Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Electronic Supplementary Information for:

Direct Formation of β-Glycosides of *N*-Acetyl Glycosamines Mediated by Rare Earth Metal Triflates

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2-Bromoethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside (7).

Donor **3** (197 mg, 0.51 mmol) and 2-bromoethanol (**6**) (0.11 mL, 1.54 mmol) were coupled according to the general procedure with $Sc(OTf)_3$ (37 mg, 0.075 mmol) as catalyst in dry CH_2Cl_2 (3 mL). After 27 h TLC analysis indicated no further reaction. The reaction mixture was worked up as described in the general procedure and purified by column chromatography (1:2 pentane/EtOAc) to give the desired glycoside **7** (153 mg, 67 %) as white crystals. R_f (EtOAc): 0.50; Mp(uncorr.): 166-167 °C (EtOAc/pentane). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 5.45 (d, 1H, $J_{NH,2}$ 8.4 Hz, N*H*), 5.31 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 9.6 Hz, H3), 5.06 (t, 1H, H4), 4.77 (d, 1H, $J_{1,2}$ = 8.4 Hz, H-1), 4.25 (dd, 1H, $J_{5,6a}$ 4.8 Hz, $J_{6a,6b}$ 12.2 Hz, H6a), 4.19-4.12 (m, 2H, H6b, OC*H*HCH$_2$Br), 3.90-3.80 (m, 2H, H2, OCH*H*CH$_2$Br), 3.71 (ddd, 1H, $J_{5,6b}$ 2.2 Hz, H5), 3.49-3.46 (m, 2H, OCH$_2$C*H*$_2$Br), 2.09, 2.03, 2.02,, 1.97 (s, 12H, COC*H*$_3$). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 171.1, 170.9, 170.7, 169.6 (*C*O), 101.2 (C1), 72.4, 72.2 (C3, C5), 69.7, 68.8 (C2, C4), 62.3 (C6), 54.9 (O*C*H$_2$CH$_2$Br), 30.8 (OCH$_2$*C*H$_2$Br), 23.6, 21.0, 20.9, 20.8 (C(O)*C*H$_3$); HRMS: calcd for $C_{16}H_{24}NO_9{}^{79}BrNa$: 476.0532, found: 476.0533. $[\alpha]_D^{21}$ -11.8 (*c* 1.0, $CHCl_3$).

Cyclohexyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside (9).

Donor **3** (200 mg, 0.51 mmol) and cyclohexanol (**8**) (0.16 mL, 1.52 mmol), freshly distilled from sodium, were coupled according to the general procedure with $Sc(OTf)_3$ (37 mg, 0.076 mmol) as catalyst in dry CH_2Cl_2 (2.5 mL). After 48 h TLC analysis indicated no further reaction. The reaction

mixture was worked up as described in the general procedure and purified by column chromatography (1:3 pentane/EtOAc → EtOAc) to give the desired cyclohexyl glycoside **9** (184 mg, 84 %) as colourless crystals. R_f(EtOAc): 0.53. Mp(uncorr.): 180-181 °C (EtOAc/pentane); LRMS(ES+): calcd. for $C_{20}H_{24}NO_9Na$: 452.2, found: 452.0. Spectral data was in accordance with previously reported results.[i]

***N*-(9-Fluorenylmethoxycarbonyl)-(2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl)-L-serine methyl ester (11).**

Donor **3** (129 mg, 0.33 mmol) and *N*-(9-fluorenylmethyl-oxycarbonyl)-L-serine methyl ester (**10**) (169 mg, 0.50 mmol) were coupled according to the general procedure with $Sc(OTf)_3$ (25 mg, 0.050 mmol) as catalyst in dry CH_2Cl_2 (3 mL). After 72 h TLC analysis indicated no further reaction. The reaction mixture was worked up as described in the general procedure and purified by column chromatography (1:4 pentane/EtOAc → EtOAc) which gave glycoside **11** (111 mg, 50 %) as pale yellow crystals. R_f(EtOAc): 0.56; Mp(uncorr.): 162-165 °C (EtOAc/pentane); ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.72 (dd, 2H, *J* 3.4 Hz, *J* 7.4 Hz, Fmoc Ph), 7.58 (d, 2H, *J* 5.0 Hz, Fmoc Ph), 7.34 (t, 2H, *J* 7.4 Hz, Fmoc Ph), 7.27 (t, 2H, *J* 7.4 Hz, Fmoc Ph), 5.67 (d, 1H, $J_{NH,CH\text{-}Ser}$ 7.6 Hz, N*H*-Ser), 5.41 (d, 1H, $J_{NH,2}$ 8.0 Hz, N*H*Ac), 5.17 (t, 1H, $J_{2,3} = J_{3,4}$ 10.0 Hz, H3), 4.97 (t, 1H, H4), 4.56 (d, 1H, $J_{1,2}$ 8.4 Hz, H1), 4.43-4.38 (m, 3H, C*H*-Ser, CH_2Fmoc), 4.20-4.12 (m, 3H, H6a, C*H* Fmoc, C*H*H-Ser), 4.05 (dd, 1H, $J_{5,6b}$ 2.4 Hz, $J_{6a,6b}$ 12.4 Hz, H6b), 3.79-3.71 (m, 2H, H2, CH*H*-Ser), 3.70 (s, 3H, CO_2CH_3), 3.60 (ddd, 1H, $J_{5,6a}$ 4.8 Hz, H5), 2.01, 1.97, 1.96, 1.78 (s, 12H, COCH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 171.1, 170.9, 170.4, 169.6 (*C*OCH_3, *C*O_2CH_3), 156.3 (*C*O Fmoc), 144.1, 143.9, 141.6 (*C*-ipso Fmoc), 128.0, 127.4, 125.4, 120.3 (Ar Fmoc), 101.0 (C1), 72.4, 72.2 (C3, C5), 69.1, 68.7 (C4, *C*H_2-Ser), 67.1 (*C*H_2 Fmoc), 62.3 (C6), 54.6, 54.4 (C2, *C*H-Ser), 53.0 (CO_2*C*H_3), 47.4 (*C*H Fmoc), 23.4, 20.9, 20.9, 20.8 (CO*C*H_3); HRMS(ES+): calcd. for $C_{33}H_{38}N_2O_{13}Na$: 693.2272; found: 693.2243. $[\alpha]_D^{21}$ 3.5 (*c* 1.0, $CHCl_3$).

_O_-(2-Acetamido-3,4,6-tri-_O_-acetyl-2-deoxy-D-glucopyranosyl)-β-(1-6)-1,2;3,4-di-_O_-isopropylidene-α-D-galactopyranose (13).

Donor **3** (734 mg, 1.89 mmol) and 1,2;3,4-di-*O*-isopropylidene-α-D-galactopyranose (**12**) (220 mg, 0.85 mmol) were coupled according to the general procedure with $Sc(OTf)_3$ (63 mg, 0.13 mmol) as catalyst in dry CH_2Cl_2 (3 mL). After 20 h TLC analysis indicated no further reaction. The reaction mixture was worked up as described in the general procedure and purified by column chromatography (acetone/pentane 2:5) to give the desired disaccharide **13** (0.387 g, 78%) as a white powder. R_f(acetone/pentane 4:5) 0.47; Mp(uncorr.): 72-74 °C (acetone/pentane). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 5.59 (d, 1H, $J_{NH,2}$ 8.8 Hz, N*H*Ac), 5.50 (d, 1H, $J_{1',2'}$ 5.0 Hz, H1), 5.14 (t, 1H, $J_{2',3'} = J_{3,4}$ 9.6 Hz, H3'), 5.08 (t, 1H, H4'), 4.68 (d, 1 H, $J_{1',2'}$ 8.4 Hz, H1'), 4.56 (dd, 1H, $J_{3,4}$ 2.4 Hz, $J_{2,3}$ 7.6 Hz, H3), 4.29 (dd, 1H, H2), 4.25 (dd, 1H, $J_{6'a,6'b}$ 12.4 Hz, $J_{6a,5}$ 4.6 Hz, H6'a), 4.14-4.09 (m, 2H, H4, H6'b), 4.04-3.92 (m, 3H, H2', H6a, H5'), 3.72 (dd, 1H, $J_{6a,6b}$ 13.2 Hz, $J_{5,6b}$ 9.2 Hz, H6b), 3.66 (ddd, 1H, $J_{5',6'b}$ 2.4 Hz, H5'), 2.06, 2.00, 1.99, 1.94 (s, 12H, C(O)C*H*$_3$), 1.47 (s, 3H, O_2CMeC*H*$_3$), 1.42 (s, 3H, O_2CC*H*$_3$Me), 1.30 (s, 6H, O_2CMeC*H*$_3$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 171.1, 170.9, 170.6, 169.5 (*C*O), 109.6, 108.8 ($(CH_3)_2CO_2$), 102.1 (C1'), 96.4 (C1), 73.4 (C3'), 72.0 (C5'), 71.2 (C4), 70.8 (C3), 70.5 (C2), 69.2 (C6), 68.7 (C4'), 68.5 (C2'/C5), 62.3 (C6'), 54.3 (C2'/C5), 26.3, 26.1, 25.2, 24.5 , 23.5, 20.9, 20.9 20.8 (C(O)*C*H$_3$); $[\alpha]_D^{21}$ -51.3 (*c* 1.0, $CHCl_3$). Spectral data was in accordance with previously reported results.[ii]

Methyl _O_-(2-acetamido-3,4,6-tri-_O_-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (15):

Donor **3** (210 mg, 0.54 mmol, microwave heating; 410 mg, 0.9 mmol, conventional heating), methyl glucopyranoside **14** (100 mg, 0.22 mmol), and $Sc(OTf)_3$ (16 mg, 0.023 mmol) was dissolved in dry CH_2Cl_2 (2 mL) and heated to 80°C for 3 h. by microwave irradiation or to reflux for 72 h by conventional heating. The mixture was diluted with CH_2Cl_2 and washed with water followed by extraction with CH_2Cl_2 as described in the general procedure. The combined organic extracts were dried over $MgSO_4$ and purified by column chromatography (EtOAc/pentane 1:1 → 1:0) to give the desired disaccharide

16 (128 mg, 75 %, microwave heating; 145 mg, 85% conventional heating) as a white solid. R_f(EtOAc) 0.6. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.29-7.19 (m, 15H, Ar*H*), 5.33 (d, 1H, $J_{NH,2}$ 8.4 Hz, N*H*), 5.20 (t, 1H, $J_{2',3'} = J_{3',4'}$ 10.0 Hz, H3'), 4.97 (t, 1H, H4'), 4.90 (d, 1H, J_{gem} 10.8 Hz, PhC*H*H), 4.76 (d, 1H, J_{gem} 10.8 Hz, PhC*H*H), 4.72 (d, 1H, J_{gem} 10.8 Hz, PhCH*H*), 4.70 (d, 1H, J_{gem} 12.0 Hz, PhC*H*H), 4.61 (d, 1H, $J_{1',2'}$ 8.0 Hz, H1'), 4.58 (d, 1H, J_{gem} 12.0 Hz, PhCH*H*), 4.52 (d, 1H, $J_{1,2}$ 3.2 Hz, H1), 4.50 (d, 1H, J_{gem} 10.8 Hz, PhCH*H*), 4.14 (dd, 1H, $J_{5'6'a}$ 4.8 Hz, $J_{6'a,6'b}$ 12.0 Hz, H6'a), 4.02 (dd, 1H, $J_{5',6'b}$ 2.4 Hz, H6'b), 3.98 (d, 1H, $J_{6a,6b}$ 10.2 Hz, H6a), 3.90 (t, 1H, H3), 3.78 (q, 1H, H2'), 3.70-3.57 (m, 3H, H5', H5, H6b), 3.44 (dd, 1H, $J_{2,3}$ 9.6 Hz, H2), 3.40 (t, 1H, $J_{3,4}$ 9.6 Hz, H4), 3.28 (s, 3H, OCH_3), 1.94, 1.74 (s, 12H, C(O)CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.0, 169.6 (*C*O), 139.0, 138.3, 128.7, 128.1, 127.8 (Ar), 100.8 (C1'), 98.3 (C1), 82.2 (C3), 80.0 (C2), 77.6 (C4), 75.9 (Ph*C*H_2), 74.8 (Ph*C*H_2), 73.6 (Ph*C*H_2), 72.5 (C3'), 72.1, 69.7 (C5, C5'), 68.9 (C4'), 67.9 (C6), 62.4 (C6'), 55.4 (O*C*H_3), 54.9 (C2'), 23.5, 20.9, 20.9 (C(O)*C*H_3). Spectral data is in accordance with previously reported values.[iii]

Methyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (17).

Acceptor **16** (103 mg, 0.22 mmol) and donor **3** (345 mg, 0.89 mmol) were coupled according to the general procedure with $Sc(OTf)_3$ (66 mg, 0.13 mmol) as catalyst in dry CH_2Cl_2. After 72 h TLC analysis indicated no further reaction. The reaction mixture was worked up as described in the general procedure and purified by column chromatography (EtOAc/pentane 1:5 → EtOAc) to give the desired disaccharide **17** (37 mg, 21%) and unreacted acceptor (**16**) (68 mg). R_f(EtOAc) 0.55. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.44-7.15 (m, 15H, Ar-*H*), 4.92 (d, 1H, *J* 11.3 Hz, PhC*H*Ha), 4.87 (m, 1H, H4'), 4.82 (m, 1H, H3'), 4.77 (d, 1H, *J* 12.2 Hz, PhC*H*Hb), 4.70 (d, 1H, PhCH*H*a), 4.64 (d, 1H, *J* 12.0, PhC*H*Hc), 4.57 (d, 1H, PhCH*H*c), 4.56 (d, 1H, $J_{1,2}$ 3.6 Hz, H1), 4.53 (d, 1H, $J_{NH,2'}$ 9.2 Hz, N*H*), 4.36 (d, 1H, $J_{1',2'}$ 8.4 Hz, H1'), 4.31 (d, 1H, PhCH*H*b), 4.02 (dd, 1H, $J_{5',6a'}$ 4.4 Hz, $J_{6a',6b'}$ 12.4 Hz, H6a'), 3.80-3.72 (m, 4H, H2', H3, H4, H6b'), 3.59-3.53 (m, 2H, H5, H6a), 3.43-3.34 (m, 3H, H2, H5', H6b), 3.29 (s, 3H, OCH_3), 1.93, 1.91, 1.86, 1.64 (s, 12 H, C(O)CH_3). ^{13}C-NMR

($CDCl_3$, 100 MHz) δ 170.9, 170.8, 170.0, 169.6 (*C*O), 139.8, 138.5, 138.0, 129.2, 129,1,, 129.0, 128.6, 128.4, 128.3, 128.0, 127.3, 127.2 (Ar), 100.7 (C1'), 98.6 (C1), 80.3 (C3), 79.1 (C2), 77.5 (C4), 75.2, 74.0, 73.7 (Ph*C*H_2), 73.1 (C3'), 71.6 (C5'), 69.6 (C5), 68.7 (C4'), 67.8 (C6) , 62.1 (C6'), 55.6 (O*C*H_3), 54.8 (C2'), 23.4 (NHC(O)*C*H_3), 20.8 (OC(O)*C*H_3). $[\alpha]_D^{22}$ 14 (*c* 1.0, $CHCl_3$); HRMS(ES+): calcd for $C_{42}H_{51}NO_{14}Na$: 816.3208; found, 816.3203.

Methyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (17) by microwave irradiation.

Donor **3** (168 mg, 0.43 mmol) and methyl glucoside **16** (100 mg, 0.23 mmol) were dissolved in CH_2Cl_2 (1.2 mL) before $Sc(OTf)_3$ (16 mg, 0.032 mmol) was added. The reaction mixture was heated by microwave irradiation to 80 °C for 8 h. After this period of time more donor (**3**) (167 mg, 0.43 mmol) and $Sc(OTf)_3$ (16 mg, 0.032 mmol) were added and the mixture heated as before for another 8 h. The reaction mixture was loaded directly onto a column of silicagel and purified as mentioned above. This gave desired disaccharide (**17**) (73 mg, 43%) and unreacted acceptor (**16**) (37 mg, recovered yield of **17**: 68%).

Allyl 2,3,6-tri-*O*-benzyl-α-D-galactopyranoside (19):

To a stirred solution of benzylidene **24** (1.33 g, 2.7 mmol) in CH_2Cl_2 (10 mL) was added triethylsilane (3.55 mL, 22.2 mmol) and triflouroacetic acid (1.83 mL, 24.6 mmol). The mixture was stirred for 5 min at 0 ˚C and then at ambient temperature for 24 h before neutralised with $NaHCO_3$ (sat. aq) and extracted with CH_2Cl_2. The resulting product was purified by column chromatography (silica, EtOAc/pentane 1:4). This gave the desired tribenzylated galactoside **19** as a colourless oil (813 mg, 61 %). R_f(EtOAc/pentane 1:4) 0.20. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.39-7.26 (m, 15H, Ar*H*), 5.99-5.90 (m, 1H, CH_2CH=CH_2), 5.32 (dq, *J* 1.6 Hz, J_{vic} 17.2 Hz, CH=C*H*H), 5.21 (b d, J_{vic} 10.0 Hz, CH=CH*H*), 4.88 (d, 1H, $J_{1,2}$ 4.8 Hz, H1), 4.81 (d, 1H, J_{gem} 11.6 Hz, PhC*H*H), 4.80 (d, 1H, J_{gem} 12.0 Hz, PhC*H*H), 4.71 (d, 1H, J_{gem} 11.6 Hz, PhCH*H*), 4.66 (d, 1H, J_{gem} 12.0 Hz, PhCH*H*), 4.60 (d,

1H, J_{gem} 12.0 Hz, PhC*H*HO6), 4.56 (d, 1H, PhCH*H*O6), 4.18 (ddt, J_{vic} 5.2 Hz, J_{gem} 13.2 Hz, OC*H*HCH=CH_2), 4.09 (b s, 1H, H4), 4.04 (ddt, 1H, J_{vic} 6.8 Hz, OCH*H*CH=CH_2), 3.97 (b t, 1H, $J_{5,6a}$ = $J_{5,6b}$ 5.6 Hz, H5), 3.93-3.86 (m, 2H, H2, H3), 3.74 (dd, 1H, $J_{6a,6b}$ 10.0 Hz, H6a), 3.68 (dd, 1H, H6b). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 138.8, 138.5, 138.4, 128.7, 128.6, 128.2, 128.1, 127.9 (Ar), 134.2 (*C*H=CH_2), 118.3 (CH=*C*H_2), 96.5 (C1), 78.0, 76.1 (C2, C3), 73.8, 73.6, 73.1 (Ph*C*H_2), 69.9 (C6), 68.9 (C5), 68.6 (*C*H_2CH=CH_2), 68.4 (C4). HRMS(ES+): calcd. for: $C_{30}H_{34}O_6Na$: 513.2253; found 513.2258. Spectral data was largely in accordance with previously published values.[iv]

_O_-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-2-acetamido-2-deoxy-α/β-D-glucopyranose (26):

A balloon of H_2-gas was applied to a vigorously stirred solution of protected disaccharide **23** (120 mg, 0.16 mmol) and $Pd(OH)_2$/C (10%, 25 mg) in acetic acid (2 mL). The reaction mixture was stirred overnight before the catalyst was removed by filtration through a bed of Celite®. The remaining acetic acid was carefully removed by repeated co-evaporation with toluene before the residue was dissolved in methanol (3 mL) to which had been added a catalytic amount of Na-metal. The reaction mixture was stirred overnight at 40 °C before diluted with H_2O (5 mL) and neutralised with Amberlite (IR-120 H+). The solvents were removed under reduced pressure and the crude product underwent ^{13}C-NMR analysis (D_2O, 100 MHz) to confirm the linkage being 1→3.**Error! Bookmark not defined.**[a] HRMS(ES+): calcd. for $C_{16}H_{28}N_2O_{11}Na$: 447.1591; found: 447.1593.

Benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α/β-D-glucopyranoside from anomeric mixture of donors (5αβ):

An anomeric mixture of D-*N*-acetyl glucosamine tetraacetate (**3αβ**) (α/β 4.6:1, 200 mg, 0.51 mmol), BnOH (**4**) (0.16 mL, 1.54 mmol), and $Sc(OTf)_3$ were dissolved in CH_2Cl_2 (1.45 mL). The mixture was heated to 110 °C under microwave conditions for 5 hours. The reaction mixture was diluted with CH_2Cl_2, washed with $NaHCO_3$ (sat. aq.), and dried ($MgSO_4$) before purified by

column chromatography (EtOAc/pentane 1:1 → 2:1) to give an anomeric mixture of benzyl glycosides **5αβ** (α/β 21/79, 180 mg, 80%).

Data for α-anomer (less polar than β-anomer): R_f(EtOAc) 0.61. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40-7.31 (m, 5H, Ar*H*), 5.63 (d, 1H, $J_{2,NH}$ 9.2 Hz, N*H*), 5.23 (t, 1H, $J_{2,3;3,4}$ 10.2 Hz, H3), 5.13 (t, 1H, H4), 4.94 (d, 1H, $J_{1,2}$ 3.6 Hz, H1), 4.71 (d, 1H, J_{gem} 11.6 Hz, PhC*H*HO), 4.52 (d, 1H, PhCH*H*O), 4.35 (ddd, 1H, H2), 4.23 (dd, 1H, $J_{5,6a}$ 4.4 Hz, $J_{6a,6b}$ 12.4 Hz, H6a), 4.03 (dd, 1H, $J_{5,6b}$ 2.4 Hz, H6b), 3.99-3.95 (m, 1H, H5), 2.10, 2.01, 2.00, 1.89 (s, 12H, C(O)CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ171.6, 170.9, 170.1, 169.5 (*C*O), 136.7, 128.9, 128.6, 128.5 (Ar), 96.9 (C1), 71.5 (C3), 70.5 (Ph*C*H_2O), 68.3, 68.2 (C4, C5), 62.1 (C6), 52.0 (C2), 23.4, 21.0, 20.9, 20.8 (C(O)*C*H_3). $[\alpha]_D^{21}$ 113 (*c* 1.0, $CHCl_3$), HRMS(ES+): calcd. for $C_{21}H_{27}NO_9Na$: 460.1584; found: 460.1594.

Treatment of benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranose (5) with either $Sc(OTf)_3$ or acetic acid:

To benzyl glucoside (**5**) (100 mg, 0.23 mmol) in CH_2Cl_2 (0.75 mL) was added either $Sc(OTf)_3$ (17 mg, 0.034 mmol) or CH_3CO_2H (13 μL, 0.23 mmol) before the reaction mixture was heated to 110 °C under microwave irradiation for 5 h. The reaction mixture was then diluted with CH_2Cl_2 (20 mL) and washed with $NaHCO_3$ (aq. sat. 20 mL), dried ($MgSO_4$), concentrated under reduced pressure (full recovery of material) and analysed by NMR spectroscopy to be starting material **5**.

Treatment of benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranose (5) with $Sc(OTf)_3$ and acetic acid:

To benzyl glucoside (**5**) (100 mg, 0.23 mmol) in CH_2Cl_2 (0.75 mL) was added $Sc(OTf)_3$ (17 mg, 0.034 mmol) and CH_3CO_2H (13 μL, 0.23 mmol) before the reaction mixture was heated to 110 °C under microwave irradiation for 5 h. The reaction mixture was then diluted with CH_2Cl_2 (20 mL) and washed with $NaHCO_3$ (aq. sat. 20 mL), dried ($MgSO_4$), concentrated under reduced pressure (near full recovery of material) and analysed by NMR spectroscopy to be an anomeric mixture of benzyl glycosides (**5αβ**).

[i] F. Iglesias-Guerra, I. Romero, F. Alcudia, J. M. Vega-Pérez, *Carbohydr. Res.*, 1998, **308**, 57-62
[ii] D.A. Griffith, S.J. Danishefsky, *J. Am. Chem. Soc.,* 1990, **112**, 5811-5819
[iii] A. F. G. Bongat, M. N. Kamat, A.V. Demchenko, *J. Org. Chem.*, 2007, **72**, 1480-1483.
[iv] K. Nunokawa, S. Onaka, T. Yamaguchi, T. Ito, S. Watase, M. Nakamoto, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 1601-1602.