Supporting Information for
Conversion of Epoxides to 1,3-Dioxolanes Catalyzed by Tin (II)
Chloride

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Acetone used in this study was dried over B_2O_3 and distilled prior to use.¹ Anhydrous $SnCl_2$ (98%) was used as received from commercial suppliers. Epoxides **3h**,² **5**,³ **9**,⁴ and **11**⁴ were prepared following literature procedures. All reactions involving air- or moisture-sensitive materials were performed in oven-dried glassware under an argon atmosphere. Purifications were done using medium pressure liquid chromatography (MPLC) performed with columns of silica gel (230-400 mesh) at 40-100 psi, using various solvent mixtures (such as 50:1 hexanes:ethyl acetate), a Fluid Metering, Inc. solvent pump, and a refractive index / UV detector. All coupling constant values are in Hz.

Preparation of 2-cyclohexyloxirane (3h).² Vinylcyclohexane (4.34 mL, 3.47 g, 31.7 mmol) was added dropwise through an addition funnel to a cold solution of *m*-CPBA (8.63 g, 70-75%, 35.0 mmol) and Na_2HPO_4 (9.958 g, 70.1 mmol) in CH_2Cl_2 (150 mL). After 1.75 hours at room temperature, more *m*-CPBA (2.0 g) and CH_2Cl_2 (40 mL) added to the flask. The mixture was stirred overnight at room temperature. The solids were filtered off and the filtrate was treated with Na_2SO_3 and H_2O and extracted with ether (2×). The organics were washed (H_2O , brine, sat. Na_2CO_3) and dried over Na_2SO_4 . The ether and CH_2Cl_2 were removed by distillation at atmospheric pressure and the crude product was purified by distillation under reduced pressure (bp = 74 – 76 °C @ 25 mmHg) to yield desired epoxide **3h** as a colorless oil (1.632 g, 41%). **IR** (neat): 1256, 1131, 979, 944, 880, 859, 837, and 802 cm^{-1} . **1H NMR** ($CDCl_3$, 300 MHz): δ 2.71 (m, 2H), 2.52 (m, 1H), 1.90 (m, 1H), 1.8-1.6 (m, 4H), and 1.3-1.0 (m, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 56.4, 45.7, 40.2, 29.5, 28.6, 26.2, 25.5, and 25.4.

Preparation of 2-(9-methoxymethoxynonyl)oxirane (3i). ω -Undecylenyl alcohol (5 mL, 4.25 g, 25 mmol) and dimethoxymethane (25 mL) were added to a 100 mL round-bottomed flask.

LiBr (0.305 g, 3.5 mmol) and TsOH·H₂O (0.082 g, 0.43 mmol) were then added. The flask was capped and the mixture was stirred at room temperature. After 60 h the reaction was quenched with brine and extracted with ether (3×). The combined organics were washed with 5% NaHCO₃ solution and brine, dried over MgSO₄ and concentrated. Distillation of the crude product (bp = 80 °C @ 0.2 mmHg) gave pure 11-methoxymethoxy-1-undecene (4.8 g, 90%). **IR** (neat, NaCl): 3076, 1640, 1213, 1148, 1111, 1046, 993, and 914 cm⁻¹. **¹H NMR** (CDCl₃, 300 MHz): δ 5.85 (ddt, *J* = 17.5, 10.0, 6.5, 1H), 4.98 (ddt, *J* = 17.5, 1.5, 1.5, 1H), 4.91 (ddt, *J* = 10.0, 1.5, 1.5, 1H), 4.61 (s, 2H), 3.51 (t, *J* = 6.5, 2H), 3.35 (s, 3H), 2.04 (dt (app q), *J* = 6.5, 6.5, 2H), 1.58 (pentet, *J* = 6.5, 2H), and 1.4-1.2 (m, 12H). **¹³C NMR** (CDCl₃, 75 MHz): δ 139.1, 114.0, 96.3, 67.8, 55.1, 33.9, 29.8, 29.6, 29.5 (2C), 29.2, 29.0, and 26.3. Anal. Calcd for C₁₃H₂₆O₂: C, 72.84; H, 12.23. Found: C, 72.90; H, 12.41.

11-methoxymethoxyundec-1-ene (3.225 g, 15 mmol), Na₂HPO₄ (4.259 g, 30 mmol), and CH₂Cl₂ (75 mL) were added sequentially to a 200 mL round-bottomed flask cooled in an ice bath. *m*-CPBA (4.065 g, 16.5 mmol) was added and the mixture was warmed to room temperature. After 4 h more *m*-CPBA (0.175 g) was added and the mixture was stirred overnight. After TLC analysis showed no starting material the reaction was quenched with Na₂SO₃ and H₂O, then extracted with ether (3×). The combined organic layers were washed with H₂O, Na₂CO₃ solution (2×) and brine. The solution was then dried over Na₂SO₄ and concentrated. MPLC of the crude product (9:1 hexanes:ethyl acetate) gave pure epoxide **3i** (3.017 g, 87%). **IR** (neat, NaCl): 1257, 1213, 1147, 1110, 1045, and 918 cm⁻¹. **¹H NMR** (CDCl₃, 300 MHz): δ 4.60 (s, 2H), 3.51 (t, *J* = 6.5, 2H), 3.35 (s, 3H), 2.90 (tdd, *J* = 5.0, 4.0, 2.6, 1H), 2.74 (dd, *J* = 5.0, 4.0, 1H), 2.46 (dd, *J* = 5.0, 2.6, 1H), and 1.7-1.2 (m, 16H). **¹³C NMR** (CDCl₃, 75 MHz): δ 96.1, 67.5, 54.8, 52.1, 46.8,

32.3, 29.6, 29.3(2C), 29.26, 29.2, 26.1, and 25.8. Anal. Calcd for C₁₃H₂₆O₃: C, 67.79; H, 11.38. Found: C, 67.50; H, 11.65.

Preparation of 2-(9-benzyloxynonyl)oxirane (3j). NaH (60% in mineral oil, 1.28 g, 32.0 mmol) was washed with hexanes (3×) then ω-undecylenylalcohol (5.0 mL, 4.25 g, 25.0 mmol) was added as a solution in DMF (50 mL). After 1.5 h benzyl bromide (3.8 mL, 5.46 g, 31.9 mmol) was added dropwise and the mixture was stirred overnight. The reaction was quenched with NH₄Cl solution and extracted with ether (3×). The combined organic layers were washed with H₂O and brine, dried over MgSO₄, and concentrated. The crude product was purified using flash chromatography (19:1 hexanes: ethyl acetate) to yield pure 10-undecenyloxymethylbenzene (5.08 g, 78%). **IR** (neat, NaCl): 3065, 3029, 1639, 1203, 1102, 1027, 734, and 696 cm⁻¹. **¹H NMR** (CDCl₃, 300 MHz): δ 7.30 (m, 5H), 5.80 (ddt, *J* = 17.0, 10.0, 6.7, 1H), 4.98 (ddt, *J* = 17.0, 2.3, 1.5, 1H), 4.91 (ddt, *J* = 10.0, 2.3, 1.2, 1H), 4.49 (s, 2H), 3.45 (t, *J* = 7.0, 2H), 2.03 (dt, *J* = 7.6, 6.7, 2H), 1.6 (pentet, *J* = 6.7, 2H), and 1.4-1.2 (m, 12H). **¹³C NMR** (CDCl₃, 75 MHz): δ 138.8, 138.5, 128.0, 127.3, 127.2, 114.0, 72.7, 70.3, 33.3, 29.8, 29.5, 29.4(2C), 29.1, 28.9, and 26.2.

10-undecenyloxymethylbenzene (3.106 g, 11.9 mmol), Na₂HPO₄ (3.407 g, 24.0 mmol), and CH₂Cl₂ (60 mL) were added sequentially to a 200 mL flask that was cooled in an ice bath. *m*-CPBA (3.254 g, 13.0 mmol) was added and the mixture was allowed to warm to room temperature. After 4 h more *m*-CPBA (0.225 g) was added and the reaction was stirred overnight. After TLC analysis showed no starting material, the reaction was quenched with Na₂SO₃ and H₂O then extracted with ether (3×). The combined organic layers were washed with H₂O, Na₂CO₃ solution (2×) and brine. The solution was dried over Na₂SO₄ then

concentrated to yield **3j** (2.58 g, 93%) in sufficient purity for subsequent reactions. An analytical sample was prepared using MPLC (9:1 hexanes:ethyl acetate). **IR** (neat, NaCl): 3032, 1101, 833, 736, and 697 cm^{-1} . **^1H NMR** (CDCl_3 , 300 MHz): δ 7.4-7.2 (m, 5H), 4.49 (s, 2H), 3.45 (t, J = 6.7, 2H), 2.90 (tdd, J = 5.3, 4.1, 2.6, 1H), 2.74 (dd, J = 5.0, 4.1, 1H), 2.46 (dd, J = 5.0, 2.6, 1H), and 1.7-1.2 (m, 16H). **^{13}C NMR** (CDCl_3 , 75 MHz): δ 138.5, 128.1, 127.4, 127.2, 72.7, 70.4, 52.3, 47.0, 32.4, 29.7, 29.44, 29.40, 29.38(2C), 26.2, and 26.0. Anal. Calcd for $\text{C}_{18}\text{H}_{28}\text{O}_2$: C, 78.21; H, 10.21. Found: C, 78.27; H, 10.22.

Preparation of *tert*-Butyldimethyl-9-oxiranylnonyloxysilane (3k). TBSCl (2.51 g, 16.7 mmol) and imidazole (1.23 g, 18.0 mmol) were added to a 100 mL three-necked flask with a stir bar. The flask was cooled in an ice bath and dry DMF (30 mL) was added via syringe. ω -Undecylenylalcohol (3.0 mL, 2.55 g, 15.0 mmol) was added dropwise, and the mixture was warmed to room temperature and stirred for 72 h. The reaction was then quenched with water and extracted with hexanes (3 $\times$). The combined organic layers were washed with water and brine, then dried over MgSO_4 . Concentration of the solution yielded crude product that was purified using flash chromatography (50:1 hexanes:ethyl acetate) to yield *tert*-Butyldimethyl-10-undecenyloxysilane (3.15 g, 74%). **IR** (neat, NaCl): 3078, 1641, 1255, 1101, 1006, 907, 836, 775, 721, and 661 cm^{-1} . **^1H NMR** (CDCl_3 , 300 MHz): δ 5.80 (ddt, J = 17.0, 10.3, 6.8, 1H), 4.98 (ddt, J = 17.0, 5.3, 1.5, 1H), 4.91 (ddt, J = 10.3, 3.5, 1.5, 1H), 3.59 (t, J = 6.5, 2H), 2.02 (dtt, J = 6.5, 6.5, 1.5, 2H), 1.6-1.2 (m, 14H), 0.89 (s, 9H), and 0.05 (s, 6H). **^{13}C NMR** (CDCl_3 , 75 MHz): δ 139.1, 114.0, 63.3, 33.9, 33.0, 29.7, 29.54, 29.52, 29.2, 29.0, 26.1(2C), 25.9, 18.5, and -5.1. Anal. Calcd for $\text{C}_{17}\text{H}_{36}\text{OSi}$: C, 71.76; H, 12.75. Found: C, 71.52; H, 13.00.

tert-Butyldimethyl-10-undecenylloxysilane (3.305 g, 11.6 mmol), Na₂HPO₄ (4.30 g, 30.0 mmol), and CH₂Cl₂ (75 mL) were added to a 200 mL round-bottomed flask that was cooled in an ice bath. *m*-CPBA (3.40 g, 19.7 mmol) was added and the mixture was warmed to room temperature. After two hours, the reaction was quenched with Na₂SO₃ and H₂O and extracted with ether (3×). Combined organic layers were washed with H₂O, Na₂CO₃ solution, and brine. After drying over Na₂SO₄ the solution was concentrated and the residue was purified with flash chromatography (19:1 hexanes:ethyl acetate) to yield pure epoxide **3k** (3.26 g, 93%). **IR** (neat, NaCl): 1256, 1099, 1006, 939, 918, 836, 722, and 662 cm⁻¹. **¹H NMR** (CDCl₃, 300 MHz): δ 3.59 (t, *J* = 6.6, 2H), 2.90 (tdd, *J* = 5.3, 3.8, 2.9, 1H), 2.74 (dd, *J* = 5.0, 3.8, 1H), 2.46 (dd, *J* = 5.0, 2.9, 1H), 1.6-1.2 (m, 16H), 0.89 (s, 9H), 0.05 (s, 6H). **¹³C NMR** (CDCl₃, 75 MHz): δ 63.3, 52.4, 47.1, 32.9, 32.5, 29.6, 29.54, 29.47, 29.4, 26.0(3C), 25.8, 18.4, and -5.2. Anal. Calcd for C₁₇H₃₆O₂Si: C, 67.94; H, 12.07. Found: C, 67.76; H, 12.39.

Preparation of 2-[9-(4-methoxybenzyloxy)nonyl]oxirane (3l). NaH (60 % in mineral oil, 0.72 g, 18 mmol) was added to a 100 mL flask and washed with hexanes (3×). Dry THF (30 mL) was added while the flask was cooled in an ice bath. ω-Undecenylalcohol (3.0 mL, 2.55 g, 15.0 mmol) was added dropwise. The mixture was warmed to room temperature and stirred for 30 minutes. The flask was then cooled in an ice bath and *p*-methoxybenzyl chloride (2.25 mL, 2.60 g, 16.6 mmol) in dry THF (10 mL) was added slowly and the mixture was allowed to warm to room temperature. The reaction was stirred for 72 hours then quenched with NH₄Cl solution and extracted with ether (3×). The combined organic layers were washed with water and brine then dried over MgSO₄. After filtration and concentration the crude product thus obtained was purified using flash chromatography (30:1 hexanes:ethyl acetate) to yield pure 1-

methoxy-4-(10-undecenylloxymethyl)benzene (3.483 g, 80%). **IR** (neat, NaCl): 3074, 1640, 1613, 1586, 1513, 1248, 1208, 1173, 1099, 1038, 994, 910, 821, 756, and 722 cm⁻¹. **¹H NMR** (CDCl₃, 300 MHz): δ 7.25 (m, 2H), 6.85 (m, 2H), 5.80 (ddt, *J* = 17.0, 10.3, 6.7, 1H), 4.97 (ddt, *J* = 17.0, 2.0, 1.5, 1H), 4.91 (ddt, *J* = 10.3, 2.0, 1.2, 1H), 4.42 (s, 2H), 3.79 (s, 3H), 3.42 (t, *J* = 6.8, 2H), 2.04 (dt, *J* = 7.6, 6.7, 2H), 1.59 (pentet, *J* = 7.0, 2H), and 1.4-1.2 (m, 12H). **¹³C NMR** (CDCl₃, 75 MHz): δ 158.8, 138.9, 130.5, 128.9, 113.9, 113.5, 72.4, 70.0, 55.0, 33.8, 29.7, 29.5, 29.43, 29.41, 29.1, 28.9, and 26.2. Anal. Calcd for C₁₉H₃₀O₂: C, 78.57; H, 10.41. Found: C, 78.39; H, 10.70.

1-methoxy-4-(10-undecenylloxymethyl)benzene (2.902 g, 9.99 mmol), Na₂HPO₄ (2.85 g, 20.1 mmol), and CH₂Cl₂ (50 mL) were added to a flask with stir bar in an ice bath. *m*-CPBA (3.71 g, 21.5 mmol) was added and the reaction was warmed to room temperature. After 24 hours more *m*-CPBA (1.0 g) was added. Four hours later the reaction was quenched with Na₂SO₃ and water, then extracted with ether (3×). The combined organics were washed with water followed by Na₂CO₃ (2×) and brine. The organics were then dried over Na₂SO₄ and concentrated to yield **31** in sufficient purity for subsequent reactions (2.94 g, 96%). An analytical sample was purified using MPLC (6:1 hexanes:ethyl acetate). **IR** (neat, NaCl): 1616, 1511, 1249, 1174, 1098, 1040, and 825 cm⁻¹. **¹H NMR** (CDCl₃, 300 MHz): δ 7.23 (m, 2H), 6.85 (m, 2H), 4.42 (s, 2H), 3.79 (s, 3H), 3.42 (t, *J* = 6.5, 2H), 2.89 (tdd, *J* = 5.0, 4.1, 2.9, 1H), 2.74 (dd, *J* = 5.0, 4.1, 1H), 2.46 (dd, *J* = 5.0, 2.9, 1H), and 1.6-1.2 (m, 16H). **¹³C NMR** (CDCl₃, 75 MHz): δ 158.8, 130.6, 129.0, 113.5, 72.4, 70.1, 55.2, 52.3, 47.1, 32.5, 29.7, 29.51, 29.50, 29.42, 29.40, 26.2, and 26.0. Anal. Calcd for C₁₉H₃₀O₃: C, 74.47; H, 9.87. Found: C, 74.32; H, 10.08.

Preparation of 2,2-dimethyl-3-nonyloxirane (13). Decyltriphenylphosphonium bromide (15.97 g, 33 mmol) was added to a dry 250-mL round-bottomed three-necked flask with a magnetic stir bar. Dry DMSO (85 mL) was added and the flask was cooled in an ice bath. *n*-BuLi (13.4 mL, 2.5 M in hexanes, 33 mmol) was added dropwise. The mixture turned deep red and was stirred for one hour and warmed to room temperature. Dry acetone (2.7 mL, 2.14 g, 37 mmol) was added dropwise, and the mixture was stirred overnight. The reaction was quenched with NH₄Cl solution (50 mL) and extracted with hexanes (3×). The combined organic layers were dried over Na₂SO₄. The crude product was filtered through silica with pentane and concentrated to yield the pure 2-methyl-2-dodecene (2.503 g, 42%). **IR** (neat, NaCl): 1672, 983, 830, and 720 cm⁻¹. **¹H NMR** (CDCl₃, 300 MHz): δ 5.10 (t of septets, *J* = 7.0, 1.5, 1H), 1.95 (dt, *J* = 6.7, 6.5, 2H), 1.68 (d, *J* = 1.2, 3H), 1.59 (broad s, 3H), 1.4-1.2 (m, 14H), and 0.88 (t, *J* = 6.7, 3H). **¹³C NMR** (CDCl₃, 75 MHz): δ 130.9, 124.9, 32.0, 30.0, 29.8, 29.5(2C), 28.2, 25.8, 22.8, 22.5, 17.7, and 14.2.

2-methyl-2-dodecene (1.663 g, 9.1 mmol), Na₂HPO₄ (2.848 g, 20 mmol), and CH₂Cl₂ (50 mL) were added sequentially to a 100-mL flask cooled in an ice bath. *m*-CPBA (2.718 g, 16 mmol) was added and the mixture was allowed to warm to room temperature. After 2 h TLC analysis showed no starting material. The reaction was quenched with saturated Na₂SO₃ solution and H₂O, and extracted with ether (3×). The combined organic layers were washed with H₂O, saturated Na₂CO₃ (2×), and brine. The solution was dried over Na₂SO₄ and concentrated to yield pure epoxide **13** (1.68 g, 85%). **IR** (neat, NaCl): 1247, 1120, 894, and 733 cm⁻¹. **¹H NMR** (CDCl₃, 300 MHz): δ 2.70 (t, *J* = 6.0, 1H), 1.6-1.2 (m, 16H) 1.31 (s, 3H), 1.26 (s, 3H), and 0.89 (t, *J* = 6.5, 3H). **¹³C NMR** (CDCl₃, 75 MHz): δ 64.6, 58.2, 31.9, 29.6, 29.57, 29.56, 29.4, 28.9,

26.6, 25.0, 22.7, 18.8, and 14.2. Anal. Calcd for C₁₃H₂₆O: C, 78.72; H, 13.21. Found: C, 78.93; H, 13.28.

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