Thioglycuronides: Synthesis and Application in the Assembly of Acidic Oligosaccharides

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General Procedures: ^1H and ^{13}C NMR spectra were recorded on a Jeol JNM-FX-200 (200/50.1 MHz), a Bruker AV-400 (400/100 MHz) and a Bruker DMX-600 (600/150 MHz) spectrometer. Chemical shifts are given in ppm (δ) relative to tetramethylsilane as internal standard. Coupling constants are given in Hz. All given ^{13}C spectra are proton decoupled. Mass spectra were recorded with PE/SCIEX API 165 with electrospray interface and Q-Star Applied Biosystems Q-TOF (TOF-section). Optical rotations were measured on a Propol automatic polarimeter. IR-spectra were recorded on a Shimadzu FTIR-8300. Melting points were measured on a Büchi Schmelzpunktbestimmungsapparat nach dr. Tottoli (+ pat 320.388) and were uncorrected. Traces of water in the donor and acceptor glycosides, diphenylsulfoxide, benzenesulfinylpiperidine and TTBP were removed by co-evaporation with toluene. Benzenesulfinylpiperidine¹ and TTBP² were synthesised as described by Crich *et al.* Dichloromethane (DCM, Baker p.a.) was boiled under reflux over P_2O_5 for 2h and distilled immediately prior to use. Trifluoromethanesulfonic anhydride was distilled from P_2O_5 . Molecular sieves $3\text{\AA}$ were flame dried before use. Solvents used for flash chromatography and TLC were of technical grade and distilled before use. Flash chromatography was performed on Baker silica gel (0.063 – 0.200 mm). TLC-analysis was conducted on DC-fertigfolien (Schleicher & Schuell, F1500, LS254) with detection by UV-absorption (254 nm) were applicable and by spraying with 20% sulfuric acid in ethanol followed by charring at $\sim 150^\circ\text{C}$ or by spraying with a solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot\text{H}_2\text{O}$ (25 g/l) in 10% sulfuric acid in ethanol followed by charring at $\sim 150^\circ\text{C}$.

General Procedure for the TEMPO/BAIB Mediated Oxidation:

To a vigorously stirred solution of 0.3 mmol thioglycoside in 1 ml DCM and 0.5 ml H₂O was added 0.06 mmol TEMPO (0.2 eq) and 0.75 mmol BAIB (2.5 eq). Stirring was allowed until TLC indicated complete conversion of the starting material to a lower running spot (~ 45 min). The reaction mixture was quenched by the addition of 10 ml Na₂S₂O₃ solution (10% in H₂O). The mixture was then extracted twice with EtOAc (10 ml) and the combined organic layers were dried (MgSO₄), filtered and concentrated. Flash column chromatography using EtOAc/petroleum ether/AcOH) afforded the pure glycuronic acids.

General Procedure for the Esterification using Diazomethane:

A solution of 0.2 mmol thio uronic acid in 1 ml DMF was treated with a freshly prepared ethereal solution of diazomethane³ (~0.03 M) until the evolution of gas ceased [CAUTION: diazomethane is highly explosive]. The reaction mixture was then treated with 1 ml AcOH and concentrated *in vacuo*. Flash column chromatography using EtOAc/petroleum ether afforded the methyl uronates.

N.B.: NMR-spectroscopy of the various unprotected carboxylic acids sometimes showed low intensity of the C-5 signals. In all cases, the intensity of the peak was restored after methylation of the carboxylate.

Ethyl 2,3,4-tri-*O*-benzyl-1-thio- β -D-glucopyranosiduronic acid **10**: TLC: 50%

EtOAc/PE (5% AcOH); MP: 125°C; $[\alpha]_D^{22}$: -22.4 ($c = 1$, CDCl₃); IR (neat, cm⁻¹):

1074, 1454, 1726; ¹H NMR (400 MHz, MeOD) δ = 1.25 (t, 3H, $J = 7.4$ Hz, CH₃ SEt), 2.62 – 2.75 (m, 2H, CH₂ SEt), 3.39 (t, 1H, $J = 9.2$ Hz, H-2), 3.67 (t, 1H, $J = 8.7$ Hz, H-3), 3.75 (t, 1H, $J = 9.2$ Hz, H-4), 3.93 (d, 1H, $J = 9.6$ Hz, H-5), 4.59 (d, 1H, $J = 10.0$ Hz, H-1), 4.62 – 4.86 (m, 6H, 3xCH₂Ph), 7.22 – 7.31 (m, 15H, H Arom); ¹³C NMR (100 MHz, MeOD) δ = 15.6 (CH₃ SEt), 25.8 (CH₂ SEt), 75.9 (CH₂ Bn), 76.2 (CH₂ Bn), 76.7 (CH₂ Bn), 79.0 (C-5), 81.0 (C-4), 82.5 (C-2), 86.6 (C-1), 86.7 (C-3), 128.6 – 129.3 (CH Arom), 139.3 (C_q Bn), 139.5 (C_q Bn), 139.8 (C_q Bn), 172.0 (C=O COOH); HRMS: (M + NH₄⁺) calcd 509.19924, found 509.19894.

Methyl (ethyl 2,3,4-tri-*O*-benzyl-1-thio- β -D-glucopyranosid) uronate **12**: TLC: 25%

EtOAc/PE; MP: 125°C $[\alpha]_D^{22}$: -10.2 ($c = 1$, CDCl_3); IR (neat, cm^{-1}): 1026, 1074,

1284, 1745; ^1H NMR (400 MHz, MeOD) δ = 1.30 (t, 3H, CH_3 SEt), 2.75 (m, 2H, CH_2 SEt), 3.47 (t, 1H, $J = 9.2$ Hz, H-2), 3.69 (t, 1H, $J = 8.8$ Hz, H-3), 3.89 (d, 1H, $J = 9.6$ Hz, H-5), 4.50 (d, 1H, $J = 9.6$ Hz, H-1), 4.61 (d, 1H, $J = 10.8$ Hz, CHHPh), 4.73 (d, 1H, $J = 10.4$ Hz, CHHPh), 4.77 (d, 1H, $J = 10.8$ Hz, CHHPh), 4.84 (d, 1H, $J = 10.8$ Hz, CHHPh), 4.90 (d, 1H, $J = 11.2$ Hz, CHHPh), 4.92 (d, 1H, $J = 10.0$ Hz, CHHPh), 7.29 (m, 15H, H Arom); ^{13}C NMR (100 MHz, MeOD) δ = 14.9 (CH_3 SEt), 25.0 (CH_2 SEt), 52.3 (CH_3 COOMe), 75.0 (CH_2 Bn), 75.4 (CH_2 Bn), 76.0 (CH_2 Bn), 78.1 (C-5), 81.2 (C-4), 81.2 (C-2), 85.8 (C-1 and C-3), 127.8 – 128.4 (CH Arom), 137.8 (C_q Bn), 138.2 (C_q Bn), 168.7 (C=O COOMe); HRMS: ($\text{M} + \text{NH}_4^+$) calcd 540.2414, found 540.2422.

Ethyl 2,3-di-*O*-benzyl-1-thio- β -D-glucopyranosiduronic acid **11**: TLC: 50%

EtOAc/PE (5% AcOH); $[\alpha]_D^{22}$: -24.6 ($c = 1$, CHCl_3); IR (neat, cm^{-1}): 1085, 1251,

1712, 1776, 3386; ^1H NMR (400 MHz, MeOD) δ = 1.23 (t, 3H, $J = 7.6$ Hz, CH_3 SEt), 2.59 – 2.74 (m, 2H, CH_2 SEt), 3.51 (t, 1H, $J = 9.4$ Hz, H-2), 3.51 (t, 1H, $J = 8.8$ Hz, H-3), 3.75 (t, 1H, $J = 9.2$ Hz, H-4), 3.81 (d, 1H, $J = 9.6$ Hz, H-5), 4.52 (d, 1H, $J = 9.6$ Hz, H-1), 4.62 (d, 1H, $J = 10.4$ Hz, CHHPh), 4.75 (d, 1H, $J = 11.2$ Hz, CHHPh), 4.78 (d, 1H, $J = 10.8$ Hz, CHHPh), 4.90 (d, 1H, $J = 10.8$ Hz, CHHPh), 7.06 – 7.31 (m, 10H, H Arom); ^{13}C NMR (100 MHz, MeOD) δ = 15.5 (CH_3 SEt), 25.6 (CH_2 SEt), 73.3 (C-5), 76.2 (CH_2 Bn), 76.5 (CH_2 Bn), 80.0 (C-4), 82.0 (C-2), 86.4 (C-1), 87.0 (C-3), 128.5 – 129.9 (CH Arom), 139.4 (C_q Bn), 140.0 (C_q Bn), 172.2 (C=O COOMe); HRMS: ($\text{M} + \text{NH}_4^+$) calcd 436.1788, found 436.1793.

Methyl (ethyl 2,3-di-*O*-benzyl-1-thio- β -D-glucopyranosid) uronate **13**: TLC 50%

EtOAc/PE; $[\alpha]_D^{22}$: -30.8 ($c = 1$, CHCl_3); IR (neat, cm^{-1}): 1026, 1062, 1174, 1209,

1357, 1438, 1454, 1496, 1747, 2329, 2866; ^1H NMR (400 MHz, CDCl_3) δ = 1.32 (t, 3H, $J = 7.6$ Hz, CH_3 SEt), 2.68 – 2.34 (m, 2H, CH_2 SEt), 2.89 (bs, 1H, OH), 3.41 (t, 1H, $J = 9.2$ Hz, H-2), 3.56 (t, 1H, $J = 8.6$ Hz, H-3), 3.80 (s, 3H, CH_3 COOMe), 3.83 (s, 1H, H-5), 3.90 (t, 1H, $J = 9.4$ Hz, H-4), 4.52 (d, 1H, $J = 9.6$ Hz, H-1), 4.75 (d, 1H, $J = 10.0$ Hz, CHHPh), 4.88 (s, 2H, CH_2Ph), 4.89 (d, 1H, $J = 11.2$ Hz, CHHPh), 7.13

– 7.35 (m, 10H, H Arom); ^{13}C NMR (100 MHz, CDCl_3) δ = 15.0 (CH_3 SEt), 25.2 (CH_2 SEt), 52.7 (CH_3 COOMe), 71.9 (C-4), 75.5 (CH_2 Bn), 76.2 (CH_2 Bn), 77.6 (C-5), 80.6 (C-2), 85.1 (C-3), 85.9 (C-1), 126.6 – 128.8 (CH Arom), 137.8 (C_q Bn), 138.4 (C_q Bn), 169.6 (C=O COOMe); HRMS: ($\text{M} + \text{NH}_4^+$) calcd 450.1945, found 450.1930.

Phenyl 2,3,4-tri-*O*-benzoyl-1-seleno- α -D-galactopyrosiduronic acid **15**: TLC: 50% EtOAc/PE (5% AcOH); IR (neat, cm^{-1}): 1026, 1068, 1091, 1178, 1211, 1257, 1315, 1450, 1583, 1600, 1724; ^1H NMR (400 MHz, MeOD) δ = 4.89 (s, 1H, H-5), 5.44 (d, 1H, J = 10.0 Hz, H-1), 5.66 (t, 1H, J = 9.8 Hz, H-2), 5.74 (dd, 1H, J = 9.6 Hz, J = 3.2 Hz, H-3), 6.21 (d, 1H, J = 2.4 Hz, H-4), 7.08 – 7.96 (m, 20H, H Arom); ^{13}C NMR (100 MHz, MeOD) δ = 69.8 (C-2), 71.1 (C-4), 74.0 (C-3), 77.5 (C-5), 80.9 (C-1), 127.2 (C_q SePh), 129.1 – 137.7 (CH Arom), 130.2 (C_q Bz), 130.5 (C_q Bz), 130.6 (C_q Bz), 166.6 (C=O Bz or COOH), 169.5 (C=O Bz or COOH); HRMS: ($\text{M} + \text{NH}_4^+$) calcd 664.1080, found 664.1098.

Methyl (phenyl 2,3,4-tri-*O*-benzoyl-1-seleno- α -D-galactopyrosid) uronate **16**: TLC: 30% EtOAc/PE; IR (neat, cm^{-1}): 1001, 1024, 1066, 1091, 1178, 1211, 1257, 1438, 1450, 1600, 1726; ^1H NMR (400 MHz, CDCl_3) δ = 4.63 (s, 1H, H-5), 5.20 (d, 1H, J = 9.6 Hz, H-1), 5.58 (dd, 1H, J = 9.6 Hz, J = 3.2 Hz, H-3), 5.73 (t, 1H, J = 9.8 Hz, H-2), 6.18 (dd, 1H, J = 2.8 Hz, J = 0.8 Hz, H-4), 7.20 – 7.99 (m, 20H, H Arom); ^{13}C NMR (100 MHz, CDCl_3) δ = 52.6 (CH_3 COOMe), 68.0 (C-3), 69.2 (C-4), 72.4 (C-2), 76.8 (C-5), 80.2 (C-1), 125.7 (C_q SePh), 128.2 – 136.7 (CH Arom), 128.8 (C_q Bz), 164.9 (C=O Bz or COOMe), 165.4 (C=O Bz or COOMe), 166.1 (C=O Bz or COOMe); HRMS: ($\text{M} + \text{NH}_4^+$) calcd 678.1237, found 678.1235.

Phenyl 4-*O*-benzyl-2,3-*O*-isopropylidene-1-thio- α -D-mannopyraniduronic acid **18**: TLC: 50% EtOAc/PE (5% AcOH); $[\alpha]_D^{22}$: +104.0 (c = 1, CHCl_3); ^1H NMR (400 MHz, MeOD) δ = 1.33 (s, 3H, Me isoprop.), 1.42 (s, 3H, Me isoprop.), 3.97 (dd, 1H, J = 7.4 Hz, J = 6.0 Hz, J = 5.6 Hz, H-4), 4.26 (dd, 1H, J = 5.4 Hz, J = 4.0 Hz, J = 3.6 Hz, H-2), 4.32 (t, 1H, J = 5.6 Hz, H-3), 4.59 (d, 1H, J = 7.2 Hz, H-5), 4.67 (d, 1H, J = 11.6 Hz, CHHPh), 4.75 (d, 1H, J = 11.6 Hz, CHHPh), 5.68 (d, 1H, J

= 3.2 Hz, H-1), 7.07 – 7.55 (m, 10H, H Arom); ^{13}C NMR (100 MHz, MeOD) δ = 26.5 (CH_3 isoprop), 28.1 (Me isoprop), 71.9 (C-5), 73.7 (CH_2 Bn), 76.1 (C-2), 77.2 (C-4), 77.9 (C-3), 84.7 (C-1), 111.0 (C_q isoprop), 128.8 – 133.0 (CH Arom), 134.3 (C_q SPh), 139.1 (C_q Bn), 172.3 (C=O); HRMS: ($\text{M} + \text{NH}_4^+$) calcd 434.1632, found 434.1695.

Methyl (phenyl 4-*O*-benzyl-2,3-*O*-isopropylidene-1-thio- α -D-mannopyranid) uronate

19: TLC: 30% EtOAc/PE; $[\alpha]_{\text{D}}^{22}$: +43.0 ($c = 0.6$, CHCl_3); IR (neat, cm^{-1}): 1043, 1093, 1234, 1735; ^1H NMR (400 MHz, CDCl_3) δ = 1.29 (s, 3H, Me isoprop), 1.42 (s, 3H, Me isoprop), 3.63 (s, 3H, CH_3 COOMe), 3.90 (dd, 1H, $J = 7.8$ Hz, $J = 6.4$ Hz, $J = 6.0$ Hz, H-4), 4.22 (dd, 1H, $J = 5.6$ Hz, $J = 3.6$ Hz, H-2), 4.27 (t, 1H, $J = 5.8$ Hz, H-3), 4.56 (d, 1H, $J = 8.4$ Hz, H-5), 4.59 (d, 1H, $J = 12.4$ Hz, CHHPh), 4.72 (d, 1H, $J = 11.2$ Hz, CHHPh), 5.60 (d, 1H, $J = 3.6$ Hz, H-1), 7.17 – 7.47 (m, 10H, H Arom); ^{13}C NMR (100 MHz, CDCl_3) δ = 26.1 (CH_3 isoprop), 27.7 (CH_3 isoprop), 52.3 (CH_3 COOMe), 70.7 (C-5), 72.9 (CH_2 Bn), 75.0 (C-2), 76.0 (C-4), 76.7 (C-3), 83.7 (C-1), 110.0 (C_q isoprop), 127.6 – 131.9 (CH Arom), 132.8 (C_q SPh), 137.5 (C_q Bn), 169.4 (C=O); HRMS: ($\text{M} + \text{NH}_4^+$) calcd 448.1788, found 448.1833.

Ethyl 2,3-di-*O*-benzoyl-1-thio- β -D-glucopyranosylduronic acid **22**: TLC: 50%

EtOAc/PE (5% AcOH); IR (neat, cm^{-1}): 1072, 1272, 1450, 1604, 1720; ^1H NMR (400 MHz, MeOD) δ = 1.22 (t, 3H, $J = 7.6$ Hz, CH_3 SEt), 2.67 – 2.77 (m, 2H, CH_2 SEt), 4.07 (t, 1H, $J = 9.4$ Hz, H-4), 4.13 (d, 1H, $J = 10.0$ Hz, H-5), 4.93 (d, 1H, $J = 9.2$ Hz, H-1), 5.35 (t, 1H, $J = 9.8$ Hz, H-2), 5.62 (t, 1H, $J = 9.2$ Hz, H-3), 7.09 – 7.92 (m, 10H, H Arom); ^{13}C NMR (100 MHz, MeOD) δ = 15.3 (CH_3 SEt), 25.0 (CH_2 SEt), 71.0 (C-4), 71.8 (C-2), 77.4 (C-3), 80.1 (C-5), 84.7 (C-1), 128.9 – 134.3 (CH Arom), 129.7 (C_q Bz), 130.2 (C_q Bz), 166.5 (C=O Bz or COOH), 167.2 (C=O Bz or COOH); HRMS: ($\text{M} + \text{H}^+$) calcd 469.09276, found 469.09314.

Methyl (ethyl 2,3-di-*O*-benzoyl-1-thio- β -D-glucopyranosyd) uronate **24**: TLC: 30%

EtOAc/PE; $[\alpha]_{\text{D}}^{22}$: +63.6 ($c = 1$, CHCl_3); IR (neat, cm^{-1}): 1066, 1272, 1724, 3471; ^1H NMR (400 MHz, CDCl_3): δ = 1.20 (t, 3H, $J = 7.6$ Hz, CH_3 SEt), 2.72 (m, 2H, CH_2 SEt), 3.82 (s, 3H, CH_3

COOMe), 4.14 (d, 1H, $J = 10.0$ Hz, H-5), 4.21 (t, 1H, $J = 9.2$ Hz, H-4), 4.80 (d, 1H, $J = 10.0$ Hz, H-1), 5.46 (t, 1H, $J = 9.8$ Hz, H-2), 5.62 (t, 1H, $J = 9.2$ Hz, H-3), 7.28 – 7.96 (m, 10H, H Arom); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 14.6$ (CH_3 SEt), 24.3 (CH_2 SEt), 52.7 (CH_3 COOMe), 69.8 (C-2), 70.3 (C-4), 76.0 (C-3), 78.3 (C-5), 84.2 (C-1), 128.2 – 133.2 (CH Arom), 129.0 (C_q Bz), 165.2 (C=O Bz or COOMe), 166.3 (C=O Bz or COOMe), 168.7 (C=O Bz or COOMe); HRMS: ($\text{M} + \text{NH}_4^+$) calcd 483.10841, found 483.10828.

Phenyl 2,3-di-*O*-benzoyl-1-thio- α -D-glucopyranosydruronic acid **23**: TLC: EtOAc (2% AcOH); $[\alpha]_D^{22}$: +61.8 ($c = 1$; CHCl_3); IR (neat, cm^{-1}): 707, 1066, 1271, 1712; ^1H NMR (400 MHz, MeOD): $\delta = 4.12$ (t, 1H, $J = 9.4$ Hz, H-4), 5.26 (d, 1H, $J = 10.0$ Hz, H-5), 5.29 (t, 1H, $J = 10.0$ Hz, H-1), 5.37 (t, 1H, $J = 9.4$ Hz, H-2), 5.74 (t, 1H, $J = 9.2$ Hz, H-3), 7.21 – 8.06 (m, 15H, H Arom); ^{13}C NMR (100 MHz, MeOD): $\delta = 70.1$ (C-4), 70.9 (C-2), 76.6 (C-3), 78.9 (C-5), 86.1 (C-1), 128.1 – 133.5 (CH Arom), 129.2 (C_q Bz), 132.2 (C_q SPh), 165.5 (C=O Bz), 166.3 (C=O Bz), 170.4 (C=O COOH); HRMS: ($\text{M} + \text{H}^+$) calcd 469.09276, found 469.09314.

Methyl (phenyl 2,3-di-*O*-benzoyl-1-thio- β -D-glucopyranosyd) uronate **25**: TLC: 30% EtOAc/PE; $[\alpha]_D^{22}$: +63.3 ($c = 1$, CHCl_3); IR (neat, cm^{-1}): 707, 1066, 1272, 1724, 3471; ^1H NMR (400 MHz, CDCl_3) $\delta = 3.52$ (bs, 1H, OH), 3.87 (s, 3H, CH_3 COOMe), 4.13 (d, 1H, $J = 9.6$ Hz, H-5), 4.18 (t, 1H, $J = 9.2$ Hz, H-4), 4.99 (d, 1H, $J = 10.0$ Hz, H-1), 5.41 (t, 1H, $J = 9.8$ Hz, H-2), 5.58 (t, 1H, $J = 9.0$ Hz, H-3), 7.26 – 8.02 (m, 15H, H Arom); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 53.0$ (CH_3 COOMe), 69.7 (C-4), 70.3 (C-2), 76.2 (C-3), 78.0 (C-5), 86.9 (C-1), 128.4 – 133.4 (CH Arom), 128.9 (C_q Bz), 129.0 (C_q Bz), 131.9 (C_q SPh), 165.0 (C=O Bz or COOMe), 166.5 (C=O Bz or COOMe), 168.8 (C=O Bz or COOMe); HRMS: ($\text{M} + \text{H}^+$) calcd 517.0928, found 517.0933.

Ethyl 2-azido-3-*O*-benzoyl-2-deoxy-1-thio- β -D-glucopyranosiduronic acid **27**: TLC: 50% EtOAc/PE (5% AcOH); $[\alpha]_D^{22}$: -0.8 ($c = 1$, CHCl_3); IR (neat, cm^{-1}): 1026, 1068, 1116, 1261, 1421, 1716, 2108; ^1H NMR (400 MHz, MeOD) $\delta = 1.31$ (t, 3H, $J = 7.0$ Hz, CH_3 SEt), 2.79 (m, 2H, CH_2 SEt), 3.67 (t, 1H, $J = 10.0$ Hz, H-2), 3.91 (t, 1H, $J = 9.4$ Hz, H-4), 3.98 (d, 1H, $J = 9.6$ Hz, H-5),

4.69 (d, 1H, $J = 10.4$ Hz, H-1), 5.25 (t, $J = 9.4$ Hz, H-3), 7.47 – 8.11 (m, 5H, H Arom); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 15.5$ (CH_3 SEt), 25.5 (CH_2 SEt), 65.1 (C-2), 71.2 (C-4), 77.9 (C-3), 80.1 (C-5), 85.7 (C-1), 129.6 – 134.5 (CH Arom), 167.3 (C=O Bz), 172.0 (C=O COOH); HRMS: ($\text{M} + \text{H}^+$) calcd 368.09108, found 368.09232

Methyl (ethyl 2-azido-3-*O*-benzoyl-2-deoxy-1-thio- β -D-glucopyranosid) uronate **28**:

TLC: 30% EtOAc/PE; $[\alpha]_D^{22}$: -2.0 ($c = 0.8$, CHCl_3); IR (neat, cm^{-1}): 1091, 1211, 1265, 1450, 1732, 2110; ^1H NMR (400 MHz, CDCl_3) $\delta = 1.36$ (t, 3H, $J = 7.6$ Hz, CH_3 SEt), 2.82 (m, 2H, CH_2 SEt), 3.62 (t, 1H, $J = 10.0$ Hz, H-2), 3.82 (s, 3H, CH_3 COOMe), 4.00 (d, 1H, $J = 9.6$ Hz, H-5), 4.05 (t, 1H, $J = 9.4$ Hz, H-4), 4.55 (d, 1H, $J = 10.0$ Hz, H-1), 5.26 (t, 1H, $J = 9.6$ Hz, $J = 9.2$ Hz, H-3), 7.45 – 8.10 (m, 5H, H Arom); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 14.9$ (CH_3 SEt), 25.2 (CH_2 SEt), 52.9 (CH_3 COOMe), 63.6 (C-2), 70.2 (C-4), 76.7 (C-3), 78.1 (C-5), 85.2 (C-1), 128.5 – 133.6 (CH Arom), 129.1 (C_q Bz), 166.4 (C=O Bz or COOMe), 168.7 (C=O Bz or COOMe); ESI-MS: 404.1 ($\text{M} + \text{Na}^+$).

Phenyl

3-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-phthalimido-1-thio- β -D-

glucopyranosiduronic acid **30**: TLC: EtOAc (5% AcOH); $[\alpha]_D^{22}$: +39.6 ($c = 1$,

CHCl_3); IR (neat, cm^{-1}): 1085, 1251, 1386, 1593, 1712, 1776, 3386; ^1H NMR (400 MHz, CDCl_3) $\delta = -0.19$ (s, 3H, Me TBDMS), 0.14 (s, 3H, Me TBDMS), 0.66 (s, 9H, *t*-Bu TBDMS), 3.65 (t, 1H, $J = 9.2$ Hz, H-4), 3.93 (d, 1H, $J = 10.0$ Hz, H-5), 4.26 (t, 1H, $J = 10.2$ Hz, H-2), 4.49 (t, 1H, $J = 9.2$ Hz, H-3), 5.65 (d, 1H, $J = 10.4$ Hz, H-1), 7.22 – 7.24 (m, 3H, H(Ar SPh), 7.38 – 7.40 (m, 2H, H(Ar SPh), 7.84 – 7.93 (m, 4H, H(Ar NPhth)); ^{13}C NMR (100 MHz, CDCl_3) $\delta = -5.0$ (Me TBDMS), -3.4 (Me TBDMS), 18.7 (C_q *t*-Bu), 26.2 (*t*-Bu), 57.6 (C-2), 74.8 (C-4), 75.1 (C-3), 81.0 (C-5), 85.8 (C-1), 124.3 – 135.8 (CH Arom), 132.9 (C_q SPh), 134.2 (C_q NPhth), 169.0 (C=O NPhth), 169.7 (C=O NPhth), 177.2 (C=O COOH); HRMS: ($\text{M} + \text{NH}_4^+$) calcd 547.1929, found 547.1987.

Methyl (phenyl 3-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranosid) uronate **31**: TLC: 50% EtOAc/PE (5% AcOH); $[\alpha]_D^{22}$: +93.2 (c = 1, CHCl₃); IR (neat, cm⁻¹): 1384, 1110, 1710; ¹H NMR (400 MHz, CDCl₃) δ = -0.30 (s, 3H, Me TBDMS), 0.02 (s, 3H, Me TBDMS), 0.61 (s, 9H, *t*Bu TBDMS), 3.10 (bs, 1H, OH), 3.76 (dd, 1H, *J* = 11.0 Hz, *J* = 8.4 Hz, *J* = 5.6 Hz, H-4), 3.81 (s, 3H, CH₃ COOMe), 4.02 (d, 1H, *J* = 10.0 Hz, H-5), 4.24 (t, 1H, *J* = 10.2 Hz, H-2), 4.43 (dd, 1H, *J* = 9.6 Hz, *J* = 8.4 Hz, H-3), 5.55 (d, 1H, *J* = 10.8 Hz, H-1), 7.13 – 7.84 (m, 10H, H Arom); ¹³C NMR (100 MHz, CDCl₃) δ = -5.3 (Me TBDMS), -4.1 (Me TBDMS), 17.8 (C_q *t*Bu), 25.5 (*t*Bu TBDMS), 52.8 (Me), 55.6 (C-2), 72.9 (C-3), 73.1 (C-4), 77.7 (C-5), 84.5 (C-1), 123.2 – 134.2 (CH Arom), 131.7 (C_q SPh), 132.1 (C_q Phth), 169.7 (C=O NPhth or COOMe); ESI-MS: 566.2 (M + Na⁺).

Phenyl 2,3-di-*O*-benzyl-1-thio- β -D-galactopyranosiduronic acid **33**: TLC: 50% EtOAc/PE (5% AcOH); $[\alpha]_D^{22}$: -11.2 (c = 0.8, CHCl₃); IR (neat, cm⁻¹): 1027, 1086, 1725; ¹H NMR (400 MHz, CDCl₃) δ = 3.62 (dd, 1H, *J* = 8.8 Hz, *J* = 3.2 Hz, *J* = 2.8 Hz, H-3), 3.74 (t, 1H, *J* = 9.4 Hz, H-2), 4.06 (s, 3H, H-5), 4.43 (bs, 1H, H-4), 4.64 (d, 1H, *J* = 9.6 Hz, H-1), 4.65 (d, 1H, *J* = 11.6 Hz, CHHPh), 4.73 (d, 1H, *J* = 11.2 Hz, CHHPh), 4.75 (d, 1H, *J* = 10.0 Hz, CHHPh), 4.82 (d, 1H, *J* = 10.4 Hz, CHHPh), 5.57 (bs, 1H, COOH), 7.12 – 7.58 (m, 15H, H Ar); ¹³C NMR (100 MHz, CDCl₃) δ = 67.4 (C-4), 72.2 (CH₂ Bn), 75.8 (CH₂ Bn), 76.2 (C-2), 76.6 (C-5), 81.5 (C-3), 87.8 (C-1), 127.9 – 132.6 (CH Arom), 132.9 (C_q SPh), 137.2 (C_q Bn), 137.9 (C_q Bn), 169.9 (C=O COOH); HRMS: (M + Na⁺) calcd 467.15229, found 467.15396

Methyl (phenyl 2,3-di-*O*-benzyl-1-thio- β -D-galactopyranosid) uronate **34**: TLC: 50% EtOAc/PE; $[\alpha]_D^{22}$: -8.4 (c = 0.6, CHCl₃); IR (neat, cm⁻¹): 1026, 1083, 1716; ¹H NMR (400 MHz, CDCl₃) δ = 2.49 (s, 1H, OH), 3.63 (dd, 1H, *J* = 8.8 Hz, *J* = 3.2 Hz, H-3), 3.77 (t, 1H, *J* = 9.0 Hz, H-2), 3.84 (s, 3H, CH₃ COOMe), 4.07 (s, 1H, H-5), 4.39 (s, 1H, H-4), 4.59 (d, 1H, *J* = 10.0 Hz, H-1), 4.68 (d, 1H, *J* = 11.2 Hz, CHHPh), 4.73 (d, 2H, *J* = 10.0 Hz, CHHPh, CHHPh), 4.83 (d, 1H, *J* = 10.4 Hz, CHHPh), 7.13 – 8.01 (m, 15H, H Ar); ¹³C NMR (100 MHz, CDCl₃) δ = 52.7 (CH₃ COOMe), 67.8 (C-4), 72.2 (CH₂ Bn), 75.8 (CH₂ Bn), 76.3 (C-2), 76.7 (C-5), 81.7 (C-3), 87.8 (C-1), 127.8 – 132.8 (CH Arom),

133.1 (C_q SPh), 137.2 (C_q Bn), 138.0 (C_q Bn), 168.2 (C=O); HRMS: (M + H⁺) calcd 503.14972, found 503.14988.

Phenyl 2-*O*-benzoyl-3-*O*-benzyl-1-thio-β-D-galactopyranosiduronic acid **36**: TLC:

50% EtOAc/PE (5% AcOH); [α]_D²²: +52.8 (c = 1, CHCl₃); IR (neat, cm⁻¹): 1026, 1068, 1091, 1263, 1431, 1600, 1720; ¹H NMR (400 MHz, MeOD) δ = 3.80 (d, 1H, *J* = 9.6 Hz, H-3), 4.21 (s, 1H, H-5), 4.53 (d, 1H, *J* = 12.4 Hz, CHHPh), 4.54 (s, 1H, H-4), 4.64 (d, 1H, *J* = 12.0 Hz, CHHPh), 4.90 (d, 1H, *J* = 8.4 Hz, H-1), 5.49 (t, 1H, *J* = 9.8 Hz, H-2), 7.00 – 7.93 (m, 15H, H Arom); ¹³C NMR (100 MHz, MeOD) δ = 67.0 (C-4), 69.7 (C-2), 70.5 (CH₂ Bn), 78.1 (C-5), 79.4 (C-3), 86.6 (C-1), 127.1 – 133.0 (CH Arom), 129.8 (C_q SPh), 133.9 (C_q Bz), 137.8 (C_q Bn), 165.6 (C=O Bz or COOH); ESI-MS: 503.3 (M + Na⁺).

Methyl (phenyl 2-*O*-benzoyl-3-*O*-benzyl-1-thio-β-D-galactopyranosid) uronate **37**:

TLC: 50% EtOAc/PE; [α]_D²²: +28.8 (c = 1, CHCl₃); IR (neat, cm⁻¹): 1213, 1265, 1662, 1726, 1760; ¹H NMR (400 MHz, CDCl₃) δ = 3.74 (dd, 1H, *J* = 9.2 Hz, *J* = 2.8 Hz, H-3), 3.84 (s, 3H, OMe COOMe), 4.18 (s, 1H, H-5), 4.50 (d, 1H, *J* = 12.0 Hz, CHHPh), 4.51 (s, 1H, H-4), 4.67 (d, 1H, *J* = 12.4 Hz, CHHPh), 4.74 (d, 1H, *J* = 10.4 Hz, H-1), 5.52 (t, 1H, *J* = 9.2 Hz, H-2), 7.02 – 8.02 (m, 15H, H Arom); ¹³C NMR (100 MHz, CDCl₃) δ = 52.6 (CH₃ COOMe), 67.3 (C-4), 68.9 (C-2), 71.2 (CH₂ Bn), 77.0 (C-5), 78.3 (C-3), 86.6 (C-1), 127.8 – 133.1 (CH Arom), 129.6 (C_q SPh), 132.4 (C_q Bz), 136.6 (C_q Bn), 165.1 (C=O Bz or COOMe), 167.9 (C=O Bz or COOMe); HRMS: (M + H⁺) calcd 512.1738, found 512.1797.

Ethyl 3-*O*-benzoyl-2-*O*-benzyl-1-thio-α/β-L-idopyranosiduronic acid **39**: TLC: 50%

EtOAc/PE (5% AcOH); IR (neat, cm⁻¹) 1716, 1066; α-anomer: ¹H NMR (400 MHz, MeOD): δ = 1.27 (t, 3H, *J* = 7.6 Hz, CH₃ SEt), 2.68 (m, 2H, CH₂ SEt), 3.87 (s, 1H, H-3), 4.14 (m, 1H, H-4), 4.68 (d, 1H, *J* = 12.0 Hz, CHHPh), 4.80 (d, 1H, *J* = 12.0 Hz, CHHPh), 5.08 (s, 1H, H-5), 5.26 (s, 1H, H-2), 5.52 (s, 1H, H-1), 8.17-7.12 (m, 10H, H Arom); ¹³C NMR (100 MHz, CDCl₃): δ = 15.5 (CH₃ SEt), 27.3 (CH₂ SEt), 69.0 (C-4), 70.2 (C-5), 71.0 (C-2), 73.4 (CH₂ Bn), 76.8 (C-3), 84.0 (C-1), 134.4-

128.7 (CH Arom), 130.8 (C_q Bz), 138.9 (C_q Bn), 166.9 (C=O Bz or COOMe), 173.2 (C=O Bz or COOMe);

β-anomer: ¹H NMR (400 MHz, CDCl₃): δ = 1.30 (t, 3H, *J* = 7.6 Hz, CH₃ SEt), 2.78 (m, 2H, CH₂ SEt), 3.82 (s, 1H, H-3), 4.08 (m, 1H, H-4), 4.57 (s, 1H, H-5), 4.76 (d, 1H, *J* = 12.0 Hz, CHHPh), 4.81 (d, 1H, *J* = 12.0 Hz, CHHPh), 5.21 (s, 1H, H-1), 5.22 (s, 1H, H-2), 8.17-7.12 (m, 10H, H Arom); ¹³C NMR (100 MHz, CDCl₃): δ = 15.5 (CH₃ SEt), 26.4 (CH₂ SEt), 67.8 (C-4), 71.3 (C-2), 73.4 (CH₂ Bn), 76.4 (C-3), 77.2 (C-5), 83.0 (C-1), 134.4-128.7 (CH Arom), 130.7 (C_q Bz), 139.0 (C_q Bn), 167.3 (C=O Bz or COOMe), 172.4 (C=O Bz or COOMe); HRMS: (M + NH₄⁺) calcd 450.1581, found 450.1568.

Methyl (ethyl 3-O-benzoyl-2-O-benzyl-1-thio-α/β-L-idopyranosid) uronate **40**:

TLC: 50% EtOAc/PE; IR (neat, cm⁻¹): 1091, 1720, 1760; **α-anomer:** ¹H NMR (400

MHz, CDCl₃) δ = 1.30 (t, 3H, *J* = 7.6 Hz, CH₃ SEt), 2.66 (m, 2H, CH₂ SEt), 2.93 (bd, 1H, *J* = 11.2 Hz, OH), 3.79 (s, 3H, CH₃ COOMe), 3.88 (s, 1H, H-3), 4.10 (m, 1H, H-4), 4.63 (d, 1H, *J* = 12.0 Hz, CHHPh), 4.83 (d, 1H, *J* = 12.0 Hz, CHHPh), 5.28 (s, 1H, H-5), 5.32 (s, 1H, H-2), 5.56 (s, 1H, H-1), 7.12 - 8.00 (m, 10H, H Arom); ¹³C NMR (100 MHz, CDCl₃): δ = 14.8 (CH₃ SEt), 26.7 (CH₂ SEt), 52.1 (CH₃ COOMe), 68.1 (C-4), 68.3 (C-5), 69.5 (C-2), 72.0 (CH₂ Bn), 73.6 (C-3), 83.0 (C-1), 127.5 - 133.4 (CH Arom), 128.8 (C_q Bz), 136.9 (C_q Bn), 164.7 (C=O Bz or COOMe), 169.6 (C=O Bz or COOMe); **β-anomer:** ¹H NMR (400 MHz, CDCl₃): δ = 1.30 (t, 3H, *J* = 7.6 Hz, CH₃ SEt), 2.75 (m, 2H, CH₂ SEt), 2.87 (bd, 1H, *J* = 11.6 Hz, OH), 3.79 (s, 3H, CH₃ COOMe), 3.99 (s, 1H, H-3), 4.06 (m, 1H, H-4), 4.60 (s, 1H, H-5), 4.72 (d, 1H, *J* = 12.0 Hz, CHHPh), 4.80 (d, 1H, *J* = 11.6 Hz, CHHPh), 5.15 (s, 1H, H-1), 5.28 (s, 1H, H-2), 8.00-7.12 (m, 10H, H Arom); ¹³C NMR (100 MHz, CDCl₃): δ = 14.7 (CH₃ SEt), 25.6 (CH₂ SEt), 52.1 (CH₃ COOMe), 67.3 (C-4), 69.9 (C-2), 72.4 (CH₂ Bn), 74.2 (C-3), 76.0 (C-5), 81.9 (C-1), 127.5 - 133.4 (CH Arom), 128.7 (C_q Bz), 136.9 (C_q Bn), 165.1 (C=O Bz or COOMe), 168.7 (C=O Bz or COOMe); HRMS: (M + NH₄⁺) calcd 464.1737, found 464.1739.

Methyl (phenyl 4-*O*-acetyl-2,3-di-*O*-benzoyl-1-thio- β -D-galactopyranosid) uronate

41: A solution of 138 mg compound **25** (0.3 mmol) in 2 ml pyridine and 0.7 ml Ac₂O was stirred for 3h before 3 ml MeOH was added. The reaction mixture was concentrated under reduced pressure and several times co-evaporated with toluene. Flash column chromatography using EtOAc/petroleum ether afforded 153 mg of the title compound **41** (0.3 mmol, quant) as a colourless oil. TLC: 25% EtOAc/PE; MP: 178°C; $[\alpha]_D^{22}$: +59.0 (*c* = 1, CHCl₃); IR (neat, cm⁻¹): 1066, 1093, 1226, 1257, 1708; ¹H NMR (400 MHz, CDCl₃) δ = 1.94 (s, 3H, Ac), 3.80 (s, 3H, CH₃ COOMe), 4.23 (d, 1H, *J* = 10.0 Hz, H-5), 5.99 (d, 1H, *J* = 10.0 Hz, H-1), 5.40 (t, 1H, *J* = 10.0 Hz, H-2), 5.45 (t, 1H, *J* = 10.2 Hz, H-4), 5.73 (t, 1H, *J* = 9.4 Hz, H-3), 7.31 – 7.96 (m, 15H, H Arom); ¹³C NMR (100 MHz, CDCl₃) δ = 20.4 (Ac), 52.9 (CH₃ COOMe), 69.4 (C-4), 69.9 (C-2), 73.6 (C-3), 76.4 (C-5), 86.5 (C-1), 128.4 – 133.4 (CH Arom), 128.5 (C_q SPh), 131.3 (C_q Bz), 164.8 (C=O Ac, Bz or COOMe), 165.5 (C=O Ac, Bz or COOMe), 166.9 (C=O Ac, Bz or COOMe); HRMS: (*M* + H⁺) calcd 551.13703, found 551.13885

Methyl (phenyl 4-*O*-acetyl-2,3-di-*O*-benzyl-1-thio- β -D-galactopyranosid) uronate **44:**

A solution of 734 mg compound **34** (1.53 mmol) in 5 ml pyridine and 2 ml Ac₂O was stirred for 3h before 5 ml MeOH was added. The reaction mixture was concentrated under reduced pressure and several times co-evaporated with toluene. Flash column chromatography using EtOAc/petroleum ether afforded 798 mg of the title compound **44** (1.53 mmol, quant) as a colourless oil. TLC: 25% EtOAc/PE; $[\alpha]_D^{22}$: -32.0 (*c* = 1, CHCl₃); IR (neat, cm⁻¹): 1230, 1749; ¹H NMR (400 MHz, CDCl₃) δ = 2.11 (s, 3H, Ac), 3.67 (m, 2H, H-2, H-5), 3.78 (s, 3H, CH₃ COOMe), 4.52 (d, 1H, *J* = 11.2 Hz, CHHPh), 4.63 (d, 1H, *J* = 9.6 Hz, H-1), 4.74 (d, 1H, *J* = 10.4 Hz, CHHPh), 4.75 (d, 1H, *J* = 9.6 Hz, CHHPh), 4.77 (d, 1H, *J* = 10.0 Hz, CHHPh), 5.82 (d, 1H, *J* = 1.2 Hz, H-4), 7.25 – 7.40 (m, 15H, H Arom); ¹³C NMR (100 MHz, CDCl₃) δ = 20.8 (Ac), 52.6 (CH₃ COOMe), 67.6 (C-4), 72.0 (CH₂ Bn), 75.6 (C-3), 76.1 (CH₂ Bn), 76.7 (C-2 or C-5), 80.6 (C-5 or C-2), 87.8 (C-1), 127.8 – 128.8 (CH Arom), 137.2 (C_q Bn), 138.0 (C_q Bn), 167.0 (C=O Ac or COOMe), 169.9 (C=O Ac or COOMe); HRMS: (*M* + H⁺) calcd 523.17850, found 523.18024

Methyl 2,3,4-tri-*O*-benzyl-6-(methyl (4-acetyl-2,3-di-*O*-benzoyl-β-*D*-glucopyranosid) uronate)-α-*D*-glucopyranoside **43**: A solution of 54 mg methyl (phenyl 4-*O*-acetyl-2,3-di-*O*-benzoyl-1-thio-β-*D*-glucopyranosid)

uronate **39** (0.1 mmol), 29 mg benzenesulfinylpiperidine (0.14 mmol, 1.4 eq) in 2.5 ml DCM was stirred over 100 mg activated MS3Å for 30 min. The mixture was cooled to -60°C before 22 µl triflic acid anhydride (0.13 mmol, 1.3 eq) was added. The mixture was allowed to warm to -40°C in 15 min followed by addition of 93 mg methyl 2,3,4-tri-*O*-benzyl-β-*D*-galactopyranoside **42** (0.2 mmol, 2 eq) in 0.5 ml DCM. Stirring was continued and the reaction mixture was allowed to warm to 0°C. Subsequently the reaction was quenched by addition of 0.16 ml triethylamine. Flash chromatography (15% EtOAc/PE) and removal of the eluent afforded 57 mg of the title compound **43** (0.063 mmol, 63%) as a colourless oil. TLC: 20% EtOAc/toluene; MP: 168°C (decomp.); $[\alpha]_D^{22}$: +40.4 ($c = 1$, CHCl₃); IR (neat, cm⁻¹): 1024, 1066, 1091, 1220, 1276, 1730; ¹H NMR (400 MHz, CDCl₃) δ = 1.94 (s, 3H, Ac), 3.18 (s, 3H, Me(OMe)), 3.35 (m, 1H, $J = 9.2$ Hz, H-4), 3.40 (dd, 1H, $J = 9.6$ Hz, $J = 3.2$ Hz, H-2), 3.69 (m, 2H, H-5, H-6), 3.76 (s, 3H, CH₃ COOMe), 4.14 (d, 1H, $J = 9.6$ Hz, H-5', H-6), 4.31 (d, 1H, $J = 11.2$ Hz, CHHPh), 4.47 (d, 1H, $J = 3.6$ Hz, H-1), 4.56 (d, 1H, $J = 8.4$ Hz, CHHPh), 4.58 (d, 1H, $J = 9.6$ Hz, CHHPh), 4.68 (d, 2H, $J = 10.8$ Hz, 2xCHHPh), 4.74 (d, 1H, $J = 6.8$ Hz, H-1'), 4.90 (d, 1H, $J = 10.8$ Hz, CHHPh), 5.45 – 5.51 (m, 2H, $J = 9.6$ Hz, $J = 6.4$ Hz, H-2', H-4'), 5.68 (t, 1H, $J = 9.4$ Hz, H-3'); ¹³C NMR (100 MHz, CDCl₃) δ = 7.08 – 7.91 (m, 25H, H Arom); ¹³C NMR (100 MHz, CDCl₃) δ = 20.4 (Ac), 52.8 (CH₃ COOMe), 54.9 (Me(OMe)), 68.5 (C-6), 69.3 (C-2' or C-4'), 69.5 (C-5), 71.4 (C-4' or C-2'), 72.2 (C-3'), 72.7 (C-5'), 73.2 (CH₂ Bn), 74.6 (CH₂ Bn), 75.4 (CH₂ Bn), 77.4 (C-4), 79.7 (C-2), 81.8 (C-3), 97.8 (C-1), 101.1 (C-1'), 127.4 – 133.4 (CH Arom), 128.3 (C_q Bz), 129.0 (C_q Bz), 138.1 (C_q Bn), 138.7 (C_q Bn), 163.2 (C=O Bz or Ac or COOMe), 164.7 (C=O Bz or Ac or COOMe), 165.6 (C=O Bz or Ac or COOMe), 167.1 (C=O Bz or Ac or COOMe), 169.2 (C=O Bz or Ac or COOMe); HRMS: (M + Na⁺) calcd 927.31984. found 927.32434

Methyl (4-methoxyphenyl 2,4-di-*O*-benzyl-3-(methyl (4-*O*-acetyl-2,3-di-*O*-benzyl- α -D-galactopyranosyluronate)- β -D-galactopyranid) uronate **46**: A solution of 52 mg methyl (phenyl 4-*O*-acetyl-2,3-di-*O*-benzyl-1-thio- β -D-galactopyranosid) uronate **44** (0.1 mmol), 29 mg benzenesulfinylpiperidine (0.14 mmol, 1.4 eq) and 74 mg tri-*tert*-butylpyrimidine (0.3 mmol, 3 eq) in 2.5 ml DCM was stirred over 100 mg activated MS3Å for 30 min. The mixture was cooled to -60°C before 22 μ l triflic acid anhydride (0.13 mmol, 1.3 eq) was added. The mixture was allowed to warm to -40°C in 15min followed by addition of 74 mg methyl (4-methoxyphenyl 2,4-di-*O*-benzyl- β -D-galactopyranosid) uronate **45** (0.15 mmol, 1.5 eq) in 0.5 ml DCM. Stirring was continued and the reaction mixture was allowed to warm to 0°C. Subsequently the reaction was quenched by addition of 0.16 ml triethylamine. Flash chromatography (15% EtOAc/PE) and removal of the eluent afforded 51 mg (0.056 mmol, 57%, BSP) of the title compound **46** as a colourless oil. TLC: 20% EtOAc/toluene; $[\alpha]_D^{22}$: +67.8 ($c = 1$, CHCl₃); IR (neat, cm⁻¹): 1026, 1089, 1215, 1506, 1747; ¹H NMR (400 MHz, CDCl₃) δ = 2.01 (s, 3H, Ac), 3.58 (s, 3H, CH₃ COOMe), 3.67 (s, 3H, CH₃ COOMe), 3.76 (s, 3H, Me(*p*MP)), 3.89 (m, 2H, H-3, H-2'), 3.96 (dd, 1H, $J = 10.0$ Hz, $J = 3.2$ Hz, H-3'), 4.12 (t, 2H, $J = 8.8$ Hz, H-2, H-5), 4.28 (s, 1H, H-4), 4.42 (d, 1H, $J = 11.2$ Hz, CHHPh), 4.50 (d, 1H, $J = 11.2$ Hz, CHHPh), 4.63 (d, 1H, $J = 11.8$ Hz, CHHPh), 4.64 (d, 1H, $J = 11.4$ Hz, CHHPh), 4.72 (d, 1H, $J = 11.2$ Hz, CHHPh), 4.80 (d, 1H, $J = 7.6$ Hz, H-1), 4.84 (d, 1H, $J = 11.2$ Hz, CHHPh), 4.90 (d, 1H, $J = 1.2$ Hz, H-5'), 5.04 (d, 1H, $J = 11.6$ Hz, CHHPh), 5.08 (d, 1H, $J = 11.2$ Hz, CHHPh), 5.27 (d, 1H, $J = 3.2$ Hz, H-1'), 5.50 (bs, 1H, H-4'), 6.77 – 7.43 (m, 24H, H Arom); ¹³C NMR (100 MHz, CDCl₃) δ = 20.7 (Ac), 52.1 (CH₃ COOMe), 52.4 (CH₃ COOMe), 55.6 (Me *p*MP), 68.6 (C-4'), 69.0 (C-5'), 71.9 (CH₂ Bn), 73.9 (C-4), 74.0 (C-5), 74.4 (C-3 or C-2'), 74.7 (CH₂ Bn), 74.9 (CH₂ Bn), 75.4 (CH₂ Bn), 75.6 (C-3'), 76.4 (C-2' or C-3), 76.9 (C-2), 95.3 (C-1'), 103.3 (C-1), 114.4 (Ar *p*MP), 118.8 (Ar *p*MP), 127.2 – 128.5 (CH Arom), 137.7 (C_q Bn), 137.9 (C_q Bn), 138.3 (C_q Bn), 151.3 (C_q *p*MP), 155.4 (C_q *p*MP), 168.0 (C=O Ac or COOMe), 168.1 (C=O Ac or COOMe), 169.7 (C=O Ac or COOMe); HRMS: ($M + H^+$) calcd 924.38010, found 924.38050.

Methyl (ethyl 2,3-di-*O*-benzyl-4-*O*-(6-*O*-acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy- α -D-glucopyranosyl)-1-thio- β -D-glucopyranosid) uronate **48**: A solution of 128 mg 6-*O*-acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy- α/β -D-glucopyranose **47** (0.3 mmol), 170 mg diphenylsulfoxide (0.84 mmol, 2.5 eq) and 223 mg tri-*tert*-butylpyrimidine (0.9 mmol, 3 eq) in 3 ml DCM was stirred over 100 mg activated MS3Å for 30 min. The mixture was cooled to -60°C before 69 μ l triflic acid anhydride (0.42 mmol, 1.4 eq) was added. The mixture was allowed to warm to -40°C in 1h followed by addition of 173 mg methyl (ethyl 2,3-di-*O*-benzyl-1-thio- β -D-galactopyranosid) uronate **13** (0.4 mmol, 1.5 eq) in 1 ml DCM. Stirring was continued and the reaction mixture was allowed to warm to 0°C. Subsequently the reaction was quenched by addition of 0.16 ml triethylamine. Flash chromatography (10% EtOAc/PE) and removal of the eluent afforded 169 mg of the title compound **48** (0.2 mmol, 67%) as a colourless oil. TLC: 20% EtOAc/toluene; $[\alpha]_D^{22}$: +14.6 ($c = 1$, CHCl₃); IR (neat, cm⁻¹): 1028, 1074, 1209, 1236, 1361, 1444, 1741, 2108; ¹H NMR (400 MHz, CDCl₃) δ = 1.23 (t, 3H, $J = 7.6$ Hz, CH₃ SEt), 2.01 (s, 3H, Ac), 2.73 – 2.78 (m, 2H, CH₂ SEt), 3.50 (t, 1H, $J = 9.2$ Hz, H-2), 3.52 (m, 1H, $J = 8.8$ Hz, H-4'), 3.58 (bd, 1H, $J = 10.0$ Hz, H-5'), 3.75 (s, 3H, CH₃ COOMe), 3.78 (t, 1H, $J = 8.8$ Hz, H-3), 3.88 (t, 1H, $J = 9.2$ Hz, H-3'), 3.91 (d, 1H, $J = 9.6$ Hz, H-5), 4.13 (t, 1H, $J = 9.4$ Hz, H-4), 4.28 (bs, 2H, H-6'), 4.51 (t, 2H, $J = 9.4$ Hz, H-1, CHHPh), 4.65 (d, 1H, $J = 10.0$ Hz, CHHPh), 4.80 (d, 1H, $J = 11.2$ Hz, CHHPh), 4.86 (s, 2H, CH₂ Bn), 4.90 (d, 1H, $J = 10.8$ Hz, CHHPh), 4.93 (d, 1H, $J = 10.4$ Hz, CHHPh), 5.03 (d, 1H, $J = 10.8$ Hz, CHHPh), 5.53 (d, 1H, $J = 3.6$ Hz, H-1'), 7.24 – 7.71 (m, 20H, H Arom); ¹³C NMR (100 MHz, CDCl₃) δ = 14.8 (CH₃ SEt), 20.8 (Ac), 25.0 (CH₂ SEt), 52.7 (Me OMe), 62.1 (C-6'), 63.2 (C-2'), 69.6 (C-5'), 74.9 (CH₂ Bn), 75.1 (C-4), 75.1 (CH₂ Bn), 75.2 (CH₂ Bn), 75.4 (CH₂ Bn), 77.4 (C-4'), 77.8 (C-5), 80.0 (C-3'), 81.2 (C-2), 85.5 (C-3), 85.6 (C-1), 97.7 (C-1'); 124.7 – 131.0 (CH Arom), 137.5 (C_q Bn), 138.1 (C_q Bn), 168.3 (C=O (Ac, COOMe), 170.6 (C=O Ac, COOMe), ESI-MS: 864.4 (M + Na⁺).

3-*O*-Benzoyl-2-*O*-(methyl (4-*O*-(6-*O*-acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy- α -D-glucopyransyl)-2,3-di-*O*-benzyl- α -D-glucopyransid) uronate)-5,6-*O*-isopropylidene-D-galactono-1,4-lacton **50**: A solution of 84 mg methyl (ethyl 2,3-di-*O*-benzyl-4-*O*-(6-*O*-acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy- α -D-glucopyranosyl)-1-thio- β -D-glucopyranosid) uronate **48** (0.1 mmol), 29 mg benzenesulfonylpiperidine (0.14 mmol, 1.4 eq) and 74 mg tri-*tert*-butylpyrimidine (0.3 mmol, 3 eq) in 2.5 ml DCM was stirred over 100 mg activated MS3Å for 30 min. The mixture was cooled to -60°C before 22 μ l triflic acid anhydride (0.13 mmol, 1.3 eq) was added. The mixture was allowed to warm to -40°C in 15min followed by addition of 62 mg 3-*O*-benzoyl-5,6-*O*-isopropylidene-D-galactono-1,4-lacton **49** (0.2 mmol, 2 eq) in 0.5 ml DCM. Stirring was continued and the reaction mixture was allowed to warm to 0°C. Subsequently the reaction was quenched by addition of 0.16 ml triethylamine. Flash chromatography (15% EtOAc/PE) and removal of the eluent afforded 38 mg of the title compound **50** (0.035 mmol, 35%) as a colorless oil (α/β = 4/1). TLC: 20% EtOAc/toluene; IR (neat, cm^{-1}): 1174, 1296, 1676, 1743, 2106; α -anomer: ^1H NMR (600 MHz, CDCl_3) δ = 1.41 (s, 3H, Me isoprop), 1.43 (s, 3H, CH_3 isoprop), 2.00 (s, 3H, Ac), 3.19 (dd, 1H, J = 10.4 Hz, J = 3.7 Hz, H-2''), 3.44 – 3.45 (m, 2H, H-4'', H-5''), 3.45 (s, 3H, CH_3 COOMe), 3.66 (t, 1H, J = 8.2 Hz, H-2'), 3.68 – 3.71 (m, 2H, J = 9.5 Hz, J = 9.4 Hz, H-2', H-3''), 3.97 (dd, 1H, J = 8.5 Hz, J = 6.5 Hz, H-6), 4.00 (t, 1H, J = 9.3 Hz, H-4'), 4.08 (t, 1H, J = 9.1 Hz, H-3'), 4.11 – 4.14 (m, 2H, H-6, H-6''), 4.20 – 4.23 (m, 2H, J = 9.8 Hz, J = 5.2 Hz, H-5', H-6''), 4.43 (dd, 1H, J = 5.9 Hz, J = 2.9 Hz, H-4), 4.51 (d, 1H, J = 10.9 Hz, CHHPh), 4.56 (dt, 1H, J = 6.7 Hz, J = 2.9 Hz, J = 2.7 Hz, H-5), 4.65 (d, 1H, J = 11.3 Hz, CHHPh), 4.71 (d, 1H, J = 10.5 Hz, CHHPh), 4.73 (d, 1H, J = 10.5 Hz, CHHPh), 4.79 (d, 1H, J = 10.9 Hz, CHHPh), 4.81 (d, 1H, J = 6.7 Hz, H-2), 4.82 (d, 1H, J = 10.3 Hz, CHHPh), 4.84 (d, 1H, J = 11.0 Hz, CHHPh), 5.08 (d, 1H, J = 10.6 Hz, CHHPh), 5.52 (d, 1H, J = 3.7 Hz, H-1''), 5.61 (d, 1H, J = 3.5 Hz, H-1'), 5.89 (t, 1H, J = 6.5 Hz, H-3''), 7.23 – 8.09 (m, 25H, H Ar); ^{13}C NMR (151.2 MHz, CDCl_3) δ = 20.8 (Ac), 25.4 (CH_3 isoprop), 25.9 (CH_3 isoprop), 52.4 (CH_3 COOMe), 62.2 (C-6''), 63.1 (C-2''), 65.1 (C-6), 69.5 (C-5), 70.5 (C-5'), 72.4

(CH₂ Bn), 74.3 (C-3), 74.6 (C-2, C-5), 74.8 (CH₂ Bn), 74.9 (C-4'), 75.2 (CH₂ Bn), 75.4 (CH₂ Bn), 77.4 (C-4''), 78.6 (C-2'), 80.0 (C-4), 80.7 (C-3''), 81.0 (C-3'), 96.1 (C-1'), 97.9 (C-1''), 110.7 (C_q isoprop), 125.2 – 134.0 (CH Arom), 137.2 (C_q Bn), 137.6 (C_q Bn), 138.1 (C_q Bn), 138.4 (C_q Bn), 165.4 (C=O Ac, Bz or COOMe), 169.1 (C=O Ac, Bz or COOMe), 170.7 (C=O Ac, Bz or COOMe); HRMS: (M + H⁺) calcd 1119.44449, found 1119.44702.

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