Supporting Information

Stereoselection in Radical Cyclization of β -Alkoxyvinyl Sulfoxides:

Synthesis of Tetrahydrofuranyl Allyl Carbinols

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Experimental

General Methods

All reactions were performed under argon atmosphere. ^1H and ^{13}C NMR spectra were measured on 300 MHz and 500 MHz spectrometers. Chemical shift values were recorded in parts per million using the residual undeuterated solvent as an internal reference and coupling constants in hertz. Infrared spectra (IR) were recorded on a Perkin Elmer 16F PC FT-IR spectrophotometer and frequencies are given in reciprocal centimeters. Mass spectra (MS and HRMS) were recorded using chemical ionization (CI), electron impact (EI), or fast atom bombardment (FAB) method. High Performance Liquid Chromatography (HPLC) analyses were carried out on AGILENT 1100 series using a Hibar® RT 250-4 column (Merck, Licrosorb, Si-60, 5 μm , detection at 254 nm). Optical rotation data were obtained on a digital polarimeter at 589 nm (sodium D line).

The progress of reactions was checked on TLC plates (Merck Kiesel-gel 60F₂₅₄, layer thickness 0.25mm), and the spots were visualized under 254 nm UV light and/or charring after dipping the TLC plates into a *p*-anisaldehyde solution (ethanol 67.5 mL, *p*-anisaldehyde 1.85 mL, acetic acid 0.75 mL, and sulfuric acid 2.5 mL). Column chromatography was performed on E. Merck silica gel 60 (9385, 230-400 mesh) or Kanto Chem. Co. Silica gel 60 (Cat. No. 37562-79, spherical, 40-50 μm).

All solvents used in reactions were dried under nitrogen atmosphere. THF and toluene was distilled from Na-benzophenone. CH_2Cl_2 , acetonitrile and triethylamine were distilled from CaH_2 . The following dry solvents were purchased from Aldrich Chem. Co.: THF, CH_2Cl_2 , MeOH, toluene, and pyridine.

(3S)-4-Benzyloxybutane-1,3-diol.

(3S)-4-Benzyloxybutane-1,3-diol was prepared from L-malic acid by modification of the known sequence.^{1, 2} The 1,2-diol derived from the undesired minor dioxolane isomer was removed by treatment of the mixture with NaIO₄ (10 Mol%): $[\alpha]^{19}_D -10.55$ (*c* 3.68, MeOH) [lit.³ $[\alpha]^{22}_D -7.68$ (*c* 3.67, MeOH)] ; IR (neat) ν 3380 (br), 2928, 1716, 1452, 1276, 1202, 1096, 698 cm⁻¹; ¹H NMR (CDCl₃) δ 7.40–7.27 (m, 5H), 4.58 (s, 2H), 4.08 (m, 1H), 3.84 (t, *J* = 5.2 Hz, 1H), 3.52 (dd, *J* = 9.5, 3.6 Hz, 1H), 3.42 (dd, *J* = 9.4, 7.5 Hz, 1H), 2.93 (br. s, 1H), 2.64 (br. s, 1H), 1.75–1.65 (m, 2H); ¹³C NMR (CDCl₃) δ 138.17, 128.89, 128.27, 128.18, 74.74, 73.79, 70.64, 61.36, 35.20; MS *m/z* 196 (*M*⁺), 177, 160, 137, 122, 121, 108, 107, 105, 92, 91 (100), 89, 75, 65, 57.

Tosylate 6.

To a solution of (3S)-4-benzyloxybutane-1,3-diol (1.50 g, 7.64 mmol) and triethylamine (2.13 mL, 15.3 mmol) in dry CH₂Cl₂ (15 mL) was added *p*-toluenesulfonyl chloride (1.74g, 9.13 mmol) at 0 °C. The reaction mixture was stirred for 12 h at 0 °C, and then it was quenched with aqueous 1 N HCl (10 mL). The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (20 mL x 2). The combined organic layers were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with a mixture of hexane and ethyl acetate (2:1) to give the tosylate **6** (2.25 g, 84% yield) as an oil: $[\alpha]^{23}_D -5.2$ (*c* 1.40, CHCl₃); IR (neat) ν 3530 (br.), 2924, 1720, 1598, 1452, 1358, 1274, 1176, 1098, 948, 816, 766, 700, 664 cm⁻¹; ¹H NMR (CDCl₃) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.39–7.27 (m, 7H), 4.53 (s, 2H), 4.24–4.14 (m, 2H), 3.91 (m, 1H), 3.47 (dd, *J* = 9.5, 3.3 Hz, 1H), 3.32 (dd, *J* = 9.5, 7.3 Hz, 1H), 2.44 (s, 3H), 1.96–1.73 (m, 2H); ¹³C NMR (CDCl₃) δ 145.2, 138.1, 133.4, 130.3, 128.9, 128.3, 128.1, 74.4, 73.8, 67.8, 67.1, 32.9, 22.0; MS *m/z* 262, 181, 167, 165, 156, 139, 107, 92, 91, 79, 77, 65, 63, 51.

Sulfoxide **9a**.

To a solution of the alcohol **6** (600 mg, 1.71 mmol) and (+)-(*R*)-ethynyl *p*-tolyl sulfoxide (**7**, 703 mg, 2.5 equiv) in dry CH₂Cl₂ (17 mL, 0.1 M) was added *N*-methylmorpholine (0.188 mL, 1.0 equiv) at 0 °C. After stirring for 12 h at ambient temperature, aqueous 1 N HCl (3 mL) was added. The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂. The combined organic layers were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with a mixture of hexane and ethyl acetate (1:1) to give the *E*-β-alkoxyvinyl sulfoxide **9a** (847 mg, 90%): [α]_D²⁰ -40.5 (*c* 1.45, CHCl₃); IR (neat) ν 2924, 1722, 1620, 1600, 1494, 1452, 1360, 1176, 1098, 1038, 950, 812, 758, 664 cm⁻¹; ¹H NMR (CDCl₃) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.38–7.27 (m, 9H), 7.15 (d, *J* = 12.3 Hz, 1H), 5.77 (d, *J* = 12.3 Hz, 1H), 4.50 (s, 2H), 4.21 (m, 1H), 4.09 (t, *J* = 5.7 Hz, 2H), 3.54 (dd, *J* = 10.5, 3.6 Hz, 1H), 3.47 (dd, *J* = 10.6, 5.8 Hz, 1H), 2.43 (s, 3H), 2.41 (s, 3H), 1.98 (m, 2H); ¹³C NMR (CDCl₃) δ 157.66, 145.51, 142.45, 141.12, 137.73, 133.04, 130.42, 130.23, 128.96, 128.37, 128.30, 128.16, 124.79, 113.98, 78.91, 73.94, 71.55, 66.34, 31.10, 22.08, 21.76; HRMS (FAB) calcd for C₂₇H₃₁O₆S₂ (M⁺+H) 515.1562, found 515.1577.

Sulfoxide **9b**.

The alcohol **6** (200 mg, 0.57 mmol) was dissolved in anhydrous THF (6 mL) and the solution was cooled with stirring to -78 °C under argon atmosphere. Lithium hexamethyldisilylazide (0.685 mL, 1.2 equiv, 1.0 M solution in THF) was added dropwise and the reaction mixture was stirred for 30 minutes before being allowed to warm to -20 °C for an additional 30 minutes. The reaction mixture was then cooled back to -78 °C, and (+)-(*R*)-ethynyl *p*-tolyl sulfoxide (**7**, 281 mg, 1.71 mmol, 3.0 equiv) in THF (2 mL) was added dropwise. The reaction mixture was then allowed to warm up to -20 °C. After stirring for 1 h at -20 °C, the reaction mixture was partitioned between water and diethyl ether. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. According to ¹H NMR analysis, the crude product was a

mixture of **9a** and **9b** in the ratio of 3:97 as determined from the NMR signals at 5.77 and 5.26 ppm respectively. The residue was purified by flash chromatography on silica gel with a mixture of hexane and ethyl acetate (1:1 ~ 1:2) to give the *Z*- β -alkoxyvinyl sulfoxide **9b** (150.5 mg, 51%) as an oil: ^1H NMR (CDCl_3) δ 7.80 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.33–7.21 (m, 7H), 6.63 (d, J = 5.6 Hz, 1H), 5.26 (d, J = 5.6 Hz, 1H), 4.51 (s, 2H), 4.19–4.10 (m, 3H), 3.59 (dd, J = 10.6, 3.4 Hz, 1H), 3.52 (dd, J = 10.6, 6.9 Hz, 1H), 2.44 (s, 3H), 2.37 (s, 3H), 2.03–1.95 (m, 2H); ^{13}C NMR (CDCl_3) δ 145.0, 145.6, 142.9, 141.0, 137.8, 132.9, 130.5, 130.1, 128.9, 128.3, 128.3, 127.9, 124.3, 113.0, 80.4, 73.8, 72.7, 66.5, 31.5, 22.1, 21.7.

Sulfoxide **9c**.

The compound **9c** was obtained from **6** (600 mg) and (–)-(*S*)-ethynyl *p*-tolyl sulfoxide (**8**) following the procedure as described for **9a** as an oil in 96% yield: $[\alpha]_D^{21} +56.5$ (c 2.125, CHCl_3); IR (neat) ν 2924, 1724, 1620, 1494, 1452, 1360, 1270, 1178 (strong), 1098, 1038, 950, 760, 664 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.77 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 7.38–7.24 (m, 9H), 7.12 (d, J = 12.5 Hz, 1H), 5.72 (d, J = 12.5 Hz, 1H), 4.54, 4.47 (ABq, J = 12.0 Hz, 2H), 4.24–4.02 (m, 3H), 3.56 (dd, J = 10.6, 3.3 Hz, 1H), 3.47 (dd, J = 10.6, 6.5 Hz, 1H), 2.46 (s, 3H), 2.39 (s, 3H), 2.00–1.91 (m, 2H); ^{13}C NMR (CDCl_3) δ 158.0, 145.7, 142.4, 141.1, 137.8, 132.9, 130.5, 130.2, 128.9, 128.4, 128.3, 128.0, 124.7, 113.7, 79.0, 73.8, 71.8, 66.4, 31.2, 22.1, 21.8.

Sulfoxide **9d**.

The compound **9d** was prepared from **6** (600 mg) and (–)-(*S*)-ethynyl *p*-tolyl sulfoxide (**8**) following the procedure as described for **9b**. According to ^1H NMR analysis the crude product was a mixture of **9c** and **9d** in the ratio of 7:93 as determined from the NMR signals at 5.72 and 5.29 ppm respectively. Purification by flash chromatography on silica gel with a mixture of hexane and ethyl acetate (1:1 ~ 1:2) furnished the *E*- β -alkoxyvinyl sulfoxide **9c** (19.2 mg, 7%) and the *Z*- β -alkoxyvinyl sulfoxide **9d** (150.2 mg, 51%): ^1H NMR (CDCl_3) δ 7.74 (d, J = 8.3 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.40–7.24 (m, 9H), 6.62 (d, J = 5.6 Hz, 1H), 5.29 (d, J = 5.6 Hz, 1H), 4.56, 4.52 (ABq, J = 12.0 Hz, 2H), 4.20–4.08 (m, 3H), 3.54 (m, 2H), 2.42 (s, 3H), 2.39 (s, 3H), 1.99–1.94 (m, 2H); ^{13}C NMR (CDCl_3) δ 153.7, 145.5, 142.9, 141.1, 137.8, 133.1, 130.4, 130.2, 129.0, 128.3, 128.3, 128.2, 124.4, 113.3, 80.1, 74.0, 72.6, 66.3, 31.3, 22.0, 21.8.

General procedure for the iodide substitution.

To a solution of the tosylate **9a** (847 mg, 1.65 mmol) in acetone (16 mL, 0.1 M) was added NaI (740 mg, 4.94 mmol, 3 equiv) at room temperature. Then the reaction mixture was heated under reflux for 3 h. The mixture was concentrated under reduced pressure, and the residue was partitioned between ethyl acetate and saturated aqueous NaCl solution. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (20 ml x 2). The combined organic layers were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with a mixture of hexane and ethyl acetate to give the iodide **10a** as a colorless oil.

Iodide 10a.

The iodide **10a** was obtained from **9a** (553 mg) after flash chromatography (hexane/EtOAc 3:2) as a colorless oil in 83% yield: $[\alpha]_D^{21} -104.2$ (*c* 1.70, CHCl₃); IR (neat) ν 2922, 1722, 1620, 1492, 1452, 1370, 1213, 1184, 1118, 1088, 1040, 810, 740, 698 cm⁻¹; ¹H NMR (CDCl₃) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.39–7.26 (m, 8H), 5.84 (d, *J* = 12.5 Hz, 1H), 4.53 (s, 2H), 4.24 (m, 1H), 3.54 (m, 2H), 3.25–3.11 (m, 2H), 2.41 (s, 3H), 2.19–2.00 (m, 2H); ¹³C NMR (CDCl₃) δ 157.9, 142.5, 141.2, 137.7, 130.2, 129.0, 128.4, 128.2, 124.8, 113.9, 82.6, 74.0, 71.4, 35.0, 30.1, 21.8, 1.2.

Iodide 10b.

The iodide **10b** was obtained from **9b** (151 mg) after flash chromatography (hexane/EtOAc 1:1) as a colorless oil in 83% yield: ¹H NMR (CDCl₃) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.35–7.22 (m, 11H), 6.84 (d, *J* = 5.6 Hz, 1H), 5.37 (d, *J* = 5.6 Hz, 1H), 4.54 (s, 2H), 4.23 (m, 1H), 3.60 (d, *J* = 5.2 Hz, 2H), 3.34–3.30 (m, 2H), 2.38 (s, 3H), 2.25–1.95 (m, 2H); ¹³C NMR (CDCl₃) δ 154.5, 142.9, 141.1, 137.9, 130.2, 128.9, 128.3, 127.9, 124.4, 112.9, 84.2, 73.9, 72.5, 35.2, 21.8, 1.8.

Iodide 10c.

The iodide **10c** was obtained from **9c** (847 mg) after flash chromatography (hexane/EtOAc 3:2) as a colorless oil in 84% yield: $[\alpha]_D^{23} +29.2$ (*c* 1.00, CHCl₃); IR (neat) ν 3030, 2920, 2862, 1618, 1492, 1452, 1372, 1214, 1178, 1118, 1084, 1038, 808, 740, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 7.43 (d, *J* = 8.2 Hz, 2H), 7.38–7.19 (m, 8H), 5.83 (d, *J* = 12.5 Hz, 1H), 4.53 (ABq, *J* = 12.0 Hz, 2H), 4.26 (m, 1H), 3.59 (dd, *J* = 10.6, 3.8 Hz, 1H), 3.53 (dd, *J* = 10.6, 6.3 Hz, 1H), 3.27–3.12 (m, 2H), 2.38 (s, 3H), 2.16–1.99 (m, 2H); ¹³C NMR (CDCl₃) δ 158.4, 142.5, 141.1, 137.9, 130.2, 128.9, 128.4, 128.0, 124.7, 113.6, 82.7, 73.9, 71.6, 35.1, 30.1, 21.8, 1.3; HRMS (FAB) calcd for C₂₀H₂₄IO₃S (M⁺+H) 471.0491, found 471.0481.

Iodide 10d.

The iodide **10d** was obtained from **9d** (150 mg) after flash chromatography (hexane/EtOAc 1:1) as a colorless oil in 83% yield: ¹H NMR (CDCl₃) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.37–7.25 (m, 7H),

6.82 (d, $J = 5.6$ Hz, 1H), 5.38 (d, $J = 5.6$ Hz, 1H), 4.59, 4.54 (ABq, $J = 12.0$ Hz, 2H), 4.18 (m, 1H), 3.64–3.59 (m, 2H), 3.30–3.13 (m, 2H), 2.40 (s, 3H), 2.20–1.97 (m, 2H); ^{13}C NMR (CDCl_3) δ 153.7, 145.5, 142.9, 141.1, 137.8, 133.1, 130.4, 130.2, 129.0, 128.3, 128.3, 128.2, 124.4, 113.3, 80.1, 74.0, 72.5, 66.3, 31.3, 22.0, 21.8.

General procedure for the radical cyclization of β -alkoxyvinyl sulfoxides.

To a stirred solution of the β -alkoxyvinyl sulfoxide **10a** in dry toluene (0.025 M) were added $n\text{-Bu}_3\text{SnH}$ (1.2 equiv) and Et_3B (1.5 equiv, 1.0 M solution in n -hexane) at -20°C . The resulting mixture was stirred for 30 min under air at the same temperature. Concentration and flash chromatography on silica gel (Kanto, Silica gel 60, Spherical) with a mixture of hexane and ethyl acetate furnished the 2,5-disubstituted tetrahydrofurans **11** and **12**.

The product ratio of *cis* and *trans* tetrahydrofurans (**11:12** and **13:14**) was determined by HPLC analysis: Licrosorb, Hibar RT 250-4, Si-60, hexane/ EtOAc =50:50, flow rate=2 ml/min, column temp= 24.1°C , detection at 254 nm.

Sulfoxides **11** and **12** from **10a**.

A 94:6 mixture of the sulfoxides **11** and **12** was obtained from **10a** (332 mg) after flash chromatography (hexane/ethyl acetate 1:1 ~ 1:2) as a colorless oil in 95% yield.

Sulfoxide **11** from **10b**.

The sulfoxide **11** was obtained from **10b** after flash chromatography (hexane/ethyl acetate 1:1 ~ 1:2) as a colorless oil in 88% yield. The product ratio was determined as 99:1 by HPLC analysis.

11: $[\alpha]_D^{23} +42.7$ (c 1.0, CHCl_3); IR (neat) ν 3030, 2866, 1718, 1494, 1452, 1366, 1272, 1204, 1086, 1042, 810, 740, 698 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.56 (d, $J = 8.1$ Hz, 1H), 7.37–7.25 (m, 7H), 4.57 (ABq, $J = 12.3$ Hz, 2H), 4.11 (p, $J = 5.8$ Hz, 1H), 4.02 (qui, $J = 6.4$ Hz, 1H), 3.50 (d, $J = 4.9$

Hz, 2H), 3.22 (dd, $J = 13.0, 6.1$ Hz, 1H), 2.88 (dd, $J = 13.0, 6.1$ Hz, 1H), 2.41 (s, 3H), 2.13–1.79 (m, 4H); ^{13}C NMR (CDCl_3) δ 141.9, 140.9, 138.6, 130.3, 128.8, 128.1, 128.0, 124.7, 79.2, 74.8, 73.8, 73.1, 63.2, 31.2, 28.3, 21.8; MS m/z 204 [$\text{M}^+ - \text{CH}_3\text{C}_6\text{H}_4\text{SOH}$ (140)], 113, 98, 95, 91, 83 (100), 65, 55; HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{25}\text{O}_3\text{S}$ ($\text{M}^+ + \text{H}$) 345.1524, found 345.1531.

Sulfoxide **13** from **10c**.

The sulfoxide **13** was obtained from **10c** after flash chromatography (hexane/ethyl acetate 1:2 ~ 0:1) as an colorless oil in 95% yield. The product ratio was determined as 99:1 by HPLC analysis.

13: $[\alpha]_D^{23} -143.0$ (c 1.0, CHCl_3); IR (neat) ν 3030, 2868, 1720, 1598, 1494, 1452, 1364, 1204, 1088, 1046, 906, 812, 738, 700 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.47 (d, $J = 8.2$ Hz, 2H), 7.34–7.26 (m, 7H), 4.58 (s, 2H), 4.44 (qui, $J = 6.5$ Hz, 1H), 4.19 (m, 1H), 3.56 (dd, $J = 10.2, 4.3$ Hz, 1H), 3.50 (dd, $J = 10.2, 4.8$ Hz, 1H), 2.89 (d, $J = 6.4$ Hz, 2H), 2.39 (s, 3H), 2.14–1.61 (m, 4H); ^{13}C NMR (CDCl_3) δ 141.9, 141.7, 138.7, 130.3, 128.8, 128.0, 124.2, 79.2, 74.0, 73.7, 72.8, 65.0, 31.7, 28.2, 21.8; HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{25}\text{O}_3\text{S}$ ($\text{M}^+ + \text{H}$) 345.1524, found 345.1521.

Sulfoxides **13** and **14** from **10d**.

The sulfoxides **13** and **14** was obtained from **9d** after flash chromatography (hexane/ethyl acetate 1:2 ~ 0:1) as a colorless oil in 85% yield. The product ratio was determined as 92:8 by HPLC analysis.

Aldehyde **15**.

To an acetonitrile solution (6 mL) of the sulfoxide **13** (299.3 mg, 0.87 mmol) was added pyridine (354 μL , 4.34 mmol) and trifluoroacetic anhydride (245 μL , 1.73 mmol) under nitrogen at 0 °C. After stirring at the same temperature for 30 min, solid KOAc (512 mg, 5.21 mmol, 6 equiv) and water (100 μL) were added to the reaction mixture. The resulting suspension was stirred at 0 °C for 2 h. Saturated aqueous NaHCO_3 solution was added to the mixture at 0 °C and the solution was extracted with ethyl acetate. The organic phase was washed with 1 N HCl, saturated aqueous NaHCO_3 , and brine. The organic layer was then dried over anhydrous MgSO_4 , filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/ethyl acetate 2:1 ~ 3:2) afforded the aldehyde **15** (160.1 mg, 84%) as a colorless oil: $[\alpha]_D^{25} +54.1$ (c 0.93, CHCl_3) [Lit.⁴ $[\alpha]_D^{20}$ (enantiomer) -42.9 (c 1.04, CHCl_3)]; IR (neat) ν 3442, 2868, 1730, 1452, 1366, 1270, 1082, 802, 740, 700 cm^{-1} ; ^1H NMR (CDCl_3) δ 9.69 (d, $J = 1.7$ Hz, 1H), 7.38–7.26 (m, 5H), 4.58 (s, 2H), 4.32–4.22 (m, 2H), 3.58 (dd, $J = 10.1, 4.0$ Hz, 1H), 3.52 (dd, $J = 10.1, 5.4$ Hz, 1H), 2.18–1.60 (m, 4H); ^{13}C NMR (CDCl_3) δ 203.75, 138.41, 128.79, 128.08, 83.93,

80.39, 73.85, 72.92, 28.25, 28.16; MS m/z 220 (M^+), 191, 173, 155, 143, 129, 114, 107, 99, 92, 91 (100), 83, 77, 69, 65.

Carbinol 16.

To a solution of the aldehyde **15** (92.3 mg, 0.42 mmol) and $MgBr_2 \cdot Et_2O$ (325 mg, 1.26 mmol) in CH_2Cl_2 (4 mL) was added allyltributylstannane (260 μL , 0.84 mmol) at room temperature. After stirring for 3 h at room temperature, the organic layer was washed with aqueous 1 N HCl, extracted with CH_2Cl_2 (10 mL x 2), dried over $MgSO_4$, and concentrated. The residue was purified by flash chromatography on silica gel with a mixture of hexane and ethyl acetate (4:1) to give the carbinol **16** (108.3 mg, 99% yield) as a colorless oil: $[\alpha]_D^{24}$ -0.64 (c 0.94, $CHCl_3$); IR (neat) ν 3454 (br.) 2868, 1720, 1640, 1452, 1274, 1204, 1074, 912, 738, 698 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.38–7.25 (m, 5H), 5.88 (ddt, J = 17.2, 10.1, 7.0 Hz, 1H), 5.14–5.05 (m, 2H), 4.59, 4.54 (ABq, J = 12.2 Hz, 2H), 4.20–4.12 (m, 1H), 3.93–3.85 (m, 1H), 3.49 (dd, J = 10.0, 3.9 Hz, 1H), 3.48 (m, 1H), 3.45 (dd, J = 10.0, 4.6 Hz, 1H), 2.80 (d, J = 6.2 Hz, 1H), 2.27 (dt, J = 7.0, 1.1 Hz, 2H), 1.97–1.80 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 138.36, 135.50, 128.83, 128.14, 117.38, 82.41, 78.88, 74.24, 73.77, 72.73, 39.35, 28.49, 28.42; MS m/z 262 (M^+), 244, 221, 191, 173, 155, 141, 129, 113, 101, 99, 91 (100), 83, 71, 65, 57, 55; HRMS (CI) calcd for $C_{16}H_{23}O_3$ ($M^+ + H$) 263.1647, found 263.1655.

Carbinol 17.

To a solution of the aldehyde **15** (136.8 mg, 0.62 mmol) and $BF_3 \cdot Et_2O$ (236 μL , 1.86 mmol) in CH_2Cl_2 (6 mL) was added allyltributylstannane (385 μL , 1.24 mmol) at $-78^\circ C$. After stirring for 3 h at $-78^\circ C$, the organic layer was washed with aqueous 1 N HCl, extracted with CH_2Cl_2 (10 mL x 2), dried over $MgSO_4$, and concentrated. The residue was purified by flash chromatography on silica gel with a mixture of hexane and ethyl acetate (4:1) to give a 8:92 mixture of the *syn* (**16**) and the *anti* (**17**) carbinols (108.3 mg, 99% yield) as colorless oil. Diastereomeric ratio of the product was determined by capillary GC analysis.

To a solution of the carbinol mixture (143.3 mg, 0.55 mmol) obtained above in CH_2Cl_2 (4 mL) was added triethylamine (304 μL , 2.18 mmol), Ac_2O (78 μL , 0.83 mmol) and DMAP (3.3 mg, 0.03 mmol) at room temperature. After 3 h, the reaction mixture was treated with saturated NH_4Cl solution and extracted with CH_2Cl_2 (5 mL x 2). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel with a mixture of hexane and ethyl acetate (7:1) to provide the acetate of **17** (125.1 mg, 75%): $[\alpha]_D^{24}$ +6.46 (c 1.02, $CHCl_3$); IR (neat) ν 2862, 1740, 1454, 1370, 1238, 1088, 1028, 918, 738, 698 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.34–7.26 (m, 5H), 5.75 (ddt, J = 17.0, 10.1,

7.0, 1H), 5.10–5.01 (m, 2H), 4.97 (dt, $J = 8.1, 5.0$ Hz, 1H), 4.58, 4.54 (ABq, $J = 12.3$ Hz, 2H), 4.12 (m, 1H), 3.98 (m, 1H), 3.45 (d, $J = 5.2$ Hz, 2H), 2.43–2.29 (m, 2H), 2.00 (s, 3H), 1.98–1.87 (m, 2H), 1.78–1.69 (m, 2H); ^{13}C NMR (CDCl_3) δ 170.87, 138.68, 134.18, 128.77, 128.06, 127.98, 117.98, 80.36, 79.13, 74.40, 73.71, 73.02, 35.88, 28.28, 27.30, 21.51; MS m/z 304 (M^+), 261, 244, 203, 191, 183, 173, 155, 143, 138, 129, 123, 105, 91, 79, 65, 55; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{24}\text{O}_4$ (M^+) 304.1674, found 304.1679.

After hydrolysis of the acetate described above with 1 N NaOH in MeOH, an analytically pure sample of **17** was obtained by flash chromatography in 97% yield: $[\alpha]_{\text{D}}^{23} +1.74$ (c 1.04, CHCl_3); IR (neat) ν 3450 (br.), 2868, 1640, 1452, 1364, 1074, 912, 738, 698 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.35–7.30 (m, 5H), 5.85 (ddt, $J = 17.1, 10.1, 7.0$ Hz, 1H), 5.15–5.06 (m, 2H), 4.60, 4.54 (ABq, $J = 12.3$ Hz, 2H), 4.14 (m, 1H), 3.97–3.87 (m, 2H), 3.60 (dd, $J = 10.0, 3.5$ Hz, 1H), 3.42 (dd, $J = 10.0, 4.4$ Hz, 1H), 2.91 (br. s, 1H), 2.29–2.13 (m, 2H), 2.02–1.77 (m, 4H); ^{13}C NMR (CDCl_3) δ 138.25, 135.21, 128.84, 128.17, 128.14, 117.55, 82.93, 78.59, 73.72, 72.52, 72.18, 37.97, 28.50, 24.78; MS m/z 262 (M^+), 221, 191, 155, 141, 129, 113, 101, 99, 91, 79, 71, 65, 57, 55; HRMS (CI) calcd for $\text{C}_{16}\text{H}_{23}\text{O}_3$ ($\text{M}^+ + \text{H}$) 263.1647, found 263.1650.

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¹H NMR spectrum of **11**

¹³C NMR spectrum of **11**

¹H NMR spectrum of **13**

¹³C NMR spectrum of **13**

¹H NMR spectrum of **15**

¹³C NMR spectrum of **15**

¹H NMR spectrum of **16**

DEPT135 NMR spectrum of **16**

¹H NMR spectrum of **17**

¹³C NMR spectrum of **17**