Electronic Supplementary Material (ESI) for ChemComm.

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

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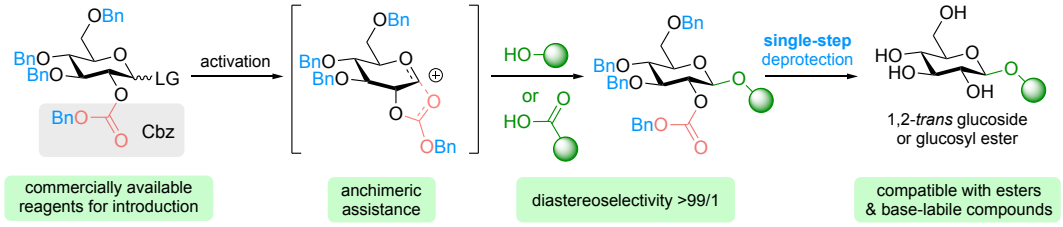
Paul Kosma, and Hannes Mikula*



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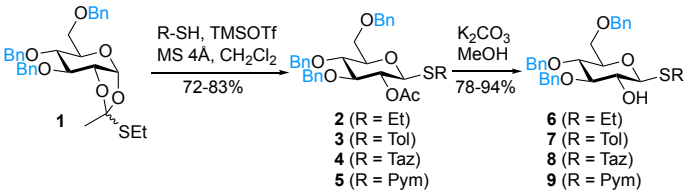
1) General Remarks

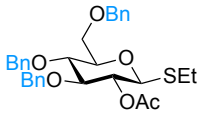
All reactions were performed under an argon atmosphere. Anhydrous solvents were obtained using a PURESOLV system of *it-innovative technology*. Molecular sieves (3Å) were activated before use by heating at 200 °C under vacuum. Analytical thin layer chromatography (TLC) was performed using plates cut 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. ^{1}H and ^{13}C 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



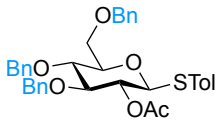
Ethyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucoside (2)



To a solution of thioorthoester **1** (16 g, 29.8 mmol) in dry CH_2Cl_2 (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 NEt_3 (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%); R_f 0.45 (hexanes/EtOAc = 5/1); ^{1}H NMR (200 MHz, $CDCl_3$) 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); ^{13}C NMR (50 MHz, $CDCl_3$) 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]

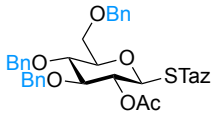
General procedure for the preparation of 2-OAc thioglucosides (compounds 3-5). To a solution of thioorthoester **1** (2.68 g, 5 mmol) in dry CH_2Cl_2 (80 mL) molecular sieve (3Å, 2 g) and thiol (R-SH) (40 mmol) were added. After stirring at room temperature for 30 min and subsequent cooling to 0 °C, 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 NEt_3 (0.8 mL) and the mixture was filtrated over Celite, washed with aq. NaOH (1%) and water. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes/EtOAc gradient elution + 0.1% NEt_3) to obtain the desired product.

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



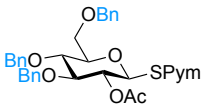
3 was obtained as a white solid (2.40 g, 80%); R_f 0.64 (hexanes/EtOAc = 3/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.49-7.27 (m, 15H), 7.14 (d, *J* = 8.2 Hz, 2H), 5.15-5.04 (m, 1H), 4.92 (d, *J* = 11.6 Hz, 1H), 4.90 (d, *J* = 10.8 Hz, 1H), 4.78 (d, *J* =11.6 Hz, 1H), 4.69 (d, *J* = 10.6 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%); R_f 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, 3C), 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]

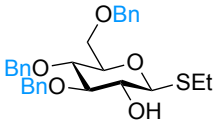
2-Pyrimidyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucoside (5):



5 was obtained as a yellowish solid (2.12 g, 72%); R_f 0.44 (hexanes/EtOAc = 3/2); ^{1}H NMR (200 MHz, $(CD_3)_2CO$) 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, $(CD_3)_2CO$) 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), 128.8 (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 $C_{33}H_{34}N_2NaO_6S^+$ $[M+Na]^+$ 609.2030, found 609.2042.

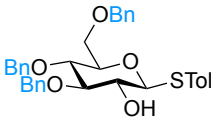
General procedure for de-acetylation of 2-OAc thioglucosides. To a solution/suspension of the 2-OAc thioglucoside (1 mmol) in dry MeOH (5 mL) K_2CO_3 (28 mg, 0.2 mmol) was added and the reaction mixture was stirred at room temperature until the starting material had completely dissolved (up to 72 h). 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% NEt_3) to obtain the desired product.

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



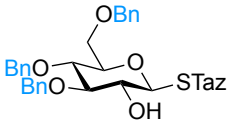
6 was obtained as a white solid (420 mg, 85%); R_f 0.21 (hexanes/EtOAc = 4/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.31-7.16 (m, 13H), 7.11-7.08 (m, 2H), 4.86 (d, *J* = 11.3 Hz, 1H), 4.77 (d, *J* = 11.3 Hz, 1H), 4.76 (d, *J* = 12.1 Hz, 1H), 4.58-4.42 (m, 3H), 4.22 (d, *J* = 9.1 Hz, 1H), 3.67 (dd, *J* = 1.8, 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); ^{13}C NMR (50 MHz, $CDCl_3$) 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)



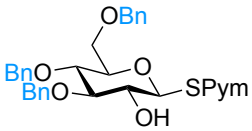
7 was obtained as a white solid (523 mg, 94%); R_f 0.49 (hexanes/EtOAc = 4/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.38-7.19 (m, 15H), 7.07 (d, *J* = 7.8 Hz, 2H), 4.97-4.79 (m, 3H), 4.67-4.50 (m, 3H), 4.45 (d, *J* = 9.4 Hz, 1H), 3.81-3.75 (m, 2H), 3.64-3.40 (m, 4H), 2.33 (s, 3H), 1.97 (bs, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 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):



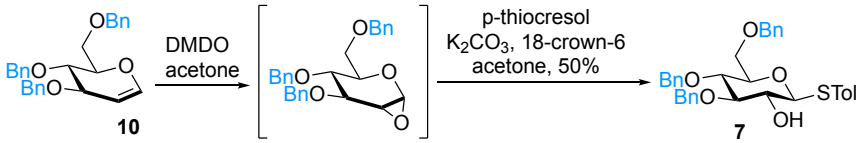
8 was obtained as a white solid (430 mg, 78%); R_f 0.27 (hexanes/EtOAc = 3/2); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.31-7.02 (m, 15H), 5.08 (d, *J* = 9.2 Hz, 1H), 4.90 (d, *J* = 11.2 Hz, 1H), 4.75 (d, *J* = 11.3 Hz, 1H), 4.74 (d, *J* = 10.9 Hz, 1H), 4.53 (d, *J* = 12.1 Hz, 1H), 4.46 (d, *J* = 10.9 Hz, 1H), 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); ^{13}C NMR (50 MHz, $CDCl_3$) 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)



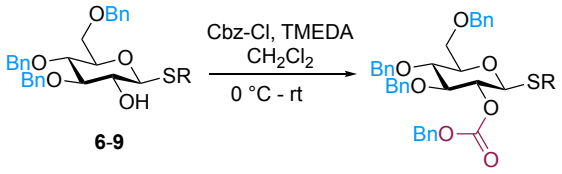
9 was obtained as a yellowish solid (479 mg, 88%); R_f 0.21 (hexanes/EtOAc = 3/2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.9 Hz, 2H), 7.43-7.41 (m, 2H), 7.36-7.26 (m, 11H), 7.24-7.22 (m, 2H), 6.96 (t, *J* = 5.0 Hz, 1H), 5.65 (d, *J* = 9.8 Hz, 1H), 5.04 (d, *J* = 11.4 Hz, 1H), 4.93 (d, *J* = 11.4 Hz, 1H), 4.90 (d, *J* = 10.8 Hz, 1H), 4.63 (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); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.3 (s, 1C), 157.6 (d, 2C), 138.7 (s, 1C), 138.3 (s, 1C), 138.2 (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 $C_{31}H_{32}N_2NaO_5S^+$ $[M+Na]^+$ 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), K_2CO_3 (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%); R_f 0.49 (hexanes/EtOAc = 4/1); ^{1}H NMR (200 MHz, $CDCl_3$) 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); ^{13}C NMR (50 MHz, $CDCl_3$) δ 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]

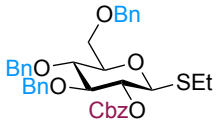
c. Introduction of benzyloxycarbonyl (Cbz) at *O*-2



11 (R = Et), 45% (81% brsm)
12 (R = Tol), 33% (88% brsm)
13 (R = Taz), 53% (77% brsm)
14 (R = Pym), 61% (90% brsm)

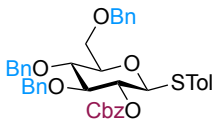
General procedure. To a solution of the 2-OH thioglucoside (0.5 mmol) in dry CH_2Cl_2 (5 mL), cooled to 0 °C, TMEDA (58 mg, 0.5 mmol) was added, followed by Cbz-Cl (127 mg, 0.75 mmol). The reaction mixture was stirred for 48 h, poured into water (20 mL) and extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4 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*-benzyloxycarbonyl-1-thio-β-D-glucoside (11)



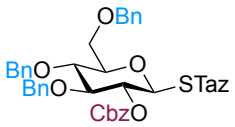
11 was obtained as a white solid (420 mg, 45%); R_f 0.42 (hexanes/EtOAc = 6/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2H), 7.26-7.23 (m, 6H), 7.22-7.17 (m, 8H),7.15-7.12 (m, 2H), 7.11-7.08 (m, 2H), 5.11 (s, 2H), 4.79-4.75 (m, 1H), 4.72 (d, *J* = 10.9 Hz, 1H), 4.69 (d, *J* = 11.0 Hz, 1H), 4.62 (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); ^{13}C NMR (150 MHz, $CDCl_3$) 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 $C_{37}H_{40}NaO_7S^+$ $[M+Na]^+$ 651.2387, found 651.2402.

p-Tolyl 3,4,6-tri-*O*-benzyl-2-*O*-benzyloxycarbonyl-1-thio-β-D-glucoside (12)



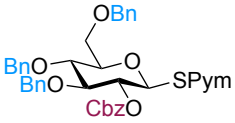
12 was obtained as a white solid (523 mg, 33%); R_f 0.47 (hexanes/EtOAc = 6/1); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.43-7.34 (m, 11H), 7.33-7.25 (m, 7H), 7.24-7.17 (m, 4H), 7.07 (d, *J* = 8.2 Hz, 2H), 5.23 (d, *J* = 12.1 Hz, 1H), 5.16 (d, *J* = 12.1, 1H), 4.78 (t, *J* = 11.1 Hz, 2H), 4.74 (dd, *J* = 9.9, 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), 3.750-3.69 (m, 2H), 3.66 (t, *J* = 9.2 Hz, 1H), 3.55-3.45 (m, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) 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 $C_{42}H_{42}NaO_7S^+$ $[M+Na]^+$ 713.2543, found 713.2570.

1,3-Thiazolin-2-yl 3,4,6-tri-*O*-benzyl-2-*O*-benzyloxycarbonyl-1-thio-β-D-glucoside (13)



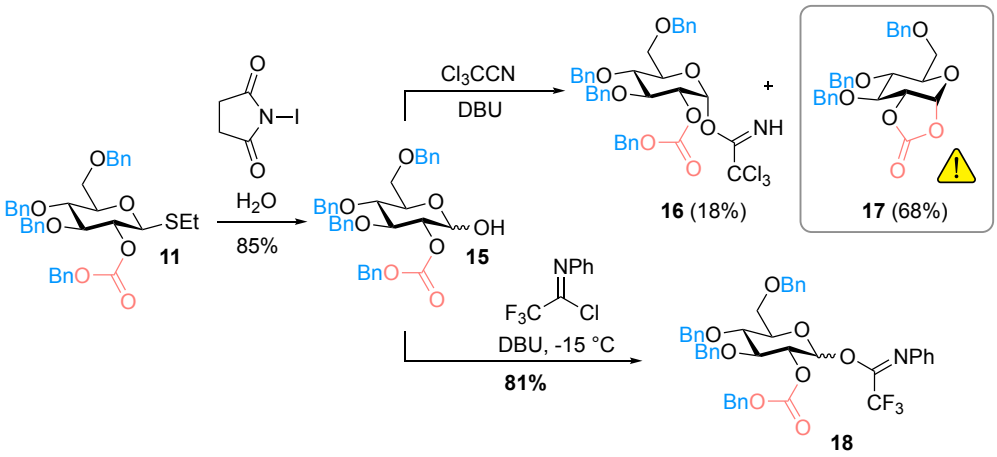
13 was obtained as a white solid (430 mg, 53%); R_f 0.48 (hexanes/EtOAc = 3/2); ^{1}H NMR (200 MHz, $(CD_3)_2CO$) δ 7.43-7.23 (m, 20H), 5.56 (d, *J* = 10.6 Hz, 1H), 5.23 (s, 2H), 4.90-4.80 (m, 3H), 4.72 (d, *J* = 11.3 Hz, 1H), 4.68 (d, *J* = 10.6 Hz, 1H), 4.62 (d, *J* = 11.8 Hz, 1H), 4.56 (d, *J* = 11.8 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); ^{13}C NMR (50 MHz, $(CD_3)_2CO$) 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), 84.8 (d, 1C), 83.6 (d, 1C), 80.3 (d, 1C), 78.4 (d, 1C), 76.8 (d, 1C), 75.9 (t, 1C), 75.5 (t, 1C), 73.7 (t, 1C), 70.5 (t, 1C), 69.5 (t, 1C), 65.1 (t, 1C), 35.7 (t, 1C); HRMS calcd for $C_{38}H_{39}NNaO_7S_2^+$ $[M+Na]^+$ 708.2060, found 708.2078.

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

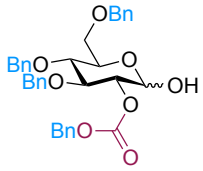


14 was obtained as a yellowish solid (479 mg, 61%); R_f 0.66 (hexanes/EtOAc = 3/2); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.48 (d, *J* = 4.8 Hz, 2H), 7.24-7.10 (m, 20H), 7.08 (t, *J* = 5.4 Hz, 1H), 5.70 (d, *J* = 10.7 Hz, 1H), 5.08 (d, *J* = 12.2 Hz, 1H), 5.04 (d, *J* = 12.2 Hz, 1H), 4.81 (dd, *J* = 10.3, 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); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) 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), 135.6 (d, 1C), 128.5 (d, 2C), 128.3 (d, 1C), 128.2 (d, 4C), 128.15 (d, 2C), 128.1 (d, 2C), 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 $C_{39}H_{38}N_2NaO_7S^+$ $[M+Na]^+$ 701.2292, found 701.2306.

d. Synthesis of glucosyl imidates

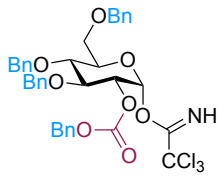


3,4,6-Tri-*O*-benzyl-2-*O*-benzyloxycarbonyl-α,β-D-glucose (15)



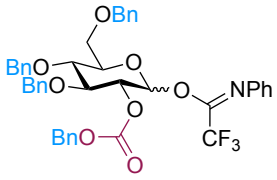
To a solution of glucosyl donor **11** (300 mg, 0.477 mmol) in MeCN/H_2O (9:1, 4 mL), N-iodosuccinimide (215 mg, 0.954 mmol) was added. The reaction mixture was stirred for 5 min at rt, quenched with an aqueous saturated solution of $Na_2S_2O_3$, diluted with CH_2Cl_2, and washed with $Na_2S_2O_3$-solution and brine. The organic phases were combined, dried over Na_2SO_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%). ^{1}H NMR (400 MHz, CD_2Cl_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); ^{13}C NMR (100 MHz, CD_2Cl_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 $C_{35}H_{36}NaO_8^+$ $[M+Na]^+$ 607.2302, found 607.2301.

3,4,6-Tri-*O*-benzyl-2-*O*-benzyloxycarbonyl-α-D-glucopyranosyl trichloroacetimidate (16)



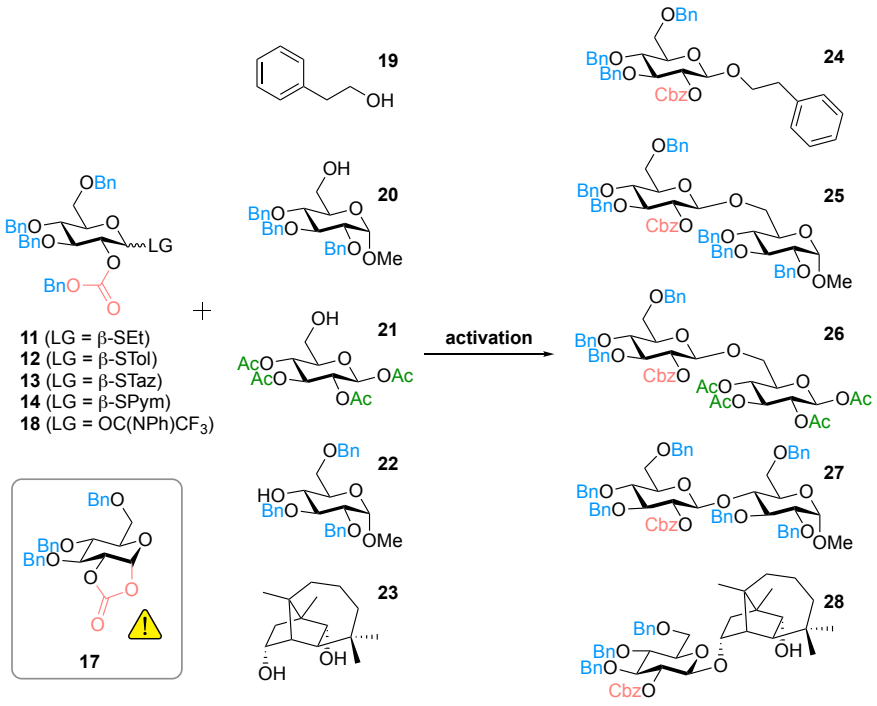
To a solution of compound **15** (994 mg, 1.7 mmol) in CH_2Cl_2 (25 mL), trichloroacetonitrile (736 mg, 5.1 mmol), and DBU (39 mg, 255 µmol) were added. The reaction mixture was stirred at room temperature for 2 h and then concentrated. The residue was purified by column chromatography (hexanes/ EtOAc, gradient elution) to afford **16** as a colorless viscous liquid (220 mg, 18%). ^{1}H NMR (200 MHz, $(CD_3)_2CO$) 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); ^{13}C NMR (50 MHz, $(CD_3)_2CO$) 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), 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 $C_{37}H_{36}Cl_3NNaO_8^+$ $[M+Na]^+$ 750.1, found 750.1.

3,4,6-Tri-*O*-benzyl-2-*O*-benzyloxycarbonyl-α,β-D-glucopyranosyl-1-(N-phenyl)-2,2,2-trifluoroacetimidate (18)



To a solution of compound **15** (20 mg, 34 µmol) in CH_2Cl_2 (1 mL), N-phenyltrifluoroacetimidoyl chloride[10] (63 mg, 303 µmol) and DBU (1.5 mg, 10 µmol) were added at -15 °C. The reaction mixture was stirred for 16 h 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%). ^{1}H NMR (600 MHz, CD_2Cl_2): 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); ^{13}C NMR (100 MHz, CD_2Cl_2) 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 $C_{43}H_{40}F_3NNaO_8^+$ $[M+Na]^+$ 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 CH_2Cl_2 (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 CH_2Cl_2. To quench the reaction, the solution was washed with 1 mL of aqueous saturated $NaHCO_3$ or Na_2SO_3 solution, and 0.5 mL water. The organic layer was separated, dried over Na_2SO_4 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).

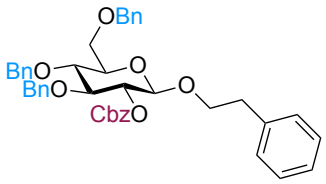
General procedure for glycosylation reactions with N-phenyltrifluoroacetimidoyl glucosyl donor

To a solution of the glucosyl donor (0.03 mmol) and the acceptor (0.05-0.06 mmol) in dry CH_2Cl_2 (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 NEt_3. 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

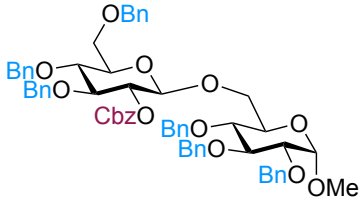
Procedure	Activator	Temperature	LG
A	NIS (2 eq.) TfOH (0.2 eq.)	-10 °C	SEt, STol
B	I_2 (2 eq.)	rt	SEt
C	TMSOTf (2 eq.)	-10 °C	SPym
D	AgOTf (2 eq.)	0 °C or rt	SPym, STaz
E	TMSOTf (0.1 eq.)	-10 °C	$OC(NPh)CF_3$

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



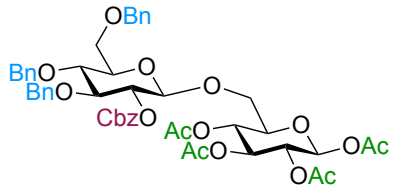
To a solution of glucosyl donor **14** (81.5 mg, 0.12 mmol) and 2-phenylethanol (22.0 mg, 0.18 mmol) in dry CH_2Cl_2 (2.5 mL) molecular sieve (3Å, 250 mg) was added and the reaction mixture was stirred overnight at room temperature. After cooling to -10°C, TMSOTf (43 µl, 0.24 mmol) was added and stirring 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 Et_3N, diluted with CH_2Cl_2 and filtrated over Celite. The filtrate was washed with water and brine, dried over Na_2SO_4 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.; R_f 0.39 (hexanes/EtOAc = 4/1); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) 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); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) 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 $C_{43}H_{44}NaO_8^+$ $[M+Na]^+$ 711.2928, found 711.2932.

Methyl 2,3,4,9,10,12-hexa-*O*-benzyl-8-*O*-benzyloxycarbonyl-α-D-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 CH_2Cl_2 (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 Et_3N, the mixture was diluted with CH_2Cl_2 and filtrated over Celite. The filtrate was washed with water and brine, dried over Na_2SO_4 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%); R_f 0.64 (hexanes/ EtOAc = 2/1); ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.41-7.31 (m, 11H), 7.30-7.22 (m, 16H), 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); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 154.80 (s, 1C), 139.53 (s, 1C), 139.00 (s, 1C), 138.87 (s, 1C), 138.62 (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 (d, 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 $C_{63}H_{66}NaO_{13}^+$ $[M+Na]^+$ 1053.4396, found 1053.4392.

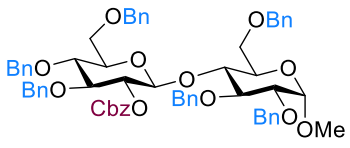
1,2,3,4-Tetra-*O*-acetyl-9,10,12-tri-*O*-benzyl-8-*O*-benzyloxycarbonyl-gentiobioside (26)



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 CH_2Cl_2 (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 $NaHCO_3$ and Na_2SO_3 solution (1:1). The mixture was diluted with CH_2Cl_2 and filtrated over Celite. The filtrate was washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes/EtOAc gradient elution) to obtain **26** (225 mg, 77%); R_f 0.29 (hexanes/ EtOAc = 2/1); ^{1}H NMR (600 MHz, CD_2Cl_2) 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); ^{13}C NMR

(100 MHz, CD_2Cl_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), 128.02 (d, 1C), 127.97 (d, 1C), 100.96 (d, 1C), 92.11 (d, 1C), 83.12 (d, 1C), 78.06 (d, 1C), 77.59 (d, 1C), 75.59 (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 $C_{49}H_{54}NaO_{17}^+$ $[M+Na]^+$ 937.3254, found: 937.3251

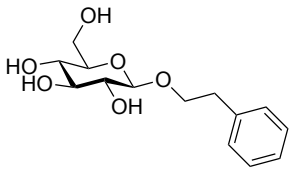
Methyl 2,3,6,9,10,12-hexa-*O*-benzyl-8-*O*-benzyloxycarbonyl-α-D-cellobioside (27)



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_2Cl_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_2Cl_2 and filtrated over Celite. The filtrate was washed with water and brine, dried over Na_2SO_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); ^1H NMR (600 MHz, CD_2Cl_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 (ddd, *J* = 9.8, 4.4, 1.9, 1H); ^{13}C NMR (150 MHz, CD_2Cl_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 $C_{63}H_{66}NaO_{13}^+$ $[M+Na]^+$ 1053.4396, found 1053.4392.

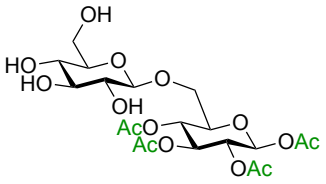
f. Deprotection

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



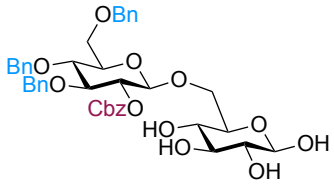
To a suspension of compound **24** (20 mg, 0.03 mmol) in dry ethanol (1 mL) one small tip of a spatula of Pd/C was added under an argon atmosphere. The argon balloon was changed for a balloon filled with H_2 and the reaction mixture was stirred for 4 h at rt. The reaction mixture was filtered through 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 a H_2 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%). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 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); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 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 $C_{20}H_{30}NaO_{15}^+$ $[M+Na]^+$ 533.1477, found: 533.1482.

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

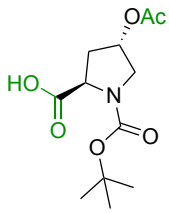


To a suspension of the disaccharide **26** (80 mg, 0.09 mmol) in dry methanol (20 mL) KCN (3 mg, 0.05 mmol) was added at 0 °C. The reaction mixture was slowly warmed to room temperature and stirring was continued for 4 h. Water was added and the reaction mixture was concentrated to a third of its volume. The residue was diluted with MeCN/H_2O (1:1) and purified by preparative HPLC to obtain compound **31**, as an anomeric mixture (50 mg, 75 %). ^{1}H NMR (600 MHz, MeOD) δ 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 (ddd, *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); ^{13}C 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 $C_{41}H_{46}NaO_{13}^+$ $[M+Na]^+$ 769.2831, found: 769.2829

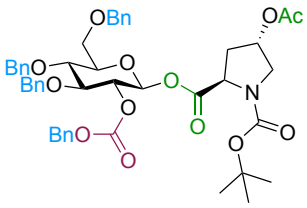
g. Synthesis of glycosyl esters

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%); ^{1}H NMR (400 MHz, $CDCl_3$)[1] 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); ^{13}C NMR (100 MHz, $CDCl_3$)[1] 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 $C_{12}H_{19}NNaO_6^+$ $[M+Na]^+$ 296.1, found 296.0.

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

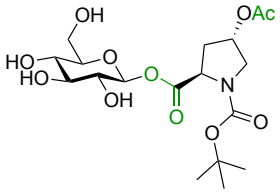


To a solution of glucosyl donor **11** (100 mg, 0.16 mmol) and *trans*-N-(*tert*-butoxycarbonyl)-4-acetoxy-L-proline (65 mg, 0.24 mmol) in dry CH_2Cl_2 (3 mL) molecular sieve 3Å (150 mg) was added and the reaction mixture was stirred for 2 h at room temperature. After cooling to -10°C, NIS (72 mg, 0.32 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_2SO_3 solution (1:1). The mixture was diluted with CH_2Cl_2 and filtrated over Celite. The filtrate was washed with water and brine, dried over Na_2SO_4 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); ^{1}H NMR (400 MHz, CD_2Cl_2)[2] 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

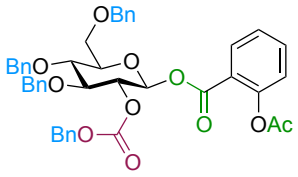
(m, 1H), 2.04 (s, 3H), 1.43 (s, 3H), 1.36 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2)[2] δ 171.19 (s, 1C), 171.10 (s, 1C), 170.62 (s, 1C), 170.52 (s, 1C), 154.68 (s, 2C), 154.38 (s, 1C), 153.55 (s, 1C), 138.52 (s, 1C), 138.48 (s, 1C), 138.43 (s, 4C), 135.80 (s, 1C), 135.52 (s, 1C), 129.09 (d, 2C), 129.04 (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), 80.97 (s, 1C), 80.64 (s, 1C), 77.60 (d, 1C), 77.55 (d, 1C), 76.83 (d, 1C), 76.65 (d, 1C), 76.35 (d, 1C), 76.25 (d, 1C), 75.71 (t, 2C), 75.35 (t, 2C), 73.79 (t, 1C), 73.76 (t, 1C), 73.07 (d, 1C), 72.18 (d, 1C), 70.46 (t, 1C), 70.41 (t, 1C), 68.65 (t, 1C), 68.57 (t, 1C), 58.23 (d, 1C), 57.98 (d, 1C), 52.76 (t, 1C), 52.39 (t, 1C), 36.75 (t, 1C), 35.74 (t, 1C), 28.46 (q, 2C), 28.18 (q, 4C), 21.23 (q, 2C); ESI-MS calcd for $C_{47}H_{53}NNaO_{13}^+$ $[M+Na]^+$ 862.3, found 862.1.

trans-N-(_tert_-butoxycarbonyl)-4-acetoxy-L-proline, ß-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_2O 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 $C_{18}H_{29}NNaO_{11}^+$ $[M+Na]^+$ 458.2, found 458.1.

Acetylsalicylic acid, 3,4,6-tri-*O*-benzyl-2-*O*-benzyloxycarbonyl-β-D-glucopyranosyl ester (36)

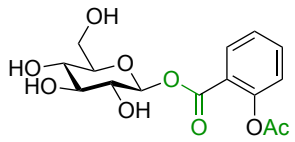


To a solution of glucosyl donor **11** (100 mg, 0.16 mmol) and acetylsalicylic acid (**33**) (43 mg, 0.24 mmol) in dry CH_2Cl_2 (3 mL) molecular sieve 3Å (150 mg) was added and the reaction mixture was stirred for 2 h at room temperature. After cooling to -10°C, NIS (72 mg, 0.32 mmol) and TfOH (5 mg, 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_2SO_3 solution (1:1). The mixture was diluted with CH_2Cl_2 and filtrated over Celite. The filtrate was washed with water and brine, dried over Na_2SO_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_2Cl_2)

[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, 2H), 3.77 (d, *J* = 2.8 Hz, 2H), 3.69 (dt, *J* = 9.8, 2.8 Hz, 1H), 2.3 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) 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), 128.89 (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 $C_{44}H_{42}NaO_{11}^+$ [M+Na]$^+$ 769.3, found 769.3.

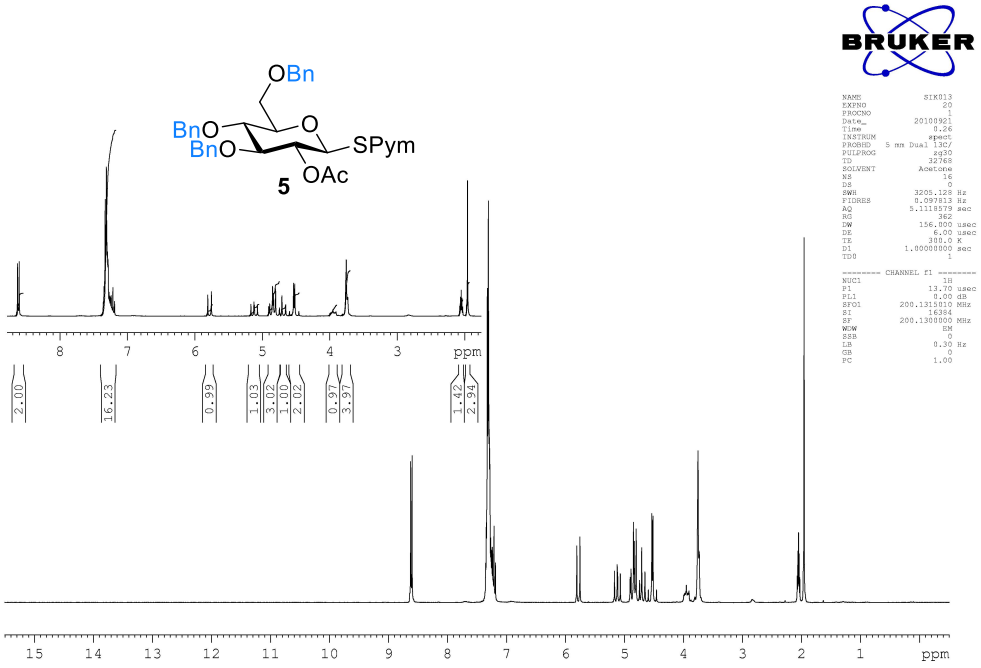
Acetylsalicylic acid, ß-D-glucopyranosyl ester (37)



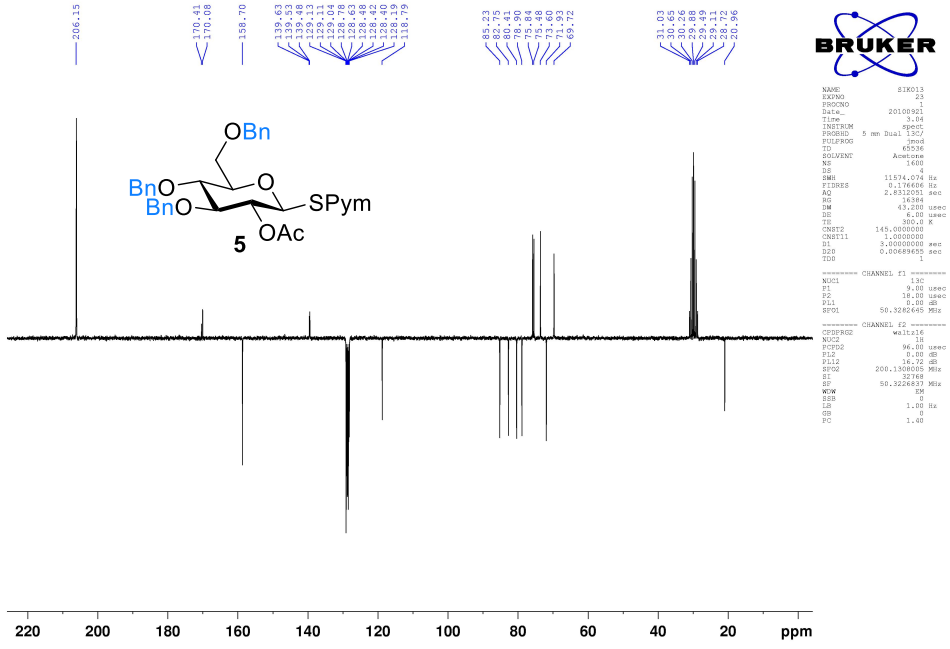
To a suspension of compound **36** (98 mg, 0.13 mmol) in dry ethanol (1.5 mL) three small tips of a spatula of Pd/C were added under an argon atmosphere. The argon balloon was changed for a H_2-balloon and the mixture was stirred for 16 h at rt. The reaction mixture was filtered through a syringe filter and the filtrate was concentrated. The residue was dissolved in MeCN/H_2O and purified by preparative HPLC to yield **37** as a white solid (29 mg, 65%). ^{1}H 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); ^{13}C 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 $C_{15}H_{18}NaO_{19}^+$ [M+Na]$^+$ 365.1, found 365.0.

3) NMR Spectra

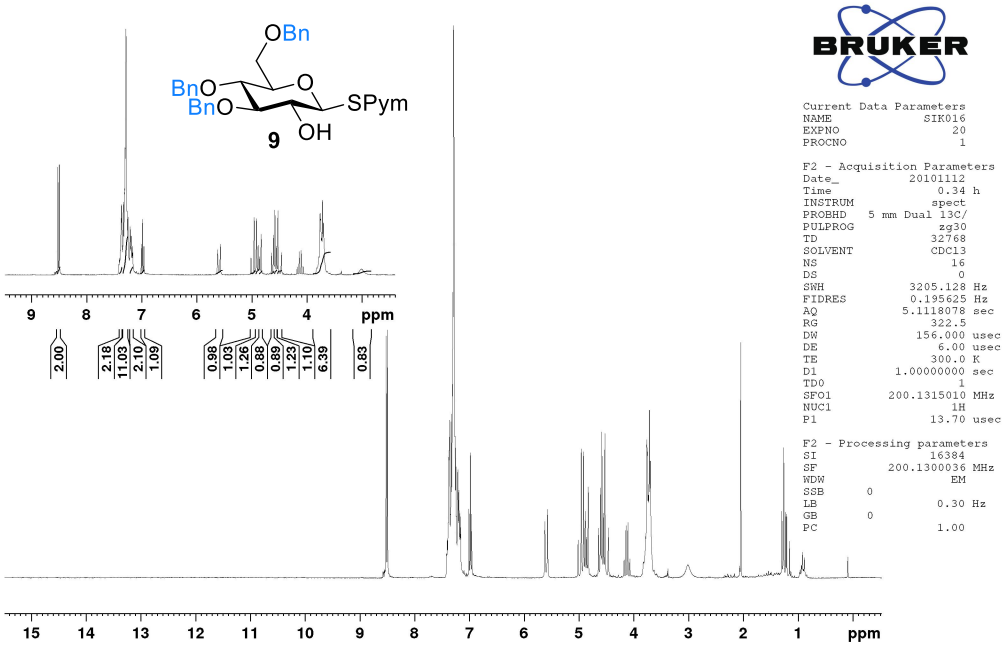
^{1}H NMR (d_6-acetone, 200 MHz)



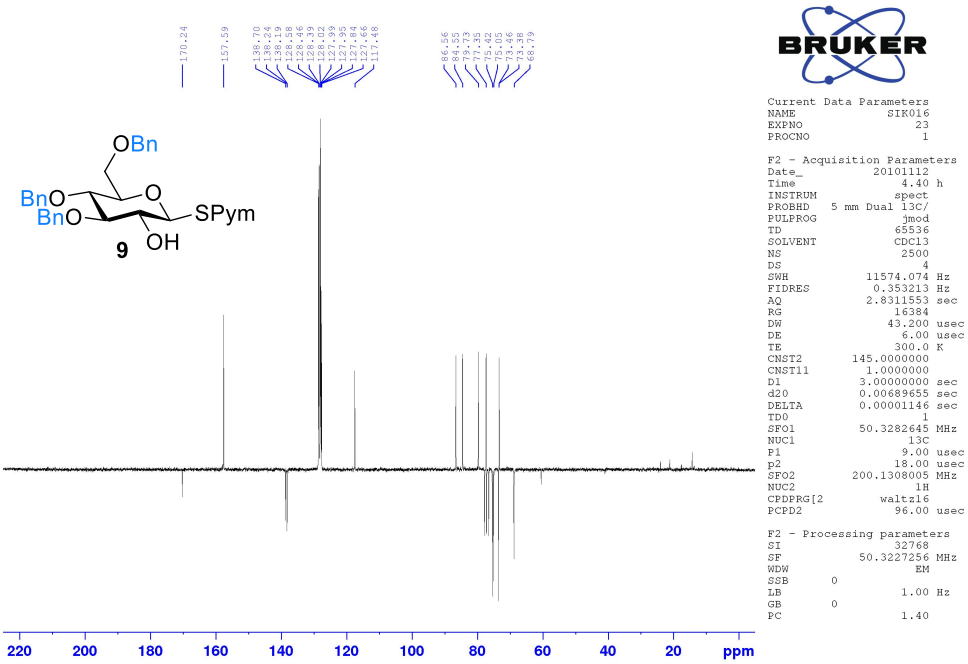
^{13}C NMR (d_6-acetone, 50 MHz)

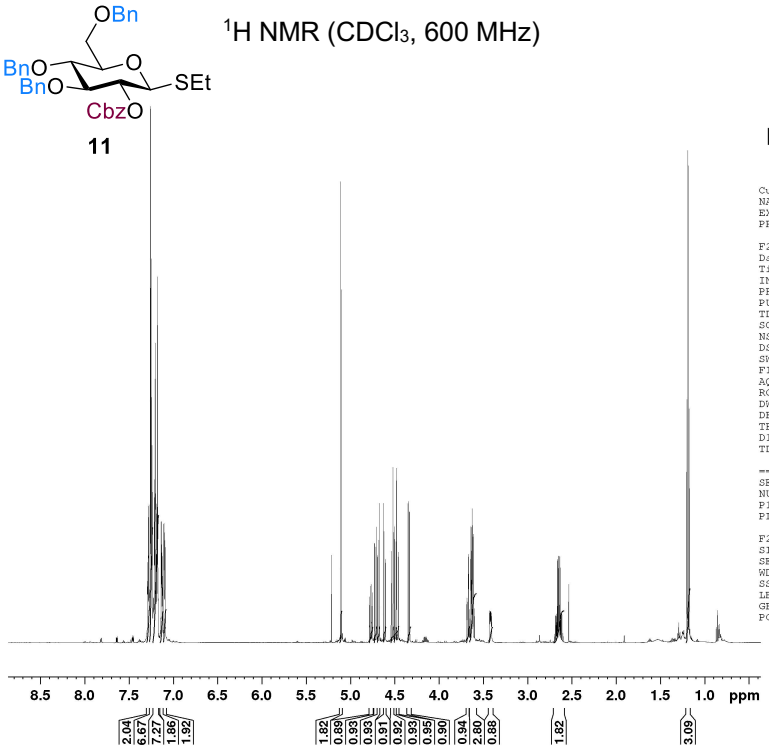


^{1}H NMR ($CDCl_3$, 200 MHz)



^{13}C NMR ($CDCl_3$, 50 MHz)




OBn
BnO
BnO
O
SEt
CbzO
11
1H NMR (CDCl3, 600 MHz)
BRUKER
Current Data Parameters
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EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
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Time 15.45
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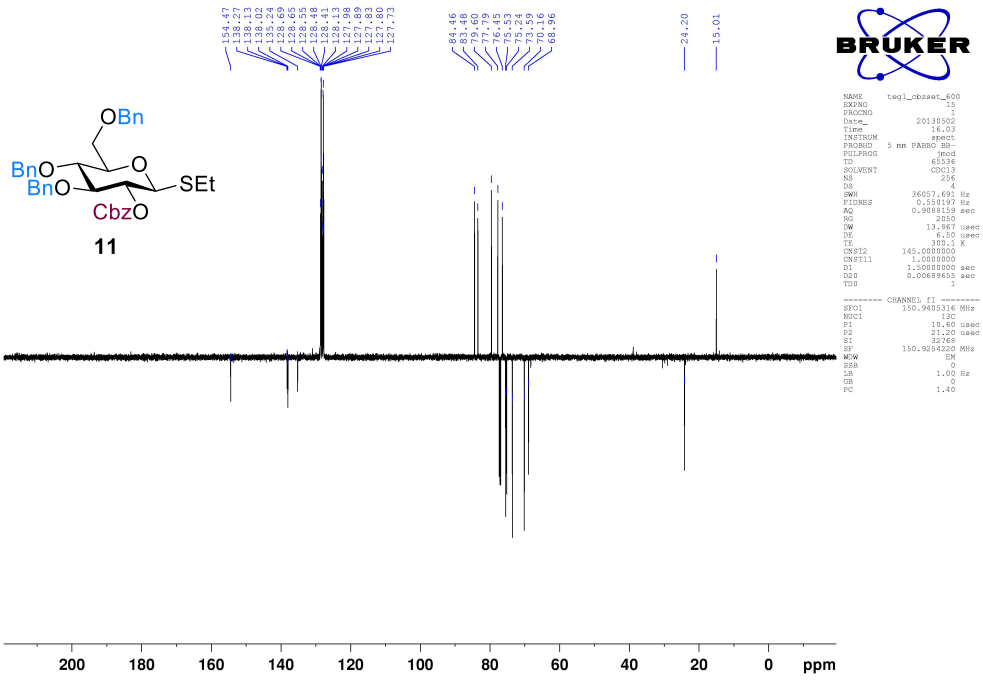
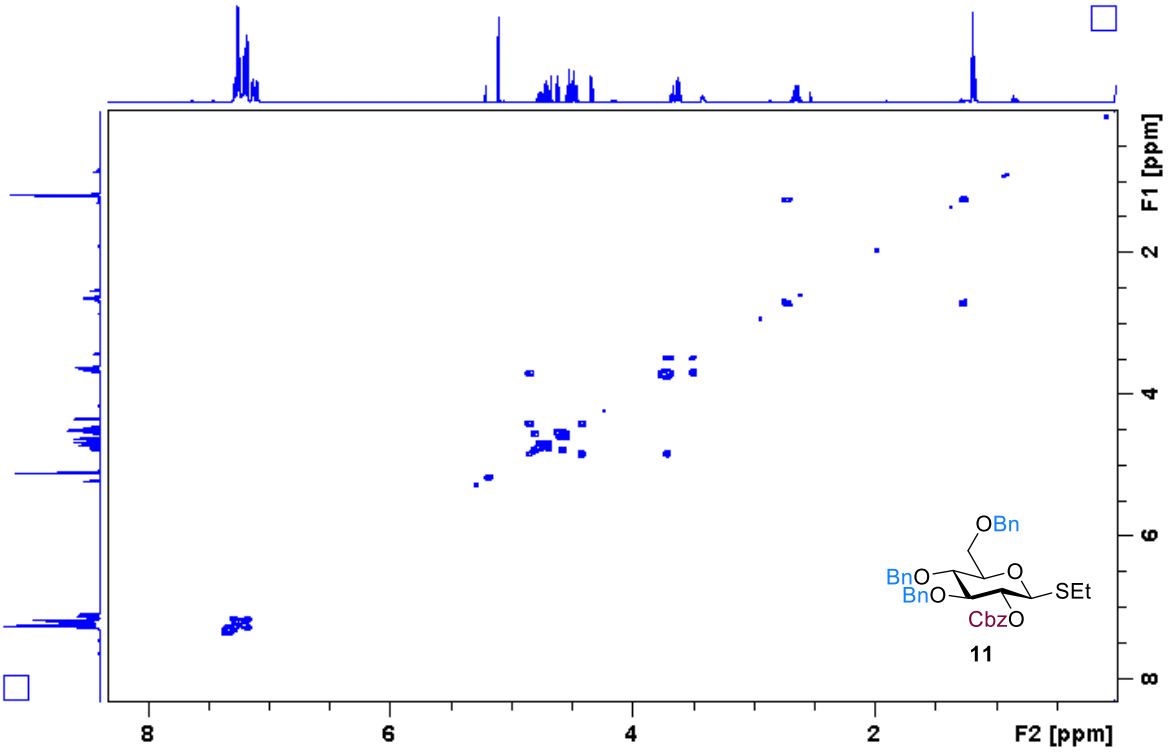
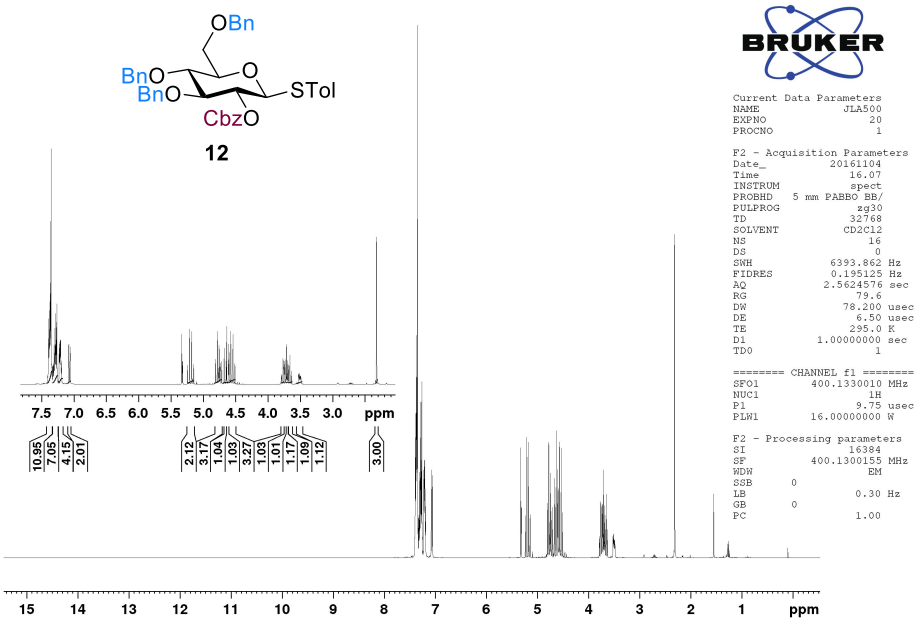
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 4
SWH 5630.631 Hz
FIDRES 0.085917 Hz
AQ 5.8195968 sec
RG 90.5
DW 88.800 usec
DE 6.50 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
SFO1 600.2227148 MHz
NUC1 1H
P1 12.50 usec
PLW1 18.00000000 W
F2 - Processing parameters
SI 65536
SF 600.2200624 MHz
WDW GM
SSB 0
LB -0.10 Hz
GB 0.1
PC 1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.04 6.67 7.27 1.86 1.92 1.82 0.89 0.93 0.93 0.91 0.92 0.93 0.95 0.90 0.94 2.80 0.88 1.82 3.09


13C NMR (CDCl3, 150 MHz)
154.47 138.27 138.13 138.02 137.98 128.69 128.65 128.55 128.48 128.41 128.13 127.98 127.89 127.83 127.80 127.73
84.46 83.48 79.60 77.79 76.45 75.53 75.24 73.59 70.16 68.96
24.20
15.01
OBn
BnO
BnO
O
SEt
CbzO
11
BRUKER
NAME tegl_cbzset_600
EXPNO 15
PROCNO 1
Date_ 20130502
Time 16.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 36057.691 Hz
FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 2050
DW 13.867 usec
DE 6.50 usec
TE 300.1 K
CNST2 145.0000000
CNST11 1.0000000
D1 1.50000000 sec
D20 0.00689655 sec
TD0 1
CHANNEL f1
SFO1 150.9405316 MHz
NUC1 13C
P1 10.60 usec
P2 21.20 usec
SI 32768
SF 150.9254220 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm

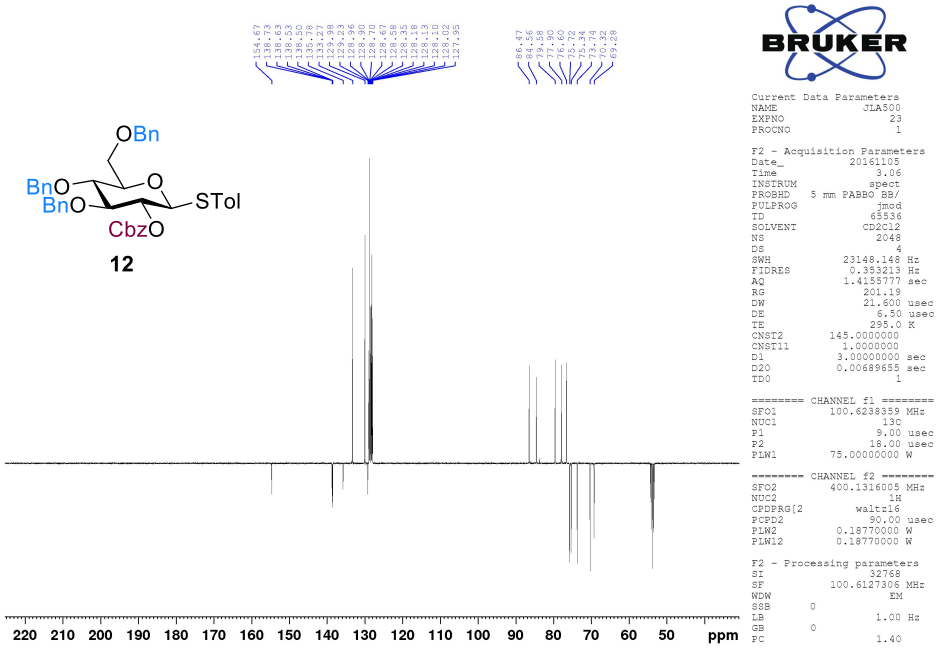
H,H-COSY ($CDCl_3$, 600 MHz)



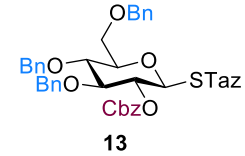
^{1}H NMR (CD_2Cl_2, 400 MHz)



^{13}C NMR (CD_2Cl_2, 100 MHz)



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



13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EXPNO                     10
PROCNO                     1

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Time                   1.57 h
INSTRUM               spect
PROBHD    5 mm Dual 13C/
PULPROG                zg30
TD                    32768
SOLVENT             Acetone
NS                        16
DS                         0
SWH                 3205.128 Hz
FIDRES              0.195625 Hz
AQ                  5.1118078 sec
RG                      574.7
DW                    156.000 usec
DE                      6.00 usec
TE                     300.0 K
D1                 1.00000000 sec
TD0                        1
SFO1              200.1315010 MHz
NUC1                      1H
P1                     13.70 usec

F2 - Processing parameters
SI                        16384
SF                200.1300007 MHz
WDW                       EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
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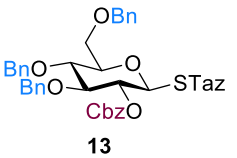
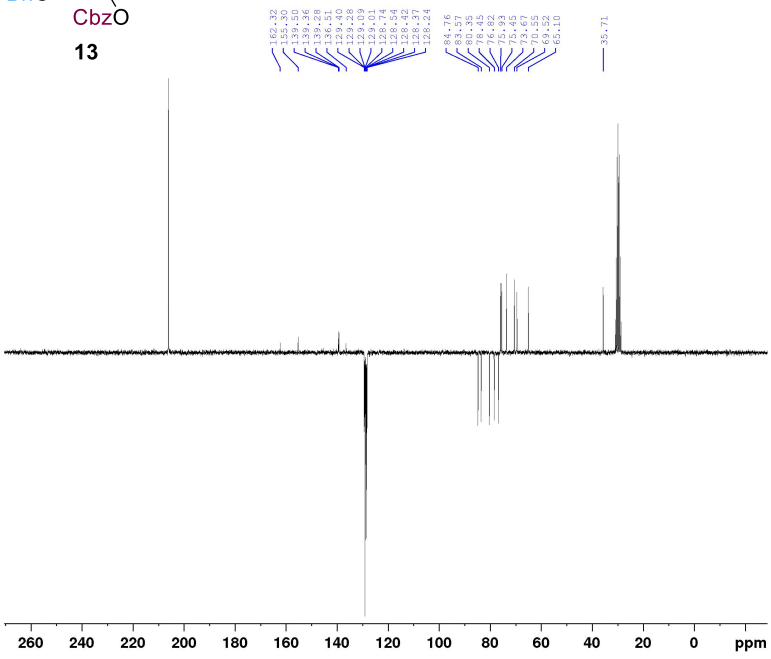
^{13}C NMR (d_6-acetone, 50 MHz)



13

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Current Data Parameters
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EXPNO                     13
PROCNO                     1

F2 - Acquisition Parameters
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PULPROG               jmod
TD                    65536
SOLVENT             Acetone
NS                      2500
DS                         4
SWH                15060.241 Hz
FIDRES              0.459602 Hz
AQ                  2.1757953 sec
RG                     16384
DW                    33.200 usec
DE                      6.00 usec
TE                     300.0 K
CNST2             145.0000000
CNST11              1.0000000
D1                 3.00000000 sec
d20                0.00689655 sec
DELTA              0.00001146 sec
TD0                        1
SFO1              50.3287677 MHz
NUC1                      13C
P1                     9.00 usec
p2                    18.00 usec
SFO2             200.1308005 MHz
NUC2                      1H
CPDPRG[2             waltz16

F2 - Processing parameters
SI                        32768
SF                50.3226849 MHz
WDW                       EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.40
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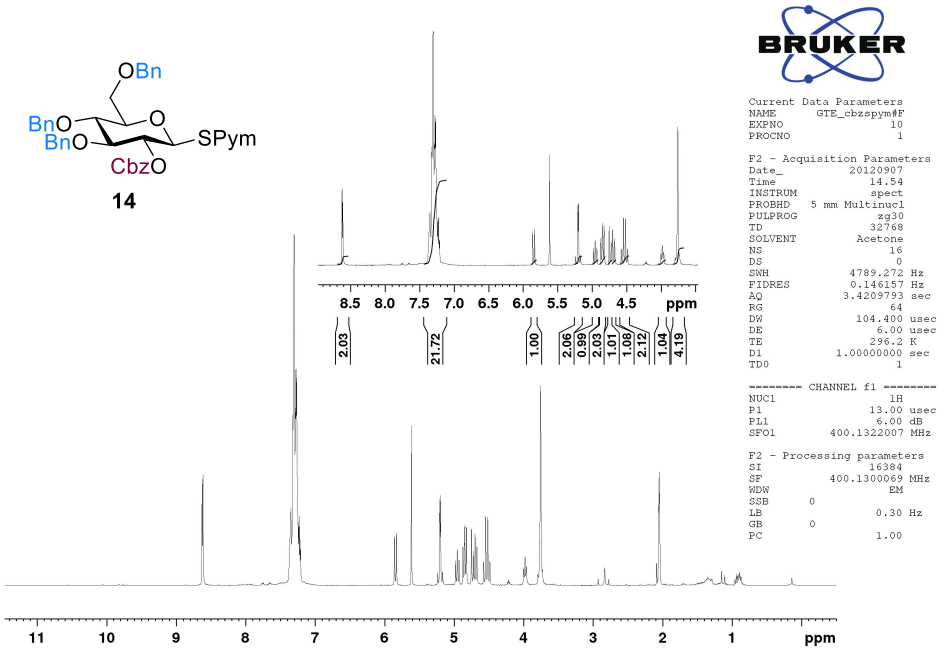
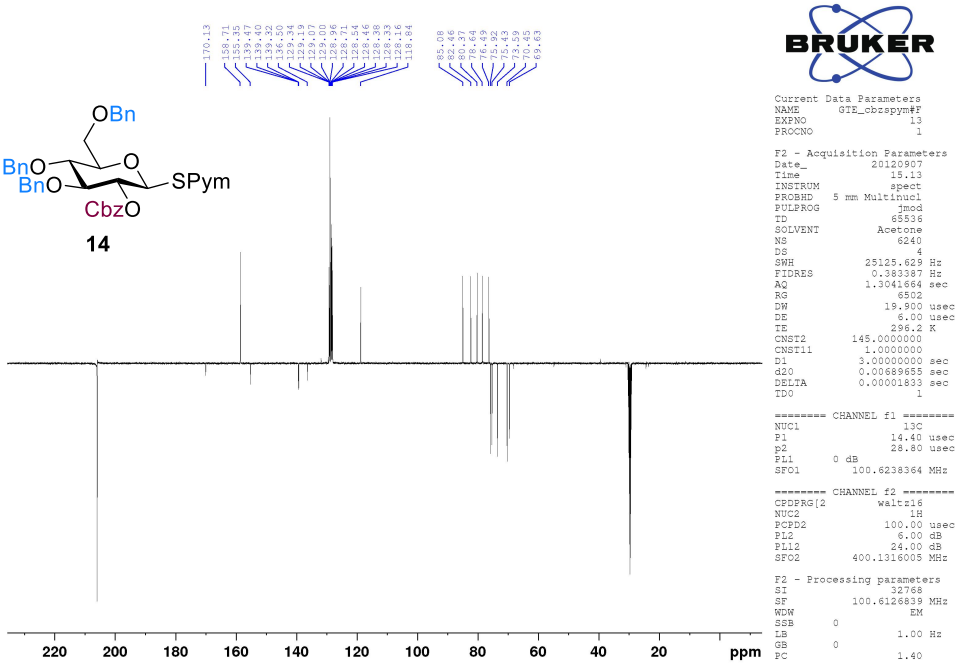
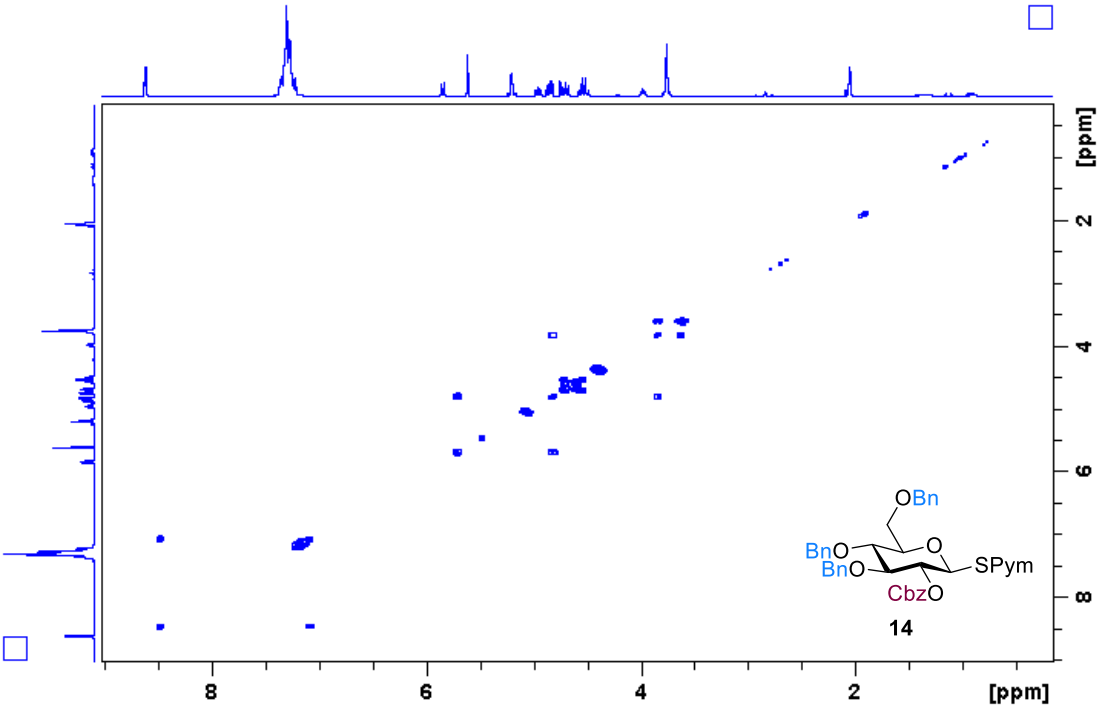
^{1}H NMR (d_6-acetone, 400 MHz)



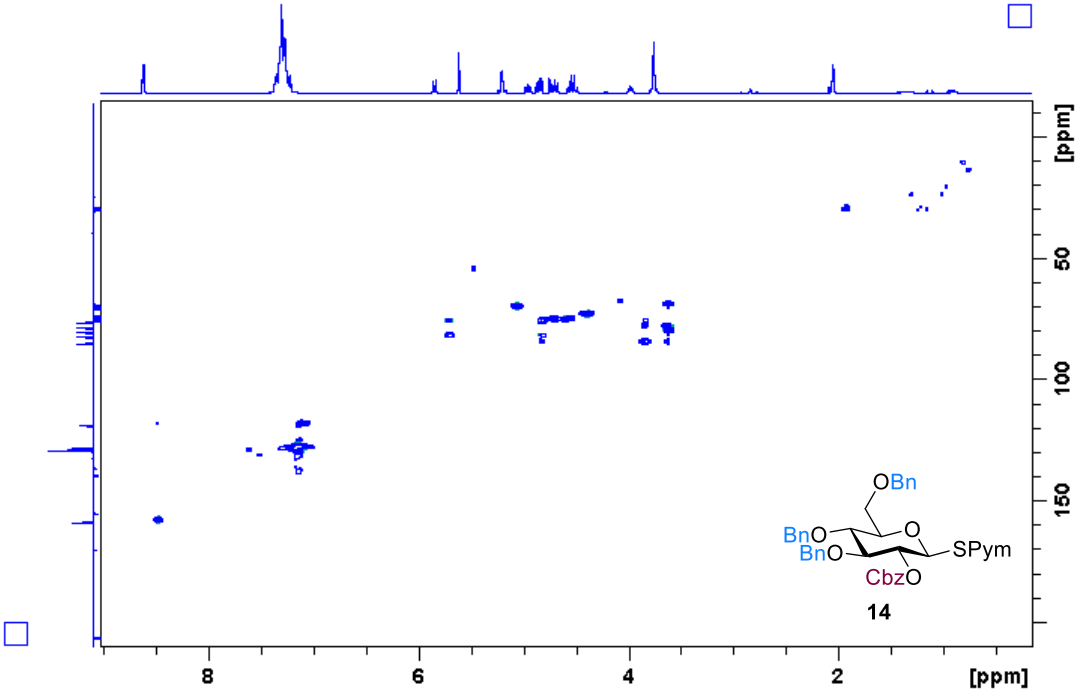
^{13}C NMR (d_6-acetone, 100 MHz)



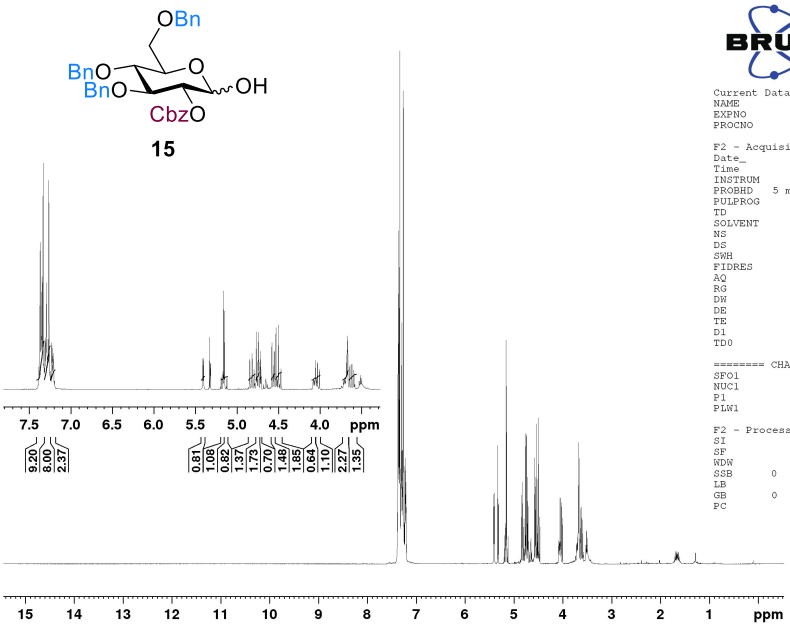
H,H-COSY (*d*$_6$-acetone, 400 MHz)



HSQC (*d*$_6$-acetone, 400 MHz)



^{1}H NMR (CD_2Cl_2, 400 MHz)



BRUKER

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EXPNO                     10
PROCNO                     1

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Time                  11.30
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG               zg30
TD                   32768
SOLVENT             CD2Cl2
NS                       16
DS                        0
SWH                6393.862 Hz
FIDRES            0.195125 Hz
AQ                2.5624576 sec
RG                    45.28
DW                   78.200 usec
DE                    6.50 usec
TE                   295.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             400.1330010 MHz
NUC1                       1H
P1                       9.75 usec
PLW1             16.00000000 W

F2 - Processing parameters
SI                       16384
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WDW                         EM
SSB                       0
LB                        0.30 Hz
GB                        0
PC                        1.00
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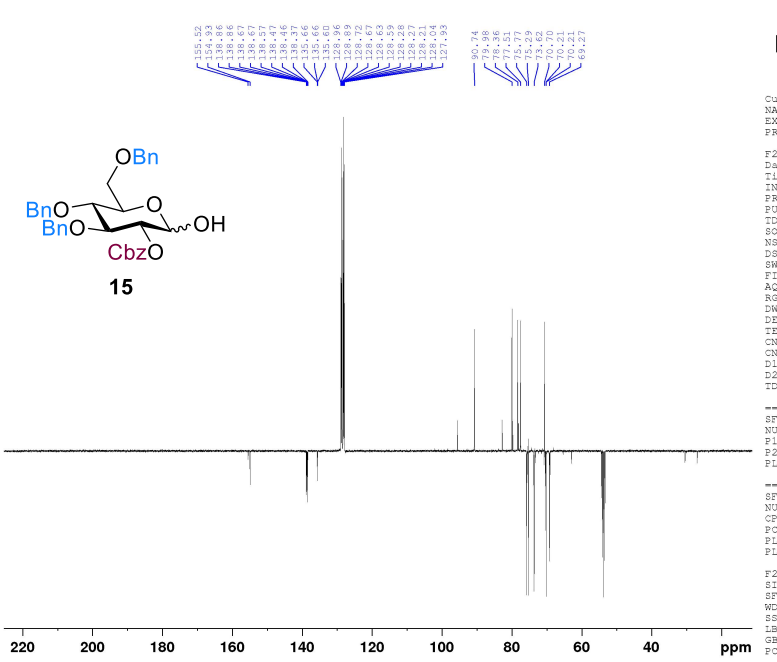
^{13}C NMR (CD_2Cl_2, 100 MHz)



BRUKER

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Current Data Parameters
NAME                  JLA500
EXPNO                     13
PROCNO                     1

F2 - Acquisition Parameters
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Time                  14.04
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG             zgmod
TD                   65536
SOLVENT             CD2Cl2
NS                     2048
DS                        4
SWH               23148.148 Hz
FIDRES            0.353213 Hz
AQ                1.4155777 sec
RG                   201.19
DW                   21.600 usec
DE                    6.50 usec
TE                   295.0 K
CNST2            145.0000000
CNST11             1.0000000
D1                 3.00000000 sec
D20                0.00689655 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             100.6238359 MHz
NUC1                      13C
P1                       9.00 usec
P2                      18.00 usec
PLW1             75.00000000 W

======== CHANNEL f2 ========
SFO2             400.1316005 MHz
NUC2                       1H
CPDPRG[2              waltz16
PCPD2                   90.00 usec
PLW2              0.18770000 W
PLW12             0.18770000 W

F2 - Processing parameters
SI                       32768
SF                100.6127312 MHz
WDW                         EM
SSB                       0
LB                        1.00 Hz
GB                        0
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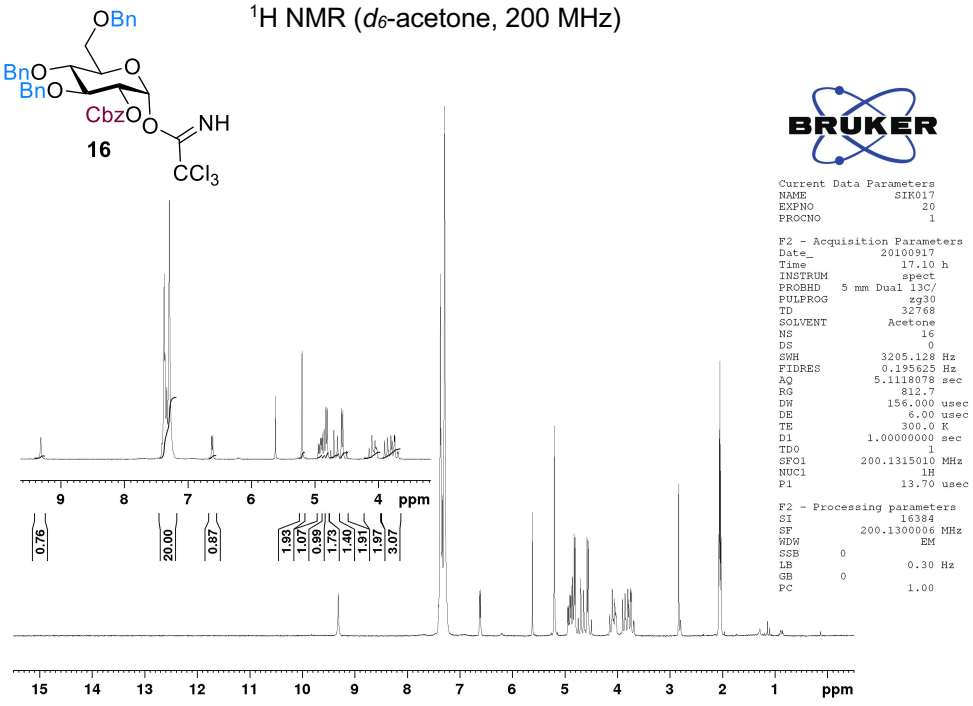
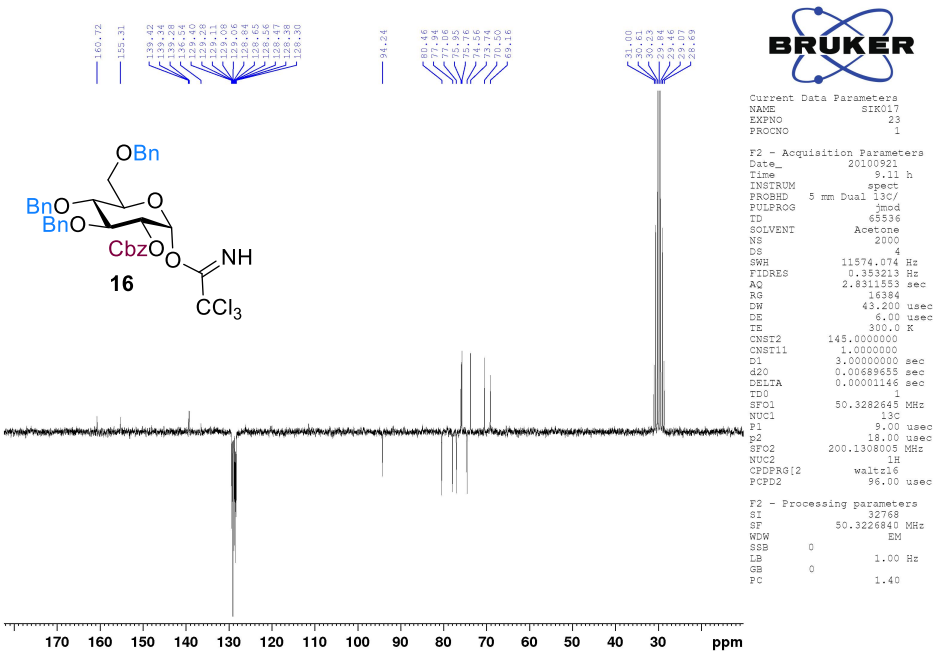
```

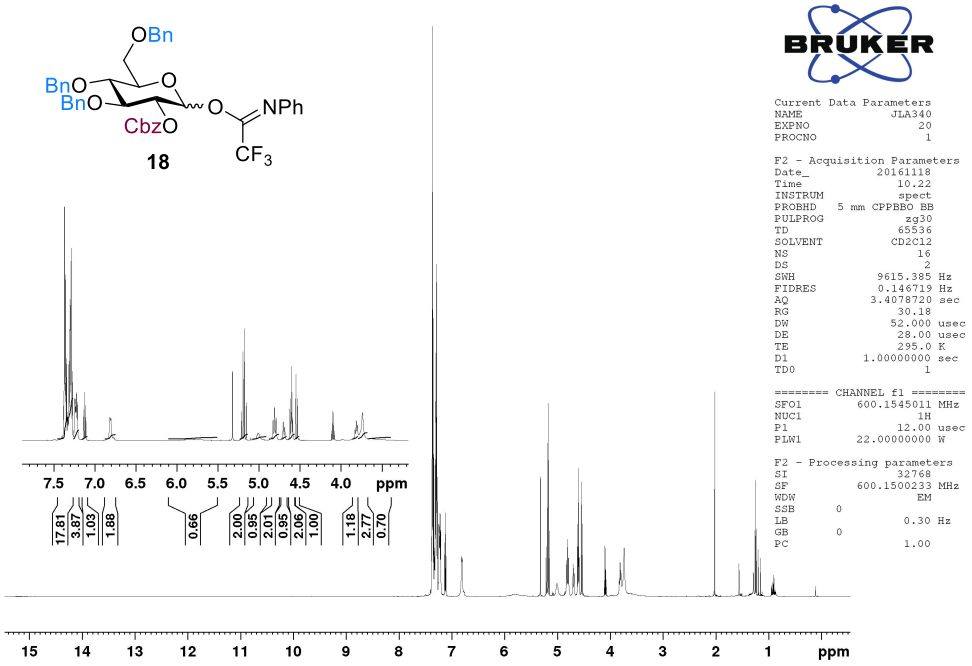
^{1}H NMR (d_6-acetone, 200 MHz)



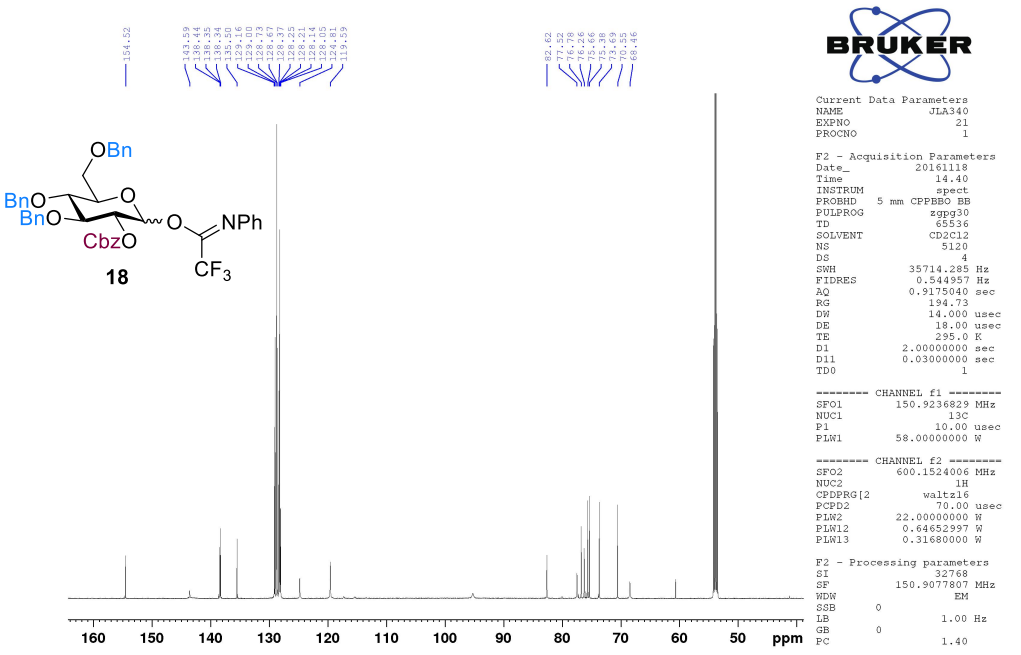
^{13}C NMR (d_6-acetone, 50 MHz)



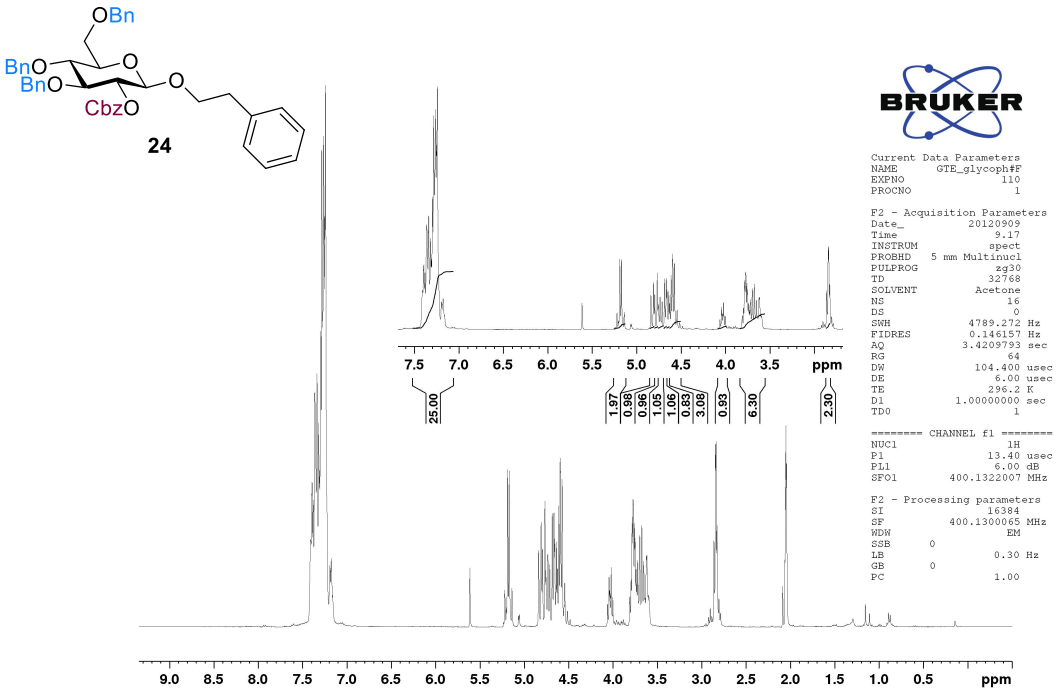
^{1}H NMR (CD_2Cl_2, 600 MHz)



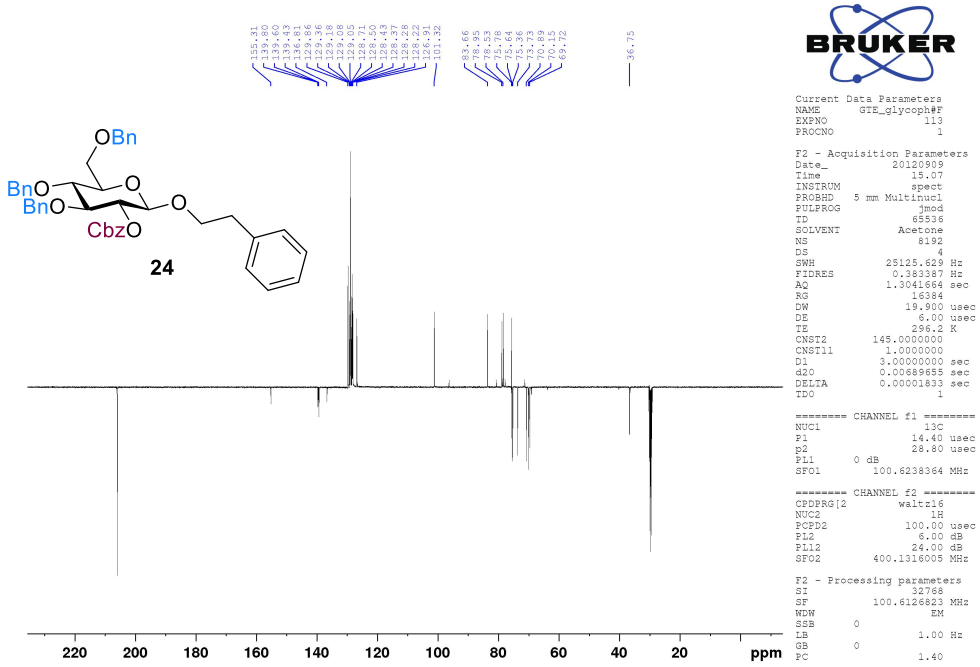
^{13}C NMR (CD_2Cl_2, 150 MHz)



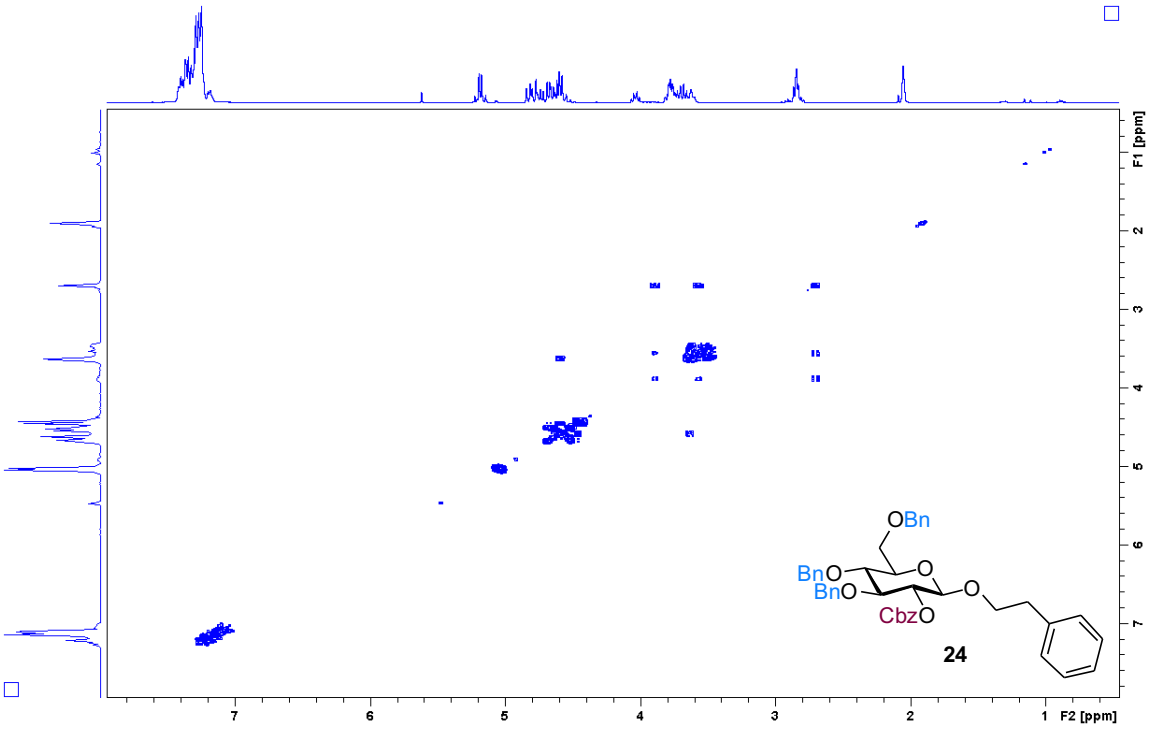
^{1}H NMR (d_6-acetone, 400 MHz)



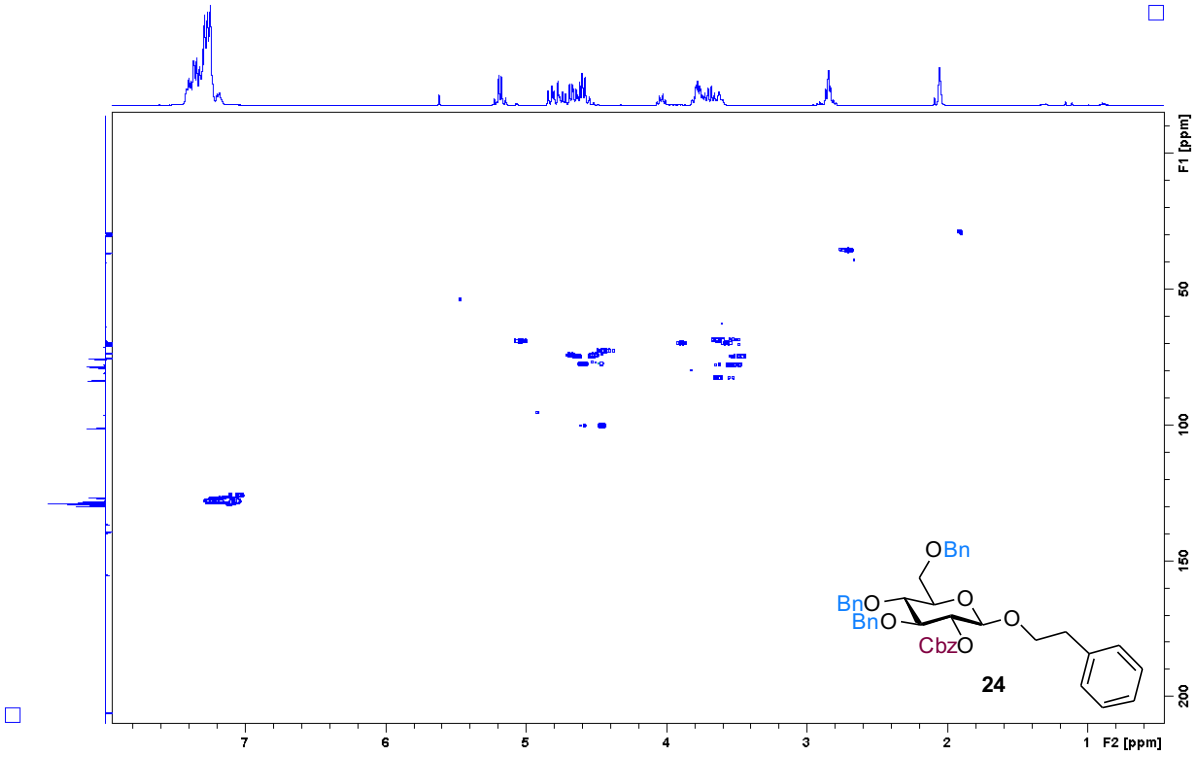
^{13}C NMR (d_6-acetone, 100 MHz)



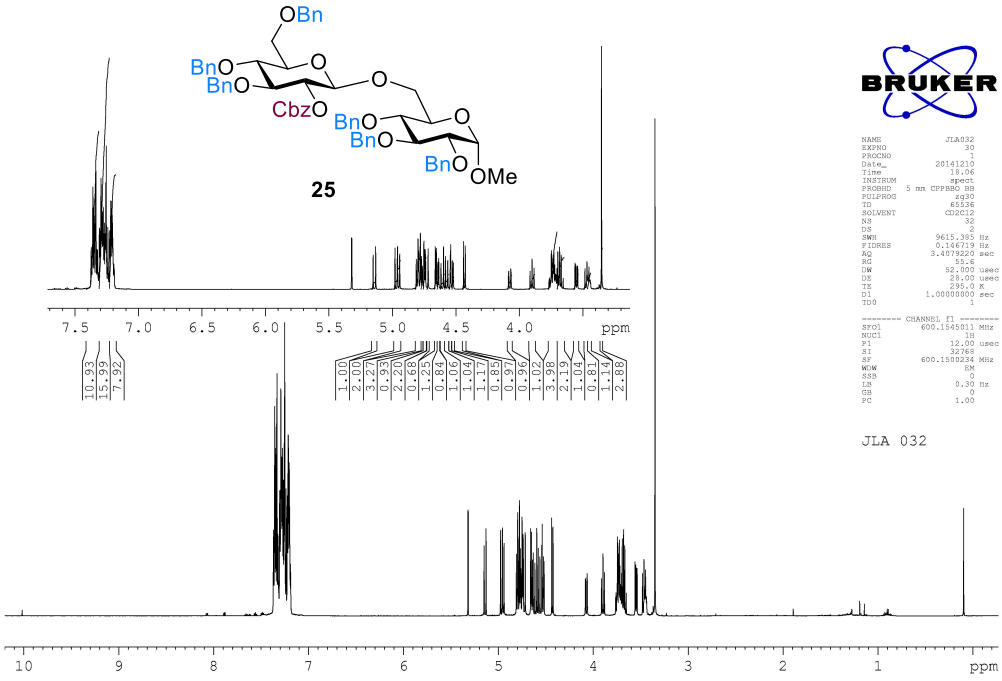
H,H COSY (*d*$_6$-acetone, 400 MHz)



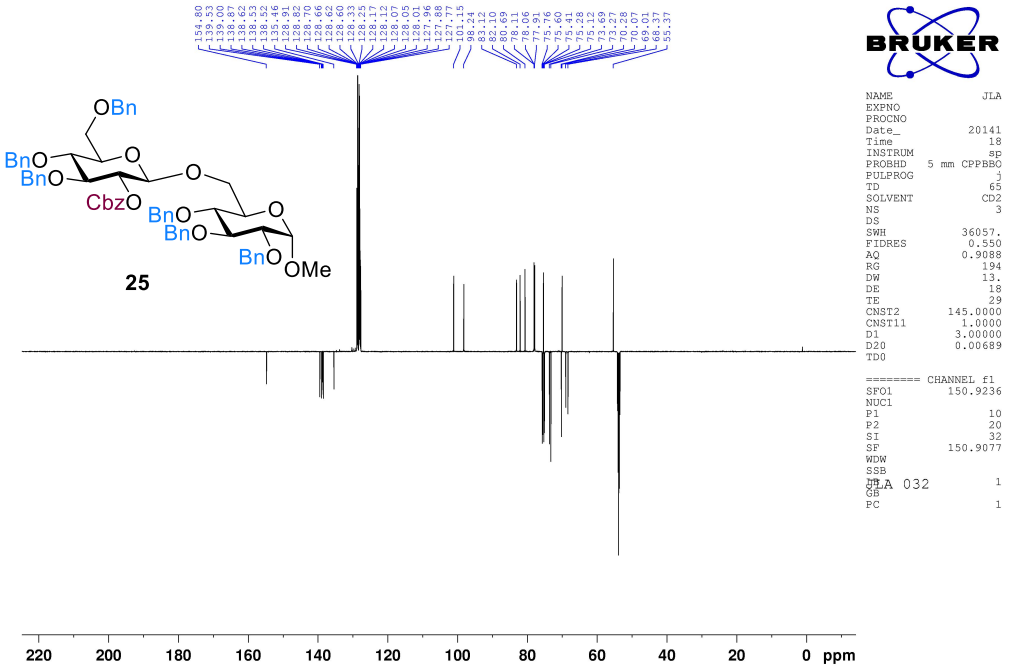
HSQC (*d*$_6$-acetone, 400 MHz)



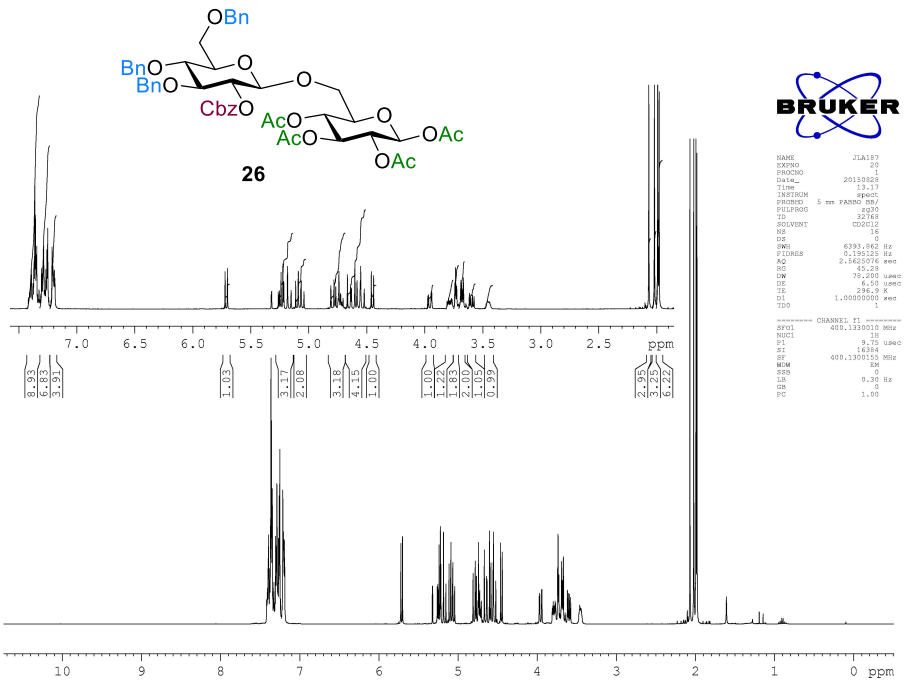
^{1}H NMR (CD_2Cl_2, 600 MHz)



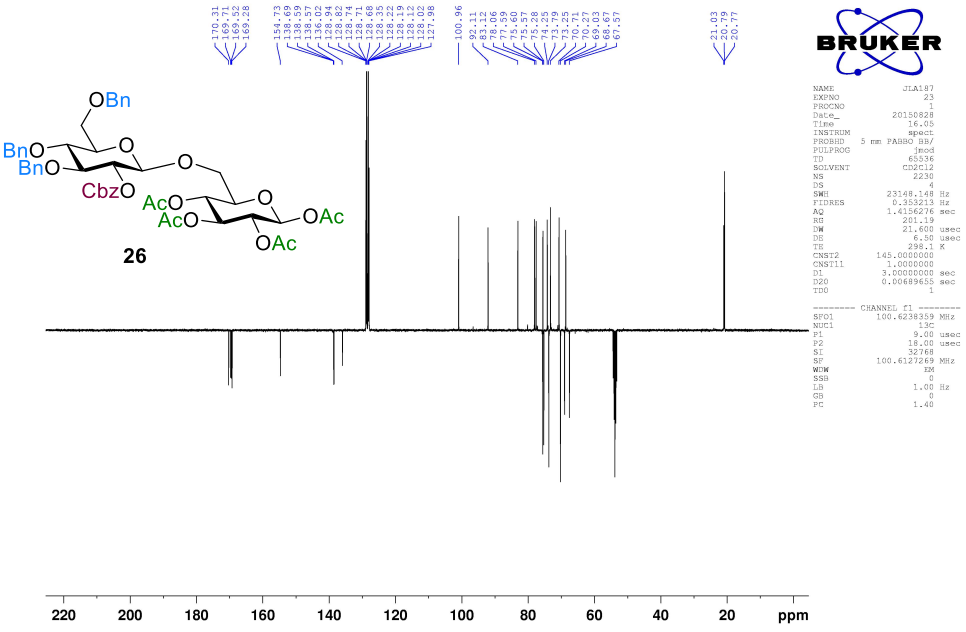
^{13}C NMR (CD_2Cl_2, 150 MHz)



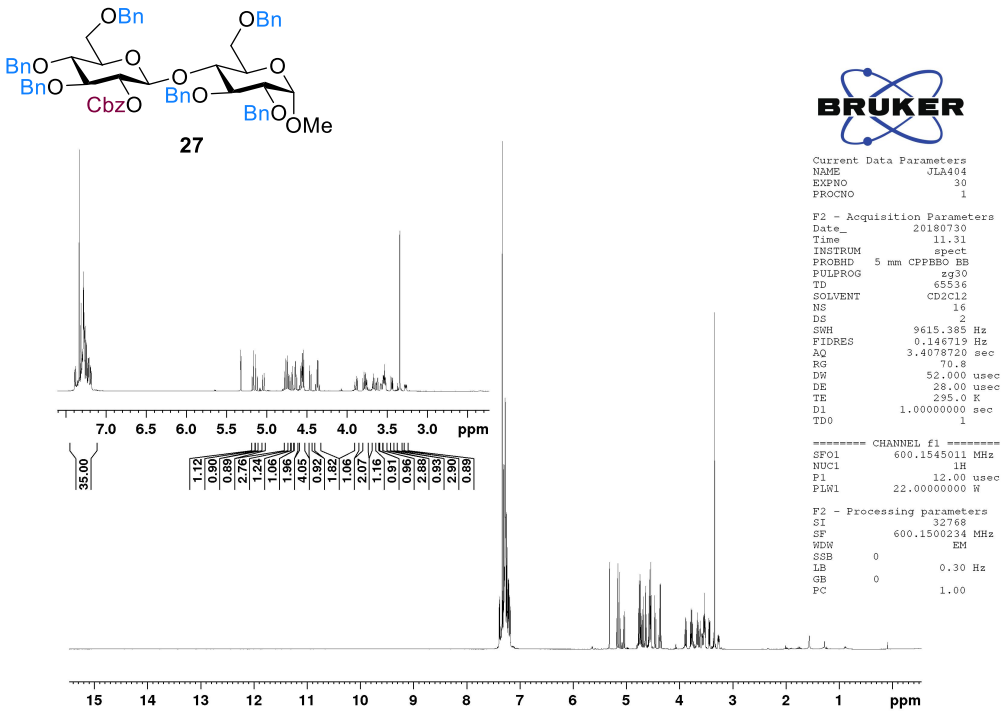
^{1}H NMR (CD_2Cl_2, 400 MHz)



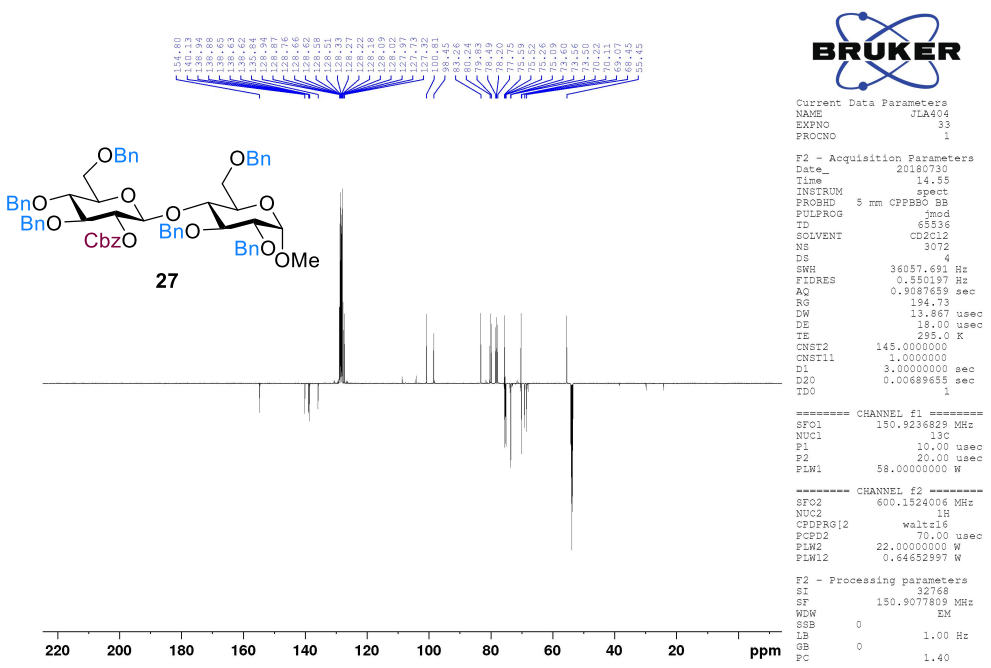
^{13}C NMR (CD_2Cl_2, 100 MHz)



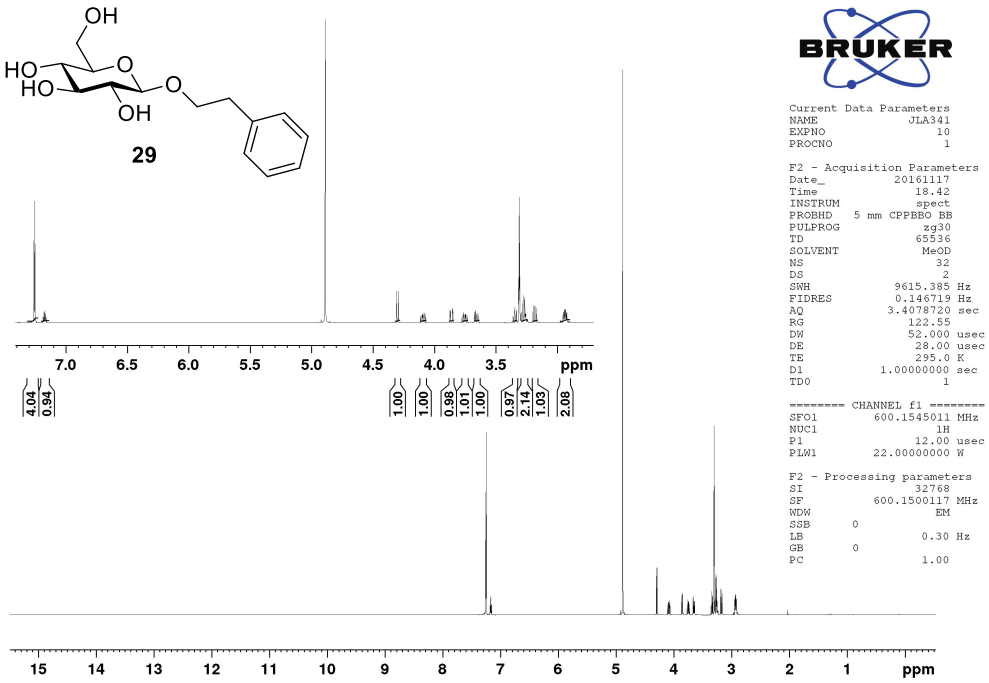
^{1}H NMR (CD_2Cl_2, 600 MHz)



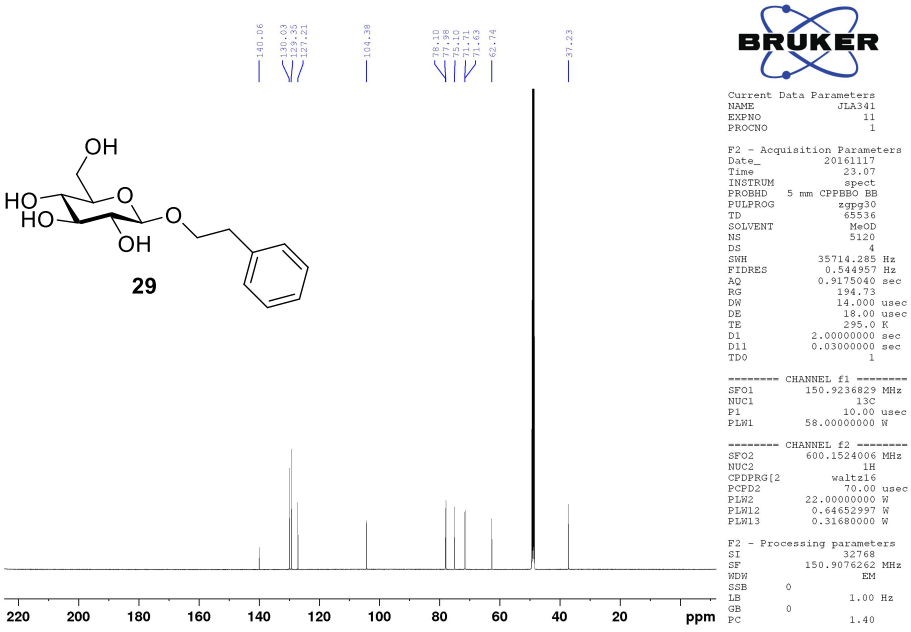
^{13}C NMR (CD_2Cl_2, 100 MHz)



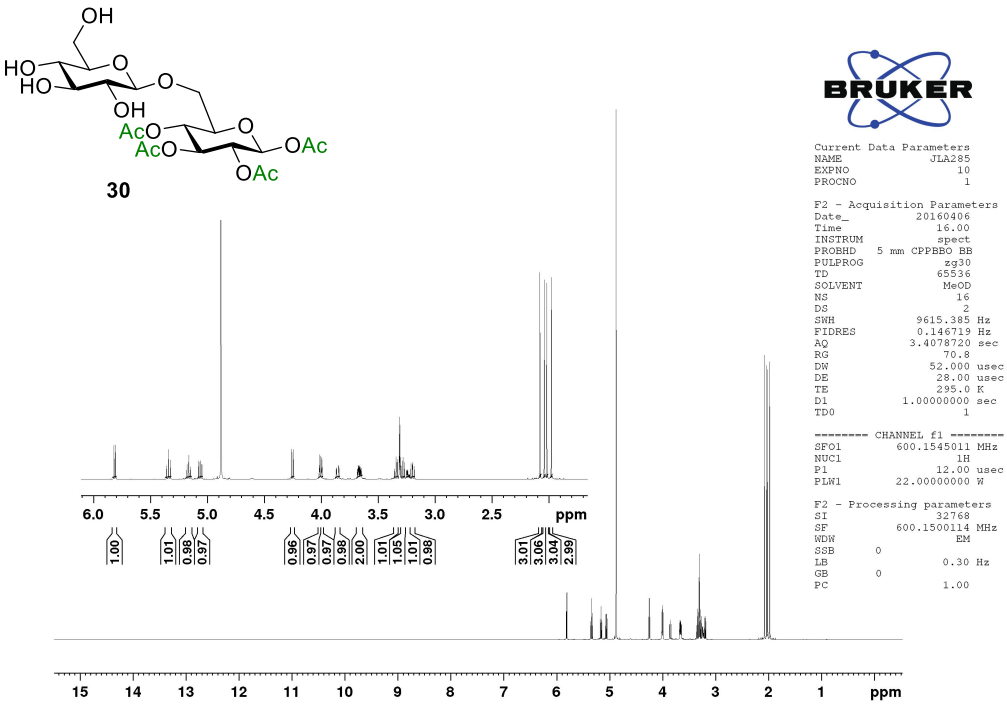
^{1}H NMR (CD_2Cl_2, 600 MHz)



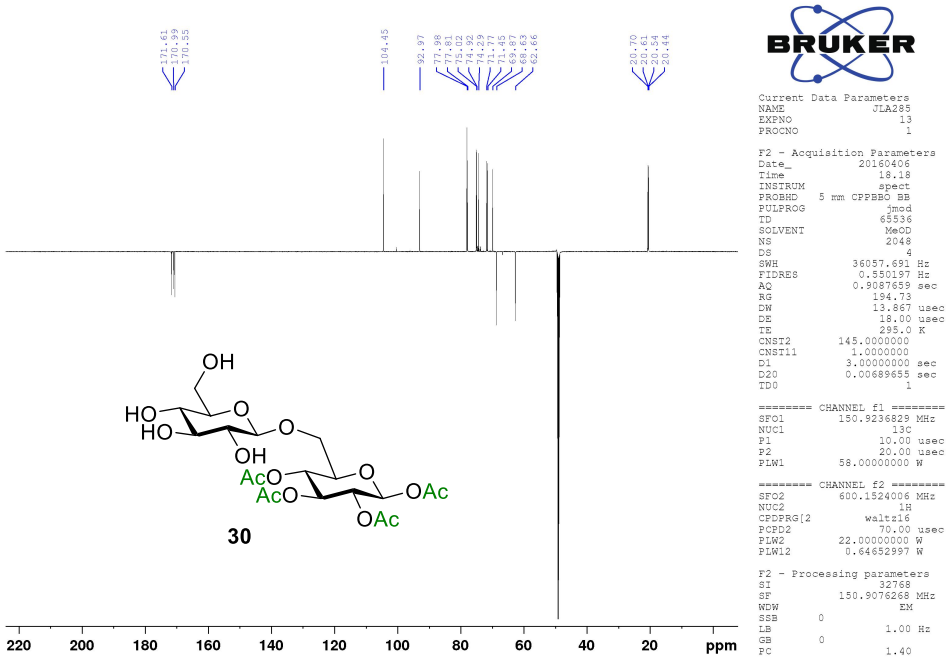
^{13}C NMR (CD_2Cl_2, 150 MHz)



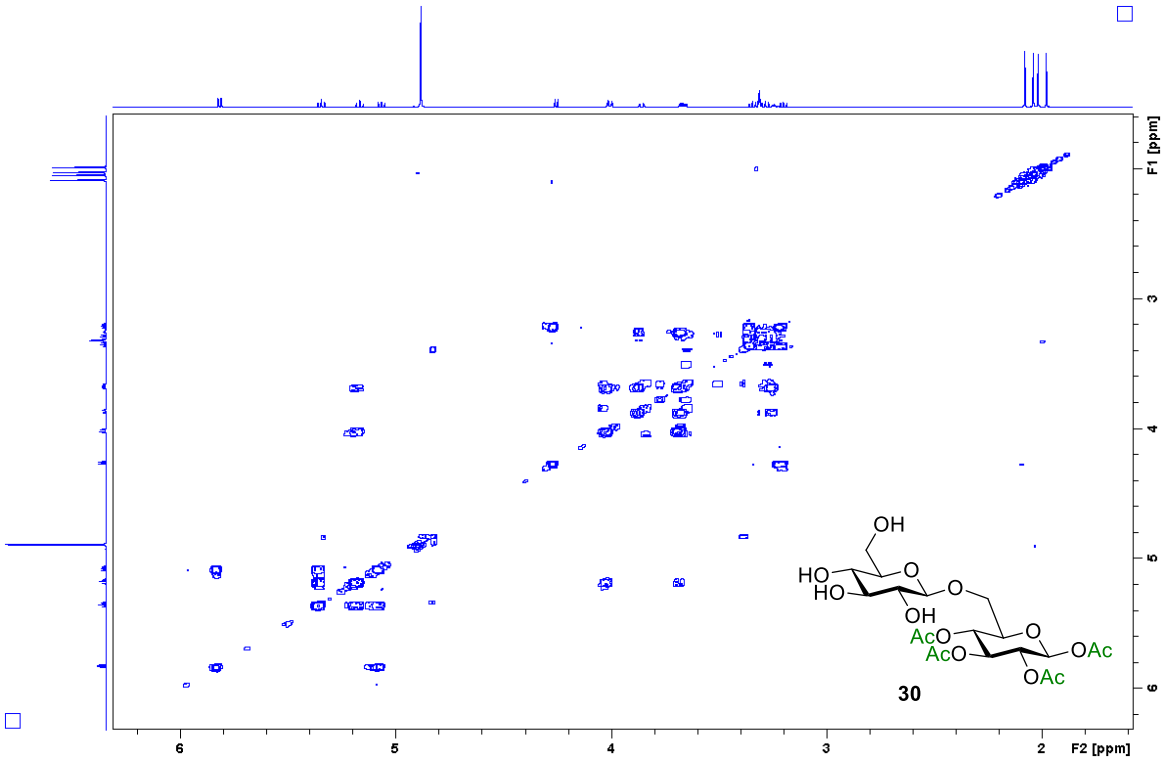
^{1}H NMR (CD_3OD, 600 MHz)



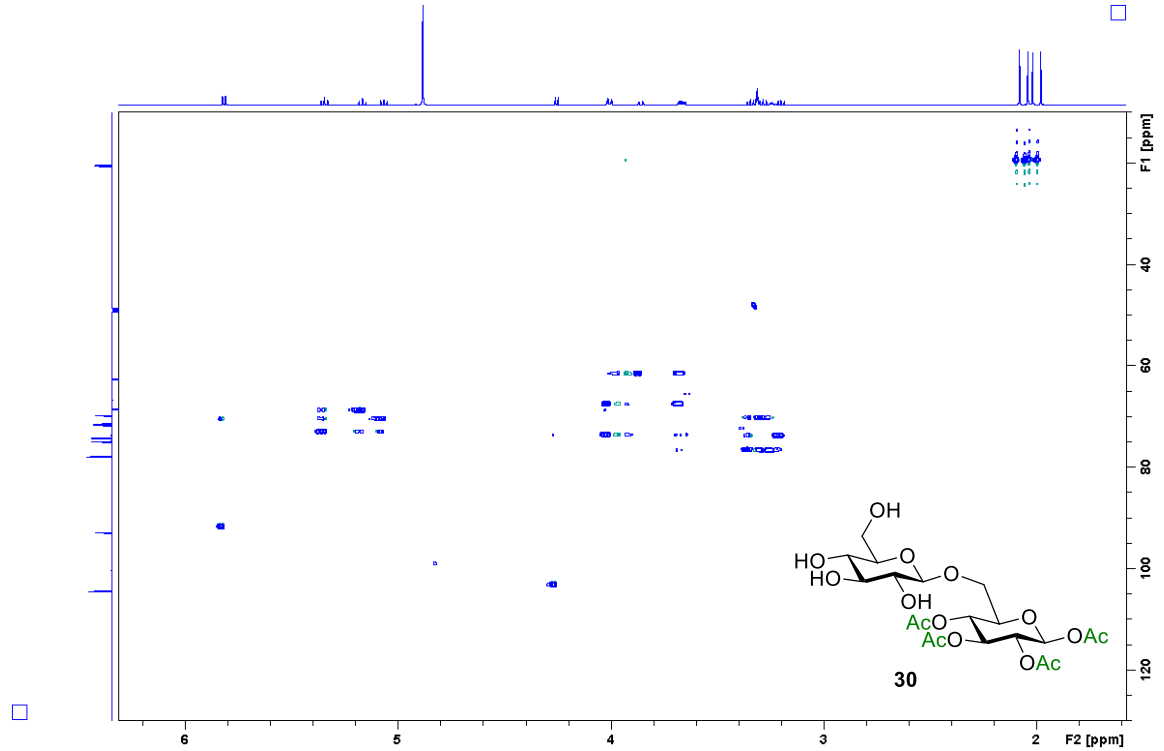
^{13}C NMR (CD_3OD, 150 MHz)

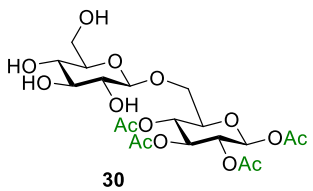


H,H-COSY (CD_3OD, 600 MHz)



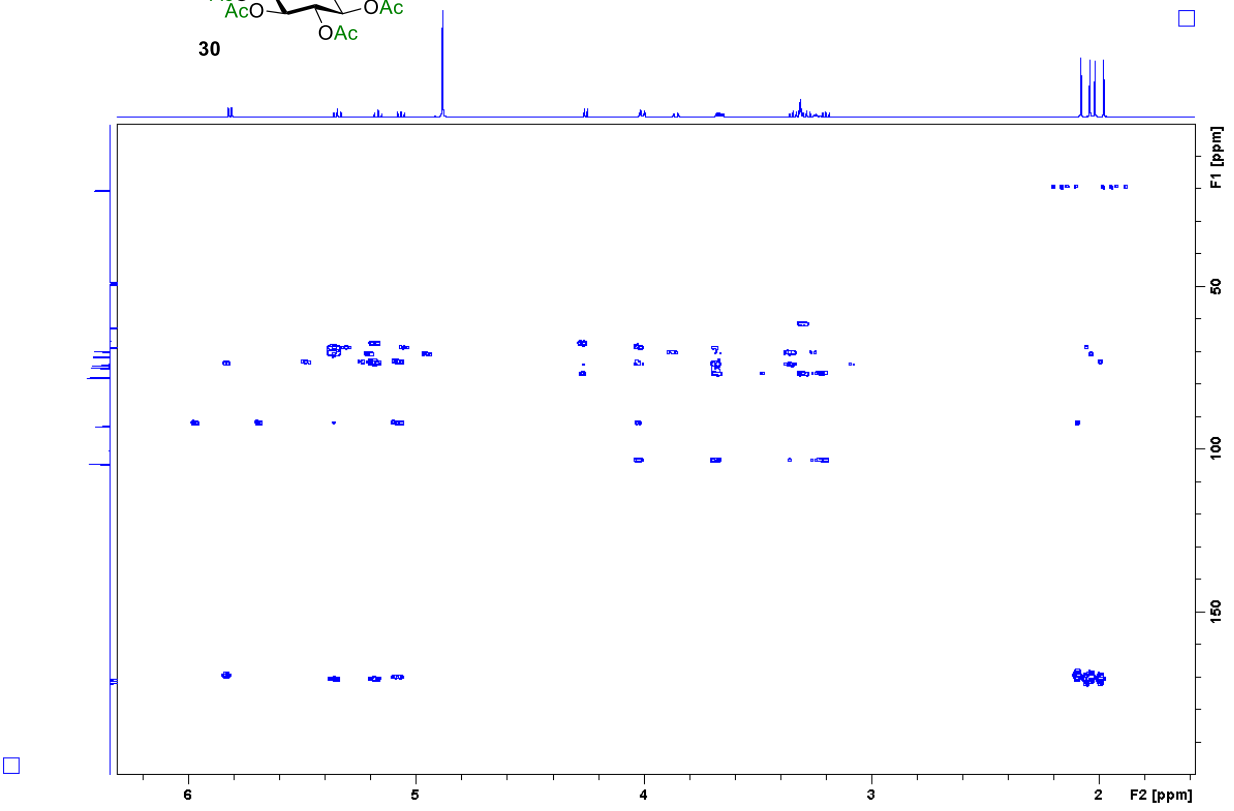
HSQC (CD_3OD, 600 MHz)



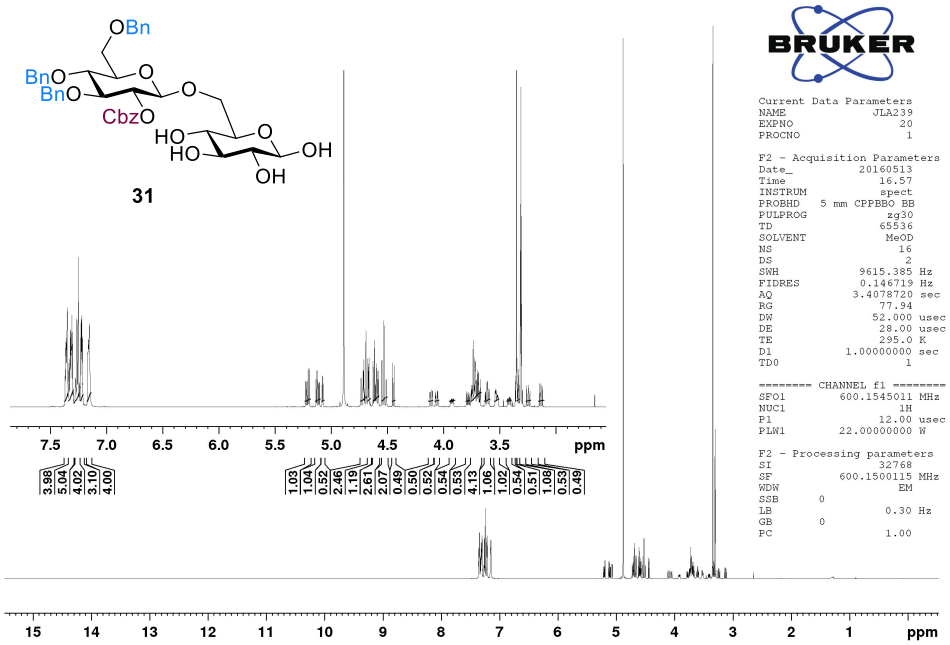


30

HMBC (CD_3OD, 600 MHz)



^{1}H NMR (CD_3OD, 600 MHz)



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Current Data Parameters
NAME                  JLA239
EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_              20160513
Time                  16.57
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG               zg30
TD                   65536
SOLVENT               MeOD
NS                       16
DS                        2
SWH                9615.385 Hz
FIDRES             0.146719 Hz
AQ                 3.4078720 sec
RG                    77.94
DW                   52.000 usec
DE                   28.00 usec
TE                   295.0 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1             600.1545011 MHz
NUC1                     1H
P1                   12.00 usec
PLW1            22.00000000 W

F2 - Processing parameters
SI                    32768
SF               600.1500115 MHz
WDW                      EM
SSB          0
LB                    0.30 Hz
GB           0
PC                    1.00
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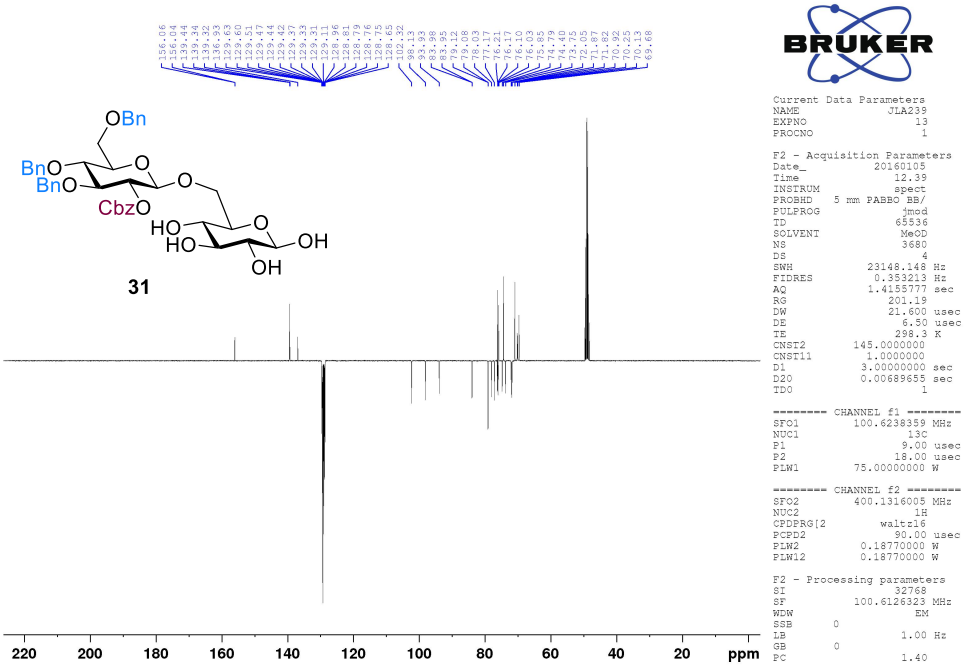
^{13}C NMR (CD_3OD, 100 MHz)



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Current Data Parameters
NAME                  JLA239
EXPNO                     13
PROCNO                     1

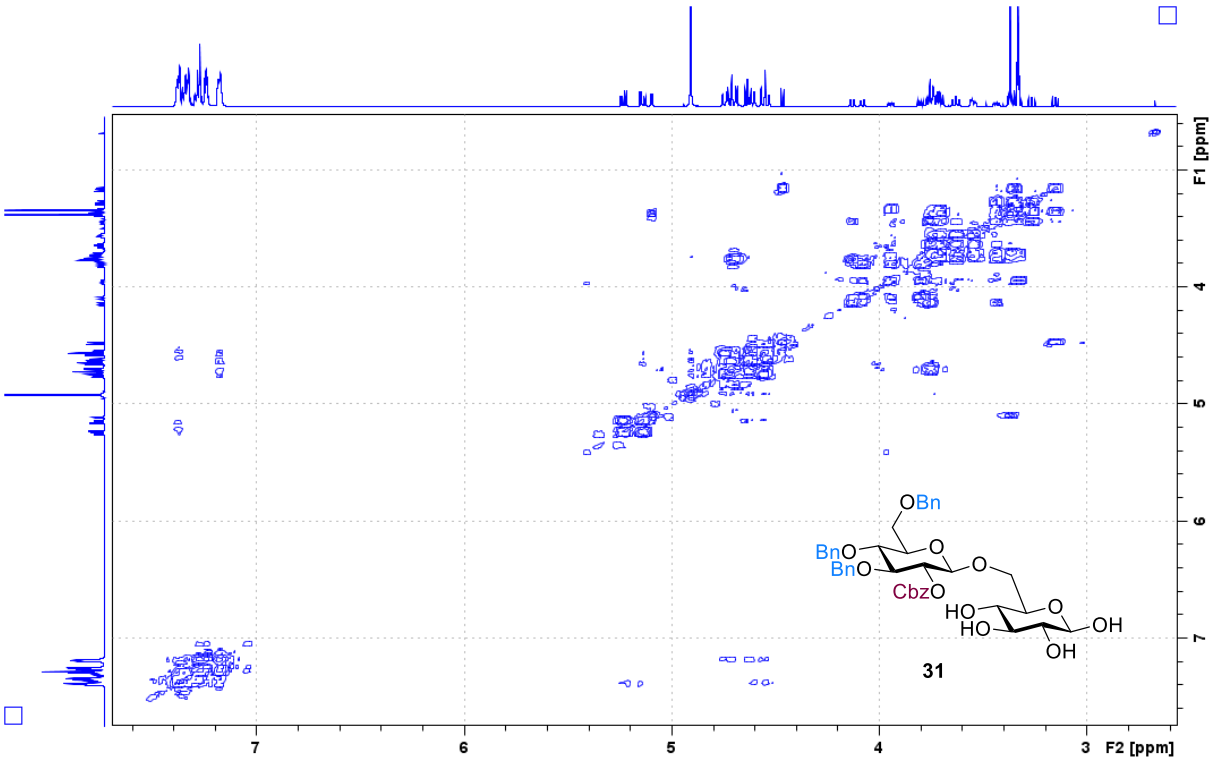
F2 - Acquisition Parameters
Date_              20160105
Time                  12.39
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG               jmod
TD                   65536
SOLVENT               MeOD
NS                     3680
DS                        4
SWH               23148.148 Hz
FIDRES             0.353213 Hz
AQ                 1.4155777 sec
RG                   201.19
DW                   21.600 usec
DE                    6.50 usec
TE                   298.3 K
CNST2            145.0000000
CNST11             1.0000000
D1                 3.00000000 sec
D20                0.00689655 sec
TD0                       1

======== CHANNEL f1 ========
SFO1             100.6238359 MHz
NUC1                     13C
P1                    9.00 usec
P2                   18.00 usec
PLW1            75.00000000 W

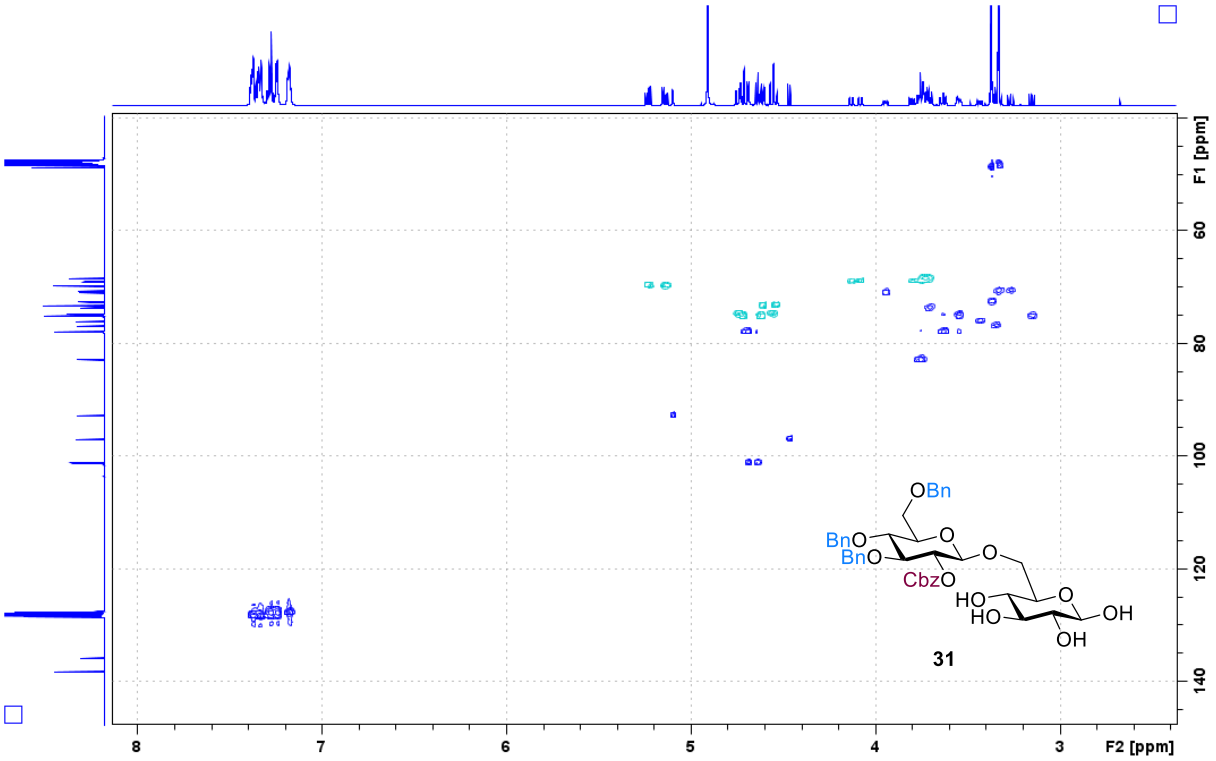
======== CHANNEL f2 ========
SFO2             400.1316005 MHz
NUC2                     1H
CPDPRG[2              waltz16
PCPD2                90.00 usec
PLW2             0.18770000 W
PLW12            0.18770000 W

F2 - Processing parameters
SI                    32768
SF               100.6126323 MHz
WDW                      EM
SSB          0
LB                    1.00 Hz
GB           0
PC                    1.40
```

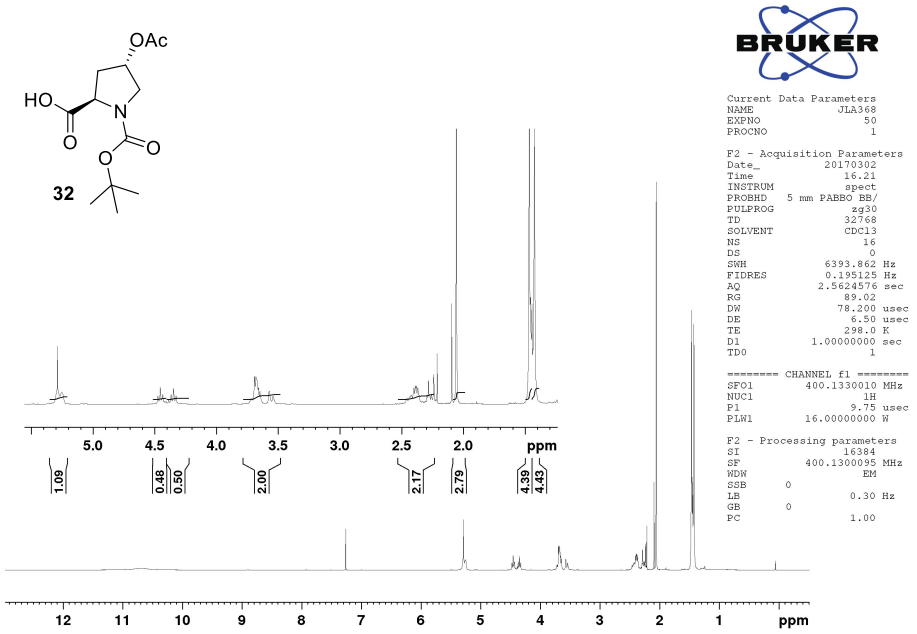
H,H-COSY (CD_3OD, 600 MHz)



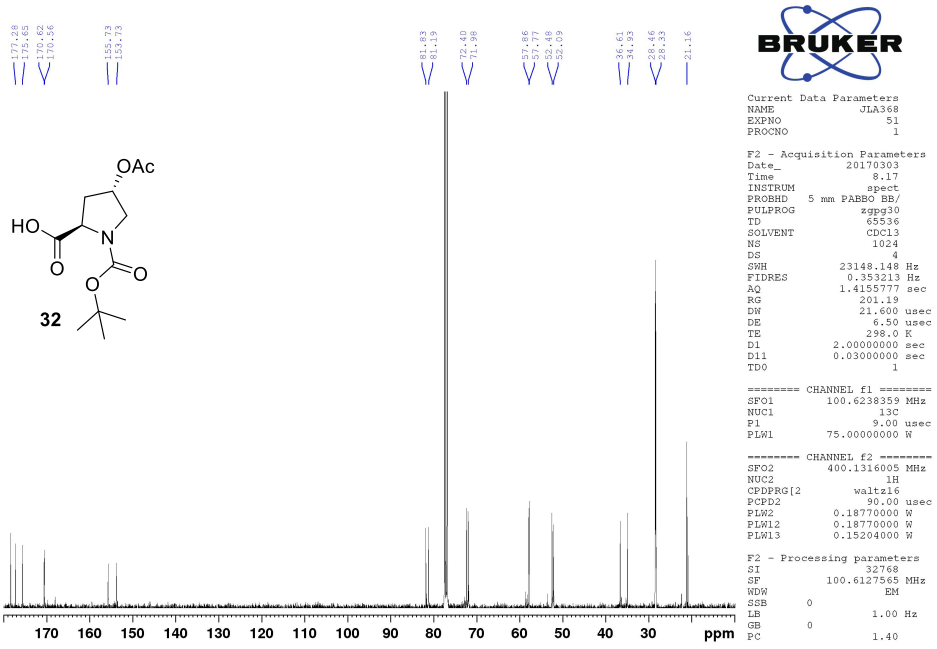
HSQC (CD_3OD, 600 MHz)



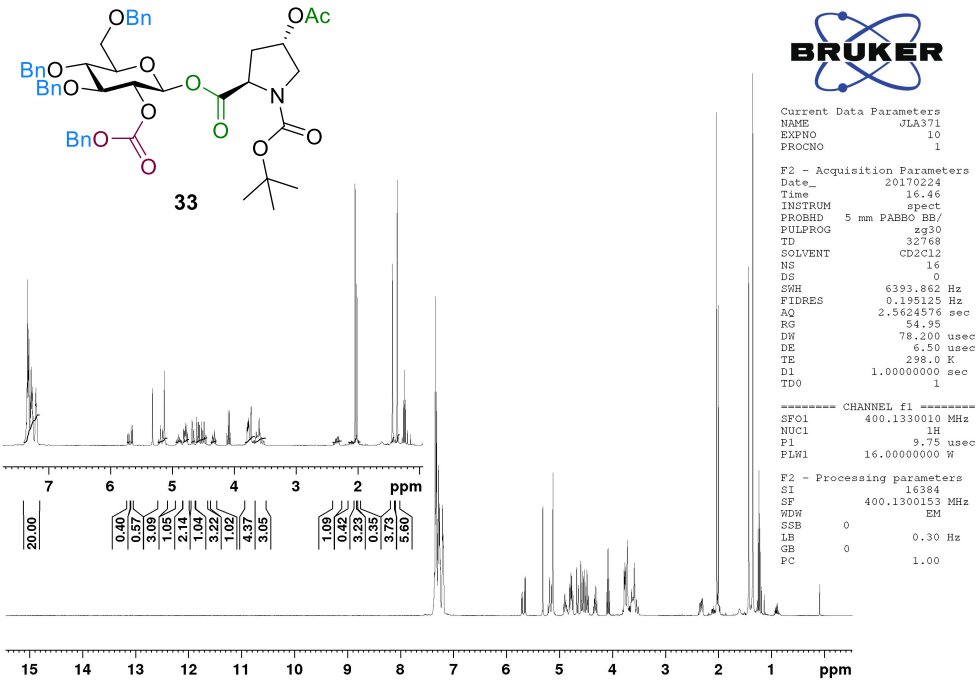
^{1}H NMR ($CDCl_3$, 400 MHz)



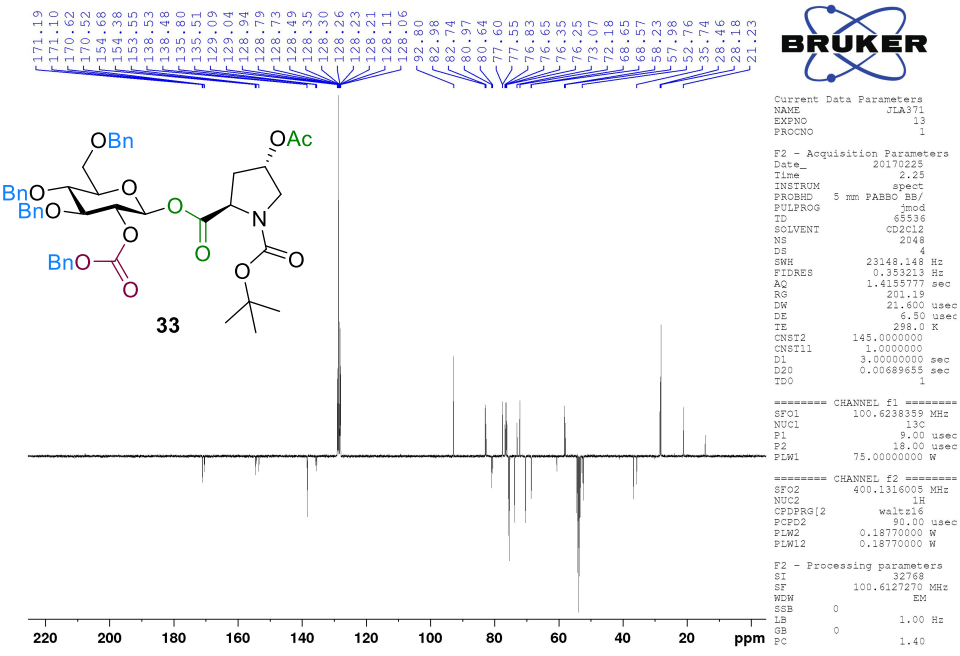
^{13}C NMR ($CDCl_3$, 100 MHz)



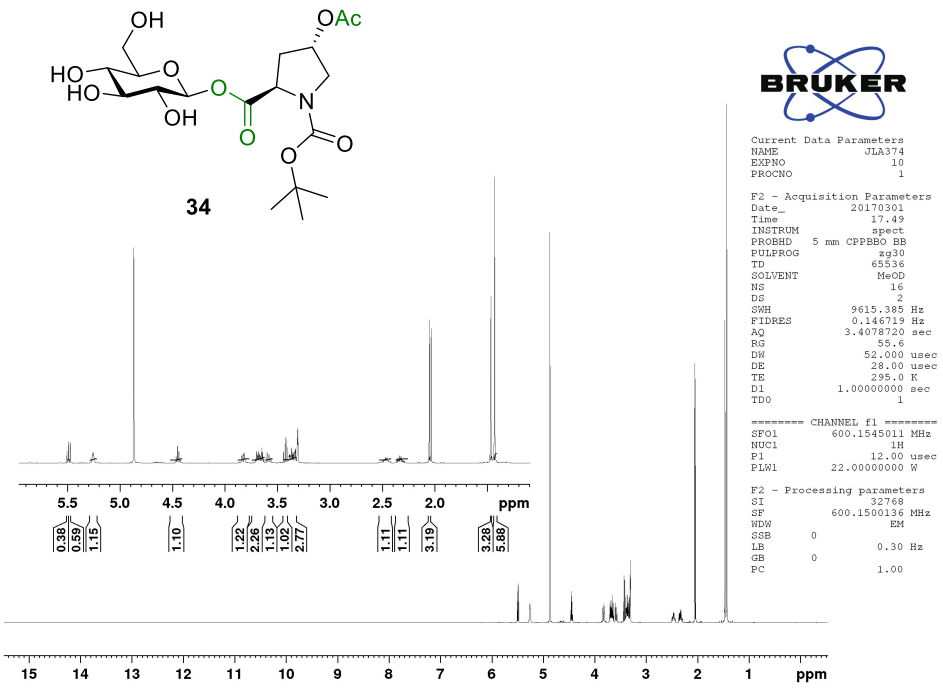
^{1}H NMR (CD_2Cl_2, 400 MHz)



^{13}C NMR (CD_2Cl_2, 100 MHz)



^{1}H NMR (CD_3OD, 600 MHz)



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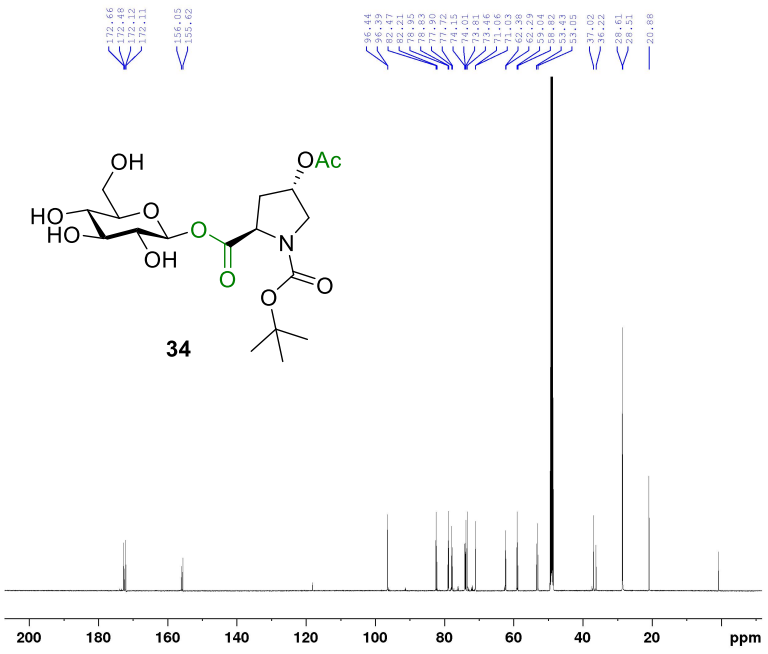
Current Data Parameters
NAME                  JLA374
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20170301
Time                  17.49
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG                zg30
TD                    65536
SOLVENT                MeOD
NS                       16
DS                        2
SWH                9615.385 Hz
FIDRES            0.146719 Hz
AQ                3.4078720 sec
RG                     55.6
DW                  52.000 usec
DE                  28.00 usec
TE                    295.0 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1          600.1545011 MHz
NUC1                      1H
P1                   12.00 usec
PLW1          22.00000000 W

F2 - Processing parameters
SI                        32768
SF                600.1500136 MHz
WDW                          EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    1.00
```

^{13}C NMR (CD_3OD, 150 MHz)



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```
Current Data Parameters
NAME                  JLA374
EXPNO                     11
PROCNO                     1

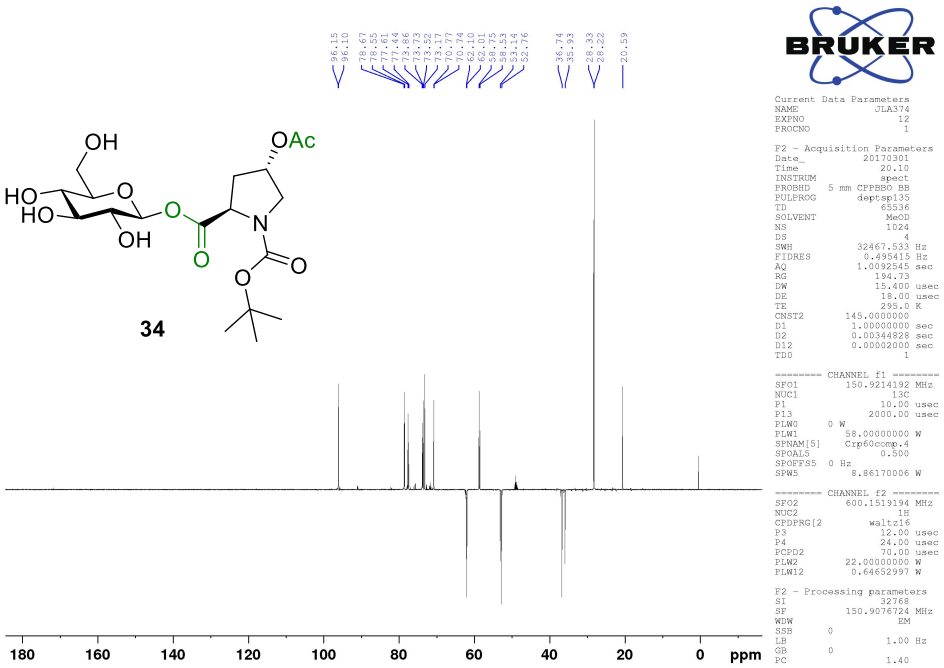
F2 - Acquisition Parameters
Date_              20170301
Time                  19.33
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG             zgpg30
TD                    65536
SOLVENT                MeOD
NS                     2048
DS                        4
SWH               35714.285 Hz
FIDRES            0.544957 Hz
AQ                0.9175040 sec
RG                    194.73
DW                  14.000 usec
DE                  18.00 usec
TE                    295.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1          150.9236829 MHz
NUC1                      13C
P1                   10.00 usec
PLW1          58.00000000 W

======== CHANNEL f2 ========
SFO2          600.1524006 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2                70.00 usec
PLW2          22.00000000 W
PLW12          0.64652997 W
PLW13          0.31680000 W

F2 - Processing parameters
SI                        32768
SF                150.9076294 MHz
WDW                          EM
SSB                       0
LB                    1.00 Hz
GB                        0
PC                    1.40
```

DEPT NMR (CD_3OD, 150 MHz)



Current Data Parameters
NAME JLA374
EXPNO 12
PROCNO 1

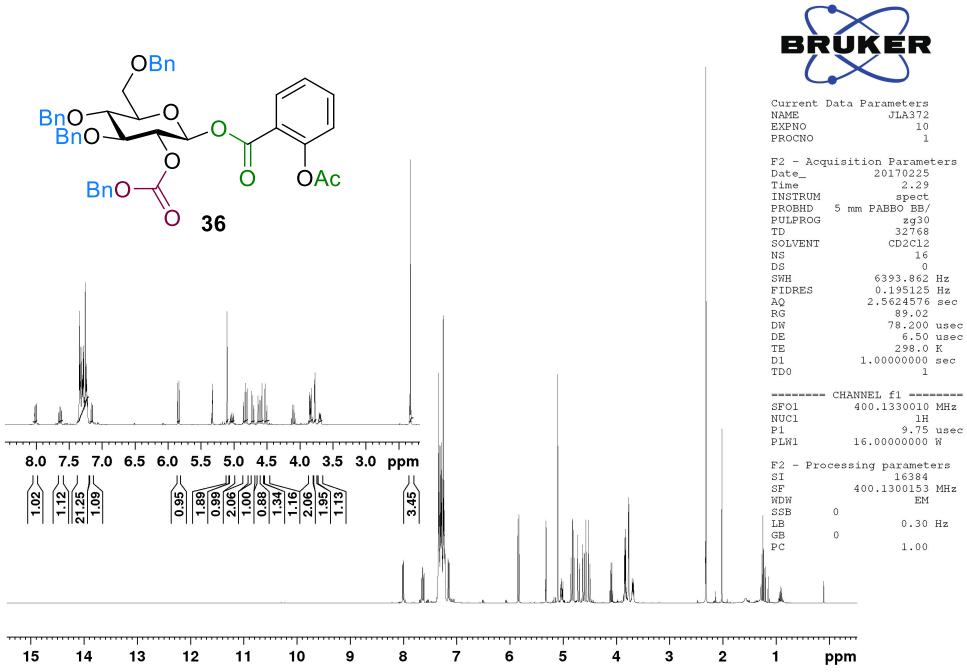
F2 - Acquisition Parameters
Date_ 20170301
Time 20.10
INSTRUM spect
PROBHD 5 mm CPFBBO BB
PULPROG deptsp135
TD 65536
SOLVENT MeOD
NS 1024
DS 4
SWH 32467.533 Hz
FIDRES 0.495415 Hz
AQ 1.0092545 sec
RG 194.73
DW 15.400 usec
DE 18.00 usec
TE 295.0 K
CNST2 145.0000000
D1 1.00000000 sec
D2 0.00344828 sec
D12 0.00002000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9214192 MHz
NUC1 13C
P1 10.00 usec
P13 2000.00 usec
PLW0 0 W
PLW1 58.00000000 W
SPNAM[5] Crp60comp.4
SPOAL5 0.500
SPOFFS5 0 Hz
SPW5 8.86170006 W

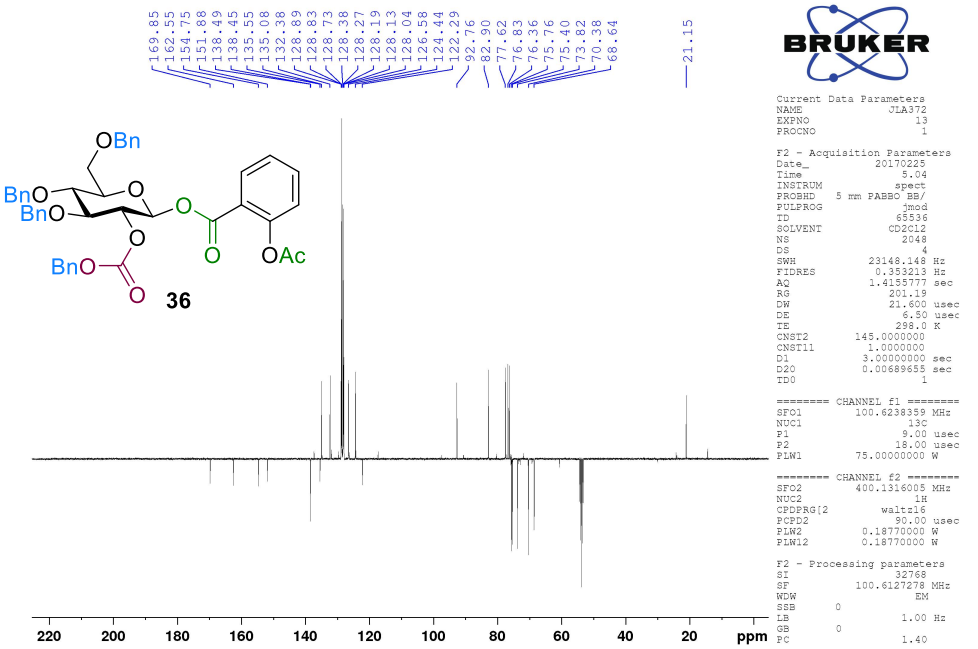
======== CHANNEL f2 ========
SFO2 600.1519194 MHz
NUC2 1H
CPDPRG[2 waltz16
P3 12.00 usec
P4 24.00 usec
PCPD2 70.00 usec
PLW2 22.00000000 W
PLW12 0.64652997 W

F2 - Processing parameters
SI 32768
SF 150.9076724 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

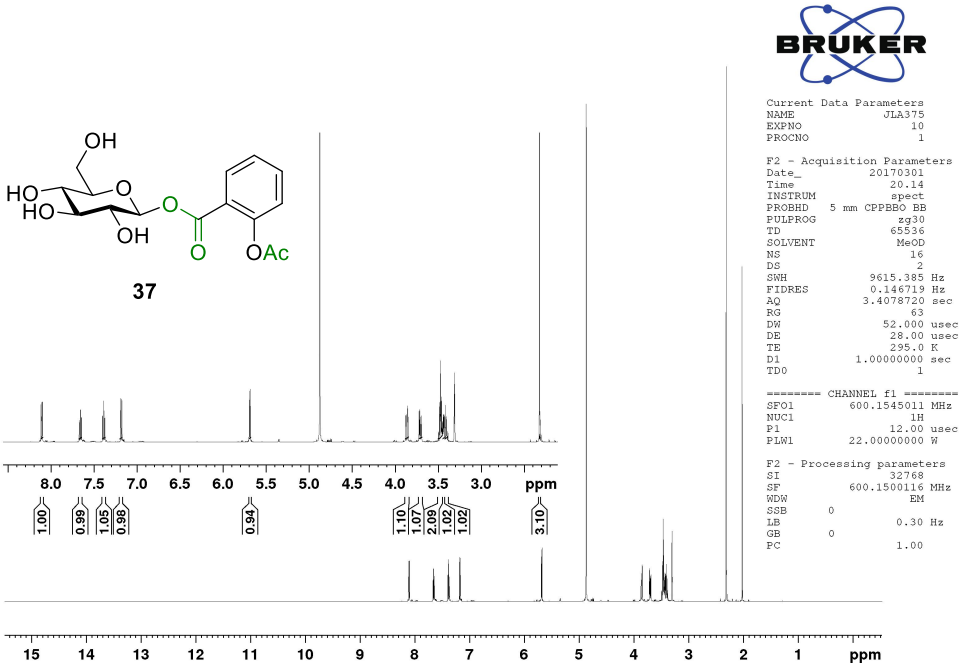
^{1}H NMR (CD_2Cl_2, 400 MHz)



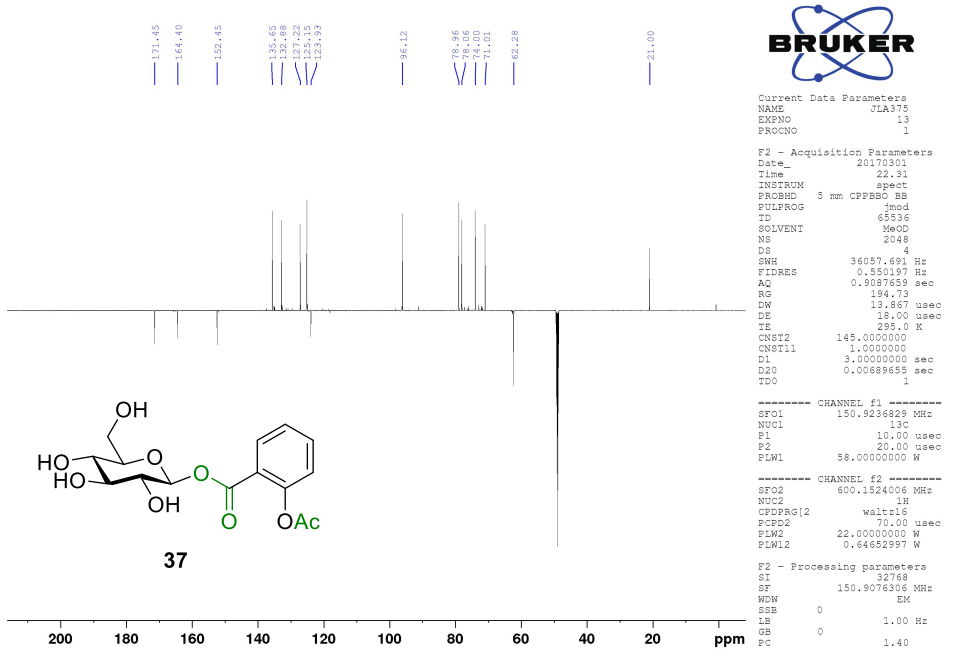
^{13}C NMR (CD_2Cl_2, 100 MHz)



^{1}H NMR (CD_3OD, 600 MHz)



^{13}C NMR (CD_3OD, 150 MHz)



4) References

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