Supporting Information

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Proton NMR (^{1}H NMR) spectra were recorded at 500 MHz. Chemical shifts are expressed in parts per million (δ) and are referenced to residual protium in the NMR solvent: $CD_3S(O)CD_2H$, δ 2.49; DOH, δ 4.80. Carbon NMR (^{13}C NMR) spectra were recorded at 125 MHz. Chemical shifts (δ ppm) are referenced to the carbon signal for the solvent: DMSO-d_6, δ 39.51; carbon spectra recorded in D_2O are referenced to an external standard of DMSO-d_6.

***N*-(*p*-Methoxybenzyl)-L-serine benzyl ester (2).** Serine benzyl ester hydrochloride (8.0 g, 34.5 mmol, 1.0 equiv) and $NaBH_3CN$ (2.39 g, 38 mmol, 1.1 equiv) were suspended in CH_3OH (38 mL). *p*-Anisaldehyde (4.6 mL, 38 mmol, 1.1 equiv) was added over a period of 5 min and the suspension was stirred at rt for 8 h. The CH_3OH was removed by rotary evaporation and the crude material was partitioned between $NaHCO_3$ and CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 and the combined organic extracts were dried (Na_2SO_4), filtered and concentrated . The product was purified by chromatography (silica gel, 250 mL), eluting with 1/1 hexane/EtOAc. The product was obtained as a clear, colorless oil (7.7 g, 70%). TLC (SiO_2, 100% EtOAc): R_f = 0.45. ^{1}H NMR (DMSO-d_6): δ 7.38-7.31 (m, 5 H), 7.17 (d, *J* = 8.6 Hz, 2 H), 6.84 (d, *J* = 8.6 Hz, 2 H), 5.13 (s, 2 H), 4.86 (t, *J* = 5.8 Hz, 1 H), 3.71 (s, 3 H), 3.68 (d, *J* = 13.0 Hz, 1 H), 3.59 (t, *J* = 5.8 Hz, 2 H), 3.52 (d, *J* = 13.0 Hz, 1 H), 3.28 (br t, *J* = 5.0 Hz, 1 H), 2.35 (br s, 1 H). ^{13}C NMR (DMSO-d_6): δ 173.1, 158.2, 136.3, 132.1, 129.2, 128.4, 127.9, 127.8, 113.5, 65.4, 62.6, 62.2, 55.0, 50.3. IR (cm^{-1}): 3200, 3042, 2954, 1733. EIMS: Calcd for $(M + H)^+$, 316; found, 316.

***N*-(*p*-Methoxybenzyl)-2,2-dioxo-1,2,3-oxathiazolidinone-(4S)-carboxylic acid benzyl ester (3).** The protected serine derivative **2** (7.7 g, 24.4 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (240 mL). Pyridine (9.8 mL, 122 mmol, 5 equiv) was added and the solution was cooled to –78 °C. $SOCl_2$ (1.9 mL, 26.8 mmol, 1.1 equiv) was added over a period of 5 min and the solution was stirred at –78 °C for 5 min. The ice bath was removed and the reaction allowed to warm to rt. The reaction was quenched by the addition of HCl (1%, 200 mL). The aqueous layer was extracted with CH_2Cl_2 and the combined organic extracts were washed with $NaHCO_3$, dried (Na_2SO_4), filtered, and concentrated. The sulfamidite was dissolved in CH_3CN (60 mL) and the solution was cooled to 0 °C. $NaIO_4$ (5.75 g, 26.8 mmol, 1.1 equiv) was added followed by $RuCl_3 \cdot xH_2O$ (50 mg, 0.24 mmol, 0.01 equiv). The reaction

was initiated by addition of H_2O (60 mL) and the reaction was stirred at 0 °C for 5 min. The ice bath was removed and the reaction was stirred for an additional 10 min. The reaction solution was partitioned between CH_2Cl_2 and $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 and the combined organic extracts were dried (Na_2SO_4), filtered, and concentrated. The product was purified by chromatography (silica gel, 200 mL), eluting with 7/3 hexane/EtOAc. The sulfamidate **3** was obtained as a white solid (8.1 g, 90%). TLC (SiO_2, 1/1 hexane/EtOAc): R_f = 0.45. ^{1}H NMR (DMSO-d_6): δ 7.40 (m, 5 H), 7.24 (d, *J* = 8.7 Hz, 2 H), 6.86 (d, *J* = 8.7 Hz, 2 H), 5.14 (d, *J* = 12.8 Hz, 1 H), 5.11 (d, *J* = 12.8 Hz, 1 H), 4.79 (dd, *J* = 7.6, 9.2 Hz, 1 H), 4.74 (dd, *J* = 4.0, 9.2 Hz, 1 H), 4.53 (dd, *J* = 4.0, 7.6 Hz, 1 H), 4.36 (d, *J* = 14.3 Hz, 1 H), 4.31 (d, *J* = 14.3 Hz, 1 H), 3.73 (s, 3 H). ^{13}C NMR (DMSO-d_6): δ 168.1, 159.1, 135.2, 130.3, 128.5, 128.3, 128.2, 126.4, 113.8, 68.1, 67.1, 59.4, 55.1, 50.1. IR (cm^{-1}): 2959, 1748, 1613, 1514. HREIMS: calcd for $(M)^+$, 377.0933; found, 377.0943. Anal: calcd for $C_{18}H_{19}NO_6S$: C, 57.28; H, 5.07; N, 3.71; S, 8.50. Found: C, 56.90; H, 4.77; N, 3.76; S, 8.82.

2,2-Dioxo-1,2,3-oxathiazolidinone-(4S)-carboxylic acid benzyl ester (4). The protected sulfamidate **3** (8.1 g, 21.5 mmol, 1.0 equiv) was dissolved in CH_3CN (150 mL). H_2O (50 mL) was added with stirring, followed by $(NH_4)_2Ce(NO_3)_6$ (35 g, 65 mmol, 3 equiv). The reaction was stirred at rt for ca. 20 min, after which TLC (SiO_2, 1/1 hexane/EtOAc) showed complete conversion to a more polar product (R_f = 0.40). The reaction solution was partitioned between $NaHCO_3$ and CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 and the combined organic extracts were dried (Na_2SO_4), filtered, and concentrated. The product was purified by chromatography (silica gel, 200 mL), eluting with 8/2 hexane/EtOAc to 7/3. Sulfamidate **4** was obtained as a clear, colorless oil (4.5 g, 95%). ^{1}H NMR (DMSO-d_6): δ 8.59 (d, *J* = 6.0 Hz, 1 H), 7.42-7.32 (m, 5 H), 5.22 (d, *J* = 12.5 Hz, 1 H), 5.19 (d, *J* = 12.5 Hz, 1 H), 4.81-4.70 (m, 3 H, -CH_2O). ^{13}C NMR (DMSO-d_6): δ 168.4, 135.4, 128.5, 128.3, 128.0, 70.2, 67.0, 55.6. IR (cm^{-1}): 3269, 2958, 1746, 1188. HREIMS: cald for $(M)^+$, 257.0358; found, 257.0346. Anal: calcd for $C_{10}H_{11}NO_5S$: C, 46.69; H, 4.31; N, 5.44; S, 12.46. Found: C, 46.74; H, 4.53; N, 5.38; S, 12.78.

2,2-Dioxo-1,2,3-oxathiazolidinone-(4S)-carboxylic acid (5). The protected sulfamidate **4** (1.25 g, 4.86 mmol, 1.0 equiv) was dissolved in EtOAc (50 mL). Palladium on carbon (10% wt, 260 mg, 0.24 mmol, 0.05 equiv) was added, and the suspension was stirred under an atmosphere of hydrogen for ca. 30 min, after which TLC (SiO_2, 1/1 hexane/EtOAc) showed complete conversion to a product that did not migrate by TLC. The suspension was filtered over Celite and concentrated. The sulfamidate **5** was used without further purification (805 mg, 100%). ^{1}H NMR (DMSO-d_6): δ 8.40 (br s, 1 H), 4.72 (dd, *J* = 7.8, 8.7 Hz, 1 H), 4.65 (dd, *J* = 4.8, 8.6 Hz, 1 H), 4.60 (dd, *J* = 4.9, 7.8 Hz, 1 H). ^{13}C NMR (DMSO-d_6): δ 170.0,

70.6, 55.7. HREIMS: calcd for $(M + H)^+$, 167.9967; found, 167.9959. Anal: calcd for $C_3H_5NO_5S$: C, 21.56; H, 3.02; N, 8.38; S, 19.18. Found: C, 21.52; H, 2.88; N, 8.33; S, 18.89.

2-Acetamido-1,2-dideoxy-1-thio-β-D-glucose (9). 2-Acetamido-3,4,6-tri-*O*-acetyl-1-*S*-acetyl-2-deoxy-1-thio-β-D-glucopyranose[11] (100 mg, 0.25 mmol, 1.0 equiv) was dissolved in CH_3OH (5 mL). Sodium methoxide (1.0 mL, 500 mM in CH_3OH, 0.50 mmol, 2 equiv) was added and the reaction was stirred at rt for 2 h. The reaction was quenched by the addition of $NaHCO_3$ (42 mg, 0.50 mmol, 2 equiv). The solvent was removed by rotary evaporation and the product was used without purification. (65 mg, 100%). ^{1}H NMR (D_2O): δ 4.62 (d, *J* = 9.6 Hz, 1 H), 3.80 (dd, *J* = 2.1, 12.3 Hz, 1 H), 3.62 (dd, *J* = 5.9, 12.3 Hz, 1 H), 3.48 (m, 1 H), 3.40-3.30 (m, 3 H). ^{13}C NMR (D_2O): δ 174.2, 82.3, 80.0, 76.6, 70.8, 62.0, 61.6, 22.9. Mass spectrometry (EI, ESI, FAB) afforded signals corresponding to the symmetric disulfide.

1-Deoxy-1-thio-α-D-glucose (10). 2,3,4,6-Tetra-*O*-acetyl-1-*S*-acetyl-1-thio-α-D-glucopyranose[12] (140 mg, 0.34 mmol, 1.0 equiv) was dissolved in CH_3OH (8 mL). Sodium methoxide (1.4 mL, 500 mM in CH_3OH, 0.68 mmol, 2 equiv) was added and the reaction was stirred at rt for 2 h. The reaction was quenched by the addition of $NaHCO_3$ (57 mg, 0.68 mmol, 2 equiv). The solvent was removed by rotary evaporation and the product was used without purification. (74 mg, 100%). ^{1}H NMR (D_2O): δ 5.56 (d, *J* = 5.3 Hz, 1 H), 4.09 (dt, *J* = 3.6, 9.9 Hz, 1 H), 3.75 (m, 3 H), 3.48 (dd, *J* = 5.4, 9.2 Hz, 1 H), 3.32 (t, *J* = 9.6 Hz, 1 H). ^{13}C NMR (D_2O): δ 83.7, 74.1, 72.2, 70.3, 70.1, 61.0. Mass spectrometry (EI, ESI, FAB) afforded signals corresponding to the symmetric disulfide.

***S*-β-D-Glucopyranosyl-L-cysteine (11).** The sodium salt of 1-thio-β-D-glucose (**8**) (360 mg, 1.65 mmol, 1.0 equiv) was dissolved in H_2O (8 mL). In a second flask, solid $NaHCO_3$ (345 mg, 4.1 mmol, 2.5 equiv) was added to **5** (275 mg, 1.65 mmol, 1.0 equiv). The reaction was initiated by addition of the sodium thiolate solution to the flask containing **5**, thus affording the following concentrations of reactants at the onset of the reaction: **5**, 0.2 M; **8**, 0.2 M; $NaHCO_3$, 0.5 M. The reaction was stirred at rt for 4 h, then concentrated by rotary evaporation under reduced pressure. To hydrolize the sulfamidate, the crude material was dissolved in HCl (5 M, 10 mL). The hydrolysis reaction was incubated at 37 °C for 24 h, then concentrated by rotary evaporation under reduced pressure. The product was dissolved in H_2O (10 mL) and the pH was brought to neutral by the addition of solid $NaHCO_3$ (ca. 600 mg). Product **11** was purified over a column of Biogel P-2 (fine, column dimensions 2.5 cm ID × 70 cm L) eluting with H_2O (20 mL/h). Fractions containing the desired product were identified by TLC with ninhydrin staining. Product **11** was obtained as a white solid (430 mg, 90%). ^{1}H NMR (D_2O, HCl salt): δ 4.40 (d, *J* = 9.9 Hz, 1 H), 4.23 (dd, *J* = 4.2, 7.6 Hz, 1 H), 3.70 (dd, *J* = 2.3, 12.5 Hz, 1 H), 3.52 (dd, *J* = 5.6, 12.7 Hz, 1 H), 3.36-3.30 (m, 3 H), 3.28 (dd, *J* = 4.2, 15.6 Hz, 1 H), 3.21 (dd, *J* = 9.2, 9.7 Hz, 1 H), 3.07 (dd, *J* = 7.6, 15.7 Hz). ^{13}C NMR (D_2O, HCl

salt): δ 170.2, 85.3, 80.3, 77.4, 72.2, 68.9, 61.4, 53.6, 30.2. HRFABMS: calcd for $(M + H)^+$, 284.0804; found, 284.0805.

***S*-2-Acetamido-2-deoxy-β-D-glucopyranosyl-L-cysteine (12).** The sodium salt of 1-thio-*N*-acetyl-β-D-glucosamine (**9**) (420 mg, 1.62 mmol, 1.0 equiv) was dissolved in H_2O (8 mL). In a second flask, solid $NaHCO_3$ (340 mg, 4.1 mmol, 2.5 equiv) was added to **5** (270 mg, 1.62 mmol, 1.0 equiv). The reaction was initiated by addition of the sodium thiolate solution to the flask containing **5**, thus affording the following concentrations of reactants at the onset of the reaction: **5**, 0.2 M; **9**, 0.2 M; $NaHCO_3$, 0.5 M. The reaction was stirred at rt for 4 h, then concentrated by rotary evaporation under reduced pressure. To hydrolize the sulfamidate, the crude material was dissolved in HCl (5 M, 10 mL). The hydrolysis reaction was incubated at 37 °C for 24 h, then concentrated by rotary evaporation under reduced pressure. The product was dissolved in H_2O (10 mL) and the pH was brought to neutral by the addition of solid $NaHCO_3$ (ca. 600 mg). Product **12** was purified over a column of Biogel P-2 (fine, column dimensions 2.5 cm ID × 70 cm L) eluting with H_2O (20 mL/h). Fractions containing the desired product were identified by TLC with ninhydrin staining. Product **12** was obtained as a white solid (470 mg, 90%). ^{1}H NMR (D_2O, HCl salt): δ 3.97 (d, *J* = 10.5 Hz, 1 H), 3.67 (dd, *J* = 4.2, 7.2 Hz, 1 H), 3.17 (dd, *J* = 2.0, 12.5 Hz, 1 H), 3.12 (t, *J* = 10.2 Hz, 1 H), 3.01 (dd, *J* = 5.3, 12.4 Hz, 1 H), 2.90 (t, *J* = 9.2 Hz, 1 H), 2.82-2.76 (m, 2 H), 2.74 (dd, *J* = 4.4, 15.3 Hz, 1 H), 2.48 (dd, *J* = 7.3, 15.5 Hz, 1 H). ^{13}C NMR (D_2O, HCl salt): δ 174.9, 169.5, 83.3, 79.1, 74.5, 69.4, 60.6, 54.2, 52.9, 29.8, 22.1. HRFABMS: calcd for $(M + H)^+$, 325.1069; found, 325.1057.

***S*-α-D-Glucopyranosyl-L-cysteine (13).** The sodium salt of 1-thio-α-D-glucose (**10**) (205 mg, 0.94 mmol, 1.0 equiv) was dissolved in H_2O (4.7 mL). In a second flask, solid $NaHCO_3$ (200 mg, 2.4 mmol, 2.5 equiv) was added to **5** (157 mg, 0.94 mmol, 1.0 equiv). The reaction was initiated by addition of the sodium thiolate solution to the flask containing **5**, thus affording the following concentrations of reactants at the onset of the reaction: **5**, 0.2 M; **10**, 0.2 M; $NaHCO_3$, 0.5 M. The reaction was stirred at rt for 4 h, then concentrated by rotary evaporation under reduced pressure. To hydrolize the sulfamidate, the crude material was dissolved in HCl (5 M, 10 mL). The hydrolysis reaction was incubated at 37 °C for 12 h, then concentrated by rotary evaporation under reduced pressure. The product was dissolved in H_2O (10 mL) and the pH was brought to neutral by the addition of solid $NaHCO_3$ (ca. 400 mg). Product **13** was purified over a column of Biogel P-2 (fine, column dimensions 2.5 cm ID × 70 cm L) eluting with H_2O (20 mL/h). Fractions containing the desired product were identified by TLC with ninhydrin staining. Product **13** was obtained as a white solid (225 mg, 85%). ^{1}H NMR (D_2O, HCl salt): δ 5.27 (d, *J* = 5.6 Hz, 1 H), 4.28 (dd, *J* = 4.0, 6.2 Hz, 1 H), 3.78 (m, 1 H), 3.72-3.64 (m, 2 H), 3.55 (dd, *J* = 6.1, 12.6 Hz, 1 H), 3.33 (t, *J* = 9.6 Hz, 1 H), 3.20 (t, *J* =

9.6 Hz, 1 H), 3.17 (dd, *J* = 6.4, 15.3 Hz, 1 H), 3.07 (dd, *J* = 4.1, 15.4 Hz, 1 H). ^{13}C NMR (D_2O, HCl salt): δ 170.1, 87.1, 73.5, 73.1, 70.9, 69.7, 60.7, 53.3, 31.0. HRFABMS: calcd for $(M + Na)^+$, 306.0623; found, 306.0631.