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Supporting Information

Conformational Disorder in the Crystal Structure of Methyl 2-Acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (Methyl β-Chitobioside)

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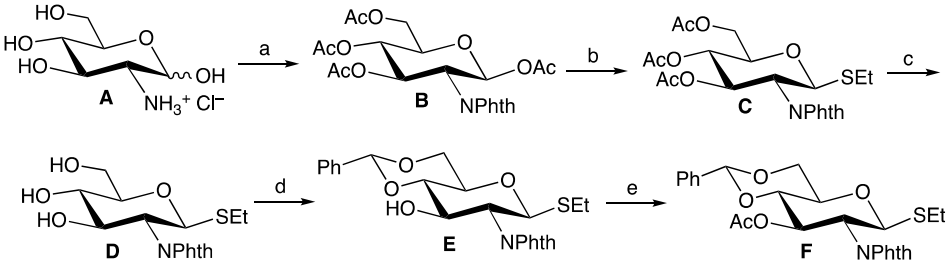
Preparation of Methyl 2-Acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (Methyl β-Chitobioside) (IV)

Preparation of Donor F (Scheme 1)

*1,3,4,6-Tetra-O-acetyl-2-deoxy-2-N-phthalimido-β-D-glucopyranose (**B**)*[1]. To a solution of D-glucosamine hydrochloride (**A**) (10 g, 46.5 mmol) in methanol-distilled water (60 mL, 1:2 *v*/*v*) was added sodium hydroxide (1.9 g, 46.5 mmol) and the reaction mixture was allowed to stir at rt for 1 h. The reaction mixture was then cooled to 15 ºC and a solution of phthalic anhydride (8 g, 54.0 mmol) in acetone (40 mL) was added to it slowly maintaining the temperature below 15 ºC. After stirring at rt for 2 h, solid $NaHCO_3$ (8 g, 95.2 mmol) was added in portions and the reaction mixture was allowed to stir at 50 ºC for 30 min. The reaction mixture was then stirred at rt for 12 h. The reaction mixture was neutralized with cold HCl maintaining the temperature below 20 ºC. On cooling the resulting reaction mixture, 2-deoxy-2-*N*-phthalimido-α/β-D-glucopyranose precipitated as a white solid. The solid product was collected by filtration, washed with cold distilled water, and dried. To a suspension of crude product in acetic anhydride (100 mL, 1.06 mol) was added anhydrous sodium acetate (24 g, 291.1 mmol) and the reaction mixture was refluxed for 30 min. After cooling, the reaction mixture was diluted with CH_2Cl_2 (200 mL) and washed successively with distilled water and satd. aqueous $NaHCO_3$. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to a yellow syrup. Column chromatography of the crude product on silica gel, using hexane-EtOAc (8:1 *v*/*v*) as the eluant, gave pure compound **B**[1] (18.4 g, 83%) as a white solid.

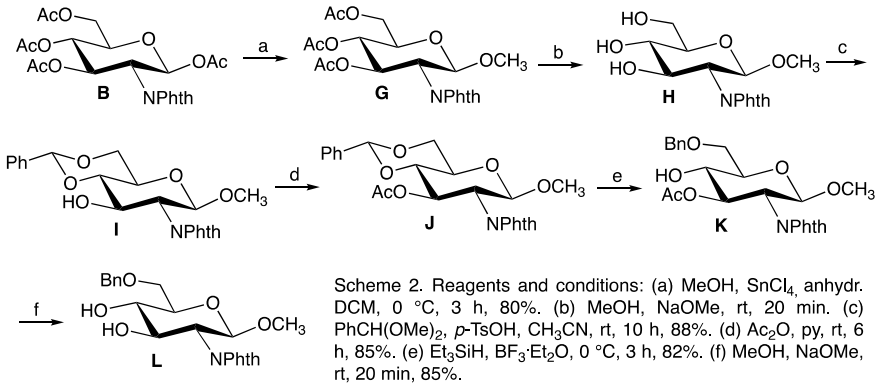
*Ethyl 3,4,6-Tri-O-acetyl-2-deoxy-2-N-phthalimido-1-thio-β-D-glucopyranoside (**C**)*[2]. To a stirred solution of **B** (12 g, 25.9 mmol) in anhydrous CH_2Cl_2 (40 mL) were added 4Å molecular sieves (4 g), EtSH (7.6 mL, 103.7 mmol) and $BF_3{\cdot}Et_2O$ (9.8 mL, 77.7 mmol), and the resulting



Scheme 1. Reagents and conditions: (a) (i) NaOH, MeOH:H_2O, rt, 1 h; (ii) phthalic anhydride, acetone, 15 °C, 2 h; (iii) $NaHCO_3$, 50 °C, 30 min; (iv) HCl, 20 °C, 1 h, filtered; (v) NaOAc, Ac_2O, refluxed, 30 min, 83%. (b) EtSH, DCM, $BF_3{\cdot}Et_2O$, 5 °C, 5 h, 85%. (c) MeOH, NaOMe, rt, 20 min. (d) $PhCH(OMe)_2$, *p*-TsOH, CH_3CN, rt, 6 h, 88%. (e) Ac_2O, py, rt, 6 h, 85%.

reaction mixture was stirred at 5 ºC for 5 h. The reaction mixture was filtered and the washed with CH_2Cl_2 (150 mL). The organic layer was washed with satd. aqueous $NaHCO_3$ and distilled water, dried over anhydrous Na_2SO_4, and concentrated. The crude product was purified on silica gel using hexane-EtOAc (5:1*v*/*v*) as the eluant to afford pure compound (**C**)[2] (10.2 g, 85%) as a yellow oil.

*Ethyl 4,6-O-Benzylidene-2-deoxy-2-N-phthalimido-1-thio-β-D-glucopyranoside (**E**)*[3]. A solution of **C** (3 g, 6.3 mmol) in 0.05 *M* CH_3ONa in CH_3OH (25 mL) was stirred at rt for 20 min. The reaction mixture was neutralized with batchwise addition of Dowex HCR (H^+) ion-exchange resin, vacuum-filtered, and the filtrate was concentrated to dryness to give an amorphous solid



Scheme 2. Reagents and conditions: (a) MeOH, $SnCl_4$, anhydr. DCM, 0 °C, 3 h, 80%. (b) MeOH, NaOMe, rt, 20 min. (c) $PhCH(OMe)_2$, *p*-TsOH, CH_3CN, rt, 10 h, 88%. (d) Ac_2O, py, rt, 6 h, 85%. (e) Et_3SiH, $BF_3{\cdot}Et_2O$, 0 °C, 3 h, 82%. (f) MeOH, NaOMe, rt, 20 min, 85%.

(**D**) in quantitative yield. To a solution of the crude mass in anhydrous CH_3CN (15 mL) were added benzaldehyde dimethylacetal (2.3 mL, 12 mmol) followed by *p*-TsOH (300 mg, 1.78 mmol), and the reaction mixture was stirred at rt for 10 h. The reaction was quenched with Et_3N (1 mL) and the reaction mixture was evaporated to dryness. The crude mass was purified on silica gel using hexane-EtOAc (3:1*v*/*v*) as the eluant to give pure compound (**E**)[3] (2.43 g, 88%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80–7.26 (m, 9 H, Ar-H), 5.57 (s, 1 H, PhC*H*), 5.42–5.39 (d, *J* = 10.6 Hz, 1 H, H-1), 4.66–4.40 (m, 1 H, H-4), 4.39–4.29 (m, 2 H, H-6_a, H-6_b), 3.83 (t, *J* = 10.1 Hz each, 1 H, H-3), 3.69–3.60 (m, 1 H, H-5), 3.58 (t, *J* = 9.2 Hz each, 1 H, H-2), 2.71–2.63 (m, 2 H, S*CH*$_2$CH$_3$), 1.21 (t, *J* = 7.4 Hz each, 3 H, SCH$_2$*CH*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 167.9 (2 Phth), 134.4–123.5 (Ar-C), 102.2 (Ph*C*H), 82.3 (C-1), 82.1 (C-4), 70.5 (C-3), 69.7 (C-6), 68.8 (C-5), 55.6 (C-2), 24.4 (S*C*H$_2$CH$_3$), 15.1 (SCH$_2$*C*H$_3$).

*Ethyl 3-O-Acetyl-4,6-O-benzylidene-2-deoxy-2-N-phthalimido-1-thio-β-D-glucopyranoside (**F**)*[4]*.* To a solution of **E** (2 g,4.5 mmol) in pyridine (15 mL) was added acetic anhydride (10 mL, 108.1 mmol), and and the reaction mixture was stirred at rt for 6 h. The solvents were removed under reduced pressure to give the crude product, which was purified on silica gel using hexane-EtOAc (3:1*v*/*v*) as the eluant to give pure compound **F**[4] (1.9 g, 85%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87–7.26 (m, 9 H, Ar-H), 5.92 (t, *J* = 9.3 Hz each, 1 H, H-3), 5.59 (d, *J* = 8.0 Hz, 1 H, H-1), 5.55 (s, 1 H, PhC*H*), 4.43–4.34 (m, 2 H, H-2, H-5), 3.81–3.75 (m, 3 H, H-4, H-6_{ab}), 2.71–2.66 (m, 2 H, S*CH*$_2$CH$_3$), 1.89 (s, 3 H, COC*H*$_3$), 1.20 (t, *J* = 7.4 Hz each, 3 H, SCH$_2$C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3 (*C*OCH$_3$), 167.5, 167.6 (2 *C*O, Phth), 134.3–123.6 (Ar-C), 102.0 (Ph*C*H), 82.0 (C-1), 79.6 (C-4), 70.9 (2 C, C-3, C-5), 69.0 (C-6), 54.6 (C-2), 24.7 (S*C*H$_2$CH$_3$), 20.9 (CO*C*H$_3$), 15.3 (SCH$_2$*C*H$_3$).

Preparation of Acceptor L (Scheme 2)

*Methyl 3,4,6-Tri-O-acetyl-2-deoxy-2-N-phthalimido-β-D-glucopyranoside (**G**)*[5]*.* To a stirred solution of **B** (5 g, 10.47 mmol) and methanol (0.636 mL, 15.70 mmol) in anhydrous CH_2Cl_2 (30 mL) was stirred under nitrogen for 30 min. To the reaction mixture was added stannic chloride (4.80 mL, 10.91 g, 41.89 mmol) dropwise at 0 °C, and the reaction was continued at rt. After 3 h, TLC (10:1 chloroform-acetone) showed the formation of a single compound. The reaction mixture was added to a satd. aqueous solution of $NaHCO_3$ and the mixture was extracted with $CHCl_3$. The organic extract was washed with distilled water, dried over anhydrous Na_2SO_4, and

concentrated. Crystallization from methanol gave **G**[5] (4.2 g, 80%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85–7.74 (m, 4 H, Ar-H), 5.81–5.76 (t, *J* = 9.3 Hz each, 1 H, H-3), 5.31 (d, *J* = 8.0 Hz, 1 H, H-1), 5.21–5.16 (t, 1 H, H-2), 4.36–4.28 (m, 2 H, H-4, H-6$_b$), 4.21–4.18 (dd, 1 H, H-6$_a$), 3.89–3.87 (m, 1 H, H-5), 3.45 (s, 3 H, OC*H*$_3$), 2.12, 2.03, 1.86 (3 s, 9 H, 3 COC*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0, 170.4, 169.7, (3 *C*OCH$_3$), 167.5, 167.6 (2 *C*O, Phth), 134.5–123.8 (Ar-C), 99.2 (C-1), 72.0 (C-4), 71.0 (C-3), 69.2 (C-6), 62.5 (C-5), 57.3 (O*C*H$_3$) 54.7 (C-2), 21.0, 20.8, 20.6 (3 CO*C*H$_3$).

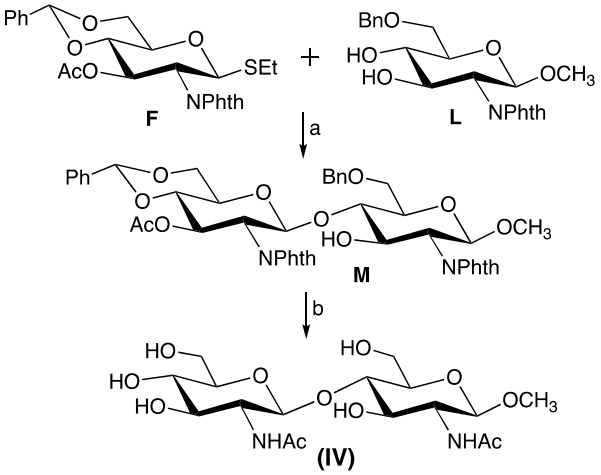
*Methyl 4,6-O-Benzylidene-2-deoxy-2-N-phthalimido-β-D-glucopyranoside (**I**)*[3]. A solution of **G** (3 g, 6.67 mmol) in 0.05 *M* CH_3ONa in CH_3OH (25 mL) was stirred at rt for 20 min. The reaction mixture was neutralized with batchwise addition of Dowex HCR (H^+) ion-exchange resin, vacuum-filtered, and the filtrate was evaporated to dryness to give an amorphous solid (**H**) in quantitative yield. To a solution of the crude mass in anhydrous CH_3CN (15 mL) were added benzaldehyde dimethylacetal (2.3 mL, 12 mmol) followed by *p*-TsOH (300 mg, 1.78 mmol), and the resulting reaction mixture was stirred at rt for 10 h. The reaction was quenched with the addition of Et_3N (1 mL) and the reaction mixture was evaporated to dryness. The crude mass was purified on silica gel using hexane-EtOAc (3:1*v*/*v*) as the eluant to give pure compound **I**[3] (2.43 g, 88%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–7.36 (m, 9 H, Ar-H), 5.56 (s, 1 H, PhC*H*), 5.18 (d, *J* = 8.0 Hz, 1 H, H-1), 4.63–4.58 (t, 1 H, H-3), 4.40–4.38 (dd, 1 H, H-6$_a$), 4.23–4.19 (t, 1 H, H-2), 3.85–3.80 (m, 1 H, H-5), 3.61–3.57 (m, 2 H, H-4, H-6$_b$), 3.43 (s, 3 H, OC*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4 (2 *C*O, Phth), 134.3–126.5 (Ar-C), 102.1 (C-1), 100.0 (Ph*C*H), 82.4 (C-4), 68.9 (C-3), 68.7 (C-6), 66.4 (C-5), 57.3 (O*C*H$_3$) 56.8 (C-2).

*Methyl 3-O-Acetyl-4,6-O-benzylidene-2-deoxy-2-N-phthalimido-β-D-glucopyranoside (**J**)*[3]. To a solution of **I** (2 g,4.86 mmol) in pyridine (15 mL) was added acetic anhydride (10 mL, 97.2 mmol),and the reaction mixture was stirred at rt for 6 h. The solvents were evaporated under reduced pressure to give a crude product, which was purified on silica gel using hexane-EtOAc (3:1*v*/*v*) as the eluant to furnish pure compound **J**[3] (1.9 g, 85%) as a white solid.

*Methyl 3-O-Acetyl-6-O-benzyl-2-deoxy-2-N-phthalimido-β-D-glucopyranoside (**K**)*[3]. To a solution of **J** (2.0 g, 4.41 mmol) in CH_2Cl_2 (15 mL) were added triethylsilane (4.22 mL, 26.46 mmol) and $BF_3{\cdot}Et_2O$ (0.544 mL, 4.41 mmol), and the reaction mixture was stirred at 0 ºC for 3 h. The reaction mixture was poured into distilled water (200 mL) and the mixture was extracted with CH_2Cl_2 (100 mL). The organic layer was washed successively with satd. aqueous $NaHCO_3$ and distilled water, dried over anhydrous Na_2SO_4, and concentrated. The solvents were removed under reduced pressure and the crude product was purified on silica gel using hexane-EtOAc (1:1 *v*/*v*) as the eluant to give pure compound **K**[3] (1.2 g, 82%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87–7.36 (m, 9 H, Ar-H), 5.70–5.65 (t, *J* = 9.3 Hz each, 1 H, H-3), 5.46 (d, *J* = 8.0 Hz, 1 H, H-1), 4.70 (d, *J* = 12.0 Hz, 1 H, PhC*H*$_2$), 4.65 (d, *J* = 12.0 Hz, 1 H, PhC*H*$_2$), 4.60 (t, 1 H, H-2), 4.34 (m, 1 H, H-5), 3.90–3.70 (m, 3 H, H-4, H-6$_{ab}$), 3.44 (s, 3 H, OC*H*$_3$), 1.93 (s, 3 H, COC*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3 (*C*OCH$_3$), 168.4 (2 *C*O, Phth), 134.4–123.7 (Ar-C), 99.2 (C-1), 74.3 (C-4), 74.0 (C-3), 73.8 (C-6), 71.8 (C-5), 57.1 (O*C*H$_3$), 54.7 (C-2), 20.9 (*C*OCH$_3$).

*Methyl 6-O-Benzyl-2-deoxy-2-N-phthalimido-β-D-glucopyranoside (**L**)*[6]. A solution of **K** (3 g, 6.3 mmol) in 0.05 *M* CH_3ONa in CH_3OH (25 mL) was stirred at rt for 20 min. The reaction mixture was neutralized with batchwise addition of Dowex HCR (H^+) ion-exchange resin, vacuum-

filtered, and the filtrate was evaporated to dryness to give an amorphous solid in quantitative yield. The crude product was purified on silica gel using hexane-EtOAc (1:1 *v*/*v*) as the eluant to give pure compound **L**^{6} (1.6 g, 85%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–7.35 (m, 9 H, Ar-H), 5.14 (d, *J* = 8.0 Hz, 1 H, H-1), 4.64 (d, *J* = 12.0 Hz, 1 H, PhCH_2), 4.61 (d, *J* = 12.0 Hz, 1 H, PhCH_2), 4.31 (t, 1 H, H-2), 4.15–4.10 (m, 1 H, H-5), 3.83–3.78 (m, 2 H, H-6$_{ab}$), 3.64–3.60 (m, 2 H, H-3, H-4), 3.41 (s, 3 H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.5, 167.6 (2 *C*O, Phth), 134.3–123.6 (Ar-C), 99.4 (C-1), 74.3 (C-4), 74.0 (C-3), 73.8 (C-6), 71.9 (C-5), 57.0 (O*C*H$_3$), 56.3 (C-2).



Scheme 3. Reagents and conditions: (a) NIS, TMSOTf, anhydr. DCM, –40 °C, 1 h, 82%. (b) (i) NH_2NH_2, EtOH, 70 °C, 24 h; (ii) Ac_2O, py, rt, 3 h; (iii) CH_3OH, NaOMe, rt, 3 h; (iv) H_2, Pd/C, MeOH, rt, 24 h, 60%.

Condensation of Donor **F** and Acceptor **L** To Give Disaccharide (IV) (Scheme 3)

*Methyl 3-O-Acetyl-4,6-benzylidine-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-(1→4)-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (**M**)*[7]. To a solution of **L** (200 mg, 0.48 mmol) and **F** (351 mg, 0.72 mmol) in anhydrous CH_2Cl_2 (5 mL) was added 4Å molecular sieves (2.0 g), and the reaction mixture was cooled to –40 ºC. To the cooled reaction mixture were added *N*-iodosuccinimide (180 mg, 0.79 mmol) and TMSOTf (13µL, 0.07 mmol), and the reaction mixture was stirred at –40 ºC for 1 h. The reaction mixture was filtered through a Celite® pad and the pad was washed with CH_2Cl_2 (100 mL). The organic layer was washed successively with 5% aqueous $Na_2S_2O_3$, satd. aqueous $NaHCO_3$ and distilled water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified on silica gel using hexane-EtOAc (1:1 *v*/*v*) as the eluant to give pure **M**[7] (200 mg, 82%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.10 (m, 18 H, Ar-H), 5.91–5.85 (t, 1 H, H-3_B), 5.58–5.56 (d, *J* = 8.0 Hz, 1 H, H-1_B), 5.49 (s, 1 H, PhC*H*), 5.03–5.01 (d, *J* = 8.0 Hz, H-1_A), 4.38–4.36 (m, 3 H, -CH_2-, 2 PhCH_2, H-5_B), 4.14–4.09 (m, 4 H, H-3_A, H-6_{abA}, H-2_A), 3.91 (m, 1 H, H-4_B), 3.76–3.65 (m, 4 H, H-6_{abB}, H-4_A, H-2_B), 3.34 (s, 3 H, OCH_3), 3.29 (m, 1 H, H-5_A), 1.88 (COCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1 (COCH_3), 167.5, 167.6 (2 *C*O, Phth), 134.3–123.9 (Ar-C), 101.9 (C-1_A), 99.6 (Ph*C*H), 99.1 (C-1_B), 81.9 (C-4_A), 78.8 (C-3_B), 74.2 (C-3_A), 73.1 (PhCH_2), 70.0 (C-4_B), 69.6 (C-6_A), 68.4 (C-5_A), 68.0 (C-6_B), 66.3 (C-5_B), 56.7 (OCH_3), 55.9 (C-2_B), 55.5 (C-2_A), 20.7 (COCH_3).

*Methyl 2-Acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (**IV**).* To a solution of **M** (200 mg, 0.23 mmol) in EtOH (2 mL) was added NH_2NH_2 (0.5 mL, 15.64 mmol), and the reaction mixture was stirred at 70 ºC for 24 h. The solvents were removed under reduced pressure, and the crude product was dissolved in pyridine (3 mL) and acetic anhydride (1 mL, 10.58 mmol) and the solution kept at rt for 3 h. The solvents were removed under reduced pressure to give the crude acetylated product in quantitative yield after purification on a silica gel column using ethyl acetate-hexane (1:1 *v*/*v*) as the solvent. To a solution of acetylated product was added CH_3OH and CH_3ONa, and the reaction mixture was stirred at rt for 3 h. The reaction mixture was neutralized with Dowex HCR (H^+) ion-exchange resin, filtered, and

concentrated *in vacuo* to dryness to afford a crude product. To a solution of the *N*-acetylated product in CH_3OH (5 mL) was added Pd-C (50 mg), and the reaction mixture was stirred at rt under a positive pressure of H_2 for 24 h. The reaction mixture was then filtered through a Celite® pad, the pad was washed with CH_3OH/H_2O (20 mL, 2:1 *v*/*v*), and the filtrates were collected and concentrated under reduced pressure. The deprotected product was purified on a column (2.5 cm x 100 cm) containing Dowex 50 x 8 (200-400 mesh) ion-exchange resin in the Ca^{2+} form[8] using distilled water as the eluant to give pure disaccharide (**IV**) (80 mg, 60%). ^{1}H NMR (800 MHz, ^2H_2O): δ 4.53–4.52 (d, 1 H, H-1_B), 4.38–4.37 (d, 1 H, H-1_A), 3.86–3.84 (dd, 1 H, H-6_{Aa}), 3.81–3.79 (dd, 1 H, H-6_{Ba}), 3.70–3.59 (m, 5 H, H-2_A, H-2_B, H-6_{Ab}, H-6_{Bb}, H-3_B), 3.55–3.50 (m, 3 H, H-3_A, H-5_B, H-4_A), 3.45 (s, 3 H, OCH_3), 3.45–3.41 (m, 2 H, H-5_A, H-4_B), 2.01 (s, 3 H, NHCOCH_3), 1.97 (s, 3 H, NHCOCH_3). ^{13}C NMR (200 MHz, ^2H_2O): δ 174.6 (2 NH*C*OCH$_3$), 101.8 (C-1_A), 101.4 (C-1_B), 79.4 (C-4_A), 75.9 (C-5_A), 74.5 (C-5_B), 73.4 (C-6_A), 72.6 (C-3_B), 69.7 (C-6_B), 60.5 (C-3_B), 60.1 (C-6_A), 57.1 (O*C*H$_3$), 55.5 (C-2_B), 54.8 (C-2_A), 22.1 (2 NH*C*OCH$_3$). HRMS (ESI-TOF) *m/z* $[M+Na]^+$: calcd. for $C_{17}H_{30}N_2O_{11}Na$, 461.1742; found, 461.1744.

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