Asymmetric Total Syntheses of (+)-Mycoepoxydiene and Related Natural Product (–)-1893A: Application of One-Pot Ring-Opening/Cross/Ring-Closing Metathesis to Construct their 9-Oxabicyclo[4.2.1]nona-2,4-diene Skeleton

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Supporting Information

Contents

General methods. Melting points are uncorrected. Specific rotations were measured in a 10 mm or 100 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 on Merck Kieselgel 60 F_{254} plates. The crude reaction mixtures and extractive materials were purified by chromatography on Daisogel IR-60 (Daiso) or Wakogel C-300 (Wako). Unless otherwise described, reactions were carried out at ambient temperature. Combined organic extracts were dried over anhydrous Na_2SO_4. Solvents were removed from the reaction mixture or combined organic extracts by concentration under reduced pressure using an evaporator with bath at 35–45 °C.

(1*S*,2*S*,3*R*,4*R*)-2-Acetoxymethyl-3-hydroxymethyl-7-oxabicyclo[2.2.1]hept-5-ene ((+)-10). The following reaction was carried out according Bloch's procedure.[1] To a stirred solution of **9**[2] (3.91 g, 25.0 mmol) in vinyl acetate (78 mL) was added lipase PS (Amano) (0.782 g). The mixture was stirred for 15 h, and the enzyme was removed by filtration and washed with EtOAc. The combined filtrate and washings were concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:2) to provide 4.10 g (83%) of (+)-**10** as white crystals: mp 49-51 °C (lit.[1] mp 44 °C); TLC R_f 0.17 (EtOAc:hexane, 1:1); $[\alpha]_D^{24}$ +8.1 (*c* 2.16, MeOH) [lit.[1] $[\alpha]_D^{20}$ +7.8 (*c* 1.0, MeOH)]; IR (KBr) 3400, 2940, 1740 cm^{-1}; ^{1}H NMR (270 MHz) δ 1.78 (br, 1H, OH), 1.87-2.08 (m, 2H), 2.09 (s, 3H), 3.66 (m, 1H), 3.86 (m, 1H), 4.04 (dd, 1H, *J* = 9.3, 10.9 Hz), 4.31 (dd, 1H, *J* = 5.5, 10.9 Hz), 4.81 (s, 1H),

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[1] Cinquin, C.; Schaper, I.; Mandville, G.; Bloch, R. *Synlett* **1995**, 339-340.

[2] Das, J.; Vu, T.; Harris, D. N.; Ogletree, M. L. *J. Med. Chem.* **1988**, *31*, 930-935.

4.90 (s, 1H), 6.37-6.42 (m, 2H); ^{13}C NMR (68 MHz) □ 21.0, 39.2, 42.0, 61.7, 64.2, 80.4, 80.5, 135.3, 135.7, 171.0; HRMS calcd for $C_{10}H_{14}O_4$ (M^+) *m/z* 198.0892, found 198.0899; HPLC analysis (column, Daicel Chiralcel OD+OD-H, *i*-PrOH:hexane = 1:30, flow rate = 0.5 mL/min); t_R (min) = 30.1 for the 4-*t*-butylbenzoate of (–)-**10**, 36.2 for the 4-*t*-butylbenzoate of (+)-**10**.[3] Compound (+)-**10** was determined to be 96% ee.

(1*R*,2*R*,3*S*,4*S*)-2-(*t*-Butyldiphenylsilyloxy)methyl-3-hydroxymethyl-7-oxabicyclo[2.2.1]hept-5-ene ((+)-7). To a cooled (0°C) stirred solution of (+)-**10** (4.79 g, 24.2 mmol) in DMF (100 mL) were added imidazole (3.95 g, 58.6 mmol) and TBDPSCl (10.1 mL, 39.1 mmol). The mixture was stirred for 23 h, diluted with EtOAc (200 mL), and washed with H_2O (200 mL □ 3). The organic layer was dried and concentrated in vacuo to provide crude silyl ether (11.8 g), which was used directly in the next step. In a small scale experiment, crude silyl ether was purified by column chromatography on silica gel (EtOAc:hexane, 1:6) and obtained as a colorless oil: TLC R_f 0.87 (EtOAc:hexane, 1:1); [□]$_D^{22}$ +6.8 (*c* 1.87, $CHCl_3$); IR 2940, 1740 cm^{-1}; ^{1}H NMR (300 MHz) □ 1.06 (s, 9H), 1.84-1.94 (m, 2H), 1.98 (s, 3H), 3.65 (dd, 1H, *J* = 9.4, 9.5 Hz), 3.78 (dd, 1H, *J* = 5.3, 9.5 Hz), 3.89 (dd, 1H, *J* = 10.2, 10.5 Hz), 4.23 (dd, 1H, *J* = 4.7, 10.5 Hz), 4.77 (br s, 1H), 4.95 (br s, 1H), 6.34 (dd, 1H, *J* = 1.3, 5.8 Hz), 6.39 (dd, 1H, *J* = 1.3, 5.8 Hz), 7.36-7.46 (m, 6H), 7.65-7.69 (m, 4H); ^{13}C NMR (68 MHz) □ 19.2, 20.9, 26.8 □ 3, 39.0, 42.5, 62.9, 64.0, 80.3, 80.4, 127.7 □ 4, 129.7 □ 2, 133.4, 133.5, 135.1, 135.5 □ 4, 135.9, 170.8; HRMS calcd for $C_{22}H_{23}O_4Si$ (M^+–*t*-C_4H_9) *m/z* 379.1366, found 379.1362.

To a stirred solution of crude silyl ether obtained above (11.8 g) in MeOH (100 mL) was added NaOMe (1.0 M solution in MeOH, 4.84 mL, 4.84 mmol). The mixture was stirred for 2 h, diluted with saturated brine (200 mL), and extracted with EtOAc (400 mL □ 3). The combined extracts were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:3) to provide 8.80 g (92%) of (+)-**7** as white crystals: mp 65-67 °C; TLC R_f 0.38 (EtOAc:hexane, 1:1); [□]$_D^{21}$ +17.7 (*c* 4.23, $CHCl_3$); IR 3440, 2940 cm^{-1}; ^{1}H NMR (270 MHz) □ 1.05 (s, 9H), 1.91-2.00 (m, 2H), 2.90 (br, 1H, OH), 3.67 (dd, 1H, *J* = 5.9, 11.0 Hz), 3.76 (dd, 1H, *J* = 6.4, 10.4 Hz), 3.84-3.91 (m, 2H), 4.65 (br s, 1H), 4.74 (br s, 1H), 6.35 (dd, 1H, *J* = 1.7, 5.9 Hz), 6.37 (dd, 1H, *J* = 1.5, 5.9 Hz), 7.25-7.47 (m, 6H), 7.65-7.69 (m, 4H); ^{13}C NMR (68 MHz) □ 19.1, 26.8 □ 3, 42.5, 42.7, 62.6, 64.4, 80.8, 81.2, 127.8 □ 4, 129.9 □ 2, 132.9 □ 2, 135.5 □ 4, 135.6, 135.8; HRMS calcd for $C_{20}H_{21}O_3Si$ (M^+–*t*-C_4H_9) *m/z* 337.1260, found 337.1258.

(1*S*,2*S*,3*R*,4*R*)-2-Acetoxymethyl-3-[(1*RS*)-1-ethoxyethoxy]methyl-7-oxabicyclo[2.2.1]hept-5-ene ((+)-11). To a stirred solution of (+)-**10** (2.04 g, 10.3 mmol) in CH_2Cl_2 (40 mL) were added ethyl vinyl ether (1.5 mL, 16 mmol) and PPTS (265 mg, 1.06 mmol). The mixture was stirred for 1 h, diluted with saturated aqueous $NaHCO_3$ (200 mL), and extracted with CH_2Cl_2 (100 mL □ 4). The combined extracts were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:5 to 1:2) to provide 2.71 g (97%) of (+)-**11** (d.r. = *ca.* 1:1) as a pale yellow oil: TLC R_f 0.80 (EtOAc:hexane, 1:1); [□]$_D^{27}$ +7.3 (*c* 3.69, $CHCl_3$); IR 2940, 1740 cm^{-1}; ^{1}H NMR (270 MHz)

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[3] The 4-*t*-butylbenzoate sample was prepared by treatment of (+)-**10** or (–)-**10** with *t*-BuBzCl in pyridine.

□ 1.21 (t, 3H, *J* = 7.2 Hz), 1.32 (d, 3H □ 1/2, *J* = 5.1 Hz), 1.34 (d, 3H □ 1/2, *J* = 5.5 Hz), 1.93-1.98 (m, 2H), 2.09 (s, 3H), 3.35 (m, 1H □ 1/2), 3.50 (q, 2H □ 1/2, *J* = 7.2 Hz), 3.51 (q, 2H □ 1/2, *J* = 7.2 Hz), 3.61-3.75 (m, 1H □ 1/2 + 1H), 3.95 (m, 1H), 4.30 (m, 1H), 4.70 (q, 1H □ 1/2, *J* = 5.1 Hz), 4.71 (q, 1H □ 1/2, *J* = 5.5 Hz), 4.81 (br s, 1H), 4.85 (br s, 1H □ 1/2), 4.87 (br s, 1H □ 1/2), 6.36 (dd, 1H, *J* = 1.5, 5.9 Hz), 6.40 (dd, 1H, *J* = 1.8, 5.9 Hz); ^{13}C NMR (68 MHz) □ 15.3, 19.78 □ 1/2, 19.84 □ 1/2, 21.0, 38.9, 40.1, 61.2, 64.0 □ 1/2, 64.2 □ 1/2, 64.5, 80.4, 80.7, 99.8 □ 1/2, 100.0 □ 1/2, 135.1, 135.9, 170.9; HRMS calcd for $C_{13}H_{19}O_5$ (M^+–CH_3) *m/z* 255.1233, found 255.1239.

(1*R*,2*R*,3*S*,4*S*)-2-[(1*RS*)-(1-Ethoxyethoxy)]methyl-3-hydroxymethyl-7-oxabicyclo[2.2.1]hept-5-ene ((+)-12). To a stirred solution of (+)-**11** (2.71 g, 10.0 mmol) in MeOH (50 mL) was added NaOMe (1.0 M solution in MeOH, 2.0 mL, 2.0 mmol). The mixture was stirred for 2 h, diluted with saturated brine (250 mL), and extracted with EtOAc (100 mL □ 4). The combined extracts were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:3) to provide 2.30 g (quant.) of (+)-**12** (d.r. = *ca*. 1:1) as a colorless oil: TLC R_f 0.29 (EtOAc:hexane, 1:1); [□]$_D^{22}$ +9.8 (*c* 0.710, $CHCl_3$); IR 3440, 2940 cm^{-1}; ^{1}H NMR (270 MHz) □ 1.22 (t, 3H, *J* = 7.0 Hz), 1.34 (d, 3H □ 1/2, *J* = 5.1 Hz), 1.35 (d, 3H □ 1/2, *J* = 5.1 Hz), 1.89-2.04 (m, 2H), 2.83 (br, 1H □ 1/2, OH), 2.95 (br, 1H □ 1/2, OH), 3.45-3.88 (m, 6H), 4.69-4.77 (m, 3H), 6.37-6.43 (m, 2H); ^{13}C NMR (68 MHz) □ 15.3, 19.7, 40.1 □ 1/2, 40.3 □ 1/2, 42.7 □ 1/2, 42.8 □ 1/2, 61.1 □ 1/2, 61.4 □ 1/2, 62.5, 65.1 □ 1/2, 65.5 □ 1/2, 81.1 □ 1/2, 81.2 □ 1/2, 81.3, 99.9 □ 1/2, 100.0 □ 1/2, 135.5, 135.9; HRMS calcd for $C_{10}H_{15}O_3$ (M^+–OC_2H_5) *m/z* 183.1021, found 183.1016.

(1*S*,2*S*,3*R*,4*R*)-2-(*t*-Butyldiphenylsilyloxy)methyl-3-[(1*RS*)-1-ethoxyethoxy]methyl-7-oxabicyclo[2.2.1]hept-5-ene ((–)-13). To a cooled (0°C) stirred solution of (+)-**12** (2.30 g, 10.0 mmol) in DMF (40 mL) were added imidazole (1.50 g, 22.0 mmol) and TBDPSCl (2.9 mL, 11 mmol). The mixture was sitrred for 1 h, diluted with EtOAc (200 mL), and washed with H_2O (100 mL □ 3). The organic layer was dried and concentrated in vacuo to provide 6.12 g of crude (–)-**13** (d.r. = *ca*. 1:1), which was used directly in the next step. For the one-pot ROM/CM/RCM reaction, crude (–)-**13** was purified by column chromatography on silica gel (EtOAc:hexane, 1:5) and obtained in quantitative yield as a colorless oil: TLC R_f 0.81 (EtOAc:hexane, 1:1); [□]$_D^{22}$ –10.2 (*c* 1.97, $CHCl_3$); IR 2940 cm^{-1}; ^{1}H NMR (270 MHz) □ 1.06 (s, 9H), 1.12 (t, 3H □ 1/2, *J* = 7.1 Hz), 1.15 (t, 3H □ 1/2, *J* = 7.1 Hz), 1.20 (d, 3H □ 1/2, *J* = 5.4 Hz), 1.24 (d, 3H □ 1/2, *J* = 5.3 Hz), 1.83-1.97 (m, 2H), 3.21-3.81 (m, 6H), 4.57 (q, 1H □ 1/2, *J* = 5.4 Hz), 4.60 (q, 1H □ 1/2, *J* = 5.3 Hz), 4.82 (br s, 1H), 4.93 (br s, 1H □ 1/2), 4.94 (br s, 1H □ 1/2), 6.36 (br s, 2H), 7.38-7.43 (m, 6H), 7.64-7.68 (m, 4H); ^{13}C NMR (68 MHz) □ 15.2, 19.2, 19.8, 26.8 □ 3, 40.0, 42.4, 60.9 □ 1/2, 61.0 □ 1/2, 63.3, 64.5 □ 1/2, 64.8 □ 1/2, 80.3, 80.7, 99.7 □ 1/2, 100.0 □ 1/2, 127.7 □ 4, 129.7 □ 2, 133.6, 133.7, 135.5 □ 6; HRMS calcd for $C_{24}H_{29}O_4Si$ (M^+– *t*-C_4H_9) *m/z* 409.1835, found 409.1830.

(1*S*,2*S*,3*R*,4*R*)-2-(*t*-Butyldiphenylsilyloxy)methyl-3-hydroxymethyl-7-oxabicyclo[2.2.1]hept-5-ene ((–)-7). A solution of crude (–)-**13** obtained above (6.12 g) in THF (40 mL) and 60% aqueous AcOH (120 mL) was stirred for 5 h and concentrated in vacuo with aid of EtOH. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:2) to provide 3.82 g (97% from (+)-**12**) of (–)-**7** as white crystals: mp 65-67 °C; [□]$_D^{22}$ –14.0 (*c* 1.46, $CHCl_3$).

***exo-cis*-2,3-Bis(acetoxymethyl)-7-oxabicyclo[2.2.1]hept-5-ene (14).** To a cooled (0 °C) stirred solution of **8**[4] (3.01 g, 18.1 mmol) in THF (60 mL) was added $LiAlH_4$ (1.36 g, 36.8 mmol) in four portions over a period of 2 h. The mixture was stirred for 20 h and quenched with H_2O (1.4 mL), 10 wt% aqueous NaOH (1.4 mL), and H_2O (4.2 mL), successively. The precipitated solids were removed by filtration through a Celite-pad and washed well with EtOAc. The combined filtrate and washings were concentrated in vacuo to provide crude **9** (2.56 g), which was used directly in the next step.

A solution of crude **9** (2.56 g) in Ac_2O (20 mL) and pyridine (20 mL) was stirred for 17 h and concentrated in vacuo with aid of toluene. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:3) to provide 2.92 g (67%) of **14** as white crystals: mp 101-102 °C; TLC R_f 0.57 (EtOAc:hexane, 1:1); IR (KBr) 2940, 1740 cm^{-1}; ^1H NMR (270 MHz) δ 1.97-2.09 (m, 2H), 2.09 (s, 6H), 4.02 (dd, 2H, J = 9.5, 10.9 Hz), 4.29 (dd, 2H, J = 5.3, 10.9 Hz), 4.82 (s, 2H), 6.40 (s, 2H); ^{13}C NMR (68 MHz) δ 21.0 × 2, 39.2 × 2, 63.8 × 2, 80.5 × 2, 135.6 × 2, 170.8 × 2; HRMS calcd for $C_{12}H_{17}O_5$ (M^++H) m/z 241.1076, found 241.1076.

(1*R*,2*R*,3*S*,4*S*)-2-Acetoxymethyl-3-hydroxymethyl-7-oxabicyclo[2.2.1]hept-5-ene ((–)-10). To a stirred solution of **14** (1.48 g, 6.15 mmol) in H_2O (60 mL) and THF (60 mL) was added lipase PS (Amano) (591 mg). The mixture was stirred for 20 days, diluted with saturated brine (300 mL), and extracted with EtOAc (50 mL × 8). The combined extracts were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:2) to provide 1.07 g (88%) of (–)-**10** and 93 mg (6.3%) of **14** was recovered. Compound (–)-**10** was obtained as white crystals: mp 49-51 °C; $[\alpha]_D^{24}$ –7.7 (*c* 1.48, MeOH). As described for the HPLC analysis of (+)-**10**, compound (–)-**10** was determined to be 95% ee.

Preparation of (–)-7 from (–)-10. As described for the preparation of (+)-**7** from (+)-**10**, compound (–)-**10** (1.02 g, 5.12 mmol) was converted to 1.90 g (94%) of (–)-**7**.

(1*S*,2*S*,3*R*,4*R*)-2-(*t*-Butyldiphenylsilyloxy)methyl-3-(methyldithiocarbonyloxy)methyl-7-oxabicyclo[2.2.1]hept-5-ene ((–)-15). To a cooled (0 °C) stirred solution of (–)-**7** (3.67 g, 9.30 mmol) in THF (75 mL) was added NaH (*ca.* 60% in oil, 0.558 g, 14.0 mmol). After being stirred for 30 min, the mixture was cooled to 0 °C, and CS_2 (1.12 mL, 18.6 mmol) and MeI (1.15 mL, 18.6 mmol) were added successively. The mixture was stirred for 2 h, quenched with H_2O (2 mL), diluted with saturated brine (200 mL), and extracted with CH_2Cl_2 (100 mL × 3). The combined extracts were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:20) to provide 4.33 g (96%) of (–)-**15** as a pale yellow oil: TLC R_f 0.57 (EtOAc:hexane, 1:3); $[\alpha]_D^{23}$ –8.7 (*c* 1.70, $CHCl_3$); IR 2940 cm^{-1}; ^1H NMR (270 MHz) δ 1.06 (s, 9H), 1.99 (dt, 1H, J = 7.1, 8.4 Hz), 2.15 (ddd, 1H, J = 5.1, 8.4, 10.6 Hz), 2.52 (s, 3H), 3.70 (dd, 1H, J = 8.4, 9.9 Hz), 3.78 (dd, 1H, J = 7.1, 9.9 Hz), 4.49 (t, 1H, J = 10.6 Hz), 4.84 (br s, 1H), 4.86 (br s, 1H), 4.94 (dd, 1H, J = 5.1, 10.6 Hz), 6.38 (dd, 1H, J = 1.5, 5.9 Hz), 6.40 (dd, 1H, J = 1.5, 5.9 Hz), 7.35-7.44 (m, 6H), 7.65-7.69 (m, 4H); ^{13}C NMR (68 MHz) δ 19.1 × 2, 26.8 × 3, 38.8, 42.7, 63.3, 73.8, 80.3, 80.5, 127.7 × 4, 129.7 × 2, 133.3 × 2, 135.1, 135.5 × 4, 136.1, 215.8; HRMS calcd for $C_{22}H_{23}O_3S_2Si$ (M^+–*t*-C_4H_9) m/z 427.0858, found 427.0859.

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[4] (a) Woodward, R. B.; Baer, H. *J. Am. Chem. Soc.* **1948**, *70*, 1161-1166. (b) *Chem. Abstr.* **1966**, *65*, 16924e.

(1*R*,2*S*,3*R*,4*S*,5*R*,6*S*)-2-(*t*-Butyldiphenylsilyloxy)methyl-5,6-dihydroxy-3-(methyldithiocarbonyloxy)methyl-7-oxabicyclo[2.2.1]heptane ((–)-16). To a cooled (0 °C) stirred solution of (–)-**15** (3.03 g, 6.25 mmol) in 80% aqueous acetone (60 mL) were added OsO_4 (0.05 M solution in *t*-BuOH, 6.3 mL, 0.31 mmol) and $Me_3NO{\cdot}2H_2O$ (2.34 g, 31.3 mmol). The mixture was stirred for 20 h, quenched with 1 M aqueous $NaHSO_3$ (1 mL), diluted with EtOAc (300 mL), and washed with 1 M aqueous $NaHSO_3$ (150 mL × 2). The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:2) to provide 2.76 g (85%) of (–)-**16** as a colorless oil: TLC R_f 0.06 (EtOAc:hexane, 1:3); $[\alpha]_D^{24}$ –17.0 (*c* 1.87, $CHCl_3$); IR 3360, 2940 cm^{-1}; ^1H NMR (270 MHz) δ 1.04 (s, 9H), 2.04 (m, 1H), 2.28 (m, 1H), 2.50 (s, 3H), 3.13 (br, 2H, OH × 2), 3.62 (d, 2H, *J* = 7.7 Hz), 3.87 (d, 1H, *J* = 6.0 Hz), 3.91 (d, 1H, *J* = 6.0 Hz), 4.21 (d, 1H, *J* = 1.1 Hz), 4.26 (d, 1H, *J* = 1.1 Hz), 4.43 (t, 1H, *J* = 11.0 Hz), 4.83 (dd, 1H, *J* = 5.5, 11.0 Hz), 7.35-7.44 (m, 6H), 7.65-7.69 (m, 4H); ^{13}C NMR (68 MHz) δ 19.1 × 2, 26.8 × 3, 39.8, 43.3, 61.8, 71.7, 74.1, 74.3, 84.3, 84.6, 127.8 × 4, 129.8 × 2, 133.0 × 2, 135.5 × 4, 215.5; HRMS calcd for $C_{22}H_{25}O_5S_2Si$ (M^+–*t*-C_4H_9) *m*/*z* 461.0913, found 461.0903.

(1*R*,2*S*,3*S*,4*S*,5*R*,6*S*)-2-(*t*-Butyldiphenylsilyloxy)methyl-5,6-dihydroxy-3-methyl-7-oxabicyclo-[2.2.1]heptane ((+)-17). The following reaction was carried out under Ar. To a refluxing solution of (–)-**16** (2.76 g, 5.32 mmol) in toluene (50 mL) was added dropwise a solution of AIBN (262 mg, 1.60 mmol) and *n*-Bu_3SnH (2.9 mL, 11 mmol) in toluene (50 mL) over 30 min. The mixture was refluxed for an additional 1 h and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:10 to 1:1) to provide 1.94 g (89%) of (+)-**17** as a colorless oil: TLC R_f 0.14 (EtOAc:hexane, 1:1); $[\alpha]_D^{25}$ +10.4 (*c* 2.04, $CHCl_3$); IR 3440, 2940 cm^{-1}; ^1H NMR (270 MHz) δ 0.88 (d, 3H, *J* = 6.6 Hz), 1.05 (s, 9H), 1.82-1.88 (m, 2H), 3.31 (br, 2H, OH × 2), 3.59 (d, 2H, *J* = 6.2 Hz), 3.85 (br, 2H), 3.86 (d, 1H, *J* = 1.5 Hz), 4.31 (d, 1H, *J* = 1.8 Hz), 7.35-7.46 (m, 6H), 7.63-7.67 (m, 4H); ^{13}C NMR (68 MHz) δ 13.3, 19.1, 26.7 × 3, 34.4, 43.4, 62.1, 74.1, 74.3, 84.4, 88.8, 127.5 × 4, 129.5 × 2, 133.3, 133.4, 135.3 × 4; HRMS calcd for $C_{20}H_{23}O_4Si$ (M^+–*t*-C_4H_9) *m*/*z* 355.1366, found 355.1368.

(2*R*,3*S*,4*S*,5*S*)-3-(*t*-Butyldiphenylsilyloxy)methyl-2,5-bis(hydroxymethyl)-4-methyl-tetrahydrofuran ((+)-18). To a stirred solution of (+)-**17** (2.51 g, 6.09 mmol) in benzene (50 mL) was added $Pb(OAc)_4$ (4.05 g, 9.14 mmol). The mixture was stirred for 45 min, and the precipitated solids were removed by filtration through a Celite-pad and washed well with EtOAc. The combined filtrate and washings were concentrated in vacuo to provide crude dialdehyde monohydrate (3.85 g), which was used immediately in the next step.

To a cooled (0 °C) stirred solution of crude dialdehyde monohydrate (3.85 g) in MeOH (70 mL) was added $NaBH_4$ (2.3 g, 61 mmol). After being stirred for 1 h, the mixture was cooled to 0 °C, and 35% aqueous H_2O_2 (4 mL) was added. The mixture was stirred for 1 h, quenched with saturated aqueous Na_2SO_3 (15 mL) at 0 °C, diluted with saturated brine (200 mL), and extracted with CH_2Cl_2 (200 mL × 3). The combined extracts were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:1) to provide 2.04 g (81%) of (+)-**18** as a colorless oil: TLC R_f 0.10 (EtOAc:hexane, 1:1); $[\alpha]_D^{26}$ +10.3 (*c* 1.68, $CHCl_3$); IR 3400, 2940 cm^{-1}; ^1H NMR (270 MHz) δ 0.93 (d, 3H, *J* = 6.8 Hz), 1.05 (s, 9H), 2.21-2.32 (m, 4H), 3.53 (dd, 1H, *J* = 4.4, 11.7 Hz), 3.59 (dd,

1H, *J* = 4.9, 11.7 Hz), 3.64-3.75 (m, 3H), 3.79 (dd, 1H, *J* = 3.4, 11.7 Hz), 3.80 (dd, 1H, *J* = 2.7, 11.7 Hz), 4.07 (m, 1H), 7.36-7.45 (m, 6H), 7.64-7.67 (m, 4H); ^{13}C NMR (68 MHz) 12.3, 19.1, 26.8 3, 35.8, 45.4, 62.7, 63.1, 65.1, 82.4, 86.2, 127.7 4, 129.7 2, 133.1, 133.2, 135.5 4; HRMS calcd for $C_{20}H_{25}O_4Si$ (M^+–*t*-C_4H_9) *m*/*z* 357.1522, found 357.1519.

(2*R*,3*S*,4*S*,5*S*)-3-(*t*-Butyldiphenylsilyloxy)methyl-4-methyl-2,5-bis[(*p*-toluenesulfonyloxy)-methyl]tetrahydrofuran ((+)-19). The following reaction was carried out under Ar. To a cooled (0 °C) stirred solution of (+)-**18** (2.04 g, 4.92 mmol) in THF (100 mL) was added *n*-BuLi (2.44 M solution in hexane, 5.0 mL, 12 mmol). The mixture was stirred for 1 h and TsCl (2.35 g, 12.3 mmol) was added at 0 °C. After being stirred for 30 min, the mixture was diluted with saturated aqueous NH_4Cl (250 mL) and extracted with CH_2Cl_2 (120 mL 3). The combined extracts were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:5) to provide 2.82 g (79%) of (+)-**19** as a pale yellow oil: TLC R_f 0.68 (EtOAc:hexane, 1:1); $[]_D^{26}$ +6.3 (*c* 1.42, $CHCl_3$); IR 2940 cm^{-1}; ^{1}H NMR (270 MHz) 0.86 (d, 3H, *J* = 6.6 Hz), 0.99 (s, 9H), 2.05-2.20 (m, 2H), 2.43 (s, 3H), 2.44 (s, 3H), 3.56 (dd, 1H, *J* = 6.2, 10.3 Hz), 3.63 (dd, 1H, *J* = 4.8, 10.3 Hz), 3.73 (m, 1H), 3.89 (dd, 1H, *J* = 4.7, 10.3 Hz), 3.91 (dd, 1H, *J* = 4.7, 9.9 Hz), 4.00 (dd, 1H, *J* = 4.4, 10.3 Hz), 4.03 (dd, 1H, *J* = 3.7, 9.9 Hz), 4.10 (m, 1H), 7.29-7.45 (m, 10H), 7.58-7.61 (m, 4H), 7.74-7.81 (m, 4H); ^{13}C NMR (68 MHz) 12.1, 19.1, 21.7 2, 26.8 3, 36.5, 45.3, 62.1, 70.1, 71.3, 79.1, 82.9, 127.8 4, 127.9 4, 129.9 6, 132.7 2, 132.8, 133.0, 135.5 4, 144.8, 144.9; HRMS calcd for $C_{34}H_{37}O_8S_2Si$ (M^+–*t*-C_4H_9) *m*/*z* 665.1699, found 665.1695.

(2*R*,3*S*,4*S*,5*S*)-3-(*t*-Butyldiphenylsilyloxy)methyl-2,5-bis(iodomethyl)-4-methyltetrahydro-furan ((+)-20). To a stirred solution of (+)-**19** (2.82 g, 3.90 mmol) in 2-butanone (60 mL) was added NaI (2.05 g, 13.7 mmol). The mixture was refluxed for 12 h, diluted with EtOAc (220 mL), and washed with saturated aqueous $Na_2S_2O_3$ (70 mL 2) and saturated brine (70 mL). The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:20) to provide 2.36 g (96%) of (+)-**20** as a colorless oil: TLC R_f 0.71 (EtOAc:hexane, 1:3); $[]_D^{27}$ +0.5 (*c* 1.81, $CHCl_3$); IR 2940 cm^{-1}; ^{1}H NMR (270 MHz) 0.96 (d, 3H, *J* = 6.6 Hz), 1.06 (s, 9H), 2.19-2.33 (m, 2H), 3.23 (dd, 1H, *J* = 5.1, 10.6 Hz), 3.30 (dd, 1H, *J* = 4.8, 10.3 Hz), 3.38 (dd, 1H, *J* = 5.1, 10.6 Hz), 3.39 (dd, 1H, *J* = 4.8, 10.3 Hz), 3.59 (dt, 1H, *J* = 6.6, 5.1 Hz), 3.67 (dd, 1H, *J* = 6.6, 10.4 Hz), 3.72 (dd, 1H, *J* = 5.1, 10.4 Hz), 3.96 (dt, 1H, *J* = 5.5, 4.8 Hz), 7.37-7.48 (m, 6H), 7.64-7.68 (m, 4H); ^{13}C NMR (68 MHz) 10.0, 11.6, 12.6, 19.1, 26.8 3, 40.5, 49.1, 62.5, 80.8, 84.7, 127.8 4, 129.8 2, 132.0 2, 135.6 4; HRMS calcd for $C_{20}H_{23}I_2O_2Si$ (M^+–*t*-C_4H_9) *m*/*z* 576.9557, found 576.9558.

(2*S*,3*S*,4*S*,5*R*)-3-(*t*-Butyldiphenylsilyloxy)methyl-4-methyl-2,5-di(2-propenyl)tetrahydrofuran ((+)-6). The following reaction was carried out under Ar. To a stirred solution of (+)-**20** (2.00 g, 3.15 mmol) in benzene (80 mL) was added vinylMgBr (1.0 M solution in THF, 25 mL, 25 mmol). The mixture was stirred for 20 h, diluted with saturated aqueous NH_4Cl (200 mL), and extracted with EtOAc (100 mL 2). The combined extracts were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (toluene:hexane, 1:2) to provide 1.22 g (89%) of (+)-**6** as a colorless oil: TLC R_f 0.57 (toluene:hexane, 3:1); $[]_D^{23}$ +5.7 (*c* 0.830, $CHCl_3$); IR 2940, 1640 cm^{-1}; ^{1}H NMR (270

MHz) δ 0.93 (d, 3H, *J* = 7.0 Hz), 1.04 (s, 9H), 1.92-2.39 (m, 6H), 3.53 (dt, 1H, *J* = 5.1, 7.0 Hz), 3.61 (dd, 1H, *J* = 6.6, 10.3 Hz), 3.68 (dd, 1H, *J* = 5.9, 10.3 Hz), 3.89 (dt, 1H, *J* = 5.5, 5.9 Hz), 4.99-5.12 (m, 4H), 5.71-5.95 (m, 2H), 7.35-7.42 (m, 6H), 7.64-7.68 (m, 4H); ^{13}C NMR (68 MHz) δ 12.2, 19.2, 26.8 × 3, 38.8, 39.4, 40.4, 48.0, 62.7, 80.1, 84.3, 116.6, 116.8, 127.7 × 4, 129.6 × 2, 133.5 × 2, 135.1, 135.2, 135.6 × 4; HRMS calcd for $C_{24}H_{29}O_2Si$ (M^+–*t*-C_4H_9) *m/z* 377.1937, found 377.1942.

(1*R*,6*S*,7*S*,8*S*)-7-(*t*-Butyldiphenylsilyloxy)methyl-8-methyl-9-oxabicyclo[4.2.1]non-3-ene ((+)-5). The following reaction was carried out with bubbling Ar. To a stirred solution of (+)-**6** (850 mg, 1.96 mmol) in benzene (650 mL) was added a solution of 2nd generation Grubbs catalyst **22** (25 mg, 0.029 mmol) in benzene (2 mL). The mixture was refluxed for 4 h and a solution of **22** (25 mg, 0.029 mmol) in benzene (2 mL) was added. The mixture was refluxed for 2 h and then DMSO (0.21 mL, 2.9 mmol) was added.[5] After being refluxed for 16 h, the mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:80) to provide 689 mg (86%) of (+)-**5** as a colorless oil: TLC R_f 0.28 (EtOAc:hexane, 1:20); $[\alpha]_D^{22}$ +5.8 (*c* 0.675, $CHCl_3$); IR 2940 cm^{-1}; ^{1}H NMR (270 MHz) δ 0.92 (d, 3H, *J* = 7.3 Hz), 1.04 (s, 9H), 2.15-2.64 (m, 6H), 3.59 (dd, 1H, *J* = 9.2, 9.9 Hz), 3.73 (dd, 1H, *J* = 6.2, 9.9 Hz), 3.98 (m, 1H), 4.36 (m, 1H), 5.50-5.63 (m, 2H), 7.35-7.43 (m, 6H), 7.63-7.67 (m, 4H); ^{13}C NMR (68 MHz) δ 15.4, 19.2, 26.8 × 3, 38.4, 39.1, 40.2, 48.4, 63.9, 81.5, 86.0, 127.2, 127.5, 127.7 × 4, 129.6 × 2, 133.8 × 2, 135.5 × 4; HRMS calcd for $C_{22}H_{25}O_2Si$ (M^+–*t*-C_4H_9) *m/z* 349.1624, found 349.1616.

(1*R*,3*RS*,4*RS*,6*S*,7*S*,8*S*)-3,4-Dibromo-7-(*t*-butyldiphenylsilyloxy)methyl-8-methyl-9-oxabicyclo[4.2.1]nonane (23). To a cooled (–78 °C) stirred solution of (+)-**5** (780 mg, 1.91 mmol) in Et_2O (30 mL) was added a solution of bromine (0.10 mL, 2.0 mmol) in Et_2O (1 mL). The mixture was stirred at –78 °C for 1 h, diluted with EtOAc (100 mL), and washed with saturated aqueous $Na_2S_2O_3$ (50 mL × 2) and saturated brine (50 mL). The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:60) to provide 1.03 g (96%) of **23** (d.r.= *ca.* 5:6) as a pale yellow oil: TLC R_f 0.28 (EtOAc:hexane, 1:20); IR 2940 cm^{-1}; ^{1}H NMR (270 MHz) δ 0.89 (d, 3H × 5/11, *J* = 8.1 Hz), 0.91 (d, 3H × 6/11, *J* = 7.0 Hz), 1.05 (s, 9H × 6/11), 1.06 (s, 9H × 5/11), 1.76-1.87 (m, 1H × 5/11), 2.06-2.26 (m, 2H), 2.34-2.61 (m, 2H + 1H × 6/11), 2.97-3.08 (m, 1H), 3.54-3.78 (m, 2H), 3.83-4.12 (m, 2H), 4.23-4.61 (m, 2H), 7.35-7.43 (m, 6H), 7.63-7.67 (m, 4H) ; HRMS calcd for $C_{22}H_{25}Br^{81}BrO_2Si$ (M^+–*t*-C_4H_9) *m/z* 508.9970, found 508.9974.

(1*R*,6*S*,7*S*,8*S*)-7-(*t*-Butyldiphenylsilyloxy)methyl-8-methyl-9-oxabicyclo[4.2.1]nona-2,4-diene ((+)-24). To a heated (75 °C) stirred solution of *t*-BuOK (933 mg, 8.31 mmol) in *t*-BuOH (20 mL) was added a solution of **23** (942 mg, 1.66 mmol) in *t*-BuOH (5 mL). The mixture was stirred at 75 °C for 30 min, diluted with H_2O (200 mL), and extracted with EtOAc (100 mL × 3). The combined extracts were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:80) to provide 356 mg (53%) of (+)-**24** as a colorless oil: TLC R_f 0.28 (EtOAc:hexane, 1:20); $[\alpha]_D^{22}$ +12.3 (*c* 0.840, $CHCl_3$); IR 2940 cm^{-1}; ^{1}H NMR (270 MHz) δ 0.93 (d, 3H, *J* = 7.0 Hz), 1.04

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[5] Byproducts derived from catalyst were removed effectively by treatment with DMSO, see: Ahn, Y. M.; Yang, K.; Georg, G. I. *Org. Lett.* **2001**, *3*, 1411-1413.

(s, 9H), 2.62-2.78 (m, 2H), 3.62 (dd, 1H, *J* = 6.6, 10.3 Hz), 3.69 (dd, 1H, *J* = 8.8, 10.3 Hz), 4.19 (dd, 1H, *J* = 1.5, 4.8 Hz), 4.55 (dd, 1H, *J* = 3.9, 5.3 Hz), 5.81-5.89 (m, 2H), 6.05-6.22 (m, 2H), 7.35-7.43 (m, 6H), 7.63-7.67 (m, 4H); ^{13}C NMR (68 MHz) 14.0, 19.1, 26.5 3, 50.2, 57.0, 62.5, 80.7, 85.9, 124.6, 124.7, 127.7 4, 129.6 2, 133.6 2, 135.5 4, 137.8, 139.0; HRMS calcd for $C_{22}H_{23}O_2Si$ (M^+–*t*-C_4H_9) *m/z* 347.1467, found 347.1465.

(1*R*,6*S*,7*S*,8*S*)-7-Hydroxymethyl-8-methyl-9-oxabicyclo[4.2.1]nona-2,4-diene ((+)-4). To a cooled (0 °C) stirred solution of (+)-**24** (356 mg, 0.880 mmol) in THF (8 mL) was added *n*-Bu_4NF (1.0 M solution in THF, 1.14 mL, 1.14 mmol). The mixture was stirred for 2 h and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:4) to provide 146 mg (quant.) of (+)-**4** as a colorless oil: TLC R_f 0.28 (EtOAc:hexane, 1:1); $[]_D^{19}$ +20.4 (*c* 1.21, $CHCl_3$); IR 3400, 2940 cm^{-1}; ^{1}H NMR (270 MHz) 1.07 (d, 3H, *J* = 7.0 Hz), 1.93 (br, 1H, OH), 2.60-2.79 (m, 2H), 3.67 (dd, 1H, *J* = 7.3, 10.3 Hz), 3.68 (dd, 1H, *J* = 6.2, 10.3 Hz), 4.23 (dd, 1H, *J* = 2.9, 5.1 Hz), 4.53 (dd, 1H, *J* = 3.5, 5.3 Hz), 5.82-5.90 (m, 2H), 6.11-6.19 (m, 2H); ^{13}C NMR (68 MHz) 13.8, 49.0, 57.9, 61.7, 81.3, 85.4, 124.9, 125.1, 137.9, 138.0; HRMS calcd for $C_{10}H_{14}O_2$ (M^+) *m/z* 166.0994, found 166.0993.

(1*S*,2*S*,3*R*,4*R*)-2-(*t*-Butyldiphenylsilyloxy)methyl-3-(*p*-toluenesulfonyl)oxymethyl-7-oxabicyclo[2.2.1]hept-5-ene ((–)-27). To a cooled (0°C) stirred solution of (–)-**7** (101 mg, 0.255 mmol) in CH_2Cl_2 (2 mL) were added Et_3N (0.224 mL, 2.41 mmol), TsCl (72.9 mg, 0.382 mmol), and 4-DMAP (4.4 mg, 0.036 mmol). The mixture was sitrred for 22 h, diluted with EtOAc (20 mL), and washed with H_2O (15 mL 3). The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:10) to provide 143 mg (quant.) of (–)-**27** as a colorless oil: TLC R_f 0.66 (EtOAc:hexane, 1:2); $[]_D^{23}$ –19.1 (*c* 1.52, $CHCl_3$); IR 2960 cm^{-1}; ^{1}H NMR (270 MHz) 1.00 (s, 9H), 1.87-2.05 (m, 2H), 2.40 (s, 3H), 3.58 (d, 2H, *J* = 7.7 Hz), 3.94 (t, 1H, *J* = 9.7 Hz), 4.38 (dd, 1H, *J* = 4.6, 9.7 Hz), 4.70 (br s, 1H), 4.78 (br s, 1H), 6.30 (dd, 1H, *J* = 1.5, 5.8 Hz), 6.35 (dd, 1H, *J* = 1.5, 5.8 Hz), 7.25 (d, 2H, *J* = 8.1 Hz), 7.37-7.45 (m, 6H), 7.65-7.69 (m, 4H), 7.71 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR (68 MHz) 19.0, 21.6, 26.7 3, 39.6, 42.7, 63.2, 70.7, 80.2, 80.3, 127.8 4, 129.8 4, 129.9 2, 132.8, 133.1 2, 135.0, 135.4 4, 136.0, 144.7; HRMS calcd for $C_{27}H_{27}O_5SSi$ (M^+–*t*-C_4H_9) *m/z* 491.1349, found 491.1340.

(1*S*,2*S*,3*S*,4*R*)-2-(*t*-Butyldiphenylsilyloxy)methyl-3-methyl-7-oxabicyclo[2.2.1]hept-5-ene ((+)-26). To a heated (90 °C) stirred solution of $NaBH_4$ (98.7 mg, 2.55 mmol) in DMPU (1 mL) was added a solution of (–)-**27** obtained above (143 mg) in DMPU (2 mL). The mixture was sitrred at 90 °C for 2 h, diluted with EtOAc (10 mL), and washed with H_2O (10 mL 3). The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:30) to provide 110 mg (76% from (–)-**7**) of (+)-**26** as a colorless oil: TLC R_f 0.75 (EtOAc:hexane, 1:4); $[]_D^{22}$ +1.9 (*c* 1.73, $CHCl_3$); IR 2940 cm^{-1}; ^{1}H NMR (270 MHz) 0.95 (d, 3H, *J* = 7.0 Hz), 1.06 (s, 9H), 1.69-1.81 (m, 2H), 3.66 (dd, 1H, *J* = 9.7, 9.8 Hz), 3.77 (dd, 1H, *J* = 5.5, 9.8 Hz), 4.43 (s, 1H), 4.94 (s, 1H), 6.34 (s, 2H), 7.37-7.45 (m, 6H), 7.65-7.69 (m, 4H); ^{13}C NMR (68 MHz) 14.4, 19.2, 26.9 3, 33.4, 42.3, 63.9, 80.5, 84.9, 127.6 4, 129.6 2, 133.8, 133.9, 135.4 2, 135.5 4; HRMS calcd for $C_{20}H_{21}O_2Si$ (M^+–*t*-C_4H_9) *m/z* 321.1311, found 321.1311.

Mixture of (2*R*,3*S*,4*S*,5*S*)-2-[(1*Z*)-Buta-1,3-diene-1-yl]-4-(*t*-butyldiphenylsilyloxy)methyl-3-methyl-5-vinyltetrahydrofuran (25a), (2*S*,3*S*,4*S*,5*R*)-2-[(1*Z*)-Buta-1,3-diene-1-yl]-3-(*t*-butyldiphenylsilyloxy)methyl-4-methyl-5-vinyltetrahydrofuran (25b), and *E*-isomers (25c and 25d) (Entry 1 in Table 1). To a stirred solution of (+)-**26** (24.9 mg, 65.8 μmol) in benzene (6.6 mL) were added 1,3-butadiene (1.0 M solution in benzene, 0.13 mL, 0.13 mmol) and a solution of $Cl_2Ru(PCy_3)_2$=CHPh (**21**) (2.7 mg, 3.3 μmol) in benzene (0.5 mL). The mixture was stirred for 10 min, diluted with EtOAc (5 mL), and washed with H_2O (3 mL). The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:60) to provide 16.8 mg (60%) of inseparable mixture of **25a-d** as a colorless oil: TLC R_f 0.74 (EtOAc:hexane, 1:6); IR 2940 cm^{-1}; ^1H NMR (270 MHz) δ 0.96, 0.97 (2d, total 3H, J = 7.0 Hz), 1.05, 1.06, 1.07 (3s, total 9H), 2.03-2.20 (m, 2H), 3.58 (m, 2H), 3.90-4.02, 4.35-4.42 (2m, total 1.35H), 4.48 (t, 0.30H, J = 9.0 Hz, minor *Z*-isomer), 4.87 (ddd, 0.35H, J = 0.9, 5.0, 8.6 Hz, major *Z*-isomer), 5.02-5.29 (m, 4H), 5.42 (m, 0.30H, minor *Z*-isomer), 5.48 (m, 0.35H, major *Z*-isomer), 5.64-5.93 (m, 1.35H), 5.98-6.38 (m, 1.35H), 6.57-6.73 (m, 0.65H, *Z*-isomers), 7.35-7.47 (m, 6H), 7.64-7.70 (m, 4H); HRMS calcd for $C_{28}H_{36}O_2Si$ (M^+) *m/z* 432.2475, found 432.2485.

Preparation of (+)-4 from 25a-d (Entry 2 in Table 2). The following reaction was carried out with bubbling Ar. To a stirred solution of **25a-d** (*Z*/*E* = 1.8:1, 51.8 mg, 0.120 mmol) in benzene (40 mL) was added a solution of 2nd generation Grubbs catalyst **22** (5.5 mg, 6.5 μmol) in benzene (0.5 mL). The mixture was refluxed while each solution of **22** (5.5 mg, 6.5 μmol) in benzene (0.5 mL) was added three times over a period of 3 days. Then DMSO (92 μL, 1.3 mmol) was added to the mixture. After being refluxed for 17 h, the dark solution was passed through a pad of silica gel (EtOAc:hexane, 1:15). The filtered solution was concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:80) to provide inseparable mixture of (+)-**24** and byproducts (20.3 mg).

To a cooled (0 °C) stirred solution of the mixture obtained above (20.3 mg) in THF (1 mL) was added *n*-Bu_4NF (1.0 M solution in THF, 60 μL, 60 μmol). The mixture was stirred for 17 h and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:3) to provide 5.7 mg (29% from **25a-d**) of (+)-**4** as a colorless oil.

One-Pot ROM/CM/RCM Reaction of (+)-26 for Preparation of (+)-4. To a stirred solution of 1,3-butadiene (1.0 M solution in benzene, 2.5 mL, 2.5 mmol) in benzene (210 mL) was added a solution of $Cl_2Ru(PCy_3)_2$=CHPh (**21**) (20.9 mg, 25.4 μmol) in benzene (0.5 mL). The mixture was stirred for 10 min and a solution of (+)-**26** (480 mg, 1.27 mmol) in benzene (5 mL) was added. After being stirred for 30 min, the mixture was heated to reflux and bubbled a stream of Ar. The mixture was refluxed while each solution of 2nd generation Grubbs catalyst **22** (21.5 mg, 25.4 μmol) in benzene (0.5 mL) was added five times over a period of 4 days. Then DMSO (0.56 mL, 7.5 mmol) was added to the mixture. After being refluxed for 18 h, the dark solution was passed through a pad of silica gel (EtOAc:hexane, 1:15). The filtered solution was concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:80) to provide inseparable mixture of (+)-**24** and byproducts (175 mg).

To a cooled (0 °C) stirred solution of the mixture obtained above (175 mg) in THF (3 mL) was added *n*-

Bu_4NF (1.0 M solution in THF, 1.3 mL, 1.3 mmol). The mixture was stirred for 80 min and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:4) to provide 49.0 mg (23% from (+)-**26**) of (+)-**4** as a colorless oil.

(1*S*,2*S*,3*S*,4*R*)-2-Hydroxymethyl-3-methyl-7-oxabicyclo[2.2.1]hept-5-ene ((+)-28). To a cooled (0 °C) stirred solution of (+)-**26** (127 mg, 0.335 mmol) in THF (3 mL) was added *n*-Bu_4NF (1.0 M solution in THF, 0.40 mL, 0.40 mmol). The mixture was stirred for 3 h and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:1) to provide 39.3 mg (84%) of (+)-**28** as a colorless oil: TLC R_f 0.32 (EtOAc:hexane, 1:1); $[\alpha]_D^{22}$ +18.2 (*c* 1.09, $CHCl_3$); IR 3400, 2940 cm^{-1}; ^1H NMR (270 MHz) δ 1.07 (d, 3H, *J* = 7.0 Hz), 1.67-1.86 (m, 2H), 2.10 (br, 1H, OH), 3.61 (dd, 1H, *J* = 8.8, 10.3 Hz), 3.81 (dd, 1H, *J* = 5.0, 10.3 Hz), 4.48 (br s, 1H), 4.88 (br s, 1H), 6.33 (dd, 1H, *J* = 1.5, 5.9 Hz), 6.37 (dd, 1H, *J* = 1.5, 5.9 Hz); ^{13}C NMR (68 MHz) δ 14.5, 33.6, 41.7, 62.5, 80.6, 84.7, 135.0, 135.8; HRMS calcd for $C_8H_{13}O_2$ (M^++H) *m/z* 141.0916, found 141.0914.

One-Pot ROM/CM/RCM Reaction of (+)-28 for Preparation of (+)-4. To a stirred solution of (+)-**28** (14.4 mg, 0.103 mmol) in benzene (34 mL) were added 1,3-butadiene (1.0 M solution in benzene, 0.21 mL, 0.21 mmol) and a solution of $Cl_2Ru(PCy_3)_2$=CHPh (**21**) (8.4 mg, 10 μmol) in benzene (0.5 mL). After being stirred for 45 min, the mixture was heated to reflux and bubbled a stream of Ar. The mixture was refluxed while each solution of 2nd generation Grubbs catalyst **22** (4.4 mg, 5.1 μmol) in benzene (0.5 mL) was added four times over a period of 4 days. Then DMSO (92 μL, 1.3 mmol) was added to the mixture. After being refluxed for 18 h, the dark solution was passed through a pad of silica gel (EtOAc:hexane, 1:1). The filtered solution was concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:4) to provide 3.1 mg (18%) of (+)-**4** as a colorless oil.

One-Pot ROM/CM/RCM Reaction of (–)-13 for Preparation of (1*R*,6*S*,7*S*,8*R*)-7-(*t*-Butyldiphenylsilyloxy)methyl-8-hydroxymethyl-9-oxabicyclo[4.2.1]nona-2,4-diene ((+)-30). To a stirred solution of 1,3-butadiene (1.0 M solution in benzene, 2.8 mL, 2.8 mmol) in benzene (70 mL) was added a solution of $Cl_2Ru(PCy_3)_2$=CHPh (**21**) (17.2 mg, 20.9 μmol) in benzene (0.5 mL). The mixture was stirred for 15 min and a solution of (–)-**13** (898 mg, 1.93 mmol) in benzene (5 mL) was added. After being stirred for 30 min, the mixture was heated to reflux and bubbled a stream of Ar. The mixture was refluxed while each solution of 2nd generation Grubbs catalyst **22** (17.8 mg, 20.9 μmol) in benzene (0.5 mL) was added four times over a period of 2 days. Then DMSO (0.31 mL, 4.2 mmol) was added to the mixture. After being refluxed for 17 h, the dark solution was passed through a pad of silica gel (EtOAc:hexane, 1:10). The filtered solution was concentrated in vacuo to provide a mixture of crude **29** (d.r. = *ca.* 1:1) and byproducts (257 mg), which was used directly in the next step: TLC R_f 0.53 (EtOAc:hexane, 1:4); ^1H NMR (270 MHz) for compound **29** δ 1.05 (s, 9H), 1.11 (t, 3H $\times$ 1/2, *J* = 7.3 Hz), 1.14 (t, 3H $\times$ 1/2, *J* = 7.0 Hz), 1.19 (d, 3H $\times$ 1/2, *J* = 5.1 Hz), 1.20 (d, 3H $\times$ 1/2, *J* = 5.5 Hz), 2.74-2.81 (m, 2H), 3.29-3.67 (m, 6H), 4.49 (m, 1H), 4.56 (q, 1H $\times$ 1/2, *J* = 5.5 Hz), 4.59 (q, 1H $\times$ 1/2, *J* = 5.1 Hz), 4.63 (m, 1H), 5.82-5.89 (m, 2H), 6.08-6.17 (m, 2H), 7.38-7.43 (m, 6H), 7.63-7.66 (m, 4H).

To a stirred solution of the mixture obtained above (257 mg) in MeOH (5 mL) was added PPTS (66.8

mg, 0.266 mmol). The mixture was stirred for 4 h, diluted with H_2O (20 mL), and extracted with CH_2Cl_2 (20 mL × 3). The combined extracts were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:7) to provide 65.5 mg (22% from (–)-**13**) of (+)-**30** as a colorless oil: TLC R_f 0.52 (EtOAc:hexane, 1:2); $[\alpha]_D^{19}$ +1.7 (*c* 1.45, $CHCl_3$); IR 3440, 2930 cm^{-1}; ^1H NMR (270 MHz) δ 1.06 (s, 9H), 2.63 (br, 1H, OH), 2.82-2.89 (m, 2H), 3.66-3.85 (m, 4H), 4.38 (dd, 1H, *J* = 2.6, 5.1 Hz), 4.47 (dd, 1H, *J* = 2.6, 5.5 Hz), 5.81-5.90 (m, 2H), 6.01-6.15 (m, 2H), 7.36-7.45 (m, 6H), 7.64-7.68 (m, 4H); ^{13}C NMR (68 MHz) δ 19.1, 26.8 × 3, 57.2, 57.5, 61.3, 62.8, 81.0, 81.1, 124.9, 125.1, 127.8 × 4, 129.9 × 2, 132.9 × 2, 135.5 × 4, 137.7, 137.8; HRMS calcd for $C_{22}H_{23}O_3Si$ (M^+–*t*-C_4H_9) *m/z* 363.1417, found 363.1413.

(1*R*,6*S*,7*S*,8*R*)-7-(*t*-Butyldiphenylsilyloxy)methyl-8-(*p*-toluenesulfonyl)oxymethyl-9-oxa-bicyclo[4.2.1]nona-2,4-diene ((–)-31). To a cooled (0°C) stirred solution of (+)-**30** (61.6 mg, 0.146 mmol) in CH_2Cl_2 (2 mL) were added Et_3N (49 μL, 0.35 mmol), TsCl (33.6 mg, 0.176 mmol), and 4-DMAP (8.9 mg, 0.073 mmol). The mixture was sitrred for 18 h, diluted with EtOAc (5 mL), and washed with 1 M aqueous HCl (5 mL), saturated aqueous $NaHCO_3$ (5 mL), and saturated brine (5 mL), successively. The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:15) to provide 85.1 mg (quant.) of (–)-**31** as a colorless oil: TLC R_f 0.37 (EtOAc:hexane, 1:4); $[\alpha]_D^{23}$ –4.0 (*c* 1.66, $CHCl_3$); IR 2940 cm^{-1}; ^1H NMR (270 MHz) δ 1.00 (s, 9H), 2.41 (s, 3H), 2.76 (dq, 1H, *J* = 4.0, 7.0 Hz), 2.94 (m, 1H), 3.53 (dd, 1H, *J* = 7.0, 10.0 Hz), 3.60 (dd, 1H, *J* = 7.0, 10.0 Hz), 4.04 (t, 1H, *J* = 9.5 Hz), 4.09 (dd, 1H, *J* = 5.9, 9.5 Hz), 4.40-4.43 (m, 2H), 5.79-5.89 (m, 2H), 5.99-6.06 (m, 2H), 7.25 (d, 2H, *J* = 8.2 Hz), 7.36-7.45 (m, 6H), 7.56-7.61 (m, 4H), 7.70 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR (68 MHz) δ 19.1, 21.7, 26.8 × 3, 54.9, 55.5, 61.3, 68.5, 79.6, 80.8, 125.2 × 2, 127.8 × 4, 129.8 × 2, 129.9 × 4, 132.8, 132.9, 133.0, 135.5 × 4, 137.2, 137.8, 144.7; HRMS calcd for $C_{29}H_{29}O_5SSi$ (M^+–*t*-C_4H_9) *m/z* 517.1505, found 517.1501.

Preparation of (+)-24 from (–)-31. To a heated (90 °C) stirred solution of $NaBH_4$ (78.4 mg, 2.02 mmol) in DMPU (1 mL) was added dropwise a solution of (–)-**31** (116 mg, 0.202 mmol) in DMPU (2 mL) over 15 min. The mixture was sitrred at 90 °C for an additional 10 min, diluted with EtOAc (5 mL), and washed with H_2O (5 mL × 3). The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:20) to provide 61.9 mg (76%) of (+)-**24** as a colorless oil.

Mixture of (1*R*,6*S*,7*S*,8*S*)-7-[(1*S*)- (32) and (1*R*)-1-(2-Furyl)-1-hydroxymethyl]-8-methyl-9-oxabicyclo[4.2.1]nona-2,4-diene (33). To a cooled (0 °C) stirred solution of (+)-**4** (146 mg, 0.878 mmol) in CH_2Cl_2 (3 mL) was added Dess-Martin periodinane (560 mg, 1.32 mmol). The mixture was stirred for 2 h, diluted with EtOAc (40 mL), and washed with saturated aqueous $Na_2S_2O_3$ (20 mL × 2) and saturated aqueous $NaHCO_3$ (20 mL). The organic layer was dried and concentrated in vacuo to provide crude aldehyde (165 mg), which was used immediately in the next step: TLC R_f 0.57 (EtOAc:hexane, 1:1); IR 2940, 1720 cm^{-1}; ^1H NMR (270 MHz) δ 1.10 (d, 3H, *J* = 6.8 Hz), 3.15 (d of quint, 1H, *J* = 2.0, 6.8 Hz), 3.26 (ddd, 1H, *J* = 2.4, 4.4, 6.8 Hz), 4.34 (dd, 1H, *J* = 2.0, 4.9 Hz), 5.07 (dd, 1H, *J* = 4.4, 5.4 Hz), 5.85-5.94 (m, 2H), 6.07-6.19 (m, 2H), 9.69 (d, 1H, *J* = 2.4 Hz).

The following reaction was carried out under Ar. To a cooled (0 °C) stirred solution of crude aldehyde (165 mg) in THF (6 mL) was added furyllithium (0.30 M solution in THF, prepared from *n*-BuLi and furan, 3.0 mL, 0.90 mmol). The mixture was stirred at 0 °C for 40 min, diluted with 5% aqueous $NaHCO_3$ (60 mL), and extracted with EtOAc (30 mL × 3). The combined extracts were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:10) to provide 87.9 mg (43%) of inseparable mixture of **32** and **33** (d.r. = *ca.* 3:2) as a pale yellow oil: TLC R_f 0.47 (EtOAc:hexane, 1:1); IR 3400, 2940 cm^{-1}; ^1H NMR (270 MHz) δ 1.06 (d, 3H δ 2/5, J = 7.3 Hz), 1.21 (d, 3H δ 3/5, J = 7.0 Hz), 2.10 (br, 1H, OH), 2.64 (m, 1H δ 2/5), 2.86-3.06 (m, 2H δ 3/5), 3.01 (m, 1H δ 2/5), 4.14 (t, 1H δ 3/5, J = 5.7 Hz), 4.26 (dd, 1H δ 2/5, J = 2.4, 4.9 Hz), 4.30 (d, 1H δ 3/5, J = 4.4 Hz), 4.66 (dd, 1H δ 3/5, J = 3.8, 10.8 Hz), 4.69 (d, 1H δ 2/5, J = 8.1 Hz), 4.79 (t, 1H δ 2/5, J = 4.8 Hz), 5.66-5.93 (m, 2H), 6.08-6.22 (m, 2H), 6.27-6.35 (m, 2H), 7.37 (m, 1H).

(1*R*,6*S*,7*R*,8*S*)-7-(Furan-2-carbonyl)-8-methyl-9-oxabicyclo[4.2.1]nona-2,4-diene ((–)-34). To a cooled (0 °C) stirred solution of mixture of **32** and **33** (d.r.=*ca.* 3:2, 87.9 mg, 0.383 mmol) in CH_2Cl_2 (2 mL) was added MnO_2 (1.75 g, 19.8 mmol). The mixture was stirred for 1 h, and insoluble materials were removed by filtration through a Celite-pad and washed well with CH_2Cl_2. The combined filtrate and washings were concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:8) to provide 63.2 mg (72%) of (–)-**34** as a colorless oil: TLC R_f 0.53 (EtOAc:hexane, 1:1); $[\alpha]_D^{21}$ –7.0 (*c* 0.505, $CHCl_3$); IR 2960, 1680 cm^{-1}; ^1H NMR (270 MHz) δ 0.88 (d, 3H, J = 7.5 Hz), 3.28 (quint, 1H, J = 7.5 Hz), 4.02 (dd, 1H, J = 5.5, 7.5 Hz), 4.35 (d, 1H, J = 4.4 Hz), 5.32 (t, 1H, J = 5.5 Hz), 5.88-5.99 (m, 2H), 6.11 (m, 1H), 6.25 (m, 1H), 6.55 (dd, 1H, J = 1.5, 3.7 Hz), 7.24 (d, 1H, J = 3.7 Hz), 7.59 (d, 1H, J = 1.5 Hz); ^{13}C NMR (68 MHz) δ 15.7, 55.9, 60.6, 76.1, 87.1, 112.8, 117.7, 125.3, 126.4, 137.4, 138.7, 146.8, 153.3, 186.1; HRMS calcd for $C_{14}H_{14}O_3$ (M^+) *m/z* 230.0943, found 230.0938.

Preparation of (+)-32 from (–)-34. The following reaction was carried out under Ar. To a cooled (–78 °C) stirred solution of (–)-**34** (63.2 mg, 0.207 mmol) in THF (2 mL) was added L-Selectride (1.0 M solution in THF, 1.1 mL, 1.1 mmol). The mixture was stirred at –78 °C for 15 min and 35% aqueous H_2O_2 (1 mL) was added. After being stirred for 1 h, the mixture was quenched with saturated aqueous Na_2SO_3 (2 mL). The resulting mixture was diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (10 mL × 5). The combined extracts were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:8) to provide 54.4 mg (85%) of (+)-**32** as a colorless oil: TLC R_f 0.47 (EtOAc:hexane, 1:1); $[\alpha]_D^{18}$ +82.5 (*c* 1.85, $CHCl_3$); IR 3400, 2940 cm^{-1}; ^1H NMR (270 MHz) δ 1.21 (d, 3H, J = 7.0 Hz), 1.90 (d, 1H, J = 3.8 Hz, OH), 2.86-3.06 (m, 2H), 4.14 (t, 1H, J = 5.7 Hz), 4.30 (d, 1H, J = 4.4 Hz), 4.66 (dd, 1H, J = 3.8, 10.8 Hz), 5.67-5.90 (m, 2H), 6.02-6.08 (m, 2H), 6.28 (dd, 1H, J = 0.7, 3.3 Hz), 6.34 (dd, 1H, J = 1.8, 3.3 Hz), 7.38 (dd, 1H, J = 0.7, 1.8 Hz); ^{13}C NMR (68 MHz) δ 13.7, 52.1, 56.4, 66.3, 76.1, 86.4, 106.4, 109.7, 123.9, 124.6, 136.6, 138.2, 141.7, 155.8; HRMS calcd for $C_{14}H_{16}O_3$ (M^+) *m/z* 232.1099, found 232.1091.

Preparation of (–)-34 from (+)-4 via Weinreb amide 35. To a cooled (0 °C) stirred solution of (+)-**4** (21.7 mg, 0.130 mmol) in CH_2Cl_2 (1 mL) was added Dess-Martin periodinane (84.5 mg, 0.199 mmol). The mixture was stirred for 1 h, diluted with EtOAc (2 mL), and washed with saturated aqueous

$Na_2S_2O_3$ (2 mL × 3). The organic layer was dried and concentrated in vacuo to provide crude aldehyde (90.2 mg), which was used immediately in the next step.

To a stirred solution of crude aldehyde (90.2 mg) in *t*-BuOH (2 mL) was added a solution of NH_2SO_3H (37.8 mg, 0.390 mmol) and Na_2HPO_4 (55.4 mg, 0.390 mmol) in H_2O (2 mL). Then $NaClO_2$ (35.3 mg, 0.390 mmol) was added to the mixture. After being stirred for 30 min, the mixture was diluted with H_2O (4 mL) and extracted with CH_2Cl_2 (2 mL × 4). The combined extracts were dried and concentrated in vacuo to provide crude acid (102 mg), which was used immediately in the next step.

To a stirred solution of crude acid (102 mg) in CH_2Cl_2 (2 mL) were added Me(MeO)NH·HCl (50.7 mg, 0.520 mmol), 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (49.8 mg, 0.260 mmol), 1-hydroxybenzotriazole (35.1 mg, 0.260 mmol), 4-DMAP (2.0 mg, 0.016 mmol), and Et_3N (0.11 mL, 0.78 mmol). The mixture was stirred for 16 h, diluted with EtOAc (4 mL), and washed with H_2O (4 mL × 3). The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:5) to provide 49.9 mg of inseparable mixture of **35** and byproducts: TLC R_f 0.33 (EtOAc:hexane, 1:1); ^{1}H NMR (270 MHz) for compound **35** δ 0.96 (d, 3H, J = 7.0 Hz), 3.09-3.16 (m, 2H), 3.19 (s, 3H), 3.66 (s, 3H), 4.31 (d, 1H, J = 4.8 Hz), 5.23 (t, 1H, J = 5.5 Hz), 5.84-5.92 (m, 2H), 6.05 (m, 1H), 6.24 (m, 1H).

The following reaction was carried out under Ar. To a cooled (0 °C) stirred solution of the mixture obtained above (49.9 mg) in THF (2 mL) was added furyllithium (0.30 M solution in THF, prepared from *n*-BuLi and furan, 1.3 mL, 0.39 mmol). The mixture was stirred at 0 °C for 40 min, diluted with 5% aqueous $NaHCO_3$ (4 mL), and extracted with EtOAc (2 mL × 3). The combined extracts were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:10) to provide 12.8 mg (43% from (+)-**4**) of (–)-**34** as a colorless oil

(1*R*,6*S*,7*R*,8*S*)-7-[(2*S*,6*RS*)-6-Hydroxy-3-oxo-6-hydro-2*H*-pyran-2-yl]-8-methyl-9-oxabicyclo-[4.2.1]nona-2,4-diene ((+)-36). The following reaction was carried out under Ar. To a cooled (0 °C) stirred solution of (+)-**32** (23.3 mg, 0.101 mmol) in CH_2Cl_2 (1 mL) were added a solution of $VO(acac)_2$ (4.0 mg, 15 μmol) in CH_2Cl_2 (0.3 mL) and *t*-BuOOH (6.63 M solution in isooctane, 90 μL, 0.60 mmol). The mixture was stirred for 3 h, quenched with Me_2S (50 μL), and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:3) to provide 22.3 mg (90%) of (+)-**36** (d.r. = *ca.* 1:2) as a colorless oil: TLC R_f 0.24 (EtOAc:hexane, 1:1); $[\alpha]_D^{19}$ +80.1 (*c* 1.74, $CHCl_3$); IR 3350, 2940, 1700 cm^{-1}; ^{1}H NMR (270 MHz) δ 1.10 (d, 3H × 2/3, J = 6.6 Hz), 1.11 (d, 3H × 1/3, J = 7.4 Hz), 2.74-2.91 (m, 2H), 4.06-4.24 (m, 2H), 4.62-4.72 (m, 1H), 5.63 (m, 1H), 5.80-5.90 (m, 2H), 5.98-6.09 (m, 1H), 6.08 (d, 1H × 2/3, J = 10.3 Hz), 6.13 (dd, 1H × 1/3, J = 1.5, 10.3 Hz), 6.37-6.51 (m, 1H), 6.87 (dd, 1H × 2/3, J = 3.3, 10.3 Hz), 6.92 (dd, 1H × 1/3, J = 1.8, 10.3 Hz); ^{13}C NMR (68 MHz) signals attributable to the major isomer δ 14.5, 51.5, 52.6, 73.5, 78.1, 85.3, 87.7, 124.3, 124.7, 127.4, 136.5, 139.7, 144.3, 196.4, signals attributable to the minor isomer δ 14.5, 52.4, 52.9, 73.5, 77.7, 85.4, 90.6, 124.5, 124.7, 128.5, 136.4, 139.5, 147.4, 196.0; HRMS calcd for $C_{14}H_{16}O_4$ (M^+) *m/z* 248.1049, found 248.1046.

(1*R*,6*S*,7*R*,8*S*)-7-[(2*S*,6*R*)- ((+)-37) and (2*S*,6*S*)-6-(*t*-Butyldimethylsilyloxy)-3-oxo-6-hydro-2*H*-pyran-2-yl]-8-methyl-9-oxabicyclo[4.2.1]nona-2,4-diene ((+)-38). To a cooled (0 °C) stirred

solution of (+)-**36** (22.3 mg, 0.091 mmol) in CH_2Cl_2 (1 mL) were added Et_3N (0.10 mL, 0.72 mmol), 4-DMAP (6.6 mg, 0.054 mmol), and TBSCl (54.6 mg, 0.362 mmol). The mixture was stirred for 18 h, diluted with saturated brine (20 mL), and extracted with CH_2Cl_2 (10 mL × 3). The combined extracts were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:15) to provide 15.2 mg (46%) of (+)-**37** and 6.1 mg (19%) of (+)-**38**. Compound (+)-**37** was obtained as a colorless oil: TLC R_f 0.40 (EtOAc:hexane, 1:3); $[\alpha]_D^{22}$ +39.4 (*c* 1.03, $CHCl_3$); IR 2940, 1700 cm^{-1}; ^1H NMR (270 MHz) δ 0.17 (s, 6H), 0.92 (s, 9H), 1.12 (d, 3H, *J* = 6.6 Hz), 2.76-2.92 (m, 2H), 4.07 (dd, 1H, *J* = 1.5, 10.3 Hz), 4.23 (d, 1H, *J* = 4.4 Hz), 4.64 (t, 1H, *J* = 5.7 Hz), 5.62 (q, 1H, *J* = 1.5 Hz), 5.78-5.90 (m, 2H), 6.00 (m, 1H), 6.07 (dd, 1H, *J* = 1.5, 10.3 Hz), 6.48 (m, 1H), 6.83 (dd, 1H, *J* = 1.5, 10.3 Hz); ^{13}C NMR (68 MHz) δ –5.2, –3.9, 14.3, 17.9, 25.6 × 3, 51.9, 53.2, 77.3, 77.9, 85.3, 91.2, 124.1, 124.7, 127.7, 136.4, 140.2, 149.3, 196.1. Compound (+)-**38** was obtained as a colorless oil: TLC R_f 0.50 (EtOAc:hexane, 1:3); $[\alpha]_D^{25}$ +113 (*c* 0.515, $CHCl_3$); IR 2940, 1700 cm^{-1}; ^1H NMR (270 MHz) δ 0.17 (s, 6H), 0.92 (s, 9H), 1.09 (d, 3H, *J* = 6.6 Hz), 2.71-2.87 (m, 2H), 4.22 (d, 1H, *J* = 4.4 Hz), 4.61 (d, 1H, *J* = 9.2 Hz), 4.72 (t, 1H, *J* = 5.9 Hz), 5.54 (d, 1H, *J* = 3.3 Hz), 5.79-5.90 (m, 2H), 6.00 (m, 1H), 6.01 (d, 1H, *J* = 10.3 Hz), 6.47 (m, 1H), 6.78 (dd, 1H, *J* = 3.3, 10.3 Hz); ^{13}C NMR (68 MHz) δ –5.2, –4.6, 14.5, 17.9, 25.6 × 3, 51.3, 53.2, 73.6, 77.3, 85.4, 87.8, 124.3, 124.6, 126.1, 136.8, 140.1, 145.7, 196.9.

(1*R*,6*S*,7*R*,8*S*)-7-[(2*S*,3*S*,6*R*)-6-(*t*-Butyldimethylsilyloxy)-3-hydroxy-3,6-dihydro-2*H*-pyran-2-yl]-8-methyl-9-oxabicyclo[4.2.1]nona-2,4-diene ((+)-39). To a cooled (0 °C) stirred solution of (+)-**37** (15.1 mg, 41.6 μmol) in MeOH (0.5 mL) and CH_2Cl_2 (0.5 mL) was added $CeCl_3 \cdot 7H_2O$ (94 mg, 0.25 mmol). After being stirred at 0 °C for 10 min, the mixture was cooled to –78 °C, and then $NaBH_4$ (9.0 mg, 0.25 mmol) was added. The mixture was stirred at –78 °C for 20 min, diluted with saturated brine (20 mL), and extracted with EtOAc (10 mL × 3). The combined extracts were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:10) to provide 13.2 mg (86%) of (+)-**39** as white crystals: mp 88-89 °C; TLC R_f 0.21 (EtOAc:hexane, 1:3); $[\alpha]_D^{19}$ +136 (*c* 0.830, $CHCl_3$); IR 3380, 2940 cm^{-1}; ^1H NMR (270 MHz) δ 0.14 (s, 6H), 0.91 (s, 9H), 1.09 (d, 3H, *J* = 7.0 Hz), 1.69 (d, 1H, *J* = 10.0 Hz, OH), 2.79-2.95 (m, 2H), 3.53 (dd, 1H, *J* = 1.5, 10.6 Hz), 3.69 (m, 1H), 4.27 (d, 1H, *J* = 4.8 Hz), 4.35 (t, 1H, *J* = 5.8 Hz), 5.30 (d, 1H, *J* = 1.1 Hz), 5.80 (d, 1H, *J* = 9.9 Hz), 5.81-5.93 (m, 2H), 6.01-6.14 (m, 2H), 6.30 (m, 1H); ^{13}C NMR (68 MHz) δ –5.0, –3.9, 14.6, 18.0, 25.7 × 3, 51.6, 52.7, 63.6, 74.8, 77.5, 86.4, 92.9, 124.6, 125.0, 129.5, 133.4, 136.9, 138.8; HRMS calcd for $C_{20}H_{32}O_4Si$ (M^+) *m*/*z* 364.2070, found 364.2078.

(1*R*,6*S*,7*R*,8*S*)-7-[(2*S*,3*S*,6*R*)-3-Acetoxy-6-(*t*-butyldimethylsilyloxy)-3,6-dihydro-2*H*-pyran-2-yl]-8-methyl-9-oxabicyclo[4.2.1]nona-2,4-diene ((+)-40). To a stirred solution of (+)-**39** (22.7 mg, 62.2 μmol) in pyridine (0.5 mL) and Ac_2O (0.5 mL) was added 4-DMAP (3.4 mg, 28 μmol). The mixture was stirred for 20 min, diluted with EtOAc (20 mL), and washed with 1 M aqueous HCl (10 mL), saturated aqueous $NaHCO_3$ (10 mL), and saturated brine (10 mL), successively. The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:15) to provide 22.6 mg (89%) of (+)-**40** as a colorless oil: TLC R_f 0.39 (EtOAc:hexane, 1:3); $[\alpha]_D^{20}$ +201 (*c* 0.835, $CHCl_3$); IR 2940, 1730 cm^{-1}; ^1H NMR (270 MHz) δ 0.15 (s, 6H), 0.91 (s, 9H),

1.08 (d, 3H, *J* = 6.6 Hz), 2.00 (s, 3H), 2.83-2.99 (m, 2H), 3.66 (dd, 1H, *J* = 1.8, 10.8 Hz), 4.26 (t, 1H, *J* = 5.9 Hz), 4.27 (d, 1H, *J* = 4.4 Hz), 4.87 (dt, 1H, *J* = 5.1, 1.8 Hz), 5.33 (d, 1H, *J* = 1.1 Hz), 5.81-5.93 (m, 3H), 5.99-6.09 (m, 3H); ^{13}C NMR (68 MHz) –4.9, –3.9, 14.2, 18.1, 21.2, 25.8 3, 50.6, 52.9, 65.1, 72.9, 76.4, 86.3, 92.7, 124.4, 124.9, 125.5, 135.3, 137.3, 138.0, 170.8; HRMS calcd for $C_{18}H_{25}O_5Si$ (M^+) *m/z* 406.2176, found 406.2175.

(1*R*,6*S*,7*R*,8*S*)-7-[(2*S*,3*S*,6*RS*)-3-Acetoxy-6-hydroxy-3,6-dihydro-2*H*-pyran-2-yl]-8-methyl-9-oxabicyclo[4.2.1]nona-2,4-diene ((+)-41). A solution of (+)-**40** (21.5 mg, 52.9 mol) in THF (1 mL) and 2 M aqueous HCl (1 mL) was stirred for 1 h. The mixture was diluted with H_2O (10 mL) and extracted with CH_2Cl_2 (10 mL 3). The combined extracts were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:2) to provide 15.5 mg (quant.) of (+)-**41** (d.r. = *ca.* 1:8) as white crystals: mp 142-143 °C; TLC R_f 0.23 (EtOAc:hexane, 1:1); $[]_D^{21}$ +304 (*c* 0.570, $CHCl_3$); IR (KBr) 3420, 2960, 1710 cm^{-1}; ^{1}H NMR (270 MHz) for the major isomer 1.14 (d, 3H, *J* = 6.6 Hz), 2.01 (s, 3H), 2.79 (br, 1H, OH), 2.80-2.91 (m, 2H), 4.14 (dd, 1H, *J* = 2.0, 10.8 Hz), 4.28 (t, 1H, *J* = 5.5 Hz), 4.29 (d, 1H, *J* = 4.4 Hz), 4.84 (dd, 1H, *J* = 2.0, 5.7 Hz), 5.46 (br, 1H), 5.82-5.94 (m, 2H), 6.02-6.09 (m, 2H), 6.05 (d, 1H, *J* = 10.1 Hz), 6.20 (dd, 1H, *J* = 5.7, 10.1 Hz); ^{13}C NMR (68 MHz) for the major isomer 13.8, 21.1, 50.0, 52.7, 64.3, 67.9, 77.5, 86.3, 88.6, 124.4, 125.6, 125.9, 130.7, 137.4, 137.8, 170.6; HRMS calcd for $C_{16}H_{20}O_5$ (M^+) *m/z* 292.1311, found 292.1304.

(1*R*,6*S*,7*R*,8*S*)-7-[(2*S*,3*S*,6*S*)- ((+)-42) and (2*S*,3*R*,6*S*)-6-(*t*-Butyldimethylsilyloxy)-3-hydroxy-3,6-dihydro-2*H*-pyran-2-yl]-8-methyl-9-oxabicyclo[4.2.1]nona-2,4-diene ((+)-43). To a cooled (0 °C) stirred solution of (+)-**38** (3.3 mg, 9.1 mol) in MeOH (1 mL) was added $CeCl_3 \cdot 7H_2O$ (20 mg, 55 mol). The mixture was stirred at 0 °C for 10 min, and $NaBH_4$ (1.0 mg, 27 mol) was added. After being stirred at 0 °C for 15 min, the mixture was diluted with saturated brine (20 mL), and extracted with EtOAc (10 mL 5). The combined extracts were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:8) to provide 2.1 mg (63%) of (+)-**42** and 1.0 mg (30%) of (+)-**43**. Compound (+)-**42** was obtained as white crystals: mp 151-152 °C; TLC R_f 0.20 (EtOAc:hexane, 1:3); $[]_D^{23}$ +149 (*c* 0.125, $CHCl_3$); IR (KBr) 3380, 2940 cm^{-1}; ^{1}H NMR (270 MHz) 0.13 (s, 3H), 0.14 (s, 3H), 0.90 (s, 9H), 1.16 (d, 3H, *J* = 6.6 Hz), 1.53 (d, 1H, *J* = 10.0 Hz, OH), 2.75-2.88 (m, 2H), 3.65 (m, 1H), 4.01 (dd, 1H, *J* = 1.5, 10.6 Hz), 4.28 (d, 1H, *J* = 4.4 Hz), 4.37 (t, 1H, *J* = 5.5 Hz), 5.33 (d, 1H, *J* = 2.9 Hz), 5.82 (dd, 1H, *J* = 2.9, 9.9 Hz), 5.86-5.95 (m, 2H), 6.06 (m, 1H), 6.14 (dd, 1H, *J* = 5.9, 9.9 Hz), 6.31 (m, 1H); ^{13}C NMR (68 MHz) –5.2, –4.5, 14.1, 18.3, 25.7 3, 51.2, 52.5, 62.9, 69.9, 77.1, 86.3, 89.0, 124.5, 125.4, 128.2, 130.4, 137.3, 138.5; HRMS calcd for $C_{20}H_{32}O_4Si$ (M^+) *m/z* 364.2070, found 364.2071. Compound (+)-**43** was obtained was a colorless oil: TLC R_f 0.30 (EtOAc:hexane, 1:3); $[]_D^{23}$ +92.2 (*c* 0.260, $CHCl_3$); IR 3400, 2960 cm^{-1}; ^{1}H NMR (270 MHz) 0.12 (s, 3H), 0.13 (s, 3H), 0.90 (s, 9H), 1.14 (d, 3H, *J* = 7.0 Hz), 1.50 (d, 1H, *J* = 10.0 Hz, OH), 2.54 (dt, 1H, *J* = 9.5, 6.0 Hz), 2.84 (m, 1H), 3.74 (t, 1H, *J* = 9.5 Hz), 3.94 (m, 1H), 4.21 (d, 1H, *J* = 4.4 Hz), 4.82 (t, 1H, *J* = 6.0 Hz), 5.29 (d, 1H, *J* = 1.1 Hz), 5.71 (dt, 1H, *J* = 10.3, 2.6 Hz), 5.82 (dd, 1H, *J* = 1.1, 10.3 Hz), 5.85-5.92 (m, 2H), 6.06 (m, 1H), 6.37 (m, 1H); ^{13}C NMR (68 MHz) –5.3, –4.5, 13.8, 18.3, 25.7 3, 53.4, 55.2, 68.9, 70.5, 76.8, 85.2, 88.7, 124.8, 125.4, 129.0, 131.5, 137.6, 139.8; HRMS calcd for $C_{20}H_{32}O_4Si$ (M^+)

m/z 364.2070, found 364.2067.

Preparation of (+)-41 from (+)-42. To a stirred solution of (+)-**42** (1.9 mg, 5.2 μmol) in pyridine (0.5 mL) and Ac_2O (0.5 mL) was added 4-DMAP (2.8 mg, 23 μmol). The mixture was stirred for 15 min, diluted with EtOAc (20 mL), and washed with 1 M aqueous HCl (10 mL), saturated aqueous $NaHCO_3$ (10 mL), and saturated brine (10 mL), successively. The organic layer was dried and concentrated in vacuo to provide crude acetate (2.3 mg), which was used directly in the next step. The crude acetate was obtained as a colorless oil: TLC R_f 0.52 (EtOAc:hexane, 1:3); IR 2960, 1730 cm^{-1}; ^1H NMR (270 MHz) δ 0.13 (s, 3H), 0.15 (s, 3H), 0.90 (s, 9H), 1.14 (d, 3H, *J* = 6.6 Hz), 2.00 (s, 3H), 2.79-2.92 (m, 2H), 4.11 (dd, 1H, *J* = 2.2, 10.8 Hz), 4.26 (t, 1H, *J* = 5.5 Hz), 4.27 (d, 1H, *J* = 4.4 Hz), 4.81 (dd, 1H, *J* = 2.2, 5.9 Hz), 5.39 (d, 1H, *J* = 2.9 Hz), 5.76-5.95 (m, 3H), 6.03-6.14 (m, 3H); ^{13}C NMR (68 MHz) δ –5.3, –4.5, 13.8, 18.3, 21.1, 25.7, 50.2, 52.7, 64.6, 68.1, 77.5, 86.3, 88.8, 124.1, 124.3, 125.6, 132.4, 137.4, 138.0, 170.6.

As described for the preparation of (+)-**41** from (+)-**40**, crude acetate obtained above (2.3 mg) was treated with 2 M aqueous HCl (0.5 mL) in THF (0.5 mL) to provide 1.3 mg (80% from (+)-**42**) of (+)-**41**.

(+)-Mycoepoxydiene (1). To a cooled (0 °C) stirred solution of (+)-**41** (14.0 mg, 47.9 μmol) in CH_2Cl_2 (2 mL) was added MnO_2 (280 mg, 3.22 mmol). The mixture was stirred for 20 min, and insoluble materials were removed by filtration through a Celite-pad and washed well with CH_2Cl_2. The combined filtrate and washings were concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:3) to provide 10.6 mg (76%) of (+)-**1** as white crystals: mp 144-145 °C; TLC R_f 0.29 (EtOAc:hexane, 1:1); $[\alpha]_D^{20}$ +227 (*c* 0.072, MeOH); IR (KBr) 2940, 1740, 1720, 1630 cm^{-1}; ^1H NMR (270 MHz) δ 1.14 (d, 3H, *J* = 7.0 Hz), 2.03 (s, 3H), 2.99-3.10 (m, 2H), 4.28 (t, 1H, *J* = 5.9 Hz), 4.32 (d, 1H, *J* = 4.4 Hz), 4.49 (dd, 1H, *J* = 2.4, 11.2 Hz), 5.08 (dd, 1H, *J* = 2.4, 6.0 Hz), 5.87-5.95 (m, 2H), 6.01-6.14 (m, 2H), 6.22 (d, 1H, *J* = 9.9 Hz), 7.03 (dd, 1H, *J* = 6.0, 9.9 Hz); ^{13}C NMR (68 MHz) δ 14.1, 20.7, 50.0, 52.6, 63.1, 75.9, 77.6, 86.4, 124.4, 125.1, 126.3, 136.9, 137.5, 140.2, 162.2, 170.0; HRMS calcd for $C_{16}H_{18}O_5$ (M^+) *m/z* 290.1154, found 290.1155; HPLC analysis (column, Daicel Chiralcel OD+OD-H, *i*-PrOH:hexane = 1:5, flow rate = 0.5 mL/min); t_R (min) = 51.1 for (–)-**1**, 59.5 for (+)-**1**. Compound (+)-**1** was determined to be 94% ee.

4-*epi*-Mycoepoxydiene ((–)-44). As described for the preparation of (+)-**1** from (+)-**39**, compound (+)-**43** (4.8 mg, 13 μmol) was converted to 2.5 mg (65% from (+)-**43**) of (–)-**44**. Compound (–)-**44** was obtained as a white solid: TLC R_f 0.39 (EtOAc:hexane, 1:1); $[\alpha]_D^{20}$ –54.7 (*c* 0.055, $CHCl_3$); IR 2920, 1740, 1730, 1635 cm^{-1}; ^1H NMR (270 MHz) δ 1.18 (d, 3H, *J* = 7.0 Hz), 2.16 (s, 3H), 2.64 (dt, 1H, *J* = 10.9, 6.6 Hz), 2.89 (m, 1H), 4.29 (d, 1H, *J* = 4.4 Hz), 4.49 (t, 1H, *J* = 5.9 Hz), 4.59 (ddd, 1H, *J* = 1.1, 3.4, 10.9 Hz), 5.12 (dd, 1H, *J* = 3.4, 5.1 Hz), 5.85-5.95 (m, 2H), 6.06 (m, 1H), 6.13 (m, 1H), 6.19 (d, 1H, *J* = 9.8 Hz), 6.74 (ddd, 1H, *J* = 1.1, 5.1, 9.8 Hz); ^{13}C NMR (68 MHz) δ 14.1, 20.8, 53.2, 53.3, 65.9, 76.1, 79.2, 86.1, 124.6, 124.8, 127.3, 136.6, 137.8, 139.4, 163.0, 171.3; HRMS calcd for $C_{16}H_{18}O_5$ (M^+) *m/z* 290.1154, found 290.1154.

(1*R*,6*S*,7*S*,8*S*)-7-[(1*RS*)-1-Hydroxy-1-[(2*RS*)-5-oxo-2-hydro-2-furyl]methyl]-8-methyl-9-oxa-bicyclo[4.2.1]nona-2,4-diene (46). To a cooled (0 °C) stirred solution of (+)-**4** (27.5 mg, 0.165 mmol) in CH_2Cl_2 (1 mL) was added Dess-Martin periodinane (210 mg, 0.496 mmol). The mixture was stirred

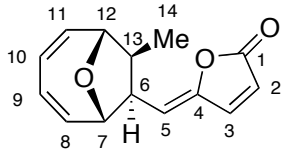
for 1 h, diluted with EtOAc (5 mL), and washed with saturated aqueous $Na_2S_2O_3$ (5 mL × 3) and saturated aqueous $NaHCO_3$ (10 mL). The organic layer was dried and concentrated in vacuo to provide crude aldehyde (29.6 mg), which was used immediately in the next step.

The following reaction was carried out under Ar. To a cooled (–78 °C) stirred solution of crude aldehyde (29.6 mg) in CH_2Cl_2 (1 mL) were added 2-(trimethylsilyloxy)furan (**45**) (82 μL, 0.50 mmol) and TESOTf (15 μL, 0.066 mmol). The mixture was stirred at –78 °C for 1 h and TESOTf (15 μL, 0.066 mmol) was added. The mixture was stirred at –78 °C for 40 min and TESOTf (7.5 μL, 0.033 mmol) was added. After being stirred at –78 °C for 20 min, the mixture was quenched with 1M aqueous HCl (1 mL), diluted with H_2O (5 mL), and extracted with CH_2Cl_2 (5 mL × 5). The combined extracts were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:toluene, 1:2) to provide 24.5 mg (60%) of **46** (d.r. = *ca.* 8:1) as white solids: TLC R_f 0.19 (EtOAc:toluene, 1:1); IR 3420, 2920, 1750 cm^{-1}; ^1H NMR (300 MHz) for major isomer δ 1.15 (d, 3H, J = 6.8 Hz), 2.39 (br, 1H, OH), 2.71-2.83 (m, 2H), 3.92 (m, 1H), 4.26 (dd, 1H, J = 1.7, 4.9 Hz), 4.87 (t, 1H, J = 4.8 Hz), 5.02 (q, 1H, J = 1.9 Hz), 5.87-5.94 (m, 2H), 6.09-6.20 (m, 2H), 6.22 (dd, 1H, J = 1.9, 5.8 Hz), 7.47 (dd, 1H, J = 1.9, 5.8 Hz); ^{13}C NMR (75 MHz) for major isomer δ 14.5, 50.4, 56.3, 70.2, 79.4, 85.0, 85.7, 122.6, 125.3, 125.5, 137.0, 138.1, 154.0, 172.9; HRMS calcd for $C_{14}H_{16}O_4$ (M^+) m/z 248.1049, found 248.1041.

(–)-1893A (2) and its *E*-isomer ((–)-47). To a stirred solution of **46** (8.9 mg, 0.036 mmol) in pyridine (1 mL) was added MsCl (11 μL, 0.14 mmol). After being stirred for 30 min, the mixture was heated to 80 °C and stirred for 2 days. The mixture was diluted with EtOAc (3 mL) and washed with 1M aqueous HCl (3 mL), saturated aqueous $NaHCO_3$ (3 mL), and saturated brine (3 mL). The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:7) to provide 5.2 mg (63%) of (–)-**2** and 1.1 mg (13%) of (–)-**47**. Compound (–)-**2** was obtained as white crystals: mp 91-92 °C; TLC R_f 0.72 (EtOAc:toluene, 1:1); $[\alpha]_D^{22}$ –293 (c 0.32, acetone), $[\alpha]_D^{23}$ –285 (c 0.064, acetone); IR (KBr) 2960, 1780, 1750, 1660 cm^{-1}; ^1H NMR (300 MHz, CD_3COCD_3) δ 1.01 (d, 3H, J = 7.0 Hz), 2.85 (m, 1H), 3.71 (ddd, 1H, J = 3.1, 7.5, 10.6 Hz), 4.26 (dd, 1H, J = 3.6, 5.1 Hz), 4.43 (dd, 1H, J = 3.1, 5.1 Hz), 5.56 (d, 1H, J = 10.6 Hz), 5.85-5.92 (m, 2H), 6.12-6.26 (m, 2H), 6.29 (d, 1H, J = 5.5 Hz), 7.75 (d, 1H, J = 5.5 Hz); ^1H NMR (270 MHz, $CDCl_3$) δ 1.03 (d, 3H, J = 7.3 Hz), 2.86 (d of quint., 1H, J = 3.9, 7.3 Hz), 3.84 (ddd, 1H, J = 2.4, 7.3, 10.7 Hz), 4.29 (dd, 1H, J = 3.9, 4.9 Hz), 4.45 (dd, 1H, J = 2.4, 5.1 Hz), 5.40 (d, 1H, J = 10.7 Hz), 5.87-5.96 (m, 2H), 6.08-6.24 (m, 2H), 6.27 (d, 1H, J = 5.1 Hz), 7.37 (d, 1H, J = 5.1 Hz); ^{13}C NMR (75 MHz, CD_3COCD_3) δ 15.5, 52.6, 54.8, 83.6, 85.4, 115.4, 120.1, 125.7, 126.1, 138.1, 138.9, 145.3, 150.9, 170.1; ^{13}C NMR (68 MHz, $CDCl_3$) δ 15.3, 50.7, 54.8, 83.4, 84.5, 115.3, 119.8, 125.3, 125.6, 136.4, 137.6, 143.5, 149.7, 163.6; HRMS calcd for $C_{14}H_{14}O_3$ (M^+) m/z 230.0943, found 230.0942. Compound (–)-**47** was obtained as white crystals: mp 112-115 °C; TLC R_f 0.81 (EtOAc:toluene, 1:1); $[\alpha]_D^{23}$ –148 (c 0.095, acetone); IR (KBr) 2960, 1750, 1660 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.05 (d, 3H, J = 7.3 Hz), 2.79 (d of quint., 1H, J = 3.4, 7.3 Hz), 3.40 (ddd, 1H, J = 3.4, 7.3, 11.7 Hz), 4.34 (dd, 1H, J = 3.4, 5.1 Hz), 4.46 (dd, 1H, J = 3.4, 5.1 Hz), 5.86 (dd, 1H, J = 2.0, 11.7 Hz), 5.91-5.98 (m, 2H), 6.11-6.20 (m, 2H), 6.24 (dd, 1H, J = 2.0, 5.4 Hz), 7.59 (d, 1H, J = 5.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 15.4, 52.7, 53.5, 82.7, 85.0, 114.5, 120.9, 125.1, 126.0, 136.4, 137.8, 139.1,

150.4, 165.9; HRMS calcd for $C_{14}H_{14}O_3$ (M^+) *m/z* 230.0943, found 230.0941.

Preparation of (–)-2 from (–)-47. To stirred solution of (–)-**47** (0.8 mg, 3.5 μmol) in pyridine (1 mL) was added MsCl (3 μL, 35 μmol). The mixture was stirred at 90 ℃ for 2 days, diluted with EtOAc (5 mL), and washed with H_2O (3 mL × 2) and saturated brine (3 mL). The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:7) to provide 0.5 mg (63%) of (–)-**2** and 0.2 mg (25%) of (–)-**47** was recovered.



1893A (**2**)

Table S1. NMR data of natural 1893A (**2**) and synthetic (–)-**2** (in CD_3COCD_3)

	^{13}C NMR		^{1}H NMR (multiplicity, $J_{H/H}$ Hz)	
No	natural (125 MHz)[a]	synthetic (75 MHz)	natural (500 MHz)[a]	synthetic (300 MHz)
1	170.1	170.1		
2	120.1	120.1	6.28 (d, 5.5)	6.29 (d, 5.5)
3	145.2	145.3	7.74 (d, 5.5)	7.75 (d, 5.5)
4	150.9	150.9		
5	115.4	115.4	5.54 (d, 11)	5.56 (d, 10.6)
6	54.9	54.8	3.71 (ddd, 3.5, 7, 11)	3.71 (ddd, 3.1, 7.5, 10.6)
7	83.7	83.6	4.43 (dd, 3.5, 5.5)	4.43 (dd, 3.1, 5.1)
8	138.1	138.1	6.18 (dd, 5.5, 8.5)	6.12~6.26 (m)
9	126.1	126.1	5.85 (dd, 7, 8.5)	5.85~5.92 (m)
10	125.7	125.7	5.89 (dd, 7, 8.5)	5.85~5.92 (m)
11	138.9	138.9	6.23 (dd, 5, 8.5)	6.12~6.26 (m)
12	85.4	85.4	4.25 (dd, 3.5, 5)	4.26 (dd, 3.6, 5.1)
13	52.5	52.6	2.83 (ddq, 3.5, 7, 7)	2.85 (m)
14	15.5	15.5	1.02 (d, 7)	1.01 (d, 7.0)

[a] ref) Chen, G.; Lin, Y.; Wen, L.; Vrijmoed, L. L. P.; Jones, E. B. G. *Tetrahedron* **2003**, *59*, 4907-4909.