1, 42.3, 40.0, 39.8, 39.5, 37.0, 36.7, 36.2, 35.8, 31.9, 28.2, 28.0, 27.9, 24.3, 23.8, 22.8, 22.6, 21.0, 19.4, 18.7, 11.9. HRMS-ESI (m/z): [M + Na]+ calcd for C₅₄H₇₃N₃NaO₅⁺, 866.5442; found, 866.5443.

The α/β ratio of 32 was determined to be >19/1 by HPLC analysis (Table 3, Entry 2). HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 24/1 gradient to 19/1. For β anomer standard of 36 obtained from low concentration glycosylation, retention time = 23.4 min (Figure S25-1). For 36 obtained from one-pot in situ adduct transformation and glycosylation, retention time of α anomer = 12.5 min and no β anomer was detected at 23.4 min (Figure S25-2). β-Anomer of cholesteryl galactoside 36 was synthesized from cholesterol 33 and donor 30 based on the low concentration glycosylation procedure.⁷

![Figure S25-1. HPLC chromatogram of β anomer standard 36.](image-url)
Figure S25-2. HPLC chromatogram for crude product 36 from one-pot in situ adduct transformation and glycosylation procedure.

2.5.16 Methyl 2-Azido-3,4,6-tri-O-benzyl-2-deoxy-α-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (37)

α-Anomer of disaccharide 37 was (30 mg, 55%) synthesized from glucosyl acceptor 4 (28 mg, 0.06 mmol) and 2-azido-2-deoxythioglucoside donor 31 (70 mg, 0.12 mmol) according to one-pot in situ adduct transformation and glycosylation procedure with 2-azido-2-deoxythioglucoside donor (Table 3, entry 3 in main text). For α-anomer 37, Rf 0.3 (hexanes/EtOAc 2.5/1); [α]D25 +46.8 (c 0.513, CHCl3); 1H NMR (500 MHz, CDCl3): δ 7.37 – 7.24 (m, 28H, ArH), 7.15 – 7.17 (m, 2H, ArH), 5.00 (d, J = 3.5 Hz, 1H, H-1’), 4.98 (d, J = 10.8 Hz, 1H), 4.94 (d, J = 11.2 Hz, 1H, benzyl-H), 4.85 (d, J = 3.0 Hz, 2H), 4.81 – 4.78 (m, 2H), 4.77 (d, J = 2.7 Hz, 1H), 4.66 (d, J = 12.0 Hz, 1H, benzyl-H), 4.61 – 4.55 (m, 3H, including H-1), 4.48 (d, J = 11.0 Hz, 1H, benzyl-H), 4.42 (d, J = 12.1 Hz, 1H, benzyl-H), 4.00 (t, J = 9.3 Hz, 1H, H-3), 3.92 (dd, J = 8.6, 10.2 Hz, 1H, H-3’), 3.82 (dd, J = 4.5, 11.3 Hz, 1H, H-6’), 3.79 – 3.72 (m, 2H), 3.72 – 3.66 (m, 2H), 3.63 (dd, J = 3.3, 10.8 Hz, 1H, H-6’), 3.59 – 3.51 (m, 3H), 3.37 (s, 3H, OCH3), 3.33 (dd, J = 3.5, 10.3 Hz, 1H); 13C NMR (125 MHz, CDCl3): δ 138.7, 138.3, 138.1,
138.0, 137.9, 137.8, 128.43, 128.37, 128.14, 128.05, 128.03, 127.96, 127.87, 127.85, 127.82, 127.76, 127.69, 127.65, 127.63, 127.61, 127.60, 98.2 (C-1’, J_{CH} = 171.3 Hz), 97.9 (C-1, J_{CH} = 167.4 Hz), 82.0, 80.1, 79.8, 78.2, 77.7, 75.8, 75.2, 74.9, 73.5, 73.4, 70.7, 69.9, 68.1, 66.4, 63.5, 55.2 (OCH₃). HRMS-ESI (m/z): [M + Na]⁺ calcd for C₅₅H₅₉N₃NaO₁₀⁺, 944.4093; found, 944.4094.

The α/β ratio of 37 was determined to be 9/1 by HPLC analysis (Table 3, Entry 4). HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 77/23. For β anomer standard of 37, retention time = 9.5 min (Figure S27-1). For 37 obtained from one-pot in situ adduct transformation and glycosylation procedure, retention time of α anomer = 12.0 min; β anomer = 9.6 min (Figure S27-2). β-Anomer of disaccharide 37₁₈ was synthesized from 31 and 4 according to the low concentration glycosylation procedure.⁷

![Figure S27-1. HPLC chromatogram of β-anomer of 37.](image1)

![Figure S27-2. HPLC chromatogram of α-anomer of 37.](image2)
2.5.17 2-Azido-3,4,6-tri-O-benzyl-2-deoxy-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (38)

α-Anomer of disaccharide 38 was (27 mg, 84%) synthesized from galactosyl acceptor 15 (12 mg, 0.045 mmol) with 2-azido-2-deoxythioglucoside donor 31 (50 mg, 0.09 mmol) according to one-pot in situ adduct transformation and glycosylation procedure (Table 3, entry 4 in article). For α-anomer of 38, Rf 0.2 (hexanes/EtOAc 3/1); [α]D25 +37.4 (c 0.643, CHCl3); 1H NMR (500 MHz, CDCl3): δ 7.39 – 7.23 (m, 13H, ArH), 7.18 – 7.13 (m, 2H, ArH), 5.51 (d, J = 5.0 Hz, 1H, H-1), 4.99 (d, J = 3.5 Hz, 1H, H-1′), 4.86 (s, 2H), 4.79 (d, J = 10.9 Hz, 1H, OCHPh), 4.66 – 4.59 (m, 2H), 4.52 (d, J = 10.8 Hz, 1H, OCHPh), 4.48 (d, J = 12.1 Hz, 1H, OCHPh), 4.34 – 4.29 (m, 2H), 4.03 – 3.97 (m, 2H, including H-3′), 3.90 – 3.86 (m, 1H), 3.82 (dd, J = 10.3, 6.4 Hz, 1H), 3.80 – 3.73 (m, 2H), 3.71 (dd, J = 8.7, 5.0 Hz, 1H), 3.66 (dd, J = 10.8, 1.8 Hz, 1H), 3.33 (dd, J = 10.3, 3.5 Hz, 1H, H-2′), 1.53 (s, 3H, isopropylidene-CH3), 1.43 (s, 3H, isopropylidene-CH3), 1.34 (s, 3H, isopropylidene-CH3), 1.33 (s, 3H, isopropylidene-CH3); 13C NMR (125 MHz, CDCl3): δ 138.0, 137.8, 128.40, 128.36, 128.35, 128.0, 127.9, 127.81, 127.77, 127.71, 127.68, 109.2, 108.6, 98.2 (C-1′, JCH = 170.0 Hz), 96.2 (C-1, JCH = 178.8 Hz), 79.9, 78.2, 75.2, 74.9, 73.5, 70.8, 70.7, 70.61, 70.55, 68.1, 66.8, 66.2, 63.4 (C-2′), 26.1, 25.94, 24.92, 24.4. HRMS-ESI (m/z): [M + Na]+ calcd for C39H47N3NaO10+, 740.3154; found, 740.3155.

The α/β ratio of 38 was determined by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 17/3 gradeint to 7/3. For β anomer standard of 38, retention time = 19.8 min (Figure S26-1). For 38 obtained from one-pot in situ adduct transformation and glycosylation procedure, retention time for α anomer = 17.5 min and β anomer = 20.2 min, thus
\( \alpha/\beta \) ratio: > 15/1 (Figure S26-2). \( \beta \)-Anomer of disaccharide 38\textsuperscript{19} was synthesized from 31 and 15 according to the low concentration glycosylation procedure.\textsuperscript{7}

![Figure S26-1. HPLC chromatogram of \( \beta \)-anomer of 38.](image)

![Figure S26-2. HPLC chromatogram for crude product 38 obtained from one-pot in situ adduct transformation and glycosylation procedure.](image)

2.5.18 Cholesteryl 2-Azido-3,4,6-tri-O-benzyl-2-deoxy-\( \alpha \)-D-glucopyranoside (39).

\[ 
\begin{align*}
\text{BnO} & \quad \text{BnO} \\
\text{N}_3 & \quad \text{OBn}
\end{align*}
\]

\( \alpha \)-Anomer of cholesteryl 2-azido-2-deoxyglucoside 39 was (39 mg, 54%) synthesized as a white greasy solid from reaction of cholesterol 33 (33 mg, 0.085 mmol) with 2-azido-2-
deoxythioglucoside donor 31 (100 mg, 0.17 mmol) according to one-pot in situ adduct transformation and glycosylation procedure (Table 3, entry 5 in article). For α-anomer 39, Rf 0.6 (hexanes/EtOAc 5/1); [α]D²⁵ +22.0 (c 0.8, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 7.39 – 7.25 (m, 13H), 7.17 – 7.14 (m, 2H), 5.30 (d, J = 4.7 Hz, 1H), 5.08 (d, J = 3.5 Hz, 1H, H-1’), 4.88 (q, J = 10.7 Hz, 2H), 4.81 (d, J = 10.8 Hz, 1H), 4.63 (d, J = 12.0 Hz, 1H), 4.53 – 4.46 (m, 2H), 4.06 – 4.00 (m, 1H, H-3’), 3.97 – 3.91 (m, 1H), 3.80 – 3.75 (m, 1H), 3.73 – 3.68 (m, 1H), 3.68 – 3.63 (m, 1H), 3.55 – 3.46 (m, 1H), 3.30 (dd, J = 10.3, 3.5 Hz, 1H, H-2’), 2.40 – 2.30 (m, 2H), 2.04 – 1.91 (m, 3H), 1.90 – 1.78 (m, 2H), 1.62 – 1.31 (m, 13H), 1.20 – 1.02 (m, 9H), 0.95 – 0.84 (m, 11H), 0.68 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 140.5, 138.04, 137.95, 137.8, 128.434, 128.425, 128.36, 128.0, 127.9, 127.82, 127.80, 127.7, 122.0, 96.3 (C-1’, JCH = 168.0 Hz), 80.2, 78.4, 78.2, 75.3, 75.1, 73.5, 70.7, 68.4, 63.3, 56.8, 56.2, 50.1, 42.3, 40.0, 39.8, 39.5, 37.0, 36.7, 36.2, 35.8, 31.93, 31.87, 28.2, 28.0, 27.8, 24.3, 23.82, 22.81, 22.6, 21.0, 19.4, 18.7, 11.9; HRMS-ESI (m/z): [M + Na]⁺ calcd for C₅₄H₇₃N₃NaO₅⁺, 866.5442; found, 866.5433.

The α/β ratio of 39 was determined to be >19/1 by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 24/1 gradient to 19/1. For β anomer standard of 39, retention time = 13.6 min (Figure S28-1). For 39 obtained from one-pot in situ adduct transformation and glycosylation procedure, retention time of α anomer = 22.3 min and no β anomer was detected at 13.6 min (Figure S28-2). β-Anomer of cholesteryl 2-azido-2-deoxy glucoside 39 was obtained from the donor 31 and the cholesterol acceptor 33 using the low concentration glycosylation procedure.
2.5.19 4-Azido-2,3-di-O-benzyl-4,6-dideoxy-\(\alpha\)-D-fucopyranosyl-(1→6)-1,2:3,4-di-O-isopropylidene-\(\alpha\)-D-galactopyranose (40)

\(\alpha\)-Anomer of disaccharide 40 (53 mg, \(\alpha\) only, 76%) was synthesized from reaction of galactosyl acceptor 15 (41 mg, 0.158 mmol) with D-Fuc4N\(_3\) donor 32 (50 mg, 0.105 mmol) using the one-pot \textit{in situ} adduct transformation and glycosylation procedure (Table 3, entry 6 in article). For \(\alpha\)-anomer of 40, \(R_t\) 0.48 (Hexanes/EtOAc = 2/1); \([\alpha]\)\(_{D}^{25}\) +3.32 (c 2.85, CHCl\(_3\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)): 6 = 7.41 – 7.27 (m, 10H, ArH), 5.52 (d, \(J = 5.0\) Hz, 1H, H-1), 4.87 (d, \(J = 3.5\) Hz, 1H, H-1’), 4.83 (d, \(J = 11.5\) Hz, 1H, benzyl-H), 4.76 (d, \(J = 11.5\) Hz, 1H, benzyl-H), 4.74 (d, \(J = 11.5\) Hz, 1H, benzyl-H), 4.70 (d, \(J = 11.5\) Hz, 1H, benzyl-H), 4.58 (dd, \(J = 8.0, 2.5\) Hz, 1H), 4.31 (dd, \(J = 2.4\) Hz, 1H), 4.28 (dd, \(J = 8.0, 2.0\) Hz, 1H), 4.07 – 3.99 (m, 3H), 3.84 (dd, \(J = 10.0, 3.5\) Hz, 1H), 3.73 (d, \(J = 3.5, 2H\)), 3.72 (d, \(J = 3.6, 1H\)), 1.51 (s, 3H, CH\(_3\)), 1.44 (s, 3H, CH\(_3\)), 1.33 (s, 3H, CH\(_3\)), 1.31 (s, 3H, CH\(_3\)), 1.22 (d, \(J = 6.4\) Hz, 3H, CH\(_3\)); \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 138.5, 138.3, 128.4, 128.3, 127.7, 127.7, 127.6, 109.3, 109.3, 108.53, 108.5, 97.4 (C-1), 96.3 (C-1’), 78.0, 75.9,
73.1, 72.9, 71.0, 70.7, 70.6, 66.7, 66.2, 65.0, 64.5, 26.1, 26.0, 24.9, 24.6, 17.3; HRMS (ESI): calcd for C\textsubscript{32}H\textsubscript{41}N\textsubscript{3}O\textsubscript{9}Na\textsuperscript{+} [M + Na\textsuperscript{+}] requires 634.2735, found 634.2757 m/z. The α-anomer of disaccharide 40 was obtained as the only anomer and HPLC analysis was not performed for this reaction.

2.5.20 Methyl 4-Azido-2,3-di-O-benzyl-4,6-dideoxy-α-D-fucopyranosyl-(1→3)-4-O-benzyl-2,6-dideoxy-α-D-ribo-hexopyranoside (41)

Disaccharide 41 (71 mg, 70\%, α only) was synthesized from glycosylation of methyl α-digitoside acceptor 34 (40.6 mg, 0.161 mmol) with 4-azido-4-deoxy-1-thio-D-fucopyranosyl donor 32 (91.8 mg, 0.193 mmol) according to one-pot \textit{in situ} adduct transformation and glycosylation procedure (Table 3, entry 7 in article). For 41, \(R_f\) 0.30 (Hexanes/EtOAc = 5/1); \([\alpha]_D^{35} +75.10\) (c 1.75, CHCl\textsubscript{3}); \(^1\text{H} NMR (500 MHz, CDCl\textsubscript{3}): \delta 7.38\) (t, \(J = 8.5\) Hz, 4H, ArH), 7.34 – 7.22 (m, 11H, ArH), 5.11 (d, \(J = 3.0\) Hz, 1H, H-1‘), 4.83 (d, \(J = 12\) Hz, 1H), 4.80 (d, \(J = 12\) Hz, 1H), 4.71 (d, \(J = 11.5\) Hz, 1H), 4.66 (d, \(J = 12.0\) Hz, 1H), 4.62 (d, \(J = 2.5\) Hz, 1H, H-1), 4.590 (dd, \(J = 7.0, 12.0\) Hz, 2H), 3.91 (dd, \(J = 6.5, 13.5\) Hz, 1H), 3.87 (dd, \(J = 3.0, 9.5\) Hz, 1H), 3.55 (d, \(J = 2.5\) Hz, 1H ), 3.21 (s, 3H, OCH\textsubscript{3}), 3.18 (dd, \(J = 2.5, 8.5\) Hz, 1H), 2.24 (dd, \(J = 2.0, 15.0\) Hz, 1H, H-2\textsuperscript{eq}), 1.72 (dt, \(J = 4.0, 15.0\) Hz, 1H, H-2\textsuperscript{ax}), 1.27 (d, \(J = 6.5\) Hz, 1H, CH\textsubscript{3}), 1.04 (d, \(J = 6.5\) Hz, 1H, CH\textsubscript{3}); \(^{13}\text{C} NMR (100 MHz, CDCl\textsubscript{3}): \delta 138.9, 138.4, 138.3, 128.3, 128.2, 128.1, 127.6, 127.6, 127.5, 127.3, 127.2, 127.2, 97.2 (C-1), 93.8 (C-1‘), 79.9, 77.4, 76.1, 73.0, 71.8, 71.4, 67.34, 65.1, 64.4, 63.3, 54.9, 31.3, 17.97, 17.2; HRMS (ESI): calcd for C\textsubscript{34}H\textsubscript{41}N\textsubscript{3}O\textsubscript{7}Na\textsuperscript{+} [M + Na\textsuperscript{+}] requires 626.2837, found 626.2864 m/z. The α-anomer of disaccharide 41 was obtained as the only anomer and no HPLC analysis was performed for this reaction.
2.5.21 Methyl 2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl-(1→6)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (43)

Mixture of thioglucoside donor 2 (100 mg, 0.15 mmol) and flame-dried molecular sieve (4Å, 300 mg) was suspended in dried CH2Cl2 (3 mL) such that the final concentration of 2 was 50 mM. Then, NFM (60 µL, 0.6 mmol) was added to the mixture. The resulting mixture was stirred at room temperature for 10 min and at 0 °C for additional 20-30 min. Subsequently, NIS (50.6 mg, 0.225 mmol) and TMSOTf (27 µL, 0.15 mmol) were added, and the reaction progress was monitored by TLC. Upon activation of glycosyl donor and formation of imidinium ion intermediate (by TLC examination), acceptor 42 (104.5 mg, 0.225 mmol) was added. The mixture was stirred at 0 °C. Upon completion of the glycosylation reaction (~24 h), the reaction was quenched by addition of Et3N. Workup procedure: NaHCO3 and Na2S2O3(s) were added to the mixture, followed by stirring until the deep red color of the reacting solution changed to pale yellow. The resulting mixture was dried (over MgSO4), filtered, and concentrated for flash chromatography purification over silica gel (Elution: hexanes/EtOAc 7:1) to furnish the glycosylation product. The disaccharide 43 (106 mg, 0.11 mmol, 70%, α:β 16:1 from NMR) was obtained as a glassy solid and no β-anomer was isolated in the reaction.11 For α-anomer of 43, 1H NMR (400 MHz, CDCl3): δ 7.27 – 7.18 (m, 33H, Ar-H), 7.11 – 7.08 (m, 2H, Ar-H), 5.69 (d, J = 3.6 Hz, 1H, H-1'), 5.02 (d, J = 11.6 Hz, 1H), 4.87 (d, J = 10.8 Hz, 1H), 4.81 – 4.75 (m, 4H), 4.69 (d, J = 12.0 Hz, 1H), 4.60 (d, J = 3.6 Hz, 1H), 4.57 (d, J = 1.2 Hz, 1H, H-1'), 4.54 (s, 1H), 4.52 (d, J = 3.6 Hz, 1H), 4.49 (d, J = 2.8 Hz, 2H), 4.42 (d, J = 10.8 Hz, 1H), 4.27 (d, J = 12.0 Hz, 1H), 4.12 – 4.01 (m, 2H), 3.93 – 3.81 (m, 3H), 3.73 – 3.64 (m, 3H), 3.59 (dd, J = 3.6, 8.8 Hz, 1H), 3.49 (dd, J = 3.6, 10.0 Hz, 2H), 3.40 (d, J = 1.6 Hz, 1H), 3.37 (s, 3H, CH3); 13C NMR (100 MHz, CDCl3): δ 139.0, 138.8, 138.6, 138.2, 138.1, 138.04, 138.00, 128.5, 128.37, 128.35, 128.30, 128.27, 128.25, 128.1, 128.0, 127.87, 127.86, 127.75, 127.67, 127.61, 127.5, 127.4, 127.3, 127.1,
126.8, 97.8 ($^{1}J_{CH} = 166.2$ Hz), 96.70 ($^{1}J_{CH} = 168.4$ Hz), 82.10, 82.08, 80.3, 79.5, 77.7, 75.6, 75.0, 74.5, 73.5, 73.4, 73.3, 72.4, 71.0, 69.6, 69.1, 68.3, 55.2.

2.5.22 Methyl 2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (45)

![Diagram of 45]

Mixture of donor 2 (100 mg, 0.15 mmol) and flame-dried molecular sieve (4Å) (0.3 mg) was suspended in dried CH$_2$Cl$_2$ (3 mL). Then, NFM (120 µL, 1.2 mmol) was added to the mixture. The resulting mixture was stirred at room temperature for 10 min and at -20 °C for additional 20-30 min. Subsequently, NIS (50.6 mg, 0.225 mmol) and TMSOTf (27 µL, 0.15 mmol) were added, and the reaction progress was monitored by TLC. Upon activation of glycosyl donor and formation of imidinium ion adduct (by TLC examination), acceptor 40 (104.5 mg, 0.225 mmol) was added. The mixture was stirred at -20 °C. Upon completion of the glycosylation reaction (~24 h), the reaction was quenched by addition of NaHCO$_3$. Workup procedure: NaHCO$_3$ and Na$_2$S$_2$O$_3$(s) were added to the mixture, followed by stirring until the deep red color of the reacting solution changed to pale yellow. The resulting mixture was dried (over MgSO$_4$), filtered, and concentrated for flash chromatography purification over silica gel (Elution: hexanes/EtOAc 1/0 to 5/1) to furnish the glycosylation product. Disaccharide 41 (91 mg, 61%, α:β >19:1 from NMR) was obtained after chromatography purification (Elution: hexanes/EtOAc 5:1). For α-anomer 45, $R_f$ 0.28 (hexanes/EtOAc 3/1); $[\alpha]_D^{17} +90.0$ (c 0.33, CHCl$_3$); $^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.37 – 7.20 (m, 25H, Ar-H), 7.17 – 7.10 (m, 10H, Ar-H), 5.48 (d, $J = 3.6$ Hz, 1H, anemic proton), 4.90 (d, $J = 10.8$ Hz, 1H), 4.83 (d, $J = 10.8$ Hz, 1H), 4.78 (d, $J = 11.6$ Hz, 1H), 4.75 (d, $J = 2.4$ Hz, 1H, anemic proton), 4.70 (d, $J = 10.8$ Hz, 1H), 4.66 (s, 1H), 4.63 (d, $J = 2.8$ Hz, 1H), 4.60 (s, 1H), 4.54 – 4.42 (m, 4H), 4.34 (d, $J = 10.8$ Hz, 1H), 4.20 (t, $J = 2.0$ Hz, 1H), 4.03 (q, $J = 19.2$ Hz, 2H), 3.94 – 3.87 (m, 2H), 3.83 – 3.79 (m, 1H), 3.75 – 3.65 (m, 4H), 3.60 (t, $J = 9.2$ Hz, 1H), 3.54 (dd, $J = 3.6$, 9.6 Hz, 1H), 3.30 (s, 3H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.0, 138.7,
138.6, 138.4, 138.2, 138.0, 128.5, 128.43, 128.37, 128.32, 128.31, 128.29, 128.1, 128.04, 127.96, 127.85, 127.81, 127.76, 127.70, 127.62, 127.50, 127.48, 127.4, 127.2, 100.1 (\(J_{CH} = 168.9\) Hz), 97.2 (\(J_{CH} = 169.8\) Hz), 81.5, 80.6, 79.7, 77.5, 75.6, 75.1, 75.0, 74.9, 73.5, 73.45, 73.1, 72.7, 72.3, 71.2, 70.7, 69.4, 68.6, 54.7; HRMS-ESI (\(m/z\)): [M + Na]\(^{+}\) calcd for C\(_{62}\)H\(_{66}\)NaO\(_{11}\)\(^{+}\), 1009.4503; found, 1009.4548. The α:β ratio of 40 was >19:1 based on the estimation from \(^1\)H NMR spectroscopy.

2.5.23 Methyl 2,3,6-Tri-O-benzyl-\(\alpha\)-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzyl-\(\alpha\)-D-glucopyranoside (46).

For \(\alpha\)-disaccharide 46, \(R_f\) 0.43 (hexanes/EtOAc/CH\(_2\)Cl\(_2\) 2/1/1); \([\alpha]\)\(^D\)\(^{30}\) +55.34 (c 1.012, CHCl\(_3\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.33-7.20 (m, 30H, Ar-H), 4.98-4.94 (m, 3H, including one aromatic proton), 4.92 (dd, \(J = 2.0, 11.0\) Hz, 1H), 4.82 (dd, \(J = 2.5, 11.0\) Hz, 1H), 4.73 – 4.63 (m, 5H), 4.55 – 4.52 (m, 3H, including one aromatic proton), 4.48 (d, \(J = 12.0\) Hz, 1H), 3.99 (td, \(J = 2.5, 9.0\) Hz, 1H), 3.84 – 3.73 (m, 5H), 3.70 (d, \(J = 11.5\) Hz, 1H), 3.66 (dd, \(J = 3.5, 9.5\) Hz, 1H), 3.62 – 3.57 (m, 3H), 3.51 (dt, \(J = 9.5, 2.5\) Hz, 1H), 3.43 (dt, \(J = 9.5, 2.5\) Hz, 1H), 3.34 (s, 3H, CH\(_3\)); \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 138.8, 138.7, 138.4, 138.3, 138.1, 138.0, 128.5, 128.38, 128.36, 128.33, 128.31, 128.30, 128.04, 127.95, 127.8, 127.7, 127.63, 127.56, 98.0 (\(J_{CH} = 166.4\) Hz), 97.2 (\(J_{CH} = 168.1\) Hz), 82.1, 80.6, 80.1, 79.6, 77.8, 75.8, 75.7, 75.6, 75.1, 75.01, 74.96, 73.5, 73.43, 73.37, 73.33, 73.30, 72.14, 72.10, 72.07, 70.6, 70.3, 70.1, 69.5, 66.1, 55.1; HRMS-ESI (\(m/z\)): [M + Na]\(^{+}\) calcd for C\(_{55}\)H\(_{60}\)NaO\(_{11}\)\(^{+}\), 919.4028; found, 919.4041.
2.5.24 Methyl 2,3,4,6-Teta-O-benzyl-α-D-gluco-pyranosyl-(1→4)-2,3,6-tri-O-benzyl-α-D-gluco-pyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-gluco-pyranoside (47):

Trisaccharide 47 was (48 mg, 60%) synthesized from glycosylation of disaccharide 46 (100 mg, 0.12 mmol) with donor 2 (109 mg, 0.17 mmol) according to the glycosylation protocol for preparation of 43. The trisaccharide 47 was obtained as a white glassy solid by flash chromatography purification (Elution: hexanes/EtOAc 7/1 to 5/1) and no other anomer was obtained. For trisaccharide 47, Rf 0.19 (hexanes/EtOAc 3/1); [α]D30 +71.6 (c 0.475, CHCl3); 1H NMR (500 MHz, CDCl3): δ 7.33 -7.19 (m, 43H, Ar-H), 7.14 – 7.10 (m, 7H Ar-H), 5.68 (d, J = 3.5 Hz, 1H, anomic proton), 4.99-4.92 (m, 4H, including one aromatic proton), 4.86-4.73 (m, 5H), 4.70-4.67 (m, 2H), 4.61-4.41 (m, 10H, including one aromatic proton), 4.27 (dd, J = 3.0, 12.0 Hz, 1H), 4.07-3.97 (m, 3H), 3.90-3.87 (m, 2H), 3.81-3.79 (m, 3H), 3.74-3.70 (m, 2H), 3.66-3.56 (m, 4H), 3.48-3.42 (m, 3H), 3.38-3.35 (m, 4H, including CH3); 13C NMR (125 MHz, CDCl3): δ 139.1, 138.9, 138.8, 138.6, 138.4, 138.3, 138.24, 138.19, 138.16, 138.0, 128.5, 128.44, 128.38, 128.34, 128.29, 128.25, 128.19, 128.03, 127.99, 127.93, 127.87, 127.85, 127.83, 127.74, 127.65, 127.60, 127.58, 127.52, 127.48, 127.38, 127.29, 127.0, 126.9, 98.0 (1JCH = 165.5 Hz), 96.8 (1JCH = 172.3 Hz), 96.8 (1JCH = 168.6 Hz), 82.2, 82.1, 81.7, 80.2, 80.1, 79.5, 77.8, 77.7, 75.8, 75.5, 75.1, 75.0, 74.1, 73.5, 73.4, 73.2, 73.1, 72.9, 72.3, 71.0, 70.5, 69.9, 69.2, 68.3, 65.9, 55.3. HRMS-ESI (m/z): [M + Na]+ calcd for C89H94NaO16+, 1441.6434; found, 1441.6431.
2.5.25 Methyl D-Glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→6)-α-D-glucopyranoside (48).

Protected trisaccharide 47 (147 mg, 0.10 mmol) dissolved in 4:1:0.5 MeOH/EtOAc/AcOH solvent mixture was treated with Pd/C (100 mg) under H₂ (1 atm). The reaction mixture was stirred at RT for 2 days and then filter (over celite) to remove Pd/C. The resulting filtrate was concentrated and purified by FPLC (Elution: 1:1 MeOH:H₂O, flow rate 0.5 mL/min) to obtain the trisaccharide 48 as a white glassy solid (30 mg, 56%). For 48, Rf 0.09 (CH₂Cl₂/MeOH/H₂O 2/1/0.05); [α]D₃⁵ +28.8 (c 0.35, MeOH); ¹H NMR (500 MHz, CD₃OD): δ 5.15 (d, J = 4.0 Hz, 1H, anomeric H), 4.85 (d, J = 4.0 Hz, 1H, anomeric H overlap with residual H₂O signals), 4.67 (d, J = 4.0 Hz, 1H, reducing end H-1), 3.92 – 3.88 (m, 2H), 3.86 – 3.64 (m, 8H), 3.61 (td, J = 3.0, 9.5 Hz, 2H), 3.54 (t, J = 9.5 Hz, 1H), 3.47 – 3.43 (m, 2H), 3.42 (s, 3H, CH₃), 3.41 (m, 1H), 3.35 (dd, J = 10.0, 11.5 Hz, 1H), 3.27 (t, J = 9.0 Hz, 1H); ¹³C NMR (125 MHz, CD₃OD): δ 103.0 (¹JCH 172.5 Hz), 101.5 (¹JCH 171.3 Hz), 100.0 (¹JCH 168.85 Hz), 81.8, 75.4, 75.2, 75.1, 74.9, 74.4, 73.5, 72.3, 72.1, 72.0, 71.6, 67.8, 62.9, 62.1, 56.0 (OCH₃); HRMS-ESI (m/z): [M + Na]⁺ calcd for C₁₉H₃₄NaO₁₆+, 541.1739; found, 541.1745.

3 Reference
2004, 126, 12374-12385 (donor 9, α-disaccharide 23).


4 NMR spectra
\(^1\)H NMR of 3-\(\text{O}\)-[3,4,6-tri-\(\text{O}\)-benzyl-2-\(\text{O}\)-(2-naphthylmethyl)-\(\alpha\)-D-glucopyranosyl]-1,2-\(\text{O}\)-cyclohexyldiene-\(\text{sn}\)-glycerol (5)
$^{13}$C NMR of 3-O-[3,4,6-tri-O-benzyl-2-O-(2-naphthylmethyl)-a-D-glucopyranosyl]-1,2-O-cyclohexyldene-sn-glycerol (5)

$^{13}$C non-decoupling:

$J_{\text{CH}} = 167.8$ Hz
$^1$H NMR of methyl 2,3,4,6-tetra-$O$-benzyl-$\alpha$-D-glucopyranosyl-(1→6)-2,3,4-tri-$O$-benzyl-$\alpha$-D-glucopyranoside (6)
$^{13}$C NMR of methyl 2,3,4,6-tetra-$O$-benzyl-$\alpha$-D-glucopyranosyl-(1→6)-2,3,4-$O$-benzyl-$\alpha$-D-glucopyranoside (6)

$^{13}$C non-decoupling:

$J_{CH} = 167.8$ Hz

$J_{CH} = 166.3$ Hz
Crude $^1$H NMR of D-glucopyranosyl imidinium ion (7) at -20 °C
Crude $^1$H NMR of D-glucopyranosyl imidinium ion (7) at -20 °C
Crude $^1$H NMR of $\alpha$-D-glucopyranosyl iodide (8) at 0 °C
Crude $^{13}$C NMR of α-D-glucopyranosyl iodide (8) at 0 °C

$^{13}$C non-decoupling:

$J_{CH} = 177.3$ Hz
Crude COSY NMR of α-D-glucopyranosyl iodide (8) at 0 °C
Crude HSQC NMR of α-D-glucopyranosyl iodide (8) at 0 °C
$^1$H NMR of methyl 2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-(1→4)-2,3-O-isopropylidene-α-L-rhamnopyranoside (19)
$^{13}$C NMR of methyl 2,3,4,6-tetra-$O$-benzyl-$\alpha$-D-glucopyranosyl)-(1→4)-2,3-$O$-isopropylidene-$\alpha$-L-rhamnopyranoside (19)

$^{13}$C non-decoupling:

$J_{\text{CH}} = 167.9$ Hz

$J_{\text{CH}} = 167.4$ Hz
$^1$H NMR of diosgeninyl 2,3,4,6-tetra-$O$-benzyl-$\alpha$-D-glucopyranoside (20)
$^{13}$C NMR of diosgeninyl 2,3,4,6-tetra-O-benzyl-$\alpha$-D-glucopyranoside (20)
COSY NMR of diosgeninyl 2,3,4,6-tetra-O-benzyl-α-D-glucopyranoside (20)
HSQC NMR of diosgeninyl 2,3,4,6-tetra-O-benzyl-α-D-glucopyranoside (20)
$^1$H NMR of $p$-tolyl 2,3,4,6-tetra-$O$-benzyl-$\alpha$-$D$-glucopyranosyl-(1→6)-2,3-di-$O$-benzoyl-$4$-$O$-benzyl-$1$-thio-$\beta$-$D$-glucopyranoside (21)
$^{13}$C NMR of $\rho$-tolyl 2,3,4,6-tetra-O-benzyl-$\alpha$-D-glucopyranosyl-(1→6)-2,3-di-O-benzoyl-4-O-benzyl-1-thio-$\beta$-D-glucopyranoside (21)

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$^{13}$C non-decoupling:

$J_{CH} = 168.8$ Hz
$^1$H NMR of 6-O-acetyl-2,3,4-tri-O-benzyl-$\alpha$-D-glucopyranosyl-(1→6)-1,2,3,4-di-O-isopropylidene-$\alpha$-D-galactopyranose (22)
$^{13}$C NMR of 6-$O$-acetyl-2,3,4-tri-$O$-benzyl-$\alpha$-D-glucopyranosyl-(1→6)-1,2:3,4-$O$-diisopropylidene-$\alpha$-D-galactopyranose (22)

$^{13}$C non-decoupling:

$J_{\text{CH}} = 168.0 \text{ Hz}$

$J_{\text{CH}} = 178.4 \text{ Hz}$

![Chemical structure of 22](image)
$^1$H NMR of methyl 6-O-acetyl-2,3,4-tri-O-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (23)
\(^{13}\text{C}\) NMR of methyl 6-\(O\)-acetyl-2,3,4-tri-\(O\)-benzyl-\(\alpha\)-D-glucopyranosyl-(1\(\rightarrow\)6)-2,3,4-tri-\(O\)-benzyl-\(\alpha\)-D-glucopyranoside (23)

\(^{13}\text{C}\) non-decoupling:

\(J_{\text{CH}} = 168.5\) Hz

\(J_{\text{CH}} = 167.1\) Hz
$^1$H NMR of methyl 6-$O$-benzoyl-2,3,4-tri-$O$-benzyl-$\alpha$-$D$-glucopyranosyl-(1→6)-2,3,4-tri-$O$-benzyl-$\alpha$-$D$-glucopyranoside (24)
$^{13}$C NMR of methyl 6-<sup>O</sup>-benzoyl-2,3,4-tri-<sup>O</sup>-benzyl-<sup>α</sup>-D-glucopyranosyl-(1→6)-2,3,4-tri-<sup>O</sup>-benzyl-<sup>α</sup>-D-glucopyranoside (24)
$^{1}$H NMR of methyl 2,3,4-tri-\(O\)-benzyl-6-\(O\)-(tertbutyldiphenylsilyl)-\(\alpha\)-D-glucopyranosyl-(1→6)-2,3,4-tri-\(O\)-benzyl-\(\alpha\)-D-glucopyranoside 25
$^{13}$C NMR of methyl 2,3,4-tri-O-benzyl-6-O-(tertbutyldiphenylsilyl)-α-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside 25

$^{13}$C non-decoupling:

$J_{\text{CH}} = 166.3$ Hz
$^1$H NMR of methyl 4-\(O\)-acetyl-2,3,6-tri-\(O\)-benzyl-\(\alpha\)-D-glucopyranosyl-(1\(\rightarrow\)6)-2,3,4-tri-\(O\)-benzyl-\(\alpha\)-D-glucopyranoside 26
$^{13}$C NMR of methyl 4-$\text{O}$-acetyl-2,3,6-tri-$\text{O}$-benzyl-$\alpha$-$\text{D}$-glucopyranosyl-(1$\rightarrow$6)-2,3,4-tri-$\text{O}$-benzyl-$\alpha$-$\text{D}$-glucopyranoside 26
$^1$H NMR of methyl 2,3,4,6-tetra-$O$-benzyl-$\alpha$-$D$-galactopyranosyl-(1$\rightarrow$6)-2,3,4-$O$-benzyl-$\alpha$-$D$-glucopyranoside (27)
$^{13}$C NMR of methyl 2,3,4,6-tetra-$O$-benzyl-$\alpha$-D-galactopyranosyl-(1$\rightarrow$6)-2,3,4-tri-$O$-benzyl-$\alpha$-D-glucopyranoside (27)

$^{13}$C non-decoupling:

$J_{\text{CH}}$ and $J_{\text{CH}} = 168.3$ Hz
$^1$H NMR of methyl 2,3,4,6-tetra-\(O\)-benzyl-\(\alpha\)-D-galactopyranosyl-(1→6)-1,2:3,4-di-\(O\)-isopropylidene-\(\alpha\)-D-galactopyranose (28)
$^{13}$C NMR of methyl 2,3,4,6-tetra-$O$-benzyl-$\alpha$-D-galactopyranosyl-(1$\rightarrow$6)-1,2:3,4- di-$O$-isopropylidene-$\alpha$-D-galactopyranose (28)

$^{13}$C non-decoupling:

$J_{\text{CH}} = 168.5$ Hz
$^1$H NMR of 2,3,4-tri-$O$-benzyl-$\alpha$-D-xylopyranosyl-(1$\rightarrow$6)-1,2,3,4-di-$O$-isopropylidene-$\alpha$-D-galactopyranoside (29)

29 ($\alpha/\beta = 5:1$ from HPLC)
$^{13}$C NMR of 2,3,4-tri-$O$-benzyl-$\alpha$-D-xylopyranosyl-(1$\rightarrow$6)-1,2,3,4-di-$O$-isopropylidene-$\alpha$-D-galactopyranoside (29)

$^{13}$C non-decoupling:

$J_{CH} = 167.6$ Hz

29 ($\alpha/\beta = 5:1$ from HPLC)
$^1$H NMR of methyl 6-$O$-2-azido-3,4,6-tri-$O$-benzyl-2-deoxy-$\alpha$-D-galactopyranosyl-(1$\rightarrow$6)-2,3,4-tri-$O$-benzyl-$\alpha$-D-glucopyranoside (35)
$^{13}$C NMR of methyl 6-0-2-azido-3,4,6-tri-O-benzyl-2-deoxy-α-D-galactopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (35)

$^{13}$C non-decoupling:

$J_{CH} = 171.0$ Hz

$J_{CH} = 166.9$ Hz
$^{1}H$ NMR of cholesteryl-2-azido-3,4,6-tri-$O$-benzyl-2-deoxy-$\alpha$-D-galactopyranoside (36)
$^{13}$C NMR of cholesteryl-2-azido-3,4,6-tri-O-benzyl-2-deoxy-$\alpha$-D-galactopyranoside (36)

$^{13}$C non-decoupling:

$J_{CF} = 168.5$ Hz
$^1$H NMR of methyl 2-azido-3,4,6-tri-$O$-benzyl-2-deoxy-$\alpha$-$D$-glucopyranosyl-(1→6)-2,3,4-tri-$O$-benzyl-$\alpha$-$D$-glucopyranoside (37)
$^{13}$C NMR of methyl 2-azido-3,4,6-tri-$O$-benzyl-2-deoxy-$\alpha$-D-glucopyranosyl-(1→6)-2,3,4-tri-$O$-benzyl-$\alpha$-D-glucopyranoside (37)

$^{13}$C non-decoupling:

$J_{CH} = 171.3$ Hz

37 ($\alpha/\beta = 9/1$)
$^1$H NMR of 2-azido-3,4,6-tri-$O$-benzyl-2-deoxy-$\alpha$-D-glucopyranosyl-(1$\rightarrow$6)-1,2:3,4-di-$O$-isopropylidene-$\alpha$-D-galactopyranoside (38)
$^{13}$C NMR of 2-azido-3,4,6-tri-O-benzyl-2-deoxy-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranoside 38

$^{13}$C non-decoupling:

$J_{CH} = 170.0$ Hz
$^1$H NMR of cholesteryl-2-azido-3,4,6-tri-O-benzyl-2-deoxy-$\alpha$-D-glucopyranoside (39)
$^{13}$C NMR of cholesteryl-2-azido-3,4,6-tri-O-benzyl-2-deoxy-α-D-glucopyranoside (39)

$^{13}$C non-decoupling:

$J_{CH} = 168.0$ Hz
$^1$H NMR spectrum of D-Fuc$\text{N}_3$ thioglycosyl building block (32)
$^{13}$C NMR spectrum of D-Fuc4N$_3$ thioglycosyl building block (32)

$^{13}$C non-decoupling:
$J_{CH} = 155.5$ Hz
$^1$H NMR spectrum of $\alpha$-anomer of 2,6-dideoxy acceptor (34)
$^{13}$C NMR spectrum of $\alpha$-anomer of 2,6-dideoxy acceptor (34)

$^{13}$C non-decoupling:

$J_{\text{CH}} = 167.1$ Hz
$^1$H NMR spectrum of 4-azido-2,3-di-O-benzyl-4,6-dideoxy-$\alpha$-D-fucopyranosyl-(1→6)-1,2:3,4-di- $O$-isopropylidene-$\alpha$-D-galactopyranose (40)
$^{13}$C NMR spectrum of 4-azido-2,3-di-$O$-benzyl-4,6-dideoxy-$\alpha$-$D$-fucopyranosyl-(1→6)-1,2:3,4-di-$O$-isopropylidene-$\alpha$-$D$-galactopyranose (40)

$^{13}$C non-decoupling:

$J_{C\text{H}'} = 168.13$ Hz

![13C NMR spectrum of 4-azido-2,3-di-$O$-benzyl-4,6-dideoxy-$\alpha$-$D$-fucopyranosyl-(1→6)-1,2:3,4-di-$O$-isopropylidene-$\alpha$-$D$-galactopyranose (40)]
COSY NMR spectrum of 4-azido-2,3-di-O-benzyl-4,6-dideoxy-α-D-fucopyranosyl-(1→6)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (40)
$^1$H NMR spectrum of methyl 4-azido-2,3-di-$O$-benzyl-4,6-dideoxy-$\alpha$-D-fucopyranosyl-(1$\rightarrow$3)-4-$O$-benzyl-2,6-dideoxy-$\alpha$-D-ribo-hexopyranoside (41)
$^{13}$C NMR spectrum of methyl 4-azido-2,3-di-$O$-benzyl-4,6-dideoxy-$\alpha$-D-fucopyranosyl-(1$\rightarrow$3)- 4-$O$-benzyl-2,6-dideoxy-$\alpha$-D-ribo-hexopyranoside (41)

$^{13}$C non-decoupling:

$J_{\text{CH'}} = 167.9$ Hz
COSY NMR spectrum of methyl 4-azido-2,3-di-O-benzyl-4,6-dideoxy-\(\alpha\)-D-fucopyranosyl-(1\(\rightarrow\)3)-4-O-benzyl-2,6-dideoxy-\(\alpha\)-D-ribo-hexopyranoside (41)
HSQC NMR spectrum of methyl 4-azido-2,3-di-O-benzyl-4,6-dideoxy-α-D-fucopyranosyl-(1→3)-4-O-benzyl-2,6-dideoxy-α-D-ribo-hexopyranoside (41)
$^1$H NMR spectrum of methyl 2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl-(1→6)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (43)
$^{13}$C NMR spectrum of methyl 2,3,4,6-tetra-$O$-benzyl-$\alpha$-$D$-glucopyranosyl-(1$\rightarrow$6)-2,3,6-tri-$O$-benzyl-$\alpha$-$D$-glucopyranoside (43)
$^1$H NMR spectrum of methyl 2,3,4,6-tetra-\textit{O}-benzyl-\textit{\alpha}-D-glucopyranosyl-(1\textsubscript{→}2)-3,4,6-tri-\textit{O}-benzyl-\textit{\alpha}-D-mannopyranoside (45)
$^{13}$C NMR spectrum of methyl 2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (45)
$^1$H NMR spectrum of methyl 2,3,6-tri-$O$-benzyl-$\alpha$-D-glucopyranosyl-(1$\rightarrow$6)-2,3,6-tri-$O$-benzyl-$\alpha$-D-glucopyranoside (46)
$^{13}$C NMR spectrum of methyl 2,3,6-tri-$O$-benzyl-$\alpha$-$D$-glucopyranosyl-(1$\rightarrow$6)-2,3,6-tri-$O$-benzyl-$\alpha$-$D$-glucopyranoside (46)
$^1$H NMR spectrum of methyl 2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranosyl-(1→6)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (47)
$^{13}$C NMR spectrum of methyl 2,3,4,6-tetra-$O$-benzyl-$\alpha$-D-glucopyranosyl-(1$\rightarrow$4)-2,3,6-tri-$O$-benzyl-$\alpha$-D-glucopyranosyl-(1$\rightarrow$6)-2,3,6-tri-$O$-benzyl-$\alpha$-D-glucopyranoside (47)
HSQC NMR spectrum of methyl 2,3,4,6-tetra-\(O\)-benzyl-\(\alpha\)-D-glucopyranosyl-(1\(\rightarrow\)4)-2,3,6-tri-\(O\)-benzyl-\(\alpha\)-D-glucopyranosyl-(1\(\rightarrow\)6)-2,3,6-tri-\(O\)-benzyl-\(\alpha\)-D-glucopyranoside (47)
$^1$H NMR spectrum of methyl α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→6)-α-D-glucopyranoside (48)
$^{13}$C NMR spectrum of methyl $\alpha$-D-glucopyranosyl-$\rightarrow$(1$\rightarrow$4)$\alpha$-D-glucopyranosyl-$\rightarrow$(1$\rightarrow$6)$\alpha$-D-glucopyranoside (48)
HSQC NMR spectrum of methyl α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→6)-α-D-glucopyranoside (48)
High resolution mass spectrometry of glucosyl chloride 10'}
High resolution mass spectrometry of glucosyl chloride 12'