

Experimental

Thin layer chromatography (TLC) was performed using silica gel 60 coated aluminum sheets containing fluorescence indicator (Merck KGaA, Darmstadt, Germany) and analyzed by UV light (254 nm) and by charring either in anisaldehyde solution (1% v/v 4-methoxybenzaldehyde, 2% v/v concentrated H₂SO₄ in EtOH), in aqueous KMnO₄ solution or in a molybdate solution (a 0.02 M solution of ammonium cerium sulfate dihydrate and ammonium molybdate tetrahydrate in aqueous 10% H₂SO₄) with heating. Reversed phase medium pressure liquid chromatography (RP-MPLC) was performed on a Teledyne Isco Combiflash Rf200 system with pre-packed RediSep Column (C18 15.5g Gold, Teledyne Isco). Dichloroethane was dried and stored over activated molecular sieves 4 Å. Other commercial chemicals and solvents and reagents were used without further purification. Cu(OTf)₂ was purchased from ABCR (Karlsruhe, Germany), GlcNAc from Dextra Laboratories (UK), deuterated solvents were obtained from Eurisotop (Saarbrücken, Germany). Optical rotation was measured using a P-2000 polarimeter (Jasco, Gross-Umstadt, Germany) at 589 nm and melting points were determined on a Stuart melting point apparatus SMP3 (Staffordshire, United Kingdom) with a heating rate of 2 °C/min. Nuclear magnetic resonance (NMR) spectroscopy was performed on Bruker Fourier 300, Bruker Avance III 400 or 500 UltraShield spectrometers at 300/400/500 MHz (¹H) or 75/101/126 MHz (¹³C), respectively. Chemical shifts are given in ppm and were calibrated on residual solvent peaks as internal standard. Multiplicities were specified as s (singlet), d (doublet), t (triplet) or m (multiplet). The signals were assigned with the help of ¹H,¹H-COSY, DEPT-135-edited ¹H,¹³C-HSQC experiments. Analytical HPLC-MS was performed on a Thermo Dionex Ultimate 3000 HPLC coupled to a Bruker amaZon SL for low resolution mass spectra or on a Bruker maxis 4G hr-QqToF spectrometer for high resolution, and the data were analyzed using DataAnalysis (Bruker Daltonics, Bremen, Germany).

Acetylation of N-acetyl D-glucosamine

2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy- α/β -D-glucopyranose (**2 α/β**). GlcNAc was acetylated in analogy to the synthesis of **2 α/β** starting from glucosamine hydrochloride reported^[1] by Lobry de Bruyn and van Ekenstein. GlcNAc (**1a**, 20.0 g, 90.4 mmol) was added portion-wise to a suspension of NaOAc (8.16 g, 99.4 mmol) in refluxing Ac₂O (110 mL). The reaction was stirred for 2 h at reflux, then cooled to r.t. and quenched with crushed ice. After extraction with EtOAc (3 x 200 mL), the combined organic layers were dried over Na₂SO₄, filtered and the volatiles were removed *in vacuo*. The light brown residue was recrystallized from EtOH to give the title compound **2 α/β** as colorless solid (24.6 g, 70%) in a α/β ratio of 5:1. This material was used in all glycosylation reactions reported here. For analytical purposes, pure **2 α** was obtained after purification by column chromatography and ¹H- and ¹³C-NMR data are included in the supporting information.

2-Methyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy- α -D-glucopyrano)[1,2-*d*]-oxazoline (**3**). Acetylated *N*-acetyl D-glucosamine **2 α/β** (α/β = 5:1, 1.00 g, 2.56 mmol) was stirred under nitrogen atmosphere with Cu(OTf)₂ (1.11 g, 3.08 mmol) in dry 1,2-dichloroethane (26 mL) for 7 h at 84 °C. The reaction was cooled to r.t., Et₃N (1.00 mL, 7.2 mmol) was added and stirred for 15 min. The volatiles were removed *in vacuo* and the residue was purified by flash chromatography on silica (toluene + 1% Et₃N to EtOAc + 1% Et₃N) to give **3** as a yellowish oil (622 mg, 74%). *R*_f=0.39 (EtOAc + 1% Et₃N); ¹H-NMR (500 MHz, CDCl₃, 25 °C): δ =5.95 (d, *J* = 7.3 Hz, 1H, H1), 5.27 – 5.24 (m, 1H, H5), 4.98 – 4.86 (m, 1H, H4), 4.18 – 4.15 (m, 2H, H6a, H2), 4.14 – 4.10 (m, 1H, H6b), 3.67 – 3.51 (m, 1H, H3), 2.05 (s, 3H, OAc), 2.04 – 2.01 (m, 6H, OAc, CH₃), 2.01 (s, 3H, OAc); ¹³C NMR (126 MHz, CDCl₃, 25 °C): δ =107.7 (CO), 169.6 (CO), 169.3 (CO), 166.8 (OCN), 99.5 (C1), 70.5 (C5), 68.5 (C4), 67.6 (C3),

65.1 (C2), 63.5 (C6), 21.0 (OAc), 21.0 (OAc), 20.9 (OAc), 14.1 ($\underline{\text{C}}\text{H}_3$). NMR data of **3** correspond to the reported values.^[2]

Typical procedure for glycosylation with catalytic amount of Cu(OTf)₂

2'-cyanoethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy- β -D-glucopyranoside (**4a**). A dry two-necked round bottom flask equipped with a reflux condenser was charged with donor **2a/β** (5.97 g, 15.3 mmol), Cu(OTf)₂ (830 mg, 2.30 mmol) and a stirring bar. The flask was evacuated and dried, followed by the addition of dry 1,2-dichloroethane (90 mL) and 2-cyanoethanol (3.85 mL, 46.0 mmol). The mixture was heated to reflux for 48 h, cooled to r.t. and quenched with brine (90 mL). The phases were separated and the aqueous layer was extracted with CH₂Cl₂ (3 x 100 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and the volatiles removed in vacuo. The residue was purified by flash chromatography on silica using EtOAc as solvent and **4a** (4.20 g, 69%) was obtained as colorless solid containing trace amounts of the α -anomer (< 6%). *R*_f=0.18 (EtOAc); mp: degradation >170 °C; [α]_D²²=−8.0 (c=0.2 in CH₂Cl₂); ¹H-NMR (400 MHz, CDCl₃, 25 °C): δ =5.88 (d, *J* = 8.6 Hz, 1H, NH), 5.31 (dd, *J* = 10.0, 9.3 Hz, 1H, H3), 5.06 (t, *J* = 9.7 Hz, 1H, H4), 4.82 (d, *J* = 8.4 Hz, 1H, H1), 4.31 – 4.19 (dd, *J* = 12.3, 4.8 Hz, 1H, H6a), 4.13 (dd, *J* = 12.3, 2.4 Hz, 1H, H6b), 4.08 – 3.98 (m, 1H, 1H of OCH₂CH₂CN), 3.86 (dt, *J* = 10.7, 8.5 Hz, 1H, H2), 3.82 – 3.68 (m, 2H, H5, 1H of OCH₂CH₂CN), 2.73 – 2.56 (m, 2H, CH₂CH₂CN), 2.08 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.98 (s, 3H, NHAc). ¹³C-NMR (101 MHz, CDCl₃, 25 °C): δ =171.0 (CO), 170.8 (CO), 170.7 (CO), 169.5 (CO), 117.8 (CN), 100.8 (C1), 72.2 (C5), 72.1 (C3), 68.7 (C4), 64.2 (OCH₂CH₂CN), 62.1 (C6), 54.6 (C2), 23.4 (NHAc), 20.9 (OAc), 20.8 (OAc), 20.7 (OAc), 19.2 (OCH₂CH₂CN). MS: [C₁₇H₂₄N₂O₉+Na]⁺ calcd: 423.1, found: 423.2; HRMS: [C₁₇H₂₄N₂O₉+H]⁺ calcd: 401.1555, found: 401.1560.

n-Propyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy- β -D-glucopyranoside (**4b**) was synthesized analogously to **4a** and purified by RP-MPLC (A: H₂O + 0.1% HCOOH; B: MeCN + 0.1% HCOOH; 0-20 min 5-20% B, 20-30 min 20%B, flow rate 30 mL/min). *n*-Propyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy- β -D-glucopyranoside (β -**4b**) was obtained as colorless solid (25 mg; 0.06 mmol; 31%). R_f =0.46 (SiO₂, EtOAc); mp: 147.0-148.5 °C; $[\alpha]_D^{22}$ =−19.0 (c=0.2 in CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, 25 °C): δ =5.70 (s, 1H, NH), 5.30 (t, J = 9.7 Hz, 1H, H3), 5.05 (t, J = 9.1 Hz, 1H, H4), 4.69 (d, J = 7.8 Hz, 1H, H1), 4.25 (dd, J = 12.2, 4.0 Hz, 1H, H6a), 4.12 (d, J = 12.2 Hz, 1H, H6b), 3.82 (m, 2H, CH₂+H2), 3.75 – 3.64 (m, 1H, H5), 3.43 (d, J = 8.5 Hz, 1H, CH₂), 2.07 (s, 3H, CH₃), 2.02 (s, 3H, CH₃), 2.01 (s, 3H, CH₃), 1.94 (bs, 3H, CH₃), 1.64 – 1.52 (bs, 2H, CH₂), 0.88 (t, J = 7.1 Hz, 3H, CH₃). ¹³C NMR (126 MHz, CDCl₃, 25 °C): δ =171.0 (CO), 170.9 (CO), 170.4 (CO), 169.6 (CO), 100.8 (C1), 72.5 (C3), 71.9 (C5), 71.7 (CH₂), 68.9 (C4), 62.3 (C6), 55.0 (C2), 23.6 (NHAc), 22.8 (CH₂), 20.9 (OAc), 20.9 (OAc), 20.8 (OAc), 10.5 (CH₃). HRMS: [C₁₇H₂₇NO₉+H]⁺ calcd: 390.1759, found: 390.1759. *n*-Propyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy- α -D-glucopyranoside (α -**4b**) was obtained as colorless oil (18 mg; 0.05 mmol; 23%). R_f =0.53 (SiO₂, EtOAc); $[\alpha]_D^{22}$ =112.5 (c=0.4 in CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, 25 °C): δ =5.67 (d, J = 9.5 Hz, 1H, NH), 5.21 (t, J = 10.0 Hz, 1H, H3), 5.11 (t, J = 9.8 Hz, 1H, H4), 4.82 (d, J = 3.6 Hz, 1H, H1), 4.33 (td, J = 10.1, 3.6 Hz, 1H, H2), 4.23 (dd, J = 12.3, 4.6 Hz, 1H, H6a), 4.09 (dd, J = 12.3, 2.4 Hz, 1H, H6b), 3.94 (ddd, J = 10.2, 4.8, 2.4 Hz, 1H, H5), 3.63 (dt, J = 9.9, 6.8 Hz, 1H, CH₂), 3.40 (dt, J = 9.8, 6.6 Hz, 1H, CH₂), 2.09 (s, 3H, Ac-CH₃), 2.02 (s, 3H, Ac-CH₃), 2.01 (s, 4H, Ac-CH₃), 1.95 (s, 3H, NHAc-CH₃), 1.63 (h, J = 7.1 Hz, 2H, CH₂), 0.95 (t, J = 7.4 Hz, 3H, CH₃). ¹³C NMR (126 MHz, CDCl₃, 25 °C): δ =171.6 (CO), 170.8 (CO), 170.1 (CO), 169.5 (CO), 97.2 (C1), 71.6 (C3), 70.2 (CH₂), 68.3 (C4), 67.8 (C5), 62.2 (C6), 52.0 (C2), 23.4 (NHAc), 22.7 (CH₂), 20.9 (OAc), 20.9 (OAc), 20.8 (OAc), 10.8 (CH₃). HRMS: [C₁₇H₂₇NO₉+H]⁺ calcd: 390.1759, found: 390.1759.

2'-Chloroethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranoside (**4c**) was synthesized analogously to **4a** and purified by RP-MPLC (A: H₂O + 0.1% HCOOH; B: MeCN + 0.1% HCOOH; 0-50 min 5-20% B, flow rate 30 mL/min). 2'-Chloroethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside (β-**4c**) was obtained as colorless solid (35 mg; 0.09 mmol; 42%). *R*_f=0.45 (SiO₂, EtOAc); mp: 153.0-154.2 °C; [α]_D²²=−22.0 (c=0.2 in CH₂Cl₂); ¹H NMR (300 MHz, DMSO-*d*₆, 25 °C): δ=7.95 (d, *J* = 9.1 Hz, 1H, NH), 5.08 (dd, *J* = 10.5, 9.4 Hz, 1H, H3), 4.82 (t, *J* = 9.7 Hz, 1H, H4), 4.69 (d, *J* = 8.5 Hz, 1H, H1), 4.18 (dd, *J* = 12.3, 4.8 Hz, 1H, H6a), 4.02 (dd, *J* = 12.3, 2.4 Hz, 1H, H6b), 3.95 – 3.63 (m, 6H, H2, H5, 4xCH₂), 2.01 (s, 3H, OAc), 1.96 (s, 3H, OAc), 1.91 (s, 3H, OAc), 1.76 (s, 3H, NHAc). ¹³C NMR (126 MHz, CDCl₃, 25 °C): δ=170.9 (CO), 170.8 (CO), 170.8 (CO), 169.5 (CO), 101.2 (C1), 72.3 (C3), 72.1 (C5), 69.9 (CH₂), 68.7 (C4), 62.2 (C6), 54.8 (C2), 43.2 (CH₂), 23.6 (NHAc), 20.9 (2C, OAc), 20.8 (OAc). HRMS: [C₁₆H₂₄ClNO₉+H]⁺ calcd: 410.1212, found: 410.1216.

2'-Chloroethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranoside (α-**4c**) was obtained as colorless oil (13 mg; 0.03 mmol; 15%). *R*_f=0.41 (SiO₂, EtOAc); [α]_D²²=105.5 (c=0.4 in CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, 25 °C): δ=5.77 (d, *J* = 9.4 Hz, 1H, NH), 5.24 (dd, *J* = 10.7, 9.5 Hz, 1H, H3), 5.13 (t, *J* = 9.8 Hz, 1H, H4), 4.90 (d, *J* = 3.6 Hz, 1H, H1), 4.37 (td, *J* = 10.1, 3.5 Hz, 1H, H2), 4.24 (dd, *J* = 12.3, 4.6 Hz, 1H, H6a), 4.12 (dd, *J* = 12.3, 2.4 Hz, 1H, H6b), 4.05 (ddd, *J* = 10.1, 4.6, 2.4 Hz, 1H, H5), 3.98 (dt, *J* = 11.0, 4.7 Hz, 1H, CH₂), 3.76 (dt, *J* = 11.0, 5.3 Hz, 1H, CH₂), 3.70 (t, *J* = 5.0 Hz, 2H, 2 x CH₂), 2.10 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.96 (s, 3H, NHAc). ¹³C NMR (126 MHz, CDCl₃, 25 °C): δ=171.5 (CO), 170.8 (CO), 170.3 (CO), 169.4 (CO), 97.9 (C1), 71.3 (C3), 68.9 (CH₂), 68.3 (C5), 68.1 (C4), 62.1 (C6), 52.0 (C2), 43.1 (CH₂), 23.4 (NHAc), 20.9 (OAc), 20.9 (OAc), 20.8 (OAc). HRMS: [C₁₆H₂₄ClNO₉+H]⁺ calcd: 410.1212, found: 410.1216.

2'-Bromoethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranoside (**4d**) was

synthesized analogously to **4a** and purified by RP-MPLC (A: H₂O + 0.1% HCOOH; B: MeCN + 0.1% HCOOH; 0-30 min 5-20% B, 20-40 min 20%B, flow rate 30 mL/min). 2'-Bromoethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy- β -D-glucopyranoside (**β -4d**) was obtained as yellowish solid (33 mg; 0.07 mmol; 35%). R_f =0.40 (SiO₂, EtOAc); mp: degradation >152 °C; $[\alpha]_D^{22}$ =−17.0 (c=0.2 in CH₂Cl₂); ¹H NMR (300 MHz, DMSO-*d*₆, 25 °C): δ =7.94 (d, J = 9.1 Hz, 1H, NH), 5.08 (dd, J = 10.5, 9.4 Hz, 1H, H3), 4.83 (t, J = 9.7 Hz, 1H, H4), 4.70 (d, J = 8.5 Hz, 1H, H1), 4.18 (dd, J = 12.2, 4.8 Hz, 1H, H6a), 4.03 (dd, J = 12.2, 2.4 Hz, 1H, H6b), 3.99 – 3.90 (m, 1H), 3.89 – 3.80 (m, 1H), 3.79 – 3.66 (m, 1H), 3.62 – 3.48 (m, 2H, CH₂), 2.02 (s, 3H, OAc), 1.97 (s, 3H, OAc), 1.91 (s, 3H, OAc), 1.76 (s, 3H, NHAc). ¹³C NMR (126 MHz, CDCl₃, 25 °C): δ =171.0 (CO), 170.9 (CO), 170.8 (CO), 169.5 (CO), 101.1 (C1), 72.3 (C3), 72.1 (C5), 69.7 (CH₂), 68.6 (C4), 62.2 (C6), 54.8 (C2), 30.9 (CH₂), 23.7 (NHAc), 20.9 (OAc), 20.9 (OAc), 20.8 (OAc). HRMS: [C₁₆H₂₄BrNO₉+H]⁺ calcd: 454.0707, found: 454.0710. 2'-Bromoethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy- α -D-glucopyranoside (**α -4d**) was obtained as yellowish solid (9 mg; 0.02 mmol; 10%). R_f =0.33 (SiO₂, EtOAc); mp: 114.5-116.8 °C; $[\alpha]_D^{22}$ =64.0 (c=0.2 in CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, 25 °C): δ =5.83 (d, J = 9.1 Hz, 1H, NH), 5.24 (t, J = 10.0 Hz, 1H, H3), 5.13 (t, J = 9.8 Hz, 1H, H4), 4.90 (bs, 1H, H1), 4.37 (t, J = 9.8 Hz, 1H, H2), 4.23 (dd, J = 12.4, 4.5 Hz, 1H, H6a), 4.11 (dd, J = 12.3, 2.3 Hz, 1H, H6b), 4.09 – 4.02 (m, 2H, H5+CH₂), 3.82 (bs, 1H, CH₂), 3.55 (bs, 2H, CH₂), 2.10 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.97 (s, 3H, NHAc). ¹³C NMR (126 MHz, CDCl₃, 25 °C): δ =171.5 (CO), 170.8 (CO), 170.3 (CO), 169.5 (CO), 97.8 (C1), 71.3 (C3), 68.6 (CH₂), 68.4 (C5), 68.1 (C4), 62.0 (C6), 52.0 (CH₂), 30.8 (NHAc), 20.9 (OAc), 20.9 (OAc), 20.8 (OAc). HRMS: [C₁₆H₂₄BrNO₉+H]⁺ calcd: 454.0707, found: 454.0710.

NMR data of **β -4d**^[3] correspond to the reported values.

Benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranoside (**4e**) was synthesized analogously to **4a** and purified by RP-MPLC (A: H₂O + 0.1% HCOOH; B: MeCN + 0.1% HCOOH; 0-3 min 5-15% B, 3-40 min 30%B, flow rate 30 mL/min). Benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside (β-**4e**) was obtained as colorless solid (34 mg; 0.08 mmol; 38%). *R*_f=0.46 (SiO₂, EtOAc); mp: 163.0-165.0 °C; [α]_D²²=−48.0 (c=0.2 in CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, 25 °C): δ=7.47 – 7.15 (m, 5H, H-Ar), 5.65 (bs, 1H, NH), 5.21 (t, *J* = 9.9 Hz, 1H, H3), 5.08 (t, *J* = 9.4 Hz, 1H, H4), 4.88 (d, *J* = 11.9 Hz, 1H, CH₂), 4.64 (d, *J* = 8.2 Hz, 1H, H1), 4.59 (d, *J* = 12.1 Hz, 1H, CH₂), 4.27 (dd, *J* = 12.2, 4.4 Hz, 1H, H6a), 4.15 (dd, *J* = 12.1, 1.9 Hz, 1H, H6b), 3.98 (dd, *J* = 7.8, 7.2 Hz, 1H, H2), 3.80 – 3.54 (m, 1H, H5), 2.09 (s, 3H, OAc), 2.00 (s, 3H, OAc), 2.00 (s, 3H, OAc), 1.90 (s, 3H, NHAc). ¹³C NMR (126 MHz, CDCl₃, 25 °C): δ=171.0 (CO), 170.9 (CO), 170.5 (CO), 169.5 (CO), 137.0 (C-Ar), 128.6 (2C, CH-Ar), 128.2 (CH-Ar), 128.2 (2C, CH-Ar), 99.5 (C1), 72.5 (C3), 71.9 (C5), 70.8 (CH₂), 68.7 (C4), 62.2 (C6), 54.6 (C2), 23.4 (NHAc), 20.9 (OAc), 20.8 (OAc), 20.7 (OAc). HRMS: [C₂₁H₂₇NO₉+H]⁺ calcd: 438.1759, found: 438.1764. Benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranoside (α-**4e**) was obtained as colorless oil (4 mg; 0.01 mmol; 4%). *R*_f=0.51 (SiO₂, EtOAc); [α]_D²²=86.0 (c=0.2 in CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, 25 °C): δ=7.42 – 7.30 (m, 5H, H-Ar), 5.65 (d, *J* = 9.5 Hz, 1H, NH), 5.23 (dd, *J* = 10.7, 9.5 Hz, 1H, H3), 5.14 (t, *J* = 9.8 Hz, 1H, H4), 4.94 (d, *J* = 3.6 Hz, 1H, H1), 4.72 (d, *J* = 11.8 Hz, 1H, CH₂), 4.52 (d, *J* = 11.8 Hz, 1H, CH₂), 4.35 (ddd, *J* = 10.7, 9.6, 3.7 Hz, 1H, H2), 4.23 (dd, *J* = 12.3, 4.4 Hz, 1H, H6a), 4.03 (dd, *J* = 12.3, 2.4 Hz, 1H, H6b), 3.97 (ddd, *J* = 10.1, 4.4, 2.4 Hz, 1H, H5), 2.10 (s, 3H, OAc), 2.02 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.90 (s, 3H, NHAc). ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ=171.5 (CO), 170.9 (CO), 170.0 (CO), 169.4 (CO), 136.7 (C-Ar), 128.9 (2C, CH-Ar), 128.6 (CH-Ar), 128.4 (2C, CH-Ar), 96.8 (C1), 71.5 (C3), 70.4 (CH₂), 68.2 (C4), 68.2 (C5), 62.0 (C6), 52.0 (C2), 23.3 (NHAc), 20.9 (OAc), 20.9 (OAc), 20.8 (OAc). HRMS: [C₂₁H₂₇NO₉+H]⁺ calcd: 438.1759, found: 438.1763.

NMR data of β -**4e**^[4] correspond to the reported values.

2'-Phenylethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranoside (**4f**) was synthesized analogously to **4a** and purified by RP-MPLC (A: H₂O + 0.1% HCOOH; B: MeCN + 0.1% HCOOH; 0-2 min 10-20% B, 2-5 min 20%B, 5-35 min 20-40% B, flow rate 30 mL/min). 2'-Phenylethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy- β -D-glucopyranoside (β -**4f**) was obtained as colorless solid (39 mg; 0.09 mmol; 42%). *R*_f=0.46 (SiO₂, EtOAc); mp: 168.5-170.9 °C; [α]_D²²=−26.0 (c=0.2 in CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, 25 °C): δ =7.30 – 7.23 (m, 2H, H-Ar), 7.23 – 7.15 (m, 3H, H-Ar), 5.51 (d, *J* = 8.5 Hz, 1H, NH), 5.24 (t, *J* = 9.9 Hz, 1H, H3), 5.05 (t, *J* = 9.4 Hz, 1H, H4), 4.63 (d, *J* = 8.1 Hz, 1H, H1), 4.25 (dd, *J* = 12.2, 4.5 Hz, 1H, H6a), 4.19 – 4.06 (m, 2H, H6b+CH₂), 3.84 (dd, *J* = 8.4 Hz, 1H, H2), 3.75 – 3.54 (m, 2H, CH₂+H5), 2.97 – 2.82 (m, 2H, CH₂), 2.07 (s, 3H, OAc), 2.01 (s, 6H, 2 x OAc), 1.83 (s, 3H, NHAc). ¹³C NMR (126 MHz, CDCl₃, 25 °C): δ =171.0 (CO), 170.9 (CO), 170.5 (CO), 169.5 (CO), 138.7 (C-Ar), 129.1 (2C, CH-Ar), 128.4 (2C, CH-Ar), 126.4 (CH-Ar), 100.8 (C1), 72.5 (C3), 71.9 (C5), 70.5 (CH₂), 68.7 (C4), 62.2 (C6), 54.8 (C2), 36.0 (CH₂), 23.4 (NHAc), 20.9 (OAc), 20.9 (OAc), 20.7 (OAc). HRMS: [C₂₂H₂₉NO₉+H]⁺ calcd: 452.1915, found: 452.1921. 2'-Phenylethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy- α -D-glucopyranoside (α -**4f**) was obtained as colorless solid (19 mg; 0.04 mmol; 20%). *R*_f=0.46 (SiO₂, EtOAc); mp: 89.3-90.8 °C; [α]_D²²=82.0 (c=0.2 in CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, 25 °C): δ =7.36 – 7.29 (m, 2H, H-Ar), 7.26 – 7.21 (m, 3H, H-Ar), 5.40 (d, *J* = 9.3 Hz, 1H, NH), 5.15 (dd, *J* = 10.5, 9.5 Hz, 1H, H3), 5.06 (t, *J* = 9.8 Hz, 1H, H4), 4.76 (bs, 1H, H1), 4.26 (dt, *J* = 10.9, 5.5 Hz, 1H, H2), 4.12 (dd, *J* = 12.4, 4.3 Hz, 1H, H6a), 4.04 – 3.88 (m, 2H, H6b+CH₂), 3.71 – 3.64 (m, 1H, CH₂), 3.61 (ddd, *J* = 10.1, 4.3, 2.3 Hz, 1H, H5), 2.92 (t, *J* = 6.0 Hz, 2H, CH₂), 2.07 (s, 3H, OAc), 2.01 (s, 3H, OAc), 2.00 (s, 3H, OAc), 1.79 (s, 3H, NHAc). ¹³C NMR (126 MHz, CDCl₃, 25 °C): δ =171.5 (CO), 170.8 (CO), 170.0 (CO), 169.4 (CO), 138.8 (C-Ar), 129.1 (2C, CH-Ar), 128.7 (2C, CH-Ar), 126.7 (CH-Ar), 97.3 (C1), 71.5

(C3), 68.9 (CH₂), 68.0 (C4), 67.9 (C5), 61.9 (C6), 51.9 (C2), 35.9 (CH₂), 23.33 (NHAc), 20.9 (OAc), 20.9 (OAc), 20.7 (OAc). HRMS: [C₂₂H₂₉NO₉+H]⁺ calcd: 452.1915, found: 452.1918.

NMR data of β -**4f**^[5] correspond to the reported values. In a large scale reaction β -**4f** (931 mg; 2.06 mmol; 40%) and α -**4f** (98 mg; 0.21 mmol; 4%) were isolated after 10 h reaction time.

3'-Phenyl-*n*-propyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranoside (**4g**) was synthesized analogously to **4a** and purified by RP-MPLC (A: H₂O + 0.1% HCOOH; B: MeCN + 0.1% HCOOH; 0-3 min 5-20% B, 3-10 min 20%B, 10-40 min 20-40% B, flow rate 30 mL/min). 3'-Phenyl-*n*-propyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy- β -D-glucopyranoside (β -**4g**) was obtained as colorless solid (33 mg; 0.07 mmol; 34%). *R*_f=0.48 (SiO₂, EtOAc); mp: 139.6-141.6 °C; [α]_D²²=−27.0 (c=0.2 in CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, 25 °C): δ =7.31 – 7.23 (m, 2H, CH-Ar), 7.21 – 7.11 (m, 3H, CH-Ar), 5.85 (bs, 1H, NH), 5.30 (t, *J* = 9.9 Hz, 1H, H3), 5.07 (t, *J* = 9.5 Hz, 1H, H4), 4.68 (d, *J* = 8.2 Hz, 1H, H1), 4.25 (dd, *J* = 12.2, 4.6 Hz, 1H, H6a), 4.12 (dd, *J* = 12.2, 2.1 Hz, 1H, H6b), 4.01 – 3.79 (m, 2H, H2, CH₂), 3.78 – 3.62 (m, 1H, H5), 3.61 – 3.33 (m, 1H, CH₂), 2.76 – 2.52 (m, 2H, 2 x CH₂), 2.06 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.96 (s, 3H, CH₃-NHAc), 1.96 – 1.81 (m, 2H, CH₂). ¹³C NMR (126 MHz, CDCl₃, 25 °C): δ =171.0 (CO), 170.9 (CO), 170.6 (CO), 169.5 (CO), 141.7 (C-Ar), 128.6 (2C, CH-Ar), 128.5 (2C, CH-Ar), 126.0 (CH-Ar), 100.8 (C1), 72.5 (C3), 71.8 (C5), 69.0 (CH₂), 68.8 (C4), 62.3 (C6), 55.0 (C2), 32.1 (CH₂), 31.2 (CH₂), 23.5 (NHAc), 20.9 (2C, OAc), 20.8 (OAc). HRMS: [C₂₃H₃₁NO₉+H]⁺ calcd: 466.2072, found: 452.2074. 3'-Phenyl-*n*-propyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy- β -D-glucopyranoside (α -**4g**) was obtained as colorless sticky oil (4 mg; 0.009 mmol; 4%). *R*_f=0.48 (SiO₂, EtOAc); [α]_D²²=74.0 (c=0.2 in CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, 25 °C): δ =7.35 – 7.28 (m, 2H, CH-Ar), 7.25 – 7.15 (m, 3H, CH-Ar), 5.64 (d, *J* = 9.5 Hz, 1H,

NH), 5.21 (dd, $J = 10.7, 9.4$ Hz, 1H, H3), 5.15 – 5.03 (m, 1H, H4), 4.82 (d, $J = 3.6$ Hz, 1H, H1), 4.33 (ddd, $J = 10.7, 9.5, 3.6$ Hz, 1H, H2), 4.21 (dd, $J = 12.3, 4.6$ Hz, 1H, H6a), 4.05 (dd, $J = 12.3, 2.3$ Hz, 1H, H6b), 3.90 (ddd, $J = 10.2, 4.6, 2.4$ Hz, 1H, H5), 3.71 (dt, $J = 9.9, 6.6$ Hz, 1H, CH₂), 3.45 (dt, $J = 9.9, 6.4$ Hz, 1H, CH₂), 2.78 – 2.63 (m, 2H, CH₂), 2.06 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.02 – 1.93 (m, 5H, NHAc, CH₂). ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ =171.6 (CO), 170.8 (CO), 170.0 (CO), 169.5 (CO), 141.2 (C-Ar), 128.7 (2C, CH-Ar), 128.5 (2C, CH-Ar), 126.3 (CH-Ar), 97.4 (C1), 71.6 (C3), 68.29 (C4), 67.9 (C5+CH₂), 62.1 (C6), 52.1 (C2), 32.5 (CH₂), 30.8 (CH₂), 29.9 (NHAc), 20.9 (OAc), 20.9 (OAc), 20.8 (OAc). MS: [C₂₃H₃₁NO₉+H]⁺ calculated: 466.2, found: 466.2.

Phenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranoside (**4h**) was synthesized analogously to **4a** and purified by RP-MPLC (A: H₂O + 0.1% HCOOH; B: MeCN + 0.1% HCOOH; 0-45 min 5-30% B, flow rate 30 mL/min). Phenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy- β -D-glucopyranoside (β -**4h**) was obtained as colorless solid (15 mg; 0.04 mmol; 17%). R_f =0.47 (SiO₂, EtOAc); mp: 177.8-180.8 °C; $[\alpha]_D^{22}$ =−21.0 (c=0.2 in CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, 25 °C): δ =7.34 – 7.19 (m, 2H, CH-Ar), 7.05 (t, $J = 7.3$ Hz, 1H, CH-Ar), 6.99 (d, $J = 8.0$ Hz, 2H, CH-Ar), 5.78 (d, $J = 8.4$ Hz, 1H, NH), 5.41 (t, $J = 9.8$ Hz, 1H, H3), 5.27 (d, $J = 8.1$ Hz, 1H, H1), 5.14 (t, $J = 9.4$ Hz, 1H, H4), 4.28 (dd, $J = 12.2, 5.2$ Hz, 1H, H6a), 4.22 – 4.06 (m, 2H, H6b, H2), 3.97 – 3.80 (m, 1H, H5), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.95 (s, 3H, NHAc). ¹³C NMR (126 MHz, CDCl₃, 25 °C): δ =171.0 (CO), 170.8 (CO), 170.6 (CO), 169.6 (CO), 157.1 (C-Ar), 129.7 (2C, CH-Ar), 123.3 (CH-Ar), 117.0 (2C, CH-Ar), 99.1 (C1), 72.2 (C3), 72.1 (C5), 68.7 (C4), 62.3 (C6), 54.9 (C2), 23.5 (NHAc), 20.9 (OAc), 20.9 (OAc), 20.8 (OAc). HRMS: [C₂₀H₂₅NO₉+H]⁺ calcd: 424.1602, found: 424.1606. Phenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy- β -D-glucopyranoside (α -**4h**) was obtained as yellowish oil (9 mg; 0.02 mmol; 10%). R_f =0.53 (SiO₂, EtOAc); $[\alpha]_D^{22}$ =143.5 (c=0.4 in CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, 25 °C): δ =7.35 –

7.28 (m, 2H, CH-Ar), 7.14 – 7.03 (m, 3H, CH-Ar), 5.84 (d, $J = 9.3$ Hz, 1H, NH), 5.58 (d, $J = 3.4$ Hz, 1H, H1), 5.44 (dd, $J = 10.8, 9.4$ Hz, 1H, H3), 5.22 (t, $J = 9.7$ Hz, 1H, H4), 4.53 (ddd, $J = 10.8, 9.3, 3.4$ Hz, 1H, H2), 4.30 – 4.17 (m, 1H, H6a), 4.11 – 3.99 (m, 2H, H5, H6b), 2.07 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.96 (s, 3H, NHAc). ^{13}C NMR (126 MHz, CDCl_3 , 25 °C): δ =171.7 (CO), 170.8 (CO), 170.3 (CO), 169.5 (CO), 155.9 (C-Ar), 129.9 (CH-Ar), 123.3 (CH-Ar), 116.5 (CH-Ar), 95.7 (C1), 71.2 (C3), 68.6 (C5), 68.0 (C4), 61.8 (C6), 52.1 (C2), 23.4 (NHAc), 20.9 (OAc), 20.8 (OAc), 20.8 (OAc). HRMS: $[\text{C}_{20}\text{H}_{25}\text{NO}_9+\text{H}]^+$ calcd: 424.1602, found: 424.1604.

NMR data of β -**4h**^[6] correspond to the reported values.

i-Propyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranoside (**4i**) was synthesized analogously to **4a** and purified by RP-MPLC (A: $\text{H}_2\text{O} + 0.1\%$ HCOOH; B: MeCN + 0.1% HCOOH; 0-40 min 5-20% B, flow rate 30 mL/min). *i*-Propyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy- β -D-glucopyranoside (β -**4i**) was obtained as colorless solid (13 mg; 0.03 mmol; 16%). R_f =0.38 (SiO_2 , EtOAc); mp: 173.3-174.8 °C; $[\alpha]_{\text{D}}^{22} = -28.0$ ($c=0.2$ in CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ =5.56 (bs, 1H, NH), 5.41 (t, $J = 10.0$ Hz, 1H, H3), 5.03 (t, $J = 9.1$ Hz, 1H, H4), 4.84 (d, $J = 8.0$ Hz, 1H, H1), 4.25 (dd, $J = 12.2, 4.2$ Hz, 1H, H6a), 4.11 (d, $J = 12.0$ Hz, 1H, H6b), 3.93 (bs, 1H, CH), 3.78 – 3.55 (m, 2H, H5+H2), 2.07 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.94 (s, 3H, NHAc), 1.22 (d, $J = 5.3$ Hz, 3H, CH_3), 1.13 (d, $J = 5.1$ Hz, 3H, CH_3). ^{13}C NMR (126 MHz, CDCl_3 , 25 °C): δ =170.9 (2C, CO), 169.7 (2C, CO), 99.3 (C1), 72.8 (CH), 72.3 (C3), 71.8 (C5), 69.1 (C4), 62.5 (C6), 55.7 (C2), 23.4 (NHAc, CH_3), 22.2 (CH_3), 21.0 (OAc), 20.9 (OAc), 20.8 (OAc). HRMS: $[\text{C}_{17}\text{H}_{27}\text{NO}_9+\text{H}]^+$ calcd: 390.1759, found: 390.1755. *i*-Propyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy- β -D-glucopyranoside (α -**4i**) was obtained as colorless oil (9 mg; 0.02 mmol; 11%). R_f =0.45 (SiO_2 , EtOAc); $[\alpha]_{\text{D}}^{22} = 140.0$ ($c=0.2$ in CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ =5.62 (d, $J = 9.5$ Hz, 1H, NH), 5.20 (dd, $J = 10.7, 9.5$ Hz, 1H, H3), 5.10 (t, $J = 9.8$

Hz, 1H, H4), 4.93 (d, J = 3.7 Hz, 1H, H1), 4.31 (ddd, J = 10.7, 9.5, 3.8 Hz, 1H, H2), 4.22 (dd, J = 12.2, 4.7 Hz, 1H, H6a), 4.08 (dd, J = 12.2, 2.4 Hz, 1H, H6b), 4.02 (ddd, J = 10.1, 4.6, 2.4 Hz, 1H, H5), 3.89 (hept, J = 6.2 Hz, 1H, CH), 2.09 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.95 (s, 3H, NHAc), 1.24 (d, J = 6.2 Hz, 3H, CH₃), 1.15 (d, J = 6.1 Hz, 3H, CH₃). ¹³C NMR (126 MHz, CDCl₃, 25 °C): δ =171.6 (CO), 170.9 (CO), 170.0 (CO), 169.5 (CO), 95.8 (C1), 71.6 (C3), 71.2 (CH), 68.4 (C4), 67.9 (C5), 62.2 (C6), 52.0 (C2), 23.4 (NHAc), 23.3 (CH₃), 21.8 (CH₃), 20.9 (OAc), 20.9 (OAc), 20.8 (OAc). HRMS: [C₁₇H₂₇NO₉+H]⁺ calcd: 390.1759, found: 390.1754.

NMR data of β -**4i**^[7] correspond to the reported values.

Typical procedure for selective α -glycoside formation with equimolar catalyst

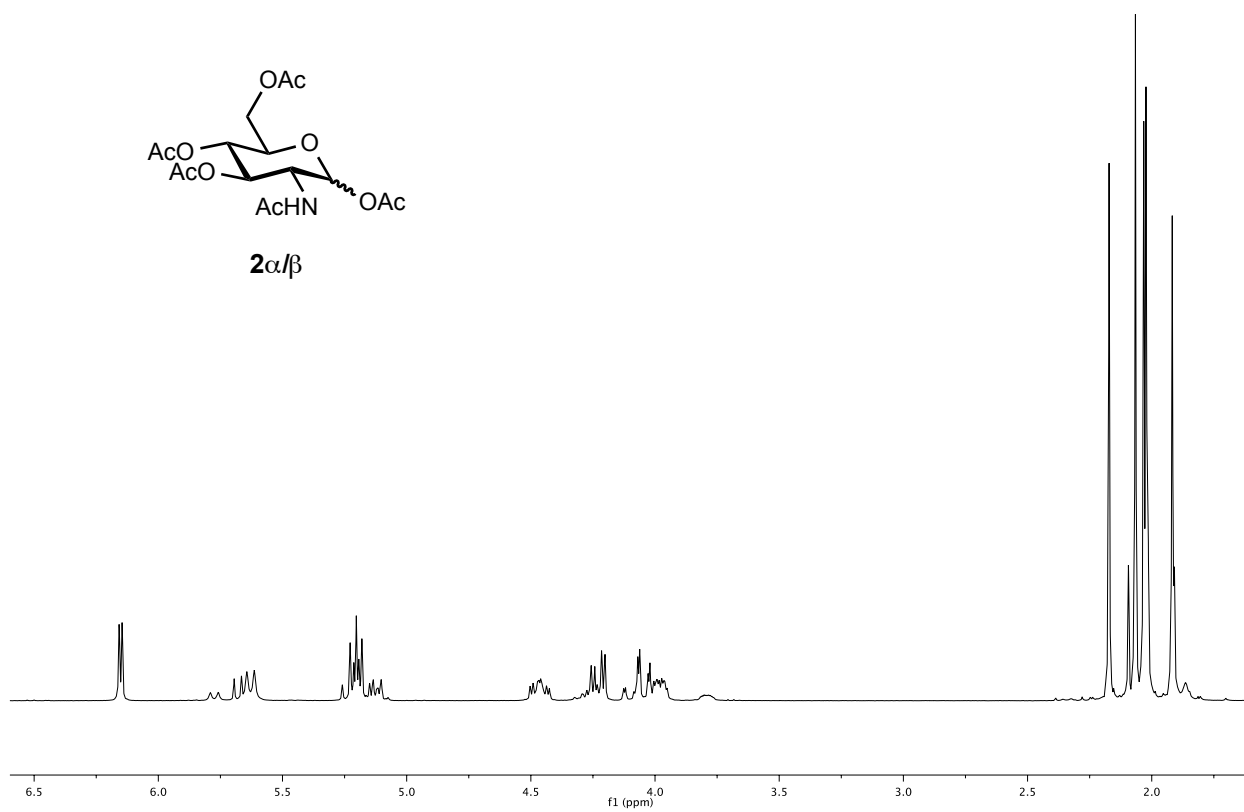
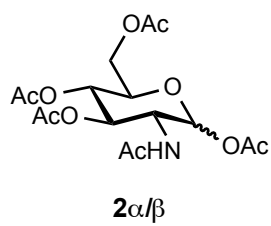
Donor **2a/β** (80.0 mg, 0.20 mmol), Cu(OTf)₂ (74.0 mg, 0.20 mmol) and the corresponding acceptor (1.02 mmol) were stirred under nitrogen atmosphere in dry 1,2-dichloroethane (4 mL) at 84 °C. After full conversion and anomerization was observed by LCMS the mixture was cooled to r.t. and quenched with brine (4 mL). The phases were separated and the aqueous layer was extracted with CH₂Cl₂ (5 x 6 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and the volatiles removed in vacuo. The residue was purified by flash chromatography on silica (toluene/*i*PrOH 95:5 to toluene/*i*PrOH 90:10). This method was applied for α -**4b**, α -**4h** and α -**4i**.

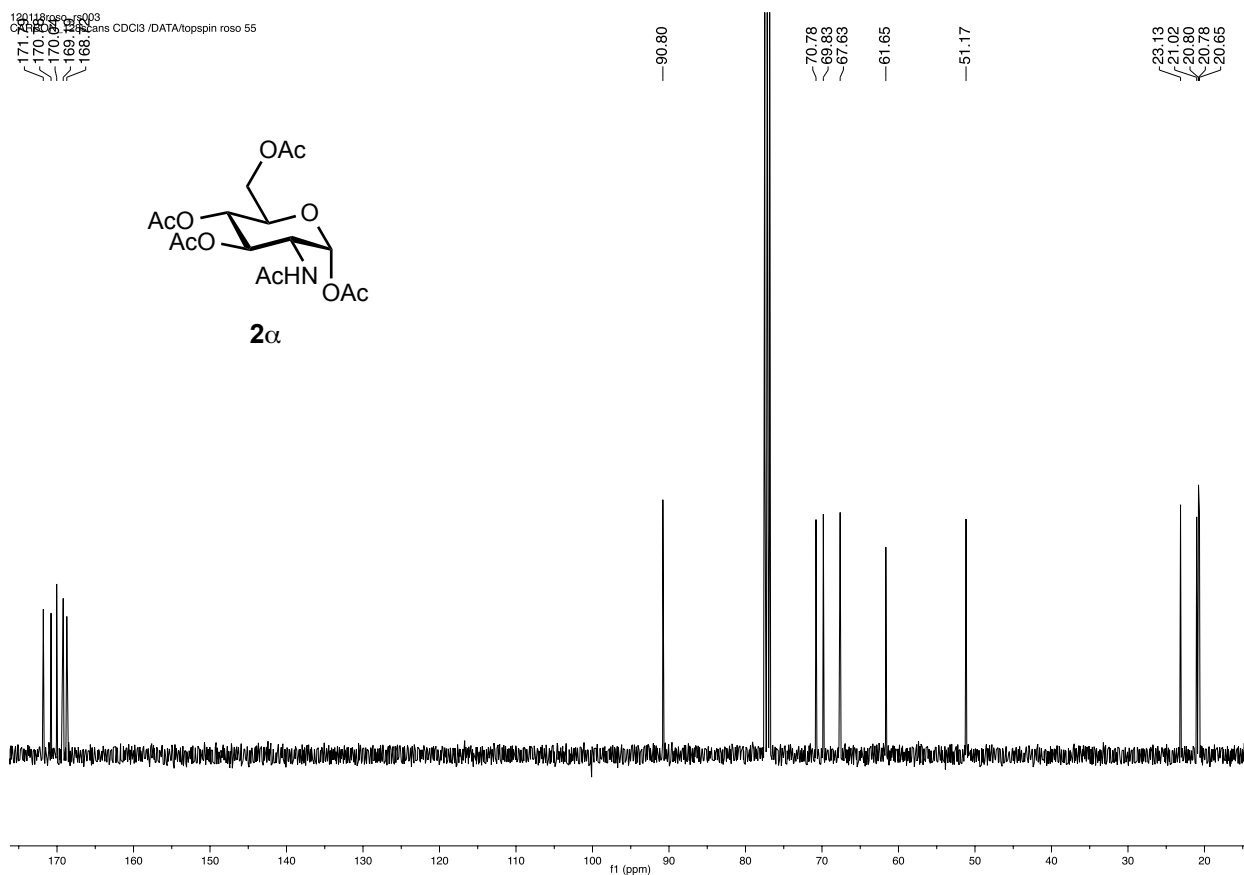
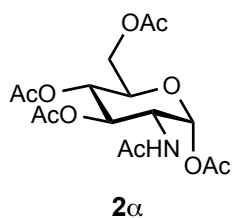
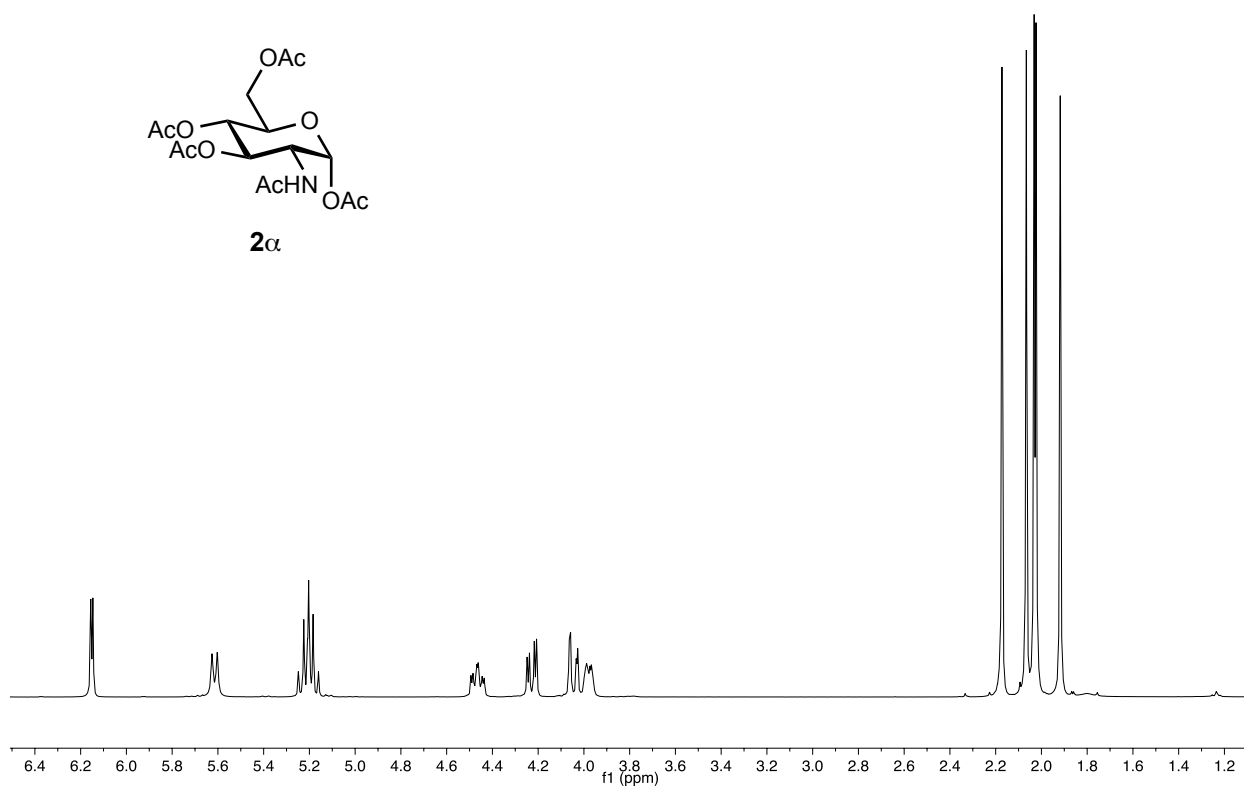
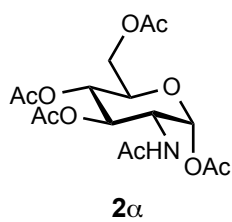
Typical procedure for selective β -glycoside formation with equimolar catalyst

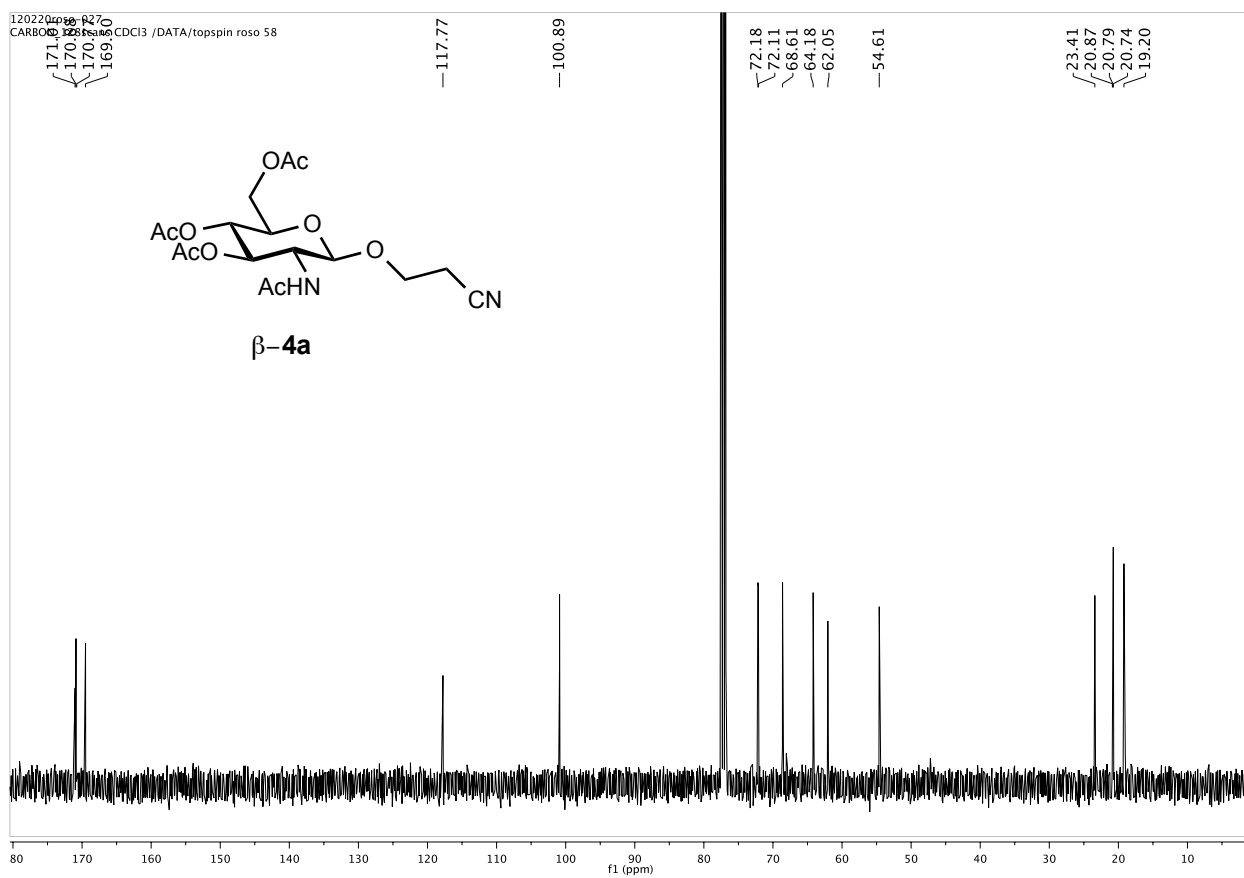
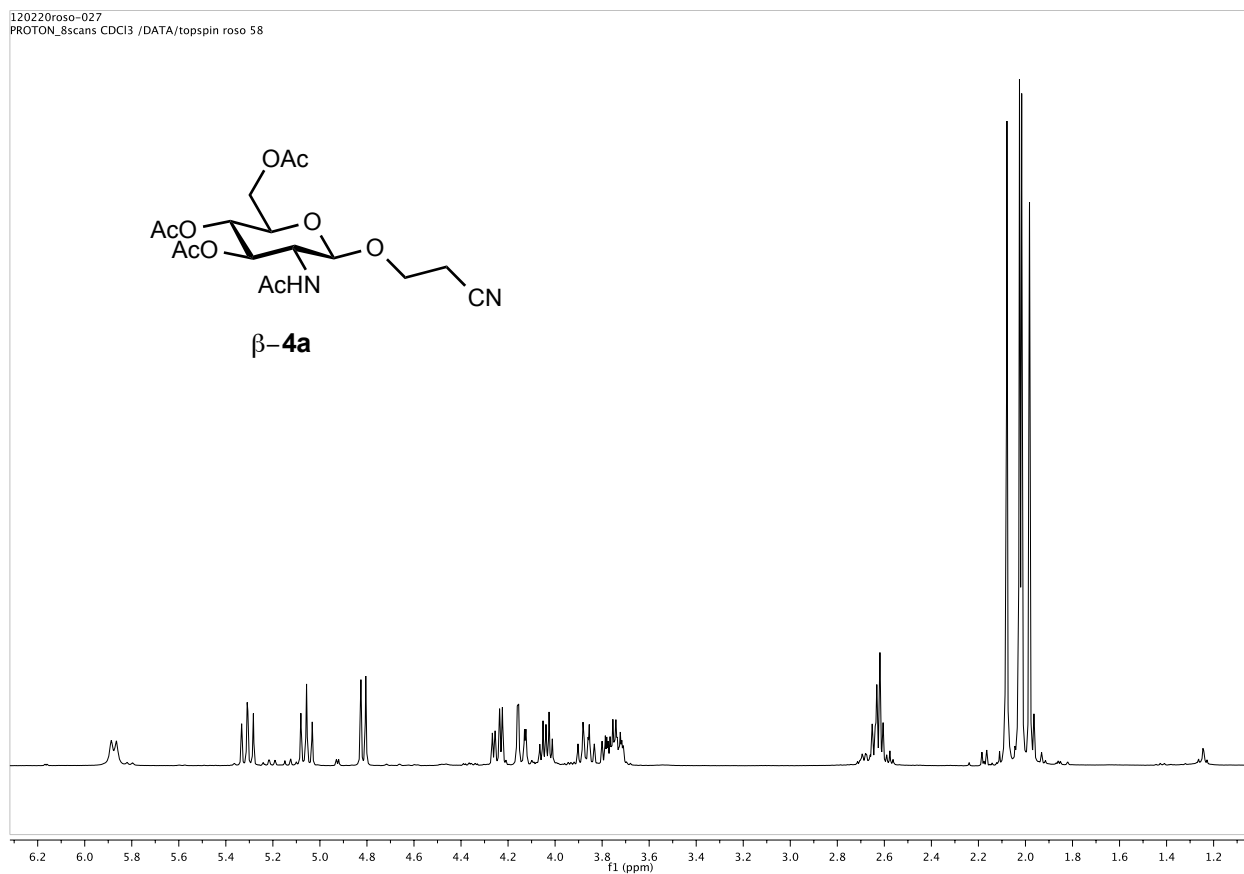
Donor **2a/β** (80.0 mg, 0.20 mmol) and Cu(OTf)₂ (74.0 mg, 0.20 mmol) were stirred under nitrogen atmosphere in dry 1,2-dichloroethane (4 mL) at 84 °C for 4 h. The reaction mixture was then cooled to 40 °C and the corresponding acceptor (1.02 mmol) was added and stirred for 2-4 h. The mixture was cooled to r.t. and quenched with brine (4 mL). The phases were separated and the aqueous layer was extracted with CH₂Cl₂ (5 x 6 mL). The

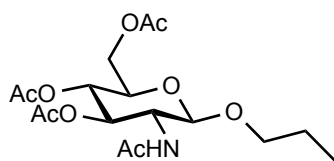
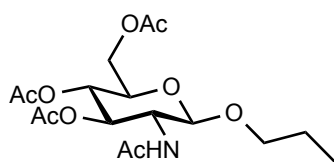
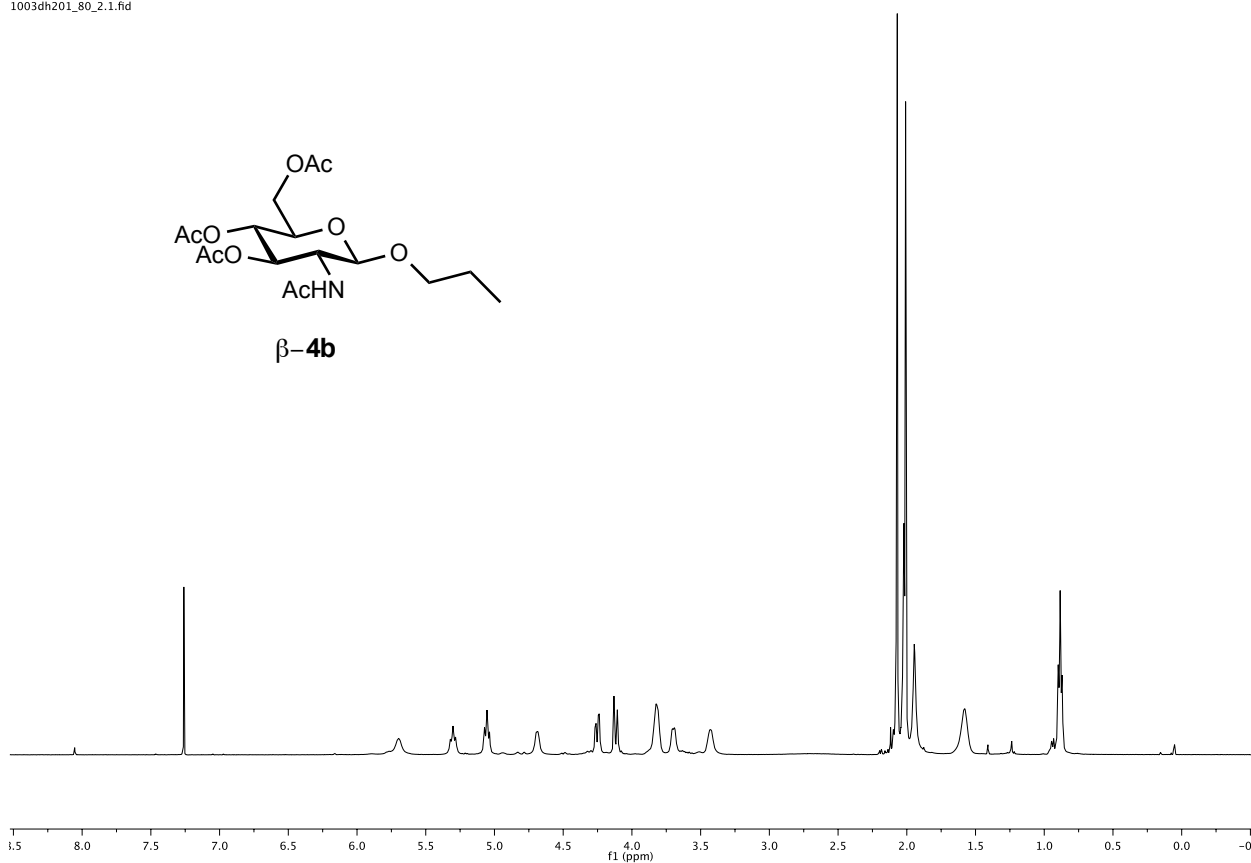
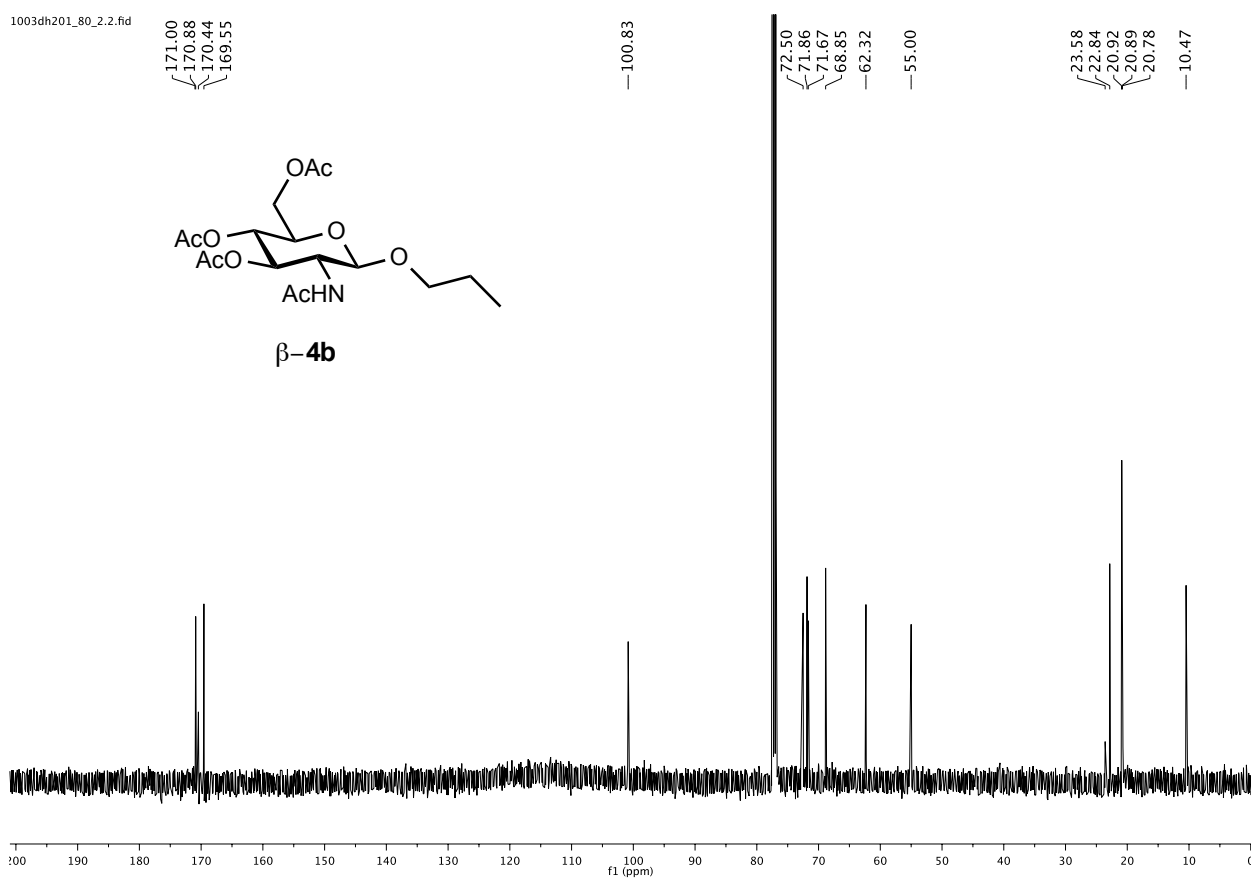
combined organic layers were dried over anhydrous Na_2SO_4 , filtered and the volatiles removed in vacuo. The residue was purified by flash chromatography on silica (toluene/*i*PrOH 95:5 to toluene/*i*PrOH 90:10). This method was applied for β -**4b**, β -**4h** and β -**4i**.

Transcripts of ^1H and ^{13}C NMR spectra

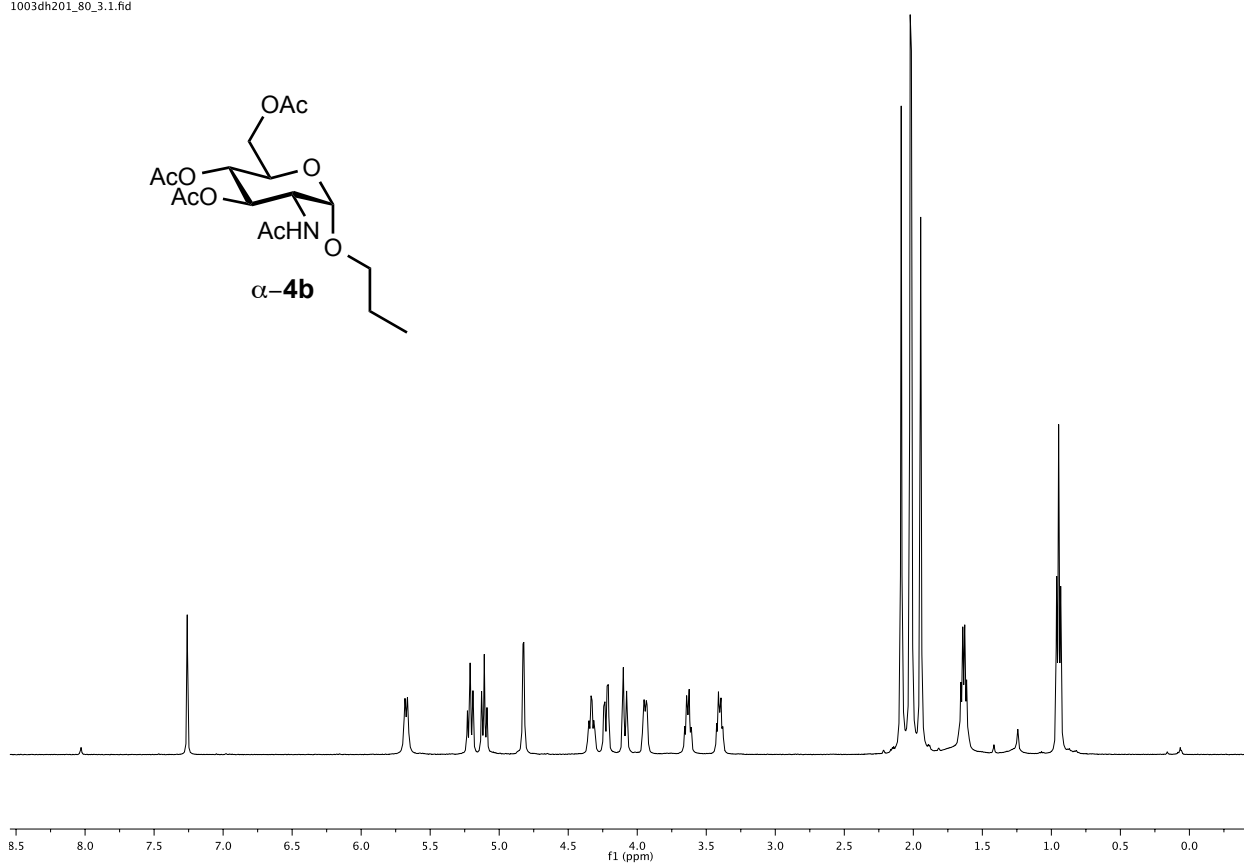




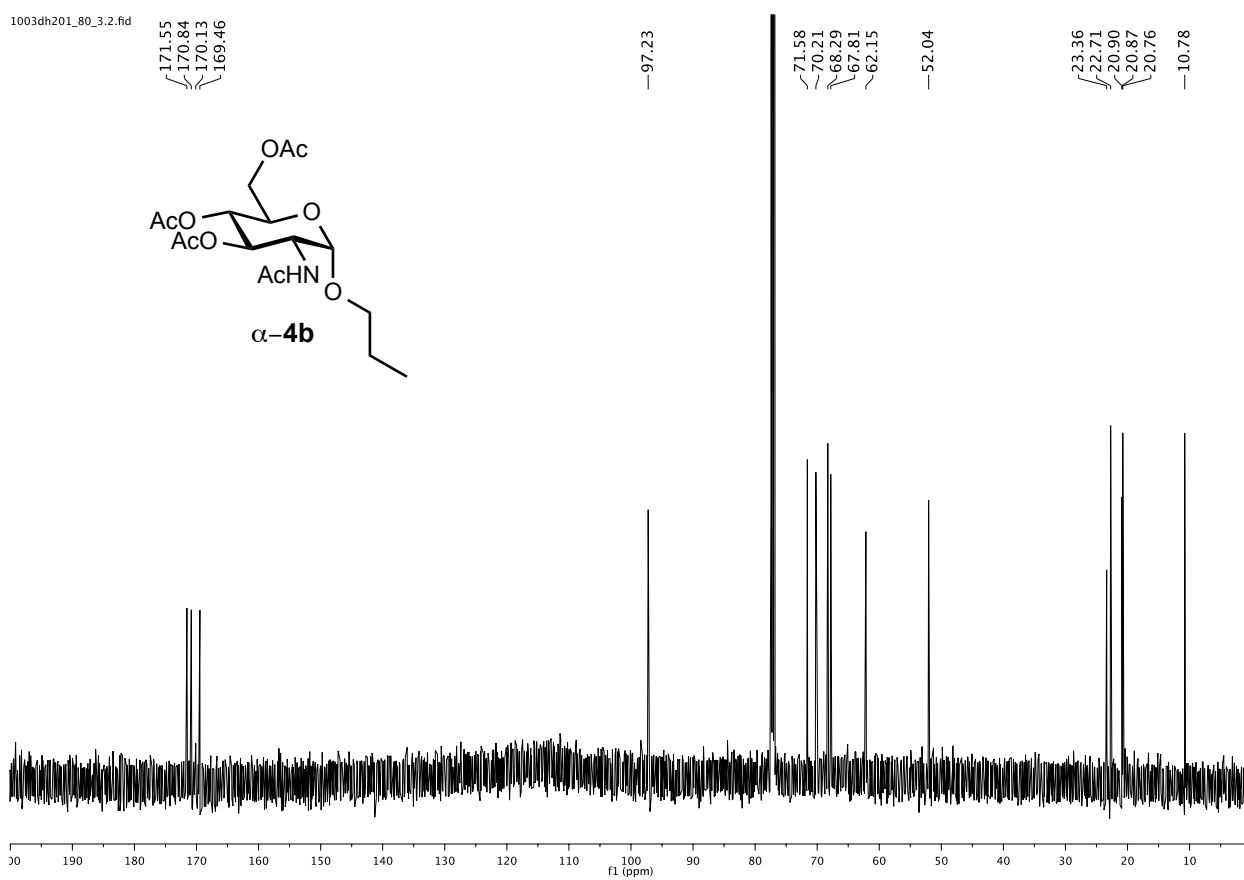


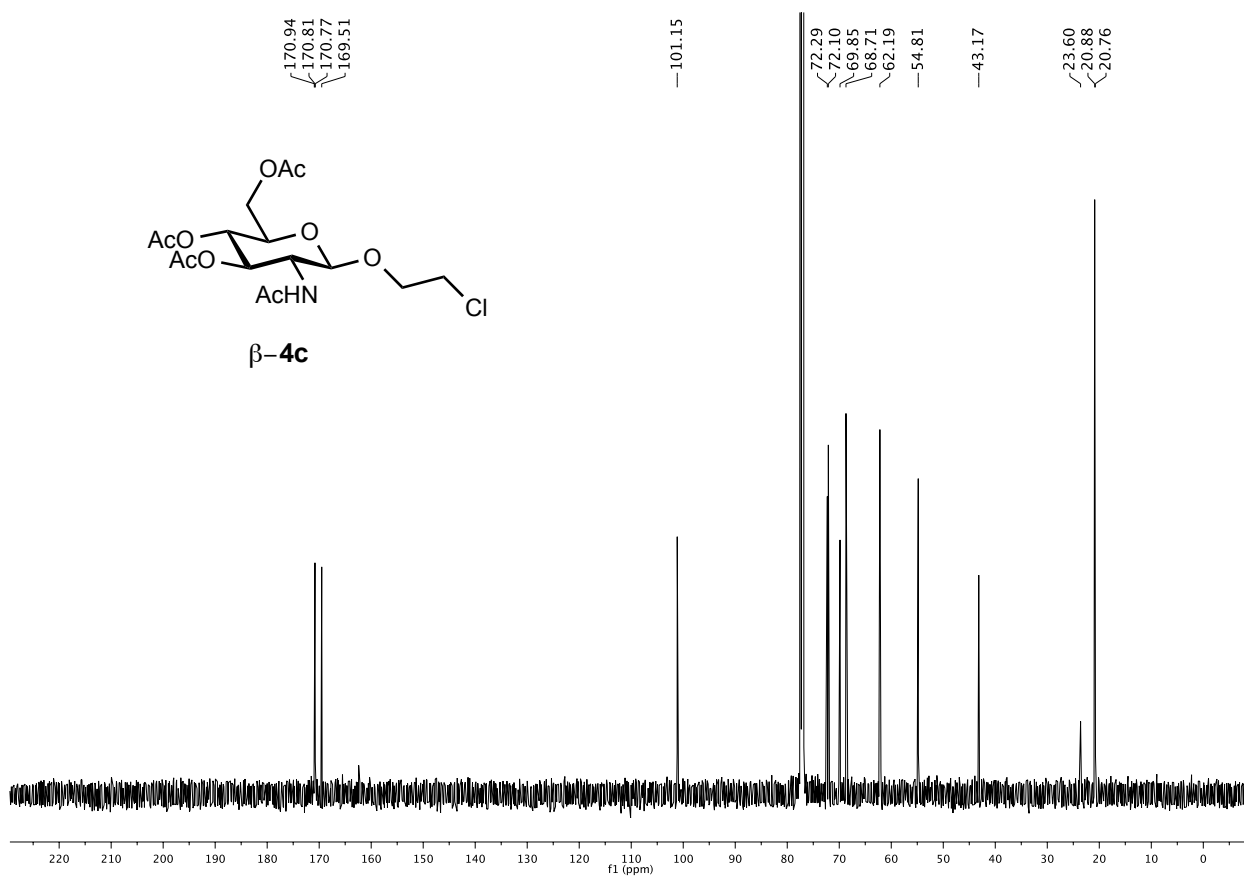
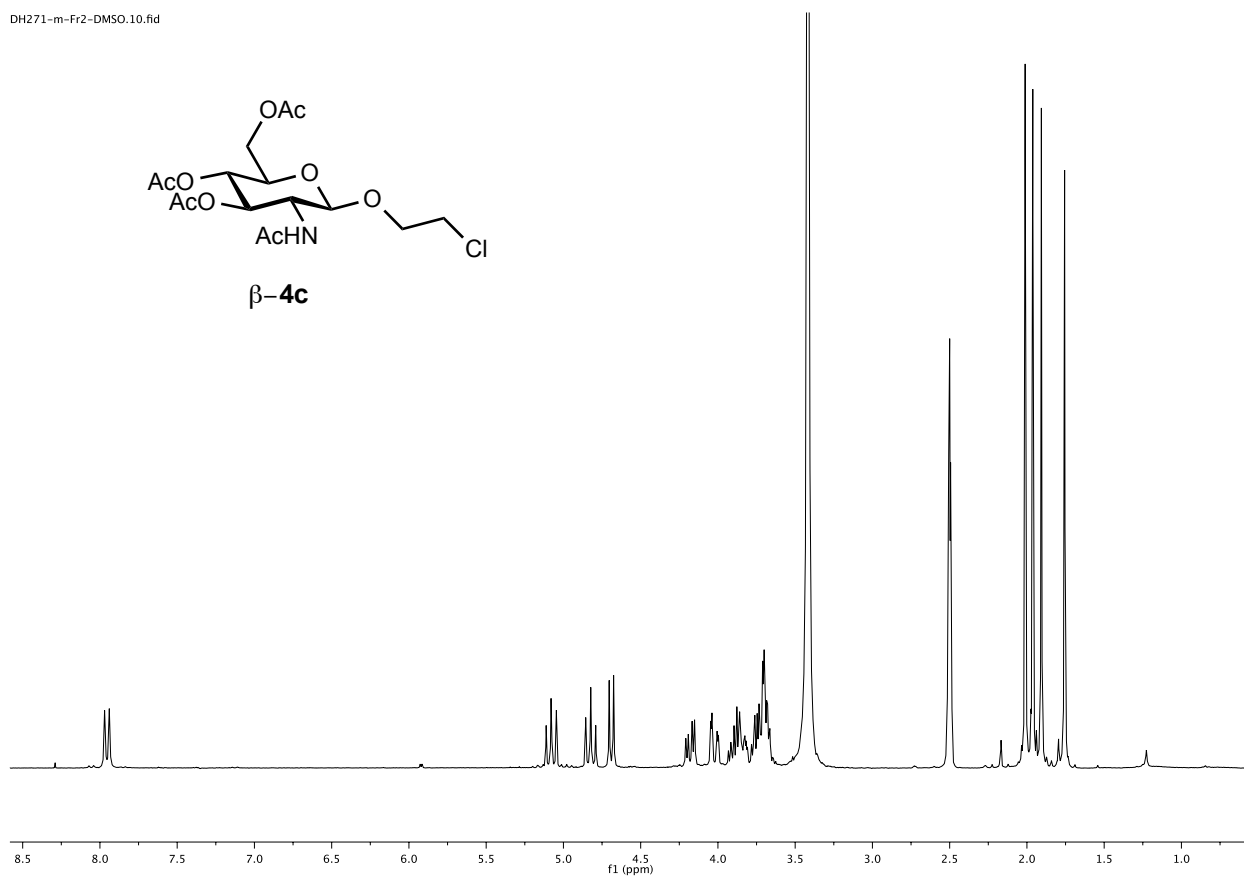
 β -4b β -4b

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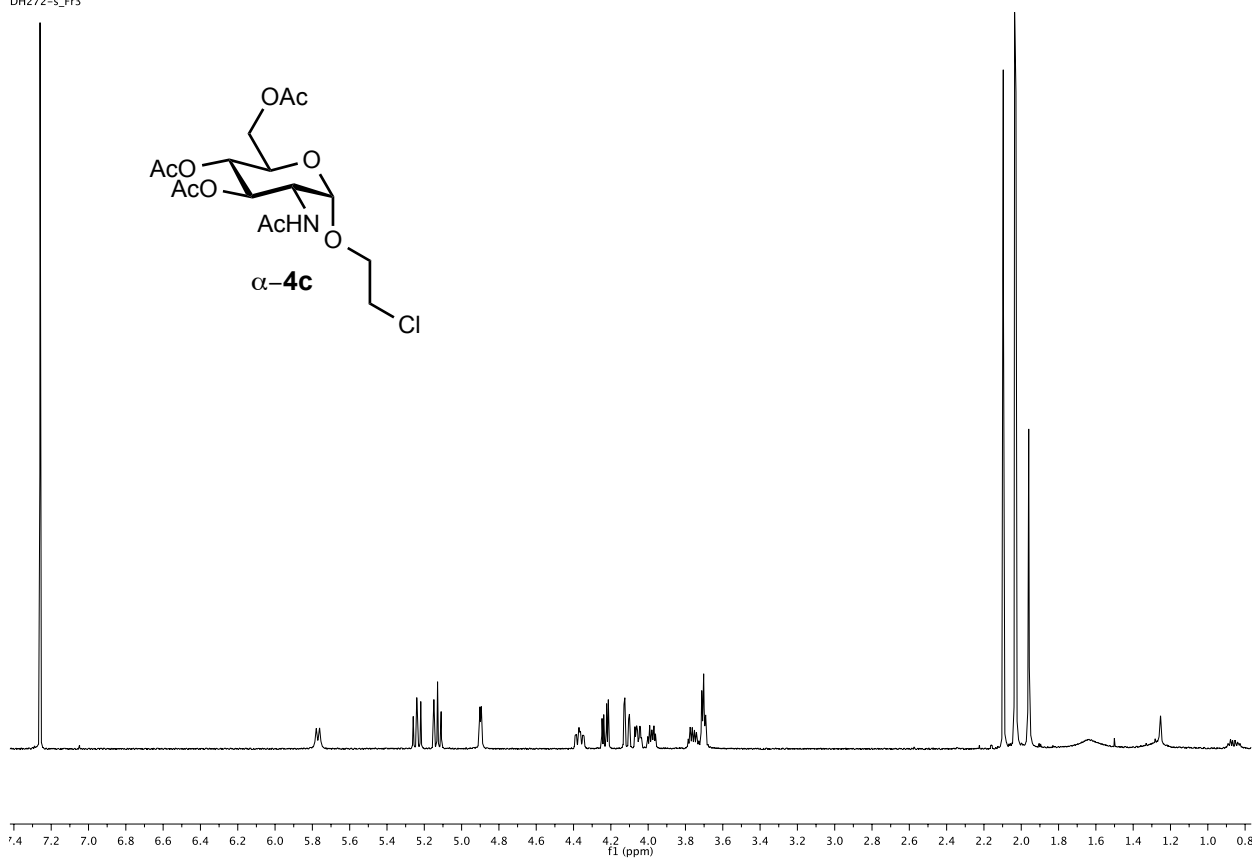


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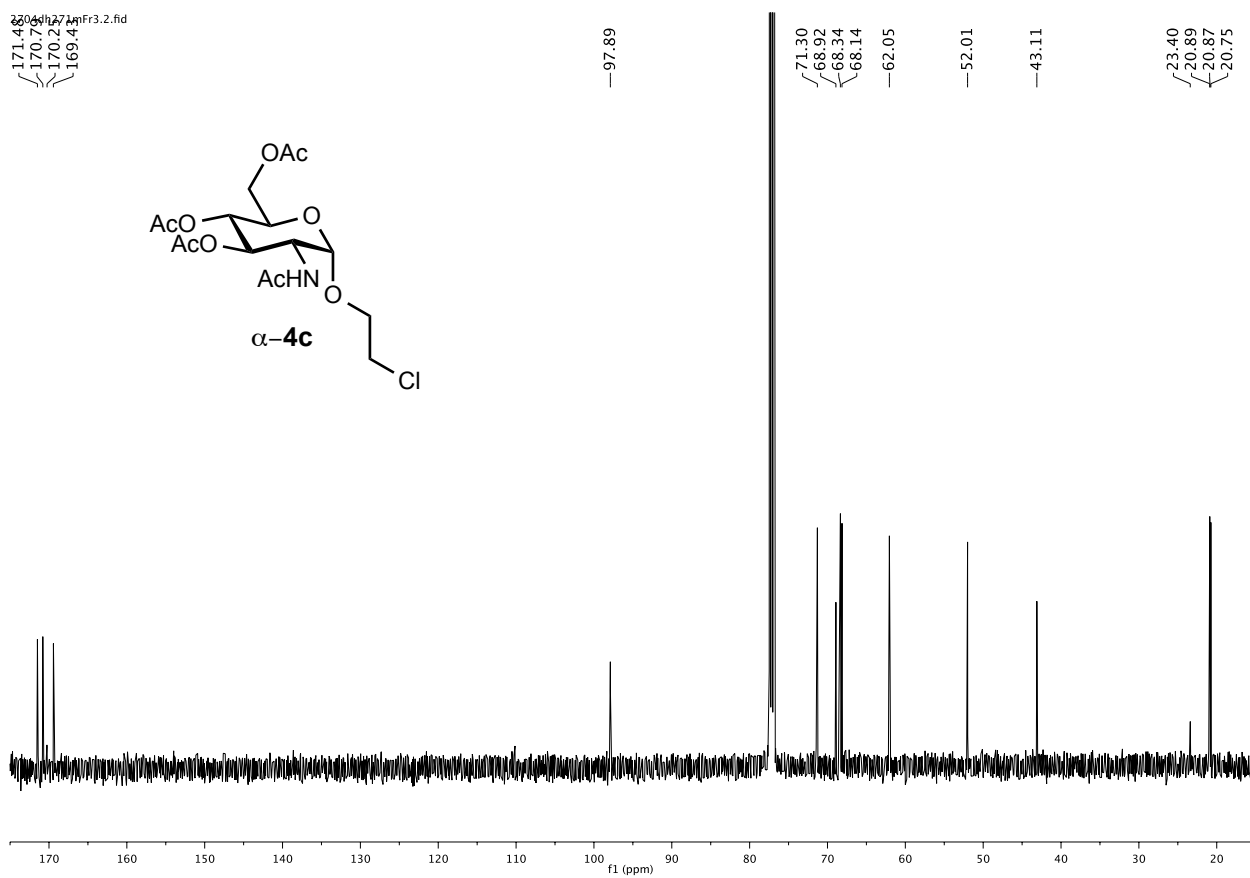




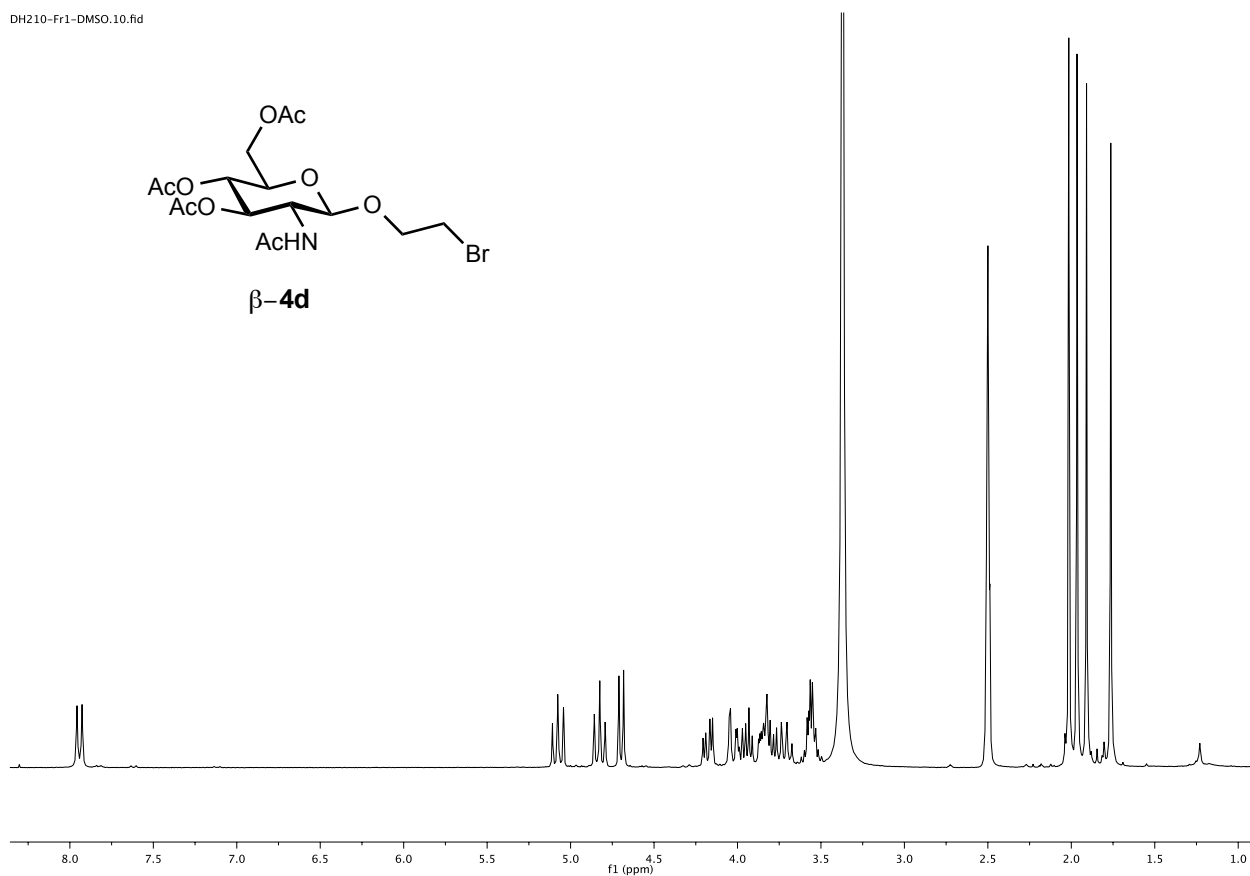
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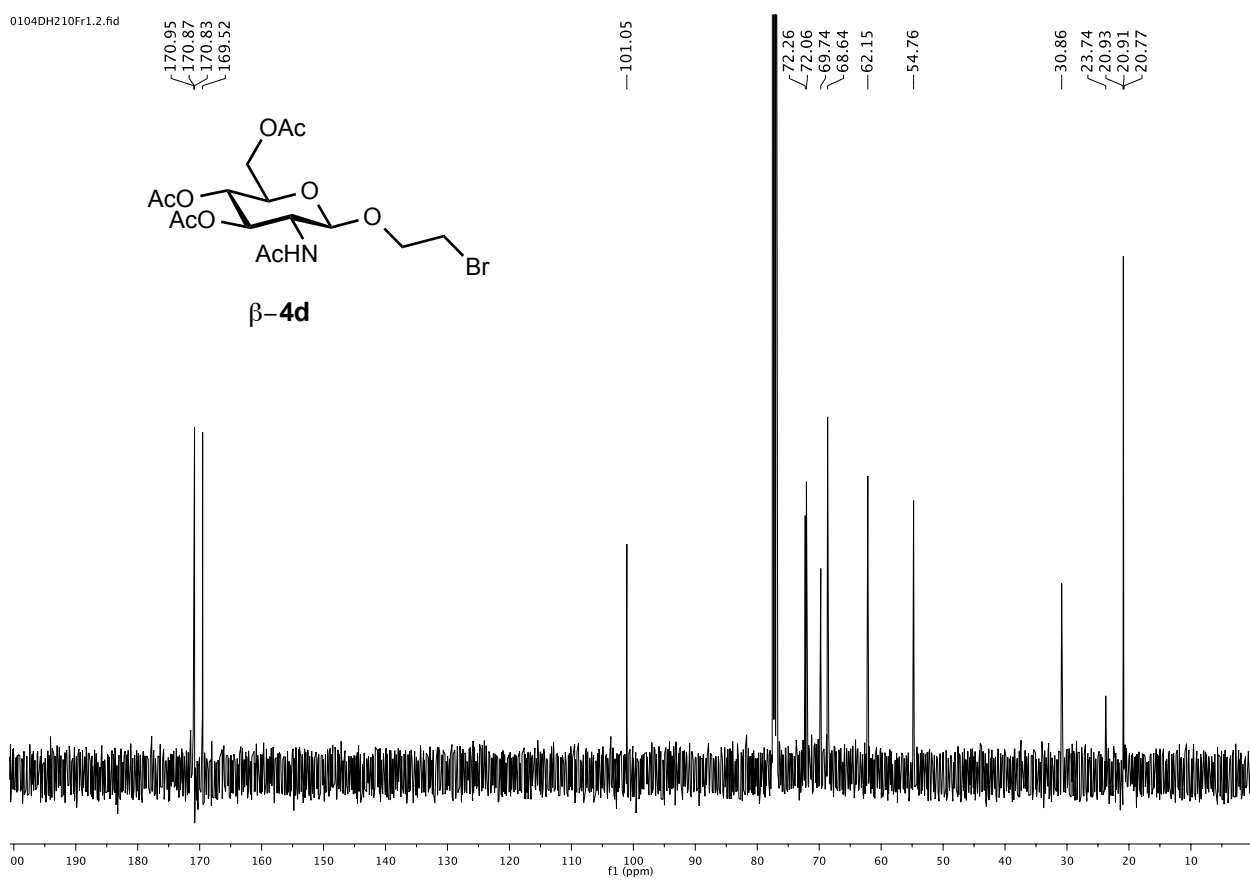
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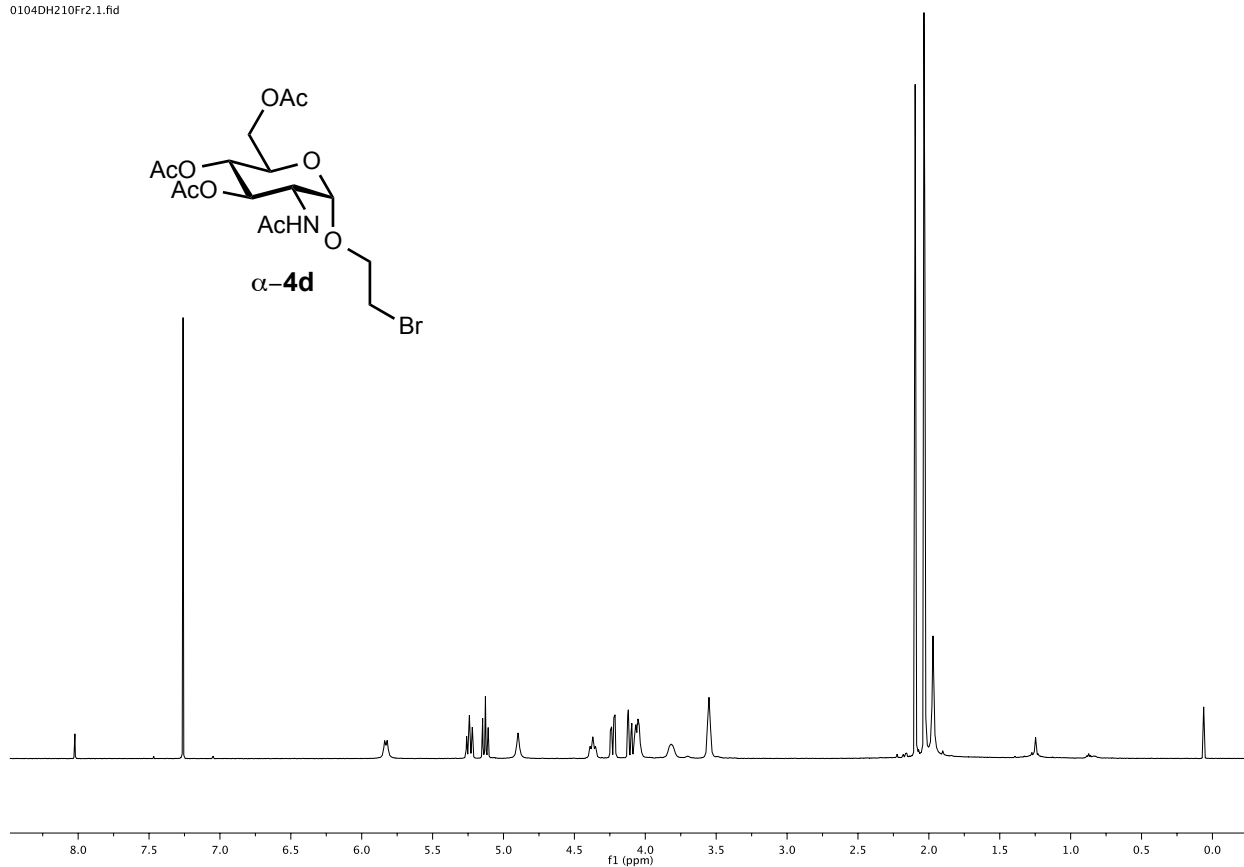
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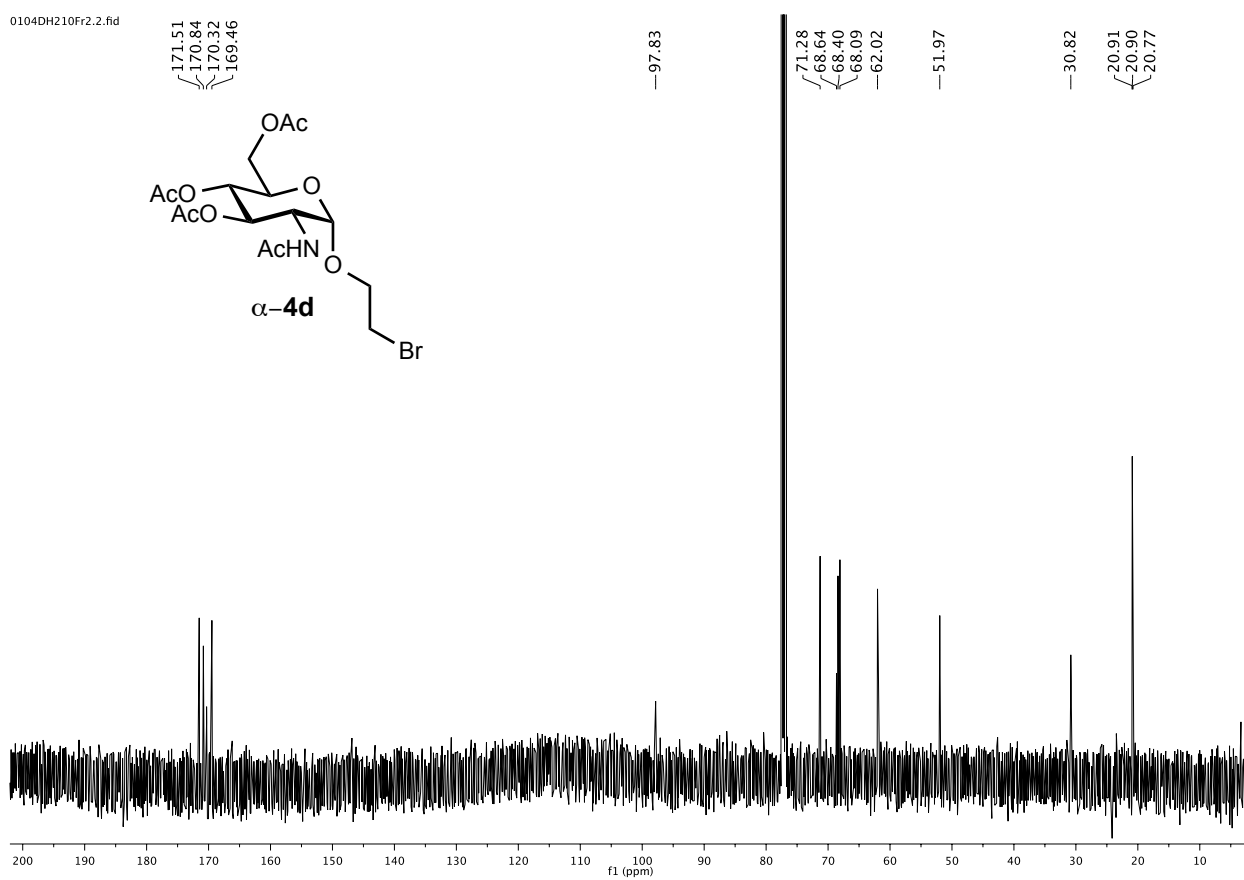
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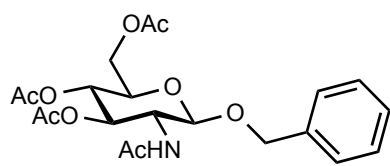
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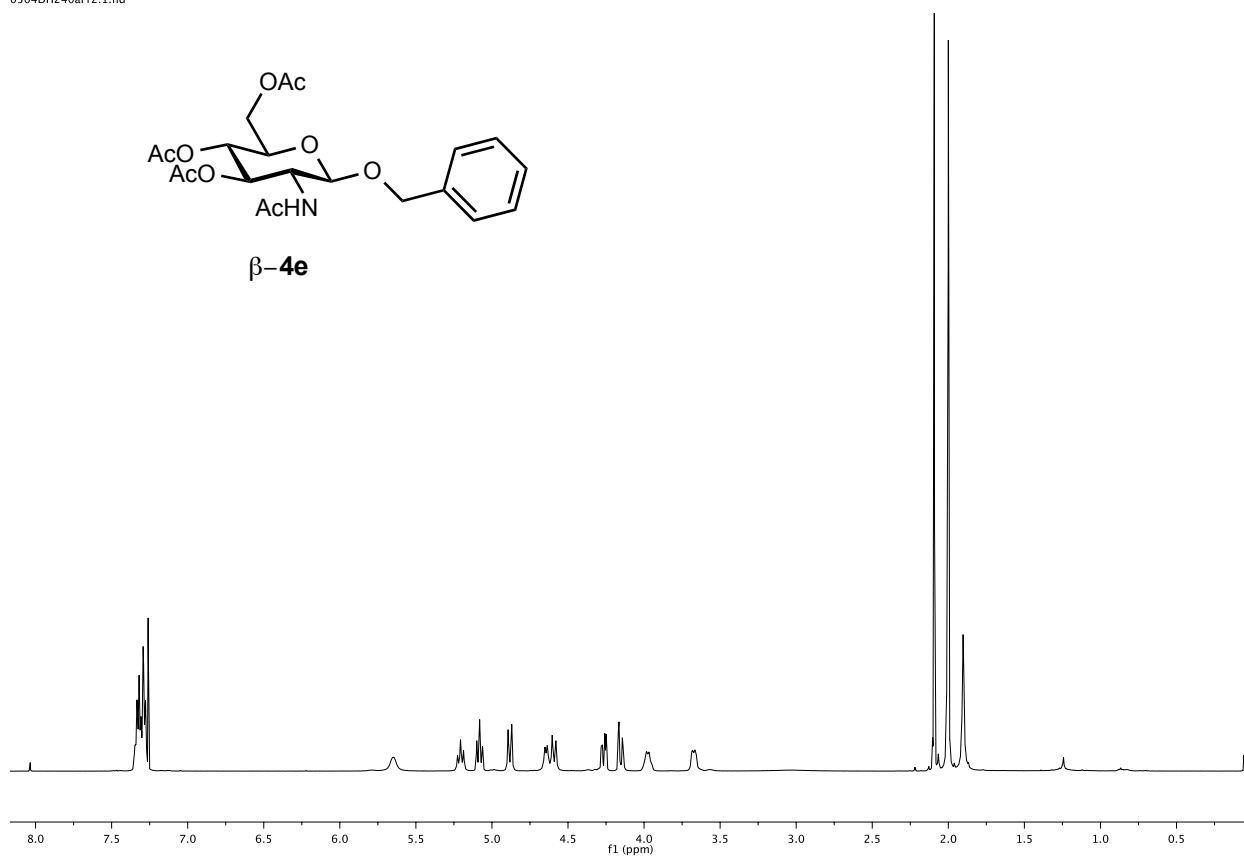
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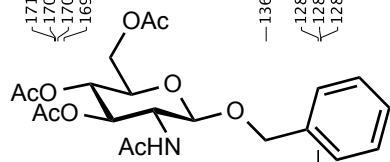
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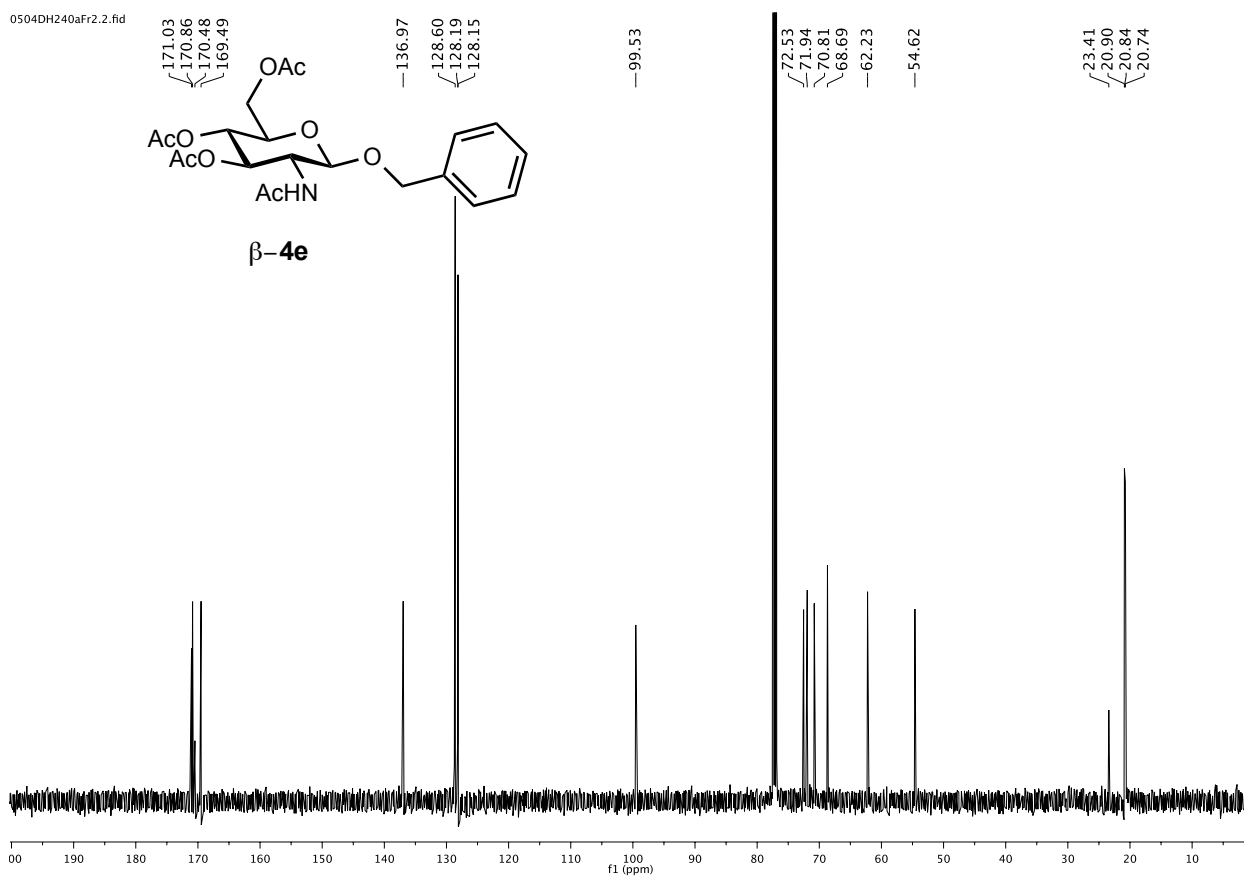
β -4e

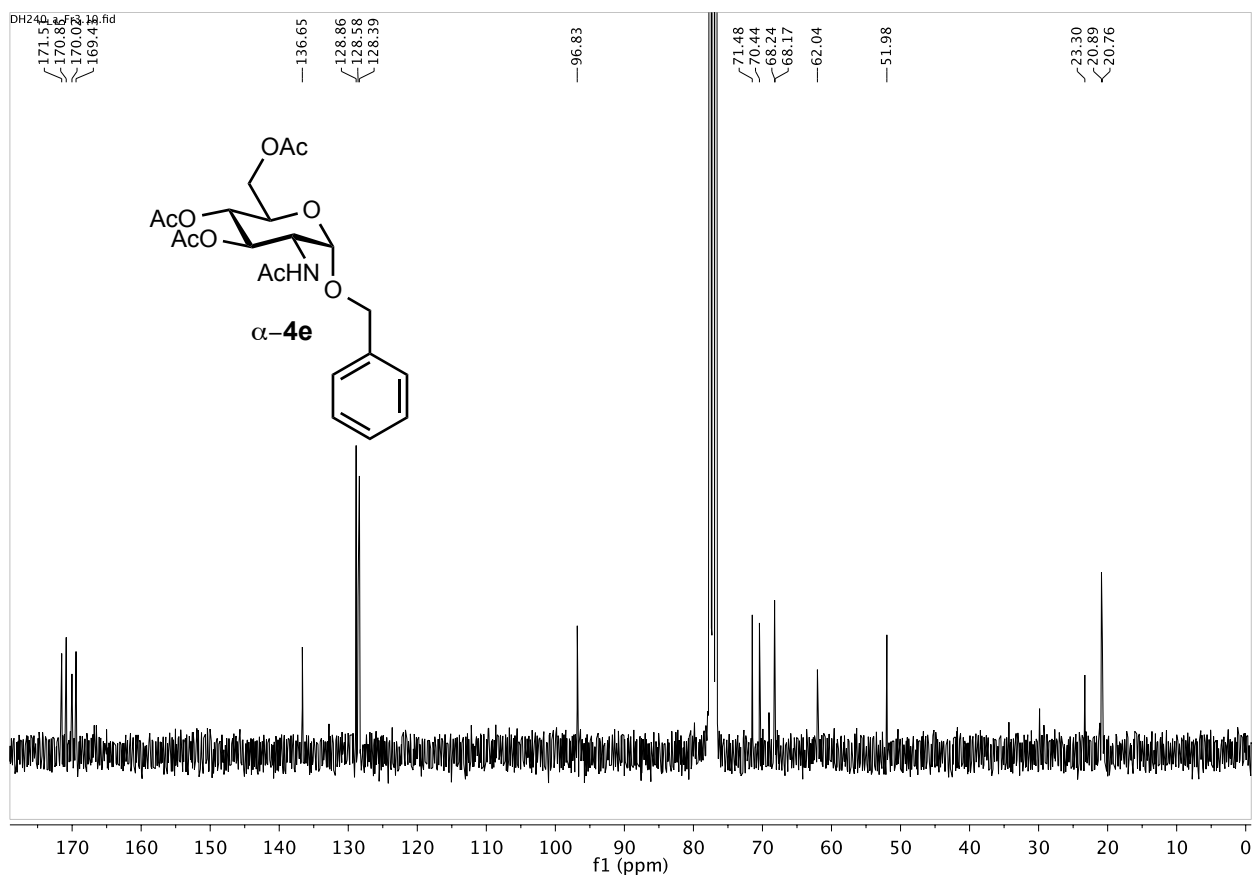
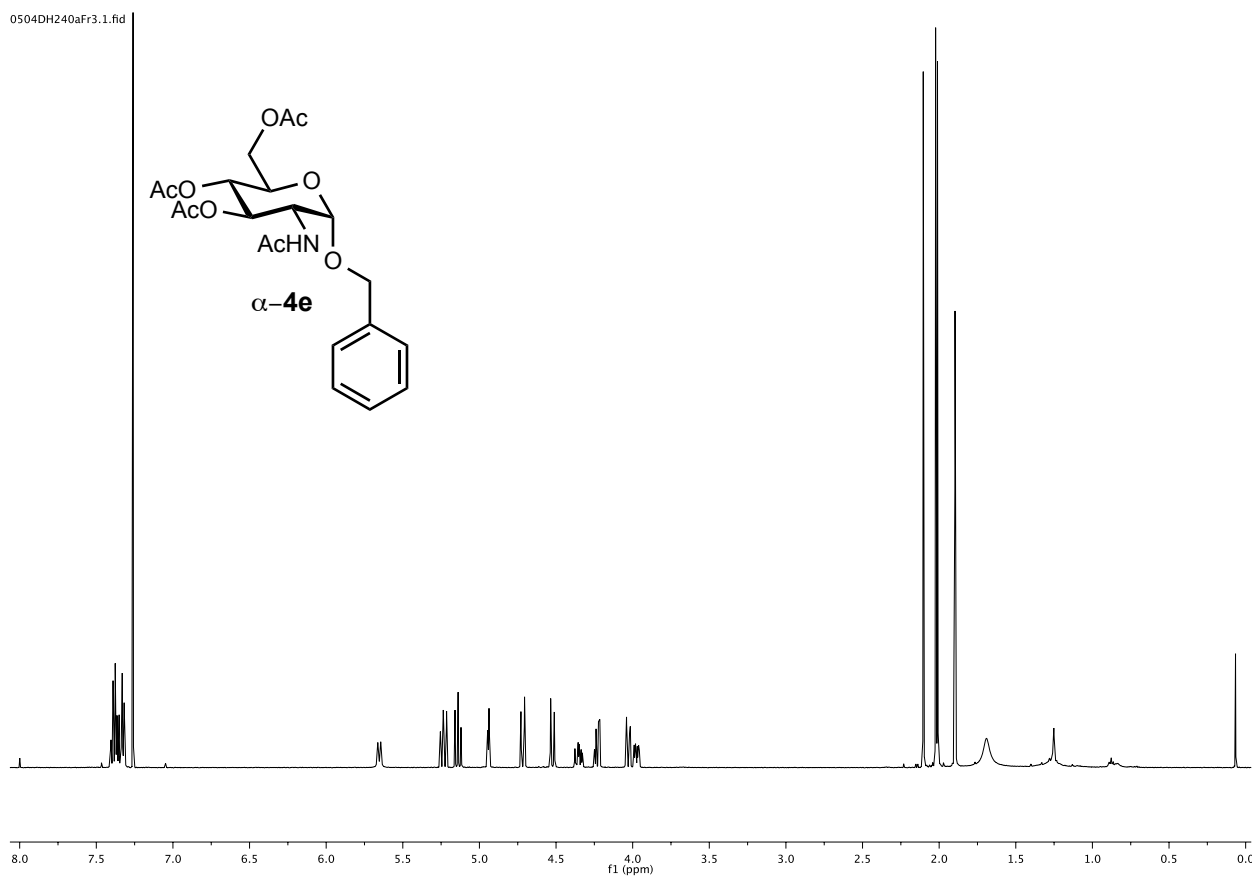


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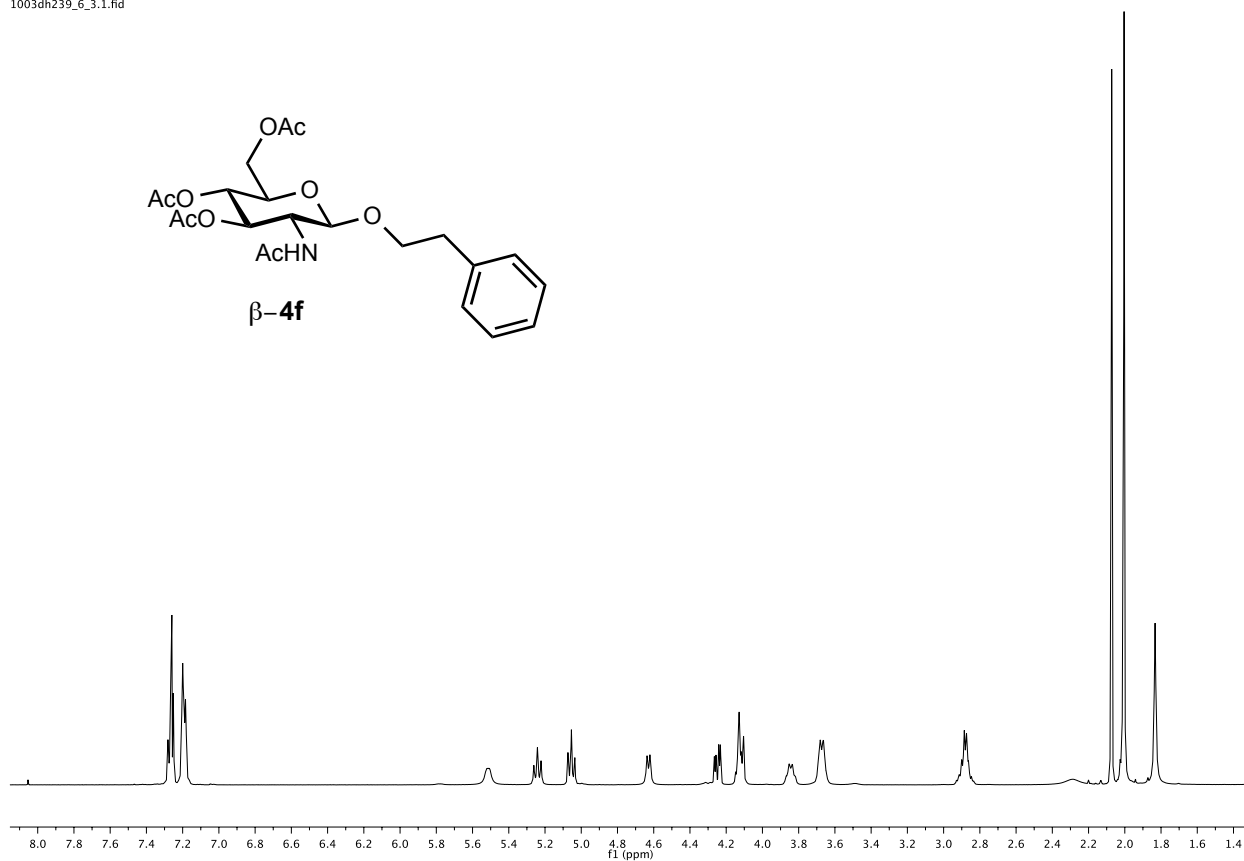
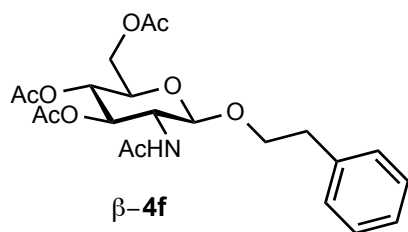


β -4e

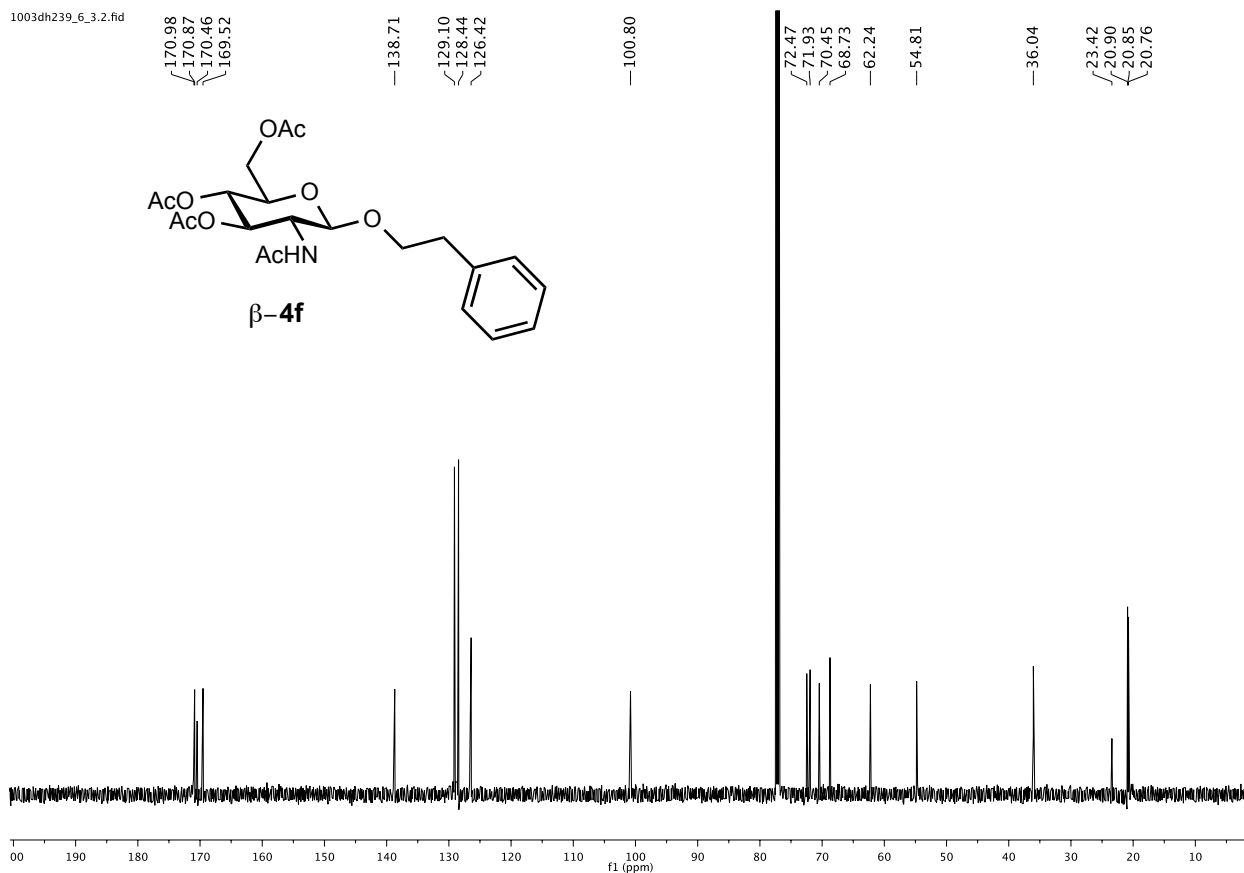
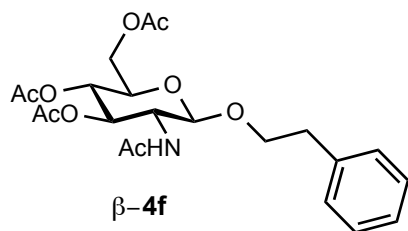




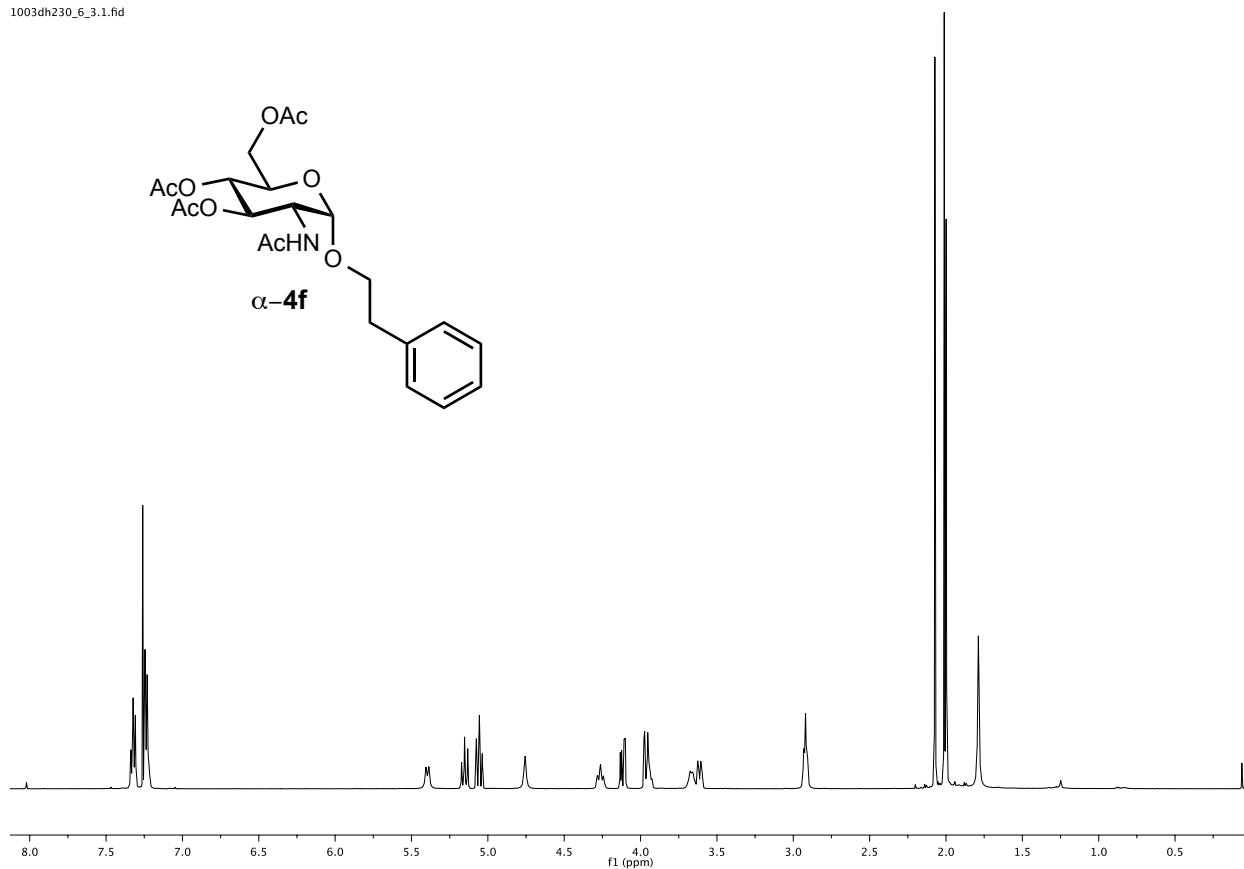
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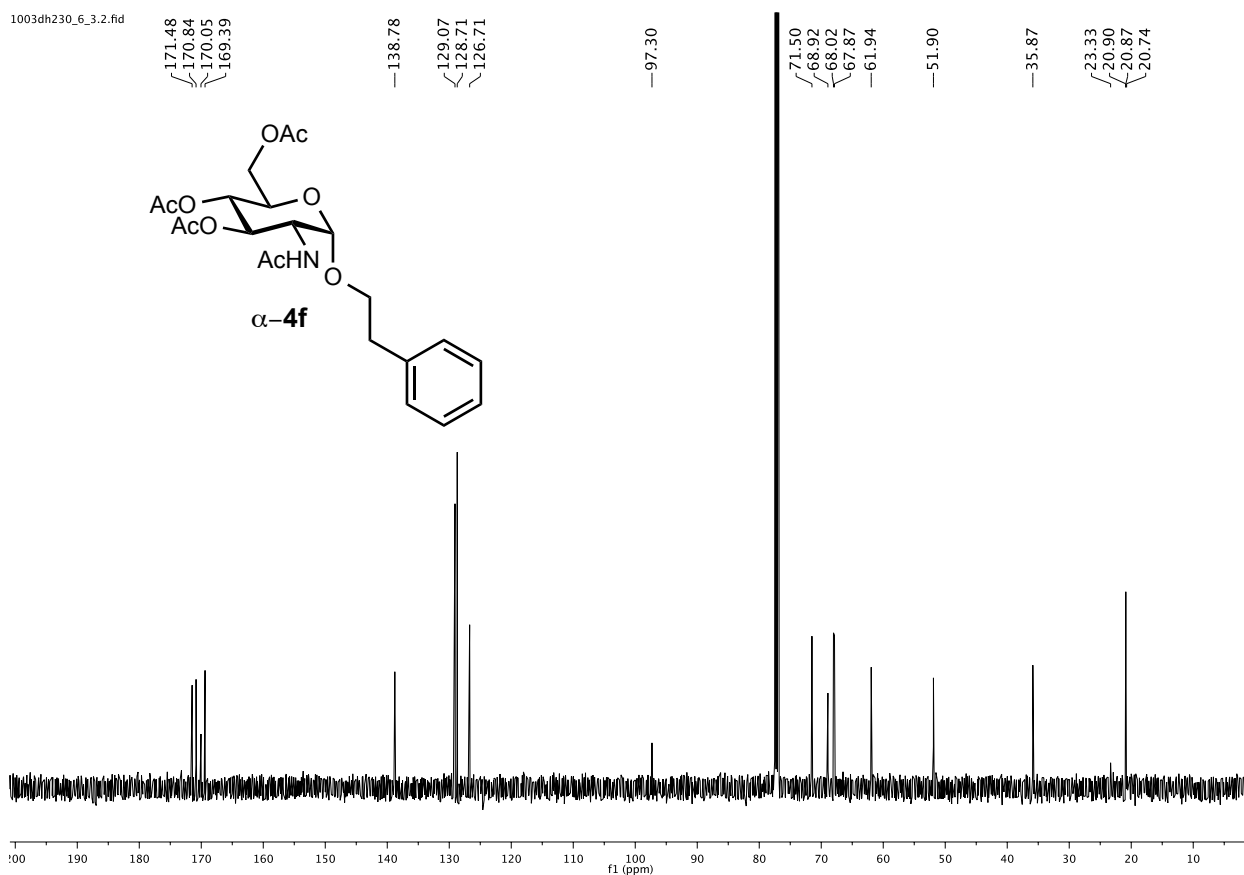
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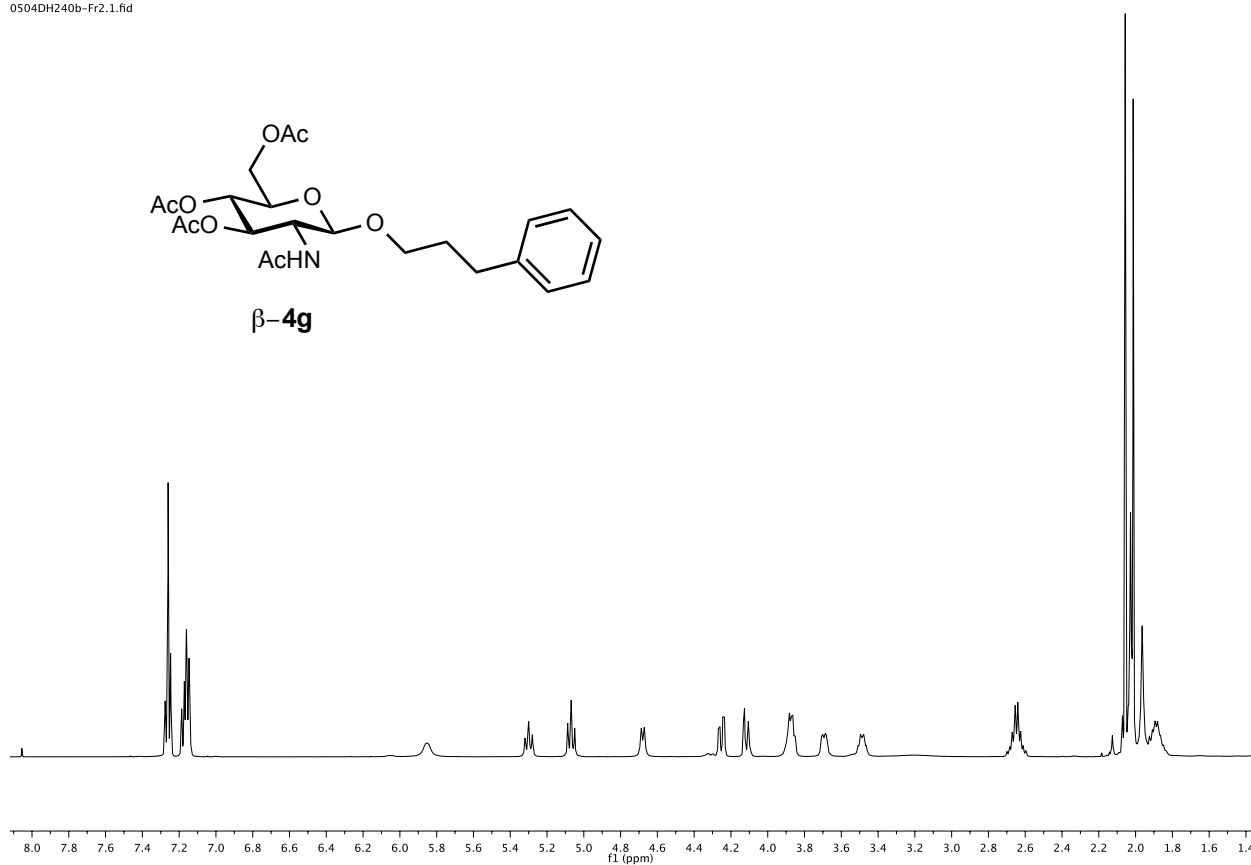
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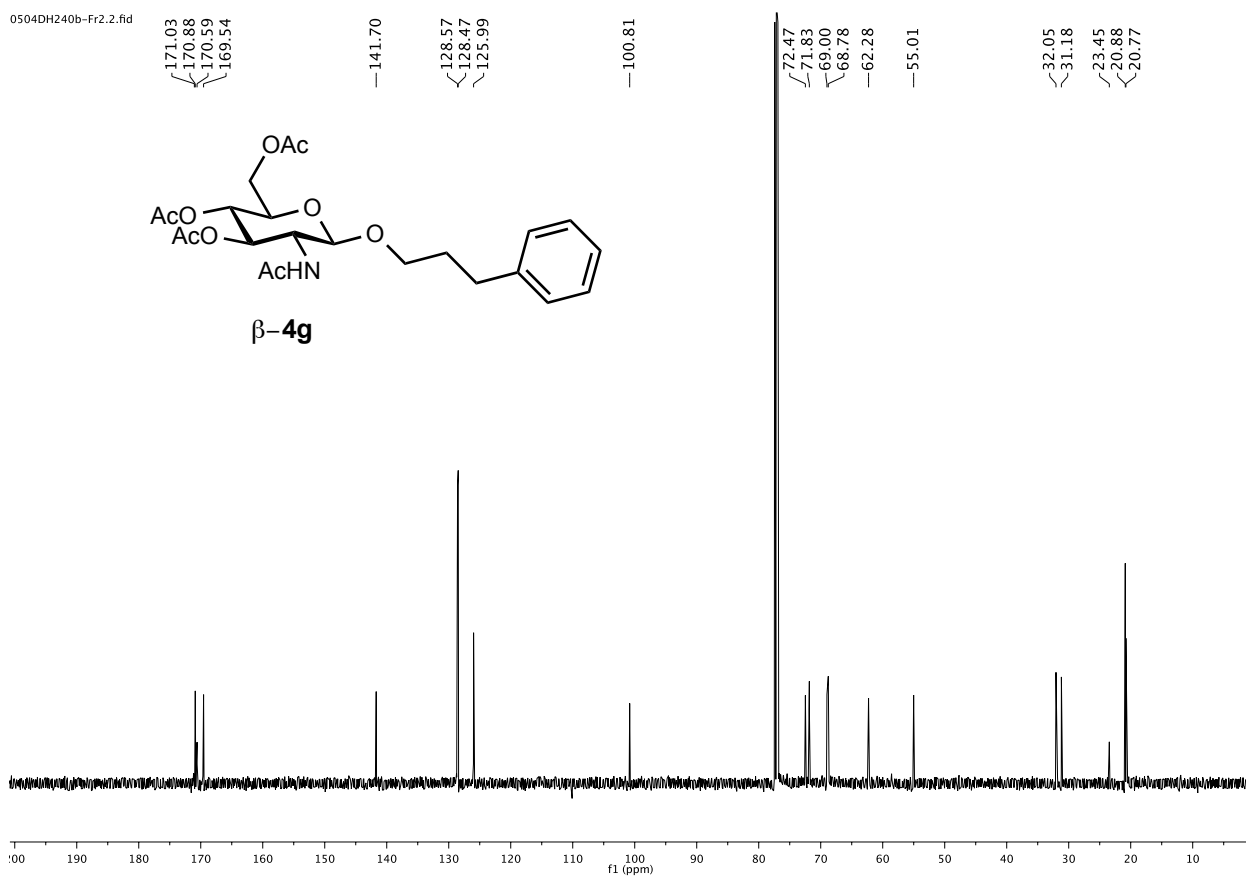
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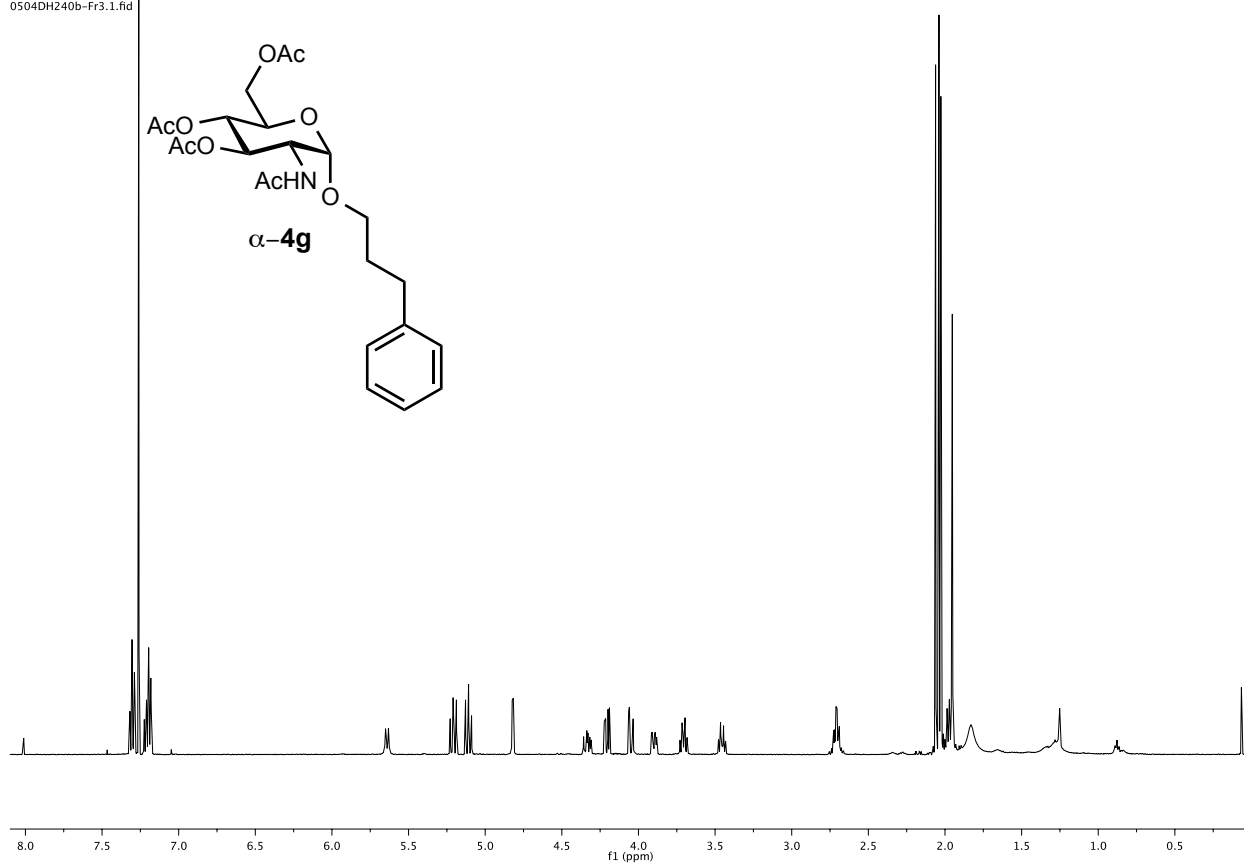
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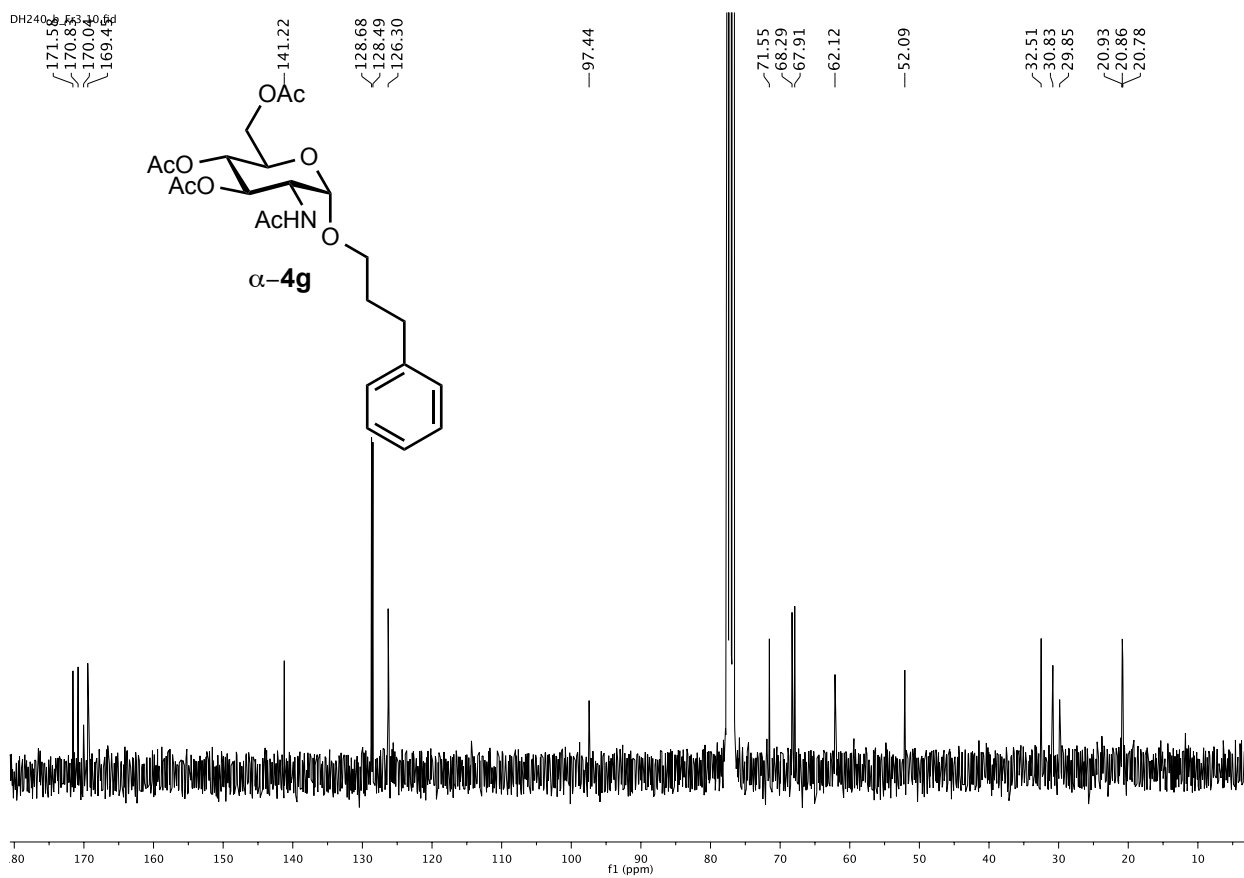
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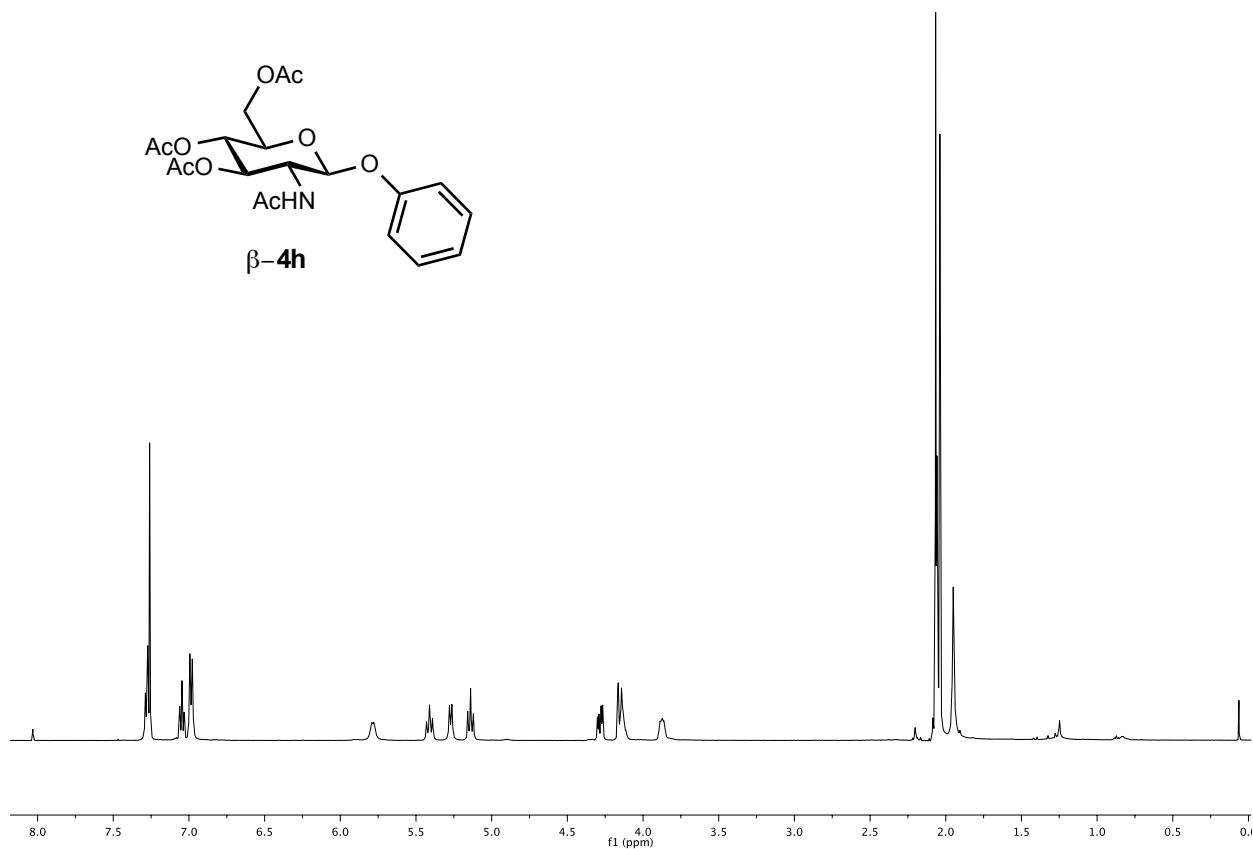
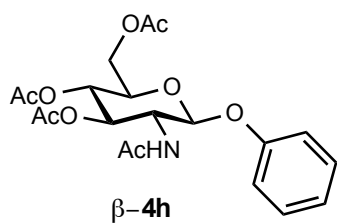
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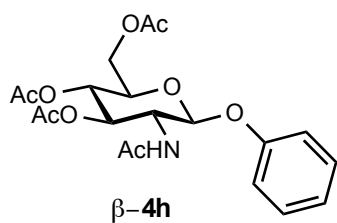
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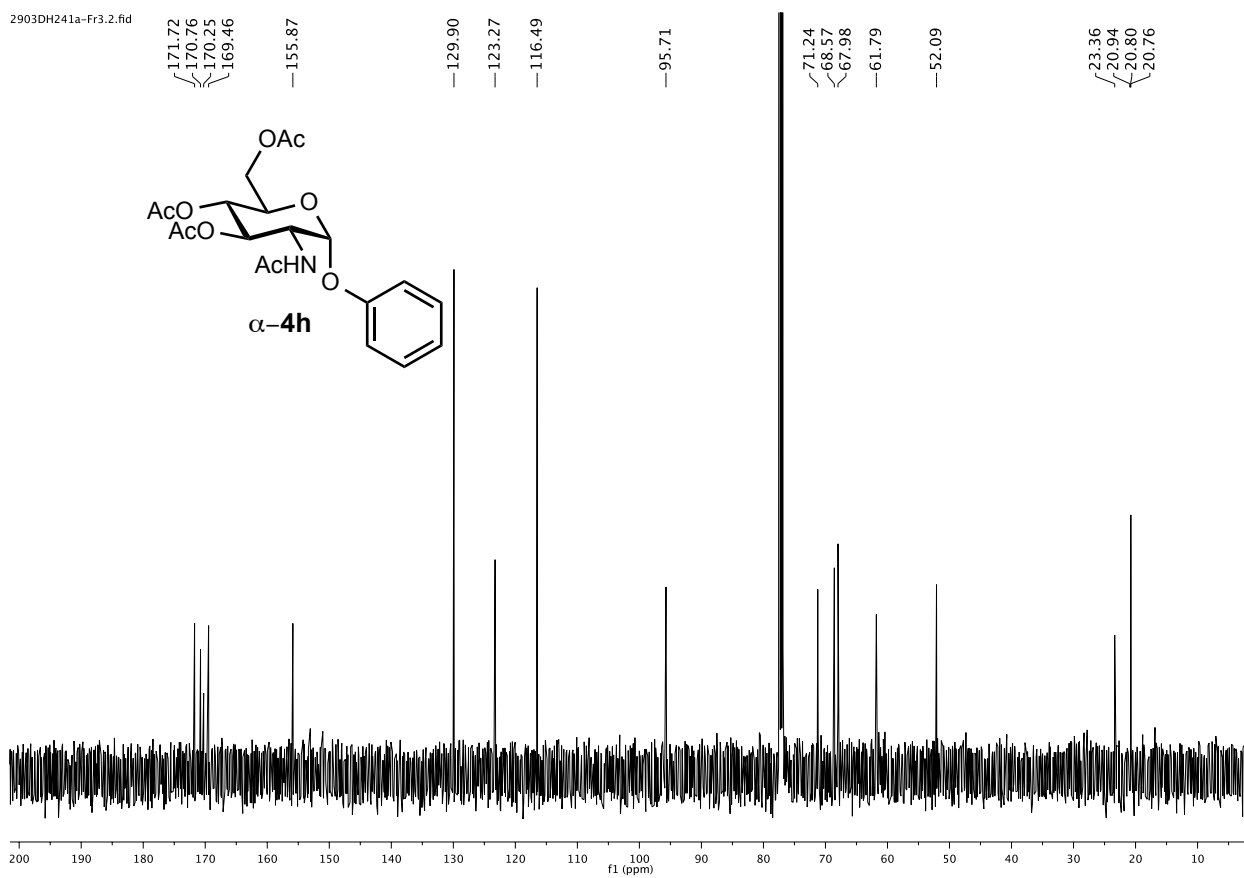
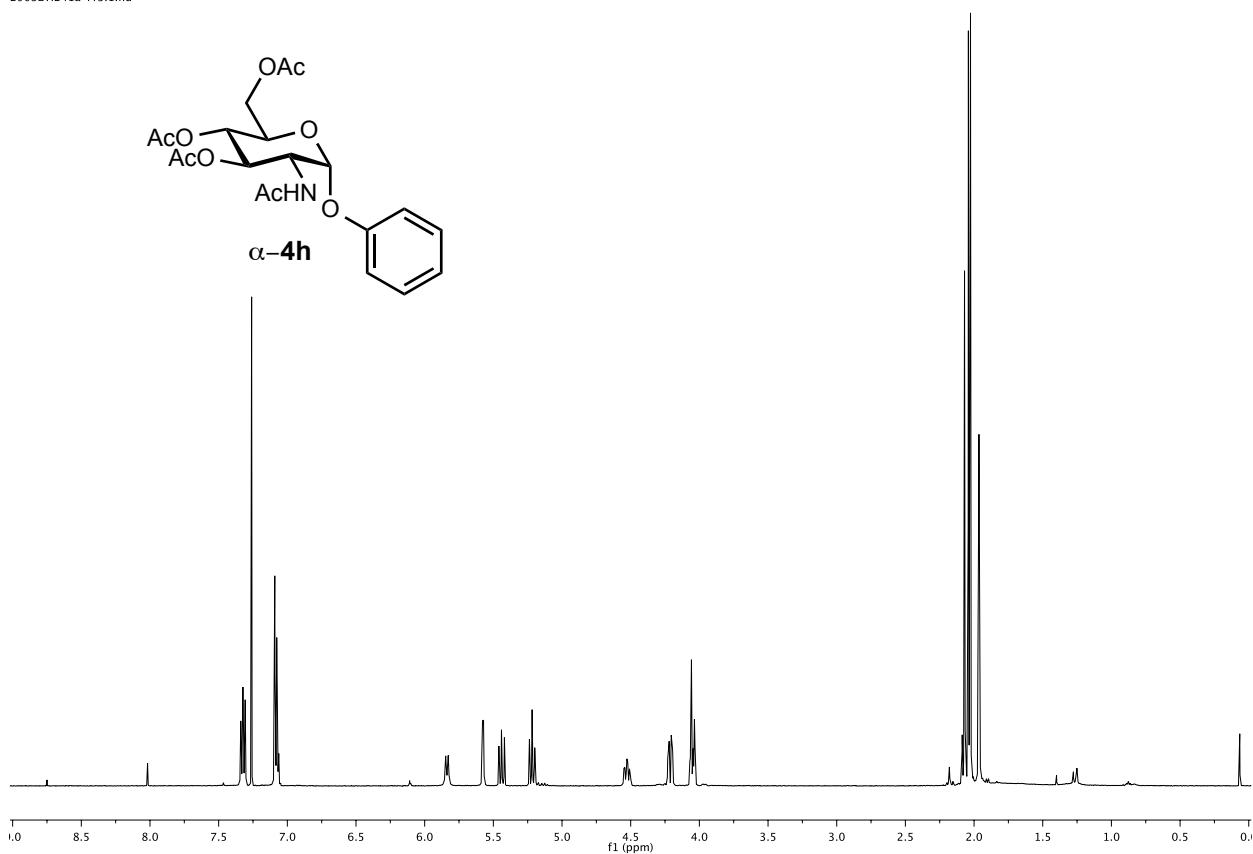


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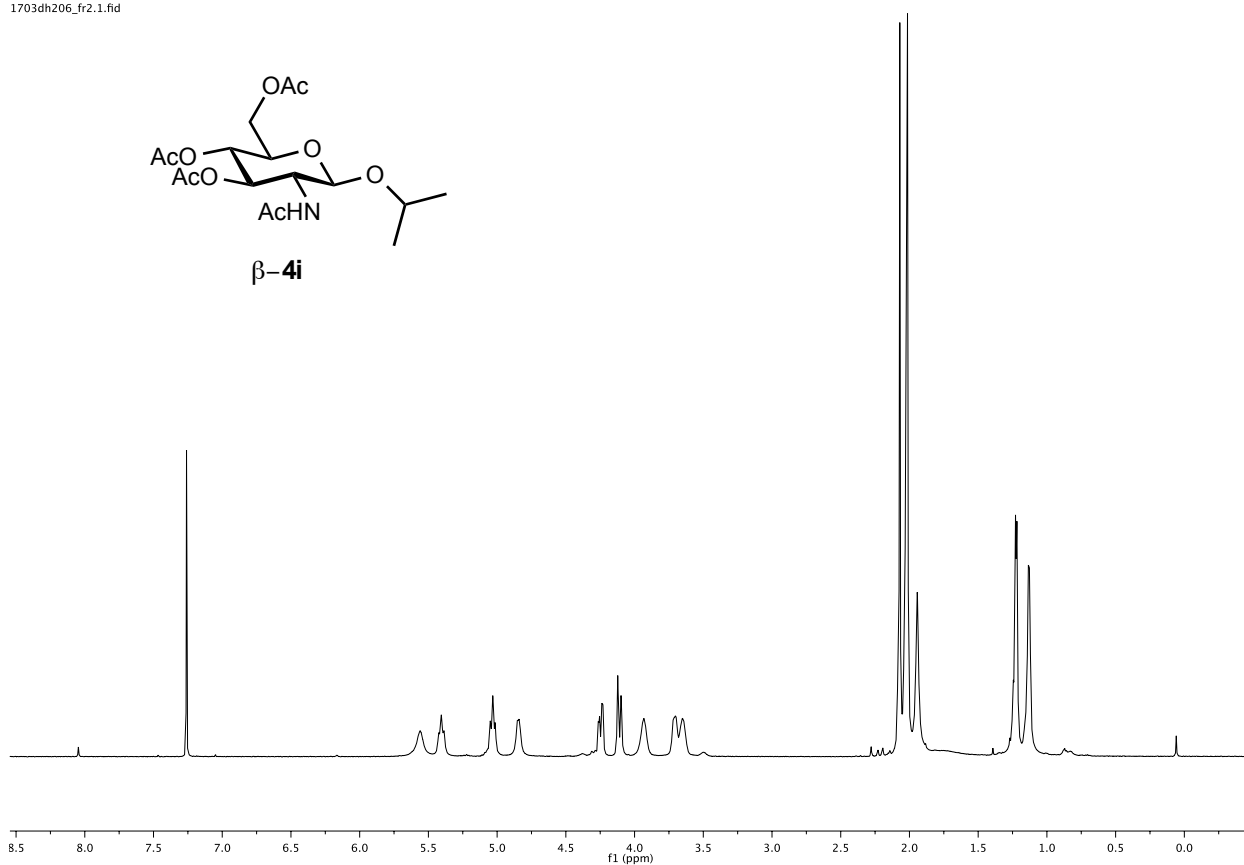


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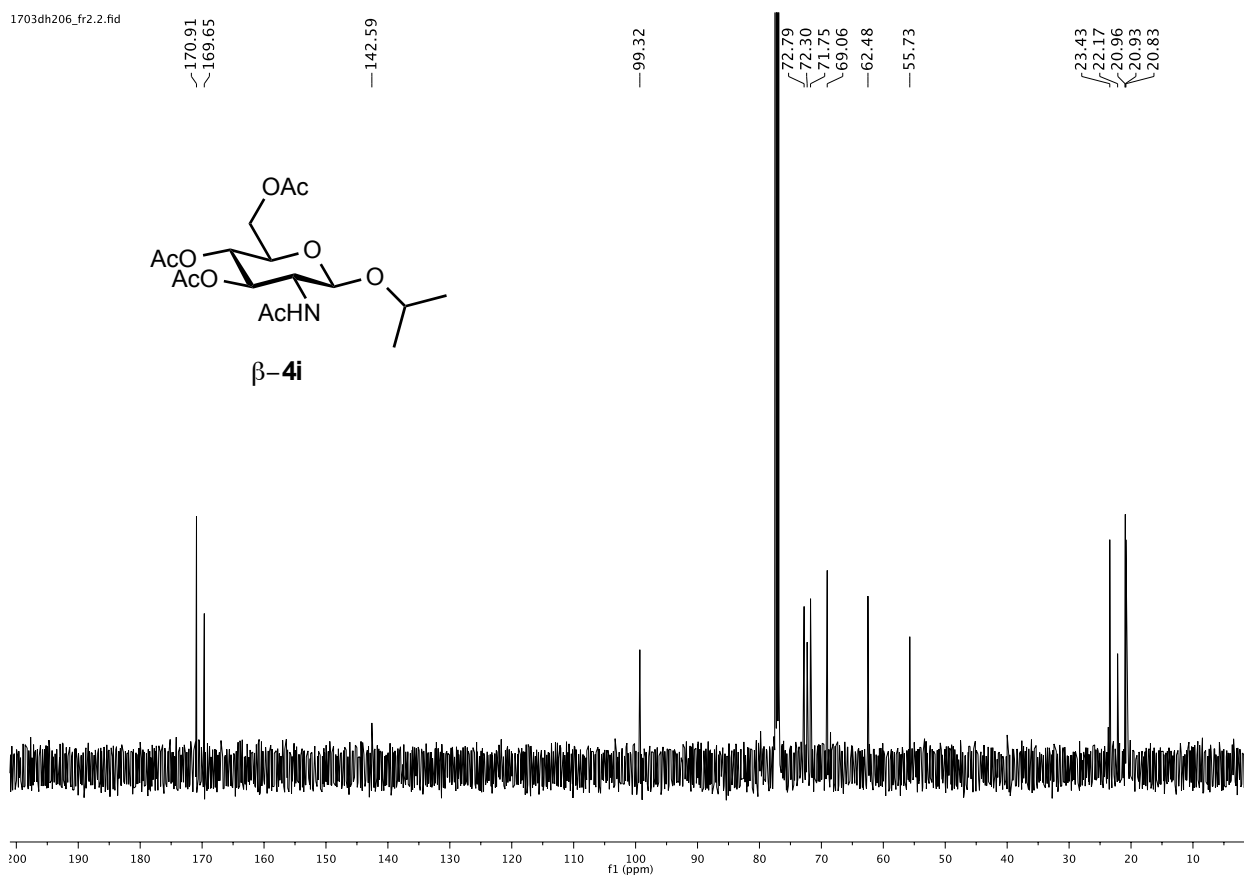




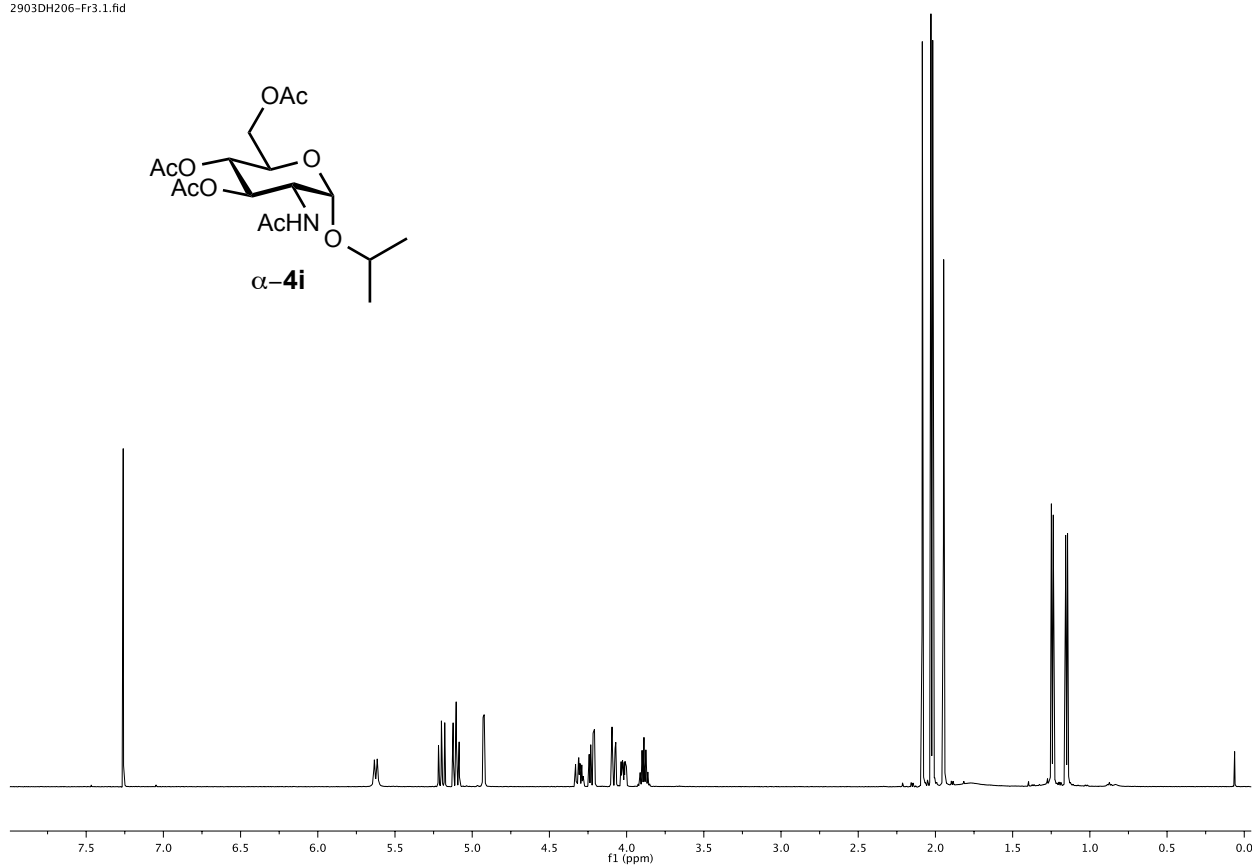
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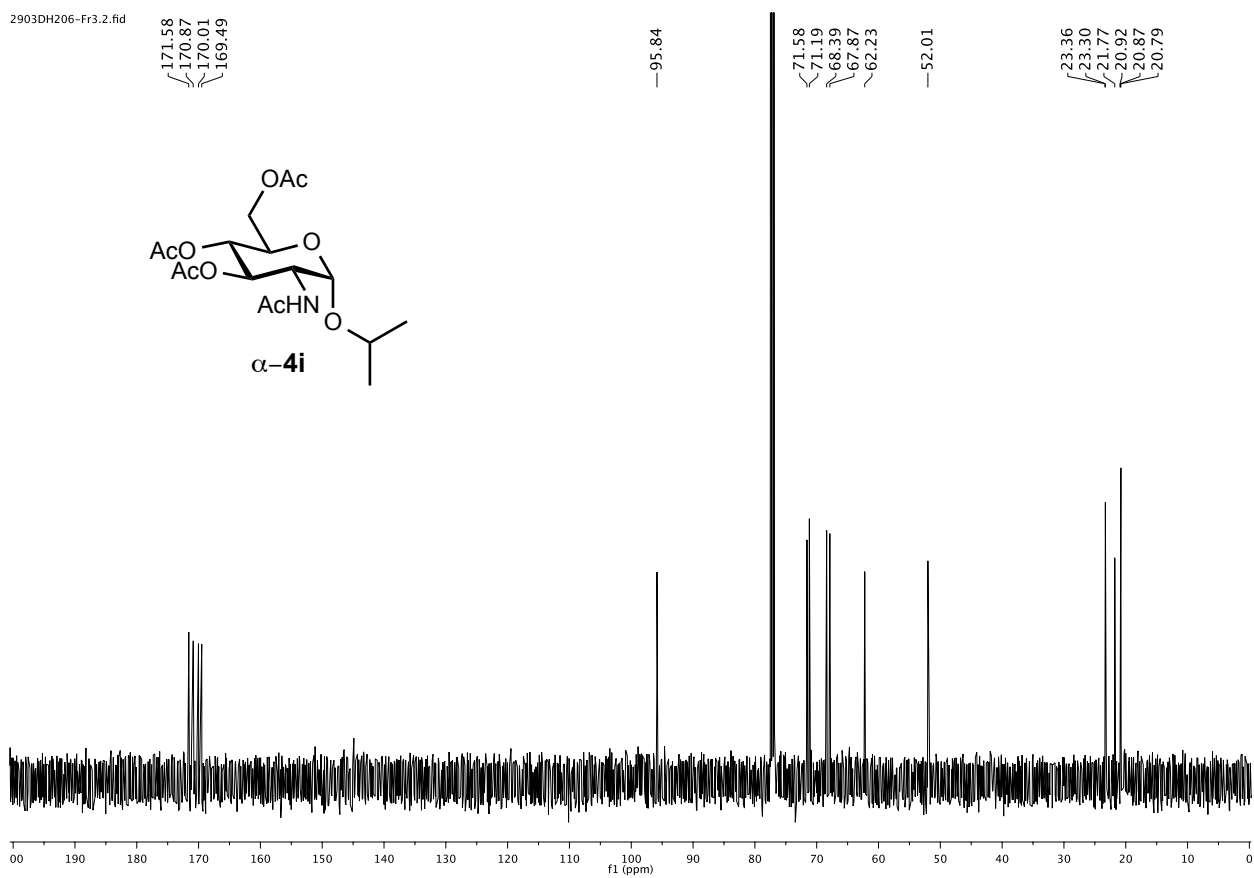
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2903DH206-Fr3.2.fid



References

1. C. A. L. de Bruyn, W. A. van Ekenstein, *Recueil des Travaux Chimiques des Pays-Bas et de la Belgique*. **1899**, 18(3), 77–85.
2. D. J. Chambers, G. R. Evans, A. J. Fairbanks, *Tetrahedron*. **2004**, 60(38), 8411 - 8419.
3. J. Dahmen, T. Frejd, G. Gronberg, T. Lave, G. Magnusson, G. Noori, *Carbohydr Res*. **1983**, 116(2), 303 - 307.
4. B. Aguilera, A. Fernández-Mayoralas, C. Jaramillo, *Tetrahedron*. **1997**, 53(16), 5863 - 5876.
5. A. E. Zemlyakov, V. O. Kur'yanov, V. V. Tsikalov, E. A. Aksenova, V. Y. Chirva, *Chem Nat Compd*. **1997**, 33(1), 61-66.
6. E. J. Cocinero, E. C. Stanca-Kaposta, M. Dethlefsen, B. Liu, D. P. Gamblin, B. G. Davis, J. P. Simons, *Chem Eur J*. **2009**, 15(48), 13427-34.
7. V. Wittmann, D. Lennartz, *Eur J Org Chem*. **2002**, 1363–1367.