Experimental Section

General

Specific rotations were measured in a 10 mm cell. ^{1}H NMR spectra were recorded at 270 MHz or at 300 MHz with tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded at 68 MHz or at 75 MHz. All spectra were recorded in $CDCl_3$ as solvent, unless otherwise described. Thin-layer chromatography (TLC) was performed with a glass plate coated with Kieselgel 60 F_{254} (Merck). The crude reaction mixtures and extractive materials were purified by chromatography on silica gel Daisogel IR-60 (Daiso Co., Ltd.) or Wakogel C300 (Wako Pure Chemical Industries). Unless otherwise described, reactions were carried out at ambient temperature. Combined organic extracts were dried over anhydrous Na_2SO_4. Solvents were removed from reaction mixture or combined organic extracts by concentration under reduced pressure using an evaporator with a water bath at 35–45 °C.

(3*R*,4*S*,5*R*)-5,6-(Isopropylidene)dioxy-4-[(4-methoxyphenyl)methoxy]-3-methyl-1-hexene (10)

To a cooled (0 °C), stirred solution of **9**[1] (698 mg, 3.75 mmol) in DMF (15 mL) was added NaH (60% in oil, 301 mg, 7.53 mmol). The mixture was stirred for 30 min and 4-methoxybenzyl chloride (0.77 mL, 5.7 mmol) was added at 0 °C. The mixture was stirred for 2 h and quenched with saturated aqueous NH_4Cl. This was diluted with Et_2O (30 mL) and washed with saturated brine. The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/toluene/triethylamine, 1:100:1) to provide 1.07 g (93%) of **10** as a colorless oil; TLC, R_f 0.70 (EtOAc/hexane, 1:2); $[\alpha]^{27}_{D}$ +43.2 (*c* 1.64, $CHCl_3$); ^{1}H NMR (270 MHz) δ 1.07 (d, J = 7.0 Hz, 3H), 1.35, 1.43 (2s, 3H $\times$ 2), 2.37 (m, 1H), 3.51 (dd, J = 5.0, 5.5 Hz, 1H), 3.80 (s, 3H), 3.88 (dd, J = 7.3, 8.1 Hz, 1H), 3.97 (dd, J = 6.4, 8.1 Hz, 1H), 4.16 (ddd, J = 5.0, 6.4, 7.3 Hz, 1H), 4.55, 4.65 (2d, J = 11.0 Hz, 1H $\times$ 2), 5.00–5.10 (m, 2H),

5.85 (ddd, *J* = 7.7, 10.3, 17.2 Hz, 1H), 6.87 (m, 2H), 7.26 (m, 2H); ^{13}C NMR (75 MHz) δ 15.31, 25.43, 26.60, 40.37, 55.22, 65.62, 74.14, 76.87, 82.08, 108.60, 113.70 × 2, 114.55, 129.41 × 2, 130.76, 141.19, 159.13; IR (neat) 2990, 1615, 1515 cm^{-1}; HRMS calcd for $C_{18}H_{26}O_4$ (M^+) *m/z* 306.1831, found 306.1832.

(3*R*,4*S*,5*R*)-5,6-(Isopropylidene)dioxy-4-[(4-methoxyphenyl)methoxy]-3-methyl-1-hexanol (11)

The following reaction was carried out under argon. To a cooled (0 °C), stirred solution of **10** (1.95 g, 6.36 mmol) in THF (30 mL) was added $BH_3 \cdot SMe_2$ (0.25 mL, 2.5 mmol). The mixture was stirred for 2 h and then quenched with EtOH followed by the addition of 1 M aqueous NaOH (6 mL) and 35% H_2O_2 (2 mL). The mixture was stirred vigorously for 3.5 h and 10 % aqueous $Na_2S_2O_3$ (100 mL) was added. This was extracted with CH_2Cl_2. The combined organic layers were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:5) to provide 1.59 g (77%) of **11** as a colorless oil; TLC, R_f 0.14 (EtOAc/hexane, 1:2); $[\alpha]^{24}_D$ +25.5 (*c* 1.82, $CHCl_3$); ^{1}H NMR(300 MHz) δ 0.97 (d, *J* = 7.1 Hz, 3H), 1.34, 1.42 (2s, 3 H × 2), 1.52 (m, 1H), 1.75 (m, 1H), 1.97 (m, 1H), 2.17 (br s, 1H), 3.50 (dd, *J* = 3.3, 5.9 Hz, 1H), 3.55–3.74 (m, 2H), 3.79 (s, 3H), 3.89 (dd, *J* = 6.8, 7.8 Hz, 1H), 4.04 (dd, *J* = 6.3, 7.8 Hz, 1H), 4.17 (ddd, *J* = 5.9, 6.3, 6.8 Hz, 1H), 4.55, 4.59 (2d, *J* = 11.0 Hz, 1H × 2), 6.87 (m, 2H), 7.25 (m, 2H); ^{13}C NMR (75 MHz) δ 15.23, 25.23, 26.63, 32.52, 36.55, 55.24, 61.21, 66.77, 73.61, 76.69, 82.58, 108.52, 113.77 × 2, 129.36 × 2, 130.46, 159.20; IR (neat) 3400, 2940, 1615, 1515 cm^{-1}; HRMS calcd for $C_{18}H_{28}O_5$ (M^+) *m/z* 324.1937, found 324.1934

Ethyl (2*E*,5*R*,6*S*,7*R*)-7,8-(isopropylidene)dioxy-6-[(4-methoxyphenyl)methoxy]-5-methyl-2-octenoate (12)

The following reaction was carried out under argon. To a cooled (–78 °C), stirred solution of oxalyl chloride (0.49 mL, 5.6 mmol) in CH_2Cl_2 (9 mL) was added DMSO

(0.80 mL, 11 mmol). The mixture was stirred at –78 °C for 30 min. To this was added **11** (603 mg, 1.86 mmol) in CH_2Cl_2 (5 mL) at –78 °C. The mixture was stirred at –78 °C for 1 h and then Et_3N (2.6 mL, 19 mmol) was added and gradually warmed to rt. The mixture was stirred for 30 min. This was diluted with saturated brine (30 mL) and extracted with CH_2Cl_2. The combined organic layers were dried and concentrated in vacuo to give crude aldehyde, which was used in the next step without purification.

To a stirred solution of the crude aldehyde obtained above in benzene (14 mL) was added $Ph_3P{=}CHCO_2Et$ (1.98 g, 5.68 mmol). The mixture was stirred for 14 h and concentrated in vacuo. The residue was triturated with excess petroleum ether. The precipitated $Ph_3P{=}O$ was removed by filtration and washed well with cooled petroleum ether. The combined filtrate and washings were concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:15) to provide 616 mg (84%) of **12** as a colorless oil; TLC, R_f 0.68 (EtOAc/hexane, 1:2); $[\alpha]^{27}_D$ –9.1 (*c* 1.41, $CHCl_3$); ^{1}H NMR (300 MHz) δ 0.95 (d, *J* = 6.8 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.35, 1.42 (2s, 3H × 2), 1.98 (m, 1H), 2.13 (m, 1H), 2.38 (m, 1H), 3.49 (dd, *J* = 2.9, 5.8 Hz, 1H), 3.81 (s, 3H), 3.89 (dd, *J* = 6.3, 7.8 Hz, 1H), 4.04 (dd, *J* = 6.3, 7.8 Hz, 1H), 4.11 (q, *J* = 6.3, 6.5 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.50, 4.59 (2d, *J* = 11.0 Hz, 1H × 2), 5.81 (d, *J* = 15.6 Hz, 1H), 6.86–6.97 (m, 3H), 7.25 (m, 2H); ^{13}C NMR (75 MHz) δ 14.24, 14.43, 25.22, 26.65, 35.00, 36.53, 55.24, 60.17, 66.70, 73.74, 76.87, 81.64, 108.57, 113.77 × 2, 122.75, 129.24 × 2, 130.53, 147.73, 159.20, 166.44; IR (neat) 2980, 1715, 1650, 1615, 1515 cm^{-1}; HRMS calcd for $C_{22}H_{32}O_6$ (M^+) *m/z* 392.2199, found 392.2204.

(2*E*,5*R*,6*S*,7*R*)-7,8,-(Isopropylidene)dioxy-6-[(4-methoxyphenyl)methoxy]-5-methyl-2-octen-1-ol (13)

The following reaction was carried out under argon. To a cooled (–78 °C), stirred solution of **12** (911 mg, 2.32 mmol) in CH_2Cl_2 (15 mL) was added DIBALH (5.1 mL of 1.0 M in toluene, 5.1 mmol). The mixture was stirred at –78 °C for 30 min and

DIBALH (1.2 mL of 1.0 M in toluene, 1.2 mmol). The mixture was stirred at –78 °C for 30 min and quenched with H_2O. This was diluted with CH_2Cl_2 (10 mL), and then an aqueous solution (10 mL) of potassium sodium (+)-tartrate tetrahydrate (3.6 g) was added. The mixture was stirred vigorously for 12 h and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:10) to provide 789 mg (97%) of **13** as a colorless oil; TLC, R_f 0.25 (EtOAc/hexane, 1:2); $[\alpha]^{24}_D$ +6.5 (*c* 1.87, $CHCl_3$); ^{1}H NMR (300 MHz) δ 0.93 (d, *J* = 6.8 Hz, 3H), 1.35, 1.42 (2s, 3H $\times$ 2), 1.68 (br s, 1H), 1.83 (m, 1H), 2.00 (m, 1H), 2.24 (m, 1H), 3.52 (dd, *J* = 3.3, 5.5 Hz, 1H), 3.80 (s, 3H), 3.90 (dd, *J* = 6.9, 7.9 Hz, 1H), 4.02 (dd, *J* = 6.5, 7.9 Hz, 1H), 4.08 (d, *J* = 2.2 Hz, 2H), 4.13 (q, *J* = 6.5 Hz, 1H), 4.52, 4.61 (2d, *J* = 11.0 Hz, 1H $\times$ 2), 5.63–5.65 (m, 2H), 6.88 (m, 2H), 7.25 (m, 2H); ^{13}C NMR (68 MHz) δ 14.37, 25.22, 26.64, 35.56, 36.66, 55.23, 63.55, 66.49, 73.78, 77.06, 81.49, 108.42, 113.72 $\times$ 2, 129.18 $\times$ 2, 130.74, 131.31 $\times$ 2, 159.10; IR (neat) 3400, 2940, 1615, 1515 cm^{-1}; HRMS calcd for $C_{20}H_{30}O_5$ (M^+) *m/z* 350.2093, found 350.2099

(2*E*,5*R*,6*S*,7*R*)-7,8-(Isopropylidene)dioxy-6-[(4-methoxyphenyl)methoxy]-5-methyl-1-pivaloyloxy-2-octene (14)

To a cooled (0 °C), stirred solution of **13** (325 mg, 0.927 mmol) in pyridine (6.5 mL) were added Et_3N (0.19 mL, 1.4 mmol) and PivCl (0.17 mL, 1.4 mmol). The mixture was stirred for 1 h and then Et_3N (0.039 mL, 0.28 mmol) and PivCl (0.034 mL, 0.28 mmol) were added. The mixture was stirred for 1 h and then concentrated with the aid of toluene. This was diluted with EtOAc (10 mL) and washed with saturated brine. The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:40) to provide 386 mg (97%) of **14** as a colorless oil; TLC, R_f 0.83 (EtOAc/hexane, 1:2); $[\alpha]^{25}_D$ +5.6 (*c* 1.82, $CHCl_3$); ^{1}H NMR (300 MHz) δ 0.92 (d, *J* = 6.8 Hz, 3H), 1.20 (s, 9H), 1.35, 1.42 (2s, 3H $\times$ 2), 1.85

(m, 1H), 2.01 (m, 1H), 2.25 (m, 1H), 3.50 (dd, *J* = 3.2, 5.5 Hz, 1H), 3.80 (s, 3H), 3.88 (dd, *J* = 6.2, 8.0 Hz, 1H), 4.02 (dd, *J* = 6.2, 8.0 Hz, 1H), 4.12 (q, *J* = 6.2 Hz, 1H), 4.50–4.54 (m, 3H), 4.59 (d, *J* = 11.0 Hz, 1H), 5.56 (dt, *J* = 15.4, 6.0 Hz, 1H), 5.71 (td, *J* = 6.9, 15.4 Hz, 1H), 6.87 (m, 2H), 7.25 (m, 2H); ^{13}C NMR (75 MHz) δ 14.24, 25.23, 26.65, 27.16 × 3, 35.42, 36.73, 38.69, 55.20, 64.79, 66.57, 73.79, 76.97, 81.59, 108.45, 113.70 × 2, 125.91, 129.16 × 2, 130.76, 134.03, 159.12, 178.26; IR (neat) 2980, 1730, 1610, 1515 cm^{-1}; HRMS calcd for $C_{25}H_{38}O_6$ (M^+) *m/z* 434.2668, found 434.2666

(2*R*,3*S*,4*R*,6*E*)-3-[(4-Methoxyphenyl)methoxy]-4-methyl-8-pivaloyloxy-6-octene-1,2-diol (15)

Compound **14** (386 mg, 0.889 mmol) was dissolved in a mixture of AcOH, H_2O, and THF (3:1:1, v/v, 8 mL). The solution was stirred at 40 °C for 18 h and then concentrated in vacuo with the aid of toluene and EtOH. The residue was purified by column chromatography on silica gel (acetone/hexane, 1:5) to provide 333 mg (95%) of **15** as a colorless oil; TLC, R_f 0.35 (acetone/hexane, 1:2); $[\alpha]^{26}_D$ +0.2 (*c* 1.54, $CHCl_3$); ^{1}H NMR (270 MHz) δ 0.99 (d, *J* = 6.6 Hz, 3H), 1.20 (s, 9H), 1.88–2.10 (m, 4H), 2.23 (m, 1H), 3.42 (t, *J* = 4.9 Hz, 1H), 3.69–3.78 (m, 3H), 3.80 (s, 3H), 4.48–4.58 (m, 4H), 5.56 (dt, *J* = 15.4, 6.0 Hz, 1H), 5.72 (dt, *J* = 15.4, 6.8 Hz, 1H), 6.88 (m, 2H), 7.25 (m, 2H); ^{13}C NMR (75 MHz) δ 14.41, 27.14 × 3, 34.71, 36.98, 38.72, 55.24, 63.81, 64.84, 71.69, 74.12, 82.84, 113.85 × 2, 125.99, 129.33 × 2, 130.40, 133.87, 159.27, 178.46; IR (neat) 3400, 2970, 1730, 1615, 1515 cm^{-1}; HRMS calcd for $C_{22}H_{34}O_6$ (M^+) *m/z* 394.2355, found 394.2348.

(3*S*,4*R*,6*E*)-1,1-Dibromo-3-[(4-methoxyphenyl)methoxy]-4-methyl-8-pivaloyloxy-1,6-octadiene (16)

To a cooled (0 °C), stirred solution of **15** (281 mg, 0.712 mmol) in MeOH (4 mL) was added a solution of $NaIO_4$ (305 mg, 0.142 mmol) in H_2O (2 mL). The mixture was stirred for 30 min and then diluted with H_2O (7 mL) and extracted with CH_2Cl_2. The combined organic layers were dried and concentrated in vacuo to give crude aldehyde,

which was used in the next step without purification.

The following reaction was carried out under argon. To a cooled (0 °C), stirred solution of CBr_4 (826 mg, 2.49 mmol) in CH_2Cl_2 (3 mL) was added a solution of PPh_3 (1.31 g, 4.98 mmol) in CH_2Cl_2 (1 mL). The mixture was stirred at 0°C for 15 min and then cooled to –78 °C. Then a solution of the crude aldehyde obtained above in CH_2Cl_2 (1 mL) was added at –78 °C. The mixture was stirred at –78 °C for 1 h and diluted with saturated aqueous $NaHCO_3$ (6 mL). This was extracted with CH_2Cl_2. The combined organic layers were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:18) to provide 302 mg (82%) of **16** as a colorless oil; TLC, R_f 0.69 (EtOAc/hexane, 1:3); $[\alpha]^{27}_D$ –4.4 (*c* 1.72, $CHCl_3$); ^{1}H NMR (300 MHz) δ 0.94 (d, *J* = 6.8 Hz, 3H), 1.19 (s, 9H), 1.76 (m, 1H), 1.88 (m, 1H), 2.24 (m, 1H), 3.81 (s, 3H), 3.90 (dd, *J* = 5.4, 8.5 Hz, 1H), 4.29 (d, *J* = 11.5 Hz, 1H), 4.48 (d, *J* = 5.9 Hz, 2H), 4.52 (d, *J* = 11.5 Hz, 1H), 5.52 (dt, *J* = 15.4, 5.9 Hz, 1H), 5.65 (dt, *J* = 15.4, 6.7 Hz, 1H), 6.44 (d, *J* = 8.5 Hz, 1H), 6.88 (m, 2H), 7.26 (m, 2H); ^{13}C NMR (75 MHz) δ 14.94, 27.19 $\times$ 3, 35.42, 37.54, 38.70, 55.24, 64.78, 70.60, 81.59, 91.33, 113.70 $\times$ 2, 126.10, 129.47 $\times$ 2, 130.17, 133.26, 138.95, 159.18, 178.28; IR (neat) 2970, 1730, 1615, 1515 cm^{-1}; HRMS calcd for $C_{22}H_{30}O_4BrBr^{81}$ (M^+) *m/z* 518.0490, found 518.0499.

(2*E*,5*R*,6*S*)-8,8-Dibromo-6-[(4-methoxyphenyl)methoxy]-5-methyl-2,7-octadien-1-ol (17)

The following reaction was carried out under argon. To a cooled (–78 °C), stirred solution of **16** (249 mg, 0.480 mmol) in CH_2Cl_2 (5 mL) was added DIBALH (1.1 mL of 1.0 M in toluene, 1.1 mmol). The mixture was stirred at –78 °C for 30 min and quenched with H_2O. This was diluted with CH_2Cl_2 (10 mL), and then an aqueous solution (10 mL) of potassium sodium (+)-tartrate tetrahydrate (745 mg) was added. The mixture was stirred vigorously for 14 h and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried

and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:5) to provide 202 mg (97%) of **17** as a colorless oil; TLC, R_f 0.29 (EtOAc/hexane, 1:3); $[\alpha]^{25}_D$ –9.5 (*c* 1.59, $CHCl_3$); ^{1}H NMR (300 MHz) δ 0.95 (d, *J* = 6.6 Hz, 3H), 1.54 (br s, 1H), 1.75 (m, 1H), 1.88 (m, 1H), 2.21 (m, 1H), 3.81 (s, 3H), 3.89 (dd, *J* = 5.5, 8.7 Hz, 1H), 4.05 (d, *J* = 3.4 Hz, 2H), 4.28, 4.53 (2d, *J* = 11.5 Hz, 1H × 2), 5.56–5.60 (m, 2H), 6.45 (d, *J* = 8.7 Hz, 1H), 6.88 (m, 2H), 7.26 (m, 2H); ^{13}C NMR (75 MHz) δ15.05, 35.35, 37.64, 55.24, 63.59, 70.54, 81.59, 91.34, 113.68 × 2, 129.52 × 2, 130.17, 130.71, 130.91, 138.95, 159.18; IR (neat) 3400, 2940, 1615, 1515 cm^{-1}; HRMS calcd for $C_{17}H_{22}O_3BrBr^{81}$ (M^+) *m/z* 433.9915, found 433.9913.

(3*S*,4*R*,6*E*)-1,1-Dibromo-8-(*t*-butyldiphenylsilyloxy)3-[(4-methoxyphenyl)methoxy]-4-methyl-1,6-octadiene (18)

To a cooled (0 °C), stirred solution of **17** (202 mg, 0.466 mmol) in DMF (2 mL) were added imidazole (76.1 mg, 1.12 mmol) and TBDPSCl (0.15 mL, 0.56 mmol). The mixture was stirred for 1.5 h and then diluted with EtOAc (10 mL) and washed with saturated brine. The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:35) to provide 303 mg (97%) of **18** as a colorless oil; TLC, R_f 0.74 (EtOAc/hexane, 1:3); $[\alpha]^{26}_D$ –2.2 (*c* 1.48, $CHCl_3$); ^{1}H NMR (300 MHz) δ 0.95 (d, *J* = 6.6 Hz, 3H), 1.05 (s, 9 H), 1.74 (m, 1H), 1.87 (m, 1H), 2.22 (m, 1H), 3.78 (s, 3H), 3.91 (dd, *J* = 5.6, 8.5 Hz, 1H), 4.14 (d, *J* = 3.7 Hz, 2H), 4.29, 4.52 (2d, *J* = 11.5 Hz, 1H × 2), 5.48–5.66 (m, 2H), 6.44 (d, *J* = 8.5 Hz, 1H), 6.87 (m, 2H), 7.25 (m, 2H), 7.35–7.41 (m, 6H), 7.64–7.70 (m, 4H); ^{13}C NMR (75 MHz) δ 15.00, 19.21, 26.83 × 3, 35.40, 37.77, 55.22, 64.37, 70.65, 81.84, 91.21, 113.70 × 2, 127.60 × 4, 128.57, 129.44 × 2, 129.56 × 2, 130.28, 130.79, 133.82 × 2, 135.51 × 4, 139.13, 159.17; IR (neat) 3080, 2940, 1610, 1515 cm^{-1}; HRMS calcd for $C_{29}H_{31}O_3BrBr^{81}Si$ (M^+–*t*-Bu) *m/z* 615.0389, found 615.0404.

(3*S*,4*R*,6*E*)-8-(*t*-Butyldiphenylsilyloxy)3-[(4-methoxyphenyl)methoxy]-4-methyl-6-octen-1-yne (6)

The following reaction was carried out under argon. To a cooled (–78 °C), stirred solution of **18** (1.68 g, 2.50 mmol) in THF (30 mL) was added BuLi (3.1 mL of 2.46 M in hexane, 7.5 mmol). The mixture was stirred at –78 °C for 30 min and quenched with saturated aqueous NH_4Cl. This was diluted with saturated NH_4Cl (100 mL) and extracted with EtOAc. The combined organic layers were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:100) to provide 1.02 g (80%) of **6** as a colorless oil; TLC, R_f 0.66 (EtOAc/hexane, 1:3); $[\alpha]^{26}_D$ –50.9 (*c* 1.62, $CHCl_3$); ^{1}H NMR (270 MHz) δ 0.99 (d, *J* = 7.0 Hz, 3H), 1.05 (s, 9H), 1.82 (m, 1H), 1.95 (m, 1H), 2.34 (m, 1H), 2.46 (d, *J* = 2.0 Hz, 1H), 3.78 (s, 3H), 3.93 (dd, *J* = 2.0, 4.8 Hz, 1H), 4.13 (d, *J* = 4.0 Hz, 2H), 4.39, 4.73 (2d, *J* = 11.4 Hz, 1H $\times$ 2), 5.47–5.65 (m, 2H), 6.85 (m, 2H), 7.28 (m, 2H), 7.36–7.42 (m, 6H), 7.64–7.70 (m, 4H); ^{13}C NMR (68 MHz) δ 15.09, 19.21, 26.84 $\times$ 3, 35.07, 38.24, 55.23, 64.45, 70.26, 71.67, 74.50, 82.07, 113.72 $\times$ 2, 127.60 $\times$ 4, 128.81, 129.55 $\times$ 2, 129.61 $\times$ 2, 130.02, 130.74, 133.87 $\times$ 2, 135.52 $\times$ 4, 159.19; IR (neat) 3290, 3070, 2930, 1615, 1515 cm^{-1}; HRMS calcd for $C_{33}H_{40}O_3Si$ (M^+) *m/z* 512.2747, found 512.2742.

(3*R*,4*S*)-4,5-(Isopropylidene)dioxy-3-methyl-1-pentanol (21)[2]

To a cooled (0 °C), stirred solution of **20**[3] (12.6 g, 58.2 mmol) in Et_2O (250 mL) was added $LiAlH_4$ (2.22 g, 58.5 mmol). The mixture was stirred at 0 °C for 1 h and $LiAlH_4$ (0.66 g, 17 mmol) was added. The mixture was stirred at 0 °C for 1 h and $LiAlH_4$ (0.66 g, 17 mmol) was added. The mixture was stirred at 0 °C for 1 h and then quenched with H_2O (4 mL), followed by successive addition of 15% aqueous NaOH (4 mL) and H_2O (14 mL). After being stirred, the mixture was filtered through a Celite pad. The combined filtrate and washings were concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:20) to provide 9.75 g (96%) of **21** as a colorless oil. ; TLC, R_f 0.21 (EtOAc/hexane, 1:2); $[\alpha]^{26}_D$ +19.0 (*c* 1.70, $CHCl_3$); ^{1}H NMR (270 MHz) δ 0.99 (d, *J* = 6.6 Hz, 3H), 1.36, 1.42 (2s, 3H $\times$ 2), 1.43 (m, 1H), 1.66 (m, 1H), 1.84 (m, 1H), 1.95 (br s, 1H), 3.61–3.80 (m, 3H), 4.01 (m,

2H); ^{13}C NMR (75 MHz) δ 15.12, 25.28, 26.38, 32.70, 35.53, 60.30, 67.13, 79.62, 108,73; IR (neat) 3400, 2990 cm^{-1}; HRMS calcd for $C_8H_{15}O_3$ (M^+–CH_3) *m/z* 159.1021, found 159.1024.

Ethyl (2*E*,5*R*,6*S*)-6,7-(isopropylidene)dioxy-5-methyl-2-heptenoate (22)

To a cooled (0 °C) solution of **21** (5.52 g, 31.7 mmol) in CH_2Cl_2 (110 mL) were added molecular sieves (MS) 4A (11.1 g), NaOAc (1.31 g, 16.0 mmol), and pyridinium chlorochromate (PCC) (10.3 g, 47.8 mmol). The mixture was stirred for 2 h and the mixture was transferred to a short column packed with silica gel. The column was eluted with exccess Et_2O. The ethereal elute was concentrated in vacuo to provide 4.16 g (76%) of aldehyde.

The following reaction was carried out under argon. To a cooled (0 °C), stirred suspension of NaH (60% in oil, 1.53 g, 38 mmol) in THF (50 mL) was added $(EtO)_2P(O)CH_2CO_2Et$ (16 mL, 81 mmol). The mixture was stirred for 1 h, and a solution of the aldehyde (4.16 g) obtained above in THF (10 mL) was added at 0 °C. The mixture was stirred for 1 h and quenched with saturated aqueous NH_4Cl. This was diluted with H_2O (400 mL) and extracted with CH_2Cl_2. The combined organic layers were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:20) to provide 4.67 g (80%) of **22** as a colorless oil (a small amount of the *Z*-isomer was separated from the *E*-isomer **22**); TLC, R_f 0.70 (EtOAc/hexane, 1:2); $[\alpha]^{23}_D$ +5.0 (*c* 1.58, $CHCl_3$); ^{1}H NMR (270 MHz) δ 0.98 (d, *J* = 6.6 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.35, 1.41 (2s, 3H × 2), 1.81 (m, 1H), 2.03 (m, 1H), 2.31 (m, 1H), 3.63 (m, 1H), 3.92–4.04 (m, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 5.85 (dt, *J* = 15.4, 1.5 Hz, 1H), 6.92 (ddd, *J* = 7.0, 8.1, 15.4 Hz, 1H); ^{13}C NMR (68 MHz) δ 14.22, 15.23, 25.28, 26.40, 35.56, 35.68, 60.21, 67.09, 79.13, 108.79, 122.96, 146.89, 166.36; IR (neat) 2990, 1715, 1650 cm^{-1}; HRMS calcd for $C_{13}H_{22}O_4$ (M^+) *m/z* 242.1518, found 242.1518.

(2*E*,5*R*,6*S*)-6,7-(Isopropylidene)dioxy-5-methyl-2-hepten-1-ol (23)

The following reaction was carried out under argon. To a cooled (–78 °C), stirred solution of **22** (1.08 g, 4.47 mmol) in CH_2Cl_2 (20 mL) was added DIBALH (11 mL of 1.0 M in toluene, 11 mmol). The mixture was stirred at –78 °C for 20 min and quenched with H_2O. This was diluted with CH_2Cl_2 (10 mL), and then an aqueous solution (30 mL) of potassium sodium (+)-tartrate tetrahydrate (7.90 g) was added. The mixture was stirred vigorously for 3.5 h and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried and concentrated in vacuo to give crude **23**, which was used in the next step without purification. In a small-scale experiment, pure **23** was obtained by column chromatography on silica gel (EtOAc/hexane, 1:4) as a colorless oil; TLC, R_f 0.29 (EtOAc/hexane, 1:2); $[\alpha]^{23}_D$ +8.2 (*c* 1.72, $CHCl_3$); ^{1}H NMR (270 MHz) δ 0.97 (d, *J* = 7.0 Hz, 3H), 1.35, 1.40 (2s, 3 H $\times$ 2), 1.69 (m, 1H), 1.80–1.93 (m, 2H), 2.15 (m, 1H), 3.62 (t, *J* = 7.3 Hz, 1H), 3.92 (dt, *J* = 7.3, 6.2 Hz, 1H), 4.00 (dd, *J* = 6.2, 7.3 Hz, 1H), 4.10 (m, 2H), 5.62–5.69 (m, 2H); ^{13}C NMR (68 MHz) δ 15.38, 25.43, 26.49, 35.62, 36.34, 63.44, 67.44, 79.59, 108.56, 130.36, 130.91; IR (neat) 3400, 2990 cm^{-1}; HRMS calcd for $C_{11}H_{20}O_3$ (M^+) *m/z* 200.1412, found 200.1401.

(2*S*,3*R*,5*E*)-3-Methyl-5-heptene-1,2,7-triol (24)

To a cooled (0 °C), stirred solution of the crude **23** obtained above in MeOH–H_2O (1:1, 20 mL) was added Amberlyst 15 (182 mg). The mixture was stirred at 40 °C for 21 h and then the resin was filtered off. The filtrate was concentrated in vacuo to give crude **24**, which was used in the next step without purification. In a small-scale experiment, pure **24** was obtained by column chromatography on silica gel (acetone/toluene, 1:3) as a colorless oil; TLC, R_f 0.22 (acetone/toluene, 1:1); $[\alpha]^{22}_D$ +0.80 (*c* 1.32, MeOH); ^{1}H NMR (270 MHz) δ 0.94 (d, *J* = 6.6 Hz, 3H), 1.68 (m, 1H), 1.78 (br s, 3H), 1.97 (m, 1H), 2.23 (m, 1H), 3.53–3.70 (m, 3H), 4.10–4.12 (m, 2H), 5.66–5.72 (m, 2H); ^{13}C NMR (68 MHz) δ 14.37, 35.56, 36.08, 63.58, 65.05, 74.81, 130.85, 130.94; IR (neat) 3350, 2930 cm^{-1}; HRMS calcd for $C_8H_{14}O_2$ (M^+–H_2O) *m/z* 142.0994,

found 142.0993.

(2*E*,5*R*,6*S*)-6-[(4-Methoxyphenyl)methoxy]-5-methyl-2-heptene-1,7-diol (25)

To a cooled (0 °C), stirred solution of the crude **24** obtained above in DMF (15 mL) were added 4-methoxybenzaldehyde dimethylacetal (0.70 mL, 6.9 mmol) and $TsOH \cdot H_2O$ (43.1 mg, 0.227 mmol). The mixture was stirred at 40 °C for 22 h under reduced pressure with aspirator. This was diluted with saturated aqueous $NaHCO_3$ (40 mL) and extracted with CH_2Cl_2. The combined organic layers were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:3) to provide 1.09 g of the 4-methoxybenzylidene acetal, which was used immediately in the next step.

The following reaction was carried out under argon. To a cooled (–78 °C), stirred solution of the acetal obtained above (1.09 g) in CH_2Cl_2 (25 mL) was added DIBALH (12 mL of 1.0 M in toluene, 12 mmol). The mixture was stirred at –78 °C for 20 min and quenched with H_2O. This was diluted with CH_2Cl_2 (25 mL), and then an aqueous solution (50 mL) of potassium sodium (+)-tartrate tetrahydrate (8.32 g) was added. The mixture was stirred vigorously for 3 h and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (acetone/hexane, 1:4) to provide 0.990 g (80%, 4 steps from **22**) of **25** as a colorless oil; TLC, R_f 0.50 (acetone/toluene, 1:1); $[\alpha]^{22}_D$ +3.1 (*c* 1.50, $CHCl_3$); ^{1}H NMR (270 MHz) δ 0.94 (d, *J* = 6.2 Hz, 3H), 1.80–1.91 (m, 4H), 2.28 (m, 1H), 3.39 (m, 1H), 3.60 (dd, *J* = 6.2, 11.4 Hz, 1H), 3.67 (dd, *J* = 4.2, 11.4 Hz, 1H), 3.81 (s, 3H), 4.07 (m, 2H), 4.49, 4.56 (2d, *J* = 11.2 Hz, 1H $\times$ 2), 5.55–5.70 (m, 2H), 6.89 (m, 2H), 7.27 (m, 2H); ^{13}C NMR (68 MHz) δ 15.26, 34.32, 35.33, 55.26, 62.03, 63.55, 72.13, 82.82, 113.86 $\times$ 2, 129.35 $\times$ 2, 130.56, 130.65, 131.20, 159.24; IR (neat) 3350, 2940, 1615, 1515 cm^{-1}; HRMS calcd for $C_{16}H_{24}O_4$ (M^+) *m/z* 280.1675, found 280.1677.

(2*S*,3*R*,5*E*)-7-(*t*-Butyldiphenylsilyloxy)-2-[(4-methoxyphenyl)methoxy]-3-methyl-

5-hepten-1-ol (26)

The following reaction was carried out under argon. To a cooled (–78 °C), stirred solution of **25** (1.31 g, 4.69 mmol) in CH_2Cl_2 (40 mL) were added Et_3N (1.1 mL, 8.0 mL), TBDPSCl (1.0 mL, 4.0 mmol), and a solution of DMAP (57.3 mg, 0.469 mmol) in CH_2Cl_2 (1 mL). The mixture was stirred while gradually wamred to –20 °C over 2 h and then quenched with saturated aqueous $NaHCO_3$. This was diluted with saturated aqueous $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2. The combined organic layers were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:7) to provide 1.77 g (73%) of **26** as a colorless oil along with 0.18 g of recovered **25** (13%); TLC, R_f 0.43 (EtOAc/hexane, 1:2); $[\alpha]^{21}_D$ +0.8 (*c* 1.89, $CHCl_3$); ^{1}H NMR (270 MHz) δ 0.94 (d, *J* = 6.6 Hz, 3H), 1.06 (s, 9H), 1.63 (br s, 1H), 1.85 (m, 2H), 2.27 (m, 1H), 3.39 (ddd, *J* = 4.0, 4.5, 6.3 Hz, 1H), 3.59 (dd, *J* = 6.3, 11.5 Hz, 1H), 3.67 (dd, *J* = 4.0, 11.5 Hz, 1H), 3.80 (s, 3H), 4.16 (d, *J* = 4.0 Hz, 2H), 4.47, 4.56 (2d, *J* = 11.0 Hz, 1H $\times$ 2), 5.49–5.65 (m, 2H), 6.88 (m, 2H), 7.33 (m, 2H), 7.42–7.44 (m, 6H), 7.65–7.71 (m, 4H); ^{13}C NMR (68 MHz) δ 15.02, 19.21, 26.81 $\times$ 3, 34.47, 35.33, 55.23, 62.17, 64.45, 72.22, 82.96, 113.86 $\times$ 2, 127.60 $\times$ 4, 129.18 $\times$ 2, 129.35 $\times$ 2, 129.55, 130.56, 130.62, 133.82 $\times$ 2, 135.52 $\times$ 4, 159.21; IR (neat) 3400, 2930, 1615, 1515 cm^{-1}; HRMS calcd for $C_{28}H_{33}O_4Si$ (M^+–*t*-Bu) *m/z* 461.2148, found 461.2139.

Compound 18 from 26.

To a cooled (0°C), stirred solution of **26** (623 mg, 1.20 mmol) in CH_2Cl_2 (12 mL) was added Dess–Martin periodinane (1.01 g, 2.38 mmol). The mixture was stirred vigorously for 40 min and diluted with 10% aqueous $Na_2S_2O_3$ (30 mL) at 0 °C. The mixture was stirred for 30 min, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried and concentrated in vacuo to give crude aldehyde, which was used in the next step without further purification.

To a cooled (0°C), stirred solution of CBr_4 (1.40 g, 4.22 mmol) in CH_2Cl_2 (10 mL) was added a solution of PPh_3 (2.21 g, 8.43 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at 0 °C for 10 min and a solution of the crude aldehyde obtained above in CH_2Cl_2 (3 mL) was added at –78 °C. The mixture was stirred at –78 °C for 1 h and quenched with saturated aqueous $NaHCO_3$. This was diluted with saturated aqueous $NaHCO_3$ (40 mL) and extracted with CH_2Cl_2. The combined organic layers were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (Et_3N/hexane, 1:100) to provide 621 mg (77%) of **18**.

(*E*)-4-Iodo-3-buten-1-ol (29*E*)[4]

A solution of Bu_3SnH (4.3 mL, 16 mmol), 2,2'-azobisisobutyronitrile (183 mg, 1.11 mmol), and 3-butyn-1-ol (0.74 g, 10.6 mmol) in benzene (5 mL) was stirred at 80 °C for 47 h. After being cooled to ambient temperature, the solution was diluted with CH_2Cl_2 (100 mL). To this solution was added I_2 (4.06 g, 16.0 mmol) at 0 °C. The mixture was stirred at 0 °C for 30 min and then washed with 20% aqueous $Na_2S_2O_3$ (50 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were concentrated in vacuo. The residue was dissolved in Et_2O (100 mL) and 10% aqueous KF (50 mL) was added. After being vigorously stirred for 3 h, insoluble precipitates formed were filtered off and washed with Et_2O. From the combined filtrate and washings, the organic layer was separated. The aqueous layer was extracted with Et_2O. The combined organic layers were dried and concentrated in vacuo. The residue was dissolved in MeOH (20 mL) and MeONa (16 mL of 1.0 M in MeOH, 16 mmol) was added. The mixture was heated under reflux for 23 h, and the solvent was removed by evaporation. The residue was diluted with saturated aqueous NH_4Cl (100 mL) and extracted with CH_2Cl_2. The combined organic layers were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:5) to provide 1.56 g (74%) of **29*E*** as a colorless oil; TLC, R_f 0.53 (EtOAc/hexane, 1:2); ^{1}H NMR (300 MHz) δ 1.53

(br s, 1H), 2.33 (ddt, *J* = 1.4, 7.3, 6.2 Hz, 2H), 3.69 (t, *J* = 6.2 Hz, 2H), 6.17 (dt, *J* = 14.5 Hz, 1.4 Hz, 1H), 6.55 (dt, *J* = 14.5, 7.3 Hz, 1H); ^{13}C NMR (68 MHz) δ 39.05, 60.85, 77.23, 142.60; IR (neat) 3400, 2950, 1610 cm^{-1}; HRMS calcd for C_4H_7IO (M^+) *m/z* 197.9542, found 197.9544.

(*E*)-1-Iodo-4-(triphenylmethoxy)-1-butene (7)

To a cooled (0 °C), stirred solution of **29*E*** (323 mg, 1.63 mmol) in pyridine (15 mL) were added chlorotriphenylmethane (546 mg, 1.96 mmol) and DMAP (38.1 mg, 0.312 mmol). The mixture was stirred for 25 h and then chlorotriphenylmethane (95.3 mg, 0.342 mmol) and DMAP (41.6 mg, 0.342 mmol) were added. The mixture was stirred for 12 h at 60 °C and concentrated in vacuo. The residue was diluted with $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2. The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:100) to provide 718 mg (100%) of **7** as a colorless oil; TLC, R_f 0.48 (toluene/hexane, 1:2); ^{1}H NMR (300 MHz) δ 2.32 (dt, *J* = 7.1, 6.6 Hz, 2H), 3.11 (t, *J* = 6.6 Hz, 2H), 6.05 (d, *J* = 14.4 Hz, 1H), 6.55 (dt, *J* = 14.4, 7.1 Hz, 1H), 7.19–7.32 (m, 9H), 7.41–7.45 (m, 6H); ^{13}C NMR (75 MHz) δ 36.57, 62.13, 76.49, 86.54, 126.94 × 3, 127.76 × 6, 128.57 × 6, 143.31, 144.00 × 3; IR (neat) 3060, 2920, 1600 cm^{-1}; HRMS calcd for $C_{23}H_{21}IO$ (M^+) *m/z* 440.0637, found 440.0637.

(2*E*,5*R*,6*S*,9*E*)-1-(*t*-Butyldiphenylsilyloxy)-6-[(4-methoxyphenyl)methoxy]-5-methyl-12-(triphenylmethoxy)-2,9-dodecadien-7-yne (30)

The following reaction was carried out under argon. To a stirred solution of **6** (85.0 mg, 0.165 mmol) and **7** (87.2 mg, 0.198 mmol) in Et_3N (2 mL) were added $Pd(PPh_3)_4$ (9.6 mg, 8.3 μmol) and CuI (3.6 mg, 19 μmol). The mixture was stirred for 2.5 h and then diluted with saturated aqueous $NaHCO_3$ (10 mL). This was extracted with CH_2Cl_2. The combined organic layers were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:100) to provide 124 mg (91%) of **30** as a colorless oil; TLC, R_f 0.27 (EtOAc/hexane, 1:20);

$[\alpha]^{25}_{D}$ –36.8 (*c* 1.73, $CHCl_3$); ^{1}H NMR (300 MHz) δ 0.98 (d, *J* = 6.6 Hz, 3H), 1.04 (s, 9H), 1.81 (m, 1H), 1.96 (m, 1H), 2.30–2.46 (m, 3H), 3.14 (t, *J* = 6.7 Hz, 2H), 3.76 (s, 3H), 4.02 (dd, *J* = 1.2, 4.6 Hz, 1H), 4.12 (d, *J* = 4.1 Hz, 2H), 4.39, 4.71 (2d, *J* = 11.5 Hz, 1H × 2), 5.47–5.65 (m, 3H), 6.18 (dt, *J* = 15.8, 7.1 Hz, 1H), 6.83 (m, 2H), 7.22–7.46 (m, 23H), 7.65–7.69 (m, 4H); ^{13}C NMR (75 MHz) δ 15.26, 19.20, 26.81 × 3, 33.80, 35.22, 38.49, 55.20, 62.74, 64.47, 70.17, 72.41, 85.16, 86.39, 86.56, 110.99, 113.63 × 2, 126.94 × 3, 127.58 × 4, 127.76 × 6, 128.62 × 6, 129.03, 129.56 × 4, 130.25, 130.56, 133.85 × 2, 135.51 × 4, 141.32, 144.13 × 3, 159.07; IR (neat) 3040, 2935, 1615, 1515 cm^{-1}; HRMS calcd for $C_{56}H_{60}O_4Si$ (M^+) *m/z* 824.4261, found 824.4244.

(2*E*,5*R*,6*S*,7*Z*,9*E*)-1-(*t*-Butyldiphenylsilyloxy)-6-[(4-methoxyphenyl)methoxy]-5-methyl-12-(triphenylmethoxy)-2,7,9-dodecatriene (31)

A solution of **30** (58.9 mg, 0.0714 mmol) in 1-hexene (1 mL) was stirred under atmospheric hydrogen for 2 h in the presence of Lindlar catalyst (5.9 mg) and quinoline (3 μL, 0.03 mmol). The catalyst was removed by filtration through a Celite pad, washed with EtOAc and the combined filtrate and washings were concentrated in vacuo. The residue was purified by column chromatography on silica gel (toluene/hexane, 1:1) to provide 38.8 mg (66%) of **31** as a colorless oil. 18.3 mg (31%) of **30** was recovered; TLC, R_f 0.28 (EtOAc/hexane, 1:20); $[\alpha]^{25}_{D}$ –4.0 (*c* 1.66, $CHCl_3$); ^{1}H NMR (270 MHz) δ 0.93 (d, *J* = 6.2 Hz, 3H), 1.04 (s, 9H), 1.66–1.79 (m, 2H), 2.24 (m, 1H), 2.37 (q, *J* = 6.6 Hz, 2H), 3.11 (t, *J* = 6.6 Hz, 2H), 3.77 (s, 3H), 3.99 (dd, *J* = 6.2, 9.5 Hz, 1H), 4.12 (d, *J* = 4.8 Hz, 2H), 4.20, 4.49 (2d, *J* = 11.7 Hz, 1H × 2), 5.27 (t, *J* = 9.5 Hz, 1H), 5.44–5.65 (m, 2H), 5.75 (m, 1H), 6.18–6.27 (m, 2H), 6.82 (m, 2H), 7.19–7.45 (m, 23H) 7.65–7.69 (m, 4H); ^{13}C NMR (75 MHz) δ 15.23, 19.20, 26.81 × 3, 33.57, 35.45, 38.46, 55.20, 63.17, 64.51, 69.56, 77.43, 86.43, 113.57 × 2, 126.89 × 3, 127.20, 127.58 × 4, 127.71 × 6, 128.64 × 6, 129.13, 129.31 × 2, 129.41, 129.52 × 2, 130.28, 131.02, 132.39, 133.31, 133.85 × 2, 135.50 × 4, 144.21 × 3, 158.92; IR (neat) 3020, 2930, 1615, 1515 cm^{-1}; HRMS calcd for $C_{56}H_{62}O_4Si$ (M^+) *m/z* 826.4417, found

826.4416.

(2*E*,5*R*,6*S*,7*Z*,9*E*)-6-[(4-Methoxyphenyl)methoxy]-5-methyl-12-(triphenylmethoxy)-2,7,9-dodecatrien-1-ol (32)

To a cooled (0 °C) solution of **31** (57.5 mg, 0.0695 mmol) in THF (1 mL) was added tetrabutylammonium fluoride (0.077 mL of 1.0 M solution in THF, 0.077 mmol). The mixture was stirred for 2.5 h. This was diluted with H_2O (10 mL) and extracted with CH_2Cl_2. The combined organic layers were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:5) to provide 40.9 mg (100%) of **32** as a colorless oil; TLC, R_f 0.37(EtOAc/hexane, 2:1); $[\alpha]^{24}_D$ –2.4 (*c* 1.67, $CHCl_3$); ^{1}H NMR (270 MHz) δ 0.93 (d, *J* = 6.6 Hz, 3H), 1.48 (br s, 1H), 1.64–1.86 (m, 2H), 2.24 (m, 1H), 2.41 (q, *J* = 6.5 Hz, 2H), 3.13 (t, *J* = 6.5 Hz, 2H), 3.78 (s, 3H), 3.96–4.02 (m, 3H), 4.19, 4.49 (2d, *J* = 11.7 Hz, 1H × 2), 5.26 (t, *J* = 9.5 Hz, 1H), 5.50–5.64 (m, 2H), 5.76 (m, 1H), 6.18–6.32 (m, 2H), 6.83 (m, 2H), 7.19–7.31 (m, 11H), 7.42–7.46 (m, 6H); ^{13}C NMR (68 MHz) δ 15.26, 33.60, 35.42, 38.30, 55.23, 63.15, 63.73, 69.54, 77.20, 86.45, 113.57 × 2, 126.91 × 3, 127.19, 127.74 × 6, 128.63 × 6, 128.95, 129.38 × 2, 130.48, 130.94, 131.45, 132.46, 133.41, 144.21 × 3, 158.96; IR (neat) 3400, 3030, 2930, 1615, 1515 cm^{-1}; HRMS calcd for $C_{40}H_{44}O_4$ (M^+) *m/z* 588.3240, found 588.3243.

(2*E*,5*R*,6*S*,7*Z*,9*E*)-6-[(4-Methoxyphenyl)methoxy]-5-methyl-12-(triphenylmethoxy)-2,7,9-dodecatrien-1-al (5)

To a cooled (0 °C), stirred solution of **32** (38.1 mg, 0.0647 mmol) in CH_2Cl_2 (1 mL) was added MnO_2 (411 mg, 4.73 mmol). The mixture was stirred for 30 min, and the insoluble materials were filtered off and washed well with EtOH. The combined filtrate and washings were concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:15) to provide 31.4 mg (83%) of **5** as a colorless oil; TLC, R_f 0.30 (EtOAc/hexane, 1:5); $[\alpha]^{24}_D$ –7.9 (*c* 1.52, $CHCl_3$); ^{1}H NMR (300 MHz) δ 0.95 (d, *J* = 6.8 Hz, 3H), 1.88 (m, 1H), 2.07 (m, 1H), 2.41 (q, *J* = 6.6 Hz,

2H), 2.52 (m, 1H), 3.14 (t, *J* = 6.6 Hz, 2H), 3.79 (s, 3H), 4.04 (dd, *J* = 5.9, 9.5 Hz, 1H), 4.19, 4.50 (2d, *J* = 11.6 Hz, 1H × 2), 5.26 (t, *J* = 9.5 Hz, 1H), 5.80 (m, 1H), 6.03 (dd, *J* = 7.9 15.5 Hz, 1H), 6.20–6.32 (m, 2H), 6.73 (m, 1H), 6.83 (m, 2H), 7.18–7.31 (m, 11H), 7.42–7.45 (m, 6H), 9.43 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (75 MHz) δ 15.45, 33.57, 36.04, 37.88, 55.24, 63.03, 69.60, 76.85, 86.46, 113.63 × 2, 126.81, 126.91 × 3, 127.71 × 6, 127.91, 128.62 × 6, 129.43 × 2, 130.58, 133.18, 134.06, 134.18, 144.18 × 3, 157.87, 159.05, 193.99; IR (neat) 3030, 2930, 1690, 1615, 1515 cm^{-1}; HRMS calcd for $C_{40}H_{42}O_4$ (M^+) *m/z* 586.3083, found 586.3066.

(1*S*,2*S*,3*S*,6*S*,7*S*,8*R*)-2-Formyl-7-[(4-methoxyphenyl)methoxy]-8-methyl-3-[2-(triphenylmethoxy)ethyl]bicyclo[4.3.0]non-4-ene (4)

Compound **5** (29.5 mg, 0.0503 mmol) was dissolved in degassed toluene (5 mL), and a crystal of BHT was added. The solution was transferred into a 20 mL sealed tube equipped with a screwed stopper, and the tube was filled with argon. The tube was heated to 150 °C for 5 h. After being cooled to ambient temperature, the solution was concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:15) to provide 22.1 mg (75%) of **4**; TLC, R_f 0.36 (EtOAc/hexane, 1:5); $[\alpha]^{24}_D$ +45.3 (*c* 0.945, $CHCl_3$); ^{1}H NMR (270 MHz) δ 1.05 (d, *J* = 5.8 Hz, 3H), 1.07 (m, 1H), 1.72 (m, 2H), 1.96 (m, 2H), 2.35 (m, 1H), 2.57 (m, 2H), 2.66 (m, 1H), 3.12–3.18 (m, 3H), 3.80 (s, 3H), 4.46, 4.54 (2d, *J* = 11.2 Hz, 1H × 2), 5.56 (m, 1H), 5.73 (m, 1H), 6.87 (m, 2H), 7.23–7.32 (m, 11H), 7.41–7.44 (m, 6H), 9.68 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (68 MHz) δ 18.28, 29.72, 32.42, 33.81, 36.71, 39.62, 43.42, 53.62, 55.23, 61.13, 72.02, 86.50, 92.06, 113.75 × 2, 126.93 × 3, 127.74 × 6, 128.58 × 6, 128.66, 129.21 × 2, 130.36, 130.65, 144.13 × 3, 159.15, 204.92; IR (neat) 3020, 2930, 1720, 1615, 1515 cm^{-1}; HRMS calcd for $C_{40}H_{42}O_4$ (M^+) *m/z* 586.3083, found 586.3083.

(1*R*,2*S*,3*S*,6*S*,7*S*,8*R*)-2-Hydroxymethyl-7-[(4-methoxyphenyl)methoxy]-8-methyl-3-[2-(triphenylmethoxy)ethyl]bicyclo[4.3.0]non-4-ene (33)

To a cooled (0 °C), stirred solution of **4** (17.8 mg, 0.0303 mmol) in EtOH (1 mL) was

added $NaBH_4$ (1.1 mg, 0.029 mmol). The mixture was stirred for 2 h and then quenched with saturated aqueous NH_4Cl. This was diluted with H_2O (10 mL) and extracted with CH_2Cl_2. The combined organic layers were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:5) to provide 17.7 mg (99%) of **33** as a colorless oil; TLC, R_f 0.33 (EtOAc/hexane, 1:3); $[\alpha]^{24}_D$ +64.5 (*c* 0.830, $CHCl_3$); ^{1}H NMR (300 MHz) δ 1.04 (d, *J* = 6.6 Hz, 3H), 1.09 (m, 1H), 1.53 (m, 1H), 1.62 (m, 2H), 1.73 (m, 1H), 1.84 (m, 1H), 1.93 (m, 1H), 2.28 (m, 1H), 2.43 (m, 1H), 2.47 (m, 1H), 3.12 (dd, *J* = 6.1, 7.3 Hz, 1H), 3.18 (m, 2H), 3.54 (m, 2H), 3.79 (s, 3H), 4.47, 4.55 (2d, *J* = 11.2 Hz, 1H $\times$ 2), 5.48 (m, 1H), 5.66 (m, 1H), 6.87 (m, 2H), 7.20–7.32 (m, 11H), 7.43–7.46 (m, 6H); ^{13}C NMR (75 MHz) δ 18.37, 30.20, 31.52, 34.81, 36.85, 39.72, 42.65, 43.52, 55.24, 61.92, 62.82, 72.05, 86.56, 92.12, 113.73 $\times$ 2, 126.88 $\times$ 3, 127.73 $\times$ 6, 128.64 $\times$ 6, 129.23 $\times$ 2, 129.44, 129.74, 130.86, 144.26 $\times$ 3, 159.07; IR (neat) 3400, 3020, 2930, 1615, 1515 cm^{-1}; HRMS calcd for $C_{40}H_{44}O_4$ (M^+) *m/z* 588.3240, found 588.3233.

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