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Supporting Information

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Introduction of 2,2,2-trichloroethyl-Protected Sulfates into Monosaccharides using a Sulfuryl Imidazolium Salt and its application to the Synthesis of Sulfated Carbohydrates

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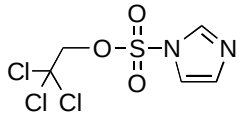
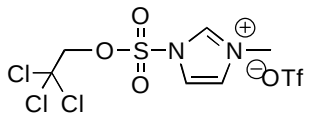
General Information: All reactions were carried out under argon with freshly distilled solvents unless otherwise noted. Tetrahydrofuran (THF) and Et_2O were distilled from sodium metal in the presence of benzophenone under argon. CH_2Cl_2 was distilled from calcium hydride under nitrogen. All commercially available reagents were obtained from Aldrich Chemical Company (Oakville, Ontario, Canada) and were used as received, with the exception of TMSOTf, which was immediately distilled into a Schlenk tube and stored under argon. Flash chromatography was performed using silica gel 60Å (234-400 mesh) obtained from Silicycle (Laval, Quebec, Canada). ^1H, ^{19}F, ^{13}C and 2D spectra were recorded on a Brüker Avance 300MHz or Brüker Avance 500 MHz spectrometer. Chemical shifts (d) for ^1H NMR spectra are reported in parts per million (ppm) relative to Me_4Si (0.0 ppm) or DMSO-d_6 (2.49 ppm) and are reported as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broadened), integration, coupling constant in Hz, and assignment. Chemical shifts (d) for ^{13}C spectra are reported in ppm relative to $CDCl_3$ (d 77.0, central peak) or DMSO-d_6 (d 39.5, central peak). Chemical shifts (d) for ^{19}F spectra are reported in ppm relative to an external fluoroform standard (d 0.0, $CFCl_3$). All melting points were obtained using a Fisher-Johns apparatus and are uncorrected. Electron impact mass spectra were acquired with a JEOL HX110 double focusing mass spectrometer operated at a mass resolution of ~1000 for nominal mass work and ~10,000 for elemental composition determinations. Typical source conditions were: source temp=200^{o}C and electron energy of 70eV. Ammonia was used as the CI reagent gas for positive ion CI. All samples were introduced by direct insertion. Positive and negative ion electrospray (ESI) experiments were performed with a Waters/Micromass QTOF Ultima Global mass spectrometer. Samples were infused at 1μL/min in 1:1 CH_3CN/H_2O+0.2% formic acid for +ve ion work or 1:1 CH_3CN/H_2O for –ve ion work. Typical operating conditions were: source temp=80^{o}C, capillary voltage=3.5kV, cone voltage=60-160V and mass resolution of ~9000.



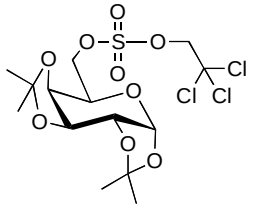
2,2,2-Trichloroethoxysulfuryl imidazole 8: To imidazole (21.17 g, 0.31 mol) in dry THF (50 mL) at 0^{o}C was added dropwise a solution of 2,2,2-trichloroethylsulfonylchloride **7** (20 mL, 0.15 mol) in THF (20 mL). The reaction was

stirred at 0°C for 1 h, warmed to room temperature and stirred for an additional hour. The salts were removed by suction filtration, washed with THF and the filtrate was condensed to a yellow crude oil. Flash chromatography (33:67 EtOAc/hexanes) provided a white solid (35.9 g, 86%). Melting point 46-48°C; ^{1}H NMR (300 MHz, $CDCl_3$) *d* 8.04, (s, 1H, ImH), 7.41, 7.23 (2m, 2H, ImH), 4.68 (s, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 136.90, 131.66, 117.97, 91.53, 80.05; HRMS (EI) *m/z* = 277.9090, $C_5H_5N_2SO_3Cl_3$ requires 277.9087.



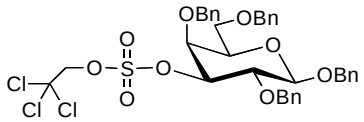
2,2,2-trichloroethoxysulfuryl-*N*-methylimidazolium triflate 6: To a solution of 2,2,2-trichloroethoxysulfurylimidazole **8** (10.6 g, 36 mmol) in Et_2O (140 mL) at 0°C was added dropwise methyl triflate (4.6 mL, 41 mmol). The reaction was stirred for 3 h at 0°C during which time a white precipitate formed. The desired product was isolated by suction filtration (filtrate re-precipitated 1x) and washed with cold Et_2O to afford a light white solid (14.6 g, 91%). Melting point 146-148°C; ^{1}H NMR (300 MHz, CD_3OD) *d* 9.97, 8.34, 7.91 (3s, 3H, ImH), 5.41 (s, 2H, CH_2), 4.07 (s, 3H, CH_3); ^{13}C NMR (75 MHz, CD_3OD) *d* 139.53, 125.87, 120.73, 120.43 (q, J_{CF} = 318.7 Hz, CF_3), 91.52, 82.08, 36.42; ^{19}F NMR (282 MHz, CD_3OD) *d* -79.6; ESI of cation *m/z* = 294.9423, $C_6H_8Cl_3N_2O_3S^+$ requires 294.9635.

General Procedure for Synthesis of Sulfated Carbohydrates: All sulfations commenced with the following procedure as described for **2**. For reactions incomplete after 24h, additional equivalents of *N*-methyl imidazole and 2,2,2-trichloroethoxysulfuryl-*N*-methylimidazolium triflate salt **6** (1 eq. each) were added at intervals of approximately 12 h until no starting material remained by TLC, unless otherwise described.

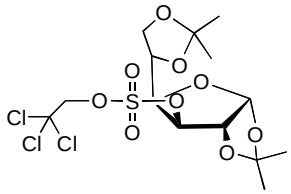


1:2,3:4-di-*O*-isopropylidine-6-*O*-trichloroethylsulfogalactose 2: *General Procedure*: To 1:2,3:4 di-isopropylidinegalactose **1** (0.25 g, 0.97 mmol) in THF (4.2 mL, 0.23 M) at 0°C was added *N*-methyl imidazole (0.19 mL, 2.39 mmol) followed by 2,2,2-trichloroethoxysulfuryl-*N*-methylimidazolium triflate **6** (0.85 g, 1.92 mmol). The reaction was stirred at 0°C, gradually warmed to room temperature by allowing the ice bath to melt, and then stirred overnight. After 24 h, the system was quenched with water and extracted with EtOAc. The combined organics were washed with $NaHCO_3$, brine, and dried over $MgSO_4$ and condensed to brown crude oil. (*Note*: work up was not performed for all products, reaction contents were instead applied directly to silica gel column). Flash chromatography (25:75 EtOAc/hexanes) yields desired product as a

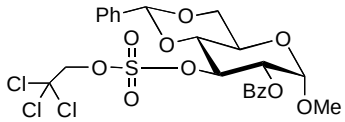
white solid (0.4 g, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) *d* 5.55 (d, 1H, *J* = 4.9 Hz, H1), 4.82, 4.79 (AB, 2H, *J* = 10.8 Hz, CH_2CCl_3), 4.76 (dd, 1H, *J* = 7.8, 2.5 Hz, H3), 4.51 (m, 2H, H6, H6'), 4.38 (dd, 1H, *J* = 4.9, 2.5 Hz, H2), 4.26 (dd, 1H, *J* = 7.8, 1.7 Hz, H4), 4.15 (m, 1H, H5), 1.56 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.35 (s, 6H, 2xCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 109.89 109.00, 96.00, 92.53, 79.46, 72.02, 70.50, 70.35, 70.10, 65.50, 25.90, 25.8, 24.74, 24.32; Melting Point 70-72^{o}C; HRMS (ESI) *m/z* = 471.0060, $C_{14}H_{22}Cl_3O_9S$ $(M+H)^+$ requires 471.0050.



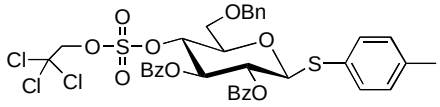
1,2,4,6-tetra-*O*-benzyl-3-trichloroethylsulfogalactose 14: Prepared according to the general procedure. Carbohydrate **4** (0.5 g, 0.93 mmol), THF (6 mL, 016 M), *N*-methyl imidazole (0.22 mL, 2.8 mmol), 2,2,2-trichloroethoxysulfuryl-*N*-methylimidazolium triflate **6** (0.86 g, 1.9 mmol), reaction time 2 d. Desired product isolated as a white solid (0.65 g, 94%). ^{1}H NMR (300 MHz, $CDCl_3$) *d* 3.55-3.64 (m, 3H, H5, H6, H6'), 3.93, (dd, 1H, *J* = 10.0, 7.6 Hz, H2), 4.30 (d, 1H, *J* = 3.0 Hz, H4), 4.40-4.49 (m, 4H, CH_2CCl_3, CH_2Ph), 4.50 (d, 1H, *J* = 7.6 Hz, H1), 4.57 (dd, 1H, *J* = 10.1, 3.1 Hz, H3), 4.59-4.66 (m, 3H, CH_2Ph), 4.87 (d, 1H, *J* = 11.4 Hz, CH_2Ph), 4.95 (d, 1H, *J* = 11.9 Hz, CH_2Ph), 5.00 (d, 1H, *J* = 11.0Hz, CH_2Ph), 7.25-7.37 (m, 20H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 67.95, 71.04, 72.70, 73.43, 73.87, 75.09, 75.29, 76.38, 79.34, 85.65, 92.37, 102.18, 127.75, 127.81, 127.84, 127.88, 127.95, 128.01, 128.11, 128.27, 128.38, 128.41, 128.49, 136.77, 137.43, 137.51, 137.59; Melting point 52-54^{o}C; HRMS (ESI) *m/z* = 768.1581, $C_{36}H_{41}NO_9SCl_3$ $(M+NH_4)^+$ requires 768.1568.



1:2,5:6-di-*O*-acetone-3-*O*-trichloroethylsulfoglucofuranose 15: Prepared according to the general procedure. Carbohydrate **9** (0.25 g, 0.96 mmol), in THF (4.2 mL, 0.23 M), *N*-methyl imidazole (0.15 mL, 1.9mmol), 2,2,2-trichloroethoxysulfuryl-*N*-methylimidazolium triflate **6** (0.85 g, 1.9 mmol). Desired product isolated as a white solid, (0.41 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) *d* 5.98 (d, 1H, *J* = 3.7 Hz, H1), 5.10 (1/2AB, 1H, *J* = 10.5 Hz, CH_2CCl_3), 5.07 (d, 1H, *J* = 2.8 Hz, H3), 5.00 (d, 1H, *J* = 3.7 Hz, H2), 4.81 (1/2AB, 1H, *J* = 10.5, CH_2CCl_3), 4.29 (m, 1H, H5), 4.18 (m, 2H, H4, H6), 4.08 (dd, 1H, *J* = 9.1, 3.8 Hz, H6'), 1.54, 1.46, 1.38, 1.34 (4s, 4x3H, 4xCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 112.67, 109.95, 104.88, 92.45, 85.29, 82.44, 79.58, 79.53, 71.54, 67.39, 26.91, 26.45, 26.05, 25.00; Melting point 100-102^{o}C; HRMS (ESI) *m/z* = 471.0059, $C_{14}H_{22}Cl_3O_9S$ $(M+H)^+$ requires 471.0050.

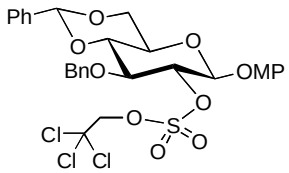


Methyl-2-*O*-benzoyl-3-*O*-trichloroethylsulfo-4:6-*O*-benzylidine-a-D-glucopyranoside 16: To sugar **10** (1.0 g, 2.6 mmol) in THF (11 mL, 0.24 M) at 0°C was added *N*-methyl imidazole (0.66 mL, 8.3 mmol) followed by 2,2,2-trichloroethoxysulfuryl-*N*-methylimidazolium triflate **6** (3.0 g, 6.76 mmol). The reaction was stirred at 0°C, gradually warmed to room temperature by allowing the ice bath to melt, and then stirred overnight. After 24 h and 36 h, additional aliquots of *N*-methyl imidazole (0.22 mL, 2.8 mmol) and 2,2,2-trichloroethoxysulfuryl-*N*-methylimidazolium triflate **6** (0.1.2 g, 2.7 mmol) were added at room temperature. Upon completion by TLC (approx. 48 h) the reaction was quenched with water and extracted with EtOAc. The combined organics were washed with $NaHCO_3$, brine, and dried over $MgSO_4$ and condensed to brown crude oil. Flash chromatography (33:67 EtOAc/hexanes) yields desired product as a white solid (1.467 g, 94%). ^{1}H NMR (300 MHz, $CDCl_3$) *d* 3.44 (s, 3H, OCH_3), 3.86 (dd, 1H, $J_1 = J_2 = 10.3$ Hz, $H6_{ax}$), 3.89 (dd, 1H, $J_1 = J_2 = 9.5$ Hz, H4), 4.05 (ddd, 1H, $J = 9.9, 9.7, 4.7$ Hz, H5), 4.41 (dd, 1H, $J = 10.4, 4.8$ Hz, $H6_{eq}$), 4.43, 4.50 (AB, 2H, $J = 11.1$ Hz, CH_2CCl_3), 5.18 (dd, 1H, $J = 9.5, 3.6$ Hz, H2), 5.22 (d, 1H, $J = 3.6$ Hz, H1), 5.36 (dd, 1H, $J_1 = J_2 = 9.5$ Hz, H3), 7.38-7.40 (m, 3H, ArH), 7.46-7.53 (m, 4H, ArH), 7.59-7.61 (m, 1H, ArH), 8.19 (d, 2H, $J = 7.4$ Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 55.67, 62.27, 68.74, 71.62, 78.67, 79.64, 80.62, 94.23, 97.77, 102.59, 126.35, 128.42, 129.64, 130.19, 133.60, 136.09, 165.71; Melting point (dec.) 130-132°C; HRMS (ESI) *m/z* = 597.0133, $C_{23}H_{23}Cl_3O_{10}S$ $(M+H)^+$ requires 597.0156.

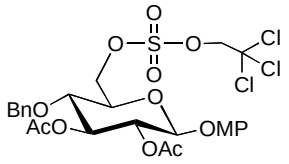


***p*-Tolyl-2,3-di-*O*-benzoyl-4-*O*-trichloroethylsulfo-6-*O*-benzyl-1-thio-ß-D-glucopyranoside 17:** To sugar **11** (0.41 g, 0.70 mmol) in THF (3 mL, 0.24 M) at 0°C was added *N*-methyl imidazole (0.17 mL, 2.1 mmol) followed by 2,2,2-trichloroethoxysulfuryl-*N*-methylimidazolium triflate **6** (3.0 g, 1.7 mmol). The reaction was stirred at 0°C, gradually warmed to room temperature by allowing the ice bath to melt, and then stirred overnight. After 24 h and 36 h, additional aliquots of *N*-methyl imidazole (0.06 mL, 0.76 mmol) and 2,2,2-trichloroethoxysulfuryl-*N*-methylimidazolium triflate **6** (0.3 g, 0.68 mmol) were added at room temperature. Upon completion by TLC (approx. 48 h), reaction contents were applied directly to a silica column, and were purified by flash chromatography (25:75 EtOAc/hexanes). Product was isolated as a white waxy compound (5.034 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) *d* 2.31 (s, 3H, CH_3), 3.81-3.94 (m, 3H, H5, H6, H6'), 4.45, 4.57 (AB, 2H, $J = 11.1$ Hz, CH_2Ph), 4.60, 4.66 (AB, 2H, $J = 11.8$ Hz, CH_2CCl_3), 4.86 (d, 1H, $J = 9.9$ Hz, H1), 5.14 (dd, 1H, $J_1 = J_2 = 9.5$ Hz, H4), 5.31 (dd, 1H, $J_1 = J_2 = 9.7$ Hz, H2), 5.80 (dd, 1H, $J_1 = J_2 = 9.4$ Hz, H3), 7.03 (d, 2H, $J = 7.9$ Hz, ArH), 7.24-7.39 (m, 11H, ArH), 7.45-7.54 (m, 2H, ArH), 7.92 (d, 4H, $J = 7.8$ Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 21.3, 68.1, 70.6, 73.7, 73.8, 77.5, 79.2, 80.2, 86.1, 92.4, 127.4, 127.9, 128.0, 128.5, 128.7, 129.1, 129.9, 130.0, 130.2, 133.5, 133.7,

134.1, 137.8, 139.0; Melting point (dec.) 112-114°C; HRMS (ESI) *m/z* = 795.0659, $C_{36}H_{34}O_{10}S_2Cl_3$ $(M+H)^+$ requires 795.0659.



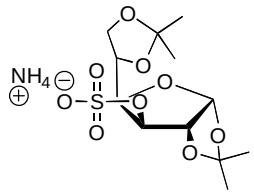
***p*-Methoxyphenyl-2-*O*-trichloroethylsulfo-3-*O*-benzyl-4:6-*O*-benzylidine-ß-D-glucospyranoside 18:** To carbohydrate **12** (0.2 g 0.43 mmol) in THF (2 mL, 0.25 M) at 0°C was added *N*-methyl imidazole (0.2 mL, 2.5 mmol) followed by 2,2,2-trichloroethoxysulfuryl-*N*-methylimidazolium triflate **6** (1.0 g, 2.25 mmol). After 24 h, reaction was incomplete by TLC, additional base and triflate **6** were added (0.2 mL, 2.5 mmol, and 1.0 g, 2.25 mmol) respectively. Upon completion (48 h) the reaction contents were directly applied to a silica gel column. Flash chromatography (20:80 EtOAc/hexanes) provided a white solid (0.26 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) *d* 3.57 (ddd, 1H, *J* = 9.7, 9.5, 5.0 Hz, H5), 3.80 (s, 3H, CH_3), 3.86 (dd, 1H, $J_1 = J_2 = 10.4$ Hz, $H6_{ax}$), 3.88 (dd, 1H, $J_1 = J_2 = 9.2$ Hz, H4), 3.98 (dd, 1H, $J_1 = J_2 = 9.1$ Hz, H3), 4.43 (dd, 1H, *J* = 10.5, 5.0 Hz, $H6_{eq}$), 4.68, 4.71 (AB, 2H, *J* = 11.1 Hz, CH_2CCl_3), 4.85 (m, 1H, H2), 4.87, 5.01 (AB, 2H, *J* = 11.2 Hz, CH_2Ph), 5.02 (d, 1H, *J* = 7.8 Hz, H1), 5.61 (s, 1H, CHPh), 6.85-6.88 (m, 2H, ArH), 7.06-7.09 (m, 2H, ArH), 7.33-7.50 (m, 10H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 55.54, 66.19, 66.30, 74.61, 77.87, 79.86, 81.21, 83.89, 92.57, 99.89, 101.36, 114.59, 118.77, 125.88, 127.92, 128.09, 128.11, 128.25, 128.27, 128.28, 128.38, 129.13, 136.63, 137.12, 150.16, 155.99; Melting point 105-107°C; HRMS (EI) *m/z* = 674.0546, $C_{29}H_{29}Cl_3O_{10}S$ requires 674.0547.



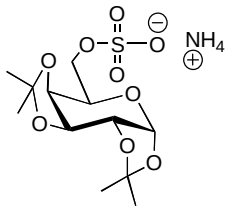
***p*-Methoxyphenyl-2,3-di-*O*-acetyl-4-*O*-benzyl-6-*O*-trichloroethylsulfo-ß-D-glucopyranoside 19:** To carbohydrate **13** (0.81 g, 1.76 mmol) in THF (8 mL, 0.22 M) at 0°C was added *N*-methyl imidazole (0.42 mL, 5.29 mmol) followed by 2,2,2-trichloroethoxysulfuryl-*N*-methylimidazolium triflate **6** (1.9 g, 4.28 mmol). The reaction was stirred at 0°C, gradually warmed to room temperature by allowing the ice bath to melt, and then stirred overnight. After 24 h and additional aliquots of *N*-methyl imidazole (0.42 mL, 5.29 mmol) and 2,2,2-trichloroethoxysulfuryl-*N*-methylimidazolium triflate **6** (1.0 g, 2.25 mmol) were added at room temperature. Upon completion by TLC (approx. 36 h), reaction contents were applied directly to a silica column, and were purified by flash chromatography (33:67 EtOAc/hexanes). Product was isolated as a white solid (0.96 g, 81%). ^{1}H NMR (300 MHz, $CDCl_3$) *d* 2.04 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 3.78 (m, 5H, OCH_3, H4, H6), 4.45 (dd, 1H, *J* = 10.6, 3.7 Hz, H5), 4.65-4.72 (m, 5H, CH_2CCl_3, CH_2Ph, H6'), 5.02 (d, 1H, *J* = 7.8 Hz, H1), 5.16 (dd, 1H, *J* = 9.5, 7.9 Hz, H2), 5.34 (m, 1H, H3), 6.81-6.84 (m, 2H, ArH), 6.91-6.94 (m, 2H, ArH), 7.30-7.40 (m,

5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 20.55, 20.68, 55.55, 71.18, 71.45, 72.34, 74.52, 74.60, 74.94, 79.60, 92.28, 99.73, 114.59, 118.27, 128.04, 128.40, 128.66, 136.53, 150.53, 155.73, 169.47, 169.83; Melting point 110-112^{o}C; HRMS (ESI) *m/z* = 688.0812 $(M+NH_4)^+$ $C_{26}H_{33}NO_{12}SCl_3$ requires 688.0789.

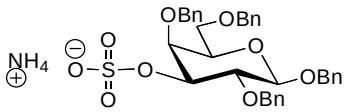
General Procedure for Deprotection of the Sulfate Moiety: All deprotections were performed with the following procedure (*note:* reaction equivalents are doubled when two trichloroethyl bearing sulfate groups are to be deprotected).



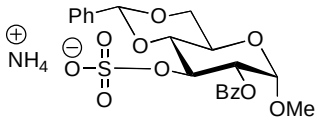
1:2,5:6-di-*O*-acetone-3-*O*-sulfoglucofuranose 22: *General Procedure:* To a suspension of ammonium formate (0.16 g, 2.5 mmol) in MeOH (2.5 mL, 1.0 M) was added protected carbohydrate **15** (0.2 g, 0.42 mmol) followed by zinc dust (0.2 g, 3.1 mmol). The reaction was stirred for 7 h at room temperature, at which point no starting material was detected by TLC. The reaction was filtered through Celite, and condensed to crude product. Flash chromatography (20:4:1 CH_2Cl_2/MeOH/NH_4OH) afforded a white solid, which was lyophilized (3x) to yield a light white product (0.14 g, 94%). ^{1}H NMR (300 MHz, DMSO-d_6) *d* 1.23 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 3.91-3.96 (m, 1H, H6), 3.78-3.83 (m, 1H, H6'), 4.20-4.26 (m, 2H, H4, H5), 4.45 (d, 1H, *J* = 2.7 Hz, H3), 4.76 (d, 1H, *J* = 3.8 Hz, H2), 5.84 (d, 1H, *J* = 3.8 Hz, H1), 7.08 (brs, 4H, NH_4); ^{13}C NMR (75 MHz, DMSO-d_6) *d* 25.61, 26.42, 26.74, 26.94, 65.09, 73.03, 78.49, 79.63, 83.04, 104.73, 107.76, 111.05; HRMS (ESI) *m/z* = 339.0738, $C_{12}H_{19}O_9S$ requires 339.0750.



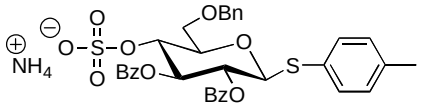
1:2,3:4-di-*O*-isopropylidine-6-*O*-sulfogalactose 20: Carbohydrate **2** (0.20 g, 0.43 mmol), MeOH (2.5 mL), HCO_2NH_4 (0.16 g, 2.6 mmol), Zn (0.22 g, 3.4 mmol), reaction time 6 h. ^{1}H NMR (300 MHz, DMSO-d_6) *d* 1.27 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 3.71-3.81 (m, 2H, H6, H6'), 3.94 (brdd, J_1 = J_2 = 5.7 Hz, H5), 4.22 (brd, 1H, *J* = 8.0 Hz, H4), 4.32 (dd, 1H, *J* = 4.8, 2.1 Hz, H2), 4.57 (dd, 1H, *J* = 8.0, 1.9 Hz, H3), 5.43 (d, 1H, *J* = 5.0 Hz, H1), 7.09 (brs, 4H, NH_4); ^{13}C NMR (75 MHz, DMSO-d_6) *d* 24.59, 25.26, 26.15, 26.28, 65.06, 66.27, 70.13, 70.33, 70.73, 95.94, 108.15, 108.56; HRMS (ESI) *m/z* = 339.0754, $C_{12}H_{19}O_9S$ requires 339.0750.



1,2,4,6-tetra-*O*-benzyl-3-sulfogalactose 21: Carbohydrate **14** (0.13 g, 0.18 mmol), MeOH (1.1 mL), HCO_2NH_4 (0.07 g, 1.1 mmol), Zn (0.08 g, 1.2 mmol), reaction time 8 h. ^{1}H NMR (300 MHz, DMSO-d_6) *d* 3.42-3.51 (m, 3H, H2, H6, H6'), 3.73 (dd, 1H, $J_1 = J_2 =$ 6.2 Hz, H5), 4.21 (d, 1H, *J* = 2.6 Hz, H4), 4.34 (dd, 1H, *J* = 9.8, 2.9 Hz, H3), 4.43, 4.46 (AB, 2H, *J* = 12.2 Hz, CH_2Ph), 4.52 (d, 1H, *J* = 11.5 Hz, CH_2Ph), 4.56 (d, 1H, *J* = 7.9 Hz, H1), 4.58 (d, 1H, *J* = 12.6 Hz, CH_2Ph), 4.67 (d, 1H, *J* = 11.5 Hz, CH_2Ph), 4.78 (d, 1H, *J* = 12.3 Hz, CH_2Ph), 4.80 (d, 1H, *J* = 11.5 Hz, CH_2Ph), 4.97 (d, 1H, *J* = 11.4 Hz, CH_2Ph), 7.08 (brs, 4H, NH_4), 7.22-7.39 (m, 20H, ArH); ^{13}C NMR (75 MHz, DMSO-d_6) *d* 68.83, 70.31, 72.60, 72.60, 73.71, 74.20, 74.53, 77.85, 78.70, 102.05, 127.36, 127.60, 127.74, 127.78, 127.82, 127.99, 128.17, 128.38, 128.49, 128.59, 138.28, 138.58, 139.51, 139.56; HRMS (ESI) *m/z* = 619.1982, $C_{34}H_{35}O_9S$ requires 619.2002.

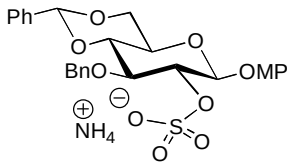


Methyl-2-*O*-benzoyl-3-*O*-sulfo-4:6-*O*-benzylidine-a**-D-glucopyranoside 23**:
Carbohydrate **16** (0.2 g, 0.33 mmol), MeOH (2.0 mL), HCO_2NH_4 (0.13 g, 2.06 mmol), Zn (0.15 g, 2.29 mmol), reaction time 6h. ^{1}H NMR (300 MHz, DMSO-d_6) *d* 3.31 (s, 3H, CH_3), 3.70-3.85 (m, 3H, H4, H5, $H6_{ax}$), 4.25 (dd, 1H, *J* = 9.5, 3.6 Hz, $H6_{eq}$), 4.78 (brdd, $J_1 = J_2 =$ 9.3 Hz, H3), 4.90 (dd, 1H, *J* = 9.8, 3.6 Hz, H2), 5.04 (d, 1H, *J* = 3.5 Hz, H1), 5.64 (s, 1H, CHPh), 7.09 (s, 4H, NH_4), 7.36-7.38 (m, 3H, ArH), 7.47-7.52 (m, 4H, ArH), 7.62-7.68 (m, 1H, ArH), 8.14 (d, 2H, *J* = 7.5 Hz, ArH); ^{13}C NMR (75 MHz, DMSO-d_6) *d* 55.11, 63.01, 68.18, 72.88, 73.04, 79.36, 97.66, 100.55, 126.64, 128.22, 128.67, 128.94, 130.08, 130.43, 133.54, 138.08, 166.13; HRMS (ESI) *m/z* = 465.0837, $C_{21}H_{21}O_{10}S$ requires 465.0855.

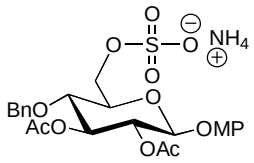


***p*-Tolyl-2,3-di-*O*-benzoyl-4-*O*-sulfo-6-*O*-benzyl-1-thio-ß-D-glucopyranoside 24**:
Carbohydrate **17** (0.11 g, 0.14 mmol), MeOH (1.0 mL), HCO_2NH_4 (0.06 g, 0.95 mmol), Zn (0.09 g, 1.3 mmol), reaction time 4 h. ^{1}H NMR (300 MHz, DMSO-d_6) *d* 3.57 (dd, 1H, *J* = 11.5, 8.0 Hz, H6), 4.01 (brdd, $J_1 = J_2 =$ 8.8 Hz, H5), 4.11 (brd, *J* = 11.5 Hz, H6'), 4.25 (dd, 1H, $J_1 = J_2 =$ 9.6 Hz, H4), 4.52 (s, 2H, CH_2Ph), 5.11 (dd, 1H, $J_1 = J_2 =$ 9.7 Hz, H2), 5.39 (d, 1H, *J* = 9.9 Hz, H1), 5.65 (dd, 1H, $J_1 = J_2 =$ 9.3 Hz, H3), 7.02 (d, 2H, *J* = 8.0 Hz, ArH), 7.08 (brs, 4H, NH_4), 7.27-7.41 (m, 9H, ArH), 7.47-7.66 (m, 4H, ArH), 7.80-7.87 (m, 4H, ArH); ^{13}C NMR (75 MHz, DMSO-d_6) *d* 20.96, 70.62, 71.44, 72.58, 72.80, 74.89, 78.62, 83.81, 127.64, 127.80, 128.48, 129.10, 129.13, 129.23, 129.57, 129.75, 129.92,

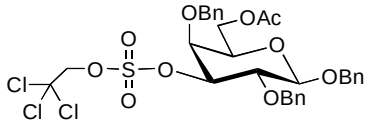
130.37, 131.66, 137.41, 139.08, 164.99, 165.63; HRMS (ESI) *m/z* = 663.1337, $C_{34}H_{31}O_{10}S_2$ requires 663.1359.



***p*-Methoxyphenyl-2-*O*-sulfo-3-*O*-benzyl-4:6-O-benzylidine-ß-D-glucospyranoside 25**: Carbohydrate **18** (0.20 g, 0.30 mmol), MeOH (1.8 mL), HCO_2NH_4 (0.11 g, 1.8 mmol), Zn (0.16 g, 2.45 mmol), reaction time 5 h. ^{1}H NMR (300 MHz, DMSO-d_6) *d* 3.61-3.68 (m, 2H, H5, $H6_{ax}$), 3.72 (s, 3H, CH_3), 3.85 (dd, 1H, *J* = 8.5, 4.0 Hz, H3), 4.11-4.17 (m, 1H, H4), 4.23-4.25 (m, 1H, $H6_{eq}$), 4.51 (dd, 1H, $J_1 = J_2$ = 4.3 Hz, H2), 4.70, 4.90 (AB, 2H, *J* = 12.2 Hz, CH_2Ph), 5.40 (d, 1H, *J* = 4.6 Hz, H1), 5.70 (s, 1H, CHPh), 6.88 (d, 2H, *J* = 9.1 Hz, ArH), 7.02 (d, 2H, *J* = 9.0 Hz, ArH), 7.09 (brs, 4H, NH_4), 7.23-7.33 (m, 3H, ArH), 7.38-7.41 (m, 7H, ArH); ^{13}C NMR (75 MHz, DMSO-d_6) *d* 55.70, 65.11, 68.81, 71.59, 77.13, 79.14, 79.76, 99.98, 100.59, 114.83, 118.96, 126.43, 127.53, 128.02, 128.31, 128.40, 129.11, 138.03, 139.14, 150.98, 155.00; HRMS (ESI) *m/z* = 543.1305, $C_{27}H_{27}O_{10}S$ requires 543.1325.

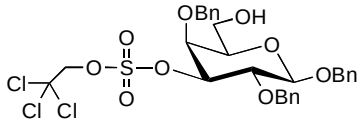


***p*-Methoxyphenyl-2,3-di-*O*-acetyl-4-*O*-benzyl-6-*O*-sulfoglucose 26:** Carbohydrate **19** (0.16 g, 0.24 mmol), MeOH (1.4 mL), HCO_2NH_4 (0.09 g, 1.42 mmol), Zn (0.12 g, 1.84 mmol), reaction time 5 h. ^{1}H NMR (300 MHz, DMSO-d_6) *d* 1.95 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 3.66 (dd, 1H, $J_1 = J_2$ = 9.6 Hz, H4), 3.71 (s, 3H, OCH_3), 3.91 (brd, 1H, *J* = 9.7 Hz, H5), 4.03 (brs, 2H, H6, H6'), 4.52, 4.71 (AB, 2H, *J* = 10.8 Hz, CH_2Ph), 4.88 (dd, 1H, *J* = 9.7, 8.1 Hz, H2), 5.28 (d, 1H, *J* = 8.0 Hz, H1), 5.28 (dd, 1H, $J_1 = J_2$ = 9.6 Hz, H3), 6.87 (d, 2H, *J* = 9.2 Hz, ArH), 6.96 (d, 2H, *J* = 9.1 Hz, ArH), 7.09 (brs, 4H, NH_4), 7.27-7.37 (m, 5H, ArH); ^{13}C NMR (75 MHz, DMSO-d_6) *d* 20.75, 20.87, 55.73, 64,41, 71.81, 73.44, 73.80, 74.08, 75.35, 98.75, 114.95, 118.27, 128.04, 128.53, 128.66, 138.31, 150.95, 155.25, 169.54, 169.92; HRMS (ESI) *m/z* = 539.1205, $C_{24}H_{27}O_{12}S$ requires 539.1223.

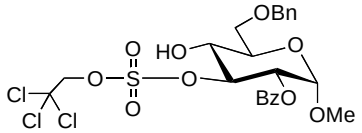


1,2,4-Tri-*O*-benzyl-3-trichloroethylsulfo-6-*O*-acetylgalactose 27: A solution of AcOH:Ac_2O (3 mL, 1:5 v/v) was added to freshly fused $ZnCl_2$ (0.67 g, 4.9 mmol) with stirring. After 1.5 h, carbohydrate **14** (1.0 g, 1.3 mmol) in AcOH:Ac_2O solution (8 mL, 1:5 v/v) was added slowly via syringe. After 3 h, no starting material remained by TLC. The reaction was cooled to 0^{o}C and slowly quenched with ice. The product was extracted

with EtOAc, washed with $NaHCO_3$ and condensed to a clear, colourless oil. Flash chromatography (25:75 EtOAc/hexanes) afforded a clear, colourless oil (0.89 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) *d* 2.03 (s, 3H, CH_3), 3.63 (dd, 1H, $J_1 = J_2 = 6.6$ Hz, H5), 3.98 (dd, 1H, $J = 9.9, 7.6$ Hz, H2), 4.04 (dd, 1H, $J = 11.1, 6.2$ Hz, H6), 4.25 (d, 1H, $J = 2.9$ Hz, H4), 4.31 (dd, 1H, $J = 11.1, 6.2$ Hz, H6'), 4.50 (brs, 2H, CH_2CCl_3), 4.52 (d, 1H, $J = 7.7$ Hz, H1), 4.60 (dd, 1H, $J = 9.9, 2.9$ Hz, H3), 4.65 (d, 1H, $J = 11.0$ Hz, CH_2Ph), 4.67 (d, 1H, $J = 11.3$ Hz, CH_2Ph), 4.68 (d, 1H, $J = 11.8$ Hz, CH_2Ph), 4.96 (d, 1H, $J = 11.5$ Hz, CH_2Ph), 4.97 (d, 1H, $J = 11.8$ Hz, CH_2Ph), 5.06 (d, 1H, $J = 11.0$ Hz, CH_2Ph), 7.28-7.41 (m, 15H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 20.63, 61.86, 71.00, 71.27, 73.01, 75.14, 75.15, 76.20, 79.44, 85.41, 92.28, 101.96, 127.96, 127.99, 128.06, 128.09, 128.39, 128.50, 128.55, 136.54, 136.96, 137.31, 170.20; HRMS (ESI) *m/z* = 720.1215, $C_{31}H_{37}Cl_3NO_{10}S$ $(M+NH_4)^+$ requires 720.1204.

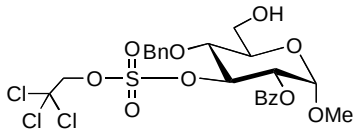


1,2,4-Tri-*O*-benzyl-3-trichloroethylsulfogalactose 28: Carbohydrate **27** (0.19 g, 0.27 mmol) was subjected to a 0.025 M solution of NaOMe in MeOH (1.7 mL). After 3 h, no starting material remained by TLC. Residual solvent was removed *in vacuo*, the residue was dissolved in ethyl acetate, washed with water, $NaHCO_3$ and brine, and condensed to a clear, colourless oil. Flash chromatography (25:75 EtOAc/hexanes) provided a white foam (0.15 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$) *d* 3.44-3.53 (m, 2H, H5, H6), 3.72-3.80 (m, 1H, H6'), 3.98 (dd, 1H, $J = 10.1, 7.6$ Hz, H2), 4.26 (d, 1H, $J = 3.0$ Hz, H4), 4.50 (s, 2H, CH_2CCl_3), 4.55 (d, 1H, $J = 7.6$ Hz, H1), 4.61 (dd, 1H, $J = 10.1, 3.1$ Hz, H3), 4.66 (d, 1H, $J = 11.9$ Hz, CH_2Ph), 4.67 (d, 1H, $J = 11.0$ Hz, CH_2Ph), 4.71 (d, 1H, $J = 11.8$ Hz, CH_2Ph), 4.95 (d, 1H, $J = 11.7$ Hz, CH_2Ph), 4.96 (d, 1H, $J = 11.9$ Hz, CH_2Ph), 5.07 (d, 1H, $J = 11.0$ Hz, CH_2Ph), 7.28-7.44 (m, 15H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 61.17, 71.32, 72.63, 73.88, 74.86, 75.16, 76.39, 77.46, 85.60, 92.29, 102.37, 127.95, 127.99, 128.01, 128.06, 128.30, 128.39, 128.49, 128.51, 128.53, 128.67, 128.80, 136.71, 137.03, 137.34; HRMS (ESI) m/z = 661.0857, $C_{29}H_{31}Cl_3O_9S$ $(M+H)^+$ requires 661.0833.

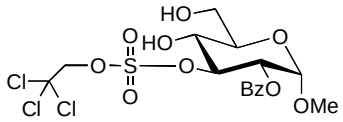


Methyl-2-*O*-benzoyl-3-*O*-trichloroethylsulfo-6-*O*-benzyl-a**-D-glucopyranoside 29:** Carbohydrate **16** (0.5 g, 0.86 mmol) in CH_2Cl_2 (11 mL, 0.08 M) and activated 4Å molecular sieves (1.2 g) were stirred for 1 h at room temperature. The solution was cooled to –78^{o}C and Et_3SiH (0.41 mL, 2.6 mmol) and TfOH (0.26 mL, 2.9 mmol) were added successively. The reaction was stirred at –78^{o}C for 1h, quenched with NEt_3 (1 mL) and methanol (1 mL), diluted with $CHCl_3$ then warmed to room temperature. Solids were removed by filtering reaction contents through Celite, the organic layer was washed with $NaHCO_3$, dried over $MgSO_4$ and condensed to a clear yellow oil. Flash chromatography (25:75 EtOAc/ hexanes) provided a clear colourless glassy compound (0.48 g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$) *d* 3.13-3.16 (brs, 1H, OH), 3.40 (s, 3H, OCH_3), 3.41-3.79 (m, 1H, H6), 3.85-3.92 (m, 2H, H5, H6'), 4.02 (brdd, 1H, $J = 9.0$ Hz,

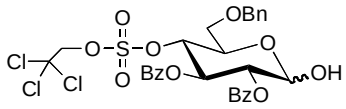
H4), 4.63, 4.76 (AB, 2H, J = 12.0 Hz, CH_2Ph), 4.73, 4.75 (AB, 2H, J = 11.0 Hz, CH_2CCl_3), 5.09-5.13 (m, 2H, H1, H2), 5.26 (dd, 1H, $J_1 = J_2 = 9.2$ Hz, H3), 7.36-7.61 (m, 8H, ArH), 8.16 (dd, 2H, J = 8.4, 1.3 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 55.50, 68.83, 69.70, 70.74, 70.90, 73.82, 79.77, 85.83, 92.48, 96.91, 127.77, 128.05, 128.46, 128.53, 128.74, 130.09, 133.55, 137.11; HRMS (ESI) *m/z* = 599.0302, $C_{23}H_{26}Cl_3O_{10}S$ $(M+H)^+$ requires 599.0132.



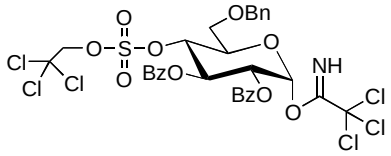
Methyl-2-*O*-benzoyl-3-*O*-trichloroethylsulfo-4-*O*-benzyl-a**-D-glucopyranoside 30:** Carbohydrate **16** (0.6 g, 1.0 mmol) in CH_2Cl_2 (20 mL, 0.05 M) and activated 4Å molecular sieves (2 g) were stirred for 1 h at room temperature. The solution was cooled to –78°C and Et_3SiH (0.50 mL, 3.0 mmol) and $PhBCl_2$ (0.46 mL, 3.5 mmol) were added successively. The reaction was stirred at –78°C for 1 h, quenched with NEt_3 (1 mL) and methanol (1 mL), diluted with $CHCl_3$ then warmed to room temperature. Solids were removed by filtering reaction contents through Celite, the organic layer was washed with $NaHCO_3$, dried over $MgSO_4$ and condensed to a clear yellow oil. Flash chromatography (25:75 EtOAc/hexanes) provided a white foam (0.52 g, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) *d* 3.38 (s, 3H, CH_3), 3.85 (m, 4H, H4, H5, H6, H6'), 4.53, 4.63 (AB, 2H, J = 11.1 Hz, CH_2CCl_3), 4.70, 4.99 (AB, 2H, J = 10.7 Hz, CH_2Ph), 5.12 (d, 1H, J = 3.6 Hz, H1), 5.14 (dd, 1H, J = 9.7, 3.6 Hz, H2), 5.45 (dd, 1H, $J_1 = J_2 = 9.3$ Hz, H3), 7.31-7.50 (m, 7H, ArH), 7.58-7.63 (m, 1H, ArH), 8.16-8.19 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 55.38, 60.91, 70.63, 71.36, 74.99, 75.02, 79.82, 85.53, 92.34, 96.87, 128.13, 128.19, 128.48, 128.72, 133.62, 136.92, 165.74; HRMS (ESI) *m/z* = 616.0588, $C_{23}H_{29}Cl_3NO_{10}S$ $(M+NH_4)^+$ requires 616.0578.



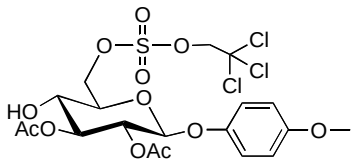
Methyl-2-*O*-benzoyl-3-*O*-trichloroethylsulfo-a**-D-glucopyranoside 31:** A suspension of carbohydrate **16** (0.30 g, 0.5 mmol) in 1:2 CH_2Cl_2/MeOH (2.4 mL, 4.8 mL) was equipped with a reflux condenser and placed in an oil bath at 40°C. The suspension was stirred until all starting material had dissolved then *p*-TsOH (9.0 mg, 0.05 mmol) was added. The temperature was increased to 45°C and the reaction was stirred O/N (approximately 16 hours) until no starting material remained by TLC. The reaction was neutralized with NEt_3 and condensed to a yellow oil. Flash chromatography (60:40 EtOAc/hexanes) provided a white foam (0.24 g, 94%). ^{1}H NMR (300 MHz, $CDCl_3$) *d* 3.14 (s, 3H, CH_3), 3.78-3.84 (m, 1H, H5), 3.97 (brd, J = 3.3 Hz, 2H, H6, H6'), 4.06 (dd, 1H, $J_1 = J_2 = 9.3$ Hz, H4), 4.63, 4.71 (AB, 2H, J = 10.9 Hz, CH_2CCl_3), 5.09-5.15 (m, 2H, H1, H2), 5.30 (dd, 1H, $J_1 = J_2 = 9.1$ Hz, H3), 7.46 (t_{app}, 2H, J = 7.5 Hz, ArH), 7.61 (t_{app}, 1H, J = 7.4 Hz, ArH), 8.15 (d, 2H, J = 7.1 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 55.51, 61.68, 68.96, 70.56, 70.90, 79.81, 85.73, 92.32, 96.96, 128.52, 128.65, 130.07, 133.66, 165.68; HRMS (ESI) *m/z* = 508.9852, $C_{16}H_{20}Cl_3O_{10}S$ $(M+H)^+$ requires 508.9843.



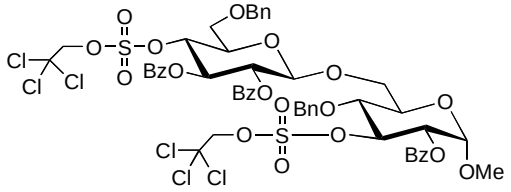
2,3-di-*O*-benzoyl-4-trichloroethylsulfo-6-*O*-benzyl-D-glucose 32: To carbohydrate **17** (0.2 g 0.25 mmol) in acetone / H_2O (9:1, 5.1mL) at 0^oC was added NBS (0.18 g, 1.0 mmol). The reaction was stirred for 20 min at 0^oC, at which point no starting material remained by TLC. Solvents were evaporated at room temperature *in vacuo* until turbidity developed. The remaining residue was dissolved in EtOAc, washed with H_2O, $NaHCO_3$ and brine, dried over $MgSO_4$ and condensed to a clear, colourless oil. Flash chromatography (33:67 EtOAc/hexanes) provided a white foam (0.13 g, 74%). ^1H NMR (300 MHz, $CDCl_3$) *d* 3.61 (brs, 1H, OH), 3.84 (d, 2H, *J* = 3.0 Hz, H6, H6'), 4.40-4.46 (m, 1H, H5), 4.37, 4.79 (AB, 2H, *J* = 14.1 Hz, CH_2CCl_3), 4.61, 4.68 (AB, 2H, *J* = 11.4 Hz, CH_2Ph), 5.20 (dd, 1H, *J* = 10.2, 3.6 Hz, H2), 5.24 (dd, 1H, $J_1 = J_2 = 9.7$ Hz, H4), 5.70 (brs, 1H, H1), 6.19 (dd, 1H, $J_1 = J_2 = 9.8$ Hz, H3), 7.33-7.55 (m, 9H, ArH), 7.97 (d, 2H, *J* = 7.2 Hz, ArH), 8.04 (d, 2H, *J* = 7.2 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 67.62, 68.02, 69.51, 72.02, 73.76, 73.83, 79.51, 79.99, 89.99, 92.23, 127.85, 128.03, 128.36, 128.61, 128.5, 128.80, 129.85, 129.92, 133.44, 137.20, 165.53, 165.79; HRMS (ESI) *m/z* = 689.0443, $C_{29}H_{28}Cl_3O_{11}S$ $(M+H)^+$ requires 689.0418.



2,3-di-*O*-benzoyl-4-trichloroethylsulfo-6-*O*-benzyl-a**-D-glucopyranotrichloracetimidate 33:** To carbohydrate **32** (0.4 g, 0.58 mmol) in CH_2Cl_2 (5 mL, 0.13 M) at –40^oC was added trichloroacetonitrile (0.93 mL, 9.28 mmol), followed by a slow dropwise addition of DBU (0.12 mL, 1.0 M solution in CH_2Cl_2). The reaction was stirred at –40^oC for 2 h then gradually warmed to –10^oC over 1 h, at which point no starting material remained by TLC. The solvent was removed *in vacuo* at room temperature, and crude material was applied directly to a short silica gel column. Flash chromatography (25:75 EtOAc/hexanes) afforded a white foam (0.38 g, 80%). ^1H NMR (300 MHz, $CDCl_3$) *d* 3.91 (brs, 2H, H6, H6'), 4.37 (brd, 1H, *J* = 10.0 Hz, H5), 4.55, 4.66 (AB, 2H, *J* = 11.1 Hz, CH_2CCl_3), 4.62, 4.72 (AB, 2H, *J* = 11.7 Hz, CH_2Ph), 5.49 (dd, 1H, *J* = 10.1, 3.6 Hz, H2), 5.49 (dd, 1H, $J_1 = J_2 = 9.8$ Hz, H4), 6.24 (dd, 1H, $J_1 = J_2 = 9.9$ Hz, H3), 6.79 (d, 1H, *J* = 3.5 Hz, H1), 7.31-7.54 (m, 11H, ArH), 7.94 (d, 2H, *J* = 7.3 Hz, ArH), 8.05 (d, 2H, *J* = 7.3 Hz, ArH), 8.65 (s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) *d* 66.93, 69.53, 70.56, 71.15, 73.76, 77.34, 78.34, 80.09, 90.49, 92.19, 92.79, 127.81, 128.01, 128.24, 128.34, 128.36, 128.60, 129.79, 129.90, 129.96, 133.52, 133.57, 137.29, 160.27, 165.08, 165.61.

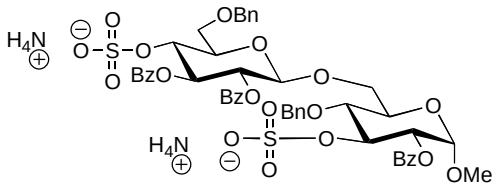


***p*-Methoxyphenyl-2,3-di-*O*-acetyl-6-*O*-trichloroethylsulfo-ß-D-glucopyranoside 34:** To carbohydrate **19** (0.220 g, 0.28 mmol) in CCl_4/H_2O (15 mL, 9.5 mL) was added NBS (0.157 g, 0.88 mmol) and $CaCO_3$ (0.149 g, 1.5 mmol). The system was purged with argon for 15 minutes and the reaction was irradiated with a 250 W incandescent lamp for 1h. The reaction was poured into ice water (50 mL) and extracted with $CHCl_3$. Combined organics were dried over $MgSO_4$ and concentrated to crude residue. Flash chromatography (50:50 EtOAc/hexanes) provided a white foam (0.173 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) *d* 2.10 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 3.09 (d, 1H, *J* = 4.3 Hz, OH), 3.78 (s, 3H, OCH_3), 3.78-3.87 (m, 2H, H4, H5), 4.61 (dd, 1H, J_1 = 10.9 Hz, J_2 = 4.5 Hz, H6), 4.67 (s, 2H, CH_2), 4.70 (dd, 1H, $J_1 = J_2$ = 10.5 Hz, H6'), 5.02 (d, 1H, *J* = 7.7 Hz, H1), 5.10 (brdd, 1H, $J_1 = J_2$ = 8.7 Hz, H3), 5.20 (brdd, 1H, $J_1 = J_2$ = 8.6 Hz, H2), 6.03 (d, 2H, *J* = 9.1 Hz, ArH), 6.94 (d, 2H, *J* = 9.1 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 20.55, 20.71, 55.57, 68.40, 70.69, 71.55, 73.20, 75.81, 79.60, 92.27, 99.82, 114.60, 118.24, 150.55, 155.73, 169.33, 171.82; HRMS (ESI) *m/z* = 598.0320 $(M+NH_4)^+$ $C_{19}H_{27}NO_{12}SCl_3$ requires 598.0314.



Methyl-(2,3-di-*O*-benzoyl-4-trichloroethylsulfo-6-*O*-benzyl-ß-D-glucopyranoside)-(1 ® 6)-(2-*O*-benzoyl-3-*O*-trichlorethylsulfo-4-*O*-benzyl-a-D-glucopyranoside) 35: Donor **33** (0.36 g, 0.43 mmol) and acceptor **30** (0.22 g, 0.36 mmol) were dissolved in CH_2Cl_2 (9.4 mL). Powdered 4Å molecular sieves were added, and the mixture was stirred at room temperature for 1.5 h. The solution was then cooled to –40°C, stirred for an additional 30 min. TMSOTf (72 µL, 1.0 M solution in CH_2Cl_2) was added dropwise. The reaction was stirred for 30 min at –40°C at which point no starting acceptor remained by TLC. The reaction was quenched with NEt_3 (0.1 mL), warmed to room temperature, filtered through Celite and condensed to a yellow crude oil. Flash chromatography (25:75 EtOAc/hexanes) followed by gravity chromatography (80:20 PhH/EtOAc) provided product as a white foam (0.38 g, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) *d* 3.24 (s, 3H, OCH_3), 3.73 (dd, 1H, $J_1 = J_2$ = 9.5 Hz, $H4_{(II)}$), 3.81 (dd, 1H, *J* = 10.9, 4.1 Hz, H6), 3.86-3.98 (m, 4H, $H5_{(I)}$, $H5_{(II)}$, H6, H6'), 4.20 (dd, 1H, *J* = 10.9, 1.8 Hz, H6'), 4.34, 4.59 (AB, 2H, *J* = 10.7 Hz, CH_2Ph), 4.43, 4.52 (AB, 2H, *J* = 11.1 Hz, CH_2CCl_3), 4.53, 4.63 (AB, 2H, *J* = 11.1 Hz, CH_2CCl_3), 4.68, 4.71 (AB, 2H, *J* = 11.9 Hz, CH_2Ph), 4.78 (d, 1H, *J* = 7.8 Hz, $H1_{(I)}$), 5.03 (d, 1H, *J* = 3.1 Hz, $H1_{(II)}$), 5.25 (brdd, 1H, $J_1 = J_2$ = 9.3 Hz, $H4_{(I)}$), 5.35 (dd, 1H, $J_1 = J_2$ = 9.7 Hz, $H3_{(II)}$), 5.53 (dd, 1H, *J* = 9.6, 7.8 Hz, $H2_{(I)}$), 5.87 (dd, 1H, $J_1 = J_2$ = 9.4 Hz, $H3_{(I)}$), 7.18 (d, 2H, *J* = 5.7 Hz, ArH), 7.27-7.61 (m, 17H, ArH), 7.93, 8.00, 8.15 (3d, 3x2H, *J* = 7.2 Hz, ArH). ^{13}C NMR (125 MHz, $CDCl_3$) *d* 55.29, 67.78,

67.92, 69.40, 71.21, 71.74, 72.18, 73.45, 73.73, 74.17, 75.44, 79.43, 79.80, 80.82, 85.56, 92.29, 92.38, 96.73, 100.96, 127.78, 127.85, 128.00, 128.28, 128.44, 128.48, 128.53, 128.86, 129.72, 130.07, 130.24, 133.50, 133.63, 133.69, 136.90, 137.57, 164.80, 165.61, 165.82; HRMS (ESI) *m/z* = 1269.0546, $C_{52}H_{51}Cl_6O_{20}S_2$ $(M+H)^+$ requires 1269.0546.



Methyl-(2,3-di-*O*-benzoyl-4-sulfo-6-*O*-benzyl-ß-D-glucopyranoside)-(1 ® 6)-(2-*O*-benzoyl-3-*O*-sulfo-4-*O*-benzyl-a**-D-glucopyranoside) 36**: To disaccharide **35** (0.05 g, 0.039 mmol) in reagent grade MeOH (0.4 mL) was added ammonium formate (0.03 g, 0.48 mmol) followed by zinc dust (0.04 g, 0.55 mmol). The reaction was stirred for 9h at room temperature, at which point no starting material was detected by TLC. The reaction was filtered through Celite, and condensed to crude product. Flash chromatography (20:4:1 CH_2Cl_2/MeOH/NH_4OH) afforded a white solid, which was lyophilized (3x) to yield a light white product (0.038 g, 92%). ^{1}H NMR (500MHz, DMSO-d_6) *d* 2.99 (s, 3H, OCH_3), 3.28 - 3.32 (m, 1H, $H3_{(II)}$), 3.56-3.59 (m, 3H, $H6'_{(I)}$, $H4_{(II)}$, $H5_{(II)}$), 3.65 (dd, 1H, J_1 = 10.7 Hz, J_2 = 5.5 Hz, $H6'_{(II)}$), 3.87 (br-dd, 1H, $J_1 = J_2$ = 9.4 Hz, $H5_{(I)}$), 4.01 (br-d, 1H, J = 9.4 Hz, $H6_{(II)}$), 4.06 (d, 1H, J = 10.3 Hz, $CH_2PH_{(I)}$), 4.08 (d, 1H, J = 10.0 Hz, $H6_{(I)}$), 4.26 (dd, 1H, $J_1 = J_2$ = 9.5 Hz, $H4_{(I)}$), 4.52 , 4.55 (AB, 2H, J = 11.9 Hz, $CH_2PH_{(I)}$), 4.68 – 4.72 (m, 2H, $H1_{(II)}$, $H2_{(II)}$), 4.85 (d, 1H, J = 10.3 Hz, $CH_2PH_{(II)}$), 4.96 (d, 1H, J = 8.0 Hz, $H1_{(I)}$), 5.09 (dd, 1H, J_1 = 9.8 Hz, J_2 = 8.0 Hz, $H2_{(I)}$), 5.57 (dd, 1H, $J_1 = J_2$ = 9.5 Hz, $H3_{(I)}$), 7.10 (br-s, 8H, NH_4), 7.14 – 7.20 (m, 7H, ArH), 7.25 – 7.38 (m, 8H, ArH), 7.43 – 7.46 (m, 2H, ArH), 7.48 – 7.52 (m, 2H, ArH), 7.57 – 7.59 (m, 1H, ArH), 7.76 – 7.80 (m, 4H, ArH), 8.07 – 8.09 (m, 1H, ArH); ^{13}C NMR (125 MHz, D_2O) *d* 54.87, 67.61, 68.33, 69.00, 71.43, 71.89, 73.26, 73.37, 73.48, 74.25, 74.83, 75.43, 78.89, 96.67, 100.33, 127.81, 128.25, 128.41, 128.45, 128.57, 128.58, 128.70, 128.74, 128.79, 128.88, 129.43, 129.51, 129.90, 133.93, 134.32, 136.96, 137.40, 166.99, 167.43, 167.62; HRMS (ESI) m/z = 1006.2000, $C_{48}H_{46}O_{20}S$ requires 1006.2024.