**Experimental**

*General.* Infrared spectra were recorded on a Perkin-Elmer 1710 infrared spectrometer. $^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker WP 200 SY and Bruker AVS 400 in deuterated chloroform unless otherwise stated, with tetramethylsilane as internal standard. Mass spectra were recorded on a Finnigan MAT 312 (70 eV) or a VG Autospec spectrometer. Microanalyses were performed in the Department of Organic Chemistry of the University of Hannover. Preparative column chromatography was performed on J. T. Baker silica gel (particle size 30 - 60 µm). Analytical TLC was carried out on aluminum-backed 0.2-mm silica gel 60 $F_{254}$ plates (E. Merck). Diethyl ether (E) and THF were distilled over sodium and benzophenone before use. $CH_2Cl_2$ (DCM) was distilled over $CaH_2$ before use. DMF was dried over BaO and distilled over $CaH_2$ before use. Methyl *tert.*-butyl ether (MTBE), ethyl acetate (EA), cyclohexane (CH) and light petroleum (PE, bp 40-60 °C) were distilled before use. Compounds ***rac*-4** was prepared as described in ref. 8, compounds ***rac*-5**, **6** and **6'** were prepared as described in ref. 6c, compounds ***meso*-15**, ***meso*-16**, **17** and **18** were prepared as described in ref. 13.

*(4-Benzyloxy-6-hydroxy-5,5-dimethyl-tetrahydro-pyran-2-yl)-acetic acid methyl ester* (**7**). To a solution of lactone **6** (62 mg, 0.22 mmol) in MeOH (1.2 ml) was added $K_2CO_3$ (37 mg, 0.36 mmol). The resulting mixture was stirred for 6 h at r.t. and then neutralized with 2 N HCl. MTBE was added, the organic layer was washed with brine and dried ($MgSO_4$). After removal of the solvent the residue was purified by column filtration to afford **7** (68 mg, 99%), unseparable mixture of anomers (α:β, 1.5:1), colourless liquid, $[\alpha]_D^{20}$ = +47.3° (*c* 1, $CHCl_3$). IR ($CHCl_3$) ν 3000, 2984, 2952, 2932, 1732, 1436, 1328, 1264, 1228, 1180, 1072, 1028 cm$^{-1}$; $^1$H NMR (α-anomer) (400 MHz) δ 7.35-7.24 (m, 5 H, Ar-*H*), 4.75 (bs, 1 H, HOC*H*O), 4.62/4.47 (d, $^2J$ =11.8 Hz, 2 H, C$H_2$Ph), 4.48-4.40 (m, 1 H, OC*H*CH$_2$), 3.72 (dd, $^3J$ = 11.5 Hz, $^3J$ = 4.7 Hz, 1 H, *H*COBn), 3.68 (s, 3 H, CO$_2$C$H_3$), 2.92 (d, $^3J$ = 2.6 Hz, 1 H, O*H*), 2.58 (dd, $^2J$ = 15.8 Hz, $^3J$ = 8.4 Hz, 1 H, C$H_2$CO$_2$CH$_3$), 2.49 (dd, $^2J$ = 15.8 Hz, $^3J$ = 5.2 Hz, 1 H, C$H_2$CO$_2$CH$_3$), 1.95-1.88 (m, 1 H, CHC$H_2$CH$_{eq}$), 1.55-1.43 (m, 1 H, CHC$H_2$CH$_{ax}$), 1.08/1.00 (s, 3 H, C(C$H_3$)$_2$); $^1$H NMR (β-anomer) (400 MHz) δ 7.35-7.24 (m, 5 H, Ar-*H*), 4.63/4.44 (d, $^2J$ =11.8 Hz, 2 H, C$H_2$Ph), 4.36 (d, $^3J$ = 6.4 Hz, 1 H, HOC*H*O), 3.90-3.81 (m, 1 H, OC*H*CH$_2$), 3.68 (s, 3 H, CO$_2$C$H_3$), 3.22 (d, $^3J$ = 6.4 Hz, 1 H, O*H*), 3.18 (dd, $^3J$ = 11.5 Hz, $^3J$ = 4.7 Hz, 1 H, *H*COBn), 2.68 (dd, $^2J$ = 15.8 Hz, $^3J$ = 7.8 Hz, 1 H, C$H_2$CO$_2$CH$_3$), 2.47 (dd, $^2J$ = 15.8 Hz, $^3J$ = 4.6 Hz, 1 H, C$H_2$CO$_2$CH$_3$), 1.95-1.88 (m, 1 H, CHC$H_2$CH$_{eq}$), 1.48-1.38 (m, 1 H, CHC$H_2$CH$_{ax}$), 1.06/0.94 (s, 3 H, C(C$H_3$)$_2$); $^{13}$C NMR (100 MHz) δ 171.88 (4°, *C*O$_2$CH$_3$), 139.06 (4°, Ar-*C*), 128.27 (3°, m-Ar-*C*), 127.46 (3°, p-Ar-*C*), 127.41 (3°, o-Ar-*C*), 100.28 (3°, HO*C*HO), 77.30 (3°, *C*HOBn), 71.45 (2°, *C*H$_2$Ph), 64.97 (3°, O*C*HCH$_2$), 51.75 (1°, O*C*H$_3$), 40.58 (2°, *C*H$_2$CO$_2$CH$_3$), 39.06 (4°, *C*(CH$_3$)$_2$), 22.98/18.62 (1°, C(*C*H$_3$)$_2$); MS (50 °C) *m/z* 308 (M$^+$, 1), 280 (1), 275 (1), 219 (4), 199 (2), 184 (5), 171 (3), 170 (3), 162 (12), 154 (100), 149 (9), 145 (3), 139 (3), 129 (4), 128 (4), 123 (2), 111 (7); HRMS calcd for $C_{17}H_{24}O_5$: 308.1625, found 308.1624.

*5-Benzyloxy-6-[1,3]dithian-2-yl-3-hydroxy-6-methyl-heptanoic acid methyl ester* (**8**). To a solution of acetal **7** (75 mg, 0.24 mmol) in $MeNO_2$ (2.4 ml) was added HS(CH$_2$)$_3$SH (50 µl, 0.48 mmol). The solution was cooled to –20 °C, $BF_3{\cdot}Et_2O$ (90 µl, 0.73 mmol) was added slowly. The mixture was allowed to reach –15 °C within 0.5 h. Then MTBE and sat. aq. $NaHCO_3$ solution were added. The layers were separated quickly and the aqueous layer was neutralized with conc. HCl solution and extracted with MTBE. The combined organic phase was washed with brine, dried ($Na_2SO_4$/$Na_2CO_3$, 2:1) and evaporated. Purification by column chromatography (MTBE/PE, 1:4 → 1:1) afforded **8** (91 mg, 95%), white solid, mp 45-48 °C, $[\alpha]_D^{20}$ = -5.0° (*c* 1, $CHCl_3$). IR ($CHCl_3$) ν 3564, 2998, 2976, 2956, 2900, 1724, 1436, 1364, 1276, 1176, 1092, 1068 cm$^{-1}$; $^1$H NMR (400 MHz) δ 7.40-7.25 (m, 5 H, Ar-*H*), 4.83/4.79 (d, $^2J$ = 11.8 Hz, 2 H, C$H_2$Ph), 4.28-4.19 (m, 1 H, C*H*OH), 4.21 (s, 1 H, SC*H*S), 4.09 (dd, $^3J$ = 10.1 Hz, $^3J$ = 2.2 Hz, 1 H, C*H*OBn), 3.70 (s, 3 H, OC$H_3$), 3.18 (bd, $^3J$ = 3.6 Hz, 1 H, O*H*), 2.90-2.79 (m, 3 H, SC$H_2$CH$_2$C$H_2$S), 2.77-2.69 (m, 1 H, SC$H_2$CH$_2$CH$_2$S), 2.53 (dd, $^2J$ = 16.5 Hz, $^3J$ = 3.5 Hz, 1 H, C$H_2$CO$_2$CH$_3$), 2.46 (dd, $^2J$ = 16.5 Hz, $^3J$ = 8.6 Hz, 1 H, C$H_2$CO$_2$CH$_3$), 2.09-2.00 (m, 1 H, SCH$_2$C$H_2$CH$_2$S), 1.88-1.75 (m, 1 H, SCH$_2$C$H_2$CH$_2$S), 1.74-1.66 (m, 1 H, BnOCHC$H_2$), 1.62-1.53 (m, 1 H, C$H_2$CHOBn), 1.17/1.06 (s, 3 H, C(C$H_3$)$_2$); $^{13}$C NMR (100 MHz) δ 173.31 (4°, *C*O$_2$CH$_3$), 139.22 (4°, Ar-*C*), 128.31 (3°, m-Ar-*C*), 127.33 (3°, p-Ar-*C*), 127.28 (3°, o-Ar-*C*), 79.57 (3°, *C*HOBn), 75.00 (2°, *C*H$_2$Ph), 65.12 (3°, *C*OH), 59.16 (3°, S*C*HS), 51.74 (1°, O*C*H$_3$), 43.47 (4°, *C*(CH$_3$)$_2$), 41.75 (2°, *C*H$_2$CO$_2$CH$_3$), 37.62 (2°, BnOCH*C*H$_2$), 31.54/31.32 (2°, S*C*H$_2$CH$_2$*C*H$_2$S), 26.31 (2°, SCH$_2$*C*H$_2$CH$_2$S), 21.04/20.96 (1°, C(*C*H$_3$)$_2$); MS (100 °C) *m/z* 398 (M$^+$, 2), 367 (M$^+$–OCH$_3$, 2), 291 (20), 272 (2), 257 (2), 253 (2), 219 (3), 187 (16), 173 (9), 161 (29), 129 (6), 121 (11), 119 (99), 107 (5), 106 (5), 91 (100); HRMS calcd for $C_{20}H_{30}O_4S_2$: 398.1586, found 398.1584.

*7-Benzyloxy-8-[1,3]dithian-2-yl-5-hydroxy-8-methyl-3-oxo-nonanoic acid tert.-butyl ester* (**9**). To a solution of diisopropyl amine (9.7 ml, 69.4 mmol) in THF (59 ml) was added *n*-BuLi (42.8 ml, 68.6 mmol, 1.6 M solution in hexane) dropwise at 0 °C. After 15 min the solution was cooled to –78 °C and acetic acid *t*-butyl ester (9.33 ml, 69.4 mmol) was added dropwise. The solution was stirred for 45 min at –78 °C, then a solution of **8** (5.60 g, 14.0 mmol) in THF (59 ml) was added. The mixture was allowed to reach 0 °C within 2 h, treated with glacial acetic acid (3.7 ml, 64.4 mmol) and diluted with EA and $H_2O$. The layers were separated and the aqueous phase extracted with EA (2×). The combined organic layer was dried ($MgSO_4$), the solvent removed and the crude product purified by column chromatography (MTBE/PE, 1:4 → 1:1) to give **9** (6.40 g, 94%), colourless liquid, $[\alpha]_D^{20}$ = +

1.0° (*c* 1, $CHCl_3$). IR ($CHCl_3$) ν 3576, 3001, 2980, 2928, 2904, 1732, 1708, 1648, 1452, 1368, 1252, 1148, 1092 $cm^{-1}$; $^1H$ NMR (400 MHz) δ 7.40-7.25 (m, 5 H, Ar-*H*), 4.80 (s, 2 H, C$H_2$Ph), 4.34-4.26 (m, 1 H, C*H*OH), 4.21 (s, 1 H, SC*H*S), 4.07 (dd, $^3J$ = 10.1 Hz, $^3J$ = 2.0 Hz, 1 H, C*H*OBn), 3.35 (s, 2 H, COC$H_2$CO$_2$), 3.09 (d, $^3J$ = 3.3 Hz, 1 H, O*H*), 2.90-2.79 (m, 3 H, SC$H_2$CH$_2$C$H_2$S), 2.78-2.63 (m, 3 H, SC$H_2$CH$_2$CH$_2$S, CH(OH)C$H_2$CO), 2.09-2.01 (m, 1 H, SCH$_2$C$H_2$CH$_2$S), 1.87 (m, 1 H, BnOCHC$H_2$), 1.70 (ddd, $^2J$ = 12.8 Hz, $^3J$ = 10.5 Hz, $^3J$ = 2.0 Hz, 1 H, SCH$_2$C$H_2$CH$_2$S), 1.58-1.49 (m, 1 H, BnOCHC$H_2$), 1.46 (s, 9 H, OC(C$H_3$)$_3$), 1.17/1.07 (s, 3 H, C(C$H_3$)$_2$); $^{13}C$ NMR (100 MHz) δ 204.19 (4°, *C*O), 166.07 (4°, *C*O$_2$), 139.21 (4°, Ar-*C*), 128.34 (3°, m-Ar-*C*), 127.38 (3°, p-Ar-*C*), 127.33 (3°, o-Ar-*C*), 82.26 (4°, O*C*(CH$_3$)$_3$), 79.56 (3°, *C*HOBn), 75.05 (2°, *C*H$_2$Ph), 64.71 (3°, *C*OH), 59.17 (3°, S*C*HS), 51.07 (2°, CO*C*H$_2$CO$_2$), 50.52 (2°, CH(OH)*C*H$_2$CO), 43.48 (4°, *C*(CH$_3$)$_2$), 37.48 (2°, BnOCH*C*H$_2$), 31.55/31.34 (2°, SC$H_2$CH$_2$*C*H$_2$S), 27.97 (1°, OC(*C*H$_3$)$_3$), 26.33 (2°, SCH$_2$*C*H$_2$CH$_2$S), 21.08/ 21.00 (1°, C(*C*H$_3$)$_2$); MS (80°C) *m/z* 483 ($M^+$+1, 1), 409 (2), 374 (2), 318 (20), 300 (2), 259 (4, 247 (2), 216 (3), 187 (9), 173 (6), 161 (33), 139 (2), 119 (100), 106 (4), 91 (100), 86 (5); HRMS calcd for $C_{14}H_{22}O_4S_2$: 318.0960, found 318.0962.

*7-Benzyloxy-8-[1,3]dithian-2-yl-3,5-dihydroxy-8-methyl-nonanoic acid tert.-butyl ester* (**10**). A solution of $Me_4NBH(OAc)_3$ (27.8 g, 105 mmol) in MeCN (50 ml) and AcOH (50 ml) was stirred for 30 min at r.t. and then cooled to –35 °C. A solution of **9** (6.40 g, 13.2 mmol) in MeCN/ AcOH (1:2.5, 17 ml) was added slowly. The mixture was stored for 3 d at –35 °C and 1 d at –25 °C. The mixture was then treated with aq. sodium tartrate solution (0.5 M, 290 ml, 128 mmol) at 0 °C. The cooling bath was removed and the suspension diluted with MTBE. Solid $NaHCO_3$ was added carefully (gas evolution!) in portions until pH 7 was reached. The mixture was added carefully to a two-phase system of sat. aq. $NaHCO_3$ solution and MTBE. The aqueous layer was extracted with MTBE (3×). The combined organic phase was washed with brine, dried ($MgSO_4$) and concentrated. Purification by column chromatography gave a non-separable mixture of ***anti*-10** and ***syn*-10** (6.26 g, 97%). Data for ***anti*-10**, colourless oil, $[\alpha]_D^{20}$ = -16.2° (*c* 1, $CHCl_3$). IR ($CHCl_3$) ν 3500, 2980, 2928, 2852, 1712, 1452, 1424, 1368, 1232, 1152, 1092 $cm^{-1}$; $^1H$ NMR (400 MHz) δ 7.40-7.24 (m, 5 H, Ar-*H*), 4.82/4.78 (d, $^2J$ = 11.8 Hz, 2 H, C$H_2$Ph), 4.34-4.27 (m, 1 H, C*H*OH), 4.23 (s, 1 H, SC*H*S), 4.17-4.09 (m, 1 H, C*H*OH), 4.05 (dd, $^3J$ = 9.8 Hz, $^3J$ = 2.0 Hz, 1 H, C*H*OBn), 3.70 (bs, 1 H, O*H*), 3.15 (bs, 1 H, O*H*), 2.88-2.78 (m, 3 H, SC$H_2$CH$_2$C$H_2$S), 2.77-2.67 (m, 1 H, SC$H_2$CH$_2$CH$_2$S), 2.46-2.31 (m, 2 H, C$H_2$CO$_2$), 2.07-2.00 (m, 1 H, SCH$_2$C$H_2$CH$_2$S), 1.87-1.75 (m, 1 H, SCH$_2$C$H_2$-CH$_2$S), 1.75-1.49 (m, 4 H, BnOCHC$H_2$, C$H_2$CHOH), 1.45 (s, 9 H, OC(C$H_3$)$_3$), 1.07/0.81 (s, 3 H, C(C$H_3$)$_2$); $^{13}C$ NMR (100 MHz) δ 172.33 (4°, *C*O$_2$), 139.34 (4°, Ar-*C*), 128.29 (3°, m-Ar-*C*), 127.34 (3°, o-Ar-*C*), 127.31 (3°, p-Ar-*C*), 81.32 (4°, O*C*(CH$_3$)$_3$), 80.15 (3°, *C*HOBn), 74.90 (2°, *C*H$_2$Ph), 66.00 (3°, *C*OH), 65.95 (3°, *C*OH), 59.25 (3°, S*C*HS), 43.50 (4°, *C*(CH$_3$)$_2$), 42.87 (2°, *C*H$_2$CO$_2$), 42.14 (2°, BnOCHC$H_2$), 38.45 (2°, *C*H$_2$CHOH), 31.50/31.29 (2°, SC$H_2$CH$_2$*C*H$_2$S), 28.10 (1°, OC(*C*H$_3$)$_3$), 26.32 (2°, SCH$_2$*C*H$_2$CH$_2$S), 21.08/21.00 (1°, C(*C*H$_3$)$_2$); MS (170 °C) *m/z* 411($M^+$–OBu$^t$, 2), 376 (3), 320 (2), 302 (2), 290 (2), 261 (7), 249 (3), 213 (3), 190 (12), 187 (14), 161 (28), 158 (11), 141 (15), 119 (100), 107 (4), 106 (4), 91 (100), 87 (4), 81 (3), 73 (4); HRMS calcd for $C_{21}H_{31}O_4S_2$: 411.1664, found 411.1666.

*[6-(2-Benzyloxy-3-[1,3]dithian-2-yl-3-methyl-butyl)-2,2-dimethyl-[1,3]dioxan-4-yl]-acetic acid tert.-butyl ester* (**11**). To a solution of **10** (6.20 g, 12.8 mmol) in 2,2-dimethoxypropane (25 ml) was added a catalytic amount of *p*-TsOH·$H_2O$ and the resulting mixture was stirred at r.t. for 16 h. $Et_3N$ (5 drops) was added, the solvent was removed and the residue purified by column chromatography (MTBE/PE, 1:10 → 1:1) to yield starting material (700 mg, 11%) and **11** (5.90 g, 88%), white solid, mp 81-86 °C, $[\alpha]_D^{20}$ = +6.6° (*c* 1, $CHCl_3$). IR ($CHCl_3$) ν 2980, 2932, 2904, 1720, 1452, 1368, 1228, 1152, 1124 , 1096, 1028 $cm^{-1}$; $^1H$ NMR (200 MHz) δ 7.38-7.24 (m, 5 H, Ar-*H*), 4.77 (s, 2 H, C$H_2$Ph), 4.29 (s, 1 H, SC*H*S), 4.27-4.18 (m, 1 H, CH$_2$C*H*O(C(CH$_3$)$_2$)CH$_2$), 4.12-4.01 (m, 1 H, CH(OBn)CH$_2$C*H*), 3.95 (dd, $^3J$ = 8.4 Hz, $^3J$ = 3.2 Hz, 1 H, C*H*OBn), 2.88-2.76 (m, 3 H, SC$H_2$CH$_2$C$H_2$S), 2.67 (ddd, $^2J$ = 14.2 Hz, $^3J$ = 12.0 Hz, $^3J$ = 2.5 Hz, 1 H, SC$H_2$CH$_2$-CH$_2$S), 2.49-2.30 (m, 2 H, C$H_2$CO$_2$), 2.11-2.01 (m, 1 H, SCH$_2$C$H_2$CH$_2$S), 1.90-1.60 (m, 5 H, SCH$_2$C$H_2$CH$_2$S, CH-(OBn)C$H_2$, CHC$H_2$CH), 1.45 (m, 9 H, OC(C$H_3$)$_3$), 1.38/ 1.37 (s, 3 H, OC(C$H_3$)$_2$O), 1.14/1.05 (s, 3 H, C(C$H_3$)$_2$); $^{13}C$ NMR (50 MHz) δ 170.21 (4°, *C*O$_2$), 139.43 (4°, Ar-*C*), 128.27 (3°, m-Ar-*C*), 127.19 (3°, p-Ar-*C*), 126.84 (3°, o-Ar-*C*), 100.40 (4°, *C*O$_2$(CH$_3$)$_2$), 80.46 (4°, O*C*(CH$_3$)$_3$), 79.75 (3°,*C*HOBn), 74.47 (2°, *C*H$_2$Ph), 63.85 (3°, CH(OBn)CH$_2$*C*H), 63.71 (3°, CH$_2$*C*HO(C(CH$_3$)$_2$)CH$_2$), 59.12 (3°, S*C*HS), 43.53 (4°, *C*(CH$_3$)$_2$), 42.20 (2°, *C*H$_2$CO$_2$), 38.35 (2°, CH(OBn)*C*H$_2$), 38.24 (2°, CH*C*H$_2$-CH), 31.52/31.25 (2°, S*C*H$_2$CH$_2$*C*H$_2$S), 28.05 (1°, OC-(*C*H$_3$)$_3$), 26.32 (2°, SCH$_2$*C*H$_2$CH$_2$S), 25.24 (1°, OC(*C*H$_3$)$_2$-O), 25.16 (1°, OC(*C*H$_3$)$_2$O), 21.12/20.60 (1°, C(*C*H$_3$)$_2$); MS (130 °C) *m/z* 524 ($M^+$, 3), 509 (3), 416 (5), 393 (11), 360 (11), 356 (11), 302 (10), 279 (6), 244 (6), 216 (3), 173 (10), 167 (10), 161 (23), 160 (19), 149 (23), 141 (7), 121 (9), 119 (96), 91 (100), 84 (4), 71 (6); HRMS calcd for $C_{28}H_{44}O_5S_2$: 524.2630, found 524.2633.

*3-[1,3]Dithian-2-yl-1-[6-(2-hydroxy-ethyl)-2,2-dimethyl-[1,3]dioxan-4-yl]-3-methyl-butan-2-ol* (**12**). To a solution of ester **11** (4.61 g, 8.86 mmol) in THF (70 ml) was added a solution of $LiAlH_4$ (13.3 ml, 13.3 mmol, 1.0 M in THF) dropwise at 0 °C. The mixture was stirred for 2 h at r.t. and was then cooled to 0 °C. EA (1.1 ml) was added dropwise followed by $H_2O$ (0.5 ml), 2 N NaOH (0.5 ml) and $H_2O$ (1.55 ml). The mixture was filtered and the residue washed with MTBE and a small amount of MeOH (1 ml). The filtrate was dried ($Na_2SO_4$/$Na_2CO_3$, 1:1), evaporated and purified by column filtration (MTBE/PE, 1:2) to yield 2-[6-(2-benzyloxy-3-[1,3]dithian-2-yl-3-methyl-butyl)-2,2-

dimethyl-[1,3]dioxan-4-yl]-ethanol (3.98 g, 99%), colourless oil, $[\alpha]_D^{20}$ = –0.7° (*c* 1, $CHCl_3$). IR ($CHCl_3$) ν 3516, 3060, 2984, 2928, 2852, 1496, 1452, 1424, 1380, 1264, 1164, 1088 , 1036 $cm^{-1}$; $^1H$ NMR (200 MHz) δ 7.39-7.24 (m, 5 H, Ar-*H*), 4.77 (s, 2 H, C*H*$_2$Ph), 4.29 (s, 1 H, SC*H*S), 4.16-3.90 (m, H, $CH_2CHO(C(CH_3)_2)CH_2$, CH(OBn)-$CH_2CH$, C*H*OBn), 3.75 (t, $^3J$ = 5.5 Hz, 2 H, C*H*$_2$OH), 2.88-2.76 (m, 4 H, SC*H*$_2$CH$_2$C*H*$_2$S, O*H*), 2.75-2.58 (m, 1 H, SC*H*$_2$CH$_2$CH$_2$S), 2.11-1.97 (m, 1 H, SCH$_2$C*H*$_2$CH$_2$S), 1.90-1.55 (m, 6 H, SCH$_2$C*H*$_2$CH$_2$S, CH(OBn)C*H*$_2$, CHC*H*$_2$CH, C*H*$_2$CH$_2$OH), 1.51-1.40 (m, 1 H, CHC*H*$_2$CH), 1.39/1.38 (s, 3 H, OC(C*H*$_3$)$_2$O), 1.14/1.05 (s, 3 H, C(C*H*$_3$)$_2$); $^{13}C$ NMR (50 MHz) δ 139.44 (4°, Ar-*C*), 128.34 (3°, m-Ar-*C*), 127.27 (3°, p-Ar-*C*), 127.90 (3°, o-Ar-*C*), 100.44 (4°, *C*O$_2$(CH$_3$)$_2$), 79.81 (3°,*C*HOBn), 74.54 (2°, *C*H$_2$Ph), 66.80 (3°, CH(OBn)CH$_2$*C*H), 64.11 (3°, CH$_2$*C*HO(C(CH$_3$)$_2$)CH$_2$), 61.21 (2°, *C*H$_2$OH), 59.17 (3°, S*C*HS), 43.59 (4°, *C*(CH$_3$)$_2$), 38.68 (2°, CH(OBn)*C*H$_2$), 38.43 (2°, CH*C*H$_2$CH), 37.64 (2°, *C*H$_2$CH$_2$OH), 31.58/ 31.30 (2°, S*C*H$_2$CH$_2$*C*H$_2$S), 26.37 (2°, SCH$_2$*C*H$_2$CH$_2$S), 25.43 (1°, OC(*C*H$_3$)$_2$O), 25.33 (1°, OC(*C*H$_3$)$_2$O), 21.17/ 20.64 (1°, C(*C*H$_3$)$_2$); MS (80 °C) *m/z* 524 ($M^+$, 3), 439 (4), 346 (16), 289 (6), 274 (18), 251 (3), 230 (2), 216 (3), 190 (13), 187 (6), 173 (6), 161 (25), 160 (23), 145 (4), 128 (5), 121 (9), 119 (96), 101 (5), 92 (10), 91 (100), 83 (6); HRMS calcd for $C_{24}H_{38}O_4S_2$: 454.2211, found 454.2214.

To a suspension of Li (700 mg, 101 mmol) in THF (10 ml) was added a solution of 4,4'-di-*tert*.-butyldiphenyl (24.4 g, 91.6 mmol) in THF (42 ml). The surface of lithium was scratched to start the reaction (indicated by green colour). After 10 min the deep-green suspension was diluted with THF (15 ml) and stirring was continued for 14 h at r.t. to complete reaction. To a solution of 2-[6-(2-benzyloxy-3-[1,3]dithian-2-yl-3-methyl-butyl)-2,2-dimethyl-[1,3]dioxan-4-yl]-ethanol (4.05 g, 8.9 mmol) in THF (70 ml) was added the freshly prepared LDBB solution at –78 °C. The mixture was allowed to reach –50 °C within 30 min. $H_2O$ (10 ml) was added, the mixture was warmed up to r.t. and filtered. The organic phase was dried ($Na_2SO_4/Na_2CO_3$, 1:1), evaporated and chromatographed (MTBE/PE, 1:9 → 1:1) to afford diol **12** (3.182 g, 98%), highly viscous oil, $[\alpha]_D^{20}$ = +1.2° (*c* 1, $CHCl_3$). IR ($CHCl_3$) ν 3616, 3516, 2988, 2904, 1464, 1424, 1384, 1228, 1160, 1124, 1084, 1056 $cm^{-1}$; $^1H$ NMR (200 MHz) δ 4.27 (s, 1 H, SC*H*S), 4.24-3.96 (m, 3 H, C*H*OH, CH$_2$C*H*O(C(CH$_3$)$_2$)CH$_2$), C*H*O(C(CH$_3$)$_2$)CH$_2$CH$_2$OH), 3.84-3.58 (bs, 1 H, O*H*), 3.77 (t, $^3J$ = 5.5 Hz, 2 H, C*H*$_2$OH), 3.18-3.00 (bd, $^3J$ = 7.0 Hz, 1 H, O*H*), 2.96-2.78 (m, 4 H, SC*H*$_2$CH$_2$C*H*$_2$S), 2.18-2.02 (m, 1 H, SCH$_2$C*H*$_2$CH$_2$S), 1.93-1.43 (m, 7 H, SCH$_2$C*H*$_2$CH$_2$S, CH(OH)C*H*$_2$, CHC*H*$_2$CH, C*H*$_2$CH$_2$OH), 1.38/1.37 (s, 3 H, OC(C*H*$_3$)$_2$O), 1.08/1.02 (s, 3 H, C(C*H*$_3$)$_2$); $^{13}C$ NMR (50 MHz) δ 100.66 (4°, *C*O$_2$(CH$_3$)$_2$), 71.64 (3°,*C*HOH), 67.04 (3°, CH$_2$*C*HO(C(CH$_3$)$_2$CH$_2$, 64.52 (3°, *C*HO(C(CH$_3$)$_2$)-CH$_2$CH$_2$OH), 61.05 (2°, *C*H$_2$OH), 59.33 (3°, S*C*HS), 42.37 (4°, *C*(CH$_3$)$_2$), 37.67 (2°, CH(OH)*C*H$_2$), 37.64 (2°, CH*C*H$_2$CH), 36.18 (2°, *C*H$_2$CH$_2$OH), 31.57/31.43 (2°, S*C*H$_2$CH$_2$*C*H$_2$S), 26.39 (2°, SCH$_2$*C*H$_2$CH$_2$S), 24.89 (1°, OC(*C*H$_3$)$_2$O), 24.80 (1°, OC(*C*H$_3$)$_2$O), 21.27/21.18 (1°, C(*C*H$_3$)$_2$); MS (80 °C) *m/z* 364 ($M^+$, 2), 349 (1), 273 (1), 205 (3), 187 (1), 162 (3), 161 (2), 160 (2), 138 (3), 126 (3), 121 (9), 119 (14), 110 (14), 107 (4), 101 (22), 95 (10), 91 (5), 86 (100), 82 (36), 79 (11), 74 (39); HRMS calcd for $C_{17}H_{32}O_4S_2$: 364.1742, found 364.1743.

*4-[2-(tert.-Butyl-dimethyl-silanyloxy)-3-[1,3]dithian-2-yl-3-methyl-butyl]-6-[2-(tert.-butyl-diphenyl-silanyloxy)-ethyl]-2,2-dimethyl-[1,3]dioxane* (**13**). To a solution of diol **12** (4.57 g, 12.5 mmol) and imidazole (2.05 g, 30.1 mmol) in DCM (60 ml) was added TPSCl (3.6 ml, 13.8 mmol) dropwise and the resulting mixture was stirred for 2 h at r.t. Water (30 ml) was added, the aqueous layer was extracted with MTBE (2×), the combined organic phase washed with brine and dried ($Na_2SO_4/Na_2CO_3$, 1:1). After removal of the solvent *anti* and *syn* acetonide were separated by column chromatography. Data for *anti* acetonide 1-{6-[2-(*tert.*-butyl-diphenyl-silanyloxy)-ethyl]-2,2-dimethyl-[1,3]dioxan-4-yl}-3-[1,3]dithian-2-yl-3-methyl-butan-2-ol (6.79 g, 90%), colourless oil, $[\alpha]_D^{20}$ = -1.8° (*c* 1, $CHCl_3$). IR ($CHCl_3$) ν 3512, 3072, 2988, 2928, 2852, 1448, 1428, 1380, 1228, 1112 , 956, 824 $cm^{-1}$; $^1H$ NMR (200 MHz) δ 7.71-7.62 (m, 4 H, o-Ar-*H*), 7.43-7.31 (m, 6 H, Ar-*H*), 4.28 (s, 1 H, SC*H*S), 4.22-3.99 (m, 3 H, C*H*OH, CH$_2$C*H*O(C(CH$_3$)$_2$)CH$_2$, C*H*O(C(CH$_3$)$_2$)CH$_2$CH$_2$OTPS), 3.87-3.62 (m, 2 H, C*H*$_2$OTPS), 2.95-2.82 (m, 4 H, SC*H*$_2$CH$_2$C*H*$_2$S), 2.76 (s, 1 H, O*H*), 2.17-2.01 (m, 1 H, SCH$_2$C*H*$_2$CH$_2$S), 1.95-1.49 (m, 7 H, SCH$_2$C*H*$_2$CH$_2$S, CH-(OH)C*H*$_2$, CHC*H*$_2$CH, C*H*$_2$CH$_2$OTPS), 1.34 (s, 6 H, OC-(C*H*$_3$)$_2$O), 1.09 (s, 3 H, C(C*H*$_3$)$_2$), 1.03 (s, 12 H, Si-Ph$_2$C(C*H*$_3$)$_3$, C(C*H*$_3$)$_2$); $^{13}C$ NMR (50 MHz) δ 135.54 (3°, o-Ar-*C*), 133.94/133.90 (4°, Ar-*C*), 129.55 (3°, p-Ar-*C*), 127.62 (3°, m-Ar-*C*), 100.42 (4°, *C*O$_2$(CH$_3$)$_2$), 71.63 (3°, *C*HOH), 64.55 (3°, CH$_2$*C*HO(C(CH$_3$)$_2$)CH$_2$), 63.66 (3°, *C*HO(C(CH$_3$)$_2$))CH$_2$CH$_2$OTPS), 60.10 (2°, *C*H$_2$OTPS), 59.37 (3°, S*C*HS), 42.39 (4°, *C*(CH$_3$)$_2$), 38.93 (2°, *C*H$_2$CH$_2$OTPS), 37.90 (2°, CH(OH)*C*H$_2$), 36.14 (2°, CH*C*H$_2$CH), 31.58/31.45 (2°, S*C*H$_2$CH$_2$*C*H$_2$S), 26.86 (1°, SiPh$_2$C(*C*H$_3$)$_3$), 26.43 (2°, SCH$_2$*C*H$_2$CH$_2$S), 24.94/24.85 (1°, OC(*C*H$_3$)$_2$O), 21.19/ 19.95 (1°, C(*C*H$_3$)$_2$), 19.20 (4°, SiPh$_2$*C*(CH$_3$)$_3$); MS (120 °C) *m/z* 603 ($M^+$+1, 2), 525 (8), 487 (4), 376 (3), 350 (100), 318 (10), 271 (6), 255 (5), 229 (6), 199 (14), 180 (5), 155 (2), 135 (4), 121 (14), 119 (16), 106 (5), 105 (7); HRMS calcd for $C_{27}H_{45}O_4S_2Si$: 525.2317, found 525.2308. Data for *syn* acetonide (683 mg, 9%). IR ($CHCl_3$) ν 3672, 3482, 3072, 2996, 2932, 2900, 1472, 1428, 1380, 1164, 1112 , 956, 820 $cm^{-1}$; $^1H$ NMR (200 MHz) δ 7.75-7.62 (m, 4 H, o-Ar-*H*), 7.44-7.31 (m, 6 H, Ar-*H*), 4.28 (s, 1 H, SC*H*S), 4.24-3.99 (m, 3 H, C*H*OH, CH$_2$C*H*O(C(CH$_3$)$_2$)CH$_2$, C*H*O(C(CH$_3$)$_2$)CH$_2$CH$_2$OTPS), 3.91-3.76 (m, 1 H, C*H*$_2$OTPS), 3.75-3.61 (m, 1 H, C*H*$_2$OTPS), 3.05-2.91 (bs, 1 H, O*H*), 2.90-2.82 (m, 4 H, SC*H*$_2$CH$_2$C*H*$_2$S), 2.17-2.02 (m, 1 H, SCH$_2$C*H*$_2$CH$_2$S), 1.95-1.51 (m, 7 H, SCH$_2$C*H*$_2$CH$_2$S, CH(OH)C*H*$_2$, CHC*H*$_2$CH, C*H*$_2$CH$_2$OTPS), 1.43/ 1.37 (s, 3 H, OC(C*H*$_3$)$_2$O), 1.05 (s, 9 H, SiPh$_2$C(C*H*$_3$)$_3$), 1.08/1.02 (s, 6 H, C(C*H*$_3$)$_2$); $^{13}C$ NMR (50 MHz) δ 135.52/ 134.80 (3°, o-Ar-*C*), 135.36/ 133.90 (4°, Ar-*C*), 129.54 (3°, p-Ar-*C*), 127.64 (3°, m-Ar-*C*), 98.73 (4°, *C*O$_2$(CH$_3$)$_2$), 71.40 (3°, *C*HOH), 67.42 (3°, CH$_2$*C*HO(C(CH$_3$)$_2$)CH$_2$), 65.72 (3°, *C*HO(C(CH$_3$)$_2$)CH$_2$-

$CH_2$OTPS), 59.62 (2°, *C*$H_2$OTPS), 59.21 (3°, S*C*HS), 42.35 (4°, *C*$(CH_3)_2$), 39.26 (2°, *C*$H_2CH_2$OTPS), 36.66 (2°, CH(OH)*C*$H_2$), 36.49 (2°, CH*C*$H_2$CH), 31.50/31.39 (2°, S*C*$H_2CH_2C$*H*$_2$S), 30.22 (1°, OC(*C*$H_3$)$_2$O), 26.57 (1°, $SiPh_2C(CH_3)_3$), 26.38 (2°, $SCH_2CH_2CH_2S$), 21.05 (1°, OC(*C*$H_3$)$_2$O), 19.95/19.68 (1°, C(*C*$H_3$)$_2$), 19.18 (4°, $SiPh_2C(CH_3)_3$); MS (140 °C) 603 *m/z* ($M^+$+1, 1), 602 ($M^+$, 2), 588 (3), 526 (2), 487 (12), 469 (4), 437 (3), 379 (1), 350 (5), 326 (7), 256 (21), 225 (12), 199 (31), 183 (10), 161 (11), 134 (11), 119 (100), 107 (9), 91 (13), 81 (6), 75 (5).

To a solution of 1-{6-[2-(*tert.*-butyl-diphenyl-silanyloxy)-ethyl]-2,2-dimethyl-[1,3]dioxan-4-yl}-3-[1,3]dithian-2-yl-3-methyl-butan-2-ol (120 mg, 0.2 mmol) and imidazole (35 mg, 0.52 mmol) in DMF (0.6 ml) was added TBSOTf (55 µl, 0.24 mmol) and the mixture was stirred for 2 h at 60 °C. The mixture was cooled down to r.t. and added to a mixture of $H_2O$/MTBE (1:1, 30 ml). The aqueous layer was extracted with MTBE (2×), the combined organic phase washed with brine, dried ($Na_2SO_4$/$Na_2CO_3$, 2:1) and concentrated. The residue was purified by chromatography (MTBE/PE, 1:40) to afford **13** (141 mg, 99%), highly viscous oil, $[\alpha]_D^{20}$ = +0.5° (*c* 1, $CHCl_3$). IR ($CHCl_3$) ν 3072, 2956, 2932, 2900, 2856, 1472, 1428, 1380, 1256, 1168, 1108, 1004, 832 $cm^{-1}$; $^1$H NMR (400 MHz) δ 7.70-7.63 (m, 4 H, o-Ar-*H*), 7.44-7.34 (m, 6 H, Ar-*H*), 4.33 (s, 1 H, SC*H*S), 4.11-4.02 (m, 1 H, C*H*O(C$(CH_3)_2$)$CH_2CH_2$-OTPS), 3.99 (dd, $^3J$ = 5.3 Hz, $^3J$ = 2.4 Hz, 1 H, C*H*OTBS), 3.91-3.83 (m, 1 H, $CH_2$C*H*O(C$(CH_3)_2$)$CH_2$), 3.82-3.75 (m, 1 H, C*H*$_2$OTPS), 3.72-3.65 (m, 1 H, C*H*$_2$OTPS), 2.92-2.80 (m, 4 H, SC*H*$_2CH_2$C*H*$_2$S), 2.11-2.03 (m, 1 H, $SCH_2$C*H*$_2$-$CH_2$S), 1.90-1.65 (m, 4 H, $SCH_2$C*H*$_2CH_2$S, CH(OTBS)-C*H*$_2$, C*H*$_2CH_2$OTPS), 1.62-1.47 (m, 2 H, CHC*H*$_2$CH), 1.40-1.30 (m, 1 H, CH(OTBS)C*H*$_2$), 1.35/1.30 (s, 3 H, OC(C*H*$_3$)$_2$O), 1.04 (s, 9 H, $SiPh_2C(CH_3)_3$), 1.03/0.99 (s, 3 H, C(C*H*$_3$)$_2$), 0.91 (s, 9 H, $Si(CH_3)_2C(CH_3)_3$), 0.15/0.09 (s, 3 H, Si(C*H*$_3$)$_2$C$(CH_3)_3$); $^{13}$C NMR (100 MHz) δ 135.57/135.56 (3°, o-Ar-*C*), 133.96/133.90 (4°, Ar-*C*), 129.56 (3°, p-Ar-*C*), 127.63/127.61 (3°, m-Ar-*C*), 100.06 (4°, *C*$O_2$-$(CH_3)_2$), 74.02 (3°, *C*HOTBS), 65.31 (3°, $CH_2$*C*HO-(C$(CH_3)_2$)$CH_2$), 63.34 (3°, *C*HO(C$(CH_3)_2$)$CH_2CH_2$OTPS), 60.07 (2°, *C*$H_2$OTPS), 58.41 (3°, S*C*HS), 43.45 (4°, *C*$(CH_3)_2$), 41.00 (2°, CH(OTBS)*C*$H_2$), 38.95 (2°, *C*$H_2CH_2$-OTPS), 38.87 (2°, CH*C*$H_2$CH), 31.39/31.04 (2°, S*C*$H_2$-$CH_2C$*H*$_2$S), 26.86 (1°, $SiPh_2C(CH_3)_3$), 26.44 (2°, $SCH_2$-*C*$H_2CH_2$S), 26.19 (1°, $Si(CH_3)_2C(CH_3)_3$), 25.40/ 24.98 (1°, OC(*C*$H_3$)$_2$O), 20.36/20.06 (1°, C(*C*$H_3$)$_2$), 19.21 (4°, $SiPh_2$-*C*$(CH_3)_3$), 18.50 (2°, $Si(CH_3)_2C(CH_3)_3$), -3.24/-4.35 (1°, Si(*C*$H_3$)$_2$C$(CH_3)_3$); FAB-MS *m/z* 739($M^+$+Na, 17), 717 ($M^+$+1, 8), 701 (11), 659 (56), 601 (60), 511 (36), 479 (15), 439 (20), 397 (23), 339 (53), 269 (100), 255 (59), 239 (81); HRMS calcd for $C_{39}H_{64}O_4S_2Si_2$: 716.3784, found 716.3745.

*2-Hydroxymethyl-6-trityloxymethyl-tetrahydro-pyran-4-one* (**19**). To a solution of alcohol **18** (1.55 g, 7.68 mmol) in DCM (8 ml) were added $Et_3N$ (1.70 ml, 12.2 mmol), 4-DMAP (93 mg, 0.76 mmol) and trityl chloride (2.73 g, 9.97 mmol) at r.t. and the mixture was stirred for 24 h. The resulting yellow suspension was poured into E (500 ml) and then suction-filtered. The filtrate was washed with 1 N HCl (50 ml), brine (25 ml) and dried ($MgSO_4$). After removal of the solvent the resulting yellow oil was purified by column filtration (E/PE, ~3:2) to afford acetic acid 4-oxo-6-trityloxymethyl-tetrahydro-pyran-2-yl methyl ester,white powder (2.87 g, 84%), mp 130-134 °C, $[\alpha]_D^{21}$ = –20.1° (*c* 1, $CHCl_3$). IR (KBr) ν 3058, 2935, 2873, 1742, 1723, 1491, 1449, 1232, 1159, 1079, 1042, 766, 749, 703 $cm^{-1}$; $^1$H NMR (200 MHz) δ 7.49-7.40 (m, 6 H, o-Ar-*H*), 7.35-7.21 (m, 9 H, m/p-Ar-*H*), 4.25-4.18 (m, 2 H, C*H*$_2$OAc), 3.99-3.78 (m, 2 H, C*H*OC*H*), 3.25 (dd, $^2J$ = 10 Hz, $^3J$ = 5 Hz, 1 H, C*H*$_2$OTr), 3.14 (dd, $^2J$ = 10 Hz, $^3J$ = 5 Hz, 1 H, C*H*$_2$OTr), 2.47-2.35 (m, 4 H, C*H*$_2$C(=O)C*H*$_2$), 2.09 (s, 3 H, OC(=O)C*H*$_3$); $^{13}$C NMR (50 MHz) δ 205.78 (4°, $CH_2$*C*O), 170.68 (4°, O*C*(=O)$CH_3$), 143.73 (4°, Ar-*C*), 128.66 (3°, o-Ar-*C*), 127.82 (3°, m-Ar-*C*), 127.08 (3°, p-Ar-*C*), 86.60 (4°, *C*$Ph_3$), 76.17 (3°, *C*$HCH_2$OTr), 74.50 (3°, *C*$HCH_2$OAc), 66.10 (2°, *C*$H_2$OTr), 65.94 (2°, *C*$H_2$OAc), 44.57 (2°, *C*$H_2CHCH_2$OTr), 43.80 (2°, *C*$H_2CHCH_2$OAc), 20.79 (1°, OC(=O)*C*$H_3$); MS (100 °C) *m/z* 444 ($M^+$, 3), 367 (6), 295 (13), 243 (100), 165 (50), 125 (14), 105 (31); HRMS calcd for $C_{28}H_{28}O_5$: 444.1937, found 444.1928.

To a solution of acetic acid 4-oxo-6-trityloxymethyl-tetrahydro-pyran-2-yl methyl ester (2.68 g, 6.04 mmol) in MeOH (60 ml) and $H_2O$ (2.6 ml) was added $K_2CO_3$ (876 mg, 6.34 mmol) at 0 °C. The mixture was stirred for 2 h at 0 °C and then diluted with $H_2O$ (80 ml). The aqueous layer was extracted with E (2×350 ml). The combined organic phase was dried ($MgSO_4$) and the solvent was removed to give alcohol **19** (2.41 g, 99%), white foam, mp 109.5-110 °C (crystals from E/PE). $[\alpha]_D^{22}$ = –8.7° (*c* 1, $CHCl_3$). IR (KBr) ν 3442, 3057, 2923, 2873, 1719, 1597, 1491, 1449, 1224, 1156, 1073, 1035, 766, 749, 709 $cm^{-1}$; $^1$H NMR (200 MHz) δ 7.50-7.40 (m, 6 H, o-Ar-*H*), 7.38-7.20 (m, 9 H, m/p-Ar-*H*), 3.95-3.70 (m, 3 H, C*H*$_2$OH, C*H*$CH_2$OTr), 3.66-3.51 (m, 1 H, C*H*$CH_2$OH), 3.34 (dd, $^2J$ = 10 Hz, $^3J$ = 5 Hz, 1 H, C*H*$_2$OTr), 3.20 (dd, $^2J$ = 10 Hz, $^3J$ = 5 Hz, 1 H, C*H*$_2$OTr), 2.56-2.23 (m, 4 H, C*H*$_2$C(=O)C*H*$_2$), 2.06 (dd, $^3J$ = 6 Hz, $^3J$ = 7 Hz, 1 H, O*H*); $^{13}$C NMR (50 MHz) δ 206.55 (4°, $CH_2$*C*O), 143.62 (4°, Ar-*C*), 128.61 (3°, o-Ar-*C*), 127.83 (3°, m-Ar-*C*), 127.13 (3°, p-Ar-*C*), 86.70 (4°, *C*$Ph_3$), 77.11 (3°, *C*$HCH_2$OH), 76.04 (3°, *C*$HCH_2$OTr), 66.12 (2°, *C*$H_2$OTr), 65.18 (2°, *C*$H_2$OH), 44.66 (2°, *C*$H_2CHCH_2$OTr), 43.26 (2°, *C*$H_2CHCH_2$OH); MS (110 °C) *m/z* 402 ($M^+$, 4), 325 (1), 324 (4), 243 (23), 222 (24), 210 (12), 137 (73), 121 (100), 91 (59); HRMS calcd for $C_{26}H_{26}O_4$: 402.1831, found 402.1834.

*(2-Hydroxymethyl-6-trityloxymethyl-tetrahydro-pyran-4-ylidene)-acetic acid ethyl ester* (**20a**). To a suspension of NaH (25 mg, 0.63 mmol, 60% suspension in mineral oil) in toluene (6 ml) was added ethyl diisopropoxyphosphono-acetate (0.18 ml, 0.75 mmol) dropwise within 15 min under water-cooling. The solution was stirred for 15 min at r.t. and was then cooled to –50 °C. A solution of ketone **19** (196 mg, 0.49 mmol) in toluene (4 ml) was added dropwise within 30 min. The mixture was allowed to reach –35 °C within 1 h and was then stored for 17 h at –25 °C. The

mixture was then warmed up to 0 °C slowly and added to $H_2O$/EA (1:1, 20 ml). The aqueous layer was extracted with EA (2×). The combined organic phase was washed with brine, dried ($MgSO_4$) and concentrated. The crude product was purified by chromatography to yield **20a** (222 mg, 96%, *E:Z* = 9:1), white solid, mp 98-101 °C, $[\alpha]_D^{21}$ = +26.5° (*c* 1, $CHCl_3$). IR (KBr) ν 3445, 3059, 2926, 2871, 1713, 1651, 1491, 1449, 1376, 1206, 1178, 1152, 1095, 1034, 708 $cm^{-1}$; $^1H$ NMR (200 MHz) δ 7.50-7.40 (m, 6 H, o-Ar-*H*), 7.36-7.22 (m, 9 H, m/p-Ar-*H*), 5.75 (s, 1 H, C*H*$CO_2$), 4.15 (q, $^3J$ = 7 Hz, 2 H, OC$H_2$$CH_3$), 3.76 (d, $^2J$ = 14 Hz, 1 H, C$H_2$$CHCH_2OH_{eq}$), 3.75-3.45 (m, 4 H, C*H*OC*H*C$H_2$OH), 3.29 (dd, $^2J$ = 9 Hz, $^3J$ = 5 Hz, 1 H, C$H_2$OTr), 3.10 (dd, $^2J$ = 9 Hz, $^3J$ = 5 Hz, 1 H, C$H_2$OTr), 2.34 (d, $^2J$ = 12 Hz, 1 H, C$H_2$$CHCH_2$OTr), 2.20 (t, $^{2/3}J$ = 12.5 Hz, 1 H, C$H_2$$CHCH_2$OTr), 2.07 (dd, $^3J$ = 7.5 Hz, $^3J$ = 4.5 Hz, 1 H, O*H*), 1.95 (t, $^{2/3}J$ = 12.5 Hz, 1 H, C$H_2$CH-$CH_2OH_{ax}$), 1.28 (t, $^3J$ = 7 Hz, 3 H, $CH_2$C$H_3$); $^{13}C$ NMR (50 MHz) δ 166.30 (4°, *C*$O_2$), 156.18 (4°, *C*$CHCO_2$), 143.78 (4°, Ar-*C*), 128.62 (3°, o-Ar-*C*), 127.76 (3°, m-Ar-*C*), 127.01 (3°, p-Ar-*C*), 116.50 (3°, *C*$HCO_2$), 85.52 (4°, *C*$Ph_3$), 77.74 (3°, *C*$HCH_2OH$), 77.11 (3°, *C*$HCH_2$OTr), 66.47 (2°, *C*$H_2$OTr), 65.80 (2°, *C*$H_2OH$), 59.74 (3°, *C*$H_2CH_3$), 39.70 (2°, *C*$H_2CHCH_2$OTr), 31.53 (2°, *C*$H_2$CH-$CH_2OH$), 14.22 (1°, $CH_2$*C*$H_3$); MS (150 °C) *m/z* 472 ($M^+$, 1), 453 (2), 440 (7), 395 (3), 259 (5), 243 (100), 229 (8), 199 (15), 165 (14), 153 (9); HRMS calcd for $C_{30}H_{32}O_5$: 472.2250, found 472.2259. Anal. Calcd for $C_{30}H_{32}O_5$ C: 76.25, H: 6.83 Found C: 76.26, H: 7.00.

*(2-Hydroxymethyl-6-trityloxymethyl-tetrahydro-pyran-4-ylidene)-acetic acid isopropyl ester* (**20b**). NaH (25 mg, 0.625 mmol), isoproyl diisopropoxyphosphonoacetate (200 mg, 0.75 mmol) and ketone **19** (200 mg, 0.497 mmol) in toluene (15 ml) were allowed to react as described for **20a**. Reaction time: 7 d at –8 °C, yield after chromatography (EA/CH, 1:4): 240 mg (99%), white foam, mp 50 °C, $[\alpha]_D^{20}$ = +29.3° (*c* 1, $CHCl_3$). IR ($CHCl_3$) ν 3592, 3060, 3004, 2980, 2928, 1704, 1648, 1448, 1372, 1244, 1176, 1152, 1104, 1040 $cm^{-1}$; $^1H$ NMR (400 MHz) δ 7.48-7.40 (m, 6 H, o-Ar-*H*), 7.35-7.20 (m, 9 H, m/p-Ar-*H*), 5.73 (s, 1 H, C*H*$CO_2$), 5.03 (sept., 1 H, $^3J$ = 6.2 Hz, OC*H*$(CH_3)_3$), 3.79 (d, $^2J$ = 14.0 Hz, 1 H, C$H_2$$CHCH_2OH_{eq}$), 3.74-3.47 (m, 4 H, C*H*OC*H*C$H_2$OH), 3.29 (dd, $^2J$ = 9.3 Hz, $^3J$ = 5.1 Hz, 1 H, C$H_2$OTr), 3.10 (dd, $^2J$ = 9.3 Hz, $^3J$ = 5.1 Hz, 1 H, C$H_2$OTr), 2.34 (d, $^2J$ = 15.0 Hz, 1 H, C$H_2$$CHCH_2$OTr), 2.20 (t, $^{2/3}J$ = 13.0 Hz, 1 H, C$H_2$$CHCH_2$OTr), 2.22-2.13 (bs, 1 H, O*H*), 1.95 (t, $^{2/3}J$ = 12.7 Hz, 1 H, C$H_2$CHC$H_2$-OH), 1.27/1.26 (d, $^3J$ = 4.8 Hz, 3 H, (C$H_3$)$_2$); $^{13}C$ NMR (100 MHz) δ 165.83 (4°, *C*$O_2$), 155.77 (4°, *C*$CHCO_2$), 143.80 (4°, Ar-*C*), 128.65 (3°, o-Ar-*C*), 127.76 (3°, m-Ar-*C*), 127.02 (3°, p-Ar-*C*), 116.00 (3°, *C*$HCO_2$), 84.54 (4°, *C*$Ph_3$), 77.75 (3°, *C*$HCH_2OH$), 77.11 (3°, *C*$HCH_2$OTr), 67.00 (3°, *C*$H(CH_3)_2$), 66.49 (2°, *C*$H_2$OTr), 65.82 (2°, *C*$H_2OH$), 39.70 (2°, *C*$H_2CHCH_2$OTr), 31.50 (2°, *C*$H_2$CH-$CH_2OH$), 21.88 (1°, CH(*C*$H_3$)$_2$); MS (150 °C) *m/z* 486 ($M^+$, 0.1), 433 (0.2), 409 (0.8), 279 (1), 259 (2), 243 (100), 228 (3), 213 (9), 171 (5), 165 (23), 153 (14), 149 (8), 105 (6), 91 (1), 77 (3); HRMS calcd. for $C_{31}H_{34}O_5$: 486.2406, found 486.2408.

*2-(2-Triisopropylsilanyloxymethyl-6-trityloxymethyl-tetrahydro-pyran-4-ylidene)-ethanol* (**21**). To a solution of isopropyl ester **20b** (200 mg, 0.411 mmol) and imidazole (78.0 mg, 1.15 mmol) in DMF (0.8 ml) was added TIPSCl (118 µl, 0.55 mmol) dropwise at r.t. and the mixture was stirred for 1 h. Then MTBE and $H_2O$ were added, the aqueous layer was extracted with MTBE (2×) and the combined organic phase washed with brine and dried ($Na_2SO_4$). The solvent was removed and the residue purified by column filtration (MTBE/PE, 1:35) to afford (2-triisopropylsilanyloxymethyl-6-trityloxymethyl-tetrahydro-pyran-4-ylidene)-acetic acid isopropyl ester (262 mg, 99%), highly viscous oil, $[\alpha]_D^{20}$ = +13.6° (*c* 1, $CHCl_3$). IR ($CHCl_3$) ν 3060, 2928, 2964, 1700, 1648, 1448, 1384, 1236, 1156, 1108, 996 $cm^{-1}$; $^1H$ NMR (400 MHz) δ 7.49-7.41 (m, 6 H, o-Ar-*H*), 7.32-7.20 (m, 9 H, m/p-Ar-*H*), 5.71 (s, 1 H, C*H*$CO_2$), 5.04 (sept., 1 H, $^3J$ = 6.2 Hz, OC*H*$(CH_3)_3$), 3.84 (d, $^2J$ = 15.0 Hz, 1 H, C$H_2$$CHCH_2OH_{eq}$), 3.83-3.79 (m, 1 H, C$H_2$OTIPS), 3.77-3.72 (m, 1 H, C$H_2$OTIPS), 3.66-3.59 (m, 1 H, C*H*$CH_2$OTIPS), 3.51-3.44 (m, 1 H, C*H*$CH_2$OTr), 3.25 (dd, $^2J$ = 9.3 Hz, $^3J$ = 5.1 Hz, 1 H, C$H_2$OTr), 3.05 (dd, $^2J$ = 9.3 Hz, $^3J$ = 5.5 Hz, 1 H, C$H_2$OTr), 2.29 (d, $^2J$ = 13.3 Hz, 1 H, C$H_2$$CHCH_2$OTr), 2.18 (t, $^{2/3}J$ = 11.8 Hz, 1 H, C$H_2$$CHCH_2$OTr), 1.97 (t, $^{2/3}J$ = 12.2 Hz, 1 H, C$H_2$CH-$CH_2OH$), 1.26/1.25 (d, $^3J$ = 3.4 Hz, 3 H, (C$H_3$)$_2$), 1.05 (bs, 21 H, Si(C*H*(C$H_3$)$_2$)$_3$); $^{13}C$ NMR (100 MHz) δ 165.96 (4°, *C*$O_2$), 156.67 (4°, *C*$CHCO_2$), 144.01 (4°, Ar-*C*), 128.76 (3°, o-Ar-*C*), 127.75 (3°, m-Ar-*C*), 126.96 (3°, p-Ar-*C*), 115.66 (3°, *C*$HCO_2$), 86.48 (4°, *C*$Ph_3$), 78.54 (3°, *C*$HCH_2$OTIPS), 77.20 (3°, *C*$HCH_2$OTr), 66.89 (3°, *C*$H(CH_3)_2$), 66.78 (2°, *C*$H_2$OTr), 65.62 (2°, *C*$H_2$OTIPS), 40.04 (2°, *C*$H_2CHCH_2$OTr), 32.56 (2°, *C*$H_2CHCH_2$-OTIPS), 21.96 (1°, CH(*C*$H_3$)$_2$), 18.00 (1°, Si(CH(*C*$H_3$)$_2$)$_3$), 12.00 (3°, Si(*C*$H(CH_3)_2$)$_3$); FAB-MS *mz* 642 ($M^+$, 68), 641 (75), 631 (20), 559 (100); HRMS calcd for $C_{40}H_{54}O_5Si$: 642.3740, found 642.3693.

To a solution of (2-triisopropylsilanyloxymethyl-6-trityloxymethyl-tetrahydro-pyran-4-ylidene)-acetic acid isopropyl ester (2.28 g, 3.55 mmol) in toluene (24 ml) was added DIBAH (9.5 ml, 9.5 mmol, 1 M solution in hexane) dropwise at –65 °C. The mixture was allowed to reach –20 °C within 1 h, then treated with sodium/potassium tartrate (20 ml) and stirred for 30 min at r.t. The resulting mixture was diluted with $H_2O$ and E and the aqueous layer was extracted with E (3×). The combined organic phase was washed with brine and dried ($MgSO_4$). The solvent was removed to give **21** (2.02 g, 97%), white foam, $[\alpha]_{365}^{21}$ = –1.6 ° (*c* 1, $CHCl_3$). IR ($CHCl_3$) ν 3612, 3088, 3060, 3000, 2944, 2892, 2864, 1672, 1488, 1464, 1448, 1384, 1364, 1308, 1240, 1148, 1120, 996 $cm^{-1}$; $^1H$ NMR (200 MHz) δ 7.51-7.40 (m, 6 H, o-Ar-*H*), 7.35-7.18 (m, 9 H, m/p-Ar-*H*), 5.51 (t, $^3J$ = 7 Hz, 1 H, C*H*$CH_2OH$), 4.19 (d, $^3J$ = 7 Hz, 2 H, C$H_2OH$), 3.84 (dd, $^2J$ = 10 Hz, $^3J$ = 5 Hz, 1 H, C$H_2$O-TIPS), 3.63 (dd, $^2J$ = 10 Hz, $^3J$ = 6 Hz, 1 H, C$H_2$OTIPS), 3.66-3.32 (m, 2 H, C*H*$CH_2$OTIPS, C*H*$CH_2$OTr), 3.23 (dd, $^2J$ = 9 Hz, $^3J$ = 5.5 Hz, 1 H, C$H_2$OTr), 3.00 (dd, $^2J$ = 9 Hz,

$^3J$ = 6 Hz, 1 H, C$H_2$OTr), 2.73 (d, $^2J$ = 13 Hz, 1 H, C$H_2$CHCH$_2$OTIPS), 2.28 (d, $^2J$ = 12 Hz, 1 H, C$H_2$CH-CH$_2$OTr), 2.07 (t, $^{2/3}J$ ~ 12 Hz, C$H_2$CHCH$_2$OTr) 1.77 (t, $^{2/3}J$ = 13 Hz, 1 H, C$H_2$CHCH$_2$OTIPS), 1.60 (bs, 1 H, *OH*), 1.07 (bs, 21 H, Si(C*H*(C$H_3$)$_2$)$_3$); $^{13}$C NMR (50 MHz) δ 143.98 (4°, Ar-*C*), 138.06 (4°, *C*CHCH$_2$OH), 128.68 (3°, o-Ar-*C*), 127.64 (3°, m-Ar-*C*), 126.82 (3°, p-Ar-*C*), 122.74 (3°, *C*HCH$_2$OH), 86.32 (4°, *C*Ph$_3$), 78.27 (3°, *C*HCH$_2$OTr), 77.41 (3°, *C*HCH$_2$OTIPS), 66.71/66.19 (2°, *C*H$_2$OTr, *C*H$_2$OTIPS), 58.19 (3°, *C*H$_2$OH), 39.29 (2°, *C*H$_2$CHCH$_2$OTr), 31.75 (2°, *C*H$_2$CHCH$_2$OTIPS), 17.92 (1°, Si(CH(C$H_3$)$_2$)$_3$), 11.87 (3°, Si(*C*H(CH$_3$)$_2$)$_3$); MS (70 °C) *m/z* 586 (0, M$^+$), 274 (40), 260 (9), 243 (56), 197 (100), 183 (31), 173 (51), 165 (35), 131 (37), 105 (90), 77 (64).

*4-[2-(tert.-Butyl-diphenyl-silanyloxy)-ethylidene]-2-triisopropylsilanyloxymethyl-6-trityloxymethyl-tetrahydro-pyran* (**22**). To a solution of **21** (2.07 g, 3.53 mmol) and imidazole (650 mg, 9.55 mmol) in DMF (7.1 ml) was added TPSCl (1.13 ml, 4.4 mmol) and the mixture was stirred for 90 min at r.t. $H_2O$ (60 ml) was added and the aqueous layer was extracted with E (3×150 ml). The combined organic phase was washed with brine, dried ($MgSO_4$) and evaporated. The crude product was purified by chromatography (PE/E, 35:1) to afford **22** (2.71 g, 93%), colourless, highly viscous foam, $[\alpha]_D^{21}$ = +1.8° (*c* 1, $CHCl_3$). IR ($CHCl_3$) ν 3068, 3000, 2944, 2892, 2864, 1596, 1488, 1461, 1448, 1428, 1388, 1112, 1068, 880 cm$^{-1}$; $^1$H NMR (200 MHz) δ 7.77-7.65 (m, 4 H, o-Ar-*H*/TPS), 7.51-7.20 (m, 21 H, m/p-Ar-*H*), 5.48 (t, $^3J$ = 6.5 Hz, 1 H, C*H*CH$_2$OTPS), 4.25 (d, $^3J$ = 6.5 Hz, 2 H, C$H_2$OTPS), 3.74 (dd, $^2J$ = 10 Hz, $^3J$ = 5 Hz, 1 H, C$H_2$OTIPS), 3.61-3.49 (m, 2 H, C$H_2$OTIPS, C*H*CH$_2$OTr), 3.32-3.18 (m, 2 H, C*H*CH$_2$OTIPS, C$H_2$OTr), 2.98 (dd, $^2J$ = 9 Hz, $^3J$ = 5 Hz, 1 H, C$H_2$OTr), 2.43 (d, $^2J$ = 14 Hz, 1 H, C$H_2$CHCH$_2$OTIPS), 2.25 (d, $^2J$ = 13 Hz, 1 H, C$H_2$CHCH$_2$OTr), 1.99 (t, $^{2/3}J$ = 12 Hz, C$H_2$CHCH$_2$OTr) 1.60 (t, $^{2/3}J$ = 12 Hz, 1 H, C$H_2$CHCH$_2$OTIPS), 1.04 (s, 9 H, SiC(C$H_3$)$_3$), 1.01 (bs, 21 H, Si(C*H*(C$H_3$)$_2$)$_3$); $^{13}$C NMR (50 MHz) δ 144.10 (4°, Ar-*C*/Tr), 138.06 (4°, *C*CHCH$_2$OTPS), 135.55 (3°, o-Ar-*C*/TPS), 133.90 (4°, Ar-*C*/TPS), 129.54 (3°, p-Ar-*C*/TPS), 128.77 (3°, o-Ar-*C*/Tr), 127.70 (3°, m-Ar-*C*/Tr), 127.60 (3°, m-Ar-*C*/TPS), 126.88 (3°, p-Ar-*C*/Tr), 123.35 (3°, *C*HCH$_2$OTPS), 86.37 (4°, *C*Ph$_3$), 78.17 (3°, *C*HCH$_2$OTIPS), 77.39 (3°, *C*HCH$_2$OTr), 66.85/ 66.67 (2°, *C*H$_2$OTr, *C*H$_2$OTIPS), 60.11 (3°, *C*H$_2$OTPS), 39.25 (2°, *C*H$_2$CHCH$_2$OTr), 31.82 (2°, *C*H$_2$CHCH$_2$OTIPS), 26.86 (1°, SiPh$_2$C(*C*H$_3$)$_3$), 19.16 (4°, SiPh$_2$*C*(CH$_3$)$_3$), 17.97 (1°, Si(CH(*C*H$_3$)$_2$)$_3$), 11.92 (3°, Si(*C*H(CH$_3$)$_2$)$_3$); FAB-MS *m/z* 824 (0, M$^+$), 823 (1), 325 (4), 243 (100), 197 (24), 165 (23), 135 (29).

*Trifluoro-methanesulfonic acid 4-[2-(tert-butyl-diphenyl-silanyloxy)-ethylidene]-6-triisopropylsilanyloxymethyl-tetrahydro-pyran-2-yl methyl ester* (**23**). To a solution of **22** (2.67 g, 3.24 mmol) in DCM (32 ml) and MeOH (5.3 ml) was added anhydrous $ZnBr_2$ (8.76 g, 40 mmol) in three portions at 0 °C. After complete addition the cooling bath was removed, the mixture stirred for 1.5 h at r.t. and then cooled to 0 °C again. Sat. aq. $NaHCO_3$ solution and E were added carefully. The aqueous layer was extracted with E (3×), the combined organic phase was washed with brine (2×) and dried ($MgSO_4$). The solvent was removed and the residue purified by chromatography (PE/E, 7:2) to give pure *Z*-{4-[2-(tert.-butyl-diphenyl-silanyloxy)-ethylidene]-6-triisopropylsilanyloxymethyl-tetrahydro-pyran-2-yl}-methanol (1.73 g, 92%), colourless, highly viscous oil, $[\alpha]_D^{22}$ = +2.9° (*c* 1, $CHCl_3$). IR ($CHCl_3$) ν 3592, 3420, 3072, 3052, 3000, 2944, 2892, 2864, 1588, 1428, 1408, 1252, 1196, 1140, 1112, 1040, 1012 cm$^{-1}$; $^1$H NMR (400 MHz) δ 7.70-7.66 (m, 4 H, o-Ar-*H*), 7.44-7.35 (m, 6 H, m/p-Ar-*H*), 5.47 (t, $^3J$ = 6.5 Hz, 1 H, C*H*CH$_2$OTPS), 4.24 (d, $^3J$ = 6.5 Hz, 2 H, C$H_2$OTPS), 3.72 (dd, $^2J$ = 10.5 Hz, $^3J$ = 5.5 Hz, 1 H, C$H_2$OTIPS), 3.66-3.60 (m, 1 H, C$H_2$OH), 3.58 (dd, $^2J$ = 10.5 Hz, $^3J$ = 5.5 Hz, 1 H, C$H_2$OTIPS), 3.55-3.42 (m, 2 H, C*H*CH$_2$OH, C$H_2$OH), 3.25 (m, 1H, C*H*CH$_2$OTIPS), 2.37 (dd, $^2J$ = 14 Hz, $^3J$ = 1.5 Hz, 1 H, C$H_2$CHCH$_2$OTIPS), 2.07-1.99 (m, 3 H, C$H_2$CHCH$_2$OH, O*H*), 1.63 (t, $^{2/3}J$ = 13 Hz, 1 H, C$H_2$CHCH$_2$OTIPS), 1.05-1.01 (m, 30 H, SiC-(C$H_3$)$_3$, Si(C*H*(C$H_3$)$_2$)$_3$); $^{13}$C NMR (50 MHz) δ 135.51 (3°, o-Ar-*C*), 135.28 (4°, *C*CHCH$_2$OTPS), 133.80 (4°, Ar-*C*), 129.52 (3°, p-Ar-*C*/TPS), 127.56 (3°, m-Ar-*C*), 123.70 (3°, *C*HCH$_2$OTPS), 78.99 (3°, *C*HCH$_2$OH), 78.10 (3°, *C*H-CH$_2$OTIPS), 66.57 (2°, *C*H$_2$OTIPS), 65.81 (2°, *C*H$_2$OH), 60.00 (3°, *C*H$_2$OTPS), 37.43 (2°, *C*H$_2$CHCH$_2$OH), 31.43 (2°, *C*H$_2$CHCH$_2$OTIPS), 26.78 (1°, SiPh$_2$C(*C*H$_3$)$_3$), 19.09 (4°, SiPh$_2$*C*(CH$_3$)$_3$), 17.88 (1°, Si(CH(*C*H$_3$)$_2$)$_3$), 11.87 (3°, Si(*C*H(CH$_3$)$_2$)$_3$); MS (130 °C) *m/z* 582 (0, M$^+$), 527 (M$^+$–C$_4$H$_9$, 3), 526 (7), 507 (4), 447 (6), 351 (6), 283 (23), 199 (39), 173 (100), 135 (16), 93 (35); HRMS calcd. for $C_{30}H_{45}O_4Si_2$: 525.2856, found 525.2857.

To a solution of *Z*-{4-[2-(tert.-butyl-diphenyl-silanyloxy)-ethylidene]-6-triisopropylsilanyloxymethyl-tetrahydro-pyran-2-yl}-methanol (583 mg, 1.00 mmol) and 2,6-di-*tert.*-butyl-4-methylpyridine (308 mg, 1.50 mmol) in DCM (35 ml) was added $Tf_2O$ (0.20 ml, 1.2 mmol) dropwise at –78 °C. After 15 min the mixture was diluted with E (20 ml), the mixture was warmed up to 0 °C and suction-filtered. The filtrate was washed with 1 N HCl and brine. The organic phase was dried ($MgSO_4$), concentrated and purified immediately by chromatography (PE/E, ~6:1) to afford unstable triflate **23** (710 mg, 99%), colourless oil.

*4-(2-(tert.-Butyl-dimethyl-silanyloxy)-3-methyl-3-{2-[6-triisopropylsilanyloxymethyl-4-(2-(tert.-butyl-diphenyl-silanyloxy)-ethylidene)-tetrahydro-pyran-2-ylmethyl]-[1,3]dithian-2-yl}-butyl)-2,2-dimethyl-6-(2-(tert.-butyl-diphenyl-silanyloxy)-ethyl)-[1,3]dioxane* (**24**). To a solution of dithiane **13** (370 mg, 0.515 mmol) in THF (4.5 ml) was added *t*-BuLi (0.354 ml, 0.566 mmol, 1.6 M solution in pentane) at –78 °C, followed by HMPA (0.270 ml, 1.55 mmol). The mixture was stirred for 5 min at –78 °C, then triflate **23** (368 mg, 0.515 mmol) was added. The mixture was allowed to reach –50 °C within 1 h. 2 N NaOH was added, the mixture was stirred for 30 min at r.t. and then diluted with MTBE and $H_2O$. The aqueous layer was extracted with MTBE, the combined organic phase

was washed with brine and dried ($Na_2SO_4/Na_2CO_3$, 2:1). After removal of the solvent the crude product was purified by chromatography (MTBE/PE, 1:60 → EA/CH, 1:25) to yield **24** (414 mg, 63%), white foam. $^1$H NMR (400 MHz) δ 7.70-7.64 (m, 8 H, o-Ar-*H*), 7.44-7.34 (m, 12 H, Ar-*H*), 5.45 (t, $^3J$ = 6.4 Hz, 1 H, C*H*$CH_2$OTPS), 4.28-4.18 (m, 3 H, *H*-3, C$H_2$OTPS), 4.12-4.03 (m, 1 H, *H*-7), 3.91-3.63 (m, 4 H, *H*-1, *H*-5, *H*-11), 3.58-3.46 (m, 1 H, *H*-1a, *H*-16a), 3.28-3.13 (m, 2 H, *H*-15, *H*-16b), 3.09-2.58 (m, 4 H, SC$H_2$$CH_2$C$H_2$S), 2.55-2.42 (m, 2 H, *H*-14a, *H*-12a), 2.39-2.21 (m, 1 H, *H*-12b), 2.14-2.04 (m, 1 H, $SCH_2$C$H_2$$CH_2$S), 2.00-1.49 (m, 6 H, *H*-4a, *H*-6a, *H*-10, *H*-14b, $SCH_2$C$H_2$$CH_2$S), 1.37-1.28 (m, 4 H, *H*-2, *H*-4b, *H*-6b), 1.43 (s, 6 H, OC(C$H_3$)$_2$), 1.06-0.98 (m, 45 H, C(C$H_3$)$_2$, $SiPh_2$C(C$H_3$)$_3$, Si(C*H*(C$H_3$)$_2$)$_3$), 0.92-0.87 (m, 9 H, $Si(CH_3)_2$C(C$H_3$)$_3$), 0.19-0.07 (m, 6 H, Si(C$H_3$)$_2$C($CH_3$)$_3$).

*2-[6-(2-(tert.-Butyl-dimethyl-silanyloxy)-3-{2-[4-(2-hydroxy-ethylidene)-6-hydroxymethyl-tetrahydro-pyran-2-ylmethyl]-[1,3]dithian-2-yl}-3-methyl-butyl)-2,2-dimethyl-[1,3]dioxan-4-yl]-ethanol* (**25**). To a solution of silyl ether **24** (53 mg, 0.041 mmol) in THF (2 ml) was added TBAF/AcOH (0.82 ml, 0.82 mmol) [prepared from TBAF (1 equiv, 1 M solution in THF) and glacial acetic acid (1 equiv)]. The mixture was stirred for 2 d at r.t. and then MTBE and $H_2O$ were added. The organic layer was washed with sat. aq. $NaHCO_3$ solution (2×10 ml). The combined aqueous layer was extracted with MTBE and the combined organic phase washed with brine and dried ($Na_2SO_4/Na_2CO_3$, 1:1). After removal of the solvent the product was purified by chromatography (MTBE → MTBE/MeOH, 8:1) to afford triol **25** (19 mg, 73%), white foam. $^1$H NMR (400 MHz) δ 5.52 (t, $^3J$ = 6.9 Hz, OC*H*$CH_2$OH), 4.26-4.12 (m, 4 H), 4.11-3.72 (m, 4 H), 3.67-3.51 (m, 2 H), 3.45-3.37 (m, 1 H), 3.09-2.68 (m, 4 H, SC$H_2$$CH_2$C$H_2$S), 2.59-2.41 (m, 2 H, *H*-14a, *H*-12a), 2.36-2.09 (m, 8 H), 2.00-1.57 (m, 12 H), 1.47/1.36 (s, 3 H, OC(C$H_3$)$_2$), 1.24/1.16 (s, 3 H, C(C$H_3$)$_2$), 0.89 (s, 9 H, $Si(CH_3)_2$C(C$H_3$)$_3$), 0.16/0.11 (s, 3 H, Si(C$H_3$)$_2$C($CH_3$)$_3$).

*[6-(2-{2-(tert.-Butyl-dimethyl-silanyloxy)-3-[6-(2-(tert.-butyl-diphenyl-silanyloxy-ethyl)-2,2-dimethyl-[1,3]dioxan-4-yl]-1,1-dimethyl-propyl}-[1,3]dithian-2-ylmethyl)-4-(2-(tert.-butyl-diphenyl-silanyloxy)-ethylidene)-tetrahydro-pyran-2-yl]-methanol* (**26**). To a solution of triol **25** (16 mg, 0.024 mmol) in DCM (0.4 ml) was added imidazole (5 mg, 0.07 mmol) at 0 °C. The resulting solution was cooled to –30 °C and TPSCl (12.5 µl, 0.048 mmol) was added dropwise. The mixture was allowed to reach 0 °C within 2 h and MTBE and $H_2O$ were added. The aqueous layer was extracted with MTBE and the combined organic layer was washed with brine and dried ($Na_2SO_4/Na_2CO_3$, 1:1). After removal of the solvent the residue was purified by chromatography (MTBE/PE, 1:3 → 1:1) to give **26** (19 mg, 71%), white foam. $^1$H NMR (400 MHz) 7.70-7.64 (m, 8 H, o-Ar-*H*), 7.45-7.35 (m, 12 H, m-Ar-*H*, p-Ar-*H*), 5.48 (t, $^3J$ = 5.4 Hz, C*H*$CH_2$OTPS), 4.30-4.15 (m, 4 H), 4.11-3.75 (m, 4 H), 3.55-3.37 (m, 2 H), 3.34-3.16 (m, 1 H), 3.09-2.40 (m, 8 H), 2.33-2.27 (m, 1 H), 2.18-1.49 (m, 9 H), 1.47/1.36 (s, 3 H, OC(C$H_3$)$_2$), 1.24/1.16 (s, 3 H, C(C$H_3$)$_2$), 1.04 (s, 18 H, $SiPh_2$C(C$H_3$)$_3$), 0.90 (s, 9 H, $Si(CH_3)_2$C(C$H_3$)$_3$), 0.17/0.12 (s, 3 H, Si(C$H_3$)$_2$C($CH_3$)$_3$).