Supporting Information:

Lactone **5**. To a solution of methoxy acetal **1** (40 mg, 0.123 mmol) and 1,3-propanedithiol (16 µL, 0.16 mmol) was added $BF_3{\cdot}Et_2O$ (17 µL, 0.135 mmol) in MeCN (1.2 mL) at 0 °C. The solution was stirred 0.5 h at this temperature and then diluted with MTB ether. After addition of $NaHCO_3$ and sat. aq. $NaHCO_3$ at 0 °C the aqueous phase was separated, carefully neutralized with conc. HCl solution and extracted with MTBE, until no product was detectable in the aqueous layer (tlc). The combined organic layers were washed with brine, dried (Na_2SO_4:Na_2CO_3 = 2:1) and evaporated. The crude product was diluted in CH_2Cl_2 and PPTS (15 mg, 0.061 mmol) was added. The mixture was stirred 1 h at room temperature and neutralized with Et_3N. Flash chromatography (SiO_2, MTBE) afforded the lactone **5** (24 mg, 80%) as a clear oil. $[\alpha]_D^{20}$ = -2.6° (c 0.1, $CHCl_3$); IR ($CHCl_3$) ν 3682, 3608, 3501, 2979, 2907, 1734, 1514, 1424, 1366, 1230, 1174, 1078, 930 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.59 (m, 1 H, CO_2CH), 4.37-4.26 (s, 2 H, SC*H*S and C*H*OH), 2.98-2.80 (m, 5 H, $SCH_2CH_2CH_2S$ and CH_2CO_2), 2.50 (dd, ^2J = 17.2 Hz, ^3J = 7.5 Hz, 1 H, CH_2CO_2), 2.32-2.25 (m, 1 H, $CHCH_2CH(OH)$), 2.23-2.03 (m, 3 H, $SCHSCH_2CH$ and $SCH_2CH_2CH_2S$ and O*H*), 1.91-1.76 (m, 2 H, $SCHSCH_2CH$ and $SCH_2CH_2CH_2S$), 1.68-1.57 (m, 1 H, $CHCH_2CH(OH)$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.49 (4°, CO_2), 73.26 (3°, CO_2CH), 63.57 (3°, *C*HOH), 42.64 (3°, SCHS), 41.25 (4°, $C(CH_3)_2$), 39.41 (2°, CH_2CO_2), 37.74 (2°, $CHCH_2CH(OH)$), 30.74/29.77 (2°, $SCH_2CH_2CH_2S$), 25.83 (2°, $SCH_2CH_2CH_2S$); MS (140 °C) *m/z* 248 (M^+, 40), 230 (2), 197 (2), 183 (2), 171 (2), 159 (19), 145 (16), 133 (26), 123 (5), 119 (100), 106 (11), 97 (11), 73 (24); HRMS calcd for $C_{10}H_{16}O_3S_2$ (M^+) 248.0541, found 248.0543.

Triol **7**. To a solution of methoxy acetal **1** (100 mg, 0.31 mmol) in THF (2.5 mL) at 0 °C $LiAlH_4$ (0.37 mL, 0.37 mmol, 1.0 M solution in THF) slowly was added and stirrred for 1 h at ambient temperature. The mixture was cooled to 0 °C and quenched as follows: Addition of (i) 50 µL EtOAc, (ii) 20 µl H_2O , 20 µl 2 N aqueous NaOH solution and (iv) 50 µl H_2O. The precipitate formed was removed by filtration. The filtrate was dried (Na_2SO_4: Na_2CO_3 = 1:1), concentrated *in vacuo* and the crude product was purified by column chromatography (SiO_2, MTBE) to leave alkohol **6** (91 mg, 99%) as a colourless oil.

To a solution of methoxy acetal **1** (66 mg, 0.22 mmol) and 1,3-propanedithiol (29 µL, 0.27 mmol) was added $BF_3{\cdot}Et_2O$ (123 µL, 1.0 mmol) in MeCN (2.2 mL) at -20 °C. The solution was warmed up to room temperature and stirred for 2.5 h and then diluted with EtOAc. After addition of $NaHCO_3$ and sat. aq. $NaHCO_3$ at 0 °C the aqueous phase was separated, carefully neutralized with conc. HCl solution, saturated with NaCl and extracted with EtOAc, until no product was detectable in the aqueous layer (tlc). The combined organic layers were dried (Na_2SO_4:Na_2CO_3 = 2:1) and evaporated. Flash chromatography (SiO_2, MTBE → MTBE:MeOH = 8:1) afforded the triol **7** (40 mg, 71%) as a clear oil. $[\alpha]_D^{20}$ = -0.8° (c 0.05, $CHCl_3$); IR ($CHCl_3$) ν 3618, 3452, 2999, 2942, 1425, 1331, 1277, 1242, 1073, 908 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.30-4.14 (m, 3 H, SC*H*S and C*H*OHCH$_2$C*H*-OH), 3.91-3.24 (m, 5 H, CH_2OH u. O*H* (3×)), 2.98-2.78 (m, 4 H, $SCH_2CH_2CH_2S$), 2.17-2.08 (m, 1 H, SCH_2CH_2-CH_2S), 2.02-1.56 (m, 7 H, $SCH_2CH_2CH_2S$ and CH_2CH-$(OH)CH_2CH(OH)CH_2CH_2OH$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.37 (3°, $SCHSCH_2CHOH$), 65.74 (3°, *C*HOH-CH_2CH_2OH), 61.08 (2°, CH_2OH), 44.10 (3°, SCHS), 43.22/42.87/38.57 (2°, $CH_2CH(OH)CH_2CH(OH)CH_2CH_2$-OH), 30.33/30.03 (2°, $SCH_2CH_2CH_2S$), 25.93 (2°, SCH_2-CH_2CH_2S); MS (140 °C) *m/z* 252 (M^+, 3), 234 (37), 207 (3), 189 (3), 171 (3), 159 (20), 145 (12), 133 (22), 127 (25), 119 (100), 109 (11), 106 (14), 101 (13), 83 (9), 73 (24); HRMS calcd for $C_{10}H_{20}O_3S_2$ (M^+) 252.0854, found 252.0855.

α,β-Unsaturated ester **8**. To a solution of ester **1** (1.35 g, 4.16 mmol) in CH_2Cl_2 (30 mL) was added DIBAH (6.2 mL, 6.2 mmol, 1.0 M solution in hexane) dropwise at -78 °C and stirred 0.5 h. At this temperature a solution of Ph_3PCHCO_2Me (4.86 g, 13.56 mmol) in CH_2Cl_2 (12 mL) was added and the solution warmed up to ambient temperature. After 16 h the mixture was concentrated *in vacuo* and purified by column chromatography (SiO_2, MTBE:PE = 1:1 → 3:1) to yield ester **8** (1.06 g, 73%, (α : β ≅ 8 : 1) as a colourless oil. $[\alpha]_D^{20}$ = -28.3° (c 0.5, $CHCl_3$); IR ($CHCl_3$) ν 2999, 2951, 2938, 1718, 1660, 1613, 1514, 1438, 1249, 1175, 1122, 1042, 984 cm^{-1}; Data for the α-anomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.28-7.21 (m, 2 H, Ar-*H*), 6.98 (dt, ^3J = 15.7 Hz, ^3J = 7.4 Hz, 1 H, $CHCHCO_2CH_3$), 6.89-6.84 (m, 2 H, Ar-*H*), 5.90 (d, ^3J = 15.7 Hz, 1 H, $CHCHCO_2CH_3$), 4.83 (d, ^3J = 3.1 Hz, 1 H, CH_3OCH), 4.46 (s, 2 H, CH_2Ar), 3.91-3.76 (m, 5 H, CH_3OAr and C*H*OAr and $CHCH_2CHCH$), 3.73 (s, 3 H, CO_2CH_3), 3.30 (s, 3 H, CH_3OCH), 2.49-2.32 (m, 2 H, $CHCH_2CHCH$), 2.20-2.13 (m, 1 H, CH_3OCHCH_2-eq), 2.07-2.00 (m, 1 H, CH_2CHCH_2CHCH-eq), 1.58-1.48 (m, 1 H, CH_3OCHCH_2-ax), 1.30 (q, $^{2/3}J$ = 11.8 Hz, CH_2CH-CH_2CHCH-ax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.73 (4°, CO_2CH_3), 159.18 (4°, Ar-*C*), 145.05 (3°, $CHCHCO_2CH_3$), 130.68 (4°, Ar-*C*), 129.15 (3°, m-Ar-*C*), 123.23 (3°, CH-$CHCO_2CH_3$), 113.85 (3°, o-Ar-*C*), 99.29 (3°, CH_3OCH), 70.38 (3°, *C*HOAr), 69.62 (2°, CH_2Ar), 66.53 (3°, $CHCH_2$-CHCH), 55.28 (1°, CH_3OCH), 54.72 (1°, CH_3OAr), 51.44 (1°, CO_2CH_3), 38.64 (2°, $CHCH_2CHCH$), 37.72/36.36 (2°, CH_3OCHCH_2 u. CH_2CHCH_2CHCH); MS (100 °C) *m/z* 350 (M^+, 1), 318 (2), 300 (1), 280 (1), 251 (1), 228 (1), 198 (1), 181 (3), 150 (7), 137 (20), 121 (100), 97 (6), 91 (3), 85 (4), 81 (6), 77 (4); HRMS calcd for $C_{18}H_{22}O_5$ (M^+-CH_3OH) 318.1467, found 318.1467.

Diol **9**. To a solution of methoxy acetal **8** (1.08 g, 3.08 mmol) and 1,3-propanedithiol (400 µL, 4 mmol) was added $BF_3{\cdot}Et_2O$ (495 µL, 4 mmol) in MeCN (16 mL) at 0 °C. The solution was warmed up to room temperature, stirred for 0.5 h and then diluted with MTB ether. After addition of $NaHCO_3$ and sat. aq. $NaHCO_3$ at 0 °C the aqueous phase was separated, carefully neutralized with conc. HCl solution and extracted with MTB ether (5 ×).

The combined organic layers were washed with brine, dried (Na_2SO_4) and evaporated. Flash chromatography (SiO_2, MTB:PE = 3:1) afforded the lactone **9** (660 mg, 70%) as a clear oil. $[\alpha]_D^{20}$ = -7.2° (c 1, $CHCl_3$); IR ($CHCl_3$) ν 3688, 3609, 3502, 2999, 2950, 2907, 1717, 1660, 1437, 1279, 1230, 1173, 1042 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.97 (dt, ^3J = 15.7 Hz, ^3J = 7.4 Hz, 1 H, C*H*CHCO$_2$CH$_3$), 5.95-5.87 (m, 1 H, CHC*H*CO$_2$CH$_3$), 4.29-4.21 (m, 2 H, C*H*(OH)CH$_2$CHCH and SC*H*S), 4.10 (qui, ^3J = 6.2 Hz, 1 H, SCHSCH$_2$C*H*OH), 3.73 (s, 3 H, OC*H*$_3$), 3.52-3.25 (bs, 1 H, O*H*), 2.96-2.80 (m, 4 H, SC*H*$_2$CH$_2$C*H*$_2$S), 2.49-2.35 (m, 2 H, C*H*$_2$CHCH), 2.11-2.08 (m, 1 H, SCH$_2$C*H*$_2$CH$_2$S), 2.03 (m, 3 H, SCH$_2$C*H*$_2$CH$_2$S and C(OH)C*H*$_2$CH(OH) u. O*H*), 1.66 (m, 2 H, SCHSC*H*$_2$CHOH), 1.51-1.39 (m, 1 H, C(OH)C*H*$_2$CH(OH)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.90 (4°, *C*O$_2$CH$_3$), 145.51 (3°, *C*HCHCO$_2$CH$_3$), 123.40 (3°, CH*C*HCO$_2$CH$_3$), 67.54/65.84 (3°, *C*H(OH)CH$_2$*C*H-(OH)), 51.55 (1°, O*C*H$_3$), 44.08 (3°, S*C*HS), 42.64/42.54 (2°, *C*H$_2$CH(OH)*C*H$_2$*C*H(OH)), 40.30 (2°, *C*H$_2$CHCH), 30.24/29.99 (2°, S*C*H$_2$CH$_2$*C*H$_2$S), 25.87 (2°, SCH$_2$*C*H$_2$-CH$_2$S); MS (130 °C) *m/z* 306 (M^+, 8), 288 (8), 257 (5), 228 (5), 207 (16), 189 (18), 167 (15), 159 (13), 145 (14), 133 (33), 119 (100), 106 (16), 101 (24), 97 (20), 81 (31); HRMS calcd for $C_{13}H_{22}O_4S_2$ (M^+) 306.0960, found 306.0962.

Alcohol ***trans*-10**. To a mixture of NaH (5.7 mg, 0.143 mmol, 60% in paraffin) in THF (0.3 mL) a solution of **9** (20 mg, 0.065 mmol) in THF (0.3 mL) was added dropwise at -78 °C. The mixture was warmed up to 0 °C over 2.5 h and quenched with 2 N HCl/MeOH (1/2, 1 mL). After dilution with MTB ether and water, the phases were separated and the aqueous layer was extracted with MTB ether (3 ×). The combined organic layers were washed with brine, dried (Na_2SO_4), concentrated *in vacuo* and purified by flash chromatography (SiO_2, MTB:PE = 3:1) to afford *C*-glycosides ***trans*-10** and ***cis*-10** (15.5 mg, 78%, 81:19) as a clear oil. $[\alpha]_D^{20}$ = -10.3° (c 0.3, $CHCl_3$); IR (neat) ν 3612, 2940, 1733, 1511, 1434, 1366, 1306, 1273, 1172, 1082, 1025, 909 cm^{-1}; Data for the *C*-glycoside ***trans*-10**: ^1H NMR (400 MHz, $CDCl_3$) δ 4.58-4.50 (m, 1 H, C*H*CH$_2$CO$_2$CH$_3$), 4.19 (dd, ^3J = 10.2 Hz, ^3J = 3.1 Hz, 1 H, SC*H*S), 4.08-3.99 (m, 1 H, SCHSCH$_2$C*H*), 3.97-3.90 (m, 1 H, C*H*OH), 3.71 (s, 3 H, OC*H*$_3$), 2.94-2.80 (m, H, SC*H*$_2$CH$_2$C*H*$_2$S), 2.75 (dd, ^2J = 15.1 Hz, ^3J = 8.4 Hz, 1 H, C*H*$_2$CO$_2$CH$_3$), 2.50 (dd, ^2J = 15.1 Hz, ^3J = 6.4 Hz, 1 H, C*H*$_2$CO$_2$CH$_3$), 2.18-2.05 (m, 2 H, SCH$_2$C*H*$_2$CH$_2$S and SCHSC*H*$_2$CH), 1.99-1.77 (m, 5 H, SCH$_2$C*H*$_2$CH$_2$S and C*H*$_2$CH(OH)C*H*$_2$ and O*H*), 1.72-1.63 (m, 1 H, SCHS-C*H*$_2$CH), 1.36-1.25 (m, 1 H, C*H*$_2$CHCH$_2$CO$_2$CH$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.46 (4°, *C*O$_2$CH$_3$), 68.06 (3°, SCHSCH$_2$*C*H), 66.07 (3°, *C*HOH), 64.13 (3°, *C*HCH$_2$CO$_2$CH$_3$), 51.74 (1°, O*C*H$_3$), 43.40 (3°, S*C*HS), 41.01 (2°, *C*H$_2$CO$_2$CH$_3$), 39.81/37.67/37.55 (2°, *C*H$_2$CH-(OH)*C*H$_2$ and SCHSC*H*$_2$CH), 30.25/29.79 (2°, S*C*H$_2$-CH$_2$*C*H$_2$S), 26.08 (2°, SCH$_2$*C*H$_2$CH$_2$S); MS (70 °C) *m/z* 306 (M^+, 2), 121 (1), 119 (2), 106 (4), 97 (1), 88 (3), 86 (21), 84 (32), 81 (2), 74 (4), 73 (100), 71 (1); HRMS calcd for $C_{13}H_{22}O_4S_2$ (M^+) 306.0960, found 306.0959. The relative configuration of alcohol ***trans*-10** was confirmed by spectroscopic comparison with related 2,6-*trans*-*C*-glycosides (reference 11f) and *C*-glycoside ***cis*-10**. NOE experiments were not possible because of the complex multiplicities in combination with the chemical shifts.

Alcohol ***cis*-10**. To a mixture of NaH (10.4 mg, 0.261 mmol, 60% in parrafine) in THF (1 mL) a solution of **9** (80 mg, 0.261 mmol) in THF (2 mL) was added dropwise at -40 °C. The mixture was warmed up to room temperature over 1 h, stirred 7 h and quenched with 2 N HCl/MeOH (1/2, 2 mL). After dilution with MTB ether and water, the phases were separated and the aqueous layer was extracted with MTB ether (3 ×). The combined organic layers were washed with brine, dried (Na_2SO_4), concentrated *in vacuo* and purified by flash chromatography (SiO_2, MTB:PE = 3:1) to afford *C*-glycosides ***trans*-10** and ***cis*-10** (49 mg, 61%, 2:98) as a clear oil. $[\alpha]_D^{20}$ = -0.6° (c 0.1, $CHCl_3$); IR (neat) ν 3400, 2941, 2914, 1734, 1512, 1435, 1373, 1311, 1273, 1198, 1145, 1079, 1029, 909 cm^{-1}; Data for the *C*-glycoside ***cis*-10**: ^1H NMR (400 MHz, $CDCl_3$) δ 4.18 (dd, ^3J = 9.9 Hz, ^3J = 4.8 Hz, 1 H, SC*H*S), 3.91-3.82 (m, 1 H, C*H*OH), 3.81-3.74 (m, 1 H, SCHSCH$_2$C*H*), 3.70 (s, 3 H, OC*H*$_3$), 3.68-3.60 (m, 1 H, C*H*CH$_2$CO$_2$CH$_3$), 2.92-2.80 (m, H, SC*H*$_2$CH$_2$C*H*$_2$S), 2.62 (dd, ^2J = 15.0 Hz, ^3J = 7.6 Hz, 1 H, C*H*$_2$CO$_2$CH$_3$), 2.45 (dd, ^2J = 15.0 Hz, ^3J = 5.6 Hz, 1 H, C*H*$_2$CO$_2$CH$_3$), 2.15-2.06 (m, 1 H, SCH$_2$C*H*$_2$CH$_2$S), 2.05-1.77 (m, 5 H, SCH$_2$C*H*$_2$CH$_2$S and C*H*$_2$CH(OH)C*H*$_2$ and SCHSC*H*$_2$CH), 1.70-1.60 (bs, 1 H, O*H*), 1.24-1.13 (m, 2 H, C*H*$_2$CH(OH)C*H*$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.37 (4°, *C*O$_2$CH$_3$), 72.11/71.73 (3°, SCHSCH$_2$*C*H u. *C*HCH$_2$CO$_2$CH$_3$), 67.66 (3°, *C*HOH), 51.67 (1°, O*C*H$_3$), 43.41 (3°, S*C*HS), 41.45 (2°, *C*H$_2$CO$_2$CH$_3$), 40.98/40.71/ 40.56 (2°, *C*H$_2$CH(OH)*C*H$_2$ and SCHSC*H*$_2$CH), 30.24/ 29.85 (2°, S*C*H$_2$CH$_2$*C*H$_2$S), 26.01 (2°, SCH$_2$*C*H$_2$CH$_2$S); MS (120 °C) *m/z* 306 (M^+, 100), 275 (7), 199 (17), 181 (30), 159 (29), 145 (25), 141 (13), 133 (14), 123 (9), 119 (87), 113 (6), 107 (9), 97 (12), 84 (21), 81 (38), 73 (36); HRMS calcd for $C_{13}H_{22}O_4S_2$ (M^+) 306.0960, found 306.0960. The relative stereochemistry of alcohol ***cis*-10** was confirmed by a NOE experiment: Irradiation of the proton at the new stereogenic centre (3.68-3.60 ppm, C*H*CH$_2$CO$_2$CH$_3$) led to enhancement of the signals at 3.81-3.74 ppm (9.4%, SCHSCH$_2$C*H*) and 3.91-3.82 ppm (3.4%, C*H*OH).

Benzoate ester **11**. To a mixture of ***cis*-10** (31 mg, 0.1 mmol), PPh_3 (365 mg, 1.4 mmol) and *p*-nitrobenzoic acid (50 mg, 0.3 mmol) in toluene (1.8 mL) DEAD (32 µL, 0.2 mmol) was added at 0 °C. The mixture was stirred for 1 h at ambient temperature, quenched with water and diluted with MTB ether. The aqueous layer was extracted with MTB ether (2 ×) and the combined organic layers were washed with brine, dried over Na_2SO_4, concantrated *in vacuo* and purified by column chromatography (SiO_2, MTB:PE = 1:3) to give **11** (39 mg, 85%) as yellow oil. $[\alpha]_D^{20}$ = -1.6° (c 0.2, $CHCl_3$); IR ($CHCl_3$) ν 3111, 3080, 2973, 2949, 2904, 1722, 1608, 1528, 1437, 1348, 1274, 1201, 1117, 1103, 1078, 1014 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.34-8.30 (m, 2 H, Ar-*H*), 8.26-8.22 (m, 2 H, Ar-*H*), 5.50 (qui, ^2J = 2.8 Hz, 1 H, C*H*OAr), 4.28-4.19 (m, 2

H, SC*H*S and SCHSCH$_2$C*H*), 4.14-4.06 (m, 1 H, C*H*CH$_2$CO$_2$CH$_3$), 3.71 (s, 3 H, OC*H*$_3$), 2.94-2.79 (m, H, SC*H*$_2$CH$_2$C*H*$_2$S), 2.60 (dd, ^2J = 15.1 Hz, ^3J = 8.0 Hz, 1 H, C*H*$_2$CO$_2$CH$_3$), 2.45 (dd, ^2J = 15.1 Hz, ^3J = 5.3 Hz, 1 H, C*H*$_2$CO$_2$CH$_3$), 2.16-2.07 (m, 1 H, SCH$_2$C*H*$_2$CH$_2$S), 2.05-1.76 (m, 5 H, SCH$_2$C*H*$_2$CH$_2$S and C*H*$_2$CH(OH)C*H*$_2$ and SCHSC*H*$_2$CH), 1.70-1.58 (m, 2 H, C*H*$_2$CH(OH)C*H*$_2$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 171.25 (4°, *C*O$_2$CH$_3$), 163.65 (4°, *C*O$_2$Ar), 150.65 (4°, Ar-*C*), 135.68 (4°, Ar-*C*), 130.82 (3°, Ar-*C*), 123.66 (3°, Ar-*C*), 69.51/69.37/68.97 (3°, SCHSCH$_2$*C*H and *C*HCH$_2$CO$_2$CH$_3$ and *C*HOAr), 51.76 (1°, OCH$_3$), 43.25 (3°, S*C*HS), 41.54 (2°, *C*H$_2$CO$_2$CH$_3$), 40.98 (2°, SCHS*C*H$_2$CH), 35.26/35.10 (2°, *C*H$_2$CH(OAr)-*C*H$_2$), 30.39/29.98 (2°, SCH$_2$CH$_2$*C*H$_2$S), 25.99 (2°, SCH$_2$*C*H$_2$CH$_2$S); MS (150 °C) *m/z* 455 (M$^+$, 16), 313 (1), 288 (2), 253 (12), 194 (10), 181 (21), 150 (100), 145 (8), 119 (14), 104 (19), 97 (3), 84 (28), 81 (15), 73 (65).