In situ Formation of β-Glycosyl Imidinium Triflate from Participating Thioglycosyl Donors: Elaboration to Disarmed-Armed Iterative Glycosylation

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Table S3: General DMF-modulated glycosylation procedure

Table S1: Temperature optimization for modulated glycosylation of 3 with 1

Table S2: Selected NMR data for reaction intermediates 40a, 40b, and 41

Table S3: Exact amounts of glycoside substrates and promoters

Methyl 4-O-(2-O-Benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-2,3,6-tri-O-benzyl-α-D-glucopyranoside 18

4-(r-Butyl)-2-methylphenyl 4-O-(2-O-Benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-thio-β-D-galactopyranoside 21

4-(r-Butyl)-2-methylphenyl 4-O-(2-O-Benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-thio-β-D-galactopyranoside 22

p-Tolyl 2-O-Benzoyl-3,4,6-tri-O-benzyl-thio-α-D-mannopyranoside 14

p-Tolyl 2-O-Benzoyl-3,4,6-tri-O-benzyl-thio-α-D-mannopyranoside 15

4-r-Butyl-2-methylphenyl 2,3-O-Isopropyldiene-thio-α-L-rhamnopyranoside 17

Table S1: Temperature optimization for modulated glycosylation of 3 with 1

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4-(r-Butyl)-2-methylphenyl 4-O-(2-O-Benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-thio-β-D-galactopyranoside 21

4-(r-Butyl)-2-methylphenyl 4-O-(2-O-Benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-thio-β-D-galactopyranoside 22

p-Tolyl 4-O-(2-O-Benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-2,3,6-tri-O-benzyl-thio-β-D-galactopyranoside 19

p-Tolyl 6-O-(2-O-Benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-thio-β-D-galactopyranoside 20

p-Tolyl 6-O-(2-O-Benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-thio-β-D-galactopyranoside 21

p-Tolyl 4-O-(6-O-Acetyl-2,3-di-O-benzoyl-4-O-benzyl-β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-thio-β-D-galactopyranoside 23

p-Tolyl 6-O-(6-O-Acetyl-2,3-di-O-benzoyl-4-O-benzyl-β-D-glucopyranosyl)-2,3-di-O-benzoyl-4-O-benzyl-thio-β-D-glucopyranoside 24

p-Tolyl 2-O-(2-O-Benzoyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-3,4,6-tri-O-benzyl-thio-α-D-mannopyranoside 25

p-Tolyl 3-O-(2-O-Benzoyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-2,4,6-tri-O-benzyl-thio-α-D-mannopyranoside 26

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p-Tolyl 6-O-[3,4,6-Tri-O-acetyl-2-(2,2,2-trichloroethoxy carbonylamino)-2-deoxy-β-D-glucopyranosyl]-2,3,4-tri-O-benzyl-thio-β-D-glucopyranoside \(29\)----------------------------- S26 S79
p-Tolyl 6-O-[3,4,6-Tri-O-acetyl-2-(2,2,2-trichloroethoxy carbonylamino)-2-deoxy-β-D-glucopyranosyl]-3-O-benzyl-4-O-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy carbonylamino)-thio-β-D-glucopyranoside \(30\)----------------------------- S26 S81
p-Tolyl 6-O-(2-O-Benzoyl-3,4,6-tri-O-benzyl-α-D-galactopyranosyl)-2,3,4-tri-O-benzyl-thio-β-D-galactopyranoside \(31\)----------------------------- S27 S83
p-Tolyl 2-O-Benzoyl-3,4-di-O-benzyl-thio-α-D-mannopyranoside \(33\)----------------------------- S28 S85
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Methyl 2-O-Benzoyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→6)-2-O-benzoyl-3,4-di-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside \(36\)----------------------------- S31 S89
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Section A: Experimental section

Reagent-grade chemicals were purchased from commercial vendors and used without purification. Dichloromethane (CH₂Cl₂) was dried by Asianwong solvent system (AWS-1000). N,N-Dimethylformamide (DMF) was stocked with flame-dried molecular sieves (MS) under N₂. Progress of reactions was monitored by thinlayer 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. Silica gel (Geduran Si-60, 0.063-0.200 mm) for chromatography was obtained from Merck. NMR spectra were recorded at 300 MHz and 75 MHz spectrometers in Bruker console or 400/500/600 MHz and 100/125/150 MHz in Varian console as specified. Coupling constants in Hz was calculated from chemical shifts of ¹H NMR spectra.

Preparations of glycosyl substrates 1, 7, 8, 9, 10, 11a, 11b, 12, 13, 13ba, 14a, 16, 32, 33a, and 34 were referred to literature methods. Diacetonide galactose 3 was purchased from common vendors. Naming of the saccharide molecules follows the nomenclature rules of carbohydrate from IUPAC.¹¹

**p-Tolyl 2-O-benzoyl-3,4,6-tri-O-benzyl-α-D-thiomannopyranoside 2:**

A solution of per-O-acetyl mannosyl acetate s2a (33.6 g, 86.0 mmol) in CH₂Cl₂ (35 mL) was cooled to 0 °C and treated with 33% HBr in AcOH (34 mL) under N₂. After stirring at 0 °C for 30 min, the reaction mixture was brought to RT. Upon the completion of the reaction as checked by TLC (ca. 2 h), the reaction mixture was diluted with EtOAc (20 mL × 2) and poured into a separatory funnel. The organic phase was then washed with satd. NaHCO₃ (15 mL × 2), brine (50 mL), dried (over
MgSO₄), filtered, concentrated, and dried under vacuo for 5h. The crude was taken up in dried CH₃CN (98 mL), treated with tetrabutyl ammonium bromide (TBAB) (5 g, 15.7 mmol), 2,6-lutidine (18.2 mL, 157 mmol), and MeOH (9.5 mL). The reaction was stirred overnight at RT under N₂. Upon completion of the reaction, the solvent was reduced by rotary evaporator. The residue was taken up by EtOAc (100 mL × 2), which was washed with satd. NaHCO₃ (150 mL × 2), H₂O (50 mL) and brine (50 mL), dried over MgSO₄, filtered, and concentrated to give crude per-O-acetylated orthoester s2b (28.3 g, 78.4 mmol). The per-O-acetylated orthoester s2b was dissolved in MeOH/CH₂Cl₂ solution mixture, then treated with Na(s) at RT. Upon completion of deacetylation, the reaction mixture was concentrated and dried under vacuo for 4h. The crude mixture was dissolved in DMF and cooled at 0 °C bath under N₂. The reaction mixture was treated with sodium hydride (NaH, 13.2 g, 331 mmol) (60% in mineral oil) and benzyl bromide (BnBr, 40 mL, 331 mmol). Upon completion of the reaction, ice was added to quench excessive NaH. The reaction crude was subsequently diluted with EtOAc and H₂O in the separation funnel, then washed with satd. NaHCO₃ and brine, dried over MgSO₄, filtered, and concentrated for column chromatography purification (Elution: CH₂Cl₂/EtOAc/Hexane 1/0/3 stepwise to 1/1/3) to give per-O-benzylmannosyl orthoester s2c (35.1g). The per-O-benzylated mannosyl orthoester s2c (10.12 g, 20 mmol) in CH₂Cl₂ was treated with p-thiocresol (6.21 g, 50 mmol) was cooled to 0 °C, then BF₃.OEt₂ (6.3 mL, 50 mmol) was added to the mixture. Upon completion of the reaction, the reaction crude was diluted with EtOAc, washed with satd. NaHCO₃ and brine in chill, dried over MgSO₄, filtered, and concentrated for column chromatography purification (Elution: EtOAc/Hexane 1/19 stepwise to 3/17) to give 2-O-acetyl thiomannoside s2d (5.2 g, 8.7 mmol) as yellow syrup. The 2-O-acetyl thiomannoside s2d (7.8 g, 13 mmol) in CH₂Cl₂/MeOH mixture solution was treated with Na(s). Upon completed deacetylation, the reaction was neutralized with IR-120 (H⁺), filtered, and concentrated for column chromatography purification (Elution: recycled EtOAc/Hexane 0~25% stepwise to 25~50%) to give
the 2-hydroxyl unprotected thiomannoside (6.08g, 10.9mmol). The 2-hydroxyl unprotected thiomannoside (6.08g, 10.9mmol) in CH₂Cl₂ was subsequently treated with benzoyl chloride (BzCl) (2.56 mL, 21.8 mmol), Et₃N (4.5 mL, 32.7 mmol) and DMAP (133 mg, 1.09 mmol) under N₂. Upon completion of the benzoylation, the reaction mixture was diluted with satd. NaHCO₃, then washed with EtOAc, H₂O and brine, dried over MgSO₄, filtered, and concentrated for column chromatography purification (Elution: recycled EtOAc/Hexane 0~25%) to yield target thiomannoside donor 2 (6.11 g, 9.27 mmol). For thiomannnoside 2: [α]D³⁵ +77.11 (c 0.42, CHCl₃) ; Rf 0.35 (EtOAc/Hexane 1:3); ¹H NMR (300 MHz, CDCl₃): δ 8.05 (dd, J = 7.8, 1.5 Hz, 2 H), 7.54 (t, J = 7.5 Hz, 1 H), 7.39-7.25 (m, 17 H), 7.23-7.20 (m, 2 H), 7.05 (d, J = 8.1 Hz, 2 H), 5.87 (dd, J = 2.7, 1.8 Hz, 1 H, H-2), 5.58 (d, J = 1.5 Hz, 1 H, H-1), 4.90 (d, J = 10.8 Hz, 1 H), 4.81 (d, J = 11.4 Hz, 1 H), 4.70 (d, J = 11.7 Hz, 1 H), 4.58 (t, J = 11.4 Hz, 2 H), 4.49 (d, J = 11.7 Hz, 1 H), 4.40 (dd, J = 9.3, 2.1 Hz, 1 H), 4.16 (t, J = 9.6 Hz, 1 H), 4.06 (dd, J = 9, 2.7 Hz, 1 H), 3.95 (dd, J = 10.8, 4.2 Hz, 1 H), 3.79 (dd, J = 10.5, 1.5 Hz, 1 H), 2.29 (s, 3 H, CH₃); ¹³C NMR (75 MHz, CDCl₃): δ 166.0 (C=O), 138.8, 138.7, 138.4, 138.1, 133.7, 132.8, 130.4, 130.3, 130.2, 128.9, 128.81, 128.77, 128.6, 128.5, 128.3, 128.2, 128.0, 127.9, 87.1 (C-1’), 79.0, 75.8, 75.0, 73.8, 73.0, 72.1, 71.0, 69.5, 21.6; HRMS (m/z): [M + Na]⁺ calcd. for C₄₁H₄₀NaO₆S⁺, 683.2438; found, 683.2450.

6-O-(2-O-Benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose 4

Disaccharide 4 was prepared from thioglucoside 1 and diacetonide galactose acceptor 3 by general modulated glycosylation procedure. Purification of 4 was
performed by column chromatography (Elution: EtOAc/CH$_2$Cl$_2$/Hexane 1:2:10 stepwise to 1:2:7). For 4: [α]$_D^{35}$ -30.00 (c 0.36, CHCl$_3$); $R_f$ 0.275 (EtOAc/CH$_2$Cl$_2$/Hexane 1:2:5); $^1$H NMR (300 MHz, CDCl$_3$): δ 8.03 (d, $J = 7.5$ Hz, 2 H), 7.53 (t, $J = 7.2$ Hz, 1 H), 7.42-7.27 (m, 10 H), 7.12 (s, 5 H), 5.38 (d, $J = 4.8$ Hz, 1 H, H-1), 5.30 (t, $J = 8.1$ Hz, 1 H, H-2'), 4.82 (d, $J = 10.8$ Hz, 1 H), 4.46 (d, $J = 11.1$ Hz, 1 H), 4.68-4.63 (m, 3 H), 4.59-4.55 (m, 2 H), 4.39 (dd, $J = 7.8$, 1.8 Hz, 1 H), 4.19-4.17 (m, 1 H), 4.10 (d, $J = 8.1$ Hz, 1 H), 4.02 (dd, $J = 10.8$, 5.1 Hz, 1 H), 3.82-3.71 (m, 6 H), 3.56 (d, $J = 1.8$ Hz, 1 H), 1.38 (s, 3 H, CH$_3$), 1.21 (s, 3 H, CH$_3$), 1.17 (s, 6 H, CH$_3$ $\times$ 2); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 165.6 (C=O), 138.5, 138.3, 138.2, 133.2, 130.4, 130.3, 128.8, 128.7, 128.6, 128.34, 128.31, 128.19, 128.15, 128.1, 109.5 (quaternary-C), 108.8 (quaternary-C), 101.8, 96.6, 83.3, 78.4, 75.7, 75.5, 74.1, 74.0, 69.1, 68.4, 67.7, 26.4, 26.1, 25.3, 24.6; HRMS-ESI ($m/z$): [M + Na]$^+$ calcd. for C$_{46}$H$_{51}$NaO$_{12}$, 819.3351; found, 819.3343.

2-O-Benzoyl-3,4,6-tri-O-benzyl-D-mannopyranosyl-α(1→6)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose 5

Disaccharide 5 was prepared from thiomannoside 2 and galactose acceptor 3 by general modulated glycosylation procedure. Purification of 5 was performed by column chromatography (Elution: EtOAc/CH$_2$Cl$_2$/Hexane 1:2:15 stepwise to 1:2:10).

For disaccharide 5: [α]$_D^{35}$ -18.34 (c 0.52, CHCl$_3$); $R_f$ 0.375 (EtOAc/CH$_2$Cl$_2$/Hexane 1:2:5); $^1$H NMR (300 MHz, CDCl$_3$): δ 8.07 (d, $J = 8.1$ Hz, 2 H), 7.53 (t, $J = 7.5$ Hz, 1 H), 7.40-7.18 (m, 17 H), 5.67 (s, 1 H), 5.52 (d, $J = 4.8$ Hz, 1 H, H-1), 5.04 (s, 1 H), 4.86 (d, $J = 10.8$ Hz, 1 H), 4.78 (t, $J = 11.1$ Hz, 2 H), 4.63-4.51 (m, 4 H), 4.31 (dd, $J$ =
4.8, 1.8 Hz, 1 H), 4.24 (d, \( J = 8.1 \) Hz, 1 H), 4.12 (s, 2 H), 3.99-3.91 (m, 3 H), 3.87-3.71 (m, 3 H), 1.53 (s, 3H, CH₃), 1.43 (s, 3 H, CH₃), 1.34 (d, \( J = 6.6 \) Hz, 6 H, CH₃ × 2); \(^{13}\)C NMR (75 MHz, CDCl₃): \( \delta \) 166.0 (C=O), 138.9, 138.8, 138.5, 130.4, 130.3, 128.8, 128.73, 128.71, 128.68, 128.4, 128.03, 127.97, 127.93, 127.86, 109.8 (quaternary-C), 109.0 (quaternary-C), 98.4, 96.7, 78.6, 75.7, 74.7, 73.8, 72.2, 72.0, 71.2, 71.02, 70.97, 69.4, 69.3, 66.6, 66.4, 26.6, 26.4, 25.3, 24.9; HRMS-ESI (m/z): [M + Na]⁺ calcd. for C₄₆H₅₁NaO₁₂, 819.3351; found, 819.3339.

\( p \)-Tolyl 6-\( O \)-Acetyl-2,3-di-\( O \)-benzoyl-4-\( O \)-benzyl-thio-\( \beta \)-D-glucopyranoside 6:

Known thioglucoside \( s6 \) (1.0 g, 1.71 mmol) in EtOAc (4 mL) was treated with Ac₂O (0.2 mL, 2.05 mmol), Et₃N (0.35 mL, 2.56 mmol), and DMAP (20 mg, 0.171 mmol). Upon completion of acetylation, the reaction mixture was diluted with EtOAc and washed with satd. NaHCO₃, H₂O, brine, dried (over MgSO₄), filtered, and concentrated for column chromatography purification (Elution: EtOAc/Hexane 1:4) to furnish 6 (quantitative). For compound 6: \( [\alpha]_D^{35} \) +63.1 (c 0.30, CHCl₃); \( R_f \) 0.4 (EtOAc/Hexane 3/7); \(^1\)H-NMR (400 MHz, CDCl₃): \( \delta \) 7.96–7.91 (m, 4 H), 7.53–7.48 (m, 2 H), 7.39–7.34 (m, 6 H), 7.20-7.17 (m, 3 H), 7.13–7.08 (m, 4 H), 5.73 (t, \( J = 9.6 \) Hz, 1 H), 5.32 (t, \( J = 10.0 \) Hz, 1 H), 4.84 (d, \( J = 10.0 \) Hz, 1 H, H-1), 4.56 (d, \( J = 11.2 \) Hz, 1 H), 4.50–4.46 (m, 2H), 4.25 (dd, \( J = 12.0 \), 4.8 Hz, 1 H), 3.83–3.74 (m, 2 H), 2.33 (s, 3 H, CH₃), 2.09 (s, 3 H, CH₃C=O); \(^{13}\)C-NMR (100 MHz, CDCl₃): \( \delta \) 171.1 (C=O), 166.1 (C=O), 165.8 (C=O), 139.0, 137.3, 134.1, 133.73, 133.70, 130.3, 130.2, 130.1, 129.8, 128.90, 128.88, 128.8, 128.7, 128.6, 86.7 (C-1), 77.6, 76.9, 76.1, 75.3, 71.2, 63.3, 21.7, 21.4; HRMS-ESI (m/z): [M + Na]⁺ calcd. for C₃₆H₃₄NaO₈S, 649.1867; found, 649.1900.
**p-Tolyl 2,4,6-Tri-**$O$**-benzyl-thio-α-D-mannopyranoside 13a:**

Unprotected thiomannoside $s_{13aa}$[8] (2 g, 7 mmol) was treated with Bu$_2$SnO (2.3 g, 9.3 mmol) in MeOH (23.3 mL) and heated to 85 °C. Upon Until a clear reaction mixture solution clearly was observed, the reaction mixture was cooled to RT, concentrated, and dried high vacuum ca 2h. The reaction residue was treated with cesium fluoride (1.3 g, 8.4 mmol), $p$-methoxybenzyl chloride (1.4 mL, 10.2 mmol) in DMF. Upon completion of the alkylation, the reaction mixture was filtered and the filtrate was concentrated for column chromatography purification (Elution: EtOAc/Hexane 1/2 stepwise to 1/0) to furnish crude 3-OH protected thiomannoside $s_{13ab}$ (1.78 g). The thiomannoside $s_{13ab}$ (1.78 g, 4.38 mmol) in dried DMF was treated with benzyl bromide (BnBr) (2.4 mL, 19.7 mmol) and sodium hydride (NaH) (800 mg in 60% mineral oil, 19.7 mmol). Upon completion of the benzylation, the DMF was removed by high vacuo rotary evaporator and the residue was taken up with EtOAc. The organic phase was washed with water and, brine, dried over MgSO$_4$, concentrated, and dried under vacuo for ca 4 h to furnish fully protected thiomannoside $s_{13ac}$. $p$-Methoxybenzyl ether (PMB) protection in $s_{13ac}$ was removed by treatment with 2,3-dichloro-5,6-dicyano quinone (DDQ) (835 mg, 3.68 mmol) in 10:1 EtOAc/H$_2$O (10/1) mixture. Upon completion of the PMB deprotection, the crude reaction mixture was diluted with EtOAc, and the organic phase was washed with Na$_2$S$_2$O$_3$(aq), NaOH(aq), water and brine. After drying (over MgSO$_4$) and filtration, the EtOAc solution was concentrated for column chromatography.
purification (Elution: EtOAc/CH$_2$Cl$_2$/Hexane 1/2/15 stepwise to 1/2/13) to furnish target thiomannoside acceptor 13a (473 mg, 12%, three steps unoptimized). For thiomannoside 13a: $[\alpha]_D^{35} +115.1$ (c 0.40, CHCl$_3$); $R_f$ 0.27 (EtOAc/CH$_2$Cl$_2$/Hexane 1:2:6); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.38-7.21 (m, 17H), 7.04 (d, $J = 8.1$ Hz, 2H), 5.61 (s, 1H, H-1), 4.87 (d, $J = 10.8$ Hz, 1H), 4.74 (d, $J = 11.4$ Hz, 1H), 4.64 (d, $J = 12$ Hz, 1H), 4.54 (d, $J = 11.1$ Hz, 1H), 4.48 (dd, $J = 11.7$, 4.8 Hz, 2H), 4.33-4.28 (m, 1H), 4.03-3.96 (m, 2H), 3.86-3.72 (m, 3H), 2.44 (d, $J = 9$ Hz, 1H), 2.30 (s, 3H); $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ 138.8, 138.7, 132.8, 130.7, 130.2, 129.0, 128.8, 128.7, 128.5, 128.43, 128.37, 128.2, 127.9, 85.7 (C-1), 80.0, 77.3, 75.3, 73.8, 72.7, 72.5, 72.4, 69.6, 21.6 (CH$_3$); HRMS-ESI (m/z): [M + Na]$^+$ calcd. for C$_{34}$H$_{36}$NaO$_5$S, 579.2176; found, 579.2192.

$p$-Tolyl 6-$O$-Benzoyl-2,4-di-$O$-benzyl-thio-$\alpha$-$D$-mannopyranoside 13b:

Per-$O$-acetyl thiomannoside s13ba$^{[9]}$ (15.2 g, 39 mmol) in MeOH/CH$_2$Cl$_2$ mixture (150 mL) was treated with Na(s) (120 mg) for deacetylation. Upon completion of deacetylation, the reaction solution was neutralized with IR-120 (H$^+$), and the mixture was filtered to remove resin, followed by concentration (by rotary evaporator) and dried (under vacuo) to give crude unprotected thiomannoside s13bb. The thiomannoside s13bb (11.1 g, 39 mmol) in anhydrous CH$_3$CN (300 mL) was treated
with benzaldehyde dimethyl acetal (11.7 mL, 78.0 mmol) and p-toluensulfonic acid (TsOH, 740 mg, 3.9 mmol) to form the 4,6-O-benzylidene protected thiomannoside. Upon completion of the acetalation, the reaction was quenched by neutralization with Et₃N. The 4,6-O-benzylidene protected thiomannoside was precipitated in the reaction solution, and it was obtained by filtration and washing the precipitate with minimal amount of hexane/Et₂O mixture. The washed precipitate was dried under vacuo to give benzylidene acetal derivative s13bc (11.9 g). The acetal derivative s13bc (11.9 g, 32.0 mmol) suspended in toluene (160 mL) was treated with dibutyl tin oxide (Bu₂SnO, 11.9 g, 48.0 mmol) and refluxed at 145 °C for 8–10 h under Dean-Stark trap. The volume of toluene was then reduced approximately by half and the reaction mixture was cooled to RT. After then, 2-(bromomethyl)-naphthalene (2-NAP-Br, 10.54 g, 48.0 mmol), cesium fluoride (CsF, 7.2 g, 48.0 mmol), and CH₃CN (80 mL) were added and resulting mixture was stirred at 70 °C for ca. 11 h. Upon the completion of alkylation, the reaction mixture was filtered (over celite), and concentrated for column chromatography purification (Elution: EtOAc/CH₂Cl₂/Hexane 0.1:1:3 stepwise to 0.3:2:2) to furnish amorphous white solid of the 2-naphthylmethyl derivative s13bd (12.3 g). The derivative s13bd (10.24 g, 19.9 mmol) in BH₃·THF solution (1 M, 59.7 mL, 59.7 mmol) was treated with trimethylsilyl triflate (TMSOTf) (180 μL) at 0 °C. Upon completion of the reductive ring opening, the mixture was neutralized with Et₃N, followed by addition of MeOH. The resulting mixture was then concentrated for column chromatography purification (Elution: EtOAc/Hexane 1/5 stepwise to 1/1) to yield 2,6-dihydroxyl thiomannoside s13be (8.8 g). The 2,6-dihydroxyl thiomannoside s13be (9.44 g, 18.3 mmol) in 10% NaOH (13.3 mL) THF solution was treated with BnBr (2.2 mL, 18.3 mmol) and TBAB (5.9 g, 18.3 mmol) and the mixture was stirred vigorously. Upon the completion of benzylation, THF was removed by rotary evaporator. The residual aqueous mixture was extracted with EtOAc, which was washed with H₂O, brine, dried over MgSO₄, and concentrated for column chromatography purification (Elution:
EtOAc/CH₂Cl₂/Hexane 1/1/5) to give surprisingly 2-\textit{O}-benzyl thiomannoside. The C2 position of benzyl function was confirmed by $^1$H, $^{13}$C, HSQC, and HMBC spectroscopy (HSQC and HMBC spectra were unpublished data). To the 2-\textit{O}-benzyl thiomannoside in CH₂Cl₂ was added BzCl (2.6 mL, 22.0 mmol), Et₃N (4 mL, 29.4 mmol), and DMAP (180 mg, 1.47 mmol). Upon completion of the benzylation, satd. NaHCO₃ was added to the mixture and the product was extracted with EtOAc. The EtOAc solution was washed with H₂O, brine, dried over MgSO₄, filtered, and concentrated for column chromatography purification to give fully protected thiomannoside \textbf{s13bf}. The thiomannoside \textbf{s13bf} (10.45 g, 14.7 mmol) was treated with DDQ (10 g, 44.1 mmol) in 10/1 v/v EtOAc/H₂O mixture. Upon completion of the deprotection, the reaction mixture was diluted with EtOAc, which was washed with satd. Na₂S₂O₃, water, dried over MgSO₄, filtered, and concentrated for column chromatography purification (Elution: EtOAc/Hexane 1:10) to furnish thiomannoside \textbf{13b} (6.2 g, 68% from \textbf{s13be}). For thiomannoside \textbf{13b}: $[\alpha]_D^{35} +126.4$ (c 0.44, CHCl₃); $R_f$ 0.3 (EtOAc/Hexane 1:4); $^1$H-NMR (300 MHz, CDCl₃): $\delta$ 7.99 (d, $J = 7.8$ Hz, 2H), 7.54 (t, $J = 7.5$ Hz, 1H), 7.39-7.19 (m, 14H), 6.98 (d, $J = 7.8$ Hz, 2H), 5.62 (s, 1H), 4.94 (d, $J = 11.1$ Hz, 1H), 4.73 (d, $J = 11.4$ Hz, 1H), 4.64 (d, $J = 8.1$ Hz, 1H), 4.58-4.47 (m, 4H), 1.11-4.04 (m, 2H), 3.80 (t, $J = 9$ Hz, 1H), 2.58 (d, $J = 9.3$ Hz, 1H, OH), 2.26 (s, 3H, CH₃); $^{13}$C-NMR (75 MHz, CDCl₃): $\delta$ 166.7 (C=O), 138.4, 138.2, 137.8, 133.3, 132.6, 130.3, 130.2, 129.0, 128.9, 128.7, 128.53, 128.48, 128.3, 128.2, 85.4 (C-1), 70.1, 77.0, 75.4, 72.8, 72.5, 70.7, 64.4, 21.5 (CH₃); HRMS-EI (m/z): [M + Na]$^+$ calcd. for C₃₄H₃₄NaO₆S, 593.1968; found, 593.1979.

\textit{p}-Tolyl 2-\textit{O}-Benzyo1-4,6-di-\textit{O}-benzyl-thio-\textit{\alpha}-D-mannopyranoside 14:

\[
\begin{array}{c}
\text{s14a} \quad \text{BH}_3\text{THF, TMSOTf} \\
\end{array}
\]

Fully protected thiomannoside \textbf{s14a}[69] in BH₃THF solution (10.8 mL, 10.8
mmol) was treated with TMSOTf (78.0 μL, 0.43 mmol) at 0 °C. Upon completion of the reductive cleavage of acetal function, the reaction was quenched with Et₃N, followed by addition of MeOH to react with excess borane reagent. The resulting mixture was concentrated for column chromatography purification (Elution: EtOAc/CH₂Cl₂/Hexane 1:2.5:10 stepwise to 1:2.5:7) to produce thiomannoside 14.

For thiomannoside 14: [α]D³⁵ +81.4 (c 0.52, CHCl₃); R₇ 0.19 (EtOAc/Hexane 1/3); ¹H NMR (300 MHz, CDCl₃): δ 7.34-7.23 (m, 17 H), 7.09 (d, J = 8.1 Hz, 2 H), 5.43 (s, 1 H, H-1), 4.95 (d, J = 11.1 Hz, 1 H), 4.73-4.58 (m, 5 H), 4.13 (d, J = 9.3 Hz, 1 H), 4.06-3.98 (m, 2 H), 3.89 (dd, J = 9, 2.7 Hz, 2 H), 3.80 (s, 2 H), 2.32 (s, 3 H), 1.99 (s, 1 H, OH); ¹³C NMR (75 MHz, CDCl₃): δ 138.8, 138.5, 138.4, 138.2, 132.9, 130.5, 130.3, 128.9, 128.5, 128.4, 128.3, 128.21, 128.19, 86.8 (C-1), 80.5, 76.8, 75.7, 75.2, 73.6, 72.7, 72.6, 62.6, 21.6 (CH₃); HRMS-ESI (m/z): [M + Na]+ calcd. for C₃₄H₃₆NaO₅S, 579.2176; found, 579.2179.

**p-Tolyl 2-O-Benzoyl-2-O-benzyl-2-(2,2,2-trichloroethoxycarbonylamino)-2-deoxy-thio-β-D-glucopyranoside 15:**

Per-O-acetyl-2-(2,2,2-trichloroethoxycarbonylamino)-2-deoxy-β-D-thioglucopyranoside 7 (9.44 g, 16.1 mmol) was treated with Na(s) in CH₂Cl₂/MeOH mixture at 0 °C. Upon the completion of the reaction, the reaction was neutralized with IR-120 (H⁺), filtered, concentrated, and dried under vacuo to obtain the thioglucoside **s15a** (7.24 g, 98%). **s15a** (5.24 g, 11.4 mmol) was treated with benzaldehyde dimethyl acetal (2.2 mL, 14.8 mmol) and TsOH (230 mg, 1.2 mmol) in dried CH₃CN (48 mL).
Upon completion of the acetal formation, the reaction was neutralized by Et$_3$N, filtered, concentrated to produce 4,6-\textit{O}-benzylidene-2-(2,2,2-trichloroethoxycarbonyl amino)-2-deoxy-\textit{\beta}-D-thioglucopyranoside \textit{s15b} (4.67 g, 75\%). \textit{s15b} (2.5 g, 4.55 mmol) in dried CH$_2$Cl$_2$ (23 mL) was treated with BzCl (0.8 mL, 6.83 mmol), Et$_3$N (1.3 mL, 9.1 mmol), and DMAP (56 mg, 0.46 mmol). Upon completion of benzylation, the reaction mixture was diluted with EtOAc. The EtOAc solution was washed with satd. NaHCO$_3$, H$_2$O, brine, dried (over MgSO$_4$), filtered, and concentrated. The fully protected 2-(2,2,2-trichloroethoxycarbonylaminoo)-2-deoxy-\textit{\beta}-D-thioglucopyranoside \textit{s15c} (2 g, 68\%) was obtained by precipitation of the concentrated solution in Hexane/EtOAc mixture. The 2-amino-2-deoxy-\textit{\beta}-D-thioglucopyranoside \textit{s15c} (2 g, 3.1 mmol) in BH$_3$ THF (15.5 mL, 15.5 mmol) was treated with TMSOTf (112 \(\mu\)L, 0.62 mmol) at 0°C. Upon completion of the reductive cleavage of acetal function, excessive borane reagent was quenched with Et$_3$N and MeOH. The resulting mixture was concentrated for column chromatography purification (Elution: EtOAc/Hexane 1/4) to furnish C6 hydroxyl unprotected thioglucosaminyl acceptor \textit{15} (1.41 g, 70\%). For \textit{15}: $[\alpha]_{D}^{35}$ –6.2 (c 0.42, CHCl$_3$); $R_f$ 0.25 (EtOAc/Hexane 1/2); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.99 (d, $J$ = 7.8 Hz, 2 H), 7.58 (t, $J$ = 7.2 Hz, 1 H), 7.44-7.38 (m, 4 H), 7.12-7.00 (m, 7 H), 5.98 (d, $J$ = 9.9 Hz, 1 H, NH), 5.60 (t, $J$ = 9.9 Hz, 1 H, H-2), 4.74 (d, $J$ = 10.5 Hz, 1 H), 4.63 (q, $J$ = 11.7 Hz, 2 H), 4.50 (s, 2 H), 3.98 (q, $J$ = 10.2 Hz, 1 H), 3.85-3.66 (m, 3 H), 3.48 (d, $J$ = 9.3 Hz, 1 H), 2.28 (s, 3 H, CH$_3$), 2.08 (s, 1 H, OH); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 167.2 (C=O), 154.9 (C=O), 138.8, 137.5, 134.0, 130.4, 130.2, 129.5, 129.3, 129.0, 128.8, 128.7, 128.4, 95.8 (CCl$_3$), 88.2 (C-1), 79.6, 75.8, 75.3, 74.8, 62.0, 55.8, 21.6 (CH$_3$); HRMS-EI (m/z): [M + Na]$^+$ calcd. for C$_{30}$H$_{30}$Cl$_3$NNaO$_2$S, 676.0701; found, 676.0719.

(4-\textit{t}-Butyl-2-methylphenyl) 2,3-\textit{O}-Isopropylidene-thio-\textit{\alpha}-L-rhamnopyranoside \textit{17}
L-Rhamnose (5 g, 30.5 mmol) in acetic anhydride (Ac₂O, 17.3 mL, 183 mmol) was treated with dried TsOH (580 mg, 3.05 mmol) in ice bath. Upon completion of acetylation, the anhydride reagent was quenched with MeOH under ice bath ca 1 h and concentrated. After then, the concentrated residue was diluted with EtOAc, washed with ca. 10% NaOH, brine, ice, and dried over MgSO₄. The solution was filtered, concentrated, and dried under vacuo to give crude per-O-acetyl rhamnosyl acetate. The crude acetate in dried CH₂Cl₂ was cooled to −10 °C and treated with (4-t-butyl-2-methyl)-thiophenol (3.2 mL, 17.6 mmol) and BF₃·OEt₂ (3 mL, 23.4 mmol). Upon completion of thioglycosidation, the reaction was quenched with 10% NaOH(aq) at 0 °C and the mixture was washed with 10% NaOH(aq), chilled H₂O, brine, dried over MgSO₄, filtered, and concentrated for column chromatography purification (Elution: EtOAc/Hexane 1/8) to furnish per-O-acetyl thiorhamnoside s₁₇a (4.34 g, 74%). s₁₇a (4.34 g, 8.6 mmol) in MeOH/CH₂Cl₂ mixture (35 mL, MeOH/CH₂Cl₂ 1/2) was treated with Na(s). Upon completion of the deacetylation, the reaction mixture was neutralized with IR-120 (H⁺), and filtered to remove resin. The filtrate was concentrated and dried under vacuo to give crude deacetylated thiorhamnoside intermediate. The crude thiorhamnoside intermediate in dried acetone (29 mL) was then treated with 2,2-dimethoxypropane (2.1 mL, 17.2 mmol) and TsOH (170 mg, 0.86 mmol). Upon completion of the acetalation, the reaction was neutralized with Et₃N, and followed by concentration for column chromatograph purification (Elution: EtOAc/CH₂Cl₂/Hexane 1:1:6 stepwise to 1:1:5) to furnish thiorhamnoside acceptor 17 (2.17 g, 69%, α/β 10:1). For thiorhamnoside 17: [α]D³⁵ −170.0 (c 0.50, CHCl₃); Rₜ 0.423 (EtOAc/CH₂Cl₂/Hexane 1:1:2); ¹H-NMR (300 MHz, CDCl₃): δ 7.59 (d, J = 2.1 Hz, 1 H, ArH), 7.21 (dd, J = 7.8, 1.8 Hz, 1 H, ArH), 7.14 (d, J = 8.1 Hz, 1 H, ArH),
5.74 (s, 1 H, H-1), 4.40 (d, J = 5.4 Hz, 1 H), 4.18-4.06 (m, 2 H), 3.50-3.43 (m, 1 H),
2.88 (d, J = 3.6 Hz, 1 H), 1.55 (s, 3 H, CH₃), 1.39 (s, 3 H, CH₃), 1.30 (s, 9 H, tBu-H),
1.24 (d, J = 6 Hz, 3 H, CH₃ × 2);¹³C-NMR (75 MHz, CDCl₃): δ 150.1, 136.9, 132.5,
130.4, 130.1, 125.3, 110.2 (quaternary-C), 83.3 (C-1), 79.0, 77.4, 75.7, 67.4, 34.9,
31.8, 28.6, 26.9, 20.6, 17.6; HRMS-ESI (m/z): [M + Na]+ calcd. for C₂₀H₃₀NaO₄S,
389.1757; found, 389.1761.

**Table S1:** Temperature optimization for DMF-modulated glycosylation of diacetonide galactose acceptor 3 with thioglucoside 1.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Donor (equiv)</th>
<th>DMF (equiv)</th>
<th>T (°C)ᵃ</th>
<th>Time (h)</th>
<th>Product, 4</th>
<th>Yield%</th>
<th>α/β ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 (1.2)</td>
<td>1.2</td>
<td>0</td>
<td>4</td>
<td>50</td>
<td>β only</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1 (1.2)</td>
<td>1.2</td>
<td>−10</td>
<td>4</td>
<td>75</td>
<td>β only</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1 (1.2)</td>
<td>1.2</td>
<td>−20</td>
<td>5</td>
<td>75</td>
<td>β only</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1 (1.2)</td>
<td>1.2</td>
<td>−40</td>
<td>5</td>
<td>71</td>
<td>β only</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1 (1.2)</td>
<td>1.2</td>
<td>−60</td>
<td>6</td>
<td>60</td>
<td>β only</td>
<td></td>
</tr>
</tbody>
</table>

ᵃ T= temperature at pre-activation and coupling reaction

**Table S2:** Characteristic NMR data for reaction intermediates 40α, 40β, and 41

<table>
<thead>
<tr>
<th>Entry</th>
<th>Selected NMR data</th>
<th>Observed reaction intermediates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>40α</td>
</tr>
<tr>
<td>1</td>
<td>¹H signal at C-1/ppm (²J₁H/Hz)</td>
<td>6.19 (s)</td>
</tr>
<tr>
<td>2</td>
<td>¹H signal at C-2/ppm</td>
<td>5.22</td>
</tr>
<tr>
<td>3</td>
<td>¹H signal at C-1/ppm (²J₁CH/Hz)</td>
<td>103.0 (183 )</td>
</tr>
<tr>
<td>4</td>
<td>¹H signal of imidate /ppm</td>
<td>8.75</td>
</tr>
</tbody>
</table>

**General DMF-modulated glycosylation procedure for participating thioglycosyl donors** (refer to Table 2 in main text): 1.2 Equiv of thioglycoside donor (1, 2, 6, 7, or 8), DMF (1.2 equiv), and activated molecular sieve (4 Å) were suspended in dried CH₂Cl₂. The mixture was stirred at RT for 5 min and cooled to −30, −20 or −10 °C at
least 15 min in cooling reactor (Eyela model: PCL 1810 or PCL 1800). Subsequently, 1.2 equiv of NIS and 1.2 (or 1.8 for thiomannoside donors) equiv of TMSOTf (for most of thioglycoside acceptors used) or TfOH (for glycosylation of 13b) were added. Upon completion of pre-activation at −30, −20 or −10 °C, acceptors (9–17, 1 equiv) was added to reaction solution. The temperature for each coupling reaction needed optimization. Upon completion of glycosylation, the reaction was quenched with satd. NaHCO₃ and solid Na₂S₂O₃, then stirred vigorously at RT until the dark red coloration of the solution turning to pale yellow. The mixture was dried by MgSO₄ powder, followed by filtration and concentration to give crude concentrate for column chromatography purification giving the glycosylation products 18–32. Exact amount of substrates and reagents used were given in Table S3.

Table S3: Amounts of glycosyl substrates and promoting reagents used in DMF-modulated glycosylations

<table>
<thead>
<tr>
<th>Entry</th>
<th>Donor, (mg, mmol)</th>
<th>Acceptor, (mg, mmol)</th>
<th>NIS (mg, mmol)</th>
<th>TMSOTf (μL, mmol)</th>
<th>T₁, T₂ (°C)</th>
<th>Product, mg, yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1, 150, 0.23</td>
<td>9, 88, 0.19</td>
<td>55.8, 0.25</td>
<td>41, 0.23</td>
<td>-10, -10</td>
<td>18, 125, 65</td>
</tr>
<tr>
<td>2</td>
<td>1, 250, 0.38</td>
<td>10, 176, 0.32</td>
<td>93, 0.41</td>
<td>68, 0.38</td>
<td>-10, -10</td>
<td>19, 216, 67</td>
</tr>
<tr>
<td>3</td>
<td>1, 172, 0.26</td>
<td>11a, 120, 0.22</td>
<td>64, 0.28</td>
<td>47, 0.260</td>
<td>-10, -10</td>
<td>20, 164, 70</td>
</tr>
<tr>
<td>5</td>
<td>1, 143, 0.22</td>
<td>16, 100, 0.18</td>
<td>53, 0.23</td>
<td>39, 0.22</td>
<td>-10, -10</td>
<td>21, 137, 70</td>
</tr>
<tr>
<td>6</td>
<td>1, 150, 0.227</td>
<td>17, 69, 0.19</td>
<td>55.8, 0.25</td>
<td>41, 0.23</td>
<td>-10, -10</td>
<td>22, 84, 55</td>
</tr>
<tr>
<td>7</td>
<td>6, 200, 0.3</td>
<td>11a, 141, 0.25</td>
<td>72, 0.3</td>
<td>86, 0.48</td>
<td>-20, -10</td>
<td>23, 178, 66</td>
</tr>
<tr>
<td>8</td>
<td>6, 200, 0.3</td>
<td>11b, 149, 0.25</td>
<td>72, 0.3</td>
<td>86, 0.48</td>
<td>0, 10</td>
<td>24, 172, 63</td>
</tr>
<tr>
<td>9</td>
<td>2, 500, 0.758</td>
<td>12, 384, 0.69</td>
<td>188, 0.828</td>
<td>206, 1.14</td>
<td>-20, 0</td>
<td>25, 339, 61</td>
</tr>
<tr>
<td>10</td>
<td>2, 200, 0.303</td>
<td>13a, 141, 0.253</td>
<td>74.7, 0.329</td>
<td>82.1, 0.46</td>
<td>-20, -20</td>
<td>26, 166, 60</td>
</tr>
<tr>
<td>11</td>
<td>2, 2000, 3.03</td>
<td>13b, 1440, 2.53</td>
<td>717, 3.16</td>
<td>767, 4.56</td>
<td>-20, 0</td>
<td>27, 2050, 73</td>
</tr>
<tr>
<td>12</td>
<td>2, 150, 0.23</td>
<td>14, 105, 0.19</td>
<td>55.8, 0.25</td>
<td>61, 0.34</td>
<td>-10, -10</td>
<td>28, 128, 62</td>
</tr>
<tr>
<td>13</td>
<td>7, 182, 0.31</td>
<td>11a, 144, 0.26</td>
<td>76.5, 0.34</td>
<td>56.1, 0.31</td>
<td>-10, -10</td>
<td>29, 183, 64</td>
</tr>
<tr>
<td>14</td>
<td>7, 100, 0.17</td>
<td>15, 94, 0.14</td>
<td>42, 0.19</td>
<td>31, 0.17</td>
<td>-10, -10</td>
<td>30, 64, 40</td>
</tr>
</tbody>
</table>
\( T_1 \) = pre-activation temperature; \( T_2 \) = coupling temperature. b2.5 M stock solution of triflic acid (TfOH in Et\(_2\)O) was used as acid promoter.

Methyl 4-\( O \)-(2-\( O \)-Benzoyl-3,4,6-tri-\( O \)-benzyl-\( \beta \)-\( D \)-glucopyranosyl)-2,3,6-tri-\( O \)-benzyl-\( \alpha \)-\( D \)-glucopyranoside 18:

Disaccharide 18 was prepared from thioglucoside 1 and methyl glucoside 9 (Table S3, entry 1). Purification of 18 was achieved by standard column chromatography (Elution: EtOAc/CH\(_2\)Cl\(_2\)/Hexane 0.5:4:7 stepwise to 1:4:5). For disaccharide 18: \([\alpha]_D^{35} +30.6 \) (c 0.36, CHCl\(_3\)); \( R_f 0.35 \) (EtOAc/CH\(_2\)Cl\(_2\)/Hexane 1/4/5); \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \( \delta 7.88 \) (d, \( J = 7.2 \) Hz, 2H, Ar\( H \)), 7.56 (t, \( J = 7.5 \) Hz, 1H, Ar\( H \)), 7.43–7.35 (m, 6H, Ar\( H \)), 7.32–7.18 (m, 20H, Ar\( H \)), 7.14–7.05 (m, 6H, Ar\( H \)), 5.23 (dd, \( J = 9.3 \), 8.1 Hz, 1H), 5.08 (d, \( J = 11.4 \) Hz, 1H), 4.81 (s, 1H), 4.77 (s, 1H), 4.75–4.68 (m, 2H), 4.66–4.63 (m, 1H), 4.60–4.54 (m, 3H), 4.50 (dd, \( J = 9.9 \), 6.3 Hz, 2H), 4.45 (d, \( J = 12.3 \) Hz, 1H), 4.36 (d, \( J = 12.3 \) Hz, 1H), 4.26 (d, \( J = 12.0 \) Hz, 1H), 3.91–3.82 (m, 2H), 3.76–3.68 (m, 2H), 3.63–3.59 (m, 2H), 3.56–3.49 (m, 2H), 3.45–3.35 (m, 3H), 3.25 (s, 3H, OCH\(_3\)); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \( \delta \) 165.3, 140.1, 138.9, 138.8, 138.5, 138.4, 138.2, 133.6, 130.2, 129.0, 128.90, 128.87, 128.79, 128.76, 128.70, 128.61, 128.57, 128.5, 128.44, 128.37, 128.3, 128.24, 128.20, 128.12, 128.08, 128.07, 127.9, 127.5, 100.8 (C-1’), 98.8 (C-1), 83.3, 80.7, 79.3, 78.6, 77.2, 75.9, 75.8, 75.6, 75.3, 74.7, 74.0, 73.9, 70.0, 69.2, 68.2, 55.7; HRMS-ESI (m/z): [M + Na]\(^+\) calcd. for C\(_{62}\)H\(_{64}\)NaO\(_{12}\), 1023.4290; found, 1023.4347.

\( p \)-Tolyl 4-\( O \)-(2-\( O \)-Benzoyl-3,4,6-tri-\( O \)-benzyl-\( \beta \)-\( D \)-glucopyranosyl)-2,3,6-tri-\( O \)-benzyl-thio-\( \beta \)-\( D \)-glucopyranoside 19:
Disaccharide 19 was prepared from thiogluicosides 1 and 10 (Table S3, entry 2). Purification of 19 was achieved by standard column chromatography (Elution: EtOAc/CH₂Cl₂/Hexane 1:1:15). For disaccharide 19: [α]D<sup>35</sup> +10.1 (c 0.34, CHCl₃); R<sub>f</sub> 0.47 (EtOAc/CH₂Cl₂/Hexane 1:1:4).<sup>1</sup>H-NMR (300 MHz, CDCl₃): δ 7.92 (d, J = 7.8 Hz, 2 H, ArH), 7.55 (t, J = 7.2 Hz, 1H, ArH), 7.43-7.22 (m, 25H, ArH), 7.20-7.16 (m, 5H, ArH), 7.10-7.09 (m, 5H, ArH), 6.97 (d, J = 7.8 Hz, 2H, ArH), 5.25 (t, J = 8.4 Hz, 1 H), 5.14 (d, J = 11.4 Hz, 1H), 4.80-4.65 (m, 6H), 4.60 (s, 1H), 4.55 (d, J = 10.2 Hz, 2H), 4.47 (d, J = 9.9 Hz, 1H), 4.38-4.32 (m, 3H), 3.96 (t, J = 9.6 Hz, 1H), 3.85-3.48 (m, 8H), 3.42-3.35 (m, 2H), 3.2 (d, J = 9.3 Hz, 1H), 2.26 (s, 3H, CH₃); <sup>13</sup>C-NMR (75 MHz, CDCl₃): δ 165.3 (C=O), 139.7, 138.74, 138.7, 138.6, 138.4, 138.2, 138.0, 133.6, 133.1, 130.1, 130.0, 128.92, 128.88, 128.8, 128.70, 128.69, 128.66, 128.6, 128.5, 128.32, 128.29, 128.21, 128.16, 128.1, 128.03, 128.01, 127.9, 127.5, 100.9 (C-1’), 88.1 (C-1), 85.3, 83.3, 80.7, 79.0, 78.6, 77.0, 75.78, 75.74, 75.5, 75.3, 74.7, 73.9, 73.8, 69.1, 68.6, 21.5 (CH₃); HRMS-ESI (m/z): [M + Na]<sup>+</sup> calcd. for C<sub>68</sub>H<sub>68</sub>NaO₁₁S, 1115.4374; found, 1115.4436.

**p-Tolyl** 6-O-(2-O-Benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-thio-β-D-glucopyranoside 20:

Disaccharide 20 was prepared from thiogluicosides 1 and 11a (Table S3, entry 3). Purification of 20 was achieved by standard column chromatography (Elution: EtOAc/CH₂Cl₂/Hexane 1:1:6). For disaccharide 20: [α]D<sup>35</sup> +4.9 (c 0.32, CHCl₃); R<sub>f</sub>
0.45 (EtOAc/Hexane 1:2); \( ^1 \)H-NMR (300 MHz, CDCl\(_3\)): \( \delta \) 7.92 (d, \( J = 6.9 \) Hz, 2H, Ar\( H \)), 7.50–7.43 (m, 3H, Ar\( H \)), 7.38–7.18 (m, 25H, Ar\( H \)), 7.13–7.11 (m, 7H, Ar\( H \)), 7.07–7.03 (m, 2H, Ar\( H \)), 5.36 (t, \( J = 7.8 \) Hz, 1H), 4.84 (d, \( J = 3.3 \) Hz, 1H), 4.81 (d, \( J = 2.4 \) Hz, 1H), 4.78 (s, 1H), 4.69–4.64 (m, 3H), 4.62 (s, 1H), 4.60 (s, 1H), 4.57 (s, 1H), 4.54–4.48 (m, 2H), 4.40 (d, \( J = 10.8 \) Hz, 1H), 4.13 (d, \( J = 10.8 \) Hz, 1H), 3.85–3.71 (m, 5H), 3.57 (t, \( J = 7.2 \) Hz, 2H), 3.41 (p, \( J = 9.6 \) Hz, 3H), 2.30 (s, 3H, CH\(_3 \)); 13C-NMR (75 MHz, CDCl\(_3\)): \( \delta \) 165.5 (C\( =O \)), 138.8, 138.6, 138.4, 138.3, 138.21, 138.17, 133.4, 133.3, 130.2, 130.1, 130.1, 128.9, 128.80, 128.76, 128.70, 128.6, 128.4, 128.2, 128.1, 128.0, 101.3 (C-1’), 87.9 (C-1), 87.0, 83.3, 80.7, 79.2, 78.5, 77.8, 76.0, 75.8, 75.7, 75.5, 75.4, 75.2, 74.2, 74.0, 69.3, 68.0, 21.6 (CH\(_3 \)); HRMS-ESI (m/z): [M + Na\(^+ \)] calcd. for C\(_{68}\)H\(_{68}\)NaO\(_{11}\)S, 1115.4374; found, 1115.4436.

\( p \)-Tolyl 6-O-(2-O-Benzoyl-3,4,6-tri-O-benzyl-\( \beta \)-D-glucopyranosyl)-2,3,4-tri-O-benzyl-thio-\( \beta \)-D-galactopyranoside 21:

\[
\text{Disaccharide 21 was prepared from thiogluco}
\]

(Table S3, entry 5). Purification of 21 was achieved by standard column chromatography (Elution: EtOAc/CH\(_2\)Cl\(_2\)/Hexane 1:3:11). For disaccharide 21: [\( \alpha \)]\(_D\)\(^+\) 17.5 (c 0.42, CHCl\(_3\)); \( R_f \) 0.41 (EtOAc/CH\(_2\)Cl\(_2\)/Hexane 1:2:5); \( ^1 \)H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 7.95 (d, \( J = 7.2 \) Hz, 2H, Ar\( H \)), 7.50 (t, \( J = 7.2 \) Hz, 1H, Ar\( H \)), 7.42 (t, \( J = 8.4 \) Hz, 3H, Ar\( H \)), 7.37–7.21 (m, 24H, Ar\( H \)), 7.20–7.15 (m, 2H, Ar\( H \)), 7.11 (s, 5H, Ar\( H \)), 6.97 (d, \( J = 7.8 \) Hz, 2H, Ar\( H \)), 5.27 (t, \( J = 8.7 \) Hz, 1H), 4.82 (dd, \( J = 11.4 \) Hz, 9 Hz, 2H), 4.75–4.64 (m, 5H), 4.61–4.58 (m, 2H), 4.54 (s, 1H), 4.47 (d, \( J = 5.7 \) Hz, 1H), 4.43 (d, \( J = 3.3 \) Hz, 1H), 4.39 (d, \( J = 3.6 \) Hz, 2H), 4.01 (dd, \( J = 7.5 \) Hz, 1H), 3.84–3.71 (m, 7H), 3.52–3.47 (m, 1H), 3.41 (t, \( J = 6.0 \) Hz, 1H), 3.33 (dd, \( J = 9.3, 2.7 \) Hz, 1H), 2.25
\( \text{\(^{13}\)}\text{C-NMR (75 MHz, CDCl}_3\): }  \delta 165.6 (C=O), 139.2, 138.8, 138.6, 138.40, 138.36, 138.2, 137.8, 133.7, 133.0, 130.3, 130.2, 130.1, 130.0, 129.0, 128.84, 128.82, 128.8, 128.73, 128.71, 128.7, 128.5, 128.4, 128.35, 128.30, 128.2, 128.09, 128.07, 128.0, 127.9, 127.7, 101.5 (C-1’), 88.3 (C-1), 84.5, 83.1, 78.2, 77.3, 76.0, 75.55, 75.47, 75.45, 74.8, 74.3, 73.9, 73.4, 72.6, 68.9, 67.8, 21.6 (CH\(_3\)); HRMS-ESI (m/z): [M + Na\(^+\) calcd. for C\(_{68}\)H\(_{68}\)NaO\(_{11}\)S, 1115.4374; found, 1115.4465.

4-(\(t\)-Butyl)-2-methylphenyl 4-O(2-O-Benzoyl-3,4,6-tri-O-benzyl-\(\beta\)-D-gluco pyranosyl)-2,3-O-isopropylidene-thio-\(\alpha\)-L-rhamnopyranoside 22:

Disaccharide 22 was prepared from thioglucoside 1 and thiorhamnoside 17 (Table S3, entry 6). Purification of 22 was achieved by column chromatography purification (Elution: EtOAc/Hexane 1:15). For disaccharide 22: \([\alpha]_D^{35} \) -77.9 (c 0.83, CHCl\(_3\)); \(R_f\) 0.3 (EtOAc/Hexane 1:4); \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta 8.11 (d, J = 6.9 \text{ Hz}, 2H, \text{Ar}\_H), 7.61-7.56 (m, 1H, \text{Ar}\_H), 7.51 (d, J = 2.1 \text{ Hz}, 1H, \text{Ar}\_H), 7.45 (t, J = 7.8 \text{ Hz}, 2H, \text{Ar}\_H), 7.33-7.09 (m, 17H, \text{Ar}\_H), 5.63 (s, 1H), 5.26 (t, J = 8.1 \text{ Hz}, 1H), 4.99 (d, J = 7.8 \text{ Hz}, 1H), 4.84 (d, J = 10.8 \text{ Hz}, 1H), 4.76-4.68 (m, 2H), 4.65-4.53 (m, 3H), 4.22 (d, J = 5.7 \text{ Hz}, 1H), 4.07-4.00 (m, 2H), 3.89-3.74 (m, 4H), 3.63 (dd, J = 9.9, 7.5 \text{ Hz}, 1H), 3.52 (d, J = 9.3 \text{ Hz}, 1H), 2.34 (s, 3H, CH\(_3\)), 1.48 (s, 3H, CH\(_3\)), 1.28-1.26 (m, 15H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta 166.0 (C=O), 150.1, 138.6, 138.5, 138.4, 137.1, 133.5, 132.4, 130.8, 130.4, 128.9, 128.84, 128.76, 128.7, 128.44, 128.41, 128.3, 128.09, 128.06, 125.3, 109.7 (quaternary-C), 101.0 (C-1’), 83.4 (C-1), 80.8, 78.4, 77.4, 75.8, 75.4, 74.5, 74.0, 69.1, 66.3, 34.9, 31.8, 28.4, 26.8, 20.6, 18.0; HRMS-ESI (m/z): [M + Na\(^+\)] calcd. for C\(_{54}\)H\(_{62}\)NaO\(_{16}\)S, 925.3956; found, 925.4029.
**p-Tolyl 6-O-(6-O-Acetyl-2,3-di-O-benzoyl-4-O-benzyl-β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-thio-β-D-glucopyranoside 23:**

Disaccharide 23 was prepared from thioglucosides 6 and 11a by the general DMF-modulated glycosylation procedure (Table S3, entry 7). The disaccharide 23 was obtained as white semisolid after column chromatography purification (Elution: EtOAc/Hexane 1:4). For disaccharide 23: [α]D

\[ \text{+28.0 (c 0.80, CHCl}_3\text{)}; \]

\( R_f \) 0.3 (EtOAc/Hexane 3:7); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.97 (d, \( J = 8.0 \text{ Hz, 2H, ArH} \)), 7.81 (d, \( J = 8.0 \text{ Hz, 2H, ArH} \)), 7.53–7.47 (m, 4H, ArH), 7.40–7.37 (m, 5H), 7.34–7.13 (m, 19H, ArH), 7.09–7.07 (m, 2H, ArH), 5.70 (t, \( J = 9.2 \text{ Hz, 1H} \)), 5.44–5.39 (m, 1H), 4.87–4.71 (m, 5H), 4.66 (d, \( J = 10.4 \text{ Hz, 1H} \)), 4.60–4.53 (m, 3H), 4.50 (d, \( J = 1.6 \text{ Hz, 1H} \)), 4.45 (d, \( J = 12.0 \text{ Hz, 1H} \)), 4.39 (d, \( J = 11.2 \text{ Hz, 1H} \)), 4.27 (dd, \( J = 12.4, 4.0 \text{ Hz, 1H} \)), 3.78 (d, \( J = 9.2 \text{ Hz, 1H} \)), 3.67 (d, \( J = 9.2 \text{ Hz, 1H} \)), 3.60–3.56 (m, 1H), 3.43–3.35 (m, 3H), 2.34 (s, 3H, CH\(_3\)), 2.05 (s, 3H, CH\(_3\)CO); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 171.2 (C=O), 166.1 (C=O), 165.7 (C=O), 138.8, 138.53, 138.48, 138.3, 137.3, 133.7, 133.5, 133.3, 130.4, 130.22, 130.18, 130.0, 129.82, 129.76, 128.90, 128.87, 128.85, 128.83, 128.75 128.7, 128.6, 128.3, 128.24, 128.18, 128.13, 128.10, 127.9, 127.8, 101.2 (C-1'), 88.2 (C-1), 81.0, 79.2, 76.2, 76.1, 75.8, 75.7, 75.3, 75.2, 75.1, 73.5, 72.5, 68.2, 63.1, 21.6, 21.4; HRMS-ESI (m/z): [M + Na]\(^+\) calcd. for C\(_{63}\)H\(_{61}\)NaO\(_{15}\)S, 1081.3803; found, 1081.3784.

**p-Tolyl 6-O-(6-O-Acetyl-2,3-di-O-benzoyl-4-O-benzyl-β-D-glucopyranosyl)-2,3-di-O-benzoyl-4-O-benzyl-thio-β-D-glucopyranoside 24:**
Disaccharide 24 was prepared from thioglucosides 6 and 11b by the general DMF-modulated glycosylation procedure (Table S3, entry 8). Purification of 24 was achieved by column chromatography purification (Elution: EtOAc/Hexane 1:4). For disaccharide 24: $[\alpha]_D^{35} +41.5$ (c 0.13, CHCl$_3$); $R_f$ 0.2 (EtOAc/Hexane 1.5 two times); $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.98 (d, $J = 6.8$ Hz, 2H, ArH), 7.90 (dd, $J = 14.4$, 7.2 Hz, 4H, ArH), 7.83 (d, $J = 7.2$ Hz, 2H, ArH), 7.54–7.46 (m, 4H, ArH), 7.43–7.30 (m, 9H), 7.27 (t, $J = 7.6$ Hz, 2H, ArH), 7.21–7.20 (m, 3H, ArH), 7.17–7.10 (m, 6H, ArH), 6.95–6.93 (m, 2H, ArH), 5.74 (t, $J = 9.2$ Hz, 1H), 5.61 (t, $J = 9.2$ Hz, 1H), 5.46 (dd, $J = 9.6$, 1.6 Hz, 1H), 5.27 (t, $J = 10.0$ Hz, 1H), 4.80 (d, $J = 7.6$ Hz, 1H), 4.76 (d, $J = 8.0$ Hz, 2H), 4.63–4.50 (m, 4H), 4.34–4.27 (m, 3H), 4.16 (d, $J = 11.2$ Hz, 1H), 3.94 (t, $J = 9.6$ Hz, 1H), 3.84 (dd, $J = 8.7$, 3.3 Hz, 1H), 3.75–3.69 (m, 2H), 3.64 (dd, $J = 10.0$, 6.4 Hz, 1H), 2.33 (s, 3H, CH$_3$), 2.08 (s, 3H, CH$_3$CO); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.1 (C=O), 166.1 (C=O), 166.0 (C=O), 165.7 (C=O), 165.6 (C=O), 139.0, 137.6, 137.3, 134.1, 133.8, 133.6, 130.3, 130.24, 130.21, 130.18, 130.16, 129.9, 129.8, 128.93, 128.89, 128.8, 128.74, 128.69, 128.6, 128.3, 101.3 (C-1), 86.7 (C-1), 79.4, 76.9, 76.2, 76.1, 75.7, 75.22, 75.15, 73.6, 72.5, 71.2, 68.2, 63.1, 21.7, 21.4; HRMS-ESI (m/z): [M + Na]$^+$ calcd. for C$_{63}$H$_{57}$NaO$_{15}$S, 1109.3389; found, 1109.3373.

$p$-Tolyl 2-O-(2-O-Benzoyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-3,4,6-tri-O-benzyl-thio-α-D-mannopyranoside 25:
Disaccharide 25 was prepared from thiomannosides 2 and 12 by the general DMF-modulated glycosylation procedure for participating donor (Table S3, entry 9). 25 was purified by standard column chromatography (Et₂O/CH₂Cl₂/Hexane 0.5:2:10 stepwise to 0.1:2:8). For disaccharide 25: [α]D

\[ \alpha \] \text{D} \left( \alpha \right) +42.5 (c 0.33, CHCl₃); R<sub>f</sub> 0.4 (Et₂O/CH₂Cl₂/Hexane 1:1:4); \text{¹}H-NMR (300 MHz, CDCl₃): δ 8.07 (d, \( J = 7.5 \) Hz, 2H, ArH), 7.54 (t, \( J = 7.2 \) Hz, 1H, ArH), 7.39-7.12 (m, 34H, ArH), 7.00 (d, \( J = 8.1 \) Hz, 2H, ArH), 5.76 (s, 1H), 5.58 (s, 1H), 5.17 (s, 1H), 4.90 (d, \( J = 10.8 \) Hz, 1H), 4.82 (d, \( J = 10.8 \) Hz, 1H), 4.76-4.61 (m, 5 H), 4.57 (s, 1H), 4.49 (s, 1H), 4.46-4.40 (m, 3H, 3.85-3.71 (m, 3H), 3.63 (d, \( J = 10.5 \) Hz, 1H), 2.54 (s, 3H, CH₃); \text{¹³}C-NMR (75 MHz, CDCl₃): δ 165.9 (C=O), 138.94, 138.85, 138.8, 138.5, 138.1, 133.5, 132.8, 130.7, 130.4, 130.2, 128.9, 128.81, 128.75, 128.70, 128.67, 128.52, 128.46, 128.33, 128.25, 128.2, 128.1, 128.0, 127.9, 127.8, 100.2 (C-1’), 88.0 (C-1), 80.4, 78.5, 75.7, 75.6, 75.3, 74.8, 73.6, 73.3, 72.8, 72.6, 72.1, 69.7, 69.5, 69.3, 21.5 (CH₃); HRMS-ESI (m/z): [M + Na]<sup>+</sup> calcd. for C₆₈H₆₈NaO₁₁S, 1115.4374; found, 1115.4451.

\( p \)-Tolyl 3-O-(2-O-Benzoyl-3,4,6-tri-O-benzyl-\( \alpha \)-D-mannopyranosyl)-2,4,6-tri-O-benzyl-thio-\( \alpha \)-D-mannopyranoside 26:

Disaccharide 26 was prepared from thiomannosides 2 and 13a by the general DMF-modulated glycosylation procedure (Table S3, entry 10). Purification of 26 was performed with column chromatography (Elution: Et₂O/CH₂Cl₂/Hexane 1:1:16 stepwise to 1:1:11). For disaccharide 26: [α]D

\[ \alpha \] \text{D} \left( \alpha \right) +46.9 (c 0.35, CHCl₃); R<sub>f</sub> 0.4 (Et₂O/CH₂Cl₂/Hexane 1:1:4); \text{¹}H NMR (300 MHz, CDCl₃): δ 8.06 (d, \( J = 7.2 \) Hz, 2H,
ArH), 7.53 (t, J = 7.5 Hz, 1H, ArH), 7.38–7.16 (m, 34H, ArH), 7.03 (d, J = 8.1 Hz, 2H, ArH), 5.78 (t, J = 2.1 Hz, 1H), 5.56 (s, 1H), 5.38 (d, J = 1.2 Hz, 1H), 4.89 (d, J = 10.8 Hz, 1H), 4.78 (dd, J = 12.3, 10.8 Hz, 2H), 4.72–4.63 (m, 3H), 4.58–4.45 (m, 6H), 4.30 (dd, J = 9, 3.6 Hz, 1H), 4.20–4.12 (m, 4H), 4.04 (t, J = 9.6 Hz, 1H), 4.97 (d, J = 9.6 Hz, 1H), 3.87–3.70 (m, 4H), 2.28 (s, 3H, CH3); 13C-NMR (75 MHz, CDCl3): δ 165.8 (C=O), 139.0, 138.8, 138.7, 138.3, 138.2, 137.9, 133.5, 132.6, 130.9, 130.3, 130.2, 130.1, 128.84, 128.79, 128.76, 128.71, 128.67, 128.6, 128.44, 128.42, 128.2, 128.01, 127.97, 127.89, 127.87, 127.85, 100.2 (C-1’), 85.9 (C-1), 79.2, 78.5, 75.6, 75.4, 74.8, 73.9, 73.7, 73.2, 72.8, 71.8, 69.6, 69.5, 21.5 (CH3); HRMS-ESI (m/z): [M + Na]+ calcd. for C68H68NaO11S, 1115.4374; found, 1115.4472.

*p*-Tolyl 3-O-(2-O-Benzoyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-6-O-benzoyl-2,4-di-O-benzyl-thio-α-D-mannopyranoside 27:

Disaccharide 27 was prepared from thiomannosides 2 and 13b by the general DMF-modulated glycosylation procedure (Table S1, entry 11). Purification of 27 was performed with column chromatography (Elution: EtOAc/CH2Cl2/Hexane 0.2:2:8 stepwise to 0.4:2:8). For disaccharide 27: [α]D35 +50.2 (c 0.33, CHCl3); Rf 0.44 (EtOAc/Hexane 1/2); 1H NMR (300 MHz, CDCl3): δ 8.08 (d, J = 7.2 Hz, 2H, ArH), 8.00 (d, J = 7.2 Hz, 2H, ArH), 7.53 (dd, J = 13.8, 7.2 Hz, 2H, ArH), 7.39–7.16 (m, 31H, ArH), 7.00 (d, J = 8.1 Hz, 2H, ArH), 5.79 (s, 1 H), 5.57 (s, 1 H), 5.40 (s, 1 H), 4.89 (t, J = 10.8 Hz, 2H), 4.76 (d, J = 11.4 Hz, 1H), 4.72 (t, J = 12.3 Hz, 2H), 4.60–4.52 (m, 7H), 4.50–4.46 (m, 1H), 4.24–4.10 (m, 4H), 4.06 (d, J = 5.7 Hz, 2H), 3.83–3.75 (m, 2H), 2.26 (s, 3H); 13C-NMR (75 MHz, CDCl3): δ 166.7 (C=O), 165.9 (C=O), 138.9, 138.7, 138.24, 138.17, 138.1, 137.8, 133.6, 133.3, 132.4, 130.6, 130.3, 128.9,
Disaccharide 28 was prepared from thiomannosides 2 and 14 by the general DMF-modulated glycosylation procedure for participating donors (Table S3, entry 12). Purification of 28 was performed with column chromatography (Elution: EtOAc/CH2Cl2/Hexane 1:2:20 stepwise to 1:2:10). For disaccharide 28: [α]D\textsubscript{35} +30.8 (c 0.34, CHCl\textsubscript{3}); \textit{Rf} 0.325 (EtOAc/CH\textsubscript{2}Cl\textsubscript{2}/Hexane 1:2:10); \textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}): δ 8.08 (dd, \textit{J} = 8.1, 0.9 Hz, 2H, Ar\textit{H}), 7.52 (t, \textit{J} = 7.5 Hz, 1H, Ar\textit{H}), 7.39–7.12 (m, 34H, Ar\textit{H}), 7.07 (d, \textit{J} = 8.1 Hz, 2H, Ar\textit{H}), 5.74 (s, 1H), 5.53 (d, \textit{J} = 1.5 Hz, 1H), 5.07 (d, \textit{J} = 1.8 Hz, 1H), 4.95 (d, \textit{J} = 1.1 Hz, 1H), 4.89 (d, \textit{J} = 1.1 Hz, 1H), 4.79–4.69 (m, 3H), 4.64–4.59 (m, 3H), 4.54 (s, 1H), 4.50–4.43 (m, 3H), 4.27 (dd, \textit{J} = 9.6, 3.6 Hz, 1H), 4.11 (d, \textit{J} = 6 Hz, 2H), 4.04–3.97 (m, 3H), 3.89–3.79 (m, 3H), 3.70 (t, \textit{J} = 9.9 Hz, 2H), 2.16 (s, 3H, CH\textsubscript{3}); \textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}): δ 165.9 (C=O), 139.1, 138.9, 138.8, 138.5, 138.3, 137.9, 133.4, 131.9, 131.3, 130.4, 130.3, 128.86, 128.84, 128.79, 128.74, 128.71, 128.6, 128.5, 128.32, 128.3, 128.20, 128.16, 128.02, 127.96, 127.90, 127.86, 98.7 (C-1'), 86.3 (C-1), 80.7, 78.2, 76.5, 75.7, 75.6, 75.0, 74.6, 72.6, 72.3, 72.0, 71.7, 69.3, 69.1, 67.3, 21.4 (CH\textsubscript{3}); HRMS-ESI (m/z): [M + Na]\textsuperscript{+} calcd. for C\textsubscript{68}H\textsubscript{68}NaO\textsubscript{12}S, 1129.4167; found, 1129.4195.
p-Tolyl 6-O-[3,4,6-Tri-O-acetyl-2-(2,2,2-trichloroethoxycarbonylamino)-2-deoxy-β-D-glucopyranosyl]-2,3,4-tri-O-benzyl-thio-β-D-glucopyranoside 29:

Disaccharide 29 was prepared from thioglicosaminyl donor 7 and thioglicoside acceptor 11a by the general DMF-modulated glycosylation procedure for participating donors (Table S3, entry 13). Purification of 29 was performed by column chromatography purification (Elution: EtOAc/CH₂Cl₂/Hexane 0.2:1:2 stepwise to 0.5:1:2). For disaccharide 29: [α]D₃₅₅ = -0.6 (c 0.33, CHCl₃); Rf 0.36 (EtOAc/CH₂Cl₂/Hexane 1:1:2); ¹H-NMR (300 MHz, CDCl₃): δ 7.48 (d, J = 8.1 Hz, 2H, ArH), 7.39–7.30 (m, 13H, ArH), 7.25–7.21 (m, 4H, ArH), 5.05–4.98 (m, 2H), 4.89 (dd, J = 10.8, 6.3 Hz, 2H), 4.84 (s, 1H), 4.81 (s, 1H), 4.74–4.67 (m, 3H), 4.62 (d, J = 8.4 Hz, 2H), 4.55 (d, J = 10.5 Hz, 2H), 4.26 (dd, J = 12.3, 4.5 Hz, 1H), 4.09 (t, J = 12.6 Hz, 2H), 3.76–3.66 (m, 3H), 3.63–3.59 (m, 1H), 3.52–3.44 (m, 2H), 3.41–3.32 (m, 1H), 2.34 (s, 3H, CH₃), 2.07 (s, 3H, CH₃C=O), 2.03 (s, 3H, CH₃C=O), 2.01 (s, 3H, CH₃C=O); ¹³C-NMR (75 MHz, CDCl₃): δ 171.2 (C=O), 170.9 (C=O), 170.0 (C=O), 154.6 (OC=O), 138.8, 138.6, 138.3, 138.2, 133.2, 130.7, 129.8, 129.0, 128.95, 128.9, 128.6, 128.5, 128.4, 128.3, 101.4 (C-1’), 95.9 (CCl₃), 88.1 (C-1), 87.1, 81.2, 80.1, 78.2, 76.3, 75.8, 75.4, 74.9, 72.7, 72.0, 69.2, 68.3, 62.4, 56.3, 21.5 (CH₃), 21.2 (CH₃C=O), 21.12 (CH₃C=O), 21.10 (CH₃C=O); HRMS-ESI (m/z): [M + Na⁺] calcd. for C₄₉H₅₄Cl₃NaNO₁₄S, 1040.2223; found, 1040.2437.

p-Tolyl 6-O-[3,4,6-Tri-O-acetyl-2-(2,2,2-trichloroethoxycarbonylamino)-2-deoxy-β-D-glucopyranosyl]-3-O-benzoyl-4-O-benzyl-2-(2,2,2-trichloroethoxycarbonyl}
amino)-2-deoxy-thio-β-D-glucopyranoside 30:

Disaccharide 30 was prepared from thioglucosaminyl donor 7 and thioglucosaminyl acceptor 15 by the general DMF-modulated glycosylation procedure for participating donors (Table S1, entry 14). Purification of 30 was performed by column chromatography (EtOAc/CH₂Cl₂/Hexane 1:3:2). For disaccharide 30: [α]D³⁵ −5.3 (c 0.35, CHCl₃); Rf 0.36 (EtOAc/CH₂Cl₂/Hexane 1:3:2); ¹H NMR (300 MHz, CDCl₃): δ 8.01 (d, J = 7.5 Hz, 2H, ArH), 7.58 (t, J = 7.2 Hz, 1H, ArH), 7.46-7.40 (m, 4H, ArH), 7.17-7.00 (m, 7H, ArH), 6.06 (bs, 1H, carbamate-H), 5.59 (t, J = 8.7 Hz, 1H), 5.40 (s, 1H, carbamate-H), 5.28 (t, J = 9.6 Hz, 1H), 5.06 (t, J = 9.3 Hz, 1H), 4.79-4.65 (m, 4 H), 4.58-4.40 (m, 4H), 4.28 (dd, J = 12.3, 3.9 Hz, 1H), 4.15 (d, J = 11.4 Hz, 1H), 4.00-3.91 (m, 2H), 3.74-3.66 (m, 5H), 2.32 (s, 3H, CH₃), 2.06 (s, 3H, CH₃C=O), 2.03 (s, 3H, CH₃C=O), 2.1 (s, 3H, CH₃C=O); ¹³C NMR (75 MHz, CDCl₃): δ 171.2 (C=O), 170.9 (C=O), 169.9 (C=O), 167.0 (C=O), 154.7 (C=O), 154.5 (C=O), 138.8, 137.4, 134.0, 133.6, 130.3, 129.3, 128.9, 128.76, 128.5, 128.4, 100.5 (C-1’), 95.8 (CCl₃), 95.7 (CCl₃), 87.6 (C-1), 79.0, 76.3, 75.0, 74.6, 72.5, 72.0, 69.1, 67.3, 62.3, 56.0, 55.4, 30.0, 21.5 (CH₃), 21.1 (CH₃C=O), 21.00 (CH₃C=O), 20.97 (CH₃C=O); HRMS-ESI (m/z): [M + Na]⁺ calcd. for C₄₅H₄₈Cl₆N₂O₁₆S, 1137.0748; found, 1139.0757.

p-Tolyl 6-O-(2-O-Benzoyl-3,4,6-tri-O-benzyl-β-D-galactopyranosyl)-2,3,4-tri-O-benzyl-thio-β-D-galactopyranoside 31:
Disaccharide 31 was prepared from 2-\textit{O}-benzoyl thiogalactoside 8 and thiogalactoside 16 by general DMF-modulated glycosylation procedure (Table S1, entry 15). For disaccharide 31: \([\alpha]_D^{35} +17.6\) (c 0.75, CHCl\(_3\)); \(R_f\) 0.4 (EtOAc/Hexane 1:4); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.97 (d, \(J = 7.6\) Hz, 2H, Ar\(H\)), 7.51 (t, \(J = 7.2\) Hz, 1H, Ar\(H\)), 7.40 (d, \(J = 8.0\) Hz, 4H, Ar\(H\)), 7.36-7.21 (m, 25H, Ar\(H\)), 7.14 (bs, 5H, Ar\(H\)), 6.95 (d, \(J = 7.6\) Hz, 2H, Ar\(H\)), 5.61 (t, \(J = 8.8\) Hz, 1H), 4.98 (d, \(J = 11.6\) Hz, 1H), 4.81 (d, \(J = 11.2\) Hz, 1H), 4.65-4.60 (m, 5H), 4.53 (d, \(J = 7.6\) Hz, 1H), 4.48-4.31 (m, 6H), 4.02-3.98 (m, 2H), 3.85 (s, 1H), 3.77 (t, \(J = 9.6\) Hz, 1H), 3.72 (dd, \(J = 10.0, 4.8\) Hz, 1H), 3.63-3.57 (m, 3H), 3.54-3.51 (m, 1H), 3.41 (t, \(J = 6.0\) Hz, 1H), 3.32 (d, \(J = 9.2\) Hz, 1H), 2.25 (s, 3H, CH\(_3\)); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 165.7 (C=O), 139.4, 138.91, 138.87, 138.67, 138.2, 138.0, 137.7, 133.6, 132.8, 130.5, 130.4, 130.2, 130.0, 129.9, 128.74, 128.71, 128.68, 128.46, 128.40, 128.3, 128.12, 128.09, 128.05, 127.94, 127.90, 127.6, 101.8 (C-1'), 88.3 (C-1), 84.5, 80.3, 77.3, 76.0, 75.0, 74.8, 74.03, 73.99, 73.3, 72.9, 72.6, 72.5, 72.1, 68.7, 67.4, 21.6 (CH\(_3\)). HRMS-ESI (m/z): [M + Na]\(^+\) calcd. for C\(_{68}\)H\(_{68}\)NaO\(_{11}\)S, 1115.4375; found, 1115.4376.

\(p\)-Tolyl 2-\textit{O}-Benzoyl-3,4-di-\textit{O}-benzyl-thio-\(\alpha\)-\textit{d}-mannopyranoside 33
Acetal derivative s13bc (5.0 g, 13.4 mmol) suspended in toluene (67 mL) was treated with di-butyl tin oxide (Bu₂SnO, 5.0 g, 20.1 mmol) and the solution was heated to reflux with Dean-Stark trap for 4 h (at 145 °C). The volume of toluene was then reduced approximately by half and the reaction mixture was cooled to RT. After then, benzyl bromide (2.4 ml, 20.1 mmol), cesium fluoride (CsF, 3.0 g, 20.1 mmol), and CH₃CN (33 mL) were added and the resulting mixture was stirred at 70 °C for ca. 16 h. Upon the completion of alkylation, the reaction mixture was filtered (over celite), and concentrated for column chromatography purification (Elution EtOAc/Hexane 1/8 stepwise to 1/3) to afford s33a (4.72 g, 10.17 mmol). s33a (3.36 g, 7.2 mmol) was treated with BzCl (1.3 mL, 10.8 mmol), Et₃N (2 mL, 14.4 mmol) and DMAP (85 mg, 0.7 mmol) in CH₂Cl₂. Upon completion of the reaction, the mixture was diluted with satd. NaHCO₃, then the mixture was extracted with EtOAc (∗ 2). The EtOAc solution was then washed with H₂O and brine, dried over MgSO₄, filtered, and concentrated for column chromatography purification (Elution: Ether/CH₂Cl₂/Hexane 0.08/1/4 stepwise to 0.1/1/4) to furnish fully protected mannoside derivative s33b (3.18 g, 5.6 mmol). The derivative s33b (0.755 g, 1.33 mmol) in BH₃·THF solution (1 M, 5.32 mL, 5.32 mmol) was treated with trimethylsilyl triflate (TMSOTf) (49 μL) at 0 °C. Upon completion of the reductive acetal cleavage, the mixture was neutralized with Et₃N, excess borane was quenched with addition of MeOH. The resulting mixture was then concentrated for column chromatography purification (Elution: EtOAc/Hexane 1:8 stepwise to 1:6) to afford thiomannoside acceptor 33 (0.71 g, 1.24 mmol). For monosaccharide 33: [α]D 35 +40.8 (c 0.34, CHCl₃); Rf 0.34 (EtOAc/Hexane 1/2); ¹H-NMR (300 MHz, CDCl₃): δ 8.06 (d, J = 6.9 Hz, 2 H), 7.56 (t, J = 7.5 Hz, 1 H), 7.46-7.41 (m, 2 H), 7.37-7.25 (m, 12 H), 7.09 (d, J = 8.1 Hz, 2 H), 5.85-5.83 (m, 1 H), 5.50 (d, J = 1.5 Hz, 1 H), 4.94 (d, J = 10.8 Hz, 1 H), 4.79 (d, J = 11.4 Hz, 1 H), 4.67 (d, J = 11.1 Hz, 1 H), 4.60 (d, J = 11.4 Hz, 1 H), 4.27-4.24 (m, 1 H), 4.11-4.01 (m, 2 H), 3.85 (s, 2 H), 2.30 (s, 3 H), 1.97 (s, 1 H); ¹³C-NMR (75 MHz, CDCl₃): δ 166.0, 138.7, 138.5, 138.0, 133.8, 133.2, 130.4,
Methyl 2-O-Benzoyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside 35

Trisaccharide 35 was prepared from one pot disarmed-armed glycosylation method. In the first step, thiomannoside donor 2 (200 mg, 0.303 mmol) and DMF (23.5 μL, 0.303 mmol) were treated with NIS (74.7 mg, 0.329 mmol) and TMSOTf (83 μL, 0.455 mmol) in dried CH₂Cl₂ at –20 °C. Upon the completion of the pre-activation (ca. 0.5 h), thiomannoside acceptor 12 (141 mg, 0.253 mmol) was added to the mixture, which was stirred at –20 °C for ca. 7.5 h. Progress of the reaction was monitored by TLC (Rᵣ of disaccharide product = 0.4, developed with 1/1/4 v/v Et₂O/CH₂Cl₂/Hexane). Upon the completion of glycosylation (ca. 7.5 h), methyl mannoside 32 (117 mg, 0.253 mmol), DMF (55 μL, 0.708 mmol), NIS (68.8 mg, 0.303 mmol) and TMSOTf (82 μL, 0.455 mmol) was added to the mixture and the reaction temperature was stirred raised at 10 °C for ca. 14.5 h. Followed by standard workup (as described in general modulated glycosylation procedure) and column chromatography purification (Elution: EtOAc/CH₂Cl₂/Hexane 1/2/12 stepwise to 1/1/8), target trisaccharide 35 was obtained as white glassy solid (126.7 mg, 35%). For 35: [α]ᵣ <sup>35</sup> +10.0 (c 0.32, CHCl₃); Rᵣ 0.47 (EtOAc/CH₂Cl₂/Hexane
1/1/4; ¹H-NMR (300 MHz, CDCl₃): δ 8.09 (d, J = 7.8 Hz, 2 H), 7.55 (t, J = 7.5 Hz, 1 H), 7.39-7.10 (m, 49 H), 7.05 (t, J = 8.1 Hz, 1 H), 5.77 (s, 1 H), 5.25 (s, 1 H), 5.12 (s, 1 H), 4.88-4.82 (m, 4 H), 4.77 (d, J = 11.1 Hz, 1 H), 4.70-4.45 (m, 14 H), 4.37 (d, J = 12.0 Hz, 1 H), 4.12-4.06 (m, 3 H), 4.01-3.93 (m, 4 H), 3.87-3.69 (m, 9 H), 3.60 (d, J = 1 H), 3.23 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 165.9, 139.0, 138.9, 138.8, 138.5, 133.5, 130.5, 130.4, 128.84, 128.82, 128.76, 128.6, 128.4, 128.3, 128.14, 128.08, 128.0, 127.94, 127.86, 101.1, 100.2, 99.9, 80.1, 79.7, 78.5, 75.7, 75.52, 75.45, 75.3, 75.2, 74.8, 73.8, 73.7, 72.7, 72.6, 72.5, 72.1, 72.0, 70.0, 69.8, 69.5, 55.1; HRMS-ESI (m/z): [M + Na]⁺ calcd. for C₈₉H₉₂NaO₁₇, 1455.6227; found, 1455.6222.

Methyl 2-O-Benzoyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→6)-2-O-benzoyl-3,4-di-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside 36

Trisaccharide 36 was prepared from one pot disarmed-armed glycosylation method. In the first step, thiomannoside donor 2 (200 mg, 0.303 mmol) and DMF (23.5 µL, 0.303 mmol) were treated with NIS (74.7 mg, 0.329 mmol) and TMSOTf (83 µL, 0.455 mmol) in dried CH₂Cl₂ at −20 °C. Upon the completion of donor activation (ca. 0.5 h), thiomannoside acceptor 33 (141 mg, 0.253 mmol) was added to the mixture, which was stirred at 0 °C for ca. 4.5 h. Progress of the reaction was monitored by TLC examination (Rf of disaccharide product = 0.55, developed with 1/1/3 v/v Et₂O/CH₂Cl₂/Hexane). Upon the completion of the glycosylation (ca. 4.5 h), the reaction temperature was decreased to −20 °C, methyl mannoside acceptor 32
(105.8 mg, 0.228 mmol), NIS (68.8 mg, 0.303 mmol) and TMSOTf (68.6 µL, 0.380 mmol) were added to the mixture and the mixture was stirred at −20 °C for ca. 2 h. Followed by standard workup (as described in general modulated glycosylation procedure) and column chromatography purification (Elution: EtOAc/CH2Cl2/Hexane 1/2/10 stepwise to 1/2/7), trisaccharide 36 was obtained as a white glassy solid (181.2 mg, 55%). For trisaccharide 36: [α]D35 +21.1 (c 1.05, CHCl3); Rf 0.30 (EtOAc/Hexane 1/3); 1H-NMR (400 MHz, CDCl3): δ 8.12 (dd, J = 7.2, 1.6 Hz, 2 H), 8.08 (d, J = 7.6 Hz, 2 H), 7.55-7.46 (m, 5 H), 7.36-7.17 (m, 36 H), 7.15-7.06 (m, 7 H), 5.79 (s, 2 H), 5.24 (s, 1 H), 5.15 (s, 1 H), 4.88-4.82 (m, 4 H), 4.79-4.75 (m, 3 H), 4.70-4.59 (m, 5 H), 4.52-4.42 (m, 6 H), 4.14-4.09 (m, 4 H), 4.03-3.98 (m, 2 H), 3.93-3.86 (m, 3 H), 3.83-3.69 (m, 7 H), 3.64 (d, J = 10.4 Hz, 1 H), 3.33 (s, 3 H); 13C NMR (100 MHz, CDCl3): δ 165.97, 165.95, 138.94, 138.88, 138.6, 138.5, 138.2, 133.6, 133.5, 130.6, 130.44, 130.37, 130.3, 129.0, 128.83, 128.79, 128.77, 128.75, 128.70, 128.69, 128.6, 128.5, 128.4, 128.3, 128.1, 128.03, 128.02, 127.97, 127.9, 100.3, 99.7, 98.5, 80.4, 78.9, 78.6, 75.7, 75.6, 75.5, 74.9, 74.61, 74.59, 74.2, 73.82, 73.80, 72.6, 72.3, 72.16, 72.15, 71.8, 69.6, 69.4, 69.3, 69.1, 66.7, 55.2; HRMS MALDI-TOF (m/z): [M + Na]+ calcd. for C89H90NaO18, 1469.6019; found, 1469.5842.

Methyl 6-O-Acetyl-2,3-di-O-benzoyl-4-O-benzyl-β-D-glucopyranosyl-(1→6)-2,3-di-O-benzoyl-4-benzyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzyl-β-D-glucopyranoside 37

Trisaccharide 37 was prepared from one pot disarmed-armed glycosylation
method. In first step, thiogluicoside 6 (200 mg, 0.319 mmol) and DMF (30 µL, 0.389 mmol) were treated with NIS (72 mg, 0.319 mmol) and TMSOTf (86 µL, 0.479 mmol) in dried CH₂Cl₂ at −10 °C. Upon the completion of pre-activation, thiogluicoside acceptor 11b was added to the mixture and the reaction temperature was raised to 0 °C. The mixture was stirred at 0 °C for ca 6 h and the reaction was monitored by TLC examination (Rf of disaccharide = 0.27, developed by 1/4 v/v EtOAc/Hexane × 2). Upon the completion of the first glycosylation, DMF (20 µL, 0.319 mmol), NIS (72 mg, 0.319 mmol) and TMSOTf (85 µL, 0.479 mmol) were added to the reaction mixture to react with the disaccharide for ca. 1 h at 0 °C. Upon the completion of the disaccharide activation, methyl glycoside acceptor 34 (151 mg, 0.256 mmol) was added to the mixture and the reaction temperature was raised to 10 °C. The reaction mixture was stirred at 10 °C for ca. 8 h. After standard workup (as described in general modulated glycosylation procedure) and column chromatography purification (Elution: EtOAc/CH₂Cl₂/Hexane 1/22), target trisaccharide 37 was obtained as a light yellow glassy substance (255 mg, 52%). For trisaccharide 37: [α]D 35 +35.7 (c 2.1, CHCl₃); Rf 0.23 (EtOAc/Hexane: 1/4 × 2); 1H NMR (400 MHz,CDCl₃): δ 7.86 (d, J = 7.2 Hz, 2 H), 7.82 (d, J = 7.2 Hz, 2 H, ArH), 7.74 (t, J = 8.4 Hz, 4 H, ArH), 7.41-7.34 (m, 3 H), 7.31-7.14 (m, 22 H, ArH), 7.09-7.02 (m, 10 H), 6.91-6.86 (m, 4 H, ArH), 5.63 (t, J = 9.6 Hz, 1 H), 5.52 (t, J = 9.6 Hz, 1 H), 5.35-5.26 (m, 2 H), 4.80-4.78 (m, 2 H), 4.61 (t, J = 12.8 Hz, 2 H), 4.51-4.48 (m, 3 H), 4.44-4.38 (m, 3 H), 4.29-4.17 (m, 4 H), 4.09-3.95 (m, 3 H), 3.83-3.69 (m, 3 H), 3.64-3.48 (m, 5 H), 3.35-3.27 (m, 2 H), 3.17 (s, 3 H), 2.00 (s, 3 H, CH₃); 13C NMR (100 MHz, CDCl₃): δ 171.0, 166.0, 165.6, 165.4, 139.2, 138.62, 138.57, 137.4, 137.2, 133.7, 133.6, 133.3, 130.07, 130.05, 130.0, 129.8, 129.6, 128.84, 128.78, 128.70, 128.67, 128.6, 128.5, 128.3, 128.2, 127.83, 127.77, 101.5, 101.1, 98.4, 82.2, 80.1, 77.6, 76.4, 76.0, 75.9, 75.7, 75.5, 75.4, 75.2, 75.03, 74.96, 73.69, 73.65, 72.5, 72.2, 69.8, 68.3, 68.2, 63.0, 55.6, 21.3; HRMS-ESI (m/z): [M + Na]⁺ calcd. for C₈₄H₆₂NaO₂₁, 1449.5241; found, 1449.5242.
Per-O-acetyl glucosyl acetate \textit{s38a}[^{2}] (31.1 g, 79.7 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (20 mL) was cooled to 0 °C and treated with 33% HBr in AcOH (31.0 mL) under N\textsubscript{2}. After 30 min, the reaction mixture was brought to RT. Upon completion of the bromination, the reaction mixture was extracted with EtOAc, and the EtOAc solution was washed with H\textsubscript{2}O, 8% NaOH (aq), NaCl, dried (over MgSO\textsubscript{4}), filtered, and concentrated, and dried under \textit{vacuo} to give crude bromide derivative. The bromide derivative dissolved in CH\textsubscript{3}CN (75 mL) was treated with TBAB (4.9 g, 15.2 mmol), 2,6-lutidine (17.6 mL, 152 mmol), and MeOH (9.2 mL). The reaction mixture was stirred at RT under N\textsubscript{2} overnight. Upon completion of the orthoester formation, the solvent was reduced by rotary evaporator. The residue was dissolved by EtOAc, which was washed with satd. NaHCO\textsubscript{3}, H\textsubscript{2}O, brine, followed by dried over MgSO\textsubscript{4}, filtered, and concentrated to give per-O-acetyl glucosyl orthoester \textit{s38b} (32.5 g). \textit{s38b} (32.5 g) in MeOH/CH\textsubscript{2}Cl\textsubscript{2} mixture (120 mL, MeOH/CH\textsubscript{2}Cl\textsubscript{2} 2/1) was treated with Na(s) (120 mg) at RT. Upon completion of deacetylation, the reaction mixture was concentrated and dried under \textit{vacuo} for 4 h. The crude deacetyl compound (14.3 g, 60.5 mmol) was then dissolved in dried DMF (120 mL) and the solution was cooled to 0 °C under N\textsubscript{2}. The solution was treated with (7.3 g, 181.5 mmol) (60% in mineral oil), followed by iodomethane (MeI) (11.3 mL, 182 mmol). Upon completion of methylation, H\textsubscript{2}O was added to quench the reaction. The reaction mixture was diluted with EtOAc, and the resulting solution was washed with H\textsubscript{2}O, brine, dried over MgSO\textsubscript{4}, filtered, and concentrated for column chromatography purification (EtOAc/Hexane 3/7) to furnish per-O-methyl
glucosyl orthoester \textbf{s38c} (7.20 g). \textbf{s38c} (7.20 g, 25.9 mmol) in dried CH₂Cl₂ (52 mL) was treated with \(p\)-thiocresol (4.8 g, 38.9 mmol) at 0°C, followed by treatment with BF₃.OEt₂ (4.93 mL, 39 mmol). Upon completion of the reaction, the reaction mixture was diluted with 8% NaOH(aq), and the reaction solution was washed with satd. NaHCO₃, EtOAc, brine, dried over MgSO₄, filtered, and concentrated for column chromatography purification (Elution: EtOAc/CH₂Cl₂/Hexane 1/4/9 stepwise to 1/3/7) to give 2-\(O\)-acetyl-3,4,6-tri-\(O\)-methyl thioglucoside \textbf{s33d} (7.1 g, 74%) as yellow syrup. \textbf{s33d} (6.8 g, 18.4 mmol) in CH₂Cl₂/MeOH (120 mL) was treated with Na(s) (150 mg). Upon completion of deacetylation, the reaction was neutralized with IR-120 (H⁺), filtered, concentrated, and column chromatography purification (EtOAc/Hexane 1/3 stepwise to 1/2) to furnish (4.6 g, 76%). The preceding derivative in CH₂Cl₂ was treated with BzCl (2.4 mL, 20.1 mmol), Et₃N (3.7 mL, 26.8 mmol) and DMAP (170 mg, 1.4 mmol) under N₂. Upon completion of benzoylation, the reaction solution was diluted with satd. NaHCO₃, followed by extraction with EtOAc. The EtOAc solution was washed with H₂O, brine, dried over MgSO₄, filtered, and recrystallized to obtain target 2-\(O\)-benzoyl-3,4,6-tri-\(O\)-methyl-\(\beta\)-D-thioglucoside \textbf{38} (4.02 g, 69%). For thioglucoside \textbf{38}: \([\alpha]_D^{35} +33.8 \ (c \ 0.5, \ \text{CHCl}_3); \ R_f \ 0.375 \ (\text{EtOAc/Hexane 1/2}); \ ^1\text{H} \ \text{NMR} \ (300 \ \text{MHz, \ CDCl}_3) \ : \ \delta \ 8.09 \ (d, \ J = 7.5 \ \text{Hz, 2H, ArH}), \ 7.56 \ (t, \ J = 7.2 \ \text{Hz, 1H, ArH}), \ 7.44 \ (t, \ J = 7.5 \ \text{Hz, 1H, ArH}), \ 7.35 \ (d, \ J = 7.8 \ \text{Hz, 2H, ArH}), \ 7.05 \ (d, \ J = 7.8 \ \text{Hz, 2H, ArH}), \ 5.15 \ (t, \ J = 9.6 \ \text{Hz, 1H}), \ 4.70 \ (d, \ J = 10.2 \ \text{Hz, 1H}), \ 3.70-3.60 \ (m, 2H), \ 3.54-3.41 \ (m, \ 11H), \ 3.35-3.29 \ (m, 1H), \ 2.28 \ (s, \ 3H, \ \text{CH}_3); \ ^{13}\text{C-NMR} \ (75 \ \text{MHz, CDCl}_3) : \ \delta \ 165.4 \ (C=O), \ 138.1, \ 133.5, \ 133.0, \ 130.2, \ 130.0, \ 129.8, \ 129.7, \ 128.7, \ 87.0 \ (C-1), \ 86.6, \ 79.5, \ 79.3, \ 72.7, \ 71.6, \ 60.8, \ 60.7, \ 59.7, \ 21.3; \ \text{HRMS-ESI} \ (m/z): \ [M + \text{Na}]^+ \ \text{calcd. for C}_{23}\text{H}_{28}\text{NaO}_6\text{S}, \ 455.1499; \ \text{found}, \ 455.1493.
6-Chlorohexyl 2-O-benzoyl-3,4,6-tri-O-methyl \( \beta \)-D-glucopyranoside 42:

![Chemical structure of 42](image)

6-Chlorohexyl glucoside 42 was prepared from glycosylation of chlorohexanol 39 with thioglucoside 38 under the general DMF-modulated glycosylation procedure. The glucoside 42 was purified by column chromatography (Elution: EtOAc/CH\(_2\)Cl\(_2\)/Hexane 1/2/15). For 42: \([\alpha]_D^{35}\) +8.2 (c 0.41, CHCl\(_3\)); \(R_f\) 0.5 (EtOAc/CH\(_2\)Cl\(_2\)/Hexane 1:2:5); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.08 (d, \(J = 7.2\) Hz, 2H, Ar\(H\)), 7.59 (t, \(J = 7.2\) Hz, 1H, Ar\(H\)), 7.46 (t, \(J = 7.8\) Hz, 2H. Ar\(H\)), 5.13 (dd, \(J = 9.3, 7.8\) Hz, 1H, H-2), 4.46 (d, \(J = 8.1\) Hz, 1H, H-1), 3.91–3.86 (m, 1H), 3.71–3.67 (m, 1H), 3.61–3.56 (m, 4H), 3.50 (s, 3H), 3.47–3.38 (m, 6H), 3.35–3.29 (m, 3H), 1.50–1.43 (m, 4H), 1.26–1.16 (m, 4H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta\) 165.6 (C=O), 133.5, 130.5, 130.1, 128.8, 101.5 (C-1), 85.2, 79.7, 75.4, 74.0, 71.7, 69.9, 60.9, 60.8, 59.8, 45.3, 32.8, 29.6, 26.8, 25.5; HRMS (m/z): [M + Na]+ calcd. for C\(_{22}\)H\(_{33}\)ClNaO\(_7\), 467.1807; found,467.1801.

**Determination of RRV for thioglycosides: \([^{s2}\]**

The RRV calculation formula: 

\[
K_1 \frac{K_2}{K_2} = \ln\left(\frac{[A_1,\tau]}{[A_1,0]}\right) \div \ln\left(\frac{[A_2,\tau]}{[A_2,0]}\right)
\]

0.3 g of particle molecular sieve was flame-dried for 5 times. Tested thioglycoside \(A_2\) (0.02 mmol) and reference thioglycoside \(A_1\) (0.02 mmol) were dissolved in 2 mL CH\(_2\)Cl\(_2\) and stirred in RT for 10 min, 100 \(\mu\)L of reaction solution was removed for determination of time-zero absorbance \([A_{1,0}]\) and \([A_{2,0}]\). The remainder of the reaction solution was treated with 4 \(\mu\)L MeOH (0.1 mmol) and particle molecular sieve stirred in 0 °C. 0.5 M NIS solution (40 \(\mu\)L, 0.02 mmol) and 0.1 M TMSOTf solution (20 \(\mu\)L, 0.002 mmol) were added to the reaction solution and stirred for 2 h. Upon the reaction completed, the reaction mixture was treated with few drops of 10% NaHCO\(_3\)/Na\(_2\)SO\(_3\)
solution. After stirring for 15 min, the reaction temperature was raised to RT. The mixture was dried over MgSO₄, filtered and concentrated. The crude residue was dissolved in 2 mL CH₂Cl₂ for determination of final absorbance \([A_{1,t}]\) and \([A_{2,t}]\) at 2 h reaction. As an example, the HPLC traces from thioglucoside 11b and reference compound 1 before and after the reaction were given (Figure S1). The RRV of tested thioglycoside was calculated by substitution of the absorbance values (before and after the reaction) and the RRV value of the reference compound from literature into the equation above (Table S4).

**Figure S1.** HPLC traces of thioglucoside 11b and 1 before and after the glycosylation in RRV determination.
Table S4. Reference thioglycosides and thioglycosides for RRV measurement

<table>
<thead>
<tr>
<th>Reference thioglycosides $A_1$</th>
<th>Thioglycosides for RRV measurement $A_2$</th>
<th>Reference thioglycosides $A_1$</th>
<th>Thioglycosides for RRV measurement $A_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Structure 1" /></td>
<td>$6, 10, 11a, 17$</td>
<td><img src="image2" alt="Structure 2" /></td>
<td>$16$</td>
</tr>
<tr>
<td><img src="image3" alt="Structure 3" /></td>
<td>$1, 11b, 12$</td>
<td><img src="image4" alt="Structure 4" /></td>
<td>$15$</td>
</tr>
<tr>
<td><img src="image5" alt="Structure 5" /></td>
<td>$2, 13a, 13b, 14$</td>
<td><img src="image6" alt="Structure 6" /></td>
<td>$2, 33$</td>
</tr>
</tbody>
</table>
Section B: NMR spectra:

$^1$H spectrum of $p$-tolyl 2-O-benzoyl-3,4,6-tri-O-benzyl-thio-$\alpha$-D-mannopyranoside 2
$^{13}$C spectrum of $p$-tolyl 2-O-benzoyl-3,4,6-tri-O-benzyl-thio-α-D-mannopyranoside 2
$^1$H spectrum of 6-O-(2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose 4
$^{13}$C spectrum of 6-O-(2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose 4
$^1$H spectrum of 6-O-(2-O-benzoyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose 5
$^{13}$C spectrum of 6-O-(2-O-benzoyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose 5
$^1$H spectrum of $p$-tolyl 6-0-acetyl-2,3-di-0-benzoyl-4-0-benzyl-thio-β-D-gluco-
pyranoside 6
$^{13}$C spectrum of $p$-tolyl 6-O-acetyl-2,3-di-O-benzoyl-4-O-benzyl thio-$\beta$-D-gluco-pyranoside 6
$^1$H spectrum of $p$-tolyl 2,4,6-tri-O-benzyl-thio-$\alpha$-D-mannopyranoside 13a
\(^{13}\)C spectrum of \(p\)-tolyl 2,4,6-tri-O-benzyl-thio-\(\alpha\)-D-mannopyranoside 13a
$^1\text{H}$ spectrum of $p$-tolyl 6-$O$-benzoyl-2,4-di-$O$-benzyl-thio-$\alpha$-$D$-mannopyranoside 13b
$^{13}$C spectrum of $p$-tolyl 6-$O$-benzoyl-2,4-di-$O$-benzyl-thio-$\alpha$-D-mannopyranoside 13b
$^1$H spectrum of $p$-tolyl 2,3,4-tri-$O$-benzyl-thio-$\alpha$-$D$-mannopyranoside 14
$^{13}\text{C}$ spectrum of $p$-tolyl 2,3,4-tri-$O$-benzyl-thio-$\alpha$-D-mannopyranoside 14
$^1$H spectrum of $p$-tolyl 3-$O$-benzoyl-4-$O$-benzyl-2-(2,2,2-trichloroethoxycarbonylamino)-2-deoxy-thio-$\beta$-D-glucopyranoside 15
$^{13}$C spectrum of $p$-tolyl 3-$O$-benzoyl-4-$O$-benzyl-2-(2,2,2-trichloroethoxycarbonyl amino)-2-deoxy-thio-$\beta$-D-glucopyranoside 15
$^1$H spectrum of 4-(t-butyl)-2-methylphenyl 2,3-\textit{O}-isopropylidene-thio-\textit{\alpha}-l-rhamno pyranoside 17
$^{13}$C spectrum of 4-(t-butyl)-2-methylphenyl 2,3-$O$-isopropylidene-thio-$\alpha$-L-rhamno pyranoside 17
$^1$H spectrum of methyl 4-O-(2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-2,3,6-tri-O-benzyl-α-D-glucopyranoside 18
$^{13}$C spectrum of methyl $4-O-(2-O$-benzoyl-$3,4,6$-tri-$O$-benzyl-$\beta$-D-glucopyranosyl)-$2,3,6$-tri-$O$-benzyl-$\alpha$-D-glucopyranoside 18
$^1$H spectrum of $p$-tolyl 4-$O$-(2-$O$-benzoyl-3,4,6-tri-$O$-benzyl-$\beta$-$D$-glucopyranosyl)-2,3,6-tri-$O$-benzyl-thio-$\beta$-$D$-glucopyranoside 19
$^{13}$C spectrum of $p$-toly 4-$O$-(2-$O$-benzoyl-3,4,6-$O$-benzyl-$\beta$-D-glucopyranosyl)-2,3,6-$O$-benzyl-thio-$\beta$-D-glucopyranoside 19
$^1$H spectrum of $p$-tolyl 6-$O$-(2-$O$-benzoyl-3,4,6-$tri$-$O$-benzyl-$\beta$-$D$-glucopyranosyl)-$2,3,4$-$tri$-$O$-benzyl-thio-$\beta$-$D$-glucopyranoside 20
$^{13}$C spectrum of $p$-tolyl 6-\(O\)-(2-\(O\)-benzoyl-3,4,6-\(O\)-benzyl-\(\beta\)-D-glucopyranosyl)-2,3,4-\(O\)-benzyl-thio-\(\beta\)-D-glucopyranoside 20
\(^1\)H spectrum of \(p\)-tolyl 6-\(O\)-(2-\(O\)-benzoyl-3,4,6-\(O\)-benzyl-\(\beta\)-D-glucopyranosyl)-2,3,4-\(O\)-benzyl-thio-\(\beta\)-D-galactopyranoside 21
$^{13}$C spectrum of $p$-tolyl 6-$O$-(2-$O$-benzoyl-3,4,6-tri-$O$-benzyl-$\beta$-$D$-glucopyranosyl)-
2,3,4-tri-$O$-benzyl-thio-$\beta$-$D$-galactopyranoside 21
$^1$H spectrum of 4-($t$-butyl)-2-methylphenyl 4-$O$-($2$-$O$-benzoyl-3,4,6-tri-$O$-benzyl-$\beta$-$D$-glucopyranosyl)-2,3-$O$-isopropylidene-thio-$\alpha$-$L$-rhamnopyranoside 22
$^{13}$C spectrum of 4-$t$-butyl-2-methylphenyl 4-$O$-(2-$O$-benzoyl-3,4,6-tri-$O$-benzyl-$\beta$-D-glucopyranosyl)-2,3-$O$-isopropylidene-thio-$\alpha$-L-rhamnopyranoside 22
\(^1\)H spectrum of \(p\)-tolyl 6-\(O\)-(6-\(O\)-acetyl-2,3-di-\(O\)-benzoyl-4-\(O\)-benzyl-\(\beta\)-D-glucopyranosyl)-2,3,4-tri-\(O\)-benzyl-thio-\(\beta\)-D-glucopyranoside 23
$^{13}$C spectrum of $p$-tolyl 6-$O$-(6-$O$-acetyl-2,3-di-$O$-benzoyl-4-$O$-benzyl-$\beta$-D-gluco pyranosyl)-2,3,4-tri-$O$-benzyl-thio-$\beta$-D-glucopyranoside 23
$^1$H spectrum of $p$-tolyl 6-$O$-(6-$O$-acetyl-2,3-di-$O$-benzoyl-4-$O$-benzyl-$\beta$-D-gluco pyranosyl)-2,3-di-$O$-benzoyl-4-$O$-benzyl-thio-$\beta$-D-glucopyranoside 24
$^{13}$C spectrum of $p$-tolyl 6-$O$-(6-$O$-acetyl-2,3-di-$O$-benzoyl-4-$O$-benzyl-$\beta$-$D$-glucopyranosyl)-2,3-di-$O$-benzoyl-4-$O$-benzyl-thio-$\beta$-$D$-glucopyranoside 24
$^1$H spectrum of $p$-tolyl 2-O-(2-O-benzoyl-3,4,6-tri-O-benzyl-$\alpha$-L-mannopyranosyl)-3,4,6-tri-O-benzyl-thio-$\alpha$-D-mannopyranoside 25
\(^{13}\)C spectrum of \(p\)-tolyl 2-\(O\)-(2-\(O\)-benzoyl-3,4,6-tri-\(O\)-benzyl-\(\alpha\)-D-mannopyranosyl)-3,4,6-tri-\(O\)-benzyl-thio-\(\alpha\)-D-mannopyranoside 25
$^1$H spectrum of $p$-tolyl 3-\textit{O}-(2-\textit{O}-benzoyl-3,4,6-\textit{O}-benzyl-\textit{\alpha}-\text{D}-mannopyranosyl)-2,4,6-\textit{O}-benzyl-thio-\textit{\alpha}-\text{D}-mannopyranoside 26
$^{13}$C spectrum of $p$-tolyl 3-$O$-(2-$O$-benzoyl-3,4,6-$tri-O$-benzyl-$\alpha$-$D$-mannopyranosyl)-2,4,6-$tri-O$-benzyl-thio-$\alpha$-$D$-mannopyranoside 26
$^1$H spectrum of $p$-tolyl 3-$O$-(2-$O$-benzoyl-3,4,6-$tri$-$O$-benzyl-$\alpha$-$D$-mannopyranosyl)-6-$O$-benzoyl-2,4-$di$-$O$-benzyl-thio-$\alpha$-$D$-mannopyranoside 27
$^{13}$C spectrum of $p$-tolyl 3-O-(2-O-benzoyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-
-6-O-benzoyl-2,4-di-O-benzyl-thio-α-D-mannopyranoside 27
$^1$H spectrum of $p$-tolyl 6-$O$-(2-$O$-benzoyl-3,4,6-$O$-benzyl-$\alpha$-D-mannopyranosyl)-2,3,4-$O$-benzyl-thio-$\alpha$-D-mannopyranoside 28
$^{13}$C spectrum of $p$-tolyl 6-$O$-(2-$O$-benzoyl-3,4,6-$O$-benzyl-$\alpha$-$D$-mannopyranosyl)-2,3,4-$O$-benzyl-thio-$\alpha$-$D$-mannopyranoside 28
$^1$H spectrum of $p$-tolyl 6-$O$-[3,4,6-tri-$O$-acetyl-2-(2,2,2-trichloroethoxycarbonyl amino)-2-deoxy-$\beta$-D-glucopyranosyl]-2,3,4-tri-$O$-benzyl-thio-$\beta$-D-glucopyranoside 29
$^{13}$C spectrum of $p$-tolyl 6-$O$-[3,4,6-tri-$O$-acetyl-2-(2,2,2-trichloroethoxycarbonyl amino)-2-deoxy-$\beta$-$D$-glucopyranosyl]-2,3,4-tri-$O$-benzyl-thio-$\beta$-$D$-glucopyranoside 29
$^1$H spectrum of $p$-tolyl 6-$O$-[3,4,6-tri-$O$-acetyl-2-(2,2,2-trichloroethoxycarbonylamino)-2-deoxy-$\beta$-$D$-glucopyranosyl]-3-$O$-benzoyl-4-$O$-benzyl-2-(2,2,2-trichloroethoxycarbonylamino)-2-deoxy-thio-$\beta$-$D$-glucopyranoside 30
$^{13}$C spectrum of $p$-tolyl 6-$O$-[3,4,6-tri-$O$-acetyl-2-(2,2,2-trichloroethoxycarbonyl amino)-2-deoxy-$\beta$-$D$-glucopyranosyl]-3-$O$-benzoyl-4-$O$-benzyl-2-(2,2,2-trichloroethoxycarbonylamino)-2-deoxy-thio-$\beta$-$D$-glucopyranoside 30
$^1$H spectrum of $p$-tolyl 6-$O$-(2-benzoyl-3,4,6-tri-$O$-benzyl-$\beta$-$D$-galactopyranosyl)-
2,3,4-tri-$O$-benzyl-thio-$\beta$-$D$-galactopyranoside 31
$^{13}$C spectrum of $p$-tolyl 6-O-(2-benzoyl-3,4,6-tri-O-benzyl-β-D-galactopyranosyl)-2,3,4-tri-O-benzyl-thio-β-D-galactopyranoside 31
$^1$H spectrum of $p$-tolyl 2-<i>O</i>-benzoyl-3,4-di-<i>O</i>-benzyl-thio-<i>α</i>-<i>D</i>-mannopyranoside 33
$^{13}$C spectrum of $p$-tolyl 2-O-benzoyl-3,4-di-O-benzyl-thio-α-D-mannopyranoside 33
$^1$H spectrum of methyl 2-O-benzoyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside 35
$^{13}$C spectrum of methyl 2-$O$-benzoyl-3,4,6-tri-$O$-benzyl-$\alpha$-D-mannopyranosyl-(1$\rightarrow$2)-3,4,6-tri-$O$-benzyl-$\alpha$-D-mannopyranosyl-(1$\rightarrow$2)-3,4,6-tri-$O$-benzyl-$\alpha$-D-mannopyranosyl side 35
$^1$H spectrum of methyl 2-O-benzoyl-3,4,6-tri-O-benzyl-$\alpha$-D-mannopyranosyl-(1→6)-2-O-benzoyl-3,4-di-O-benzyl-$\alpha$-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-$\alpha$-D-mannopyranoside 36
$^{13}$C spectrum of methyl 2-$O$-benzoyl-3,4,6-tri-$O$-benzyl-$\alpha$-$D$-mannopyranosyl-(1$\rightarrow$6)-2-$O$-benzoyl-3,4-di-$O$-benzyl-$\alpha$-$D$-mannopyranosyl-(1$\rightarrow$2)-3,4,6-tri-$O$-benzyl-$\alpha$-$D$-mannopyranoside 36
$^1$H spectrum of methyl 6-O-acetyl-2,3-di-O-benzoyl-4-O-benzyl-β-D-glucopyranosyl-(1→6)-2,3-di-O-benzoyl-4-benzyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzyl-β-D-glucopyranoside 37
$^{13}$C spectrum of methyl 6-O-acetyl-2,3-di-O-benzoyl-4-O-benzyl-β-D-gluco pyranosyl-(1→6)-2,3-di-O-benzoyl-4-benzyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzyl-β-D-glucopyranoside 37
$^1$H spectrum of $p$-tolyl 2-$O$-benzoyl-3,4,6-tri-$O$-methyl-thio-$\beta$-$D$-glucopyranoside 38
$^{13}$C spectrum of $p$-tolyl 2-$O$-benzoyl-3,4,6-tri-$O$-methyl-thio-$\beta$-$D$-glucopyranoside 38
$^1$H spectrum of 6-chlorohexyl 2-O-benzoyl-3,4,6-tri-O-methyl-β-D-glucopyranoside
$^{13}$C spectrum of 6-chlorohexyl 2-\(O\)-benzoyl-3,4,6-tri-\(O\)-methyl-\(\beta\)-D-glucopyranoside
$^1$H NMR spectrum of crude pre-activation mixture of 38 (refer to Fig 2 and scheme 3 in main context)
$^{13}$C NMR spectrum of crude pre-activation mixture of 38 (refer to Fig 2 and scheme 3 in main context)
$^{13}$C non-decoupling NMR spectrum of crude pre-activation mixture of 38 (refer to Fig 2 and scheme 3 in main context)
HSQC spectrum of crude pre-activation mixture of 38 (refer to Fig 2 and scheme 3 in main context)
HMBC spectrum of crude pre-activation mixture of 38 (see Fig S1 in following page for selected expansion)
**Figure S2.** Selected 1H NMR spectrum of pre-activation mixture of 38

**Figure S3.** HMBC spectrum of β-glucosyl imidinium triflate 40β in reaction mixture

**Figure S4.** Proposed mechanism for modulated glycosylations
Figure S5. (a) Selected $^1$H NMR spectrum of pre-activation of 38. (b) Selected $^1$H NMR spectrum of the crude reaction after adding acceptor 39.
Crude $^1$H spectrum of the reaction mixture after addition of 39 (formation of 42)
Reference:


