Supporting Information for:

"Selective Rhenium-Catalyzed Oxidation of Secondary Alcohols With Methyl Sulfoxide in the Presence of Ethylene Glycol, A Convenient One-Pot Synthesis of Ketals"

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General Considerations. All experiments were performed in an efficient fume hood. Solvents and reagents were purchased from the Aldrich Chemical Company and used without further purification. Silica gel 60, 70-230 mesh was used for column chromatography. Dichloromethane was purchased from Baker. Potassium perrhenate ($KReO_4$) was purchased from Johnson-Matthey. Deuterated solvents were purchased from Aldrich or Norell, and were used without further purification. The complex $Re(O)Cl_3(PPh_3)_2$ (**I**) was prepared according to the published procedure: Johnson, N. P.; Lock, C. J. L.; Wilkinson, G. *Inorg. Synth.* **1967**, *9*, 145).

NMR spectra were acquired at ambient temperatures (18 ± 2 ˚C), unless otherwise noted, using a Varian Gemini 200 Fourier transform spectrometer. The ^1H NMR spectra in $CDCl_3$ were referenced to TMS. The $^{13}C\{^1H\}$ NMR spectra were recorded at 50 MHz and referenced relative to the $^{13}C\{^1H\}$ peaks of the solvent. Spectra are reported as δ (ppm) (number of hydrogens, multiplicity, coupling constants (Hz)).

General Experimental Procedures for Alcohol Oxidation

Method A: To a mixture of the alcohol (1 mmol), ethylene glycol (0.22 mL, 4 mmol), dimethyl sulfoxide (0.15 mL, 2.1 mmol) and $Re(O)Cl_3(PPh_3)_2$ (42 mg, 0.05 mmol) was added toluene (5 mL). The flask was equipped with a Dean-Stark trap and the solution was refluxed. Additional portions of ethylene glycol (0.44 mL, 8 mmol) were added to the reaction mixture after 1 hr and 3 hr. After a total reaction time of 5 hours, the reaction was removed from the heat and allowed to cool. The reaction mixture was then washed with saturated $NaHCO_3$ (10 mL) and water (10 mL). The organic layer was dried over $MgSO_4$ and the volatiles were removed *in vacuo*.

Method B: To a mixture of substrate (1 mmol), ethylene glycol (0.22 mL, 4 mmol), dimethyl sulfoxide (0.15 mL, 2.1 mmol), 2,4,6-collidine (3.3 μL, 0.025 mmol) and $Re(O)Cl_3(PPh_3)_2$ (42 mg, 0.05 mmol) was added toluene (5 mL). The flask was equipped with a Dean-Stark trap and the solution was refluxed. After a total reaction time of 1 and 3 hours, additional portions of ethylene glycol (0.44 mL, 8 mmol) were added to the reaction mixture. After a total reaction time of 5 hours, the reaction was removed from the heat and allowed to cool. The reaction mixture was then washed with saturated $NaHCO_3$ (10 mL) and water (10 mL). The organic layer was dried over $MgSO_4$ and the volatiles were removed *in vacuo*.

2-Dodecanone Ethylene Ketal: 2-Dodecanol (0.22 mL, 1 mmol) was reacted using the conditions of Method A. The product was purified by silica gel chromatography using CH_2Cl_2 as the eluent. The ketal was obtained as a colorless oil (197 mg, 0.86 mmol, 86%): ^{1}H-NMR ($CDCl_3$) δ 0.88 (3H, t, J = 6.8 Hz), 1.08-1.45 (16H, m), 1.31 (3H, s), 1.61 (2H, m), 3.93 (4H, s); ^{13}C-NMR ($CDCl_3$) δ 13.9, 22.5, 23.5, 23.9, 29.1, 29.4, 29.6, 31.7, 39.1, 64.4, 110.0.

2-Undecyl-1,3-dioxolane: 1-Dodecanol (186 mg, 1 mmol) was reacted using the conditions of Method A with modifications to the procedure described below. The total reaction time was 23 hours and additional portions of ethylene glycol (0.44 mL, 8 mmol) were added after a total reaction time of 1, 3 , 5 , 7 and 9 hours. Additional portions of DMSO were added after a total reaction time of 3 and 7 hours. The product was purified by silica gel chromatography using CH_2Cl_2 as the eluent. The acetal was obtained as a colorless oil (193 mg, 0.85 mmol, 85%): ^{1}H-NMR ($CDCl_3$) δ 0.88 (3H, t, J = 6.8 Hz), 1.26 (18H, m), 1.65 (2H, m), 3.78-4.02 (4H, m), 4.84, (1H, t, J = 4.8 Hz); ^{13}C-NMR ($CDCl_3$) δ 13.9, 22.5, 23.9, 29.4, 31.8, 33.8, 64.7, 104.6.

Geranylacetone Ethylene Ketal: 1-Geranyl-2-prapanol (196 mg, 1 mmol) was reacted using the conditions of Method A. The product was purified by silica gel chromatography using CH_2Cl_2 as the eluent. The ketal was obtained as a colorless oil (195 mg,, 0.82 mmol, 82%): ^{1}H-NMR ($CDCl_3$) δ 1.33 (3H, s), 1.60 (6H, s), 1.68 (3H, s), 1.88-2.21 (6H, m), 3.94 (4H, s), 5.12 (2H, m); ^{13}C-NMR ($CDCl_3$) δ 15.7, 17.5, 22.4, 23.6, 25.5, 26.5, 38.9, 39.5, 64.4, 109.8, 123.8, 124.2, 131.1, 135.0.

Estrone Ethylene Ketal: β-Estradiol (272 mg, 1mmol) was reacted using the conditions of Method A. The ketal and ketone products were not separable by chromatography under the conditions investigated. The product mixture was dissolved in

methanol (10 mL), and treated with $NaBH_4$ (39 mg, 1 mmol) to reduce the remaining ketone. The solution stirred for 30 minutes, and was then concentrated to a volume of 2 mL *in vacuo*. The residue was diluted with 10 mL CH_2Cl_2 and washed with water (10 mL). The organic solution was dried over $MgSO_4$, and the volatiles were removed *in vacuo*. The product was purified by silica gel chromatography using 2% MeOH/CH_2Cl_2 as the eluent. The ketal was obtained as a white solid (258 mg, 0.82 mmol, 82%): ^{1}H-NMR ($CDCl_3$) δ 0.88 (3H, s), 1.15-2.35 (9H, m), 2.65-2.85 (2H, m), 3.93 (4H, m), 5.83 (1H, s), 6.55 (1H, s), 6.61 (1H, d, J = 8 Hz), 7.12 (1H, d, J = 8 Hz); ^{13}C-NMR ($CDCl_3$) δ 14.1, 22.1, 25.9, 26.7, 29.4, 30.6, 34.1, 38.9, 43.4, 46.0, 49.2, 64.4, 65.1, 112.6, 115.2, 119.6, 126.3, 132.4, 138.0, 153.4.

2-Phenyl-1,3-dioxolane: Benzyl alcohol (153 mg, 1 mmol) was reacted using the conditions of Method B. The product was purified by silica gel chromatography using CH_2Cl_2 as the eluent. The acetal was obtained as a light yellow oil (131 mg, 0.87 mmol, 87%). ^{1}H- and ^{13}C-NMR matched those of authentic material: Aldrich FT-NMR **1**(2),229C.

2-(4-Nitrophenyl)-1,3-dioxolane: 4-Nitrobenzyl alcohol (153 mg, 1 mmol) was reacted using the conditions of Method A. The product was purified by silica gel chromatography using CH_2Cl_2 as the eluent. The acetal was obtained as a pale yellow solid (180 mg, 0.92 mmol, 92%): ^{1}H-NMR ($CDCl_3$) δ 4.10 (4H, m), 5.89 (1H, s), 7.65 (2H, d, J = 8.5 Hz), 8.23 (2H, d, 8.4 Hz); ^{13}C-NMR δ 65.3, 102.1, 123.4, 127.3, 144.9, 148.3.

2-Methyl-2-(4-nitrophenyl)-1,3-dioxolane: 1-(4-Nitrophenyl)-1-ethanol (167 mg, 1 mmol) was reacted using the conditions of Method A. The product was purified by silica gel chromatography using CH_2Cl_2 as the eluent. The ketal was obtained as a pale yellow solid (183 mg, 0.88 mmol, 88%): ^{1}H-NMR ($CDCl_3$) δ 1.66 (3H, s), 3.79 (2H, m), 4.10 (2H, m), 7.68 (2H, d, J = 8.7 Hz), 8.20 (2H, d, J = 8.7 Hz); ^{13}C-NMR ($CDCl_3$) δ 27.2, 64.5, 107.9, 123.4, 126.3, 147.5, 150.5.

(-)-Menthone Ethylene Ketal: a) (1R, 2S, 5R)-(-)-Menthol (156 mg, 1 mmol) was reacted using the conditions of Method A with modifications to the workup described below. After the reaction was complete, the solution was diluted with CH_2Cl_2 (10 mL) and combined with the contents of the Dean-Stark trap in a separatory funnel and the solution was washed with saturated $NaHCO_3$ (10 mL). The solution was then dried over Na_2SO_4, and the volatiles were removed *in vacuo*. The product was purified by bulb to bulb distillation. A colorless oil was obtained containing ketal as a 6 : 1 mixture of diastereomers (133 mg, 0.67 mmol, 67%): ^{1}H-NMR ($CDCl_3$) δ 0.68-1.08 (11H, m), 1.29-1.45 (2H, m), 1.47-1.80 (4H, m), 2.10 (1H, h, J = 6.6 Hz), 3.79-4.05 (4H, m); ^{13}C-NMR ($CDCl_3$) δ 18.1, 21.9, 23.2, 24.5, 30.3, 34.4, 44.5, 49.1, 64.1, 64.4, 111.6, and ketone (26 mg, 0.17 mmol, 17%). ^{1}H- and ^{13}C-NMR matched those of authentic material: Aldrich FT-NMR **1**(1),672A. b) (1R, 2S, 5R)-(-)-Menthol (156 mg, 1 mmol) was reacted using the conditions of Method B with modifications to the procedure described below. The reaction refluxed for a total of 7 hours, and after the reaction was complete, the solution was diluted with CH_2Cl_2 (10 mL) and combined with the contents of the Dean-Stark trap in a separatory funnel and the solution was washed with saturated

$NaHCO_3$ (10 mL). The solution was then dried over Na_2SO_4, and the volatiles were removed *in vacuo*. The product was purified by bulb to bulb distillation. A colorless oil was obtained containing ketal as a 6 : 1 mixture of diastereomers (161 mg, 0.81 mmol, 81%), and ketone (13 mg, 0.08 mmol, 8%).

5α-Cholestan-3-one Ethylene Ketal: a) (+)-Dihydrocholesterol (389 mg, 1mmol) was reacted using the conditions of Method A. The product was purified by silica gel chromatography using CH_2Cl_2 as the eluent. The ketal was obtained as a white solid (400 mg, 0.93 mmol, 93%): ^{1}H-NMR ($CDCl_3$) δ 0.65 (3H, s), 0.81 (3H, s), 0.86 (3H, d, J = 6.8 Hz), 0.89 (3H, d, J = 6.6 Hz), 0.69-2.00 (31H, m), 3.93 (4H, s); ^{13}C-NMR ($CDCl_3$) δ 11.2, 11.9, 18.5, 21.0, 22.5, 23.6, 24.0, 27.8, 28.2, 28.4, 31.0, 31.8, 35.3, 35.5, 35.9, 37.8, 39.3, 39.9, 42.4, 43.5, 53.9, 56.1, 63.9, 109.2. b) (+)-Dihydrocholesterol (389 mg, 1mmol) was reacted using the conditions of Method B. The product was purified by silica gel chromatography using CH_2Cl_2 as the eluent. The ketal was obtained as a white solid (430 mg, 1.00 mmol, 100%).

2,2,4-Trimethyl-1-hydroxy-3-pentanone: To a mixture of 2,2,4-trimethyl-1,3-pentanediol (146 mg, 1 mmol), ethylene glycol (0.22 mL, 4 mmol), dimethyl sulfoxide (85 μL, 1.2 mmol), 2,4,6-collidine (6.6 μL, 0.05 mmol) and $Re(O)Cl_3(PPh_3)_2$ (42 mg, 0.05 mmol) was added toluene (5 mL). A Dean-Stark trap was attached and the solution was refluxed. An additional portion of ethylene glycol (0.44 mL, 8 mmol) was added after 1 hr. The reaction was removed from the heat after a total of 3 hours and was allowed to cool. The solution was diluted with CH_2Cl_2 (10 mL) and combined with the contents of the Dean-Stark trap in a separatory funnel. The solution was washed with saturated $NaHCO_3$ (10 mL), dried over Na_2SO_4 and the volatiles were removed *in vacuo*. The product was purified by bulb to bulb distillation. The ketone was obtained as a colorless oil (128 mg, 0.89 mmol, 89%): ^{1}H-NMR ($CDCl_3$) δ 1.06 (6H, d, J = 6.6 Hz), 2.76 (1H, bs), 3.10 (1H, h, J = 6.6 Hz), 3.55 (2H, s); ^{13}C-NMR ($CDCl_3$) δ 19.7, 20.8, 34.4, 49.5, 69.2, 221.5.

1,7-Dioxaspiro[5.5]undecane: To a mixture of 1,5,9-nonanetriol (30 mg, 0.2 mmol), ethylene glycol (76 μL, 0.8 mmol), dimethyl sulfoxide (14.5 μL, 0.2 mmol), 2,4,6-collidine (1.1 μL, 0.0085 mmol) and $Re(O)Cl_3(PPh_3)_2$ (7 mg, 0.0085 mmol) was added toluene (3 mL). A Dean-Stark trap was attached and the solution was refluxed for 3 hours. After cooling, the solution and the contents of the Dean-Stark trap were loaded directly onto a silica gel column using CH_2Cl_2 as the eluent. After all of the toluene had passed through the column, an additional 30 ml of CH_2Cl_2 was eluted. Then 1% MeOH/CH_2Cl_2 was used as the eluent. The fractions containing the desired product were collected, and the solvent was removed by distillation. The spiroketal was obtained as a pale yellow oil (15 mg, 0.096 mmol, 57%). The ^{1}H- and ^{13}C-NMR matched those of authentic material: Aldrich FT-NMR **1**(1),407B.