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Supplemental Material

An experiment on the optical purity of (-)-10-mercaptoisoborneol (2)

A DMF (2 mL) solution of (-)-10-mercaptoisoborneol (2) (300 mg, 1.61 mmol) was added dropwise to a slurry of 60% sodium hydride (129 mg, 3.22 mmol), which was washed 3 times with dry ether (5 mL), in dry DMF (10 mL) at 0 °C. After being stirred for 30 min, benzyl bromide (330 mg, 1.93 mmol) was added dropwise and then stirred for 10 h. The reaction mixture was quenched with a saturated ammonium chloride solution. The solvent was removed *in vacuo*. The residue was added water (20 mL) and then the aqueous layer was extracted with ethyl acetate (50 mL x 3). The combined organic layer was washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. Silica gel chromatography of the residue (eluted with hexane : ethyl acetate = 15 : 1) gave the *S*-benzyl ether of 2 (440 mg, 99% yield). *S*-Benzyl ether of 2: colorless oil; $[\alpha]_D^{27}$ = -60.3 (1.17, $CHCl_3$); IR ($CHCl_3$) 3600-3500, 2950, 1490, 1450, 1385, 1065, 1045, 1025, 990, 875 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.33–7.23 (m, 5H), 3.82 (dt, *J* = 7.3 and 3.4 Hz, 1H), 3.76 (d, A part of AB, *J* = 13.4 Hz, 1H), 3.70 (d, B part of AB, *J* = 13.4 Hz, 1H), 2.67 (d, A part of AB, *J* = 11.0 Hz, 1H), 2.51 (d, B part of AB, *J* = 11.0 Hz, 1H), 2.06 (d, *J* = 3.4 Hz, 1H), 1.78-1.61 (m, 4H), 1.53-1.41 (m, 1H), 1.29-1.13 (m, 1H), 1.07-0.95 (m, 1H), 0.98 (s, 3H), 0.79 (s, 3H); MS FAB(+) *m/z* 276 (M^+, 22); Anal. Calcd for $C_{17}H_{24}OS$: C, 73.86; H, 8.75. Found : C, 73.87; H, 8.86.

The 98% ee of (-)-2 was determined by a chiral HPLC analysis [DAICEL CHIRALCEL OD (25 x 0.46); eluent: hexane / isopropanol = 99 / 1; flow rate: 1 mL/min.; Temp.: 25 °C; detector: 254 nm, *S*-benzyl ether of (+)-2: 14.1 min., *S*-benzyl ether of (-)-2: 15.8 min.].

A General Procedure for the Tandem Michael Addition - MPV Reduction (Table 1, 3a-d)

To a dichloromethane (or benzene) solution (20 mL) of (-)-10-mercaptoisoborneol (2) (100 mg, 0.54 mmol) was added dropwise dimethyl aluminum chloride (0.94 M hexane solution, 0.57 mL, 0.54 mol) at room temperature (ca. 20 °C). After being stirred for 1 h, dichloromethane (or benzene) (5 mL) solution of an α,β-unsaturated ketone **1a-d** (0.45 mmol) was added dropwise and then the mixture was stirred for hours indicated in Table 1 at room temperature (ca. 20 °C) (if necessary, a Cryobath CB-80, Neslab Co. Ltd., was used to control the temperature). The reaction mixture was quenched with a saturated ammonium chloride solution, then the aqueous layer was extracted with dichloromethane (or ethyl acetate) (50 mL x 3). The organic layer was washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. Silica gel chromatography of the residue (eluted with hexane : ethyl acetate = 7 : 1 - 10 : 1) gave a product **3a-d** in the yield shown in Table 1.

(1*R*)-3-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-1,3-diphenyl-1-propanol (3a)

colorless oil; $[\alpha]_D^{22}$ = +124.4 (1.05, $CHCl_3$); IR ($CHCl_3$) 3640-3170, 3605, 2960, 1735, 1492, 1450, 1410, 1045, 905, 550 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.42-7.15 (m, 10H), 4.95 (dt, *J* = 8.6 and 4.0 Hz, 1H), 3.96 (dd, *J* = 9.1 and 6.0 Hz, 1H), 2.63 (d, A part of AB, *J* = 13.2 Hz, 1H), 2.53 (d, *J* = 2.0 Hz, 1H), 2.35-2.07 (m, 3H), 2.16 (d, B part of AB, *J* = 13.2 Hz, 1H),

2.01 (t, J = 4.6 Hz, 1H), 2.05-1.59 (m, 3H), 1.52-1.38 (m, 1H), 1.36-1.20 (m, 1H), 0.86 (s, 3H), 0.72 (s, 3H); ^{13}C-NMR (67.5 MHz, $CDCl_3$) 217.86, 144.03, 142.98, 128.32, 127.87, 126.97, 125.88, 71.59, 60.63, 48.38, 47.66, 45.75, 43.20, 42.95, 27.42, 26.67, 26.53, 19.86, 19.79; MS (20 eV) *m/z* 394 (M^+, 0.7), 211 (23), 210 (100), 193 (10), 185 (12), 107 (22), 105 (75), 104 (11); HRMS calcd for $C_{25}H_{30}O_2S$: 394.1967, found 394.1962.

(2*S*,4*R*)-4-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-4-phenyl-2-butanol (3b)

colorless oil; $[\alpha]_D^{20}$ = +134.5 (2.53, $CHCl_3$); IR ($CHCl_3$) 3650-3260, 3610, 2970, 1735, 1710, 1450, 1410, 1375, 1360, 1125, 1060, 1050, 935 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.41-7.17 (m, 5H), 4.15-3.95 (m, 2H), 2.61 (d, A part of AB, J = 13.2 Hz, 1H), 2.49-2.15 (br s, 1H), 2.31 (ddd, A part of AB, J = 18.3, 4.7 and 3.1 Hz, 1H), 2.21 (d, B part of AB, J = 13.2 Hz, 1H), 2.01 (t, J = 2.2 Hz, 1H), 1.95-1.83 (m, 3H), 1.83 (d, B part of AB, J = 18.3 Hz, 1H), 1.83-1.65 (m, 1H), 1.59-1.45 (m, 1H), 1.39-1.13 (m, 1H), 1.20 (d, J = 6.3 Hz, 3H), 0.88 (s, 3H), 0.75 (s, 3H); MS (70 eV) *m/z* 332 (M^+, 10), 185 (50), 137 (16), 109 (18), 105 (100), 81 (16), 79 (16); HRMS calcd for $C_{20}H_{28}O_2S$: 332.1810, found 332.1819.

(1*R*)-3-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-3-(*p*-methoxyphenyl)-1-phenyl-1-propanol (3c)

colorless oil; $[\alpha]_D^{23}$ = +122.6 (0.31, $CHCl_3$); IR ($CHCl_3$) 3700, 3600, 3550-3390, 2960, 1740, 1610, 1510, 1420, 1300, 1180, 1040, 835, 550 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.35-7.23 (m, 5H), 7.25 (d, J = 8.3 Hz, 2H), 6.85 (d, J = 8.3 Hz, 2H), 4.92 (br dd, J = 9.0 and 5.4 Hz, 1H), 3.93 (dd, J = 8.7 and 6.2 Hz, 1H), 3.80 (s, 3H), 2.64 (d, A part of AB, J = 13.2 Hz, 1H), 2.48 (br s, 1H), 2.40-2.10 (m, 2H), 2.20 (d, B part of AB, J = 13.2 Hz, 1H), 2.05-1.69 (m, 4H), 1.53-1.42 (m, 1H), 1.37-1.22 (m, 2H), 0.90 (s, 3H), 0.76 (s, 3H); MS FAB(+) *m/z* 425 (M^++H, 4); HRMS (FAB(+)) calcd for $C_{26}H_{33}O_3S$ (M^++H): 425.2151, found 425.2152.

(1*R*)-3-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-1-phenyl-3-(*p*-tolyl)-1-propanol (3d)

colorless oil; $[\alpha]_D^{23}$ = +126.0 (0.44, $CHCl_3$); IR ($CHCl_3$) 3700, 3600, 3550-3400, 2960, 1740, 1600, 1510, 1450, 1410, 1300, 1000, 920, 620 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.36-7.09 (m, 9H), 4.94 (br dt, J = 7.4 and 3.9 Hz, 1H), 3.95 (dd, J = 9.0 and 6.3 Hz, 1H), 2.64 (d, A part of AB, J = 13.2 Hz, 1H), 2.51 (d, J = 3.9 Hz, 1H), 2.33 (s, 3H), 2.35-2.15 (m, 2H), 2.22 (d, B part of AB, J = 13.2 Hz, 1H), 2.01 (t, J = 4.6 Hz, 1H), 1.95-1.70 (m, 2H), 1.53-1.43 (m, 2H), 1.35-1.25 (m, 2H), 0.90 (s, 3H), 0.76 (s, 3H); MS FAB(+) *m/z* 409 (M^++H, 10); HRMS (FAB(+)) calcd for $C_{26}H_{33}O_2S$ (M^++H): 409.2201, found 409.2189.

A General Procedure for Reductive Desulfurization with the Raney Nickel - Sodium Hypophosphite Combination System (Method A)

To a solution [acetate buffer (pH 5.2) : ethanol = 1 : 2, 9 mL] of an MPV product **3a-d** was added Raney Ni W-2 (ethanol suspension, 2 mL). To a resultant solution was added sodium hypophosphite monohydrate (in water solution, 2 mL) immediately and stirred for minutes indicated in Table 1 at room temperature. The reaction mixture was filtered with celite and then evaporated. To this solution was added water (20 mL), then aqueous layer was extracted with dichloromethane (30 mL x 3), washed brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. Preparative TLC of the residue (eluted with hexane : ethyl acetate = 3 : 1) gave a

secondary alcohol in the yield shown in Table 1.

(*R*)-1,3-Diphenylpropanol (4a) (Lit. Table 1, footnote f)

(1*R*)-3-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-1,3-diphenyl-1-propanol (**3a**) (50.8 mg, 0.129 mmol) and sodium hypophosphite monohydrate (136.7 mg, 1.29 mmol) were used. **4a**: $[\alpha]_D^{22}$ = +16.2 (1.17, MeOH); [96% ee, chiral HPLC analysis; DAICEL CHIRALCEL OD (25 x 0.46); eluent: hexane / isopropanol = 95 / 5; flow rate: 1 mL/min.; Temp.: 25 °C; detector: 254 nm, (*S*)-**4a**: 21.0 min., (*R*)-**4a**: 25.0 min.].

(*S*)-4-Phenylbutan-2-ol (4b)

(2*S*,4*R*)-4-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-4-phenyl-2-butanol (**3b**) (38 mg, 0.11 mmol) and sodium hypophosphite monohydrate (180 mg, 1.65 mmol) were used. **4b**: colorless oil; $[\alpha]_D^{22}$ = +18.8 (0.86, $CHCl_3$); IR ($CHCl_3$) 3680-3230, 3625, 3075, 2985, 2948, 1603, 1495, 1455, 1370, 1120, 1045, 950, 850 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.32-7.12 (m, 5H), 3.83 (sextet, *J* = 6.2 Hz, 1H), 2.82-2.60 (m, 2H), 1.87-1.67 (m, 2H), 1.56 (br s, 1H), 1.23 (d, *J* = 6.2 Hz, 3H); MS (70 eV) *m/z* 150 (M^+, 7), 132 (32), 117 (82), 92 (48), 91 (100), 78 (27); HRMS calcd for $C_{10}H_{14}O$: 150.1045, found 150.1050. [97% ee, chiral HPLC analysis; DAICEL CHIRALCEL OD (25 x 0.46); eluent: hexane / isopropanol = 95 / 5; flow rate: 1 mL/min.; Temp.: 25 °C; detector: 254 nm, (*R*)-**4b**: 12.4 min., (*S*)-**4b**: 18.0 min.].

(*R*)-3-(*p*-Methoxyphenyl)-1-phenylpropanol (4c)

(*R*)-3-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-3-(*p*-methoxyphenyl)-1-phenyl-1-propanol (**3c**) (24 mg, 0.057 mmol) and sodium hypophosphite monohydrate (0.57 mmol, 60 mg) were used. **4c**: colorless needles, mp 96-97 °C (hexane); $[\alpha]_D^{28}$ = +17.1 (0.14, $CHCl_3$); IR ($CHCl_3$) 3600, 3450 (br), 3000, 2925, 2850, 1615, 1510, 1450, 1290, 1170, 1060, 830 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.36-7.25 (m, 5H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.67 (dd, *J* = 7.8 and 5.5 Hz, 1H), 3.78 (s, 3H), 2.75-2.55 (m, 2H), 2.17-1.91 (m, 3H); MS [FAB(+)] *m/z* 242 (M^+, 20). Anal. Calcd for $C_{16}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.13; H, 7.72. [96% ee, chiral HPLC analysis; DAICEL CHIRALPAK AS (25 x 0.46); eluent: hexane / isopropanol = 95 / 5; flow rate: 1 mL/min.; Temp.: 25 °C; detector: 254 nm, (*S*)-**4c**: 13.7 min., (*R*)-**4c**: 18.1 min.].

(*R*)-1-Phenyl-3-(*p*-tolyl)propanol (4d)

(*R*)-3-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-1-phenyl-3-(*p*-tolyl)-1-propanol (**3d**) (32 mg, 0.077 mmol) and sodium hypophosphite monohydrate (82 mg, 0.77 mmol) were used. **4d**: colorless needles; mp 73-74 °C (hexane); $[\alpha]_D^{25}$ = +22.6 (0.45, $CHCl_3$); IR ($CHCl_3$) 3600, 3440 (br), 3000, 2930, 2860, 1510, 1450, 1380, 1050, 910, 560 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.35-7.24 (m, 5H), 7.08 (s, 4H), 4.67 (dd, *J* = 7.8 and 5.6 Hz, 1H), 2.71-2.62 (m, 2H), 2.31 (s, 3H), 2.29-1.99 (m, 2H), 1.88 (br s, 1H); MS [FAB(+)] *m/z* 226 (M^+, 5). Anal. Calcd for $C_{16}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.33; H, 8.25. [98% ee, chiral HPLC analysis; DAICEL CHIRALCEL OD (25 x 0.46); eluent: hexane / isopropanol = 95 / 5; flow rate: 1 mL/min.; Temp.: 25 °C; detector: 254 nm, (*R*)-**4d**: 14.2 min., (*S*)-**4d**: 16.9 min.].

Tandem Michael Addition - MPV Reduction Reaction (Table 1, 3e-g)

The same procedure as described on the general procedure was carried out using (-)-10-mercaptoisoborneol (150 mg, 0.81 mmol), dimethyl aluminum chloride (0.94 M hexane solution, 0.81 mL, 0.86 mol), and an α,β-unsaturated ketone **1e-g** (0.67 mmol). Silica gel chromatography of the crude product (eluted with hexane : ethyl acetate = 6 : 1 - 8 : 1) gave a product **3e-g** in the yield shown in Table 1.

(*S*)-4-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-4-metyl-2-pentanol (3e)

colorless oil; $[\alpha]_D^{22}$ = +43.5 (0.40, $CHCl_3$); IR ($CHCl_3$) 3680, 3600-3225, 2965, 2930, 1735, 1455, 1415, 1370, 1280, 1140, 1040, 925 cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 4.17-4.02 (m, 1H), 3.80 (br s, 1H), 2.83 (d, A part of AB, J = 11.9 Hz, 1H), 2.49 (d, B part of AB, J = 11.9 Hz, 1H), 2.36 (ddd, A part of AB, J = 18.3, 4.3 and 2.5 Hz, 1H), 2.19-1.78 (m, 3H), 1.86 (d, B part of AB, J = 18.3 Hz, 1H), 1.62-0.83 (m, 4H), 1.35 (s, 3H), 1.32 (s, 3H), 1.18 (d, J = 6.3 Hz, 3H), 1.06 (s, 3H), 0.91 (s, 3H); MS (70 eV) *m/z* 284 (M^+, 26), 185 (100), 109 (47), 108 (42), 85 (72), 81 (49), 67 (41), 57 (91), 55 (54); HRMS calcd for $C_{16}H_{28}O_2S$: 284.1810, found 284.1817.

(*S*)-4-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-2-butanol (3f)

colorless oil; $[\alpha]_D^{16}$ = +32.0 (0.32, $CHCl_3$); IR ($CHCl_3$) 3655-3210, 3625, 2980, 1735, 1455, 1410, 1390, 1375, 1280, 1120, 1050 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) 3.96 (sextet, J = 6.2 Hz, 1H), 2.82 (d, A part of AB, J = 13.1 Hz, 1H), 2.69 (t, J = 7.2 Hz, 2H), 2.55 (d, B part of AB, J = 13.1 Hz, 1H), 2.37 (ddd, A part of AB, J = 18.3, 4.6 and 2.5 Hz, 1H), 2.22-1.87 (m, 3H), 1.88 (d, B part of AB, J = 18.3 Hz, 1H), 1.75 (q, J = 7.2 Hz, 2H), 1.66 (br s, 1H), 1.59-1.48 (m, 1H), 1.48-1.31 (m, 1H), 1.22 (d, J = 6.2 Hz, 3H), 1.05 (s, 3H), 0.91 (s, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz) 217.67, 66.99, 60.88, 47.75, 43.39, 43.06, 38.14, 31.03, 29.11, 26.79, 26.71, 23.39, 20.12 (2 carbons); MS (70 eV) *m/z* 256 (M^+, 65), 185 (26), 183 (100), 113 (39), 109 (55), 107 (46), 93 (26), 81 (52), 79 (36), 67 (46), 55 (49); HRMS calcd for $C_{14}H_{24}O_2S$: 256.1497, found 256.1490.

(*S*)-1-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-3-octanol (3g)

colorless oil; $[\alpha]_D^{17}$ = +27.1 (2.01, $CHCl_3$); IR ($CHCl_3$) 3630, 3680-3255, 2980, 2950, 1740, 1710, 1465, 1450, 1415, 1385, 1375, 1280, 1050 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.82-3.68 (m, 1H), 2.84 (d, A part of AB, J = 13.0 Hz, 1H), 2.70 (br t, J = 7.3 Hz, 2H), 2.52 (d, B part of AB, J = 13.0 Hz, 1H), 2.37 (ddd, A part of AB, J = 18.4, 4.7 and 2.7 Hz, 1H), 2.14-1.89 (m, 4H), 1.88 (d, B part of AB, J = 18.4 Hz, 1H), 1.84-1.62 (m, 2H), 1.59-1.21 (m, 10H), 1.05 (s, 3H), 0.91 (s, 3H), 0.89 (t, J = 6.6 Hz, 3H); MS (70 eV) *m/z* 312 (M^+, 34), 185 (72), 183 (100), 109 (57), 107 (43), 81 (68), 69 (55), 67 (56), 55 (80); HRMS calcd for $C_{18}H_{32}O_2S$: 312.2123, found 312.2114.

Benzoylation of the Hydroxy group of 3e-g

(*S*)-2-Benzoyloxy-4-[(1*S*,4*R*)-2-oxobornane-10-sulfenyl]-4-methyl-2-pentane (Table 1, entry 8, 9)

To a pyridine solution (5 mL) of **3e** (79 mg, 0.28 mmol) was added dropwise benzoyl chloride (0.039 mL, 0.34 mmol) at 0 °C and the mixture was allowed to warm up to room temperature and stirred for 1 h. After removal of the solvent under reduced pressure, water (20 mL) was added the residue. The mixture was extracted with ether (20 mL x 3). The combined extract was dried

($MgSO_4$), filtered and concentrated *in vacuo*. Silica gel chromatography of the residue (hexane : ethyl acetate = 10 : 1) gave (*S*)-2-benzoyloxy-4-[(1*S*,4*R*)-2-oxobornane-10-sulfenyl]-4-methyl-2-pentane (105 mg, 96%) as colorless oil. IR ($CHCl_3$); 2970, 2940, 1735, 1710, 1450, 1315, 1280, 1115 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.09-8.02 (m, 2H), 7.59-7.52 (m, 1H), 7.49-7.40 (m, 2H), 5.49-5.38 (m, 1H), 2.81 (d, A part of AB, J = 12.4 Hz, 1H), 2.47 (d, B part of AB, J = 12.4 Hz, 1H), 2.37 (ddd, A part of AB, J = 18.3, 4.6 and 3.2 Hz, 1H), 2.19-1.91 (m, 5H), 1.85 (d, B part of AB, J = 18.3 Hz, 1H), 1.42-1.24 (m, 2H), 1.37 (d, J = 6.3 Hz, 3H), 1.34 (s, 3H), 1.32 (s, 3H), 1.04 (s, 3H), 0.90 (s, 3H); MS (70 eV) *m/z* 388 (M^+, 1), 122 (28), 105 (100), 83 (11), 77 (53), 51 (24); HRMS calcd for $C_{23}H_{32}O_3S$: 388.2073, found 388.2072.

(*S*)-2-Benzoyloxy-4-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]butane (Table 1, entry 10)

The same procedure described above was carried out using **3f** (83 mg, 0.32 mmol), pyridine (10 mL), benzoyl chloride (0.11 mL, 0.969 mmol) for 12 h. Silica gel chromatography of the residue (eluted with hexane : ethyl acetate = 8 : 1) gave (*S*)-2-benzoyloxy-4-[(1*S*,4*R*)-2-oxobornane-10-sulfenyl]butane (111 mg, 96%) as colorless oil. IR ($CHCl_3$): 3545, 3075, 2975, 1730, 1710, 1603, 1450, 1410, 1390, 1370, 1355, 1315, 1280, 1110, 1050, 1025 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.07-8.01 (m, 2H), 7.60-7.52 (m, 1H), 7.49-7.41 (m, 2H), 5.31-5.20 (m, 1H), 2.82 (d, A part of AB, J = 13.0 Hz, 1H), 2.74-2.57 (m, 2H), 2.54 (d, B part of AB, J = 13.0 Hz, 1H), 2.42 (ddd, A part of AB, J = 18.3, 4.7 and 2.9 Hz, 1H), 2.15-1.87 (m, 5H), 1.86 (d, B part of AB, J = 18.3 Hz, 1H), 1.53-1.42 (m, 1H), 1.42-1.29 (m, 1H), 1.38 (d, J = 6.3 Hz, 3H), 1.03 (s, 3H), 0.90 (s, 3H); MS (70 eV) *m/z* 360 (M^+, 31), 238 (52), 183 (82), 109 (35), 105 (100), 81 (38), 77 (58), 55 (48); HRMS calcd for $C_{21}H_{28}O_3S$: 360.1759, found 360.1765.

(*S*)-3-Benzoyloxy-1-[(1*S*,4*R*)-2-oxobornane-10-sulfenyl]octane (Table 1, entry 11)

The same procedure described above was carried out using **3g** (168.2 mg, 0.54 mmol), pyridine (7 mL), benzoyl chloride (0.125 mL, 1.08 mmol) for 13 h. Silica gel chromatography of the residue (eluted with hexane : ethyl acetate = 10 : 1) gave (*S*)-3-benzoyloxy-1-[(1*S*,4*R*)-2-oxobornane-10-sulfenyl]-3-octane (219.9 mg, 98%) as colorless oil. IR ($CHCl_3$) 2975, 2950, 2890, 2875, 1740, 1710, 1450, 1315, 1270, 1110, 1025 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.12-7.98 (m, 2H), 7.64-7.32 (m, 3H), 5.27-5.18 (m, 1H), 2.80 (d, A part of AB, J = 13.1 Hz, 1H), 2.71-2.48 (m, 2H), 2.53 (d, B part of AB, J = 13.1 Hz, 1H), 2.36 (ddd, A part of AB, J = 18.2, 4.6 and 2.7 Hz, 1H), 2.12-1.83 (m, 5H), 1.85 (d, B part of AB, J = 18.2 Hz, 1H), 1.79-1.54 (m, 2H), 1.52-1.13 (m, 8H), 1.02 (s, 3H), 0.89 (s, 3H), 0.87 (br t, J = 6.8 Hz, 3H); MS (70 eV) *m/z* 416 (M^+, 9), 295 (36), 183 (43), 110 (30), 109 (41), 105 (100), 81 (50), 77 (54), 69 (38), 67 (44), 55 (46); Anal. calcd for $C_{25}H_{36}O_3S$: C, 72.07; H, 8.71. Found: C, 72.23; H, 8.80.

Reductive Desulfurization with Raney Nickel in EtOH (Table 1, Method B)

(*S*)-2-Benzoyl-4-methylpentane (4e)

To an ethanol solution (4 mL) of (*S*)-2-benzoyloxy-4-methyl-4-[(1*S*,4*R*)-2-oxobornane-10-sulfenyl]pentane (51.7 mg, 0.13 mmol) was added Raney Ni W-2 (ethanol suspension, 2 mL) and then stirred 2 h at room temperature. The reaction mixture was

filtered with celite and concentrated *in vacuo*. A preparative TLC gave (*S*)-2-benzoyl-4-methylpentane (**4e**) (10 mg, 75%) as colorless oil. $[\alpha]_D^{22}$ = +37.1 (0.16, $CHCl_3$); IR ($CHCl_3$): 3545, 3080, 2970, 1700, 1603, 1450, 1315, 1275, 1170, 1110, 1070, 1020, 910 cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$): δ 8.12-8.00 (m, 2H), 7.63-7.38 (m, 3H), 5.34-5.17 (m, 1H), 1.84-1.63 (m, 2H), 1.33 (d, *J* = 6.3 Hz, 3H), 1.50-1.24 (m, 1H), 0.94 (d, *J* = 6.3 Hz, 3H), 0.93 (d, *J* = 6.3 Hz, 3H); MS: (70 eV) *m/z* 206 (M^+, 0.1), 123 (12), 105 (100), 84 (69), 77 (34), 69 (36), 51 (12); HRMS calcd for $C_{13}H_{18}O_2$: 206.1307, found 206.1326. [98% ee, chiral HPLC analysis; DAICEL CHIRALCEL OB (25 x 0.46); eluent: hexane / isopropanol = 99 / 1; flow rate: 0.2 mL/min.; Temp.: 25 °C; detector: 254 nm, (*R*)-**4e**: 19.4 min., (*S*)-**4e**: 20.8 min.].

(*S*)-2-Benzoyloxybutane (4f)

To an ethanol solution (10 mL) of (2*S*)-2-benzoyloxy-4-[(1*S*,4*R*)-2-oxobornane-10-sulfenyl]butane (28 mg, 0.08 mmol) was added Raney Ni W-2 (ethanol suspension, 5 mL) and then refluxed 2 h at 90 °C. The reaction mixture was filtered with celite and concentrated *in vacuo*. Preparative TLC gave (*S*)-2-benzoylbutane (10 mg, 73%) as colorless oil. $[\alpha]_D^{25}$ = +39.7 (0.12, $CHCl_3$); IR ($CHCl_3$) 2980, 2950, 2890, 1705, 1445, 1380, 1350, 1270, 1170, 1100, 1065, 1015, 965, 880 cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 8.21-8.00 (m, 2H), 7.62-7.38 (m, 3H), 5.10 (sextet, *J* = 6.3 Hz, 1H), 1.85-1.55 (m, 2H), 1.34 (d, *J* = 6.3 Hz, 3H), 0.98 (t, *J* = 7.6 Hz, 3H); MS (70 eV) *m/z* 178 (M^+, 0.6), 123 (45), 105 (100), 77 (39), 73 (10), 56 (20), 51 (15); HRMS calcd for $C_{11}H_{14}O_2$: 178.0994, found 178.0999. [98% ee, chiral HPLC analysis; DAICEL CHIRALCEL OB (25 x 0.46); eluent: hexane / isopropanol = 99 / 1; flow rate: 0.2 mL/min.; Temp.: 25 °C; detector: 254 nm, (*R*)-**4f**: 22.3 min., (*S*)-**4f**: 25.1 min.].

(*R*)-3-Benzoyloxyoctane (4g)

The same procedure described on the synthesis of **4e**, was carried out using (*S*)-3-benzoyloxy-1-[(1*S*,4*R*)-2-oxobornane-10-sulfenyl]-3-octane (40 mg, 0.096 mmol), Raney Ni W2 (suspension, 1.5 mL), and ethanol (7 mL) for 31 h to give **4g** (17.5 mg, 77 %) as colorless oil. $[\alpha]_D^{23}$ = -8.0 (0.28, $CHCl_3$); IR ($CHCl_3$) 3530, 3075, 2975, 2950, 2860, 1705, 1603, 1450, 1315, 1280, 1110, 1065, 1020, 920 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.10-8.03 (m, 2H), 7.59-7.52 (m, 1H), 7.49-7.41 (m, 2H), 5.08 (quintet, *J* = 6.2 Hz, 1H), 1.77-1.56 (m, 4H), 1.46-1.22 (m, 6H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.87 (br t, *J* = 6.7 Hz, 3H); MS (70 eV) *m/z* 234 (M^+, 0.6), 123 (23), 112 (16), 105 (100), 77 (28), 70 (11); HRMS calcd for $C_{15}H_{22}O_2$: 234.1620, found 234.1601. [97% ee, chiral HPLC analysis; DAICEL CHIRALCEL OF (25 x 0.46); eluent: hexane / isopropanol = 1000 / 1; flow rate: 1.0 mL/min.; Temp.: 24 °C; detector: 254 nm, (*R*)-**4g**: 15.8 min., (*S*)-**4g**: 19.3 min.].

(1*S*,2*R*,4*R*)-10-Mercaptoisoborneol-2-d

(1*S*,2*R*,4*R*)-10-Mercaptoisoborneol-2-d was prepared by Eliel's procedure[6a] using lithium aluminum deuteride (>98% D) (45%, 2 steps). white powder; $[\alpha]_D^{27}$ = -58.1 (0.98, $CHCl_3$); IR ($CHCl_3$) 3600-3400, 2975, 2170, 1450, 1385, 1080, 965 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.78 (dd, A part of AB, *J* = 12.7 and 9.7 Hz, 1H), 2.57 (dd, B part of AB, *J* = 12.7 and 5.2 Hz, 1H),

2.07 (s, 1H), 1.83-1.62 (m, 4H), 1.49-1.39 (m, 1H) 1.32-1.21 (m, 1H), 1.28 (dd, J = 9.7 and 5.2 Hz, 1H), 1.10-1.01 (m, 1H) 1.05 (s, 3H), 0.83 (s, 3H); MS FAB(+) *m/z* 170 (M^++H-H_2O, 70); HRMS calcd for $C_{10}H_{16}DS$ (M^++H-H_2O): 170.1114, found 170.1121.

4-[(1*S*, 2*R*,4*R*)-2-Hydroxybornane-10-sulfenyl]-2-butanone-2-d (6)

To a dry THF solution (10 mL) of (1*S*,2*R*,4*R*)-10-mercaptoisoborneol-2-d (200 mg, 1.07 mmol) was added dropwise triethylamine (5.37 mmol, 0.75 mL) at room temperature. After being stirred for 30 min and methyl vinyl ketone (112 mg, 1.60 mmol) was added dropwise and then stirred for 4 h at room temperature. The reaction mixture was quenched with a saturated ammonium chloride solution. The solvent was removed *in vacuo*. The residue was added water (20 mL) and then the aqueous layer was extracted with ethyl acetate (50 mL x 3). The organic layer was washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. Silica gel chromatography of the residue (eluted with hexane : ethyl acetate = 4 : 1) gave **6** (275 mg, 100% yield) as colorless oil. **6**: $[\alpha]_D^{27}$ = -23.3 (0.18, $CHCl_3$); IR ($CHCl_3$) 3600-3450, 2955, 1710, 1660, 1360, 1080 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.80 (d, A part of AB, J = 11.1 Hz, 1H), 2.78 (br t, J = 3.7 Hz, 4H), 2.57 (d, B part of AB, J = 11.1 Hz, 1H), 2.46 (s, 1H), 2.18 (s, 3H), 1.82-1.45 (m, 4H), 1.55-1.44 (m, 1H), 1.28-1.15 (m, 1H), 1.09-1.01 (m, 1H), 1.06 (s, 3H), 0.84 (s, 3H); MS FAB(+) *m/z* 257 (M^+, 29); HRMS calcd for $C_{14}H_{23}DO_2S$: 257.1560, found 257.1542.

5-[(1*S*, 2*R*,4*R*)-2-Hydroxybornane-10-sulfenyl]-3-pentenone (7)

The same procedure described above carried out using (-)-10-mercaptoisoborneol (**2**) (200 mg, 1.07 mmol), ethyl vinyl ketone (135 mg, 1.61 mmol), triethylamine (5.37 mmol, 0.75 mL) and dry THF (10 mL), to give **7** (288 mg, 99% yield) as colorless oil. **7**: $[\alpha]_D^{25}$ = -42.1 (3.35, $CHCl_3$); IR ($CHCl_3$) 3600-3450, 2950, 1710, 1450, 1105, 1065, 875 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.86 (br dt, J = 7.6 and 3.6 Hz, 1H), 2.85-2.68 (m, 4H), 2.80 (d, A part of AB, J = 10.8 Hz, 1H), 2.57 (d, B part of AB, J = 10.8 Hz, 1H), 2.50 (d, J = 3.6 Hz, 1H), 2.46 (q, J = 7.3 Hz, 2H), 1.83-1.62 (m, 4H), 1.55-1.43 (m, 1H), 1.29-1.13 (m, 1H), 1.11-0.98 (m, 1H), 1.08 (t, J = 7.3 Hz, 3H), 1.06 (s, 3H), 0.84 (s, 3H) ; MS FAB(+) *m/z* 270 (M^+, 62); HRMS calcd for $C_{15}H_{26}O_2S$: 270.1653, found 270.1640.

A crossover experiment (Scheme 2)

Dimethylaluminum chloride (0.52 mL, 0.94 M hexane solution, 0.49 mmol) was added dropwise to a dry dichloromethane solution (10 mL) of **6** (63 mg, 0.25 mmol) and **7** (66 mg, 0.25 mmol), and then stirred for 22 h at room temperature. The reaction mixture was quenched with a saturated ammonium chloride solution and then extracted with ethyl acetate (50 mL x 3). The organic layer was washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. Silica gel chromatography of the residue (eluted with hexane : ethyl acetate = 10 : 1) gave **8** (58 mg, 92% yield) and **9** (60 mg, 91% yield).

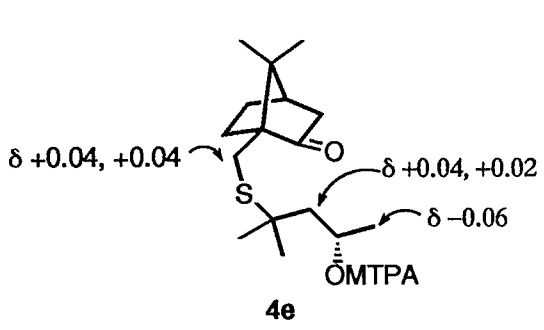
(*S*)-4-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-2-butanol-2-d (**8**): colorless oil; $[\alpha]_D^{27}$ = +31.5 (0.50, $CHCl_3$); IR ($CHCl_3$) 3605, 3500-3400, 2960, 1740, 1450, 1405, 1370, 1040, 930 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.82 (d, A part of AB, J = 13.0 Hz, 1H), 2.69 (t, J = 7.2 Hz, 2H), 2.54 (d, B part of AB, J = 13.0 Hz, 1H), 2.37 (ddd, A part of AB, J = 18.4, 4.6 and 2.6 Hz, 1H),

2.17-1.92 (m, 4H), 1.87 (d, B part of AB, J = 18.4 Hz, 1H), 1.75 (t, J = 7.2 Hz, 2H), 1.58-1.48 (m, 1H), 1.42-1.32 (m, 1H), 1.21 (s, 3H), 1.05 (s, 3H), 0.91 (s, 3H); MS FAB(+) *m/z* 258 (M^++H, 100); HRMS calcd for $C_{14}H_{24}DO_2S$ (M^++H): 258.1638, found 258.1660.

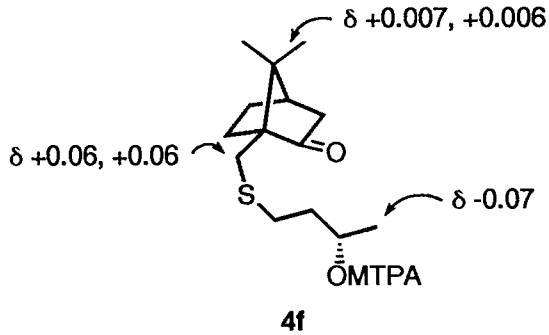
(*S*)-5-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-3-pentanol (**9**): colorless oil; $[\alpha]_D^{24}$ = +35.8 (1.44, $CHCl_3$); IR ($CHCl_3$) 3600, 3450 (br), 2960, 1730, 1410, 1045, 960 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.68-3.65 (m, 1H), 2.82 (d, A part of AB, J = 13.1 Hz, 1H), 2.70 (br t, J = 14.4 Hz, 2H), 2.55 (d, B part of AB, J = 13.1 Hz, 1H), 2.37 (ddd, A part of AB, J = 18.4, 4.7 and 2.5 Hz, 1H), 2.11-1.92 (m, 4H), 1.88 (d, B part of AB, J = 18.4 Hz, 1H), 1.82-1.62 (m, 2H), 1.58-1.22 (m, 4H), 1.05 (s, 3H), 0.96 (t, J = 7.4 Hz, 3H), 0.91 (s, 3H); MS FAB(+) *m/z*; 271 (M^++H, 75); HRMS calcd for $C_{15}H_{27}O_2S$ (M^++H): 271.1732, found 271.1714.

The determination of the configuration on the alcoholic carbon by modified Mosher's Method

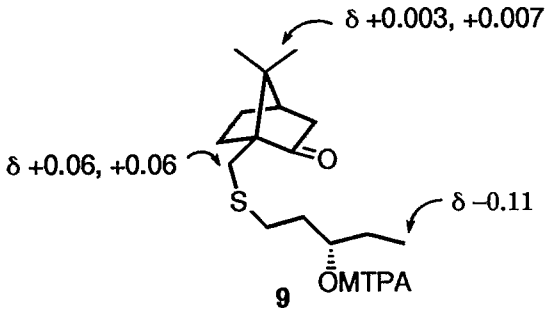
The configurations on the alcoholic carbons of **4e**, **4f**, and **9** shown below were determined by modified Mosher's method (Ohtani, I.: Kusumi, T. et al. *J. Am. Chem. Soc.* **1991**, *113*, 4092-4096).



4e



4f



9

Oxidation of 3b to the corresponding sulfone for X-ray crystallographic analysis

(2*S*,4*R*)-4-[(1*S*,4*R*)-2-Oxobornane-10-sulfonyl]-4-phenyl-2-butanol

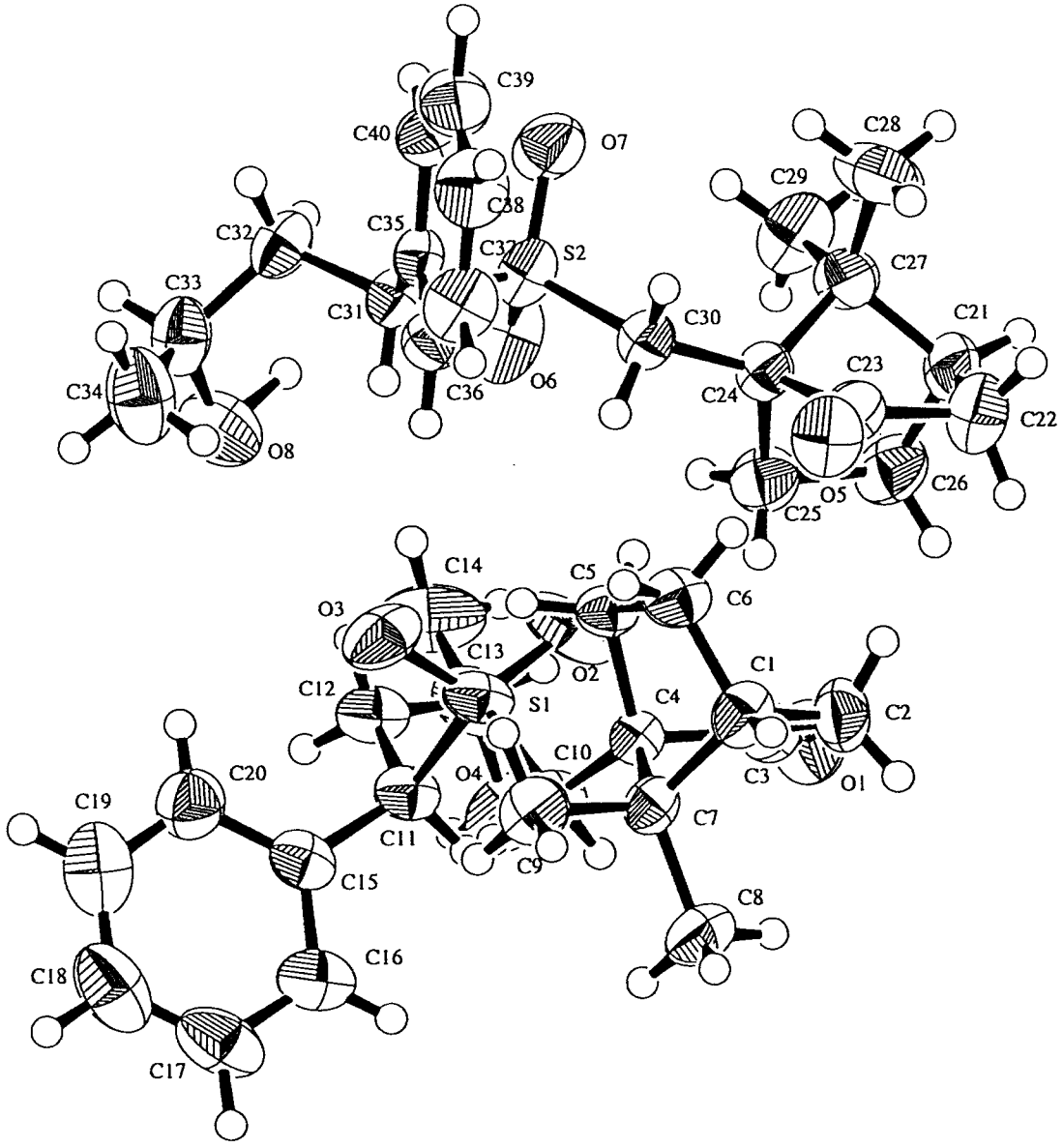
To a solution of (2*S*,4*R*)-4-[(1*S*,4*R*)-2-oxobornane-10-sulfenyl]-4-phenyl-2-butanol (**3b**) (165 mg, 0.50 mmol) in methanol / water = 5 : 2 (28 mL) was added oxone (1.53 g, 2.50 mmol) and then the mixture was stirred for 12 h at room temperature. The solvent was removed *in vacuo*. The residue was added water (20 mL) and then the aqueous layer was extracted with ethyl acetate (50 mL x 3). The combined organic layer was washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. Silica gel chromatography of the residue (eluted with hexane : ethyl acetate = 1 : 1) gave the (2*S*,4*R*)-4-[(1*S*,4*R*)-2-oxobornane-10-sulfonyl]-4-

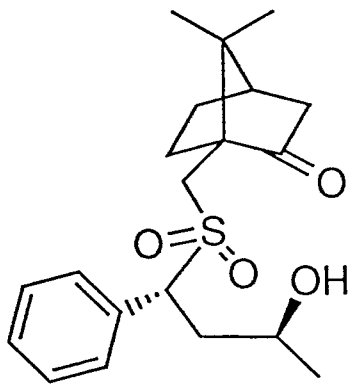
phenyl-2-butanol (175 mg, 97% yield). Recrystallization of the product (37 mg) from ether gave colorless needles (31 mg) for the X-ray crystallographic analysis. colorless needles: mp 110 °C (Et_2O); $[\alpha]_D^{28}$ = +74.0 (0.24, $CHCl_3$); IR ($CHCl_3$) 3600, 3510 (br), 2960, 1740, 1600, 1310, 1120, 930 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.54-7.48 (m, 2H), 7.43-7.36 (m, 3H), 4.98 (t, *J* = 7.2 Hz, 1H), 4.13-4.02 (m, 1H), 3.17 (d, A part of AB, *J* = 15.1 Hz, 1H), 2.62 (ddd, A part of AB, *J* = 14.3, 6.9 and 5.2 Hz, 1H), 2.34 (d, B part of AB, *J* = 15.1 Hz, 1H), 2.40-1.87 (m, 8H), 1.45-1.38 (m, 1H), 1.22 (d, *J* = 6.2 Hz, 3H), 0.89 (s, 3H), 0.66 (s, 3H); MS FAB(+) *m/z* 365 (M^++1, 47); Anal. Calcd for $C_{20}H_{28}O_4S$: C, 65.90; H, 7.74. Found : C, 65.52; H, 7.79.

The monoclinic crystal were observed with a couple of two different conformers: Crystal data for (2*S*,4*R*)-4-[(1*S*,4*R*)-2-oxobornane-10-sulfonyl]-4-phenyl-2-butanol: $C_{20}H_{28}O_4S$, M = 364.50, monoclinic, space group $P2_1$ (#4), a = 10.148(1), b = 17.681(1), c = 10.6260(8) Å, β = 91.320(7)°, V = 1906.0(2) $Å^3$, Z = 4, D_c = 1.270 g/cm^3, μ = 16.80 cm^{-1}, T = 297 K, 3126 measured reflections, 2945 unique reflections, 2714 reflections with $I > 3\sigma(I)$ used in refinement, direct methods and Fourier techniques, R = 0.037, R_w = 0.055. The data were collected using a Rigaku AFC7R diffractometer with graphite-monochromated Cu-Kα radiation (λ = 1.54178 Å) by the ω-2θ scan technique in the range 59.15 < 2θ <59.87°. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

MOPAC calculation

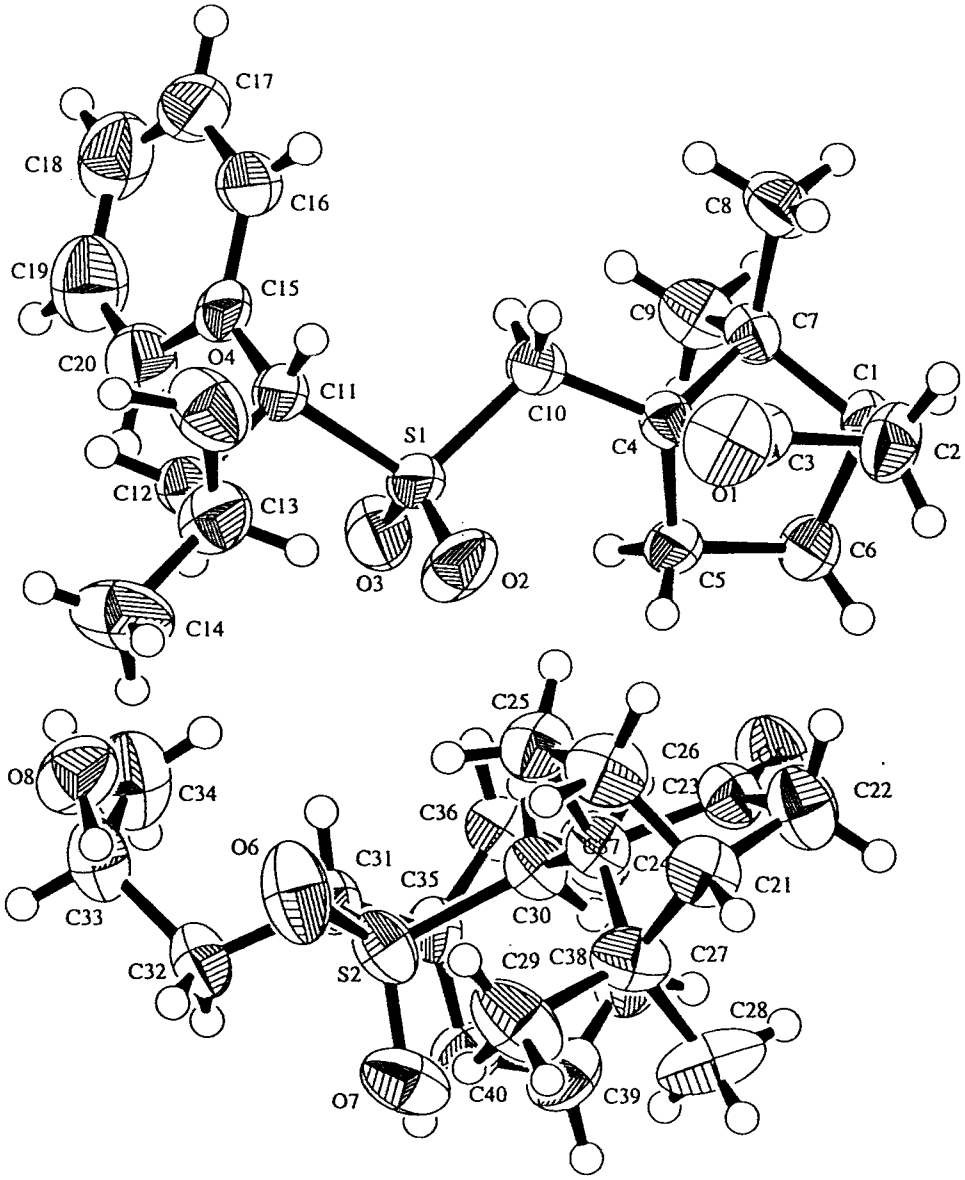
The minimization of structures and the calculation of heat of formations were performed with a software, Builder and MOPAC (PM3 ver. 6) on Insight II system (Biosym Technologies, Scranton Road, San Diego, CA 92121-2777) in 4.3BSD UNIX system using a hardware, IRIS work station (4DRPC^2 extreme, Silicon Graphics Inc., 2011 N. Shoreline Blvd., Mountain View, CA 94039-7311).

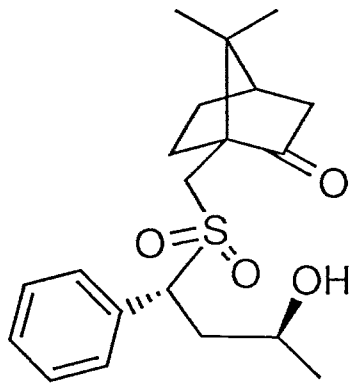




The corresponding sulfone of **3b**

Conformer 2





The corresponding sulfone of **3b**


Heat of Formation (PM3 Calculation, MOPAC ver. 6)
-172.14 Kcal/mol
-173.96 Kcal/mol