Experimental Section (Supplemental Material):

15: 3-Buten-1-ol **14** (25.08 g, 347.8 mmol), triethylamine (2.32 g, 22.9 mmol), and solid NaOH (20.55 g, 518.3 mmol) were stirred together in hexanes (250 mL) at 50^{0}C for 30 min. Benzyl bromide (64.71 g, 378.3 mmol) in 50 mL of hexanes was then added slowly over a period of 30 min. The mixture was then heated to reflux for 3 h. After cooling, 300 mL of water was added. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layers were dried, filtered, and concentrated. The residue was purified by flash column chromatography using hexanes and ethyl acetate (9:1) to give **15** (55.44 g, 341.7 mmol) as clear oil in 98% yield. ^{1}H NMR ($CDCl_3$): 2.36 (q, J = 7.3 Hz, 2H), 3.52 (t, J = 7.2 Hz, 2H), 4.52 (s, 2H), 5.09 (m, 2H), 5.78-5.92 (m, 1H), 7.23-7.40 (m, 5H).

16: **15** (449 mg, 2.77 mmol) was dissolved in 20 mL of CH_2Cl_2. MCPBA (1.30 g, 3.77 mmol) was then added. The mixture was stirred at room temperature for 16h. The crude mixture was worked up with saturated Na_2CO_3 and CH_2Cl_2. The product was purified by flash column chromatography using hexanes and ethyl acetate (4:1) to give **16** (449 mg, 2.52 mmol) as clear oil in 91% yield. ^{1}H NMR ($CDCl_3$): 1.70-1.82 (m, 1H), 1.85-1.96 (m, 1H), 2.52 (m, 1H), 2.78 (t, J = 4.7 Hz, 1H), 3.06 (m, 1H), 3.62 (t, J = 6.2 Hz, 2H), 4.53 (s, 2H), 7.23-7.38 (m, 5H). ^{13}C NMR ($CDCl_3$): 32.7, 46.7, 49.7, 66.8, 72.8, 127.3, 128.1, 129.3, 138.1. IR ($CHCl_3$, cm^{-1}): 3017s, 2864, 1495, 1102s. MS (FD) 178 (M^+, 100). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.20; H, 7.96.

17: To a stirred solution of **16** (2.71 g, 15.2 mmol) in 12 mL of DMSO was added lithium acetylide ethylenediamine complex (2.40 g, 90%, 23.5 mmol) under nitrogen at room temperature. The mixture was then stirred for approximately 40 min. Water (80 mL) and ethyl acetate (80 ml) were added. The organic layer was separated, washed with water (2 x 50 mL), dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography using hexanes and ethyl acetate (7 : 3) to give **17** (2.83 g, 13.85 mmol) in 91%. ^{1}H NMR ($CDCl_3$): 1.88 (m, 2H), 2.01 (t, J = 3Hz, 1H), 2.36 (m, 2H), 3.62-3.78 (m, 2H), 3.94-4.01 (m, 1H), 4.50 (s, 2H), 7.22-7.38 (m, 5H). IR ($CHCl_3$, cm^{-1}): 3487, 3307, 3012, 2867, 1420, 1087. MS (FD) 204 (M^+, 100). HRMS (FAB) Calcd for $C_{13}H_{17}O_2$ (M + H): 205.1229; Found: 205.1231. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.33; H, 7.56.

18: Compound **17** (2.83 g, 13.8 mmol) from previous step was dissolved in 100 mL of CH_2Cl_2. To this solution were added acetic anhydride (12 ml), acetic chloride (12 mL) and pyridine (1.9 mL) at room temperature. After stirred for 30 min, the volatiles were removed by reduced pressure. The residue was worked up with water and diethyl ether. The cure was purified by flash chromatography using hexanes and ethyl acetate (4 : 1) to give **18** (3.08 g, 12.5 mmol) in 91% yield. ^{1}H NMR ($CDCl_3$): 1.90-2.10 (m, 6H), 2.50 (m, 2H), 3.51 (t, J = 7.2 Hz, 2H), 4.43 (s, 2H), 5.11 (m, 1H), 7.22-7.40 (m, 5H). IR ($CHCl_3$, cm^{-1}): 3309, 3010, 2866, 1734, 1375, 1245. MS (FAB) 247 (M^++1, 100). Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.13; H, 7.36.

13: To a stirred solution of **17** (2.22 g, 10.8 mmol) in 50 mL of $CHCl_3$ were added $CH_2(OMe)_2$ (15 mL) and P_2O_5 (3.00 g). The mixture was vigorously stirred at room temperature, and the progress of the reaction was monitored by TLC. After completion of the reaction (5 h), the mixture was poured into a ice-cold Na_2CO_3 solution (10%). The residue in the reaction flask was washed with $CHCl_3$ and Na_2CO_3 solution. The organic layer was separated, washed with water, dried and concentrated. The residue was purified by flash column chromatography using hexanes and ethyl acetate (3 : 1) to give **13** (2.11 g, 8.5 mmol) in 79% yield. ^1H NMR ($CDCl_3$): 1.94 (m, 2H), 1.98 (t, J = 2.9 Hz, 1H), 2.37-2.58 (m, 2H), 3.37 (s, 3H), 3.58 (m, 2H), 3.89 (m, 1H), 4.49 (s, 2H), 4.67 (dd, J = 15.2 Hz, 7.3 Hz, 2H), 7.22-7.40 (m, 5H). MS (FD) 428 (M^+-H, 100). IR ($CHCl_3$, cm^{-1}): 3308, 3012, 2951, 1453, 1365, 1101, 1037. Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.56; H, 7.85.

19: A solution of acetylene **13** (882 mg, 3.6 mmol) and chromium carbene complex **12** (1.30 g, 3.8 mmol) in 35 mL of benzene was deoxygenated by the freeze-vacuum-thaw method (-196^{0}C / 20^{0}C, 3 cycles). The mixture was then stirred under nitrogen at 70^{0}C for 14 h. The mixture was transferred to a new flask and stirred under air for 20 min. The volatiles were removed by reduced pressure and the residue was purified by flash chromatography using hexanes, CH_2Cl_2 and ethyl acetate (3 : 3 : 1) to give **19** (378 mg, 0.89 mmol) in 25% yield, along with an unidentified product (528 mg). ^1H NMR ($CDCl_3$): 1.86 (m, 2H), 2.82-3.15 (m, 2H), 3.28 (s, 3H), 3.58 (m, 2H), 3.85 (s, 3H), 3.97 (s, 3H), 4.16 (m, 1H), 4.52 (s, 2H), 4.70 (dd, J = 21.0 Hz, 7.4 Hz, 2H), 6.51 (s, 1H), 6.82 (d, J = 7.5 Hz, 1H), 7.18-7.42 (m, 6H), 7.87 (d, J = 7.5 Hz, 1H), 8.04 (s, 1H). MS (FD) 426 (M^+, 100).

The same reaction was also carried out in THF solution. Thus, the reaction of **13** (814 mg, 3.3 mmol) and **12** (1.00 g, 2.9 mmol) in 30 mL of THF at 60^{0}C for 16 h gave rise to **19** (306 mg, 0.72 mmol) in 22% yield, along with an unidentified product (458 mg).

20: A solution of acetylene **18** (908 mg, 3.7 mmol) and chromium carbene complex **12** (1.05 g, 3.1 mmol) in 30 mL of THF was deoxygenated by the freeze-vacuum-thaw method (-196^{0}C / 20^{0}C, 3 cycles). The mixture was then stirred under nitrogen at 60^{0}C for 15 h. The mixture was transferred to a new flask and stirred under air for 20 min. The volatiles were removed by reduced pressure and the residue was purified by flash chromatography using hexanes, CH_2Cl_2 and ethyl acetate (3 : 3 : 1) to give **20** (966 mg, 2.3 mmol) in 74% yield, along with an unidentified product (85 mg). ^1H NMR ($CDCl_3$): 1.86-2.06 (m, 2H), 2.07 (s, 3H), 2.93 (dd, J = 12.1 Hz, 7.5 Hz, 1H), 3.16 (dd, J = 12.1 Hz, 3.6 Hz, 1H), 3.53 (m, 1H), 3.60 (m, 1H), 3.87 (s, 3H), 3.98 (s, 3H), 4.50 (s, 2H), 4.99 (m, 1H), 6.58 (s, 1H), 6.86 (d, J = 7.5 Hz, 1H), 7.20-7.40 (m, 6H), 7.51 (s, 1H), 7.90 (d, J = 7.5 Hz, 1H). MS (ESI) 425 (M^++1, 65).

21: Compound **20** (952 mg, 2.24 mmol) was dissolved in 50 mL of acetone. K_2CO_3 (620 mg, 4.5 mmol) and iodomethane (3.0 mL) were then added. The mixture was then heated to reflux for 3 h. The solid was removed by filtration. The filtrate was

evaporated to dryness that was purified by flash chromatography using hexanes, CH_2Cl_2 and ethyl acetate (3 : 3 : 1) to give **21** (795 mg, 1.81 mmol) in 81% yield. ^1H NMR ($CDCl_3$): 1.80-2.00 (m, 2H), 1.92 (s, 3H), 3.06 (m, 2H), 3.51 (m, 2H), 3.81 (s, 3H), 3.90 (s, 3H), 3.96 (s, 3H), 4.44 (s, 2H), 5.40 (m, 1H), 6.66 (s, 1H), 6.83 (d, J = 7.4 Hz, 1H), 7.20-7.36 (m, 5H), 7.38 (t, J = 7.5 Hz, 1H), 7.64 (d, J = 7.5 Hz, 1H).

22: Compound **21** (795 mg, 1.81 mmol) was dissolved in 8 mL of methanol. Saturated K_2CO_3 solution (8 mL) was added. The mixture was then stirred at room temperature for 6 h. CH_2Cl_2 (50 mL) and water (20 mL) were added. The organic layer was separated, and washed with water, dried and concentrated. The residue was purified by flash chromatography using hexanes, CH_2Cl_2 and ethyl acetate (2 : 2 : 1) to give **22** (607 mg, 1.53 mmol) in 85% yield. ^1H NMR ($CDCl_3$): 1.81 (dd, J = 11.1 Hz, 6.0 Hz, 2H), 2.94 (m, 2H), 3.60-3.80 (m, 3H), 3.83 (s, 3H), 3.91 (s, 3H), 3.95 (s, 3H), 4.16 (m, 1H), 4.50 (s, 2H), 6.67 (s, 1H), 6.83 (d, J = 7.8 Hz, 1H), 7.20-7.38 (m, 5H), 7.39 (t, J = 7.9 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H). MS (ESI) 397 (M^++1, 100). Anal. Calcd for $C_{24}H_{28}O_5$: C, 72.71; H, 7.12. Found: C, 73.30; H, 6.92.

10: To a stirred solution of **22** (534 mg, 1.35 mmol) in 25 mL of diethyl ether were added $CH_2(OMe)_2$ (0.23 mL, 2.60 mmol) and $BF_3 \cdot Et_2O$ (0.49 mL, 3.87 mmol) under nitrogen. The mixture was stirred at room temperature for 3 h. All starting material had been consumed. 30 mL of $NaHCO_3$ solution (10%) and 30 mL of diethyl ether were added. The organic layer was separated, washed with water, dried and concentrated. The residue was purified by flash chromatography using hexanes and ethyl acetate (4 : 1) to give **10** (468 mg, 1.15 mmol) in 85% yield. ^1H NMR ($CDCl_3$): 1.99 (dd, J = 12.4 Hz, 5.9 Hz, 2H), 2.68 (dd, J = 16.4 Hz, 11.0 Hz, 1H), 3.06 (dd, J = 16.4 Hz, 4.0 Hz, 1H), 3.68-4.00 (m, 3H), 3.77 (s, 3H), 3.83 (s, 3H), 3.98 (s, 3H), 4.55 (s, 2H), 4.81 (d, J = 16.1 Hz, 1H), 5.20 (d, J = 16.0 Hz, 1H), 6.81 (d, J = 7.6 Hz, 1H), 7.26-7.37 (m, 6H), 7.64 (d, J = 8.0 Hz, 1H). MS (ESI) 409 (M^++1, 100).

23: To a stirred solution of **10** (136 mg, 0.33 mmol) in 6 mL of CH_2Cl_2 were added 4A molecular sieves (100 mg) and $LiClO_4$ (50 mg). The mixture was stirred at room temperature for 15 min before DDQ (91 mg, 0.40 mmol) was introduced. The resulting mixture was stirred for another 14 min, yielding a brown suspension. At this point, allyltriphenyltin (155 mg, 0.40 mmol) was introduced. After stirring at room temperature for 3 h, CH_2Cl_2 (30 mL) and $NaHCO_3$ (5%, 30 mL) were added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (20 mL x 2). The combined organic layers were washed with water, dried, filtered and then concentrated. The residue was purified by flash chromatography using hexanes and ethyl acetate (3 : 1) to give compound **23** (140 mg, 0.31 mmol) in 94% yield. ^1H NMR ($CDCl_3$): 1.88-2.06 (m, 2H), 2.57-2.66 (m, 2H), 2.76-2.86 (m, 1H), 3.06 (dd, J = 16.4 Hz, 4.0 Hz, 1H), 3.64-3.79 (m, 2H), 3.82 (s, 3H), 3.83 (s, 3H), 4.00 (s, 3H), 4.10-4.22(m, 1H), 4.50 (d, J = 11.8 Hz, 1H), 4.55 (d, J = 11.8 Hz, 1H), 5.07-5.22 (m, 3H), 5.96-6.10 (m, 1H), 6.82 (d, J = 7.8 Hz, 1H), 7.25-7.40 (m, 6H), 7.64 (d, J = 8.4 Hz, 1H). MS (FIA) 448 (M^+, 25). HRMS (FAB) Calcd for $C_{28}H_{33}O_5$ (M + H): 449.2328; Found: 449.2331.

24: Compound **23** (138 mg, 0.31 mmol) was dissolved in 14 mL of ethanol. Pd/C catalyst (10% on carbon, 30 mg) was added. The reaction flask was then charged with hydrogen using a balloon. The mixture was stirred at room temperature for 2 days until all starting material was consumed. The catalyst was removed by filtration. The filtrate was evaporated. The residue was purified by flash chromatography using hexanes, CH_2Cl_2 and ethyl acetate (2 : 1 : 1) to give **24** (86 mg, 0.24 mmol) in 77% yield. ^1H NMR ($CDCl_3$): 1.00 (t, J = 7.3 Hz, 3H), 1.50-1.70 (m, 2H), 1.80-2.02 (m, 5H), 2.68 (dd, J = 16.9 Hz, 11.2 Hz, 1H), 3.03 (dd, J = 16.9 Hz, 3.5 Hz, 1H), 3.79 (s, 3H), 3.83 (s, 3H), 3.90 (m, 2H), 4.00 (s, 3H), 4.13-4.22 (m, 1H), 5.13 (dd, J = 10.4 Hz, 3.4 Hz, 1H), 6.82 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 8.1 Hz, 1H), 7.63 (d, J = 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$): 13.5, 19.4, 28.9, 35.2, 38.4, 56.0, 60.6, 61.0, 61.9, 66.0, 72.3, 105.4, 114.5, 119.2, 123.6, 125.7, 129.3, 129.8, 147.9, 149.0, 156.0. IR ($CHCl_3$, cm^{-1}): 3500br, 2961, 2935, 1572, 1338, 1060. MS (FD) 360 (M^+, 95). HRMS (FAB) Calcd for $C_{21}H_{29}O_5$ (M + H): 361.2015; Found: 361.2019.

26: To a stirred solution of **24** (56 mg, 0.156 mmol) in a solvent mixture of acetone and acetic acid (2 : 1, 3 ml) was added a solution of CrO_3 (140 mg, 1.400 mmol) in 0.3 mL of water at room temperature. The mixture was then stirred at room temperature for 40 min. Water (10 mL) and CH_2Cl_2 (10 mL) were added. The organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (5 mL x 3). The combined organic layers were washed with water, dried, filtered and concentrated to give a yellow residue that contained rather pure compound **25**. ^1H NMR ($CDCl_3$): 0.96 (t, J = 7.5 Hz, 3H), 1.23 (m, 2H), 1.45-1.80 (m, 4H), 2.30 (dd, J = 17.0 Hz, 11.0 Hz, 1H), 2.68 (d, J = 7.5 Hz, 2H), 2.78 (dd, J = 17.0 Hz, 3.5 Hz, 1H), 4.00 (s, 3H), 4.27 (m, 1H), 4.85 (dd, J = 10.0 Hz, 3.0 Hz, 1H), 7.27 (d, J = 7.6 Hz, 1H), 7.66 (t, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H). MS (FIA) 344 (M^+, 100).

Without further purification, the crude **25** was re-dissolved in 10 ml of methanol. H_2SO_4 (10 drops) was added. The mixture was stirred at room temperature for 4 h. CH_2Cl_2 (10 mL) and water (5 mL) were added. The organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (5 mL x 3). The combined organic layers were washed with water, dried, filtered and concentrated. Purification of the residue by flash chromatography using hexanes, CH_2Cl_2 and ethyl acetate (4 : 3 : 3) to give **26** (24 mg, 0.067 mmol) in 43% yield. ^1H NMR ($CDCl_3$): 0.95 (t, J = 7.3 Hz, 3H), 1.40-1.65 (m, 2H), 1.67-1.80 (m, 2H), 2.29 (ddd, J = 18.8 Hz, 9.4 Hz, 2.0 Hz, 1H), 2.62 (d, J = 7.2 Hz, 2H), 2.73 (dd, J = 18.8 Hz, 3.5 Hz, 1H), 3.71 (s, 3H), 3.98 (s, 3H), 4.20-4.32 (m, 1H), 4.82 (dd, J = 10.0 Hz, 2.5 Hz, 1H), 7.26 (d, J = 8.4 Hz, 1H), 7.62 (t, J = 8.0 Hz, 1H), 7.72 (d, J = 7.1 Hz, 1H). MS (FIA) 358 (M^+, 15).

27: To a solution of **26** (11.0 mg, 0.031 mmol) in CH_2Cl_2 (5 ml) was added dropwise a solution of BBr_3 (1 M in CH_2Cl_2, 0.3 ml, 0.30 mmol) at -78^{0}C under nitrogen. The resulting mixture was stirred at -78^{0}C for 10 min and then 0^{0}C for 10 min. The mixture was then quenched with 5 mL of $NaHCO_3$ solution (10%) and 10 mL of CH_2Cl_2. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (5 ml x 3). The Combined organic layers were washed with water, dried, filtered and concentrated. The residue was purified by flash chromatography using hexanes, CH_2Cl_2

and ethyl acetate (3 : 1 : 1) to give a yellow compound **27** (9.1 mg, 0.026 mmol) in 85% yield. The following spectrum data are identical with those of the literature.[5, 9] ^{1}H NMR ($CDCl_3$): 0.99 (t, J = 7.1 Hz, 3H), 1.48-1.68 (m, 2H), 1.77 (m, 2H), 2.30 (ddd, J = 19.0 Hz, 10.4 Hz, 2.0 Hz, 1H), 2.63 (d, J = 6.7 Hz, 2H), 2.81 (dd, J = 19.0 Hz, 3.0 Hz, 1H), 3.72 (s, 3H), 4.27 (m, 1H), 4.81 (m, 1H), 7.26 (d, J = 7.5 Hz, 1H), 7.56 (m, 2H), 12.00 (s, 1H). MS (FIA) 344 (M^+, 100).