Asymmetric Catalysis on the Intramolecular Cyclopropanation of α -Diazo- β -Ketosulfones

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General Information. ^1H and ^{13}C NMR spectra were recorded on a JEOL AL-400 spectrometer. ^1H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) with the solvent resonances as internal standards. The following abbreviations were used to explain the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; band, several overlapping signals; b, broad. IR spectra were recorded on a JASCO FT/IR-8300. Melting points (mp) are uncorrected, recorded on a Yamato capillary melting point apparatus. Optical rotations were measured using a 2 ml cell with a 1 dm path length on a JASCO DIP-1000. Chiral HPLC analysis was performed on a JASCO PU-980 and UV-970. Mass spectra and elemental analyses were provided at the Materials Characterization Central Laboratory, Waseda University. All reactions were carried out under an argon atmosphere with dry, freshly distilled solvents under anhydrous conditions, unless otherwise noted. All reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and phosphomolybdic acid and heat as developing agents. E. Merck silica gel (60, particle size 0.040-0.063 mm) was used for flash column chromatography. Preparative thin-layer chromatography (PTLC) separations were carried out on self-made 0.3 mm E. Merck silica gel plates (60F-254).

Materials. THF was distilled from sodium/benzophenone ketyl, and methylene chloride (CH_2Cl_2), benzene, and toluene from calcium hydride. Toluene was distilled from sodium. DMF was distilled from CaH_2 under reduced pressure. $(\text{CuOTf})_2\text{C}_6\text{H}_6$ and all other reagents were purchased from Aldrich, TCI, or Kanto Chemical co. Ltd.

Caution! : Although authors prepared ca. 50 g of **4b** from **3b** according to the procedure below without any trouble, diazo compounds are potentially explosive and therefore must be handled with caution.

(4*S*)-2, 2'-(1-Methylethylidene)bis[4-(1-methylethyl)-4, 5-dihydrooxazole] (**2a**),^{7a} (4*S*)-2, 2'-(1-Methylethylidene)bis(4-phenylmethyl-4, 5-dihydrooxazole) (**2b**),^{7b} (4*S*)-2, 2'-(1-Methylethylidene)bis[4-(1, 1-dimethylethyl)-4, 5-dihydrooxazole] (**2c**),^{7a} (4*S*)-2, 2'-(1-Ethylpropylidene)bis[4-(1-methylethyl)-4, 5-dihydrooxazole] (**2d**)^{7c} were prepared by the literature methods (see the corresponding references).

7 (a) Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726-728. (b) Denmark, S. E.; Nakajima, N.; Nicaise, O. J.-C.; Faucher, A.-M.; Edwards, J. P. *J. Org. Chem.* **1995**, *60*, 4884-4892. (c) von Matt, P.; Lloyd-Jones, G. C.; Minidis, A. B. E.; Pfaltz, A.; Macko, L.; Neuburger, M.; Zehnder, M.; Rueegger, H.; Pregosin, P. S. *Helv. Chim. Acta* **1995**, *78*, 265-284.

(4S)-2, 2'-(1-Phenylmethyl-2-phenylethylidene)bis[4-(1-methylethyl)-5-dihydrooxazole (2e)

Dibenzylcyanomalonate (1.86 g, 7.55 mmol) was dissolved in PhCl (100 ml) and to the solution was added L-valinol (2.34 g, 22.7 mmol), and ZnCl_2 (3.09 g, 22.7 mmol). The reaction mixture was refluxed for 1 day. The reaction mixture was cooled to ambient temperature, quenched with a solution of ethylenediamine (20 ml) in H_2O (100 ml). Then the mixture was stirred for 1h. After extraction with CH_2Cl_2 (100 ml x 1, 50ml x 2), the combined organic layer was dried over Na_2SO_4 , evaporated, and residue was purified by flash chromatography (hexane/ethyl acetate=9:1) to afford pure **2e** (3.04g, 96%) in the form of a white solid.: $R_f=0.39$ (hexane/ethyl acetate=3/1); $[\alpha]_D^{23} +86.9$ (c 1.03, CHCl_3); mp 70-71 °C (ethyl acetate); IR (KBr): 3087, 2971, 2943, 2460, 2407, 2114, 1673, 1602, 1458, 1444, 1323, 1302, 1237, 1176, 1146, 894, 732 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3); $\delta=7.35\text{-}7.16$ (m, 12H), 4.25-4.06 (m, 2H), 3.94-3.81 (m, 4H), 3.40 (d, $J=14\text{Hz}$, 2H), 3.19 (d, $J=14\text{Hz}$, 2H), 1.69 (m, 2H), 0.86 (d, $J=6.6\text{Hz}$, 6H), 0.82 (d, $J=6.6\text{Hz}$, 6H); ^{13}C NMR (100 MHz, CDCl_3); $\delta=166.1, 136.9, 130.4, 127.8, 126.5, 72.0, 69.8, 48.3, 39.3, 32.5, 19.0, 18.0$; FAB MS $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{35}\text{N}_2\text{O}_2$: 419.2700, found: 419.2713.

Methyl (1R)-2-oxobicyclo[3.1.0]hexane-1-carboxylate (1a)

A toluene azeotroped $[\text{CuOTf}]_2 \cdot \text{C}_6\text{H}_6$ (4.3 mg, 0.0085 mmol) was placed in a dried flask (10 ml) under Ar atmosphere and to this flask was added a solution of toluene azeotroped ligand **2a** (7.4 mg, 0.028 mmol) in toluene (0.5 ml x 3) via a canula. The mixture was stirred at room temperature for 1h and then to the light blue solution was added a solution of toluene azeotroped methyl 2-diazo-3-oxo-6-heptenoate (34.0 mg, 0.187 mmol) in toluene (0.5 ml x 3) via a canula. The reaction mixture was stirred at 50 °C for 4h, then cooled to room temperature, quenched with NH_4OH aqueous solution (2 ml), extracted with ether (2 ml), and CH_2Cl_2 (2 ml x 3). The combined organic layer was washed with brine (5 ml), dried over Na_2SO_4 , and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=8/1) to afford the known methyl (1R)-2-oxobicyclo [3.1.0]hexane-1-carboxylate **1a** (16.5 mg, 56% ee, 57%) as a viscous oil. $R_f=0.19$ (hexane/ethyl acetate=4/1). Ee was determined by ^1H NMR using chiral shift reagent ($\text{Eu}(\text{hfc})_3$).

1-Methyl-1-phenylethyl (1R)-2-oxobicyclo[3.1.0]hexane-1-carboxylate (1b)

A toluene azeotroped $[\text{CuOTf}]_2 \cdot \text{C}_6\text{H}_6$ (5.3 mg, 0.011 mmol) was placed in a dried flask (10 ml) under Ar atmosphere and to this flask was added a solution of toluene azeotroped ligand **2a** (10.3 mg, 0.039 mmol) in toluene (0.5 ml x 3) via a canula. The mixture was stirred at room temperature for 1h and then to the light blue solution was added a solution of toluene azeotroped 1-methyl-1-phenylethyl 2-diazo-3-oxo-6-heptenoate (30.3 mg, 0.106 mmol) in toluene

(0.5 ml x 3) via a canula. The reaction mixture was stirred at room temperature for 2h, but the reaction did not occurred. Hence, the reaction mixture was stirred at 50 °C for 1h, then cooled to room temperature, quenched with NH₄OH aqueous solution (2 ml), extracted with ether (2 ml), and CH₂Cl₂ (2 ml x 3). The combined organic layer was washed with brine (5 ml), dried over Na₂SO₄, and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=12/1) to afford 1-methyl-1-phenylethyl (1*R*)-2-oxobicyclo[3.1.0]hexane-1-carboxylate **1b** (21.1 mg, 48% ee, 77%) as a viscous oil. **1b** was successfully converted to the known **1a**, hence, the absolute configuration was determined by comparison of the optical rotation. Ee was determined by HPLC (254 nm); Daicel Chiral Cell OD-H 0.46 cm ϕ x 25 cm; hexane/isopropanol=9/1; flow rate=0.5 ml/min; retention time : 15.1 min for **1b**, 17.1 min for *ent*-**1b**; R_f =0.52 (hexane/ethyl acetate=2/1); $[\alpha]_D^{25}$ -29.6 (c 0.48, CHCl₃, 48% ee); IR(neat): 2984, 1758, 1730, 1448, 1380, 1324, 1306, 1268, 1194, 1142, 1096, 1032, 764, 702 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ =7.45-7.40 (m, 2H), 7.36-7.30 (m, 2H), 7.26-7.21 (m, 1H), 2.58-2.52 (m, 1H), 2.30-2.15 (m, 3H), 2.03-1.95 (m, 2H), 1.81 (s, 3H), 1.79 (s, 3H), 1.33 (t, J =5.1Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ =206.9, 166.7, 145.6, 128.2, 126.9, 124.3, 82.9, 38.6, 33.8, 32.5, 28.8, 28.4, 21.6, 21.0; HRMS(FAB): m/z calcd for C₁₆H₁₈O₃H⁺ 259.1334, found 259.1311.

(1-Methyl-1-phenylethyl 2-diazo-3-oxo-6-heptenoate)

Procedure A : To a solution of 1-methyl-1-phenylethyl 3-oxo-6-heptenoate (598.3 mg, 2.30 mmol) in CH₃CN (20 ml) was added triethylamine (0.95 ml, 6.81 mmol) at 0 °C, and then a solution of *p*-toluenesulfonyl azide (908.0 mg, 4.60 mmol) in CH₃CN (2.5 ml x 2) via a canula. The reaction mixture was stirred at room temperature for 3h. The light yellow reaction mixture was quenched with 3*N* KOH aqueous solution (20 ml), extracted with ether (20 ml), and CH₂Cl₂ (10 ml x 3). The combined organic layer was washed with brine (30 ml), dried over Na₂SO₄, and evaporated. The residue was purified by flash chromatography (hexane/CH₂Cl₂=1/1) to afford 1-methyl-1-phenylethyl 2-diazo-3-oxo-6-heptenoate (610.0 mg, 93%) as a yellow oil: R_f =0.56 (hexane/EA=4/1); IR(neat): 2984, 2136, 1720, 1656, 1384, 1368, 1314, 1274, 1212, 1134, 1100, 1032, 994, 764, 698 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ =7.38-7.26 (m, 5H), 5.79(ddt, J =17.1, 10.3, 6.6Hz, 1H), 5.02 (ddt, J =17.1, 1.7, 1.7Hz, 1H), 4.95 (ddt, J =10.3, 1.7, 1.2Hz, 1H), 2.88 (t, J =7.3Hz, 2H), 2.38-2.31 (m, 2H), 1.85 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ =192.1, 159.8, 144.7, 136.8, 128.4, 127.3, 124.0, 115.2, 83.9, 39.3, 28.8, 28.2; HRMS(FAB): m/z calcd for C₁₆H₁₈N₂O₃H⁺ 287.1395, found 287.1410.

(1-Methyl-1-phenylethyl 3-oxo-6-heptenoate)

To a suspension of NaH (60%, 138.1 mg, 3.45 mmol) in THF (30 ml) was added a solution of toluene azeotroped 1-methyl-1-phenylethyl 3-oxo-butyrate (634.6 mg, 2.88 mmol) in THF (2 ml x 3) via a canula at 0 °C. To this reaction mixture was added *n*BuLi (1.59 M in hexane, 1.80 ml, 2.86mmol) at 0 °C, and then was added allylbromide (0.25 ml, 2.88 ml) at -78 °C. The reaction mixture was warmed to room temperature and stirred for 2h. The reaction was stopped

with saturated aqueous NH_4Cl solution (20 ml), extracted with ether (5 ml), and CH_2Cl_2 (10 ml x 3). The combined organic layer was washed with brine (10 ml), dried over Na_2SO_4 , and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=15/1) to afford 1-methyl-1-phenylethyl 3-oxo-6-heptenoate (624.0 mg, 83 %) as a viscous oil: R_f =0.49 (hexane/EA=4/1); IR(neat): 2984, 1742, 1716, 1408, 1368, 1320, 1274, 1138, 1104, 1078, 916, 764, 700 cm^{-1} ; ^1H NMR(400 MHz, CDCl_3): δ =7.39-7.23 (m, 5H), 5.80 (ddt, J =17.1, 10.3, 6.6Hz, 1H), 5.03 (ddt, J =17.1, 1.7, 1.7Hz, 1H), 4.99 (ddt, J =10.3, 1.7, 1.2Hz, 1H), 3.42 (s, 2H), 2.63 (t, J =7.3Hz, 2H), 2.39-2.30 (m, 2H), 1.79 (s, 6H); ^{13}C NMR(100 MHz, CDCl_3): δ =202.0, 165.5, 145.0, 136.5, 128.2, 127.1, 124.2, 115.4, 83.1, 50.4, 42.1, 28.4, 27.4; HRMS(FAB): m/z calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3\text{H}^+$ 261.1490, found 261.1523.

(1-Methyl-1-phenylethyl 3-oxobutyrate)

To a stirred solution of 1-methyl-1-phenylethyl alcohol (1.94 g, 14.3 mmol) and $\text{CH}_3\text{CO}_2\text{Na}$ (114.4 mg, 1.39 mmol) in toluene (5 ml) was added diketene (1.2 ml, 15.6 mmol) at 60°C , and the mixture was stirred at 130°C for 2h. The reaction mixture was quenched with saturated aqueous NaHCO_3 solution (5 ml), extracted with CH_2Cl_2 (10 ml x 3). The combined organic layer was washed with brine (10 ml), dried over Na_2SO_4 , and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=10/1) to afford 1-methyl-1-phenylethyl 3-oxobutyrate (2.89 g, 92%) as a viscous oil: R_f =0.40 (hexane/ethyl acetate=4/1); IR(neat): 2984, 1742, 1720, 1450, 1386, 1366, 1322, 1274, 1198, 1136, 1104, 766, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =7.40-7.25 (m, 5H), 3.42 (s, 2H), 2.25 (s, 3H), 1.80 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ =200.8, 165.4, 145.0, 128.2, 127.1, 124.2, 83.1, 51.2, 30.2, 28.5; HRMS(FAB): m/z calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3\text{H}^+$ 221.1177, found 221.1153.

1-Phenylsulfonyl-5-hexene-2-one

To a solution of methylphenyl sulfone (0.923 g, 5.91 mmol) in THF (60 ml) was added $n\text{BuLi}$ (1.59 M, 7.40 ml, 11.8 mmol) at 0°C , and stirred for 10 min. To this stirred solution was added methyl 4-pentenoate (0.710 g, 6.22 mmol) in THF (1 ml x 2) via a canula. The reaction mixture was stirred at 0°C for 0.5h, and quenched with saturated aqueous NH_4Cl solution (50 ml), extracted with Et_2O (30 ml x 1), and CH_2Cl_2 (30 ml x 2). The combined organic layer was washed with brine (100 ml), dried over Na_2SO_4 , and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=6/1) to afford 1-phenylsulfonyl-5-hexene-2-one (1.22 g, 82%) as a colorless oil: R_f =0.18 (hexane/ethyl acetate=4/1); IR(neat): 3076, 2988, 2932, 1724, 1644, 1448, 1400, 1368, 1324, 1236, 1156, 1086, 1070, 1026, 1000, 918, 796, 762, 738, 690 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =7.89 (d, J =8.1Hz, 2H), 7.69 (t, J =7.6Hz, 1H), 7.58 (dd, J =8.1Hz, 7.6Hz, 2H), 5.77 (ddt, J =16.8, 10.3, 6.6Hz, 1H), 5.03 (dd, J =16.8, 1.2Hz, 1H), 5.01 (dd, J =10.3, 1.2Hz, 1H), 4.16 (s, 2H), 2.83 (t, J =7.1Hz, 2H), 2.33 (dt, J =7.1, 6.6Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ =197.2, 138.5, 136.0, 134.2, 129.3, 128.2, 115.8, 66.9, 43.5, 27.1; HRMS(FAB): m/z calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3\text{SH}^+$ 239.0742, found 239.0744.

1-Diazo-1-phenylsulfonyl-5-hexen-2-one (3a)

3a was prepared by **Procedure A**. Purification by flash chromatography (hexane/ethyl acetate=20/1) afforded 1-diazo-1-phenylsulfonyl-5-hexen-2-one **3a** (85%) as a yellow solid: $R_f=0.32$ (hexane/ethyl acetate=4/1); mp=41-43 °C; IR(KBr): 2122, 1661, 1447, 1331, 1228, 1185, 1157, 1083 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): $\delta=7.98$ (d, $J=8.1\text{Hz}$, 2H), 7.68 (t, $J=7.6\text{Hz}$, 1H), 7.59 (dd, $J=8.1, 7.6\text{Hz}$, 2H), 5.72 (ddt, $J=16.7, 10.5, 6.6\text{Hz}$, 1H), 4.96 (dd, $J=16.7, 1.2\text{Hz}$, 1H), 4.95 (dd, $J=10.5, 1.2\text{Hz}$, 1H), 2.66 (t, $J=7.3\text{Hz}$, 2H), 2.31 (dt, $J=7.3, 6.6\text{Hz}$, 2H); ^{13}C NMR (100 MHz, CDCl_3): $\delta=187.5, 141.9, 135.9, 134.1, 129.5, 127.2, 115.9, 38.3, 27.6$; HRMS(FAB): m/z calcd for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_3\text{SH}^+$ 265.0647, found 265.0644.

(1R, 5R)-1-Phenylsulfonyl-2-oxobicyclo[3.1.0]hexane (4a)

A toluene azeotroped $[\text{CuOTf}]_2 \cdot \text{C}_6\text{H}_6$ (1.2 mg, 0.00238 mmol, 10 mol % as CuOTf) was placed in a dried flask (10 ml) under Ar atmosphere and to this flask was added a solution of toluene azeotroped ligand **2a** (1.9 mg, 0.00714 mmol, 15 mol %) in toluene (0.5 ml x 2) via a canula. The mixture was stirred at room temperature for 0.5h and then to the light blue solution was added a solution of toluene azeotroped 1-diazo-1-phenylsulfonyl-5-hexen-2-one **3a** (12.6 mg, 0.0476 mmol) in toluene (0.5 ml x 2) via a canula. The reaction mixture was stirred at room temperature for 2h, quenched with NH_4OH aqueous solution (2 ml), extracted with ether (5 ml) and CH_2Cl_2 (5 ml x 2). The combined organic layer was washed with brine (10 ml), dried over Na_2SO_4 , and evaporated. The residue was purified by preparative TLC (benzene/ethyl acetate=2/1) to afford (1R, 5R)-1-phenylsulfonyl-2-oxobicyclo[3.1.0]hexane **4a** (10.3 mg, 65% ee, 91%) as a white solid. The absolute configuration was determined by X-ray crystallographic analysis of the recrystallized **4a**. Ee was determined by HPLC (254 nm); Daicel Chiral Cell OD-H 0.46 cm ϕ x 25 cm; hexane/isopropanol=3/1; flow rate=0.5 ml/min; retention time : 21.3 min for **4a**, 23.3 min for *ent-4a*: $R_f=0.35$ (hexane/ethyl acetate=1/1); mp=114-115 °C (hexane/ CH_2Cl_2); $[\alpha]_D^{23.5} -62.1$ (c 0.60, CHCl_3 , 100% ee); IR(KBr): 1731, 1446, 1304, 1149, 1034 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): $\delta=8.05$ (d, $J=8.1\text{Hz}$, 2H), 7.65 (t, $J=7.3\text{Hz}$, 1H), 7.56 (dd, $J=8.1, 7.3\text{Hz}$, 2H), 3.09-3.01 (m, 1H), 2.33-2.15 (m, 4H), 2.10-1.96 (m, 1H), 1.54 (dd, $J=5.6, 3.8\text{Hz}$, 1H); ^{13}C NMR (100 MHz, CDCl_3): $\delta=203.2, 139.3, 133.6, 128.8, 128.6, 53.1, 33.6, 31.1, 20.5, 20.3$; HRMS(FAB): m/z calcd for $\text{C}_{12}\text{H}_{12}\text{O}_3\text{SH}^+$ 237.0585, found 237.0545.

1-(2, 4, 6-trimethylphenylsulfonyl)-5-hexen-2-one

To a solution of methyl-2, 4, 6-trimethylphenyl sulfone (497.5 mg, 2.51 mmol) in THF (20 ml) was added nBuLi (1.57 M, 3.20 ml, 5.02 mmol) at 0 °C, and stirred at room temperature for 1h. To the resultant stirred orange suspension was

added ethyl 4-pentenoate (324.3 mg, 2.53 mmol) in THF (2 ml x 2) via a canula at 0°C. The reaction mixture was stirred at 0°C for 1h, and quenched with saturated aqueous NH₄Cl solution (20 ml), extracted with Et₂O (5 ml x 1), and CH₂Cl₂ (10 ml x 3). The combined organic layer was washed with brine (20 ml), dried over Na₂SO₄, and evaporated. The residue was purified by flash chromatography (benzene/ethyl acetate=400/1) to afford 1-(2, 4, 6-trimethylphenylsulfonyl)-5-hexen-2-one (567.4 mg, 81%) as a white solid: R_f=0.11 (hexane/ethyl acetate=6/1); mp=86 °C; IR(KBr): 3002, 2977, 2948, 2920, 1715, 1604, 1441, 1401, 1282, 1236, 1173, 929, 739 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ=6.98 (s, 2H), 5.77 (ddt, *J*=17.1, 10.3, 6.6Hz, 1H), 5.04 (ddt, *J*=17.1, 1.7, 1.7Hz, 1H), 4.99 (ddt, *J*=10.3, 1.7, 1.2Hz, 1H), 4.14 (s, 2H), 2.84 (t, *J*=7.3Hz, 2H), 2.63 (s, 6H), 2.36-2.30 (m, 2H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ=197.5, 143.9, 140.0, 136.1, (132.8), 132.4, 115.8, 66.399, 43.9, 27.2, 22.9, 21.1; HRMS(FAB):*m/z* calcd for C₁₅H₂₀O₃SH⁺ 281.1211, found 281.1233.

1-Diazo-1-(2, 4, 6-trimethylphenylsulfonyl)-5-hexen-2-one (3b)

3b was prepared by the previously described **Procedure A**.

Purification by flash chromatography (hexane/ethyl acetate=50/1) afforded 1-diazo-1-(2, 4, 6-trimethylphenylsulfonyl)-5-hexen-2-one **3b** (quant.) as a yellow solid: R_f=0.60 (hexane/ethyl acetate=4/1) ; mp=115 °C; IR(KBr): 2116, 1674, 1326, 1235, 1175, 1147, 910, 665, 597 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ=7.01 (s, 2H), 5.65 (ddt, *J*=17.1, 10.3, 6.6Hz, 1H), 4.95-4.88 (m, 2H), 2.65 (s, 6H), 2.50 (t, *J*=7.6 Hz, 2H), 2.33 (s, 3H), 2.28-2.21 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ=188.2, 144.1, 140.0, 135.8, 134.9, 132.5, 115.7, 38.0, 27.6, 22.6, 21.1; HRMS(FAB):*m/z* calcd for C₁₅H₁₈N₂O₃SH⁺ 307.1116, found 307.1161.

(1*R*, 5*R*)-2-oxo-1-(2, 4, 6-trimethylphenylsulfonyl)bicyclo[3.1.0]hexane (4b)

The enantioselective cyclopropanation of **3b** with **2e** was carried out at room temperature for 2h, then at 50 °C for 2.5h according to the previously described procedure for **4a** with **2a**. Purification by preparative TLC (benzene/ethyl acetate=10/1) to afford (1*R*, 5*R*)-2-oxo-1-(2,4,6-trimethylphenylsulfonyl)bicyclo[3.1.0]hexane **4b** (93% ee, 87%) as a white solid. The absolute configuration was determined by X-ray crystallographic analysis of the recrystallized **4b**. Ee was determined by HPLC (254 nm); Daicel Chiral Cell AS-H 0.46 cm φ × 25 cm; hexane/isopropanol=3/1; flow rate=0.2 ml/min; retention time : 61.8 min for **4b**, 65.9 min for *ent*-**4b**; R_f=0.30 (hexane/ethyl acetate=2/1); mp=110 °C (hexane/CH₂Cl₂); [α]_D²³ -29.1 (c 0.89, CHCl₃, 99% ee); IR(KBr): 2969, 1728, 1605, 1297, 1272, 1252, 1211, 1137, 1034, 959, 870, 673, 513 cm⁻¹; ¹H NMR (400MHz, CDCl₃): δ=6.97(s, 2H), 2.96-3.02 (m, 1H), 2.69 (s, 6H), 2.37 (dd, *J*=5.6, 8.8Hz, 1H), 2.30 (s, 3H), 2.29-2.19 (m, 3H), 2.10-2.04 (m, 1H), 1.63 (t, *J*=5.6Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ=203.9, 143.2, 140.8, 133.0, 132.1, 55.1, 33.5, 31.6, 23.2, 21.0, 20.6, 20.5; HRMS(FAB):*m/z* calcd for C₁₅H₁₈O₃SH⁺ 279.1055, found 279.1053.

5-methyl-1-(2, 4, 6-trimethylphenylsulfonyl)-5-hexen-2-one

The previously described procedure for **1-(2, 4, 6-trimethylphenylsulfonyl)-5-hexen-2-one** afforded the title compound. Purification by flash chromatography (hexane/ethyl acetate=9/1) afforded 5-methyl-1-(2, 4, 6-trimethylphenylsulfonyl)-5-hexen-2-one (80%) as a white solid: R_f =0.36 (hexane/ethyl acetate=4/1); mp=74-76 °C; IR(KBr): 2943, 1719, 1601, 1314, 1177, 1156, 1142, 735, 514 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =6.98 (s, 2H), 4.74 (s, 1H), 4.66 (s, 1H), 4.15 (s, 2H), 2.87 (t, J =7.6Hz, 2H), 2.63 (s, 6H), 2.31 (s, 3H), 2.28 (t, 7.6Hz, 2H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ =197.7, 143.9, 143.5, 140.0, 132.8, 132.3, 110.7, 66.8, 43.0, 31.0, 22.9, 22.6, 21.1; HRMS(FAB): m/z calcd for $\text{C}_{16}\text{H}_{22}\text{O}_3\text{SH}^+$ 295.1368, found 295.1368.

1-Diazo-5-methyl-1-(2, 4, 6-trimethylphenylsulfonyl)-5-hexen-2-one (3c)

3c was prepared by the previously described **Procedure A**. Purification by flash chromatography (hexane/ethyl acetate=50/1) afforded 1-diazo-5-methyl-1-(2, 4, 6-trimethylphenylsulfonyl)-5-hexen-2-one **3c** (66%) as a yellow solid: R_f =0.48 (hexane/ethyl acetate=4/1); mp=85-86 °C; IR(KBr): 2970, 2942, 2114, 1673, 1652, 1602, 1458, 1444, 1323, 1302, 1269, 1237, 1176, 1146, 894, 665, 597, 536 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =7.01 (s, 2H), 4.67 (s, 1H), 4.48 (s, 1H), 2.66 (s, 6H), 2.54 (t, J =7.6 Hz, 2H), 2.32 (s, 3H), 2.19 (t, 7.6Hz, 2H), 1.62 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ =188.3, 144.1, 143.4, 140.0, 134.9, 132.5, 110.4, 37.1, 31.1, 22.6, 21.1; HRMS(FAB): m/z calcd for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_3\text{SH}^+$ 321.1273, found 321.1300.

(1R, 5R)-5-Methyl-2-oxo-1-(2, 4, 6-trimethylphenylsulfonyl)bicyclo[3.1.0]hexane (4c)

The enantioselective cyclopropanation of **3c** with **2e** was carried out at 50°C for 2h according to the previously described procedure for **4a** with **2a**. Purification by flash chromatography (hexane/ethyl acetate=10/1) to afford (1R, 5R)-5-methyl-2-oxo-1-(2,4,6-trimethylphenylsulfonyl)bicyclo[3.1.0]hexane **4c** (98% ee, 90%) as a white solid. The absolute configuration was determined by X-ray crystallographic analysis of the recrystallized derivative of **4c**, (1R, 5R)-2-(4-Bromobenzoyloxyimino)-5-methyl-1-(2, 4, 6-trimethylphenylsulfonyl)bicyclo[3.1.0]hexane **4c-X** (see below). Ee was determined by HPLC (254 nm); Dical Chiral Cell AS-H 0.46 cm ϕ $\times$ 25 cm; hexane/isopropanol=3/1; flow rate=0.5 ml/min; retention time : 14.6 min for *ent*-**4c**, 17.3 min for **4c**; R_f =0.30 (hexane/ethyl acetate=2/1); mp=123-125 °C (hexane/ CH_2Cl_2); $[\alpha]_D^{28}$ -138.6 (c 0.61, CHCl_3 , 100% ee); IR(KBr): 2937, 2877, 1739, 1603, 1562, 1454, 1300, 1138, 661 cm^{-1} ; ^1H NMR (400MHz, CDCl_3): δ =6.96 (s, 2H), 2.65 (s, 6H), 2.38 (d, J =5.4Hz, 1H), 2.30 (s, 3H), 2.26-2.07 (m, 4H), 1.84 (s, 3H), 1.80 (d, J =5.4Hz, 1H); ^{13}C NMR (100MHz, CDCl_3): δ =204.3, 142.9, 140.3, 135.2, 131.9, 58.4, 41.8, 33.7, 29.2, 28.3, 23.2, 21.1, 18.8; HRMS(FAB): m/z calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3\text{SH}^+$ 293.1211, found 293.1225.

(1*R*, 5*R*)-5-Methyl-2-oxo-1-(2, 4, 6-trimethylphenylsulfonyl)bicyclo[3.1.0]hexane oxime

(1*R*, 5*R*)-5-Methyl-2-oxo-1-(2, 4, 6-trimethylphenylsulfonyl)bicyclo[3.1.0]hexane **4c** (396.7 mg, 1.357 mmol), $\text{NH}_2\text{OH} \cdot \text{HCl}$ (295.5 mg, 4.252 mmol), and $\text{CH}_3\text{CO}_2\text{Na}$ (580.5 mg, 7.077 mmol) were added in EtOH (13.0 ml) under Ar atmosphere, and the reaction mixture was stirred at room temperature for 48h. The reaction mixture was evaporated, and the white residue was dissolved in CH_2Cl_2 (10 ml), and precipitated materials was filtered off. The filtrate was evaporated, and the residue was purified by flash chromatography (hexane/Et₂O=4/1) to afford (1*R*, 5*R*)-5-methyl-2-oxo-1-(2, 4, 6-trimethylphenylsulfonyl)bicyclo[3.1.0]hexane oxime (406.2 mg, 97%) as a white solid: R_f =0.40 (benzene/ethyl acetate=10/1); mp=135-137 °C; $[\alpha]_D^{35}$ -112.0 (c 1.48, CHCl_3 , 98% ee); ^1H NMR (400 MHz, CDCl_3): δ =6.90 (s, 2H), 6.70 (s, 1H), 3.01-2.93 (m, 1H), 2.64 (s, 6H), 2.29 (s, 3H), 2.23 (d, J =5.2 Hz, 1H), 2.08-1.89 (m, 3H), 1.78 (s, 3H), 1.49 (d, J =5.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ =161.2, 142.3, 139.9, 137.1, 131.6, 54.7, 40.2, 31.2, 28.6, 23.4, 23.2, 21.0, 18.5; IR (KBr): 3176, 1655, 1637, 1604, 1560, 1509, 1459, 1300, 1138, 935 cm^{-1} ; HRMS (FAB): m/z calcd for $\text{C}_{16}\text{H}_{22}\text{NO}_3\text{S}[\text{M} + \text{H}]^+$ 308.1321, found 308.1286.

(1*R*, 5*R*)-2-(4-Bromobenzoyloxyimino)-5-methyl-1-(2, 4, 6-trimethylphenylsulfonyl)bicyclo[3.1.0]hexane (4c-X)

To a solution of (1*R*, 5*R*)-5-methyl-2-oxo-1-(2, 4, 6-trimethylphenylsulfonyl)bicyclo[3.1.0]hexane oxime (35.0 mg, 0.1140 mmol) and DMAP (19.1 mg, 0.1563 mmol) in CH_2Cl_2 (2 ml) was added a solution of *p*-bromobenzoylchloride (30.2 mg, 0.1376 mmol) in CH_2Cl_2 (0.5 ml x 3) via a cannula at room temperature, and the mixture was stirred at room temperature for 20.5h. The reaction mixture was quenched with saturated aqueous NH_4Cl solution (5 ml), extracted with ether (10 ml), and CH_2Cl_2 (10 ml x 2). The combined organic layer was washed with brine (5 ml), dried over Na_2SO_4 , and evaporated. The residue was purified by preparative TLC (benzene/ethyl acetate=10/1) to afford (1*R*, 5*R*)-2-(4-Bromobenzoyloxyimino)-5-methyl-1-(2, 4, 6-trimethylphenylsulfonyl)bicyclo[3.1.0]hexane (53.6 mg, 96%) as a white solid: R_f =0.56 (benzene/ethyl acetate=10/1); mp 146-148 °C (hexane/ethyl acetate); $[\alpha]_D^{35}$ -28.3° (c 0.835, CHCl_3 , 98% ee); IR (KBr): 1754, 1655, 1637, 1591, 1560, 1509, 1459, 1305, 1255, 1140, 1087, 1065, 905 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =7.77 (d, J =8.5Hz, 2H), 7.54 (d, J =8.5 Hz, 2H), 6.99 (s, 2H), 3.16-3.05 (m, 1H), 2.72 (s, 6H), 2.41 (d, J =5.6 Hz, 1H), 2.31 (s, 3H), 2.23-2.01 (m, 3H), 1.85 (s, 3H), 1.65 (d, J =5.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ =169.5, 161.5, 142.7, 140.4, 136.1, 132.0, 131.7, 130.8, 128.2, 127.8, 54.9, 41.3, 31.2, 28.8, 25.4, 23.6, 21.2, 18.4; HRMS (FAB): m/z calcd for $\text{C}_{23}\text{H}_{25}\text{NO}_4\text{SBr}[\text{M} + \text{H}]^+$ 490.0688, found 490.0676.

5-Bromo-1-(2, 4, 6-trimethylphenylsulfonyl)-5-hexen-2-one

The previously described procedure for **1-(2, 4, 6-trimethylphenylsulfonyl)-5-hexen-2-one** afforded the title compound. Purification by flash chromatography (hexane/ethyl acetate=6/1) afforded 5-bromo-1-(2, 4, 6-trimethylphenylsulfonyl)-5-hexen-2-one (75%) as a white solid: R_f =0.33 (hexane/ethyl acetate=4/1); mp 85-86 °C; IR (KBr): 3012, 2980, 2941, 1717, 1600, 1452, 1401, 1300, 1187, 1137, 1054, 1034, 968 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =6.99 (s, 2H), 5.63 (dt, J =1.2, 1.7Hz, 1H), 5.42 (d, J =1.7Hz, 1H), 4.16 (s, 2H), 3.01 (t, J =7.6Hz, 2H), 2.71 (dt, 1.2, 7.6Hz, 2H), 2.63 (s, 6H), 2.32 (s, 3H); ^{13}C NMR (100MHz, CDCl_3): δ =196.3, 144.0, 139.9, 132.7, 132.4, 131.7, 118.0, 67.0, 43.2, 35.1, 22.9, 21.1; HRMS(FAB): m/z calcd for $\text{C}_{15}\text{H}_{19}\text{O}_3\text{SH}^+$ 359.0317, found 359.0293.

5-Bromo-1-diazo-1-(2, 4, 6-trimethylphenylsulfonyl)-5-hexen-2-one (3d)

Procedure B : To a suspension of NaH (60%, 22.7 mg, 0.57 mmol) in a mixed solvent of benzene (1.5 ml) and THF (0.5 ml) was added 5-bromo-1-(2, 4, 6-trimethylphenylsulfonyl)-5-hexen-2-one (177.4 mg, 0.49 mmol) in benzene (1 ml x 3) via a canula at 0 °C. The reaction mixture was stirred at 0 °C for 1h. To the resultant white suspension was added a solution of *p*-toluenesulfonyl azide (108.9 mg, 0.55 mmol) in benzene (1 ml x 3) via a canula at 0 °C. The reaction mixture was stirred at room temperature for 6h, filtered through celite, and evaporated. The residue was purified by preparative TLC (hexane/ethyl acetate=4/1), and a small amount of *p*-toluenesulfonyl azide contaminated was removed by short column chromatography (hexane/ CH_2Cl_2 =1/1) to afford 5-bromo-1-diazo-1-(2, 4, 6-trimethylphenylsulfonyl)-5-hexen-2-one **3d** (93.0 mg, 49%) as a yellow solid: R_f =0.45 (hexane/ethyl acetate=4/1); mp 107 °C; IR (KBr): 2946, 2101, 1675, 1599, 1459, 1397, 1327, 1291, 1240, 1191, 1143, 1031, 901, 854 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =7.01 (s, 2H), 5.52-5.49 (m, 1H), 5.35 (d, J =1.7Hz, 1H), 2.70-2.61 (m, 4H), 2.66 (s, 6H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ =186.9, 144.2, 140.1, 134.8, 132.5, 131.5, 118.1, 37.4, 35.2, 22.6, 21.1; HRMS(FAB): m/z calcd for $\text{C}_{15}\text{H}_{17}\text{BrN}_2\text{O}_3\text{SH}^+$ 385.0221, found 385.0203.

(1*R*, 5*R*)-5-Bromo-2-oxo-1-(2, 4, 6-trimethylphenylsulfonyl)bicyclo[3.1.0]hexane (4d)

The enantioselective cyclopropanation of **3d** with **2e** was carried out at 50 °C for 2.5h according to the previously described procedure for **4a** with **2a**. Purification by flash chromatography (hexane/ethyl acetate=15/1) afforded (1*R*, 5*R*)-5-bromo-2-oxo-1-(2,4,6-trimethylphenylsulfonyl)bicyclo[3.1.0]hexane **4d** (63%) as a white solid. The absolute configuration was determined by X-ray crystallographic analysis of the recrystallized **4d**. Ee was determined by HPLC (254 nm); Daicel Chiral Cell OD-H 0.46 cm ϕ $\times$ 25 cm; hexane/isopropanol=3/1; flow rate=0.5 ml/min; retention time : 17.7 min for *ent*-**4d**, 19.5 min for **4d**; mp=159 °C (hexane-ethyl acetate); R_f =0.40 (hexane/ethyl acetate=2/1);

$[\alpha]_D^{29}$ -98.5 (c 0.40, CHCl_3 , 98% ee); IR (KBr): 1746, 1309, 1260, 1233, 1201, 1142 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =6.98 (s, 2H), 2.91 (d, J =6.6Hz, 1H), 2.65 (s, 6H), 2.72-2.64 (m, 2H), 2.37-2.17 (m, 2H), 2.32 (s, 3H), 2.19 (d, J =6.6Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ =200.6, 143.6, 140.7, 134.2, 132.1, 56.6, 40.9, 35.1, 32.9, 31.2, 23.4, 21.1; HRMS(FAB): m/z calcd for $\text{C}_{15}\text{H}_{17}\text{BrO}_3\text{SH}^+$ 357.0160, found 357.0198.

6-methyl-1-(2, 4, 6-trimethylphenylsulfonyl)-5-hepten-2-one

The previously described procedure for **1-(2, 4, 6-trimethylphenylsulfonyl)-5-hexen-2-one** afforded the title compound. Purification by flash chromatography (hexane/ethyl acetate=6/1) afforded 6-methyl-1-(2, 4, 6-trimethylphenylsulfonyl)-5-hepten-2-one (85%) as a viscous oil: R_f =0.44 (hexane/ethyl acetate=4/1); IR(neat): 2976, 2940, 1722, 1604, 1452, 1402, 1380, 1320, 1188, 1178, 1150, 1054, 582 cm^{-1} ; ^1H NMR(400MHz, CDCl_3): δ =6.98 (s, 2H), 5.06-4.99 (m, 1H), 4.13 (s, 2H), 2.75 (t, J =7.3 Hz, 2H), 2.63 (s, 6H), 2.32 (s, 3H), 2.25 (dt, J =7.3, 7.1Hz, 2H), 1.66 (d, J =1.0Hz, 3H), 1.59 (s, 3H); ^{13}C NMR(100MHz, CDCl_3): δ =198.0, 143.8, 139.9, 133.1, 132.8, 132.3, 121.9, 66.7, 44.8, 25.6, 22.8, 22.0, 21.1, 17.6; HRMS(FAB): m/z calcd for $\text{C}_{17}\text{H}_{24}\text{O}_3\text{SH}^+$ 309.1524, found 309.1528.

1-Diazo-6-methyl-1-(2, 4, 6-trimethylphenylsulfonyl)-5-hepten-2-one (3e)

3e was prepared by the previously described **Procedure A**. Purification by preparative TLC (1st time; hexane/ethyl acetate=4/1, 2nd time; hexane/ CH_2Cl_2 =1/1) afforded 1-diazo-6-methyl-1-(2, 4, 6-trimethylphenylsulfonyl)-5-hepten-2-one **3e** (75%) as a yellow solid: R_f =0.56(hexane/ethyl acetate=4/1); mp=63-68 $^\circ\text{C}$; IR(KBr): 2960, 2110, 1667, 1458, 1328, 1271, 1242, 1187, 1147, 671 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =7.00 (s, 2H), 4.93-4.86 (m, 1H), 2.65 (s, 6H), 2.43 (t, 7.3Hz, 2H), 2.32 (s, 3H), 2.20 (dt, 7.3, 7.3Hz, 2H), 1.63 (d, 1.0Hz, 3H), 1.51 (s, 3H); ^{13}C NMR (100MHz, CDCl_3): δ =188.5, 143.9, 140.0, 134.9, 133.5, 132.3, 121.4, 39.1, 25.6, 22.6, 22.5, 21.0, 17.5; HRMS(FAB): m/z calcd for $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_3\text{SH}^+$ 335.1429, found 335.1427.

(1R, 5S)-6, 6-Dimethyl-2-oxo-1-(2, 4, 6-trimethylphenylsulfonyl)bicyclo[3.1.0]hexane (4e)

The enantioselective cyclopropanation of **3e** was carried out with 10 mol% of $[\text{CuOTf}]_2 \cdot \text{C}_6\text{H}_6$ (20 mol% as CuOTf) and 30 mol% of **2e** at room temperature for 5h according to the previously described procedure for **4a** with **2a**. Purification by preparative TLC (benzene/ethyl acetate=10/1) afforded (1R, 5S)-6, 6-dimethyl-2-oxo-1-(2, 4, 6-trimethylphenylsulfonyl)bicyclo[3.1.0]hexane **4e** (84%) as a white solid. The absolute configuration was determined by X-ray crystallographic analysis of the recrystallized **4e**. Ee was determined by HPLC (254 nm); Daicel Chiral Cell AS-H 0.46 cm ϕ $\times$ 25 cm; hexane/isopropanol=3/1; flow rate=0.5 ml/min; retention time : 11.7 min for *ent*-**4e**, 15.5 min for **4e**; R_f =0.40 (hexane/ethyl acetate=2/1); mp 139-140 $^\circ\text{C}$ (hexane-ethyl acetate); $[\alpha]_D^{28}$ -53.2 (c 0.47, CHCl_3 ,

100% ee); IR(KBr):2940, 1728, 1604, 1458, 1378, 1306, 1233, 1141, 1100, 848, 655 cm^{-1} ; ^1H NMR(400MHz, CDCl_3): δ =6.91 (s, 2H), 2.84 (d, J =6.8Hz, 1H), 2.71 (s, 6H), 2.32-2.02 (m, 3H), 2.27 (s, 3H), 1.93-1.86 (m, 1H), 1.75 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ =205.6, 142.9, 140.1, 134.7, 131.9, 65.0, 44.0, 39.5, 36.0, 22.9, 22.3, 21.0, 18.1, 17.6; HRMS(FAB): m/z calcd for $\text{C}_{17}\text{H}_{22}\text{O}_3\text{SH}^+$ 307.4286, found 307.1406.

Ethyl 2-(triphenylmethoxymethyl)propenoate

To a solution of ethyl 2-(hydroxymethyl)propenoate (8.32 g, 63.9 mmol) in CH_2Cl_2 (100 ml) was added pyridine (6.4 ml, 79.5 mmol), and after 5min was added triphenylmethyl chloride (19.4 g, 69.5 mmol) at 0 $^\circ\text{C}$. The reaction mixture was stirred at room temperature for 15h, quenched with saturated aqueous NH_4Cl solution (100 ml) at 0 $^\circ\text{C}$, extracted with CH_2Cl_2 (30 ml x 3). The combined organic layer was washed with brine (50 ml), dried over Na_2SO_4 , and evaporated. The residue was purified by flash chromatography (hexane/ CH_2Cl_2 =10/1) to afford ethyl 2-(triphenylmethoxymethyl)propenoate (23.3 g, 98%) as a white solid: R_f =0.52 (hexane/ethyl acetate=4/1); mp=73-75 $^\circ\text{C}$ (CH_2Cl_2); IR(KBr): 1709, 1490, 1449, 1305, 1151, 1079, 769, 754, 702, 630 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =7.35-7.33 (m, 6H), 7.16-7.12 (m, 6H), 7.08-7.04 (m, 3H), 6.23 (d, J =1.8 Hz, 1H), 6.08 (d, J =1.8 Hz, 1H), 3.98 (q, J =7.08 Hz, 2H), 3.79 (s, 2H), 1.06 (t, J =7.08 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ =165.5, 143.7, 137.8, 128.4, 127.7, 126.9, 124.2, 86.9, 62.2, 60.4, 14.1; HRMS (FAB): m/z calcd for $\text{C}_{25}\text{H}_{24}\text{O}_3$ 372.1726, found 372.1740.

2-Triphenylmethoxymethyl-2-propenol

To a solution of ethyl 2-(triphenylmethoxymethyl)propenoate (9.81 g, 26.3 mmol) in CH_2Cl_2 (100 ml) was added diisobutylaluminum hydride (6.4 ml, 79.5 mmol) at -78 $^\circ\text{C}$, and the reaction mixture was stirred at -78 $^\circ\text{C}$ for 1h. The reaction mixture was quenched with methanol (1 ml) at -78 $^\circ\text{C}$ and the mixture was warmed to room temperature. To the reaction mixture was added saturated aqueous Rochelle salt solution (100 ml) at room temperature, and the mixture was stirred for 3h, extracted with CH_2Cl_2 (30 ml x 3). The combined organic layer was washed with brine (100 ml), dried over Na_2SO_4 , and evaporated. The residue was purified by flash chromatography (hexane/ CH_2Cl_2 =3/1) to afford 2-triphenylmethoxymethyl-2-propenol (8.69 g, 99%) as a white solid: R_f =0.31 (hexane/ethyl acetate=4/1); mp=90-92 $^\circ\text{C}$ (CH_2Cl_2); IR (KBr): 3369, 3054, 1490, 1448, 1065, 1030, 903, 765, 742, 703, 632 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =7.46-7.43 (m, 6H), 7.32-7.27 (m, 6H), 7.25-7.21 (m, 3H), 5.25 (d, J =1.2 Hz, 1H), 5.16 (d, J =1.2 Hz, 1H), 4.13 (d, J =6.1 Hz, 2H), 3.70 (s, 2H), 1.74 (t, J =1.74, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ =145.6, 143.7, 128.5, 127.8, 127.0, 111.7, 87.0, 65.3, 64.5; HRMS(EI): m/z calcd for $\text{C}_{23}\text{H}_{22}\text{O}_2$ 330.1621, found 330.1639.

1-Bromo-2-triphenylmethoxymethyl-2-propene

To a solution of 2-triphenylmethoxymethyl-2-propenol (1.03 g, 3.11 mmol) in CH_2Cl_2 (30 ml) was added CBr_4 (1.45

g, 4.37 mmol), and then PPh_3 (983 mg, 3.74 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 30min, quenched with saturated aqueous NaHCO_3 solution (50 ml) at 0 °C, extracted with CH_2Cl_2 (10 ml x 3). The combined organic layer was washed with brine (30 ml), dried over Na_2SO_4 , and evaporated. The residue was purified by flash chromatography (hexane/ CH_2Cl_2 =15/1) to afford 1-bromo-2-triphenylmethoxymethyl-2-propene (1.22 g, 99%) as a viscous oil: R_f =0.63 (hexane/ethyl acetate=4/1); IR(neat): 1492, 1450, 1212, 1084, 1066, 766, 746, 732, 708, 672, 632 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =7.33-7.31 (m, 6H), 7.28-7.26 (m, 6H), 7.12-7.09 (m, 3H), 5.19 (s, 1H), 5.08 (s, 1H), 3.76 (s, 2H), 3.62 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ =143.7, 142.6, 128.4, 127.7, 126.9, 115.8, 86.8, 64.1, 33.3; HRMS (FAB): m/z calcd for $\text{C}_{23}\text{H}_{21}\text{O}_3\text{Br}$ 392.0776, found 392.0782.

Methyl 4-triphenylmethoxymethyl-4-pentenoate

To a suspension of NaH (234 mg, 3.90 mmol) in THF (30 ml) was added a solution of ethyl phenylsulfonylacetate (854 mg, 3.74 mmol) in THF (30 ml) at 0°C, and after 15min was added a solution of ethyl 1-bromo-2-triphenylmethoxymethyl-2-propene (1.22 g, 3.12 mmol) in THF (10 ml) via a canula at 0 °C. The reaction mixture was stirred at room temperature for 3h, quenched with saturated aqueous NH_4Cl solution (20 ml) at 0°C, extracted with CH_2Cl_2 (10 ml x 3). The combined organic layer was washed with brine (20 ml), dried over Na_2SO_4 , and evaporated. The residue was purified by flash chromatography (hexane/ CH_2Cl_2 =4/1) to afford a 2:1 (57% : 29%) mixture of ethyl 2-phenylsulfonyl-4-triphenylmethoxymethyl-4-pentenoate and ethyl phenylsulfonylacetate (1.45 g) as a viscous oil. The mixture was used for next step without further purification: R_f =0.25 (hexane/ethyl acetate=4/1); ^1H NMR (400 MHz, CDCl_3): δ =7.72 (d, J =7.81 Hz, 2H), 7.58-7.49 (m, 1H), 7.42 (dd, J =7.81, 7.57 Hz, 2H), 7.38-7.29 (m, 6H), 7.22-7.11 (m, 9H), 5.10 (s, 1H), 4.86 (s, 1H), 4.21 (dd, J =13.3, 3.91 Hz, 1H), 4.04 (q, J =7.08 Hz, 2H), 3.43 (d, J =3.17 Hz, 2H), 2.70 (td, J =13.3, 3.91 Hz, 2H), 1.01 (t, J =7.08 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ =165.1, 143.5, 140.5, 137.1, 134.0, 129.0, 128.8, 127.7, 127.6, 126.9, 126.8, 114.6, 87.0, 69.1, 66.6, 30.7, 13.8; HRMS (FAB): m/z calcd for $\text{C}_{33}\text{H}_{32}\text{O}_5\text{SH}^+$ 541.2050, found 541.2033.

To a solution of the mixture obtained as above (5.30 g) in methanol (30 ml) and THF (3 ml) was added Na_2HPO_4 (5.57 g, 39.2 mmol) and 5% Na-Hg (19.3 g) at 0 °C. The reaction mixture was stirred at room temperature for 3h, filtered through celite, and evaporated. To the residue was added saturated aqueous NH_4Cl solution (20 ml), and the mixture was extracted with CH_2Cl_2 (15 ml x 3). The combined organic layer was washed with brine (10 ml), dried over Na_2SO_4 , and evaporated. The residue was purified by flash chromatography (hexane/ CH_2Cl_2 =5/1) to afford methyl 4-triphenylmethoxymethyl-4-pentenoate (3.12 g, 82%, 2 steps) as a colorless oil: R_f =0.50 (hexane/ethyl acetate=4/1); IR (neat): 1738, 1492, 1450, 1222, 1158, 910, 734, 708 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =7.47-7.41 (m, 6H), 7.31-7.27 (m, 6H), 7.25-7.19 (m, 3H), 5.25 (s, 1H), 4.92 (s, 1H), 3.62 (s, 3H), 3.54 (s, 2H), 2.42-2.34 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ =173.4, 144.9, 144.0, 128.5, 127.7, 126.9, 110.4, 86.8, 66.5, 51.6, 32.4, 28.5; HRMS (EI): m/z calcd for $\text{C}_{25}\text{H}_{26}\text{O}_3$ 386.1883, found 386.1878.

1-(2, 4, 6-Trimethylphenylsulfonyl)-5-triphenylmethoxymethyl-5-hexen-2-one

The previously described procedure for **1-(2, 4, 6-trimethylphenylsulfonyl)-5-hexen-2-one** afforded the title compound. Purification by flash chromatography (hexane/CH₂Cl₂=3/1) afforded 1-(2, 4, 6-trimethylphenylsulfonyl)-5-triphenylmethoxymethyl-5-hexen-2-one (98%) as a viscous oil: *R*_f=0.18 (hexane/ethyl acetate=4/1); IR(neat): 2940, 1772, 1602, 1492, 1450, 1402, 1322, 1222, 1188, 1150, 912, 854, 766, 732, 706, 632 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ=7.36-7.34 (m, 6H), 7.20-7.16 (m, 6H), 7.13-7.10 (m, 3H), 6.83 (s, 2H), 5.13 (s, 1H), 4.78 (s, 1H), 3.95 (s, 2H), 3.42 (s, 2H), 2.68 (t, *J*=7.57 Hz, 2H), 2.48(s, 6H), 2.19-2.16 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ=197.4, 144.3, 143.8, 143.7, 139.8, 132.7, 132.2, 128.4, 127.7, 126.8, 110.8, 86.7, 66.6, 66.4, 42.8, 26.7, 22.8, 21.0; HRMS(FAB): *m/z* calcd for C₃₅H₃₆O₄SH⁺ 553.2412, found 553.2396.

1-Diazo-1-(2, 4, 6-trimethylphenylsulfonyl)-5-triphenylmethoxymethyl-5-hexene-2-one (3f)

3f was prepared by the previously described **Procedure B**. Purification by flash chromatography (hexane/CH₂Cl₂=3/1) afforded 1-diazo-1-(2, 4, 6-trimethylphenylsulfonyl)-5-triphenylmethoxymethyl-5-hexene-2-one **3f** (79%) as a yellow oil: *R*_f=0.32 (hexane/ethyl acetate=4/1); IR(neat): 3064, 2940, 2108, 1724, 1680, 1602, 1566, 1522, 986, 902, 854, 632 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ=7.32-7.30 (m, 6H), 7.17-7.07 (m, 9H), 6.83 (s, 2H), 5.07 (s, 1H), 4.60 (s, 1H), 3.36 (s, 2H), 2.50 (s, 6H), 2.38 (dd, *J*=7.32, 7.08 Hz, 2H), 2.14 (s, 3H), 2.10 (dd, *J*=7.81, 7.32 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ=187.7, 144.2, 143.9, 143.7, 139.8, 134.7, 132.3, 128.3, 128.3, 127.6, 126.8, 110.4, 86.6, 66.3, 37.0, 26.8, 22.4. 20.9; HRMS(FAB): *m/z* calcd for C₃₅H₃₄N₂O₄SH⁻ 577.2161, found 577.2145.

(1*R*, 5*S*)-2-oxo-1-(2, 4, 6-trimethylphenylsulfonyl)-5-triphenylmethoxymethylbicyclo[3.1.0]hexane (4f)

The enantioselective cyclopropanation of **3f** was carried out at 50 °C for 13h and then 70 °C for 7h according to the previously described procedure for **4a** with **2a**. Purification by flash chromatography (hexane/ethyl acetate=1/1) afforded (1*R*, 5*S*)-2-oxo-1-(2, 4, 6-trimethylphenylsulfonyl)-5-triphenylmethoxymethylbicyclo[3.1.0]hexane **4f** (91% ee, 98%) as a white solid: *R*_f=0.67 (hexane/ethyl acetate=1/1); mp=154-156 °C(CH₂Cl₂); [α]_D²⁴ -70.6 (c 1.79, CHCl₃, 91% ee); IR(KBr): 3449, 2939, 2368, 2345, 2099, 1735, 1602, 1490, 1448, 1311, 1189, 1141, 1064, 705 cm⁻¹; ¹H NMR (400MHz, CDCl₃): δ=7.52-7.49 (m, 6H), 7.33-7.22 (m, 9H), 6.99 (s, 2H), 3.93 (dd, *J*=10.2, 0.98 Hz, 1H), 3.83 (d, *J*=10.2, 1H), 2.55 (s, 6H), 2.28-2.09 (m, 8H), 1.72 (dd, *J*=5.37, 0.98 Hz, 1H); ¹³C NMR (100MHz, CDCl₃): δ=143.9, 143.0, 140.5, 131.9, 128.7, 127.8, 127.8, 127.8, 127.0, 87.0, 64.0, 58.4, 44.3, 33.5, 27.6, 25.0, 23.3, 21.1; HRMS(FAB): *m/z* calcd for C₃₅H₃₄O₄SH⁺ 551.2256, found 551.2233.

After converting **4f** to the corresponding deprotected compound ((**1R, 5S**)-2-oxo-1-(2, 4, 6-trimethylphenylsulfonyl)-5-hydroxymethylbicyclo[3.1.0]hexane, see below), ee was determined by HPLC (254 nm); Dical Chiral Cell OD-H 0.46 cm ϕ $\times$ 25 cm; hexane/isopropanol=3/1; flow rate=0.2 ml/min); retention time : 32.4 min for *ent*-**4f**, 42.3 min for **4f**.

(1R, 5S)-2-oxo-1-(2, 4, 6-trimethylphenylsulfonyl)-5-hydroxymethylbicyclo[3.1.0]hexane

To a stirred solution of **4f** (4.0 mg, 7.3×10^{-3} mmol) in methanol (1 ml) was added *p*-toluenesulfonic acid (1.0 mg, 5.3×10^{-3} mmol) portionwise at room temperature over night. The reaction was quenched with triethylamine (0.5 ml), and evaporated. The residue was purified by flash chromatography (hexane/ CH_2Cl_2 =1/2) to afford (**1R, 5S**)-2-oxo-1-(2, 4, 6-trimethylphenylsulfonyl)-5-hydroxymethylbicyclo[3.1.0]hexane as a white crystal. Recrystallization (CH_2Cl_2) gave a pure compound (2.2 mg, 98%): R_f =0.22 (hexane/ethyl acetate=1/1); mp=87-90°C (CH_2Cl_2); $[\alpha]_D^{27}$ -107.5 (c 1.42, CHCl_3 , 100% ee); IR(KBr): 2930, 2368, 2345, 1735, 1449, 1311, 1141, 1075, 705 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =6.98 (s, 2H), 4.17 (d, J =3.2 Hz, 2H), 3.01 (t, J =4.88 Hz, 1H), 2.62 (s, 6H), 2.54 (d, J =5.62 Hz, 1H), 2.35-2.15 (m, 6H), 1.98 (ddd, J =12.9, 8.78, 1.71 Hz, 1H), 1.87 (d, J =5.62 Hz, 1H); ^{13}C NMR(400 MHz, CDCl_3): δ =203.3, 143.5, 140.4, 132.0, 77.2, 62.4, 58.4, 48.1, 33.8, 27.0, 23.1, 22.6, 21.1; HRMS(FAB): m/z calcd for $\text{C}_{16}\text{H}_{20}\text{O}_4\text{SH}^+$: 309.1160; found: 309.1155.

(1R, 5S)-2-oxo-1-(2, 4, 6-trimethylphenylsulfonyl)-5-(3, 5-dinitrobenzoyloxymethyl)bicyclo[3.1.0]hexane (4f-X)

To a stirred solution of (**1R, 5S**)-2-oxo-1-(2, 4, 6-trimethylphenylsulfonyl)-5-hydroxymethylbicyclo[3.1.0]hexane (50.2 mg, 0.16 mmol), pyridine (0.02 ml, 0.25 mmol), and DMAP (2.1 mg, 1.7×10^{-2} mmol) in CH_2Cl_2 (3 ml) was added 3, 5-dinitrobenzoylchloride (45.0 mg, 0.20 mmol) portionwise at room temperature. The reaction was quenched with saturated aqueous NH_4Cl solution (2 ml), and the mixture was extracted with CH_2Cl_2 (2 ml $\times$ 3). The combined organic layer was washed with brine (5 ml), dried over Na_2SO_4 , and evaporated. The residue was purified by recrystallization (hexane/ CH_2Cl_2) to afford pure (**1R, 5S**)-2-oxo-1-(2, 4, 6-trimethylphenylsulfonyl)-5-(3, 5-dinitrobenzoyloxymethyl)bicyclo[3.1.0]hexane (77.9 mg, 95%) as a pale yellow crystal: R_f =0.75 (hexane/ethyl acetate=1/1); mp=168-171 °C; $[\alpha]_D^{24}$ -89.0 (c 1.47, CHCl_3 , 100% ee); IR(KBr): 1738, 1632, 1546, 1348, 1310, 1278, 1168, 1140, 720, 662 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =9.29 (d, J =1.95 Hz, 2H), 9.23 (d, J =1.95 Hz, 1H), 6.98 (s, 2H), 5.24 (d, J =11.9 Hz, 1H), 4.96 (d, J =11.9 Hz, 1H), 2.66 (s, 6H), 2.42-2.22 (m, 8H), 1.96 (d, J =5.37 Hz, 1H); ^{13}C NMR(400 MHz, CDCl_3): δ =202.7, 162.3, 148.5, 143.5, 140.7, 134.0, 133.4, 132.1, 129.7, 122.4, 66.7, 57.8, 41.7, 33.3, 26.9, 24.1, 23.3, 21.1; HRMS(FAB): m/z calcd for $\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_9\text{SH}^+$: 503.1124; found: 503.1105.

1-Methyl-2, 5-cyclohexadiene-1-acetaldehyde

To a stirred suspension of methoxymethyltriphenylphosphonium chloride (16.1 g, 47.0 mmol) in Et₂O (20 ml) was added 1.00 M THF solution of NaHMDS (50.0 ml, 50.0 mmol) at 0 °C. After 5 min, a solution of 1-methyl-2, 5-cyclohexadiene-1-carboxaldehyde* (4.41 g, 36.1 mmol) in Et₂O (10 ml) was added to the red brown reaction mixture dropwise via a canula at 0 °C. The reaction mixture was quenched with saturated aqueous NH₄Cl solution (60 ml), extracted with Et₂O (20 ml x 3). The combined organic layer was washed with brine (60 ml), dried over Na₂SO₄, and evaporated. The residue was purified by flash chromatography (hexane/diethyl ether=40/1) to afford crude 1-(2-methoxyethenyl)-1-methyl-2, 5-cyclohexadiene, (¹H NMR (400 MHz, CDCl₃): δ=5.76-5.71 (m, 2H), 5.72 (d, *J*=6.8 Hz, 1H), 5.62 (ddd, *J*=2.8, 3.4, 10.3 Hz, 2H), 4.24 (d, *J*=6.8 Hz, 1H), 3.55 (s, 3H), 2.65-2.52 (m, 2H), 1.24 (s, 3H)), containing a small amount of triphenylphosphineoxide. To a solution of the crude vinyl ether in THF (50 ml) and H₂O (50 ml) was added acetic acid (200 ml), and the mixture was stirred at 50 °C for 2h. The reaction mixture was quenched with diethyl ether (90 ml) and H₂O (90 ml), stirred for a while, and the organic layer was separated. To the organic layer was added saturated aqueous NaHCO₃ solution (100 ml) slowly, and then was added solid NaHCO₃ portionwise with stirring until evolution of CO₂ ceased. The mixture was extracted with Et₂O (50 ml x 2), and the combined organic layer was washed with brine (90 ml), dried over Na₂SO₄, and evaporated. The residue was purified by flash chromatography (hexane/diethyl ether=40/1) to afford 1-methyl-2, 5-cyclohexadiene-1-acetaldehyde (2.66 g, 54% (2steps)) as a colorless oil: R_f=0.16 (hexane/ether=20/1); IR(neat): 3024, 2968, 2872, 2824, 2736, 1724, 1404, 1098, 948, 718 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ=9.60 (t, *J*=3.2 Hz, 1H), 5.78 (ddd, *J*=2.8, 3.4, 10.3 Hz, 2H), 5.58 (ddd, *J*=1.6, 2.0, 10.3 Hz, 2H), 2.70-2.55 (m, 2H), 2.31 (d, *J*=3.2 Hz, 2H), 1.15 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ=203.6, 132.1, 124.2, 54.9, 34.8, 30.0, 26.2.

*Arseniyadis, S.; Yashunsky, D. V.; Dorado, M. M. ; Alves, R. B.; Wang, Q.; Potier, P. *Tetrahedron* **1996**, 52, 6215-6232.

1-Methyl-1-(2-oxo-3-phenylsulfonyl)propyl-2, 5-cyclohexadiene

To a solution of methylphenylsulfone (229.0 mg, 1.47 mmol) in THF (10 ml) was added 1.59 M hexane solution of n-BuLi (0.92 ml, 1.46 mmol) at 0 °C. After stirring the reaction mixture at 0 °C for 20 min, a solution of 1-methyl-2, 5-cyclohexadiene-1-acetaldehyde (200.0 mg, 1.47 mmol) in THF (5 ml) was added to the yellow reaction mixture dropwise via a canula at 0 °C. After stirring at 0 °C for 30 min, the reaction mixture was quenched with saturated aqueous NH₄Cl solution (15 ml), extracted with Et₂O (5 ml), and then CH₂Cl₂ (10 ml x 2). The combined organic layer was washed with brine (15 ml), dried over Na₂SO₄, and evaporated to afford crude 1-(2-hydroxy-3-phenylsulfonyl)propyl-1-methyl-2, 5-cyclohexadiene, containing a small amount of methylphenylsulfone, which was used for next step without further purification: R_f=0.16 (hexane/ethyl acetate=4/1); ¹H NMR (400 MHz, CDCl₃):

δ =7.90 (d, J =7.9Hz, 2H), 7.66 (t, J =7.3Hz, 1H), 7.56 (dd, J =5.7, 7.9 Hz, 2H), 5.58-5.56 (m, 2H), 5.46 (ddd, J =2.0, 3.1, 10.3 Hz, 1H), 5.32 (ddd, J =2.0, 3.1, 10.3 Hz, 1H), 4.15-4.09 (m, 1H), 3.34 (dd, J =2.4, 14.4 Hz, 1H), 3.19 (dd, J =9.0, 14.4 Hz, 1H), 3.17 (s, 1H), 2.54-2.22 (m, 2H), 1.66 (dd, J =6.3, 14.4 Hz, 1H), 1.50 (dd, J =5.6, 14.4 Hz, 1H), 1.01 (s, 3H).

To a solution of the crude 1-(2-hydroxy-3-phenylsulfonyl)propyl-1-methyl-2, 5-cyclohexadiene in CH_2Cl_2 (20 ml) was added Dess-Martin's periodinane (1.87 g, 4.41 mmol) portionwise, and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with diethyl ether (20 ml), saturated aqueous NaHCO_3 solution (20 ml), and saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution (20 ml). The organic layer was separated, washed with brine (20 ml), dried over Na_2SO_4 , and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=6/1) to afford 1-methyl-1-(2-oxo-3-phenylsulfonyl)propyl-2, 5-cyclohexadiene (299.4 mg, 70% (2steps)) as a colorless oil: R_f =0.27 (hexane/ethyl acetate=4/1); IR(neat): 3020, 2964, 2928, 2884, 1722, 1448, 1324, 1312, 1154, 1086, 1042, 730, 688 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =7.87 (d, J =7.9Hz, 2H), 7.67 (t, J =7.3 Hz, 1H), 7.57 (dd, J =5.7, 7.9 Hz, 2H), 5.71 (ddd, J =2.8, 3.4, 10.3 Hz, 2H), 5.57 (ddd, J =1.6, 2.0, 10.3 Hz, 2H), 4.17 (s, 2H), 2.70 (s, 2H), 2.62-2.45 (m, 2H), 1.14 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ =196.9, 138.6, 134.1, 132.1, 129.1, 128.3, 124.2, 67.4, 56.1, 36.0, 30.1, 26.0; HRMS(FAB): calcd $\text{C}_{16}\text{H}_{18}\text{O}_3\text{SH}^+$ 291.1055, found 291.1069.

1-(3-Diazo-2-oxo-3-phenylsulfonylpropyl)-1-methyl-2, 5-cyclohexadiene (**5a**)

5a was prepared by the previously described **Procedure A**. Purification by flash chromatography (hexane/ethyl acetate=10/1) afforded 1-(3-diazo-2-oxo-3-phenylsulfonylpropyl)-1-methyl-2, 5-cyclohexadiene **5a** (87%) as a yellow solid: R_f =0.33 (hexane/ethyl acetate=4/1); mp=77-80°C; IR(KBr): 2116, 1648, 1334, 1203, 1154, 759, 729, 683, 630 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =8.00 (d, J =7.9Hz, 2H), 7.66 (t, J =7.3 Hz, 1H), 7.57 (dd, J =5.7, 7.9 Hz, 2H), 5.63 (ddd, J =2.8, 3.4, 10.3 Hz, 2H), 5.46 (ddd, J =1.6, 2.0, 10.3 Hz, 2H), 2.49 (s, 2H), 2.44-2.25 (m, 2H), 1.10(s, 3H); ^{13}C NMR(100 MHz, CDCl_3): δ =185.9, 141.7, 133.9, 131.4, 129.1, 127.7, 124.3, 51.2, 36.9, 29.5, 25.9; HRMS(FAB): calcd $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_3\text{SH}^+$ 317.0960, found 317.0970.

(1*S*, 5*R*, 6*R*, 7*S*)-1-Methyl-8-oxo-7-phenylsulfonyltricyclo[4.3.0.0^{5,7}]non-2-ene (**6a**)

The enantioselective cyclopropanation of **5a** with **2e** was carried out at room temperature for 5h according to the previously described procedure for **4a** with **2a**. Purification by preparative TLC (hexane/ethyl acetate=4/1) to afford (1*S*, 5*R*, 6*R*, 7*S*)-1-methyl-8-oxo-7-phenylsulfonyltricyclo[4.3.0.0^{5,7}]non-2-ene **6a** (66% ee, 81%) as a white solid. The absolute configuration was determined by X-ray crystallographic analysis of the recrystallized **6a**. Ee was determined by HPLC (254 nm); Daicel Chiral Cell AS-H 0.46 cm ϕ $\times$ 25 cm; hexane/isopropanol=3/1; flow rate=0.5 ml/min);

retention time : 31.3 min for **6a**, 38.1 min for **ent-6a**; $R_f=0.23$ (hexane/ethyl acetate=4/1); mp=127-129°C (hexane/CH₂Cl₂); $[\alpha]_D^{21}$ -27.3 (c 1.22, CHCl₃, 96% ee); IR(KBr): 1739, 1454, 1432, 1316, 1262, 1146, 1089, 1050, 942, 774, 746, 728, 694 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ =7.98 (d, J =7.9 Hz, 2H), 7.66 (t, J =7.3 Hz, 1H), 7.58 (dd, J =5.7, 7.9 Hz, 2H), 5.67-5.66 (m, 2H), 2.87 (d, J =9.3 Hz, 1H), 2.74-2.69 (m, 1H), 2.61-2.53 (m, 1H), 2.44 (d, J =17.3 Hz, 1H), 2.16 (dd, J =1.5, 17.3 Hz, 1H), 1.97 (dd, J =1.5, 19.5 Hz, 1H), 1.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ =203.3, 139.3, 135.4, 133.6, 128.9, 128.4, 124.3, 59.8, 59.6, 40.1, 31.0, 29.5, 27.8, 19.9; HRMS(EI): calcd C₁₆H₁₆O₃S 288.0820, found 288.0828.

1-Methyl-1-[2-oxo-3-(2, 4, 6-trimethylphenylsulfonyl)propyl]-2, 5-cyclohexadiene

To a solution of methyl-2, 4, 6-trimethylphenyl sulfone (436.8 mg, 2.20 mmol) in THF (12 ml) was added 1.59 M hexane solution of n-BuLi (1.39 ml, 2.21 mmol) slowly at 0 °C. After stirring the yellow reaction mixture at rt for 1 h, a solution of 1-methyl-2, 5-cyclohexadiene-1-acetaldehyde (299.7 mg, 2.20 mmol) in THF (8 ml) was added to the yellow reaction mixture dropwise via a canula at 0 °C. After stirring at 0 °C for 30 min, the reaction mixture was quenched with saturated aqueous NH₄Cl solution (15 ml), extracted with Et₂O (5 ml), and then CH₂Cl₂ (10 ml x 2). The combined organic layer was washed with brine (15 ml), dried over Na₂SO₄, and evaporated to afford crude 1-[2-hydroxy-3-(2, 4, 6-trimethylphenylsulfonyl)propyl]-1-methyl-2, 5-cyclohexadiene, containing a small amount of 2, 4, 6-trimethylphenylsulfone, which was used for next step without further purification: $R_f=0.32$ (hexane/ethyl acetate=4/1); ¹H NMR (400 MHz, CDCl₃): δ =6.96 (s, 2H), 5.61-5.69 (m, 2H), 5.49 (ddd, J =2.0, 3.1, 10.3 Hz, 1H), 5.35 (ddd, J =2.0, 3.1, 10.3 Hz, 1H), 4.22-4.28 (m, 1H), 3.38 (dd, J =2.4, 14.4 Hz, 1H), 3.36 (d, J =2.0 Hz, 1H), 3.13 (dd, J =9.0, 14.4 Hz, 1H), 2.63 (s, 6H), 2.31 (s, 3H), 2.50-2.29 (m, 2H), 1.69 (dd, J =5.6, 14.4 Hz, 1H), 1.52 (dd, J =6.1, 14.4 Hz, 1H), 1.03 (s, 3H).

To a solution of the crude 1-[2-hydroxy-3-(2, 4, 6-trimethylphenylsulfonyl)propyl]-1-methyl-2, 5-cyclohexadiene in CH₂Cl₂ (30 ml) was added Dess-Martin's periodinane (2.81 g, 6.64 mmol) portionwise, and the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was quenched with Et₂O (30 ml), saturated aqueous NaHCO₃ solution (30 ml), and saturated aqueous Na₂S₂O₃ solution (30 ml). The organic layer was separated, washed with brine (30 ml), dried over Na₂SO₄, and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=8/1) to afford 1-methyl-1-[2-oxo-3-(2, 4, 6-trimethylphenylsulfonyl)propyl]-2, 5-cyclohexadiene (563.6 mg, 77% (2steps)) as a white solid: $R_f=0.41$ (hexane/ethyl acetate=4/1); mp=88-90 °C; IR(KBr): 1723, 1601, 1456, 1396, 1361, 1311, 1146, 1033, 852, 759, 742, 731, 715, 704, 623 cm⁻¹; ¹H NMR (400MHz, CDCl₃): δ =6.96 (s, 2H), 5.71 (ddd, J =2.8, 3.4, 10.3 Hz, 2H), 5.58 (ddd, J =1.6, 2.0, 10.3 Hz, 2H), 4.14 (s, 2H), 2.73 (s, 2H), 2.61 (s, 6H), 2.53-2.61 (m, 2H), 2.30 (s, 3H), 1.15 (s, 3H); ¹³C NMR (100MHz, CDCl₃): δ =197.3, 143.8, 140.0, 132.8, 132.3, 132.2, 124.0, 67.4, 56.6, 36.1, 30.1, 26.0, 22.9, 21.1; HRMS(FAB): calcd C₁₉H₂₄O₃SH⁺ 333.1524, found 333.1530.

1-[3-Diazo-2-oxo-3-(2, 4, 6-trimethylphenylsulfonyl)propyl]-1-methyl-2, 5-cyclohexadiene (**5b**)

5b was prepared by the previously described **Procedure A**. Purification by flash chromatography (hexane/ethyl acetate=50/1) afforded 1-[3-diazo-2-oxo-3-(2, 4, 6-trimethylphenylsulfonyl)propyl]-1-methyl-2, 5-cyclohexadiene **5b** (94%) as a yellow solid: R_f =0.47 (hexane/ethyl acetate=4/1); mp=96-99 °C; IR(KBr): 2109, 1658, 1457, 1328, 1149, 714, 671, 608 cm^{-1} ; ^1H NMR (400MHz, CDCl_3): δ =6.98 (s, 2H), 5.64 (ddd, J =2.8, 3.4, 10.3 Hz, 2H), 5.40 (ddd, J =1.6, 2.0, 10.3 Hz, 2H), 2.65 (s, 6H), 2.51-2.31 (m, 2H), 2.42 (s, 2H), 2.31 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (100MHz, CDCl_3): δ =186.6, 143.8, 140.3, 134.8, 132.1, 131.4, 124.3, 51.1, 36.8, 29.4, 25.9, 22.7, 21.1; HRMS(FAB): calcd $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_3\text{SH}^+$ 359.1429, found 359.1405.

(1*S*, 5*R*, 6*R*, 7*S*)-1-Methyl-8-oxo-7-(2, 4, 6-trimethylphenylsulfonyl)sulfonyltricyclo[4.3.0.0^{5,7}]non-2-ene (**6b**)

The enantioselective cyclopropanation of **6a** with **2e** was carried out at room temperature for 1h and at 50°C for 27h according to the previously described procedure for **4a** with **2a**. Purification by preparative TLC (hexane/ethyl acetate=4/1) to afford (1*S*, 5*R*, 6*R*, 7*S*)-1-methyl-8-oxo-7-(2, 4, 6-trimethylphenylsulfonyl)sulfonyltricyclo[4.3.0.0^{5,7}]non-2-ene **6b** (93% ee, 61%) as a white solid. The absolute configuration was determined by X-ray crystallographic analysis of the recrystallized **6b**. Ee was determined by HPLC (254 nm); Daicel Chiral Cell AS-H 0.46 cm ϕ $\times$ 25 cm; hexane/isopropanol=3/1; flow rate=0.5 ml/min; retention time : 17.4 min for **6b**, 21.5 min for *ent*-**6b**; R_f =0.39 (hexane/ethyl acetate=4/1); mp=157-158°C (hexane/ CH_2Cl_2); $[\alpha]_D^{25}$ -21.0 (c 1.82, CHCl_3 , 93% ee); IR(KBr): 1732, 1603, 1455, 1373, 1307, 1267, 1164, 1142, 1055, 854, 715, 682, 669 cm^{-1} ; ^1H NMR(400MHz, CDCl_3): δ =6.97 (s, 2H), 5.73-5.65 (m, 2H), 2.85 (d, J =3.2Hz, 1H), 2.85-2.84 (m, 1H), 2.68 (s, 6H), 2.68-2.60 (m, 1H), 2.48 (d, J =17.3 Hz, 1H), 2.30 (s, 3H), 2.13 (dd, J =0.7, 17.3 Hz, 1H), 2.11 (dd, J =1.5, 19.5 Hz, 1H), 1.51 (s, 3H); ^{13}C NMR(100MHz, CDCl_3): δ =203.8, 143.3, 140.6, 135.5, 132.8, 132.1, 124.5, 61.9, 59.5, 40.1, 31.1, 29.2, 27.7, 23.4, 21.1, 20.0; HRMS(FAB): calcd $\text{C}_{19}\text{H}_{22}\text{O}_3\text{SH}^+$ 331.1368, found 331.1335.

Ethyl (*E*)-3-(1-methyl-2, 5-cyclohexadienyl)propenoate

To a solution of potassium *tert*-butoxide (2.164 g, 19.3 mmol) in THF (100 ml) was added ethyl diethylphosphonate (5.47 ml, 27.6 mmol) dropwise at 0°C, and the reaction mixture was cooled to -78°C. To the reaction mixture was added a solution of 1-methyl-2, 5-cyclohexadiene-1-carboxaldehyde (1.904 g, 15.6 mmol) in THF (5 ml) via a canula at -78°C. The solution was stirred at -78°C for 10 min, then warmed to 0°C and stirred for 30 min. The reaction mixture

was quenched with saturated aqueous NH_4Cl solution (60 ml), extracted with Et_2O (50 ml x 1), and CH_2Cl_2 (50 ml x 2). The combined organic layer was washed with brine (100 ml), dried over Na_2SO_4 , and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=10/1) to afford ethyl (*E*)-2-(1-methyl-2, 5-cyclohexadienyl)propenoate (2.644 g, 88%) as a colorless oil: R_f =0.45 (hexane/ethyl acetate=10/1); IR(neat): 3024, 2980, 2932, 2876, 1720, 1646, 1456, 1422, 1368, 1310, 1288, 1268, 1254, 1206, 1178, 1114, 1100, 1038, 990, 948, 916, 864 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =6.88 (d, J =15.6Hz, 1H), 5.77 (ddd, J =10.3, 3.4, 2.0Hz, 2H), 5.72 (d, J =15.6Hz, 1H), 5.52 (ddd, J =10.3, 2.0, 1.5Hz, 2H), 4.18 (q, J =7.1Hz, 2H), 2.67-2.62 (m, 2H), 1.28 (t, J =7.1Hz, 3H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ =167.0, 154.8, 130.5, 123.8, 118.5, 60.3, 38.9, 27.9, 26.1, 14.3; HRMS(FAB): m/z calcd for $\text{C}_{12}\text{H}_{16}\text{O}_2\text{H}^+$ 193.1228, found 193.1240.

Ethyl 3-(1-methyl-2, 5-cyclohexadienyl)propanate

To a solution of ethyl (*E*)-3-(1-methyl-2, 5-cyclohexadienyl)propenoate (311.0 mg, 1.62 mmol) in MeOH (16 ml) was added $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (54.4 mg, 0.229 mmol), then NaBH_4 (176.0 mg, 4.65 mmol) portionwise at 0°C . The reaction mixture was stirred at 0°C for 1.5h, quenched with saturated aqueous NH_4Cl solution (15 ml), extracted with ethyl acetate (15 ml x 3), and the combined organic layer was washed with brine (20 ml), dried over Na_2SO_4 , and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=10/1) to afford ethyl 3-(1-methyl-2, 5-cyclohexadienyl)propanate (288.0 mg, 92%) as a colorless oil: R_f =0.73 (hexane/ethyl acetate=4/1); IR(neat): 3016, 2964, 2928, 2868, 2820, 1736, 1456, 1422, 1392, 1374, 1354, 1292, 1236, 1208, 1182, 1122, 1102, 1038, 1026, 948 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =5.73 (ddd, J =10.5, 3.4, 2.3 Hz, 2H), 5.36 (ddd, J =10.5, 2.0, 1.6Hz, 2H), 4.09 (q, J =7.1 Hz, 2H), 2.61-2.55 (m, 2H), 2.19 (dd, J =8.4, 8.3 Hz, 2H), 1.63 (dd, J =8.4, 8.3Hz, 2H), 1.24 (t, J =7.1 Hz, 3H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ =174.2, 132.8, 123.9, 60.1, 37.3, 36.0, 30.9, 30.0, 26.3, 14.3; HRMS(FAB): m/z calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2\text{H}^+$ 195.1385, found 195.1384.

1-Methyl-1-(3-oxo-4-phenylsulfonylbutyl)-2, 5-cyclohexadiene

The previously described procedure for **1-phenylsulfonyl-5-hexene-2-one** afforded the title compound. Purification by flash chromatography (hexane/ethyl acetate=5/1) afforded 1-phenylsulfonyl-5-hexene-2-one (88%) as a colorless oil: R_f =0.20 (hexane/ethyl acetate=4/1); IR(neat): 3016, 2956, 2928, 2864, 1722, 1448, 1370, 1324, 1154, 1088, 1066, 744, 690 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =7.88 (d, J =8.2 Hz, 2H), 7.68 (t, J =7.6 Hz, 1H), 7.57 (dd, J =8.2, 7.6 Hz, 2H), 5.73 (ddd, J =10.5, 3.4, 2.2 Hz, 2H), 5.30 (ddd, J =10.5, 2.0, 1.4 Hz, 2H), 4.12 (s, 2H), 2.63-2.57 (m, 2H), 2.55 (dd, J =7.8, 7.5 Hz, 2H), 1.56 (dd, J =7.8, 7.5 Hz, 2H), 1.05 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ =198.6, 138.7, 134.1, 132.8, 129.2, 128.3, 124.2, 67.0, 41.3, 35.9, 35.6, 29.9, 26.3; HRMS(FAB): m/z calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3\text{SH}^+$ 305.1211, found 305.1165.

1-(4-Diazo-3-oxo-4-phenylsulfonylbutyl)-1-methyl-2, 5-cyclohexadiene (7a)

7a was prepared by the previously described **Procedure A**. Purification by flash chromatography (hexane/ethyl acetate=20/1) afforded 1-(4-diazo-3-oxo-4-phenylsulfonylbutyl)-1-methyl-2, 5-cyclohexadiene **7a** (90%) as a yellow oil: IR(neat): 3016, 2960, 2928, 2864, 2116, 1666, 1448, 1370, 1338, 1314, 1292, 1216, 1156, 1118, 726 cm^{-1} ; R_f =0.39 (hexane/ethyl acetate=4/1); ^1H NMR (400 MHz, CDCl_3): δ =7.97 (d, J =8.1 Hz, 2H), 7.67 (t, J =7.3 Hz, 1H), 7.57 (dd, J =8.1, 7.3 Hz, 2H), 5.69 (ddd, J =10.5, 3.4, 2.3 Hz, 2H), 5.26 (ddd, J =10.5, 2.0, 1.4 Hz, 2H), 2.68-2.45 (m, 2H), 2.41 (dd, J =7.8, 7.6 Hz, 2H), 1.57 (dd, J =7.8, 7.6 Hz, 2H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ =188.7, 141.8, 134.0, 132.7, 129.2, 127.4, 124.1, 36.1, 36.1, 35.8, 29.9, 26.3; HRMS(FAB): m/z calcd for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_3\text{SH}^+$ 331.1116, found 331.1095.

(1R, 5S, 6S, 7R)-1-Methyl-8-oxo-7-phenylsulfonyltricyclo[4.4.0.0^{5,7}]dec-2-ene (8a)

The enantioselective cyclopropanation of **7a** with **2a** was carried out at rt for 3.5h according to the previously described procedure for **4a** with **2a**. Purification by flash chromatography (hexane/ethyl acetate=15/1) afforded (1R, 5S, 6S, 7R)-1-methyl-8-oxo-7-phenylsulfonyltricyclo[4.4.0.0^{5,7}]dec-2-ene **8a** (78%) as a white solid. The absolute configuration was determined by X-ray crystallographic analysis of the recrystallized **8a**. Ee was determined by HPLC (254 nm); Daicel Chiral Cell OD-H 0.46 cm ϕ $\times$ 25 cm; hexane/isopropanol=9/1; flow rate=0.5 ml/min; retention time : 17.4 min for **ent-8a**, 20.6 min for **8a**; R_f =0.23 (hexane/ethyl acetate=4/1); mp 138-139 $^\circ\text{C}$ (hexane/ CH_2Cl_2); $[\alpha]_D^{23}$ +128.7 (c 0.99, CHCl_3 , 99% ee); IR(KBr): 3017, 2969, 1708, 1449, 1307, 1148, 1088, 958 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =7.85 (d, J =8.1 Hz, 2H), 7.65 (t, J =7.3 Hz, 1H), 7.55 (dd, J =8.1, 7.3 Hz, 2H), 5.51 (ddd, J =10.5, 3.4, 2.5 Hz, 1H), 5.22 (dd, J =10.5, 1.2 Hz, 1H), 2.53 (dd, J =9.9, 1.2 Hz, 1H), 2.45-2.34 (m, 1H), 2.27 (ddd, J =18.8, 7.3, 1.5 Hz, 1H), 2.22-2.10 (m, 2H), 2.04 (ddd, J =13.2, 11.4, 7.3 Hz, 1H), 1.96 (ddd, J =19.5, 3.2, 2.5 Hz, 1H), 1.57 (ddd, J =13.2, 6.6, 1.5, 1H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ =201.2, 139.4, 133.6, 132.0, 128.8(2C), 128.8(2C), 124.0, 48.3, 36.9, 36.8, 29.7, 29.0, 29.0, 22.8, 19.3; HRMS(FAB): m/z calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3\text{SH}^+$ 303.1055, found 303.1050.

1-Methyl-1-[3-oxo-4-(2, 4, 6-trimethylphenylsulfonyl)butyl]-2, 5-cyclohexadiene

The previously described procedure for **1-(2, 4, 6-trimethylphenylsulfonyl)-5-hexen-2-one** afforded the title compound. Purification by flash chromatography (hexane/ethyl acetate=25/1) afforded 1-methyl-1-[3-oxo-4-(2, 4, 6-trimethylphenylsulfonyl)butyl]-2, 5-cyclohexadiene (95%) as a white solid: R_f =0.28 (hexane/ethyl acetate=4/1);

mp=67-70°C; IR(KBr): 3003, 2930, 2878, 1716, 1456, 1380, 1314, 1152, 1057, 1034, 740, 705 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ=6.97 (s, 2H), 5.72 (ddd, *J*=10.0, 3.4, 2.3 Hz, 2H), 5.30 (ddd, *J*=10.0, 2.0, 1.6 Hz, 2H), 4.11 (s, 2H), 2.70-2.48 (m, 10H), 2.31 (s, 3H), 1.55 (dd, *J*=7.8, 7.6 Hz, 2H), 1.05 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ=198.9, 143.8, 140.0, 132.8, 132.3, 132.3, 124.1, 67.0, 41.5, 35.8, 35.6, 29.9, 26.3, 22.9, 21.1; HRMS(FAB): *m/z* calcd for C₂₀H₂₆O₃SH⁺ 347.1681, found 347.1683.

1-[4-Diazo-3-oxo-4-(2, 4, 6-trimethylphenylsulfonyl)butyl]-1-methyl-2, 5-cyclohexadiene (**7b**)

7b was prepared by the previously described **Procedure A**. Purification by flash chromatography (hexane/ethyl acetate=50/1) afforded 1-[4-diazo-3-oxo-4-(2, 4, 6-trimethylphenylsulfonyl)butyl]-1-methyl-2, 5-cyclohexadiene **7b** (85%) as a yellow solid: *R*_f=0.48 (hexane/ethyl acetate=4/1); mp=94-97°C; IR(KBr): 3015, 2946, 2925, 2867, 2102, 1667, 1457, 1372, 1326, 1299, 1242, 1181, 1146, 718 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ=6.98 (s, 2H), 5.65 (ddd, *J*=10.5, 3.4, 2.3 Hz, 2H), 5.20 (ddd, *J*=10.5, 2.0, 1.5 Hz, 2H), 2.63 (s, 6H), 2.63-2.40 (m, 2H), 2.32 (s, 3H), 2.25 (dd, *J*=7.6, 7.5 Hz, 2H), 1.49 (dd, *J*=7.6, 7.5 Hz, 2H), 0.99 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ=189.3, 143.9, 140.0, 135.0, 132.6, 132.4, 124.1, 35.9, 35.8, 35.6, 30.0, 26.3, 22.6, 21.1; HRMS(FAB): *m/z* calcd for C₂₀H₂₄N₂O₃SH⁺ 373.1586, found 373.1570.

(1*R*, 5*S*, 6*S*, 7*R*)-1-Methyl-8-oxo-7-(2, 4, 6-trimethylphenylsulfonyl)tricyclo[4.4.0.0^{5,7}]dec-2-ene (**8b**)

The enantioselective cyclopropanation of **7b** with **2a** was carried out at rt for 27h according to the previously described procedure for **4a** with **2a**. Purification by flash chromatography (hexane/ethyl acetate=20/1) afforded (1*R*, 5*S*, 6*S*, 7*R*)-1-methyl-8-oxo-7-(2, 4, 6-trimethylphenylsulfonyl)tricyclo[4.4.0.0^{5,7}]dec-2-ene **8b** (97% ee, 69%) as a white solid. The absolute configuration was determined by comparison of the optical rotation of (1*S*, 6*R*)-1-methyl-8-oxobicyclo[4.4.0]dec-2-ene, which had been derived from **8a** and **8b** (see below). Ee was determined by HPLC (254 nm); Dical Chiral Cell OD-H 0.46 cm φ×25 cm; hexane/isopropanol=9/1; flow rate=0.5 ml/min; retention time : 12.7 min for *ent*-**8b**, 17.0 min for **8b**; *R*_f=0.37 (hexane/ethyl acetate=4/1); mp 122-124°C (hexane/CH₂Cl₂); [α]_D²¹ +134.1 (c 1.10, CHCl₃, 100% ee); IR(KBr): 1692, 1459, 1308, 1142, 1102 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ=6.95 (s, 2H), 5.56 (ddd, *J*=10.5, 3.4, 2.7 Hz, 1H), 5.23 (d, *J*=10.5 Hz, 1H), 2.63 (s, 6H), 2.53-2.40 (m, 2H), 2.40-2.25 (m, 4H), 2.25-2.00 (m, 4H), 1.65-1.55 (m, 1H), 1.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ=201.4, 143.2, 140.5, 132.8, 132.1, 132.0, 124.2, 50.8, 36.9, 36.9, 29.3, 28.9, 28.7, 23.6, 22.7, 21.1, 19.3; HRMS(FAB): *m/z* calcd for C₂₀H₂₄O₃SH⁺ 345.1524, found 345.1520.

(1*S*, 6*R*)-1-Methyl-8-oxobicyclo[4.4.0]dec-2-ene

To a stirred solution of **8a** (152.0 mg, 0.503 mmol) in MeOH (8.5 ml) was added Na₂HPO₄ (285.0 mg, 2.01 mmol) and sodium amalgam (ca. 3g) at room temperature. After 3h, the reaction mixture was filtered through celite, and the filtered material and celite were washed with Et₂O (80 ml). The combined filtrate was washed with saturated aqueous NaHCO₃ solution (40 ml), and the separated aqueous layer was extracted with CH₂Cl₂ (30 ml x 2). The combined organic layer was washed with brine (80 ml), dried over Na₂SO₄, and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=20/1) to afford (1*S*, 6*R*)-1-methyl-8-oxobicyclo[4.4.0]dec-2-ene (36.7 mg, 45%) as a colorless oil. **8b** was also converted to the same compound (53%): R_f=0.54 (hexane/ethyl acetate=4/1); [α]_D²⁴+72.9 (c 1.14, CHCl₃, 95% ee, from **8a**); [α]_D²³+76.9 (c 1.19, CHCl₃, 100% ee, from **8b**); IR(neat): 3016, 2928, 2872, 1718, 1454, 1422, 1268, 1232, 754, 716 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ=5.68 (ddd, *J*=10.0, 3.7, 2.5Hz, 1H), 5.47 (ddd, *J*=10.0, 2.2, 1.6 Hz, 1H), 2.36 (dd, *J*=14.0, 6.1 Hz, 1H), 2.33-2.25 (m, 3H), 2.08-2.01 (m, 2H), 2.00-1.80 (m, 3H), 1.68 (ddd, *J*=13.8, 8.8, 5.9 Hz, 1H), 1.45 (dddd, *J*=13.3, 6.8, 6.6, 6.1 Hz, 1H), 1.17 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ=212.8, 134.8, 126.0, 43.2, 41.4, 38.2, 37.9, 34.2, 27.9, 24.6, 22.2; HRMS(FAB): *m/z* calcd for C₁₁H₁₆OH⁺ 165.1279, found 165.1251.