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General Chemical Procedures. Proton nuclear magnetic resonance (^{1}H NMR) and carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with $CDCl_3$ as the solvent at 400 MHz and 100 MHz respectively (Brüker AC 400). Chemical shifts are given in parts per million (ppm) downfield from internal reference tetramethylsilane in δ-units, and coupling constants (*J*-values) are given in hertz (Hz). Selected data are reported in the following manner: chemical shift; multiplicity; coupling constants; and assignment. Infrared (IR) spectra were recorded on a Mattson Galaxy Series 3000 FT infrared spectrometer. Liquid samples were measured as neat films on NaCl plates; solid samples were measured as KBr pellets. The reported frequencies are given in reciprocal centimeters (cm^{-1}) with the following relative intensities: s (strong, 70-100%), m (medium, 40-70%), w (weak, 20-40%), br (broad). Optical rotations were obtained on a Perkin-Elmer 241 polarimeter using a cell 1 dm in length and are reported as follows: $[\alpha]^{temp}_{wavelength}$, (concentration in g/100 mL, solvent). Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, NY, or Galbraith Laboratories, Inc., Knoxville, TN. Flash column chromatography refers to the method of Still[42] using Merck 230-400 mesh silica gel. Gradient elution refers to applying the compound as a solution in hexanes to the hexanes-equilibrated column, then eluting with progressively more polar hexanes / EtOAc solutions. Analytical thin layer chromatography (TLC) was performed using Merck 60-F-254 0.25 mm precoated silica gel plates. Compounds were visualized using ultraviolet light, iodine vapor, or cerium molybdate / sulfuric acid / methanol. Preparative thin layer chromatography (PTLC) was performed using Merck 60-F-254 0.50 or 1.00 mm precoated silica gel plates. High performance liquid chromatography (HPLC) was performed on a Beckman System Gold 126 chromatograph using a 4.6 x 250 mm Beckman Ultrasphere ODS column. Preparative HPLC was performed on a Waters Delta Prep 4000. The detector wavelength was set to 254 nm. Ethyl ether and tetrahydrofuran were distilled directly prior to use from sodium / benzophenone ketyl. Dichloromethane (CH_2Cl_2), benzene, and toluene were dried and stored under nitrogen over 4Å molecular sieves. Organic amines were distilled from CaH_2 and stored over solid KOH pellets

under nitrogen. Unless otherwise specified, solutions of common inorganic salts used in work-ups are aqueous solutions. All moisture sensitive reactions were carried out using oven-dried or flame-dried round-bottomed (rb) flasks and glassware under an atmosphere of dry nitrogen.

Synthesis of Benzylic Bromide 5.

4-Bromo-2-(*tert*-butyl)dimethylsilyloxy-5-methoxybenzaldehyde (4b). To a flame-dried 100-mL rb flask containing 2.76 g (12.0 mmol) 4-bromo-2-hydroxy-5-methoxybenzaldehyde (**4a**)[11] in 50 mL anhydrous CH_2Cl_2 at rt was added 2.03 g (29.9 mmol, 2.50 equiv) imidazole, 2.25 g (14.9 mmol, 1.25 equiv) (*tert*-butyl)chlorodimethylsilane, and 4-*N*,*N*-dimethylaminopyridine (DMAP) (100 mg, 0.8 mmol, 0.1 equiv). The mixture was allowed to stir at rt for 75 min, at which time TLC analysis indicated complete consumption of starting material, and the formation of a less polar product (R_f 0.75, 2:1 hexanes / EtOAc). The reaction mixture was then poured into a separatory funnel containing 50 mL CH_2Cl_2 and 50 mL saturated NH_4Cl, the layers were separated, and the organic phase was washed with 50 mL brine, dried (Na_2SO_4), and concentrated under reduced pressure to give 4.13 g (99%) of the silylated bromophenol as a colorless low-melting solid. **^{1}H NMR** 0.27 [s, 6H, Si(CH_3)$_2$], 1.02 [s, 9H, SiC(CH_3)$_3$], 3.89 (s, 3H, OCH_3), 7.14 (s, 1H, 6-H), 7.28 (s, 1H, 3-H), 10.35 (s, 1H, C*H*O). **^{13}C NMR** -4.4, 18.3, 25.7, 56.7, 108.9, 120.1, 125.6, 126.5, 151.0, 152.9, 189.1.

4-Bromo-2-(*tert*-butyl)dimethylsilyloxy-5-methoxybenzyl bromide (5). To a flame-dried 200-mL rb flask containing **4b** (4.10 g, 13.1 mmol) in 100 mL anhydrous methanol at 0 °C was added 0.50 g (13 mmol, 1.0 mol equiv) $NaBH_4$ over a period of 3 min. After 20 min at 0 °C, TLC analysis indicated complete consumption of starting material, and the formation of a more polar product (R_f 0.42, 2:1 hexanes / EtOAc). Water (75 mL) was added, and the methanol was removed by rotary evaporation. The resultant aqueous residue was extracted with EtOAc (2 x 100 mL), and the combined organic layers were dried (Na_2SO_4), and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, hexanes / EtOAc, 5:1) afforded 4.10 g (98%) of the benzylic alcohol as a colorless low-melting solid. **^{1}H NMR** 0.23 [s, 6H,

$Si(CH_3)_2$], 1.00 [s, 9H, $SiC(CH_3)_3$], 3.85 (s, 3H, OCH_3), 4.63 (d, 2H, J = 6.1, CH_2OH), 6.94 (s, 1H, 6-H), 6.99 (s, 1H, 3-H). **^{13}C NMR** -4.3, 18.1, 25.7, 56.8, 61.3, 110.0, 112.1, 123.2, 131.6, 147.3, 150.7. This alcohol was then brominated in the following manner. To a flame-dried 100-mL rb flask containing triphenylphosphine (1.27 g, 4.84 mmol, 1.05 equiv) in 25 mL anhydrous DMF at 0 ℃ was added bromine (0.24 mL, 4.8 mL, 1.1 equiv) through an addition funnel. To this reaction mixture was added 4-bromo-2-(*tert*-butyl)dimethylsilyloxy-5-methoxybenzyl alcohol in 10 mL DMF through the addition funnel over 30 min. The reaction mixture was allowed to stir at 0 ℃ for 60 min, at which time TLC analysis indicated complete consumption of starting material, and the formation of a less polar product (R_f 0.81, 2:1 hexanes / EtOAc). Hexane (100 mL) was then added, and the contents of the flask were transferred to a separatory funnel containing 50 mL of saturated NH_4Cl, rinsing with an additional 50 mL hexanes and 10 mL water. The layers were separated, and the organic phase was washed with 20 mL 10% $Na_2S_2O_3$, dried (Na_2SO_4), and concentrated under reduced pressure. Purification by trituration at 0 ℃ (2 x 30 mL ea. hexanes) to remove residual triphenylphosphine oxide, followed by flash column chromatography (silica gel, hexanes / EtOAc, gradient elution) afforded 1.51 g (80%) of the benzylic bromide as a colorless low-melting solid. **^{1}H NMR** 0.28 [s, 6H, $Si(CH_3)_2$], 1.05 [s, 9H, $SiC(CH_3)_3$], 3.87 (s, 3H, OCH_3), 4.48 (s, 2H, CH_2Br), 6.79 (s, 1H, 6-H), 7.01 ppm (s, 1H, 3-H). **^{13}C NMR** -4.2, 18.2, 25.7, 56.8, 112.1, 113.9, 114.0, 123.6, 128.1, 147.8, 150.5.

Synthesis of Racemic Compounds 8c, 8d, 12 and 16.

6-[4-Bromo-2-(*tert*-butyl)dimethylsilyloxy-5-methoxyphenyl]methyl-3,5,5-trimethylcyclohex-2-en-1-one (7b). This compound was prepared from isophorone (0.17 g, 1.2 mmol) in the manner previously described for enone **7a**, affording 0.34 g (60%) of the alkylation product (R_f 0.40, 2:1 hexanes / EtOAc) as a colorless, low-melting solid. **^{1}H NMR** 0.20 and 0.22 [2s, 2 x 3H, $Si(CH_3)_2$], 0.99 [s, 9H, $SiC(CH_3)_3$], 1.00 and 1.02 (2s, 2 x 3H, geminal-CH_3's), 1.92 (s, 3H, 3-CH_3), 2.16 and 2.23 (ABq, 2H, J_{AB} = 18.6, 4-H), 2.42 (dd,

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1H, J = 8.1, 5.4, 6-H), 2.78 and 2.84 (d of ABq, 2H, J_{AB} = 14.3, J_A = 8.2, J_B = 5.3, benzylic-CH_2), 3.81 (s, 3H, OCH_3), 5.82 (d, 1H, J = 1.0, 2-H), 6.72 (s, 1H, 6'-H), 6.93 (s, 1H, 3'-H). **^{13}C NMR** -4.1, 18.3, 24.1, 24.2, 25.7, 25.9, 28.7, 36.7, 44.9, 56.8, 57.5, 108.2, 114.4, 123.1, 125.0, 131.5, 147.5, 150.2, 157.7, 201.4.

6-(2-Acetoxy-4-bromo-5-methoxyphenyl)methyl-3,5,5-trimethyl-1-methylidenecyclohexene (12). This compound was prepared from enone **7b** (42.0 mg, 0.0900 mmol) in the manner previously described for acetoxy diene **8b-OAc**, affording 18.4 mg (52%) of the acetoxy-diene as a colorless oil. **^{1}H NMR** 0.87 and 1.11 (2s, 2 x 3H, geminal-CH_3's), 1.78 (s, 3H, 3-CH_3), 2.26 (s, 3H, acetate-CH_3), and (d of ABq, 2H, J_{AB} = , J_A = , J_B = , benzylic-CH_2), 3.83 (s, 3H, OCH_3), 4.03 and 4.58 (2s, 2 x 1H, methylidene-CH_2), 5.82 (s, 1H, 2-H), 6.52 (s, 1H, 6'-H), 7.19 (s, 1H, 3'-H). **^{13}C NMR** 19.8, 20.1, 20.7, 22.9, 30.6, 33.1, 35.0, 47.4, 56.6, 108.6, 111.7, 114.5, 123.0, 125.9, 133.0, 134.0, 143.0, 143.4, 153.6, 170.1. **IR** (neat) 1733 (s). **Anal.** ($C_{20}H_{25}BrO_3$) C, H.

6-(4-Bromo-2-hydroxy-5-methoxyphenyl)methyl-3,5,5-trimethyl-1-methylidenecyclohex-2-ene (8c). This compound was prepared from acetoxy diene **12** (6.80 mg, 0.0200 mmol) in the manner previously described for diene **8b**, affording 5.8 mg (96%) of the phenolic diene as a colorless, low-melting solid. **^{1}H NMR** 0.87 and 1.15 (2s, 2 x 3H, geminal-CH_3's), 1.70 and 2.25 (ABq, 2H, J_{AB} = 14.0, 4-H), 1.80 (s, 3H, 3-CH_3), 1.95 (dd, 1H, J = 11.5, 3.3, 6-H), 2.17 and 2.79 (d of ABq, 2H, J_{AB} = 13.4, J_A = 13.3, J_B = 3.4, benzylic-CH_2), 3.82 (s, 3H, OCH_3), 4.15 and 4.63 (2s, 2 x 1H, methylidene-CH_2), 5.87 (s, 1H, 2-H), 6.52 (s, 1H, 6'-H), 6.99 (s, 1H, 3'-H). **^{13}C NMR** 22.7, 23.7, 30.3, 31.6, 33.2, 41.2, 52.3, 57.0, 108.7, 112.2, 115.3, 120.5, 122.1, 128.0, 137.3, 144.4, 148.5, 149.9. **IR** (neat) 3434 (br, m).

5-[4-Bromo-2-(*tert*-butyl)dimethylsilyloxy-5-methoxyphenyl]methyl-4,4-dimethylcyclopent-2-en-1-one (7c). This compound was prepared from enone **6c** (0.13 g, 1.2 mmol) and bromide **5** (1.00 g, 2.44 mmol, 2.00 equiv) in the manner previously described for enone **7a**, affording 0.427 g (81%) of the benzylated enone as a colorless syrup (R_f 0.57, 2:1

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hexanes / EtOAc). **^{1}H NMR** 0.20 and 0.23 [2s, 2 x 3H, Si(C*H*$_3$)$_2$], 0.97 [s, 9H, SiC(C*H*$_3$)$_3$], 1.00 and 1.08 (2s, 2 x 3H, geminal-C*H*$_3$'s), 2.60-2.70 (m, 2H, 5-H and benzylic-C*H*), 3.07 (dd, 1H, J = 13.3, 3.1, benzylic-C*H*), 3.83 (s, 3H, OC*H*$_3$), 6.04 (d, 1H, J = 5.9, 2-H), 6.83 (s, 1H, 6'-H), 6.98 (s, 1H, 3'-H), 7.38 (d, 1H, J = 5.7, 3-H).

2-(4-Bromo-2-hydroxy-5-methoxyphenyl)methyl-3,3-dimethyl-1-methylidene-cyclopentane (8d). The intermediate ketone was prepared from enone **7c** (0.15 g, 0.33 mmol) in the manner previously described for the 6-membered homologue, affording 0.14 g (91%) of the desired product as a colorless, low-melting solid. **^{1}H NMR** 0.21 [s, 6H, Si(C*H*$_3$)$_2$], 0.90 and 0.91 (2s, 2 x 3H, geminal-C*H*$_3$'s), 0.98 [s, 9H, SiC(C*H*$_3$)$_3$], 1.67-1.78 (m, 2H, 4-H), 2.14-2.32 (m, 2H, 5-H), 2.36 (dd, 1H, J = 7.8, 6.0, 2-H), 2.51 (dd, 1H, J = 14.5, 8.0) and 2.91 (dd, 1H, J = 14.5, 5.5) [benzylic-C*H*$_2$], 3.83 (s, 3H, OC*H*$_3$), 6.81 (s, 1H, 6'-H), 6.95 (s, 1H, 3'-H). This intermediate was then methylenated in the following manner. To a flame-dried 25-mL rb flask was added 340 mg (0.90 mmol) of $CeCl_3 \cdot 7\ H_2O$, and the flask was heated to 140 °C under vacuum for 2 h, after which time the solid was cooled to rt, and 3 mL of THF was added. After stirring for 2 h at rt, the slurry was cooled to -78 °C and (trimethyl)silylmethyllithium (0.78 mL of a 1.00 M solution in pentane, 0.78 mmol) was added. After 30 min, 2-[4-bromo-2-(*tert*-butyl)dimethylsilyloxy-5-methoxyphenyl]methyl-3,3-dimethylcyclopentanone (15.0 mg, 0.030 mmol) in 1 mL THF was added, and the mixture was allowed to stir at -78 °C for 4 h, before quenching with 5 mL saturated NH_4Cl. The reaction mixture was extracted with 40 mL ether, and the organic phase was dried (Na_2SO_4), and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, hexanes / EtOAc 9:1) gave 15 mg (83%) of the tertiary alcohol intermediate as a colorless oil. Compound **8d** was prepared from this alcohol intermediate (7.3 mg, 0.014 mmol) in the manner previously described for **8a**, affording 3.0 mg (66%) of the desired product as a colorless oil. **^{1}H NMR** 0.92 and 0.96 (2s, 2 x 3H, geminal-C*H*$_3$'s), 1.53 (m, 2H, 4-H), 2.39 (m, 3H, 2,5-H), 2.57 and 2.67 (d of ABq, 2H, J_{AB} = 14.5, J_A = 8.5, J_B = 5.4, benzylic-C*H*$_2$), 3.81 (s, 3H, OC*H*$_3$), 4.50 (s, 1H, O*H*), 4.66 and 4.84 (2s, 2 x 1H, methylidene-C*H*$_2$), 6.74 (s, 1H, 6'-H), 6.99 (s, 1H, 3'-H). **^{13}C NMR** 21.9, 28.0, 29.1, 29.4,

38.8, 41.6, 53.7, 57.0, 106.5, 108.5, 114.8, 120.2, 128.2, 148.0, 150.1, 155.5. **Anal.** ($C_{16}H_{21}BrO_2$) C, H.

6-[4-Bromo-2-(*tert*-butyl)dimethylsilyloxy-5-methoxyphenyl]methyl-3-ethoxy-5,5-dimethylcyclohex-2-en-1-one (14). This compound was prepared from 3-ethoxy-5,5-dimethylcyclohex-2-en-1-one (1.30 g, 7.73 mmol) and benzyl bromide **5** (1.53 g, 3.73 mmol) in the manner previously described for enone **7a**, affording 1.71 g (92%) of the desired β-ethoxy enone as a colorless, low-melting solid. **^{1}H NMR** 0.20 and 0.22 [2s, 2 x 3H, $Si(CH_3)_2$], 0.99 [s, 9H, $SiC(CH_3)_3$], 1.01 and 1.04 (2s, 2 x 3H, geminal-CH_3's), 1.37 (t, 3H, J = 6.9, OCH_2CH_3), 2.28 and 2.34 (ABq, 2H, J_{AB} = 17.6, 4-H), 2.43 (dd, 1H, J = 6.6, 6.4, 6-H), 2.84 and 2.85 (d of ABq, 2H, J_{AB} = 5.8, J_A = 2.6, J_B = 1.1, benzylic-CH_2), 3.82 (s, 3H, OCH_3), 3.90 (q, 2H, J = 7.0, OCH_2CH_3), 5.32 (br s, 1H, 2-H), 6.77 (s, 1H, 6'-H), 6.93 (s, 1H, 3'-H).

4-[4-Bromo-2-(*tert*-butyl)dimethylsilyloxy-5-methoxyphenyl]methyl-3,5,5-trimethylcyclohex-2-en-1-one (15). To a flame-dried 50-mL rb flask containing 6-[4-bromo-2-(*tert*-butyl)dimethylsilyloxy-5-methoxyphenyl]methyl-3-ethoxy-5,5-dimethylcyclohex-2-en-1-one (1.01 g, 2.02 mmol) in 10 mL ether at -78 °C was added methyllithium (4.33 mL of a 1.40 M solution in ether, 6.06 mmol, 3.00 equiv). After 3 h at -78 °C, 1.0 M $NaHSO_4$ (5mL) was added, and the reaction mixture was allowed to stir overnight, warming to rt. The biphasic reaction mixture was then extracted with EtOAc (100 mL), and the organic phase was washed with brine (50 mL), dried (Na_2SO_4), and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, hexanes / EtOAc, gradient elution) afforded 0.850 g (90%) of the desired enone as a colorless, low-melting solid. **^{1}H NMR** 0.24 and 0.26 [2s, 2 x 3H, $Si(CH_3)_2$], 1.01 [s, 9H, $SiC(CH_3)_3$], 1.04 and 1.14 (2s, 2 x 3H, geminal-CH_3's), 1.41 (d, 3H, J = 1.1, 3-CH_3), 2.11 and 2.50 (ABq, 2H, J_{AB} = 17.7, benzylic-CH_2), 2.35-2.43 (m, 2H, 6-H), 3.22 (br d, 1H, $J \approx$ 8.0, 4-H), 3.80 (s, 3H, OCH_3), 5.83 (br s, 1H, 2-H), 6.57 (s, 1H, 6'-H), 6.98 (s, 1H, 3'-H).

4-(4-Bromo-2-hydroxy-5-methoxyphenyl)methyl-3,5,5-trimethyl-1-methylidenecyclohex-2-ene (16). This compound was prepared from 4-[4-bromo-2-(*tert*-

butyl)dimethylsilyloxy-5-methoxyphenyl]methyl-3,5,5-trimethylcyclohex-2-en-1-one (100 mg, 0.2 mmol) in the manner previously described for olefin **8a**, affording 43 mg (57%) of the desired diene as a colorless oil. **^{1}H NMR** 0.87 and 1.07 (2s, 2 x 3H, geminal-CH_3's), 1.38 (s, 3H, 3-CH_3), 1.95 and 2.48 (ABq, 2H, J_{AB} = 17.6, 6-H), 2.02 (dd, 1H, J = 11.6, 4.5, 4-H), 2.46 and 2.94 (d of ABq, 2H, J_{AB} = 17.0, J_A = 13.1, J_B = 4.0, benzylic-CH_2), 3.80 (s, 3H, OCH_3), 4.74 (br s, 2H, methylidene-C*H* and O*H*), 4.81 (s, 1H, methylidene-C*H*), 5.93 (s, 1H, 2-H), 6.67 (s, 1H, 6'-H), 7.00 (s, 1H, 3'-H). **^{13}C NMR** 14.2, 24.7, 27.4, 27.8, 32.7, 38.9, 50.7, 57.0, 108.9, 110.6, 115.0, 120.5, 125.2, 128.3, 142.2, 142.4, 148.4, 150.2. **IR** (neat) 3437 (br, m).

Synthesis of Allylic Bromide 18 and Compound 19.

***trans*-Methyl 4-bromo-2-(*tert*-butyl)dimethylsilyloxy-5-methoxycinnamate (17).** To a flame-dried 25-mL 3-necked rb flask at rt equipped with a reflux condenser and an addition funnel was added sodium hydride (0.23 g of a 60% dispersion in mineral oil, 5.8 mmol, 1.0 equiv). Anhydrous benzene (2 mL) was added, and then trimethylphosphonoacetate (1.06 g, 5.80 mmol, 1.00 equiv) in 1 mL benzene was added dropwise through the addition funnel over a period of 45 min. The reaction mixture was vigorously stirred for an additional 90 min at rt before aldehyde **4b** (2.00 g, 5.80 mmol) in 5 mL benzene was added dropwise over 90 min. The reaction mixture was allowed to stir an additional 90 min at rt before heating to 65 °C for 5 min. Upon cooling to rt, the product was isolated by repetitive washing of the solid residue with benzene (6 x 25 mL) at 65°C, cooling, and decanting, until TLC analysis of the wash solution indicated the absence of any product. The combined organic washings were dried (Na_2SO_4), and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, hexanes / EtOAc, 5:1) afforded 2.05 g (88%) of the desired *trans*-cinnamate as a colorless, low-melting solid. **^{1}H NMR** 0.21 [s, 6H, Si(CH_3)$_2$], 1.03 [s, 9H, SiC(CH_3)$_3$], 3.80 (s, 3H, ArOCH_3), 3.87 (s, 3H, CO_2CH_3), 6.38 (d, 1H, J = 16.2, CH=C*H*CO_2Me), 7.00 (s, 1H, 6'-H), 7.06 (s, 1H, 3'-H), 7.97 (d, 1H, J = 16.3, C*H*=CHCO_2Me).

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3-[4-Bromo-2-(*tert*-butyl)dimethylsilyloxy-5-methoxyphenyl]prop-2-enyl bromide (18). To a flame-dried 200-mL rb flask containing cinnamate **17** (2.00 g, 4.98 mmol) in 20 mL ether at -40 °C was added DIBAL-H (17 mL of a 1.0 M solution in hexanes, 17 mmol, 3.5 equiv), at a rate such that the reaction temperature did not rise above -30 °C. After 20 min, the reaction mixture was poured into a 250-mL erlynmeyer flask containing 50 mL ice-cold 1.0 M $NaHSO_4$, and the resultant biphasic mixture was stirred 5 min before extraction with EtOAc (3 x 50 mL). The combined organic solutions were washed with 50 mL brine, dried (Na_2SO_4), and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, hexanes / EtOAc, 5:1) afforded 1.57 g (85%) of the desired allylic alcohol as a colorless low-melting solid. **^{1}H NMR** 0.18 [s, 6H, Si(CH_3)$_2$], 1.00 [s, 9H, SiC(CH_3)$_3$], 3.77 (s, 3H, OCH_3), 4.32 (t, 2H, J = 6.8, CH_2OH), 6.30 (dt, 1H, J = 15.8, 7.0, ArCH=CHCH$_2$OH), 6.84 (dt, 1H, J = 16.0, 1.1, ArCH=CHCH$_2$OH), 6.98 and 7.00 (2s, 2 x 1H, 6',3'-H). This alcohol (1.50 g, 4.04 mmol) was brominated using triphenylphosphine dibromide in the manner previously described for bromide **5**. Purification by trituration at 0 °C (2 x 30 mL hexanes) to remove residual triphenylphosphine oxide, followed by flash column chromatography (silica gel, hexanes / EtOAc, gradient elution) afforded 1.57 g (90%) of the desired allylic bromide as a colorless syrup. **^{1}H NMR** 0.20 [s, 6H, Si(CH_3)$_2$], 1.01 [s, 9H, SiC(CH_3)$_3$], 3.86 (s, 3H, OCH_3), 4.14 (d, 2H, J = 7.0, CH_2Br), 6.33 (dt, 1H, J = 15.8, 7.2, ArCH=CHCH$_2$Br), 6.88 (d, 1H, J = 16.0, ArCH=CHCH$_2$Br), 6.94 and 7.00 (2s, 2 x 1H, 6',3'-H).

6-[*trans*-(4-Bromo-2-hydroxy-5-methoxyphenyl)-1-propenyl]-3,5,5-trimethyl-1-methylidenecyclohex-2-ene (19). The intermediate enone was prepared from isophorone (0.40 g, 2.9 mmol) and bromide **18** (0.50 g, 1.2 mmol) in the manner previously described for enone **7a**, affording 452 mg (80%) of the desired enone as a yellow oil. **^{1}H NMR** 0.16 an 0.17 [2s, 2 x 3H, Si(CH_3)$_2$], 0.97 and 1.09 (2s, 2 x 3H, geminal-CH_3's), 1.00 [s, 9H, SiC(CH_3)$_3$], 1.92 (s, 3H, 3-CH_3), 2.34-2.52 (m, 2H, allylic-CH_2), 3.85 (s, 3H, OCH_3), 5.85 (d, 1H, J = 1.2, 2-H), 6.21 (ddd, 1H, J = 15.8, 7.1, 7.1, ArCHCH), 6.59 (d, 1H, J = 16.0, ArCHCH), 6.93 and 6.94 (2s, 2 x 1H, Ar-H). This enone (50.0 mg, 0.10 mmol) was then methylenated in

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the manner previously described for olefin **8a**, affording 23.0 mg (60%) of the desired triene as a colorless oil. **^{1}H NMR** 0.88 and 1.04 (2s, 2 x 3H, geminal-C*H*$_3$'s), 1.74 (s, 3H, 3-C*H*$_3$), 3.83 (s, 3H, OC*H*$_3$), 4.62 and 4.81 (2s, 2 x 1H, methylidene-C*H*$_2$), 5.13 (s, 1H, O*H*), 5.85 (s, 1H, 2-H), 6.07 (ddd, 1H, J = 15.4, 6.9, 6.9, ArCHC*H*), 6.32 (d, 1H, J = 16.2, ArC*H*CH), 6.76 (s, 1H, 6'-H), 7.03 (s, 1H, 3'-H). **^{13}C NMR** . **IR** (neat) 3442 (br, m).

Synthesis of Compound 24.

6-(Benzofurazan-5-yl)methyl-3,5,5-trimethyl-1-methylidenecyclohex-2-ene (24). A flame-dried 200-mL rb flask equipped with a reflux condenser was charged with 5-methylbenzofurazan (1.04 g, 7.72 mmol), carbon tetrachloride (75 mL), and AIBN (10 mg, catalytic). *N*-Bromosuccinamide (1.44 g, 8.10 mmol, 1.05 equiv) was added, and the mixture was heated to reflux 4 h in the presence of an incandescent sunlamp. Upon cooling to rt, the solvent was removed under reduced pressure, and the resultant yellow residue was purified by flash column chromatography (silica gel, hexanes / EtOAc, 5:2), affording 0.92 g (56%) of the desired benzofurazan-5-yl-methyl bromide (R$_f$ 0.55, 2:1 hexanes / EtOAc) as a white solid. **^{1}H NMR** 4.51 (s, 2H, C*H*$_2$Br), 7.44 (d, 1H, J = 10.4, 6-H), 7.80 (s, 1H, 4-H), 7.85 (d, 1H, J = 10.4, 7-H). The title compound was then prepared from isophorone (1.48 mL, 9.83 mmol) and benzofurazan-5-yl-methyl bromide (0.84 g, 3.9 mmol) in three steps in the manner previously described for olefin **8a** through the intermediate enone 6-(benzofurazan-5-yl)methyl-3,5,5-trimethylcyclohex-2-en-1-one. **^{1}H NMR** 1.01 and 1.18 (2s, 2 x 3H, geminal-C*H*$_3$'s), 1.94 (s, 3H, 3-C*H*$_3$), 2.20 and 2.35 (ABq, 2H, J_{AB} = 18.5, 4-H), 2.45 (dd, 1H, J = 8.9, 3.2, 6-H), 2.80 and 3.10 (d of ABq, 2H, J_{AB} = 14.1, J_A = 3.1, J_B = 8.9) [benzylic-C*H*$_2$], 5.87 (s, 1H, 2-H), 7.36 (d, 1H, J = 9.2, 6'-H), 7.57 (s, 1H, 2'-H), 7.72 (d, 1H, J = 9.2, 5'-H). Peterson methylenation of this enone as previously described afforded the desired diene as a pale orange oil (R$_f$ 0.41, 2:1 hexanes / EtOAc) in 33% overall yield from isophorone. **^{1}H NMR** 0.90 and 1.14 (2s, 2 x 3H, geminal-C*H*$_3$'s), 1.72 and 2.13 (ABq, 2H, J_{AB} = 18.3, 4-H), 1.78 (s, 3H, 3-C*H*$_3$), 2.02 (dd, 1H, J = 11.4, 3.1) and 2.95 (dd, 1H, J = 12.8, 2.9) [benzylic-C*H*$_2$], 2.33 (dd, 1H, J =

12.7, 12.6, 6-H), 4.02 and 4.54 (2s, 2 x 1H, methylidene-CH_2), 5.83 (s, 1H, 2-H), 7.16 (d, 1H, J = 9.2, 6'-H), 7.37 (s, 1H, 2'-H), 7.67 (d, 1H, J =9.3, 5'-H). **^{13}C NMR** 28.2, 32.0, 32.4, 37.0, 39.6, 44.4, 54.9, 108.8, 111.1, 111.7, 118.5, 130.1, 130.9, 137.9, 139.7, 142.2, 143.1. **IR** (neat) 2960 (br, w), 1651 (m). **Anal.** ($C_{17}H_{20}N_2O$) C, H, N.

Synthesis of Enantiomerically Pure Compounds 28b, 30 and 31.

(1*R*,3*R*)-3-(4-Bromo-2-hydroxy-5-methoxyphenyl)methyl-1-hydroxy-4,4-dimethyl-2-methylidenecyclohexane (28b) and (1*S*,3*R*)-3-(4-Bromo-2-hydroxy-5-methoxyphenyl)methyl-1-hydroxy-4,4-dimethyl-2-methylidenecyclohexane (1-epi-28b). To a flame-dried 25-mL rb flask containing **26a** (0.75 g, 1.7 mmol) in 3.5 mL anhydrous CH_2Cl_2 at rt was added SeO_2 (0.090 g, 0.83 mmol, 0.50 equiv) and anhydrous (*tert*-butyl)hydroperoxide (1.1 mL of a 3.0 M solution in 2,2,4-trimethylpentane, 3.3 mmol, 2.0 equiv), and the mixture was allowed to stir at rt for 40 h, at which time the solvent was removed by rotary evaporation. Purification by flash column chromatography (silica gel, hexanes / EtOAc, gradient elution) afforded 741 mg (95%) of an inseparable 1:1 mixture of diastereomeric allylic alcohols as a colorless syrup. A portion (40.0 mg, 0.090 mmol) of this diastereomeric mixture was dissolved in 1 mL THF, cooled to 0 °C, and treated with TBAF (98 μL of a 1.0 M solution in THF, 0.10 mmol, 1.2 equiv). After 10 min, the reaction was quenched by the addition of pH 7 potassium phosphate buffer (5 mL), and extracted with hexanes (2 x 25 mL). The combined organic extracts were dried (Na_2SO_4), and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, hexanes / EtOAc, gradient elution) yielded a mixture of free phenols, separable by flash column chromatography (silica gel, hexanes / EtOAc, gradient elution), to give 14.0 mg (46%) of the less polar 1*R*,3*R* diastereomer **28b**, along with 13.0 mg (43%) of the more polar 1*S*,3*R* diastereomer as colorless, low-melting solids. Data for **28b**: **^{1}H NMR** 0.93 and 1.12 (2s, 2 x 3H, geminal-CH_3's), 1.70 (m, 2H, 1-H), 1.94 (m, 3H, 6,3-H), 2.65 and 3.00 (d of ABq, 2H, J_{AB} = 14.0, J_A = 3.1, J_B = 14.0, benzylic-CH_2) 3.84 (s, 3H, OCH_3), 4.37 (br s, 1H, 5-H), 4.39 and 4.92 (2s, 2 x 1H, methylidene-CH_2), 6.58 (s, 1H, 6'-H),

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7.02 (s, 1H, 3'-H). **^{13}C NMR** 14.2, 21.1, 25.5, 26.3, 28.2, 30.0, 42.2, 57.1, 62.6, 112.1, 114.2, 115.3, 120.0, 127.8, 147.1, 147.8, 150.1. Data for **1-epi-28b**: **^{1}H NMR** 1.00 and 1.02 (2s, 2 x 3H, geminal-CH_3's), 2.45 (dd, 1H, J = 11.5, 3.2, 3-H), 2.70 and 2.88 (d of ABq, 2H, J_{AB} = 14.1, J_A = 13.1, J_B = 4.2, benzylic-CH_2) 3.80 (s, 3H, OCH_3), 4.40 (br dd, 1H, $J \approx$ 11.5, 4.5, 5-H), 4.47 and 4.86 (2s, 2 x 1H, methylidene-CH_2), 6.61 (s, 1H, 6'-H), 7.94 (s, 1H, 3'-H).

(3*R*)-1-Debromo-5-oxo-cyclocymopol monomethyl ether, (*tert*-butyl)dimethylsilyl ether (29). The inseparable mixture of diastereomeric allylic alcohols described above was carried on to the next step without further purification. To a flame-dried 50-mL rb flask containing a 1:1 mixture of the silyl-protected phenols (350 mg, 0.74 mmol) in 25 mL CH_2Cl_2 with 2% pyridine at rt was added Dess-Martin periodinane reagent (330 mg, 0.77 mmol, 1.1 equiv), and the mixture was stirred for 5 min. The reaction mixture was then transferred to a 125-mL erlenmeyer flask containing 50 mL 1:1 saturated $NaHCO_3$ / 10% $Na_2S_2O_3$, and the mixture was stirred for an additional 90 min. The mixture was then extracted with CH_2Cl_2 (2 x 40 mL), and the organic phase was washed with brine (40 mL), dried (Na_2SO_4), and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, hexanes / EtOAc, 9:1) afforded 289 mg (85%) of the desired enone as a colorless, low-melting solid. **^{1}H NMR** 0.23 [(s, 6H, Si(CH_3)$_2$], 1.00 [s, 9H, SiC(CH_3)$_3$], 1.12 and 1.15 (2s, 2 x 3H, geminal-CH_3's), 1.62 (dddd, 1H, J = 9.9, 6.6, 5.4, 1.3, 1-H_{eq}), 2.01 (dddd, 1H, J = 14.0, 13.8, 8.9, 2.3, 1-H_{ax}), 2.24 and 2.50 (d of ABq, 2H, J_{AB} = 11.9, J_A = 11.9, J_B = 2.8, benzylic-CH_2), 2.46 and 2.48 (ABq, 2H, J_{AB} = 5.4, 6-H), 3.07 (dd, 1H, J = 13.3, 3.6, 3-H), 3.80 (s, 3H, OCH_3), 4.46 (d, 1H, J = 1.6) and 5.54 (d, 1H, J = 1.8) [methylidene-CH_2], 6.41 (s, 1H, 6'-H), 6.93 (s, 1H, 3'-H). **^{13}C NMR** -4.1, 18.3, 25.9, 27.0, 27.8, 30.7, 32.9, 33.5, 36.7, 53.1, 56.8, 108.2, 115.6, 122.0, 122.8, 130.1, 146.7, 147.7, 149.7, 202.9.

(3*R*,5*R*)-1-Debromo-5-hydroxy-5-methylcyclocymopol monomethyl ether (30). To a flame-dried 25-mL rb flask containing a solution of enone **29** (28 mg, 0.060 mmol) in 6 mL THF at -70 °C was added methyllithium (120 μL of a 1.4 M solution in ether, 0.17 mmol, 2.8

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equiv), and the mixture was allowed to stir for 5 min before quenching with 10 mL saturated NH_4Cl. Upon warming to rt, the reaction mixture was extracted with EtOAc, and the organic phase was washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure gave a 3:1 (3*R*,5*S* : 3*R*,5*R*) mixture of the diastereomeric tertiary alcohols. Purification by flash column chromatography (silica gel, hexanes / EtOAc, gradient elution) afforded 20.6 mg (71%) of the more polar, major 3*R*,5*S* isomer (**30**), along with 6.9 mg (24%) of the less polar, minor 3*R*,5*R* isomer, as colorless, low-melting solids. Data for **(3*R*,5*S*) isomer:** **^{1}H NMR** 0.21 and 0.23 (s, 6H, Si(CH_3)$_2$], 0.84 [s, 9H, SiC(CH_3)$_3$], 0.84 and 1.04 (2s, 2 x 3H, geminal-CH_3's), 1.39 (s, 3H, 5-CH_3), 2.43 (br dd, 1H, $J \approx$ 11.3, 2.9, 3-H), 2.72 and 2.85 (d of ABq, 2H, J_{AB} = 16.1, J_A = 3.1, J_B = 11.5, benzylic-CH_2) 3.77 (s, 3H, OCH_3), 4.57 and 5.16 (2s, 2 x 1H, methylidene-CH_2), 6.63 (s, 1H, 6'-H), 6.93 (s, 1H, 3'-H). Data for **(3*R*,5*R*) isomer:** **^{1}H NMR** 0.19 and 0.24 (s, 6H, Si(CH_3)$_2$], 0.77 and 1.08 (2s, 2 x 3H, geminal-CH_3's), 1.03 [s, 9H, SiC(CH_3)$_3$], 1.36 (s, 3H, 5-CH_3), 2.65 and 2.82 (d of ABq, 2H, J_{AB} = 16.0, J_A = 3.0, J_B = 11.8, benzylic-CH_2), 2.97 (br dd, 1H, $J \approx$ 11.7, 2.5, 3-H), 3.79 (s, 3H, OCH_3), 4.64 and 4.96 (2s, 2 x 1H, methylidene-CH_2), 6.73 (s, 1H, 6'-H), 6.92 (s, 1H, 3'-H). Removal of the silyl ether of the (3*R*,5*R*) isomer under standard conditions (TBAF, THF, 0 °C) afforded the desired phenol **30** as a colorless oil. **^{1}H NMR** 0.77 and 1.08 (2s, 2 x 3H, geminal-CH_3's), 1.36 (s, 3H, 5-CH_3), 2.65 and 2.82 (d of ABq, 2H, J_{AB} = 16.0, J_A = 3.0, J_B = 11.8, benzylic-CH_2), 2.97 (br dd, 1H, $J \approx$ 11.7, 2.5, 3-H), 3.79 (s, 3H, OCH_3), 4.64 and 4.96 (2s, 2 x 1H, methylidene-CH_2), 6.73 (s, 1H, 6'-H), 6.92 (s, 1H, 3'-H).

(3*R*)-1-Debromo-5,6-dehydro-5-methylcyclocymopol monomethyl ether, acetate (31). To a flame-dried 10-mL rb flask containing the 3:1 diastereomeric mixture of tertiary alcohols (3.0 mg, 0.010 mmol) in 1 mL anhydrous benzene at rt was added Burgess' reagent [(methoxycarbonylsulfamoyl)triethylammonium hydroxide, inner salt] (4.2 mg, 0.020 mmol, 2.5 equiv), and the mixture was allowed to stir for 12 h. Removal of the solvent under reduced pressure gave the crude diene, which was subjected to the standard conditions for deprotection of the silyl ether, trapping the intermediate phenoxide as the acetate (TBAF, THF,

Ac_2O, 0 °C). Purification by flash column chromatography (silica gel, hexanes / EtOAc, gradient elution) afforded 4.8 mg (74%) of the desired diene as a colorless oil. **^{1}H NMR** 0.87 and 1.09 (2s, 2 x 3H, geminal-CH_3's), 1.81 (s, 3H, 5-CH_3), 2.26 (s, 3H, acetate-CH_3), 2.77 (dd, 1H, J = 12.8, 3.1, benzylic-*H*), 3.83 (s, 3H, OCH_3), 4.13 and 4.75 (2s, 2 x 1H, methylidene-CH_2), 5.53 (br s, 1H, 3-H), 6.45 (s, 1H, 6'-H), 7.18 (s, 1H, 3'-H).

Synthesis of Enantiomerically Pure Compounds 34a, 34b, 35 and 36.

(5*R*,6*S*)-6-[4-Bromo-2-(*tert*-butyl)dimethylsilyloxy-5-methoxyphenyl)methyl-5-methylcyclohex-2-en-1-one (33a). To a solution of lithium diisopropylamide (4.7 mL of a 2.0 M solution in THF, 9.3 mmol, 2.2 equiv) in 15 mL THF and 4.4 mL of anhydrous HMPA at -35 °C was added dropwise ketosulfoxide **32a** in 5 mL THF. The reaction mixture was stirred at -35 °C for 3 h, after which benzyl bromide **5** was added dropwise as a solution in 10 mL THF. The reaction mixture was allowed to stir for an additional 2 h at -35 °C, quenched with 1 M $NaHSO_4$ (15 mL) and extracted with ether (50 mL). The organic layer was washed with water (3 x 15 mL) and brine (1 x 15 mL), then dried (Na_2SO_4) and concentrated under reduced pressure to afford 2.37 g of the intermediate ketosulfoxide as a pale yellow oil, which was used directly in the next step without purification. A solution of the intermediate ketosulfoxide (2.37 g, 4.20 mmol) and $CaCO_3$ (0.40 g, 3.9 mmol) in 90 mL of CCl_4 was brought to reflux for 3 h. Upon cooling to rt, the reaction mixture was filtered and the solvent was removed under reduced pressure. Purification by flash column chromatography (silica gel, hexanes / EtOAc, 95:5) afforded 550 mg (30%) of the desired enone **33a** as a colorless syrup. **^{1}H NMR** 0.18 and 0.22 [2s, 2 x 3H, Si(CH_3)2], 1.03 [s, 9H, SiC(CH_3)3], 1.05 (d, 3H, J = 8.0, 5-CH_3), 2.07 (m, 2H, 4-H_{ax}, 5-H), 2.50 (dd, J =13.5, 5.6, 1H, 6-H), 2.65 (m, 1H, 4-H_{eq}), 2.91 (m, 2H, benzylic-CH_2), 3.80 (s, 3H, OCH_3), 6.02 (d, 1H, J = 9.4, 2-H), 6.70 (s, 1H, 6'-H), 6.85 (ddd, 1H, J = 9.6, 4.1, 3.2, 3-H), 6.98 (s, 1H, 3'-H).

(2*S*,3*R*)-1-Methylidene-2-(2-hydroxy-4-bromo-5-methoxyphenyl)methyl-3-methylcyclohexane (34a). This compound was prepared from ketone **32a** (51 mg, 0.12

mmol) in the manner previously described for **8a**, affording 9.0 mg (58%) of the desired olefin as a colorless oil. **^{1}H NMR** 0.94 (d, 3H, J = 7.1), 1.35 (m, 1H, 4-H_{ax}), 1.49 (m, 2H, 4-H_{eq}, 5-H_{ax}), 1.85 (m, 2H, 3-H, 5-H_{eq}), 2.11 (ddd, 1H, J = 13.4, 4.1, 4.1, 6-H_{ax}), 2.28 (m, 2H, 2-H, 6-H_{eq}), 2.76 and 2.80 (d of ABq, 2H, J_{AB} = 14.1, J_A = 6.4, J_B = 8.3, benzylic-CH_2), 3.82 (s, 3H, OCH_3), 4.50 (s, 1H, O*H*), 4.53 and 4.68 (2s, 2 x 1H, methylidene-CH_2), 6.63 (s, 1H, 6'-H), 6.97 (s, 1H, 3'-H). **^{13}C NMR** 19.5, 23.1, 28.2, 32.2, 33.3, 34.3, 50.5, 57.0, 108.5, 110.0, 114.8, 120.2, 128.2, 147.9, 149.0, 150.0. **IR** (neat) 3435 (br, s), 2930 (m), 1496 (s), 1400 (s), 1199 (s). **Anal.** ($C_{19}H_{23}BrO_2$) C, H.

(2*R*,3*S*)-2-(4-Bromo-2-hydroxy-5-methoxyphenyl)methyl-3-methyl-1-methylidenecyclohexane (34b). This compound was prepared from enone **33b** in the manner previously described for enantiomer **34a**. The ^{1}H NMR spectral data and TLC elution properties for this compound were identical to that obtained for its enantiomer (**34a**). **Anal.** ($C_{19}H_{23}BrO_2$) C, H.

(5*R*,6*S*)-6-(2-Acetoxy-4-bromo-5-methoxyphenyl)methyl-3,5-dimethyl-1-methylidenecyclohex-2-ene (35). To a suspension of copper(I) iodide (1.36 mg, 0.007 mmol, 1 mol%) in 0.5 mL of ether at 0 °C was added methylmagnesium bromide (220 μL of a 3.0 M solution in ether, 0.67 mmol, 1.0 equiv), causing the solution to turn dark. A solution of enone **33a** (310 mg, 0.67 mmol) in 1 mL ether was added over a period of 2 minutes keeping the temperature below 5 °C. After the addition was complete, the mixture was stirred at 0 °C for an additional 30 minutes, at which time phenylselenenyl bromide (157 mg, 0.670 mmol) in 0.5 mL THF was added, keeping the temperature below 10 °C. The resulting mixture was stirred for 10 minutes, poured into water (2 mL) and extracted with ether (5 mL). The organic phase was washed twice with water (2 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The resultant oil was dissolved in 2 mL of CH_2Cl_2 and 162 μL of pyridine, and to this a solution of hydrogen peroxide 35% (181 μL) in 162 μL of water was added dropwise, keeping the temperature between 30-35 °C and warming when necessary to initiate the reaction. The mixture was stirred at rt for 30 minutes, and then poured into a separatory funnel containing CH_2Cl_2-

saturated $NaHCO_3$ (40 mL). The layers were separated, and the organic solution was washed successively with 10% HCl (20 mL) and brine (20 mL), and dried (Na_2SO_4). The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel, hexanes / EtOAc, 9:1), affording 157 mg (60%) of the desired (5*R*,6*S*)-6-[4-bromo-2-(*tert*-butyl)dimethylsilyloxy-5-methoxyphenyl)methyl-5-methylcyclohex-2-en-1-one as a colorless oil. **^{1}H NMR** 0.15 and 0.20 [2s, 2 x 3H, $Si(CH_3)_2$], 0.97 [s, 9H, $SiC(CH_3)_3$], 0.95 (d, 3H, J = 8.0, 5-CH_3), 1.90 (s, 3H, 3-CH_3), 1.95 (m, 2H), 2.38 (m, 1H), 2.59 (m, 1H, 6-H), 2.87 (m, 2H, benzylic-CH_2), 3.79 (s, 3H, OCH_3), 5.86 (s, 1H, 2-H), 6.69 (s, 1H, 6'-H), 6.96 (s, 1H, 3'-H). Compound **35** was prepared from the above enone (63 mg, 0.14 mmol) in the manner previously described for diene **8b**, affording 6.4 mg (60%) of acetoxy diene **35** as a colorless oil. **^{1}H NMR** 0.85 (d, 3H, 5-CH_3), 1.67 (m, 2H), 1.76 (s, 3H, 3-CH_3), 2.20 (dd, 1H), 2.27 (s, 3H, acetate-CH_3), 2.49 (m, 3H), 3.86 (s, 3H, OCH_3), 4.40 and 4.71 (2s, 2 x 1H, methylidene-CH_2), 5.86 (s, 1H, 3-H), 6.64 (s, 1H, 6'-H), 7.21 (s , 1H, 3'-H). **^{13}C NMR** 20.0, 20.8, 23.9, 30.6, 33.2, 35.8, 46.9, 56.6, 108.6, 111.7, 114.0, 123.8, 126.8, 133.1, 134.2, 142.7, 143.5, 153.4, 169.3. **HRMS** Calcd for $C_{19}H_{23}BrO_3$: m/z 379.0909; Found: m/z 379.0909.

(2*S*,3*R*,5*R*)-2-(4-Bromo-2-hydroxy-5-methoxyphenyl)methyl-3,5-dimethyl-1-methylidenecyclohexane (36). This intermediate ketone was prepared from methylcuprate addition to enone **33a** (100 mg, 0.23 mmol) in the manner previously described, affording 68 mg (65%) of the desired ketone as a colorless oil. **^{1}H NMR** 0.22 (s, 6H, $Si(CH_3)_2$), 0.97 (d, 3H, J = 7.3, 3-CH_3), 0.99 (d, 3H, J = 7.8, 5-CH_3), 1.00 [m, 18H, 3,3,5-CH_3 and $SiC(CH_3)_3$], 1.57-2.32 (m, 6H, 3,4,5,6-H), 2.44 (dd, 1H, J = 12.5, 7.0, 2-H), 2.85 (d, 2H, J = 7.3, benzylic-CH_2), 3.81 (s, 3H, OCH_3), 6.72 (s, 1H, 6'-H), 6.95 (s, 1H, 3'-H). This ketone (56 mg, 0.12 mmol) was then methylenated in the manner previously described for **8a**, affording 14 mg (37%) of the desired olefin as a colorless oil. **^{1}H NMR** 0.92 (d, 3H, J = 6.9, 3-CH_3), 0.94 (d, 3H, J = 5.2, 5-CH_3), 1.52 (m, 1H, 3-H), 1.68 and 1.70 (ABq, 2H, J_{AB} = 13.4, 4-H), 1.71 (m, 1H, 5-H), 1.90 (m, 1H, 6-H_{eq}), 2.14 (dd, 1H, J = 13.3, 2.9, 6-H_{ax}), 2.20 (dd, 1H, J = 7.4, 7.4, 2-H), 2.72 and 2.77 (d of ABq, 2H, J_{AB} = 13.8, J_A = 6.7, J_B = 8.3, benzylic-CH_2), 3.82 (s, 3H,

OCH_3), 4.50 and 4.68 (2s, 2 x 1H, methylidene-CH_2), 4.55 (s, 1H, O*H*), 6.61 (s, 1H, 6'-H), 6.98 (s, 1H, 3'-H). **^{13}C NMR** 20.0, 22.6, 28.3, 33.4, 34.2, 35.9, 40.0, 50.2, 57.0, 108.6, 110.7, 114.9, 120.3, 128.2, 147.9, 148.4, 150.1. **IR** (neat) 3437 (br, s), 2951 (m), 2910 (m), 1496 (s), 1400 (s), 1199 (s). **Anal.** ($C_{19}H_{23}BrO_3$) C, H.

Synthesis of Compound 37.

3-Ethoxy-5,5-dimethyl-6-(4-nitrophenyl)methylcyclohex-2-en-1-one (37). This compound was prepared from 3-ethoxy-5,5-dimethylcyclohex-2-en-1-one (0.43 g, 2.6 mmol) and *p*-nitrobenzyl bromide (0.61 g, 2.8 mmol, 1.1 equiv) in the manner previously described for **8a**, affording 0.71 g (90%) of the desired enone as a colorless, low-melting solid. **^{1}H NMR** 1.03 and 1.17 (2s, 2 x 3H, geminal-CH_3's), 1.36 (t, 3H, J = 6.9, OCH_2CH_3), 2.28 and 2.34 (ABq, 2H, J_{AB} = 17.6, 4-H), 2.81 and 3.82 (d of ABq, 2H, J_{AB} = 13.8, J_A = 2.6, J_B = 5.8, benzylic-CH_2), 3.90 (q, 2H, J = 7.0, OCH_2CH_3), 5.30 (s, 1H, 2-H), 7.49 (d, 2H, J = 8.2, 2',6'-H), 8.11 (d, 2H, J = 8.2, 3',5'-H).