Supplemental material.

Materials and methods.

Chemical synthesis of sulfated monosaccharide. TLC was carried out on precoated 60 F_{254} silica gel alumina plates (Merck) using UV-light and/or 8% H_2SO_4 and/or AMC-solution (ammonium molybdate, cerium (IV) sulfate, 10% H_2SO_4 [5:0.1:100, w/w/v] for visualization. Flash column chromatography was performed on silica gel (Merck, pore size 60 Å, particle size 40-63 mm). NMR spectra were recorded in $CDCl_3$ (internal Me_4Si $\delta = 0.00$ ppm) at 25 °C on a Varian instrument (400 MHz for ^1H and 101 MHz for ^{13}C or 500 MHz for ^1H and 126 MHz for ^{13}C). Coupling constants are given in Hertz (Hz). All reactions containing air- and moisture-sensitive reagents were carried out under an argon atmosphere. Organic phases were dried over $MgSO_4$ before evaporation, which was performed under reduced pressure at temperatures not exceeding 40 °C.

2-Acetamido-1,3,4-tri-*O*-acetyl-6-*O*-triphenylmethyl-2-deoxy-α-D-glucopyranose (Fig. 1A, structure **5**). Compound **5** was prepared from 2-acetamido-2-deoxy-D-glucose (5.0 g, 22.6 mmol) according to a literature procedure (1) as a white solid (9 g, 68%); R_f = 0.48 (toluene/EtOAc 5:95); ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.16 (m, 15H, Ar), 6.29 (d, J = 3.7 Hz, 1H, H-1), 5.57 (d, J = 9.0 Hz, 1H, N*H*Ac), 5.35 (dd, J = 10.3, 9.6 Hz, 1H, H-4), 5.18 (dd, J = 11.0, 9.5 Hz, 1H, H-3), 4.54 (ddd, J = 11.0, 9.0, 3.7 Hz, 1H, H-2), 3.88 (ddd, J = 10.3, 4.2, 2.3 Hz, 1H, H-5), 3.28 (dd, J = 10.7, 2.3 Hz, 1H, H-6a), 3.03 (dd, J = 10.6, 4.2 Hz, 1H, H-6b), 2.17 (s, 3H, C*H*$_3$CO), 2.04 (s, 3H, C*H*$_3$CO), 1.95 (s, 3H, C*H*$_3$CO). 1.73 (s, 3H, C*H*$_3$CO); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 170.1, 168.8, 168.7, 143.6, 128.8, 127.9, 127.1, 91.2, 86.7, 71.4, 71.3, 68.0, 61.6, 51.5, 23.2, 21.1, 20.9, 20.6.

2-Acetamido-1,3,4-tri-*O*-acetyl-2-deoxy-α-D-glucopyranose (Fig. 1A, **6**). Compound **6** was prepared from **5** (620 mg, 1.05 mmol) according to a literature procedure (1) as a white solid

(285 mg, 78%); R_f = 0.34 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (d, *J* = 3.6 Hz, 1H, H-1), 5.61 (d, *J* = 8.9 Hz, 1H, N*H*Ac), 5.28 (dd, *J*= 10.9, 9.5 Hz, 1H, H-3), 5.15 (t, *J* = 9.8 Hz, 1H, H-4), 4.45 (ddd, *J* = 11.0, 9.0, 3.7 Hz, 1H, H-2), 3.80 (ddd, *J* = 10.1, 4.1, 2.2 Hz, 1H, H-5), 3.69 (dd, *J* = 12.8, 2.3 Hz, 1H, H-6a), 3.59 (td, *J* = 12.3, 10.6, 4.5 Hz, 1H, H-6b), 2.18 (s, 3H, C*H*$_3$CO), 2.07 (s, 3H, C*H*$_3$CO), 2.06 (s, 3H, C*H*$_3$CO), 1.94 (s, 3H, C*H*$_3$CO); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 170,1, 170.0, 168.9, 90.8, 72.2, 70.7, 68.04, 61.1, 51.3, 23.2, 21.1, 20.9, 20.8.

2-Acetamido-1,3,4-tri-*O*-acetyl-2-deoxy-6-*O*-sulfate-*α*-D-glucopyranose (Fig. 1A, **7**). Sulfation of compound **6** (100 mg, 0.29 mmol) according to a literature procedure (2) gave **7** (ammonium salt) as a transparent oil (115 mg, 90%); R_f = 0.54 (EtOAc/MeOH/NH_4OH 8:2:1); NMR data were in accordance with those reported in the literature (2).

2-Acetamido-2-deoxy-6-*O*-sulfate-D-glucopyranose (Fig. 1A, **1**). Deprotection (2) of compound **7** (600 mg, 1.4 mmol) using NaOMe (200 mg, 3.7 mmol) in MeOH gave **1** (ammonium salt) as a powder (400 mg, 95%); R_f = 0.3 (EtOAc/MeOH/NH_4OH 6:4:1); ^{1}H NMR (500 MHz, D_2O) δ 5.11 (d, *J* = 3.6 Hz, 1H, H-1α), 4.64 (d, *J* = 8.5 Hz, 0.7H, H-1β), 4.27-4.22 (m, 0.7H, H-6β), 4.20-4.16 (m, 2H, H-6α), 4.15-4.10 (m, 0.7H, H-6β), 3.96 (dt, *J* = 10.1, 3.6 Hz, 1H, H-5α), 3.81 (dd, *J* = 10.8, 3.4 Hz, 1H, H-2α), 3.67 (dd, *J* = 10.7, 9.0 Hz, 1H, H-3α), 3.64-3.55 (m, 1.4H, H-5β, H-2β), 3.49-3.37 (m, 2.4H, H-4α, H-3β, H-4β), 1.95 (s, 5H, C*H*$_3$CO); ^{13}C NMR (126 MHz, D_2O) δ 175.1, 95.7, 91.6, 74.5, 74.4, 71.3, 70.4, 70.3, 70.2, 67.8, 57.2, 54.6, 22.6.

Benzyl 2-Acetamido-2-deoxy-*β*-D-glucopyranose (Fig. 1A, **8**). Compound **8** was prepared according to a literature procedure (3) using 2-acetamido-2-deoxy-D-glucose (1.50 g, 6.8 mmol), NaH (408 mg, 10.2 mmol), LiBr (887 mg, 10.2 mmol), and BnBr (1.2 ml, 10.2 mmol). The pure *β*-anomer was achieved through acetylation and deacetylation steps as the

main product (1.2 g, 60% over 3 steps); R_f = 0.37 (EtOAc/MeOH 4:1); NMR data were in accordance with those reported in the literature (3).

Benzyl 2-Acetamido-4,6-*O*-benzylidene-*2*-deoxy-*β*-D-glucopyranose (Fig. 1A, **9**). Compound **9** was prepared from the reaction of benzyl glycoside **8** (370 mg, 1.19 mmol) with $PhCH(OMe)_2$ (5 ml) and formic acid (5 ml) (4) as a white solid (356 mg, 74%); R_f = 0.4 (EtOAc); NMR data were in accordance with those reported in the literature (3).

Benzyl 2-Acetamido-4,6-*O*-benzylidene-*2*-deoxy-3-*O*-sulfate-*β*-D-glucopyranose (Fig. 1A, **10**). Compound **9** (100 mg, 0.25 mmol) was dissolved in anhydrous pyridine (10 ml) and $SO_3{\cdot}NEt_3$ complex (135 mg, 0.75 mmol) was added. The reaction mixture was stirred at 85 ℃ for 2.5 hours and then concentrated and purified by silica gel chromatography (EtOAc/MeOH/NH_4OH 8:2:1) affording sulfated product **10** (ammonium salt) as a white powder (107 mg, 86%); R_f = 0.48 (EtOAc/MeOH/NH_4OH 8:2:1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.67 – 7.55 (m, 2H, Ar), 7.41 – 7.26 (m, 8H, Ar), 5.63 (s, 1H), 4.85 (d, J = 12.1 Hz, 1H, C*H*$_2$Ph), 4.82 (d, J = 8.4 Hz, 1H, H-1), 4.71 (dd, J = 10.1, 9.3 Hz, 1H, H-3), 4.62 (d, J = 12.1 Hz, 1H, C*H*$_2$Ph), 4.31 (dd, J = 10.3, 4.9 Hz, 1H, H-6a), 4.00 (dd, J = 10.1, 8.4 Hz, 1H, H-2), 3.84 (t, J = 10.2 Hz, 1H, H-6b), 3.75 – 3.69 (m, 1H, H-4), 3.58 (td, J = 9.7, 5.0 Hz, 1H, H-5), 2.00 (s, 3H, C*H*$_3$CO); ^{13}C NMR (101 MHz, CD_3OD) δ 173.8, 139.2, 139.0, 129.6, 129.3, 128.9, 128.7, 128.7, 127.6, 102.6, 102.3, 81.0, 78.3, 72.3, 69.6, 67.4, 56.7, 23.3.

2-Acetamido-*2*-deoxy-3-*O*-sulfate-D-glucopyranose (Fig. 1A, **2**). Compound **10** (105 mg, 0.21 mmol) was dissolved in EtOH (10 ml) and 10% Pd/C (112 mg) was added. Hydrogenolysis was carried out under an H_2 atmosphere (15 bar) for 2.5 hours at room temperature. The mixture was filtered and concentrated under vacuum. The residue was purified by silica gel chromatography (EtOAc/MeOH/NH_4OH 6:4:1) affording **2** (ammonium salt) as a powder (61 mg, 90%); R_f = 0.36 (EtOAc/MeOH/NH_4OH 6:4:1); ^{1}H NMR (400

MHz, D_2O) δ 5.26 (d, J = 3.5 Hz, 1H, H-1α), 4.85 (d, J = 8.5 Hz, 0.7H, H-1β), 4.53 (dd, J = 10.6, 9.0 Hz, 1H, H-3α), 4.38 (dd, J = 10.4, 8.8 Hz, 0.7H, H-3β), 4.06 (dd, J = 10.7, 3.5 Hz, 1H, H-2α), 3.96-3.54 (m, 7.5H), 2.05 (s, 3H, CH_3CO-α), 2.04 (s, 2H, CH_3CO-β); ^{13}C NMR (101 MHz, D_2O) δ 174.7, 174.4, 94.4, 91.0, 81.5, 79.5, 75.4, 71.4, 68.7, 68.5, 60.5, 60.4, 55.2, 52.6, 22.2, 22.0.

2-Acetamido-1,3,4,6-tetra-*O*-acetyl-*2*-deoxy-β-D-galactopyranose (Fig. 1B, **11**). Compound **11** (7.5 g, 83%) was prepared from D-galactosamine hydrochloride (5 g, 23.3 mmol) as described in the literature (5).

Benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-*2*-deoxy-β-D-galactopyranose (Fig. 1B, **12**). Compound **12** (1.4 g, 78%) was prepared from compound **11** (1.6 g, 4.1 mmol) as described in the literature (5).

Benzyl 2-Acetamido-4,6-*O*-benzylidene-*2*-deoxy-*β*-D-galactopyranose (Fig. 1B, **13**). Compound **13** (907 mg, 71%, over 2 steps) was prepared from deacetylation of **10** (1.4 g, 3.2 mmol) followed by benzylidenation (4) as described for compound **9**; R_f = 0.52 (EtOAc/MeOH 8:2); NMR data were in accordance with those reported in the literature (5).

Benzyl 2-Acetamido-4,6-*O*-benzylidene-*2*-deoxy-3-*O*-sulfate-*β*-D-galactopyranose (Fig. 1B, **14**). Compound **13** (385 mg, 0.965 mmol) and $SO_3{\cdot}NEt_3$ complex (523 mg, 2.89 mmol) were dissolved in anhydrous pyridine (30 ml) and the mixture stirred for 2.5 hours. The reaction mixture was then concentrated and the residue purified by silica gel chromatography (EtOAc/MeOH/NH4OH 8:2:1) affording **14** (ammonium salt) as a white powder (450 mg, 94%); R_f = 0.37 (EtOAc/MeOH/NH_4OH 8:2:1); NMR data were in accordance with those reported in the literature (5).

2-Acetamido-2-deoxy-3-*O*-sulfate-D-galactopyranose (Fig. 1B, **3**). Compound **14** (360 mg, 0.725 mmol) was dissolved in EtOH (25 ml), 10% Pd/C (337 mg) was added and the mixture was stirred under an H_2 atmosphere (15 bars) for 2.5 hours at room temperature. The mixture was filtered and concentrated. The residue was purified by silica gel chromatography (EtOAc/MeOH/NH_4OH 5:5:1) affording compound **3** (ammonium salt) as a powder (205 mg, 89%); R_f = 0.39 (EtOAc/MeOH/NH_4OH 5:5:1); ^1H NMR (400 MHz, CD_3OD) δ 5.22 (d, J = 3.5 Hz, 1H, H-1α), 4.64 (d, J = 8.3 Hz, 0.6H, H-1β), 4.58 (dd, J = 11.3, 2.9 Hz, 1H, H-3α), 4.34 (dd, J = 11.3, 3.6 Hz, 1H, H-2α), 4.31–4.28 (m, 1.6H, H-3β, H-4α), 4.26–4.23 (m, 0.6H, H-4β), 4.09–4.04 (m, 1H, H-5α), 4.01 (dd, J = 10.9, 8.3 Hz, 0.6H, H-2β), 3.77–3.70 (m, 1.3H, H-6β), 3.70 (m, 2H, H-6α), 3.59–3.54 (m, 0.6H, H-5β), 1.98 (s, 2H, C*H*$_3$CO-β), 1.97 (s, 3H, C*H*$_3$CO-α); ^{13}C NMR (101 MHz, CD_3OD) δ 174.5, 173.7, 97.6, 92.8, 79.1, 76.3, 76.3, 71.6, 68.9, 67.9, 62.6, 62.4, 53.6, 50.4, 23.1, 22.9.

Benzyl 2-acetamido-3,4-*O*-isopropylidene-2-deoxy-*β*-D-galactopyranose (Fig. 1B, **15**). Compound **12** (490 mg, 1.1 mmol) was deacetylated using NaOMe (20 mg) in MeOH (15 ml). The mixture was neutralized and concentrated and the resulting white solid, 2,2-dimethoxypropane (5ml), and p-toluenesulfonic acid monohydrate (18 mg, 0.1 mmol) were dissolved in DMF (8 ml). The mixture was stirred under reflux for 5 hours, then cooled to room temperature, followed by addition of NEt_3 (1.2 ml). After concentration, the crude residue was dissolved in MeOH/H_2O (10:1, 12 ml) and stirred for 15 minutes at 65 ℃. The solution was concentrated and the residue was purified by silica gel chromatography (EtOAc/MeOH 95:5) to give product 15 as a white solid (295 mg, 75% over 2 steps); R_f = 0.49 (EtOAc/MeOH 95:5); ^1H NMR (500 MHz, CD_3OD) δ 7.48–7.06 (m, 5H, Ar), 4.90 (d, J = 12.1 Hz, H, C*H*$_2$Ph), 4.62 (d, J = 12.2 Hz, 1H, C*H*$_2$Ph), 4.48 (d, J = 8.8 Hz, 1H, H-1), 4.24–4.13 (m, 2H, H-4, H-5), 3.90–3.80 (m, 4H, H-2, H-3, H-6), 1.96 (s, 3H, C*H*$_3$CO), 1.53

(s, 3H, C*H*$_3$), 1.33 (s, 3H, C*H*$_3$); ^{13}C NMR (126 MHz, CD_3OD) δ 173.4, 139.1, 129.3, 128.9, 128.7, 111.1, 101.1, 78.1, 75.2, 74.5, 71.4, 62.6, 55.7, 28.4, 26.6, 22.9.

Benzyl 2-acetamido-3,4-*O*-isopropylidene-2-deoxy-6-*O*-sulfate-*β*-D-galactopyranose (Fig. 1B, **16**). Compound **15** (290 mg, 0.826 mmol) and $SO_3{\cdot}NEt_3$ complex (250 mg, 1.38 mmol) were dissolved in anhydrous DMF (20 ml) and the reaction mixture was heated at 55 ℃ for 2 hours. H_2O (2 ml) was added to decompose excess sulfation reagent. The reaction mixture was concentrated and purified by silica gel chromatography (EtOAc/MeOH/NH_4OH 8:2:1) affording **16** (ammonium salt) as a white solid (355 mg, 96%); R_f = 0.3 (EtOAc/MeOH/NH_4OH 8:2:1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.43–7.26 (m, 5H, Ar), 4.88 (d, J = 12.1 Hz, 1H, C*H*$_2$Ph), 4.62 (d, J = 12.1 Hz, 1H, C*H*$_2$Ph), 4.47 (d, J = 8.7 Hz, 1H, H-1), 4.31-4.25 (m, 3H, H-6, H-4), 4.2 –4.14 (m, 2H, H-3, H-5), 3.90 (t, J = 8.6 Hz, 1H, H-2), 1.97 (s, 3H, C*H*$_3$CO), 1.55 (s, 3H, C*H*$_3$), 1.35 (s, 3H, C*H*$_3$); ^{13}C NMR (101 MHz, CD_3OD) δ 173.4, 138.9, 129.3, 129.0, 128.7, 111.3, 101.1, 78.2, 74.4, 72.7, 71.5, 68.0, 55.4, 28.3, 26.6, 22.9.

Benzyl 2-acetamido-2-deoxy-6-*O*-sulfate-*β*-D-galactopyranose Fig. 1B, **17**). Compound **16** (50 mg, 0.11 mmol) was dissolved in a solution of acetic acid/water (4:1, 2 ml). The reaction was stirred at 55 ℃ for 40 minutes. The solution was then concentrated and the residue was purified by silica gel chromatography (EtOAc/MeOH/NH4OH 6:4:1) to yield compound **17** (ammonium salt) as a white solid (41 mg, 91%); R_f = 0.39 (EtOAc/MeOH/NH_4OH 6:4:1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.60–7.15 (m, 5H, Ar), 4.88 (d, J = 12.1 Hz, 1H, C*H*$_2$Ph), 4.63 (d, J = 12.2 Hz, 1H, C*H*$_2$Ph), 4.45 (d, J = 8.4 Hz, 1H, H-1), 4.30–4.17 (m,2H, H-6), 4.03 (dd, J = 10.7, 8.4 Hz, 1H, H-2), 3.91 (dd, J = 3.3, 1.0 Hz, 1H, H-4), 3.81 (td, J = 6.3, 1.1 Hz, 1H, H-5), 3.60 (dd, J = 10.7, 3.3 Hz, 1H, H-3), 1.97 (s, 3H, C*H*$_3$CO); ^{13}C NMR (101 MHz, CD_3OD) δ 174.0, 139.2, 129.3, 128.9, 128.6, 102.3, 74.4, 72.9, 71.6, 69.3, 67.6, 54.1, 23.0.

2-Acetamido-2-deoxy-6-*O*-sulfate-D-galactopyranose (Fig. 1B, **4**). Compound **17** (55 mg, 0.135 mmol) was dissolved in EtOH (5 ml) and 10% Pd/C (68 mg) was added. Hydrogenolysis was carried out under an H_2 atmosphere (10 bar) for 1 hour, where after the reaction mixture was filtered and the filtrate concentrated. The residue was purified by silica gel chromatography (EtOAc/MeOH/NH_4OH 55:45:10) affording **4** (ammonium salt) as a white powder (40 mg, 92%); R_f = 0.32 (EtOAc/MeOH/NH_4OH 6:4:1); ^{1}H NMR (400 MHz, D_2O) δ 5.09 (d, J = 3.7 Hz, 1H, H-1α), 4.52 (d, J = 8.3 Hz, 0.7H, H-1β), 4.28–4.13 (m, 1H, H-5α), 4.12–3.96 (m, 4.4H, H-6α, H-6β, H-2α), 3.92–3.90 (m, 0.7H, H-5β), 3.86–3.76 (m, 2.4H, H-3α, H-3β, H-4β), 3.77–3.72 (m, 0.7H, H-2β), 3.59 (ddd, J = 10.8, 3.8, 1.6 Hz, 0.7H, H-4β), 1.90 (s, 2H, C*H*$_3$CO-β), 1.85 (s, 3H, C*H*$_3$CO-α); ^{13}C NMR (101 MHz, D_2O) δ 174.9, 174.6, 95.3, 91.0, 72.7, 70.8, 68.3, 68.2, 67.6, 67.5, 67.2, 67.1, 53.4, 50.0, 22.1, 21.9.

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