$SnCl_4$ and $TiCl_4$ catalysed anomerisation of acylated *O*- and *S*-glycosides: analysis of factors that lead to higher α:β anomer ratios and reaction rates

Wayne Pilgrim,[1,2] Paul V. Murphy[1,*]

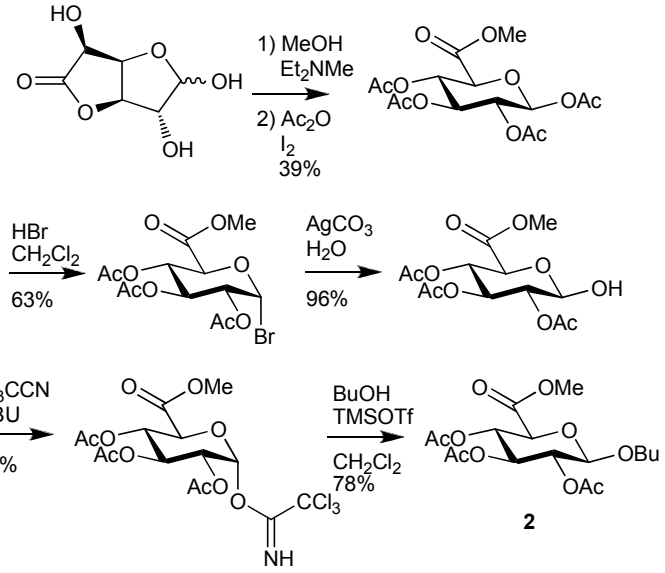
[1]*School of Chemistry, National University of Ireland, Galway.* [2] *Centre for Synthesis and Chemical Biology, School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland.*

email: paul.v.murphy@nuigalway.ie

Index

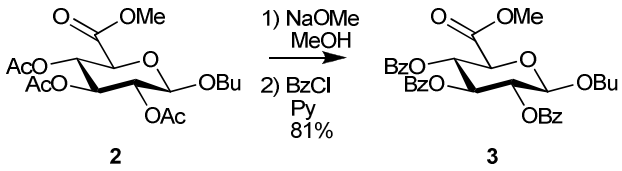
Synthesis of 1-18

The synthesis of **15-18** was described previously.[1] The synthesis of **2** was carried out from D-glucurono-3,6-lactone as shown in Scheme S1.[1,2] Trichloroacetimidates were used for O-glycoside synthesis.[3]



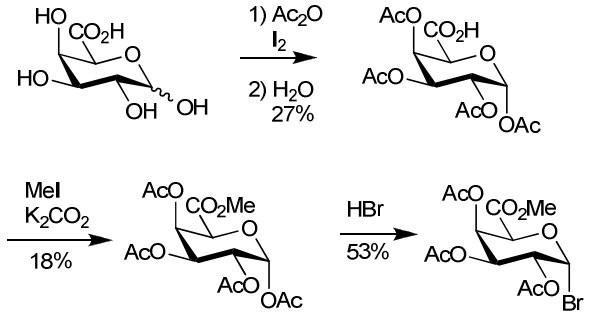
Scheme S1. Synthesis of **2**

Removal of the acetates from **2** using sodium methoxide in anhydrous methanol and subsequent reaction of the deacetylated intermediate with benzoyl chloride and pyridine gave **3** (Scheme S2).

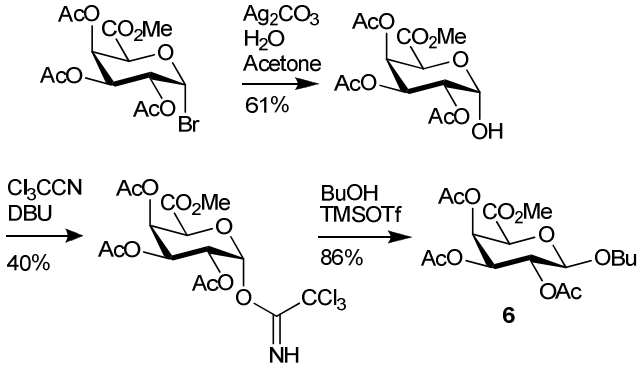


Scheme S2. Preparation of **3**

The synthesis of galacturonic acid **6** was carried out starting from galacturonic acid as shown in Scheme S3 and S4.

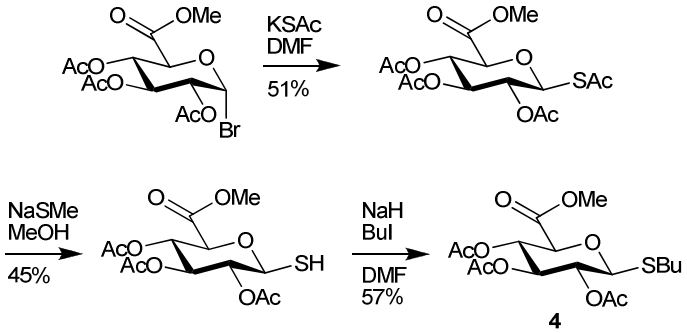


Scheme S3 Synthesis of galacturonic acid derivatives



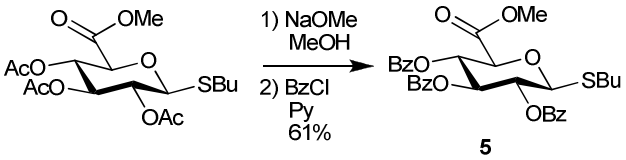
Scheme S4 Synthesis of **6**

The synthesis of thioglycoside substrates were achieved by a direct anomeric alkylation of a glycosyl thiol. The synthesis of both α- and β-glycosyl thiols have been reported from the corresponding β- or α-halides.[4] Thioglycoside **4** was obtained as a 1:9 (α/β) mixture by this route.



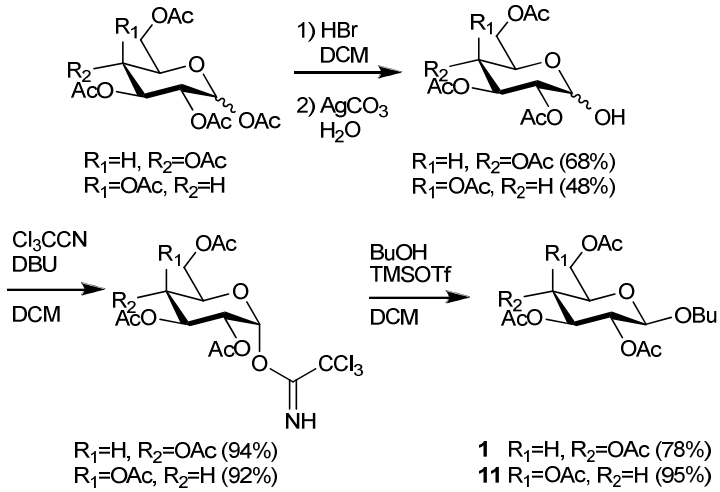
Scheme S5. Synthesis of **4**

Replacement of the acetates from **4** and introduction of benzoyl protecting groups gave **5** (Scheme S6).



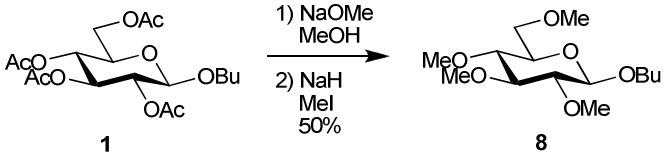
Scheme S6 Synthesis of **5**

The synthesis of **1** and **11** is shown in Scheme S7.



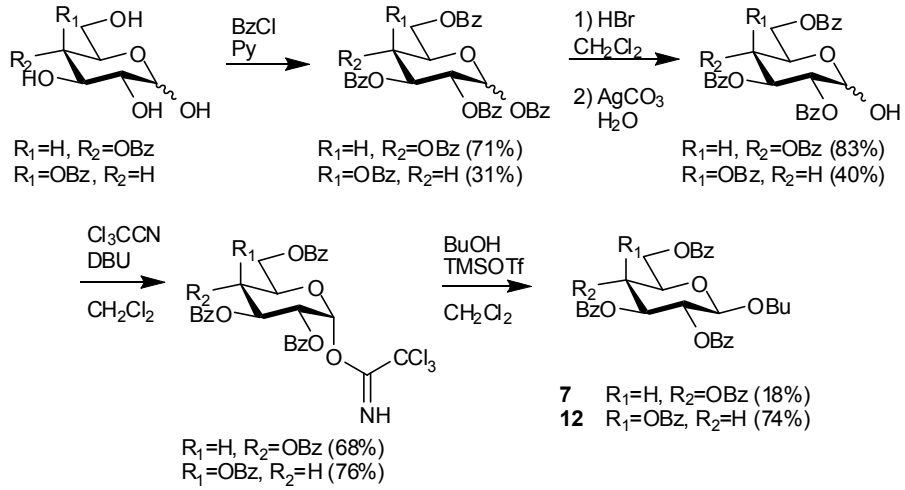
Scheme S7 Synthesis of **1** and **11**

Glucoside **8** was prepared from **1** (Scheme S8).



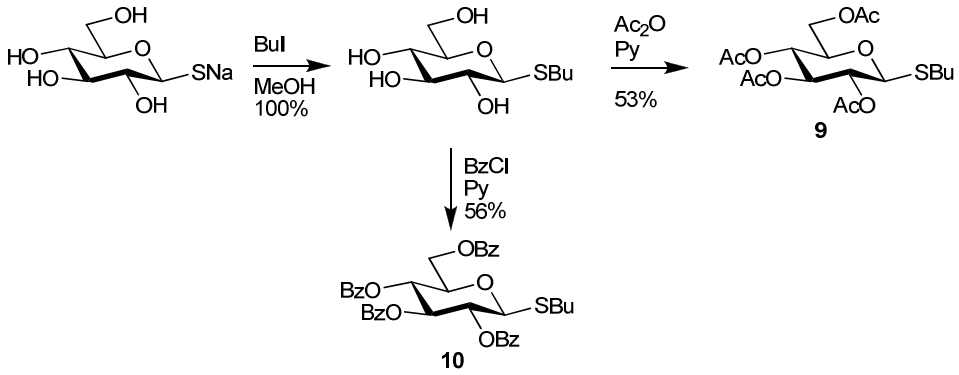
Scheme S8. Synthesis of **8**

Benzoyl protected glycoside **7** was prepared from D-glucose following a published procedure.[5] The synthesis of galactoside **12** from galactose followed the same synthetic scheme.



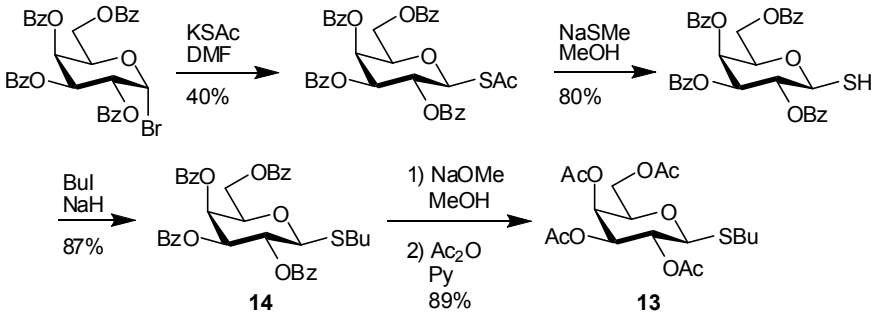
Scheme S9 Synthesis of **7**

Synthesis of thioglucosides **9** and **10** employed a direct anomeric alkylation of commercially available sodium thioglucose and subsequent protection (Scheme S10).



Scheme S10. Preparation of **9** and **10**

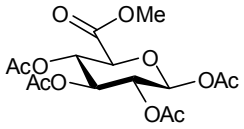
Thio-galactosides **13** and **14** were obtained via the galactosyl bromide (Scheme S11).



Scheme S11. Synthesis of **13** and **14**

General Experimental Conditions

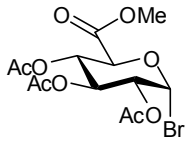
Optical rotations were determined at the sodium D line at 20°C. NMR spectra were recorded (30 °C) with 400, 500, or 600 MHz spectrometers. Chemical shifts are reported relative to internal Me_4Si in $CDCl_3$ (δ 0.0) or HOD for D_2O (δ 4.72, 30 °C) for ^1H and Me_4Si in $CDCl_3$ (δ 0.0) or $CDCl_3$ (δ 77.0) for ^{13}C. ^1H NMR signals were assigned with the aid of COSY. ^{13}C NMR signals were assigned with the aid of DEPT, gHSQCAD and/or gHMBCAD. Coupling constants are reported in hertz. The IR spectra were recorded using thin film on a NaCl plate or with ATR attachment. Low and high resolution mass spectra were in positive and/or negative mode as indicated in each case. Thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel and spots visualized by UV and charring with H_2SO_4-EtOH (1:20), or cerium molybdate. Flash chromatography was carried out with silica gel 60 (0.040-0.630 mm) and using a stepwise solvent polarity gradient correlated with TLC mobility. CH_2Cl_2, MeOH, and THF reaction solvents were used as obtained from a Pure Solv™ Solvent Purification System. Anhydrous DMF, pyridine, and toluene were used as purchased. Chromatography solvents were used as obtained from suppliers.



1,2,3,4-Tetra-O-β-D-glucopyranuronic acid, methyl ester[2]

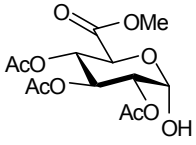
D-Glucurono-6,3-lactone (10 g, 56.8 mmol) was suspended in dry methanol (160 mL), to this dimethylethylamine (0.1 mL) was added. The reaction was stirred for 16 h until all the glucuronolactone was dissolved. The solvent was evaporated and the foam was used without purification. Acetic anhydride (50 mL) and sodium acetate (5 g, 61 mmol) were added and the suspension was stirred for 4 days. The reaction was poured onto ice water (300 mL) and stirred overnight. The precipitate was separated by filtration, washed with water and recrystallised from absolute ethanol gave the title compound as a white solid (8.5 g, 39%); R_f 0.57 (1:1 EtOAc-cyclohexane); $[\alpha]_D$ +9.31 (c 1.16, $CHCl_3$); IR (film) cm^{-1}: 2958, 1757, 1439, 1370, 1215, 1039; ^1H NMR ($CDCl_3$, 600 MHz): δ 5.77 (1H, d, *J* 7.7 Hz, H-1), 5.31 (1H, t, *J* 9.3 Hz, H-3), 5.25 (1H, t, *J* 9.3 Hz, H-4), 5.14 (1H, dd, *J* 9.3 Hz, *J* 7.7 Hz, H-2), 4.18 (1H, d, 9.3 Hz, H-

5), 3.76 (3H, s, OC*H*$_3$), 2.13 (3H, s), 2.05 (6H, s), 2.04 (3H, s) (each OAc); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 169.9, 169.4, 169.2, 168.8, 166.8 (each C=O), 91.4 (C-1), 73.0 (C-5), 71.8 (C-3), 70.1 (C-2), 68.9 (C-4), 53.0 (O*C*H$_3$), 20.8, 20.6, 20.5, 20.5 (each OAc); ES-HRMS calcd for $C_{15}H_{20}O_{11}Na$ 399.0903, found *m/z* 399.0885 $[M+Na]^+$; Anal. Calcd for $C_{15}H_{20}O_{11}$: C, 47.88; H, 5.36. Found: C, 47.89; H, 5.31.



1-Bromo-2,3,4-tri-O-acetyl-α-D-glucopyranuronic acid, methyl ester.[6]

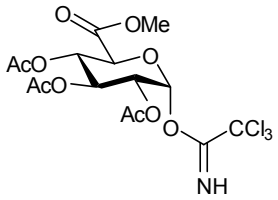
1,2,3,4-Tetra-*O*-β-D-glucopyranuronic acid, methyl ester (4.0 g, 10.5 mmol) was dissolved in CH_2Cl_2 (8 mL) and cooled to 0 °C. To this HBr (33% in AcOH, 16 mL) was added and the reaction allowed to attain room temperature over 4 h. The reaction mixture was diluted with Et_2O, washed with water, satd $NaHCO_3$, water, brine, dried over $MgSO_4$, and the solvent removed under reduced pressure. Recrystallisation of the residue from absolute ethanol gave the title compound (2.66 g, 63%) as a white solid; R_f 0.69 (1:1 EtOAc-cyclohexane); IR (film) cm^{-1}: 2975, 1752, 1370, 1213, 1115, 1044; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.64 (1H, d, *J* 4.1 Hz, H-1), 5.61 (1H, t, *J* 10.0 Hz, H-3), 5.24 (1H, t, *J* 10.0 Hz, H-4), 4.86 (1H, dd, 10.0, 4.1 Hz, H-2), 4.58 (1H, d, 10.0 Hz, H-5), 3.76 (3H, s, OC*H*$_3$), 2.10 (3H, s), 2.06 (3H, s), 2.05 (3H, s) (each OAc); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.6, 169.5, 169.3, 166.6 (each C=O), 85.3 (C-1), 72.0 (CH), 70.3 (CH), 69.3 (CH), 68.5 (CH), 53.0 (O*C*H$_3$), 20.6 (2s), 20.4 (each OAc).



2,3,4-Tri-*O*-acetyl-α-D-glucopyranuronic acid, methyl ester[7]

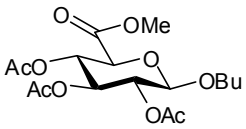
1-Bromo-2,3,4-tri-*O*-acetyl-α-D-glucopyranuronic acid, methyl ester (989 mg, 2.46 mmol) was dissolved in acetone (20 mL) and water (2 mL) and to this Ag_2CO_3 (338 mg, 1.23 mmol) was added and the reaction stirred for 16 h at room temperature. The reaction was filtered through Celite, which was rinsed with CH_2Cl_2, the organic layer

was decanted, dried over $MgSO_4$ and the solvent was removed to give the title compound (720 mg, 96 %) as a white solid; R_f 0.27 (EtOAc-cyclohexane 1:1); Mp 81 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.61-5.30 (2H, m, H-1, H-4), 5.18 (1H, dd, *J* 10.0 Hz, *J* 9.0 Hz, H-3), 4.95 (1H, dd, *J* 4.0 Hz, *J* 10.0 Hz, H-2), 4.59 (1H, d, *J* 10.0 Hz, H-5), 3.74 (3H, s, OC*H*$_3$), 2.04 (3H, s), 2.03 (3H, s), 2.02 (3H, s) (each OAc).



2,3,4-Tri-O-acetyl-1-(2,2,2-trichloroethanimidate)-α-D-glucopyranuronic acid, methyl ester.[8]

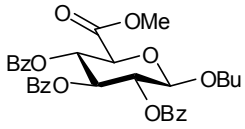
The hemiacetal precursor 2,3,4-tri-*O*-acetyl-α-D-glucopyranuronic acid, methyl ester (360 mg, 1.06 mmol) was dissolved in CH_2Cl_2 (20 mL) and cooled to 0 °C. To this Cl_3CCN (1.06 mL, 10.6 mmol), and DBU (10 drops) was added. The reaction was stirred at 0 °C for 5 h, concentrated to 5 mL and chromatography of the residue (EtOAc-cyclohexane 1:2) gave the title compound (385 mg, 75%) as a white solid. R_f 0.63 (EtOAc-cyclohexane 1:1); Mp 112 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.74 (1H, s, NH), 6.64 (1H, d, *J* 4.0 Hz, H-1), 5.63 (1H, t, *J* 10.0 Hz, H-4), 5.27 (1H, t, *J* 10.0 Hz, H-3), 5.15 (1H, dd, *J* 10.0 Hz, *J* 4.0 Hz, H-2), 4.50 (1H, d, *J* 10.0 Hz, H-5), 3.75 (3H, s, OC*H*$_3$), 2.05 (3H, s), 2.04 (3H, s), 2.01 (3H, s) (each OAc).



Butyl 2,3,4-tri-O-acetyl-β-D-glucopyranosiduronic acid, methyl ester 2[9]

A mixture of trichloroacetimidate precursor (385 mg, 0.795 mmol) and molecular sieves 4 Å (50 mg) were placed under reduced pressure for 1 h. Dichloromethane (4 mL) and *n*-BuOH (109μL, 1.19 mmol) were added and the solution was stirred for 40 min at room temperature. The solution was cooled to 0 °C and TMSOTf (0.05M, 0.0795 mmol, 1.6 mL) was added, the reaction stirred for a further 40 min. Solid $NaHCO_3$ (50 mg) was added and the mixture stirred for 20 min, then filtered through Celite, which was rinsed with CH_2Cl_2. The solvent was removed under reduced

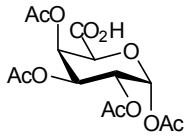
pressure and chromatography of the residue (EtOAc-cyclohexane 1:4) gave **2** as a white solid (284 mg, 78%); R_f 0.37 (EtOAc-cyclohexane, 1:1); $[\alpha]_D$ -27.5 (c 1.35, $CHCl_3$); Mp 85.8-85.0 °C; IR (film) cm^{-1}: 2958, 1755, 1373, 1221, 1040, 893; ^1H NMR ($CDCl_3$, 400 MHz): δ 5.23 (2H, m, H-3, H-4), 4.99 (1H, dd, *J* 9.0 Hz, *J* 7.8 Hz, H-2), 4.54 (1H, d, *J* 7.8 Hz, H-1), 4.03 (1H, d, *J* 9.4 Hz, H-5), 3.90 (1H, dt, *J* 9.6 Hz, *J* 6.3 Hz, CH*H*O), 3.76 (3H, s, OC*H*$_3$), 3.47 (1H, dt, *J* 9.6 Hz, *J* 6.7 Hz, CH*H*O), 2.03 (3H, s, OAc), 2.02 (6H, s, OAc), 1.55 (2H, m), 1.34 (2H, m), 0.89 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.1, 169.3, 169.2, 167.3 (each C=O), 100.8 (C-1), 72.6 (C-5), 72.1 (C-3/4), 71.2, (C-2), 70.1 (O*C*H$_2$), 69.5 (C-3/4), 52.8 (O*C*H$_3$), 31.3 (*C*H$_2$), 20.6 (2s), 20.5 (each OAc), 18.9 (*C*H$_2$), 13.7 (*C*H$_3$). ESI-HRMS calcd for $C_{17}H_{26}O_{10}Na$ 413.1424, found *m/z* 413.1440 $[M+Na]^+$.



Butyl 2,3,4-tri-O-benzoyl-β-D-glucopyranosiduronic acid, methyl ester 3

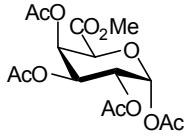
Glucuronide **2** (67 mg, 0.265 mmol) was dissolved in MeOH (3 mL) and NaOMe (1M in MeOH, 0.1 mL) was added and the mixture stirred for 1 h at room temperature. The reaction mixture was acidified with amberlite to pH 6, filtered and the solvent was removed under reduced pressure. The resulting syrup was taken up in pyridine (3 mL) and cooled to 0 °C. To this benzoyl chloride (223 mg, 1.59 mmol, 185 µL) was added and the reaction allowed to attain room temperature for 16 h. The reaction mixture was diluted with Et_2O washed with 1M HCl, water, brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Purification by flash chromatography (EtOAc-cyclohexane 1:4) gave **3** (123 mg, 81%) as a colourless oil; R_f 0.39 (EtOAc-cyclohexane 2:5); $[\alpha]_D$ -4.04 (c 4.1, $CHCl_3$); IR (film) cm^{-1}: 3066, 2957, 1733, 1450, 1098; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.96 (2H, dd, *J* 8.4 Hz, *J* 1.3 Hz, Ar-H), 7.93 (2H, dd, *J* 8.4 Hz, *J* 1.3 Hz, Ar-H), 7.87 (2H, dd, *J* 8.4 Hz, *J* 1.3 Hz, Ar-H), 7.50 (2H, td, *J* 7.5 Hz, *J* 0.7 Hz, Ar-H), 7.43 (1H, tt, *J* 7.5 Hz, *J* 1.2 Hz, Ar-H), 7.37 (4H, td, *J* 7.8 Hz, *J* 1.5 Hz, Ar-H), 7.29 (2H, t, *J* 7.8 Hz, Ar-H), 5.92 (1H, t, *J* 9.4 Hz, H-3), 5.71 (1H, t, *J* 9.4 Hz, H-4), 5.54 (1H, dd, *J* 9.4 Hz, *J* 7.4 Hz, H-2), 4.87 (1H, d, *J* 7.4 Hz, H-1), 4.37 (1H, d, *J* 9.4 Hz, H-5), 3.97 (1H, dt, *J* 9.7 Hz, *J* 6.4 Hz, CH*H*O), 3.69 (3H, s, OC*H*$_3$), 3.55 (1H, dt, *J* 9.7 Hz, *J* 6.7 Hz, C*H*HO), 1.52 (2H, m), 1.26 (2H, m), 0.76 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.4,

165.6, 165.1, 164.9 (each C=O), 133.3, 133.2, 133.1, 129.75, 129.72, 129.67, 129.8, 128.8, 128.8, 128.4, 128.3, 128.3 (each Ar-C), 101.1 (C-1), 72.9 (C-5), 72.2 (C-3), 71.6 (C-2), 70.2 (C-4), 70.1 (*C*H), 52.8 (OC*H*$_3$), 31.3 (*C*H$_2$), 18.8 (*C*H$_2$), 13.5 (*C*H$_3$); ES-HRMS calcd for $C_{32}H_{32}O_{10}Na$ 599.1893, found *m/z* 599.1893 $[M+Na]^+$.



1,2,3,4-Tetra-O-α-D-galactopyranuronic acid[10]

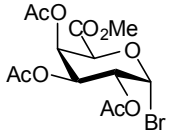
Galacturonic acid monohydrate (10.74 g, 55.4 mmol) was dried under vacuum for 4 h, 150 mL of Ac_2O was added followed by I_2 (702 mg, 2.76 mmol) and the reaction stirred at room temp for 2 h. The reaction was concentrated to 30 mL and the residue diluted with Et_2O, washed with sodium thiosulfate, water, brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. The resulting syrup was taken up in THF (60 mL) and water (60 mL), the reaction was stirred for 16 h at room temperature. The solvent was removed under reduced pressure to give the title compound (5.42 g, 27%) as a white solid; R_f 0.27 (EtOAc-cyclohexane 1:1); IR (film) cm^{-1}: 3507, 2945, 1756, 1370, 1217, 1039; ^1H NMR ($CDCl_3$, 500 MHz): δ 9.31 (1H, bs, OH), 6.37 (1H, d, *J* 3.4 Hz, H-1), 5.75 (1H, m, H-4), 5.30 (1H, dd, *J* 10.8 Hz, *J* 3.1 Hz, H-3), 5.23 (1H, dd, *J* 10.8 Hz, *J* 3.4 Hz, H-2), 4.71 (1H, d, *J* 0.7 Hz, H-5), 2.07 (3H, s), 2.02 (3H, s), 1.92 (3H, s), 1.90 (3H, s) (each OAc); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.4, 170.2, 170.1, 169.1, 168.6 (each C=O), 89.5 (C-1), 70.5 (C-5), 68.7 (C-4), 67.3 (C-3), 66.2 (C-2), 20.8, 20.7, 20.6 (2s) (each OAc); ES-HRMS calcd for $C_{14}H_{18}O_{11}Na$ 385.0747, found *m/z* 385.0755 $[M+Na]^+$.



1,2,3,4-Tetra-O-α-D-galactopyranuronic acid, methyl ester[11]

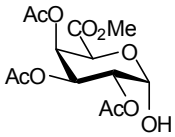
1,2,3,4-Tetra-*O*-α-D-galactopyranuronic acid (5.42 g, 14.9 mmol) and K_2CO_3 (10.3 g, 74.9 mmol) were dissolved in THF (100 mL) to this MeI (4.25 g, 29.9 mmol, 1.86 mL) and 18-Crown-6 were added and the reaction stirred for 16 h at room temperature. The reaction was diluted with Et_2O washed with water, brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Chromatography

(EtOAc-cyclohexane 1:2) gave the title compound (1.00 g, 18 %) as a colourless oil; R_f 0.27 (EtOAc-cyclohexane 1:1); IR (film) cm^{-1}: 2958, 1755, 1438, 1372, 1224, 1078, 940, 730; ^1H NMR ($CDCl_3$, 500 MHz): δ 6.37 (1H, d, *J* 2.8 Hz, H-1), 5.68 (1H, m, H-4), 5.25 (2H, m, H-2, H-3), 4.67 (1H, d, *J* 1.2 Hz, H-5), 3.63 (3H, s, OC*H*$_3$), 2.03 (3H, s), 1.99 (3H, s), 1.90 (3H, s), 1.89 (3H, s) (each OAc); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.6, 169.4, 169.3, 168.2, 166.3 (each C=O), 89.2 (C-1), 70.4 (C-5), 68.3 (C-4), 66.7, 65.7 (C-3 and C-4), 52.4 (O*C*H$_3$), 20.4, 20.2, 20.1 (2s) (each OAc); ES-HRMS calcd for $C_{15}H_{20}O_{11}Na$ 399.0903, found *m/z* 399.0912 $[M+H]^+$.



1-Bromo-2,3,4-tri-O-acetyl-α-D-galactopyranuronic acid, methyl ester

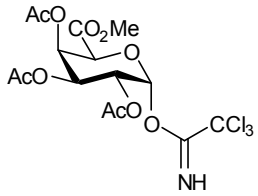
1,2,3,4-Tetra-*O*-α-D-galactopyranuronic acid, methyl ester (500 mg, 1.31 mmol) was dissolved in CH_2Cl_2 (2 mL) and cooled to 0 °C. To this HBr (33% in AcOH, 4 mL) was added and the reaction stirred for a further 4 h. The reaction mixture was diluted with Et_2O, washed with water, satd $NaHCO_3$, water, brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure to give the title compound (282 mg, 53%) as a colourless oil; R_f 0.58 (EtOAc-cyclohexane 1:1); IR (film) cm^{-1}: 2992, 2957, 1755, 1372, 1220, 1093, 1013; ^1H NMR ($CDCl_3$, 500 MHz): δ 6.72 (1H, d, *J* 3.9 Hz, H-1), 5.77 (1H, dd, *J* 3.2 Hz, *J* 1.2 Hz, H-4), 5.40 (1H, dd, *J* 10.6 Hz, *J* 3.2 Hz, H-3), 5.05 (1H, dd, *J* 10.6 Hz, *J* 3.9 Hz, H-2), 4.84 (1H, d, *J* 1.2 Hz, H-5), 3.73 (3H, s, OC*H*$_3$), 2.06 (3H, s), 1.97 (6H, s) (each OAc); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.7, 169.5, 169.3, 165.7 (each C=O), 87.2 (C-1), 72.3 (C-5), 67.8 (C-4), 67.5 (C-3), 67.1 (C-2), 52.8 (O*C*H$_3$), 20.5, 20.4, 20.3 (each OAc).



2,3,4-Tri-O-acetyl-α-D-galactopyranuronic acid, methyl ester

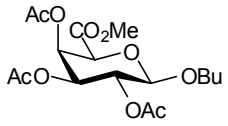
2,3,4-Tri-*O*-acetyl-1-bromo-α-D-galactopyranuronic acid, methyl ester (280 mg, 0.696 mmol) was dissolved in acetone (4 mL) and water (1 mL), to this Ag_2CO_3 (96 mg, 0.348 mmol) was added and the reaction stirred for 16 h at room temperature.

The reaction was filtered through Celite, which was rinsed with CH_2Cl_2 and concentrated to give the title compound (145 mg, 61 %) as a colourless oil; $[\alpha]_D$ +96.2 (c 0.51, $CHCl_3$); IR (film) cm^{-1}: 3462, 2958, 1752, 1372, 1299, 1065, 1030, 906; ^1H NMR ($CDCl_3$, 500 MHz): δ 5.76 (1H, dd, *J*, 3.3 Hz, *J* 1.2 Hz, H-4), 5.60 (1H, t, *J* 3.5 Hz, H-1), 5.42 (1H, dd, *J* 10.8 Hz, *J* 3.3 Hz, H-3), 5.14 (1H, dd, *J* 10.8 Hz, *J* 3.3 Hz, H-2), 4.87 (1H, d, *J* 1.2 Hz, H-5). 4.63 (1H, brs, O*H*), 3.72 (3H, s, OC*H*$_3$), 2.07 (3H, s), 2.06 (3H, s), 1.96 (3H, s) (each OAc); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.3, 170.0, 169.8, 168.2 (each C=O), 90.7 (C-1), 69.1 (C-4), 68.1 (C-5), 67.8 (C-2), 67.0 (C-3), 52.7 (O*C*H$_3$), 20.7, 20.5, 20.4 (each OAc); ES-HRMS calcd for $C_{13}H_{18}O_{10}Na$ 357.0798, found *m/z* 357.0807 $[M+Na]^+$.



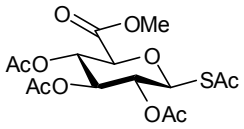
2,3,4-Tri-O-acetyl-1-(2,2,2-trichloroethanimidate)-α-D-galactopyranuronic acid, methyl ester

2,3,4-Tri-*O*-acetyl-α-D-galactopyranuronic acid, methyl ester (145 mg, 0.426 mmol) was dissolved in CH_2Cl_2 (5 mL) and cooled to 0 °C. To this Cl_3CCN (4.26 mmol, 42 μL), and DBU (5 drops) were added, and the reaction was stirred for 5 h, concentrated to 1 mL and purified by flash chromatography (EtOAc-cyclohexane 1:2) to give the title compound (82 mg, 40%) as a white solid; R_f 0.37 (EtOAc-cyclohexane 1:1); Mp 122.4 - 122.8 °C; $[\alpha]_D$ +123.8 (c 3.8, $CHCl_3$); IR (film) cm^{-1}: 2957, 1754, 1678, 1371, 1222, 1075, 1017; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.72 (1H, s, NH), 6.75 (1H, d, *J* 3.4 Hz, H-1), 5.87 (1H, dd, *J* 3.1 Hz, *J* 1.1 Hz, H-4), 5.48 (1H, dd, *J* 10.8 Hz, *J* 3.1 Hz, H-3), 5.42 (1H, dd, *J* 10.8 Hz, *J* 3.4 Hz, H-2), 4.82 (1H, d, *J* 1.1 Hz, H-5), 3.76 (3H, s, OC*H*$_3$), 2.13 (3H, s), 2.03 (3H, s), 2.02 (3H, s) (each OAc); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.8 (2s), 169.6, 166.4, 160.6 (each C=O), 93.4 (C-1), 70.7 (C-5), 68.6 (C-4), 67.1 (C-3), 66.5 (C-2), 52.8 (O*C*H$_3$), 20.6, 20.5, 20.4 (each OAc). ES-HRMS calcd for $C_{15}H_{18}O_{10}NCl_3Na$ 499.9894, found *m/z* 499.9916 $[M+Na]^+$.



Butyl 2,3,4-tri-O-acetyl-β-D-galactopyranosiduronic acid, methyl ester 6

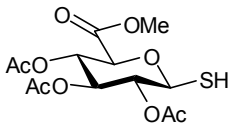
A mixture of trichloroacetamide precursor (82 mg, 0.169 mmol) and molecular sieves 4 Å (50 mg) were placed under reduced pressure for 1 h. CH_2Cl_2 (2 mL) and *n*-BuOH (0.381 mmol, 35 μL) were added and the solution was stirred for 40 min at room temperature. The solution was cooled to 0 °C, to this TMSOTf (0.05M in CH_2Cl_2, 0.017 mmol, 0.34 mL) was added and the reaction stirred for a further 40 min. Solid $NaHCO_3$ (50 mg) was added and the mixture stirred for 20 min, then filtered through Celite, which was rinsed with CH_2Cl_2. The solvent was removed under reduced pressure and the residue purified by flash chromatography (EtOAc-cyclohexane 1:4) to give **6** (58 mg, 86%) as a colourless oil; R_f 0.37 (EtOAc-cyclohexane 1:1); $[\alpha]_D$ +8.55 (c 1.45, $CHCl_3$); IR (film) cm^{-1}: 2050, 2874, 1705, 1647, 1369, 1219, 1046; ^1H NMR ($CDCl_3$, 500 MHz): δ 5.70 (1H, dd, *J* 3.5 Hz, *J* 1.2 Hz, H-4), 5.24 (1H, dd, *J* 10.5 Hz, *J* 8.0 Hz, H-2), 5.07 (1H, dd, *J* 10.5 Hz, *J* 3.5 Hz, H-3), 4.48 (1H, d, *J* 8.0 Hz, H-1), 4.30 (1H, d, *J* 1.2 Hz, H-5), 4.00 (1H, dt, *J* 9.5, *J* 6.2 Hz, OCH*H*), 3.76 (3H, s, OC*H*$_3$), 3.49 (1H, dt, *J* 9.5, *J* 6.8 Hz, OC*H*H), 2.11 (3H, s), 2.04 (3H, s), 1.99 (3H, s) (each OAc), 1.58 (2H, m), 1.35 (2H, m), 0.90 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.1, 169.9, 169.2 (each C=O), 166.5 (C-6), 101.2 (C-1), 72.4 (C-5), 70.6, (C-3), 70.1 (O*C*H$_2$), 68.6 (C-2), 68.4 (C-4), 50.7 (O*C*H$_3$), 31.3 (*C*H$_2$), 20.7, 20.6, 20.5 (each OAc), 18.9 (*C*H$_2$), 13.7 (*C*H$_3$); ES-HRMS calcd for $C_{17}H_{26}O_{10}Na$ 413.1424, found *m/z* 413.1438 $[M+Na]^+$.



Methyl 2,3,4-tri-O-acetyl-1-β-thioacetyl-D-glucopyranosiduronate[4]

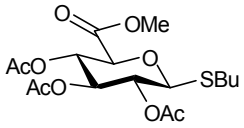
1-Bromo-2,3,4-tri-*O*-acetyl-α-D-galactopyranuronic acid, methyl ester (2.66 g, 6.62 mmol) was dissolved in DMF (20 mL) and KSAc (0.92 g, 8.07 mmol) was added and the reaction stirred at room temperature for 3 h. The solvent was removed under reduced pressure, and the residue filtered through silica (EtOAc-cyclohexane 1:1). The solvent was removed and the title compound was recovered by recrystallisation from absolute EtOH to give the title compound (1.34 g, 51%) as an off white solid; R_f

0.59 (EtOAc-cyclohexane 3:1); $[\alpha]_D$ +17.2 (c 2.16, $CHCl_3$); Mp 163.6-164.0 °C; IR (film) cm^{-1}: 2956, 1654, 1711, 1375, 1217, 1077, 1036; ^1H NMR ($CDCl_3$, 600 MHz): δ 5.33 (1H, t, *J* 9.7 H, H-3), 5.30 (1H, d, *J* 10.4 Hz, H-1), 5.20 (1H, t, *J* 9.7 Hz, H-4), 5.14 (1H, dd, *J* 10.4 Hz, *J* 9.7 Hz, H-2), 4.16 (1H, d, *J* 9.7 Hz, H-5), 3.73 (3H, s, C*H*-*3*), 2.38 (3H, s, SAc), 2.03 (3H, s, OAc), 2.02 (6H, s, OAc); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 191.7, 169.8, 169.3, 169.2, 166.7 (each C=O), 80.2 (C-1), 76.5 (C-5), 73.1 (C-3), 69.3 (C-4), 68.7 (C-2), 52.9 (O*C*H_3), 30.8 (SAc), 20.5 (2s), 20.4 (each OAc); ES-HRMS calcd for $C_{15}H_{20}O_{10}SNa$ 415.0675, found *m/z* 415.0656 $[M+Na]^+$; Anal. Calcd for $C_{15}H_{20}O_{10}S$: C, 45.92; H, 5.14: S, 8.17. Found: C, 45.88; H, 5.04: S, 8.08.



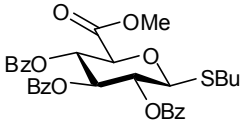
Methyl 2,3,4-tri-O-acetyl-1-β-thio-D-glucopyranosiduronate[4]

Methyl 2,3,4-tri-*O*-acetyl-1-β-thio-D-glucopyranosiduronate (400 mg, 1.01 mmol) was dissolved in $CHCl_3$-MeOH 1:1 (8 mL) and cooled to 0 °C. Nitrogen was bubbled through the solution for 5 min, followed by the addition of NaSMe (70 mg, 1.01 mmol). The reaction was stirred for 5 min at 0 °C and then poured onto 1% aq HCl (40 mL), and extracted with CH_2Cl_2 (2 x 30 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. Recrystallisation from absolute EtOH gave the title compound as an orange solid (217 mg, 61%); R_f 0.52 (EtOAc-cyclohexane 3:1); $[\alpha]_D$ -2.77 (c 0.94, $CHCl_3$); Mp 122.6-122.9 °C; IR (film) cm^{-1}: 2955, 2559, 1752, 1375, 1218, 1072, 1036; ^1H NMR ($CDCl_3$, 400 MHz): δ 5.24 (2H, m, H-3, H-4), 5.00 (1H, m, H-2), 4.58 (1H, t, *J* 9.9 Hz, H-1), 4.05 (1H, d, *J* 9.6 Hz, H-5), 3.76 (3H, s, OC*H*$_3$), 2.38 (1H, d, *J* 9.9 Hz, SH), 2.08 (3H, s), 2.03 (3H, s), 2.02 (3H, s) (each OAc); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.9, 169.5, 169.3, 166.7 (each C=O), 79.0 (C-1), 76.6 (C-5), 73.2 (C-2), 72.8, 69.3 (C-3 and C-4), 53.0 (O*C*H_3), 20.7, 20.6, 20.5 (each OAc).



Methyl 1-β-thiobutyl-2,3,4-tri-*O*-acetyl-D-glucopyranosiduronate 4

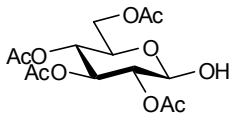
Methyl 2,3,4-tri-*O*-acetyl-1-β-thio-D-glucopyranosiduronate (50 mg, 0.140 mmol) was dissolved in DMF (2 mL) and cooled to 0 °C. To this NaH (5.4 mg, 0.140 mmol) was added and the reaction stirred for 5 min, followed by the addition of BuI (25.8 mg, 0.140 mmol, 16 μL) and the mixture was allowed to warm to room temperature for 2 h. The reaction mixture was diluted with Et_2O, washed with water, brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Chromatography (EtOAc-cyclohexane 1:1) gave **4** (39 mg, 57%) as a yellow solid; R_f 0.43 (EtOAc-cyclohexane 1:1); IR (film) cm^{-1}: 2954, 2858, 1754, 1374, 1219, 1071, 1036; ^1H NMR ($CDCl_3$, 500 MHz): δ 5.27 (1H, t, *J* 9.2 Hz, H-3), 5.22 (1H, t, *J* 9.2 Hz, H-4), 5.05 (1H, dd, *J* 10.0 Hz, *J* 9.2 Hz, H-2), 4.51 (1H, d, *J* 10.0 Hz, H-1), 4.03 (1H, d, *J* 9.2 Hz, H-5), 3.75 (3H, s, OC*H*$_3$), 2.73 (1H, ddd, *J* 12.3 Hz, *J* 8.1 Hz, *J* 6.5 Hz, SC*H*H), 2.66 (1H, ddd, *J* 12.3 Hz, *J* 8.1 Hz, *J* 6.5 Hz, SC*H*H), 2.06 (3H, s, OAc), 2.02 (6H, s, OAc), 1.57 (2H, m), 1.40 (2H, m), 0.91 (3H, t, *J* 7.3 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.0, 169.3, 169.2, 166.9 (each C=O), 83.8 (C-1), 76.4 (C-5), 73.2 (C-3), 69.6 (C-2), 69.4 (C-4), 52.8 (O*C*H$_3$), 31.5 (*C*H$_2$), 29.6 (S*C*H$_2$), 21.8 (*C*H$_2$), 20.7, 20.6, 20.5 (each OAc), 13.5 (*C*H$_3$); ES-HRMS calcd for $C_{17}H_{26}O_9SNa$ 429.1195, found *m/z* 429.1214 $[M+Na]^+$.



Methyl 1-β-thiobutyl-2,3,4-tri-*O*-benzoyl-D-glucopyranosiduronate 5

Thioglycoside **4** (66 mg, 0.160 mmol) was dissolved in MeOH (3 mL) and NaOMe (1M in MeOH, 0.1 mL) was added and the reaction stirred for 1 h at room temperature. The reaction mixture was acidified with amberlite to pH 6, filtered and the solvent was removed under reduced pressure. The resulting syrup was taken up in pyridine (2 mL) and cooled to 0 °C, to this benzoyl chloride (0.15 mL, 1.44 mmol) was added and the reaction allowed to warm to room temperature for 16 h. The reaction was diluted with Et_2O, washed with 1M HCl, water, brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Chromatography

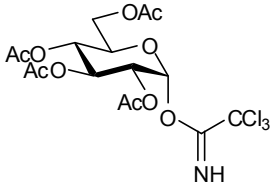
(EtOAc-cyclohexane 1:4) gave **5** (57 mg, 61 %) as a white solid; R_f 0.43 (EtOAc-cyclohexane 2:5); $[\alpha]_D$ -5.75 (c 2.85, $CHCl_3$); Mp 149.8-150.3 °C; IR (film) cm^{-1}: 3067, 2957, 1732, 1451, 1276, 1093; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.94 (2H, d, *J* 8.5 Hz, Ar-H), 7.92 (2H, d, *J* 8.5 Hz, Ar-H), 7.84 (2H, d, *J* 8.5 Hz, Ar-H), 7.51 (2H, td, *J* 7.5 Hz, *J* 1.2 Hz, Ar-H), 7.43 (1H, t, *J* 7.5 Hz, Ar-H), 7.37 (4H, t, *J* 7.8 Hz, Ar-H), 7.29 (2H, t, *J* 7.8 Hz, Ar-H), 5.92 (1H, t, *J* 9.8 Hz, H-3), 5.68 (1H, t, *J* 9.8 Hz, H-4), 5.58 (1H, t, *J* 9.8 Hz, H-2), 4.83 (1H, d, *J* 9.8 Hz, H-1), 4.34 (1H, d, *J* 9.8 Hz, H-5), 3.70 (3H, s, OC*H*$_3$), 2.80 (1H, ddd, *J* 12.4 Hz, *J* 8.1 Hz, *J* 6.4 Hz, SC*H*H), 2.75 (1H, ddd, *J* 12.4 Hz, *J* 7.9 Hz, *J* 7.0 Hz, SC*H*H), 1.59 (2H, m), 1.38 (2H, m), 0.88 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.0, 165.6, 165.1, 165.0 (each C=O), 133.4, 133.3, 129.83, 129.78, 129.76, 129.12, 128.81, 128.75, 128.4, 128.34, 128.30 (each Ar-C), 84.2 (C-1), 76.7 (C-5), 73.5 (C-3), 70.2, 70.1 (C-2 and C-4), 52.8 (O*C*H$_3$), 31.5 (S*C*H$_2$), 29.7 (*C*H$_2$), 21.8 (*C*H$_2$), 13.5 (*C*H$_3$); ES-HRMS calcd for $C_{32}H_{32}O_9SNa$ 615.1665, found *m/z* 615.1655 $[M+Na]^+$.



2,3,4,6-Tetra-*O*-acetyl-D-glucopyranose

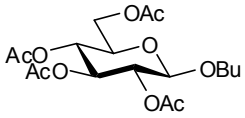
β-D-Glucose pentaacetate (2 g, 5.13 mmol) was dissolved in CH_2Cl_2 (4 mL) and cooled to 0 °C. To this HBr (33% in AcOH, 8 mL) was added and the reaction stirred at room temperature for 6 h. The reaction mixture was diluted with Et_2O washed with water, $NaHCO_{3\ (sat)}$, water, brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure to give a colourless oil. This was taken up in acetone (90 mL) and water (10 mL), to this Ag_2CO_3 (705 mg, 2.56 mmol) was added and the reaction stirred for 16 h at room temperature. The reaction mixture was filtered through Celite, which was rinsed with CH_2Cl_2, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Recrystallisation from absolute EtOH gave the title compound (1.209 g, 68%) as a white solid; R_f 0.40 (EtOAc-cyclohexane 3:1); $[\alpha]_D$ +15.7 (c 1.55, $CHCl_3$); Mp 107.9-108.4 °C; IR (film) cm^{-1}: 3450, 2955, 1753, 1369, 1225, 1038; ^1H NMR ($CDCl_3$, 500 MHz): δ 5.26 (1H, t, *J* 9.7 Hz, H-3), 5.08 (1H, t, *J* 9.7 Hz, H-4), 4.88 (1H, dd, *J* 9.7 Hz, *J* 8.4 Hz, H-2), 4.74 (1H, t, *J* 8.4 Hz, H-1), 4.26 (1H, dd, *J* 12.4 Hz, *J* 4.9 Hz, H-6a), 4.16 (1H, dd, *J* 12.4 Hz, *J* 2.3 Hz, H-6b), 3.76 (1H, ddd, *J* 9.7 Hz, *J* 4.9 Hz, *J* 2.3 Hz, H-5), 3.51 (1H, d, *J* 8.4 Hz, O*H*), 2.10 (3H, s),

2.09 (3H, s), 2.03 (3H, s), 2.02 (3H, s) (each OAc); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.9, 170.7, 170.0, 169.4 (each C=O), 95.6 (C-1), 73.3 (C-2), 72.2, 72.1 (C-3 and C-5), 68.5 (C-4), 62.0 (C-6), 20.7 (2s), 20.6 (2s) (each OAc).



2,3,4,6-Tetra-*O*-acetyl-1-(2,2,2-trichloroethanimidate)-α-D-glucopyranoside

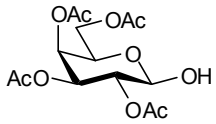
2,3,4,6-Tetra-*O*-acetyl-D-glucopyranose (400 mg, 1.15 mmol) was dissolved in CH_2Cl_2 (5 mL) and cooled to 0 °C. To this Cl_3CCN (11.5 mmol, 0.91 mL), and DBU (5 drops) were added. The reaction was stirred for 4 h at 0 °C, then concentrated to 2 mL and purified by flash chromatography (EtOAc-cyclohexane 1:4) to give the title compound (533 mg, 94%) as a white solid; R_f 0.42 (EtOAc-cyclohexane 1:1); Mp 47.8 – 48.1 °C; $[\alpha]_D$ +58.9 (c 2.9, $CHCl_3$); IR (film) cm^{-1}: 3321, 2961, 1752, 1370, 1224, 1039; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.70 (1H, s, NH), 6.57 (1H, d, *J* 3.7 Hz, H-1), 5.57 (1H, t, *J* 9.9 Hz, H-3), 5.18 (1H, t, *J* 9.9 Hz H-4), 5.14 (1H, dd, *J* 9.9 Hz, *J* 3.7 Hz, H-2), 4.28 (1H, dd, *J* 12.4 Hz, *J* 4.2 Hz, H-6a), 4.22 (1H, ddd, *J* 9.9 Hz, *J* 4.2 Hz, *J* 2.1 Hz, H-5), 4.14 (1H, dd, *J* 12.4 Hz, *J* 2.1 Hz, H-6b), 2.08 (3H, s), 2.05 (3H, s), 2.03 (3H, s), 2.02 (3H, s) (each OAc); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.5, 169.9, 169.8, 169.4, 160.8 (each C=O), 92.9 (C-1), 70.0 (C-5), 69.9 (C-3), 69.7 (C-2), 67.8 (C-4), 61.4 (C-6), 20.6 (2s), 20.5, 20.4 (each OAc); ES-HRMS calcd for $C_{18}H_{28}O_{10}Na$ 427.1580, found *m/z* 427.1585 $[M+Na]^+$.



Butyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside 1[12]

A mixture of 2,3,4,6-tetra-*O*-acetyl-1-(2,2,2-trichloroethanimidate)-α-D-glucopyranoside (444 mg, 0.902 mmol) and molecular sieves 4 Å (50 mg) were placed under reduced pressure for 1 h. CH_2Cl_2 (4 mL) and *n*-BuOH (9.02 mmol, 0.83 mL) were added and the solution was stirred for 40 min at room temperature. The solution was cooled to 0 °C and TMSOTf (0.05N, 0.090 mmol, 1.8 mL) was added and the reaction stirred for a further 30 min. Solid $NaHCO_3$ (50 mg) was added and the mixture stirred for 20 min, then filtered through Celite, which was rinsed with CH_2Cl_2. The solvent was removed under reduced pressure and the residue purified by

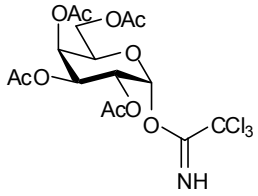
flash chromatography (EtOAc-cyclohexane 1:4) to give **1** as white solid (284 mg, 78%); R_f 0.20 (EtOAc-cyclohexane 2:5); Mp 47.8-48.1 °C; $[\alpha]_D$ -15.0 (c 1.15, $CHCl_3$); IR (film) cm^{-1}: 3435, 3299, 2959, 2875, 1750, 1372, 1227; ^1H NMR ($CDCl_3$, 500 MHz): δ 5.21 (1H, t, *J* 9.6 Hz, H-3), 5.08 (1H, t, *J* 9.6 Hz, H-4), 4.98 (1H, dd, *J* 9.6 Hz, *J* 8.0 Hz, H-2), 4.50 (1H, d, *J* 8.0 Hz, H-1), 4.27 (1H, dd, *J* 12.3 Hz, *J* 4.8 Hz, H-6a), 4.14 (1H, dd, *J* 12.3 Hz, *J* 2.4 Hz, H-6b), 3.88 (1H, dt, *J* 9.7 Hz, *J* 6.3 Hz, OC*H*H), 3.70 (1H, ddd, *J* 9.6 Hz, *J* 4.8 Hz, *J* 2.4 Hz, H-5), 3.49 (1H, dt, *J* 9.7 Hz, *J* 6.8 Hz, OCH*H*), 2.09 (3H, s), 2.04 (3H, s), 2.02 (3H, s), 2.00 (3H, s) (each OAc), 1.56 (2H, m), 1.35 (2H, m), 0.91 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.6, 170.2, 169.3, 169.2 (each C=O), 100.8 (C-1), 72.8 (C-3), 71.7 (C-5), 71.3 (C-2), 69.8 (O*C*H_2), 68.5 (C-4), 62.0 (C-6), 31.3 (*C*H_2), 20.6, 20.5 (2s), 20.4, 18.9 (*C*H_2), 13.6 (*C*H_3); ES-HRMS calcd for $C_{18}H_{28}O_{10}Na$ 427.1580, found *m/z* 427.1585 $[M+Na]^+$.



2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranose

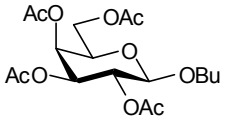
β-D-Galactose pentaacetate (2 g, 5.13 mmol) was dissolved in CH_2Cl_2 (4 mL) and cooled to 0 °C. To this HBr (33% in AcOH, 8 mL) was added and the reaction stirred at room temperature for 6 h. The reaction mixture was diluted with Et_2O washed with water, $NaHCO_{3\ (sat)}$, water, brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure to give the α-bromide (1.96 g, 93%) as a colourless oil. This was taken up in acetone (90 mL) and water (10 mL) and Ag_2CO_3 (705 mg, 2.56 mmol) was added and the reaction stirred for 16 h at room temperature. The reaction mixture was filtered through Celite, which was rinsed with CH_2Cl_2, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Recrystallisation from absolute EtOH gave the title compound (804 mg, 47%) as a white solid; R_f 0.20 (EtOAc-cyclohexane 1:1); $[\alpha]_D$ +22 (c 1.7, $CHCl_3$); IR (film) cm^{-1}: 3440, 2973, 1744, 1371, 1228, 1049; ^1H NMR ($CDCl_3$, 500 MHz): δ 5.41 (1H, m, H-4), 5.07 (2H, m, H-2, H-3), 4.69 (1H, ddd, *J* 9.1 Hz, *J* 4.5 Hz, *J* 3.4 Hz, H-1), 4.16 (2H, m, H-6a, H-6b), 3.96 (1H, td, *J* 6.6 Hz, *J* 0.9 Hz, H-5), 3.46 (1H, d, *J* 9.1 Hz, OH), 2.16 (3H, s), 2.11 (3H, s), 2.06 (3H, s), 2.00 (3H, s) (each OAc); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.3, 170.4, 170.1, 169.9 (each C=O), 96.1 (C-1), 71.2, 71.1, 70.3 (C-2, 3, and 5), 67.1 (C-

4), 61.4 (C-6), 20.8, 20.7, 20.6, 20.5 (each OAc); ES-HRMS calcd for $C_{14}H_{20}O_{10}Na$ 371.0954, found *m/z* 371.0958 $[M+Na]^+$.



2,3,4,6-Tetra-*O*-acetyl-1-(2,2,2-trichloroethanimidate)-α-D-galactopyranoside

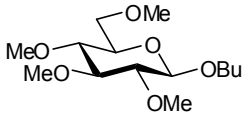
2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranose (657 mg, 1.89 mmol) was dissolved in CH_2Cl_2 (7 mL) and cooled to 0 °C. To this Cl_3CCN (1.89 mL, 18.9 mmol), and DBU (5 drops) were added. The reaction was stirred for 4 h at 0 °C, then concentrated to 2 mL and purified by flash chromatography (EtOAc-cyclohexane 1:4) to give the title compound (857 mg, 92%) as a yellow oil; R_f 0.44 (1:1 EtOAc-cyclohexane); $[\alpha]_D$ -6.9 (c 9.0, $CHCl_3$); IR (film) cm^{-1}: 3319, 1749, 1676, 1371, 1233, 1070; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.67 (1H, s, NH), 6.61 (1H, d, *J* 3.5 Hz, H-1), 5.56 (1H, dd, *J* 3.1 Hz, *J* 1.1 Hz, H-4), 5.43 (1H, dd, *J* 10.8 Hz, *J* 3.1 Hz, H-3), 5.34 (1H, dd, *J* 10.8 Hz, *J* 3.5 Hz, H-2), 4.44 (1H, t, *J* 6.7 Hz, H-5), 4.17 (1H, dd, *J* 11.3 Hz, *J* 6.7 Hz, H-6a), 4.09 (1H, dd, *J* 11.3 Hz, *J* 6.7 Hz, H-6b), 2.17 (3H, s), 2.03 (3H, s), 2.02 (3H, s), 2.01 (3H, s) (each OAc); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.2, 170.1, 170.0, 169.9 (each C=O), 161.0 (C=N), 93.6 (C-1), 69.0 (C-5), 67.5, 67.4 (C-3 and C-4), 67.0 (C-2), 61.3 (C-6), 20.6 (3s), 20.5 (each OAc); ES-HRMS calcd for $C_{16}H_{20}O_{10}NCl_3Na$ 514.0050, found *m/z* 514.0026 $[M+Na]^+$.



Butyl 2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside 11[13]

A mixture of trichloroacetamide precursor (836 mg, 1.70 mmol) and molecular sieves 4 Å (50 mg) were placed under reduced pressure for 1 h. CH_2Cl_2 (8 mL) and *n*-BuOH (0.46 mL, 5.09 mmol) were added and the solution was stirred for 40 min at room temperature. The solution was cooled to 0 °C and TMSOTf (0.1N, 0.169 mmol, 1.7 mL) was added and the reaction stirred for a further 30 min. Solid $NaHCO_3$ (50 mg) was added and the mixture stirred for 20 min, then filtered through Celite, which was rinsed with CH_2Cl_2. The solvent was removed under reduced pressure and the residue purified by flash chromatography (EtOAc-cyclohexane 1:4) to give **11** as a colourless

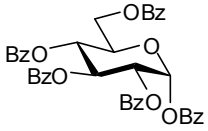
oil (654 mg, 95%); R_f 0.35 (EtOAc-cyclohexane 1:1); $[\alpha]_D$ -6.9 (c 9.0, $CHCl_3$); IR (film) cm^{-1}: 3437, 2959, 2875, 1747, 1431, 371, 1230, 1070; ^1H NMR ($CDCl_3$, 500 MHz): δ 5.35 (1H, dd, *J* 3.4 Hz, *J* 0.8 Hz, H-4), 5.15 (1H, dd, *J* 10.5 Hz, *J* 8.0 Hz, H-2), 5.00 (1H, dd, *J* 10.5 Hz, *J* 3.4 Hz, H-3), 4.43 (1H, d, *J* 8.0 Hz, H-1), 4.15 (1H, dd, *J* 11.2 Hz, *J* 6.5 Hz, H-6a), 4.09 (1H, dd, *J* 11.2 Hz, *J* 6.9 Hz, H-6b), 3.86 (2H, m, H-5, OC*H*H), 3.45 (1H, dt, *J* 9.6 Hz, *J* 6.8 Hz, OCH*H*), 2.11 (3H, s), 2.01 (6H, s), 1.94 (3H, s) (each OAc), 1.52 (2H, m), 1.31 (2H, m), 0.87 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.3, 170.2, 170.0, 169.3 (each C=O), 101.2 (C-1), 70.9 (C-3), 70.5 (C-5), 69.8 (C*H*$_2$O), 68.9 (C-2), 67.0 (C-4), 61.2 (C-6), 31.3 (*C*H$_2$), 20.6, 20.5 (2s), 20.4, 18.8 (*C*H$_2$), 13.6 (*C*H$_3$); ES-HRMS calcd for $C_{18}H_{28}O_{10}Na$ 427.1580, found *m/z* 427.1566 $[M+Na]^+$.



Butyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside 8

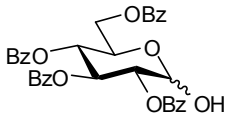
Glucoside **1** (100 mg, 0.248 mmol) was dissolved in MeOH (3 mL) to this NaOMe (1M in MeOH, 5 drops) was added. The reaction was stirred for 2 h at room temperature, acidified with amberlite to pH 6, filtered and the solvent was removed under reduced pressure to give a colourless oil. The oil was taken up in DMF (3 mL) and cooled to 0 °C, to this NaH (1.48 mmol, 59 mg) was added followed by MeI (1.48 mmol, 92 μL) and the reaction allowed to warm to room temperature over 16 h. The reaction was diluted with Et_2O washed with water, brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Chromatography (EtOAc-cyclohexane 2:5) gave **8** (36 mg, 50%) as a colourless oil; R_f 0.18 (EtOAc-cyclohexane 1:4); $[\alpha]_D$ -21.4 (c 1.6, $CHCl_3$); IR (film) cm^{-1}: 3933, 2834, 1460, 1374, 1091; ^1H NMR ($CDCl_3$, 500 MHz): δ 4.21 (1H, d, *J* 7.8 Hz, H-1), 3.90 (1H, dt, *J* 9.5 Hz, *J* 6.5 Hz, OC*H*H), 3.63 (1H, dd, *J* 10.6 Hz, *J* 2.0 Hz, H-6a), 3.62 (3H, s, OC*H*$_3$), 3.62 (3H, s, OC*H*$_3$), 3.55 (1H, dd, *J* 10.6 Hz, *J* 5.0 Hz, H-6b), 3.52 (3H, s, OC*H*$_3$), 3.48 (1H, dt, *J* 9.5 Hz, *J* 6.9 Hz, OCH*H*), 3.40 (3H, s, OC*H*$_3$), 3.26 (1H, ddd, *J* 8.6 Hz, *J* 5.0 Hz, *J* 2.0 Hz, H-5), 3.15 (1H, t, *J* 8.6 Hz, H-3), 3.11 (1H, t, *J* 8.6 Hz, H-4), 2.98 (1H, dd, *J* 7.8 Hz, *J* 8.6 Hz, H-2), 1.59 (2H, m), 1.39 (2H, m), 0.92 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 103.4 (C-1), 86.4 (C-3), 83.8 (C-2), 79.5 (C-4), 74.6 (C-5), 71.5

(C-6), 69.6 (O*C*H_3), 60.7, 60.4, 60.3, 59.3 (each O*C*H_3), 31.7 (*C*H_2), 19.2 (*C*H_2), 13.8 (*C*H_3); ES-HRMS calcd for $C_{14}H_{28}O_6Na$ 315.1784, found *m/z* 315.1772 $[M+Na]^+$.



α-D-Glucopyranose pentabenzoate

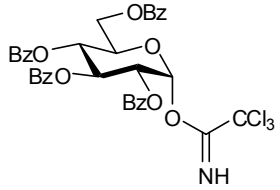
D-Glucose (1.00 g, 5.56 mmol) in pyridine (12 mL) was cooled to 0 °C, to this benzoyl chloride (4.85 g, 34.5 mmol, 4 mL) was added portion wise and the reaction was allowed to warm to room temperature over 16 h. The reaction mixture was diluted with EtOAc, washed with 1M HCl, water, brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Recrystallisation from acetone/water gave the title compound (2.75 g, 71%) as a white solid; R_f 0.50 (CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.17 (2H, d, *J* 7.8 Hz, Ar-H), 8.04 (2H, t, *J* 7.2 Hz, Ar-H), 7.95 (2H, d, *J* 7.9 Hz, Ar-H), 7.88 (4H, d, *J* 7.9 Hz, Ar-H), 7.67 (1H, t, *J* 7.5 Hz, Ar-H), 7.57-7.29 (14H, m, Ar-H), 6.85 (1H, d, *J* 3.4 Hz, H-1), 6.32 (1H, t, *J* 9.9 Hz, H-3), 5.86 (1H, t, *J* 9.9 Hz, H-4), 5.68 (1H, dd, *J* 9.9 Hz, *J* 3.4 Hz, H-2), 4.61 (2H, m, H-5, H-6a), 4.49 (1H, dd, *J* 12.8 Hz, *J* 4.7 Hz, H-6b); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.1, 165.9, 165.3, 165.1, 164.4 (each C=O), 133.9, 133.5 (2s), 133.3, 133.1, 132.9, 130.0, 129.9, 129.8 (2s), 129.7, 129.6, 129.5, 129.0, 128.8 (2s), 128.7, 128.5, 128.4 (3s), 128.3 (each Ar-C), 90.0 (C-1), 70.5 (2s, CH), 70.4 (CH), 68.8 (C-4), 62.5 (C-6); ES-HRMS calcd for $C_{41}H_{32}O_{11}Na$ 723.1842, found *m/z* 723.1852 $[M+Na]^+$.



2,3,4,6-Tetra-O-benzoyl-D-glucopyranose

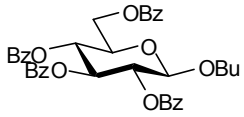
α-D-Glucopyranose pentabenzoate (4 g, 5.71 mmol) was dissolved in CH_2Cl_2 (20 mL) and cooled to 0 °C. To this HBr (33% in AcOH, 10 mL) was added and the reaction stirred at room temperature for 6 h. The reaction mixture was diluted with Et_2O washed with water, $NaHCO_{3\,(sat)}$, water, brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure to give a colourless oil. This was taken up in acetone (100 mL) and water (2 mL), to this Ag_2CO_3 (788 mg, 2.86 mmol) was added

and the reaction stirred for 16 h at room temperature. The reaction mixture was filtered through Celite, which was rinsed with CH_2Cl_2, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Chromatography (EtOAc-cyclohexane 1:4) gave the title compound (2.81 g, 83%) as a white solid (α:β = 3:1); R_f 0.31 (EtOAc-cyclohexane 1:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04 (2H, d, *J* 7.3 Hz, Ar-H), 7.98 (2H, d, *J* 7.3 Hz, Ar-H), 7.94 (2H, d, *J* 7.3 Hz, Ar-H), 7.88 (2H, d, *J* 7.3 Hz, Ar-H), 7.55-7.25 (12H, m, Ar-H), 6.26 (1H, t, *J* 9.9 Hz, H-3), 5.74 (1H, m, H-4), 5.32 (1H, dd, *J* 9.9 Hz, *J* 3.2 Hz, H-2), 4.67 (2H, m, H-5, H-6a), 4.43 (1H, dd, *J* 12.5 Hz, *J* 4.4 Hz, H-6b), 3.74 (1H, d, *J* 3.2 Hz, H-1), 1.76 (1H, brs, OH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.3, 165.9, 165.8, 165.3 (each C=O), 133.4 (2s), 133.1, 129.9, 129.8 (4s), 129.7, 128. (3s), 128.3 (2s) (each Ar-C), 90.5 (C-1), 72.3 (C-2), 70.1 (C-3), 69.5 (C-4), 67.8 (C-5), 62.9 (C-6).



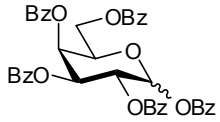
2,3,4,6-Tetra-O-benzoyl-1-(2,2,2-trichloroethanimidate)-α-D-glucopyranoside 3

2,3,4,6-Tetra-*O*-benzoyl-D-glucopyranose (2.22 g, 3.73 mmol) was dissolved in CH_2Cl_2 (80 mL) and cooled to 0 °C. To this Cl_3CCN (3.74 mL, 37.3 mmol), and DBU (5 drops) were added. The reaction was stirred for 4 h at 0 °C, then concentrated to 4 mL and purified by flash chromatography (EtOAc-cyclohexane 1:4) to give the title compound (1.87 g, 68%) as a colourless oil; R_f 0.26 (EtOAc-cyclohexane 1:4); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.56 (1H, s, NH), 7.96 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.89 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.87 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.79 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.49 (1H, t, *J* 7.4 Hz, Ar-H), 7.44 (2H, t, *J* 7.5 Hz, Ar-H), 7.35 (3H, t, *J* 7.7 Hz, Ar-H), 7.29 (4H, t, *J* 7.8 Hz, Ar-H), 7.23 (2H, t, *J* 7.8 Hz, Ar-H), 6.77 (1H, d, *J* 3.7 Hz, H-1), 6.20 (1H, t, *J* 10.0 Hz, H-3), 5.74 (1H, t, *J* 10.0 Hz, H-4), 5.55 (1H, dd, *J* 10.0 Hz, *J* 3.7 Hz, H-2), 4.58 (1H, m, H-5, H-6a), 4.42 (1H, dd, *J* 12.5 Hz, *J* 5.1 Hz, H-6b); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.0, 165.6, 165.4, 165.2 (C=O), 160.5 (C=N), 133.5, 133.3, 133.1, 129.9, 129.8, 129.7, 128.4 (2s), 128.3 (each Ar-C), 93.1 (C-1), 70.7 (2s, C-2, C-5), 70.2 (C-3), 68.7 (C-4), 62.5 (C-6).



Butyl 2,3,4,6-tetra-O-benzoyl-β-D-glucopyranoside 7

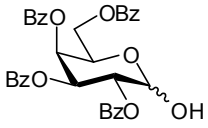
A mixture of trichloroacetamide precursor (543 mg, 0.735 mmol) and molecular sieves 4 Å (50 mg) were placed under reduced pressure for 1 h. CH_2Cl_2 (4 mL) and *n*-BuOH (101 µL, 1.10 mmol) were added and the solution was stirred for 40 min at room temperature. The solution was cooled to 0 °C and TMSOTf (0.05 N, 0.074 mmol, 1.5 mL) was added and the reaction stirred for 30 min. Solid $NaHCO_3$ (50 mg) was added and the mixture stirred for a further 20 min, then filtered through Celite, which was rinsed with CH_2Cl_2. The solvent was removed under reduced pressure and the residue purified by flash chromatography (EtOAc-cyclohexane 1:4) to give **7** as a colourless oil (188 mg, 18%); R_f 0.29 (EtOAc-cyclohexane 1:4), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.02 (2H, dd, *J* 8.4 Hz, *J* 1.2 Hz, Ar-H), 7.96 (2H, dd, *J* 8.4 Hz, *J* 1.2 Hz, Ar-H), 7.90 (2H, dd, *J* 8.4 Hz, *J* 1.2 Hz, Ar-H), 7.83 (2H, dd, *J* 8.4 Hz, *J* 1.2 Hz, Ar-H), 7.50 (3H, m, Ar-H), 7.39 (5H, m, Ar-H), 7.33 (2H, t, *J* 7.8 Hz, Ar-H), 7.26 (2H, t, *J* 7.7 Hz, Ar-H), 5.92 (1H, t, *J* 9.7 Hz, H-3), 5.68 (1H, t, *J* 9.7 Hz, H-4), 5.53 (1H, dd, *J* 9.7 Hz, *J* 7.8 Hz, H-2), 4.85 (1H, d, *J* 7.8 Hz, H-1), 4.65 (1H, dd, *J* 12.1 Hz, *J* 3.3 Hz, H-6a), 4.53 (1H, dd, *J* 12.1 Hz, *J* 5.3 Hz, H-6b), 4.17 (1H, ddd, *J* 9.7 Hz, *J* 5.3 Hz, *J* 3.3 Hz, H-5), 3.91 (1H, dt, *J* 9.7 Hz, *J* 6.4 Hz, OC*H*H), 3.56 (1H, dt, *J* 9.7 Hz, *J* 6.7 Hz, OCH*H*), 1.51 (2H, m, CH_2), 1.23 (2H, m, CH_2), 0.74 (3H, t, *J* 7.4 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 125 Mz): δ 166.2, 165.8, 165.2, 165.1 (each C=O), 133.4, 133.2, 133.1 (2s), 129.8 (2s), 129.7, 128.4, 128.3 (3s), 101.3 (C-1), 73.0 (C-3), 72.2 (C-5), 71.9 (C-2), 70.0 (OCH_2), 69.9 (C-4), 63.3 (C-6), 31.4 (CH_2), 18.9 (CH_2), 13.5 (CH_3);



D-Galactopyranose pentabenzoate[14]

D-Galactose (3g, 16.7 mmol) in pyridine (90 mL) was cooled to 0 °C and benzoyl chloride (14.65 g, 104 mmol, 12 mL) was added portion wise and the reaction was allowed to warm to room temperature over 16 h. The reaction mixture was diluted with EtOAc, washed with 1M HCl, water, brine, dried over $MgSO_4$, and the solvent

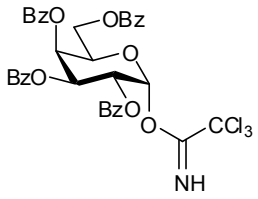
was removed under reduced pressure. Chromatography (EtOAc-cyclohexane 2:5) gave the title compound (3.60 g, 31%) (α:β ratio of 1:2) as a white solid; R_f 0.53 (EtOAc-cyclohexane 1:1); IR (film) cm^{-1}: 3063, 1728, 1265, 1108, 1068, 708; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.13-7.79 (18H, m, Ar-H), 7.65-7.20 (32H, m, Ar-H), 6.96 (1H, d, *J* 3.6 Hz, H-1α), 6.29 (1H, d, *J* 8.3 Hz, H-1β), 6.19 (1H, dd, *J* 3.2 Hz, *J* 0.9 Hz, H-4α), 6.12 (2H, m), 6.03 (1H, dd, *J* 10.7 Hz, *J* 3.6 Hz), 5.79 (1H, dd, *J* 10.3 Hz, *J* 3.5 Hz), 4.83 (1H, t, *J* 7.1 Hz), 7.67 (1H, dd, *J* 11.2 Hz, *J* 6.5 Hz), 4.58 (1H, t, *J* 6.5 Hz), 4.46 (1H, dd, *J* 11.2 Hz, *J* 6.5 Hz), 4.43 (1H, dd, *J* 11.3 Hz, *J* 6.9 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.2, 166.0, 165.7, 165.5 (2s), 165.4, 165.3, 164.7, 164.5, 133.9, 133.8, 133.7 (2s), 133.6, 133.4 (3s), 133.3, 133.2 (2s), 130.2 (2s), 130.0 (3s), 129.9, 129.8 (3s), 129.7, 128.8 (2s), 128.7 (3s), 128.5 (3s), 128.4 (2s), 128.3 (2s), 128.2, 128.1, 93.1, 90.7, 72.5, 71.6, 69.5, 68.8, 68.6, 68.5, 68.0, 67.7, 61.9, 61.8; ES-HRMS calcd for $C_{41}H_{32}O_{11}Na$ 723.1842, found *m/z* 723.1852 $[M+Na]^+$.



2,3,4,6-Tetra-O-benzoylgalactopyranose[15]

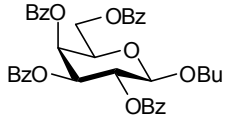
D-Galactopyranose pentabenzoate (5 g, 6.76 mmol) was dissolved in CH_2Cl_2 (5 mL) and cooled to 0 °C. To this HBr (33% in AcOH, 15 mL) was added and the reaction stirred at room temperature for 6 h. The reaction mixture was diluted with Et_2O washed with water, $NaHCO_{3\,(sat)}$, water, brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure to give a colourless oil. The residue was dissolved in acetone (230 mL) and water (20 mL) to this Ag_2CO_3 (929 mg, 3.38 mmol) was added and the reaction stirred for 16 h at room temperature. The reaction mixture was filtered through Celite, which was rinsed with CH_2Cl_2, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Chromatography (EtOAc-cyclohexane 1:4) gave the title compound (1.98 g, 40%) as a white solid (α:β = 3:1); R_f 0.32 (EtOAc-cyclohexane 2:5); ^1H NMR ($CDCl_3$, 500 MHz): δ 8.09 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 8.02 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.99 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.80 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H),7.62 (1H, t, *J* 7.4 Hz, Ar-H), 7.56-7.36 (9H, m, Ar-H), 7.24 (2H, t, *J* 8.1 Hz, Ar-H), 6.08 (2H, m, H-4, H-3), 5.85 (1H, d, *J* 3.5 Hz, H-1), 5.72 (1H, m, H-2), 4.88 (1H, t, *J* 6.5 Hz, H-5), 4.62 (1H, dd, *J* 11.4 Hz, *J* 6.5 Hz, H-6a), 4.40 (1H, dd, *J* 11.4 Hz, *J* 6.5 Hz, H-6b); ^{13}C NMR ($CDCl_3$, 125

MHz): δ 166.1, 166.0, 165.7, 165.5 (each C=O), 133.5, 133.4, 133.2, 133.1, 123.0, 129.9 (2s), 129.8 (4s), 129.7 (2s), 128.6, 128.5 (2s), 128.4 (2s), 128.3, 128.2 (each Ar-C), 91.1 (C-1), 69.5 (C-2), 69.3, 68.0 (C-3 and C-4), 67.0 (C-5), 62.4 (C-6); ES-HRMS calcd for $C_{34}H_{28}O_{10}Na$ 619.1580, found *m/z* 619.1565 $[M+Na]^+$.



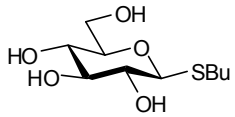
2,3,4,6-Tetra-O-benzoyl-1-(2,2,2-trichloroethanimidate)-α-D-galactopyranoside 16

2,3,4,6-Tetra-*O*-benzoylgalactopyranose (990 mg, 1.66 mmol) was dissolved in CH_2Cl_2 (20 mL) and then cooled to 0 °C. To this Cl_3CCN (1.67 mL, 16.6 mmol), and DBU (5 drops) was added. The reaction was stirred for 4 h at 0 °C, then concentrated to 2 mL and chromatography (EtOAc-cyclohexane 1:4) gave the title compound (939 mg, 76%) as a colourless oil; R_f 0.41 (EtOAc-cyclohexane 2:5); $[\alpha]_D$ +105 (c 6.05, $CHCl_3$); IR (film) cm^{-1}: 3338, 3066, 2969, 1728, 1269, 1104, 711; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.64 (1H, s, NH), 8.10 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.98 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.96 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.81 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.63 (1H, tt, *J* 7.4 Hz, *J* 1.1 Hz, Ar-H), 7.50 (4H, m, Ar-H), 7.45-7.29 (5H, m, Ar-H), 7.26 (2H, t, *J* 7.9 Hz, Ar-H), 6.93 (1H, d, *J* 3.6 Hz, H-1), 6.17 (1H, d, *J* 3.3 Hz, H-4), 6.09 (1H, dd, *J* 10.7 Hz, *J* 3.3 Hz, H-3), 5.98 (1H, dd, *J* 10.7 Hz, *J* 3.6 Hz, H-2), 4.88 (1H, t, *J* 6.5 Hz, H-5), 4.62 (1H, dd, *J* 11.5 Hz, *J* 6.5 Hz, H-6a), 4.45 (1H, dd, *J* 11.5 Hz, *J* 6.5 Hz, H-6b); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.9, 165.6, 165.5, 165.4 (each C=O), 160.6 (C=N), 133.7, 133.5, 133.3, 133.2, 129.9, 129.8, 129.7 (2s), 128.9 (2s), 128.7 (2s), 128.4, 128.3 (2s) (each Ar-C), 93.8 (C-1), 69.7 (C-5), 68.5, 68.4 (C-3 and C-4), 67.9 (C-2), 62.2 (C-6); ES-HRMS calcd for $C_{36}H_{28}O_{10}NCl_3Na$ 762.0676, found *m/z* 762.0686 $[M+Na]^+$.



Butyl 2,3,4,6-tetra-O-benzoyl-β-D-galactopyranoside 12

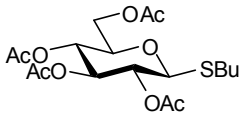
A mixture of the trichloroacetamide precursor (150 mg, 0.203 mmol) and molecular sieves 4 Å (50 mg) were placed under reduced pressure for 1 h. CH_2Cl_2 (4 mL) and *n*-BuOH (28 μL, 0.304 mmol) were added and the solution was stirred for 40 min at room temperature. The solution was cooled to 0 °C and TMSOTf (0.05N, 0.030 mmol, 0.6 mL) was added and the reaction stirred for a further 30 min. Solid $NaHCO_3$ (50 mg) was added and the mixture stirred for 20 min, then filtered through Celite, which was rinsed with CH_2Cl_2. The solvent was removed under reduced pressure and the residue purified by flash chromatography (EtOAc-cyclohexane 1:4) to give the title compound as a colourless oil (120 mg, 74%); R_f 0.41 (EtOAc-cyclohexane 2:5); $[\alpha]_D$ +72.5 (c 3.4, $CHCl_3$); IR (film) cm^{-1}: 3066, 2959, 1727, 1267, 1102, 1027; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.10 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 8.03 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.96 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.89 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.61 (1H, tt, *J* 7.4 Hz, *J* 1.2 Hz, Ar-H), 7.55 (1H, tt, *J* 7.4 Hz, *J* 1.2 Hz, Ar-H), 7.52-7.36 (8H, m, Ar-H), 7.24 (2H, t, *J* 7.9 Hz, Ar-H), 6.00 (1H, dd, *J* 3.4 Hz, *J* 0.7 Hz, H-4), 5.79 (1H, dd, *J* 10.4 Hz, *J* 7.9 Hz, H-2), 5.61 (1H, dd, *J* 10.4 Hz, *J* 3.4 Hz, H-3), 4.81 (1H, d, *J* 7.9 Hz, H-1), 4.69 (1H, dd, *J* 11.3 Hz, *J* 6.5 Hz, H-6a), 4.43 (1H, dd, *J* 11.3 Hz, *J* 6.8 Hz, H-6b), 4.32 (1H, m, H-5), 3.97 (1H, dt, *J* 9.8 Hz, *J* 6.3 Hz, OC*H*H), 3.59 (1H, dt, *J* 9.8 Hz, *J* 6.8 Hz, OCH*H*), 1.54 (2H, m). 1.26 (2H, m), 0.75 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.0, 165.6 (2s), 165.2 (each C=O), 133.5, 133.2 (2s), 133.1, 130.0, 129.8, 129.7, 129.6, 128.6, 128.4, 128.3, 128.2 (each Ar-C), 101.8 (C-1), 71.8 (C-3), 71.3 (C-5), 70.2 (O*C*H$_3$), 70.0 (C-2), 68.2 (C-4), 62.0 (C-6), 31.4 (*C*H$_2$), 18.9 (*C*H$_2$), 13.5 (*C*H$_3$); ES-HRMS calcd for $C_{38}H_{36}O_{10}Na$ 675.2206, found *m/z* 675.2224 $[M+Na]^+$.



β-Butyl-1-D-thioglucopyranoside[17]

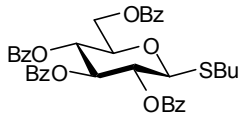
Sodium thioglucose (1 g, 4.58 mmol) was dissolved in 60 mL of MeOH and BuI (0.625 mL, 5.50 mmol) was added and the reaction stirred at room temperature for 1 h. The solvent was removed and the residue purified by chromatography (MeOH-CH_2Cl_2 1:9) to give the title compound (1.15 g, 100%) as a colourless oil; R_f 0.18 (MeOH- CH_2Cl_2 1:9); $[\alpha]_D$ -64 (c 1.15, MeOH); IR (film) cm^{-1}: 3422, 2928, 2872,

1647, 1057, 1035; ^{1}H NMR (D_2O, 500 MHz): δ 4.60 (1H, d, *J* 9.6 Hz, H-1), 3.96 (1H, d, *J* 12.3 Hz, H-6a), 3.78 (1H, dd, *J* 12.3 Hz, *J* 5.2 Hz, H-6b), 3.53 (3H, m, H-3, H-4, H-5), 3.39 (1H, t, *J* 9.6 Hz, H-2), 2.83 (2H, m, OC*H*$_2$), 1.69 (2H, m, C*H*$_2$), 1.48 (2H, m, C*H*$_2$), 0.98 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR (D_2O, 125 MHz): δ 85.3 (C-1), 79.8 (C-5), 77.3 (C-3), 72.4 (C-2), 69.6 (C-4), 61.0 (C-6), 31.6 (*C*H$_2$), 29.7 (S*C*H$_2$), 21.4 (*C*H$_2$), 13.1 (*C*H$_3$); ES-HRMS calcd for $C_{10}H_{20}O_5SNa$ 275.0929, found *m/z* 275.0918 $[M+Na]^+$.



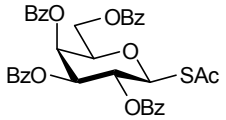
Butyl 2,3,4,6-tetra-O-acetyl-1-β-D-thioglucopyranoside 9[18]

β-Butyl-1-D-thioglucopyranoside (250 mg, 0.992 mmol) was dissolved in pyridine (2 mL) and cooled to 0 °C, to this Ac_2O (2 mL) was added and the reaction allowed to warm to room temperature over 16 h. The reaction mixture was diluted with Et_2O washed with water, 1 M HCl, water, brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Chromatography (EtOAc-cyclohexane 2:5) gave **9** (222 mg, 53%) as a yellow oil; R_f 0.43 (EtOAc-cyclohexane 2:5); IR (film) cm^{-1}: 2959, 2873, 1756, 1372, 1228, 1039; ^{1}H NMR ($CDCl_3$, 500 MHz): δ5.22 (1H, t, *J* 9.7 Hz, H-3), 5.08 (1H, t, *J* 9.7 Hz, H-4), 5.03 (1H, t, *J* 9.7 Hz, H-2), 4.48 (1H, d, *J* 9.7 Hz, H-1), 4.24 (1H, dd, *J* 12.3 Hz, *J* 5.0 Hz, H-6a), 4.14 (1H, dd, *J* 12.3 Hz, *J* 2.4 Hz, H-6b), 3.71 (1H, ddd, *J* 9.7 Hz, *J* 5.0 Hz, *J* 2.4 Hz, H-5), 2.71 (1H, ddd, *J* 12.5 Hz, *J* 8.0 Hz, *J* 6.8 Hz, SC*H*H), 2.65 (1H, ddd, *J* 12.5 Hz, *J* 8.0 Hz, *J* 7.1 Hz, SCH*H*), 2.08 (3H, s), 2.06 (3H, s), 2.02 (3H, s), 2.01 (3H, s) (each OAc), 1.59 (2H, m), 1.40 (2H, m), 0.92 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.6, 170.1, 169.4, 169.3 (each C=O), 83.6 (C-1), 75.9 (C-5), 73.9 (C-3), 69.9 (C-2), 68.4 (C-4), 62.2 (C-6), 31.7 (S*C*H$_2$), 29.7 (*C*H$_2$), 21.8, 20.7 (2s), 20.6 (each OAc), 20.5 (*C*H$_2$), 13.5 (*C*H$_3$); ES-HRMS calcd for $C_{18}H_{28}O_9SNa$ 443.1352, found *m/z* 443.1346 $[M+Na]^+$.



Butyl 2,3,4,6-tetra-O-benzoyl-1-β-thiobutylglucopyranoside 10[19]

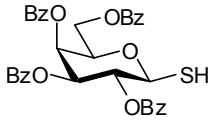
Butyl 2,3,4,6-tetra-*O*-acetyl-1-β-D-thioglucopyranoside (140 mg, 0.556 mmol) was dissolved in pyridine (3 mL) and cooled to 0 °C. To this benzoyl chloride (468 mg, 3.33 mmol, 387 μL) was added dropwise till the red colour persisted, and the reaction was allowed to warm to room temperature over 16 h. The reaction mixture was diluted with Et_2O washed with water, 1 M HCl, water, brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Chromatography (EtOAc-cyclohexane 2:5) gave **10** (209 mg, 56%) as a white solid; R_f 0.34 (EtOAc-cyclohexane 2:5); $[\alpha]_D$ +16.5 (c 4.3, $CHCl_3$); Mp 107.3 – 107.4 °C; IR (film) cm^{-1}: 3066, 2957, 1728, 1599, 1269, 1094; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.02 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.95 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.90 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.81 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.51 (4H, m, Ar-H), 7.37 (4H, m, Ar-H), 7.33 (2H, t, *J* 7.8 Hz, Ar-H), 7.26 (2H, t, *J* 7.8 Hz, Ar-H), 5.93 (1H, t, *J* 9.7 Hz, H-3), 5.67 (1H, t, *J* 9.7 Hz, H-4), 5.57 (1H, t, *J* 9.7 Hz, H-2), 4.86 (1H, d, *J* 9.7 Hz, H-1), 4.64 (1H, dd, *J* 12.1 Hz, *J* 3.1 Hz, H-6a), 4.50 (1H, dd, *J* 12.1 Hz, *J* 5.5 Hz, H-6b), 4.19 (1H, ddd, *J* 9.7 Hz, *J* 5.5 Hz, *J* 3.1 Hz, H-5), 2.76 (1H, ddd, *J* 12.3 Hz, *J* 8.3 Hz, *J* 6.6 Hz, SC*H*H), 2.71 (1H, ddd, *J* 12.3 Hz, *J* 8.3 Hz, *J* 6.6 Hz, SCH*H*),1.57 (2H, m), 1.32 (2H, m), 0.82 (3H, t, *J* 7.4 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.0, 165.8, 165.2, 165.1 (each C=O), 134.5, 133.4, 133.21, 133.16, 133.1, 130.5, 129.80, 129.78, 129.7, 128.8, 128.4, 128.3, 128.2 (each Ar-C), 84.0 (C-1), 76.3 (C-5), 74.1 (C-3), 70.7 (C-2), 69.7 (C-4), 63.3 (C-6), 31.7 (CH_2), 29.8 (SCH_2), 21.8 (CH_2), 13.4 (CH_3); ES-HRMS calcd for $C_{38}H_{36}O_9SNa$ 691.1978, found *m/z* 691.1953 $[M+Na]^+$.



1-Deoxy-1-thio-2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl acetate

D-Galactopyranose pentabenzoate (3.60 g, 5.14 mmol) was dissolved in CH_2Cl_2 (7 mL) and cooled to 0 °C, to this HBr (33% in AcOH) (35 mL) was added and the reaction allowed to warm to room temperature over 6 h. The reaction mixture was

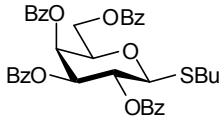
diluted with EtOAc, washed with water, $NaHCO_{3\ (sat)}$, water, brine, dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure to give the α-bromide as a white solid. The solid was dissolved in DMF (50 mL) and KSAc (645 mg, 5.66 mmol) and the reaction stirred at room temperature for 1 h. The reaction was diluted with EtOAc, washed with water, brine, dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Chromatography (EtOAc-cyclohexane 2:5) gave the title compound (1.34 g, 40%) as a yellow solid; R_f 0.29 (EtOAc-cyclohexane 2:5); $[\alpha]_D$ +153.5 (c 1.1, $CHCl_3$); IR (film) cm^{-1}: 3057, 1726, 1599, 1266, 1097, 709; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.07 (2H, dd *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 8.01 (2H, dd *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.92 (2H, dd *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.76 (2H, dd *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.62 (1H, tt, *J* 7.5 Hz, *J* 1.2 Hz, Ar-H), 7.51 (4H, m, Ar-H), 7.42 (3H, m, Ar-H), 7.37 (2H, t, *J* 7.8 Hz, Ar-H), 7.23 (2H, t, *J* 7.9 Hz, Ar-H), 6.61 (1H, dd, *J* 3.4 Hz, *J* 0.7 Hz, H-4), 5.91 (1H, t, *J* 10.0 Hz, H-2), 5.72 (1H, dd, *J* 10.0 Hz, *J* 3.4 Hz, H-3), 5.64 (1H, d, *J* 10.0 Hz, H-1), 4.61 (1H, dd, *J* 11.3 Hz, *J* 6.5 Hz, H-6a), 4.50 (1H, td, *J* 6.5 Hz, *J* 0.7 Hz, H-5), 4.38 (1H, dd, *J* 11.3 Hz, *J* 6.5 Hz, H-6b), 2.33 (3H, s, SAc); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 192.0, 166.0, 165.5, 165.4, 165.3 (each C=O), 133.6, 133.5, 133.3, 133.2, 130.0, 129.8 (2s), 129.7, 129.4, 129.0, 128.8, 128.7, 128.6, 128.4 (2s), 128.3 (each Ar-C), 81.0 (C-1), 75.8 (C-5), 72.7 (C-3), 68.3 (C-4), 67.6 (C-2), 62.0 (C-6), 30.8 (SAc); ES-HRMS calcd for $C_{36}H_{30}O_{10}S$ 677.1457, found *m/z* 677.1456 $[M+Na]^+$.



2,3,4,6-Tetra-O-benzoyl-1-thio-β-D-galactose

1-Deoxy-1-thio-2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl acetate (250 mg, 0.382 mmol) was dissolved in MeOH-$CHCl_3$ 1:1 (8 mL), $N_{2\ (g)}$ was bubbled through for 5 min and the mixture then cooled to 0 °C. To this NaSMe (26.7 mg, 0.382 mmol) was added and the reaction stirred for at 0 °C for 10 min, the reaction was then poured onto 1% HCl (20 mL) and extracted with CH_2Cl_2. Chromatography (EtOAc-cyclohexane 1:4) gave the title compound (207 mg, 88%) as a yellow solid; R_f 0.29 (EtOAc-cyclohexane 2:5); $[\alpha]_D$ +113.9 (c 6.05, $CHCl_3$); Mp 86.6 – 86.7 °C; IR (film) cm^{-1}: 3064, 2970, 2565, 1728, 1600, 1270, 1099; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.09 (2H, d, *J* 7.3 Hz, Ar-H), 8.02 (2H, d, *J* 7.3 Hz, Ar-H), 7.96 (2H, d, *J* 7.3 Hz, Ar-H),

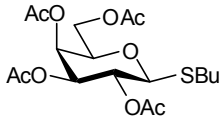
7.77 (2H, d, *J* 7.3 Hz, Ar-H), 7.62 (1H, t, *J* 7.5 Hz, Ar-H), 7.52 (4H, m, Ar-H), 7.41 (3H, t, *J* 7.8 Hz, Ar-H), 7.37 (2H, t, *J* 7.8 Hz, Ar-H), 7.22 (2H, t, *J* 7.8 Hz, Ar-H), 6.05 (1H, d, *J* 3.2 Hz, H-4), 5.78 (1H, t, *J* 9.8 Hz, H-2), 5.64 (1H, dd, *J* 9.8 Hz, *J* 3.2 Hz, H-3), 4.93 (1H, t, *J* 9.8 Hz, H-1), 4.66 (1H, dd, *J* 10.9 Hz, *J* 6.0 Hz, H-6a), 4.40 (2H, m, H-5, H-6b), 2.57 (1H, d, *J* 9.8 Hz, SH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.0, 165.5, 165.4 (2s) (each C=O), 133.6, 133.4, 133.3, 133.2, 129.9, 129.8, 129.7, 129.3, 129.0, 128.9, 128.7, 128.6, 128.4, 128.2 (each Ar-C), 79.4 (C-1), 75.6 (C-5), 72.3 (C-3), 71.9 (C-2), 68.3 (C-4), 62.1 (C-6); ES-HRMS calcd for $C_{34}H_{28}O_9SNa$ 635.1352, found *m/z* 635.1321 $[M+Na]^+$.



Butyl 2,3,4,6-tetra-O-benzoyl-1-thio-β-D-galactopyranoside 14[18]

The thiol precursor 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-galactose (75 mg, 0.122 mmol) was dissolved in DMF (2 mL) and cooled to 0 °C. To this NaH (6 mg, 0.146 mmol) was added and the reaction stirred for 5 min, followed by the addition of BuI (21 μL, 0.185 mmol) and the reaction stirred at 0 °C for 2 h. The reaction was diluted with Et_2O, washed with water, brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Chromatography (EtOAc-cyclohexane 1:4) gave **14** (71 mg, 87%) as a yellow solid; R_f 0.32 (EtOAc-cyclohexane 2:5); $[\alpha]_D$ +57.0 (c 3.35, $CHCl_3$); Mp 159.9 – 160.9 °C; IR (film) cm^{-1}: 3065, 2957, 2863, 1721, 1600, 1268, 1101; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.08 (2H, dd, *J* 8.2 Hz, *J* 1.2 Hz, Ar-H), 8.02 (2H, dd, *J* 8.2 Hz, *J* 1.2 Hz, Ar-H), 7.95 (2H, dd, *J* 8.2 Hz, *J* 1.2 Hz, Ar-H), 7.78 (2H, dd, *J* 8.2 Hz, *J* 1.2 Hz, Ar-H), 7.62 (1H, tt, *J* 7.5 Hz, *J* 1.2 Hz, Ar-H), 7.55 (1H, tt, *J* 7.5 Hz, *J* 1.2 Hz, Ar-H), 7.48 (3H, m, Ar-H), 7.42 (3H, t, *J* 7.7 Hz, Ar-H), 7.38 (2H, t, *J* 7.8 Hz, Ar-H), 7.24 (2H, t, *J* 7.9 Hz, Ar-H), 6.03 (1H, dd, *J* 3.3 Hz, *J* 0.5 Hz, H-4), 5.85 (1H, t, *J* 10.0 Hz, H-2), 5.64 (1H, dd, *J* 10.0 Hz, *J* 3.3 Hz, H-3), 4.86 (1H, d, *J* 10.0 Hz, H-1), 4.66 (1H, dd, *J* 11.2 Hz, *J* 6.5 Hz, H-6a), 4.41 (1H, dd, *J* 11.2 Hz, *J* 6.5 Hz, H-6b), 4.36 (1H, td, *J* 6.5 Hz, *J* 0.5 Hz, H-5), 2.85 (1H, ddd, *J* 12.5 Hz, *J* 8.6 Hz, *J* 6.3 Hz, SC*H*H), 2.77 (1H, ddd, *J* 12.5 Hz, *J* 8.6 Hz, *J* 6.3 Hz, SCH*H*), 1.65 (2H, m), 1.38 (2H, m), 0.88 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.0, 165.5, 165.4, 165.3 (each C=O), 133.6, 133.2, 130.0, 129.8, 129.6, 129.4, 129.3, 129.1, 128.8, 128.6, 128.4, 128.3, 128.2 (each Ar-C), 84.4 (C-1), 75.1 (C-5), 72.8 (C-

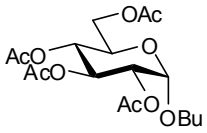
3), 68.4 (C-4), 68.3 (C-2), 62.3 (C-6), 31.9 (*C*H_2), 29.9 (S*C*H_2), 21.9 (*C*H_2), 13.5 (*C*H_3); ES-HRMS calcd for $C_{38}H_{36}O_9SNa$ 691.1978, found *m/z* 691.1960 $[M+Na]^+$.



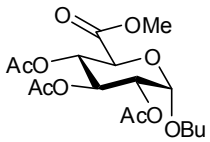
Butyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-galactopyranoside 13[18]

Thioglycoside **14** (104 mg, 0.155 mmol) was dissolved in MeOH (2 mL) and NaOMe (1M, 0.05 mL) was added. The reaction was stirred for 30 min at room temperature, acidified with amberlite, to pH 6, filtered and the solvent was removed under reduced pressure to give a colourless oil. The oil was taken up in pyridine (1.5 mL) and cooled to 0 °C, to this Ac_2O (1 mL) was added and the reaction allowed to warm to room temperature over 16 h. The reaction was diluted with Et_2O washed with water, 1M HCl, water, brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Chromatography (EtOAc-cyclohexane 1:2) gave **13** (58 mg, 89%) as a colourless oil; R_f 0.44 (EtOAc-cyclohexane 1:1); $[\alpha]_D$ -5.07 (c 4.9, $CHCl_3$); IR (film) cm^{-1}: 2959, 1749, 1370, 1227, 1053; ^1H NMR ($CDCl_3$, 500 MHz): δ 5.43 (1H, dd, *J* 3.3 Hz, *J* 0.8 Hz, H-4), 5.23 (1H, t, *J* 10.0 Hz, H-2), 5.05 (1H, dd, *J* 10.0 Hz, *J* 3.3 Hz, H-3), 4.48 (1H, d, *J* 10.0 Hz, H-1), 4.16 (1H, dd, *J* 11.3 Hz, *J* 6.6 Hz, H-6a), 4.11 (1H, dd, *J* 11.3 Hz, *J* 6.6 Hz, H-6b), 3.93 (1H, td, *J* 6.6 Hz, *J* 0.8 Hz, H-5), 2.73 (1H, ddd, *J* 12.5 Hz, *J* 7.7 Hz, *J* 6.9 Hz, SC*H*H), 2.67 (1H, ddd, *J* 12.5 Hz, *J* 7.7 Hz, *J* 6.9 Hz, SCH*H*), 2.15 (3H, s), 2.07 (3H, s), 2.04 (3H, s), 1.98 (3H, s) (each OAc), 1.60 (2H, m), 1.42 (2H, m), 0.92 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.3, 170.1, 170.0, 169.5 (C=O), 84.2 (C-1), 74.4 (C-5), 71.9 (C-3), 67.3, 67.2 (C-2 and C-4), 61.5 (C-6), 31.7 (*C*H_2), 29.8 (S*C*H_2), 21.8 (*C*H_2), 20.7, 20.6 (2s), 20.5 (each OAc), 13.5 (*C*H_3); ES-HRMS calcd for $C_{18}H_{28}O_9SNa$ 443.1352, found *m/z* 443.1351 $[M+Na]^+$.

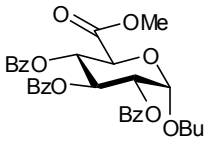
Analytical data for α-anomers of 1-18 with assignments



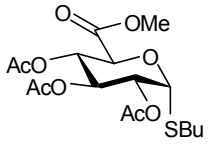
Butyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside 1α (α:β = 10:1); R_f 0.24 (EtOAc-petroleum spirits 1:4); IR (film) cm^{-1}: 2959, 1748, 1367, 1221, 1037; ^1H NMR ($CDCl_3$, 500 MHz): δ 5.50 (1H, t, *J* 9.8 Hz, H-3), 5.09 (1H, d, *J* 3.7 Hz, H-1), 5.05 (1H, t, *J* 9.8 Hz, H-4), 4.86 (1H, dd, *J* 9.8 Hz, *J* 3.7 Hz, H-2), 4.29 (1H, dd, *J* 12.3 Hz, *J* 4.6 Hz, H-6a), 4.15 (1H, dd, *J* 12.3 Hz, *J* 2.3 Hz, H-6b), 4.04 (1H, ddd, *J* 10.2, *J* 4.6 Hz, *J* 2.3 Hz, H-5), 3.70 (1H, dt, *J* 9.8 Hz, *J* 6.5 Hz, OC*H*H), 3.45 (1H, dt, *J* 9.8 Hz, *J* 6.5 Hz, OCH*H*), 2.18 (3H, s), 2.11 (3H, s), 2.08 (3H, s), 2.06 (3H, s) (each OAc), 1.59 (2H, m), 1.40 (2H, m), 0.94 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.7, 170.2, 170.1, 169.6 (each C=O), 95.6 (C-1), 71.0 (C-2), 70.3 (C-3), 68.7 (C-4), 68.4 (O*C*H_2), 67.1 (C-5), 62.0 (C-6), 31.3 (*C*H_2), 20.7 (2s), 20.6 (each OAc), 19.2 (*C*H_2), 13.7 (*C*H_3); ES-HRMS calcd for $C_{18}H_{28}O_{10}Na$ 427.1580, found *m/z* 427.1559 $[M+Na]^+$.



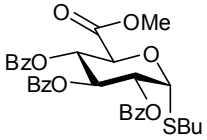
Butyl 2,3,4-tri-*O*-acetyl-α-D-glucopyranosiduronic acid, methyl ester 2α (α:β = 16:1); R_f 0.21 (EtOAc-petroleum spirits 1:4); IR (film) cm^{-1}: 2960, 1754, 1439, 1371, 1219, 1051; ^1H NMR ($CDCl_3$, 500 MHz) δ5.55 (1H, t, *J* 10.0 Hz, H-3), 5.28 (1H, d, *J* 3.6 Hz, H-1), 5.21 (1H, t, *J* 10.0 Hz, H-4), 4.90 (1H, dd, *J* 10.0 Hz, *J* 3.6 Hz, H-2), 4.39 (1H, d, *J* 10.0 Hz, H-5), 3.80 (3H, s, OC*H*$_3$), 3.77 (1H, m, OCH*H*), 3.50 (1H, dt, *J* 9.9 Hz, *J* 6.5 Hz, OC*H*H), 2.09 (3H, s), 2.07 (3H, s), 2.06 (3H, s) (each OAc), 1.60 (2H, m), 1.40 (2H, m), 0.94 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.7, 170.5, 170.2, 169.1 (each C=O), 96.1 (C-1), 70.7 (C-2), 69.7 (C-4), 69.6 (C-3), 69.3 (O*C*H_2), 68.0 (C-5), 53.5 (O*C*H_3), 31.2 (*C*H_2), 20.7 (OAc), 20.6 (2s) (each OAc), 19.1 (*C*H_2), 13.9 (*C*H_3); ES-HRMS calcd for $C_{17}H_{30}O_{10}N$ 408.1870, found *m/z* 408.1870 $[M+NH_4]^+$.



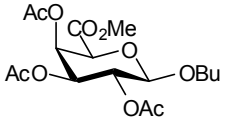
Butyl 2,3,4-tri-*O*-benzoyl-α-D-glucopyranosiduronic acid, methyl ester 3α (α:β = 24:1); R_f 0.38 (EtOAc-petroleum spirits 1:4); IR (film) cm^{-1}: 2958, 1730, 1263, 1107, 1069; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.97 (4H, m, Ar-H), 7.89 (2H, dd, *J* 8.1 Hz, *J* 0.9 Hz, Ar-H), 7.52 (2H, m, Ar-H), 7.44 (1H, t, *J* 7.4 Hz, Ar-H), 7.43 (4H, m, Ar-H), 7.31 (2H, t, *J* 7.8 Hz, Ar-H), 6.20 (1H, t, *J* 10.0 Hz, H-3), 5.64 (1H, t, *J* 10.0 Hz, H-4), 5.43 (1H, d, *J* 3.7 Hz, H-1), 5.32 (1H, dd, *J* 10.0 Hz, 3.7 Hz, H-2), 4.62 (1H, d, *J* 10.0 Hz, H-5), 3.83 (1H, dt, *J* 9.9 Hz, *J* 6.5 Hz, OC*H*H), 3.69 (3H, s, OCH_3), 3.51 (1H, dt, *J* 9.9. Hz, *J* 6.5 Hz, OC*H*H), 1.59 (2H, m), 1.37 (2H, m), 0.84 (3H, t, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.3, 165.7, 165.6, 165.3 (each C=O), 133.4, 133.2, 129.9, 129.8, 129.7, 129.1, 129.0, 128.9, 128.4 (2s), 128.3 (each Ar-C), 96.3 (C-1), 71.5 (C-2), 70.3 (C-4), 69.8 (C-3), 69.2 (O*C*H_2), 68.6 (C-5), 52.9 (O*C*H_3), 31.3 (*C*H_2), 19.1 (*C*H_2), 13.6 (*C*H_3); ES-HRMS calcd for $C_{32}H_{36}O_{10}N$ 594.2339, found *m/z* 594.2326 $[M+NH_4]^+$.



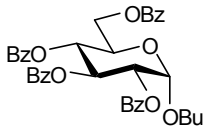
Methyl 1-α-thiobutyl-2,3,4-tri-*O*-acetyl-D-glucopyranosiduronate 4α (α:β = 4:1); R_f 0.27 (EtOAc-petroleum spirits 1:4); IR (film) cm^{-1}: 2958, 1753, 1438, 1372, 1220, 1042, 899; ^1H NMR ($CDCl_3$, 500 MHz): δ 5.81 (1H, d, *J* 5.5 Hz, H-1), 5.39 (1H, t, *J* 9.5 Hz, H-3), 5.22 (1H, t, *J* 9.5 Hz, H-4), 5.04 (1H, dd, *J* 9.5 Hz, *J* 5.5 Hz, H-2), 4.81 (1H, d, *J* 9.5 Hz, H-5), 3.80 (3H, s, OCH_3), 2.61 (2H, m, SCH_2), 2.10 (3H, s), 2.08 (3H, s), 2.06 (3H, s) (each OAc), 1.58 (2H, m), 1.41 (2H, m), 0.91 (3H, t, *J* 7.4 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.2 (3s), 168.7 (each C=O), 82.3 (C-1), 70.3 (C-3), 69.7, 69.5, 68.5 (C-2, C-4, C-5), 53.3 (O*C*H_3), 31.4 (*C*H_2), 30.3 (*C*H_2), 21.8, 20.7, 20.6 (each OAc), 13.5 (*C*H_3); ES-HRMS calcd for $C_{17}H_{30}O_9NS$ 424.1641, found *m/z* 424.1628 $[M+NH_4]^+$.



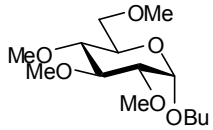
Methyl 1-α-thiobutyl-2,3,4-tri-*O*-benzoyl-D-glucopyranosiduronate 5α (α:β = 7:1); R_f 0.73 (EtOAc-petroleum spirits 1:4); IR (film) cm^{-1}: 2957, 1727, 1259, 1091, 1026, 910; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.01 (2H, dd, *J* 8.0 Hz, *J* 1.2 Hz, Ar-H), 7.95 (2H, dd, *J* 8.0 Hz, *J* 1.2 Hz, Ar-H), 7.91 (2H, dd, *J* 8.0 Hz, *J* 1.2 Hz, Ar-H), 7.52 (4H, m, Ar-H), 7.39 (2H, t, *J* 7.6 Hz, Ar-H), 7.34 (4H, m, Ar-H), 6.16 (1H, d, *J* 5.3 Hz, H-1), 6.09 (1H, t, *J* 8.9 Hz, H-3), 5.78 (1H, t, *J* 8.9 Hz, H-4), 5.56 (1H, dd, *J* 8.9 Hz, *J* 5.3 Hz, H-2), 5.16 (1H, d, *J* 8.9 Hz, H-5), 3.77 (3H, s, OC*H*$_3$), 2.82 (1H, ddd, *J* 12.8 Hz, *J* 7.9 Hz, *J* 6.5 Hz, SC*H*H), 2.76 (1H, ddd, *J* 14.9 Hz, *J* 7.9 Hz, *J* 7.0 Hz, SCH*H*), 1.69 (2H, m), 1.46 (2H, m), 0.95 (3H, t, *J* 7.4 Hz, C*H*$_3$). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.3, 165.4, 165.3, 165.2 (each C=O), 133.5, 133.4, 130.0, 129.9, 129.8 (3s), 128.9 (2s), 128.8, 128.5, 128.4 (3s), 128.3 (each Ar-C), 82.0 (C-1), 70.9 (C-3), 69.8 (C-5), 69.5 (2s, C-2 and C-4), 52.8 (O*C*H$_3$), 31.6 (*C*H$_2$), 30.6 (S*C*H$_2$), 21.9 (*C*H$_2$), 13.5 (*C*H$_3$): ES-HRMS calcd for $C_{32}H_{32}O_9SNa$ 615.1665, found *m/z* 615.1652 $[M+Na]^+$.



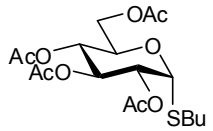
Butyl 2,3,4-tri-*O*-acetyl-α-D-galactopyranosiduronic acid, methyl ester 6α (α:β = 19:1); R_f 0.15 (EtOAc-petroleum spirits 1:4); IR (film) cm^{-1}: 2958, 1752, 1372, 1224, 1158, 1068, 1030; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.77 (1H, dd, *J* 3.4 Hz, *J* 1.3 Hz, H-4), 5.41 (1H, dd, *J* 10.9 Hz, *J* 3.4 Hz, H-3), 5.24 (1H, d, *J* 3.6 Hz, H-1), 5.16 (1H, dd, *J* 10.9 Hz, *J* 3.6 Hz, H-2), 4.63 (1H, d, *J* 1.3 Hz, H-5), 3.76 (3H, s, OC*H*$_3$), 3.74 (1H, dt, *J* 9.9 Hz, *J* 6.5 Hz, OCH*H*), 3.47 (1H, dt, *J* 9.9 Hz, *J* 6.7 Hz, OC*H*H), 2.10 (3H, s), 2.07 (3H, s), 2.00 (3H, s) (each OAc), 1.57 (2H, m), 1.36 (2H, m), 0.92 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.2, 167.0, 169.8, 167.6 (each C=O), 96.4 (C-1), 69.2 (C-4), 69.0 (O*C*H$_2$), 68.4 (C-5), 67.8 (C-2), 67.3 (C-3), 52.7 (O*C*H$_3$), 31.3 (*C*H$_2$), 20.7, 20.6 (2s) (each OAc), 19.2 (*C*H$_2$), 13.7 (*C*H$_3$); ES-HRMS calcd for $C_{17}H_{26}O_{10}Na$ 413.1424, found *m/z* 413.1431 $[M+Na]^+$.



Butyl 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranoside 7α (α:β = 14:1); NMR ($CDCl_3$, 500 MHz): δ 8.05 (2H, d, *J* 7.5 Hz, Ar-H), 7.99 (2H, d, *J* 7.5 Hz, Ar-H), 7.95 (2H, d, *J* 7.3 Hz, Ar-H), 7.87 (2H, d, *J* 7.4 Hz, Ar-H), 7.55 (1H, t, *J* 7.4 Hz, Ar-H), 7.49 (2H, m, Ar-H), 7.41 (3H, t, *J* 7.8 Hz, Ar-H), 7.36 (4H, m, Ar-H), 7,28 (2H, t, *J* 7.7 Hz, Ar-H), 6.21 (1H, t, *J* 9.8 Hz, H-3), 5.68 (1H, t, *J* 9.8 Hz, H-4), 5.35 (1H, d, *J* 3.7 Hz, H-1), 5.32 (1H, dd, *J* 9.8 Hz, *J* 3.7 Hz, H-1), 4.61 (1H, m, H-6a), 4,48 (2H, m, H-5, H-6b), 3.81 (1H, dt, *J* 9.8 Hz, *J* 6.5 Hz, OCH*H*), 3.51 (1H, dt, *J* 9.8 Hz, *J* 6.6 Hz, OC*H*H), 1.60 (2H, m), 1.35 (2H, m), 0.83 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): 166.4, 165.9, 165.8, 165.4 (each C=O), 133.4 (2s), 133.2, 129.9, 129.7 (2s), 129.6, 129.1, 129.0, 128.8, 128.4, 128.3 (each Ar-C), 96.0 (C-1), 72.0 (C-2), 70.7 (C-3), 69.7 (C-4), 68.7 (O*C*H$_2$), 67.7 (C-5), 63.3 (C-6), 31.3 (*C*H$_2$), 19.2 (*C*H$_2$), 13.6 (*C*H$_3$).

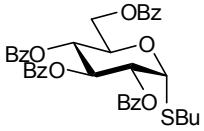


Butyl 2,3,4,6-tetra-*O*-methyl-α-D-glucopyranoside 8α (α:β = 13:1); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.77 (1H, d, *J* 2.0 Hz, H-1), 3.92 (2H, m), 3.83 (1H, m), 3.69 (2H, m), 3.66 (3H, s), 3.62 (2H, m), 3.60 (3H, s), 3.57 (3H, s), 3.53 (2H, m), 1.66 (2H, m), 1.40 (2H, m), 0.94 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 96.3 (C-1), 83.4 (CH), 81.7 (CH), 79.6 (CH), 71.1 (C-6), 69.9, 67.8 (O*C*H$_2$), 60.8 (O*C*H$_3$), 60.4 (O*C*H$_3$), 59.2 (O*C*H$_3$), 58.6 (O*C*H$_3$), 31.5 (*C*H$_2$), 19.8 (*C*H$_2$), 13.8 (O*C*H$_3$).

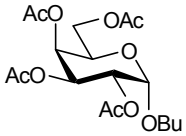


Butyl 2,3,4,6-tetra-*O*-acetyl-1-α-D-thioglucopyranoside 9α (α:β = 2:1); R_f 0.25 (EtOAc-petroleum spirits 1:4); IR (film) cm^{-1}: 2960, 2873, 1723, 1451, 1265, 1107, 1095, 1069, 1026; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.66 (1H, d, *J* 5.8 Hz, H-1), 5.38 (1H, t, *J* 9.7 Hz, H-3), 5.05 (2H, m, H-2, H-4), 5.46 (1H, ddd, *J* 10.2 Hz, *J* 4.7 Hz, *J*

2.2 Hz, H-5), 4.33 (1H, dd, *J* 12.4 Hz, *J* 4.7 Hz, H-6a), 4.12 (1H, dd, *J* 12.4 Hz, *J* 2.2 Hz, H-6b), 2.54 (2H, m, SC*H*$_2$), 2.16 (3H, s), 2.09 (3H, s), 2.08 (3H, s), 2.05 (3H, s), (each OAc), 1.58 (2H, m), 1.40 (2H, m), 0.92 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.6, 169.9 (2s), 169.6 (each C=O), 82.0 (C-1), 70.8 (*C*H), 70.5 (*C*H), 68.6 (*C*H), 67.5 (*C*H), 62.0 (CH), 31.4 (S*C*H$_2$), 29.8 (*C*H$_2$), 21.9 (*C*H$_2$), 20.8, 20.7 (2s), 20.6 (each OAc), 13.6 (*C*H$_3$); ES-HRMS calcd for $C_{18}H_{28}O_9SNa$ 443.1352, found *m/z* 443.1360 $[M+Na]^+$.

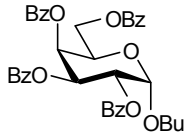


Butyl 2,3,4,6-tetra-*O*-benzoyl-1-α-thiobutylglucopyranoside 10α (α:β = 4:1); R_f 0.44 (EtOAc-petroleum spirits 1:4); IR (film) cm^{-1}: 2958, 1726, 1267, 1093, 1069, 1027, 708; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.05 (2H, d, *J* 7.3 Hz, Ar-H), 7.98 (2H, d, *J* 7.3 Hz, Ar-H), 7.95 (2H, d, *J* 7.3 Hz, Ar-H), 7.87 (2H, d, *J* 7.3 Hz, Ar-H), 7.56 (1H, t, *J* 7.3 Hz, Ar-H), 7.51 (2H, t, *J* 7.4 Hz, Ar-H), 7.45-7.35 (7H, m, Ar-H), 7.30 (2H, t, *J* 7.8 Hz, Ar-H), 6.07 (1H, t, *J* 10.0 Hz, H-3), 5.91 (1H, d, *J* 5.8 Hz, H-1), 5.66 (1H, t, *J* 10.0 Hz, H-4), 5.50 (1H, dd, *J* 10.0 Hz, *J* 5.8 Hz, H-2), 4.87 (1H, ddd, *J* 10.0 Hz, *J* 5.6 Hz, *J* 2.8 Hz, H-5), 4.59 (1H, dd, *J* 12.2 Hz, *J* 2.8 Hz, H-6a), 4.52 (1H, dd, *J* 12.2 Hz, *J* 5.6 Hz, H-6b), 2.59 (2H, m, SC*H*$_2$), 1.56 (2H, m), 1.30 (2H, m), 0.82 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.1, 165.6, 165.4, 165.3 (each C=O) 133.4, 133.2, 133.1, 130.0, 129.9, 129.7 (2s), 128.4 (3s), 128.3 (each Ar-C), 82.3 (C-1), 71.7 (C-2), 70.9 (C-3), 69.6 (C-4), 68.2 (C-5), 63.1 (C-6), 31.4 (*C*H$_2$), 29.9 (S*C*H$_2$), 22.0 (*C*H$_2$), 13.5 (*C*H$_3$); ES-HRMS calcd for $C_{38}H_{36}O_9SNa$ 691.1978, found *m/z* 691.1982 $[M+Na]^+$.

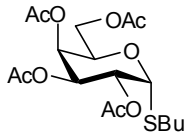


Butyl 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranoside 11α. (α:β = 15:1); R_f 0.65 (EtOAc-Petroleum Spirits 1:1); IR (film) cm^{-1}: 2961, 2937, 1744, 1369, 12171044, 912; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.46 (1H, d, *J* 3.1 Hz, H-1), 5.36 (1H, m), 5.10 (2H, m), 4.22 (1H, t, *J* 6.6 Hz, H-5), 4.11 (1H, dd, *J* 9.3 Hz, *J* 4.5 Hz, H-6a), 4.08 (1H, dd *J* 9.3 Hz, *J* 5.4 Hz, H-6b), 3.69 (1H, dt, *J* 9.7 Hz, *J* 6.5 Hz, OC*H*H), 3.43 (1H,

dt, *J* 9.7 Hz, *J* 6.5 Hz, OCH*H*), 2.14 (3H, s), 2.07 (3H, s), 2.05 (3H, s), 1.99 (3H, s) (each OAc), 1.58 (2H, m), 1.39 (2H, m), 0.93 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.4 (2s), 170.2, 170.0(each C=O), 96.1 (C-1), 68.4, 68.3, 68.2, 67.7 (C-2, C-3, C-4), 66.2 (C-5), 61.9 (C-6), 31.3 (*C*H$_2$), 20.8, 20.7, 20.6 (each OAc), 19.2 (*C*H$_2$), 13.7 (*C*H$_3$); ES-HRMS calcd for $C_{18}H_{32}O_{10}N$ 422.2026, found *m/z* 422.2032 $[M+NH_4]^+$.

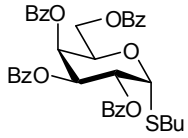


Butyl 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranoside 12α (α:β = 11:1); R_f 0.44 (EtOAc-petroleum spirits 1:4); IR (film) cm^{-1}: 2960, 2873, 1725, 1602, 1267, 1108, 1095, 1069, 1027; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.09 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 8.02 (2H, dd, *J* 8.5 Hz, *J* 1.3 Hz, Ar-H), 7.98 (2H, dd, *J* 8.5 Hz, *J* 1.3 Hz, Ar-H), 7.79 (2H, dd, *J* 8.4 Hz, *J* 1.2 Hz, Ar-H), 7.62 (1H, t, *J* 7.5 Hz, Ar-H), 7.57-7.36 (9H, m, Ar-H), 7.24 (2H, t, *J* 7.8 Hz, Ar-H), 6.04 (1H, d, *J* 3.3 Hz, H-4), 6.00 (1H, dd, *J* 10.6 Hz, *J* 3.3 Hz, H-3), 5.68 (1H, dd, *J* 10.6 Hz, *J* 3.6 Hz, H-2), 5.41 (1H, d, *J* 3.6 Hz, H-1), 4.65 (1H, m, H-5), 4.60 (1H, dd, *J* 11.0, *J* 7.1 Hz, H-6a), 4.40 (1H, dd, *J* 11.0 Hz, *J* 5.6 Hz, H-6b), 3.80 (1H, dt, *J* 9.7 Hz, *J* 6.5 Hz, OC*H*H), 3.50 (1H, dt, *J* 9.5 Hz, *J* 6.2 Hz, OCH*H*), 1.59 (2H, m), 1.34 (2H, m), 0.83 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.1, 166.0, 165.7, 165.6 (each C=O), 133.5, 133.3, 133.2, 133.1, 129.9, 129.8, 129.7, 128.6, 128.4 (2s), 128.2 (each Ar-C), 96.6 (C-1), 69.4 (C-2), 69.3 (C-4), 68.6 (O*C*H$_2$), 68.5 (C-3), 66.9 (C-5), 62.7 (C-6), 31.4 (*C*H$_2$), 19.2 (*C*H$_2$), 13.7 (*C*H$_3$); ES-HRMS calcd for $C_{38}H_{40}O_{10}N$ 670.2652, found *m/z* 670.2631 $[M+NH_4]^+$.

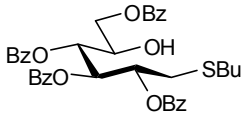


Butyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-galactopyranoside 13α (α:β = 2:1); R_f 0.28 (EtOAc-petroleum spirits 1:4); IR (film) cm^{-1}: 2960, 1751, 1368, 1224, 1038, 913; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.72 (1H, d, *J* 5.4 Hz, H-1), 5.45 (1H, dd, *J* 3.0 Hz, *J* 0.8 Hz, H-4), 5.27 (1H, dd, *J* 10.8 Hz, *J* 5.4 Hz, H-2), 5.22 (1H, dd, *J* 10.8 Hz, *J* 3.0 Hz, H-3), 4.59 (1H, t, *J* 6.6 Hz, H-5), 4.11 (2H, m, H-6a, H-6b), 2.53 (2H, m, SC*H*$_2$), 2.15

(3H, s), 2.08 (3H, s), 2.05 (3H, s) (each OAc), 1.58 (2H, m), 1.40 (2H, m), 0.92 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.3, 170.2, 170.1, 169.8 (each C=O), 82.2 (C-1), 68.2, 68.0 (2s) (C-2, C-3, C-4), 66.5 (C-5), 61.9 (C-6), 31.4 (*C*H$_2$), 29.5 (S*C*H$_2$), 22.0 (*C*H$_2$), 20.8, 20.7, 20.6 (each OAc), 13.6 (*C*H$_3$); ES-HRMS calcd for $C_{18}H_{28}O_9SNa$ 443.1352, found *m/z* 443.1353 $[M+Na]^+$.



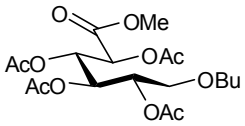
Butyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α-D-galactopyranoside 14α (α:β = 4:1); R_f 0.27 (EtOAc-petroleum spirits 1:4); IR (film) cm^{-1} 2960, 1726, 1451, 1316, 1266, 1177, 1095, 1069, 1026; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.09 (2H, d, *J* 7.4 Hz, Ar-H), 8.03 (2H, d, *J* 8.2 Hz, Ar-H), 7.99 (2H, d, *J* 7.6 Hz, Ar-H), 7.79 (2H, d, *J* 8.3 Hz, Ar-H), 7.62 (1H, t, *J* 7.4 Hz, Ar-H), 7.56 (1H, t, *J* 7.5 Hz, Ar-H), 7.49 (3H, m, Ar-H), 7.42 (5H, m, Ar-H), 7.24 (2H, t, *J* 7.9 Hz, Ar-H), 6.05 (2H, m), 5.88 (2H, m), 5.04 (1H, t, *J* 6.4 Hz, H-5), 4.61 (1H, dd, *J* 11.6 Hz, *J* 7.4 Hz, H-6a), 4.49 (1H, dd, *J* 11.6 Hz, *J* 5.1 Hz, H-6b), 2.62 (1H, ddd, *J* 12.7 Hz, *J* 8.5 Hz, *J* 6.3 Hz, SCH*H*), 2.55 (1H, ddd, *J* 12.7 Hz, *J* 8.5 Hz, *J* 7.0 Hz, SC*H*H), 1.54 (2H, m), 1.27 (2H, m), 0.81 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): 166.0, 165.7, 165.5, 165.4 (each C=O), 133.6, 133.4, 133.2 (2s), 129.9 (2s), 129.8, 129.7 (2s), 129.5, 129.1, 129.0 (2s), 128.6, 128.4 (3s), 128.3, 128.2 (each Ar-C), 82.5 (C-1), 69.1, 69.0 (2s) (C-2, C-3, and C-4), 67.3 (C-5), 62.7 (C-6), 31.4 (S*C*H$_2$), 29.6 (*C*H$_2$), 22.0 (*C*H$_2$), 13.5 (*C*H$_3$); ES-HRMS calcd for $C_{38}H_{40}O_9SN$ 686.2424, found *m/z* 686.2416 $[M+NH_4]^+$.



Trapping experiment: (2R, 3R, 4S, 5R) 1,3,4,5-Tetra-O-benzoylhexan-2-ol-6-thiobutyl ether 27

β-thioglucoside **10** (90 mg, 0.134 mmol) and $Na(CN)BH_3$ (169 mg, 2.69 mmol) was dried under vacuum for 3 h. To this $TiCl_4$ (0.8 mL of a 0.342 M solution in chloroform, 0.268 mmol) was added and the mixture stirred at room temperature for 16 h, followed by the addition of satd aq $NaHCO_3$ (3 mL) and solid $NaHCO_3$ (50 mg) and the reaction stirred for a further 15 min. The organic layer was washed with

water, dried ($MgSO_4$) and the solvent was removed under reduced pressure. Purification via flash chromatography (EtOAc-Petroleum Spirits 1:1) to give the title compound (27 mg, 30%). R_f 0.16 (EtOAc-Petroleum Spirits 1:4); IR (film) cm^{-1}: 3485, 3065, 2926, 1724, 1263, 1108, 1069, 1026, 708; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.40 (2H, dd, *J* 8.4 Hz, *J* 1.2 Hz, Ar-H), 7.98 (2H, dd, *J* 8.4 Hz, *J* 1.2 Hz, Ar-H), 7.95 (2H, dd, *J* 8.4 Hz, *J* 1.2 Hz, Ar-H), 7.88 (2H, dd, *J* 8.3 Hz, *J* 1.2 Hz, Ar-H), 7.52 (2H, m, Ar-H), 7.39 (8H, m, Ar-H), 7.26 (2H, m, Ar-H), 6.18 (1H, dd, *J* 6.0 Hz, *J* 2.8 Hz, H-4), 5.71 (2H, m, H-3, H-5), 4.56 (1H, dd, *J* 12.0 Hz, *J* 2.9 Hz, H-1a), 4.35 (1H, dd, *J* 12.0 Hz, *J* 2.9 Hz, H1b), 4.18 (1H, m, H-2), 3.69 (1H, m), 3.02 (1H, dd, *J* 14.4 Hz, *J* 5.3 Hz, H-6a), 2.94 (1H, dd, *J* 14.4 Hz, *J* 6.6 Hz, H-6b), 2.56 (2H, t, *J* 7.5 Hz, S*CH*$_2$), 1.51 (2H, m, C*H*$_2$), 1.30 (2H, m, C*H*$_2$), 0.82 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz), δ 167.0, 166.6, 165.8, 165.5 (each C=O), 133.7, 133.5, 133.1, 133.0, 130.0, 129.9, 129.7, 129.6, 128.7, 128.5 (3s), 128.3, 128.2 (each Ar-C), 72.2 (C-3/5), 72.0 (C-4), 71.5 (C-3/5), 68.6 (C-2), 65.3 (C-1), 32.7 (C-6), 32.4 (S*C*H$_2$), 31.5 (*C*H$_2$), 21.8 (*C*H$_2$), 13.5 (*C*H$_3$); ES-HRMS calcd for $C_{38}H_{38}O_9SNa$ 693.2134, found *m/z* 693.2131 $[M+Na]^+$.



Methyl (2S, 3S, 4R, 5S) 2,3,4,5-Tetra-O-acetyl-6-O-butylhex-2-olanoate 26

β-Glucoside **2** (90 mg, 0.230 mmol) and $Na(CN)BH_3$ (169 mg, 2.69 mmol) was dried under vacuum for 3 h. To this $CHCl_3$ (1.0 mL) was added followed by $TiCl_4$ (0.8 mL of a 0.342 M solution in chloroform, 0.268 mmol) was added and the mixture stirred at room temperature for 16 h, followed by the addition of $NaHCO_{3\ (sat)}$ (3 mL) and solid $NaHCO_3$ (50 mg) and the reaction stirred for a further 15 min. The organic layer was washed with water, dried ($MgSO_4$) and the solvent was removed under reduced pressure, Purification via flash chromatography gave compounds **2** and **25** as an inseparable mixture. The mixture was taken up in Pyridine (2 mL) and Ac_2O (2 mL) was added and the reaction stirred at room temperature for 16 h. Purification via flash chromatography (EtOAc-Petroleum Spirits 1:4) gave **26** as a colourless oil (5 mg, 5 %). R_f 0.82 (EtOAc-Petroleum Spirits 1:4); IR (film) cm^{-1}: 2957, 2855, 1749, 1370, 1209, 1036, 910; ^1H NMR ($CDCl_3$, 500 MHz): δ 5.64 (1H, dd, *J* 6.6 Hz, *J* 4.2 Hz, H-4), 5.49 (1H, dd, *J* 6.9 Hz, *J* 4.2 Hz, H-3), 5.15 (1H, m, H-5), 5.11 (1H, d, *J* 7.0

Hz, H-2), 3.74 (3H, s, OC*H*$_3$), 3.50 (2H,d, *J* 4.4 Hz, H-6), 3.46 (1H, dt, *J* 9.2 Hz, *J* 6.4 Hz, OCH*H*), 3.38 (1H, dt, *J* 9.2 Hz, *J* 6.6 Hz, OC*H*H), 2.13 (3H, s), 2.10 (3H, s), 2.08 (3H, s), 2.07 (3H, s) (each OAc), 1.50 (2H, m), 1.38 (2H, m), 0.92 (3H, t, *J* 7.4 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 170.2, 169.8, 169.5, 167.5 (each C=O), 71.4 (O*C*H$_2$), 70.9 (C-5), 69.6 (C-3), 69.3 (C-2), 69.2 (C-4), 68.6 (C-6), 52.8 (O*C*H$_3$), 31.5 (*C*H$_2$), 20.9, 20.6 (2s), 20.4 (each OAc), 19.2 (*C*H$_2$), 13.9 (*C*H$_3$); ES-HRMS calcd for $C_{19}H_{30}O_{11}Na$ 457.1672 found *m/z* 457.1686 $[M+Na]^+$.

References for supporting information section

1 O'Brien, C.; Polakova, M.; Pitt, N.; Tosin, M.; Murphy, P. V. *Chem. Eur. J.* **2007**, *13*, 902-909.

2 Graf von Roedern, E.; Lohof, E.; Hessler, G.; Hoffmann, M.; Kessler, H. *J. Am. Chem. Soc.* **1996**, *118*, 10156-10167.

3 Schmidt, R. R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 212-235.

4 (a) Yamamoto, K.; Watanabe, N.; Matsuda, H.; Oohara, K.; Araya, T.; Hashimoto, M.; Miyairi, K.; Okazaki, I.; Saito, M.; Shimizu, T.; Kato, H.; Okuno, T. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 4932-4935. (b) Fulton, D. A.; Stoddart, J. F. *J. Org. Chem.* **2001**, *66*, 8309-8319. (c) Bernardes, G. J. L.; Gamblin, D. P.; Davies, B. G. *Angew. Chem. Int. Ed.* **2006**, *45*, 4007-4011. (d) Wallace, O. B.; Springer, D. M. *Tetrahedron Lett.* **1998**, *39*, 2693-2694. (e) MacDougall, J. M.; Zhang, X.-D.; Polgar, W. E.; Khroyan, T. V.; Toll, L.; Cashman, J. R. *J. Med. Chem.* **2004**, *47*, 5809-5815.

5 Mbadugha, B. N. A.; Menger, F. M. *Org. Lett.* **2003**, *5*, 4041-4044.

6 Bollenback, G. N.; Long, J. W.; Benjamin, D. G.; Lindquist, J. A. *J. Am. Chem. Soc.* **1955**, *77*, 3310-3315.

7 Tietze, L. F.; Seele, R. *Carbohydr. Res.* **1986**, *148*, 349-352.

8 Brown, R. T.; Scheinmann, F.; Stachulski, A. V. *J. Chem. Res., Synop.* **1997**, 370-371.

9 Timell, T. E.; Enterman, W.; Spencer, F.; Soltes, E. J. *Can. J. Chem.* **1965**, *43*, 2296-2305.

10 Györgydeák, Z.; Thiem, J. *Carbohydr. Res.* **1995**, *268*, 85-92.

11 Pippen, E. L.; McCready, R. M. *J. Org. Chem.* **1951**, *16*, 262-268.

12 Antkowiak, R.; Antkowiak, W. Z.; Banczyk, I.; Mikolajczyk, L. *Can. J. Chem.* **2003**, *81*, 118-124.

13 Prata, C.; Mora, N.; Lacombe, J.-M.; Maurizis, J. C.; Pucci, B. *Tetrahedron Lett.* **1997**, *38*, 8859-8862.

14 Tiwari, P.; Misra, A. K. *Carbohydr. Res.* **2006**, *341*, 339-350.

15 Caputo, R.; Kunz, H.; Mastroianni, D.; Palumbo, G.; Pedatella, S.; Solla, F. *Eur. J. Org. Chem.* **1999**, *1999*, 3147-3150.

16 Lopez, R.; Montero, E.; Sanchez, F.; Canada, J.; Fernandez-Mayoralas, A. *J. Org. Chem.* **1994**, *59*, 7027-7032.

17 van Doren, H. A.; van der Geest, R.; Kellogg, R. M.; Wynberg, H. *Carbohydr. Res.* **1989**, *194*, 71-77.

18 Pakulski, Z.; Pierozynski, D.; Zamojski, A. *Tetrahedron* **1994**, *50*, 2975-2992.

19 Lahmann, M.; Oscarson, S. *Can. J. Chem.* **2002**, *80*, 889-893.