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Supporting Information

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One-step Stereocontrol of Three Contiguous Chiral Centers in Acyclic Systems: Tuning Effect of Additive in Tandem Asymmetric Michael Addition - MPV Reduction

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Supporting Information

Experimental

General. Melting points were taken on a micro hot-stage apparatus (Yanagimoto) and were uncorrected. Infrared (IR) spectra were recorded on a JASCO IR-810 or a Shimadzu FTIR-8300 diffraction grating infrared spectrophotometer and ^{1}H-NMR spectra were obtained on a JEOL JNM-EX270, a JEOL JNM-AL300, a Varian XL-300, a Varian Unity INOVA-400 spectrometer, or a Varian GEMINI 2000/200 with tetramethylsilane as an internal standard. ^{13}C-NMR spectra were obtained on a Varian Unity INOVA-400 spectrometer or a Varian GEMINI 2000/200 with $CDCl_3$ as an internal standard. Mass spectra (MS) were determined on a JEOL JMS-SX 102A QQ or a JEOL JMS-GC-mate mass spectrometer. Combustion analysis was done on a Perkin Elmer Series II CHNS/O Analyzer 2400. Specific rotations were recorded on a Horiba SEPA-200 automatic digital polarimeter. Chiral HPLC analyses were performed with a Shimadzu LC-9A and LC-10A Liquid Chromatograph series using a Daicel chiral column (CHIRALCEL OD). Their data were recorded with Shimadzu C-R6A Chromatopac. Acetate buffer was adjusted with a Horiba pH meter F-13. Wakogel C-200 (silica gel) (100-200 mesh, Wako) was used for open column chromatography. Flash column chromatography was performed with Silica Gel 60N (Kanto Chemical Co., Inc.). Kieselgel 60 F-254 plates (Merck) were used for thin layer chromatography (TLC). Preparative TLC (PTLC) was done with Kieselgel 60 F-254 plate (0.25 mm, Merck) or Silica gel 60 F-254 plate (0.5 mm, Merck). When necessary, compounds were further purified by a recycle HPLC (JAI LC-908) on GPC column (JAIGEL 1H and 2H) after purification on silica gel. Some diastereomeric mixtures were separated by a recycle HPLC (JAI LC-908) on SiO_2 gel column (Kusano Si-10) after purification on silica gel.

Materials. Tetrahydrofuran (THF) and ether was distilled from sodium benzophenone ketyl, and dichloromethane was distilled from CaH_2, after ten washing with water to remove methanol contaminants. Most of the reagents were obtained from Wako pure Chemical Industries, Ltd., Nakalai Tesque, Inc., Aldrich Chemical Inc. (*S*)-(+)-camphorsulfonic acid monohydrate and (*R*)-(-)-camphorsulfonic acid were commercially available. (-)-10-Mercaptoisoborneol (98 %ee) was prepared by Eliel's procedure[1] from (*S*)-(+)-camphorsulfonic acid monohydrate, which was purchased from Wako Pure Chemical Industries, Ltd., and used without further purification. Dimethylaluminum chloride (hexane solution) was purchased from Kanto Chemical Co., Inc.

Determination of the optical purity of (-)-10-Mercaptoisoborneol [(-)-1]. A DMF (2 ml) solution of (-)-10-mercaptoisoborneol [(-)-**1**] (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 the reaction 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 and the solvent was removed in vacuo. Water (20 ml) was added to the residue and the aqueous layer was extracted with ethyl acetate (50 ml x 3). The combined organic layer was washed with brine, dried over magnesium sulfate, filtered and concentrated in vacuo. Silica gel chromatography of the residue (hexane : ethyl acetate=15 : 1) gave the *S*-benzyl ether of (-)-**1** (440 mg, 99 % yield). *S*-Benzyl ether of (-)-**1**: colorless oil; $[\alpha]_D^{27}$ = -60.3 (1.17, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.33-7.23 (m, 5 H), 3.82 (dt, J = 7.3 and 3.4 Hz, 1H), 3.76 (d, A part of AB, J_{AB} = 13.4 Hz, 1H), 3.70 (d, B part of AB, J_{AB} = 13.4 Hz, 1H), 2.67 (d, A part of AB, J_{AB} = 11.0 Hz, 1H), 2.51 (d, B part of AB, J_{AB} = 11.0, 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); IR ($CHCl_3$) 3600, 3500, 2950, 1490, 1450, 1385, 1065, 1045, 1025, 990, 875 cm^{-1}; 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 ee of (-)-**1** was determined to be 98 % by 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 (+)-**1**: 14.1 min., *S*-benzyl ether of (-)-**1**: 15.8 min.].

A typical procedure for the Tandem Michael-MPV reaction in the absence of additive.

To a dichloromethane solution (20 ml) of (-)-10-mercaptoisoborneol [(-)-**1**] (100 mg, 0.54 mmol) was added dropwise dimethylaluminum chloride (1.05 M hexane solution, 0.51 ml, 0.54 mmol) at 0 °C. After the reaction stirred for 0.5 h, a dichloromethane (5 ml) solution of an α,β-unsaturated ketone **2** (0.36 mmol) was added dropwise, and the mixture was stirred for hours indicated in Table 1 or 2 at room temperature under a nitrogen atmosphere. The reaction mixture was quenched with a saturated ammonium chloride solution and the aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over magnesium sulfate, filtered and concentrated in vacuo. Purification of the residue by silica gel column chromatography (hexane : ethyl acetate = 10 : 1- 20 : 1) gave the products **3** as diastereomeric mixture in the yields shown in Table 1 or 2.

A typical procedure for the Tandem Michael-MPV reaction in the presence of additive.

To a dichloromethane solution (20 ml) of (-)-10-mercaptoisoborneol [(-)-**1**] (100 mg, 0.54 mmol) was added dropwise dimethylaluminum chloride (1.05 M hexane solution, 0.51 ml, 0.54 mmol) at 0 °C. After the reaction stirred for 0.5 h, a dichloromethane (5 ml) solution of an α,β-unsaturated ketone **2** (0.36 mmol) was added dropwise, followed by the addition of a dichloromethane (7 ml) solution of an additive (0.54 mmol), and the mixture was stirred for hours indicated in Table 2 at room temperature under a nitrogen atmosphere. The reaction mixture was quenched with a saturated ammonium chloride solution, and the aqueous layer was extracted with ethyl acetate. The combined organic layer were washed with a saturated sodium hydrogen carbonate solution followed by brine, and dried over magnesium sulfate, filtered and concentrated in vacuo. Purification of the residue by silica gel column chromatography (hexane : ethyl acetate = 10 : 1 - 20 : 1) gave the products **3** as diastereomeric mixture in the yields shown in Table 2.

The obtained diastereomers (**3**) were separated by a recycle HPLC.

(1*R*,2*R*,3*R*)-2-Methyl-[(1*S*,4*R*)-2-oxobornane-10-thio]-1,3-diphenyl-1-propanol (3Aa). Colorless oil; $[\alpha]_D^{27}$ = +157.7 (2.44, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.41-7.20 (m, 10 H), 5.56 (br s, 1H), 3.96 (d, *J* = 10.6 Hz, 1H), 2.87 (d, *J* = 4.4 Hz, 1H), 2.62 (d, A part of AB, J_{AB} = 13.3 Hz, 1H), 2.33 (ddd, A part of AB, J_{AB} = 18.9 Hz, *J* = 4.6 and 3.6 Hz, 1H), 2.26 (d, B part of AB, J_{AB} = 13.3 Hz, 1H), 2.21-2,15 (m, 1H), 2.03 (t, *J* = 4.7 Hz, 1H), 1.99-1.85 (m, 1H), 1.85 (d, B part of AB, J_{AB} = 18.9 Hz, 1H), 1.78-1.68 (m, 1H), 1.62-1.55 (m, 1H), 1.38-1.25 (m, 1H), 0.88 (s, 3H), 0.77 (s, 3H), 0.54 (d, *J* = 6.9 Hz, 3H); IR ($CHCl_3$) 3500, 2960, 1730, 1480, 1445, 1055, 985 cm^{-1}; MS FAB(+) *m*/*z* 409 (M^++H, 16); HRMS calcd for $C_{26}H_{33}O_2S$ (M^++H): 409.2202, found 409.2216.

(1*R*,2*S*,3*R*)-2-Methyl-[(1*S*,4*R*)-2-oxobornane-10-thio]-1,3-diphenyl-1-propanol (3Ba). Colorless oil; $[\alpha]_D^{25}$ = +145.6 (1.00, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.52-7.19 (m, 10 H), 4.77 (d, *J* = 8.7 Hz, 1H), 4.56 (d, *J* = 3.3 Hz, 1H), 3.55 (br s, 1H), 2.55 (d, A part of AB, J_{AB} = 12.9 Hz, 1H), 2.35 (d, B part of AB, J_{AB} = 12.9 Hz, 1H), 2.27-2.15 (m, 1H), 2.32 (ddd, A part of AB, J_{AB} = 18.4 Hz, *J* = 4.8 and 2.2 Hz, 1H), 2.04-1.87 (m, 3H), 1.85 (d, B part of AB, J_{AB} = 18.4 Hz, 1H), 1.70-1.59 (m, 1H), 1.39-1.29 (m, 1H), 0.95 (s, 3H), 0.77 (s, 3H), 0.64 (d, *J* = 7.1 Hz, 3H); IR ($CHCl_3$) 3502, 3062, 3035, 3008, 2958, 1735, 1600, 1492, 1454, 1415, 1377, 1319, 1299, 1014 cm^{-1}; MS (20 eV) *m*/*z* 408 (M^+, 1), 390 (9), 273 (16), 239 (15), 224 (100), 207 (31), 184 (14), 118 (49), 105 (56); HRMS calcd for $C_{26}H_{32}O_2S$ (M^+): 408.2123, found 408.2120.

(1*R*,2*R*,3*R*)-2-Methyl-3-[(1*S*,4*R*)-2-oxobornane-10-thio]-1-phenyl-3-(*p*-tolyl)-1-propanol (3Ab). Pale yellow oil; $[\alpha]_D^{20}$ = +164.8 (1.75, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.41-7.09 (m, 9H), 5.55 (br s, 1H), 3.93 (d, *J* = 10.5 Hz, 1H), 2.97 (d, *J* = 4.0 Hz, 1H), 2.60 (d, A part of AB, J_{AB} = 13.4 Hz, 1H), 2.37-2.34 (m, 1H), 2.33 (s, 3H), 2.28 (d, B part of AB, J_{AB} = 13.4 Hz, 1H), 2.19-2.13 (m, 1H), 2.03

(t, J = 4.4 Hz, 1H), 1.97-1.91 (m, 1H), 1.85 (d, J =18.3 Hz, 1H), 1.77-1.72 (m, 1H), 1.63-1.58 (m, 1H), 1.38-1.32 (m, 1H), 0.89 (s, 3H), 0.78 (s, 3H), 0.54 (d, J = 6.8 Hz, 3H); IR ($CHCl_3$) 3500, 3010, 2965, 2930, 1736, 1512, 1452, 1415, 1390, 1234, 1020 cm^{-1}; MS FAB(+) *m/z* 422 (M^+, 2); HRMS calcd for $C_{27}H_{34}O_2S$ (M^+): 422.2280, found 422.2271.

(1*R*,2*R*,3*R*)-3-(4-Methoxylphenyl)-2-methyl-3-[(1*S*,4*R*)-2-oxobornane-10-thio]-1-phenyl-1-propanol (3Ac). Colorless oil; $[\alpha]_D^{21}$ = +92.0 (0.65, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.40-7.20 (m, 7H), 6.86-6.83 (m, 2H), 5.53 (br s, 1H), 3.92 (d, J = 10.3 Hz, 1H), 3.80 (s, 3H), 2.84 (br s, 1H), 2.60 (d, A part of AB, J_{AB} = 13.3 Hz, 1H), 2.37-2.29 (m, 1H), 2.25 (d, B part of AB, J_{AB} = 13.3 Hz, 1H), 2.17-2.10 (m, 1H), 2.04-2.02 (m, 1H), 1.94-1.89 (m, 1H), 1.85 (d, J = 18.4 Hz, 1H), 1.81-1.73 (m, 1H), 1.63-1.55 (m, 1H), 1.38-1.29 (m, 1H), 0.90 (s, 3H), 0.78 (s, 3H), 0.54 (d, J = 6.8 Hz, 3H); IR ($CHCl_3$) 3500, 3020, 3008, 2963, 1736, 1609, 1510, 1250, 1175, 1034 cm^{-1}; MS FAB(+) *m/z* 461 (M^++Na, 69); HRMS calcd for $C_{27}H_{34}O_3SNa$ (M^++Na): 461.2126, found 461.2132.

(1*R*,2*R*,3*R*)-3-(4-Chlorophenyl)-2-methyl-3-[(1*S*,4*R*)-2-oxobornane-10-thio]-1-phenyl-1-propanol (3Ad). Pale yellow oil; $[\alpha]_D^{19}$ = +107.6 (0.85, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.45-7.21 (m, 9H), 5.55 (br s, 1H), 3.97 (d, J = 10.7 Hz, 1H), 2.87 (br s, 1H), 2.57 (d, A part of AB, J_{AB} = 13.3 Hz, 1H), 2.38-2.30 (m, 1H), 2.26 (d, B part of AB, J_{AB} = 13.3 Hz, 1H), 2.13-2.08 (m, 1H), 2.07-2.04 (m, 1H), 1.99-1.94 (m, 1H), 1.86 (d, J = 18.4 Hz, 1H), 1.82-1.72 (m, 1H), 1.65-1.56 (m, 1H), 1.39-1.26 (m, 1H), 0.90 (s, 3H), 0.79 (s, 3H), 0.52 (d, J = 6.9 Hz, 3H); IR ($CHCl_3$) 3500, 3008, 2966, 1734, 1491, 1452, 1390, 1236, 1089, 1014 cm^{-1}; MS FAB(+) *m/z* 442 (M^+, 3); HRMS calcd for $C_{26}H_{31}ClO_2S$ (M^+): 442.1733, found 442.1737.

(1*R*,2*R*,3*R*)-2-Ethyl-3-[(1*S*,4*R*)-2-oxobornane-10-thio]-1,3-diphenyl-1-propanol (3Ae). Colorless oil; $[\alpha]_D^{26}$ = +137.6 (0.46, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.41-7.19 (m, 10H), 5.51 (br s, 1H), 4.13 (d, J = 9.8 Hz, 1H), 3.03 (br s, 1H), 2.61 (d, A part of AB, J_{AB} = 13.2 Hz, 1H), 2.38-2.29 (m, 1H), 2.28 (d, B part of AB, J_{AB} = 13.2 Hz, 1H), 2.08-2.02 (m, 1H), 1.97-1.87 (m, 2H), 1.85 (d, J = 18.4 Hz, 1H), 1.83-1.75 (m, 1H), 1.61-1.52 (m, 1H), 1.38-1.13(m, 3H), 0.90 (s, 3H), 0.78 (s, 3H), 0.44 (t, J = 7.6 Hz, 3H); IR ($CHCl_3$) 3500, 3010, 2964, 1736, 1452, 1416, 1321, 1198, 1026 cm^{-1}; MS FAB(+) *m/z* 445 (M^++Na, 100); HRMS calcd for $C_{27}H_{34}O_2SNa$ (M^++Na): 445.2177, found 445.2171.

(1*R*,2*R*,3*R*)-2-Ethyl-3-[(1*S*,4*R*)-2-oxobornane-10-thio]-1-phenyl-3-(*p*-tolyl)-1-propanol (3Af). Pale yellow oil; $[\alpha]_D^{24}$ = +122.0 (0.83, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.44-7.11 (m, 9H), 5.49 (br s, 1H), 4.10 (d, J = 9.8 Hz, 1H), 3.02 (br d, J = 3.3 Hz, 1H), 2.59 (d, A part of AB, J_{AB} = 13.4 Hz, 1H), 2.38-2.28 (m, 1H), 2.34 (s, 3H), 2.29 (d, B part of AB, J_{AB} = 13.4 Hz, 1H), 2.07-1.91 (m, 3H), 1.89-1.77 (m, 1H), 1.85 (d, J = 18.4 Hz, 1H), 1.62-1.53 (m, 1H), 1.38-1.12 (m, 3H), 0.92 (s, 3H), 0.79 (s, 3H), 0.46 (t, J = 7.5 Hz, 3H); IR ($CHCl_3$) 3500, 2964, 1734, 1512, 1450, 1415, 1390, 1375, 1321, 1300, 1280, 1236, 1026 cm^{-1}; MS FAB(+) *m/z* 459 (M^++Na, 100); HRMS calcd for $C_{28}H_{36}O_2SNa$ (M^++Na): 459.2334, found 459.2350.

(1*R*,2*R*,3*R*)-2-Ethyl-3-(4-methoxylphenyl)-3-[(1*S*,4*R*)-2-oxobornane-10-thio]-1-phenyl-1-propanol (3Ag). Colorless oil; $[\alpha]_D^{25}$ = +85.6 (0.29, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.39-7.18 (m, 7H), 6.88-6.84 (m, 2H), 5.48 (br s, 1H), 4.09 (d, J = 9.8 Hz, 1H), 3.81 (s, 3H), 3.79 (br s, 1H), 2.59 (d, A part of AB, J_{AB} = 13.2 Hz, 1H), 2.36-2.29 (m, 1H), 2.28 (d, B part of AB, J_{AB} = 13.2 Hz, 1H), 2.05-1.80 (m, 4H), 1.85 (d, J = 18.5 Hz, 1H), 1.61-1.57 (m, 1H), 1.38-1.17 (m, 3H), 0.92 (s, 3H), 0.78 (s, 3H), 0.45 (t, J = 7.5 Hz, 3H); IR ($CHCl_3$) 3500, 3020, 3009, 2963, 1736, 1608, 1510, 1425, 1300, 1250, 1175, 1034 cm^{-1}; MS FAB(+) *m/z* 475 (M^++Na, 62); HRMS calcd for $C_{28}H_{36}O_3SNa$ (M^++Na): 475.2283, found 475.2292.

(1*R*,2*R*,3*R*)-3-(4-Chlorophenyl)-2-ethyl-3-[(1*S*,4*R*)-2-oxobornane-10-thio]-1-phenyl-1-propanol (3Ah). Colorless oil; $[\alpha]_D^{25}$ = +105.7 (0.57, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.39-7.21 (m, 9H), 5.49 (br s, 1H), 4.12 (d, J = 10.0 Hz, 1H), 3.01 (br s, 1H), 2.55 (d, A part of AB, J_{AB} = 13.3 Hz, 1H), 2.36-2.24 (m, 1H), 2.27 (d, B part of AB, J_{AB} = 13.3 Hz, 1H), 2.06-1.79 (m, 4H), 1.85 (d, J = 18.3 Hz, 1H), 1.62-1.57 (m, 1H), 1.39-1.13 (m, 3H), 0.92 (s, 3H), 0.78 (s, 3H), 0.43 (t, J = 7.5 Hz, 3H); IR ($CHCl_3$) 3500, 3008, 2964, 2934, 1736, 1489, 1452, 1416, 1390, 1260, 1236, 1091, 1015 cm^{-1}; MS FAB(+) *m/z* 479 (M^++Na, 100); HRMS calcd for $C_{27}H_{33}ClO_2SNa$ (M^++Na): 479.1787, found 479.1798.

(1*R*,2*R*,3*R*)-3-[(1*S*,4*R*)-2-Oxobornane-10-thio]-1,3-diphenyl-2-propyl-1-propanol (3Ai). Colorless oil; $[\alpha]_D^{18}$ = +125.7 (1.86, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.41-7.18 (m, 10H), 5.48

(br s, 1H), 4.09 (d, J = 9.9 Hz, 1H), 2.92 (br d, J = 3.6 Hz, 1H), 2.60 (d, A part of AB, J_{AB} = 13.4 Hz, 1H), 2.38-2.28 (m, 1H), 2.28 (d, B part of AB, J_{AB} = 13.4 Hz, 1H), 2.10-2.01 (m, 2H), 1.98-1.87 (m, 1H), 1.84 (d, J = 18.2 Hz, 1H), 1.85-1.74 (m, 1H), 1.61-1.53 (m, 1H), 1.38-1.21(m, 3H), 1.15-0.65 (m, 2H), 0.91 (s, 3H), 0.77 (s, 3H), 0.42 (t, J = 7.3 Hz, 3H); IR ($CHCl_3$) 3500, 3008, 2962, 1736, 1490, 1452, 1236, 1198, 1045 cm^{-1}; MS FAB(+) *m/z* 459 (M^++Na, 100); HRMS calcd for $C_{28}H_{36}O_2SNa$ (M^++Na): 459.2334, found 459.2340.

(1*R*,2*R*,3*R*)-2-Benzyl-3-[(1*S*,4*R*)-2-oxobornane-10-thio]-1,3-diphenyl-1-propanol (3Aj). Colorless oil; $[\alpha]_D^{19}$ = +97.8 (0.45, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.35-7.15 (m, 11H), 7.01-6.97 (m, 2H), 6.59-6.56 (m, 2H), 5.38 (br s, 1H), 4.01 (d, J = 7.3 Hz, 1H), 2.86 (d, J = 4.0 Hz, 1H), 2.78-2.31 (m, 4H), 2.54 (d, A part of AB, J_{AB} = 13.0 Hz, 1H), 2.27 (d, B part of AB, J_{AB} = 13.0 Hz, 1H), 2.04-1.81 (m, 3H), 1.58-1.23 (m, 3H), 0.96 (s, 3H), 0.79 (s, 3H); IR ($CHCl_3$) 3500, 3008, 2963, 2360, 1736, 1493, 1452, 1319, 1198 cm^{-1}; MS FAB(+) *m/z* 507 (M^++Na, 100); HRMS calcd for $C_{32}H_{36}O_2SNa$ (M^++Na): 507.2334, found 507.2343.

(1*R*,2*R*,3*S*)-2-Methyl-1-[(1*S*,4*R*)-2-oxobornane-10-thio]-1-phenyl-3-pentanol (3Ak). Colorless oil; $[\alpha]_D^{22}$ = +190.4 (1.25, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31-7.19 (m, 5H), 4.21-4.16 (m, 1H), 3.82 (d, J = 10.6 Hz, 1H), 2.57 (d, A part of AB, J_{AB} = 13.2 Hz, 1H), 2.39 (br d, J = 3.5 Hz, 1H), 2.30 (ddd, A part of AB, J_{AB} = 18.4 Hz, J = 4.6, 3.3 Hz, 1H), 2.14 (d, B part of AB, J_{AB} = 13.2 Hz, 1H), 2.01 (t, J = 4.5 Hz, 1H), 1.94-1.85 (m, 2H), 1.84 (d, B part of AB, J_{AB} = 18.4 Hz, 1H), 1.72-1.49 (m, 3H), 1.47-1.28 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H), 0.85 (s, 3H), 0.73 (s, 3H), 0.69 (d, J = 6.8 Hz, 3H); IR ($CHCl_3$) 3506, 3031, 3012, 2966, 2881, 1735, 1600, 1488, 1454, 1415, 1392, 1377, 1319, 1122 1064 cm^{-1}; MS (70 eV) *m/z* 360 (M^+, 13), 273 (89), 185 (64), 147 (57), 118 (88), 91 (100); HRMS calcd for $C_{22}H_{32}O_2S$ (M^+): 360.2123, found 360.2126.

(1*R*,2*S*,3*S*)-2-Methyl-1-[(1S,4R)-2-oxobornane-10-thio]-1-phenyl-3-pentanol (3Bk). Colorless oil; $[\alpha]_D^{22}$ = +162.9 (1.50, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.48 (d type, J = 7.1 Hz, aromatic 2H), 7.33 (t type, J = 7.5 Hz, aromatic 2H), 7.23 (t type, J = 7.3 Hz, aromatic 1H), 4.43 (d, J = 4.4 Hz, 1H), 3.58-3.53 (m, 1H), 3.13 (d, J = 4.6 Hz, 1H), 2.44 (d, A part of AB, J_{AB} = 13.0 Hz, 1H), 2.33 (d, B part of AB, J_{AB} = 13.0 Hz, 1H), 2.32 (ddd, A part of AB, J_{AB} = 18.5 Hz, J = 4.9, 2.8 Hz, 1H), 2.03 (t, J = 4.4 Hz, 1H), 2.00-1.83 (m, 3H), 1.86 (d, B part of AB, J_{AB} = 18.5 Hz, 1H), 1.69-1.59 (m, 2H), 1.46-1.33 (m, 2H), 0.99 (t, J = 7.3 Hz, 3H), 0.92 (s, 3H), 0.82 (d, J = 6.9 Hz, 3H), 0.75 (s, 3H); IR ($CHCl_3$) 3502, 3028, 3008, 2966, 2877, 1735, 1600, 1488, 1450, 1415, 1388, 1323, 1126, 1064 cm^{-1}; MS (70 eV) *m/z* 360 (M+, 11), 273 (86), 185 (62), 151 (53), 119 (79), 91 (100); HRMS calcd for $C_{22}H_{32}O_2S$ (M^+): 360.2123, found 360.2124.

(1*R*,2*R*,3*S*)-2,4-Dimethyl-1-[(1*S*,4*R*)-2-oxobornane-10-thio]-1-phenyl-3-pentanol (3Al). Colorless oil; $[\alpha]_D^{23}$ = +172.5 (0.66, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33-7.19 (m, 5H), 3.82 (d, J = 10.6 Hz, 1H), 3.83-3.79 (m, 1H), 2.57 (d, A part of AB, J_{AB} = 13.1 Hz, 1H), 2.39 (d, J = 4.8 Hz, 1H), 2.30 (ddd, A part of AB, J_{AB} = 18.3 Hz, J = 4.8, 3.3 Hz, 1H), 2.12 (d, B part of AB, J_{AB} = 13.1 Hz, 1H), 2.08-1.99 (m, 2H), 1.93- 1.84 (m, 1H), 1.83 (d, B part of AB, J_{AB} = 18.3 Hz, 1H), 1.76-1.63 (m, 2H), 1.56-1.49 (m, 1H), 1.35-1.28 (m, 1H), 1.08 (d, J = 3.3 Hz, 3H), 0.85 (d, J = 6.8 Hz, 3H), 0.84 (s, 3H), 0.72 (s, 3H), 0.69 (d, J =6.8 Hz, 3H); IR ($CHCl_3$) 3541, 3062, 3012, 2958, 1735, 1600, 1492, 1469, 1415, 1373, 1315, 1296 cm^{-1}; MS (70 eV) *m/z* 374 (M^+, 2), 273 (100), 185 (21), 147 (33), 118 (35), 109 (21), 91 (24), 73 (9); HRMS calcd for $C_{23}H_{34}O_2S$ (M^+): 374.2279, found 374.2274.

(1*R*,2*S*,3*S*)-2,4-Dimethyl-1-[(1*S*,4*R*)-2-oxobornane-10-thio]-1-phenyl-3-pentanol (3Bl). Colorless oil; $[\alpha]_D^{23}$ = +146.4 (2.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.52 (d type, J = 7.1 Hz, aromatic 2H), 7.34 (t type, J = 7.5 Hz, aromatic 2H), 7.24 (t type, J = 7.2 Hz, aromatic 1H), 4.53 (d, J = 3.1 Hz, 1H), 3.56 (dd, J = 8.8, 3.1 Hz, 1H), 3.11 (br s, 1H), 2.46 (d, A part of AB, J_{AB} = 13.0 Hz, 1H), 2.35 (d, B part of AB, J_{AB} = 13.0 Hz, 1H), 2.32 (ddd, A part of AB, J_{AB} = 18.4 Hz, J = 4.8, 2.7 Hz, 1H), 2.04-1.78 (m, 4H), 1.87 (d, B part of AB, J_{AB} = 18.4 Hz, 1H), 1.66-1.60 (m, 2H), 1.40-1.34 (m, 1H), 1.06 (t, J = 6.8 Hz, 3H), 0.93 (s, 3H), 0.89 (d, J = 6.8 Hz, 3H), 0.76 (d, J = 6.9 Hz, 3H), 0.76 (s, 3H); IR ($CHCl_3$) 3502, 3058, 2966, 2877, 1735, 1600, 1492, 1469, 1450, 1415, 1373, 1323, 1296, 1280, 995 cm^{-1}; MS (70 eV) *m/z* 374 (M^+, 4), 273 (100), 205 (8), 185 (26), 147 (38), 118 (55), 109 (45), 91 (57), 73 (25), 55 (22); HRMS calcd for $C_{23}H_{34}O_2S$ (M^+): 374.2279, found 374.2273.

(1*S*,2*R*,3*R*)-1-Cyclohexyl-2-methyl-3-[(1*S*,4*R*)-2-oxobornane-10-thio]-3-phenyl-1-propanol

(3Am). Colorless oil; $[\alpha]_D^{24}$ = +160.3 (0.70, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33-7.18 (m, 5H), 3.92-3.89 (m, 1H), 3.83 (d, *J* = 10.6 Hz, 1H), 2.57 (d, A part of AB, J_{AB} = 13.2 Hz, 1H), 2.32 (br, OH, 1H), 2.30 (ddd, A part of AB, J_{AB} = 18.3 Hz, *J* =4.8, 3.3 Hz, 1H), 2.19-2.14 (m, 1H), 2.12 (d, B part of AB, J_{AB} = 13.2 Hz, 1H), 2.07-1.98 (m, 2H), 1.93- 1.59 (m, 6H), 1.83 (d, B part of AB, J_{AB} = 18.3 Hz, 1H), 1.55-1.37 (m, 2H), 1.34-1.10 (m, 4H), 1.04-0.86 (m, 2H), 0.84 (s, 3H), 0.72 (s, 3H), 0.67 (d, *J* = 6.8 Hz, 3H); IR ($CHCl_3$) 3533, 3028, 2927, 2854, 1735, 1600, 1492, 1450, 1415, 1299, 975 cm^{-1}; MS (70 eV) *m*/*z* 414 (M^+, 3), 396 (1), 273 (100), 230 (23), 184 (15), 147 (32), 118 (65), 83 (66), 55 (52); HRMS calcd for $C_{26}H_{38}O_2S$ (M^+): 414.2592, found 414.2588.

(1*S*,2*S*,3*R*)-1-Cyclohexyl-2-methyl-3-[(1*S*,4*R*)-2-oxobornane-10-thio]-3-phenyl-1-propanol (3Bm). Colorless oil; $[\alpha]_D^{24}$ = +123.2 (1.46, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.51(d type, *J* = 7.1 Hz, aromatic 2H), 7.33 (t type, *J* = 7.3 Hz, aromatic 2H), 7.23 (t type, *J* = 7.4 Hz, aromatic 1H), 4.49 (d, *J* = 3.1 Hz, 1H), 3.52 (d, *J* = 8.1 Hz, 1H), 3.09 (br s, 1H), 2.47 (d, A part of AB, J_{AB} = 12.9 Hz, 1H), 2.34 (d, B part of AB, J_{AB} = 12.9 Hz, 1H), 2.31 (ddd, A part of AB, J_{AB} = 18.4 Hz, *J* = 4.9, 2.7 Hz, 1H), 2.06-1.83 (m, 4H), 1.86 (d, B part of AB, J_{AB} = 18.4 Hz, 1H), 1.80-1.59 (m, 6H), 1.50-1.09 (m, 7H), 0.94 (s, 3H), 0.77 (d, *J* = 6.9 Hz, 3H), 0.75 (s, 3H); IR ($CHCl_3$) 3502, 3062, 3028, 2993, 2931, 1735, 1600, 1492, 1450, 1415, 1319, 1299, 987, 968 cm^{-1}; MS (70 eV) *m*/*z* 414 (M^+, 4), 396 (2), 273 (100), 230 (38), 184 (22), 151 (39), 118 (79), 95 (73), 55 (60); HRMS calcd for $C_{26}H_{38}O_2S$ (M^+): 414.2592, found 414.2586.

(1*S*,2*S*,3*S*)-1-Cyclohexyl-2-methyl-3-[(1*S*,4*R*)-2-oxobornane-10-thio]-3-phenyl-1-propanol (3Dm). Colorless oil; $[\alpha]_D^{27}$ = -72.9 (1.45, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40 (d type, *J* = 7.1 Hz, aromatic 2H), 7.31-7.19 (m, 3H), 4.36 (d, *J* = 4.2 Hz, 1H), 2.92 (d, *J* = 9.0 Hz, 1H), 2.54 (d, A part of AB, J_{AB} = 13.2 Hz, 1H), 2.40 (d, B part of AB, J_{AB} = 13.2 Hz, 1H), 2.33 (ddd, A part of AB, J_{AB} = 18.3 Hz, *J* = 4.6, 2.5 Hz, 1H), 2.23-2.15 (m, 1H), 2.03-1.89 (m, 3H), 1.82 (d, B part of AB, J_{AB} = 18.3 Hz, 1H), 1.80-1.63 (m, 5H), 1.43-1.09 (m, 9H), 0.98 (s, 3H), 0.86 (s, 3H), 0.84 (d, *J* = 7.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 217.6, 139.4, 129.7 (2), 127.8 (2), 126.9, 77.5, 61.0, 53.0, 47.7, 43.5, 43.1, 40.9, 39.9, 30.9, 28.2, 26.9, 26.8, 26.6, 26.5, 26.2, 24.6, 20.3, 20.1, 12.5; IR ($CHCl_3$) 3548, 3035, 2993, 2931, 2854, 1735, 1600, 1492, 1450, 1415, 1319, 1299, 983, 968, 910 cm^{-1}; MS (70 eV) *m*/*z* 414 (M^+, 2), 396 (2), 273 (100), 230 (17), 212 (14), 184 (16), 151 (24), 129 (18), 118 (64), 91 (65), 81 (55), 67 (49), 55 (80); HRMS calcd for $C_{26}H_{38}O_2S$ (M^+): 414.2592, found 414.2595.

(1*S*,2*R*,3*R*)-1-Cycloheptyl-2-methyl-3-[(1*S*,4*R*)-2-oxobornane-10-thio]-3-phenyl-1-propanol (3An). White crystals; mp 70-72 °C (hexane / dichloromethane); $[\alpha]_D^{26}$ = +110.5 (0.40, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.42-7.19 (m, 5H), 3.93 (br dd, *J* = 7.0, 1.9 Hz, 1H), 3.82 (d, *J* = 10.6 Hz, 1H), 2.58 (d, A part of AB, J_{AB} = 13.3 Hz, 1H), 2.32 (dd, *J* = 2.7, 1.9 Hz, 1H), 2.25 (dd, *J* = 2.7, 1.9 Hz, 1H), 2.08 (d, B part of AB, J_{AB} = 13.3 Hz, 1H), 2.08-1.00 (m, 20H), 0.82 (s, 3H), 0.72 (s, 3H), 0.65 (d, *J* = 6.8 Hz, 3H); IR ($CHCl_3$) 2927, 2854, 1735, 1492, 1454, 1373, 1195 cm^{-1}; MS (70 eV) *m*/*z* 428 (M^+, 1), 313 (2), 273 (100), 259 (5), 244 (9); HRMS calcd for $C_{27}H_{40}O_2S$ (M^+): 428.2749, found 428.2744.

(1*R*,2*R*,3*S*)-1-(4-Methoxylphenyl)-2,4-dimethyl-1-[(1*S*,4*R*)-2-oxobornane-10-thio]-3-pentanol (3Ao). Colorless oil; $[\alpha]_D^{28}$ = +191.0 (0.86, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.23 (dt type, *J* = 8.8, 2.5 Hz, aromatic 2H), 6.84 (dt type, *J* = 8.8, 2.5 Hz, aromatic 2H), 3.81-3.75 (m, 5H), 2.54 (d, A part of AB, J_{AB} = 13.2 Hz, 1H), 2,34 (d, *J* = 5.1 Hz, 1H), 2.30 (ddd, A part of AB, J_{AB} = 18.3 Hz, *J* = 4.6, 3.3 Hz, 1H), 2.13 (d, B part of AB, J_{AB} = 13.2 Hz, 1H), 2.02-1.85 (m, 3H), 1.84 (d, B part of AB, J_{AB} = 18.3 Hz, 1H), 1.75-1.65 (m, 2H), 1.57-1.49 (m, 1H), 1.35-1.28 (m, 1H), 1.07 (d, *J* = 6.4 Hz, 3H), 0.86 (s, 3H), 0.85 (d, *J* = 6.7 Hz, 3H), 0.74 (s, 3H), 0.68 (d, *J* = 6.7 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 218.1, 158.4, 135.0, 129.7 (2), 113.6 (2), 76.8, 60.8, 55.6, 55.2, 47.8, 43.3, 43.2, 40.8, 31.1, 27.7, 26.8 (2), 20.4, 19.9, 19.8, 18.8, 10.6; IR ($CHCl_3$) 3529, 2993, 2962, 2877, 2839, 1735, 1608, 1596, 1512, 1465, 1415, 1373, 1253, 1176, 825 cm^{-1}; MS (70 eV) *m*/*z* 404 (M^+, 1), 303 (12), 187 (11), 149 (100), 133 (16), 121 (36), 105 (16), 77 (18), 55 (12); HRMS calcd for $C_{24}H_{36}O_3S$ (M^+): 404.2385, found 404.2389.

(1*R*,2*S*,3*S*)-1-(4-Methoxylphenyl)-2,4-dimethyl-1-[(1*S*,4*R*)-2-oxobornane-10-thio]-3-pentanol (3Bo). Colorless oil; $[\alpha]_D^{27}$ = +145.9 (1.58, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.43 (dt type, *J* = 8.4, 2.5 Hz, aromatic 2H), 6.86 (dt type, *J* = 8.8, 2.5 Hz, aromatic 2H), 4.46 (d, *J* = 3.1 Hz, 1H), 3.81 (s, 3H), 3.54-3,52 (m, 1H), 3.07 (br d, *J* = 4.9 Hz, 1H), 2.46 (d, A part of AB, J_{AB} = 12.9 Hz, 1H), 2.34 (d,

B part of AB, J_{AB} = 12.9 Hz, 1H), 2.31 (ddd, A part of AB, J_{AB} = 18.5 Hz, J = 4.8, 2.7 Hz, 1H), 2.04-1.78 (m, 5H), 1.86 (d, B part of AB, J_{AB} = 18.5 Hz, 1H), 1.65-1.58 (m, 1H), 1.39-1.33 (m, 1H), 1.05 (d, J = 6.8 Hz, 3H), 0.94 (s, 3H), 0.88 (d, J = 6.8 Hz, 3H), 0.77 (d, J = 7.0 Hz, 3H), 0.76 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 218.1, 158.3, 134.3, 129.9 (2), 113.5 (2), 78.0, 60.7, 55.2, 54.8, 47.9, 44.0, 43.2, 43.1, 29.8, 28.9, 26.8, 26.7, 20.8, 19.9, 19.8, 14.9, 11.6; IR ($CHCl_3$) 3502, 3020, 2962, 2877, 2839, 1735, 1608, 1581, 1508, 1465, 1415, 1377, 1242, 1176, 829 cm^{-1}; MS (70 eV) *m*/*z* 404 (M^+, 4), 303 (16), 187 (11), 159 (7), 149 (100), 133 (16), 121 (26), 105 (16), 91 (16), 55 (9); HRMS calcd for $C_{24}H_{36}O_3S$ (M^+): 404.2385, found 404.2388.

(1*S*,2*R*,3*S*)-1-(4-Methoxylphenyl)-2,4-dimethyl-1-[(1*S*,4*R*)-2-oxobornane-10-thio]-3-pentanol (3Co). Colorless oil; $[\alpha]_D^{28}$ = -109.5 (0.74, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.27 (dt type, J = 8.6, 2.6 Hz, aromatic 2H), 6.85 (dt type, J = 8.8, 2.6 Hz, aromatic 2H), 3.81 (s, 3H), 3.77 (d, J = 8.6 Hz, 1H), 2.98 (br d, J = 9.0 Hz, 1H), 2.45 (d, A part of AB, J_{AB} =13.1 Hz, 1H), 2.32 (ddd, A part of AB, J_{AB} = 18.2 Hz, J = 4.8, 2.0 Hz, 1H), 2.31 (d, B part of AB, J_{AB} = 13.1 Hz, 1H), 2.09-1.89 (m, 4H), 1.81 (d, B part of AB, J_{AB} = 18.2 H, 1H), 1.72-1.60 (m, 2H), 1.38-1.26 (m, 2H), 1.08 (d, J = 6.8 Hz, 3H), 0,97 (s, 3H), 0.89 (d, J = 6.6 Hz, 3H), 0.84 (s, 3H), 0.76 (d, J = 6.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 217.4, 158.4, 134.0, 129.4 (2), 113.7 (2), 78.3, 60.9, 56.7, 55.2, 47.7, 43.5, 43.1, 41.2, 31.3, 28.2, 26.8 (2), 20.3, 20.2, 19.6, 18.9, 10.1; IR ($CHCl_3$) 3552, 3031, 3020, 2958, 2873, 2839, 1735, 1608, 1512, 1465, 1415, 1373, 1303, 1249, 1176, 829 cm^{-1}; MS (70 eV) *m*/*z* 404 (M^+, 3), 303 (17), 187 (10), 149 (100), 133 (15), 121 (28), 91 (16), 77 (17), 67 (11), 55 (12); HRMS calcd for $C_{24}H_{36}O_3S$ (M^+): 404.2385, found 404.2388.

(1*S*,2*S*,3*S*)-1-(4-Methoxylphenyl)-2,4-dimethyl-1-[(1*S*,4*R*)-2-oxobornane-10-thio]-3-pentanol (3Do). Colorless oil; $[\alpha]_D^{27}$ = -99.0 (0.74, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33 (dt type, J = 8.8, 2.5 Hz, aromatic 2H), 6.83 (dt type, J = 6.6, 2.5 Hz, aromatic 2H), 4.36 (d, J = 4.0 Hz, 1H), 3.80 (s, 3H), 2.93 (ddd, J = 9.4, 6.1 and 2.6 Hz, 1H), 2.53 (d, A part of AB, J_{AB} = 13.2 Hz, 1H), 2.39 (d, B part of AB, J_{AB} = 13.2 Hz, 1H), 2.33 (ddd, A part of AB, J_{AB} = 18.3 Hz, J = 4.6, 2.6 Hz, 1H), 2.10 (ddq, J = 9.4, 7.0 and 4.0 Hz, 1H), 2.05-1.90 (m, 3H), 1.82 (d, B part of AB, J_{AB} = 18.3 Hz, 1H), 1.75 (d of septet, J = 7.0, 2.6 Hz, 1H), 1.62 (br d, J = 6.1 Hz, 1H), 1.44-1.29 (m, 2H), 0.99 (s, 3H), 0.92 (d, J = 7.0 Hz, 3H), 0.87 (s, 3H), 0.83 (d, J = 6.8 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) 217.6, 158.4, 131.2, 130.7 (2), 113.2 (2), 77.5, 61.0, 55.2, 52.3, 47.8, 43.5, 43.1, 41.7, 29.3, 28.2, 26.9, 26.8, 20.4, 20.3, 20.2, 13.9, 12.2; IR ($CHCl_3$) 3691, 3208, 2962, 2839, 1735, 1608, 1581, 1508, 1465, 1415, 1373, 1299, 1249, 1176, 995, 825 cm^{-1}; MS (70 eV) *m*/*z* 404 (M^+, 4), 303 (22), 187 (9), 149 (100), 133 (14), 121 (26), 105 (14), 91 (16), 77 (16), 67 (10), 55 (10); HRMS calcd for $C_{24}H_{36}O_3S$ (M^+): 404.2385, found 404.2389.

(1*R*,2*R*,3*S*)-1-(4-Chlorophenyl)-2,4-dimethyl-1-[(1*S*,4*R*)-2-oxobornane-10-thio]-3-pentanol (3Ap). Colorless oil; $[\alpha]_D^{27}$ = +196.4 (0.89, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 4H), 3.83 (d, J = 10.6 Hz, 1H), 3.80 (ddd, J = 9.5, 5.0 and 2.1 Hz, 1H), 2.51 (d, A part of AB, J_{AB} = 13.2 Hz, 1H), 2.38 (d, J = 5.0 Hz, 1H), 2.31 (ddd, A part of AB, J_{AB} = 18.5 Hz, J = 4.8, 3.3 Hz, 1H), 2.13 (d, B part of AB, J_{AB} = 13.2 Hz, 1H), 2.04-1.87 (m, 3H), 1.85 (d, B part of AB, J_{AB} = 18.5 Hz, 1H), 1.76-1.64 (m, 2H), 1.58-1.51 (m, 1H), 1.37-1.30 (m, 1H), 1.07 (d, J = 6.6 Hz, 3H), 0.87 (s, 3H), 0.85 (d, J = 6.8 Hz, 3H), 0.75 (s, 3H), 0.67 (d, J = 6.8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 218.1, 141.9, 132.3, 130.1 (2), 128.4 (2), 76.6, 60.8, 55.5, 47.9, 43.3, 43.1, 40.6, 31.1, 27.9, 26.8, 26.7, 20.4, 19.9, 19.8, 18.8, 10.7; IR ($CHCl_3$) 3525, 3020, 2989, 2962, 2877, 1735, 1596, 1488, 1473, 1415, 1377, 1091, 817 cm^{-1}; MS (70 eV) *m*/*z* 408 (M^+, 2), 307 (100), 183 (39), 152 (99), 117 (96), 109 (45), 71 (68); HRMS calcd for $C_{23}H_{33}ClO_2S$ (M^+): 408.1890, found 408.1894.

(1*R*,2*S*,3*S*)-1-(4-Chlorophenyl)-2,4-dimethyl-1-[(1*S*,4*R*)-2-oxobornane-10-thio]-3-pentanol (3Bp). Colorless oil; $[\alpha]_D^{25}$ = +132.8 (0.88, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.47 (dt type, J = 8.5, 2.3 Hz, aromatic 2H), 7.31 (dt type, J = 8.5, 2.3 Hz, aromatic 2H), 4.52 (d, J = 2.9 Hz, 1H), 3.56 (ddd, J = 8.9, 5.3 and 3.1 Hz, 1H), 3.06 (d, J = 5.3 Hz, 1H), 2.41 (d, A part of AB, J_{AB} = 12.9 Hz, 1H), 2.34 (d, B part of AB, J_{AB} = 12.9 Hz, 1H), 2.32 (ddd, A part of AB, J_{AB} = 18.6 Hz, J = 4.8, 3.0 Hz, 1H), 1.87 (d, B part of AB, J_{AB} = 18.6 Hz, 1H), 2.06-1.78 (m, 5H), 1.67-1.60 (m, 1H), 1.41-1.35 (m, 1H), 1.05 (d, J = 6.8 Hz, 3H), 0.94 (s, 3H), 0.87 (d, J = 6.8 Hz, 3H), 0.77 (s, 3H), 0.73 (d, J = 7.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 218.1, 141.1, 132.2, 130.3 (2), 128.3 (2), 77.7, 60.7, 54.9, 48.0, 44.1, 43.2, 43.1, 29.6, 29.0, 26.8, 26.7, 20.9, 19.9 (2), 14.6, 11.2; IR ($CHCl_3$) 3521, 3012, 2962, 2877, 1735,

1600, 1488, 1469, 1415, 1373, 1319, 1296, 1137, 1091, 821 cm^{-1}; MS (70 eV) *m*/*z* 408 (M^+, 5), 307 (100), 185 (46), 152 (70), 141 (26), 117 (78), 109 (86), 81 (68), 69 (65), 55 (54); HRMS calcd for $C_{23}H_{33}ClO_2S$ (M^+): 408.1890, found 408.1891.

(1*S*,2*R*,3*S*)-1-(4-Chlorophenyl)-2,4-dimethyl-1-[(1*S*,4*R*)-2-oxobornane-10-thio]-3-pentanol (3Cp). Colorless oil; $[\alpha]_D^{27}$ = -117.6 (0.84, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 4H), 3.80 (d, *J* = 8.6 Hz, 1H), 2.90 (d, *J* = 9.0 Hz, 1H), 2.43 (d, A part of AB, J_{AB} = 13.1 Hz, 1H), 2.33 (ddd, A part of AB, J_{AB} = 18.3 Hz, *J* = 4.9, 2.2 Hz, 1H), 2.29 (d, B part of AB, J_{AB} = 13.1 Hz, 1H), 2.06-1.99 (m, 2H), 1.96-1.91 (m, 2H), 1.81 (d, B part of AB, J_{AB} = 18.3 Hz, 1H), 1.72-1.63 (m, 1H), 1.56 (br s, 1H), 1.41-1.27 (m, 2H), 1.09 (d, *J* = 6.8 Hz, 3H), 0.97 (s, 3H), 0.89 (d, *J* = 6.6 Hz, 3H), 0.85 (s, 3H), 0.76 (d, *J* = 6.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 217.2, 140.9, 132.4, 129.8 (2), 128.5 (2), 78.1, 60.9, 56.5, 47.7, 43.5, 43.1, 41.1, 31.4, 28.4, 26.9, 26.8, 20.3, 20.2, 19.5, 18.9, 10.0; IR ($CHCl_3$) 3548, 3035, 3012, 2962, 2877, 1735, 1600, 1488, 1415, 1377, 1091, 825 cm^{-1}; MS (70 eV) *m*/*z* 408 (M^+, 4), 307 (100), 185 (41), 152 (63), 117 (70), 109 (85), 81 (60), 73 (52), 55 (48); HRMS calcd for $C_{23}H_{33}ClO_2S$ (M^+): 408.1890, found 408.1889.

(1*R*,2*R*,3*S*)-2,4-Dimethyl-1-[(1*S*,4*R*)-2-oxobornane-10-thio]-1-(*p*-tolyl)-3-pentanol (3Aq). Colorless oil; $[\alpha]_D^{27}$ = +165.6 (3.72, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.20 (d type, *J* = 8.1Hz, aromatic 2H), 7.11 (d type, *J* = 7.9 Hz, aromatic 2H), 3.79 (d, *J* = 10.4 Hz, 2H), 2.54 (d, A part of AB, J_{AB} = 13.3 Hz, 1H), 2.40 (br d, *J* = 4.2 Hz, 1H), 2.34-2.27 (m, 1H), 2.33 (s, 3H), 2.15 (d, B part of AB, J_{AB} = 13.3 Hz, 1H), 2.06-1.97 (m, 2H), 1.94-1.85 (m, 1H), 1.84 (d, *J* = 18.5 Hz, 1H), 1.76-1.67 (m, 2H), 1.57-1.49 (m, 1H), 1.35-1.28 (m, 1H), 1.07 (d, *J* = 6.4 Hz, 3H), 0.86 (s, 3H), 0.84 (d, *J* = 7.0 Hz, 3H), 0.74 (s, 3H), 0.69 (d, *J* = 7.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 218.1, 139.9, 136.4, 128.9 (2), 128.6 (2), 76.8, 60.8, 56.0, 47.8, 43.2, 43.1, 40.6, 31.1, 27.8, 26.8, 26.7, 21.1, 20.5, 19.9, 19.8, 18.8, 10.6; IR ($CHCl_3$) 3514, 3004, 2962, 2877, 1735, 1604, 1512, 1469, 1415, 1377, 1315, 1296, 1222, 1203, 1110, 1064 cm^{-1}; MS (70 eV) *m*/*z* 388 (M^+, 3), 287 (80), 204 (15), 165 (11), 161 (33), 133 (100), 132 (59), 109 (27), 105 (72), 81 (26), 73 (30), 55 (47); HRMS calcd for $C_{24}H_{36}O_2S$ (M^+): 388.2436, found 388.2434.

(1*R*,2*S*,3*S*)-2,4-Dimethyl-1-[(1*S*,4*R*)-2-oxobornane-10-thio]-1-(*p*-tolyl)-3-pentanol (3Bq). Colorless oil; $[\alpha]_D^{26}$ = +127.8 (2.04, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40 (d type, *J* = 8.1 Hz, aromatic 2H), 7.15 (d type, *J* = 7.9 Hz, aromatic 2H), 4.48 (d, *J* = 3.1 Hz, 1H), 3.54 (ddd, *J* = 8.6, 5.2 and 3.3 Hz, 1H), 3.11 (d, *J* = 5.2 Hz, 1H), 2.45 (d, A part of AB, J_{AB} = 13.0 Hz, 1H), 2.36 (d, B part of AB, J_{AB} = 13.0 Hz, 1H), 2.35 (s, 3H), 2.31 (ddd, A part of AB, J_{AB} = 18.3 Hz, *J* = 4.9, 2.5 Hz, 1H), 2.04-1.78 (m, 5H), 1.86 (d, B part of AB, J_{AB} = 18.3 Hz, 1H), 1.66-1.59 (m, 1H), 1.40-1.34 (m, 1H), 1.05 (d, *J* = 7.0 Hz, 3H), 0.94 (s, 3H), 0.88 (d, *J* = 6.6 Hz, 3H), 0.76 (s, 3H), 0.76 (d, *J* = 7.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 218.1, 139.3, 136.2, 128.8 (4), 78.0, 60.7, 55.2, 47.9, 44.0, 43.2, 43.1, 29.8, 29.0, 26.7, 26.6, 21.0, 20.8, 20.0, 19.9, 14.9, 11.6; IR ($CHCl_3$) 3502, 3008, 2962, 2877, 1735, 1600, 1508, 1465, 1415, 1377, 1319, 1296, 1207, 1110 cm^{-1}; MS (70 eV) *m*/*z* 388 (M^+, 1), 287 (52), 204 (13), 165 (11), 161 (16), 133 (100), 132 (42), 109 (22), 105 (64), 81 (30), 73 (37), 55 (44); HRMS calcd for $C_{24}H_{36}O_2S$ (M^+): 388.2436, found 388.2439.

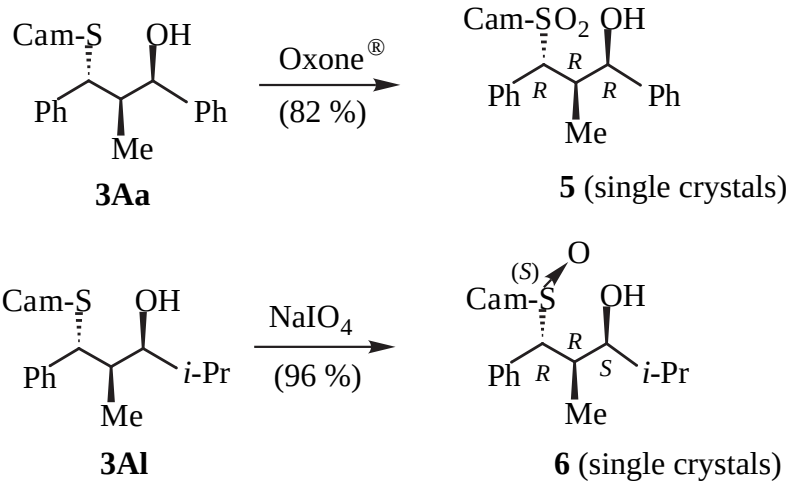
Chemical Conversion of 3Al into 1,3-Mercapto Alcohol 4l.

(1*R*,2*R*,3*S*)-1-Mercapto-2,4-dimethyl-1-phenyl-3-pentanol (4l). To a suspension of lithium aluminum hydride (29 mg, 0.75 mmol) in tetrahydrofuran (1 ml) was added dropwise a solution of **3Al** (94 mg, 0.25 mmol) in tetrahydrofuran (3 ml) at 0 °C, and the reaction mixture was stirred for 2 h at room temperature under a nitrogen atmosphere. After being stirred for 2 h, the reaction mixture was diluted diethyl ether, and quenched with sat. sodium sulfate solution at 0 °C, and then dried over magnesium sulfate, and filtrated, concentrated under reduced pressure to give a crude diol. To a solution of a crude diol in dichloromethane (3 ml) was added $BF_3 \cdot OEt_2$ (32 μl, 0.25 mmol), and the resulting mixture was stirred at room temperature under a nitrogen atmosphere for 2.5 h until all starting material were disappeared on TLC analysis. If the starting material remained, the additional $BF_3 \cdot OEt_2$ (16 μl, 0.13 mmol) was added. Then, 1-dodecanethiol (1.2 ml, 5.02 mmol) was added and the resultant mixture was stirred for 5.5 h at room temperature. At this stage, if the reaction has not

been completed, the additional $BF_3 \cdot OEt_2$ (16 μl, 0.13 mmol) was added. The reaction mixture was poured into water, and extracted with ethyl acetate. The combined organic layer was washed with brine, and dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification of the residue by silica gel column chromatography (hexane : ethyl acetate = 10 : 1) gave **4l** (46 mg, 82 % over 2 steps). Colorless needles; mp 61-63 °C (hexane / diethyl ether); $[\alpha]_D^{25}$ = +141.3 (1.05, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.34-7.28 (m, 4H), 7.25-7.20 (m, 1H), 4.03 (dd, *J* = 10.3, 5.3 Hz, 1H), 3.75 (ddd, *J* = 9.3, 5.8 and 2.2 Hz, 1H), 2.10 (qdd, *J* = 10.3, 6.8 and 2.2 Hz, 1H), 1.84 (d, *J* = 5.3 Hz, 1H), 1.71 (d of septet, *J* = 9.3, 6.6 Hz, 1H), 1.58 (s, 1H), 1.08 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.68 (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 144.8, 128.6 (2), 127.4 (2), 127.1, 77.2, 47.6, 41.9, 31.8, 20.2, 18.8, 10.5; IR ($CHCl_3$) 3691, 3062, 3004, 2962, 2939, 2873, 1600, 1492, 1454, 1380, 1315, 1126 cm^{-1}; MS (70 eV) *m*/*z* 224 (M^+, 9), 206 (10), 190 (20), 147 (52), 123 (88), 119 (63), 91 (100), 83 (20), 73 (23), 55 (21); HRMS calcd for $C_{13}H_{20}OS$ (M^+): 224.1235, found 224.1229; Anal. Calcd for $C_{13}H_{20}OS$: C, 69.59; H, 8.98. Found: C, 69.31; H, 9.05. [98 %ee, chiral HPLC analysis; DICEL CHIRALCEL OD (25 x 0.46); eluent: hexane / isopropanol = 100 / 1; flow rate: 1.0 ml/min.; Temp.: 27 °C; detector: 254 nm, (-):13.3 min., (+):17.1 min.].

Determination of the absolute configuration of major isomer (3Aa and 3Al)

The major diastereomers **3Aa** and **3Al** were converted into crystalline sulfone (**5**), sulfoxide (**6**) by oxidation, respectively. Absolute configurations of the major isomers **3Aa** and **3Al** were determined by X-ray crystallographic analyses of **5** and **6**.



3Aa **5** (single crystals)

3Al **6** (single crystals)

(1*R*,2*R*,3*R*)-2-Methyl-3-[(1*S*,4*R*)-2-oxobornane-10-sulfonyl]-1,3-diphenyl-1-propanol (5). To a solution of **3Aa** (12 mg, 0.028 mmol) in methanol (2 ml) was added Oxone® (52 mg, 0.084 mmol), and stirred at room temperature for 24 h. After being stirred for 24 h, the solvent was removed under reduced pressure. The residue was added water, and extracted with ethyl acetate. The combined organic layer was washed with brine, and dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification of the residue by silica gel column chromatography (hexane : ethyl acetate = 4 : 1) gave **5** (10 mg, 82 % yield). The obtained sulfone (**5**) was recrystallized from ethyl acetate / hexane to give single crystals for X-ray analysis. Colorless needles; mp 186-187 °C (ethyl acetate / hexane); $[\alpha]_D^{18}$ = +94.3 (0.095, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.53-7.24 (m, 10H), 5.69 (br s, 1H), 4.81 (d, *J* = 9.7 Hz, 1H), 3.08 (d, A part of AB, J_{AB} = 15.0, 1H), 2.91-2.84 (m, 1H), 2.85 (d, *J* = 5.6 Hz, 1H), 2.36-2.25 (m, 1H), 2.24 (d, B part of AB, J_{AB} = 15.0, 1H), 2.05-1.94 (m, 4H), 1.91 (d, *J* = 18.6 Hz, 1H), 1.47-1.39 (m, 1H), 0.88 (s, 3H), 0.60 (d, *J* = 6.9 Hz, 3H), 0.56 (s, 3H); IR ($CHCl_3$) 3500, 3008, 2962, 1734, 1454, 1375, 1310, 1248, 1200, 1132, 1045 cm^{-1}; MS FAB(+) *m*/*z* 441 (M^++H, 6); HRMS calcd for $C_{26}H_{33}O_4S$ (M^++H): 441.2100, found 441.2105.

(1*R*,2*R*,3*S*)-2,4-Dimethyl-1-[(1*S*,4*R*,S_S)-2-oxobornane-10-sulfinyl]-1-phenyl-3-pentanol (6). To a solution of **3Al** (52 mg, 0.138 mmol) in methanol (10 ml) was added sodium periodate (35 mg, 0.166 mmol) and the resultant mixture was stirred at room temperature for 24 h. After being stirred for 24 h, the solvent was removed under reduced pressure. The residue was added with water and extracted with ethyl acetate. The combined organic layer was washed with brine, and dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification of the residue by preparative PTLC (hexane : ethyl acetate = 1 : 1) gave **6** as a diastereomeric mixture (52 mg, 96 % yield). This diastereomeric mixture (**6**) were separated partly by HPLC, which was recrystallized from diethyl ether / hexane to give a single crystal for X-ray analysis. Colorless needles; mp 158-160 °C (hexane / diethyl ether); $[\alpha]_D^{27}$ = +43.3 (0.22, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42-7.33 (m, 5H), 4.00-3.96 (m, 1H), 3.92 (d, *J* = 11.4 Hz, 1H), 2.84 (d, A part of AB, J_{AB} = 14.0, 1H), 2.68-2.59 (m, 1H), 2.42 (d, *J* = 5.3 Hz, 1H), 2.36 (ddd, A part of AB, J_{AB} = 18.5, *J* = 4.9, 2.4 Hz, 1H), 2.12-1.76 (m, 5H), 1.91 (d, B part of AB, J_{AB} = 18.5, 1H), 1.56 (d, B part of AB, J_{AB} = 14.0, 1H), 1.47-1.41 (m, 1H), 1.11 (d, *J* = 6.4 Hz, 3H), 0.93 (d, *J* = 6.9 Hz, 3H), 0.82 (s, 3H), 0.78 (d, *J* = 6.9 Hz, 3H), 0.75 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 218.2, 133.2, 130.2 (2), 128.2 (2), 128.1, 75.9, 68.7, 59.5, 50.2, 48.2, 42.9, 42.8, 36.1, 31.5, 27.1, 26.3, 20.5, 19.7, 19.1, 18.6, 10.7; IR ($CHCl_3$) 3691, 3564, 3035, 2954, 1735, 1600, 1496, 1473, 1415, 1323, 1296 cm^{-1}; MS FAB(+) *m*/*z* 391 (M^++H, 67); HRMS calcd for $C_{23}H_{35}O_3S$ (M^++H): 391.2313, found 391.2307; Anal. Calcd for $C_{23}H_{34}O_3S$: C, 70.73; H, 8.77. Found: C, 70.44; H, 8.91.

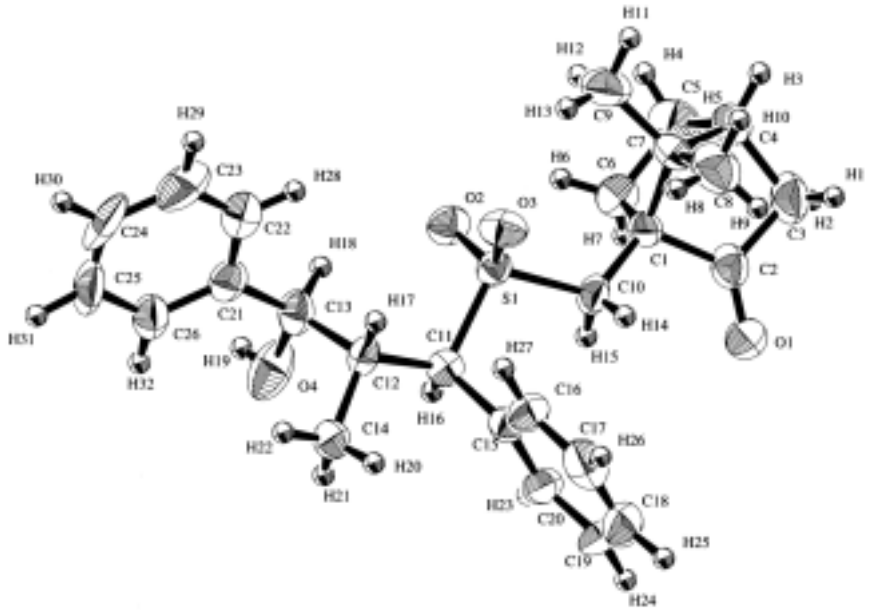


Fig. 1. ORTEP drawing of sulfone **5.**

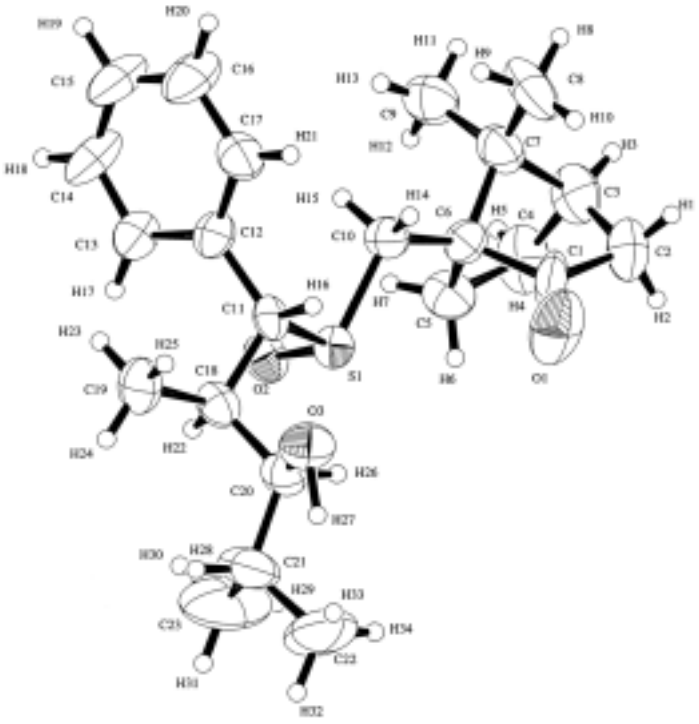


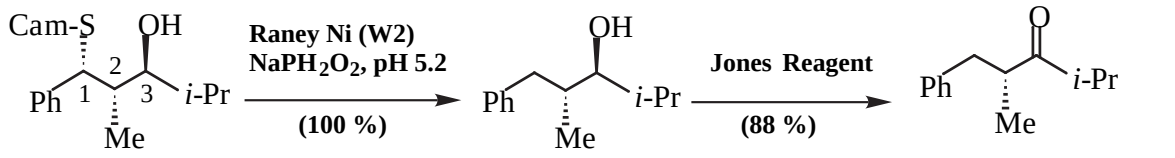
Fig. 2. ORTEP drawing of sulfoxide **6.**

Table 1. Crystal Data of Sulfone **5** and Sulfoxide **6**.

	Sulfone **5**	Sulfoxide **6**
Formula	$C_{26}H_{32}O_4S$	$C_{23}H_{34}O_3S$
Formula Weight	440.60	390.58
Crystal color, Habit	Colorless, prismatic	Colorless, needles
Crystal Dimensions (mm)	0.2 x 0.2 x 0.2	0.15 x 0.10 x 0.20
Crystal System	orthorhombic	monoclinic
Lattice Type	Primitive	Primitive
Space Group	$P2_12_12_1$ (#19)	$P2_1$ (#4)
Z value	4	4
Lattice parameters	a = 12.670(4) Å	a = 11.340(2) Å
	b = 21.494(5) Å	b = 10.921(3) Å
	c= 8.662(3) Å	c= 19.141(2) Å
		β = 105.70(1) °
Volume	V = 2359.1(10) $Å^3$	V = 2281.8(8) $Å^3$
D*calc* [g/cm^3]	1.240	1.137
F_{000}	944.00	848.00
Radiation	CuKα (λ = 1.54178Å)	CuKα (λ = 1.54178Å)
Unique Data	1114	3611
Observed Data	285 (I>3σ(I))	488 (I>2σ(I))
R ; R_W	0.038 ; 0.041	0.127 ; 0.161
Goodness of Fit	1.16	1.13

Determination of the absolute configuration of the minor isomer (3Bl)

The minor isomer **3Bl** was desulfurized reductively using the Raney Ni – $NaPH_2O_2$ combination system[2] to give secondary alcohol (**7Bl**). Then, the obtained **7Bl** was led to the known compound **8Bl**[3] by Jones oxidation. The specific rotation of **8Bl** was identical with that reported in the literature,[3] therefore, the absolute stereochemistry of minor isomer (**3Bl**) was established as shown in the following Scheme.



3Bl **7Bl** **8Bl**

$[\alpha]_D^{27}$ = -86.7

(Lit.[3] ; $[\alpha]_D^{20}$ = -83.8)

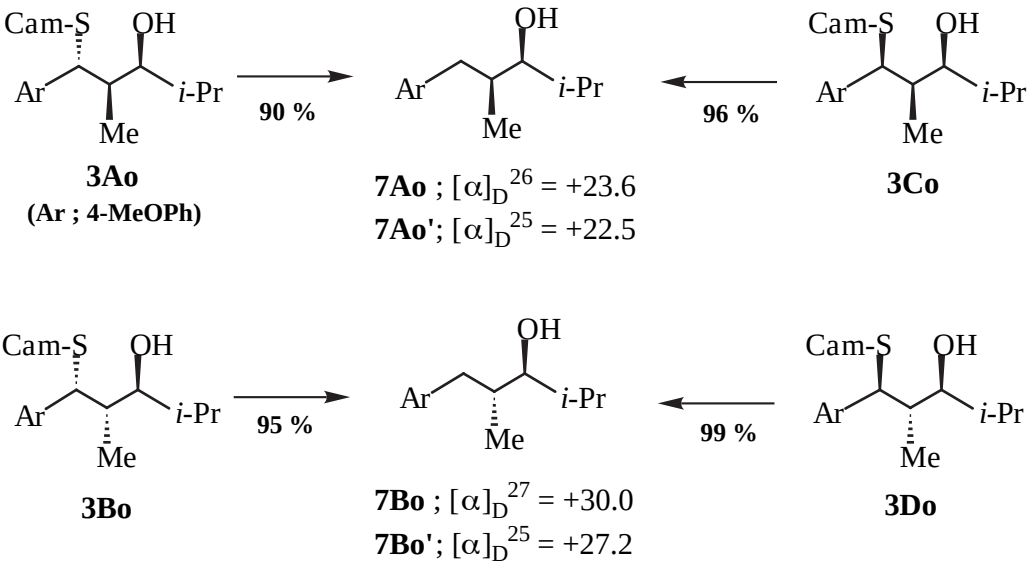
(2*R*,3*S*)-2,4-Dimethyl-1-phenyl-3-pentanol (7Bl). To a solution of a **3Bl** (61 mg, 0.16 mmol) in an acetate buffer (pH 5.2) and ethanol (1 : 2, 9 ml) was added freshly prepared Raney Ni (W-2) (suspension in ethanol, 20 ml), followed by the addition of water (1 ml) solution of sodium hypophosphite monohydrate (10 eq) immediately, and the resultant solution was stirred for 0.5 h at room temperature. The reaction mixture was filtered with celite (washing with methanol), and the solvent was removed in vacuo. Water was added to this residue, then the aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with brine, and dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification of the residue by the preparative TLC (hexane : ethyl acetate = 5 : 1) gave **7Bl** (31 mg, 100 %). Pale yellow oil; $[\alpha]_D^{20}$ = +27.8 (0.63, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.30-7.25 (m, 2H), 7.20-7.16 (m, 3H), 3.17 (t, *J* = 5.7 Hz, 1H), 3.05 (dd, A part of AB, J_{AB} = 13.4 Hz, *J* = 3.5 Hz, 1H), 2.30 (dd, B part of AB, J_{AB} = 13.4 Hz, *J* = 10.1 Hz, 1H), 1.94-1.82 (m, 2H), 1.40 (br s, 1H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.81 (d, *J* = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 141.4, 129.3 (2), 128.2 (2), 125.7, 80.9, 38.2, 37.9, 30.1, 20.0, 16.2, 16.1; IR ($CHCl_3$) 3687, 3629, 3606, 3471, 3082, 3062, 3028, 3008, 2966, 2931, 2873, 1600, 1492, 1465, 1380, 1083, 1049 cm^{-1}; MS (70 eV) *m/z* 192 (M^+, 2), 174 (7), 131 (26), 118 (33), 91 (100), 83 (14), 73 (16), 55 (25); HRMS calcd for $C_{13}H_{20}O$ (M^+): 192.1514, found 192.1505.

(2*R*)-2,4-Dimethyl-1-phenylpentan-3-one (8Bl). To a solution of **7Bl** (14 mg, 0.073 mmol) in an acetone (2 ml) was added Jones reagent until the reaction color was changed to green from brown at 0 °C, and the resultant mixture stirred for 0.5 h at 0 °C. The reaction mixture was quenched with isopropanol, and neutralized with sat. sodium hydrogen carbonate solution, then the solvent was removed in vacuo. Water was added to this residue, and extracted with ethyl acetate. The combined organic layer was washed with brine, and dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification of the residue by preparative TLC (hexane : ethyl acetate = 15 : 1) gave **8Bl** (12 mg, 88 %). Colorless oil; $[\alpha]_D^{27}$ = -86.7 (1.06, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.28-7.11 (m, 5H), 3.04-2.92 (m, 2H), 2.59-2.46 (m, 2H), 1.08 (d, *J* = 6.8 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 7.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 217.9, 140.0, 129.0 (2), 128.3 (2), 126.2, 46.5, 40.4, 39.5, 18.0, 17.7, 17.2; IR ($CHCl_3$) 3085, 3062, 3035, 2970, 2935, 2873, 1708, 1604, 1496, 1465, 1380, 1122, 1014 cm^{-1}; MS (20 eV) *m/z* 190 (M^+, 32), 147 (100), 119 (78), 91 (58), 71 (35); HRMS calcd for $C_{13}H_{18}O$ (M^+): 190.1358, found 190.1363.

Determination of the absolute configuration of another minor isomers (3Co, 3Do)

Fortunately, we could separate each diastereomer (**3Ao**, **3Bo**, **3Co**, **3Do**) using HPLC about compounds **3o**. The compound **7Ao'** obtained from reductive desulfurization of **3Co** was identical to

7Ao obtained from reductive desulfurization of **3Ao**. In the case of **3Do**, **7Bo'** (from **3Do**) was identical to **7Bo** (from **3Bo**). Consequently, we could determine the absolute configurations of **3Co** and **3Do**.



(2*S*,3*S*)-1-(4-Methoxylphenyl)-2,4-Dimethyl-3-pentanol (7Ao). The same procedure for reductive desulfurization of **3Ao** as the experiment for **7Bl**; 90 % yield. Colorless oil; $[\alpha]_D^{26}$ = +23.6 (1.65, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.10 (dt type, *J* = 8.8, 2.5 Hz, aromatic 2H), 6.83 (dt type, *J* = 8.8, 2.5 Hz, aromatic 2H), 3.80 (s, 3H), 3.06 (dd, *J* = 8.1, 3.2 Hz, 1H), 2.67 (dd, A part of AB, J_{AB} = 13.6 Hz, *J* = 6.7 Hz, 1H), 2.46 (dd, B part of AB, J_{AB} = 13.6 Hz, *J* = 8.2 Hz, 1H), 1.92 (dd of quintet, *J* = 8.2, 6.7 and 3.2 Hz, 1H), 1.79-1.67 (m, 1H), 1.29 (br s, 1H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 157.7, 133.1, 123.0 (2), 113.6 (2), 79.2, 55.2, 39.8, 37.1, 31.3, 19.2, 19.0, 12.4; IR ($CHCl_3$) 3568, 3020, 3005, 2962, 2935, 2912, 2873, 2839, 1612, 1512, 1465, 1380, 1299, 1242, 1180, 1114, 975 cm^{-1}; MS (70 eV) *m*/*z* 222 (M^+, 9), 161 (16), 121 (100), 91 (9), 77 (9); HRMS calcd for C14H22O2 (M+): 222.1620, found 222.1616.

(2*S*,3*S*)-1-(4-Methoxylphenyl)-2,4-Dimethyl-3-pentanol (7Ao'). The same procedure for reductive desulfurization of **3Co** as the experiment for **7Bl**; 96 % yield. Colorless oil; $[\alpha]_D^{25}$ = +22.5 (1.11, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.10 (dt type, *J* = 8.8, 2.5 Hz, aromatic 2H), 6.83 (dt type, *J* = 8.8, 2.5 Hz, aromatic 2H), 3.80 (s, 3H), 3.06 (dd, *J* = 8.1, 3.2 Hz, 1H), 2.67 (dd, A part of AB, J_{AB} = 13.6 Hz, *J* = 6.7 Hz, 1H), 2.46 (dd, B part of AB, J_{AB} = 13.6 Hz, *J* =8.2 Hz, 1H), 1.92 (dd of quintet, *J* = 8.2, 6.7 and 3.2 Hz, 1H), 1.79-1.67 (m, 1H), 1.29 (br s, 1H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 157.7, 133.1, 123.0 (2), 113.6 (2), 79.2, 55.2, 39.8, 37.1, 31.3, 19.2, 19.0, 12.4; IR ($CHCl_3$) 3568, 3024, 3008, 2962, 2935, 2912, 2873, 1612, 1512, 1465, 1380, 1299, 1242, 1180, 1114, 975 cm^{-1}; MS (70 eV) *m*/*z* 222 (M^+, 11), 161 (18), 121 (100), 91 (8), 77 (9); HRMS calcd for $C_{14}H_{22}O_2$ (M^+): 222.1620, found 222.1617.

(2*R*,3*S*)-1-(4-Methoxylphenyl)-2,4-Dimethyl-3-pentanol (7Bo). The same procedure for reductive desulfurization of **3Bo** as the experiment for **7Bl**; 95 % yield. Colorless oil; $[\alpha]_D^{27}$ = +30.0 (0.57, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.10 (dt type, *J* = 8.7, 2.5 Hz, aromatic 2H), 6.83 (dt type, *J* = 8.7, 2.5 Hz, aromatic 2H), 3.79 (s, 3H), 3.16 (br t, *J* = 5.7 Hz, 1H), 2.97 (dd, A part of AB, J_{AB} = 13.5 Hz, *J* =3.6 Hz, 1H), 2.26 (dd, B part of AB, J_{AB} = 13.5 Hz, *J* = 10.0 Hz, 1H), 1.93-1.77 (m, 2H), 1.38 (br s, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.80 (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 157.7, 133.3, 130.2 (2), 113.6 (2), 80.8, 55.2, 38.3, 37.0, 30.1, 20.0, 16.2, 16.1; IR ($CHCl_3$) 3568, 3024, 2962, 2935, 2873, 2839, 1612, 1512, 1465, 1365, 1299, 1245, 1180, 1114, 987 cm^{-1}; MS (70 eV) *m*/*z* 222 (M^+, 8), 161 (27), 121 (100), 91 (10), 77 (11); HRMS calcd for $C_{14}H_{22}O_2$ (M^+): 222.1620, found 222.1615.

(2*R*,3*S*)-1-(4-Methoxylphenyl)-2,4-Dimethyl-3-pentanol (7Bo'). The same procedure for reductive desulfurization of **3Do** as the experiment for **7Bl**; 99 % yield. Colorless oil; $[\alpha]_D^{25}$ = +27.2 (0.94,

$CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.10 (dt type, J = 8.7, 2.5 Hz, aromatic 2H), 6.83 (dt type, J = 8.7, 2.5 Hz, aromatic 2H), 3.79 (s, 3H), 3.16 (br t, J = 5.7 Hz, 1H), 2.97 (dd, A part of AB, J_{AB} = 13.5 Hz, J = 3.6 Hz, 1H), 2.26 (dd, B part of AB, J_{AB} = 13.5 Hz, J =10.0 Hz, 1H), 1.93-1.77 (m, 2H), 1.38 (br s, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.92 (d, J = 6.6 Hz, 3H), 0.80 (d, J = 6.8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 157.7, 133.3, 130.2 (2), 113.6 (2), 80.8, 55.2, 38.3, 37.0, 30.1, 20.0, 16.2, 16.1; IR ($CHCl_3$) 3568, 3020, 2962, 2935, 2873, 2839, 1612, 1512, 1465, 1369, 1299, 1245, 1180, 1114, 987 cm^{-1}; MS (70 eV) *m*/*z* 222 (M^+, 8), 161 (27), 121 (100), 91 (10), 77 (10); HRMS calcd for $C_{14}H_{22}O_2$ (M^+): 222.1620, found 222.1616.

The configurations of **3Aa**, **3Al**, **3Bl**, **3Ao**, **3Bo**, **3Co**, and **3Do** were eatablished by the above experiments. The configurations of the other diastereomers **3A**-**D** were assigned by comparison of their ^{1}H-NMR data with those of the above determined diastereomers**.**

References in Experimental Section

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