Supporting Information

A Mild, Chemoselective Protocol for the Removal of Thioketals and Thioacetals Mediated By Dess-Martin Periodinane.

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Experimental section: ^1H and ^{13}C NMR spectra were taken in CDCl_3 at 400 MHz and 75 MHz respectively. Chemical shifts are reported in parts per million using the solvent internal standard (chloroform, 7.24 and 77.00 ppm, respectively). Infrared resonance spectra were recorded on a NexusTM 670 FTIR spectrometer. High resolution mass spectra were obtained on a FiniganTM MAT-90 spectrometer. CH_3CN , CH_2Cl_2 , MeOH, and THF were obtained from a dry solvent system (alumina) and used without further drying. DMP was prepared by known methods,¹ or purchased from Aldrich, Inc.² All other reagents were used as supplied. All reactions were carried out in oven-dried glassware, open to the atmosphere unless otherwise noted. Analytical thin layer chromatography was performed on Sorbent Technologies 0.20 mm silica gel 60 Å plates. Flash chromatography³ was performed on Sorbent Technologies 32-63 μm 60 Å silica gel. Melting points are uncorrected.

General Experimental Procedures.

General experimental procedure for Dess-Martin periodinane mediated hydrolysis of thioketals/thioacetals. A representative experimental procedure for the formation of acetophenone (**2b**) from 2-methyl-2-phenyl-1,3-dithiane (**1b**) is illustrated.

Compound 2b. To a sample of **1b** (210 mg, 1.0 mmol) in 5.0 mL 8:1:1 $\text{CH}_3\text{CN}:\text{CH}_2\text{Cl}_2:\text{H}_2\text{O}$ (0.2 M) was added freshly prepared Dess-Martin periodinane⁴ (420 mg, 2.0 mmol, 2.0 equiv.) in one portion. The reaction mixture was stirred at ambient temperature,

exposed to air, for 2 hours until complete consumption of starting material as observed by TLC analysis. The reaction was diluted with 50% aq. NaHCO_3 , the layers were separated, and the aqueous layer was extracted $3 \times$ into CH_2Cl_2 . The combined organic layers were washed with brine, dried over MgSO_4 , filtered, and concentrated under

(1) (a) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277-7287. (b) Ireland, R. E.; Liu, L. *J. Org. Chem.* **1993**, *58*, 2899.

(2) Aldrich catalog number 27,462-3 (Dess-Martin periodinane). See article text for results utilizing this reagent.

(3) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.

(4) Degradation of prepared DMP reagent after prolonged storage at $-20\text{ }^\circ\text{C}$ (>4 months) has been observed.

reduced pressure. Purification by flash chromatography (silica, 5% EtOAc/hexanes) affords 112 mg (92%) of desired ketone **2b**, which possesses spectral data identical to that of acetophenone.

General experimental procedure for Dess-Martin periodinane mediated direct thioacetal to acetal conversion. The illustrated experimental procedure for the formation of **3b** from thioacetal **1k** is representative.

6,6-Dimethoxy-hexan-1-ol (3b). To a sample of **1k** (200 mg, 1.0 mmol) in 5.0 mL 8:1:1 CH₃CN:CH₂Cl₂:MeOH (0.2 M) under argon was added freshly

prepared Dess-Martin periodinane⁴ (420 mg, 2.0 mmol, 2.0 equiv.) in one portion. The reaction mixture was stirred at ambient temperature for 12 hours until complete consumption of starting material as observed by TLC. The reaction was diluted with 50% aq. NaHCO₃, the layers were separated, and the aqueous layer was extracted 3 × into CH₂Cl₂. The combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by flash chromatography (silica, 30→50% EtOAc/hexanes) provides 143 mg (88%) of desired acetal **3b** as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 1.32 (4H, m), 1.54 (4H, m), 3.26 (6H, s), 3.58 (2H, t, J = 6.8), 3.83 (1H, bs), 4.32 (1H, t, J = 5.8); ¹³C NMR (75 MHz, CDCl₃) δ 24.2, 25.4, 32.2, 52.5, 62.5, 104.4; IR (neat) ν_{max} 3422, 2939, 1725, 1464, 1385, 1128, 1054, 915, 734; HRMS(CI, NH₃) *m/z* calc'd for C₈H₁₉O₃ [M+H]⁺ 163.1334, found: 163.1327.

Spectroscopic Characterization of Selected Novel Compounds.

***tert*-Butyl-(2-((3*S*)-methyl-(6*S*)-[2-(4-methyl-pent-1-enyl)-[1,3]dithian-2-ylmethyl]-tetrahydro-pyran-(2*R*)-yl)-ethoxy)-diphenyl-silane (1a).** Prepared from the lithium anion of thioacetal **1g** by the known procedure.⁵

Purification by flash chromatography (5% EtOAc/hexanes) yields desired product (90%) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 0.87 (9H, d, J = 6.8), 1.03 (9H, s), 1.22-1.36 (3H, m), 1.58-1.69 (3H, m), 1.72-1.81 (2H, m), 1.87-1.96 (3H, m), 2.24 (1H, dd, J = 5.6, 14.4), 2.56-2.70 (3H, m), 2.72-2.85 (3H, m), 3.44 (1H, tt, J = 6.8, 12.4), 3.77-3.84 (2H, m), 4.00 (1H, dt, J = 4.6, 9.2), 5.38 (1H, d, J = 15.0), 5.83 (1H, dt, J = 7.0, 15.0), 7.34-7.38 (6H, m), 7.64-7.68 (4H, m); ¹³C NMR (75 MHz, CDCl₃) δ 18.2, 19.0, 22.2, 22.3, 25.1, 26.7, 26.8, 26.9, 27.0, 28.2, 29.9, 33.7, 35.7, 41.4, 44.6, 53.8, 60.9, 68.2, 73.4, 127.6, 129.5, 133.4, 133.5, 134.2, 135.7; IR (neat) ν_{max} 3070, 2953, 2929, 2856, 1462, 1427, 1111, 1084, 702; HRMS(CI, NH₃) *m/z* calc'd for C₃₅H₅₃O₂S₂Si₁ [M+H]⁺ 597.3256, found: 597.3231, [α]_D = + 27.78 (c=0.39, CHCl₃).

(5) Enders, D.; Schüßeler, T. *Tetrahedron Lett.* **2002**, 43, 3467-3470.

(+/-)-8-[1,3]Dithian-2-yl-oct-1-en-4-ol (1l). To an argon-filled round bottom flask were added 270 mg aldehyde **1j** (1.3 mmol), 0.32 mL

allyltrimethylsilane (2.0 mmol, 1.5 equiv.), and 6.6 mL CH_2Cl_2 (0.2 M), and the solution was cooled to $-78\text{ }^\circ\text{C}$. $\text{BF}_3 \cdot \text{OEt}_2$ (0.34 mL, 2.6 mmol, 2.0 equiv.) was added dropwise, and the reaction mixture was allowed to warm to $0\text{ }^\circ\text{C}$. After 24 hours, the reaction was quenched with saturated aq. NaHCO_3 . The layers were separated, and the aqueous layer was extracted $3 \times$ into CH_2Cl_2 . The combined organic layers were washed with H_2O , washed with brine, then dried over MgSO_4 . Following filtration, the organic layers concentrated *in vacuo*. Flash chromatography (silica, 10 $\rightarrow$ 20% EtOAc/hexanes) yields 250 mg (78%) of desired thioacetal **1l** as a pale yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 1.46-1.68 (4H, m), 1.75 (2H, dt, $J = 6.9, 7.6$), 1.81 (2H, m), 2.10 (3H, m), 2.26 (1H, m), 2.81, (4H, m), 3.61 (1H, m), 4.02 (1H, t, $J = 6.9$), 5.10 (2H, d, $J = 13.2$), 5.79 (1H, dt, $J = 7.4, 13.2$); ^{13}C NMR (75 MHz, CDCl_3) δ 25.1, 25.9, 26.4, 30.3, 35.2, 36.3, 41.9, 47.4, 70.3, 118.2, 134.8; IR (neat) ν_{max} 3409, 3073, 2932, 2856, 1639, 1457, 1422, 1275, 997, 909; HRMS (EI) m/z calc'd for $\text{C}_{12}\text{H}_{22}\text{O}_1\text{S}_2$ $[\text{M}]^+$ 246.1112, found: 246.1126.

(6S)-((2R)-Benzyloxy-2-[1,3]dithian-2-yl-ethyl)-(3S)-methyl-tetrahydro-pyran-2-one (1o). Prepared from the corresponding aldehyde by a known procedure.⁶

Purification by flash chromatography (30% EtOAc/hexanes) yields **1o** as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 1.13 (3H, d, $J = 6.8$), 1.35-1.47 (1H, m), 1.51-1.62 (1H, m), 1.74-2.02 (6H, m), 2.06-2.13 (1H, m), 2.24-2.33 (1H, m), 2.79-2.91 (4H, m), 4.05 (1H, ddd, $J = 3.6, 8.0, 13.2$), 4.27 (1H, dddd, $J = 3.2, 8.0, 11.6, 14.8$), 4.36 (1H, d, $J = 3.6$), 4.47 (1H, d, $J = 11.4$), 4.85 (1H, d, $J = 11.4$), 7.25-7.36 (5H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 15.7, 25.3, 26.1, 26.8, 30.3, 30.4, 32.7, 38.4, 52.3, 73.4, 73.8, 76.7, 127.9, 128.4, 128.5, 138.1, 176.3; IR (neat) ν_{max} 3583, 2932, 1739, 1454, 1242, 1182, 1080, 737; HRMS(EI) m/z calc'd for $\text{C}_{19}\text{H}_{27}\text{O}_3\text{S}_2$ $[\text{M}]^+$ 366.1323, found: 366.1345; $[\alpha]_D = +115.17$ ($c = 0.44$, CHCl_3).

2-[(5R)-Benzyloxy-(3S)-(tert-butyl-dimethylsilanyloxy)-6-(tert-butyl-diphenyl-silanyloxy)-hexyl]-2-styryl-[1,3]dithiane (1p). Prepared from the lithium anion of thioacetal **1s**

by the known procedure.⁵ Purification by flash chromatography (5% EtOAc/hexanes) yields **1p** (21%) as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ -0.02 (3H, s), -0.01 (3H, s), 0.85 (9H, s), 1.03 (9H, s), 1.52-1.71 (4H, m), 1.80-2.04 (4H, m), 2.62-2.72 (2H, m), 2.84-2.96 (2H, m), 3.58-3.74 (3H, m), 3.86-3.96 (1H, m), 4.42 (1H, d, $J = 11.4$), 4.64 (1H, d, $J = 11.4$), 6.14 (1H, d, $J = 15.6$), 6.75 (1H, d, $J = 15.6$), 7.24-7.40 (15H, m), 7.62 (5H, m); ^{13}C NMR (75 MHz, CDCl_3) δ -4.7, -4.1, 17.9, 19.1, 25.3, 25.8, 25.9, 26.7, 27.1,

(6) Marshall, J. A.; Belletire, J. L. *Tetrahedron Lett.* **1971**, 12, 871-874.

30.8, 31.8, 36.8, 39.7, 54.9, 49.0, 66.6, 68.8, 71.8, 77.3, 126.6, 127.3, 127.5, 127.7, 128.3, 128.6, 129.7, 132.8, 133.3, 133.6, 135.7, 136.5, 139.1; IR (neat) ν_{max} 3068, 3027, 2929, 2856, 1469, 1427, 1253, 1109, 700; HRMS(CI, NH_3) m/z calc'd for $\text{C}_{47}\text{H}_{65}\text{O}_3\text{S}_2\text{Si}_2$ $[\text{M}+\text{H}]^+$ 797.3913, found: 797.3819; $[\alpha]_{\text{D}} = +8.99$ ($c=0.55$, CHCl_3).

1-((6R)-[2-(*tert*-Butyl-diphenyl-silanyloxy)-ethyl]-(5S)-methyl-tetrahydro-pyran-(2S)-yl)-6-methyl-hept-3-en-2-one (2a). Prepared by general Dess-Martin periodinane hydrolysis procedure using **1a**, with a 12-hour reaction time. Purification by flash chromatography (10% EtOAc/hexanes)

yields **2a** (91%) as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 0.88 (6H, d, $J = 6.4$), 0.92 (3H, d, $J = 6.4$), 1.02 (9H, s), 1.23-1.50 (3H, m), 1.59-1.82 (5H, m), 2.02 (2H, ddd, $J = 1.2, 7.6, 8.4$), 2.70 (1H, dd, $J = 7.0, 7.0$), 2.80 (1H, dd, $J = 6.0, 6.0$), 3.47 (1H, dddd, $J = 3.6, 7.8, 9.2, 9.2$), 3.67-3.78 (2H, m), 4.22 (1H, dt, $J = 6.0, 7.0$), 6.03 (1H, d, $J = 15.8$), 6.73 (1H, ddd, $J = 7.2, 15.8, 15.8$), 7.31-7.48 (6H, m), 7.63-7.67 (4H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 18.2, 19.0, 22.3, 26.3, 26.7, 27.4, 27.7, 33.2, 35.3, 41.6, 43.4, 60.6, 67.9, 73.8, 127.6, 129.5, 129.6, 131.6, 134.2, 135.6, 146.8, 198.8; IR (neat) ν_{max} 2929, 2955, 2857, 1694, 1670, 1627, 1463, 1386, 1111, 702; HRMS(CI, NH_3) m/z calc'd for $\text{C}_{32}\text{H}_{47}\text{O}_3\text{Si}_1$ $[\text{M}+\text{H}]^+$ 507.3294, found: 507.3286; $[\alpha]_{\text{D}} = +17.07$ ($c=0.41$, CHCl_3).

(+/-)-6-Hydroxy-non-8-enal (2l). Prepared by general Dess-Martin periodinane hydrolysis procedure using thioacetal **1l**, with a 2-hour reaction time. Purification by flash chromatography (25→40% EtOAc/hexanes) yields **2l** (85%) as

a pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 1.30-1.55 (4H, m), 1.59-1.76 (2H, m), 2.13 (1H, m), 2.29 (1H, m), 2.43 (2H, m), 3.61 (1H, m), 5.18 (2H, d, $J = 12.4$), 5.80 (1H, dt, $J = 6.8, 12.4$), 9.78 (1H, s); ^{13}C NMR (75 MHz, CDCl_3) δ 24.9, 25.4, 26.5, 35.0, 36.1, 71.7, 116.2, 130.8, 202.6; IR (neat) ν_{max} 3420, 2980, 2950, 2840, 1720, 1350, 1092, 997; HRMS(CI, NH_3) m/z calc'd for $\text{C}_9\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$ 157.1229, found: 157.1237.

Compound 2o. Prepared by general Dess-Martin periodinane hydrolysis procedure using thioacetal **1o**, with a 12-hour reaction time. Purification by flash chromatography (30% EtOAc/hexanes) yields **2o** (68%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3)

δ 1.19 (3H, d, $J = 6.8$), 1.44-1.73 (3H, m), 1.83-1.89 (1H, m), 1.91-2.09 (2H, m), 2.42-2.49 (1H, m), 4.20 (1H, dddd, $J = 0.8, 2.8, 4, 10.8$), 4.43 (1H, dddd, $J = 2.8, 5.6, 10.8$), 4.52 (1H, d, $J = 11.2$), 4.74 (1H, d, $J = 11.2$), 7.27-7.36 (5H, m), 9.65 (1H, d, $J = 0.8$); ^{13}C NMR (75 MHz, CDCl_3) δ 16.0, 25.5, 27.0, 33.1, 35.7, 73.2, 73.5, 77.2, 79.8, 128.3, 128.6, 137.1, 175.5, 202.0; IR (neat) ν_{max} 3020, 2937, 2877, 1497, 1455, 1382, 1190, 934; HRMS(CI, NH_3) m/z calc'd for $\text{C}_{16}\text{H}_{21}\text{O}_4$ $[\text{M}+\text{H}]^+$ 277.1439, found: 277.1442; $[\alpha]_{\text{D}} = +103.83$ ($c=0.47$, CHCl_3).

Compound 2p. Prepared by general Dess-Martin periodinane hydrolysis procedure using thioacetal **1p**, with a 12-hour reaction time. Purification by flash chromatography (10% EtOAc/hexanes) yields **2p** (82%) as a pale yellow oil.

^1H NMR (400 MHz, CDCl_3) δ -0.03 (3H, s), -0.02 (3H, s), 0.89 (9H, s), 1.05 (9H, s), 1.56-1.92 (4H, m), 2.68 (2H, t, J = 8.0), 3.60-3.78 (3H, m), 3.96-4.02 (1H, m), 4.44 (1H, d, J = 11.4), 4.66 (1H, d, J = 11.4), 6.69 (1H, d, J = 16.8), 7.24-7.43 (14H, m), 7.48-7.54 (3H, m), 7.64-7.68 (4H, m); ^{13}C NMR (75 MHz, CDCl_3) δ -4.6, -4.2, 19.8, 25.9, 26.7, 29.6, 31.7, 35.6, 39.7, 66.4, 68.5, 71.9, 77.3, 126.4, 127.5, 127.7, 127.8, 128.34, 128.39, 128.4, 129.0, 129.8, 130.5, 133.6, 138.7, 139.0, 142.4, 200.4; IR (neat) ν_{max} 3584, 3401, 2959, 2842, 1647, 1620, 1410, 1119, 742; HRMS(CI, NH_3) m/z calc'd for $\text{C}_{44}\text{H}_{59}\text{O}_4\text{Si}_2$ $[\text{M}+\text{H}]^+$ 707.3952, found: 707.3863; $[\alpha]_{\text{D}} = +14.16$ ($c=0.60$, CHCl_3).

Acetic acid 6,6-dimethoxy-hexyl ester (3a). Prepared by general Dess-Martin periodinane direct thioacetal to acetal procedure using thioacetal **1h**, 8:1:1 $\text{CH}_3\text{CN}:\text{CH}_2\text{Cl}_2:\text{MeOH}$

solvent mixture, with starting material consumption after a 9-hour reaction time. Purification by flash chromatography (10→15% EtOAc/hexanes) yields **3a** (91%) as a pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 1.35 (4H, m), 1.59 (4H, m), 2.02 (3H, s), 3.29 (6H, s), 4.03 (2H, t, J = 6.6), 4.33 (1H, t, J = 5.6); ^{13}C NMR (75 MHz, CDCl_3) δ 20.7, 24.0, 25.6, 28.3, 32.1, 52.4, 64.2, 104.3, 171.1; IR (neat) ν_{max} 2946, 2863, 2830, 1739, 1464, 1386, 1366, 1240, 1131, 1053; HRMS(CI, NH_3) m/z calc'd for $\text{C}_{10}\text{H}_{21}\text{O}_4$ $[\text{M}+\text{H}]^+$ 205.1440, found: 205.1448.

2-Phenethyl-[1,3]dioxolane 3c. Prepared by general Dess-Martin periodinane direct thioacetal to acetal procedure using thioacetal **1t**, 8:1:1 $\text{CH}_3\text{CN}:\text{CH}_2\text{Cl}_2$:ethylene glycol solvent mixture, with starting material consumption after a 12-hour reaction time. Purification by

flash chromatography (4% EtOAc/hexanes) yields **3c** (74%) as a pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 1.98 (2H, ddd, J = 4.6, 5.9, 10.3), 2.75 (2H, dd, J = 5.9, 10.3), 3.86 (2H, dd, J = 3.5, 5.3), 3.99 (2H, dd, J = 3.5, 5.3), 4.89 (1H, t, J = 4.6), 7.18-7.29 (5H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 30.0, 35.4, 64.9, 103.8, 125.9, 128.4, 141.7; IR (neat) ν_{max} 3062, 3026, 2954, 2882, 1603, 1496, 1454, 1410, 1180, 1139, 1031; HRMS(CI, NH_3) m/z calc'd for $\text{C}_{11}\text{H}_{15}\text{O}_2$ $[\text{M}+\text{H}]^+$ 179.1072, found: 179.1061.

5,5-Dimethyl-2-styryl-[1,3]dioxane 3d. To an argon-filled round bottom flask were added thioacetal **1s** (200 mg, 0.90 mmol), neopentyl glycol (940 mg, 9.0 mmol, 10 equiv.), and 4.5 mL CH_2Cl_2 (0.20 M). DMP (760 mg, 1.8 mmol, 2.0 equiv.) was added in one portion, and the reaction was stirred at rt for 35

minutes, until starting material was consumed by TLC analysis. The reaction was quenched with saturated aq. NaHCO_3 , extracted 3 $\times$ into CH_2Cl_2 , and the combined organic layers were washed with brine, dried over MgSO_4 , filtered, and concentrated *in vacuo*. Purification by flash chromatography (5→10% EtOAc/hexanes) affords 170 mg (88% yield) of **3d** as a white solid: ^1H NMR (400 MHz, CDCl_3) δ 0.74 (3H, s), 1.23 (3H,

s), 3.53 (2H, d, J = 10.6), 3.68 (2H, d, J = 10.6), 5.02 (1H, d, J = 4.6), 6.21 (1H, dd, J = 4.6, 16.2), 6.76 (1H, d, J = 16.2), 7.22-7.40 (5H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 21.8, 22.9, 30.1, 77.3, 100.9, 125.6, 126.9, 128.2, 128.5, 133.5, 136.1; IR (neat) ν_{max} 3054, 2950, 2856, 1466, 1451, 1392, 1369, 1153, 1099, 1014, 984, 970, 929; HRMS(CI, NH_3) m/z calc'd for $\text{C}_{14}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$ 219.1385, found: 219.1376; m.p. = 51 °C.