2-O-Benzoyloxycarbonyl protected glycosyl donors: A revival of carbonate-mediated anchimeric assistance for diastereoselective glycosylation

Julia Weber, Dennis Svatunek, Simon Krauter, Gregor Tegl, Christian Hametner, Paul Kosma, and Hannes Mikula*

Table of Contents

1) General Remarks ........................................................................................................................................... S2
2) Experimental Procedures ................................................................................................................................. S3
3) NMR Spectra ................................................................................................................................................. S19
4) References ......................................................................................................................................................... S47

Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2019
1) General Remarks

All reactions were performed under an argon atmosphere. Anhydrous solvents were obtained using a PURESOLV system of *it-innovative technology*. Molecular sieves (3Å) were activated before use by heating at 200 °C under vacuum. Analytical thin layer chromatography (TLC) was performed using plates cut from aluminum sheets (silica gel 60 F-254). Visualization was achieved under a 254 nm or 365 nm UV light and by immersion in a solution of ceric ammonium molybdate in ethanol/sulfuric acid followed by heating with a heat gun. Chromatographic separation was carried out on a 3000 series HPLC-UV system (Dionex UltiMate 3000, Thermo Scientific) using a Chiralpak IB column (Cellulose tris-(3,5-dimethylphenylcarbamate) immobilized on 5 µm silica-gel, 4.6x250mm, Chiral Technologies Europe) and n-heptane/iPrOH gradient elution (flow rate: 1 mL/min, 0-4 min: 4% iPrOH, 4-25 min: 4 to 20% iPrOH linear gradient, 25-30 min: 20% iPrOH, 30-30.1 min: 20 to 4% iPrOH linear gradient, 30.1-35 min: 4% iPrOH). Preparative column chromatography was performed on a Büchi Sepacore Flash System (2 x Büchi Pump Module C-605, Büchi Pump Manager C-615, Büchi UV Photometer C-635, Büchi Fraction Collector C-660) or a Grace Reveleris Prep Purification System using silica gel 60 (40-63 µm) as obtained from Merck and distilled solvents. 1H and 13C NMR spectra were recorded on a Bruker DPX 200-MHz, an Avance DRX-400 MHz or an Avance IIIHD 600-MHz spectrometer equipped with a Prodigy BBO cryo probe (Bruker, Germany). Data were recorded and evaluated using TOPSPIN 3.5 (Bruker Biospin). Chemical shifts are reported in ppm (δ) relative to tetramethylsilane and calibrated using solvent residual peaks. Multiplicities are abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), b (broad signal). All chemicals were purchased either from ABCR (Germany) or Sigma-Aldrich (Austria/Germany). HR-MS analysis was carried out from methanol solutions (concentration: 10 ppm) by using an HTC PAL system autosampler (CTC Analytics AG, Zwingen, Switzerland), an Agilent 1100/1200 HPLC with binary pumps, degasser and column thermostat (Agilent Technologies, Waldbronn, Germany) and Agilent 6230 AJS ESI–TOF mass spectrometer (Agilent Technologies, Palo Alto, United States). 3,4,6-Tri-O-benzyl-1,2-O-(1-ethylthioethylidene)-α-D-glucopyranose (1)\(^1\), dimethyldioxirane (DMDO)\(^2\), methyl 2,3,4-tri-O-benzyl-1-O-β-D-glucopyranoside (20)\(^3-5\), and methyl 2,3,6-tri-O-benzyl-1-O-β-D-glucopyranoside (22)\(^6\) were synthesized following known procedures.
2) Experimental Procedures

a. Synthesis of 2-OH thioglucosides 6-9 applying the orthoester strategy

![Chemical structures](image)

Ethyl 2-O-acetyl-3,4,6-tri-O-benzyl-1-thio-β-D-glucoside (2)

To a solution of thioorthoester 1 (16 g, 29.8 mmol) in dry CH₂Cl₂ (150 mL) molecular sieve (3Å, 4 g) was added and the suspension was stirred at room temperature for 1 h. After cooling to 0 °C, TMSOTf (0.27 mL, 1.5 mmol) was added and stirring was continued at room temperature for 4 h. The reaction was quenched by addition of NEt₃ (4 mL) and the mixture was filtrated over Celite and concentrated under reduced pressure. The residue was purified by filtration over silica (hexanes/EtOAc gradient elution) to obtain 2 as a highly viscous oil (13.3 g, 83%); Rf 0.45 (hexanes/EtOAc = 5/1); ¹H NMR (200 MHz, CDCl₃) δ 7.41-7.26 (m, 15H), 5.15-5.05 (m, 1H), 4.88 (d, J = 11.1 Hz, 1H), 4.86 (d, J = 10.5 Hz, 1H), 4.76 (d, J = 11.2 Hz, 1H), 4.68 (d, J = 11.9 Hz, 1H), 4.64 (d, J = 10.9 Hz, 1H), 4.62 (d, J = 12.2 Hz, 1H), 4.43 (d, J = 10.0 Hz, 1H), 3.86-3.68 (m, 4H), 3.63-3.48 (m, 1H), 2.88-2.65 (m, 2H), 2.03 (s, 3H), 1.32 (t, J = 7.5 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 169.3 (s, 1C), 138.0 (s, 1C), 138.0 (s, 1C), 137.8 (s, 1C), 128.2 (d, 1C), 128.15 (d, 1C), 128.0 (d, 1C), 127.85 (d, 1C), 127.7 (d, 1C), 127.5 (d, 1C), 84.2 (d, 1C), 83.4 (d, 1C), 79.4 (d, 1C), 77.6 (d, 1C), 75.1 (t, 1C), 75.0 (t, 1C), 73.3 (t, 1C), 71.5 (d, 1C), 68.6 (t, 1C), 23.6 (t, 1C), 20.8 (q, 1C), 14.8 (q, 1C); NMR data matched that reported.[¹]

General procedure for the preparation of 2-OAc thioglucosides (compounds 3-5). To a solution of thioorthoester 1 (2.68 g, 5 mmol) in dry CH₂Cl₂ (80 mL) molecular sieve (3Å, 2 g) and thiol (R-SH) (40 mmol) were added. After stirring at room temperature for 30 min and subsequent cooling to 0 °C, TMSOTf (0.28 g, 1.25 mmol) was added and the reaction mixture was stirred at room temperature for 12 h. The reaction was quenched by addition of NEt₃ (0.8 mL) and the mixture was filtrated over Celite, washed with aq. NaOH (1%) and water. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes/EtOAc gradient elution + 0.1% NEt₃) to obtain the desired product.
p-Tolyl 2-O-acetyl-3,4,6-tri-O-benzyl-1-thio-β-D-glucoside (3)

3 was obtained as a white solid (2.40 g, 80%); Rf 0.64 (hexanes/EtOAc = 3/1); \(^1\)H NMR (200 MHz, CDCl\(_3\)) δ 7.53 (d, J = 8.2 Hz, 2H), 7.49-7.27 (m, 15H), 7.14 (d, J = 8.2 Hz, 2H), 5.15-5.04 (m, 1H), 4.92 (d, J = 11.6 Hz, 1H), 4.90 (d, J = 10.8 Hz, 1H), 4.78 (d, J = 10.6 Hz, 1H), 4.69 (d, J = 8.2 Hz, 1H), 4.66 (d, J = 10.10 Hz, 1H), 3.97-3.83 (m, 2H), 3.82-3.74 (m, 2H), 3.69-3.57 (m, 1H), 2.41 (s, 3H), 2.12 (s, 3H); \(^13\)C NMR (50 MHz, CDCl\(_3\)) δ 169.5 (s, 1C), 138.3 (s, 1C), 138.1 (s, 2C), 137.9 (s, 1C), 133.2 (d, 2C), 129.6 (d, 2C), 128.5 (d, 4C), 128.4 (d, 2C), 128.0 (d, 2C), 127.9 (d, 3C), 127.8 (d, 1C), 127.7 (d, 2C), 127.6 (d, 1C), 86.1 (d, 1C), 84.4 (d, 1C), 84.2 (d, 1C), 79.4 (d, 1C), 77.8 (d, 1C), 75.3 (t, 1C), 75.1 (t, 1C), 73.5 (t, 1C), 71.8 (d, 1C), 68.9 (t, 1C), 21.1 (q, 1C), 21.0 (q, 1C); NMR data matched that reported.[7]

1,3-Thiazolin-2-yl 2-O-acetyl-3,4,6-tri-O-benzyl-1-thio-β-D-glucoside (4)

4 was obtained as a white solid (2.13 g, 72%); Rf 0.40 (hexanes/EtOAc = 3/2); \(^1\)H NMR (200 MHz, CDCl\(_3\)) δ 7.41-7.13 (m, 15), 5.34 (d, J = 10.4 Hz, 1H), 5.20-5.07 (m, 1H), 4.84-4.50 (m, 6H), 4.29-4.08 (m, 2H), 3.88-3.67 (m, 4H), 3.67-3.56 (m, 1H), 3.35 (t, J = 8.1 Hz, 2H), 1.97 (s, 3H); \(^13\)C NMR (50 MHz, CDCl\(_3\)) δ 169.6 (s, 1C), 163.6 (s, 1C), 138.1 (s, 2C), 137.9 (s, 1C), 128.5 (d, 2C), 128.4 (d, 2C), 128.3 (d, 2C), 128.0 (d, 2C), 127.9 (d, 3C), 127.8 (d, 1C), 127.6 (d, 1C), 85.3 (d, 1C), 83.8 (d, 1C), 83.3 (d, 1C), 79.7 (d, 1C), 77.7 (d, 1C), 75.3 (t, 1C), 75.1 (t, 1C), 73.4 (t, 1C), 71.4 (d, 1C), 68.4 (t, 1C), 64.2 (t, 1C), 35.1 (t, 1C), 20.9 (q, 1C); NMR data matched that reported.[8]

2-Pyrimidyl 2-O-acetyl-3,4,6-tri-O-benzyl-1-thio-β-D-glucoside (5):

5 was obtained as a yellowish solid (2.12 g, 72%); Rf 0.44 (hexanes/EtOAc = 3/2); \(^1\)H NMR (200 MHz, (CD\(_3\))\(_2\)CO) δ 8.61 (d, J = 4.9 Hz, 2H), 7.36-7.24 (m, 15H), 7.21 (t, J = 4.9 Hz, 1H), 5.78 (d, J = 10.7 Hz, 1H), 5.12 (dd, J = 10.6, 9.0 Hz, 1H), 4.88 (d, J = 11.4 Hz, 1H), 4.86 (d, J = 10.9 Hz, 1H), 4.77 (d, J = 11.4, 1H), 4.68 (d, J = 10.9 Hz, 1H), 4.57 (d, J = 12.1 Hz, 1H), 4.49 (d, J = 12.1 Hz, 1H), 4.00-3.89 (m, 1H), 3.82-3.69 (m, 4H), 1.96 (s, 3H); \(^13\)C NMR (50 MHz, (CD\(_3\))\(_2\)CO) δ 170.4 (s, 1C), 170.1 (s, 1C), 158.7 (d, 2C), 139.6 (s, 1C), 139.53 (s, 1C), 139.47 (s, 1C), 129.13 (d, 2C), 129.11 (d, 2C), 129.0 (d, 2C), 129.8 (d, 2C), 128.6 (d, 2C), 128.5 (d, 2C), 128.42 (d, 1C), 128.40 (d, 1C), 128.2 (d, 1C), 118.8 (d, 1C), 85.2 (d, 1C), 82.7 (d, 1C), 80.4 (d, 1C), 78.9 (d, 1C), 75.8 (t, 1C), 75.5 (t, 1C), 73.6 (t, 1C), 71.9 (d, 1C), 69.7 (t, 1C), 21.0 (q, 1C); HRMS calcd for C\(_{33}\)H\(_{34}\)N\(_2\)NaO\(_6\)S\(^+\) [M+Na]\(^+\) 609.2030, found 609.2042.
**General procedure for de-acetylation of 2-OAc thioglycosides.** To a solution/suspension of the 2-OAc thioglycoside (1 mmol) in dry MeOH (5 mL) K₂CO₃ (28 mg, 0.2 mmol) was added and the reaction mixture was stirred at room temperature until the starting material had completely dissolved (up to 72 h). The reaction mixture was quenched by addition of acidic cation exchange resin (Amberlite® IR120H), filtrated and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes/EtOAc gradient elution + 0.1% NEt₃) to obtain the desired product.

**Ethyl 3,4,6-tri-O-benzyl-1-thio-β-D-glucoside (6)**

6 was obtained as a white solid (420 mg, 85%); Rₚ 0.21 (hexanes/EtOAc = 4/1); ¹H NMR (200 MHz, CDCl₃) δ 7.31-7.16 (m, 13H), 7.11-7.08 (m, 2H), 4.86 (d, J = 11.3 Hz, 1H), 4.77 (d, J = 11.3 Hz, 1H), 4.76 (d, J = 12.1 Hz, 1H), 4.58-4.42 (m, 3H), 4.22 (d, J = 9.1 Hz, 1H), 3.67 (dd, J = 1.8, 10.9 Hz, 1H), 3.61 (dd, J = 4.5, 10.9 Hz, 1H), 3.56 - 3.39 (m, 4H), 2.70-2.60 (m, 2H), 1.24 (t, J = 4.0 Hz, 3H); ¹³C NMR (50 MHz, CDCl₃) δ 138.7 (s, 1C), 138.3 (s, 1C), 138.1 (s, 1C), 128.6 (d, 2C), 128.5 (d, 2C), 128.4 (d, 2C), 128.1 (d, 2C), 128.0 (d, 2C), 127.9 (d, 1C), 127.8 (d, 3C), 127.7 (d, 1C), 86.2 (d, 1C), 86.1 (d, 1C), 79.5 (d, 1C), 77.5 (d, 1C), 75.3 (t, 1C), 75.2 (t, 1C), 73.5 (t, 1C), 73.4 (d, 1C), 69.1 (t, 1C), 24.4 (t, 1C), 15.5 (q, 1C); NMR data matched that reported.[9]

**p-Tolyl 3,4,6-tri-O-benzyl-1-thio-β-D-glucoside (7)**

7 was obtained as a white solid (523 mg, 94%); Rₚ 0.49 (hexanes/EtOAc = 4/1); ¹H NMR (200 MHz, CDCl₃) δ 7.50 (d, J = 8.2 Hz, 2H), 7.38-7.19 (m, 15H), 7.07 (d, J = 7.8 Hz, 2H), 4.97-4.79 (m, 3H), 4.67-4.50 (m, 3H), 4.45 (d, J = 9.4 Hz, 1H), 3.81-3.75 (m, 2H), 3.64-3.40 (m, 4H), 2.33 (s, 3H), 1.97 (bs, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 138.6 (s, 1C), 138.6 (s, 1C), 138.6 (s, 1C), 138.5 (s, 1C), 138.2 (s, 1C), 133.8 (d, 2C), 129.9 (d, 2C), 128.60 (d, 2C), 128.56 (d, 2C), 128.5 (d, 2C), 128.1 (d, 2C), 128.08 (d, 2C), 127.9 (d, 2C), 127.8 (d, 2C), 127.7 (d, 1C), 127.6 (s, 1C), 88.2 (d, 1C), 86.0 (d, 1C), 79.6 (d, 1C), 77.5 (d, 1C), 75.5 (t, 1C), 75.2 (t, 1C), 73.6 (t, 1C), 72.6 (d, 1C), 69.1 (t, 1C), 21.3 (q, 1C); NMR data matched that reported.[7]

**1,3-Thiazolin-2-yl 3,4,6-tri-O-benzyl-1-thio-β-D-glucoside (8):**

8 was obtained as a white solid (430 mg, 78%); Rₚ 0.27 (hexanes/EtOAc = 3/2); ¹H NMR (200 MHz, CDCl₃) δ 7.31-7.02 (m, 15H), 5.08 (d, J = 9.2 Hz, 1H), 4.90 (d, J = 11.2 Hz, 1H), 4.75 (d, J = 11.3 Hz, 1H), 4.74 (d, J = 10.9 Hz, 1H), 4.53 (d, J = 12.1 Hz, 1H), 4.46 (d, J = 10.9 Hz, 1H), 4.42 (d, J = 12.1 Hz, 1H), 4.13-4.01 (m, 2H), 3.72-3.44 (m, 6H), 3.22 (t, J = 8.1 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 164.5 (s, 1C), 137.6 (s, 1C), 137.1 (s, 1C), 137.0 (s, 1C), 127.4 (d, 2C), 127.33 (d, 2C), 127.30 (d, 2C), 126.94 (d, 2C), 126.87 (d, 2C), 126.8 (d, 2C), 126.7 (d, 2C), 126 (d, 1C), 85.5 (d, 1C), 84.5 (d, 1C), 78.7 (d, 1C), 75.9 (d, 1C), 74.4 (t, 1C), 74.0 (t, 1C), 73.3 (d, 1C), 72.4 (t, 1C), 67.6 (t, 1C), 62.8 (t, 1C), 34.3 (t, 1C); NMR data matched that reported.[8]
2-Pyrimidyl 3,4,6-tri-O-benzyl-1-thio-β-D-glucoside (9)

9 was obtained as a yellowish solid (479 mg, 88%); Rt 0.21 (hexanes/EtOAc = 3/2); ¹H NMR (600 MHz, CDCl₃) δ 8.51 (d, J = 4.9 Hz, 2H), 7.43-7.41 (m, 2H), 7.36-7.26 (m, 11H), 7.24-7.22 (m, 2H), 6.96 (t, J = 5.0 Hz, 1H), 5.65 (d, J = 9.8 Hz, 1H), 5.04 (d, J = 10.8 Hz, 1H), 4.93 (d, J = 10.8 Hz, 1H), 4.90 (d, J = 12.2 Hz, 1H), 4.62 (d, J = 10.8 Hz, 1H), 4.53 (d, J = 12.2 Hz, 1H), 3.82-3.72 (m, 6H); ¹³C NMR (50 MHz, CDCl₃) δ 170.3 (s, 1C), 157.6 (d, 2C), 138.7 (s, 1C), 138.3 (s, 1C), 128.3 (d, 2C), 128.2 (s, 1C), 128.5 (d, 2C), 128.4 (d, 2C), 128.3 (d, 2C), 128.02 (d, 2C), 127.96 (d, 2C), 127.9 (d, 2C), 127.7 (d, 2C), 127.6 (d, 1C), 117.5 (d, 1C), 86.6 (d, 1C), 84.6 (d, 1C), 79.6 (d, 1C), 77.4 (d, 1C), 75.4 (t, 1C), 75.0 (t, 1C), 73.4 (t, 1C), 73.3 (d, 1C), 68.8 (t, 1C); HRMS calcd for C₃₁H₃₂N₂NaO₅S⁺ [M+Na⁺] 567.1924, found 567.1909.

b. p-Tolyl 3,4,6-tri-O-benzyl-1-thio-β-D-glucoside (7) via DMDO Epoxidation of 10

3,4,6-Tri-O-benzyl-D-glucal (10, 1.25 g, 3 mmol) was reacted with DMDO (78.7 mL, 0.046 M in acetone) at 0 °C for 30 min. The solvent was evaporated and the residue was dissolved in dry acetone (100 mL). After addition of p-thiocresol (HSTol, 1.86 g, 15 mmol), K₂CO₃ (4.15 g, 30 mmol) and 18-crown-6 (80 mg, 0.3 mmol), the reaction mixture was heated to reflux for 2 h, subsequently filtrated and evaporated. The residue was purified by column chromatography (hexanes/EtOAc gradient elution) to yield 7 as a white solid (0.84 g, 50%); Rt 0.49 (hexanes/EtOAc = 4/1); ¹H NMR (200 MHz, CDCl₃) δ 7.50 (d, J = 8.2 Hz, 2H), 7.38-7.19 (m, 15H), 7.07 (d, J = 7.8 Hz, 2H), 4.97-4.79 (m, 3H), 4.67-4.50 (m, 3H), 4.45 (d, J = 9.4 Hz, 1H), 3.81-3.75 (m, 1H), 3.64-3.40 (m, 4H), 2.33 (s, 3H), 1.97 (bs, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 138.6 (s, 1C), 138.6 (s, 1C), 138.5 (d, 2C), 133.8 (d, 2C), 129.9 (d, 2C), 128.60 (d, 2C), 128.56 (d, 2C), 128.5 (d, 2C), 128.1 (d, 2C), 128.08 (d, 2C), 127.9 (d, 2C), 127.8 (d, 2C), 127.7 (d, 1C), 127.6 (s, 1C), 88.2 (d, 1C), 86.0 (d, 1C), 79.6 (d, 1C), 77.5 (d, 1C), 75.5 (t, 1C), 75.2 (t, 1C), 73.6 (t, 1C), 72.6 (d, 1C), 69.1 (t, 1C), 21.3 (q, 1C); NMR data matched that reported.[⁷]
c. Introduction of benzylxycarbonyl (Cbz) at O-2

General procedure. To a solution of the 2-OH thioglucoside (0.5 mmol) in dry CH₂Cl₂ (5 mL), cooled to 0 °C, TMEDA (58 mg, 0.5 mmol) was added, followed by Cbz-Cl (127 mg, 0.75 mmol). The reaction mixture was stirred for 48 h, poured into water (20 mL) and extracted with CH₂Cl₂. The combined organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes/EtOAc gradient elution) to yield the desired Cbz-protected thioglucoside.

Ethyl 3,4,6-tri-O-benzyl-2-O-benzylxycarbonyl-1-thio-β-D-glucoside (11)

11 was obtained as a white solid (420 mg, 45%); Rf 0.42 (hexanes/EtOAc = 6/1); ¹H NMR (600 MHz, CDCl₃) δ 7.30-7.27 (m, 2H), 7.26-7.23 (m, 6H), 7.22-7.17 (m, 8H), 7.15-7.12 (m, 2H), 7.11-7.08 (m, 2H), 5.11 (s, 2H), 4.79-4.75 (m, 1H), 4.72 (d, J = 10.9 Hz, 1H), 4.69 (d, J = 11.0 Hz, 1H), 4.62 (d, J = 11.0 Hz, 1H), 4.53 (d, J = 12.2 Hz, 1H), 4.50 (d, J = 10.9 Hz, 1H), 4.47 (d, J = 12.1 Hz, 1H), 4.34 (d, J = 10.0 Hz, 1H), 3.68 (dd, J = 11.0, 2.1 Hz, 1H), 3.66-3.59 (m, 3H), 3.42 (ddd, J = 9.2, 4.4, 1.8 Hz, 1H), 2.70-2.60 (m, 2H), 1.19 (t, J = 7.5 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 154.4 (s, 1C), 138.2 (s, 1C), 138.0 (s, 1C), 137.9 (s, 1C), 135.1 (s, 1C), 128.6 (d, 1C), 128.6 (d, 1C), 128.4 (d, 3C), 128.37 (d, 3C), 128.3 (d, 2C), 128.0 (d, 2C), 127.9 (d, 2C), 127.8 (d, 2C), 127.71 (d, 2C), 127.69 (d, 1C), 127.6 (d, 1C), 84.3 (d, 1C), 83.4 (d, 1C), 79.5 (d, 1C), 77.7 (d, 1C), 76.3 (d, 1C), 75.4 (t, 1C), 75.1 (t, 1C), 73.5 (t, 1C), 70.0 (t, 1C), 68.8 (t, 1C), 23.8 (t, 1C), 14.9 (q, 1C); HRMS calcd for C₃₇H₄₀NaO₇S⁺ [M+Na⁺] 651.2387, found 651.2402.

p-Toly 3,4,6-tri-O-benzyl-2-O-benzylxycarbonyl-1-thio-β-D-glucoside (12)

12 was obtained as a white solid (523 mg, 33%); Rf 0.47 (hexanes/EtOAc = 6/1); ¹H NMR (400 MHz, CD₂Cl₂) δ 7.43-7.34 (m, 11H), 7.33-7.25 (m, 7H), 7.24-7.17 (m, 4H), 7.07 (d, J = 8.2 Hz, 2H), 5.23 (d, J = 12.1 Hz, 1H), 5.16 (d, J = 12.1, 1H), 4.78 (t, J = 11.1 Hz, 2H), 4.74 (dd, J = 9.9, 8.8 Hz, 1H), 4.66 (d, J = 11.3 Hz, 1H), 4.62 (d, J = 10 Hz, 1H), 4.61-4.50 (m, 3H), 3.77 (dd, J = 10.9, 2.0 Hz, 1H), 3.75-3.69 (m, 2H), 3.66 (t, J = 9.2 Hz, 1H), 3.55-3.45 (m, 1H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 154.7 (s, 1C), 138.7 (s, 1C), 138.6 (s, 1C), 138.52 (s, 1C), 138.50 (s, 1C), 135.8 (s, 1C), 133.3 (d, 2C), 130.0 (d, 2C), 129.2 (s, 1C), 129.0 (d, 1C), 128.9 (d, 1C), 128.69 (d, 4C), 128.67 (d, 2C), 128.6 (d, 2C), 128.4 (d, 2C), 128.2 (d, 2C), 128.13 (d, 1C), 128.10 (d, 3C), 128.0 (d, 1C), 127.9 (d, 1C), 86.5 (d, 1C), 84.6 (d, 1C), 79.6 (d, 1C), 77.9 (d, 1C), 76.6 (d, 1C), 75.7 (t, 1C), 75.3 (t, 1C), 73.7 (t, 1C), 70.3 (t, 1C), 69.3 (t, 1C), 21.2 (q, 1C); HRMS calcd for C₄₂H₄₂NaO₇S⁺ [M+Na⁺] 713.2543, found 713.2570.
1,3-Thiazolin-2-yl 3,4,6-tri-O-benzyl-2-O-benzyl oxycarbonyl-1-thio-β-D-glucoside (13)

13 was obtained as a white solid (430 mg, 53%); Rf: 0.48 (hexanes/EtOAc = 3/2); 1H NMR (200 MHz, (CD3)2CO) δ 7.43-7.23 (m, 20H), 5.56 (d, J = 10.6 Hz, 1H), 5.23 (s, 2H), 4.90-4.80 (m, 3H), 4.72 (d, J = 11.3 Hz, 1H), 4.68 (d, J = 10.6 Hz, 1H), 4.62 (d, J = 11.8 Hz, 1H), 4.56 (d, J = 11.8 Hz, 1H), 4.24-4.12 (m, 2H), 3.94 (t, J = 8.9 Hz, 1H), 3.84-3.68 (m, 4H), 3.44 (t, J = 8.2 Hz, 2H); 13C NMR (50 MHz, (CD3)2CO) δ 162.3 (s, 1C), 155.3 (s, 1C), 139.5 (s, 1C), 139.4 (s, 1C), 139.3 (s, 1C), 136.5 (s, 1C), 129.4 (d, 2C), 129.3 (d, 1C), 129.1 (d, 6C), 129.0 (d, 2C), 128.7 (d, 2C), 128.5 (d, 4C), 128.4 (d, 1C), 128.3 (d, 1C), 128.2 (d, 1C), 128.1 (d, 2C), 127.6 (d, 1C), 127.5 (d, 1C), 127.4 (d, 1C), 127.3 (d, 1C), 118.0 (d, 1C), 84.2 (d, 1C), 81.6 (d, 1C), 79.5 (d, 1C), 77.8 (d, 1C), 75.6 (d, 1C), 75.0 (t, 1C), 74.6 (t, 1C), 72.7 (t, 1C), 69.6 (t, 1C), 68.8 (t, 1C); HRMS calcd for C38H39NNaO7S2 [M+Na]+ 708.2060, found 708.2078.

2-Pyrimidyl 3,4,6-tri-O-benzyl-2-O-benzyl oxycarbonyl-1-thio-β-D-glucoside (14)

14 was obtained as a yellowish solid (479 mg, 61%); Rf: 0.66 (hexanes/EtOAc = 3/2); 1H NMR (400 MHz, (CD3)2CO) δ 8.48 (d, J = 4.8 Hz, 2H), 7.24-7.10 (m, 20H), 7.08 (t, J = 5.4 Hz, 1H), 5.70 (d, J = 10.7 Hz, 1H), 5.08 (d, J = 12.2 Hz, 1H), 5.04 (d, J = 12.2 Hz, 1H), 4.81 (dd, J = 10.3, 9.3 Hz, 1H), 4.72 (d, J = 10.7 Hz, 1H), 4.70 (d, J = 11.0 Hz, 1H), 4.59 (d, J = 10.9 Hz, 1H), 4.54 (d, J = 11.1 Hz, 1H), 4.42 (d, J = 11.9 Hz, 1H), 4.36 (d, J = 12.1 Hz, 1H), 3.84 (t, J = 8.3 Hz, 1H), 3.66-3.56 (m, 4H); 13C NMR (100 MHz, (CD3)2CO) δ 169.4 (s, 1C), 157.9 (d, 2C), 154.5 (s, 1C), 138.6 (d, 1C), 138.5 (d, 1C), 138.4 (d, 1C), 136.6 (d, 1C), 128.5 (d, 2C), 128.3 (d, 1C), 128.2 (d, 1C), 128.1 (d, 2C), 128.0 (d, 1C), 127.9 (d, 2C), 127.7 (d, 2C), 127.6 (d, 2C), 127.54 (d, 1C), 127.49 (d, 1C), 127.3 (d, 1C), 118.0 (d, 1C), 84.2 (d, 1C), 81.6 (d, 1C), 79.5 (d, 1C), 77.8 (d, 1C), 75.6 (d, 1C), 75.0 (t, 1C), 74.6 (t, 1C), 72.7 (t, 1C), 69.6 (t, 1C), 68.8 (t, 1C); HRMS calcd for C38H38N2NaO7S+ [M+Na]+ 701.2292, found 701.2306.
d. Synthesis of glucosyl imidates

To a solution of glucosyl donor 11 (300 mg, 0.477 mmol) in MeCN/H\(_2\)O (9:1, 4 mL), N-iodosuccinimide (215 mg, 0.954 mmol) was added. The reaction mixture was stirred for 5 min at rt, quenched with an aqueous saturated solution of Na\(_2\)S\(_2\)O\(_3\), diluted with CH\(_2\)Cl\(_2\), and washed with Na\(_2\)S\(_2\)O\(_3\)-solution and brine. The organic phases were combined, dried over Na\(_2\)SO\(_4\) and concentrated. The residue was purified by column chromatography (hexanes/ EtOAc, gradient elution) to obtain the desired product 15 as a mixture of α,β-isomers (~4:1 as determined by NMR, 235 mg, 85\%).

**1H NMR (400 MHz, CD\(_2\)Cl\(_2\))**: δ 7.41-7.32 (m, 9H), 7.32-7.25 (m, 8H), 7.24-7.18 (m, 3H), 5.41 (d, J = 3.5 Hz, 1H), 5.18 (d, J = 12.1 Hz, 1H), 5.14 (d, J = 12.1 Hz, 1H), 4.86-4.78 (m, 1H), 4.77-4.73 (m, 2H), 4.73-4.70 (m, 1H), 4.56 (d, J = 11.3 Hz, 1H), 4.52 (q, J = 23.9, 11.9 Hz, 2H), 4.09-3.99 (m, 2H), 3.74-3.66 (m, 2H), 3.62 (dd, J = 9.76, 8.96 Hz, 1H); 13C NMR (100 MHz, CD\(_2\)Cl\(_2\)): α-(15): δ 154.93 (s, 1C), 138.86 (s, 1C), 138.67 (s, 1C), 138.46 (s, 1C), 135.66 (s, 1C), 128.96 (d, 1C), 128.89 (d, 1C), 128.72 (d, 2C), 128.67 (d, 2C), 128.63 (d, 2C), 128.59 (d, 2C), 128.28 (d, 2C), 128.27 (d, 2C), 128.21 (d, 3C), 128.04 (d, 2C), 127.93 (d, 1C), 90.74 (d, 1C), 79.98 (d, 1C), 78.36 (d, 1C), 77.51 (d, 1C), 75.77 (t, 1C), 75.29 (t, 1C), 73.62 (t, 1C), 70.70 (d, 1C), 70.21 (t, 1C), 69.21 (t, 1C); β-(15): δ 155.52 (s, 1C), 138.57 (s, 1C), 138.46 (s, 1C), 138.37 (s, 1C), 135.60 (s, 1C), 128.96 (d, 1C), 128.89 (d, 1C), 128.72 (d, 2C), 128.67 (d, 2C), 128.63 (d, 2C), 128.59 (d, 2C), 128.28 (d, 2C), 128.27 (d, 2C), 128.21 (d, 3C), 128.04 (d, 2C), 127.93 (d, 1C), 95.61 (d, 1C), 82.79 (d, 1C), 79.76 (d, 1C), 78.07 (d, 1C), 75.64 (t, 1C), 75.29 (t, 1C), 73.76 (t, 1C), 70.70 (d, 1C), 70.41 (t, 1C), 69.09 (t, 1C); HRMS calcd for C\(_{35}\)H\(_{38}\)NaO\(_8\)\([M+Na]^{+}\) 607.2302, found 607.2301.
3,4,6-Tri-O-benzyl-2-O-benzylxycarbonyl-α-0-glucopyranosyl trichloroacetimidate (16)

To a solution of compound 15 (994 mg, 1.7 mmol) in CH₂Cl₂ (25 mL), trichloroacetonitrile (736 mg, 5.1 mmol), and DBU (39 mg, 255 µmol) were added. The reaction mixture was stirred at room temperature for 2 h and then concentrated. The residue was purified by column chromatography (hexanes/ EtOAc, gradient elution) to afford 16 as a colorless viscous liquid (220 mg, 18%). ¹H NMR (200 MHz, (CD₃)₂CO) δ 9.31 (s, 1H), 7.44–7.19 (m, 20H), 6.62 (d, J = 3.5 Hz, 1H), 5.20 (s, 2H), 4.96–4.84 (m, 2H), 4.56 (d, J = 4.5 Hz, 2H), 4.76–4.61 (m, 1H), 4.60–4.48 (m, 2H), 4.19–3.99 (m, 2H), 3.92–3.65 (m, 3H); ¹³C NMR (50 MHz, (CD₃)₂CO) δ 160.72 (s, 1C), 155.31 (s, 1C), 139.42 (s, 1C), 139.34 (s, 1C), 139.28 (s, 1C), 136.53 (s, 1C), 129.40 (d, 2C), 129.28 (d, 1C), 129.11 (d, 4C), 129.08 (d, 3C), 129.06 (d, 3C), 128.84 (d, 2C), 128.65 (d, 1C), 128.56 (d, 1C), 128.47 (d, 1C), 128.37 (d, 1C), 128.30 (d, 1C), 128.24 (d, 1C), 94.24 (d, 1C), 80.46 (d, 1C), 77.94 (d, 1C), 77.06 (d, 1C), 75.95 (t, 1C), 75.76 (t, 1C), 74.55 (d, 1C), 73.74 (t, 1C), 70.50 (t, 1C), 69.16 (t, 1C); ESI-MS calcd for C₃₇H₅₀Cl₅NaOs⁺ [M+Na]⁺ 778.2598, found 778.2607.

3,4,6-Tri-O-benzyl-2-O-benzylxycarbonyl-α,β-0-glucopyranosyl-1-(N-phenyl)-2,2,2-trifluoroacetimidate (18)

To a solution of compound 15 (20 mg, 34 µmol) in CH₂Cl₂ (1 mL), N-phenyltrifluoroacetimidoyl chloride[¹⁰] (63 mg, 303 µmol) and DBU (1.5 mg, 10 µmol) were added at -15 °C and then concentrated. The residue was purified by column chromatography (hexanes/ EtOAc, gradient elution) to afford 18 as a colorless viscous liquid (21 mg, 81%). ¹H NMR (600 MHz, CD₂Cl₂): δ 7.42–7.26 (m, 18H), 7.26–7.19 (m, 4H), 7.15–7.09 (m, 1H), 6.86–6.77 (m, 2H), 6.10–5.52 (m, 1H), 5.18 (q, J = 23.4; 12.0 Hz, 2H), 5.05–4.96 (m, 1H), 4.81 (t, J = 11.8 Hz, 2H), 4.69 (d, J = 11.4 Hz, 1H), 4.60 (d, J = 11.8 Hz, 1H), 4.59 (d, J = 10.9 Hz, 1H), 4.54 (d, J = 11.8 Hz, 1H), 3.81 (t, J = 9.3 Hz, 1H), 3.78–3.68 (m, 3H), 3.66–3.39 (m, 1H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 154.52 (s, 1C), 143.59 (s, 1C), 138.44 (s, 1C), 138.35 (s, 1C), 138.34 (s, 1C), 135.50 (s, 1C), 129.16 (d, 2C), 129.00 (d, 3C), 128.73 (d, 6C), 128.67 (d, 2C), 128.37 (d, 2C), 128.25 (d, 2C), 128.20 (d, 3C), 128.14 (d, 2C), 128.05 (d, 2C), 124.81 (d, 1C), 119.59 (d, 1C), 82.61 (d, 1C), 77.52 (d, 1C), 76.77 (d, 1C), 76.26 (d, 1C), 75.65 (t, 1C), 75.38 (t, 1C), 73.69 (t, 1C), 70.55 (t, 1C), 68.46 (t, 1C); HRMS calcd for C₃₃H₄₀F₃N₃NaOs⁺ [M+Na⁺] 778.2598, found 778.2607.
e. Glycosylation reactions (analytical and preparative)

General procedure for glycosylation reactions with thioglucosyl donors

To a solution of the glucosyl donor (0.05 mmol) and the acceptor (0.05 or 0.075 mmol) in dry CH₂Cl₂ (1 mL) molecular sieve (3Å, 100 mg) was added and the reaction mixture was stirred for 14 h at room temperature. After cooling to the appropriate temperature, activator (see Table S1) was added and stirring was continued in the dark for 24 h. Samples of the reaction mixture (100 µl) were taken after 3 h and 24 h and diluted with 1.9 mL CH₂Cl₂. To quench the reaction, the solution was washed with 1 mL of aqueous saturated NaHCO₃ or Na₂SO₃ solution, and 0.5 mL water. The organic layer was separated, dried over Na₂SO₄ and concentrated. The residue was diluted in 3 mL acetonitrile and 1 mL was taken and filtered through a syringe filter. This sample was analyzed by HPLC-UV using previously isolated material as a reference (external and internal calibration).

General procedure for glycosylation reactions with N-phenyl trifluoroacetimidoyl glucosyl donor

To a solution of the glucosyl donor (0.03 mmol) and the acceptor (0.05-0.06 mmol) in dry CH₂Cl₂ (2 mL) molecular sieve (3Å, 100 mg) was added and the reaction mixture was stirred for 2 h at room temperature. After cooling to the appropriate temperature, activator (see Table S1) was added and stirring was continued for 2 h. The reaction was quenched by addition of NEt₃. A sample of the reaction mixture (100 µl) was taken, diluted with 0.9 mL MeCN and filtered through a syringe filter. This sample was then analyzed by HPLC-UV using isolated material as a reference (external and internal calibration).
Table S1. Glycosylation methods

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Activator</th>
<th>Temperature</th>
<th>LG</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>NIS (2 eq.)</td>
<td>-10 °C</td>
<td>SEt, STol</td>
</tr>
<tr>
<td></td>
<td>TfOH (0.2 eq.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>I₂ (2 eq.)</td>
<td>rt</td>
<td>SEt</td>
</tr>
<tr>
<td>C</td>
<td>TMSOTf (2 eq.)</td>
<td>-10 °C</td>
<td>SPym</td>
</tr>
<tr>
<td>D</td>
<td>AgOTf (2 eq.)</td>
<td>0 °C or rt</td>
<td>SPym, STaz</td>
</tr>
<tr>
<td>E</td>
<td>TMSOTf (0.1 eq.)</td>
<td>-10 °C</td>
<td>OC(NPh)CF₃</td>
</tr>
</tbody>
</table>

2-Phenylethyl 3,4,6-tri-O-benzyl-2-O-benzylxloxy carbonyl-β-D-glucopyranoside (24)

To a solution of glucosyl donor 14 (81.5 mg, 0.12 mmol) and 2-phenylethanol (22.0 mg, 0.18 mmol) in dry CH₂Cl₂ (2.5 mL) molecular sieve (3Å, 250 mg) was added and the reaction mixture was stirred overnight at room temperature. After cooling to -10°C, TMSOTf (43 µl, 0.24 mmol) was added and stirring was continued for 16 h at -10 °C. Analysis by TLC indicated remaining starting material, thus additional phenylethanol (1 eq.) and TMSOTf (2 eq.) were added. After 2 h the reaction mixture was slowly warmed to room temperature and stirred for 16 h. The reaction was quenched by addition of Et₃N, diluted with CH₂Cl₂ and filtrated over Celite. The filtrate was washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes/EtOAc gradient elution) to obtain the title compound 24 (43 mg, 53 %) as a colorless solid: Rf 0.39 (hexanes/EtOAc = 4/1); ¹H NMR (400 MHz, (CD₃)₂CO) δ 7.44-7.14 (m, 25H), 5.21 (d, J = 12.3 Hz, 1H), 5.16 (d, J = 12.3 Hz, 1H), 4.83 (d, J = 11.1 Hz, 1H), 4.78 (d, J = 11.4 Hz, 1H), 4.73 (t, J = 8.7 Hz, 1H), 4.67 (d, J = 7.9 Hz, 1H), 4.62 (d, J = 7.6 Hz, 1H), 4.63-4.53 (m, 3H), 4.07-3.98 (m, 1H), 3.83-3.57 (m, 6H), 2.87-2.80 (m, 2H); ¹³C NMR (100 MHz, (CD₃)₂CO) δ 155.3 (s, 1C), 139.8 (s, 1C), 139.6 (s, 1C), 139.4 (s, 2C), 136.8 (s, 1C), 129.9 (d, 2C), 129.4 (d, 2C), 129.2 (d, 2C), 129.1 (d, 4C), 129.0 (d, 4C), 128.7 (d, 2C), 128.5 (d, 2C), 128.4 (d, 2C), 128.3 (d, 2C), 128.2 (d, 2C), 126.9 (d, 1C), 101.3 (d, 1C), 83.7 (d, 1C), 78.9 (d, 1C), 78.5 (d, 1C), 75.8 (d, 1C), 75.6 (t, 1C), 75.4 (t, 1C), 73.7 (t, 1C), 70.9 (t, 1C), 70.2 (t, 1C), 69.7 (t, 1C), 36.8 (t, 1C). HRMS calcd for C₄₃H₄₄NaO₈⁺ [M+Na]⁺ 711.2928, found 711.2932.
Methyl 2,3,4,9,10,12-hexa-O-benzyl-8-O-benzylxoycarbonyl-α-L-gentiobioside (25)

To a solution of glucosyl donor 11 (200 mg, 0.32 mmol) and the glucosyl acceptor 20 (148.7 mg, 0.32 mmol) in dry CH₂Cl₂ (6 mL) molecular sieve 3Å (300 mg) was added and the reaction mixture was stirred for 2 h at room temperature. After cooling to -10 °C, NIS (143 mg, 0.64 mmol) and TfOH (10 mg, 0.06 mmol) were added and stirring was continued for 14 h. The reaction was quenched by addition of Et₃N, the mixture was diluted with CH₂Cl₂ and filtrated over Celite. The filtrate was washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes/EtOAc gradient elution) to obtain the desired product 25 (314 mg, 87%); Rf 0.64 (hexanes/ EtOAc = 2/1); ¹H NMR (600 MHz, CD₂Cl₂) δ 7.41-7.31 (m, 1H), 7.30-7.22 (m, 1H), 7.22-7.17 (m, 8H), 5.14 (d, J = 12.1 Hz, 1H), 4.96 (t, J = 11.0 Hz, 2H), 4.82-4.76 (m, 4H), 4.76-4.71 (m, 3H), 4.66 (d, J = 4.9 Hz, 1H), 4.64 (d, J = 4.3 Hz, 1H), 4.61 (d, J = 12.0 Hz, 1H), 4.57 (d, J = 10.9 Hz, 1H), 4.54 (d, J = 2.2 Hz, 1H), 4.52 (d, J = 3.2 Hz, 1H), 4.43 (d, J = 8.0 Hz, 1H), 4.07 (dd, J = 10.5, 1.5 Hz, 1H), 3.89 (t, J = 9.3 Hz, 1H), 3.77-3.70 (m, 4H), 3.70-3.64 (m, 2H), 3.55 (dd, J = 9.6, 3.5 Hz, 1H), 3.49-3.42 (m, 2H), 3.35 (s, 3H); ¹³C NMR (150 MHz, CD₂Cl₂) δ 154.80 (s, 1C), 139.53 (s, 1C), 139.00 (s, 1C), 138.87 (s, 1C), 138.62 (s, 1C), 138.60 (s, 1C), 138.53 (s, 1C), 138.52 (s, 1C), 135.46 (s, 1C), 128.91 (d, 2C), 128.82 (d, 1C), 128.70 (d, 6C), 128.66 (d, 2C), 128.62 (d, 2C), 128.60 (d, 3C), 128.32 (d, 2C), 128.25 (d, 4C), 128.17 (d, 2C), 128.12 (d, 3C), 128.01 (d, 1C), 128.05 (d, 2C), 128.01 (d, 2C), 127.95 (d, 1C), 127.88 (d, 1C), 127.77 (d, 1C), 101.15 (d, 1C), 98.24 (d, 1C), 83.12 (d, 1C), 82.10 (d, 1C), 80.69 (d, 1C), 78.11 (d, 1C), 78.06 (d, 1C), 77.91 (d, 1C), 75.76 (t, 1C), 75.60 (t, 1C), 75.41 (t, 1C), 75.28 (t, 1C), 75.12 (t, 1C), 73.68 (t, 1C), 73.27 (t, 1C), 70.27 (t, 1C), 70.07 (d, 1C), 69.00 (t, 1C), 68.37 (t, 1C), 55.37 (q, 1C); HRMS calcd for C₆₃H₆₆NaO₂₅⁺ [M+Na⁺] 1053.4396, found 1053.4392.

1,2,3,4-Tetra-O-acetyl-9,10,12-tri-O-benzyl-8-O-benzylxoycarbonyl-α-L-gentiobioside (26)

To a solution of glucosyl donor 11 (200 mg, 0.32 mmol) and 1,2,3,4-tetra-O-acetylglucose (21) (166 mg, 0.48 mmol) in dry CH₂Cl₂ (6 mL) molecular sieve 3Å (600 mg) was added and the reaction mixture was stirred for 2 h at room temperature. After cooling to -10 °C, NIS (143 mg, 0.64 mmol) and TfOH (10 mg, 0.06 mmol) were added and stirring was continued for 14 h at -10 °C. The reaction was quenched by addition of an aqueous saturated NaHCO₃ and Na₂SO₄ solution (1:1). The mixture was diluted with CH₂Cl₂ and filtrated over Celite. The filtrate was washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes/EtOAc gradient elution) to obtain 26 (225 mg, 77%); Rf 0.29 (hexanes/ EtOAc = 2/1); ¹H NMR (600 MHz, CD₂Cl₂) δ 7.43-7.32 (m, 9H), 7.31-7.23 (m, 7H), 7.22-7.17 (m, 4H), 5.71 (d, J = 8.2 Hz, 1H), 5.28-5.14 (m, 3H), 5.12-5.02 (m, 2H), 4.82-4.86 (m, 3H), 4.67-4.51 (m, 4H), 4.45 (d, J = 7.8 Hz, 1H), 3.95 (dd, J = 11.3, 2.3 Hz, 1H), 3.82-3.75 (m, 1H), 3.75-3.71 (m, 2H), 3.70-3.65 (m, 2H), 3.59 (dd, J = 11.1, 4.9 Hz, 1H), 3.49-3.41 (m, 1H), 2.07 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H); ¹³C NMR
(100 MHz, CD$_2$Cl$_2$) δ 170.31 (s, 1C), 169.71 (s, 1C), 169.52 (s, 1C), 169.28 (s, 1C), 154.73 (s, 1C), 138.69 (s, 1C), 138.59 (s, 1C), 138.57 (s, 1C), 136.03 (s, 1C), 128.94 (d, 2C), 128.82 (d, 1C), 128.73 (d, 2C), 128.70 (d, 2C), 128.68 (d, 4C), 128.35 (d, 2C), 128.22 (d, 2C), 128.19 (d, 2C), 128.12 (d, 1C), 127.97 (d, 1C), 100.96 (d, 1C), 92.11 (d, 1C), 83.12 (d, 1C), 78.06 (d, 1C), 77.59 (t, 1C), 75.95 (t, 1C), 75.56 (d, 1C), 75.28 (t, 1C), 74.25 (d, 1C), 73.78 (t, 1C), 73.25 (d, 1C), 70.71 (d, 1C), 70.27 (t, 1C), 69.02 (t, 1C), 68.67 (d, 1C), 67.57 (t, 1C), 21.03 (q, 1C), 20.79 (q, 2C), 20.76 (q, 1C); HRMS calcd for C$_{63}$H$_{66}$NaO$_{17}$+ [M+Na]$^+$ 937.3254, found: 937.3251

Methyl 2,3,6,9,10,12-hexa-O-benzyl-8-O-benzoxycarbonyl-α-D-cellobioside (27)

To a solution of glucosyl donor 14 (100 mg, 0.15 mmol) and the glucosyl acceptor 22 (103 mg, 0.22 mmol) in dry CH$_2$Cl$_2$ (3 mL) molecular sieve 3Å (100 mg) was added and the reaction mixture was stirred for 2 h at room temperature. After cooling to 0 °C, AgOTf (77 mg, 0.30 mmol) was added and stirring was continued for 3 h. The reaction was quenched by addition of an aqueous saturated NaHCO$_3$, diluted with CH$_2$Cl$_2$ and filtrated over Celite. The filtrate was washed with water and brine, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes/EtOAc gradient elution) to obtain 27 (100 mg, 66%); R$_f$ 0.68 (hexanes/ EtOAc = 2/1); $^1$H NMR (600 MHz, CD$_2$Cl$_2$) δ 7.43-7.13 (m, 35H), 5.16 (d, J = 12.2 Hz, 1H), 5.12 (d, J = 12.1 Hz, 1H) 5.04 (d, J = 11.8 Hz, 1H), 4.78-4.74 (m, 3H), 4.72 (dd, J = 9.6, 8.2, 1H), 4.68 (d, J = 11.6 Hz, 1H), 4.65-4.62 (m, 2H), 4.58-4.53 (m, J = 4.3 Hz, 4H), 4.45 (d, J = 11.7 Hz, 1H), 4.37 (d, J = 12.1 Hz, 1H), 4.34 (d, J = 12.1 Hz, 1H), 3.88 (t, J = 9.5 Hz, 1H), 3.78 (t, J = 9.3 Hz, 1H), 3.76 (dd, J = 11.1, 3.2, 1H), 3.67 (t, J = 9.3, 1H), 3.62 (dd, J = 10.9, 1.8, 1H), 3.59-3.56 (m, 1H), 3.55-3.51 (m, 3H), 3.43 (dd, J = 9.5, 3.6 Hz, 1H), 3.34 (s, 3H), 3.27 (dd, J = 9.8, 4.4, 1.9, 1H); $^{13}$C NMR (150 MHz, CD$_2$Cl$_2$) δ 154.79 (s, 1C), 140.13 (s, 1C), 138.94 (s, 1C), 138.87 (s, 1C), 138.64 (s, 1C), 138.62 (s, 1C), 138.60 (s, 1C), 135.84 (s, 1C), 128.94 (d, 1C), 128.87 (d, 1C), 128.76 (d, 2C), 128.65 (d, 4C), 128.62 (d, 2C), 128.58 (d, 2C), 128.51 (d, 2C), 128.33 (d, 3C), 128.27 (d, 2C), 128.22 (d, 2C), 128.18 (d, 2C), 128.09 (d, 2C), 128.02 (d, 2C), 127.97 (d, 6C), 127.73 (d, 1C), 127.32 (d, 1C), 100.81 (d, 1C), 98.45 (d, 1C), 83.26 (d, 1C), 80.23 (d, 1C), 79.83 (d, 1C), 78.49 (d, 1C), 78.20 (d, 1C), 77.75 (d, 1C), 75.59 (d, 1C), 75.52 (t, 1C), 75.26 (t, 1C), 75.09 (t, 1C), 73.60 (t, 1C), 73.56 (t, 1C), 73.50 (t, 1C), 70.22 (d, 1C), 70.11 (t, 1C), 69.07 (t, 1C), 68.45 (t, 1C), 55.45 (q, 1C); HRMS calcd for C$_{63}$H$_{66}$NaO$_{17}$+ [M+Na]$^+$ 1053.4396, found 1053.4392.
f. Deprotection

2-Phenylethyl-β-o-glucopyranoside (29)

To a suspension of compound 24 (20 mg, 0.03 mmol) in dry ethanol (1 mL) one small tip of a spatula of Pd/C was added under an argon atmosphere. The argon balloon was changed for a balloon filled with H₂ and the reaction mixture was stirred for 4 h at rt. The reaction mixture was filtered through a syringe filter and the filtrate was concentrated. The residue was dissolved in water and purified by preparative HPLC to yield 29 as a white solid (7 mg, 87%). The obtained material was identical with reference material of 29 previously prepared using a known procedure for Königs-Knorr glucosylation of 2-phenylethanol.[11]

1,2,3,4-Tetra-O-acetyl-gentiobioside (30)

To a suspension of disaccharide 26 (50 mg, 0.05 mmol) in dry ethanol (3 mL) two small tips of a spatula of Pd/C were added under an argon atmosphere. The argon balloon was changed for a balloon filled with H₂ and the mixture was stirred for 1 h at rt. The reaction mixture was filtered through a syringe filter and the filtrate was concentrated. The residue was dissolved in water and purified by preparative HPLC to yield 28 as a white solid (20 mg, 71%). 1H NMR (600 MHz, CD₂Cl₂) 5.81 (d, J = 8.5 Hz, 1H), 5.34 (t, J = 9.7 Hz, 1H), 5.16 (t, J = 9.5 Hz, 1H), 5.06 (dd, J = 9.5, 8.4 Hz, 1H), 4.25 (d, J = 7.9 Hz, 1H), 4.03-3.98 (m, 2H), 3.86 (dd, J = 11.9, 2.2, 1H), 3.69-3.64 (m, 2H), 3.34 (t, J = 8.9 Hz, 1H), 3.28 (t, J = 9.1 Hz, 1H), 3.26-3.22 (m, 1H), 3.20 (dd, J = 9.1, 7.9 Hz, 1H), 2.08 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H); 13C NMR (150 MHz, CD₂Cl₂) 5.171.61 (s, 2C), 170.99 (s, 1C), 170.55 (s, 1C), 104.45 (d, 1C), 92.97 (d, 1C), 77.98 (d, 1C), 77.81 (d, 1C), 75.01 (d, 1C), 74.91 (d, 1C), 74.28 (d, 1C), 71.77 (d, 1C), 71.45 (d, 1C), 69.87 (d, 1C), 68.63 (t, 1C), 62.65 (t, 1C), 20.70 (q, 1C), 20.61 (q, 1C), 20.54 (q, 1C), 20.44 (q, 1C); HRMS calcd. for C₂₀H₃₀N₃O₁₅ [M+Na]⁺ 533.1477, found: 533.1482.

9,10,12-Tri-O-benzyl-8-O-benzoyloxycarbonyl-gentiobioside (31)

To a suspension of the disaccharide 26 (80 mg, 0.09 mmol) in dry methanol (20 mL) KCN (3 mg, 0.05 mmol) was added at 0 °C. The reaction mixture was slowly warmed to room temperature and stirring was continued for 4 h. Water was added and the reaction mixture was concentrated to a third of its volume. The residue was diluted with MeCN/H₂O (1:1) and purified by preparative HPLC to obtain compound 31, as an anomeric mixture (50 mg, 75%). 1H NMR (600 MHz, MeOD) 7.38-7.34 (m, 4H), 7.33-7.29 (m, 5H), 7.28-7.24 (m, 4H), 7.23-7.20 (m, 3H), 7.17-7.13 (m, 4H), 5.21 (dd, J = 12.5, 5.7 Hz, 1H), 5.12 (dd, J = 12.0, 5.0 Hz, 1H), 5.07 (d, J = 3.5 Hz, 0.5H), 4.75-4.68 (m, 2.5H), 4.67-4.65 (m, 1H), 4.64-4.57 (m, 2.5H), 4.52 (t, J = 11.6 Hz, 2H), 4.44 (d, J = 7.6 Hz, 0.5H), 4.11 (dd, J = 11.4, 2.1 Hz, 0.5H), 4.06 (dd, J = 11.2, 2.3 Hz, 0.5H), 3.92 (dd, J = 10.1, 5.2, 2.0 Hz, 0.5H), 3.78 (dd, J = 11.2, 5.0 Hz, 0.5H), 3.76-3.66 (m, 4H), 3.61 (td, J = 9.4, 2.3 Hz, 1H), 3.55-3.50 (m, 1H), 3.44-3.39 (m, 0.5H), 3.36-3.32 (m, 1.5H), 3.24 (dd, J = 9.5, 8.9 Hz, 0.5H), 3.13 (dd, J = 9.2, 7.8 Hz, 0.5H); 13C NMR...
(150 MHz, MeOD) δ 156.09 (s, 1C), 156.08 (s, 1C), 139.5 (s, 4C), 139.4 (s, 1C), 139.3 (s, 1C), 137.0 (s, 2C), 129.7 (d, 2C), 129.6 (d, 2C), 129.53 (d, 2C), 129.49 (d, 2C), 129.46 (d, 2C), 129.45 (d, 2C), 129.41 (d, 2C), 129.35 (d, 2C), 129.33 (d, 4C), 129.15 (d, 4C), 129.0 (d, 3C), 128.84 (d, 3C), 128.83 (d, 2C), 128.80 (d, 2C), 129.78 (d, 2C), 128.76 (d, 2C), 128.68 (d, 2C), 102.32 (d, 1C), 102.31 (d, 1C), 98.13 (d, 1C), 93.95 (d, 1C), 84.0 (d, 1C), 83.9 (d, 1C), 79.11 (d, 2C), 79.08 (d, 2C), 78.0 (d, 1C), 77.2 (d, 1C), 76.2 (d, 1C), 76.17 (t, 2C), 76.10 (d, 1C), 76.03 (d, 1C), 75.9 (t, 2C), 74.8 (d, 1C), 74.4 (t, 2C), 73.8 (d, 1C), 72.07 (d, 1C), 71.85 (d, 1C), 71.81 (d, 1C), 70.9 (t, 2C), 70.2 (t, 1C), 70.1 (t, 1C), 69.65 (t, 2C), HRMS calcd for C₄₁H₆₆NaO₁₃⁺ [M+Na]⁺ 769.2831, found: 769.2829

g. Synthesis of glycosyl esters

trans-N-(tert-butoxycarbonyl)-4-acetoxy-L-proline (32)

The title compound was prepared according to a procedure described by Wong[12] and obtained as a white solid (588 mg, 99%); ¹H NMR (400 MHz, CDCl₃) δ 5.41-5.16 (m, 1H), 4.48 (t, J = 7.7 Hz, 0.5H), 4.36 (t, J = 7.9 Hz, 0.5H), 3.83-3.44 (m, 2H), 2.58-2.24 (m, 2H), 2.06 (s, 3H), 1.46 (s, 4.5H), 1.42 s (4.5H); ¹³C NMR (100 MHz, CDCl₃) δ 177.28 (s, 1C), 175.65 (s, 1C), 170.62 (s, 1C), 170.56 (s, 1C), 155.73 (s, 1C), 153.73 (s, 1C), 81.83 (s, 1C), 81.19 (s, 1C), 72.40 (d, 1C), 71.98 (d, 1C), 57.86 (d, 1C), 57.77 (d, 1C), 52.48 (t, 1C), 52.09 (t, 1C), 36.61 (t, 1C), 34.93 (t, 1C), 28.46 (q, 3C), 28.33 (q, 3C), 21.15 (q, 2C); ESI-MS calcd for C₁₂H₁₉NNaO₆⁺ [M+Na]⁺ 296.1, found 296.0.

trans-N-(tert-butoxycarbonyl)-4-acetoxy-L-proline, 3,4,6-tri-O-benzyl-2-O-benzylloxycarbonyl-β-D-glucopyranosyl ester (33)

To a solution of glucosyl donor 11 (100 mg, 0.16 mmol) and trans-N-(tert-butoxycarbonyl)-4-acetoxy-L-proline (65 mg, 0.24 mmol) in dry CH₂Cl₂ (3 mL) molecular sieve 3Å (150 mg) was added and the reaction mixture was stirred for 2 h at room temperature. After cooling to -10°C, NIS (72 mg, 0.32 mmol) and TFOH (5 mg, 0.03 mmol) were added and stirring was continued for 2 h at -10 °C. The reaction was quenched by addition of an aqueous saturated NaHCO₃ and Na₂SO₃ solution (1:1). The mixture was diluted with CH₂Cl₂ and filtrated over Celite. The filtrate was washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes/EtOAc gradient elution) to obtain the desired product 31 (71 mg, 53%); Rf 0.45 (hexanes/ EtOAc = 2/1); ¹H NMR (400 MHz, CD₂Cl₂) δ 7.41-7.15 (m, 20H), 5.71 (d, J = 8.2 Hz, 0.4H), 5.65 (d, J = 8.2 Hz, 0.6H), 5.24-5.09 (m, 3H), 4.95-4.84 (m, 1H), 4.83-4.73 (m, 2H), 4.66 (d, J = 10.9 Hz, 1H), 4.62-4.43 (m, 3H), 4.37-4.28 (m, 1H), 3.82-3.68 (m, 4H), 3.66-3.49 (m, 3H), 2.39-2.27 (m, 1H), 2.16-1.96

¹ mixture of two rotamers
(m, 1H), 2.04 (s, 3H), 1.43 (s, 3H), 1.36 (s, 6H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) $^2$ δ 171.19 (s, 1C), 171.10 (s, 1C), 170.62 (s, 1C), 170.52 (s, 1C), 154.68 (s, 2C), 154.38 (s, 1C), 153.55 (s, 1C), 138.52 (s, 1C), 138.48 (s, 1C), 138.43 (s, 4C), 135.80 (s, 1C), 135.52 (s, 1C), 129.09 (d, 2C), 129.04 (d, 2C), 128.94 (d, 2C), 128.79 (d, 2C), 128.73 (d, 10C), 128.49 (d, 2C), 128.35 (d, 4C), 128.30 (d, 2C), 128.26 (d, 2C), 128.23 (d, 4C), 128.21 (d, 4C), 128.11 (d, 2C), 128.06 (d, 2C), 92.80 (d, 2C), 82.98 (d, 1C), 82.74 (d, 1C), 82.47 (s, 1C), 78.95 (d, 1C), 78.83 (d, 1C), 77.90 (d, 1C), 77.72 (d, 1C), 74.15 (d, 1C), 74.01 (d, 1C), 73.81 (d, 1C), 73.46 (d, 1C), 71.06 (d, 1C), 71.03 (d, 1C), 62.38 (t, 1C), 62.29 (t, 1C), 59.04 (d, 1C), 58.82 (d, 1C), 53.43 (t, 1C), 53.05 (t, 1C), 37.02 (t, 1C), 36.22 (t, 1C), 28.61 (q, 3C), 28.51 (q, 3C), 20.88 (q, 2C)$^2$; ESI-MS calcd for C$_{18}$H$_{28}$NNaO$_{13}$ $^+$ [M+Na]$^+$ 458.2, found 458.1.

trans-N-(tert-butoxycarbonyl)-4-acetoxyl-proline, $\beta$-$d$-glucopyranosyl ester (34)

To a suspension of compound 33 (71 mg, 0.085 mmol) in dry ethanol (1.5 mL) were added two small tips of a spatula of Pd/C under argon atmosphere. The argon balloon was changed for a balloon filled with a H$_2$ and the reaction mixture was stirred at rt for 16 h. The reaction mixture was filtered through a syringe filter and concentrated. The residue was dissolved in a mixture of MeCN/H$_2$O and purified by preparative HPLC to yield 32 as a white solid (30 mg, 81%). 1H NMR (600 MHz, MeOD) δ 5.50 (d, $J$ = 8.2 Hz, 0.4H), 5.48 (d, $J$ = 8.2 Hz, 0.6H), 5.29-5.22 (m, 1H), 4.45 (q, $J$ = 15.4, 7.8 Hz, 1H), 3.86-3.78 (m, 1H), 3.72-3.62 (m, 2H), 3.61-3.55 (m, 1H), 3.43 (t, $J$ = 8.8 Hz, 1H), 3.40-3.32 (m, 3H), 2.51-2.42 (m, 1H), 2.37-2.27 (m, 1H), 2.05 (s, 3H), 1.46 (s, 3H), 1.43 (s, 6H); $^{13}$C NMR (150 MHz, MeOD) δ 172.66 (s, 1C), 172.48 (s, 1C), 172.12 (s, 1C), 172.11 (s, 1C), 156.05 (s, 1C), 155.62 (s, 1C), 96.44 (d, 1C), 96.39 (d, 1C), 82.47 (s, 1C), 82.21 (s, 1C), 78.95 (d, 1C), 78.83 (d, 1C), 77.90 (d, 1C), 77.72 (d, 1C), 74.15 (d, 1C), 74.01 (d, 1C), 73.81 (d, 1C), 73.46 (d, 1C), 71.06 (d, 1C), 71.03 (d, 1C), 62.38 (t, 1C), 62.29 (t, 1C), 59.04 (d, 1C), 58.82 (d, 1C), 53.43 (t, 1C), 53.05 (t, 1C), 37.02 (t, 1C), 36.22 (t, 1C), 28.61 (q, 3C), 28.51 (q, 3C), 20.88 (q, 2C)$^2$; ESI-MS calcd for C$_{18}$H$_{28}$NNaO$_{13}$ $^+$ [M+Na]$^+$ 458.2, found 458.1.

Acetylsalicylic acid, 3,4,6-tri-O-benzyl-2-O-benzyloxy carbonyl-$\beta$-$d$-glucopyranosyl ester (36)

To a solution of glucosyl donor 11 (100 mg, 0.16 mmol) and acetylsalicylic acid (33) (43 mg, 0.24 mmol) in dry CH$_2$Cl$_2$ (3 mL) molecular sieve 3Å (150 mg) was added and the reaction mixture was stirred for 2 h at room temperature. After cooling to -10°C, NIS (72 mg, 0.32 mmol) and TfOH (5 mg, 0.03 mmol) were added and stirring was continued for 2 h at -10°C. The reaction was quenched by addition of an aqueous saturated NaHCO$_3$ and Na$_2$SO$_4$ solution (1:1). The mixture was diluted with CH$_2$Cl$_2$ and filtrated over Celite. The filtrate was washed with water and brine, dried over Na$_2$SO$_4$ and concentrated. The residue was purified by column chromatography (hexanes/EtOAc gradient elution) to obtain the desired product 34 (100 mg, 84%); Rf 0.67 (hexanes/EtOAc = 2/1); $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $^2$ mixture of two rotamers.

---

$^2$ mixture of two rotamers
δ 8.01 (dd, J = 8.0, 1.8 Hz, 1H), 7.64 (td, J = 7.8, 1.6 Hz, 1H), 7.37-7.20 (m, 21H), 7.15 (dd, J = 8.2, 0.8 Hz, 1H), 5.84 (d, J = 8.2 Hz, 1H), 5.09 (s, 2H), 5.06-4.99 (m, 1H), 4.82 (t, J = 10.7 Hz, 2H), 4.71 (d, J = 10.9 Hz, 1H), 4.62 (d, J = 10.9 Hz, 1H), 4.58 (d, J = 12.1 Hz, 1H), 4.51 (d, J = 12.1 Hz, 1H), 3.83 (dd, J = 6.8, 2.5 Hz, 1H), 3.77 (d, J = 2.8 Hz, 2H), 3.69 (dt, J = 9.8, 2.8 Hz, 1H), 2.3 (s, 3H); 13C NMR (100 MHz, CD2Cl2) δ 169.85 (s, 1C), 162.55 (s, 1C), 154.75 (s, 1C), 151.88 (s, 1C), 138.49 (s, 1C), 138.45 (s, 2C), 135.55 (s, 1C), 135.08 (d, 1C), 132.38 (d, 1C), 132.89 (d, 2C), 128.83 (d, 1C), 128.73 (d, 6C), 128.38 (d, 4C), 128.27 (d, 4C), 128.19 (d, 1C), 128.13 (d, 1C), 128.04 (d, 1C), 126.58 (d, 1C), 124.44 (d, 1C), 122.29 (s, 1C), 92.76 (d, 1C), 82.90 (d, 1C), 77.63 (d, 1C), 76.83 (d, 1C), 76.36 (d, 1C), 75.76 (t, 1C), 75.40 (t, 1C), 73.82 (t, 1C), 70.38 (t, 1C), 68.64 (t, 1C), 21.14 (q, 1C); ESI-MS calcd for C44H42NaO11+ [M+Na]+ 769.3, found 769.3.

**Acetylsalicylic acid, β-D-glucopyranosyl ester (37)**

To a suspension of compound 36 (98 mg, 0.13 mmol) in dry ethanol (1.5 mL) three small tips of a spatula of Pd/C were added under an argon atmosphere. The argon balloon was changed for a H2-balloon and the mixture was stirred for 16 h at rt. The reaction mixture was filtered through a syringe filter and the filtrate was concentrated. The residue was dissolved in MeCN/H2O and purified by preparative HPLC to yield 37 as a white solid (29 mg, 65%). 1H NMR (600 MHz, MeOD) δ 8.11 (dd, J = 7.9, 1.7 Hz, 1H), 7.66 (td, J = 7.8, 1.5 Hz, 1H), 7.39 (td, J = 7.6, 1.1 Hz, 1H), 7.18 (dd, J = 8.2, 0.9 Hz, 1H), 5.69 (d, J = 7.9 Hz, 1H), 3.86 (dd, J = 12.2, 2.1 Hz, 1H), 3.71 (dd, J = 12.3, 5.0 Hz, 1H), 3.51-3.45 (m, 2H), 3.44-3.42 (m, 1H), 3.42-3.38 (m, 1H), 2.32 (s, 3H); 13C NMR (150 MHz, MeOD) δ 171.45 (s, 1C), 164.40 (s, 1C), 152.45 (s, 1C), 135.65 (d, 1C), 132.88 (d, 1C), 127.22 (d, 1C), 125.15 (d, 1C), 123.93 (s, 1C), 96.12 (d, 1C), 78.97 (d, 1C), 78.06 (d, 1C), 73.99 (d, 1C), 71.01 (d, 1C), 62.28 (t, 1C), 21.00 (q, 1C); ESI-MS calcd for C15H18NaO19+ [M+Na]+ 365.1, found 365.0.
3) NMR Spectra

$^1$H NMR ($d_6$-acetone, 200 MHz)

$^{13}$C NMR ($d_6$-acetone, 50 MHz)
$^1$H NMR (CDCl$_3$, 600 MHz)

$^{13}$C NMR (CDCl$_3$, 150 MHz)
H,H-COSY (CDCl₃, 600 MHz)
\(^1\text{H NMR (CD}_2\text{Cl}_2, 400\text{ MHz)}\)

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

\(12\)

\[^{13}\text{C NMR (CD}_2\text{Cl}_2, 100\text{ MHz)}\)

\[
\begin{align*}
\text{O} & \quad \text{Bn} \\
\text{Bn} & \quad \text{O} \\
\text{O} & \quad \text{CbzO} \\
\end{align*}
\]

\(12\)
^1H NMR (d$_6$-acetone, 200 MHz)

13C NMR (d$_6$-acetone, 50 MHz)
H,H-COSY (d6-acetone, 400 MHz)

HSQC (d6-acetone, 400 MHz)
$^1$H NMR (CD$_2$Cl$_2$, 400 MHz)

$^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz)
$^1$H NMR (d$_6$-acetone, 200 MHz)

$^{13}$C NMR (d$_6$-acetone, 50 MHz)
H,H COSY ($d_6$-acetone, 400 MHz)

HSQC ($d_6$-acetone, 400 MHz)
$^1$H NMR (CD$_2$Cl$_2$, 600 MHz)

$^{13}$C NMR (CD$_2$Cl$_2$, 150 MHz)
$^1$H NMR (CD$_2$Cl$_2$, 400 MHz)

$^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz)
$^1$H NMR (CD$_2$Cl$_2$, 600 MHz)

$^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz)
$^1$H NMR (CD$_2$Cl$_2$, 600 MHz)

13C NMR (CD$_2$Cl$_2$, 150 MHz)
**1H NMR (CD$_3$OD, 600 MHz)**

![1H NMR Spectrum](image)

**13C NMR (CD$_3$OD, 150 MHz)**

![13C NMR Spectrum](image)
HMBC (CD$_3$OD, 600 MHz)
$^{1}H$ NMR (CD$_3$OD, 600 MHz)

$^{13}C$ NMR (CD$_3$OD, 100 MHz)
H,H-COSY (CD$_3$OD, 600 MHz)

HSQC (CD$_3$OD, 600 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
$^{1}H$ NMR (CD$_2$Cl$_2$, 400 MHz)

$^{13}C$ NMR (CD$_2$Cl$_2$, 100 MHz)
$^1$H NMR (CD$_3$OD, 600 MHz)

$^{13}$C NMR (CD$_3$OD, 150 MHz)
DEPT NMR (CD$_3$OD, 150 MHz)
$^1$H NMR (CD$_2$Cl$_2$, 400 MHz)

$^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz)
$^1$H NMR (CD$_3$OD, 600 MHz)

$^{13}$C NMR (CD$_3$OD, 150 MHz)
4) References