SUPPORTING INFORMATION

for

**"A Zirconocene-Mediated Route to Enantiopure 9-Oxabicyclononanes
Functionalized on Both Carbon Bridges"**

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(17 Pages)

Periodinane Oxidation/Sodium Borohydride Reduction of **8**. A

magnetically stirred mixture of **8** (107 mg, 0.38 mmol) and sodium bicarbonate (638 mg, 7.6 mmol) in CH₂Cl₂ (20 mL) was treated with the Dess-Martin periodinane (486 mg, 1.14 mmol). After 3 h at rt, the resulting white suspension was filtered through a pad of Celite (hexanes/ethyl acetate 8:1 rinse) and the filtrate was evaporated to leave a residue that was dissolved in methanol (10 mL). After the addition of sodium borohydride (43 mg, 1.14 mmol) at 0 °C, the reaction mixture was stirred for 30 min at this temperature, quenched with saturated NH₄Cl solution, and freed of methanol under reduced pressure. After extraction of the product into ethyl acetate, the combined organic layers were dried, filtered, and evaporated. Purification of the residue by chromatography on silica gel (elution with hexanes/ethyl acetate 2:1) gave **9a** as a colorless oil (94 mg, 88%); IR (neat, cm⁻¹) 3552, 1612, 1586; ¹H NMR (300 MHz, CDCl₃) 7.27 (d, *J* = 8.5 Hz, 2 H), 6.88 (d, *J* = 8.6 Hz, 2 H), 5.71 (ddd, *J* = 17.0, 10.4, 6.5 Hz, 1 H), 5.26 (d, *J* = 17.1 Hz, 1 H), 5.13 (d, *J* = 10.4 Hz, 1 H), 4.90 (d, *J* = 4.6 Hz, 1 H), 4.68 (d, *J* = 11.9 Hz, 1 H), 4.56 (d, *J* = 11.9 Hz, 1 H), 4.52-4.41 (m, 1 H), 4.10 (ddd, *J* = 11.1, 7.0, 4.7 Hz, 1 H), 3.80 (s, 3 H), 3.60 (dd, *J* = 7.0, 3.8 Hz, 1 H), 3.48 (s, 3 H), 2.93 (d, *J* = 10.7 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) 159.4, 135.8, 129.6, 129.5 (2C), 116.6, 113.8 (2C), 102.6, 82.9, 79.0, 72.7, 71.3, 55.6, 55.2; ES HRMS *m/z* (M+Na)⁺ calcd 303.1203, obsd 303.1215; [α]_D²² +109.7 (c 0.4, CHCl₃).

TBS Protection of 9a. A mixture of **9a** (64 mg, 0.23 mmol), imidazole (63 mg, 0.92 mmol), DMAP (3 mg, 0.02 mmol), and *tert*-butyldimethylsilyl chloride (69 mg, 0.46 mmol) in CH₂Cl₂ (5 mL) was stirred for 2 days at rt, filtered through a short column of silica gel (hexanes/ethyl acetate 10:1 rinse), and evaporated. Chromatography of the residue on silica gel (elution with hexanes/ethyl acetate 10:1) afforded **9b** as a colorless oil (78 mg, 87%); IR (neat, cm⁻¹) 1613, 1514, 1249; ¹H NMR (300 MHz, CDCl₃) 7.26 (d, *J* = 8.5 Hz, 2 H), 6.85 (d, *J* = 8.6 Hz,

2 H), 5.72 (ddd, $J = 17.0, 10.3, 6.5$ Hz, 1 H), 5.25 (d, $J = 17.1$ Hz, 1 H), 5.10 (d, $J = 10.4$ Hz, 1 H), 4.80 (d, $J = 4.4$ Hz, 1 H), 4.73 (d, $J = 12.6$ Hz, 1 H), 4.54 (d, $J = 12.6$ Hz, 1 H), 4.50-4.47 (m, 1 H), 4.06 (dd, $J = 6.6, 4.4$ Hz, 1 H), 3.80 (s, 3 H), 3.54 (dd, $J = 6.6, 4.0$ Hz, 1 H), 3.46 (s, 3 H), 0.94 (s, 9 H), 0.12 (s, 3 H), 0.11 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3) 159.1, 136.4, 130.3, 129.3 (2C), 116.3, 113.6 (2C), 103.3, 82.9, 78.9, 72.8, 71.9, 55.5, 55.2, 25.9 (3C), 18.4, -4.7, -4.9; ES HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 417.2068, obsd 417.2070; [^{22}D] +108.7 (c 1.32, CHCl_3).

Anomerization of 9b. A sample of **9a** (512 mg, 1.29 mmol) in 1% methanolic HCl (130 mL) was stirred overnight at rt, cooled to 0 °C, and neutralized with saturated NaHCO_3 solution. After methanol removal under reduced pressure, the remaining oil was triturated with ethyl acetate, the combined organic layers were dried and evaporated, and the residue was taken up in CH_2Cl_2 (10 mL), mixed with imidazole (263 mg, 3.86 mmol), DMAP (32 mg, 0.31 mmol), and *tert*-butyldimethylsilyl chloride (292 mg, 1.94 mmol), and stirred for 2 days at rt. The resulting white heterogeneous mixture was filtered through a short pad of silica gel (CH_2Cl_2 rinse), evaporated, and chromatographed on silica gel (elution with hexanes/ethyl acetate 10:1) to give **10** as a colorless oil (345 mg, 67%) and return unreacted **9b** (44 mg, 9%); IR (neat, cm^{-1}) 1613, 1514, 1250; ^1H NMR (300 MHz, CDCl_3) 7.24 (d, $J = 8.7$ Hz, 2 H), 6.86 (d, $J = 8.6$ Hz, 2 H), 5.83 (ddd, $J = 17.2, 10.3, 6.4$ Hz, 1 H), 5.36 (d, $J = 17.1$ Hz, 1 H), 5.16 (d, $J = 10.3$ Hz, 1 H), 4.73 (s, 1 H), 4.58 (d, $J = 11.5$ Hz, 1 H), 4.48 (t, $J = 7.2$ Hz, 1 H), 4.42 (d, $J = 11.5$ Hz, 1 H), 4.11 (d, $J = 4.0$ Hz, 1 H), 3.80 (s, 3 H), 3.80-3.77 (m, 1 H), 3.37 (s, 3 H), 0.92 (s, 9 H), 0.10 (s, 6 H); ^{13}C NMR (75 MHz, CDCl_3) 159.2, 138.0, 130.1, 129.2 (2C), 116.9, 113.7 (2C), 108.6, 82.1, 81.7, 74.7, 72.0, 55.2, 55.1, 25.8 (3C), 18.2, -4.7, -4.8; ES HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 417.2068, obsd 417.2099; [^{22}D] +12.0 (c 1.22, CHCl_3).

PMB Protection of 12a. A cold (0 °C) suspension of sodium hydride (1.59 g, 40 mmol) in dry THF (20 mL) was treated with **12a** (6.9 g, 26.5 mmol) dissolved in dry THF (60 mL) and stirred for 20 min at 0 °C and for 10 min at rt. Following a return to 0 °C, *p*-methoxybenzyl bromide (6.9 g, 34 mmol) in THF (20 mL) containing tetra-*n*-butylammonium iodide (1.0 g, 2.7 mmol) was introduced. The reaction mixture was stirred at rt for 3 h, quenched with saturated NH₄Cl solution (100 mL) at 0 °C, and extracted with ethyl acetate. The combined organic layers were dried and evaporated, leaving a residue that was chromatographed on silica gel (elution with hexanes/ethyl acetate 2:1) to furnish 7.0 g (70%) of **12b** as a white solid, mp 75-77 °C; IR (neat, cm⁻¹) 1614, 1514, 1462; ¹H NMR (300 MHz, CDCl₃) 7.32 (d, *J* = 8.7 Hz, 2 H), 6.89 (d, *J* = 8.7 Hz, 2 H), 5.74 (d, *J* = 3.8 Hz, 1 H), 4.70 (d, *J* = 11.9 Hz, 1 H), 4.56-4.51 (m, 1 H), 4.53 (d, *J* = 11.5 Hz, 1 H), 4.35 (dt, *J* = 7.1, 3.1 Hz, 1 H), 4.12 (dd, *J* = 8.7, 3.1 Hz, 1 H), 4.02-3.92 (m, 2 H), 3.86 (dd, *J* = 8.7, 4.5 Hz, 1 H), 3.80 (s, 3 H), 1.58 (s, 3 H), 1.39 (s, 3 H), 1.37 (s, 3 H), 1.35 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) 159.2, 129.5 (2C), 129.3, 113.5 (2C), 112.5, 109.2, 103.6, 77.7, 77.5, 76.9, 74.5, 71.4, 64.7, 54.9, 26.5, 26.3, 25.9, 24.8; ES HRMS *m/z* (M+Na)⁺ calcd 403.1727, obsd 403.1717; [²⁰D] +95.5 (c 1.0, CHCl₃).

Conversion of 12b to 13. To a cold (0 °C) solution of **12b** (54.8 g, 144 mmol) in methanol (600 mL) were added concentrated HCl (0.6 mL) and water (6 mL). The reaction mixture was stirred for 2 h in the cold, maintained at rt for 3 h, returned to 0 °C, neutralized with saturated NaHCO₃ solution, and evaporated. The product was extracted into ethyl acetate, the combined organic layers were dried and evaporated, and the residue was chromatographed on silica gel (elution with hexanes/ethyl acetate 1:5) to give the diol as a colorless oil (28.7 g, 59%); IR (neat, cm⁻¹) 3444, 1613, 1514; ¹H NMR (300 MHz, CDCl₃) 7.30 (d, *J* = 8.6 Hz, 2 H), 6.89 (d, *J* = 8.6 Hz, 2 H), 5.76 (d, *J* = 3.7 Hz, 1 H), 4.72 (d, *J* = 11.1 Hz, 1 H), 4.59

(t, $J = 4.0$ Hz, 1 H), 4.49 (d, $J = 11.0$ Hz, 1 H), 4.09 (dd, $J = 8.9, 3.2$ Hz, 1 H), 4.01-3.97 (m, 1 H), 3.90 (dd, $J = 8.9, 4.3$ Hz, 1 H), 3.80 (s, 3 H), 3.77-3.61 (m, 2 H), 2.46 (br s, 2 H), 1.59 (s, 3 H), 1.36 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3) 159.2, 129.6 (2C), 128.8, 113.6 (2C), 112.7, 103.8, 78.7, 77.1, 76.2, 71.5, 70.8, 62.8, 54.9, 26.5, 26.3; ES HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 363.1414, obsd 363.1418; $[\text{I}]_{\text{D}}^{22} +96.4$ (c 1.32, CHCl_3).

A solution of the above diol (24.0 g, 70.5 mmol) and *p*-toluenesulfonyl chloride (54.1 g, 282 mmol) in pyridine (150 mL) was stirred at rt for 2 days, diluted with ethyl acetate, and washed sequentially with 1N HCl, saturated NaHCO_3 solution, and brine prior to drying and solvent evaporation. The residue was purified by chromatography on silica gel (elution with hexanes/ethyl acetate 1:1) to afford the ditosylate as a colorless oil (43.9 g, 96%); IR (neat, cm^{-1}) 1612, 1514, 1458; ^1H NMR (300 MHz, CDCl_3) 7.72 (d, $J = 8.3$ Hz, 2 H), 7.65 (d, $J = 8.4$ Hz, 2 H), 7.28 (br d, $J = 8.0$ Hz, 4 H), 7.24 (d, $J = 8.7$ Hz, 2 H), 6.87 (d, $J = 8.7$ Hz, 2 H), 5.44 (d, $J = 3.5$ Hz, 1 H), 4.99-4.94 (m, 1 H), 4.59 (d, $J = 11.2$ Hz, 1 H), 4.42 (d, $J = 11.2$ Hz, 1 H), 4.43-4.40 (m, 1 H), 4.13-4.01 (m, 3 H), 3.82 (s, 3 H), 3.82-3.75 (m, 1 H), 2.44 (s, 6 H), 1.48 (s, 3 H), 1.30 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3) 159.6, 145.2, 144.9, 133.8, 132.2, 129.9 (2C), 129.7 (4C), 129.7 (2C), 129.1, 127.9 (2C), 113.9 (2C), 113.3, 104.2, 77.8, 77.7 (2C), 77.3, 71.7, 66.9, 55.2, 26.8, 26.5, 21.6 (2C); ES HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 671.1591, obsd 671.1562; $[\text{I}]_{\text{D}}^{22} +42.8$ (c 1.16, CHCl_3).

A heterogeneous mixture of the ditosylate from above (46.6 g, 71.8 mmol), sodium iodide (108 g, 720 mmol), and zinc dust (47 g, 719 mmol) in DMF (500 mL) was refluxed overnight, diluted with water, filtered, diluted with ethyl acetate, and washed with brine. After drying and evaporation of the organic phase, the residue was chromatographed on silica gel (elution with hexanes/ethyl acetate 5:1) to furnish **13** as a colorless oil (19.2 g, 87%); IR (neat, cm^{-1}) 1613, 1514, 1374; ^1H NMR

(300 MHz, CDCl₃) 7.28 (d, J = 8.8 Hz, 2 H), 6.88 (d, J = 8.7 Hz, 2 H), 5.79 (ddd, J = 17.2, 10.4, 6.7 Hz, 1 H), 5.73 (d, J = 3.8 Hz, 1 H), 5.44 (d, J = 17.0 Hz, 1 H), 5.25 (d, J = 10.3 Hz, 1 H), 4.67 (d, J = 11.9 Hz, 1 H), 4.56 (d, J = 11.9 Hz, 1 H), 4.54-4.52 (m, 1 H), 4.48-4.43 (m, 1 H), 3.81 (s, 3 H), 3.48 (dd, J = 9.0, 4.3 Hz, 1 H), 1.61 (s, 3 H), 1.35 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) 159.0, 134.6, 129.1 (3C), 118.1, 113.4 (2C), 112.3, 103.3, 81.1, 78.6, 77.1, 71.4, 54.8, 26.3, 26.1; ES HRMS m/z (M+Na)⁺ calcd 329.1359, obsd 329.1379; [²²D] +59.9 (c 1.61, CHCl₃).

Conversion of 13 to 10. A solution of **13** (21.2 g, 69.2 mmol) in methanolic 1% HCl (1300 mL) was stirred overnight, cooled to 0 °C, neutralized with saturated NaHCO₃ solution, and evaporated. The residue was extracted with ethyl acetate, the combined organic layers were dried and evaporated, and the residue was chromatographed on silica gel (elution with hexanes/ethyl acetate 3:2) to give the hydroxy methyl acetal as a colorless oil (15.4 g, 79%) consisting of an inseparable 8:1 mixture of α - and β -anomers. This mixture was therefore dissolved in CH₂Cl₂ (200 mL), treated sequentially with imidazole (11.2 g, 165 mmol), DMAP (672 mg, 0.55 mmol) and *tert*-butyldimethylsilyl chloride (10.8 g, 71.7 mmol), and stirred at rt for 2 days prior to dilution with ethyl acetate and washing with water and brine. The organic solution was dried and evaporated to leave a residue that was chromatographed on silica gel (elution with hexanes/ethyl acetate 10:1). There was isolated 19.2 g (88%) of **10** and 2.4 g (11%) of **9b**.

Ring Contraction of 10. A cold (-78 °C) solution of zirconocene dichloride (4.6 g, 15.7 mmol) in toluene (30 mL) was treated with *n*-butyllithium (18.2 mL of 1.67 M, 30.4 mmol) and stirred for 1 h at this temperature. After the introduction of **10** (2.0 g, 5.1 mmol) as a solution in toluene (120 mL), the reaction mixture was stirred at rt for 3 h, cooled to 0 °C, and exposed to boron trifluoride etherate (3 mL, 24 mmol). After 30 min, 1 N HCl was added and the product was extracted into

ethyl acetate. The combined organic layers were washed with saturated NaHCO₃ solution, dried, and evaporated. The residue was chromatographed on silica gel (elution with hexanes/ethyl acetate 7:1) to give **11** as a colorless oil (1.2 g, 65%): IR (neat, cm⁻¹) 3454, 1613, 1514; ¹H NMR (300 MHz, CDCl₃) 7.27 (d, *J* = 8.3 Hz, 2 H), 6.86 (d, *J* = 8.6 Hz, 2 H), 5.79 (ddd, *J* = 17.3, 10.5, 8.4 Hz, 1 H), 5.25 (d, *J* = 10.5 Hz, 2 H), 5.14 (d, *J* = 17.3 Hz, 1 H), 4.66 (d, *J* = 11.3 Hz, 1 H), 4.45 (d, *J* = 11.4 Hz, 1 H), 4.41-4.36 (m, 1 H), 4.09 (td, *J* = 6.2, 1.0 Hz, 1 H), 3.94 (dd, *J* = 6.0, 1.9 Hz, 1 H), 3.80 (s, 3 H), 2.99 (br t, *J* = 8.4 Hz, 1 H), 1.80 (d, *J* = 6.8 Hz, 1 H), 0.93 (s, 9 H), 0.13 (s, 3 H), 0.12 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) 151.9, 133.9 (2C), 130.4, 129.4 (2C), 118.5, 113.7, 76.2, 76.0, 75.1, 71.3, 55.2, 45.8, 25.8 (3C), 18.2, -4.7, -5.0; ES HRMS *m/z* (M+Na)⁺ calcd 387.1962, obsd 387.1955; [α]_D²² +10.6 (c 1.44, CHCl₃).

Oxidation of 11 and Acetylide Addition to the Cyclobutanone. A mixture of **11** (144 mg, 0.39 mmol) and sodium bicarbonate (655 mg, 7.8 mmol) in CH₂Cl₂ (40 mL) was treated with the Dess-Martin periodinane (496 mg, 1.17 mmol), stirred at rt for 3 h, filtered through a pad of Celite (hexanes rinse) and evaporated. The residue was taken up in THF (2 mL) and added at 0 °C to the Grignard of trimethylsilylacetylene. This reagent was prepared by treating a solution of the alkyne (0.18 mL, 1.3 mmol) in THF (1.5 mL) with *n*-butyllithium (0.7 mL of 1.67 M, 1.17 mmol) at -78 °C, gradual warming to 0 °C, and treatment with an excess of magnesium bromide etherate. The white suspension was stirred at 0 °C for 30 min prior to use.

The original reaction mixture was stirred for 3 h at 0 °C, quenched with saturated NH₄Cl solution (5 mL), and extracted with ethyl acetate. The combined organic layers were dried and evaporated to leave a residue that was purified chromatographically on silica gel (elution with hexanes/ethyl acetate 10:1). There was isolated 118 mg (65%) of **14a** as a colorless oil; IR (neat, cm⁻¹) 3511, 2169,

1613; ^1H NMR (300 MHz, CDCl_3) 7.23 (d, $J = 8.6$ Hz, 2 H), 6.86 (d, $J = 8.6$ Hz, 2 H), 6.01-5.89 (m, 1 H), 5.14 (d, $J = 16.0$ Hz, 1 H), 5.13 (d, $J = 11.4$ Hz, 1 H), 4.48 (d, $J = 11.4$ Hz, 1 H), 4.43 (d, $J = 11.4$ Hz, 1 H), 4.36 (d, $J = 4.8$ Hz, 1 H), 3.81 (s, 3 H), 3.81-3.74 (m, 1 H), 3.31 (s, 1 H), 2.99 (t, $J = 8.2$ Hz, 1 H), 0.94 (s, 9 H), 0.17 (s, 9 H), 0.15 (s, 3 H), 0.14 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3) 159.2, 135.3, 130.1, 129.2 (2C), 116.9, 113.6 (2C), 103.8, 92.7, 76.2, 73.6, 71.0, 68.2, 59.1, 55.2, 26.8 (3C), 18.4, -0.1 (3C), -4.6, -4.9; ES HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 483.2357, obsd 483.2375; $[\alpha]_{\text{D}}^{22} +3.0$ (c 1.0, CHCl_3).

Cyclobutanediol 14b. A 42 mg (0.09 mmol) sample of **14a** was placed in 1% methanolic HCl (5 mL), stirred for 4 h at rt, cooled to 0 °C, and neutralized with saturated NaHCO_3 solution. After the removal of methanol under reduced pressure, the residue was leached with ethyl acetate, and the combined organic phases were dried and evaporated. Product purification was completed by chromatography on silica gel (elution with hexanes/ethyl acetate 2:1) and delivered 21 mg (68%) of **14b** as a white solid, mp 118-119 °C; IR (neat, cm^{-1}) 3313, 1612, 1511; ^1H NMR (300 MHz, CDCl_3) 7.26 (d, $J = 8.6$ Hz, 2 H), 6.90 (d, $J = 8.6$ Hz, 2 H), 5.95 (ddd, $J = 17.2, 10.5, 7.8$ Hz, 1 H), 5.17 (d, $J = 10.2$ Hz, 1 H), 5.14 (d, $J = 17.2$ Hz, 1 H), 4.52 (d, $J = 11.3$ Hz, 1 H), 4.45 (d, $J = 11.3$ Hz, 1 H), 4.22 (br d, $J = 4.7$ Hz, 1 H), 3.88-3.78 (m, 1 H), 3.82 (s, 3 H), 3.24 (br s, 1 H), 2.95 (br t, $J = 7.9$ Hz, 1 H), 2.98-2.93 (m, 1 H), 0.17 (s, 9 H); ^{13}C NMR (75 MHz, CDCl_3) 159.6, 134.5, 129.6 (2C), 129.2, 117.3, 114.0 (2C), 103.4, 93.4, 73.5, 71.7, 71.6, 67.6, 58.7, 55.3, -0.1 (3C); ES HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 369.1493, obsd 369.1476; $[\alpha]_{\text{D}}^{22} +19.1$ (c 1.0, CHCl_3).

Thermal Rearrangement of 14b. A 20 mg (0.06 mmol) sample of **14b** dissolved in benzene (4 mL) was heated at reflux for 4 h, freed of solvent, and chromatographed on silica gel (elution with hexanes-ethyl acetate 4:1) to give **15 (R = SiMe₃)** as a colorless oil (20 mg, 100%); IR (neat, cm^{-1}) 3452, 1652, 1612; ^1H

NMR (300 MHz, CDCl₃) 7.25 (d, *J* = 8.6 Hz, 2 H), 6.86 (d, *J* = 8.6 Hz, 2 H), 6.29 (d, *J* = 2.2 Hz, 1 H), 5.85-5.76 (m, 1 H), 5.68 (ddd, *J* = 11.3, 5.8, 1.9 Hz, 1 H), 5.02 (d, *J* = 2.3 Hz, 1 H), 4.64 (d, *J* = 11.7 Hz, 1 H), 4.59 (d, *J* = 11.7 Hz, 1 H), 4.39-4.36 (m, 1 H), 4.19-4.15 (m, 1 H), 3.79 (s, 3 H), 3.16 (br dd, *J* = 15.9, 6.0 Hz, 1 H), 2.85 (dd, *J* = 15.9, 8.6 Hz, 1 H), 0.13 (s, 9 H); ¹³C NMR (75 MHz, CDCl₃) 200.3, 161.0, 159.3, 134.8, 131.2 (2C), 130.0, 129.7, 128.6, 113.7 (2C), 79.5, 75.7, 72.8, 55.2, 30.2, -2.6 (3C); ES HRMS *m/z* (M+Na)⁺ calcd 369.1493, obsd 369.1513; [_D²²] -39.6 (c 0.82, CHCl₃).

Oxymercuration-Demercuration of 15 (R = SiMe₃). A cold (0 °C) solution of **15 (R = SiMe₃)** (27.8 mg, 0.08 mmol) in acetonitrile (4 mL) was treated with mercuric trifluoroacetate (68 mg, 0.16 mmol) and stirred for 2 h at this temperature. To this mixture was added ethanol (4 mL), sodium bicarbonate (134 mg, 1.6 mmol), and 1,3-propanedithiol (0.04 mL, 0.4 mmol), and stirring was maintained for 4 h at rt. The heterogeneous white mixture was filtered through a pad of Celite (hexanes rinse) and evaporated. The residue was purified by chromatography on silica gel (elution with hexanes/ethyl acetate 4:1) to give **16** as a white solid, mp 53-54 °C (21.7 mg, 78%); IR (neat, cm⁻¹) 1751, 1612, 1514; ¹H NMR (500 MHz, CDCl₃) 7.33 (d, *J* = 8.5 Hz, 2 H), 6.91 (d, *J* = 8.6 Hz, 2 H), 5.80 (ddd, *J* = 12.2, 6.8, 2.2 Hz, 1 H), 5.71-5.67 (m, 1 H), 4.65 (d, *J* = 11.7 Hz, 1 H), 4.59 (d, *J* = 11.7 Hz, 1 H), 4.45 (s, 1 H), 4.11 (d, *J* = 5.5 Hz, 1 H), 3.84 (s, 3 H), 2.94 (d, *J* = 17.9 Hz, 1 H), 2.55 (d, *J* = 18.6 Hz, 1 H), 2.24 (dd, *J* = 17.9, 6.9 Hz, 1 H), 2.23 (d, *J* = 18.6 Hz, 1 H), 0.17 (s, 9 H); ¹³C NMR (125 MHz, CDCl₃) 217.0, 159.7, 131.7, 130.8, 130.0 (2C), 127.1, 114.3 (2C), 81.8, 77.5, 75.5, 70.4, 55.7, 43.1, 39.7, -4.0 (3C); ES HRMS *m/z* (M+Na)⁺ calcd 369.1493, obsd 369.1502; [_D²⁰] -85.8 (c 1.18, CHCl₃).

Three-Step Desilylation of 14a. A mixture of **14a** (118 mg, 0.26 mmol) and K₂CO₃ (54 mg, 0.39 mmol) in methanol (5 mL) was stirred for 1 h at rt, cooled

to 0 °C, and quenched with saturated NH₄Cl solution. The methanol was carefully removed under reduced pressure and the aqueous phase was extracted with CH₂Cl₂. The combined organic phases were dried and evaporated. The residue was purified by chromatography on silica gel (elution with hexanes - ethyl acetate 10:1) to give the unsubstituted alkyne as a colorless oil (86 mg, 85%) that was used directly.

The above material (86 mg, 0.22 mmol) in benzene (5 mL) was refluxed for 2 h, cooled to rt, and evaporated. The residue was chromatographed on silica gel (elution with hexane - ethyl acetate 10:1) to provide the cyclooctadienone as a colorless oil (74 mg, 86%); IR (neat, cm⁻¹) 1703, 1612, 1514; ¹H NMR (300 MHz, CDCl₃) 7.26 (d, *J* = 8.4 Hz, 1 H), 6.87 (d, *J* = 8.6 Hz, 2 H), 6.11-6.03 (m, 1 H), 5.88-5.75 (m, 3 H), 4.79 (d, *J* = 2.7 Hz, 1 H), 4.62 (dd, *J* = 6.8, 2.8 Hz, 1 H), 4.56 (d, *J* = 11.6 Hz, 1 H), 4.49 (d, *J* = 11.6 Hz, 1 H), 3.81 (s, 3 H), 2.93-2.80 (m, 2 H), 0.93 (s, 9 H), 0.13 (s, 3 H), 0.05 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) 202.2, 159.1, 137.3 (2C), 133.8, 130.2, 129.4, 129.1, 127.2, 113.6 (2C), 81.8, 74.5, 70.7, 55.2, 29.0, 25.8, 18.6 (3C), -4.7, -5.2; ES HRMS *m/z* (M+Na)⁺ calcd 411.1962, obsd 411.1968; [α]_D²⁰ +0.17 (c 1.0 CHCl₃).

A solution of the preceding ketone (74 mg, 0.19 mmol) in 1% methanolic HCl (10 mL) was stirred at rt for 1.5 h, cooled to 0 °C, and quenched with saturated NaHCO₃ solution. The methanol was carefully removed under reduced pressure and the product was extracted into CH₂Cl₂. The combined organic layers were dried and evaporated to leave a residue that was chromatographed on silica gel (elution with hexanes - ethyl acetate 2:1) to give **15 (R = H)** as a white solid, mp 73-74 °C (21 mg, 40%) and **i** as a colorless oil (20 mg, 38%).

For **15** (**R** = **H**): IR (neat, cm^{-1}) 3472, 1698, 1610; ^1H NMR (300 MHz, CDCl_3) 7.26 (d, J = 8.6 Hz, 2 H), 6.87 (d, J = 8.6 Hz, 2 H), 6.34 (ddd, J = 12.6, 7.3, 5.1 Hz, 1 H), 6.00 (dd, J = 12.6, 2.7 Hz, 1 H), 5.88-5.77 (m, 2 H), 4.87 (s, 1 H), 4.65 (d, J = 11.7 Hz, 1 H), 4.57-4.53 (m, 1 H), 4.55 (d, J = 11.6 Hz, 1 H), 3.99 (br s, 1 H), 3.81 (s, 3 H), 3.09-3.02 (m, 1 H), 2.88-2.76 (m, 1 H); ^{13}C NMR (300 MHz, CDCl_3) 201.1, 159.3, 141.6, 132.9 (2C), 129.9, 129.7, 128.0, 127.4, 113.8 (2C), 77.9, 74.4, 71.8, 55.2, 28.7; ES HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 297.1097, obsd 297.1094; $[\text{J}]_{\text{D}}^{20}$ -61.3 (c 1.1, CHCl_3).

For **i**: IR (neat, cm^{-1}) 3458, 1711, 1612; ^1H NMR (300 MHz, CDCl_3) 7.28 (d, J = 8.4 Hz, 2 H), 6.89 (d, J = 8.6 Hz, 2 H), 5.92-5.65 (m, 2 H), 4.82 (dd, J = 8.2, 3.1 Hz, 0.5 H), 4.68 (d, J = 11.9 Hz, 1 H), 4.70-4.63 (m, 0.5 H), 4.54 (s, 0.5 H), 4.48 (d, J = 2.6 Hz, 0.5 H), 4.43 (d, J = 11.9 Hz, 0.5 H), 4.42 (d, J = 11.9 Hz, 0.5 H), 3.82 (s, 1.5 H), 3.81 (s, 1.5 H), 3.74-3.68 (m, 1 H), 3.57-3.54 (m, 0.5 H), 3.41 (s, 1.5 H), 3.34 (s, 1.5 H), 3.32-3.23 (m, 0.5 H), 2.86 (dd, J = 12.6, 6.5 Hz, 0.5 H), 2.78-2.77 (m, 0.5 H), 2.74-2.48 (m, 2 H), 2.28-2.13 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) 206.3, 206.1, 159.5, 159.4, 133.5, 132.7, 129.8, 129.6, 129.3, 129.1, 127.4, 113.94, 113.90, 82.0, 80.6, 77.9, 77.5, 72.4, 71.6, 70.2, 70.1, 56.62, 56.57, 55.3, 44.6, 40.4, 34.4, 32.3; ES HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 329.1359, obsd 329.1360; $[\text{J}]_{\text{D}}^{20}$ -60.9 (c 1.2, CHCl_3).

Oxymercuration - Demercuration of 15 (R = H). Reaction of **15** (**R** = **H**) (14 mg, 0.05 mmol) with mercuric trifluoroacetate (43 mg, 0.1 mmol) in the predescribed manner furnished 7 mg (91%) of **17a** as a colorless oil; IR (neat, cm^{-1}) 3410, 1714, 1434; ^1H NMR (500 MHz, CDCl_3) 5.95-5.91 (m, 1 H), 5.81-5.77 (m, 1 H), 4.70 (t, J = 7.3 Hz, 1 H), 4.54 (d, J = 1.7 Hz, 1 H), 3.84 (s, 1 H), 3.23 (dd, J = 15.1, 8.2 Hz, 1 H), 3.15 (d, J = 4.0 Hz, 1 H), 2.77-2.71 (m, 1 H), 2.29 (dt, J = 15.1, 0.9 Hz, 1 H), 1.91 (dd, J = 18.2, 5.3 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3)

206.1, 125.6, 125.2, 75.0, 74.6, 69.0, 42.7, 30.1; ES HRMS m/z (M+Na)⁺ calcd 177.0522, obsd 177.0535; $[\alpha]_D^{20}$ +22 (c 0.6, CHCl₃).

Cyclooctadienone 15 (R = CH₃). To a mixture of cyclobutanol **11** (235 mg, 0.64 mmol) and NaHCO₃ (1.08 g, 12.8 mmol) in CH₂Cl₂ (64 mL) was added the Dess-Martin periodinane (819 mg, 1.92 mmol). After 3 h of stirring at rt, the white suspension was filtered through a pad of celite (hexane rinse) and the filtrate was evaporated. For the preparation of propynylmagnesium bromide, propyne was bubbled into cold (-78 °C) THF (5 mL) for 15 min and this solution was treated with *n*-butyllithium (2 mL of 1.67 M, 3.34 mmol) and stirred for 30 min at this temperature before being warmed to 0 °C and treated with an excess of MgBr₂•OEt₂. After an additional 20 min of stirring at 0 °C, the cyclobutanone was introduced as a solution in THF (5 mL). The reaction mixture was stirred at 0 °C for 2 h, quenched with saturated NH₄Cl solution (5 mL), and extracted with ethyl acetate. The combined organic layers were dried and evaporated. Chromatography of the residue on silica gel (elution with hexanes - ethyl acetate 15:1) furnished 180 mg (69%) of the cyclobutanol adduct **ii** as a colorless oil; IR (neat, cm⁻¹) 3510, 1638, 1613; ¹H NMR (300 MHz, CDCl₃) 7.23 (d, *J* = 8.7 Hz, 2 H), 6.86 (d, *J* = 8.6 Hz, 2 H), 5.96 (ddd, *J* = 17.3, 10.3, 8.3 Hz, 1 H), 5.17-5.10 (m, 2 H), 4.47 (d, *J* = 11.6 Hz, 1 H), 4.42 (d, *J* = 11.6 Hz, 1 H), 4.33 (d, *J* = 4.5 Hz, 1 H), 3.81 (s, 3 H), 3.24 (dd, *J* = 4.8, 8.2 Hz, 1 H), 3.29 (s, 1 H), 2.99 (t, *J* = 8.3 Hz, 1 H), 1.88 (s, 3 H), 0.94 (s, 9 H), 0.15 (s, 3 H), 0.14 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) 159.1, 135.7, 130.1, 129.1 (2C), 116.8, 113.6 (2C), 83.9, 77.7, 76.4, 73.1, 70.8, 67.5, 59.4, 55.2, 25.8 (3C), 18.4, 3.7, -4.6, -5.0; ES HRMS m/z (M+Na)⁺ calcd 425.2119, obsd 425.2120; $[\alpha]_D^{20}$ 0 (c 1.1, CHCl₃).

A cold (0 °C) solution of **ii** (92 mg, 0.23 mmol) in methanol (7 mL) was treated with concentrated HCl (0.07 mL), warmed directly to 0 °C, stirred for 2 h, returned to 0 °C, and quenched with saturated NaHCO₃ solution. After the careful removal of methanol under reduced pressure and extraction with CH₂Cl₂, the combined organic layers were dried and concentrated, and the residue was chromatographed on silica gel. Elution with hexanes - ethyl acetate 1.5:1 delivered 54 mg (82%) of **iii** as a white solid, mp 62-64 °C; IR (neat, cm⁻¹) 3414, 1639, 1613; ¹H NMR (300 MHz, CDCl₃) 7.26 (d, *J* = 8.6 Hz, 2 H), 6.89 (d, *J* = 8.6 Hz, 2 H), 6.02-5.90 (m, 1 H), 5.17-5.11 (m, 2 H), 4.52 (d, *J* = 11.5 Hz, 1 H), 4.45 (d, *J* = 11.5 Hz, 1 H), 4.18 (br d, *J* = 4.3 Hz, 1 H), 3.83-3.79 (m, 1 H), 3.81 (s, 3 H), 3.23 (br s, 1 H), 2.97-2.92 (m, 2 H), 1.88 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) 159.5, 134.9, 129.6 (2C), 129.2, 117.1, 113.9 (2C), 84.5, 77.5, 73.7, 71.6, 71.4, 67.3, 58.8, 55.2, 3.7; ES HRMS *m/z* (M+Na)⁺ calcd 311.1254, obsd 311.1270; [²⁰D] +3.7 (c 1.4, CHCl₃).

A 54 mg (0.19 mmol) sample of **iii** was dissolved in benzene (5 mL), refluxed for 5 h, cooled to rt, and evaporated under reduced pressure. Chromatography of the residue (silica gel, elution with hexanes - ethyl acetate 3:1) gave **15 (R = CH₃)** as a colorless oil (50 mg, 93%); IR (neat, cm⁻¹) 3436, 1650, 1612; ¹H NMR (300 MHz, CDCl₃) 7.25 (d, *J* = 8.7 Hz, 2 H), 6.86 (d, *J* = 8.6 Hz, 2 H), 6.02 (s, 1 H), 5.95-5.86 (m, 1 H), 5.70 (ddd, *J* = 11.5, 5.8, 2.2 Hz, 1 H), 5.10-5.08 (m, 1 H), 4.65 (d, *J* = 11.6 Hz, 1 H), 4.60 (d, *J* = 11.6 Hz, 1 H), 4.38-4.37 (m, 2 H), 3.80 (s, 3 H), 3.31 (dd, *J* = 15.3, 4.5 Hz, 1 H), 2.59 (dd, *J* = 15.5, 9.1 Hz, 1 H), 1.99 (d, *J* = 0.8 Hz, 3 H); ¹³C NMR (75 MHz, CDCl₃) 198.5, 159.2, 157.4, 131.8, 130.2, 129.6 (2C), 126.8, 125.6, 113.7 (2C), 78.8, 76.4, 73.3, 55.2, 33.4, 28.0; ES HRMS *m/z* (M+Na)⁺ calcd 311.1254, obsd 311.1271; [²⁰D] -140.3 (c 1.2, CHCl₃).

Oxymercuration - Demercuration of 15 (R = CH₃). Reaction of **15 (R = CH₃)** (49 mg, 0.17 mmol) with mercuric trifluoroacetate (145 mg, 0.34 mmol) in CH₃CN (8 mL) as described above led to the isolation of **17b** (23 mg, 79%) and **18b** (7 mg, 14%).

For **17b**: colorless oil; IR (neat, cm⁻¹) 3417, 1732, 1714; ¹H NMR (500 MHz, CDCl₃) 5.98-5.95 (m, 1 H), 5.87-5.83 (m, 1 H), 4.63 (d, *J* = 1.7 Hz, 1 H), 3.88 (s, 1 H), 3.09 (d, *J* = 1.0 Hz, 1 H), 2.84 (d, *J* = 14.7 Hz, 1 H), 2.44 (d, *J* = 14.7 Hz, 1 H), 2.42 (dd, *J* = 18.1, 2.4 Hz, 1 H), 2.06 (dd, *J* = 18.1, 4.7 Hz, 1 H), 1.60 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) 206.6, 126.4, 125.0, 75.8, 74.3, 73.9, 48.5, 36.8, 30.4; ES HRMS *m/z* (M+Na)⁺ calcd 191.0679, obsd 191.0687; [²⁰D]_D²⁰ +27 (c 1.2, CHCl₃).

For **18b**: colorless oil; IR (neat, cm⁻¹) 1754, 1613, 1514; ¹H NMR (300 MHz, CDCl₃) 7.28 (d, *J* = 8.7 Hz, 2 H), 6.87 (d, *J* = 8.7 Hz, 2 H), 5.68-5.66 (m, 2 H), 4.61 (d, *J* = 11.7 Hz, 1 H), 4.54 (d, *J* = 11.7 Hz, 1 H), 4.52 (d, *J* = 2.5 Hz, 1 H), 4.04-4.01 (m, 1 H), 3.80 (s, 3 H), 2.81 (d, *J* = 16.9 Hz, 1 H), 2.45 (d, *J* = 18.5 Hz, 1 H), 2.38 (d, *J* = 18.5 Hz, 1 H), 2.38-2.30 (m, 1 H), 1.57 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) 214.8, 159.4, 130.1, 129.6 (2C), 128.6, 126.8, 113.9 (2C), 82.2, 77.2, 76.3, 70.3, 55.3, 47.5, 44.8, 29.0; ES HRMS *m/z* (M+Na)⁺ calcd 311.1254, obsd 311.1268; [²⁰D]_D²⁰ -75.5 (c 0.33, CHCl₃).

Cyclooctadienone 15 (R = C₆H₅). A 220 mg (0.60 mmol) sample of cyclobutanol **11** was oxidized with the Dess-Martin periodinane (763 mg, 1.8 mmol) in the prescribed manner and the resulting cyclobutanone was treated directly with phenylacetylenylmagnesium bromide. The latter reagent was prepared by the addition of *n*-butyllithium (1.8 mL of 1.67 M, 3 mmol) to a cold (-78 °C) solution of phenylacetylene (0.36 mL, 3.3 mmol) in dry THF (6 mL). The resulting solution was stirred in the cold for 30 min, warmed to 0 °C, treated with an excess of MgBr₂•OEt₂, and allowed to proceed for 20 min at this temperature prior to addition

to the ketone dissolved in THF (8 mL). The addition reaction was allowed to proceed at 0 °C for 2.5 h prior to work-up. There was isolated 195 mg (70%) of **iv** as a colorless oil; IR (neat, cm^{-1}) 3504, 1638, 1613; ^1H NMR (300 MHz, CDCl_3) 7.46-7.43 (m, 2 H), 7.37-7.23 (m, 5 H), 6.87 (d, $J = 8.6$ Hz, 2 H), 6.05 (ddd, $J = 17.5, 10.4, 8.2$ Hz, 1 H), 5.19 (d, $J = 17.4$ Hz, 1 H), 5.17 (d, $J = 10.2$ Hz, 1 H), 4.51 (d, $J = 11.7$ Hz, 1 H), 4.45 (d, $J = 11.6$ Hz, 1 H), 3.88-3.79 (m, 2 H), 3.81 (s, 3 H), 3.44 (s, 1 H), 3.11 (t, $J = 8.1$ Hz, 1 H), 0.97 (s, 9 H), 0.19 (s, 3 H), 0.17 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3) 159.1, 135.4, 131.8 (2C), 130.0, 129.1 (2C), 128.4, 128.2 (2C), 122.4, 117.1, 113.7 (2C), 87.7, 87.6, 76.4, 73.4, 70.9, 68.2, 59.5, 55.2, 25.8 (3C), 18.4, -4.6, -4.9; ES HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 487.2275, obsd 487.2257; $[\text{J}_\text{D}^{20}] +18.5$ (c 1.17, CHCl_3).

Desilylation of **iv** (72 mg, 0.15 mmol) in the prescribed manner afforded **v** (46 mg, 85%) as a white solid, mp 124-126 °C; IR (CHCl_3 , cm^{-1}) 3440, 1612, 1514; ^1H NMR (300 MHz, CDCl_3) 7.46-7.42 (m, 2 H), 7.32-7.26 (m, 5 H), 6.90 (d, $J = 8.6$ Hz, 2 H), 6.05 (ddd, $J = 18.6, 10.9, 7.8$ Hz, 1 H), 5.21 (d, $J = 10.0$ Hz, 1 H), 5.16 (d, $J = 17.9$ Hz, 1 H), 4.55 (d, $J = 11.4$ Hz, 1 H), 4.48 (d, $J = 11.5$ Hz, 1 H), 4.34-4.31 (m, 1 H), 3.92 (dd, $J = 7.5, 5.0$ Hz, 1 H), 3.83 (s, 3 H), 3.37 (s, 1 H), 3.07 (t, $J = 7.7$ Hz, 1 H), 3.01 (d, $J = 4.4$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) 159.6, 134.6, 131.8 (2C), 129.6 (2C), 129.1, 128.6 (2C), 128.2, 122.2, 117.4, 114.0 (2C), 88.2, 87.3, 73.7, 71.6, 71.5, 67.8, 59.0, 55.2; ES HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 373.1410, obsd 373.1417; $[\text{J}_\text{D}^{20}] +31$ (c 1.098, CHCl_3).

A solution of **v** (77 mg) in benzene (5 mL) was refluxed for 5 h and processed in the usual manner to give 76 mg (99%) of **15** (**R** = **C₆H₅**) as a

colorless oil; IR (neat, cm^{-1}) 3440, 1644, 1612; ^1H NMR (300 MHz, CDCl_3) 7.42-7.37 (m, 5 H), 7.25 (d, $J = 8.6$ Hz, 2 H), 6.86 (d, $J = 8.6$ Hz, 2 H), 6.43 (s, 1 H), 6.08-5.99 (m, 1 H), 5.78-5.73 (m, 1 H), 5.30-5.26 (m, 1 H), 4.68 (d, $J = 11.7$ Hz, 1 H), 4.63 (d, $J = 11.6$ Hz, 1 H), 4.47-4.41 (m, 2 H), 3.79 (s, 3 H), 3.69-3.62 (m, 1 H), 3.19 (dd, $J = 15.4, 9.4$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) 198.6, 159.2, 157.3, 141.5, 131.3, 130.2, 129.5 (2C), 129.4 (2C), 128.6, 127.5, 126.7 (2C), 126.4, 113.7 (2C), 78.9, 76.6, 73.5, 55.2, 31.9; ES HRMS m/z ($\text{M}+\text{Na}$)⁺ calcd 373.1410, obsd 373.1413; $[\text{D}]_{\text{D}}^{20} -56$ (c 1.0, CHCl_3).

Oxymercuration - Demercuration of 15 ($\text{R} = \text{C}_6\text{H}_5$). Reaction of **15** ($\text{R} = \text{C}_6\text{H}_5$) (45 mg, 0.13 mmol) with mercuric trifluoroacetate (111 mg, 0.26 mmol) in CH_3CN (5 mL) as described above led to the isolation of **17c** (18.6 mg, 62%) and **18c** (12 mg, 27%).

For **17c**: white solid, mp 173-175 $^\circ\text{C}$; IR (CHCl_3 , cm^{-1}) 3419, 1728, 1522; ^1H NMR (500 MHz, CDCl_3) 7.47-7.44 (m, 2 H), 7.41-7.38 (m, 2 H), 7.32-7.29 (m, 1 H), 6.04-6.00 (m, 1 H), 5.90-5.86 (m, 1 H), 4.83 (d, $J = 1.8$ Hz, 1 H), 3.91 (d, $J = 5.5$ Hz, 1 H), 3.12 (d, $J = 7.4$ Hz, 1 H), 3.09 (d, $J = 14.9$ Hz, 1 H), 2.78 (d, $J = 14.9$ Hz, 1 H), 2.61 (dd, $J = 18.1, 2.1$ Hz, 1 H), 2.46 (dd, $J = 18.1, 5.2$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) 205.7, 146.7, 128.6, 127.5 (2C), 126.5, 124.9 (2C), 123.2, 76.3, 75.7, 74.4, 49.3, 37.5; ES HRMS m/z ($\text{M}+\text{Na}$)⁺ calcd 253.0835, obsd 253.0820; $[\text{D}]_{\text{D}}^{20} +90.7$ (c 1.05, CHCl_3).

For **18c**: white solid, mp 126-128 $^\circ\text{C}$; IR (neat, cm^{-1}) 1755, 1613, 1514; ^1H NMR (300 MHz CDCl_3) 7.52-7.40 (m, 2 H), 7.38-7.26 (m, 5 H), 6.90 (d, $J = 8.6$ Hz, 2 H), 5.81-5.71 (m, 2 H), 4.70 (d, $J = 2.0$ Hz, 1 H), 4.68 (d, $J = 11.7$ Hz, 1 H), 4.63 (d, $J = 11.8$ Hz, 1 H), 4.16-4.15 (m, 1 H), 3.81 (s, 3 H), 2.97 (d, $J = 17.4$ Hz, 1 H), 2.84 (d, $J = 18.5$ Hz, 1 H), 2.77 (d, $J = 18.6$ Hz, 1 H), 2.73-2.57 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) 213.5, 159.4, 146.1, 130.1, 129.5 (2C), 128.4 (2C), 127.4, 126.9, 124.3 (2C), 123.3, 113.9 (2C), 83.4, 82.0, 77.2, 70.3, 55.3,

47.8, 46.6; ES HRMS m/z (M+Na)⁺ calcd 373.1410, obsd 373.1413; [α]_D²⁰ -30.6 (c 1.36, CHCl₃).

Thermal Rearrangement of 19. A solution of **19** (26 mg, 0.056 mmol) in benzene (4 mL) was refluxed for 5 h, freed of solvent, and chromatographed on silica gel (elution with hexanes/ethyl acetate 30:1) to give **20** as a colorless oil (18 mg, 69%); IR (neat, cm⁻¹) 1681, 1613, 1514; ¹H NMR (300 MHz, CDCl₃) 7.23 (d, J = 8.6 Hz, 2 H), 6.84 (d, J = 8.6 Hz, 2 H), 5.85-5.74 (m, 1 H), 5.47-5.39 (m, 1 H), 4.55 (d, J = 11.6 Hz, 1 H), 4.55-4.52 (m, 1 H), 4.31 (d, J = 11.7 Hz, 1 H), 4.13 (d, J = 5.0 Hz, 1 H), 3.79 (s, 3 H), 1.63 (dd, J = 7.0, 1.7 Hz, 3 H), 0.92 (s, 9 H), 0.20 (s, 9 H), 0.08 (s, 3 H), 0.06 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) 187.3, 159.0, 130.4, 130.0, 129.4 (2C), 127.0, 113.5 (2C), 101.2, 98.6, 82.1, 74.7, 69.8, 55.2, 25.8 (3C), 18.4, 13.6, -0.9 (3C), -4.8, -5.0; ES HRMS m/z (M+Na)⁺ calcd 483.2357, obsd 483.2346; [α]_D²² -25.8 (c 1.0, CHCl₃).