Supplementary Information

Allyl 2-O-(3,4,6-tri-O-benzyl-β-D-mannopyranosyl)-3,4,6-tri-O-benzyl-β-D-mannopyranoside (7). Glycosyl acceptor **5** (1.0 g, 2.0 mmol) and silver zeolite[12] (3.3 g) in dichloromethane (4 mL) was stirred for 20 min at room temperature. Freshly prepared 3,4,6 tri-O-benzyl-α-D-arabino-hexopyranos-2-ulosyl bromide[7] (2.6 g, 5 mmol) was dissolved in dichloromethane (2 mL) and was added dropwise to the suspension containing the glycosyl acceptor. The reaction was stirred for 16 hr, filtered through celite and concentrated to a yellow syrup. This syrup was dissolved in tetrahydrofuran (30 mL) and cooled to –78 ºC under argon. L-Selectride (1M THF, 8 mL) was then added dropwise and the reaction was stirred for 5 min, the dry ice bath was removed and the reaction was allowed to warm to room temperature. The reaction mixture was quenched after 15 min with methanol (2mL) and diluted with dichloromethane. Washing with a solution of hydrogen peroxide (5%) and sodium hydroxide (1M) followed by thiosulfate (5%) and brine solutions gave a clear colourless organic solution. This was dried over sodium sulfate and concentrated to a colourless oil. The oil was taken up in a 1:1 solution of toluene and ethyl acetate (2 mL) and passed through a plug of aluminium oxide (neutral, activated Brockman I, 3 cm) and the aluminium oxide was washed with the equivalent solution (90 mL). The combined filtrates were concentrated and subjected to column chromatography in 8:1 toluene:ethylacetate to give **7** as a colourless syrup (1.47g, 78%), $[\alpha]_D$ –4.6 °(c 0.6, $CHCl_3$); ^{1}NMR (500 MHz, $CDCl_3$) δ 7.39-7.12 (30 H, Ar), 5.85 (dddd, 1 H, $^3J_{trans}$ 16.6, $^3J_{cis}$ 10.7, $J_{vic}\approx J_{vic}$ 5.0 Hz, $OCH_2C\underline{H}CH_2$), 5.20 (dddd, 1 H, $J_{gem}\approx {}^4J_a\approx {}^4J_b\approx$ 1.5 Hz, $OCH_2CHC\underline{H}_2$), 5.13 (dddd, 1 H, $J^4{}_a\approx J^4{}_b\approx$ 1.5 Hz, $OCH_2CHC\underline{H}_2$), 4.95 (s, 1 H, H-1'), 4.94 (d, 1 H, J 10.5 Hz, $OC\underline{H}_2Ph$), 4.91 (d, 1 H, J 11.6 Hz, $OC\underline{H}_2Ph$), 4.86 (d, 1 H, J 10.8 Hz, $OC\underline{H}_2Ph$), 4.82 (d, 1 H, J 11.9 Hz, $OC\underline{H}_2Ph$), 4.62 (d, 1 H, J 11.9 Hz, $OC\underline{H}_2Ph$), 4.61 (d, 1 H, J 12.1 Hz, $OC\underline{H}_2Ph$), 4.54 (d, 1 H, J 10.7 Hz, $OC\underline{H}_2Ph$), 4.54 (d, 1 H, J 12.1, $OC\underline{H}_2Ph$), 4.50 (d, 1 H, $J_{2,3}$ 3.4 Hz, H-2), 4.46-4.43 (4 H, $OC\underline{H}_2Ph$), 4.41 (1 H, s, H-1), 4.38 (dddd, 1 H, J_{gem} 13.0, $OC\underline{H}_2CHCH_2$), 4.33 (d, 1 H, $J_{2,3}$ 2.9 Hz, H-2'), 4.00 (dddd, 1 H, $OC\underline{H}_2CHCH_2$), 3.90 (dd, 1

H, $J_{3,4} \approx J_{4,5}$ 9.5 Hz, H-4'), 3.79-3.75 (3 H, H-6a, H-4, H-6a'), 3.72 (dd, 1 H, $J_{5,6b}$ 5.5, J_{gem} 10.7 Hz, H-6b), 3.64 (dd, 1 H, $J_{5\text{-}6b}$ 6.1, J_{gem} 10.5 Hz, H-6b'), 3.56 (dd, 1H, H-3'), 3.53 (dd, 1 H, $J_{3,4}$ 6.6, H-3), 3.49 (ddd, 1 H, $J_{5,6a}$ 1.5, H-5'), 3.40 (ddd, 1 H, $J_{5,6a}$ 1.5, H-5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4-138.1, 133.8, 128.6-127.5, 117.1, 100.1 ($^1J_{C\text{-}H}$ 163 Hz, C1'), 99.3 ($^1J_{C\text{-}H}$ 154 Hz, C1), 81.5, 80.4, 80.3, 75.6, 75.2, 75.1, 75.1, 74.5. 74.1, 73.5, 73.4, 70.8, 70.7, 70.1, 70.1, 70.0, 69.5, 67.7; Anal. Calc. For $C_{57}H_{62}O_{11}$; C, 74.16; H, 6.77; O, 19.07; Found; C, 73.87; H, 6.91.

Allyl (3,4,6-tri-O-*p*-chlorobenzyl-β-D-mannopyranosyl)(1→2)(3,4,6-tri-O-benzyl-β-D-mannopyranosyl)(1→2)-3,4,6-tri-O-benzyl-β-D-mannopyranoside(12). Glycosyl donor (**11**) (820 mg 1.3 mmol), glycosyl acceptor (**7**) (380 mg, 0.41 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (330 mg, 1.6 mmol) were dried together under vacuum for 1 hr in a pear shaped flask (25 ml). The contents were then dissolved in acetonitrile (1.5 mL), activated 3Å molecular sieves (500 mg) and a stir bar were then added. The suspension was stirred for 30 min and the temperature was moderated by an ambient temperature water bath. Silver triflate (355 mg, 1.4 mmol) was added and the reaction was stirred in the dark for 1 hr. The reaction was then diluted with dichloromethane and filtered through celite. Combined filtrates were washed with a solution of sodium bicarbonate, dried over sodium sulphate and concentrated. Column chromatography in 9:1 toluene/ethyl acetate gave the crude ketone as a colourless syrup (rf 0.35 4:1 toluene/ethylacetate). The syrup was then taken up in THF (10 ml) and cooled to –78 °C under argon. L-Selectride (3 mL, 1 M) was added dropwise and the cooling bath removed. Once the reaction had reached ambient temperature methanol (2mL) was added. The reaction was diluted with dichloromethane and washed with 5% hydrogen peroxide/1M NaOH followed by 5% thiosulfate/brine to give a clear solution, which after drying over sodium sulphate, and concentration gave a colourless oil. This was taken up in a 1:1 solution of toluene/ethyl acetate (2 mL) and passed through a plug of aluminium oxide (neutral, activated Brockman I, 3 cm) and the aluminium oxide was washed with the equivalent solution (90 mL). The combined filtrates were

concentrated and column chromatography in 9:1 toluene/ethyl acetate gave **12** (390 mg, 65%); $[\alpha]_D$ – 64 °(c 0.6, $CHCl_3$); ^{1}NMR (600 MHz, $CHCl_3$) δ 7.45-6.87 (42 H, Ar), 5.86 (dddd, 1 H, $^3J_{trans}$ 17.2, $^3J_{cis}$ 10.4, J_{vic}≈J_{vic} 5.6 Hz, $OCH_2C\underline{H}CH_2$), 5.20 (dddd, J_{gem}≈^4J_a≈^4J_b≈ 1.5 Hz, $OCH_2CHC\underline{H}_2$), 5.16 (s, 1 H, H-1''), 5.14 (dddd, 1 H, ^4J_a≈^4J_b≈1.1 Hz, $OCH_2CHC\underline{H}_2$), 5.11 (s, 1 H, H-1'), 4.92 (d, 1 H, J 10.8 Hz, $OC\underline{H}_2Ph$), 4.92 (d, 1 H, J 10.5 Hz, $OC\underline{H}_2Ph$), 4.92 (d, 1 H, J 10.2 Hz, $OC\underline{H}_2Ph$), 4.72 (d, 1 H, J 11.7 Hz, $OC\underline{H}_2Ph$), 4.71 (d, 1 H, J 9.2 Hz, $OC\underline{H}_2Ph$), 4.68 (d, 1 H, $J_{2,3}$ 3.3 Hz, H-2'), 4.63 (d, 1 H, J 11.9 Hz, $OC\underline{H}_2Ph$), 4.62 (d, 1 H, $J_{2,3}$ 2.5 Hz, H-2), 4.51 (d, 1 H, J 10.3 Hz, $OC\underline{H}_2Ph$), 4.50 (d, 1 H, J 11.5 Hz, $OC\underline{H}_2Ph$), 4.44 (s, 1 H, H-1), 4.44-4.38 (6H, 5 $OC\underline{H}_2Ph$, $OC\underline{H}_2CHCH_2$), 4.29 (d, 1 H, J 9.7, $OC\underline{H}_2Ph$), 4.28 (d, 1 H, J 12.6 Hz, $OC\underline{H}_2Ph$), 4.25 (d, 1 H, $J_{2,3}$ 2.9, H-2''), 4.17 (d, 1 H, J 10.3 Hz, $OC\underline{H}_2Ph$), 4.04 (d, 1 H, J 12.1 Hz, $OC\underline{H}_2Ph$), 3.99 (dddd, 1 H, J_{gem} 12.8, OCH2CHCH2), 3.91 (dd, $J_{3,4}$≈$J_{4,5}$ 9.5 Hz, H-4'), 3.82 (d, 1 H, J 12.0 Hz, $OC\underline{H}_2Ph$), 3.80 (dd, $J_{3,4}$≈$J_{4,5}$ 9.0 Hz, H-4''), 3.77 (dd, J_{gem} 11.1, H-6a'), 3.72 (dd, $J_{5,6}$ 5.7, H-6b'), 3.27-3.67 (ABX, 2 H, H6a, H-6b), 3.65-3.62 (3 H, H-4, H-6a'', H-6b'') 3.60 (dd, 1H, $J_{3,4}$ 7.9, H-3'), 3.58 (dd, 1 H, $J_{2,3}$ 3.5, $J_{3,4}$ 7.5, H-3), 3.50 (ddd, 1 H, $J_{5,6a}$ 1.1, H-5'), 3.46(ddd, 1 H, $J_{5,6a}$ 2.8, $J_{5,6b}$ 4.3, H-5''), 3.39 (dd, 1 H, H-3''), 3.37 (ddd, 1 H, $J_{5,6a}$ 2.2, $J_{5,6b}$ 4.0, $J_{4,5}$ 8.7, H-5) ^{13}C NMR (125 mHz, CDCl3) 139.1, 139.0, 138.8, 138.8, 138.6, 137.7, 137.4, 134.3, 134.0, 133.9, 133.6, 130.0-128.2, 118.2, 101.4 ($^1J_{C-H}$ 156 Hz), 100.7 ($^1J_{C-H}$ 164 Hz), 100.6 ($^1J_{C-H}$ 161 Hz), 83.8, 81.3, 81.1, 76.1, 76.1, 75.9, 75.8, 75.7, 75.4, 75.0, 74.9, 74.2, 74.1, 73.3, 73.1, 71.1, 70.8, 70.6, 70.5, 70.4, 70.1, 69.8, 69.4, 67.9; Anal. Calc. For $C_{84}H_{87}Cl_3O_{16}$; C, 69.15; H, 6.01; O, 17.55; Cl, 7.29; Found; C, 69.26; H, 6.13

Allyl (3,4,6-tri-O-*p*-chlorobenzyl-β-D-mannopyranosyl)(1→2)(3,4,6-tri-O-*p*-chlorobenzyl-β-D-mannopyranosyl)(1→2)(3,4,6-tri-O-benzyl-β-D-mannopyranosyl)(1→2)-3,4,6-tri-O-benzyl-β-D-mannopyranoside(13). Glycosyl donor (**11**) (290 mg, 0.47 mmol), glycosyl acceptor (**12**) (180 mg, 0.12 mmol) and 2,6-di-tert-butyl-4-methylpyridine (106 mg, 0.52 mmol) were dried together under vacuum for 1 hr in a pear shaped flask (25ml). The contents were then dissolved in pivaloylnitrile (900 μL), activated 4 Å molecular sieves (300mg) and a stir bar were then added. The suspension was stirred

for 30 min at room temperature under argon and the temperature was moderated by an ambient temperature water bath. Silver triflate was added and the reaction was stirred in the dark for an additional 1 hr. The reaction was diluted with dichloromethane and filtered through celite. Combined filtrates were washed with a solution of sodium bicarbonate, dried over sodium sulphate and concentrated. Column chromatography in 8:1 toluene:ethylacetate gave the crude ketone as a colourless syrup (rf 0.35 4:1 toluene/ethylacetate).The syrup was then taken up in THF (10 mL) and cooled to –78 °C under argon. L-Selectride (2 mL, 1 M) was added dropwise and the cooling bath removed. Once the reaction had reached ambient temperature methanol (1 mL) was added. The reaction was diluted with dichloromethane and washed with 5% hydrogen peroxide/1M NaOH followed by 5% thiosulfate/brine to give a clear solution. After drying over sodium sulphate, concentration gave a colourless oil which was taken up in a 1:1 solution of toluene ethyl acetate (2 mL), passed through a plug of aluminium oxide (neutral, activated Brockman I, 3 cm) and the aluminium oxide was washed with the equivalent solution (90 mL). The combined filtrates were concentrated and column chromatography in 9:1 toluene/ethyl acetate gave **13** (120 mg, 48%), $[\alpha]_D$ -68° (c 0.6, $CHCl_3$); ^1H NMR (600 MHz $CDCl_3$) δ 7.45-6.88 (54 H, Ar), 5.82 (dddd, 1 H, $^3J_{trans}$ 16.7, $^3J_{cis}$ 10.8, $J_{vic} \approx J_{vic}$ 5.7 Hz, $OCH_2C\underline{H}CH_2$), 5.48 (s, 1 H, H-1''), 5.19 (dddd, 1 H, $J_{gem} \approx {}^4J_a \approx {}^4J_b \approx$ 1.1 Hz, $OCH_2CHC\underline{H}_2$), 5.16 (s, 1 H, H-1'''), 5.13 (1 H, dddd, $J_{gem} \approx {}^4J_a \approx {}^4J_b \approx$ 1.1 Hz, $OCH_2CHC\underline{H}_2$), 5.11 (s, 1 H, H-1'), 4.88 (d, 2 H, J 10.6 Hz, $2C\underline{H}_2Ph$), 4.84 (d, 1 H, $J_{2,3}$ 3.3 Hz, H2'), 4.80 (d, 1 H, J 11.4 Hz, $C\underline{H}_2Ph$), 4.78 (d, 1 H, J 10.3 Hz, $C\underline{H}_2Ph$), 4.72 (d, 2 H, J 11.2 Hz, $2C\underline{H}_2Ph$), 4.57 (d, 1 H, J 12.5 Hz, $C\underline{H}_2Ph$), 4.56 (d, 1 H, J 12.3 Hz, $C\underline{H}_2Ph$), 4.52 (d, 1 H, J 12.1 Hz, $C\underline{H}_2Ph$), 4.52 (d, 1 H, $J_{2,3}$ 3.1 Hz, H2), 4.47 (d, 1 H, J 11.2 Hz, $C\underline{H}_2Ph$), 4.47 (d, 1 H, $J_{2\text{-}3}$ 3.3 Hz, H-2''), 4.45 (d, 1 H, J 12.8 Hz, $C\underline{H}_2Ph$), 4.41 (d, 1 H, J 11.4 Hz, $C\underline{H}_2Ph$), 4.40 (s, 1 H, H-1), 4.40 (d, 1 H, J 10.8 Hz, $C\underline{H}_2Ph$), 4.38 (d, 2 H, J 12.0 Hz, $2C\underline{H}_2Ph$), 4.38 (dddd 1 H, $OC\underline{H}_2CHCH_2$), 4.36 (d, 1 H, J 13.5 Hz, $C\underline{H}_2Ph$), 4.32 (d, 1 H, H2'''), 4.31 (d, 1 H, J 12.4 Hz, $C\underline{H}_2Ph$), 4.30 (d, 2 H, J 10.0 Hz, $C\underline{H}_2Ph$), 4.30 (d, 1 H, J 9.6 Hz, $C\underline{H}_2Ph$), 4.26 (d, 1 H, J 12.1 Hz, $C\underline{H}_2Ph$), 4.08 (d, 1 H, J 12.1 Hz, $C\underline{H}_2Ph$), 3.96(dddd, 1 H, J_{gem} 12.5 Hz, $OC\underline{H}_2CHCH_2$), 3.92 (dd, $J_{3,4} \approx J_{4,5}$ 9.3 Hz, H-

4''), 3.90 (d, 1 H, J 12.1 Hz, C<u>H</u>$_2$Ph), 3.83 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ 9.3 Hz, H-4'''), 3.75 (d, 1 H, J 11.1 Hz, C<u>H</u>$_2$Ph), 3.76-3.60 (12 H, H-4, H-6a, H-6b, H-3',H-4', H-6a', H-6b', H-6a'', H-6b'', H-6a''', H-6b''', C<u>H</u>$_2$Ph), 3.58 (ddd, 1 H, H-5''), 3.56 (dd, 1 H, $J_{4,5}$ 9.4 Hz, H-3), 3.50 (ddd, 1 H, H-5'''), 3.49 (1 H, ddd, H-5'), 3.46 (dd, 1 H, $J_{3,4}$ 9.5 Hz, H-3''), 3.44 (dd, 1 H, $J_{2,3}$ 2.9, $J_{3,4}$ 9.2 Hz, H3'''), 3.33 (ddd, 1 H, $J_{4,5}$ 9.5 $J_{5,6a}$ 1.7, $J_{5,6b}$ 4.0 Hz, H-5) ^{13}C NMR (125 MHz, $CDCl_3$), 138.9, 138.8, 138.7, 138.6, 138.5, 138.5, 137.9, 137.6, 137.5, 137.4, 137.4, 137.2, 134.3, 134.9, 134.9, 133.7, 133.6, 129.8-128.4, 118.1, 101.8 ($^1J_{C\text{-}H}$ 163 Hz, C1''), 101.4 ($^1J_{C\text{-}H}$ 162 Hz, C1'''), 100.9 ($^1J_{C\text{-}H}$ 161 Hz, C1'), 100.4 ($^1J_{C\text{-}H}$ 155 Hz, C1''), 83.7, 82.3, 81.4, 81.0, 76.2, 76.1, 75.9, 75.9, 75.8, 75.3, 75.1, 75.0, 74.9, 74.9, 74.2, 74.2, 73.5, 73.3, 73.1, 71.1, 71.2, 71.0, 71.0, 70.7, 70.5, 70.3, 70.2, 69.9, 69.8, 69.5, 69.3, 68.1 Electrospray ms Calc 1995 Found (M+Na) 2018 isotope intensities correct for Cl_6

3-(2-Aminoethylthio)-propyl (3,4,6-tri-O-*p*-chlorobenzyl-β-D-mannopyranosyl)(1→2)(3,4,6-tri-O-*p*-chlorobenzyl-β-D-mannopyranosyl)(1→2)(3,4,6-tri-O-benzyl-β-D-mannopyranosyl)(1→2)-3,4,6-tri-O-benzyl-β-D-mannopyranoside (14). Allyl tetratrasaccharide (70 mg) (**13**) was added to a quartz vessel and dissolved in a minimum amount of dichloromethane (400 μL). Methanol (5 mL) was then added followed by 2-aminoethanethiol hydrochloride (1.0 g) the reaction was stirred until dissolution was complete. Irradiation 365nm was carried out for 3 hrs and then the solution was diluted with dichloromethane and washed with 1M sodium hydroxide. The combined organic layer was dried, concentrated and subjected to column chromatography in dichloromethane containing 2% methanol giving **14** (53 mg, 74%); $[\alpha]_D$ -51.7° (c 0.4, $CHCl_3$);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45-6.89 (54 H, Ar), 5.48 (s, 1 H, H-1''), 5.16 (s, 1 H, H-1'''), 5.08 (s, 1 H, H-1'), 4.88 (d, 1 H, J 10.3 Hz, OC<u>H</u>$_2$Ph), 4.87 (d, 1 H, J 11.0 Hz, OC<u>H</u>$_2$Ph), 4.81 (d, 1 H, J 10.4 Hz, OC<u>H</u>$_2$Ph), 4.81 (d, 1 H, $J_{2,3}$ 3.3 Hz, H-2'), 4.78 (d, 1 H, J 10.3 Hz, OC<u>H</u>$_2$Ph), 4.71 (d, 2 H, J 11.4 Hz, OC<u>H</u>$_2$Ph), 4.57 (d, 1 H, J 12.5 Hz, OC<u>H</u>$_2$Ph), 4.56 (d, 1 H, J 12.3 Hz, OC<u>H</u>$_2$Ph), 4.53 (d, 1 H, $J_{2,3}$ 2.7 Hz, H-2), 4.53 (d, 1 H, J 12.5 Hz, OC<u>H</u>$_2$Ph), 4.46 (d, 1 H, J 10.4 Hz, OC<u>H</u>$_2$Ph), 4.45 (d, 1 H, $J_{2,3}$ 3.1 Hz, H-2''), 4.45 (d, 1 H, J 11.9 Hz, OC<u>H</u>$_2$Ph),

4.39 (d, 1 H, J 11.4 Hz, OC$\underline{H}_2$Ph), 4.38 (d, 2 H, J 11.5 Hz, OC$\underline{H}_2$Ph), 4.38 (d, 1 H, J 12.5 Hz, OC$\underline{H}_2$Ph), 4.37 (s, 1 H, H-1), 4.35 (d, 1 H, J 12.1 Hz, OC$\underline{H}_2$Ph), 4.32 (d, 1 H, J 12.1 Hz, OC$\underline{H}_2$Ph), 4.31 (d, 1 H, J 9.9 Hz, OC$\underline{H}_2$Ph), 4.31 (d, 1 H, H2'''), 4.31 (d, 1 H, J 11.1 Hz, OC$\underline{H}_2$Ph), 4.29 (d, 1 H, J 10.3, C$\underline{H}_2$Ph), 4.25 (d, 1 H, J 12.3, OC$\underline{H}_2$Ph), 4.07 (d, 1 H, J 11.9 Hz, OC$\underline{H}_2$Ph), 3.98 (dt, 1 H, J_{gem}, 9.5, J_{vic} 6.1 Hz, OC$\underline{H}_2$CH$_2$), 3.91 (dd, 1 H, $J_{4,5}\approx J_{3,4}$ 9.3 Hz, H-4''), 3.89 (d, 1 H, J 11.9 Hz, OC$\underline{H}_2$Ph), 3.83 (dd, 1 H $J_{4,5}\approx J_{3,4}$ 9.4 Hz, H-4'''), 3.75-3.61 (12 H, H-4, H-6a, H-6b, H-3', H-4', H-6a', H-6b', H-6a'', H-6b'', H-6a''', H-6b''', OC$\underline{H}_2$Ph), 3.59-3.57 (2 H, H-3, H-5''), 3.52-3.48 (2 H, H-5''', OC$\underline{H}_2$CH$_2$), 3.47-3.41 (3 H, H-3'', H-3'', H-5'), 3.34 (ddd, $J_{5,6a}$2.0, $J_{5,6b}$ 4.4, $J_{4,5}$ 9.7 Hz, H-5), 2.78 (t, 2 H, J_{vic} 6.4, C$\underline{H}_2$NH$_3^+$), 2.53 (t, 2 H, J_{vic} 6.4, SC$\underline{H}_2$CH$_2$NH$_3^+$), 2.50 (t, 2 H, J_{vic} 7.0, OCH$_2$CH$_2$C$\underline{H}_2$S), 1.89-1.78 (m, 2 H, OCH$_2$C$\underline{H}_2$CH$_2$S);^{13}C NMR (125 MHz, CDCl$_3$) δ 139.9, 138.7, 138.6, 138.4, 138.4, 138.3, 137.7, 137.5, 137.3, 137.3, 137.1, 137.0, 134.0, 134.0, 133.9, 133.8, 133.6, 129.9-128.4, 102.4($^1J_{C-H}$ 155 Hz, C1), 101.7 ($^1J_{C-H}$ 161 Hz, C1'), 101.1 ($^1J_{C-H}$ 164 Hz, C1'''), 100.3 ($^1J_{C-H}$ 165 Hz, C1''), 83.6, 82.4, 81.4, 80.9, 76.3, 76.2, 75.9, 75.8, 75.8, 75.3, 75.1, 74.9,74.8, 74.8, 74.2, 74.1, 73.5, 73.4, 73.3, 70.8, 70.6, 70.4, 70.3, 70.1, 69.9, 69.7, 69.1, 69.0. 68.0, 39.4, 30.4, 29.7, 29.4, 28.8 Electrospray ms Calc 2072 Found (M+H) 2073, isotope intensities for Cl$_6$ correct

3-(2-Aminoethylthio)-propyl (β-D-mannopyranosyl)(1→2)(β-D-mannopyranosyl)(1→2)(β-D-mannopyranosyl)(1→2)-β-D-mannopyranoside (1). The protected tetrasaccharide (**14**) (20 mg) was dissolved in THF (5 mL) and *t*-butanol (200 μl). The solution was added in one portion to a solution of ammonia (~50 mL) and sodium metal (50 mg) at –78 °C. The flask previously containing (**14**) was rinsed with THF (5mL) and this solution was added to the ammonia solution. After 1 minute the reaction was quenched with methanol and the ammonia allowed to evaporate at room temperature. The remaining THF was removed under vacuum and the resulting white solid was taken up in water (5 mL). The suspension was loaded onto a Amberlite IRC 50 (NH_4^+) column (1.5 cm by 15 cm), washed with water (50 mL) and eluted with ammonium hydroxide (0.5 M). The fractions containing **1** were

concentrated and lyophilized to a white solid. Further purification by HPLC on a Hypersil (Hypercarb 5μ) column using a water (0.01% TFA)/Methanol gradient gave homogenous material (6 mg, 77%) $[\alpha]_D$ -53° (c 0.15,H_2O); ^{1}H NMR (600 MHz, D_2O) δ 5.03 (s, 1 H, H-1''), 4.93 (s, 1 H, H-1'''), 4.88 (s, 1 H, H-1'), 4.72 (s, 1 H, H-1), 4.39 (d, 1 H, $J_{2,3}$ 3.1 Hz, H-2''), 4.32 (d, 1 H, $J_{2,3}$ 3.3 Hz, H-2'), 4.24 (d, 1 H, $J_{2,3}$ 3.1 Hz, H-2), 4.15 (d, 1 H, $J_{2,3}$ 3.1 Hz, H-2'''), 3.99 (dt, 1 H, J_{gem} 10.1 Hz, J_{vic} 6.2, OC$\underline{H}_2$CH_2), 3.93 (d, 1 H, J_{gem} 12.3 Hz, H-6a'''), 3.93 (d, 1 H, J_{gem} 12.5 Hz, H-6a'), 3.92 (d, 1 H, J_{gem} 12.3 Hz, H-6a), 3.92 (d, 1 H, J_{gem} 12.3 Hz, H-6a''), 3.75 (d, 1 H, $J_{5,6}$ 6.2 Hz, H-6b''), 3.73 (d, 1 H, $J_{5,6}$ 6.7 Hz, H-6b), 3.73 (d, 1 H, $J_{5,6}$ 6.9 Hz, H-6b'''), 3.73 (dt, J_{vic}, 6.2 Hz, OC$\underline{H}_2$CH_2), 3.71 (d, 1 H, $J_{5,6}$ 5.7 Hz, H-6b'), 3.67 (dd, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 3.65 (dd, 1 H, $J_{3,4}$ 9.7 Hz, H-3'), 3.62 (dd, 1 H, $J_{3,4}$ 8.8 Hz, H-3''), 3.60 (dd, 1 H, $J_{3,4}$ 8.8 Hz, H-3'''), 3.59 (dd, 1 H, $J_{3,4}\approx J_{4,5}$ 9.8 Hz, H-4''), 3.56 (dd, 1 H, $J_{3,4}\approx J_{4,5}$ 9.5 Hz, H-4'''), 3.50 (dd, 1 H, $J_{3,4}\approx J_{4,5}$ 9.7 Hz, H-4'), 3.47 (dd, 1 H, $J_{3,4}\approx J_{4,5}$ 9.7 Hz, H-4), 3.39-3.34 (m, 4-H, H-5, H-5', H-5'', H-5'''), 3.24 (t, 2 H, J_{vic} 6.6 Hz, $CH_2NH_3^+$), 2.87 (t, 2 H, $SCH_2CH_2NH_3^+$), 2.69-2.67(m, 2 H, $OCH_2CH_2C\underline{H}_2S$), 1.94-1.91(m, 2H, $OCH_2C\underline{H}_2CH_2S$); ^{13}C NMR (125 MHz, D_2O) δ 101.9 ($^1J_{C\text{-}H}$ 163 Hz, C1''), 101.8 ($^1J_{C\text{-}H}$ 163 Hz, C1'''), 101.6 ($^1J_{C\text{-}H}$ 163 Hz, C1'), 100.8 ($^1J_{C\text{-}H}$ 160 Hz, C1''), 79.7 (C2''), 79.7 (C2'), 79.0 (C2), 77.1, 76.9, 76.9, 76.8 (C-5, C-5', C-5'', C5'''), 73.7 (C3'''), 73.0 (C3''), 72.6 (C3'), 72.6 (C3), 71.1 (C2'''), 69.1 (O$\underline{C}H_2CH_2$), 68.2 (C4), 67.8 (C4'), 67.6 (C4''), 67.5 (C4'''), 61.9, 61.5, 61.4, 61.3 (C6, C6', C6'', C6'''), 39.0($\underline{C}H_2NH_3^+$), 29.3 ($S\underline{C}H_2CH_2NH_3^+$), 28.9 ($OCH_2CH_2C\underline{H}_2S$), 28.2 ($OCH_2\underline{C}H_2$)