PMB Ether 7. A suspension of **6** (500 mg, 2.69 mmol) and NaH (60%, 538 mg, 13.5 mmol) in dry DMF (38 mL) was stirred for 30 min at 0 °C to rt under N_2, treated with *p*-methoxybenzyl bromide (1.86 mL, 10.7 mmol) at 0 °C, stirred overnight at rt, quenched with water, diluted with hexanes/ethyl acetate (1:1), washed with brine, dried, and concentrated *in vacuo*. Purification of the residue on silica gel (hexanes/ethyl acetate 20:1) gave **7** as a colorless oil (822 mg, 100%); IR (neat, cm^{-1}) 1613, 1514, 1369; ^1H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.6 Hz, 2 H), 6.87 (d, *J* = 8.6 Hz, 2 H), 5.90-5.76 (m, 1 H), 5.14-5.07 (m, 2 H), 4.57 (d, *J* = 10.9 Hz, 1 H), 4.39 (d, *J* = 10.9 Hz, 1 H), 4.27-4.18 (m, 1 H), 4.02 (dd, *J* = 8.0, 5.8 Hz, 1 H), 3.80 (s, 3 H), 3.71-3.62 (m, 1 H), 3.50 (t, *J* = 7.9 Hz, 1 H), 2.38-2.32 (m, 2 H), 1.82-1.42 (m, 2 H), 1.39 (s, 3 H), 1.35 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 134.4, 130.9, 129.6, 117.6, 114.0, 108.5, 75.3, 73.8, 71.3, 70.2, 55.4, 38.9 (2 C), 27.2, 26.0; HRMS ES *m/z* $(M + Na)^+$ calcd 329.1729, obsd 329.1730; $[\alpha]_D^{19}$ -48.7 (*c* 3.55, $CHCl_3$).

Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.58; H, 8.60.

Diol 8. A solution of **7** (4.0 g, 13.1 mmol) in acetic acid: THF:H_2O (1:1:1) (66 mL) was stirred for 8 h at 45-50 °C, freed of solvent *in vacuo*, diluted with CH_2Cl_2, and washed with saturated $NaHCO_3$ solution. The aqueous layer was re-extracted with CH_2Cl_2, the combined organic layers were washed with brine, dried, and evaporated, and the residue was purified by column chromatography on silica gel (hexanes/ethyl acetate 1:2) to give **8** (3.22 g, 92%) as a colorless oil; IR (neat, cm^{-1}) 3402, 1612, 1514; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.6 Hz, 2 H), 6.87 (d, *J* = 8.6 Hz, 2 H), 5.86-5.73 (m, 1 H), 5.13-5.07 (m, 2 H), 4.57 (d, *J* = 11.1 Hz, 1 H), 4.42 (d, *J* = 11.1 Hz, 1 H), 3.98-3.91 (m, 1 H), 3.79 (s, 3 H), 3.79-3.72 (m, 1 H), 3.58 (dd, *J* = 11.1, 3.0 Hz, 1 H), 3.41 (dd, *J* = 11.1, 6.8 Hz, 1 H), 2.81 (br s, 2 H), 2.47-2.31 (m, 2 H), 1.73-1.65 (m, 1 H), 1.56 (ddd, *J* = 14.6, 8.0, 3.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 134.2, 130.2, 129.5, 117.6, 113.9, 75.5, 70.9, 69.1, 66.9, 55.2, 38.0, 36.3; HRMS ES *m/z* (M + Na)$^+$ calcd 289.1410, obsd 289.1404; $[\alpha]_D^{20}$ -61.1 (*c* 1.55, $CHCl_3$).

Hydroxy Pivalate 9. To a stirred solution of **8** (413 mg, 1.55 mmol) in pyridine (5 mL) and CH_2Cl_2 (10 mL) was added pivaloyl chloride (0.23 mL, 1.86 mmol) at 0 °C under N_2. The mixture was allowed to warm to rt, stirred overnight, diluted with ethyl acetate, washed with 1N HCl, saturated $NaHCO_3$ solution, and brine, then dried and concentrated. The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate 7:1) to give **9** (496 mg, 91%); IR (neat, cm^{-1}) 3488, 1729, 1613; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.6 Hz, 2 H), 6.88 (d, *J* = 8.7 Hz, 2 H), 5.89-5.73 (m, 1 H), 5.15-5.07 (m, 2 H), 4.59 (d, *J* = 11.1 Hz, 1 H), 4.43 (d, *J* = 11.1 Hz, 1 H), 4.13-3.96 (m, 3 H), 3.80 (s, 3 H), 3.83-3.75 (m, 1 H), 2.71 (br s, 1 H), 2.50-2.29 (m, 2 H), 1.72-1.58 (m, 2 H), 1.21 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.4, 159.2, 134.1, 130.2, 129.4, 117.5, 113.8, 75.2, 68.2, 66.8, 55.2, 38.7, 38.1, 36.8, 27.1; HRMS ES *m/z* (M + Na)$^+$ calcd 373.1985, obsd 373.2007; $[\alpha]_D^{19}$ -35.5 (*c* 1.85, $CHCl_3$).

Unsaturated Epoxide 10. To a cooled (0 °C), stirred solution of **9** (6.66 g, 19 mmol) in pyridine (7.7 mL) and CH_2Cl_2 (95 mL) were added DMAP (230 mg, 1.9 mmol) and methanesulfonyl chloride (4.4 mL, 57 mmol) under N_2. The solution was allowed to warm to rt, stirred overnight, diluted with ethyl acetate, washed with 1N HCl and brine, and dried. The solvent was removed and the residue was purified by column chromatography on silica gel (hexanes/ethyl acetate 8:1) to give the mesylate as a colorless oil (7.9 g, 97%); IR (neat, cm^{-1}) 1734, 1515, 1350; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.5 Hz, 2 H), 6.88 (d, *J* = 8.6 Hz, 2 H), 5.88-5.74 (m, 1 H), 5.19-5.09 (m, 3 H), 4.57 (d, *J* = 10.4 Hz, 1 H), 4.45 (d, *J* = 10.2 Hz, 1 H), 4.41 (dd, *J* = 12.2, 3.1 Hz, 1 H), 4.07 (dd, *J* = 12.5, 5.6 Hz, 1 H), 3.79 (s, 3 H), 3.77-3.68 (m, 1 H), 3.01 (s, 3 H), 2.43-2.34 (m, 2 H), 1.91 (ddd, *J* = 14.9, 9.4, 2.4 Hz, 1 H), 1.73 (ddd, *J* = 14.8, 10.2, 3.2 Hz, 1 H), 1.22 (s, 9 H); ^{13}C

NMR (75 MHz, $CDCl_3$) δ 177.7, 159.1, 133.5, 130.3, 129.6, 117.8, 113.7, 77.3, 73.6, 70.6, 65.4, 55.1, 38.7, 38.6, 37.7, 36.5, 27.0; HRMS ES *m/z* $(M + Na)^+$ calcd 451.1761, obsd 451.1728; $[\alpha]_D^{19}$ -26.6 (*c* 2.98, $CHCl_3$).

Anal. Calcd for $C_{21}H_{32}O_7S$: C, 58.86; H, 7.53. Found: C, 59.04; H, 7.60.

The mesylate (1.0 g, 2.3 mmol) was dissolved in MeOH (117 mL), treated with K_2CO_3 (484 mg, 3.50 mmol) and stirred overnight at rt. The mixture was diluted with ethyl acetate, washed with brine, dried, and freed of solvent. The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate 7:1) to give epoxide **30** (518 mg, 89%); IR (neat, cm^{-1}) 1613, 1514, 1302; ^1H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.5 Hz, 2 H), 6.87 (d, *J* = 8.7 Hz, 2 H), 5.92-5.78 (m, 1 H), 5.15-5.06 (m, 2 H), 4.53 (d, *J* = 11.3 Hz, 1 H), 4.45 (d, *J* = 11.3 Hz, 1 H), 3.80 (s, 3 H), 3.63 (q, *J* = 5.9 Hz, 1 H), 3.07-3.01 (m, 1 H), 2.73 (t, *J* = 4.5 Hz, 1 H), 2.46 (dd, *J* = 5.1, 2.7 Hz, 1 H), 2.44-2.38 (m, 2 H), 1.88-1.79 (m, 1 H), 1.75-1.67 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 134.4, 130.6, 129.2, 117.4, 113.8, 76.0, 70.5, 55.2, 49.5, 46.8, 38.3, 36.6; HRMS EI *m/z* (M^+) calcd 248.1412, obsd 248.1432; $[\alpha]_D^{20}$ -23.3 (*c* 1.39, $CHCl_3$).

Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.51; H, 8.06.

Conversion of 10 to 11. A cold (-78 ˚C), stirred solution of **10** (1.34 g, 5.40 mmol) in ethyl acetate (54 mL) was exposed to a stream of ozone. The completion of reaction was carefully monitored by TLC. After 7 min, Ph_3P (1.42 g, 5.40 mmol) was introduced and the mixture was allowed to warm to rt, stirred overnight, and freed of solvent. The resulting aldehyde was taken up in MeOH (54 mL), cooled to 0 ˚C, and treated with $NaBH_4$ (408 mg, 10.8 mmol) at 0 ˚C. After 30 min, H_2O was added, methanol was removed *in vacuo*, and the residue was diluted with CH_2Cl_2, washed with 1N HCl, saturated $NaHCO_3$ solution, and brine prior to drying and concentration *in vacuo*. The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate 1:1) to give the alcohol. Since separation from triphenylphosphine oxide was not readily achieved, the mixture of these two compounds was used in the pivaloylation step.

To a stirred solution of crude alcohol in pyridine (4.4 mL) and CH_2Cl_2 (11 mL) was added pivaloyl chloride (1.33 mL, 10.8 mmol) at 0 °C under N_2. The mixture was allowed to warm to rt, stirred for 5 h, diluted with hexanes, and filtered through a short silica gel pad, which was washed with hexanes/ethyl acetate (5:1). The filtrate was concentrated and the residue was purified by silica gel column chromatography (hexanes/ethyl acetate 20:1) to give **11** (980 mg, 54%) and **12** (416 mg, 23%), both as colorless oils.

For **11**: IR (neat, cm^{-1}) 1726, 1612, 1514; ^1H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.6 Hz, 2 H), 6.87 (d, *J* = 8.6 Hz, 2 H), 4.50 (d, *J* = 11.1 Hz, 1 H), 4.42 (d, *J* = 11.1 Hz, 1 H), 4.19 (t, *J* = 6.4 Hz, 2 H), 3.79 (s, 3 H), 3.73-3.65 (m, 1 H), 3.06-3.00 (m, 1 H), 2.76 (dd, *J* = 4.9, 4.1 Hz, 1 H), 2.47 (dd, *J* = 5.0, 2.7 Hz, 1 H), 1.94 (q, *J* = 6.3 Hz, 2 H), 1.89-1.71 (m, 2 H), 1.17 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.4, 159.3, 130.3, 129.4, 113.6, 73.3, 70.8, 61.0, 55.2, 49.1, 46.7, 38.7, 36.8, 33.4, 27.2; HRMS ES *m/z* $(M + Na)^+$ calcd 359.1829, obsd 359.1863; $[\alpha]_D^{20}$ +39.6 (*c* 2.13, $CHCl_3$).

For **12**: IR (neat, cm^{-1}) 1725, 1612, 1514; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.6 Hz, 2 H), 6.88 (d, *J* = 8.6 Hz, 2 H), 4.55 (d, *J* = 11.0 Hz, 1 H), 4.42 (d, *J* = 11.0 Hz, 1 H), 4.18 (t, *J* = 6.5 Hz, 2 H), 4.00-3.82 (m, 1 H), 3.80 (s, 3 H), 3.80-3.74 (m, 1 H), 3.48 (d, *J* = 5.4 Hz, 2 H), 2.00-1.91 (m, 2 H), 1.89-1.73 (m, 2 H), 1.20 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.4, 159.4, 129.6, 129.5, 114.0, 75.1, 70.7, 70.4, 60.6, 55.2, 49.3, 38.7, 38.2, 32.7, 27.1; HRMS ES *m/z* $(M + Na)^+$ calcd 359.1829, obsd 359.1864; $[\alpha]_D^{20}$ -17.9 (*c* 1.08, $CHCl_3$).

Acetylenic Carbinol 13. To a cooled (-78 °C), stirred solution of trimethylsilylacetylene (3.8 mL, 26.77 mmol) in THF (67 mL) was added *n*-BuLi (1.45 M solution in hexane, 14.8 mL, 21.42 mmol) dropwise under N_2. After 30 min at -78 °C, $BF_3 \cdot Et_2O$ (3.9 g, 42.84 mmol) was added to the reaction mixture. The mixture was stirred for 20 min at -78 °C and to this reaction mixture was added a solution of epoxide **11** (3.6g, 10.71 mmol) in THF (40 mL). After 1 h at -78 °C, the mixture was quenched with saturated NH_4Cl solution, extracted with ethyl acetate, washed with brine, and dried over Na_2SO_4. The solvent was removed *in vacuo* and the resulting oil was used for the next step without added purification. In one instance, a small aliquot was chromatographed to allow for characterization; colorless oil; IR (neat, cm^{-1}) 3491, 2175, 1728; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, J = 8.5 Hz, 2 H), 6.87 (d, J = 8.6 Hz, 2 H), 4.53 (d, J = 10.9 Hz, 1 H), 4.43 (d, J = 10.9 Hz, 1 H), 4.22-4.13 (m, 2 H), 3.90-3.85 (m, 1 H), 3.79 (s, 3 H), 3.79-3.73 (m, 1 H), 2.43 (dd, J = 16.8, 5.8 Hz, 1 H), 2.35 (dd, J = 16.8, 6.6 Hz, 1 H), 1.97-1.85 (m, 2 H), 1.84-1.70 (m, 2 H), 1.19 (s, 9 H), 0.15 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.4, 159.4, 129.8, 129.5, 114.0, 103.2, 87.2, 75.5, 70.7, 69.2, 60.7, 55.2, 39.9, 38.7, 32.8, 28.9, 27.2, 0.1; HRMS ES m/z $(M + Na)^+$ calcd 457.2381, obsd 457.2346; $[\alpha]_D^{20}$ -15.9 (c 1.30, $CHCl_3$).

A solution of the unpurified silylacetylene from above and TBAF (1 M solution in THF, 32 mL, 32mmol) in THF (107 mL) was stirred for 1 h at 0 °C. Water was added and the mixture was diluted with ethyl acetate, washed with brine, dried, and evaporated. The residue was purified by silica gel column chromatography (hexanes/ethyl acetate 3:1) to give **13** (3.7 g, 95% for the two steps); IR (neat, cm^{-1}) 3494, 1725, 1613; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, J = 8.5 Hz, 2 H), 6.87 (d, J = 8.6 Hz, 2 H), 4.55 (d, J = 10.9 Hz, 1 H), 4.41 (d, J = 10.9 Hz, 1 H), 4.17 (t, J = 6.5 Hz, 2 H), 4.13-3.80 (m, 1 H), 3.79 (s, 3 H), 3.79-3.74 (m, 1 H), 3.40 (s, 1 H), 2.42-2.26 (m, 2 H), 2.01 (t, J = 2.6 Hz, 1 H), 1.98-1.87 (m, 2 H), 1.84-1.71 (m, 2 H), 1.19 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.4, 159.5, 129.6 (2 C), 114.0, 80.8, 76.0, 70.7, 70.5, 69.4, 60.7, 55.3, 40.0, 38.7, 32.7, 27.3, 27.2; HRMS ES *m/z* (M + Na)$^+$ calcd 385.1985, obsd 385.1975; $[\alpha]_D^{20}$ -23.9 (*c* 0.97, $CHCl_3$).

Acetylenic Acetal 14. A suspension of **13** (20 mg, 0.055 mmol) and molecular sieves (40 mg) in dry CH_2Cl_2 (5 mL) was stirred for 20 min under N_2 prior to the addition of DDQ (19 mg, 0.083 mmol) at rt. The reaction mixture was stirred for 3 h and saturated $NaHCO_3$ solution was introduced prior to dilution with ethyl acetate, washing with brine, drying, and solvent evaporation. The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate 10:1) to give **14** (17 mg, 85%) as a colorless oil; IR (neat, cm^{-1}) 1726, 1615, 1518; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.7 Hz, 2 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 5.48 (s, 1 H), 4.23 (t, *J* = 6.5 Hz, 2 H), 4.02-3.89 (m, 2 H), 2.64 (ddd, *J* = 16.6, 5.2, 2.7 Hz, 1 H), 2.43 (ddd, *J* = 16.6, 8.1, 2.7 Hz, 1 H), 2.03 (t, *J* = 2.5 Hz, 1 H), 2.00-1.85 (m, 3 H), 1.56-1.41 (m, 1 H), 1.20 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.6, 160.1, 131.0, 127.5, 113.7, 100.8, 80.0, 74.9, 73.8, 70.6, 60.8, 55.4, 38.8, 36.1, 35.0, 27.3, 25.8; HRMS ES *m/z* (M + Na)$^+$ calcd 383.1829, obsd 383.1820; $[\alpha]_D^{16}$ +36.5 (*c* 0.69, $CHCl_3$).

Vinylstannane 15. To a stirred solution of **14** (40 mg, 0.11 mmol) in benzene (22 mL) were added *n*-Bu_3SnH (0.3 mL, 1.1 mmol) and AIBN (2 mg, 0.01 mmol) at rt under N_2. The reaction mixture was gently refluxed with stirring for 2 h. The solvent was removed and the residue was purified by column chromatography on silica gel (hexanes/ethyl acetate 50:1) to give **15** (71 mg, 99%) as a colorless oil; IR (neat, cm^{-1}) 1730, 1615, 1518; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.7 Hz, 2 H), 6.87 (d, *J* = 8.7 Hz, 2 H), 6.14-5.93 (m, 2 H), 5.47 (s, 1 H), 4.26-4.19 (m, 2 H), 3.95-3.81 (m, 2 H), 3.80 (s, 3 H), 2.79-2.52 (m, 1 H), 2.41-2.32 (m, 1 H), 2.03-1.83 (m, 2 H), 1.68-1.45 (m, 7 H), 1.42-1.22 (m, 7 H), 1.20 (s, 9 H), 1.03-0.82 (m, 15 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.4, 160.0, 144.0, 131.5, 127.3, 113.5, 100.5, 76.3, 73.6, 60.7, 55.3, 44.4, 38.7, 36.4, 35.0, 29.1, 27.2, 13.7, 9.4; HRMS ES *m/z* (M + Na)$^+$ calcd 675.3042, obsd 675.3019; $[\alpha]_D^{17}$ +8.0 (*c* 0.69, $CHCl_3$).

Vinyl Iodide 4. To a cooled (0 °C), stirred solution of **15** (207 mg, 0.318 mmol) in CH_2Cl_2 (11 mL) was added iodine (161 mg, 0.636 mmol). After 10 min at 0 °C, the reaction mixture was diluted with ethyl acetate, washed with saturated $Na_2S_2O_3$ and 10% KF solutions, and brine. The organic layer was dried, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate 20:1) to give **4** (149 mg, 96%); IR (neat, cm^{-1}) 1725, 1614, 1518, 1249; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.7 Hz, 2 H), 6.89 (d, *J* = 8.7 Hz, 2 H), 6.60 (dt, *J* = 14.6, 7.4 Hz, 1 H), 6.15 (d, *J* = 14.5 Hz, 1 H), 5.46 (s, 1 H), 4.21 (t, *J* = 6.5 Hz, 2 H), 3.95-3.82 (m, 2 H), 3.80 (s, 3 H), 2.48-2.26 (m, 2 H), 2.04-1.84 (m, 2 H), 1.63-1.54 (m, 1 H), 1.44 (q, *J* = 11.1 Hz, 1 H), 1.20 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.4, 160.0, 141.6, 130.9, 127.3, 113.6, 100.5, 77.3, 75.1, 73.5, 60.6, 55.3, 42.2, 38.7, 36.2, 34.9, 27.2; HRMS ES *m/z* (M + Na)$^+$ calcd 511.0952, obsd 511.0963; $[\alpha]_D^{19}$ +3.5 (*c* 0.49, $CHCl_3$).

Lactone 17. To a vigorously stirred suspension of CuI (6.54 g, 34.32 mmol) in dry ether (50 mL) was added MeLi (1.4 M solution in ether, 49 mL, 68.66 mmol) dropwise at -20 °C under N_2. The resulting solution was stirred for 30 min at -20 °C and **16** (4.03 g, 11.44 mmol) dissolved in THF (20 mL) was introduced at -30 °C. After 35 min at this temperature, the mixture was quenched with saturated NH_4Cl solution, extracted with ethyl acetate, washed with brine, dried, and concentrated. Purification of the residue on silica gel (hexanes/ethyl acetate 6:1) gave **17** (3.74 g, 89%), the enantiomeric form of which has previously been prepared in the same manner;[16] $[\alpha]_D^{17}$ -27.4 (*c* 1.2, $CHCl_3$).

Hydroxy Ester 18. To a stirred solution of **17** (93 mg, 0.38 mmol) in dry CH_2Cl_2 was added Dibal-H (1 M solution in hexane, 0.57 mL, 0.57 mmol) dropwise at -78 °C under N_2. After 1 h, the reaction mixture was quenched with methanol, allowed to warm to rt, treated with Rochelle's salt solution and stirred until two clear layers were visible. The mixture was extracted with CH_2Cl_2 and the combined organic layers were dried and concentrated. The resulting lactol was dissolved directly in dry benzene (7.6 mL), treated with (methoxycarbonylmethylene)triphenylphosphorane (367 mg, 1.14 mmol), and stirred for 3 h at 100 °C. The solvent was evaporated and the residue was preadsorbed from CH_2Cl_2 on to silica gel and purified by silica gel column chromatography (hexanes/ethyl acetate 8:1) to give **18** (115 mg, quantitative); IR (neat, cm^{-1}) 3491, 1724, 1428; ^1H NMR (300 MHz, $CDCl_3$) δ 7.67-7.64 (m, 4 H), 7.48-7.32 (m, 6 H), 6.99-6.89 (m, 1 H), 5.83 (dt, *J* = 15.6, 1.3 Hz, 1 H), 3.73 (s, 3 H), 4.13-3.65 (m, 1 H), 3.55 (dd, *J* = 9.9, 7.5 Hz, 1 H), 3.49-3.41 (m, 1 H), 2.63 (d, *J* = 3.7 Hz, 1 H), 2.55-2.46 (m, 1 H), 2.15-2.04 (m, 1 H), 1.81-1.68 (m, 1 H), 1.07 (s, 9 H), 0.76 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 148.1, 135.5, 132.9, 129.9, 127.8, 122.4, 75.0, 65.9, 51.4, 35.4, 35.2, 26.8, 19.2, 15.4; HRMS ES *m/z* $(M + Na)^+$ calcd 449.2119, obsd 449.2124; $[\alpha]_D^{20}$ -2.8 (*c* 0.99, $CHCl_3$).

Allylic Alcohol 20. A solution of **18** (510 mg, 1.20 mmol) and (4-methoxybenzyl) trichloroacetimidate (676 mg, 2.39 mmol) in CH_2Cl_2 (12 mL) was cooled to 0 °C and camphorsulfonic acid (28 mg, 0.12 mmol) was added under N_2. The reaction mixture was stirred at 0 °C for 2 h and at rt overnight, diluted with ethyl acetate, and washed with 1N HCl and brine. The organic layer was dried and evaporated. The residual **19** was used for the next step without further purification.

To a cooled (-78 °C), stirred solution of unpurified **19** in CH_2Cl_2 (26 mL) was added Dibal-H (1M solution in hexane, 5.2 mL, 5.21 mmol) under N_2. After 2 h at -78 °C, the reaction mixture was quenched with MeOH and the temperature of reaction mixture was allowed to 20 °C. Saturated Rochelle's salt solution was added and the resulting mixture was stirred overnight. The aqueous layer was extracted with CH_2Cl_2 and the combined organic layers were washed with brine, dried, and evaporated. Purification was realized on silica gel (hexanes/ethyl acetate 5:1) to afford **20** (386 mg, 60% for 2 steps); IR (neat, cm^{-1}) 3420, 1612; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76-7.72 (m, 4 H), 7.50-7.46 (m, 2 H), 7.45-7.40 (m, 4 H), 7.30-7.27 (m, 2 H), 6.92-6.89 (m, 2 H), 5.68-5.60 (m, 2 H), 4.68 (d, *J* = 11.2 Hz, 1 H), 4.45 (d, *J* = 11.2 Hz, 1 H), 4.11-4.10 (m, 2 H), 3.85 (s, 3 H), 3.84-3.71 (m, 2 H), 3.33 (ABq, Δv = 9.7 Hz, *J* = 5.3 Hz, 1 H), 2.33-2.29 (m, 1 H), 1.97-1.91 (m, 2 H), 1.44 br s, 1 H), 1.12 (s, 9 H), 0.92 (d, *J* = 6.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 135.6, 133.5 (2 C), 131.8, 131.0, 130.3, 129.6, 129.3, 127.6, 113.6, 83.1, 72.2, 64.1, 63.7, 55.2, 35.0, 34.7, 26.8, 19.2, 15.7; HRMS ES *m/z* (M + Na)$^+$ calcd 541.2750, obsd 541.2748; $[\alpha]_D^{17}$ +12.7 (*c* 1.32, $CHCl_3$).

Acetate 21. To a stirred solution of **20** (74 mg, 0.14 mmol) in CH_2Cl_2 (7 mL) were added pyridine (0.033 mL, 0.41 mmol), DMAP (2.0 mg, 0.014 mmol) and acetic anhydride (0.040 mL, 0.41 mmol) at rt under N_2. The reaction mixture was stirred for 1 h and diluted with ethyl acetate. The organic layer was washed with brine, dried, filtered, and evaporated. Purification on silica gel (hexanes/ethyl acetate 15:1) gave **21** (76 mg, 97%); IR (neat, cm^{-1}) 1739, 1613, 1514; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.0 Hz, 4 H), 7.47-7.35 (m, 6 H), 7.27-7.23 (m, 2 H), 6.89-6.84 (m, 2 H), 5.73-5.64 (m, 1 H), 5.58-5.48 (m, 1 H), 4.63 (d, *J* = 11.2 Hz, 1 H), 4.50 (d, *J* = 6.3 Hz, 2 H), 4.40 (d, *J* = 11.2 Hz, 1 H), 3.82 (s, 3 H), 3.80-3.72 (m, 2 H), 3.28 (q, *J* = 4.9 Hz, 1 H), 2.32-2.09 (m, 1 H), 2.07 (s, 3 H), 1.95-1.85 (m, 2 H), 1.07 (s, 9 H), 0.86 (d, *J* = 6.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 159.0, 135.6, 135.1, 133.5 (2 C), 131.0, 129.6, 129.3, 127.7, 125.2, 113.6, 83.1, 72.2, 65.3, 64.1, 55.2, 35.1, 34.5, 26.8, 21.0, 19.2, 15.8; HRMS ES *m/z* (M + Na)$^+$ calcd 583.2850, obsd 583.2875; $[\alpha]_D^{17}$ +14.4 (*c* 0.39, $CHCl_3$).

Dibromide 22. To a cooled (0 °C), solution of **21** (76 mg, 0.14 mmol) in THF (6.8 mL) was added TBAF (1 M solution in THF, 0.3 mL, 0.27 mmol) under N_2. After 4 h at 0 °C, the mixture was diluted with ethyl acetate and washed with water and brine. The organic layer was dried, filtered, and evaporated. The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate 1:1) to afford the acetoxy alcohol (44 mg, 100%); IR (neat, cm^{-1}) 3449, 1736, 1612; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2 H), 6.91-6.87 (m, 2 H), 5.77-5.67 (m, 1 H), 5.63-5.54 (m, 1 H), 4.56-4.47 (m, 4 H), 3.81 (s, 3 H), 3.73 (dd, *J* = 11.7, 3.2 Hz, 1 H), 3.60 (dd, *J* = 11.7, 5.8 Hz, 1 H), 3.31-3.26 (m, 1 H), 2.34-2.26 (m, 1 H), 2.06 (s, 3 H), 1.97-1.89 (m, 3 H), 0.90 (d, *J* = 6.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 159.3, 134.3, 130.4, 129.4, 125.6, 113.9, 82.9, 71.8, 65.0, 61.2, 55.2, 35.6, 33.8, 21.0, 15.0; HRMS ES *m/z* (M + Na)$^+$ calcd 345.1672, obsd 345.1660; $[\alpha]_D^{17}$ +1.9 (*c* 0.54, $CHCl_3$).

A mixture of the above compound (52 mg, 0.16 mmol) and IBX (226 mg, 0.81 mmol) in THF/DMSO (9:1, 5.4 mL) was stirred for 4 h at rt, diluted with hexanes, filtered through Celite, and rinsed with hexanes/ethyl acetate (3:1). The filtrate was transferred to a separatory funnel and washed with brine. The organic layer was dried, filtered, and evaporated to leave a residue that was purified by column chromatography on silica gel (hexanes/ethyl acetate 5:1). There was isolated 46 mg (90%) of the aldehyde; IR (neat, cm^{-1}) 1732, 1613, 1514; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.62 (d, *J* = 2.8 Hz, 1 H), 7.27-7.24 (m, 2 H), 6.90-6.86 (m, 2 H), 5.70-5.52 (m, 2 H), 4.59 (d, *J* = 11.4 Hz, 1 H), 4.49 (d, *J* = 5.2 Hz, 2 H), 4.43 (d, *J* = 11.4 Hz, 1 H), 3.81 (s, 3 H), 3.48 (dd, *J* = 5.8, 2.8 Hz, 1 H), 2.35-2.24 (m, 1 H), 2.05 (s, 3 H), 2.05-1.97 (m, 2 H), 0.93 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.3, 170.8, 159.6, 133.3, 129.7, 129.3, 126.5, 113.9, 86.4, 72.6, 64.9, 55.3, 34.9, 34.7, 21.0, 15.5; HRMS ES *m/z* (M + Na)$^+$ calcd 343.1516, obsd 343.1539; $[\alpha]_D^{18}$ +64.0 (*c* 0.65, $CHCl_3$).

To a cooled (0 °C), stirred solution of carbon tetrabromide (377 mg, 1.14 mmol) in CH_2Cl_2 (4 mL) was added triphenylphosphine (596 mg, 2.27 mmol) in CH_2Cl_2 (4 mL) under Ar. After 10 min, the reaction mixture was cooled to -78 °C and a solution of the above aldehyde (91 mg, 0.28 mmol) in CH_2Cl_2 (6 mL) was introduced into the yellowish ylide solution. The mixture was stirred for 2 h at -78 °C, quenched with saturated $NaHCO_3$ solution, and extracted with ethyl acetate. The combined organic layers were washed with brine, dried, and evaporated to leave a residue that was purified by column chromatography on silica gel (hexanes/ethyl acetate 20:1) to afford **22** (132 mg, 98%); IR (neat, cm^{-1}) 1739, 1612, 1514; ^1H NMR (300 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2 H), 6.90-6.85 (m, 2 H), 6.39 (d, *J* = 8.9 Hz, 1 H), 5.73-5.60 (m, 1 H), 4.52 (d, *J* = 11.5 Hz, 1 H), 4.49 (d, *J* = 6.5 Hz, 2 H), 4.30 (d, *J* = 11.5 Hz, 1 H), 3.83 (dd, *J* = 9.0, 7.3 Hz, 1 H), 3.81 (s, 3 H), 2.40-2.32 (m, 1 H), 2.05 (s, 3 H), 1.98-1.88 (m, 1 H), 1.87-1.76 (m, 1 H), 0.88 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 159.3, 138.5, 133.9, 130.2, 129.5, 125.9, 113.8, 92.0, 82.1, 70.6, 65.1, 55.3, 37.4, 35.2, 21.0, 14.9; HRMS ES *m/z* $(M + Na)^+$ calcd 498.9913, obsd 498.9902; $[\alpha]_D^{19}$ +9.1 (*c* 0.69, $CHCl_3$).

Acetylenic Alcohol 5. To a cooled (-78 °C), stirred solution of **22** (64 mg, 0.13 mmol) in THF (6.7 mL) was added *n*-BuLi (2.5 M solution in hexane, 0.32 mL, 0.80 mmol) dropwise under Ar. After 30 min, the reaction mixture was quenched with saturated NH_4Cl solution and extracted with ethyl acetate. The organic layer was washed with brine, dried, and evaporated to leave a residue that was purified by column chromatography on silica gel (hexanes/ethyl acetate 5:1) to give **5** (33 mg, 90%); IR (neat, cm^{-1}) 3286, 1613, 1514; ^1H NMR (300 MHz, $CDCl_3$) δ 7.29-7.26 (m, 2 H), 6.90-6.85 (m, 2 H), 5.85-5.54 (m, 2 H), 4.74 (d, *J* = 11.4 Hz, 1 H), 4.42 (d, *J* = 11.4 Hz, 1 H), 4.05 (d, *J* = 4.3 Hz, 2 H), 3.91 (dd, *J* = 5.7, 2.1 Hz, 1 H), 3.80 (s, 3 H), 2.46 (d, *J* = 2.1 Hz, 1 H), 2.32-2.25 (m, 1 H), 2.03-1.84 (m, 2 H), 1.46 (br s, 1 H), 1.00 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 131.0, 130.5, 129.9, 129.6, 113.7, 81.4, 74.8, 72.0, 70.2, 63.6, 55.2, 37.7, 35.4, 15.1; HRMS ES *m/z* $(M + Na)^+$ calcd 297.1461, obsd 297.1465; $[\alpha]_D^{18}$ +95.9 (*c* 0.32, $CHCl_3$).

Sonagashira Coupling of 4 to 5. To a stirred mixture of $Pd(PPh_3)_2Cl_2$ (8.4 mg, 0.012 mmol) and CuI (4.6 mg, 0.024 mmol) in Et_3N (2 mL) were added solutions of **4** (67 mg, 0.137 mmol) in Et_3N (2 mL) and of **5** (33 mg, 0.120 mmol) in Et_3N (2 mL) under Ar at rt. After 4 h, the reaction mixture was filtered through Celite and the filtrate was concentrated. The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate 3:1) to give **23** (62 mg, 82%) as a yellow syrup; IR (neat, cm^{-1}) 3505, 1726, 1614; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.6 Hz, 2 H), 7.28 (d, *J* = 8.6 Hz, 2 H), 6.90-6.85 (m, 4 H), 6.21 (dt, *J* = 15.9, 7.6 Hz, 1 H), 5.69-5.60 (m, 3 H), 5.48 (s, 1 H), 4.72 (d, *J* = 11.5 Hz, 1 H), 4.42 (d, *J* = 11.5 Hz, 1 H), 4.23 (t, *J* = 6.4 Hz, 2 H), 4.13-4.02 (m, 3 H), 3.96-3.84 (m, 2 H), 3.80 (s, 6 H), 2.57-2.42 (m, 1 H), 2.40-2.27 (m, 2 H), 2.03-1.85 (m, 4 H), 1.66-1.61 (m, 1 H), 1.51-1.41 (m, 1 H), 1.32 (br s, 1 H), 1.20 (s, 9 H), 1.00 (d, *J* = 6.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.4, 159.8, 159.2, 139.5, 131.0, 130.8, 130.7, 130.2, 129.5, 127.3, 113.7, 111.9, 100.5, 86.2, 85.2, 75.6, 73.6, 72.7, 70.2, 63.6, 60.0, 55.2 (2 C), 39.4, 38.7, 38.0, 36.4, 35.5, 34.9, 27.2, 15.3; HRMS ES *m/z* $(M + Na)^+$ calcd 657.3398, obsd 657.3399; $[\alpha]_D^{18}$ +47.8 (*c* 0.25, $CHCl_3$).

Compound 26. To a solution of **23** (21 mg, 0.033 mmol) in 3 mL of ethyl acetate/pyridine/1-octene (10:1:1) was added Lindlar catalyst (4 mg). The reaction mixture was stirred for 5.5 h under a balloon of H_2 at rt and filtered through a Celite pad. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (hexanes/ethyl acetate 3:1) to afford an inseparable mixture of **24** and **25** (ratio 1.9:1) (20 mg, 95%).

The above mixture of **24** and **25** (24.5 mg, 0.0385 mmol) and IBX (54 mg, 0.19 mmol) in THF/DMSO (9:1, 4 mL) was stirred for 4 h at rt, diluted with hexanes, filtered through Celite, and concentrated. The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate 5:1) to afford a mixture of the corresponding aldehydes (20.9 mg, 85%). This mixture (14 mg, 0.0221 mmol) together with BHT (3.0 mg, 4.4 μmol) and toluene (2.2 mL) was placed in a sealed tube and heated at 195 °C for 26 h. The mixture was cooled to rt, diluted with MeOH (2.2 mL) and treated with $NaBH_4$ (4 mg, 0.1 mmol) at 0 °C. After 1 h, the mixture was quenched with saturated $NaHCO_3$ solution and diluted with ethyl acetate. The organic layer was washed with brine, dried, and concentrated. The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate/dichoromethane 4:1:1) to give **26** (6.0 mg, 66% from **24**); IR (neat, cm^{-1}) 3433, 1728, 1614; ^1H NMR (500 MHz, C_6D_6) δ 7.57 (d, *J* = 8.6 Hz, 2 H), 7.27 (d, *J* = 8.6 Hz, 2 H), 6.83-6.79 (m, 4 H), 5.98 (ddd, *J* = 9.9, 4.9, 2.4 Hz, 1 H), 5.88 (dd, *J* = 9.9, 2.1 Hz, 1 H), 5.40 (s, 1 H), 4.41-4.33 (m, 2 H), 4.31-4.21 (m, 2 H), 3.73-3.69 (m, 1 H), 2.25-2.18 (m, 1 H), 2.09-2.02 (m, 1 H), 1.87-1.78 (m, 2 H), 1.74-1.57 (m, 4 H), 1.48-1.20 (m, 3 H), 1.18 (s, 9 H), 1.05 (d, *J* = 6.9 Hz, 3 H); ^{13}C NMR (75 MHz, C_6D_6) δ 178.1, 160.8, 160.0, 132.8, 132.5, 132.2, 132.0, 129.9, 129.6, 114.4, 114.2, 101.5, 87.4, 75.7, 74.2, 71.5, 63.5, 61.3, 55.1, 44.9, 42.5, 39.1, 38.2, 37.6, 37.0, 35.8, 35.6, 33.2, 30.6, 30.4, 27.7, 14.6; HRMS ES *m/z* $(M + Na)^+$ calcd 659.3554, obsd 659.3532.