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TOTAL SYNTHESIS OF (-)-PERIPLANONE-B, NATURAL MAJOR SEX-EXCITANT PHEROMONE OF THE AMERICAN COCKROACH, PERIPLANETA AMERICANA†

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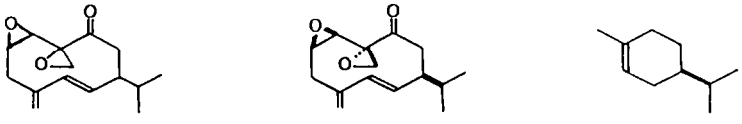
Abstract: The total synthesis of (-)-periplanone-B **1**, the major sex excitant and attractant pheromone of the American cockroach was accomplished starting from (+)-dihydrolimonene **2**. Intramolecular alkylation of the substituted α-phenylthioacrylate **10** gave rise to the (E)-cyclodecene **11**. Second key reaction was the reductive elimination of vicinal phenylthiobenzoate **14** to provide the conjugated diene **15**. Overall yield of **1** through 28 steps was 0.5 %.

INTRODUCTION

In 1952, Roth and Willis discovered that virgin females of American cockroach, Periplaneta americana L., produce an extraordinarily potent sex pheromone.[1] Since then, a large number of biological studies as well as extensive efforts to isolate and identify its active components have been performed.[2] Early attempts to isolate the pure material encountered difficulties as the pheromone is extremely active (threshold $<10^{-7}$ μg) and the insect stores it only very minute amount. In 1974, Persoons et al. succeeded in isolating two active components, periplanone-A (ca. 20 μg) and -B (ca. 200 μg) from more than 75,000 virgin females after efforts to improve the method for massive rearing of cockroach and extraction of material.[3] They characterized periplanone-B spectroscopically and assigned a ten-membered germacrenoid structure i (stereochemistry unknown) tentatively.[4] The relative stereochemistry of (±)-periplanone-B **1** was determined through Still's first total synthesis of **1** together with possible diastereomers[5] and its absolute configuration as



i 1 2

Fig. I

†Synthesis of medium- and macro-cyclic compounds part 6: part 5, see T. Kitahara and K. Mori, Tetrahedron **40**, 2935 (1984).

†Pheromone Synthesis part 102: part 101, see K. Mori, B. G. Hazra, R, J. Pfeiffer, A. K. Gupta and B. S. Lindgren, Tetrahedron in the press.

††Research fellow on leave from Japan Tobacco Inc. in 1984-1986.

shown in **1** was established by the combination of X-ray analysis and chiroptical studies of a resolved synthetic intermediate.[6] The second total synthesis of (±)-**1** was reported by Schreiber and Santini in 1984[7] and more recently two additional syntheses of (±)-**1** were published.[8,9] Nevertheless, there have never been any paper on chiral synthesis of **1** and therefore chiroptical data of **1** was not sufficient (e.g., optical rotation of **1** is not known yet).

In connection with our continuing interest in the synthesis of optically active pheromones and medium-ring systems, we started our research to afford the substantial amount of **1** in optically active form for obtaining complete chiroptical data and for the biological study. In our preliminary communication,[10] we reported the total synthesis of natural (-)-periplanone-B via the route without differentiation of protective groups of two hydroxyl groups starting from (+)-dihydrolimonene **2**[11] readily available in large quantity. Here, we wish to describe the improved synthesis of (-)-**1** in detail.

STRATEGY

Our synthetic planning was based on using two key processes **a** and **b**. The process **a** is intramolecular alkylation of a substituted α-phenylthioacrylate **D** to provide the (E)-cyclodecene derivative **C** exclusively.[12] The other key process **b** is reductive elimination[13] of vicinal phenylthio-benzoate **B** to furnish the conjugated diene system of the intermediate **A**. The precursor for cyclization should be obtained by the extension of two carbon unit to both termini of the keto acetal **3** which could be derived from (+)-dihydrolimonene **2**[12b] (Scheme I).

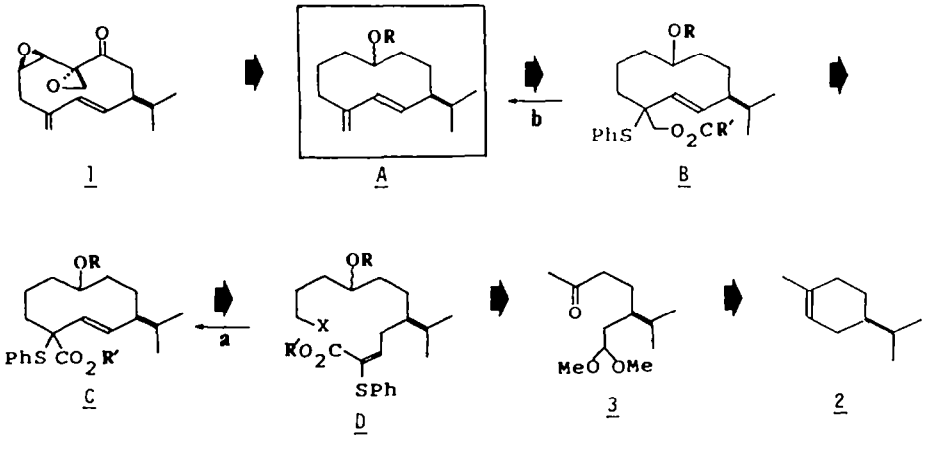
SYNTHESIS

Overall synthetic route to (-)-periplanone-B **1** is shown in Scheme II.

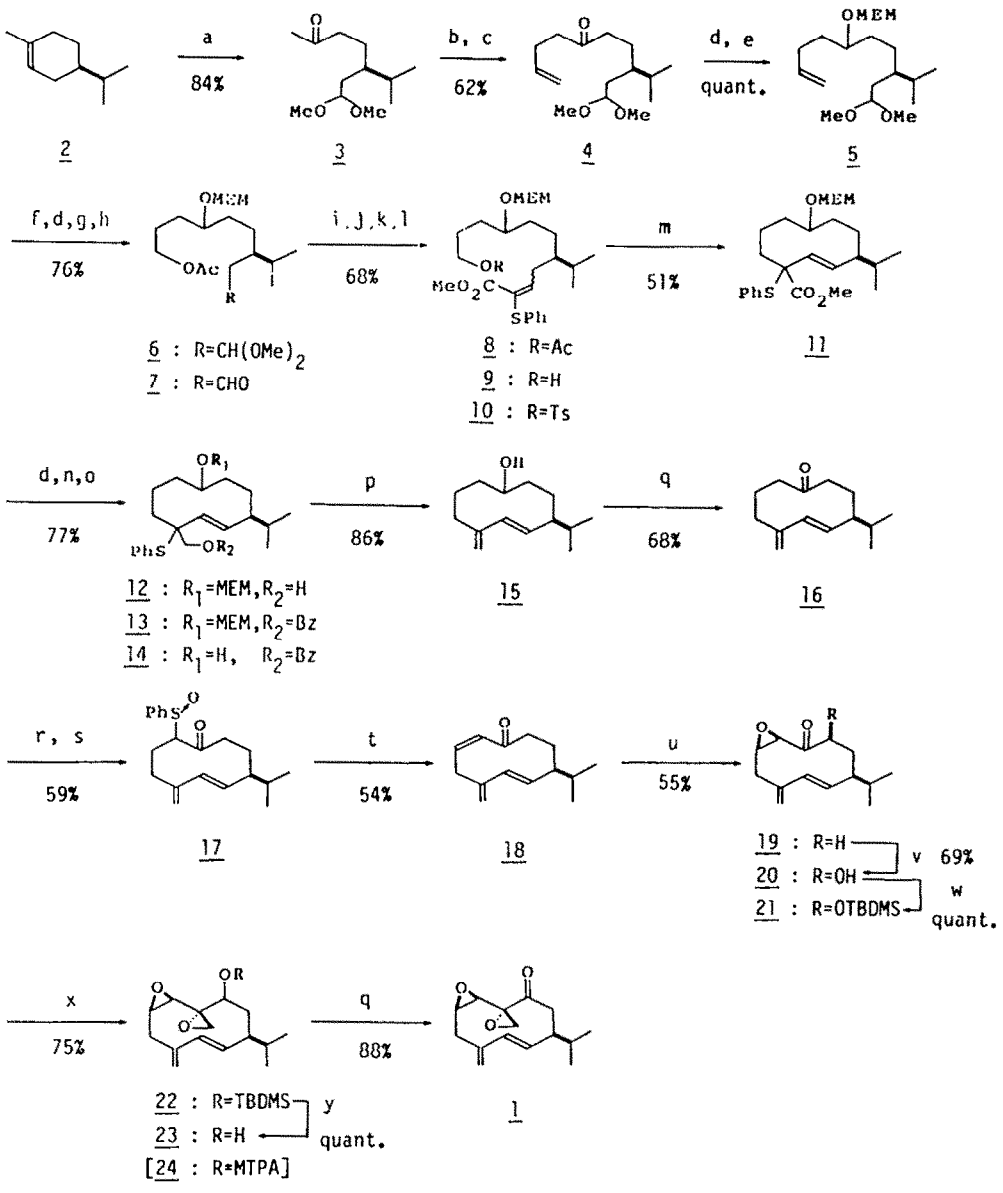
Ozonolysis of (+)-dihydrolimonene **2** was followed by reductive workup with Me_2S in methanol in the presence of p-TsOH to give a keto acetal **3** (84 %). Optical purity of **2** was determined as follows: Ozonolysis of **2** followed by oxidative workup with Jones' reagent gave a keto acid **25**, which was purified as the acetal methyl ester **26a**. Alkaline hydrolysis provided an acetal acid **26b**, which was converted to its (R)- and (S)-1-(1-naphthyl)ethylamide **27a,b** using DCC. Hplc analysis showed optical purity of **26b** (2) to be 98 % e.e. (Scheme III)

The methyl ketone **3** was methoxycarbonylated with $CO(OMe)_2$ and NaH in refluxing dioxane and the resulting enolate was directly quenched with methyl bromoacetate to give the crude keto diester **28** (q.y.) Decarbomethoxylation under Krapcho's condition[14], however, gave the desired keto ester **29** in only 34 % yield along with acid-cleavage product **30**.

(Scheme IV)

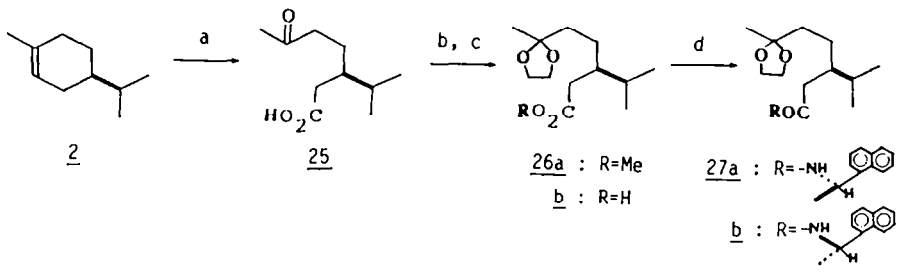


Scheme I Synthetic Plan



a) O_3, MeOH, -20°; Me_2S, p-TsOH. b) $(MeO)_2CO$, NaH, dioxane, reflux/24 h; $CH_2=CHCH_2Br$, reflux/2 h. c) 5 % KOH in 40 % MeOH aq., 90°/2 h. d) LAH, Et_2O. e) MEMCl, $EtN(i\text{-}Pr)_2$, CH_2Cl_2, 40°/20 h. f) OsO_4-$NaIO_4$, Et_2O-H_2O, rt/4 h. g) Ac_2O-Py. h) 75 % AcOH aq., 40°/1 h. i) LDA, $PhSCH_2CO_2Me$, THF, -70°/10 min. j) Ac_2O-AcONa, 130°/30 min. k) 1 % MeONa in MeOH, rt/1 h. l) p-TsCl, Py, 0--5°/7 h. m) $NaN(TMS)_2$, DME, reflux, 50 min. n) PhCOCl, DMAP, Py, THF, rt/24 h. o) TMSCl-NaI, MeCN, -8°/ 40 min. p) Na-naphthalene, THF, -70°/6 min. q) PCC, Molecular sieves 3A, CH_2Cl_2, rt/1 h. r) $LiN(TMS)_2$, $PhSSO_2Ph$, THF, -10°/15 min. s) $NaIO_4$, MeOH-H_2O, rt/20 h. t) $CaCO_3$, BHT, toluene, reflux/4 h. u) t-BuOOH, KH, THF, rt/1 h. v) $LiN(TMS)_2$, THF, -70°/30 min; MoO_5·HMPA·Py, -22°/15 min. w) t-$Bu(Me)_2SiCl$, imidazole, DMF, 40°/16 h. x) $Me_3S^+I^-$, n-BuLi, THF, -5°/30 min. y) n-Bu_4NF, THF, rt/30 min.

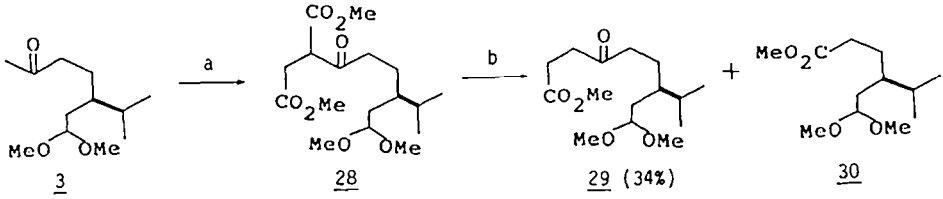
Scheme II Overall Synthetic Scheme of (-)-Periplanone-B



a) O_3, MeOH; Jones' reagent, acetone. b) ethylene glycol, p-TsOH, benzene; MeONa, MeOH. c) KOH, EtOH. d) (R)-, (S)-naphthylethylamine, DCC, CH_2Cl_2.

Scheme III Determination of optical purity of 2.

Thus, the enolate anion derived from 3 was trapped with allyl bromide and the crude product was treated with aq. methanolic KOH under reflux to give an olefinic ketone **4** in 62 % yield. Remieux-Johnson oxidation[15] of **4**, $LiAlH_4$ reduction, acetylation and subsequent workup with 6N HCl aq. gave an aldehyde **31** (84 %). Condensation of **31** with lithium enolate of methyl phenylthioacetate, dehydration with hot Ac_2O-AcONa and methanolysis of the resulting diacetate with MeONa-MeOH provided a diol ester **32** (79 %). Selective monotosylation of primary OH in **32** was essential, but conventional method using p-TsCl-pyridine gave the undesired ditosylate **34** and furan **35** predominantly. While, the diol was selectively monotosylated with p-TsCl, DMAP and Et_3N in CH_2Cl_2 at -15°† to give an unstable monotosylate whose secondary OH was immediately protected as THP ether to give **33**, the precursor for cyclization. The yield of this selective monotosylation was greatly dependent on the reaction scale. Selectivity was very high at 5 g scale and the yield of **33** was more than 80 % (highest 84 %). The reaction, however, gave more side products, **34** and **35**, at preparative scale (more than 20 g) and the yield of 33 became lower than 50 %. Although the synthesis was continued further and the cyclized product **36** was obtained in moderate yield, some modification should be done for the preparative scale synthesis. Thus, different protective groups should be used for discriminating two hydroxyl groups of **37**. A protective group for the secondary OH must be stable during mild acid hydrolysis of dimethyl acetal and selectively removable at later stage. MEM group was the candidate. Versatility of MEM was proved by the following experiment. The alcohol **14** was converted to MEM ether **13** in usual manner. Mineral acid hydrolysis did not give the alcohol **14** in good yield because labile benzoate was also hydrolyzed partly. While, MEM group was cleanly cleaved to give **14** under Rigby's procedure[16] with slight modification using TMS-NaI at -10° in 86 % yield. (Scheme V)

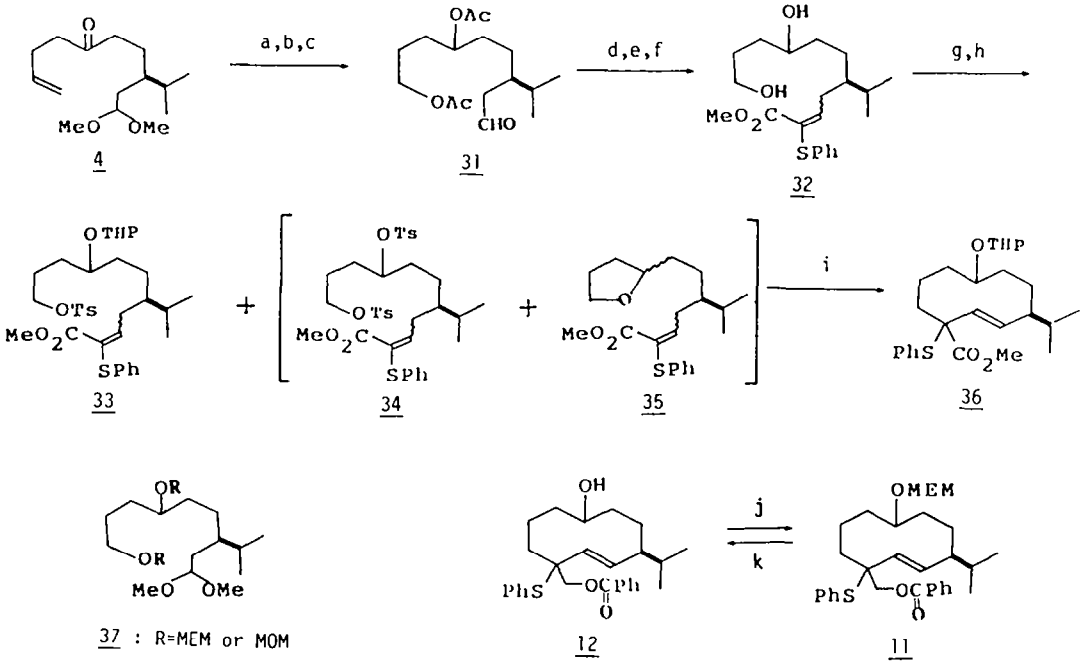


a) $(MeO)_2CO$, NaH, dioxane, reflux/24 h; $BrCH_2CO_2Me$, reflux/1 h. b) NaCl, DMSO-H_2O, 140°/9 h.

Scheme IV

†Reaction temperature was critical for the selective monotosylation and side reaction could not be suppressed at higher than -5°. Using DMAP was also essential to accelerate the reaction at low temperature.

The olefinic ketone **4** was reduced with $LiAlH_4$ and treated with MEMCl-EtN(i-Pr)$_2$ in CH_2Cl_2 to give a MEM ether **5** (q.y.) Olefin cleavage was carried out in the same manner as before (vide supra) gave the acetal **6** with different protective groups (76 %). Dimethyl acetal group was selectively hydrolyzed with 75 % AcOH aq. at 50° for 60 min to give the aldehyde **7**, which was condenced with $PhSCH_2CO_2Me$ and dehydrated to give the ester **8** (70 %). Both cleavage of acetate and tosylation of the primary OH was very simple process to give the precursor **10** for cyclization. Cyclization was effected by adding a soln of **10** in DME to a refluxing soln of $NaN(TMS)_2$ in DME over 50 min to give the cyclodecene **11** (51 %).† Crude mixture of cyclized products was reduced with $LiAlH_4$ to afford the alcohol **12** (56 % from **10**). Benzoylation of **12** with C_6H_5COCl-DMAP in pyridine followed by the treatment with TMSCl-NaI at -10° gave the substrate **14** for the second key step, reductive elimination to the conjugated diene. Lithium-ammonia reduction of **14** was entirely non-chemoselective and gave a mixture of **14**, the diene **15** and overreduction product, the dihydroderivative of **15**, (ca. 1:1:2) even using limited amount of lithium. Alternatively, treating **14** with freshly prepared sodium naphthalenide in THF at -70° for 5 min gave cleanly the dienol **15** as a sole product (86 %).†† Both reagents were employed by Sowerby and Coates for the preparation of isolated exo-methylene group from vicinal phenylthioben-



a) OsO_4-$NaIO_4$, Et_2O-H_2O. b) LAH, Et_2O. c) Ac_2O, Py; 6N HCl aq. d) LDA, $PhSCH_2CO_2Me$, THF, -70°/10 min. e) Ac_2O-AcONa, 140°/1 h. f) MeONa, MeOH. g) p-TsCl, DMAP, Et_3N, CH_2Cl_2, -15°/3 h. h) DHP, PPTS, CH_2Cl_2. i) $NaN(TMS)_2$, DME, reflux/50 min. j) MEMCl, EtN(i-Pr)$_2$, CH_2Cl_2. k) TMSCl, NaI, MeCN.

Scheme V

†Longer reaction period caused lowering the yield of the desired product **11** probably because the non-enolizable ester group of the product **11** was degraded by base. Shorter reaction time than 30 min caused the formation of the dimer. We also examined to use several other bases and solvents such as $KN(TMS)_2$, $LiN(TMS)_2$, THF, dioxane etc, but all these combinations gave much worse result. Details on model study of the cyclization step is described in ref. 12c.

††Quick removal of thiophenol from the quenched reaction mixture was crucial to get the pure product, because the presence of thiophenol for ca. 30 min at room temperature caused isomerization of (E)-diene to (Z)-diene and radical polymerization to reduce the yield of the desired product. Detailed procedure for the isolation of (E)-diene is described in experimental.

zoate.[13] Nonetheless, there has not been known to prepare the conjugated diene system efficiently using these reagent. Ours is the first example to apply sodium naphthalenide reduction for the formation of labile conjugated diene successfully.

PCC-MS-3A oxidation[17] of **15** afforded the dienone **16** (68 %), the Schreiber's intermediate, in optically active form; $[\alpha]_D^{22}$ -362° (c=1.22, n-hexane).

Regioselective sulfenylation of **16**, oxidation with $NaIO_4$ and pyrolytic elimination were carried out in the same manner as reported[7,8] to give the volatile trienone **18** (32 %). Stereoselective epoxidation of **18** provided the epoxy dienone **19** as a major product containing ca. 1/8 of α-epoxy isomer after chromatography (55 %). Direct introduction of carbonyl group at C-10 by Schreiber's procedure[7] using selena-Pummerer rearrangement[19] was unsuccessful by our hands. Instead, α-hydroxylation of **19** with Mimoun's reagent,[20] MoO_5·HMPA·pyridine by Vedejs' procedure[21] gave the ketol **20** cleanly.† Recrystallization from n-hexane-i-Pr_2O gave pure **20** free from α-epoxy isomer (69 %). Silylation of **20** gave crystalline **21**. Stereoselective epoxide formation with dimethylsulfonium methylide and subsequent desilylation with n-Bu_4NF afforded (-)-periplanol-B **23** (75 % from **20**). Hplc analysis of its (R)- and (S)-MTPA ester proved that the optical purity of **23** is 99.90 % e.e. Finally, oxidation of **23** with PCC-MS-3A[17] gave (-)-periplanone-B **1** (88 %), m.p. 57.0-57.5°, $[\alpha]_D^{22}$ -553° (c=0.113, n-hexane). (Lit.[10] $[\alpha]_D^{22}$ -667°, see experimental section) Spectral data of the synthetic (-)-**1** (IR, MS, 500 MHz ^1H NMR, 125 MHz ^{13}C NMR, UV) were in accord with structure. ^1H NMR spectra of the synthetic and natural periplanone-B[3b] were completely identical. Synthetic (-)-**1** showed potent excitant and attractant activity against male cockroach and as active as (±)-periplanone-B (threshold 10^{-7} μg). Detailed result on biological study of (-)-**1** will be reported elsewhere.

In summary, the total synthesis of (-)-periplanone-B was accomplished in 28 steps starting from (+)-dihydrolimonene. The key step, ten-membered ring formation proceeded very smoothly to give the desired (E)-cyclodecene **11** in good yield. The other key reaction, preparation of the conjugated diene was executed via reductive elimination cleanly to afford the dienol **15**. Substantial amount of (-)-**1** was obtained as a pure crystalline product. Overall yield of (-)-**1** was 0.5 %.

EXPERIMENTAL

All b.ps and m.ps were uncorrected. UV spectra were recorded on a Hitachi U-3200 spectrophotometer. IR spectra were measured as films for oils or as KBr discs for solids on a Jasco IRA-102 spectrometer. Unless otherwise stated, ^1H NMR spectra were recorded with TMS as an internal standard at 60 MHz on a Hitachi R-24A spectrometer or at 90 MHz on a Hitachi RH-90 spectrometer. 500 MHz ^1H NMR and 125 MHz ^{13}C NMR spectra were measured with TMS as an internal standard as C_6D_6 soln on a Bruker AM-500 spectrometer. Optical rotations were measured on a Jasco DIP 140 polarimeter. CD spectra were measured on a Jasco J-20C polarimeter. GLC-Mass spectra were recorded on a JEOL DX-300 spectrometer at 70 eV. Merck Kieselgel 60 (particle size 0.063-0.200 mm) or Fuji-Davison BW-820 MH were used for SiO_2 column chromatography, unless otherwise stated. Neutral alumina (Woelm) were used for Al_2O_3 column chromatography.

(R)-3-(1-Methylethyl)-6-oxoheptanal dimethylacetal **3**. A mixture of (R)-(+)-limonene [$[\alpha]_D^{23}$ +113.7° (c=1.98, EtOH); 200 g, 1.47 mol] and platinum oxide (0.6 g) in MeOH (800 ml) was stirred vigorously below 20° under 1 atom of hydrogen. Hydrogenation was monitored by GLC. After the starting material was disappeared (ca. 1.1 eq. of hydrogen was absorbed), the reaction mixture was filtered. The filtrate contains (+)-dihydrolimonene **2** with small amount of tetrahydro derivative in a ratio of 94:6. To the filtrate was added CH_2Cl_2 (200 ml) and the mixture was ozonized at ca. -40° until **2** was not detected on TLC. After flashing off the excess ozone with nitrogen for 30 min, the reaction mixture was cooled to -60°. To this was added slowly Me_2S (300 ml, 4.08 mol) and then a soln of p-TsOH (20 g) in MeOH (100 ml) below -50° over 30 min. The mixture was stirred for 30 min at -60° and then at ambient temp for 5 h. The reaction mixture was neutralized with excess $NaHCO_3$ soln, concentrated to ca. 300 ml and extracted with ether. The extract was washed with water and brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was distilled over K_2CO_3 to give **3** (266 g, 83.8 %). b.p. 99°/1.6 Torr; n_D^{21} 1.4370; $[\alpha]_D^{21}$ +1.08° (c=1.30, Et_2O); νmax (film) 2960 (s), 2920 (sh), 2840 (m), 1715 (s), 1465 (m), 1385 (m), 1365 (s), 1190 (m), 1165 (m), 1125 (s), 1055 (s) cm^{-1}; δ (60 MHz, CCl_4) 0.80 (6H, d, J=7 Hz), 1.0-1.8 (6H, m), 2.00 (3H, s), 2.30 (2H, m), 3.13 (3H, s), 3.15 (3H, s), 4.22 (1H, t, J=6 Hz). (Found: C, 66.57; H, 10.96. Calc for $C_{12}H_{24}O_3$: C, 66.63; H, 11.18 %).

†The stereochemistry at C-2 of **20** could be assigned as S by the 500 MHz ^1H NMR analysis. The large coupling constants of $J_{2,3ax}=J_{3ax,4}=11.1$ Hz indicated axial-axial relationships of each set of H-2 and H-3, and H-3 and H-4, respectively. The comparison of **23** (periplanol-B, SiO_2, 20% EtOAc-n-hexane, Rf 0.2) with 10-epi-periplanol-B (Rf 0.3) obtained by $NaBH_4$ reduction of **1**[22] on TLC also supported this assignment.

Determination of optical purity of **2**. A portion (ca. 6 ml, corresponding to 1 g of **2**) of the above ozonized mixture was concentrated, and oxidized with Jones' reagent in acetone (10 ml). To this was added ether and the resulting suspension was filtered. The filtrate was concentrated and partitioned with ether and water. The organic layer was extracted with sat. $NaHCO_3$ soln and aq layer was washed with ether. The aq layer was acidified to pH 6 and reextracted with ether 3 times. The extract was dried over $MgSO_4$, and concentrated in vacuo to give crude keto acid **25** (0.91 g). To this were added ethylene glycol (1.2 g) and p-TsOH (15 mg) in benzene (10 ml) and heated with continuous azeotropic drying overnight. The reaction mixture was washed successively with sat $NaHCO_3$ soln, water, and brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was treated with NaOMe (28 % in MeOH, 1 ml) in MeOH (10 ml) for 3 h and then concentrated to remove MeOH. This was chromatographed over SiO_2 (25 g) to afford 0.62 g (35 % from **2**) of a pure methyl (R)-6,6-ethylenedioxy-3-(1-methylethyl)-heptanoate **26a**, n_D^{22} 1.4482; $[\alpha]_D^{26}$ +4.8° (c=1.47, $CHCl_3$); νmax (film) 2960 (s), 2890 (s), 1735 (s), 1460 (s), 1435 (s), 1375 (s), 1335 (s), 1250 (s), 1220 (s), 1190 (s), 1165 (s), 1120 (s), 1050 (s), 945 (m), 855 (s), 785 (w) cm^{-1}; δ (90 MHz, $CDCl_3$) 0.85 (3H, d, J=6.6 Hz), 0.87 (3H, d, J=6.6 Hz), 1.30 (3H, s), 1.2-1.7 (6H, m), 2.22 (2H, t, J=6.2 Hz), 3.66 (3H, s), 3.92 (4H, s); MS m/z 229 (10%, M^+-Me), 213 (3%, M^+-MeO), 197 (5), 143 (5), 109 (6), 87 (100), 69 (8), 55 (7), 42 (40). HRMS Found: 229.1432, 213.1486. Calc for $C_{12}H_{21}O_4$: 229.1440; for $C_{12}H_{21}O_3$: 213.1490. A soln of **26a** (0.5 g, 2.1 mmol) in 4 % KOH/EtOH was heated under reflux for 1 h. The cooled mixture was concentrated to remove ethanol and then diluted with water. The soln was acidified to pH 6 with N-HCl and extracted with ether. The extract was dried over $MgSO_4$ and concentrated in vacuo to afford 0.41 g (87 %) of a crude **26b**. To a soln of **26b** (50 mg) in dry CH_2Cl_2 (0.3 ml) were added (R)-1-(1-naphthyl)ethylamine (94 mg) and DCC (50 mg), and the mixture was stirred for 1 h. The reaction mixture was filtered, washed with water and brine, dried over $MgSO_4$, and used directly for Hplc analysis (Shimadzu LC-2, Column: Nucleosil® 50-5 (25 cm x 4.6 mm); Solvent: n-hexane–THF (3:1); flow rate: 0.77 ml/min; Detector: SPD-1, 254 nm): Rt 20.09 min (97.55 %), Rt 16.78 min (2.45 %). An (S)-naphthylethylamide drivative of **26b** was prepared and analyzed in the same manner to show a diastereomer ratio of 2.52:97.48. The optical purity of **26b** was therefore 98.2 % e.e.

(R)-3-(1-Methylethyl)-6-oxo-9-decenal dimethylacetal **4**. To a stirred suspension of NaH (60% mineral oil dispersion, 55.8 g, 1.40 mol, washed with dry pentane) in dry dioxane (700 ml) were added dimethyl carbonate (200 ml, 2.09 mol) and dry MeOH (4.7 ml, 0.11 mol) and the mixture was stirred vigorously under reflux. To this was added a soln of **3** (150 g, 0.69 mol) in dry dioxane over 4 h and the mixture was refluxed with vigorous stirring overnight. To the resulting pasty suspension was added dropwise allyl bromide (67.7 ml, 0.78 mol) over 30 min and the mixture was stirred under reflux for 90 min. The cooled reaction mixture was diluted with ice-water, neutralized to pH 7 with acetic acid and concentrated in vacuo to remove dioxane. The residue was poured into cold water and extracted with ether. The extract was washed with sat $NaHCO_3$ soln and brine, dried over $MgSO_4$ and concentrated. The residual brown oil was added to a soln of KOH (45 g, 0.80 mol) in water (800 ml) and MeOH (500 ml) and the mixture was stirred under reflux for 2 h. The cooled mixture (-10°) was neutralized to pH 6-7 with AcOH, concentrated in vacuo to remove MeOH and extracted with ether. The extract was washed with water, sat $NaHCO_3$ soln and brine, dried over $MgSO_4$ and concentrated. The residue was distilled over K_2CO_3 to give **4** (110 g, 62 %), b.p. 128-130°/0.35 Torr; $n_D^{21.5}$ 1.4486; $[\alpha]_D^{21.5}$ +0.70° (c=1.22, Et_2O); νmax (film) 3100(w), 2960 (s), 2910 (s), 1715 (s), 1645 (m), 1470 (s), 1440 (s), 1415 (m), 1390 (s), 1370 (s), 1195 (s), 1125 (s), 1070 (s), 1000 (m), 960 (m), 915 (m), 820 (w) cm^{-1}; δ (CCl_4) 0.85 (6H, d, J=7 Hz), 1.0-1.9 (6H, m), 2.1-2.6 (6H, m), 3.20 (3H, s), 3.22 (3H, s), 4.32 (1H, t, J=6 Hz), 4.8-5.2 (2H, m), 5.7 (1H, m). (Found: C, 69.84; H, 10.73. Calc for $C_{15}H_{28}O_3$: C, 70.27; H, 11.01 %).

(3R,6RS)-6-(2-Methoxyethoxymethoxy)-3-(1-methylethyl)-9-decenal dimethylacetal **5**. To a stirred suspension of $LiAlH_4$ (7.3 g, 0.19 mol) in dry ether was added dropwise a soln of **4** (100 g, 0.39 mol) in dry ether (100 ml) below 10° and the mixture was stirred for 1 h. To this was added carefully water (7.3 ml), 15 % NaOH soln (14.6 ml) and water (7.3 ml) and the mixture was filtered through a celite pad. The slurry was washed with THF (100 ml) and the combined filtrate was dried over $MgSO_4$ and concentrated. The residue was dissolved in dry toluene and concentrated to remove water thoroughly. To a soln of crude alcohol (102 g) and diisopropylethylamine (71 g, 0.55 mol) in dry CH_2Cl_2 (300 ml) was added MEMCl (63 g, 0.51 mol) at once and the mixture was stirred under reflux for 24 h. The cooled reaction mixture was washed with water and brine, dried over $MgSO_4$ and concentrated to give **5** (133.3 g, 99.4%). This was pure enough (TLC, NMR and IR) using for the next step. Analytical sample was obtained by Florisil chromatography. **5**: n_D^{24} 1.4498; $[\alpha]_D^{24}$ +3.5° (c=0.30, n-hexane); νmax (film) 3100 (w), 2950 (s), 2900 (s), 2850 (m), 1640 (w), 1465 (m), 1385 (m), 1370 (m), 1225 (w), 1200 (m), 1120 (s), 1050 (s), 1000(m), 915 (m), 850 (w) cm^{-1}; δ (60 MHz, CCl_4) 0.80 (6H, d, J=7 Hz), 0.97-2.50 (12H, m), 3.15 (6H, s), 3.23 (3H, s), 3.3-3.8 (5H, m), 4.28 (1H, t, J=6 Hz), 4.55 (2H, s), 4.6-5.1 (2H, m), 5.6 (1H, m). (Found: C, 65.75; H, 10.83. Calc for $C_{19}H_{38}O_5$: C, 65.86; H, 11.05 %).

(3R,6RS)-9-Acetoxy-6-(2-methoxyethoxymethoxy)-3-(1-methylethyl)-nonanal dimethylacetal **6**. To a suspension of OsO_4 (4 g, 16.2 mmol, 3 mol %) and $NaIO_4$ (227 g, 1.06 mol) in ether (1 l) and water (1 l) was added the olefin **5** (186 g, 0.538 mol) and the mixture was stirred vigorously for ca. 7 h until **5** was not detected on TLC. The reaction mixture was filtered through a celite pad and the precipitate was washed thoroughly with ether. Organic layer was separated and the aq layer was extracted with ether. The combined ether layer was washed with excess 10 % Na_2S soln. Aq layer containing black precipitate was filtered and the filtrate was extracted with ether. The combined ether layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was dissolved in dry toluene and evaporated in vacuo to remove water. A soln of crude aldehyde (175 g) in dry ether (200 ml) was added dropwise to a stirred suspension of $LiAlH_4$ (13.2 g, 0.35 mol) in dry ether (800 ml) below 10° and the mixture was stirred for further 30 min. The usual workup gave a crude alcohol (163 g). A mixture of the crude alcohol and Ac_2O (90 ml, 0.94 mol) in pyridine (500 ml) was allowed to stand overnight. The reaction mixture was concentrated in vacuo, poured into water and extracted with ether. The extract was washed with water, sat $CuSO_4$ soln, water, sat $NaHCO_3$ soln and brine, dried over $MgSO_4$ and concentrated to give **6** (180.6 g, 76 %). This was pure enough (IR, NMR and TLC) and used for the next step without further purification. Analytical sample was obtained by SiO_2 chromatography. **6**: n_D^{22} 1.4438; $[\alpha]_D^{22}$ +5.2° (c=0.64, Et_2O); νmax (film) 2930 (s), 2900 (sh), 2820 (sh), 1740 (s), 1455 (m), 1385 (m), 1370 (m), 1240 (s), 1195 (m), 1120 (s), 1045 (s), 985 (s), 845 (w), 780 (w) cm^{-1}; δ (60 MHz, CCl_4) 0.85 (6H, d, J=7 Hz), 1.1-1.8 (12H, m), 1.98 (3H, s), 3.20 (6H, s), 3.30 (3H, s), 3.3-3.6 (5H, m), 4.00 (2H, m), 4.20-4.45 (1H, deformed t), 4.64-4.72 (2H, m). (Found: C, 60.93; H, 10.21. Calc for $C_{20}H_{40}O_7$: C, 61.19; H, 10.27 %).

Methyl (2EZ,5R,8RS)-11-acetoxy-8-(2-methoxyethoxymethoxy)-5-(1-methylethyl)-2-phenylthio-2-undecenoate **8**. A soln of **6** (90.9 g, 0.263 mol) in 75 % AcOH soln (450 ml) was stirred at 30° for 1 h and poured onto ice. The mixture was neutralized with cold NaOH soln (172 g in 500 ml of water) and then with powdered Na_2CO_3 to ca. pH 7.0-7.5 under ice-cooling, then was extracted with ether. The extract was washed with water, sat $NaHCO_3$ soln, water and brine, dried over $MgSO_4$ and concentrated to give the aldehyde **7** (81.7 g, quantitative yield): νmax (film) 2950 (s), 2900 (s), 2720 (w), 1740 (s), 1720 (sh),

1460 (m), 1390 (m), 1365 (m), 1240 (s), 1200 (m), 1110 (s), 1040 (s), 995 (s), 930 (m), 850 (w) cm^{-1}; δ (60 MHz, CCl_4) 0.88 (6H, br.d, J=6 Hz), 1.1-1.9 (10H, m), 1.99 (3H, s), 2.15-2.40 (2H, m), 3.60 (3H, s), 3.3-3.7 (5H, m), 4.00 (2H, m), 4.63-4.70 (2H, each br.s), 9.82 (1H, t, J=2.5 Hz). The crude aldehyde was dissolved in dry toluene, concentrated in vacuo to remove water thoroughly and used for the next step without further purification. To a soln of LDA, prepared from i-Pr_2NH (39.1 ml, 0.279 mol) and n-BuLi (1.72 N in n-hexane, 161 ml, 0.277 mol) in dry THF (920 ml) was added a soln of $PhSCH_2CO_2Me$ (50.2 g, 0.299 mol) in dry THF (100 ml) below -60° under Ar atomosphere and the mixture was stirred for 20 min. To this was added dropwise a soln of 7 in dry THF (50 ml) below -60° and the mixture was stirred for 30 min. The reaction mixture was quenched with excess sat NH_4Cl soln and concentrated in vacuo. The residue was poured into cold water and extracted with ether. The extract was washed with water and brine, dried over $MgSO_4$ and concentrated. The residue was mixed with anhydrous NaOAc (15.6 g, 0.183 mol) and Ac_2O (500 ml, 5.3 mol) and the mixture was stirred at ca. 130° for 40 min. The cooled reaction mixture was poured onto ice, neutralized with aq NaOH (286 g, 7.15 mol in 500 ml of water) and then extracted with ether. The extract was washed with brine, dried over $MgSO_4$ and concentrated. The crude product (156 g) was chromatographed over SiO_2 (800 g). Elution with n-hexane-THF (95:5) gave $PhSCH_2CO_2Me$, n-hexane-THF (9:1) gave diacetate (by-product by the replacement of MEM group with acetyl group during dehydration) (23 g, 21 %). Further elution with n-hexane-THF (8:2-7:3) gave 82 g (70 % from 5) of **8**, n_D^{22} 1.5088; $[\alpha]_D^{22}$ -6.32° (c=0.895, Et_2O); νmax (film) 2950 (s), 2940 (sh), 2870 (s), 1735 (s), 1715 (s), 1600 (w), 1580 (w), 1475 (m), 1450 (m), 1435 (m), 1380 (w), 1360 (m), 1245 (s), 1130 (m), 1105 (m), 1040 (s), 740 (m), 695 (w) cm^{-1}; δ (60 MHz, CCl_4) 0.86 (6H, d, J=7 Hz), 1.1-1.8 (10H, m), 1.92 (3H, s), 2.2-2.6 (2H, m), 3.23 (3H, s), 3.3-3.7 (4H, m), 3.50 (3H, s), 3.7-4.1 (3H, m), 4.55 (2H, br.s), 7.10 (5H, br.s), 7.25 (1H, m). (Found: C, 63.24; H, 8.39. Calc for $C_{27}H_{42}O_7S$: C, 63.50; H, 8.29 %).

Methyl (2EZ,5R,8RS)-11-hydroxy-8-(2-methoxyethoxymethoxy)-5-(1-methylethyl)-2-phenylthio-2-undecenoate **9**. A soln of **8** (81.7 g, 0.161 mol) and 1 % NaOMe in dry MeOH (812 ml) was stirred at room temp for 1 h. The reaction mixture was neutralized with 2N HCl to pH 7 and methanol was removed in vacuo. The residue was poured into water and extracted with ether. The extract was washed with brine, dried over $MgSO_4$ and concentrated to give **9** (75.4 g). Analytical sample was obtained by SiO_2 chromatography. **9**: n_D^{22} 1.5191; $[\alpha]_D^{22}$ -5.13° (c=0.88, Et_2O); νmax (film) 3450 (br.m), 3070 (w), 2950 (s), 2890 (s), 1720 (s), 1605 (w), 1585 (w), 1480 (m), 1440 (m), 1385 (w), 1365 (m), 1250 (s), 1200 (m), 1100 (s), 1040 (s), 850 (w), 740 (m), 695 (m) cm^{-1}; δ (60 MHz, CCl_4) 0.87 (6H, d, J=7 Hz), 1.1-1.8 (10H, m), 2.12 (1H, br.s, -OH), 2.3-2.6 (2H, m), 3.26 (3H, s), 3.3-3.8 (7H, m), 3.53 (3H, s), 4.58 (2H, br.s), 7.0-7.5 (6H, m). (Found: C, 63.67; H, 8.61. Calc for $C_{25}H_{40}O_6S$: C, 64.07; H, 8.60 %).

Methyl (2EZ,5R,8RS)-8-(2-methoxyethoxymethoxy)-5-(1-methylethyl)-2-phenylthio-11-p-toluenesulfonyloxy-2-undecenoate **10**. To a soln of **9** (75 g, 0.16 mol), Et_3N (21g, 0.21 mol) and DMAP (4 g, 0.03 mol) in dry CH_2Cl_2 (320 ml) was added a soln of p-TsCl (36.6 g, 0.19 mol) in dry CH_2Cl_2 (50 ml) and the mixture was stirred below 0° for 7 h. The reaction mixture was washed with water, sat $NaHCO_3$ soln and brine, dried over $MgSO_4$ and concentrated to give 96.7 g (97 %) of **10**, νmax (film) 3080 (w), 2960 (s), 2890 (s), 1725 (s), 1600 (m), 1585 (m), 1480 (m), 1440 (m), 1365 (s), 1255 (s), 1190 (s), 1180 (s), 1100 (s), 1040 (s), 960 (m), 920 (m), 820 (m), 745 (s), 690 (m), 665 (m) cm^{-1}; δ (60 MHz, CCl_4) 0.82 (6H, d, J=7 Hz), 1.1-1.9 (10H, m), 2.39 (3H, s), 2.15-2.7 (2H, m), 3.20 (3H, s), 3.2-3.7 (5H, m), 3.50 (3H, s), 3.7-4.1 (2H, m), 4.50 (2H, br.s), 7.13 (5H, br.s), 7.2-7.4 (1H, m), 7.25 (2H, d, J=8 Hz), 7.80 (2H, d, J=8 Hz). This was used for the next step without further purification.

Methyl (1RS,2E,4S,7RS)-7-(2-methoxyethoxymethoxy)-4-(1-methylethyl)-1-phenylthio-2-cyclodecen-1-ylcarboxylate **11**. Four necked round bottomed flask (2 l) was equipped with a mechanical stirrer, an efficient condenser and two sets of pressure-equalizing dropping funnel (200 ml) whose bottom was connected to the top of a short Liebig-condenser (ca. 10 cm of length). The top of the refluxing condenser was connected with two dropping funnels using three-way stopcock and silicon tubing to equalize the pressure of nitrogen. Freshly prepared $NaN(TMS)_2$ (7.2 g, 38 mmol) was placed in this flask and dissolved in dry DME (1 l) under nitrogen flow. The soln was stirred under vigorous reflux and to this was added dropwise a soln of **10** (20 g, 32.2 mmol) in dry DME (380 ml) over 40-50 min and the mixture was stirred for an additional 5 min. The reaction mixture was cooled with ice-bath to room temp, quenched with sat NH_4Cl soln and concentrated in vacuo to remove DME. The residue was diluted with water and extracted with ether. The extract was washed with water and brine, dried over $MgSO_4$ and concentrated to give crude **11** (10.7 g). This was chromatographed over SiO_2 (100 g, n-hexane-EtOAc=9/1-7/3) to give pure **11** (7.3 g, 51 %). n_D^{22} 1.5269; $[\alpha]_D^{22}$ -137° (c=0.92, Et_2O); νmax (film) 3070 (w), 2950 (s), 2880 (s), 1730 (s), 1650 (w), 1585 (w), 1460 (s), 1440 (s), 1390 (m), 1370 (m), 1230 (s), 1200 (s), 1170 (s), 1140 (s), 1100 (s), 1050 (s), 985 (s), 850 (w), 755 (m), 695 (m) cm^{-1}; δ (60 MHz, CCl_4) 0.7-1.0 (6H, m), 1.0-2.2 (12H, m), 3.25 and 3.32 (total 3H, two s), 3.3-3.8 (5H, m), 3.53 and 3.58 (total 3H, two s), 4.49 and 4.52 (total 2H, two s), 5.45-5.95 (2H, m), 7.27 (5H, br.s). (Found: C, 66.39; H, 8.46. Calc for $C_{25}H_{38}O_5S$: C, 66.63; H, 8.50 %).

(1RS,2E,4S,7RS)-7-(2-Methoxyethoxymethoxy)-4-(1-methylethyl)-1-phenylthio-2-cyclodecene-1-methanol **12**. To a stirred suspension of $LiAlH_4$ (1.8 g, 47 mmol) in dry ether (300 ml) was added a soln of **11** (13.9 g, 30.9 mmol) in dry ether (50 ml) over 10 min with ice-cooling and the mixture was stirred for 1 h. To this was added carefully water (1.8 ml), 15 % aqueous NaOH (3.6 ml) and water and the mixture was filtered. The precipitate was washed thoroughly with THF (100 ml). The combined filtrate was dried over $MgSO_4$, passed through short column of Florisil and concentrated to give **12** (12.9 g, 99 %) as viscous gum. This was pure enough (TLC) to use for the next step. νmax (film) 3450 (s), 3050 (w), 2930 (s), 2870 (s), 1650 (w), 1580 (m), 1460 (s), 1440 (s), 1385 (s), 1370 (s), 1305 (m), 1240 (m), 1200 (s), 1100 (s), 1050 (s), 985 (s), 920 (m), 845 (m), 745 (s) cm^{-1}; δ (90 MHz, $CDCl_3$) 0.8 (6H, m), 1.1-2.0 (11H, m), 2.45 (1H, m), 3.4 (5H, m), 3.6 (4H, m), 4.7 (3H, m), 5.4 (1H, d, J=16 Hz), 5.7 (1H, m), 7.45 (5H, m); MS: m/z 317 (2 %, M^+-MEMO), 298 (20, M^+-MEMOH-H_2O), 255 (15), 207 (20), 189 (35), 89 (100), 59 (80), 44 (70). HRMS Found 317.1911, 298.1751. Calc for $C_{20}H_{29}OS$: 317.1939; for $C_{20}H_{26}S$: 298.1755.

Direct reduction of crude **11** containing small amount of an acid derived by hydrolysis during cyclization gave better yield of **12**. Thus, treatment of crude **11** (29 g from 56 g of **10**; obtained by 3 batches of cyclization) with $LiAlH_4$ gave **12** (21 g, 56% from **10**) after chromatography over SiO_2 (50 g, n-hexane-EtOAc=7/3).

(1RS,2E,4S,7RS)-7-Hydroxy-4-(1-methylethyl)-1-phenylthio-2-cyclodecene-1-methyl benzoate **14**. To a soln of **12** (34.0 g, 81 mmol) and DMAP (10 g, 80 mmol) in dry pyridine (130 ml) and dry THF (340 ml) was added dropwise benzoyl chloride (18.6 ml, 0.16 mol) below 10° and the mixture was stirred for 24 h at room temp. To this was added methanol (16 ml, 0.4 mol) and the mixture was stirred for 3 h. The reaction mixture was poured into ice-water and concentrated in vacuo to remove THF and pyridine. The residue was poured into water and extracted with ether. The extract was washed with water and brine, dried

over $MgSO_4$ and concentrated. The residue was dissolved in dry toluene and concentrated in vacuo twice to remove water and pyridine completely. The crude benzoate (homogeneity was checked by TLC) was dissolved in dry acetonitrile (700 ml). To this were added NaI (25.5 g, 0.170 mol) and then TMSCl (21.2 ml, 0.167 mol) at once at -10° and the mixture was stirred for 45 min. To this was added sat $NaHCO_3$ soln and the mixture was diluted with water and extracted with ether. The extract was washed with sat $NaHCO_3$ soln, water and brine, dried over $MgSO_4$ and concentrated. The residue (35 g) was chromatographed over SiO_2 (200 g, n-hexane-EtOAc=9/1~6/4) to give 27.9 g (78 % from **12**) of **14**, νmax (film) 3450 (br.s), 3070 (m), 2950 (s), 2880 (s), 1720 (s), 1605 (m), 1585 (m), 1450 (s), 1315 (s), 1260 (s), 1175 (s), 1115 (s), 1070 (s), 1025 (s), 990 (s), 845 (w), 780 (br.s), 750 (s), 710 (s), 695 (s) cm^{-1}; δ (60 MHz, CCl_4) 0.6-1.0 (6H, m), 1.0-2.2 (13H, m), 3.60 (1H, m), 4.18 (2H, br.s), 5.1-6.1 (2H, m), 7.0-7.6 (8H, m), 7.8-8.2 (2H, m); MS m/z 316 (1 %, M^+-BzOH), 298 (15, M^+-BzOH-H_2O), 255 (10), 189 (30), 145 (40), 122 (40), 105 (100), 91 (35), 77 (55). HRMS Found 316.1906, 298.1804. Calc for $C_{20}H_{28}OS$: 316.1890; for $C_{20}H_{26}S$: 298.1755.

(1RS,4S,5E)-7-Methylene-4-(1-methylethyl)-5-cyclodecen-1-ol **15**. To a stirred suspension of freshly prepared Na sand (3.9 g, 0.17 gatom) in dry THF (700 ml) was added naphthalene (22 g, 0.17 mol) at once under Ar atomosphere and the mixture was stirred at room temp for ca. 5 h until metalic sodium was dissolved completely. To the resulting dark green soln of sodium naphthalenide was added a soln of **14** (12.3 g, 28.1 mmol) at once below -70° and the mixture was stirred for 5 min. To this were added excess sat NH_4Cl soln at -70° and then ether and brine. Organic layer was separated and the aq layer was extracted with ether quickly. The combined organic layer was washed with 5 % NaOH (x 2) and brine (x 2), dried over $MgSO_4$ and concentrated. The residue was quickly chromatographed over alumina (activity grade II, 100 g). Elution with n-hexane-EtOAc (95/5) gave naphthalene. Further elution with n-hexane-EtOAc (8/2) gave pure **15** (5.0 g, 86 %) as a 1 to 1 mixture of C-1 epimers. n_D^{22} 1.5118; $[\alpha]_D^{22}$ -253° (c=1.85, n-hexane); νmax (film) 3375 (s), 3100 (w), 2990 (w), 1650 (sh), 1640 (w), 1615 (w), 1470 (m), 1450 (m), 1390 (w), 1375 (w), 1180 (w), 1060 (w), 995 (m), 945 (w), 890 (m) cm^{-1}; δ (500 MHz, C_6D_6) 0.86 (6H, m), 1.17-1.67 (9H, m), 2.20 (2.5H, m), 2.30 (0.5H, m), 3.45 (0.5H, br.m), 3.79 (0.5H, br.m), 4.86 (1H, br.s), 4.88 (0.5H, br.s), 4.92 (0.5H, br.s), 5.27 (0.5H, dd, J=16.0 Hz, 9.8 Hz), 5.40 (0.5H, dd, J=16.1 Hz, 9.8 Hz), 5.89 (1H, br.d, J=16.1 Hz); Glc (Jeol DX-300 GC-MS, column, OV-101 (fused silica) 50 m at 150° + 4°/min, carrier gas, He, 1 ml/min; Rt 13.1 min (50 %), 13.3 min (50 %). MS m/z 208 (7 %, M^+), 190 (40, M^+-H_2O), 147 (100), 91 (85). HRMS Found: 208.1812. Calc for $C_{14}H_{24}O$: 208.1827.

(4S,5E)-7-Methylene-4-(1-methylethyl)-5-cyclodecen-1-one **16**. To a stirred suspension of PCC (24 g, 0.11 mol) and finely powdered molecular sieves 3A (60 g) in dry CH_2Cl_2 was added **15** (12.0 g, 57.7 mmol) with ice-cooling and the mixture was stirred vigorously at room temp for 30 min. To this was added ether (300 ml) and the precipitate was crushed well. The mixture was filtered through celite-Florisil pad and the slurry was washed well with ether. The combined filtrate was passed through short Florisil column and solvent was removed in vacuo. The residue was chromatographed over alumina (activity grade II, n-hexane-EtOAc=95/5) to give pure **16** (8.16 g, 69 %) as a syrup which crystallized in a refrigerator. n_D^{22} 1.5080; $[\alpha]_D^{22}$ -362° (c=1.22, n-hexane); UV (n-hexane): λmax 237.0 nm (ε 14,800), 221.2 nm (12,000); CD (c=2.0 x 10^{-3} mol/l, MeOH, t=25°): [Δε (λ, nm)] -23 (214), 0 (238), +3.5 (250), 0 (267), -1.4 (286); νmax (film) 3100 (w), 2980 (s), 2900 (s), 1715 (s), 1650 (w), 1615 (w), 1465 (m), 1430 (s), 1390 (m), 1365 (m), 1330 (w), 1260 (w), 1215 (w), 1190 (m), 1160 (w), 1120 (m), 1100 (m), 1055 (m), 1025 (w), 985 (s), 880 (m), 870 (w), 800 (m) cm^{-1}; δ (500 MHz, C_6D_6) 0.78 (3H, d, J=6.7 Hz), 0.80 (3H, d, J=6.7 Hz), 1.21 (1H, m), 1.33 (1H, m), 1.46 (1H, m), 1.57 (1H, m), 1.80-1.90 (3H, m), 1.99 (1H, ddd, J=2.0, 7.2, 12.9 Hz), 2.10 (1H, dq, J=2.7, 11.8 Hz), 2.27 and 2.29 (2H, two t, J=12.8 Hz), 2.54 (1H, dt, J=4.8, 12.9 Hz), 4.82 (1H, brs), 4.85 (1H, brs), 5.24 (1H, dd, J=10.4, 15.9 Hz), 5.90 (1H, d, J=15.9 Hz). m/z 206 (25 %, M^+), 188 (40), 173 (35), 145 (100), 91 (55). HRMS Found: 206.1651. Calc for $C_{14}H_{22}O$: 206.1671.

(4S,5E)-7-Methylene-4-(1-methylethyl)-10-phenylsulfinyl-5-cyclodecen-1-one **17**. To a soln of hexamethyldisilazane (1.5 ml, 7.0 mmol) in dry THF (30 ml) was added 1.55N n-BuLi in n-hexane (4.5 ml, 7.0 mmol) at -10° under Ar atomosphere and the mixture was stirred for 10 min. To this was added dropwise a soln of **16** (1.10 g, 5.35 mmol) in dry THF (2 ml) at -70° and the mixture was stirred for 1 h. Then, reaction temp of the resulting enolate was raised to -20° and this was added at once to a soln of phenylthiobenzenesulfonate (1.8 g, 7.0 mmol) in dry THF (30 ml) at room temp and the mixture was stirred for 5 min. (The reaction temp was kept between -5° to 5° and in ca. 1 min after the addition of the enolate reaction mixture became turbid). To this was added sat NH_4Cl soln and the reaction mixture was extracted with ether. The extract was washed with sat $NaHCO_3$ soln and brine, dried over $MgSO_4$ and concentrated. The crude sulfenylated product was revealed to contain phenylthiobistrimethylsilylamide as by-product. This was dissolved in a soln of $NaIO_4$ (3.1 g, 14 mmol) in MeOH-H_2O (5:1, 140 ml) and the mixture was stirred vigorously for 22 h. The reaction mixture was filtered and the precipitate was washed with ether. The combined filtrate was concentrated in vacuo and the residue was diluted with water and extracted with ether. The extract was washed with brine, dried over $MgSO_4$ and concentrated. The residue was chromatographed over neutral alumina (activity grade II, 50 g). Elution with n-hexane-EtOAc (6/4) gave 1.06 g (59 %) of a sulfoxide **17**, νmax (film) 3100 (w), 3080 (w), 2980 (s), 1700 (s), 1650 (w), 1635 (w), 1615 (m), 1585 (w), 1470 (m), 1445 (s), 1420 (m), 1390 (m), 1370 (m), 1345 (m), 1330 (m), 1310 (m), 1230 (m), 1180 (m), 1130 (m), 1090 (s), 1055 (s), 985 (s), 895 (w), 755 (s), 695 (m) cm^{-1}; δ (60 MHz, CCl_4) 0.7-1.1 (6H, m), 1.1-2.8 (10H, m), 3.1-3.8 (1H, m), 4.80 and 4.88 (2H, two br.s), 5.0-5.3 (1H, m), 5.92 (1H, br.d, J=16 Hz), 7.46 and 7.48 (5H, two br.s). This was employed in the next step without further purification.

(2Z,6E,8S)-5-Methylene-8-(1-methylethyl)-2,6-cyclodecadien-1-one **18**. A mixture of the sulfoxide **17** (1.1 g, 3.3 mmol), 2,6-di-t-butyl-p-cresol (BHT, 70 mg) and the powdered anhydrous $CaCO_3$ (700 mg) was stirred vigorously under reflux for 6 h under Ar atomosphere and then concentrated to ca. 5 ml under atomospheric pressure. The cooled reaction mixture was filtered through celite and the filtrate was diluted with n-hexane. This was chromatographed over neutral alumina (activity grade II, 20 g) with n-hexane-EtOAc (100/0-9/1) gave fractions containing **18** which contains the minor isomers (0.74 g, 54 %). In another small scale-run crude product was chromatographed over neutral alumina to give analytical sample of **18**. n_D^{24} 1.5116; $[\alpha]_D^{24}$ -360° (c=0.63, n-hexane); νmax (film) 3100 (w), 3040 (m), 2960 (s), 2890 (s), 1695 (s), 1655 (w), 1635 (m), 1615 (m), 1470 (m), 1460 (m), 1445 (m), 1420 (m), 1395 (m), 1370 (m), 1315 (w), 1180 (m), 1170 (m), 1120 (m), 1080 (s), 985 (s), 925 (m), 895 (s), 845 (m), 825 (m), 805 (w), 730 (m) cm^{-1}; δ (500 MHz, C_6D_6, C_6H_6=7.24 ppm as standard) 0.88 (3H, d, J=6.7 Hz), 0.89 (3H, d, J=6.7 Hz), 1.45 (1H, m), 1.54 (2H, m), 1.91 (1H, dd, J=14.1, 5.0 Hz), 2.0-2.2 (2H, m), 2.57 (1H, dd, J=12.1, 6.7 Hz), 3.69 (1H, dd, J=12.1, 10.7 Hz), 4.80 and 4.87 (2H, two s), 5.32 (1H, dd, J=14.8, 11.4 Hz), 5.43 (1H, ddd, J=12.1, 11.4, 6.7 Hz), 5.78 (1H, d, J=14.8 Hz), 5.88 (1H, d, J=11.4 Hz); MS m/z 204 (10 %, M^+), 186 (50), 171 (60), 169 (60), 143 (100), 130 (60), 91 (50), 77 (35). HRMS Found: 204.1519. Calc for $C_{14}H_{20}O$: 204.1514.

(4S,5E,9R,10R)-9,10-Epoxy-7-methylene-4-(1-methylethyl)-5-cyclodecen-1-one **19**. To a suspension of KH (240 mg, 6.1 mmol) in dry THF (40 ml) was added a 4.17N soln of t-BuOOH in toluene (3 ml, 12 mmol) below -5° and the mixture was stirred for 5 min. To this was added dropwise a soln of crude **18** (250 mg, 1.23 mmol) in dry THF (10 ml) at 0° and the mixture was stirred for 1 h. The reaction mixture was poured into ice-water and extracted with ether. The extract was washed with aq Na_2SO_3, water and brine, dried over $MgSO_4$ and concentrated. The residue was chromatographed over neutral alumina (activity grade II, 30 g). Elution with n-hexane-EtOAc (9/1-8/2) gave 149 mg (55 %) of **19**, m.p. 39-41°; $[\alpha]_D^{22.5}$ -347° (c=1.30, n-hexane); νmax (film) 3120 (w), 2990 (s), 2960 (s), 2910 (s), 1730 (s), 1655 (w), 1620 (w), 1475 (m), 1455 (m), 1420 (s), 1375 (m), 1260 (w), 1190 (w), 1145 (m), 1090 (m), 1070 (m), 1030 (m), 985 (s), 900 (m), 865 (w), 810 (s) cm^{-1}; δ (500 MHz, C_6D_6)) 0.75 (3H, d, J=6.2 Hz), 0.78 (3H, d, J=6.2 Hz), 1.29 (2H, m), 1.36 (1H, m), 1.64 (1H, dd, J=16.7 Hz, 6.0 Hz), 1.85 (1H, dd, J=16.7 Hz, 12.3 Hz), 2.09 (1H, m), 2.35 (1H, dd, J=12.7 Hz, 9.8 Hz), 2.52 (1H, dd, J=12.7 Hz, 3.5 Hz), 2.79 (1H, ddd, J=9.9 Hz, 4.7 Hz, 3.5 Hz), 3.03 (1H, d, J=4.7 Hz), 4.74 (1H, s), 4.76 (1H, s), 5.10 (1H, dd, J=16.2 Hz, 10.3 Hz), 5.66 (1H, d, J=16.2 Hz). This was a crystalline product, however, its Glc analysis showed to be a mixture of **19** and (9S,10S)-isomer (6.6:1). Glc (OV-101, 50 m, at 150°+4°/min Rt 20.5 min [13%, (9S,10S)-isomer], 21.1 min (87 %, **19**). MS m/z 220 (10 %, M^+), 202 (25), 177 (30), 159 (75), 131 (55), 95 (100), 91 (60). HRMS Found: 220.1494. Calc for $C_{14}H_{20}O_2$: 220.1465. (9S,10S)-isomer: MS, m/z 220 (10 %, M^+), 202 (18), 177 (24), 159 (58), 131 (50), 95 (100), 91 (55).

(2S,4S,5E,9R,10R)-9,10-Epoxy-2-hydroxy-7-methylene-4-(1-methylethyl)-5-cyclodecen-1-one **20**. To a soln of $LiN(TMS)_2$ prepared from $(TMS)_2NH$ (0.26 ml, 1.23 mmol) and 1.72N n-BuLi in n-hexane (0.71 ml, 1.23 mmol) in dry THF (5 ml) was added dropwise a soln of **19** (180 mg, 0.82 mmol) in dry THF (2 ml) at -70° under Ar atomosphere and the mixture was stirred for 1 h and then temp was raised to -22° (CCl_4-dry ice bath temp). To this was added crystalline $MoO_5 \cdot HMPA \cdot C_5H_5N$ freshly prepared by Vedejs' method[20] (700 mg, 1.64 mmol) quickly and the mixture was stirred for 15 min. To this was added 10 % Na_2SO_3 soln, ether and brine successively and the ether layer was separated. Aq layer was extracted with ether. Combined extract was washed with brine, dried over $MgSO_4$ and concentrated to give crude crystals. Recrystallization from n-hexane-i-Pr_2O gave 134 mg (69 %) of pure crystalline **20**, m.p. 116.5-117.5°; $[\alpha]_D^{26}$ -389° (c=0.0883, Et_2O); νmax 3340 (br), 3020 (w), 2950 (s), 2860 (m), 1715 (s), 1610 (w), 1450 (m), 1415 (m), 1385 (m), 1255 (m), 1085 (m), 1040 (m), 1010 (m), 980 (s), 965 (s), 905 (m), 805 (m), 760 (w) cm^{-1}; δ (500 MHz, C_6D_6) 0.70 (3H, d, J=6.6 Hz), 0.80 (3H, d, J=6.6 Hz), 1.34 (1H, m), 1.45 (1H, m), 1.49 (1H, ddd, J=12.5 Hz, 5.2 Hz, 1.5 Hz), 1.6 (1H, -OH), 2.18 (1H, dt, J=12.5 Hz, 9.8 Hz), 2.27 (1H, dd, J=13.1 Hz, 10.2 Hz), 2.49 (1H, dd, J=13.1 Hz, 3.3 Hz), 2.72 (1H, ddd, J=10.2 Hz, 4.6 Hz, 3.3 Hz), 3.37 (1H, d, J=4.6 Hz), 3.61 (1H, br.t, J=9.8 Hz, 1.5 Hz), 4.70 (1H, br.s), 4.73 (1H, br.s), 4.93 (1H, dd, J=16.2 Hz, 10.3 Hz), 5.60 (1H, d, J=16.2 Hz). This was proved to be free from (9S,10S)-isomer by spectral data.

(2S,4S,5E,9R,10R)-2-t-Butyldimethylsilyloxy-9,10-epoxy-7-methylene-4-(1-methylethyl)-5-cyclodecen-1-one **21**. To a soln of **20** (134 mg, 0.57 mmol) in dry DMF (5 ml) was added t-Bu(Me)$_2$SiCl (102 mg, 0.68 mmol) at once and the mixture was stirred overnight at 40°. The reaction mixture was diluted with cold water and extracted with n-hexane. The extract was washed with water and brine, dried over $MgSO_4$ and concentrated. The residue was chromatographed over neutral alumina (activity grade II, 5 g, n-hexane-EtOAc) to give 203 mg (quantitative yield) of crystalline **21**, m.p. 61.5-62.0°; $[\alpha]_D^{26}$ -301° (c=0.184, n-hexane); νmax (KBr) 3070 (w), 2950 (s), 2925 (s), 2880 (s), 2850 (s), 1720 (s), 1610 (w), 1460 (s), 1415 (m), 1385 (m), 1360 (m), 1250 (s), 1090 (s), 1065 (s), 980 (s), 970 (s), 900 (m), 835 (s), 770 (s), 715 (m) cm^{-1}; δ (500 MHz, C_6D_6) 0.06 (3H, s), 0.07 (3H, s), 0.72 (3H, d, J=6.7 Hz), 0.79 (3H, d, J=6.6 Hz), 0.91 (9H, s), 1.30 (1H, m), 1.59 (1H, m), 1.74 (1H, ddd, J=2.0, 5.2, 12.7 Hz), 2.35 (1H, dd, J=9.6, 13.0 Hz), 2.54 (1H, dd, J=3.6, 13.0 Hz), 2.57 (1H, dt, J=12.7, 11.1 Hz), 2.84 (1H, ddd, J=3.6, 4.4, 9.6 Hz), 3.61 (1H, d, J=4.4 Hz), 4.00 (1H, dd, J=2.0, 11.1 Hz), 4.74 (1H, br.s), 4.77 (1H, br.s), 5.01 (1H, dd, J=10.5, 16.1 Hz), 5.69 (1H, d, J=16.1 Hz); MS: m/z 293 (15 %, M^+-t-Bu), 275 (20, M^+-t-Bu-H_2O), 265 (5), 249 (7), 173 (13), 129 (27), 107 (35), 93 (30), 75 (100), 73 (67). HRMS Found: 293.1562. Calc for $C_{16}H_{25}O_3Si$:293.1573; Found: 275.1444. Calc for $C_{16}H_{23}O_2Si$: 275.1468.

(1S,3S,4E,8R,9R,10R)-1-t-Butyldimethylsilyloxy-8,9-epoxy-6-methylene-10,10-methylenoxy-3-(1-methylethyl)-4-cyclodecene [(-)-Periplanol-B t-butyldimethylsilyl ether] **22**. To a stirred suspension of $Me_3S^+I^-$ (31 mg, 0.15 mmol) in dry THF (0.4 ml) was added dropwise 1.5N n-BuLi in n-hexane (0.095 ml, 0.14 mmol) at -15°. Cooling bath was removed and the mixture was stirred for 10 min at room temp until the soln became clear, and then cooled to -10°. To this was added a soln of **21** (25.0 mg, 0.071 mmol) in dry THF (0.5 ml) at -5° and the mixture was stirred for 10 min. The reaction mixture was diluted with water and extracted with ether. The extract was washed with water and brine, dried over $MgSO_4$ and concentrated. The residue was chromatographed over neutral alumina (activity grade II, 10 g, n-hexane-EtOAc=95/5) to give 19.6 mg (75 %) of pure crystalline **22**, m.p. 45.5-47.5°; $[\alpha]_D^{26}$ -322.5° (c=0.0772, n-hexane); νmax (KBr) 3090 (w), 2960 (s), 2940 (s), 2870 (s), 1790 (w), 1655 (w), 1615 (m), 1465 (s), 1390 (m), 1365 (s), 1250 (s), 1165 (m), 1090 (s),1035 (m), 990 (s), 915 (s), 895 (s), 850 (s), 835 (s), 815 (s), 770 (s), 720 (m) cm^{-1}; δ (500 MHz, C_6D_6) 0.04 (6H, s), 0.84 (3H, d, J=6.4 Hz), 0.85 (3H, d, J=6.4 Hz), 0.91 (9H, s), 1.40 (1H, m), 1.53 (1H, dd, J=12.2, 4.9 Hz), 1.71 (1H, dt, J=10.4, 12.2 Hz), 1.79 (1H, m), 2.64 (1H, dd, J=11.4, 3.9 Hz), 2.65 (1H, d, J=6.0 Hz), 2.82 (1H, d, J=6.0 Hz), 2.86 (1H, dt, J=10.3, 3.9 Hz), 3.13 (1H, dd, J=11.4, 10.3 Hz), 3.22 (1H, br.d, J=3.9 Hz), 3.98 (1H, br.d, J=10.4 Hz), 4.87 (2H, br.s), 6.02 (1H, dd, J=16.2, 2.2 Hz), 6.03 (1H, d, J=16.2 Hz). MS: m/z 307 (5 %, M^+-t-Bu), 289 (6, M^+-t-Bu-H_2O), 277 (20), 173 (15), 143 (25), 131 (20), 117 (20), 105 (20), 91 (20), 75 (100), 73 (45). HRMS Found: 307.1732. Calc for $C_{17}H_{27}O_3Si$: 307.1729; Found: 289.1612. Calc for $C_{17}H_{25}O_2Si$: 289.1624.

(1S,3S,4E,8R,9R,10S)-8,9-Epoxy-6-methylene-10,10-methylenoxy-3-(1-methylethyl)-4-cyclodecen-1-ol [(-)-Periplanol-B] **23**. To a soln of **22** (54 mg, 0.15 mmol) in dry THF (1 ml) was added a N soln of n-Bu_4NF in THF (2 ml, 0.2 mmol) and the mixture was stirred for 10 min. The reaction mixture was diluted with brine and extracted with ether three times. The combined extract was washed with brine, dried over Na_2SO_4 and concentrated to give crystalline **23** (39 mg, quantitative yield). Recrystallization from i-Pr_2O-n-hexane gave pure **23**, m.p. 116.0°; $[\alpha]_D^{26}$ -462° (c=0.135, Et_2O); νmax (KBr) 3500 (s), 3070 (w), 3030 (w), 2950 (s), 2925 (s), 2870 (s), 1800 (w), 1645 (m), 1610 (w), 1455 (m), 1415 (m), 1385 (s), 1365 (s), 1280 (m), 1265 (m), 1160 (m), 1135 (m), 1085 (m), 1055 (s), 1040 (m), 1015 (m), 980 (s), 950 (s), 915 (s), 895 (s), 835 (m), 815 (s), 790 (s), 715 (m), 700 (m), 515 (s) cm^{-1}; δ (500 MHz, C_6D_6) 0.70 (1H, br.s, -OH), 0.818 (3H, d, J=6.7 Hz), 0.826 (3H, d, J=6.6 Hz), 1.26 (1H, dd, J=10.4, 5.8 Hz), 1.35 (1H, m), 1.44 (1H, q, J=10.4 Hz), 1.63 (1H, m), 2.40 (1H, d, J=5.9 Hz), 2.60 (1H, dd, J=12.2, 4.0 Hz), 2.70 (1H, d, J=5.9 Hz), 2.76 (1H, dt, J=12.2, 4.0 Hz), 3.01 (1H, d, J=4.0 Hz), 3.04 (1H, t, J=12.2 Hz), 3.58 (1H, dd, J=10.4, 4.2 Hz), 4.86 (1H, br.s), 4.87 (1H, br.s,), 5.90 (1H, dd, J=16.2, 2.2 Hz), 5.95 (1H, d, J=16.2 Hz). (Found: C, 71.67; H, 8.42. Calc for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86 %).

Optical purity of (-)-Periplanol-B. The optical purity of **23** was determined by the Hplc analysis of its MTPA ester

prepared by the acylation with (R)-MTPACl or (S)-MTPACl in a described manner. The MTPA ester was analyzed on Hewlet Packerd (HP) 1090 liquid chromatograph equipped with diode array detector and HP 3390A integrator. (Column: HP Hypersil® Silica 5μm, 100 x 2.1 mm; Solvent: n-hexane-THF (99.5:0.5); Flow rate: 0.2 ml/min; detected at 227 nm) Rt **23**-(R)-MTPA: 9.91 min (99.95 %), 13.67 min (0.05 %); **23**-(S)-MTPA 9.91 min (0.05 %), 13.67 min (99.95 %). The optical purity of **23** was therefore 99.90 % e.e.

(3S,4E,8R,9R,10S)-8,9-Epoxy-6-methylene-10,10-methylenoxy-3-(1-methylethyl)-4-cyclodecen-1-one [(3S,8R,9R,10S)-(-)-periplanone-B] **1**. PCC (35 mg, 0.16 mmol) was dissolved into dry CH_2Cl_2 (2 ml) in the presence of powdered MS-3A (80 mg). To this was added crystalline **23** (20.2 mg, 0.081 mol), and the mixture was stirred at room temp for 1 h. To this was added ether (10 ml) and the mixture was passed through a short Florisil column. The solvent was removed in vacuo and the residue was chromatographed over neutral alumina (activity grade II, 5 g, n-hexane-EtOAc=85/15) to give crystalline (-)-**1** (19.6 mg, 98 %). Recrystallization from n-hexane gave 17.6 mg (88 %) of pure **1**, m.p. 57.0-57.5°; $[\alpha]_D^{26}$ -553° (c=0.113, n-hexane) [In our preliminary communication, we reported the optical rotation of (-)-periplanone-B[1] with higher value (-667°). Later, we obtained more **1** (total ca. 50 mg) and carefully recrystallized from n-hexane. Pure sample was weighed accurately using micro-balance (Limit 0.001 mg). Thus, specific rotation reported here must be correct value.]; UV (n-hexane): λmax 225.4 nm (ε 14,300); CD (c=6.1 x 10^{-4} mol/l, n-hexane, t=25°): [Δε (λ, nm)] -27 (273), -2.5 (390); νmax [FT-IR (Nicolet 60SX spectrometer), KBr] 2960 (s), 2934 (m), 2873 (m), 1707 (s), 1620 (w), 1451 (m), 1308 (m), 1018 (m), 982 (m), 911 (m), 897 (m), 845 (m), 814 (m) cm^{-1}; δ (500 MHz, CS_2) 0.87 (3H, d, J=6.5 Hz), 0.91 (3H, d, J=6.5 Hz), 1.56 (1H, m), 2.04 (1H, m), 2.06 (1H, m), 2.55 (1H, m), 2.58 (2H, m), 2.63 (1H, d, J=6.0 Hz), 2.68 (1H, ddd, J=8.0 Hz, 6.0 Hz, 4.0 Hz), 2.84 (1H, d, J=6.0 Hz), 3.52 (1H, d, J=4.0 Hz), 4.87 (1H, br.s), 5.02 (1H,br.s), 5.78 (1H, dd, J=16.0, 10.0 Hz), 5.91 (1H, d, J=16.0 Hz); (500 MHz, C_6D_6) 0.70 (3H, d, J=6.8 Hz), 0.72 (3H, d, J=6.9 Hz), 1.30 (1H, m), 1.94 (1H, dd, J=9.8, 5.7 Hz), 2.02 (1H, d, J=5.7 Hz), 2.05 (1H, m), 2.35 (1H, dd, J=11.0, 9.8 Hz), 2.56 (1H, dd, J=12.2, 4.0 Hz), 2.63 (1H, d, J=5.7 Hz), 2.74 (1H, dt, J=10.2, 4.0 Hz), 2.86 (1H, dd, J=12.2, 10.2 Hz), 3.84 (1H, d, J=4.0 Hz), 4.78 (1H, br.s), 4.81 (1H, br.s), 5.91 (1H, dd, J=16.0, 9.0 Hz), 5.96 (1H, d, J=16.0 Hz). Its ^1H NMR spectrum (CS_2) was identical with that reported for natural **1**.[3] ^{13}C NMR: δ (125 MHz, C_6D_6) 20.08 (q), 20.17 (q), 32.41 (d), 36.09 (t), 39.65 (t), 46.19 (t), 50.93 (d), 52.82 (d), 59.44 (2C, d and s), 115.80 (t), 131.78 (d), 134.97 (d), 141.87 (s), 209.09 (s). GLC (OV-101, 50 m capillary, at 150°+4°/min; carrier gas, He, 1 ml/min) Rt 22.4 min (single peak); MS m/z 248 (10 %, M^+), 230 (10), 187 (20), 159 (20), 145 (20), 133 (25), 121 (30), 119 (25), 111 (35), 107 (35), 105 (45), 91 (80), 79 (65), 77 (60), 69 (35), 55 (46), 42 (73), 38 (100). HRMS Found: 248.1429. Calc for $C_{15}H_{20}O_3$: 248.1413.

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