Supporting Information
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Supporting Information

Additive-Controlled Stereoselective Glycosylations of Oxazolidinone Protected Glucosamine and Galactosamine Thioglycoside Donors Based on Preactivation Protocol

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**General Procedures.** All chemicals were purchased as reagent grade and used without further purification, unless otherwise noted. Dichloromethane (CH$_2$Cl$_2$) and pyridine were distilled over calcium hydride (CaH$_2$). All glycosylation reactions were carried out under anhydrous conditions with freshly distilled solvents, unless otherwise noted. Reactions were monitored by analytical thin-layer chromatography on silica gel 60-F$_{254}$ precoated on aluminium plates (E. Merck). Spots were detected under UV (254 nm) and/or by staining with acidic ceric ammonium molybdate. Solvents were evaporated under reduced pressure and below 40 °C (bath). Organic solutions of crude products were dried over anhydrous Na$_2$SO$_4$. Column chromatography was performed on silica gel (200-300 mesh). $^1$H-NMR spectra were recorded on an Advance DRX Bruker-400 or Varian INOVA-500 spectrometer at 25 °C. Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in deuterated chloroform. $^{13}$C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl$_3$ ($\delta = 77.00$ ppm). Mass spectra were recorded using a PE SCLEX QSTAR spectrometer. High-resolution mass spectrometry was performed on a Bruker APEX IV. Elemental analysis data were recorded on a Vario EL-III elemental analyzer.

**Preparation of glycosyl donor 2**

Reagents and conditions: (a) TolSH, SnCl$_4$, CH$_2$Cl$_2$, reflux, 93%; (b) NaOH, H$_2$O, reflux, 100%; (c) triphosgene, NaHCO$_3$, CH$_3$CN/H$_2$O, 81%; (d) Ac$_2$O, Py, DMAP, CH$_2$Cl$_2$, 88%.

$p$-Tolyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-1-thio-β-D-galactopyranoside
SnCl₄ (2.7 mL, 23.1 mmol, 0.9 eq.) was added to a stirred solution of D-galacosamine pentaacetate 2a (10.0 g, 25.7 mmol, 1 eq.) and p-toluenethiol (3.8 g, 30.8 mmol, 1.2 eq.) in dichloromethane (200 mL). The reaction mixture was heated at reflux overnight, cooled to room temperature and quenched by the addition of saturated aqueous NaHCO₃ (250 mL). The aqueous layer was separated and extracted with dichloromethane (2 × 250 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered and evaporated. The residue obtained was recrystallized in petroleum ether/ethyl acetate to give 2b (10.8 g, 93%) as a white solid. \( R_f = 0.5 \) (ethyl acetate). Compound 2b was used for the next reaction directly.

\( p \)-Tolyl 2-amino-2-deoxy-1-thio-\( \beta \)-D-galactopyranoside (2c)

Compound 2b (5.0 g, 11.0 mmol) was dissolved in 2N NaOH (100 mL), the turbid solution was heated at reflux for 24 h. The reaction mixture was cooled to room temperature and quenched by 2N HCl (100 mL), then evaporated to give the crude product 2c. The crude product was directly used for the next reaction.

\( p \)-Tolyl 2-amino-2,3-N,O-carbonyl-2-deoxy-1-thio-\( \beta \)-D-galactopyranoside (2d)

Compound 2c (3.1 g, 11.0 mmol) was dissolved in MeCN (100 mL), and NaHCO₃ (sat. aq., 50 mL) was added. The mixture was cooled to 0 °C, and triphosgene (1.3 g, 4.4 mmol, 0.4 eq.) was added to the vigorously stirred mixture. After 1 h, EtOAc (150 mL) containing ethylenediamine (2.1 mL, 30.9 mmol, 2.8 eq.) was added and the stirring was continued for 15 min. The aqueous layer was separated and extracted with EtOAc (2 × 75 mL). The combined organic layer was washed with brine, dried over Na₂SO₄, filtered and evaporated. The residue obtained was purified by column chromatography (petroleum ether/ethyl acetate, 1:5) to give 2d (2.8 g, 81%) as a white solid. \( R_f = 0.1 \) (petroleum ether/ethyl acetate, 1:3). \(^1\)H NMR (400 MHz, \((\text{CD}_3)_2\text{CO})\) δ 7.47-7.50 (m, 2H), 7.16 (d, 2H, \( J = 8.0 \) Hz), 6.73 (s, 1H), 4.87 (d, 1H, \( J = 9.6 \) Hz, H-1), 4.57 (d, 1H, \( J = 4.4 \) Hz), 4.37 (d, 1H, \( J = 4.0 \) Hz), 4.32 (dd, 1H, \( J = 2.0, 11.2 \) Hz), 3.89-3.94 (m, 2H), 3.78-3.82 (m, 3H), 2.32 (s, 3H); \(^{13}\)C NMR (100 MHz, \((\text{CD}_3)_2\text{CO})\) δ 165.7 (C-O), 147.8 (C=O), 134.3 (C), 112.9 (C), 110.7 (C), 80.2 (C), 70.1 (C), 69.4 (C), 68.1 (C), 67.3 (C), 50.0 (C), 44.7 (C), 38.9 (C), 37.8 (C), 21.0 (C).
MHz, (CD$_3$)$_2$CO) $\delta$ 159.49, 138.79, 133.59, 130.43, 129.47, 86.59, 83.50, 81.06, 65.63, 62.20, 54.70, 21.02; (ESI) Calcd for C$_{28}$H$_{35}$N$_2$O$_{10}$S$_2$ [2M + H]$^+$: 623.1728. Found: 623.1729.

$p$-Tolyl

$N$-acetyl-2-amino-2,3-$N,O$-carbonyl-4,6-$O$-diacetyl-2-deoxy-1-thio-$\beta$-D-galactopyranoside (2)

To a stirred solution of compound 2d (2.8 g, 9.0 mmol, 1 eq.) in dichloromethane (50 mL) containing a catalytic amount of 4-(dimethylamino) pyridine, was added pyridine (7.2 mL, 89.7 mmol, 10 eq.) and acetic anhydride (8.4 mL, 89.7 mmol, 10 eq.). The reaction mixture was stirred at room temperature for 5 h, quenched by the addition of saturated aqueous NaHCO$_3$ (50 mL), and extracted with CH$_2$Cl$_2$ (2 × 50 mL). The combined organic layer was washed with brine, dried over Na$_2$SO$_4$, filtered and evaporated. The residue was purified by column chromatography (petroleum ether/ethyl acetate, 3:1) to give 2 (3.4 g, 88%) as a white solid. $R_f$ = 0.25 (petroleum ether/ethyl acetate, 1.5:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 (d, 2H, $J$ = 8.4 Hz), 7.11 (d, 2H, $J$ = 8.0 Hz), 5.66 (t, 1H, $J$ = 2.0 Hz), 4.81 (d, 1H, $J$ = 8.4 Hz, H-1), 4.50 (dd, 1H, $J$ = 8.8, 11.6 Hz), 4.27 (dd, 1H, $J$ = 2.4, 11.6 Hz), 4.19 (dd, 1H, $J$ = 6.0, 11.6 Hz), 4.10 (dd, 1H, $J$ = 7.2, 11.6 Hz), 3.91-3.94 (m, 1H), 2.59 (s, 3H), 2.33 (s, 3H), 2.17 (s, 3H), 2.00 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.07, 170.21, 169.34, 153.19, 138.34, 133.26, 129.70, 129.52, 88.69, 78.06, 75.60, 64.96, 61.70, 56.40, 24.76, 21.05, 20.54, 20.51; HRMS (ESI) Calcd for C$_{20}$H$_{23}$NO$_8$SNa [M + Na]$^+$: 460.1037. Found: 460.1049.

Separation and characterization details for glycosylation reactions and glycoside products listed in Table 3 that were not presented as examples in the text.

Coupling of 2 with 4 afforded $\alpha$-anomer 11 or $\beta$-anomer 12

Methyl

(N-acetyl-2-amino-2,3-$N,O$-carbonyl-4,6-diacetyl-2-deoxy-$\alpha$-D-galactopyranosyl)-
(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (11)

The product was purified by column chromatography (petroleum ether/ethyl acetate, 3:1) to give 11, yields with different additives were listed in Table 3. \( R_f = 0.3 \) (petroleum ether/ethyl acetate, 1.5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.24-7.38 (m, 15H), 5.77 (d, 1H, \( J = 2.8 \) Hz, H-1'), 5.55 (s, 1H), 5.00 (d, 1H, \( J = 10.8 \) Hz), 4.86 (d, 1H, \( J = 11.2 \) Hz), 4.80 (d, 1H, \( J = 10.8 \) Hz), 4.77 (d, 1H, \( J = 11.2 \) Hz), 4.68 (d, 1H, \( J = 12.0 \) Hz), 4.52-4.59 (m, 3H), 4.14-4.19 (m, 2H), 4.09 (dt, 1H, \( J = 1.2, 6.4 \) Hz), 3.96-4.01 (m, 2H), 3.69-3.80 (m, 3H), 3.51 (dd, 1H, \( J = 3.6, 9.6 \) Hz), 3.35 (s, 3H), 3.28 (t, 1H, \( J = 9.2 \) Hz), 2.41 (s, 3H), 2.13 (s, 3H), 1.98 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 171.21, 170.25, 169.31, 152.66, 138.67, 138.04, 137.99, 128.45, 128.41, 128.37, 128.07, 127.93, 127.91, 127.86, 127.82, 127.59, 97.80, 96.32, 81.88, 79.76, 77.07, 75.58, 74.61, 73.21, 72.04, 69.94, 68.18, 67.02, 65.64, 61.59, 55.94, 55.18, 23.63, 20.60, 20.56; MS (ESI) 795 [M + NH\(_4\)]\(^+\), 800 [M + Na\(^+\)], 816 [M + K\(^+\)]; Anal. Calcd for C\(_{41}\)H\(_{47}\)NO\(_{14}\): C, 63.31; H, 6.09; N, 1.80. Found: C, 63.06; H, 6.11; N, 1.77.

Methyl (N-acetyl-2-amino-2,3-N,O-carbonyl-4,6-diacetyl-2-deoxy-β-D-galactopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (12)

The product was purified by column chromatography (petroleum ether/ethyl acetate, 1.5:1) to give 12, yields with different additives were listed in Table 3. \( R_f = 0.1 \) (petroleum ether/ethyl acetate, 1.5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.22-7.37 (m, 15H), 5.60 (s, 1H), 4.99 (d, 1H, \( J = 11.2 \) Hz), 4.88 (d, 1H, \( J = 11.6 \) Hz), 4.80 (d, 2H, \( J = 12.4 \) Hz), 4.66 (d, 1H, \( J = 12.4 \) Hz), 4.64 (d, 1H, \( J = 4.0 \) Hz, H-1'), 4.55 (d, 1H, \( J = 11.2 \) Hz), 4.50 (d, 1H, \( J = 7.2 \) Hz, H-1'), 4.30 (dd, 1H, \( J = 7.2, 12.0 \) Hz), 3.95-4.19 (m, 6H), 3.78 (dd, 1H, \( J = 2.0, 10.0 \) Hz), 3.57-3.62 (m, 2H), 3.38 (s, 3H), 2.45 (s, 3H), 2.10 (s, 3H), 2.01 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 170.89, 170.30, 169.25, 153.45, 138.82, 138.70, 138.20, 128.42, 128.35, 128.12, 127.92, 127.87, 127.64, 127.58, 127.55, 102.74, 98.10, 82.17, 79.88, 77.32, 76.00, 75.59, 74.48, 73.39, 72.49, 69.59, 67.76, 63.99, 61.25, 57.03, 55.18, 24.91, 20.60, 20.54; MS (ESI) 795 [M + NH\(_4\)]\(^+\), 800 [M + Na\(^+\)], 816 [M + K\(^+\)]; Anal. Calcd for C\(_{41}\)H\(_{47}\)NO\(_{14}\): C, 63.31; H, 6.09;
Coupling of 2 with 7 afforded a mixture of α-anomer 13 and β-anomer 14

Methyl (N-acetyl-2-amino-2,3-N,O-carbonyl-4,6-diacetyl-2-deoxy-α- and β-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-α-D-galactopyranoside (13) and (14)

The product was purified by column chromatography (petroleum ether/ethyl acetate, 4:1 to 3:1) to give 13 and 14, yields and α/β ratios with different additives were listed in Table 3. 13: \( R_f = 0.4 \) (petroleum ether/ethyl acetate, 1.5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.28-7.41 (m, 15H), 5.73 (s, 1H, H-1'), 5.47 (s, 1H), 4.64-4.84 (m, 7H), 4.56 (t, 1H, \( J = 7.2 \) Hz), 4.49 (d, 1H, \( J = 11.6 \) Hz), 4.21-4.23 (m, 2H), 3.92 (t, 1H, \( J = 10.0 \) Hz), 3.80-3.87 (m, 3H), 3.60 (dd, 1H, \( J = 5.6, 11.2 \) Hz), 3.40-3.41 (m, 2H), 3.37 (s, 3H), 2.47 (s, 3H), 2.10 (s, 3H), 1.91 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 172.14, 169.98, 169.28, 152.92, 138.15, 137.96, 128.39, 128.24, 128.02, 127.68, 127.47, 98.13, 96.48, 75.52, 74.51, 73.70, 72.98 (2C), 71.62, 68.65, 67.86, 67.56, 65.62, 60.82, 56.31, 55.37, 23.85, 20.59 (2C); HRMS (ESI) Calcd for C\(_{41}\)H\(_{47}\)NO\(_{14}\)Na [M + Na]\(^+\): 800.2889. Found: 800.2901.

14: \( R_f = 0.3 \) (petroleum ether/ethyl acetate, 1.5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.42-7.44 (m, 2H), 7.28-7.35 (m, 13H), 5.54 (s, 1H), 4.85 (d, 1H, \( J = 12.0 \) Hz), 4.82 (d, 1H, \( J = 12.0 \) Hz), 4.71 (d, 1H, \( J = 7.6 \) Hz, H-1'), 4.65 (d, 1H, \( J = 12.0 \) Hz), 4.61 (d, 1H, \( J = 3.6 \) Hz, H-1'), 4.58 (d, 1H, \( J = 12.0 \) Hz), 4.56 (d, 1H, \( J = 11.2 \) Hz), 4.51 (d, 1H, \( J = 12.0 \) Hz), 4.28 (dd, 1H, \( J = 7.6, 12.0 \) Hz), 4.11-4.18 (m, 2H), 3.91-3.97 (m, 3H), 3.80-3.86 (m, 3H), 3.71 (dd, 1H, \( J = 5.2, 10.4 \) Hz), 3.64 (dd, 1H, \( J = 6.4, 10.4 \) Hz), 3.36 (s, 3H), 2.25 (s, 3H), 2.13 (s, 3H), 2.00 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 171.58, 170.23, 169.29, 153.53, 138.73, 138.53, 138.53, 138.35, 128.47, 128.39, 128.36, 128.09, 128.03, 127.80, 127.75, 127.55, 127.43, 104.40, 98.70, 78.05, 77.90, 76.27, 73.99, 73.78, 73.38, 72.53, 69.94, 68.79, 64.05, 61.09, 56.46, 55.37, 24.76, 20.57, 20.54; HRMS (ESI) Calcd for C\(_{41}\)H\(_{47}\)NO\(_{14}\)Na [M + Na]\(^+\): 800.2889. Found: 800.2908.

Coupling of 2 with 8 afforded a mixture of α-anomer 15 and β-anomer 16
Methyl (N-acetyl-2-amino-2,3-N,O-carbonyl-4,6-diacetyl-2-deoxy-α- and β-D-galactopyranosyl)-(1→2)-3-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (15) and (16)

The product was purified by column chromatography (dichloromethane/ethyl acetate, 12:1 to 8:1) to give 15 and 16, yields and α/β ratios with different additives were listed in Table 3. 15: \( R_f = 0.3 \) (petroleum ether/ethyl acetate, 1.5:1); \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.47-7.49 (m, 2H), 7.31-7.38 (m, 8H), 5.75 (d, 1H, \( J = 2.4 \) Hz, H-1'), 5.59 (s, 1H), 5.18 (s, 1H), 4.99 (d, 1H, \( J = 11.2 \) Hz), 4.79 (d, 1H, \( J = 3.6 \) Hz, H-1), 4.58 (d, 1H, \( J = 11.2 \) Hz), 4.46 (dd, 1H, \( J = 2.4, 12.4 \) Hz), 4.31 (dd, 1H, \( J = 4.4, 10.0 \) Hz), 4.16 (dd, 1H, \( J = 2.8, 12.4 \) Hz), 3.93-4.06 (m, 3H), 3.62-3.86 (m, 5H), 3.37 (s, 3H), 2.52 (s, 3H), 2.08 (s, 3H), 1.99 (s, 3H); \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \( \delta \) 171.21, 170.14, 152.57, 138.33, 137.20, 129.01, 128.50, 128.47, 128.28, 128.16, 125.94, 103.32, 97.29, 94.15, 83.16, 75.50, 75.25, 72.12, 69.04, 68.04, 65.62, 62.21, 61.17, 55.67, 55.11, 23.69, 20.72, 20.58; MS (ESI) 686 [M + H]^+ , 708 [M + Na]^+ , 724 [M + K]^+ ; Anal. Calcd for C\(_{34}\)H\(_{39}\)NO\(_{14}\): C, 59.56; H, 5.73; N, 2.04. Found: C, 59.43; H, 6.02; N, 1.80. 16: \( R_f = 0.1 \) (petroleum ether/ethyl acetate, 1.5:1); \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.44-7.47 (m, 2H), 7.35-7.39 (m, 3H), 7.22-7.31 (m, 5H), 5.58 (s, 1H), 5.55 (s, 1H), 4.99 (d, 1H, \( J = 7.6 \) Hz, H-1'), 4.94 (d, 1H, \( J = 11.6 \) Hz), 4.83 (d, 1H, \( J = 3.6 \) Hz, H-1), 4.60 (d, 1H, \( J = 11.6 \) Hz), 4.28-4.34 (m, 2H), 4.08-4.21 (m, 3H), 3.96-4.02 (m, 2H), 3.89 (dt, 1H, \( J = 4.8, 10.0 \) Hz), 3.74 (t, 1H, \( J = 10.0 \) Hz), 3.71 (dd, 1H, \( J = 3.6, 9.2 \) Hz), 3.62 (t, 1H, \( J = 9.2 \) Hz), 3.45 (s, 3H), 2.26 (s, 3H), 2.14 (s, 3H), 2.06 (s, 3H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 170.86, 170.31, 169.87, 153.36, 138.87, 137.30, 128.97, 128.31, 128.23, 127.56, 126.94, 126.02, 103.95, 101.43, 99.99, 82.87, 79.07, 78.10, 75.99, 74.74, 72.55, 69.13, 64.14, 61.98, 61.41, 57.29, 55.29, 24.65, 20.63, 20.55; HRMS (ESI) Calcd for C\(_{34}\)H\(_{39}\)NO\(_{14}\)Na [M + Na]^+: 708.2263. Found: 708.2269.