SUPPORTING INFORMATION

for

Synthesis of Stereoisomeric Medium-Ring α,α' -Dihydroxy Cycloalkanones

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Select experimental details and copies of the high field ^1H and ^{13}C NMR spectra
of all new compounds.

(82 pages)

2-(*tert*-Butyldimethylsilyloxy)cycloheptanone (6b). *tert*-

Butyldimethylchlorosilane (1.04 g, 6.91 mmol) was added in one portion to a magnetically stirred solution of **6a** (590 mg, 4.6 mmol), imidazole (470 mg, 6.91 mmol), and DMAP (56 mg, 0.46 mmol) in CH₂Cl₂ (44 mL). The reaction mixture was heated to reflux for 24 h, allowed to return to rt, quenched with saturated NaHCO₃ solution, and transferred to a separatory funnel. The aqueous phase was extracted with CH₂Cl₂ (3x), and the combined organic solutions were dried and concentrated. Chromatography of the residue on silica gel (elution with 20:1 hexane/ethyl acetate) furnished 1.11 g (98%) of **6b** as a colorless oil; IR (neat, cm⁻¹) 1710, 1472, 1253; ¹H NMR (300 MHz, CDCl₃) δ 4.26 (dd, *J* = 7.1, 2.4 Hz, 1 H), 2.66 (dt, *J* = 15.4, 6.5 Hz, 1 H), 2.39-2.29 (m, 1 H), 1.92-1.56 (series of m, 7 H), 1.39-1.32 (m, 1 H), 0.90 (s, 9 H), 0.05 (s, 3 H), 0.04 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) δ 213.7, 79.0, 40.3, 33.7, 28.2, 25.7, 24.9 (3C), 22.7, 18.1, -5.0, -5.1; ES HRMS *m/z* (M+Na)⁺ calcd 265.1594, obsd 265.1601.¹⁷

Borohydride Reduction of 7. A solution of **7** (200 mg, 0.42 mmol) in methanol (3 mL) was cooled to 0 °C and treated with sodium borohydride (22 mg, 0.57 mmol) in one portion. After 30 min, the reaction mixture was quenched with water, allowed to warm to rt, and extracted with CH₂Cl₂ (3 x 25 mL). The combined organic phases were dried and concentrated, and the two resultant products were separated chromatographically (silica gel, elution with 10:1 hexanes/ethyl acetate) to give 142 mg (71%) of **8** and 52 mg (26%) of **9**, both as colorless oils.

For **8**: IR (neat, cm⁻¹) 3468, 1472, 1361, 1254; ¹H NMR (300 MHz, CDCl₃) δ 3.94-3.91 (m, 1 H), 3.88-3.86 (m, 1 H), 3.83-3.81 (m, 1 H), 1.92-1.42 (series of m, 8 H),

0.96 (s, 9 H), 0.93 (s, 9 H), 0.14 (s, 3 H), 0.12 (s, 3 H), 0.09 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 79.1, 72.0, 71.8, 30.2, 29.3, 26.25 (3C), 26.20 (3C), 22.6, 20.3, 18.5, 18.4, -4.0, -4.3, -4.4 (2C); ES HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 397.2564, obsd 397.2587.

For **9**: IR (neat, cm^{-1}) 3355, 1472, 1360, 1255; ^1H NMR (300 MHz, CDCl_3) δ 4.07-4.05 (m, 1 H), 3.88-3.83 (m, 1 H), 3.58 (d, $J = 7.2$ Hz, 1 H), 2.03-1.46 (series of m, 8 H), 0.96 (s, 9 H), 0.93 (s, 9 H), 0.13 (s, 6 H), 0.11 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 82.1, 74.4, 72.8, 33.1, 32.7, 26.3 (3C), 26.2 (3C), 23.8, 22.1, 18.5 (2C), -3.5, -4.2, -4.3, -4.4; ES HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 397.2564, obsd 397.2559.

***syn,anti*-Cycloheptane-1,2,3-triol. A. By Desilylation of 8.** A solution of **8** (3.0 g, 8.1 mmol) in THF (90 mL) was blanketed with N_2 and cooled to 0 °C prior to the addition of tetrabutylammonium fluoride solution (17.7 mL of 1 M in THF, 17.7 mmol). The reaction mixture was stirred for 12 h, quenched with saturated NaHCO_3 solution, and extracted with ether (3 x 90 mL). The combined organic phases were dried and concentrated, and the residue was chromatographed on silica gel (elution with 1:1 hexane/ethyl acetate) to give **10** as a faintly yellow oil (930 mg, 80%); IR (neat, cm^{-1}) 3394, 1454, 1030; ^1H NMR (300 MHz, CDCl_3) δ 4.12-4.11 (m, 1 H), 3.82-3.78 (m, 1 H), 3.53 (dd, $J = 8.5, 3.3$ Hz, 1 H), 1.98-1.93 (m, 1 H), 1.84-1.41 (series of m, 7 H); ^{13}C NMR (75 MHz, CDCl_3) δ 79.1, 71.9, 70.8, 33.2, 30.7, 24.0, 21.5; ES HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 169.0835, obsd 169.0827.

B. By Desilylation of 9. Analogous treatment of **9** (300 mg, 0.81 mmol) with TBAF provided 92 mg (80%) of **10**.

Desilylation of 7. A cold (0 °C) solution of **7** (250 mg, 0.67 mmol) in THF (30

mL) was blanketed with N₂, treated with tetrabutylammonium fluoride in THF (1.5 mL of 1 M, 1.5 mmol), and stirred for 12 h prior to quenching with saturated NaHCO₃ solution and extraction with ether (3 x 90 mL). After the combined organic phases were dried and concentrated, the residue was chromatographed on silica gel (elution with 1:1 hexane/ethyl acetate) to give 45 mg (50%) of **11** and 23 mg (24%) of **12**, both as faintly yellowish oils.

For **11**: IR (neat, cm⁻¹) 3414, 1710, 1452, 1270; ¹H NMR (300 MHz, CDCl₃) δ 4.25 (dd, *J* = 9.8, 2.9 Hz, 2 H), 3.10 (s, 2 H), 2.12-2.04 (m, 2 H), 1.98-1.90 (m, 2 H), 1.79-1.25 (series of m, 4 H); ¹³C NMR (75 MHz, CDCl₃) δ 214.2, 77.4 (2C), 32.2 (2C), 26.9 (2C); ES HRMS *m/z* (M+Na)⁺ calcd 167.0678, obsd 167.0674.

For **12**: IR (neat, cm⁻¹) 3418, 1703, 1647, 1451; ¹H NMR (300 MHz, CDCl₃) δ 4.45 (d, *J* = 1.5 Hz, 1 H), 4.26-4.22 (m, 1 H), 2.75-2.69 (m, 1 H), 2.53-2.46 (m, 1 H), 2.23-2.18 (m, 1 H), 1.99-1.93 (m, 1 H), 1.88-1.79 (m, 2 H), 1.74-1.61 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ 212.2, 80.8, 73.1, 41.0, 34.2, 23.0, 22.9; ES HRMS *m/z* (M+Na)⁺ calcd 167.0678, obsd 167.0669.

Borohydride Reduction of 11. An 8 mg (0.26 mmol) sample of **11** was reduced in methanol (1.5 mL) at 0 °C with sodium borohydride (29 mg, 0.86 mmol) in the predescribed manner to give 30 mg (78%) of **10**.

Silylation of 12. A stirred solution of **12** (1.0 g, 7.0 mmol), imidazole (720 mg, 10.6 mmol), and DMAP (86 mg, 70 mmol) in CH₂Cl₂ (39 mL) was treated with *tert*-butyldimethylchlorosilane (1.59 g, 10.6 mmol) in one portion, and the stirred reaction mixture was heated at reflux for 48 h, cooled to rt, quenched with saturated NaHCO₃

solution, and extracted with CH₂Cl₂ (3x). The combined organic layers were dried and evaporated to leave a mixture that was separated by chromatography on silica gel (elution with 20:1 hexane/ethyl acetate). There was isolated 26 mg (42%) of **13** and 38 mg (40%) of **14**, both as colorless oils.

For **13**: IR (neat, cm⁻¹) 3460, 1705, 1472, 1397; ¹H NMR (300 MHz, CDCl₃) δ 4.40 (s, 1 H), 4.20 (d, *J* = 5.3 Hz, 1 H), 4.08 (s, 1 H), 2.73-2.72 (m, 1 H), 2.44-2.37 (m, 1 H), 2.08-2.03 (m, 1 H), 1.98-1.92 (m, 1 H), 1.86-1.58 (series of m, 4 H), 0.87 (s, 9 H), 0.06 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃) δ 211.6, 81.2, 74.8, 40.9, 35.9, 26.1 (3C), 23.4, 22.9, 18.4, -4.4, -4.6; ES HRMS *m/z* (M+Na)⁺ calcd 281.1543, obsd 281.1533.

For **14**: IR (neat, cm⁻¹) 1723, 1472, 1252; ¹H NMR (300 MHz, CDCl₃) δ 4.35 (s, 1 H), 3.92-3.90 (m, 1 H), 2.57-2.38 (m, 2 H), 2.08-1.97 (m, 2 H), 1.79-1.46 (series of m, 4 H), 0.95 (s, 9 H), 0.89 (s, 9 H), 0.13 (s, 3H), 0.08 (s, 3 H), 0.07 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃) δ 211.3, 84.9, 75.8, 41.6, 35.3, 26.3 (3C), 25.7 (3C), 23.8, 22.8, 18.8, 18.5, -4.2, -4.4, -4.6, -4.8; ES HRMS *m/z* (M+Na)⁺ calcd 395.2408, obsd 395.2435.

***trans*-2-(*tert*-Butyldimethylsilyloxy)-7-(hydroxy)cycloheptanone (15).** A cold (-78 °C) solution of **6b** (1.65 g, 6.82 mmol) in dry THF (8.2 mL) was treated with lithium hexamethyldisilazide (47.1 mL of 1 M in THF, 47.1 mmol), then stirred for 1 h in the cold before the introduction of chlorotrimethylsilane (1.21 mL, 9.55 mmol). Stirring was maintained for 2 h at rt prior to quenching with saturated NaHCO₃ solution. The product was extracted into ether (3 x 100 mL), the combined organic phases were dried, and the concentrate was redissolved in CH₂Cl₂ (138 mL). This solution was treated with *m*-chloroperbenzoic acid (2.08 g, 8.17 mmol) at 0 °C, stirred for 4 h, warmed to rt, and

quenched with saturated K_2CO_3 solution. The product was extracted into ether (3 x 50 mL) and the combined organics were dried and evaporated. The residue was chromatographed on silica gel (elution with 20:1 hexane/ethyl acetate) to give **15** as a colorless oil (264 mg, 15%); IR (neat, cm^{-1}) 3492, 1712, 1471; ^1H NMR (300 MHz, CDCl_3) δ 4.64 (dd, $J = 5.5, 2.5$ Hz, 1 H), 4.55 (dd, $J = 6.6, 1.5$ Hz, 1 H), 2.30-2.24 (m, 1 H), 1.95-1.91 (m, 2 H), 1.76-1.65 (m, 4 H), 1.57-1.50 (m, 1H), 0.96 (s, 9 H), 0.12 (s, 3 H), 0.09 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 215.0, 77.9, 74.7, 34.4, 32.0, 26.0 (3C), 25.0, 23.7, 18.4, -4.5, -4.9; ES HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 281.1543, obsd 281.1531.

***cis*-2,7-Dihydroxycycloheptanone (20).** A mixture of **19** (25 mg, 0.09 mmol) and dry THF (2.6 mL) was cooled to 0 °C, treated with a 1 M solution of tetra-*n*-butylammonium fluoride in THF (0.1 mL, 0.1 mmol), stirred at rt for 30 min, and quenched with saturated NaHCO_3 solution prior to extraction with ether (3 x 15 mL). The combined organic layers were dried and evaporated. Purification of the residue was achieved by chromatography on silica gel (elution with 1:1 hexane/ethyl acetate). There was isolated 6 mg (46%) of **20** as a colorless solid, mp 87 °C; IR (neat, cm^{-1}) 3406, 1711, 1451; ^1H NMR (300 MHz, CDCl_3) δ 4.41 (dd, $J = 7.6, 4.5$ Hz, 2 H), 3.39 (br s, 2 H), 2.06-2.00 (m, 2 H), 1.83-1.76 (m, 2 H), 1.69-1.59 (m, 4 H); ^{13}C NMR (75 MHz, CDCl_3) δ 214.9, 74.9 (2C), 33.7 (2C), 24.8 (2C); ES HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 167.0678, obsd 167.0684.

***trans*-2,8-Dihydroxycyclooctanone (23).** To a solution of **22** (22 mg, 0.14 mmol) in ethanol (2 mL) was added 10% palladium on carbon (2 mg). Hydrogen was bubbled through this mixture for 10 min and stirring was maintained for 30 min under 1

atm of H₂. The reaction mixture was filtered through Celite, and the pad was rinsed with CH₂Cl₂. The combined filtrates were freed of solvent and the residue was chromatographed on silica gel (elution with 20% ethyl acetate in hexane) to give **23** (21 mg, 94%) as a white solid, mp 78-79 °C; IR (neat, cm⁻¹) 3419, 1700, 1653; ¹H NMR (500 MHz, CDCl₃) δ 4.62 (dd, *J* = 6.0, 2.9 Hz, 2 H), 2.47-2.40 (m, 2 H), 2.09-2.01 (m, 2 H), 1.79-1.71 (m, 2 H), 1.60-1.54 (m, 2 H), 1.39-1.31 (m, 2 H) (OH not seen); ¹³C NMR (125 MHz, CDCl₃) δ 218.7, 75.7 (2C), 33.5 (2C), 24.9 (2C), 21.0; ES HRMS *m/z* (M+Na)⁺ calcd 181.0835, obsd 181.0837.

***syn,anti*-Cyclooctane-1,2,3-triol (24).** A solution of **23** (13.5 mg, 0.085 mmol) in anhydrous ether (1 mL) was treated with a solution of lithium aluminum hydride (0.13 mL of 1 M in ether, 0.13 mmol) at -78 °C. The reaction mixture was stirred in the cold for 3 h, allowed to warm to rt, quenched with sodium sulfate decahydrate, and filtered through a pad of Celite. After rinsing of the pad with ethyl acetate/methanol (5:1), the combined filtrates were chromatographed on silica gel (elution with 10:1 ethyl acetate/methanol) to give **24** (5.8 mg, 42%) as a white solid, mp 73-75 °C; IR (neat, cm⁻¹) 3390, 1458, 1058; ¹H NMR (500 MHz, CDCl₃) δ 4.04 (br s, 1 H), 3.92 (br s, 1 H), 3.75 (br s, 1 H), 3.11 (br s, 1 H), 2.44 (br s, 2 H), 1.92-1.44 (series of m, 10 H); ¹³C NMR (125 MHz, CDCl₃) δ 76.2, 71.4, 70.2, 33.7, 30.3, 27.5, 23.0, 22.7; ES HRMS *m/z* (M+Na)⁺ calcd 183.0992, obsd 183.0992.

2-Hydroxycyclooctanone (25). To a solution of **21** (400 mg, 0.14 mmol) in ethanol (5 mL) was added 10% palladium on carbon (10 mg). Hydrogen was bubbled through the suspension for 10 min and stirring was maintained for 3 h under 1 atm of H₂.

After filtration through Celite and rinsing of the pad with CH₂Cl₂, the combined filtrates were evaporated to leave **25** as a waxy solid, mp 114-118 °C (395 mg, 97%); IR (neat, cm⁻¹) 3478, 1698, 1464; ¹H NMR (500 MHz, CDCl₃) δ 4.11 (dd, *J* = 6.5, 2.8 Hz, 1 H), 2.63 (dt, *J* = 12.2, 3.8 Hz, 1 H), 2.39-2.22 (m, 2 H), 1.96-1.85 (m, 2 H), 1.78-1.55 (m, 4 H), 1.34-1.27 (m, 2 H), 0.89-0.81 (m, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ 217.8, 76.5, 376, 29.4, 29.1, 25.8, 24.8, 22.4; ES HRMS *m/z* (M+Na)⁺ calcd 168.0886, obsd 168.0883.⁸

***trans*-2-(Benzyloxy)-8-(hydroxy)cyclooctanone (28).** A solution of **27** (5.40 g, 23 mmol) in dry THF (77 mL) was treated with lithium hexamethyldisilazide (30 mL of 1 M in THF, 30 mmol) at -78 °C and the solution was stirred at this temperature for 1 h, treated dropwise with chlorotrimethylsilane (3.79 g, 35 mmol), stirred overnight at rt, and quenched with saturated NaHCO₃ solution. The product was extracted into ethyl acetate (3x), and the combined organic phases were washed with brine, dried, and evaporated.

The resulting yellowish oil was dissolved in acetone (150 mL) containing suspended NaHCO₃ (19.5 g, 233 mmol). The stirred slurry was treated slowly with a solution of oxone (42.90 g, 70 mmol) in 238 mL of water at 0 °C, stirred overnight at rt, and diluted with ethyl acetate. The separated aqueous layer was extracted with ethyl acetate and the combined organic phases were washed with 10% HCl, saturated NaHCO₃ solution, and brine. After drying and concentration, the residue was purified chromatographically on silica gel (elution with 3% ethyl acetate in hexane) to afford **28** as a colorless oil (2.85 g, 50% over two steps); IR (neat, cm⁻¹) 3484, 1701, 1114; ¹H NMR (300 MHz, CDCl₃) δ 7.41-7.29 (m, 5 H), 4.58 (d, *J* = 11.8 Hz, 1 H), 4.55-4.51 (m,

2 H), 4.25-4.23 (m, 1 H), 3.56-3.55 (m, 1 H), 2.94-2.82 (m, 1 H), 2.23-2.14 (m, 1 H), 2.05-1.95 (m, 1 H), 1.89-1.52 (series of m, 5 H), 1.46-1.26 (m, 1 H), 0.95-0.82 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 218.1, 137.4, 128.6 (2C), 128.0, 127.4 (2C), 83.7, 74.5, 72.1, 35.1, 28.2, 24.6, 21.5, 19.4; ES HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 271.1305, obsd 271.1298.

***trans*-2,8-Dihydroxycyclooctanone (23).** **A. Deprotection of 26.** A solution of **26** (370 mg, 1.34 mmol) in dry THF (15 mL) was treated with a THF solution of tetrabutylammonium fluoride (1.61 mL of 1 M, 1.61 mmol), stirred for 30 min, and concentrated in vacuo. The residue was chromatographed on silica gel (elution with 50% hexane in ethyl acetate) to give **23** as a white solid identical in all respects with the dihydroxy ketone prepared above.

B. Deprotection of 28. A solution of **28** (100 mg, 0.40 mmol) in dry ethanol (3 mL) was admixed with 10% palladium on carbon (15 mg) and hydrogenolyzed for 2 h as described above. There was isolated 51 mg (80%) of **23**, identical in all respects to the material generated earlier.

Reduction of 33. B. With Diisobutylaluminum Hydride. A solution of **33** (11 mg, 0.04 mmol) in dry THF (0.5 mL) was cooled to 0 °C, treated with Dibal-H (40 μL of 1 M, 0.04 mmol), stirred for 10 min, and quenched with saturated NaHCO_3 solution. The separated aqueous phase was extracted with ether (3 x 15 mL), and the combined organic layers were dried and concentrated. Chromatography of the residue on silica gel (elution with 20:1 hexane/ethyl acetate) returned 6.6 mg (67%) of **35**, spectroscopically identical to the compound formed in part A.

C. With L-Selectride in THF. A solution of **33** (48 mg, 0.18 mmol) in THF (2.25 mL) was treated with L-Selectride (190 μ L of 1 M, 0.19 mmol), stirred for 10 min, and worked up in the prescribed manner. There was isolated 32 mg of **35** (32 mg, 67% or 89% based on recovered **33**).

D. With Sodium Borohydride in Methanol. A solution of **33** (48 mg, 0.18 mmol) in methanol (2 mL) was treated with sodium borohydride (6.5 mg, 0.18 mmol), stirred for 10 min, and processed in the prescribed manner to provide 28 mg (59%) of **34** and 18 mg (39%) of **35**, both as yellowish oils.

For **34**: IR (neat, cm^{-1}) 3447, 1717, 1472; ^1H NMR (300 MHz, CDCl_3) δ 4.51 (dd, $J = 9.2, 4.1$ Hz, 1 H), 4.27 (dd, $J = 7.6, 4.4$ Hz, 1 H), 2.30-1.26 (series of m, 10 H), 0.93 (s, 9H), 0.11 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 216.2, 74.9, 74.2, 36.1, 26.1 (3C), 24.2, 22.2, 21.8, 18.7, -4.2, -4.6; ES HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 295.1699, obsd 295.1692.

3-(tert-Butyldimethylsilyloxy)-2-methylenecyclooctanone (39). A solution of **37** (162 mg, 0.60 mmol) and IBX (200 mg, 0.72 mmol) in an 8:1 solution of THF and DMSO (3.1 mL) was stirred at rt for 12 h, quenched with saturated NaHCO_3 solution, transferred to a separatory funnel, and extracted with ether (3 x 30 mL). Following drying and concentration of the combined organic layers, the residue was chromatographed on silica gel (elution with 20:1 hexane/ethyl acetate) to afford 150 mg (94%) of **39** as a colorless oil; IR (neat, cm^{-1}) 1689, 1471, 1253; ^1H NMR (300 MHz, CDCl_3) δ 5.84 (d, $J = 0.8$ Hz, 1 H), 5.64 (t, $J = 1.6$ Hz, 1 H), 4.75 (dd, $J = 9.3, 4.8$ Hz, 1 H), 2.68-2.60 (m, 2 H), 1.93-1.29 (series of m, 8 H), 0.95 (s, 9 H), 0.12 (s, 3 H), 0.10 (s, 3

H) ^{13}C NMR (75 MHz, CDCl_3) δ 206.5, 153.0, 119.2, 71.6, 41.1, 40.3, 28.1, 27.2, 26.2 (3C), 23.1, 18.6, -4.4, -4.6; ES HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 291.1750, obsd 291.1763.

2-(*tert*-Butyldimethylsilyloxy)-8-methylenecyclooctanone (40). Oxidation of **38** (62 mg, 0.23 mmol) with IBX (77 mg, 0.28 mol) in 8:1 THF/DMSO (1.2 mL) according to the predescribed protocol afforded 36 mg (60%) of **40** as a colorless oil; IR (neat, cm^{-1}) 1688, 1606, 1463; ^1H NMR (300 MHz, CDCl_3) δ 5.72 (d, J = 2.0 Hz, 1 H), 5.26 (s, 1 H), 4.53 (dd, J = 6.6, 3.8 Hz, 1 H), 3.26-3.20 (m, 2 H), 1.95-1.54 (series of m, 8 H), 0.93 (s, 9 H), 0.07 (s, 6 H); ^{13}C NMR (75 MHz, CDCl_3) δ 208.6, 150.1, 122.5, 78.4, 38.3, 30.5, 29.7, 26.1 (3C), 25.6, 20.8, 18.6, -4.6, -4.7; ES HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 291.1750, obsd 291.1763.

***cis*-2,8-Dihydroxymethylenecyclooctane (43).** A solution of **42** (57.5 mg, 0.21 mmol) in THF (2.5 mL) was cooled to 0 $^\circ\text{C}$, treated with a 1 M solution of TBAF in THF (0.26 mL), stirred for 30 min, and processed in the usual way to deliver 23 mg (70%) of **43** as a colorless oil; IR (neat, cm^{-1}) 3506, 1460, 1444; ^1H NMR (300 MHz, CDCl_3) δ 5.24 (s, 2 H), 4.37 (dd, J = 8.9, 5.2 Hz, 2 H), 2.46 (s, 2 H), 2.08-2.02 (m, 2 H), 1.89-1.82 (m, 2 H), 1.78-1.70 (m, 2 H), 1.61-1.47 (m, 2 H), 1.40-1.32 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 154.1, 113.9, 75.3 (2C), 35.8 (2C), 26.9, 2.4 (2C); ES HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 179.1042, obsd 179.1036.

Ozonolysis of 43. A solution of **43** (22 mg, 0.14 mmol) in CH_2Cl_2 (12 mL) was ozonolyzed at -78 $^\circ\text{C}$ until a faint blue color persisted. Oxygen was then bubbled through until a clear solution was added, the mixture was allowed to warm to rt, and the usual workup ensued. There was isolated 7.5 mg (30%) of **36**, which was spectroscopically

identical to material reported above.

^1H NMR Spectrum of Compound 7

¹H NMR Spectrum of Compound 8

¹H NMR Spectrum of Compound **10**

¹H NMR Spectrum of Compound II

¹H NMR Spectrum of Compound **13**

¹H NMR Spectrum of Compound **14**

¹H NMR Spectrum of Compound 15

¹H NMR Spectrum of Compound 16

¹H NMR Spectrum of Compound 17

¹H NMR Spectrum of Compound 19

¹H NMR Spectrum of Compound 20

¹H NMR Spectrum of Compound 22

S27

¹H NMR Spectrum of Compound 25a

¹H NMR Spectrum of Compound 26

¹H NMR Spectrum of Compound 28

¹H NMR Spectrum of Compound 30

¹H NMR Spectrum of Compound 32

¹H NMR Spectrum of Compound 33

¹H NMR Spectrum of Compound 36

¹H NMR Spectrum of Compound 37

¹H NMR Spectrum of Compound 38

¹H NMR Spectrum of Compound 39

¹H NMR Spectrum of Compound 40

¹H NMR Spectrum of Compound **41**

S44

¹H NMR Spectrum of Compound 43

¹H NMR Spectrum of Compound **44**

Wed

211 980

33.974	
33.651	

18 18 18 24 76

25 25 25 25 100

176

2- 986
4- 266
5- 267

¹H NMR Spectrum of Compound **10**

¹H NMR Spectrum of Compound II

S51

¹H NMR Spectrum of Compound 14

wdw
-----212.861

¹H NMR Spectrum of Compound 20

218.966
PPM

99.778

77.489
77.066
76.643
76.239

33.002
24.463
20.436

¹H NMR Spectrum of Compound 23

¹H NMR Spectrum of Compound 32

¹H NMR Spectrum of Compound 33

¹H NMR Spectrum of Compound 35

¹H NMR Spectrum of Compound 36

¹H NMR Spectrum of Compound 38

¹H NMR Spectrum of Compound 39

¹H NMR Spectrum of Compound 42

¹H NMR Spectrum of Compound 43

¹H NMR Spectrum of Compound 44