Supporting Information

Methyl 2,3,4,6-Tetra-S,O,O,O-acetyl-2-thio-α-D-mannopyranoside (2). A solution of 1.0 g (2.69 mmol) of methyl 4,6-O-benzylidene-2-3-di-S,O-acetyl-α-D-mannopyranoside **1** in 10 mL of methanol was treated with 3 drops of acetyl chloride and then stirred at room temperature for 1 h. The reaction was quenched with 2 mL of pyridine and concentrated to an oil. The crude diol was dissolved in 10 mL of pyridine and 2 mL of acetic anhydride (2 mL). After 30 min the reaction mixture was diluted with 50 mL of petroleum ether and washed with dilute 2 N hydrochloric acid (3 X 30 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated to an oil, which was chromatographed on silica with 2:100 methanol / dichloromethane as the eluant to afford 978 mg of **2** as an oil (98% yield): ^{1}H NMR ($CDCl_3$) δ 5.56 (dd, *J* = 4.7, 9.9, H-3), 5 .07 (t, J = 9.9, H-4), 4.75 (d, *J* = 1.3, H-1), 4.25 (dd, *J* = 1.5, 4.7, H-2), 4.21 (dd, *J* = 7.4, 12.3, H-6), 4.08 (dd, *J* = 2.4, 9.8, H-6'), 3.95 (ddd, J = 2.6, 4.9, 10.1, H-5), 3.39 (s, OC$\underline{H}_3$), 2.36 (s, SCOC$\underline{H}_3$), 2.10 (s, OCOC$\underline{H}_3$), 2.02 (s, OCOC$\underline{H}_3$), 1.95 (s, OCOC$\underline{H}_3$); ^{13}C NMR ($CDCl_3$) δ 193.8 (S-C=O), 171.07, 170.19, 170.01, 101.46 (C-1), 69.06, 67.40, 62.80, 55.85, 47.61, 30.97, 21.15; IR (film) 1747 and 1702 (S-C=O) cm^{-1}.

Phenyl 2,3,4,6-Tetra-S,O,O,O-acetyl-1,2-dithio-α-D-mannopyranoside (3). Borontrifluoride etherate (50 μl, 0.40 mmol) was added to a solution of 42 mg (0.114 mmol) of methyl 2,3,4,6-tetra-S,O,O,O-acetyl-2-thio-α-D-mannopyranoside (**2**) in 0.3 mL of dichloromethane and 0.45 mL of thiophenol at room temperature. The resulting solution was stirred for 1.5 days. The reaction mixture was concentrated and then directly chromatographed on silica with 1:100 ethylacetate / dichloromethane as the

eluant to remove a higher R_f impurity. Rechromatography of the material with R_f ~0.1 - 0.2 (previous eluant) on silica with 300:1 dichloromethane / methanol as the eluant afforded 26 mg of **3** (50% yield) as an oil. Crystallization of a portion from toluene / petroleum ether gave a white solid, mp 103-104 ºC: ^{1}H NMR ($CDCl_3$) δ 7.52-7.47 (m, two *o*-Ar-H's), 7.32-7.26 (m, three *m* - and *p*-Ar-H's), 5.34 (dd, *J* = 4.6, 9.7, H-3), 5.52 (s, H-1), 5.13 (t, *J* = 9.9, H-4), 4.58 (ddd, *J* = 2.6, 5.2, 9.9, H-5), 4.51 (dd, *J* = 1.3, 4.5, H-2), 4.25 (dd, *J* = 5.1, 12.1, H-6), 4.09 (dd, *J* = 2.2, 12.3, H-6'), 2.37 (s, SCOC$\underline{H}_3$), 2.08 (s, OCOC$\underline{H}_3$), 2.07 (s, SCOC$\underline{H}_3$), 1.99 (s, SCOC$\underline{H}_3$); ^{13}C NMR ($CDCl_3$) δ 193.71 (S-C=O), 170.97, 170.12,170.02, 133.6, 132.63, 129.55, 128.55, 88.23 (J_{C-H} = 173), 70.21, 69.68, 67.61, 62.79, 49.08, 30.95, 21.11; IR (film) 1752, 1701 (S-C=O) cm^{-1}; FAB-MS m/z 463 (MLi^+); Anal. Calcd for $C_{20}H_{24}O_8S_2$: C, 52.62; H, 5.30; S, 14.04; Found: C, 52.18; H, 5.27; S, 13.94.

Oligomerization of 3. Sodium methoxide (0.75ml, 1.07 mmol) was added to a solution of 220 mg (0.484 mmol) of phenyl 2,3,4,6-tetra-S,O,O,O-acetyl-1,2-dithio-α-D-mannopyranoside (**3**) in 5 mL of methanol. After 80 min the reaction mixture was neutralised with Dowex H^+ resin, filtered, and then concentrated to an oil. The crude product was chromatographed on Iatrobeads with 1:16, 1:8, 1:6 and finally 1:5 methanol / dichloromethane as the eluant to afford 10 mg of phenyl 1,2-dithio-α-D-mannopyranoside **6** (7% yield, positive iodine/sodium azide test for mercaptan), 33 mg of thiomannobioside **7** (30% yield), 24 mg of thiomannotrioside **8** (23% yield) and 21 mg of thiomannotetroside **9** (12% yield), respectively: ^{1}H NMR (CD_3OD) of **6** δ 7.55-7.50 (m, two *o*-Ar-H's), 7.35-7.28 (m, three *m* - and *p*-Ar-H's), 5.55 (s, H-1), 4.11 - 4.04 (m, H-5), 4.01 (dd, *J* = 4.5, 10.9, H-3), 3.82-3.72 (m, 3H), 3.60 (dd, *J* = 2.9, 1.5, H-2);); ^{13}C NMR

(CD_3OD) of **6** 136.2, 133.4, 130.4, 129.0, 91.6 (C-1), 76.5, 72.0, 68.7, 62.6 (C-2 obscured by MeOH-d_3); δ IR of **6** 3432, 2527 (SH) cm^{-1}; FAB-MS of **6** (as disulfide) m/z 597 ($MMNa-2H^+$); ^1H NMR (CD_3OD) of **7** δ 7.56-7.50 (m, two *o*-Ar-H's), 7.35-7.28 (m, three *m* - and*p*-Ar-H's), 5.64 (s, H-1), 5.60 (s, H-1'), 4.15 - 4.04 (m, 2H), 3.94 - 3.84 (m, 2H), 3.79 - 3.49 (m, 7H), 3.35-3.31 (m, 1H); ^{13}C NMR (CD_3OD) of **7** δ 136.27, 133.54, 130.37, 128.95, 91.21 (J_{C-H} = 170.5), 89.58 (J_{C-H} = 169), 76.37, 76.15, 72.34, 71.86, 70.13, 68.70, 62.87, 62.49, 55.95; IR (film) of **7** 3384, 2562 (SH) cm^{-1}; FAB-MS of **7** m/z 473 (MLi^+), 489 $(M+23)^+$; ^1H NMR (CD_3OD) of **8** δ 7.55-7.50 (m, two *o*-Ar-H's), 7.34-7.26 (m, three *m* - and *p*-Ar-H's), 5.73 (s, H-1), 5.64 (S, H-1'), 5.55 (s, H-1''), 4.14-3.86 (m, 6H), 3.83-3.32 (m, 12H); ^{13}C NMR (CD_3OD) of **8** δ 136.24, 133.48, 130.34, 128.87, 91.15, 89.24, 89.15, 76.33, 76.25, 75.99, 72.85, 72.53, 71.84, 70.22, 70.03, 69.19, 63.15, 62.87, 62.78, 55.94, 55.57; FAB-MS of **8** m/z 651 (MLi^+), 667 (MNa^+); IR (film) of **8** 3377, 2565 cm^{-1}; ^1H NMR (CD_3OD) of **9** δ 7.55-7.50 (m, two *o*-Ar-H's), 7.32-7.27 (m, three *m*- and *p*-Ar-H's), 5.74 (s, H-1), 5.72 (s, H-1'), 5.64 (s, H-1''), 5.55 (s, H-1'''), 4.1-3.84 (m, 10H), 3.78-3.35 (m, 14H); ^{13}C NMR (CD_3OD) of **9** δ 136.23, 133.48. 130.34, 128.89, 91.12, 89.28, 89.04, 88.74, 76.34, 76.22, 75.98, 72.89, 72.53, 71.84, 70.59, 70.11, 69.99, 69.24, 63.34, 63.18, 62.84, 55.93, 55.78; FAB-MS of **9** m/z 845 (MNa^+).

Per-acetylation of disaccharide 7. A solution of 8 mg (0.017 mmol) of disaccharide **7** in 2 mL of pyridine was treated with 0.5 mL of acetic anhydride. After 1 h, the reaction mixture was washed with 1N hydrochloric acid (3 X 15 mL) and water (15 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated to a residue. The crude product was chromatographed on silica with 1:50 methanol / dichloromethane as the eluant to afford 6 mg of the peracetate (46%): ^1H NMR ($CDCl_3$)

δ 7.5-7.43 (m, two *o*-Ar-H's), 7.38-7.28 (m, three *m*- and *p*-Ar-H's), 5.67 (s, H-1) 5.50-5.30 (m, H-4, H-4', H-1', H-3), 5.05 (t, *J* = 9.8, H-3'), 4.51 (ddd, *J* = 2.5, 5.1, 9.1, H-5), 4.41-4.81 (m, H-5', H-2), 4.27 (dd, *J* = 5.3, 12.4, H-6), 4.18 (dd, *J* = 5.9, 12.1, H-6'), 4.10 (dd, *J* = 9.7, 2.7, H-6''), 3.99 (dd, *J* = 12.2, 2.3, H-6'''), 3.84 (dd, *J* = 1.8, 4.4, H-2'), 2.38 (s, SCOC$\underline{H}_3$), 2.09, 2.08, 2.08, 2.05, 2.00, 1.97 (six s, OCOC$\underline{H}_3$); ^{13}C NMR ($CDCl_3$) δ 194.97 (S$\underline{C}$=O), 172.65, 171.96, 171.52 (three O$\underline{C}$=O, three hidden), 135.11, 133.60, 131.24, 129.97 (four Ar-C's), 89.49 (C-1'), 86.92 (C-1), 72.73, 71.85, 71.77, 70.77, 68.86, 64.28, 64.13, 52.12 and 50.13 (C-2 and C-2'), 32.53 (SCO$\underline{C}H_3$), 22.73 and 22.58 (two OCO$\underline{C}H_3$, four hidden); IR (film) 1747, 1697 (S-C=O) cm^{-1}.

Phenyl 2,3,4,6-Tetra-O,O,O,S-acetyl-1,6-dithio-α-D-mannopyranoside (11). A solution of 5 g (13 mmol) of mannose pentaacetate (**10**) in 1.8 mL (0.014 mol) of borontrifluoride etherate and 15 mL of thiophenol was stirred overnight. The reaction mixture was chromatographed on silica with 0.8:1 ether / petroleum ether as the eluant to afford 5.2 g of phenyl 2,3,4,6-tetra-O-acetyl-1-thio-α-D-mannopyranoside (92%) as an oil: ^{1}H NMR ($CDCl_3$) δ 7.52-7.47 (m, two *o*-Ar-H's), 7.25-7.35 (m, three *m*- and *p*-Ar-H's), 5.5 (app s, H-1, H-2), 5.28-5.38 (m, H-3, H-4), 4.55 (ddd, *J* = 2.6, 5.2, 10, H-5), 4.32 (dd, *J* = 6, 12, H-6) 4.12 (dd, *J* = 2.6, 12, H-6'), 2.16, 2.10, 2.06, 2.03 (four s, OCOC$\underline{H}_3$); ^{13}C NMR ($CDCl_3$) δ 172.40, 171.79, 171.71, 171.64, 134.55, 134.01, 131.14, 131.06, 87.60, 72.83, 71.48, 71.33, 68.32, 64.38, 22.80, 22.64, 22.58; IR (film) 1750 cm^{-1}.

A suspension of 152 mg (0.34 mmol) of the phenyl 1-thiomannoside in methanol was stirred with few drops of sodium methoxide at room temperature for 30 min. The

reaction was quenched with Dowex acid resin and filtered. The filtrate was concentrated to a residue and dried. The crude product was dissolved in 1 mL of pyridine, treated with 96 mg (0.47 mmol) of*p*-toluenesulfonyl chloride, and then stirred overnight. The reaction mixture was treated with a few drops of acetic anhydride. After 30 min the reaction mixture was concentrated to residue and dissolved in 25 mL of dichloromethane. The resulting solution was washed with water (20 mL), aqueous hydrochloric acid (2 x 20 mL) and water (20 mL) again. The organic layer was dried over anhydrous sodium sulfate and concentrated to a residue. The crude product was chromatographed on silica with 66:1 dichloromethane / ether as the eluant to afford 127 mg of phenyl 6-O-*p*-toluenesulfonyl-2,3,4-tri-O-acetyl-1-thio-α-D-mannopyranoside (66%): ^{1}H NMR ($CDCl_3$) δ 7.73 (d, *J* = 8.3, two Ar-H), 7.42-7.48 (m, two Ar-H), 7.27-7.32 (m, five Ar-H), 5.43-5.46 (m, H-2), 5.35 (d, *J* = 1.5, H-1), 5.17-5.29 (m, H-3, H-4), 4.55 (ddd, *J* = 1.3, 4.5, 5.9, H-5), 4.14 (d, *J* = 4.4, H-6, H-6'), 2.43 (s, Ar-$\underline{CH_3}$), 2.12 , 2.01, 1.99 (three s, OCO$\underline{CH_3}$); ^{13}C NMR ($CDCl_3$) 170.37, 170.25, 170.18, 145.44, 133.1, 130.37, 129.72, 128.55, 124.74, 86.34, 71.29, 69.77, 68.34, 66.34, 22.13, 21.33, 21.18.

A solution of 111 mg (0.195 mmol) of of phenyl 6-O-*p*-toluenesulfonyl-2,3,4-tri-O-acetyl-1-thio-α-D-mannopyranoside in 2 mL of acetone was treated with 180 mg (1.58 mmol) of potassium thiolacetate, and the resulting suspension was heated at reflux for 3 h. The reaction mixture was concentrated to residue and dissolved in 20 mL of dichloromethane, which was washed with water (3 x 15 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated to a residue, which was chromatographed with 1:3.2 ether / petroleum ether as the yield to afford 62 mg of phenyl

2,3,4,6-tetra-O,O,O,S-acetyl-1,6-dithio-α-D-mannopyranoside, **11** (70%): ^{1}H NMR ($CDCl_3$) δ 7.47-7.52 (m, two Ar-H), 7.26-7.35 (m, three Ar-H), 5.47 (br s, H-2), 5.43 (br s, H-1), 5.25-5.28 (m, H-3, H-4), 4.34-4.46 (m, H-5), 3.25 (dd, *J* = 2.9, 14.2, H-6), 3.07 (dd, *J* = 14.1, 7.5, H-6) 2.31 (s, SCOC$\underline{H}_3$), 2.15 , 2.12, 2.01 (three s, OCOC$\underline{H}_3$); ^{13}C NMR ($CDCl_3$) δ 195.19, 170.54, 170.41, 170.41, 170.31, 132.55, 129.62, 129.55, 128.48, 86.21, 71.51, 71.34, 69.77, 69.14, 30.89, 30.70, 21.38, 21.30, 21.13; IR (film) 1751 (O-C=O), 1696 (S-C=O) cm^{-1} ; FAB-MS m/z 463 (MLi^+).

Pseudo-trisaccharide 12. Methanolic solutions of **3** (20 mg, 0.043 mmol), **11** (50 mg, 0.11 mmol) and sodium methoxide (260 μl of 1.29N solution, 0.34 mmol) were degassed in vacuo at -78°C. The sodium methoxide solution was added to the solution of **11** and, after 20 min, the resulting solution was added to the solution of **3**. After 2 days the reaction was quenched with Dowex acid resin and concentrated to a residue. The crude product was chromatographed on Iatrobeads with 100:6, 100:10, and then 100:15 dichloromethane / methanol as the eluant to give 7 mg (41%) of the phenylthio-disulfide **13**, 10 mg (23%) of the symmetrical 6-thiomannose disulfide **14**, and 5 mg (23%) of the pseudo-trisaccharide **12** (yield based on **3**): ^{1}H NMR (CD_3OD) of **13** δ 7.47–7.68 (m, four Ar-H's), 7.15-7.40 (m, six Ar-H's), 5.42 (d, *J* = 1.4, H-1), 4.26 (td, *J* = 9, 2, H-5), 4.10 (dd, *J* = 1.4, 2.8, H-2), 3.65 (dd, *J* = 9, 2.8, H-3), 3.55 (t, *J* = 9, H-4), 3.29 (dd, *J* = 14.6, 2, H-6), 2.97 (dd, overlapped with MeOH-d_3, *J* = 14.2, 9, H-6); ^{1}H NMR (CD_3OD) of **14** δ 7.48–7.62 (m, two Ar-H's), 7.19-7.40 (m, three Ar-H's), 5.39 (br s, H-1), 4.27 (br t, *J* = 7.9, H-5), 4.10 (br s, H-2), 3.68 (dd, *J* = 9.5, 1.2, H-3), 3.62 (app t, *J* = 9.5, H-4), 3.32 (app dd, overlapped with MeOH-d_3, *J* = 13.7, 2, H-6), 2.88 (dd, *J* = 9.0, 13.7, H-6);

^{13}C NMR (CD_3OD) of **14** δ 136.10, 133.37, 130.31, 128.79, 90.78, 74.03, 73.67, 73.32, 72.0, 42.26; FAB-MS of **14** m/z 581 (MLi^+). ^1H NMR of **12** (CD_3OD) δ 7.5-7.6 (m, four Ar-H's), 7.23-7.47 (m, six Ar- H's), 5.78 (d, *J* = 2.5, H-1'), 5.45 and 5.43 (two d, *J* = 2.5, H-1, H-1''), 4.12-4.28 (m, H-5, H-5', H-5''), 4.02-4.12 (m, 4H), 3.85-3.95 (m, 2H), 3.6-3.8 (m, 5H), 3.15-3.22 (dd, *J* = 14, 4, one H-6), 3.75-3.91 (m, two H-6); ^{13}C NMR of **12** (CD_3OD) δ 136.2, 136.3, 133.42, 133.05, 130.41, 130.33, 128.81, 90.88 and 90.66 (C-1, C-1''), 84.69 (C-1'), 75.75, 74.19, 74.02, 73.89, 73.30, 72.63, 71.97, 71.53, 69.54, 62.87 and 61.77 (C-2', C-6'), 43.06 (C-6''), 33.94 (C-6); FAB-MS of **12** m/z 774 (MNa^+).

Glycopeptide 16. Methanolic solutions of **3** (27 mg, 0.059 mmol), N-(*tert*-butoxylcarbonyl)-D-serine methyl ester **15** (17 mg, 0.072 mmol, available from Aldrich) and sodium methoxide (16 μL of 1.29N solution, 0.189 mmol) were deoxygenated in vacuo at -78°C. The sodium methoxide solution was added to the solution of **3** and **15**. After 1 day the reaction was qunched with acid resin and concentrated to a residue. The crude product was chromatographed on silica with 7:100 methanol / dichloromethane as the eluant to afford 6 mg of the glycopeptide **16** (25%): ^1H NMR (CD_3OD) δ 7.08 (d, *J* = 6, N-H), 5.42 (br s, H-1), 4.35-4.45 (m, H-α), 3.68-3.95 (m, 5H and OCH_3), 3.43 (br d, *J* = 4, H-2), 3.08 (d, *J* = 5, H-β); ^{13}C NMR (CD_3OD) δ 89.08 (C-1), 76.19, 71.87, 68.57, 62.56 (C-6), 55.96 (C-α), 53.11 (OCH_3), 51.07 (C-2), 35.15 (SCH_2), 28.97 (*t*-Bu); FAB-MS m/z 414 (MH^+); IR (film) 3371 (OH), 1740 (O=C-OCH_3), 1688 (OC=O-N) cm^{-1} (SH and NH not observed).