Supporting Information Available.

Preparation of 5aR: The following reaction was carried out under Ar. To a cold (–78 °C) solution of CuBr·Me_2S (251 mg, 1.22 mmol) in THF–Me_2S (2:1) (3 mL) was added vinylmagnesium bromide (1.04 M solution in THF, 2.30 mL, 2.39 mmol). The solution was stirred for 1h at –78 °C, and a solution of **2a** (101 mg, 0.24 mmol) in THF (1 mL) was added. The solution was stirred for 10 min at –78 °C and quenched with saturated aqueous NH_4Cl. After stirring for 10 min, the solution was diluted with EtOAc (30 mL) and washed with saturated aqueous NH_4Cl (5 mL × 5). The organic layer was dried and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:16) to give 96 mg (90%, d.r. = >99:1) of **5aR** as a colorless oil: TLC, Rf 0.69 (EtOAc/hexane=1:2); $[\alpha]^{25.5}_D$ +8.0° (*c* 1.15, $CHCl_3$); IR (neat) 2940, 1740, 1640, 1500 cm^{-1}; ^1H NMR (300 MHz) δ 1.01 (d, *J* = 6.8 Hz, 3H), 2.24 (d, *J* = 6.3 Hz, 3H), 2.13 (dd, *J* = 7.3, 15.4 Hz, 1H), 2.25 (dd, *J* = 7.0, 15.4 Hz, 1H), 2.56-2.68 (m, 1H), 3.38 (s, 3H), 3.57 (dd, *J* = 3.7, 9.5 Hz, 1H), 3.69-3.79 (m, 1H), 3.87 (t, *J* = 9.4 Hz, 1H), 4.53 (d, *J* = 3.7 Hz, 1H), 4.62, 4.66 (2d, *J* = 3.5 Hz, 1H × 2), 4.77 (t, *J* = 9.7 Hz, 1H), 4.77 (d, *J* = 12.2 Hz, 1H), 4.86-5.02 (m, 3H), 5.73 (ddd, *J* = 6.7, 10.4, 17.3 Hz, 1H), 7.23-7.31 (m, 10H), ^{13}C NMR (75 MHz) δ17.45, 19.64, 33.87, 47.11, 55.25, 65.32, 73.40, 74.98, 75.14, 78.97, 79.90, 98.06, 113.44, 127.45, 127.63 ×2, 127.93, 128.13 ×2, 128.26 × 2, 128.44 ×2, 137.98, 138.65, 142.27, 171.34; Anal. Calcd for $C_{27}H_{34}O_6$: C, 71.34; H, 7.54. Found: C, 71.32; H, 7.55.

Hydrolysis of 5aR: A solution of **5aR** (81 mg, 0.18 mmol) in MeOH–4M aq. KOH (1:1) (2 mL) was refluxed for 6 h. After completion of the reaction (as assessed by TLC monitoring), the solution was cooled to room temperature and diluted with water (5 mL)

The entire solution was extracted with $CHCl_3$ (5 mL × 5), and the combined extracts were dried and concentrated to give 60 mg (94%) of **13**. The pH of the aqueous layer was adjusted to pH 2 by adding 1M aq. HCl, this was then extracted with $CHCl_3$ (5 mL × 5). The combined extracts were dried and concentrated to give 19.5 mg (96%) of **12** as a colorless oil: TLC, Rf 0.25 (EtOAc/hexane=1:1); $[\alpha]^{30.0}_D$ -17.4° (*c* 0.58, $CHCl_3$); lit. $[\alpha]^{24}_D$ -17.42° (*c* 2.06, $CHCl_3$); IR (neat) 3400-2800 (br), 2680, 1710, 1600, 1580 cm^{-1}; ^1H NMR (300 MHz) δ 1.09 (d, *J* = 6.6 Hz, 3H), 2.31 (dd, *J* = 7.6, 15.1 Hz, 1H), 2.42 (dd, *J* = 7.1, 15.1 Hz, 1H), 2.62-2.76 (m, 1 H), 4.97-5.09 (m, 2H), 5.79 (ddd, *J* = 6.8, 10.3, 17.1 Hz); ^{13}C NMR (75 MHz) δ 19.04, 34.07, 41.01, 113.57, 142.09, 178.86.

ORTEP Drawing of 4bR.