Supporting Information

for

Bis(oxazolines) based on glycopyranosides – steric, configurational and conformational influences on stereoselectivity

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General methods

Dry solvents were obtained by distillation over appropriate drying reagents under a nitrogen atmosphere (CH\textsubscript{2}Cl\textsubscript{2} was distilled from calcium hydride), or purchased in dried form from commercial sources (DMF and benzene from Acros, abs. ethanol from Fisher Scientific). All reactions involving reagents sensitive to air and moisture were carried out under a nitrogen atmosphere (glove box and/or Schlenk techniques). Reactions were monitored by TLC on 60 F254 aluminium plates (Merck) with detection by UV light and/or charring with 10% sulfuric acid in ethanol or a mixture of cerium(IV) sulfate and molybdophosphoric acid in 8% sulfuric acid. Flash chromatography was performed on Merck silica (grain size 40–63 µm). NMR spectra were recorded on an AVS 400 instrument (Bruker) at 400 MHz (\textsuperscript{1}H) or at 100 MHz (\textsuperscript{13}C) respectively. Deuterated chloroform was used as solvent and spectra were calibrated against the residual solvent peaks (CHCl\textsubscript{3}: 7.24 ppm for \textsuperscript{1}H and 77 ppm for \textsuperscript{13}C). Chemical shifts δ are given in ppm, coupling constants J are given in Hz. Electrospray mass (ESI) spectra were recorded on a Micromass LCT device (Waters). Optical rotations were recorded on a Perkin-Elmer 451 instrument under following standard conditions: Room temperature, wavelength 589.3 nm (sodium D line), cell length 1 dm, solvent and sample concentration (in 10 mg/ml) are given with the individual experiment.
Ethyl 4,6-O-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-glucopyran-3-ulose (8)

Oxalyl chloride (2.65 g, 1.79 mL, 20.84 mmol) was dissolved in dry CH₂Cl₂ (60 mL) at −78 °C. Dimethylsulfoxide (2.04 g, 1.85 mL, 26.05 mmol) was added slowly and the reaction mixture stirred for 15 min at −78 °C. Thioglucoside 7 (2.30 g, 5.21 mmol) dissolved in dry CH₂Cl₂ (10 mL) was then added slowly and the reaction mixture stirred for further 20 min at −78 °C. Et₃N (5.00 mL) was added and the mixture allowed to warm to room temperature. The mixture was diluted with CH₂Cl₂, washed successively with saturated aqueous NaHCO₃ solution and brine, and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel (eluent: PE/EtOAc 4:1) to yield 8 (1.95 g, 4.43 mmol, 85%) as a colourless foam.

Rf 0.76 (2:1 PE/EtOAc); ¹H NMR (CDCl₃, 400 MHz): δ = 7.84–7.87 (m, 2H, Phth), 7.70–7.75 (m, 2H, Phth), 7.47–7.50 (m, 2H, Ph), 7.32–7.36 (m, 3H, Ph), 5.64 (d, 1H, J₁,₂ = 10.2 Hz, H-1), 5.58 (s, 1H, CHPh), 4.96 (d, 1H, J₁,₂ = 10.2 Hz, H-2), 4.52 (dd, 1H, J₁,₂ = 10.2 Hz, J₅,₆ = 4.7 Hz, J₆,₆’ = 10.2 Hz, H-6), 4.42 (d, 1H, J₄,₅ = 9.9 Hz, H-4), 4.01 (ddd ≈ td, 1H, J₄,₅ ≈ J₅,₆ = 9.9 Hz, J₆,₆’ = 10.2 Hz, H-5), 3.92 (dd ≈ t, 1H, J₅,₆ = 9.9, J₆,₆’ = 10.2 Hz, H-6’), 2.68–2.78 (m, 2H, SCH₂CH₃), 1.22 (t, 3H, J = 7.5 Hz, SCH₂CH₃) ppm;

¹³C NMR (CDCl₃, 100 MHz): δ = 191.4 (C, C3), 167.04 (C, NCO), 136.1 (C, arom.), 134.4, 134.3 (CH, arom.), 131.5, 131.5 (C, arom.), 129.3, 128.2, 126.3, 123.8, 123.7, (CH, arom.), 101.9 (CH, PhCH), 84.0 (CH, C-1), 82.0 (CH, C-4), 71.2 (CH, C-5), 68.9 (CH₂, C-6), 59.1 (CH, C-2), 24.7 (CH₂, SCH₂CH₃), 14.8 (CH₃, SCH₂CH₃) ppm; HRMS (ESI): calculated for C₂₃H₂₆N₂O₆S 457.1428, found 457.1439 [M + NH₄]⁺.
Ethyl 4,6-O-benzylidene-2-deoxy-2-phthalimido-1-thio-3-trifluoromethane-sulfonyl-β-D-glucopyranoside (9)

Thioglucoside 7 (1.00 g, 2.27 mmol) was dissolved in dry CH₂Cl₂ (15 mL), cooled to −20 °C and pyridine (1.54 g, 1.58 mL, 19.52 mmol) was added. Trifluoromethanesulfonic anhydride (1.28 g, 0.75 mL, 4.54 mmol) was dissolved in dry CH₂Cl₂ (5 mL) and added slowly to the reaction mixture at −20 °C. The mixture was allowed to warm up to 10 °C and diluted with CH₂Cl₂ and HCl (1 M). The mixture was washed successively with saturated aqueous NaHCO₃ solution and brine. The organic layer was dried over Na₂SO₄ and the solvent removed under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: PE/EtOAc 3:1) to yield 9 (1.22 g, 2.13 mmol, 96%) as a colourless foam.

R, 0.78 (3:1 PE/EtOAc); ¹H NMR (CDCl₃, 400 MHz): δ = 7.87–7.92 (m, 2H, Phth), 7.73–7.78 (m, 2H, Phth), 7.45–7.48 (m, 2H, Ph), 7.33–7.39 (m, 3H, Ph), 5.76 (dd, 1H, J₂,₃ = 9.5 Hz, J₃,₄ = 9.2 Hz, H-3), 5.61 (s, 1H, CHPh), 5.46 (d, 1H, J₁,₂ = 10.2 Hz, H-1), 4.58 (t ≈ dd, 1H, J₁,₂ = 10.2 Hz, J₂,₃ = 9.5 Hz, H-2), 4.45 (dd, 1H, J₅,₆ = 4.4 Hz, J₆,₆’ = 9.9 Hz, H-6), 3.92 (dd ≈ t, 1H, J₃,₄ = 9.2 Hz, J₄,₅ = 9.9 Hz, H-4), 3.84 (dd ≈ t, 1H, J₅,₆ ≈ J₆,₆’ = 9.9 Hz, H-6’), 3.77 (ddd ≈ td, 1H, J₄,₅ ≈ J₅,₆ = 9.9 Hz, J₆,₆’ = 4.4 Hz, H-5), 2.59–2.73 (m, 2H, SCH₂CH₃), 1.18 (t, 3H, J = 7.5 Hz, SCH₂CH₃) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 167.9, 166.6 (C, NCO), 136.1 (C, arom.), 134.6 (CH, arom.), 131.3, 131.0 (C, arom.), 129.1, 128.2, 125.8, 124.0, 123.6 (CH, arom.), 101.3 (CH, PhCH), 82.9 (CH, C3), 81.8 (CH, C-1), 78.5 (CH, C-4), 70.2 (CH, C-5), 68.3 (CH₂, C-6), 53.6 (CH, C-2), 24.3 (CH₂, SCH₂CH₃), 14.7 (CH₃, SCH₂CH₃) ppm; HRMS (ESI): calculated for C₂₄H₂₂F₃NNaO₈S₂ 596.0631, found 596.0681 [M + Na]⁺.
Ethyl 4,6-O-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-allopyranoside (10)

From ulose 8: Compound 8 (480 mg, 1.09 mmol) was dissolved in dry THF (20 mL) and cooled to −78 °C. A solution of L-selectride® (1 M, THF, 1.31 mL) was added slowly and the reaction mixture stirred for 2 h at −78 °C. The reaction was quenched with water, the solvent removed under reduced pressure and the residue twice co-evaporated with toluene. The residue was purified by flash chromatography on silica gel (eluent: PE/EtOAc 3:1) to yield 10 (330 mg, 760 μmol, 70%) as a colourless powder.

From Triflate 9: Compound 9 (200 mg, 350 μmol) was dissolved in dry DMF (10 mL). Successively, 15-crown-5 (230 mg, 210 μL, 1.05 mmol) and NaNO₂ (70 mg, 1.05 mmol) were added. The reaction mixture was heated to 50 °C and stirred for 24 h. The solvent was removed under reduced pressure and the residue co-evaporated twice with toluene. The residue was purified by flash chromatography on silica gel (eluent: PE/EtOAc 3:1) to yield 10 (96 mg, 220 μmol, 63%) as a colourless powder.

Rf 0.51 (3:1 PE/EtOAc); [α]D²⁰ = −58.1 (c = 1.15, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ = 7.83–7.88 (m, 2H, Phth), 7.70–7.75 (m, 2H, Phth), 7.45–7.48 (m, 2H, Ph), 7.33–7.37 (m, 3H, Ph), 6.01 (d, 1H, J₁,₂ = 10.5 Hz, H-1), 5.59 (s, 1H, CHPh), 4.40–4.44 (m, 3H, 2-H, 3-H, H-6), 4.23 (ddd ≈ td, 1H, J₄,₅ = 9.5 Hz, J₅,₆ = 10.2 Hz, J₆,₆′ = 5.1 Hz, H-5), 3.79 (dd ≈ t, 1H, J₅,₆ ≈ J₆,₆′ = 10.2 Hz, H-6′), 3.75 (dd, 1H, J₃,₄ = 2.3 Hz, J₄,₅ = 9.5 Hz, H-4), 3.17 (br. s, 1 H, 3-OH), 2.62–2.74 (m, 2H, SCH₂CH₃), 1.21 (t, 3H, J = 7.5 Hz, SCH₂CH₃) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 168.8 167.7 (C, NCO), 136.9 (C, arom.), 134.3, 134.2 (CH, arom.), 131.8, 131.2 (C, arom.), 129.2, 128.3, 126.2 ppm.
123.7, 123.6 (CH, arom.), 101.9 (CH, PhCH), 79.1 (CH, C-1), 78.9 (CH, C-4), 69.3
(CH, C-3), 69.0 (CH, C-6), 66.4 (CH, C-5), 55.2 (CH, C-2), 24.7 (CH, SCH₂CH₃),
14.9 (CH, SCH₂CH₃) ppm; HRMS (ESI): calculated for C₂₃H₂₃NO₆SNa 464.1138,
found 464.1141 [M + Na]+.

**Ethyl 2-amino-4,6-O-benzylidene-2-deoxy-1-thio-β-d-allopyranoside (11)**

![Chemical Structure](image)

N-Protected allosamine 10 (500 mg, 1.13 mmol) and ethylenediamine (2.80 mL,
4.07 g, 67.80 mmol) were dissolved in abs. ethanol (50 mL) and the reaction mixture
refluxed for 16 h (TLC: EtOAc). The solvent was removed under reduced pressure
and the residue co-evaporated twice with toluene. The residue was purified by flash
chromatography on silica gel (eluent: CH₂Cl₂/MeOH 20:1) to yield 11 (320 mg, 1.02
mmol, 90%) as a colourless powder.

Rᶠ 0.21 (20:1 CH₂Cl₂/MeOH); [α]₂⁰ = −54.2 (c = 1.06, CHCl₃); ¹H NMR (CDCl₃, 400
MHz): δ = 7.44–7.49 (m, 2H, Ph), 7.32–7.39 (m, 3H, Ph), 5.53 (s, 1H, CHPh), 4.59
(d, 1H, J₁₂ = 10.2 Hz, H-1), 4.34 (dd, 1H, J₅₆ = 5.1 Hz, J₆₆’ = 10.2 Hz, H-6), 4.22 (dd
≈ t, 1H, J₂₃ = 2.7 Hz, J₃₄ = 2.3 Hz, H-3), 3.96 (ddd ≈ td, 1H, J₄₅ ≈ J₅₆ = 9.9 Hz, J₅₆ =
5.1 Hz, H-5), 3.70 (dd ≈ t, 1H, J₅₆ ≈ J₆₆’ = 10.2 Hz, H-6’), 3.52 (dd, 1H, J₃₄ = 2.3 Hz,
J₄₅ = 9.9 Hz, H-4), 2.74 (dd, 1H, J₁₂ = 10.2 Hz, J₂₃ = 2.7 Hz, H-2), 2.60–2.72 (m, 2H,
SCH₂CH₃), 1.28 (t, 3H, J = 7.5 Hz, SCH₂CH₃) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ =
137.1 (C, Ph), 129.2, 128.3, 126.1 (CH, Ph), 101.8 (CH, PhCH), 85.9 (CH, C-1),
79.6 (CH, C-4), 69.1 (CH₂, C-6), 68.2 (CH, C-3), 66.0 (CH, C-5), 54.1 (CH, C-2),
24.5 (CH₂, SCH₂CH₃), 15.2 (CH₃, SCH₂CH₃) ppm; HRMS (ESI): calculated for
C₁₅H₁₃NO₄SNa 334.1083, found 334.1079 [M + Na]+.
Allosamine 11 (200 mg, 640 μmol) was dissolved in dry CH₂Cl₂ (40 mL) under a nitrogen atmosphere and cooled to 0 °C. Successively Et₃N (180 μL, 130 g, 1.28 mmol) and dimethylmalonyl dichloride (50 μL, 60 mg, 320 μmol) were added (TLC: EtOAc). After approximately 2 h the solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel (eluent: PE/EtOAc 1:1) to yield 12 (230 mg, 320 μmol, quant.) as colourless crystals.

Rᵣ 0.51 (1:1 PE/EtOAc); [α]ᵣ²⁰ = −90.3 (c = 0.80, CHCl₃); ¹H NMR (CDCl₃, 400 MHz):
δ = 7.42–7.44 (m, 4H, Ph), 7.33–7.35 (m, 6H, Ph), 6.86 (d, 2H, J₂,NH = 8.8 Hz, NH), 5.55 (s, 2H, CHPh), 4.75 (d, 2H, J₁₂ = 9.9 Hz, H-1), 4.35 (dd, 2H, J₅₆ = 5.1 Hz, J₆₆ = 10.2 Hz, H-6), 4.20–4.26 (m, 4H, 2-H, H-3), 3.95 (ddd ≈ td, 2H, J₄₅ ≈ J₅₆ = 9.5 Hz, J₆₆ = 5.1 Hz, H-5), 3.72 (dd ≈ t, 2H, J₅₆ ≈ J₆₆ = 10.2 Hz, H-6'), 3.62 (dd, 2H, J₃₄ = 2.0 Hz, J₄₅ = 9.5 Hz, H-4), 2.73 (br. s, 2H, 3-OH), 2.68–2.71 (m, 4H, SCH₂CH₃), 1.48 [s, 6H, (CH₃)₂C], 1.25 (t, 6H, J = 7.5 Hz, SCH₂CH₃) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 172.9 (C, CONH), 136.8 (C, Ph), 129.2, 128.3, 126.1 (CH, Ph), 101.6 (CH, PhCH), 82.1 (CH, C-1), 78.6 (CH, C-4), 68.9 (CH₂, C-6), 67.9 (CH, C-3), 66.2 (CH, C-5), 51.1 (CH, C-2), 49.9 [C, (CH₃)₂C], 23.9 [CH₃, (CH₃)₂C], 23.8 (CH₂, SCH₂CH₃), 14.8 (CH₃, SCH₂CH₃) ppm; HRMS (ESI): calculated for C₃₅H₄₇N₂O₁₀S₂ 719.2667, found 719.2661 [M + H]⁺.
$N,N'$-Bis(ethyl 3-O-acetyl-4,6-O-benzylidene-2-deoxy-1-thio-$\beta$-D-allopyranosid-2-yl)dimethylmalonamide (13)

Bis(amide) 12 (190 mg, 260 $\mu$mol) was dissolved in pyridine (20 mL) and acetic anhydride (250 $\mu$L, 270 mg, 2.64 mmol) added slowly. The reaction mixture was stirred for 16 h at room temperature (TLC: PE/EtOAc 1:1). The solvent was removed under reduced pressure and the residue co-evaporated twice with toluene. The residue was purified by flash chromatography on silica gel (eluent: PE/EtOAc 2:1) to yield 13 (200 mg, 250 $\mu$mol, 96%) as a colourless foam.

$R_f$ 0.43 (1:1 PE/EtOAc); $[\alpha]_D^{20} = -81.2$ (c = 0.93, CHCl$_3$); $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 7.36–7.39 (m, 4H, Ph), 7.30–7.33 (m, 6H, Ph), 6.70 (d, 2H, $J_{2,NH}$ = 8.8 Hz, NH), 5.57 (dd $\approx$ t, 2H, $J_{2,3}$ $\approx$ $J_{3,4}$ = 2.7 Hz, H-3), 5.53 (s, 2H, CHPh), 4.73 (d, 2H, $J_{1,2}$ = 10.5 Hz, H-1), 4.35 (dd, 2H, $J_{5,6}$ = 4.7 Hz, $J_{6,6'}$ = 10.2 Hz, H-6), 4.30 (ddd $\approx$ td, 2H, $J_{1,2}$ = 10.5 Hz, $J_{2,3}$ = 3.0 Hz, $J_{2,NH}$ = 8.8 Hz, H-2), 3.90 (ddd $\approx$ td, 2H, $J_{4,5}$ $\approx$ $J_{5,6}$ = 9.5 Hz, $J_{5,6}$ = 4.7 Hz, H-5), 3.74 (dd, 2H, $J_{5,6'}$ $\approx$ $J_{6,6'}$ = 10.2 Hz, H-6$'$), 3.73 (dd, 2H, $J_{3,4}$ = 2.7 Hz, H-3), 2.69–2.76 (m, 4H, SC$_2$H$_2$CH$_3$), 1.40 (s, 6H, (CH$_3$)$_2$C], 2.17 (s, 6H, CH$_3$CO), 1.26 (t, 6H, $J$ = 7.5 Hz, SCH$_2$CH$_3$) ppm; $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ = 172.7 (C, CONH), 169.5 (C, CH$_3$CO), 136.8 (C, Ph), 129.0, 128.2, 125.9 (CH, Ph), 101.3 (CH, PhCH), 82.3 (CH, C-1), 76.9 (CH, C-4), 68.97 (CH, C-3), 68.94 (CH$_2$, C-6), 67.4 (CH, C-5), 50.2 (CH, C-2), 49.5 [C, (CH$_3$)$_2$C], 23.9 [CH$_3$, (CH$_3$)$_2$C], 23.8 (CH$_2$, SCH$_2$CH$_3$), 20.8 (CH$_3$, CH$_3$CO), 14.9 (CH$_3$, SCH$_2$CH$_3$) ppm; HRMS (ESI): calculated for C$_{39}$H$_{56}$N$_2$O$_{12}$NaS$_2$ 825.2703, found 825.2689 [M + Na]$^+$. 
3-O-Ac alloBox (14)

A mixture of bis(amide) 13 (130 mg, 160 μmol) and MS 4 Å (130 mg) in dry CH₂CH₂ (5 mL) was stirred for 1 h under a nitrogen atmosphere. NIS (88 mg, 390 μmol) was added, and the mixture cooled to −30 °C. Then, TfOH (1.8 μL, 20 μmol) was added, and the mixture was stirred for 1 h at −30 °C. The reaction was quenched by addition of Et₃N (100 μL), filtered through Celite®, diluted with CH₂Cl₂, washed successively with saturated aqueous NaHCO₃ solution and aqueous sodium thiosulfate solution (3 M), and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel (eluent: EtOAc) to yield 14 (100 mg, 150 μmol, 94%) as a colourless solid.

R₉ 0.05 (1:1 PE/EtOAc); [α]D²⁰ = +192.8 (c = 0.76, CHCl₃); 'H NMR (CDCl₃, 400 MHz): δ = 7.38–7.41 (m, 4H, Ph), 7.32–7.34 (m, 6H, Ph), 5.83 (d, 2H, J₁,₂ = 6.8 Hz, H-1), 5.64 (dd, 2H, J₂,₃ = 5.8 Hz, J₃,₄ = 2.3 Hz, H-3), 4.38 (dd, 2H, J₅,₆ = 5.1 Hz, J₆,₆' = 10.5 Hz, H-6), 5.56 (s, 2H, CHPh), 4.28 (ddd ≈ td, 2H, J₄,₅ = J₅,₆' = 9.5 Hz, J₅,₆ = 5.1 Hz, J₆,₆' = 10.2 Hz, H-5), 4.14 (dd, 2H, J₁,₂ = 6.8 Hz, J₂,₃ = 5.8 Hz, H-2), 3.69 (dd, 2H, J₃,₄ = 2.3 Hz, J₄,₅ = 9.5 Hz, H-4), 3.41 (dd ≈ t, 2H, J₅,₆ ≈ J₆,₆' = 10.2 Hz, H-6'), 2.10 (s, 6H, CH₃CO), 1.52 [s, 6H, (CH₃)₂C], ppm; 'C NMR (CDCl₃, 100 MHz): δ = 170.3 (C, CH₃CO), 169.5 (C, O–C=N), 136.8 (C, Ph), 129.1, 128.2, 125.9 (CH, Ph), 103.1 (CH, C-1), 101.5 (CH, PhCH), 75.0 (CH, C-4), 68.9 (CH₂, C-6), 64.1 (CH, C-3), 60.4 (CH, C-2), 59.6 (CH, C-5), 40.1 [C, (CH₃)₂C], 23.1 [CH₃, (CH₃)₂C], 20.9 (CH₃, CH₃CO) ppm; HRMS (ESI): calculated for C₃₅H₃₈N₂O₁₂Na 701.2322, found 701.2321 [M + Na]⁺.
\(N,N^\prime\)-Bis(ethyl 3,4,6-tri-O-acetyl-2-deoxy-1-thio-\(\beta\)-d-allopyranosid-2-yl)dimethylmalonamide (15)

The benzylidene-protected bis(amide) \(13\) (515 mg, 720 \(\mu\)mol) was dissolved in 60% aqueous acetic acid (10 mL) and the solution stirred at 100 °C for 3 h. The solvent was evaporated and the residue was co-evaporated twice with toluene (10 mL). The crude product was dissolved in pyridine (100 mL) and a catalytic amount of DMAP added. Acetic anhydride (2.05 mL, 2.21 g, 21.6 mmol) was added slowly and the reaction mixture was stirred for 16 h at room temperature (TLC: EtOAc). The solvent was removed under reduced pressure and the residue twice co-evaporated with toluene (100 mL). The residue was purified by flash chromatography on silica gel (eluent: PE/EtOAc 1:1) to yield \(15\) (440 g, 550 \(\mu\)mol, 77%) as a colourless foam.

\[ R_f \, 0.61 \, (\text{EtOAc}; \, [\alpha]_D^{20} = -37.3 \, (c = 1.10, \, \text{CHCl}_3) \]; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 6.69 \, (d, \, 2H, \, J_{2,NH} = 8.8 \, \text{Hz}, \, \text{NH}), \, 5.54 \, (dd \approx t, \, 2H, \, J_{2,3} \approx J_{3,4} = 2.7 \, \text{Hz}, \, \text{H-3}), \, 4.91 \, (dd, \, 2H, \, J_{3,4} = 2.7 \, \text{Hz}, \, J_{4,5} = 10.2 \, \text{Hz}, \, \text{H-4}), \, 4.69 \, (d, \, 2H, \, J_{1,2} = 10.2 \, \text{Hz}, \, \text{H-1}), \, 4.30 \, (ddd \approx td, \, 2H, \, J_{1,2} = 10.2 \, \text{Hz}, \, J_{2,3} = 3.0 \, \text{Hz}, \, J_{2,NH} = 8.8 \, \text{Hz}, \, \text{H-2}), \, 4.25 \, (dd, \, 2H, \, J_{5,6} = 4.7 \, \text{Hz}, \, J_{6,6'} = 10.2 \, \text{Hz}, \, \text{H-6}), \, 4.13-4.19 \, (m, \, 4H, \, \text{H-6}, \, \text{H-6'}), \, 3.96 \, (ddd \approx td, \, 2H, \, J_{4,5} = 10.2, \, J_{5,6} = 7.1 \, \text{Hz}, \, J_{5,6'} = 4.0 \, \text{Hz}, \, \text{H-5}), \, 2.64-2.73 \, (m, \, 4H, \, \text{SCH}_2\text{CH}_3), \, 2.14 \, (s, \, 6H, \, \text{CH}_3\text{CO}), \, 2.04 \, (s, \, 6H, \, \text{CH}_3\text{CO}), \, 1.95 \, (s, \, 6H, \, \text{CH}_3\text{CO}), \, 1.35 \, [s, \, 6H, \, (\text{CH}_3)_2\text{C}], \, 1.25 \, (t, \, 6H, \, J = 7.5 \, \text{Hz}, \, \text{SCH}_2\text{CH}_3) \, \text{ppm}; \, ^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 172.7 \, (\text{C, CONH}), \, 170.7, \, 169.4, \, 169.1 \, (\text{C, CH}_3\text{CO}), \, 81.6 \, (\text{CH, C-1}), \, 72.6 \, (\text{CH, C-5}), \, 69.1 \, (\text{CH, C-3}), \, 66.6 \, (\text{CH, C-4}), \, 62.6 \, (\text{CH}_2, \, \text{C-6}), \, 49.8 \, [\text{C, (CH}_3)_2\text{C}], \, 49.3 \, (\text{CH, C-2}), \, 24.1 \, [\text{CH}_3, \, (\text{CH}_3)_2\text{C}], \, 23.8 \, (\text{CH}_2, \, \text{SCH}_2\text{CH}_3), \, 20.7, \, 20.6, \, 20.5 \, (\text{CH}_3, \, \text{CH}_3\text{CO}), \, 14.9 \, (\text{CH}_3, \, \text{SCH}_2\text{CH}_3) \, \text{ppm}; \, \text{HRMS (ESI)}: \) calculated for \(\text{C}_{33}\text{H}_{51}\text{N}_2\text{O}_{16}\text{S}_2\) 795.2680, found 795.2692 [M + H]*.
**Ac alloBox (16)**

A mixture of the per-acetylated bis(amide) 15 (270 mg, 340 μmol) and MS 4 Å (300 mg) in dry CH₂CH₂ (10 mL) was stirred for 1 h under a nitrogen atmosphere. NIS (184 mg, 820 μmol) was added, and the mixture cooled to −30 °C. Then, TfOH (2.96 μL, 50 μmol) was added, and the mixture stirred for 1 h at −30 °C. The reaction was quenched with Et₃N (200 μL), filtered through Celite®, diluted with CH₂Cl₂, washed successively with saturated aqueous NaHCO₃ solution and aqueous sodium thiosulfate solution (3 M), and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel (eluent: EtOAc) to yield 16 (210 mg, 310 μmol, 91%) as a colourless solid.

**R**<sub>f</sub> 0.09 (EtOAc); [α]<sub>D</sub><sup>20</sup> = +139.5 (c = 1.25, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ = 6.01 (d, 2H, <i>J</i><sub>1,2</sub> = 7.5 Hz, H-1), 5.28 (dd ≈ t, 2H, <i>J</i><sub>2,3</sub> ≈ <i>J</i><sub>3,4</sub> = 4.7 Hz, H-3), 5.20 (dd, 2H, <i>J</i><sub>3,4</sub> ≈ <i>J</i><sub>4,5</sub> = 5.6 Hz, H-4), 4.24 (dd, 2H, <i>J</i><sub>1,2</sub> = 7.5 Hz, <i>J</i><sub>2,3</sub> = 4.4 Hz, H-2), 4.15–4.19 (m, 4H, H-6, H-6´), 4.02–4.07 (m, 2H, H-5), 2.09, 2.06, 2.05 (s, 6H, CH₃CO), 1.52 [s, 6H, (CH₃)₂C] ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 170.5, 170.0, 169.9 (C, CH₃CO), 169.3 (C, O–C=N), 101.2 (CH, C-1), 70.1 (CH, C-5), 65.7 (CH, C-4), 65.3 (CH, C-3), 63.7 (CH₂, C-6), 62.7 (CH, C-2), 39.2 [C, (CH₃)₂C], 24.1 [CH₃, (CH₃)₂C], 20.8, 20.7, 20.6 (CH₃, CH₃CO) ppm; HRMS (ESI): calculated for C<sub>29</sub>H<sub>38</sub>N₂O<sub>16</sub> 671.2000, found 671.2305 [M + H]<sup>+</sup>. 
Ethyl 4,6-O-benzylidene-2-deoxy-3-O-[methyl thio(thiocarbonyl)]-2-phthalimido-1-thio-β-D-glucopyranoside (17)

Thioglucoside 7 (1.00 g, 2.27 mmol) was dissolved in dry DMF (15 mL). Sodium hydride (180 mg of 60% dispersion in mineral oil, 4.54 mmol) was added and the reaction mixture stirred for 30 min at room temperature. Carbon disulfide (280 µL, 4.54 mmol) was added and the mixture stirred for an additional 15 min. Subsequently, methyl iodide (280 µL, 4.54 mmol) was added and the stirring continued for 30 min. The reaction mixture was poured onto ice and extracted with EtOAc. The organic phase was washed twice with water, dried over Na₂SO₄ and concentrated. Flash chromatography on silica gel (eluent: PE/EtOAc 3:1) yielded 17 (1.06 g, 1.99 mmol, 88%) as a white foam.

Rf 0.46 (2:1 PE/EtOAc); [α]D²⁰ = −5.5 (c = 1.0, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ = 7.82–7.84 (m, 2H, arom.), 7.70–7.73 (m, 2H, arom.), 7.40–7.43 (m, 2H, arom.), 7.31–7.36 (m, 3H, arom.), 6.81 (dd ≈ t, 1H, J₂,₃ ≈ J₃,₄ = 9.5 Hz, H-3), 5.64 (d, 1H, J₁,₂ = 10.2 Hz, H-1), 5.55 (s, 1H, CHPh), 4.51 (dd ≈ t, 1H, J₁,₂ ≈ J₂,₃ = 10.2 Hz, H-2), 4.43 (dd, 1H, J₃,₄ = 4.1 Hz, J₆,₆* = 10.2 Hz, H-6), 3.95 (dd ≈ t, 1H, J₃,₄ ≈ J₄,₅ = 9.2 Hz, H-4), 3.80–3.97 (m, 2H, H-5, H-6*), 2.63–2.74 (m, 2H, SCH₂CH₃), 2.36 (s, 3H, SCH₃), 1.19 (t, 3H, J = 7.5 Hz, SCH₂CH₃) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 215.4 (C, OC(SMe)=S), 167.9 (C, NCO), 167.0 (C, NCO), 136.7 (C, arom.), 134.3 (CH, arom.), 134.1 (CH, arom.), 134.1 (CH, arom.), 131.7 (C, arom.), 131.2 (C, arom.), 129.0 (CH, arom.), 128.1 (2 CH, arom.), 128.1 (2 CH, arom.), 123.7 (CH, arom.), 123.5 (CH, arom.), 101.4 (CH, PhCH), 81.7 (CH, C-1), 79.5 (CH, C-4), 78.3 (CH, C-3), 70.4 (CH, C-5), 68.6 (CH₂, C-6), 53.8 (CH, C-2), 24.3 (CH₂, SCH₂CH₃), 19.9 (CH₃, SCH₃), 14.8
(CH$_3$, SCH$_2$CH$_3$) ppm; HRMS (ESI) calculated for C$_{25}$H$_{25}$NO$_6$S$_3$Na 554.0742, found 554.0740 [M + Na]$^+$. 

**Ethyl 4,6-O-benzylidene-2,3-dideoxy-2-phthalimido-1-thio-β-D-glucopyranoside (18)**

Xanthogenate 17 (500 mg, 940 µmol) was dissolved in dry benzene (10 mL) under a nitrogen atmosphere and Bu$_3$SnH (470 µL, 1.76 mmol) added. Then AIBN (~20 mg) was added and the reaction mixture refluxed for 15 min. After removal of the solvent the residue was diluted with n-hexane and extracted five times with acetonitrile. After removal of the solvent, the residue was purified by flash chromatography on silica gel (eluent: PE/EtOAc 3:1) to yield 18 (380 mg, 900 µmol, 96%) as a white foam. $R_f$ 0.69 (2:1 PE/EtOAc); $[\alpha]_D^{20} = -3.8$ (c = 1.0, CHCl$_3$); $^1$H NMR (CDCl$_3$, 400 MHz): δ = 7.84–7.86 (m, 2H, arom.), 7.70–7.74 (m, 2H, arom.), 7.45–7.48 (m, 2H, arom.), 7.31–7.38 (m, 3H, arom.), 5.55 (s, 1H, CHPh), 5.41 (d, 1H, $J_{1,2} = 10.2$ Hz, H-1), 4.42 (ddd, 1H, $J_{1,2} = 10.2$ Hz, $J_{2,3} = 12.2$ Hz, $J_{2,3'} = 4.4$ Hz, H-2), 4.36 (dd, 1H, $J_{5,6} = 4.1$ Hz, $J_{6,6'} = 10.2$ Hz, H-6), 3.79 (dd ≈ t, 1H, $J_{5,6'} ≈ J_{6,6'} = 10.2$ Hz, H-6'), 3.64 – 3.75 (m, 2H, H-4, H-5), 2.60 – 2.75 (m, 3H, H-3, SCH$_2$CH$_3$), 2.30 (ddd ≈ td, 1H, $J_{2,3'} = 4.4$ Hz, $J_{3,3'} = 11.6$ Hz, $J_{3',4} = 4.1$ Hz, H-3'), 1.18 (t, 3H, $J = 7.5$ Hz, SCH$_2$CH$_3$) ppm; $^{13}$C NMR (CDCl$_3$, 100 MHz): δ = 167.9 (C, NCO), 167.2 (C, NCO), 137.2 (C, arom.), 134.2 (2 CH, arom.), 131.7 (C, arom.), 129.1 (CH, arom.), 128.3 (2 CH, arom.), 126.1 (2 CH, arom.), 123.6 (CH, arom.), 123.4 (CH, arom.), 101.7 (CH, PhCH), 83.0 (CH, C-1), 76.6 (CH, C-4), 73.7 (CH, C-5), 69.0 (CH$_2$, C-6), 49.6 (CH, C-2), 32.7 (CH$_2$, C-3), 24.3 (CH$_2$, SCH$_2$CH$_3$), 14.9 (CH$_3$, SCH$_2$CH$_3$) ppm; HRMS (ESI) calculated for C$_{23}$H$_{23}$NO$_6$SNa 448.1195, found 448.1203 [M + Na]$^+$. 

13
Ethyl 2-amino-4,6-O-benzylidene-2,3-dideoxy-1-thio-β-D-glucopyranoside (19)

The N-protected 3-deoxy sugar 18 (180 mg, 420 µmol) and ethylene diamine (1.05 mL, 25.40 mmol) were dissolved in absolute ethanol (50 mL) and the resulting mixture refluxed for 2 h (TLC: EtOAc). The solvent was evaporated and the residue co-evaporated twice with toluene. Flash chromatography on silica gel (eluent: EtOAc) yielded 19 (120 mg, 390 µmol, 93%) as a white solid.

\[ R_f = 0.28 \] (EtOAc); \[ [\alpha]_{D}^{20} = -63.7 \] (c = 1.6, CHCl₃); 'H NMR (CDCl₃, 400 MHz): \( \delta = 7.44–7.47 \) (m, 2H, arom.), 7.31–7.37 (m, 3H, arom.), 5.52 (s, 1H, CHPh), 4.30 (dd, 1H, \( J_{5,6} = 4.7 \) Hz, \( J_{6,6} = 10.5 \) Hz, H-6), 4.23 (d, 1H, \( J_{1,2} = 9.5 \) Hz, H-1), 3.74 (dd \( \approx t \), 1H, \( J_{4,5} \approx J_{5,6} = 10.5 \) Hz, H-6'), 3.63 (ddd, 1H, \( J_{3,4} = 8.8 \) Hz, \( J_{3,4} = 4.1 \) Hz, H-4), 3.41 (dd \( \approx td \), 1H, \( J_{4,5} \approx J_{5,6} = 10.2 \) Hz, \( J_{5,6} = 4.7 \) Hz, H-5), 2.85–2.91 (m, 1H, \( J_{1,2} = 9.5 \) Hz, \( J_{2,3} = 11.6 \) Hz, \( J_{2,3} = 4.4 \) Hz, H-2), 2.68–2.77 (m, 2H, SCH₂CH₃), 2.42 (ddd \( \approx td \), 1H, \( J_{2,3} = 4.4 \) Hz, \( J_{3,3} = 11.9 \) Hz, \( J_{3,4} = 4.1 \) Hz, H-3'), 1.50–1.60 (m, 3H, H-3, NH₂), 1.30 (t, 3H, \( J = 7.5 \) Hz, SCH₂CH₃) ppm; 'C NMR (CDCl₃, 100 MHz): \( \delta = 137.2 \) (C, arom.), 129.0 (CH, arom.), 128.3 (2 CH, arom.), 126.1 (2 CH, arom.), 101.7 (CH, PhCH), 90.9 (CH, C-1), 76.5 (CH, C-4), 73.8 (CH, C-5), 69.0 (CH₂, C-6), 51.6 (CH, C-2), 37.8 (CH₂, C-3), 24.6 (CH₂, SCH₂CH₃), 15.3 (CH₃, SCH₃) ppm; HRMS (ESI) calculated for C₁₅H₂₂NO₃S 296.1320, found 296.1323 [M + H]+.
The 3-deoxygenated aminosugar 19 (310 mg, 1.05 mmol) was dissolved under a nitrogen atmosphere in dry CH₂Cl₂ (25 mL) and the solution cooled to 0 °C. Then, Et₃N (280 µL, 2.00 mmol) and dimethylmalonyl dichloride (70 µL, 500 µmol) were added subsequently. After approximately 2 h (monitored by TLC: EtOAc), the solvent was removed in vacuo, and the product purified by flash chromatography on silica gel (eluent: PE/EtOAc 1:1) to yield 20 (340 mg, 500 µmol, quant.) as a white solid.

R₉ 0.50 (1:1 PE/EtOAc); [α]D²⁰ = −76.8 (c = 1.0, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ = 7.42–7.45 (m, 4H, arom.), 7.31–7.36 (m, 6H, arom.), 6.58 (d, 2H, J₂,ΝH = 8.8 Hz, NH), 5.50 (s, 1H, CHPh), 4.48 (d, 2H, J₁,₂ = 10.2 Hz, H-1), 4.30 (dd, 2H, J₅,₆ = 4.7 Hz, J₆,₆’ = 10.5 Hz, H-6), 4.09 (ddd, 2H, J₁,₂ = 10.2 Hz, J₂,₃ = 11.6 Hz, J₂,₃’ = 4.4 Hz, H-2), 3.74 (dd ≈ t, 2H, J₅,₆’ ≈ J₆,₆’ = 10.2 Hz, H-6’), 3.62 (ddd, 2H, J₃,₄ = 8.8 Hz, J₃,₄’ = 4.0 Hz, J₄,₅ = 9.2 Hz, H-4), 3.41 (ddd ≈ td, 2H, J₄,₅ ≈ J₅,₆’ = 9.2 Hz, J₅,₆ = 4.7 Hz, H-5), 2.66–2.75 (m, 4H, SCH₂CH₃), 2.47 (ddd ≈ td, 2H, J₂,₃’ = 4.4 Hz, J₃,₃’ = 11.9 Hz, J₃,₄’ = 4.0 Hz, H-3’), 1.66–1.75 (m, 2H, J₂,₃ = 11.6 Hz, J₃,₃’ = 11.9 Hz, J₃,₄ = 8.8 Hz, H-3), 1.45 (s, 6H, CH₃), 1.25 (t, 6H, J = 7.5 Hz, SCH₂CH₃) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 172.8 (C, CONH), 137.1 (C, Ph), 129.0, 128.2, 126.0 (CH, Ph), 101.5 (CH, PhCH), 86.2 (CH, C-1), 75.6 (CH, C-4), 74.0 (CH, C-5), 68.8 (CH₂, C-6), 49.6 (CH, C-2), 48.6 [C, (CH₃)₂C], 35.8 (CH₂, C-3), 23.9 (CH₂, SCH₂CH₃), 23.8 [CH₃, (CH₃)₂C], 14.9 (CH₃, SCH₃) ppm; HRMS (ESI) calculated for C₃₅H₄₆N₂O₈S₂Na 709.2593, found 709.2610 [M + Na]⁺.
A mixture of the benzylidene-protected bis(amide) 20 (150 mg, 220 µmol) and MS 4 Å (150 mg) in dry CH₂CH₂ (5 mL) was stirred for 1 h under a nitrogen atmosphere. NIS (118 mg, 520 µmol) was added, and the mixture cooled to −30 °C. Then, TfOH (3 μL, 30 µmol) was added, and the reaction mixture stirred for 1 h at −30 °C. The reaction was quenched with Et₃N (100 µL), filtered through Celite®, diluted with CH₂Cl₂, washed successively with saturated aqueous NaHCO₃ solution and aqueous sodium thiosulfate solution (3 M), and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel (eluent: EtOAc) to yield 21 (109 mg, 190 µmol, 89%) as a white solid.

R₁ 0.17 (EtOAc); [α]₂₀ = +160.6 (c = 0.98, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ = 7.44–7.48 (m, 4H, arom.), 7.30–7.37 (m, 6H, arom.), 5.86 (d, 2H, J₁₂ = 7.1 Hz, H-1), 5.54 (s, 2H, CHPh), 4.35 (dd, 2H, J₅₆ = 4.0 Hz, J₆₆ = 9.9 Hz, H-6), 4.08–4.14 (m, 2H, H-2), 3.62–3.75 (m, 6H, H-4, H-5, H-6'), 2.63 (ddd, 2H, J₂₃ = 7.5 Hz, J₃₃' = 13.3 Hz, J₅₄ = 4.4 Hz, H-3'), 1.63 (ddd, 2H, J₂₃ = 8.8 Hz, J₃₃' = 13.3 Hz, J₅₄ = 7.8 Hz, H-3), 1.45 (s, 6H, CH₃) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 168.2 (C, O-C=N), 137.1 (C, arom.), 129.0 (CH, arom.), 128.2 (2 CH, arom.), 126.1 (2 CH, arom.), 102.6 (CH, C-1), 101.6 (CH, PhCH), 73.7 (CH, C-4), 68.8 (CH₂, C-6), 65.8 (CH, C-5), 59.3 (CH, C-2), 39.1 [C, (CH₃)₂C]), 32.4 (CH₂, C-3), 23.2 [CH₃, (CH₃)₂C] ppm; HRMS (ESI) calculated for C₃₁H₃₅N₂O₈ 563.2393, found 563.2385 [M + H]⁺.
The benzylidene-protected bis(amide) 20 (1.17 g, 1.70 mmol) was dissolved in acetic acid (25 mL, 60%) and the solution stirred at 100 °C for 3 h. The solvent was evaporated and the residue twice co-evaporated with toluene (25 mL). The crude product was dissolved in pyridine (150 mL) and a catalytic amount of DMAP added. Acetic anhydride (3.21 mL, 3.47 g, 34.00 mmol) was added slowly and the reaction mixture stirred for 5 h at room temperature (TLC: PE/EtOAc 1:2). The solvent was removed under reduced pressure and the residue twice co-evaporated with toluene (200 mL). The residue was purified by flash chromatography on silica gel (eluent: PE/EtOAc 1:2) to yield 22 (1.07 g, 1.58 mmol, 93%) as a colourless foam.

Rf 0.28 (1:2 PE/EtOAc); [α]D20 = −13.2 (c = 1.0, CHCl3); 1H NMR (CDCl3, 400 MHz):
δ = 6.57 (d, 2H, J2,NH = 7.5 Hz, NH), 4.76 (ddd ≈ dt, 2H, J3,4 ≈ J4,5 = 10.5 Hz, J3’,4 = 4.7 Hz, H-4), 4.45 (d, 2H, J1,2 = 9.9 Hz, H-1), 4.14-4.17 (m, 4H, H-6, H-6’), 3.91-4.01 (m, 2H, H-2), 3.60 (m, 2H, H-3´), 3.03 (s, 6H, CH3CO), 2.00 (s, 6H, CH3CO), 1.54-158 (m, 2H, H-3), 1.39 [s, 6H, (CH3)2C], 1.23 (t, 6H, J = 7.5 Hz, SCH2CH3) ppm; 13C NMR (CDCl3, 100 MHz): δ = 172.8 (C, CONH), 170.7, 169.5 (C, CH3CO), 85.5 (CH, C-1), 77.9 (CH, C-5), 66.3 (CH, C-4), 62.8 (CH2, C-6), 49.5 [C, (CH3)2C]], 48.2 (CH, C-2), 35.4 (CH2, C-3), 24.0 (CH2, SCH2CH3), 23.9 [CH3, (CH3)2C], 20.8, 20.7 (CH3, CH3CO), 14.9 (CH3, SCH3) ppm; HRMS (ESI) calculated for C29H47N2O12S2 679.2570, found 679.2597 [M + H]+.

N,N’-Bis(ethyl 4,6-di-O-acetyl-2-amino-2,3-dideoxy-1-thio-β-D-glucopyranosid-2-yl)dimethylmalonamide (22)
A mixture of the 3-deoxygenated, per-acetylated bis(amide) 22 (500 mg, 740 µmol) and MS 4 Å (500 mg) in dry CH$_2$CH$_2$ (20 mL) was stirred for 1 h under a nitrogen atmosphere. NIS (400 mg, 1.78 mmol) was added, and the mixture cooled to −30 °C. Then, TfOH (15 µL, 30 µmol) was added, and the reaction mixture stirred for 1 h at −30 °C. The reaction was quenched with Et$_3$N (500 µL), filtered through Celite®, diluted with CH$_2$Cl$_2$, washed successively with saturated aqueous NaHCO$_3$ solution and aqueous sodium thiosulfate solution (3 M), and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel (eluent: EtOAc) to yield 23 (360 mg, 650 µmol, 88%) as a white solid.

$R_f$ 0.04 (EtOAc); $[\alpha]_D^{20} = +82.3$ (c = 1.23, CHCl$_3$); $^1$H NMR (CDCl$_3$, 400 MHz): δ = 5.90 (d, 2H, J$_{1,2}$ = 7.6 Hz, H-1), 4.95 (m, 2H, H-4), 4.16 (dd, 2H, J$_{5,6}$ = 3.0, J$_{6,6'}$ = 12.1, H-6), 4.11–4.13 (m, 2H, H-2), 4.07 (dd, 2H, J$_{5,6}$ = 5.3, J$_{6,6'}$ = 12.1, H-6'), 3.78 (ddd ≈ dt, 2H, J$_{4,5}$ = 7.9, J$_{5,6}$ = 3.0, J$_{6,6'}$ = 5.3, H-5), 2.20-2.29 (m, 2H, H-3'), 2.07 (ddd, 2H, J$_{2,3}$ = 6.6 Hz, J$_{3,3'}$ = 15.8 Hz, J$_{3,4}$ = 5.1 Hz, H-3), 2.01 (s, 6H, CH$_3$CO), 1.99 (s, 6H, CH$_3$CO), 1.54 [s, 6H, (CH$_3$)$_2$C] ppm; $^{13}$C NMR (CDCl$_3$, 100 MHz): δ = 170.5, 170.0 (C, CH$_3$CO), 168.4 (C, O-C=O), 100.5 (CH, C-1), 68.4 (CH, C-5), 65.5 (CH, C-4), 63.8 (CH$_2$, C-6), 60.0 (CH, C-2), 38.8 [C, (CH$_3$)$_2$C], 26.8 (CH$_2$, C-3), 23.9 [CH$_3$, (CH$_3$)$_2$C], 21.1, 20.6 (CH$_3$, CH$_3$CO) ppm; HRMS (ESI) calculated for C$_{25}$H$_{36}$N$_2$O$_{12}$ 555.2190, found 555.2188 [M + H]$^+$. 

**Ac 3-O-Deoxy glucoBox (23)**

![Chemical structure of Ac 3-O-Deoxy glucoBox (23)](image-url)
The acetoformic anhydride necessary for the 3-O-formylation was prepared by stirring 1 eq. of acetic anhydride and 1.5 eq. of formic acid at 60 °C for 2 h. Then, the gluco-configured bis(amide) 24 (250 mg, 260 μmol) was dissolved in pyridine (15 mL) and a catalytic amount of DMAP added. The reaction mixture was cooled to –20 °C and acetoformic anhydride (310 mg, 3.50 mmol) added dropwise. The reaction mixture was subsequently stirred for 1 h at –20 °C (TLC: PE/EtOAc 1:1). The solvent was removed under reduced pressure and the residue twice co-evaporated with toluene (20 mL). The residue was purified by flash chromatography on silica gel (eluent: PE/EtOAc 2:1) to yield 25 (264 mg, 340 μmol, 98%) as a colourless foam.

$R_f 0.53 \ (1:1 \ \text{PE/EtOAc}); \ \left[\alpha\right]_\text{D}^{20} = -91.6 \ (c = 1.16, \ \text{CHCl}_3); \ ^1\text{H NMR} \ (\text{CDCl}_3, 400 \ \text{MHz}): \ \delta = 8.12 \ (s, 2H, \text{OC(O})H), 7.42–7.44 \ (m, 4H, \text{Ph}), 7.31-7.36 \ (m, 6H, \text{Ph}), 6.69 \ (d, 2H, J_{2,NH} = 9.2 \ Hz, \text{NH}), 5.50 \ (s, 2H, \text{CHPh}), 5.46 \ (dd \approx t, 2H, J_{2,3} \approx J_{3,4} = 9.56 \ Hz, \text{H-3}), 4.77 \ (d, 2H, J_{1,2} = 10.2 \ Hz, \text{H-1}), 4.33 \ (dd, 2H, J_{5,6} = 5.1 \ Hz, J_{6,6} = 10.2 \ Hz, \text{H-6}), 4.17 \ (dd, 2H, J_{1,2} = 10.2 \ Hz, J_{2,3} = 9.5 \ Hz, \text{H-2}), 3.73-3.79 \ (m, 4H, \text{H-4}, \text{H-6}'), 3.58 \ (ddd \approx dt, 2H, J_{4,5} \approx J_{5,6} = 9.9 \ Hz, J_{5,6} = 5.1 \ Hz, \text{H-5}), 2.62–2.76 \ (m, 4H, \text{SCH}_2\text{CH}_3), 1.38 \ [s, 6H, (\text{CH}_3)_2\text{C}], 1.24 \ (t, 6H, J = 7.5 \ Hz, \text{SCH}_2\text{CH}_3) \ \text{ppm}; \ ^{13}\text{C NMR} \ (\text{CDCl}_3, 100 \ \text{MHz}): \ \delta = 173.4 \ (\text{C, CONH}), 161.4 \ (\text{CH, OC(O})H), 136.6 \ (\text{C, Ph}), 129.1, 128.2, 126.1 \ (\text{CH, Ph}), 101.5 \ (\text{CH, PhCH}), 84.2 \ (\text{CH, C-1}), 78.3 \ (\text{CH, C-4}), 73.1 \ (\text{CH, C-3}), 70.4 \ (\text{CH, C-5}), 68.4 \ (\text{CH}_2, \text{C-6}), 53.4 \ (\text{CH, C-2}), 50.6 \ [\text{C, (CH}_3)_2\text{C}], 24.2 \ [\text{CH}_3, (\text{CH}_3)_2\text{C}], 24.0
(CH₂, SCH₂CH₃), 14.8 (CH₃, SCH₂CH₃) ppm; **HRMS** (ESI): calculated for C₃₇H₄₇N₂O₁₂NaS₂ 775.2570, found 775.2579 [M + H]⁺.

**3-O-Formyl glucoBox (26)**

![Chemical structure of 3-O-Formyl glucoBox (26)](attachment:image.png)

A mixture of the 3-O-formylated bis(amide) 25 (410 mg, 530 μmol) and MS 4 Å (400 mg) in dry CH₂CH₂ (20 mL) was stirred for 1 h under a nitrogen atmosphere. NIS (290 mg, 1.27 mmol) was added, and the mixture cooled to −30 °C. Then, TfOH (6.5 μL, 70 μmol) was added, and the mixture stirred for 1 h at −30 °C. The reaction was quenched with Et₃N (400 μL), filtered through Celite®, diluted with CH₂Cl₂, washed successively with saturated aqueous NaHCO₃ solution and aqueous sodium thiosulfate solution (3 M), and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel (eluent: EtOAc) to yield 26 (290 mg, 456 μmol, 85%) as a colourless solid.

**R** f 0.29 (EtOAc); [α]D²⁰ = −3.49 (c = 0.93, CHCl₃); **¹H NMR** (CDCl₃, 400 MHz): δ = 8.12 (s, 2H, OC(O)H), 7.42−7.46 (m, 4H, Ph), 7.32−7.36 (m, 6H, Ph), 6.01 (d, 2H, J₁,₂ = 7.5 Hz, H-1), 5.52 (s, 2H, CHPh), 5.26 (dd, 2H, J₂,₃ = 3.4 Hz, J₃,₄ = 7.1 Hz, H-3), 4.38 (dd, 2H, J₅,₆ = 4.7 Hz, J₆,₆´ = 10.2 Hz, H-6), 4.16 (dd, 2H, J₁,₂ = 7.5 Hz, J₂,₃ = 3.4 Hz, H-2), 3.73−3.84 (m, 4H, H-4, H-5), 3.65 (dd ≈ t, 2H, J₅,₆´ ≈ J₆,₆´ = 9.9 Hz, H-6´), 1.53 [s, 6H, (CH₃)$_2$C] ppm; **¹³C NMR** (CDCl₃, 100 MHz): δ = 169.7 (C, O–C=N), 160.0 (CH, OC(O)H), 136.6 (C, Ph), 129.1, 128.2, 126.0 (CH, Ph), 101.9 (CH, PhCH), 101.5 (CH, C-1), 77.8 (CH, C-4), 74.1 (CH, C-3), 68.4 (CH₂, C-6), 67.2 (CH, C-2), 20
63.0 (CH, C-5), 39.2 [C, (CH₃)₂C], 23.2 [CH₃, (CH₃)₂C ppm; **HRMS** (ESI): calculated for C₃₅H₃₅N₂O₁₂ 651.2190, found 701.651.2178 [M + H]⁺.

**Determination of enantiomeric excesses by gas chromatography on a chiral stationary phase:** A racemic sample of the product was analysed by GC on the chiral stationary phase to obtain the retention times of both enantiomers. Then an enantiomerically enriched sample was injected and the enantiomeric excess was determined from the resulting chromatogram by peak integration.

**Analytical data for the cyclopropanation products**

Absolute configurations were assigned by the sign of the optical rotation of the respective compound and comparison with literature data.

**Ethyl (1S,2S)-2-phenylcyclopropanecarboxylate** (*trans* 6) [1]

[α]₀²⁰ = +223 (c = 1.0, CHCl₃); **¹H NMR** (CDCl₃, 400 MHz): δ = 7.07–7.28 (m, 5H, Ph), 4.15 (q, 2H, J = 7.1 Hz, OCH₂CH₃), 2.50 (ddd, 1H, J = 4.2, 6.5, 9.3 Hz, PhCH), 1.89 (ddd, 1H, J = 4.2, 5.3, 8.4 Hz, CHCO₂Et), 1.58 (ddd, 1H, J = 4.6, 5.3, 9.3 Hz, CH₂), 1.29 (ddd, 1H, J = 4.7, 6.2, 8.6 Hz, CH₂), 1.27 (3H, t, J = 7.1 Hz, OCH₂CH₃) ppm; **¹³C NMR** (CDCl₃, 100 MHz): δ = 173.3 (C, CHCO₂Et), 140.0 (C, Ph), 128.4, 126.4, 126.0 (CH, Ph), 160.6 (CH₂, OCH₂CH₃), 26.1 (CH, CHPh), 24.1 (CH, CHCO₂Et), 17.0 (CH₂, CH₂), 4.2 (CH₃, OCH₂CH₃) ppm; **MS** (EI): calculated for C₁₈H₁₄O₂ 190.0994, found 190.0980 [M⁺].

**Retention times (GC):**

racemic mixture: \( t_R = 67.45 \text{ min}, t_R = 68.28 \text{ min} \)

product: \( t_R = 67.75 \text{ min (minor), } t_R = 68.36 \text{ min (major)}\).
Ethyl (1S,2R)-2-phenylcyclopropanecarboxylate (cis 6) [1]

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[a]_D^{20} = +26 \quad (c = 1.0, \text{CHCl}_3); \quad ^1H \text{ NMR (CDCl}_3, 400 \text{ MHz): } \delta = 7.17–7.26 \quad (m, 5\text{H, Ph}), 3.86 \quad (q, 2\text{H, } J = 7.2 \text{ Hz, OCH}_2\text{CH}_3), 2.54–2.61 \quad (m, 1\text{H, PhCH}), 2.07 \quad (ddd, 1\text{H, } J = 5.6, 7.8, 9.3 \text{ Hz, CHCO}_2\text{Et}), 1.70 \quad (ddd, 1\text{H, } J = 5.2, 5.5, 7.5 \text{ Hz, CH}_2), 1.26 \quad (ddd, 1\text{H, } J = 5.1, 7.9, 8.6 \text{ Hz, CH}_2), 0.96 \quad (t, 3\text{H, } J = 7.1 \text{ Hz, OCH}_2\text{CH}_3) \text{ ppm}; \quad ^{13}C \text{ NMR (CDCl}_3, 100 \text{ MHz,): } \delta = 171.0 \quad (\text{C, CHCO}_2\text{Et}), 136.5 \quad (\text{C, Ph}), 129.3, 127.8, 126.6 \quad (\text{CH, Ph}), 60.1 \quad (\text{CH}_2, \text{OCH}_2\text{CH}_3), 25.4 \quad (\text{CH, PhCH}), 21.8 \quad (\text{CH, CHCO}_2\text{Et}), 14.0 \quad (\text{CH}_3, \text{OCH}_2\text{CH}_3), 11.1 \quad (\text{CH}_2, \text{CH}_2) \text{ ppm; MS (El): calculated for C}_{12}\text{H}_{14}\text{O}_2 190.0994, found 190.0980 [M]^+.
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RetentionPolicy (GC):

racemic mixture: \( t_R = 63.53 \text{ min, } t_R = 65.67 \text{ min} \)

product: \( t_R = 63.62 \text{ min (major), } t_R = 65.89 \text{ min (minor).} \)

References

I. Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. J. Am. Chem. Soc. 1991, 113, 726–728. doi:10.1021/ja00002a080