***Z*-3-({(1*S*,2*R*,4*R*)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylthio)propenamide** A solution of 10-mercapto-2-*exo*-borneol[8] (8.0 g, 43 mmol) in MeOH/H_2O (9:1, 50 mL) was added dropwise to a solution of propiolamide[11] (3.0 g, 43 mmol) in MeOH/H_2O (9:1, 150 mL) with stirring at –20 °C. After being stirred at –20 °C for 15 min, Et_3N (15 drops) was added to the reaction mixture. The mixture was stirred at rt for 8 h and MeOH was evaporated. The aqueous layer was extracted with AcOEt (200 mL x 3). Combined extracts were washed with brine, dried over $MgSO_4$ and concentrated. The residue [10.8 g, a mixture of *Z* and *E* isomers (7:3) by ^{1}H-NMR] was recrystallized from AcOEt/hexane to give *Z*-3-({(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methyl-thio)propenamide (6.1 g, 56%) as colorless needles. mp 155–156 °C. $[\alpha]_D^{26}$ –25.1° (*c* 1.00, MeOH). IR (KBr) 3432, 3305, 3214, 2952, 2916, 1643, 1564, 1564, 1305 cm^{-1}. ^{1}H-NMR ($CDCl_3/CD_3OD$, 1:1) δ 0.89 and 1.06 (each 3H, s, Me x 2), 1.0–1.1 (1H, m, bornyl H), 1.2–1.3 (1H, m, bornyl H), 1.55–1.65 (1H, m, bornyl H), 1.7–1.8 (4H, m, bornyl H), 2.67 (1H, d, *J* = 12.6 Hz, 10-H^a), 3.17 (1H, d, *J* = 12.6 Hz, 10-H^b), 3.85 (1H, dd, *J* = 7.8 and 3.7 Hz, 2-H), 5.87 (1H, d, *J* = 10.0 Hz, CH=), 7.14 (1H, d, *J* = 10.0 Hz, CH=). MS *m/z* 255 (M^+). *Anal.* Calcd for $C_{13}H_{21}NO_2S$: C, 61.14; H, 8.29; N, 5.49. Found: C, 60.90; H, 8.32; N, 5.27.

***Z*-3-({(1*S*,2*R*,4*R*,R_S)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulfinyl)propenamide (2)** A solution of *m*-CPBA (80%, 1.264 g, 5.86 mmol) in dry CH_2Cl_2 (20 mL) was added dropwise to a solution of *Z*-3-({(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylthio)propenamide (1.271 g, 4.99 mmol) in dry CH_2Cl_2 (50 mL) with stirring at –20 °C under argon. After being stirred at –20 °C for 3 h, the reaction mixture was diluted with $CHCl_3$ (50 mL) and the organic layer was washed with 5% $NaHCO_3$ (50 mL) followed by brine (40 mL), dried over $MgSO_4$ and concentrated. The residue was recrystallized from AcOEt/MeOH/hexane to give **2** (1.02 g, 76%) as colorless prisms. mp 210–212 °C. $[\alpha]_D^{26}$ +330.1° (*c* 1.01, MeOH). IR (KBr) 3315, 3306, 3292, 3276, 3204, 2938, 2913, 1688, 1660, 1611, 1399, 1081, 1033 cm^{-1}. ^{1}H-NMR ($CDCl_3/CD_3OD$, 1:1) δ 0.87 and 1.08 (each 3H, s, Me x 2), 1.15–1.25 (1H, m, bornyl H), 1.5–1.6 (1H, m, bornyl H), 1.75–2.0 (5H, m, bornyl H), 3.02 (1H, d, *J* = 12.8 Hz, 10-H^a), 3.44 (1H, d, *J* = 12.8 Hz, 10-H^b), 4.04 (1H, dd, *J* = 7.9 and 4.2 Hz, 2-H), 6.51 (1H, d, *J* = 9.8 Hz, CH=), 6.79 (1H, d, *J* = 9.8 Hz, CH=). MS *m/z* 272 ($M^+ + 1$), 255 ($M^+ - O$). *Anal.* Calcd for $C_{13}H_{21}NO_3S$: C, 57.53; H, 7.80; N, 5.16. Found: C, 57.73; H, 7.77; N, 5.14.

Typical Procedure for Asymmetric Diels-Alder Reaction of a Dienophile (1 or 2) with a Diene (3–12) under Atmospheric Pressure Conditions A solution of a dienophile (**1**[7] or **2**) (0.20–0.83 mmol) and **3** (4.1–17 mmol) in dry CH_2Cl_2 (3–40 mL) or in dry CH_2Cl_2/MeOH (1:1) (3–40 mL) was stirred in a sealed tube under the conditions as shown in Table 1. After evaporation of the solvent, the residue was purified by column chromatography on silica gel with hexane followed by hexane/AcOEt (1:1) or AcOEt (for the reaction of **1** with **3**) or with hexane followed by $CHCl_3$/MeOH (10:1) (for the reaction of **2** with **3**). The ratio of products were determined by ^{1}H-NMR spectroscopy of the crude mixture.

Typical Procedure for Asymmetric Diels-Alder Reaction of a Dienophile (1 or 2) with a Diene (3–12) under High-Pressure Conditions A solution of a dienophile (**1** or **2**) (0.21–2.21 mmol) and **3** (4.1–22.8 mmol) in dry CH_2Cl_2 (10 mL) or in dry CH_2Cl_2/MeOH (1:1) (10 mL) was placed in a Teflon tube plugged with a Teflon stopper. The tube was placed in a high-pressure reactor and pressurized to 1.2 Gpa under the conditions as shown in Table 1. The pressure was released and the reaction mixture was

concentrated. The ratio of products was determined by ^{1}H-NMR spectroscopy of the crude mixture. Tl mixture from the reaction of **1** or **2** with **3** was purified by the procedure described as above. Tl products, yield and diastereomer excess are listed in Table 1.

(1*R*,*R*$_S$)-Methyl 3-*endo*-({(1*S*,2*R*,4*R*)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulf nyl)bicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylate (13a): Colorless plates. mp 136–139 °C (lit.,[6] m 130 °C). $[\alpha]_D^{26}$ –1.9° (*c* 0.33, $CHCl_3$) (lit.,[6] $[\alpha]_D^{20}$ +4.44° (*c* 1, $CHCl_3$)). IR ($CHCl_3$) 3392, 2955, 173 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.82 and 1.11 (each 3H, s, Me x 2), 1.1–1.9 (7H, m, bornyl H), 1.42 (1H, d, = 9.3 Hz, 7-H^a), 1.68 (1H, d, *J* = 9.3 Hz, 7-H^b), 2.94 (1H, d, *J* = 12.6 Hz, 10'-H^a), 3.05 (1H, d, *J* = 12. Hz, 10'-H^b), 3.35–3.4 (2H, m, 1-H and 2-H), 3.53 (1H, br s, 4-H), 3.63 (1H, dd, *J* = 8.8 and 3.3 Hz, 3-H 3.64 (3H, s, OMe), 4.03 (1H, dd, *J* = 8.0 and 4.1 Hz, 2'-H), 4.2-4.25 (1H, br, OH), 6.33 (1H, dd, *J* = 5. and 2.8 Hz, CH=), 6.49 (1H, dd, *J* = 5.5 and 2.8 Hz, CH=).

(1*R*,*R*$_S$)-3-*endo*-({(1*S*,2*R*,4*R*)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulfinyl)bicy-clo[2.2.1]hept-5-ene-2-*endo*-carboxamide (13b): Colorless needles. mp 277–278 °C. $[\alpha]_D^{26}$ +28.3° (0.73, MeOH). IR (KBr) 3374, 3206, 2967, 1660, 1391, 1074, 1031 cm^{-1}. ^{1}H-NMR ($CDCl_3$/CD_3OD 1:1) δ 0.82 and 1.08 (each 3H, s, Me x 2), 1.1–1.2 (1H, m, bornyl H), 1.4–1.45 (1H, m, bornyl H), 1.5 (1H, d, *J* = 11.0 Hz, 7-H^a), 1.6–1.85 (5H, m, bornyl H), 1.71 (1H, d, *J* = 10.9 Hz, 7-H^b), 2.95 (1H, d, *J* = 12.8 Hz, 10'-H^a), 3.01 (1H, d, *J* = 12.6 Hz, 10'-H^b), 3.36 (1H, br s, 1-H), 3.43 (1H, dd, *J* = 8.8 and 3.4 Hz, 2-H), 3.47 (1H, br s, 4-H), 3.56 (1H, dd, *J* = 8.8 and 3.4 Hz, 3-H), 4.02 (1H, dd, *J* = 8.2 and 4.0 Hz 2'-H), 6.31 (1H, dd, *J* = 5.7 and 2.9 Hz, CH=), 6.49 (1H, dd, *J* = 5.8 and 2.8 Hz, CH=). MS *m/z* 338 (M^+ + 1), 337 (M^+). *Anal.* Calcd for $C_{18}H_{27}NO_3S$: C, 64.06; H, 8.06, N, 4.15. Found: C, 64.04; H, 8.04; N 4.19.

(1*S*,*R*$_S$)-3-*exo*-({(1*S*,2*R*,4*R*)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulfinyl)bicy-clo[2.2.1]hept-5-ene-2-*exo*-carboxamide (14b): Crystalline mass (a mixture of **13b/14b**, 95:5). For **14b** ^{1}H-NMR ($CDCl_3$/CD_3OD, 1:1) δ (a mixture of **13b/14b**, 95:5): 0.83 and 1.07 (each 3H, s, Me x 2), 2.82 (1H, d, *J* = 12.8 Hz, 10'-H^a), 3.01 (1H, d, *J* = 12.6 Hz, 10'-H^b), 3.10 (1H, br s, 1-H), 3.41 (1H, d, *J* = 8.8 Hz, 2-H), 6.29 (1H, dd, *J* = 5.7 and 2.9 Hz, CH=), 6.36 (1H, dd, *J* = 5.7 and 2.9 Hz, CH=).

(1*R*,*R*$_S$)-Methyl 3-*endo*-({(1*S*,2*R*,4*R*)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulfi-nyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylate (13c): Colorless oil (a mixture of **13c/14c/ 15c/1**, 80:13:2:5) . For **13c**: ^{1}H-NMR ($CDCl_3$) (a mixture of **13c/14c/15c/1**, 80:13:2:5) δ 0.85 and 1.13 (each 3H, s, Me x 2), 1.1–1.9 (7H, m, bornyl H), 3.08 (1H, d, *J* = 12.6 Hz, 10'-H^a), 3.20 (1H, d, *J* = 12.6 Hz, 10'-H^b), 3.53 (1H, dd, *J* = 9.2 and 4.5 Hz, 2-H), 3.67 (3H, s, OMe), 3.85 (1H, dd, *J* = 9.2 and 4.5 Hz, 3-H), 3.99 (1H, dd, *J* = 8.6 and 4.1 Hz, 2'-H), 5.31 (1H, ddd, *J* = 4.5, 1.3 and 1.3 Hz, 1-H), 5.35 (1H, ddd, *J* = 4.5, 1.2 and 1.2 Hz, 4-H), 6.64 (1H, dd, *J* = 5.8 and 1.7 Hz, CH=), 6.83 (1H, dd, *J* = 5.8 and 1.5 Hz, CH=).

(1*S*,*R*$_S$)-Methyl 3-*exo*-({(1*S*,2*R*,4*R*)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulfi-nyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylate (14c): Colorless oil (a mixture of **13c/14c/15c/1**, 80:13:2:5) . For **14c**: ^{1}H-NMR ($CDCl_3$) (a mixture of **13c/14c/15c/1**, 80:13:2:5) δ 2.85 (1H, d, *J* = 8.1 Hz, 2-H), 2.90 (1H, d, *J* = 12.8 Hz, 10'-H^a), 3.09 (1H, d, *J* = 8.1 Hz, 3-H), 3.11 (1H, d, *J* = 13.0 Hz, 10'-H^b), 3.75 (3H, s, OMe), 4.05 (1H, dd, *J* = 8.4 and 4.2 Hz, 2'-H), 5.43 (1H, br s, 1-H), 5.64 (1H, br s, 4-H), 6.52 (1H, dd, *J* = 5.8 and 1.7 Hz, CH=), 6.54 (1H, dd, *J* = 5.8 and 1.7 Hz, CH=).

(1*S*,R_S)-Methyl 3-*endo*-({(1*S*,2*R*,4*R*)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulfinyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylate (15c): Colorless oil (a mixture of **13c/14c/15c/1**, 80:13:2:5) . For **15c**: ^{1}H-NMR ($CDCl_3$) (a mixture of **13c/14c/15c/1**, 80:13:2:5) δ 3.74 (3H, s, OMe), 5.07 (1H, m, 1-H), 5.23 (1H, m, 4-H), 6.42 (1H, dd, *J* = 5.8 and 1.7 Hz, CH=), 6.72 (1H, dd, *J* = 5.8 and 1.7 Hz, CH=).

(1*R*,R_S)-3-*endo*-({(1*S*,2*R*,4*R*)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulfinyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-*endo*-carboxamide (13d): Colorless plates. mp 182–185 °C (CH_2Cl_2/hexane). $[\alpha]_D^{26}$ +33.6° (*c* 0.75, MeOH). IR (KBr) 3376, 3192, 2945, 1696, 1659, 1392, 1323, 1075, 1028 cm^{-1}. ^{1}H-NMR ($CDCl_3$/CD_3OD) δ 0.81 and 1.09 (each 3H, s, Me x 2), 1.1–1.2 (1H, m, bornyl H), 1.35–1.45 (1H, m, bornyl H), 1.6–1.9 (5H, m, bornyl H), 2.97 (1H, d, *J* = 12.6 Hz, 10'-H^a), 3.07 (1H, d, *J* = 12.6 Hz, 10'-H^b), 3.50 (1H, dd, *J* = 8.8 and 4.7 Hz, 2-H), 3.72 (1H, dd, *J* = 8.8 and 4.3 Hz, 3-H), 3.99 (1H, dd, *J* = 8.3 and 4.1 Hz, 2'-H), 5.30 (1H, dd, *J* = 4.6 and 1.0 Hz, 1-H), 5.33 (1H, br d, *J* = 4.3 Hz, 4-H), 6.59 (1H, dd, *J* = 5.9 and 1.6 Hz, CH=), 6.86 (1H, dd, *J* = 5.9 and 1.6 Hz, CH=). MS *m/z* 272 ($M^+ - C_4H_4O + 1$), 68 (C_4H_4O). *Anal.* Calcd for $C_{17}H_{25}NO_4S$: C, 60.15; H, 7.42, N, 4.13. Found: C, 60.15; H, 7.12; N, 3.99.

(1*R*,R_S)-Methyl 3-*endo*-({(1*S*,2*R*,4*R*)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulfinyl)-1-methoxy-7-oxabicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylate (13e): Colorless oil (a mixture of **13e/14e**/unidentified compound/**1**, 49:13:29:9) . For **13e**: ^{1}H-NMR ($CDCl_3$) (a mixture of **13e/14e**/unidentified compound/**1**, 49:13:29:9) δ 0.84 and 1.12 (each 3H, s, Me x 2), 1.0–1.9 (7H, m, bornyl H), 2.83 (1H, d, *J* = 12.8 Hz, 10'-H^a), 3.20 (1H, d, *J* = 12.6 Hz, 10'-H^b), 3.34 (1H, d, *J* = 9.6 Hz, 2-H), 3.5–3.6 (1H, m, 3-H), 3.60 and 3.68 (each 3H, s, OMe x 2), 4.06 (1H, dd, *J* = 9.6 and 4.7 Hz, 2'-H), 5.17 (1H, dd, *J* = 4.5 and 1.9 Hz, 4-H), 6.68 (1H, d, *J* = 5.8 Hz, 6-H), 6.88 (1H, dd, *J* = 5.6 and 1.9 Hz, 5-H).

(1*S*,R_S)-Methyl 3-*exo*-({(1*S*,2*R*,4*R*)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulfinyl)-1-methoxy-7-oxabicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylate (14e): Colorless oil (a mixture of **13e/14e**/unidentified compound/**1**, 49:13:29:9) . For **14e**: ^{1}H-NMR ($CDCl_3$) (a mixture of **13e/14e**/unidentified compound/**1**, 49:13:29:9) δ 0.85 and 1.11 (each 3H, s, Me x 2), 2.35 (1H, d, *J* = 12.6 Hz, 10'-H^a), 2.93 (1H, d, *J* = 7.7 Hz, 2-H), 2.99 (1H, d, *J* = 12.8 Hz, 10'-H^b), 3.10 (1H, d, *J* = 7.9 Hz, 3-H), 3.76 and 3.84 (each 3H, s, OMe x 2), 5.44 (1H, d, *J* = 1.9 Hz, 4-H), 6.50 (1H, d, *J* = 5.8 Hz, 6-H), 6.65 (1H, dd, *J* = 5.7 and 2.0 Hz, 5-H).

(1*R*,R_S)-3-*endo*-({(1*S*,2*R*,4*R*)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulfinyl)-1-methoxy-7-oxabicyclo[2.2.1]hept-5-ene-2-*endo*-carboxamide (13f): Colorless needles. mp 182–184 °C. $[\alpha]_D^{26}$ –35.1° (*c* 0.77, MeOH). IR (KBr) 3380, 3204, 2954, 1697, 1662, 1341, 1075, 1033 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.82 and 1.11 (each 3H, s, Me x 2), 1.0–1.9 (7H, m, bornyl H), 3.09 (1H, d, *J* = 12.4 Hz, 10'-H^a), 3.24 (1H, d, *J* = 12.2 Hz, 10'-H^b), 3.33 (1H, d, *J* = 9.0 Hz, 2-H), 3.65 (3H, s, OMe), 4.0–4.05 (1H, m, 2'-H), 4.02 (1H, dd, *J* = 9.1 and 4.6 Hz, 3-H), 5.23 (1H, dd, *J* = 4.5 and 1.9 Hz, 4-H), 5.32 (1H, br s, NH), 6.33 (1H, br s, NH), 6.56 (1H, d, *J* = 5.8 Hz, 6-H), 7.00 (1H, dd, *J* = 5.3 and 1.9 Hz, 5-H). MS *m/z* 369 (M^+). *Anal.* Calcd for $C_{18}H_{27}NO_5S$: C, 58.51; H, 7.37; N, 3.79. Found: C, 58.16; H, 7.30; N, 3.91.

(1*R*,R_S)-Methyl 3-*endo*-({(1*S*,2*R*,4*R*)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulfinyl)bicyclo[2.2.2]oct-5-ene-2-*endo*-carboxylate (16a) Colorless needles. mp 149–151 °C. $[\alpha]_D^{26}$ –

18.9° (*c* 0.33, $CHCl_3$). IR (KBr) 3423, 2926 1735, 1719, 1647, 1429, 1162, 1078 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.82 and 1.10 (each 3H, s, Me x 2), 1.1–1.2 (1H, m, bornyl H), 1.25–1.9 (6H, m, bornyl H), 2.73 (1H, d, *J* = 13.2 Hz, 10'-H^a), 3.0–3.05 (1H, m, 1- or 4-H), 3.00 (1H, d, *J* = 12.6 Hz, 10'-H^b), 3.14 (1H, dd, *J* = 9.9 and 2.2 Hz, 3-H), 3.25 (1H, dd, *J* = 9.9 and 2.2 Hz, 2-H), 3.3–3.4 (1H, m, 4- or 1-H), 3.64 (3H, s, OMe), 4.02 (1H, ddd, *J* = 8.2, 4.4, and 3.3 Hz, 2'-H), 4.13 (1H, d, *J* = 2.7 Hz, OH), 6.39 (1H, ddd, *J* = 10.7, 6.3, and 1.9 Hz, 5- or 6-H), 6.43 (1H, ddd, *J* = 9.3, 6.3, and 1.9 Hz, 6- or 5-H). MS *m/z* 349 (M^+ – OH), 335 (M^+ – CH_3O). *Anal.* Calcd for $C_{20}H_{30}O_4S$: C, 65.57; H, 8.11. Found: C, 65.54; H, 8.25.

(1*R*,*R*$_S$)-3-*endo*-(1*S*,2*R*,4*R*)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulfinyl)bicyclo[2.2.2]oct-5-ene-2-*endo*-carboxamide (16b) Colorless plates. mp 268 °C (decomp). $[\alpha]_D^{27}$ –12.8° (*c* 0.35, $CHCl_3$). IR (KBr) 3380, 2940, 1661, 1408, 1075, 966 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.81 and 1.09 (each 3H, s, Me x 2), 1.05–1.1 (1H, m, bornyl H), 1.35–1.85 (6H, m, bornyl H), 2.82 (1H, d, *J* = 13.2 Hz, 10'-H^a), 2.95–3.0 (1H, m, 1- or 4-H), 2.99 (1H, d, *J* = 13.2 Hz, 10'-H^b), 3.03 (1H, brd, *J* = 10.4 Hz, 3-H), 3.21 (1H, dd, *J* = 9.9 and 2.7 Hz, 2-H), 3.35–3.5 (1H, m, 4- or 1-H), 4.01 (1H, ddd, *J* = 7.7, 3.8, and 3.8 Hz, 2'-H), 4.08 (1H, d, *J* = 2.7 Hz, OH), 5.38 (1H, br, NH), 5.77 (1H, br, NH), 6.49 (1H, dd, *J* = 7.1 and 7.1 Hz, 5- or 6-H), 6.59 (1H, ddd, *J* = 7.7, 6.3, and 1.1 Hz, 6- or 5-H). MS *m/z* 351 (M^+). *Anal.* Calcd for $C_{19}H_{29}NO_3S$: C, 64.92; H, 8.32, N, 3.99. Found: C, 64.97; H, 8.27; N, 3.92.

(1*R*,*R*$_S$)-Methyl 9,10-Dihydro-12-*endo*-{(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulfinyl-9,10-ethanoanthracene-11-*endo*-carboxylate (17) Yellow plates. mp 236–238 °C. $[\alpha]_D^{27}$ +9.06° (*c* 0.20, $CHCl_3$). IR (KBr) 3396, 2938 1732, 1458, 1232, 1076, 1053, 1000 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.74 and 1.04 (each 3H, s, Me x 2), 0.8–1.9 (7H, m, bornyl H), 2.69 (1H, d, *J* = 12.6 Hz, 10'-H^a), 3.01 (1H, d, *J* = 12.6 Hz, 10'-H^b), 3.33 (1H, dd, *J* = 9.9 and 2.2 Hz, 11- or 12-H),), 3.38 (1H, dd, *J* = 9.9 and 1.6 Hz, 11- or 12-H), 3.61 (3H, s, OMe), 4.01 (1H, ddd, *J* = 7.1, 4.4 and 2.7 Hz, 2'-H), 4.15 (1H, d, *J* = 2.7 Hz, OH), 4.70 (1H, d, *J* = 2.2 Hz, 9- or 10-H), 5.09 (1H, d, *J* = 2.2 Hz, 4- or 1-H), 7.1–7.25 (4H, m, ArH x 4), 7.3–7.35 (2H, m, ArH x 2), 7.4–7.45 (1H, m, ArH), 7.45–7.5 (1H, m, ArH). MS *m/z* 463 (M^+ – 1). *Anal.* Calcd for $C_{28}H_{32}O_4S$: C, 72.38; H, 6.94. Found: C, 72.15; H, 6.87.

Methyl 4-Hydroxybenzoate (18) Colorless plates. mp 125–128 °C (lit.,[12] mp 127 °C). IR (KBr) 3312, 1681, 1607, 1589, 1514, 1435, 1279, 850 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 3.81 (3H, s, OMe), 5.97 (1H, s, OH), 6.97 (2H, d, *J* = 8.8 Hz, ArH x 2), 7.87 (2H, d, *J* = 8.8 Hz, ArH x 2). MS *m/z* 152 (M^+). HRMS calcd for $C_8H_8O_2$: 152.0473. Found: 152.0484.

Methyl *E*-3-({(1*S*,2*R*,4*R*,*R*$_S$)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulfinyl)propenoate (19) Colorless oil. $[\alpha]_D^{29}$ –98.6° (*c* 0.37, $CHCl_3$). IR (neat) 3436, 2953, 1728, 1296, 1078, 1037 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.85 and 1.08 (each 3H, s, Me x 2), 0.8–1.9 (7H, m, bornyl H), 2.58 (1H, d, *J* = 13.2 Hz, 10'-H^a), 3.27 (1H, d, *J* = 13.2 Hz, 10'-H^b), 3.62 (1H, d, *J* = 3.3 Hz, OH), 3.83 (3H, s, OMe), 4.12 (1H, ddd, *J* = 8.2, 3.7, and 3.7 Hz, 2'-H), 6.71 (1H, d, *J* = 14.8 Hz, CH=), 7.63 (1H, d, *J* = 15.3 Hz, CH=). ^{13}C-NMR ($CDCl_3$) δ 20.0 (CH_3), 20.6 (CH_3), 27.3 (CH_2), 30.8 (CH_2), 38.7 (CH_2), 45.2 (CH), 48.6 (C), 51.7 (C), 52.6 (OCH_3), 55.1 (CH_2), 77.1 (CH), 126.0 (CH), 149.8 (CH), 164.3 (CO). MS *m/z* 287 (M^+ + 1), 270 (M^+ – O). HRMS calcd for $C_{14}H_{22}O_4S$: 286.1239. Found: 286.1257.

Methyl *E*-3-({(1*S*,2*R*,4*R*,*S*$_S$)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulfinyl)propenoate (20) Colorless oil. $[\alpha]_D^{27}$ +77.5° (*c* 0.34, $CHCl_3$). IR (neat) 3408, 2953, 1728, 1296, 1076, 1037

cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.84 and 1.12 (each 3H, s, Me x 2), 0.8–1.9 (7H, m, bornyl H), 2.59 (1H, d, *J* = 14.3 Hz, 10'-H^a), 3.08 (1H, d, *J* = 3.8 Hz, OH), 3.51 (1H, d, *J* = 13.7 Hz, 10'-H^b), 3.83 (3H, s, OMe), 4.08 (1H, ddd, *J* = 7.1, 3.7, and 3.7 Hz, 2'-H), 6.69 (1H, d, *J* = 14.8 Hz, CH=), 7.71 (1H, d, *J* = 14.8 Hz, CH=). ^{13}C-NMR ($CDCl_3$) δ 20.8 (CH_3), 21.1 (CH_3), 28.1 (CH_2), 32.4 (CH_2), 40.8 (CH_2), 45.4 (CH), 49.9 (C), 53.0 (C), 53.3 (OCH_3), 53.6 (CH_2), 76.7 (CH), 126.0 (CH), 151.5 (CH), 164.5 (CO). MS *m/z* 287 (M^+ + 1), 270 (M^+ – O). HRMS calcd for $C_{14}H_{22}O_4S$: 286.1239. Found: 286.1261.

(1*S*)-Methyl 5,6-*exo*-Dihydroxy-3-*endo*-({(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}-methylsulfonyl)-1-methoxy-7-oxabicyclo[2.2.1]heptane-2-*endo*-carboxylate (21e) A mixture of the sulfoxide **(1)** (419 mg, 1.46 mmol) and 2-methoxyfuran **(5)** (453 mg, 4.62 mmol) in dry CH_2Cl_2 (10 mL) was placed in a Tefron tube plugged with a Tefron stopper. The tube was placed in a high-pressure reactor and pressurized to 1.2 GPa at rt for 3 days. The pressure was released and the reaction mixture was concentrated to give a colorless oil (784 mg). A part of the resulting residue (327 mg) was subjected to the following reaction promptly because of the instability of the adducts. 0.1 M Solution of OsO_4 in *t*-BuOH (0.43 mL, 0.043 mmol) and triethylamine *N*-oxide dihydrate (377 mg, 3.4 mmol) were added to a solution of the crude adducts (327 mg) in acetone (18 mL) at 0 °C. The mixture was allowed to warm to rt with stirring for 3 h 20 min and concentrated. The residue was purified by flash column chromatography on silica gel with AcOEt and by subsequent recrystallization from CH_2Cl_2 to give **21e** (141 mg) as colorless plates. Calculated yield of **21e** from **1** was 53%. mp 189-191 °C. $[\alpha]_D^{25}$ +5.86° (*c* 4.15, $CHCl_3$). IR (KBr) 3356, 2956, 1732, 1332, 1073 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.80 and 1.09 (each 3H, s, Me x 2), 1.1–1.9 (7H, m, bornyl H), 2.57 (1H, d, *J* = 12.6 Hz, 10'-H^a), 2.8–3.0 (1H, br, OH), 3.13 (1H, d, *J* = 12.6 Hz, 10'-H^b), 3.4–3.85 (2H, br, OH x 2), 3.52 (1H, dd, *J* = 11.5, 4.9 Hz, 3-H), 3.58 (1H, dd, *J* = 11.5, 1.1 Hz, 2-H), 3.67 and 3.75 (each 3H, s, OMe x 2), 4.04 (1H, dd, *J* = 8.5, 4.1 Hz, 2'-H), 4.07 (1H, d, *J* = 6.6 Hz, 5-H), 4.58 (1H, dd, *J* = 4.9, 1.1 Hz), 4.76 (1H, d, *J* = 6.0 Hz, 6-H). MS *m/z* 434 (M^+). *Anal.* Calcd for $C_{19}H_{30}O_9S$: C, 52.52; H, 6.96. Found: C, 52.53; H, 6.86.

(1*S*)-5,6-*exo*-Dihydroxy-3-*endo*-({(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}-methylsulfonyl)-1-methoxy-7-oxabicyclo[2.2.1]heptane-2-*endo*-carboxamide (21f) 0.1 M Solution of OsO_4 in *t*-BuOH (0.80 mL, 0.080 mmol) and triethylamine *N*-oxide dihydrate (1.20 g, 10.8 mmol) were added at 0 °C to an acetone/MeOH (10:3, 39 mL) solution of the crude adducts, which were prepared from dienophile **(2)** (600 mg, 2.21 mmol) and 2-methoxyfuran **(5)** (2.1 mL, 22.8 mmol) in CH_2Cl_2/MeOH (1:1, 10 mL). After being stirred for 21 h at 0 °C, the reaction mixture was concentrated. The residue was purified by flash column chromatography on silica gel with $CHCl_3$/MeOH (20:1) and by subsequent recrystallization from CH_2Cl_2/hexane/MeOH to give **21f** (586 mg, 63%) as colorless needles. mp 200–202 °C. $[\alpha]_D^{26}$ –19.5° (*c* 0.81, MeOH). IR (KBr) 3462, 3184, 2956, 1675, 1651, 1325, 1163 cm^{-1}. ^{1}H-NMR ($CDCl_3$/MeOH) δ 0.84 and 1.09 (each 3H, s, Me x 2), 1.1–1.25 (1H, m, bornyl H), 1.4-1.55 (1H, m, bornyl H), 1.7–1.9 (5H, m, bornyl H), 2.91 (1H, d, *J* = 12.6 Hz, 10'-H^a), 3.09 (1H, d, *J* = 12.6 Hz, 10'-H^b), 3.50 (1H, dd, *J* = 11.0, 1.1 Hz, 2-H), 3.56 (1H, dd, *J* = 11.0, 4.9 Hz, 3-H), 3.69 (3H, s, OMe), 4.02 (1H, dd, *J* = 8.2, 3.8 Hz, 2'-H), 4.14 (1H, d, *J* = 6.6 Hz, 6- or 5-H), 4.47 (1H, dd, *J* = 4.9, 1.1 Hz, 4-H), 4.66 (1H, d, *J* = 6.0 Hz, 5- or 6-H). MS *m/z* 404 (M^+ + 1). *Anal.* Calcd for $C_{18}H_{29}NO_8S$: C, 51.53; H, 6.97; N, 3.34. Found: C, 51.29; H, 7.09; N, 3.39.

(1*S*)-Methyl 5,6-*O*,*O*-Isopropylidene-5,6-*exo*-dihydroxy-3-*endo*-({(1*S*,2*R*,4*R*)-2-hydroxy-7,7-di methylbicyclo[2.2.1]heptan-1-yl}methylsulfonyl)-1-methoxy-7-oxabicyclo[2.2.1]-heptane-2-*endo*-carboxylate (22) 2,2-Dimethoxypropane (450 mg, 4.3 mmol) and catalytic amount of *p*-toluenesulfoni acid were added to a solution of **21e** (187 mg, 0.43 mmol) in acetone (7 mL) and the reaction mixture wa refluxed for 5 h. After concentration of the reaction mixture, CH_2Cl_2 (50 mL) was added to the residue The organic layer was washed with saturated $NaHCO_3$ (50 mL) and brine (50 mL), dried over $MgSO_4$ and concentrated to give a brownish oil (192 mg). The residue was purified by flash colum chromatography on silica gel with hexane/AcOEt (1:1) and by subsequent recrystallization from CH_2Cl_2 to give **22** (130 mg, 64%) as colorless needles. mp 164–167 °C. $[\alpha]_D^{26}$ –6.67° (*c* 5.21, $CHCl_3$). IR (KBr 3364, 2946, 1735, 1626, 1374, 1316, 1155, 1021 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.80 and 1.10 (each 3H, s Me x 2), 1.1–1.9 (7H, m, bornyl H), 1.32 and 1.53 (each 3H, s, Me x 2), 2.55 (1H, d, *J* = 12.1 Hz, 10'-H^a) 3.11 (1H, d, *J* = 12.6 Hz, 10'-H^b), 3.50 (1H, d, *J* = 11.0 Hz, 2-H), 3.56 (1H, dd, *J* = 11.5, 5.0 Hz, 3-H) 3.67 and 3.76 (each 3H, s, OMe x 2), 3.88 (1H, br d, *J* = 2.2 Hz, OH), 4.0–4.1 (1H, m, 2'-H), 4.41 (1H, d *J* = 6.0 Hz, CH=), 4.63 (1H, dd, *J* = 5.0, 1.1 Hz, 4-H), 5.10 (1H, d, *J* = 5.5 Hz, CH=). MS *m/z* 434 (M^+ - CH_3O). *Anal.* Calcd for $C_{22}H_{34}O_9S$: C, 55.68; H, 7.22. Found: C, 55.87; H, 7.22.

(1*S*)-2-*endo*-Crotonyloxymethyl-5,6-*O*,*O*-isopropylidene-5,6-*exo*-dihydroxy-3-*endo*-({(1*S*, 2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulfonyl)-1-methoxy-7-oxabicyclo[2.2.1]heptane (24) $LiAlH_4$ (6.4 mg 0.17 mmol) was added portionwise to a solution of **22** (26.7 mg, 0.056 mmol in THF (5 mL) and the reaction mixture was stirred at –20 °C under nitrogen for 3 h. The reaction wa quenched with anhydrous Na_2SO_4 followed by saturated Na_2SO_4 and the whole mixture was stirred at r for 30 min. The precipitates were filtered off and washed with acetone followed by $CHCl_3$. The combine filtrate was dried over $MgSO_4$ and concentrated to give a colorless oil (25.7 mg). The crude product wa subjected to next reaction without purification because of its instability on silica gel. For **23**: ^{1}H-NMF ($CDCl_3$) δ 0.83 and 1.12 (each 3H, s, Me x 2), 1.1–1.9 (7H, m, bornyl H), 1.32 and 1.53 (each 3H, s, M x 2), 2.6-2.8 (1H, m, 2-H), 3.00 (1H, d, *J* = 13.2 Hz, 10'-H^a), 3.33 (1H, d, *J* = 12.6 Hz, 10'-H^b), 3.48 (1H dd, *J* = 11.5, 5.5 Hz, 3-H), 3.64 (3H, s, OMe), 3.8-3.95 (2H, m, C*H*$_2$OH), 3.95–4.05 (1H, m, 2'-H), 4.4((1H, d, *J* = 5.5 Hz, CH=), 4.60 (1H, d, *J* = 5.5, Hz, 4-H), 5.14 (1H, d, *J* = 6.1 Hz, CH=). MS *m/z* 415 (M^+ – CH_3O), 399 (M^+ – CH_3O – OH).

Crotonic anhydride (34 μL, 0.21 mmol) was added dropwise to a mixture of **23** (25.7 mg), pyridine (1 μL, 0.22 mmol) and catalytic amount of 4-dimethylaminopyridine in benzene (1 mL) and the mixture wa stirred at rt for 22 h. CH_2Cl_2 was added to the reaction mixture and washed with 1N HCl. The combine organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified b flash column chromatography on silica gel with hexane/AcOEt (9:1 to 3:1), AcOEt gave **24** (8.8 mg 30%) as colorless needles. mp 162–164 °C. $[\alpha]_D^{28}$ –74.3° (*c* 2.72, $CHCl_3$). IR (KBr) 3416, 2955, 1724 1656, 1372, 1308, 1176, 1078 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.83, 1.13 and 1.32 (each 3H, s, Me x 3), 1.4– 1.9 (7H, m, bornyl H), 1.54 (3H, s, Me), 1.89 (3H, dd, *J* = 7.1, 1.6 Hz, C*H*$_3$CH), 2.71 (1H, d, *J* = 12.6 Hz 10'-H^a), 2.88 (1H, ddd, *J* = 11.5, 9.1, 5.2 Hz, 2-H), 3.37 (1H, d, *J* = 12.6 Hz, 10'-H^b), 3.51 (1H, dd, *J* = 11.8, 5.8 Hz, 3-H), 3.62 (3H, s, OMe), 3.84 (1H, br d, *J* = 3.3 Hz, OH), 4.00 (1H, ddd, *J* = 8.2, 4.4, 3.3 Hz, 2'-H), 4.28 (1H, dd, *J* = 11.8, 9.1 Hz, C*H*HO), 4.36 (1H, dd, *J* = 11.8, 5.2 Hz, C*H*HO), 4.37 (1H, d,

= 5.5 Hz, CH=), 4.62 (1H, d, J = 5.5 Hz, 4-H), 5.16 (1H, d, J = 5.5 Hz, CH=), 5.83 (1H, dq, J = 15.4, 1.6 Hz, CH_3CH=C*H*), 7.05 (1H, dq, J = 15.4, 6.8 Hz, CH_3C*H*=CH). MS *m/z* 483 ($M^+ - CH_3O$). *Anal.* Calcd for $C_{25}H_{38}O_9S$: C, 58.34; H, 7.44. Found: C, 58.38; H, 7.32.

(–)-COTC (25) 80% Aqueous TFA (3 mL) was added to **24** (158 mg, 0.31 mmol) at –20 °C and the whole mixture was stirred at the same temperature for 7 h. The reaction mixture was concentrated. The residue was washed with hexane and crystallized from AcOEt/MeOH/hexane to give **25** (22 mg, 29%) as colorless needles. mp 176–178 °C (lit.,[9] mp 181 °C and lit.,[3c] mp 179–181 °C). $[\alpha]_D^{28}$ –109.7° (*c* 0.23, MeOH) (lit.,[9] $[\alpha]_D^{24}$ –109° (*c* 1.5, MeOH) and lit.,[3c] $[\alpha]_D$ –108° (*c* 0.23, MeOH)). IR (KBr) 3423, 3204, 2944, 1713, 1687, 1654 cm^{-1}. ^{1}H-NMR (CD_3OD) δ 1.89 (3H, dd, J = 7.1, 1.6 Hz, Me), 4.28 (1H, d, J = 2.2 Hz, 6-H), 4.36 (1H, ddd, J = 3.3, 2.7, 2.2 Hz, 5-H), 4.64 (1H, dd, J = 3.0, 1.9 Hz, 4-H), 4.75 (1H, ddd, J = 13.7, 1.6, 1.6 Hz, C*H*HO), 4.86 (1H, ddd, J = 13.7, 2.2, 1.6 Hz, C*H*HO), 5.89 (1H, dq, J = 15.9, 1.6 Hz, CH_3CH=C*H*), 6.70 (1H, br s, 3-H), 7.02 (1H, dq, J = 15.5, 6.9 Hz, CH_3C*H*=CH). MS *m/z* 213 ($M^+ - C_2H_5$).

(–)-Gabosine C (26) 80% Aqueous TFA (10 mL) was added at –20 °C to **23**, which was prepared from **22** (447 mg, 0.94 mmol) and $LiAlH_4$ (108 mg, 2.83 mmol) in THF (50 mL), and the whole mixture was stirred at the same temperature for 6 h. The reaction mixture was concentrated. The residue was purified by PLC on cellulose with *n*-BuOH/EtOH/H_2O (4:1:2) to give **26** (84 mg, 51% from **22**) as colorless needles. mp 114–115 °C (lit.,[10a,c] mp 113–114 °C and lit.,[10b] mp 112–113 °C). $[\alpha]_D^{28}$ –166° (*c* 0.17, H_2O) (lit.,[10a] $[\alpha]_D^{20}$ –168° (*c* 1.0, H_2O), lit.,[10b] $[\alpha]_D^{20}$ –170° (*c* 1.0, H_2O) and lit.,[10c] $[\alpha]_D^{20}$ –165.7° (*c* 0.2, H_2O)). IR (KBr) 3456, 2924, 1687 cm^{-1}. ^{1}H-NMR (CD_3OD) δ 4.2–4.3 (3H, m, 6-H, C*H*$_2$OH), 4.36 (1H, ddd, J = 3.3, 2.8, 2.2 Hz, 5-H), 4.63 (1H, m, 4-H), 6.68 (1H, m, 3-H). ^{13}C-NMR (CD_3OD) δ 59.4 (CH_2), 69.4 (CH), 76.9 (CH), 77.8 (CH), 137.8 (C), 145.1 (CH), 199.3 (CO). MS *m/z* 174 (M^+), 156 ($M^+ - H_2O$), 138 ($M^+ - 2H_2O$).

X-Ray Crystallographic Analysis of 13b A colorless plate crystal of $C_{18}H_{27}NO_3S$ having approximate dimentions of 0.40 x 0.30 x 0.05 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation and 12 kW rotating anode generator. Crystal data for **13b**: monoclinic, space group, $P2_1$ with a = 10.971(3) Å, b = 7.338(2) Å, c = 12.159(3) Å, β = 116.08(2)°, V = 879.1(4) Å^3, and Z = 2 (d_{calcd} = 1.275 g cm^{-3}), μ(MoK_α) = 2.98 cm^{-1} absorption corrected by ω scans; 2290 unique reflections; 2181 with $I > 3.00\sigma(I)$ were used in refinement; R = 4.3%, R_w = 4.4%.

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REFERENCES AND NOTES

† Dedicated to Professor James P. Kutney on the occasion of his 70th birthday.

‡ Fellow of the Science and Technology Agency of Japan, on leave from National Institute of Healtl Sciences.

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